



Florida Department of Environmental Protection

Bob Martinez Center
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Charlie Crist
Governor

Jeff Kottkamp
Lt. Governor

Michael W. Sole
Secretary

December 19, 2008

Philip A. Block, Ph.D.
Remediation Technology Manager
FMC Corporation
1735 Market Street
Philadelphia, Pennsylvania 19103

Re: **Klozur[®] CR**

Dear Dr. Block:

The Division of Waste Management (Division) hereby accepts Klozur[®] CR, a proprietary blend of sodium persulfate and calcium peroxide, for the remediation of petroleum and other suitable contaminants in groundwater and soil, in situ and ex situ. Although these ingredients are available individually, the combination offers the convenience of a single package and self-activation of the persulfate component by the high pH of the calcium peroxide.

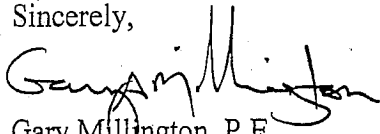
FMC indicates that Klozur[®] CR destroys contaminants in a two-stage process. In the first stage, the persulfate oxidizes contaminants. In the second stage, the calcium peroxide provides oxygen for longer-term aerobic biodegradation. A proprietary information voucher is provided as Enclosure 1, regulatory information as Enclosure 2, supplemental information as Enclosure 3, and Underground Injection Control notification as Enclosure 4.

The Division of Waste Management does not provide endorsement of specific or brand name remediation products or processes. It does, however, recognize the need to determine their acceptability in the context of environmental regulations, safety and the protection of public health. For that reason, the Division issues an "acceptance" letter, not an approval. In no way shall an acceptance be construed as certification of performance. Additionally, vendors, upon receipt of an acceptance, must market their product or process on its own merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace.

Remedial Action Plans that propose the use of an accepted product or process should include a copy of the acceptance letter in the plan's appendix, and reference it in the text of the document. It is not a requirement that a particular remediation product or process have an official acceptance letter in order for it to be proposed in a site-specific Remedial Action Plan. The plan, however, must contain sufficient information about the product or process to show that it meets all applicable rules and regulations.

The Division reserves the right to revoke its acceptance of a product or process if it has been falsely represented. Additionally, Division acceptance of any product or process does not imply it has been deemed applicable for all cleanup situations, or that it is preferred over other treatment or cleanup techniques in any particular case. A site-specific evaluation of applicability and cost-effectiveness must be considered for any product or process, whether conventional or innovative, and adequate site-specific design details must be provided in a Remedial Action Plan submitted for Department review and approval. Questions about hazardous waste cleanup applications should be directed to Gary Millington, and questions about petroleum cleanup applications should be directed to Rick Ruscito.

Sincerely,



Gary Millington, P.E.
Division of Waste Management
Bureau of Waste Cleanup
Program and Technical Support Section
gary.millington@dep.state.fl.us
(850) 245-7502



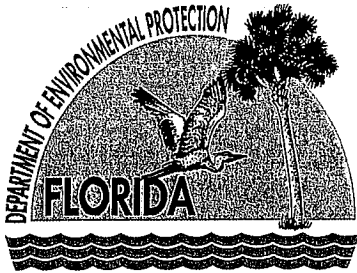
Rick Ruscito, P.E.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6
rruscito@ene.com
(850) 877-1133, extension 3722

Enclosures: (1) Proprietary Information Voucher for Klozur[®] CR
(2) Regulatory Information
(3) Supplemental Information
(4) Underground Injection Control Notification Memorandum

c: Tom Conrardy - FDEP/Tallahassee
Rob Cowdery - FDEP/Tallahassee

ENCLOSURE 1

PROPRIETARY INFORMATION VOUCHER



Florida Department of
Environmental Protection

Bob Martinez Center
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Charlie Crist
Governor

Jeff Kottkamp
Lt. Governor

Michael W. Sole
Secretary

December 19, 2008

Philip A. Block, Ph.D.
Remediation Technology Manager
FMC Corporation
1735 Market Street
Philadelphia, Pennsylvania 19103

Re: **Proprietary Information Voucher for Klozur[®] CR**

Dear Dr. Block:

On November 21, 2008 the Division of Waste Management received from FMC Corporation a confidential disclosure stating the ratio of sodium persulfate to calcium peroxide in the proprietary blend of these two chemicals known as Klozur[®] CR. This ratio, in combination with earlier non-proprietary information provided by FMC on February 15, 2005 about the chemical composition of its sodium persulfate, was used by the Division to identify the groundwater parameters that must be monitored in the temporary injection zone of discharge when Klozur[®] CR is used to remediate petroleum and other suitable contaminants at a contaminated site.

