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Phosphogypsum

PROCEEDINGS OF
THE INTERNATIONAL SYMPOSIUM ON PHOSPHOGYPSUM

Utilization and/or Disposal of Phosphogypsum
Potential Barriers to Utilization

Lake Buena Vista, Florida
5-7 November 1980

Editors:
David P. Borris
Patricia W. Boody

FLORIDA INSTITUTE OF PHOSPHATE RESEARCH
BARTOW, FLORIDA

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FINAL REPORT

David P. Borris and Patricia W. Boody

FLORIDA INSTITUTE OF PHOSPHATE RESEARCH
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PREFACE

We intentionally sought to process and deliver the symposium proceedings to the potential user as soon as possible. To do this, we decided to have the author assume full responsibility for submitting manuscripts in camera ready format. The manuscripts did not receive full, conventional editorial processing, and consequently you may find typographical errors and differences in format. The views expressed in each paper are those of the author and not necessarily those of the sponsoring organizations. Trade names are used solely for information and convenience of the reader and do not imply official endorsement by the sponsoring organizations.

INTRODUCTION

Since the end of World War II, the increase in the world's population has created a dependence on fertilizer as a partial solution for the hunger crisis. As one of the raw materials for fertilizers, phosphate has assumed strategic importance; requirements for this mineral have placed new demands on the phosphate industry including the necessity for developing new technology for producing phosphoric acid 'from phosphate rock. At the same pace as the quest for new technology, Americans have become increasingly concerned with conservation of natural resources. Pollution abatement-'and preservation of natural areas for a variety of activities are key conservation issues that have had an important impact on the phosphoric acid industry and in the utilization of by-product materials. These proceedings from the First International Symposium on Phosphogypsum present the results of discussions and presentations by individual researchers in diverse areas demonstrating both the problems and potential uses associated with by-product gypsum from the phosphoric acid industry.

The phosphoric acid industry is world-wide. Phosphate deposits are scattered throughout the world, and even where there are no natural deposits, countries import rock for producing acid. Although there are several methods of producing phosphoric acid including the thermal method, hydrochloric, and nitric acidulation, the wet process or sulfuric acidulation of phosphate rock is most commonly used. The phosphate content-of the rock is converted by concentrated sulfuric acid to phosphoric acid and calcium sulfate, $Ca_3(PO_4)_2 + 3H_2SO_4 - 2H_3PO_4 + 3CaSO_4$.

Calcium sulfate is separated from the phosphoric acid by filtration. By-product calcium sulfate can exist in several different crystal forms, among them anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 - ½H_2O$) and gypsum, or dihydrate ($CaSO_4 - 2H_2O$). Proportions of calcium and phosphate vary according to the source and grade of the phosphate rock; in addition, there are approximately 5Ø other impurities in the rock which contaminate the two end products. Several advances in the technology of phosphoric acid production have been utilized.

One of the earliest processes was the Dorroco Strong Acid Process which consisted of a series of separate reactors with an air-induced cooling system for creating the conditions for gypsum crystallization. The Prayon Dihydrate Process used today makes use of a multi-compartment reactor. Each compartment contains an agitator and aging tank for gypsum crystallization. The Fisons Dihydrate Process incorporates the aging tank in the reactor vessel. The Phone-Poulenc Process also follows the concept of a single tank reactor, as do the Kellogg-Lopker Process, R.L. Somerville and Isothermal phosphoric acid reactors. The phosphate c tent of the acid produced in these dihydrate processes is usually 32% - 33% P_2O_5.

In producing a higher P_2O_5 concentration, the hemihydrate calcium sulfate is produced as the by-product. Fisons also has a hemihydrate process which uses two reactors instead of the one reactor used in the dihydrate process. Occidental and the Tennessee Valley Authority have also developed hemihydrate processes.

In Japan where there are no natural gypsum deposits, the industry has had an incentive to produce a higher quality, cleaner, by-product gypsum for use in construction. Nissan Chemical Industries, Ltd., Nippon Kokan KK, and Mitsubishi Chemical Industries, Inc. have developed processes which acidulate the rock under hemihydrate conditions, recrystallize to the dihydrate form without separating the hemihydrate, and finally separate the product. Fisons, Nissan and other companies have developed a recrystallization process which has two independent filters. The processes acidulate the rock under hemihydrate conditions, separate the product, recrystallize the hemihydrate to dihydrate calcium sulfate, filter and recycle the liquors to the first process. A third method for recrystallization acidulates the rock under dihydrate conditions, separates the product, recrystallizes from dihydrate to hemihydrate, filters and returns the liquors to the process. This method has been investigated by Marchon and used commercially by Central Glass Company and Societe de Prayon, whose process is known as Central-Prayon process.

For each ton of phosphoric acid produced by these wet processes, there are approximately 4.5 tons of gypsum produced. In central Florida, the phosphoric acid industry has stockpiled over 328 million tons and currently produces 33 million tons of gypsum each year. This is a substantial amount of waste to be disposed of - either by discharge into water, land storage, or utilization. Along coastal areas, as in Australia, the gypsum slurry is pumped directly into the surrounding oceans. Although the impurities in the gypsum are potentially harmful, tidal fluctuations and currents quickly disperse that material. This disposal method disregards implications of increasing the acidity and background levels of heavy metals and fluorine. In Florida and many other locations, gypsum slurry is pumped to lagoons for gypsum to settle out, is tacked on land, or used as fill for mining cuts. Environmental regulations strictly control these methods to prevent groundwater contamination and public exposure to radioactive materials associated with phosphate rock.

The Florida Institute of Phosphate Research is concerned with the reclamation and utilization of phosphogypsum. Although Florida's production rate of by-product gypsum exceeds the United States' use of gypsum by 50%, Florida is a major importer of mined gypsum. Before phosphogypsum can be substituted for natural gypsum, however, impurities incorporated into the material must be removed or inactivated. In line with the Institute's goals, an investigation is being sponsored to evaluate potential uses of phosphogypsum in the building industry as plaster, wallboard or sheetrock, in the cement industry as a cement component or retarder, or in the fertilizer industry as a sulfur source for sulfuric acid and lime.

One of FIPR's concerns with by-product phosphogypsum is the enriched amount of Radium-226, parent isotope of Radium-222. FIPR is seeking ways to recover or remove impurities, including radium, which may diminish the useful potential of the by-product gypsum. The removal of radium to mitigate the radium concentrations associated with gypsum stacks should serve two purposes: (1) allow the material to be used more effectively and (2) reduce the environmental impact of land disposal, therefore eliminating the potential for groundwater contamination.

In addition to basic research, the Institute sponsored this International Symposium on Phosphogypsum to discuss potential benefits, problems, disposal methods and uses for phosphogypsum associated with the fertilizer industry. The utilization of phosphogypsum is not only a scientific/engineering problem, it also has economic and political consideration as well. The symposium began with a commentary challenge by Jacob Varn, Secretary of the Florida Department of Environmental Regulation. Varn communicated the state's concerns with gypsum pond contamination of groundwater and the potential radiation hazard if the phosphogypsum were substituted for natural gypsum in building materials. Thirty-six papers were presented in six technical areas including agriculture, civil engineering, chemical recovery and purification, environmental effects, regulatory effects, and world-wide production and utilization of phosphogypsum.

Agricultural research shows that phosphogypsum is successful as a nutrient source of sulfur, calcium and phosphorus. Phosphogypsum can also be used to reclaim sodic soils and improve soil water infiltration. Although agricultural use has not been large, the potential shortages of sulfur make gypsum land plaster more promising.

In countries such as Japan and France, phosphogypsum is already being used for construction of roadways and landfills and as a building material for houses. French research is in the final stages of determining viable methods of removing the radium impurities associated with phosphogypsum. Phosphogypsum could potentially be substituted for other chemical gypsums in artificial reef construction and artificial islands.

Phosphogypsum can be used as a source of sulfur for sulfuric acid. Several processes exist that produce sulfuric acid and Portland cement. As an elemental sulfur source, phosphogypsum could be processed for use in wood-sulfur composites , creating rot-resistant and water-resistant materials, for reinforcing bamboo, for structural concrete, for sulfur foam, for sulfur asphalt pavements, etc. As uses of sulfur increase, and as supplies diminish and prices rise, phosphogypsum will be considered more favorably by potential users.

The editors wish to acknowledge the technical support and symposium preparations made by Patricia Corcoran and the College of Extended Studies staff at the University of Central Florida. We would also like to thank Karl Johnson and the Fertilizer Institute for their input in developing the program and publicity and for the gracious reception they provided on November 6, 1980. We also want to express our thanks to Homer Hooks and the Florida Phosphate Council for publicizing and providing the welcoming reception on November 5, 1980. We appreciate the hard work and efforts of the Institute staff, especially Jane Waters and Janice Crowder and all others associated with the event.

WELCOME

Dr. David P. Borris

It is my sincere wish that each of you have a most enjoyable time as we attempt to remove 'potential 'barriers to the utilization of phosphogypsum. Through the Florida Institute of Phosphate Research, the State of Florida is seeking better ways' to responsibly develop its phosphate resources, including by-products of the various production processes.

Phosphogypsum is a by-product of the wet-acid production of phosphoric acid. Wet process phosphoric acid plants are concentrated in Polk County to the south and west of Bartow: The area contains about 15 plants (Figure 1). Phosphogypsum is slurried from the phosphoric acid production facility to extensive storage areas where it dries in stacks as high as 9Ø feet tall. An aerial perspective of the stacks dramatically emphasizes the magnitude of the phosphogypsum stockpiled at a single plant. In general, chemical analysis reveals that the material is approximately 92% pure gypsum with acid, insoluble phosphatic material, radium, and fluorine being the principal contaminants. On an individual state basis, the central Florida phosphate district's annual output of by-product gypsum can be calculated from the amount of wet-acid production. In 1979, Florida's production represented a significant portion of the total amount of gypsum produced in the United States (Figure 2). Florida's production rate exceeds 33 million tons per year.

Location plays an important role in seeking viable solutions for the utilization of phosphogypsum. The distribution of the 1Ø largest gypsum mines in the United States in 198Ø is illustrated in Figure 3. Those states shaded horizontally produce 71% of America's total mined gypsum. None of these states are in the Southeast; in fact, there is no active gypsum mining in the area. Yet, despite high transportation costs, the ninth largest processing plant consuming mined gypsum is located in Florida.

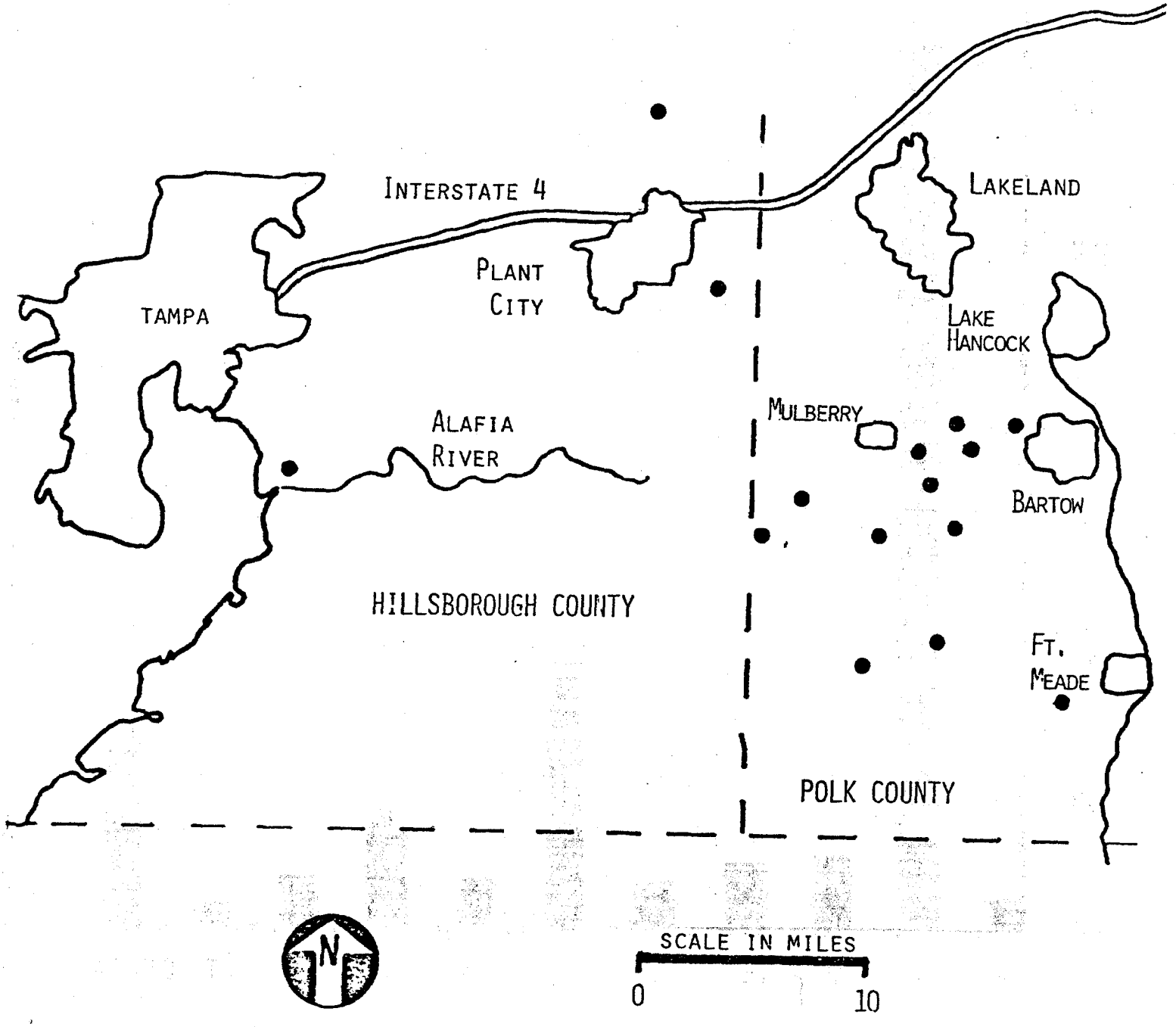
Annual Gypsum consumption in the United States stood at about 22.5 million tons in 1979 (Figure 4). Approximately 66% was mined domestically, and 33% was imported, mostly from Canada. Of the 22.5 million tons, about 71% went for production of wallboard, while 19% was used as a retardant in portland cement. For agricultural application, by-product gypsum is a significant competitor with mined gypsum, but only a tiny fraction (2%) of the annual production is used agriculturally.

The Florida phosphate region's annual production rate of 33 million tons currently exceeds the total utilization of the combined domestic and imported mined gypsum in the United States by 5Ø%. Over 33Ø million tons of by-product gypsum are stockpiled in central Florida. By the year 2ØØØ, this amount will exceed one billion tons. Developing economically feasible uses for this readily available mineral resource is a major priority of the Florida Institute of Phosphate Research.

By-product gypsum has a wide variety of uses throughout the world including the production of Portland cement and sulfuric acid, plaster and wallboard, road-bed material, composite materials consisting of gypsum combined with various wastes and extenders, and lime and sulfuric acid. Agricultural applications include its use as a sulfur fertilizer, a soil amendment, and as an animal feed supplement. There is also demonstrated potential for microbial reduction for the recovery of sulfur and chemical recovery of the sulfur, phosphate, radium and fluoride. These topics and several others will be discussed during the symposium.

Let us as members of the international scientific community be cognizant of the earth's limitations. Our management of the planet's natural resources has a profound effect on the integrity of the biosphere. As a community, let us work together to develop solutions for the use of this resource.

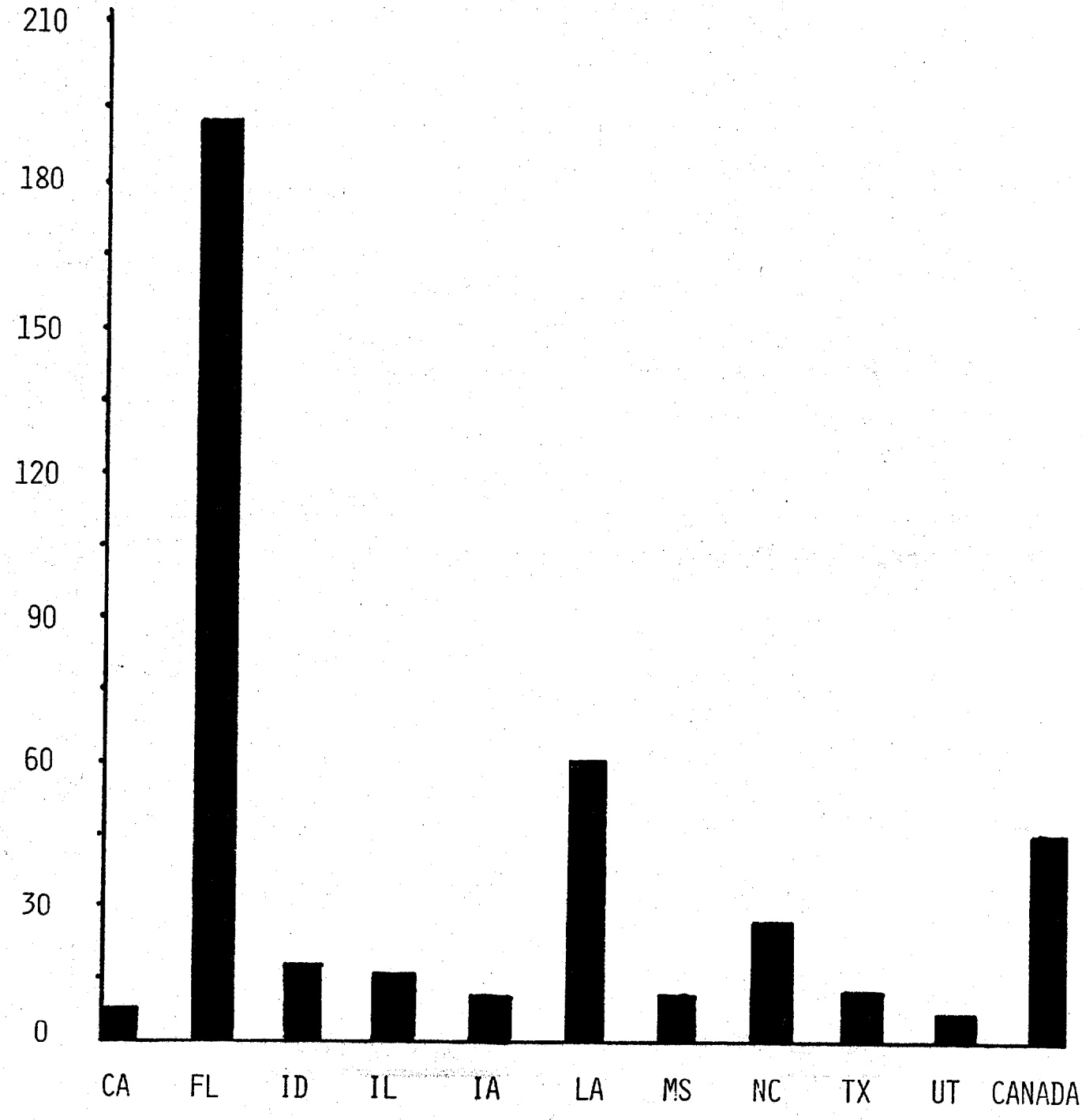
LOCATION OF WET-PROCESS PHOSPHORIC ACID CHEMICAL PLANTS AND BY-PRODUCT GYPSUM STACKS



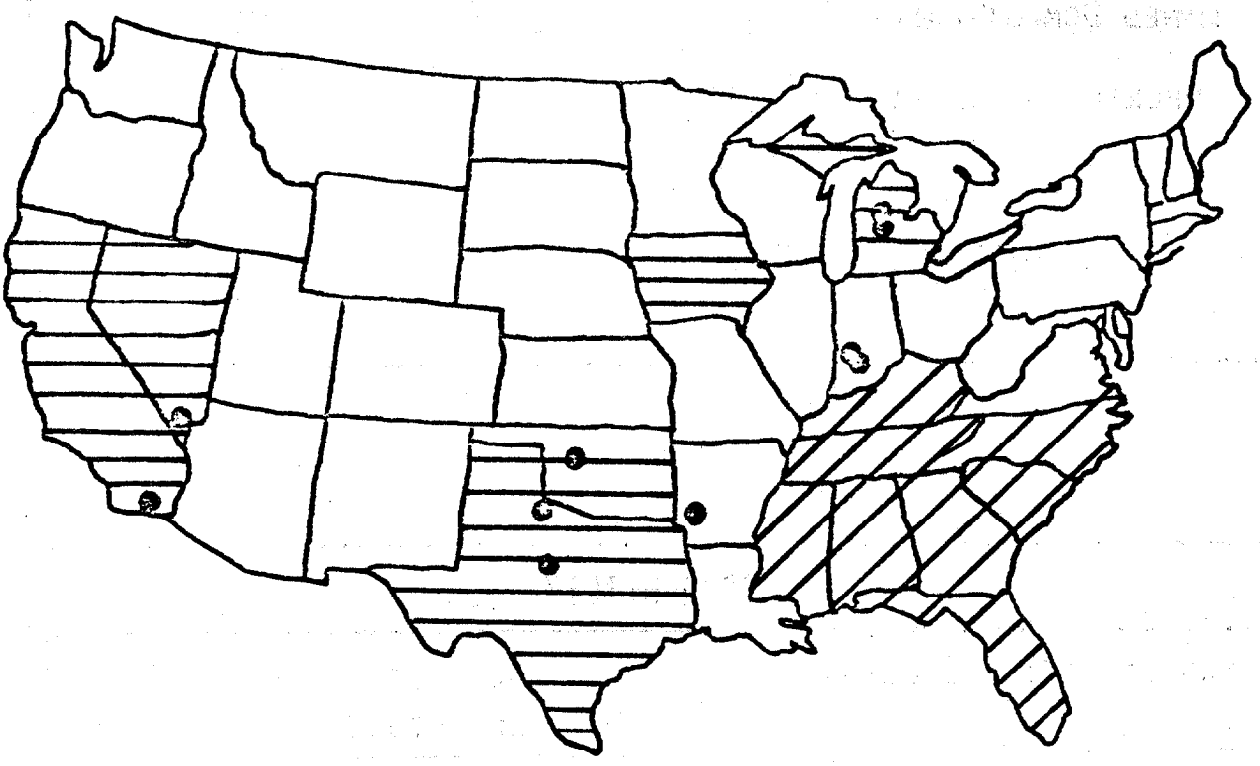
NATIONAL DISTRIBUTION OF STOCKPILED BY-PRODUCT GYPSUM

FOR THE PERIOD 1973-1980

(1,000,000 SHORT TONS)



GYPSUM MINES IN THE UNITED STATES IN 1980



● THESE 10 MINES ACCOUNTED FOR 47% OF THE TOTAL

THESE STATES ACCOUNTED FOR 71% OF THE TOTAL GYPSUM MINED

THESE STATES HAVE NO CURRENT GYPSUM MINING

GYPSUM 1979

	Million Tons	Value $M
Mined Domestically	14.7	$101
Imported - 93% (Canada 74%) (Mexico 19%)	7.8	
TOTAL CONSUMPTION	22.5	

GYPSUM UTILIZATION

Product ($1.1 Billion)	Gypsum Used Million s-tons	%
Wallboard	16	71
Portland Cement (Retarder)	4.2	19
Agriculture (50% By-product Gypsum)	1.5	7
Plaster	.8	3
	22.5 Total Consumed	

CHEMICAL NATURE OF PHOSPHOGYPSUM AS PRODUCED BY VARIOUS WET PROCESS PHOSPHORIC ACID PROCESSES

by

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INTRODUCTION

The advent of industrial pollution, created in the 1960's, was followed by concerted efforts by government and industry to reach a reasonable and practical goal for attaining pollution abatement. In the 1970's, the public was convinced that modern technology - the creator and culprit of such pollution - had proven its capabilities in effectively and economically solving the problem of pollution. Great and bold strides in water and air pollution abatement were successfully taken by industry and government alike.

Against a small group of disillusioned and radical environmentalists and a similar group of irresponsible, "gung-ho" industrialists, the great majority of the people recognized that great environmental improvements were and are being made. The public today not only sees this progress made in the areas of air and water pollution, but also feels the "pinch" and the accompanying social and economic repercussions of this type of life improvement. After all, it was the public that ultimately paid for this; it was also the public that took the hardships of life changes whether due to life-style or to employment.

The phosphate mining and processing industry in Florida - this giant food producer in the USA and the world - through its responsible leadership and proper backing and understanding by the state and federal governments, has been able to go through the 60's and 70's and is prepared to meet the challenges of the 80's. Such accomplishments as SO_2 emission compliance with best available technology, zero effluent digcharge, neutralization and pH control of waste waters, fluorine scrubbing, slimes pond design and control, reclamation of disturbed lands, etc. are all accomplishments attained through a combined and conscientious effort of the industry and government. Each of these accomplishments involved not only a substantial expenditure of money but hard work on the part of technologists and engineers to develop the methods; hard work on the part of sociologists and economics to evaluate the socio-economic impact; hard work on the part of the government to find legal means of compliance that can be realistic and attainable whether these were new permissible emissions or now compliance schedules.

And the upward fight is still going on. In human health new medicines cure old diseases; then suddenly new diseases create the need for new cures. It appears to be like the mythical Sisyphean effort. In phosphates we made significant inroads; we solved the air pollution in order to create water pollution problems. It appears now that we solved our water pollution problems but we have ahead of us a major problem of solid waste - "phosphogypsum." Like Sisyphus, we cannot rest for one moment; we have to pick up the ball and start climbing again. The fact that today, in this room, we have assembled technologists and engineers from all over the world to discuss this subject, is a living proof of Technology's desire and capability to solve this problem.

This paper will attempt to present, in a general overview manner, the present state-of-the-art on phosphogypsum waste, the processes available for making phos acid and then the relationship to this waste. Finally, we will attempt to look into the future analytically and outline the thinks that have to be developed to solve this problem.

THE PRESENT STATE-OF-THE-ART

The present state-of-the-art of phosphogypsum, as it relates to the Fertilizer Industry, offers the following three alternates:

(I) Waste Disposal

(2) By-product Exploitation

(3) Replacing Sulfuric Acid Acidulation with other mineral acids not precipitating calcium in a solid form

From the three alternates, solid waste disposal is the only method used exclusively in the United States and in most of the world.

Waste Disposal

In the past, disposal was practiced by pumping the waste in the form of a slurry directly into a body of water - preferably the sea. There, eventually, the soluble $CaSO_4$ combined with existing currents and this was considered to be sufficient for dispersing the waste. This practice has since been abandoned as inefficient and detrimental to the environment. The present widely used practice consists of containing the gypsum at the site by employing the so-called "peripheral discharge" technique whereby the gypsum slurry is pumped on top of a specially designed, earthy-type solids-liquid separating field (commonly known as a "gyp-pile" or "gyp-stack"). The liquid component readily separates from, the fast-settling gypsum solids. The liquid - mostly acidic water - is then recycled after it is cooled into a cooling pond. Figure shows a typical arrangement of this system. This system as applied today has the following advantages:

(1) It represents the best, fully developed, technology available.

(2) It is economical.

(3) It is feasible and operational.

(4) It is capable of using a closed circuit, zero discharge, system.

However, this system has the following disadvantages:

(1) It is aesthetically unacceptable.

(2) It can create acidic run-off water streams.

(3) It leaves a pile exposed to a radium emission, the long-term effects of which are presently unknown.

(4) If not operated properly with controls or built with safe design standards, it can create a serious dike break.

Regarding the much-discussed and argued radiation, it is very important that as scientists and engineers (whether employed by the government for setting or enforcing compliance regulations or employed by the industry for production) we face the true, pragmatic dimension of the problem. This means that we have to do the following:

(1) Inform the public without alarming.

(2) Get the facts straight.

(3) Give Technology and Industry proper time and backing to solve the problem.

We know that during the acidulation of rock, uranium is quantitatively dissolved and reports with the acid. A number of uranium extraction plants are already in operation. However, radium, a natural decay product of uranium, is precipitated with the gypsum sd $TsD\emptyset_4$ and can product radioactive emissions such as radon gas, etc. The literature reports the following measurements:

TABLE 1. Radiation - nCi/Kg

Rock Origin	Rock As Is	Theoretically Computed Gypsum	Actually Measured Gypsum
Florida	35.0	23.5	20
Morocco	37.5	25.0	31
Togo	35.0	23.0	20
Kola	3.0	2.0	2
Natural Gypsum	----		1

Against this background, some countries reportedly have established some characterization limits as follows:

Radiation	Regulation/Characterization
< 10 nCi/Kg	Free Use
10-25 nCi/Kg	Compulsory declaration
> 25 nCi/Kg	Compulsory registration

From all the above discussion it can be readily concluded that while we have to admit that we have a problem, the true dimensions, parameters, and solutions to this problem would require a careful and extensive study. At the same time, we can also conclude that the present state-of-the-art for phosphogypsum waste disposal may not be satisfactory and cannot be maintained as such in the future without significant changes in the total disposal system. In addition, the other two alternates of by-product exploitation and sulfuric acid replacement have to be thoroughly evaluated.

By-product Exploitation

The literature is full of processes and patents describing various methods and technologies capable of producing a number of by-products from phosphogypsum. A limited but growing number of full-scale plants producing sulfur by-products and sulfuric acid, cement, wallboard and other building material exist in Europe, Japan and other countries. We know that the thermal decomposition of phosphogypsum to produce sulfur, SO_2 and other by-products is technically feasible. Purification of gypsum to produce wallboard material is also a reality. Unfortunately, in the United States no such full-scale plant operation exists. In the late 60's the Elcor Corp. in Texas attempted to do that at a time when the sulfur prices were climbing. Unfortunately, this venture failed. With the present sulfur prices, a number of companies and agencies were re-evaluating this project.

The reasons given for the slow development of sulfur and cement by-products from phosphogypsum were in the past convincing. The abundance of inexpensive high quality gypsum in the USA, coupled with the co-existing inexpensive transportation, were inhibiting such a development. This situation, however, has changed in the last five years. Natural gypsum companies having to ship their raw materials from, say, Nova Scotia to Jacksonville, Florida, started looking carefully at the "Florida Phosphogypsum Mountains." Similarly and for the same reasons, the fertilizer producers, under the heavy burden of a high-priced sulfur, re-evaluate thermal decomposition.

Zellars-Williams, Inc. recently received a grant from the Florida Institute of Phosphate Research to provide a complete technical and economic analysis of the most promising available processes. Capital, operating cost and profitability will be evaluated and a bench or pilot scale demonstration of the optimum processes will be carried out.

In conclusion, the alternate of by-product exploitation from phosphogypsum even though not yet developed in the USA, appears to be the best long-term, practical and perhaps economic solution, especially as it relates to sulfur and sulfur compounds required by the Fertilizer Industry to make sulfuric acid. It is intersting to note here that in the next decade the amount of by-product gypsum of a better quality, originating from the SO_2 scrubbing of coal-fired power plants, will be tremendously increased. Thus, unless the Fertilizer Industry accelerates its development of phosphogypsum, they may find themselves in competition with the power plants.

Replacing Sulfuric Acid

It is well known that the phosphogypsum problem is the product of existing phosphoric acid technology. For every ton of P_2O_5 we produce we co-produce about five tons of gypsum. The paradox that exists in our technology is that the SO component of sulfuric acid "goes for the ride." Chemically, we need the hydrogen ion and the energy to make H_3PO_4. The SO_4 component enters the picture because we designed our plants as large filtration plants to filter our the residue of calcium,

namely $CaSO_4$. The nitrophos technology has been investigated extensively. Similarly, the technology of hydrochloric acid acidulation has been studied. In both of these, the calcium impurity stays with the phosphoric acid as the corresponding soluble salt of Ca. Our efforts to fully develop either one of these processes failed because the same philosophy of filtration keeps creeping in.

On a long-term basis and as it relates to a specific case, this technology cannot be ignored. Solvent extraction, ion exchange and fractional crystallization should be perhaps looked upon again if we have to stay away from sulfur either because of price or because of gypsum disposal. However, with the present state-of-the-art and presently existing developments, replacing sulfuric acid can be a long-term uphill fight. The energy provided by sulfur to produce SO_2 is of paramount importance to the Fertilizer Industry as it exists today in order to produce part of its total energy and steam requirements. In addition to this, a nitric or chloride acidulation technology may create new pollution problems - this time with the disposal of such corrosive chemicals as $CaCl_2$ and $Ca(NO_3)_2$.

In conclusion, it appears that the present state-of-the-art shows that:

(a) The sulfuric acid technology and thus the co-production of phosphogypsum is going to be with us for quite a while.

(b) Phosphogypsum disposal as presently done has to be improved or otherwise abandoned in the future.

(c) Phosphogypsum by-product exploitation will have to be developed as part of the new disposal with perhaps emphasis in the production of sulfur or sulfurous compounds for producing H_2SO_4.

AVAILABLE PROCESSES AND THEIR RELATION TO PHOSPHOGYPSUM

It should be pointed out here that all the processes available for phosphoric acid manufacture have been developed primarily for obtaining high P_2O_5 recovery and high filtration rate. This is understandable since phosphoric acid is the raw material for fertilizers and therefore the efficiency and cost of the phosphoric acid plant is the main concern. As a matter of fact, the filtration characteristics of the produced gypsum determine the size and type of the filter equipment, the cost of which as an integrated installed unit operation may comprise as much as 50% of the total plant cost. These two parameters alone work against any purification of the gypsum residue. In addition to this, the recently introduced processing of low quality rock forces further this design toward precipitating a lot of undesired impurities with the phosphogypsum waste. Based on these two parameters, the existing phos acid technology still varies around the optimization of the acid manufactured rather than that of the gypsum. Numerous processes have been introduced or promoted for the "cleaning" of phosphogypsum after acid production, primarily in countries where natural gypsum, as a raw material for wallboard and cement retarder, was in short supply.

In this part of our paper we would like to present the conventional phosphoric acid processes that are available today and emphasize their relationship to the quantity and quality of the gypsum produced. Following this, we will attempt to present a number of other processes that are supplemental or "add-on" modifications to the main phos acid process and aim at optimizing the quality and by-product recovery of phosphogypsum. Naturally, we will present a limited number of them because of the limitations of time for this presentation.

Conventional Phos Acid Methods

Even though the commercial name or trademark may be different, there are essentially only three basic conventional processes presently used all around the world. We will use, understandably, the chemical names of these processes to avoid any complaints of partiality.

These processes are: dihydrate, hemihydrate, and a hemi-dihydrate combination otherwise known as the recrystallization hemihydrate process.

Di-hydrate Process (DH)

This process is widely used in the world. It is the one process most used in the USA. Reportedly, in the past at least, it required a low capital, had a very low production cost and had a great flexibility in using various qualities of phosphate rock. It is capable of producing an acid from which uranium can be extracted. It is designed for a 28-30% P_2O_5 acid and a high filtration rate which for Florida rock was as high as 1.0-1.2 TPD P_2O_5/ft^2. Against these advantages, however, it is still the process that makes the dirtiest gypsum requiring high free sulfuric acid and yielding a cake with as much as 0.5-1.0% P_2O_5 (dry

basis) in the filter cake. Figure 2 shows a typical dihydrate process. Such a process is commercially known as Prayon, Dorco, Fissons, Lurgi, etc.

Typical phosphogypsum analysis forms a good quality rock under good operating conditions as follows:

TABLE II. Typical Di-hydrate Phosphogypsum Analysis

CaO	=	32.50%
SO_3	=	44.00
P_2O_5	=	0.65
F	=	1.20
SiO_2	=	0.50
Fe_2O_3	=	0.10
Al_2O_3	=	0.10
MgO	=	0.10
Cryst. H_2O	=	19.00 (approx.)

Its yield of dry phosphogypsum is about 4.9 T/ton of P_2O_5 produced. This gypsum, as is, cannot be used without pre-treatment or cleaning for either the wallboard industry or cement. It will require washing, lime neutralization, calcination and granulation to assist in solids handling and feeding of the cement kiln.

Hemihydrate Process (HH)

Next to the dihydrate process, this is the one process relatively widely used in Europe, Japan and Africa. It has drawn considerable attention recently due to its energy savings in producing 40-52% P_2O_5 acid.

Reportedly, it is of a higher capital for attack and filtration, has a higher production cost mainly due to higher production and maintenance costs, and it can used a coarse phosphate rock material. It is designed for purer phos acid product with higher P_2O_5 concentration (as high as 52%) and with low post-precipitation properties. Steam and energy savings are reportedly high. Presently there is no fully developed method for extracting uranium out of this process's acid. Due to the higher acid concentration and the resulting high viscosity (as well as finer crystal) filtration rates are considerably lower than those obtained by the dihydrate process. Against this disadvantage, however, the energy savings of this system can amount to about $20/ton P_2O_5 if not more. Figure 3 shows a typical flowsheet of this process.

Typical phosphogypsum analysis resulting from a good quality rock under good operating conditions is as follows:

TABLE III. Typical Hemihydrate Phosphogypsum Analysis

CaO	=	36.9%
SO_3	=	50.3
P_2O_5	=	1.5
F	=	0.8
SiO_2	=	0.7
Fe_2O_3	=	0.1
Al_2O_3	=	0.3
Cryst. $H_2Ø$	=	9.Ø% (approx.)

It should be noticed that even though this gypsum is higher in $CaSO_4$ content due to low content in crystalline water, its impurity level is still not satisfactory. The process yield in dry phospho-gypsum is about 4.3 T/ton P_2O_5 produced. Such processes are available and in operation in Europe, Japan, Africa, etc. and are commercialized under the trade name Fissons, Lurgi, Nissan, etc. This phosphogypsum will still require some washing, lime neutralization and granulation to assist in solids handling and feeding of the kiln.

Hemi-Dihydrate Process (HDH)

This process is perhaps the only one that, based on current technology, combines the advantages of the dihydrate process with the requirements of a clean gypsum residue as produced by the hemihydrate method. There are a number of installations of this process in Europe and Japan. It is presently economically attractive because it combines the savings of producing 4Ø-52% acid with the advantages of making a very clean phosphogypsum.

Reportedly it requires a higher capital investment; but when such investment is considered as part of an integrated phos acid-gypsum plant, it appears to be very attractive. Production and maintenance costs, as expected, are still higher than that of dihydrate; but when considered in relation to the energy savings of a concentrated acid and the very clean phosphogypsum procued, the overall economics may look very promising - if anything, for the future at least.

Figure 4 shows a typical flowsheet of this process. This process is commercially promoted by Fissons, Lurgi, Nissan and others. A typical phosphogypsum analysis resulting from a good quality rock under good operating conditions is as follows:

TABLE IV. Typical Hemi-Dihydrate Phosphogypsum Analysis

CaO	=	32.20%
SO_3	=	46.50
P_2O_5	=	0.25
F	=	0.50
SiO_2	=	0.40
Fe_2O_3	=	0.05
Al_2O_3	=	0.30
Cryst. H_2O	=	20.00% (approx.)

The process yield in dry phosphogypsum is about 4.9 T/ton P_2O_5 produced. This gypsum still requires some washing with lime; and because of its dihydrate nature, it will also require calcination and granulation.

Phosphogypsum Cleaning or By-product Recovery Processes

As mentioned before, none of the available phos acid processes is capable of producing a clean phosphogypsum product that can be used "as is" as wallboard or other raw material. There are numerous available processes and patents suitable for cleaning phosphogypsum, to make either wallboard material or "plaster of paris." Similarly, there is a great number of processes claimed to be fully developed and economically attractive for manufacturing cement and sulfuric acid from phosphogypsum. We have already mentioned that Zellars-Williams, Inc., under contract for the Florida Institute of Phosphate Research, is carrying out a comprehensive investigation in determining the most optimum technical and economic processes that can be used in Florida. Therefore, we will like to take this opportunity and invite those companies or firms that desire to have their process evaluated to submit to us pertinent process data.

Due to the limitations of time and space, a limited number of such processes will be discussed below.

Donau Chemie Ag Process

Figure 5 presents the main elements of this process which is claimed to be suitable for cleaning phosphogypsum prior to calcination. In this process[5,6] the gypsum slurry from the phos acid plant is purified in a two-stage, counter-current hydro-cyclone operation giving a 20-fold washing effect. The classified and purified neutralized gypsum passes over a system of drum filters and centrifuges for further dewatering prior to drying in a flash dryer. The dry product is then calcinized in a rotary calciner to the desired hemihydrate or anhydrite form. Reportedly, the product's purity is 99% $CaSO_4 \cdot 0.5H_2O$ and can be used for plaster blocks of 6, 8 and 10cm thickness.

Rhone-Poulenc Process

Figure 6 presents the Rhone-Poulenc phosphogypsum cleaning process, incorporating flotation and a two-step classification. It is shown that this process employs washing and lime neutralization as a first step. If the phosphogypsum is reasonably pure (high grade apatite feed), further purification may be unnecessary as the main impurities are soluble and are removed with the water when the slurry is filtered and centrifuged prior to calcination. However, if purification is necessary, this can be done in one of two ways - either hydrocyclone washing and classification or flotation can be employed. Reportedly, with hydrocyclone the gypsum recovery is 70-90% and the soluble impurities removal over 90%. When flotation is employed, the removal of impurities is 85-90% and the gypsum recovery 90-96%.

Muller-Kuhne Cement - H_2SO_4 Process[5,6]

Figure 7 shows the Muller process. In it, gypsum is ground and blended with coke and clay and then thermally decomposed in a kiln as shown. The reactions taking place are:

(1) $CaSO_4 \rightarrow CaS + 2CO_2$

(2) $CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$

(3) $2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2$

To compensate for side reaction of: $3CaS + CaSO_4 \rightarrow 4CaO + 4S$

$CaS + 2SO_2 \rightarrow CaSO_4 + 2S$

a slight excess of coke is used. The strength of the cement by-produce made by this process is related to the P_2O_5 content of the phosphogypsum used.

OSW-Krupp Cement - H_2SO_4 Process[5,6]

Figure 8 shows a similar process capable of making Portland cement and sulfuric acid from phosphogypsum. This process claims that for a 1000 TPD capacity to total plant investment (including phosphogypsum handling and H_2SO_4 storage) is $50MM (1976). A SO_2 conversion of 99.5% is guaranteed. Portland cement made by this process conforms to DIN standard 1164.

FUTURE OUTLOOK AND NEEDED DEVELOPMENTS

It is quite obvious that the future of phosphogypsum, whether viewed as a disposal or as a recovery problem, is critical to the very existence and economics of the wet process phosphoric acid industry.

For years we have designed our plants as filtration plants with maximum P_2O_5 recovery and minimum capital aimed at recovering the P_2O_5 product only. It is now time to take a hard look at gypsum not as a waste product but instead as a valuable by-product. A couple of years ago we had the same situation with the fluorine waste. We have successfully made inroads into this problem with the development of the fluosilicates. If we are motivated enough and look into the future perceptively as to what is coming, we will then be able to prepare ourselves.

Research and development as well as up-to-date economics are urgently needed to realistically appraise the technology of phosphogypsum. Industry should realize that we are going through a transition period and that the economics of P_2O_5 have to be re-evaluated in relation to the phosphogypsum by-product, either as a disposal cost (negative cash flow) or as a by-product exploitation (positive cash flow). As we mentioned before, if we do not do this work now, we may find out later that it may be too late or much more difficult. We should not ignore the fact that if coal were to be used extensively by the power plants (as the present energy situation indicates) the amount and quality of recovery-gypsum produced by these plants can be in competition with the phosphate industry. New phosphoric acid processes have to be developed urgently that either incorporate the production of clean phosphogypsum or rely on its by-product value to pay for the clean-up that may be required. At the same time, the physical chemistry of the crystallization of $CaSO_4$ should be studied. A radium profile should be obtained from the rock to the acid and the various size fractions of gypsum. Classification of the fine fraction of gypsum (reportedly containing more Ra) should be studied.

In developing countries using low analysis fertilizers with relatively short distance distribution networks, the use of single superphosphate should be looked upon as a means of providing them with the P_2O_5 source without having to suffer the pollution penalty and high capital cost of a phos acid plant.

At the same time, government and respective agencies have to realize that since no immediate danger exists to the public's health, a realistic schedule, proper incentives and industry's support are all elements necessary for the Fertilizer Industry to go through this transitional technological crisis.

ACKNOWLEDGMENT

The author wishes to express his thanks to the management of Zellars-Williams, Inc. for permission to present this paper.

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AUTHOR'S BIOGRAPHY

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TABLE I
RADIATION - nCi/kg

ROCK ORIGIN	ROCK AS IS	THEOR. COMP. IN GYP.	ACTUAL MEAS. IN GYP.
FLORIDA	35.0	23.5	20
MOROCCO	37.5	25.0	31
TOGO	35.0	23.0	20
KOLA	3.0	2.0	2
NAT.GYPSUM	–	–	1

TABLE II

TYPICAL DI-HYDRATE PHOSPHOGYPSUM ANALYSIS

CaO	-	32.50 %
SO_3	-	44.00 %
P_2O_5	-	0.65 %
F	-	1.20 %
SiO_2	-	0.50 %
Fe_2O_3	-	0.10 %
Al_2O_3	-	0.10 %
MgO	-	0.10 %
CRYSTAL. H_2O	-	19.00 % (APPROX.)

PHOSPHOGYPSUM YIELD - 4.9 T/TON OF P_2O_5

TABLE III

TYPICAL HEMI-HYDRATE PHOSPHOGYPSUM ANALYSIS

CaO	-	36.9 %
SO_3	-	50.3 %
P_2O_5	-	1.5 %
F	-	0.8 %
SiO_2	-	0.7 %
Fe_2O_3	-	0.1 %
Al_2O_3	-	0.3 %
CRYSTAL. H_2O	-	9.0 % (APPROX.)

PHOSPHOGYPSUM YIELD - 4.3 T/TON P_2O_5

TABLE I V

TYPICAL HEMI-DI-HYDRATE PHOSPHOGYPSUM ANALYSIS

CaO	-	32.20 %
SO_3	-	46.50 %
P_2O_5	-	0.25 %
F	-	0.50 %
SiO_2	-	0.40 %
Fe_2O_3	-	0.50 %
Al_2O_3	-	0.30 %
CRYSTAL. H_2O	-	20.00 % (APPROX.)

PHOSPHOGYPSUM YIELD - 4.9 T/TON P_2O_5

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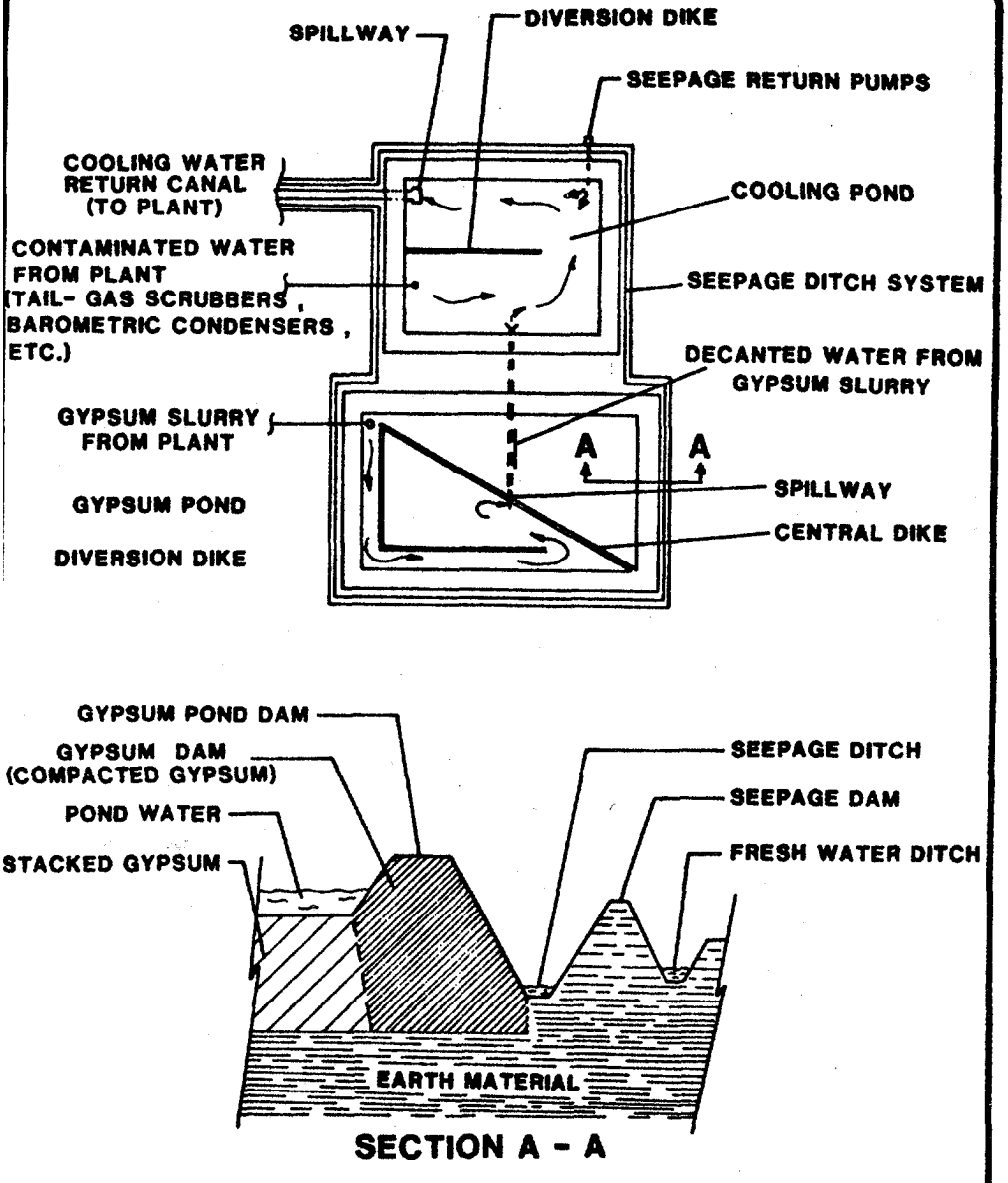


FIGURE 1. TYPICAL GYPSUM PILE & LAYOUT

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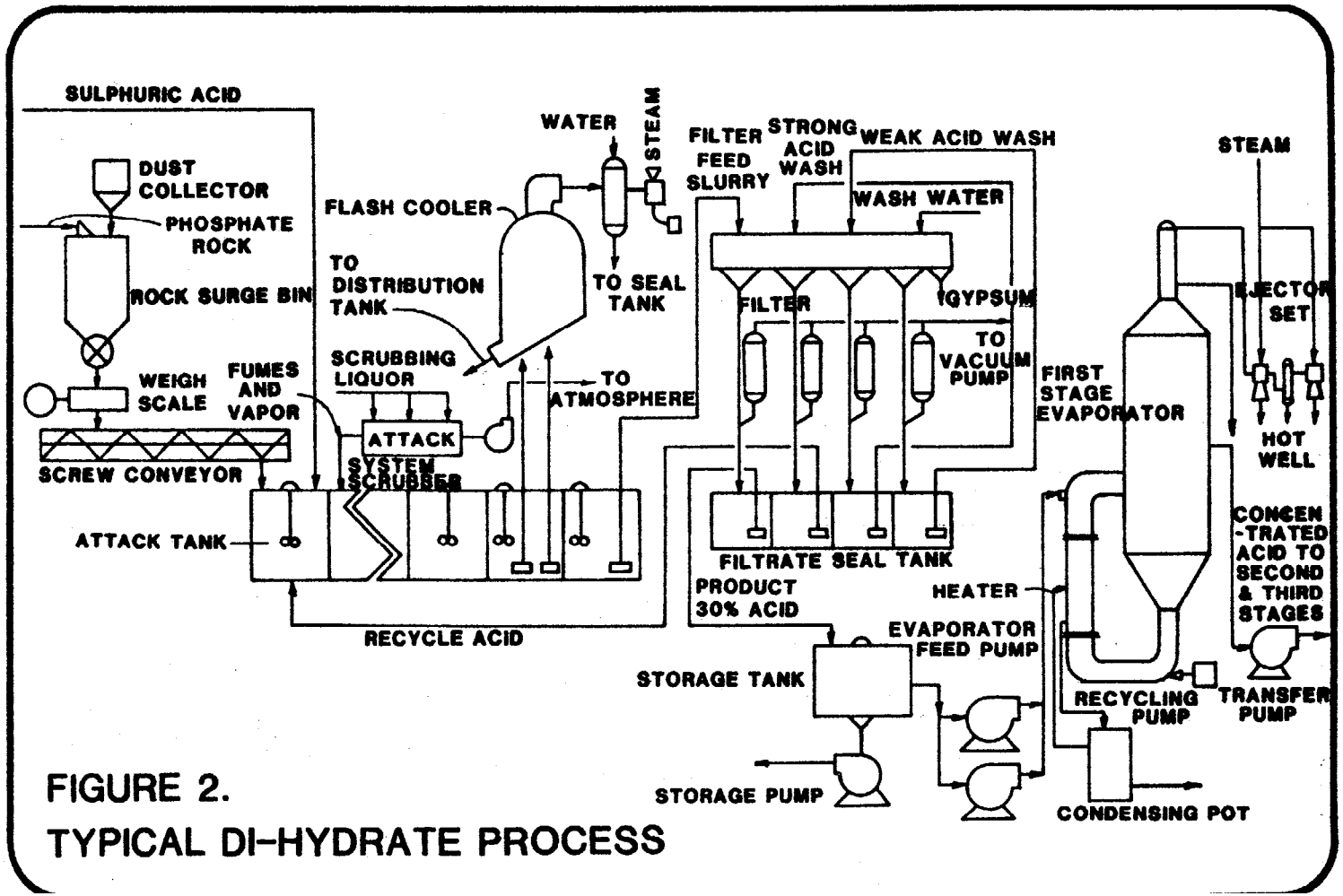


FIGURE 2.
TYPICAL DI-HYDRATE PROCESS

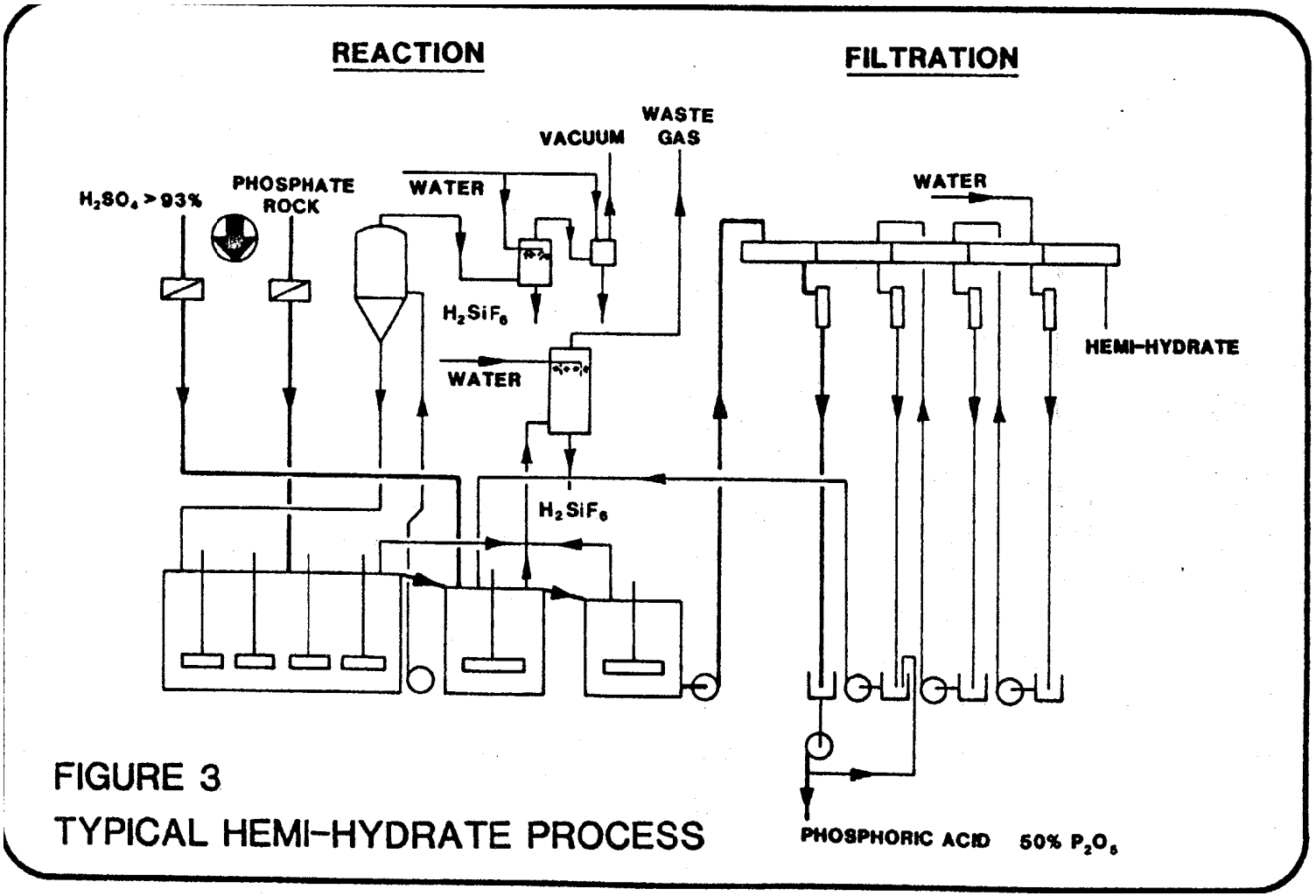


FIGURE 3
TYPICAL HEMI-HYDRATE PROCESS

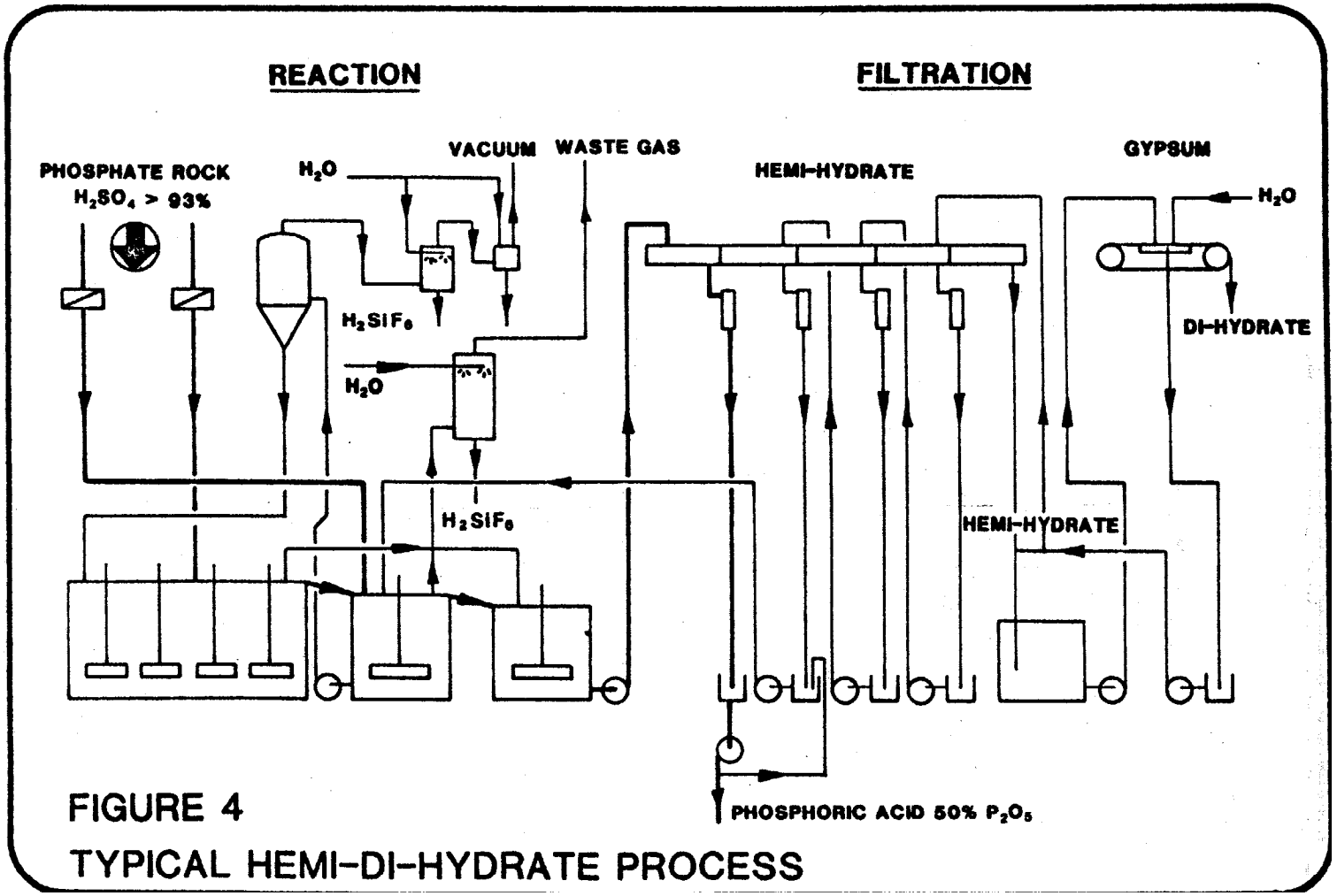


FIGURE 4

TYPICAL HEMI-DI-HYDRATE PROCESS

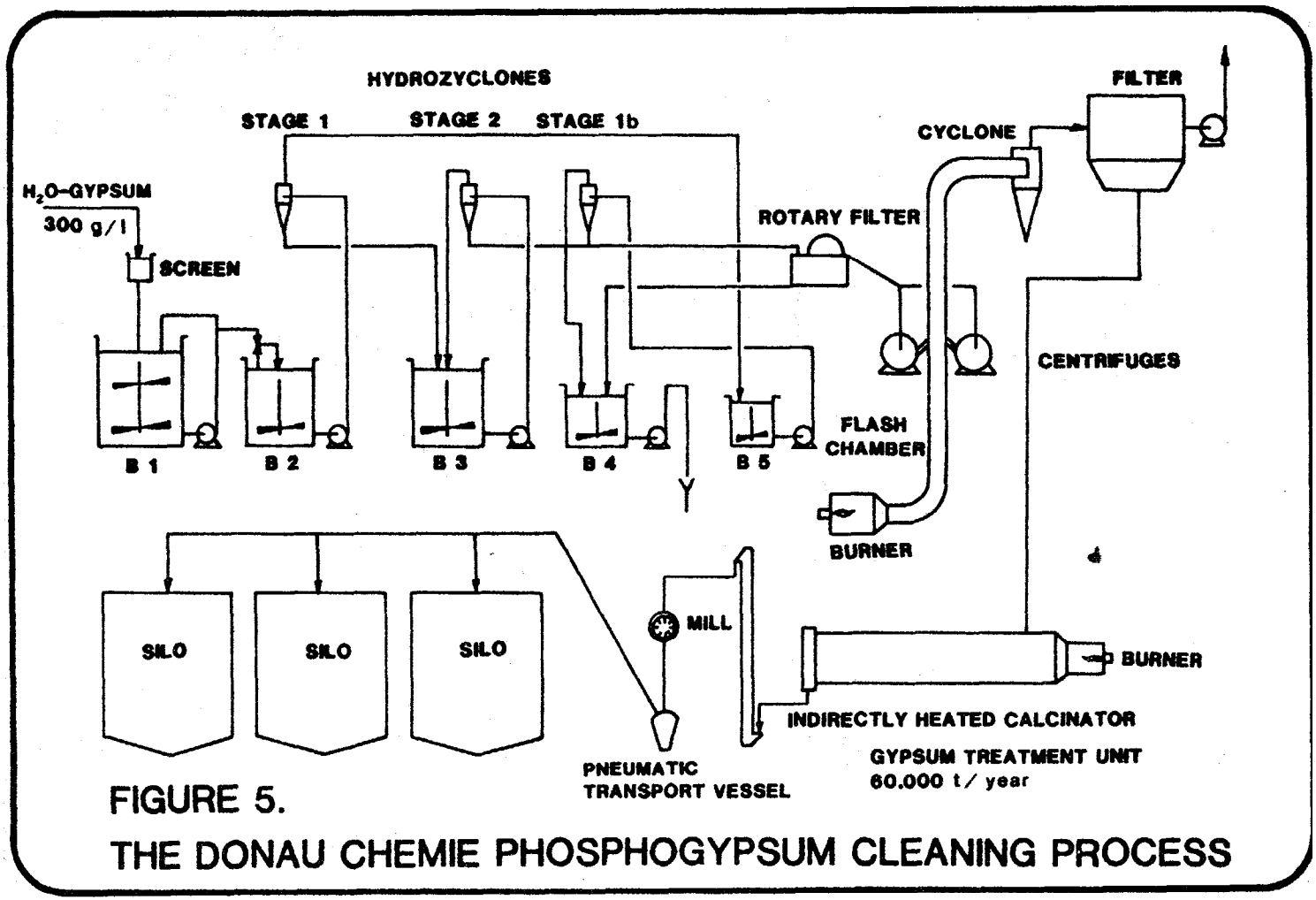


FIGURE 5.

THE DONAU CHEMIE PHOSPHOGYPSUM CLEANING PROCESS

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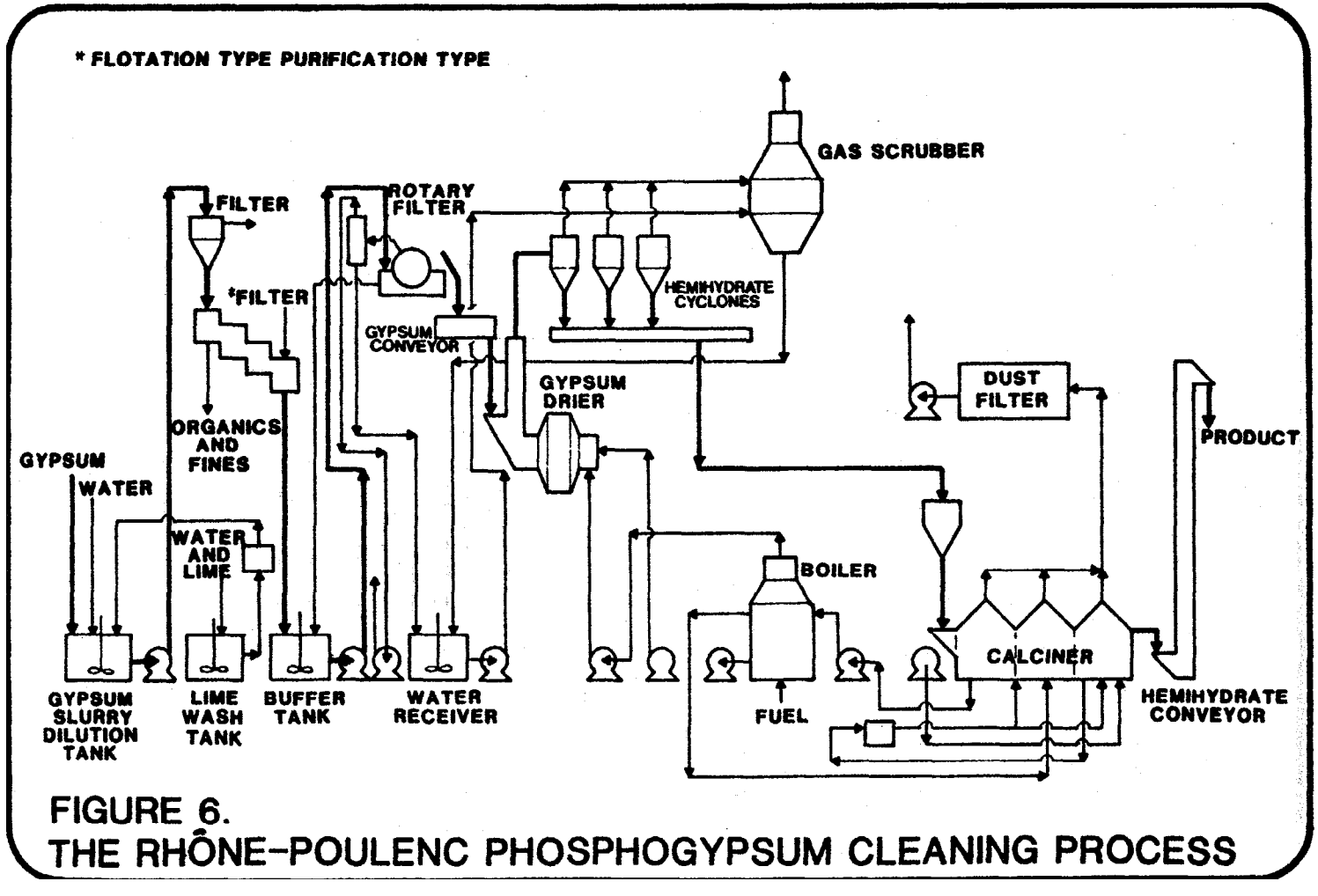


FIGURE 6.
THE RHÔNE-POULENC PHOSPHOGYPSUM CLEANING PROCESS

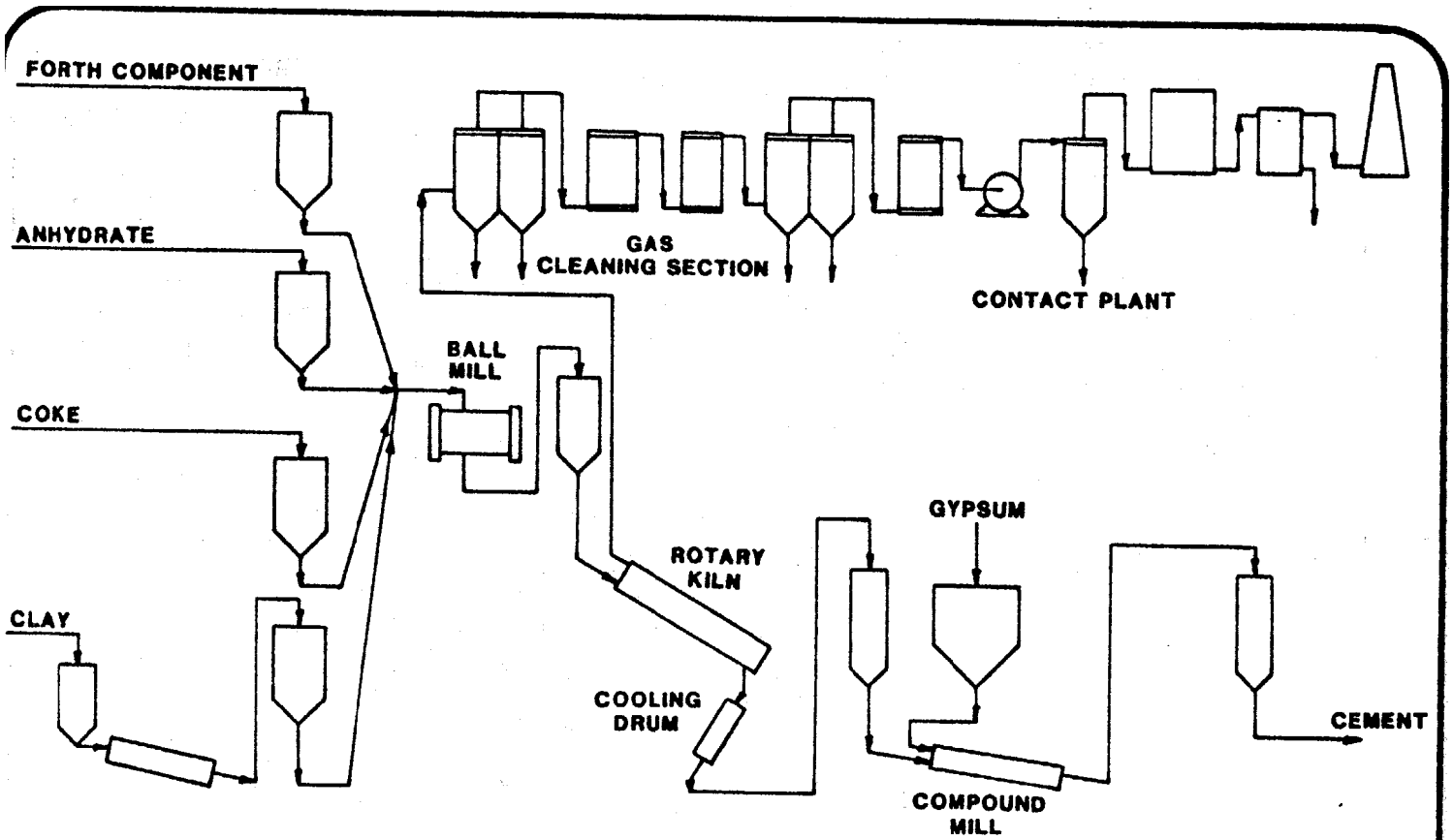


FIGURE 7. THE MÜLLER-KÜHNE CEMENT-H_2SO_4 PROCESS

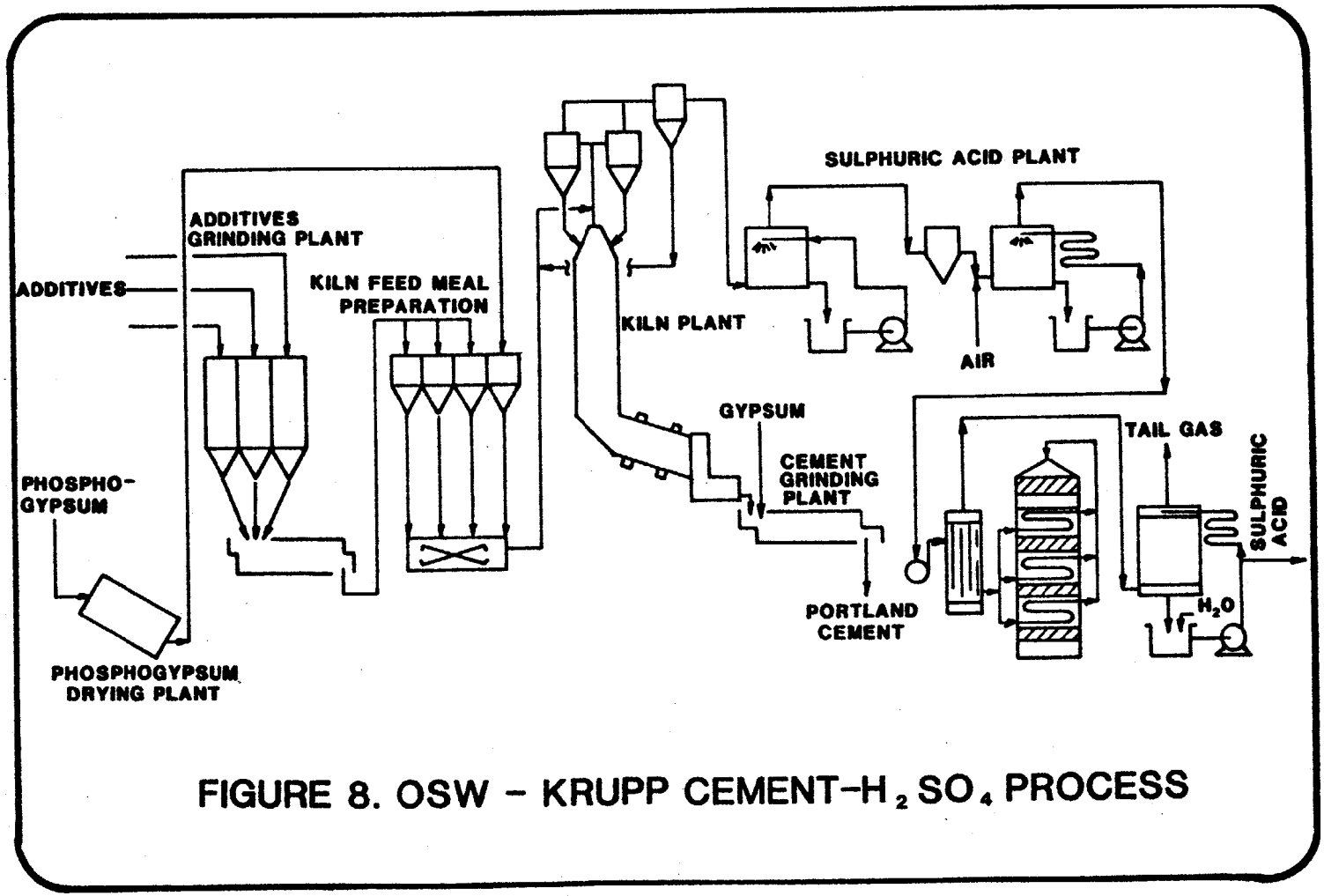


FIGURE 8. OSW - KRUPP CEMENT-H_2SO_4 PROCESS

NISSAN HEMI PHOSPHOGYPSUM

by

Walter E. Goers
The Heyward - Robinson Co.
New York, New York

INTRODUCTION

The manufacture of wet process phosphoric acid by the reaction of phosphate rock with sulfuric acid is a process practiced for the past 60+ years. Calcium sulfate with two molecules of H_2O (gypsum) is a by-product of this industry. However the unfortunate fact is that the phosphogypsum obtained as a by-product cannot be used as a substitute for natural gypsum without a costly extensive pretreatment operation. The phosphogypsum contains too high a level of P_2O_5 which interferes with the physical properties of the plaster board.

If by-product phosphogypsum from the wet process phosphoric acid industry was to be used as a substitute for naturally-occurring gypsum, it was apparent that the basic chemistry would have to be modified.

Picture in your mind for a few minutes the country of Japan, a small land mass of approximately 143,000 square miles with a population density of 780. In fact, its capital, Tokyo, is the most populated city in the world -- 14 million. By contrast, the USA has an area of. 3,700,000 square miles with a population density of 58. A second point to consider when thinking of Japan, is that it is a land of relatively few natural resources. Mountains cover six of every seven square miles and only 15% of the land is suitable for farming. Now further imagine having to provide housing facilities, industrial facilities, and highways for all these masses of people without a native source of gypsum for wallboard manufacture and as a cement retarder.

Nissan Chemical faced this challenge some 28 years ago when they first developed what has become to be known as the Nissan Phosphoric Acid Processes. These processes were the first in the world to produce a high-quality phosphogypsum suitable for use by the construction industry with the fertilizer grade phosphoric acid as a by-product.

This paper will briefly outline the Nissan concept for obtaining high-quality phosphogypsum while producing phosphoric acid. The reasons for the high level of P_2O_5 in by-product conventional phosphogypsum making it unusable will be discussed in detail. How the Nissan Process greatly reduces the levels of P_2O_5 will also be presented.

The industrial use of phosphogypsum in the U.S. has been hampered by the abundance of natural sources of gypsum and the economic penalty to make phosphogypsum useable. Even if the present methods of producing P_2O_5 were abandoned in the U.S. and the Nissan Processes were universally adopted, the fertilizer industry would produce gypsum in quantities that by far exceeds demand. I will therefore mention other advantages of the Nissan phosphogypsum that apply to the unreused portion.

Wet Process Acid

The conventional wet process phosphoric acid plant design consists of two basic process steps -- Digestion (Reaction) and Filtration. Digestion conditions are carried out at process parameters which ensure

a stable slurry in the form of calcium sulfate dihydrate (gypsum) crystal. This two-step dihydrate process, while relatively simple in concept, does not produce a phosphogypsum by-product of suitable quality for use in wallboard and as a cement retarder. Very little improvement can be attained in phosphogypsum quality because the operating conditions must be within the ranges of a stable dihydrate parameter, leaving little room for variation.

Nissan realized that the basic wet process phosphoric acid chemistry has to be modified if a high-quality phosphogypsum is to be realized. Thus the development of the Nissan "H" Phosphoric Acid Process in 1952, and the evolved Nissan "C" Concentrated Acid Process.

The Nissan Processes react phosphate rock with sulfuric acid using digestion parameters which produce a stable calcium sulfate slurry with one-half molecule of water (hemihydrate) crystals. The temperature is maintained at 194° - 200°F with a P_2O_5 level of 30% in the acid media in the "H" Process and up to 50% with the "C" Process. If the process chemistry ended with rock digestion, a phosphogypsum of low quality would also be attained after separation by a filter with the Nissan Process.

It is a well-known chemical phenomenon that a recrystallization step greatly enhances solid product quality. The Nissan Processes take advantage of this fact in a step known as "hydration." In "hydration," the hemihydrate crystal slurry is subjected to variation in the process parameters causing the hemi to dissolve and recrystallize in the dihydrate form. As will be demonstrated later in this presentation, this step is the difference between good and poor quality phosphogypsum.

The Nissan Hemi Phosphoric Acid Processes then consist of three basic steps -- digestion, hydration and filtration. There are, at present, some 35 Nissan "H" Process plants in operation or under construction. Some of these plants were selected for the high-quality phosphogypsum product. High-quality gypsum means low P_2O_5 in the gypsum and consequently high yields of P_2O_5 in the wet process phosphoric acid.

P_2O_5 Losses in Phosphogypsum

Now that I have briefly discussed the Nissan Hemi Process, let's take a closer look into the P_2O_5 contamination of phosphogypsum. The P_2O_5 content of phosphogypsum is present in three forms -- water soluble, citrate soluble and citrate insoluble. It is interesting to discuss the reason for the presence of these three forms of P_2O_5 in the phosphogypsum and the operating conditions in a wet process plant that cause the problems.

Water soluble P_2O_5 is present due to the incomplete displacement washing or draining of the mother liquor from the filter cake retained on the filter cloth. The extent of P_2O_5 in this form can be lessened by growing rapidly filterable-readily washable types of gypsum crystals. The amount of wash water and number of counter current washes which can

be economically passed through the filter also will limit levels of water soluble P_2O_5 which can be attained. The origin of the phosphate rock also may play a role in this type of P_2O_5 presence in phosphogypsum.

Citrate soluble P Ø is predominantly present in the form of phosphate substitution in the crystal lattice of the calcium sulfate. This type of P_2O_5 is chemically bound and thus cannot be washed or leached out of the phosphogypsum. Citrate soluble P_2O_5 appears to be fairly well independent of the source of phosphate rock. Its level can be somewhat lessened by attempting to achieve "so called" ideal crystallization conditions. However, at the normal dynamic conditions existing in a typical digester reactor vessel, very little can be done about the phenomenon of phosphate substitution. This type of phosphogypsum P_2O_5 is of the most importance and will be discussed to some degree in a moment.

Citrate insoluble P_2O_5 is in the form of unattached phosphate rock. This type of P_2O_5 loss to phosphogypsum is typically very low in all the commercial wet phosphoric acid processes which have all adopted mechanical techniques to minimize its presence.

(Just a note in summary. As you increase the production rate of a typical phosphoric acid plant beyond its design capacity, the levels of all three forms of P_2O_5 in the phosphogypsum will tend to increase.)

Phosphate Substitution

Getting back to phosphate substitution, the following basic facts have been thoroughly presented in crystallographic literature:

1) $CaSO_4 \cdot 2H_2O$ has been shown to be isotypic to $CaHPO_4 \cdot 2H_2O$; which means that

   (a) the two compounds have the same architecture (packaging arrangement of constituent ions; and

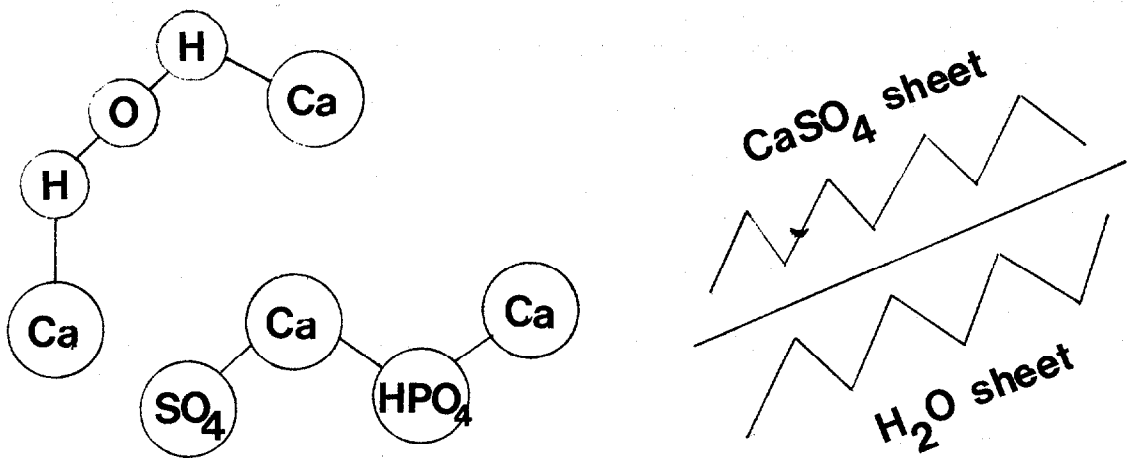
   (b) $HPO_3^=$ ion and the sulfate ion exist in a tetrahedral unit (4 oxygens) of nearly identical size and equal charge; therefore

(2) the isomorphous substitution of phosphate for sulfate is a logical consequence of these structural similarities.

(Note: Phosphate ions $(HPO_4^=)$ have been conclusively proven to be present in the-phosphate slurry matrix.)

The calcium sulfate - dicalcium phosphate substituted molecules are arranged in sheet structures which influences the shape of the crystals. A plate-type crystal is favored by this type of structural arrangement.

The following sketch graphically shows this type of structure:



Factors Affecting Phosphate Substitution

The following digestion operating parameters affect level of phosphate substitution:

(1) Excess Sulfuric Acid. The higher the concentration of free sulfate ions existing in the slurry media, the less likely the phosphate ions substitute for the sulfate ions in the crystal lattice. The level of excess sulfuric acid, of course, is limited by the sulfate coating possibilities of the phosphate rock, the level of free H_2SO_4 in the product phosphoric acid and economics.

(2) P2O5 Content of Mother Liquor. Though not an important effect, the increase in P_2O_5 content of mother liquor entails a higher concentration of $HPO_4^{=}$ ion which will increase the probability of phosphate substitution. The concentration of P_2O_5 in the mother liquor is generally maintained at a level consistent with stable forms of calcium sulfate - either hemi or dihydrate.

(3) Attack Rate. The phosphate rock attack rate is defined as the time the reaction slurry is retained in the digestion vessel. The longer the time in digestion, that is the larger the reaction volume per unit of P_2O_5, the less the tendency is for phosphate substitution. The physical size of the digestion system is, of course, dictated by economic considerations.

(4) Temperature. An increase in reaction temperature will decrease tendency for phosphate substitution. If the temperature could be varied at will, an increase in temperature (i.e. from 50 to 100°C) the tendency for phosphate substitution could be approximately halved. However, at the temperature ranges permitted to maintain stable calcium sulfate hydrates, the effect of temperature is minimal.

(5) Percent Solids. From slurry contents of 0-10% solids, a change in percent solids will have an appreciable effect on phosphate substitution. An increase in percent solids in this range will lessen tendency for phosphate substitution. In the percent solids range typical of commercial phosphate rock digestion systems (35-40%), a change in solids level has a minimal effect on phosphate substitution.

These five digestion operating parameters are the major criteria which can affect phosphate substitution.

In summary, any variation in parameters tending to improve quality of crystallization tends to reduce phosphate substitution.

Nissan Hydration Step

As discussed previously, there is very little a conventional dihydrate phosphoric acid producer can do to lower the level of the citrate soluble P_2O_5 in the phosphogypsum. The dynamic non-ideal digestion reaction conditions, coupled with the rapid crystallization growth, does not allow time for the phosphate ions in solution to get away from the calcium sulfate crystal lattice. If reaction parameters are less dynamic and more conducive to uniform crystal growth, the substitution of the phosphate ions can be more readily rejected by the sulfate ions.

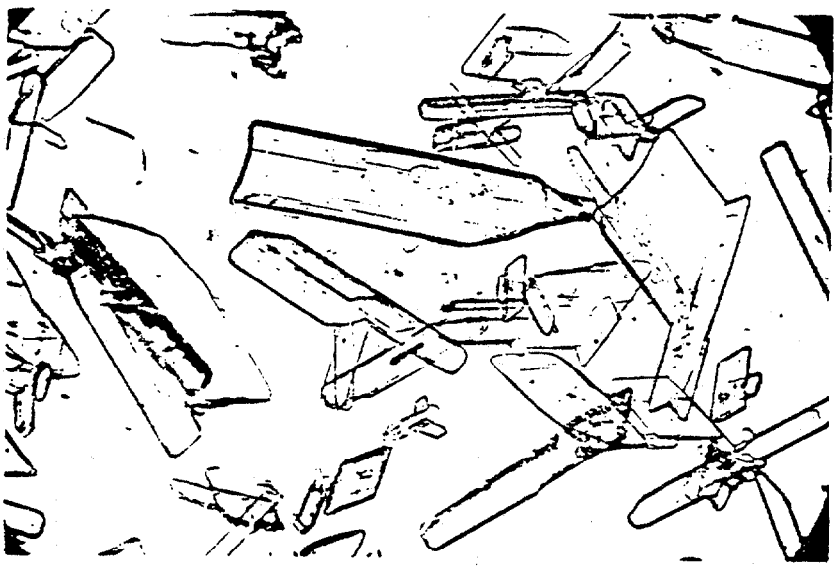
It was this realization that led Nissan Chemical in the early 1950's to add a Hydration Step to the conventional dihydrate process. In the hydration vessel, the reaction slurry is cooled to a temperature where the hemihydrate of calcium sulfate dissolves. Please refer to the calcium sulfate transition diagram. When the hemihydrate crystalline structure dissolves, the occluded phosphate ions pass back into the acid media. The environmental conditions in the hydration vessel are more oriented towards parameters which promote the slower growth of crystals; i.e., less dynamic surroundings. Now, as the calcium sulfate recrystallizes in the dihydrate form, the sulfate ions have an opportunity to oppose the phosphate ion substitution in the crystal lattice. It is this phenomenon which permits Nissan to obtain a gypsum crystal holding very little citrate soluble P_2O_5.

The recrystallization of calcium sulfate attains one further advantage - crystal structure. The dihydrate crystals obtained from the Nissan Hydration Step are large single plate type structures. The dihydrate crystals from a conventional-digestion crystallization step are, in the case of Florida Rock, an agglomeration of small crystals, the so-called "raspberry" appearance, The crystalline structure of the gypsum is also an important criterion for its applicability as a raw material for wallboard.

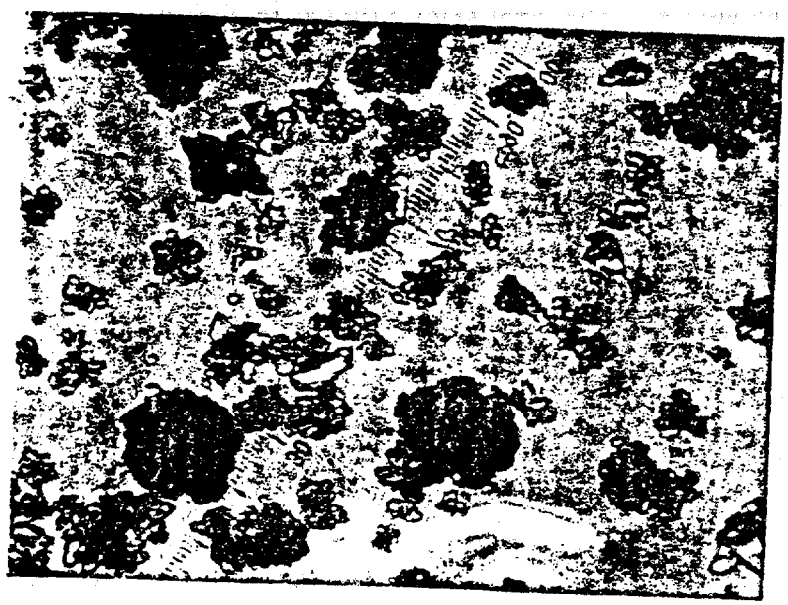
The micro-photographs of Nissan and typical dihydrate gypsum crystals vividly indicate the difference in the crystalline structure.

200 X

NISSAN



DIHYDRATE



Phosphogypsum Comparisons

As discussed throughout this paper, the Nissan Hemi Phosphoric Acid Process was developed to provide a source of high-quality material for the construction industry. The table on the following page compares P_2O_5 analyses of Nissan and typical dihydrate phosphogypsum. The data are for gypsum obtained from Central Florida phosphate rock, and are averages for commercial phosphoric acid plants.

Two other items of interest are indicated in comparison table: W/S P_2O_5 and moisture content.

The considerably lower water soluble P_2O_5 and moisture contents can most probably be explained by the different structure of the calcium sulfate dihydrate crystals. The large single plate type crystals which are a feature of the Nissan Process form a filter cake which is more easily filterable, and more readily washable, and drains to much lower moisture content.

PHOSPHOGYPSUM ANALYSES COMPARISONS

CENTRAL FLORIDA PHOSPHATE ROCK

ITEM	NISSAN	TYPICAL DIHYDRATE
W/S P_2O_5 - %	0.10	0.60
C/S P_2O_5 - %	0.20	0.60
C/I P_2O_5 - %	0.10	0.10
Total P_2O_5 - %	0.40	1.30
Moisture Content -%	18	28

Final Thoughts

Not enough is currently known to determine if a high-quality phosphogypsum can economically replace natural gypsum in the U.S. There undoubtedly will be some local areas where phosphogypsum will present a lower cost or competitive alternative for use by the construction industry. However, even if the assumption is made that phosphogypsum will find little use in plaster board manufacture, there are other potential advantages of the Nissan phosphogypsum -- minimal leaching into underground waters, dry stacking feasibility and Portland cement manufacture.

Many individuals familiar with the phosphate industry are very concerned about leaching of phosphoric acid into underground waters. The Nissan phosphogypsum greatly alleviates this possibility. It is also not likely that the phosphate industry can forever continue to dump phosphogypsum and may very well lend itself more readily to dry disposal methods.

Considerable efforts in the past have been made to develop a Portland cement clinker process from phosphogypsum. Two small commercial plant installations have been constructed and operated. One of the essential criteria for a Portland Cement clinker process from phosphogypsum is that the P_2O_5 content be lower than Ø.5%. The Nissan phosphogypsum thus could be used "as is" without any extensive pretreatment.

In summary, it appears that regardless of the ultimate end use or disposal of phosphogypsum, a high-quality material presents fewer problems in handling.

THE DIHYDRATE METHOD OF PROCESSING ORE PHOSPHATE IN THE PRODUCTION OF NPK FERTILIZER WITH UTILIZATION OF PHOSPHOGYPSUM

by

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INTRODUCTION

The wet phosphoric acid, which is most often obtained by dihydrate methods comprising decomposition of phosphate raw materials with sulfuric acid, is a principal semi-product in the production of complex fertilizers. The dihydrate methods are characterized by enormous amounts of waste phosphogypsum and by a low concentration of produced wet phosphoric acid containing from 27 to 29% by weight of P_2O_5. By way of example, the works fabricating 330,000 tons of P_2O_5 per year in fertilizer products are charged with the waste phosphogypsum in an amount of about 2.2 million tons per year, having moisture of 18-28% by weight from phosphorites and 35-40% by weight from apatites. The waste, the main component of which is dihydrate calcium sulfate, contains also 6-15% by weight mineral impurities adsorbed at the surface of crystals, occluded in crystalline concretions and incorporated into the crystal lattice of calcium sulfate isomorphically or in the form of a solid solution. These impurities, mainly fluorine compounds (1.5-2.5% by weight) and phosphate compounds (0.82% by weight), create disturbances in all hitherto elaborated, very expensive methods for the utilization of phosphogypsum [1,2].

In spite of the constant progress in the technology of fabricating wet phosphoric acid, it is impossible to reduce the total content of P_2O_5 in the phosphogypsum considerably below 1 weight % simply because of physical and chemical principles of the conventional process. Even with such low levels of P_2O_5 in the waste phosphogypsum, the losses involved are of about 50,000 tons per year calculated in terms of phosphate raw material for the production of 330,000 tons of P_2O_5 per year.

Studies of the influence of the ammonium ion on the crystallization of phosphogypsum have shown that the growth of phosphogypsum crystals was three times as large and their homogeneity considerably increased., As a result, the filtration time became shorter by about 30% and total content of P_2O_5 in the waste significantly decreased [2,3,4,5,6,7].

It was proven in the model test, and on the basis of the equilibrium investigations, that the ammonium ion contained in the liquid phase of reaction pulp results in the increase of temperature of equilibrium phase transition:

$$CaSO_4 \cdot 2H_2O \quad -CaSO_4 \cdot 1/2\ H_2O^* + 3/2\ H_2O \qquad (1)$$

by 10-30° with regard to the temperature of traditional dihydrate process [2,5,8,9]. These results indicated that it is possible to produce ammonium phosphate and phosphoric acid in the solution containing up to 40% weight of P_2O_5 by dihydrate method.

On the basis of the found correlation and of examination results on the adsorption of phosphate ion HPO_4^{-2} on the phosphogypsum surface [2,8,9] the method of decreasing the losses of P_2O_5 was elaborated. This method [10] consists in the fact a solution ofsulfuric acid is

introduced into the washing liquids. The presence of H_2SO_4 in the washings causes a desorption of phosphate ions which are absorbed upon the surface of phosphogypsum crystals and in the capillary spaces of the filter cake.

Results of the model investigation on the conversion of phosphogypsum by gaseous ammonia and carbon dioxide to soil chalk and solution of ammonium sulfate have proven the possibility of full utilization of the waste phosphogypsum. The phosphogypsum can be converted in the crystallizer with the forced circulation of the pulp and adiabatic cooling system [11].

The above-mentioned results, together with a new method and apparatus for the utilization of phosphogypsum in the single stage conversion process using ammonia and carbon dioxide, have provided for elaborating a waste-free method illustrated schematically in Figure 2.

The mineral phosphate raw material is subjected to decomposition by the action of an aqueous solution of ammonium sulfate and sulfuric acid according to the following stoichiometric reaction:

$$Ca_5/PO_4/3 + 4H_2SO_4 + /NH_4/_2SO_4 + 10\ H_2O$$

$$5CaSO_4 \cdot 2H_2O + 2NH_4H_2PO_4 + H_3PO_4 + HF$$

The process is conducted in the typical reaction system of the wet phosphoric acid plant in which the reaction pulp is cooled adiabatically, the pulp circulating at a ratio of 8:1 up to 10:1. It is possible for the decomposition process to be carried out at P_2O_5 concentration 34-36% weight. The phosphate raw material and sulfuric acid diluted with filter washings are introduced into the reaction system. The phosphogypsum formed in the decomposition stage is counter-current washed on the filter and for the last but one washing zone the solution of sulfuric acid is introduced into the washing liquid in an amount of 10-20% of the production quantity used in the decomposition process.

The sulfuric acid passes in a counter-current through the washing zones and changes dissociation conditions in solutions contained in the rinsing tanks and in the filter cake. Mixing the solution of sulfuric acid with filter washings results in an advantageous increase of the temperature of washing liquids on the filter, this increase being caused by the exothermic effect of sulfur acid dilution. The elevated concentration of P_2O_5 contained in the decomposed solution will be kept under the stipulation that the amount of washing water supplied to the filter is decreased by about 10-15% when compared to the conventional dihydrate methods. This is achieved in the method under consideration by introducing a suitable amount of sulfuric acid solution having predetermined concentration onto the filter. By that means good washing off of phosphogypsum, as well as a reduction of blocking and depositing effects on filter cloths, are simultaneously attained. As a result, the utilization period of these cloths is considerably extended. The sulfuric acid may also be introduced into the tanks containing rinsing liquids, into the condenser tanks or directly onto the filter cake. It

is also possible to by-pass a part of the acid used in the decomposition process as well as to employ waste sulfuric acid originating from another technological process, e.g. post-hydrolytic sulfuric acid from an installation of titanium oxide.

Filtered phosphogypsum washing using the counter-current method with sulfuric acid solution and with post-conversion solution containing ammonium sulfate (30-40% weight of $NH_4{}_2SO_4$) undergoes the conversion to chalk and ammonium sulfate solution according to the reaction

$$5CaSO_4 2H_2O + 10NH_3 + 5CO_2 + aq \xrightarrow{30\text{-}60^\circ C} 5CaCO_3 + 5NH_4{}_2SO_4 + aq \qquad (3)$$

The forms of P_2O_5 contained in phosphogypsum absorbed, occluded, built in into the crystal lattice of phosphogypsum (with the exception of undecomposed raw material) are transferred to a liquid phase, thus coming back to the decomposition process. These forms of P_2O_5 are transferred to ammonium sulfate solution according to the reaction

$$CaHPO_4 . 2H_2O + NH_4{}_2SO_4 \longrightarrow CaSO_4 . 2H_2O + NH_4{}_2HPO_4 \qquad (4)$$

Measurements of solubility of $[HPO_4{}^{-2}]$% by weight P_2O_5 ion showed the following dependence on process parameters:

$$[HPO_4{}^{-2}] = 0.214 + 6.4.10^{-3}x_1 - 3,11.10^{-3}x_2 + 7,83.10^{-3}x_3 + 0,95x_4 \qquad (5)$$

$$R = 0,9156;\ F_{calc} = 25,91 > F_{0,01,4,25} = {}^{2,16}$$

where:

x_1 - temperature 20-70°C

x_2 - ammonium sulfate concentration 28-44% by weight $NH_4{}_2SO_4$

x_3 - ammonium carbonate concentration 0.3-4.4% by weight $NH_4{}_2CO_3$

x_4 - concentration of one excess NH_3 0.2-0.3% by weight NH_3

From the relationship determined regressively by means of the smallest squares method one can conclude that it is possible to obtain about 0.5-0.7% by weight P_2O_5 content in the filtrate. This enables increase of the general phosphorus efficiency of the method by about 6-10%.

The filtrate obtained in this process, containing 30-40% by weight $NH_4{}_2SO_4$, is used for washing the filter cloths and phosphogypsum filter cake and a part of it is introduced directly into the node of multicomponent fertilizer production. The solution after decomposition containing ammonium phosphate, phosphoric acid and ammonium sulfate is at first concentrated and then transformed into granulated complex mineral fertilizers. The stage of fabrication of the fertilizer consists in ammonization of the solution remaining after decomposition and introduction of potassium salts or other mineral additions according to requirements of the agriculture. The final product is a mineral fertilizer NPK in which the ratio of assimilable components $N:P_2O_5:K_2O$

can be modified within the range of from 0.3:1:1 to 1:1:1. The described technological system makes it possible to fabricate multicomponent fertilizers of NPK-type 15:15:15, 13:16:16 and NPKMg-type 13:13:13-3MgO. Another final product is fertilizer chalk containing 72-75% by weight of $CaCO_3$ and 2-10% by weight of $NH_4{}_2SO_4$ according to needs. This variant has been examined on industrial scale in an installation having a production capacity of 110,000 tons of P_2O_5 per year and the total capacity of 5-reactor cascade system equal to 850 m^3. In that system the circulation of reaction pulp was carried out by means of an adiabatic evaporation with a circulation ration of 8:1.

The filtration was performed on a Prayon-type filter having a surface of 80m^2. The filtrated solution was used to produce a complex fertilizer (NPK), the composition of which was 8-24-24 and 15:15:15, and the fertilizer properties of this product were subject to production-type field examinations. This technology was being tested during long-term (about three months) research work, with the concentrations of about 27-29% by weight of P_2O_5 as well as 32-36% by weight of P_2O_5 when using for the decomposition process the raw materials Marokko II and Floryda 68 BPL. The change in dissolubility of $CaSO_4 \cdot 2H_2O$ and of mineral impurities manifested itself by the growth of dimensions of phosphogypsum crystals and their better homogeneity. In the case of decomposing Marokko II raw material a length of crystals was of 100-700 μm and width was of 20-150 m, said crystal having the form of beams and rhomb twins with very food filtration properties [12].

The modification of washing waste phosphogypsum with solution sulfuric acid was employed in the traditional dihydrate method in the two plants having the capacity of 110,000 tons of P_2O_5 per year and it annually brings economies in the consumption of about 7.5 thousand tons of the phosphate rock. The process of conversion of the phosphogypsum to the chalk and ammonium sulfate solution has been examined on a semi-technical scale in an installation having a capacity of 24 tons of phosphogypsum per day.

Expected advantages of this method. The method enables H_2SO_4 consumption to be 20% lower than in the case of dihydrate methods applied in industry. Because of P_2O_5 regeneration in the conversion process the total P_2O_5 efficiency of the method is equal to 96%. The energy being necessary for concentration post-decomposition solution is decreased by more than 40% when compared with the conventional wet phosphoric acid method. The new method enables fabrication of the NPK fertilizers having the ratio of assimilable components NPK of 1:1:1 without the necessity of using urea and ammonium nitrate and makes utilization of waste phosphogypsum to the soil chalk possible.

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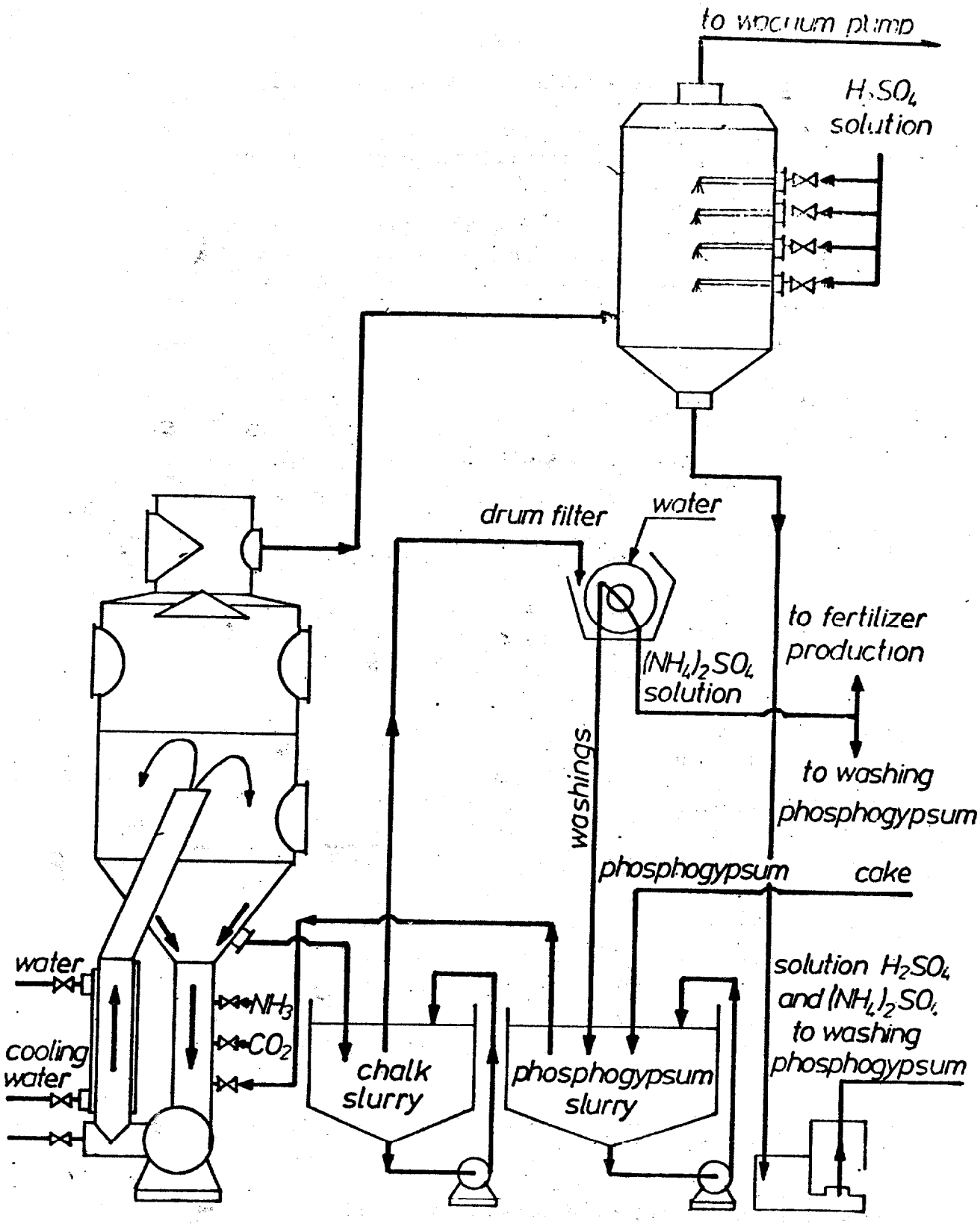
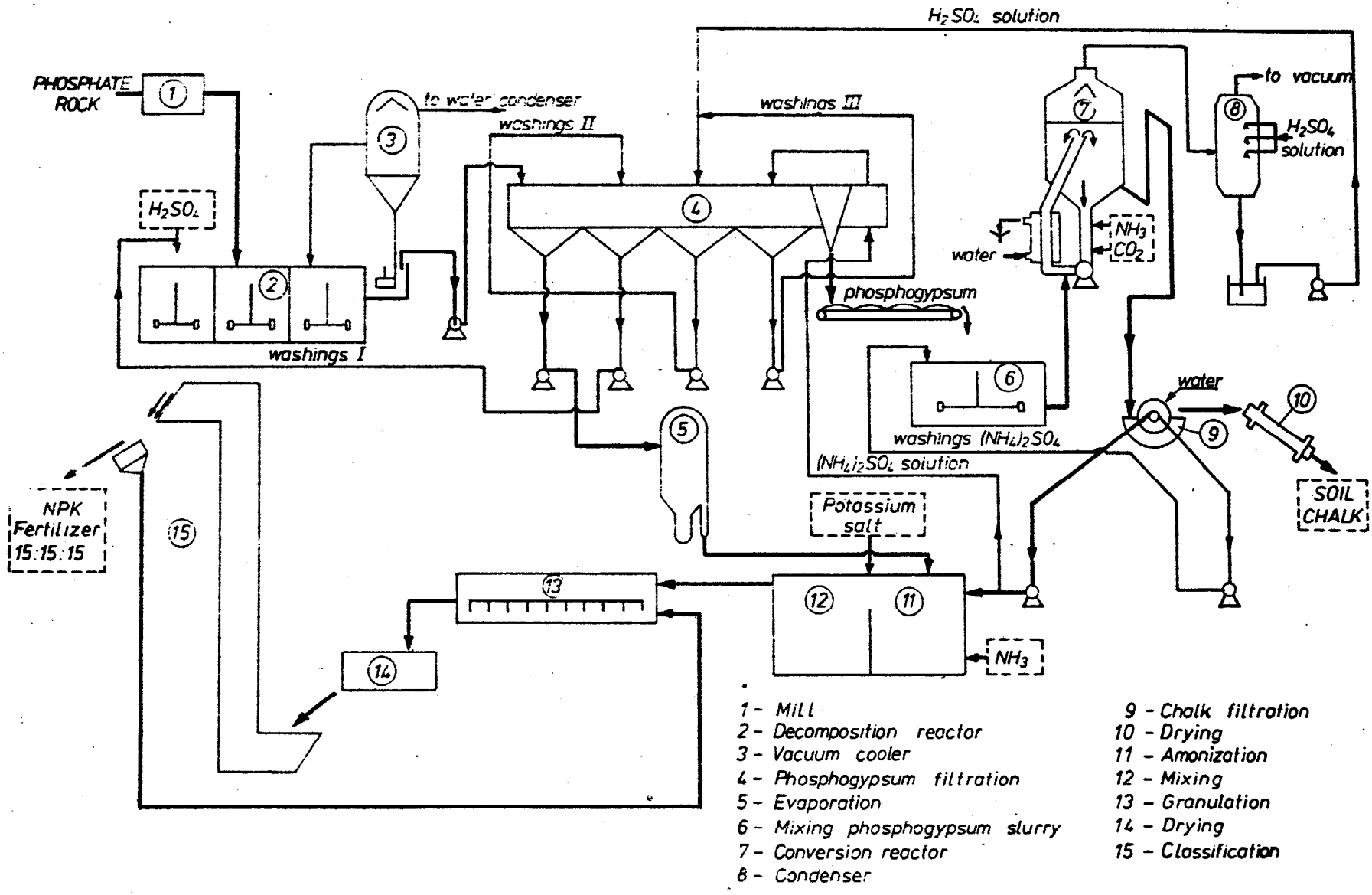


Fig. 1 Technological diagram of the phosphogypsum conversion by NH_3 and CO_2 to soil chalk and ammonium sulphate solution



1 - Mill
2 - Decomposition reactor
3 - Vacuum cooler
4 - Phosphogypsum filtration
5 - Evaporation
6 - Mixing phosphogypsum slurry
7 - Conversion reactor
8 - Condenser
9 - Chalk filtration
10 - Drying
11 - Amonization
12 - Mixing
13 - Granulation
14 - Drying
15 - Classification

Fig. 2 Simplified flow diagram for simultaneous manufacturing of complex multicomponent mineral NPK fertilizer and soil chalk

Economics of Utilizing Phosphogypsum

GYPSUM INDUSTRY IN THE UNITED STATES

(AN OVERVIEW - INCLUDING POTENTIAL FOR USE OF CHEMICAL GYPSUM)

by

F.C. Appleyard

INTRODUCTION

The purpose of my being here with you today is to discuss the gypsum industry of the United States - to provide a generalized overview - and also, to provide a basis for placing in perspective any consideration which might be given to the use of by-product or chemical gypsum as a raw material by our industry.

You will note that I will be using the term "chemical" gypsum rather than "by-product" gypsum. This is because from where we sit, we see by-product or synthetic or chemically produced gypsum resulting from a number of sources, and chemical gypsum seems a broader, more appropriate term.

As a broad outline, I will touch briefly on the following areas:

- What Is The Gypsum Industry
- How Is It Structured
- Where Does It Find Its Raw Material
- What Processing Steps Are Involved
- Size Of The Industry - What Are Its Products
- Where And How Are They Marketed
- What Are The Basic Economic Factors
- Gypsum Rock Specifications
- Sources Of Chemical Gypsum
- Potential For Use of Chemical Gypsum

What Is The Gypsum Industry. As with most industries, the gypsum industry can be categorized in many ways. First of all, gypsum is one of the so-called "industrial minerals" with the industry being built around its physical and chemical properties, and in particular, the relative ease of converting it into a cementitous material. Because of this trait - and the numerous construction products which are based upon this property - it is usually classified in the United States among the building or construction material industries.

Due to its plentiful supply and wide distribution - both geologically and geographically - gypsum is a low value mineral, with any given source being extremely sensitive to extraction and transportation costs, leading to the term "place value" as a first consideration in determining its economic viability. We usually consider the value of gypsum in the ground before mining to be very low, measured in cents per ton, and in many cases, as being zero.

Most of our products compete in the market place against other materials, and while we like to think that our products have superior qualities, we are constantly called upon to demonstrate and prove this superiority.

As with the fertilizer industry, we are capital intensive. Also, as with your business, our markets are cyclical, with both of these factors impacting in a major way upon our balance sheets.

Although the industry has carved out a respectable position in our industrialized society, it should be noted that none of its end use products can be classified as being essential to human life, and that most products - with the exception of Portland cement retarder - compete in the market place with other materials.

And finally, we are an energy intensive industry, leading to strong motivation in the area of energy conservation and for methods of using lower cost fuels.

How Is The Industry Structured. The wide geographic distribution of our primary raw material (gypsum) and of our markets results in a highly fractured situation which tends to limit the size of our mining operations and manufacturing plants. Annual gypsum usage at any given operation might range from 100,000 to as much as 500,000 tons, but the average is more in the 200,000 - 300,000 ton range.

(Figure 1) - Illustrative of this situation, gypsum mining and/or manufacturing took place at some 115 different locations in 1979, including six from which chemical gypsum was sold. In this total are 65 different mining operations, with the output of mined rock ranging from only 5,000 to 10,000 tons per mine per year on up to nearly 1,000,000 tons. There are 74 different manufacturing locations of which 34 are operated in combination with a mine. The other 40 have no adjacent mine rock source, with their gypsum being transported to the plant location either by water or overland by truck or rail from distant mines.

(Figure 2) - This has led to the development of several multi-plant organizations. Between them, these companies as shown in Figure 2 own and operate 64 of the 115 mines, plants or combination mines and plants shown on the preceding Figure 1, and it can be estimated that in total, they mine approximately 80% of the rock produced and ship perhaps a similar percentage of the finished products.

With only six exceptions, the 74 gypsum manufacturing plants control their own source of gypsum, with the result that there is no market for crude or unprocessed gypsum rock. Thus, the major gypsum manufacturers are vertically integrated, including mining and the manufacture of the' paper used 'for wallboard. It should be pointed out that no mine exists in the United States for the purpose of marketing gypsum (except in a captive situation) to manufacturing plants.

The first product of a gypsum mine is Portland cement retarder rock, or in a few cases, agricultural gypsum (sometimes called landplaster). Of the 65 mines operating in 1979, approximately 35 produced and sold only uncalcined gypsum for Portland cement retarder or agricultural use. However, as noted above, their combined tonnage and sales represented only a small portion of the U.S. total.

Many gypsum manufacturing plants are multi-product operations, shipping both uncalcined and calcined products. The product mix, obviously, at any given location will usually reflect the markets available within an economic shipping distance.

One further observation that may be pertinent is that as a general rule, and because of the direct mine to manufacturing plant relationship , no profit is allocated to the mining operation for that proportion of their production transferred to a manufacturing plant, even when the mine is physically separated from the manufacturing plant. Instead, profits are taken at the final product stage.

Where Does The Industry Find Its Raw Materials. As noted earlier, gypsum deposits are quite widely distributed, both in a geologic and geographic sense. Based upon commonly known geologic principles, this map-(Figure 3) shows the major broad areas in-the United States where geological conditions are such that calcium sulfate might be found. I say calcium sulfate because it can exist either in its anhydrous form - anhydrite, or dihydrate form - gypsum, with anhydrite being by far the more prevalent.

(Figure 4) - This map shows the location of the principal gypsum mining areas in North America. Not shown are the offshore locations which in 1979 supplied 33% of the gypsum used, or the transportation routes involved.

With respect to imported gypsum, it should be emphasized that this does not reflect any shortage of reserves in the United States. Rather, it is the result of the lack of gypsum deposits in the large market areas paralleling the Atlantic, Gulf and Pacific Coasts, and the fact that foreign deposits located near deep water can be shipped via large bulk carriers to our coasts for less cost than land transportation from inland United States deposits.

(Figure 5) - This table illustrates where the imported gypsum originated, with about 90% of the Canadian production coming from Nova Scotia and the balance from Newfoundland. Mexico is the number two foreign source shipping from two mines, the largest of which is on San' Marcos Island in the Gulf of Lower California, and the other being at La Borreguita in the State of San Luis Potosi, shipping by rail to the Port of Tampico on the Gulf of Mexico.

Considering both the domestic and foreign locations which presently supply the industry, known reserves are extensive, and are backed up with the potential for developing enormous additional sources. Thus, reserves of natural gypsum are not considered to be a problem.

What Processing Steps Are Involved. The basic steps involved in a typical gypsum operation are:

(1) Mining (Surface Or Underground)
(2) Rock Transportation (Applied To Approximately 45% of the Gypsum Used)
(3) Rock Preparation
(4) Calcination
(5) Formulating and Manufacturing

Transportation refers primarily to ocean shipping from foreign sources, and to the movement on the Great Lakes of crude gypsum from two different mines to six different manufacturing plants. Also, in a few cases, it includes overland transportation by truck or rail over distances varying from approximately 50 miles to as much as 500 miles.

(Figure 6) - This generalized flow diagram shows the steps involved in a typical plant from rock preparation, through formulation and/or manufacturing. The three most critical areas are calcination, the formulation of the slurry mix in the manufacture of wallboard, and the drying of excess moisture from the wallboard, and many of our operating practices and raw material specifications are based on minimizing problems in these areas.

Significantly, this chart does not show a definite beneficiation step, although this possibility is indicated between the primary and secondary crushing stages. Also, the "possible screen waste" box represents a crude form of beneficiation by either dry or wet screening. To the degree necessary, grade control is accomplished by selective mining and/or blending, plus screening in some cases. Heavy media separation, although technically feasible, is currently employed at only one U.S.A. location.

The thermodynamic properties of gypsum are such that the removal of free moisture, as well as the calcination and board drying steps, must be carried out at relatively low temperatures. Disassociation of the chemically combined water begins at about 120°F (depending upon the humidity index) and in the drying of free moisture, care must be taken that the temperature of the material does not greatly exceed this figure. The same situation exists in the board drying kiln where the excess water used in slurrying the stucco - the hemihydrate form of calcium sulfate or $CaSO_4 \cdot 1/2\ H_2O$ - must be dried without raising the temperature of the gypsum core to the point where it would begin to dehydrate.

Briefly stated, the most critical technology in gypsum processing is that of heat transfer - to devise means to most efficiently use the BTU content available in the fuel, but at the same time to stay within relatively low temperature limits and to uniformly distribute this heat.

As is evident from the flow diagram shown in Figure 6, a basic point in any consideration of chemical gypsum as a substitute for natural gypsum is the fact that all existing plants are designed to handle a relatively dry gypsum rock rather than a filter cake or centrifuged material with 12 to 20% free moisture. By itself, this situation would seem to suggest two alternative courses: (1) dry and agglomerate the fine, wet chemical gypsum to make a produce which could be handled in a existing gypsum plant; or (2) modify the rock preparation section to handle the fine wet material.

Neither of these courses have as yet been commercially demonstrated in the United States, although some testing has been done, and of course, phosphogypsum is being used abroad in the manufacture of building materials as we shall hear later on in this program.

Size of the Industry - What Are Its Products. In terms of tonnage the table shown in Figure 7 shows the apparent total gypsum supply in the United States in 1979, and in general terms, where it came from. Note that 4% or 828,000 tons of chemicalgypsum were reported as used, about 90% of which, I believe, was phosphogypsum with all of this tonnage being sold into the agricultural market. Note also that the total of 23,231,000 tons used was well below the 30-33,000,000 tons of phosphogypsum which I understand is produced annually in Florida, and which is but a minor part of the 250-300 million tons already stockpiled in your gypsum "stacks" in the central part of the state.

Figure 8 shows the tonnage of gypsum used by major end product. Of particular interest is the fact that 75% of the volume is calcined, with 71% being used in the manufacture of prefabricated products, almost all of which were wallboard.

The trend of gypsum usage over the past 15 years is shown in Figure 9, and it averages out to 3.0% per year growth for the entire industry. Again referring to imported gypsum, it consistently ranges from 33 to 38 percent of the total used. Also apparent from this charge is the cyclical nature of our business.

One further comment regarding the size of the gypsum industry is a stab at what the future may hold. These figures are based on projections made by the U.S. Bureau of Mines as part of their analysis of the strengths and weaknesses of our country's mineral resource data base, and should be fairly realistic. An average annual growth of 2.4% is projected as compared to 3.0% over the past 15 years, and it is of some interest to note that the total consumption of 36,000,000 tons projected for the year 2,000 is approximately equal to today's annual production of phosphogypsum.

The end uses for gypsum can be categorized in three different product areas - construction, industrial and agricultural. As illustrated in Figure 11, 92% of the value of all gypsum products in 1979 was in pre-fabricated products, nearly all of which were in the wallboard sector of the business. From an earlier table, we saw that this sector consumed 71% of the tonnage used. Similarly, Portland cement retarder gypsum utilized 17% of the gypsum used, but yielded only 3% of the total value.

Where and How Are Gypsum Products Marketed. As discussed above, the two most important product areas (in both volume and value) are construction or building materials and Portland cement retarder. Portland cement rock is sold directly by the gypsum producer to a cement plant, usually under some type of long-term contract. Depending upon the size of the cement plant, annual shipment to any given location will range from approximately 20,000 tons per year to 60-80,000 tons per year. Both truck and rail freight are used, and in a few cases, direct water shipments are made. In many cases, freight costs are higher than the cost of the material.

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As is evident from the flow diagram shown in Figure 6, a basic point in any consideration of chemical gypsum as a substitute for natural gypsum is the fact that all existing plants are designed to handle a relatively dry gypsum rock rather than a filter cake or centrifuged material with 12 to 20% free moisture. By itself, this situation would seem to suggest two alternative courses: (1) dry and agglomerate the fine, wet chemical gypsum to make a produce which could be handled in a existing gypsum plant; or (2) modify the rock preparation section to handle the fine wet material.

Neither of these courses have as yet been commercially demonstrated in the United States, although some testing has been done, and of course, phosphogypsum is being used abroad in the manufacture of building materials as we shall hear later on in this program.

Gypsum Rock Specifications. As was noted earlier, only minimal beneficiation is employed in the gypsum industry, a situation which is possible because of the common occurrence of large deposits of relatively clean mineral. Wallboard is made from gypsum ranging in purity from the high 70's to the high 90's, but the average is somewhere in the mid to high 80's. Gypsum purity is a definite factor in most gypsum products, being more critical in some than in others. But in the manufacture of wallboard in particular, the nature of the impurities can be more important than gypsum purity.

The chart in Figure 15 shows the principal mineral impurities usually found associated with gypsum, and also indicates the range in the amount of each which we consider to be acceptable. With respect to wallboard, we are particularly critical of soluble salts such as chlorides and sulfates, preferring to hold the total of such minerals to less than 0.05%. Clay minerals, especially if they are hydrous, also adversely affect wallboard manufacture, and must be controlled at 1 to 2%.

Therefore, for natural gypsum, a specification would include a gypsum content from 85 to 90% with impurities not to exceed the ranges shown in Figure 15, and with particular emphasis on soluble salts and clay minerals as discussed above.

Sources Of Chemical Gypsum. It should be pointed out that the fertilizer industry is not the only generator of chemical gypsum, although at the present time, of course, you are by far the largest producer. As indicated in Figure 16, there are other industries where gypsum is also a direct by-product (or co-product) such as citric acid and hydrofluoric acid, but of much greater impact are pollution control systems which yield calcium sulfate as a solid waste., One can speculate that over the next ten years as flue gas desulfurization becomes a common requirement, it could generate annual tonnages approaching that of phosphogypsum, although depending on the technology used much of this would have no potential use.

The primary reason in pointing out these other sources is that chemical gypsum also has "place value" and to a degree, we can visualize each industry source and each geographical location as competing for whatever uses currently exist, or may be developed in the future for calcium sulfate.

Potential For Use of Phosphogypsum. Just as I started this discussion with the question, "What is the gypsum industry," any evaluation of the potential use by the industry of phosphogypsum should be prefacted with another question: "What is phosphogypsum?" However, I believe that this will be discussed in, depth in subsequent papers, so in the following comments I will not attempt to get into details, but instead, will offer a few broad opinions and conclusions.

The impurities commonly associated with natural gypsum were listed in Figure 15; however, in Figure 17 I list those found in various samples of phosphogypsum as analyzed over the years by our Research Department. All of these samples were material produced here in the United States, with most of them coming from Florida.

Although you may take issue with any of the specific numbers shown, the point I want to emphasize is the different nature of these impurities. We are used to working with the impurities occurring in natural gypsum, and over the years have developed specific data as to how and why each impacts upon the quality of the final product. Also, we have learned how much can be tolerated and the how's and wherefore's of mitigating their adverse impact.

We have no such background of experience with phosphogypsum, although we have done some laboratory work on it and are familiar with the fact that it is used on a commercial scale in Japan and a few other countries.

However, from our understanding of this foreign experience, and from the laboratory work, we think there are three problem areas regarding the commercial use of phosphogypsum in the United States:

(1) Location or "place value" - that is, the concentration of tonnage in central Florida vs. the widespread occurrence of natural' gypsum (and probably other chemical gypsum sources as well).

(2) Its physical properties.

(3) Its chemical properties.

With respect to place value, there are three manufacturing plants in Florida plus six cement plants, all of which use imported gypsum delivered by ship. Between them, they serve the Florida market requirement, for gypsum, and use perhaps an average of 1.2 million tons per year. Even if all this usage could be converted to phosphogypsum, it obviously would not materially impact on the phosphate industry's gypsum output.

Similarly, there are three gypsum plants in Georgia using imported water borne rock, but the cost of land transportation to reach them is probably prohibitive.

Regarding the physical properties of phosphogypsum, the cost of drying is a deterrent, as would be redesigning our raw material handling systems.

However, of much greater concern are the adverse chemical properties of chemical gypsum which from our experience can be summarized as being: (1) excessive P_2O_5 content, (2) low pH, and (3) high radioactivity level. These comment are particularly applicable to your central Florida production, but apply to a greater or lesser degree to all U.S.A. produced phosphogypsum.

Excessive P_2O_5 adversely affects the setting time and strength development charcteristic of calcined gypsum, which in turn cannot be tolerated on today's high speed wallboard machines, the successful operation of which depends upon careful control of these two conditions.

As I expect you know from your own plant operations, the low pH of phosphogypsum results in a corrosion problem which probably is minor in the total context of a phosphoric acid operation, but which introduces a whole new line of problems to a gypsum operation where we have very little, if any, difficulty from corrosion. Also, it is essential to the manufacture of good quality wallboard that the pH of the stucco be essentially neutral, that is between a value of 6.5 to 7.5; however, as noted in Figure 17, test results which we have seen run well below this level.

