



Department of Environmental Protection

Jeb Bush
Governor

Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Colleen M. Castille
Secretary

February 25, 2005

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

Re: **Klozür™ Activated Persulfate**

Dear Dr. Block:

The Bureau of Petroleum Storage Systems hereby accepts Klozür™ Activated Persulfate for the remediation of petroleum and other suitable contaminants in groundwater and soil, in situ and ex situ, via chemical oxidation. As FMC has indicated, Klozür™ is sodium persulfate that is used in combination with an activator to destroy contaminants. The activator can be divalent metals such as ferrous sulfate, chelated metals such as chelated iron, hydrogen peroxide, pH modifiers, or heat.

This acceptance applies only to the regulatory jurisdiction and the remediation needs of the Bureau of Petroleum Storage Systems, which is primarily the cleanup of subsurface petroleum contamination pursuant to Chapter 62-770, Florida Administrative Code (F.A.C.). Other state agencies and local governments may choose to recognize this acceptance if their needs and regulations are similar. This Bureau, however, is not responsible for applications beyond its jurisdiction.

For vadose remediation, where the underlying groundwater will not be affected by the leaching of Klozür™, there are no special concerns beyond those that would normally need to be addressed in preparing a Remedial Action Plan and conducting a cleanup in accordance with Chapters 62-770 and 62-777, F.A.C. However, for injection-type, in situ groundwater remediation, via direct injection of Klozür™ into an aquifer, there are underground injection control regulations that must be observed. Since injection-type, in situ aquifer remediation is likely to be the most common application of this product, the bulk of the regulatory requirements discussed herein will be directed to that topic.

"More Protection, Less Process"

Visit Our Internet Site At: www.dep.state.fl.us/waste/categories/pcp/default.htm

Printed on recycled paper.

The Bureau recognizes Klozür™ as a viable product for the remediation of petroleum contaminated sites in Florida. There are no objections to its use provided: (a) the considerations of this letter are taken into account; (b) a site-specific Remedial Action Plan is submitted pursuant to Chapter 62-770, F.A.C., and approved by the Department for each site where the use of Klozür™ is proposed; and (c) the Remedial Action Plan specifies the injection zone of discharge size and duration for sodium, sulfate, total dissolved solids, pH, iron and manganese, and proposes adequate groundwater monitoring for them pursuant to Rule 62-522.300(2)(c), F.A.C. Some major regulatory considerations that apply to Klozür™ are discussed in Enclosure 1.

While the Department of Environmental Protection does not provide endorsement of specific or brand name remediation products or processes, it does recognize the need to determine their acceptability from an environmental standpoint with respect to applicable rules and regulations, and the interests of public health and safety. Vendors must then market the products and processes on their own merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace. In no way, however, shall this regulatory acceptance letter be construed as Department certification of performance. Additionally, the Department emphasizes a distinction between its regulatory “acceptance” letters and an approval. Products and processes are accepted but they are not approved.

Also, 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 and appropriate rules and regulations, especially those of the Florida Administrative Code pertaining to underground injection control.

Those who prepare Remedial Action Plans are advised to include a copy of this letter in the appendix, and call attention to it in the text of their document. In this way, technical reviewers will be informed that you have contacted the Department of Environmental Protection to inquire about the environmental acceptability of Klozür™. To aid those reviewers, the Bureau of Petroleum Storage Systems provides supplemental information as Enclosure 2.

The Department reserves the right to revoke its acceptance of a product or process if it has been falsely represented. Additionally, Department 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

Philip A. Block, Ph.D.
February 25, 2005
Page 3

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. You may contact me at (850) 877-1133, extension 29, if there are any questions.

Sincerely,

Rick Ruscito, P.E.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

Rebecca S. Lockenbach
FDEP Section Leader
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

c: Tom Conrardy - FDEP/Tallahassee

ppl #258
inn_125.doc
2/25/05

REGULATORY CONSIDERATIONS

For Klozür™ applications, the major regulatory considerations are listed below.