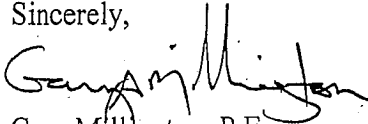
The disclosure, having been made once, does not have to be repeated each time a site-specific Remedial Action Plan proposing the use of Klozur[®] CR is submitted. Instead, it will suffice hereafter for site-specific Remedial Action Plans to: (1) indicate the overall concentration of Klozur[®] CR in the fluid to be injected; (2) indicate the volume of the fluid to be injected; (3) include a copy of the acceptance letter, which includes this voucher, and (4) provide for groundwater monitoring of the chemical species and parameters associated with Klozur[®] CR in the temporary injection zone of discharge per the advice of this letter.

Philip A. Block, Ph.D.
December 19, 2008
Voucher
Page 2

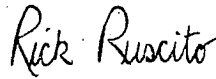
Klozur® CR
Proprietary Information

Questions about hazardous waste cleanup applications should be directed to Gary Millington, and questions about petroleum cleanup applications should be directed to Rick Ruscito.

Sincerely,



Gary Millington, P.E.
Division of Waste Management
Bureau of Waste Cleanup
Program and Technical Support Section
gary.millington@dep.state.fl.us
(850) 245-7502



Rick Ruscito, P.E.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6
rruscito@ene.com
(850) 877-1133, extension 3722

REGULATORY INFORMATION

- a. Regulations: Chapters of the Florida Administrative Code (F.A.C.) that may be applicable, either in part or in their entirety, include but are not necessarily limited to Chapter 62-550, F.A.C., for primary and secondary water quality standards; Chapter 62-520, F.A.C. for groundwater classes and standards; Chapter 62-522, F.A.C., for groundwater permitting and monitoring requirements; Chapter 62-528, F.A.C., for underground injection control, particularly Part V, for Class V, Group 4 aquifer remediation projects; Chapters 62-770, 62-780, 62-782, and 62-785 F.A.C., for cleanup criteria; and Chapter 62-777, F.A.C., for cleanup target levels.

Users of Klozur® CR shall comply with all applicable regulations. This includes meeting applicable groundwater cleanup target levels for the contaminants of concern, the residual concentrations of Klozur® CR ingredients, and any byproducts of concern produced by chemical and biological reactions induced by the ingredients during the timeframe of the cleanup project. For the "ingredients of concern" in Klozur® CR that are present in excess of their groundwater standards, the timeframe is that which is permitted for a temporary injection zone of discharge.

- b. Underground Injection Control permit: Per Rule 62-528.630(2)(c), F.A.C., Class V injection-type aquifer remediation wells are exempt from the permitting requirements of Rule 62-528.635, F.A.C., when authorized by a Department-approved Remedial Action Plan or other enforceable mechanism, provided the requirements of the rules governing the remediation project, as well as the construction, operation, and monitoring requirements of Chapter 62-528, F.A.C., are met. Per Rule 62-528.630(2)(c), F.A.C., the issuance of an enforceable, site-specific Remedial Action Plan Approval Order by the Department for injection-type aquifer remediation constitutes the granting of a Class V injection well construction/clearance permit.
- c. Underground Injection Control notification: Remedial Action Plans proposing in situ, injection-type aquifer remediation shall include information pursuant to Rules 62-528.630(2)(c)1 through 6, F.A.C., for the inventory purposes of the Underground Injection Control program. Reviewers of those plans, upon issuance of an enforceable Remedial Action Plan Approval Order by the Department, must submit a completed copy of the Underground Injection Control inventory notification memorandum in Enclosure 4.
- d. General information about temporary injection zones of discharge: For in situ aquifer remediation, the composition of an injected fluid must meet the primary and secondary drinking water standards set forth in Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapter 62-520, F.A.C., pursuant to underground injection control Rule 62-528.600(2)(d), F.A.C. Aquifer remediation fluids that do not meet these requirements must seek permission for a temporary injection zone of discharge. Depending on the chemical composition and the physical properties of the fluid, it will be necessary to obtain an injection zone of discharge by either one or both of the following methods: by Rule 62-522.300(2)(c), F.A.C., or by variance from Rule 62-522.300(3), F.A.C.