Overriding all other concerns is the radioactivity problem. Although there currently is not EPA mandated radioactivity standard for gypsum, discussions are closing in on a maximum figure of 5 pica-curies per gram range. And one can even anticipate that the regulators could, in their infinite wisdom, establish a standard for chemical gypsum not to exceed that of natural gypsum. How to close the gap between such a standard and the average of perhaps 25 pica-curies/gram common to most phosphogypsum appears to us to be a major problem.

There is not time, nor did I intend in this presentation to get into the technical details which might be considered for cleaning up your present phosphogypsum or of modifying a phosphoric acid plant to produce an improved gypsum. We are aware, of course, that the Japanese in particular have developed certain modifications, and we also have monitored various technologies for cleaning up typical Prayon Process products. However, it is questionable if these modified phosphogypsums have been improved sufficiently to meet our U.S.A. requirements - especially with regard to radioactivity.

A fundamental point, it seems to me, is that in your present operations the phosphogypsum is a sort of dumping ground for all of the impurities in the phosphate rock, including organics. This is a logical situation if you are to protect the quality of your primary product, but it suggests that if gypsum is to also be produced as a product which must meet its own specifications, modification of the total process would be required, with such modification being over and above that which has so far been adopted in Japan and other countries.

To accomplish this would seem to require a major process research project to investigate both its technical and economic feasibility. It is not clear whether or not such an effort would be warranted; however, if it is to be considered, it probably should be done by looking at specific situations rather than on an industry-wide basis.

It is not my intent to take a negative attitude in considering the phosphogypsum problem. However, when one looks at the volume of already stockpiled material, as well as the annual rate at which it is being added to, one must conclude that the gypsum industry as we know it in the United States cannot be of much help in adsorbing this material. One can conceive of very limited additional use in a few isolated cases, but to accomplish even this minor step appears to require research and process modification costs which at this stage of our understanding of the problems involved do not appear to have economic incentive.

ACKNOWLEDGMENTS

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Various Technical and Research Personnel of U.S. Gypsum Company.

GYPSUM MINE & MANUFACTURING PLANTS - UNITED STATES - 1979

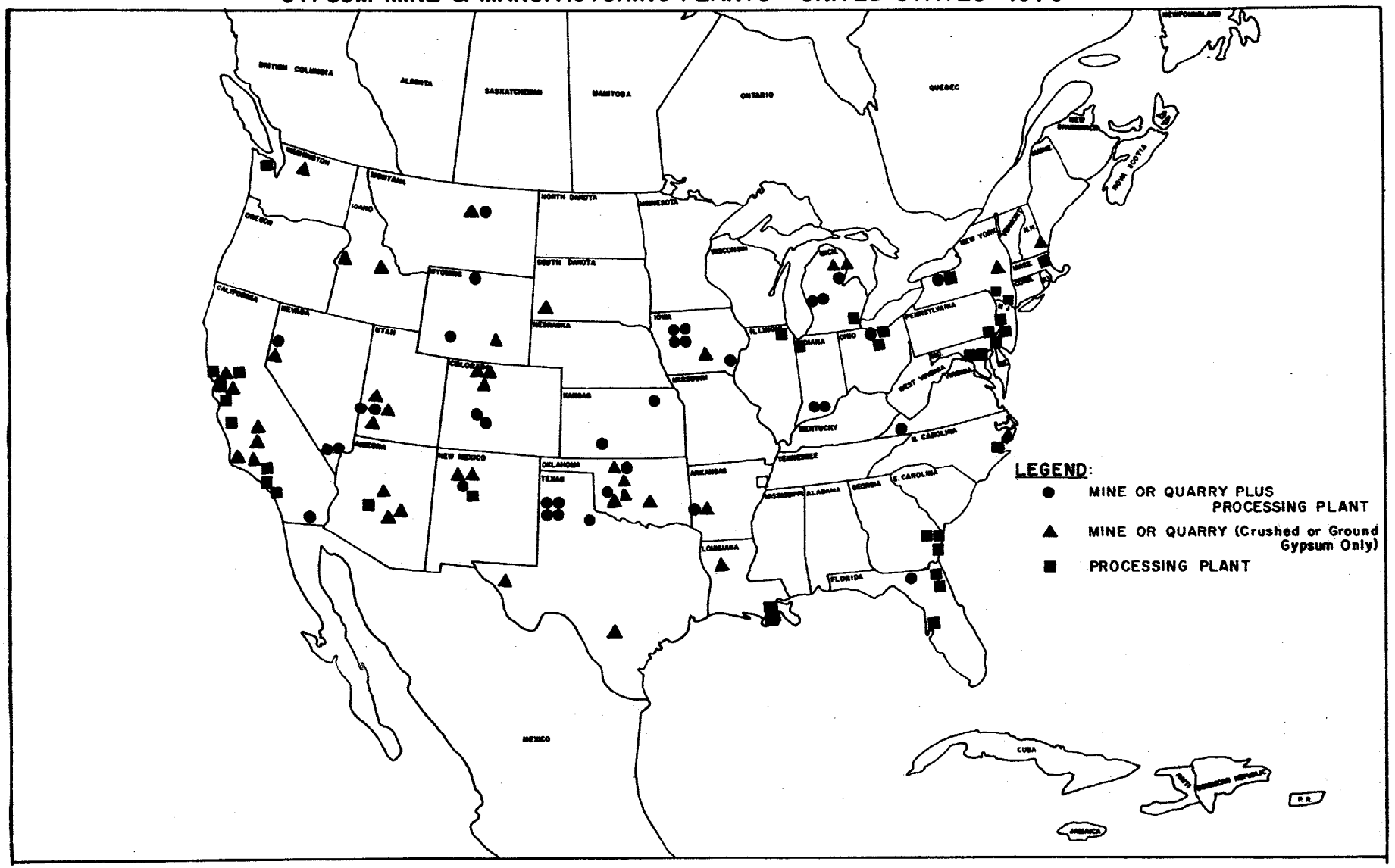


FIGURE 1

0-5000 2-72

GYPSUM PRODUCERS (MULTI-PLANT) (1)

UNITED STATES - 1979

Company	Number of Plants
United States Gypsum	23
National Gypsum Company	20
Georgia-Pacific Corporation	9
The Flintkote Company	6
Celotex Division (Jim Walters Company)	4
Domtar Gypsum American, Inc.	2
Pacific Coast Building Products	2
Temple Industries	2

(1) Each Mine, Manufacturing Plant Or Combination Mine & Plant Counted As One Unit.

Source: U. S. Bureau of Mines

FIGURE 2

FIGURE 3

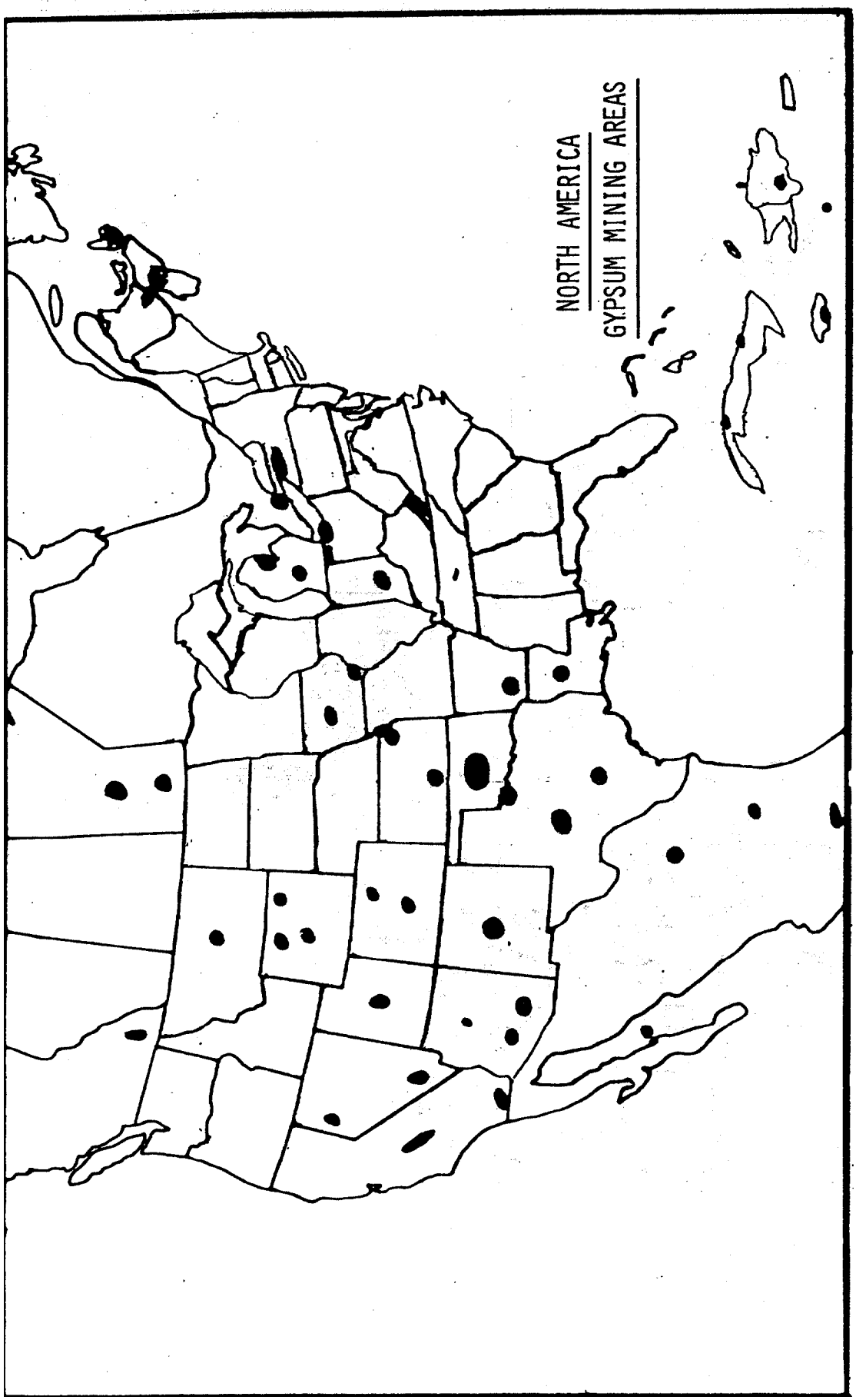


FIGURE 4


GYPSUM-ANHYDRITE
POSSIBILITIES
SALT DOME PROVINCE
NEWFOUNDLAND
QUEBEC
ONTARIO
MANITOBA
BRITISH COLUMBIA
ALBERTA
SASKATCHEWAN
MINNESOTA
WISCONSIN
MICHIGAN
ILLINOIS
IOWA
MISSOURI
KANSAS
NEBRASKA
COLORADO
UTAH
NEVADA
CALIFORNIA
OREGON
WASHINGTON
IDAHO
MONTANA
WYOMING
NORTH DAKOTA
SOUTH DAKOTA
OKLAHOMA
TEXAS
NEW MEXICO
ARKANSAS
LOUISIANA
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
TENNESSEE
KENTUCKY
S. CAROLINA
N. CAROLINA
PENNSYLVANIA
NEW YORK
MAINE
NEW BRUNSWICK
MEXICO
CUBA
HAITI
DOMINICAN REPUBLIC
JAMAICA

IMPORTED GYPSUM

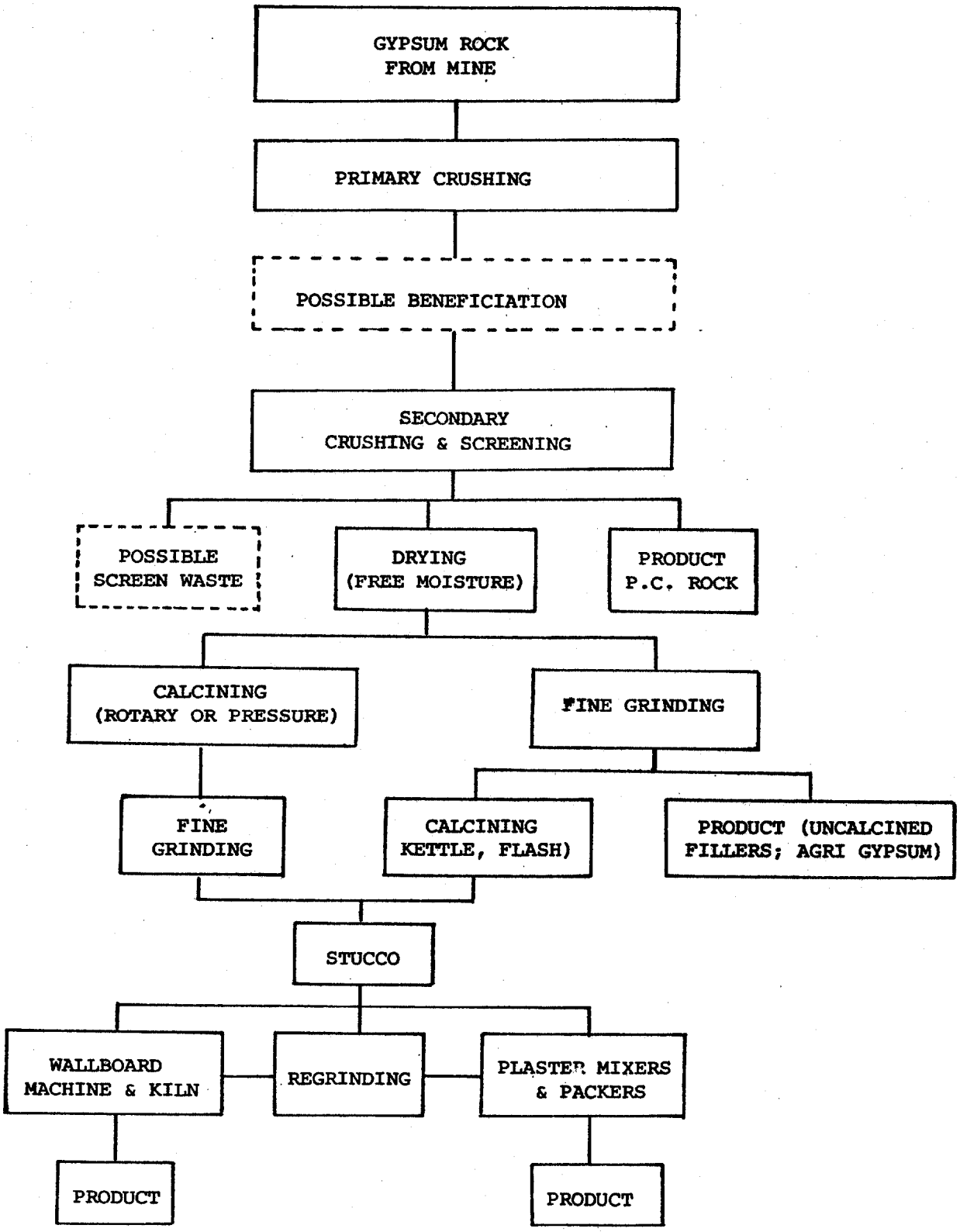
1979

Country	Short Tons
Canada	5,700,000
Mexico	1,851,000
Spain	125,000
Dominican Republic	80,000
Norway	12,000
Jamaica	5,000
	7,773,000

Source: U.S. Bureau of Mines

FIGURE 6

GYPSUM PROCESSING



GYPSUM SUPPLY

UNITED STATES - 1979

	Short Tons	%
Domestic Mined	14,630,000	63
Imported	7,773,000	33
By Product Sold	828,000	4
	23,231,000	100

Source: U.S. Bureau of Mines

FIGURE 7

GYPSUM USAGE

UNITED STATES - 1979

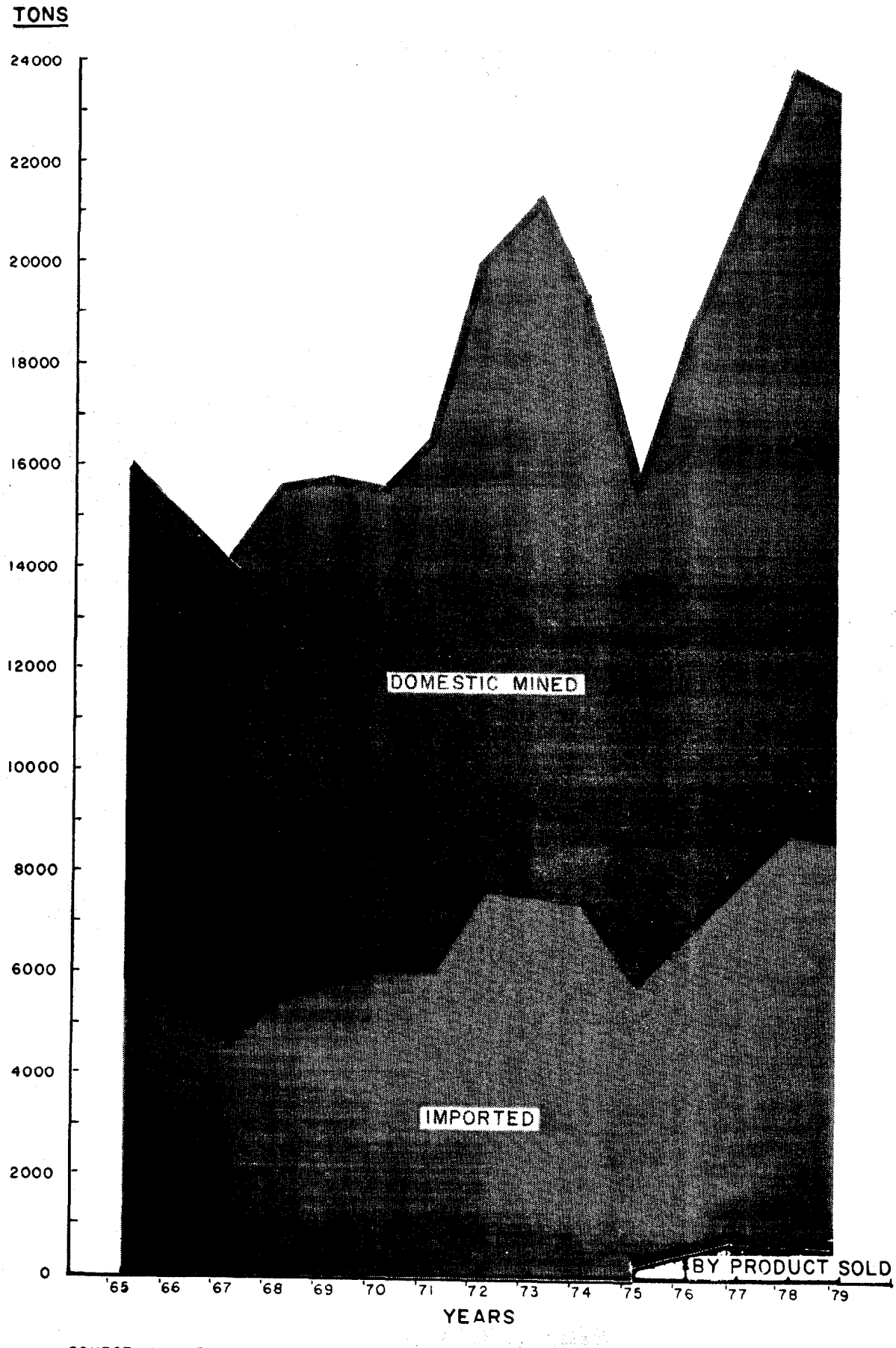
	Short Tons	%
UNCALCINED		
Portland Cement Retarder	4,024,000	17
Agricultural (1)	1,700,000	7
Fillers & Miscellaneous	124,000	1
Sub-Total	5,848,000	25
CALCINED		
Prefabricated Products	16,728,000	71
Building Plasters	520,000	2
Industrial Plasters	456,000	2
Sub-Total	17,704,000	75
GRAND TOTAL	23,552,000	100

(1) Includes 828,000 tons of by-product gypsum

Source: U. S. Bureau of Mines

FIGURE 8

CRUDE GYPSUM - APPARENT SUPPLY



SOURCE: U.S. BUREAU OF MINES

GYPSUM USAGE

UNITED STATES

PROJECTED TO YEAR 2000

(Short Tons)

	1979	2000	% Change
UNCALCINED			
Portland Cement Retarder	4,024,000	6,500,000	+ 62
Agricultural	1,700,000	3,400,000	+100
Fillers & Miscellaneous	124,000	200,000	+ 61
CALCINED			
Prefabricated Products	16,728,000	25,000,000	+ 49
Building Plasters	520,000	400,000	- 23
Industrial Plasters	456,000	500,000	+ 10
Sub-Total	17,704,000	25,900,000	+ 46
Grand Total	23,552,000	36,000,000	+ 53

FIGURE 10

GYPSUM END USES

	Approx. 1979 Value $000,000	%
CONSTRUCTION PRODUCTS		
Wallboard Tile & Block	1,285	92
Plasters	27	2
Sub-Total	1,312	94
INDUSTRIAL PRODUCTS		
Portland Cement Retarder	38	3
Molding Plaster Casting Plaster Oil Well Cement	24	2
Mineral Fillers & Extenders Water Treatment Glass Batch Additive	4	-
Sub-Total	66	5
AGRICULTURAL PRODUCTS		
Soil Conditioner Calcium Source Insecticide Carrier Animal Feed Supplement	14	1
GRAND TOTAL	1,392	100

MAJOR COST FACTORS

1/2" GYPSUM WALLBOARD

1979 AVERAGE

	% of Total
*Stucco (Less Energy)	11
Paper (Less Energy)	21
Other Raw Materials	5
Total Energy	23
Maintenance, Supplies, Etc.	6
Direct Operating Labor	4
Overhead	6
Warehouse & Loading	2
Outbound Freight	22
	100

*Includes Cost of Gypsum Rock

GYPSUM COMMODITY PRICES

FOB PLANT

	Average 1979
Wallboard (1/2" Thick)	$ 71.60/MSF
Portland Cement Rock	$ 10.70/Ton

FIGURE 13

1/2" GYPSUM WALLBOARD

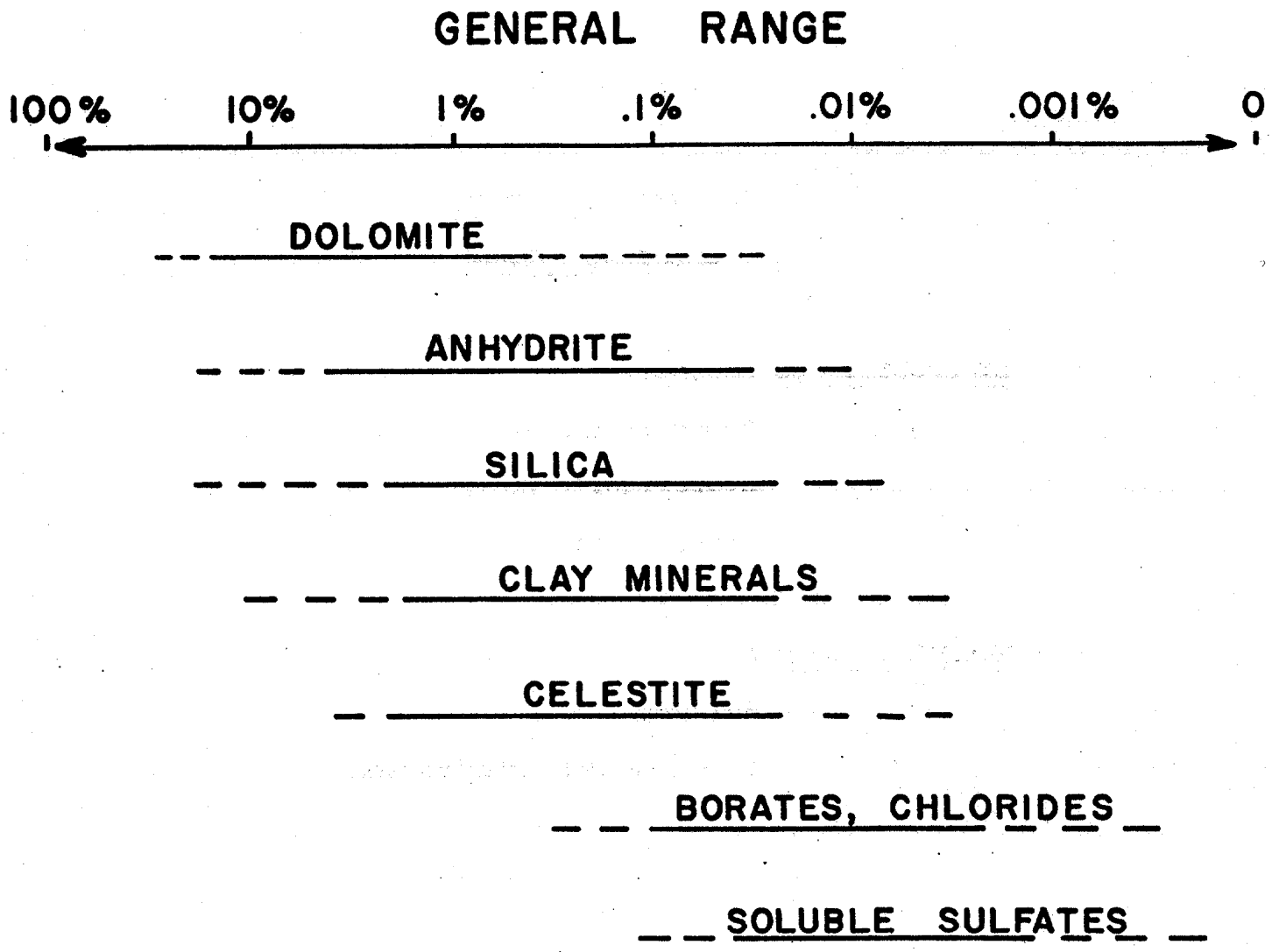
PRICE - COST TREND

(1967 = 100)

Year	Realized Price	Cost
1967	100	100
1969	87	101
1972	84	110
1975	99	146
1976	103	160
1977	129	179
1978	165	196
1979	182	218

FIGURE 15

COMMON IMPURITIES IN GYPSUM DEPOSITS



POTENTIAL SOURCES

CHEMICAL GYPSUM

BY-PRODUCT (CO-PRODUCT)

Phosphoric Acid

Hydrofluoric Acid

Citric Acid

POLLUTION CONTROL

Sulfuric Acid

Flue Gas Desulfurization

PHOSPHOGYPSUM

TYPICAL ANALYSIS*

Gypsum	85 - 93%
P_2O_5	0.2 - 1.7%
F	0.4 - 1.3%
SiO_2	1.4 - 8.4%
Soluble Salts	0.1 - 5.3%
pH	3.1 - 5.3
Radioactivity (R_{226})	15 - 29 Pc/Gm

* All samples from U.S.A. produced material

Source: U.S. Gypsum Research Laboratory

GYPSUM BUILDING PRODUCTS IN NORTH AMERICA: CAN PHOSPHOGYPSUM COMPETE WITH ALTERNATIVES?

by

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INTRODUCTION

Phosphogypsum is being produced in North America at a rate that exceeds that of gypsum from any other source. It is well-recognized that the utilization of this material in conventional gypsum products could provide an attractive method of disposing of some of this material, while at the same time offering an alternative supply to natural gypsum. In an assessment of the feasibility of using phosphogypsum, however, it is important to consider the most likely end use, and whether or not phosphogypsum is really suitable for that use in view of its properties. In this context it is also important to examine the alternatives to phosphogypsum presently available.

Considering first the potential uses of gypsum, it would appear from Table I that prefabricated products (primarily gypsum board) and Portland cement represent the two largest uses (1). The present discussion pertains primarily to gypsum board production which provides the only possibility of consuming significant quantities.

Judging from the difference in the gypsum industry between North America and Europe or Japan, it is obvious that the ample supply of natural gypsum has seriously restricted the use of phosphogypsum on this continent. This is compounded by the poor quality of the phosphogypsum. Also, natural gypsum is not the only competitor to phosphogypsum. As is illustrated in Table II, gypsum is presently produced in substantial quantities from HF production (2), TiO_2 Production (3), Purification of organic (citric, tartaric, etc.) and inorganic (boric) acids, and from the desulfurization of flue gases (4). Although flue gas desulfurization (FGD) gypsum is not presently available in large quantities, it is expected to change in the near future. For example, it has been estimated (4) that as of 1978, it would be economically attractive for 30 U.S. power companies to choose FGD systems resulting in 2.7 million tons of gypsum. It is expected that sources of FGD gypsum will be increasing at a much faster rate than was predicted in 1978.

COMPARISON OF PHOSPHOGYPSUM TO ALTERNATIVES

The following discussion is a comparison of phosphogypsum to the other types of gypsum with respect to problems encountered in making gypsum board. As is shown in Table III, these gypsums are compared under the following three general categories: availability, bulk physical properties and chemical properties.

Availability. Considering just the availability aspect, only phospho-, fluoro-, or FGD gypsum will be produced in sufficient quantities to affect the market in the near future.

Transportation costs play an important role in the sale and manufacture of gypsum products. Gypsum board plants are presently located in market areas, near either mine sites or convenient shipping routes. Substitution of natural gypsum with by-product gypsum will therefore occur only where natural gypsum is transported long distances.

In order for substitution to occur, the by-product gypsum will therefore occur only where natural gypsum is transported long distances. In order for substitution to occur, the by-product gypsum source must also be near a board plant or convenient shipping. In general, the by-product gypsums are near shipping routes and should therefore be competitive with-natural gypsum. Since FGD gypsum is produced in built-up areas, it will be near the market area as well and therefore may have some advantage.

Before discussing the physical and chemical properties, it should be pointed out that present gypsum board plants operate at quite high speeds (200 ft/minute). It is therefore imperative that the board slurries be very predictable with respect to the flow and setting properties. Any by-product gypsum source which results in variability of these properties, especially if the variation is detrimental, will not be used for board manufacture.

Bulk Physical Properties. The bulk physical properties of by-product gypsum are quite different from natural gypsum since they are produced in solution. The main problems associated with these properties are:

- extra drying prior to calcination;
- poor handling in hoppers, bins, etc.;
- abnormal calcination properties;
- abnormal stucco flow properties.

All of the above problems result from the size and shape of the by-product gypsum crystals produced. Even after conventional dewatering procedures, fine acicular or platelike gypsum crystals will retain substantial quantities of water, water which must be removed prior to hemihydrate production. The abnormal crystal size and shape also result in smaller kettle loadings and altered kettle operating conditions. In addition, slurries prepared using the resultant stucco have peculiar rheological properties, in particular poor flow characteristics at normal water-stucco ratios. The above problems represent serious barriers to utilization of the material.

The approach used to overcome these problems is to remove the small size crystals, to grow large gypsum crystals, and then to grind the material either before or after calcination. In this way, the final stucco particles are similar in size and shape to those derived from natural gypsum. A comparison of phosphogypsum to its higher volume, competitors in this respect is quite useful. Fluorogypsum, since it is produced as anhydrite, solidifies as a solid mass, is subsequently ground and therefore is less of a problem. Several FGD systems are presently available which have specifically included processing steps aimed at the production of large crystals and as a result produce the. required product. Similar process modifications have not yet been undertaken by phosphogypsum producers.

Chemical Properties. Although the bulk physical properties of synthetic gypsums are important, it is their chemical properties which most seriously hinder their utilization; In general, the materials are of high $CaSØ_4.2H_2O$ content, one exception being fluorogypsum (major contaminant - anhydrite, $CaSO_4$)(5). The pH can be somewhat variable with problems being encountered at either extreme. Neutralization is possible in most cases, although with phosphogypsum, HPO_4^{2-} trapped in the gypsum matrix causes the pH of a neutralized gypsum to drop upon calcination to hemihydrate, or upon subsequent hydration (6).

In comparing the chemical properties of synthetic gypsums, it is useful to divide the impurities found into two types - those which can be washed from the gypsum, and those trapped within the gypsum matrix. The source of these contaminants can be the original ore, chemicals added during processing , contaminants in raw materials, chemical waste dumped into the gypsum pond, etc.

Considering the impurities which can be removed by washing, phosphogypsum is similar to synthetic gypsum from other sources. Utilization of any of these products would be greatly facilitated if these impurities would be removed either during production or by subsequent treatment. Some of the problems associated with the presence of these impurities are as follows:

(1) abnormal dehydration characteristics (aridization);
(2) abnormal hydration characteristics;
(3) poor strength of gypsum core;
(4) poor humidified deflection;
(5) poor paper bond;
(6) efflorescence and poor paint adhesion.

Phosphogypsum contains substantial quantities of these types of contaminants, and in this respect is worse than the other by-product gypsums. In addition, little effort has been made by producers to clean phosphogypsum, A similar comment can be made with respect to fluorogypsum. Only with FGD gypsum is progress being made.

The most serious problem associated with phosphogypsum is the second type of chemical impurity mentioned above, i.e. those trapped within the gypsum crystal. It is known that both the HPO_4^{2-} (7) or ALF_5^{2-} (8) ions can be isomorphically incorporated into the gypsum lattice. The radium contamination also falls into this category.

Some of the problems associated with these types of impurities are:

(1) insensitivity to retarder;
(2) rapid set, slow set, uncontrolled set;
(3) incomplete hydration;
(4) crystal habit modification;
(5) poor strength;
(6) poor bond to paper;
(7) altered calcination properties;
(8) pH;
(9) discolouration, efflorescence;
(10) radioactivity.

Many of the above are related. Since the gypsum product develops strength through the intergrowth of long gypsum needles, interference in growth along one axis of the gypsum crystals will 'result in crystal habit modification and usually a reduction in strength. Figure 1 illustrates the crystal. habit modification obtained when gypsum is grown in the presence of small amounts of phosphate. This modification is the result of the interference of HPO_4^{2-} on the crystallization process and greatly reduces the strength of the set gypsum matrix. This effect is important for gypsum board, where the density of the board is adjusted to give acceptable strengths at minimum weight. In this respect, North American board differs considerably from European board, since the latter is normally 35% higher in density (Ø.95 vs. Ø.7Ø g/cm^3 (5) and as a result would be expected to have approximately 2½ times the compressive strength. The lighter North American board is not so amenable to phosphogypsum, since the strength to weight ratio is quite critical.

These co-crystalline impurities also affect the thermal stability of the host gypsum, even when present at quite low concentrations. Work in our laboratories has shown that the temperature of conversion of soluble to insoluble anhydrite can be raised more than 3ØØ°C (39Ø-4ØØ°C to 72Ø°C) by the presence of 2% P_2O_5 (1Ø). Figure 2 illustrates the point by showing the set time of the hemihydrate slurry to be considerably longer at a $Ca(OH)_2/P_2O_5$ ratio of approximately 1.Ø.

The difficulties encountered in removing these types of impurities are quite substantial. Processes involving a phase change prior to filtration (two step processes, for example, Central-Prayon (11), Nissan (12)) generally result in purer products since during the phase change impurities are removed from the $CaSO_4$ crystals.

Although the problems just discussed can be quite severe, solutions have been found for most, either through a clean-up procedure during gypsum production or by subsequent chemical treatment (11,12,13).

In genera?, this type of impurity is much more significant in phosphogypsum than the other by-product gypsums. This is especially true when one considers the category into which the Ra-226 impurity falls. Unless specific actions are taken, phosphogypsum will contain the impurities which interface with the setting process as well as the radium. In terms of this type of impurity, phosphogypsum is far less attractive than the other alternatives.

SUMMARY

The obvious market for phosphogypsum in North America is gypsum board and to a lesser extent Portland cement. At the present time, phosphogypsum would have to compete in these markets primarily with natural gypsum. This is theoretically possible because phosphogypsum is generally available near market areas. However, international experience has demonstrated that phosphogypsum can only be used when it is properly processed or reprocessed. Unfortunately, phosphogypsum in North America is treated as a waste material instead of a resource and is not properly processed. This is one of the main reasons why phosphogypsum is not competitive.

Other by-product gypsums are of local significance only. However, it is quite possible that FGD gypsum will be available in large quantities in the near future. In contrast to phosphogypsum, it is expected that FGD gypsum will be processed to give a material with good qualities. In that state, FGD gypsum will become a serious competitor for natural gypsum as well as phosphogypsum.

The radiation problem associated with phosphogypsum has not received much discussion in this presentation. In spite of the many problems associated with phosphogypsum utilization, the major barrier to its use in North America is the Ra-226 content, If the regulations (14) recently proposed are actually introduced, it is doubtful that phosphogypsum will be competitive with natural gypsum under any circumstances.

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TABLE I.

GYPSUM CONSUMPTION (1)

PRODUCT	PER CENT	10^6 T/Y (USA)
GYPSUM BOARD, etc.	69·6	15·2
PORTLAND CEMENT	18·4	4·0
AGRICULTURE	7·8	1·7
BUILDING PLASTER	1·9	0·4
INDUSTRIAL PLASTER	1·7	0·4
OTHER	0·6	0·1
	100·0	21·8

TABLE II

ALTERNATIVES TO PHOSPHOGYPSUM

PRODUCT	PRODUCTION RATE 10^6 T/Y (USA)	GROWTH POTENTIAL
PHOSPHOGYPSUM	> 35	GOOD
NATURAL	20 - 25	GOOD
FGD	VERY SMALL AT PRESENT 3 PROBABLE 30 POSSIBLE (4)	EXCELLENT
FLUORO	UP TO 2·0 (2)	GOOD
TiO_2	UP TO 0·8 (1976) (3)	POOR
OTHER	< 1·0	

TABLE III

PROBLEMS ASSOCIATED WITH GYPSUM SOURCE IN BOARD PRODUCTION.

	NATURAL	PHOSPHO	FGD	FLUORO	TiO_2	OTHER
AVAILABILITY						
TRANSPORTATION	●	●		●	●	●
SUPPLY					●	●
BULK PROPERTIES						
COLOUR		●	?	●		●
MOISTURE CONTENT		●	●	●	●	●
CRYSTAL SIZE & SHAPE		●	?	?	?	?
CHEMICAL PROPERTIES						
pH		●		●		●
$CaSO_4\ 2H_2O$ CONTENT	?			●		
SURFACE IMPURITIES		●	●	●	●	●
CO-CRYSTALLINE IMPURITIES		●		●		

TABLE IV

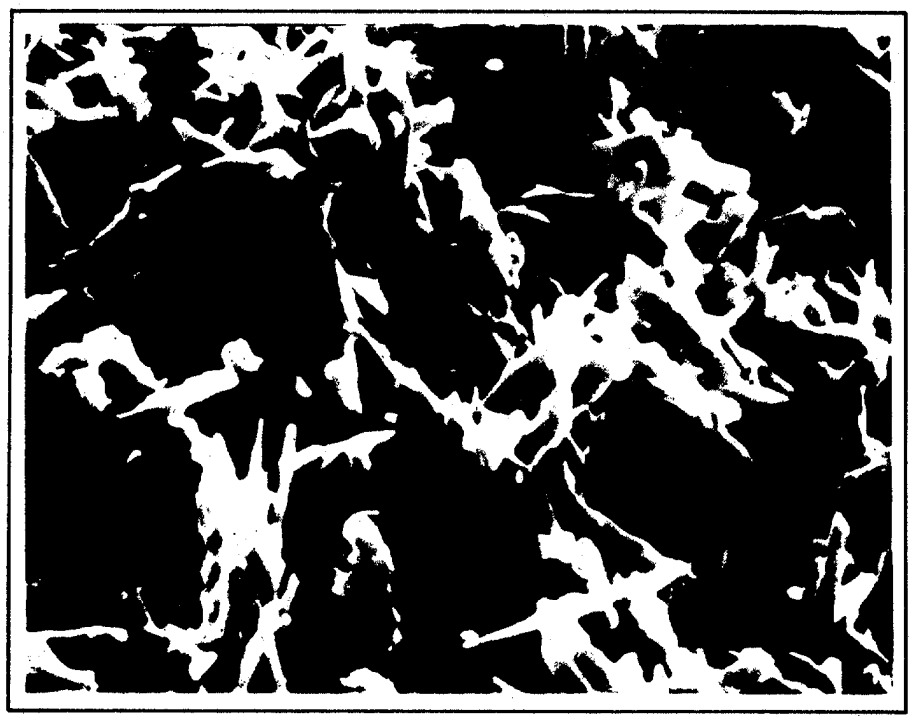
EFFECTS OF CO-CRYSTALLINE IMPURITIES ON THERMAL STABILITY

		IMPURITY	TEMPERATURE °C
(HPO_4^{2-} (10))		% P_2O_5	$CaSO_4$ (III) → $CaSO_4$ (II)
PURE GYPSUM		0	402
PHOSPHOGYPSUM	1.	4·29	732
	2.	3·83	723
	3.	2·87	725
	4.	2·05	720
(AlF_5^{2-} (8))		% Al	$CaSO_4 . 2H_2O \rightarrow CaSO_4 . {}^1/_2 H_2O$
PURE GYPSUM		0	120 - 125 °C
GYPSUM plus AlF_5^{2-}		0.04 - 0.05	145 - 150 °C

FIGURE 1



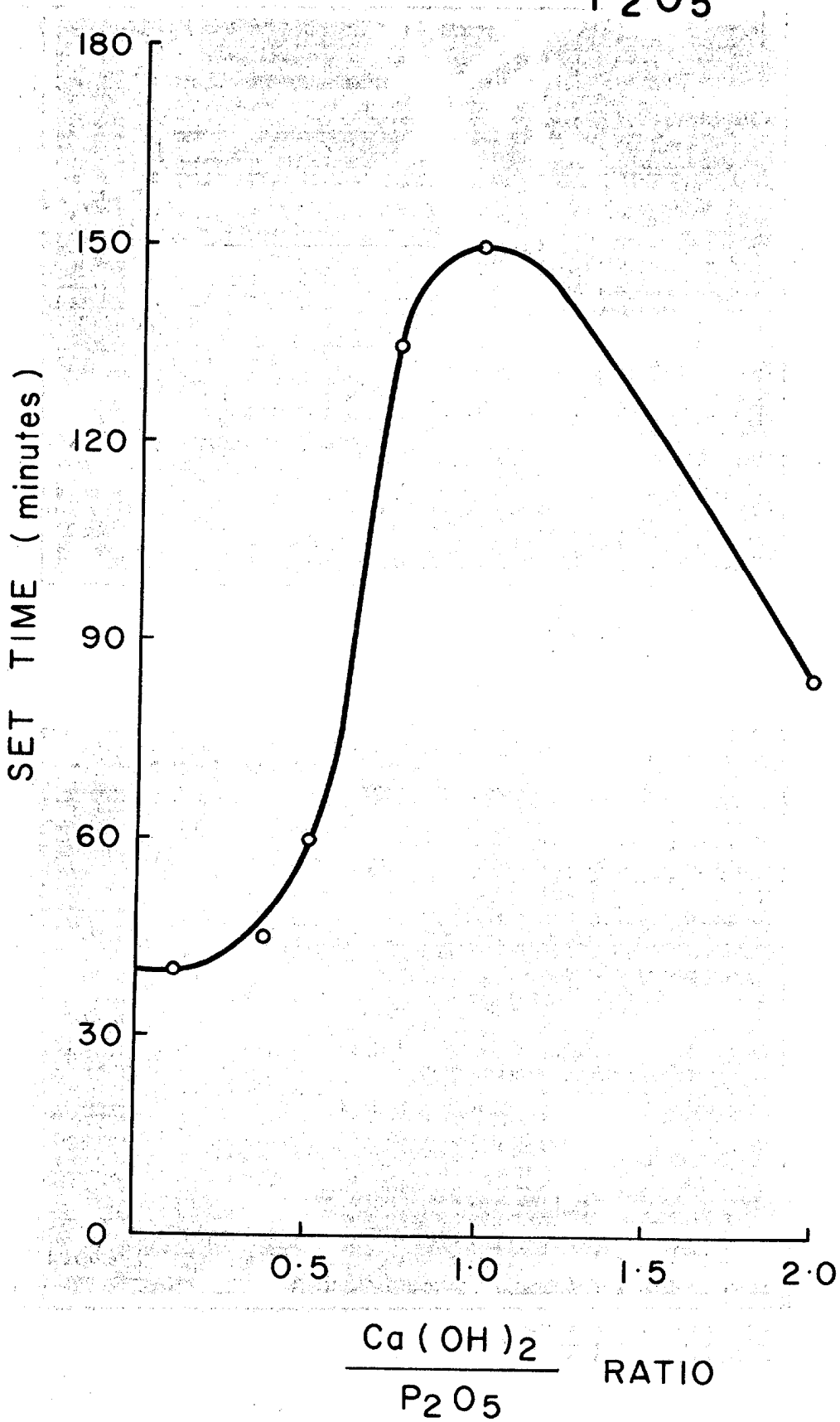
NATURAL



PHOSPHO

FIGURE 2

EFFECT OF SET TIME ON $\frac{Ca(OH)_2}{P_2O_5}$ RATIO



OPTIONS FOR CONSERVING GYPSUM IN THE PRODUCTION OF HYDRAULIC CEMENT AND GYPSUM PRODUCTS

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INTRODUCTION

This paper summarizes an economic analysis of production technology in several gypsum using industries. The object of this research is to investigate the feasibility of three potential options by which society can conserve the nonrenewable resource gypsum within the limits of known or foreseeable technologies. By known technology we mean either methods of production currently in use or methods used in the past. Foreseeable technology, however, is a rather inchoate concept, and we must try to pin it down. What we mean by the term "Foreseeable technology" is production methods that require the direct use of a relevant exhaustible resource; but if the resource becomes more costly, it may be used more efficiently.

To clarify further, our "foreseeable technology" stops far short of the halcyon "Age of Substitutability" envisioned several centuries hence by Goeller and Weinberg (1976) (cf. also Goeller (1979). In that golden age, all currently conceivable production methods would be obsolete. Society's material requirements would be met by "unlimited nonrenewable resources, renewable resources, and the non-dissipative use of rarer minerals. Similarly, society's energy requirements would be fulfilled from breeder reactors, fusion and solar energy. The Goeller-Weinberg "Age of Substitutability" is basically a closed, homeostatic materials and energy system. Of course, even such an idealized state would have to surmount the entrophy law, a principle repeatedly stressed by Georgescu-Roegen (1971), (1979).

There appear to be five foreseeable avenues by which society can conserve an increasingly costly exhaustible resource: (1) by micro-economic substitution of labor and/or reproducible capital for the resource in question, (3) by factor-saving technological progress that reduces particularly the input requirement of the exhaustible resource; (4) by substitution in production of renewable resources or materials based on renewable resources; and (5) by substitution in final demand goods that embody little or none of the exhaustible resource for goods embodying much of it. Of these avenues, we explore the first three.

Trends in Input Costs and Input Use. We deliberately focus on industries that use primarily the exhaustible resource gypsum to produce a reasonable homogenous output or output mix. The form of the natural resource input and the four-digit manufacturing industries in which it is processed are:

Resource Input	Resource-Using Industry (S.I.C. Code)
Gypsum (uncalcined)	Hydraulic Cement (3241)
Gypsum (calcined)	Gypsum Products (3275)

We construct annual series on the current dollar value of net output attributable to' the use of capital, labor and natural resource inputs by adding, each year, purchases of the natural resources input to value added. We then construct for each year in each industry a Divisia aggregate input price index by which the current dollar value of net output is deflated.

Details are discussed in Appendix I.

The sample means of relataive input cost shares appear below, where M_K, M_L, M_N refer to arithmetic mean cost shares of capital, labor, the natural resource.

Industry	M_K	M_L	M_N
Hydraulic Cement	.647	.337	,Ø16
Gypsum Products	.435	.222	.343

The input levels and their prices during the period 1954-1974 are presented in Appendix II. Perhaps the best summary measure of changes in input prices is the estimated trend coefficient from the regression

$$\ell n\, P_{i(t)} = a + bt + c_{i(t)}$$

in which b is an estimate of the proportional rate of change of P_i. We clearly recognize that such an estimate is a summary measure and it is an incomplete description of actual movements in factor costs. Indeed this regression, estimated by ordinary least squares, consistently produces a low Durbin-Watson statistic, a striking indication that the assumption of smooth proportional change misspecifies the actual pattern of input prices. However, we are interested here only in a simple summary measure, not a structural explanation.

The estimated coefficients and their standard errors appear in Table 1. The sample, period is 1954-1974. The cost of capital outlay was trendless in both industries. Hourly labor costs are quite a different story; both industries experienced average annual increases in the range of 5.Ø to 6%. The price of natural resource inputs also increased in a statistically significant sense. The broad patterns of factor price change are clear: labor cost increased relative to the cost of capital in each industry similarly, labor became increasingly expensive relative to natural resources.

Such changes in factor costs should induce responses in relative input use. The trends in employment of labor, capital and natural resources are shown in Table 2. Both industries expanded their stocks of real capital assets at average annual rates of about 3%. Employment decreased somewhat in both industries. And each industry was marked by substantial increases in the use if natural resource inputs. Comparison of the trend coefficients shows that each industry was characterized by the joint substitution of capital and natural resources against labor. This pattern of input use is entirely compatible with the evolution of relative factor costs.

The pervasive substitution of capital and natural resources for labor is an important fact for it emphasizes a considerable scope for variation in factor proportions. The substitution process is, of course, reversible, and during a period of sustained increases in natural resource costs there is little doubt that such resources would be conserved. The observed evolution in factor proportions could be

attributable either to purely price-induced substitution in a static technological framework, or to factor-saving technological change. We now propose two statistical models which may be used to explain the observed patterns of input use.

Transcendental Logarithmic Cost Models. The models that follow are based on three assumptions:

(1) Input prices are predetermined variables for extrepreneurs.

(2) Industry production functions exhibit constant returns to scale.

(3) Entrepreneurs minimize cost, subject to (1) and (2).

A reasonably general, constant-returns-to-scale translog cost function is given by:

$$(1a) \qquad \ell n\, C(P_i,q,t) = a_0 + \ell n\, q + \sum_i a_i \ell n\, P_i + \tfrac{1}{2} \sum_i \sum_j Y_{ij} \ell n\, P_i \ell n\, P_j + Bt + \sum_i B_i\, t \ell n\, P_i$$

Where a_0, a_i, Y_{ij}, B, and B_i are technological parameters, C is total cost, q is physical output, t is an index of technology, and P_i and P_j are input prices. Subscribes i and j index the inputs capital (K), labor (L), natural resources (N). If technological progress is assumed to be neutral and to occur at a constant proportional rate, (1a) takes the simpler form

$$(1b) \qquad \ell n\, C(P_i,q,t) = a_0^* + \ell n\, q + \sum_i a_i \ell n\, P_i + \tfrac{1}{2} \sum_i \sum_j Y_{ij}^* \ell n\, P_i \, n\, P_j + B^* t$$

The restrictions on the parameters of (1a) and (1b) are discussed in Moroney and Trapani (1980).

The rate of technological progress is conceptually the rate at which the unit cost function shifts downward when factor prices are constant. Expressing (1a) as a unit cost function, the rate of technological progress is

$$(3) \qquad R_{1a} = - \frac{\partial \ell\, n(C/q)}{\partial t} = - (B + \sum_i B_i \ell n\, P_i)$$

The term -B is the nonprice-induced part of the overall rate, and the other terms are the price-induced components. Note that the overall rate of technical change is variable, and that it varies directly with P_i if B_i zero.

From equation (1b) the proportional rate of Hicks-neutral technological process is

$$(4) \qquad R_{1b} = - \frac{\partial \ell\, n(C/q)}{\partial t} = - B^*$$

The assumption of cost minimization yields an explicit set of factor demand equations. In particular, the Samuelson-Shephard lemma ensures that at a point of cost minimization the demand for the ith factor is

$$(5) \qquad \hat{X}_i = \partial C(\cdot) / \partial P_i \qquad i = K, L, N$$

Thus the equilibrium cost share of the ith factor is

$$(6) \qquad \hat{M}_i = P_i \hat{X}_i / \xi P_i X_i = \partial \ell n\, C(\cdot) / \partial \ell n\, P_i$$

One may differentiate (1a) with respect to $\ell n\, P_i$ to obtain the minimum cost input demand equations

$$(7a) \qquad \hat{M}_i = a_i + \xi Y_{ij} \ell n\, P_i + B_i t \qquad (i, j = K,L,N)$$

Differentiation of (1b) yields the alternative minimum cost input demand equations

$$(7b) \qquad \hat{M}^*_i = a^*_i + Y^*_{ij} \ell n\, P_i \qquad (i, j = K,L,N)$$

Notice that relative input cost shares in (7a) respond to changes in technology:, Technology change is factor using or factor saving as B_i Ø. Relative shares in (7b) depend only on factor prices, just as we would expect when technical change is neutral,.

For the purpose of estimation, disturbance terms are added to the cost equations (1a) and (1b), and to the factor demand equations (7a) and (7b). Equations (1a) and (7a) and equations (1b) and (7b) are then estimated as separate simultaneous systems.

The central purpose of estimating the parameters of the cost functions (1a) and (1b) is to estimate the overall rate of technical progress, the direction of factor-saving bias, and technical input substitutability. The most widely-used measure of input substitutability is the Allen partial elasticity of substitution.

The cross elasticities of substitution are given by:

$$(8) \qquad \sigma_{ij} = (Y_{ij}/M_i M_j) + 1 \qquad \text{for } i \neq j$$

and own elasticities of substitution by

$$(9) \qquad \sigma_{ii} = (Y_{ii} + M_i^2 - M_i)/M_i^2$$

The cross elasticities indicate which inputs are substitutes or complements for one another in the production process. The greater the substitutability of other factors for the input in question, the greater the opportunity for resource conservation.

There are two other potentially important avenues for resource conservation. First, the neutral component of technological progress, B in equation (3) and B* in equation (4), shows the uniform rate of

reduction in unit input requirements in response to improved technology. Second, the price-induced components, B_j in equation (3), show the reduction in unit input requirements of the specific factors in response to factor-saving technological change.

The three most potential sources of input conservation may be developed by writing the cost-minimizing, constant-output input demand as

$$(10) \qquad x_i = X_i (P_L, P_K, P_N, t).$$

Differentiating (10) totally with respect to time it can be shown that

$$(11) \qquad \dot{x}_i/x_i = M_L \sigma_{iL} (\dot{P}_L/P_L) + M_K \sigma_{iK} (\dot{P}_K/P_K) + M_N \sigma_{iN} (\dot{P}_N/P_N) + \partial \ell n \, x_i/\partial t$$

The proportional change in factor demand is thus expressed in terms of relative shares, substitution elasticities, relative variation in factor prices, and technological change. Equation (11) could be used to stimulate the relative change in input usage in response to altnernative paths of factor prices, given statistical estimates of σ_{ij} and the technical change parameters.

Parameter Estimates. These systems are estimated by the iterative Zellner efficient method for the sample period 1954-1974. The partial elasticities of substitution, evaluated at sample means, appear in Table 3. Asymptotic standard errors are listed in parentheses below the estimated substitution elasticities.

The results indicate that capital and labor are, in general, substitutes in both industries studied here, This means that producers in these industries have had some options for substituting capital for labor in the production process. These substitution possibilities may explain, in part, the trends regarding capital and labor employment in these industries in the face of rising relative labor costs. The results regarding substitution among the other inputs is mixed. There does not appear to be much opportunity for substituting capital for natural resources in the production of gypsum products or hydraulic cement even though these results are somewhat sensitive to model specification. The inference regarding labor and natural resource substitutions are also dependent upon model specification. If the model allows for non-neutral technical then labor and natural resources are complementary in both gypsum products and hydraulic cement. However, if the model is constrained to neutral technical change, labor and natural resources are substitutes in the production hydraulic cement but independent in the production of gypsum products.

The sensitivity of the estimated elasticities to model specification appears to be, in part, due to the importance of non-neutral technical change in these industries. All of the parameters measuring the extent of non-neutral technical change were significant as seen in Table 4. The estimated biases in technical change are generally small,

but are estimated with high precision as indicated by their relatively small asymptotic standard errors. Both industries display labor-saving, and natural resource-using innovations consistent with the movements in relative input prices described in Table 1.

Implications for Commodity Inflation and Resource Usage. Having estimated the translog cost parameters, we proceed to investigate two questions of importance for economic policy. First, what is the impact of rising input costs on the rate of commodity inflation? Second, if natural resource prices were to increase relative to those of capital and labor, to what extent would natural resources be conserved?

One may approach the first question by noting that with constant returns to scale in production, the price of a commodity may be expressed as

$$(12) \qquad P = \sum_i P_i \, (X_i/q)$$

where P_i is the price of the ith input and (X_i/q) is the physical input-output coefficient. Differentiating (12) with respect to time, one obtains

$$(13) \qquad dP/dt = \dot{P} = \sum_i [P_i d(X_i/q)/dt + (X_i/q)\, d\, P_i/dt]$$

If output is held constant,

$$(14) \qquad \dot{P}/P = \sum_i M_{i(t)} \, (\dot{X}_i/X_i) + \sum M_{i(t)} \, (\dot{P}_i/P_i)$$

Assume that technical change is Hicks neutral and occurs at a constant exponential rate B^*, and substitute equations (11) into (14) to obtain

$$(15) \quad \dot{P}/P = \sum_i M_{i(t)} \, [(\dot{X}_i/X_i)_{\substack{\text{technology} \\ \text{constant}}} - B^* \,] + \sum M_{i(t)} \, (\dot{P}_i/P_i)$$

It has been shown Moroney and Toevs (1979) that $\sum_i M \, (\dot{X}_i/X_i) = 0$, so that equation (15) may be simplified to

$$(16) \quad \dot{P}/P = \sum_i M_{i(t)} \, (\dot{P}_i/P_i) - B^*$$

We simulate equation (16) for both industries. In particular, we assume that wage rates and unit capital costs increase by 8 and 4% per year, respectively, and that natural resource prices rise at either 10 or 15 percent annually. These rates of natural resource inflation are, of course, much higher than any experienced historically, but may be useful as a guide in the presence of severe resource shortages.

As shown in Table 5, a 10% increase in natural resource prices would provoke comparatively high rates of inflation in the most resource-intensive industry, gypsum products. Notice also that the commodity inflation rate is elevated by a 15% increase in natural resource prices. In each industry commodity inflation accelerates throughout the simulation period. Although there is generally substitution of capital and/or labor for the increasingly dear natural resource, it is insufficient to prevent a rising natural resource cost share, and thus a quickening of commodity inflation. Since these commodities are used as material inputs to other industries, rapid resource price inflation could stimulate far-ranging inflationary impacts throughout the economy.,

We now consider the closely related question: During an epoch of rising resource prices, would substantial, price-induced conservation of natural resources occur? Recall that the opportunity for conservation, for constant commodity output, hinges on input cost shares and technical input substitution. Accordingly, we simulate the change in demand for natural resources (equation 11) using the estimated substitution elasticities in Table 3 and the estimated rates of Hicks-neutral technical change in Table 4. Again, the simulations are based on the assumptions that input prices follow the paths $(\dot{P}_L/P_L) = .08$, $(\dot{P}_K/P_K) = .04$, and $(\dot{P}_N/P_N) = .10$ and .15. Recall, however that during our sample period the typical pattern of factor price change was $(\dot{P}_L/P_L)(\dot{P}_N/P_N)$ This induced labor-saving and natural resource-using technological change, a tendency that would quite likely be reversed during a period of relatively rapid growth in natural resource prices.

The simulated changes in constant-output factor demand are obtained with the use of equation (11). The optimal (cost-minimizing) levels of input use readily follow from these percentage changes, and appear in Table 6.

Consider first the simulated levels of constant-output factor demand if natural resource prices increase at 10%, capital cost at 4%, and labor cost at 8%. In both industries there would be some growth of real investment and a higher optimal capital stock. Employment levels of labor and gypsum would remain relatively stable in both gypsum products and hydraulic cement.

Consider now the simulations based on natural resource prices increasingly by 15% annually - a rate that would mean resource costs double relative to capital costs in 6-1/2 years, and double relative to labor costs in ten years. In each industry, employment would increase sharply; yet in the face of such steep increases in resource prices, there would be basically no change in the use of calcined gypsum to produce gypsum products, although a modest reduction in uncalcined gypsum could result in hydraulic cement. Overall the opportunities for price-induced resource conservation are painfully meagre in these industries. Thus, the lion's share of resource conservation must be sought in factor-saving technological change. If the estimated magnitudes of input-saving technology in Table 4 are a reasonable guide, we cannot expect much relief from this quarter.

Summary and Conclusions. This research addresses three broad issues. First, we wish to determine trends in relative costs and relative use of capital, labor and natural resources in in two industries that process gypsum. During the period 1954-1974, hourly labor costs in these industries increased by roughly 5% per year. Capital costs , on the other hand, were practically trendless in both industries. We may expect the cost of capital to rise during the foreseeable future because both nominal interest rates and inflation in capital goods prices are likely to remain above historical levels. Natural resource prices typically increased by 1½ to 2½% annually. Broadly speaking, labor became more costly relative to capital and natural resources.

The observed changes in relative input costs (Table 1) induced a pervasive substitution of capital and natural resources against labor (Table 2). If natural resources were to become increasingly costly relative to capital and labor, this pattern of substitution would cease.

Our second objective is to analyze the observed trends in the capital-labor -- natural resources input mix using a neoclassical economic framework. We assume that entrepreneurs attempt to minimize cost subject to predetermined factor prices and constant-returns-to-scale production functions. We develop the analysis using two versions of translog cost functions. One model is based on the assumption that technological change is Hicks neutral. The other allows for biased technical change induced by the evolution of input prices.

The estimated partial elasticities of substitution between capital and labor, capital and natural resources, and labor and natural resources are quite sensitive to the alternative model specifications. Economic theory would suggest that they should be. Using either model, capital and labor are substitutes in both industries. The estimated elasticities between capital and natural resources and between labor and natural resources suggest that there is little opportunity for conservation from input substitution.

Our third objective is to simulate the impacts of factor prices on commodity prices and factor use. To do so, we adopt a setting of natural resource scarcity that has not yet been experienced in this country: natural resource prices are assumed to rise at either 1Ø or 15% per year, while the costs of capital and labor are postulated to increase, respectively, by 4 and 8%. As one would expect, commodity prices are more responsive to resource prices in the more resource-intensive sectors.

Finally, consider the issue of resource conservation. If we adopt the counter-historical assumption of increasing relative costs of mineral resources, we find that the post World War II trends of increasing resource use per unit of output would end. Indeed, neoclassical factor substitution would lead to moderate conservation of gypsum in producing hydraulic cement (Table 6). But little or no reduction in resource use per unit of output would be achieved in gypsum products.

We embarked on this research with the expectation that factor substitution and technological change would be pervasive options for conserving prospectively scarce mineral resources. The evidence from our simulations, however, is that these options are apparently quite limited. The most promising paths to mineral conservation may be found in substitution among semi-finished materials, and in-changes in the structure of final demand.

Table 1. Trends in the Costs of Capital, Labor, and Natural Resource Inputs in Manufacturing Industries

Industry	$\%\Delta P_K$	$\%\Delta P_L$	$\%\Delta P_N$	$\%\Delta P_S$
Hydraulic Cement (3241)	-.00268	.06115	.01498	
	(.00802)	(.00363)	(.00229)	
Gypsum Products (3275)	-.01283	.05038	.02649	
	(.00890)	(.00349)	(.00366)	

Table 2. Trends in Employment of Capital, Labor and Natural Resource Inputs in Manufacturing Industries

Industry	$\%\Delta K^*$	$\%\Delta L^*$	$\%\Delta N^*$	$\%\Delta Q^*$
Hydraulic Cement (3241)	.03245	-.02029	.03165	.01520
	(.00797)	(.00184)	(.00163)	(.00323)
Gypsum Products (3275)	.02570)	-.00569	.01442	.01570
	(.00620)	(.00230)	(.00495)	(.00195)

Note: Estimated standard errors are listed in parentheses beneath the estimated regression coefficients.

All regressions were characterized by positively autocorrelated residuals, according to a Durbin-Watson test. The first-order autocorrelation coefficient, ρ, was estimated, and the original estimated standard errors were adjusted upward (multiplied) by the factor $(1 + 2\hat{\rho})^{\frac{1}{2}}$. For 'the rationale of this adjustment see Wold [1953, p. 44].

Table 3. Partial Elasticities of Substitution Between Capital (K), Labor (L), Natural Resources (N), and Scrap (S) in U. S. Four-Digit Manufacturing Industries

	Hydraulic Cement		Gypsum Products	
	Non-neutral	Neutral	Non-neutral	Neutral
σ_{KL}	.18 (.13)	.65 (.02)	.47 (.21)	.83 (.07)
σ_{KN}	.24 (.32)	- .38 (.23)	1.40 (.35)	.08 (.12)
σ_{LN}	-1.02 (.62)	1.08 (.18)	- .67 (.15)	- .18 (.14)
σ_{KK}	- .10 (.07)	- .33 (.01)	-1.35 (.28)	- .49 (.12)
σ_{LL}	- .30 (.24)	-1.30 (.05)	.11 (.41)	-1.35) (.13)
σ_{NN}	11.94 (10.39)	-7.40 (12.23)	-1.34 (.40)	.01 (.17)

Table 4. Estimates of the Rate and Bias of Technological Change in U. S. Four-Digit Manufacturing Industries

Industry	Bias: β_L	β_K	β_N	Non-neutral Rate
Hydraulic Cement:	-.00431 (.00093)	.00352 (.00097)	.00079 (.00017	.00072
Gypsum Products	-.00303 (.00117)	-.00543 (.00177)	.00846 (.00185)	.00000

Note: The non-neutral rate is computed from equation (3) of text, and is evaluated at the sample means of factor prices.

The neutral rate is not reported here. Our procedure-for deflating the the value of output resulted its estimated value being biased toward zero. For a discussion of this problem see Moroney and Trapani (1980).

Table 5. Simulated Commodity Inflation Rates in Natural Resource Using Industries

	Hydraulic Cement (3241)		Gypsum Products (3275)	
	% ΔP_N = 10	% ΔP_N = 15	% ΔP_N = 10	% ΔP_N = 15
1975	5.7%	5.8%	7.2%	9.2%
1980	5.8	5.9	7.5	10.1
1985	5.9	5.1	7.8	11.1
1990	6.0%	6.2%	8.2%	12.1%

Note: The simulated commodity inflation rates are based on the assumptions that % ΔP_L = 8 and % ΔP_K = 4 in all industries.

Table 6. Simulated Levels of Input Use in Natural Resource Using Industries

Gypsum Products (3275)

	$\%\Delta P_N = 10$			$\%\Delta P_N = 15$		
	Capital (Millions of 1967 $)	Labor (Million Manhours)	Gypsum (Million Short Tons)	Capital (Millions of 1967 $)	Labor (Million Manhours)	Gypsum (Million Short Tons)
1974	586	23.0	11.0	586	23.0	11.0
1980	617	21.6	10.9	619	22.1	10.8
1985	641	20.7	10.9	634	22.2	10.7
1990	660	20.1	10.9	600	22.9	10.7

Hydraulic Cement (3241)

	$\%\Delta P_N = 10$			$\%\Delta P_N = 15$		
	Capital (Millions of 1967 $)	Labor (Million (Manhours)	Gypsum (Million Short Tons)	Capital (Millions of 1967 $)	Labor (Million Manhours)	Gypsum (Million Short Tons)
1974	3,375	60.7	4.06	3,375	60.7	4.06
1980	3,587	55.4	4.06	3,587	55.8	3.59
1985	3,787	51.4	3.92	3,796	52.3	2.95
1990	4,010	47.9	3.71	4.037	49.3	2.32

MEASUREMENT OF VARIABLES

In this section we describe the procedures employed to measure each variable to be used in the analysis. Data are developed for the years 1954-1974.

Value of Input (VO). This variable is conceptually the contribution to the nominal value of production of capital, labor and the natural resource input(s) employed by the industry. We have deliberately selected industries that make comparatively intensive use of labor, reproducible capital, and homogeneous natural resource inputs. And we assume that the economic contributions of these agents are separable from those of other intermediate inputs. Value of output is measured here as the sum of value added (VA) and the total cost of the natural resource ($P_n N$). That is,

$$(1) \quad VO = VA + P_n.N$$

when scrap and the natural resource input are conceptually separate inputs.

Value added (VA) is reported for the 4-digit industries in the Census of Manufactures and Annual Survey of Manufacturers for the years under review. The measurement of natural resource price and input series is discussed below.

Price Deflator For Value Of Output. For each industry we construct a Divisia aggregate input price index. Under the assumptions of constant returns to scale and cost minimization for the industry, an aggregate input price index is the appropriate deflator for the nominal value of output (Arrow 1974); and if the underlying production technology is consistent with a translog cost function (either homothetic or nonhomothetic, but characterized by Hicks-neutral technological change), the Divisia input price index is an exact deflator for the nominal value of outpit (Diewart 1976). It appears to be a reasonably accurate deflator for a wide range of production technologies.

The aggregate Divisia input price in period t relative to that in period t-l is

$$P_I(t)/P_I(t-1) = [P_i(t)/P_i(t-1)]^{1/2}(S_i(t) + S_i(t-1))$$

for t = 1, ---, 2Ø and i = K,L,N.(and S in industries 3312 and 3351). The index is defined such that $P_i(o) = 1$, and each year's index is linked to the base year (1954) through chain multiplication. The nominal value of output in each year is deflated by the aggregate input price index, thereby yielding a time series of real output expressed in 1954 dollars.

Real Capital Stock (K*). The nominal capital stock is measured as gross book value of capital assets when reported by Census of Manufactures and Annual Survey of Manufactures. For several years (1954-56, 1958-61, 1965-66) these figures were not reported and had to

be approximated. Data on new capital expenditures, available in the Annual Survey of Manufactures, and an adjustment for fully depreciated capital, permitted the approximation of gross book value in all of these years for the industries under study.

To deflate gross book value of assets we employed a composite price deflator, which adjusts for the price of structures and the price of durable equipment. That is, the gross book value for an industry is separated into two components: structures (plant and structures) and nonstructures (machinery and equipment). This disaggregation permits the consideration of the separate price movements in new structural additions and in new nonstructural investments. In addition, structures have substantially longer useful lives than nonstructures, so it is necessary to employ a different deflator for each type of asset.

Consider first the method used to obtain a gross book value deflator for nonstructurers in a specific manufacturing industry. A nonstructure that is in service less than n years is included in gross book value, where n is the average useful life of a nonstructure. (These life expectancies, which average 12 years, are obtained from the U.S. Department of Treasury publication, Tax Information on Depreciation.) The formula used to calculate the deflator for the non-structure component of gross book value in year T, DnT is:

$$DnT = \sum_{t=T-n}^{T} \frac{Nit \quad dnT}{\sum_{t=T-n}^{T} NIt}$$

where dnt is the Implicit Price Deflator for Producers' Durable Equipment in year t (compiled and reported by the Department of Commerce in the Survey of Current Business) and NIt is constant dollar nonstructure investment in year t. Thus, the weights are determined by the relative importance of each year's investment in total non-depreciated investment of nonstructures.

Since nonstructure investment is reported for 4-digit manufacturing industries beginning in 1947, a less precise method of computing D_{nt} for the years 1954 to 1947 + (n-l) was employed. It was assumed that the annual industry investment in nonstructures for years prior to 1947 is in the same proportion to total manufacturing investment in nonstructures as its average for the years 1947 through 1965. Total manufacturing investment in nonstructures is known for the years prior to 1947. It is computed as the sum of lines 8,9,1Ø,15,16,17,2Ø,21,23,29 and 3Ø in Tables 5.4 of Office of Business Economics, National Income and Product Accounts of the United States, 1929-1965. Thus, one can approximate industry-specific investment for these years.

APPENDIX 2

DATA TABLES

1958 and 1966 were estimated by

$$R_{67} = R_{57} (1 + g)^{9}.$$

Data required for the cost of labor computation are reported in Census of Manufactures and the Annual Survey of Manufactures.

Natural Resource Inputs (N*) and Prices (Pn). The data on resource input and resource input prices are taken from the Minerals' Yearbook unless otherwise noted.

a. Uncalcined Gypsum To Hydraulic Cement (SIC 3241). Consumption of uncalcined gypsum (in short tons) as cement retarder is the resource input series employed.

The price is computed as the average value (dollars per short ton) of uncalcined gypsum sold for Portland cement retarder.

b. Calcined Gypsum to Gypsum Products (SIC 3275). Total calcined gypsum produced (short tons) is used as the resource input series. Commodity experts at the Bureau of Mines stated that essentially all calcined gypsum is for use in gypsum products, so the industrial disposition of this natural resource is known with accuracy.

The price series is computed as average value of calcined gypsum at the processing plant. Since the calcining of gypsum and its subsequent use in gypsum products is almost always a continuous process in a common production site, the computed price series reflects with accuracy the unit cost to the input purchaser.

Consider now the structures component of gross book value. We assume that structures have a useful life of forty years. A deflation procedure similar to that just developed is unfruitful because yearly investment in structures is reported for 4-digit industries only since the year 1947. The only workable alternative is to assume that for each industry the ratio of investment in structures has been constant since 1913. This assumption, although somewhat restrictive, has a precedent in the literature. For example, George Stigler (1963) and Daniel Creamer, et al. (1960), used it to derive gross book value deflators for specific industries.

The construction price index, $d_S m$ used to build a deflator for the gross book value of structures is the Boeckh's Price Index of Commercial Construction. The measured used for total manufacturing investment in structures is the "Industrial and Commercial Construction Put in Place" series. Both are reported in the Statistical Abstract of the United States. The deflator for gross book value of structures in year T, D_{ST}, is:

$$D_{ST} = \sum_{t=T-n}^{T} \frac{SI_t \, d_{ST}}{\sum_{t=T-n}^{T} SI_t}$$

where SI_t is the constant dollar investment in structures undertaken by all manufacturing industries in year t. Given the assumption made above, the resulting deflator will be applicable to all the sample industies.

The two components of gross book value cannot be individually deflated because reported gross book value is not always disaggregated into structures and nonstructures. Therefore, a composite deflator is calculated as a weighted average of the nonstructures deflator and the structures deflator. In each manufacturing industry the weights are the average relative shares of structures and nonstructures in gross book value during the period 1967-1974. The resulting figures are used industry by industry to deflate the series on the gross book value of capital assets, forming the constant dollar gross book value series that serve as our measures of capital stocks.

Cost of Capital (P_K). The cost of capital is computed as a residual rate of return to capital.

$$P_K = \frac{VA - P_L \cdot L^*}{K^*}$$

where $P_L \cdot L^*$ represents total labor costs.

Labor Input (L*). Labor input is measured as the sum of (i) total man hours of production employees, plus (ii) 2,000 man hours per non-production employee per year. Data required for this computation are reported in the Census of Manufacturers and Annual Survey of Manufactures.

Cost of Labor (P_L). The cost of labor is computed as the sum of total payroll plus total supplements divided by total manhours (L*). Supplemental labor costs are divided into legally required expenditures and payments for voluntary programs. The legally required portion consists primarily of Federal Old Age and Survivor's Insurance, Unemployment Compensation and Workers' Compensation. Payments for voluntary programs include those not specifically required by legislation, whether they were employee initiated or as the result of collective bargaining (e.g. employer portion of insurance premiums, pension plans, stock purchase plans on which the employer payment is not subject to withholding tax, etc.).

Total supplements were reported for the years 1954-56 and 1958-66 and were therefore approximated. The procedure was to estimate the rate of growth (g) of the ratio of total supplements to total payroll (R) and apply this ratio to total payroll.

TABLE 1A

UNCALCINED GYPSUM TO HYDRAULIC CEMENT

Year	Real Value of Output (3241) (Million 1954$)	Uncalcined Gypsum Consumed (Million ST)	Uncalcined Gypsum Per Unit Of Ouput (ST/$)	Price of Uncalcined Gypsum ($/ST)	Share In Total Input Cost
1974	864.295	4.058	.0047	5.94	.01981
73	845.190	4.148	.0049	5.35	.01971
72	847.028	3.924	.0046	4.95	.01755
71	788.413	3.386	.0043	4.78	.01611
70	810.409	3.358	.0041	4.74	.01615
69	830.955	3.464	.0042	4.58	.01677
68	823.951	3.439	.0042	4.66	.01786
67	838.357	3.154	.0038	4.66	.01645
66	848.376	3.372	.0040	4.61	.01773
65	846.351	3.152	.0037	4.68	.01661
64	839.214	3.034	.0036	4.28	.01479
63	839.231	2.898	.0035	4.46	.01466
62	829.266	2.765	.0033	4.47	.01424
61	810.459	2.763	.0034	4.27	.01382
60	807.152	2.543	.0031	4.42	.01361
59	794.023	2.757	.0035	4.30	.01487
58	751.882	2.416	.0032	4.23	.01337
57	713.178	2.273	.0032	4.21	.01392
56	663.691	2.394	.0036	4.02	.01560
55	584.776	2.226	.0038	3.92	.01647
54	533.391	2.051	.0038	3.75	.01587

SOURCES: See Appendix 2.

TABLE 2A

CAPITAL USE IN HYDRAULIC CEMENT

Year	Real Capital Stock (Million 1967 $)	Capital Per Unit of Output ($/$)	Price of Capital	Share In Total Input Cost
1974	3374.85	3.904	.2021	.56061
73	3255.83	3.852	.1983	.57363
72	3250.21	3.837	.2047	.60126
71	2984.51	3.785	.2093	.62186
70	3044.17	3.756	.2050	.63325
69	3134.43	3.772	.1938	.64229
68	3083.16	3.742	.1910	.65649
67	3105.31	3.704	.1906	.66268
66	3088.58	3.640	.1878	.66167
65	3060.29	3.616	.1942	.66946
64	2996.35	3.570	.2000	.68242
63	3008.35	3.585	.2032	.69330
62	2943.97	3.550	.2060	.69892
61	2813.77	3.472	.2121	.69951
60	2680.91	3.321	.2089	.67826
59	2530.85	3.187	.2093	.66459
58	2370.27	3.152	.2179	.67626
57	2195.90	3.079	.2064	.65954
56	1928.74	2.906	.2036	.63666
55	1597.90	2.732	.2034	.61356
54	1411.05	2.645	.2084	.60669

SOURCES: See Appendix 2.

TABLE 3A

LABOR USE IN HYDRAULIC CEMENT

Year	Labor Input (Mill Man Hours)	Labor Per Unit of Output (Man Hrs/$)	Price of Labor ($/Man Hour)	Share In Total Input Cost
1974	60.7	.0702	8.410	.41958
73	60.6	.0717	7.556	.40666
72	61.3	.0723	6.882	.38119
71	58.6	.0743	6.206	.36203
70	61.1	.0754	5.656	.35060
69	62.2	.0748	5.185	.34094
68	62.6	.0759	4.668	.32565
67	65.3	.0779	4.389	.32087
66	68.1	.0802	4.128	.32060
65	69.1	.0816	4.033	.31393
64	70.4	.0839	3.777	.30279
63	70.0	.0834	3.679	.29204
62	70.7	.0852	3.521	.28684
61	72.3	.0892	3.383	.28667
60	79.1	.0979	3.217	.30813
59	84.4	.1063	3.027	.32054
58	82.1	.1092	2.888	.31037
57	81.6	.1144	2.751	.32654
56	84.8	.1278	2.529	.34774
55	84.8	.1450	2.311	.36997
54	82.4	.1545	2.220	.37744

SOURCES: See Appendix 2.

TABLE 1B

CALCINED GYPSUM TO GYPSUM PRODUCTS

Year	Real Value of Output (3275) (Million 1954$)	Calcined Gypsum Consumed (Million ST)	Calcined Gypsum Per Unit of Output (ST/$)	Price of Calcined Gypsum ($/ST)	Share In Total Input Cost
1974	362.68	10.993	.0303	18.71	.40456
73	385.23	12.592	.0327	16.31	.40944
72	377.24	12.005	.0318	16.32	.39997
71	347.60	9.562	.0275	15.96	.34148
70	329.27	8.449	.0257	15.63	.32291
69	348.22	9.324	.0267	15.39	.35273
68	344.23	8.844	.0257	15.07	.35987
67	321.34	7.879	.0245	14.66	.32464
66	336.42	8.434	.0250	14.20	.33555
65	352.47	9.320	.0264	14.27	.34668
64	348.65	9.440	.0270	14.39	.34988
63	338.31	9.181	.0271	14.34	.34739
62	333.02	8.819	.0265	14.45	.33878
61	313.01	8.246	.0263	14.33	.32913
60	312.67	8.591	.0275	14.08	.34484
59	314.81	9.268	.0294	12.06	.33353
58	289.38	8.122	.0280	11.25	.29626
57	282.10	7.801	.0276	10.70	.29635
56	296.29	8.608	.0290	10.61	.31538
55	281.38	8.848	.0314	10.01	.33003
54	241.48	7.618	.0315	10.00	.32812

SOURCES: See Appendix 2.

TABLE 2B

CAPITAL USE IN GYPSUM PRODUCTS

Year	Real Capital Stock (Million 1967 $)	Capital Per Unit of Output ($/$)	Price of Capital	Share In Total Input Cost
1974	586.25	1.616	.2850	.32871
73	556.84	1.445	.2780	.30869
72	553.52	1.467	.2963	.33485
71	584.52	1.681	.3101	.40566
70	591.42	1.796	.3018	.43646
69	595.95	1.711	.2760	.40439
68	582.78	1.693	.2714	.42714
67	596.66	1.856	.2726	.45723
66	594.84	1.768	.2680	.44673
65	587.99	1.668	.2863	.43882
64	561.77	1.611	.3032	.43870
63	547.92	1.619	.3136	.45342
62	544.63	1.635	.3230	.46768
61	508.42	1.624	.3406	.48232
60	481.60	1.540	.3349	.45988
59	545.56	1.444	.3382	.45876
58	430.46	1.487	.3622	.50561
57	420.42	1.490	.3358	.50128
56	416.35	1.405	.3309	.47572
55	362.71	1.289	.3327	.44977
54	303.18	1.255	.3476	.45394

SOURCES: See Appendix 2.

TABLE 3B

LABOR USE IN GYPSUM PRODUCTS

Year	Labor Input (Mill Man Hours)	Labor Per Unit of Output (Man Hrs/54 $)	Price of Labor ($/Man Hour)	Share In Total Input Cost
1974	23.0	.0634	5.896	.26673
73	25.6	.0664	5.523	.28187
72	25.5	.0676	5.094	.26518
71	23.8	.0685	4.748	.25286
70	22.8	.0692	4.316	.24063
69	24.2	.0695	4.083	.24288
68	23.4	.0679	3.371	.21299
67	21.8	.0678	3.560	.21813
66	24.2	.0719	3.211	.21772
65	26.0	.0737	3.165	.21450
64	26.6	.0763	3.086	.21142
63	25.4	.0750	2.972	.19919
62	25.5	.0766	2.855	.19354
61	24.5	.0783	2.763	.18855
60	25.8	.0825	2.655	.19528
59	27.0	.0857	2.578	.20771
58	24.8	.0857	2.464	.19813
57	24.6	.0872	2.317	.20237
56	27.3	.0921	2.216	.20890
55	27.9	.0991	2.118	.22020
54	25.3	.1048	2.000	.21794

SOURCE: See Appendix 2.

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Uses of Phosphogypsum in Agriculture

AGRICULTURAL USE OF PHOSPHOGYPSUM ON NORTH CAROLINA CROPS

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INTRODUCTION

Sulfur (S) is an essential element in the life processes of all living things, including microorganisms, higher plants and animals and man. This element is universally distributed over the earth. Sulfur is present in the soil in both organic and inorganic forms. The organic forms are components of living and dead microorganisms and of the residues of higher forms of life that constitute the soil organic matter. The inorganic forms are minerals that were contained in the original rocks from which soils were formed or they may have developed during the degradation of these rocks. Or they may be end products of microbial decomposition of sulfur containing organic compounds in the soil organic matter.

Further, sulfur occurs throughout the universe as the element (S), as a gaseous constituent of the atmosphere (SO_2), as pyrite (FeS_2), as sulfates, of which gypsum ($CaSO_4 \cdot 2H_2O$ and anhydrite ($CaSO_4$) are the most common mineral forms, and in natural sour gases as H_2S. Large quantities of magnesium (Mg), sodium (Na), and potassium (K) sulfates are found in salt deposits derived from the waters of ancient seas, and in less concentrated but similar deposits in the unleached soils of arid regions.

The atmosphere contains about Ø.Ø25 ppm sulfur as SO_2. The average over-dried soil contains about Ø.Ø5% sulfur. The dry matter of the average microbe contains about Ø.15% sulfur, that of the average plant about Ø.7Ø%, and that of the average man about 1%. Living organisms serve as concentrating agents for sulfur, but much higher concentrations of sulfur are found in mineral forms of the element, the sulfur content of gypsum being 18.6%, anhydrite 23.5%, pyrite 53.3%, and the large deposits of elemental sulfur about 99.5%.

Soil-Sulfur Relationships. Although sulfur is considered one of the essential elements for plant growth, attention should be given at this point to soil-plant relationships with this element. Attention today, primarily, will be given to sulfate (SO_4) relationships.

Because of its anionic nature and the solubility of most of its common salts, leaching losses of sulfates are generally rather large. However, their tendency to disappear from soils varies widely. As an example, University of Georgia researchers showed that cotton, grown for five years on two texturally different soils, responded differently to sulfur applications at Ø,4,8,16 and 32 lbs/A per year. On the silt loam soil no responses to added sulfur were observed at the end of the five-year experiment. On the sandy loam soil, however, a sulfur deficiency developed during the fourth cropping year at the zero level of added sulfur. Further evidence as to why differential responses to sulfate sulfur applications occur with different soils are shown in Tables 1 and 2.

These data show the real possibility of sulfur deficiencies occurring when surface layers of soil are low in available sulfur. These conditions frequently occur in the southeastern United States where annual rainfall may exceed 5Ø or so inches each year.

Development of Sulfur Needs. Changes in cropping patterns, fertilizer sources, environmental safeguards and possibly other factors may aggravate the need for sulfur. These conditions, as spelled out by personnel of the Sulfur Institute, are the balance between all additions of this nutrient in precipitation, atmosphere, irrigation water, crop residues, fertilizers and other agricultural chemicals, and all losses through crop removal and leaching.

The importance of incidental additions of sulfur in precipitation and atmospheric processes depends upon the composition of fuels, distance from emitting sources, and pollution control measures. High yielding varieties, high plant populations and improved management practices (including heavier rates of fertilization, irrigation and double cropping) all contribute to greater withdrawal of soil sulfur. The increasing need and popularity of high-analysis fertilizers low in sulfur is reducing the amount being provided unintentionally in fertilizer programs. Leaching losses will vary depending upon soil characteristics, precipitation distribution patters, ground cover, etc.

Nearly 30 years ago, the Southern Regional Sulfur Project was begun (1952) to study sulfur supplies and requirements for crops and to assess the importance of technological changes on the sulfur nutrition of crops (5). Field experiments were widely distributed in the South and were conducted on diverse soil types with crops common to the area. The results of these field experiments represent fairly accurately the need for sulfur as a plant nutrient in the south. It was concluded that yields would decline on 63% of the soils if sulfur-free fertilizers were used exclusively for seven years or less. This decline would be progressive. There were no responses to supplemental sulfur in the first year of the experiments, but in each of six succeeding years some new fields showed positive needs for sulfur.

The consensus of the many investigations on this project was that farm operators of the South can no longer rely on incidental additions of sulfur from rainwater, atmosphere, insecticides and fertilizers if crop production is to be maintained or increased. Planned additions of sulfur are mandatory.

Use of Gypsum on North Carolina Crops.

Use on Corn. Recently, Rabufetti and Kamprath completed several field experiments on eastern North Carolina experiment stations evaluating sulfur requirements of corn. Response of corn to selected sulfur and nitrogen rates was noted. At the Coastal Plain Tobacco Research Station, Kinston, N.C. the soil was a Goldsboro loamy sand, classified as an Aquic Paleudult, fine loamy, siliceous thermic. The A horizon is 25 cm thick and has a low capacity for available water and a high leaching potential. At the Central Crops Research Station, Clayton, N.C. the soil is a Wagram loamy sand, 0 to 2% slope, classified as an Arenic Paleudult, fine loamy, siliceous thermic. It has a loamy sand A horizon ranging from 50 to 60 cm thick and a sandy clay loam B horizon. Gypsum was used in all studies to supply sulfur. Grain yield for the different treatments at the two locations are given in Tables 3 and 4.

These investigators conclude that the effect of sulfur on corn yields (either grain or total dry matter production) was highly dependent on the rate of nitrogen applied. For nitrogen rates of about 150 to 200 pounds per acre and for yield levels like those obtained at each site, the additions of 30 to 60 pounds of sulfur per acre will increase grain yields 5 to 9% at Kinston and from 6 to 14% at Clayton. The higher response to sulfur fertilization at Clayton was probably due to the overall lower native sulfur supply in the rooting zone explored by corn in the Wagram soil as compared to the Goldsboro soil at Kinston.

Reneau and Hawkins recently report results from numerous field tests of sulfur by corn and soybeans, Available sulfur from seven representative Virginia soils sampled at three different depths (0-25 cm, 25-50 cm and 50-75 cm) ranged from 2.2 to 25.0 kg/ha in the top layer, 1.0 to 117 kg/ha for the next depth and 1.0 to 166 kg/ha from the deepest depth.

They suggest that corn will probably respond to sulfur application in Coastal Plain soils that are moderately well to well-drained, low in organic matter, and belong to the fine-loamy or coarser textured families of soils with extractable soil sulfur concentrations of 6-7 kg/ha or less in the surface horizon. Soils with the same characteristics, but with extractable sulfur between 7 and 15 kg/ha, are expected to respond under certain conditions related to soil moisture, accumulation of sulfur in the subsurface horizons, and the depth to these sulfur enriched horizons.

Use on Tobacco. Flue-cured tobacco is grown in 64 of North Carolina's 100 counties. Its sales generated over one billion dollars in 1979. A crop as important as this one is seldom underfertilized; in fact, it is still frequently over-fertilized. Occasionally one will see a sulfur deficiency but not often because most tobacco fertilizer manufacturers intentionally include 7 to 8% sulfur to supply this necessary element. A sulfur deficiency appears as light yellow leaves before the crop has reached maturity and the plants remain small, especially on deep sandy soils. Gypsum can be economically applied to alleviate this nutrient deficiency.

Use on Small Grain. Occasionally it is noted that wheat does not respond as expected from a spring topdressing of nitrogen, especially on deep sandy surfaces of Coastal Plain soils. A topdressing with gypsum, as shown in the slide, caused a greening of the wheat on a Wagram loamy sand during March 1979 at the Central Crops Research Crops Station, Clayton, N.C.

A plausible explanation of the situation above is supported by work of Rhue. Soft red winter wheat (Blueboy variety) was planted in October 1969 on a Wagram soil. Fifty pounds per acre of sulfur using gypsum was applied at planting time. Although moisture stress during April to June of 1970 prevented the achievement of high grain yields, the movement of sulfate sulfur (SO_4) during the winter and early spring was noteworthy. Sulfate from gypsum had leached from the top six inches of the Wagram loamy sand 150 days after application.

The movement of SO_4 from gypsum into the 6-12 inch and 12 to 18 inch depth with time is shown in Figures 1 and 2. A considerable amount of SO_4 apparently leached into the 6-12 inch depth during the first 44 days after application. As the SO_4 moved out of the 6-12 inch depth, it accumulated to some extent in the 12-18 inch depth. Furthermore, the SO_4 from gypsum had completely leached from this lower depth 186 days after application.

When sampled on March 23, the sulfur content of wheat grown on the Wagram soil was significantly increased at all three sulfur rates (10,20 and 40 lbs/A) when compared to the no sulfur treatment. By May 21, however, 1% sulfur content was only significantly higher with the 40 lbs. per acre rate.

Although dry matter was not significantly increased by sulfur application at any sampling there was a trend for dry matter to increase with increasing rate of sulfur at the first sampling (March 23) only. Rainfall was optional for growth during the period preceding the first sampling but was well below average during the months of April and May. Consequently, dry matter was more affected by climatic conditions after March and this probably explains the lack of response to sulfur at the second and third sampling (April 27, May 21). The yields also failed to show significant differences and no trends were discernible.

Where leaching of SO_4 occurs, as with the Wagram soil, fall application of sulfur as gypsum at rates as low as 40 lbs. sulfur per acre may result in little or no additional SO_4 available in the early spring when growth beings. Improved efficiengy of sulfur uptake should occur on sandy soils by applying the sulfur as a topdressing in early spring. On the other hand, where subsoils with high SO_4 levels are within the root zone of crop plants, little benefit appears likely from application of any sulfur.

In 1970-71, Blueboy wheat was again planted at this same site to evaluate the effect of source and time of application of sulfur. A response to sulfur was noted, as much as seven bushels per acre increase from fall applied sulfur to ten bushels per acre increase from spring applied sulfur (Table 5).

Use on Coastal Bermudagrass. It has been generally recognized that sulfur is an important element in crop production. Numerous investigators (11,12) in the southern United States have discussed the problems related to supplying the sulfur needs of forage plants. As a group, legumes tend to be more sensitive to sulfur supply than grasses. Therefore, forage grasses (such as coastal bermuda) have received less attention, with the data on sulfur response of this group of plants still being rather limited. Woodhouse presents enlightening and useful information about sulfur responses of coastal bermudagrass (Cynodon doctylon). A long time field experiment evaluating the response of this important forage grass to selected N, P, K and lime variables on a Eustis loamy sand was completed in 1968. The response to sulfur at all rates of nitrogen (0 to 672 kg/ha) is presented in Table 6.

Sulfur-nitrogen relationships in forages have been evaluated, For example Stewart and Whitfield concluded from their results, and in an examination of other published data, that the N/S ratio is a very good criterion in assessing the sulfur status of plants. They also proposed that a sulfur deficiency may be suspected when the N/S ratio in the forage exceeds 17. Woodhouse presents the N/S ratio in the following table over the seven-year period for the plus sulfur treatment, across six nitrogen rates (Table 7).

There is a definite positive relationship between the N/S ratio and the rate of nitrogen applied. These data suggest the possibility that low sulfur uptake may have been a factor in the lack of response to the higher rates of nitrogen at this site. N/S for the no-sulfur treatment (>90:1) is extremely high, due no doubt in part to the high rate of nitrogen applied with this treatment. In all probability if no sulfur had been used at any nitrogen rate, the N/S ratio would have been undesirably wide.

The high N/S ratios found in this experiment suggest the need for consideration of the nutritive value of such forage. Allway and Thompson have reviewed this aspect of forages and conclude, from the limited data available, that the optimum N/S ratio for ruminant nutrition is 10:1 to 15:1, which is generally lower than that considered necessary for optimum growth. When these standards are applied to the data in Table 7, all forage produced at rates of nitrogen above about 300 kg N/ha becomes suspect as an unsupplemented feed for ruminants.

It has been the experience of both research workers and farmers in the Southeast that, although coastal bermuda is quite responsive to nitrogen fertilization, high forage yields are not always matched by correspondingly high animal production. Most cases of poor animal performance on this grass may be attributed to such factors as lack of palatability, low intake, low digestibility. The data from this experiment suggest that low sulfur , or high N/S, may also be a factor and one which should be investigated whenever conditions appear conducive to the development of low sulfur in coastal bermudagrass.

Use on Peanuts. Peanuts (Arachis hypogaea) possess a unique nutritional habit. Supplemental calcium (CA) must be supplied to the "peg," a modified stem that penetrates the soil surface to form the fruit or nut. It is an accepted practice that Ca should be applied to or near the soil surface to large-seeded Virginia-type peanuts to promote better fruit development. Numerous reports (16,17,18,19,20) have shown that supplemental Ca improved quality and yield of large-seeded peanuts. In view of these effects, the use of supplemental Ca on large seeded peanuts will continue. Historically, finely ground landplaster was the principal supplemental Ca source use for peanuts in the Virginia-North Carolina peanut producing belt. Recently, two other sources of landplaster have entered the market for possible use on peanuts. These two materials were adapted for bulk-spreading.

The U.S. Gypsum Company developed a granular landplaster called 420 Landplaster Bulk (420-Bulk) and Texasgulf, Inc. merchandised a gypsum by-product (Tg Gypsum) from their phosphate processing operations at Aurora, North Carolina. This by-product is known by several names: Texasgulf Gypsum, Tg Gypsum, Phosphogypsum, or wet landplaster.

The relative effectiveness of Bagged-LP (fine ground landplaster), 420-Bulk, and Tg Gypsum on peanut yields were compared in 1977 and 1978 field experiments by Hallock and Allison (21). Their research was conducted on private farm fields located in Southampton County, Virginia. Florigiant peanuts were grown on Kenansville l.f.s. (Arenic Hapludult) in 1977 and on Rumford l.f.s. (Typic Hapludult) in 1978. All supplemental Ca sources were applied by hand on the soil surface. No incorporation occurred except by natural forces until the layby cultivation just prior to fruiting.

The average yields and crop values obtained from the supplemental Ca treatments applied in 1977 and 1978 are shown in Tables 8 and 9. The two-year results indicate, in general, that 420-Bulk and Tg Gypsum were as effective as Bagged-LP for supplemental Ca sources from peanuts.

Daughtry and Cox have also reported on the use of by-product gypsum in North Carolina field tests as a source of supplemental Ca on Virginia-type peanuts. Three forms of gypsum, ie., conventional (finely ground), granular and phosphogypsum, produced no difference in yield, seed grade and value when applied at flowering. The following year (1974) further evaluated the same three sources of gypsum on peanuts. The results are shown in Table 10. Cox concluded that there were no differences in yield and grades in these two field tests where he had used three different kinds of gypsum.

Use on Cotton. Although the cotton acreage in North Carolina is relatively small (approximately 50,000 acres) there are occasional sulfur deficiencies noted in the crop. This condition has occurred, as with some other crops discussed above, on Coastal Plain soils with deep loamy sand surfaces. Unless sulfur from some outside source has been recently added, this crop will show a yellowing of the most recently fully developed leaves. Many growers tend to confuse this yellow color with a nitrogen deficiency. The slide shows a typical sulfur deficiency of cotton that had been fertilized with a sulfur-free clear liquid mixed fertilizer. An economical side-dressing of gypsum to supply 20-25 lbs. of sulfur per acre would have quickly corrected this condition.

Use on Other Crops. At least two other North Carolina crops appear to be benefitting from supplemental calcium. Shelton has noticed a condition of "needle drop" on Fraiser fir, a highly desirable Christmas tree grown on the higher elevations of western North Carolina. This condition has been corrected by adding supplemental calcium, the most practical source being gypsum. In fact, Dr. Shelton tells me that he knows of at least one grower who brings phosphogypsum from Florida for his plantings.

Another important crop of western North Carolina is fresh market apples, particularly the cultivar Red Delicious. Shelton has noted that many orchards have low calcium levels in the leaf tissue. He has attempted to increase the level to above the so-called "critical level" with use of limestone. He has not been very successful using this calcium source. He is currently encouraged with the use of gypsum as a supplemental source of Ca. Although Shelton has not concluded his investigations, he believes that gypsum will be a very feasible means of coping with this nutrient need.

SUMMARY

Sulfur especially - and to a more limited degree, calcium - have sometimes improved crop yield and/or quality when applied to numerous crops as a fertilizer supplement in the southeastern United States. This report presents examples of soil and crop characteristics, climatic conditions and management considerations for achieving maximum benefit to these supplemental nutrient applications.

Particular emphasis is given to how gypsum has been effective in supplying either sulfur or calcium or both in meeting the above described needs for numerous North Carolina crops. Finally, data is presented showing where phosphogypsum has been equally effective as conventionally used, finely ground gypsum to supplying these nutrients. A large potential market exists in North Carolina for use of phospho-gypsum as a satisfactory source of sulfur and calcium for optimum crop production.

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Table 1. Chemical and physical properties of selected North Carolina Soils (2).

Soil	Depth cm	Texture	pH	Sulfate S ppm
Georgeville	0 - 15	si.cl.l.	5.9	6.0
(Typic	15 - 30	si.cl.l	5.9	25.0
Hapludult)	30 - 45	cl.l.	-	22.0
Wagram	0 - 15	l.s.	6.0	2.0
	15 - 30	l.s.	4.9	3.0
(Arenic	30 - 45	l.s.	-	3.0
Paleudult)	45 - 60	s.cl.l.	-	70.0

Table 2. Chemical and physical properties of selected North Carolina Soils (3).

Soil	Depth cm	Texture	pH	Sulfate S ppm	Organic S ppm
Durham	0 - 15	c.s.l.	5.7	7	20
	15 - 30	c.s.l.	5.3	7	
(Typic	30 - 45	c.s.l.	5.2	8	
Hapludult)	45 - 60	s.cl.l.	5.2	32	
	60 - 75	s.cl.	4.5	78	
	75 - 90	s.cl.	4.1	137	
Marlboro	0 - 15	f.s.l.	5.7	1	31
	15 - 30	f.s.l.	5.5	36	
(Typic	30 - 45	f.s.cl.l.	5.2	157	
Paleudult)	45 - 60	f.s.cl.l.	4.7	234	
	60 - 75	f.s.cl.l.	4.5	284	
	75 - 90	f.s.cl.l.	4.4	263	

Table 3. Yield of corn grain as affected by nitrogen and sulfur rates at Kinston, North Carolina, 1974.

Nitrogen	Sulfur, lb/acre				Nitrogen means
	0	20	40	60	
lb/acre	Yield, bu/acre				
50	100.7	99.6	98.3	88.9	96.9
100	111.6	114.0	113.2	111.6	112.6
150	113.7	113.4	125.1	127.6	120.0
200	120.3	129.0	121.3	127.6	124.5
Sulfur means	111.6	114.0	114.5	114.0	113.7

LSD (5%) N or S means: 7.14
LSD (5%) N x S: 6.15

Table 4. Yield of corn grain as affected by nitrogen and sulfur rates at Clayton, North Carolina, 1975.

Nitrogen	Sulfur, lb/acre			Nitrogen means
	0	30	60	
lb/acre	Yield, bu/acre			
50	87.1	81.2	82.0	83.5
200	96.9	102.5	110.4	103.3
Sulfur means	92.0	91.9	96.2	93.4

LSD (5%) N means: 5.58
LSD (5%) S means: NS
LSD (5%) N x S: 9.67

Table 5. Effect of selected sources of sulfur on wheat yield, Hoke County*, North Carolina, 1970-71.

Source of Sulfur	Rate	Time of Application	
		Fall (Nov.)	Spring (Feb.)
	lbs/A	bu/A	bu/A
None	0	32	32
Gypsum	20	34	38
	40	39	40
	80	39	42
Sol-U-Sul	20	30	33
	40	33	32
	80	40	-

*Applied to a Wagram loamy sand.

Table 6. Effect of sulfur on coastal bermudagrass yield, Lee County, North Carolina.

Year	Forage Yield	
	No S	S*
	kg/ha**	kg/ha
1958	8764a	10,625b
1959	9216a	10,091a
1960	7080a	9,462b
1961	8065a	14,310b
1962	6561a	13,515b
1963	3819a	14,480b
1964	5891a	11,789b
1965	8547a	10,608b

* 28 kg/ha S applied annually 1958-61, and 56 kg/ha S applied 1962-65.
** Entries in the same year with the same letter are not significantly different at the 5% level of probability.

Table 7. Effect of N rate on the N/S ratio of coastal bermudagrass for two S rates*, Lee County, North Carolina, 1959-65.

N Rate	% N/% S Ratio**	
kg/ha		
0	9.9:1	
56	9.0:1	$Y = 8.504 + .00618\ X + .0000316\ X^2$
112	9.1:1	
224	10.8:1	$R^2 = .9722$
448	20.0:1	
672	27.0:1	

* 28 kg/ha S applied annually 1958-61, and 56 kg/ha S applied 1962-65.
** Where no sulfur was applied at 672 kg/ha N, the N/S ratio was >90:1.

Table 8. Effect of calcium source on yield and value of Florigiant peanuts, Holland, Virginia, 1978.

Source	Yield*	Value
	kg/ha	$/ha
Check	2335	682
Bagged LP	2695	1025
420-Bulk	3077	1271
Tg Gypsum	2970	1272

Broadcast 907 kg/ha $CaSO_4$
* Avg. of 5/2, 6/2 and 6/29 application date.

Table 9. Effect of calcium source on yield and value of Florigiant peanuts, Holland, Virginia, 1978.

Source	Yield*	Value
	kg/ha	$/ha
Check	2655	1109
Bagged LP	3232	1400
420-Bulk	3518	1536
Tg Gypsum	3370	1475

Broadcast 907 kg/ha $CaSO_4$
Avg. of 5/25, 6/15 and 6/30 application date.

Table 10. Effect of Ca source on yield and grade of North Carolina peanuts, 1974.

County	Source	Yield*	SMK**	ELK**	OK**
		lbs/A	%	%	%
Bladen	Regular	2506	72.5	29.6	1.9
	Granular	2580	72.3	29.5	2.0
	Phosphogypsum	2378	71.3	28.3	2.6
Bertie	Regular	3913	67.8	27.8	3.2
	Granular	2818	68.8	30.8	2.7
	Phosphogypsum	3876	69.9	30.8	2.3

*Avg. from 250 and 750 lbs. actual $CaSO_4$ per acre.
**SMK - Sound mature kernels, ELK - Extra large kernels, OK - Other kernels.

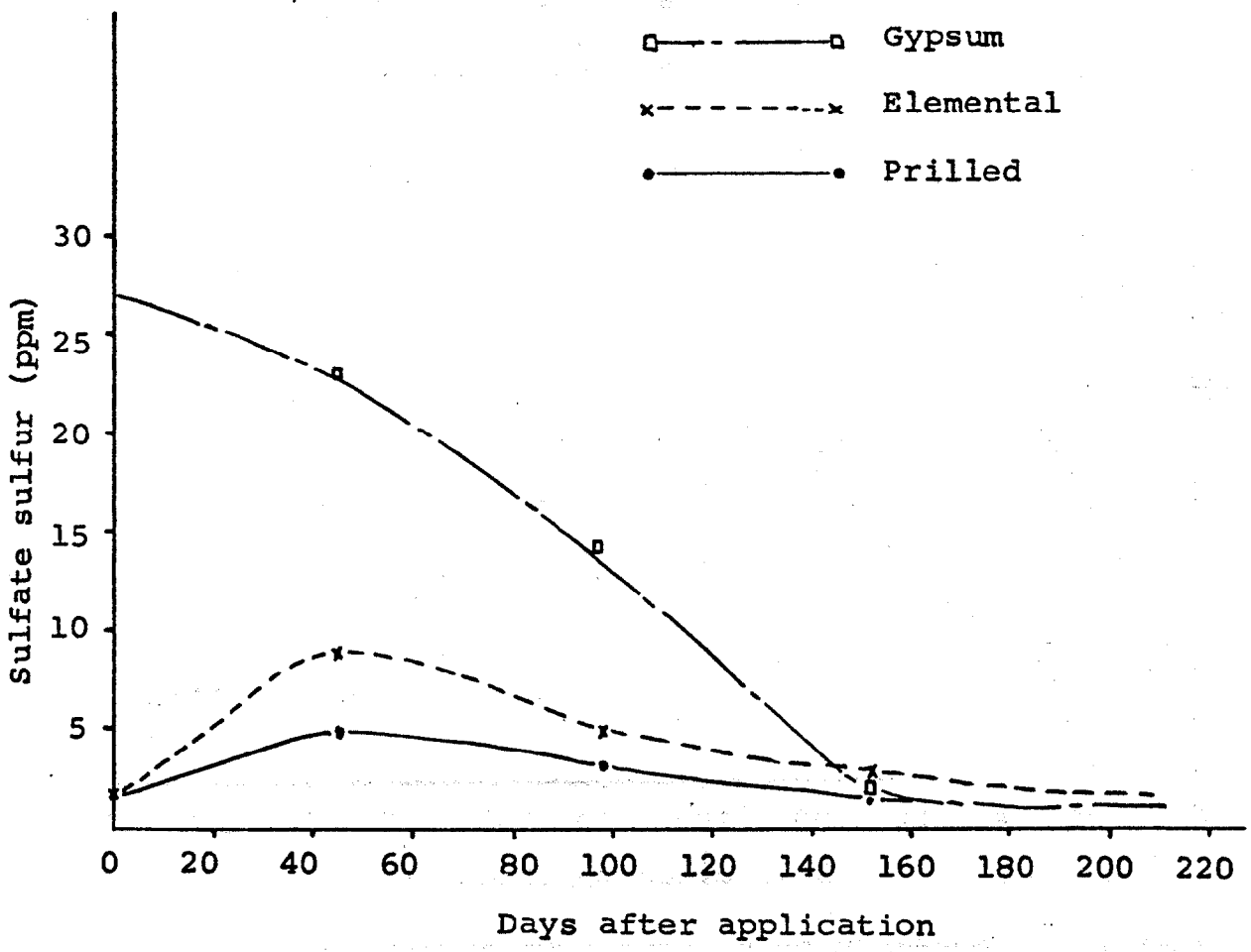


Figure 1. Sulfate sulfur content of the 0-6 inch depth of the Wagram soil

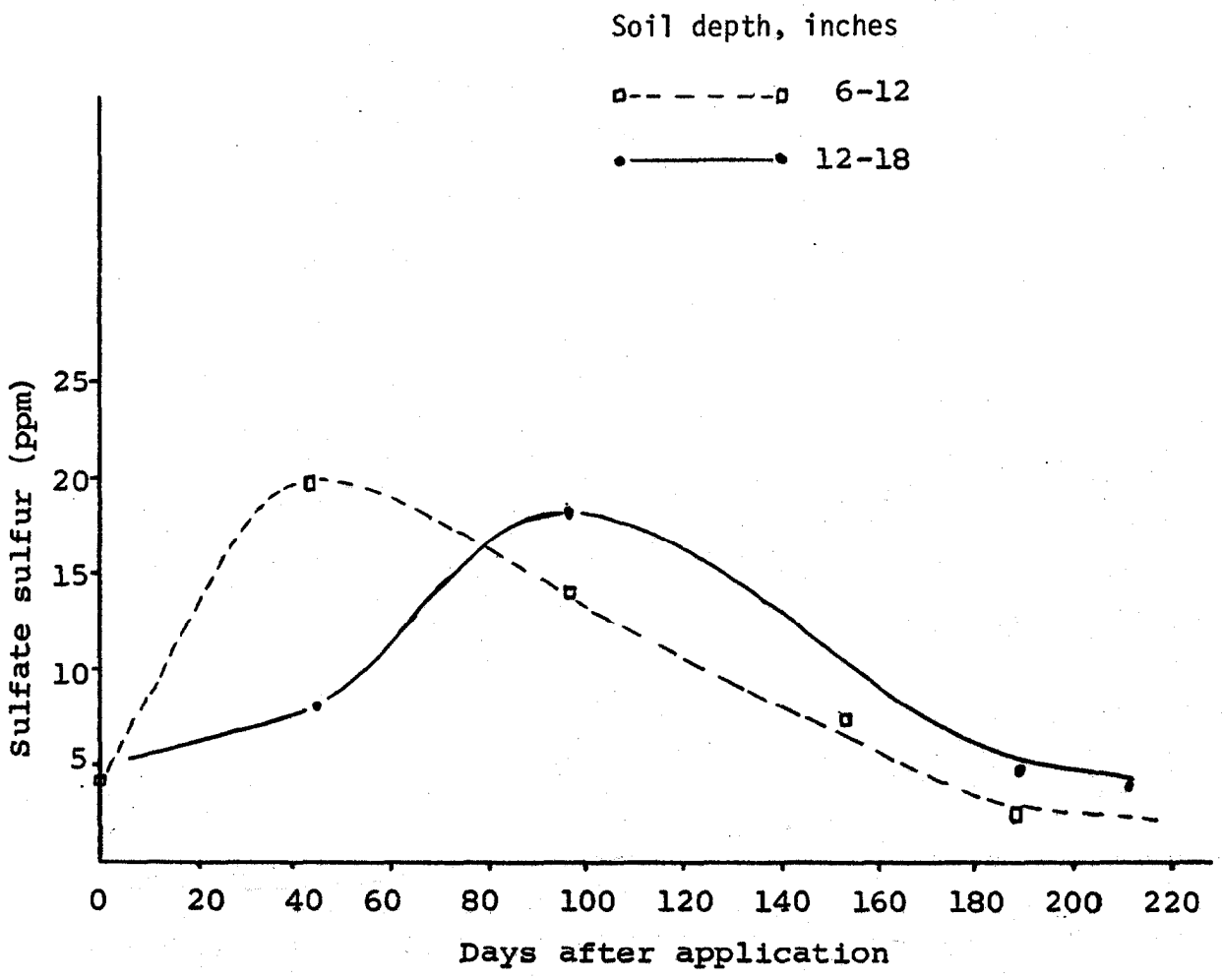


Figure 2. Movement of sulfate from gypsum through the Wagram soil

GYPSUM USAGE IN IRRIGATED AGRICULTURE

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INTRODUCTION

Gypsum, because of its general availability and low cost, is the most used source of calcium to reclaim sodic soils and, of electrolyte to maintain adequate water infiltration. Its use for sodic soil reclamation dates back to the early 1900's. Recognition that improvement in soil hydraulic properties occurred because. the calcium released by gypsum dissolution replaced exchangeable sodium (Kelly and Brown 1934) led to several methods to determine gypsum requirement based on cation exchange capacity and the desired change in exchangeable sodium fraction, E_{Na} (U.S. Salinity Laboratory Staff 1954). The use of gypsum to increase water infiltration is also-an old practice. Field trials, conducted in Australia between 1921 and 1933 on soils which contained little exchangeable sodium, demonstrated that surface application of gypsum reduced soil crusting, thereby increasing water infiltration and, in turn, crop yield (Sims and Rooney 1965). Between 1963 and 1965 an estimated 44,500 ha of fallow soil was treated with gypsum to improve dryland wheat yields in the Wimmera and Southern Mallee Districts of Victoria, Australia. Current research in Australia on gypsum usage is being conducted by the Soils Division of CSIRO at Canberra (Kowalik et al, 1979). Doneen (1948) reported that 270,000 Mg of gypsum were applied to the soil in 1945 by farmers in the San Joaquin Valley of California to improve infiltration. The addition of gypsum to the dilute Friant-Kern irrigation water - or to the associated, irrigated, non-sodic soils irrigated therewith - for the purpose of improving infiltration was a common practice in the 1950's on the east side of the Central Valley of California between, Fresno and Bakersfield (personal communication, Robert Ayers 1980). The beneficial effect of gypsum on infiltration rate is directly related to the added electrolyte levels in the soil solution. Fireman and Bodman (1939) established that increasing the electrolyte concentration of the water applied to non-sodic soils increased their saturated hydraulic conductivity. Thus, the agricultural use of gypsum as a source of electrolyte and of calcium to improve water flow into and through soils is well established.

Research findings since 1950 have clarified the effects of, exchangeable ion composition and electrolyte concentration on clay swelling and soil particle dispersion, the two basic mechanisms which account for changes in soil -hydraulic properties. After describing these interactions in greater detail, they will be related to the equilibrium chemistry of the gypsum-soil-water system and the kinetics of gypsum dissolution. The final section of this paper discusses the potential beneficial effects of the phosphoric acid content of phos-phogypsum.

Clay Swelling and Dispersion., The clay content of a soil, because of its large surface area, is the most important soil component which influences soil hydraulic properties. Exchangeable cations are constrained within the electrical influence of the negatively charged clay particle: they are attracted to the charged surface, and they tend to diffuse from the surface, where their concentration is high, into the bulk solution where it is low. Consequently, clay particles act as

miniature osmometers and imbibe water to lower the ion concentration near charged surfaces. This water uptake is referred to as swelling. Sodium montmorillonite swells freely; large swelling pressures develop between sodium montmorillonite platelets and single platelets tend to persist in dilute solutions. Increasing the electrolyte concentration decreases swelling. Divalent calcium ions are more strongly adsorbed to the clay surface than monovalent sodium, reducing the tendency of calcium clay to swell. Individual calcium montmorillonite platelets tend to aggregate into packets, or tactoids, of several (4-9) clay platelets with a Ø.45 nm film of water on each internal surface (Norrish and Quirk 1954; Blackmore and Miller 1961; Shomer and Mingelgrin 1978). The film thickness is independent of the electrolyte concentration (Norrish 1954) and remains the same even in distilled water. Thus, swelling of a calcium montmorillonite system occurs between the external surfaces of the tactoids.

Several physical properties of a mixed Na/Ca montmorillonite system indicate that the initial increments ofadsorbed sodium are not distributed evenly over all surfaces: Using viscosity and-light transmission measurements, Shainberg and Otoh (1968) found that the size of the calcium montmorillonite tactoid changed little when $E_{Na} < Ø.2$. Higher levels of E_{Na} caused tactoid breakdown. On the other hand, the initial increment of exchangeable Na^+ for $E_{Na} < Ø.2$, caused a disproportionate increase in the electrophoretic mobility (Bar-On et. al, 197Ø). The same was true for the electrolyte concentration required to flocculate Na/Ca montmorillonite suspensions as can be seen in Figure 1. (Note that the abscissa of Figure 1 is expressed in terms of the sodium adsorption ratio, R_{Na} 1/. For the purpose of this discussion, it is sufficiently accurate to assume $E_{Na} \sim Ø.Ø1\ R_{Na}$.) These observations are explained by the "demixing" of the adsorbed ions in Na/Ca montmorillonite system, where the initial increments ($E_{Na} < Ø.2$) of sodium adsorption occur on the external surface of the tactoid, and adsorbed calcium is located on interlayer surfaces between individual clay platelets. Consequently, the size of the tactoid remains about the same, but its mobility is increased because the sodium ions on the outer surface of the tactoid impart it to a mobility similar to that of sodium montmorillonite. Demixing also increases the stability of the Na/Ca clay suspension more than if sodium were distributed evenly over all surfaces.

The relation between the concentration required to flocculate illite suspensions and R_{Na} is more nearly linear than that for montmorillonite suspensions (Fig 1). However, illite is more easily dispersed than montmorillonite. The flocculation values for Na/Ca montmorillonite with E_{Na} values of Ø.Ø5, Ø.1Ø, and Ø.2Ø are 3.Ø, 4.Ø and 7.Ø mol m^{-3} respectively. The corresponding values for illite are 6, 1Ø, and[c]18 mol m^{-3} (The abbreviation mol represents the amount of electrolyte in [c]moles of either positive or negative charge). These

1/ The sodium adsorption ration, $RNa = (C_{Na}/C_{Ca})^{0.5}$ where the ion concentrations, Ci, are expressed in mol m^{-3}.

observations suggest that soils with illitic clays are more sensitive to dispersion and clay movement than those with montmorillonitic clays. The difference in the flocculation value is probably due to a smaller attraction force in Na-illite. Consideration of the shape of the Na-illite particle explains this observation. An electromicrograph (Green et al., 1978) revealed that Na-illite particles had an average thickness of about 10.0 nm and that the planar surfaces were terraced. Upon close approach of the particles, the unavoidable mismatch of the terraces would lead to poor contact between the edges and the surfaces leading to smaller edge-to-face attraction forces (van Olphen 1977) and, consequently, a higher flocculation for Na-illite than for Na-montmorillonite.

Soil Particle Stability. Demixing in montmorillonite and its effect on tactoid size and mobility and its parallels in more complex soil systems (Rahman and Rowe11 1979) which contain such clay minerals as kaolinite, vermiculite and illite, in addition to montmorillonite. These minerals exist as thick quasi-crystals consisting of a stack of individual clay platelets regardless of the exchangeable cation. Consequently, external surfaces predominate. The selectivity of both vermiculite and illite for adsorbed sodium is greater than of montmorillonite (Rhoades 1967, Shainberg et al. 1980). Thus, for soils containing a mixture of these clay minerals, including montmorillonite, the initial increments of exchangeable sodium will be adsorbed on external surfaces. The associated enhancement of swelling between external surfaces weakens interparticle bonds, enhancing the freedom of adjacent soil particles to move. In the words of McNeal (1974), "This process, whereby soil particles become essentially independent entities, is termed dispersion."

Differences of opinion remain as the relative importance of swelling or dispersion in the reduction of the hydraulic conductivity, K, of soils. McNeal and Coleman (1966) found a good correlation between K and microscopic swelling of the soil clay fraction. Using a swelling model based on double-layer theory, Russo and Bresler (1977) closely approximated the effects of solution and exchange compositions on the K of a loam soil. The double-layer theory was modified to account for the influence of E_{Na} on the number of clay platelets in a tactoid. Frenkel et al. (1978) and Pupisky and Shainberg (1979) clearly demonstrated that clay movement and consequent pore blockage are the main causes of reduced K of several soils ($0.1 < E_{Na} < 0.15$) with different clay mineralogies when irrigated with distilled water where swelling was small.

Aggregate breakdown and soil-particle dispersion can be substantial even below an E_{Na} of 0.10. Emerson and Bakker (1973) demonstrated that soil aggregates from the subsoil of three illitic, red brown clay soils spontaneously dispersed in 0.001 M salt solutions when the initial E_{Na} was less than 0.06. Similar data-were reported for the dispersivity of a montmorillonitic, halloysitic-kaolinitic, and micaceous soil (Verlasco-Molina et al. 1971) Infiltration rates of a montmorillonitic soil decreased with decreasing salt concentration at E levels as low as 0.02 (Oster and Schroer 1979). Thus, a small amount of adsorbed sodium markedly increased the dispersivity of the soil clay fraction in dilute solutions.

Collis-George and Smiles (1963) reported flocculation values for a soil clay fraction (Figure 2) which were greater than those for montmorillonite but less than for illite (Figure 1). Their relationship between electrolyte concentration and R_{Na} for flocculation was the same as that reported by Quirk and Schofield 1955) for threshold concentrations required to maintain less than a 1Ø to 15% decrease in the K of a Sawyer soil in which the clay fraction was predominantly illite. This suggests that when concentrations are too low to maintain flocculated conditions, K decreases because of clay dispersion and consequent blockage of the water conducting pores. However, as reported by Quirk and Schofield (1955), the electrolyte concentration at which the column effluents become turbid due to the presence of clay were from one-third to one-tenth of the threshold concentrations. They ranged from 2 to 25 mol m^{-3} as E_{Na} increased from Ø to 1.Ø. Consequently, deflocculation and clay dispersion within the soil matrix of-their soil occurred at lower electrolyte concentrations than those required for the reverse process of flocculation. This irreversibility supports concepts recently discussed by Emerson (1977) and Quirk (1978). They suggested that at low water contents, the clay fraction in soil is in intimate contact with the cements or stabilizing agents such as organic matter, and iron and aluminum oxides. Thus, dispersion of soil aggregates (or granules) within a soil would be expected to occur at a lower electrolyte concentration than that required to flocculate a clay suspension. Bradfield (1936) summarized the situation as follows: "granulation is flocculation plus."

A closer relationship between clay flocculation and soil dispersion may be expected to occur at the soil surface. Here the soil aggregates are unconfined by the soil matrix and excess water can exist under irrigation or where rainfall exceeds infiltration. In addition, the soil surface is also subject to rapid wetting, the mechanical action of raindrops, flowing water and fillage operations. The infiltration rates of undisturbed columns of Heimdal loam, a montmorillonitic soil, cropped to alfalfa and irrigated for 19 months with waters of different compositions (Oster and Shroer 1979) were very sensitive to electrolyte concentration and exchangeable sodium. The dashed line in Fig. 2, which is based on their data, represents those combinations of electrolyte concentration and R_{Na} which are projected to result in an infiltration of 1.4 mm h^{-1} which was 5% of the rate, 28 mm h^{-1} , obtained for the Heimdal soil columns irrigated with water with an electrolyte concentration of 3Ø $mol_c m^{-3}$ and an R_{Na} of 2.Ø. At the soil surface, aggregate breakdown followed by dispersion of finer particles results in a compacted zone of higher bulk density and thin clogged pores as the result of fine particle lodgment in soil voids (Chen and Banin 1975; Chen et al., 198Ø). The water permeability of this surface layer can be reduced two or three orders of magnitude below that of the undispersed soil beneath (McIntyre 1958).

Proper management to limit the undesired effects of soil and irrigation water chemistry on soil hydraulic properties involves the joint consideration of both electrolyte and E_{Na} levels (Rhoades 1977). Useful methods exist to estimate the electrolyte and exchange composition which may develop in the soil as the result of irrigation with waters of known

composition for either the steady (Miyamoto 198Ø; Suarez 1981) or the transient chemical states (Jury et al. 1978). Alternatively, soil chemical analysis can be used to assess existing conditions (U.S. Laboratory Staff 1954). If adverse combinations of electrolyte concentration or E_{Na} are deemed likely to occur, a soil amendment such as gypsum can be used to increase electrolyte concentration or to reduce E_{Na}. Its effectiveness depends on its solubility and its rate of dissolution.

Gypsum Solubility. Gypsum solubility depends on both the composition of the soil solution and exchange phase. The Gibbs phase rule provides a convenient means to determine the number of independent variables, F, of a chemical system. According to this rule F = C - P - R + 2 where C, P and R represent the total number of components, phases and independent reactions between the components, respectively, and where the numeral two represents the additional degrees of freedom due to temperature and pressure. The gypsum-water-Na system contains four components ($CaSO_4.2H_2O(S)$, $CaSO_4(aq)$, $Na_2SO_4(aq)$ and H_2O (1), and two phases (liquid and solid). These is one independent reaction

$$CaSO_4.2H_2O(S) = CaSO_4(aq) + 2H_2O(1). \quad (1)$$

Thus, F equals three, and the activity of one component - or the ratio of two - must be specified, in addition to temperature and pressure, to fully specify the chemical composition of the system. The addition of an exchanger phase entails the addition of two components, exchangeable sodium and calcium, and the exchange reaction

$$Na_2SO_4(aq) + CaX_2 = 2\ NaX + CaSO_4(aq) \quad (2)$$

where X represents one mole of negative charge of the exchanger phase. F for this system also equals three: the two additional components are compensated by the addition of one phase and one independent reaction. Consequently, specification of the concentration ratio, R_{Na}, in addition to temperature and pressure, fully specifies the concentration of all aqueous and exchangeable components provided the effects of ionic strength are also taken into account. The introduction of magnesium adds two components, $MgSO_4$ (aq) and MgX_2 and the exchange reaction

$$CaSO_4(aq) + MgX_2 = MgSO_4(aq) = CaX_2. \quad (3)$$

Consequently F increases to four. The corresponding additional ratio, which is convenient to specify, is $C_{Mg}/C_{Ca'}$

The electrolyte concentration of the soil solution in equilibrium with gypsum increases with R_{Na} and C_{Mg}/C_{Ca} as shown in Fig. (3). The equilibrium compositions were calculated using a computer model (Oster and Rhoades 1975) which accounts for the effects of ionic strength and ion speciation (Tanji 1969). Both ion ratios cover the range commonly found in soils. The electrolyte concentration increase with increasing R_{Na} is approximately linear for any given ratio of C_{Mg}/C_{Ca} The dashed line represents the relationship between electrolyte concentration and R_{Na} required for flocculation as reported by Collis-George and Smiles (1963). Clearly, the electrolyte concentrations of gypsiferous soils

under equilibrium conditions are more than adequate to keep soils flocculated and hence to maintain or to improve existing soil hydraulic properties. In many circumstances, the initial hydraulic conductivity of sodic soils is very low, and the increase in hydraulic conductivity with the addition of gypsum is inadequate to accomplish reclamation within a reasonable period of time. Use of $CaCl_2$ or H_2SO_4 in combination with gypsum increases the extent of improvement and often hastens reclamation (Prather et al., 1978).

Numerical simulations of reclamation, assuming the reaction rates of gypsum dissolution and exchange are sufficiently rapid to maintain soil solution and exchangeable ion compositions which are in equilibrium with gypsum as water moves through the soil, show that the amount of gypsum dissolved is a linear function of the exchangeable sodium replaced (Oster and Frenkel 1980). The combination of Eq. 1 and 2 represents an equilibrium reaction which does not go to completion. Thus, more than one mole of charge of gypsum must dissolve to replace one mole of exchangeable sodium. Typical values are 1.4, 1.3 and 1.2 moles of charge per mole of exchangeable sodium replaced at final E_{Na}'s of 0.05, 0.10 and 0.15. Gypsum requirement for sodic soils based on the quantitative replacement of exchangeable sodium should be increased by the appropriate amount depending on the desired final level of exchangeable sodium.

The water requirement for reclamation with gypsum is less than that estimated from its solubility in distilled water, 2.6 kg m^{-3}. As shown in Fig. 3 the equilibrium electrolyte concentration increases with R_{Na} and C_{Mg}/C_{Ca} In addition to these parameters, the water requirement will also depend on the cation exchange capacity because it acts as a sink for calcium until both the gypsum dissolution and exchange reactions achieve equilibrium. The larger the sink, the smaller the change in R_{Na} per unit of gypsum dissolved, and the greater the amount of gypsum dissolved per unit of applied water, or its effective solubility. Numerical simulations of representative situations indicate that a reasonably accurate estimate of water requirement can be made assuming a threefold increase in effective solubility, or 7.8 kg of gypsum per m^3 of water.

