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Regulatory Issues and Assumptions Associated with Polymers for Subsurface Barriers Surrounding Buried Waste*

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ABSTRACT

One of the options for control of contaminant migration from buried waste sites is the construction of a subsurface barrier that consists of a wall of low permeability material. Subsurface barriers will improve remediation performance by removing pathways for contaminant transport due to groundwater movement, meteorological water infiltration, vapor- and gas-phase transport, transpiration, etc. Subsurface barriers may be used to "direct" contaminant movement to collection sumps/lysimeters in cases of unexpected remediation failures or transport mechanisms, to contain leakage from underground storage tanks, and to restrict in-situ soil cleanup operation and chemicals. Brookhaven National Laboratory is currently investigating advanced polymer materials for subsurface barriers. This report addresses the regulatory aspects of using of non-traditional polymer materials as well as soil-bentonite or cement-bentonite mixtures for such barriers.

The regulatory issues fall into two categories. The first category consists of issues associated with the acceptability of subsurface barriers to the Environmental Protection Agency (EPA) as a method for achieving waste site performance improvement.

The second category encompasses those regulatory issues concerning health, safety and the environment which must be addressed regarding barrier installation and performance, especially if non-traditional materials are to be used. Since many of EPA's concerns regarding subsurface barriers focus on the chemicals used during installation of these barriers we discuss the results of a search of the Federal Register and the Code of Federal Regulations for references in Titles 29 and 40 pertaining to key chemicals likely to be utilized in installing non-traditional barrier materials. The use of polymeric materials in the construction industry has been accomplished with full compliance with the applicable health, safety, and environmental regulations. Therefore, it is anticipated that such compliance is achievable when using these materials as subsurface barriers, the installation of which is essentially a construction operation. We also discuss here EPA's injection well regulations, which may apply to installation of subsurface barriers.

INTRODUCTION

One of the options for control of contaminant migration from buried waste sites is the construction of a subsurface barrier that consists of a wall of low permeability material. Subsurface barriers will improve remediation performance by removing pathways for contaminant transport due to groundwater movement, meteorological water infiltration, vapor- and gas-phase transport, transpiration, etc. Subsurface barriers may be used to "direct" contaminant movement to collection sumps/lysimeters in cases of unexpected remediation failures or transport mechanisms, to contain leakage from underground storage tanks, and to restrict in-situ soil cleanup operation and chemicals. (See, for example, Figure 1.) They may be used alone or in combination with techniques such as groundwater pumping, subsurface drains, and *in-situ* biological or chemical treatment methods. Slurry walls are the most commonly used subsurface barriers because they are relatively inexpensive, but grouted barriers such as grout curtains and sheet piling cut-off barriers are also used.[1] The purpose of this report is to identify the regulatory issues and assumptions associated with the use of barriers in the vadose zone to improve the performance of buried waste sites.

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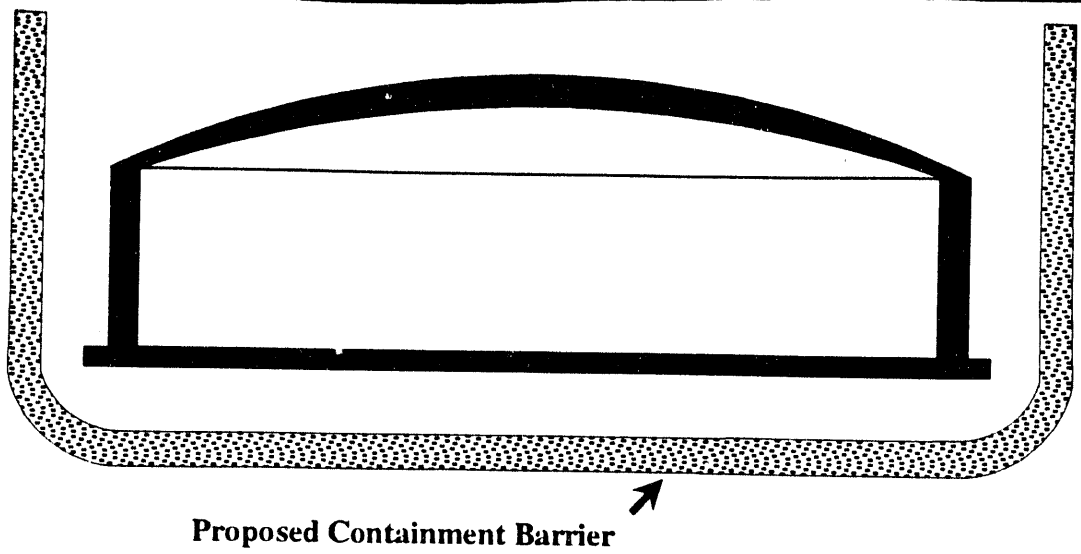

