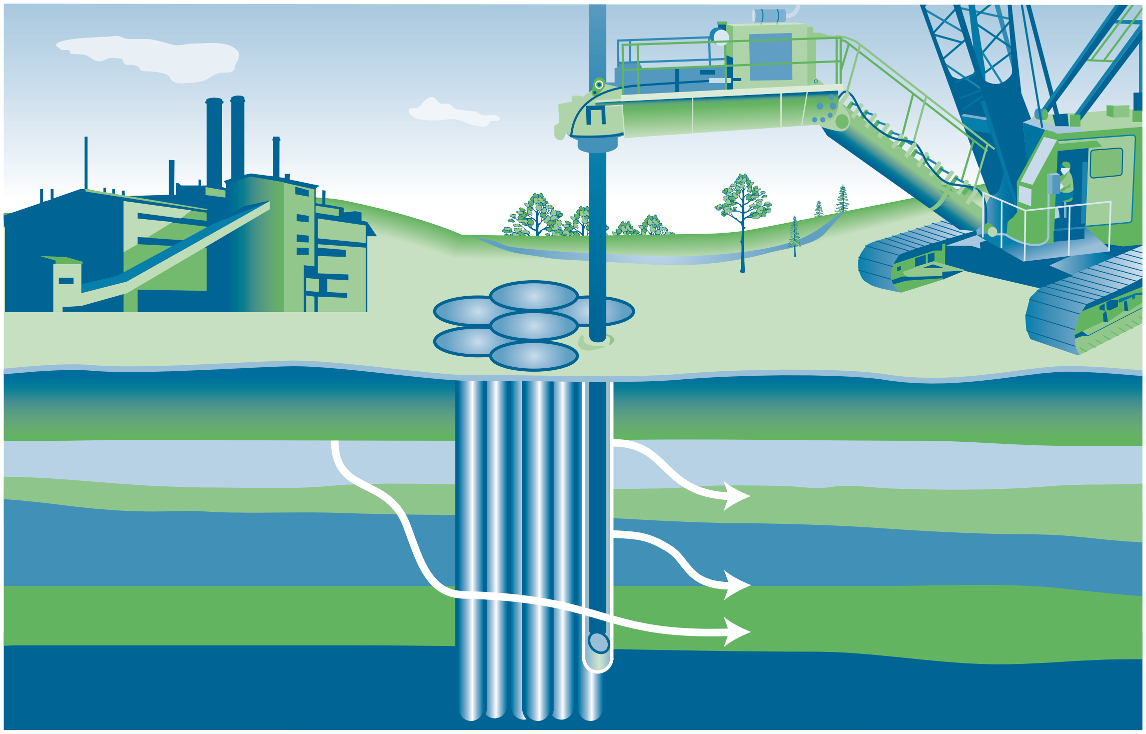
Technical/Regulatory Guidance

Development of Performance Specifications for Solidification/Stabilization



July 2011

Prepared by
The Interstate Technology & Regulatory Council
Solidification/Stabilization Team

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- South Dakota Department of Environment and Natural Resources
- Tennessee Department of Environment and Conservation
- Texas Commission on Environmental Quality
- Utah Department of Environmental Quality
- Vermont Department of Environmental Conservation
- Virginia Department of Environmental Quality
- West Virginia Department of Environmental Protection
- Wisconsin Department of Natural Resources

EXECUTIVE SUMMARY

The ITRC Solidification/Stabilization (S/S) Team was formed in 2009 to develop the technical and regulatory guidance needed to support the use of S/S technologies for the on-site treatment of contaminated soil, sediment, sludge, and waste (i.e., contaminated material). S/S remedies are designed to reduce the flux of contamination that leaches from a contaminant source to within acceptable parameters set forth in a site-specific remediation goal.

Abundant literature describes the S/S process and test methods for design and implementation. However, guidance on applicable contaminants, effectiveness, comprehensive performance specifications, and long-term performance is not widely available. Because these issues have long been a concern of regulators and site owners, the lack of readily available guidance represents a regulatory barrier with respect to the use of S/S technologies. Of particular concern is the assessment of contaminant leaching to the environment and the relationship of leaching test results to the performance of the remedy over time.

S/S technology may be applicable for a wide range of contaminants. To determine site- and contaminant-specific potential effectiveness of S/S technology, performance specifications should be used to ensure protectiveness of the remedy. Performance specifications refer to the collection of performance-related parameters, tests, and criteria used to develop an S/S treatment recipe that meets performance goals (i.e., the design targets that describe a treated material that will meet specific site remediation goals). These specifications have two purposes: (a) to guide the evaluation of the ability of the treated material to meet remediation goals and (b) to establish a minimal set of properties for evaluation during field operations to verify consistency with materials characterized in the laboratory.

As an illustration of performance specifications, leachability may be considered a primary performance parameter used to assess the ability of a material to retain a specific set of site contaminants of concern. Several different performance tests have been used to measure leachability of S/S materials, including both recognized and draft U.S. Environmental Protection Agency methods. The resultant eluate concentrations represent performance measurements describing the leachability of the S/S material. These performance measurements are typically compared to a set of predefined concentrations or action levels used as performance criteria to determine whether the solid material will leach beyond acceptable limits.

A key part of the S/S process is the role of treatability studies in providing site-specific information to evaluate the technology and to develop process design parameters and scale up for full-scale implementation. Treatability testing typically involves characterizing the untreated contaminated material and evaluating the technology performance under different operating conditions. Testing may include both bench-scale and pilot testing, although full-scale pilot testing may be considered during startup of field implementation. Once treatability testing is completed, a plan for treating the full extent of the contaminated material in the implementation phase is based on those testing results.

During implementation, achievement of material performance goals is documented through quality control testing for both compliance with material performance specifications and consistency through construction. Once a remedy has been implemented and safeguards are put in place, long-term stewardship programs are typically used to verify the remedy continues to meet material performance goals and therefore remains effective and protective of human health and the environment.

Long-term stewardship of a completed S/S remedy may include monitoring of environmental media in contact with and potentially affected by the remedy, monitoring of institutional controls, monitoring and maintenance of engineering controls, financial assurances, and periodic review(s) by the controlling environmental agency. Because the most common impact from a treated mass is to groundwater, the key long-term stewardship component is typically groundwater monitoring programs. Groundwater modeling is a valuable method for assisting in the design and evaluation of a groundwater monitoring program. An S/S remedy should be considered successful if it meets material performance goals designed to meet site groundwater cleanup criteria at established points of compliance and groundwater monitoring data show that the cleanup criteria have been met.

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1. INTRODUCTION

Solidification/stabilization (S/S) is a well-established remediation technology for treatment of contaminated soil, sediment, sludge, and waste (i.e., contaminated material). S/S is a process of blending treatment reagents[1] into contaminated material to impart physical and/or chemical changes that result in reduced environmental impact of the contaminated material to groundwater and/or surface water. Section 2 of this document provides an overview of S/S technology. S/S is one of the most common in situ technologies used at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites for source control and was the second most commonly used in situ source treatment control in fiscal years 2005–2008 (EPA 2010d).

1.1 Document Purpose

Abundant literature describes the S/S process in technical papers, guidance manuals, and case study applications; research into mineralogical and chemical process aspects; and test methods for design and implementation. However, guidance on comprehensive performance specifications, applicable contaminants, effectiveness, and long-term performance is not widely available.

Because these issues have long been a concern of regulators and site owners, the lack of readily available guidance represents a regulatory barrier with respect to the use of S/S technologies. Of particular concern is the assessment of contaminant leaching to the environment and the relationship of leaching test results to the performance of the remedy over time. Therefore, the Interstate Technology & Regulatory Council (ITRC) S/S Team has developed, and presents in this guidance document, an approach to the development of performance specifications to meet the need to confidently identify and select appropriate performance specifications for design, implementation, and monitoring of S/S remedies.

1.2 Document Scope

This document specifically focuses on processes and approaches for the treatment of contaminated materials on site, mixed with inorganic cementitious/pozzolanic reagents (the most common application of S/S) and cured in place to create a solid mass with a reduced potential for leaching and typically a lowered hydraulic conductivity. Therefore, the technology as discussed in this document is based on on-site, in situ S/S applications. Although the processes and approaches presented can often be applied more broadly to other types of S/S applications, these applications are generally not discussed in this document.

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[1] The terms “binder,” “reagent,” and “additive” are sometimes used interchangeably with respect to S/S. In this document the term “reagent” is used as a general term describing a product used to accomplish S/S treatment; “additive” refers to a product used to target specific compounds.

The approach developed by the ITRC S/S Team for developing, testing, and evaluating appropriate site-specific performance specifications and the considerations for designing appropriate long-term stewardship programs for S/S remedies will provide a useful tool for establishing an appropriate degree of treatment and regulatory confidence in the performance data to support decision making. To provide guidance on applying this approach, this document includes the following:

- an overview of the S/S technology with numerous references for more detailed information on each step in the S/S process (design, testing, implementation, etc.)
- a process for selecting appropriate performance specifications to allow practitioners to apply a consistent assessment methodology that considers the physical (e.g., strength, hydraulic conductivity), chemical (e.g., constituent retention and transport mechanisms) and site- or scenario-specific management characteristics (e.g., infiltration rate, water contact mode) of the treated materials to meet remedial action objectives (RAOs) and minimize post-treatment impacts to groundwater
- the use of treatability tests to demonstrate compliance with performance specifications and consistency between laboratory and field samples results
- a process for ensuring achievement of material performance goals through compliance with performance specifications during implementation
- long-term stewardship considerations to aid practitioners and regulators in determining site-specific approaches that provide relevant and reliable measures of remedy success
- potential stakeholder concerns in general and those concerns that may impact the development of performance specifications
- appendices to facilitate the understanding, evaluation, and selection of key performance specifications and long-term stewardship strategies described in the document text and illustrated using case study examples

This document does *not* include the following:

- S/S technology selection considerations (it assumes that the technology has already been selected for further evaluation)
- sufficient details on the technology to support detailed design and implementation of S/S as a remedy or detailed review of work plans for design and implementation of S/S (such as dust control and health and safety issues)
- regulatory requirements for materials taken off site or relocated on site after treatment, which may involve additional considerations such as Resource Conservation and Recovery Act (RCRA) waste generation or land disposal restriction (LDR) regulations
- recommendations of performance specification values or cleanup criteria applicable to S/S remediation projects

1.3 Intended Audience

This guidance can be used by regulators, site owners, and environmental practitioners as follows:

- State regulators with oversight responsibility for remediation projects where S/S is proposed, implemented, or monitored can use this guidance to do the following:

  - evaluate site-specific proposed performance specifications
  - evaluate site-specific treatability study work plans with respect to technology design
  - review construction-complete reports to ensure performance specifications were met during implementation
  - assess predicted long-term performance
  - review long-term stewardship work plans and reports
  - anticipate potential stakeholder concerns

- Environmental practitioners who prepare plans and designs, implement S/S, or monitor S/S long-term performance can use this guidance to apply an appropriate degree of treatment, develop long-term monitoring programs, and understand regulator expectations for this technology.

- Site owners with responsibility for remediation and long-term management can use this guidance to understand state regulator expectations, long-term performance, and potential stakeholder concerns.

Other audiences include the regulated community, community stakeholders, and federal regulators. This guidance will provide these readers with a common understanding of the application and limitations of S/S for site cleanup as well as an understanding of common regulator expectations for performance and monitoring criteria to measure its effectiveness.

1.4 Framing the Guidance Document

The ITRC S/S Team used several sources of input to formulate the scope and content of this document. During September and October 2009, the team conducted a survey of state regulators to identify uncertainties that may pose a potential barrier to the use of the technology. In addition, the team informally surveyed industry practitioners to ascertain real or perceived regulatory barriers and experiences in implementing S/S technology. Additional input on S/S was provided through technical sessions with the broader ITRC membership conducted in the spring of 2010. Team members reviewed and evaluated the results of these surveys to identify key issues to discuss in this document.

1.4.1 State Survey

Thirty-one states responded to the survey, with 26 states reporting implementation of S/S technologies as follows:

- the majority of states reported using the technology for treating contaminated material in situ and above the groundwater table
- the majority of identified S/S projects were performed to treat source areas
- the second greatest reported use of S/S technology was for controlling migration of nonaqueous-phase liquid (NAPL)

Only a few states that completed the survey reported having established regulations or policies related to S/S treatment; exceptions include regulations in Illinois and New Hampshire and S/S policy in Kansas. None of the responding states reported having published S/S-specific guidance;

however, some of the states that did not respond to the survey have or may have guidance or policies related to S/S. For example, Louisiana has a rule specifically related to the treatment of oil and gas exploration and production waste (Louisiana Administrative Code, Title 43, Part XIX, Chapter 313).

Most states reported using at least one parameter, such as strength, hydraulic conductivity, or leaching potential, for remedy performance specifications. However, the parameters and criteria were not consistently applied across the responding states. In addition, some states noted that S/S may not be allowed for some contaminants or is considered too difficult to implement. When asked to select one or more topics of most value for inclusion in an ITRC guidance document, 71% of reporting states identified developing performance criteria, 61% identified an approach to assessing performance, and 30% identified a discussion of ex situ versus in situ implementation.

1.4.2 Industry Concerns

A screening poll was conducted by team members of select industry practitioners to identify key regulatory barriers encountered by industry practitioners when implementing S/S. Some of the identified perceived regulatory barriers were as follows:

- requirements to achieve drinking water standards within or near the treated material
- understanding and effectively working with federal RCRA and LDR regulations to benefit S/S implementation
- length of time for review of S/S work plans (where required)
- determining appropriate locations for points of compliance (POCs)

When asked what information ITRC guidance could provide to break down these perceived regulatory barriers, the industry responders indicated the following:

- an understanding of the mechanics and limitations of S/S technology for reducing contaminant mobility, but not necessarily achieving drinking water standards
- flexibility to use S/S under the EPA Area of Contamination (AOC) Policy (EPA 1998) for RCRA cleanups regarding the consolidation and in situ treatment of materials within a defined AOC without triggering LDR (see box on page 5)

1.4.3 Other Concerns

Based on their collective experience, ITRC S/S Team members also identified monitoring of long-term performance as another barrier to the use of S/S technology because of the uncertainty regarding long-term durability of the treated material and potential for release of contaminants to groundwater. This same issue was identified as a barrier to use of S/S by the broader ITRC membership and in the United Kingdom (Environment Agency 2004a).

In reviewing all of the input on regulatory barriers as described above, ITRC S/S Team members identified the following key points to be addressed by this technical and regulatory guidance document to eliminate the barriers to technology usage:

- approach to identify and evaluate appropriate performance specifications, tests, and parameters
- appropriate implementation and post-implementation sampling and testing
- long-term stewardship to measure and verify long-term performance

Regulators and site owners must evaluate remedial technologies against appropriate criteria to determine the most effective, implementable, and appropriate technology for a site. Perceived barriers regarding the uncertainties of the evaluation and performance of the S/S technology could influence the selection of realistic, efficient, and cost-effective remedial technologies. However, the degree and likely sources of uncertainty for S/S are not different from those for many other remedial technologies. Common sources of uncertainty include errors, variations or heterogeneities in data inputs from site assessment and site models, subsurface materials and contamination levels, leaching test results, decision-support information, implementation, conceptual models, performance projections, and monitoring data. These uncertainties present challenges with respect to their impact on the effectiveness and performance evaluation process; however, the degree of uncertainty a project may tolerate should be balanced with the associated risks determined on a site-by-site basis. Data uncertainties can be minimized through (a) adequate site characterization to define heterogeneity in the subsurface, (b) well-designed treatability programs focusing on collection of appropriately representative materials to determine how best to

RCRA and S/S

Hazardous wastes that are treated using S/S technology may be subject to regulation under RCRA and as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA). RCRA regulates the disposal of hazardous waste and sets treatment standards. The LDRs included in the HSWA prohibit land disposal of hazardous waste without prior treatment as specified in the regulations. Land disposal is defined by RCRA as "'placement' of hazardous waste in a landfill, surface impoundment, waste pile, injection well, land treatment facility, salt dome formation, salt bed formation, underground mine or cave, and concrete bunker or vault" (EPA 1993c). LDRs may apply to a cleanup if "placement" occurs after the effective date of the regulations.

A simple approach to determine whether RCRA and LDRs apply to a cleanup is to step through a series of four questions:

1. Does the cleanup action constitute placement?
2. If placement occurs, is the waste a RCRA hazardous waste?
3. If the waste is a RCRA hazardous waste, is it also restricted under the LDRs?
4. Was the waste originally disposed or released after the effective date of the regulation?

When considering the first question, "placement" occurs if waste is disposed off site, such as in a landfill. For on-site disposal, determining "placement" relies on the concept of an area of contamination (AOC) or the defined areal extent of contiguous contamination. The movement of waste within the confines of an individual AOC does not, in itself, constitute "placement." But once a waste has been removed from the AOC, it cannot be returned without "placement" taking place. In the case of the fourth question, if the waste was originally disposed or released after the effective date of the regulations, then the LDRs already apply and those wastes must meet the LDR requirements regardless of whether or not they are confined to an AOC.

The focus of this guidance document is to present a process for developing performance criteria for S/S treatment that is not itself directly linked to RCRA or LDR regulations. Because the process for development of performance criteria also may be applied to ex situ treatment of contaminated material, site managers considering ex situ application of S/S should work closely with the regulating agency(s) to determine whether and how RCRA and LDRs may apply.

apply the treatment and the most appropriate methods for evaluation of treatment effectiveness, (c) appropriate performance specifications acting as a guide for the evaluation of S/S material performance, (d) quality control (QC) and consistency testing during implementation to provide field observation and verification during construction, and (e) long-term stewardship as a benchmark for demonstrating and monitoring long-term performance. This document provides background information and guidance which can reduce the uncertainties listed above associated with evaluation of the S/S process such that barriers to S/S technology use may be minimized.

1.5 Document Organization

The document is organized following the general sequence of an S/S remediation project:

- Section 2 presents an overview of S/S technology.
- Section 3 describes the behavior of treated materials in subsurface environments and defines performance specifications, key performance parameters, and available performance tests.
- Section 4 establishes a flowchart of the S/S design and implementation process, used as a guide for subsequent sections, and describes how performance specifications are used.
- Sections 5 and 6 describe the treatability testing and implementation in the context of using performance specifications.
- Section 7 discusses long-term stewardship considerations following implementation.
- Section 8 addresses potential stakeholder concerns related to the development of performance specifications for S/S-treated materials.

Appendixes are included at the end of the document to present additional information as follows:

- Appendix A—common equipment used for S/S implementation
- Appendix B—emerging EPA leaching approaches, including examples addressing contaminant release from S/S-treated materials
- Appendix C—case studies of S/S technology applications with particular emphasis on the role of groundwater modeling in long-term stewardship strategies

2. SOLIDIFICATION/STABILIZATION TECHNOLOGY OVERVIEW

This section presents a brief overview of S/S. In-depth information on S/S can be found in the literature cited in this document and elsewhere. Several useful references on the technology include Conner (1990 and 1997), the United Kingdom Environment Agency[2] (2004a, 2004b), EPA (1986, 1989, 1999a, 2009b, 2010d), Paria and Yuet (2006), Electric Power Research Institute (EPRI 2009a), and several state-of-the-practice reports produced by the U.K. Engineering and Physical Sciences Research Council's Stabilization/Solidification Treatment and Remediation Network (STARNET), available at www-starnet.eng.cam.ac.uk. These documents also contain numerous literature references for in-depth information on many technical aspects of S/S.

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[2] Environment Agency is the environmental regulatory body of the United Kingdom.

2.1 Technology Description

S/S is a remediation technology used to treat contaminated material. Typically, S/S includes processes that mix inorganic cementitious/pozzolanic reagents into contaminated material to transform it into a durable, solid, low–hydraulic conductivity material that reduces the rate of contaminant migration through leaching. Although solidification and stabilization are defined separately, they are often implemented simultaneously through a single treatment process. EPA defines each as follows (EPA 2000):

> Solidification involves the processes that encapsulate contaminated material to form a solid material and restricts contaminant migration by decreasing the surface area exposed to leaching and/or by coating the contaminated material with low-permeability materials. Solidification can be accomplished by mechanical processes that mix the material and one or more reagents. Solidification entraps the contaminated material within a granular or monolithic matrix.
>
> Stabilization involves the processes where chemical reactions occur between the reagents and contaminated material to reduce the leachability of contaminated material into a stable insoluble form. Stabilization chemically binds free liquids and immobilizes contaminated materials or reduces their solubility through a chemical reaction. The physical nature of the contaminated material may or may not be changed significantly by this process.

The on-site application of S/S technology, as discussed in this document, leaves treated material in place. Therefore, long-term stewardship is often required and is discussed in detail in Section 7 of this document.

2.2 Contaminant Types Treated Using S/S

S/S technology has been used to treat both inorganic and organic contaminants (EPA 1993a). Inorganic contaminants include metals such as arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, antimony, uranium, and zinc. Common organic contaminants present in soil or waste include pesticides/herbicides, petroleum or polycyclic aromatic hydrocarbons (PAHs), volatile organic chemicals (VOCs), polychlorinated biphenyls (PCBs), and dioxins/ furans.

Early literature concerning effectiveness of S/S on organic hazardous constituents noted the possibility of the interference by organics with the setting of cement-based mixtures, and as a result, a majority of S/S remedies were used for source control of inorganic contaminants (EPA 2007b), possibly leading readers to conclude that S/S treatment is not effective on organics. However, current published case studies and other literature indicate that S/S technology can be effective or potentially effective for a wide range of contaminants (see Table 2-1).

Frequently, contaminants at a site may be a complex mix of chemicals including both inorganic and organic contaminants. The presence of multiple contaminants can complicate the determination and application of this technology for effective S/S. Some examples of sites with both inorganic and organic contaminants include manufactured gas plant (MGP) sites, wood-treating sites, refineries, oil recycling facilities, and pesticide/herbicide manufacturing plants.

Table 2-1. Documented effectiveness of S/S treatment for chemical groups

Chemical groups	**Citations for treatment effectiveness**[a]		
	EPA 1993a[b]	**EPA 2009b**[b]	**Other references**[c]
Organic chemicals			
HVOCs[d]	N	N	D, with pretreatment (Paria and Yuet 2006)
N-HVOCs[d]	N	N	D, with pretreatment (Paria and Yuet 2006)
HSVOCs[d]	D	D	
N-HSVOCs, N-VOCs[d]	D	D	
PCBs	P	D	
Pesticides	P	D	
Dioxins/furans	P	P	D (Bates, Akindele, and Sprinkle 2002, PASSiFy Project 2010)
Organic cyanides	P	P*	D (Wilk 2007)
Organic corrosives	P	P*	D (Wilk 2007)
Pentachlorophenol	–	–	D (Bates, Akindele, and Sprinkle 2002, Wilk 2007)
Creosotes, coal tar	–	–	D (Bates, Akindele, and Sprinkle 2002,Wilk 2007)
Heavy oils	–	–	D (Wilk 2003)
Inorganic chemicals			
Volatile metals	D	D*	
Nonvolatile metals	D	D	
Asbestos	D	D*	
Radioactive materials	D	D	
Inorganic corrosives[d]	D	D*	
Inorganic cyanides[d]	D	D*	
Mercury	D	D*	EPA 2007b
Reactive chemicals			
Oxidizers	D	D*	
Reducers	D	D*	

[a] Key:

- N = no expected effectiveness, P = potential effectiveness, D = demonstrated effectiveness.
- P*/D* = S/S effectiveness was specifically stated in EPA 1993a but not in EPA 2009b; effectiveness is assumed to be the same in 2009. EPA 2007b documents the selection and use of S/S at National Priorities List (NPL) sites, but EPA does not indicate the effectiveness of the remedy.
- – = This chemical was not specifically discussed in EPA 1993a or 2009b, but effectiveness has been documented in other references (see rightmost column).

[b] See EPA references (EPA 1993a, 1993c, 2009b) on use of S/S for organics and inorganics and for site remediation.

[c] Other references provide S/S effectiveness for specific chemical groups for which EPA (1993a, 2009b) has not specifically stated S/S effectiveness as “D.”

[d] Halogenated volatile chemicals (HVOCs) include solvents, gases; nonhalogenated volatile chemicals (N-HVOCs) include ketones/furans, aromatics; halogenated semivolatile chemicals (HSVOCs) include PCBs, pesticides, chlorinated benzenes, chlorinated phenols; nonhalogenated semivolatile chemicals (N-HSVOCs) include PAHs, nonchlorinated phenols; inorganic corrosives include hydrochloride (HCL), sulfuric acid, sodium hydroxide, potassium hydroxide; inorganic cyanides include salts of cyanide (CN^-). N-VOCs = nonvolatile organic compounds.

Table 2-1 summarizes how broad classes of inorganic and organic chemicals generally respond to S/S treatment. This information is based on EPA reports evaluating the effectiveness of S/S treatment technologies at Superfund sites (EPA 1993a, 2009b). For contaminant types not included in these EPA documents (such as creosote and coal tars), additional documentation was used to indicate effectiveness as shown in the table. In some cases, discrepancies exist in the documented effectiveness reported in EPA references and other references. For example, the EPA documents report no expected effectiveness for halogenated and nonhalogenated VOCs, while Paria and Yuet (2006) document the effectiveness of S/S used along with pretreatment of volatiles. This particular example illustrates that one integral part of a successful S/S treatment is to determine site-specific and chemical-specific effectiveness through bench-scale treatability studies (see Section 5).

2.3 General S/S Process

The S/S process involves the incorporation of reagents, additives, and water with contaminated media to produce a material with improved physical and chemical properties. The overall process commonly includes (a) the establishment of material performance specifications based on remediation goals, (b) treatability studies intended to develop an appropriate mix design of reagents and additives which addresses material performance specifications and refines implementation techniques and construction performance specifications, (c) mobilization of field equipment and implementation of the S/S mix design on a field scale, and (d) monitoring of material performance after the remediation process is completed.

2.3.1 Reagents and Additives

S/S process options can generally be grouped into cementitious reagent processes and/or surface adsorption reagent processes (organophilic clay and thermoplastics or other synthetic polymers). Cementitious reagents are the most common commercially employed S/S process options due, in part, to low cost and availability. Cementitious and/or pozzalanic reagents include portland cement, fly ash, ground granulated blast furnace slag, silica fume, cement kiln dust, various forms of lime, and lime kiln dust. Although these reagents may be used singly or in various combinations, portland cement is by far the most widely used.

Since most organic compounds do not bond with cementitious minerals produced by hydration of S/S reagents, these contaminants are typically physically entrapped with the treated material. However, the use of additives with sorptive properties can improve the efficiency of S/S treatment for organics and, along with proper mixing technique, may offset interferences noted in the literature between organic compounds and setting properties of cement-based materials (Conner 1997). For example, the adsorptive properties of organophilic clay, when added to the S/S mix design, can result in reduced leaching of the organic compounds through chemical adsorption onto clay particles (Faschan, Tittlebaum, and Cartledge 1996). The clay particles are typically not involved in cementitious setting reactions but are encapsulated into the treated material. In addition to organophilic clay, other examples of useful additives include bentonite, activated carbon, phosphates, rubber particulates, and chemical gellants.

Further detail on the types and properties of various reagents and additives can be found in Paria and Yuet (2006), Environment Agency (2004b), and Conner (1990, 1997), among others. Decisions regarding the use of reagents and additives should be made on a site-specific basis.

2.3.2 Mixing

The S/S process typically involves either the addition of reagents to water (to form a grout or paste) or the addition of dry reagents. The addition of dry reagents is more common. The selection of the type of reagent is influenced by contaminant characteristics and site conditions such as depth of mixing and moisture content. Dry addition is typically feasible for only relatively shallow mixing operations; however, the generation of fugitive dust may be a concern unless it is mitigated by use of suitable equipment and controls. The S/S process then involves mixing the dry reagent or grout or paste with the contaminated material, using mechanical mixing equipment.

2.3.2.1 Mixing equipment

The selection of the type of mixing equipment is influenced by contaminant characteristics and site conditions, such as the depth and geometry of the impacted media; the presence of subsurface debris or very dense soil; the presence of buildings, railways, utilities, and other structures; and the proximity of surface water bodies. Appendix A of this document provides an overview of equipment options for shallow and deep soil S/S applications. Detailed descriptions can be found in Al-Tabbaa and Perara (2002), Environment Agency (2004b), and EPRI (2009a), among others.

2.3.2.2 Mixing process

For shallow S/S applications with contaminated material depths of approximately 6 m (20 feet) or less, the area to be treated is typically divided into grid cells. The size of a grid cell is often determined by the area and depth that the mixing equipment can reach with minimal need for relocation, the type of equipment used for mixing, the grout batch volume capacity of the batch plant equipment, and the frequency of QC sampling and testing.

When the contaminated material is at depths greater than approximately 6 m (20 feet), the S/S project is a candidate for in situ treatment through deep soil mixing (DSM) applications using a single large-diameter auger or a multiple auger tool. In these applications, the mix column depth and diameter dictate the volume per unit of production and the corresponding grout volume/ batches required for each setup location. Figure 2-1 is a conceptual illustration of an in situ S/S DSM application.

In both shallow and deep in situ S/S applications, the overall production rate is often controlled by the production rate of the batch plant and the mixing time required for thorough homogenization of the contaminated material and reagents to achieve the desired solidification and/or stabilization reactions.

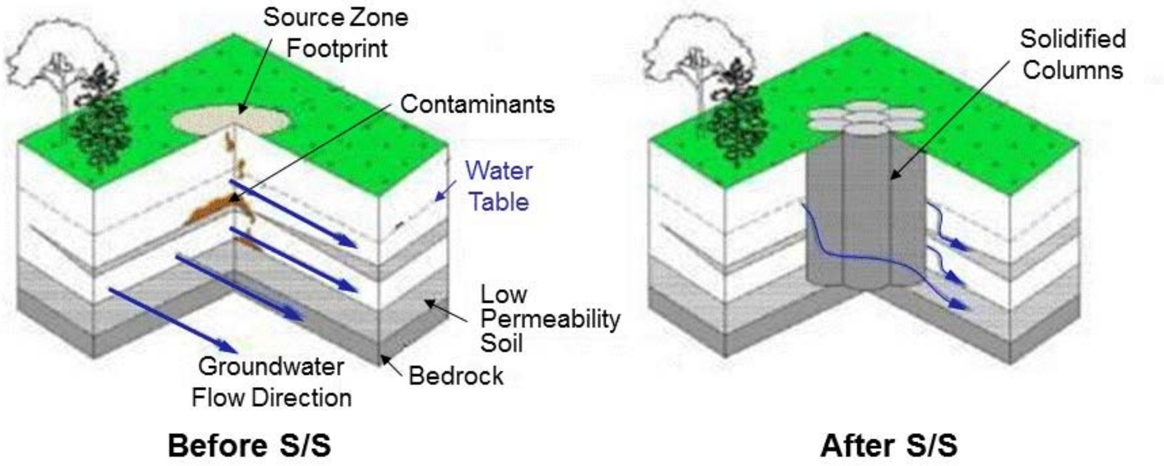

Figure 2-1. Conceptual in situ S/S model. *Source:* Modified from Palaia 2007.

If mixing occurs in situ, the treated material is left in place to "cure" or "set." When mixed ex situ, the treated material is placed into an on-site waste consolidation cell, spread into lifts of uniform thickness, compacted, and allowed to cure. Assuming the reagents and water are adequately mixed into the contaminated material, the ultimate physical and chemical properties of the treated material are determined largely by the ratio of the dry weight of reagent (content or dosage) to the initial in-place soil mass before mixing.

In addition to the mixing system, a typical S/S project also uses a batch/grout plant that consists of storage silos, metering and blending devices, and pumps. Auxiliary equipment that may be used for S/S projects includes specialty equipment such as shrouds equipped with air controls to capture fugitive emissions during the mixing operation.

2.4 S/S Technology Advantages and Limitations

Use of S/S to treat contaminated material has resulted in development of reliable information regarding effectiveness and other factors that are typically considered in the process to evaluate and select site remedial actions. In considering use of S/S technology, a sound understanding of site conditions is important, as well as an understanding of the practical outcomes and limitations of the technology.

S/S technology is applicable for a relatively broad range of contaminants and may be feasible when limitations to other technologies are imposed by site or contaminated material conditions. General non-site-specific advantages and challenges of S/S technology are listed below (Environment Agency 2004a, EPRI 2009a). As with use of any technology, site-specific conditions determine the potential feasibility and effectiveness of S/S and therefore also determine the applicability of the advantages and challenges listed.

S/S Technology Advantages
- effective in treating many inorganic contaminated materials
- has been shown effective in treating some materials contaminated with organic chemicals
- option for treating recalcitrant or mixed contaminants

- may address NAPL through S/S treatment process
- often reaches fixed treatment end point in a relatively short period of time
- can improve structural property of soil, waste, and sludge (e.g., strength) to facilitate consideration of land beneficial reuse
- applicable for in situ or ex situ treatment
- has been applied in dry or wet conditions, reducing dewatering and waste management issues
- generally uses simple, readily available equipment and materials
- on-site management of contaminated materials conserves landfill space and does not require transportation off site
- may be more cost-effective than excavation and off-site disposal

S/S Technology Challenges

- contaminants are not destroyed or removed; long-term stewardship may be required
- effectiveness for certain contaminants (such as some organics or highly mobile species) may require additional measures in testing and design
- potential changes in physical setting (e.g., groundwater flow, mounding) may need to be assessed
- uncertainties associated with prediction of long-term behavior
- options for treatment or post-treatment modifications limited by time for field performance testing and changed properties of treated material
- volume increases that occur in the treated mass may require management
- requires removal of debris or underground obstructions prior to treatment

2.5 Long-Term Performance

As outlined in Section 1, uncertainty over the long-term performance, durability, and reliability is a barrier to selection of S/S in some instances, due in part to limited knowledge of research and literature available on the subject. Several useful references address this topic in detail, both from case studies and predictive modeling (Perara et al. 2004a, EPRI 2003, Environment Agency 2004b). The combined experience of the ITRC S/S Team indicates that some in the regulatory community perceive that solidified materials will degrade over time as a result of one or more of the following: internal chemical reactions; geochemical and/or biological reactions with the surrounding environment; and physical mechanisms such as settlement, wet-dry cycling, or freeze-thaw cycling. However, degradation mechanisms for S/S materials typically are slow to manifest significant alteration of material properties which control contaminant release. Section 7.1 describes long-term durability and performance in more detail.

3. PERFORMANCE OF S/S-TREATED MATERIALS

This section provides a detailed discussion of how S/S-treated materials behave when placed in the subsurface, the key parameters that best describe performance of S/S-treated materials, and tests that can be used to measure these key parameters. The term "performance," in this context, refers to the ability of the S/S-treated material or remedy to maintain its function of minimizing release of contaminants to the environment. Thus, performance of S/S-treated materials should consider the behavior of the material both immediately after implementation as well as the longer-term aspects of material durability and site monitoring/maintenance.

3.1 S/S-Treated Materials in Subsurface Environments

Several factors may play a role in the physical and environmental performance of cement-based materials, as shown schematically in Figure 3-1. Although this figure is complex, performance relies on combinations of these factors such that small variances in the internal or external stresses typically to not lead to catastrophic failure of the treated material performance. Internal and external factors affecting S/S performance are also described in Table 3-1.

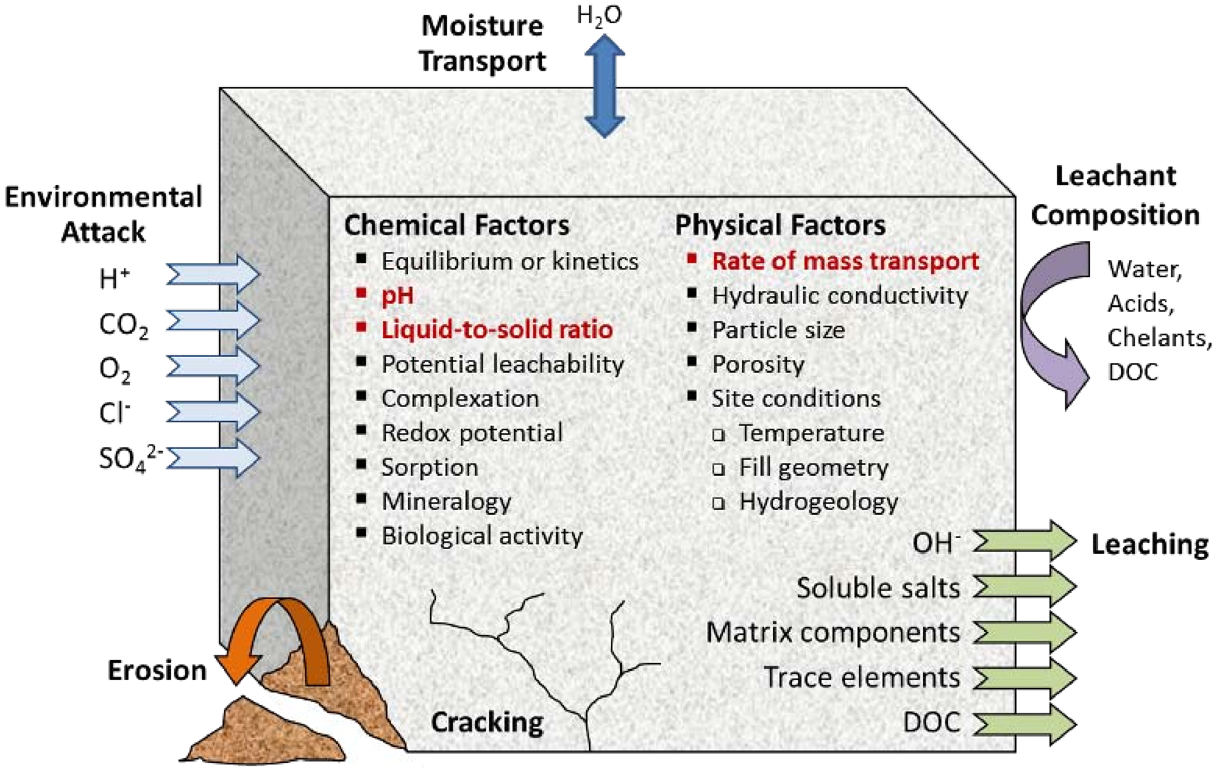

Figure 3-1. Internal and external stresses influencing the performance of S/S-treated materials. *Source:* Modified from Garrabrants and Kosson 2005.

3.1.1 Internal Stresses

Internal stresses listed within the cube include chemical and physical factors inherent to the material as well as site-specific parameters which are based on the placement of the S/S material into the subsurface. Many of the chemical and physical factors may be addressed during the treatability to maximize retention of contaminants.

The primary physical factors that can affect performance of S/S-treated material are its unit particle size (e.g., granular or monolithic material), hydraulic conductivity, and porosity. Of these, hydraulic conductivity is the most important in that the way in which groundwater contacts the material is controlled by the relative hydraulic conductivity of the soil and S/S-treated material.