- a. Groundwater cleanup standards: The onus shall be on users of Klozür™ to ensure that all applicable groundwater contaminant standards will be met at the time of project completion, for petroleum and other contaminants that may be present, any residuals associated with the ingredients of Klozür™ and any byproducts produced as a result of chemical or biochemical reactions involving those ingredients. The following chapters of the Florida Administrative Code (F.A.C.) are cited: Chapter 62-550, F.A.C., for primary and secondary water quality standards; Chapter 62-520, F.A.C. for groundwater classes and standards, and minimum criteria; 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; Chapter 62-770, F.A.C., for petroleum cleanup criteria; and Chapter 62-777, F.A.C., also for cleanup and minimum groundwater criteria.

A noteworthy aspect of the minimum criteria set forth in Chapter 62-520, F.A.C., is that it requires groundwater to be free from substances that are harmful to plants, animals, and organisms, and free from substances that are carcinogenic, mutagenic, teratogenic or toxic to human beings. In effect, these “free from” requirements form a catchall. They close what would otherwise be a loophole in the regulations by preventing injection of a potentially harmful product in the event that any of its ingredients is not regulated as a specific primary or secondary drinking water contaminant.

- b. Injection well permit: The issuance of a site-specific Remedial Action Plan Approval Order by either the Bureau of Petroleum Storage Systems or the Bureau of Waste Cleanup, for remediation via injection of Klozür™ into an aquifer, constitutes the granting of a Class V injection well permit. [62-528.630(2)(c) and 62-528.640(1)(c), F.A.C.]
- c. Groundwater injection standards: For in situ aquifer remediation, the composition of an injected fluid must meet the 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 an injection zone of discharge. Depending on the ingredients 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. For Klozür™ sodium persulfate injection at concentrations of 20 percent or less, by weight, only Rule 62-522.300(2)(c), F.A.C., needs to be observed in order to be permitted an injection zone of discharge for the following six (6) parameters: sodium, sulfate, total dissolved solids, pH, iron and manganese. At concentrations greater than 20 percent, the rule still applies to the same 6 parameters, but a variance that grants an injection zone of discharge for chromium is also necessary.
- d. Zone of discharge by rule: For the injection of Klozür™ sodium persulfate at concentrations of 20 percent or less, by weight, Rule 62-522.300(2)(c), F.A.C., applies to sodium, sulfate, total dissolved solids, pH, iron and manganese. Each site-specific Remedial Action Plan proposing its use must: (a) indicate that the concentrations of sodium, sulfate, and total

dissolved solids, iron, and manganese in the fluid to be injected will be in excess of their groundwater injection standards, and that its pH may not meet groundwater standards; (b) specify a temporary zone of discharge size; (c) specify the period of time for which the temporary zone of discharge will be needed; and (d) propose groundwater monitoring of these parameters. The current groundwater standards for the Klozür™ parameters that require a zone of discharge by rule are sodium (160 milligrams per liter, mg/L), sulfate (250 mg/L), total dissolved solids (500 mg/L), iron (0.3 mg/L), manganese (0.05 mg/L), and pH (range 6.5 to 8.5). If the groundwater's natural-occurring background level of any of these 6 parameters at a specific remediation site does not meet the established groundwater standard, then the residual level of that parameter by the time remedial action ends shall be no worse than the pre-existing, pre-injection background level.

- e. Variance: In order for Klozür™ sodium persulfate to be used for injection-type, in situ aquifer remediation at concentrations greater than 20% by weight, Rule 62-522.300(2)(c), F.A.C., still applies to 6 parameters as discussed above in paragraph d, but FMC Corporation must also obtain a variance for a deviation from Rule 62-522.300(3), F.A.C., in order to allow a temporary injection zone of discharge for chromium, which is not a prime constituent of the reagents needed for the remediation. Once granted, a variance will allow a temporary zone of discharge of specified dimensions around each injection point (usually expressed as a radius of influence) for a specified period of time. By the end of the time period, the groundwater concentration of any residual chromium in the zone of discharge must not exceed the 0.1-milligram per liter (mg/L) maximum allowed by Chapter 62-550, F.A.C. If the groundwater's natural-occurring background concentration of chromium at a specific remediation site is already in excess of the established groundwater standard, then its residual concentration at the completion of remediation shall be no greater than the pre-existing background concentration.