A simulation model, which assumed that dissolution was sufficiently rapid to maintain a saturated gypsum solution, was field tested in Arizona by Dutt et al. (1972). This study indicated fair agreement between predicted and measured results for reclamation of sodic soil with gypsum where it is mixed into the soil to a depth of 15-20 cm. However, equilibrium conditions probably do not apply to the dissolution of surface applied gypsum. Here, the kinetics of dissolution are limited due to the shallow depth of the gypsum-soil layer and to the high soil water flux rates associated with the initial stages of infiltration.

Dissolution Kinetics. Gypsum dissolution follows first-order,' reaction rate kinetics (Barton and Wilde 1971; Kemper et al. 1975). The electrolyte concentration of water flowing through a bed of gypsum particles was adequately described by a transport equation which

included terms to account for convection, diffusion and dissolution kinetics (Eq. (2) of Keisling et al 1978). This equation will be used to illustrate the potential effects of gypsum and water application rates, and the depth of mixing, on the electrolyte concentrations resulting from the application of gypsum to the soil surface. Due to the need to make several assumptions, the accuracy of the results is questionable. However, they should indicate general trends and the order of relative effects.

The mathematical solution given by Kiesling et al. (1979) assumes a constant concentration at the soil surface (taken to be zero here) and a semi-infinite profile. The average electrolyte concentration, <C>, of the soil-gypsum layer between Ø and depth L (cm) is:

$$<C> = C_s - \frac{2C_sD}{L(U-V)} \{1 - \exp \frac{L(V-U)}{2D}\} \quad (4)$$

where

$$U = (V^2 + 4aD)^{1/2}, \quad (5)$$

and where D is the dispersion coefficient ($cm^2\ s^{-1}$), V is the average pore water velocity ($cm^2\ s^{-1}$), a is the dissolution rate constant (s), and C_S is the concentration of a saturated gypsum solution, taken as 15 mol m^{-3}. The volumetric water content O, was assumed to be Ø.3 $cm^3\ cm^{-3}$. Consequently, V = q/O where q is the water application rate. Following Keisling et al.; 1978, the relationship between a and the surface area of gypsum particles per unit volume of soil, S ($cm^2\ cm^{-3}$), is

$$a = 0.0043S^{1.48} \quad (6)$$

where the average gypsum particle size and associated surface area was assumed to be Ø.4 cm and 6.6 cm^2g^{-1}. The empirical relationship between D and V for representative soils is

$$D = 0.00001 + 2V \quad (7)$$

where the numerical value represents the diffusion coefficient of salt in water.

The effect of gypsum application rate and pore water velocity on the average concentration is shown in Fig. 4 for L equal to Ø.5 cm. For a given rate of water application, the average concentration increases with gypsum application rate (Mg ha^{-1}) because the amount of gypsum, and the associated gypsum surface area, increases per unit volume of soil. Increasing the water application rate decreases the contact time available for dissolution. Consequently, the electrolyte concentration decreases with increasing water application rate for a given gypsum application. As can be seen in Fig. 5, the effect of the depth of mixing is small. For given gypsum and water application rates, the increase in gypsum surface area per unit volume of soil, as L decreases, approximately compensates for the associated decrease in contact time.

The preceding information is based on the dissolution rate of mined gypsum. According to Keren and Shainberg (1981), the rate of dissolution of phosphogypsum can be ten times greater. The effects of such an increase on electrolyte concentration is shown in Fig. 6. The concentrations for phosphogypsum are about three times greater than for mined gypsum at application rates less than 5 Mg ha^{-1}: at higher application rates, the concentrations differ by a factor of two.

The amount and type of surface applied gypsum recommended to improve infiltration will depend on existing soil chemical conditions, composition of the water, and the crop and soil management options available to the farmer; A hypothetical example illustrates some of the considerations involved for a case where: (1) the annual crop water requirement of 1.5 m is applied by sprinkler irrigation, (2) the rate of water application can be varied, (3) the electrolyte requirement, based on the chemical composition of the soil and of the irrigation water, is 2 mol m^{-3} . In the field, the amount of gypsum present in the soil surface varies with time after it has been applied and irrigation begins. Equation 4 does not provide a means to estimate the time averaged <C>after the gypsum has been applied and starts to dissolve. For the purpose of this example, I assume that a time averaged electrolyte contribution of 2 mol m^{-3} will occur if gypsum is applied at a rate corresponding to a <C> of 4 mol m^{-3}.

According to Fig. 4, application rates of mined gypsum of 5, 8 and 12 Mg ha^{-1} would be required for water application rates of Ø.5, 1 and 2 cm h^{-1}. The corresponding amount of water required per hectare to dissolve all the gypsum would be 1.5, 2.4 and 3 5 m since 2 mol m^{-3} of gypsum (molecular weight = 0.17 kg) in 10 000 m^3 of water corresponds to 3.4 Mg of gypsum. Thus, not all the gypsum is projected to dissolve if the water application rates exceed 0.5 cm h^{-1}. Consequent tillage operations would mix the remaining gypsum to depths of about 10 cm, rendering it ineffective for the following season. The application rate for phosphogypsum, for a water application rate of 1 cm h^{-1}, is 1.6 Mg ha^{-1}, and it would all dissolve after a water application of 0.5m. Consequently, several surface applications of phosphogypsum would be required during the growing season: three applications of 1.6 Mg ha^{-1} may be a recommended practice. Since an increased electrolyte level will reduce crust formation but not prevent it, repeated application could be advantageous if combined with light tillage. The combined effect on total infiltration could be considerably greater than a single application of mined gypsum without further tillage.

This simple example served to illustrate that the amendment requirements for phosphogypsum will not be the same as for gypsum, and that phosphogypsum increases the number of management options available to farmers. The example ignored many other considerations. Crop cultural practices may prevent repeated tillage. If surface applications are made on growing crops, there may be concern about the possible effects of the acid content of phosphogypsum on exposed leaves and fruit. It may be more convenient, or economical, to add the gypsum to the water rather than to the soil. The soil scientist must question the validity of Eq. 4. The boundary condition, C = Ø at L = Ø, and the assumption that C_S equals 15 mol m^{-3} in effect stipulates that $CaSO_4$

(aq) and CaX_2 are the only aqueous and exchangeable components present. Thus, the effects of exchangeable sodium and magnesium, and the compositions of the irrigation water and initial soil solution on the effective solubility of gypsum were not taken into account. The first order rate constant indicates gypsum dissolution is controlled by diffusion. The rate constant used in this example was obtained under well mixed conditions, and it may not be appropriate to apply it to a situation where the soil water flow rate and consequent degree of mixing is considerably less. Equation 4 does not account for changes with time in the mass of gypsum per unit volume of soil, whereas the mathematical formulation of Glas et al., (1979) does. However, additional experimental data obtained under appropriate experimental conditions are needed to evaluate the use of transport equations as tools to predict the gypsum requirement associated with the electrolyte effect. In addition, there is very little data available upon which to formulate a basis 'to predict the electrolyte levels required to increase aggregate stability and consequent infiltration rate.

Acid Content of Phosphogypsum. The phosphoric acid component of phosphogypsum is of direct benefit as a phosphate fertilizer. Neutralization of the acid by various soil reactions could also result in beneficial effects, particularly in calcareous soils, which typically have a high pH ($7.5 < pH < 9.5$). pH depends on the partial pressure of carbon dioxide, and soil water and exchangeable ion composition. It is reduced by the replacement of exchangeable sodium with calcium. The release of calcium, iron and aluminum as a result of soil mineral dissolution, consequent to the neutralization of phosphoric acid, will promote flocculation and interparticle bonding and further reduce soil pH. A reduction in pH increases the availability of trace metal nutrients which are typically deficient in sodic soils because of high pH. It will also increase the positive charge density of iron and aluminum oxides which are positively charged at pH values less than 8 and 10, respectively, although phosphate adsorption on the oxides could modify their effective charge (Hingston et al., 1972). Both oxides act as polycations linking clay particles together (El-Swaify and Emerson 1975). Other theoretical aspects associated with the charge of oxide surfaces were recently reviewed by Quirk (1978). Based on existing information, it is safe to conclude that the acid content of phosphogypsum is a beneficial component for calcareous sodic soils from the viewpoint of its neutralization with calcium carbonate, its effect on availability of minor nutrients and its value as a phosphate fertilizer. In addition, the acid content of phosphogypsum may act as a soil structure stabilizer depending on its effect on the charge of oxide surface.

CONCLUSION

Gypsum dissolution can provide adequate electrolyte levels in the soil solution to maintain existing hydraulic conductivities of sodic soils during their reclamation , and to increase infiltration rates of soils suspectable to crusting. The criteria governing the gypsum requirement for sodic soil reclamation, which are based on the amount of exchangeable sodium to be replaced and the efficiency of the exchange reaction, are well understood. Similarly, the electrolyte levels during reclamation are predictable and approach equilibrium levels governed by

the solubility of gypsum, because hydraulic conductivities of sodic soils are generally low and gypsum is mixed into the soil to the depth of tillage. The gypsum requirement associated with surface applications of gypsum to reduce soil crusting are not as well understood. Here the kinetics of gypsum dissolution are limiting due to the small opportunity time for dissolution. Consequently, electrolyte levels in the soil surface depend on the gypsum and water application rates, and the depth of mixing. Transport equations which account for convection, diffusion and dissolution kinetics could provide a means to assess the gypsum requirement. To date, this has not been done and the rates used are based on local experience and financial constraints.

Recent data indicate phosphogypsum dissolves faster than mined gypsum. This difference is projected to have significant effects on the optimum timing and rate of application. Phosphogypsum would be applied more frequently and in smaller amounts than mixed gypsum to achieve similar effects. In addition to its fertilizer value, the acid content of phosphogypsum is of direct benefit for increasing the availability of phosphate and of trace metal nutrients which are typically deficient in sodic soils ($E_{Na} > 0.15$) because of high pH and it may increase soil structural stability.

Can agricultural use of gypsum be increased sufficiently to utilize the phosphogypsum produced at an annual rate of 30×10^6 Mg? Since sodic soil reclamation is a practice primarily limited to new irrigated lands in arid regions, significant expansion of the use of gypsum would depend on its application in both irrigated and dryland agriculture to increase soil water infiltration. The annual production rate of phosphogypsum is sufficient to treat 73,000 km^2 (29,000 mi^2) at a rate of 4 Mg/ha, or nearly half the total area irrigated in the USA. Extensive areas are required where water infiltration - and hence crop yield - is limited by soil or rainfall, or both. Considering that most of the product is produced in Florida and that ocean transport is the cheapest mode of transportation, dryland farming areas with low rainfall within the North American Continent along the western borders of the Gulf of Mexico would be a logical target area. Market development within this area would require extensive field evaluation of local agricultural research personnel in cooperation with the phosphate fertilizer industry to determine if the economic benefits exceed the cost of phosphogypsum.

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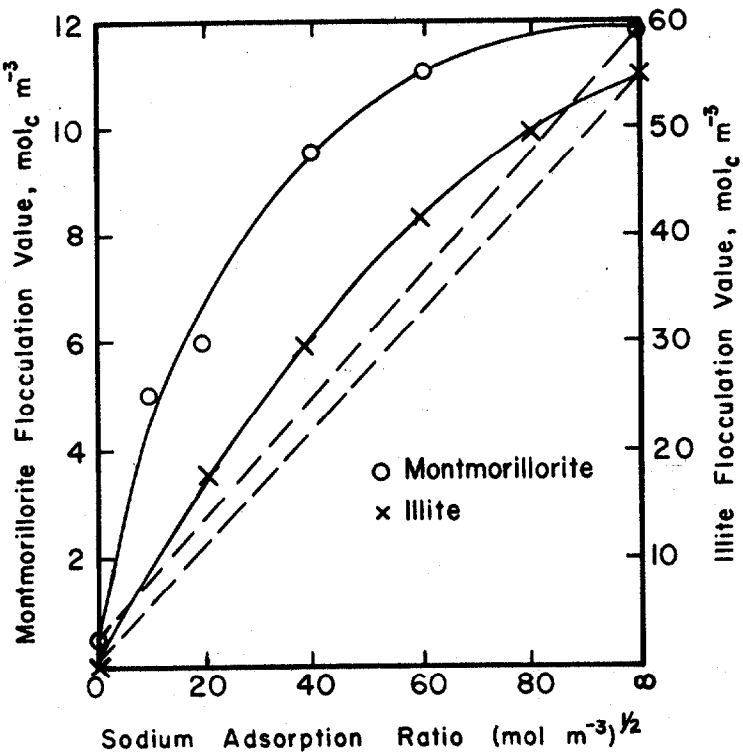


Fig. 1. Flocculation value for Wyoming montmorillonite (API 25) and Fithian illite (API 35) as a function of the sodium adsorption ratio.

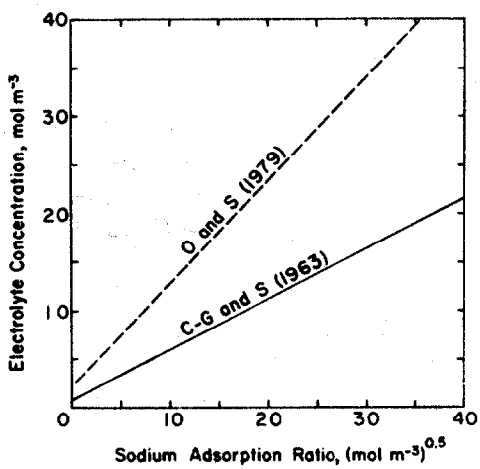


Fig. 2 The relationship between electrolyte concentration and sodium adsorption ratio that resulted in soil clay flocculation (Collis-George and Smiles, 1963; solid line) and a 95% reduction in infiltration rate (Oster and Schroer, 1979; dashed line).

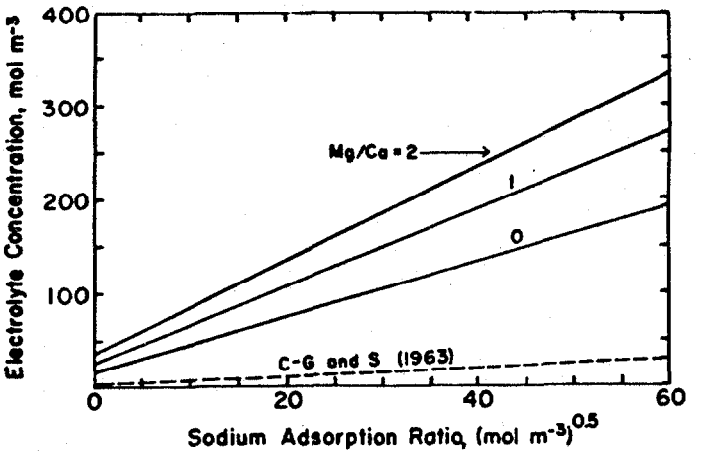


Fig. 3. The effects of sodium adsorption ratio and the concentration ratio of magnesium to calcium on the electrolyte concentration of sulfate solutions in equilibrium with gypsum. The dashed line is the same as the solid line in Fig. 2.

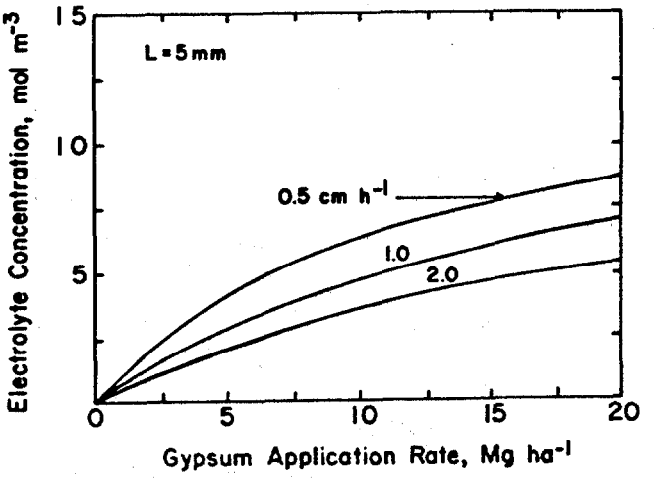


Fig. 4. Average electrolyte concentration of the soil solution, where gypsum is mixed with the soil to depth of 5 mm, as a function of gypsum and water application rates.

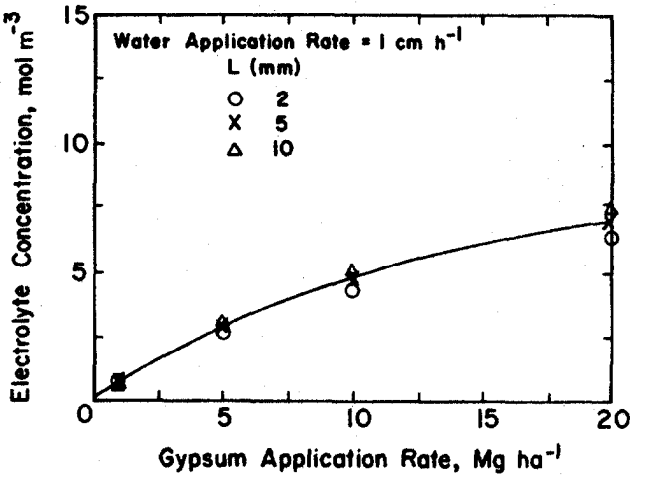


Fig. 5. The average electrolyte concentration of the soil solution as a function of gypsum application rate and depth of mixing at a water application rate of 1 cm h^{-1}.

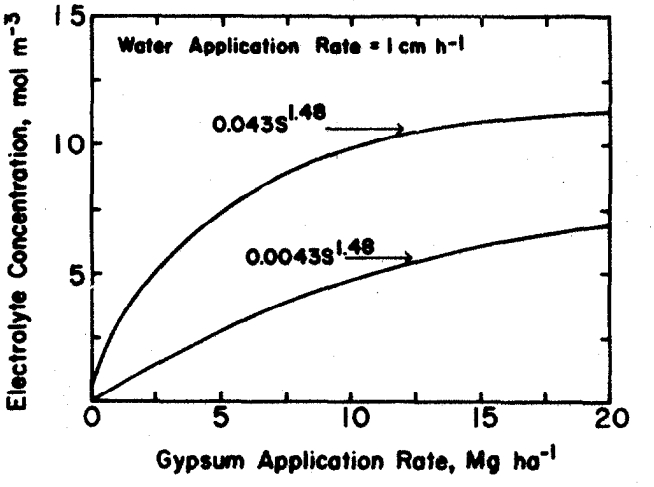


Fig. 6. The effect of a 10 fold increase in dissolution rate of gypsum on the average electrolyte concentration of the soil solution where the depth of mixing is 5 mm and the water application rate is 1 cm h^{-1}.

PROPERTIES AND VEGETATIVE STABILIZATION OF CEMENT BAG HOUSE DUST

by

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ABSTRACT

A study has been made to determine the feasibility of reclaiming cement bag house dust. The research undertook to characterize chemical, mineralogical and physical properties of the dust for its potential as a plant growth medium. A greenhouse study was established to compare mixtures of soil and paper mill sludge amendments to the dust for the establishment of vegetation.

Chemical analysis reveals absence of nitrogen, 1 ppm phosphorous, 227 ppm potassium; 48,ØØØ calcium, 516 ppm magnesium, 61Ø ppm sodium. The average pH was 12.9 and electrical conductivities ranged from 6.4 to 3Ø mmhos/cm^2. The high pH and electrical conductivities indicate that the dust is an "alkali" plant growth medium.

The dust will retain 42% available water by weight and has a 1.6 to 2.ØØ gm/cc particle density. Particle size separates range as follows: 21 to 6Ø% sand, 12 to 6Ø% silt and 16 to 24% clay. The dust is plastic, structureless and will form a crust when moistened, The formation of the crust will limit water infiltration and seeding.

In the greenhouse trials , cement dust without soil or paper mill sludge did not support grass and legume mixtures. Seedlings showed evidence of severe salt toxicity. Better establishment of grass and legume seedlings was observed on mixtures of dust with soil, dust with paper mill sludge and dust with soil and paper mill sludge. With all mixtures, pH electrical conductivities, %N, calcium and sodium contents were sufficiently ameliorated for the establishment. of grass and legume mixtures. Results indicate that cement bag house dust by itself will not support vegetation. Amendments such as soil or paper mill sludge are required in order to lessen the impact of the alkaline properties of cement bag house dust on the establishment of vegetation.

INTRODUCTION

Materials required for the production of cement are a mixture of limestone, gypsum, clay or shale. This mixture is heated to high temperature which will form a clinker. The clinker is finely ground to a fine powder or cement. In addition, waste dust is produced during the final grinding and bagging procedures. This dust is collected in stack precipitators and in the baghouse where the cement is readied for shipment. Up to a thousand tons of dust are produced per day at the study site. The cement dust is presently truck hauled for deposit in a de-activated quarry. Prior to use of the quarry, the dust was deposited on the surface of the landscape in piles up to 3Ø meters in height. Since materials for the manufacture of cement are obtained locally from open pit mines, wastes are subject to Michigan's Mine Reclamation Act (197Ø).

The study was carried out to examine the potential for establishing a stable vegetative cover on cement bag house dust waste deposits. The research undertook to characterize the chemical, mineralogical and physical properties of the dust. Greenhouse trials were used to test

various mixtures of soil and paper mill sludge for establishment of vegetation. The study was conducted at the Ford Forestry Center facilities, Michigan Technological University.

METHODS

To determine the extent of the pit and mill wastes, an inventory was made on a base map of the plant site, showing the location, aerial extent, age of the wastes and any natural revegetation. The inventory served as a means to stratify the cement bag house dust into manageable units to facilitate sampling.

Bulk samples of dust were collected from each of four sites identified in the inventory and described as fresh dust or dust deposited that day, dust 3, 15 and 30 years of age. Moisture retention was determined using pressure plant (1.3, 1, 3 and 15 bar). Available water capacity was calculated from the data. Particle size analysis was determined by procedures outlined by the Soil Survey Staff (1972), ASTM (1980) procedures were used for calculating plastic index. Mineralogy of each age class was determined by X-ray defraction.

Standard soil characterization procedures were employed for determining % N, available phosphorous, potassium, calcium, magnesium, sodium, pH, cation exchange capacity (C.E.C.) and electrical conductivity (E.C.) (Soil Survey Staff 1972).

Replicated greenhouse studies were designed to test mixtures of: fresh + 15 + 30 year old dust, fresh dust + soil; fresh dust + paper mill sludge up to 5 dry metric tons/hectare; fresh dust + soil + paper mill sludge up to 5 dry metric tons/hectare. Each replication was seeded with the following grass and legume mixture: vernal alfalfa (Medicago sativa) Fults cultivar (Puccinellia distans) and alkali sacaton (Sporobolus airoides). Each treatment was instrumented with salt sensors at 6 and 12 cms to monitor electrical conductivities by depth and time, and to determine the effect of amendments on fresh dust alkalinity.

The paper mill sludge was collected from the effluent ponds of a paper mill near the cement plant site.

RESULTS AND DISCUSSION
CHEMICAL PROPERTIES

Data on chemical concentrations of the various aged dust samples are presented in Table 1. The pH of the dust sample indicates an alkaline seed bed substrate. Alkali soils generally have a pH greater than 9.0 and are saturated with cations of sodium, calcium, potassium and magnesium. The fresh, 3 and 25 year old dust samples have pH's above 9.0 comparable to alkali soils (Buol. et. al 1980). Since the 30 year old dust samples have a lower pH, as well as less cations contributing to higher pH's, they approximate a saline soil. The decrease in pH is attributed to removal of cations such as calcium and sodium

through the natural leaching process of precipitation. Generally adequate plant growth can be obtained on natural soils with pH's less than 8.Ø. Thus the high pH of the dust samples is detrimental to the establishment and growth of vegetation. The causal elements are excesses of calcium and sodium in the soil solution that remove essential plant nutrients such as phosphates, from vegetation absorption (Black 1968, Richards 1954, Russell 1977).

Electrical conductivities (E.C.) of the saturated paste show a similar trend as pH for the different ages of the dust. The older the dust samples, the lower the E.C. values. E.C. is a measure of the osmotic pressure of the soil solution. As the salt concentrations in the soil solution increases, so does the plant cell sap. However, if the plant is unable to maintain an equilibrium state, pysiological drought or toxic cation conditions exist. The effects on the plant is reduced growth and eventual death (Russell 1977).

The major contributor to the high pH's and E.C. values is the calcium cation whose primary source is the limestone constituent of the cement. The presence of excess calcium ions in the dust when exposed to carbon dioxide may be forming bicarbonate ions. Appreciable amounts of bicarbonate can be, present only at pH above 9.5. The chemistry of the fresh, 3 & 15 year old dust samples show a bicarbonate tendency. The 3Ø year old dust with its lower pH and E.C. values indicate a non-bicarbonate condition. Other cations such as sodium, potassium and magnesium also contribute to the high pH and E.C. values.

PHYSICAL PROPERTIES

Table 2 summarizes selected physical and engineering properties of cement bag house dust considered important to our understanding of the behavior of the dust for establishment vegetation. The texture of the dust ranges from silt loam to sandy loam. The older dust contains a higher percentage of sand which reflects a possible coarse grind compared to the fresh dust. Or, the beginning of structural particles which were not properly dispersed during the characterization tests for particle size analysis. The higher sand fraction of the older dust may also reflect the breakdown of crusting which will form on fresh dust, into smaller and sand size particles. With time, crust formation will decay allowing water to properly infiltrate.

The amount of water retained in a soil will govern species selection for reclamation. Generally, sandy soils are droughty with low water retention values. Clay soils, on the other hand, will retain more water because of the greater surface area of clay size particles compared to sand size particles. All of the dust samples retain sufficient amounts of water for revegetation at saturation; (3 Bar). In fact, many of the samples reflect excess moisture at .3 Bar which could be detrimental to plant growth. The 15 Bar values represent the dryer limit of the range of available water for plants. The .3 to 3 Bar values represent the range in available water that will satisfy plant needs without undue stress on plant growth. The data in Table 2 show sufficient water is retained between .3 to 3 Bar. It is interesting to note that the .3 to

3 Bar data for all samples represents approximately two-thirds of the total available water; The 3 Bar moisture percentage represents a critical point since the amount of moisture retained decreases rapidly between 3 and 15 Bar. This relationship reflects the lack of structure and organic matter in the dust regardless of age. Site conditions such as a lack of protection from winds and solar radiation, which will increase evapotranspiration, will require amelioration in order to control rapid loss of water.

Liquid, plastic and sticky limits were calculated to determine the behavior of the dust to an applied stress. The older dust samples have higher liquid, plastic and sticky limits than the fresh dust. This is a reflection of higher clay and silt contents which will retain more water. The implication of this relationship is that moisture films become thick enough so that eohesion and adhesion is decreased and the soil mass flows. Compaction and sealing of the surface will result from equipment traffic and will limit surface infiltration rates and limit seedling establishment. Use of equipment on the dust should be minimal and then only when dry.

Research has shown that exchangeable cations such as potassium, calcium, magnesium and sodium will influence the plastic index of soils. The dust contains excessive amounts of these cations. Generally, sodium and calcium saturated soils have higher plasticity index than potassium and magnesium hydro saturated soils (Baver 1973).

The chemical and physical data, especially pH and E.C. data, were calculated to determine what species of plants would be suited to the dust. Also, these data show that nutrient toxicities exist and that amendments are needed to modify the dust prior to reclamation effects. A greenhouse investigation was undertaken to screen various amendments prior to actual field trials.

GREENHOUSE INVESTIGATION

In selecting species of plants for reclamation of the cement dust wastes particular attention was paid to the following: local climate, salt tolerance at germination, as well as after establishment, and local species adaptable to these kinds of wastes. The local climate can be characterized as cool and humid with mean annual temperatures of between 8 and 10°C. Rainfall is plentiful, with an average of 76 cm/year in the form of snow and rain. Winters are cold and snowy, whereas summer can experience droughty periods. Because of the local climate a number of species adaptable to alkali soils in the hot and dry regions of the western United States were eliminated. Table three is a listing of species that were appraised to be tolerant of the pH and E.C.'s of the cement dust.

The treatments used for the greenhouse test were based on the effect they would have on changing pH and E.C. of the dust, as well as local availability. The following treatments were implemented in one cubic foot boxes: (1) natural soil, (2) papermill sludge, applied at an equivalent of ½, 1 and 5 dry metric tons/acre, (3) soil and paper mill

sludge, and (4) 30 year old dust. All treatments involved mixing the fresh dust and dust amendments to a depth of 12 cms (plow depth). Salt sensors were placed at several levels in the boxes to monitor E.C.'s of each mixture over time and depth.

Table 4 summaries the final salt sensor data for a three-month period for several of the more promising treatments. For all treatments, the E.C. values of the surface 0-5 cms decreased significantly over the three month trial period. The effect of continued watering and vegetative establishment has removed those cations contributing to high E.C. of the treatments. This is further demonstrated at the 8-10 and 12-15 cm levels. With time leaching has moved the cations downward increasing the cation concentrations, thus E.C. values will increase. All of the treatments show this relationship with a significant increase in the final E.C. values for the 12-15 cm depth. Throughout the entire series of trials, 30 year old dust soil or paper mill sludge amendments had the lowest E.C. values. These relationships indicate a potential use of the older dust as a surface cap over the fresh dust.

During the three month trial period, inorganic fertilizers were added to overcome the lack of nutrients with the various treatments. Nitrogen was added in the form of ammonium nitrate @ 33kg/ha, phosphorous as triple super phosphate at 45 kg/ha and potassium as muriate of potash @ 65 kg/ha. E.C. of the surface 0-5 cm increased significantly for one week and then decreased as moisture contents were maintained. Although fertilizer amendments were demonstrated to be essential in maintaining proper nutrient levels for the vegetation, they should be added in small increments in order to maintain E.C. values low enough to sustain the vegetation.

Throughout the trials all treatments were evaluated for changes in visual properties of the vegetation , root and shoot development, E.C. and pH. Table 5 summarizes the results of these observations for some of the more promising treatments. Fresh dust by itself will not support vegetation. I noted the characteristic effect of alkali soils on vegetation: tip burn and lack of shoot and root development. The best treatment is the fresh dust mixed with older dust, soil and paper mill sludge. This mixture supplies nitrogen from the paper mill sludge, noted in the green vegetation color. Furthermore, the old dust and soil have ameliorated the alkali effect of the fresh dust. It appears that the soil, paper mill sludge and old dust have removed from solution excess cations contributing to high pH values. Other treatments utilizing old dust to modify the fresh dust could provide acceptable reclamation techniques to establish vegetation. But long-term effects need to be quantified.

CONCLUSIONS

Results of this study show that fresh cement bag house dust is alkaline and contains excessive amounts of actions such as calcium, sodium, magnesium and potassium. Because of this excess, pH and E.C. values are extreme and thus prohibit the establishment of vegetation. A

series of greenhouse trials were investigated whereby old dust, soil and paper mill sludge were mixed with fresh dust. Soil, paper mill sludge and old dust as a single mixture with fresh dust shows promise in an expanded field trial for reclamation. Ph, E.C.'s were less, vegetation had good root and shoot growth compared to other treatments.

Engineering properties of dust indicate that they compact readily and use of equipment should be limited to an unsaturated state of the dust to prevent compaction and puddling of the mixtures.

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TABLE 1: Chemical and Mineralogical Properties of Cement Bag House Dust by Age

AGE OF BAGHOUSE DUST	Properties											
		Chemical								Mineralogical		SAR
	pH	N	P	K	Ca	Mg	Na	EC	CEC	Calcite	Quartz	
		%	ppm					mmohs/ cm^2	MEQ/ 100 gms	%		
FRESH[2/]	11.8	0	1	227	48,000	516	610	22.9-	26.2	95	5	3.4
3 Year	11.8	0	1	602	32,000	600	680	20.6	19.21	95	5	
15 Year	12.9	0	1	637	13,527	756	210	10.6	15.50	100	0	
30 Year	8.8	0	1	550	11,450	325	84	8.1	6.85	95	5	
Pulpmill Sludge	6.5-7.0	3										

Table 2. Selected Physical and Engineering Properties of Cement Baghouse Dust and Paper Sludge

Physical Properties

BAG HOUSE	Particle Size Distribution % SAND	% SILT	% CLAY	TEXTURE[1/]	% Water by Weight .3 Bar	1 Bar	3 Bar	15 Bar	Available Water .3 -3 Bar	.3 -15Bar
DUST	7.2mm	.2-.02mm	/ .02mm							
FRESH	24	60	16	Si.L.	56	46	27	24	19	32
3 YEAR	32	42	26	L.	100	95	75	62	25	34
15 YEAR	60	24	16	S.L.	75	61	46	33	29	42
30 YEAR	64	12	24	S.L.	82	73	60	48	22	34
PAPERMILL SLUDGE					.25 gms /L. density					

ENGINEERING PROPERTIES	Liquid Limit	Plastic Limit	Sicky Limit	Plasticity Index
FRESH	64	62	82	2
3 YEAR	93	86	69	7
30 YEAR	116	101	115	15
15 YEAR	71	82	83	--

-1/ United States Dept. of Ag. Classification

Table 3: List of Some Species Tolerant to Soils With High Salts Adaptable to the Study Area in Michigan[1]

PLANTS	HIGH SALT TOLERANCE	MEDIUM SALT TOLERANCE	LOW SALT TOLERANCE
	12 - 18 mmohms	4 - 12 mmohms	2 - 4 mmohms
FORAGES (Grasses and Legumes	Alkali sacaton	White Sweet Clover	Alsike Clover
	Saltgrass	Yellow Sweet Clover	Red Clover
	Canada Wildrye	Perrenial Ryegrass	Ladino Clover
	Barley (hay)	Alfalfa	
	Birdsfeet trefoil	Tall fescue	
	Western Wheatgrass	Wheat	
	Nutall Alkaligrass	Oats	
	Fults	Orchard Grass	
		Smooth Brome	
		Reed Canary	
FIELD CROPS	Barley	Rye (grain)	Field Beans
	Rape	Sorghum (grain)	
	Sugar Beets	Corn (field)	
		Sunflower	
		Flax	

(1) Extracted from Agriculture Handbook No. 60

Table 4: Final Electrical Conductivity Values for Selected Cement Bag House Dust and Pulpmill Sludge Greenhouse Trials.

TREATMENT AND SEED	AGE OF DUST	DEPTH IN CUBIC FOOT BOXES					
		EC		EC		EC	
		Initial	Final	Initial	Final	Initial	Final
		0-5 cm		8-10 cms		12-15 cms	
		mmohms		mmohms		mmohms	
Control - no seed	Old	8.1	4.6	5.1	2.5	7.4	2.5
	Fresh	17.5	7.3	19.5	13.5	11.3	17.7
Control-seeded	Old	3.1	2.3	2.5	1.9	2.0	1.7
	Fresh	24.0	4.2	15.5	6.3	9.4	11.4
½ dry m ton/ha sludge and seeded	Old	4.2	2.6	2.4	1.8	2.1	1.7
	Fresh	35.0	12.5	15.9	13.8	16.9	18.1
1 dry m ton/ha	Old	3.1	2.7	2.9	2.7	3.0	2.4
	Fresh	19.2	10.1	18.5	19.6	16.9	19.0
5 dry m ton/ha paper mill sludge soil and seeded	Old	3.6	2.3	2.0	1.9	2.3	1.9
	Fresh	6.6	4.6	4.5	6.6	11.0	20.9

Table 5. Results of Greenhouse Trials Testing Several Mixtures of Cement Bag House Dust, Paper Mill Sludge and Natural Soil Materials

TREATMENT	SEED MIX	LENGTH OF TRIAL	COVERAGE	TOP GROWTH	ROOT GROWTH	pH FINAL	NOTES
			%	CMS	CMS		
Fresh Dust	Alfalfa, Fults cultivar, Alkali Sacaton	3 Months	10	1	.5	11.5	Crusting, tip burn, foliage green.
Old Dust	" "	3 Months	70	3	3	9.0	No crust or tip burn foliage green.
Equal Parts Old and Fresh Dust	" "	3 Months	30	1	1	10.3	No crust or tip burn, foliage green, old dust supporting seedlings.
Equal Parts Fresh Old and Soil	" "	3 Months	80	7	4	9.2	No crusting or tip burn, foliage green.
Equal Parts Fresh Old and 5 Dry M. TN/Ha Paper Mill Sludge	" "	3 Months	60	4	2	8.5	No crusting or tip burn, sludge keeps dust soft, foliage green.
Equal Parts Old, Fresh, Soil and Paper Mill Sludge @ 5 Dry M TN/Ha	" "	3 Months	90	20	12	7.8	No crusting or tip burn foliage dark green, algae growth

THE ROLE OF GYPSUM AND OTHER AMENDMENTS IN THE RECLAMATION OF STRIP-MINED LANDS IN SEMI ARID ENVIRONMENTS [1/]

by

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INTRODUCTION

Approximately 20% of the world's coal reserves or 50% of U.S. reserves are found in the Northern Great Plains states of Colorado, Montana, Wyoming and North Dakota (1). Additional important reserves are located in the Canadian provinces of Alberta and Saskatchewan. Almost all current coal extraction in this region is by surface mining techniques. Coal mining is a debilitating, but reclaimable land disturbance. The region's predominant land use is agricultural, with grazing and forage production, and small grain with oilseed crops predominating. Thus, the primary goal of reclamation of spoil banks created by surface mining is to return the land to agricultural productivity.

Much of the spoil created by surface mining in the Northern Great Plains is either sodic (containing an excess of exchangeable sodium), or saline (containing an excess of soluble salts) or both (1,2). Reclamation of sodic minespoils is made difficult by the physical properties of these materials. The climate of the region is predominantly semi-arid, and plant growth is constrained by the available water supply. Dispersion of clay materials in minespoils by elevated exchangeable sodium causes greatly reduced rainfall infiltration and compounds the effect of limited rainfall. Minespoils of the Northern Great Plains are typically fine textured, low in organic matter, and contain a predominance of clay materials that swell when wet (2).

The dominant method of reclamation of surface-mine spoils in mid- and western-North America is currently the overspreading of topsoil on leveled spoil followed by revegetation. Topsoil is stripped from the land before surface mining and is stockpiled. Reclamation laws generally require that all available non-sodic, non-saline surface soil to a thickness of from 1.5 to 2.4 m be saved and respread. Adequate thicknesses of surface soil does not always exist, however, and chemical reclamation of sodic spoil is a possible alternative to adjunct to soil spreading. In chemical reclamation, the amendment applied must supply soluble calcium or magnesium and the soil-water system must be managed so that the calcium and magnesium will replace sodium on the cation exchange complex. This displacement or cation exchange is actually a chemical reaction between solid and liquid phases of the soil-water system that increases the soluble Na. Then the replaced Na must subsequently be removed by leaching the liquid phase (the soil solution) downward with precipitation or irrigation water.

Several different chemical amendments can be used to ameliorate sodic conditions (3.4), but in terms of the combination of cost, convenience of handling and effectiveness, gypsum ($CaSO_4.2H_2O$) is one of the best and may be thought of as the "standard amendment" against which the performance of others may be compared. Gypsum usage in irrigated agriculture is reviewed elsewhere in these proceedings (5). The generation of 30×10^6 tonnes per year and a stockpile accumulation of over 270×10^6 tonnes of by-product gypsum (phosphogypsum) from phosphate fertilizer production in the U.S. (6) creates a significant and negative environmental impact, unless it can be used beneficially. This paper examines current research on the use of gypsum for reclamation of sodic minespoils. A number of experiments will be examined, and one

particular project will be discussed in detail, because it illustrates the promise and the difficulties of gypsum usage in minespoil reclamation in semi-arid environments.

Field Experiments with Gypsum and Topsoil: Methods. F.M. Sandoval and others at the USDA-SEA's Northern Great Plains Laboratory established field experiments to compare the benefits of topsoil spreading and gypsum incorporation on reclamation of mine spoils of various qualities. A meaningful measure of reclamation success is ability of the disturbed soilscape to support plant productivity at a level comparable to that of similar, undisturbed land. In these experiments, plant productivity was assessed by forage yields of crested wheatgrass (Agropyron desertorum) [Fisch.] Schult.), a perennial, drought-tolerant forage grass. The experiments were conducted at four mine sites located in Oliver and Mercer counties in central-western North Dakota. The climate is continental and semi-arid, with an average annual precipitation of 40 cm, with about 28 cm received from April through August. During the five-month, frost-free growing season, total potential evapotranspiration averages about 100 cm and the area is subject to periodic droughts.

At each of four sites, identical experiments were established on leveled minespoils with adequate surface drainage. Six main plots 6.1 by 15.2 m provided three replications for three plots with 30 cm thickness of topsoil and three with no topsoil replacement to serve as controls. The topsoil was obtained from adjacent non-mined lands and consisted of a mixture of material from A- and B-horizons. These main plots were subdivided to accommodate two subtreatments in a 2 x 2 factorial arrangement. Subtreatments were: (A) gypsum applied at 21.5 tonnes/ha and (B) no gypsum; cropping treatments were then superimposed consisting of (C) crested wheatgrass and (D) summer fallow. The fine granulated gypsum was disked into the upper 10 cm of spoil material before the 30-cm topsoil placement occurred. Crested wheatgrass was seeded in 1974 and some subplots had to be reseeded in 1975. Weeds were removed by periodic cultivation on the fallow plots during the growing seasons from 1974 through 1976. This practice is known as "summer-fallowing" in the Great Plains and is employed by conserve precipitation from one year for crop production the next year. Topsoil placement occurred in 1973, and forage yields were measured for either four or five years, from 1974 through 1978. Phosphorus fertilizer was disked into all plots and nitrogen fertilizer was applied annually. Soil samples were collected in early fall of each year and analyzed for soluble electrolyte components and other characteristics. Four samples from each depth zone of each subplot were collected and composited to form a single sample.

The standard measure of sodicity level is the exchangeable-sodium-percentage (ESP) of the soil. ESP is defined as the percentage of the soil exchange capacity that is occupied by sodium ions. In this paper, as is often done in practice , sodicity will be evaluated in terms of the more easily measured sodium-adsorption-ratio (SAR) of the saturation extract. SAR represents the liquid phase of the equilibrium cation exchange reaction. For ESP values in the range of 3 to approximately

35%, SAR values are nearly numerically equal to the corresponding equilibrium ESP value (3). The SAR is defined as $(Na)/((Ca + Mg)/2)^{1/2}$, where concentrations are in meq/liter of saturation extracts.

Results of Field Experiments. Relevant physical and chemical properties of the minespoils and covering soils at the four sites are indicated in Table 1. The minespoil near Zap, North Dakota, was the poorest medium for plant growth because it had the highest sodicity (SAR average, 27). Spoils at the Beulah and Stanton sites were intermediate with moderately sodic characteristics. The best material for plant growth was the non-sodic minespoil at the Center site. Topsoils were medium textured and minespoils were relatively fine textured. The high saturation percentages of the sodic minespoils (Table 1) is indicative of soil dispersion and poor physical condition.

The gypsum treatment contained Ca equivalent to 93% of the exchangeable Na in a 30-cm thick zone in the highly sodic minespoil at the Zap site. At the Beulah and Stanton sites, applied gypsum contained more than enough Ca to replace the exchangeable sodium in a 30-cm thickness in the moderately sodic spoils. Complete exchange never occurs, but the figures are approximately indicative of maximum chemical reclamation potential.

Results of gypsum incorporation are most easily observed as changes in soluble cation concentrations and SAR values., Data in Table 3 indicate that significant decreases of sodicity (as SAR) occurred over time in the 0-15 cm depth zone of non-covered minespoil, with or without gypsum. Lesser changes of SAR occurred with time in the upper spoil zone (30- to 61-cm depth) of topsoiled plots. The incorporation of gypsum resulted in increases with Na, Ca, and Mg concentrations. Increases in Na and Mg were the result of exchange, whereas the increase of Ca was caused by solution of gypsum. While data from the non-sodic site at Center are not shown in Table 3 because they are irrelevant to the central question of sodicity decrease, increases of soluble Ca concentration resulting from gypsum incorporation at this site were comparable to those at the two moderately-sodic spoil sites.

Decreases in sodicity may be partitioned into a part attributable to gypsum per se and a part attributable to time, which is related to the effect of water and salt movement and possibly natural weathering processes. Relative changes in sodicity with time and with treatment were calculated from appropriate data, most of which are shown in Table 3, to arrive at values shown in Table 4. Decreases in SAR over time were greater in the non-topsoiled plots than were decreases ascribable to gypsum application per se. On the basis of a 30-cm thick minespoil zone, the largest overall decrease in SAR for non-topsoiled spoils treated with gypsum was 32% (Beulah site, base SAR value, 13) which the largest overall decrease for topsoiled plots was 34% at the high-sodicity Zap site. In general, a given amount of gypsum should be expected to produce a larger reduction in sodicity when the materials have a higher, initial sodicity level. The results shown in Table 4 for topsoiled plots are consistent with this expectation. Negative values were not statistically significant in two of the three cases.

As fallowing conserves soil water, this treatment should increase the potential for leaching. The effect of the fallow treatment is best examined by reference to soluble Na, as this ionic species is the most mobile of the cations involved. The data in Table 35 indicate that only at one site (Stanton) was there some decrease of soluble Na under fallow in non-topsoiled plots at the 15 to 61 cm depths. In plots that received gypsum at the Stanton site, this expected effect was not observed in the Ø to 15 cm depth, as the soluble Na concentration was greater with fallow than with crop. Fallowing resulted in significant decreases in soluble Na in some of the topsoil at all three sites which indicates that salts were moving upward instead of downward. In general, then, fallowing was not effective in leaching soluble sodium.

Although no measurements of soil hydrologic balance and deep percolation were made in these experiments, gravimetric water content measurements were taken in the fall of 1974 and 1975 at the Stanton and Beulah sites. As a result of fallow, stored soil water had increased 9.4 and 6.Ø cm in the upper 91-cm profile depth in spoil only and topsoiled plants, respectively. This information, coupled with often observed evidence of deep percolation in summer-fallowed sites in the same region under a similar climate (7), indicates that leaching of soluble salts originally near the surface could have occurred through a depth of 3Ø cm, or more , at these study sites if the hydraulic conductivity of the minespoil were adequate. Even with the evapotranspiration of forage grasses present, appreciable leaching of soluble sodium did occur through a profile zone extending from the surface to the 3Ø cm depth of a deep covering, soil layer over minespoil under the climate pattern of the present experiments (8). Based on the results of these experiments and other evidence cited, we conclude that the chemical reclamation process is being limited by inadequate leaching-of exchanged Na, and that the hydraulic conductivity of the sodic minespoils is as much of a constraining factor as the limited amounts of precipitation available. Measurements of the hydraulic conductivity of minespoil similar in SAR value to that found at the Zap site indicate extremely low permeability to water after the spoil undergoes swelling upon wetting (8,9,1Ø). The excess of evapotranspiration over precipitation and periodic droughts definitely limit the depth to which soluble salts will be leached.

Inadequate downward leaching of Na is associated with a progressive increase of this ion in the 15- to 3Ø-cm depth zone of topsoil overlying the minespoil at all 3 sodic-spoil sites. Figure 1 illustrates this for the highly sodic Zap site. Gypsum applications enhanced the release of exchangeable Na from minespoils, which resulted in more soluble Na appearing in overlying soil. Merrill et al. (11) concluded that salt-diffusion processes were largely responsible for this upward Na migration.

Despite the apparent inadequacy of the leaching aspect of the chemical reclamation process in these experiments, the various observed decreases of sodicity were such that significant forage-yield increases were observed. Data in Table 2 indicate four-year average yield increases of 22 to 23% in response to gypsum incorporation for the spoil-only plots at the two moderately sodic sites. Of the topsoiled

plots, only the high-sodicity spoil site showed a significant (20%) yield response to gypsum. Forage yields at the non-sodic spoil site (Center) were less with gypsum than without it for plots without topsoil. The pattern of sites and topsoiling treatments displaying significant yield responses to gypsum (i.e. Stanton and Beulah without topsoil and Zap with topsoil) is consistent with the pattern of sites and treatments showing the greatest overall decreases of sodicity (as SAR, Table 4).

In comparing the relative effect of topsoil placement with gypsum application upon wheatgrass yield, it is apparent that topsoiling confers considerably larger relative yield increases than does gypsum application. However, the relative benefit of topsoiling is less pronounced as spoil quality improves. Relative yield increases, comparing topsoiled versus non-topsoiled plots, without gypsum, are 84%, 33%, 25%, and 8% for the Zap, Stanton, Beulah and Center Sites, respectively. Yields for topsoiled, high-sodicity spoil were lower than yields for comparable treatments on non-sodic spoil because 30 cm of topsoil is not enough to restore productivity to the optimum level found on high quality, undisturbed soils of the area. Spoils similar to that found at the Zap site require 75 cm or more of overspread soil material to reach the maximum plant-productivity level, according to a soil reconstruction study in the same area conducted by Power et al. (12). The experiments detailed here demonstrate the evident superiority of soil spreading over chemical reclamation by gypsum for restoring vegetative production potential to sodic minespoils under limited rainfall conditions.

Other Experiments with Chemical Reclamation. In earlier experiments conducted in western North Dakota by Power et al. (13), gypsum application was compared with the spreading of 5 cm of good quality topsoil over high-SAR minespoil. Very low growth of perennial grasses on spoil alone was improved much more by presence of the soil material than by gypsum. The results were in qualitative agreement with the four-site study detailed above.

An ongoing study recently reported by Dollhopf et al. (14) compared the effectiveness of gypsum, calcium chloride and gypsum augmented with calcium chloride and ammonium nitrate or ammonium sulfate for sodic minespoil reclamation in southeastern Montana. After amendment application , all treatments were covered with 70 cm of good quality soil material. Forage grass production was measured under irrigated and non-irrigated treatments. All treatments, from non-irrigated, non-amended checks to irrigated, amended treatments produced 5 to 15 unit decreases in a minespoil having an initial SAR of about 23. Applications of calcium chloride, which is considerably more soluble than gypsum, produced greater decreases in SAR than did gypsum. Combinations of 88% gypsum with $CaCl_2$ and either NH_4NO_3 or $(NH_4)\ SO_4$ were also more effective in lowering SAR than gypsum applied alone.

No significant plant yield responses to amendment treatments were reported by Dollhopf et al. (14). Also, no upward migration of Na from spoil into soil was observed as occurred in the North Dakota experiments. A study of the soil hydrologic balance under the irrigated treatments indicated that significant deep percolation into the minespoil did

occur. The minespoil thus appeared to have some permeability. Unlike the North Dakota minespoils which were dominated by expanding montmorillonitic clays, more than 50% of the clay-sized fraction of the minespoil in the Montana experiment was non-swelling kaolinite, which is less sensitive to sodicity. It appeared that the 70-cm thickness of overspread topsoil and the apparent ability of the minespoil to support significant downward water flux increased plant growth potential to the extent that yield responses to sodicity decreases associated with the amendments were not observed.

Chemical Reclamation and Hydraulic Conductivity. Critically limiting hydraulic conductivity of sodic minespoil undoubtedly limited the ameliorative action of gypsum in the North Dakota experiments previously discussed. The degree of deterioration of hydraulic conductivity (HC) and other physical properties depends on the exchangeable-sodium-percentage (ESP) of the soil, on the electrolyte concentration of the soil solution, and on the clay mineralogy of the soil. Hydraulic conductivity decreases as ESP of the soil increases. For a particular soil and a particular ESP, however, HC increases as electrolyte concentration in the soil solution increases. This is true because of the flocculating effect that saline solutions have on soil materials (9, 15). Increasing clay content of soil generally reduces the hydraulic conductivity. Expanding type clays, such as montmorillonite, swell progressively more as the level of sodicity increases, causing a drastic reduction in HC. Non-expanding clays, such as kaolinite, are much less sensitive to the effects of sodicity than montmorillonite, and hence, have lesser effects on soil physical properties. These background concepts are reviewed in References (3) and (15). The benefit of a chemical amendment should not be evaluated separate from hydraulic conductivity, which is both the primary indicator of the physical limitations of a sodic soil and an important indicator of amendment effectiveness. Sodic soils or minespoils restrict plant growth more because of physical limitations than because of chemical toxicity, unless significant salinity is associated with sodicity (16).

Skaptason (17) conducted a laboratory study of chemical reclamation of various sodic materials and compared the filtration rate - an indicator of relative hydraulic conductivity - of several sodic agricultural soils and sodic minespoils (Table 6). The soil materials had higher filtration rates than minespoils, both initially and after adding gypsum. The spoil with the lowest filtration rate was from the same site (Stanton) as one of the moderately sodic spoils of the North Dakota study, although the sample used by Skaptason (17) had higher SAR. These. data show that for a given level of sodicity and for the same general texture, minespoils will generally have a lower hydraulic conductivity and be more difficult to reclaim by chemical amendments than natural, sodic soils. Minespoils are geological materials typically low in effective organic matter and are almost completely structureless; mature sodic agricultural soils usually possess prismatic or columnar structure in their B-horizons. Also, sodic minespoil profiles have a much greater thickness of dispersed, high SAR materials than natural sodic soils, where the zone in need of amendment is usually

much thinner. Thus, the removal of soluble salts by leaching as part of chemical reclamation of minespoils may often be very difficult and may create saline problems downslope.

Gypsum is sparingly soluble in water (31 meq/liter) and resultant hydraulic conductivities for sodic soils after amendment are often low. By using more soluble salts like calcium chloride ($CaCl_2$), higher electrolyte levels can be maintained and HC is high enough to allow rapid removal of exchanged Na by leaching. Reclamation is quickly accomplished by applying a mixed salt (Ca-rich) solution of sufficiently high concentration followed by solutions of successive dilution (18) or by applying $CaC1_2$ (9). A comparison of chemical reclamation with gypsum versus $CaCl_2$ was made in column studies by Doering and Willis (1Ø). Amendments were incorporated in a high-sodic minespoil. Distilled water was applied and the rate of the wetting front advance was measured (Table 7). The wetting-front advance rate increased very little at gypsum incorporation rates above 2Ø tonnes/ha.3Ø cm as solubility, became limiting. With $CaCl_2$, wetting front advance rate continued to increase as rate of incorporation increased, and showed a dramatic increase at the highest rate of incorporation.

Calcium chloride is more expensive than gypsum. For a very low HC spoil of SAR value 26, Doering and Willis (9) estimated that chemical reclamation with $CaC1_2$ would have to be carried out to a 1.5m depth to allow for drainage of temporary, perched water tables and to minimize resalinization of the upper part of the profile by stored salts. If applied as Ø.75 N solution, they calculate that 148 tonnes/ha.1.5m (29.6 tonnes/ha.3Øcm), of $CaC1_2$ would be necessary, costing $32,5ØØ per ha at a current estimated cost of $22Ø per tonne. If cost of spoil leveling and irrigation application are included, this reclamation cost is above estimates for the cost of stripping, stockpiling and respreading 1.5m of soil material on regraded minespoil (19). In making this comparison, it must be remembered that soil material carries organic matter, plant nutrients, and various positive, physical-tilth qualities not conferred on minespoil by chemical reclamation.

Role of Chemical Amendments in Minespoil Reclamation. Where a sufficient quantity of soil material is available, application of gypsum is inferior to respread topsoil for reclamation of sodic strip mine spoil. Direct comparisons between topsoil spreading and use of Ca amendments more soluble than gypsum, especially calcium chloride, have not been studied. Minespoils are usually deficient in plant nutrients and in the case of minespoils involved in the North Dakota studies, phosphorus was very deficient. Where soil resources are available, soil spreading will continue to be the basic method for reclaiming strip-mined land in the Great Plains. This technique is currently mandated by regulatory practice.

Approximately 2,ØØØ ha in the northern Great Plains (based on 1977 Soil Conservation Service estimates) were strip-mined before current soil-spreading requirements were imposed. Many of these abandoned "orphan" spoils are sodic and could be chemically reclaimed to a certain level with gypsum. If hydraulic conductivity is critically limiting, then combinations of gypsum and more soluble amendments or calcium chloride alone may be indicated.

Use of chemical amendments to reclaim sodic minespoil may be feasible where the thickness of available topsoil is low or its quality is limiting. Specific testing of particular combinations of sodic minespoil and climate or proposed irrigation is necessary. Short term field-plot or column experiments combining soil spreading and chemical amendments may indicate only limited or marginal chemical effects and yield benefits. Research is needed to evaluate possible long-term, soil-morphological benefits from the incorporation of 20 tonnes/ha or more of gypsum in the upper part of the spoil immediately under a soil cover. The zone of reduced sodicity and improved structure may be slowly extended downward under the influence of a reservoir of gypsum, annual climatic cycles, and root activity.

The area of new coal land exploitable by strip-mining for which spoil is sodic and the soil resource is limiting to the extent that chemical amendment may be feasible is probably of the order of one thousand ha per year in western North America. This offers a limited by potentially beneficial use of by-product gypsum.

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Table 1. Initial characteristics of topsoils and minespoils at four sites in North Dakota.

	Center		Beulah		Stanton		Zap	
	topsoil	spoil	topsoil	spoil	topsoil	spoil	topsoil	spoil
SAR	1	1	1	11	1	12	3	27
Saturation %	40	65	32	100	42	80	42	119
EC*	1	4	1	5	1	3	2	4
pH, sat. paste	7.6	7.3	6.6	7.8	7.0	7.5	7.7	7.6
texture+	L	CL	SL	CL	L	CL	SCL	SiC
$CaCO_3$ equiv., %	7	9	1	8	2	11	4	8
org. matter, %	3.6		2.1		3.3		6.6	

* Electrical conductivity of saturation extract, millimhos/cm @25°C

\+ USDA system: L, loam; CL, clay loam; SL, sandy loam; SCL, sandy clay loam; SiC, silty clay.

Table 2. Average forage dry weight yields over 4 year period (1975 through 1978) at four sites studied.

Site and type of minespoil	No topsoil		30 cm topsoil	
	- gypsum	+ gypsum	- gypsum	+ gypsum
	---------- kg/ha ----------			
Center, non-sodic minespoil	3600 b*	2950 a	3880 b	3930 b
Beulah, moderately sodic minespoil	1980 a	2440 b	2480 b	2450 b
Stanton, moderately sodic minespoil	1930 a	2360 b	2560 b	2570 b
Zap, highly sodic minespoil	1060 a	950 a	1950 b	2330 c

* Values in rows followed by the same letter are not significantly different at the 5% level of probability: Duncan's multiple range test, using "conservative degrees of freedom".

Table 3. Soluble cation concentrations in saturation extracts of minespoils at 3 sites studied 3 months and 4 and 5 years after gypsum application. Analyses shown are for depth zones including position of gypsum incorporation - 0 to 15 cm for plots without topsoil, 30 to 61 cm for plots with topsoil.

Site:		Beulah		Stanton		Zap	
spoil sodicity:		moderate		moderate		high	
time after application:		3 mo.	4,5 yr.	3 mo.	4,5 yr.	3 mo.	4 yr.
Measure	gypsum application			PLOTS WITHOUT TOPSOIL			
SAR	No	12.8+	8.3	8.9*+	6.8*	19.4*+	16.1
	Yes	12.0+	6.9	7.7+	5.0	17.2	16.2
Na, meq/liter	No	33.7	39.1	27.3+	21.4	61.5	64.3
	Yes	48.1*+	32.5	35.1*+	22.3	75.3*+	67.9
Ca, meq/liter	No	8.7	19.8+	11.1	13.0	11.5	17.5+
	Yes	22.9*	24.4*	24.6*	25.5*	27.6*	21.1*
Mg, meq/liter	No	7.7	16.6+	8.4	8.4	11.2	15.7+
	Yes	17.3*	19.2	16.7*	14.6*	16.0*	14.3
				PLOTS WITH TOPSOIL			
SAR	No	11.9+	10.7	10.5*	9.7*	27.9*	25.2*
	Yes	11.4	11.6*	8.0	8.7	21.5	18.3
Na, meq/liter	No	35.1	42.5+	25.7	28.3+	40.9	40.5
	Yes	42.3*	43.8	33.2*	33.4*	57.4*	56.8*
Ca, meq/liter	No	10.4	18.1+	7.8	10.6	2.5	2.9
	Yes	17.1*	19.0	21.4*	19.2*	11.5*	11.9*
Mg, meq/liter	No	9.5	17.7+	6.3	8.4	2.6	3.4
	Yes	14.5*	16.4	14.7*	13.9*	10.4*	11.4*

* Indicates that a vertical pair of values (gypsum vs. no gypsum) are significantly different at the 5% level. Symbol placed at larger value of the pair.

\+ Indicates that a horizontal pair of values (3 mo. vs 4,5 yr.) are significantly different at the 5% level.

Table 4. Effect of gypsum addition upon sodicity change (as differences in SAR) in depth zones of incorporation (see Table 3) at 3 sodic minespoil sites.

Site, spoil type	depth zone, cm	base SAR	Differences in SAR: time[1] Δ SAR	time[1] Δ %	time + gypsum[2] Δ SAR	time + gypsum[2] Δ %	gypsum alone[3] Δ SAR	gypsum alone[3] Δ %
PLOTS WITHOUT TOPSOIL								
Beulah, moderate sodicity	0-15	12.8	4.5	35	5.9	46	1.4	1
	0-30	12.9	3.1	24	4.1	32	1.0	8
Stanton, moderate sodicity	0-15	8.9	2.1	4	3.9	44	1.8	20
	0-30	8.8	1.0	11	1.6	18	0.6	7
Zap, high sodicity	0-15	19.4	3.3	17	3.2	17	-0.1	- 1
	0-30	20.6	3.8	18	0.9	4	-2.9	-14
PLOTS WITH TOPSOIL								
Beulah, moderate sodicity	30-61	11.9	1.2	10	0.3	3	-0.9	- 8
Stanton, moderate sodicity	30-61	10.5	0.8	8	1.8	17	1.0	10
Zap, high sodicity	30-61	27.9	2.7	10	9.6	34	6.9	25

1/ time effect = (no gyp 3 mo.) - (no gyp 4,5 yr.).

2/ time + gypsum effect = (no gyp 3 mo.) - (gyp 4, 5 yr.)

3/ gypsum effect alone = (no gyp 4, 5 yr.) - (gyp 4, 5 yr.)

Table 5. Soluble sodium concentration in saturation extracts for topsoiled and non-topsoiled plots in North Dakota study. Data from 4 years (1974 through 1977) are averaged. Underlined pairs of values are emphasized in text discussion.

Site Depth (cm)	no gypsum grass	no gypsum fallow	gypsum grass	gypsum fallow
	meq/liter			
PLOTS WITHOUT TOPSOIL				
Beulah				
* 0-15 Spoil[1]	36.3 a[2]	39.1 a	36.0 a	39.9 a
15-30 Spoil	34.6 a	35.6 ab	40.5 b	39.1 b
30-61 Spoil	32.7 a	34.4 ab	38.0 b	39.4 b
Stanton				
* 0-15 Spoil	23.6 a	24.4 a	25.6 a	30.9 b
15-30 Spoil	31.4 c	24.4 a	33.8 c	27.3 b
30-61 Spoil	29.4 b	25.7 a	29.3 b	26.2 a
Zap				
* 0-15 Spoil	63.9 a	66.4 a	73.7 b	70.4 b
15-30 Spoil	65.0 b	61.1 b	44.8 a	44.1 a
30-61 Spoil	59.4 b	55.6 b	49.7 ab	45.1 a
PLOTS WITH TOPSOIL				
Beulah				
0-15 Soil	0.9 a	1.9 b	1.0 a	2.3 b
15-30 Soil	7.8 a	16.3 b	10.4 a	19.0 b
*30-61 Spoil	40.4 a	39.6 a	44.3 a	41.5 a
Stanton				
0-15 Soil	1.2 a	2.0 b	1.0 a	1.3 a
15-30 Soil	6.2 a	11.7 b	6.0 a	12.0 b
*30-61 Spoil	27.1 a	26.3 a	36.0 c	32.0 b
Zap				
0-15 Soil	12.1 a	15.7 b	10.9 a	16.4 b
15-30 Soil	36.9 a	37.1 a	37.1 a	44.0 b
*30-61 Spoil	41.9 b	35.2 a	54.5 c	57.5 c

1/ Asterisk (*) indicates zone of gypsum incorporation.
2/ Values within the same row which are followed by the same letter are not significantly different at the 5% probability level (Duncan's multiple range test).

Table 6. Characteristics and filtration rate test for 5 materials after incorporation of 0 or 17.9 tonnes/ha·15 cm of gypsum. After Skaptason (17).

Materials and Origin	SAR	SP% *	Rate of Incorporation	
			0	17.9
			Filtration Rate, ml/min	
Soil, non-sodic (Huntley, MT)	1-3	53	40	75
Soil, sodic (New Salem, ND)	ca. 17	50	6	89
Soil, sodic (Worden, MT)	25-35	92	5	36
Minespoil, sodic (Decker Mine, MT)	25-30	67	4	21
Minespoil, sodic (Glenharold Mine, ND)	25-30	128	1	7

* SP% is saturation percentage.

Table 7. Rate of wetting front advance in columns of minespoil amended at rates shown 100 hrs after application of water. Adapted from Doering and Willis (10).

gypsum equivalent, tonnes/ha 30 cm	gypsum		calcium chloride	
	incorporation rate, kg/m	rate of advance, cm/day	incorporation rate, kg/m	rate of advance, cm/day
2.2	0.73	0.25	0.47	0.20
6.6	2.21	0.31	1.42	0.40
13.2	4.41	0.37	2.84	0.48
22.0	7.33	0.42	4.74	0.56
44.1	14.71	0.47	9.48	0.63
88.2	29.41	0.47	18.95	2.19

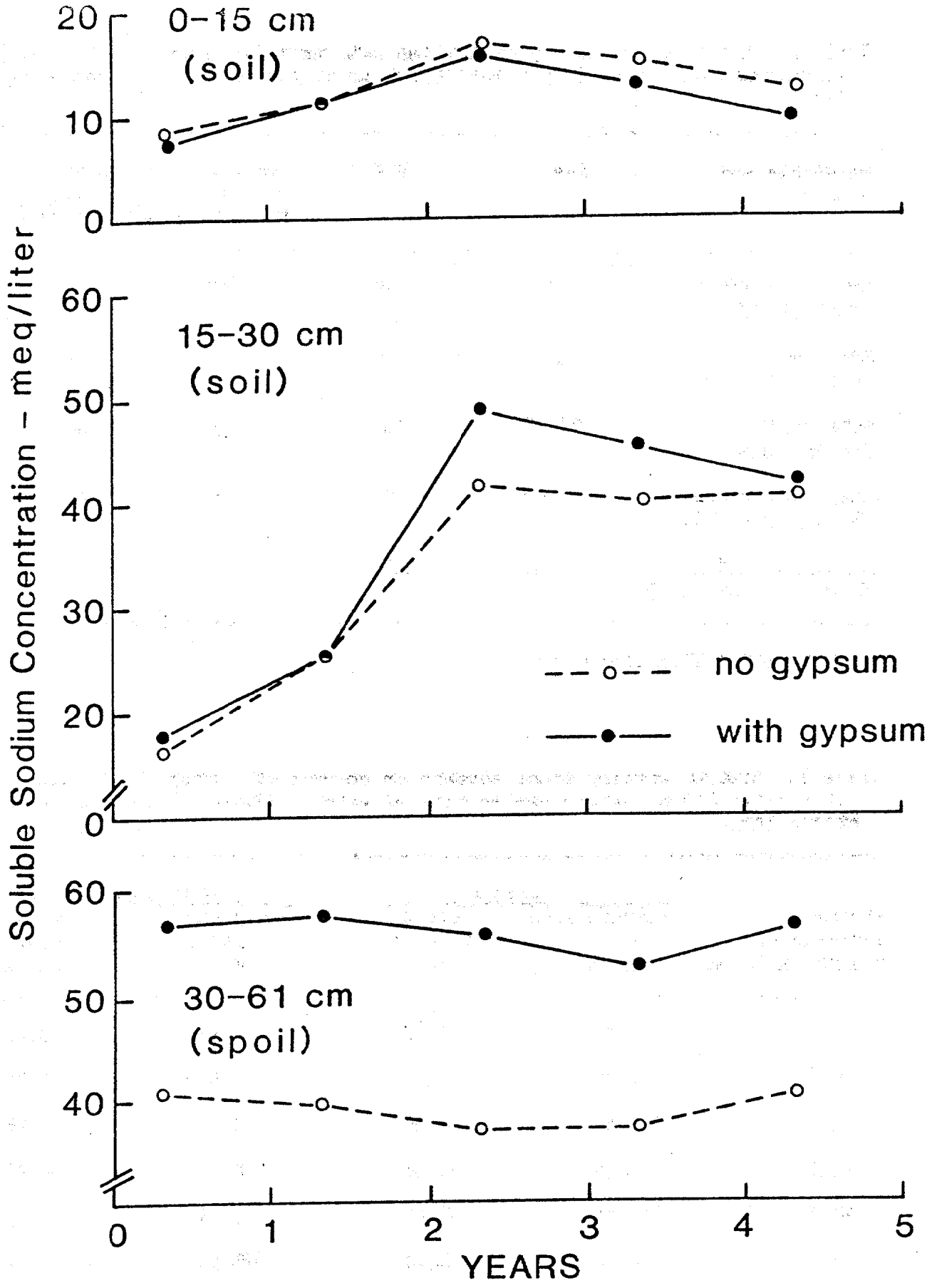


Figure 1. Soluble sodium in saturation extracts versus time after application of topsoil and gypsum at a high-sodicity minespoil site.

EFFECT OF DISSOLUTION RATE ON THE EFFICIENCY OF GYPSUM IN IMPROVING PERMEABILITY OF SODIC SOILS

by

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INTRODUCTION

Soil permeability is an important factor in soil management. A major concern in irrigation agriculture is the maintenance of sufficiently high soil permeability for salinity control. The permeability of a soil for water is dependent on both the exchangeable sodium percentage (ESP) of the soil and on the electrolyte concentration of the percolating solution, tending to decrease with increasing ESP and decreasing electrolyte concentration (Quirk and Schofield, 1955; McNeal et al., 1968; Oster and Schroer, 1979). Soil permeability can be maintained, even at high ESP values, provided that the electrolyte concentration of the irrigation water is above a critical level.

Laboratory experiments indicate that, at a certain ESP, changes in the soil structure occur when using water having electrolyte concentration below the critical level, resulting in decreased hydraulic conductivity (Chen and Banin, 1975). It appears that the effect of the ESP on soil permeability depends on soil mineralogy, texture and percolating solution concentration (Frenkel et al, 1978). The question of whether the cause of the change in soil permeability is clay migration or clay migration and swelling is still open. The difference between swelling and dispersion processes is quite important. Swelling is essentially a reversible process -- reduction in permeability can be reversed by adding electrolytes or divalent ions to the soil. Dispersion and particle migration on the other hand is essentially irreversible, causing the formation of impermeable clay layer.

The importance of dispersion in affecting soil permeability has been observed by Rhoades and Ingvalson (1969) who concluded that dispersion rather than swelling was the operative process which leads to permeability decreases in vermiculitic soils. Similarly, Frenkel et al. (1978) concluded that plugging of the soil pores by dispersed clay particles is the major cause of reduced hydraulic conductivity in montmorillionitic, vermiculitic and kaolinitic soils in the range of exchangeable sodium percentage below 20.

The rate of water intake by soil is affected both by the hydraulic properties of the soil and by changing hydraulic conductivity of the rain (or sprinkler irrigation) -- affected surface layer. Even though the thickness of the rain-affected layer rarely exceeds a few milimeters, the reduced permeability of this layer can markedly reduce infiltration (Hillel and Gardner, 1970 and McIntyre, 1958).

When saline-sodic soils are being reclaimed to remove soluble salts and exchangeable sodium, it is necessary to incorporate suitable amendments (releasing calcium) into the soil surface. Gypsum is generally the amendment which is used most, because of its availability and its low cost. Gypsum added to a sodic soil can initiate permeability changes due to both electrolyte concentration and cation exchange effects (Loveday 1976). However, if immediate improvement in infiltration and soil permeability is required, then the electrolyte effect is the important one.

The effectiveness of gypsum under various conditions is questionable. It is possible that the efficiency of gypsum as an amendment depends on its dissolution properties.

The dissolution rate of gypsum is controlled by film diffusion and follows a first-order kinetic equation. Thus, formally, the rate of dissolution of gypsum particles can be expressed as

$$\frac{dC}{dt} = K(C_s - C_t) \qquad (1)$$

where C_t is the concentration of calcium sulfate in solution at time t, C_s is the saturation concentration at the particular ionic strength, and K is the dissolution coefficient which depends linearly on the surface area of the gypsum particles and is inversely proportional to the thickness of the solution film at the gypsum fragement surface.

Integration of eq. (1) with the boundary conditions that when t = Ø, C_t = Ø, gives the increase of concentration with time:

$$\ln\left(1 - \frac{C_t}{C_s}\right) = -Kt \qquad (2)$$

where the terms have been defined.

There are two main sources of gypsum that can be used as a soil amendment: mined and industrial - the latter being a by-product of the phosphate fertilizer industry. Industrial gypsum differs from mined gypsum in its bulk density and sedimentation conditions. These differences may affect the rate of dissolution of gypsum in aqueous solutions and thus its efficiency as an amendment in the reclamation of sodic water and sodic soils. This hypothesis is tested in this study.

EXPERIMENTAL

A. The Dissolution Studies

Gypsum was obtained from three sources: (1) analytical grade; (2) a by-product of the phosphate fertilizer industry; and (3) mined gypsum from Makhtesh Ramon, Israel. The purity of the gypsum samples was determined by shaking 1.5 g of each sample with 1,ØØØ ml of distilled water for a period of 12Ø hours. The industrial and mined gypsum were analyzed for soluble salts and for insoluble residues. The gypsum content in the industrial and mined gypsum samples was 97.5%. and 99.Ø%, respectively. The content of soluble P in the industrial gypsum was Ø.Ø6%, whereas no P was found in the mined gypsum. The remaining Salt, in these gypsum sources was magnesium sulfate. The contents of Na^+, K^+, Cl^- and HCO_3 were negligible in both gypsum samples. The insoluble residues of the industrial and mined gypsum samples were found to be 1.3% and Ø.32%, respectively. Using x-rays, it was found that the main minerals in the residue of the industrial gypsum were fluorapatite and silicon, whereas in the residue of the mined gypsum it was SiO_2 and calcite.

The rate of dissolution of gypsum from the two sources was determined on particles obtained by two methods. With the first method, compressed discs were prepared; with the second method, particles of various sizes were separated from the untreated gypsum.

Gypsum discs were prepared by using a die (made by Perkin-Elmer, No. D-Ø1) to press gypsum powder into discs 13 mm in diameter. The gypsum powder was prepared by grinding some of the gypsum samples to particle size less than 44 m, followed by drying the powder at 6Ø°C for 2h before pressing. The force that was used in pressing the powder was 8,ØØØ kg for 1Ø minutes and a density of 2.11 g cm^{-3} was obtained in the gypsum discs. The external surface area of each disc as calculated from, its dimension was 3.5 cm^2. Since the density of the discs from the three sources was, the same, it was assumed that the Internal surfaces of all the gypsum discs were also the same. The gypsum discs were hard and showed no signs of crumbling when placed in water.

The dissolution rate of natural fragments of gypsum was studied on fragment sizes between 1 and 2 mm in diameter, and 4 and 5.7 mm in diameter. The gypsum fragments were obtained by sieving the gypsum through standard screens following drying at 6Ø°C for 2 hours. Some gypsum powder was absorbed on the discs and on the fragments; the powder was dissolved by washing with water.

Six discs, or 3 g of gypsum fragments, were placed in a reaction vessel containing 2ØØ ml of water. The reaction vessel was double walled; the internal dimensions, were 5.5 cm in diameter and 12 cm in depth. A pump circulated water maintained at constant temperature through the external compartment. The water in the internal reaction vessel was stirred at a constant speed of 1,4ØØ rpm. During the dissolution process, 2-ml samples of solution were removed and analyzed for calcium by using a Perkin-Elmer Atomic Adsorption spectrometer. The surface area of the gypsum discs had changed at the end of the dissolution process by about 2.3% of the initial external surface area.

B. The Simulated Rain Experiments

A loessic sodic soil from Nahal Oz was. exposed to simulated rainfall at an intensity of 27 mm/h. The texture of the soil was. 37.7, 4Ø.6 and 21.7% sand, silt and clay, respectively. The cation exchange capacity (CEC) was 17 meq/lOO g soil, and the ESP was 3Ø. The rainfall was created by means of a simulator described by Morin et al. (1967). Distilled water was used to simulate the real salt concentration in rainwater. A Z-cm-deep soil layer was packed over a layer of coarse sand in a box 29 x 5Ø cm in size. Gypsum from the two sources and of two particle sizes (powder of less than 75 m and fragments of 4.Ø to 5.7 mm in diameter), was spread on top of the soils in the amounts equivalent to 3.4 and 6.8 t/ha. The soils were first saturated from the bottom, and then the rain was applied.

C. Soil Columns

Soil columns were prepared using the F2 mm fraction of a non-calcareous soil (Golan). The texture of the soil was 11.2, 13.1 and 65.2% sand, silt and clay, respectively. The cation exchange capacity was 32.6 me/100 g soil. The soil was mixed with 0.7 - 0.8 mm quartz sand in a ration of 1:1. The purpose of mixing the soil with sand was to obtain reasonable flow rate. Columns of the soil were prepared by packing 240 g of soil into plastic cylinder (5 cm I.D.) to a bulk density 1.3 g/cm^3. The length of the soil column when wetted was 9.2 cm. The columns were initially wetted from the bottom and kept saturated. The exchangeable sodium level of the soil was adjusted by leaching with 0.5 N NaCl-$CaCl_2$ solution of SAR 20. The hydraulic conductivities (HC) of soil columns obtained with the 0.5 N solutions were taken as the "base" value. Subsequently, the columns were leached with solutions of the same SAR but of 0.02 N concentrations until steady-state conditions for HC, ionic composition and EC were obtained. Then calcium salts were added to each soil column in amounts of 2.32, 4.64 and 9.28 meq/column, which corresponded to 30, 60 and 120 percent of the exchangeable sodium in the columns. Analytical, powdered gypsum was spread at the top of the soil column at rates of 0.2, 0.4 and 0.8 g per column which corresponds to 1.0, 2.0 and 4.0 ton/ha. In similar experiments, 1.0 M solutions of CaCl at the rates of 1.16, 2.32 and 4.64 ml/column were applied at the top of the soil columns (the amounts of Ca in equivalents/column in the gypsum and $CaCl_2$ treatments were identical). Thereafter, distilled water was applied , the effluent was collected-using a fraction collector, and the effluent analyzed for volume, EC and ionic composition. At the end of the leaching with distilled water, the soil columns were sectioned into four layers, and the CEC and exchangeable sodium percent in each layer were determined.

RESULTS AND DISCUSSION

The Dissolution Studies. The changes in total calcium concentration with time for the dissolution of analytical gypsum in water at 25°C are shown in Fig. 1, Plots of -1n (1 - C_t/C_s) vs. time for the data in Fig. 1 are presented in Fig. 2.

Straight line was obtained, as predicted by eq. (2), and the dissolution coefficient (given by the slope of the lines in Fig. 2) could be calculated. This value is 1.66 x 10^{-4} sec^{-1}.

It should be noted that in solutions containing Ca^{+2} and/or SO_4^{-2} ions (in addition to NaCl), the dissolution rates of gypsum should decrease due to the common ion effect (Kemper, et al., 1975).

The dissolution rate of the industrial and the mined gypsum discs (with an external surface area of 6 x 3.5 cm^2) in water is also presented in Figure 1. The results show that, irrespective of the source of gypsum, whenever the gypsum is compressed into discs, the dissolution rate is the same. Thus, it may be calculated that the dissolution process of both industrial and mined gypsum is similar to that described for analytical gypsum.

The dissolution rate of industrial and of mined gypsum for fragment sizes of 1-2 mm and of 4-5.7 mm in diameter is presented in Fig. 3. These results indicate that the dissolution rate of the industrial gypsum is higher than that of the mined gypsum for both fragment sizes. The time that it takes to reach the value of 50% saturation of mined gypsum is nine times longer than that of the industrial gypsum for both fragment sizes.

The dissolution coefficients for the industrial and mined gypsum samples were calculated from eq. (2) and are presented in Table 1. These results indicated that the dissolution coefficient increased as the fragment size decreased for both sources of gypsum at a given amount of solid. The ratios between the dissolution coefficients of the industrial and mined gypsum samples (Table 1) for both particle sizes were found to be nearly the same. Since the dissolution mechanism and the rate of dissolution per unit surface area for the gypsum from both sources are the same (as evident from the experiment with the gypsum discs), it is suggested that the surface area parameter in the dissolution coefficient is different. This suggestion is supported by the density of the two kinds of gypsum. Whereas the bulk density of the mined gypsum fragments is 2.35 g/cm^3, that of the industrial gypsum is only 1.4 g/cm^3. Thus, for a given amount of gypsum the number of particles and the external surface area of the industrial gypsum are greater than those of mined gypsum for the same particle size. It is possible, also that in the denser particles (mined gypsum) the internal surface area is also smaller than that in the industrial gypsum.

The Simulated Rain Experiments. The infiltration rates of the loess soil as a function of the depth of rain are shown in Fig. 4 for the various gypsum treatments.

The results indicate that the gypsum source, amounts and fragment size, all have their effect on the infiltration rate (IR) of the soil. The IR of the soil without gypsum decreased very sharply as the cumulative amount of rainfall increased until it reached a constant value of 2 mm hr^{-1}. Conversely, with the spreading of 3.4 t/ha of powdered industrial and mined gypsum on the soil surface, the final infiltration rates were 7.5 and 5.5 mm hr^{-1}, respectively.

It is also evident that when coarse fragments of mined gypsum were applied, the final IR of the soil was about 2 mm/h (a value similar to that obtained for the soil without application of any gypsum), independent of the amount of gypsum applied (3.4 and 6.8 t/ha). The coarse fragments of mined gypsum were almost not effective in maintaining a high IR to the soil. Conversely, coarse fragments of industrial gypsum were effective in preventing the drop in IR of the soil, and their effectiveness increased with an increase in the amount of gypsum applied. The IR of the soil spread with the coarse fragments of industrial gypsum in amounts equivalent to 6.8 t/ha was similar to the IR of the soil spread with powdered gypsum at the rate of 3.4 t/ha. The effect of fragment size in industrial gypsum is mainly on the rate at which the IR drops with the amount of rainfall. With the coarse fragments, the IR drops more sharply than with the powdered gypsum.

The gypsum effect on the IR can be explained as follows: It has been shown (McIntyre 1958) that soil crust is the factor which determines the rate of infiltration, and its formation is associated with clay dispersion in the soil as a result of the rainfall impact. It was also found that the infiltration rate is very sensitive to the exchangeable sodium percent (ESP), and the salt concentration of the applied water (Oster and Schroer 1979). Thus, clay dispersion in the soil surface (and crust formation) is enhanced by both the impact of the rain drops and the potential of the soil clays to disperse. In our experiments the rain intensity and the mechanical impact of the rain drops were identical in all the gypsum treatments. Thus, the effect of the gypsum treatments is mainly through its effect on the chemistry of the soil surface. The potential of the soil clay to disperse increases with an increase in the ESP of the soil and with a decrease in the soil solution concentration. When the gypsum concentration in the soil solution of the soil surface is sufficiently high (5 meq/l, see Shainberg et al., 198Ø) the tendency of the soil clay to disperse is low and the IR is maintained at high values. Both the electrolyte concentration and the replacement of exchangeable sodium by calcium in the soil surface reduced the tendency of the soil to disperse and prevented it from forming a crust;

It seems that the difference between the two gypsum sources lies in the fact that the dissolution rate of the coarse fragments of the industrial gypsum is ten times higher than that of the mined gypsum (Fig. 3, Table 1). Thus, in the short time of contact between the rain. water and the soil surfaces, electrolyte concentration in the surface soil solution in the mined gypsum systems was not sufficient to prevent dispersionand crust formation. As the size of the gypsum fragments decreased, the dissolution rates of gypsum from both sources became similar and gypsum powder from both sources had a similar effect on the IR of the soil. In the experiments with the large fragments of industrial gypsum, the effect of gypsum increased with an increase in the amount of gypsum applied. This was probaby due to the uniformity of the amount of gypsum spread over the soil. In the low amount of gypsum applied (3.4 t/ha), there were bare surfaces of soil in between the gypsum fragments, and the IR rate of these surfaces dropped to 4.5 mm/h; when the amount of gypsum applied was doubled, more soil surface was covered with gypsum and the IR was maintained at values typical for powdered gypsum (7.5 mm/h).

The Column Study. The hydraulic conductivity of the sodic soil in Ø.5 N solution of SAR 2Ø was Ø.84 cm/h. Displacing the Ø.5 N solution with Ø.2 N solutions of the same SAR did not change the hydraulic conductivity of the soil. The relative hydraulic conductivity of the soil when the Ø.Ø2 N solution of SAR 2Ø was displaced with distilled water (DW) is presented in Fig. 7. It is evident that the hydraulic conductivity of the soil dropped to zero sharply.

The potential of a soil to release salt when leached with distilled water is a dominant factor which determines whether clay dispersion and loss in hydraulic conductivity (HC) can occur. Soils which release salt at a rate sufficient to maintain the concentration of soil solution. above the flocculation value of the soil clay will not disperse and will

not be sensitive to low ESP. Since this soil is chemically stable and does not release salt into the soil solution, the hydraulic conductivity of this soil decreased sharply to zero.

The composition of the exchange complex as a function of the depth of the soil for various amount of $CaSO_4$ or $CaC1_2$ salt applied is presented in Fig. 5. The efficiency of the two salts in replacing exchangeable sodium was similar and the curves in Fig. 5 represent either of the amendments. Studying the curves it is evident that the boundary between reclaimed and nonreclaimed soil is quite steep. The steepness of the ESP distributions with depth is the result of the high soil affinity for calcium ions (compared with Na). Thus, when replacing in the soil, 50% of the the exchangeable Na (the 4.64 meq/Ca treatment), the ESP at the bottom of the soil is above 15, whereas the ESP at the top of the column is below 5. Similarly, even when most of the Na has been replaced by calcium in the soil (the 9.28 meq Ca treatment) the ESP at the bottom of the profile is still 10. The soil layer with the highest percentage of sodium in the exchange complex may be the bottleneck for the flow of water when conditions promoting dispersion of the clay particles (e.g. distilled water) predominate.

The electrical conductivity of the effluent as a function of the two Ca salts is presented in Fig. 6. It is evident that the electrical conductivity of the effluent of the gypsum systems is decreasing moderately, whereas for the $CaCl_2$ systems the curves show maxima at about 1 pore volume and thereafter decrease sharply.

The relative hydraulic conductivity of the soil when leached with distilled water as a function of the amount of the two Ca salts spread at the top of the soil column is presented in Fig. 7. This soil is sensitive to the type of amendment. When $CaC1_2$ was applied, the HC of the soil dropped to zero in all rates of $CaCl_2$ treatment. Even when $CaCl_2$ was added at the rate of 120% of the amount of exchangeable Na in the soil column, the soil column was sealed upon leaching with distilled water. Conversely, when gypsum was applied at the same amounts, the soil maintained high values of hydraulic conductivity. This phenomena is explained by consideration of the chemistry of the adsorbed phase of the soil (Fig. 5) and the electrical conductivity of the effluent (Fig. 6). Even when 9.28 me $CaCl_2$ were applied to this soil, only 75% of the exchangeable Na has been replaced. Moreover, the ESP at the bottom layer of the soil dropped only to 10. This layer might become the bottleneck for the movement of water depending on the electrolyte concentration of the soil solution. The electrical conductivity of the effluent of the 9.28 me $CaCl_2$ treatment at 250 cm^3 was 0.08 mmho/cm. This low concentration of electrolytes in the soil solution does not prevent soil dispersion and clay movement and lodgment in the water conducting pores leading to a drop in the HC of the soils.

When gypsum is spread at the top of the soil, it dissolves slowly as is evident from EC breakthrough curve. The concentration of electrolytes in the effluent is maintained at values above 0.5 mmhos.cm corresponding to 5 meq/l. This concentration is above the flocculation of the clay particles (Oster and Shainberg 1980) and only limited clay

dispersion and clay movement should occur (Shainberg, et al., 198Ø). At this concentration range, swelling is the main factor causing the losses in hydraulic conductivity (Pupisky and Shainberg 1979). Thus, over this concentration range, only limited loss in hydraulic conductivity is observed.

SUMMARY AND CONCLUSION

(1) The dissolution coefficients of the analytical, industrial and mined gypsum are the same for a given surface area. However, the surface area (at a given fragment size) of the industrial gypsum is larger than that of the mined gypsum (for a given amount) and therefore, the dissolution rate is higher. As the fragment size of the gypsum becomes smaller, the difference between dissolution rates of both sources decreases.

(2) The infiltration rate of sodic soil exposed to simulated rain depends on the source, amount and size of the gypsum fragments used, The efficiency of gypsum in maintaining a high infiltration rate correlates with its rate of dissolution.

(3) The chemically stable soil is very sensitive to the type of amendment. Whereas in the $CaC1_2$ treatments, complete sealing of the soil took place, high hydraulic conductivity was maintained in the gypsum treatment. Soil, which does not have the potential to release salt, is very sensitive to low concentrations of Na in the exchange complex. Thus, the release of electrolytes by the gypsum particles is essential to maintain high hydraulic conductivity.

It is possible that calcareous soils that have moderate ESP levels will maintain reasonable physical properties through most of the profile, but will be susceptible to dispersion near the surface. This is because the soil solution electrolyte concentration may be insufficient to maintain physical structure. Application of gypsum at these surfaces will prevent crust formation under rainfall conditions.

(4) Industrial gypsum (a by-product of the phosphate fertilizer industry) is more effective than mixed gypsum in maintaining a high infiltration rate.

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Table 1: The dissolution coefficients of industrial gypsum, $K_{(PG)}$, and mined gypsum, $K_{(MG)}$, with different fragment sizes.

	Fragment size, mm	
	1.0 - 2.0	4.0 - 5.7
$K_{(PG)} \times 10^4$ (sec^{-1})	198	58
$K_{(MG)} \times 10^4$ (sec^{-1})	19	6
$\frac{K_{(PG)}}{K_{(MG)}}$	10.4	9.7

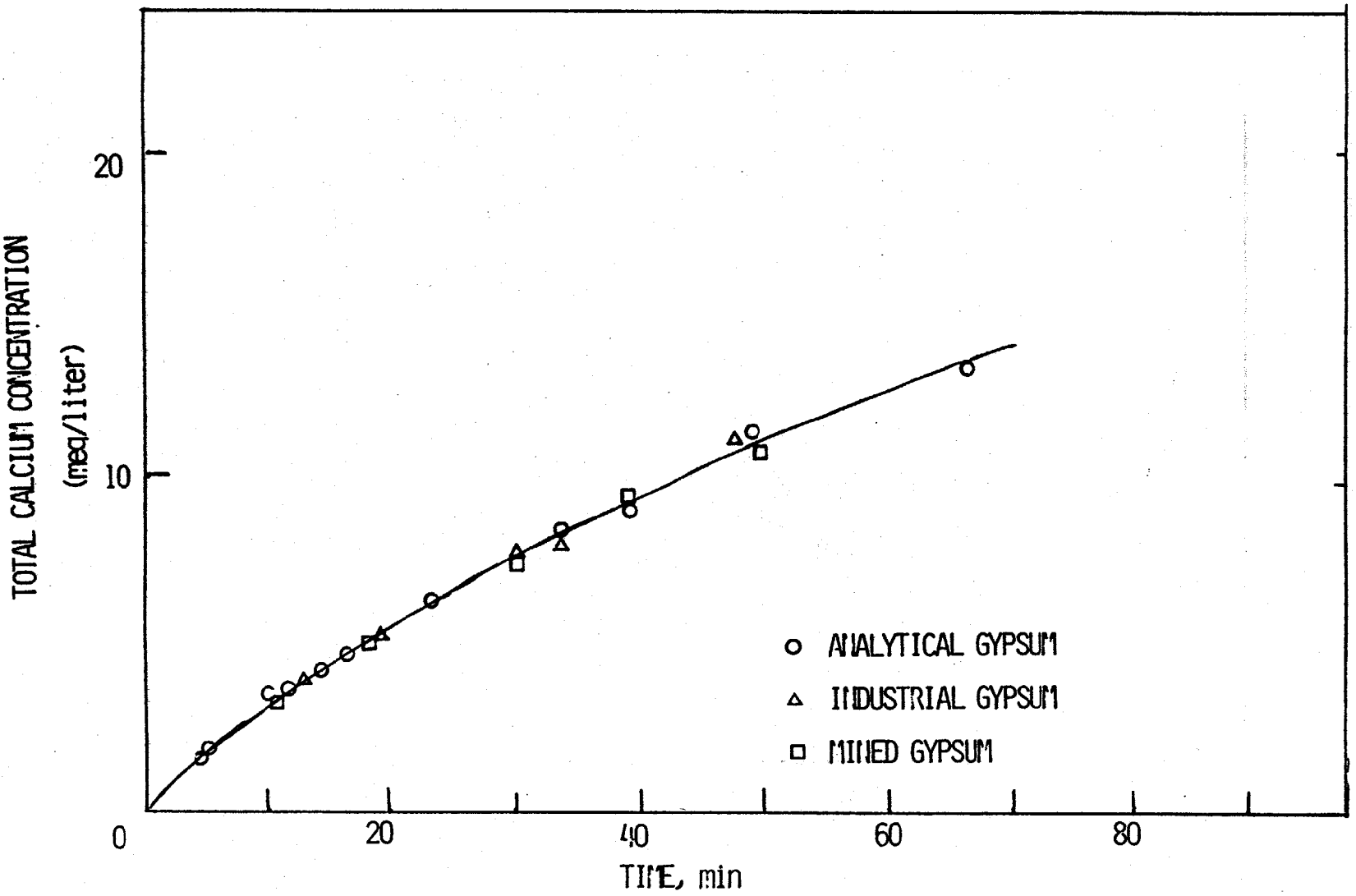


Figure 1. Calcium concentration in water, 0.05 N and 0.1 N NaCl solutions versus time plots for analytical, industrial and mined gypsum discs with an external surface area of 21 cm^2.

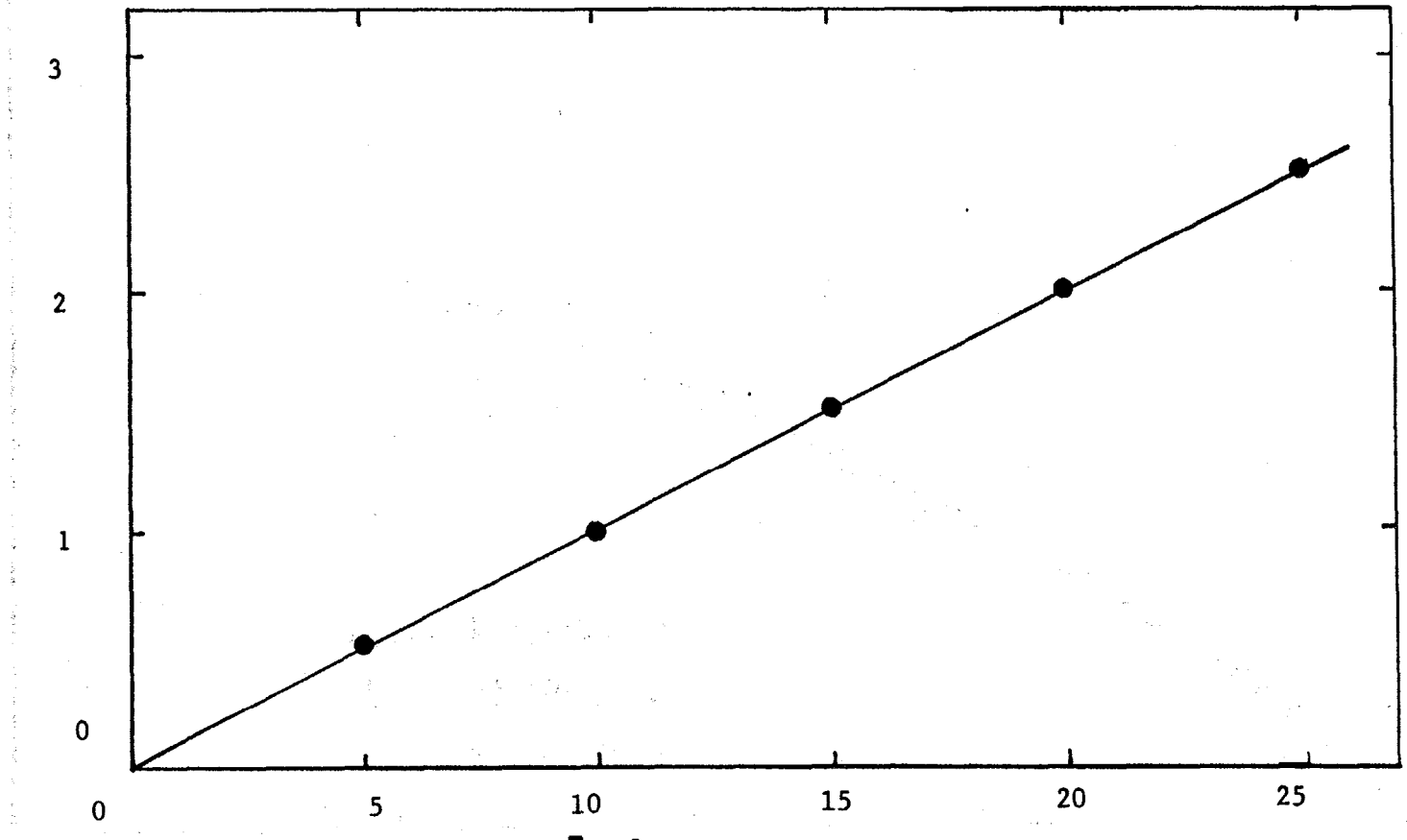


FIGURE 2. Plot of the logarithm of $1-[C_t/C_s]$ for water, 0.05 N and 0.1 N NaCl versus time for analytical gypsum discs with an external surface area of 21 cm^2.

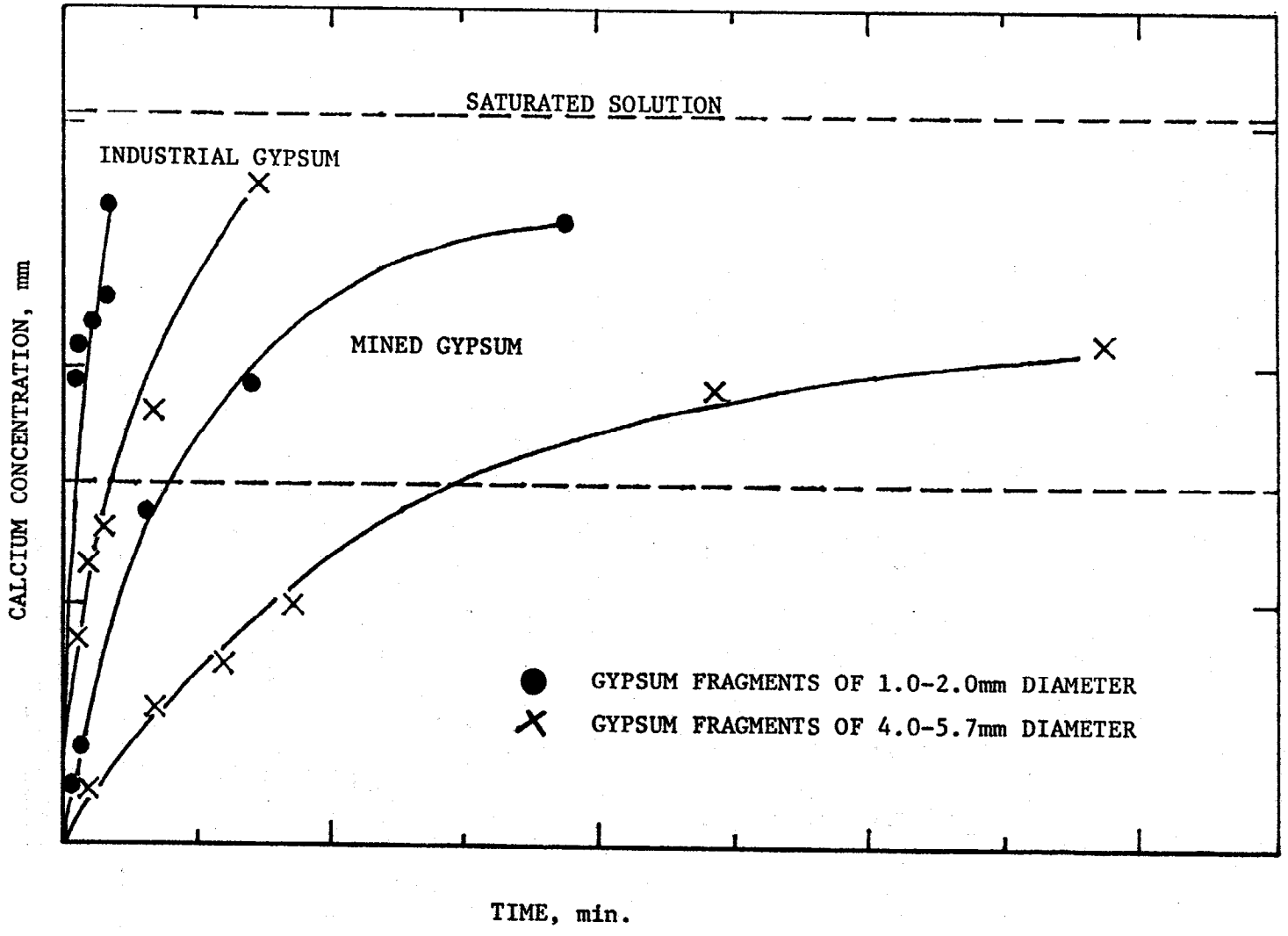
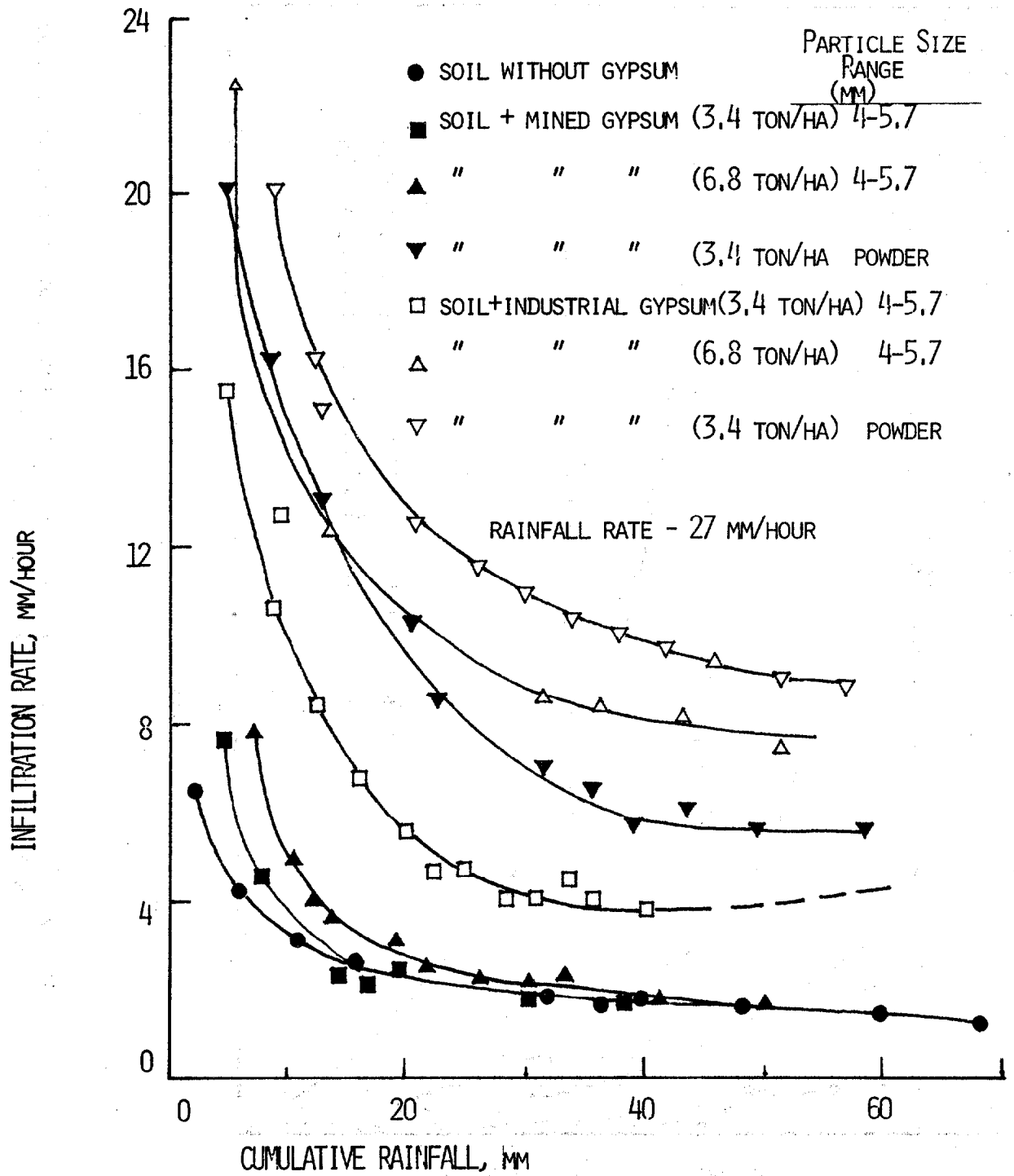


FIG. 3 Calcium concentration in water versus time plots for industrial and mined gypsum samples of two fragments' sizes.

FIGURE 4. The effect of industrial and mined gypsum (at amounts and particle sizes as indicated) on infiltration rate of loess soil, as a function of the cumulative rainfall under laboratory conditions.



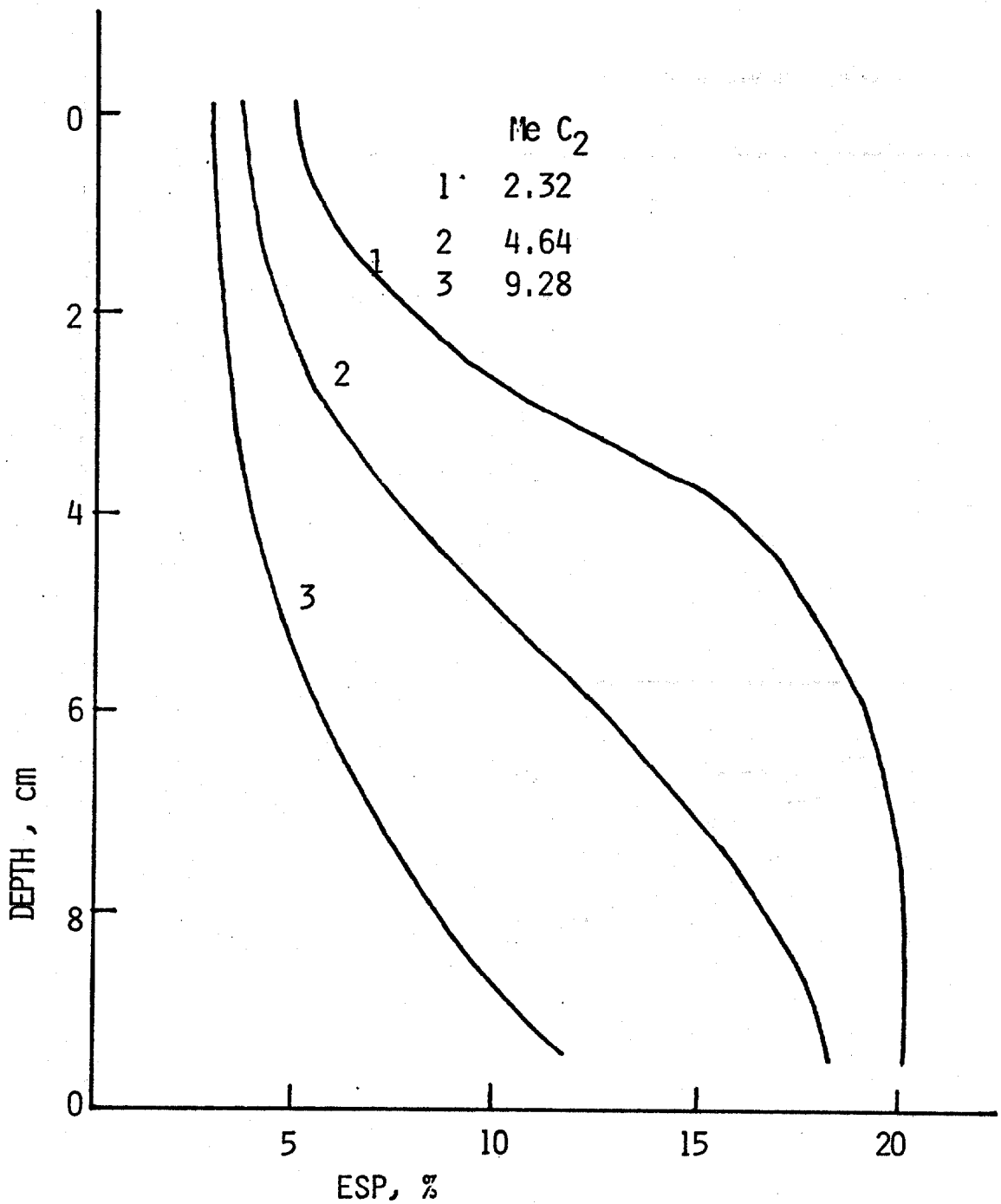


Fig. 5. The composition of the exchange complex as a function of the depth of the soil for various amount of $CaSO_4 \cdot 2H_2O$ or $CaCl_2$ salt applied.

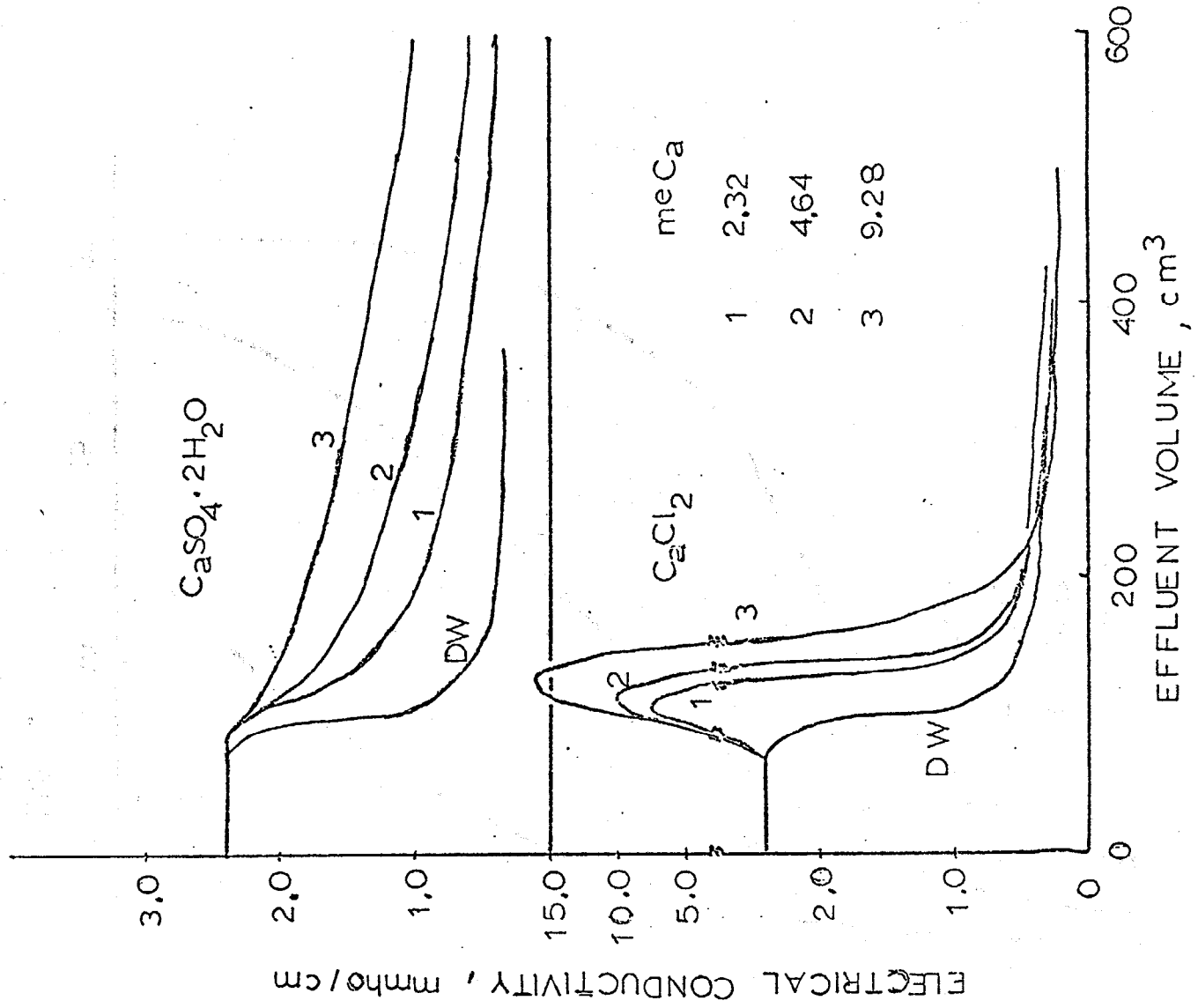


Figure 6. Electrical conductivity of the effluent as a function of both the effluent volume and the two Ca salts spread at the top of the soil column.

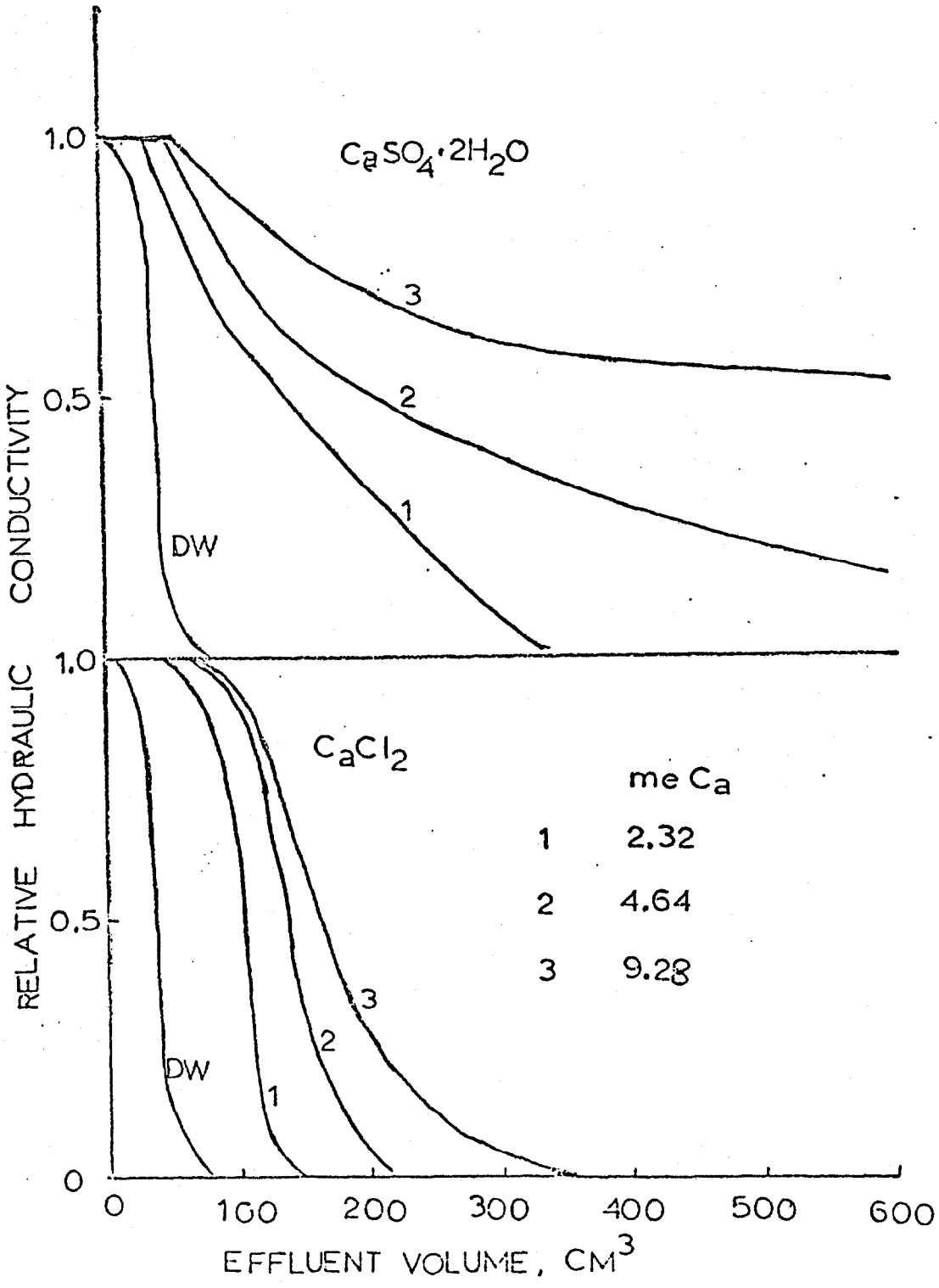


Figure 7. The relative hydraulic conductivity of the soil when leached with distilled water as a function of the two Ca salts spread at the top of the soil column.

USE OF PHOSPHOGYPSUM IN RECLAMATION OF SODIC SOILS IN INDIA

by

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INTRODUCTION

It is estimated that about one-third of the irrigated areas of the world are affected by salts. The problem of soil sodicity is one of the serious factors which adversely affects crop production and restricts economic utilization of available land resources, particularly in the arid and semiarid tropics. In India the total area under salt-affected soils is about 7.Ø million ha (1). Since the nature of the problem in different parts of India is not the sam, Bhumbla (2) has further classified these soils in four different categories.

Of the total salt-affected soils in India, 2.5 million ha occur in the Indo-Gangetic plains of Punjab, Haryana and Uttar Pradesh (U.P) i.e. in three northern states. These areas either form continguous compact blocks or are interspersed along with the normal soils. Most of these soils occur in low-lying areas where annual precipitation is more than 6Ø cm and groundwater usually contains a low amount of salts (3). These soils are predominantly sodic having high pH, high exchangeable sodium and in some cases high electrical conductivity. The distinguishing characteristics of these soils are their poor physical condition and very poor water transmission properties. Sodic soils form crusts when dry, are sticky when wet and have poor permeability to air and water.

Soil Amendments. Among inorganic amendments for reclamation of sodic soils, some are sources of calcium like gypsum, calcium chloride, phosphogypsum, rock phosphate and basic slag, while others are acids or acid-forming materials like sulfuric acid, sulfur, iron pyrites, iron sulfate, aluminum sulfate, etc. Since reclamation of sodic soils in most cases involves replacement of sodium on the exchange complex with calcium, gypsum is by far the most popular amendment. Use of gypsum as soil amendment has been known from the advent of the century. Lowering of pH by gypsum application increases the solubility of soil calcium carbonate many fold, which results in replacing exchangeable sodium of the soil and improving the physical condition. Unlike fertilizers, gypsum is applied once only as a corrective measure. Mineral gypsum is commonly recommended for the reclamation of sodic soils. India has extensive natural deposits of mineral gypsum estimated at 1216 million tonnes (4).

Besides gypsum being mined, it is also obtained as a by-product of the chemical industry producing tartaric acid, formic acid, oxalic acid, citric acid, common salt and phosphoric acid. Major quantities of by-product gypsum is known as phosphogypsum, which is obtained in the manufacture of phosphoric acid by wet process when rock phosphate is treated with sulfuric acid. For every tonne of P_2O_5 produced, 5.5 tonnes of phosphogypsum containing about 25% moisture are produced (5). While in India the annual production of 2.8 million tonnes of phospho-gypsum does not pose a serious problem for its disposal, it is a problem of much bigger dimension for other countries including the United States. There are various usages for phosphogypsum like making wallboard, cement, plaster product, sulfuric acid, manufacture of ammonium sulfate, etc. Vast areas under salt-affected soils occupying 1/3 of the irrigated acreage of the world opens up new vistas for its use in agriculture.

PHOSPHOGYPSUM

Composition. Calcium sulfate in phosphogypsum is-available as dihydrate $CaSO_4.2H_2O$, hemi-hydrate $CaSO_4.½H_2O$ and anhydrate $CaSO_4$ or it may also occur in combination of di-hydrate/hemi-hydrate, etc. depending upon the process involved in the production of phosphoric acid. The quality of phosphogypsum depends both on the process technology adopted as well as the quality of rock phosphate used. A typical analyses of phosphogypsum (6) based on Morocco rock phosphate is given in Table 1.

Phosphogypsum may also contain traces of iron, zinc, manganese, copper, etc. The presence of these elements is attributed to their presence in rock phosphate and impurities in sulfuric acid.

Percentage Purity. Phosphogypsum is high-grade gypsum having purity more than 90% on air dry basis as against 65-70% in agriculture grade mineral gypsum. The physico-chemical effects of phosphogypsum on soils is similar to that of mineral gypsum. However, it is likely to be more effective and consequently economic because of the high percentage purity when compared to agriculture grade mineral gypsum available for sodic soil reclamation in India (7).

Particle Size. The amount of gypsum dissolved in a solution depends on the particle size applied and the time allowed for dissolution besides temperature. Marshall (8) has shown that gypsum particles greater than>50μ in diameter show a solubility of 0.227% at 20°C, while particles of about 0.5μ in diameter show a solubility of 0.248%. Hildebrand (9) observed that grinding of gypsum can increase its solubility up to 20%. Khosla and Abrol (10) reported that the reactivity of gypsum increases very rapidly as fineness is increased. They explained that for sodic soils high in carbonates, large quantities of added gypsum are utilized in precipitating the surface carbonates; coarse grades of gypsum are likely to be ineffective since free carbonates would result in the formation of insoluble calcium carbonate coating on the surface of coarse gypsum particles. The neutralization of carbonates is nearly complete when gypsum of a size less than 30 mesh is added at the rate of 100% of gypsum requirement and when gypsum of a size less than 60-125 mesh is applied at the rate of 50% of gypsum requirement.

Since phosphogypsum is a fine powder of 100 mesh and above, its reactivity in sodic soils is much faster than that of mineral gypsum which is not so finely ground. Grinding of mineral gypsum builds up the cost and consequently finer grinding would mean building up the cost of the amendment still further.

Fluorine Content. Acceptance of phosphogypsum by the Government of India as an amendment for the reclamation of sodic soils did not prove an easy affair. Although use of mineral gypsum was well-accepted in the country as elsewhere in the world, the presence of fluorine in phospho-gypsum brought grave doubts among Indian Scientists and the Indian Council of Agriculture Research (ICAR) which delayed recognition of phosphogypsum ss a safe soil amendment by the Indian Government.

Research data were not available on fluorine uptake by cereals when grown on sodic soils. Phosphogypsum may contain fluorine from Ø.5 to 4.Ø%, depending on other factors. It was believed that fluorine in phosphogypsum may cause "fluorosis" to human beings as well as to cattle due to high fluorine uptake by crops when applied at the rate of Ø to 15 tonnes/ha for reclamation of sodic soils. The vast reserve of mineral gypsum in the country failed to arouse interest for an alternate source among the soil scientists. Besides, soil amendments when sold through institutional and government agencies carried a subsidy element of 5Ø to 75% for the farmers, depending on the size of their holdings. Research and extension programmes on phosphogypsum launched by Hindustan Copper Limited (HCL produced 3,ØØØ,ØØØ tonnes of phosphogypsum annually) were commendable (11). All research and extension data were presented in a meeting of scientists and the ICAR in 1977 which formed a basis for recommendation by the latter to consider phosphogypsum as an equally efficient soil amendment for the reclamation of sodic soils. Consequent upon the recommendation of ICAR, the government of India accepted phosphogypsum as a soil amendment.

INDIAN EXPERIENCE WITH PHOSPHOGYPSUM

Research. Reclamation of sodic soils picked up momentum in India only after 196Ø when the Central Soil Salinity Research Institute (CSSRI) was set up. Critical experiments were carried out on the use of amendments at the Institute with the objective of (a) determining the optimum quantity of gypsum, (b) time of application, (c) method of incorporation, (d) frequency of application, (e) relative response of different crops, and (f) interaction of amendments, fertilizers and organic manures, etc.

The use of phosphogypsum in the state of California (U.S.A.) has been reported in literature (12) but how far it has been popular as an amendment is not known. Similarly, phosphogypsum up to 2Ø tonnes/ha was used successfully in combination with manure, superphosphate and $(NH_4)_2 SO_4$ to reduce the exchangeable Na in sodic soils (13). However, work on phosphogypsum started in India only after 1973, although some work was done earlier to observe the effect of phosphogypsum as a sulfur source on oil seeds and pulses.

Mehta and Yadav (14) conducted field experiments to observe the adverse effect of phosphogypsum on crop growth due to its fluorine content. Their data showed that phosphogypsum was a promising amendment for the reclamation of sodic soils. The results of field trials conducted at several locations were summarized by Singh (15) that phosphogypsum when used as a soil amendment up to 12.5 tonnes/ha proved quite satisfactory and the yield of rice and wheat further improved in the second year. He concluded that fluorine in phosphogypsum is not available to plants; it remains in the soil as an inert material and-is eventually lost. In a recent study effects of fluorine at Ø, 25, 5Ø, 1ØØ and 2ØØ ppm as sodium fluoride was observed on rice and wheat crops (16 and 17). The authors observed that in sodic soil conditions, the effect of fluorine in phosphogypsum is considerably less because fluorine present therein is in a relatively soluble form. The application of phosphogypsum actually results in reduction of soil ESP and thereby fluorine uptake is further reduced.

The author used phosphogypsum up to 32 tonnes.ha (at double G.R. value) on sodic soils to study its effect on rice and wheat crops (18). The results given in Tables 2 and 3 lead to conclude that fluorine in phosphogypsum being rather in unavailable form may not show any adverse effect due to very little uptake by plants.

Extension. Extension work on phosphogypsum started simultaneously along with research projects. The phosphate fertilizer industry played a very important role in the initiation of research and extension work on phosphogypsum after the group discussion on utilization of phosphogypsum which was organized by the Fertilizer Association of India (FAI) in 1973. The group discussion was topical because reclamation of sodic soils was in active consideration of the government of India and a number of schemes were to be introduced on reclamation of problem soils next year. The author from HCL launched an extension programme for phosphogypsum about four years before the acceptance of phosphogypsum as soil amendment by the ICAR and the Government of India. This was a clear instance where a product was accepted by the farmers before research organizations recognized it. A collaborated demonstration programme for reclamation of sodic soils using phosphogypsum was initiated in the states of Punjab, Haryana and U.P. where the problem of sodicity was more acute. The collaborating agencies included CSSRI, Karnal, Agricultural Universities and Departments of Agriculture of the three states as well as some other agencies. The details of the programme carried out in the first three years from 1974-75 to 1976-77 are given in Table 4.

Technology Adopted. Each demonstration on farmer's field was carried out in an area of Ø.4 ha and continued for a period of two years. It is recommended to reclaim sodic soils in India during June-July and start with first crop of rice in the monsoon season. First of all, bunding and levelling were completed before the break of monsoon, i.e. by the middle of June, and phosphogypsum was applied at the rate of 1Ø-12.5 tonnes/ha based on soil test results. After mixing phosphogypsum by light harrowing, impounding of water was done for two to four weeks depending on availability of time and a minimum of 3Ø cm water was allowed to soak in. Before transplanting of rice, the standing water level of about 7 cm was drained out and fresh water was filled in the plot. Without disturbing the soil, fertilizers (½ N and full dose of P_2O_5 and K_2O) were applied along with 62.5 kg of zinc sulfate/ha. Balance N has applied in two installments, ¼ after three weeks of transplanting and the remaining after six weeks of transplanting. Since these soils are low in N, it is recommended that 25% additional N may be applied when brought under cultivation for the first time. It has been also found that $(NH_4)_2SO_4$ may be preferred over urea or calcium ammonium nitrate in the first year of reclamation (19). Instead of 1-2 plants per hill, 3-4 plants were transplanted for better plant population. Rice seedlings were 4Ø days old at transplanting as against transplanting of 21 days old seedlings in normal soils. Puddling was avoided at the time of transplanting and attempts were made not to disturb the soil beyond 15 cm depth for two years. After the harvest of rice crop, wheat was sown at all locations during Rabi season (Nov-March). At the end of Rabi season, green manuring crop (Sesbania aculeata) was raised in the same field for green manuring before second

year rotation of rice-wheat. The green manuring crop was ploughed down when it was 7-8 weeks old in the first week of June. The same cropping scheme of rice-wheat-green manuring 'was followed in the second year also for effective reclamation.

Results and Discussion. Encouraging results were obtained after the soil treatment with phosphogypsum right in the first year. Bumper crops were raised on the land where even grasses did not grow prior to initiation of the demonstration programme.