Table 3-1. Impact of internal and external factors (see Figure 3-1) on S/S performance

Factor		Impact on performance
Chemical factors	Equilibrium vs. kinetics	Equilibrium-controlled (e.g., steady-state) concentrations are generally higher than kinetic-controlled (e.g., time-based) concentrations such as some hydration and degradation reactions.
	pH	Solubility of inorganic species and organic carbon can be a strong function of pH.
	Liquid-to-solid ratio (L/S)	At low L/S, ionic strength increases, which can increase the solubility of some species.
	Maximum leachability	Fraction of total content that is leachable (i.e., availability) provides driving force for leaching.
	Complexation	Some contaminants form soluble complexes (e.g., $CdCl_2$, Pb-acetate, dissolved organic carbon [DOC]–PAHs), which increase aqueous concentrations and leaching rates.
	Redox potential	S/S mix designs may result in reducing conditions. Oxidation of reduced contaminant speciation, such as Cr(III)→Cr(IV), can increase concentrations, toxicity, and leaching rates.
	Sorption	Surface interactions with mineral phases (e.g., iron, aluminum, and manganese oxides; calcium silicates) can reduce porewater concentrations of some contaminants.
	Biological activity	Acids produced by biological activity can alter pore chemistry and locally degrade minerals.
Physical factors	Particle size	Unit particle size dictates whether material is monolithic or granular. Mean particle size of contaminated material (e.g., finely grained or gravely) may influence selection of reagents.
	Hydraulic conductivity	Water contact mode (e.g., flow through or flow around) is dictated by relative hydraulic conductivity of S/S material and surrounding soil.
	Pore structure	Materials with large, connected pores generally have higher hydraulic conductivity, whereas lower hydraulic conductivity may be seen in materials with smaller or disconnected pores.
Site conditions	Groundwater flow rate	Fast-moving groundwater limits contact time with the surface of S/S materials but may result in sufficient hydraulic head to force groundwater through the material pore structure.
	Fill geometry	Flux-based release of contaminants is proportional to the bulk surface area of the S/S fill.
	Temperature	Higher temperatures increase the rate of chemical reactions (e.g., mineral dissolution).
	Hydrogeological conditions	Determine water contact mode, liquid-to-solid ratios, infiltration rates, active surface area for leaching.
Moisture transport		Leaching from an S/S material is discontinued during drying; gas-phase reactions (e.g., oxidation, carbonation) require a pore vapor space for transport (i.e., partially dried material).
Leachant composition		Acids, chelants, and organic carbon may alter solubility of surface/near-surface minerals and contaminants.
Environmental attack		Several species in the surrounding environment may accelerate leaching or degradation of the mineral structure through pH or redox changes and expansive precipitation reactions.
Leaching		Release of mineral phases increases pore diameters and connectivity, potentially leading to increase in hydraulic conductivity and increased release rates.
Cracking		All S/S materials have cracks on the micro and macro scales; formation of larger-aperture through-cracks may increase hydraulic conductivity but does not equate to catastrophic failure as complete through-cracks simply result in two monoliths of the same performance characteristics.

Although Figure 3-1 shows many chemical factors influencing performance, the most important chemical factor with respect to S/S-treated material is the pH of the material as it relates to both leaching performance (e.g., contaminant speciation) and structural performance (e.g., dissolution of strength-providing mineral phases). In cement-based materials, alkalinity and the ability of the material to buffer acids, known as the acid neutralization capacity, are based on precipitation and dissolution of $Ca(OH)_2$ and calcium silicate hydrate minerals, which form during hydration and curing of reagents.

Inorganic constituents in the S/S mass may be initially incorporated within mineral structures (e.g., strontium or barium substituting for calcium), adsorbed to mineral surfaces or organic matter, precipitated as solids within pore spaces, or dissolved within the liquid phase held within the pore structure (i.e., the porewater). Since several of these retention mechanisms (e.g., mineral and precipitate dissolution, adsorption/desorption reactions, and aqueous solubility of inorganic species) may be strongly pH dependent, porewater pH is considered a controlling variable for the equilibrium-based leaching of many inorganic contaminants.

The pH of the alkaline porewater within the treated material directly affects retention of inorganic constituents by changing speciation of contaminants. Porewater pH also affects the sorption characteristics of the mineral surfaces of the material (van der Sloot 2002; Garrabrants, Sanchez, and Kosson 2004; Dijkstra, van der Sloot, and Comans 2006; Carter, van der Sloot, and Cooling 2009). The combined effects lead to changes in the solubility of inorganic contaminants with pH, as shown in Figure 3-2.

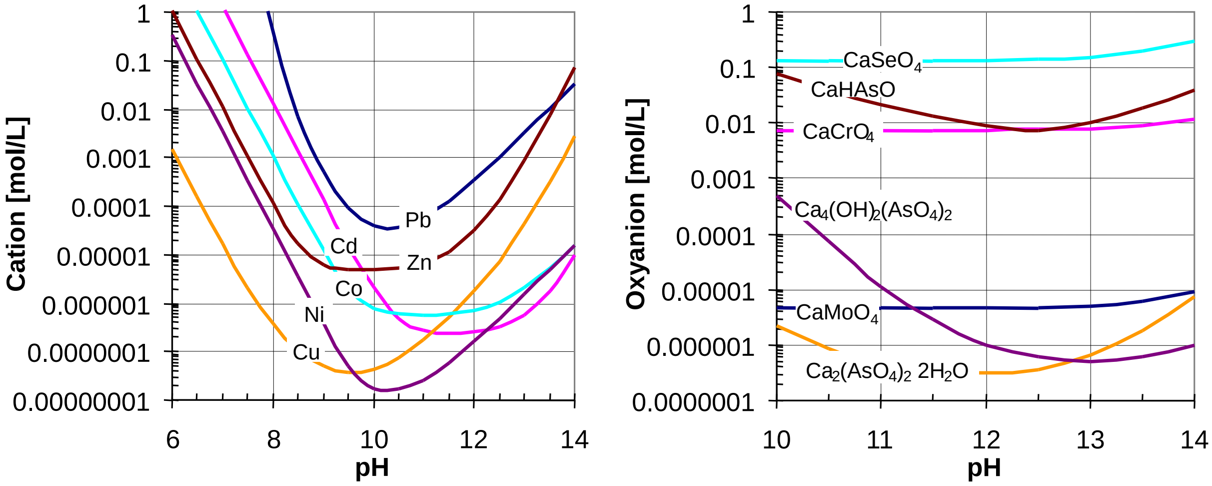

Figure 3-2. Solubility of cationic metals (hydroxides) and oxyanions (calcium salts) as a function of solution pH.

Most heavy metals form cationic hydroxide species in the porewater of S/S-treated materials. Figure 3-2 shows that the solubility of these hydroxides is strongly affected by pH and passes through a point of minimal solubility in the pH range 9–12. However, oxyanionic contaminants such as arsenates, chromates, and molybdates are less influenced by pH in the same pH range.

When organic contaminants are of concern, pH plays only an indirect but equally important role in leaching. Organic contaminants in S/S materials tend to be concentrated in isolated organic phases (e.g., tars and greases) or adsorbed to particulate organic matter. S/S formulations may include additives which specifically target organic constituents through sorption and reduce leaching. Thus, the solubility of organic contaminants is not directly affected by changes in pH. However, highly alkaline regimes promote dissolution of particulate organic matter (e.g., humic and fulvic acids) and release of DOC, which can lead to increased contaminant concentrations in the porewater (Butler 2009; Dijkstra, Meeussen, and Comans 2004; Roskam and Comans 2007, and Raber et al. 1998). DOC can form aqueous complexes with some forms of organic chemicals, especially PAHs, which in effect increase measured contaminant concentrations in the porewater (EPRI 2009b).

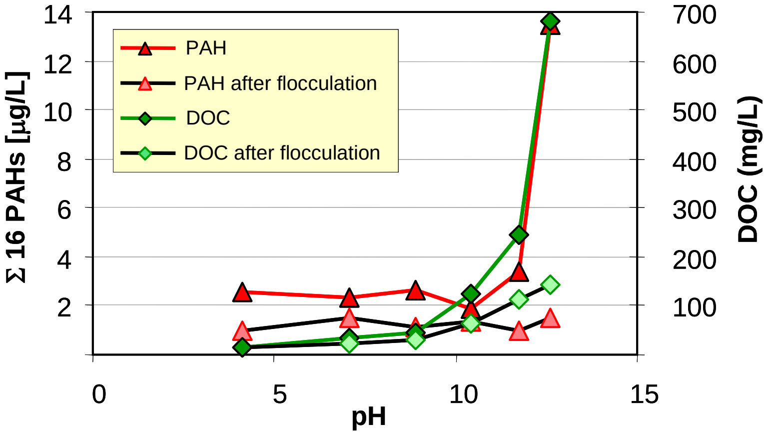

Figure 3-3. pH-dependent leaching of DOC and associated PAH concentrations from contaminated sediment. *Source:* After Roskam and Comans 2003.

To illustrate the potential for a significant effect of organic-DOC complexes at high pH, Figure 3-3 shows the relative concentrations of DOC and total PAHs measured in a leachate before and after removal of the organic carbon through flocculation.

Typically, addition of lime or portland cement to under-performing S/S recipes is thought to improve performance. In some cases, addition of portland cement can help to stabilize a material into forming a more monolithic material; however, the highly alkaline porewater in the material may result in increased leaching. Properly conducted and evaluated treatability studies (see Section 5) are essential to best tailor the properties of S/S-treated material for retention of both inorganic and organic contaminants.

3.1.2 External Stresses

External stresses include those interactions or reactions shown outside the cube in Figure 3-1 that tend to affect the long-term performance of the S/S treatment. These stresses may change the chemical or physical properties of the material and influence performance in the long run. For example, the physical durability of the S/S material may be influenced by cracking of the monolithic structure (e.g., from freeze/thaw cycles or mechanical stress), whereas the ability of the material to retain contaminants is more influenced by changes in chemistry (e.g., neutralization of porewater, precipitation reactions, changes in oxidation/reduction potential) through interaction with the surrounding environment. However, depending on the specific condition of the placement scenario, many of these aging and degradation processes are slow to develop such that S/S treatment may remain effective for extended periods.

3.1.3 S/S Placement Relative to the Water Table

Since many S/S applications extend through the unsaturated or vadose zone into the water table, the external conditions that influence an S/S material may lead to different performance outcomes.

- *Saturated zone.* Groundwater flows as a result of hydraulic gradients. Depending on the relative hydraulic conductivity between the S/S material and surrounding soils, groundwater may either percolate through an S/S mass or be diverted around an S/S mass. As long as upstream conditions (e.g., hydraulic head, groundwater composition) remain constant, material properties will not change significantly with time and release from the S/S material should be relatively predictable using a combination of equilibrium and mass transport assessments. If the hydraulic conductivity is low relative to that of the surrounding material, the rate of mass transport through the pore structure of the S/S material is often the rate-limiting step in the release process.

- *Vadose zone.* Saturation and water contact is dependent on infiltration or recharge rates so that S/S materials may be wetted only a portion of the time. The rate of infiltration is typically much slower than the flow of groundwater, resulting in relatively long residence times in the vadose zone. For materials with high hydraulic conductivity (e.g., most soils), the mode of water contact in the vadose zone is percolation through the porous material; however, materials with low hydraulic conductivity (e.g., S/S applications) may see limited percolation. Under percolation conditions, release in the vadose zone is typically dominated by equilibrium between solids and infiltrating liquids. In vadose zone placement situations, vertical transport models, such as percolation modeling approaches, may be useful in determining infiltration parameters.

  The most significant aging processes for S/S materials placed in the saturated zone are primarily the result of contact with constituents in the groundwater. For example, although the formation of ettringite during hydration of reagents may be beneficial for contaminant retention (Klemm 1998), delayed ettringite formation resulting from contact of cured material with high sulfate concentrations can lead to cracking and spalling of the monolithic material (Collepardi 2003). However, degradation processes that can strongly influence long-term performance of S/S materials are common in the vadose zone as well. Seasonal rise and fall of the water table may result in fatigue associated with cycles of wetting and drying, cycles of freezing and thawing, and interaction/reactions with soil gas components.

- *Moisture cycling (wetting/drying).* As in any cementitious material, shrinkage cracking inevitably occurs upon curing and cyclic wetting and drying. However, these cracks are not likely to compromise the integrity of the S/S material until cracking is sufficiently advanced to increase the hydraulic conductivity, resulting in a more significant preferential groundwater flow through the S/S mass. In terms of leaching, intervals of drying where no continuous external aqueous solution exists result in a lower overall release compared to continuously wetted materials; however, relaxation of diffusion profiles in the porewater may still occur which ultimately leads to redistribution of contaminants toward the surface of the S/S material (Garrabrants 2001). When the material is saturated during the next wetting period, contaminants may readily partition into the infiltrating water and be carried by gravity into the subsurface. The durability of S/S materials upon wetting and drying may be evaluated using ASTM D4843 (ASTM 2009), while the effect of wetting and drying on the leaching process may be characterized following literature approaches (Garrabrants et al.

2002; Garrabrants and Kosson 2003; Sanchez, Garrabrants, and Kosson 2003; Gervais et al. 2004).

- *Temperature cycling (freezing/thawing).* The constrained expansion of porewater upon freezing can lead to significant stress or loading in brittle small-pore material such as S/S-treated contaminated material. The stress caused by the increase in molar volume of ice over water causes a strain or deformation within the pore structure. If the strain is greater than the strength of the material, the material inelastically deforms by cracking. Testing of S/S materials for freezing and thawing durability may be conducted using ASTM C1262 (ASTM 2010a). The primary effect of freezing and thawing is an increase in hydraulic conductivity, leading to potentially higher infiltration. Since freezing occurs only above the frost line, however, subsurface applications of S/S materials are not especially susceptible to cracking via freeze/thaw cycles.

- *Gas-phase reactions.* Carbonation and oxidation are common gas-phase reactions that have the potential to change material properties and leaching characteristics over time. These reactions occur when cementitious materials are exposed to a soil gas in the unsaturated zone. Carbonation results from the reaction of carbon dioxide with hydroxides in the alkaline porewater of the S/S material, and several studies explain the carbonation process and its effects on S/S materials (Ho and Lewis 1987; Papadakis, Vayenas, and Fardis 1991; Krishnan and Sotirchos 1994; Bonen and Sarkar 1995; Ngala and Page 1997; Johannesson and Utgenannt 2001; Garrabrants, Sanchez, and Kosson 2004; van Gerven et al. 2007; Chen et al. 2009). Oxidation via the soil gas phase may be a concern, especially in the cases where a reducing agent was added to treat a redox-sensitive contaminant (e.g., chromium, arsenic, technetium, etc.). Testing of material properties for the effects of gas-phase reactions usually involves comparison of exposed materials to unexposed materials using otherwise standard performance parameter tests.

- *Physical degradation (cracking and erosion).* Although not commonly considered a significant degradation mechanism for subsurface S/S materials, the perceived catastrophic failure of S/S materials due to the cracking or erosion has been noted. The formation of cracks in S/S materials (and all cement-based materials) is expected as water is incorporated into mineral phases as a result of forces or loads working on the S/S mass due to seismic activity or to expansive precipitation reactions occurring within the pore structure as a result of aging. Discontinuous micro- and macro-scale cracks are normal and do not affect the performance of S/S materials. Wide-aperture through-cracks (i.e., a single crack traversing the entire monolith with a width sufficient to allow water to pass) may be observed. However, the effect on contaminant retention is minimal as the through-crack simply results in two monoliths with the same performance characteristics and slightly more exposed surface area. Taken to an extreme, cracking could result in erosion into a granular material; however, this case is not likely to happen for most well-designed S/S applications with the timeframe of most environmental assessment intervals. As a source of cracking and erosion, seismic activity is considered a low-probability occurrence; however, some states may have requirements concerning the ability of the S/S material to withstand seismic forces.

3.2 Performance Specifications

The performance of S/S-treated materials may be described, monitored, and demonstrated by following a few critical performance specifications. “Performance specifications” refer to the collection of performance-related parameters, tests, and criteria used to develop an S/S treatment recipe and implementation plan that meets material performance goals after implementation. The different components of a performance specification are defined as follows:

- Performance Parameters—the material properties characteristic of the ability of an S/S-treated material to carry out its intended purpose.
- Performance Tests—protocols or challenges used to characterize a performance parameter of an S/S-treated material and which return one or more measurements considered representative of the performance parameter.
- Performance Criteria—design values of a performance parameter used for comparison to performance measurements to evaluate whether acceptable performance has been achieved. Performance criteria may be regulatory goals established for cleanup of a contaminated site or material parameter values considered adequate for meeting established site remediation or regulatory goals.

As an illustration of these definitions, leachability may be considered a primary *performance parameter* used to assess the ability of a material to retain a specific set of site contaminants of concern (COCs). A common *performance test* that may be used to measure leachability of S/S materials is the EPA’s Synthetic Precipitation Leaching Procedure (SPLP), also known as SW-846 Method 1312 (EPA 1994). The resultant SPLP eluate concentrations represent *performance measurements* describing the leachability of the S/S material. These performance measurements are typically compared to a set of predefined concentrations or action levels used as *performance criteria* to determine whether the solid material will leach beyond acceptable limits.

3.3 Key Performance Parameters for S/S-Treated Materials

This section describes relevant performance criteria that may be used as indicators of the performance and long-term permanence of S/S applications and provides specific recommendations on methods to measure these criteria. Users of this document will not always include all of the performance criteria in every project, and specific recommended methods may not be useful or appropriate in every case. However, these recommended methods provide the best available determination of relevant performance criteria and, thus, are preferred in most situations.

3.3.1 Strength

The *strength* of a material represents the ability of the material structure to withstand an applied physical stress without incurring structural deformation leading to structural failure. Several different measurements of strength, including flexural, tensile, and compressive strength, may be important for S/S materials. However, compressive strength, which relates to the capacity of a material to withstand axially directed pushing forces, typically measured as unconfined compressive strength (UCS), is the most common strength parameter for S/S materials.

Compressive strength is typically monitored as an S/S performance parameter to ensure that a chemical reaction of binder and water has taken place. Criteria for minimum compressive strength are established such that the S/S material will have at least as much bearing strength as the surrounding soil to support the loads imposed by the equipment used in implementation; however, high strength values may be required depending on other considerations, such as future use of the site. A secondary purpose for testing strength during the S/S treatment process is as an indirect indicator of durability. As a rule of thumb, materials with higher initial compressive strength are typically considered to be more resistant to aging. Thus, strength may be used as an indicator during treatability studies for selecting appropriate S/S treatment additives to maximize durability as well as a monitor of performance during S/S application.

3.3.2 Hydraulic Conductivity

Hydraulic conductivity[3] is a measureable material property related to ease of movement of water through a porous medium under groundwater flow conditions governed by Darcy's Law (Bear 1972). However, the parameter that controls the mode of water contact is not simply the hydraulic conductivity of the S/S material, but the relative hydraulic conductivities of the S/S material ($K_{S/S}$) and the surrounding soil (K_{soil}). In the subsurface, groundwater flows along the path of least resistance and, thus, is diverted around lower–hydraulic conductivity materials and through material with high hydraulic conductivity. The following three possible water contact scenarios exist based on relative hydraulic conductivity between S/S-treated materials and surrounding soils:

- $K_{S/S} << K_{soil}$—For most S/S materials, the hydraulic conductivity is significantly less than that of the surrounding soil. Thus, groundwater is diverted around the compacted granular or monolithic materials of low hydraulic conductivity such that the majority of contacting water flows around the solid matrix. In such "flow-around" water contact scenarios, the material surface area exposed to leaching is minimized to the outer surface of the material, and the rate of contaminant mass transport (i.e., diffusion plus associated physical and chemical retention) through the pore structure of the low–hydraulic conductivity material limits the release into the groundwater. In these scenarios, leaching may be represented as a time-dependent flux or cumulative release of a constituent across a unit surface area.

- $K_{S/S} >> K_{soil}$—When the hydraulic conductivity of the treated material is significantly greater than that of the surrounding soil (e.g., if the treated material is unconsolidated granular or poorly engineered monolithic material), groundwater flows through the highly permeable material. In this "flow-through" or percolation water contact mode, the pore surface area of the material is exposed to groundwater. The rate of percolation may be slow enough that the release of constituents into infiltrating water may be well described by the partitioning

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[3] "Hydraulic conductivity" is often used interchangeably with the more general term "permeability" relating to the ease with which a fluid (e.g., water, oil, air, etc.) will pass through a porous medium. Although similar, permeability depends on the properties of both the material and the penetrating fluid, whereas hydraulic conductivity depends on only the properties of the material structure. Hydraulic conductivity is recommended as more appropriate as the S/S performance parameter, as it is more easily measured independent of fluid properties, and thus "permeability" will be used in this document only as a relative term (e.g., one material is more permeable than another).

between the solid and liquid phases. As groundwater passes through the material, more soluble mineral phases are dissolved, and release can be expressed as a function of the amount of liquid passing through the material (e.g., the liquid-to-solid ratio under percolation release).

- $K_{S/S} \approx K_{soil}$—In cases where the hydraulic conductivity values of the treated material and surrounding soil are approximately the same, both percolation and flow-around water contact modes exist, and both release mechanisms should be considered.

The impact of water contact mode on S/S-treated material performance is linked to leaching concentrations. Since contaminant concentrations are significantly higher for partitioning between solid and liquid phases than typical concentrations resulting from mass transport release, the mode of water contact is extremely important, and relative hydraulic conductivity of the S/S material is recommended as a key performance parameter.

Table 3-2 presents the typical hydraulic conductivity values for several material types. Permeability is used to empirically relate the hydraulic conductivity of one material to another. The hydraulic conductivity value can range from approximately 10^{-2} cm/s for sandy soils to 10^{-9} cm/s for rocks and clays. In many cases, S/S-treated materials with hydraulic conductivity values similar to silty clay (e.g., on the order of 10^{-7} cm/s) are desirable to reduce the potential for contaminant migration.

Table 3-2. Hydraulic conductivity of select porous media (*Source:* Dagan 1989)

Soil type	Hydraulic conductivity, K (cm/s)	Degree of permeability
Gravel	$>10^{-1}$	Very high
Sandy gravel, clean sand, fine sand	10^{-1}–10^{-3}	High to medium
Sand, dirty sand, silty sand	10^{-3}–10^{-5}	Low
Silt, silty clay	10^{-5}–10^{-7}	Very low
Clay, limestone, dolomite	10^{-7}–10^{-9}	Virtually impermeable

3.3.3 Leachability

“Leaching” is defined as the process of release of a constituent from a solid into a contacting liquid. The term “leachability” may be used to describe either the extent of leaching (e.g., percentage of total content that has leached) or rate of release (e.g., the time-dependent release) from materials. The mechanisms controlling the extent and rate of leaching include a combination of chemical reactions at the material surface and mass transport through the material pore structure. Chemical reactions determine the partitioning between the solid and liquid phases (e.g., using the local equilibrium assumption) whereas the mass transport (i.e., the summation of diffusion, hindered diffusion, tortuosity effects, effective surface area, etc.) describes the movement of a contaminant through the pore structure of the material to the environment. Depending on material-specific factors and release scenario conditions (see Figure 3-1), equilibrium and/or mass transfer may control the leaching process in S/S-treated materials.

Leaching of contaminants into groundwater or infiltrating precipitation may be considered the principal pathway for the release of nonvolatile contaminants into the environment. The release of VOCs is determined by a combination of both leaching and volatilization into subsurface air space. Since a principal objective of S/S treatment is to reduce contaminant mobility, leaching is a key performance parameter for S/S materials in most cases.

3.4 Performance Tests

For most performance parameters, the recorded value is somewhat determined by the test used to measure the parameter. For example, hydraulic conductivity may be determined by a falling head method or a constant head method, which can provide slightly different results. The following paragraphs discuss available test methods for each of the key performance parameters.

3.4.1 Unconfined Compressive Strength

ASTM D1633 (ASTM 2007) is a UCS measurement method specific to soil-cement material molded into cylindrical test specimens that is appropriate for monolithic S/S-treated materials. The ASTM method provides two alternative procedures based on specimen size and component particle size. UCS is expressed as the load per unit area in units of pounds per square inch (psi) or kilonewtons per square meter (kN/m^2) at structural failure of the material. The UCS of an S/S-treated material is likely to increase with curing time until setting is complete (e.g., the measured UCS values of a material cured for 3 days and 28 days are not expected to be the same). Therefore, the duration of cure time and quality of the curing conditions should be taken into consideration when interpreting the results of UCS tests.

When S/S treatment results in an encapsulated granular material, ASTM D2166 (ASTM 2006) may be used to provide an approximate measure of the compressive strength in a cohesive molded sample in terms of total stresses. For granular materials, UCS is expressed as the load per unit area in units of pounds per square inch or kilonewtons per square meter at 15% axial strain.

3.4.2 Hydraulic Conductivity

The hydraulic conductivity of S/S materials and surrounding soils may be determined by either field or laboratory tests. ASTM D5084 (ASTM 2010b) is the most common method used for determining saturated hydraulic conductivity of S/S material and saturated soils. However, if surrounding soils are unsaturated or are coarse-grained, field tests rather than laboratory methods may be needed to accurately measure hydraulic conductivity.

In general, hydraulic conductivity tests measure the rate at which water passes through a sample relative to an applied hydraulic head. The hydraulic conductivity of the material is calculated from the test results using formulas based on Darcy’s Law (Ho and Lewis 1987; Papadakis, Vayenas, and Fardis 1991; Krishnan and Sotirchos 1994; Bonen and Sarkar 1995; Ngala and Page 1997; Johannesson and Utgenannt 2001; Garrabrants, Sanchez, and Kosson 2004; van Gerven et al. 2007; Chen et al. 2009).

In the laboratory, hydraulic conductivity tests are carried out on small samples of material formed in the laboratory or field-collected during implementation. Field collection of specimens drilled or cored from cured materials should be avoided as the integrity of the sample cannot be guaranteed. Depending on the flow pattern imposed through the soil sample, the laboratory methods for measuring hydraulic conductivity may be classified as either constant-head tests with a steady-state flow regimen or falling-head tests with a non-steady-state flow regimen. The constant head test method is best applied to permeable materials ($K > 10^{-4}$ cm/s), and the falling head test is mainly used for less permeable materials ($K < 10^{-4}$ cm/s). Because of the small sample sizes, the results of these tests are considered a point representation of the material properties. If the samples used in the laboratory test are considered undisturbed specimens of field materials (e.g., soils sampled using Shelby tubes), the measured value of hydraulic conductivity may be a true representation of the in situ saturated hydraulic conductivity at a particular sampling point. Complex sites with varying soil stratigraphy may require extensive hydraulic conductivity testing to adequate characterize site materials.

3.4.3 Leachability

The leachability of a material is most often characterized from the results of one or more leaching tests. Van der Sloot, Heasman, and Quevauviller (1997) have noted that more than 50 leaching tests exist in the literature. However, of the available test methods designed for various purposes and materials, many tests differ in only minor ways such that a limited number of carefully selected tests can cover a wide range of possible exposure conditions.

Current EPA regulatory leaching tests are intended to provide a leachate that is representative of field leachates found either in a municipal solid waste landfill in the case of the Toxicity Characteristic Leaching Procedure (TCLP, EPA Method 1311) or after contact with acid rain in the case of SPLP. These leaching tests often are required at the state and federal regulatory levels for environmental purposes.[4] With respect to TCLP in particular, the EPA Science Advisory Board (EPA 1991, 1999b) and others (Kosson et al. 2002; Garrabrants and Kosson 2005) have noted several additional limitations which have bearing on leachability assessment for S/S materials. Although directed at TCLP, many of these limitations are equally applicable to SPLP.

- TCLP is over-broadly applied as the basis for leaching assessment for scenarios and materials for which the method was not designed (e.g., leaching assessments on S/S materials).
- The end-point pH of the TCLP or SPLP extraction is not required to be reported by the method; however, the final-extraction pH is essential if the test results are to be compared either between materials (e.g., treated and untreated materials) or in the context of the results other leaching tests.
- Simulation scenarios used to develop acceptance or action levels are not realistic and do not consider the long-term chemical and physical reactions (e.g., neutralization, carbonation, oxidation) which can significantly alter release and are common to many disposal or placement scenarios.

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[4] Other similar procedures (e.g., California Waste Extraction Test, or WET) may be required on a state-by-state basis.

- Like many equilibrium-based tests, the TCLP and SPLP methods require particle size reduction and, thus, do not account for time-dependent release of contaminants from monolithic low–hydraulic conductivity materials.

Both TCLP and SPLP are single-batch extraction procedures which are broadly used, in part, because they are easy to conduct and provide results that are simple to interpret relative to permissible concentration limits. However, each of these procedures yields only a single data point and provides no understanding of the underlying release-controlling mechanisms (e.g., equilibrium or mass transfer) or rate of leaching. Thus, there is no way to account for how the many influential material properties (e.g., alkaline buffering, monolithic nature of S/S materials) or external factors (e.g., groundwater diversion, low hydraulic conductivity) affect the release of contaminants into groundwater.

3.4.3.1 Flux-based leaching tests

S/S treatment technology often relies on the formation of a monolithic treated material such that the majority of the contacting groundwater flows around the treated material. Within the pore structure of S/S-treated materials, contaminants partition between solid surfaces and the porewater. Dissolved contaminants move by diffusion through the pore structure of the material toward the material surface exposed to groundwater. Since the rate of diffusion typically is slow compared to the rate of chemical reactions at the porewater/solid interface, mass transport of contaminants through the material often controls the rate of release from S/S-treated materials. Thus, leaching methods which use particle size reduction to approach equilibrium do not fully describe the dominant rate-controlling release mechanism in S/S materials. Thus, flux-based leaching tests are considered more appropriate for monolithic materials as these tests capture the time-dependent release of contaminants.

The American Nuclear Society (ANS) test method ANS 16.1, *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure* (ANS 2003), is a common flux-based test, initially designed for cement-stabilized low-activity waste in the nuclear waste industry. ANS 16.1 is often used to estimate the time-dependent release of contaminants from other solidified materials, including S/S materials. Variations on the basic tank leaching method have addressed one concern of ANS 16.1: that release rates may be suppressed if concentrations in the leachate are allowed to build up. This concern has been addressed by adjusting the schedule of exchanges to provide a net-forward rate of release (e.g., ASTM C1308 Accelerated Leach Test, 2002) or by using ion-exchange resin to remove ions from solution during longer-duration leaching intervals (e.g., the Simulated Infinite Dilution Leach Test).

3.4.3.2. Emerging EPA leaching tests

In an effort to better support environmental management decisions, the EPA Office of Resource Conservation and Recovery[5] has selected the four leaching methods of the Leaching Environmental Assessment Framework (LEAF; www.vanderbilt.edu/leaching) for inclusion into

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[5] Formerly the EPA Office of Solid Waste.

SW-846, the EPA compendium of laboratory methods (EPA 2010a). Each of the four LEAF leaching tests is design to characterize leaching as a function of a primary controlling factor shown in Figure 3-1. Preliminary versions of EPA methods or premethods[6] of the LEAF leaching test are described in brief below; details of LEAF can be found in Appendix B.

- **PreMethod 1313.** Liquid-solid partitioning (LSP) is determined as a function of the eluate pH in a short-duration, equilibrium-based, parallel-batch leaching procedure. Similar to most equilibrium-based leaching tests, the procedure requires particle size reduction to facilitate the approach to equilibrium. The method can be adapted for organic constituents if steps are taken to minimize adsorption of organics onto surfaces of the leaching vessels.

- **PreMethod 1314.** PreMethod 1314 is an equilibrium-based, up-flow percolation column test used to characterize the LSP between a high–hydraulic conductivity material and a percolating liquid phase as a function of the L/S. For S/S materials, eluate concentrations at low L/S ratio provide an estimate of porewater concentrations. A modest degree of particle size reduction is required to accommodate a column diameter of 5 cm. Column and tubing materials may be easily modified to minimize absorption of organic constituents. Methods development is ongoing to adapt collection techniques to address volatilization losses for some organic compounds.

- **PreMethod 1315.** PreMethod 1315 is a flux-based leaching test for monolith or compacted granular materials. This method is similar in structure to ANS 16.1 with minor variations in the schedule of leachant collections and interpretation of results. Test samples are cast or compacted into standard cylindrical molds and tested without particle size reduction to determine the rate of mass transport of constituents through the material. Leaching data are used to determine the mass flux and cumulative release across the material surface area exposed to the leaching solution. Although this method is specified for inorganic constituents, leachate collection modifications using absorption phases to manage low–aqueous solubility compounds and minimize volatility losses have been developed and applied to the leaching assessment of PAHs from soil/cement cores (EPRI 2009b).

- **PreMethod 1316.** The LSP is determined as a function of L/S in a manner analogous to PreMethod 1314 but conducted in short-duration, parallel-batch structure. The results provide an estimate of porewater concentrations at low L/S and show how equilibrium concentrations change as water passes through a material. Particle size reduction is required to facilitate the approach to equilibrium. PreMethod 1316 is well-suited for consistency testing in that the results of this simple, short-term leaching method provide some indication of equilibrium concentrations when the alkalinity of the material controls eluate pH. The method can be adapted for organic constituents if adsorption of organics onto surfaces of the leaching vessels is minimized.

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[6] Preliminary version denotes that this method has not been endorsed by EPA but is under consideration for inclusion in SW-846. These methods have been submitted to the EPA Office of Resource Conservation and Recovery for interlaboratory validation studies to develop precision and bias information. The four LEAF premethods are expected to be posted as draft methods on the EPA SW-846 website by the end of 2012.

The LEAF leaching methods may be used and interpreted individually; however, considerable advantages in predictive ability are provided by integration of the multiple LEAF methods with leaching assessment approaches to establish a "source term" for contaminant release. Although EPA guidance on the use of these tests remains outstanding, these alternative test methods are likely to be recommended for environmental purposes where TCLP is not required by regulation or best suited (e.g., demonstration of alternative treatment, beneficial-use applications, corrective action).

3.5 Recommended Performance Parameters and Performance Test for S/S-Treated Materials

Several test methods may be useful during the process of designing an appropriate S/S treatment formulation and implementing an S/S technology. Table 3-3 presents recommended performance parameters for treated materials, the associated performance measurement for each performance parameter, and examples of appropriate performance tests to provide the required performance measurement.

Table 3-3. Performance parameters and performance tests for S/S materials

Performance parameter	Performance measurement	Example performance test(s)
Strength	Compressive strength	ASTM D1633
Hydraulic conductivity	Hydraulic conductivity	ASTM D5084 (constant head) ASTM D5084 (falling head)
Leachability		
Treatability study	LSP as function of pH	PreMethod 1313
	LSP as function of L/S	PreMethods 1314, 1316
	Mass transfer (flux)	PreMethods 1315, 1315 (modified); ANSI 16.1
Consistency testing	LSP at natural pH, mass transfer (flux)	PreMethod 1316, SPLP, abbreviated flux tests

LSP = liquid-solid partitioning, L/S = liquid-solid ratio

Test methods for strength and hydraulic conductivity are straightforward in that the available test methods tend to be of short duration and require little to no interpretation of the results. These tests may be conducted on S/S material samples after short cure times and compared directly to performance criteria as long as it is recognized that these performance parameters will continue to develop as the S/S material ages. With respect to leachability, the proper selection of an appropriate test method is somewhat less straightforward due to the complexity of the leaching process.

The choice of one or more leaching tests depends on the degree of specificity required for the purpose of defining leachability:

- If a mechanistic understanding of the how constituents are released into the environment is desired, leachability testing should be focused on defining the leaching response of the material to the release-controlling parameters (e.g., pH, L/S, and time). This approach requires integration of the results of some multiple leaching tests over a broad range of test conditions as proposed in LEAF. With respect to S/S treatment, this level of comprehensive testing might be conducted at the bench scale during treatability testing to provide technical personnel with additional information to support selection of effective reagents and additives.

- If the purpose of leach testing is to describe leaching in the context of the most likely release scenario, a single characterization test may be used. The conditions imposed by the test should be representative of the anticipated conditions in the field.

3.5.1 Selection of Leaching Tests

Because applicability of a particular leaching test depends on the intent of the test and how the results are interpreted, no single leaching test is applicable for all purposes. For example, PreMethod 1315 is a good indicator of leachability from S/S-treated materials for use in refining S/S treatment mix designs during treatability testing and demonstrating compliance when a finalized mix design is established, but it is not a practical field test due to the 63-day testing duration. Thus, different tests may be needed at various stages in the design and implementation process (see Section 4) for different purposes.

- *Development of S/S treatment mix designs.* A well-designed S/S formulation typically is the result of a treatability study where various reagents/additives and mix designs are tested for treatment of contaminants materials (see Section 5 for more detail). Since one goal of treatability testing is to highlight differences between additives or binder recipes and to support the selection of viable candidate formulations, comparative testing of formulations with the results compared to material performance criteria is appropriate. Thus, reagent selection may be based on equilibrium tests which reflect contaminant retention, whereas mix design should also be finalized against flux-based leaching tests, which better reflect mechanisms controlling release in the field.

- *Baseline performance determination.* During the final stages of a treatability study, full detailed material characterization for leachability establishes a performance baseline for comparison of materials created during field pilot-scale studies and implementation. Recommended detailed leaching characterization at the bench scale includes the following:
    - equilibrium-based tests to predict porewater composition in the treated material (e.g., using either PreMethod 1314 or PreMethod 1316) and to determine how changes in acidity/ alkalinity will influence porewater concentrations (e.g., using PreMethod 1313)
    - mechanistic tests designed to account for the primary release-controlling mechanisms anticipated for field materials, including percolation column tests (e.g., PreMethod 1314 or ASTM D4784) for granular treated materials and flux-based tank leaching (e.g., PreMethod 1315, PreMethod 1315m, ANS 16.1) for monolithic materials with low hydraulic conductivity

    Characterization of the intrinsic leaching behavior using this approach provides a comprehensive measure of material performance for communicating with stakeholders; setting realistic, obtainable performance criteria; and comparing laboratory-derived behavior to field consistency testing during the implementation process. In addition, detailed leaching characterization can provide the source term for subsequent scenario- or site-specific impact assessment modeling.

- *Consistency testing.* Often, some measure of material consistency is required during implementation to ensure that the performance parameters of materials applied in the field are consistent with laboratory-formulated materials from the treatability study or that batch-to-batch variability is within acceptable tolerances. When the purpose of leach testing is to compare field materials to laboratory formulations, short-term compliance or consistency tests (e.g., PreMethod 1316, PreMethod 1313 at natural pH, shortened duration of PreMethod 1315, TCLP, SPLP, etc.) are recommended. The results of such tests can be used to determine batch-to-batch consistency and assess overall site compliance.

4. PERFORMANCE SPECIFICATIONS IN THE S/S DESIGN AND IMPLEMENTATION PROCESS

This section presents an overview of the material performance goals and the general role of performance specifications in the design and implementation process. The S/S design process begins after the site-specific remedial goals have been established and S/S has been selected as a suitable remedy. Detailed discussions of the individual steps in the design and implementation process are presented in Sections 5–7.