If the variance granted by the Department is not site-specific, then it may be considered as portable from one Klozür™ cleanup project to another in Florida, provided a site-specific Remedial Action Plan is submitted for each site. With a portable variance, FMC Corporation and users of Klozür™ do not have to petition for a new variance each time Klozür™ is proposed for the remediation of a site, provided there is no deviation from the terms of the variance. Instructions on how FMC can petition for a temporary injection zone of discharge variance are currently located at web page www.dep.state.fl.us/waste/categories/pcp/pages/innovative.htm.

- f. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Department has no objection to the use of some wells for the application of Klozür™. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply Klozür™ reagents. 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. Groundwater monitoring:

1. Active remediation petroleum monitoring: During the period of active remediation, groundwater shall be monitored in accordance with the requirements set forth in Section 62-770.700, F.A.C., for the petroleum contaminants of concern.
 2. Post remediation petroleum monitoring: At least one (1) year of quarterly post remediation groundwater monitoring for the petroleum contaminants of concern shall be conducted at a minimum of two (2) wells, one located in the area of maximum petroleum contamination, the other downgradient of the area of maximum petroleum contamination, pursuant to Section 62-770.750, F.A.C.
 3. Underground injection control monitoring: For Underground Injection Control purposes, when Klozür™ sodium persulfate is injected at concentrations of 20 percent or less, by weight, the groundwater must be monitored pursuant to Rule 62-522.300(2)(c), F.A.C., for the 6 parameters discussed above in paragraph *d*. And for the injection of Klozür™ sodium persulfate at concentrations greater than 20 percent, the groundwater will also have to be monitored for chromium, per the terms of an injection zone of discharge variance.
- h. Underground injection control inventory: Remedial Action Plans prescribing injection-type in situ aquifer remediation shall include information pursuant to Rule 62-528.630(2)(c)1 through 6, F.A.C., for the inventory purposes of underground injection control. Per Rule 62-528.630(2)(c), F.A.C., aquifer remediation projects involving injection wells may be authorized under the provisions of a Remedial Action Plan, provided the construction, operation, and monitoring requirements of Chapter 62-528, F.A.C., are met. A memorandum outlining the inventory information about injection-type aquifer remediation plans to be transmitted by Department reviewers to the Underground Injection Control Section is provided as Enclosure 3. Only reviewers within the Department, including its district offices, may approve in situ injection-type remediation plans in which the approval constitutes a Class V injection permit; local programs are not authorized to grant such approvals. See Enclosure 2.
- i. Operation:
1. Avoidance of migration: For injection-type, in situ aquifer remediation projects, injection of the Klozür™ reagents shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either the reagents or the petroleum contaminants in the aquifer results, pursuant to Rule 62-528.630(3), F.A.C.
 2. Underground injection control operating permit: Although an operating permit is not required for aquifer remediation wells pursuant to Rule 62-528.640(1)(b), and 62-528.640(1)(c), F.A.C., since no movement of the petroleum contamination plume is expected to accompany the treatment process, the Department requests that the information items listed in Rule 62-528.640(1)(b), F.A.C., be considered and included in Remedial Action Plan proposals as a matter of good and thorough design practice. Briefly summarized, they are: quality of water in the aquifer; quality of the injected fluid;

existing and potential uses of the affected aquifer; and well construction details. Additionally, each Remedial Action Plan should clearly indicate the total volume of the Klozür™ reagents that will be injected.

- j. Abandonment of wells: Upon issuance of a petroleum Site Rehabilitation Completion Order, or a declaration of “No Further Action”, injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C. The Underground Injection Control Section of the Department shall be notified so that the injection wells can be removed from the inventory-tracking list.
- k. Open-pit applications: While open-pit application of Klozür™ reagents is not an injection-type application, and notification of the Underground Injection Control Section therefore not required, the user of Klozür™ must still be mindful of groundwater quality. For open-pit applications, the Bureau of Petroleum Storage Systems suggests that groundwater in the application area be monitored for the same parameters that would be monitored had the application been an injection.