The yields of three demonstrations from each of the state of Punjab, Haryana and U.P. in Table 5 clearly show that a yield range of 29.64 to 65.78 g/ha of rice was obtained with the mean yield of 41.82 q/ha. The yields of wheat ranged from 19.7Ø to 61.75 h/ha with a mean of 36.94 g/ha. The figures in Table 6 illustrate the results of demonstrations of Haryana State for the year 1975-76. The range of rice yields for Haryana during 1975-76 was between 34.58 and 61.26 q/ha with the mean yield of 46.98 q/ha. These figures for wheat yields ranged from 2Ø.25 to 44.46 q/ha with the mean yield of 28.38 q/ha. These yield figures may be considered quite satisfactory in view of the nation's average yield of rice and wheat which is 13.77 and 14.77 q/ha respectively.

At yield levels given in Tables 5 and 6, it was possible to recover the cost of land development and crop cultivation in two seasons only except for the situation where the demonstrations failed. The increase in land value after reclamation was an additional but very significant gain.' The drop in soil pH after one year ranged between Ø.4 to 1.2 although the drop was in range of 1.Ø to 2.1 after first crop of rice. There was an interesting feature of these demonstrations. Under normal conditions at pH 9.2 and above it is not possible to raise wheat crop but after the application of phosphogypsum, it was possible to grow a good crop of wheat. This could be possible because application of phosphogypsum provided better physico-chemical soil environment for the growth of wheat. Since the treatments were the same for all locations, management level of farmers may be considered as the main reason for wide variations in yields among the states or within a state.

Economics of Reclamation. The detailed economics of one demonstration laid out in collaboration of Haryana Agricultural University (H.A.U.), Hissar is given in the Annexure. The soil had initial pH of 1Ø.Ø and EC 1.92 mhos and did not support any vegetation. The yields of rice and wheat in 1975-76 were 44.48 and 34.6Ø q/ha, respectively. The non-recurring expenditure on land development/reclamation came to Rs. 2454.68/ha while production cost of rice and wheat came to Rs. 2269.16 and Rs. 2237.3Ø/ha, respectively. The returns in terms of produce values of rice wheat were Rs. 3229.52 and Rs. 4Ø26.1Ø/ha, respectively. There was an overall profit of Rs. 294,47/ha from the two seasons when land reclamation/ development costs were also included in total expenditure.

Results from successful demonstrations have convincingly shown that the farmers get back their investment at the most in two seasons. The increase in land value at the minimum was Rs. 12,5ØO/ha against the development/reclamation cost of RS. 2454.68/ha. However, it must be

reckoned that the farmers who own these unproductive lands are not resourceful as their income from such lands are limited. Invariably these farmers need encouragement and financial assistance at the initial stage. Many farmers will have to create source of good quality water by installing tube-wells for which a help of greater magnitude will be required.

CONCLUSION

Earlier, the cost involved in moving phosphogypsum from factories located in the south to places of use in the north was prohibitive. The location of plants within economic freight zone for the sodic soils of northern states makes it possible to use phosphogypsum without much cost. Since soil amendments carry subsidy to the extent of 50 to 75% when sold through institutional agencies, private distribution channels cannot handle the product. It would help a lot if subsidy is made available to private distribution channels as well. The price of phosphogypsum also needs thorough consideration. A product which otherwise costs around Rs.50/tonnes finally costs Rs. 260/tonnes to the farmers without subsidy. Several measures need to be taken to bring down the ultimate price. The escalation in the basic price is a result of two elements - namely freight and packing. In case the farmers accept loose supply of phosphogypsum, it would help a lot to cut down the ultimate price because packing in HDPE bags shoots up the price considerably. The government may also consider to change the classification of phosphogypsum/mineral gypsum for rail freight purposes which would also help in reducing the delivered price of the amendment. Since phosphogypsum is used in bulk at the rate of 10 tonnes/ha or more, it becomes difficult for the farmers to lift large quantities of the material from the place of availability to the place of use. To ensure adoption of the technology of sodic soil reclamation by a willing farmer in India, it is essential that soil amendments like phosphogypsum are made available within carting distance.

SUMMARY

Phosphogypsum, a by-product of the phosphate fertilizer industry which produces several million tonnes annually, presents a challenge for its disposal. Apart from its other usages, it may also be used for reclamation of sodic soils which are increasing every year. Alkali soils occur predominantly in Punjab, Haryana and U.P. in northern India. Although research and extension work on phosphogypsum were initiated in the seventies only, available data have convincingly shown that phosphogypsum may be safely used up to 32 tonnes/ha for the reclamation of sodic soils. Application of phosphogypsum for reclamation of sodic soils gave very encouraging results in a large number of demonstrations. It was possible to recover the total investment, i.e. cost of land development and cost of production in one year, by raising two crops. The increase in land value alone was a very significant gain which is usually overlooked. Although initial soil pH dropped by 0.4 to 1.2 units only, the crop yields were obtained almost at par with those from normal soils. 'Effect of phosphogypsum application on soil characteristics, crop yield and economics of soil reclamation have been also discussed.

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T A B L E - 1

ANALYSIS OF PHOSPHOGYPSUM (per cent)

Constituents	Conventional di-hydrate process	Nissan's hemihydrate process	Central Prayons hemihydrate process
CaO	33 to 44	32.5	33.2
SO_3	45 to 46	45.6	44.8
R_2O_3	0.2 to 0.3	0.05	0.3
SiO_2	3.5 to 4.0	0.45	0.5
F	1.5	0.7	0.5
P_2O_5	1.2	0.3	0.2 to 0.3

T A B L E - 2

YIELD OF RICE (VAR. PR-106) USING DIFFERENT SOIL AMENDMENTS AT DOUBLE G.R. VALUE (1979)

AMENDMENTS	QTY. APPLIED (tonnes/ha)	INITIAL SOIL pH (1:2)	YIELD(q/ha) GRAIN	STRAW
Phosphogypsum	32.0	9.9	49.0	70.8
Pyrites	25.0	9.9	42.0	73.5

T A B L E - 3

YIELD OF WHEAT (VAR. U.P.262) USING DIFFERENT SOIL AMENDMENTS AT DOUBLE G.R. VALUE (1979 - 80)

AMENDMENTS	QTY. APPLIED (tonnes/ha)	INITIAL SOIL pH (1:2)	YIELD (q/ha) GRAIN	STRAW
Phosphogypsum	32.0	9.9	33.9	37.3
Pyrites	25.0	9.9	18.5	25.3

TABLE - 4

DEMONSTRATION PROGRAMME ON RECLAMATION OF ALKALI SOILS

STATE	PUNJAB		HARYANA		UTTAR PRADESH	
Year	No. of demons-trations	No. of Dist. covered	No. of demons-trations	No.of Dist. covered	No. of demons-trations	No.of Dist. Cover-ed
1974-75	14	9	15	3	12	7
1975-76	16	8	13	7	11	7
1976-77	17	7	11	5	18	9

TABLE - 5

FIELD DEMONSTRATIONS ON RECLAMATION OF ALKALI SOILS (1974-75)

Cultivator's Name	State	District	Soil Characteristics before phospho-gypsum application		Grain Yield (q/ha)		Demonstrations conducted in collaboration with
			pH (1:2)	EC	Rice (HYV)	Wheat (HYV)	
Diwan Chand	Haryana	Karnal	9.9	4.60	34.08	38.90	Deptt. of Agri. Haryana
Kartar Singh	Haryana	Kurukshetra	10.1	1.46	34.58	not sown	-do-
Chaman Lal	Haryana	Karnal	10.4	1.75	35.57	19.80	CSSRI, Karnal
Rajender Singh	Punjab	Sangrur	10.3	3.80	65.78	37.79	PAU, Ludhiana
Teja Singh	Punjab	Sangrur	10.5	2.30	46.68	37.05	-do-
Amar Singh	Punjab	Patiala	10.6	1.20	37.68	38.53	-do-
Shriram Katiyar	Uttar Pradesh	Kanpur	10.0	---	52.85	61.75	CSA Univ. of Agri. & Tech., Kanpur.
Ram Chander	Uttar Pradesh	Kanpur	9.8	---	39.52	42.00	-do-
Jagdish Chand	Uttar Pradesh	Etah	9.5	1.06	29.64	19.70	Deptt. of Agri., U.P.

T A B L E - 6

GRAIN YIELDS IN RICE-WHEAT ROTATION UNDER RECLAMATION DEMONSTRATIONS IN HARYANA (1975 - 76)

Cultivator's name	Village	Block	District	Soil characteristics before rice		Grain Yield (q/ha)	
				pH (1:2)	EC	Rice	Wheat
Shri Ranbir Singh	Rajthal	Narnaud	Hissar	10.0	1.92	44.48	34.60
Shri Bir Singh	Madhuwala	Tohana	Hissar	9.5	1.92	not sown	29.60
Shri Subhash Chander	Lahli	Kalanaur	Rohtak	9.7	18.65	49.77	25.69
Shri Jagdish Dhawan	Siana Saidan	Thanesar	Kurukshetra	10.6	5.75	36.19	20.25
Shri Dwarika Das	Sandholi	Thanesar	Kurukshetra	10.4	2.40	56.69	21.61
Smt. Dalbeer Kaur	Bachgaon	Thanesar	-do-	10.2	1.78	45.92	23.71
Shri Ramanand Singhla	Sikanderpur	Panipat	Karnal	10.5	3.4	61.26	44.46
Shri Ram Prakash Chhabra	Punchhigujran	Ganaur	Sonepat	10.2	13.2	34.58	27.17
					Mean yield	46.98	28.38

A N N E X U R E

ECONOMICS OF SOIL RECLAMATION

		Rs/acre
Kharif - Rice IR-8		
1.	Land levelling by tractor (4 hrs @ Rs.25/hr.)	100.00
2.	Land preparation and bunding ploughing-3 and planking-1 (Ploughing @ Rs.20 and planking @ Rs.5 each) 5 labourers @ Rs.5 per day	105.00
3.	Gypsum application (phospho-gypsum 3.5 tonnes @ Rs.200/tonne)	700.00
	Application cost	18.80
4.	Impounding of water 7 irrigations for leaching salts)	70.00
5.	Nursery raising including cost of seeds, labour, fertilisers	44.80
6.	Transplanting and gap filling	70.00
7.	Fertilisers	
	CAN 100 kg.	102.20
	Urea 115 kg.	221.26
	Superphosphate 100 kg.	100.20
	Muriate of potash 25 kg.	27.50
	Zinc sulphate 20 kg.	25.00
	Application cost	7.80

		Rs./acre
8.	Plant protection	
	BHC 10 per cent - 18 kg.	18.00
	Ferrous sulphate 0.5 kg.	4.00
	Application cost	4.00
9.	Irrigation 12 (labour & electricity charges)	120.00
10.	Harvesting, threshing & winnowing	60.00
11.	Land revenue	5.00
12.	Rental value	25.00
13.	Interest @ 14 per cent for half of the period of 4 months	83.93
	Total	1,912.49
Rabi - Wheat K-227		
1.	Land preparation (ploughing-5 @ Rs.20)	100.00
2.	Seed & seeding	
	Seed	94.00
	Seeding	25.00
3.	Fertiliser application	
	107 kg. urea	205.87
	50 kg. Shakti Khad (T.S.P)	85.00
	10 kg. zinc sulphate	12.50
	15 kg. muriate of potash	18.00
	Application cost	8.00

		Rs./acre
4.	Irrigation-8 (labour & electricity charges)	80.00
5.	Hoeing-1, 4 labour @ Rs.6 per labour day	24.00
6.	Harvesting and threshing	117.50
7.	Rental value	100.00
8.	Interest @ 14 per cent for a period of 4 months on Rs.769.87	35.92
	Total	905.79

BALANCE SHEET

Investment :

1.	Land reclamation and development cost (item 1,2,3 & 4 in Kharif)	Rs.993.80/ac. or	2,454.68/ha
2.	Cost of production of rice	Rs.918.69/ac. or	2,269.16/ha
3.	Cost of production of wheat	Rs.905.79/ac.or	2,237.30/ha
	Total	Rs.2,818.28 or	6,961.14/ha

Returns :

1.	Kharif	(i)	Main product 18.0 q. @ Rs.71.25/q	1,282.50
		(ii)	Straw sold in bulk	25.00
2.	Rabi	(i)	Main product 14.0 q.@ Rs.105/q.	1,470.00
		(ii)	Straw-16 q. @ Rs.10/q.	160.00
			Total	2,937.50/ac
			or	7,255.61/ha
	Net return for the first year of rice-wheat rotation			294.47/ha

Uses of Phosphogypsum in Civil Engineering

UPGRADING OF PHOSPHOGYPSUM FOR THE CONSTRUCTION INDUSTRY

by

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INTRODUCTION

Huge quantities of waste gypsum (phosphogypsums) arise from the production of phosphoric acid. By 1981/82 approximately 110 million tonnes are to be expected all over the world.

Processing plants for phosphogypsum in the field of building materials and cement retarder are currently in operation or under construction, as far as we are informed, in Germany, the Soviet Union, Senegal, Brazil, Belgium, Philippines, France, Korea and Japan.

The development activities towards processing of phosphogypsum for the production of building materials and as an additive for the cement industry originated essentially in Japan, where there are only scarce quantities of usable natural gypsum available. Accordingly, the development of phosphogypsum processing technologies was started in Japan as early as in 1953-1955.

The Development of the ONODA Technique. When the Japanese company ONODA Cement started its phosphoric acid production in 1955, it also took up activities for the development of a suitable phosphogypsum utilization. This development work aimed at finding an economic method of manufacturing end products that stand comparison with natural gypsum relative to their quality characteristics. This method should be independent of the respective origin of rock phosphate and of the phosphoric acid process used. Only three years later, these activities led to the construction of an industrial-scale plant with a capacity of 300 tpd of cement retarder.

The first industrial-scale plant for the processing of phosphogypsum into building materials was constructed in 1960. This plant had a capacity of 200 tpd and produced gypsum plasterboards and building plaster as end products.

As a result of the ONODA process, approximately 1,500,000 tpa of cement retarder and approximately 400,000 tpa of gypsum building materials are now produced all over the world.

In the following, the most important fields of phosphogypsum application mentioned above will be dealt with in detail, and the essential problems will be briefly described.

Cement Retarder. It is generally known that 3% to 5% of gypsum is added to the cement clinker as this is ground. Apart from a few exceptional cases, untreated phosphogypsum direct from the phosphoric acid filter cannot be used since existing impurities such as phosphates, fluorides and organic constituents affect the cement quality. In the first instance, they have a very negative effect on the setting behavior of the cement (extension of the setting time); this happens almost independent of the various cement strength values, as long as untreated phosphogypsum is used. Furthermore, the fine-grained phosphogypsum contains between approximately 20% and 30% water which makes handling extremely difficult during transport, storage and proportioning in the cement clinker mills.

Production of Building Materials. The processing of phosphogypsum by calcination into building materials containing gypsum constitutes is, no doubt, a successful type of utilization of this waste product. The most important positive characteristics of phosphogypsum are its high content of dihydrate (frequently up to 96%) and the given fineness of the material. It should be especially noted that the cost of crushing and grinding the natural gypsum currently amounts to approximately DM 5 per tonne of gypsum. It should be mentioned, however, that the impurities inherent in the phosphogypsum can affect the quality of a building material containing gypsum, even if their proportions are very low.

Particularly the various phosphates, fluorides, organic constituents, aluminum compounds and soluble salts affect the gypsum quality - mainly in respect of setting behavior of the calcined phosphogypsum, strength characteristics of the products manufactured from calcined phosphogypsum, and efflorescence phenomena in building materials containing gypsum.

A purely chemical analysis of the impurities can provide some useful information about possible applications of the phosphogypsum. This information, however, is not sufficient for a comprehensive assessment, as these impurities are partly tolerable in respect of their chemical composition and the intended use of the calcined phosphogypsum.

ONODA Technology for Cement Retarder Production. This technology, which is the result of development activities that were started in 1955, and which has been put into practice in the processing plants that are being operated, is based on the principle of converting all noxious impurities to an inactive form. Thus, the impurities are rendered harmless if the phosphogypsum is used for the production of cement retarder. For this purpose, calcareous additives are added to the phosphogypsum during and/or after its calcination. The calcined phosphogypsum is then passed through a granulation stage and processed into an end product that is suitable to be stored and transported. The technology does not require any washing stage prior to the calcination. The process as a whole comprises four main sections that are as follows:

Section 100: Phosphogypsum Preparation. In this section the phosphogypsum is mixed with a calcareous additive and, if necessary, with ready calcined phosphogypsum. Quantity and type of the calcareous additive are governed by the degree of contamination and free moisture of the particular phosphogypsum to be processed.

The question whether or not it is necessary to recycle ready calcined phosphogypsum is also dependent on the degree of free moisture. In Section 100, the phosphogypsum is to be prepared in anoptimum way so as to ensure that calcination can be carried out at reasonable costs and that the end products have the desired physical properties.

Section 200: Calcination. In Section 200, calcination is carried out in a flash calciner that works almost without any rotating or moving components. This flash calciner is comparable to a specially designed tube; its most important component parts are the phosphogypsum feeding device and the mixing chamber where the phosphogypsum is mixed with hot

gas. The selection of a flash calciner is based on its essential advantages that are as follows:

- compact design
- simple operation and monitoring
- low investment
- low maintenance requirement
- uniform-calcination conditions

The calcination conditions in the flash calciner can be varied according to the phosphogypsum qualities used (crystal sizes, impurities); thus, it is possible to obtain phosphogypsum of optimum quality for subsequent granulation.

Section 300: Granulation. In Section 300, the calcined phosphogypsum is granulated in a pan-type granulator, with water being added; this granulation is carried out in order to obtain suitable storage and transportation properties that are desired by the cement industry.

Variable granulation conditions make it possible to produce uniform granulates, and the necessary granulate strength values are adjustable via the reaction conditions in the granulation and the duration of the transport to the granulate store. According to the gypsum quality desired, the duration of transport can, for example, be varied between 10 and 20 minutes.

Section 400: Waste Gas Purification. Electrostatic filters are preferably used for waste gas purification. The type of filter is characterized by its high degree of dedusting, low power consumption and service requirements even under most unfavorable conditions. The gypsum dust removed by the filter is recycled.

Consumption Figures. In the following, some typical consumption figures and product qualities will be given, using a Korean production plant with a capacity of 500,000 tonnes of cement retarder per year as an example.

Consumption Figures

Phosphogypsum	:	868 kg (dry)
Lime	:	20 kg
Bunker fuel oil C	:	32 kg
Electric power	:	12 kWh
Process water	:	0.3 t

All values refer to one tonne of end product, free moisture 15%.

Operating Personnel : 4 per shift

Product Quality

Granulate size	:	90% between 5 mm and 20 mm
Moisture	:	10% - 15%
SO_3 content	:	42%

ONODA Technology for Building Material Production. The technology, which is the result of development activities started in 1955. and which has been worked out using the experience gained in practical operations, is based on the principle of converting noxious impurities to an inactive form and/or separating noxious impurities.

Both processing steps are carried out during and/or prior to the calcination. They are governed by the specific phosphogypsum properties and the required end product qualities.

The technology for production of building materials comprises two main sections that are as follows:

Section 100: Phosphogypsum Preparation. Impurities contained in the phosphogypsum are rendered harmless in Section 100 by adding additives. These impurities are incorporated in the crystal lattice of the calcium sulfate dihydrate in a co-crystalline form. According to the degree of contamination, the cost of the additives varies between DM 1.50 and DM 2.00 per tonne of dry phosphogypsum.

Raw phosphate particles and silicates (e.g. sand) that have not. been disintegrated are removed by wet screening. Water soluble surface-bound impurities are eliminated by washing operations.

According to experience gained in actual processing plants, a large proportion of the existing phosphogypsum impurities is concentrated in the particle size fraction below 30 microns. In Section 100 this proportion of particle sizes is therefore removed by means of separators. The phosphogypsum slurry thereby obtained which has a concentration of 500' to 700 g/l is dewatered by means of water separators until reaching a free moisture between 10% and 15%.

Remarks on Section 100. Concerning the basic operations described in Section 100, the specific type of treatment to be applied - if this is necessary at all - is dependent on the phosphogypsum quality and the particular requirements to be met by the end product.

Section 200: Calcination. The type of processing unit to be applied for calcination is essentially governed by the desired end product qualities. For economic reasons, a flash dryer is mostly used to dry the humid phosphogypsum, with the subsequent calcination being carried out in a kettle-type calciner. Alternatively, there are also calcining systems in which both drying and calcination are effected in a single unit such as a flash calciner or a rotary kiln.

In the following, some typical consumption figures and product qualities will be illustrated by the example of a production plant operating in the Republic of Korea, with a capacity of 250 tonnes of calcined phosphogypsum per day.

In this Korean plant, phosphogypsum resulting from Florida raw phosphate (Prayon dihydrate phosphoric acid process) is processed into building materials. A rotary kiln is used for calcination, with the entering phosphogypsum being taken direct from pond storage without any

pretreatment. Currently, gypsum partition blocks and gypsum plaster similar to DIN 1168 are manufactured as end products.

Consumption Figures

Additives	:	1.3Ø DM
Bunker C fuel oil	:	4Ø l
Electric power	:	28 kWh

All values refer to one tonne of calcined phosphogypsum, in unbagged condition.

Operating Personnel : 4 per shift

Product Quality (as per DIN 1168)

Gauging quantity	:	14Ø g
Initial setting	:	4 - 5 minutes
End of setting	:	8 - 1Ø minutes
Compressive strength	:	13.5 N/mm^2
Bending strength	:	4.9 N/mm^2
Combined water	:	6.6%
Blain value	:	4,ØØØ - 5,ØØØ cm^2/g

Gypsum Partition Blocks. One interesting market for the application of refined phosphogypsum is the production of gypsum partition blocks. Partition blocks made of plaster in accordance with DIN 18.163 are prefabricated building elements for light-weight, non load-bearing walls.

For many reasons, gypsum blocks are used more and more. They permit construction to be carried out quickly, with less manpower and at low cost; they meet demand for a building method that is as dry as possible; and they come up to the requirement of air humidity control, acoustics, fire protection, etc.

Production System. It can be proved that 99% of all gypsum block manufacturing plants in the industrialized countries are operating in accordance with the "push-out system with rigid chambers of highest precision and optimal surface quality."

The moulding chambers producing blocks with a tolerance of ± Ø.Ø2 mm give a product that always has the same precision. This applies to all dimensions of the gypsum blocks which are important for their erection.

The moulding chamber parts, consisting of solid welded steel or stainless steel, are rectified, highly polished with a mirror finish, and fitted with a layer of hard chromium of 1ØØ my. If an abrasive chemical gypsum (plaster) is used, the thickness of the layer of hard chromium is 16Ø my.

The moulds are supplied with different numbers of chambers (e.g. 8, 16, 24, 32); the operating cycle depends mainly on the setting behavior of the plaster used.

Below please find an example showing the production cycle:

- During the preceding cycle, the mixing water was already dosed into the mixer.
- Dosing of the plaster into the mixer begins at the moment Ø. Total dosing time Ø.5 minutes.
- Subsequently, the water and plaster are mixed for Ø.5 minutes.
- Emptying of the mixer takes Ø.3 minutes, i.e. the moulding machine will be filled after 1.3 minutes.
- After the moulding chambers have been filled, first of all the upper gypsum block tongues are shaped. During this time, the plaster in the moulding chambers will begin to set.
- Though the total setting time of the gypsum plaster may be 15 minutes, the blocks will be hard enough after a further six minutes to be pushed out of the moulding chambers in accordance with the push-out system. In other words, the blocks are already pushed out 7.3 minutes after the beginning of the production.
- Pushing out takes 1 minute. During this time, the blocks continue setting.
- After having been pushed out, the blocks will remain on the machine for about one minute. During this time, their setting goes on:
- Finally; the blocks are removed with the aid of a pneumatic spacing grab. At the same time, the next production cycle begins.

Some Characteristics and Advantages

Accuracy of manufacture ± Ø.Ø5 mm.
Plant, smooth surfaces.
Fitted with profiles (grooves and tongues) around the edges.
Handy size, 3 blocks = 1 sq. m according to DIN 18.163.
Excellent fire protection properties according to DIN 41Ø2.
Good insulation against airbourne sound.

Therefore:

Easy and simple erection using the bonding method.
No specialized personnel required.
One worker will put up 3Ø to 4Ø sq.m a day.
No plastering of wall necessary.
Immediately ready for papering or painting.
No humidity in the buildings.
Gypsum panels may be sawed, nailed, bored and milled.

Notwithstanding its many advantages, the gypsum block wall is by far the cheapest partition as compared to similar constructions of masonry, aerated concrete, sandlime bricks, gypsum plasterboard, etc. (based on German Conditions).

Processing plants for gypsum blocks using refined phosphogypsum are currently in operation or under construction in Europe, Africa and Asia. The total installed production capacity is approximately 10 million m^2/ year.

STABILIZATION OF CALCIUM SULFITE/SULFATE FOR STRUCTURAL USES

by

Louis Ruggiano and Dr. Eric Rau

INTRODUCTION

The disposal of waste calcium and sulfur compounds is a problem common to many industrial processes including the fertilizer industry. Until recently, this material was cursorily discarded without much consideration of the environmental consequences. The two largest sources of this waste are from an established industry -- the fertilizer industry and a new industry, the power generation industry, which has been required to control the SO_2 by-product from burning coal. IU Conversion Systems has pioneered in the safe environmental disposal and reuse of these utility wastes and believes that this approach can be applied to the phosphogypsum industry.

The Poz-O-Tec^R process developed by IU Conversion Systems, Inc. (IUCS), is a system of waste management by which hazardous materials are encapsulated in a pozzolanic matrix formed by the reaction of lime with fly ash. Retention within the matrix may be by chemical as well as physical forces. Chemically bound material is rendered insoluble by the formation of complex calcium silicate alumina compounds. Physically held materials are entrapped in the dense cementitious matrix which is virtually impermeable to water. Thus, the host matrix is able to retain a wide variety of wastes and prevent contact with solvents that might leach the toxics from the matrix.

Poaaolan Chemistry. By definition, pozzolans are materials which are not cementitious in themselves, but which contain constituents that will combine with lime at ordinary temperatures in the presence of water to form cementitious compounds. Natural pozzolans are usually materials of volcanic origin, but include some diatomaceous earths, and in the broadcast sense, soils. Artificial pozzolans are mainly products obtained by heating clay or shale. Today, the primary artificial pozzolan is fly ash, a residue from the combustion of pulverized coal at modern electric power plants.

When lime or lime-based additives are mixed with fly ash in the presence of water, a chemical reaction takes place producing materials whose properties are similar to the reaction products of Portland cement. The major cementitious reaction occurs between silica and lime with some alumina contributions. In addition, sulfur-bearing compounds can react with lime and alumina to form calcium sulfo-aluminohydrates. The chemical equations for these reactions are shown below:

$$SiO_2 + Al_2O_3 + Ca(OH)_2 \longrightarrow xCaO.yAl_2O_3.zSiO_2.wH_2O \quad (1)$$

$$Al_2O_3 + SO_3 + Ca(OH)_2 \longrightarrow xCaO.yAl_2O_3.aCaO.SO_3.wH_2O \quad (2)$$

The chemical reactions are complex. Initially, the fly ash surface is attacked by lime, creating a gel. This gel contains predominantly calcium, aluminum, and silica ions in solution, which combine to form insoluble hydrate complexes. Since the chemical reactions take place on the fly ash surface, the pozzolanic reactivity of the fly ash increases with greater surface area (i.e., smaller particle size).

The pozzolanic reactions described in (2) can be used to chemically fix SO scrubber sludges from electric utilities. These scrubber sludges contain $CaSO_3.\frac{1}{2}H_2O$ and/or $CaSO_4.2H_2O$ depending on scrubber conditions.

Other wastes which may contain hazardous components can be rendered innocuous by this same pozzolanic reaction. The liquid phase of the waste is utilized to form the hydration compounds that are cementitious in nature. The hydration reaction progressively seals off the pore structure in the resultant mass. Permeability is typically reduced to less than 5×10^{-6} cm/sec. Sulfur compounds may be chemically reacted to form insoluble compounds. Other solid wastes are physically entrapped in the rigid matrix which develops. The basic pH of the pozzolanic reaction renders most heavy metals insoluble.

The longevity of these reaction products has been amply demonstrated by structures (such as the Appian Way) built centuries ago during the Roman Empire.

Application to Flue Gas Desulfurization Systems. With the resurgence of coal as a fuel, it has become necessary for utilities to install and operate a growing number of flue gas desulfurization (FGD) systems for SO_2 removal. It is estimated that nearly 60,000 MW of FGD capacity will be installed by 1980.

Among the various FGD scrubber systems available, wet lime/limestone scrubbing and double alkali (indirect-lime/limestone) scrubbing have gained the widest acceptance. These scrubbing operations produce an enormous volume of low-solids-content sludge, which must be properly treated so that groundwater and surface water are not polluted by unacceptable concentrations of heavy metals and dissolved solids.

A solution to this massive sludge disposal problem is the chemical stabilization of scrubber sludge by the Poz-O-Tec process to prevent significant environmental damage and minimize land disposal requirements. The Poz-O-Tec system has received large-scale commercial acceptance on a wide variety of scrubbers. Twenty utilities have contracted to install it.

The Poz-O-Tec process is a complete waste-management system for coal-fired power plants. It blends fly ash, bottom ash (if desired), scrubber sludge, and lime. Concentrated streams from the evaporator and cooling tower sludge can also be incorporated. The stabilized material is a cementitious material and with proper placement and compaction, exhibits low permeability and superior structural properties.

Process Considerations. The fixation of power plant wastes involves more than just combining the wastes. Each of the waste materials contributes chemically and physically to the process. Variations in those materials must be considered in developing the specific process design.

Fly Ash. Fly ash is utilized in the Poz-O-Tec process for several reasons. It is a waste material which must be disposed of, and is usually available from the same plant as the sludge waste. It is a

fine-particle material and provides the alumina and silica which are necessary for the pozzolanic reactions to bind the sulfur compounds of the sludge.

The quantity of fly ash will also contribute to the final solids content of the product and affect its handling characteristics. Generally, ash-to-sludge ratios of 1:1 or higher will result in an immediately placeable material; those below that ratio will usually require interim stockpile conditioning prior to final placement.

Particle size of the ash also contributes to the process chemistry: the extremely fine particles have more surface area and therefore react faster.

Scrubber Sludge. The chemical composition of a sludge is one of the most important considerations in designing a stabilization system because it can vary greatly, even during standard power plant operation. All FGD sludges can be stabilized, but it is important to understand those characteristics of sludge which have the greatest potential effect on stabilization systems.

Sulfite/sulfate proportions primarily affect dewatering. The larger size of the sulfate particles affords easier dewatering. However, given the same ash to sludge ration, sulfate-based sludges require a numerically higher solids content of the final product to be equally handleable than do sulfite-based sludges.

The lime or limestone used in scrubbers also has an effect on process design. Poor quality reagent requires greater quantities in the scrubber to achieve the required SO_2 removal, and the high production of non-lime materials increases loads on the dewatering equipment. When in the form of grit , it causes extensive wear on piping and process equipment.

Process Additives. Most stabilization processes require that some additives be used to initiate chemical reactions. Althouqh this activator may already be present in some coal, such as lignite, it must be added separately in most cases.

For possolanic stabilization, the additive most used is lime, available as pebble lime (which requires crushing), pulverized quicklime, hydrate, or lime slurry. The important considerations for the lime are CaO and MgO content and particle size distribution.

Plant Design Considerations. Concurrent with the evaluation of process variables to achieve chemical stabilization, the physical processing systems for the plant must also be planned. A stabilization plant is a materials handling system in which liquids sludges, damp and dry solids are combined into a reactive mass.

Siting. The location of the stabilization facility will depend on land availability, location of the disposal area, and other physical and economic factors. Ideally, the landfill should be located near the power plant to minimize transportation costs for both waste materials

and the stabilized product. A 600-800 MW plant producing 1,000,000 tons per year of stabilized material will require about 60 hectares of disposal area 70m high, over a 20-year period.

Dewatering. Dewatering of the sludge is important in dry stabilization systems to produce higher final product solids. Most FGD systems, however, only thicken the sludge to 25-30% solids.

Dewatering in the stabilization facility is usually accomplished by vacuum filtration, although centrifuges have been used in some applications. Scrubber sludge can be vacuum-filtered at rates of 250-500 $kg/m^2/hr$. depending on the composition of the sludge, the filter medium, and filter aids. Sulfate sludges usually yield higher filtration rates and solids than do sulfites. Conversely, high concentrations of magnesium often result in lower filtration rates and solids. If these conditions are known at the time of design, the filtration equipment and operating parameters can be adjusted to maximize sludge dewatering.

A lime base sludge will usually dewater from 30% solids to 40-55% solids, and limestone-based sludge to 55-65% solids. Oxidized sludges are reported to achieve 80-85% solids, which when mixed with fly ash and additive, would result in a high-solids final product. This product may require water addition to achieve optimum placement density.

Materials Feeding. Feed systems for fly ash and lime involve more than just adding these materials to the sludge. For situations where there is limited ash available, controlled feed is important to conserve ash. This equipment must not only feed accurately but must control flooding.

As lime constitutes a small percentage of mix on a dry-weight basis and is the activator of the chemical stabilization reactions, accuracy of measurement and uniform dispersion of the lime in the product is absolutely necessary. Dispersion within the mix depends upon accuracy of feed, location of lime feed into the system, particle size and uniformity of mixing.

Mixing. Mixing is the combination of the waste and additives to permit adequate contact between fly ash, lime additives and sludge particles, so complete chemical action can take place. The mixer must be able to provide the required blending, even though the ratio of wet and dry materials may vary over any given period, and the mixer designed for 200 tons per hour (TPH) may only be operating at 100 TPH due to reduced station load. The specific combination of waste materials to be mixed at a facility must be evaluated for material ratios, solids content, particle size, retention time, type of additive, etc., to ascertain the proper mixing design.

Final Product Handling. The achievement of a structurally stable and environmentally compatible landfill requires a detailed materials handling and placing program, landfill preparation, and quality control procedures. In many respects, the disposal and placement procedures are as important to the overall stabilization system as the processing facility itself.

Once the processed sludge leaves the facility, it is usually placed in a surge pile. Normally, a drier final product will require less time in the surge pile prior to handling. For example, final product with solids in the range of 50-58% requires initial conditioning of several days before movement. Table I gives a range of final product solids and required conditioning times. (Please refer to Table I.)

Temperature can also affect the material cure, handling and placement operations. During winter months, with temperatures below 5°C, the chemical reactions in the material are slowed -- as in cement chemistry. As a result, greater curing times may be required for the material in the surge pile before placement in the landfill. The retarding effect of low ambient temperatures is offset by the exothermic reaction which takes place in the stockpile. These initial reactions, although slow, produce enough heat to raise the stockpile temperature, even at freezing ambience. Adequate storage capacity in the surge pile area must be included in system design for this requirement.

The processed material is then loaded into trucks for final placement in the landfill. In all instances, the stockpiled-contained material must be placed, graded and compacted at the final disposal site. The disposal sequence must be acknowledged in a timely manner to insure a monolithic stabilized product.

Material is usually placed in 30 to 60 cm lifts. The disposal site should be maintained so that a minimum surface area of fresh material is exposed to the elements. The working face should have a slight grade, so that any rainfall will tend to run off rather than collect in pockets. Should rainwater pockets occur, especially on fresh material, the material stabilization will be adversely affected, creating soft spots in the landfill.

In the landfill, the material can be placed to heights in excess of 70m. The landfill is developed in approximately 8m lifts and benched at the outer surface to provide haul roads and prevent erosion. Side slopes can be 2:1 horizontal to vertical, with 15m benches. The finished surfaces should have at least an 0.5m layer of topsoil and be revegetated to retard erosion.

At several of IUCS' installations, long-range plans call for material to be built into small mountains in excess of 70m in height, thus minimizing land area requirements.

The biggest potential environmental impact could be water runoff. For this reason, exposed surface area of freshly placed material should be kept to a minimum. Sedimentation ponds should collect the runoff discharge from the landfill area.

A good landfill operation will use monitoring wells to sample groundwater. These should be installed well in advance of the beginning of operations to obtain background data.

Environmental Considerations. The major objective of an FGD waste management program is to protect surface and subsurface water quality and resources.- This is achieved by minimizing leachate generation - potential, providing adequate runoff control measures and placing the processed material in a structural matrix. To protect surface and subsurface water quality, the landfills are designed to promote rapid surface runoff. The low permeability of the placed material (less than 5x $1Ø^{-6}$ cm/sec) contributes further to promoting runoff. All surface runoff is controlled through swales, paved ditches, piping and sedimentation basins. Discharges from the sedimentation basins are subject to National Pollution Discharge of Effluents Standard (NPDES) or state discharge criteria for pH, alkalinity, suspended solids, total dissolved solids, sulfates and sulfites. Table II presents the combined results of surface runoff quality monitoring at three disposal sites. IUCS also monitors the eight heavy metals specified in Resource Conservation and Recovery Act (RCRA). The monitoring program results show that no heavy metal contamination is expected from a stabilized FGD sludge surface runoff discharge (Table II).

The chemical characteristics of a waste material, the method of disposal, and the physical integrity of the in-place waste materials directly influence potential leachate quality. Values were obtained by the proposed American Society for Testing Materials (ASTM) Test Procedure, Leaching Test of Waste Material, Method A, a 48-hour shake test procedure.

Table III shows that leachate from an unstabilized fly ash, sulfate sludge, or sulfite sludge disposal site could be expected to exceed the EPA Interim Primary Drinking Water Standards for arsenic, cadmium, lead and selenium, and the recommended secondary standards for pH, total dissolved solids (TDS), sulfates (SO_4), copper, iron and zinc. The values for the same waste materials stabilized show that all of the primary drinking water standards would be met; however, the values of pH, TDS and SO4 would exceed the recommended secondary standards. Groundwater contamination is not seen as a problem since no leachate or permeate is expected. The combination of low permeability and positive diversion of runoff eliminates the potential for developing a hydraulic gradient which is necessary to saturate and force continuous flow.

The unconfined compressive strength of the stabilized FGD waste materials is a function of the filtercake solids, fly-ash-to-sludge ratio, in-place density, and additive content. For a given plant the above factors, with the exception of additive content, remain relatively constant on a month-to-month basis. The additive content may vary to compensate for the effect of adverse weather conditions, lowered ambient temperatures, and changes in waste material characteristics and ratios. Figure 1 shows the unconfined compressive strength of laboratory-cured samples versus in-place cured samples with typical fly-ash-to-sludge ratios and additive content (Figure 1).

Permeability of the landfilled material was also measured after several periods of time after placement. Figure 2 shows the slow pozzolanic reactions sealing the material with increasing time.

Resource Recovery. Since its conception, considerable effort has been expended to use Poz-O-Tec process material for more than landfill. Demonstration projects in which the material was used to build parking lot sub-base, pond liners, road sub-base, building aggregate and flood walls have been carried out. All of these projects have been successful.

In 1972, a parking lot sub-base for the Transpo '72 exhibition was constructed at Dulles Airport near Washington D.C. The calcium sulfate waste originated from hydrofluoric acid manufacture, acid mine drainage sludges, and FGD scrubber sludge. The placement was cored in this year and the material is still physically sound.

In 1974, an evaporative pond was constructed at Arizona Public Service. The liner strength was in excess of 750 psi and the coefficient of permeability was less than $5x\ 10^{-6}$ cm/sec.

In 1975, scrubber sludge from Southern California Edison was used for landfill, casino parking lot sub-base, and residential driveways. All are still in service.

In 1977, an 800 foot section of Pennsylvania State Road was replaced with a Poz-O-Tec sub-base with an asphalt surface. The road is subject to severe wear by trucks from Duquesne Light Company hauling bottom ash. Recent tests of the road indicate that it is holding up extremely well. Test borings were made in 1978 and again in 1980. Results indicate that all structural properties have been retained and in fact the strength is increasing. This performance is not surprising considering that similar material was used for road construction in Roman times and is still in use.

Artificial reef materials can also be produced from Poz-O-Tec process material. Since this application will be more fully described in a separate report to this conference, no details will be presented here. Suffice it to say that 500 tons of Poz-O-Tec based blocks have been produced and placed at sea. The material is environmentally stable and compatible with ocean ecology, a statement that could not be made about direct discharge of the waste to the ocean.

Another demonstration project is being constructed this month by the Corps of Engineers. A flood wall is being constructed near Louisville Gas and Electric's Can Run #6 Station. Processed material from this plant was used to construct a 25 feet wide and 200 feet long access ramp. Successful completion of this project will lead to further use in flood wall construction.

CONCLUSIONS

Pozzolanic stabilization is becoming a major process for the disposal of undesirable waste materials. Among the oldest of stone-forming reactions, the known longevity of the reaction products is adequately demonstrated.

The largest volume application today is the stabilization of SO_2 scrubber sludge and fly ash. Some 18 million tons per year capacity has now been built or contracted with continued growth expected. In this system, sludge, fly ash and lime are combined to form a strong, impermeable landfill material. Since the reaction depends on the chemical and physical properties of the reactants, careful characterization of these is necessary. Plant design must reflect these characteristics, or difficulties in operation will be met. Data obtained from the landfill corroborates design predictions from the laboratory. The results indicate that water discharge criteria for pH, alkalinity, and suspended solids are being met. Monitoring shows no contamination can be expected from the eight heavy metals considered hazardous.

The stabilized material has also been used to provide base for roads, parking lots, runways and dams. These applications have been successful. Increasing application is expected as more stabilized material becomes available across the country.

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REFERENCE

(I) Geotechnical Evaluation of Stabilized FGD Sludge Disposal by L.M. Ruggiano and E.S. Poulson. Presented at the Second Conference on Air Quality Management in the Electric Power Industry, Austin, Texas, January 198Ø.

TABLE I: Time required for stockpiling a various processed material solid content.

Solids Range (%)	Stockpile Conditioning (days)
50-58	4+
58-63	3-4
63-70	1-3
70-80	0-1

TABLE II

SURFACE RUNOFF QUALITY[1]

	Stabilized FGD Sludge	Discharge Criteria	EPA IPDWS
pH	6.5 - 10	6 - 10	N/A
Alkalinity	7 - 350	0	N/A
Suspended Solids	.01 - 10	30	N/A
TDS	900 - 3400	N/A	N/A
Sulfate	500 - 2200	N/A	N/A
Sulfite	2 - 25	N/A	N/A
Arsenic	.02	--	.05
Barium	.2	--	1.0
Cadmium	.01	--	.01
Chromium	.05	--	.05
Lead	.05	--	.05
Mercury	.001	--	.002
Selenium	.01	--	.01
Silver	.05	--	.05

*EPA Interim Primary Drinking Water Standards, effective October 15, 1979.

[1]All values in mg/l except pH.

TABLE III

LEACHATE ANALYSIS[1]

	Fly Ash	Sulfate Sludge	Sulfite Sludge	Stabilized FGD Sludge	EPA IPDWS	EPA RSDWS
pH	4-6	6-8.5	10-12.5	9.5-11.5	-	6.5-8.5
TDS	4,000-6,000	16-20,000	16-18,000	700-1,800	-	500
SO_4	800-1,200	7-10,000	7,000-9,000	300-850	-	250
Arsenic	.01-.20	<.02	<.02	.003-.02	.05	-
Barium	<.50	<.5	<.50	< .50	1.0	-
Cadmium	<.01	<.01	.01-.08	.002- <.01	.01	-
Chloride	30-40	-	500-1,000	60-120	-	250
Chromium	<.05	<.05	<.05	< .05	.05	-
Copper	2-6	-	< 1.0	.1-.5	-	1.0
Fluoride	-	-	-	< 1.0	1.4-2.4	-
Iron	80-150	-	<.2	< .20	-	.30
Lead	.2-.5	<.10	<.25	< .05	.05	-
Manganese	-	-	<.10	< .05	-	.05
Mercury	<.002	<.001	<.002	<.001	.002	-
Nitrate	-	-	-	< .50	10.0	-
Selenium	<.06	< .06	< .06	< .01	.01	-
Silver	<.05	< .05	< .05	< .05	.05	-
Zinc	7-9	-	< .10	< .10	-	5.0

[1]All values in mg/l except pH.

FIGURE 1
PERMEABILITY VS. TIME
LANDFILLED STABILIZED FGD SLUDGE
1.3:1 FLYASH TO SLUDGE RATIO
DUQUESNE LIGHT COMPANY LANDFILLS

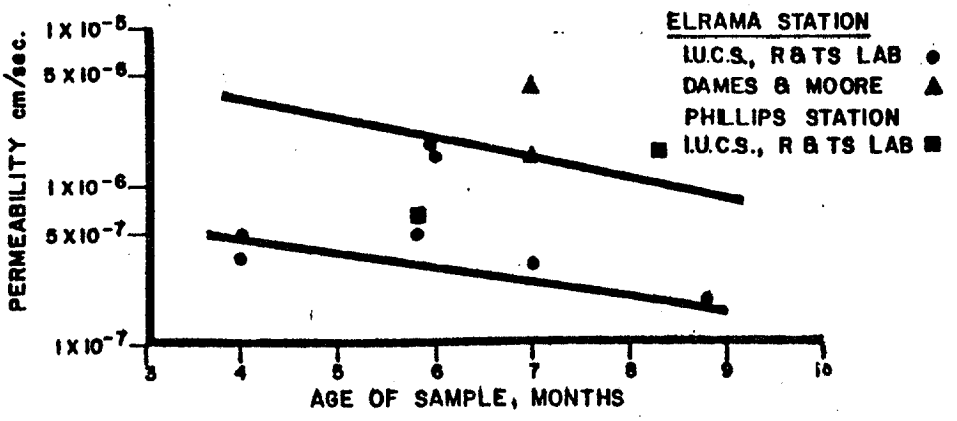
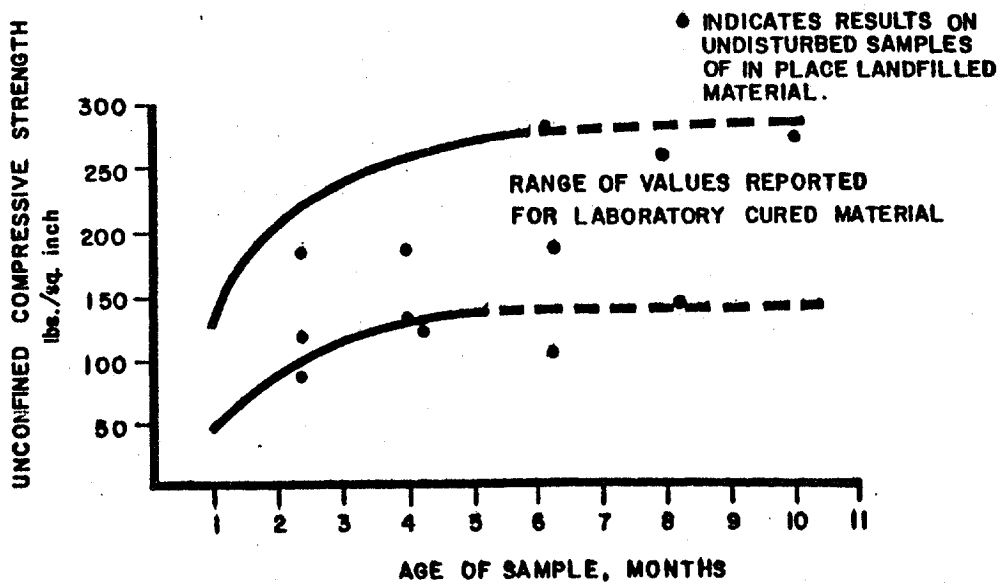


FIGURE 2
UNCONFINED COMPRESSIVE STRENGTH VS. TIME
1.3:1 FLYASH TO SLUDGE RATIO
DUQUESNE, ELRAMA STATION LANDFILL



USE AND VALORIZATION OF PHOSPHOGYPSUM IN ROAD CONSTRUCTION AND CIVIL ENGINEERING

by

E. Prandi
Setec Geotechnique

INTRODUCTION

Roadways realized in France since a score of years show in their structure more and more aggregates treated with a bituminous or a hydraulic binder.

This evolution which concerns all the courses of the roadway - subbase, base and wearing-courses - has been little by little imposed by the necessity of realizing sufficiently strong structures in acceptable economical conditions in spite of the high weight of the legal axle (13 metric tons) and the intensity of the high traffic. Therefore, the range of hydraulic binders initially limited to cement, has been extended to a set of slow-setting binders, particularly interesting for road applications.

The binders are generally constituted with a hydraulic or pouzzolanic material; their hydraulic setting is freed thanks to a catalyser, almost always a basic one. Among these new slow-setting hydraulic binders, granulated slag, flying ashes of thermic station, genuine pouzzolanes and some basic stones can be named.

The setting of the granulated slag was obtained until the commercialization of GYPSONAT with the help of fat, quick or slaked lime - 1% generally of the dry weight of the mixings. (1)

GYPSONAT is a catalyzer of the setting of the granulated slags much more efficient than lime. In effect, several varieties of GYPSONAT are now available, the last one is more especially destined to the flying ashes.

1. GYPSONAT (French patent n° 7.222.978 and followings registered by SETEC GEOTECHNIQUE)

The net catalyzer is a combination of phosphogypsum (or gypsum) and of a strong base like soda or lime. The percentage and the kind of strong base may differ with the materials to be treated or with the conditions on the site. In its most frequently used form the percentage in soda is of 7% for 93% of dry phosphogypsum.

The making from phosphogypsum includes:

(a) a physical and chemical purification of the phosphogypsum with elimination of the big impurities of the organic materials contained in the foam, and of the traces of strong acids. The pH of the phosphogypsum increases during these operations from 3 to 7 on average.

(b) a drying of the phosphogypsum, destined to expel the free water and some of the water of constitution (without reaching the percentage of water of the semi-hydrate.

(c) a pulverization of the solution of soda

(d) a sufficiently long storage (some days) during which the water cools and the water brought by the solution of soda combines itself again with the overdried phosphogypsum to give the dihydrate form again. During this operation GYPSONAT agglomerates and it is necessary to put it in an uncloding machine before delivering it to the clients.

GYPSONAT then looks like a cream white powder; its "passing" at 5Ø mm sieve is of 5Ø% on average. Its amount of water is near zero. In another type of GYPSONAT used at the back-end when the weather is cooler, or for some siliceous silts more difficult to treat, the total alkalinity is higher - about 13%. The risks of cloding have been completely suppressed by a mixing of powders; dried phosphogypsum (or gypsum), sodium sulfate and lime.

2. Properties of the New Catalyzer. The new catalyzer allows a great increase in the mechanical strengths of the mixings and their limit deformability at the breaking-point. The improvement of the mechanical properties due to GYPSONAT can 'be explained with the analysis of the hydrates which appear at the time of the setting of the granulated slag.

2.1 Catalyzing of the Granulated Slag. Granulated slag is a glassy material obtained by the brutal cooling of the melting slag. It is principally constituted with lime (4Ø-45%) silica (32-36%) and alumina (11-17%).

Granulated slag, stable in usual conditions and particularly in an acid atmosphere (carbonic dioxide) shows a hydraulic setting when in an aqueous solution with a pH greater than 11.5.

Lime and GYPSONAT give to the aqueous phase a pH sufficient to render soluble the alumina, the lime and the silica of the slag. (2)

When lime is the catalyzer, there appear principally:

(a) hydrated tetracalcic aluminate (C_4 AH_{13}); its crystals are lamellar and hexagonal; and

(b) hydrated calcium silicate (CSH) is a jelly which constitutes a filling up material.

When GYPSONAT is the catalyzer, there appear principally:

(a) ettringite or calcium trisulfo aluminate with 32 molecules of water (C_3 A S_3 H_{32}) ; its crystals are constituted with numerous very thin needles turned in all directions; and

(b) hydrated silicate of calcium as a jelly.

For the same quantity of catalyzer, lime or GYPSONAT, there appear a greater quantity of hydrates - about twice as much - when GYPSONAT is used. Mechanical strengths depend on the formed quantity of hydrates and will thus be higher, whatever the time of conservation of the test tubes is, with this latter catalyzer.

The needles of ettringite for a given mass of hydrates, are much more numerous than the hexagonal plaquettes of tetra calcic aluminate which are coarser and more directed. They give them to the material a greater deformability; ettringite, if it is too numerous, can provoke swellings in the material and destroy the binding effect brought by the granulated slag. Alumina comes essentially from the slag, calcium sulfate from GYPSONAT.

The risks of swelling will therefore be avoided if the percentages in slag and in GYPSONAT are limited.

2.2 Technical Properties

2.2.1 Comparison with Lime. Slag sands and slag gravels classically used for more than 20 years are being catalyzed with 1% of lime. The replacing of lime with GYPSONAT at the same percentage gives strengths about thrice as high as those obtained before. The increase in strength is about the same, no matter the age of the test tube at the time of the test.

The compared evolution of compressive strength is given in Chart 1 for a slag-sand mixed with sea fine sand and a slag-gravel 0/14 mm. The percentage of catalyzer is of 1% for both materials.

All kinds of strength are concerned with the increase in values: compressive strength, direct tensile strength, bending strength or fatigue.

The effect of GYPSONAT is particularly obvious for the values in bending as shown on Chart 2, strength of this slag-gravel 0/25 mm increases from 0.6 MP a with lime to 1.8 MP a with GYPSONAT after one billion loading cycles. The deformation modulus and the limit deformability before breaking are higher with GYPSONAT. The increase of the deformation modulus is of .50% with slag-gravels and .100% with slag-sands.

The evolution of the modulus is classical - modulus increases when strength increases. The increase of the deformability is less usual - it is more than 75%. It can be explained by the development of the needles of ettringite; their global direction is much more isotrope than that obtained with lime. We showed in a theory of the fatigue of slag-gravels and slag-sands that a higher isotropy of the material involved a higher deformability. (3)

2.2.2 General Results. Mechanical properties depend on granulometry and on the nature of the materials to be treated. They vary with the percentage and the reactivity of the granulated slag. All the currently used materials can nevertheless be sorted in three great families: fine or very fine sands with recent enlarging to silts, middle or coarse sands, and gravels. Table 3 summarizes the amounts of slag usually used and the results attained with 1% of GYPSONAT.

2.3 GYPSONAT Optimal Percentage. For a given age of conservation the highest strength is obtained for a quantity of GYPSONAT between Ø.8% and 2%. The optimal percentage decreases when the term of conservation increases: 2% at seven days, Ø.8 at one year.

The design structure of the works is generally determined with regard to the results of the long run. A percentage near to 1% will therefore be chosen and will give optimal characteristics.

2.4 New Catalyzer Practical Consequences. The increase of the mechanical properties brought by GYPSONAT allows a real saving of the cost of the works. This saving has multiple causes:

(a) Utilization of a wider range of aggregates, with particularly a very great valorization of all kind of sands, generally more economical than usual aggregates. The savings is besides double - concerning the costs themselves, the sands are less expensive when leaving the deposit and the distances of transport are often shorter. Concerning the energy, their content is lower (no crushing, no sieving, less transport).

(b) Reduction of the amount of granulated slag more expensive than the base sand or possibility to use less reactive slags which are more abundantly produced.

(c) Use of the new slag sands or slag gravels instead of dearer materials such as bitumen gravels in roadways or hydraulic concrete for the foundations of buildings or works.

(d) Reduction of the thickness of the structures of roadways or of storage areas being possible thanks to the increase of the mechanical properties and especially of the couple deformation modulus and limit deformation.

3. Applications

3.1 Slag Sands and Slag Gravels. Essentially used for roads at the beginning, slag-sands and slag-gravels are still used in the building of new roadways or for the overlaying of existing roads. Used only for the subbase course firstly, slag-sands now catalyzed with GYPSONAT are more and more used for the base course. Thanks to their better compactability, the subbase and base courses are often joined in a sole course; the mechanical behavior of this last one being superior to that of two separate courses.

The greater deformability of the slag-sands allows a reduction of the thickness of the wearing course in bituminous concrete and thus a saving of petrol products.

Thanks to GYPSONAT, slag-sands are more and more used to realize heavily loaded storage areas such as storage areas of harbours destined for containers.

They are used to replace industrial pavings of reinforced concrete or foundations on piles and beams. The general raft of slag-sand can be set even on very bad soils. It ensures, when its thickness is sufficient, a very great repartition of the concentrated weights brought by the work. It eases the building in the case of a foundation on piles and beams and lowers the delays of realization. Lastly, the general raft occasionally completed with a thin covering provides at the same time the paving.

Applications in this field are already very diversified - foundation-paving of detached houses, building of offices, swimming pools, sewage station tanks, dry dock, railway buildings. Slag-sands have also been used to realize quay walls. The formula of this type of slag-sand must take into account the means of densification which is essentially done with a high frequency vibrating probe.

The framing ensuring the geometry is generally blended with the final work; it thus ensures the superficial protection during the hardening of the slag-sand. Other types of wall without a lasting framing have been realized to serve as the main wall of detached houses.

3.2 Light Concrete. GYPSONAT is used in the making of light concrete, strong and thermically insulating. In this type of concrete constituted with expansed aggregates, clay or shale, all the sand is replaced with granulated slag with forms with GYPSONAT, a hydraulic binder. It is then possible to greatly lower the percentage of cement without reducing noticeably the mechanical strengths: amounts of 150 kg of cement per m^3 of concrete are sufficient to obtain compressive strengths of 20 MPa at 20 height days of conservation. The density of this light concrete goes from 1.25 T/m^3 to 1.35 T/m^3. The calorific transmission coefficient is 0.25 W/°/m.

Light concrete is a component of insulation from the outside panels for existing buildings. These panels, made of a slab of light concrete as a face and of an insulation slab such as expansed polystyrene or similar, are being fastened at the level of the stories. Their weight is 50 kg per m^2 and they divide by three or four the waste thermic coefficient of the existing wall.

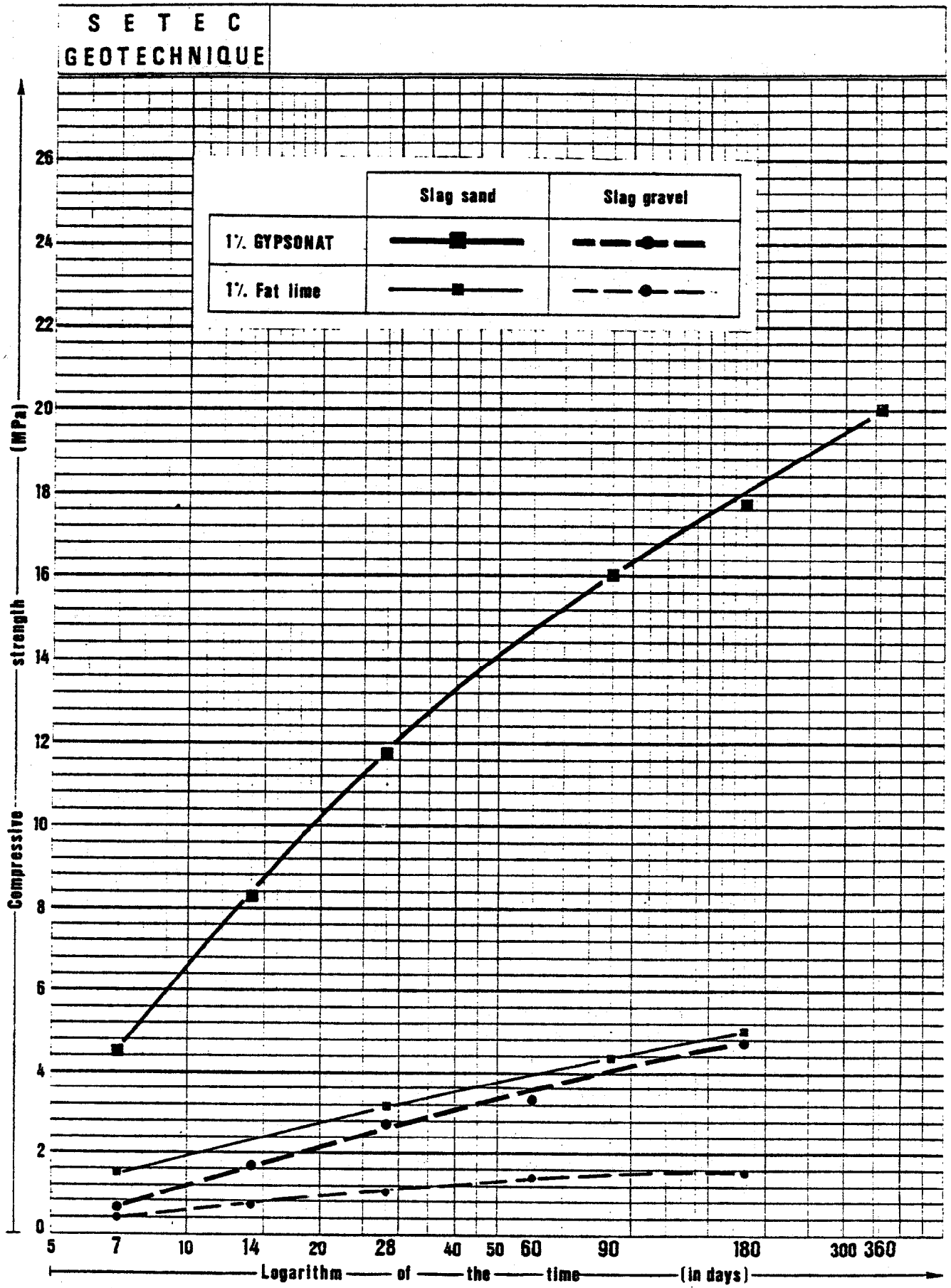
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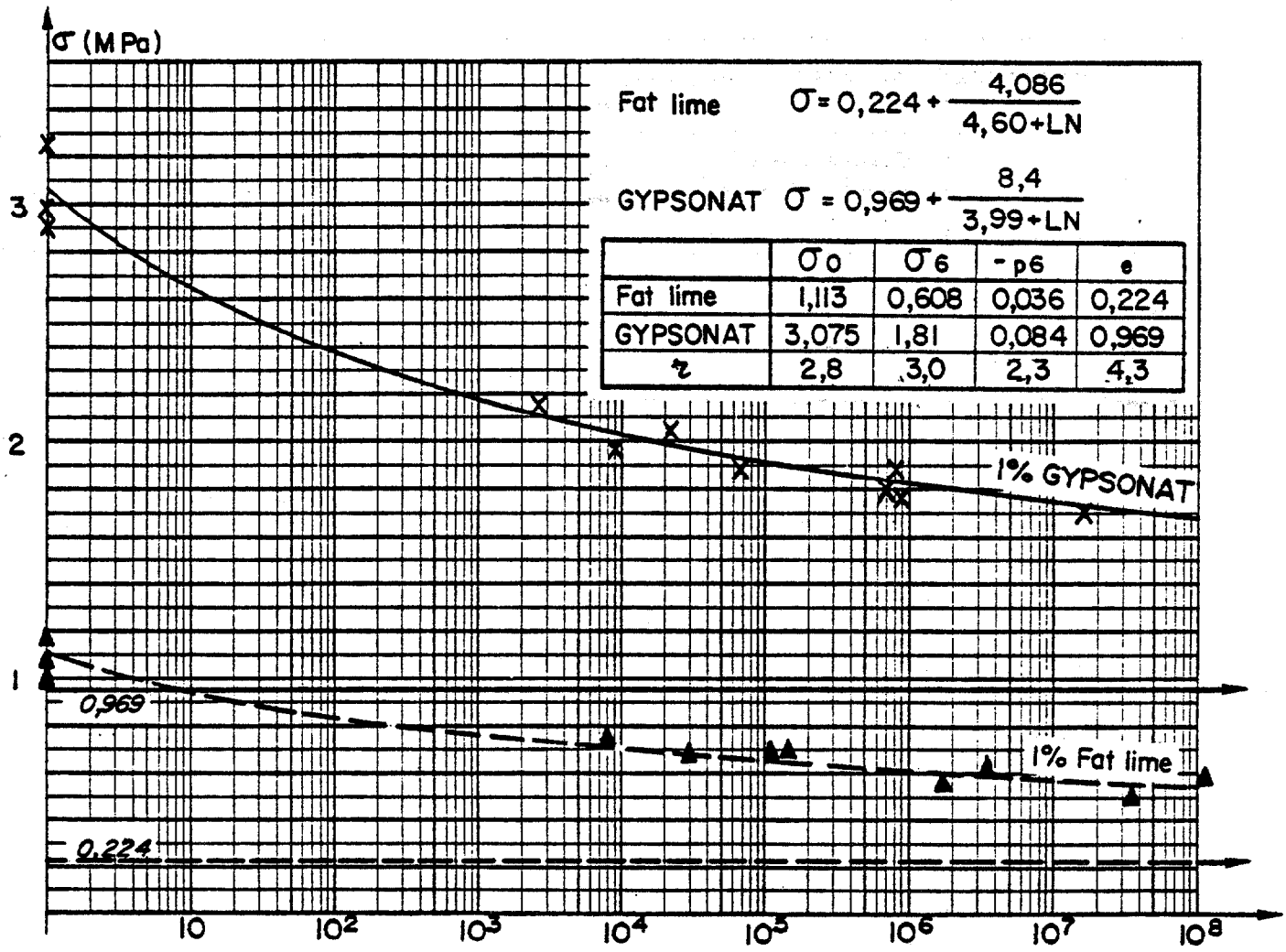
(2) VOINOVITCH, DRON "Action des differents activants sur l'hydratation du laitier granule" - Bulletin Liaison, Laboratoires Ponts et Chaussees -'Volume 83 - Mai-Juin 1976 - pp. 55-58.

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CHART 1


S E T E C
GEOTECHNIQUE
Slag sand
Slag gravel
1% GYPSONAT
1% Fat lime
Compressive strength (MPa)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
5
7
10
14
20
28
40
50
60
90
180
300
360
Logarithm of the time (in days)

S E T E C GEOTECHNIQUE		



	σ_0	σ_6	$-p_6$	e
Fat lime	1,113	0,608	0,036	0,224
GYPSONAT	3,075	1,81	0,084	0,969
τ	2,8	3,0	2,3	4,3

TABLE 3

MECHANICAL PROPRIETIES OF THE SLAG-SANDS AND SLAG-GRAVELS CATALYSED WITH 1 % OF GYPSONAT					
MATERIAL	Percentage of granulated slag (%)	STRENGTH		Deformation modulus (MPa)	Limit deformability 10^{-6}
		compressive	bending		
Fine sand	12 - 20	4 - 6	0,8-1,6	5.000- 8.000	150 - 200
Coarse sand	10 - 15	8 - 12	1,2-2,4	10.000-18.000	100 - 150
Gravel	8 - 12	10 - 20	2,0-3,0	20.000-30.000	75 - 100

DEVELOPMENTS PERFORMED BY A.P.C. - CdF CHIMIE IN THE FIELD OF PHOSPHOGYPSUM (CELLULAR GYPSUM, PAPER FILLER)

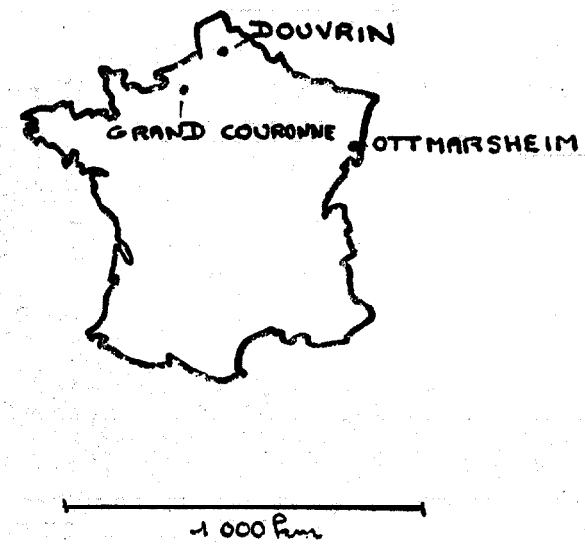
by

Dr. Philippe Pichat
Dr. Robert Sinn

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Place des Reflets
92080 Paris-Defense 2
Cedex 5, France

A.P.C.* manufactures phosphoric acid in Douvrin, Ottmarsheim and Grand Couronne. At each of these plants the phosphogypsum situation is very different. To face these situations, the Board of Directors of CdF CHIMIE sets up a Task Force** dedicated to phosphogypsum.

I will describe the situation at first in terms of operations, then in terms of R-D.



. ../2..

* At the end of 1977 the A.P.C fertilizer and nitrogen division of CdF CHIMIE was set up.

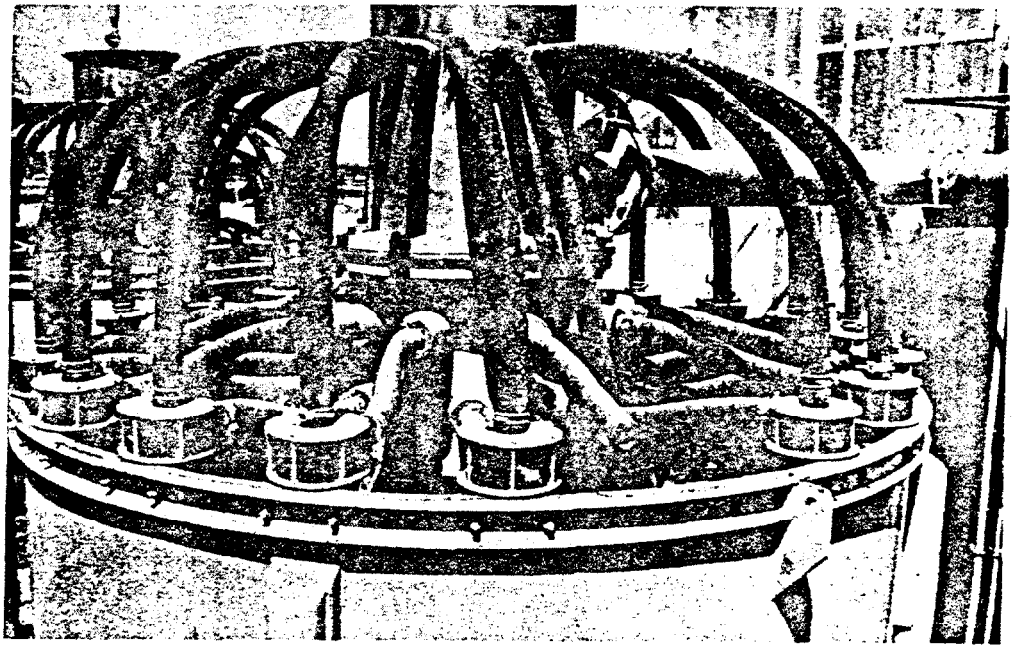
** "Groupe de Travail PG"

1/ DOUVRIN (North of France). The potential production of P Ø is 75,ØØØ T/year, which means 375,ØØØ T of phosphogypsum. A part of the gypsum production is stockpiled. There is around 2 MT. The stockpile is placed on silt which has protected the aquifer. Another part of the production is transformed into plaster after a purification treatment.

$$CaSO_4 \cdot 2\ H_2O \longrightarrow CaSO_4 \cdot 1/2\ H_2O$$

Since 1975, CdF CHIMIE operates a new type of process for manufacturing plaster. (1, 2)

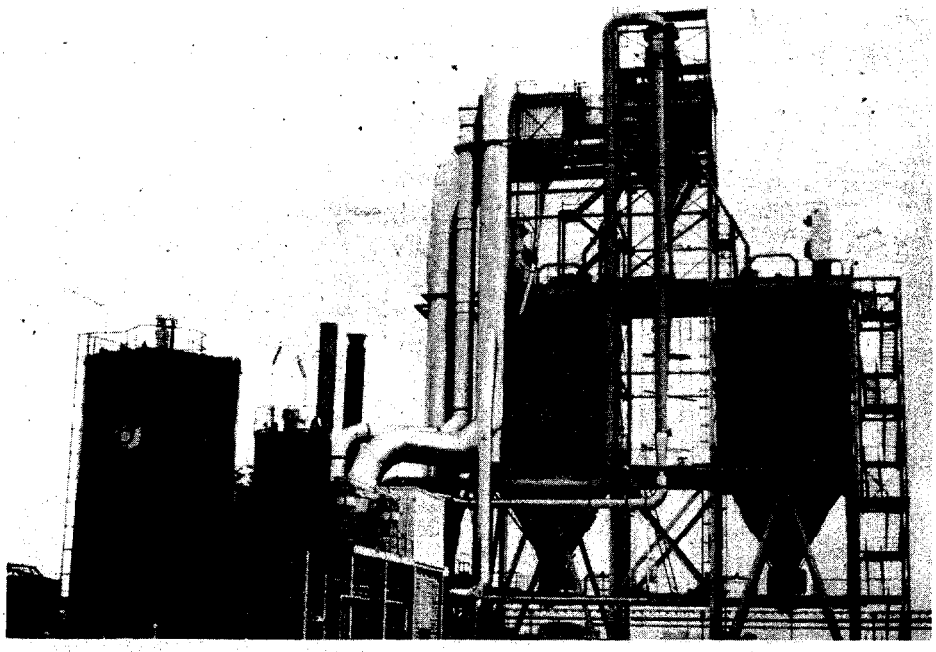
1.1 Purification. Big particles of quartz and a small amount of phosphate are removed on a filter. Traces of acids, solubles salts, organics adsorbed on the particles are removed with water. Hydrocyclones separate gypsum from the water.



Hydrocyclones

Syncristallized acids in the gypsum so obtained are neutralized by lime.

1.2 Thermal Treatment. The PG slurry is sent up from the bottom of a vertical tube with a hot air stream produced by a natural gas burner.



Production of Plaster

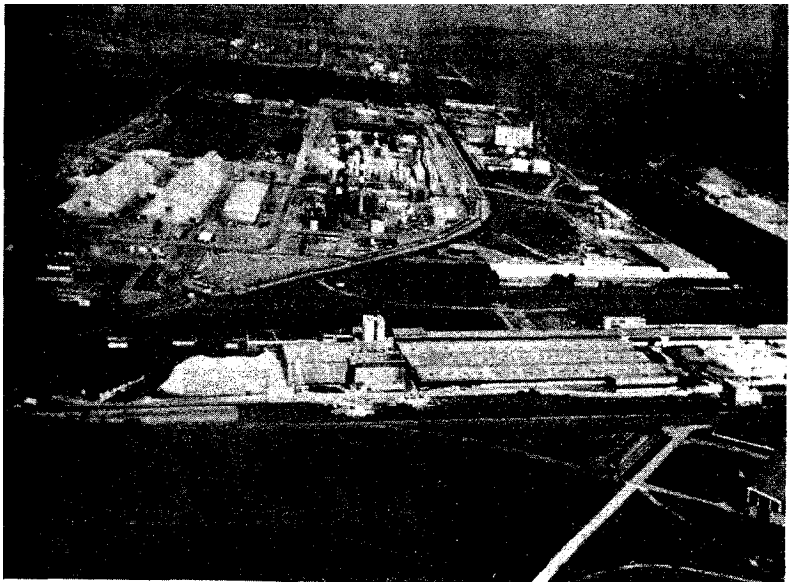
The deshydratation reaction is very fast - in approximately one second β semihydrate is obtained.

A plaster of high Blaine specific surface area is produced (~3,000 - 3,500 cm^2/g).

Its hydration is fast: solidification is complete in 8 minutes.

This high speed of hydratation is can be useful in prefabrication techniques.

2/ OTTMARSHEIM (Alsass). Phosphoric acid is produced there according to the Nissan process. The gypsum is crystallized twice and in this way purificated. There is no stockpiling at OTTMARSHEIM since the entire gypsum is used to market plasterboard by PREGYPAN, a subsidiary of LAFARGE and National gypsum groups. (3)



PREGYPAN-LAFARGE Plant
PEC-RHIN Plant

PREGYPAN manufactures around 15 Mm2 a year of a premium plasterboard which is largely exported to West Germany.

3/ GRAND COURONEE (Normandy). Grand Couronne is located on the left bank of the Seine River, some miles from ROUEN. The production of PG is around 1 Mt a year. The PG is disposed by barging (I 3ØØ T of PG) in the mouth of the Seine River (66 miles away). The trip takes around 8 and a half hours. The dumping station takes 1/2 hour. The barges circle in a well-defined area so that the dilution of the gypsum in the water is satisfactory. The regulatory agency monitors the disposal by two radars (Le HAVRE, HERREQUEVILLE) and a black device on the boat.

Another company uses the same barging system. A third company located close to the sea sends PG by a pipeline. In total around 3 MT/year of PG are produced in the lower Seine River.

This area benefits of a tradition of coastal fishing and international tourism (DEAUVILLE) and an opposition to this way of disposal has been hastered by the mass media.

A.P.C. has tried to find alternatives to this costly and controversial way of disposal. The new strategy of A.P.C. is based on the development of new application of gypsum which can use the available tonnages. The situation at GRAND COURONNE is much more complicated than the situations at DOUVRIN and. OTTMARSHEIM because the gypsum quarries of PARIS are not far away (3MT/year) and there is in the ROUEN-LE HAVRE area a production of 3MT/year of PG.

3.1 Cooperation with PREGYPAN. Mr. Moisset has exposed in detail this project (4) using the experience of OTTMARSHEIM and DOUVRIN in, GRAND, COURONNE.

R-D cooperation between LAFARGE and CdF CHIMIE has been going on for years.

2ØØ,ØØØ T a year of PG would be used to manufacture plasterboard. A.P.C. would set up a stockpiling of 5-6 MT of PG.

Extensive hydrogeological studies (5) have shown that close to the plant a site exists which is well-adapted for stockpiling.

Agronoms of A.P.C. have studied types of vegetative cover adapted to the PG.

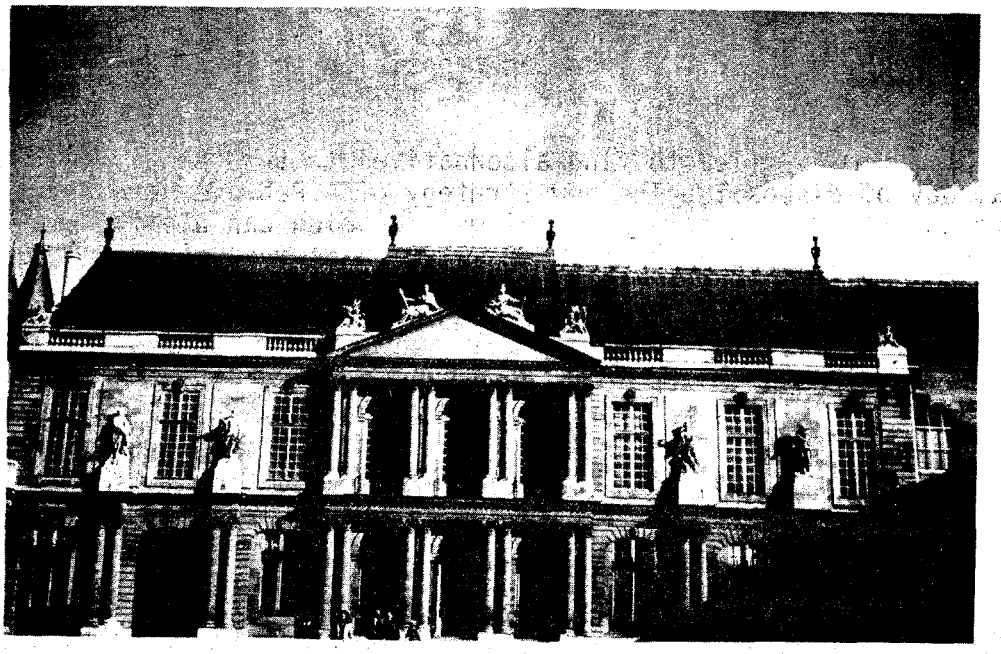
4/ R-D PROGRAM.

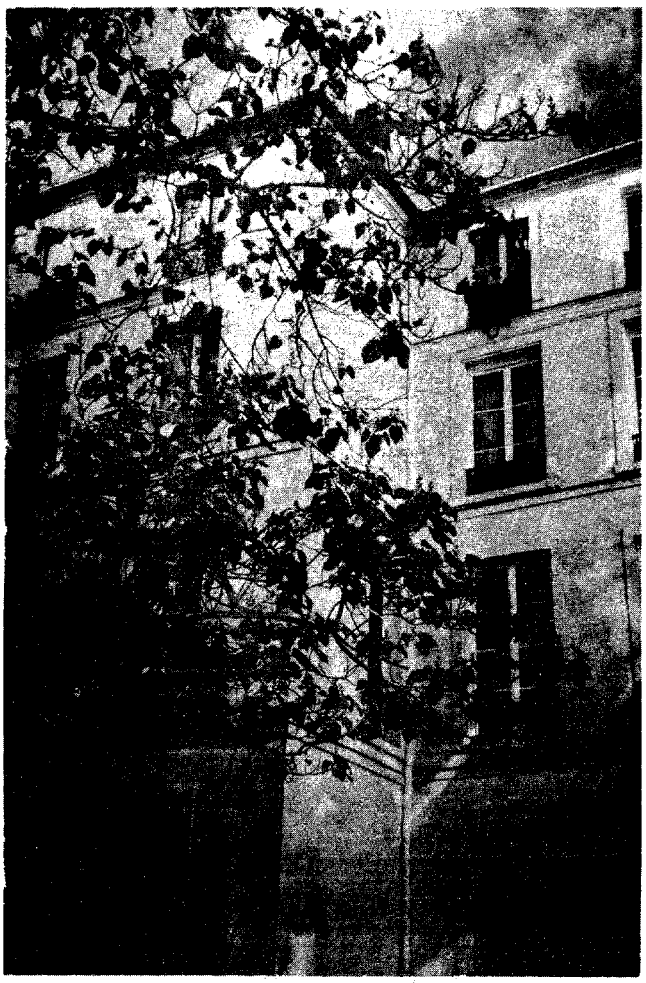
4.1. Cellular Gypsum. Latin and oriental countries have a long tradition of using gypsum. Splendid monuments made partly of gypsum can be admired in India, Egypt. In France, the use of gypsum is recorded back to the 13th century and Louis IX made regulations about performances of plaster. The use of gypsum was well-developed at the 17th and 18th century for at least three reasons.

4.1.1. Fire Protection. Many cities (e.g. London) have been destroyed by fire. A regulation of King LOUIS the fourteenth (on August 16, 1667) made the covering of internal and external pieces of wood by gypsum compulsory.

4.1.2. Energy Saving Material and Low-Cost Binder. Many people had to live with a permanent energy crisis. There was not yet coal or oil. Plaster is produced at around 150°C, hydraulic lime at around 1,000°C.

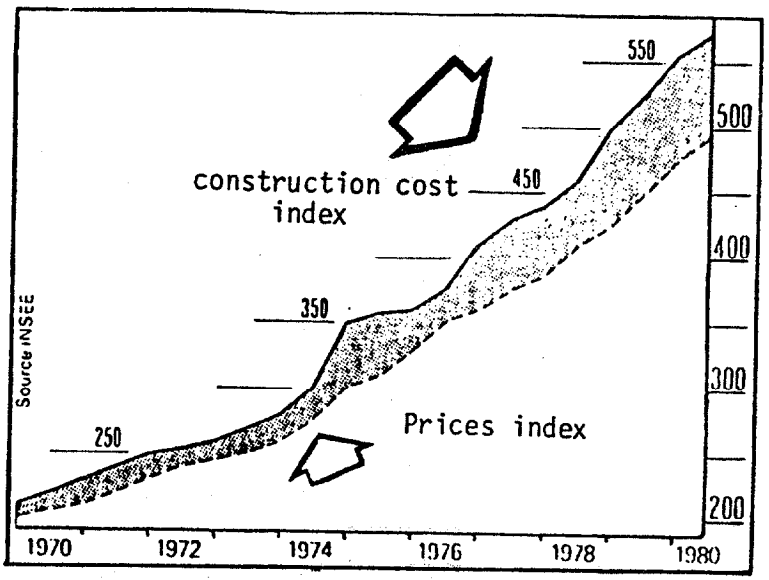
4.1.3. Architectural quality. Many buildings can be admired, for example in the Marais area of PARIS.





We have again to face an energy crisis and governments all over the world are interested in low energy content construction materials.

Populations of industrialized countries are used now (which was not the case at the 18th century) to living in warm atmospheres and buildings need more and more thermal insulation because of the rise in the cost of energy. The cost of money, the rise in the cost of construction manpower have skyrocketed the cost of construction. Governments in many countries are anxious to reduce construction costs.



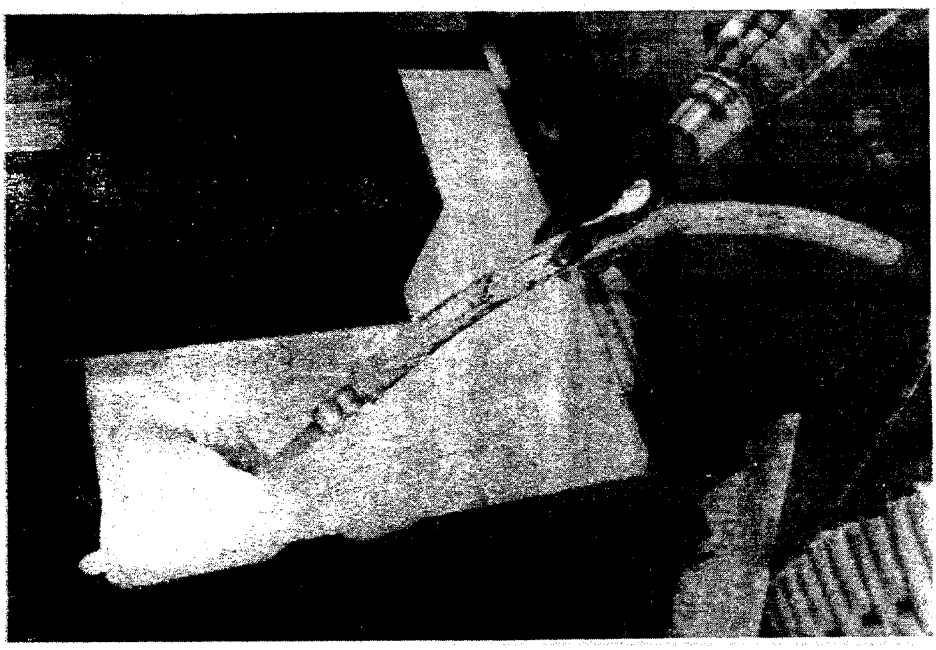
BOUYGUES and G.T.M., two leading companies in the field of construction, have developed a new construction system based on a cellular gypsum.

4.1.4. Features of the Material

- Low weight density: Ø.5 Rp = 1Ø-14 Kg/cm^2
- Thermal insulation λ = Ø.12 watt (m^2 /degre sextius)
- Flexibility of shape
- Outstanding fire protection (gypsum and its cellular form)

4.1.5. Operation

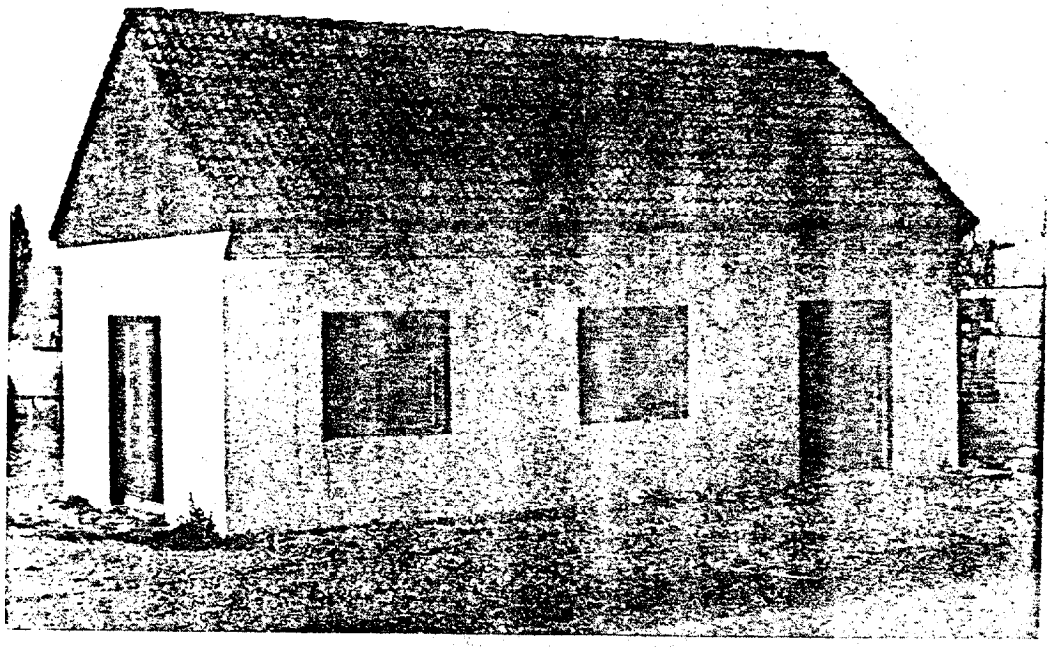
- High speed of solidification. 15 minutes after pouring, the cellular plaster is hard and the forms can be removed. The turnover of forms is very high.
- Unsophisticated equipment is used.
- Flexibility of use: Poured in place (BOUYGUES) or Prefabricated (G.T.M.) blocks easily handable by the workers characterized by a pleasant and soft touch.
- Cranes are not needed because of low weight.



Manufacture of cellular plaster

Demonstration for the French Housing and Urban Development





A cellular plaster house in DOUVRIN

According to our partners, this construction system could reduce construction prices of 20%.

A standard family house would use 25-30 T of PG. 400,000 dwellings are built in France.

4.2. Paper Filler. The price of wood is increasing. France imports a large part of its supply. Fillers are used extensively to decrease the cost of paper and increase its performances. 400,000 T are used in France.

Paper with a 20% PG content has been produced at the pilot stage in October in cooperation with paper producers. 70-80% of the PG filler particles are <10µ. The whiteness is between 65 and 70 M 60.

4.3. Agricultural Uses. A.P.C. sells some gypsum which is used in the field of:

4.3.1. Sodic Soil Reclamation (6)

4.3.2. Improvement of Drainage (6)

Price of farm land has much increased in France and it is valuable for a farmer to buy marshy lands to make it drain. But the drain pipes can be clogged. Then a large investment can be lost. With the use of PG ferric clays complexes are flocculated and drains are reopened.

4.4. Public Works - Civil Engineering (7) Low energy hydraulic binders can be made with slags, fly ashes.

CONCLUSION

A co-product may become a strategic asset for a company. A.P.C. had to develop new fields of uses. Results at the development stage have been obtained thanks to a close cooperation with companies specialized in the corresponding potential markets and companies which have the distribution channels.

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OCEAN DISPOSAL OF STABILIZED BLOCKS OF BY-PRODUCT CALCIUM SULFATE-SULFITE SLUDGES

by

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INTRODUCTION

There have been some limited successes in efforts to use $CaSO_4$ by-product from the production of phosphoric acid, HF and TiO_2 recently from flue gas desulfurization (FGD) scrubbers. But natural gypsum occurs commonly in large mineral deposits throughout most of the United States, except in the southeast, and it is mined at relatively low expense. Because of the ready availability of natural gypsum at small cost, there are only poor incentives to use industrial by-product $CaSO_4$. In addition, by-product $CaSO_4$ may be an inferior substitute for natural gypsum in some processes (Bruce, Berry and Kuntze 1981; Beretka 1981). Knight, Rotfuss and Hand (198Ø) have discussed some of the problems encountered in the commercial use of by-product $CaSO_4$ which is generally dependent on replacing currently used materials by successful economic competition. The prospects for large-scale utilization of by-product $CaSO_4$ in the United States contrast strongly with Japan, which has little or no natural gypsum and has ready potential markets for industrial by-product $CaSO_4$ sludges as economic alternatives to the import of mineral gypsum from overseas.

Very large volumes of by-product $CaSO_4$ are already being generated; 3Ø million tons of phosphogypsum annually from phosphoric acid production in the United States alone and much more will be produced as increasing numbers of large electricity generating stations burn coal and employ FGD scrubbers. In view of the market limitations in the U.S. on by-product $CaSO_4$ utilization, it is clear that there is an important problem of disposal for the excess of $CaSO_4/SO_3$ sludges; the disposal problem will grow larger with accelerating use of coal firing. In this paper we describe the investigation of a method for the ocean disposal of stabilized $CaSO_4/SO_3$ sludge from coal-fired power plant FGD scrubbers. There would appear to be similar potentials for block stabilization of by-product phosphogypsum.

There is urgency to convert from oil to coal burning, especially at northeastern power plants. An important obstacle to utilizing coal for generating electricity is the large volume of combustion by-products produced which must be disposed of. The waste disposal problem is especially critical in urban areas where disposal sites, even for municipal wastes, are rapidly disappearing. It is further compounded when the urban areas are situated along the coast. The product of the flue gas scrubber system (which removes sulfur oxides) is a voluminous filtercake of calcium sulfate-sulfite with the consistency of toothpaste - FGD sludge. The other waste of coal combustion which is produced in large quantities is ash, which occurs mainly as fine fly ash, plus about 2Ø% of coarse bottom ash.

The dumping of either the untreated FGD sludge or fly ash in the sea would be quite unacceptable, probably having deleterious environmental effects. However, IU Conversion Systems, Inc. Pa., has developed a marketable stabilized coal waste by combining the scrubber filtercake with the fly ash. Basically this system treats $CaSO_4/SO_3$ sludge and fly ash with additives and cementitious reactions convert the mix to a stable material that can range from a clay-like substance to hard blocks. The stabilization reactions taking place during the formation

of the blocks are similar to the pozzolanic reactions which occur in the forming of concrete. In the current application, this stabilized mixture is being used to fabricate solid blocks which can be used for the underwater construction of artificial fishing reefs and at the same time, resolve the problem of disposal. The bottom ash can also be included in the blocks as an aggregate.

Our research has been directed at determining the physical and chemical characteristics of the stabilized blocks of coal waste in sea water systems, their long-term integrity and what environmental effects, if any, the blocks might have. In particular, we are looking at how well the blocks serve as substrates for settlement and colonization by the plants and animals which are associated with reefs.

Laboratory Investigations. Work began four years ago with laboratory studies funded by the New York State Energy Research and Development Authority, New York State Sea Grant Institute and the Link Foundation and performed by MSRC at Stony Brook on blocks provided by IU Conversion Systems, Inc., Pa.

Small test blocks were studied in the laboratory to characterize chemical and mineralogical composition and to determine their physical and chemical properties. Of their physical properties, coal waste blocks have considerable similarities to concrete but do not have the high yield strength of concrete and are more porous and permeable. The bulk density of the blocks is about 80% that of concrete, due to the lighter fly ash used and the absence of high density aggregate materials. Compressive strength values of coal waste blocks are only a quarter of that of concrete, but in seawater some of the blocks continued to cure and slowly increased in density and in strength during a year of immersion.

Several studies have considered leaching characteristics of coal waste blocks. Calcium and sulfate at first leach fairly rapidly from test blocks in tanks of seawater. But as leaching continues, the rate of release of these major components decreases as the concentrations of the more soluble phases in the outermost layers of the blocks decrease. Leachates are also analyzed for trace elements such as iron, nickel, copper and mercury. Some elements show an initial increase in the seawater in the first days of exposure but after a few days were again taken up into the blocks; other elements did not dissolve at all. The behavior of dissolved trace elements was probably due to desorption-absorption processes; the trace elements remaining were associated with the fine materials such as fly ash in the blocks.

Using procedures recommended by the U.S. Environmental Protection Agency, in relation to disposal, bioassays were performed on block elutriates in seawater at relatively high concentrations to provide information on material toxicity. Using sand shrimp, developing fish eggs, and newly hatched fish larvae (sensitive early life stages), elutriates appeared to have no effect upon viability. Other assays were made with a unicellular plant, a marine diatom. Measurements of the daily growth, or rate of reproduction, and of photosynthesis by the plant cells indicated that the elutriates did not inhibit growth or had only transient effects for 1 to 2 days.

Inshore Habitats. The first investigations of coal waste blocks in the sea were made in an estuarine bay off Long Island Sound in about 18 feet of water. Several 1 ft^3 waste blocks were stacked into separate small habitats, "mini-reef" formations; one reef was of blocks with a high $CaSO_4$ content , a second reef consisted of blocks high in $CaSO_3$. Concrete locks were used for a control formation and a number of large natural rocks were also neatly stacked nearby. The "mini-reefs" have been periodically examined for biological colonization and photographed by SCUBA divers in a series of field experiments over a span of three years. At intervals, test blocks and encrusting organisms have been removed for laboratory analyses. The "mini-reef" study is part of the dissertation work of Frank J. Roethel, Ph.D. candidate at MSRC.

In the sea, the blocks have retained their physical integrity and although there were strong tidal flows, block edges remain sharp with little erosion. Test blocks removed from the site showed that the strength of the blocks was maintained over extended periods. The blocks high in calcium sulfite increased progressively in compressive strength from 320 to 730 psi during one year on the sea-bed.

No adverse environmental effects have been found resulting from the placement of the waste blocks. Seaweeds and animals have attached themselves and overgrown the waste blocks, as they have also on the concrete blocks and the rocks placed at the site. There appears to have developed a diverse, productive community of reef organisms on all of the blocks. At first, there were some differences in the type of settlement on the different materials, but as the blocks became more heavily overgrown and finally encapsulated by plants and encrusting animals, the initial differences in colonization between the coal waste blocks and concrete began to disappear. After a year, differences were no longer evident.

Because the coal waste materials contain trace amounts of potentially toxic elements, samples of organisms growing on the blocks were removed by SCUBA divers for trace element microchemical analysis. Samples were analyzed for Cu, Cr, Zn, Pb, Cd, Hg, Ag, Se and As using atomic absorption spectrophotometry and other methods. The collections and analyses were repeated on five occasions over two years. In no instance was there evidence of elevated levels for any of the trace metals in the biomass collected.

The continuing laboratory and field studies strongly suggest that blocks of stabilized coal combustion wastes may be environmentally acceptable in the sea. An initial economic survey indicated that the concept of block disposal in the ocean might offer savings relative to land disposal of wastes from a power plant situated on the coast or an estuary.

Demonstration Reef in Atlantic. The program has now established the larger demonstration artificial reef with 500 tons of coal waste blocks which were made by IU Conversion Systems, Inc. using methods developed by our program. The blocks have been placed two miles south of Long Island at a depth of about 70 feet in the New York Bight. This part of the program has been funded by U.S. Environmental Protection

Agency and U.S. Department of Energy, by the Electric Power Research Institute, and by New York State Energy Research and Development Authority and Power Authority of the State of New York.

In preparation for fabrication of the 500 tons of reef blocks, different coal waste mixes, stabilization additives, and curing procedures were screened to develop candidate mix designs. Large-scale experiments in block manufacture were carried out in Ohio where 1 yd^3 blocks, weighing about two tons, were made. Subsequent assessment of these experiments suggested that it might be cheaper and faster to produce smaller blocks (weighing about 60 lbs. each) using conventional concrete construction technology. This was confirmed in another large-scale investigation at the research facilities of the Besser Company in Alpena, Michigan where methods were developed to form coal wastes into blocks with block machines. The technology was successfully transferred to the commercial factory in summer 1980 by demonstration experiments at the Fizzano Bros. concrete block factory in Trevose, Pa. For these experiments only the conventional commercial machines and automatic block-handling equipment were used for coal waste block fabrication -- demonstrating engineering feasibility. In the block-making process, FGD sludge, fly ash and additives are thoroughly mixed and run into the hopper of a block machine; strong vibration is used both to feed the material into steel molds and to compact the molded blocks on pallets. The pallets of green blocks are loaded on racks holding 192 blocks each and cured for a day in steam kilns. Cured blocks are unracked, depalletized and stacked for handling as cubes of up to 144 interlocked blocks by a cubing machine, Figures I and 2. A block machine can form more than 1,500 concrete blocks per hour and our calculations suggest that single machine working three shifts per day could process the wastes from a 500 MW plant. By employing steam kilns, curing is accelerated and greater block strength can be achieved in 24 hours than in 28 days of curing at air temperature. Accelerated curing allows immediate handling by automated machines and cured blocks may be rapidly disposed of minimizing storage space.

For the full-scale manufacture of 500 tons of reef blocks, coal wastes were trucked from the Columbus and Southern Ohio Electric Co. 800 MW power plant at Conesville, Ohio and from the Indiana Power and Light Company 530 MW plant at Petersburg, Indiana. Both are modern plants with Conesville employing lime scrubbers and Petersburg using limestone. The blocks were made at the factories of Fizzano Bros. and at York Building Products in Middletown, Pa. The mixes used had fly ash to scrubber sludge ratios of 3:1 for Conesville waste and 1.5:1 for Petersburg waste. About 15,000 blocks were produced, loaded on an ocean-going, bottom opening dump barge, and released at the Atlantic demonstration project site on September 12, 1980 (Fig. 3).

Within weeks of the reef being placed on the sea-bed, numbers of barnacles, tube worms, feathery hydroids and similar encrusting organisms had begun to grow on the blocks. Such fish as sea bass, ocean pout and cunner had moved in and divers found rock crabs and an occasional lobster.

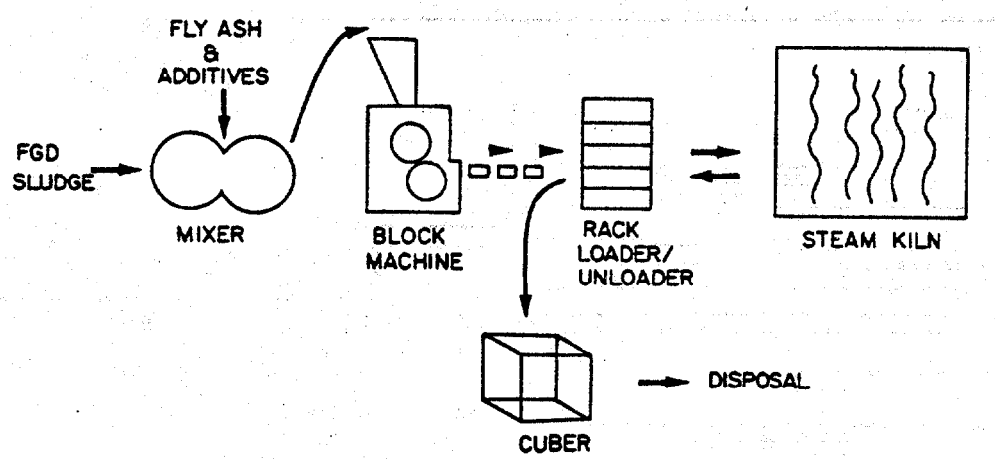
Prior to placing the reef, we made a series of baseline oceanographic cruises to characterize the project site and surrounding areas. The artificial reef will now be monitored for three or more years to assess environmental impacts which may occur and to measure the development of the biological communities which will be associated with the reef. Throughout the study, extensive testing will be performed on blocks periodically removed from the demonstration reef to evaluate their acceptability as materials for fishing reef construction from physical, chemical and biological perspectives. Other tests will be made by SCUBA divers on blocks remaining in the sea, including ultrasonic sensing for internal structural change. We hope that, if this extended program of testing and oceanographic monitoring will find the blocks to be environmentally acceptable in the ocean and without adverse effects, we may have demonstrated an economic alternative for the disposal of coal wastes which can also carry benefits for man and the marine environment.

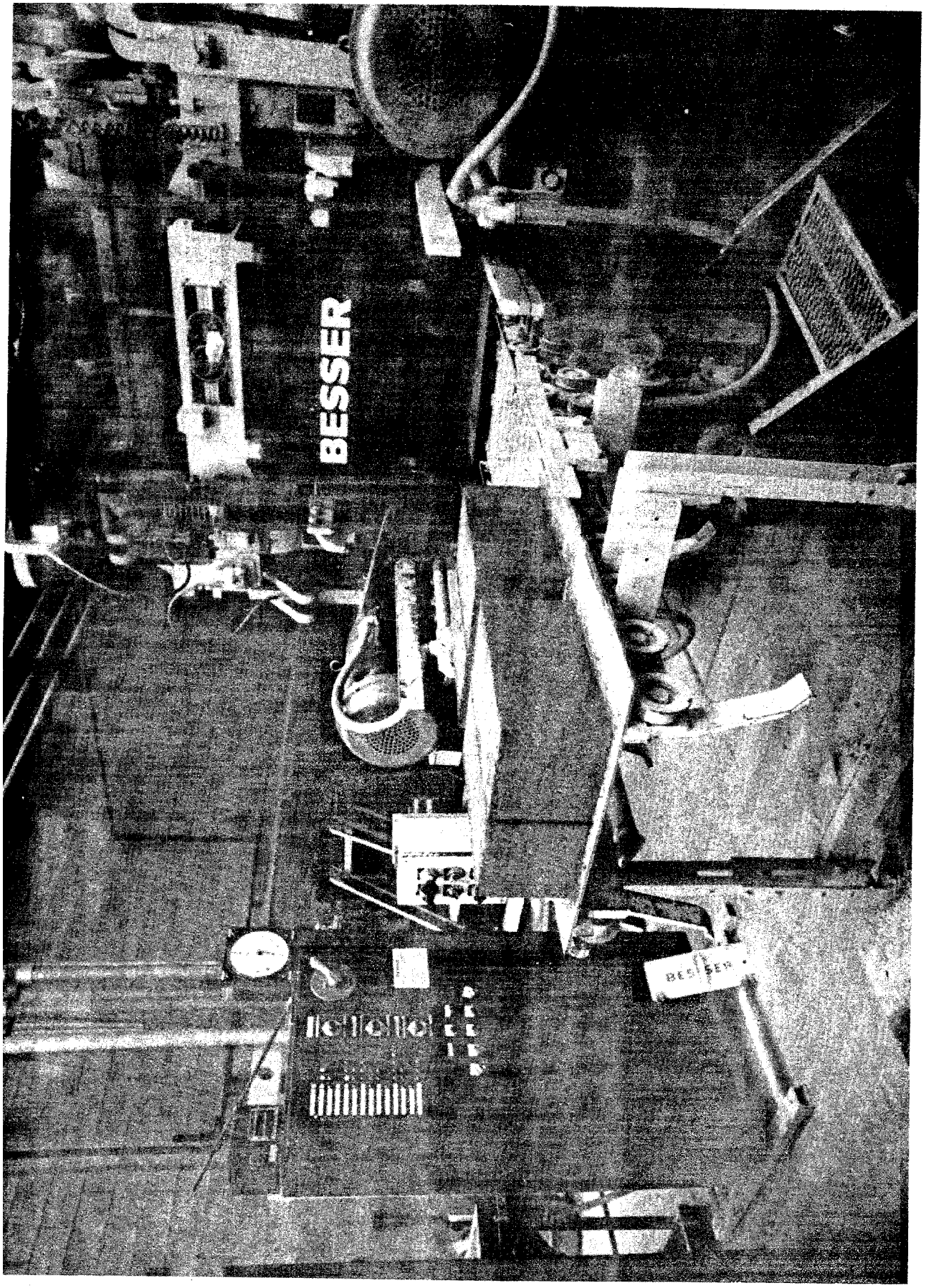
FIGURE CAPTIONS

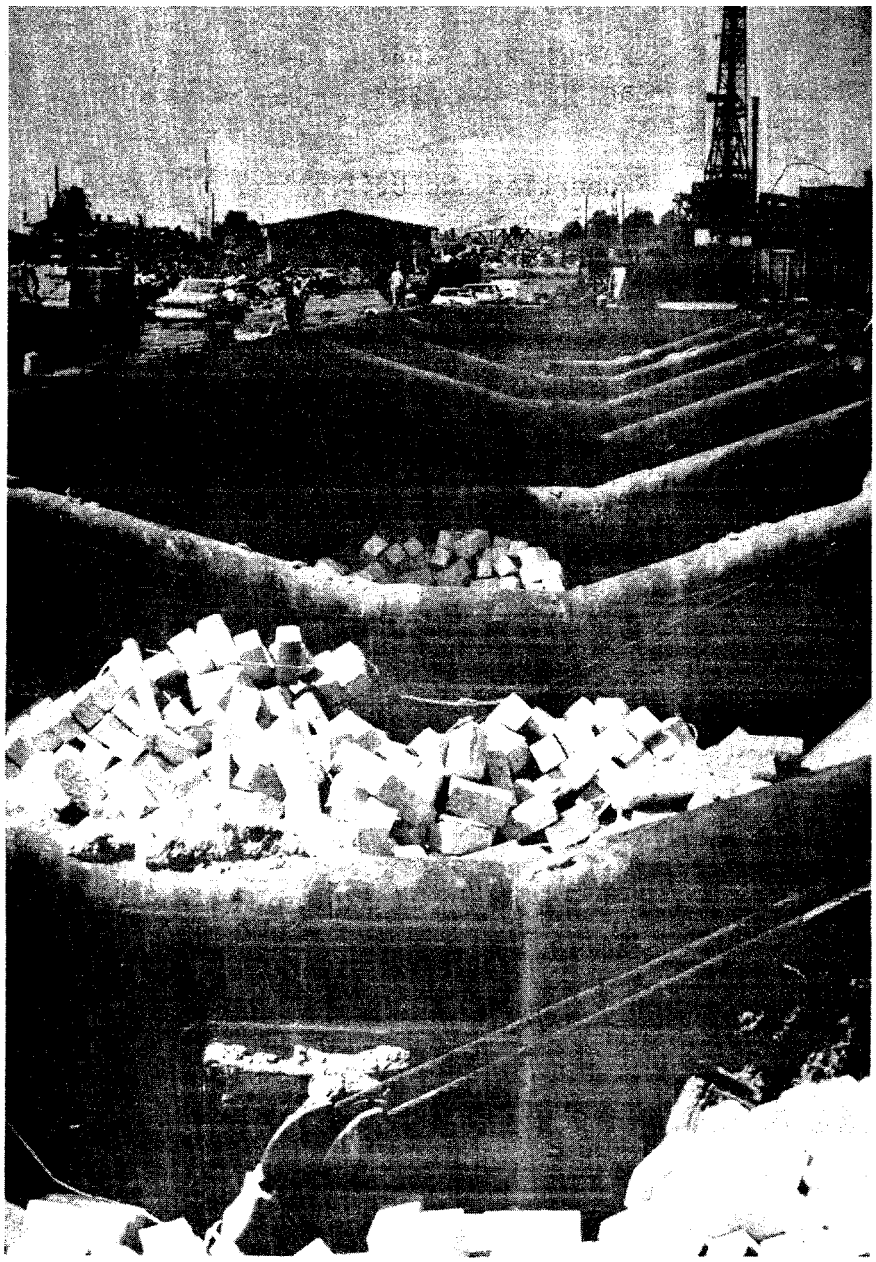
Figure I — Simplified schematic of block processing

Figure 2 — Block machine at research facilities of Besser Company, two pallets of four newly formed coal waste blocks are in the foreground

Figure 3 — Compartments of dump barge containing coal waste blocks during loading in S. Kearny, New Jersey


FLY ASH
&
ADDITIVES
FGD
SLUDGE
MIXER
BLOCK
MACHINE
RACK
LOADER/
UNLOADER
STEAM KILN
CUBER
DISPOSAL


BESSER



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Purification and Chemical Recovery from Phosphogypsum

SULFUR FROM GYPSUM

LABORATORY, BENCH-SCALE AND PILOT-PLANT STUDIES

by

Robert D. Austin

INTRODUCTION

In 1966, U.S. Phosphoric Products, Division of Tennessee Corporation, was faced with diminishing sulfur supplies and rising prices. The sulfur producers initiated a quota system, and it appeared that sulfur requirements could not be supplied at any price. As a result of this situation, a crash program was started to investigate the recovery of sulfur from gypsum.

Laboratory studies were carried out to verify and supplement the extensive technical literature which existed at that time. The parameters which seemed critical to future bench-scale and pilot-plant studies were reaction time, temperature and the effect of water in a typical reformed gas mixture.

These studies[1] were carried out in a Vycor tube containing a five-inch bed of gypsum (Figure 1). A Beckman GC2A gas chromatograph, containing both silica gel and molecular sieve columns, was used to analyze the effluent gases. The reaction tube was initially purged with helium and then heated to temperature, after which a synthetic, reformed gas containing 80% H_2 12% CO, 8% CO_2 was fed into the tube to begin the reaction. Tests were made from 700-1200°C and at various times from 15 to 120 minutes. Steam was varied in the reform gas from 1 to 90 mile percent. Additional studies were made to determine the effect of single gases such as hydrogen, carbon monoxide, hydrogen sulfide and carbon dioxide. Findings from these studies showed that the reduction products depend primarily upon the temperature of the reaction. From 700-900°C, 80 to 90% of the calcium sulfate was converted to calcium sulfide; the remaining percent being converted to H_2S, SO_2 and elemental sulfur. As the temperature was increased above 900°C, the percent reduced to CaS decreased with a corresponding increase in the evolution of H_2S and SO_2. Table I is a summary of these tests.

An increase in the amount of steam resulted in an increase in the percent of gypsum reduced to the sulfur gases at temperatures from 800°C to 1200°C. Figure 2 is a curve of these results.

The use of pure hydrogen gave results almost identical to the reform gas mixture. Carbon monoxide in tests at 900°C to 1000°C gave solids analyses similar to the reform mixture, but carbonyl sulfide, COS, was evolved in place of hydrogen sulfide. Carbon dioxide produced no reaction.

When pure hydrogen sulfide was passed over the gypsum at 900°C, SO_2 was evolved to a maximum of 94% by volume of the effluent gas stream. After the sulfur dioxide evolution had stopped, the solids analysis showed that 50% of the gypsum had been reduced -- all of it to the calcium sulfide form.

After the gypsum had been reduced to calcium sulfide, in the 800°C tests, attempts were made to convert it to calcium oxide and recover the sulfur gases. One set of tests applied steam to the calcium sulfide at 900°C. This effectively made a conversion to calcium oxide along with the evolution of sulfur dioxide and hydrogen sulfide. Another method

purged the reacted gypsum with air at temperatures from 700°C to 1200°C. At these tests, 90% of the calcium sulfide was converted to lime. Some of the remaining calcium sulfide reverted to gypsum. The best oxidation to sulfur dioxide occurred at 1100°C.

Parallel to the laboratory studies, bench-scale tests[3] were initiated to supplement the laboratory data required to design a pilot plant. Certain crucible experiments with mixtures of calcium sulfate and calcium sulfide had shown that at operating temperatures calcium sulfide becomes tacky and in no way would be fluidizable. First lime was tried as a diluent to make the calcium sulfide fluidizable which was unsuccessful; and was tried next. This turned out to bring about a three-fold benefit: It made the calcium sulfide fluidizable at elevated temperatures, it promoted conversion at lower temperatures, and also provided a heat transfer medium. Additional studies[2] were initiated at this time in order to obtain fluidization design data utilizing mixtures of sand and calcined gypsum. Figure 3 is a sketch of the equipment used in these studies which were carried out at ambient temperatures. Both overflow and under discharges were simulated. The sand used was 98% +100 mesh; whereas the gypsum was 55-65% -100 mesh. Initial studies were made with mixtures of 3 parts of sand to 1 part of calcined gypsum. Solids were fed and discharged at 3 lb./minute and air at 1 ft./second superficial velocity. The bed height was maintained at 36 inches. It was found that in the case of an underflow discharge, the bed contains about twice as much minus 100 mesh material (consequently about twice as much as gypsum) as the feed. In the case of an overflow discharge, the bed contained about 25% less gypsum than the feed and discharge. Another series of tests was run with mixtures of 50% calcined gypsum and 50% dried sand which was fluidized with air at 1 foot/second, while maintaining the bed height at 12 inches. Solids were fed and discharged at three lbs./minute. Two runs were made, once with overflow discharge and once with underflow. The results were similar to the previous runs with deeper bed and a 3:1 sand-gypsum ratio. The underflow discharge results in a uniform bed above the sparger with the bed containing almost twice as much -100 mesh (gypsum) as the feed and discharge. Overflow discharge results in a bed whose composition becomes more coarse from top to bottom with the average bed composition having 3/4 as much -100 mesh (gypsum) as the feed and discharge.

Additional bench-scale tests were made based on the overall reaction of $4CaSO_4 + CH_4 + 3H_2O$ ----> $4CaO + 4SO_2 + CO2 + 5H_2O$, with an energy requirement of 6540 Bty/lb. S. An externally-seated three-inch stainless steel cone was used to test the concept that this reaction could be carried out with gypsum in a fluidized bed with either propane or methane. With this setup, approximately 50% reduction of the gypsum at 1500°F with propane was obtained. Further experiments in the above unit were carried out with methane at 1925°F. Phosphogypsum and technical-grade calcium sulfate were compared for activity. Again, the sulfate was reduced rapidly and indicated 97% reduction of phosphogypsum and 98% reduction for the anhydrous technical-grade gypsum.

A two-tray fluid bed reactor (Figure 4) was set up for the next phase of this work. This unit was indirect-fired and used downcomers for bed height control. At 1300°F, an 80% reduction of the sulfate was

achieved. Crucible experiments had shown that 50-50 blends of calcium sulfate and calcium sulfide would be tacky and not flow as conveniently as gypsum only. One hundred percent calcium sulfide would not flow at temperatures above 1300°F.

Modifications to the system were made to improve the flow of the solids. Reform gas with excess steam was initiated as a diluent along with the desire to minimize the level of calcium sulfide intermediate by forming H_2S and lime by the reaction with steam. It was evident by stack testing and from the corrosion level in the reactor that hydrogen sulfide and SO_2 were being formed. The normal temperature range for runs made on this equipment was from 1300°F to 1500°F.

To improve the contact time of the solids to process gas, a five-tray bench unit was tried next. This unit was designed without downcomers and solids flow would be through perforated interrupter trays. Again, this unit was indirect-fired to minimize dilution of the process gas stream. This philosophy had the following advantages:

(1) A better process gas-solids contact,
(2) minimal reactor area based on required reactants and sufficient fluidization velocity, and
(3) rich product gas stream.

The five-stage unit showed an immediate improvement in the gas stream analysis temperatures of 1400-1450°F. The gas stream was 6.2% SO_2 and 1.2% H_2S. The test procedure was to absorb the SO_2 in hydrogen peroxide and H_2S in cadmium chloride solutions. Elemental sulfur condensation was evident.

To further improve mixing and solids movement, stirring devices were installed in the unit. It was felt that possibly a Hershoff-type furnace could be applicable. The mechanical agitation of the bed helped obtain some reasonable operating time and did improve our conversion efficiencies. Orsat analysis of the product gas stream indicated gas streams with up to 38% SO_2 and 13% H_2S. This unit was operated at temperatures up to 1800°F although most of the runs were made at temperatures between 1400°F and 1600°F. Solids flow and general agglomeration still remained a problem. Agglomeration of the reactants was probably exerting the most influence on the total recovery or conversion.

High fluidization velocities and stirring of the $CaSO_4$:CaS:CaO mixture did not solve the agglomeration problem, so various diluents to the gypsum were tried. Lime was tried initially without success and could not be considered as an improvement. Sand dilution was tried next and was immediately successful in maintaining solids flow with minimum clinkering. Improvement of the gas stream was also evident, thus demonstrating the previous negative effects of agglomeration. Forty percent by weight sand was found to be the minimum dilution for reasonable control of agglomeration. The five-tray unit had a total bed height of three feet, which provided a three-second gas-solids contact time, based on superficial velocity of one foot per second. At 0.94 feet per second (3.18 seconds contact time), the gas stream contained

generally 20 to 30% SO_2 and 6% H_2S. At 0.64 feet per second (4.70 seconds), the gas stream contained 50% SO_2 and 8% H_2S. Sulfate conversion to CaO and CaS ranged from 40 to 84%.

Increased residence time thus was desirable, and the reactor was increased to nine trays. Under reasonable operating conditions, at 1500"F, process gas stream analysis indicated generally good SO_2 concentrations -- 50 to 72% SO_2 and 8-9% H_2S. The higher SO_2 concentration resulted from a process gas residence time of approximately 12.5 seconds. Total conversion of the sulfate improved with the increased bed height.

An order of magnitude cost estimate was made at this time, based on a 1000-ton-per-day recovery plant. The energy of reaction could be furnished from a heat sink material that is heated in a separate vessel and thus fulfilling the desire of not diluting the product gas with combustion gases.

Fluidization tests previously described indicated that, without agglomeration, a stable fluid bed could be developed for sand-gypsum mixtures at~0.5 feet per second (incipient fluidization). Further testing indicated that classification and blow-over of the gypsum would be excessive above 1.8 feet per second. These velocities and bed action looked realistic, and the major question of conversion efficiency could only be answered in a heated bench reactor.

A six-inch diameter, 316 stainless steel pipe, 10-feet long, was set up along with a small reformer that would furnish the reducing gas to a small sparger at the base of the reactor. Figure 5 illustrates this equipment. Bed height was controlled by metering of solids at the underflow below the sparger. The reactor was run at 1500°F with various bed depths. Initial runs were batch operations and showed an acceptable sulfur gas generation, 40% SO_2 and 10% H_2S. The solid samples indicated approximately 60% conversion of sulfate with various levels of calcium sulfide remaining. These runs certainly indicated that this process technique would be applicable to our process. In general, these experiments were run at superficial velocities at approximately incipient fluidization (0.5 feet per second).

Good utilization of the reducing values was realized in this unit where the process gas stream would consistently be 90% scrubbable in caustic (SO_2, H_2S and CO_2). Bed heights from three to six feet were studied and indicated reasonably good conversions of conditions when the bed would be considered rich in calcium sulfate or lean in calcium sulfate. In either of the cases, reducing values were utilized efficiently. As a general rule, the bed which was rich in sulfate tended to form SO_2 gas in the process stream and the bed which was lean in calcium sulfate favored H_2S generation. In all cases, there was a fairly high percentage of calcium sulfide in the solids discharge. The calcium sulfide, of course, must be converted to lime and hydrogen sulfide to insure efficient utilization of all reducing values.

A process analysis indicates that SO_2 as the product would yield the lowest cost sulfur when considering a battery-limit plant. Basically, this is due to: (1) minimum reducing gas -- 1 methane converts 4 $CaSO_4$ to lime and SO_2, and (2) minimum reactor area -- reactor area controlled by superficial fluidization velocity of the reducing values.

With this goal, a pilot plant was designed. As indicated in the bench-scale fluidization work and fluid-bed technology, the unit would have to be staged to obtain essentially SO_2 as the product. The composition of a fluidized bed is technically considered homogenous where the bed is the same composition as is the solids discharging from it. With this basis requirement and the fact that the lean $CaSO_4$ bed would favor the production of H_2S, two reaction stages were planned. Countercurrent flow of the gypsum and reform process gas would enhance the recovery because the first solids stage would be rich in sulfate and favor oxidation of the sulfur values from the second solids stage, which would be maintained lean in sulfate. A third solids stage would be required to complete the sulfur recovery by stripping H_2S from the remaining calcium sulfide intermediate.

Energy would be furnished to the reactors and reactants by separate preheaters. The various vessels were designed as independent units in order that the reactions in each stage could be studied independently. To seal the stages , and for bed height control, solids transfer screws were installed. The process gas would pass from the reformer through a sparger to the second solids stage (lean sulfate) and then to a sparger in the first solids stage (rich sulfate) and finally to the product gas receiver.

Figure 6 describes the pilot-plant concept.[3] The reaction would be balanced to obtain approximately two moles of hydrogen sulfide to one mole SO_2 from the main reactor. i.e. second solid stage. This reaction requires three moles of methane for four moles of calcium sulfate. The process gas effluent ($2H_2S$ and SO_2) would react to form sulfur and water. The total energy required in either case, (1) SO_2 as product or (2) sulfur as the product, on the integrated complex is essentially equal and depends on total capitalization and general operational considerations. Operationally, it would be better to manufacture sulfur as the product. Storage, handling and use at acid plants allow for independent control with liquid sulfur.

The bench-scale data had indicated that the reaction to recover sulfur at approximately 1500°F in a fluid bed with reformed gas is possible. Bench-scale units, of course, were all indirect fired and the total reaction was dependent on the energy available through the reactor walls. The heat transfer coefficients were thus controlling. The pilot plant was designed to prove a workable process philosophy that would be readily adapted from present state-of-the-art equipment. All energy of reaction would be supplied from a heat sink material; in this case, sand would fulfill the process requirements. The sand and gypsum would be preheated, as catalysts are heated in a petroleum fluid catalyst cracker, and then transferred to the reactor bed where it would be fluidized by the reducing gases.

Following construction and initial calibration of process equipment, attempts were made to operate the pilot plant as an integrated unit. It soon became apparent that serious problems existed in three areas. There were: (1) transfer of solids between stages, (2) insufficient temperature due to system losses and inadequate thermal input from the sand, and (3) improper materials of construction.

Screw conveyors which were tried initially were subject to severe attrition and sustained frequent cracks in the housing due to expansion associated with high temperatures. Ultimately, small steam or air transfer vessels were found to be more practical than the conveyors.

A desired temperature range of 1400-1600°F was achieved in the main reaction vessel by increasing temperature and capacity of the sand preheater.

The generation of SO_2 and H_2S made the use of 316 at these temperatures completely impractical. Plasma fusion of chromium was tried in the main vessel without success due to poor bonding. Finally, 446 was used to fabricate all new vessels and other exposed equipment. During the remaining time of operation, the corrosion problem appeared to be solved.

A major portion of the pilot plant's operational time was spent dealing with these three general problem areas. Considerable data was ultimately collected relating variables such as gypsum feed rate, methane gypsum ratio, water methane ratio and temperature. Table 2 is a listing of runs in which operation was sustained sufficiently in order to obtain representative data. This data and other experimental findings are best expressed by the relationship percent conversion of gypsum equals a + b 1nG, where: a and b equals 68.45 and 21.63, respectively.

G* is a function proportional to temperature, residence time of reformed gas, ratio of moles of methane to moles of gypsum, and inversely proportional to the gypsum feed rate.

At this point in the study, due to increased availability and the declining cost of sulfur, a decision was made by management to terminate the project.

$*G = \frac{R}{f} \theta \ (\Delta T)^2$, where:

R = moles methane to moles calcium sulfate entering the system

f = calcium sulfate feed (moles per minute)

θ = residence time of the reformed gas in the fluidized bed in seconds

ΔT = reactor temperature - 1250.

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(1) R. Pyman and K. Gasser, "Recovery of Sulfur from Gypsum -- Components of Reformed Gas at Elevated Temperatures," U.S. Phosphoric Products' interoffice memorandum dated July 14, 1966.

(2) R. Nettles, "Fluidized Bed Studies," U.S. Phosphoric Products' interoffice memorandum dated August 17, 1966.

(3) R. Lister and R. Foecking, "Sulfur from Gypsum," U.S. Phosphoric Products' project report, dated December 27, 1968.