4.1 Flowchart of the S/S Design and Implementation Process

Figure 4-1 illustrates a generalized presentation of the design and implementation process for S/S technology. Although each site is different and the process may be adapted as needed, this figure is intended to serve as a roadmap through the major steps, decision points, and operations conducted for a typical S/S technology.

The flowchart consists of three columns representing inputs to the process (green shading), action items within the process (blue shading), and considerations used to inform decisions for each action item (orange shading). The basic action items shown in the center column include operation steps (blue rectangles) and milestones representing finalization of pertinent performance specifications (orange parallelograms). For many of the action items, inputs (green rounded rectangles) shown in the left column are used to inform the practitioner of key guiding information. These inputs may include both qualitative and quantitative measurements, regulations as well as other concepts related to the S/S treatment process. At each action item, considerations (white, rounded rectangles) in the right column help shape decisions by providing either established guiding information or recommended concepts.

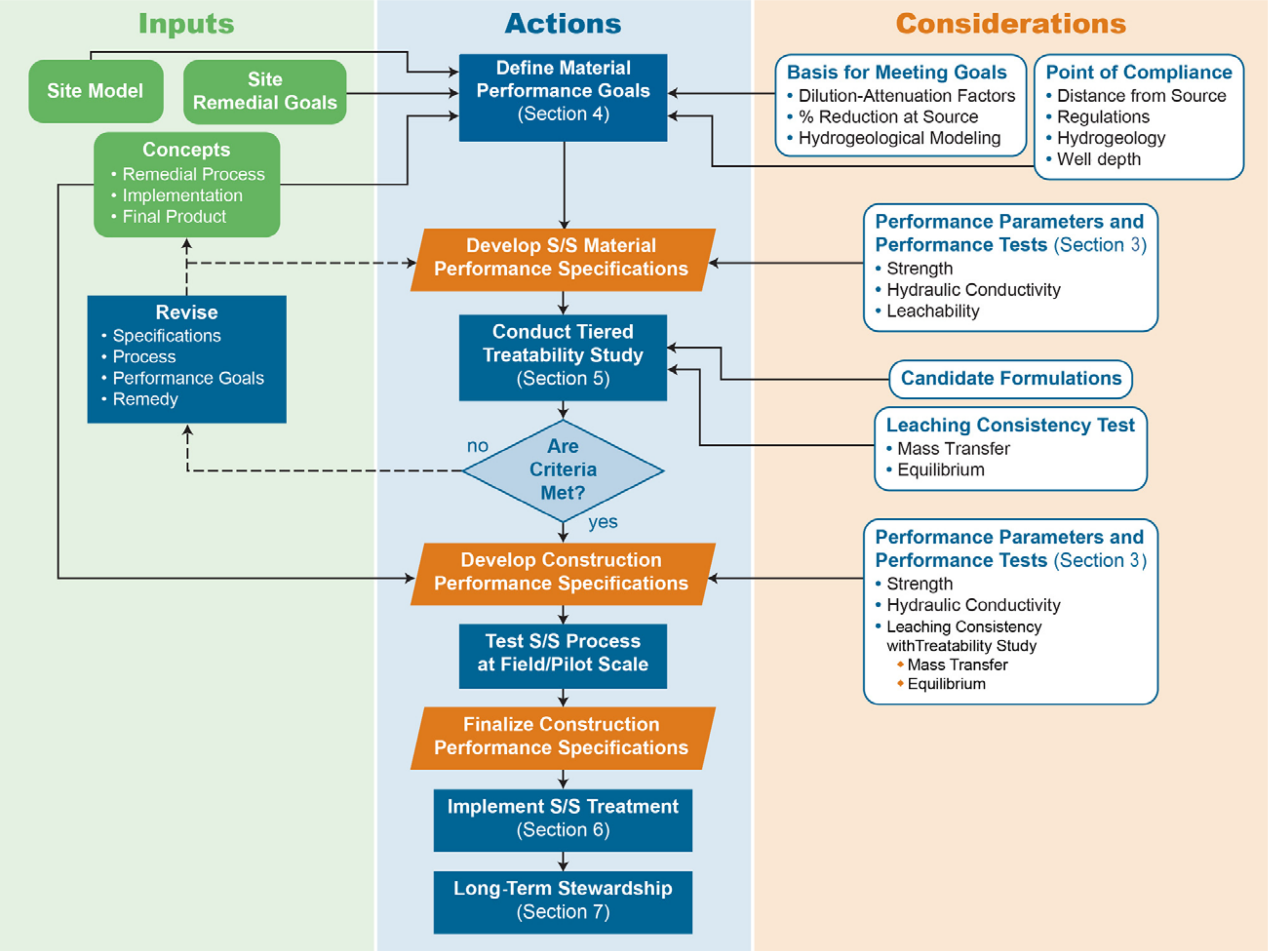

Figure 4-1. S/S design and implementation process as discussed in Sections 4–7 of this document.

4.2 Material Performance Goals

The S/S design process begins with setting material performance goals, which are design targets used to describe a treated material that is anticipated to meet specific site remediation goals. In some cases, these design targets may directly correspond with established remedial goals; however, since S/S may not be the only remedy used to meet cleanup criteria, material performance may contribution to only a portion of the remedial impact. For a groundwater remediation component, attainment of material performance goal may be established in several ways, including the following:

- demonstrating the percent reduction in concentration flux from the treated material
- calculating acceptable attenuation between the treated material and the POC
- hydrogeologic modeling to simulate groundwater flow and concentration flux attenuation

Material performance goals serve as the underlying basis for development of performance specifications that meet specific site remediation goals. The design target created by the material performance goals are used to formulate a list of characteristics for treatability testing and as a basis for the performance specifications for the design and implementation process. Several factors should be considered in the process of setting material performance goals, including the existing site model, the site remedial goals, and the vertical and horizontal location of the POC. Often, material performance goals are qualitative values (e.g., a low–hydraulic conductivity material that reduces the leaching rate by 50% while treating 90% of the contaminated material source) that serve as a framework for developing specific performance specifications.

4.2.1 Site Model

The existing conceptual site model (CSM) is composed of the primary information collected during site characterization and any supplementary data that may be collected on a site-specific basis to support a feasibility study or a remedial design. Table 4-1 shows the respective impacts of this information on development of S/S material performance goals and specifications. A firm understanding of the impact of pertinent site characteristics allows for the development of appropriate performance goals and specifications for the technology and provides insight into how the performance specifications influence the development of a long-term monitoring program for a particular site. Primary considerations beyond the site characterization that influence the formulation of performance goals and specifications include future land use and any state or federal requirements.

Table 4-1. S/S Site characterization considerations in the development of performance goals and specifications

S/S evaluation factor	Analyses/observations	Significance to technology performance and monitoring
Soil classification/ physical characteristics	Useful measurements: • Gradation • Unified Soil Classification System (USCS) classification • Atterberg limits • Moisture content • Debris content • Porosity • Density • Suspended solids • Free liquid (paint filter)	Property values for each measurement and their variability may have significant impact of overall behavior of the S/S material and on expected outcomes
Soil and groundwater	pH	Controlling variable for inorganic solubility and S/S material durability
Geochemistry	Organic content	Key variable for organic concentrations due to complexation with DOC, which is soluble at high pH (Roskam and Comans 2003, 2007)
	Contaminant levels	High concentrations of some contaminants may affect S/S cure, requiring additives to overcome interference (Conner 1997)
	Sulfate content	Sulfate attack of portland cement blends may lead to aggressive degradation through delayed ettringite formation (Little, Herbert, and Kungalli 2005)
Contaminant characterization	Leaching behavior of untreated material	Defines baseline against which treatability studies and full-scale application may be compared
	Class(es) of contaminants	Defines list of COCs, defines detection limits for analysis
	Presence/distribution of NAPLs	Defines phases/location of source and expected outcomes
Hydrogeology	Hydraulic conductivity	Controlling value in comparison to hydraulic conductivity of S/S material for mode of water contact (e.g., infiltration vs. flow-around)
	Water table depth and seasonal variability	Defines division between vadose zone, capillary fringe, and saturated zone; NAPL impacts at water table
	Geologic strata (including geometry of geology units)	Location of contaminant distribution/accumulation zones
	Groundwater flow direction and gradients	Hydraulic head on S/S mass, evaluate fate and transport with respect to POC

4.2.2 Point of Compliance

The POC, where applicable, is another factor to be considered when setting material performance goals. The POC refers to the location where the S/S-treated material must comply with site remediation goals. Often, the POC is defined with respect to compliance with groundwater remediation goals at a downgradient well located near the site boundary and screened to sample the aquifer that contacts the contaminated material. However, other possible locations for a POC may include the groundwater at the boundary of the treated material or at a surface feature (e.g., a river or lake). Indirect POCs, such as contaminants in flora or fauna, should be avoided as these are difficult to correlate to treatment of the source materials. When selected, the POC vertical and horizontal location and hydrogeology should be added to the existing CSM. Depending on the remedial goals for S/S, a POC for groundwater may or may not be a component of the project.

4.2.3 Relating Leaching Performance to Established Cleanup Goals

Often, remedial goals are established at a POC that is somewhat removed from the S/S treatment area. In these cases, it is often difficult to determine with certainty what permissible upper bounds on leaching at the treated material source will allow for attainment of goals at the POC due to limited resources regarding the ability to predict the behavior of contaminants in the subsurface between the release at the source and concentrations at the POC.

Although leaching tests can provide an estimate of leaching performance at the source of contamination, the results of leaching tests are not indicative of how released constituents travel through the subsurface. Thus, leaching test concentrations should not be considered to directly represent POC values[7] or be compared directly to water quality criteria for any purpose other than screening. In addition, flux-based leaching tests are recommended to predict release rates for monolithic materials with low hydraulic conductivity. However, current practice is to base leachability testing on single-batch extraction equilibrium tests such as SPLP or TCLP. When using equilibrium tests for leachability in the field, it is very important to consider how these results will compare with results obtained from the contaminant flux test in the laboratory since these testing methods are not the same.

Given the above statements, a remaining significant concern is how to relate leaching performance with established criteria at a POC. Figure 4-2 shows an example of how the linkage between leaching tests of S/S-treated materials and cleanup goals at a POC can be defined. In the figure, a rectangular mass of treated material is shown in the middle of an aquifer with groundwater moving with linear velocity q [m/d]. All faces of the block are exposed to groundwater. The total mass flux F released from the treated material over an exposed surface area A_{exp} is converted to a groundwater concentration C_n passing through a cross-sectional area A_n located at the treated mass.

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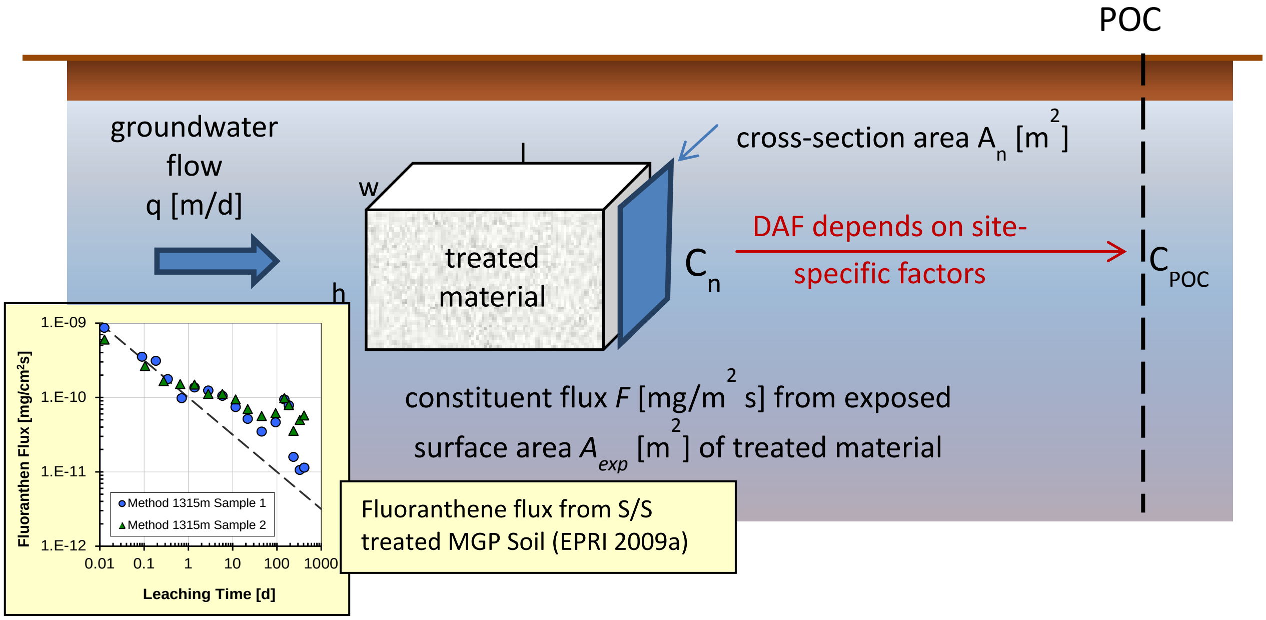
[7] The exception to this statement is the case where the POC is directly adjacent to the source material and, therefore, no dilution or attenuation is assumed to occur between the source and the POC.



Fluoranthene flux from S/S treated MGP Soil (EPRI 2009a)

Figure 4-2. Mass flux approximation showing relationship between leaching test flux and concentrations in groundwater at the treated material and at a downgradient POC.

$$C_n = \frac{F \cdot A_{exp}}{A_n \cdot q} \qquad \text{(Eq. 1)}$$

where

C_n = concentration in the groundwater (mg/L)
F = mass flux at the surface of the treated material (mg/m^2 s) (as provided by a flux-based leaching test)
A_{exp} = exposed surface area of the treated material (m^2)
A_n = cross-sectional area of groundwater (m^2)
q = linear flow rate of the groundwater (m/d)

The concentration in the groundwater is then related to a concentration at the POC through a dilution-attenuation factor (DAF). This approach is consistent with the 2010 ITRC guidance on the calculation, measurement, and use of mass flux and mass discharge in subsurface environments (ITRC 2010).

In applying a DAF, it is recognized that groundwater concentrations in the pore space just outside the material and at a POC may differ by several orders of magnitude due to dilution, dispersion, adsorption, and attenuation. The rate of transport relative to the groundwater flow and the fraction of contaminants leaving the treated material that arrive at the POC depend on several site-specific parameters:

- *site geometry*—location of the treated material relative to the water table, dimensions of the treated material, location of the well downgradient and off-center of any groundwater plume
- *soil characteristics*—pH, particulate organic matter

- *chemical retardation*—soil/water partitioning coefficients
- *hydrogeological conditions*—groundwater flow rate, hydraulic conductivity, aquifer characteristics, subsurface strata, infiltration (recharge rates)

The combined effects of these parameters are typically empirically lumped into a single DAF (a multiplier <1), which is applied to the concentration in the groundwater at the treated material (i.e., the source term) to calculate the anticipated concentration at the POC.

4.3 Performance Specifications

As discussed in Section 3, performance specifications are a critical component of an S/S remediation project, providing the basis for the development of an appropriate S/S treatment and consistency between field and laboratory materials. Two types of performance specifications are defined in this document. Although these specifications may be identical for some applications, they differ in their intended use.

- Material performance specifications are design targets developed based on the material performance goals and used during treatability studies as evaluation of whether a developed treated material will meet the material performance goals established at the start of the S/S design and implementation process. The performance parameters most commonly used in material performance specifications include UCS as a strength parameter, hydraulic conductivity (in comparison to the hydraulic conductivity of surrounding soil) as an indicator of water contact conditions, and leachability. Section 3 provides more detail on these performance parameters and example performance tests for each.

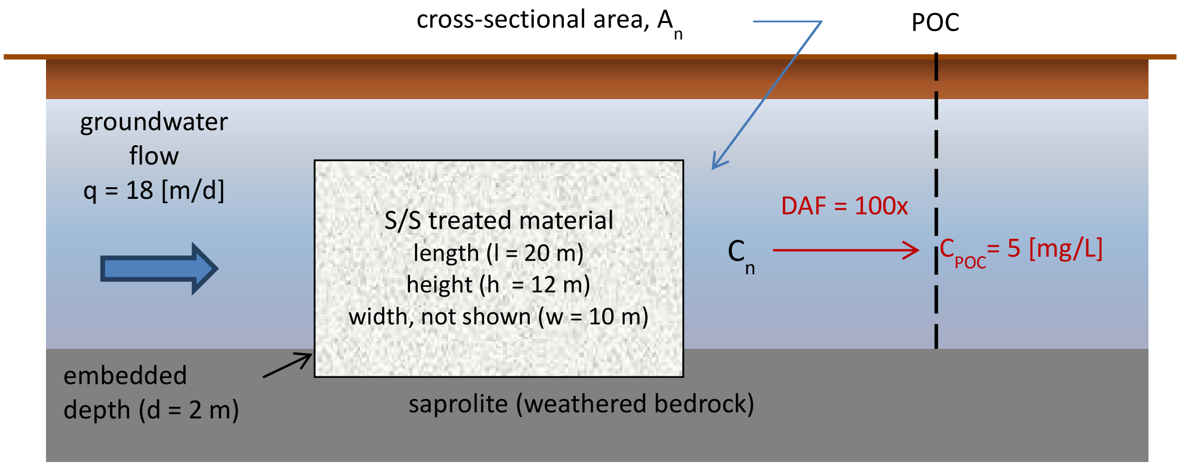
- Construction performance specifications are developed for use during field operations. These implementation targets are established at the conclusion of treatability testing or after field/ pilots studies have identified appropriate specifications for implementation of a designed S/S formulation. These performance specifications are used to verify that the treated material created in the field is consistent with the materials developed and characterized during treatability testing. Thus, the intent of testing is not to predict the performance of the material but rather to ensure that field materials behave in the same manner as the materials testing in the laboratory.

In many cases, the performance parameters used for implementation purposes are similar to those applied at the laboratory scale (e.g., UCS, hydraulic conductivity, and leachability); however, the selection of performance tests should reflect that decisions regarding acceptance of field materials must be made quickly as cured S/S-treated material is difficult to remove or retreat. Construction performance specifications should be on the selection of limited set of performance parameters already used in the treatability testing applying short-term tests which can be conducted on wet-prepared field samples after a couple of days of cure time. The results of these tests should be compared to the baseline performance developed at the end of the tiered treatability study (see Section 6.2 for information on QC).

Developing a Material Performance Specification for Leaching

This approach can be particularly useful for setting a material performance specification for leaching from an established cleanup goal and dilution-attenuation factor.

Assume: A treated mass (12 m high x 10 m wide x 20 m long) is anchored 2 m into saprolite (weathered bedrock). which acts as an aquiclude. The surface of the material not buried in saprolite is exposed surface to an aquifer moving at 18 m/d (see figure).



Since no, or relatively little, groundwater passes through the saprolite, the surface area of the treated mass embedded into saprolite does not participate in leaching, and the exposed surface area is

$$\begin{aligned} A_{\exp} &= \text{top} + 2\times\text{side} + 2\times\text{end} \\ &= w\times l + 2\times(h-d)\times l + 2\times(h-d)\times w \\ &= 10\times 20 + 2\times(12-2)\times 20 + 2\times(12-2)\times 10 = 800\left[m^2\right] \end{aligned}$$

Using the sample concept, the cross-sectional area to the groundwater flow would be

$$A_n = 1\times\text{end} = 1\times(h-d)\times w = 1\times(12-2)\times 10 = 100\left[m^2\right]$$

For a hypothetical constituent, a groundwater cleanup goal of 5 mg/L is established at a downgradient water feature (e.g., a well or surface body), and a DAF between the POC and treated material 100x is determined to be reasonable and protective. The DAF is calculated, estimated, or otherwise established to take into consideration groundwater chemistry and dynamics as well as the location of POC relative to source and groundwater flow.

Concentration at the Source: By multiplying the cleanup goal by the DAF, the maximum concentration of a constituent released from the treated material C_{max} is calculated:.

$$C_{\max} = 5\left[\frac{mg}{L}\right]\times 100 = 500\left[\frac{mg}{L}\right]$$

Maximum Flux: Using C_{max} for C_n in Eq. 1 (p. 33), the maximum allowable flux F_{max} may be determined:

$$F_{\max} = \frac{C_{\max}\times A_n\times q}{A_{\exp}} = 500\left[\frac{mg}{L}\left(\frac{10^3 L}{m^3}\right)\right]\times 100\left[m^2\right]\times 18\left[\frac{m}{d}\left(\frac{d}{24h}\,\frac{h}{3600s}\right)\right]\times\frac{1}{800\left[m^2\right]}$$

$$F_{\max} = 13.0\left[\frac{mg}{m^2 s}\right]$$

From this analysis, a conservative material performance specification of a maximum flux of 10 mg/m^2s using a flux based leaching test (e.g., ANS 16.1, EPA PreMethod 1315) can be applied with some degree of confidence that cleanup goals can be achieved based on established values.

4.4 Performance Specifications in Treatability Studies

Typically, treatability studies are bench-scale investigations used to determine whether the proposed remedial technology will be effective in meeting the remedial goals and to develop an appropriate mix design and construction performance specifications. Material performance specifications are used to provide feedback on selection of reagents and additives that result an appropriate formulation for retention of COCs. The performance parameter results from testing on laboratory-created specimens are used to refine treatment mix designs and to demonstrate compliance of the finalized mix design with material performance specifications. Comprehensive guidance on physical and chemical tests for treatability studies as applied to S/S technology is described in published guidance documents (EPA 1989, USACE 1995).

4.5 Performance Specifications During Implementation

Implementation of an S/S remedy should be performed only after determining that the S/S is consistent with the remedial goals for the project, an S/S mix design has been developed and tested that can meet the material performance goals, and a design appropriate for the size of the remedy is completed. Construction performance specifications are used to determine whether the key parameters of the material created in the field are consistent with the finalized mix design characterized during treatability studies. QC testing both for compliance with material performance specifications and consistency throughout construction is a key implementation component to document achievement of material performance goals. Key performance-related considerations for implementation of the S/S remedy at the field scale are presented in Section 6.

5. TREATABILITY TESTING PROGRAM

For many technologies including S/S, effectiveness, implementability, and cost are site specific. Site-specific treatability studies in the laboratory and/or the field provide valuable information needed to evaluate the feasibility and establish the design of treatment remedies. Treatability testing develops the S/S formula to meet project objectives and verifies the feasibility of using S/S by characterizing the untreated contaminated material and evaluating the technology performance under different operating conditions. Treatability testing provides valuable site-specific information to support selection and implementation of a remedial action. Therefore, treatability tests may be conducted both to evaluate technologies prior to selection and to develop process design parameters and scale up for full-scale implementation. Additional information for conducting treatability testing is provided in published documents and guidance (EPA 1992a, USACE 1995, Environment Agency 2004a, EPRI 2009a).

Treatability testing for S/S should be performed in a systematic manner to ensure that data generated can be used for evaluation, identification of information for further testing, and full-scale implementation.

The goal of the S/S treatability testing is typically to develop the S/S design and to verify the feasibility of using S/S at a particular site. The objectives, which should be clearly defined prior to testing, typically include the following:

- selection of correct reagent(s) (a list of common reagents is presented in Section 2.3.1)
- determination of the impact of selected reagents on other contaminants
- optimization of the reagent(s) dosages
- identification of emission of contaminants
- identification of material handling issues
- assessment of the physical and chemical uniformity of the contaminated material
- determination of the volume increase due to addition of reagent(s)
- finalization of performance criteria
- finalization of construction parameters (e.g. moisture content, slump)

A typical treatability testing program is an iterative process which determines the optimal formulation and associated design parameters that meet the project objectives. Treatability testing for S/S may include both bench-scale and pilot testing, although full-scale pilot testing may be considered during startup of field implementation. Once treatability testing is completed, a plan for treating the full extent of the contaminated material in the field is based on the results of the tests. The plan also takes into account scale-up considerations, as discussed in Section 5.4.

5.1 Reagent Selection Considerations

Potentially applicable reagents should be identified prior to bench-scale treatability testing. The identification of potentially applicable reagent depends on several factors, including contaminant to be treated, concentration of contaminants in soil/sediment and soil/sediment geotechnical properties, required performance parameters, and minimum acceptable performance criteria for the site.

Identification of potentially applicable reagents is typically based on the practitioner’s experience in implementation of S/S projects. In the absence of previous experience, a survey of technical literature to identify appropriate reagents is a good starting point for treatability testing. Because a number of candidate reagents may be identified, narrowing down the number of reagents results in reduced cost and less time-consuming treatability testing. Selection of candidate reagents requires knowledge of the following:

- interferences and chemical incompatibilities
- metal chemistry considerations
- compatibility with the disposal or reuse environment
- cost
- process track record

A more detailed discussion on the above considerations is provided in EPA’s *Technical Resource Document: Solidification/Stabilization and Its Application to Waste Materials* (EPA 1993c).

5.2 Bench-Scale Testing

Bench-scale testing is usually performed in the laboratory, where a comparatively small amount of contaminated material is tested for individual parameters of the treatment technology. In general, the testing is used to determine the efficacy of the chemistry of the process and usually consists of a series of tests using a tiered approach. In this tiered approach to treatability testing, the results of each test determine the next steps and next set of parameters and conditions to be evaluated, with the first set of tests usually covering a broad range of potential operating parameters and establishing of baseline parameters. This tiered approach (as described in EPRI 2009a) is as follows:

- <u>Tier 1</u>—testing previously identified candidate reagents (as described in Section 5.1) to narrow the range of reagents by eliminating those not meeting the performance criteria
- <u>Tier 2</u>—testing the selected reagents and combination of reagents and additives (if used) to assess contaminant immobilization
- <u>Tier 3</u>—optimizing the promising reagent or combination of reagents and additives (if used) to minimize the quantity required to meet the performance criteria
- <u>Tier 4</u>—assessing scale-up considerations for full-scale implementation and development of QC parameters, baseline consistency tests, and performance criteria acceptance limits

S/S bench-scale treatability studies include the following steps:

- prepare a work plan
- collect test samples
- characterize initial samples
    - homogenize raw materials/samples
    - perform chemical testing
    - perform physical testing
- perform treatability testing
    - conduct tests by mixing reagents with contaminated material and prepare formulations for further testing
    - optimize mix design
    - selection of mix design verification phase (three replicates)
    - prepare final mix design and test
- analyze, assess, and validate data
- prepare treatability study report

<u>5.2.1 Sample Collection</u>

Selection of the samples to be collected for bench-scale testing is critical and must be carefully planned to best represent the site conditions. Planning sample collection for treatability testing must consider a number of factors, including the following:

- appropriate locations for collection of representative samples
- methods for collecting representative samples
- type of implementation method

- whether or not samples will be composited

Sampling for treatability testing should use technical expertise to determine the most appropriate sampling locations based on previous site characterization results, operational history, and visual survey. Evaluation of site characterization data should include considerations of the following:

- contaminant types
- contaminant concentrations
- lateral variation of contamination
- depth of contamination

The sampling plan should include highly contaminated material, material representative of average site conditions, and minimally contaminated material. Sampling should also include the reasonably most difficult to treat soil that will be encountered during full-scale treatment implementation. Determination of the most difficult to treat soil depends on the physical nature of the soils as well as the COCs and the extent of blending that will occur during full-scale treatment. Although sampling using *only* the most highly contaminated or difficult to treat material provides assurance that these can be treated using S/S, it can result in overdesign and unrealistic high cost estimates. Therefore, while these samples may be used to establish the treatability of the material, additional treatability testing should be performed on material representative of average site conditions. Furthermore, the costs should be developed based on these representative samples.

Sample collection for treatability testing must also consider the lateral variation of contamination and depth of contamination. The depth of contamination also influences the selection of appropriate methods for collecting representative samples. Samples can be collected using direct-push Geoprobe equipment, hollow-stem augers, backhoes, or hand auger tools. A minimum of 40 L (10 gal) should be sampled to perform a treatability testing; however, the amount of sample will depend of the number and type of test to be performed during the study. No matter how well the site is characterized, heterogeneity makes the samples collection for treatability testing challenging. Once samples are collected, proper homogenization of the samples must be performed prior to initial (baseline) characterization.

If the site is highly variable in contaminant types and concentrations, consideration should be given to how the full-scale treatment will be implemented, such as full-scale treatment implemented separately for each impacted area versus mixing and homogenizing all material before implementing S/S. If the full-scale implementation approach dictates, compositing of samples collected for treatability testing may be required and is based on the quantity of contaminated material for each impacted area. Advantages to composite sampling include reduction in the variability in contaminant concentration and more accurate data on soil that may be treated after homogenization of all the material. Compositing is usually appropriate for nonvolatile contaminants; however, if target contaminants are volatile, care should be exercised in compositing.

5.2.2 Initial Sample Characterization

After sample collection, a baseline analysis should be performed on the samples collected for testing at the bench-scale level through a process of chemical and physical testing. The physical characterization test usually includes moisture content, grain size distribution, Atterberg limits, and compaction. Chemical characterization may include total chemical analysis of the samples collected.

5.2.3 Laboratory Testing

Selected reagents are mixed with the samples to evaluate the preliminary performance parameters (such as strength, hydraulic conductivity, and leachability). Preliminary testing in the laboratory may include testing for strength by use of a pocket penetrometer over a period of time, visual observation, chemical testing, and/or geotechnical testing (Figure 5-1). The information obtained from performing laboratory tests results in identification of reagents that can solidify/stabilize the contaminated material.

Figure 5-1. Hydraulic conductivity measurement (left) and UCS measurement (right) tests conducted in the laboratory on treatability test samples. *Source:* CETCO Contracting Services Co.

5.2.4 Data Analysis, Assessment, and Validation

Once the treatability tests are completed, if the data meet the performance criteria, pilot test studies or field demonstrations may be considered prior to full-scale implementation. If the performance criteria are not met, the specifications, process, or performance goals may need to be revised and the treatability study repeated (see Figure 3-1). If the criteria cannot be met, the remedy selection may need to be revised. Validation of the laboratory data is a step that is always included before analyzing data results. Often, data validation is provided by the laboratory.

5.3 Pilot-Test Studies/Field Demonstrations

Following selection of the design mixes obtained from bench-scale treatability testing, the next phase of the project may involve a pilot test in the field. The pilot test is intended to verify the process variables selected as part of bench-scale testing and, if required, further develop and optimize the process and construction parameters for full-scale implementation.

The pilot test scales up the design mixes developed during bench-scale treatability testing for application under actual field conditions based on the ability to meet the performance criteria, implementability, and cost. Because pilot-scale testing is intended to simulate the physical as well as chemical parameters of a full-scale testing process, the treatment unit size and the volume of contaminated material to be processed in a pilot scale is much greater than for bench-scale testing.

The development of a pilot study begins with preparation of work plans. Work plans specify the approved reagents to be used, their dosages, type of mixing devices to be employed, and data to be collected. The results obtained from the pilot testing are evaluated to confirm that performance criteria can be met in the field while implementing the full-scale system. However, if the identified performance criteria are not met during pilot testing, the reagent mix design should be adjusted as a first step. The selected performance criteria, goals, and processes should also be reevaluated if adjustment of reagents does not produce desired results.

5.4 Scale-Up Considerations

Since the S/S chemistry is already established, the scale-up from bench-scale to full-scale field implementation is generally focused on the materials-handling aspects of the S/S process. Scale-up from bench scale to full-scale field implementation should address the following:

- equipment selection and sizing
- type of equipment and mixing time/energy departed for homogenization
- chemical reagents storage and delivery methods
- evaluation of treated material consistency tests and strength gain rates
- pretreatment of soil/sediment
- presence of debris
- presence of underground utilities
- mixing and curing time and methods employed
- method and measurement for delivering correct reagent quantity
- quality assurance (QA)

Scale-up considerations are the last step of the trial approach of the treatability test programs. After completion, the next step is to implement a verification process during S/S implementation.

6. PERFORMANCE VERIFICATION DURING S/S IMPLEMENTATION

The overall success or failure of an S/S remedy depends on successful implementation of the construction phase. The following key areas should be monitored and documented as necessary during the implementation phase to ensure that performance specifications have been achieved:

- consistent preparation of the designed reagent blend in the correct proportions in accord with the mix design determined through the bench and pilot testing
- sufficient mixing of the reagents with the contaminated materials in the correct proportions to create a treated material
- sampling of treated materials to verify compliance with S/S performance specifications
- verification of treatment of the entire volume of contaminated materials

QC and QA are vital in S/S treatment to demonstrate that the treated material achieves the performance specifications of the project and that the proper reagents were mixed in accord with the approved mix design. In addition, the implementation of a QA/QC program during remedial construction allows for adjustments to be made as needed to respond to variations in material and/or site conditions. The QC plan describes the specific procedures by which the implementation of sampling and analytical procedures designed to result in reliable data are documented (LaGrega, Buckingham, and Evans 1994). The QA plan describes the procedures by which the QC implementation is audited to ensure that the work and documentation is being conducted in accord with established QC procedures.

Effective implementation of S/S requires a comprehensive construction quality assurance (CQA) program that addresses each phase of the project from bench-scale testing through full-scale field operations. Monitoring of S/S performance in the field is essential to ensure that the project objectives are met and S/S work is conducted in accord with contract requirements. Lack of an effective CQA program can lead to rapid and uncontrolled cost increases caused by the lag time between S/S sample collection and receipt of testing results due to the curing time required. A CQA program allows the owner to rapidly assess construction performance and identify potential problems early in the process to allow for field adjustments or corrections (Wittenberg and Covi 2007).

While the QA/QC procedures may vary from project to project based on the specifics of the design and performance specifications, solidification QA/QC guidance documents and published articles should be consulted when preparing a QA/QC program for S/S (EPA 1989, 1986, 1999a; Perera, Al-Tabbaa, and Johnson 2004; Perara et al. 2004b; USACE 2010; Larsson 2005; Wittenberg and Covi 2007).

6.1 Reagent and Equipment QA/QC Considerations

Reagents to be delivered in bulk to the site for full-scale S/S should be tested or otherwise verified to ensure they meet the project specifications. Reagents should be tested at the beginning and midpoint of the project to ensure that no COCs are imported with the reagents. Requirements concerning storage of reagent stockpiles may be included in construction performance specifications. Physical properties such as dry unit weight may require periodic verification if mixing involves dry reagent addition. An on-site batch plant for mixing of S/S reagents or additives is typically necessary for in situ applications that inject reagents as a liquid slurry.

For pugmills that blend dry reagents along with water, the dry reagents are typically fed from the storage silos using a screw auger. The feed rate of these augers should be calibrated at least once per day at the start of operations for that day. Reagents and additives are typically delivered to a site in bulk quantities and must be transferred to the storage pigs and silos at the pugmill or batch plant for processing. A batch plant for preparing liquid slurry may consist of mixing and staging tanks, scales, mixers and agitators, and pumps. Scales and flow meters must be field-calibrated periodically throughout the project to ensure appropriate reagent/additive injection rates. Furthermore, the addition of water, a critical reagent, should be carefully monitored and the amount recorded. Mixing and delivery procedures should include QA/QC methodology to verify that the reagents are within the mix design parameters. For reagent delivery in a water-based grout, parameters such as grout density (mud balance) and viscosity (Marsh Funnel) should be checked periodically to verify grout batch consistency with the recommended design. For pugmills where the reagents are fed in a dry state, the feed rate of the feed augers is usually calibrated in pounds/second.

S/S mixing equipment comes in many forms for shallow or deep in situ and ex situ mixing. Appendix A provides a brief description of some of the more common S/S mixing equipment. Parameters which affect the blending of contaminated materials, such as mixing speed, reagent delivery rate, soil treatment rate, and mixing time, should be incorporated into the QA/QC monitoring program to maintain consistency in mixing equipment operation. The precise location and depth of placed treated material should be recorded. For in situ treatment using vertical augers, each column is numbered and the location recorded. For ex situ treatment, the deposition location for each day’s production is recorded.

6.2 Treated Material Performance QA/QC

Procedures for ensuring sufficient mixing of contaminated materials with S/S reagents should be established in the pilot scale and/or demonstration phase and may involve consistency tests of freshly mixed materials. Depending on the type of mixing equipment and the reagent delivery method used (i.e., wet or dry), construction parameters such as mixing time, auger penetration rate and rotation speed, number of up and down auger strokes, and reagent delivery rates should be incorporated into field QC monitoring procedures. Consistency testing of freshly mixed materials based on visual observations and slump tests are commonly used during construction as control tests to identify batches or areas that appear to be outside the normal range expected and may require adjustments to the S/S mixing or reagent addition processes. For in situ mixing, overlap of treatment zones is critical to ensuring treatment of the entire volume and can be monitored through survey control and representative post S/S test pits or borings to verify complete mixing and overlap (Figure 6-1).

Observation and testing of treated material involves two types of testing as discussed in Section 4 of this document: (a) consistency testing to monitor treated material properties in real time or in a short duration to demonstrate that treated materials are consistent with properties established during treatability testing and (b) compliance testing to document that performance criteria for the treated material are met. Sampling considerations as well as field and laboratory consistency and compliance testing are briefly described in the next section.

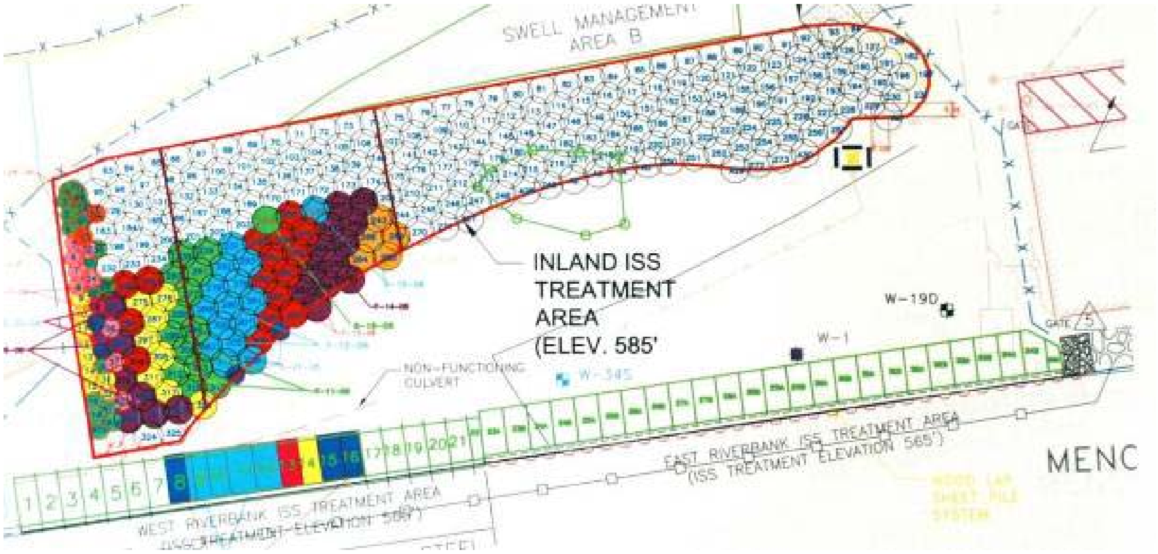


Figure 6-1. Example of overlap of in situ auger-mixed S/S. *Source:* Portland Cement Association.