SUPPLEMENTAL INFORMATION

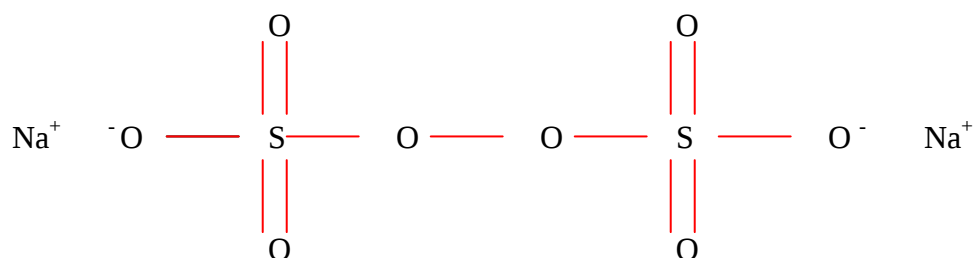
- a. Department of Environmental Protection reviewers of injection-type in situ aquifer remediation plans, regardless of whether in Tallahassee or district offices, must fill in the blanks on the Enclosure 3 memorandum, whose subject is “Proposed Injection Well(s) for In situ Aquifer Remediation at a Petroleum Remedial Action Site”. The completed form must be submitted to the Underground Injection Control Section at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400 (Mail Station 3530).

Only reviewers within the Department and its district offices may approve injection-type in situ remediation plans in which the approval constitutes the issuance of a Class V injection permit; local programs are not authorized to grant such approvals. Reason: Although an arrangement between the Environmental Protection Agency and the Department delegates underground injection control authority to the Department, it does not allow the Department to delegate that authority any further. This includes delegation to the Department’s contracted remediation review agencies such as those operated by the counties and other local governments.

- b. Pilot study: Per rule 62-770.700(2), Florida Administrative Code (F.A.C.), a pilot study proposal shall be submitted for review, and a pilot test shall be performed prior to designing a treatment system. If conditions or the situation at a site does not warrant a pilot study, then a proposal explaining the rationale for the decision not to perform a pilot study shall be submitted for review. Reviewers are encouraged to use judgment in balancing cost and the need for technical information to be obtained from a pilot study.
- c. Dosage and application: It is recommended that the dosage and details of a Klozür™ application be determined on a site-specific basis, but for information and planning purposes, the following rules-of-thumb may be helpful:

- | | |
|--|--|
| - Concentration of sodium persulfate <u>in the fluid to be injected</u> : | As recommended by FMC, typically 10 to 20%, although solutions up to 40% may be formulated. (The solubility of sodium persulfate at 25° C is 73% by weight.) |
| - Dosage: | 1 to 20 grams of Klozür™ persulfate per liter groundwater
1 to 20 grams of Klozür™ persulfate per kilogram of soil |
| - Concentration of activator <u>in the groundwater</u> for 4 chemical activator options: | (1) 100 to 700 mg/L of <u>iron</u> , when ferrous sulfate alone is activator.
(2) Same iron concentration as option 1 but also with either an ethylenediamine tetracetic acid (EDTA) or sodium citrate chelant concentration in the range of 523 to 7322 mg/L
(3) 0.14 to 42.8 <u>grams</u> /L of hydrogen peroxide
(4) Concentrations and quantities of bases such as sodium hydroxide, potassium hydroxide, and sodium carbonate, as determined by a site-specific titration of the groundwater, to raise its pH into the range of 10 to 12 |
| - Thermal activation: | Heat the groundwater to the 35° C to 60° C temperature range.
Examples: steam, resistive heating, electrical heating. |
| - Delivery methods: | Injection, either by conventional injection well or direct-push.
For remediation of soil close to surface, can be applied by tilling. |

- d. Chemical processes at work: FMC indicates that Klozür™ persulfate destroys contaminants both by direct oxidation and by free radical mechanisms involving sulfate radicals. It is also indicated that these radicals last longer (a matter of weeks to months) in the subsurface than do hydroxyl radicals.
- e. 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 [Na₂S₂O₈] at 238 grams per mole to 1 mole of benzene [C₆H₆] at 78 grams per mole. On a weight basis, this is equivalent to 45.8 grams of sodium persulfate to 1 gram of benzene.
- f. Molecular structure of sodium persulfate:



- g. Application of activator and sodium persulfate: The activator and the sodium persulfate can be applied together (simultaneously) or separately (sequentially).
- h. Oxidation potential: The persulfate anion produced by Klozür™ 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 (•OH)
	2.6 V	Sulfate Radical (SO₄•)
	2.2 V	Ozone (O ₃)
	2.1 V	Persulfate anion (S₂O₈⁻²)
	1.8 V	Hydrogen Peroxide (H ₂ O ₂)
	1.7 V	Permanganate Anion (MnO ₄ ⁻)
Lowest Oxidation Potential	1.4 V	Peroxymonosulfate Anion (HSO ₅ ⁻)

- i. Comparison to other oxidant chemistries: In addition to oxidizing strength, FMC points out these advantages of persulfate and sulfate radical oxidation.
- Radical oxidation is kinetically fast.
 - The persulfate is more stable than hydrogen or hydroxyl radical, so there is more opportunity for it to last longer and travel further in the subsurface.
 - The persulfate has less affinity for natural soil organics than permanganate, thereby making it more efficient in applications in high organic soils.

- j. Other contaminants: While the focus of the Bureau of Petroleum Storage Systems is on the application of remediation products and processes for its jurisdiction, which is essentially the cleanup of petroleum pursuant to Chapter 62-770, F.A.C., Klozür™ will be of interest to others for the remediation of other suitable contaminants. FMC indicates that those other contaminants include but are not limited to chlorinated ethenes (PCE, TCE, DCE), chlorinated ethanes (TCA, DCA, vinyl chloride), chlorinated methanes (carbon tetrachloride, chloroform, methylene chloride) and 1,4-dioxane.
- 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: Richard Deuerling, Mail Station 3530
Division of Water Facilities
Underground Injection Control Section
Florida Department of Environmental Protection
2600 Blair Stone Road, Tallahassee, FL 32399-2400

FROM: _____ (Note 1.)

DATE: _____

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

Pursuant to Rule 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 petroleum-contaminated site.

Site name: _____
Site address: _____
City/County: _____
Latitude/Longitude: _____
FDEP Facility Number: _____

Site owner's name: _____
Site owner's address: _____

Well contractor's name: _____ (Note 2.)
Well contractor's address: _____

Brief description of the in situ injection-type aquifer remediation project:

Summary of major design considerations and features of the project:

Areal extent of contamination (square feet): _____
Number of injection wells: _____
Composition of injected fluid (Note 3)
(ingredient, wt. %): _____

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

Richard Deuerling
Page Two
Date: _____

Site name: _____
FDEP facility no.: _____

A site map showing the areal extent of the groundwater contamination plume, and the location and spacing of injection wells and associated monitoring wells is attached.

The following is a summary description of the affected aquifer:

Name of aquifer: _____
Depth to groundwater (feet): _____
Aquifer thickness (feet): _____

The injection well(s) features are summarized below, and/or a schematic of the injection well(s) is attached.

Direct-push or Conventional (*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 surface
Grouted interval: _____ to _____ feet below surface
Casing diameter, if applicable (inches): _____
Cased depth, if applic.: _____ to _____ feet below surface
Casing material, if applic.: _____

The in situ injection-type aquifer remediation plan for this petroleum contaminated site is intended to meet the groundwater petroleum cleanup criteria set forth in Chapter 62-770, F.A.C. 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 contaminating petroleum 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 Chapter 62-520, 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.

-
- Note 1. Local programs are not authorized to approve underground injections into aquifers. Reason: Per agreement with EPA, the FDEP cannot delegate this authority. Local programs, after reviewing a Remedial Action Plan or an injection proposal document, should arrange for Department headquarters' execution of an approval order, and then complete this form. This form is primarily for use by state and local program technical reviewers, but petroleum remediation contractors may fill in all blanks except those labeled "FROM", "DATE", and "approval date", and "telephone number" blanks in the last paragraph. Those blanks should be completed only by a state or local program reviewer.
- Note 2. If an injection well installation contractor has not yet been selected, then indicate the name and address of the project's general remediation contractor/consultant.
- Note 3. Complete chemical analysis of injected fluid is required by Chapter 62-528, Florida Administrative Code. Proprietary formulations shall make confidential disclosure. Injected fluids must meet drinking water standards of Chapter 62-550, F.A.C., unless an exemption or variance has been granted.