



Florida Department of Environmental Protection

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Tallahassee, Florida 32399-2400

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January 3, 2008

Michael D. Lee, Ph.D.
Terra Systems Inc.
1053 Philadelphia Pike, Suite E
Wilmington, Delaware 19809

Re: Slow Release Substrate or SRSTTM

Dear Mr. Lee:

The Bureau of Waste Cleanup hereby accepts Slow Release Substrate (SRSTTM) as a product for in-situ anaerobic bioremediation of chlorinated hydrocarbons and other suitable contaminants in groundwater and soil. This acceptance is a revision of the Department's May 18, 2005 acceptance letter for Edible Oil Substrate (EOS) to reflect that the product name has been changed to Slow Release Substrate (SRSTTM). Since the product itself has not been changed, all other aspects of the previous acceptance letter remain in effect. SRSTTM consists of soybean oil as the primary substrate and also contains emulsifiers, surfactants and a tracer. SRSTTM is generally not applicable to remediation of petroleum hydrocarbons like benzene, toluene, ethylbenzene, and xylenes which are also anaerobically biodegradable.

For in-situ groundwater remediation, via direct injection of SRSTTM into an aquifer, there are underground injection control (UIC) regulations that must be observed. Since in-situ aquifer remediation via injection is likely to be the most common application of this product, the bulk of the regulatory requirements discussed herein will be directed to it.

The Bureau recognizes SRSTTM as a product for the bioremediation of 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 (RAP) is approved by the Department; (c) the approved RAP complies with Rule 62-522.300(2)(c), Florida Administrative Code (F.A.C.), in order to permit a temporary zone of discharge (ZOD) for soybean oil's total recoverable petroleum hydrocarbons (TRPH); polysorbate-80 surfactant; sodium (depending on the amount of sodium lactate); total dissolved solids (TDS); chloride (a contaminant degradation byproduct); and, if a bromine-containing tracer is used, bromide.

The Bureau does not provide endorsement of specific or brand name remediation products or processes; however, it does recognize the need to determine their acceptability in the context of environmental regulations and protection of public health and safety. In no way shall this regulatory acceptance letter be construed as Bureau certification of performance. Additionally, the Bureau emphasizes a distinction between its regulatory "acceptance" letter and an approval. Products and processes are accepted but they are not approved. Vendors and consultants must market the products and processes on their own merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace.

Remedial action plans that include use of an "accepted" product should include a copy of the acceptance letter in the RAP's appendix and reference it in the text of the document. To aid regulatory agency reviewers, supplemental information is provided as Enclosure 2. 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 RAP. The plan, however, must contain sufficient information about the product or process to show that it meets all applicable rules and regulations.

The Bureau reserves the right to revoke its acceptance of a product or process if it has been misrepresented. Additionally, Bureau 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 RAP. Please contact me at (850) 245-7502, if there are any questions.

Sincerely,



Gary Millington, P.E.
Program & Technical Support Section
Bureau of Waste Cleanup

c: T. Conrardy - FDEP/Tallahassee
R. Cowdery - FDEP/Tallahassee

History:

12/4/2002	1/29/2003	5/18/2005	1/03/2008
ppl #194	ppl #205	ppl #274	ppl #274
inn_094.doc	inn_094a.doc	inn_094b.doc	inn_094c.doc

ADDITIONAL INFORMATION

1. Groundwater cleanup standards: The onus shall be on users of SRS™ to ensure that all applicable groundwater standards will be met at the time of project completion for chlorinated hydrocarbons and any other contaminants of concern, any residuals associated with the ingredients of SRS™, and any byproducts produced as a result of chemical or biochemical reactions involving those ingredients. The following chapters of the Florida Administrative Code 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; and Chapter 62-777, F.A.C., for cleanup 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 which 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, or by Chapter 62-777, F.A.C.

2. Injection well permit: The issuance of a site-specific Remedial Action Plan Approval Order by the Florida Department of Environmental Protection, for remediation via injection of SRS™ into an aquifer, constitutes the granting of a state permit for a Class V injection well.
3. SRS™ ingredients: The Department will discuss the ingredients of SRS™, a proprietary product, only to the extent necessary for users to comply with regulations. SRS™ contains soybean oil, lecithin, polysorbate 80, glycerol monooleate, yeast extract, sodium lactate, and sodium bromide tracer in proprietary proportions. Those proportions were confidentially disclosed to the Department in August 2002, and the Department is safeguarding that disclosure in accordance with Florida Statutes that recognize the need to protect trade secrets.