6.2.1 Sampling of Treated Material

The frequency of sampling freshly treated material depends on the overall size of the S/S project, the daily treatment rate, the observed consistency of mixing by the remediation contractor, observed changes in the contaminated material properties, and other factors. A higher frequency of sampling is generally performed during the pilot phase and/or the start of S/S production to develop a test results data set confirming the ability to meet the performance criteria and further assessing the variability of the material to be treated and the variability expected in the test results. While the sampling frequency for a specific project is determined by the designer and/or the regulator, as a general guideline, it is recommended that performance sampling of treated material be conducted considering the following:

- Sample at least once per day of production and once per shift (if there are multiple shifts) and any time the batch plant or mixing equipment operator changes.
- Sample every 400–800 m^3 (500–1000 yd^3) of treated material (alternate frequencies may be appropriate based on overall volume to be treated for a site, anticipated contaminated material characteristics heterogeneity, and test results review as project progresses).
- Sample any time the contaminated material or blended material physical characteristics appear to change significantly (e.g., greater contaminant level, significant variation in moisture content, significant variation in material gradation, etc.).
- Some additional discussion on performance sampling is provided in Bates (2010), among other references.

If failing test results occur, modifications to the mix design or blending method may be required and the sampling frequency increased until acceptable results are consistently achieved. The failed material may need to be reworked or properly disposed of, if practical, based on S/S plan design. Regardless of the outcome, procedures for documenting and addressing any failures must be in place.

The method of collection of freshly mixed material (i.e., contaminated material blended with S/S reagents) depends initially on whether the material is treated in situ or ex situ. For ex situ treatment methods, a bulk sample is typically collected from the discharge of the pug mill, from a stockpile of treated material, or from a freshly treated area (e.g., when mixing excavated material within a containment area or a work pad area). The bulk sample is collected in a 20-L (5-gal) bucket and relocated to the sample preparation area for further processing, testing, and sample specimen preparation (Figure 6-2).

Figure 6-2. Field preparation of cylinder molds of freshly treated material. *Source:* Ed Bates.

For in situ mixing, fresh samples should be collected from different locations and depths within the treatment area in a statistically valid manner. Specialized sampling tools for discrete-depth interval sampling of freshly mixed soils allow for evaluation of vertical mixing homogeneity. Typically, an excavator is used to slowly push a metal tube into the freshly mixed material to the depth desired for sample retrieval (Figure 6-3). The tube is equipped with a hydraulically activated valve which is opened as the sampler reaches the desired interval.

Figure 6-3. Specialized sampler for S/S column mix areas. *Source:* Ed Bates.

Figure 6-4. Sample collection of freshly mixed material from an excavator bucket. *Source:* CETCO Contracting Services Co.

The sampler is then withdrawn from the treated material and the sample discharged to a 20-L (5-gal) bucket (Figure 6-4). Sufficient sample volume should be collected to accommodate field and laboratory testing in accord with the CQA plan. Other sampling methods exist and may be appropriate as long as the sampling can be accomplished at the location and depth interval desired. Following sample collection, specimens are prepared for field testing and/or curing and laboratory testing.

Many tests on treated material require curing in cylinder molds of a specific geometry and for a minimum period of time for hydration reactions to occur and the material to solidify. Preparation of sample specimens should follow standard procedures such as ASTM D1632 (or procedures required by specific test methods) to ensure consistent specimen preparation for the tests specified. Bulk material is typically initially screened through a 1.3-cm (0.5-inch) mesh to remove oversize particles that would interfere with the specimen testing (Figure 6-5) due to the relatively small size of test specimens. Note that the screen mesh size required may vary based on the size cylinder molds that will be prepared as specified in the ASTM cylinder preparation methods. Use of 7.6 × 15.2 cm (3 × 6 inch) or larger cylinder molds is recommended as smaller cylinder molds are more susceptible to testing variations due to sample heterogeneities. Proper preparation of cylinder molds by tamping in lifts and proper field curing conditions are critical to the testing outcomes (Figure 6-6). Specimens with voids or cured under adverse conditions typically have poor test results (i.e., lower strength and higher hydraulic conductivity).

Figure 6-5. Sieve screening of treated material sample in preparation of UCS cylinder molding. *Source:* CETCO Contracting Services Co.

Figure 6-6. Field curing of S/S material specimens in a humid atmosphere (water bath). *Source:* Ed Bates.

A sufficient number of replicate samples should be prepared in the field. These replicates are used for the following:

- evaluating curing progress within the first few days of curing
- as replicate test specimens should a failing performance test result be obtained
- samples for QA testing by an independent laboratory

6.2.2 Consistency Testing

Consistency testing is used during construction for real-time or short-term evaluation of treated material to determine whether the material properties are consistent with those established during the bench and pilot phases that result in a material that meets the project performance criteria. Therefore, it is important that the test methods, test conditions, specimen geometry, sample specimen preparation methods, and curing conditions be consistent between the bench-, pilot-, and full-scale implementation phases to reduce test results variability to the extent practical. While test results will have some inherent variability due to product heterogeneities, it is important to minimize induced variability due to specimen or test condition variability.

Tests typically used to establish compliance with performance criteria (e.g., compressive strength, hydraulic conductivity, and leachability) are performed on specimens that have been cured for 7–28 days or longer, and the tests themselves can take a few days to a few weeks to perform. Consequently, the time lag between material treatment and verification of compliance can be very long and a large volume of additional material treated before determining whether the material meets the performance criteria. Therefore, consistency test protocols are typically established in the bench and pilot phases for use during the construction phase. Consistency tests can be performed on freshly mixed material or cured specimens, and a combination of both is recommended. Real-time testing of freshly mixed material is intended to identify significant variations in material properties that can affect performance test results and may include tests such as slump, material moisture content, grout density and viscosity, mixing thoroughness (mixed material homogeneity) (Figure 6-7).

Figure 6-7. Slump test on freshly treated material. *Source:* Ed Bates.

Short-term tests on specimens as curing progresses may include, but are not limited to, strength gain rate using a pocket penetrometer, visual observation of bulk sample specimens cured in a 20-L (5-gal) bucket (Figure 6-8), and short-term leaching tests, including an SPLP test, an abbreviated monolith leaching test, or other leaching tests that may be deemed appropriate for a specific project. If SPLP tests are conducted, results are used to determine only whether the leaching of contaminants falls within the range established for this same test during the bench-scale testing, not as a performance criteria. Abbreviated monolith leaching tests are described using an example below. Use of consistency tests allows for real-time or short-term adjustment in reagent addition rates or mixing procedures to maintain material properties in a range where the risk of failing performance tests is low.

Figure 6-8. Five-gallon bucket-molded sample cleaved, exposing successful encapsulation of contaminant. *Source:* Portland Cement Association.

Leaching consistency testing example

To show consistency during implementation of an S/S remedy, leaching tests may be used to show that there is no significant deviation in leaching behavior between field samples and bench-scale samples characterized during treatability testing. Since decisions in the field to re-treat any particular zone of the implementation require a relatively rapid testing response, full-duration mass transport testing (ANS 16.1 or PreMethod 1315) may not be practical. However, these tests may be modified to shorten the duration of the test as in the treatability example above. Alternatively, batch extraction tests applied to both bench-scale and field samples may be used as a consistency indicator based on the equilibrium-based leaching behavior of samples. To further reduce testing requirements of field samples, the number of extractions in the equilibrium methods provided in LEAF (i.e., PreMethods 1313 and 1316) may be limited to target specific test conditions. (See Appendix B for more information on LEAF tests.)

This example illustrates the concept of using limited equilibrium-based leaching characterization to show consistency. The subject material is a coal combustion fly ash sampled from the same collection point over three one-month intervals. The first collection was considered to be a baseline with full characterization using PreMethod 1313. For subsequent collections, a limited version of PreMethod 1313 using four extraction points (instead of the nine used in the full characterization) was used to compare back to the baseline. Although this example does not show data conducted on materials associated with an S/S remedy, the same concept of consistency testing can be applied to S/S materials.

The data in Figure 6-9 indicate that over a three-month interval, the leaching behavior of both major constituents (i.e., those making up the matrix of the fly ash like calcium and silicon) and trace constituents is very consistent. The key to this type of consistency is not that levels change due to minor variation in material (see arsenic data), but that the general trend in data is the same. This fact indicates that the geochemical speciation of the constituents is constant in all time-dependent samples.

6.2.3 Compliance Testing

Compliance testing is used to evaluate cured material properties for direct comparison to project performance criteria. The types of compliance tests can vary on a project-specific basis based on the remedial objectives. The most common compliance tests for solidified materials are strength and hydraulic conductivity. Leachability compliance testing is used somewhat less often, and the need for compliance testing depends on the mechanism of treatment employed (i.e., solidification versus stabilization). When hydraulic conductivity reduction is the primary mechanism used for leaching reduction (i.e., solidification as opposed to chemical stabilization) and leaching performance has been adequately demonstrated in the treatability study phase, consistency tests can be used in lieu of leachability compliance tests during construction. Where stabilization reactions are the primary mechanism of treatment, leaching tests such as SPLP may be appropriate as compliance tests.

At the various stages of the S/S treatment development process, different levels of material property and leaching characterization may be needed. Thus, the performance specification, especially the selected test and performance criteria, may differ based on the stage of the remediation process. For example, compressive strength sufficient to support implementation equipment after a couple of days might be a high priority, whereas after closure, compressive strength would not be as critical as hydraulic conductivity and leachability. Likewise, leachability tests during the treatability stage of the project might include a more comprehensive leach testing scheme than can be conducted and interpreted in a timely manner for compliance testing during implementation. Therefore, during implementation a shortened testing protocol for field compliance tests for leachability is recommended.

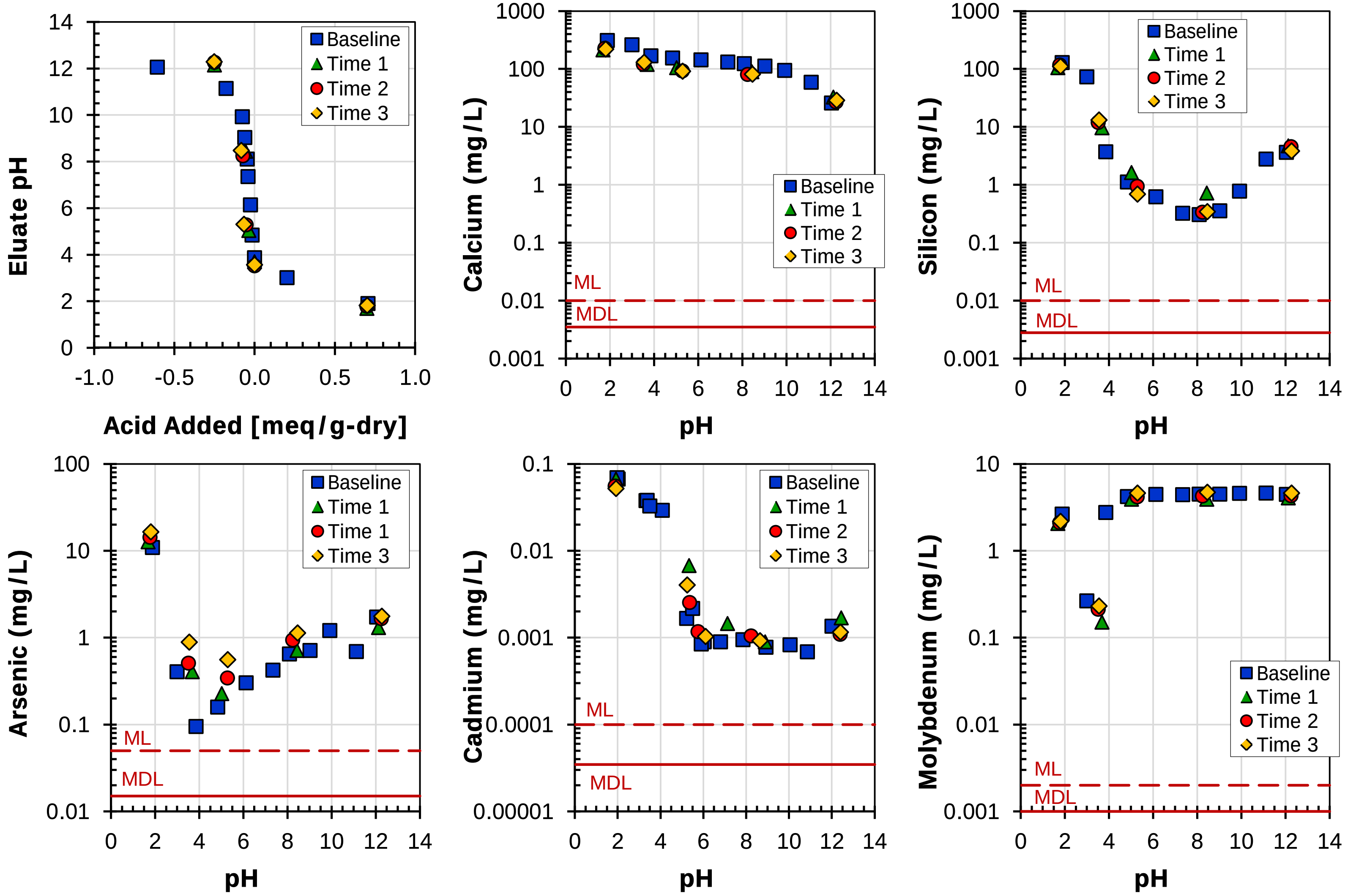


Figure 6-9. Example consistency testing using PreMethod 1313 on coal combustion fly ash samples collected at four different times from the same source.

6.3 Assessing Field Performance Test Data

Sampling and testing of treated S/S material should be performed to adequately assess representative samples from the entire area, volume, and depth of the S/S treatment area. The total number of samples collected and tested should enable statistical evaluation of test results if necessary. Sampling guidance is provided in USACE 2010.

Historic practice for many S/S projects has been to set performance criteria expressed in statements that require all results to pass, as expressed in statements such as the following:

- All specimens must exhibit UCS of not less than 344.7 kN/m^2 (50 psi) (or other site-specific performance criteria).
- Hydraulic conductivity shall not exceed 1 × 10^{-6} cm/s (or other site-specific performance criteria).

It should be noted that when provided in statements specifying or implying that all samples must meet the performance criteria, failure of any individual test result can result in the need for re-treatment. Re-treatment can be expensive and difficult on previously cured materials and may not result in significant improvement as it breaks up previously solidified material and attempts to resolidify larger particles (i.e., fractured solidified soil). This problem also underscores and demonstrates the value of preparing replicate specimens for retesting if a failing result is obtained.

Alternatively, performance criteria statements can be written to recognize that some limited variability in test results is acceptable without compromising the overall success of the remedy (see box). This approach is based on assessing failures based on the overall aggregate performance of the treated material and the potential contaminant loading from the entire S/S mass to the environment. Considerations such as the location of a failing test specimen may be of significance. For example, a poorly treated area located within the middle of an S/S monolith surrounded by properly treated material will have little or no impact on the completed remedy performance. Conversely, a poorly treated area located on the edge of the monolith will have contact with surrounding groundwater and may have a more direct influence of overall remedy performance. It is sometimes desired for in situ S/S that the outer zone of the S/S monolith receive a higher level of treatment (i.e., a richer mix) to ensure that the zone in direct contact with passing groundwater has an increased safety factor against leaching as compared to the bulk of the treated material.

Examples of tolerance intervals that may be considered for inclusion in performance criteria are as follows:

- *Strength:* Average of all performance samples must not be less than 344.7 kN/m^2 (50 psi), no individual sample shall be less than 275.8 kN/m^2 (40 psi), and no more than 20% of the performance samples shall be less than 344.7 kN/m^2 (50 psi).
- *Hydraulic conductivity:* Average of all performance samples must not be greater than 1 x 10^{-6} cm/s, no individual sample shall be greater than 1 x 10^{-5} cm/s, and no more than 20% of the performance samples shall be greater than 1 x 10^{-6} cm/s.

Note: Actual performance criteria and percent acceptable variation must be determined on a case-by-case basis.

Field construction performance specifications using tolerance intervals can be developed to allow for the inevitable variation of properties of individual test specimens. An example of the use of tolerance intervals is provided in the Peak Oil Case Study (see Appendix C). The designer and regulator should develop a consensus on what is acceptable based on the remedial objectives for the project and considering the location of failing test results, among other factors. For example, a few failing test results that meet the lower tolerance limit and that are randomly scattered throughout the S/S area may be less of a concern than a cluster of failing test results occurring in one general area (possibly indicating differing soil/contaminant conditions, inadequate reagent batch preparation, or inadequate mixing) or along the outer edge (where groundwater or infiltration exposure may be greatest).

Figure 6-10 illustrates a sample QC testing performance tracking chart. In this example, five samples out of 30 failed to meet the minimum strength performance criteria of 344.7 kN/m^2 (50 psi). Three of the five failing samples were between the tolerance limit of 275.8 kN/m^2 (40 psi) and the performance criterion of 344.7 kN/m^2 (50 psi). These failures would be considered acceptable since fewer than 20% (determined acceptable for the example site) of the samples were below the performance criterion, the failing results did not occur sequentially (which may indicate a batch process or treatment area condition requiring attention), and the average of all test results was above the performance criterion. Two results were below the tolerance limit. The areas in which the failures occurred should be evaluated (e.g. center of the matrix or on the edge of the treated matrix; failures on the edge of the matrix may be of greater concern) and testing of field replicate specimens conducted to further assess the nature of the failing test results to determine whether these areas should be retreated or additional volume surrounding the failing area warrants treatment. Additional examples are provided in the box on page 52.

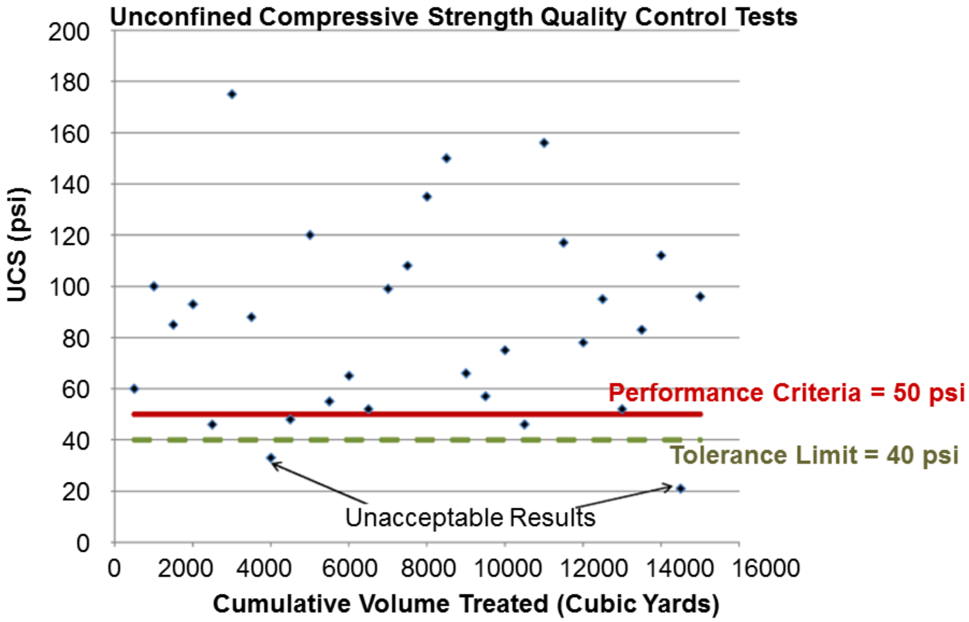


Figure 6-10. Sample QC test results tracking chart.

Additional examples of consistency testing interpretation follow using the following scenario: Implementation of an S/S remedy resulted in 100 confirmatory samples. The performance criterion for strength is assumed to be 344.7 kN/m^2 (50 psi):

- *Example 1*—95 of the samples exceeded the strength criteria of 344.7 kN/m^2 (50 psi). The five samples that did not exceed the strength criteria were all greater than 275.8 kN/m^2 (40 psi). The nonconforming samples were randomly distributed throughout the treated matrix. The determination was that the treatment was acceptable.
- *Example 2*—95 of the samples exceeded the strength criteria of 344.7 kN/m^2 (50 psi). The five samples that did not were all greater than 275.8 kN/m^2 (40 psi). The nonconforming samples were all adjacent to each other on the western edge of the treated matrix. The determination was that this area needed to be retreated.
- *Example 3*—95 of the samples exceeded the strength criteria of 344.7 kN/m^2 (50 psi). The five samples that did not were all greater than 275.8 kN/m^2 (40 psi). The nonconforming samples were all adjacent to each other in the center of the treated matrix. The determination was that the treatment was acceptable.
- *Example 4*—98 of the samples exceeded the strength criteria of 344.7 kN/m^2 (50 psi). The two samples that did not were less than 206.8 kN/m^2 (30 psi). The nonconforming samples were randomly distributed throughout the treated matrix and none on the edge. The determination was that the treatment was acceptable.
- *Example 5*—98 of the samples exceeded the strength criteria of 344.7 kN/m^2 (50 psi). The two samples that did not were less than 206.8 kN/m^2 (30 psi). The nonconforming samples were not together but on the edge of the treated matrix. The determination was that re-treatment of those areas or additional protective measures was needed.

7. LONG-TERM STEWARDSHIP

Once a remedy has been implemented and safeguards are put in place, additional work is typically necessary to verify that the remedy remains effective and protective of human health and the environment. Long-term stewardship of a completed S/S remedy may include monitoring of environmental media in contact with and potentially affected by the remedy, monitoring of institutional controls (ICs), monitoring and maintenance of engineering controls (ECs), financial assurances, and periodic review(s) by the controlling environmental agency.

The main goal of S/S remedies is to reduce the flux of contamination that leaches from a contaminant source to within acceptable parameters set forth in the site-specific remediation goal. Monitoring programs are an important part of the S/S process to determine whether the rate of leaching is within the formulated performance criteria.

Because the most common impact from a treated mass is to groundwater, this guidance focuses on development of groundwater monitoring programs following S/S implementation. The following subsections discuss long-term durability (Section 7.1), development of groundwater monitoring programs for S/S remedies (Section 7.2), typical institutional and engineering controls and their inspection and maintenance (Section 7.3), and considerations for periodic remedy reviews (Section 7.4).

7.1 Long-Term Durability and Performance of S/S-Treated Materials

7.1.1 Durability of the Monolith

As with most technologies used in the environmental field, S/S has its roots in processes and equipment developed for different purposes (Conner and Hoeffner 1998). Monoliths formed by S/S meet the definition of concrete—a mass formed by concretion or coalescence of separate particles of matter into one body. The earliest man-made concrete discovered to date is a concrete floor uncovered near Yiftah El in Galilee, Israel, dating to around 7000 BC (Kosmatka, Kerkhoff, and Panarese 2002). Notable concrete structures include Rome's Pantheon built in 118 AD, the Erie Canal constructed in 1818, and Thomas Edison houses built in 1908. Portland cement was first patented by Joseph Aspdin in 1824. Much of today's built environment relies on portland cement–based concrete. The first uses of cement-based S/S in the United States were for the disposal of radioactive or nuclear waste in the 1950s. Disposal of radioactive material by cement-based S/S, including surplus U.S. weapons plutonium, relies on mix designs that form a monolith able to last through multiple half-lives to ensure protectiveness of human health and the environment.

A number of studies and predictive modeling suggest that a properly designed S/S remedy which accounts for the contaminant properties and the disposal/management scenario conditions can be expected to last on the order of decades to centuries (Environment Agency 2004a, Perara et al. 2004b, PASSiFy Project 2010). Because contaminants remain in place, a gradual release of some contaminants over a long period of time should be anticipated. Significant or complete release over a relatively short time period would constitute a failure of the technology and would typically be the result of inadequate site or contaminant characterization, poor design, or poor implementation of the S/S remedy.

Research on the structural integrity of S/S treated monoliths has led to several conclusions: the properties of the treated material typically do not change significantly; if the properties do change, those changes do not significantly affect remedy performance; and methods for sampling the monolith impact sample quality (such as through fracturing) and thus alter the measured properties as recorded in the laboratory (PASSiFy 2010). Therefore, while monitoring of the structural integrity of the treatment monolith through direct sampling has been conducted at some sites, such as the American Creosote site in Tennessee (PASSiFY 2010), this approach is generally not recommended. However, direct evaluation of the structural integrity of the monolith could be warranted if groundwater monitoring data show unexpected increases in contaminant concentrations.

7.1.2 Long-Term Performance

Several research studies have been conducted to evaluate the long-term performance of S/S remedies. An Electric Power Research Institute (EPRI)–funded project conducted at a former MGP site 10 years after S/S implementation included geotechnical, chemical, leaching, and solid-phase geochemical analyses of samples taken from the site. Using the sampling data, contaminant transport modeling was used to predict the leaching potential at the site and concluded that the treated contaminated material still met the performance standards as designed. In addition, contaminant concentrations at the monitoring POC were predicted to continue meeting performance criteria for at least 10,000 years. Short-term groundwater monitoring results supported this hypothesis (EPRI 2003).

In another study, a research consortium led by the University of Greenwich (United Kingdom), the University of New Hampshire, and INERTEC (France) conducted a research project entitled Performance Assessment of Solidified/Stabilized Waste-forms (PASSiFy). The objective of the PASSiFy Project was to assess the time-dependent performance of the S/S remedy at 10 sites where S/S was implemented between 1989 and 2006. Contaminant classes represented by these study sites included heavy metals, PCBs, petroleum hydrocarbons, PAHs, acid wastes, creosote and coal tar constituents, and dioxins. Samples from each site were subjected to geotechnical, chemical, leaching, geochemical, and microstructural analyses. Geochemical modeling was also performed to evaluate solubility-controlling phases for metals. The report concluded that all the sites sampled were still performing well and met their RAOs (PASSiFy 2010). Additionally, the report affirmed the viability of S/S as an effective long-term treatment as long as the nature of the soils and contaminated materials are known and an effective binder system is developed (Hills et al. 2010).

7.2 Groundwater Monitoring Program

Groundwater monitoring is usually required, but may not always be (such as small-volume waste sites). Groundwater monitoring decisions are state or site specific. Considerations for monitoring plan design, monitoring parameters, locations, duration of monitoring, and monitoring data interpretation are presented in the following subsections.

Groundwater modeling using site characterization and treatability study data can be used to evaluate the anticipated flux of contaminant leaching from S/S-treated material and therefore provide valuable information for use in groundwater monitoring programs. Appendix C of this document presents discussions on the use of groundwater modeling approaches for evaluation of S/S remedies. The appendix presents selected case studies to illustrate how groundwater modeling was used on sites where S/S remedies were implemented to contribute to the design and monitoring of the remedy. In addition, other modeling methodologies are presented that may be useful to the evaluation, design, and monitoring of S/S remedies.

7.2.1 Monitoring Program Objectives and Criteria

Developing monitoring objectives and criteria provides the basis for design of a monitoring program and should use the data quality objective (DQO) process (EPA 2006). The DQO process provides a systematic approach for defining the criteria for a monitoring plan design that will yield data of acceptable quality and quantity.

7.2.1.1 Monitoring objectives

Monitoring programs are conducted to verify that the treatment was successful in preventing, reducing, or eliminating the impact of the contaminated mass on groundwater. Monitoring programs also determine whether the treatment continues to be effective over time. The monitoring plan should be designed to meet the effectiveness and protectiveness evaluation objective of the monitoring program and should also provide a basis for decisions to modify or cease monitoring.

7.2.1.2 Monitoring criteria

Groundwater cleanup criteria are a key component of the monitoring plan design and are typically established in the site remedy selection process. The criteria may include state or federal groundwater and/or surface water standards. However, it should be noted that because S/S is typically implemented as a source control remedy to minimize contaminant flux to groundwater, other technologies or approaches may be used in conjunction with S/S to meet site remedial goals.

Depending on state or federal remedial goals, cleanup criteria may be applied differently at a site. The application of cleanup criteria can range from compliance at one or more specific POCs everywhere on site within an impacted aquifer, demonstration of a percent reduction in concentration flux from the treated material, calculating acceptable attenuation between the treated material and the POC, hydrogeologic modeling to simulate groundwater flow, and concentration flux attenuation. For most sites, specific cleanup criteria for contaminants and demonstration that these criteria are met by the S/S remedy are typical regulatory requirements.

7.2.2 Monitoring Plan Design

Following the DQO process, groundwater monitoring plans should be designed for the collection of the data necessary to evaluate the S/S remedy performance and protectiveness over time. Site-specific data acquired during the site characterization and treatability study phases and developed during the design of the S/S remedy should be used in the monitoring plan design, such as the following:

- baseline conditions prior to S/S remedy implementation
- changes in site conditions, including land use, that may influence performance of the S/S remedy
- changes in site conditions resulting from the S/S remedy that may influence nature and extent or fate and transport of existing contamination adjacent to a treated mass (Environment Agency 2004a)

For example, if other sources of contamination are present, site characterization data need to be reviewed with respect to differentiating between contamination from other sources and migration from the treated material to the extent possible. Other sources of contamination may include separate sources outside the area to be treated with S/S that may already have impacted groundwater or may in the future impact groundwater at or downgradient from the S/S-treated material.

Other considerations for monitoring plan design could include site-specific conditions that may cause physical impacts to a site from the remedy implementation. For example, water table mounding or flooding is possible at a site after remedy implementation. See Appendix C for a case study example where groundwater modeling was conducted to evaluate post-implementation changes to the water table and support design of a storm-water collection system.

7.2.3 Monitoring Parameters

An integral component of monitoring plan design is determining the appropriate suite of contaminants and other parameters to monitor and evaluate for long-term performance evaluation of the S/S remedy. The COCs for groundwater or surface water will have been established prior to site remedy selection during site characterization and development of the CSM and therefore will follow through design and implementation and into the groundwater monitoring program.

One consideration in monitoring site contaminants after S/S treatment, particularly when numerous chemicals are involved, is whether all contaminants should be included in monitoring or a subset of contaminants may provide adequate representation of contaminant flux from the S/S-treated material to demonstrate compliance. This determination can be based on results of treatability studies and construction performance monitoring showing level of effectiveness of S/S treatment for each contaminant. Initial post-treatment monitoring data may also support use of a smaller subset of contaminants, or indicator contaminants, in longer-term monitoring. In any case, the selection of contaminants for groundwater monitoring should be based on the potential for contaminants to be released into groundwater and to exceed established cleanup criteria as determined from data collected during such steps as site characterization, treatability studies, construction monitoring, and groundwater modeling (if conducted).

Other groundwater parameters that could impact the stability of the S/S-treated material and may be considered for the groundwater monitoring plan include the composition of downgradient groundwater, changes in groundwater levels, or overall changes to the site. For example, pH may be a parameter of interest because for some contaminants (i.e., inorganic chemicals) solubility is directly related to the pH of groundwater. As a second example, monitoring water levels upgradient from the S/S-treated material may be important if flooding may be a concern because of a shallow groundwater table.

7.2.4 Selecting Monitoring Locations

Sufficient baseline information is necessary to evaluate changes in surrounding groundwater quality and impact on relevant receptors resulting from flux from the S/S-treated material. Therefore, monitoring points are typically located up- and downgradient of the treatment area to compare baseline versus post-treatment monitoring data and may be established on site or beyond the property limits. Exact locations of monitoring points and the number of points needed are based on site-specific factors such as the following:

- site conditions
- potential changes in the groundwater flow regime induced by the treated material
- time of travel to POCs
- presence of contamination in groundwater prior to treatment

For example, establishing downgradient monitoring well locations closer to the treated material will detect groundwater impacts sooner than wells located at a more distant POC. Closer monitoring wells where downgradient groundwater contamination exists prior to treatment may also detect improvement in groundwater quality sooner than more distant wells, making it easier to interpret relative change in mass flux.

If the S/S-treated area is adjacent to a surface water body such as a river or lake, downgradient groundwater monitoring may be more difficult or impossible. Depending on site-specific regulatory requirements, other approaches can be used to monitor groundwater discharging into the surface water, such as monitoring sediment porewater, surface water, and sediment at various depths.

Upgradient monitoring should also be considered as part of the monitoring program. Upgradient monitoring can provide insight to the interpretation of monitoring data, especially in cases where groundwater contamination exists in areas in addition to those treated with S/S. For example, if groundwater concentrations increase for both up- and downgradient monitoring, taking into consideration travel time between the two, the source of the increase may well be the upgradient groundwater going around the treated mass rather than the treatment failing.

7.2.5 Frequency and Duration of Monitoring

Guidance is generally not available specifically for S/S remedies with respect to the appropriate frequency or duration for a groundwater monitoring program. Groundwater monitoring for the first five years generally starts with quarterly monitoring and diminishes in frequency depending on results and site conditions. Five-year reviews are generally conducted as part of periodic review or required by CERCLA (EPA 2001). For state programs, monitoring requirements usually follow the same frequency of monitoring used under the CERCLA program but may vary in the requirement of five-year review periods. For example, the State of Texas only requires one five-year review (G. Beyer, personal communication, 2010). The State of Delaware requires monitoring only up to the point that eight quarters of groundwater data at the POC demonstrate attainment of the remediation goals, after which time monitoring is not required. Compliance can occur at any time before or after the first five-year review (W. Reyes, personal communication, 2010).

Monitoring frequency and duration requirements should be determined on a case-by-case basis. In keeping with the regulatory requirements, predictive modeling can be used to further identify appropriate monitoring frequency and duration. Modeling data may allow estimation of the length of time that concentrations in groundwater or surface water near the S/S-treated material may exist above acceptable levels and to predict peak concentrations over time at specific points downgradient from the S/S-treated mass (EPRI 2009a). Modeling can also take into consideration the different chemicals that may be present in the treated material in terms of their fate and transport characteristics.

Conclusions regarding compliance over time can potentially be drawn from comparison of measured concentrations with predicted peak concentrations at monitoring points. Based on consistency between measured concentrations and modeled concentrations, monitoring decisions can be evaluated, such as decisions to cease monitoring, reduce the number of chemicals monitored, and significantly reduce the frequency of monitoring and to use alternate remedial methods to address residual downgradient groundwater concentrations, such as monitored natural attenuation.

7.2.6 Interpreting Monitoring Data

Immediately following S/S implementation, dramatic improvement in groundwater quality is unlikely to be reflected in groundwater monitoring data because of reduced hydraulic conductivity of the contaminated material, fate and transport, and potential presence of other sources of contamination.

S/S treatment reduces the hydraulic conductivity of contaminated material, thereby increasing the travel time for contaminants from the center to the margin of the treated mass. The rate of release of contaminants from an S/S-treated mass may be limited by diffusion processes and will likely be significantly less than the flux from the previously untreated contaminated mass. Once released into groundwater, the fate and transport of contaminants is controlled by factors including chemical properties, groundwater and aquifer characteristics, existing biological processes, and presence of other sources of contamination. In addition, if groundwater contamination is migrating from other sources, these sources need to be considered in the evaluation of the monitoring data.

Given the variability of natural groundwater quality, monitoring data should be evaluated in terms of trends and not absolute numbers. Evaluation of groundwater concentration trends can be done through simple time versus concentration plots, or more rigorously using statistical methods for data trend analysis. For more rigorous statistical analysis, EPA's *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities Unified Guidance* (EPA 2009a) may be useful.

Evaluation of concentration trends over time can be used to show continuing compliance where concentrations do not exceed the cleanup criteria in the groundwater or at a specified POC or to show changes in concentrations over time that will demonstrate compliance or progress toward compliance. Groundwater modeling, in conjunction with treatability study data (concentration flux from the S/S-treated material as a source term), may be used to help predict peak concentrations of contaminants that may be released from an S/S-treated material and how those concentrations may change over time and distance. Modeled predictive results can be used to evaluate actual groundwater monitoring data and compliance with cleanup criteria.

If the main source of contamination is treated (per the remedial design), over time the downgradient monitoring data trends should show improvement in groundwater quality and continue showing improvement until concentrations stabilize. Should groundwater contaminant concentrations appear to increase over time, the frequency of groundwater monitoring may need to be increased to determine whether the remedy is failing or another cause for the increase exists.

An S/S remedy should be considered successful if it meets material performance goals designed to meet site groundwater cleanup criteria at established POCs and groundwater monitoring data show that the cleanup criteria have been met.

7.3 Institutional and Engineering Controls

EPA defines institutional controls as "non-engineering measures, such as administrative and/or legal controls, that help to minimize the potential for human exposure to contamination and/or to protect the integrity of a remedy by limiting land or resource use" (EDSC 2006). ICs, which may be used when contamination is first discovered and when remedies are ongoing, may also be needed when residual contamination remains on site and to meet regulatory requirements.

Engineering controls are barriers or systems that control downward migration, infiltration or seepage of surface runoff and rain, or natural leaching/migration of contaminants through the subsurface over time. The National Oil and Hazardous Substances Pollution Contingency Plan (NCP, Title 40 Code of Federal Regulations Part 300) emphasizes that ICs, such as water use restrictions, are meant to supplement ECs during all phases of cleanup and may be a necessary component of the completed remedy; ICs will rarely be the sole remedy at a site.

Site reuse has a significant influence on the design of the protective measures to ensure that any changes to land do not compromise the long-term structural and overall performance of the treated material. Requirements, such as the development of contaminated materials management plans, may also exist to protect site workers in the event of potential future excavation of the treated material. In general, ICs may include the establishment of environmental covenants to the property deed, and ECs may include the establishment of soil or impervious caps over the treated material.

ICs and ECs are intended to continue until no longer needed, which in the case of S/S is as long as the treatment material is in place. ICs usually require ongoing evaluation to determine whether they provide the restrictions necessary for the site to remain protective of human health and the environment. ECs usually require site inspections to determine performance over time. These procedures are documented in long-term operations and maintenance (O&M) plans.

7.3.1 Institutional Controls

When implemented, maintained, and enforced properly, ICs serve a critical role in the management of risks associated with residual contamination by preventing the disturbance of contaminated material, by providing notification to the appropriate governmental entities when breaches occur, and by providing important information to the local community and other interested stakeholders regarding use restrictions. ICs can include government controls, such as zoning restrictions, ordinances, and groundwater management zones; property controls, such as easements and environmental covenants; enforcement and permit tools with IC components, such as administrative orders and consent decrees; and informational devices, such as registries and fish advisories. ICs may require legal and administrative implementation, management (tracking and monitoring), and financial assurance that may require enforcement. Establishing an effective management system for ICs is a challenging task that requires planning, coordination, and funding among multiple governmental agencies, communities, and other stakeholder groups (ITRC 2008).