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Figure 1. A subsurface barrier to contain underground storage tanks.

The barrier material must be compatible with soil and waste conditions specific to the site and should have as low an effective diffusivity as is reasonably achievable to minimize or inhibit transport of moisture and contaminants. Portland cement grout curtains have been used for barriers around waste sites. However, large castings of hydraulic cements invariably result in cracking due to shrinkage and thermal stresses induced by the hydration reactions. For this and other reasons other low permeability, high integrity materials are being investigated through the DOE's integrated programs and demonstrations. The Environmental and Waste Technology Center at Brookhaven National Laboratory (BNL), with funding from the DOE's In-situ Remediation Integrated Program, is currently investigating advanced polymer materials for subsurface barriers. This report addresses the use of non-traditional organic polymer materials as well as the use of soil-bentonite or cement-bentonite mixtures for such barriers. Due to the widespread use and general acceptance of the traditional bentonite-based mixtures, barriers constructed from these materials will be considered a regulatory baseline.

The regulatory issues fall into two categories. The first category consists of issues associated with the acceptability of such barriers to the Environmental Protection Agency (EPA) as a method for achieving such improvement. Of particular importance for barriers constructed from fluids which are supposed to set *in-situ* is the chemical compatibility of the material with the wastes, leachates and geology with which it is likely to come in contact.

The second category encompasses those regulatory issues concerning health, safety and the environment which must be addressed regarding barrier installation and performance, especially if non-traditional materials are to be used. Since many of EPA's concerns regarding subsurface barriers focus on the chemicals used during installation of these barriers, we discuss the results of a search of the Federal Register and the Code of Federal Regulations for references in Titles 29 and 40 pertaining to key chemicals likely to be utilized in installing non-traditional barrier materials. [Title 29, Labor, includes Occupational Safety and Health Administration regulations and Title 40 is Protection of the Environment.] We also discuss here EPA's injection well

regulations, which may apply to installation of subsurface barriers constructed from either traditional or non-traditional materials.

ACCEPTABILITY OF SUBSURFACE BARRIERS

EPA has generally been flexible in its acceptance of any particular remediation technology for the cleanup of inactive hazardous waste disposal sites under the Comprehensive Environmental Response, Compensation, and Liability Act[2] (CERCLA) as long as the technology in question will result in attainment of the remediation standards referred to in Section 121(d) of that Act.

The selection of cleanup options under CERCLA is part of a larger process -- the "Superfund Process" -- which involves the following steps:

Preliminary Assessment
Site Inspection
Remedial Investigation (RI)
Feasibility Study (FS)
Record of Decision (ROD)
Remedial Design
Remedial Action

The selection of a remediation technology is dependent on the RI/FS portion of this process. The RI emphasizes data collection and site characterization for the purpose of defining the nature and extent of contamination at the site. The FS emphasizes data analysis and decision making using the RI data to develop response objectives and alternative remedial responses which are evaluated for engineering feasibility, public health protection, environmental impacts, and costs.[1]