Rule 62-522.300(2)(c), F.A.C., allows a temporary injection zone of discharge for closed-loop re-injection systems, the prime constituents of the reagents used to remediate site contaminants, and the secondary standards for groundwater, provided a Department-approved remedial action plan addresses the duration and size of the zone of discharge, and groundwater monitoring of the injected chemical species of concern.

In order to obtain permission for a temporary zone of discharge by way of Rule 62-522.300(2)(c), F.A.C., a site-specific Remedial Action Plan must indicate: (a) the chemical species of concern in the fluid to be injected that will be present in excess of their allowable concentrations; (b) the size of the zone that is needed; (c) the amount of time that the zone will be needed; and (d) a groundwater monitoring plan for the injected chemical species of concern. In most cases, monitoring on a quarterly basis should be sufficient. The size of the temporary injection zone of discharge in item (b) above will usually be the radius of influence when the treatment system is a single injection point. For a multiple point system, the zone of discharge can usually be expressed and illustrated as the total area of the cluster formed by all the injection points, located side-by-side with overlapping radii of influence.

- e. Specific zone of discharge information for Klozur® CR: For the injection of Klozur® CR at concentrations of 40 percent or less by weight, only the requirements of Rule 62-522.300(2)(c), F.A.C., must be met in order to obtain permission for the temporary injection zone of discharge. In such cases, the issuance of the site-specific Remedial Action Plan Approval Order also constitutes the granting of permission for the temporary injection zone of discharge.

At concentrations greater than 40 percent the rule still applies, but a variance that grants a temporary injection zone of discharge for chromium, and possibly other heavy metal impurities, will also be necessary. If in the future a variance for injection concentrations greater than 40 percent is sought, then it will be necessary for FMC Corporation to provide a breakdown of the other heavy metal impurities in its sodium persulfate that are currently grouped into a single category labeled only "as lead". However, it is anticipated that there will be few, if any, occasions in which there will be a need to inject a fluid containing more than 40% Klozur® CR. If such an occasion should arise, then additional information about a variance can be found in the February 15, 2005 acceptance letter for FMC Corporation's sodium persulfate.

The Division of Waste Management, using information provided by FMC Corporation, has done dilution calculations to create the table below. Users of Klozur® CR can refer to this table to identify the temporary injection zone of discharge parameters to be monitored for the concentration of Klozur® CR in the fluid that they propose to inject.

Temporary Injection Zone of Discharge Parameters for Concentrations of Klozur® CR in the Fluid to be Injected							
	0.062 wt% or greater	0.165 wt% or greater	20 wt% or greater	30 wt% or greater	40 wt% or greater	Obtain zone of discharge permission for this parameter by way of:	Florida Groundwater Standard
pH	X	X	X	X	X	Rule 62-522.300(2)(c)	6.5-8.5
Total Dissolved Solids	X	X	X	X	X	Rule 62-522.300(2)(c)	500 mg/L
Sulfate	X	X	X	X	X	Rule 62-522.300(2)(c)	250 mg/L
Sodium		X	X	X	X	Rule 62-522.300(2)(c)	160 mg/L
Manganese			X	X	X	Rule 62-522.300(2)(c)	0.05 mg/L
Iron				X	X	Rule 62-522.300(2)(c)	0.3 mg/L
Chromium					X	Variance	0.1 mg/L
mg/L = milligrams per liter							