Most states track and monitor ICs at some level. Tools available for tracking the status of IC implementation and maintenance may include five-year reviews and other long-term inspections and registries, state one-call systems, and third-party notification systems (ITRC 2008). Controls could be maintained in a searchable database accessible to stakeholders. The O&M plans and periodic remedy evaluations usually document reporting requirements associated with ICs (EPA 2010c).

7.3.2 Engineering Controls

Common practice for implementing S/S includes a cover system that exists between the treated material and the exposed surface to prevent human contact. The need for an EC such as a soil, gravel, or impervious cover (such as asphalt) on top of the treated material depends on land use, S/S remedy implementation (deep versus shallow), public concerns, or other factors. For deeper S/S applications where the treated material remains in the subsurface covered by on-site or imported soil, ECs are generally not necessary. For shallow S/S applications, cover systems may include soil, asphalt, gravel, geosynthetic clay liner, and/or flexible membranes. Considerations for designing and implementing covers include the following: final grading, hydraulic conductivity and stabilization of the cover system, and erosion and sediment controls permits and requirements. Similar management controls (tracking, monitoring, and documenting) as those described for ICs generally apply to ECs. Long-term inspections and reporting are usually required and documented in O&M plans and periodic remedy evaluations.

7.4 Periodic Review

Periodic reviews evaluate the performance of the S/S technology upon implementation to determine whether the remedy continues to be protective of human health and the environment. The EPA five-year review requirement for CERCLA sites is based on the review requirement for remedial actions which result in any hazardous substances, pollutants, or contaminants remaining at the site above levels that allow for unrestricted use. Many states have adopted EPA’s model of periodic reviews.

A schedule should be established for routine reviews of the monitoring results against the established objectives of the corrective action and revised accordingly, if necessary. The monitoring program should also be reviewed on a regular basis to assess whether the objectives and approach are still valid. Updates to the monitoring program may include additional monitoring locations and variation in testing parameters and frequency, if needed.

7.4.1 Long-Term Performance Evaluation

Long-term performance evaluation determines whether the remedy is still functioning as designed. Information from monitoring activities/reports, sampling and monitoring plans, and O&M plans are key documentation for the technical assessment of S/S performance and protectiveness. Evaluation of the contaminant trend versus the established criteria and remedial objectives should provide a clear understanding of remedy performance.

EPA (2001) recommends using three questions for determining the protectiveness of the remedy:

- *Question A*—Is the remedy functioning as intended by the decision documents?

- *Question B*—Are the exposure assumptions, toxicity data, cleanup levels, and RAOs used at the time of the remedy selection still valid?
- *Question C*—Has any other information come to light that could call into question the protectiveness of the remedy?

For S/S technology, some aspects to be taken in consideration while responding to the three EPA questions are discussed below.

Question A: Remedial action performance—Determining whether the remedial action continues to operate and function as designed is a key component of the remedy performance assessment. Two approaches can be used in this determination: a direct measure of the performance parameters (e.g., strength, hydraulic conductivity, leachability) versus the established performance criteria or evaluation of the groundwater concentrations at the POC. The first approach is not commonly used on S/S applications, and only a few examples of this approach exist, such as the EPRI project (EPRI 2003). Field inspections to evaluate ICs, ECs, and/or potential indicators of remedy failure (such as a settlement) are also recommended.

Question B: RAOs—In conducting five-year reviews under CERCLA, EPA recommends the evaluation of the effects of significant changes in standards and assumptions used at the time of remedy selection as changes in promulgated standards may impact the protectiveness of the remedy. Although it is unlikely that a change in a contaminant standard will require changes in implemented S/S remedies, an evaluation of any changes to groundwater standards should be evaluated. If a new standard has been established and groundwater concentrations at the POC exceed this standard, an evaluation of other remedial alternatives in addition to S/S may be required. Similarly, any changes in exposure pathway should be evaluated to determine protectiveness over time.

Question C: New information—This includes an evaluation of any changes that could have an impact on the protectiveness of the remedy, such as potential mounding, flooding, earthquakes, or land use changes.

In addition, the final remedy should contain a requirement for a contingency plan in the event that the selected remedy fails.

7.4.2 Frequency

In general, the frequency of periodic review varies over time and is either state or federally mandated. For example, CERCLA mandates that the first five-year review be conducted within five years after completion of the remedial action. Subsequent reviews must be performed no later than five years following the previous five-year review report(s).

7.4.3 Drawing Conclusions from Periodic Reviews

Typically, the conclusions of the periodic review include issues identified during the review, recommendations and follow-up actions for each identified issue, and a determination of whether the remedy is protective of human health and the environment. The conclusions are based on the technical assessment of the information discussed in Section 7.4.1. The conclusions should also present any opportunities to improve the remedy performance, including any changes in the monitoring system, if applicable. The EPA five-year review guidance provides a valuable reference for developing a review framework, including guidance on additional response actions, improving O&M activities, optimizing the remedy, enforcing access and institutional controls, performing additional studies or investigations as potential recommendations items for five-year review, and period review documentation (EPA 2001).

8. STAKEHOLDER CONCERNS

The selection and implementation of any remedial action must typically and primarily satisfy requirements mandated by the parties responsible for remediation (the regulated community) and the regulators. In addition, the opinions of the local community, local community groups, and individual neighbors should be (and sometimes must be, as required by law) considered throughout the various phases of the remediation process.

The relative impact of community involvement or action on a remediation project may be minimal or significant depending on various site-specific factors such as location relative to the community, perceived environmental or public health concerns, prior relationships between parties, prior communications (including bad press), and the remedial action activities (including noise, visible heavy equipment or truck activity, etc.). Therefore, it can be expected that the level of potential community concern or action with respect to a remedial action will be proportional to the impact it may have on the community.

Some states have mandated public notification and community input regarding contaminated sites and even in the selection of remedial methods. For example, New Jersey’s Public Notification and Outreach Requirements are included as amendments to the state’s Technical Requirements for Site Remediation (N.J.A.C. 7:26E).

The many variables relating to site remediation and the potential impact on the community should be considered early and often to avoid potential problems during the development of performance specifications and implementation. This section discusses factors important to local communities that may invariably become partners in the implementation of S/S in their communities. The scope of the discussion is not limited to performance criteria and long-term stewardship but includes all general aspects of S/S implementation (Table 8-1).

Community interest may range from very low to very high, largely depending on project location. For example, a large-scale S/S project implemented in a remote and/or secure location such as a military installation may escape notice from the nearest communities. Conversely, implementing S/S on a former MGP site located near the center of an historic or densely populated urban community will certainly be noticed. In such cases, community notification, public outreach, and meetings—and perhaps significant public relations efforts—may be required to allay the concerns of local officials and the general public.

Although community involvement in site remediation activities is not a new process, having been previously mandated and implemented at the federal level under various programs (such as CERCLA and Base Realignment and Closure), public notification and even public input on site remediation activities is becoming more common.

Table 8-1. Stakeholder considerations

Consideration	Relevance	Significance to S/S technology performance and monitoring
Acute health and safety	Implementation	Use of certain materials, especially hazardous, respirable, or toxic materials, may require special health and safety monitoring. Therefore, certain types of operations may be contraindicated due to health and safety considerations.
Current and future land use	• Proposed future land use • Local zoning/land use ordinance/regulations • Long-term stewardship • Community impacts/concerns (environmental justice, health risks, economic development)	Performance criteria may differ based on proposed future land use, affecting risk-based permissible leaching levels and remedy performance standards (e.g., compressive strength requirements should be consistent with future land use).
	• Site and surrounding land use • Institutional controls • Ecological status • Proximity to sensitive receptors (sensitive populations, water bodies, endangered species) • Local groundwater use	Performance criteria may differ based on land use (e.g., industrial park vs. greenway) and sensitive receptors, affecting risk-based permissible leaching levels and remedy performance standards.
	Potential future intrusive work (e.g., construction, boring, etc.)	May affect design strength criteria of S/S material and supplementary remediation steps (e.g., thickness of clean soil buffer, placement of geomembrane or a vapor intrusion barrier).
	Institutional controls	May affect access for long-term performance monitoring.
Groundwater and surface water regulation	Regulatory classification of groundwater and surface waters	Affects remedial goals, cleanup criteria, and determination of practicability to achieve cleanup criteria (e.g., performance criteria could include reduced leachability and hydraulic conductivity to be protective of ground and surface waters).

The introduction of communities, including local governments, individuals, local environmental advocates, and others can add a significant level of complexity to the remediation decision-making process. In addition to typical factors upon which remedial action decisions are made (effectiveness, protectiveness, cost, cost/benefit, etc.), the addition of local communities may lead to discussion of other factors, such as environmental justice, community health, impact on future land use, impact on property values, economic development, and the use of nonpermanent versus permanent remedies.

8.1 Health and Safety Issues

Health and safety is of primary importance in the design, implementation, and monitoring of all remediation methods. As a fairly unique technology and methodology, S/S has its own technology-specific health and safety aspects that require address in all phases of design (including development of performance criteria), implementation, and post-implementation monitoring. Specific factors requiring consideration are as follows:

- use of mobile heavy earthmoving equipment and (mineral and other) processing equipment
- use of various construction materials that may generate respirable and/or irritant dust and other fugitive emissions
- potential for disturbance of utilities/infrastructure, both overhead and subsurface
- disturbance and possible mobilization of contaminants to the air, soil, groundwater, or surface water
- disturbance of local soils, affecting their physical characteristics
- disturbance of local groundwater flow and quality
- natural resource damages
- implementing a process that does not "destroy" the contaminant

Some of these concerns are conditions inherent in the S/S process, which is specifically designed, in most cases, to "disturb" local groundwater flow and/or to change the physical properties of soils. Therefore, some of the health and safety concerns associated with the S/S process require specific attention to alleviate concerns of the regulatory and local communities.

8.1.1 Ensuring Health and Safety During Implementation

Maintaining a link with the public may be especially important for S/S projects that have the potential to impact the public, which may include any site at which the public is aware of an imminent short- or long-term operation. This link may include providing information to local officials, neighborhood groups, and/or neighboring property owners. Planning for public notification and outreach may include the development of a written plan or standard operating procedure that includes contact information of various stakeholders, contingency plans for various potential events/scenarios, and instructions for dealing with the media and any potential emergencies. Giving thought to potential problems of this nature and planning for certain events or emergencies prior to the implementation phase may save significant downtime or even save a project from being shut down due to local concerns.

The S/S process, especially the mixing and milling of fine-grained materials such as fly ash and cement, has the ability to generate fugitive emissions and respirable dust. Under certain conditions, fugitive emissions can present a potential exposure issue to on-site personnel and can potentially migrate beyond the work area and site boundary. Monitoring for dust and other potential fugitive emissions or vapors, accurate recordkeeping, and/or use of ECs is recommended, where appropriate. These measures ensure work place safety and provide a record of safe operating conditions during implementation. Appropriate health and safety practices also provide a means to generate positive information to release as part of keeping the public notified and assured of their safety.

8.1.2 Ensuring Long-Term Health and Safety Post-Implementation

As discussed in Section 7, S/S sites often require long-term stewardship to ensure the effectiveness of the remedy and public and environmental health. Although the long-term monitoring plan design requires regulatory oversight, the proximity of communities and sensitive populations may affect the required level of monitoring and O&M. Therefore, the key to successful S/S implementation includes an appropriate level of preimplementation planning for stakeholder issues (communication/outreach, sensitivity to specific concerns, developing relationships, etc.).

8.2 Land Use Issues

Land use is an extremely important issue to stakeholders, especially local governments, citizens, and organizations of all types. Land use management through planning and zoning laws/ordinances, building codes, land use laws, etc. is typically a primary function for local governments. Anything that affects land use affects a community. Changes in land uses have the ability to alter neighborhoods, affect tax revenues, and/or change public safety and infrastructure requirements (police, fire, utilities, water/sewer, etc.). Furthermore, any event that impacts local land use is likely to generate concern, press coverage, and local involvement.

Environmental laws and the resultant environmental remediation industry exist primarily to address the historic operations by industries, government agencies, and commercial and other operations that have impacted land with hazardous materials. Future land uses are affected by the existence of contaminated land, and if permanent remedies are not implemented, future land use of a particular site can be permanently negatively affected. Impacts to future land use can foster stakeholder concerns regarding the remediation technology, particularly when implemented proximal to populated areas, as is the case with many former MGP sites. Therefore, the remediating party and regulatory agency must address future land use impacts upon which S/S is proposed.

S/S can be engineered to accommodate a variety of land uses by considering land use in the selection of performance criteria (as described in Section 4 of this document). However, S/S may not be deemed suitable for certain uses, such as those that may impact future homeowners (residential use) or sensitive populations (day care centers, schools, etc.), usually to avoid potential public perception and other problems associated with remedies where contaminants are not removed or destroyed.

When designing S/S for use at sites in areas where local governments have identified future land reuse potential, the following stakeholder-oriented guidelines should be considered:

- Design the S/S remedy so that it does not render the site unusable unless other site conditions preclude reuse.
- Consider local community desires for the redevelopment of a particular contaminated site.
- Do not assume that conducting remediation in accord with state regulations will automatically be acceptable to the local community or in accord with local land use laws.
- Design remediation with future land use in mind. If the remedial action will accommodate potential or planned redevelopment in accord with local land use laws, the potential for local acceptance is greater.
- Anticipate community needs for information and outreach, and provide accurate information, in a simple format, using common terminology.
- Develop contingency plans for emergencies, including plans for hazard communication, and media and local government relations.

Figures 8-1, 8-2, and 8-3 depict examples of successful land reuse following S/S implementation.

Figure 8-1. Auger-mixed in situ S/S treatment of a former MGP site in Milwaukee, Wisconsin (left) and post-treatment (right). *Source:* Portland Cement Association.

Figure 8-2. Auger-mixed in situ S/S treatment of a former MGP site in at Kendall Square, Cambridge, Massachusetts (left) and after redevelopment (right). *Source:* Portland Cement Association; Carleo, Clark, and Wilk 2006.

Figure 8-3. Hercules 009 Landfill Superfund Site near Brunswick, Georgia, during S/S treatment (left) and redeveloped into an automobile dealer parking lot. *Source:* Portland Cement Association, Lear and Wilk 2008.

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Appendix A

Equipment

EQUIPMENT

A variety of mixing methods using S/S treatment equipment have been used for on-site treatment of contaminated materials, as briefly described in this appendix. Treatment can be accomplished while the material remains in place (in situ, Figure A-1) or on excavated material (ex situ, Figure A-2). Ex situ treated material can be returned to its original location or placed on another part of the project area. At some projects, material subject to S/S treatment has been excavated and placed at the final location prior to use of in situ mixing equipment to treat the relocated material.

Figure A-1. S/S treatment of contaminated soil by rotary blender at former wood-preserving site, Port Newark, N.J. *Source:* Portland Cement Association.

A.1 COMMON EX SITU MIXING EQUIPMENT

A.1.1 Pugmills

Figure A-2. Pugmilled S/S-treated soil from former wood-preserving site Port Newark, N.J., reused on site as pavement base. *Source:* Key Environmental, Inc.

Pugmills consist of a trough-like mixing chamber with two horizontal shafts with paddles affixed to the counter-rotating shafts (Figures A-3 and A-4). Material to be treated and S/S binding agents enter the mixing chamber at one end and exit the other end as a mixture. Generally, these are continuous-flow devices. Pugmills are commonly used in asphalt and concrete paving. and many are sized to be transported by tractor trailers along with binding agent silos, conveyers, hoppers, and size-screening equipment. Pugmill mixing systems are often automated, with weight belt systems and controlled feed silos to provide quality control of the mixing process.

A.1.2 Batch Mixing

A variety of vessels, in sizes ranging from 200 L (55 gal) drums to truck-sized vessels, have been used to mix batches of subject material with S/S binding agents. Batch mixing is not as common as pugmill mixing for mixing and placing treated material back on site. Care should be taken in the selection of batch-mixing equipment to ensure that mixed material can be easily discharged from the mixing vessel.

Figure A-3. Pugmill mixing S/S treatment for lead-contaminated soil at 90th South Battery Site, West Jordan, Utah. *Source:* S3 Engineers LLC.

Figure A-4. Pugmill mixer trough opened showing mixing paddles at Peak Oil Co./ Bay Drum Co. Superfund Site, Tampa, Florida. *Source:* Portland Cement Association.

A.2 COMMON IN SITU MIXING EQUIPMENT

A.2.1 Rotary Mixing

Rotary mixers are known by various names, including road reclaimer, road recycler, soil stabilizer, and pulverizer. In pavement construction, these machines recycle pavement in place. Rotary mixers consist of a milling drum on a transversely mounted shaft in a specialized piece of heavy equipment. Rotary mixers have been used in S/S treatment to mix binding agents into subject material (Figures A-5 and A-6). Material subject to S/S is placed in layers or “lifts” (200–300 mm [8–12 inches]) on an area. Binding agent(s) and additives are spread onto the lift usually by a spreader truck that precedes the rotary mixer. The rotary mixer is operated over the lift. Water can be added either in front of the rotary mixer, into a port on the mixing chamber, or spread behind the mixer as necessary. Subsequent lifts can be mixed in place over previously treated lifts to form thicker monoliths.

Figure A-5. S/S treatment of relocated dioxin-contaminated sediment by rotary mixer at Naval Construction Battalion Center, Gulfport, Mississippi.
Source: ECC.

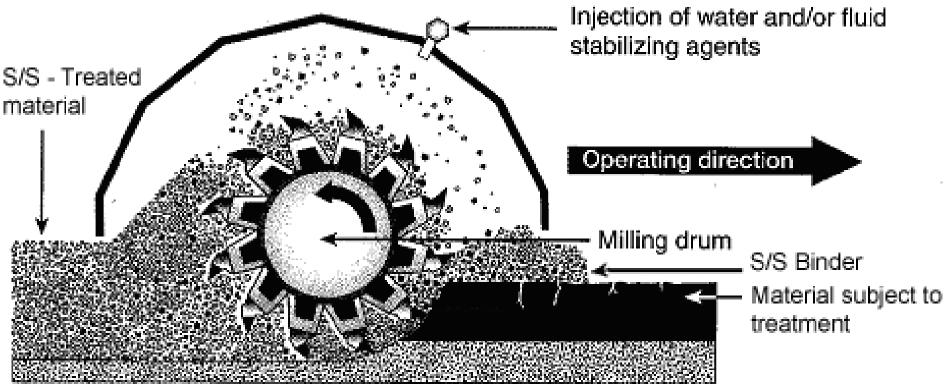

Figure A-6. Drawing of S/S treatment by rotary mixer.
Source: Modified by CETCO from Portland Cement Association Publication EB234.

A.2.2 Excavator Mixing/Bucket Mixing

S/S treatment can be performed with a common excavator (Figures A-7 and A-8). Mixing of soil, sludge, or sediment with an excavator bucket is applicable to shallow depths, generally less than 6 m (20 feet), depending on the equipment size. This approach requires no specialty mixing equipment but does require a skilled operator. Generally, the treatment area is divided into grid cells. Binding agents are added as a liquid grout or dry with the addition of supplemental water. The excavator operator mixes the binding agents into the subject material to the desired depth. Mix homogeneity is often determined by the amount of time spent mixing in one area/cell. Use of standard bucket excavators for S/S is applicable to areas where significant debris may be encountered and can be used to blend size-reduced demolition debris with the treated soil to reduce the need for off-site demolition debris disposal.

Figure A-7. Excavator bucket mixing of contaminated sediment, Sydney Tar Ponds, Nova Scotia. *Source:* CETCO Contracting Services Co.

Figure A-8. Finished surface after excavator bucket mixing, Sydney Tar Ponds, Nova Scotia.
Source: CETCO Contracting Services Co.

A.2.3 Excavator-Mounted Rake Injecting

Excavator-mounted injectors (Figure A-9) use a set of hollow “forks” or “rake” attachments to treat contaminated soil and/or sediments (Al-Tabbaa and Perara 2002a). The rakes are mounted on a conventional hydraulic excavator for in situ mixing and treatment of soil and/or sludge at depths up to 3 m (10 feet). Liquid grout is injected through the hollow “forks” and mixed in situ with soil or sediments through the rake motion of the excavator. This technology is well suited for shallow treatment of soft sediment, sludge, or soils.

Figure A-9. Rake injector (left) and grout plant and rake injector (right) for treating contaminated sediment at Koppers Co., Inc. (Charleston Plant) Superfund Site, Charleston, S.C. *Source:* Williams Environmental Services, Inc.

A.2.4 Excavator-Mounted Rotary Blending

High-speed rotary stabilization equipment is also available (Figures A-1 and A-10). This equipment mixes S/S binding agents into the soil or sludge through the rotating action of a bladed or toothed mixing head. This type of S/S is applicable to soil and sludge with a moderate to high solids content and involves processing wastes in controlled layers or directly in place. Processing steps may include preexcavation, layering, conditioning, and stabilization. Binding agents can be delivered directly to the mixing head via hydraulic or pneumatic pressure.

Figure A-10. S/S treatment by rotary blender at former wood-preserving site, Port Newark, N.J.
Source: Key Environmental, Inc.

A.2.5 Auger Mixing

Auger mixing treats an approximately 0.6–3.7 m (2–12 foot) diameter vertical soil column up to approximately 20 m (60 feet) below ground surface (bgs) by physically mixing the soil with injected grout via a rotating auger or array of augers (Figure A-11). There are two methods of auger mixing: wet and dry. In the wet method, the binders and/or fillers and/or additives are mixed with water to prepare a grout slurry, which is pumped to the mixing tool and mixed with soil in situ. The wet method is typically used for soils with moisture content less than about 60%. In the dry method, the binders and/or fillers and/or additives are delivered to the mixing tool using compressed air. Dry mixing is used commonly in low-strength soils with high moisture content. Very soft soils with high moisture content, such as soft clays, organic soils, or sludge, may dictate the use of the dry method.

Figure A-11. S/S treatment using an auger with mixing blades exposed (left) and at a depth of 22 feet as indicated by markings on auger shaft, at a former MGP plant, Milwaukee, Wisconsin. Source: Portland Cement Association.

The single-auger mixing method involves the use of a crane-mounted rotary table (turntable) or a track-mounted earth drill rig to rotate a large-diameter (as great as 3.7 m [12 feet]) cutting head. Similar to equipment used to construct cast-in-place concrete piles for bridges and dams, this equipment can treat soil to depths as great as 18 m (60 feet). As the cutting head is rotated and moved up and down, grout is injected through the hollow stem or a separate pipe. An in situ column of treated soil is created when the mixing is completed. The process is completed by executing a series of overlapping columns across the desired treatment area surface until the entire project area is treated.

Vertical drill rigs using an array of smaller-diameter helical augers while injecting binding agents can be used for deep soil mixing projects as well. For either type of vertical drilling, subsurface debris and foundations must be removed earlier to prevent damage to the drill tools. Binding agent delivery can either use the dry or wet method described above.

A.2.6 Jet Grouting

Figure A-12. Jet grouting showing exposed nozzles. *Source:* Geo-Con, Inc.

Jet grouting uses high pressure (40 MPa [6,000 psi]) to pump grout through a specialized drill tool called a "monitor" attached to a rotating drill rod. This is the most effective system for S/S applications where surgical treatment or treatment to great depths is necessary.

Jet grouting treats soil in typical 0.6–1.8 m (2–6 foot) diameter vertical columns via a rotating shaft that injects grout/air/water (in various combinations) into the subsurface as the shaft is removed (Figure A-12). Treatment to great depths (over 30 m [100 feet]) is possible. The water:solids ratio of the binding agent grout, the composition of the binders and fillers in the grout, and the quantity of grout incorporated control the ultimate strength and permeability of the columns. Similar to vertical auger mixing, the jet grouting process is repeated throughout the affected zone to develop a series of overlapping vertical elements (Figure A-13). Jet grouting is particularly useful for treating isolated zones of waste or contaminated soil and for grouting around buried utilities or below permanent structures.

Figure A-13. Exposed jet-grouted columns.
Source: Geo-Con, Inc.

Superjet grouting is a modified double-fluid jet grouting system that takes advantage of tooling design efficiencies and increased energy to create high-quality, large-diameter (3–5 m [10–15 foot]) elements. These processes entail inserting the monitor to a required depth using a rotary drilling technique and then slowly withdrawing it while injecting grout into the soil through horizontal nozzles at very high velocity (approximately 200 m/sec [650 feet/sec]). This energy erodes the soil fabric and replaces it with a mixture of grout and soil. Rotational speed and withdrawal rate of the monitor control the diameter of the columns, which encapsulate the soil particles when the grout hardens.

Appendix B

Overview of Leaching Tests and Assessment of Leachability Using the Leaching Environmental Assessment Framework

OVERVIEW OF LEACHING TESTS ANDASSESSMENT OF LEACHABILITY USING THE LEACHING ENVIRONMENTAL ASSESSMENT FRAMEWORK

B.1 INTRODUCTION

The leachability of a porous material is often determined from the results of one or more leaching tests designed to measure either the extent or the rate of contaminant release. When developing a leachability testing program, an important distinction should be made between the thermodynamics of the system and kinetics or time-dependence of the release.

In the leaching environment, the duration of the water-solid contact and the sample size define two distinct release-controlling release mechanisms: equilibrium-based release (thermodynamics) and mass transfer-based (kinetics) release.

- **Equilibrium-based release.** If the particle size of the subject material is small relative to the time that the material is in contact with a leaching solution, release continues until an equilibrium[1] is established. The equilibrium concentration is determined by the thermodynamics of the system with regard to the LSP. The partitioning between the solid and liquid phases is a function of pH, L/S, and all associated interfacial chemical reactions (e.g., dissolution, desorption, complexation). Thus, the extent of leaching can be estimated using one or more of available "equilibrium-based" leaching tests (e.g., ASTM D3987, EPA Method 1312).

- **Mass transfer-based release.** In some cases (e.g., groundwater flow around an S/S-treated material), the size of the subject material is large while the contact time with the leaching solution may be short. The rate of the partitioning reactions may be relatively fast compared to the kinetics of mass transport (van der Sloot and Dijkstra 2004; Dijkstra, van der Sloot, and Comans. 2006). [NOTE: References for this appendix are in Section B.7, beginning on p. B-24.] Therefore, the local equilibrium assumption is used to estimate concentrations within the porewater of the subject material, and one of several available mass transfer tests (e.g., ANS 16.1, EPA PreMethod 1315 currently being validated by EPA and described later in this appendix) may be used to describe the overall leaching process.

Based on the above distinction, leaching tests are designed to either (a) estimate some equilibrium between the solid and liquid phases or (b) measure the rate of mass transfer release as a function of time. In both cases, it is important to realize that the applicability of the results is limited to the conditions (e.g., particle size, leachant composition, contact time) incorporated into the test design. Equilibrium-based leaching tests do not provide information on the kinetics of contaminant release, and mass transfer-based leaching tests cannot be used to address thermodynamics.

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[1] Due to the complexity of the solid mineralogy, the assumed local equilibrium is not a true chemical equilibrium in that a dissolved mineral phase will reprecipitate; rather, it is pseudoequilibrium in that the concentration in the aqueous phase approaches a constant value with time.

Van der Sloot, Heasman, and Quevauviller (1997) noted that of the 50 or more leaching tests in the literature, most differ in only minor ways. Thus, a limited number of carefully selected leaching tests can cover a wide range of possible exposure conditions. The results of this leaching characterization can be combined with default or site-specific scenario information to provide a more robust description of contaminant release than any single test. These concepts were the basis for the development of the LEAF, a collection of leaching test methods, data management tools, and assessment approaches that can be used to characterize a subject solid material and integrated to provide a "source term" for contaminant release to the environment.

This appendix provides a more detailed description of the LEAF than that presented in Section 4 of this guidance. As illustrations of the framework applied to S/S-treated materials, example test results and interpretation of leaching data relevant are included when appropriate.

B.2 OVERVIEW OF LEACHING TESTS

Garrabrants and Kosson (2005) have reviewed leaching tests with respect to leaching assessment methodologies for cement-treated materials and have noted several other important ways to group leaching tests. One such method classification is based on whether the test is intended to provide leachates representative of field conditions (simulation tests) or an intrinsic leaching response of the material to environmental conditions (characterization tests). Procedurally, leaching test procedures may be designed as "batch extraction methods" or "dynamic leaching methods" depending on how the leaching solution is introduced to the solid material.

B.2.1 Simulation Tests

Simulation tests are designed to measure leaching under a specific set of experimental conditions, usually in an attempt to mimic field conditions. Typically, the concentrations of constituents in the leachate are compared to a set of predetermined threshold limits considered acceptable for the simulated scenario. By nature, the release conditions anticipated in the field are inherent to the design of simulation leaching tests such that test conditions and procedures need to be adapted on a case-by-case basis to best describe performance in the field. In addition, since no two leaching scenario are identical, a new test needs to be designed for each new scenario. Thus, standardization of a single simulation-based leaching procedure for applicability over a wide range of materials or release scenarios is impossible.

B.2.2 Characterization Tests

The intent of characterization leaching tests is to remove the dependence of specific field conditions from the behavior of the subject material such that the results provide information on characteristic or fundamental behavior of the subject material. Characterization tests expose the subject material to a broad range of experimental conditions so that the results may be considered to describe leaching characteristics over a range of field conditions. When site-specific parameters (e.g., fill dimension, groundwater flow rate, infiltration rate) are known, the results of characteristic leaching tests can be tailored to a particular field scenario. In other cases, results may be applied to general or default scenario parameters based on the anticipated mode of water contact (i.e., flow-around or percolation). Due to the broader range of testing conditions, characterization tests require more effort in testing and interpretation than simulation tests; however, characterization tests are generally considered to provide a more accurate and flexible assessment of leaching from solid materials. When site-specific conditions for a selected release scenario are known *a priori*, characterization tests may also provide built-in flexibility in that the range of test conditions may be tailored to conservatively cover the range of release conditions in the scenario.

B.2.3 Batch Extraction Tests

In batch extraction methods, a subsample of subject material is contacted by a single aliquot of leaching solution over a specified duration. Panels in Figure B-1 show two examples of batch tests. The basic procedure for a batch test is shown as a single-point batch test (a), while several batch extractions under different test conditions may be conducted at one time using a parallel-batch extraction structure (b). After extraction, the solid material may be discarded, recovered for analysis, or contacted with another aliquot of the same or different leaching solution. Batch extraction tests are most often performed to achieve pseudoequilibrium between the solid material and the leaching solution; therefore, the material subsample used in batch extraction tests is often particle-size-reduced by crushing or grinding to minimize the rate limitation of diffusion through large particles.

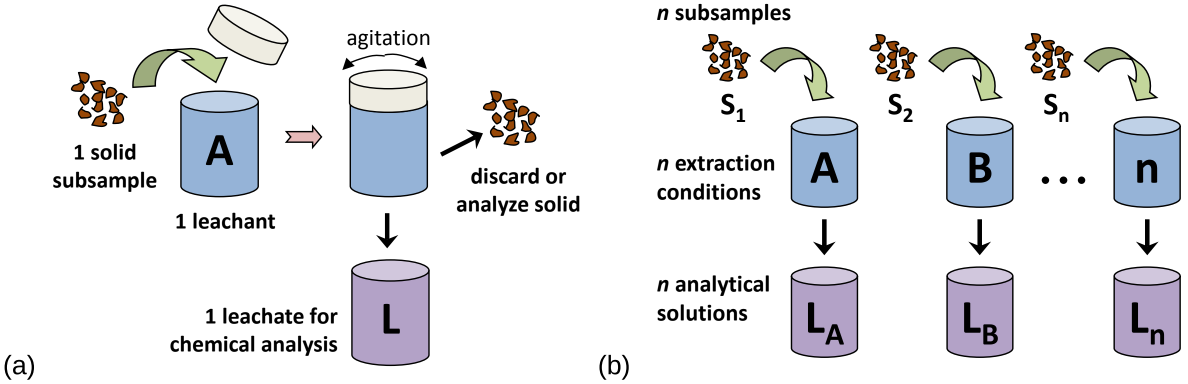

Figure B-1. Schematic representations of a two batch extraction tests: (a) single batch and (b) parallel batch. *Source:* Modified from Garrabrants and Kosson 2005.

B.2.4 Dynamic Leaching Tests

Dynamic leaching tests rely on continuous or semicontinuous refreshing of the leaching solution. Often, the purpose of dynamic leaching methods is to record time-dependent data regarding the rate of release without establishing equilibrium between the solid and liquid phases. Dynamic leaching tests may also be used to measure the rate of release during the approach to equilibrium. The panels in Figure B-2 show several approaches for conducting dynamic leaching tests, including (a) contacting the subsample with a single aliquot of leaching solution that is recirculated and analyzed periodically until equilibrium is achieved, (b) passing the leaching solution around or (c) through the subsample once in a flow-around or flow-through setup, respectively, or (d) moving the subsample progressively through a series of leaching solutions aliquots in a semidynamic process.

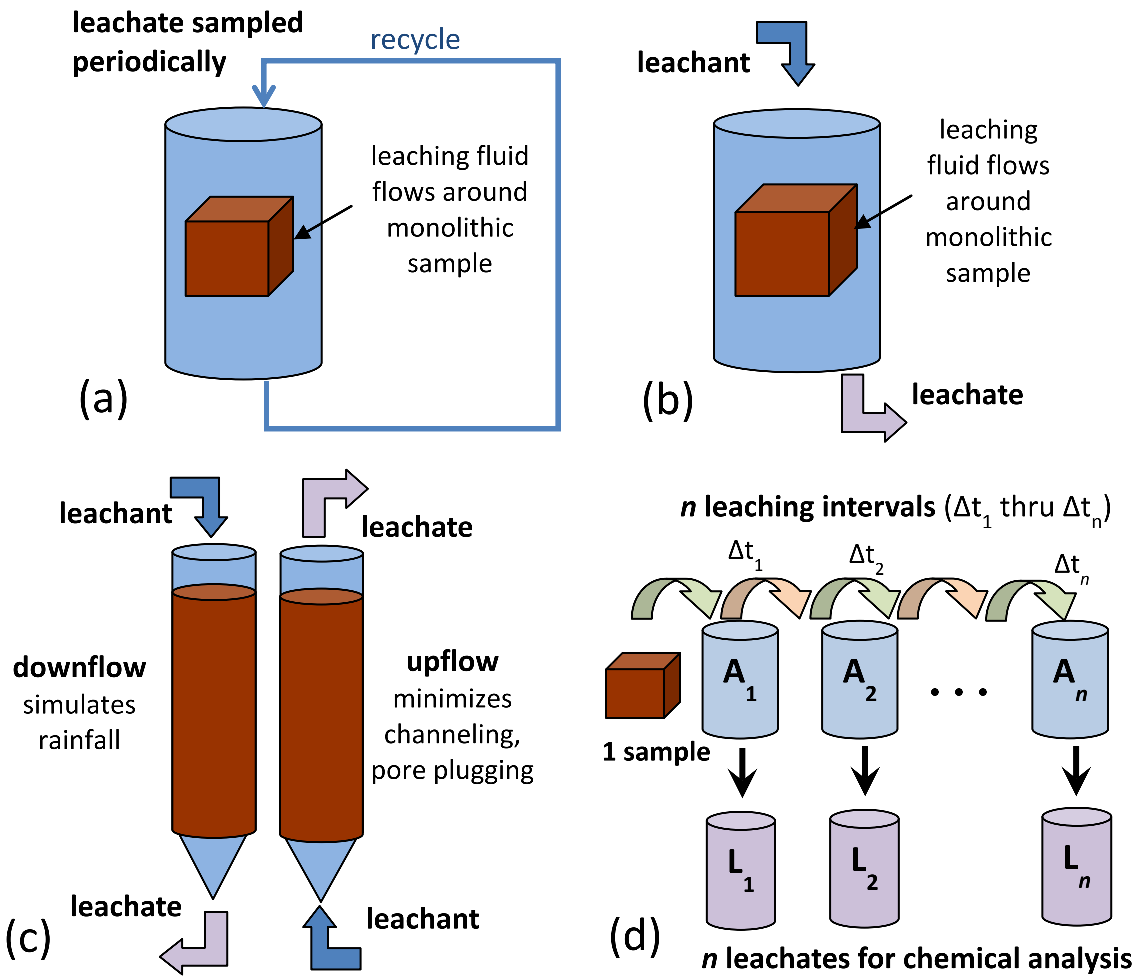

Figure B-2. Schematic representation of several dynamic leaching tests: (a) flow-around tank test with recycle, (b) single-pass flow-around tank test, (c) flow-through column test in downflow and upflow modes, and (d) semidynamic static tank test.
Source: Modified from Garrabrants and Kosson 2005.

B.3 CURRENT REGULATORY TESTING METHODS

Leaching tests for regulatory purposes have been promulgated from the EPA Office of Resource Conservation and Recovery with regard to hazardous waste classification. The EPA compendium of test methods, SW-846 (*Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*), contains two commonly used extraction procedures:

- Method 1311—Toxicity Characteristic Leaching Procedure (TCLP)
- Method 1312—Synthetic Precipitation Leaching Procedure (SPLP)

The EPA methods are single-batch, equilibrium-based simulation tests consisting of a single-batch extraction of particle-size-reduced (<9.5 mm) material with dilute acid at an L/S of 20 mL/g-dry. The test conditions for these methods are supposed to simulate release under defined regulatory scenarios. For example, TCLP mimics the result of codisposal of the tested material with municipal solid waste, while SPLP simulates the contact of the material with acid rain.

For assessment purposes, the tests are assumed to produce a leachate representative of field concentrations under the specified test conditions, and therefore, leachate concentrations may be compared directly to acceptable release concentrations. Although these tests are promulgated for hazardous waste classification (e.g., to provide a degree of protection between the public and waste materials containing potentially hazardous constituents), these leaching tests see daily use in areas for which these tests were not strictly designed.

B.4 EPA PREMETHODS—LEACHING TESTS INCLUDED IN LEAF

The characterization leaching test methods within LEAF are designed to define intrinsic leaching behavior of a wide range of solid materials. As such, the test conditions and applications are somewhat more broad-based than simulation tests. The four LEAF leaching test methods have been derived from published leaching methods (Kosson et al. 2002) and international standard methods in various states of development and validation for waste materials (CEN/TS 14405 2004, CEN/TS 14429 2005, CEN/TS 14997 2005, CEN/TS 15863 2009), construction products (CEN/TS-2 2009, CEN/TS-3 2009), and soils (ISO/TS 21268-3 2007; ISO/TS 21268-4 2007; ISO/DIS 12782 2010, parts 1–5) as well as some U.S. test methods (ASTM 4784, ASTM 1308, ANS 16.1).

Drafts of the LEAF leaching tests are currently available online (www.vanderbilt.edu/leaching) as preliminary versions of EPA test methods, denoted here as “premethods.” The following sections provide a brief description of each method, including example results and interpretation.