However, Terra Systems, Inc., in correspondence dated October 23, 2002, recognizes from a practical standpoint that a minimum amount of information will have to be disclosed for regulatory purposes. At the least, the identity of those chemical species and parameters in the fluid to be injected that do not meet their groundwater standards must be disclosed, so that users can address the requirements of Rule 62-522.300(2)(c), F.A.C., to obtain a temporary zone of discharge (ZOD).

4. Glycerol monooleate: There is no minimum groundwater criterion for the glycerol monooleate component of SRSTM. In accordance with FDA regulations (21 CFR 184.1323) it can be used in food with no limitation, and is classified by the Food and Drug Administration (FDA) as GRAS (generally regarded as safe). For these reasons, the Department believes that glycerol monooleate does not have to be a chemical of concern when SRSTM is used.
5. Zone of discharge by Rule 62-522.300(2)(c), F.A.C.: In order for SRSTM to be used for in-situ, injection-type aquifer remediation, it is necessary to first obtain a temporary ZOD for the following SRSTM components: soybean oil's total recoverable petroleum hydrocarbons (TRPH); polysorbate 80 surfactant; sodium (depending on the amount of sodium lactate used); total dissolved solids (TDS); chloride (a contaminant degradation byproduct); and, if a bromine-containing tracer is used, bromide. The zone of discharge for all six (6) of these parameters is obtained by Rule 62-522.300(2)(c), F.A.C. The Department's Underground Injection Control Program in correspondence dated April 7, 2005, regarding Office of General Counsel file number OGC 05-0356, that the soybean oil and polysorbate 80 components of SRSTM are prime constituents of the reagents needed to remediate site contaminants. Since Rule 62-522.300(2)(c), F.A.C., permits a temporary ZOD for such prime constituents, there is no need to permit the ZOD by variance.
6. Meeting the requirements of Rule 62-522.300(3)(c), F.A.C.: In order to comply with Rule 62-522.300(2)(c), F.A.C., a Department-approved Remedial Action Plan proposing the use of SRSTM must: **(a)** identify the chemical species and parameters in the fluid to be injected that do not meet their groundwater standards [TRPH, polysorbate 80, sodium (depending on the amount of sodium lactate used), TDS, chloride (if significant amounts of this degradation byproduct will be generated), and bromide (if a bromine-containing tracer is used)]; **(b)** indicate the size and duration of a temporary ZOD that is needed for these parameters; and **(c)** address groundwater monitoring of these parameters before and after injection.

For the period of time that a temporary ZOD is permitted for SRSTM parameters, a temporary departure from the groundwater standards established for those parameters by Chapters 62-520 and 62-777, F.A.C., will be tolerated when SRSTM is injected for remediation purposes. By the end of the period, the groundwater must once again meet the established standards for each of these parameters, or their natural-occurring background value, whichever is less stringent.

The current maximum allowable groundwater concentrations for these parameters are as follows: TRPH, 5 milligrams per liter (mg/L); polysorbate 80, 35 mg/L; TDS, 500 mg/L; sodium, 160 mg/L; and chloride, 250 mg/L. For bromide, the standard shall be 0.05 mg/L or less, which is the concentration of bromide in "source water" for drinking water systems, per 40 CFR (Code of Federal Regulations), Part 141,

National Primary Drinking Water Regulations that qualify systems for reduced bromide monitoring. Although the monitoring for bromide per National Primary Drinking Water Regulations arises mainly as a concern for bromate (BrO_3^-) when ozone is used for disinfection, the Department reasons that the 0.05 mg/L concentration should be a suitable target level for remediation sites as well.

7. Polysorbate 80: This is a nonionic surfactant of chemical composition $\text{C}_{64}\text{H}_{124}\text{O}_{26}$, Chemical Abstracts Service (CAS) #9005-65-6. The Food and Drug Administration lists it as a food additive. The University of Florida's Center for Environmental and Human Toxicology, in correspondence dated September 24, 2001, indicated that a Department-calculated maximum allowable groundwater concentration of 35 mg/L was reasonable.

For foaming agents (a group that includes surfactants) Chapter 62-550, F.A.C., indicates that Standard Method SM 5540 can be used for the analysis of drinking water samples. The Department, having reviewed SM 5540, believes it may be a viable method for the analysis of polysorbate 80 in groundwater samples from remediation sites as well. Method SM 5540-D applies to nonionic surfactants.