- f. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Division has no objection to the use of some wells for the application of Klozur® CR. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply Klozur® CR. This will avoid premature conclusions that the entire site meets cleanup goals. By making sure that designated tracking wells are not also used for treatment, there will be more assurance that the treatment process has permeated the entire site and that it did not remain localized to the area immediately surrounding each injection well.
- g. Avoidance of migration: For injection-type, in situ aquifer remediation projects, pursuant to Rule 62-528.630(3), F.A.C., injection of Klozur® CR shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either the Klozur® CR or the contaminants of concern in the aquifer results.
- h. Abandonment of wells: Upon issuance of a Site Rehabilitation Completion Order, injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C., and the Underground Injection Control Section of the Department shall be notified so that the treatment wells can be removed from the injection well inventory-tracking list.
- i. Open-pit applications: While open-pit application of Klozur® CR is not an injection-type application, and notification of the Underground Injection Control Section therefore not required, the user must still be mindful of groundwater quality. For open-pit applications, the Division of Waste Management suggests that groundwater in the application area be sampled for the same parameters that would have been monitored had the application been an injection.

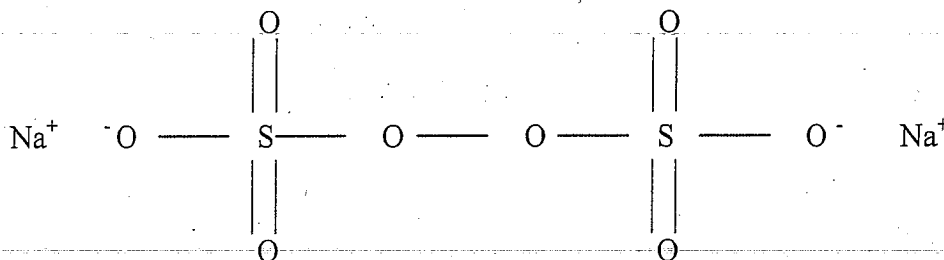
SUPPLEMENTAL INFORMATION

- a. Two components: Klozur® CR is a blend of FMC Corporation's sodium persulfate and calcium peroxide. The sodium persulfate component was accepted as Klozur™ Activated Persulfate on February 25, 2005, and the calcium peroxide component was accepted as PermeOx Plus on March 31, 2004.
- b. Uses: Klozur® CR can be used for the remediation of petroleum and other suitable contaminants. Those other contaminants include but are not necessarily limited to chlorinated ethenes (PCE, TCE, DCE), chlorinated ethanes (TCA, DCA, vinyl chloride), chlorinated methanes (carbon tetrachloride, chloroform, methylene chloride) and 1,4-dioxane.
- c. Solubility and service life: The solubility of sodium persulfate at 25° C is 73% by weight. FMC Corporation indicates that the lifetime of persulfate in the subsurface is on the order of several months. During this period, the persulfate performs a relatively quick destruction of contaminants in bulk via chemical oxidation. After this period, sulfates that were generated by the decomposition of the persulfate support the co-metabolism of residual contaminants.

The calcium peroxide component of Klozur® CR is essentially insoluble, forming a slurry when mixed with water, not a solution. FMC indicates that the calcium peroxide can release oxygen for aerobic biodegradation of contaminants for up to 9 months. Upon hydration, the calcium peroxide releases hydrogen peroxide. The hydrogen peroxide then breaks down into oxygen and water.

- d. Pilot study: The Division of Waste Management anticipates that a pilot study will usually be conducted when Klozur® CR is contemplated for use at a cleanup site, regardless of whether the contaminants of concern are petroleum or hazardous waste. In the case of petroleum, per Rule 62-770.700(2), F.A.C., it is required that a pilot study proposal be submitted for review, and that a pilot test be performed prior to the design of a full-scale treatment system. If conditions at a site do not warrant a pilot study, then a proposal explaining the rationale to forego it must be submitted for review. For hazardous waste cleanups, the decision to conduct a pilot study should be made in accordance with applicable rules and regulations.
- e. Dosage and delivery: It is recommended that Klozur® CR dosage be determined on a site-specific basis. Typical ranges are provided in the table below. As with any chemical-type remediation product, the Division of Waste Management advises that the applied dose be no greater than necessary. In this way, there can be a minimization of the risk that temporary zone of discharge time will expire before residual concentrations of the product's "ingredients of concern" have fully returned their groundwater standards or their natural-occurring background levels at the site, whichever is less stringent.