In order to assist the stakeholders in familiarizing themselves with the range of remedial technologies available, their applications and limitations, their major design and construction considerations, and their approximate costs, EPA has published various documents, often termed "handbooks" or "technical bulletins." These are not intended as regulatory promulgations with regard to the technologies addressed but as guidance documents indicating EPA's acceptance of particular technological solutions under appropriate site-specific conditions; this means two things: (1) the technologies described in these documents still need to be evaluated for their applicability to any specific facility or site needing remediation and (2) technologies other than those mentioned in these documents may be considered although they may require more supporting technical justification than those mentioned in the documents. In this section of the report we will use several of these guidance documents to demonstrate EPA's acceptance of subsurface barriers as an alternative remedial technology for containment of contamination and reduction of future potential migration of waste constituents.

Subsurface barriers constitute a subset of one of four categories of remedial technologies for controlling groundwater contamination. These categories are:

(1) groundwater pumping involving extraction or injection of water,

(2) subsurface drains for intercepting groundwater,

(3) *in-situ* treatment to remove or attenuate contaminants in place beneath the surface, and

(4) low permeability barriers constructed underground to divert groundwater flow or minimize leachate generation and plume movement.

These technologies may be used alone or in combination for controlling the movement of groundwater contamination.

EPA has considered subsurface barriers to be among the technologies potentially applicable to remediation of waste sites. For example, in an EPA handbook[1] intended for use as a basic reference tool on remedial action, EPA devotes a whole section to subsurface barriers consisting of low permeability cut-off walls or diversions which are installed below ground to contain, capture, or redirect groundwater flow in the vicinity of a site. According to this handbook, the most commonly used subsurface barriers are slurry walls, particularly soil-bentonite slurry walls, but cement-bentonite or concrete slurry walls, grouted barriers, and sheet metal piling cut-offs have also been used for the same purpose, and grouted horizontal barriers have been used to seal the bottoms of contaminated sites. The following two subsections discuss slurry walls and grouted barriers in more detail; the final subsection addresses EPA's acceptance of subsurface barrier technology.

Slurry Walls

A recent (October 1992) EPA Engineering Bulletin[3] describes the slurry wall technology. According to this bulletin, slurry walls are applicable at Superfund sites where residual contamination needs to be isolated at its source. For example, they may be used where the waste mass is too large for practical treatment, where residuals from the treatment are landfilled, and where soluble and mobile constituents pose an imminent threat to a source of drinking water. Low-permeability slurry walls may serve one or more of the following purposes: redirect groundwater flow, contain contaminated materials and contaminated groundwater, and provide increased subsurface structural integrity. Traditional soil-bentonite or cement-bentonite slurry walls can be installed quickly, and, since the use of these barriers in the construction industry for dewatering building foundations and excavations is well established, the construction requirements and practices associated with their installation are well understood. (See, for example, a handbook published by the EPA in 1984.[4]) For this reason, we will consider the traditional slurry walls as a baseline barrier technology for the purposes of this regulatory analysis.

As an example of EPA's acceptance of the slurry wall technology, the bulletin notes that in FY 1989, there were 26 records of decision (RODs) specifying the use of slurry walls as part of the remedial action. Their construction is considered a well-established technology for effectively isolating wastes and containing the migration of hazardous constituents. They may be implemented rather quickly in conjunction with other remedial actions, but long-term monitoring is needed to evaluate their effectiveness.[3]

One caution which the EPA literature on slurry walls mentions is the detrimental effect which certain chemicals can have on slurry walls containing bentonite mixtures.[1,3,4] Certain chemicals can increase the permeability of bentonite mixtures or even result in dissolution of the

material. Some organic fluids result in desiccation and cracking of the bentonite material. In any case, the EPA literature emphasizes the necessity of compatibility testing between the slurry wall material and the chemicals it is likely to come in contact with.

Grouted Barriers

Grouting refers to the injection into a rock or soil mass of fluids which reduce the water flow and strengthen the formation by solidifying or setting in place. Grouts may be injected to form subsurface barriers in unconsolidated materials. A subsurface barrier constructed in this manner is termed a grout curtain.