TABLE I

Time and Temperature Study of the
Reaction of Gypsum with Reform Gas

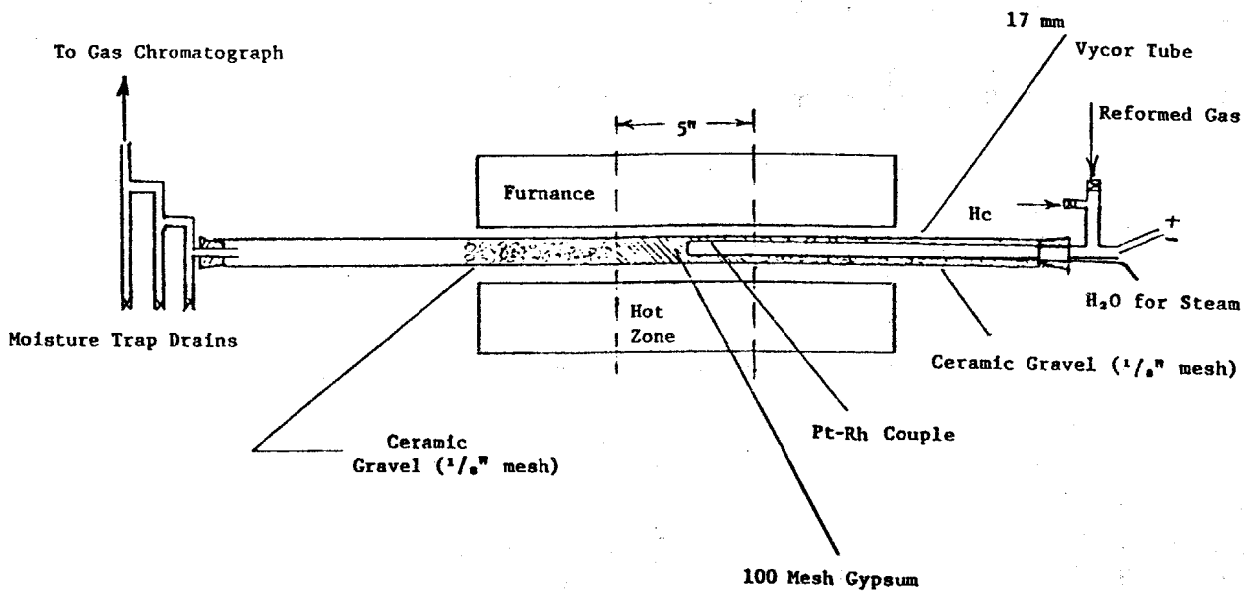
Temp. °C	Time min.	Gas				Solids				
		Max. H_2S		Max. SO_2		CaO	$SO_4^=$	$S^=$	Total % $SO_4^=$	% Conv. $SO_4^=$—CaS
		Time	%	Time	%	36.13	58.22	0.00	Conv.	
600	15									
	30	31	0.80	7	2.81	40.32	59.79	0.13	7.96	7.48
	60									
	120									
650	15									
	30	31	0.81	1	0.24	42.61	56.89	2.90	17.13	73.94
	60									
	120									
700	15									
	30	19	1.02	1	0.19	42.41	57.95	2.69	15.19	77.60
	60									
	120									
800	15									
	30	13	0.88	7	3.36	56.08	26.66	17.60	70.49	82.77
	60									
	120									
900	15									
	30	19	1.90	7	9.31	68.05	1.18	31.22	98.92	86.24
	60									
	120									
1000	15	13	2.72	1	44.41	72.23	13.33	26.05	88.55	75.75
	30	19	5.00	7	39.48	65.70	13.60	19.80	87.15	61.96
	60									
	120									
1100	15	13	1.12	1	48.00					
	30	19	3.95	7	50.66					
	60	19	8.14	1	47.44					
	120									
1160	15	13	6.76	1	58.46					
1190	30	13	13.23	1	43.05	70.04	9.64	6.88	91.45	19.97
	60									
	120									

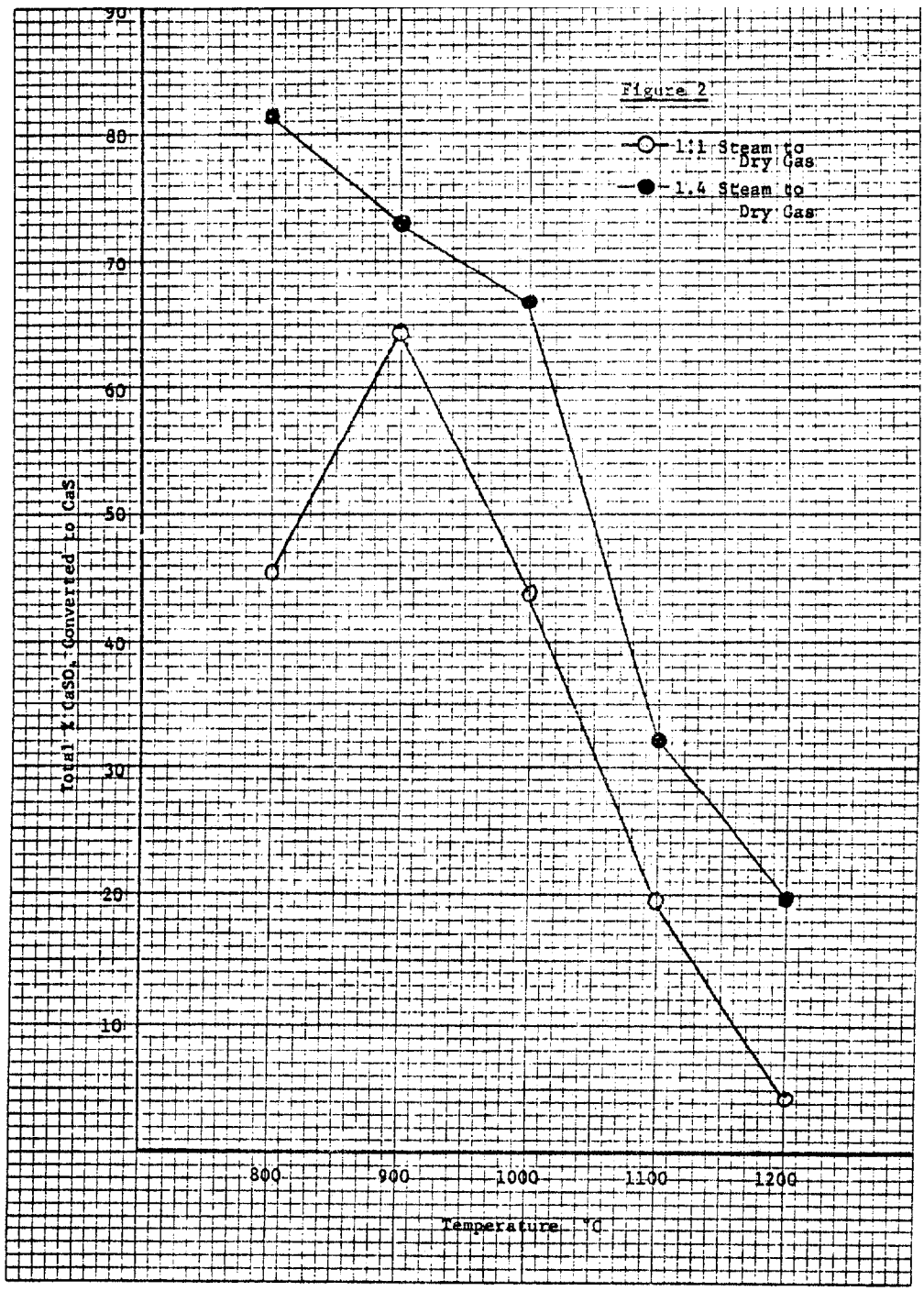
TABLE 2

Run No.	Feed Rates $CaSO_4$ #/min.	Feed Rates CH_4 #/min.	Steam to Gas Ratio v/v	Space Velocity ft./sec.	Temp. °F	Bed Height ft.	SO_4 Converted Total %	SO_4 Converted to CaS %	Gas Analysis CO_2 %	Gas Analysis H_2S %	Gas Analysis SO_2 %
1	0.31	0.0442	3.44	0.51	1480	6	95.0	44.8	35.8	34.4	17.3
2	0.4	0.0588	3.93	0.735	1420	6	85.2	47.0	38	38	19.5
3	0.31	0.0294	3.83	0.366	1600	6	87.6	27.8	25.9	14	14.4
4	0.38	0.0442	3.44	0.51	1580	6	81.4	31.1	35.6	33.4	17.2
5	0.42	0.0588	3.93	0.735	1525	8	89.5	43.0	25.2	18.8	9.4
6	0.39	0.0442	4.03	0.557	1580	7	97.7	33.3	37	38.3	18.4
7	0.425	0.0588	3.93	0.734	1610	6	90.0	33.3	25	23.6	11.6
8	0.41	0.0294	5.07	0.434	1540	7	77.9	16.9	37	37	23
9	0.44	0.0442	5.05	0.638	1550	7	82.0	31	37	37.2	18.3
10	0.67	0.0442	5.05	0.638	1520	6.75	78.1	29.1	36.8	36.5	17.7
11	0.67	0.0447	3.17	0.48	1565	7	90.5	41.5	36.1	27.8	12.7
12	1.04	0.0560	3.34	0.64	1550	5	79.5	65.5	28.3	23.2	10.2
13	0.77	0.0560	3.34	0.64	1500	6	78.8	61.7	29.5	23.5	10.9
14	0.78	0.0607	4.33	0.82	1540	6	75.4	62.9	26.6	19.8	8.9
15	0.80	0.0607	4.33	0.82	1530	6.25	86.7	35.2	24.2	14.9	7.2
16	0.93	0.0607	4.33	0.82	1485	5.5	80.3	38.7	24.6	14.1	6.2

Figure 1

APPARATUS FOR GYPSUM STUDY





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Figure 3

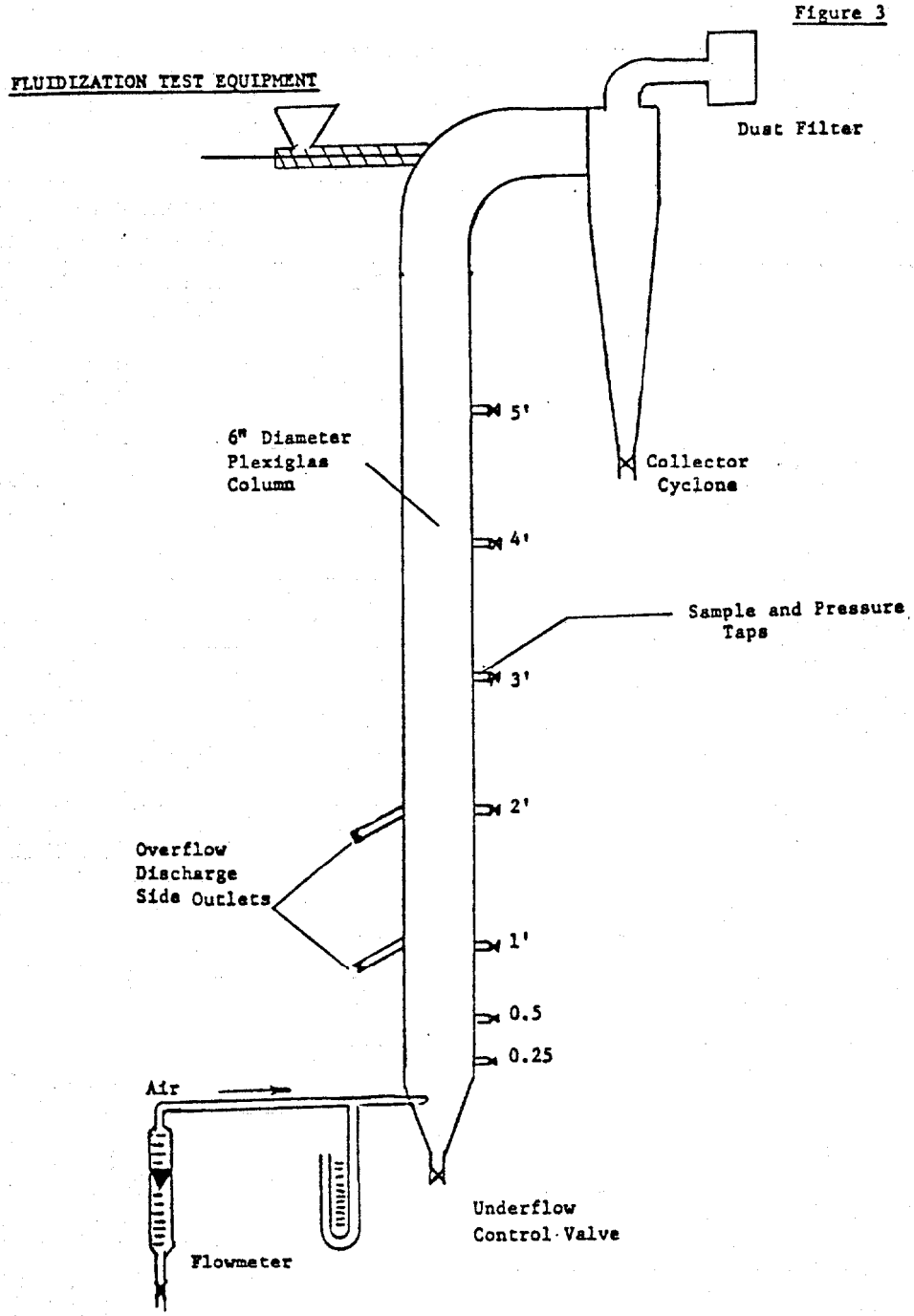

FLUIDIZATION TEST EQUIPMENT
Dust Filter
6" Diameter
Plexiglas
Column
5'
Collector
Cyclone
4'
Sample and Pressure
Taps
3'
2'
Overflow
Discharge
Side Outlets
1'
0.5
0.25
Air
Underflow
Control Valve
Flowmeter

Figure 4

TWO-TRAY FLUID-BED REACTOR

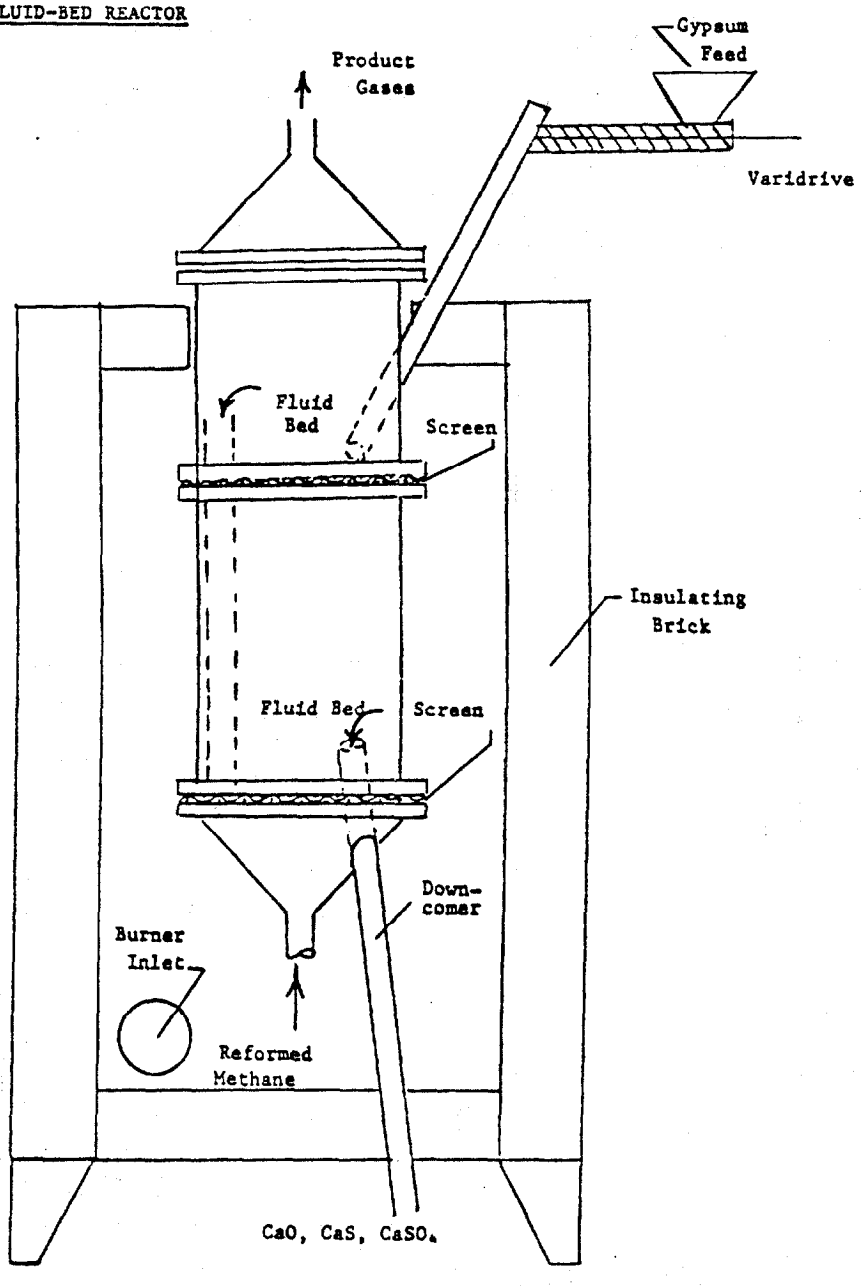


Figure 5

BENCH-SCALE FLUIDIZED REACTOR

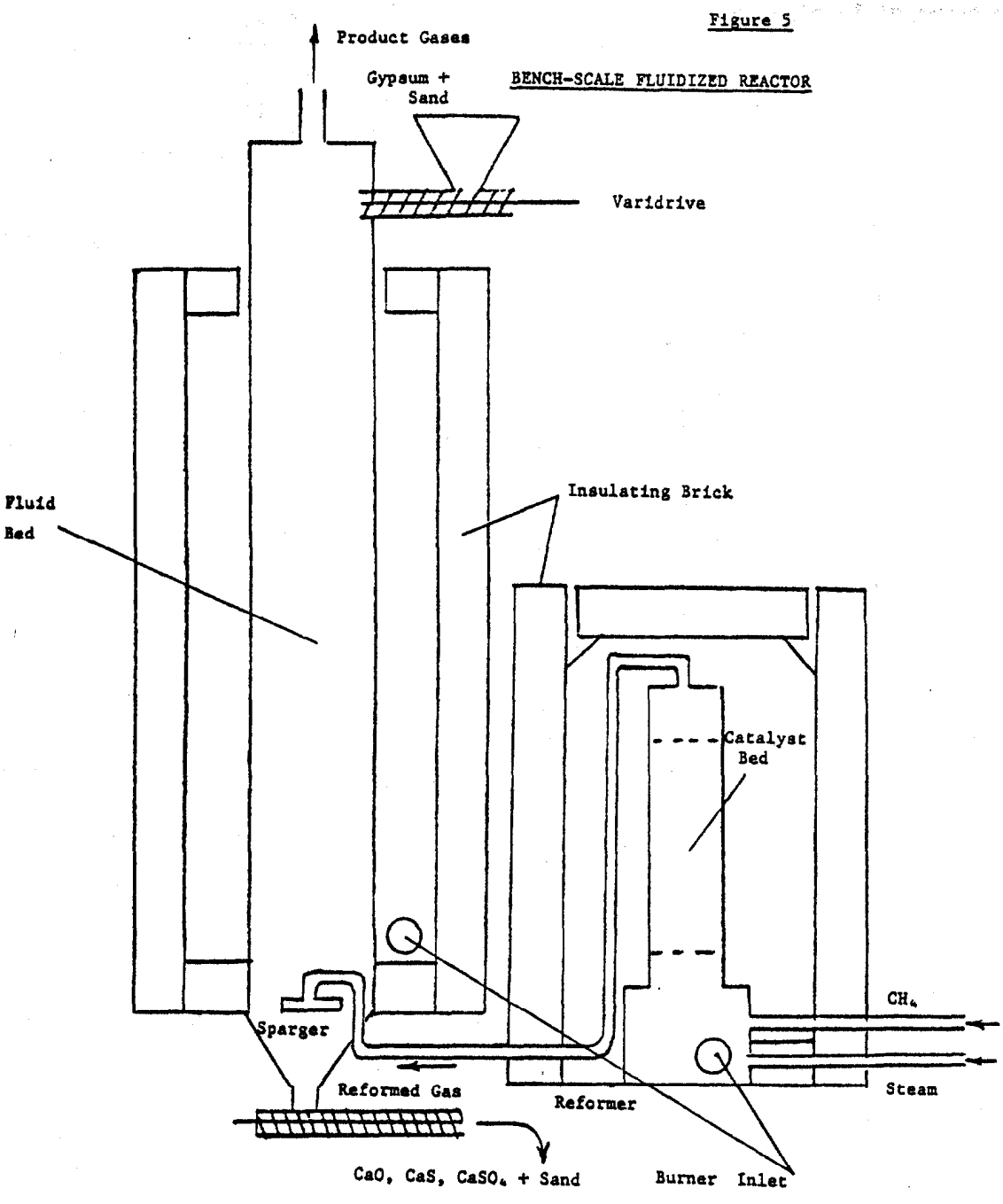
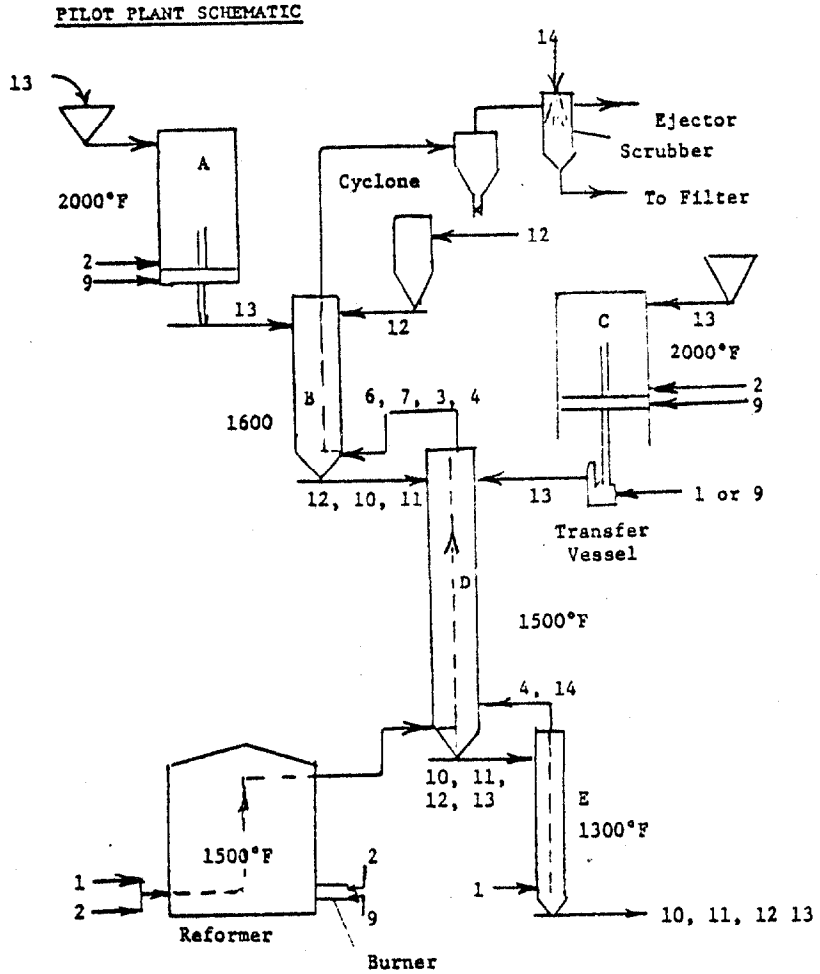


Figure 6

PILOT PLANT SCHEMATIC



1.	Steam	6.	H_2	11.	CaS
2.	CH_4	7.	CO_2	12.	$CaSO_4$
3.	SO_2	8.	CO	13.	Sand
4.	H_2S	9.	Air	14.	Water
5.	N_2	10.	CaO		

DESULFURIZATION OF PHOSPHOGYPSUM

by

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INTRODUCTION

The conversion of phosphogypsum into sulfuric acid may be attractive use for this material where conditions are appropriate since the acid can be recycled thereby fulfilling most of the sulfur requirements of the phosphoric acid manufacturer. This method of utilization is practiced in both Austria and South Africa where two industrial plants employing the OSW-Krupp process produce concentrated sulfuric acid and Portland cement in about equal amounts from phosphogypsum. The OSW-Krupp process is a derivative of the earlier Mueller-Kuhne process which was demonstrated in Germany over 60 years ago.

Although other methods of converting either mineral gypsum or phosphogypsum into sulfuric acid have been proposed, none are fully developed. Nevertheless, at least one alternate method which has been studied extensively at Iowa State University shows considerable promise. This method produces lime rather than Portland cement as a by-product and entails a lower capital investment since fewer materials are handled and a cement plant is not involved.

Both the processes in use and the proposed method involve decomposition of calcium sulfate at high temperature in the presence of reducing agents. However, the process conditions, reaction systems, and reducing agents are markedly different. To lay the groundwork for a discussion of these processes, the general principles underlying the desulfurization of calcium sulfate at high temperatures are reviewed below. Detailed descriptions of the processes of interest are then presented covering reaction systems, process flowsheets, operating conditions, and raw materials and energy requirements. In addition, problems caused by the unique properties of phosphogypsum are mentioned.

Desulfurization Principles. Since most of the methods used or proposed for desulfurizing gypsum involve reactions at high temperature, it is worth noting the changes which, take place when pure gypsum is heated to higher and higher temperatures in air. At about 180°C pure gypsum loses three-fourths of its water of hydration to form soluble anhydrite (v-$CaSO_4$). Soluble anhydrite changes to insoluble anhydrite (β-$CaSO_4$) at 360°C, and insoluble anhydrite undergoes a change in crystal structure at about 1225°C to form α-$CaSO_4$. At this temperature a small amount of anhydrite decomposes to form calcium oxide and sulfur oxides. Upon further heating, the eutectic mixture of calcium oxide and calcium sulfate melts at 1385°C.

Pure calcium sulfate is relatively stable towards decomposition at temperatures as high as 1200°C as shown by the large positive standard free energy change for reaction 1 listed in Table 1. Even at 1280°C the measured equilibrium decomposition pressure of calcium sulfate was observed to be only 0.02 atm.[2,3] Therefore, pure calcium sulfate will decompose at high temperature only as long as the gaseous products of reaction are removed and the concentrations of sulfur dioxide and oxygen in contact with the solids are kept very low. While particles of mineral gypsum have been decomposed almost quantitatively in a reasonable time by heating them to 1225°C in a stream of nitrogen, this method is not very practical for an industrial operation because, off the resulting low concentration of sulfur dioxide.[4]

A much higher concentration of sulfur dioxide can be obtained by reacting calcium sulfate with silica, alumina, or iron oxide at high temperature. This can be anticipated from the more favorable free energy change for reaction 2 (Table 1) and similar reactions involving other metal oxides compared to the free energy change for reaction 1. Moreover, it has been shown experimentally that the decomposition pressure of calcium sulfate in the presence of various metal oxides is much higher than that of pure calcium sulfate (5,6). Stinson and Mumma (7) took advantage of this principle to desulfurize phosphogypsum in a series of laboratory experiments in which the material was first mixed with fine silica sand and formed into pellets ranging in size from Ø.6 to 2.5 cm. in diameter. When pellets containing equal molar quantities of calcium sulfate and silica were calcined at 125Ø° for one hour in a small stream of air, about 9Ø% of the sulfur was volatized. Nearly 1ØØ% of the sulfur was volatilized at 125Ø°C in 15 minutes when 4% iron oxide was also incorporated in the pellets. In both cases the material was not fused. Although the concentration or sulfur dioxide in the air stream was not reported, it is estimated that the off-gases from a large calcination plant would contain at least 5% sulfur dioxide.

In the processes which have been applied on a large industrial scale, calcium sulfate is desulfurized by reaction with a solid reducing agent at high temperature. While the direct desulfurization of calcium sulfate by reaction with carbon according to reaction 3 (Table 1) appears quite favorable because of the negative free energy change accompanying this reaction, in practice it is difficult to accomplish because the formation of calcium sulfide by reaction 4 is also strongly favored. Indeed the kinetics of reaction 3 also seem to suffer in comparison with those of reaction 4 (8). Consequently when calcium sulfate particles are reacted with excess carbon-at high temperature, the solids are largely converted to calcium sulfide. This problem is circumvented in the Mueller-Kuhne process and related processes by reacting only a portion of the calcium sulfate with carbon or coke via reaction 4 (9,10). The extent of this reaction is controlled by limiting the amount of carbon or coke which is fed to about Ø.5 mole per mole of calcium sulfate. The resulting calcium sulfide is then reacted with the remaining calcium sulfate according to reaction 5. The two steps accomplish the same overall results as reaction 3 would accomplish if it could be carried out by itself.

Even though gaseous reducing agents have not been used industrially for desulfurizing gypsum, carbon monoxide and hydrogen show considerable promise. Conditions have been established which favor reactions 6 and 7 leading to desulfurization over reactions 8 and 9 forming calcium sulfide (11,12). These conditions include the use of temperatures close to 12ØØ°C, limited concentrations of carbon dioxide and water vapor. For example, 2.6mm diameter particles of mineral gypsum in a shallow bed were desulfurized rapidly and completely when a gas stream containing 3% CO, 2Ø% CO_2 and 5% SO_2 was passed through the bed at 12ØØ°C. Moreover, the reacted solids were essentially free of calcium sulfide. Temperatures much higher or lower than 12ØØ°C led to a reduced overall rate of desulfurization. Particles heated above 125Ø°C developed a glazed surface which probably interfered with gas diffusion. On the other hand, when the temperature was below the optimum value, calcium sulfide appeared in the residue with the amount increasing as the temperature fell.

Another method of desulfurization which has attracted considerable interest involves complete reduction of calcium sulfate to calcium sulfide by reactions 8 and 9 at 1000°C followed by the reaction of calcium sulfide with water and carbon dioxide at much lower temperature to form calcium carbonate and hydrogen sulfide as indicated below.[13]

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

The hydrogen sulfide can then be converted to elemental sulfur by the Claus reaction. Although an industrial scale plant was built in Texas to demonstrate this process, it was shut down after a short time.

A further discussion and review of these principles may be found in the report by Swift et al (14).

Process Producing Cement as a By-product. The initial development of the Mueller-Kuhne process which produces sulfuric acid (and about an equal amount of Portland cement as a by-product) took place in Germany during World War I when the importation of Spanish pyrites was cut off (9,10,15). A small semi-commercial plant was built at Leverkusen to utilize natural gypsum or anhydrite. The plant employed two small cement kilns and produced about 40 ton/day of acid. It operated until 1931. Further development took place in England where a full-scale commercial plant using anhydrite was built at Billingham in 1929. After several deficiencies were overcome, the plant reached an output of 300 ton/day in 1935. It was expanded later to 500 ton/day. Other commercial plants utilizing gypsum or anhydrite were subsequently put into operation in various countries (Table 2).

In the late 1960's, additional development of the Mueller-Kuhne process took place in Austria, England, East Germany, and the United States to utilize phosphogypsum (10). The effort by Oesterreichische Stickstoffwerke AG (now Chemie Linz AG) in Austria was successful and a plant which had operated on mineral anhydrite was converted to phosphogypsum in 1969. This experience led to the design of the first plant based on phosphogypsum from its inception. The plant was engineered by Krupp Chemieanlagenbau (now Krupp-Koppers GmbH) and constructed for Fedmis (Pty.) Ltd. in Phalaborwa, South Africa. It has been on stream since 1972. The process used in the Austrian and South African plants is now referred to as the OSW-Krupp process.

Other plants located in Coswig, East Germany, and Wizow, Poland, were also adapted to phosphogypsum (10,16,17). However, it is not known whether these plants presently utilize phosphogypsum. These plants and the Austrian and South African plants are the only ones known to be in operation at present. All the other plants listed in Table 2 have either shut down or been converted to other raw materials.

The Mueller-Kuhne process has been described in detail as it was applied at the Whitehaven plant in England (9). The feed for this plant was a mixture of anhydrite (78%), shale (16%), and coke (6%). These materials were dried, mixed, and then ground in tube mills. The meal was further blended to insure a properly proportioned mixture and next formed into pellets or nodules having a diameter of 6 to 12 mm. The

pellets were fed to large rotary kilns fired with coal. In the kiln, reaction 4 (Table 1) took place when the solids attained a temperature above 900°C followed by reaction 5 at somewhat higher temperatures. As a consequence of these reactions most of the sulfur was converted to sulfur dioxide and carried away in the off-gas. As the desulfurized solids continued their passage through the kiln, they were heated to 1400-1500°C where the calcium oxide reacted with the shale to form cement clinker. The clinker discharged from the kiln was cooled, blended with a small amount of gypsum, and ground to produce high-quality cement. The kiln off-gas containing about 9% sulfur dioxide was cooled and subsequently cleaned by a series of cyclones, wet scrubbers and electrostatis precipitators. The clean gas was diluted with air so that it contained about 5% sulfur dioxide as it was introduced into a conventional contact plant for the production of 98% sulfuric acid and oleum.

In adapting the Mueller-Kuhne process to phosphogypsum, serious consideration had to be given to the effect of certain impurities and the possibly high moisture content of the material (10,18,19,20). Phosphogypsum recovered as a filter cake may contain about 25% water in addition to its water of crystallization. Among various impurities, phosphate, fluoride and radium are of greatest concern. Phosphogypsum produced by a conventional dihydrate process may contain 0.45 to 1.5% P_2O_5, up to 1.5%F, and a trace of radium depending on the source of phosphate rock. While the phosphate content of phosphogypsum produced by a hemihydrate process is lower, it is not insignificant and may range up to 0.5% P_2O_5. When such materials are treated by the Mueller-Kuhne process, the phosphate is concentrated in the clinker so that the phosphate content of the clinker is about twice that of the phosphogypsum. Unfortunately, the phosphate interferes with the formation of tricalcium silicate in the clinker. Since this is the main component responsible for early strength when the cement is hydrated, cement quality suffers.

Although up to 40% of the fluorine may be converted to volatile compounds in the kiln and removed in the off-gas, the residual fluoride content of the clinker may also have a deleterious effect on cement quality (10,18,19,20). In addition, the fluorine compounds in the gas can destroy the sulfuric acid plant catalyst if not removed completely.

While the concentration of radioactive materials in phosphogypsum may be too low to cause a problem in some cases, it may be high enough in others to require special control measures. This appears to be an area which requires further study.

Because of the detrimental effects of phosphate and fluoride, the phosphogypsum used in the OSW-Krupp process should not have more than 0.5% P_2O_5 and 0.15%F (10,20). In Austria this requirement has been met by blending phosphogypsum with 'natural anhydrite. The hemihydrate used in South Africa is not a problem because it contains only 0.2 - 0.3% P_2O_5 as produced by the Central Prayon Process.

The OSW-Krupp process appears to differ from the earlier versions of the Mueller-Kuhne process in mechanical and engineering improvements which have increased the overall efficiency of the process but not changed the basic character of the method (10,21-24). A simplified flowsheet of the process (Figure 1) is similar to those for other versions of the Mueller-Kuhne process. One obvious difference is the incorporation of a Krupp countercurrent heat exchanger at the solids feed end of the rotary kiln. Such an exchanger is used at the Linz plant but not at the Phalaborwa plant. The exchanger is reported to have reduced the energy consumption of the kiln by 15-20%. Also tertiary air is supplied through the kiln shell to provide a slightly oxidizing atmosphere near the solids feed end. This measure insures that the off-gas is fully oxidized and prevents problems arising from the presence of elemental sulfur or reduced sulfur compounds in the gas. Furthermore, instrumentation for measuring and controlling kiln operating conditions has been greatly improved. To cope with the volatile fluorine compounds in the kiln gas when phosphogypsum is used, the gas is scrubbed thoroughly with water in lead--lined towers. A Peabody scrubber is used for this purpose in the Phalaborwa plant (24).

Single kilns are employed at both the Linz and Phalaborwa plants. At Linz the kiln is a multidiameter (2.8 or 3.0 m I.D.) cylinder 70.7 m in length capable of producing 200 m. ton/day of clinker without the Krupp heat exchanger and somewhat more with the heat exchanger (25). At Phalaborwa the kiln is a cylinder of uniform diameter (3.8 m I.D.) with a length of 107 m, and it is capable of producing 320-350 m. ton/day of clinker without a Krupp heat exchanger. The technology is presently available for designing and building single kilns capable of producing 600 m. ton/day of clinker when used in conjunction with a Krupp heat exchanger, and it is anticipated that kilns capable of producing 1000 m. ton/day of clinker can be built in the future (26). A 600 m. ton/day kiln would have an inside diameter of 5.5 m. and length of 120 m.

If a new plant employing the OSW-Krupp process were built now, the minimum economical size would probably be at least 500 m. ton/day (10). The capital cost of such a plant would be about five times that of a sulfur-burning plant producing an equivalent amount of acid but, of course, it would also produce cement. The plant would require approximately 60 operators and laboratory workers exclusive of administrative and maintenance personnel (10,22). Raw materials and utilities which would be consumed in producing 1 m. ton each of acid and cement are listed in Table 3. The fuel requirement is based on feeding phosphogypsum containing a total water content of 30-40% as would be the case for a wet filter cake from a phosphoric acid plant producing dihydrate. The fuel requirement would be lower if hemihydrate were fed. It is claimed that 98% sulfuric acid can be produced containing a maximum of 0.01% SO_2 and 0.0035% Fe. Also with a double adsorption sulfuric acid unit, the conversion of sulfur dioxide into sulfur trioxide should be 99.5% with a maximum concentration of 50 ppm of particulates in the gas vented to the atmosphere. Furthermore, the Portland cement should meet applicable Austrian (B3310) and German (DIN 1164) standards.

The process which has evolved in East Germany for treating phosphogypsum appears rather similar to the one described above (10,16,17).

The phosphogypsum is precalcined to remove moisture and part of the fluorine. It is mixed with clay and sand which have also been dried and with coke. The mixture is heated in a rotary kiln where the optimum temperatures for reactions 4 and 5 are 900 and 1200°C, respectively. A sintering temperature of 1420-1480°C is used for the clinker-forming reactions. The kiln gas is cleaned by three stages of electrostatic precipitation and two stages of wet scrubbing interspersed between the precipitators. The raw materials and energy requirements are similar to those reported for the previous process, but the capital cost of a plant appears higher at seven times the cost of a comparable sulfur-burning plant.

A Process for Producing Lime as a By-Product. An alternative to the Mueller-Kuhne approach is to react gypsum or anhydrite with a reducing gas at high temperature to produce sulfur dioxide and lime. The sulfur dioxide is converted into sulfuric, acid as in the Mueller-Kuhne process while the lime is recovered without further reaction. Such a process was suggested by Fleck (27) over 50 years ago when he proposed heating calcium sulfate in a rotary kiln fired with coal gas or producer gas and insufficient air for complete combustion so as to provide a reducing flame. A much later study at Iowa State University of the conditions affecting reactions 6 to 9 led to the conclusion that this type of process could best be carried out in a fluidized bed reactor with in situ combustion of fuel (11,28,29). Such a reactor would provide good contact between gases and solids and facilitate both heat and mass transfer. Also it would provide a more uniform temperature than other devices and would facilitate close control of operating conditions. Moreover, almost any hydrocarbon fuel could be burned in a fluidized bed, and by limiting the air to fuel ratio, sufficient carbon monoxide and hydrogen could be produced for the reactions with calcium sulfate. Furthermore, sufficient heat could be generated to supply the thermal requirements of reactions 6 and 7 which are highly endothermic.

The possibility of desulfurizing natural gypsum in a fluidized bed reactor heated with natural gas was demonstrated to a limited extent by Bollen (30) and by Martin, et al (31). Somewhat later a more comprehensive demonstration was conducted by Hanson, et al (32-34) with a fluidized bed reactor having an inside diameter of 25.4,cm and height of 2.6 m also heated with natural gas. Operation of this unit under appropriate conditions led to 97% desulfurization of natural anhydrite and the production of an effluent gas containing 9% sulfur dioxide. A reactive limit suitable for most applications of quicklime was produced. While these results were highly encouraging, it appeared that rather careful control of process conditions would be required. Also, previous work at Iowa State University had shown that if the temperature was too low or the reducing gas concentration too high, an appreciable amount of calcium sulfide would be formed (11). On the other hand, if the temperature was too high, the solids would sinter and reduce the rate of reaction, or the rate of reaction would also be slow if the reducing gas concentration was low. To overcome these difficulties, the two-zone fluidized bed reactor was conceived (35,36).

In a two-zone reactor, reducing conditions are maintained in one zone and oxidizing conditions in another (35,36). Because of the natural

circulation of solids in a fluidized bed, the particles are exposed alternately to oxidation and reduction. Because of the natural circulation of solids in a fluidized bed, the particles are exposed alternately to oxidation and reduction. The different zones are created by supply different ratios of air to fuel in these zones. Thus by supplying the bottom of a fluidized bed with a relatively low air-to-fuel ratio a highly reducing zone is established in the lower part of the bed, and by introducing additional excess air at an intermediate level in the bed, an oxidizing zone of established in the upper part. While the solids pass through the reducing zone, reactions 6 to 9 take place converting calcium sulfate to either calcium oxide or calcium sulfide. Then as the solids pass through the oxidizing zone, the calcium sulfide is oxidized to either calcium oxide or calcium sulfate according to the following reactions:

$$CaS + 3/2 = CaO + SO_2$$

$$CaS + 2\ O_2 = CaSO_4$$

Since the reactions producing calcium oxide and sulfur dioxide are the predominant ones, the solids are desulfurized after making several passes through both zones. In this system the reactions which produce calcium sulfide cause little difficulty, whereas in a single-zone reaction system these reactions create a serious problem.

The two-zone reactor concept was proven using a bench-scale fluidized bed reactor having an inside diameter of 12 cm and bed depth of 25-28 cm (35). In several tests conducted at 1150-1200°C, particles of natural gypsum or anhydrite were 99% desulfurized and an effluent gas containing 5 to 10% sulfur dioxide was produced. Also, the calcium sulfide content of the lime product was very low, even when the reactor was operated at temperatures at low as 1045°C, but of course the rate of reaction was reduced. Moreover, the results were not greatly affected by other changes in operating conditions which would have had a very deleterious effect in a single-zone reactor.

Although the one-zone and the two-zone systems provide greatly different reaction environments from the standpoint of chemical kinetics, they do not differ overall from the standpoint of thermodynamics. Therefore, the energy requirements and the equilibrium concentration of sulfur dioxide in the effluent gas is the same for either system. A detailed thermodynamic analysis of these systems has shown that both the fuel requirements and equilibrium concentration of sulfur dioxide are greatly affected by the overall thermal efficiency of the systems (37). Thus, by recovering the sensible heat in the products and utilizing it to preheat the reactants in an optimal manner, the fuel requirements can be cut in half and the air requirements by two-thirds. Also, the equilibrium sulfur dioxide concentration can be more than doubled. For example, if methane is used as a fuel, the maximum possible concentration of sulfur dioxide at 1200°C is 7.0% without heat recovery and 16.6% with optimal heat recovery based on published thermodynamic data.

In practice it is not possible to achieve complete heat recovery. The proposed design in Figure 2 for a plant which would produce sulfuric acid and lime from gypsum involves a compromise between heat recovery and capital cost. The fuel requirement for such a plant would be 40% greater than the absolute minimum for a plant with a complete heat recovery system. Nevertheless, with what appears to be a practical design it should be possible to produce an effluent gas with close to 12.6% sulfur dioxide. After this gas is dried and diluted with air, the gas entering the catalytic converter would contain 7% sulfur dioxide or more.

The proposed design in Figure 2 makes use of a two-zone fluidized bed reactor which is supplied with either crushed or pelletized gypsum, fuel and air. A countercurrent heat exchanger similar to the Krupp device is mounted above the reactor. As the gypsum flows downward through the exchanger it comes in direct contact with the upward flowing hot gas from the reactor. The partially cooled gas then flows to a cycline dust separator and to another heat exchanger where additional heat is given up and used to preheat combustion air for the fluidized bed reactor. The gas then continues on through an electrostatic precipitator, wet scrubber, electrostatic mist precipitator, drying tower and other components of a sulfuric acid plant much as it would in the Mueller-Kuhne process. The reacted solids are withdrawn from the fluidized bed reactor, cooled and conveyed to storage. For every ton of acid produced, 0.57 ton of lime is produced.

An industrial plant based on this design should be able to utilize a variety of fuels because the fluidized bed combustion of coal, oil and gas been demonstrated on a fairly large scale. On the other hand, the conditions required for desulfurizing gypsum and the two-zone reactor have only been tested on a small scale. Even so, at least one two-zone reactor has successfully utilized either natural gas or high volatile bituminous coal to desulfurize calcium sulfate (38). For the tests involving coal, a fluidized bed diameter of 10.8 cm and height of 46 cm were used.

In adapting this process to phosphogypsum consideration needs to be given to the higher moisture content and small particle size of this material and to the types and amounts of various impurities which are present in it. In all likelihood the material would first have to be dried and pelletized to provide particles suitable for fluidization. Many of the possible impurities such as phosphate would probably be unaffected by the process. These impurities would remain in the solids and could have some bearing on the possible uses for the by-product lime. Other possible impurities such as fluorides and iron oxides could reduce the sintering temperature of the solids to an unacceptable level. Appreciable sintering should be avoided because it could interfere with gas diffusion within individual particles and with fluidization by causing particles to stick together. A significant portion of the fluoride could be converted to volatile fluorine compounds as in the Mueller-Kuhne process. These compounds have to be removed from the effluent gas by wet scrubbing.

A substantial effort will be required to adapt the proposed process to phosphogypsum and to complete the development of the two-zone fluidized bed reactor system. In this regard, further tests should be conducted with a bench-scale fluidized bed reactor to, see whether phosphogypsum presents any unusual problems and. to establish the best combination of operating conditions for this material. If these tests are encouraging, the phosphogypsum desulfurization step should be demonstrated in a large pilot plant before building a commercial prototype plant.

Assuming that the development effort is successful and that phosphogypsum can be treated by the process shown in Figure 2, the projected quantities of calcium sulfate, fuel and other utilities required to produce 1 m. ton H_2SO_4 and Ø.57 m. ton CaO by this process are listed in Table 3. The fuel requirement for drying is based on the dehydration of a wet filter cake of the dihydrate form of phosphogypsum. While the phosphogypsum and fuel requirements for the proposed process are similar to those for the OSW-Krupp process, less electrical power and none of the cement-forming additives or coke are required.

An estimate made some years ago showed that a plant producing sulfuric acid and lime from anhydrite would require a capital investment 2.2 times greater than an equivalent plant producing acid from brimstone (28). Therefore; taking into account the additional cost of equipment for drying and pelletizing phosphogypsum, it can be anticipated that a plant based on the design of Figure 2 will cost at least 2.5 times more than a plant producing acid from sulfur.

Summary and Conclusions. Phosphogypsum is presently utilized in at least two industrial plants for the production of sulfuric acid and Portland cement. These plants employ updated versions of the Mueller-Kuhne process which was developed many years ago in Germany and England for utilizing natural gypsum and anhydrite. In this process calcium sulfate is partially reduced with coke at high temperatures in a rotary kiln to form lime which then reacts under sintering conditions with clay or shale to form cement clinker. Sulfur dioxide is also produced in the kiln, and after purification it is converted into sulfuric acid. In order to use phosphogypsum in this process, both the phosphate and fluoride contents of the material must be limited because these impurities exert a deleterious effect on the cement. Since some of the fluoride is converted into volatile fluorine compounds, the sulfur dioxide-bearing gas must be thoroughly scrubbed with water to prevent these compounds from reaching the sulfuric acid plant catalyst. The capital cost of a large plant which produces acid and cement from phosphogypsum is five to seven times that of a comparable sulfur-burning plant which produces only acid.

Other alternatives are available but require development. One promising method involves reacting calcium sulfate with reducing gases at high temperatures in a fluidized bed reactor to produce sulfur dioxide and lime. The necessary reducing gases and heat absorbed by the reaction of calcium sulfate are supplied by the in situ combustion of coal, oil or natural gas. The lime is not reacted further while the reactor off-gas is purified and converted into sulfuric acid as in the

previous process. The calcium sulfate decomposition step has been demonstrated in large bench-scale reactors with natural gypsum and anhydrite but requires further demonstration with phosphogypsum. Although some impurities present in phosphogypsum may interfere with the operation of a fluidized bed system by lowering the sintering temperature of the solids, other impurities such as phosphate should cause no problems. In general, impurities should be less of a problem than in the preceding process, unless it is necessary to produce very pure quicklime. The principal contaminants of the lime will be a few percent of phosphate and sulfate. While the capital cost of a plant for producing sulfuric acid and lime from phosphogypsum will be at least 2.5 times greater than that for a plant producing acid from sulfur., it will be much lower than that for a plant producing acid and Portland cement from phosphogypsum. The lower cost results from not having the cement manufacturing facilities including equipment for drying,, storing and handling additional raw materials and from being able to produce sulfuric acid from a gas containing a significantly higher concentration of sulfur dioxide.

Any sulfuric acid plant which makes use of phosphogypsum will require a relatively large input of energy, whereas an acid plant which uses sulfur will produce a surplus of energy in the form of by-product steam. On the other hand, by using phosphogypsum a waste disposal problem can be avoided, and a producer of phosphoric acid can be largely independent from a volatile sulfur market. For producers located in countries without indigenous sources of sulfur, the saving in foreign exchange payments can also be very important.

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Table 1. Calculated standard free energy change (ΔF^{o}) and heat of reaction (ΔH^{o}) at 1200°C for various reactions.

	Reaction	kcal./mole $CaSO_4$	
		ΔF^{o}	ΔH^{o}
1.	$CaSO_4 = CaO + SO_2 + 1/2\ O_2$	24.40	109.1
2.	$CaSO_4 + SiO_2 = CaSiO_3 + SO_2 + 1/2\ O_2$	2.09	86.7
3.	$CaSO_4 + \frac{1}{2}\ C = CaO + SO_2 + 1/2\ CO_2$	-22.97	62.3
4.	$CaSO_4 + 2\ C = CaS + 2\ CO_2$	-83.27	30.0
5.	$CaSO_4 + 1/3\ CaS = 4/3\ CaO + 4/3\ SO_2$	- 2.87	72.5
6.	$CaSO_4 + H_2 = CaO + SO_2 + H_2O$	-15.21	49.3
7.	$CaSO_4 + CO = CaO + SO_2 + CO_2$	-12.55	42.1
8.	$CaSO_4 + 4\ H_2 = CaS + 4\ H_2O$	-52.23	- 20.6
9.	$CaSO_4 + 4\ CO = CaS + 4\ CO_2$	-41.59	- 49.3

Table 2. Plants built to produce sulfuric acid and Portland cement in equal amounts from calcium sulfate.

Location	Year	Feed	Capacity, ton/day
Leverkusen, Ger.	1916	Gyp./Anh.	40
Wolfen, Ger.	1938	Anhydrite	400
Billingham, U.K.	1929	Anhydrite	500
Widnes, U.K.	1955	Anhydrite	580
Whitehaven, U.K.	1955	Anhydrite	1075
Miramas, Fr.	1937	Gypsum	70
St. Chamas, Fr.	- -	- - -	- -
Linz, Austria	1954	Phos. gypsum	230
Phalaborwa, S. Af.	1972	Phos. gypsum	350
Coswig, E. Ger.	- -	- - -	850
Wizow, Poland	1952	- - -	520

Table 3. Raw materials and utilities needed to produce 1 m. ton H_2SO_4 from phosphogypsum by two methods.

	OSW-Krupp process	Proposed process
Raw materials		
Gypsum (as $CaSO_4$), m. ton	1.64	1.50
Clay, m. ton	0.07	- -
Sand, m. ton	0.07	- -
Coke, m. ton	0.10	- -
Gypsum (add to cement), m. ton	0.04	- -
Utilities		
Cooling water, cu. m.	80	60
Electric power, kWh	230	100
Fuel - drying, 10^{-6} kcal	- -	0.9
- calcining, 10^{-6} kcal	- -	2.1
- Total, 10^{-6} kcal	2.8	3.0

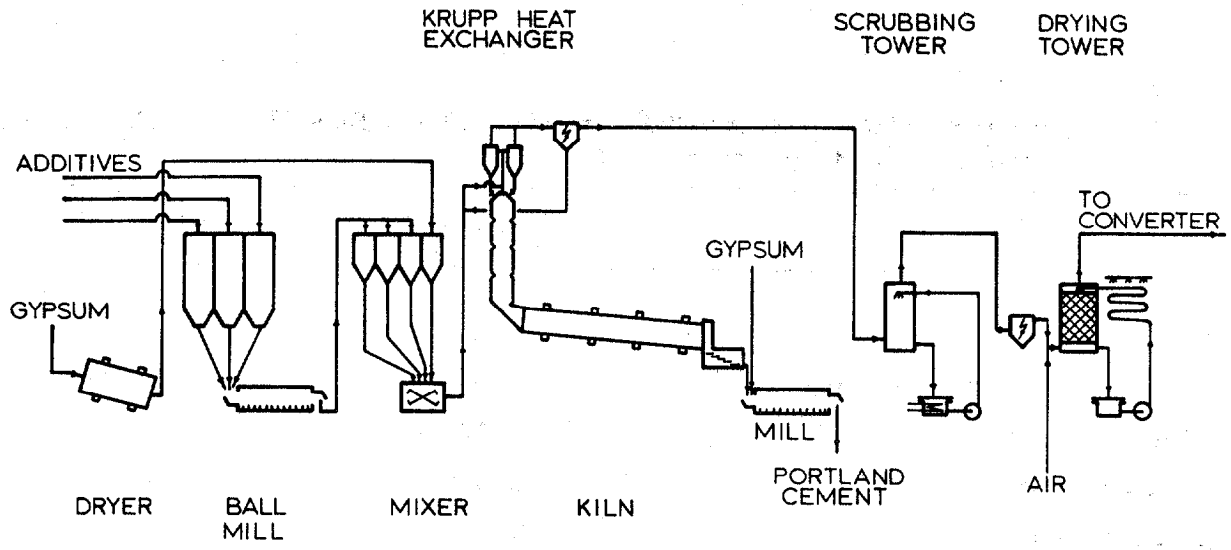


Figure 1. The OSW-Krupp process for producing sulfuric acid and Portland cement.

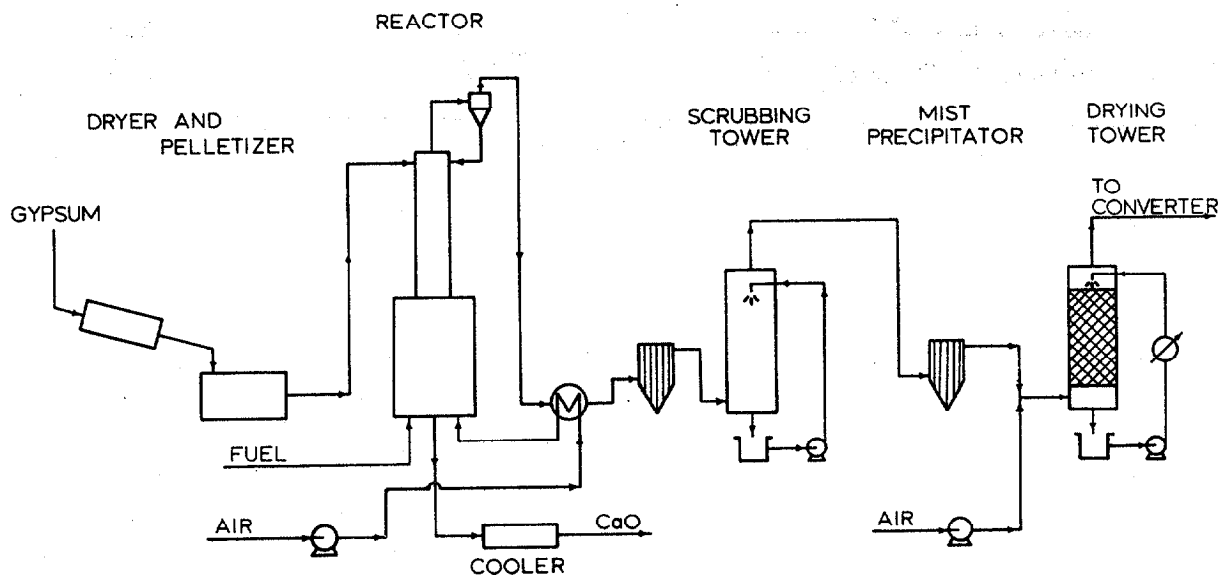


Figure 2. The proposed process for producing sulfuric acid and quick lime.

SOME ASPECTS OF SULFURIC ACID AND CLINKER CEMENT PRODUCTION FROM PHOSPHOGYPSUM

by

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INTRODUCTION

Manufacture of phosphoric acid through the wet-process route results in some 4-5 tons impure calcium sulphate per ton of acid, as P_2O_5. Phosphogypsum is a very cumbersome co-product because of storing and eventual further processing.

I described a weekly trial of applying phosphogypsum on a technical plant for sulfuric acid and clinker cement production (Przemysl Chemiczny 6, 1977). The experiment was carried out in Zaklady Chemiczne Wizow in Poland in 1973.

Replacing anhydrite with phosphogypsum appeared to be successful and gave reasons for feeding the installation with phosphogypsum at a long range. It was not a single trial, of course. You can get a lot more experimental data from my article entitled "Development of binding materials in Zaklady Chemiczne Wizow" to be published in "Cement, wapno, gips" in Poland in 1981.

Thirty years of practice with anhydrite and seven years of adaption of phosphogypsum - anhydrite mixture has given us strong experience in this area. A few big installations for sulfuric acid production were built up on the basis of a cheap and simple way to use the raw material: elemental sulfur during the 1960's in Poland. Contrary to the judgment of some economists, sulfuric acid manufacture from anhydrite survived thanks to the co-production of high quality clinker cement. Its strength amounted to over 400 kG/cm^2. It should be noted that quality of sulfuric acid from anhydrite effectively rivals the acid from sulfur. There are some advantages of sulfuric acid production from phosphogypsum such as: better protection of environment; phosphogypsum as a by-product is the cheapest raw material; it need not be milled; and its composition is far more stable than that of anhydrite.

The higher level of concentrations of water, phosphorus and fluorine in phosphogypsum compared to anhydrite is a widely known disadvantage. The Portland clinker comprises systems which have been formed from the four basic components: CaO = 22%, Al_2O_3 = 5% and Fe_2O_3 = 4%. The content of other ingredients amount to approximately 3%. In cement industry the clinker cement is being produced from the limestone $CaCO_3$. However, the sintering of Portland cement from calcium sulfate runs in other conditions for there are additional components in phosphogypsum mentioned above. In this way the clinker is a more multicomponent system.

The clinker materials are being formed along with decomposition of $CaSO_4$ and instant shortage of a free lime component. The temperature of decomposition of $CaSO_4$ is higher than of $CaCO_3$ which involves exceptional conditions of origination, new minerals and high activated silica. The chemical composition of clinker from phosphogypsum is slightly different from that one from limestone $CaCO_3$.

However, the same rules of chemical calculations have to hold. The two norms for Portland clinker from calcium sulphate are obligatory in Poland how i.e. Norm BN-64/6731-Ø3 and Norm BN-71/6731-14. According to the norm, quantity of sulfates cannot exceed 3%, sulfur in sulfides not more than Ø.5%. Compounds of phosphorus and fluorine are not being normalized. Stability and chemical composition of rotatory kiln furnace charge are the most important factors in the sulfates technology clinker production. Composition of the flour should be such that after sintering, with regard to ashes, the following clinker moduli must hold:

1. The aluminum modulus

$$M_A = \frac{Al_2O_3}{Fe_2O_3} = 3.7 \pm 0.7$$

2. The silica modulus

$$M_S = \frac{SiO_2 - SiO_2 \text{ free}}{Al_2O_3 + Fe_2O_3} = 2.6 \pm 0.3$$

3. The lime saturation modulus regarding phosphoric and fluorine compounds

$$M_N = \frac{CaO\text{-}CaO\text{free-}/1{,}65Al_2O_3 + 0{,}35Fe_2O_3 + 0{,}7SO_3 + 1{,}18P_2O_5 + 1{,}47F/}{2{,}80/SiO_2 - SiO_2\text{free}/} = \underline{0{,}88} + 0{,}3$$

4. The reducing modulus

$$M_R = \frac{CaSO_4}{C} = 19 \pm 2$$

If the above moduli are maintained together with normal concentrations of SO_3/1, 8%/, P_2O_5/ 2%/, fluorine/ Ø,35%/, the quality of clinker cement refers it to the 359 mark of cement.

It is known, however, that modulus values in clinker and furnace charge must be the same regarding to fuel ashes. Following the above, contributions of particular ingredients should be:

$CaSO_4$ - 8Ø%, SiO_2 - 1Ø%, C - 4.2%, $Al_2O_3 + Fe_2O_3$ - 3% and other components.

After solving a few mass balance, relations of the raw materials are as follows: dry phosphogypsum - 84.Ø%; fine coke - 4.6%; sand - 6.7%; coal ashes - 4.7%. The process can be easily automated when instrumental analysis is being applied. The computer analysis and control can keep the amounts of raw materials at constant level. The chemical compound of the furnace charge, its stability, and rotary kiln atmosphere are the most important factors while sintering clinker. The atmosphere should be neutral or slightly reductive. For this reason suitable proportions between the flour, fuel and air have to be kept. Theoretically, producing one kilogramme of clinker entails 19ØØ kcal at the sintering temperature i.e. 135Ø°C. Thus, the using up of coal along with drying processes amounts to 35Ø kg per one ton of clinker/calorific value - 7,ØØØ kcal per kilogramme.

Decomposition of the furnace charge and sintering minerals in a rotary kiln belongs to a difficult process. The theory of this process is not simple and requires individual description.

On the other hand, converting kiln gases into sulfuric acid need not be precisely discussed. The kiln gases contain 8% SO_2, 20.5% CO_2, 1% elemental sulfur and traces of oxygen. The gravitational and electrostatic dust cleaning is followed by washing and drying of gases. The composition of dry gases before the contact installation is 5.5% and 9.0% O_2 approximately. The contact installation is thermally self-supporting. The adsorption of SO_3 does not pose any problem. The exiting sulfuric acid contains 95-99% H_2SO_4 and 20% free of SO_3.

The Preparation of Raw Materials. It is very important to pay attention to preparation of powdered furnace charge. Its quality strongly influences the standard of clinker cement and the work of kilns. The composition and granulation of flour must be precise. However, not all components should be identically milled. Particles of anhydrite and fine coke can be larger than those of sand and coal ashes. In our plant, phosphogypsum is not being milled, and as experience shows, it can be dried until 15% of water remains. The other constituents should be dried and stored in reservoirs as shown in Figure 1.

The raw materials should be milled separately and stored in the same way. Subsequently, dried and fine all components are to be dosed to a ball mill. The output of the latter is high but efficiency is low. Frequent chemical analysis of flour must be carried out in order to correct dosing of raw materials. Well-mixed flour should be transferred to at least 5 averaging reservoirs, 1000 tons each. The next operation comprises simultaneous removal of the flour from all tanks to the distributor reservoir through the mixer. The role of the latter consists in mixing and averaging a few tons of flour. The averaging reservoirs and distributor ought to mix sufficient amounts of flour that could feed rotatory kilns within one hour. It is noticeable that ingredients of flour separate when a compressed-air dosing is being applied. There are two service ducts in Zaklady Chemiczne Wizow, i.e., anhydrite flour duct and phosphogypsum flour line. Both streams are being mixed in relation 1:1 and through an averaging system are transferred to the rotatory kilns feeding system.

Generally, phosphogypsum processing into sulfuric acid and clinker cement can be divided into the following processes:

(1) Phosphogypsum production as a by-product of phosphoric acid manufacture. Phosphogypsum contains 0.7% P_2O_5, 0.3% F and 38% water.

(2) Drying of phosphogypsum without removal of crystalline water.

(3) Storing the phosphogypsum flour. Its composition is 80.0% $CaSO_4$, 4.2% C and 10.0% SiO_2, referred to the dry mass.

(4) Sintering the furnace charge. Composition of clinker amounts: 1.8%, SO_3, 22.0% SiO_2, 66.0% CaO and 9.0% Al_2O_3 + Fe_2O_3.

(5) Sulfuric acid manufacture. Concentration of SO_2 before contact installation is 5.5%.

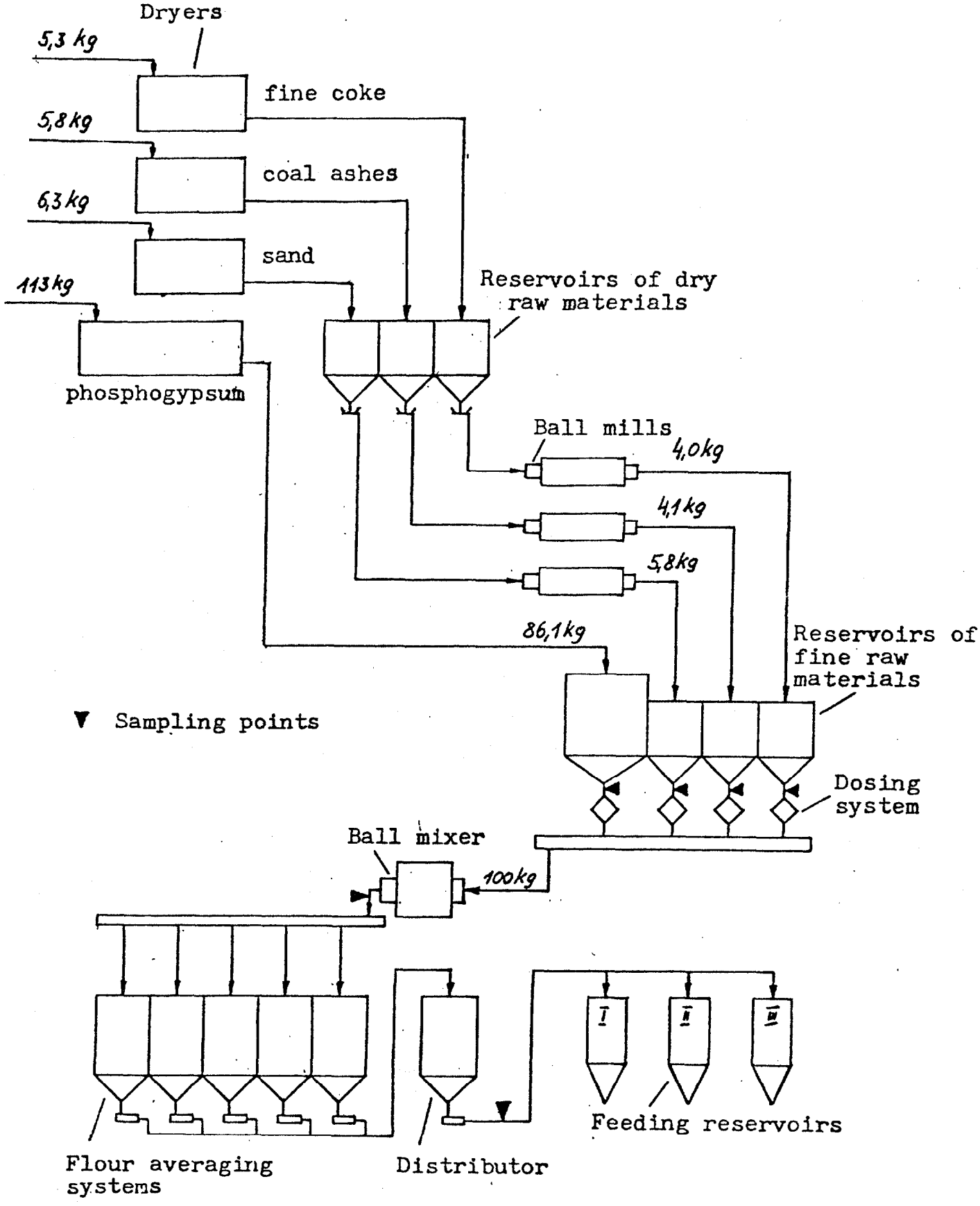
(6) Pulping of clinker cement.

To emphasize, phosphogypsum clinker mixed with those from limestone ($CaCO_3$) results in especially good clinker of high strength and other parameters. The cycling reagent between the sulfuric acid shop and phosphoric acid manufacture is the first one. Taking into account greater than theoretical spending of sulfuric acid in phosphoric acid manufacture, loss of sulfur (when phosphogypsum is being dried), it clearly shows the lack of 20% of sulfur raw material. In our manufacturing process, the mentioned deficit is being supplemented by anhydrite. In a new cement manufacturing plant based on phosphogypsum, sulfuric acid should be brought from outside. Alternatively, existing phosphogypsum stacks have to be exploited,, if available.

It is my conviction that the described technology has good prospects because of limited sulfur deposits and increasing phosphoric acid production via the wet-process route.

There is more and more phosphogypsum on this account. However, environmental protection and storage of phosphogypsum regulations are more and more stringent. An efficient and profitable solution of phosphogypsum utilization has to be looked for. Our existing experience and several years and utilization confirms the reality of phosphogypsum processing into sulfuric acid and clinker cement. (Elaborated by Kunecki)

Fig. 1. Storing and averaging systems for feeding rotatory kilns



EXTRACTION OF SUM RARE-EARTH METALS FROM PHOSPHOGYPSUM

by

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INTRODUCTION

Phosphogypsum is dump product of sulfuric acid decomposition of apatite in fertilizer production (1). Primary raw materials contain some rare-earth metals, about 60% of which are lost with phosphogypsum (2). The large potential reserves of the rare-earth metals in phosphogypsum cause necessity of the investigations carried out to search some rational methods of extraction. According to the literature data, works in this direction were-not carried out enough (3).

We have studied the possibility of extracting the sum of the rare-earth metals from phosphogypsum by two methods: (a) treatment of phosphogypsum directly by a mineral acid, in particular by sulfuric acid; (b) in the complex processing of phosphogypsum for ammonium sulfate and calcium carbonate or calcium oxide purified from admixtures.

Expediency of sulfuric acid used as a leaching agent for the rare-earth metals was based on the considerable difference between the dissolvability value of calcium sulfate (4) and some sulfuric acid salts of the rare-earth metals (4,5) in diluted H_2SO_4.

The chemical composition of the phosphogypsum under investigation (mass %) is: Ca - 16.10; SO_4 - 42.30; P_2O_5 - 1.30; Ln2O3 - 0.36 ; Si - 0.20; Fe - 0.10; Ti - 0.10; A1 - 0.02; H_2O_{total} - 40.

Note: [x)] The content (in %) of the basic rare-earth metals in, accordance with their sum is: La_2O_3 - 27.2; CeO_2 - 46.8; Nd_2O_3 - 14.8.

Calcium content in phosphogypsum, intermediate and final products (solutions) was determined by the flame photometry (6,7), and also by trilonometric titration in presence of eriochrome black, T (8,9); the sum of the rare-earth metals was determined as, it was described earlier (10), but silicon, ferrum, titanium and aluminum - by a spectral method (11).

The dependence of the extraction rate of the rare-earth metals, extracted into solution (%), on the contact period of solid and liquid phases, concentration of H_2SO_4 phase ratio (solid:liquid) and temperature were studied when the phosphogypsum was treated with sulfuric acid.

In the first series of the experiments leaching was carried out by 1- and 2-n H_2SO_4 at the ratio Solid: Liquid = 1:10 and 1:1 accordingly. The contact period was varied from 15 min to 1.5 hours. As seen from the kinetic curves given in Figure 1, equilibrium in the system under test has already been achieved after 30 minutes.

Rising in acidity of the leaching agent leads to increasing in the extraction rate of the rare-earth metals from phosphogypsum (Figure 2a), the most considerable change of e is to be observed within the range of relatively low concentration H_2SO_4 - from 0.1 to 2-n (the 2^d- curve). About 15% of the sum of the rare-earth metals is extracted into aqueous phase from phosphogypsum when being leached by 0.1-n solution of H_2SO_4 but the value e increases up to about 60% when 2-n H_2SO_4 being used.

Further increasing of H_2SO_4 concentration has no influence enough upon the efficiency of the rare-earth metals leaching from phosphogypsum. Such character of the dependence e on acidity of the leaching agent shows tendency to decrease solubility of the rare earths sulfates (La, Ce, Nd) in sulfuric acid when its concentration increases within the interval from 2 to 15-n (5).

The phase ratio has considerable influence upon the extraction rate of the rare-earth metals into solution (Figure 2 a, b). The curves given in Figure 2a show that value e for the same concentration of sulfuric acid at the ratio S:L = 1: 1Ø exceeds the extraction rate at the ratio 1:2 twice approximately. The analogous dependence of e on the ratio S:L is presented in Figure 2b as the curve it being showed in considerable degree in the variation interval of the solid and liquid phases from 1:1 to 1:15. Further decrease of the ratio S:L does not already lead to rising of the extraction rate of the rare earths into solution. This is probably connected with the rare-earth metals in phosphogypsum which substitute isomorphically calcium in the crystal lattice of $CaSO_4$ according to the data obtained (12-14).

Practically, the temperature variations of the process within 2Ø-95°C has no influence upon extraction of the rare-earth metals from phosphogypsum (Table I). This fact can be also explained by weak dependence of sulfuric acid salts solubility in diluted H_2SO_4 upon temperature (5) as well as by crystal isomorphism of the rare-earths sulfates and calcium sulfate.

Thus, all analyses carried out showed that about 5Ø-6Ø% of the sum of the rare-earth metals were extracted from phosphogypsum during one stage of leaching at optimum (1-2n H_2SO_4 S:L = 1:1O). It has been established also that it is impossible to achieve quantitative extraction of the rare earths from phosphogypsum without destruction of the crystal lattice of calcium sulfate.

Practically, the complete extraction of the rare-earth metals from phosphogypsum can be obtained in the process of complex treatment of the last into ammonium sulfate and calcium carbonate or calcium oxide purified from admixtures. The method of phosphogypsum carbonization (conversion method), described before (15), gives an opportunity to obtain ammonium sulfate and calcium carbonate contaminated with admixture of phosphorus, rare earths, silicon, ferrum and others. It is known also (16) that calcium oxide obtained under annealing, dissolves well in some ammonium salts, e.g. NH_4Cl. This effect can be used to separate calcium and the rare-earth metals.

Phosphogypsum was treated at room temperature (22 ± 2°C) by 2Ø% solution of ammonium carbonate. The quantity of $(NH_4)_2CO_3$ was estimated according to the equation of the reaction

$$CaSO_4 + (NH_4)_2\ CO_3 \rightleftharpoons CaCO_3 + (NH_4)_2\ SO_4$$

taken with 15% surplus. The process termination was defined according to the content of liquid and solid phases (content analyses for calcium, sulfate- and carbonate-ions) and also on the basis of preliminary tests

carried out to determine the influence of the intermixing period upon full interaction of $CaSO_4$ with $(NH4)_2CO_3$. After finishing the conversion process solid phase (technical calcium carbonate) was separated from liquid one, then it was washed with water and annealed at about 1000°C during three hours, The temperature conditions selected are optimum. They were established according to the data given in Figure 3a, and by thermogravimetrical analyses of technical $CaCO_3$ (Figure 4), decomposition of which began at T > 700°C. In the temperature range 850-900°C it proceeds more intensively; practically complete changing of the sample weight takes p1ace at T = 950°C and calcium is present in the annealed product in the form of oxide.

Technical calcium oxide was treated by saturated solution of ammonium chloride at the molar ratio of NH_4Cl/CaO = 2.2. In doing so the basic mass of calcium was passing into solution (Figure 3b) but admixture elements, including rare earths, were concentrated in undissolved residue. According to the data reported in the literature an aqueous solution of ammonium chloride is an effective dissolvent for calcium oxide as well as for the oxides of the rare-earth metals, especially of ceric group (17). However, when the product contained calcium oxide and rare-earth metals were dissolved as a result of formation of ammonium oxide hydrate in the process of

$$CaO + 2NH_4Cl + H_2O = CaCl_2 + 2NH_4OH$$

there were created certain conditions (pH = 8-9) for keeping the rare-earth metals in sediment. The rare-earth metals concentrate was obtained. It contained (mass %): Ca-37-.50; SO_4 - 36.04; PO_4 - 1.60; Ln_2O_3 - 5.60; Si - 1.76; Fe - 0.91; Ti - 0.89; Al - 0.37; H_2O -~10. Direct yield of the rare-earth metals into concentrate according to their content in phosphogypsum - 99.5%, degree of concentration - 15.5.

Further treatments were necessary with the purpose to separate the rare-earth metals from admixtures because of the presence of admixture elements in quantities in the rare earths concentrate. At the first stage it is advisable to clear up the efficiency of extraction of the sum rare-earth metals by means of the most simple method, viz. leaching by mineral acids; hydrochloric, nitric and sulphuric acids. For this purpose certain quantities of the concentrate were treated by diluted acid solutions during 4-5 hours at room temperature as well as when heating up to 90-100°C. Acid concentration was varied within 0.5-4.0-n, the ratio S:L - from 1:5 to 1:20. After finishing the process liquid phase was filtered, sediment was washed with water and when washed waters were joined filter liquor it was determined the content of the sum rare-earth metals, in solution.

From the data presented in Table 2 it is seen that the showing of the rare-earth metals extraction on condition of single leaching is relatively not high. The extraction rate e2 can be raised when treating the concentrate by new portions of the acid in consecutive order. However, in this case all solutions obtained were diluted highly on the rare-earth metals. The heating of the reaction mixture up to 90-100°C allows to intensify considerably the leaching process and to achieve practically the quantitative transition of the rare-earth metals into

solution at optimum (Figure 5). In particular, 3-n nitric acid at 95°C (S:L = 1:1Ø, T intermix = 4 hours) in one stage leaches more than 97% of sum of the rare-earth metals. Ln Ø content in the solution obtained makes up 3.7 g/l or 18% according to the sum of oxides (e oxide) that approximately two times more in comparison with Ln_2O_3/e oxide in the initial concentrate.

From the nitrate solutions the rare-earth metals can be extracted by means of phosphorus-organic compounds, for example, trialkylphosphine oxide (TAPhO) with the number of carbon atoms in radical from 7 to 9 (C_7 - c). The characteristic feature of the above extraction agent is its ablilty at low concentration to extract quantitatively individual rare-earth metals from weak acid nitrate solutions (18-2Ø). It was tested conformably to the extraction of the rare-earth metals from the solutions containing admixtured elements. For this extraction the solutions with concentration Ln_2O_3 = 3.7 g/l and acidity from Ø.2 to 1Ø-n HNO were prepared. The consent of Ln_2O_3 was at a rate of 3Ø% per sum of oxides in the solutions prepared.

It was studied the influence of the extraction agent concentration, acidity of aqueous solution, Ln_2O_3 concentration upon the extraction of the sum rare-earth metals into an organic phase (ξ_3). Figure 6a presents the dependence of the extraction rate upon the concentration of TAPhO in kerosene. When the tests being carried the concentration of TAPhO was varied within the range from Ø.1 to Ø.5 mole/l. The volume ratio of aqueous and organic phases V_{aq}: V_{or} is equal I. In the extraction process all volumes of the phases remained unchanged practically. By preliminary analyses it was established that equilibrium in the system was achieved when the phases being intermixed during one minute. Using Ø.5-molar solution of TAPhO in kerosene as an extraction agent the sum of the rare-earth metals is extracted completely into the organic phase from the weak acid solution. Rising of the solution acidity to 5-n HNO_3 negatively affects the extraction of metals. This fact, is confirmed by the curve (Figure 6b), and evidently, it is connected with competed influence of nitric acid as the last is extracted well by TAPhO. Under the condition of relatively high concentration nitric acid can, partly or completely, connect free extraction agent into solvate HNO_3.TAPhO [21,22] lowering or loosing extraction ability. Besides, during the extraction of the sum of the rare-earth metals by Ø.2-Ø.5-molar TAPhO from the solutions with high acidity it is observed the formation of stable emulsions making phases difficult to divide. Optimum solution acidity, which corresponds to the largest transition of the rare-earth metals into the extract; lies within Ø.4 - Ø.6n HNO_3; if the acidity of HNO_3 > 5-n the rare-earth metals extraction doesn't proceed. Increasing of lantanoides concentration in the aqueous solution (at the constant values) $[HNO_3]_{aq}$ and $[TAPhO]_{or}$ which equals Ø.5 mole/l) reduces slightly the extraction rate of metals (Figure 6c). It is probably explained by decrease of the content of the free extraction agent as it is spend on solvation of nitrate molecules of the rare-earth metals.

Reextraction of the sum rare-earth metals was carried out by I-n HCl at ratio V_{or}: V_{aq} = 1 :1. Single washing of the extract permits to extracts 90% of Ln_2O_3, two washings allow practically complete transition of rare-earth metals, into aqueous phase. Content of the basic admixture, calcium, in the sum of the rare-earth metals obtained from reextract doesn't exceed 1.10^{-2} mass %.

Thus, the investigation carried out allows to draw a conclusion. about possibility to extract very effectively the sum of the rare-earth metals in the process of the complex treatment of phosphogypsum. Optimum conditions for the extraction are: (a) when the rare-earth metals being extracted from phosphogypsum into concentrate: annealing temperature of technical calcium carbonate - 1000°C, molar ratio of NH_4 Cl/CaO for treatment of technical calcium oxide -2.2;b) when the rare-earth metals being leached from concentrate into solution by 3-n nitric acid: S:L = 1:10, T = 90-100°C,t = 4 hrs; c) when the rare-earth metals being extracted from solution by 0.5 -molar TAPhO in kerosene; V_{or} : V_{aq} = 1:1, $[HNO_3]_{aq}$ = 0.5-n, $[Ln_2O_3]_{aq}$ = 2-10 g/l.

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21. (English Text)

22. (English Text)

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Table I

Leaching of the rare earths from phosphogypsum by sulphuric acid at various temperatures

Concentration of H_2SO_4 - 2-n, S:L = I:5

Leaching period τ, hrs	Extraction rate of rare earths into solution, % to initial, at T		
	20°	60°	95°
2	36.6	45.7	46.9
4	38.7	46.9	47.8

Table 2

Leaching of sum rare-earth metals from concentrate by mineral acids solutions at room temperature

Leaching agent		Ratio S:L	Content of rare-earth metals, g		Extraction rate of rare-earth metals into solution, %
			initial concentrate	in solution after leaching	
3.I-n	HNO_3	I:IO	0.II40	0.0460	40.3
3.I-n	HCl	I:IO	0.II40	0.0465	40.8
2.0-n	H_2SO_4	I:5	0.I002	0.026I	26.I
0.5-n	H_2SO_4	I:20	0.5700	0.2440	42.7

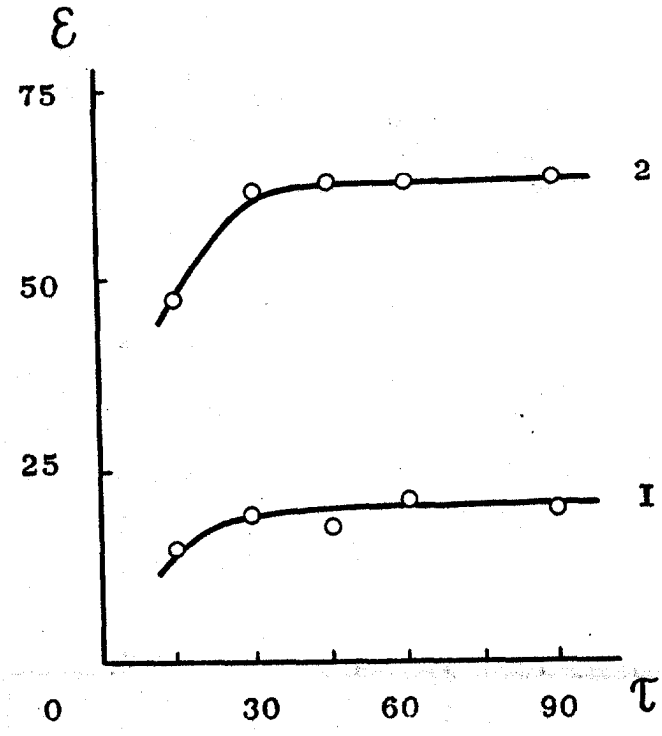


Fig. I.

Kinetic curves of leaching of the rare-earth metals from phosphogypsum by sulphuric acid.

ε - extraction rate (5); τ - period (min);

Concentration H_2SO_4 (n): I - 2.0; 2 - I.0.

Ratio S : L: I - I : I; 2 - I : I0.

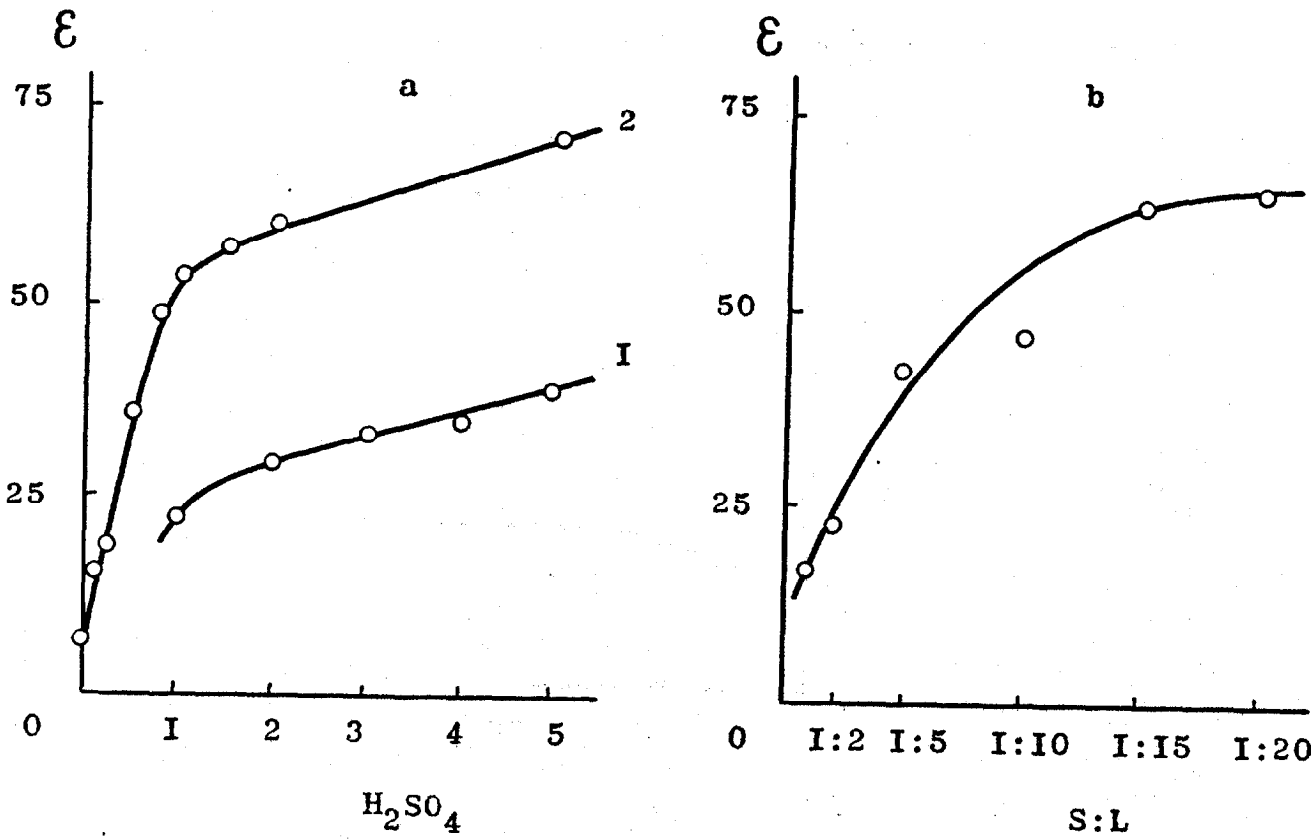


Fig. 2.

Dependence the extraction rate of the rare-earth metals ε (%) into solution on concentration of H_2SO_4 (n) (a); the ratio of solid and liquid phases when leaching by I-n H_2SO_4 (b).

Ratio S : L: I - I : 2; 2 - I : I0.

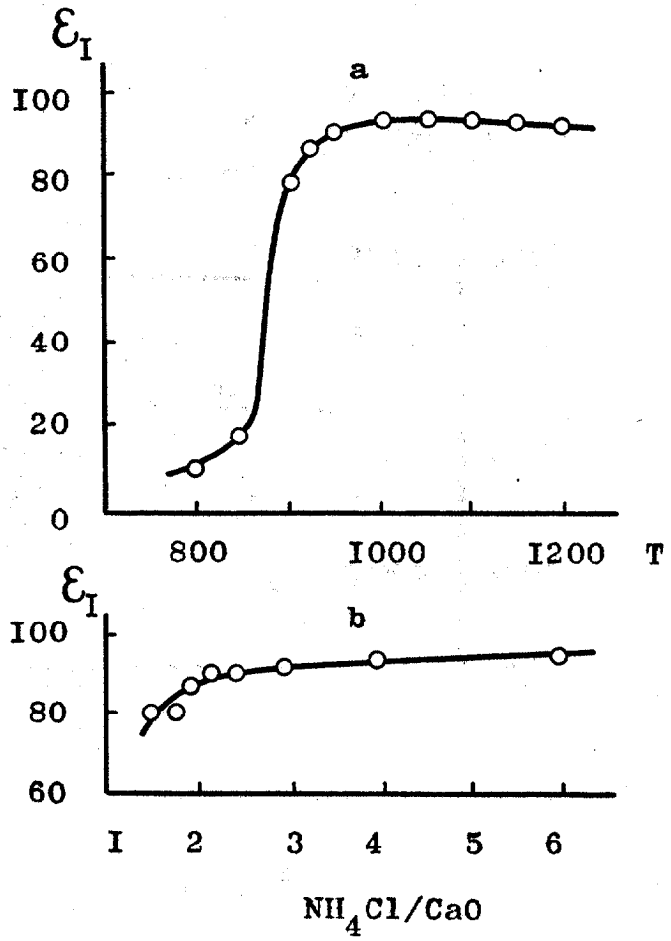


Fig. 3.

Dependence of transition degree of calcium into NH_4Cl solution $\mathcal{E}_I$ (%) on annealing temperature T (°C) of technical $CaCo_3$ obtained from phosphogypsum (a) and molar ratio of NH_4Cl/CaO (b).

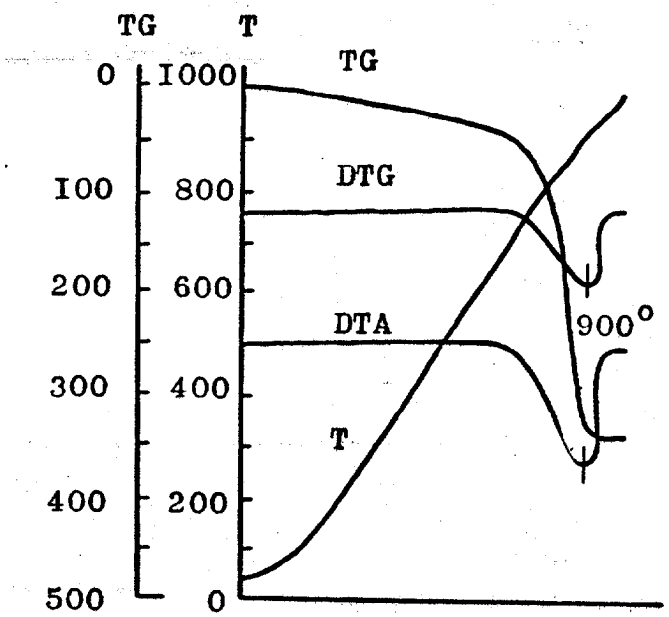


Fig. 4.

Derivatogram of heating of technical calcium carbonate obtained from phosphogypsum.

T - temperature (°C); TG - weight change of sample (mg).

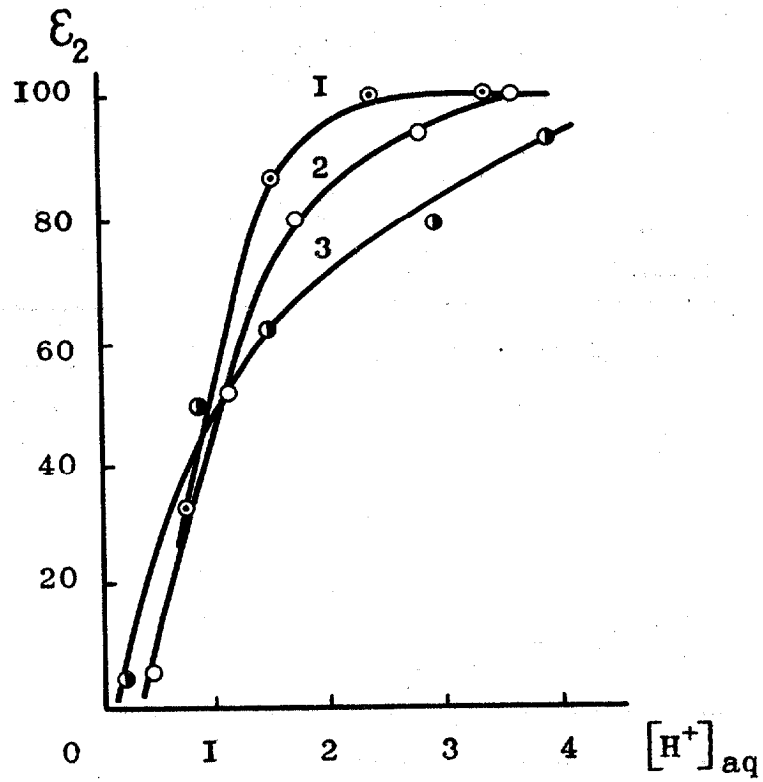


Fig. 5.

Dependence of extraction rate of rare-earth metals $\mathcal{E}_2$ (%) from concentrate into solution on acidity of leaching agent (n).

I - HCl; 2 - HNO_3; 3 - H_2SO_4.

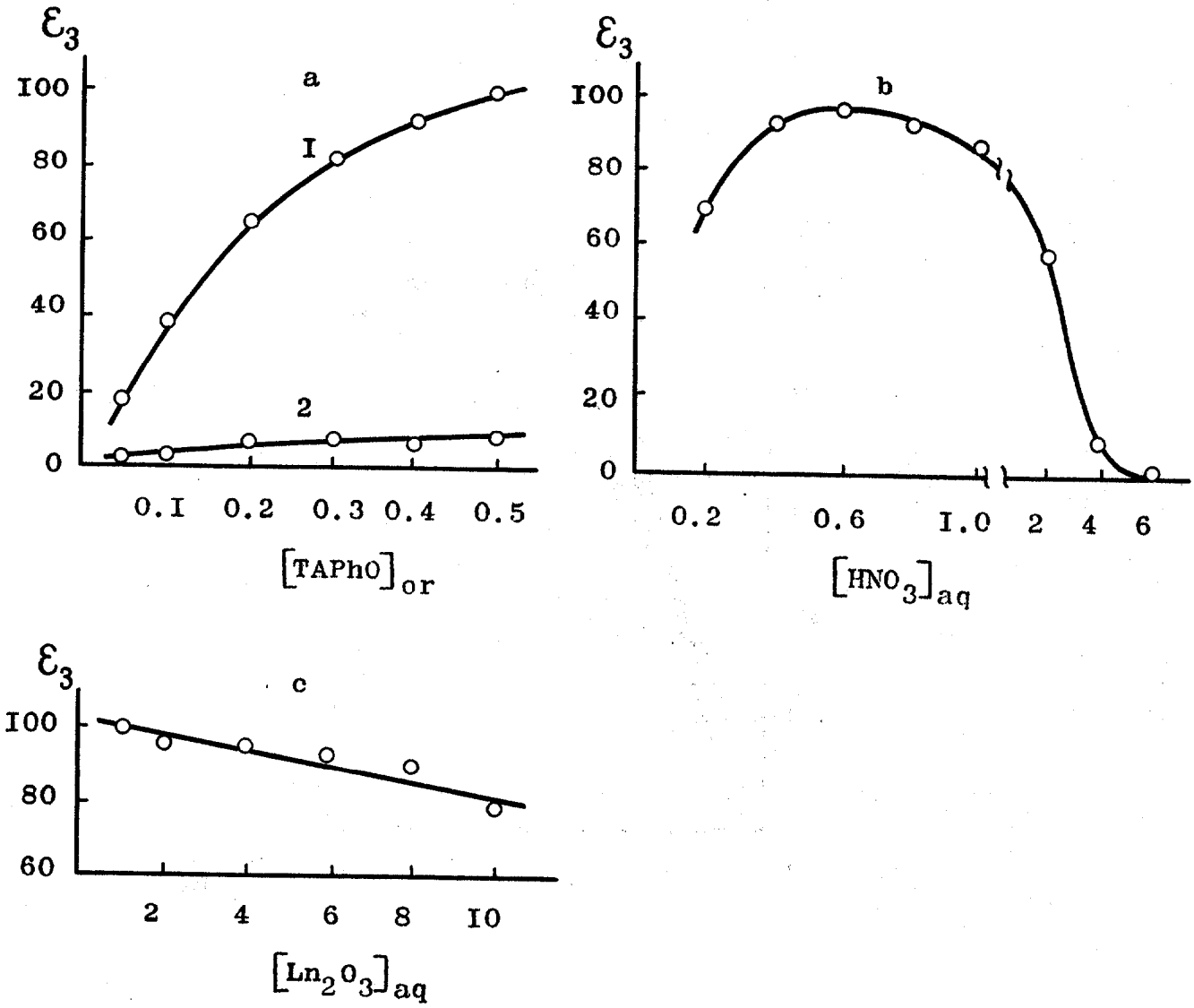


Fig. 6.

Dependence of extraction rate of rare-earth metals ε_3 (%) into organic phase on concentration of TAPhO in kerosine (mole/l) (a); HNO_3 in aqueous solution (b) (I - 0.5; 2 - 5.0-n); Ln_2O_3 in aqueous solution (g/l) (c).

URANIUM CONTROL IN PHOSPHOGYPSUM*

by

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INTRODUCTION

The more than 50 million tons of phosphate rock processed in Florida during 1980 are estimated to contain over 10 million lb of uranium. Currently, about half of this uranium is being recovered in six wet-process phosphoric acid plants. Recovery of this uranium is very difficult and costly and can be done economically only as a by-product of wet-process phosphoric acid production. Thus it seems only logical to try to dissolve as much uranium as possible during rock acidulation. Previous data, obtained during the 1950's when three plants recovered uranium from wet-process phosphoric acid, showed that only 60 to 80% of the uranium originally present in the phosphate rock reported to the acid and that the remainder reported to the gypsum residue.

This paper reviews the early data, much of which had limited distribution, with emphasis on the variables that were considered to affect uranium distribution between the acid and the gypsum. It also includes more recent test results that confirm the early data and describes an alternative route that may be particularly attractive for hemihydrate processes.

Description of the Problem. The current stockpile of phosphogypsum in Florida has been estimated at approximately 330 million tons, and it is growing at the rate of about 33 million tons per year (2). No one knows how much uranium is contained in this stockpile of gypsum, but a reasonable estimate may be made by assuming 60 to 80% dissolution of uranium, as indicated by the results of early studies and the results of a few analyses of gypsum performed recently at Oak Ridge National Laboratory (ORNL). On this basis, we estimate a concentration range of 15- to 30-ppm uranium, which indicates 10 to 20 million lb of uranium in the stockpile. Assuming a uranium price of $30.00/lb, the value of this uranium is $0.90 to $1.80/ton of gypsum.

It is very doubtful that this uranium can be recovered economically once it is incorporated into the gypsum. It thus becomes very important to divert all the uranium to the acid (or to the gypsum for subsequent recovery) during the rock acidulation.

Chemistry of the Process. The production of wet-process acid involves digesting a slurry of phosphate rock with sulfuric acid and separating the resulting phosphoric acid from the solid products of the reaction by filtration. The two major methods in use today are the dihydrate and hemihydrate processes, so-named for the mode of calcium sulfate precipitation. The dihydrate, process is by far the most widely used, but interest in hemihydrate processes is growing because of large potential savings in energy and capital costs.[3]

The overall reactions of the dihydrate and hemihydrate processes are essentially the same, -and may be represented as a two-step reaction. Equation 1 shows the dissolution of the phosphate rock in phosphoric acid to form monocalcium phosphate solution,

$$Ca_{10}F_2(PO_4)_6 + 14H_3PO_4 \rightarrow 10Ca(H_3PO_4)_2 + 2HF, \quad (1)$$

and Equation 2 shows the reaction of sulfuric acid with the monocalcium phosphate to produce a hydrated calcium sulfate which can then be separated from the phosphoric acid by filtration.

$$Ca(H_2PO_4)_2 + H_2SO_4 \cdot XH_2O \qquad CaSO_4 \cdot XH_2O + 2H_3PO_4 \qquad (2)$$

Depending on the operating conditions selected, the calcium sulfate can be crystallized as the dihydrate ($CaSO_4 \cdot 2H_2O$) or as the hemihydrate ($CaSO_4$ $1/2H_2O$). In the first case, the liquid phase will contain 28 to 30% P_2O_5 and in the latter case, it will contain 40 to 50% P_2O_5. As we will see later, the mode of crystallization has a very important bearing on the distribution of uranium between the acid and the cake.

Early Work. As early as 1954, Shaw reported that in most phosphate plants only 60 to 80% of the uranium originally present in phosphate rock reported to the acid during the manufacture of wet-process phosphoric acid, and the remainder reported to the gypsum residue. This high distribution of uranium to the gypsum residue led Dow Chemical Company into an investigation of when and how the uranium was precipitated with the gypsum during acidulation. As the first step in their study, the rock dissolution step (Equation 1) and the crystallization step (Equation 2) of the acidulation reaction were studied separately using both oxidizing and reducing conditions. The tests were then repeated with the two reactions being carried out simultaneously. The effects of excess fluoride and excess sulfate were also studied.

Figure 1. summarizes the Dow acidulation tests: As the reaction proceeded under oxidizing conditions, the uranium recovery into solution paralleled the phosphate recovery. Under normal conditions, however, the uranium recovery lagged far behind the phosphate recovery, being only 40% at 88% recovery of P_2O_5. Under reducing conditions, the uranium recovery was worse. Only 3 to 5% of the $uranium_4$ was recovered at 70% P_2O_5 recovery, and only 31% at 88% P_2O_5 recovery.

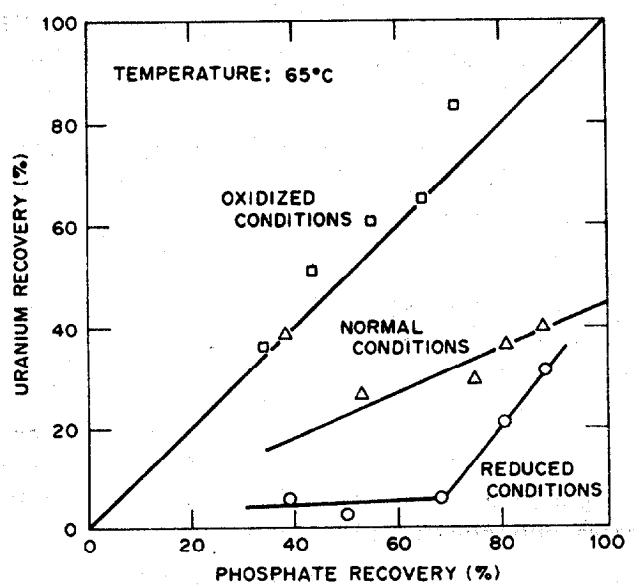


Figure 1. Recovery of Phosphate and Uranium During Acidulation of Phosphate Rock. Source: Ref. 4.

Dow concluded that uranium is present in phosphate rock primarily as U(IV) and that uranium losses to the filter cake are caused by gypsum coating of unreacted rock particles and by substitution of uranium in the crystal lattice of the gypsum. To improve uranium dissolution, Dow recommended finer grinding of the rock; minimizing the local excess of sulfuric acid during acidulation, and maintaining oxidizing conditions during acidulation.

The Blockson Chemical Company studied the distribution of uranium in their process for producing technical-grade sodium phosphates (5). On the basis of these studies, they also concluded that oxidized uranium is more soluble than reduced uranium in phosphate solutions. They reported over 90% dissolution of uranium with oxidizing conditions in acidulation, and over 95% if a small quantity of nitric acid was substituted for an equivalent quantity of sulfuric acid during the digestion.

Blockson calcined their rock before digestion to destroy organic matter. They discovered that oxygen was scavenged from the system during this step and produced reducing conditions. This increased the distribution of uranium to the gypsum to over 30% when the calcined rock was digested. They concluded this was caused by the substitution of U(IV) for calcium in the crystal lattice of the gypsum. Subsequent leaching tests indicated that recovery of uranium from gypsum required complete dissolution, and that the costs for this step were higher than the value of the uranium.

Blockson investigated two approaches to minimize the distribution of uranium to gypsum. Their first approach was to maintain oxidizing conditions during digestion of the rock. The oxidizing agents tested were air, oxygen, ozone, chlorine, nitric acid, permanganates, persulfates, chromates, hydrogen peroxide, and chlorates. All were effective, some more than others, but uranium oxidation was not selective. all ions present in a reduced state and any organic matter had to be oxidized. This increased operating costs to a point at which they offset the value of the extra uranium recovered. Their second approach was to calcine the rock in an oxidizing environment. Under optimum conditions, about 85% of the uranium reported to the acid. The cost of increasing recovery to 95% was more than the value of the extra 10% uranium recovered.

In 1968, the Chemical Separations Corporation reported a study in which they tried to divert the uranium to the gypsum by acidulating phosphate rock under reducing conditions (6). Once the uranium was distributed to the gypsum, they planned to recover it from a gypsum-water slurry using resin-in-pulp ion exchange.

In one experiment, they mixed two 10-g samples of Florida phosphate rock with 50% sulfuric acid for one hour after adding an iron nail to one sample and one gram of sodium chlorate to the other. After filtration, washing and drying, the gypsum from the test made under reducing conditions contained 165-ppm uranium compared to only 15 ppm in the gypsum from the test made under oxidizing conditions. Although this was a simple test, it further confirms and emphasizes the importance of redox potential on the distribution of uranium between the acid and the filter cake.

Table 1 indicates the wide daily variation obtained on the distribution of uranium between the acid and the gypsum at a phosphate plant during December 1952 (7). In this period, as much as 92% and as little as 51% of the uranium was found in the acid. The average distribution was 73%, which is within the range reported by Dow (4).

Table 1. Distribution of Uranium in a Commercial Plant

Date	Fraction of Uranium in Acid
December 3	0.92
5	0.91
7	0.67
12	0.55
13	0.51
14	0.56
15	0.81
16	0.83
17	0.82
Average	0.73

Distribution Profile in a Phosphate Plant. Figure 2 shows the distribution of uranium to gypsum in a phosphate plant in Florida. This plant has two identical trains for producing wet-process acid, which are fed from a common rock supply. Operating conditions are reportedly the same for the two trains. In spite of these similarities, the concentration of uranium in the gypsum from the south train is approximately twice that from the north train (approx. 34-ppm U compared to approx. 17-ppm U on an as-received basis). To date, no reason has been found for this anomaly. The results indicate the need for additional study so that a better understanding of the factors that control uranium distribution in a plant can be obtained.

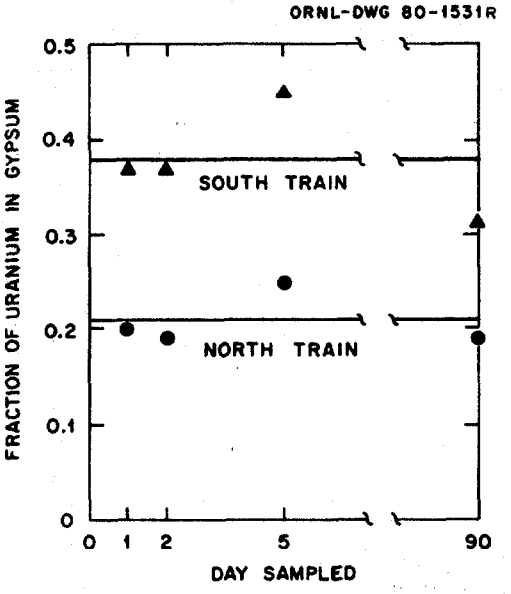


Figure 2. Uranium Distribution to Filter Cake from a Wet-Process Phosphoric Acid Plant.

Uranium in Apatite. The key to the erratic distribution of uranium to filter cake may be related to the nature of its occurrence in the phosphate rock or apatite. Altschuler found that tetravalent uranium was the predominant species in eleven apatite samples examined (Table 2)(8). From 40 to 91% of the uranium (average 65%) was present as U(IV), with the remainder presumed to be present as U(VI). The ionic radius of U(IV) (0.97 A) is almost identical to that of Ca(II) (0.99 A) and it is assumed that U(IV) substitutes for Ca(II) in the apatite structure. A uranium content of 0.01% in apatite is equivalent to only one atom of uranium for every 26,620 calcium atoms; furthermore, the positive-charge excess can easily be compensated by other ions that have replaced calcium (e.g., sodium) and are present in greater magnitude than U(IV).

Altschuler also indicated that U(VI) can be held in apatite by chemisorption as $UO_2.HPO_4$ or by exchange with surface calcium. In the latter mode, it is assumed that two moles of calcium are displaced for each mole of UO_2^{2+} taken from solution, and two moles of phosphate are

Table 2. Uranium (IV) in Bone Valley Apatite Samples[a]

Sample	Uranium Concentration (%)	Fraction of Uranium as Uranium (IV)
Black Pebble	0.010	0.91
Dark Pebble	0.0089	0.63
Fine Pebble Composite	0.016	0.81
4-8-mm Pebble Composite	0.032	0.50
	0.022	0.50
	0.015	0.42
	0.021	0.48
Apatite Pellets	0.011	0.45
	0.009	0.67
	0.0075	0.40
	0.007	0.43

[a]Source: Ref. 8.

rendered nonexchangeable. This would require the uranium to exist as a pyrophosphate, $UO_2(HPO)_2$, which is less likely than the chemisorption theory.

As apatite is decomposed and dissolved in a phosphoric acid - sulfuric acid media, phosphate ions go into solution and U(IV) , U(VI), Fe(II), and Fe(III) ions are released. Once in a solution, the relative amount of these ions is controlled by the following relationship:

$$2Fe(II) + U(V1)\ 2\ 2Fe(III) + U(IV) \qquad (3)$$

The work of Baes (9) showed that ferrous iron can readily reduce U(VI) to U(IV), especially at the concentration of phosphoric acid in the attack tank; the reduction is also catalyzed by fluoride ion from the rock.

Since Fe(III) and U(IV) form very stable complexes with fluoride and orthophosphate ions, there is a strong tendency for more U(IV) ions to form in addition to those present in the rock. These factors make it easier for uranium to substitute for calcium ions which are being released and become available for reaction with sulfate ions to form $CaSO_4.XH_2O$ crystals. Free or excess sulfate and fluoride ions can also influence the cocrystallization of uranium in the $CaSO_4$ crystal Because the mechanism of cocrystallization is not well understood, it needs additional study.

Hemihydrate Processes. Uranium recovery from the more concentrated (40 to 50% P_2O_5) acids produced by hemihydrate processes is much more difficult than recovery from the conventional (28 to 30% P_2O_5) acids produced by dihydrate processes. For example, in extraction of uranium from phosphoric acid with DEPA-TOPO (10,11) the extractant of choice for most operations involving uranium recovery from dihydrate acids, the uranium extraction coefficient decreases as the inverse fifth power of the acid concentration. Figure 3 shows that it is necessary to use a very high (and expensive) extractant concentration (approx. 1 M DEPA - 0.25 M TOPO) to obtain coefficients in the minimum usable range of 1 to 2 when extracting from approx. 40% P_2O_5 acids. Since coefficients for the upper (50% P_2O_5) range are less than one, DEPA-TOPO is not an effective extractant for uranium from these strong acids.

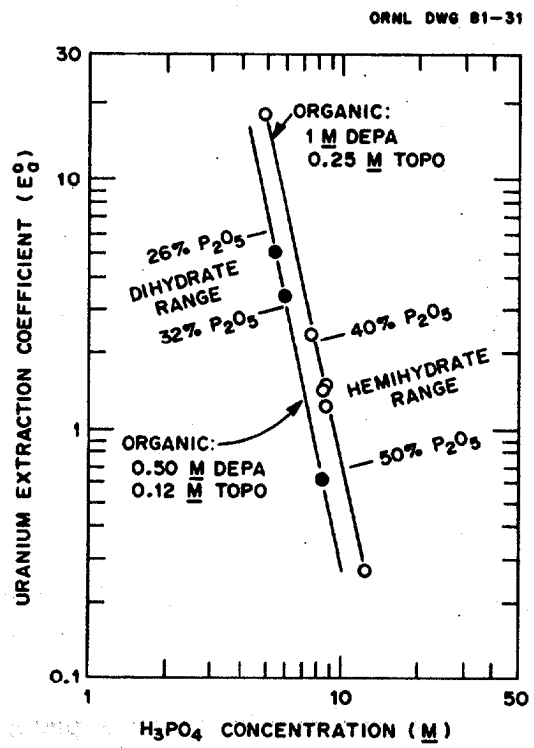


Figure 3. Effect of Acid Concentration on Uranium Extraction from Wet-Process Phosphoric Acid with DEPA-TOPO at 45°C.

Preliminary tests with our alternate OPAP (octylphenyl acid phosphate) extractant indicate that it has sufficient extraction power to be an effective extractant from these acids, at least at the lower concentration range of hemihydrate process acids. For example, the data

in Figure 4 show that the extraction power to Ø.5M OPAP is about a factor of 1Ø higher than that obtained with 1 M DEPA - Ø.25 M TOPO. However, the OPAP extraction system is plagued by stability problems that need to be resolved before an effective process can be realized (12). Our program on OPAP development at ORNL has been terminated, but it is being continued by TVA at Muscle Shoals, Alabama. Also, Earth Sciences, Inc. is operating a uranium recovery facility at a phosphate complex, owned by Western Co-operative Fertilizers, Ltd. in Calgary, which uses OPAP in the first cycle of extraction. This work may possibly lead to a resolution of these problems,

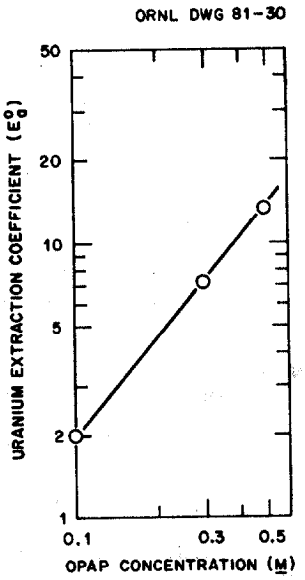


Figure 4. Effect of OPAP Concentration on Uranium Extraction from 38% P_2O_5 Wet-Process Acid Produced by a Hemihydrate Process. Temperature: 23°C

During our initial testing of hemihydrate process acids, we observed that the concentration of uranium was significantly below the levels expected. A further analysis of the problem led to the discovery of unusually large quantities of uranium in hemihydrate process filter cakes. For example, Table 3 shows 61- to 101-ppm uranium in filter cakes from two hemihydrate process plants as compared to 15 to 36 ppm in filter cakes from four dihydrate process plants.

In an effort to understand this variance, we conducted a few cursory tests to determine the variables that may affect the distribution of uranium between the acid and the filter cake during the manufacture of hemihydrate acid. On the basis of past information, the redox potential was considered to be the most important variable. However, in view of the higher distribution of uranium to hemihydrate cakes than dihydrate cakes, other factors such as temperature, crystal habit and crystal size distribution may be involved. In addition, hemihydrate can precipitate in clusters or agglomerates, which may tend to carry down more of the uranium than the dihydrate.

Table 3. Concentration of Uranium in Filter Cakes from Wet-Process Phosphoric Acid Plants

Plant	Type	Uranium in Filter Cake (ppm)
A	Di	15
B		10
C-1		12
C-2		13
D-1		18
D-2		36
X	Hemi	101
Y		61

These preliminary batch tests were made following the procedure used in TVA's foam process (13). Our test conditions were as follows:

(1) Mix 15 g of finely ground phosphate rock with 30g (23 ml) of 26% P_2O_5 wet-process acid in a 200-mL Berzelius beaker immersed in a heating bath.

(2) Add an oxidant ($NaClO_3$) or a reductant (iron metal).

(3) Add 7 mL of 98% H SO_4 dropwise over 30 min (mole ratio - H_2SO_4; Caa = 1:1).

(4) Allow 1 hour for reaction and digestion.

(5) Filter the slurry on a 5.5-cm Whatman No. 40 filter paper and Buchner funnel.

(6) Wash the cake with water (or ethanol).

(7) Air-dry the cake.

Table 4 shows that as the digestion temperature of the phosphate rock in sulfuric acid was increased from 65 (dihydrate temperature) to 98°C (hemihydrate temperature), the fraction of uranium that reported to the cake increased from 12 to 31%.

Table 4. Effect of Digestion Temperature on Uranium Distribution

Digestion Temperature (°C)	Uranium in Filter Cake	
	Concentration (ppm)	% of Total
65	26	12
85	43	21
98	74	31

In subsequent tests made at 98°C, only 20% of the uranium reported to the acid when the reaction was made under strongly reducing conditions as compared to 98% when the reaction was made under strongly oxidizing conditions (Table 5). In the tests made under oxidizing conditions, most of the organic matter was decomposed during digestion and a very clean acid was produced. The use of strongly oxidizing conditions in the attack tank could minimize the acid pretreatment required prior to uranium recovery by solvent extraction.

Table 5. Effect of Redox Potential on Uranium Distribution

Additive	EMF[a]	Concentration (mg/ml)		Uranium in Filter Cake	
		Fe^{2+}	Fe^{3+}	Concentration (ppm)	% of Total
$NaClO_3$, 10%	+0.950	0.0001	15.9	5.0	2
$NaClO_3$, 2%	+0.860	0.0001	19.4	5.7	2
None	+0.260	1.2	15.3	74.0	31
Fe°, 0.33%	+0.110	42.3	0.4	238.0	79

[a]Au vs Ag-AgCl; Digestion Temperature, 98°C.

In other tests at 98°C, 55% of the uranium remained in the cake after it was washed with ethanol compared to 31% when it was washed with water, indicating that some uranium is released from the cake as it is hydrated. This phenomenon was also observed when a sample of wet-filter cake that initially contained 101-ppm uranium was filtered to remove solution that had separated after the cake had aged for five months. The cake, after air-drying, contained 46-ppm uranium compared to 101-ppm uranium initially, and the solution removed from the cake contained 197-ppm uranium and 180-g/L phosphate.

Following this analysis, we made a few tests to determine the ease with which uranium could be leached from plant samples of hemihydrate filter cake. Figure 5 shows that approximately 60% of the uranium was

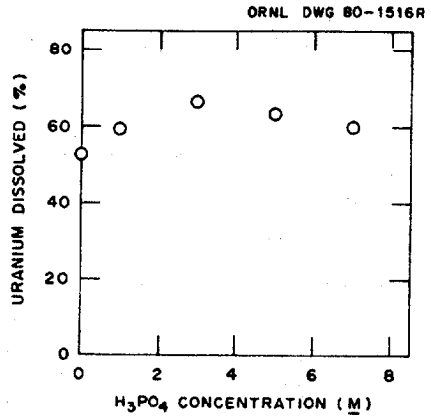


Fig. 5. Effect of H_3PO_4 Concentration on Uranium Dissolution from Hemihydrate Filter Cake; 3 grams of Filter Cake Leached for 1 h at 25°C with 10 mL of solution.

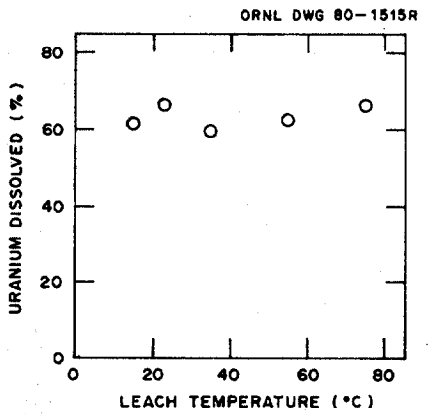


Fig. 6. Effect of Temperature on Uranium Dissolution from Hemihydrate Filter Cake; 3 grams of Filter Cake Leached for 1 h with 10 mL of 3 *M* H_3PO_4.

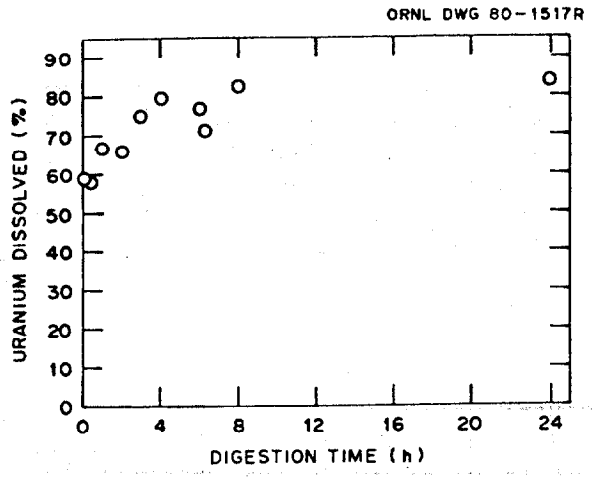


Fig. 7. Effect of Leach Time on Uranium Dissolution from Hemihydrate Cake at 25°C with 3 *M* H_3PO_4; 3 grams of Filter Cake per 10 g of Acid.

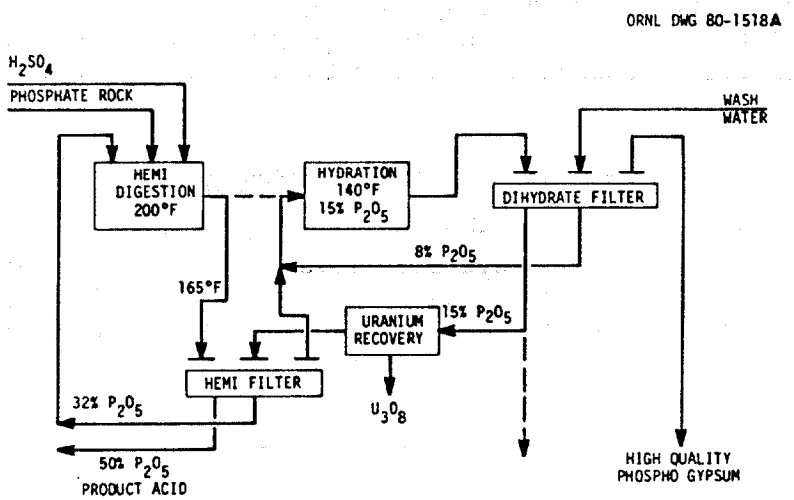


Fig. 8. Alternate Route for Uranium Recovery from Hemihydrate Acid. Source: Reference 14.

easily washed from air-dried filter cake with water or dilute phosphoric acid, which gave slightly better dissolution than water or 5 to 7M acid, showed no change in solubility over the 15 to 75°C range tested (Figure 6). The dissolution was increased to 8-0% by increasing the digestion time from 1 to 4 hours but there was little, if any, improvement beyond 4 hours (Figure 7). Although we have made no tests, we assume that recovery of the final 20% of the uranium would require complete dissolution of the cake.

Because of the difficulty of recovering uranium from the stronger acids and the higher distribution of uranium to the filter cake in hemihydrate processes, there may be a potential process advantage if most of the uranium could be diverted to the hemihydrate cake rather than the acid. The uranium would be dissolved subsequently in a dilute phosphoric acid wash stream which could be easily processed to recover the uranium. This possible alternative route to uranium recovery is shown in Figure 8 as a revision of the Nissan Hemihydrate Process (14). To be economically attractive, additional research is needed to improve the distribution of uranium to the cake and to increase its release from the cake on hydration.

CONCLUSIONS

Both earlier and recent test results show that uranium dissolution from phosphate rock is significantly higher when the rock is acidulated under oxidizing conditions than under reducing conditions. Excess sulfate and fluoride further enhance the distribution of uranium to the cake. Apparently, the U(IV) present in the crystal lattice of the apatite, plus that formed by reduction of U(VI) by Fe(II) during acidulation, is trapped or carried into the crystal lattice of the calcium sulfate crystals as they form and grow. The amount of uranium that distributes to hemihydrate filter cake is up to seven times higher than the amount that distributes to the dihydrate cake. About 60% of the uranium in hemihydrate cakes can be readily leached after hydration of the cake, but the residual uranium (20 to 30%) is very difficult to remove economically.

ACKNOWLEDGMENTS

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APPENDIX

As a spinoff of our study of the distribution of uranium in a phosphate plant (Figure 2), we found it convenient to determine the distribution of Po-210 (a highly radiotoxic uranium daughter) in the phosphate rock, wet-process acid, and phosphogypsum samples used in this study. G.N. case and W.J. McDowell of the ORNL Chemical Technology Division have recently completed development of an improved sensitive analytical method for the determination of Po-210. This technique (which will be described in a publication in the near future) is very effective for the analysis of Po-210 in phosphate products and phosphogypsum. Mr. Case kindly consented to analyze these samples for us. The results of this analysis showed Po-210 was in secular equilibrium with U-238 and Ra-226 in the phosphate rock. After acidulation, more than 99% of the Po-210 was found in the gypsum cake; the wet-process acid contained approximately one Po-210 dpm/mL. The material balance for the rock-acid- gypsum system was >90%. The significance of this almost total distribution of polonium to gypsum is that the fertilizer products produced by the wet-process route should be essentially free of this toxic nuclide.

RADIUM REMOVAL FROM PHOSPHOGYPSUM

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INTRODUCTION

If we wish to know how to remove radium from phosphogypsum, it is necessary first to assess where this radium is coming from, and secondly, to know how far we have to go in removing radium. It is understandable that if we remove radium from phosphogypsum, we will have to dispose of this radium in an acceptable way. If the requirements are to remove most of the radium from the treated phosphogypsum and if no acceptable ways of disposal are found, it will be better to leave the radium contained in phosphogypsum where it is, that means neither to extract phosphate rock or to produce phosphatic fertilizer with the existing plants technology.

Where is Radium Contained by Phosphogypsum Coming From? The phosphogypsum is the by-product of the chemical attack of phosphate rock by sulfuric acid.

$$CaH\,PO_4 \cdot 2H_2O + H_2SO_4 \longrightarrow H_3PO_4 + CaSO_4 \cdot 2H_2O$$

The sulfuric acid obtained from sulfur does not contain radioactive products. Natural phosphate rock does. Natural phosphate rock very often contains uranium salts. Generally, these salts are double phosphate salts of calcium and uranium. The average Moroccan phosphate rock contains 100 to 130 grams of uranium per metric ton of rock, while the average Florida phosphate rock contains 100 to 180 grams per metric ton of rock.

However, it is possible to find uranium in complex fluoro-apatite salts. At last, in phosphate rock deposits, you can have layers of limestone or silicates containing complex salts as vanadate of calcium and uranium.

Where we have uranium, we have radium. As we know 238U uranium decays to radium; you can find a schematic description of decay series on Figure 1. 238U uranium eventually decays to thorium then to radium, radon (which is a gas), radium A,B,C,C',C",D,E then to polonium and at last 206 Pb.

The main danger of the uranium family is not really the radiation emission by solid products which are far enough from our body, but the fact that the radon is a gas that can be inhaled by humans and that the daughters of radon are solids. They can irradiate the human body from the inside without protection.

But where does the uranium and radium go from the phosphate rock during the chemical reaction of sulfuric acid and phosphate rock? Most of the uranium goes to the phosphoric acid as soluble salts and it is well known that uranium can be extracted from the phosphoric acid.

It appears that the radium is combined as radium sulfate and can be found in (1) phosphoric acid in solid suspension, (2) phosphogypsum, and (3) the waste coming from the wash of phosphogypsum either on the main filter or in subsidiary installation used by people who want to clean phosphogypsum.

In What Combination is Radium Trapped in Phosphogypsum? If we want to extract radium from phosphogypsum, we need to know what the compound is which contains radium. Is it only radium sulfate or have we other complex salts? Is it possible to have radium co-crystallized with calcium inside the calcium sulfate crystals as we have HPO_4 -- or FPO3 -- co-crystallized with SO_4 -- ?

In order to evaluate the probability of chance to obtaining complexed radium salts, we have to go back to the basics of crystal shapes, solubility in water and ionic radius.

Radium sulfate crystallizes in rhombohedric system as does barium sulfate and hemihydrate calcium sulfate ($CaSO_4$. 1/2 H_2O). Calcium sulfate dihydrate ($CaSO_4$. $2H_2O$) crystallizes in monoclinic system. When the conditions of chemical reaction between phosphate rock and sulfuric acid are such that calcium sulfate dihydrate precipitates at low temperature (below 70°C), there is no chance to have co-crystallization of $CaSO_4$. $2H_2O$ and Ra SO_4. However, if the temperature of the reaction tan is high enough (we can say above 85-90°C), then we produce calcium sulfate hemihydrate ($CaSO_4$. 1/2 H_2O) and there is a risk that $CaSO_4$ and Ra SO_4 co-precipitate; then it will be very difficult to eliminate radium. The equilibrium between $CaSO_4$. $2H_2O$ and $CaSO_4$. 1/2 H_2O in solution is linked to temperature and the ratio of HPO_4 -- versus SO_4 -- (Figure 2).

The solubility of RaSO in water is very small: 2×10^{-5} $kg.m^{-3}$ or 2 millionth of a gram/100 cc, while the solubility of $CaSO_4$. $2H_2O$ is high: 2 $kg.m^{-3}$, 2/10 of a gram/100 cc. That means that the radium sulfate precipitates first and that the chance to see radium sulfate and dihydrate calcium sulfate co-settle is very limited.

Now, if we investigate the possible effects of ionic radius, we can find the data from PAULING in nanometers: Ba^{++} - 0.135, Ra^{++} - 0.140 , Ca^{++} - 0.099, U^{+++} - 0.111, U^{++++} - 0.097.

The small difference in ionic radius between Ca and U explains the fact that we can find several complex salts of uranium and calcium in phosphate rock and the small difference in ionic radius between Ba and Ra explains the fact that it is well known that having Ba in the reaction tank of the phosphoric acid process, helps to precipitate radium sulfate.

But the large difference in ionic radius between Ra and Ca leads to the conclusion that there is no risk to get Ra co-crystallization with Ca in $CaSO_4$. As a summary, there is no risk:

(1) To get co-crystallization of Uranium with $CaSO_4$. $2H_2O$ because most of the uranium is transferred to phosphoric acid as uranium phosphate, a soluble salt in phosphoric acid, and

(2) To get radium co-crystallization in $CaSO_4$. $2H_2O$ because of the differences in (1) solubility of the respective sulfates, (2) of ionic radius between Ra and Ca and 3) in crystalline structure.

For these reasons, the radium which is in phosphogypsum should be in the form of small crystals of radium sulfate, not bound to other crystals. However, another source of radium can be found in phosphogypsum. This source is big particles of unattacked phosphate rock which can contain some radium. Finally, a source of radiation emission is the phosphoric acid and uranium phosphate which wet the phosphogypsum.