B.4.1 PreMethod 1313

PreMethod 1313 (EPA 2010a) is an equilibrium-based leaching test designed to provide the LSP of constituents as a function of pH. The test also provides a titration curve which can be used to assess the acid or base neutralization capacity of the subject material. For most inorganic contaminants, the pH of the leaching environment can have a strong influence on the LSP, such that release concentrations under the local equilibrium assumption changes as pH shifts (e.g., when the material buffering capacity is depleted due external sources of acidity or alkalinity).

B.4.1.1 Procedure Description

The procedure consists of 10 parallel extractions of a particle-size-reduced solid material (to facilitate the approach to equilibrium) in dilute acid or base designed to provide eluates at specific pH targets over the range 2–13. A subsample of the subject material is added to each of 10 extraction vessels along with specified volumes of deionized water and aliquots of either acid or base. The final L/S of each extract is 10 mL/g-dry. The extraction vessels are sealed and tumbled end over end for a contact time that varies 24–72 hours depending on the particle size of the material.[2] After the specified contact time, eluate pH and conductivity are measured from an aliquot taken from each extraction, and the remaining solution is filtered through a 0.45-µm pore size filtration membrane. Analytical samples are saved for chemical analysis in a manner consistent with target constituents and selected analytical methods.

B.4.1.2 Modifications for Organic Contaminants

Although the procedure was initially designed to determine the pH-dependence of the LSP for inorganic contaminants, the method can be easily modified to address organic contaminants. The container materials may be altered to minimize sorption (e.g., borosilicate glass or steel vessels rather than plastic or fluoropolymer vessels), and container designs and filtration methods may be modified to minimize volatilization.

B.4.1.3 Typical Results and Interpretation

The constituent concentrations in the PreMethod 1313 eluates are plotted as a function of the final extract pH, resulting in a curve that represents the pH-dependence of the LSP across a broad range of pH values. The shape of the LSP curve (i.e., relative locations of maxima and minima) is indicative of the geochemical speciation of the constituent in the solid phase over the pH range. The LSP results for inorganic contaminants usually can be recognized as one of the four characteristic shapes described below and presented schematically in Figure B-3.

- *cationic species*—The LSP curve of cationic species (e.g., Cd) typically has a maximum concentration in the acidic pH range that decreases to lower values at alkaline pH values.
- *amphoteric species*—Although similar in shape to the LSP curve for cationic species, the LSP concentrations for amphoteric species [e.g., Pb, Cr(III), Cu] pass through a minimum in the near-neutral pH range and increase with pH into the alkaline range. The increase in LSP concentration in the alkaline range is typically associated with soluble hydroxide complexes (e.g., $[Pb(OH_3)]^-$).
- *oxyanionic species*—The LSP curves for oxyanions (e.g., $[AsO_4]^-$, $[SeO_4]^-$, $[CrO_4]^{-2}$) typically show maxima in the neutral to slightly alkaline range.
- *highly soluble species*—The LSP curve for highly soluble species (e.g., Na^+, K^+, Cl^-) is not a strong function of pH; thus, it appears to be relatively flat across the pH range.

For inorganic contaminants, the idealized LSP curves in Figure B-3 can be compared with the general shape of the test data to infer the speciation of the constituent in the solid matrix. However, geochemical speciation models should be used to confirm these observations. The eluate concentration results from PreMethod 1313 may be simulated with geochemical speciation models to infer the mineral phases, adsorption reactions, and soluble complexes that control the release of the constituent.

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[2] The contact time depends on the maximum particle size of the solid sample under the assumption that larger particles take longer to reach equilibrium.

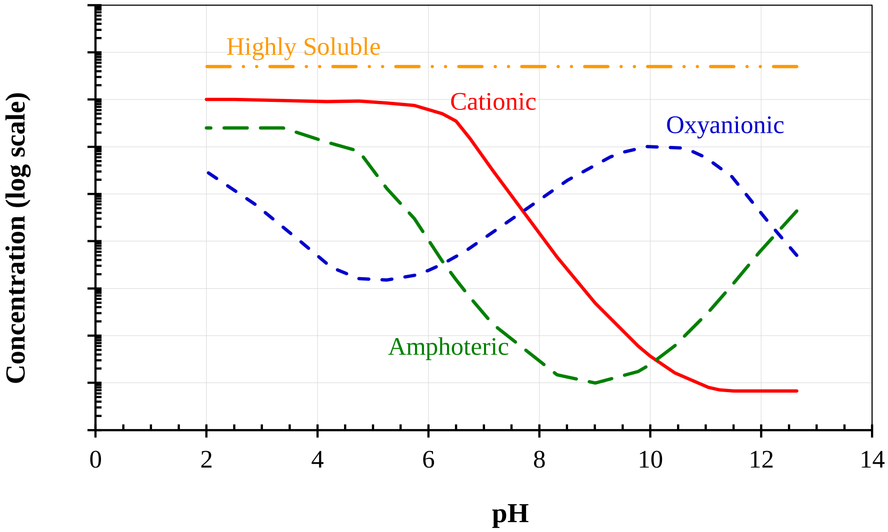

Figure B-3. Generic behaviors of several inorganic contaminant types showing generalized minima/maxima as a function of pH.

For organic contaminants, measured LSP concentrations are associated with partitioning between organic and aqueous phases, as well as complexation with dissolved carbon in the aqueous phase. The organic-aqueous partitioning of a contaminant is described in the literature using the octanol-water partitioning coefficient, K_{ow}. This partitioning is relatively tolerant of changes in pH; however, the dissolution of organic carbon, and hence the complexation with organic contaminants, are strongly dependent on pH, especially in the alkaline range. In Figure B-4, the relative concentrations of DOC and total PAHs in a leachate are shown before and after removal of the organic carbon through flocculation.

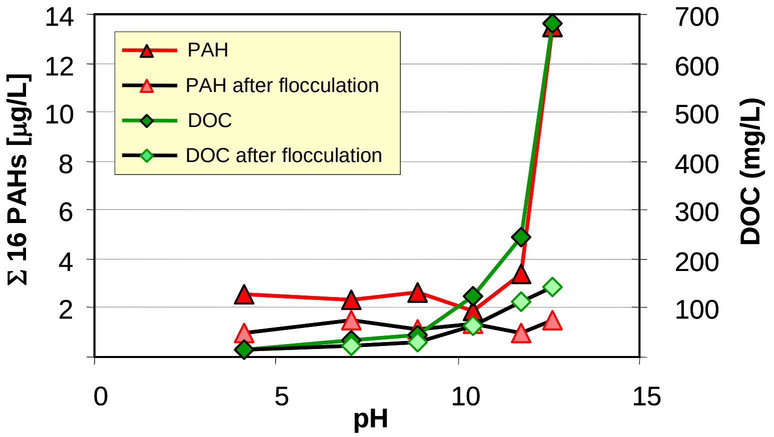

Figure B-4. pH-dependent leaching of DOC and associated PAH concentrations from contaminated sediment. *Source:* After Roskam and Comans 2003.

B.4.2 PreMethod 1314

This percolation column method (EPA 2010b) is designed to provide the LSP of constituents as a function of L/S under conditions where water percolates through the solid material.

B.4.2.1 Procedure Description

A 5 cm diameter × 30 cm column is moderately packed with solid material, and leaching solution is introduced to the column in upflow pumping mode to minimize air entrainment and flow channeling (Figure B-5). The default leaching solution for most materials is deionized water; however, a solution of 1.0 mM calcium chloride in deionized water is used when testing materials with either high clay content (to prevent deflocculation of clay layers) or high organic matter (to minimize mobilization of DOC). The liquid flow rate is be maintained at 0.5–1.0 L/S per day to increase the likelihood of local equilibrium within the column. Liquid fractions are collected as a function of the cumulative L/S and saved for chemical analysis. The cumulative mass release is plotted as a function of cumulative L/S.

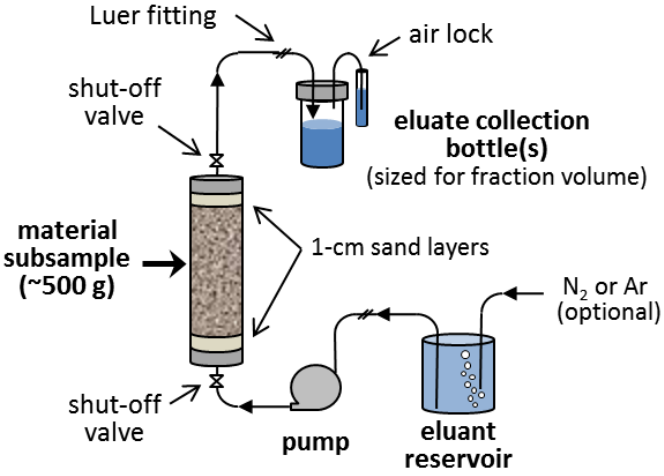

Figure B-5. Schematic of PreMethod 1314 upflow percolation column test apparatus.

B.4.2.2 Modifications for Organic Contaminants

Although this method was primarily designed to address LSP of inorganic contaminants, the method can be easily modified to address organic contaminants. The column materials need to be altered to minimize sorption (e.g., borosilicate glass or steel surfaces rather than plastic or fluoropolymer), and container designs and filtration methods should be modified to minimize volatilization.

B.4.2.3 Typical Results and Interpretation

Figure B-6 shows column eluate concentrations for calcium and chromium obtained using PreMethod 1314 on a coal combustion fly ash, along with cumulative mass release derived from the leaching test results. Eluate concentrations are compared to QC values: the method limit, which is sometimes considered a practical quantifiable limit, and the method detection limit, which indicates the lowest detectable concentrations. Cumulative release values are calculated by summing up the mass released in each eluate fraction up to the L/S value of interest (e.g., cumulative release at L/S = 2 mL/g-dry includes the mass release during the first four intervals). Cumulative release may be compared to a line with a slope of 1, which indicates solubility-controlled release in that if the solubility of the constituent is a limiting factor in the release, concentrations remain constant and doubling the liquid volume results in doubling the mass released.

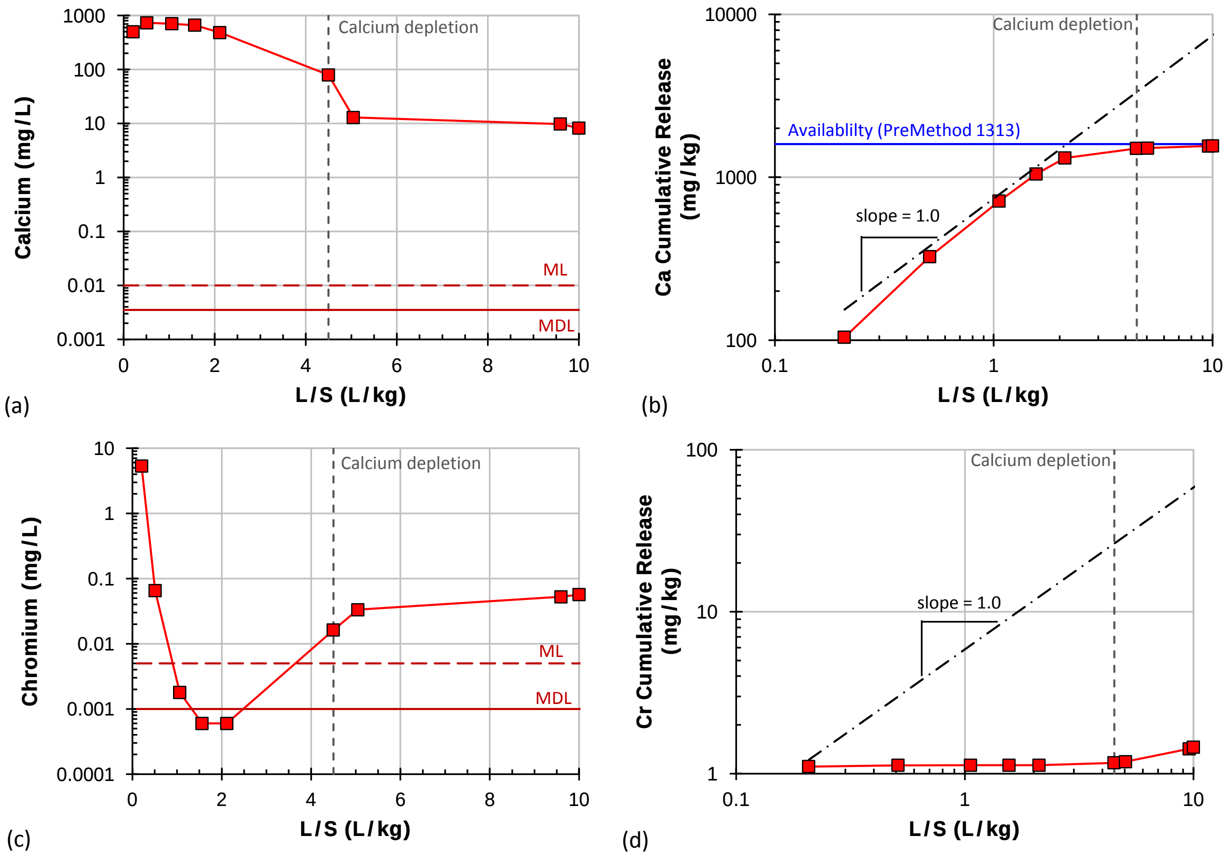

Figure B-6. Example PreMethod 1314 results for a coal combustion fly ash as a function of L/S showing (a) calcium concentration, (b) calcium release, (c) chromium concentration, and (d) chromium release.

To aid in interpretation of the results shown in Figure B-6, a vertical, dashed line is used to indicate a critical point in the leaching where calcium concentrations decrease dramatically. The change in concentration is likely due to depletion of leachable calcium, although eluate concentrations have not yet decreased to the QC limits (i.e., method limit or method detection limit). In the calcium release plot, the depletion assessment is confirmed by plotting the maximum release value from the PreMethod 1313 data, which is indicative of the available fraction of calcium in the material. Figure B-6(b) shows that the limit on calcium release in the column test corresponds to the release of the available calcium.

Comparison between calcium and chromium concentration plots shows an obvious connection between the depletion of calcium concentrations and a significant increase in chromium leaching. Since progressive L/S ratios are related to time under groundwater flow in the subsurface, chromium release is likely to increase with time as more liquid is passed through the column and calcium is depleted.

B.4.3 PreMethod 1315

PreMethod 1315 (EPA 2010c) determines mass transfer release rates of constituents containing low-permeability material under diffusion-controlled release conditions.

B.4.3.1 Procedure Description

The procedure consists of continuous leaching of a monolithic or compacted granular material in a liquid-filled tank with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen such that the sample is fully immersed in the leaching solution at a liquid–surface area ratio of 9 mL/cm^2. Monolithic samples may be cylinders or parallelepipeds; granular materials are compacted into cylindrical molds at optimum moisture content using modified Proctor compaction methods. At nine predetermined intervals, the leaching solution is exchanged with fresh reagent water, and the previous leachate is collected. For each leaching interval, the pH and conductivity are measured, and analytical samples are saved for chemical analysis. Solution concentrations are plotted as a function of time, as a mean interval flux, and as cumulative release as a function of time. Observed diffusivity and tortuosity may be estimated through analysis of the resulting leaching test data.

B.4.3.2 Modifications for Organic Contaminants

One principle of any mass transport-based leaching test is that a concentration gradient between leaching solution and the porewater within the material must be maintained as a driving force for mass transport. However, the low aqueous solubility of many organic compounds, such as PAHs, results in leaching solution concentrations that approach equilibrium quickly such that the driving force for mass transport is diminished. This condition can lead to erroneous estimation of mass transport release rates for organic contaminants. Additionally, volatile organics may be lost to headspace and vessel leaks during the procedure. Thus, the method for PreMethod 1315 testing of materials containing organic contaminants requires more extensive modification than other test methods. A modified PreMethod 1315 approach (EPRI 2009), denoted here as PreMethod 1315m, uses a siliceous gel coating within the leaching vessel to act as an absorption sink for organic constituents. The gel is coated on the inside surface of an airtight borosilicate glass jar such that organic constituents that transport through the subject material into the aqueous phase are absorbed into the gel and trapped until extracted with a solvent. Using this approach, volatility losses are minimized, and the mass release is considered to better represent the mass transfer of organic contaminants into freely moving groundwater, where concentrations typically build up.

B.4.3.3. Typical Results and Interpretation

Figure B-7 shows an example of PreMethod 1315 data for the release of aluminum from an S/S-treated wastewater stream containing heavy metals. The four panels in the figure represent a common way to present mass transfer data by including (a) the pH evolution during the leaching test since pH is an important parameter controlling porewater solubility of inorganic contaminants, (b) leachate concentrations in each test interval as a function of leaching time, (c) mass flux or the rate of release across a unit exposed surface area as a function of leaching time, and (d) cumulative mass release per unit exposed surface area as a function of leaching time. The values for mass flux and cumulative release are derived directly from leachate concentrations and compared to indicator lines with slopes of –0.5 (flux) and +0.5 (cumulative release). These lines are based on the time-dependence of a diffusion-controlled release mechanism where diffusion is related to the square root of time. In the example shown in

Figure B-7, the flux and mass release of aluminum are “consistent” with a diffusion-controlled mechanism represented by the indicator lines.[3]

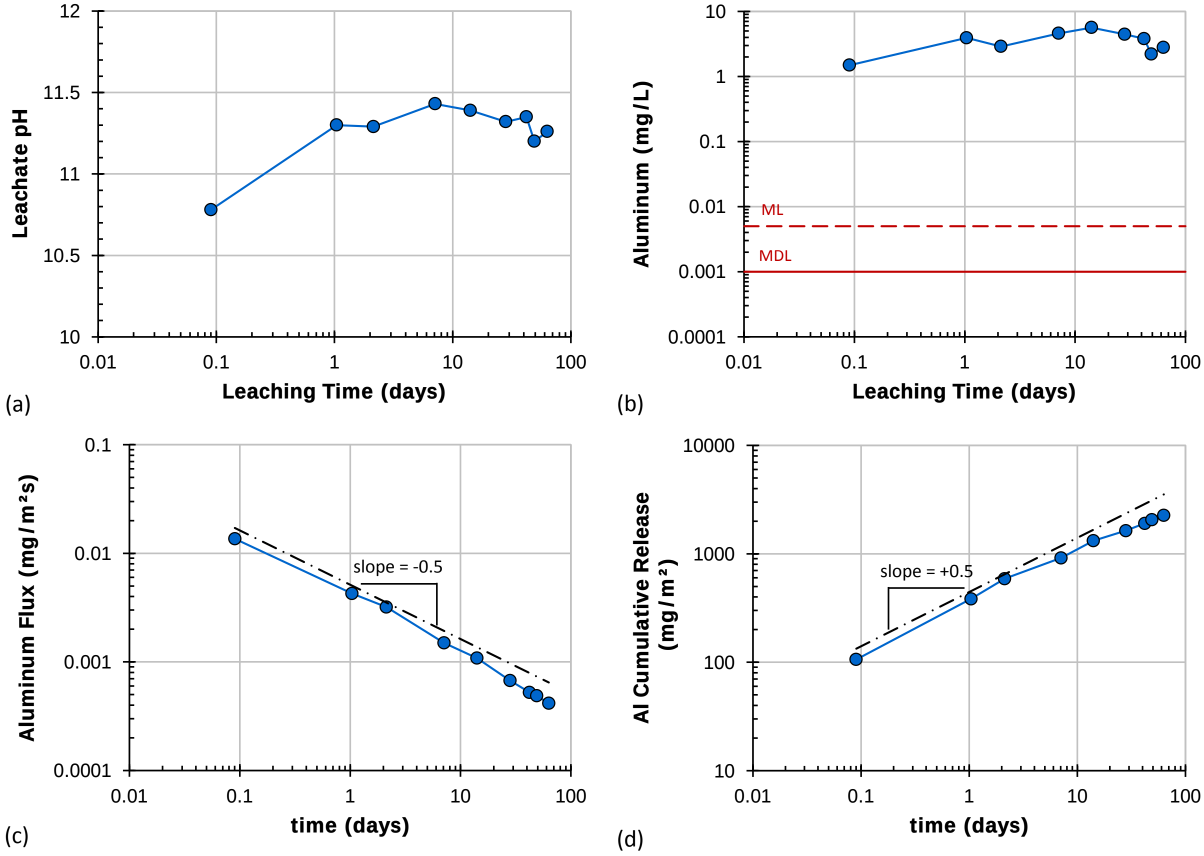

Figure B-7. Example PreMethod 1315 results for aluminum leaching from an S/S-treated material showing (a) leachate pH evolution, (b) leachate concentrations, (c) mass flux, and (d) cumulative mass release.

The release behavior of a material under conditions of mass transport can be described by either the mass flux or cumulative mass release. Either parameter may be used to provide a comparison of release behavior for different constituents as shown in Figure B-8. In this figure, the cumulative release for several select constituents from the S/S-treated wastewater is compared to the indicator line with slope of +0.5. The following generalizations may be made:

- Aluminum, selenium, and antimony cumulative releases are consistent with a diffusion-controlled mechanism.

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[3] Since other release mechanisms are also related to the square root of time and may be represented by the same lines, caution should be used during interpretation, and proclamations without supporting information that release of a species is controlled by diffusion should be avoided.

- The cumulative release of iron is not consistent with diffusion control and may be solubility-controlled. Confirmation of this observation requires additional tests or geochemical speciation modeling.

- The cumulative release curve for selenium appears to be limited to a fixed value of approximately 1,000 mg/m^2. Plotting the available content as determined by PreMethod 1313 (converted to the proper units) on the cumulative release graph shows that the release limit corresponds to the availability of selenium. Thus, the cumulative release of selenium in the PreMethod 1315 test is limited by the depletion of available selenium.

  Antimony release appears to be suppressed for the initial testing fractions but shows a significant and sudden increase between 14 and 28 days of leaching. The increase in antimony release may be due to depletion of another constituent; however, additional tests and geochemical speciation modeling may be required to confirm this observation.

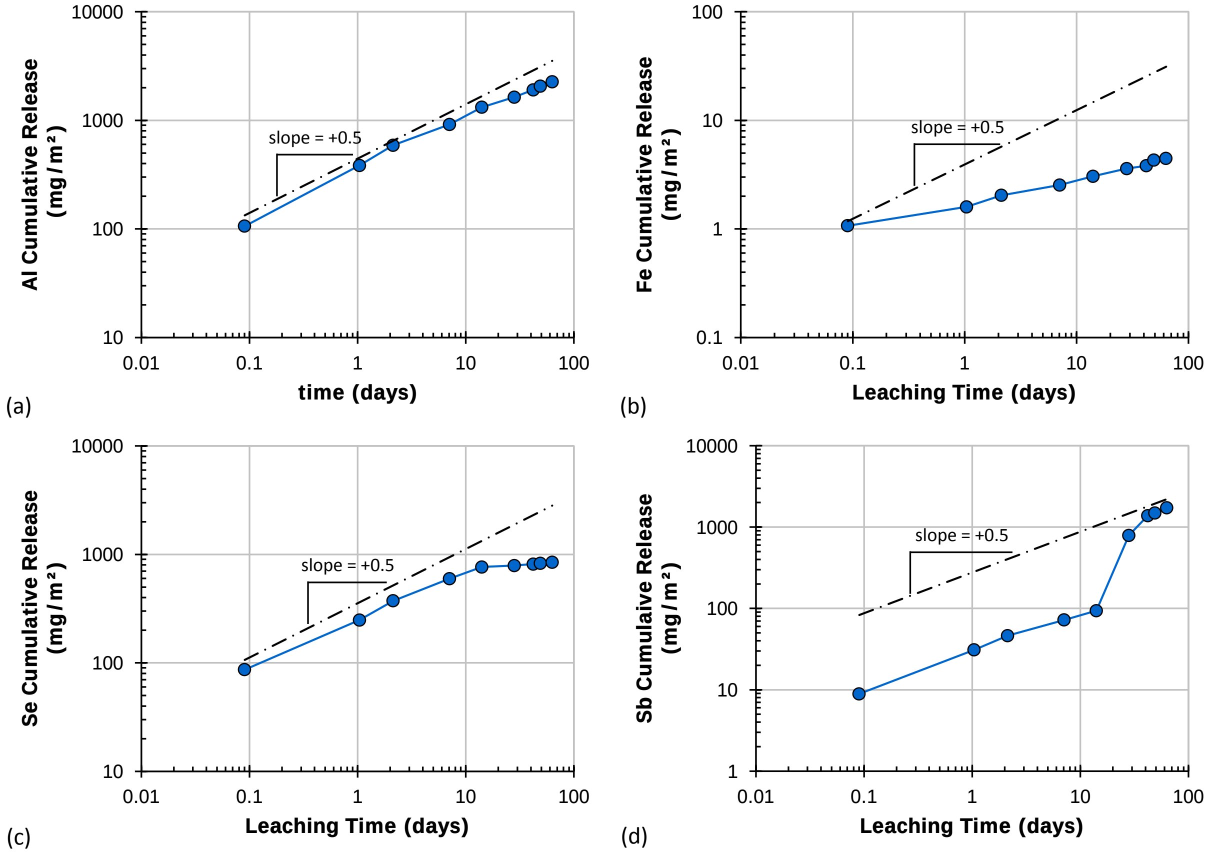

Figure B-8. Example PreMethod 1315 data showing cumulative release for (a) aluminum, (b) iron, (c) selenium, and (d) antimony.

B.4.4 PreMethod 1316

This parallel-batch equilibrium test (EPA 2010d) is designed to provide the LSP of constituents as a function of L/S at five values between 10 and 0.5 mL/g-dry. At low L/S (e.g., S/S material pore water), ionic strength is high such that the equilibrium chemistry is different from that measured under laboratory conditions of 10 mL/g-dry.

B.4.4.1 Procedure Description

This procedure consists of five parallel extractions of a particle-size-reduced solid material (to facilitate the approach to equilibrium) in reagent water. No acid or base is added so that the final extract pH reflects the buffering capacity of the solid material. Samples of solid material and volumes of deionized water are added to 10 extraction bottles at L/S values of 10, 5, 2, 1, and 0.5 mL/g-dry. The extraction vessels are sealed and tumbled end over end for a contact time between 24 and 72 hours. The contact time depends on the maximum particle size of the solid sample under the assumption that larger particles take longer to reach equilibrium. After the specified contact time, pH and conductivity of the eluates are measured, and the remaining solution is filtered through a 0.45-µm pore size filtration membrane under pressure or vacuum. Analytical samples are saved for chemical analysis depending on target constituents and selected analytical methods. The concentrations of constituents in the analytical solutions are reported and plotted as a function of L/S.

B.4.4.2 Modifications for Organic Contaminants

Although this method was primarily designed to address L/S-dependence of inorganic contaminants, the method can be easily modified to address organic contaminants. The container materials need to be altered to minimize sorption (e.g., airtight glass or steel vessels rather than plastic or fluoropolymer vessels), and container designs and filtration methods should be modified to minimize volatilization.

B.4.4.3 Typical Results and Interpretation

The results of PreMethod 1316 are similar in presentation and interpretation to those of the column test (PreMethod 1314) with leachate concentrations and release presented for each constituent. However, because this method is a parallel-batch extraction procedure, release is not cumulated over several leaching fractions as in the column tests. In PreMethod 1316, release is reported in the same manner as in the pH-dependence test (i.e., batch concentration multiplied by the corresponding L/S value for each extraction).

Figure B-9 shows PreMethod 1316 results for arsenic and boron from a contaminated smelter plant soil. As L/S values decrease from 10 mL/g-dry toward 0.5 mL/g-dry, the concentration of inorganic constituents tends to increase.[4] In some cases, the increase may be significant, one to two orders of magnitude greater than concentrations from the extract specified in typical batch extraction leaching methods (e.g., $10 \leq L/S \leq 20$).

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[4] While the concentrations of most inorganic constituents increase, some constituents in certain matrices (e.g., calcium in cement-based materials) may decrease with decreasing L/S.

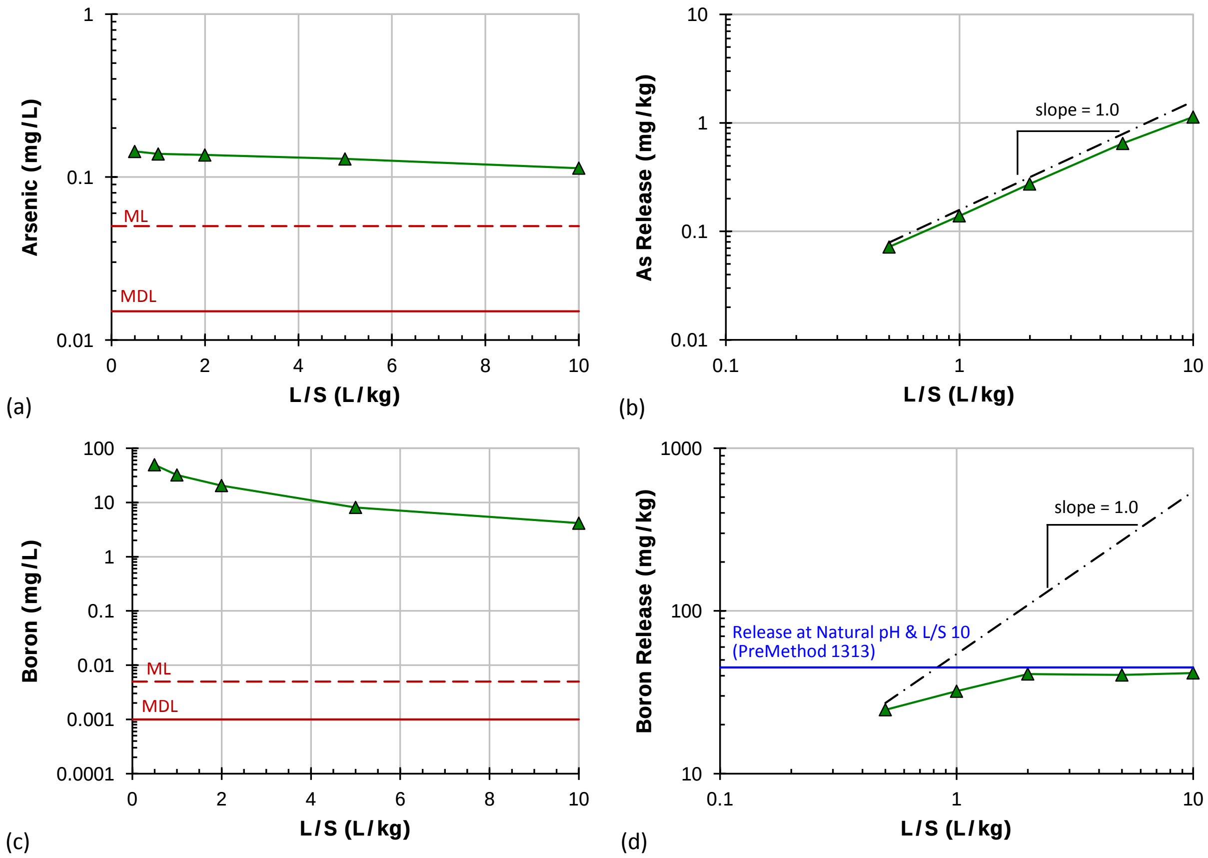


Figure B-9. Example PreMethod 1316 results as a function of L/S showing (a) arsenic concentration, (b) arsenic release, (c) boron concentration, and (d) boron release.

Plots of the mass release as a function of L/S show two distinctly different behaviors when compared to a line with a slope of 1.0 representing solubility control. Figure B-9 illustrates these two behaviors for arsenic and boron.

- *solubility control*—The arsenic release curve is consistent with the solubility line, indicating that solubility controls release. The concentration of arsenic is relatively constant such that release scales with L/S ratio. If the L/S ratio between two extractions is different by a factor of 2, the release of arsenic will also be different by a factor of 2.

- *availability control*—In contrast, the release of boron in the subject soil is limited by the available amount of boron that can be released from the material at the pH and L/S ratio imposed by PreMethod 1316. This fact can be confirmed by plotting the release value from PreMethod 1313 at natural pH (i.e., when no acid or base is added) over the release curve as shown in Figure B-9(d). The correspondence between the release at natural pH and the release asymptote in PreMethod 1316 indicates that release of boron is availability controlled.

B.5 LEACHING ASSESSMENT

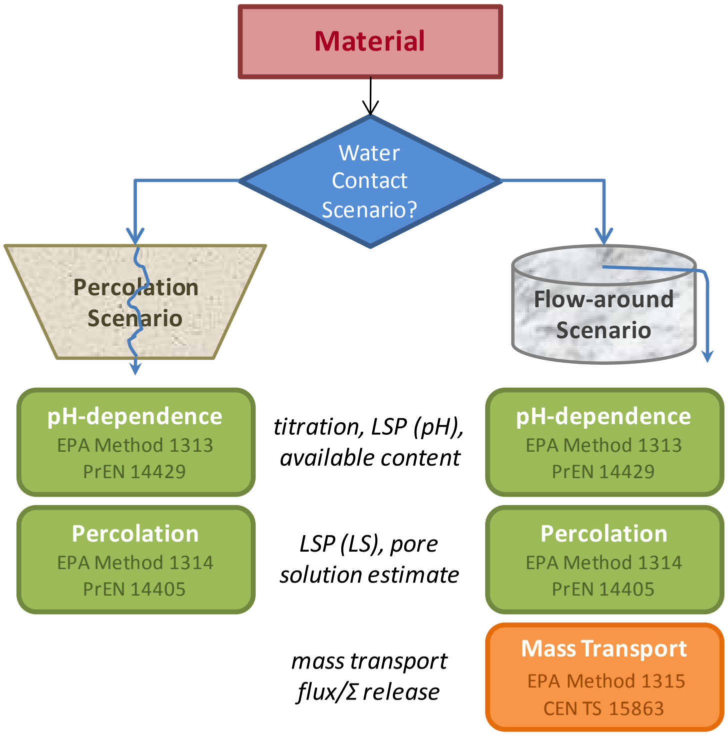
Test methods alone are not sufficient to accurately predict leaching from a source material, through the environment, to a receptor. Leaching test results need to be linked to field conditions that represent a release scenario. This linkage requires a conceptual and computational framework to extrapolate laboratory test results to field scenarios. Under the integration approach proposed by LEAF, an important distinction is made between percolation scenarios (e.g., when groundwater flows through a granular material or material with a hydraulic conductivity that is similar to that of surrounding materials) and flow-around scenarios (e.g., when groundwater is diverted around a monolith).

- In the former case, groundwater percolates through the material at a low flow rate such that partitioning between the solid and liquid phases can be described by equilibrium-based tests.
- In flow-around scenarios, the rate of release is dictated by the rate of mass transport to the groundwater/material interface such that flux-based leaching tests best describe release.

Based on this distinction, a generic testing approach has been developed for percolation scenarios and flow-around scenarios, as shown in Figure B-10. In most cases, chemical analysis should include all relevant contaminants as well as matrix constituents and organic/inorganic carbon.

In both scenarios, the most basic level of characterization is to determine the pH dependence of the LSP using PreMethod 1313. This test provides the following:

- insight into the chemical speciation of the constituents in the solid phase of the materials by evaluation of constituent release in response to different end-point pH conditions
- an estimate of the potentially leachable fraction, or availability, of a constituent determined at the maximum of the LSP curve
- a method for screening constituents to determine a list of constituents with potential environmental impact by comparing leachate concentrations to desired concentrations or action levels with the relevant release scenario pH range



Figured B-10. Flowchart indicating test method selection based on material type used in integrated assessment approach.

When used as a screening tool, pH-dependent LSP concentrations well below action levels within the relevant pH range are not likely to be an environmental concern. On the other hand, constituents with concentrations at or exceeding action levels indicate a need for further testing to quantify the impacts under percolation or mass transfer controlled conditions.

Although the test conditions of PreMethod 1313 result in a broad range of pH values, not all of the pH range is applicable for every scenario. Thus, during interpretation, the total pH range can be divided into appropriate case-specific target zones, as shown in Figure B-11. For this figure, the measured LSP curve is shown in terms of a "release basis" (i.e., mass released per unit total material mass) to allow comparison to total composition and potentially leachable (i.e., available) fraction. To convert from concentrations (mg/L) to release (mg/kg), the test method leachate concentrations (mg/L) are multiplied by the test-specific L/S (L/kg). Plotting data on the basis of mass release also allows for comparison of data from a variety of batch tests conducted at different L/Ss.

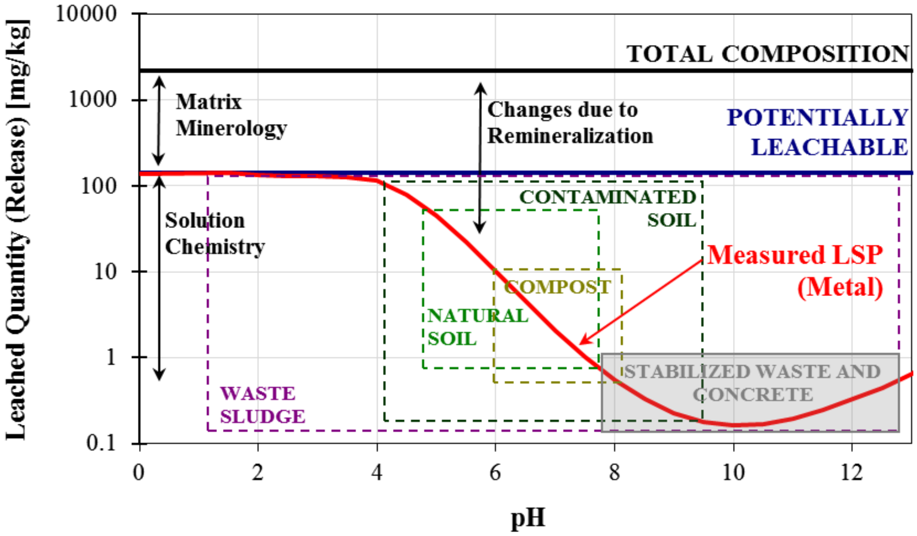


Figure B-11. Relevant pH ranges for various environmental materials superimposed over a schematic LSP pH-dependence curve.

Although the data in Figure B-11 are schematic, this comparison indicates why it is not recommended to base environmental assessment on total or available content as the mass that is released for many release scenarios is often only a small fraction of the total amount in the solid (total content) or that can be released under extreme environmental conditions (potentially available content).

B.5.1 Testing Based on Water-Contact Mode

When the mode of water contact is anticipated to be percolation through the material, release as a function of L/S using the acid/base neutralization capacity of the material is determined using a percolation test. Release from this test can be roughly related to field release as a function of the amount of liquid passing through a bed of high–hydraulic conductivity material if infiltration rates and bed parameters are known. Alternatively, similar information may be obtained through parallel-batch testing (e.g., PreMethod 1316) to determine LSP as a function L/S, although very low L/S is difficult to achieve using batch extraction approaches.

For low–hydraulic conductivity materials (e.g., monoliths, including many S/S-treated materials or well-compacted granular fills), a flux-based mass transfer test with periodic leachant renewal (e.g., ANS 16.1, PreMethod 1315) is recommended. Eluate concentrations at low L/S as resulting from a percolation column test may provide additional information by estimating porewater concentrations with the low–hydraulic conductivity material.