Typical grouting materials, either alone or in combination, are hydraulic cements, clays, bentonite, and silicates. Organic polymer grouts, while constituting only a small fraction of the grouts in use, are of greatest interest since this will be indicative of the EPA's viewpoints and requirements on using advanced polymers for barriers. The organic polymer grouts addressed in the EPA Handbook are: Acrylamide grouts, Phenolic grouts, Urethane grouts, Urea-formaldehyde grouts, Epoxy grouts, and Polyester grouts.

Acrylamide grouts have had widespread use for structural support and seepage control in mines, soil consolidation for structural foundations, and water control and soil consolidation for tunnels, wells, and mines. Grout curtains are among the specific applications of these grouts.[1] Because acrylamide grouts have been banned in Japan as a result of several cases of aquifer contamination -- acrylamide is a neurotoxin and the polymerization accelerator, dimethylaminopropionitrile, is a suspected carcinogen -- their use in this country has virtually ceased. Several relatively non-toxic acrylate grouts have effectively replaced them.[5] The newer acrylates and polyesters are the most likely candidates for barrier applications.

As with grouts formulated from more traditional cementitious or clayey materials, the compatibility of these organic polymer grouts with the hazardous wastes, soil chemistry and leachates at any particular site needs to be ascertained before selecting a grout formulation. A thorough characterization of the waste and grout chemistry, as well as the site geochemistry, is needed.[1] The EPA Handbook[1] notes that unless the setting reactions of grouts are carefully controlled, there is the possibility of release into the ground of unreacted constituents.

The EPA Handbook concludes that no detailed assessment of the performance or reliability of grout curtains for use at hazardous waste sites is possible since this is a specialty technology seldom applied to hazardous waste sites.[1]

Conclusions Regarding EPA's Acceptance of Subsurface Barrier Technologies

EPA guidance documents describe several kinds of subsurface barriers for controlling the movement of groundwater and/or contaminants at inactive waste disposal sites. We infer from this that EPA considers subsurface barrier technology to be an acceptable method of achieving such control. The selection of subsurface barriers for any given site needing remediation and the selection of a particular barrier technology must, however, be done by means of the Superfund Process, with special emphasis on the remedial investigation and feasibility study portions. Of

particular importance for barriers constructed from fluids which are supposed to set *in-situ* is the chemical compatibility of the material with the wastes, leachates and geology with which it is likely to come in contact. EPA emphasizes this compatibility in its guidance documents, noting that thorough characterization of the waste, leachate, barrier material chemistry, and site geochemistry as well as compatibility testing the barrier material with the likely disposal site chemical environment are all required. Furthermore, EPA requires that the potential release of toxic barrier material constituents be addressed as part of the characterization and testing. **This requirement for characterization and testing applies to both traditional and non-traditional materials.**

As a result of a preliminary series of telephone calls to EPA regarding EPA's acceptance of subsurface barriers constructed from polymer materials, we found that EPA's Technology Innovation Office saw no regulatory problem with the use of polymer materials for subsurface barriers as long as the final product is inert; EPA would have no further regulatory interest in what is essentially a construction operation.**

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

Since EPA approves of the technology of subterranean barriers for remedial actions the next question is what materials are deemed acceptable for barrier construction. As mentioned earlier there can be problems of cracking, durability, and chemical compatibility of conventional portland cement or bentonite grouts. The DOE has undertaken several studies of advanced polymer systems for use in subsurface barriers at buried waste sites and underground storage tanks. The list of candidate binders included in our search have or are being considered by DOE programs for subterranean barriers. Selection was based on durability of the polymer and chemical and physical characteristics of the resin (i.e., viscosity). These included methacrylates, vinyl-ester styrene, polyester styrene, furfuryl alcohol, and polyacrylic acids. Polymer systems employ a wide variety of chemicals as promoters, catalysts, and additives. These chemical ingredients are regulated under several Federal health, safety, and environmental rules. These rules include Occupational Safety and Health Administration (OSHA) rules under Title 29 and air, water, notification, and information rules administered by the EPA under Title 40. In order to ascertain which of these rules might apply to these chemical ingredients, we utilized the LEXIS-NEXIS database to search for the chemical names and Chemical Abstracts Service (CAS) Registry numbers of these ingredients in the Federal Register for the last ten years and in the most recent Code of Federal Regulations. (For a list of the chemicals searched see Ref. 6)