Radium Removal from Phosphogypsum. This reasoning gives five main ways to be followed in order to obtain a decrease of the radium content in phosphogypsum.

(1) The first one to use, when the choice is possible, is phosphate rocks with a low content of uranium. The radiation by Ra-226 can vary from one source to another source of phosphate ore from 5Ø to 2 pica-Curies per gram. But this does not help an industry which has a specific supply of ore.

(2) The second one is to wash thoroughly the residual phosphoric acid on the phosphogypsum and which contains uranium and gives radiation emission.

(3) The third one is not to have unattacked phosphate rock in phosphogypsum. In order to reach this goal, the best way is to grind the phosphate rock finely enough to be sure that every particle will be totally attacked. Another way is to screen the phosphogypsum and to reject the particles above 16Ø µmm (microns).

(4) The fourth one is to try to produce calcium sulfate dihydrate crystals as big as possible. Tests have been done on phosphogypsum from two different processes. One is a NISSAN plant where we have an average crystal size of 6Ø µmm. The second one is a DIPLO plant (which is a dihydrate process by RHONE POULENC (where the average crystal size of calcium sulfate dihydrate is 35 µmm. You can find a schematic of these two types of processes in Figures 3 and 4. These two plants, when fed with similar Moroccan phosphate rock, give phosphogypsum with different radium contents.

Measurement of radiation emission by Ra-226 gave:

23 ± Ø.6 pica-Curies per gram for the NISSAN process, and

28 ± Ø.4 pica-Curies per gram for the DIPLO process.

The standard measurement of radiation emission by Ra-226 gives a figure of 39 ± Ø.5 pico-Curies per gram for the mean Moroccan phosphate rock used by the company which manages both plants. The fact that the NISSAN process is using a double crystallization, the first one as hemihydrate, the second one as dihydrate cannot explain this difference. The only explanation we found is the following one: The phosphogypsum cake formed on the rotary filter of the phosphoric acid plant is more porous when the size of calcium sulfate crystals are washed out along with the phosphoric acid. When the calcium sulfate crystals are smaller, most of

the radium sulfate crystals stay trapped between the phosphogypsum crystals.

(5) The fifth one is a particle separation by treatment of a slurry through a hydrocyclone. In such a treatment you find the big particles with the underflow and the small particles with the overflow. You have a similar effect, but with less efficiency, by using a settling tank with or without the addition of a flotation agent. In the latter case, the efficiency is less because of the high density of radium sulfate. Many patents are recommending to treat the phosphogypsum with hydrocycloning. Among them, you can find the PROGIL and LAFARGE, CdF-CHIMIE, CERPHOS patents. Another one by M. Jan Thomas BOONTJE, claims that it is possible to decrease radiation emission of phospho-gypsum by such a treatment. We did measurements in one existing plant and in a pilot plant. You can find the results on Figures 5 and 6. On the table of Figure 5, it is possible to notice the decrease of total radiation emission in both cases when getting rid of the oversized particles above 160 μ mm, which generally are unattacked phosphate rock. On the same table of Figure 5, you can notice that each treatment through hydrocycloning gives about an equal decrease in total radiation emission. We did not go further but we intend to do it soon, in order to know if there is a limit. However, we believe each successive operations will continue to remove part of the remaining radium. The type of agitator used when the phosphogypsum is repulped into fresh water is important as more friction can help to remove small radium sulfate crystals from the surface of calcium sulfate crystals. The addition of wetting agent can help too for the same reason. We will do these tests in a common action with CdF-Chimie in the next few months.

All of the above results as shown in Figure 5 were obtained in a pilot plant. Figure 6 shows a schematic of an existing plant engineered by CdF-CHIMIE and AIR INDUSTRIE using this process. This operation incorporates the recycling of the overflow to decrease fresh water consumption. Without such recycling, it should be possible to decrease further the Ra-226 radiation emission from an actual measured 11-12 down to something below 10 pCi/gram.

On Figure 7, you can also see the effect of this hydrdcycloning process on reducing uranium content. This means that a large part of B radiation emission and some of the α radiation emission from uranium can be removed by pure washing.

You can see that we have an approach when we want to decrease the radium content of phosphogypsum. However, it is necessary to evaluate how far we have to go if we want a safe product that is not too expen-sive. The cost is not so much in the treatment itself as in the amount of water necessary for this type of treatment.

Up to now, this type of treatment (at least in France) is done by people who want to utilize phosphogypsum. However, we do not see why the phosphogypsum could not be treated instead by the phosphoric acid producer. One advantage of such a treatment by the producer should be the possible recovery of unattached phosphate and recovery of the small quantity of phosphoric acid which wets the phosphogypsum filter cake. A

second advantage would be that the radium would be distributed more uniformly over a wide area as fertilizer with no long-term local concentration. Under such conditions, radon concentration will be low and should not be noxious having open exposure to the air.

How Weak Should the Radium Content in Phosphogypsum Be? We know that the results of all the calculations and regulations are linked to hypothesis which always can be questioned. However, the actual trend in England and Germany is to propose a new building material code in Europe which suggests:

(1) To banish materials with a radiation emission above 25 pCi/gram,

(2) To control material with a radiation emission between 25 and 1Ø pCi/gram,

(3) To consider materials with a radiation emission below 1Ø pCi/gram as not radioactive materials.

We hope to reach 7 ± 1 pCi/gram in a new plant under study.

ACKNOWLEDGMENTS

We have to thank for the given information and the help for the achievement of tests the French Commissariat a L'Energie Atomique, the CdF-CHIMIE Technical Department and Laboratories and the LAFARGE S.A. Laboratory staff, B. Lelong and J.P. Caspar.

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238 Uranium Family

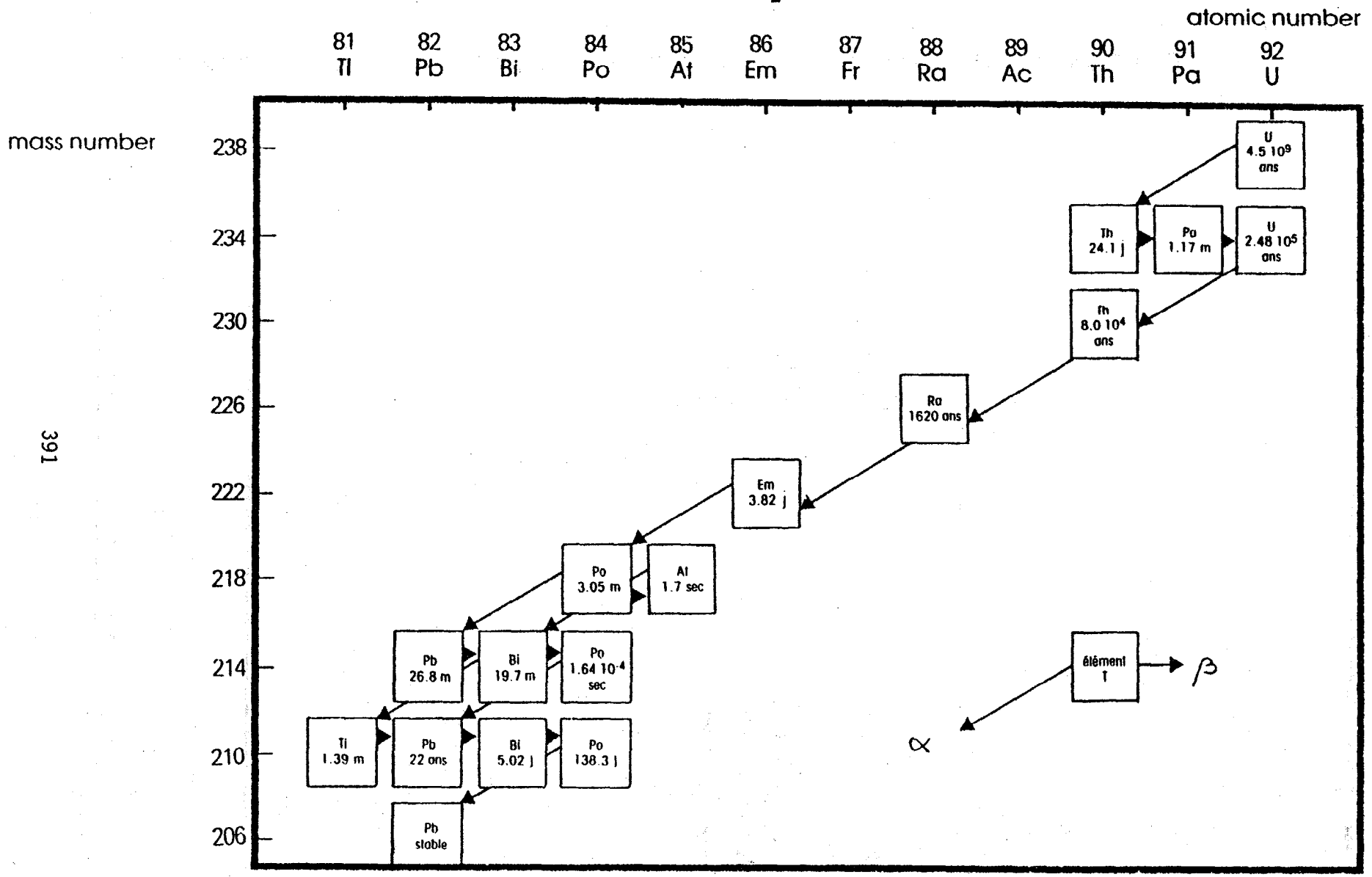


fig 1

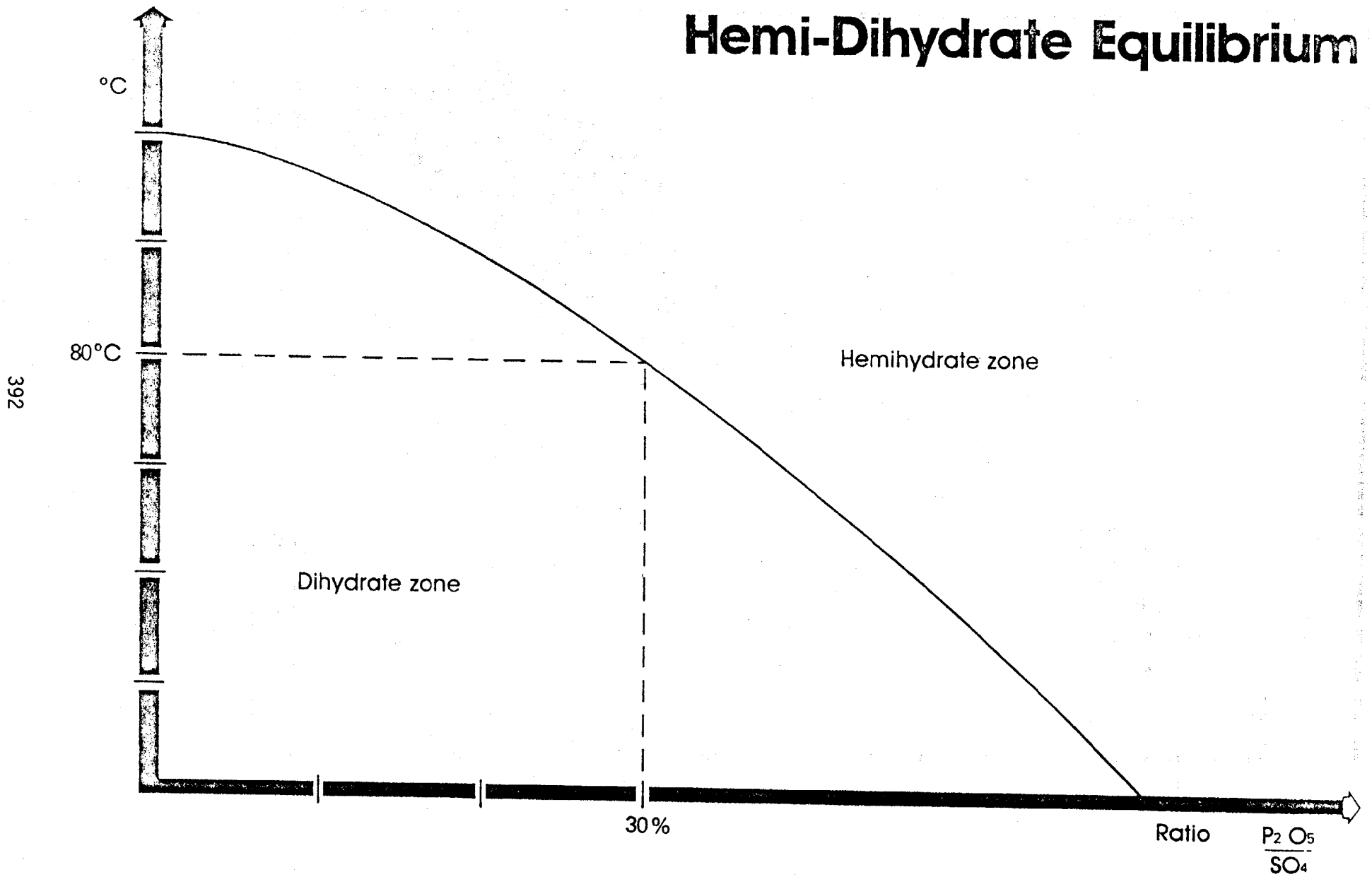

Hemi-Dihydrate Equilibrium
°C
80°C
Hemihydrate zone
Dihydrate zone
30%
Ratio
P2 O5
SO4

fig 2

Nissan Process

200 T P_2O_5/day

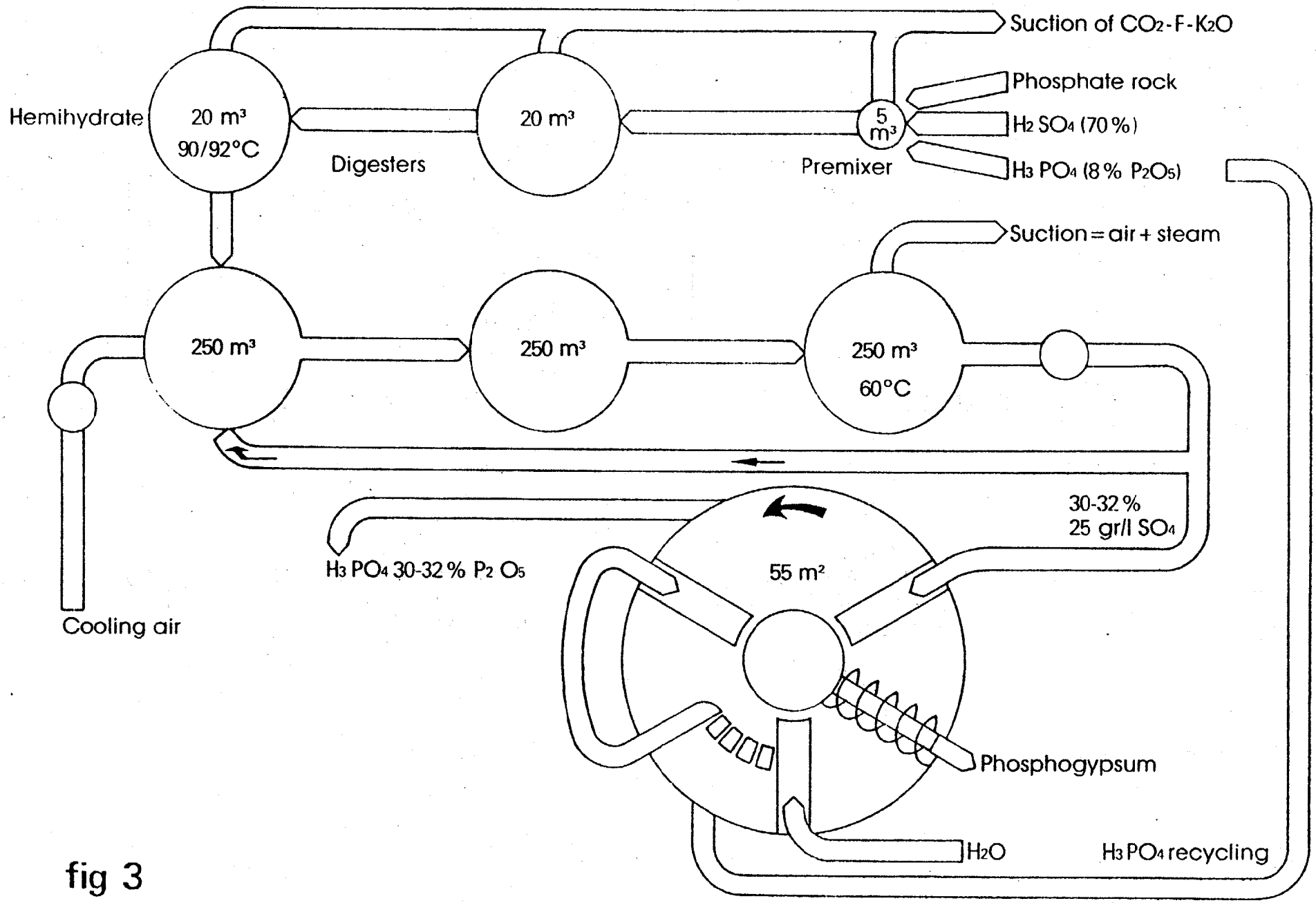


fig 3

Diplo Process
200 T P_2O_5/day

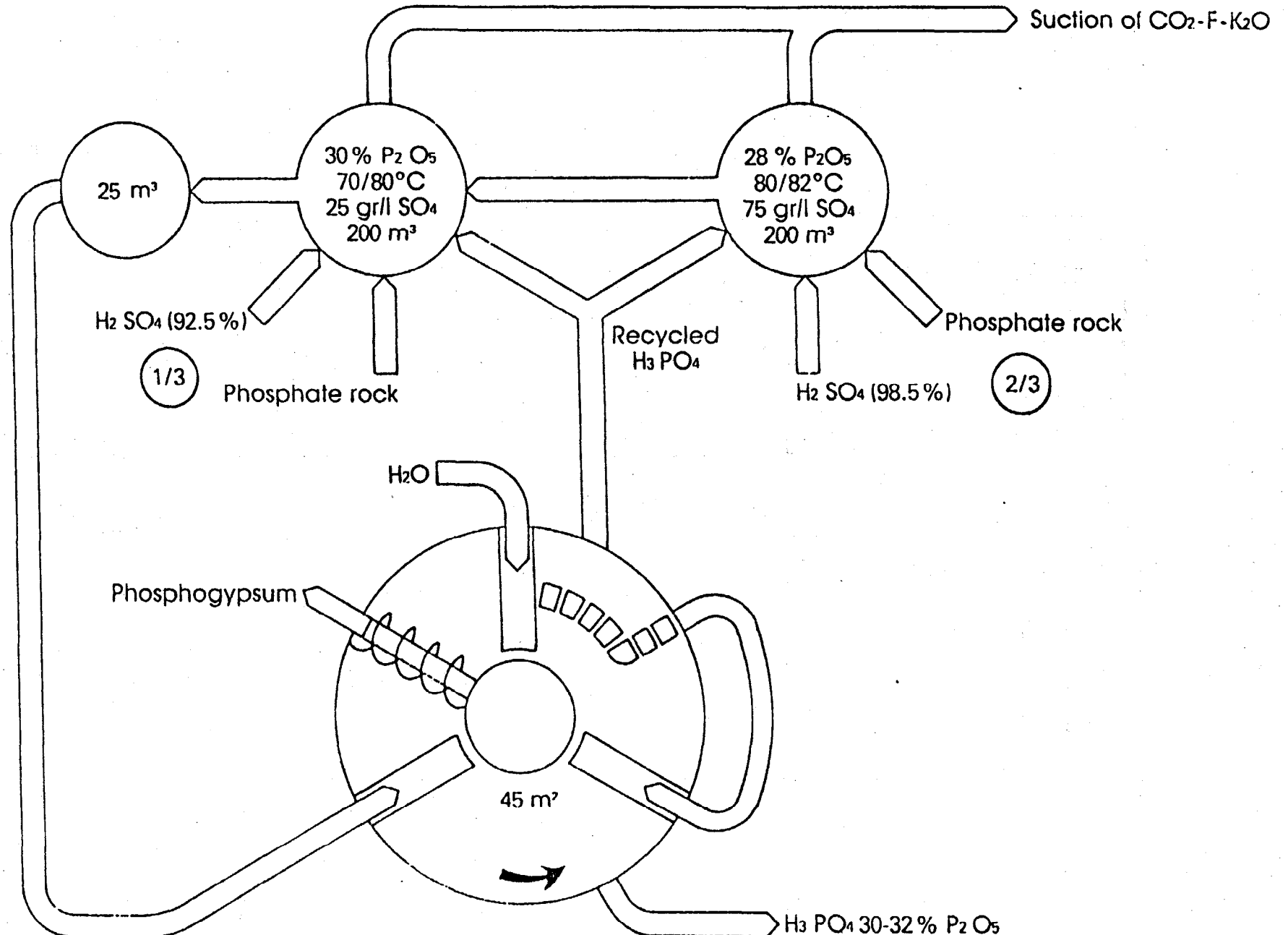


fig 4

Hydrocycloning of slurry

Gypsum	Florida rock		Morocco rock	
	total	226 Ra	total	226 Ra
Phosphate rock	122	30	122	30
Phosphogypsum : under 160 μm	63	—	102	—
After 1st treatment : over flow	174	—	239	—
under flow	72	—	80	—
After 2nd treatment : over flow	111	—	185	—
under flow	62	13	64	13
After 3rd treatment : over flow	—	—	—	—
under flow	—	—	48	8

fig 5

Hydrocycloning of slurry

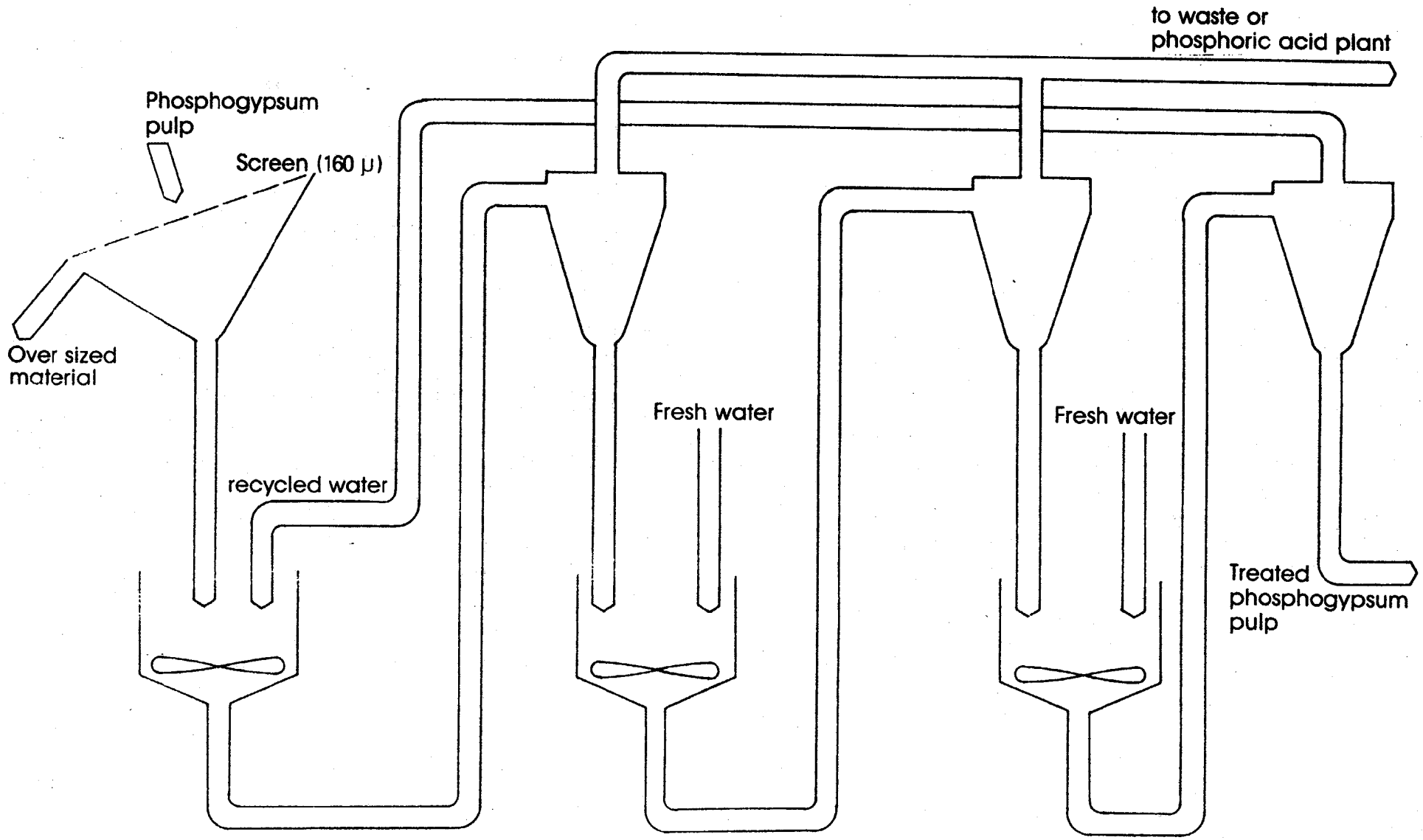


fig 6

226 Ra
Radiation emission and uranium content

	226 Ra (pCi/g)	Uranium (µg/g)
Moroccan rock	39	125
Phosphogypsum	28	17
Treated phosphogypsum	12	7.8
Stucco	16	6
Florida rock	29	87
Phosphogypsum	20	6
Treated phosphogypsum	10.5	2.4
Stucco	11	<2

fig 7

Environmental Effects of Phosphogypsum

RADIOLOGICAL CONSIDERATIONS OF PHOSPHOGYPSUM UTILIZATION IN AGRICULTURE

by

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INTRODUCTION

Gypsum ($CaSO_4 \cdot 2\ H_2O$) is an amendment that is widely used to improve the permeability of saline alkali soils. It also is used as a substitute for lime or limestone when a source of calcium is required and raising the pH of the soil is advisable. Agriculture is a minor outlet for gypsum. In 1979, 21,833,000 tons of gypsum were sold in the United States. Of this total, only 1,700,000 tons were used in agriculture. By-product gypsum accounted for 828,000 tons or nearly half of the agriculture usage (1). The balance of agricultural gypsum is supplied by quarried gypsum. Figure 1 shows annual consumption of gypsum according to use, indicating that agricultural consumption has not changed materially over the last 25 years.

The principal source of by-product gypsum is the phosphate fertilizer industry, and in the United States, Florida is the major source of phosphate rock (2). To produce phosphoric acid, the phosphate rock (commonly fluorapatite $Ca_5F(PO_4)_3$) is treated with sulfuric acid and the $CaSO_4$ (termed phosphogypsum) precipitates and is filtered from the acid. A simplified version of this reaction is shown by the following equation:

$$Ca_3(PO_4)_2 + 3\ H_2\ SO_4 + 6\ H_2O \longrightarrow 3\ CaSO_4 \cdot 2\ H_2O + 2\ H_3PO_4.$$

Florida phosphate rock may contain from 10 to 200 ppm of uranium. In the acid dissolution of the rock, the uranium tends to go into the acid solution, whereas the radium in the uranium decay chain coprecipitates with the gypsum. The radium content of phosphogypsum varies with the source of the phosphate rock. Phosphogypsum from Florida's central land pebble district generally contains about 30 pCi/g of Ra-226. The radium content of phosphogypsum from Florida's northern district averages about 15 pCi/g.

There are three areas of radiological concern associated with phosphogypsum utilization in agriculture and all of these related to its radium content. First, there is (concern over the buildup of radium in soil as a result of long-term use, and the consequent radiation exposure to agricultural workers. Secondly, and also related to this buildup, is the uncertainty regarding radium transfer to man via uptake of radium by agricultural crops. The third concern presupposes that land use will ultimately change from agricultural to residential and that the radium in the soil might then constitute a hazard to occupants of residences built on the land.

Why Gypsum is Used in Agriculture. Before discussing these radiological concerns, the reasons for using gypsum in agriculture should be reviewed. At present, phosphogypsum is most widely used in California. Much of the inland valley areas of California are arid and the soils are alkaline. Alkaline soils may either be saline - having a high content of soluble salts, or they may be alkali in which case their cation exchange sites are largely occupied by sodium ions. Alkaline soils generally are characterized by poor drainage, which is often caused by a dispersal of colloidal clay particles resulting in surface crusts and blocked soil pores.

The treatment of either saline, alkali or saline-alkali combination soils to improve drainage is called reclamation. Saline soils can usually be reclaimed by leaching. But treatment of soils with an amendment prior to leaching is recommended for alkali or saline alkali soils. The amendment most often employed is gypsum. When the dispersed particles contact the gypsum, the Na+ ions on the cation exchange sites ar replaced by Ca++ and the colloid is flocculated.

$$\begin{matrix} Na+ \\ \{\text{Micelle}\} \\ Na+ \end{matrix} + CaSO_4 \rightleftharpoons Ca++\{\text{Micelle}\} + Na_2SO_4$$

Following gypsum application and tilling (to assure mixing) the soil may be leached to remove the salt (Na_2SO_4) released. As long as the particles remain flocculated, a granular oil state and good drainage will prevail. Initial application of gypsum should provide sufficient excess to drive the reaction to completion and convert Na_2CO_3 to $CaCO_3$ and Na_2SO_4. This will reduce the soil pH and the Na_2SO_4 can be removed by leaching Regularly cultivated, the soil should not require annual applications of gypsum; when subsequent applications are used it is more for soil quality maintenance than for reclamation.

Peanut farming in the southeastern states may use gypsum as a source of calcium, often substituting it for lime or limestone when the alkalinity of the latter materials must be avoided. A supply of calcium is a major requirement for proper nutrition of this crop. Optimum peanut growth is also favored by slightly acid soil conditions (pH 5.5 - 6.5), hence the use of gypsum.

Radiological Concerns. The radiological concerns of using phosphogypsum in agriculture can be placed in perspective by considering a hypothetical case of extended heavy applications of phosphogypsum. In California, initial gypsum applications as high as ten tons/acre may be made for reclamation followed by alternate year applications of five tons/ acre for maintenance of soil quality. This initial application is about ten times the application rate typically employed in peanut farming in the southeast. Furthermore, peanuts are usually not grown on the soil every year, but are rotated with crops such as corn. As a result, gypsum is applied to these soils about every three years at application rates of one ton or less per acre.

Radium Buildup. If the radium content of the phosphogypsum was 15 pCi/g and the till depth six inches, the initial ten ton/acre and alternating five ton/acre schedule could be maintained for more than 100 years before the radium buildup would reach a proposed federal concentration limit of 5 pCi/g. This estimate is really conservative since no allowance is made for radium washout (leaching) or uptake by crops grown on the soil. Such an assumption, although conservative, may be unrealistic; without losses through runoff or uptake by plants, the soil would probably become poisoned by the buildup of salt long before the radium concentration reached 5 pCi/g. The 15 pCi/g for the radium content for phosphogypsum may be considered too low; however, most of the phosphogypsum used in California comes from Northern Florida

phosphate, and as previously noted, this source has a lower radium content than that generally quoted for Florida phosphogypsum (3). It should be noted that the proposed federal concentration limit for radium in soil of 5 pCi/g applies to lands contaminated by uranium mill tailings on which residences have been or will be constructed (4).

Terrestrial Radiation. Essentially all the gamma radiation exposure from the U-238 decay chain is due to Pb-214 and Bi-214, daughter products of Rn-222, as shown in Table 1 (5). The effect of depth on the fraction of total exposure rate from a uniformly mixed naturally occurring source has been derived by Beck (6) and is shown in Figure 2. From these data it has been estimated that a uniform concentration of 5 pCi/g of Ra-226 distributed throughout the top six inches of soil would result in an exposure rate of about 7 μR/hr.

This exposure rate must be added to that of normal background. If the average terrestrial background observed in the United States of approximately 6 R/hr (7) we added to the estimated exposure from the 5 pCi/g of Ra-226, the resulting 13 R/hr would be within the range of terrestrial exposure rates found in many populated areas. If an agricultural worker spent 40 hours a week on this soil, he would receive an estimated annual radiation dose above background of about 15 milli-rem. This dose is about 3% of the recommended limit for an individual in an unrestricted area (8).

Airborne Radon Daughters. When an Ra-226 atom decays into an Rn-222 (radon) atom the gaseous daughter atom may escape into the soil air instead of remaining in the soil matrix. Once into the soil air, the radon can diffuse up through the soil into the atmosphere. Whether the radon enters the atmosphere or remains in the soil, it undergoes the radioactive decay shown in Figure 3. Up to about 50% of the radon produced by the decay of radium may diffuse into the atmosphere depending upon atmospheric pressure and the porosity of the soil. In the atmosphere, the concentration of radon and its daughter products are determined more by the mixing rate in the atmosphere than by the concentration of radium in the soil (9).

Fall months are normally characterized by a high degree of atmospheric stability. During this period the days are often warm and there is little surface wind. After sunset, the ground cools faster than the air above it and a temperature inversion develops. As a result, radon and its daughter products accumulate near the surface during the night. During the day, vertical dispersion of this activity may be curtailed due to lack of surface wind. During the spring and early summer, windy weather is quite frequent, and surface released radon and its daughters are carried aloft by wind-induced vertical mixing. As a result of these seasonal differences in meteorology, the atmospheric radon concentration is highest during the fall months and lowest in the spring and summer. Figure 4 shows typical seasonal concentration differences observed at Livermore and the difference between morning and afternoon concentrations induced by night time temperature inversions.

Such variations have radiological monitoring implications, since it is obvious that extended sampling must be performed to accurately establish the average or typical radon daughter concentration. Once this is established for open land the measurements must be repeated when a building is constructed, since the extent of building ventilation greatly influences the radon daughter concentration. The present national emphasis on energy consumption -- weather stripping, caulking, etc. -- has reduced ventilation rates with the result that radon daughter concentrations within these energy efficient buildings have been increased.

Health Effects of Radon and Its Daughter Products. The primary hazard associated with working or living in an environment containing excessive amounts of Rn-222 and its daughters involves inhalation and subsequent deposition in lung tissue of the short-lived daughters. This concept has been established by epidemiological surveys of uranium miners who, under conditions of extreme exposure, exhibit an increased incidence of lung cancer.

Several organizations have established standards for maximum permissible concentrations in air of radon and its daughter products. The Environmental Protection Agency utilizes the concept of a working level. One working level (WL) being defined as that concentration of short-lived daughter products in a liter of air that will yield 1.3 x 10^5 million electron volts (MeV) of alpha energy in decaying through CaC'. This definition specifies the concentration of the radioactivity of concern - the daughter alpha emitters, and does not specify the necessity for equilibrium between the parent radon and its daughters. If equilibrium does exist, one WL is equivalent to 100 pCi/l of Rn-222.

An atmospheric radon daughter concentration of 0.1 pCi/l expressed as a working level would be 0.001 WL, assuming equilibrium conditions. However, such conditions are rarely achieved. At Livermore, we found an average annual percentage of secular equilibrium to be 75% in surface air based on measurements made in the Livermore Valley (10). Accordingly, an 0.1 pCi/l concentration of radon daughters at 75% of equilibrium would have an equivalent WL value of 0.00075 or 7.5 x 10^{-4} WL,

Table 2 shows that 5 pCi/g of radium in the soil would be expected to result in an airborne radon daughter concentration equivalent to an average working level of 0.012 (11). The range of concentrations shown are attributed to variations in meterology, and the degree of ventilation in basement and living areas of the building. Although this range exceeds the concentration proposed for residential exposure (12), such a guidance should not be applied to agricultural workers because of the seasonal nature of their work.

Uptake of Radium by Crops. Radium uptake expressed as the ratio of radium in dry weight foodstuff to the radium in the soil is in the range of 0.01. Assuming consumption of 80 g/day (dry weight) of foodstuff (13) grown on soil containing 5 pCi/g day. The mean daily uptake of Ra-226 in the standard U.S. diet is about 1.4 pCi, but varies at least from 0.7 to 2.1 pCi (14).

Assuming an adult's total vegetable diet consisted of items grown on soil containing 5 pCi/g of radium and that this consumption was continuous over a period of 50 years, the integrated radiation dose to the surface of the bond (the critical organ) would be 1.4 rem (15). For reference, persons in unrestricted areas are permitted to receive an annual radiation dose to the bond of about 2 rem (16).

In the case of radium associated with gypsum, the radium uptake ratio of 0.01 may be too high. When applied to the soil in a matrix containing calcium in such excess, the use of gypsum could be expected to block plant uptake of radium, as it has been demonstrated that increasing the calcium in plant nutrients reduces the uptake of other alkaline earth cations present (17). This common ion effect is illustrated by the data in Table 3, which compares the radium uptake in both root and leaf vegetables grown in test gardens containing two different levels of calcium.

Land-Use Conversion. Land use conversion from agricultural to residential would be of concern if our hypothetical application schedule would in fact result in a 5 pCi/g radium concentration in the soil. Table 2 shows this radium concentration could generate radon daughter concentrations that exceed the federal proposed guidance for residential occupancy. Although the present analysis was based on hypothesis, evidence of radium buildup in agricultural areas treated with phospho-gypsum should be monitored, since any such buildup may gain added importance as residential construction becomes more energy efficient.

SUMMARY

The radiological concerns associated with phosphogypsum utilization in agriculture have been placed in perspective by considering the consequences of a hypothetical case involving heavy long-term applications of phosphogypsum. In California, such a schedule might consist of an initial gypsum application of 10 tons/acre followed by alternate year applications of 5 tons/acre. If the radium content of the gypsum were 15 pCi/g and the till depth six inches, this schedule could be maintained for more than 100 years before the radium buildup in the soil would reach a proposed federal concentration limit of 5 pCi/g. An agricultural worker spending 40 hours a week in a field containing 5 pCi/g of radium would be exposed to terrestrial radiation of about 7μ R/hr above background. This exposure would result in an annual radiation dose of about 15 mrem, which is 3% of the recommended limit for an individual working in an uncontrolled area. Five pCi/g of radium in the soil could generate airborne daughter concentrations exceeding the concentration limit proposed for residential exposure. However, as residential exposure limits are predicted on 75% of continuous occupancy, these limits should not be applied to agricultural workers because of the seasonal nature of their work. Radium uptake by food crops grown in the hypothetical soil would result in a 50 year integrated dose to the bone surface of 1.4 rem. This dose is conservatively based on the assumption that an adult's total vegetable diet comes from this source and that consumption was continuous during the 50 year period. For comparison, individuals in unrestricted areas are permitted annual radiation doses to the bone of about 2 rem. Land use conversion from agricultural to residential has a potential for concern,

since soil containing 5 pCi/g of radium can generate airborne concentrations of radon daughters in buildings which exceed the federal guidance for residential occupancy.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of Curtis L. Graham of the Lawrence Livermore National Laboratory in performing the radiation dose calculations associated with radium uptake through the food chain.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe private owned rights. Reference herein to any specific commercial products, process or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The view and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government thereof, and shall not be used for advertising or product endorsement purposes.

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Distribution

LLNL Internal Distribution

Roger E. Batzel	L-1
C.L. Graham	L-383
C.L. Lindeken	L-385 (24)
J.L. Olsen	L-20
H.W. Patterson	L-382
W.J. Silver	L-383
A.J. Toy	L-385
TID File	L-52 (15)

Isotope	$\frac{\mu R}{h}$ / $\frac{pCi}{g}$
^{238}U + daughters	1.82
^{226}Ra + daughters	1.80
^{214}Pb (RaB)	0.20
^{214}Bi (RaC)	1.60

Table 1. Radiation Exposure rate at 1 m above ground for ^{238}U + daughters and ^{226}Ra + daughters

Soil concentration	Working level	
pCi/g ^{226}Ra	Ranges (a)	Average (b)
1.0	0.0002-0.008	0.002
3.0	0.0007-0.024	0.006
5.0	0.0024-0.04	0.012
10.0	0.0048-0.08	0.020

(a) 1 pCi/l ^{222}Rn = 0.005 WL assuming 50% of equilibrium

(b) Average based on midpoint of the range of input parameters

Table 2. Estimated airborne radon daughter working levels versus radium soil concentrations

Soil			^{226}Ra in plants, pCi/g (dry wt)	
Garden	Calcium, ppm	^{226}Ra, pCi/g	Broccoli	Turnip
1	3,100	0.477	$2.83 \times 10^{-2} \pm 34\%$	$2.55 \times 10^{-2} \pm 39\%$
2	5,200	0.482	$1.09 \times 10^{-2} \pm 100\%$	$1.32 \times 10^{-2} \pm 70\%$

Table 3. Effect of calcium on ^{226}Ra uptake by plants

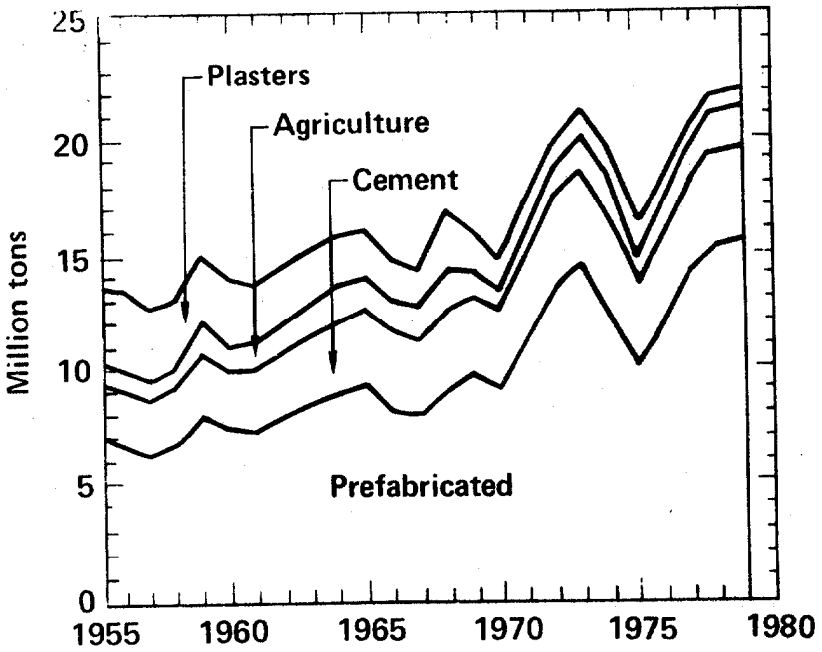


Figure 1. Sales of Gupsum Products by Use.

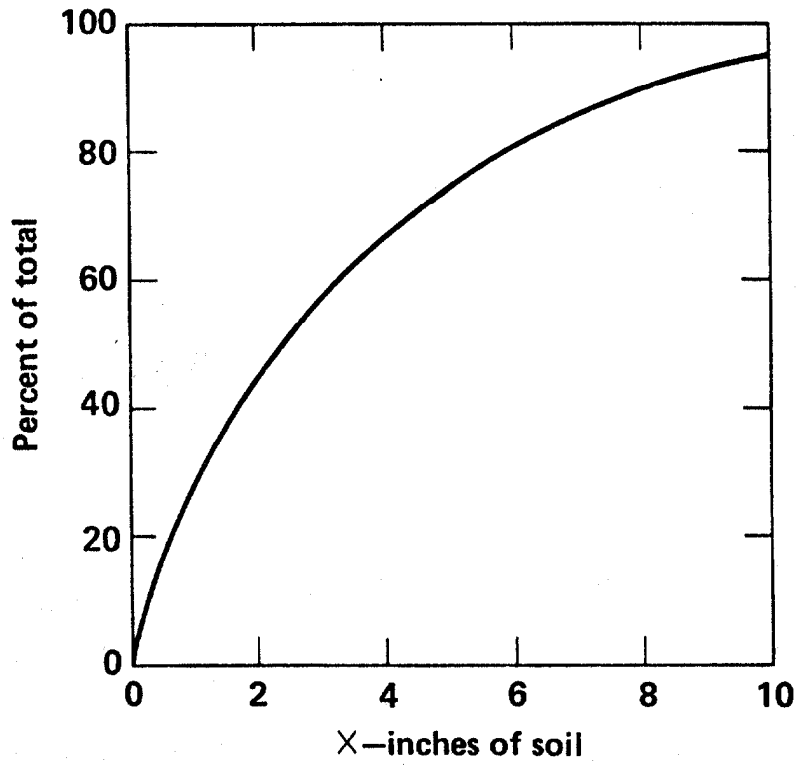


Figure 2. Percent of integral exposure rate due to natural emitter sources at various depths (from Beck, reference 5)

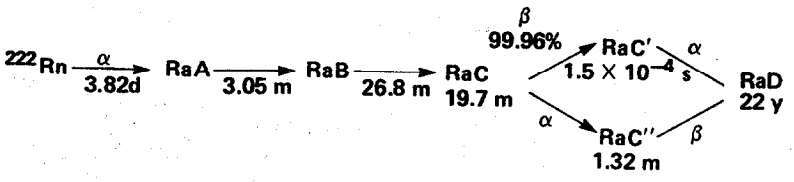


Figure 3. Radioactive decay scheme for ^{222}Rn

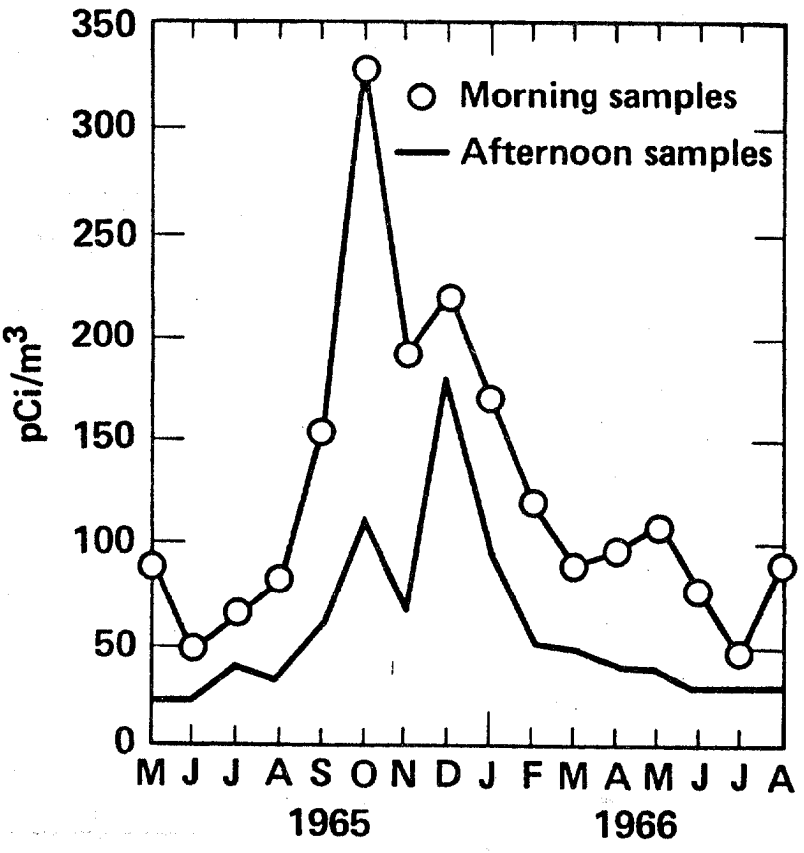


Figure 4. Morning and afternoon variations in airborne radon daughter concentrations

ASSESSMENT OF ENVIRONMENTAL IMPACTS ASSOCIATED WITH PHOSPHOGYPSUM IN FLORIDA

by

Alexander May and John J. Sweeney
U.S. Bureau of Mines

This manuscript is in preparation as a Bureau of Mines Report of Investigation which will be furnished to all participants upon completion.

Research Chemist
Supervisory Mining Engineer

INTRODUCTION

In the past 20 years there has been a constant shift in the United States toward multinutrient and mixed fertilizers in place of single-nutrient fertilizers. This trend has brought about the localization, especially in Florida and along the Gulf Coast, of large raw materials-oriented chemical companies manufacturing wet-process phosphoric acid, which is the basic material needed to product high analysis multinutrient fertilizers. The manufacture of wet-process phosphoric acid results in the generation of large quantities of waste gypsum. In the fertilizer industry this is usually referred to as phosphogypsum, which distinguishes it from the natural gypsum mineral. As a rule, 5.5 tons of phosphogypsum are produced for each ton of phosphoric acid produced.

In 1978, U.S. production of crude natural gypsum was estimated at 14.9 million tons; in addition, 700,000 tons of phosphogypsum were used. Annual domestic consumption in 1978 was at 24.4 million tons of gypsum (10)[3].

By comparison, the Florida phosphate industry generates 33 million tons of phosphogypsum annually, with only a small fraction (about 700,000 tons) used for agricultural purposes. In addition, there are 334.7 million tons of the material stacked on the ground in Florida. Projections indicate that by the year 2000, over one billion tons of this phosphogypsum will be available in Florida alone. Figure 1 shows the location of current phosphogypsum stacks in Florida.

The Environmental Protection Agency (EPA) has identified phosphogypsum as a potential hazardous waste because of its contained radium-226 and its vast tonnages. A part of the Bureau's Minerals Environmental Technology research program is to assess these types of problems and develop a data base so that through a continuing research effort potential environmental problems can be mitigated. The Bureau's Tuscaloosa Research Center conducted research to characterize phosphogypsum to determine if it is hazardous or toxic, and if so, to investigate means to mitigate the situation so that the phosphogypsum could be used in a variety of high volume applications.

ACKNOWLEDGMENTS

The authors are indebted to advice and assistance in the study to Dr. David P. Borris, Executive Director, Florida Institute of Phosphate Research. The voluntary cooperation of the following Florida phosphate companies in assisting in this study is also gratefully acknowledged: Agrico Chemical Company, American Cyanamid Company, Borden Chemical Company, C.F. Industries, Inc., Conserve, Estech General Chemical, Farmland Industries, Gardinier, Inc., International Minerals and Chemical Corporation, Occidental Chemical Company, Royster Company, U.S.S. Agri-Chemicals, and W.R. Grace and Company. Special appreciation is extended to the Environmental Protection Agency's Radiation Facility, Montgomery, Alabama, for radiological isotope analysis.

Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Criteria for Defining Hazardous/Toxic Waste. The EPA criteria defining hazardous and toxic waste were used as guidelines in this study. The EPA criterion for corrosivity is a pH equal to or less than 2, or equal to or greater than 12.5 (7). The EPA criterion for toxicity of wastes is based on an extraction procedure to identify toxic wastes likely to leach into the groundwater. The hazardous nature of the waste is judged by the concentrations of specific contaminants in the extract. The contaminants listed by EPA for consideration are eight metals and six chlorinated organic compounds (7). There are no probable sources of chlorinated organic compounds in the phosphogypsum or its precursor reactants. Therefore, organic compounds were not investigated in this study. The Bureau of Mines considered the total concentrations of trace elements in phosphogypsum, rather than consider only the toxicity due to leachable elements. Thus, emission spectrographic analysis of the gypsum solids were used to determine trace elements, both toxic and nontoxic. These analyses were correlated with the EPA leaching tests criteria, and also provided information for the assessment of the gypsum under all conditions.

The EPA regulations, proposed December 18, 1978, for the identification of hazardous wastes listed phosphogypsum as a hazardous waste because it was radioactive. To be excluded from the list, the average radium-226 concentration would have to be less than 5 picocuries per gram of solid waste or the total quantity of radium-226 would have to be less than 10 microcuries for any single discrete source (6). The final EPA regulations, issued May 19, 1980, still list phosphogypsum as a hazardous waste but defers development of final regulations for phosphogypsum pending Congressional action (7).

Phosphogypsum Production. Phosphogypsum is the major byproduct of wet-process phosphoric acid production. Phosphate rock, which is composed of apatite minerals (8), (calcium phosphates containing varying amounts of carbonate and fluoride), is digested with sulfuric acid and water to produce phosphoric acid, phosphogypsum and minor quantities of hydrofluoric acid. The reaction of the phosphate rock to produce gypsum, $CaSO_4 \cdot 2H_2O$, may be illustrated by equation (1):

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 2H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 6H_3PO_4 + 2HF \quad (1)$$

Gypsum forms monoclinic crystals that are tabular and diamond-shaped. Both habits are shown in Figure 2.

In the Prayon process commonly used in Florida, the phosphate rock, ground to pass 100 mesh, is treated with 30 to 46% phosphoric acid and 55 to 60% sulfuric acid. The slurry is circulated through reaction tanks to maintain the optimum time and temperature for the reaction and for the growth of gypsum crystals. The phosphogypsum is filtered, washed with water and pumped as a slurry to ponds from which the phosphogypsum settles to form the phosphogypsum stacks (11).

The hemi-hydrate process is similar to the Prayon process, but uses higher temperatures and acid concentrations in the reaction tanks. This favors the initial formation of hemi-hydrate which later converts to phosphogypsum: in the slurry tanks.

Figure 3 is an aerial view of a typical active phosphogypsum stack.

Inventory of Phosphogypsum. Seventeen phosphogypsum stacks were identified in Florida. Data regarding the inventory were obtained through the cooperation of the Florida Institute of Phosphate Research, and 13 phosphoric acid producing companies. The data shown in Table 1, which was current as of April 1980, showed that 334.7 million tons of phosphogypsum have accumulated in Florida over a 16.8 year average, giving an average production rate of 19.9 million tons per year. However, the present rate of generation greatly exceeds this average (4) and is now 33.3 million tons a year. At the present rate of generation, the amount of phosphogypsum accumulated by 1985 would be 500 million tons and approximately 1 billion tons by the year 2000.

Rationale of Sampling and Analyses. Of the 17 phosphogypsum stacks identified, 9 were sampled; these were identified as being representative of the variety of conditions encountered in either processing or storage. Of the nine sampled, six stacks were active and three were inactive. The rationale of the sampling program was to establish the uniformity and components of phosphogypsum in each stack and differences between stacks. This included differences 'between active and inactive stacks and between processes used in the manufacture of phosphoric acid. Of the active stacks, one produced phosphogypsum using the hemi-hydrate acid manufacturing process while the others produced phosphogypsum using the Prayon process. The phosphogypsum from one stack was washed in a different manner from the others prior to placing it on the stack, possibly making it atypical. Of the nine stacks sampled, Stack A was sampled at three locations: Stacks B and C were sampled at two locations each, while the remaining stacks were sampled at one location each.

The sampling program was designed to obtain results that would be representative of all of the phosphogypsum stacks, to show differences between stacks, and to show differences from top to bottom and across the stacks. Three types of samples were obtained:

(1) Core Samples, which were representative of the phosphogypsum in the entire length of a core. There were 13 core samples, one for each core drilled.

(2) Interval Samples, which were representative of the phospho-gypsum 10-feet depth intervals of a core. There were 90 interval samples.

(3) Sized Samples, which were representative of particle size distributions of the material in the entire length of a core. There were seven sized samples.

The rationale of the analytical tests was to characterize the phosphogypsum to assess its environmental impacts. The tests included chemical analyses for major components, pH tests for acidity, emission spectrographic analyses for minor elements, radium-226, thorium and uranium analyses for radioactivity, x-ray diffraction analyses for mineralogy, and size analyses, and density determinations for physical characterization.

One chemical analysis was made of each of the 13 core samples and one x-ray diffraction analysis was made of three of the core samples to provide the major chemical and mineralogical components of the stacks.

One spectrographic, pH and radium-226 analyses were made on each of the core samples, interval samples and sized samples to provide minor elements, acidity and radioactivity data. They also indicated differences between the stacks, differences from top to bottom and across the stacks and differences due to particle size distributions.

The three core samples obtained from Stack A, their interval samples, and sized samples were analyzed quantitatively for trace quantities of uranium and thorium. The three core samples were also analyzed for radium, uranium and thorium isotopes. These data were used to indicate the radioactive elements present and their relationships to each other within the stack.

All total, 13 core samples were obtained from approximately 1,000 feet of phosphogypsum core. Approximately 800 analyses and tests were performed to yield nearly 2,400 individual data points.

Test Procedures. To establish the free water content, samples were dried at room temperature to constant weight and then at 45°C for an additional two hours. The products were then analyzed for chemical, radiological and trace elements. Except for pH and densities, the chemical and radiological results were then calculated back to the weight basis of the samples as received. The particle size distribution was determined on the dried samples. Emission spectrographic results were reported on the basis of the dried samples.

Chemical analyses were performed in accordance with American Society for Testing and Materials, Standard Methods for Chemical Analysis of Gypsum and Gypsum Products, ASTM C471-76 (1). Fluoride and phosphorus were determined by the Association of Florida Phosphate Chemists Methods (9). Uranium was determined by the fluorometric method, ASTM D2907-70T (2) and thorium by the colorimetric method ASTM D2333 (3). Radium was determined by the radon emanation method (5) and uranium and thorium isotopes were determined by a chromatograpiric and radiological technique developed by the EPA.

Test Results. Tables 2 and 3 present the chemical analyses data. Table 4 shows the free water and Table 5 shows the pH for increment samples. Table 6 gives size distribution data. Table 7 through 10 address radium, uranium and thorium results and Table 11 lists emission spectrographic analyses.

The X-ray diffraction analyses were performed on core samples A1, B1 and F. All gave the same results. Only gypsum and alpha-quartz were detected. The limit of detection was about 5% of a mineral present. Fluorides and phosphates were present, as well as compounds of aluminum, magnesium, iron and other elements. However, these compounds were present at less than 5% and were not detected by the x-ray diffraction.

Discussion. The chemical analyses given in Tables 2 and 3 lists quantities of the major components of phosphogypsum. The analyses in Table 2 and that of sodium chloride in Table 3 were performed by the Standard Methods for Chemical Analysis of Gypsum and Gypsum Products (1). Although standard analytical methods were used, phosphogypsum differs sufficiently from gypsum to require scrutiny of the results. In the standard gypsum analysis, iron and aluminum are determined by removing silicon and acid insoluble material and then precipitating the iron and aluminum as hydroxides. The hydroxides are ignited to form oxides and the iron and aluminum oxides weighed. However, phosphogypsum contains phosphates and fluorides which accompany iron and aluminum hydroxides in their analytical determination. These precipitate as calcium phosphates and calcium fluoride. Titanium oxide may also contaminate the iron and aluminum hydroxides. The results for "iron and aluminum oxides," as designed in Reference (1) were thus higher than the actual quantity of iron and aluminum oxides present. Calcium is determined in the filtrate remaining after removing the silicon, acid insoluble material, iron, aluminum and calcium phosphates and fluorides. This calcium represented that which was present in the phosphogypsum. The other analyses were not affected.

A typical phosphogypsum composition is shown in Table 12. The results in Table 12 were from the analyses of the core samples, excluding samples C2, D and I. The core for sample C2 was taken from part of a phosphogypsum stack that had been placed in a phosphate rock mined-out area. The base of phosphate mine pits are uneven in elevation and contain overburden spoil. The unusual results for sample C2 were checked with three different composite samples. Also, the C2 interval from 10 to 20 feet and that from 70 to 80 feet were analyzed petrographically. This showed that the greater depth had high silica and low gypsum and the lower depth was vice versa. Results for C2; namely high silica, iron, aluminum, phosphorus, uranium and pH, and low calcium, sulfur and combined water, plus petrographic analyses, indicated that the core penetrated overburden spoil. Sample D was from a stack placed below ground level and sample I from a new stack. The analytical evidence indicates C2, D and I results were not completely typical of phosphogypsum due to possible contamination by overburden at the gypsum/ground interface.

The bulk densities shown in Table 3 indicated that no significant difference existed between the stacks in compaction of the phosphogypsum. The pH and radium results in Table 3 were those of the core samples. Discussion of pH and radium follows in conjunction with Tables 5 and 9.

Free water, shown in Table 4, represented moisture not bound as water of crystallization. No pattern for the seepage of water through the stacks was apparent from the data. The maximum free water content for each core occurred at depth intervals from 10 to 80 feet, but also the minimum occurred at depth intervals from 0 to 80 feet. The wettest and driest depth intervals even occurred adjacent to each other. For example, in core B1, the 60-70 foot interval was the wettest and the 70-80 foot interval the driest. In core B1 the first sample was like mud, the second like rock. Analysis of variance (ANOVA) of the data showed there was no significant difference in free water between depths and there was a significant difference between cores.

The pH values shown in Table 5 were all greater than 2.Ø and less than 12.5. Every individual pH measurement on all 1Ø-foot interval samples and the core samples given in Table 3 were also greater than 2.Ø and less than 12.5 This is significant because EPA defined a hazardous waste by the criterion of corrosivity as one that had a pH equal to or less than 2 or equal to or greater than 12.5. Therefore, all phospho-gypsum samples obtained in this investigation were not hazardous wastes by the EPA criterion of corrosivity.

Analysis of variance of the pH data showed that differences between cores and between depths were significant. This was also found when the atypical samples C2, D and I were excluded. However, when ANOVA was applied to A1, A2, A3 and also separately to B1 and B2, no significant differences were found in pH with depth or with cores. The highest pH values were for samples C1, C2 and F. All of these are from inactive stacks, the C stack being inactive 9 years and the F stack inactive 12 years. The pH values, 4.4Ø, 5.15 and 5.5Ø for C2 may be due to this core penetrating overburden spoil, as previously mentioned. Excluding these high C2 pH values, the remaining pH values from C2 average 3.66 still the highest pH value of the cores. The higher pH values for these inactive stacks indicate rain water may leach hydrogen ion and thus lower the acidity of the stacks.

Particle size distribution is shown in Table 6. In addition to the usual particle size distribution, labeled (A), and cumulative distribu-tion, labeled (B), the distribution was presented by coarse, medium and fine fractions, labeled (C). The latter fractions were used for uranium, thorium, radium and emission spectrographic analyses. These (C) fractions are also convenient summarizes of the particle size distribution data.

Uranium, thorium and radium analyses of sized samples are shown in Table 7. The uranium and thorium analyses were for total uranium and total thorium and the original data were measured in parts per million. The PPM uranium was multiplied by Ø.6781 and the PPM thorium by 4.5423 to convert them to picocuries per gram, for comparison to radium data. The factors used in the conversions were based on assuming the natural isotopic abundance of uranium and thorium isotopes. About half of the thorium data were reported as "less than 1 PPM." Since these data could not be accurately analyzed, they were included in Table 7 as NA, not available.

The average concentrations of uranium and radium for the coarse, medium and fine fractions are shown in Table 13. Radium was most concentrated in the fine fraction and (ANOVA) verified that a signifi-cant difference existed between the sizes. The results in Table 13 also indicated differences in uranium concentrations with size fractions. However, (ANOVA) indicates these differences are not significant. Insufficient data were available to statistically analyze thorium data.

Table 8 shows the isotopic analyses of radium, uranium and thorium in three samples. These results indicated that uranium-238, uranium-234 and thorium-23Ø were about in equilibrium. Radium was not in equilibrium and was more concentrated in the phosphogypsum than the radiological equilibrium with thorium-23Ø would allow.

Table 9 shows the analyses of the 10-foot interval samples for radium. The average of these data and comparison with the composite samples average are shown in Table 14.

The EPA proposed regulations of December 18, 1978 stated that 5 pCi Ra/gram or greater would cause a waste to be a hazardous waste because of radioactivity (6). However, on May 19, 1980, EPA deferred radiation limits on phosphogypsum, (7) so at this time it cannot be stated that the phosphogypsum was a radiation hazard based on EPA criteria.

Sample G was low in radium compared to the other phosphogypsum stacks. This was because the phosphate rock used to produce phosphogypsum in stack G contains about one-third the uranium and radium as the phosphate rock used to produce the phosphogypsum in the other stacks. Sample F is higher in radium than the other samples. We do not know, at this time, why this occurs.

Analysis of variance calculations were performed on the data in Table 9. Using all of the data, the ANOVA showed a significant difference in radium content at the 99% confidence level, between cores and showed that the difference in radium content was not significant with depth. The same was found when samples C2, D and I were excluded. When samples A1, A2 and A3 were examined, no significant differences were indicated between samples or between depths. The same was true with samples B1 and B2. This statistical analysis indicated that radium is uniformly distributed in each stack.

Table 10 shows uranium and thorium analyses of 10-foot increment samples. Analysis of the data indicated that uranium is also uniformly distributed in each stack. Thorium data were insufficient for an accurate statistical analysis.

Emission spectrographic analyses were performed on 13 core samples, on 90 lo-foot interval samples and on 7 sized samples, for a total of 110 samples. This yielded 1,780 individual analytical results for semi-quantitative concentrations of 30 elements. These results are summarized in Table 11.

The averages shown in Table 11 were the sums of all concentrations detected for a given element divided by the total number of analyses of the cores in which the element was detected. Thus, the data summarized concentrations only in cores in which elements were detected. For example, 57 analyses of nickel in 11 cores averaged 2 PPM of nickel. Two cores contained no nickel but these zero values were not included in calculating the 2 PPM average.

In addition to the emission spectrographic data summary in Table 11, the concentrations of each of 30 elements were tabulated by core sample versus depth. These tables are not included in this report because of the quantity of data. The emission spectrographic data, so tabulated, were statistically analyzed for 23 of the 30 elements listed in Table 11 by (ANOVA) at the 99% confidence interval. The seven elements not so analyzed were detected in less than eight samples and their data precluded the use of analysis of variance.

In every case the (ANOVA) indicated that there was no significant differences in concentrations of the elements with depth. Eleven elements, aluminum, arsenic, iron, magnesium, molybdenum, potassium, sodium, tin, titanium, tungsten and vanadium showed a significant difference in concentrations between cores. The other 12 elements showed no significant difference in concentrations between cores. When considering a single phosphogypsum stack, B and the 11 elements that showed a significant difference between cores, the ANOVA analysis indicated no difference in concentrations with depth or between cores B1 and B2.

These results indicated that trace elements were uniformly distributed in the phosphogypsum stacks. A uniform distribution of trace elements in the stacks would occur if the same quantities of trace elements were added to the stacks as were removed through leaching. However, three stacks (C, E and F) are inactive. Stack C has been idle nine years, stack E has been idle several months and stack F has been idle 12 years. In spite of about 40 inches of rainfall a year (12) for 9 and 12 years, stacks C and F also showed no significant difference in concentrations of trace elements with depth. Thus, the results indicated that trace elements were not only uniformly distributed in the stacks, but are not leached from the stacks in any significant amount. This also applied to sodium, potassium, copper and nickel whose sulfates are soluble.

The elements, arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver are listed as contaminants for characteristics of toxicity by EPA (7). Chromium, mercury and selenium were not detected in the phosphogypsum. Barium, cadmium, lead and silver were detected at concentrations far less than allowable by EPA requirements, even assuming that 100% of these elements would be extracted by the EPA procedure. The average arsenic concentration was also less than allowable by EPA requirements. However, two cores (F and H) contained 124 and 113 parts per million arsenic, respectively. If 100% of the arsenic present were extracted by the EPA extraction procedure, (7) the extracts from these cores would contain 6.20 PPM and 5.65 PPM arsenic which exceeds the EPA allowable concentration of 5.0 PPM arsenic. However, the previous analysis of the data indicated that the trace elements would not be leached from the phosphogypsum. Therefore, the phosphogypsum would not be a toxic hazardous waste by EPA definitions. Further work is in progress to perform the EPA extraction procedure and confirm this conclusion. This will be reported in a subsequent publication.

CONCLUSIONS

Based on the research conducted at the Tuscaloosa Research Center, phosphogypsum was generated at a rate of 33 million tons a year in Florida. The amount of accumulated phosphogypsum in Florida was 335 million tons, and this quantity is projected to reach over 1 billion tons by the year 2000.

Phosphogypsum was not a corrosive hazardous waste. Its pH was greater than 2.0.

The radium concentration in phosphogypsum in Florida averaged 21 picocuries per gram and its concentration was greatest in the fine sizes.

Thirty-nine elements were detected in phosphogypsum; 30 by emission spectrography, three radiologically and six by chemical analyses.

The concentrations of elements listed by EPA for toxic elements each average less than the allowable toxic elements criteria for toxic hazardous waste.

The concentrations of elements in phosphogypsum did not vary with depth.

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TABLE 1. - Phosphogypsum inventory

Gypsum stack Identification	Year began	Year discon-tinued	Years in service	Acres	Annual production million tons per year	Cumulative total, million tons
A	1965	Active	15	250	2.400	22.000
B	1947	Active	33	300	3.000	77.000
C	1956	1971	15	123	Inactive	18.900
D	1963	Active	17	340	3.700	43.080
E	1948	1980	32	50	Inactive	12.128
F	1948	1968	20	100	Inactive	5.000
G	1966	Active	14	284	3.500	21.304
H	1964	Active	15	360	1.100	16.500
I	1975	Active	5	300	5.500	17.361
J	1976	1980	4	84	Inactive	1.540
K	1961	Active	19	200	3.500	18.288
L	1954	1963	9	250	Inactive	4.000
M	1973	Active	7	60	1.302	5.860
N	1965	Active	15	400	3.016	22.709
O	1955	Active	25	90	0.750	5.830
P	1954	Active	26	528	4.600	32.200
Q	1965	Active	15	250	2.400	22.000
Totals	-	-	285	3,859	33.268	334.700

TABLE 2. - Chemical analyses[1] of core samples of phosphogypsum, major components

Core number	Feet depth of core	Percent by weight of samples as-received					
		Free water	Combined water	SiO_2 and insol.	[2]Al_2O_3 and Fe_2O_3	[3]CaO	SO_3
A1	70	16.3	15.78	3.46	3.31	24.51	37.30
A2	70	17.2	15.55	4.92	3.48	23.69	36.92
A3	70	18.7	14.66	4.86	3.56	23.15	35.62
B1	100	14.9	13.53	5.34	4.27	22.60	35.30
B2	100	14.8	12.74	13.67	2.49	20.82	31.71
C1	50	16.7	15.24	4.76	3.29	24.44	38.31
C2	80	15.1	9.70	34.15	7.51	14.04	23.48
D	70	14.1	12.02	11.01	6.31	18.66	28.55
E	90	20.7	14.29	6.66	3.41	22.47	35.64
F	30	17.6	15.73	4.48	4.38	23.32	36.17
G	60	18.9	13.19	9.57	4.07	19.22	30.54
H	80	17.2	14.18	8.99	3.74	22.26	34.58
I	30	16.0	10.72	12.90	7.48	15.61	27.55
Average	69	16.8	13.64	9.60	4.41	21.14	33.21

[1] Analyzed by ASTM C741-76 Part 5-13 Methods.

[2] Material soluble in HCl and insoluble in NH_4OH.

[3] Material soluble in HCL, soluble in NH_4OH and insoluble in oxylate solution = CaO in phosphogypsum.

TABLE 3. - Chemical analyses of core samples of phosphogypsum, minor components

Core Number	Percent by weight of samples as-received			-log [H+] pH	Density, g/ml		[1]pCi/g radium
	NaCl	P_2O_5	F		As-received	Dry at 110° C	
A1	0.01	0.67	0.49	2.30	1.57	1.08	18
A2	.01	.50	.41	2.50	1.69	1.14	17
A3	.01	.77	.40	2.55	1.63	1.12	19
B1	.03	.89	.60	2.55	1.32	1.20	20
B2	.02	.51	.64	2.65	1.40	1.22	18
C1	.01	.67	.38	2.65	1.42	1.06	20
C2	.01	2.97	.50	3.75	1.57	1.35	17
D	.01	1.85	1.05	2.85	1.49	1.31	30
E	.01	.52	.60	2.10	1.53	1.05	21
F	.01	.37	.85	3.35	1.44	1.05	38
G	.01	.32	1.81	2.70	1.56	1.19	8
H	.01	.83	.64	2.35	1.49	1.14	23
I	.01	2.48	.87	3.00	1.65	1.28	16
Average	0.01	1.03	0.71	2.72	1.52	1.17	20

[1] Picocuries per gram of composite samples as-received.

TABLE 4. - Free water of 10-foot interval samples of phosphogypsum

Interval samples, feet	SAMPLE													Row average
	A1	A2	A3	B1	B2	C1	C2	D	E	F	G	H	I	
	Percent by weight of samples as-received													
0 - 10	16.0	15.8	15.7	17.5	11.0	16.1	15.5	12.0	[2]15.6	17.8	[2]10.8	15.9	13.0	14.8
10 - 20	15.9	[2]14.9	[1]17.6	15.0	11.6	[2]15.8	14.2	10.5	16.7	[2]17.4	12.3	14.9	[1]15.4	14.8
20 - 30	15.3	15.3	13.1	15.0	[2]10.9	16.9	13.7	11.6	16.5	[1]18.2	11.9	14.7	[2]11.9	14.2
30 - 40	[1]16.4	15.0	15.3	14.9	11.3	17.0	13.2	[2]8.5	15.8	NAp	13.7	[2]13.8	NAp	14.1
40 - 50	15.1	16.0	14.4	14.6	13.3	[1]18.1	[2]11.2	12.1	15.8	NAp	11.3	14.0	NAp	14.2
50 - 60	[2]11.7	[1]16.5	16.2	14.8	12.5	NAp	13.7	13.5	[1]21.8	NAp	[1]14.1	14.9	NAp	15.0
60 - 70	15.1	15.2	[2]12.6	[1]18.1	[1]15.0	NAp	21.4	[1]13.8	16.1	NAp	NAp	[1]16.9	NAp	16.0
70 - 80	NAp	NAp	NAp	[2]13.2	13.8	NAp	[1]22.0	NAp	17.6	NAp	NAp	16.8	NAp	16.7
80 - 90	NAp	NAp	NAp	15.4	11.9	NAp	NAp	NAp	17.4	NAp	NAp	NAp	NAp	14.9
90 - 100	NAp	NAp	NAp	14.4	12.7	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	13.6
Average	15.1	15.5	15.0	15.3	12.4	16.8	15.6	11.7	17.0	17.8	12.4	15.2	13.4	[3]14.8

[1] Maximum in core.
[2] Minimum in core.
[3] Grand average all data.
NAp = Not applicable. No sample obtained.

TABLE 5. - pH of 10-foot interval samples of phosphogypsum

Depth interval, feet	SAMPLE													Depth average
	A1	A2	A3	B1	B2	C1	C2	D	E	F	G	H	I	
	pH units									I				
0 - 10	2.15	2.45	2.45	2.85	3.25	4.35	3.80	2.85	2.55	3.70	2.80	2.65	2.75	2.97
10 - 20	2.15	2.35	2.45	2.80	3.40	3.85	3.60	2.75	2.40	3.75	2.90	2.60	2.40	2.88
20 - 30	2.25	2.40	2.50	2.95	3.15	2.80	3.85	2.80	2.40	3.50	2.90	2.40	2.65	2.81
30 - 40	2.10	2.40	2.50	2.60	3.05	2.60	3.40	2.45	2.60	NAp	2.35	2.60	NAp	2.60
40 - 50	2.20	2.40	2.35	2.80	3.05	2.60	3.65	2.55	2.60	NAp	2.70	2.50	NAp	2.67
50 - 60	2.20	2.50	2.40	2.75	3.05	NAp	4.40	2.50	2.60	NAp	2.50	2.65	NAp	2.75
60 - 70	2.25	2.55	2.50	2.80	2.95	NAp	5.15	2.60	2.40	NAp	NAp	3.20	NAp	2.93
70 - 80	NAp	NAp	NAp	2.70	2.95	NAp	5.50	NAp	2.40	NAp	NAp	4.00	NAp	3.51
80 - 90	NAp	NAp	NAp	2.80	3.10	NAp	NAp	NAp	2.50	NAp	NAp	NAp	NAp	2.80
90 - 100	NAp	NAp	NAp	3.00	3.20	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	3.10
Core average	2.19	2.44	2.45	2.80	3.11	3.24	4.17	2.64	2.49	3.65	2.69	2.82	2.60	[1]2.85

[1] Grand average, all data.

NAp = Not applicable. No sample obtained.

TABLE 6. - Particle size distribution of core samples of phosphogypsum

A

Sieve opening mm		Distribution, percent by weight dried samples[1]						
		Core number						
		A1	A2	A3	B1	B2	C2	G
	Plus 0.710	4.6	10.4	6.6	2.0	1.9	7.2	4.6
Minus 0.710	Plus 0.500	3.6	9.1	5.3	4.6	5.1	7.5	4.5
Minus 0.500	Plus 0.250	6.4	12.0	9.1	15.1	35.8	20.1	11.9
Minus 0.250	Plus 0.180	3.6	4.2	5.0	11.9	27.6	8.3	7.8
Minus 0.180	Plus 0.125	4.9	9.8	6.3	13.0	12.9	25.5	8.9
Minus 0.125	Plus 0.063	15.6	11.8	15.6	24.2	11.5	12.5	24.9
Minus 0.063	Plus 0.045	12.0	13.1	13.9	11.0	3.0	8.0	6.7
Minus 0.045		49.3	29.6	38.2	18.2	2.2	10.9	30.7

B

Sieve opening mm		Cumulative distribution, percent by weight						
		Core number						
		A1	A2	A3	B1	B2	C2	G
	Plus 0.710	4.6	10.4	6.6	2.0	1.9	7.2	4.6
Minus 0.710	Plus 0.500	8.2	19.5	11.9	6.6	7.0	14.7	9.1
Minus 0.500	Plus 0.250	14.6	31.5	21.0	21.7	42.8	34.8	21.0
Minus 0.250	Plus 0.180	18.2	35.7	26.0	33.6	70.4	43.1	28.8
Minus 0.180	Plus 0.125	23.1	45.5	32.3	46.6	83.3	68.8	37.7
Minus 0.125	Plus 0.063	38.7	57.3	47.9	70.8	94.8	81.1	62.6
Minus 0.063	Plus 0.045	50.7	70.4	61.8	81.8	97.8	89.1	69.3
Minus 0.045		100.0	100.0	100.0	100.0	100.0	100.0	100.0

C

Sized samples	Distribution, percent by weight						
	Core number						
	A1	A2	A3	B1	B2	C2	G
Coarse[2]	14.6	31.5	21.0	21.7	42.8	34.8	21.0
Medium[3]	36.1	38.9	40.8	60.1	55.0	54.3	48.3
Fine[4]	49.3	29.6	38.2	18.2	2.2	10.9	30.7

[1] Dried to constant weight at 45° C.
[2] Retained on sieve opening 0.250 mm.
[3] Pass sieve opening 0.250 mm, retained on sieve opening 0.045 mm.
[4] Pass sieve opening 0.045 mm.

TABLE 7. - Uranium, thorium, and radium analyses of sized samples of phosphogypsum

Core number	Size opening mm		Designation	Picocuries per gram of samples as-received		
				[1]U	[2]Th	[3]Ra
A1		Plus 0.250	Coarse	4.3	NA	23
	Minus 0.250	Plus 0.045	Medium	3.4	NA	21
	Minus 0.045		Fine	4.3	3.8	27
	[4]Average		-	4.0	NA	24
A2		Plus 0.250	Coarse	8.4	NA	19
	Minus 0.250	Plus 0.045	Medium	3.6	NA	22
	Minus 0.045		Fine	3.4	NA	30
	[4]Average		-	5.0	NA	23
A3		Plus 0.250	Coarse	4.4	3.7	23
	Minus 0.250	Plus 0.045	Medium	4.7	NA	15
	Minus 0.045		Fine	6.1	NA	24
	[4]Average		-	5.2	NA	20
B1		Plus 0.250	Coarse	5.8	3.9	20
	Minus 0.250	Plus 0.045	Medium	8.7	11.6	26
	Minus 0.045		Fine	5.8	3.9	26
	[4]Average		-	7.5	8.5	25
B2		Plus 0.250	Coarse	9.5	3.9	15
	Minus 0.250	Plus 0.045	Medium	6.0	3.9	21
	Minus 0.045		Fine	6.0	NA	22
	[4]Average		-	7.5	NA	18
C2		Plus 0.250	Coarse	5.4	27.0	21
	Minus 0.250	Plus 0.045	Medium	20.7	7.7	16
	Minus 0.045		Fine	9.5	NA	30
	[4]Average		-	14.2	NA	19
G		Plus 0.250	Coarse	4.7	14.7	8.9
	Minus 0.250	Plus 0.045	Medium	2.5	25.8	6.7
	Minus 0.045		Fine	2.5	7.4	10.5
	[4]Average		-	3.0	17.8	8.3

1 Analyses by ASTM D2907-70T fluorometric method.
2 Analyses by ASTM D2333-68 colorimetric method.
3 Analyses by radon emanation method.
4 Weighted average based on percent in each fraction and pCi/g.
NA = Not available.

TABLE 8. - Radiological isotopic analyses of core samples of phosphogypsum

Isotope	Core		
	A1	A2	A3
	Picocuries per gram of sample as-received		
Radium	16.10	13.50	13.30
Uranium-234	2.14	1.47	2.44
Uranium-235	.17	.13	.15
Uranium-238	2.13	1.61	2.41
Thorium-227	.61	.47	.59
Thorium-228	.03	.03	.06
Thorium-230	3.30	1.95	3.91
Thorium-232	.13	.07	.11

TABLE 9. - Radium analyses of 10-foot interval samples of phosphogypsum

Depth interval, feet	SAMPLE													Depth average
	A1	A2	A3	B1	B2	C1	C2	D	E	F	G	H	I	
	Picocuries per gram of samples as-received													
0 - 10	19	26	28	13	20	19	21	22	18	37	8.9	17	24	21.0
10 - 20	25	26	21	18	16	24	26	24	20	45	8.8	20	30	23.4
20 - 30	23	27	18	15	17	20	20	34	24	44	9.7	16	23	22.4
30 - 40	18	19	17	20	20	22	18	22	21	NAp	11.2	24	NAp	19.3
40 - 50	23	18	16	15	16	25	10	34	26	NAp	8.9	27	NAp	19.9
50 - 60	19	24	18	19	18	NAp	12	26	20	NAp	10.3	26	NAp	19.2
60 - 70	18	24	16	24	16	NAp	17	33	24	NAp	NAp	24	NAp	21.8
70 - 80	NAp	NAp	NAp	14	21	NAp	[1]0.9	NAp	21	NAp	NAp	11	NAp	16.8
80 - 90	NAp	NAp	NAp	25	19	NAp	NAp	NAp	15	NAp	NAp	NAp	NAp	19.7
90 - 100	NAp	NAp	NAp	24	24	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	24.0
Core average	20.7	23.4	19.1	18.7	18.7	22.0	17.7	27.9	21.0	42.0	9.6	20.6	25.7	[2]20.91

[1] Not included in averages.

[2] Grand average, all data.

NAp = Not applicable and not included in averages. No sample obtained.

TABLE 10. - Uranium and thorium analyses of 10-foot interval samples of phosphogypsum

Depth interval feet	SAMPLE								Depth average	
	A1		A2		A3		G			
	Picocuries per gram of samples as-received									
	U	Th	U	Th	U	Th	U	Th	U	Th
20 - 30	4.0	NA	3.1	NA	4.1	3.7	2.4	14.7	3.4	NA
30 - 40	4.0	NA	2.9	NA	3.7	NA	3.2	14.7	3.5	NA
40 - 50	3.7	3.8	3.1	3.7	5.0	3.7	3.9	25.8	3.9	9.2
50 - 60	4.8	NA	3.1	NA	5.1	3.7	2.3	18.4	3.8	NA
60 - 70	4.3	NA	3.1	NA	5.9	7.4	NAp	NAp	4.4	NA
Sample average	4.2	-	3.1	-	4.8	-	3.0	-	3.8	NA

NA = Not available.
NAp = Not applicable. No sample obtained.

TABLE 11. - Emission spectrographic analyses of phosphogypsum

Element detected	Average,[1] PPM	Detected in, number of	
		Cores	Samples
Aluminum	1,360	13	110
Antimony	111	2	10
Arsenic	42	7	37
Barium	7	2	8
Bismuth	1	2	6
Boron	3	8	37
Beryllium	1	1	1
Cadmium	7	1	1
Cobalt	2	7	33
Copper	8	13	106
Iron	670	13	110
Lead	1	6	6
Magnesium	1,220	13	110
Manganese	15	13	72
Molybdenum	16	3	13
Nickel	2	11	57
Platinum	<1	2	5
Potassium	11	9	56
Rhenium	11	6	23
Silver	<1	4	6
Sodium	252	13	91
Strontium	10	11	79
Tantalum	2	2	5
Tin	4	5	13
Titanium	4,020	13	110
Tungsten	29	3	9
Vanadium	19	13	110
Yttrium	2	3	9
Zinc	9	10	50
Zirconium	10	8	12

[1] Average in cores in which element detected.

TABLE 12. - Typical composition of phosphogypsum from Florida[1]

Component	Percent by weight of samples as-received[2]		
	Average	Low	High
Moisture	17.30	14.8	20.7
Combined water	14.49	12.7	15.8
Silicon dioxide and acid insoluble	6.67	3.5	9.6
Acid soluble, NH_4OH insoluble	3.60	3.3	4.4
Calcium oxide	22.65	19.2	24.5
Sulfur trioxide	35.21	30.5	38.3
Sodium chloride	.01	.01	.03
Sum	99.93	-	-
Phosphorus pentoxide	.61	.32	.83
Fluorine	.68	.38	1.81
Aluminum oxide[3]	.29	.00	.50
Ferric oxide[3]	.10	.00	1.00
Titanium dioxide[3]	.63	.00	1.00
Calcium oxide equivalent of P_2O_5 and F[4]	1.24	.69	3.00
Sum[5]	3.55	1.39	8.14
Density, grams per ml	1.51	1.32	1.69
pH, pH units	2.57	2.10	3.35
Radium, picocuries per gram	20.2	8.00	38.00
Gypsum[6]	69.23	60.67	75.48

1 From samples A1, A2, A3, B1, B2, C1, E, F, G, and H.

2 Except for density, pH and radium.

3 Aluminum, iron and titanium analyses from emission spectrographic results.

4 As calcium dihydrogen phosphate and calcium fluoride.

5 Components that may be present in acid soluble, NH_4OH insoluble fraction of phosphogypsum.

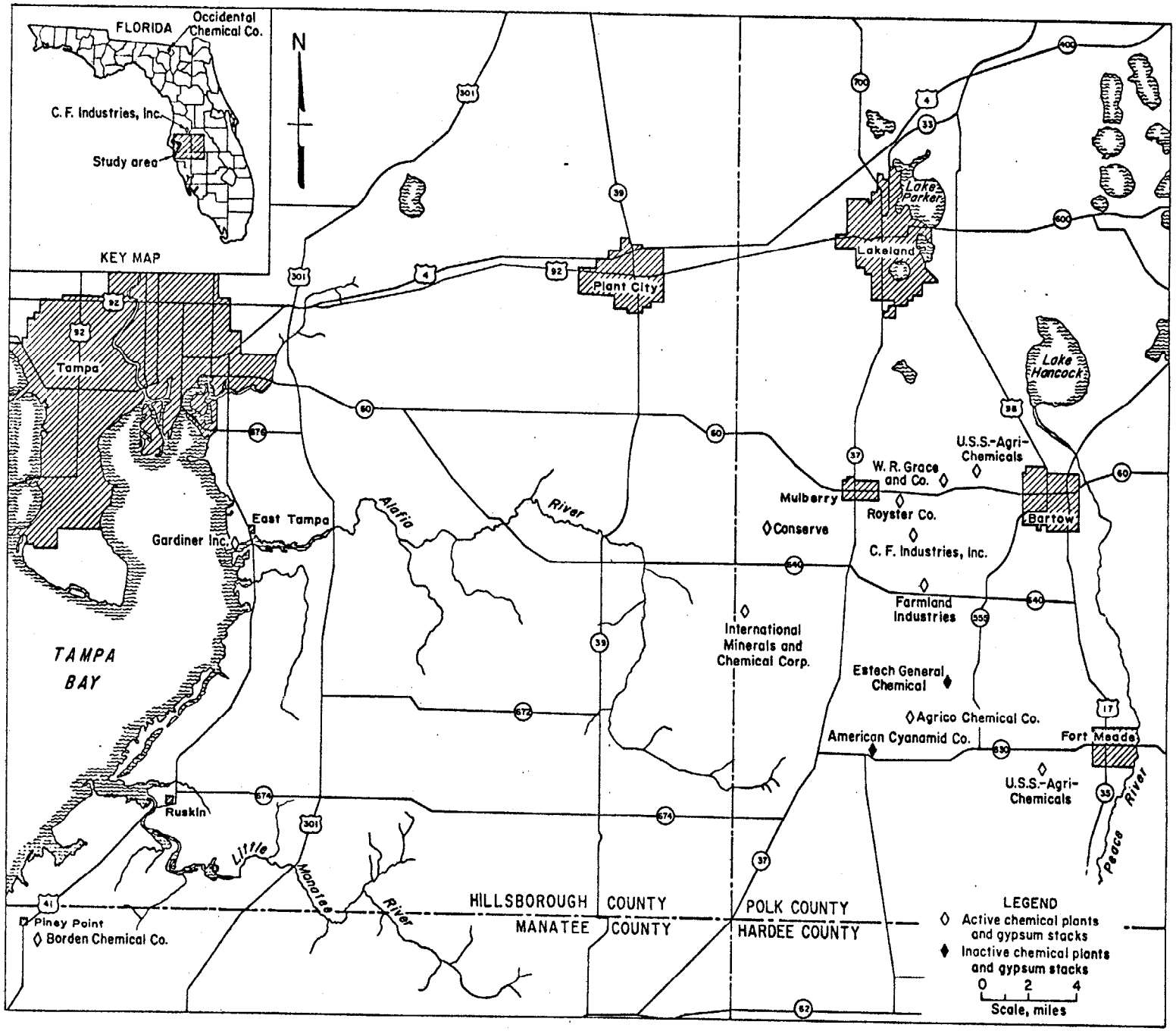
6 Calculated from percent combined water. For the average, this gives 0.10 percent calcium oxide and 3.02 percent sulfur trioxide not in gypsum.

TABLE 13. - Average uranium and radium contents of sized samples of phosphogypsum

Size	Picocuries per gram of samples as-received	
	U	Ra
Coarse...	6	19
Medium...	7	18
Fine.....	5	24

TABLE 14. - Average radium concentrations of phosphogypsum

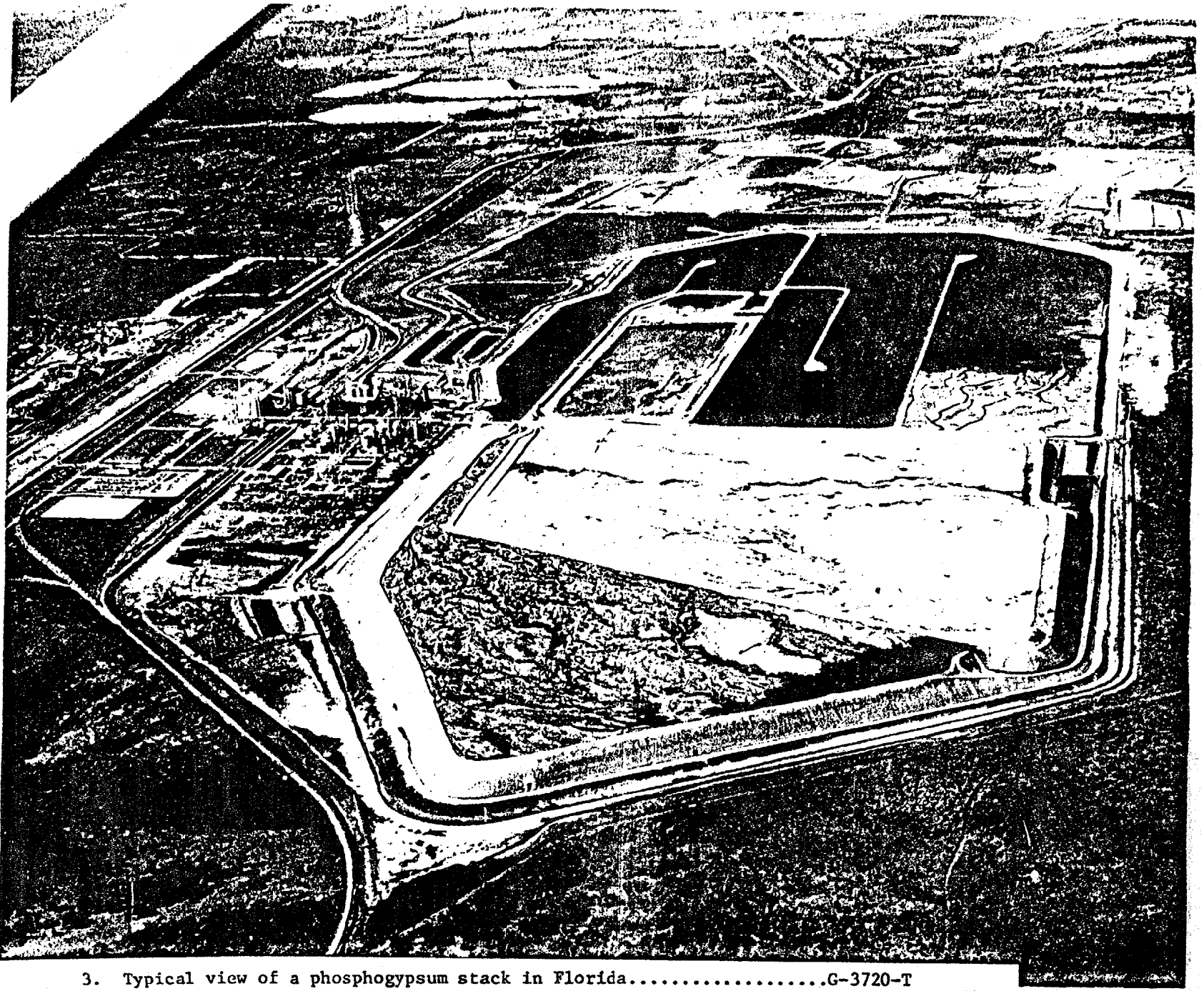
Average of samples	Picocuries per gram of samples as-received
Composite.....	20.4
10-foot interval.....	20.9
Composite (excluding C2, D, and I).	20.2
10-foot interval (excluding C2, D, and I).	20.3
Average of all data, including core samples, 10-foot increment and sized samples.	20.5



PGH-80 416

1. Location of phosphogypsum stacks in Florida.....G-3718-T





3. Typical view of a phosphogypsum stack in Florida.....G-3720-T

CONTROL OF GROUNDWATER CONTAMINATION FROM PHOSPHOGYPSUM DISPOSAL SITES

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INTRODUCTION

Phosphogypsum Disposal: An Overview. Phosphogypsum, a by-product of chemical processing and phosphoric acid production, is disposed of worldwide in accordance with one of three methods: (1) slurry discharge into the ocean or into settling ponds; (2) dry-stacking; and (3) wet-stacking using the upstream method of construction. Economic, hydro-geological and environmental considerations, as well as process and climatological constraints, generally dictate the method of disposal in a given geographic locality.

The engineering properties of phosphogypsum are ideally suited for the most widely adopted wet-stacking method of disposal which uses the upstream method of construction to raise the gypsum stack. Gypsum stacks are frequently greater than one hundred feet in height and cover several hundred acres. Process water entrained in the gypsum pores is highly acidic and contains high levels of various contaminants such as fluoride and phosphorus. Leachate seeping into the groundwater system is therefore a potential source of contamination.

Management of a gypsum stack varies from one locality to the other. For example, in relatively wet climates such as Florida, rim-ditching can be effectively used to maintain the surface of the stack ponded, and hence, promote evaporation and improve the water balance of the plant. (Rim-ditching also readily provides coarser gypsum material suitable for starter dike construction.) Moreover, stack operating features are significantly different in hot and cold climates (e.g., Middle East versus Canada), the former climate subjecting the stack to extensive heat and winds, while the latter subjects it to freeze-thaw cycles.

Figure 1 depicts typical gypsum stacks and associated process ponds. Many existing disposal facilities have been in operation for several decades and have undergone extensive expansions over the years with little prior layout planning. Process ponds abutting gypsum stacks act as surge ponds to temporarily store excess precipitation for subsequent evaporation, and as cooling ponds to allow recirculation of the process water to the plant for re-use. In some instances, cooling towers are used in lieu of cooling ponds.

An idealized gypsum stack and associated cooling/surge pond layout is shown in Figure 2. As depicted in the figure, it is desirable that the cooling pond completely surrounds the gypsum stack. This safety feature provides for containment of an accidental spill of process water ponded atop the stack. The perimeter cooling pond also acts as a relief for seepage from the gypsum stack area.

Protection of Groundwater Resources. Present and projected uses of groundwater in a given area, its degree of hydraulic connection to high quality surface waters, hydrogeologic considerations and the availability of alternative water supply sources generally dictate the degree of protection required at a given disposal site. A network of monitoring wells is generally installed around disposal facilities to detect any plume of contamination (Figure 3) and provide ample advance warning to undertake remedial measures, if needed.

Several relatively economical methods could be used to effectively control contamination, When the topography is flat and the pervious foundation is homogenous and relatively thick, a seepage collection ditch (Figure 4) around the perimeter of the gypsum stack can be fully effective if the water level in the ditch is maintained below the level of the surrounding groundwater table (Figure 4-1).

Where the previous foundation is relatively shallow and a trench can be excavated down to an underlying impervious stratum without major dewatering problems, a cutoff trench backfilled with a low permeability soil can be very effective in containing the plume of contamination from a gypsum stack and/or process water pond (Figure 5-1). Special measures should, however, be taken to relieve hydraulic pressures and avoid the formation of boils at the toe of the stack. Where dewatering is a problem or where the pervious stratum is relatively deep, a grout curtain or slurry wall can be used. These solutions are more expensive than relief ditches, but the initial construction cost may be offset by the cost of treating excess acid water which often results when seepage collection ditches are used. Seepage collection ditches can also be used when the impervious layer is relatively shallow (Figure 5-2). The ditch need only be excavated through the impervious layer and the water level in the ditch needs to be be maintained below the potentiometric surface of the underlying pervious stratum. Special measures should be taken to prevent piping of soil from the slope and bottom of the ditch.

Inceptor wells (Figure 6) perform the same function as seepage collection ditches except that the water is pumped out of wells rather than out of sumps in the ditches. Interceptor wells can be used in deep non-homogeneous deposits where ditching may be impractical. The effectiveness of interceptor wells in containing the plume of contamination is heavily dependent on their design and spacing. Piezometers should be installed between wells to monitor and control the zone of influence of each well and to determine that the collection zones overlap.

In some hydrogeologic environments, the groundwater control measures outlined in the above are not adequate in protecting underlying artesian aquifers because of vertical recharge across semi-confining units. At some sites, however, subsurface soils underlying artesian aquifers because of vertical recharge across semi-confining units. At some units, however, subsurface soils underlying a phosphogypsum disposal facility have a high leachate treatment potential due to sorption, ion exchange capacity and/or neutralization properties that protect underlying aquifers from contamination. Figure 7 presents groundwater fluoride concentration profiles with depth and distance as measured in observation wells and piezometers in the vicinity of an unlined mature gypsum stack in Florida. Collection Zone D located within the artesian aquifer did not exhibit any signs of contamination pH, fluoride, phosphorus, gross a radiation, etc. were all at background levels). This illustrates the chemical purification characteristic of the typical Floridian stratigraphic environment.

The Environmental Protection Agency (EPA) recently promulgated federal regulations and is in the process of proposing additional rules implementing the Resource Conservation and Recovery Act (RCRA) of 1976.

The strict Subtitle C regulations of RCRA which pertain to hazardous waste storage and disposal are not currently applicable to phosphate industry wastes as a result of the recently enacted Solid Waste Disposal Act Amendment of 198Ø (better known as the Bevill Amendment) which prohibits EPA from regulating these wastes until after completion of certain studies and rulemaking. On the other hand, Subtitle D regulations require each state to control the management of non-hazardous wastes in accordance with federal guidelines promulgated by EPA. These may apply to phosphogypsum disposal. The proposed regulations, as well as the EPA's Proposed Groundwater Protection Strategy, will no doubt result in implementing stricter groundwater protection measures. For example, some relatively economical methods that could be used to control contamination within an operator's property are not necessarily in compliance with EPA's regulations.

In the following, case histories are presented illustrating different groundwater control measures used and various technical designs adopted to prevent groundwater contamination at various sites of varying environmental sensitivity. Most of these case histories are from waste disposal facilities located outside the United States where regulations are flexible or non-existent, but where hydrogeologic conditions and the very proximity of vital water supply sources necessitated the design and implementation of sophisticated liner systems. In several of these projects, there was no flexibility in selecting an alternate disposal site because the chemical plant was already under construction or because of other constraints.

Case History No. 1: Compacted In-Situ Clay Liner. The layout of this South American chemical complex is depicted in Figure 8. Both the chemical plant and cooling pond were already constructed prior to selection of an optimal layout for the disposal facilities. Because of economic constraints, the disposal facilities were to be constructed in two phases.

In the first phase the surge ponds, required from a water balance standpoint for process water storage, abut the southeast wall of the gypsum stack. Although hydraulically connected to the cooling pond, the surge ponds in this case are not an integral part of the cooling system. Sludge ponds needed to store the supernatent and dispose of the precipitate after two-stage treatment of excess process water (with limestone and lime prior to discharge) are also depicted in this figure. Note how the topography has been advantageously used to minimize construction and reduce costs.

In the second phase, the gypsum stack will be expanded into the Phase I surge ponds and the latter will be relocated on the opposite bank of a nearby creek. The creek flows into a major river.

The main environmental concern in this case history was protection of the flood plain and the river from contamination by potential leachate seepage into groundwaters and subsequent discharge into surface features. The foundation consisted of a thick deposit of reddish brown colluvial lateritic soils characterized by a relatively high in-situ coefficient of permeability.

Several liner systems were evaluated for the gypsum stack and cooling/surge ponds, as depicted in Figure 9. Alternate A consists of a compacted clay liner. Alternate B incorporates an underdrain layer with a system of perforated pipes overlying the liner. This alternate was investigated for potential use beneath the gypsum stack to allow for leachate collection and removal by gravity and prevent the build-up of high hydraulic heads across the liner. This not only minimizes downward percolation but also improves stability of the stack. Alternate C consists of a leachate collection and removal system "sandwiched" between overlying and underlying clay liners.

Laboratory tests indicated that by reworking and compacting the in-situ lateritic soils a clay liner of sufficiently low permeability can be constructed. Further, the predicted quantity of leachate flowing through a three-foot clay liner and the resulting ambient groundwater and surface water quality were determined to be environmentally acceptable. Hence, Alternate A, the most economical of the three alternates considered, was selected.

There are technical difficulties associated with clay liner installations beneath gypsum stacks and acid process ponds. Clay liners are ideally suitable provided their long-term performance in an acid environment is not adversely affected. Figure 10 presents a system of stainless steel permeameters used to determine the long-term effect of acid leaching on liner performance. Also depicted in the figure is a controlled hot temperature bath used to accelerate the reaction of the soil with acid water. Typical long-term permeability test results are shown in Figure 11. As can be seen, some clays are not affected by acid water leaching, some are favorably affected as a result of cementation and/or ion exchange, while others are adversely affected by dissolution and/or ion exchange. The in-situ lateritic soils were not affected by acid water.

The three-foot clay liner was constructed in six-inch thick layers. The in-situ soil was pulverized, wetted to the desired water content, mixed with a discharrow and compacted with a sheepsfoot roller (see Figure 12). The compacted clay liner was subsequently ponded to prevent desiccation and the formation of shrinkage cracks. Permeability test pits and test ponds were monitored to document that field compaction achieved the desired liner permeability.

Construction problems with clay liners can be staggering. As noted above, once compacted the liner must be kept moist by spraying and subsequent ponding in order to avoid shrinkage cracking. When the area involved is large, maintaining the surface of the clay liner moist to avoid desiccation cracking becomes a major task, particularly if water supply sources are not readily available and evaporation losses are significant. The contractor in this instance was not able to maintain the surface of some positions of the liner wetted and extensive cracking with cracks over an inch wide and more than two feet in depth developed. This necessitated re-pulverizing and recompacting the surface of the clay liner to meet specifications, at considerable expense. With proper management and soil selection (if different soil types are available), one can minimize the potential for desiccation

cracking. Nevertheless, without adequate precautions desiccation cracking can be a significant construction problem.

The disposal facilities have been constructed and are currently operating satisfactorily. Monitor wells have been installed downstream of the gypsum stack and ponds to detect contamination if and when it occurs, to assess its environmental impact if any, and to provide an early warning for remedial measures if needed.

Case History No. 2: Clay Liner and Underdrain System. The site for this chemical complex is within an environmentally sensitive South American region. As depicted in Figure 13, two major water supply reservoirs supplying drinking water to major cities are located respectively due west and northeast of the site. Moreover, a mineral water bottling company is operating due north of the site. The site is underlain by a very thick sandy soils deposit. The impacts of groundwater contamination can therefore be staggering. An underdrain layer overlying a low permeability compacted clay liner was selected for use beneath the gypsum stack (Alternate B in Figure 9).

The layout of the chemical complex is depicted in Figure 14. The gypsum stack is to be constructed in two phases. During Phase I, the gypsum stack is located on relatively high ground some distance away from the cooling/surge pond. This allows the discharge of the gypsum stack supernatent (resulting from gypsum deposition) to flow by gravity into the cooling/surge pond both during Phases I and II. The relative ground surface elevations also allows the underdrain leachate collector pipes beneath the gypsum stack to discharge by gravity directly into the cooling/surge pond.

Several highly plastic clay borrow sources in the general vicinity were investigated for their long suitability as liners. Two of the clay borrow sources were not adversely affected by acid water leaching, and compacted samples of these clays yielded permeabilities in the 10^{-8} to 10^{-9} cm/sec range. These borrow sources were selected for use as liners beneath the gypsum stack and ponds. Technical difficulties associated with selection and construction of clay liners have already been outlined in conjunction with Case History No. 1.

There are several problems associated with the use of underdrain systems beneath gypsum stacks. In order to have an effective underdrain system, the in-situ permeability of the gypsum has to be reliably estimated. Laboratory tests on gypsum generally underestimate the effective vertical permeability of a gypsum stack because the in-situ permeability is influenced by shrinkage cracking and the presence of vortexes and vertical solution cavities that can significantly increase flow to the underdrain system.

More serious technical problems arise in designing an underdrain system that will perform satisfactorily throughout the active life of the gypsum stack and that will not be adversely affected by the process acid water. Extensive testing procedures have been developed for drainage pipes and sand/gravel drain material to ensure satisfactory long-term performance in the acid environment.

Slotted corrugated polyethylene pipes or PVC pipes can be used provided the resin is carefully selected. Several pipes manufactured with various resins have been tested by Ardaman & Associates, Inc. for chemical resistance, environmental stress cracking and in large-scale environmental simulation tests that have simulated the in-use stress and flow conditions (see Figure 15). Accelerated testing at high temperatures is necessary in the laboratory to accelerate any detrimental effects that the process water might have on the materials and hence predict satisfactory performance for the life of the facility which is generally on the order of 2Ø years. Several resins available on the market were found not suitable because of time-dependent corrosion cracking: locked-in stresses during extrusion cause stress concentrations at certain locations that, with some resins, result in progressive corrosion cracking in an acid environment even under unstressed conditions. Careful selection of resins compatible with the process water is therefore highly critical. (The pipes must also have sufficient stiffness to withstand the in-use stresses.) The cost of the pipes manufactured with a special resin is, nevertheless, small compared to that of an underdrain acid-resistant sand/gravel material even when locally available.

The most significant problem with an underdrain system is the potential cementation and clogging of drain material in an acid environment. In one project located outside the U.S.A. (Case History No. 4), extensive laboratory testing of local borrow materials indicated that the local soils exhibit significant cementation and clogging with time that hamper performance of the drain system for its intended use. The owner had to resort to a specially processed sand/gravel material at considerable expense. For Case History No. 2, a suitable local drain material was found.

The cementation of drain materials has also been observed at several disposal facilities in the U.S.A. where local soils were used in conjunction with relief wells or around perforated drain pipes installed in covered relief trenches in the vicinity of gypsum stacks and cooling ponds. As shown in Figure 16, in several instances the pipe was uncovered and a cemented layer of sand was observed around the pipe, clogging the drain and making it nonfunctional. This was particularly distressing because a lot of money had already been spent to install these drain systems and they were essentially no longer functioning two years after installation. A cemented low permeability cake formed with time around the drain pipes preventing hydraulic pressure relief and the collection of seepage.

Extensive laboratory work was recently undertaken by Ardaman & Associates, Inc. on a variety of soils using process water from several chemical plants to find materials that are not adversely affected by the process waters. It is especially important that plant specific acid water be used in these tests because the cementation is not only soil dependent but is affected by the characteristics of the acid process water. The evaluations are conducted in specially designed column tests that allow acid water to be recirculated. Probes are installed at various depths in the soil column to determine the head loss and changes in permeability along the full length of the tested sample (see Figure

17). Figure 18 presents permeability test results from two potential drain materials. Whereas one of the soils is not affected by acid water leaching, the other is shown to be adversely affected to a significant extent. More than five types of gels and crystals causing clogging have been identified so far. The cementation was found dependent on the acid water and the soil mineral it leached through. Scanning electron photomicrographs of one such cementing product is presented in Figure 19. The calcium-aluminum-sulfur octahedral crystals shown constitute a mineral that is not commonly identified. Several other cementing products with completely different composition and morphology have been observed. This dilemma cannot be easily solved technically, Finding a suitable soil for use in an underdrain system in a given chemical complex requires extensive testing. In some instances, the material has to be processed or hauled at considerable expense.

The underdrain material selected must also act as a filter for gypsum particles to prevent clogging of the drain. Figure 2Ø shows a sand meeting filter gradation requirements for gypsum and a gravel meeting gradation requirements for the sand. The use of two filter materials in an underdrain system is generally prohibitively expensive and one may have to resort to a filter fabric placed between the gypsum and gravel filter material (if sand is not used) or between the sand and perforated pipe (if gravel is not used). The filter fabric selected must be chemically resistant to acid water. Caution must be exercised in the use and selection of a filter fabric because the fabric in many instances is a source of clogging due to leaching of fine particles from the drain and subsequent deposition of cemented fine particles or crystals on the fabric.

Construction of Case History No. 2 is scheduled to start in 1981. Monitor wells will be installed at various depths and distances from the disposal facilities to monitor and detect the plume of contamination, if any, and provide ample advance warning to allow for remedial measures before the plume extends off the operator's property.

Case History No. 3: Chemical Purification Due to Favorable Hydrogeologic Conditions. At some sites, the subsurface soils may be extremely effective in "purifying" the leachate seeping out of a gypsum stack or acid process pond. In most regions of Florida where the confining bed overlying the Floridan Aquifer consists of calcareous clays and limestones, the ion exchange capacity and/or neutralization properties of the soils protect the aquifer from serious contamination. This is illustrated schematically in Figure 21 where the leachate is shown to flow through "purifying" confining beds prior to reaching the confined aquifer.

Figure 7 presented ranges in fluoride concentrations measured in observation wells installed at various depths and distances from an unlined gypsum stack and cooling pond at a chemical complex in Florida. The results clearly indicate that the disposal facilities have caused only very localized contamination of the surficial aquifer and that the facilities had no adverse impact on water quality in the lower Hawthorn Formation and the Floridan Aquifer. Fluoride levels (Figure 7) dropped very rapidly to background levels even in the shallow wells. Orthophosphate levels also dropped although somewhat less precipituously than

fluoride to background levels and gross alpha radiation was observed to be at background in all wells.

The gypsum stack and cooling/surge pond layout for a proposed chemical complex in central Florida (Case History No. 3) is shown in Figure 22. The cooling/surge pond layout completely surrounds the stack as was proposed for the idealized layout (Figure 2).

Figure 23 presents the proposed cross sections. The subsurface profile consists of a thin silty sand layer overlying a relatively impervious lo-foot thick clayey fine sand stratum. This in turn is underlain by clayey phosphatic sand, weathered limerock and phosphatic sandy clays. The bedrock complex consisting of alternating layers of calcareous clays (confining units) and limestones (aquifers) comprises the rest of the subsurface profile.

An extensive boring program was undertaken to confirm the continuity of the surficial clayey sand layer. Upon establishing its continuity, a compacted clayey sand perimeter blanket was proposed to limit lateral seepage. The continuous clayey sand layer underlying the stack and pond would therefore act as a natural "liner" that reduces downward percolation.

The design cross section also calls for installing observation wells on the gypsum stack starter dike through the underlying weathered limerock layer. These wells can also be used as relief wells in the event high hydraulic pressures are observed and/or groundwater contamination detected. Observation wells are also proposed around the perimeter of the facility. These are to be installed in the various aquifers all around the cooling/surge pond as depicted in Figure 22. These monitor wells would be used to detect any signs of contamination and provide ample time for implementing remedial measures, if needed.

The design features proposed above will not prevent leachate migration to underlying aquifers. Because of the hydraulic head difference between the surficial aquifer and the secondary artesian and Floridan aquifers, leachate from the gypsum stack and cooling pond will migrate downward to the Floridan Aquifer. Due to the low permeability of the confining units, downward migration will progress at a very slow rate. However, during this slow downward movement to the Floridan Aquifer, the leachate will be treated and purified by favorable geologic formations.

Extensive laboratory leaching studies were undertaken to predict leachate quality. These tests are performed in a battery of stainless steel permeameters (see Figure 1Ø). Constant head permeability tests with monitoring probes connected to a pressure transducer read digitally are performed under very high backpressure and the quality of leachate is determined as a function of time. The very high backpressure is needed to prevent gas bubbles from forming the soil during permeation. Otherwise flow could be impeded. Typical results for two surficial sands and a clayey sand are presented in Figure 24. As shown, the sands have very little treatment potential (particularly since the first pore volume of "acid" flow is essentially groundwater being displaced), whereas the surficial clayey sand is very effective in attenuating fluorides through adsorption by clay minerals and precipitation (when

the pH gets greater than about 5.Ø). The clayey sand is somewhat less effective with phosphorus which is mostly reduced by clay sorption. The phosphorus treatment capacity of soils, while important, is not as extensive as the fluoride treatment capacity.

Sulfate concentrations are not reduced by downward percolation through soils and one can only rely on dilution and some diffusion to reduce sulfate concentrations in the receiving aquifer to acceptable levels. At sites where dilution is not extensive and where sulfate concentrations are of concern, one may have to resort to artificial liner systems.

To account for all stratigraphic units underlying the chemical complex, a leaching study on a model stratigraphy was performed. The results are presented in Figure 25. The quality of the leachate for the life of the facility (in this case some 2Ø years, or less than two void volumes in the model test) can be used to predict water quality in the aquifer during the life of the facility and beyond. For this particular site, all concentrations of contaminants, including sulfate concentrations, were found to be at acceptable levels when aquifer dilution was taken into account.

Case History No, 4: Synthetic Liner and Underdrain System. The site of this case history is a major industrial development the Middle East. The chemical complex is located in a desert-like area along the bank of a major river (Figure 26), one of only two rivers supplying water to the whole region.

The foundation soils consisted of silty sands and fractured limerock characterized by a high in-situ coefficient of permeability. Environmental considerations indicated that a liner be installed beneath the gypsum stack.

A regional investigation revealed that no suitable clay borrow could be found for use in a compacted clay liner. Extensive laboratory tests were performed to investigate the suitability of the following artificial liners: bentonite-soil mixes, alphaltic concrete mixes and synthetic-membranes.

Bentonite-soil mixes were determined not suitable due to the high reactivity of the local soils to process waters. Asphaltic concrete mixes were found suitable because the asphalt coated particles did not exhibit sings of deterioration with process water flow. Nevertheless, economic considerations showed that synthetic liners would be more viable for this application if suitable membranes could be found.

The three-liner systems depicted in Figure 9 were investigated for potential use beneath the gypsum stack in conjunction with synthetic liners (rather than compacted clay). Alternate A was rejected because of stability (i.e., high potential for resliding at the upper liner interface) and environmental (i.e., not sufficiently safe in preventing seepage due to high hydraulic pressures) considerations. Alternate C, although highly desirable from an environmental standpoint, was rejected as a result of stability and economic considerations. Alternate B,

consisting of an underdrain layer with a system of perforated pipes overlying the synthetic liner, was therefore chosen for use beneath the gypsum stack.

Problems associated with selection of a suitable underdrain system were outlined in conjunction with Case History No. 2. Extensive processing of sand/gravel material borrowed from the river bed was essential in this instance to obtain an underdrain layer projected to perform satisfactorily in the adverse environment for extended periods of time.

The calcareous site material selected for starter dike construction was found highly reactive to acidic process waters, as illustrated in Figure 27. (Processing the river borrow material was not economically justifiable). Hence, the upstream face and base of the starter dike were to be covered with a synthetic liner. A schematic cross section is presented in Figure 28. Note that a double liner is used beneath the starter dike to avoid having numerous-welds and/or connections between the discharge pipes and the liner.

Synthetic liners are not generally desirable for use in conjunction with gypsum stacks. The life of these liners in an acid environment, under stress, is not well-documented. Extensive specialized accelerated long-term testing at elevated temperatures is required because the manufacturer's guarantee cannot be enforced when the liner is covered by 100 feet of gypsum.

Both field bonded and continuous candidate materials were tested for chemical resistance in an actual solution of process water, at elevated temperatures, to accelerate the corrosive effects of the solution. After various periods of aging, samples were measured for dimensional, weight and tensile property changes. Figures 29 and 30 present typical results. The detrimental effect of the acid water on the chlorinated polyethylene (CPE) liners had not been expected because CPE resin is known to exhibit high chemical resistance to acidic solutions. Some non-resin components of the CPE must have been affected by the process water. This underscores the need to test each candidate liner formulation. Other liner formulations produced by other manufacturers based on CPE as the base resin may indeed perform satisfactorily. The polyethylene (PE) and Ethylene Propylene Diene Monomer (EPDM) liner materials tested performed satisfactorily. The chemical resistance tests were used for screening a large number of candidate materials and narrow the field of sophisticated testing to few membranes.

Special test setups and procedures were developed to simulate actual field conditions for candidate liner and field bond evaluation. Some of these accelerated tests were continued over six months to improve predictions of long-term performance. Tensile creep tests (Figure 31) are particularly useful in this regard since the liner under the stack slope is subjected to tensile stresses and potential stress corrosion. Typical tensile creep test results are depicted in Figure 32. Hydrostatic Bell tests (Figure 33) are required to determine the long-term hydrostatic strength of the liner in an unsupported situation. Accelerated environmental simulation testing (Figure 34) with the liner subjected to in-situ compressive stresses, supported/covered on both sides by samples of in-situ soils, and saturated with process water are

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particularly recommended. Changes in liner properties effected as a result of environmental simulation testing are especially useful in assessing long-term performance under in-use conditions.

The most significant problem that the geotechnical engineer faces with the use of synthetic liners is the potential for the gypsum stack slope to slide at the surface of the liner because the surface roughness of these liners is not generally adequate from a stability standpoint. Figure 35 emphasizes the importance of the details during manufacturing and extrusion: the same material produced by the same manufacturer exhibits a 15° to 16° peak friction angle at the soil-liner interface if supplied in sheets and only 11° if supplied in rolls. Hence, the decision to use synthetic liners beneath gypsum stacks should only be made after consideration of all other alternatives. Performance monitoring is imperative from a stability standpoint when synthetic liners are used.

The chemical complex corresponding to this case history is currently under construction. The underdrain/synthetic liner system has already been installed beneath the gypsum stack site.

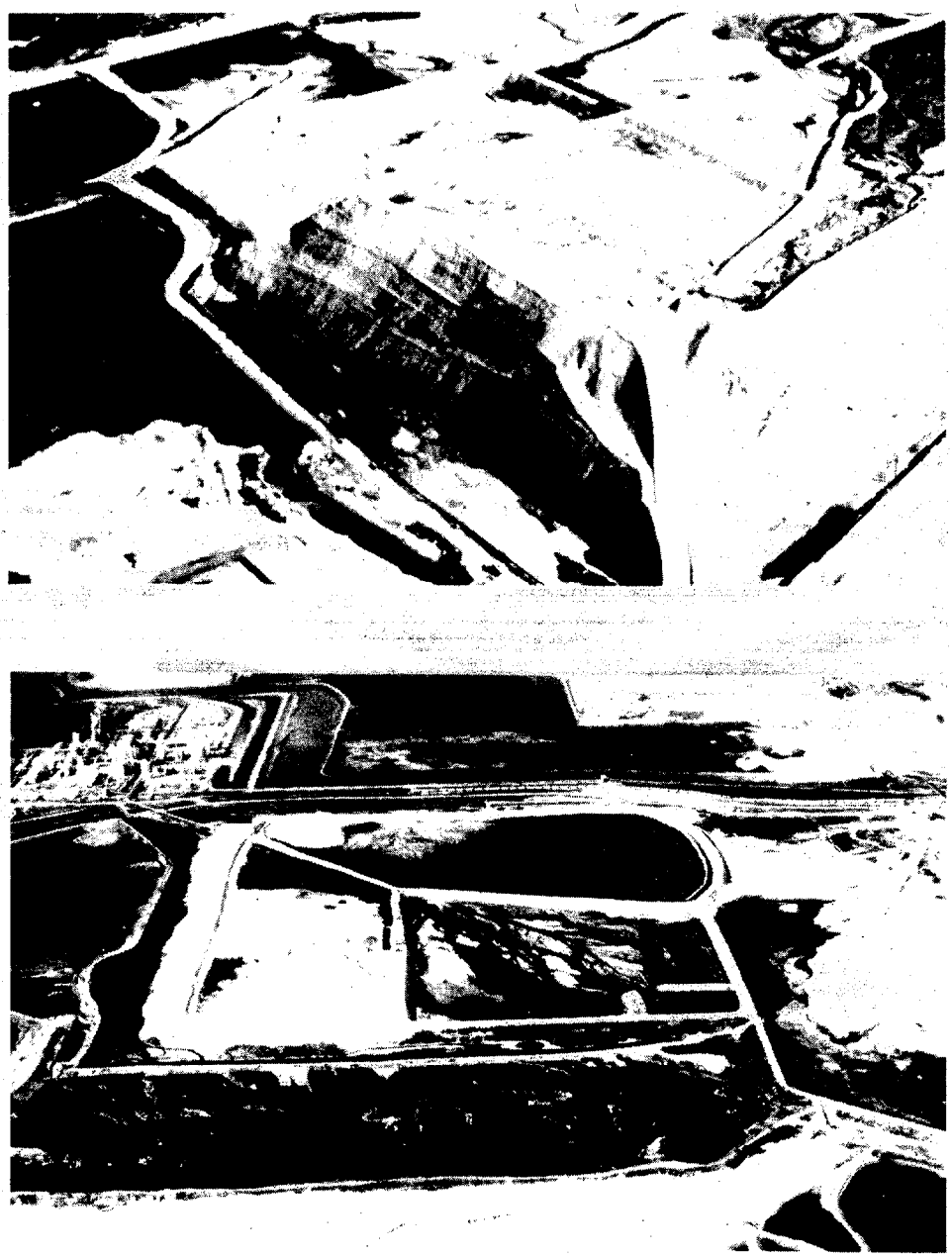
CONCLUSIONS

Environmental, geologic and hydrologic considerations generally dictate the level of groundwater protection required beneath gypsum stacks and cooling ponds. Hydrogeologic conditions should be a major criterion for selecting a site for a chemical complex, as schematically illustrated in Figure 36.

At some sites, subsurface soils have a high leachate treatment potential requiring only economical seepage control measures such as relief ditches or cut-off trenches.

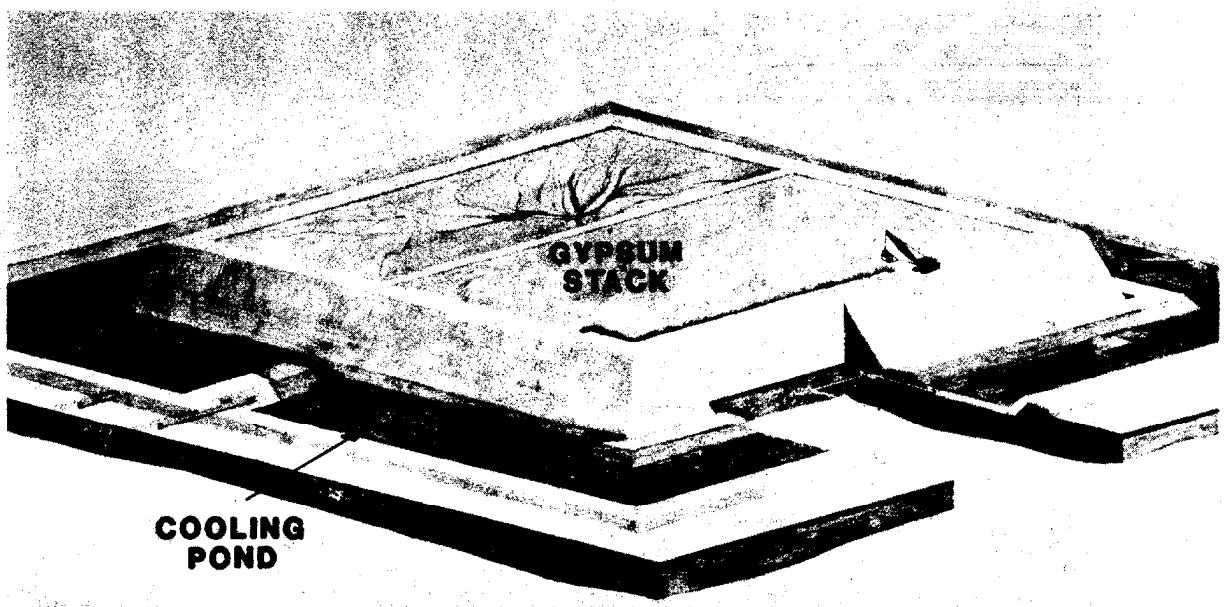
At other sites where hydrogeologic conditions are not favorable and/or where vital groundwaters or surface waters necessitate protection, liner systems may be required. Technical difficulties associated with design and construction of liner systems subjected to acidic process waters should not be underestimated - they are quite significant. One should, where feasible, avoid the use of liners by proper site selection.

A network of groundwater monitor wells around a gypsum stack/cooling pond is desirable to monitor and detect the plume of contamination, if any, and provide ample advance warning to implement remedial measures. before the plume extends off the operator's property.