8. 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 SRSTM. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply SRSTM. 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.
9. Additional nutrients: If, in the future, either Terra Systems Inc., or a user of SRSTM decides to augment SRSTM with other nutrients and/or chemicals, the injection of such nutrients and other chemicals into an aquifer must also be in accordance with the underground injection control requirements of Chapter 62-528, F.A.C., which requires that injected substances meet the drinking water standards set forth Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapter 62-520, F.A.C., which is now augmented by minimum groundwater criteria for specific chemicals listed in Chapter 62-777, F.A.C. If SRSTM is supplemented with commercially available microorganisms, then those microorganisms shall be non-pathogenic.
10. Underground injection control inventory: RAPs proposing 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 RAP, 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 the Department, including its district offices, may approve injection-type, in situ aquifer remediation plans for which the approval constitutes a Class V injection permit; local programs are not authorized to grant such approvals.

11. Operation:

- a. Avoidance of migration: For in situ injection-type aquifer remediation projects, injection of SRSTM shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either the product's ingredients or the contaminants already in the aquifer results, pursuant to Rule 62-528.630(3), F.A.C.
- b. 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 contamination plume is expected to accompany the SRSTM 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 RAP 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 RAP should clearly indicate the total volume of SRSTM that will be injected.

12. Abandonment of wells: Upon issuance of a 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.

ENCLOSURE 2

SUPPLEMENTAL INFORMATION

The information below, compiled from several sources, may be helpful to reviewers of RAPs prescribing bioremediation.

- 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, "Proposed Injection Well(s) for In-Situ Aquifer Remediation at a Remedial Action Site". The completed form must be submitted to the Underground Injection Control Section at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400.

Only the Department and its district offices may approve in-situ injection-type remediation plans in which the approval constitutes the issuance of a Class V injection permit. Local programs are not authorized to grant such approvals. 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 to others. This includes delegation to the Department's contracted remediation review agencies such as those operated by the counties and other local governments.

- b. Dosage and application rate: Terra Systems indicates that the theoretical dosage of soybean oil, the key component of SRS™, is established by the electron demand of the contaminants to be dechlorinated. (SRS™ is 60% percent soybean oil.) An example provided by Terra Systems is for perchloroethylene (PCE). As indicated by Terra Systems, biodegradation of 1 gram of the oil provides approximately 0.38 electron equivalents. One mole of PCE requires 8 electron equivalents or 0.048 electron/g PCE. If all the electrons from the soybean oil were used for PCE dechlorination, then 1 gram of the oil would support the biodegradation of 7.9 grams of PCE. The same reasoning applies to other contaminants to be degraded. The Department suggests that users of SRS™ consult Terra Systems for the determination of dosages for site-specific conditions.

Each mole of soybean oil was estimated to produce 13.7 moles of hydrogen based upon the metabolism of the various components of the soybean oil. Each mole of PCE with a molecular weight of 165.8 g requires 4 moles of hydrogen (8 g) or the equivalent of 0.048 g hydrogen per g PCE. To biodegrade one pound of PCE, 0.47 pound of soybean oil would be required based upon an estimated average molecular weight of the soybean oil of 266. Since SRS™ typically contains 60% soybean oil, each pound of SRS™ could potentially support biodegradation of 0.78 pounds of PCE. This calculation assumes that all of the hydrogen generated from the fermentation of SRS™ goes to reductive dechlorination rather than other competing electron acceptors and neglects the hydrogen

produced by other components of SRS™. The desired residence time within the treatment zone typically varies from 30 to 60 days.

As for the application rate, Terra Systems indicates that a typical rate for SRS™ is in the range of 100 to 500 gallons per injection point. For rule-of-thumb purposes only, SRS™ applied to sand and gravel aquifers has had an observed radius of influence of at least 30 feet from the point of injection. The Department suggests that users take into account their own site-specific conditions to determine if the radius of influence for their cleanup project will be more or less than 30 feet.

- c. Degradation products: Terra Systems indicates that the long chain fatty acids in SRS™ are degraded to simpler compounds such as acetic acid, propionic acid, and butyric acid by anaerobic bacteria. These compounds are further degraded to release hydrogen and electrons that are used by dechlorinating bacteria to remove chlorides, resulting in the production of relatively innocuous products such as ethane and ethene.

Cleanup time: Like any other product or process, the cleanup time for SRS™ depends on site-specific conditions, so no attempt will be made by the Department to present cleanup times as absolute. It was indicated that chlorinated solvent contaminants at one site where SRS™ was applied decreased to non-detect levels in as little as 3 months. Another site had a 66% reduction 16 months after a single application of SRS™, and a second application has since been applied to continue the cleanup. A barrier-type application of SRS™ has also been underway now for 18 months, for which reductive dechlorination of trichloroethylene to cis-dichloroethylene has been observed, but further dechlorination to vinyl chloride and ethene or ethane has been limited. In this case, Terra Systems intends to force the dechlorination to completion by the introduction of bioaugmentation.