OSHA Standards - Air Contaminants

Most of the chemical ingredients for non-traditional organic polymer barrier materials being investigated by BNL are regulated under 29 CFR §1910.1000, Air Contaminants. Employing standard industrial safety practices will keep exposure of the employees involved in the installation of subsurface barriers to the regulated air contaminants within the prescribed limits.

**Telephone conversation between B. Siskind, BNL, and R. Steimle, Federal Technology Users' Group, Technology Innovation Office, EPA, on February 10, 1993.

These safety practices may involve administrative or engineering controls -- the preferable first choice alternative -- and/or, if such controls cannot achieve full compliance or are not feasible, the use of protective equipment by the employees.

Clean Air Act [7]

In 10 CFR Part 60, EPA presents the New Source Performance Standards (NSPS) under the Clean Air Act. The NSPS regulations set minimum Federal air emission regulations for a variety of industrial categories, some of which, if broadly defined, could encompass grouting or subsurface barrier installation operations utilizing organic polymers. Furthermore, EPA could at some point in the future add such operations to its list of industrial categories. In any case, emissions of several of the ingredients for organic polymer barrier materials are regulated here, especially in Subpart VV - Standards of Performance for Equipment Leaks of Volatile Organic Compounds (VOC) in the Synthetic Organic Chemicals Industry (seven compounds) but also in Subpart DDD - Standards of Performance for VOC Emissions from the Polymer Manufacturing Industry (one compound - styrene).

Revisions of the Clean Air Act (CAA) have increased the list of designated hazardous air pollutants from eight to 189 and provided for future additions to the list. The amended CAA specifically includes cumene, N,N-dimethylaniline, and styrene; Federal Register notices have considered cumene hydroperoxide, triethanolamine, and [p-]toluenesulfonic acid in rules relating to the National Emission Standards for Hazardous Air Pollutants. Although the CAA lists specific hazardous air pollutants, it has shifted the regulation of hazardous air pollutants from health-based, substance-specific standards to technology-based standards applicable to categories of industrial sources. Under the amended CAA, a major source is one which has the potential to emit with emissions controls at least 10 TPY of any single hazardous air pollutant or at least 25 TPY of any combination of them. The EPA Administrator is authorized to set lesser quantities for a major source.

We note, however, that installation of a barrier is a limited time-span operation when compared to most industrial operations covered under NSPS and NESHAPs portions of the CAA regulations. It is not clear at present that installation of barriers using polymer grouts presently is or will at some future time be covered under either the NSPS or NESHAPs regulations.

Clean Water Act [8]

The Clean Water Act requires the EPA to establish technology-based effluent limitations on the quantities of specific pollutants which may be discharged by industrial facilities. These facilities must operate under a permit to discharge these pollutants. While we do not foresee discharges to surface waters routinely resulting from installation of barriers, we provide an overview if the potential applicability of the CWA for the sake of completeness. The CWA regulations list several of the chemical ingredients for organic polymer barrier materials:

> 40 CFR §116.4 includes styrene, zinc chloride, and methyl ethyl ketone peroxide in the list of designated hazardous substances and 40 CFR §117.3 provides the reportable quantities for these substances;

40 CFR Part 414 specifies the effluent guidelines and standards -- including those for five organic polymer barrier ingredients ([N,N-]dimethylaniline, styrene, cumene hydroperoxide, cumene, and zinc chloride) -- for point sources in the organic chemicals, plastics, and synthetic fibers industries, the definitions of which could conceivably encompass installation of organic polymer barriers.