B.5.2 Leaching Assessment Empirical Methods

Simplified, semiempirical, and semianalytical approaches, which are knowingly conservative (i.e., overpredict release), can be used for initial screening purposes with the caveat that results should be verified against field observations.

Release in a percolation scenario may be estimated directly from PreMethod 1314 results if groundwater flow rates can be related to the amount of water passing through a mass of material. In this case, time can be mapped over the L/S ratio in the test, and release can be predicted as a function of time.

For mass transfer scenarios, flux or cumulative mass release results from PreMethod 1315 can be directly scaled to the exposed surface area of a subject material. Appendix C presents an illustration of how this can be done for a subsurface material. Mass transport through the material pore structure to the exposed surface of the material dictates the rate of release under the assumptions that groundwater flows around the material such that the concentrations in the groundwater remain essentially “zero” compared to concentrations in the subject material. The concept of a zero concentration boundary condition is often referred to as the “infinite bath assumption” (Crank 1975). If groundwater concentrations build up and mass transport is suppressed due to a lack of diffusional driving force (i.e., the gradient between groundwater concentrations and porewater concentrations within the material), release may be better described by equilibrium rather than kinetics.

Example of Relating Groundwater Flow to L/S

A mass of contaminated material with dimensions of 1 × 1 × 1 m is lying in an aquifer with a linear flow rate of 0.4 m/day, or approximately 150 m/year. The dry density (ρ) of the subject material is 1,500 kg-dry/m^3. The volume (v) of the contaminant fill is 1 m^3; thus, mass of the fill (m) is 1,500 kg ($m = v * \rho$). The cross-sectional area exposed to the groundwater flow is 1 m^2 such that the volumetric flow rate of the aquifer (Q) is 150 m^3/year, or 150,000 L/year (using the conversion that 1 m^3 = 1000 L).

The percolation rate of water passing through the contaminated material is the calculated as the volumetric flow rate (Q) divided by the mass of the fill (m), which results in a percolation rate of 100 L/S per year.

For these relatively small fill dimensions, the cumulative release at an L/S of 10 mL/g-dry from PreMethod 1314 column test relates to the release from the fill at approximately 35 days of leaching. For larger contaminated fills or slower aquifer systems, the percolation rate could be significantly lower.

B.5.2.1 Reactive Transport with Geochemical Speciation

Coupled chemical reaction-transport modeling is the preferred and most robust option available to provide insight in the long-term behavior of materials under changing exposure conditions in the field (Kosson et al. 2002; van der Sloot and Dijkstra 2004; Dijkstra et al. 2005; Dijkstra, van der Sloot, and Comans 2006; Dijkstra et al. 2008). The sequence of steps ranges from problem definition, through test method selection and leaching simulation, to laboratory-to-field validation (Kosson et al. 2002, CEN EN-12920 2003).

B.5.2.2 Hydrogeological Fate and Transport Modeling

Leaching test data (e.g., mass flux from transport tests or concentrations with percolating liquid volume from column tests) may be used directly in hydrogeological fate and transport models for contaminant transport to describe release from a source (S/S-treated material) to a downgradient POC.

B.6 EXAMPLE APPLICATIONS OF LEAF LEACHING TESTS FOR S/S-TREATED MATERIALS

The following section shows several examples of applications of LEAF leaching tests. Much of the data shown in these examples are taken from privately funded research and reproduced here without reference to specific sites or material descriptions. As an illustration of S/S treatment on organic contaminants, some of these examples show testing and interpretation of S/S-treated materials containing single-ring and polycyclic aromatic hydrocarbons.

B.6.1 Example 1: S/S Treatability Study

During treatability testing, the chosen leaching test should represent the primary release mechanism anticipated in the final application. Thus, the comparison of S/S-treated materials designed to provide a low hydraulic conductivity relative to surrounding soils should be based on one of several mass transport–based tests.

In the following example, a time-shortened version of PreMethod 1315 was used to compare the flux of BTEX chemicals (e.g., benzene, toluene, ethylbenzene, xylenes) and PAHs from several S/S treatment recipes. Since the constituents of interest for assessment were volatile and semivolatile organics, the method was modified as described above and denoted as PreMethod 1315m. The goal of the treatability comparison was to downselect recipes for further characterization and testing by selecting those recipes that minimize flux while balancing all other considerations including cost of materials, ease of implementation, etc.

B.6.1.1 S/S Recipes

Five recipes of S/S treatment were formulated in the laboratory for this comparison. Prior to leach testing, the recipes were screened to ensure that each resultant material passed material performance criteria for strength and hydraulic conductivity. The five recipes included the following:

- baseline recipe, consisting of portland cement (6 wt%) and ground granulated blast furnace slag (2 wt%).
- baseline recipe with added bentonite clay (1 wt%)
- baseline recipe with added bentonite clay (2 wt%)
- baseline recipe with added organoclay (1 wt%)
- baseline recipe with added organoclay (2 wt%)

Two duplicate samples of the baseline recipe were tested in parallel to indicate the potential for variation in treatment. For all other recipes, only a single sample was tested.

B.6.1.2 Flux Comparison

Figure B-12 shows mass flux from the six treatability samples xylene, naphthalene, phenanthrene, and benzo(a)anthracene. In all, the flux of these contaminants from all S/S-treated materials follows the indicator line representing a diffusion-controlled process. Based on these results, organoclay seems to provide a better basis for retention of PAH contaminants over the other recipes; however, there is no clear trend among the various S/S recipes in the case of xylene flux. For phenanthrene, addition of 2 wt% organoclay reduced the flux over most of the test duration by a factor of ~2. Thus, it was noted that an S/S treatment recipe using organoclay would probably best minimize contaminant release. However, the costs associated with organoclay adds to the total cost of treatment for a somewhat small return on treatability. Thus, both the baseline recipe and the recipe with 2 wt% addition of organoclay were selected for further testing.

B.6.2 Example 2: Comparison of Leaching “Before” and “After” Treatment

When a qualitative demonstration of the improvement in the environmental impact at a site is required, leaching tests may be reduced to a single set of defined release conditions to provide a “before” and “after” treatment assessment. This process provides a snapshot of the release of critical constituents to answer the question, “Is leachability decreased when this remedy is applied?”

This example illustrates how LEAF leaching tests can be used to compare cumulative release from an untreated coal tar–impacted soil and an S/S-treated material based on the same soil. The soil was samples from a boring hole at a former MGP site where subsurface soils were found to contain high levels of benzene, toluene, ethylbenzene, and xylenes and PAH contaminants.

B.6.2.1 Release Scenario

Usually, interpretation of leaching data within a properly defined leaching scenario is required when the physical properties of the untreated and treated material differ greatly. For example, when freely percolating soil is treated by S/S to a low hydraulic conductivity, release for the soils should be based on a percolation scenario using PreMethod 1314 or PreMethod 1316 data, while release from the S/S-treated material should be based on mass transfer using PreMethod 1315 data. This approach requires defining a single release environment that can be applied to both release scenarios. A conceptual release scenario (Figure B-13) was defined to provide a common basis for comparison. Release from both materials was calculated for a 1 m^3 volume of material.

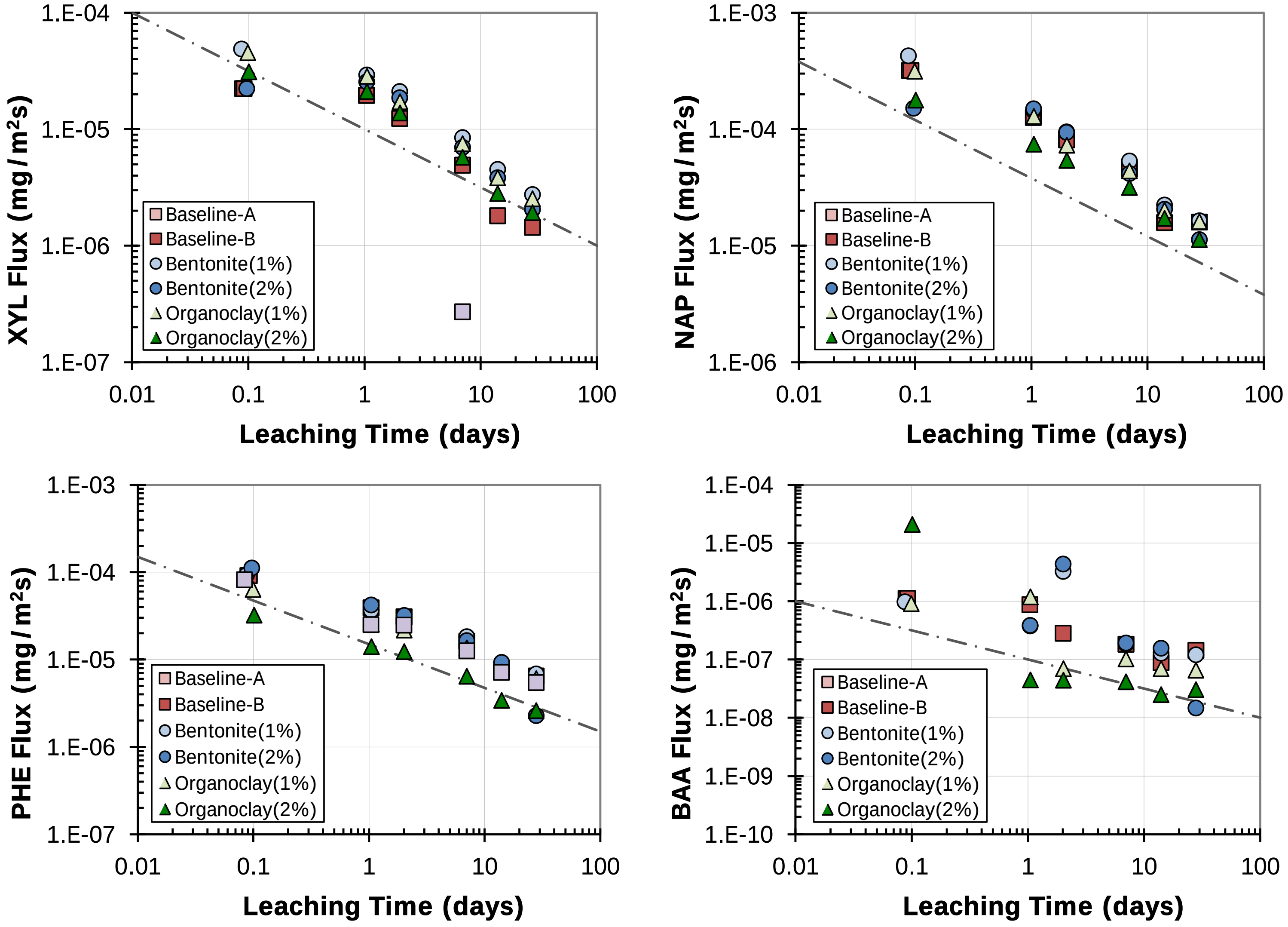


Figure B-12. Example 1: S/S treatability test results (PreMethod 1315m) for a contaminated soil from a former MGP showing xylene (XYL), naphthalene (NAP), phenanthrene (PHE), and benzo(a)anthracene (BAA) flux for a cement/slag baseline and baseline with bentonite and organoclay additives.

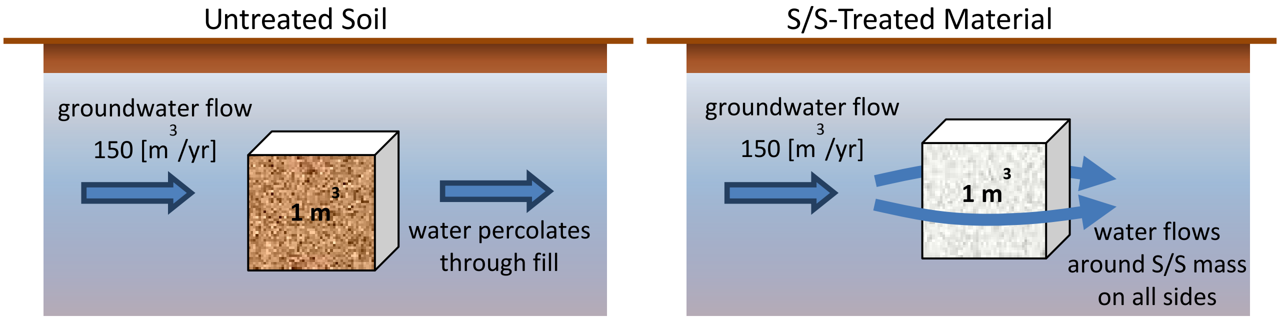


Figure B-13. Example 2: Scenario used in comparison of untreated soil and S/S-treated material.

In the case of the untreated soil (left side of Figure B-13), groundwater percolates through the contaminated "fill," and the L/S data obtained from PreMethod 1314 are related to time using the empirical approach described above. In addition, PreMethod 1314 release values were converted from units of mg/kg to units of mg/m^2 of surface area cross sectional to groundwater flow. By converting the L/S-dependent column test data to a time and area–based release, no conversions or alterations were required to the PreMethod 1315 cumulative release data for the S/S-treated material.

B.6.2.2 Release Comparison

Figure B-14 compares release for xylene and several PAHs from contaminated untreated soil and S/S-treated materials. Also shown in each panel of the figure are horizontal lines representing the "total content" of each contaminant in the soil and S/S-treated material as determined by pressurized fluid extraction using EPA Method 3545.

The data in Figure B-14 show that overall release from S/S-treated materials is several orders of magnitude less than that of the untreated material, indicating that S/S treatment of the soil is effective in reducing the rate of release. For xylene, naphthalene, and fluorene, the total content given by EPA Method 3545 is somewhat less than the cumulative release at the end of PreMethod 1314. This differential does not mean that the column test data are in error as the total content as determined by the EPA Method 3545 is operationally defined. Since the EPA method is essentially just one form of extraction technique, other, potentially more aggressive extraction techniques may yield a higher "total content."

B.6.3 Example 3: Leaching Data Linked to Hydrogeological Modeling

Often the purpose of leach testing and environmental assessment is to parameterize site- or scenario-specific release models that simulate the release of contaminants of concern integrated with hydrogeological conditions. In this case, leach testing should cover the widest possible range of test conditions so that all potential mechanisms of constituent release may be considered and combined into a groundwater fate and transport model.

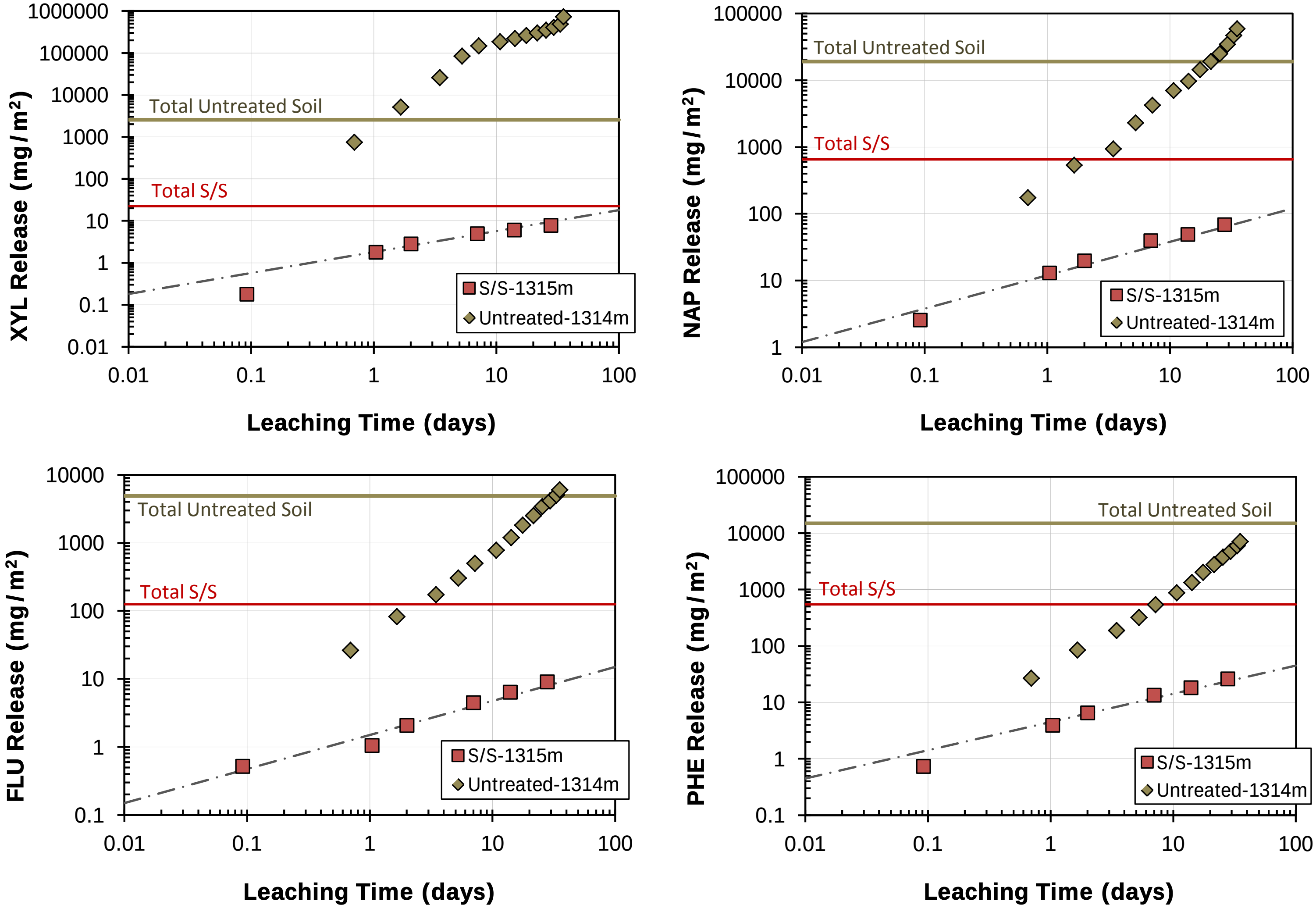


Figure B-14. Example 2: Comparison of cumulative release for untreated soil (PreMethod 1314) and cement/slag/bentonite S/S-treated materials (PreMethod 1315m) taken from a former MGP showing xylene (XYL), naphthalene (NAP), fluorene (FLU), and phenanthrene (PHE).

In the following example, leaching data on recovered cores of S/S-treated materials from a former MGP site were used as a source term for contaminant transport and combined with groundwater flow using hydrogeological fate and transport model. MIKE-SHE is an advanced integrated hydrological modeling system for simulation of water flow in entire land-based systems from rainfall to river flow. The model has the capability to integrate surface water and groundwater flow with environmental impacts to predict downgradient concentrations at a POC.

B.6.3.1 Scenario Description

MIKE-SHE was used to model groundwater flow around an S/S-treated material embedded into weathered bedrock as shown in Figure B-15. In this scenario, the majority of groundwater flows around an S/S-treated material (76 m wide × 76 m long × 10 m high) while a small fraction of groundwater is allowed to percolate through the material. The amount of water that percolates is determined in the model by the hydraulic gradient and the relative hydraulic conductivities of the S/S-treated material and surrounding soil.

The flow pattern provides an axis of symmetry along the centerline of the S/S-treated material such that the results can be displayed at two horizontal locations, as shown in the lower half of Figure B-15. Location 1 and Location 2 lay 20 m downgradient of the S/S-treated material and 12 m and 24 m off the axis of symmetry, respectively. In this scenario, the area above the S/S-treated material is capped such that the only infiltration that affects downgradient concentration is infiltration that reaches groundwater between the S/S-treated material and the POCs. However, since this infiltration will have a diluting effect only near the water table, two 5-m vertical zones of interests (i.e., Zones A and B) are established as shown in the upper half of Figure B-15. The two locations and two zones result in four POCs for this simulation, specifically named 1A, 1B, 1A, and 2B.

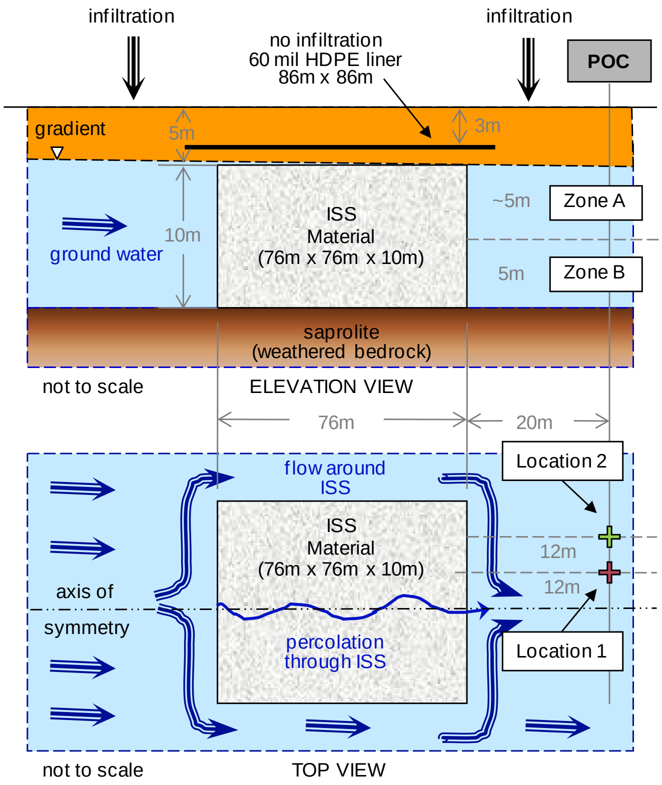


Figure B-15. Example 3: Schematic of MIKE-SHE simulation scenario showing groundwater flow around and through the S/S-treated material and combinations of location and zone (i.e., 1A, 1B, 2A, and 2B) representing four different simulation POCs).

B.6.3.2 Simulation Results

Figure B-16 shows the simulation results for POC concentrations naphthalene, phenanthrene, anthracene, fluoranthene, pyrene and benzo(a)pyrene. In the MIKE-SHE simulation, the mass of pyrene and benzo(a)pyrene released from the S/S-treated material into the groundwater is attenuated onto particulate organic matter in downgradient soils before getting to the POCs.

Thus, all concentrations at the POCs are less than 1 pg/L. For all other contaminants, the highest POC concentrations are predicted at POC 2B, which is the outermost and deepest POC. At this POC, the diluting influence of the infiltrating water is minimal, and the mass released from the material and carried by groundwater flowing around the S/S monolith has the most influence. Conversely, the lowest concentrations are predicted for POC 1A, where the dilution effect is maximized and the flow-around mass transport minimized.

While the integration leaching tests and hydrological flow models may be beyond the scope of many S/S remediation projects, simulations such as those shown in this example may be useful, not only for predicting groundwater concentration in aquifers downgradient of an S/S-treated material, but also for locating groundwater monitoring wells and establishing a monitoring plan that captures potential releases.

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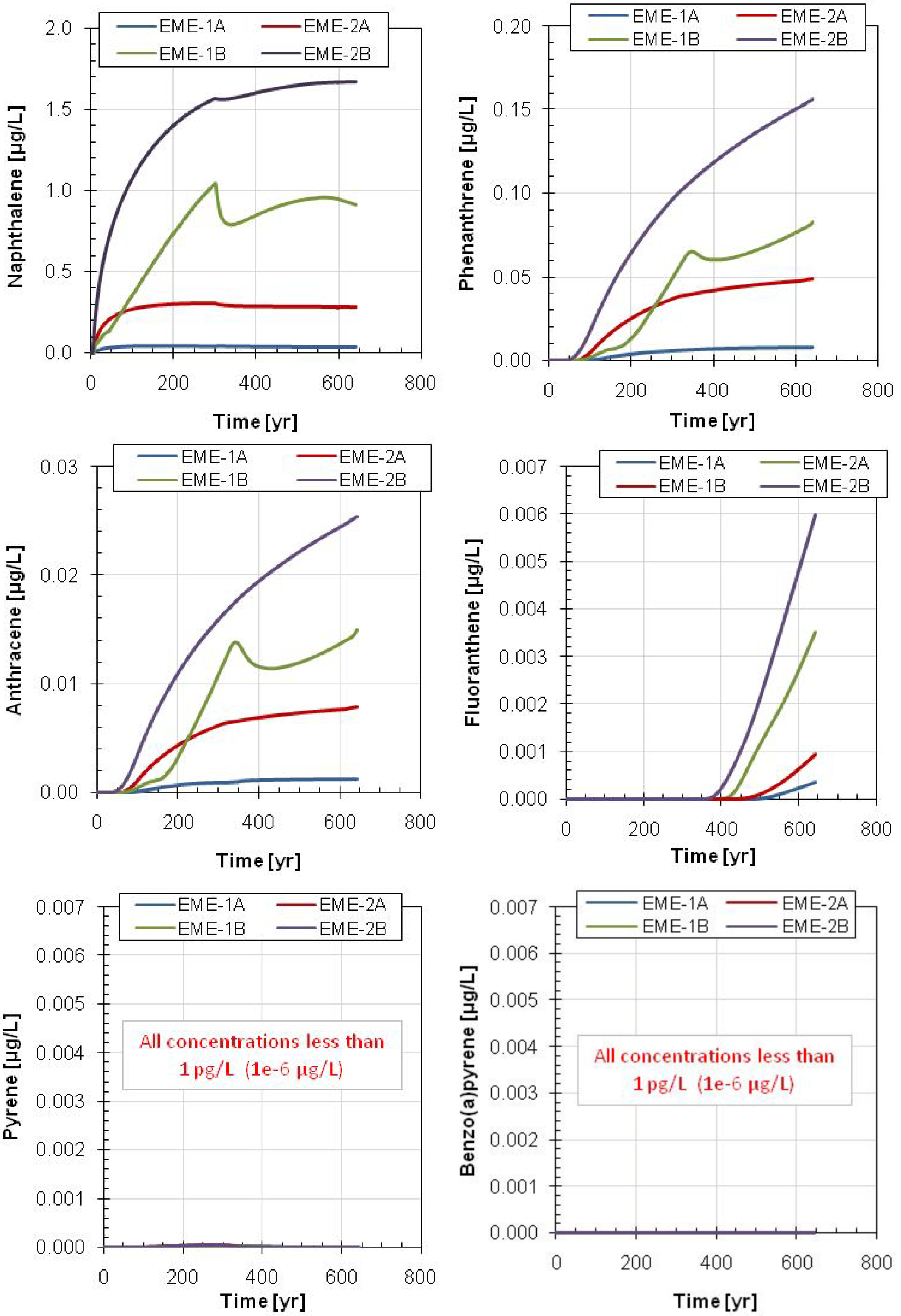

Figure B-16. Example 3: Scenario-specific simulation results using the MIKE-SHE model considering a combined "flow around + flow through" regime for naphthalene, phenanthrene, anthracene, fluoranthrene, pyrene, and benzo(a)pyrene.

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Appendix C

Groundwater Modeling Case Studies and Methods

GROUNDWATER MODELING CASE STUDIES AND METHODS

Groundwater models are mathematical conceptualizations of hydrologic and hydrogeologic flow systems. Models have become an important tool that can be used in environmental evaluations of the fate and transport of contaminants in various media, including groundwater. Models may also be a useful tool for use with S/S remedies, for example, to provide input for remedial selection and design, to evaluate potential impacts to groundwater or surface water from S/S treatment of contaminated materials, or to demonstrate in conjunction with field measurements compliance with cleanup criteria.

A wide range of groundwater models are available that have been used for environmental evaluations and can be applied to S/S remedy evaluations. These include one-, two- or three-dimensional models, numerical and/or analytical models, models to estimate the flux of contaminants that are present in unsaturated soil to underlying groundwater, water infiltration rates through caps to underlying soil and groundwater, the flux of contaminants released from a source area and transported via groundwater to a receptor or to surface water, and the containment and recovery of contamination in groundwater by one or more pumping well(s) and/or to assist in determining when groundwater monitoring may be modified or discontinued. Abundant literature is available that describes the function and capabilities of groundwater models, and therefore a detailed discussion of groundwater modeling will not be presented in this guidance document or appendix. EPA's Center for Subsurface Modeling Support (CSMOS), located at the Robert S. Kerr Center for Environmental Research in Ada, Oklahoma, provides public domain models and information on its website at www.epa.gov/ada/csmos.

The following sections in this appendix illustrate some actual uses of models for select sites and other methodologies that may be applicable to modeling for S/S remedies. Case Study #1 describes the use of modeling to estimate the degree of dilution that would be expected to occur beneath S/S-treated material as flux from the treated material entered groundwater, and how that modeling was used to predict compliance with the cleanup criteria by setting an allowable flux from the treated mass. Case Study #2 describes the use of modeling at a site where shallow groundwater indicated the possibility of groundwater mounding and flooding after S/S treatment and how modeling was used to assist in design of the site storm-water control system.

Subsection C.3 presents a graded modeling methodology that can be used to identify suitable modeling methods or codes to evaluate the efficacy of S/S remedies and estimate likely resulting potential impacts to groundwater. This is a relatively new approach, recently presented at the 2010 American Geophysical Union conference. This graded approach provides a template for selecting the modeling method or code to be used at a site such reasonably accurate results may be obtained at a lower level of effort and cost than *a priori* selection and application of more complex modeling methods and/or codes.

C.1 CASE STUDY #1—MODELING OF GROUNDWATER IMPACTS FOR AN S/S REMEDY

C.1.1 Introduction and Overview

In situ S/S applications can pose unique challenges for the management of post–environmental construction surface water and groundwater conditions. Construction of an S/S monolith may significantly alter hydrogeologic and hydrologic conditions and have potentially detrimental impacts beyond the limits of the project site. These impacts could include the following:

- Hydraulic mounding (water table rising) along the upgradient side of the monolith due to the placement of S/S material (reagent mixed with soil) with significantly lower permeabilities than the surrounding soil. This concern may be further heightened in the presence of coarse-grained soil and shallow groundwater elevations.
- Creation of localized conditions that could increase the potential for flooding due to the construction of a relatively impermeable surface that will increase surface water runoff to other areas and loss of land surface for compensating flood storage.
- Increase in the potential for flooding or surface water ponding upgradient of the S/S monolith due to hydraulic mounding and alterations to the previously existing groundwater flow paths, which could slow upgradient surface water infiltration during storm events.

Based on these considerations, it is recommended that groundwater modeling be integrated early in the design process using existing available groundwater elevation and flow data to assess the following:

- complying with local and state permitting requirements for storm-water management
- assessing potential impacts to the surrounding community
- modifying existing storm and sanitary infrastructure
- designing new groundwater and surface-water management facilities such as storm-water retention ponds and/or compensating flood storage basins
- developing final plans for site restoration and landscaping
- establishing a conceptual model for long-term groundwater monitoring

To better illustrate how groundwater modeling can be used to address the S/S design considerations outlined above, the following sections present a case study for a large S/S project at a former gasification plant site located northeast of Orlando, Florida. Pertinent topics addressed in this case study consist of the following:

- site-specific parameters that needed to be considered during model development
- key assumptions made to develop the model
- modeling methodologies and results
- development of design recommendations for surface-water and groundwater management and long-term groundwater monitoring
- design recommendations for future S/S projects

C.1.2 Site Background and Setting

In situ S/S was selected by EPA Region IV to address remaining soil and groundwater contamination from historic MGP operations at the site. Contaminant conditions included coal tar that occurred in discrete zones and various depths overlain by uncontaminated soils. The S/S operations encompassed approximately 140,000 yd^3 up to depths of approximately 30 feet bgs over an area of approximately 4–5 acres.

The study area includes the former MGP property, a number of properties that were affected by the environmental cleanup operations, and a perennial creek that drains the area (gaining stream). The creek is characterized as an urban stream and has been impacted by intensive development of the watershed. The creek discharges to a large lake at the northern edge of the site. Land use in the surrounding area consists primarily of residential homes and light commercial businesses. In this urban environment, potable water is supplied by the local municipality, and no production wells are located near the site. Figure C-1 provides a plan view of the study area, illustrating one of the major design challenges for the project: the original creek alignment passed through the design limits for the S/S monolith and needed to be rerouted prior to completing the S/S operations. The remediation limits indicated in black represent the approximate limits for the S/S monolith. As will be discussed below, rerouting the creek outside the limits of the monolith included installation of a box culvert, which required careful consideration as part of the groundwater modeling.

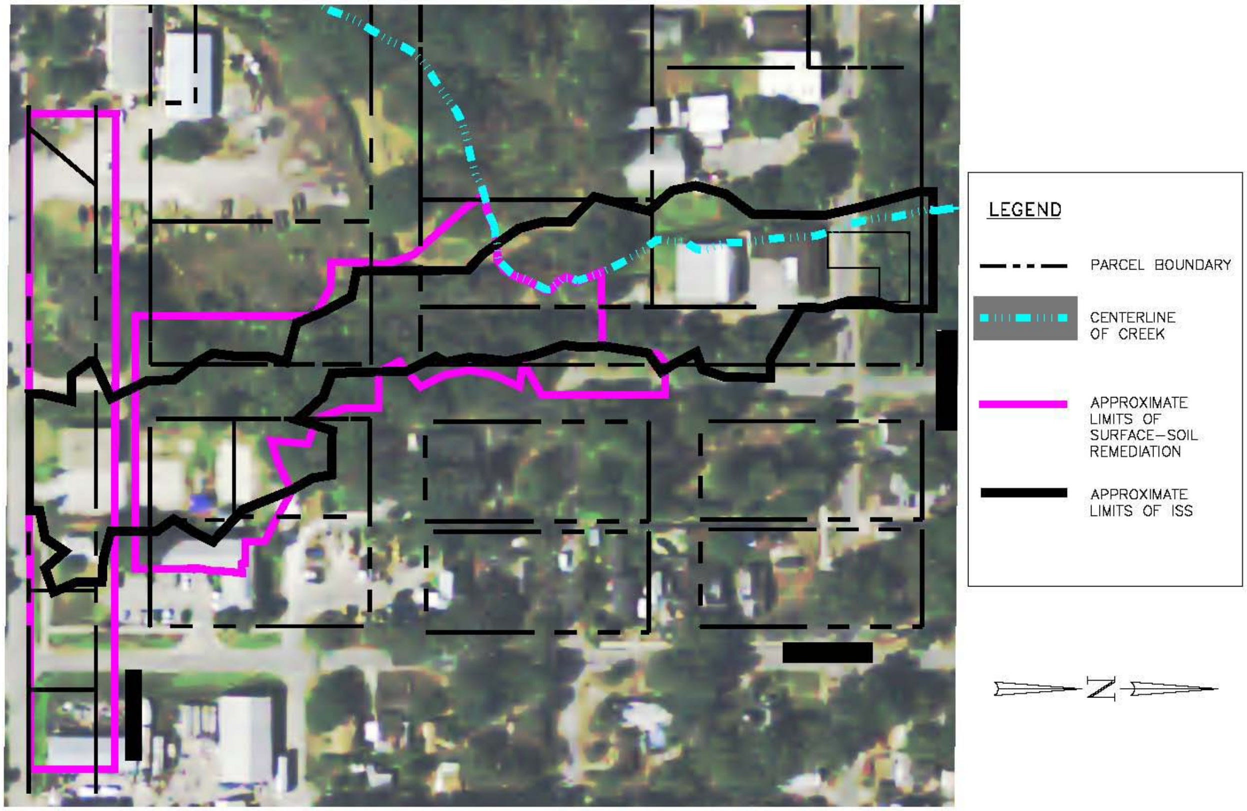

Figure C-1. Plan view of the case study area.

The climate of the area is humid subtropical, with warm wet summers and mild dry winters. Rainfall represents the largest input into the hydrologic system. The hydrostratigraphy of the site includes a shallow water table aquifer and a deep bedrock aquifer separated by a laterally continuous clay confining layer. The shallow unconfined aquifer system is present in sandy beach and shell deposits overlain by fill material. The deep confined aquifer system is present in limestone bedrock that underlies the region. The deep aquifer is the most commonly used source of groundwater in the area. Vertical gradients between the shallow and deep aquifers are upward. The shallow aquifer was the only unit modeled because the deep aquifer system was sufficiently isolated from the shallow system and not directly impacted by the S/S operations.

The shallow aquifer is within the shallow fine sand and shell encountered at the site from land surface to generally 30 feet bgs. The water table ranges 1–10 feet bgs. The general groundwater flow direction within the shallow aquifer is toward the creek with a northward component toward the lake at the end of the creek.

C.1.3 Modeling Objectives

The objectives for the modeling included the following:

- evaluate the potential for water table rise due to the construction of the S/S monolith and placement of a perennial gaining creek into a box culvert
- simulate mitigation efforts (groundwater relief drains and storm-water attenuation/retention ponds) designed to alleviate water table rise and manage surface water flow predicted by the model
- assist with design of the groundwater monitoring network

Water table rise (mounding) and potential ground surface expressions of groundwater associated with placement of the S/S monolith were of particular concern at this site for the following reasons:

- The water table at the site is 1–10 feet bgs.
- Portions of the monolith fully penetrate the shallow aquifer, preventing normal flow.
- A portion of the stream that drains the area would be diverted into a culvert, and the aquifer below the stream would be stabilized, effectively preventing groundwater discharge along a roughly 500-foot section of the stream.
- The monolith is relatively large, extending across 4–5 acres and to depths of up to 30 feet bgs to a lower clay confining layer.
- The location for the monolith is in an area that provided significant storm-water drainage for the surrounding area. This drainage included what was known as the unnamed tributary, which continuously drained from areas south of the site to the creek.

C.1.4 Modeling

Groundwater flow was modeled in three dimensions using MODFLOW. MODFLOW uses a finite-difference approximation to solve a three-dimensional head distribution in a transient, multilayer, heterogeneous, anisotropic, variable-gradient, variable-thickness, confined or unconfined flow system—given user-supplied inputs of hydraulic conductivity, formation/layer thickness, recharge, wells, and boundary conditions. The program also calculates a global water balance, including contributions from wells, rivers, and drains, and any other boundary-type packages used in the simulation. Three steady-state groundwater models were created to achieve the model objectives. The models were created prior to construction of the monolith and updated with design changes during construction:

- *calibration model*—Created and calibrated to simulate observed groundwater and surface-water conditions prior to initiation of remedial activities.
- *design model*—Created from the calibration model to simulate and predict changes in groundwater flow resulting from designed construction of the S/S monolith, associated storm-water detention ponds, and modifications to the creek. This model was used to evaluate the potential for water table rise (mounding) associated with construction activities.
- *design model with drains*—The design model was modified to include groundwater relief drains to address potential groundwater mounding and support the groundwater screening program. This model was updated during remedial construction to incorporate changes from the original design plans.

The modeled area was approximately 14,500 × 17,000 feet and bounded to the north by a lake. The east, west, and south boundaries of the model approximate the outer edge of the watershed in which the site is located (Figure C-2). The distal portions of the watershed boundary were left out of the model grid to improve computing efficiency.