- Dosage:
 - 1 to 50 grams of Klozur® CR per liter groundwater
 - 1 to 100 grams of Klozur® CR per kilogram of soil
 - 1 to 10 pounds of Klozur® CR per square foot of excavation treatment area.
 - Delivery methods:
 - Injection, either by conventional injection well or direct-push.
 - For remediation of soil, can be applied by tilling, auguring or other mechanical methods.
- f. Chemical processes at work: FMC indicates that Klozur® CR destroys contaminants by both direct oxidation and by free radical mechanisms involving sulfate radicals. It is also indicated that these radicals last longer in the subsurface than hydroxyl radicals.
- g. Stoichiometry: FMC indicates that a stoichiometric ratio for radical destruction is rather difficult to present, but that a ratio for direct oxidation can be shown by example for the complete mineralization of benzene. The ratio is 15 moles of sodium persulfate $[\text{Na}_2\text{S}_2\text{O}_8]$ at 238 grams per mole to 1 mole of benzene $[\text{C}_6\text{H}_6]$ at 78 grams per mole. On a weight basis, this is equivalent to 45.8 grams of sodium persulfate to 1 gram of benzene.
- h. Molecular structure of sodium persulfate:



- i. Oxidation potential: The persulfate anion produced by sodium persulfate is a relatively powerful oxidant, and the sulfate radical produced is more powerful still. Their oxidation potentials, in volts (V), relative to some other oxidants, are shown below.

Highest Oxidation Potential	2.7 V	Hydroxyl Radical ($\bullet\text{OH}$)
	2.6 V	Sulfate Radical ($\text{SO}_4^\bullet$)
	2.2 V	Ozone (O_3)
	2.1 V	Persulfate anion ($\text{S}_2\text{O}_8^{2-}$)
	1.8 V	Hydrogen Peroxide (H_2O_2)
	1.7 V	Permanganate Anion (MnO_4^-)
Lowest Oxidation Potential	1.4 V	Peroxymonosulfate Anion (HSO_5^-)

j. Comparison to other oxidant chemistries: In addition to oxidizing strength, FMC points out the following in regard to persulfate and sulfate radical oxidation.

- The radical oxidation is kinetically fast.
- The persulfate is more stable than hydrogen or the hydroxyl radical, so there is more of an opportunity for it to last longer and travel further in the subsurface.
- Persulfate has less affinity for natural soil organics than permanganate, thereby making it more efficient in applications in high organic soils.

k. Safety reminders:

- Use of proper protective clothing.
- Oxidation is an exothermic reaction.
- Use storage containers, tanks and piping constructed of 304 or 316 stainless steel, polyvinyl chloride, polyethylene, Plexiglas, Teflon or glass for sodium persulfate. Do not use soft metals such as copper, brass or carbon steel.
- Disposal of sodium persulfate must be handled as a hazardous waste disposal.

Memorandum**Florida Department of
Environmental Protection**

TO: Cathy McCarty, P.G.
Florida Department of Environmental Protection
Bureau of Water Facilities Regulation
Underground Injection Control Section - MS 3530
2600 Blair Stone Road, Tallahassee, FL 32399-2400

FROM: _____

DATE: _____

SUBJ: **Proposed Injection Well(s) for In Situ Aquifer
Remediation at a Remedial Action Site**

Pursuant to paragraph 62-528.630(2)(c), F.A.C., inventory information is hereby provided regarding the proposed construction of temporary injection well(s) for the purpose of in situ aquifer remediation at a contaminated site.

Facility name: _____

Facility address: _____

City/County: _____

Latitude/Longitude: _____

FDEP Facility Number: _____

Facility owner's name: _____

Facility owner's address: _____

Well contractor's name: _____

Well contractor's address: _____

Cathy McCarty, P.G.
Page 2 of 4
Date: _____

Facility name: _____
FDEP facility no.: _____

AFFECTED AQUIFER

Name of aquifer: _____
Depth to groundwater (feet): _____
Aquifer thickness (feet): _____
Areal extent of contamination (square feet): _____

INJECTION WELLS

A site map showing the location and spacing of injection wells, the areal extent of the groundwater contamination plume, and associated monitoring wells is attached. The injection well(s) features are summarized below, and/or a schematic of the injection well(s) is attached.