Safe Drinking Water Act [9]

The Safe Drinking Water Act requires drinking water from public water supply systems -- the definition of which will apply to many DOE facility water systems -- to meet certain water quality standards at the tap. Two organic polymer barrier ingredients, styrene and zinc chloride, are mentioned in connection with the primary (Parts 141 and 142) and secondary (Part 143) drinking water regulations, respectively, and both are listed in the Drinking Water Regulations and Health advisories published by the EPA. Turbidity and microbiological limits in Part 141 could be of concern during the barrier installation process for both traditional and organic polymer barrier materials.

The Safe Drinking Water Act also addresses underground injection control (UIC); 40 CFR Part 144 specifies the permitting and other program requirements for UIC programs and Part 146 sets technical criteria and standards. UIC programs are relevant to subsurface barrier installation because the barrier installation process falls within the definition of well injection as given in Part 144. Furthermore, Part 144 prohibits well injection which could result in contamination of underground sources of drinking water in violation of the primary drinking water regulations of Part 142. These regulations apply to both traditional and organic polymer barrier materials.

Note that the term "contaminant" is not limited in the definition in any way to hazardous, toxic, pathogenic, or even merely noxious contaminants! The contaminants of concern are more specifically described elsewhere in Part 144, e.g., §144.1(g), which states that "no injection shall be authorized by permit or rule if it results in the movement of any contaminant into Underground Sources of Drinking Water (USDWs ...), if the presence of that contaminant may cause a violation of any primary drinking water regulation under 40 CFR Part 142 or may adversely affect the health of persons ... " This is reiterated in ¶144.12(a), which also states, "The applicant for a permit [in cases of interest for this report, that means DOE] shall have the burden of showing that the requirements of this paragraph are met." Later paragraphs of §144.12 describe possible actions of the Regional EPA Director in the event a Class V well may cause a violation of the primary drinking water regulations or otherwise adversely affect the health of persons; these actions include requiring an individual permit, ordering preventive or corrective actions (including closure of the injection well), or take enforcement action.

These regulations apply to installation of subsurface barriers constructed from either the traditional bentonite- or portland-cement-based materials or the non-traditional organic polymer materials. Therefore, even if the chemical ingredients for the barrier material are not of concern with respect to Part 142, the physical stresses of barrier installation, as indicated in the previous subsection of this report (3.4.1) could result in turbidity or microorganisms entering drinking water.

Superfund Amendment and Reauthorization Act of 1986 (Title III)

In response to the Bhopal disaster, the Emergency Planning and Community Right-to-Know Act addresses concerns regarding the storage and handling of toxic chemicals. Part 372 delineates the requirements for submission of information relating to the use and release of toxic chemicals and lists in Subpart D these toxic chemicals. The list in §372.65 includes the following ingredients for organic polymer barrier materials: benzoyl peroxide, styrene, cumene hydroperoxide, and cumene. A related regulation under CERCLA in 40 CFR Part 302 designates hazardous substances and reportable quantities for release of these substances; the list in §302.4 includes the following ingredients for organic polymer barrier materials: styrene, cumene, methyl ethyl ketone peroxide, and zinc chloride.

Conclusions Regarding Health, Safety, and Environmental Issues

Based on discussions with representatives of the vendors of the polymer grouting materials, we note that the use of these materials in the construction industry has been accomplished with full compliance with the applicable health, safety, and environmental regulations. Therefore, it is anticipated that such compliance is achievable when using these materials as subsurface barriers, the installation of which is essentially a construction operation. With the possible exception of the SDWA, the regulatory environment should be the same as that for utilizing these materials in building a road or in installing subsurface barriers for diverting groundwater around building foundation construction activities. We emphasize that there have been no regulatory roadblocks to such uses of these materials. Applicability of the SDWA to use of these materials in DOE site remediation will need to be determined on a site-specific basis, but as we noted in our discussion of the SDWA regulations earlier in this report if a site-specific analysis shows that direct application of a drinking water standard for groundwater protection is not justified based on anticipated risk to the public, then DOE may request an exemption, variance, or alternative concentration limit. We expect that for most, if not all cases, an assessment will result in a finding of no significant impact under the SDWA.