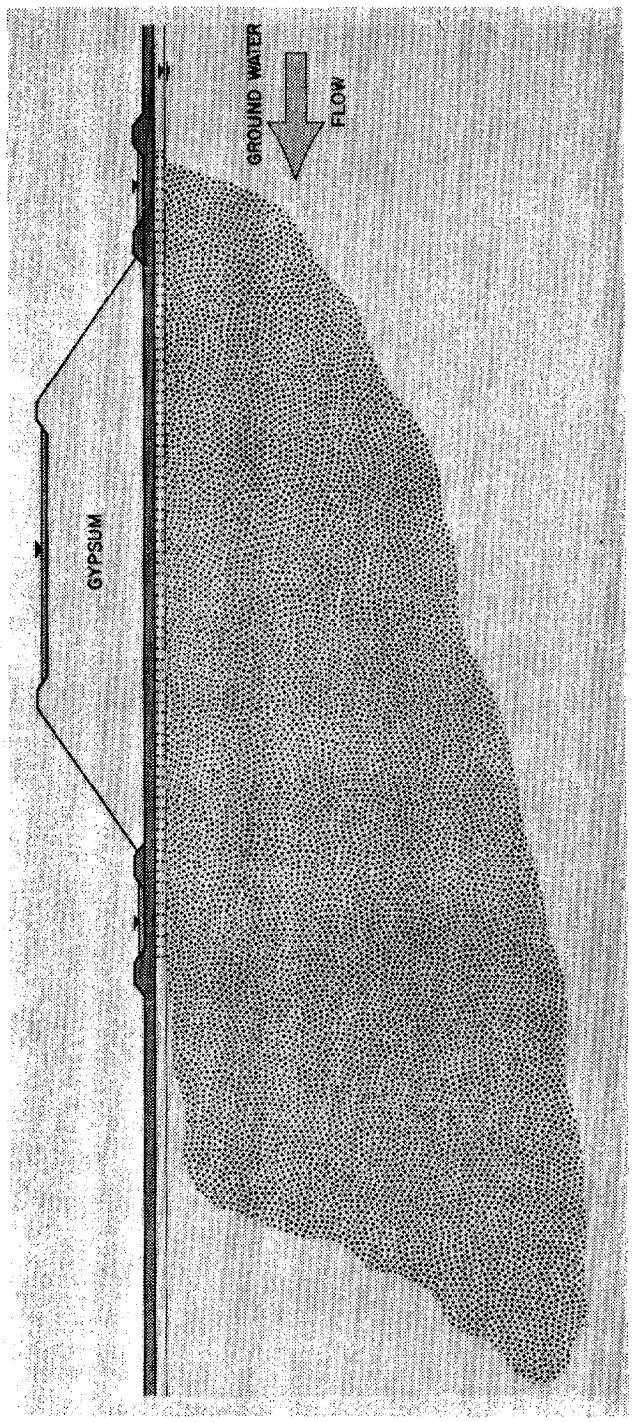
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FIGURE 1
TYPICAL GYPSUM STACKS AND
ASSOCIATED PONDS



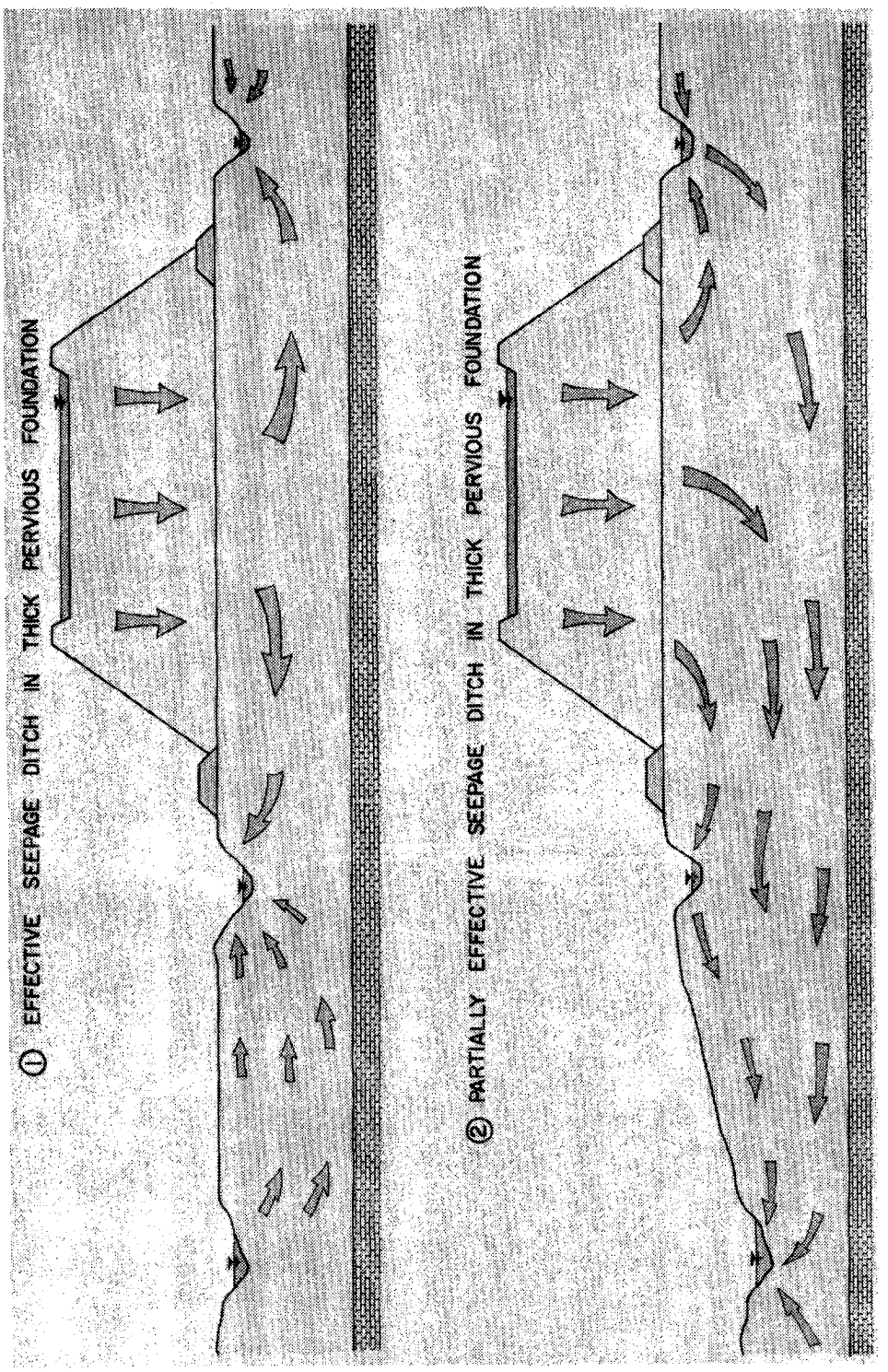
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FIGURE 2
PROPOSED LAYOUT FOR
GYPSUM STACK & COOLING POND



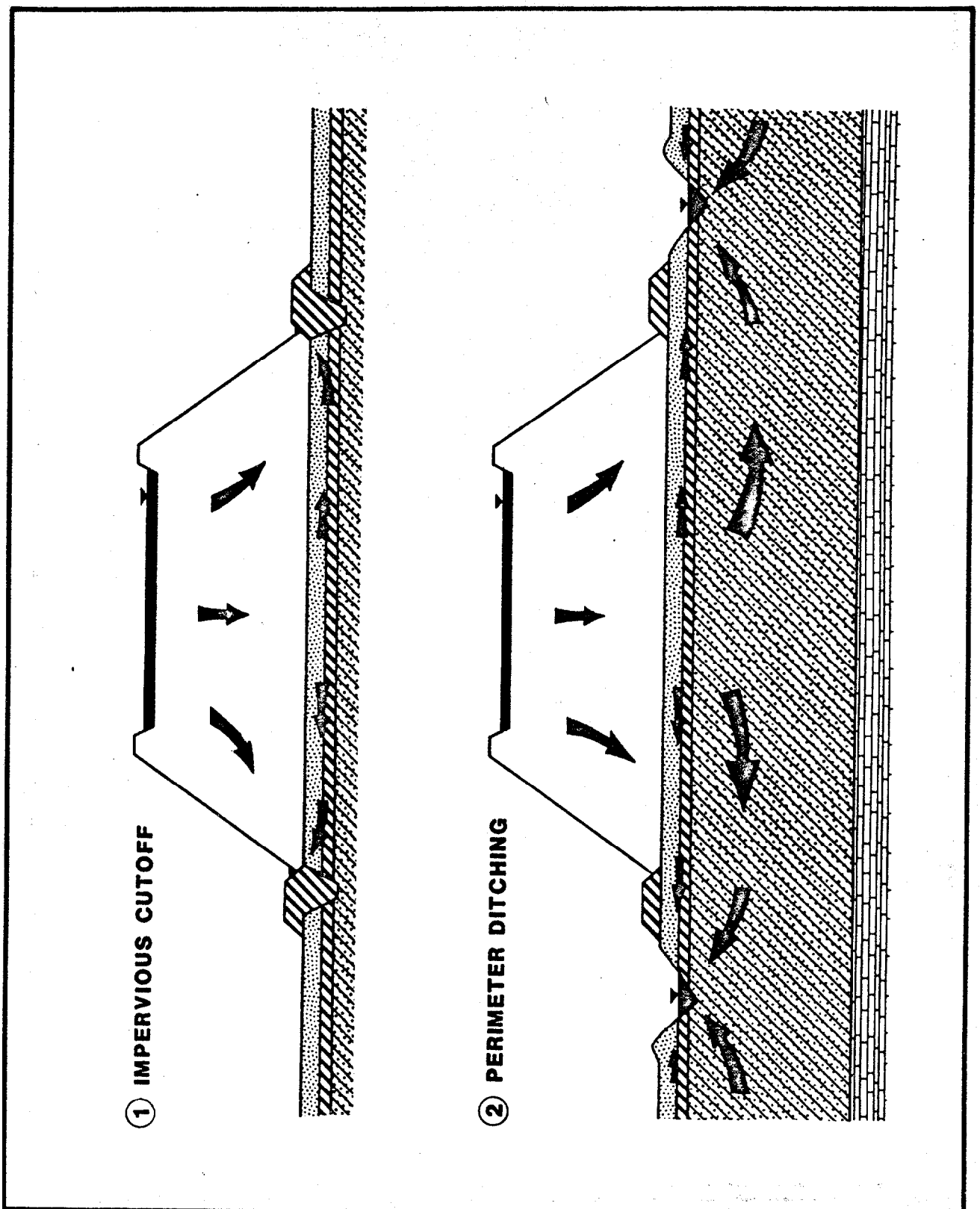
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FIGURE 3
PLUME OF CONTAMINATED GROUNDWATER



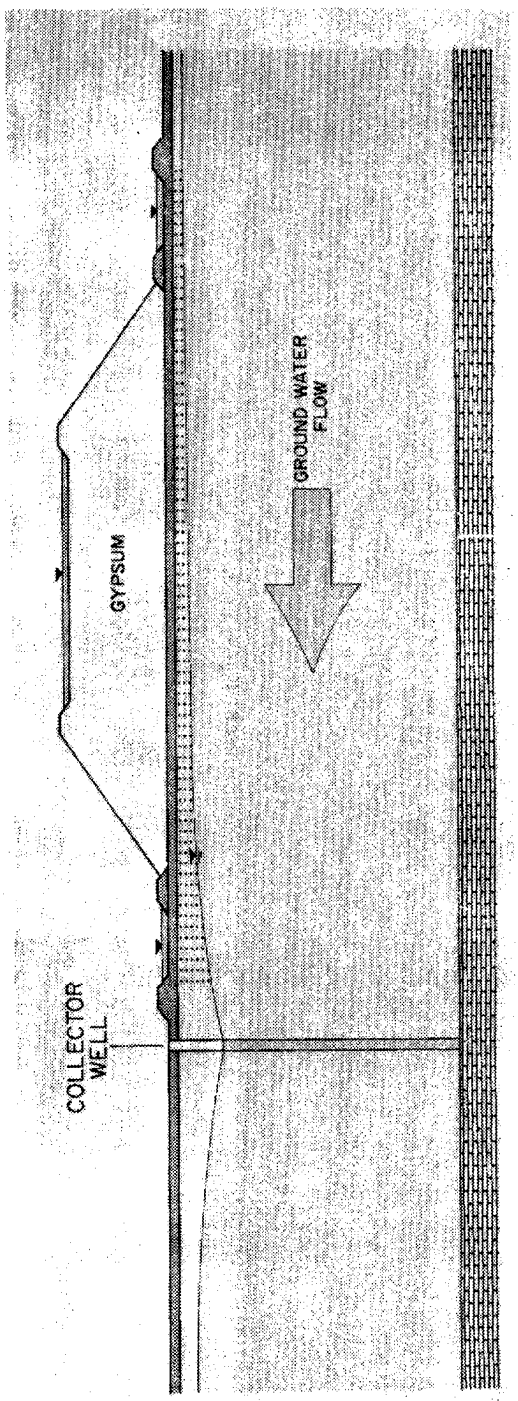
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FIGURE 4
EFFECTIVENESS OF SEEPAGE COLLECTION DITCHES AS A FUNCTION OF TOPOGRAPHY



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FIGURE 5
CONTROL OF GROUNDWATER CONTAMINATION
IMPERVIOUS STRATUM CLOSE TO SURFACE

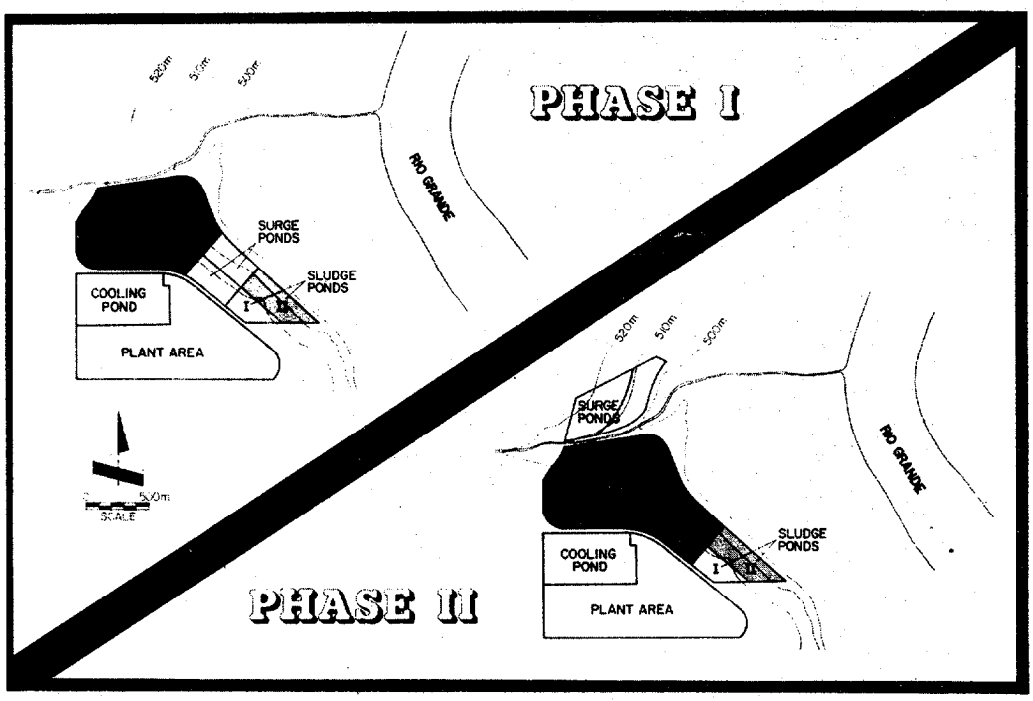


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FIGURE 6
COLLECTOR WELL INSTALLED TO
INTERCEPT CONTAMINATED GROUNDWATER

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FIGURE 7
FLUORIDE CONCENTRATION PROFILES WITH DEPTH AND DISTANCE FROM GYPSUM STACK & COOLING POND



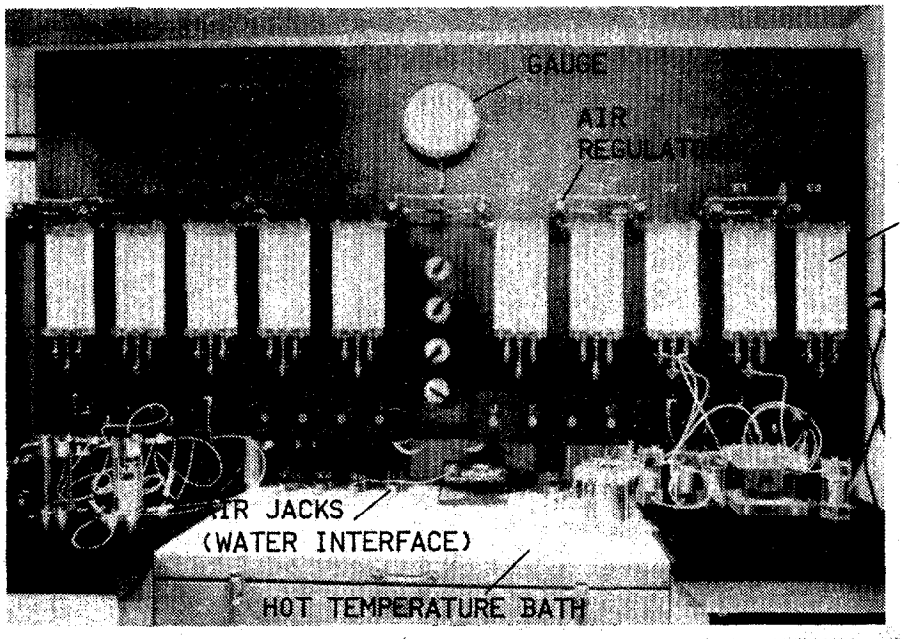
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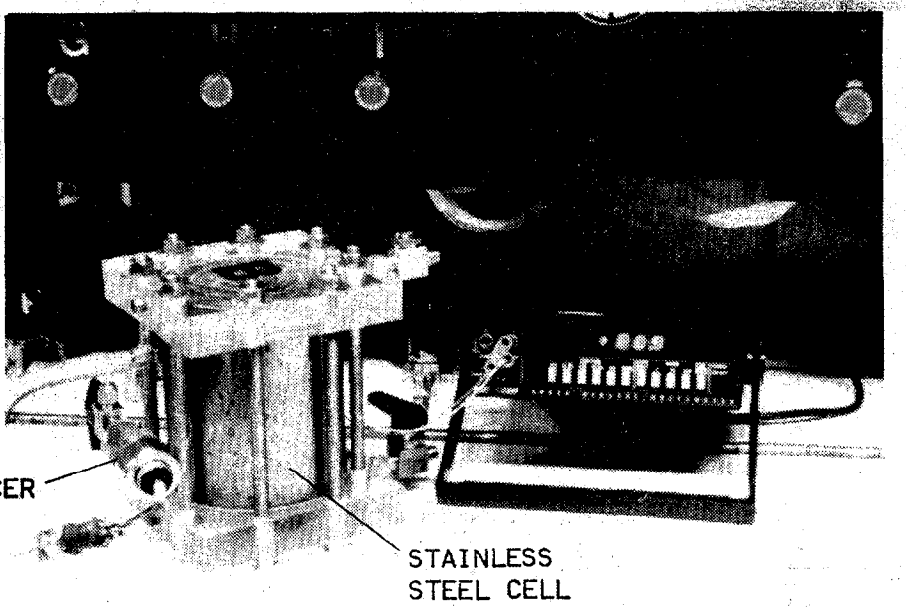
FIGURE 8
CHEMICAL COMPLEX LAYOUT
CASE HISTORY NO. 1

COMPACTED CLAY LINER SYSTEMS

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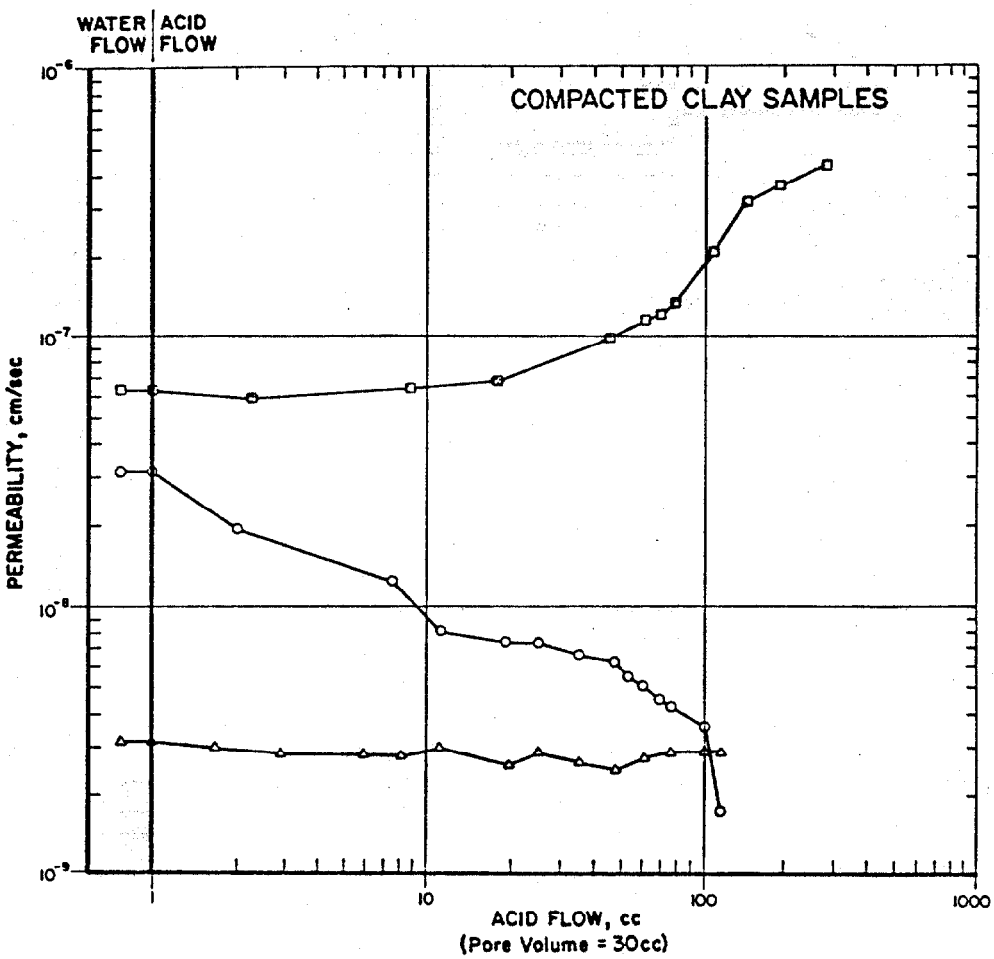
FIGURE 9
COMPACTED CLAY LINER SYSTEMS





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FIGURE 10
PERMEABILITY/LEACHING TEST EQUIPMENT
STAINLESS STEEL PERMEAMETERS

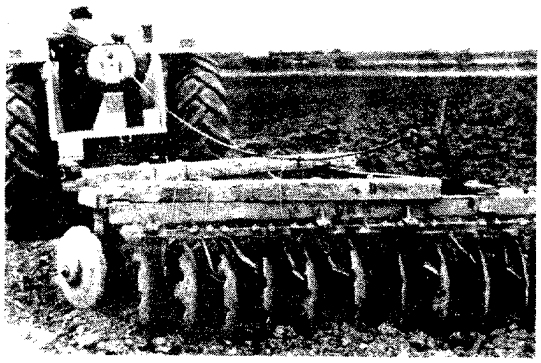


Ardaman & Associates, Inc.

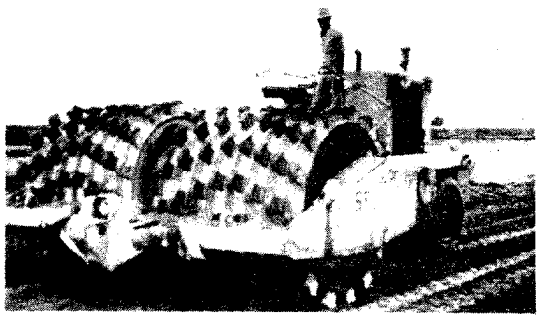
FIGURE 11
EFFECT OF ACID LEACHING ON PERMEABILITY
OF VARIOUS COMPACTED CLAY SAMPLES



(a) WETTING AFTER PULVERIZING



(b) PLOWING AND MIXING



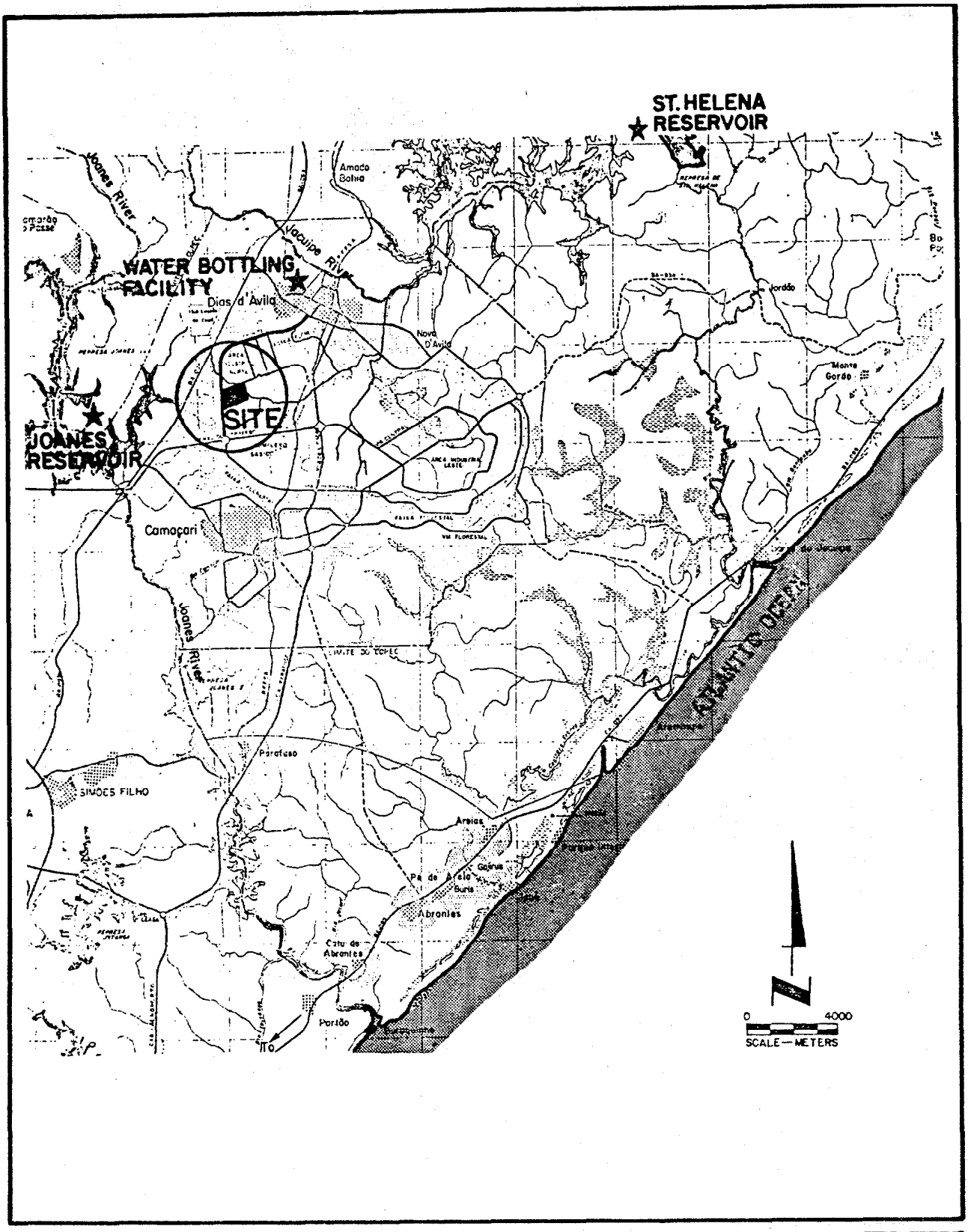
(c) SHEEPSFOOT COMPACTION



(d) PONDING TO PREVENT DESICCATION

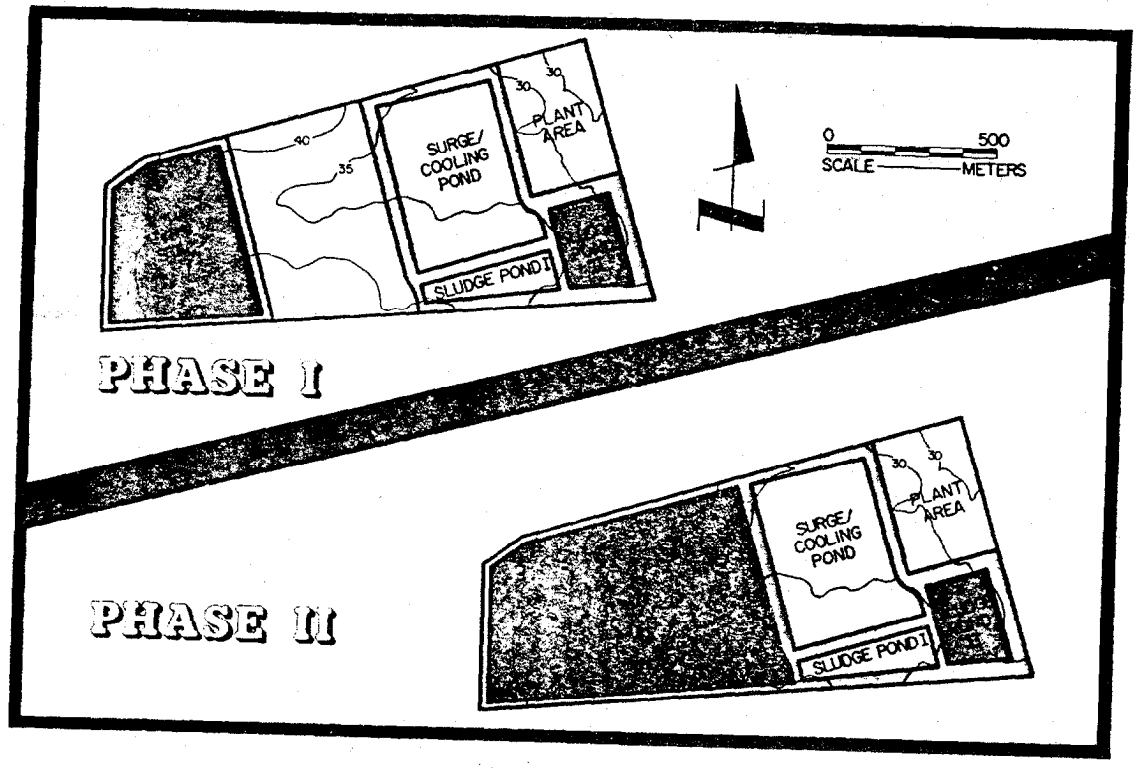
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FIGURE 12
CLAY LINER CONSTRUCTION



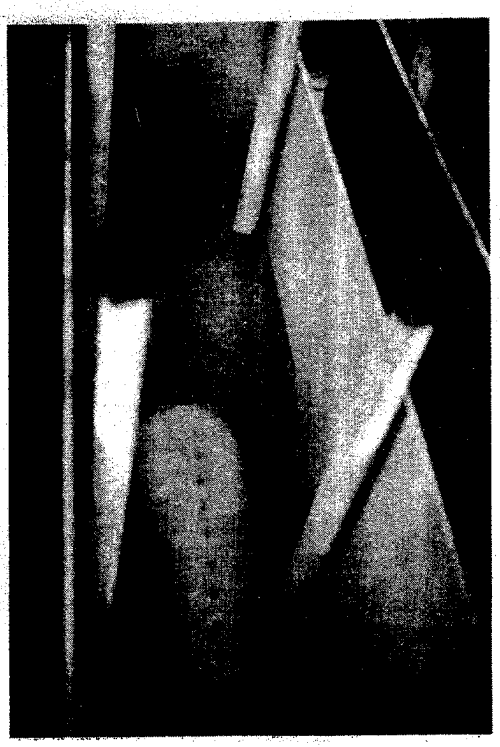
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FIGURE 13
SITE VICINITY
CASE HISTORY NO. 2

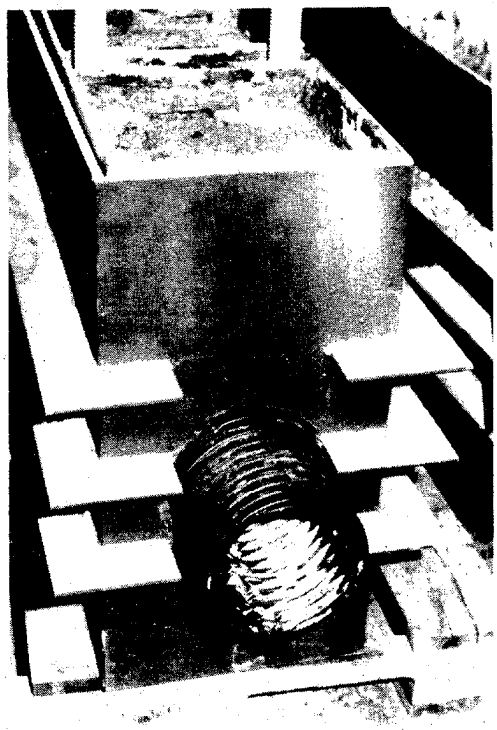


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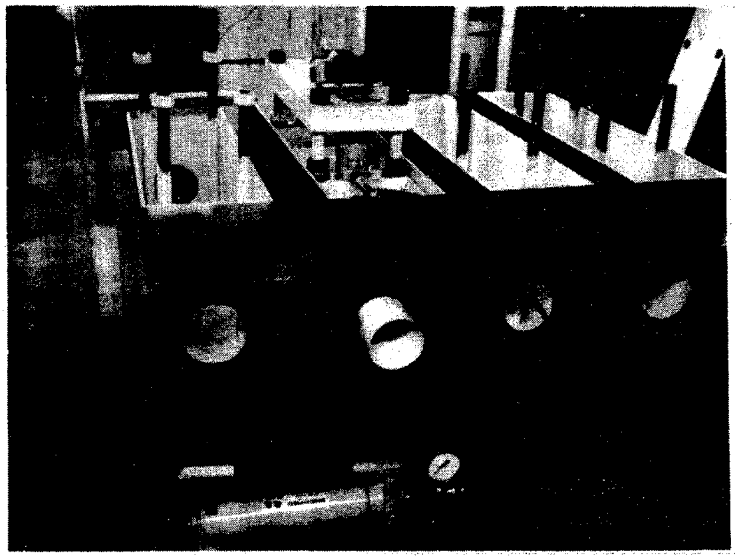
FIGURE 14
CHEMICAL COMPLEX LAYOUT
CASE HISTORY NO. 2



(a) PVC PIPE SURROUNDED WITH DRAIN MATERIAL



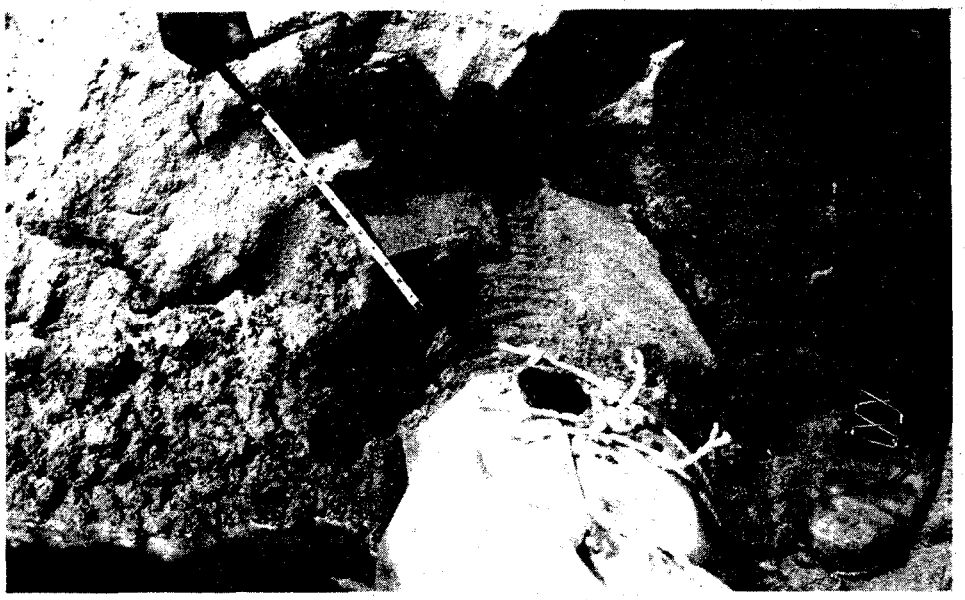
(b) PE PIPE EVALUATION TEST



(c) PIPE EVALUATION SET-UP

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FIGURE 15
ENVIRONMENTAL SIMULATION TEST
OF PIPE AND UNDERDRAIN SYSTEM



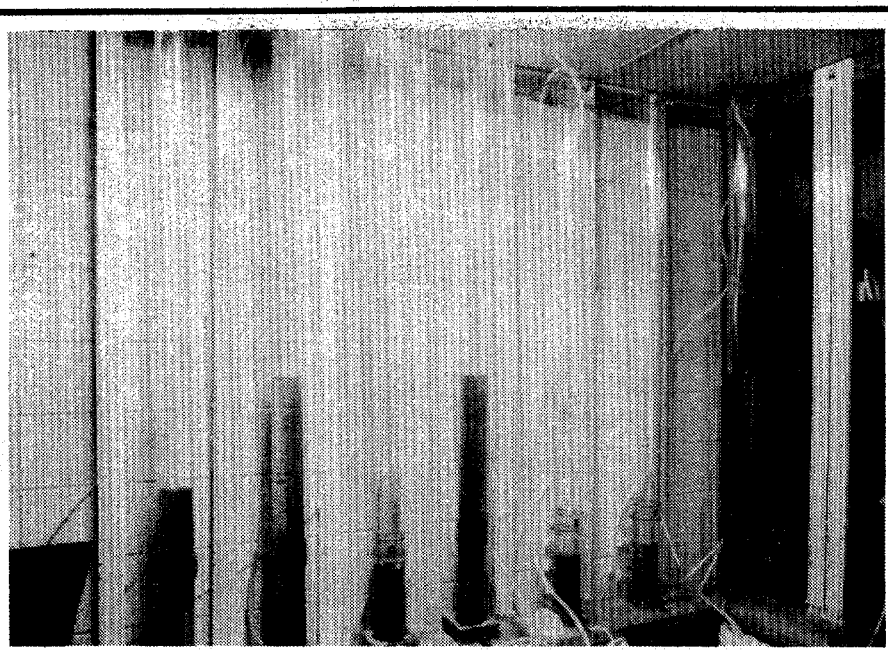
(a) CEMENTED CAKE FORMED AROUND DRAIN PIPE

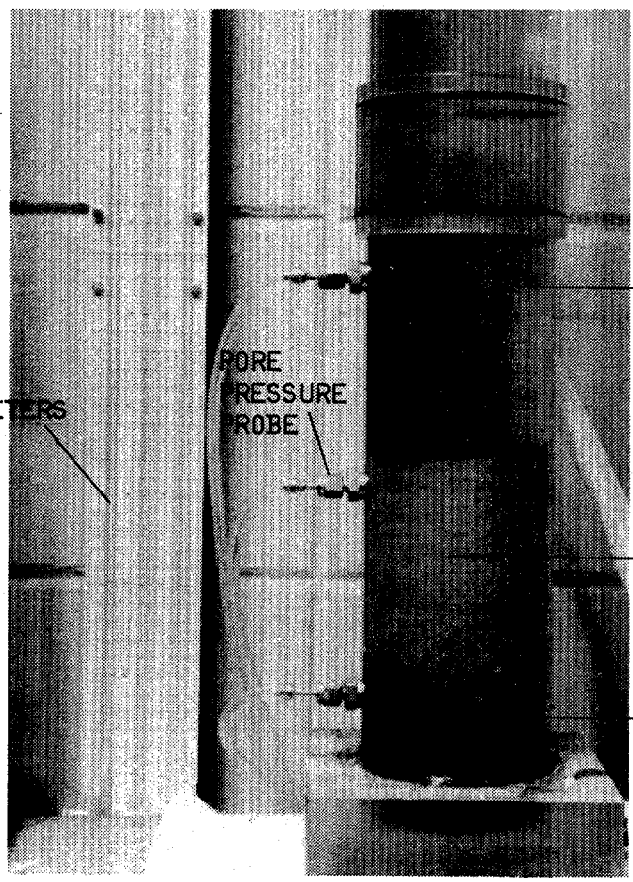


(b) CEMENTED MATERIAL

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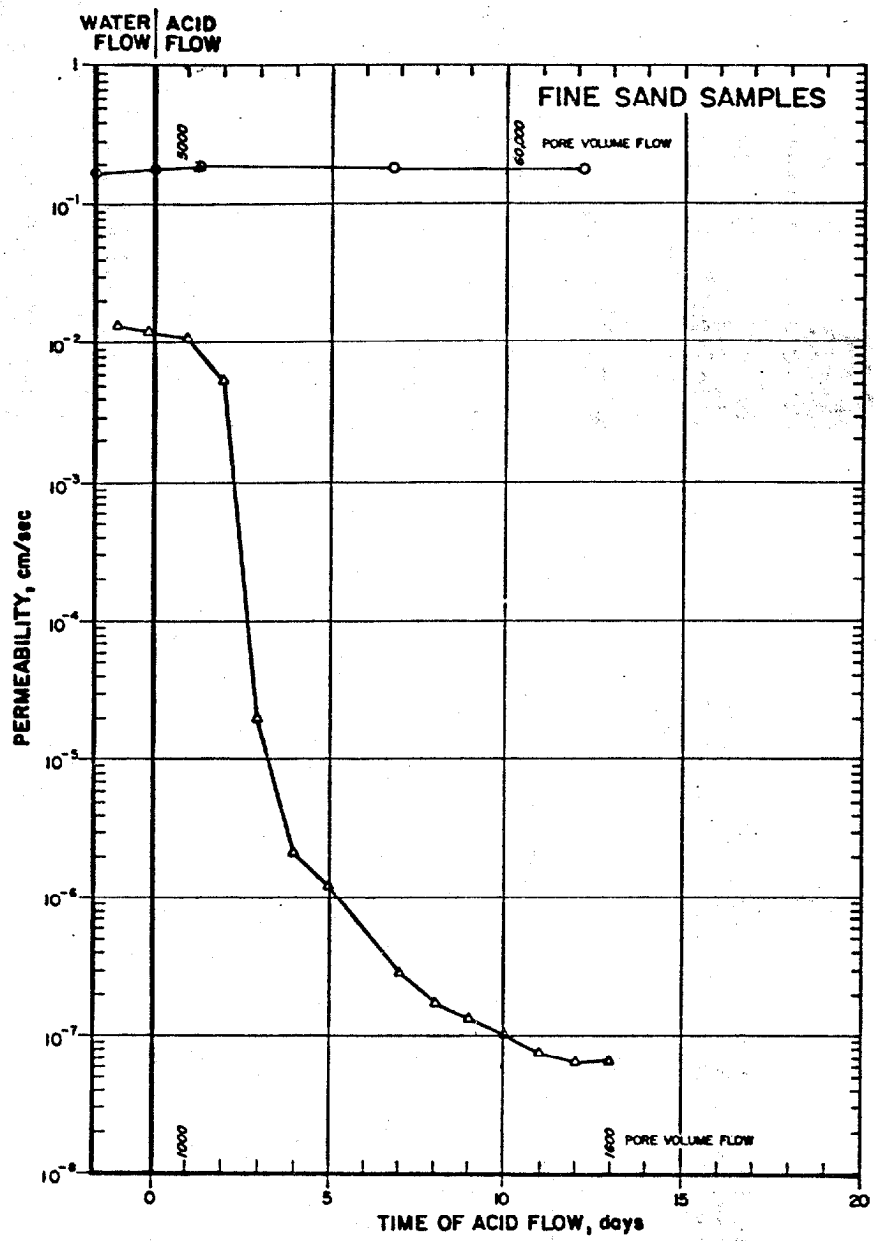
FIGURE 16
CEMENTATION OF DRAIN MATERIAL





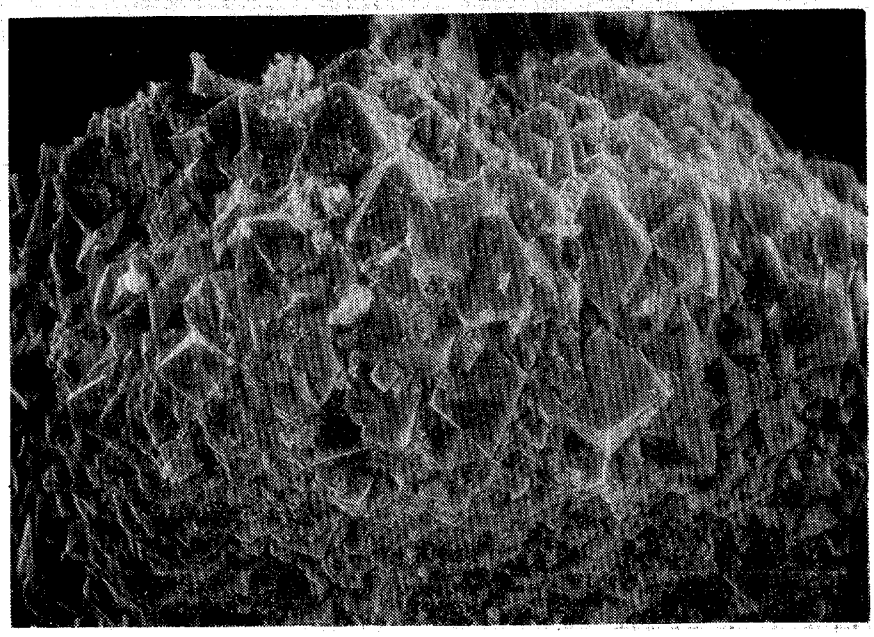
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FIGURE 17
PERMEABILITY/LEACHING TEST EQUIPMENT
FOR DRAIN MATERIAL EVALUATION

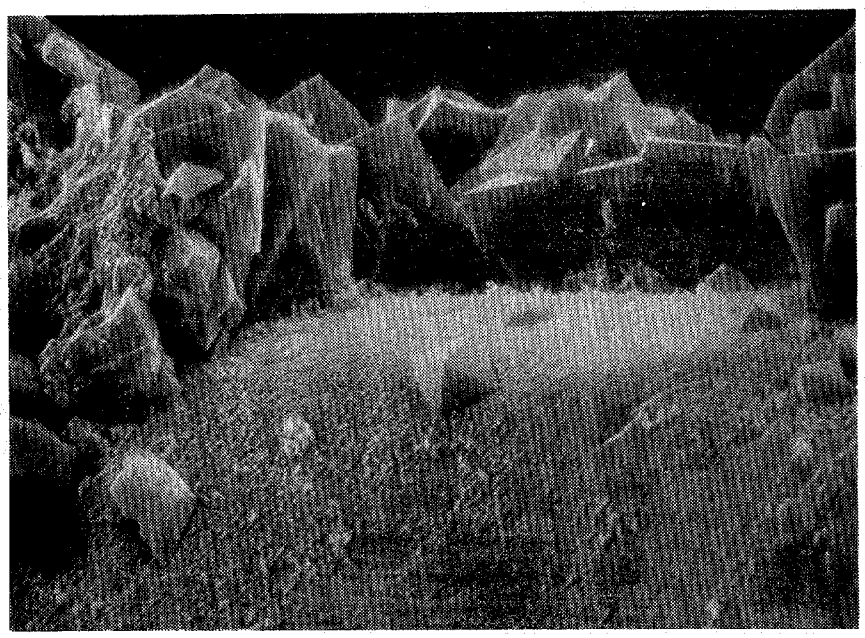


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FIGURE 18
EFFECT OF ACID LEACHING ON PERMEABILITY
OF TWO DIFFERENT DRAIN MATERIALS



a) 40μm

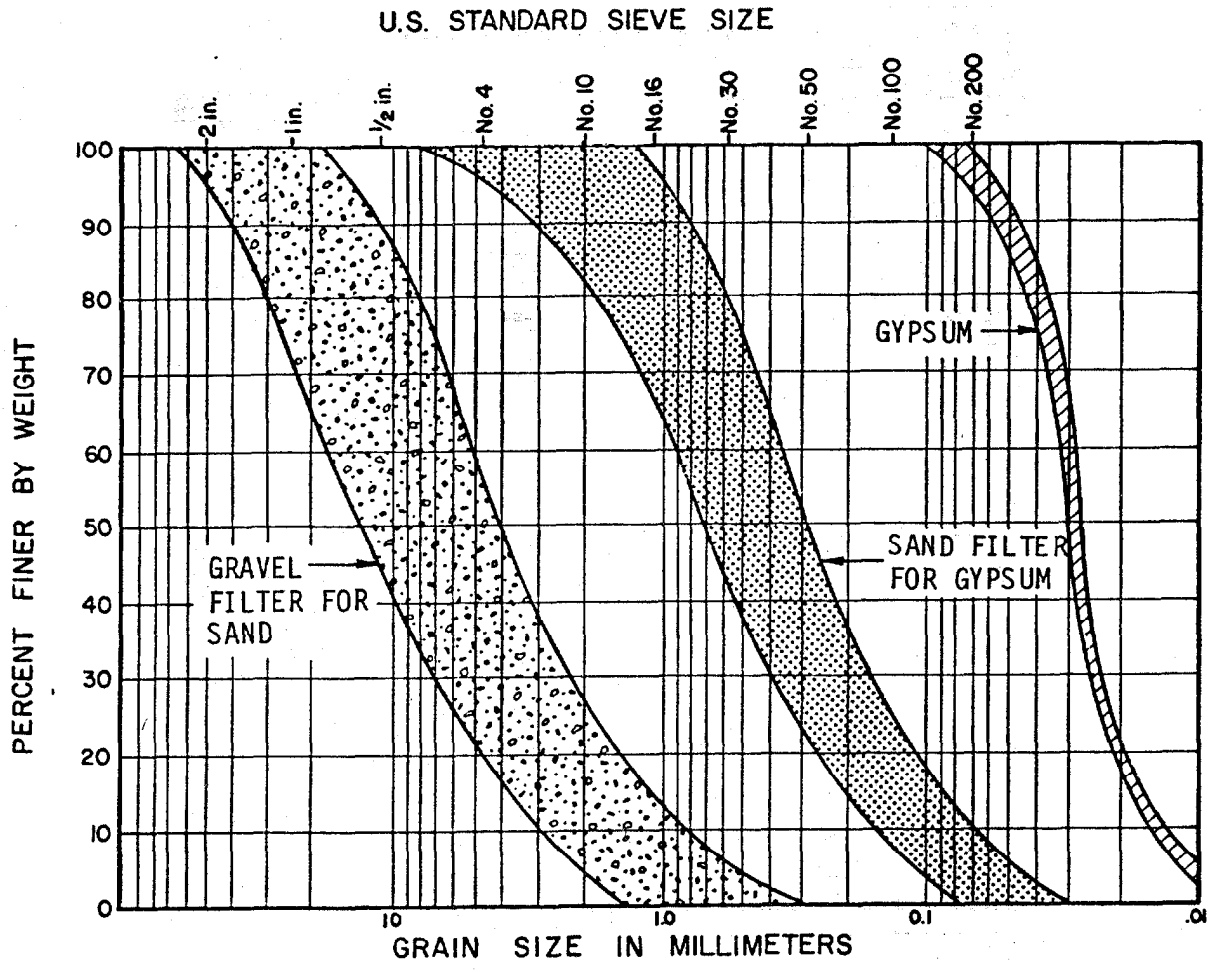


b) 10μm

Scanning Electron Photomicrographs Showing Ca-Al-S Octahedral Crystal with Silicon Dust on a Quartz Grain.

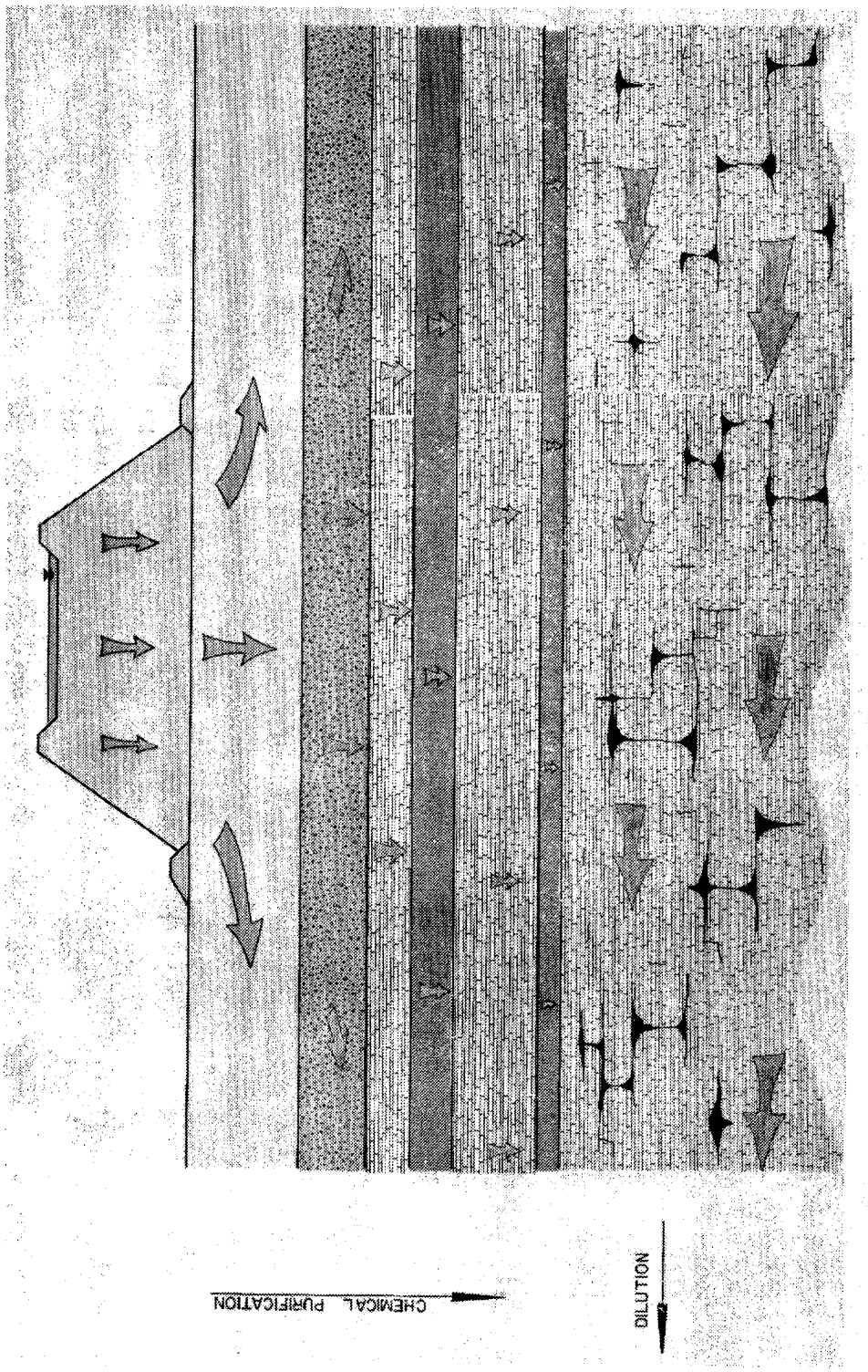
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FIGURE 19
SCANNING ELECTRON
PHOTOMICROGRAPHS



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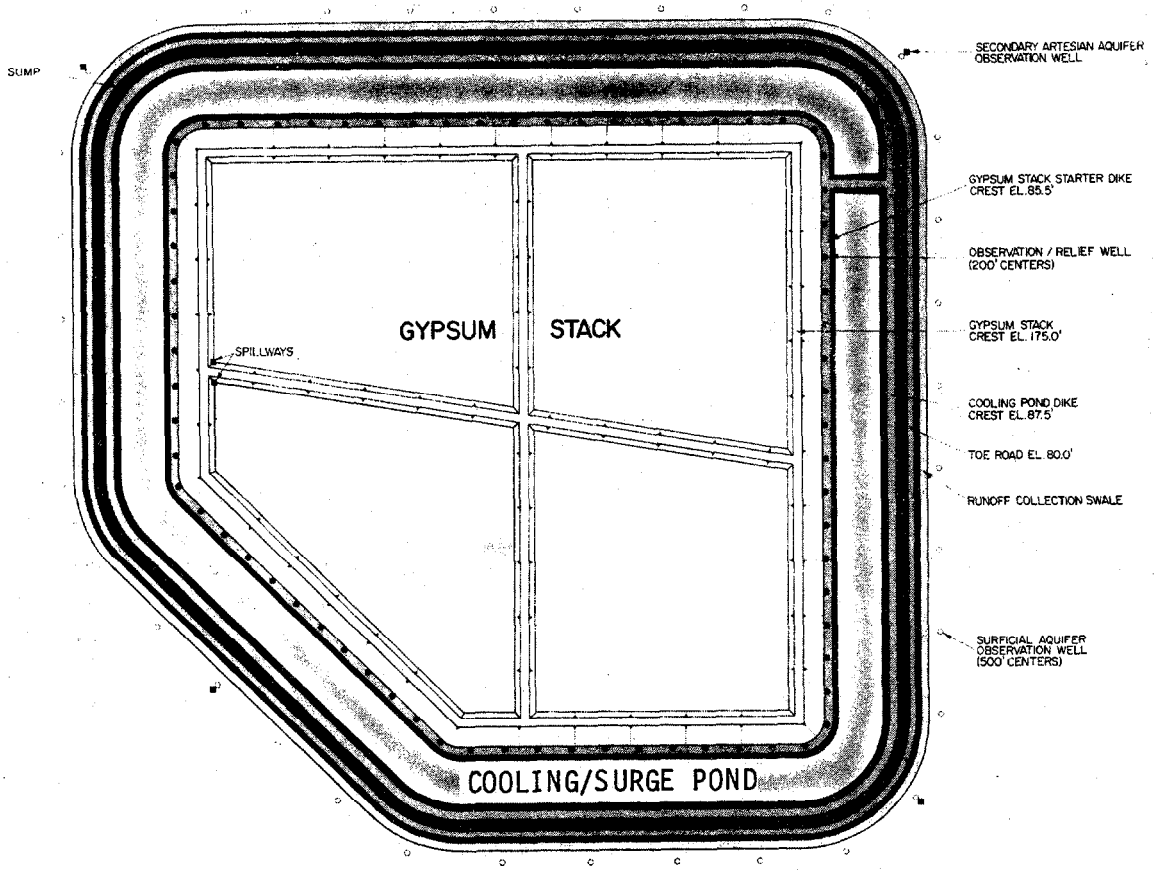
FIGURE 20
TYPICAL GRADATION REQUIREMENTS OF AN UNDERDRAIN FILTER FOR GYPSUM



EFFECT OF LEACHATE ON CONFINED AQUIFER

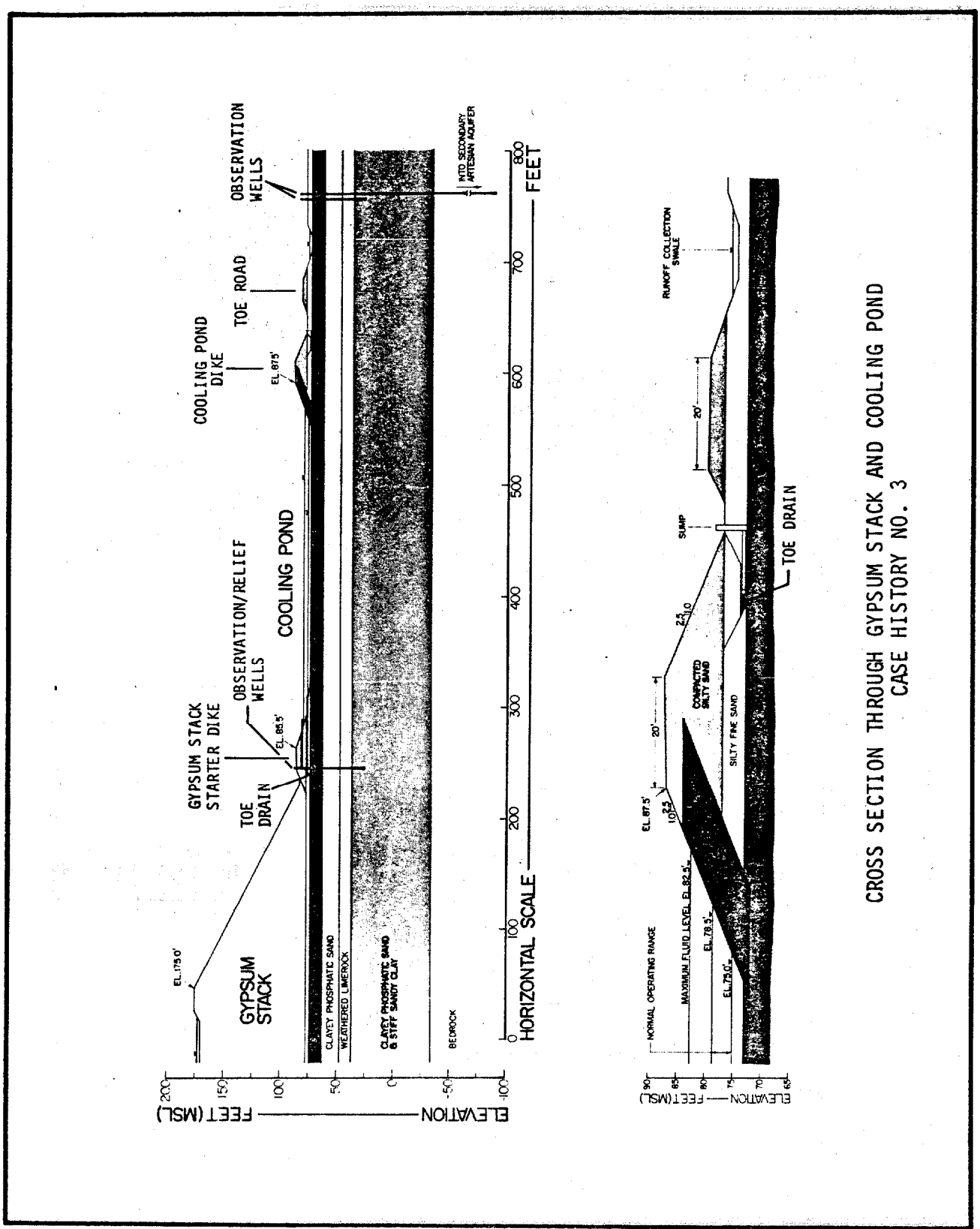
Ardaman & Associates, Inc.

FIGURE 21
EFFECT OF LEACHATE ON CONFINED AQUIFER
IN A FAVORABLE HYDROGEOLOGIC ENVIRONMENT



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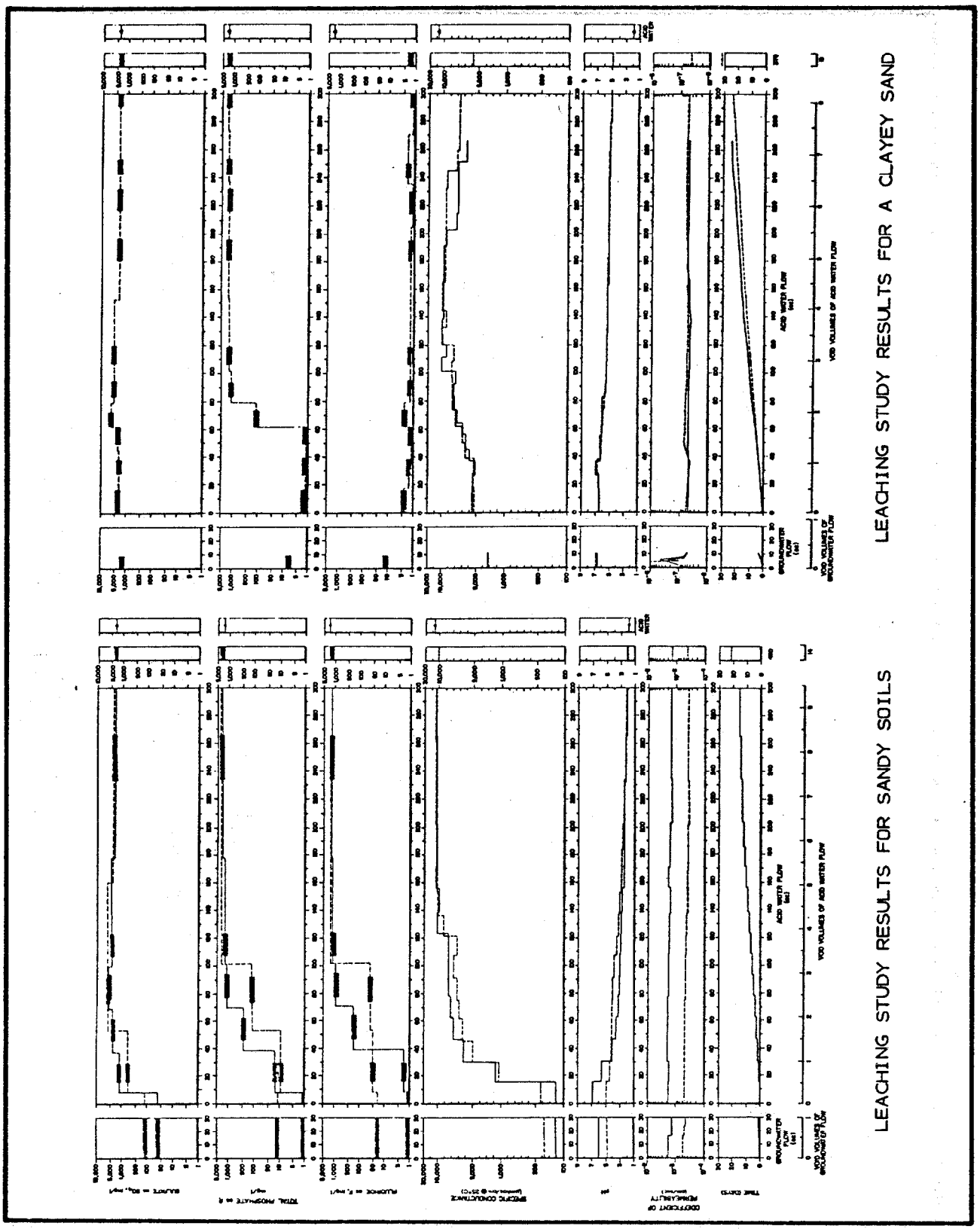
FIGURE 22
LAYOUT OF DISPOSAL FACILITIES AND MONITOR WELL NETWORK - CASE HISTORY NO. 3



CROSS SECTION THROUGH GYPSUM STACK AND COOLING POND
CASE HISTORY NO. 3

Ardaman & Associates, Inc.

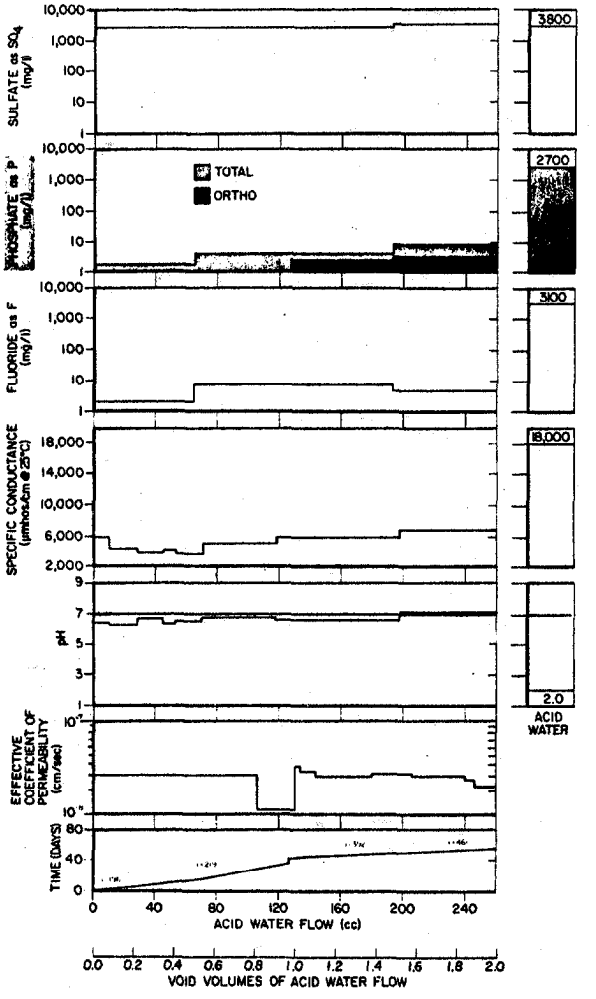
FIGURE 23
CROSS SECTION THROUGH GYPSUM STACK
AND COOLING POND - CASE HISTORY NO. 3



Ardaman & Associates, Inc.

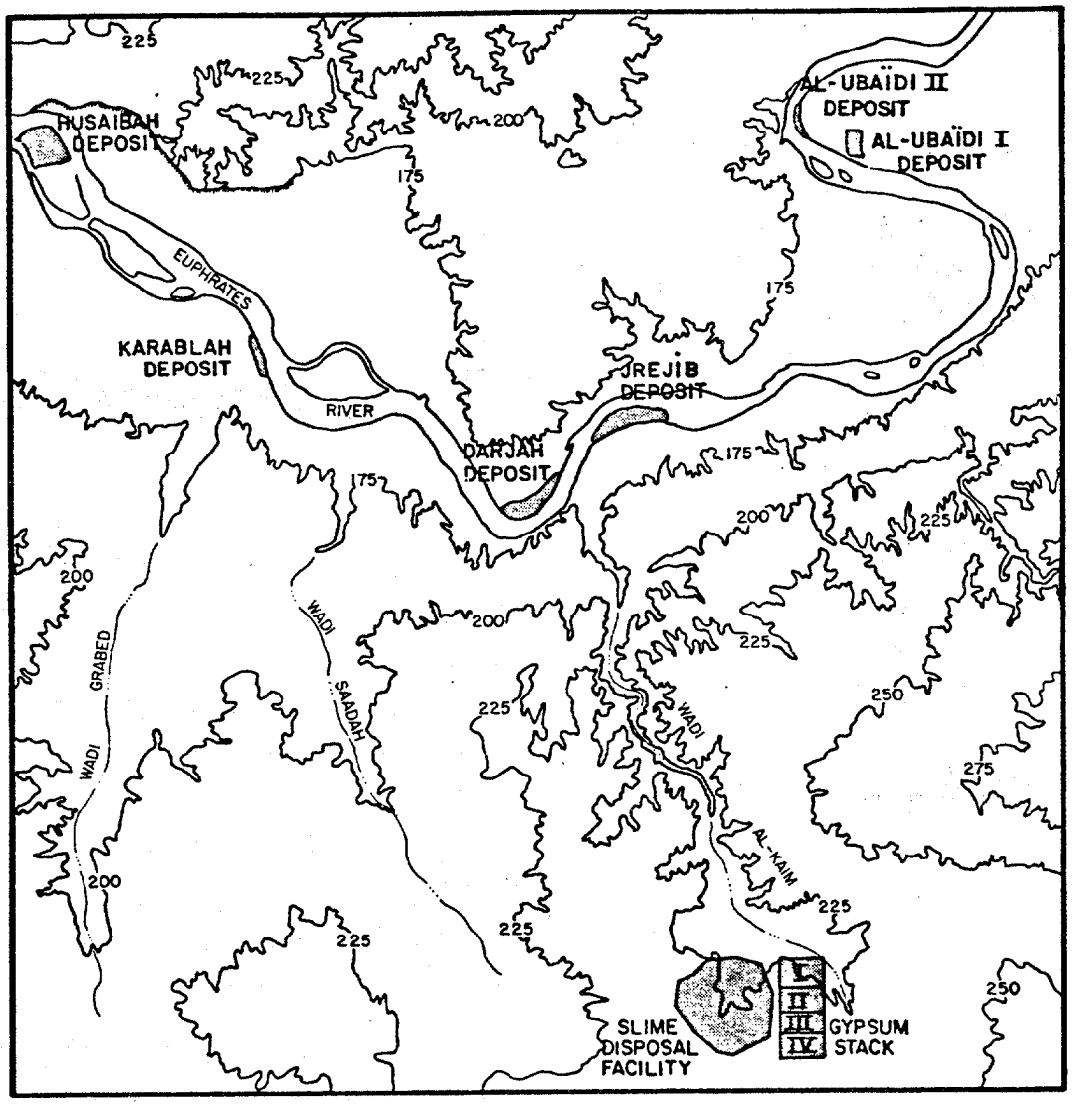
FIGURE 24
LEACHING STUDY RESULTS
FOR SANDY AND CLAYEY SOILS

SOIL TYPE		LAYER THICKNESS (cm)	MOISTURE CONTENT W_m (%)	DRY DENSITY γ_d (pcf)
FINE SAND	2	1.3	5.0	102.8
FINE SAND	1	1.3	5.0	98.1
CLAYEY SAND	3	2.8	18.5	100.9
PLASTIC CLAY	4	1.3	70.0	55.6
PHOSPHATIC CLAYEY SAND	5	22.5	25.0	99.7
PLASTIC CLAY	6	1.3	70.0	47.8



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FIGURE 25
LEACHING STUDY RESULTS
FOR MODEL STRATIGRAPHY

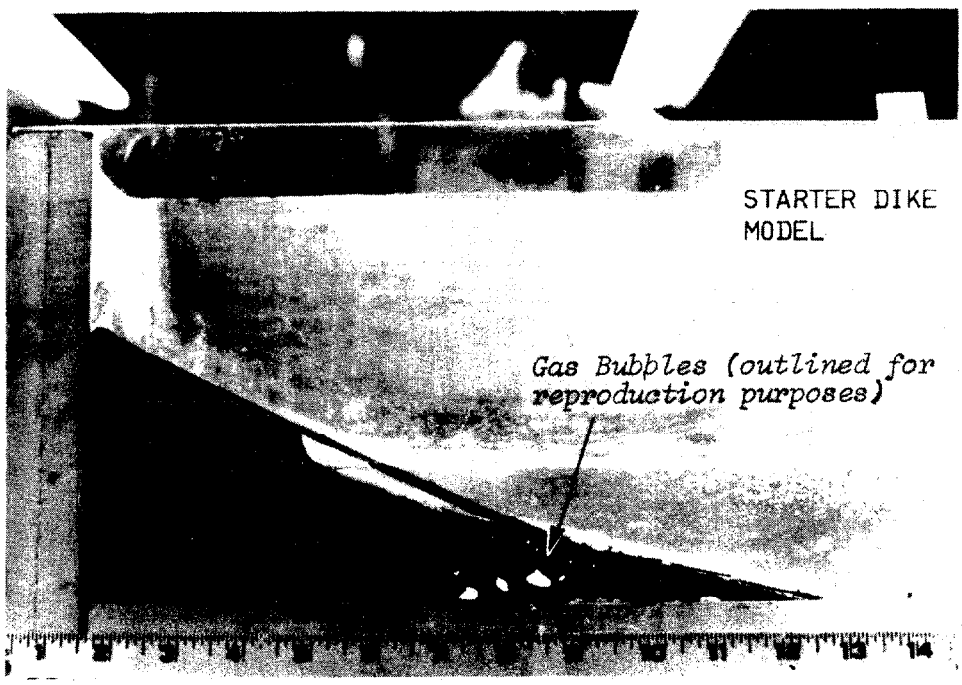


NOTE: TOPOGRAPHIC CONTOURS ARE IN m(MSL)

0 1 2
SCALE – KILOMETERS

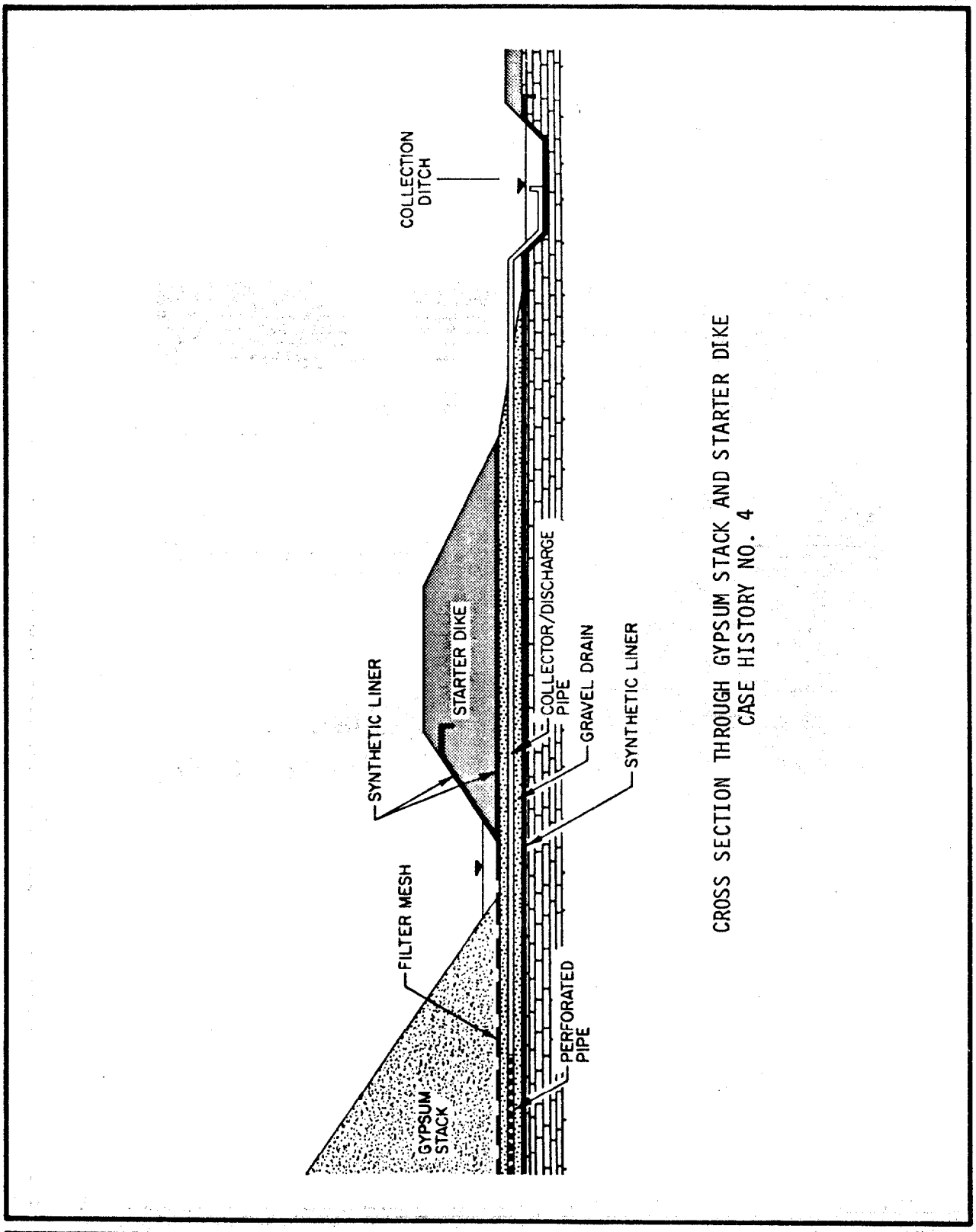
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FIGURE 26
SITE VICINITY
CASE HISTORY NO. 4



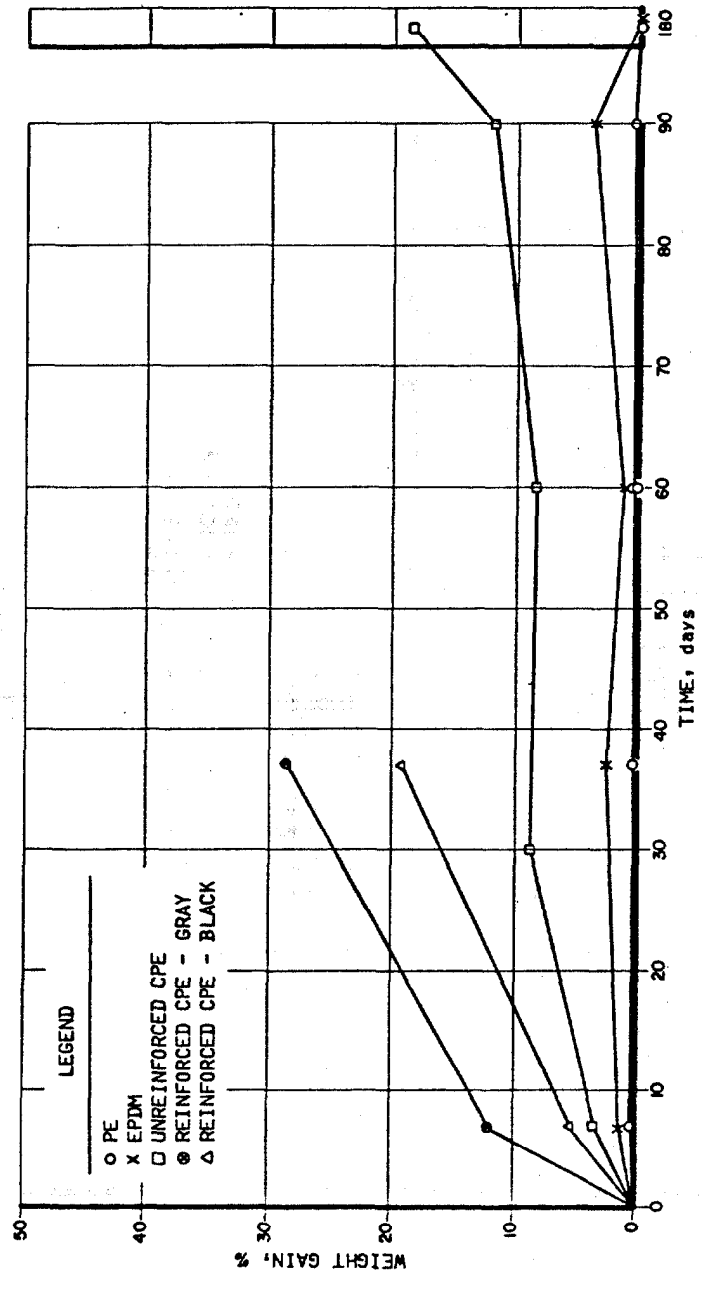
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FIGURE 27
STARTER DIKE MODEL BEHAVIOR UPON CONTACT
WITH PROCESS WATER



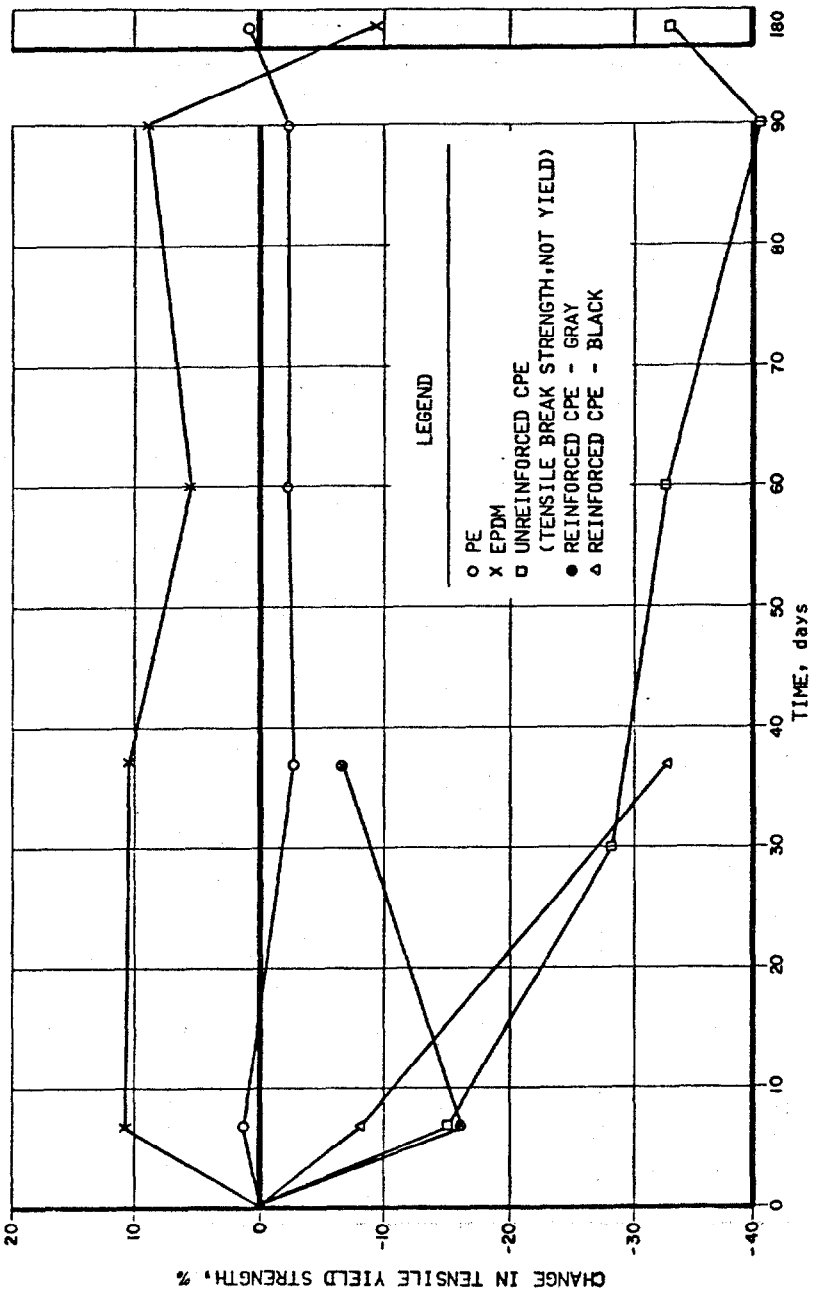
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FIGURE 28
CROSS SECTION THROUGH GYPSUM STACK AND STARTER DIKE - CASE HISTORY NO. 4



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FIGURE 29
WEIGHT GAIN OF LINER VERSUS TIME OF IMMERSION IN ACID WATER AT 71° C(160° F)

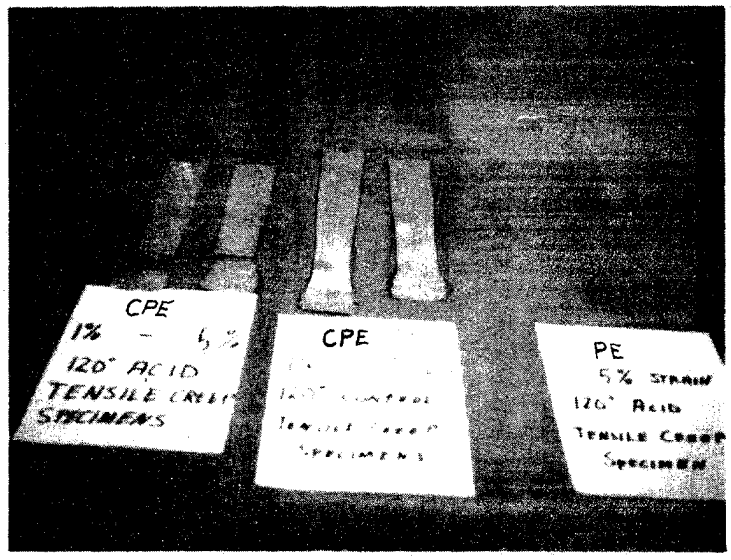


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FIGURE 30
CHANGE IN TENSILE YIELD VERSUS TIME OF IMMERSION IN ACID WATER AT 71° C(160° F)



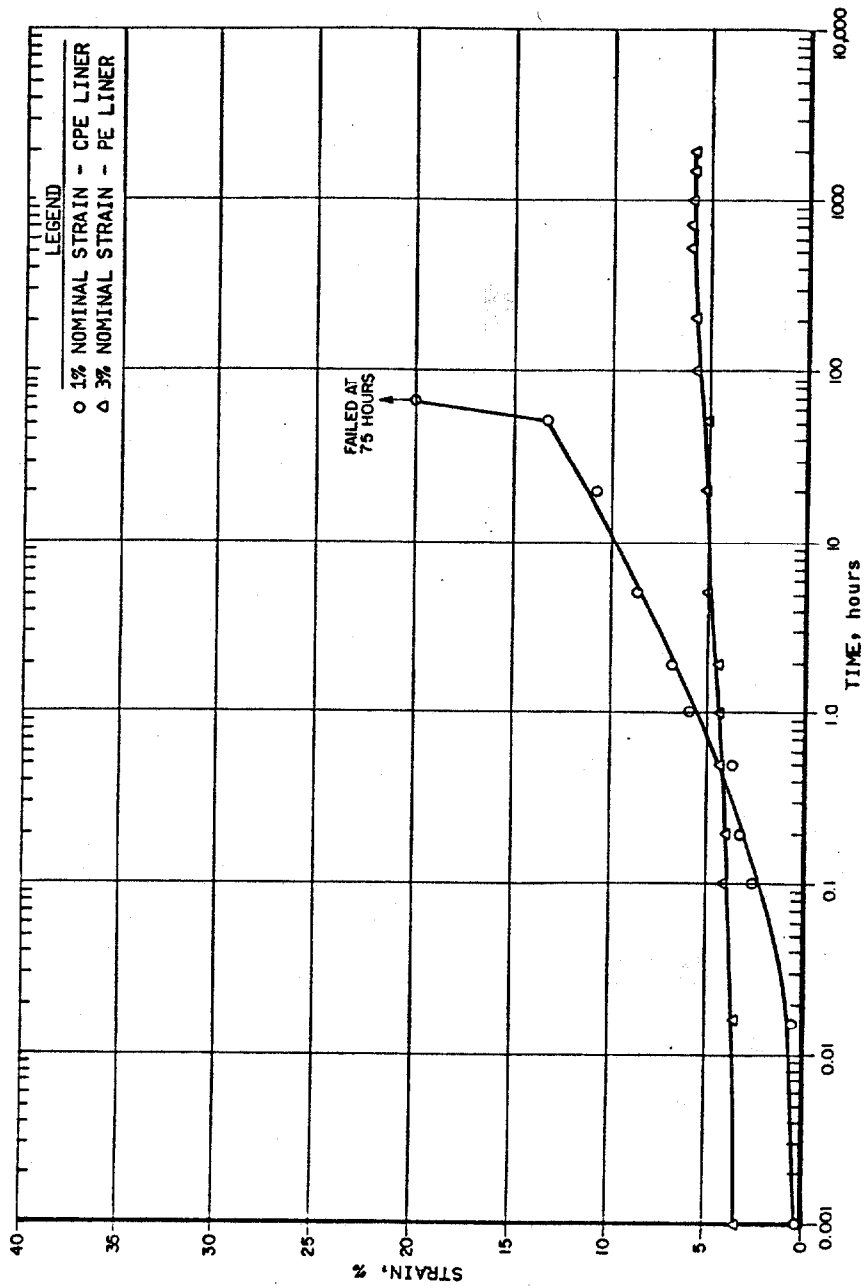
a) TENSILE CREEP TEST SET-UP



b) CREEP SPECIMENS THAT HAVE BEEN REMOVED FROM TESTING DUE TO FAILURE OR EXCESSIVE CREEP

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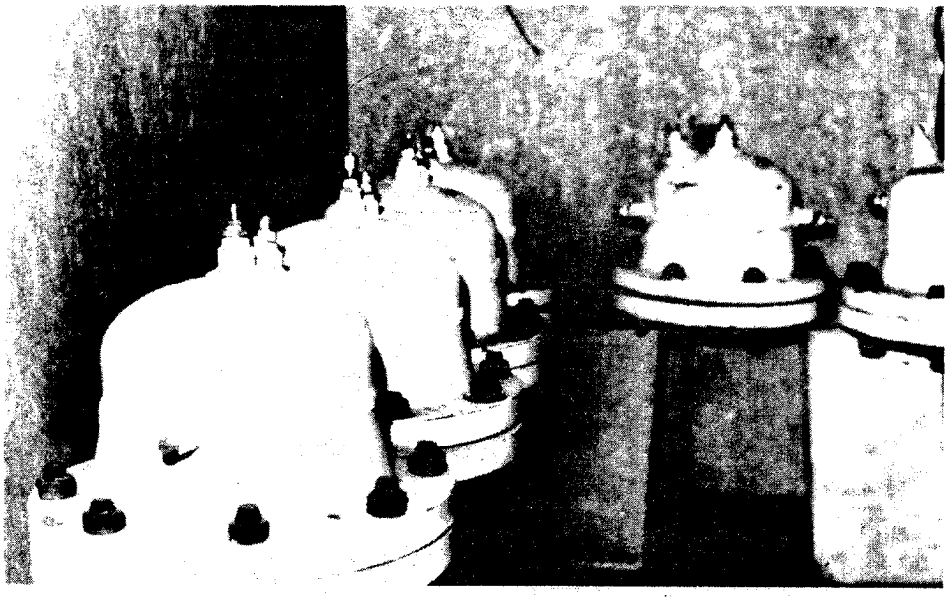
FIGURE 31
PHOTOGRAPHS OF TENSILE CREEP TESTING OF POLYMERIC LINERS



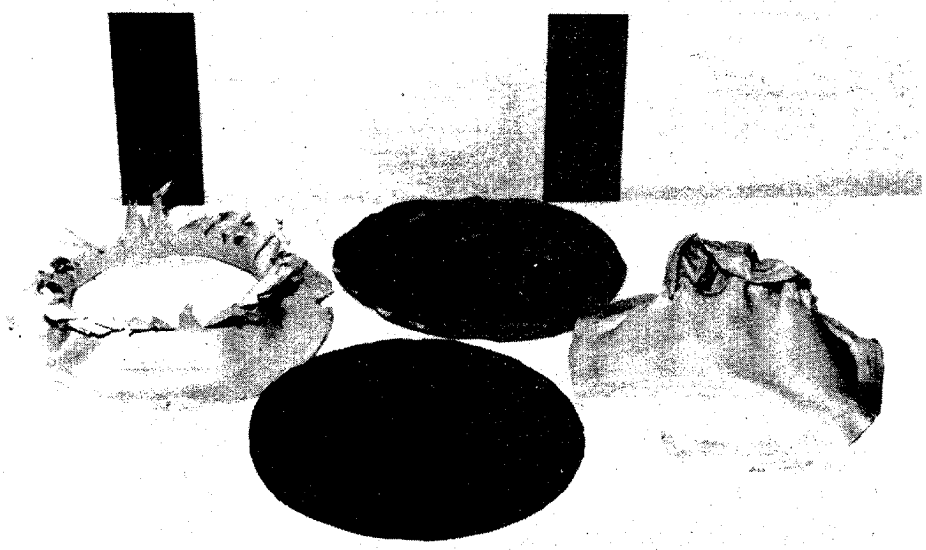
TENSILE CREEP TEST RESULTS WITH PROCESS ACID AT 49°C(120°F)

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FIGURE 32
TENSILE CREEP TEST RESULTS
WITH PROCESS ACID AT 49°C(120°F)



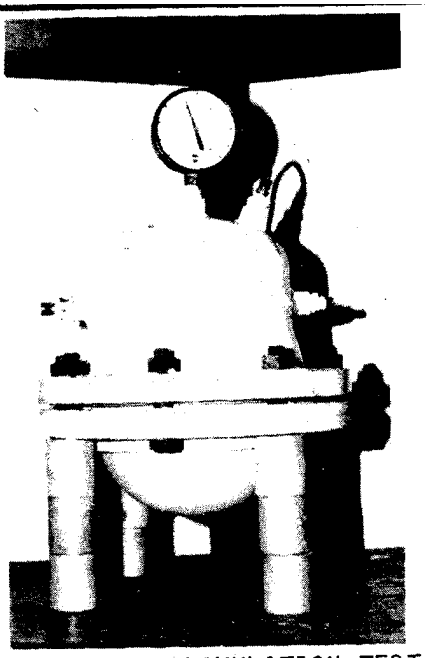
(a) HYDROSTATIC BELL TEST EQUIPMENT



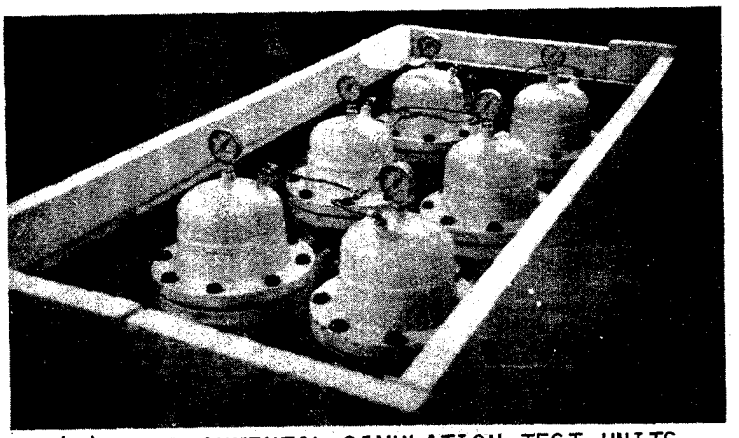
(b) CANDIDATE LINER SPECIMENS AFTER FAILURE IN HYDROSTATIC TEST

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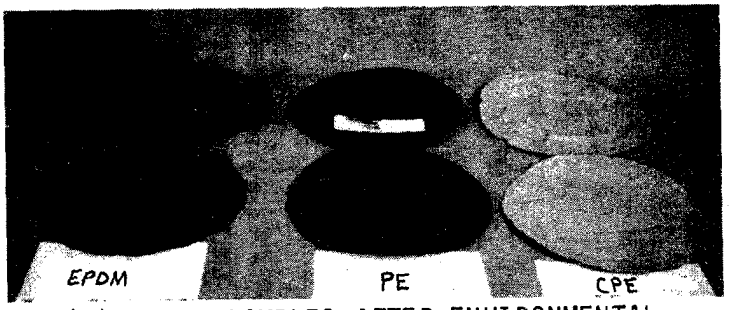
FIGURE 33
HYDROSTATIC BELL TESTING
OF POLYMERIC LINERS



(a) ENVIRONMENTAL SIMULATION TEST UNIT



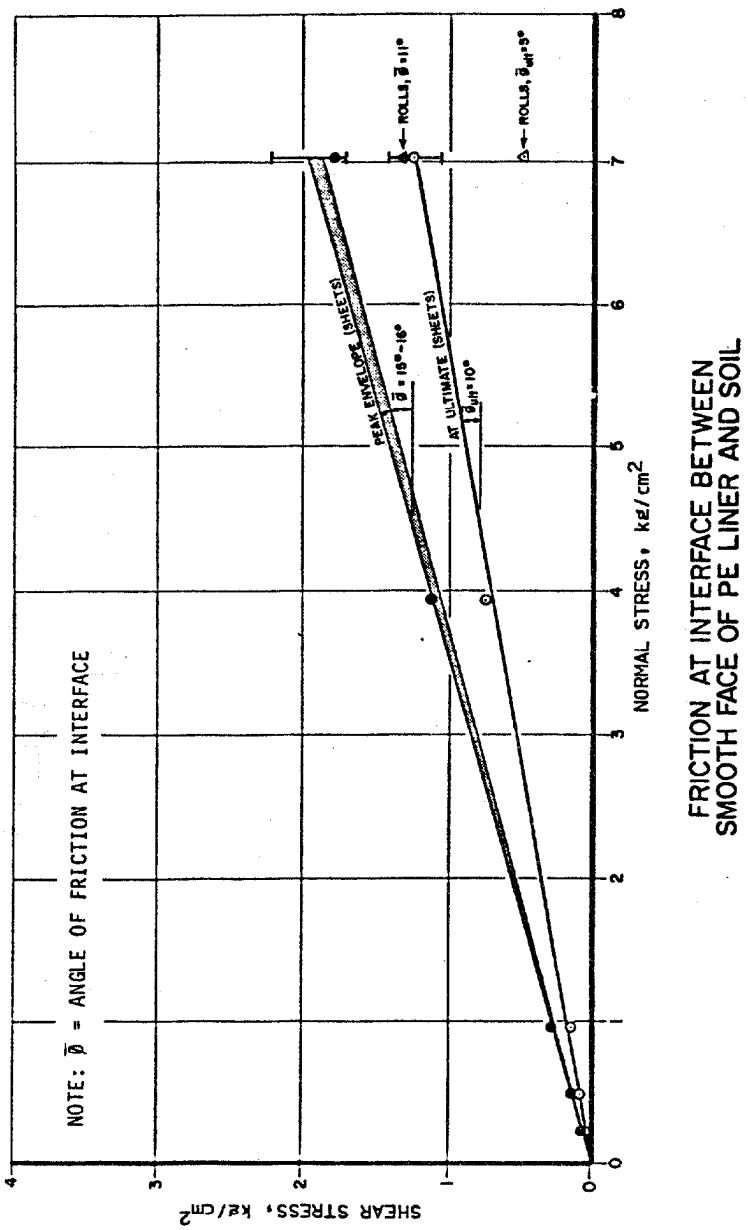
(b) ENVIRONMENTAL SIMULATION TEST UNITS IN CONTROLLED TEST ATMOSPHERE



(c) LINER SAMPLES AFTER ENVIRONMENTAL SIMULATION TESTING

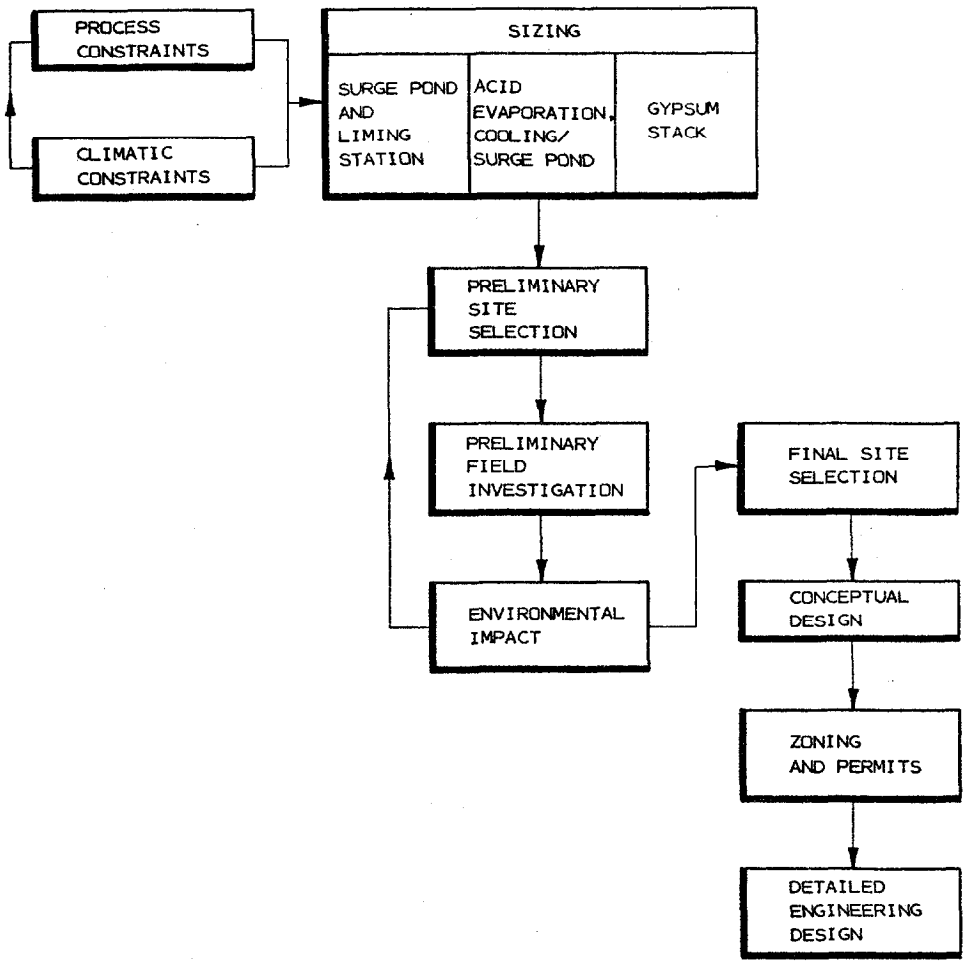
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FIGURE 34
ENVIRONMENTAL SIMULATION TESTING OF LINERS



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FIGURE 35
FRICTION AT INTERFACE BETWEEN
SMOOTH FACE OF PE LINER AND SOIL



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FIGURE 36
SITE SELECTION FLOW CHART

ASSESSMENT OF RADON EXHALATION FROM PHOSPHATE GYPSUM PILES

by

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and
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INTRODUCTION

It has been recognized for many years that phosphate deposits throughout the world contain appreciable concentrations of radioactive material originating from the decay of naturally-occurring uranium and thorium on the ore. In the United States phosphate ores, uranium concentrations range from 5 to 267 pCi per gram with the decay products of the uranium normally in equilibrium at least through radium-226 (1).

Radium-226 is a member of the uranium-238 decay series as shown in Figure 1. The first decay product of radium is radon-222 (hereafter referred to as radon), an inert gas. Radon decays with a half-life of 3.8 days to produce a series of particulates referred to as "radon daughters" or "decay products." This means that for each curie (3.7×10^{10} disintegrations per second) of the parent radionuclide such as uranium, there is also one curie of each daughter radionuclide present.

Mining and processing of phosphate ore redistribute the uranium and its decay products among the various products, by-products, effluents, and wastes of the industry. As a result of this redistribution of naturally-occurring radionuclides, there may be increased opportunity for exposure of the public.

Marketable phosphate rock which we sampled from Polk County, Florida, contained radium and uranium concentrations as noted in Table 1. Utilization of this rock in a wet-process phosphoric acid fertilizer production plant distributed the radioactivity as seen in Figure 2. As noted in the flowsheet of Figure 2, the majority of radium-226 associated with the production of phosphoric acid is deposited in the by-product gypsum. The EERF has studied the potential for population exposure to alpha-emitting radionuclides originating from radium contained in the stored gypsum. This report describes the efforts to estimate cumulative working level* months (CWLM) from radon-222 daughters produced from radium-226 in phosphate gypsum piles and how these estimates compare with CWLM from inactive uranium mill tailings piles.

Description of the Study. For many years inactive uranium mill tailings piles have been recognized as a source of relatively large quantities of radon. To test the hypothesis that phosphate gypsum piles may also be a source of relatively large amounts of radon, radon exhalation rate studies were conducted at two phosphate gypsum piles. These exhalation rate data have been converted to radon source terms so that for a nearby residence, indoor radon concentration indoor working level, and individual and population cumulative working level month estimates could be determined by utilizing atmospheric dispersion

* Working Level (WL) is defined as an atmospheric concentration of radon daughters which will deliver 1.3 x 10 million electron volts of alpha energy per liter of air. A working level month (WLM) is an exposure equivalent to 1 working level of radon daughters for 173 hours.

modeling. Similar calculations were undertaken for an inactive uranium mill tailings pile. The uranium mill tailings data used in the calculations were published in previous EPA reports (2,3,4). The results of each source category are compared.

The quantity of radon released from gypsum piles is dependent on several factors which include the radium-226 specific activity in the gypsum, the emanating power (i.e. the amount of radon released per unit generated), the atmospheric pressure , and the diffusion coefficient (which included moisture content of the gypsum) for the radon in the gypsum. High moisture content or water standing on the surface of the gypsum pile greatly reduce the exhalation rate.

Radon exhalation rates are commonly determined experimentally using either the accumulator technique (5), in which radon is collected in a metal drum, or the canister technique (6), in which radon is adsorbed on activated charcoal. Data collected by our laboratory and reported in this report were obtained using the charcoal canister technique. We use the accumulator technique as a means of calibrating the charcoal canisters employed in this report.

RESULTS

Phosphate Gypsum Pile Exhalation Rates. Exhalation rate measurements for phosphate gypsum piles were made using charcoal canisters on two active piles in Polk County, Florida. Each pile was sampled 20-30 times over a period of several weeks. Old and new sections of each pile were sampled. The old (inactive) section of each pile constitutes a portion of the overall pile that is not presently being worked (i.e., new gypsum is not being added to this section of the pile). It may include gypsum that has been present on the pile for a number of years. The new (active) section is an area of the overall pile where new material is being slurried to the pile. For the most part, canisters were placed on relatively dry areas of each pile, primarily on the outer edges of the pile. Ideally, the canisters should have been distributed over the entire pile to account for the spatial distribution of radon flux. Since these were operational piles, practical limitations precluded ideal sampling.

The exhalation rate measurements for each pile vary over almost two orders of magnitude. This variation can be explained in part by the nonuniform distribution of radium-226 in the pile material. Also the difference possibly can be accounted for by changes in average barometric pressure and total rainfall (if any) during the sampling period. For purposes of calculations in this study the arithmetic man exhalation rate, 26.7 pCi/m^2-second, was used.

Inactive Uranium Mill Tailings Pile Exhalation Rates. The exhalation rate used for the inactive uranium mill tailings pile category was obtained by averaging the results from measurements made on a pile located at Shiprock, NM (4). This exhalation rate is 93.3 pCi/m^2-second and is shown in Table 2.

Radon Source Terms. Again referring to Table 2, the radon source terms in units of Ci/yr are based on the mean exhalation rate for each source and a representative source area expressed in terms of hectares (1) hectare = 10,000m^2. Also, of interest is the radon contribution background soil would make if each pile were not present. The source terms for background soil are presented in Table 2 in the last column. In each case the pile radon source term is much greater than its corresponding background soil component.

Discussion of Source Term Results. By addressing the source size and radium-226 specific activity information in Table 2. an almost reciprocal relationship exists between radium-226 specific activity and source size which accounts for the relatively large source terms for phosphate gypsum piles. Even though radium-226 specific activity of the uranium mill tailings pile is large, the pile area is much smaller than the phosphate gypsum piles. The uranium mill tailings pile exhalation rate is much greater than either of the two phosphate gypsum pile exhalation rates, which reflects the greater radium-226 specific activity. Looking at the source terms for each category, the difference is much smaller than was seen previously with the exhalation rate comparison. The relatively large phosphate gypsum piles nullify a large portion of the difference.

Radiological Impact Assessment and Conclusion. The radon source terms are used as input into a computer code which calculates individual and population doses: The computer generated doses are converted to radon concentration, working level, and CWLM. The computer code AREAC (7) was written to output doses directly without giving radon concentrations and working level; hence the doses are transformed by hand calculations to concentration and working level. The simplifying assumption is made that over a year's period the indoor radon concentration attributable to each source will approach the annual average outdoor radon concentration resulting from atmospheric dispersion of the pile radon. Working level exposures associated with indoor radon are calculated assuming an indoor exposure at 70% equilibrium (8), 100 pCi/l radon = 0.7 working level. All reported values (Table 3) of radon concentration and working level are for a structure located 800 m from the center of the pile in the predominant wind direction.

To obtain individual CWLM estimates, the calculated indoor working level is multiplied by a CWLM conversion factor (1 WL in a structure with 75% occupancy results in 20 WL months per year) (9). As would be expected, the individual CWLM estimates for the uranium mill tailings piles are typically greater than for the phosphate gypsum piles (Table 3). The same simplifying assumptions made in calculating indoor radon concentration apply to CWLM predictions.

The population CWLM predictions (person-CWLM/year: Table 3) are noteworthy. Due to the relatively large population centers near the Polk County phosphate gypsum piles, the population CWLM for phosphate gypsum piles are significantly greater than for the model inactive uranium mill tailings pile. The Shiprock tailings pile is thought to be fairly typical in its population distribution for that source category (i.e., a low population density within 80 km of the pile). At least one

exception to the aforementioned remarks is the uranium mill tailings pile located near Salt Lake City, Utah. With a combination of a large source term and proximity to Salt Lake City, the resulting population CWLM would greatly exceed those for the two gypsum piles.

Conclusions.

(1) The maximum individual CWLM/year exposure due to radon emanations from a typical inactive uranium mill talings pile is greater than from the Florida phosphate gypsum pile studied. This is attributable to the greater radon source term associated with the inactive uranium mill tailings pile.

(2) The maximum individual CWLM/year exposure due to radon emanation from a phosphate gypsum pile is calculated to be approximately 25% of the exposure resulting from normal background in Polk County, Florida.

(3) The population CWLM/year exposure within 80 km of either of the Florida phosphate gypsum piles is as great or greater than from the inactive uranium mill tailings pile. This is a result of a greater average population density within 80 km of the Florida phosphate gypsum piles.

(4) Though the population CWLM/year exposure for the typical Florida phosphate gypsum piles is greater than for the uranium tailings pile, the exposure of an individual within this 80 km area is small compared to that from normal background radon.

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2. Horton, T.R. Estimates of Radon-222 Daughter Doses from Large-Area Sources. ANS Transactions, Vol. 27, San Francisco, CA (1977).

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9. Guimond, R.J., W.H. Ellett, J.E. Fitzgerald, S.T. Windham and P.A. Cuny. Indoor Radiation Exposure Due to Radium-226 in Florida Phosphate Lands. EPA 620/4-78-013 (1979).

Table 1
Radium and Uranium in Florida

Phosphate Rock

Material	Radium-226 (pCi/g)	Uranium (pCi/g) 234	235	238
Marketable	42	41	1.9	41

Table 2
Source Terms

Source	Pile Size (hectare)	Ra-226 Activity (pCi/g)	Exhalation Rate (pCi/m²-sec.)	Source Term (Ci/yr)	Background (Ci/yr)
Gypsum Pile A	75.4	25	26.7 (1)	620	7.0
Gypsum Pile B	81.7	27	26.7	680	7.6
Shiprock Uranium Tailings Pile	35.3	700	93.3	1,040	4.6
Polk County, Fl. Background	—	0.5	0.3	—	—

(1) The exhalation rates given for gypsum piles represents the arithmetic means for all exhalation rate measurements performed on the piles.

Table 3

Net Air Concentration, Working Level and Cumulative Working Level Months (CWLM)

Source	Indoor Radon Concentration (pCi/l)[1]	Indoor Working Level[1]	Maximum Individual CWLM/year[1]	Average Individual CWLM/year[2]	Population Within 80km	Population CWLM (Person-CWLM/year)[2]
Gypsum Pile A_3	0.19	.001	0.02	2.0×10^{-5}	1.3×10^{6}	26
Gypsum Pile B_3	0.21	.001	0.02	3.0×10^{-5}	1.2×10^{6}	36
Shiprock Tailings Pile 4	0.45	.003	0.06	2.0×10^{-4}	4.3×10^{4}	9

1. 800 meters from center of each pile for the maximum sector.
2. Within 80 km of the pile.
3. Based on McCoy AFB (Orlando, Fl.) meteorlogical data.
4. Based on Farmington, NM. meteorlogical data.

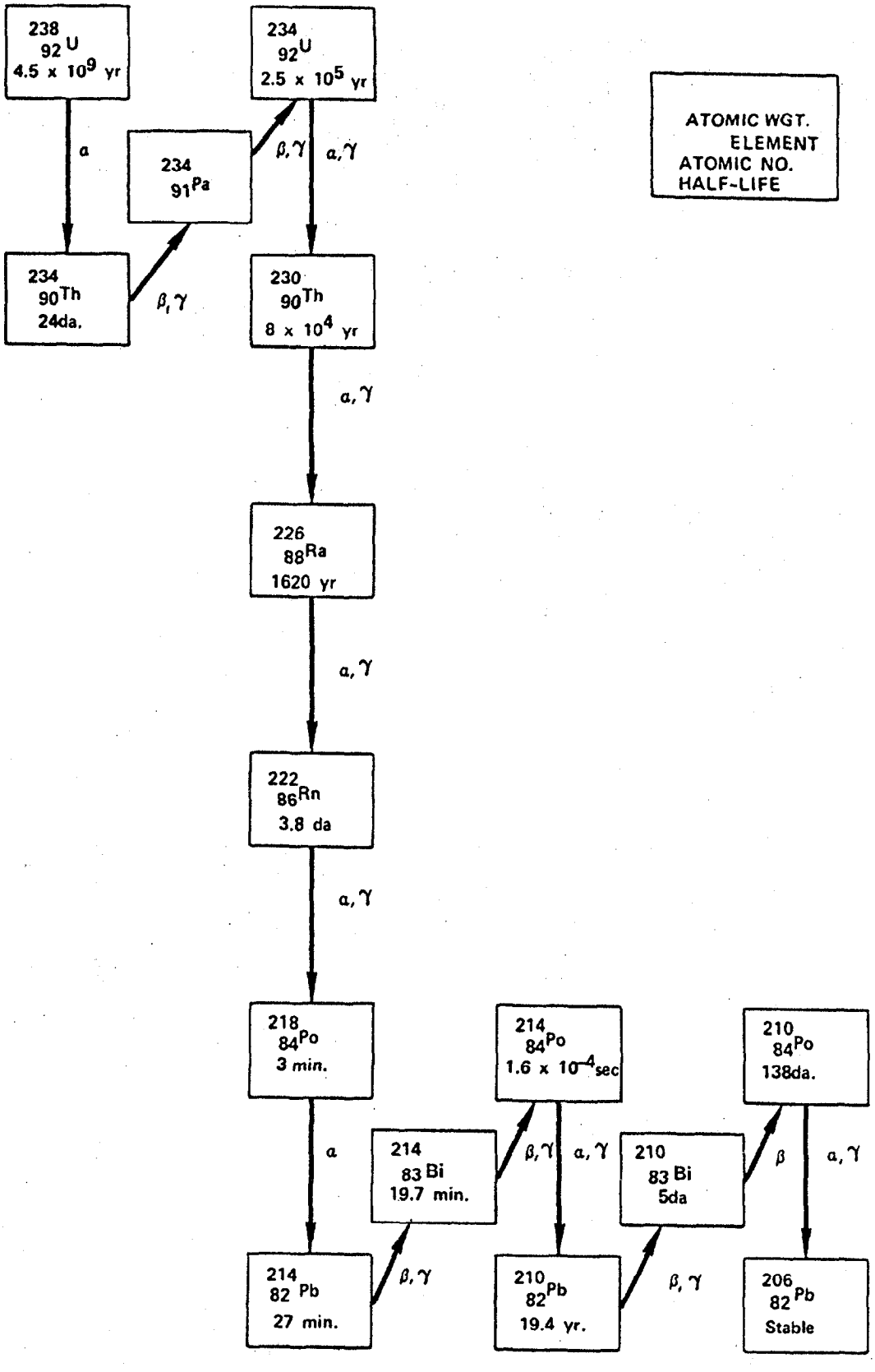


FIGURE 1. URANIUM-238 DECAY SERIES

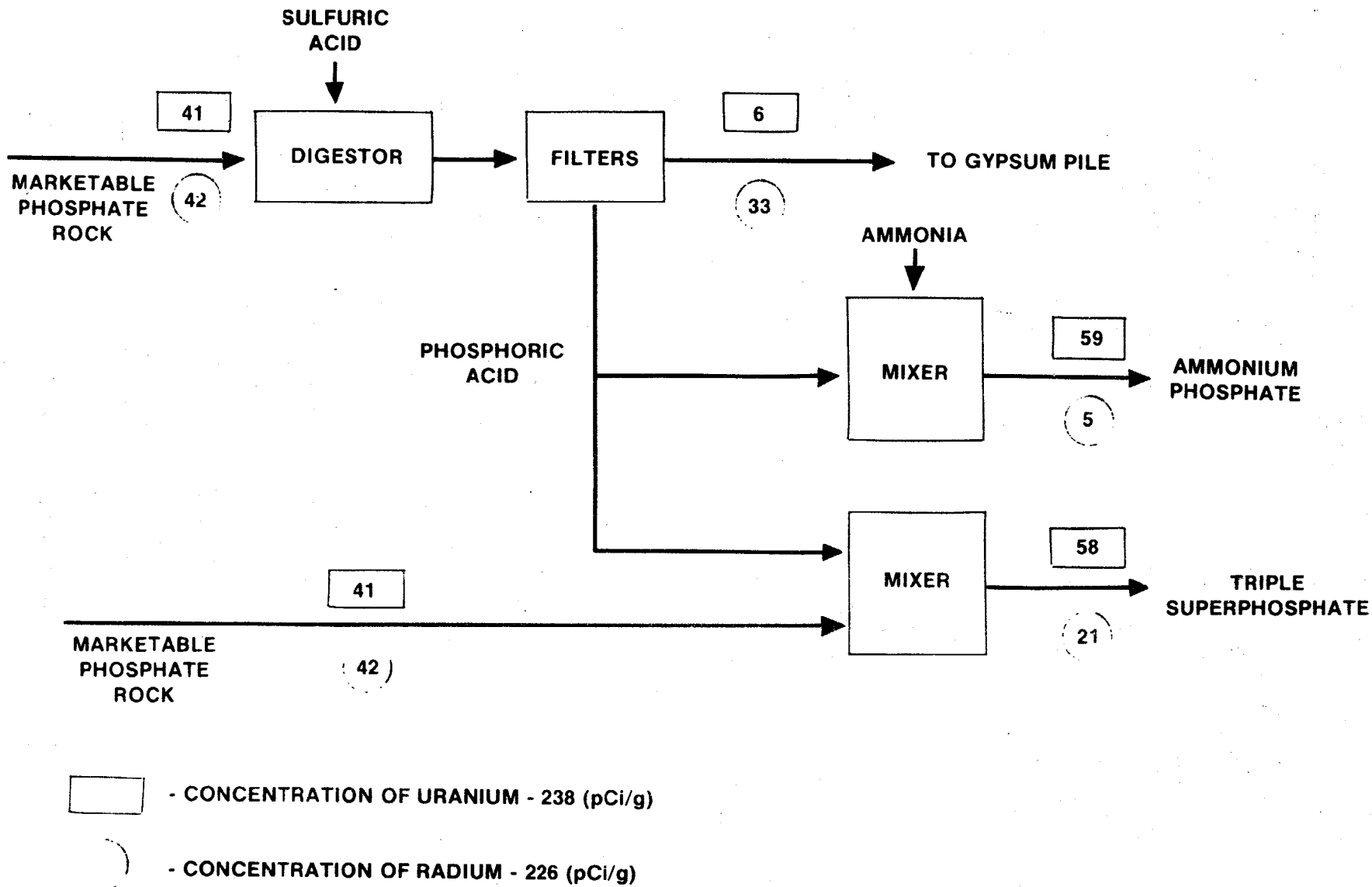


FIGURE 2. PRODUCTION FLOWSHEET FOR WET-PROCESS PHOSPHORIC ACID PLANT

RADIOLOGICAL CRITERIA FOR THE USE OF PHOSPHOGYPSUM AS A BUILDING MATERIAL

by

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National Radiological Protection Board
Harwell, Didcot, Oxon, UK

INTRODUCTION

Natural radiation is the largest contributor to the radiation exposure of humans. In the United Kingdom, for instance, more than two-thirds of the radiation dose received by the population comes, on average, from natural sources (see Table 1) (1).

Natural radiation can be grouped into four main categories by origin and mode of exposure: cosmic rays, external irradiation by terrestrial radionuclides, internal irradiation-by terrestrial radionuclides, and irradiation of lung tissues by radon decay products.

Table 2 summarizes the average radiation dose that the UK population receives from natural sources; this is not markedly different from the exposure in other countries. The subject of this paper permits attention to be restricted to external irradiation by terrestrial radionuclides and irradiation of lung tissues by radon decay products.

The important terrestrial radionuclides are potassium-40 and the radionuclides in the two decay chains headed by uranium-238 and thorium-232. The external irradiation is due to the gamma rays emitted by these radionuclides and their radioactive decay products. The external irradiation by terrestrial radionuclides inside a substantial building depends primarily on the radioactivity content of the construction materials: gamma rays from outside do not have a significant effect inside masonry dwellings.

Radium-226, itself a decay product of uranium-238, decays to the radioactive gas (radon-222) some of which may be released into the air. Radon-222, in turn, decays through a series of short-lived products which form a radioactive aerosol and irradiates lung tissues. The concentration of radon decay products inside a building depends on a number of parameters, principally the radium-226 content of the construction materials, the fraction of radon-222 emanating from the materials, the rate of radon ingress from the ground, and the ventilation rate.

The average values shown in Table 2 mask substantial variations in actual exposure. Figure 1, for example, shows the annual gamma-ray dose inside different types of houses in various parts of the UK (2). Figure 2 shows the range in exposures to radon decay products in buildings throughout the UK; the results are normalized to a ventilation rate of one air change per hour (3).

Despite some early studies which characterized in broad terms the human exposure to natural radiation, knowledge is still rather limited and much more effort is required to improve it. The need to do this has only recently become widely appreciated. Nevertheless, our present knowledge is sufficient for the conclusion to be drawn that building practice and building materials can have a substantial influence on the exposure of humans to radiation. This is an adequate reason for raising the question whether controls should be introduced to limit exposure.

Objectives of Control Measures. When radioactive substances were first used early in this century, it was thought adequate to prevent exposures that might lead to manifest harm to an individual in the short-term, for example, skin burns. These effects occur only at relatively high levels of radiation exposure, well above environmental levels. It was recognized later that radiation exposure might lead to delayed health effects, either in the exposed person, or in his descendants. For the purposes of protection, it is now assumed that the risk of occurrence of such effects is proportional to the radiation dose, and that there is no threshold below which they do not occur. In this way, risks of cancer and hereditary defects can be assessed quantitatively even for very low radiation doses, although there is no direct evidence that such risks 'can really be associated with such low doses. This is the basis for the very strict controls over the exposure of both the general public and workers to artificial sources of radiation.

There is no intrinsic difference between the radiations emitted by artificial sources and those emitted by natural sources. If radiation is assumed to cause harm, then the source is irrelevant. It would undoubtedly be foolish to subscribe to the primitive notion that natural agents are without harm simply because they are natural.

The presumption of risk from natural radiation sources is not usually a cause for alarm. Quite clearly, this is just one of a great number of risks of natural and artificial origin to which all are subject and which cannot altogether be avoided. It should be the objective of control measures, however, to minimize such risks and only to permit the introduction of a practice leading to increased radiation exposures if there is adequate justification for it.

The subject of controls for natural radiation is highly complex. In marked contrast to artificial sources, which are usually clearly defined, the components of natural radiation that should be subject to control cannot be readily identified. In the context of radiation exposure in dwellings, some argue that it should be the increment over the average indoor dose, others the increment over the average outdoor dose (4). It would seem more sensible, however, to base any control measures on the total dose in dwellings, as this reflects the total risk to persons from this source.

Account also needs to be taken of a number of opposing requirements. For example, reduction in ventilation rates in dwellings, which is desirable from the point of view of energy conservation, causes increased exposures to radon decay products. A recommendation, for instance, to control the use of a particular building material may well be misunderstood by those already living in dwellings constructed with that material: public anxiety should not be ignored.

This paper is an attempt to clarify some of the issues involved in developing such controls with specific reference to the use of phosphogypsum in plasterboard.

Basic Principles. National systems of radiological control are usually based on the recommendations of the International Commission on Radiological Protection (ICRP), the most recent recommendations of which are published in 1977 (5). Although it did not deal in depth with the problems of controlling exposures to natural radiation (further recommendations are expected on this subject) the Commission put forward and elaborated upon general criteria for radiological controls. Having in mind the risks that are assumed to be associated with exposure to low levels of radiation, the Commission propounded the following three principles;

(1) No practice shall be adopted unless its introduction produces a positive net benefit (justification);

(2) All exposures should be kept as low as reasonably achievable, economic and social factors being taken into account (optimization);

(3) The dose equivalent to individuals should not exceed the limits recommended for the appropriate circumstances by the Commission.

The first two requirements are no more than formal statements of a procedure that we all undertake, often intuitively, in reaching decisions in everyday life. They involve the weighing of costs, including the risks to health, against benefits to arrive at a decision whether a particular action is worthwhile. Whereas this process may be relatively straightforward when individuals undertake the analysis for themselves in everyday matters, even though the results of their decisions may also affect others, considerable difficulties may arise when explicit decisions have to be made by one group on behalf of others. In such cases, some form of systematic procedure is needed to avoid decisions based solely on intuition or prejudice;

In the ICRP recommendations, cost benefit analysis is recommended as the ideal mechanism for determining the acceptability of a proposal involving exposure to radiation. The aim of cost benefit analysis is to identify all the positive and negative aspects of a proposed practice, to quantify them in a common unit, usually money, and thereby determine whether the practice brings a net benefit to society as a whole.

The assessment of costs and benefits in monetary terms may be controversial as well as difficult, because judgments are often necessary on values to be assigned to elements in the analysis such as lives potentially shortened or scenic beauty destroyed. In particular, if quantified cost-benefit analysis is to be carried out, the national authority will need to consider what monetary value is to be assigned to the detriment caused by radiation. The problems of valuing radiation detriment are described elsewhere (6). Furthermore, the use of a simple sum to obtain the net benefit may well conceal potential inequities between those who gain or lose from the proposal, and costs and benefits may be distributed over different time-scales. The result of a cost-benefit analysis should therefore be regarded as only one of a number of inputs to a decision-making process.

An important aspect of the technique is that it requires the identification of all significant costs and benefits. In doing so, the national authority will see how those costs and benefits are distributed in society. One judgment that may then be made where public health is involved is whether the scope of the analysis should be restricted to the costs and benefits to the public (7).

The third requirement of the ICRP system of dose control is to prevent any one person being exposed to an unacceptably high risk. Recognizing that some exposure to natural radiation is unavoidable, the Commission advised that its dose limits do not apply to or include "normal" levels of natural radiation exposure, but only those components of natural radiation that result from man-made activities.

Extension to Natural Radiation. The ICPR system of dose limitation, although primarily concerned with the control of radiation from artificial sources, provides some useful guidance on establishing criteria for the control of exposures to natural radiation. To develop a control scheme for such exposures, it would seem convenient to consider three categories:

(1) Existing exposures , where they result from purely natural circumstances (for example, an outcrop of uranium-bearing rock) or from past practices (for example, the exposures that arise in present houses);

(2) Continued practices , where the exposures will arise in the future (for example, the exposures that will arise from the continuing use of building materials);

(3) Conceptually novel practices, although these are difficult to envisage, (for example, flying would once have been considered to fall into this category).

It would be necessary and impracticable to control all exposures to natural radiation: nobody, for example, would contemplate measuring radioactivity routinely in all building materials. If controls are contemplated it would be necessary, therefore, to have a screening mechanism which would enable the national authority to recognize situations that require radiological appraisal. The basis of control must be the dose equivalent, but more readily measurable parameters such as specific activity are essential for the implementation of practical controls. This screening mechanism is not without parallel: in the control of radioactive substances in the UK, exemption from statutory control is granted for specific activities less than a given value.

For all of the exposure categories, the process of optimization should be undertaken, this being the central element of any radiological protection scheme. Justification is also required in principle, but is difficult to envisage its being applicable to the first category of exposure. In all categories, however, there ought to be a ceiling on the dose that individuals receive: for the first category, it might be a level chosen by the national authority above which corrective action would be taken; for the second category, it might be an ad hoc dose level above which a national authority would not permit persons to be exposed; for the third category, it might be possible to consider the

exposure with regard to the existing ICRP dose limits (5). The upper dose levels that are unrelated to the ICRP limits would need to be derived from a comparison of the attendance radiation risks with the risks of everyday life, and an appraisal of what might be appropriate in the national context. In the particular circumstance of interest at this conference (namely, future exposure from building materials) a ceiling might be set on the total dose indoors, not only from the building materials, but also from other causes of exposure such as the ground and the water supply.

The clearest implication of the foregoing is that control measures should be related to dose, which is, of course, a reflection of risk. Neither are directly measureable, and in practice some other parameter that can be related to them will need to be employed. Examples are gamma-ray dose rate, concentration of radon decay products in air, and the specific activity of the materials. The last of these is the most useful parameter in the case of building materials. The validity of its use, however, will depend on how well a given value can be related to the radiation dose that might be received. The corollary of this is that a realistic model to relate the predicted dose and the measured quantity needs to be established, and where appropriate, verified by experiments.