Direct-push or HSA/Mud rotary (*circle the appropriate well type*)
Diameter of well(s) (i.e., riser pipe & screen) (inches): _____
Total depth of well(s) (feet): _____
Screened interval: _____ to _____ feet below land surface
Grouted interval: _____ to _____ feet below land surface
Casing diameter, if applicable (inches): _____
Cased depth, if applicable: _____ to _____ feet below land surface
Casing material, if applicable: _____

PROJECT DESCRIPTION

The in situ, injection-type aquifer remediation product/process remediates contaminants by:
(check those that apply)

- ☐ bioremediation,
☐ chemical oxidation, or
☐ other (describe) _____

Brief description of the project:

Summary of major design considerations and features of the project:

Number of injection wells: _____
Injection volume per well (gallons): _____
Single or multiple injection events: _____
Injection volume total (all wells, all events): _____

FLUID TO BE INJECTED

Composition of injected fluid:
(ingredient, wt. %): _____

TEMPORARY INJECTION ZONE OF DISCHARGE (ZOD)

(check those that apply)

- ☐ No ZOD needed. The fluid to be injected meets the primary and secondary groundwater standards of Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapters 62-520 and 62-777, F.A.C.
- ☐ ZOD permission by rule 62-522.200(2)(c), F.A.C., for reagent chemical species and/or parameter(s) in the fluid to be injected (or re-injected) that exceed secondary groundwater standards. ZOD permission by this rule also applies to chemical species in the fluid to be injected that exceed primary groundwater standards or minimum groundwater criteria, provided those species are prime constituents of the reagents used to remediate site contaminants. The list of chemical species and parameters for which the approved Remedial Action Plan identifies zone size, duration and groundwater monitoring are as follows:

- ☐ ZOD permission by rule 62-522.200(2)(c), F.A.C., for the following contaminants of concern that exceed their groundwater standards in the fluid to be re-injected as part of a closed-loop re-injection system for which the approved Remedial Action Plan identifies zone size, duration and groundwater monitoring:

- ☐ ZOD permission by variance because fluid to be injected contains the following impurities that are not prime constituents of the reagents used to remediate the site's contaminants, and the concentration of those impurities in the fluid to be injected are in excess of their primary groundwater standards:

☐ A variance needs to be granted before the remediation can be conducted.

☐ A variance has already been granted for the impurities listed above:

Date variance granted: _____ Zone size (feet): _____ Duration (time): _____

..... ◆◆◆

- ☐ If ZOD permission by rule 62-522.200(2)(c), F.A.C., or by variance is checked above, then a figure that delineates the ZOD is attached, or ☐ the ZOD is described as follows:

Cathy McCarty, P.G.
Page 4 of 4
Date: _____

Facility name: _____
FDEP facility no.: _____

CLEANUP CRITERIA AND ENFORCEABLE APPROVAL ORDER

In situ injection-type aquifer remediation of the contaminants of concern at this site is intended to meet the groundwater cleanup target levels established for them in accordance with applicable and appropriate chapters of the Florida Administrative Code and cited in the approved Remedial Action Plan. Additionally, all other groundwater standards will be met at the time of project completion for any residuals associated with the ingredients of the injected remediation products, and any by-products or intermediates produced as a result of the chemical or biochemical transformation of those ingredients or the contaminants of concern during their use. Applicable primary and secondary drinking water standards are set forth in Chapter 62-550, F.A.C., and additional groundwater quality criteria are set forth in Chapters 62-520 and 62-777, F.A.C.

The remediation plan estimates that site remediation will take _____ months. We will notify you if there are any modifications to the remediation strategy which will affect the injection well design or the chemical composition and volume of the injected remediation product(s).

The proposed remediation plan was approved on _____ by an enforceable approval order. A copy is attached. The remediation system installation is expected to commence within 60 days. Please call me at _____ if you require additional information.