In order to achieve regulatory compliance for installation of subsurface barriers constructed from non-traditional materials, it is useful to be aware of what regulatory issues need to be addressed if only to be dismissed as not relevant or dealt with by routine permitting or control procedures. As we have seen in this report, the chemical ingredients for the non-traditional organic polymer barrier materials are regulated under a variety of health, safety, and environmental regulations. Most of them are regulated under 29 CFR §1910.100 as air contaminants of concern for occupational safety and health. Several of them have the potential for being subject to one or both of two sets of regulations promulgated under the Clean Air Act, namely, minimum Federal air emissions regulations for a variety of industrial categories (the New Source Performance Standards -- NSPSs) and technology-based standards for hazardous air pollutants from certain industrial categories (the National Emission Standards for Hazardous Air Pollutants -- NESHAPs). Furthermore, several of these ingredients are subject to effluent limitations under the Clean Water Act and water quality standards under the Safe Drinking Water Act. In addition, several of the ingredients are subject to information requirements regarding their use release under the Emergency Planning and Community Right-to-Know Act and the Comprehensive Emergency Response, Compensation and Liability Act. Finally, the barrier installation process itself -- apart from

chemical ingredients used in the process -- may be subject to the permitting, monitoring, and technical requirements placed on underground injection control programs by regulations promulgated under the Safe Drinking Water Act. Once again, we emphasize that permits and exemptions should be available, since these materials are commonly used in the commercial sector, often in similar applications, with full regulatory compliance.

We emphasize that while the chemical ingredients for the non-traditional barrier materials are subject to these regulations, the installation of barriers using these materials may be exempt from at least some of the environmental regulations. There are a variety of grounds for exemptions from the environmental regulations.

For example, the NSPSs set emission limitations on classes of facilities at levels reflecting the best demonstrated control technology for that category of sources. It is not clear that installation of subsurface barriers falls into any of the existing industrial source categories. In addition, the NSPS must consider the cost of emissions reductions. Also, the barrier installation process for any given remediation site occurs once over a relatively short time span as opposed to most industrial activities, which are intended to continue for years or decades, e.g., a chemical production plant. Furthermore, it is not clear that the total quantities of the regulated ingredients at any given remediation site will exceed (or even approach) levels subject to regulation. For these reasons, we believe it will be possible to justify exemption of subsurface barrier installations from the NSPS. Similar arguments could be made to justify exemption from the NESHAPs, the Clean Water Act effluent limitations, and the information requirements. (For example, is there any realistic possibility that the emissions of hazardous air pollutants could even approach the 10 TPY limits under NESHAPs or the 10,000 pounds per calendar year under the community right-to-know regulations?). While these exemptions could be justified on a generic level for barrier installation operations if typical quantities of materials and emissions from unit operations are known, generic exemption from the water quality standards and from underground injection control regulations is not likely and will have to addressed on a site-specific and barrier-specific basis; **once again, note that barriers constructed from traditional materials are subject to these regulations as well.** Also, as we have already noted, the characterization and testing required for the non-traditional materials is also required for the more traditional portland-cement- and bentonite-based materials. We recommend that generic assessments of the air and water quality impacts of barrier installations, especially those involving the non-traditional materials, be conducted where possible.

Regarding the air contamination limitations under occupational safety and health regulations, we note that installation of barriers using the traditional bentonite- or portland-cement-based materials will require controls or protective measures regarding air contamination, at least with regard to airborne dust and particulates. In any case, we do not see compliance with these regulations to be an unduly onerous burden since compliance will likely involve standard industrial safety practices.

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