The exposure of individuals from a building material depends among other things on the density, the fraction of the radon formed within it that emanates, the geometry of the structural elements made from it, and the relative quantity of it in a house. Specific activity should therefore be used as a trigger for radiological assessment with a full knowledge of its limitations. It is especially important to bear in mind that an assessment should be related to the use of a material in a specified manner.

Phosphogypsum. Because of the substantial effect that building materials and practices have on exposure to natural radiation, they deserve further consideration. It would seem sensible to concentrate initially on those situations where the exposures might be expected to be elevated.

Table 3 gives the mean specific activities of building materials used in the UK (4). Phosphogypsum is included, although it is not now being used. Values are only indicative in some instances, because sampling is not complete. Phosphogypsum stands out, however, with a radium-226 content well above the others, although the potassium-40 and thorium-232 contents are not remarkable. By any radiological yardstick, it would seem appropriate to carry out a full assessment of the potential exposures that might result from the use of this material. In fact, an initial appraisal of the use of phosphogypsum as a building material was made by the National Radiological Protection Board in 1972 (8). The exposures will need to be weighed against the benefits from its use, and it will be necessary to demonstrate that any exposures are as low as reasonably achievable, and that the total dose from this and other sources indoors comply with the ad hoc limits established by the national authority. The material required for such an analysis is illustrated by reference to the use of phosphogypsum in plasterboard.

In an actual assessment, the company manufacturing the material would be expected to provide the necessary information.

Justification. The following potential benefits might be given consideration in an analysis of justification: direct cost savings for homeowners; improved technical qualities of the product; reduced spoiling of land from mining natural gypsum and disposing of phosphogypsum; reduced radiation detriment from the disposal of phosphogypsum. Only some of these are quantifiable in comparable terms.

The radiological detriment to the public in using phosphogypsum for plasterboard can be quantified to a greater extent. There are the doses to the occupants of dwellings constructed with it, the doses that might arise as a consequence of the eventual demolition of dwellings built with phosphogypsum, and the disposal of the rubble.

For illustrative purposes, the exposures arising from the use of phosphogypsum instead of natural gypsum in plasterboard are estimated here for a typical masonry house. As in the case of the initial assessment (8), the model chosen is very common in the UK. It is assumed that 270m^2 of 12.7 mm plasterboard is used overall in the ceilings, as dry lining, and doubled for non-loadbearing partitions. This is above- average utilization, but not considerably so.

The mean specific activity of radium-226 in phosphogypsum is about 630 Bq kg^{-1} and in natural gypsum about 20 Bq kg^{-1} (see Table 3); the nominal excess is therefore taken as 600 Bq kg^{-1}. This excess is expressed in terms of an increase in exposure to-gamma-rays and radon decay products.

Exposure to gamma-rays depends on the specific activity and the layout of a given type of plasterboard. Exposure to radon decay products also depends on the fraction of the radon formed in the plasterboard that emanates from it and on the ventilation rate of the house. The value of the emanating fraction is about 0.04, and the ventilation rate in British houses may be taken as one air change per hour averaged throughout the year (4).

Gamma-ray exposure varies throughout the model house, but a representative value for the extra dose equivalent is 0.15 mSv in a year, this being the mean of the upstairs and downstairs values. The extra exposure to radon decay products is 0.01 WLM in a year.

Optimization. The manufacturer of the phosphogypsum plasterboard would need to consider the possibilities for reducing radiation dose from the product. He might, for instance, investigate the possibility of reducing the radium content by physical or chemical means, or the utility of applying a better seal against radon, or the feasibility of constructing thinner boards. The purpose would be to determine the conditions under which the net cost would be at a minimum. This can be achieved either through a study of the total costs of protection measures and radiation detriment or the changes in marginal costs. In the first case, the optimum point is when the total costs are minimized, and in the second, when the marginal costs are equal though opposite, so that any further reduction in dose would not justify the incremental cost required to accomplish it.

In both of the foregoing aspects of the analysis use would be made of a value, agreeable with the national authority, of the cost of radiation detriment.

Dose Ceiling. The last step in the analysis is a comparison with the ad hoc limit on the dose from indoor exposure that the national authority might promulgate. In this step, the incremental exposures from the *use* of phosphogypsum might, for instance, be added to the average overall exposures indoors shown in Table 2 or to some other values deemed appropriately cautious.

CONCLUSIONS

The control of exposure to natural radiation is such a complex and controversial subject that any scheme for doing so can only be tentative at the present time. The suggestion put forward in this paper may merit consideration in that it has all the essential elements of the established dose limitation scheme for controlling exposure to artificial radiation sources with modifications appropriate to natural sources. Although it relies on a screening system to identify circumstances that merit assessment, it nevertheless includes justification and an optimization analysis, together with a ceiling on exposure to protect individuals.

As for the use of phosphogypsum plasterboard, in order to decide whether the practice is acceptable in a radiological sense requires an appraisal, along the lines suggested, by each national authority. On the international level, the proposal would be even more elaborate and perhaps impracticable, in that the diverse circumstances of each country would need to be taken into account.

ACKNOWLEDGMENT

We wish to acknowledge that we have drawn on discussions with members of the ICRP Task Group on Natural Radiation in writing this article.

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Table 1

Exposure of the UK population from all sources of radiation

Source	Annual per caput dose+	Percentage of total
Natural background	1100 μSv +0.16 WLM *	68
Medical irradiation	~500 μSv	31
Fallout	9.9 μSv	0.61
Consumer products	8 μSv	0.49
Occupational exposure	7.7 μSv * +0.13 mWLM	0.47
Disposal of radioactive waste	2.2 μSv	0.14

+ Apart from exposure to radon decay products, the values given are for the effective dose equivalent.

* These values are not included in the total.

Table 2

Radiation exposure from natural sources in the UK

Source	Annual per caput dose+
Cosmic rays	310 μSv
External irradiation by terrestrial radionuclides	380 μSv
Internal irradiation by terrestrial radionuclides	370 μSv
Irradiation of lung tissues by radon gas and its decay products	0.16 WLM

+ Apart from exposure to radon decay products, the values given are for the effective dose equivalent.

Table 3

Mean specific activities of some building materials in the UK

Material	Mean specific activity Bq kg^{-1}		
	Potassium-40	Radium-226	Thorium-232
Granites	1106	89	81
Sand and gravel	33	4	7
Cement	155	22	18
Clay bricks	703	52	44
White bricks (autoclaved flint and quicklime)	12	4	5
Natural gypsum	141	22	7
Lightweight blocks various aggregates	370	59	26
Phosphogypsum from sedimentary ores	41	629	18

Figure 1. Annual absorbed doses from gamma radiation in Scottish houses.

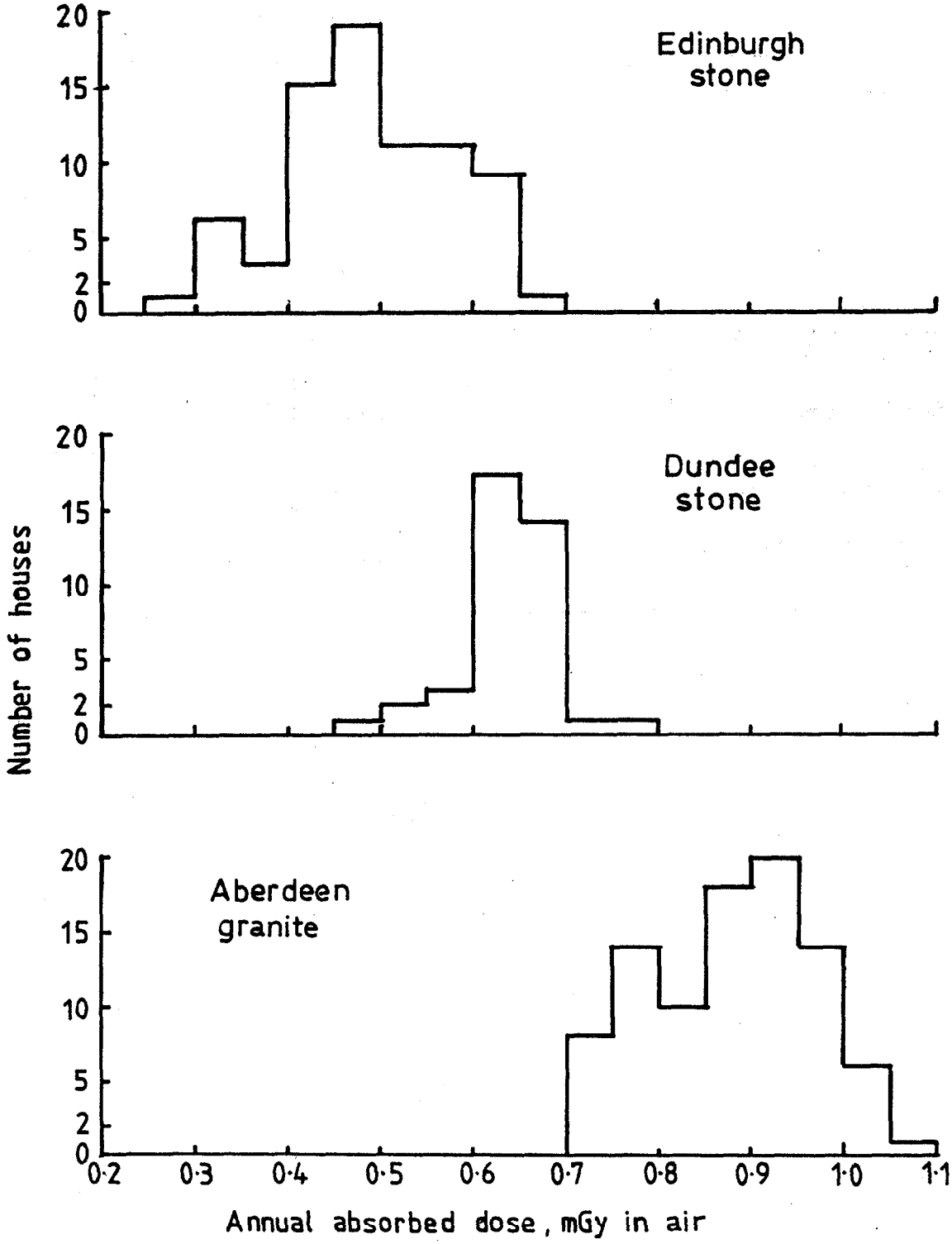
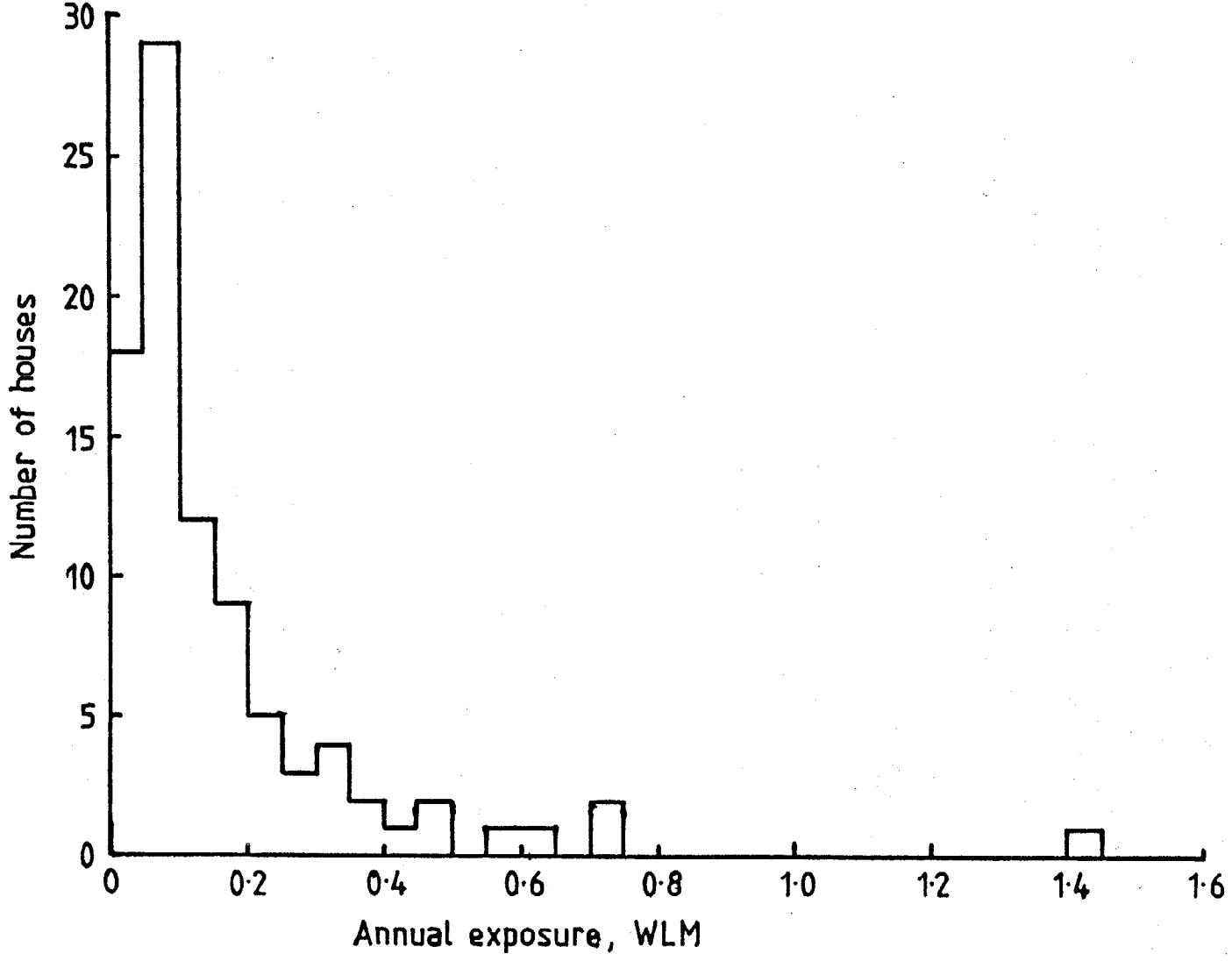


Figure 2. Annual exposures to radon decay products in houses (England & Scotland), normalised to 1 air change per hour and 90% occupancy.



EXHALATION OF RADON-222 FROM PHOSPHATE FERTILIZERS AND OTHER POROUS MATERIALS

by

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INTRODUCTION

The specific exhalation of radon from a given material is usually determined by enclosing a sample of the material in a container and following the growth of radon activity as a function of time or, more commonly, by measuring the equilibrium activity in the container.(1)

The exhalation rates determined in this way should, however, be used very cautiously in attempting to predict the radiological impact on the environment from larger amounts of material.

In the following, some of the problems connected with such measurements will be discussed.

Theory. Let is consider a plane-parallel sample of a material, Figure 1. The thickness of the sample is 2 L, the porosity c and the pore production rate of radon is f. If the dimensions of the sample parallel to the surface are much larger than the sample thickness, the (free) exhalation rate E, into a radon-free space can be written

$$E = \varepsilon f \ell . \tanh \frac{L}{\ell} \qquad (1)$$

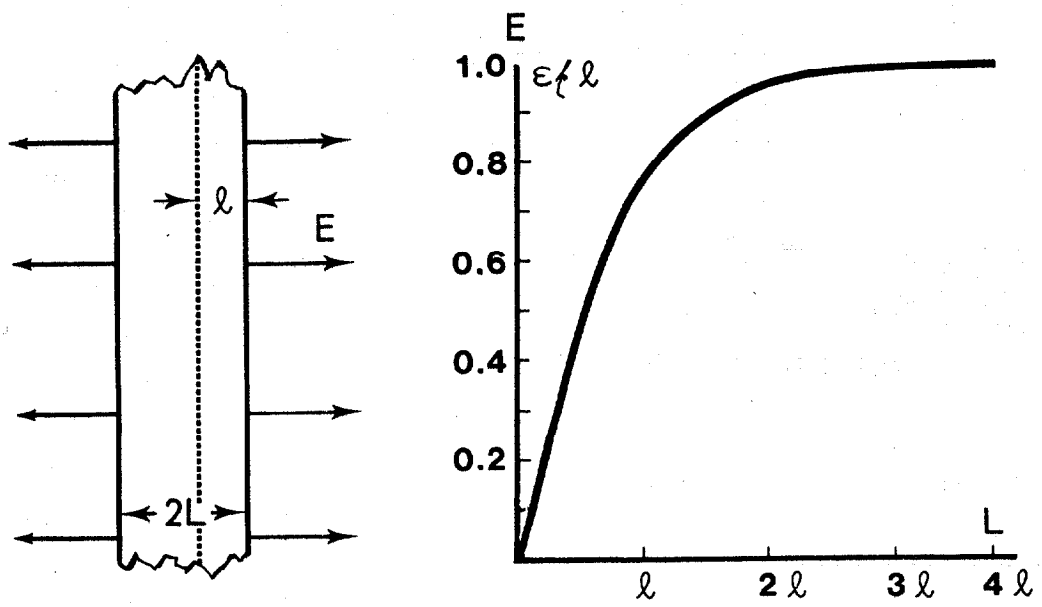


Fig. 1 Exhalation rate as a function of sample thickness L. Where ℓ is the so-called diffusion length of the material. In formulate (1) E is expressed relative to a unit area. The dependence of E on L is also shown in Figure 1. It appears, that for large values of L, the amount of radon exhaling from the surface is equal to the amount produced within a deptha from the surface.

Let us now consider a sample with a volume V_b enclosed in a vessel with a dead space volume V_d, Figure 2.

The growth of radon activity in the container can be written

$$\frac{dN}{dt} = E \cdot S - (\lambda + \lambda_d)N. \qquad (2)$$

Here N is the number of radon atoms in the container, S is the exhaling surface, λ the decay constant of radon, and λ_d a diffusion leak rate accounting for any possible escape of radon atoms from the container to the outside.

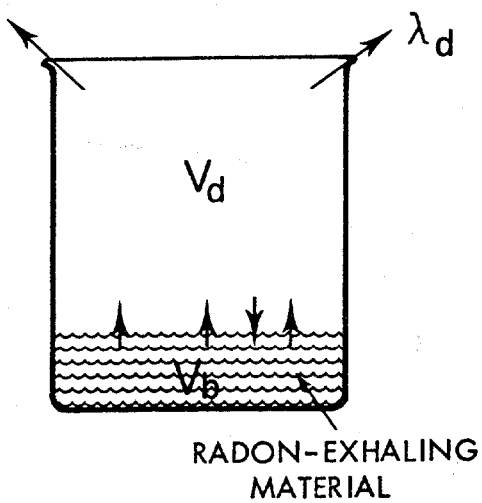


Fig. 2. Radon exhalation in closed container.

If we assume that E is constant independently of N, and that N = 0 for t = 0, equation (2) has the solution,

$$\lambda N = \frac{\lambda}{\lambda'} E \cdot S(1 - e^{-\lambda' t}), \qquad (3)$$

where $\lambda' = \lambda + \lambda_d$.

Introducing the initial increase rate in activity

$$r = \frac{d(\lambda N)}{dt} \simeq \lambda E S \quad \text{for } \lambda' t \ll 1 \qquad (4)$$

and the equilibrium activity

$$R_o = \frac{\lambda}{\lambda'} E S \qquad (5)$$

we find $$E = \frac{r}{\lambda S} \qquad (6)$$

and $$\lambda' = \frac{r}{R_o} \qquad (7)$$

It follows that a determination of the exhalation rate from the initial part of the activity growth curve is not affected by leakage of the container. The method, however, has the drawback that the activities encountered are often very low and can therefore only be determined with a considerable degree of uncertainty. A more detailed treatment of this method falls beyond the scope of the present paper and will appear elsewhere [2].

As has already been suggested, equation (3) is the solution to equation (2) only if the exhalation rate E can be considered to be constant during the build up of activity. It has previously been

demonstrated [1] that this is only approximately true, since the exhalation rate will decrease as the activity increases.

Assuming $\lambda' =$, i.e. no leaks, the equilibrium value of the net exhalation rate E' (when radon exhales into a finite volume) will under certain assumptions differ from the free exhalation rate E by an amount ΔE given by

$$\frac{\Delta E}{E} = \frac{E-E'}{E} = \frac{\tanh\beta}{\alpha\beta+\tanh\beta} \tag{8}$$

where $$\alpha = \frac{V_d}{\varepsilon V_b} = \frac{\text{dead space volume}}{\text{pore volume}}$$

and $$\beta = \frac{L}{\ell}.$$

This depression of the exhalation rate is, with a rather questionable expression, said to be caused by "back diffusion."

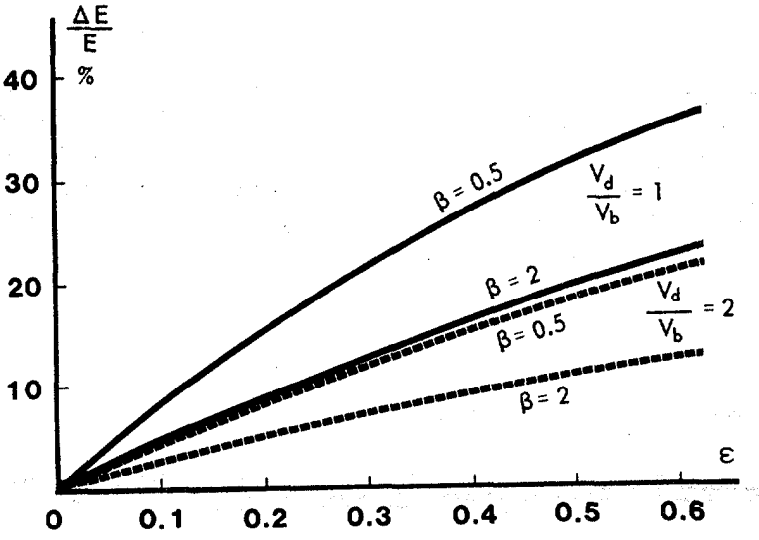


Fig. 3. Exhalation depression in closed container.

The error committed, if the net exhalation rate E' is used instead of the free exhalation rate E, is shown in Figure 3 for typical values of $\frac{V_d}{V_b}$ and B as a function of the porosity .

It appears that the error will often be of the order 10-20%.

Experimental Results. It is, however, possible to determine the free exhalation rate E by measuring the net exhalation rate E' for various dimensions of the sample.

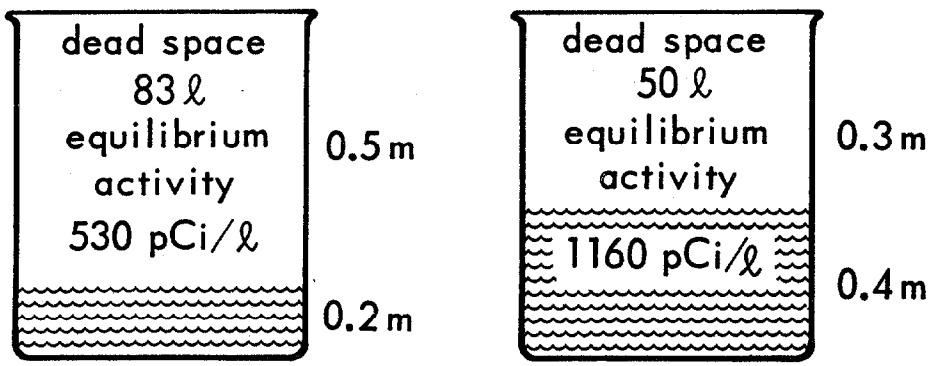


Fig. 4. Containers with radon-exhaling materials in exhalation equilibrium.

In Figure 4 are shown the results of measurements on a phosphate fertilizer product. Although the exhaling surface is the same (0.166 m^2) in the two containers, the net exhalation rates are different (approximately 10000 and 13000 atoms/$m^2 \cdot s$) because of different values of and β, as shown in the figure. The exhalation theory [1] predicts that the equilibrium activity A can be written

$$A = C \frac{\tanh\beta}{\alpha\beta + \tanh\beta} \qquad (9)$$

where C is the concentration of radon in the pores of the material.

For the two containers in question, the ratio between the equilibrium activities will thus only depend upon α and β, or Rand ε.

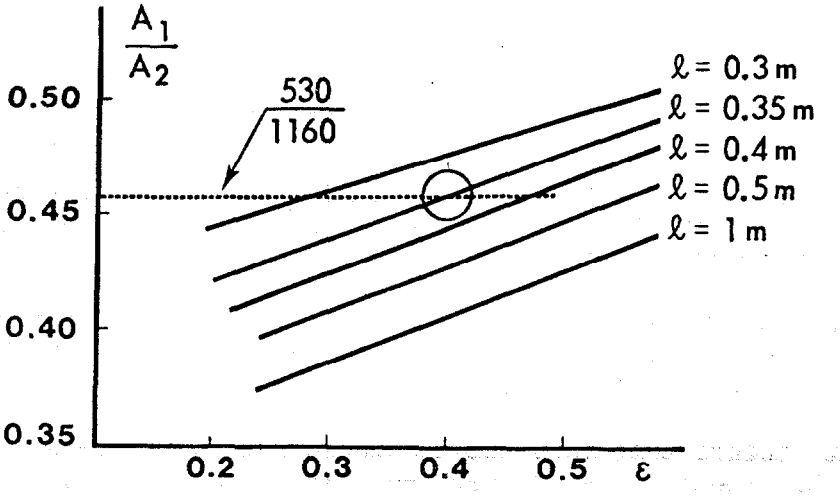


Fig. 5. Equilibrium activity ratio as a function of ε and ℓ.

In Figure 5 the equilibrium activity ratio is shown for a series of values of ℓ as a function of ε. It appears that the observed value (530.1160) should be expected for a value of a in the order of Ø.3-Ø.4 m combined with an -value of Ø.3-Ø.5.

A combination of &= Ø.35 m and ε = Ø.4Ø seems reasonable, yielding a pore concentration of 42ØØ pCi/E and a free exhalation rate of about 22ØØØ atoms/m 's.

In order to check these figures a third container was partly filled with the fertilizer as shown in Figure 6. Formula (9) predicts an equilibrium activity in the container of 133Ø pCi/ℓ, while the measurements yield a value of 123Ø pCi/ℓ. The difference of 8% may, apart from experimental uncertainties, be caused by an unconsidered effect of finite exhalation areas.

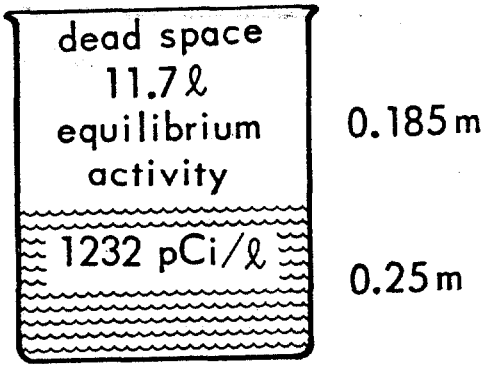


Fig. 6. Container with radon-exhaling material in exhalation equilibrium.

A series of three other fertilizers was investigated in a way similar to the one described above yielding free exhalation rates (for L>>l) of 2ØØØØ to 35ØØØØ atoms/m^2·s (Ø.Ø4-Ø.Ø7 Bq/m^2·s).

Since the diffusion lengths for all four materials are of the order of Ø.2-Ø.5 m, the free exhalation rates will have reached their maximum values for sample thickness of 1-2m. If these materials area stored in a storeroom, the resulting radon concentration in the room will, apart from the exhalation rate, depend upon the height of the free air space above the fertilizer and upon the air exchange rate, as expressed in formula (1Ø)

$$R = \frac{\lambda}{\lambda + n} \cdot \frac{E}{h} \qquad (10)$$

where R is the radon concentration, λ the decay constant of radon, n the air exchange rate, E the free exhalation rate and h the height of the air space above the fertilizer.

In Figure 7 is shown the variation of the maximum radon concentration (for n + Ø) as a function of the height of the air space for a free exhalation rate of 25ØØØ atoms/$m^2 \cdot s$.

It appears that in practice concentrations above 5Ø-15Ø pCi/ℓ are not to be expected even at very low air exchange rates.

In order to see how these results compare with actual values, a series of measurements of radon as well as radon daughters were performed in a phosphate fertilizer plant. An extract of the results are shown in Table 1.

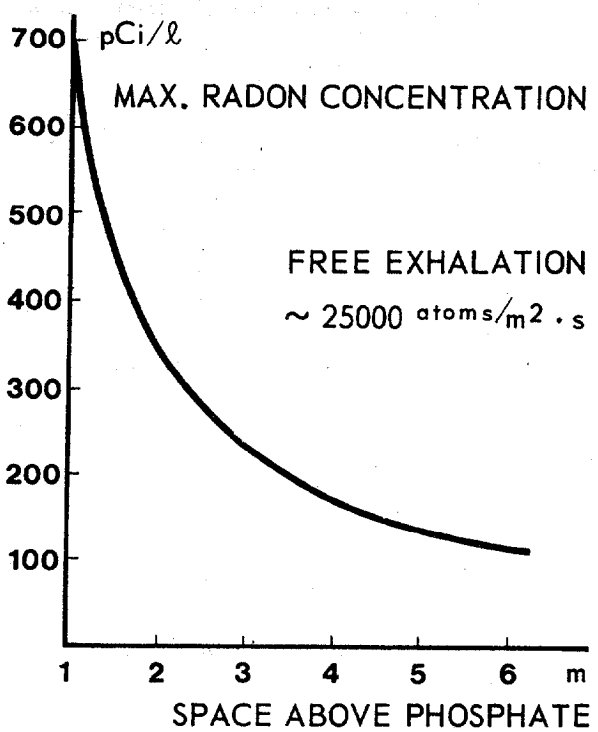


Fig. 7. Maximum radon concentration above phosphate fertilizer.

PLACE	^{222}Rn	^{218}Po	^{214}Pb	^{214}Bi	WL
		pCi/ℓ			
STORE ROOM	14.6	16.3	10.5	8.9	0.10
	19.6	21.9	17.6	15.5	0.17
	41.4	17.8	14.4	14.1	0.14
PLANT IN GENERAL	$\lesssim 1$				
OUTDOOR	0.1-1				

Table 1 Activity levels in phosphate fertilizer plant

The height of the air space above the fertilizer product varied very substantially from one place to another, but was typically of the order 10 m corresponding to an absolute maximum concentration of about 70 pCi/ℓ (for E = 25000 atoms/m^2·s).

Considering the fact that some air exchange must take place, the measured values seem to conform fairly well with the laboratory predictions.

The results, shown above, refer primarily to the conditions in plants or around storage areas, where the exhalation of radon from large amounts of fertilizers or by-products may give rise to high radon concentrations in limited locations or to an increase in the background radiation level over larger areas.

A somewhat different problem arises when the by-product phosphogypsum is made into tiles to be used as ceiling or wall covering.

A series of five different types of gypsum tiles, including one made of natural gypsum, have been examined for radon exhalation with the results shown in Table 2.

gypsum tile type	Exhalation rate	
	atoms $m^2 \cdot s$	atoms $kg \cdot s$
natural gypsum	2.5	0 31
phospho-gypsum, France	3.3	0.44
- , Kola	12.2	1.18
- , Marocco	210	25.4
- , Florida 1979	2900	121
- , Florida 1980	3400	145

Table 2 Exhalation rates from gypsum tiles

It should be mentioned that the tiles made of Florida phosphogypsum have a thickness of 2 cm, while the first four types are only 1 cm thick. The areas used in calculating the exhalation rates are the projected areas, i.e. a tile of Ø.25xØ.25 m^2 is supposed to have an exhaling area of Ø.Ø625 m^2, although it may exhale from both sides.

The figures in Table 2 should be considered as examples of the order of magnitude of the exhalation rates to expect. Only one badge of tiles (usually 8 tiles) have been examined of the first four types, while the Florida phosphogypsum tile samples consisted of 16 (1979) and 8Ø (198Ø) tiles.

It should be mentioned here that an attempt of reducing the exhalation rate by covering the tiles with a layer of epoxy resin turned out to be very ineffective, since the exhalation rate was lowered by less than 2Ø%, even when the whole surface was covered.

If the files are used in a room with a volume V to cover an area S, and if the room has an air exchange rate of n, the contribution from the tiles to the radon concentration of the room is

$$R = \frac{\lambda}{\lambda + n} \cdot E \cdot \frac{S}{V} . \qquad (11)$$

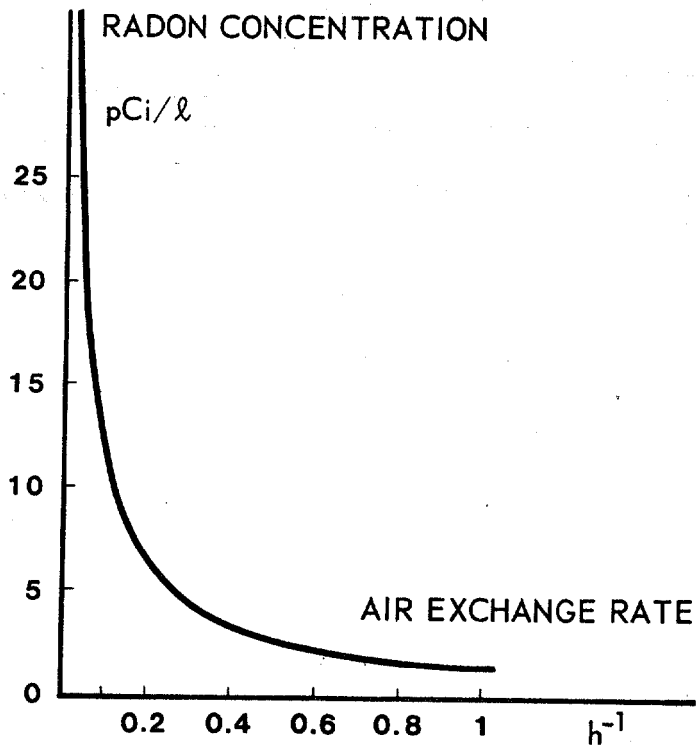


Fig. 8. Radon concentration from phospho-gypsum tiles as a function of the air exchange rate.

Setting E Ξ 3400 atoms/m^2·s (maximum value encountered), $\frac{S}{V}$ = 2 m^{-1} (corresponding to all surfaces of the room being covered with the tiles), the corresponding radon concentration as a function of n is shown in Figure 8.

It appears that for air exchange rates above Ø.2-Ø.3 h^{-1} the maximum contribution to the radon concentration is less than 5 pCi/ . If for instance only one surface of the room is covered with the tiles, the contribution is lowered by a factor of six.

It is, of course, not possible from the radon exhalation rate values to predict the corresponding levels of the radon daughters, i.e. the resulting working level in a given room. If, however, as a rather conservative estimate, an equilibrium factor F of Ø.5 is assumed, the use of the strongest exhaling tiles (E = 3400 atoms/m^2·s) to cover, say 50%, of a room with an air exchange rate of Ø.3 h^{-1} will give an additional radon daughter activity of Ø.Ø1 WL.

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Worldwide Production and Utilization of Phosphogypsum

PHOSPHOGYPSUM UTILIZATION IN JAPAN

by

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INTRODUCTION

Use of gypsum in Japan is outlined as:

(1) Population of Japan is approximately 115 million, and building of new homes ranges 250 to 300 million square meters every year, and

(2) Production of gypsum board is 310 million square meters per year which is the second largest in the world next to U.S.A., and production of cement is about 85 million tons per year which is also in the second place to U.S.S.R, and

(3) Demand for gypsum is about 5 million tons a year; meanwhile, production of wet phosphoric acid is about 550 thousand tons per year as P_2O_5.

The supply and demand of phosphatic fertilizers in the last decade is given in Table 1. Consumption of P_2O_5 in Japanese agriculture is approximately 800 thousand tons per year; this is supported by domestic production of 700 thousand tons and imported materials such as merchant grade acid and DAP of 100 thousand tons. 80% of domestic P_2O_5 production is dependent to wet phosphoric acid. There has not been a big increase of phosphate fertilizer demand domestically; hence, there has not been an increase in phosphoric acid production contrasting to a remarkable increase of gypsum usage.

Characteristics of Phosphogypsum Utilization. Utilization of phosphogypsum is characterized with several conditions specific in Japan. They are:

(1) Resource of natural gypsum in Japan is quite limited, and its quality is very poor. Accordingly, the use of domestic, natural gypsum could not substantially be potential.

Table 2 gives gypsum supply in Japan. As is clear, the proportion of natural gypsum in total gypsum supply has been very small; this supply ceased in 1977. Gypsum mines in Japan were small in production scale, and the quality was poor. The natural gypsum used for cement was replaced gradually by chemical gypsum. The production of phosphogypsum peaked in 1974. On the other hand, gypsum derived from effluent gas desulfurization appeared in 1979 and has been increasing remarkably. Other gypsum comes from hydrofluoric acid manufacture, citric acid manufacture, water treatment and synthetic fibre.

(2) Use of gypsum board increased remarkably because of its various advantages as a building material. The production of gypsum board amounts to 310 million square meters (1979). It is the second largest in the world.

(3) Production of cement is also the largest in the free world. In 1978, it exceeded 85 million tons.

Table 3 gives gypsum consumption in Japan for the same decade. The increase of gypsum consumption is steady, and the average annual increase rate through the decade is 5.3%. Increase for cement retarder is 4.3% and for gypsum board is 6.8% on an average. The proportion of gypsum usage in 1979 was 44% for cement and 36% for gypsum board. In 1976, there was a serious problem with supply-consumption imbalance in upcoming years, namely surplus production of gypsum was foreseen, caused mainly by steady increase of gypsum of effluent gas desulfurization. And in this view, new usages of gypsum were sought. Several new possible utilization for materials of building are under development; however, they are at a moment not so big to appear in this table. Such prospect of surplus has not come out as a real problem because, unfortunately, phosphoric acid production remained stagnant, and the export of gypsum had a function of adjusting the balance.

Change of gypsum demand is graphically illustrated in Figure 1.

Production of gypsum board is given in Table 4. The increase of gypsum board production is taking off together with the increase of new home building as illustrated in Figure 2. Production of cement is given in Table 5. The trend of increase, together with consumption ratio of natural gypsum and chemical gypsum, is illustrated in Figure 3.

(4) It has been an absolute requirement in the phosphoric acid industry that phosphoric plants should produce phosphogypsum suitable for utilization in the total amount and should have, creditable value.

The production and consumption statistics of phosphogypsum are given in Table 6.

Production of phosphogypsum increased consistently up to 1974 and has been keeping the level of 2.5 million tons per year. The ratio of phosphogypsum to the total gypsum supply in Japan was 60% in 1965. reached a maximum of 72% in 1969, and in 1979 was 47%, still the largest supply source. The majority of phosphogypsum is consumed in gypsum board and plaster. Its ratio was 60% to total in 1979.

Utilization of phosphogypsum in gypsum board manufacture started in 1931 using gypsum from Nissan. With the development and the industrial establishment of hemi-hydrate processes, of which the Nissan process is the most representative, the gypsum board industry favored the by-product gypsum from hemi-hydrate process plants, and made positive use of it because of its uniform, excellent quality and its stable supply. A stable and large supply of phosphogypsum, the development of architecture making positive use of gypsum board, and the requirement for such light and nonflammable building materials resulted in acute growth of the gypsum board industry. This, in turn, increased the utilization of phosphogypsum in large

quantities. The proportion of phosphogypsum to total use in this industry is now 70%. Gypsum board industry is the largest consumer of phosphogypsum.

In the cement industry, the use of phosphogypsum as a retarder started in 1956 and gradually replaced natural gypsum. During 1971 to 1973, the ratio of phosphogypsum to total reached 50%, and the ratio started to decrease because gypsum from effluent gas desulfurization filled the gap of supply as cement productions increased. In 1979 the ratio was 36%. Until several years ago, the cement industry favored granulated phosphogypsum as it is easy to handle. But now powder form is well accommodated to save energy and granulation cost.

5) Phosphoric acid plant size is comparatively small, and plants are scattered all over the country. This means transportation of bulky material is less.

The phosphoric acid plant capacity classification is given in Table 7. As is seen, average plant capacity is only 100 tons P_2O_5 a day. By the way, Table 8 shows plant usage in the last decade. The disadvantage of low plant usage ratio and small plant capacity is quite clear. The use and credit value of phosphogypsum has been important for the phosphate industry. Hemi-dihydrate processes were favored and established the dominant situation in the phosphate industry in Japan.

Figure 4 illustrates the location of phosphoric acid plants in conjunction with the location of gypsum board factory as well as cement plants. Taking into consideration the non-extensive land of Japan, the location of these three industry plants are close together.

In particular, gypsum board factories are sometimes next door to phosphoric acid plants, making the transportation of phosphogypsum easy.

Phosphogypsum Quality for the Uses

(1) General

The quality of phosphogypsum is the most important requirement for its utilization. The requirements for the quality of phosphogypsum vary to the purpose of uses. In all cases, common undesirable impurity is P_2O_5 in particular syncrystallized lattice P_2O_5 and water soluble P_2O_5 on crystal surface. A comparison of gypsum analyses from hemi-dihydrate process and dihydrate process is given in Table 9.

In hemi-dihydrate process recrystallization step is involved in which hemihydrate formed in rock acidulation is converted into dihydrate. Schematic flow of hemi-dihydrate process, typically represented by Nissan H-process and Nissan C-process is illustrated in Figure 5. In this recrystallization step, hemihydrate dissolves and dihydrate crystals are formed with

the presence of mother nuclei and low supersaturation of calcium sulfate under mild hydration conditions. This results in thorough acidulation of phosphate rock, minimized syncrystallization of P_2O_5 in gypsum crystal lattice, and uniform and chunky crystal Formation which makes cake washing easier and less water soluble P_2O_5. Hence, the process gives not only better qualified gypsum, but also higher P_2O_5 recovery in the plant operation. P_2O_5 recovery actually achieved in those plants employing hemi-dihydrate processes in Japan in 1979 is given in Table 10.

There is not a significant difference in distribution of impurities of phosphate rock into product acid and gypsum filter cake. Such distribution is slightly different from phosphate rock. An example of comparison of the distribution in the case of central Florida rock is given in Table 11. The main difference is in the distribution of aluminum.

An example analysis of phosphogypsum from a Nissan process plant is given in Table 12.

(2) Gypsum Board

There are several requirements in the physical properties of calcined gypsum which is used as a starting material of gypsum board. Table 13 shows an example of physical properties of calcined gypsum referring to several requirements from the gypsum board industry in Japan.

Consistency is correlated with the form and crystal size of gypsum before calcination. Low consistency is always desired, and chunky and uniform sized crystals promise low consistency. Low consistency is also correlated with wet tensile strength - the lower the consistency, the higher the wet tensile strength.

Chunky and uniformly sized crystals contribute to lowering of moisture in gypsum cake exfilter. It is a normal practice in gypsum board manufacture processes in Japan to centrifuge gypsum slurry after repulping the filter cake with water. The moisture content of the centrifuged gypsum cake could be minimized when gypsum is in such crystals. Low moisture content in raw material gypsum for gypsum board is quite important for decreasing heat consumption to get rid of water in the process.

Figure 6 shows gypsum crystals from hemi-hydrate and Figure 7 shows crystals from dihydrate processes. Adhesion rate is another important factor. Wet tensile strength and adhesion ratios drop sharply with the presence of water soluble P_2O_5 in gypsum. This is illustrated in Figure 8.

(3) Cement Retarder

In Portland cement production, 3.5 to 4% by weight of gypsum is added to clinker as a retarder at the milling stage. Table 14 gives an example of physical properties of cement prepared with use of Nissan phosphogypsum. Gypsum exfilter is usually repulped with water and centrifuged to reduce moisture to make its bulk handling and feeding easier. Lime is added to neutralize water soluble P_2O_5.

Figure 9 illustrates the influence of water soluble and lattice P_2O_5 on the compression strength. The same affects the initial setting time and the time between initial and final setting time. When such P_2O_5 is high, then setting is delayed undesirably.

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(Data relating to Phosphatic Fertilizers) No. 1Ø, 1979, Japan Phosphatic & Compound Fertilizers Manufacturers Association)

Table 4, Fig. 2 — Iiji M. "Gypsum Board," Gypsum and Lime, No. 167, 198Ø, P. 58-62.

Table 5, Fig. 3 — Takasaki Y. “Cement,” Gypsum and Lime, No. 167, 198Ø, P. 72-77.

Fig. 9 — Murakami, Tanaka, Sato, Gypsum and Lime, No. 91, 1968, P. 249.

Table 1 PRODUCTION/CONSUMPTION OF PHOSPHATIC FERTILIZERS IN JAPAN

UNIT : 1,000 MT P_2O_5

	71/72	72/73	73/74	74/75	75/76	76/77	77/78	78/79	79/80
Production	685	729	736	769	586	625	696	707	734
Import	34	30	59	46	41	109	69	100	97
Consumption	675	730	793	692	623	738	747	775	831
Export	48	60	25	25	16	12	12	36	30
Inventory	150	119	95	194	180	163	168	105	145

Table 2 GYPSUM SUPPLY IN JAPAN

UNIT : 1,000 MT $CaSO_4 \cdot 2H_2O$

Source	1960	1965	1970	1973	1974	1975	1976	1977	1978	1979
Quarry	-	608	527	363	305	155	38	0	0	0
Phosphoric Acid	340	1,448	2,572	3,010	3,258	2,490	2,323	2,494	2,488	2,747
Effluent Gas Desulphation	-	294	8	51	275	750	1,113	1,750	1,834	2,010
Titanium Refining	-		150	380	304	210	290	270	325	1,031
Others	-		302	702	697	610	591	673	659	
Import	-	50	162	405	74	34	29	15	20	36
Total	-	2,400	3,721	4,911	4,913	4,249	4,384	5,202	5,324	5,824

Table 3 GYPSUM CONSUMPTION IN JAPAN

UNIT : 1,000 MT $CaSO_4 \cdot 2H_2O$

Source	1965	1970	1973	1974	1975	1976	1977	1978	1979
Cement	1,095	1,782	2,190	1,890	1,919	2,051	2,305	2,592	2,659
Gypsum Board	595	1,197	1,704	1,340	1,267	1,448	1,605	1,939	2,156
Plaster	308	489	569	450	481	490	475	478	475
Pottery	67	93	104	83	73	76	80	91	92
Others	44	86	100	100	100	100	100	100	100
Export	0	0	0	30	138	365	501	406	350
Losses	65	113	194	120	117	135	157	173	182
Total	2,174	3,760	4,861	4,013	4,095	4,665	5,223	5,779	6,014
Supply	2,400	3,721	4,911	4,913	4,249	4,384	5,202	5,324	5,824
Balance	226	-39	50	900	154	-281	-21	-455	-427

Table 4 PRODUCTION OF GYPSUM BOARD IN JAPAN

	Production	Break down				Number of	
		Plain	Lath	Acoustic	Decolated	Company	Plant
	1000 M^2	%					
1955	7,354	-	-	-	-	6	6
60	35,154	69	21	10	-	11	12
65	117,026	37	60	3	-	17	22
70	213,113	37	61	2	-	14	20
75	198,171	34	48	1	17	16	23
76	208,913	37	44	1	18	16	23
77	234,641	40	41	1	18	16	23
78	261,161	43	39	1	18	17	23
79	308,130	49	32	1	17	17	24

Table 5 PRODUCTION OF CEMENT IN JAPAN

UNIT : 1,000 MT

	Production
1970	57,868
71	59,829
72	69,194
73	78,221
74	69,989
75	66,174
76	68,373
77	76,823
78	78,403
79	

Table 6 PRODUCTION/CONSUMPTION OF PHOSPHOGYPSUM

UNIT : 1,000 MT $CaSO_4 \cdot 2H_2O$

	Production	Consumption						Inventory
		Cement	Board and Plaster	Fertilizer	Export	Others	Total	
1965	1,448	339	977	-	-	56	1,372	450
66	1,732	446	1,147	23	-	71	1,687	495
67	2,033	600	1,321	24	-	34	1,979	549
68	2,370	684	1,441	27	-	84	2,236	683
69	2,434	830	1,658	27	-	38	2,553	564
70	2,572	869	1,831	28	-	9	2,737	399
71	2,614	863	1,753	25	-	-26	2,615	398
72	2,882	1,015	1,987	30	-	-44	2,988	292
73	3,010	1,036	1,903	23	-	44	3,006	296
74	3,258	859	1,589	18	-	-66	2,400	1,154
75	2,490	841	1,545	34	139	97	2,656	988
76	2,323	741	1,492	46	158	27	2,463	848
77	2,494	625	1,422	48	365	99	2,559	783
78	2,488	715	1,605	29	289	40	2,678	593
79	2,748	689	1,704	25	289	73	2,780	561

Table 7 PHOSPHORIC ACID PLANT CAPACITY IN JAPAN

Capacity MT/D	Unit	Capacity Total MT/D	Proportion %
0 - 40	2	64	3
41 - 60	6	312	13
61 - 80	4	284	12
81 - 100	5	490	21
101 - 120	0	0	0
121 -	6	1,190	51
Total	23	2,340	100

Table 8 Installed Plant Capacity of Phosphoric Acid

UNIT : 1,000 MT P_2O_5

	Capacity	Production	Usage
71/72	823	603	73 %
72/73	837	663	79
73/74	850	663	78
74/75	863	676	78
75/76	881	525	60
76/77	935	521	56
77/78	911	542	59
78/79	912	540	59
79/80	782	593	76

Table 9 Breakdown of P_2O_5 in Phosphogypsum

Process	Form of P_2O_5			
Hemi-dihydrate (NISSAN)	Undecomposed 0.07 %	Water soluble 0.05	Lattice 0.17	Total 0.29
Dihydrate	0.35	0.35	0.36	1.06

Table 10 ANNUAL OVERALL P_2O_5 RECOVERY OF HEMI-DIHYDRATE PROCESS PLANTS IN JAPAN

(1979)

Company	Capacity 1000MT/Y	Recovery %
A	18.7	97
B	85.2	98
C	32.7	97
D	44.0	98
E	67.6	97
F	20.4	98
G	33.0	97
H	78.8	98
I	27.1	97

Table 11 Distribution of Phosphate Rock Impurities

	Hemi-dihydrate		Dihydrate	
	Phosphoric acid	Gypsum	Phosphoric acid	Gypsum
Fe_2O_3	98	2	96	4
Al_2O_3	90	10	80	20
MgO	97	3	97	3
Na_2O	20	80	20	80
K_2O	10	90	10	90

Table 12 Typical Analysis of Nissan Phosphogypsum Derived from Florida 68 Rock

Total P_2O_5	0.29 %
Water soluble P_2O_5	0.05
CaO	30.41
SO_3	43.46
Crystalline Water	19.00
F	0.24
SiO_2	4.05
Fe_2O_3	0.04
Al_2O_3	0.11
MgO	0.01
Na_2O	0.08
K_2O	0.16

Table 13 Example of Test Results on the Use of Nissan Phosphogypsum in Gypsum Board

	Example	Requirements
Bulk Density (g/ml)	0.710	
Consistency (%)	72.5	<75
Setting Time (sec)		
Initial	414	
Apparent	841	
Final	2102	
pH	6.0	
Wet Tensile Strength (kg/cm^2)	12.0	>10
Adhesion Ratio	86	>50

Table 14 Example of Test Results on the Use of Nissan Phosphogypsum in Cement

		Requirement with JIS-R-5210-1973
Setting time		
Initial (hr-min)	2 - 57	>1 hr
Final (")	3 - 40	<10 hrs
Surface area (cm^2/g)	3,150	>2,500
Compression strength (kg/cm^2)		
3 days	122	>70
7 days	220	>150
Stability	good	-

Fig. 1 Change of Gypsum Demand

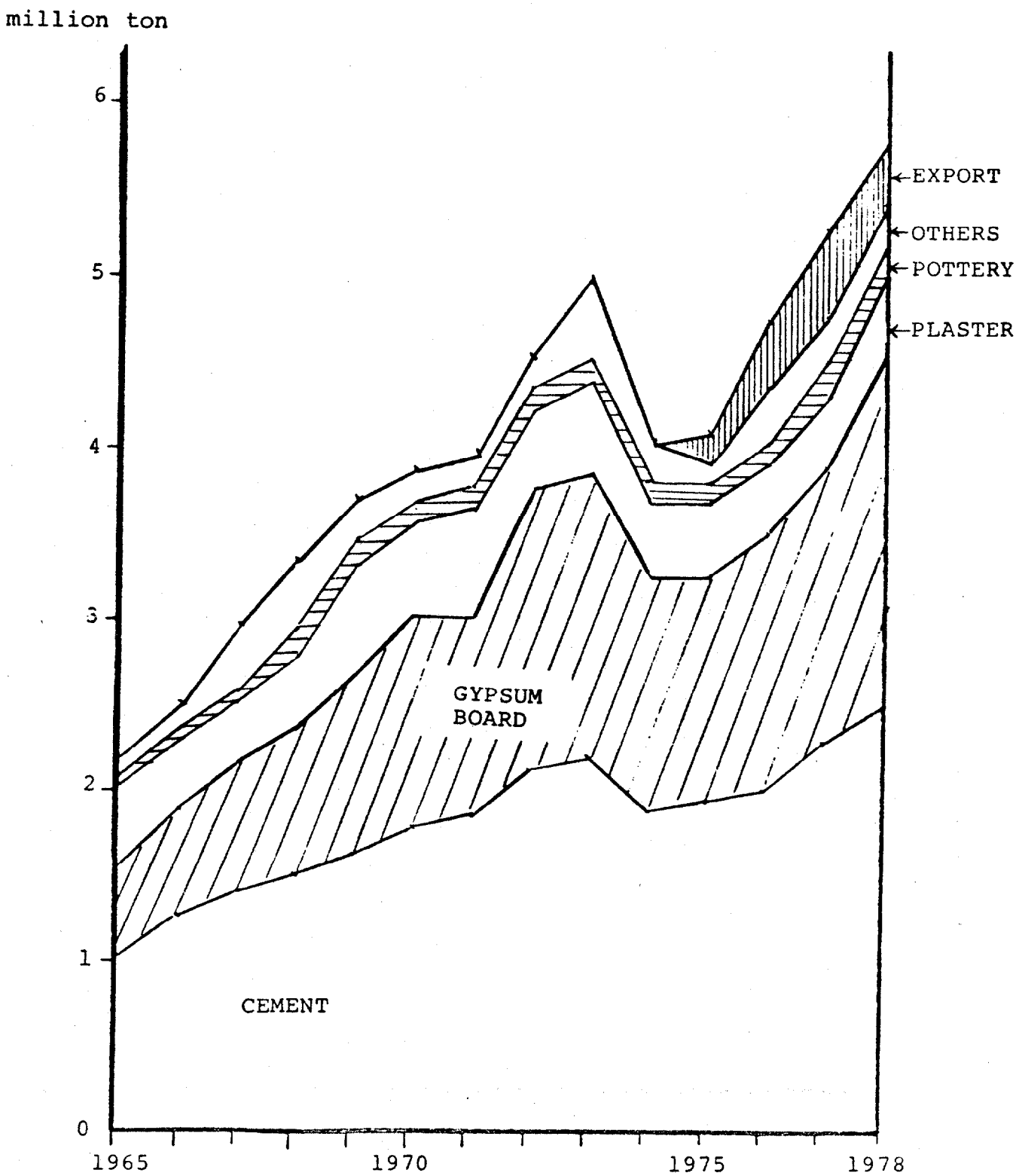


Fig. 2 Gypsum Board Production
vs. New House Floor Area

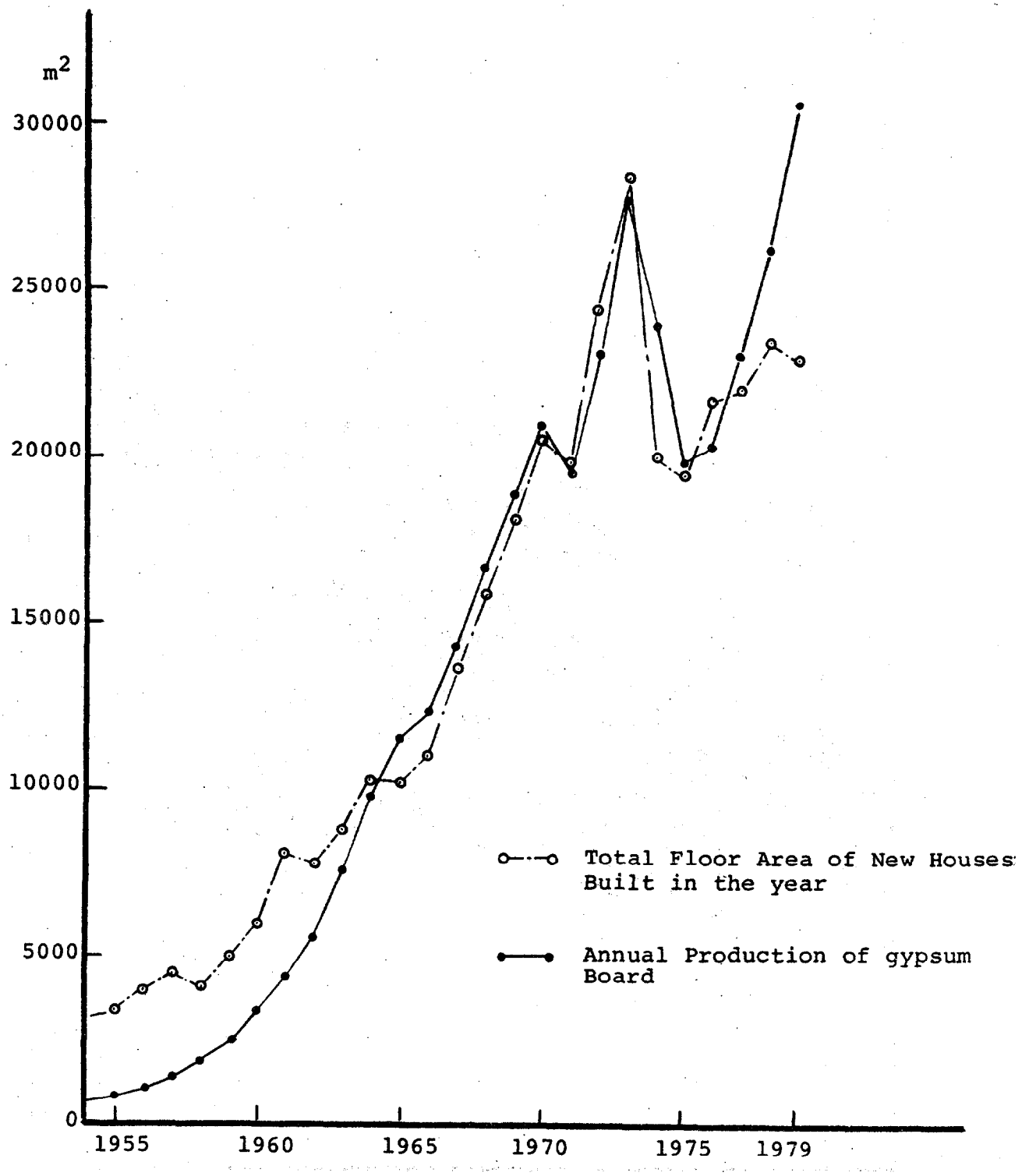


Fig. 3 Cement Production vs. Gypsum Consumption

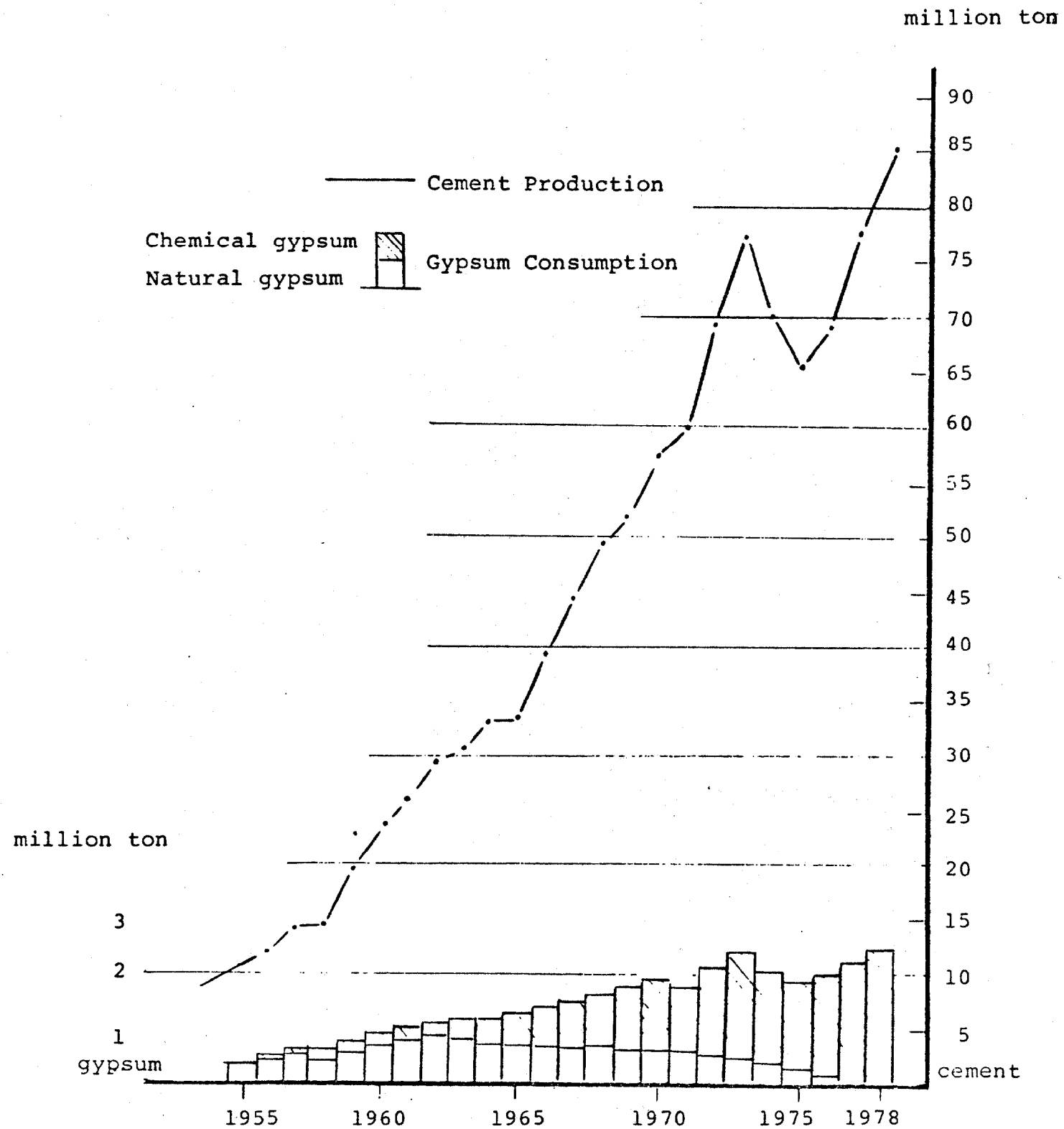


Fig. 4 Location of Phosphoric Acid Plants vs. Gypsum Board and Cement Plants in Japan

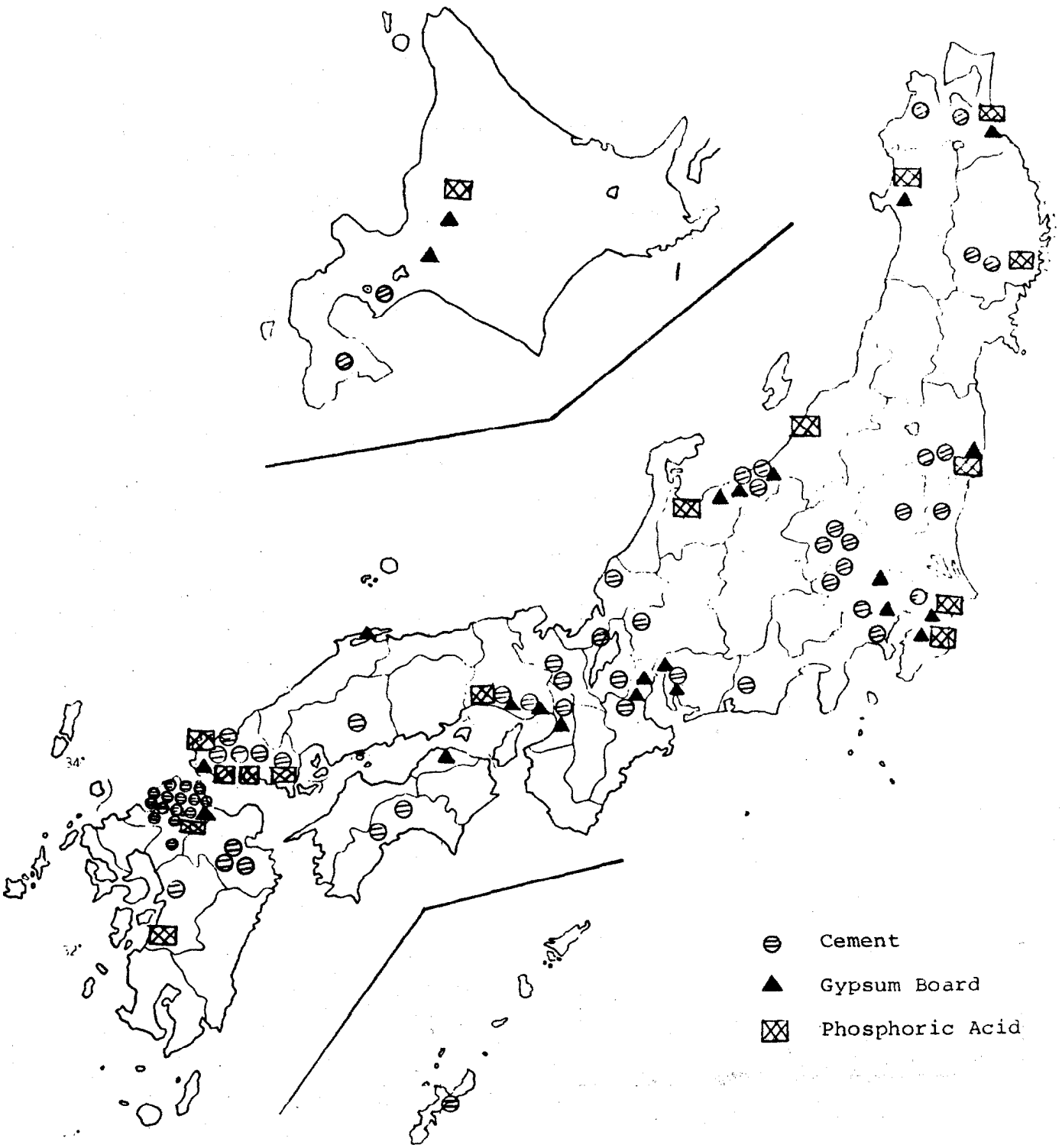


Fig. 5 HEMI-DIHYDRATE SCHEMATIC FLOW

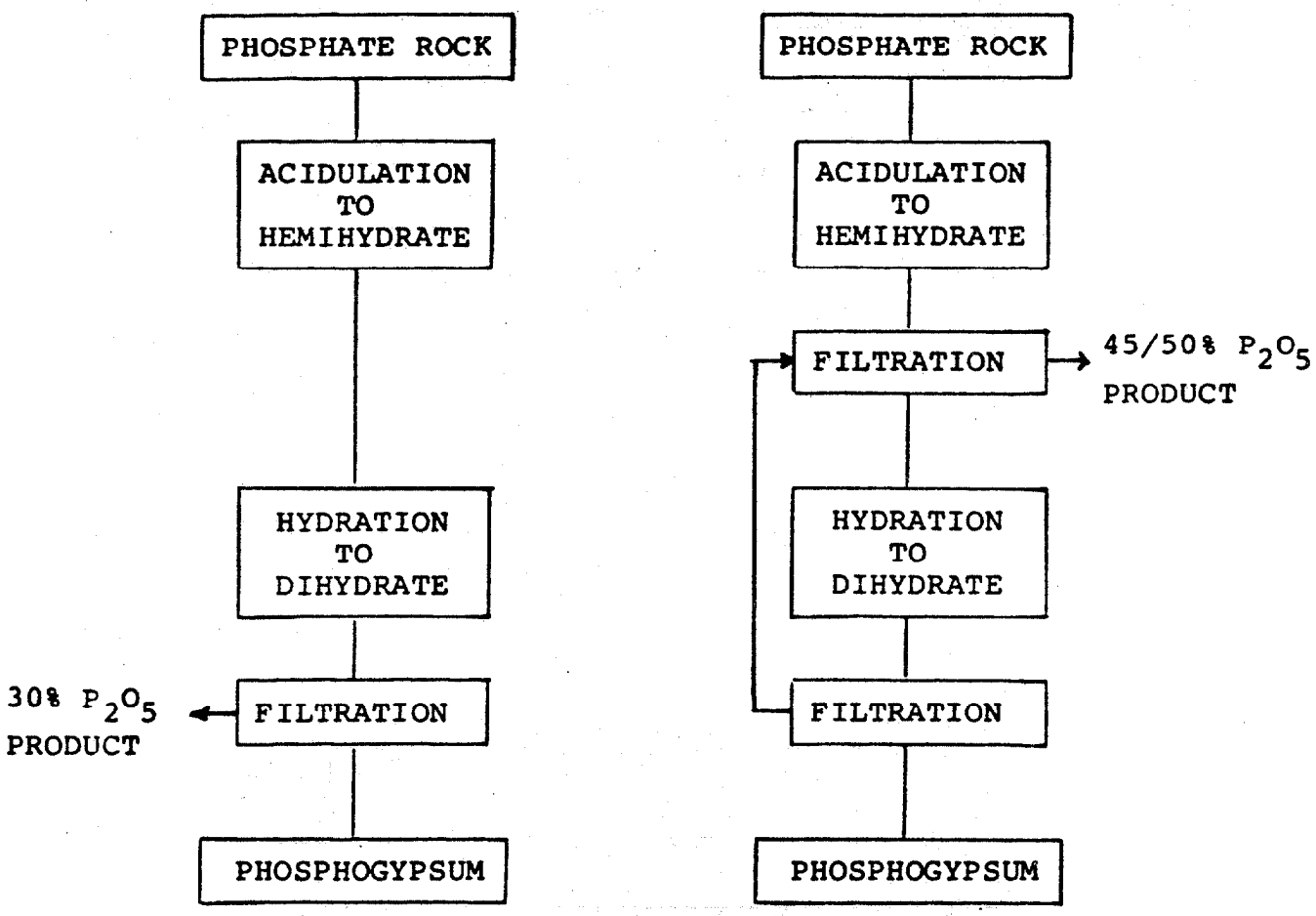


Fig. 6

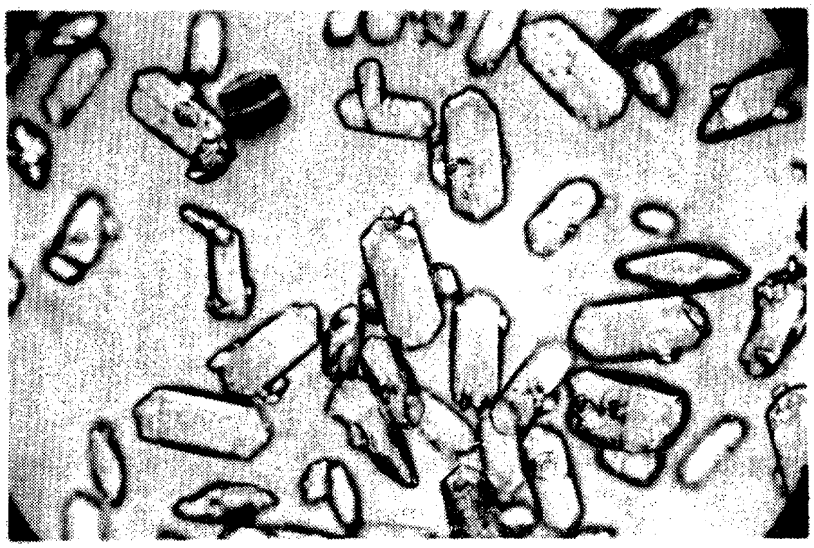


Fig. 7

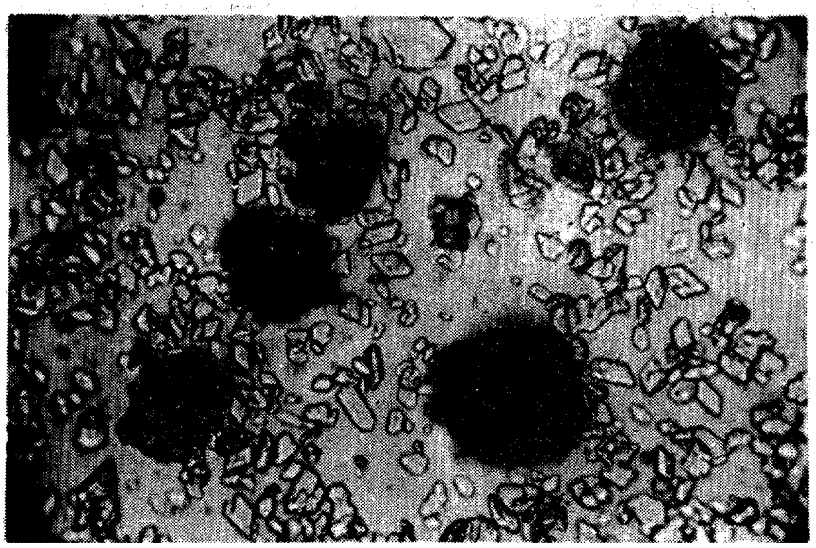
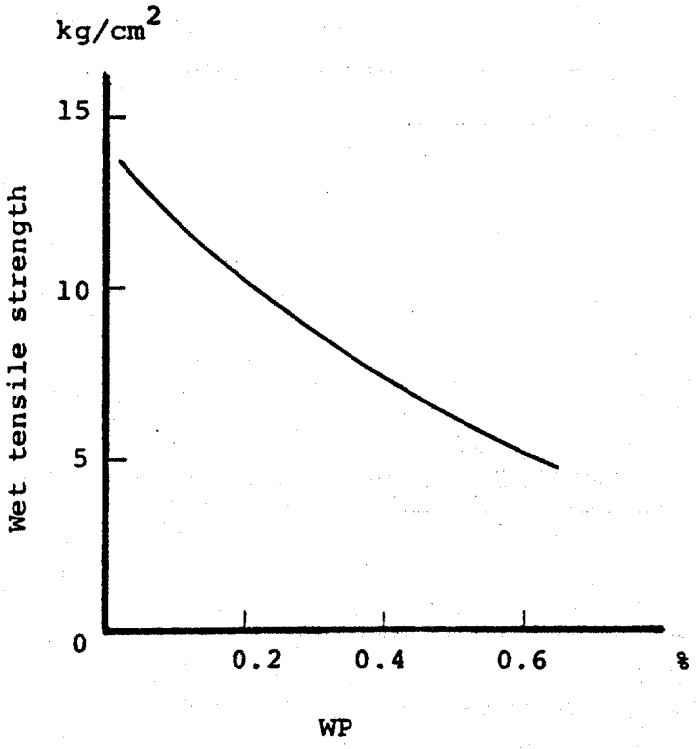


Fig. 8 Gypsum Quality vs. Gypsum Board Property



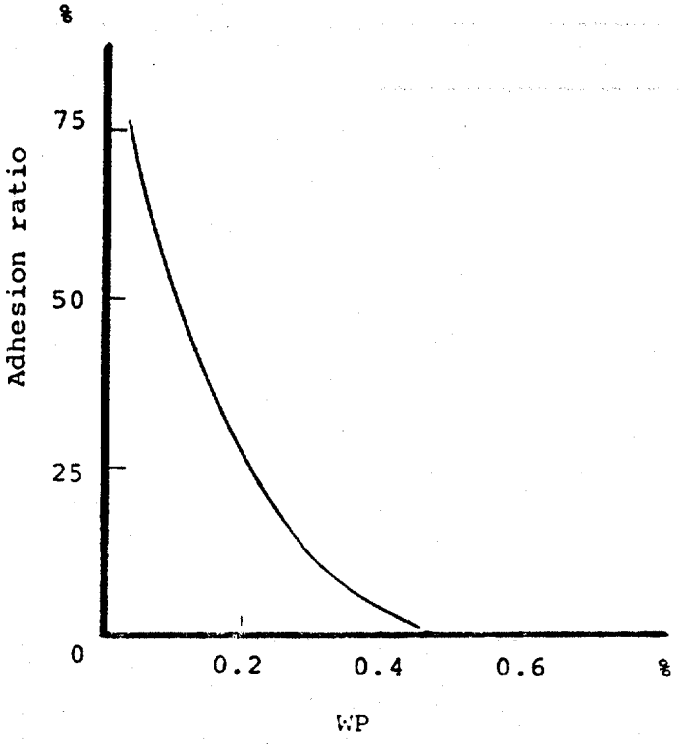
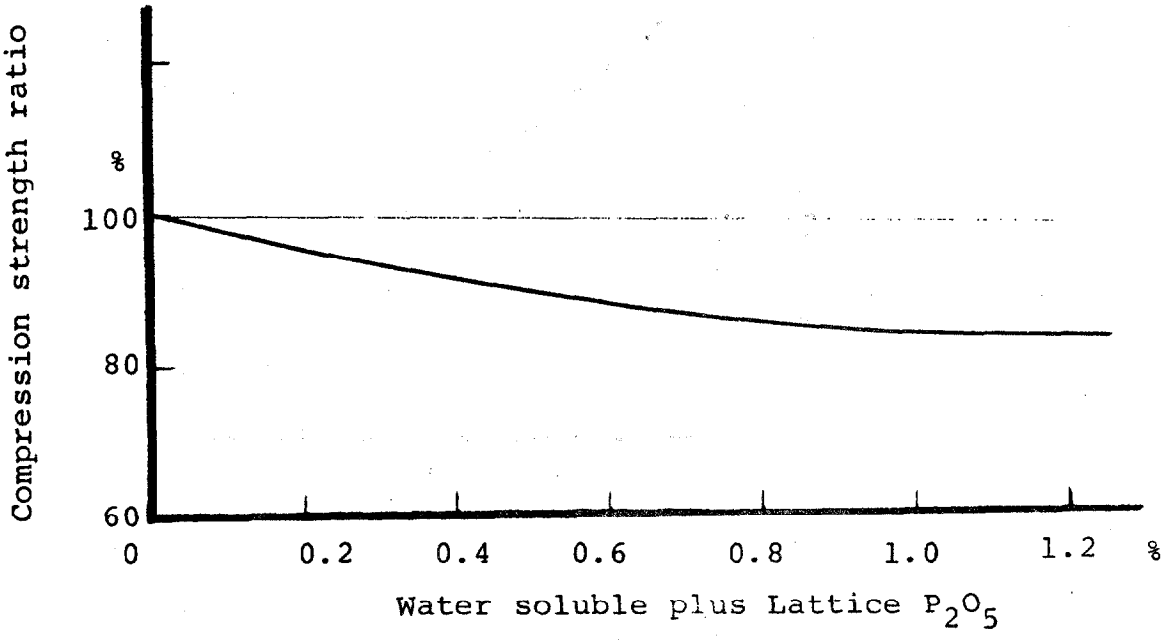


Fig. 9 Influence of Gypsum Quality on Cement



PROPERTIES AND UTILIZATION OF BY-PRODUCT GYPSUM IN AUSTRALIA

by

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SUMMARY

This paper describes the sources , chemical and physical properties, present use of and research being carried out in Australia on by-product gypsum.

INTRODUCTION

About 840,000 tons of phosphogypsum ("by-product gypsum," "chemical gypsum") is generated in Australia annually (1) at four locations. In comparison, 992,000 tons of natural gypsum were produced in 1976-77 (2) and were used for the manufacture of gypsum plasterboard, used as a retarder in the cement industry, or exported. Some 110-150,000 tons of phosphogypsum are used at present in the plaster industry and as a soil conditioner in agriculture. The bulk of the material is, however, dumped on land, into rivers, or into the sea. Due to the fact that Australia has large resources of natural gypsum, little interest has been shown previously in the utilization of phosphogypsum. However, in recent years the cost of energy and transport has rapidly increased and environmental regulations for methods of disposal are becoming more strict. As a result, commercial enterprises are becoming more interested in using this material for making plaster of Paris suitable for the building industry. Fortunately, the phosphoric acid plants and the stockpiles of phosphogypsum are located at or near major centers of population and consequently the phosphogypsum has great potential for replacing, at least in part, the natural gypsum used at present.

This paper describes the sources, chemical and physical properties, present utilization of and research carried. out in Australia on phospho-gypsum. The terminology used for the various forms of calcium sulfate and its hydrates are those described by Ridge and Beretka (3). The term "cast gypsum" refers to the hardened mixture of calcined gypsum and water.

Production and Properties of By-product Gypsum. In Australia, phosphogypsum resulting from the manufacture of phosphoric acid by wet processes, is produced at Brisbane (Qld), Kwinana (WA), Melbourne (Vic) and Newcastle (NSW). The quantities generated and utilized at present are shown in Table 1. It is seen that some 90-100,000 tons are used for the manufacture of calcined gypsum and plasterboard, and about 20-50,000 tons as a conditioner for heavy clay soils in agriculture.

By-product gypsum is also produced by other chemical processes, viz by the neutralization of waste sulfuric acid, production of common salt by the evaporation of sea water, scrubbing of flue gases, etc., but the quantities produced are relatively small and these are not discussed in, this paper.

The materials produced at Brisbane, Melbourne and Newcastle result from the Nissan process, involving two-stage precipitation of the dihydrate, and that Kwinana from the Dorr-Oliver process, with single-stage-precipitation. About 98-99% of the phosphate rock used is imported from Nauru and Christmas Island, with the remainder from Morocco for the production of special "pure" acid. Two more phosphoric

acid plants will be commissioned in 1981, one at Kwinana using the Fisons process, and the other at Geelong (Vic) employing the Prayon process. The location of existing and future plants in relation to the major cities is shown in Figure 1. The locations of the major deposits of natural gypsum are also marked in this figure.

The physico-chemical properties of phosphogypsums from Brisbane, Kwinana, Melbourne and Newcastle, designated with the symbols B,K,M and N respectively, have recently been investigated (4). Their chemical composition and pH, as compared with natural gypsum, are shown in Table 2. It is seen that all the samples contained free water in amounts varying from 1Ø-3Ø%. The amounts of CaO, SO_3 and H_2O for the materials dried at 45°C were similar to the theoretica? composition of $CaSO_4 \cdot 2H_2O$. All the phosphogypsums contained relatively high percentages of total P_2O_5 but the "soluble" and "co-crystallized P_2O_5 in samples B and N were low compared with samples K and M, The total amount of fluoride was about 1.1-1.4% and probably represents some unreacted phosphate rock, as it was about the same in all samples, The amount of water-soluble fluoride was, however, only about Ø.Ø5-Ø.Ø8 for samples, B,M and N, resulting from two-stage precipitation of the dihydrate, whereas for sample K, from single-stage precipitation, it was much higher -- namely Ø.36%. All the samples contained various amounts of Fe, Al and other impurities , irrespective of whether the gypsum resulted from the single or two-stage process. X-ray diffraction revealed that crystallographically all the specimens were identical to the mineral gypsum. The crystal habits of samples B, M and N were similar, and consisted of acidular crystals, while sample K was finer and consisted of equiaxial idiomorphic crystals.

Application of Phosphogypsum in the Plaster Industry. As indicated in Table 1, about 9Ø-1ØØ,ØØØ tons of phosphogypsum are used in Australia annually for the production of plasterboard. One company has been using the material from Brisbane since 1971, and from Newcastle since 1979. It is understood that "good quality" phosphogypsum from both locations can be used successfully for making plasterboard, after neutralization with lime and subsequent calcination. However, there have been intermittent manufacturing and quality problems experienced with calcined phosphogypsum due to the variability of the material. Recent changes to the manufacturing process, introduced in order to increase the rate of production of phosphoric acid, have resulted in phosphogypsums containing higher levels of some specific impurities, which are known to be detrimental to plaster production. The company in question is working on the problem of overcoming these difficulties.

Research. There has been relatively little published research carried out in Australia on phosphogypsum. Some research and development work has obviously been undertaken by the producers of phosphoric acid and by the large plaster and plasterboard manufacturers, but the results are considered to be confidential and are seldom published.

The CSIRO Division of Building Research had a program of research on chemical gypsum in the years 1965-67. The work was terminated because the industry showed little interest. The project was designed to discover the fundamental causes of unusual properties shown by calcined chemical gypsums (5). It was found that if calcium sulfate hemihydrate was

hydrated in mixtures contained 30% P2O5 and 5% H SO simulating the conditions in a Nissan plant, additions of HF and salts of Al and Fe greatly modified the crystal habit of the product. Furthermore, when the temperature was controlled within the range of 52.5-57.5°C, the product was almost free from P_2O_5. When work in the laboratory was repeated in the pilot plant on a larger scale, results different from the earlier ones were obtained. Some orthorhombic $CaSO_4$ appeared at 55°C and the product contained substantial amounts of P_2O_5.

A program of research on phosphogypsum was recommenced in 1978. First, the physico-chemical properties of the phosphogypsum (4) from Brisbane, Kwinana, Melbourne and Newcastle were examined in the "as received" condition. All samples were dried at 45°C and then calcined in a special rotary furnace (7) under controlled laboratory conditions. (The rotary calciner has been used in previous work in this division, and was found to give a product with properties similar to those of materials produced in commercial gypsum kettles.) Then the various properties, viz pH, chemical and mineralogical composition, particle size distribution, water requirement, setting time, kinetics of hydration, mechanical properties of cast gypsums and colour, were measured. The materials were then made slightly alkaline with CaO and the same procedures followed.

The particle size distribution of the samples after drying and calcination are shown in Table 3. It can be observed that the distributions of sizes were similar for samples B, M and N, but K was substantially finer. The other physical properties, namely induction period (defined as the time at which the rate of temperature increase of the plaster slurry exceeds 0.1°C/min), θ, setting time, water requirement, compressive strength, and density of cast cubed specimens, and colour coordinates of cast specimens, are shown in Table 4. It is seen that compared with calcined natural gypsums (cf. Table 5, samples PC-44, G4 and G5) the setting times are relatively short, the water requirements somewhat high particularly for sample M, the compressive strength low with the exception of sample B, and the colour coordinates only marginally lower.

Secondly, the change in the rate of hydration and kinetic parameters of the calcined phosphogypsums, and those treated with lime in the pH range from approximately 3-11, were examined (unpublished data) in terms of Ridge's equation (8), using the technique developed in the division (9). The other physical properties, viz settling time, water requirement, mechanical strength etc. in relation to increasing pH, were also investigated. It was found that as the pH of the slurry increased, the kinetic parameters underwent great changes. In particular, the parameter $\underline{k}$, the velocity constant, which is a measure of self-acceleration of the reaction, gradually decreased; while α_0, the measure of heterogeneous nucleation, i.e. the amount of "effective" (gypsum) nuclei present at the commencement of hydration, and θ, the period of induction, gradually increased. A typical plot of the above-mentioned parameters with pH for the calcined phosphogypsum from Brisbane, is shown in Figure 2.

In more practical terms, increasing pH resulted in increasing setting times , and little change in water requirement. The mechanical strength of cast gypsums increased until about pH 7, then decreased in the alkaline region. A typical trend for the material from Brisbane is shown in Figure 3.

Pilot plant scale experiments carried out recently (10) at the division have shown that the materials from the four Australian locations can be converted successfully to good quality calcined gypsum suitable for making cast gypsum and glass-reinforced cast gypsum boards. About 50 kg lots of phosphogypsum were co-calcined with lime in a laboratory kettle as in industry, then lightly ground. The physical properties of the resulting calcined gypsums were determined and plaster sheets were cast, reinforced with glass fibre near each face (11) ("doubly reinforced gypsum glass boards"). For comparison, batches of natural gypsums were also calcined and similar procedures followed. Due to the short setting times of the calcined phosphogypsums, small quantities (about 0.05%) of a commercial retarder (keratin) had to be added to the plaster slurry in order to facilitate the manufacture of the boards. The physical properties of the calcined materials, cast gypsum specimens and those reinforced with glass fibre are shown in Tables 5 and 6. It is seen in Table 5 that the bulk volumes and water requirements of calcined phosphogypsums were higher than those derived from natural gypsum, and they also had somewhat different particle size distributions. The induction periods and setting times were substantially shorter, but the values of compressive strength for the casts prepared from the ground calcined phosphogypsums were about the same, and in some instances (e.g. for samples K and M) were even higher than those obtained with calcined natural gypsums. The colours of cast phosphogypsum were marginally weaker.

For the plaster sheets reinforced with glass fibre (Table 6), the values of first crack, max. load and modulus of rupture were generally lower than those derived from natural gypsums. The somewhat inferior results may be due to desimentation of the slurry or to the poor bonding of calcined phosphogypsums to the glass fibers. The variability in results is not fully understood, but further work is being carried out in order to improve the properties of glass-reinforced cast phosphogypsums.

A gypsum glass board, marketed under the name of "Plasterglass" is produced commercially in Australia at present. The manufacturers of this product have expressed interest in the results presented above, but due to the structure of the plaster industry in Australia, it is unlikely that they will use calcined phosphogypsum in the near future.

Concluding Remarks. In Australia about 840,000 tons of phoshogypsum is produced annually, of which about 13-18% is used for the manufacture of plasterboard and as a soil conditioner -- the rest is dumped. Due to the fact that Australia is very rich in natural gypsum, there has been little need in the past to utilize larger quantities of phosphogypsum. However, the increasing cost of energy and transportation and stricter environmental regulations have made the utilization of phosphogypsum of immediate interest. Fortunately, the phosphoric acid plants and stockpiles of phosphogypsum are located at or near large centers of

population, and the prospects for large-scale utilization of phosphogypsum are very favorable.

Acknowledgments. Thanks are extended to my colleagues, Messrs D.N. Crook, G.A. King and L.W. Middleton. Most of the results presented in this paper are deduced from our joint publications.

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Table 1. Production and disposal of phosphogypsum in Australia

Location	Quantity (tpa)	Stockpile (tpa)	Methods of disposal
Brisbane (Pinkeba), Qld	120,000	200,000	Approx. 30,000 t is used for making gypsum plasterboard, 20-50,000 t as a soil conditioner; the rest is dumped
Kwinana, WA	119,000	nil	Discharged into the sea at Cockburn Sound
Melbourne (Yarraville), Vic	100,000	800,000	Dumped on land into disused quarries
Newcastle (Kooragang Island), NSW	500,000	300,000+	Approx. 60-70,000 t is used for making gypsum plasterboard; the rest is pumped into a pond
Total	839,000	1,300,000	

+Probably wrong figure. Quantities held in that particular pond appear to be much higher.

Table 2. Chemical analysis of samples of phospho- and natural gypsums

Components	By-product gypsum				Natural gypsum G4 and G5	$CaSO_4.2H_2O$ (theoretical)
	B	K	M	N		
pH	3.5	3.2	2.7	5.5	6.3	
Free water content (as received)	10.56	20.53	28.02	10.55	0.02	
Dried samples (45°C)						
CaO	32.9	32.2	33.4	32.7	33.15	32.58
SO_3	45.1	45.2	46.1	44.4	44.9	46.50
Total H_2O	20.6	20.5	18.8	20.4	19.96	20.92
Total P_2O_5	0.28	0.69	0.48	0.54	-	
SiO_2	0.11	0.08	0.12	0.55	0.23	
Al_2O_3	0.12	0.34	0.10	0.12)	0.02	
Fe_2O_3	0.03	0.03	0.02	0.02)		
MgO	0.04	0.01	0.06	0.08	0.03	
Na_2O	0.05	0.08	0.11	0.07		
K_2O	0.02	0.01	0.03	0.02		
CO_2					1.50	
Total F^-	1.30	1.10	1.15	1.40		
Total Cl^-					0.20	
Total	100.55	100.22	100.37	100.30	99.99	100.00
Soluble P_2O_5 (includes co-crystallized P_2O_5)	0.06	0.25	0.30	0.04		
Co-crystallized P_2O_5	0.03	0.15	0.22	0.03		
Unreacted P_2O_5 (difference of total and soluble P_2O_5)	0.22	0.44	0.18	0.50		
H_2O (free)	<0.02	0.02	0.07	0.05		
Organic C	0.10	0.14	0.10	0.18		
Water-soluble F^-	0.07	0.36	0.08	0.05		

Table 3. Particle size distribution* of dried and calcined phosphogypsums (laboratory experiments)

Sample	µm fraction (%)					
	+ 300	- 300 + 150	- 150 + 75	- 75 + 53	- 53 + 20	- 20
Dried by-product gypsum						
B	1.05	43.32	37.85	9.21	6.88	1.67
K	4.94	9.12	21.61	25.13	36.70	2.49
M	0.67	29.56	48.60	18.36	5.76	0.75
N	2.36	31.48	38.05	16.21	11.29	0.67
Calcined by-product gypsum						
B	0.63	14.17	37.68	23.57	18.24	5.71
K	1.97	4.56	19.14	21.65	43.27	9.41
M	0.53	16.90	48.85	23.71	7.60	2.36
N	0.72	17.77	55.71	13.64	8.40	3.78

*As determined by sieving in ethanol and by sedimentation balance

Table 4. Physical properties of calcined and cast phosphogypsums (laboratory experiments)

	B	K	M	N
Induction period*, θ (min)	17.8	4.3	22.0	29.3
Setting time≠ (min)	15	7	15	20
Water requirement (mL/100 g)	85	75	108	82
Compressive strength≠ (MPa)	10.52	7.19	7.26	7.42
Density (kg/m^3)	1140	1100	1080	1130
Colour coordinates, L	87.26	86.32	85.52	85.01
" " a	1.08	1.06	1.18	1.50
" " b	6.92	7.31	6.84	8.19
" " E	8.54	10.07	9.56	11.52

*Defined as the time at which the rate of temperature increase of the plaster slurry exceeds 0.1°C/min

≠As determined by the knife edge test.

≠W/S ratio, 0.7

Table 5. Physical properties of calcined and cast gypsums prepared in pilot plant

	Sample of calcined gypsum derived from										
	natural gypsum			phosphogypsum							
	PC-44*	G4	G5	B		K		M		N	
				ungr.	gr.	ungr.	gr.	ungr.	gr.	ungr.	gr.
CaO added at calcination (%)	-	-	-	0.20		0.30		0.30		0.10	
pH after calcination	6.1	6.4	6.2	-	-	-	-	-	-	-	-
pH after co-calcination with CaO	-	-	-	5.9	-	6.6	-	5.7	-	5.6	-
Bulk volume (mL/100 g)	80	74	72	81	86	93	87	83	83	84	89
Sieve analysis (%) + 300 µm	1.95	15.83	11.63	-	0.23	-	0.66	-	0.57	-	0.43
-300 + 150 µm	5.25	16.90	17.50	-	8.24	-	2.83	-	4.64	-	29.18
-150 + 75 µm	41.64	24.25	26.90	-	57.06	-	54.23	-	61.32	-	43.53
-75 + 53 µm	11.21	13.83	12.39	-	16.91	-	22.20	-	21.86	-	10.55
-53 µm	39.90	29.10	29.63	-	17.57	-	20.07	-	11.60	-	16.36
Water requirement (mL/100 g)	64	64	57	81	75	82	78	79	76	92	93
Induction period, θ (min)	35	42	26	7	8.5	-	13.5	-	26.5	36	4
Setting time (min)	34	49	32	6	8	8	7.5	14.5	9	12	15
Compressive strength (MPa)[/]	10.64	10.54	8.77	10.37	10.66	14.87	15.68	10.37	12.21	7.30	9.57
Density (kg/m^3)	1038	1072	1047	1057	1052	1067	1060	1058	1066	1081	1049
Colour, L (lightness)[≠]	92.8	91.5	91.3	-	84.8	-	86.8	-	87.4	-	91.7

*PC-44, commercial casting plaster

[/]Mean of 8 determinations. Coefficient of variation, about 5%, W/S ratio, 0.75

[≠]L = 100 denotes "perfect" white

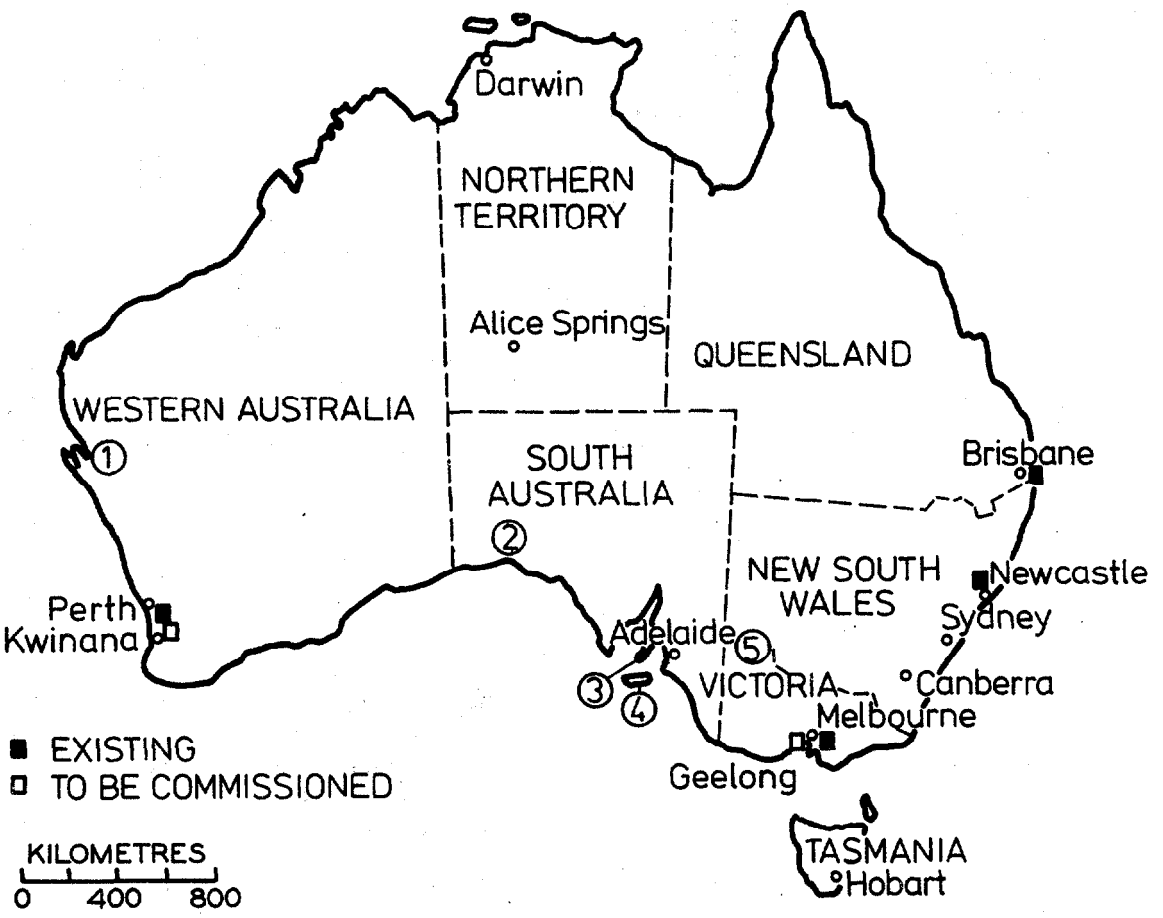
Table 6. Physical properties of doubly-reinforced gypsum glass boards*

Description of material	Symbol	Thickness (mm)	Load at first crack (N)	Max. load in bending (N)	Modulus of rupture† (MPa)	Colour, L (lightness)≠
Commercial plaster	PC-44	8.23	184	476	8.85	91.9
Mineral gypsum calcined in the pilot plant	G-4	7.61	164	418	8.97	89.5
Calcined phospho-gypsums from :	G-5	8.05	156	436	8.38	87.7
Brisbane	B	7.36	101	278	6.37	83.7
Kwinana	K	8.32	182	384	6.95	84.2
Melbourne	M	7.48	173	434	9.78	79.9
Newcastle	N	7.58	114	328	7.13	89.3

*Size of spemimens, 300 x 300 mm; tested in bending, centrepoint loading span, 250 mm

†Mean of 8 determinations. Coefficient of variation, about 12%

≠L = 100 denotes "perfect" white



LOCATION OF MAJOR GYPSUM DEPOSITS:

① LAKE Mc LEOD
② LAKE Mac DONNELL
③ STENHOUSE BAY-YORK PENINSULA
④ KANGAROO ISLAND
⑤ MILDURA

Fig. 1 Map indicating the locations of existing and future phosphoric acid plants, and the major natural gypsum deposits, in relation to main cities.

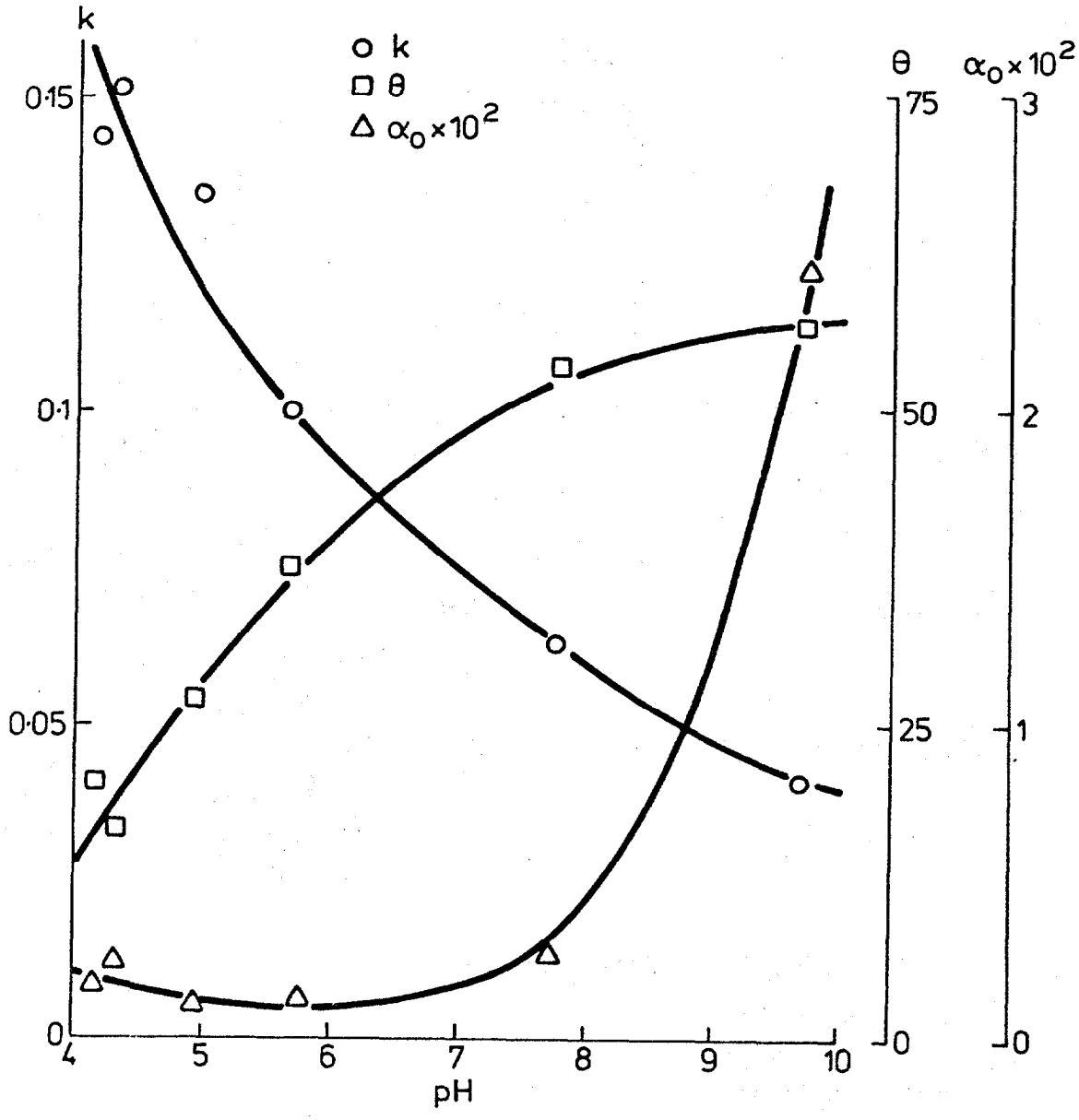


Fig. 2 The relationship between kinetic parameters and pH for calcined phosphogypsums from Brisbane, as derived from Ridge's equation. ⊙ k, a measure of self-acceleration of the reaction; ⊡ period of induction; and α_o △ a measure of the extent of heterogeneous nucleation.

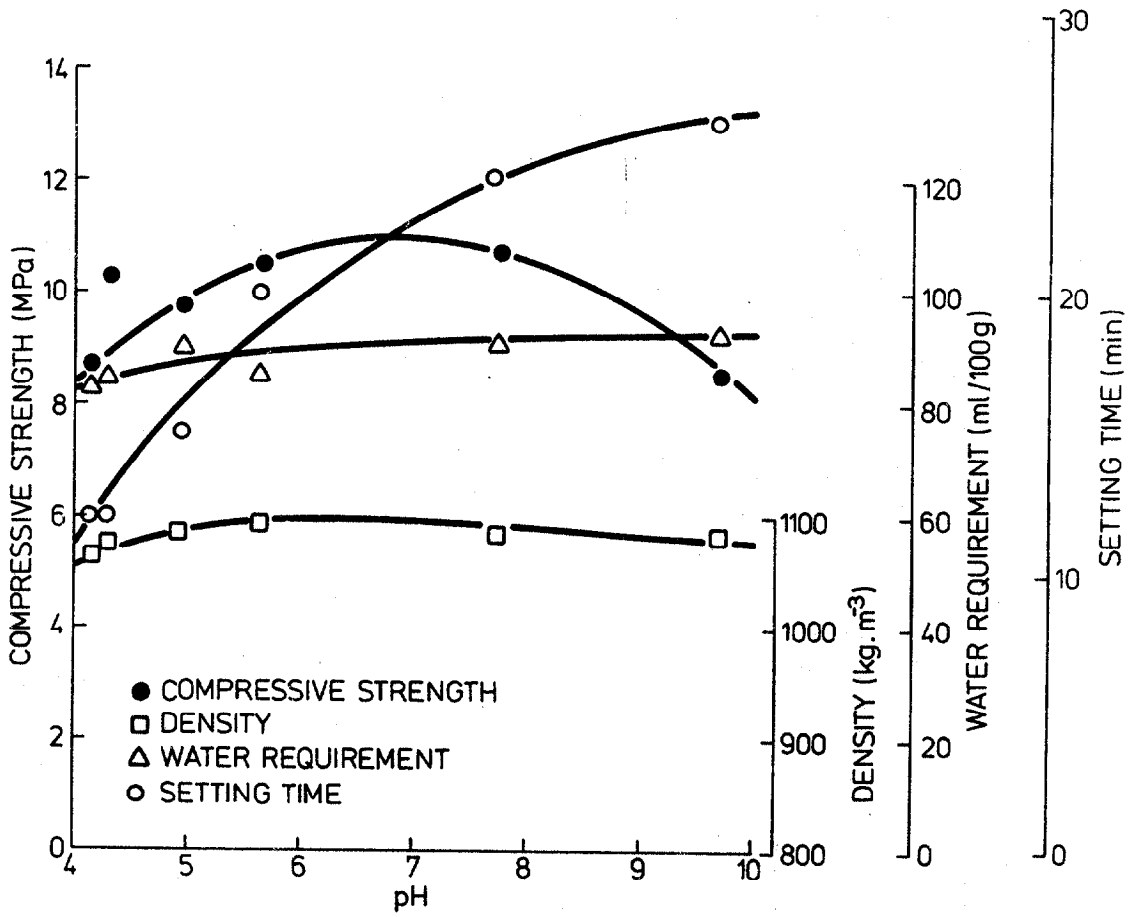


Fig. 3 The influence of pH on the physical properties of calcined and cast phosphogypsums. ● Compressive strength, MPa; ⊡ density of cast cubes (kg/m^3); △ water requirement (mL/100 g); and ◐ setting time (min.)

PHOSPHOGYPSUM IN CANADA

by

R.K. Collings

CANMET
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INTRODUCTION

Phosphogypsum, a by-product of the manufacture of phosphate fertilizer, is produced at a number of locations in Canada. Although interest has periodically been expressed in the use of this material for gypsum products and Portland cement manufacture, there is no current consumption and phosphogypsum continues to be discarded to waste dumps or to local water systems. This non-use is attributable, in part, to the fact that Canada has adequate resources of natural gypsum, and as well, to problems associated with the use of phosphogypsum by industry, not the least of which is its inherent radioactivity.

This paper outlines Canada's gypsum and phosphate fertilizer industries, notes areas of potential interest with regard to phosphogypsum utilization, describes CANMET's research on phosphogypsum, and comments on the potential radiological hazard that could result through use of phosphogypsum in gypsum products.

Gypsum Industry. Gypsum is mined in 6 of Canada's 10 provinces. Production in 1979 was 8 x 10^6 tons (70% of which was exported) mostly from Nova Scotia to consumers in the eastern United States. Canadian use is almost entirely in gypsum products and Port&and cement manufacture. Consumption by the former is about 2.2 x 10^6 t/a and, by the latter, 0.5 x 10^6 t/a.

The locations of gypsum mines are shown in Figure 1. These are listed by province in Table 1 with production and estimated consumptions in gypsum products and Portland cement. Three provinces (Quebec, Saskatchewan and Alberta) have significant requirements for gypsum but no producing mines. The Quebec requirement of approximately 0.6 x 10^6 t/a is supported by Newfoundland and Nave Scotia, whereas requirements by Saskatchewan and Alberta, about 0.5 x 10^6 t/a, are met by producers in neighboring Manitoba and British Columbia. Shipping distances are in the order of 1400 km by water in the first instance and vary from 300 to 700 km in the second.

Phosphate Fertilizer Industry. Phosphate fertilizers are produced at the nine facilities in Canada noted in Table 2. Three former producers, two in Quebec and one in British Columbia, ceased operations within the last year or two. Although there are numerous occurrences of low-grade phosphate rock in Canada, there is no commercial production. Our entire requirements are imported, largely from the United States and principally from Florida, Montana, Utah and Idaho. Imports of phosphate rock amounted to 2.9 x 10^6 tons in 1979. Production of phosphate fertilizer during the same period was about 0.9 x 10^6 tons (P_2O_5 equivalent).

Phosphogypsum. Phosphogypsum, a by-product of the manufacture of phosphate fertilizer, is produced at the nine facilities noted in Table 2. About 4.5 tons are generated for each ton of fertilizer (P_2O_5 equivalent). Production was about 4 x 10^6 tons in 1979 and although most of this amount is stored on land in large containment areas, as noted in Table 2, two plants discharge phosphogypsum into nearby water systems. The total accumulation of phosphogypsum in Canada is in the order of 50 x 10^6 tons.

Phosphogypsum is finely divided, acidic and usually contains more than 90% gypsum on a dry basis. The gypsum crystals may be needle-like to tabular, depending on impurities in the phosphate rock and its treatment during the acidulation process used in the manufacture of phosphate fertilizer. Common impurities include unreacted or partially reacted phosphate rock, organic material, calcium fluoride and quartz sand. Figure 2 shows two varieties of phosphogypsum crystals: those in 2(a) were formed from Moroccan phosphate whereas those in 2(b) were formed from Florida rock. Phosphogypsum may contain up to 50 pCi/g of radium. Radon gas emitted by this radium could be injurious to the health of persons living in homes finished with gypsum products made from this material. The presence of radium in phosphogypsum, although known for some years, did not become a matter of great concern until the last seven to eight years. Work on phosphogypsum at CANMET was undertaken before this concern became widespread.

CANMET Research. The lack of developed natural gypsum deposits in Quebec, Saskatchewan and Alberta stimulated interest by CANMET in the 1960's with the possibility of using phosphogypsum as a substitute or partial replacement for mined gypsum in gypsum products manufacture. A study based on phosphogypsum samples from producing plants in Quebec, Ontario and Alberta was initiated at that time (1). The particle size and chemical analyses of these samples are shown in Table 3. Investigative work included water washing and sizing, grinding, calcining and product fabrication and evaluation.

The CANMET study revealed a number of factors that are peculiar to phosphogypsum and associated gypsum products. These are summarized as follows:

(1) Phosphogypsum, as produced, usually is acidic (pH 3.0 t 4.0). Although it is neutralized with lime/limestone before being discharged to waste, additional neutralization is required prior to or during its conversion to gypsum plaster and plaster products (see item 3 below).

(2) Most phosphogypsums contain some unreacted phosphate rock, a significant portion of which may be concentrated in the coarser, plus 250 or 150 um sizes. Removal of these sizes prior to calcining is desirable because phosphate impurities have a detrimental effect on the setting and bond-to-paper characteristics of the calcined product during gypsum wallboard manufacture.

(3) The pH of phosphogypsum can be raised to six or more by extended water washing or by base addition; however, on calcining and subsequent hydration, the pH drops back to about three. This reversion is believed to be due to the release of acid occluded in the gypsum crystal. Acid plaster of paris and water mixtures usually set very quickly. Neutralization with a suitable base, plus retarder addition, can be employed to effectively control time of set. Sodium hydroxide was used in most tests for neutralizing because it produced consistent results. Unfortunately, if used in excess, this base tended to

to hydrolize the starch that normally is added to promote bond of the gypsum plaster-water mixture to wallboard paper, thereby rendering it less effective. The effect of excess sodium hydroxide on starch was sometimes delayed. A few gypsum wallboard samples that were very basic (pH greater than 10) showed good initial bond development, but little or no bond one week later. Regardless of the pH achieved initially by base addition, nearly all plaster samples reached a stable pH of from 6.0 to 7.0 within 24 hours.

(4) Bond of plaster-of-Paris water mixtures to gypsum wallboard paper is critical and sometimes is achieved with difficulty. Bond to paper is dependent on several factors , e.g., crystal habit, surface area, pH, impurities in the gypsum, additives, method of mixing and forming wallboard,. etc. Crystal habit, determined in part by treatment during the phosphoric acid-phosphogypsum manufacturing process and in part by impurities in the phosphate rock and resulting phosphogypsum, is important in bond development. For example, good bond to paper was obtained with the Quebec sample, which was composed of large, tabular-to-needle-like gypsum crystals (Figure 2a). By contrast, samples from Ontario and Alberta, composed of stubby crystal platelets of gypsum (Figure 2b), generally produced poor bonds. The effect of surface area on bond is difficult to evaluate. Gypsum plaster made with the Quebec sample consistently produced good bonds at lower surface areas (3000 cm^2/g). Grinding to higher surface areas (5000 cm^2/g) was required for bond development with the other samples unless the starch content was increased. Starch appears to be essential for good bond development with most phosphogypsums; the amount required in this study varied from 0.5 to 2%. Good bonds were achieved with gypsum plaster made with phosphogypsum from Ontario and Alberta that had been ground to 5000 cm^2/g or finer, with 0.5% starch addition. Equally satisfactory bonds were achieved by grinding to 3000 cm^2/g, with 1% starch. Although grinding may be performed either before or after calcining, the former is preferable because the ground gypsum is "lighter" in the calcining kettle, consequently less mechanical/electrical power is required to operate the stirring mechanism.

(5) Although the compressive strengths of the calcined products varied somewhat between tests and between samples, they generally met the requirement (5.2 MPa) of Canadian Standard Associations specification A-82 for gypsum plaster. The results of this work indicated that phosphogypsum from each of the sources studied could be upgraded to the point at which it technically could be employed as a substitute for natural gypsum in gypsum products. However, the potential health problem associated with the use of phosphogypsum for gypsum products in North America has not yet been resolved.

Phosphogypsum Use and Radiological Hazard. Phosphogypsum is used in the manufacture of gypsum products (plaster, building blocks and wallboard) in a number of countries, including Japan, France, Germany and Australia. It also was used in England from the early 1930's until fairly recently for wallboard production. Phosphogypsum is not currently used in Canada nor in the United States, partially because both countries have access to adequate sources of natural gypsum but also because of concern over the radium in this material. A 1974 EPA

report (2) notes that some phosphogypsum stockpiles may contain up to 50 pCi/g of radium, although the average content probably is closer to 25. Radium concentration in ten piles of phosphogypsum, selected at random in the United States, varied from a low of 11 to a high of 31 pCi/g.

Although limited, some information regarding radiation guidelines for phosphogypsum is available in the literature. A 1972 study by the National Radiological Protection Board of Great Britain (3) concluded that phosphogypsum could be used as a building material provided that the radium concentration in the finished components did not exceed 25 pCi/g and that production and utilization were monitored so that the population does could be assessed periodically. Adequate ventilation of houses constructed with phosphogypsum products was also stipulated.

A 1975 study by the U.S. Bureau of Mines (4) notes that the maximum permissible concentration of Ra-226 in water is 3.3 pCi/l but states that no similar data are documented for the maximum permissible concentration (MPC) of the uranium family in either tailings or soil. This report provides a number of interesting statistics, e.g.:

Radium concentration, earth's crust.....1 pCi/g

MPC for soil and building materials,
U.S. (under construction).....20 pCi/g

MPC for gypsum wall board and building blocks,
U.K. (recommended).....25 pCi/g

MPC for building materials,
U.S.S.R. (maximum permitted).....20 pCi/g

The previously noted EPA report (1) contains a number of recommendations, one of which (No. 6) is specific to phosphogypsum, i.e., that

(6) Regulations be promulgated to ensure that (a) all precipitates from process-water treatment systems are placed on gypsum piles, (b) upon abandonment, gypsum piles are stabilized to prevent future leaching or erosion, (c) as a minimum, such stabilization includes grading to promote runoff and prevent ponding, sealing to prevent infiltration, and covering with soil to permit vegetative stabilization, and (d) by-product gypsum be prohibited for use as a construction material in confined areas.

A committee on radiation protection and health, Nuclear Energy Agency, OECD, met in Paris in October 1976 to examine the radiation hazard of specific building materials and to draft radiation protection standards for such materials, especially those that could trade internationally (5). One material examined was phosphogypsum and its use in building products. An exemption formula derived and tentatively adopted at that time was as follows:

$$\frac{CK}{130} + \frac{CRa}{10} + \frac{CTh}{7} \leq 1$$

where C is the activity concentration in pCi/g of, respectively K^{40} Ra-226, and Th-232. Assuming an activity coefficient of 25 pCi/g for radium in phosphogypsum and ignoring K-40 and Th-232, 'the above equation would equate to 2.5.(25/10) which is greater than 1. This presumably would rule out international trade of gypsum products manufactured with phosphogypsum containing over 10 pCi/g.

The question of radiation guidelines and standards was discussed with various officers of the Canadian Atomic Energy Control Board and the Environmental Protection Service, Department of the Environment. At this point in time, Canada has no definitive specification for a "safe" radiation limit for phosphogypsum but this problem is under study.

Industry Interests. A letter-telephone survey of three gypsum product manufacturers and nine phosphate fertilizer producers was made recently to ascertain current interest and developments in the use of phosphogypsum.

The gypsum product manufacturers expressed continued interest in phosphogypsum as raw material for gypsum products, especially in areas having no developed sources of natural gypsum. They noted that the cost of natural gypsum in these areas currently is as much as $20 to $22/t. One or two companies have participated in co-operative research projects with the Giulini organization of West Germany. Samples of Canadian phosphogypsum were shipped to Germany for beneficiation and calcining, and on their return to Canada, they were evaluated in plant trials for gypsumboard manufacture. Although some problems were encountered in the gypsumboard trials the tests, on the whole, were successful. However, all producers expressed concern regarding the radium in phosphogypsum and the fact that we do not yet have a standard relating to permissible levels of radium in gypsum products in Canada.

The phosphate fertilizer industry similarly expressed interest in the sale of phosphogypsum for gypsum products. Some producers reported research on the use of phosphogypsum as a retarder in Portland cement, as an additive to clay soils, as a plant nutrient, and in soil reclamation following salt spills near gas wells. Results reportedly were encouraging. All producers similarly expressed concern over the radium content of phosphogypsum and the need for radiological guidelines or standards for using this material in the noted applications. This concern and frustration was aptly expressed by one respondent who noted: "Gypsum disposal (utilization) is of continuing interest, even though we are seemingly powerless to innovate our way out of the stockpile." This same respondent added that: "All routes to the utilization of phosphogypsum have proved uneconomical. This situation will remain unchanged unless North American phosphate producers switch to hemihydrate technology. The gypsum could then be used in gypsum products with little or no upgrading." The writer is here referring to processes similar to the Nippon Kokan (NKK) process that was developed in Japan some 8 to 10 years ago (6). The NKK process probably would not significantly reduce the radium content, however, and further research on this problem is necessary.

A scientist at the Ontario Research Foundation, Toronto, Ontario, in commenting on problems associated with the radioactivity of phosphogypsum, stressed that radon gas build-up could occur not only in houses constructed with phosphogypsum products, but also in manufacturing plants and in product storage areas.

CONCLUSION

While recognizing that phosphogypsum is not an ideal source material for use in gypsum products, Portland cement and the several other applications noted in this paper, technically can be so utilized. Phosphogypsum is of particular interest in those areas that have no developed sources of natural gypsum, e.g. in Canada - Alberta, Saskatchewan and Quebec. Use of phosphogypsum is contingent upon the development of standards for permissible levels of radium in each application. The development of such standards appears to be mandatory in view of the current high level of interest in phosphogypsum utilization. The development of standards of acceptability would, in turn, stimulate research on phosphogypsum beneficiation, including studies directed towards the reduction of the radium content to acceptable levels.

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TABLE 1

Gypsum Production and Estimated Consumption (1979)

Province	Gypsum Mines		Estimated Gypsum Consumption			
			Gyp. Prod. Plants		Cement Plants	
	Number	Production* Tonnes x 1000	Number	Tonnes x 1000	Number	Tonnes x 1000
Newfoundland	1	800	1		1	
Nova Scotia	6	5 640	1	200	1	25
New Brunswick	2	50	1		1	
Quebec	0	-	4	520	5	125
Ontario	3	770	3	430	6	175
Manitoba	1	130	2		2	
Saskatchewan	0	-	1	700	1	100
Alberta	0	-	3		2	
British Columbia	1	720	3	350	3	50
Total	14	8 110	19	2 200	22	475

*Preliminary statistics, 1979

TABLE 2

Phosphate Fertilizer Plants - Phosphogypsum Production

Company	Plant Location	Phosphogypsum t/a	Phosphogypsum t-accumulated
New Brunwsick			
Canada Wire and Cable Limited	Belledune	600×10^3	0*
Ontario			
Canadian Industries Limited	Courtright	900×10^3	15×10^6
International Minerals and Chemical Corporation (Canada) Limited	Port Maitland		
Alberta			
Western Co-operative Fertilizers Limited	Calgary	$1\,800 \times 10^3$	30×10^6
Western Co-operative Fertilizers Limited	Medicine Hat		
Esso Chemical Canada	Redwater		
Sherritt Gordon Mines Limited	Fort Saskatchewan		
British Columbia			
Cominco Limited	Trail	800×10^3	0*
Cominco Limited	Kimberly		5×10^6
TOTAL		$4\,100 \times 10^3$	50×10^6

*Discharged into local water systems.

TABLE 3

Sieve and Chemical Analyses - Phosphogypsum Samples

Province	Sieve Analysis Size (µm)	Wt%	Sample	Chemical Analysis - Wt% CaO	SO_3	H_2O	C	F	Water Sol	P_2O_5 Water Insol	Total
			Gypsum	32.6	46.5	20.9	-	-	-	-	-
Quebec	+ 250	4.6	Head	31.8	44.7	18.6	0 26	0.84	0.02	0.82	0.84
	-250 + 150	3.7	-250 µm, washed	-	-	18.8	0.29	0.83	0.02	0.81	0.83
	-150 + 100	3.7	-250 µm, calcined	-	-	5.7	0.24	0.58	0.02	0.52	0.54
	-100 + 75	11.8									
	-75	76.2									
	Total	100.0									
Ontario	+ 250	11.4	Head	31.3	43.1	19.6	-	1.71	0.01	0.94	0.95
	-250 + 150	13.0	+250 µm	-	-	-	-	2.76	0.01	1.02	1.03
	-150 + 100	15.4	-250 µm, washed	-	-	-	-	1.50	0.01	0.81	0.82
	-100 + 75	24.4	-250 µm, calcined	-	-	6.9	-	1.77	0.01	0.95	0.96
	-75	35.8									
	Total	100.0									
Alberta	+ 150	9.6	Head	34.0	45.8	15.9	-	0.33	0.08	0.57	0.65
	-150 + 100	19.6	-150 µm, washed	-	-	18.6	-	0.61	0.02	0.46	0.48
	-100 + 75	21.1	-150 µm, calcined	-	-	6.3	-	0.60	0.03	0.55	0.58
	-75	59.7	-150 µm, ground	-	-	-	-	-	-	-	-
			and calcined	-	-	5.8	-	0.33	0.06	0.81	0.87
	Total	100.0									

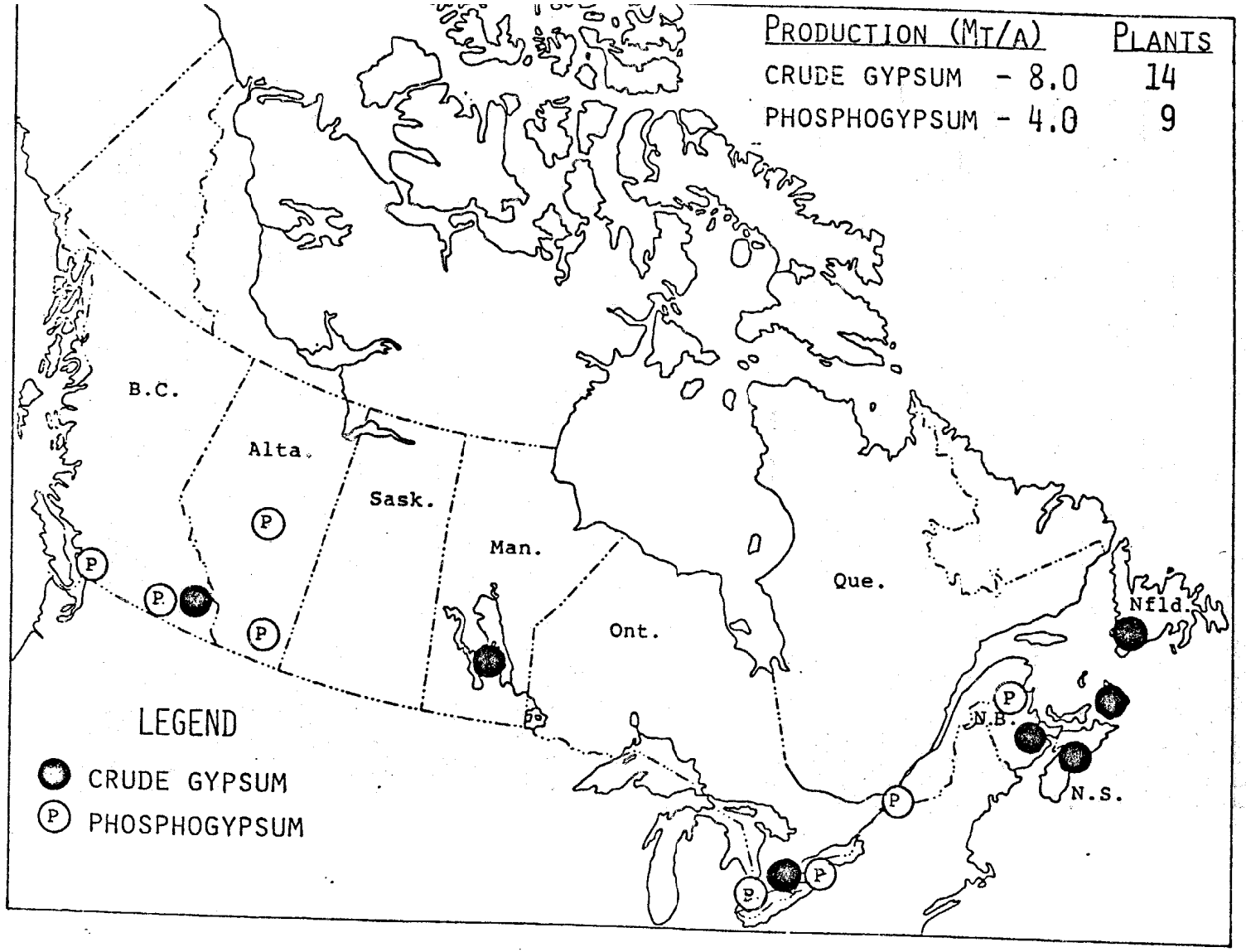


Fig. 1 - Crude gypsum mines and phosphogypsum accumulations in Canada.



(a) Quebec (50x)



(b) Ontario and Alberta (50x)

INTERNATIONAL SYMPOSIUM ON PHOSPHOGYPSUM

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