The upgradient and lateral edges of the model, representing the watershed boundaries, were no-flow (Neumann) boundaries. The lower boundary (top of clay confining layer) was also a no-flow (Neumann) boundary. The lake at the downgradient edge of the model was a constant-head (Dirichlet) boundary placed in the bottom layer of the model. Streams were represented using MODFLOW river (mixed) boundaries in the top layer of the model. The upper boundary was a time-dependent specified flux (Neumann) boundary, with specified flux rates equal to the recharge rate. Features that potentially remove water from the model, such as storm-water management ponds or groundwater relief drains, were simulated as MODFLOW drains (mixed).

For the calibration model, a sampling event was scheduled when groundwater elevations were relatively high. Water levels were collected from site wells, and river elevations were surveyed at this time so that the model would be calibrated to high-water levels and result in higher potential mounding near the monolith, thus making the model conservative with respect to predicted mounding. The calibrated steady-state model was then modified to create the design models.

C.1.5 Special Considerations for Model Construction and Input Values

Because surface expressions of groundwater were of concern, extra attention was paid to ground surface elevation and aquifer thickness in the model. The grid cells of the model near the monolith were spaced tightly (12.5 feet apart), and the top layer of the model was created by gridding and importing existing ground surface elevation data from construction plans. A surface was created in CAD (computer-aided design) based on surveyed ground surface elevations (1-foot contour interval). That surface was gridded into 12-foot cells similar to the model cells and imported to the model grid as XYZ points. Using this method, ground surface elevations near the monolith very closely approximated actual elevations. The same method was used to simulate the final construction ground surface elevations from the design plans (e.g., storm-water ponds, drainage swales, and river channel reconstruction). Figure C-2 illustrates the very tight grid spacing near the site.

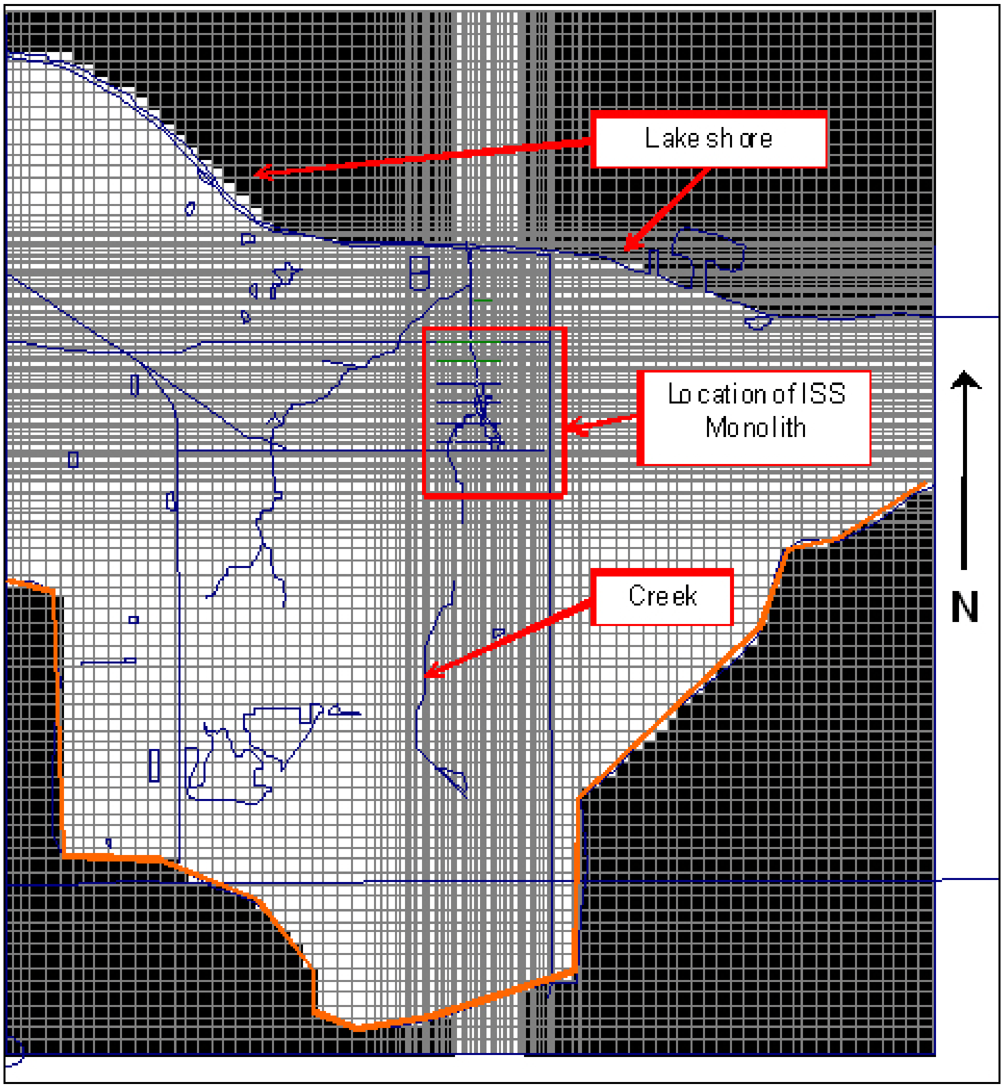

Figure C-2. Model grid. The red box indicates the location of the S/S monolith. The orange line indicates the watershed boundary. Blue lines are base map features, such as roads, streams, large ponds, and the footprint of the monolith.

The bottom of the model was created in a similar fashion to the top of layer 1. The top of clay elevation (top of confining layer) data collected from the site were surfaced in CAD, gridded, and imported into the model. Once the top and bottom of the aquifer were defined, the model was further subdivided into a three-layer model to accommodate monolith placement and spatial variations in lithology.

The creek running through the site drains the eastern half of the watershed and therefore strongly influences groundwater flow direction. Site visits also indicated that there were several pools and elevation drops giving the creek a step-like appearance as is passed though the site. To further refine groundwater flow in the model, the creek was surveyed at the same time the groundwater elevations were collected for calibration. Coordinates, top-of-water, and riverbed elevations were collected from the upper and lower ends of the creek and from pools and drops (steps).

The location of the proposed S/S monolith was added to the model by importing CAD design drawings. The hydraulic conductivity value of the monolith was originally based on construction specifications and results of bench-scale testing. The design specification for the hydraulic conductivity was 1×10^{-6} cm/s. In the design model with drains, the conductivity values were updated with QA/QC data collected during placement of the monolith. Actual hydraulic conductivities were lower than design specification. The sensitivity of this value was tested in this model by increasing and decreasing the value by a factor of 10. At this site, the changes in permeability did not affect the predicted result (i.e., it did not significantly increase the extent or magnitude of groundwater mounding). The initial conductivity value of 10^{-6} cm/s is three orders of magnitude lower than that of the surrounding sands and four orders of magnitude lower than that of the shell.

Site-specific data were used whenever possible for initial input values (such as hydraulic conductivity values derived from aquifer tests). Other initial input values were based first on regional publications or referenced from other publications if no other information was available.

C.1.6 Calibration Model Results

The calibration model (simulated flow prior to monolith construction) achieved the following targets: modeled heads were within 1 foot of observed heads near the monolith; cumulative mass balance of the model (0.00%) was less than the goal of 1% discrepancy between inputs and outputs; observed versus computed targets exhibited a linear 1:1 trend; and the graph of observed head versus modeled residuals exhibited a high degree of scatter, which indicated that the residuals were evenly distributed across the range of observed heads.

C.1.7 Design Model Results

The design model (predicted flow after placement of the monolith) suggested that groundwater mounding was likely to occur along the upgradient and side-gradient sides of the monolith and could result in surface expressions of groundwater upgradient of the site; particularly east of the site where groundwater was observed approximately 1 foot bgs. The model predicted a maximum head increase of approximately 7 feet along the eastern side-gradient edge of the monolith, as indicated in the Figure C-3.

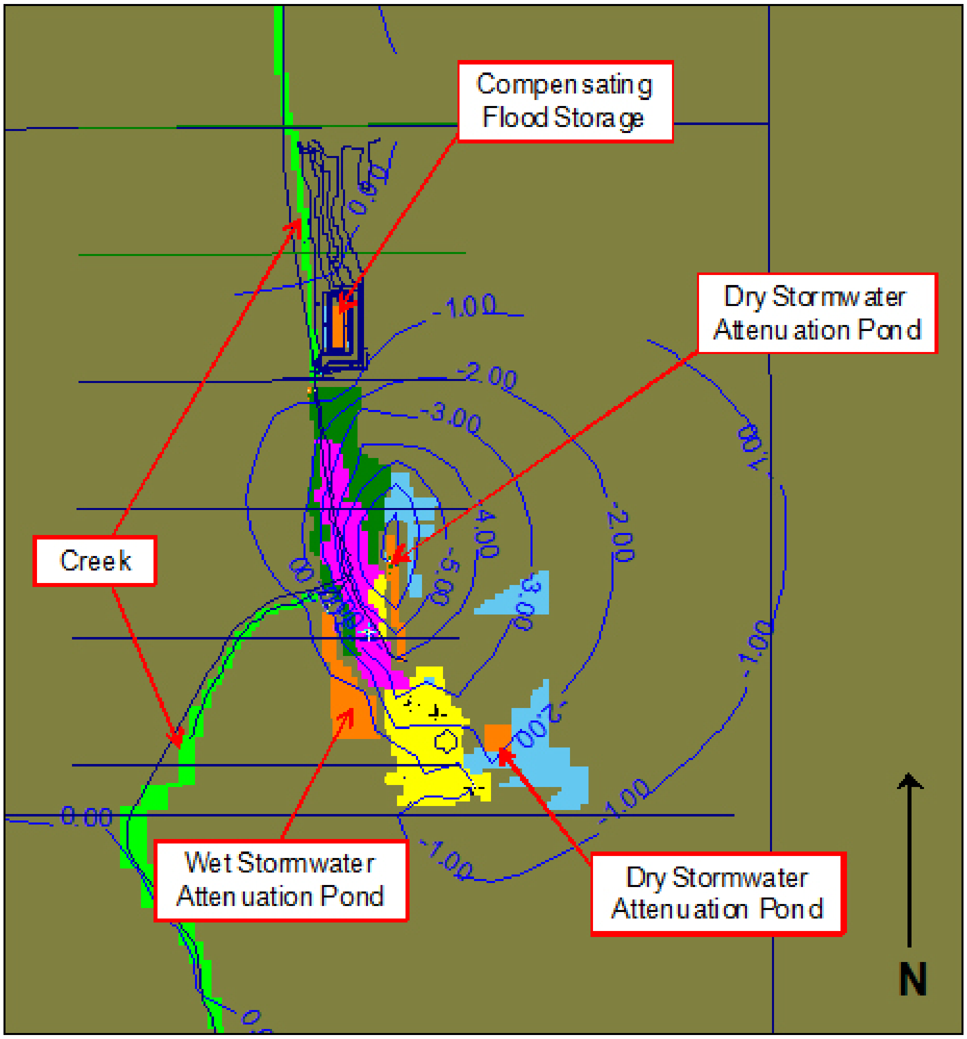

Figure C-3. Design model prediction for flooding along the eastern and upgradient portion of the monolith after installation of the monolith. Yellow, pink, and green cells represent construction phases of the monolith. Orange cells are storm-water ponds represented by drain boundary cells. Blue contours represent changes in groundwater elevation in feet relative to the original (calibration) model. Negative values indicate increasing head. Light blue cells indicate "flooded" areas where groundwater intersects land surface.

C.1.8 Simulation of Groundwater Relief Drains (Design Model with Drains)

The design model with drains (predicted flow with groundwater relief drains) was developed to alleviate predicted groundwater mounding. Two groundwater relief drains were placed in the model just upgradient of the eastern side-gradient edge of monolith to intercept groundwater and route it to a box culvert, thus reducing the risk of groundwater surface expressions. The box culvert was planned to contain the stream as it passed over the monolith. Each drain was simulated to tie into the storm-water drainage system associated with the box culvert as part of the final construction plan. To maximize groundwater relief, the drains were simulated by starting with the elevation from the tie-in location (lowest possible drain elevation). The drains were modeled as 3 × 3 foot trenches filled with gravel (1 cm/s hydraulic conductivity) that grade 0.5% toward the tie-in. Figure C-4 indicates the effect of the drains on the mounding.

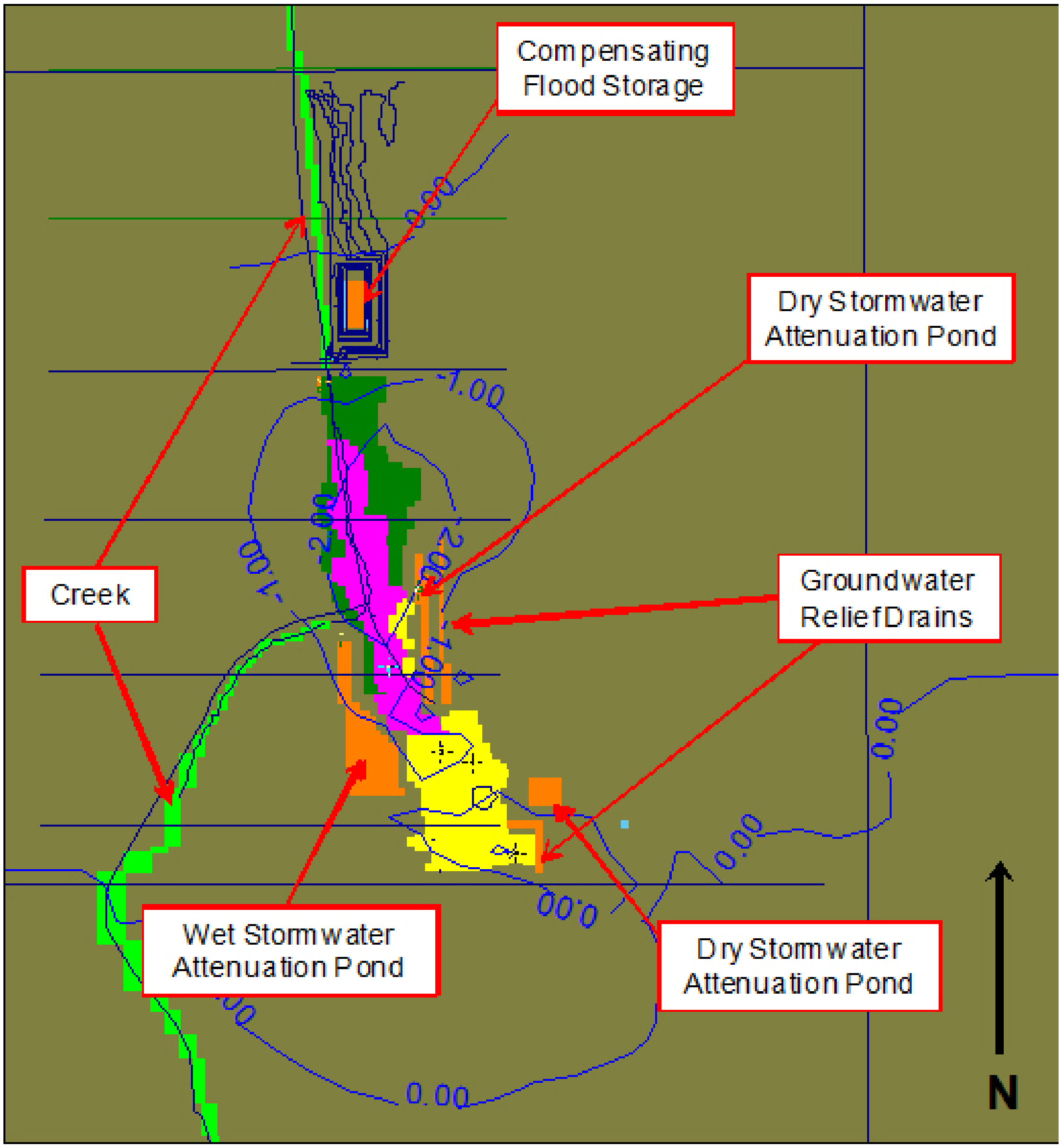

Figure C-4. Design model with drains results. Yellow, pink, and green cells represent construction phases of the monolith. Orange cells represent storm-water ponds and new groundwater relief drains represented by drain boundary cells. Blue contours represent changes in groundwater elevation in feet relative to the preconstruction (calibration) model. Negative values indicate increasing head. Light blue cells indicate "flooded" areas where groundwater intersects land surface.

Note the significant reduction in the blue cells compared to the model conditions provided in Figure C-3. The groundwater relief drains reduced the maximum increase in head from 7 feet to 2 feet, and modeled groundwater elevations remained below ground surface (eliminated surface expressions of groundwater). The model also indicated that the drains would remove water at a combined rate of approximately 10 gallons per minute (gpm) (i.e., the drains would contribute a constant flux of 10 gpm to the storm-water drains and ultimately the box culvert). This additional flux of groundwater did not require alteration of the existing storm-water design plans. As a result of this modeling effort, the groundwater relief drains were incorporated into the design and construction plans for remedial construction.

This model was updated during construction of the monolith to incorporate modifications from the original design plans and to include conductivity data from QC samples of the monolith. The model indicated these modifications would not significantly impact groundwater flow or mounding; therefore, the design of the groundwater relief drains did not require alteration. Figure C-4 is a screen capture from the last update of the design model with drains.

C.1.9 Application toward Placement of Monitoring Well Network

Prediction of post-remedial groundwater elevation contours and particle tracking were used to support development of a new monitoring well network. Projected groundwater flow contours indicated that groundwater would continue to flow toward the former stream bed after placement of the monolith and diversion into the box culvert (Figure C-5). The groundwater flow pathways and, by extension, potential post-construction plume migration pathways were generated using MODPATH to generate particle traces in the upper and lower portions of the aquifer. Particle tracking results (Figure C-6) indicated that particles from upgradient of the monolith would travel toward the monolith and either become captured by the groundwater relief drains or travel along the edge of the monolith until they reached the stream as it exited the box culvert downstream of the monolith. Particles that were not captured by the drains would move very closely along the monolith and be captured within 200 feet of the downstream edge of the monolith. This information was used to design a groundwater screening program that will be used to establish the number and locations for the final monitoring well network.

Based on the particle tracking and the projected groundwater contours, a monitoring well network with side-gradient wells located in close proximity along the length of the monolith combined with wells located directly downgradient of the monolith was considered for post-remedial groundwater monitoring. The groundwater screening program that was developed to evaluate the proposed monitoring well network targeted areas along the perimeter and directly downgradient of the monolith. At this writing, the screening program has not been completed. The data generated from the screening program will be used to calibrate a new version of the design model with drains to verify the conditions predicted by the flow model and refine recommendations for the monitoring well network.

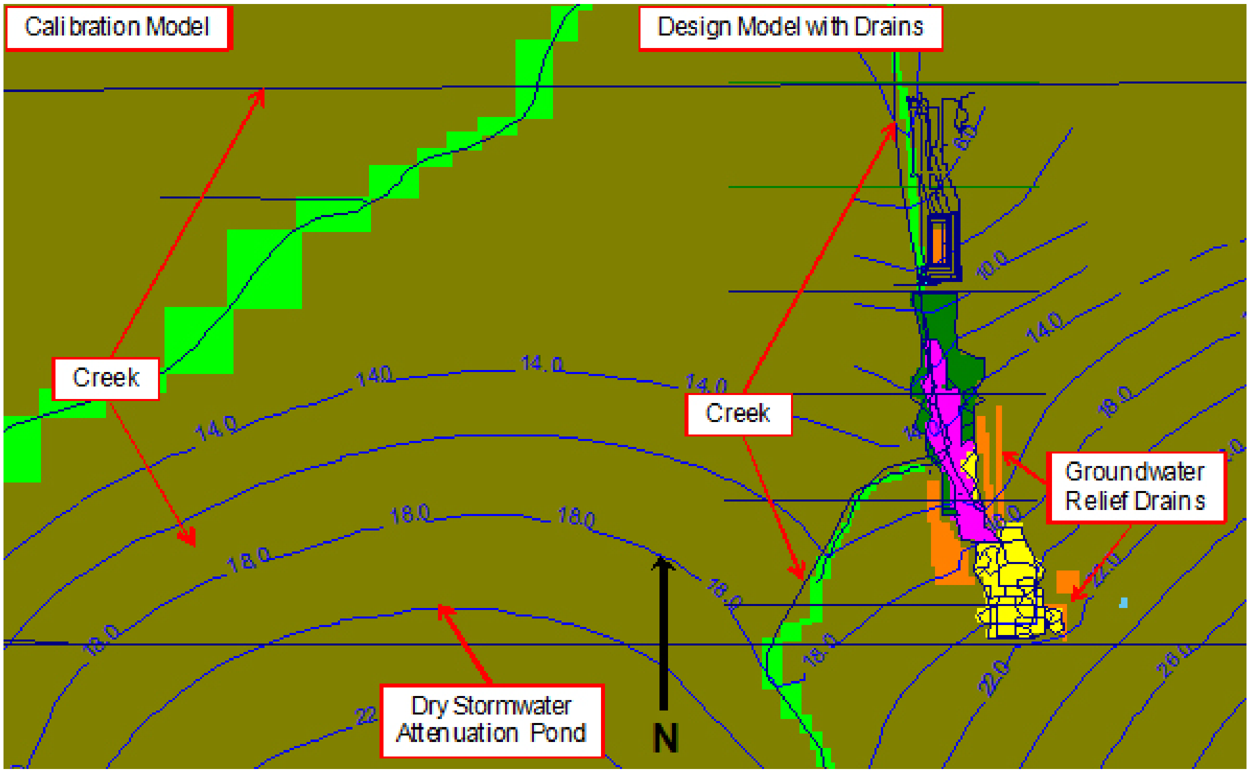

Figure C-5. Calibrated and predicted groundwater flow contours. This figure shows calibrated flow contours (on the left) and predicted groundwater elevation contours (on the right) after construction of the monolith with drains in place to mitigate increases in groundwater elevation. The green cells represent the creek, orange cells represent the storm-water attenuation ponds or relief drains, and the blue cells indicate places where the groundwater elevation could exceed land surface. Note that predicted flow contours do not deviate significantly from those of the calibrated model.

C.1.9 Recommendations and Considerations for Future S/S Projects

The groundwater modeling results discussed in the case study provided important data that were used to support the S/S design efforts for post-remedial groundwater/surface-water management. Collection of sufficient groundwater elevation and quality data should be conducted early in the design process to develop a viable CSM to guide the design efforts and support decision making for monitoring long-term performance of the S/S monolith. Plans should be included during and following the S/S operations to monitor changes in groundwater elevations and flow direction so the groundwater model can be periodically updated and initial design assumptions can be confirmed and/or revised, appropriate.

C.1.10 Case Study #1 Reference

Hennings, B. G., C. A. Robb, and R. E. Wittenberg. 2011. *Draft In Situ Stabilization/ Solidification Design Considerations and Applications for Groundwater Modeling.* Natural Resource Technology, Technical Memorandum.

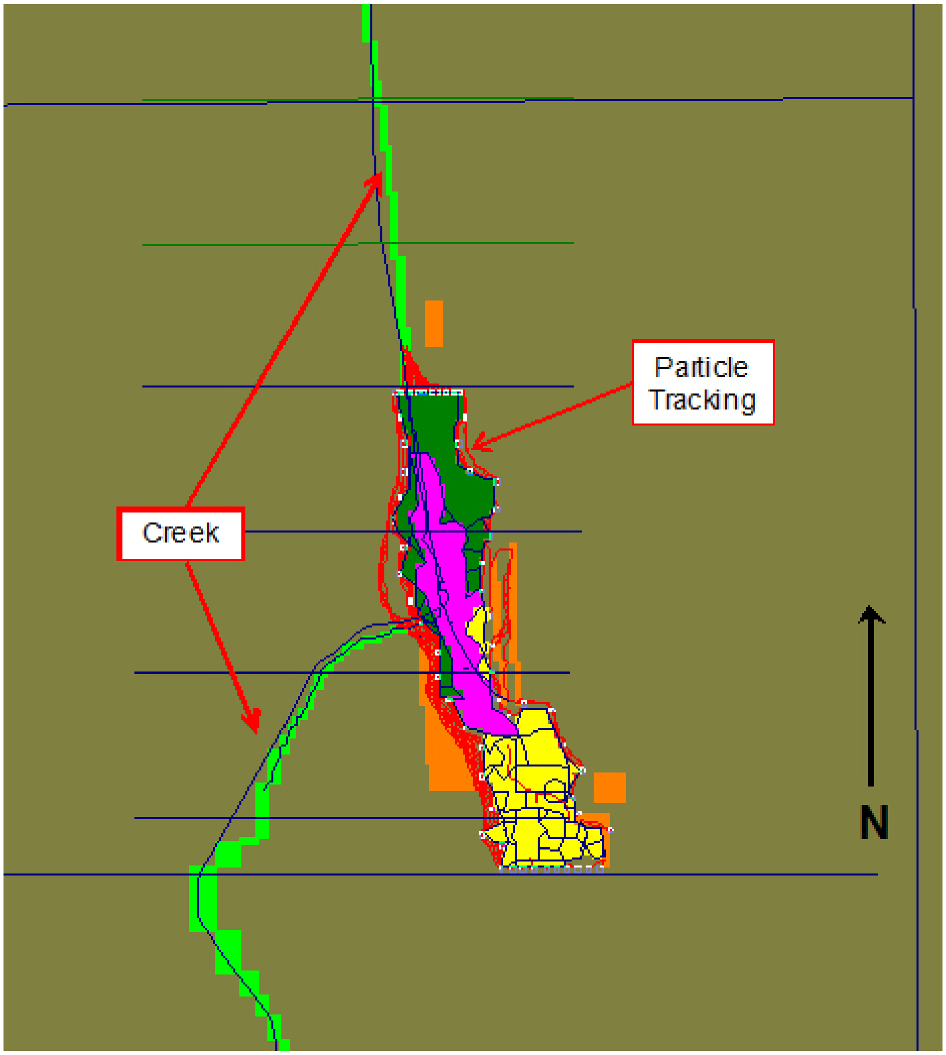

Figure C-6. Model results for particle tracking. Yellow, pink, and green cells represent the monolith. Light green cells represent the creek. Particle tracking is indicated in red. Orange cells represent storm-water attenuation ponds or the groundwater relief drains.

C.2 CASE STUDY #2—PEAK OIL/BAY DRUM SUPERFUND SITE

The Peak Oil/Bay Drum EPA Superfund site, located near Tampa, Florida, implemented S/S as part of the site remedy to treat contaminated soil, sludge, and ash. This site case study is presented as an example of groundwater modeling used to determine acceptable concentrations of site contaminants that could leach from the S/S-treated material into groundwater and still meet cleanup goals at the site POC. This concentration was then used as a performance criterion to be met during treatment.

C.2.1 Background

The site consists of two adjacent properties that represent separate historical operations, Peak Oil Company and Bay Drum Company. The separate properties were ranked by EPA and listed jointly on the NPL in 1986 as the Peak Oil/Bay Drum Superfund Site.[1] The site was divided into four operable units (OUs): OU 1, the source areas at the Peak Oil property; OU 2, groundwater beneath both properties; OU 3, the source areas at the Bay Drum property; and OU 4, wetland areas adjacent to both properties. This case study focuses on the groundwater modeling conducted to establish acceptable concentrations for contaminants in leachate from the treated material entering groundwater.

A remedial investigation and feasibility study was conducted for the site, and remedies were selected in 1993 for each of the OUs and documented in separate records of decision (RODs). The RODS for OUs 1–3 and the first EPA five-year review (see references for this case study in Section C.2.7, beginning on p. C-19) provided the site information that is summarized in the following sections. Additional work was performed during design of the remedies for OUs 1 and 3 that led to a modification to the OU 1 source (Explanation of Significant Difference) and OU 2 groundwater remedy, documented in an amendment to the 1993 ROD (EPA 2005).

The site terrain is relatively flat, ~25–45 feet above mean sea level. Land use in the area of the site is industrial or undeveloped with residences (at the time of the 1993 RODs) located at about one-third mile distant or greater.

Materials beneath the site surface include two unconsolidated sedimentary units overlying bedrock. The uppermost unconsolidated unit is the surficial sand unit, consisting of poorly graded fine sand with varying amounts of silt and gravel and is up to ~40 feet thick. Groundwater is encountered at 2–4 feet bgs. Underlying the surficial sand unit is a low-permeability unit, a component of the upper Hawthorne Group that consists of clay and clayey sand and ranges 15–40 feet thick. At the site it contains intermittent clay lenses. The Tampa Limestone and underlying Suwannee Limestone Formations compose the bedrock beneath the unconsolidated sedimentary units.

Two groundwater aquifers are identified for the site: the surficial aquifer and the deeper Upper Floridian Aquifer. The surficial aquifer is the saturated portion of the surficial sand unit; water levels and groundwater flow directions vary seasonally in response to infiltration of rainfall. The surficial aquifer does not have a current use but is hydraulically connected to area wetlands and streams. The Upper Floridian Aquifer underlies the low-permeability sedimentary unit and is associated with the Tampa Limestone and underlying Suwannee Limestone formations. Regional groundwater flow in the Upper Floridian Aquifer is to the southwest, but groundwater flow in the area of the site is to the northwest, likely in response to influence of the nearby Tampa Bypass Canal. The Upper Floridian Aquifer is also the regional municipal water supply source.

C.2.2 Site Use and Detected Contaminants

Peak Oil Company conducted an oil re-refining operation at the property (OU 1) for used oils and lubrication fluids using an acid/clay purification and filtration process. Low-pH sludge and oil-saturated clay waste containing lead were generated and stored on site in unlined lagoons. A

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[1] Additional information about this site can be found at www.epa.gov/region4/waste.npl.index.htm#FL.

1986 removal action at the Peak Oil property consisted of removal of 4,000 yd^3 of acidic oily sludge from one of the three lagoons using a mobile incinerator and generating residual ash that remained on site. The remaining two lagoons had been filled in.

Contaminants detected in Peak Oil property soil and lagoon sludge include VOCs, primarily toluene, ethylbenzene, and xylenes; semivolatile organic chemicals (SVOCs), primarily PAHs; PCBs; inorganics, notably barium, lead, chromium, and zinc; and a thick oily residue within the surficial sand unit associated with the areas of the unlined lagoons. Lead was detected in former lagoon areas at up to 2,950 mg/kg and in the residual ash at an average 3,525 mg/kg. Other inorganics detected in former lagoon areas above background concentrations included arsenic, beryllium, cadmium, cobalt, copper, manganese, mercury, and cyanide.

Bay Drum Company conducted a drum-reconditioning operation at the property (OU 3), which included a reconditioning area in a small portion of the site, with the remainder of the property used for drum storage. In the last two years of activity at the property, waste roofing shingles were stored on the property in a layer up to 19 feet thick. A 1989 removal action at the Bay Drum property removed about 70,000 yd^3 of roofing shingles, leaving 27,000 yd^3 on site due to high water table conditions, and later that year removed for off-site disposal buried drums and 4,000 yd^3 of soil and sludge contaminated with VOCs, SVOCs, pesticides, PCBs, and metals.

Contaminants detected in Bay Drum property surface and subsurface soil included VOCs, SVOCs or PAHs, PCBs, pesticides (mainly dichlorodiphenyldichloroethylene, chlordane, and ethion), and inorganics (mainly arsenic, chromium, lead, and zinc). Lead was detected in subsurface soil at up to 2,500 mg/kg. Other inorganics detected above background concentrations but not above cleanup levels included barium, chromium, and zinc.

C.2.3 Site Remedial Action Objectives

COCs for soil at the Peak Oil property include beryllium, benzo(a)pyrene, dibenzo(a,h)anthracene, lead, and PCBs for soil and lead for the residual ash. Site concentrations of COCs did not exceed remedial action objectives for the 10^{-4} to 10^{-6} risk range. Lead was detected at concentrations above the groundwater protection soil concentration of 284 mg/kg and was therefore a primary COC for leaching to groundwater.

COCs for soil at the Bay Drum property include arsenic, lead, chlordane, ethion, PCBs, and PAHs. Cleanup levels for this property were set at 10^{-4} for soil exposure for an industrial worker; concentrations for COCs did not exceed this risk criterion. Groundwater protection criteria were calculated for five COCs, including ethylbenzene, toluene, naphthalene, and lead, with only lead exceeding the groundwater protection soil concentration of 284 mg/kg. Therefore, lead was also the primary COC for groundwater.

RAOs were established for the Peak Oil/Bay Drum Site to be protective of human health and groundwater and to meet applicable or relevant and appropriate requirements. RAOs (action levels) were 521 mg/kg for lead and 180 mg/kg for chlordane in soil, with any soil exceeding these levels to be treated using S/S soil with concentrations of chlordane 9.6–180 mg/kg to be placed without treatment beneath the site cap.

C.2.4 Overview of Remedial Action

Remedial actions for both the Peak Oil and Bay Drum properties included use of S/S treatment for contaminated soil, sludge, sediment, and a residual ash pile. The main elements of source control remedial measures at both the Peak Oil and Bay Drum properties included installation of an attapulgite clay slurry wall around the contaminated soil area, excavation of soil and sludge contaminated with lead above concentrations of 521 mg/kg, S/S treatment for excavated soil/ sludge and residual ash using a pozzolanic portland cement mix, placement of a multimedia cap over the S/S-treated material, enhanced in situ bioremediation and localized air sparging for the surficial aquifer for the Peak Oil property, enhanced bioremediation of groundwater for the Bay Drum property, groundwater monitoring, ICs, and five-year reviews.

Table C-1 summarizes performance parameters and criteria developed for the site S/S treatment.

Table C-1. Performance parameters and criteria for S/S treatment

Action levels (mg/kg)	Lead		>521
	Aroclor 1260		>25
	Bis(2-ethylhexyl)phthalate		>0.58
S/S mix composition[a]	6% Portland cement, 1%–2% super triple phosphate		
S/S specifications	*Average*	*Allowance*	*Method*
Strength (USC psi)	>50	None	ASTM D 1633
Permeability (cm/s)	$<1 \times 10^{-6}$	1×10^{-5}	ASTM D 5084
Leaching lead (µg/L)	<282	<500	SPLP Method 1312

[a] C. Wilk, personal communication with S. Birdwell, RECON, January 19, 2011.

C.2.5 Modeling of Impact to Groundwater

EPA conducted groundwater modeling for the Peak Oil/Bay Drum Site to determine the maximum contaminant load and concentrations of contaminant that could leach from the S/S-treated material and still meet groundwater protection standards of 15 µg/L for lead and 2 µ/L for chlordane at the POCs. The POCs were the downgradient property boundaries, 15–30 feet downgradient for the Bay Drum property and 70–120 feet downgradient for the Peak Oil property. The modeling was conducted prior to treatment of contaminated material to support design of the S/S formulation.

EPA used the HELP3 (Hydrologic Evaluation of Landfill Performance) model to calculate the volume of rainwater infiltration through the site cap and proposed S/S monolith entering groundwater and horizontal groundwater flow through the low-permeability monolith in the saturated zone and compared to the volume of groundwater flow between the monolith and the POC to calculate a site-specific dilution factor. (The HELP3 model is typically used to analyze water balances and assist in design of landfill profiles [Schroeder et al. 1994].) EPA conducted modeling for the site in late 1999 and early 2000. Figure C-7 depicts the CSM.

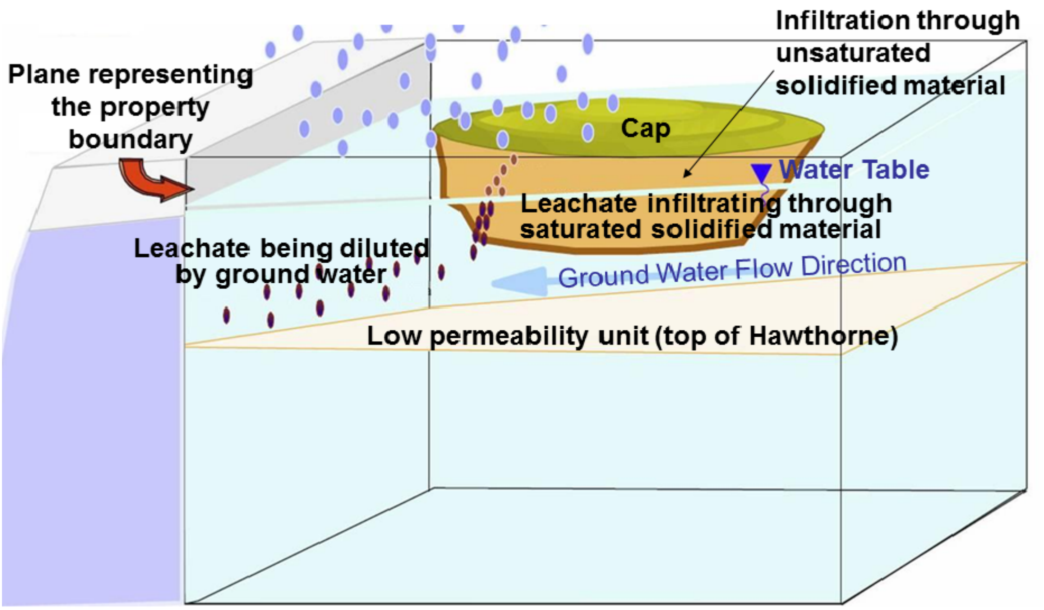


Figure C-7. Schematic of conceptual model for development of an SPLP performance standard for the solidified mass at Peak Oil and Bay Drum.

Several assumptions were made regarding infiltration and configuration of the cap and monolith forming the basis of the modeling exercise:

- Rainwater infiltrates through the site cap, moves through the S/S-treated material producing a leachate that reaches groundwater in the saturated zone along with a small volume of leachate produced by groundwater moving through the proposed low-permeability monolith, is diluted as groundwater flows beneath the site, and moves downgradient to the property boundary.
- The S/S-treated material is located within the saturated zone, and the groundwater protection standards for lead and chlordane are achieved at the property boundary.
- The multilayer cap consists of 6 inches of topsoil over 6 inches of compacted backfill over a geosynthetic clay liner with a vertical permeability of less than 10^{-7}, grass cover is on the topsoil, the cap slope is 2.
- No liner or leachate system is installed.
- The cap includes a lateral drainage layer, the landfill cover consists of a bentonite mat (geosynthetic clay liner), and chlordane is eliminated as a COC for the Peak Oil property since it was not detected in soil.
- The treated material will be located within the saturated zone.

Input values for model parameters were developed using site- and area-specific values obtained from standard climate and water resource sources, using model functions to calculate some derivative values (such as solar radiation) based on actual data, soil type characteristics (such as porosity), and design specifications for the cap and proposed monolith. The dimensional parameters for the surficial aquifer were derived based on site groundwater monitoring data and are shown on the maps of Figures C-8 and C-9. Figure C-8 shows groundwater flow directions, cap area, and groundwater flow cross-sectional lengths. Figure C-9 shows the surface soil and cap areas used to calculate recharge areas.

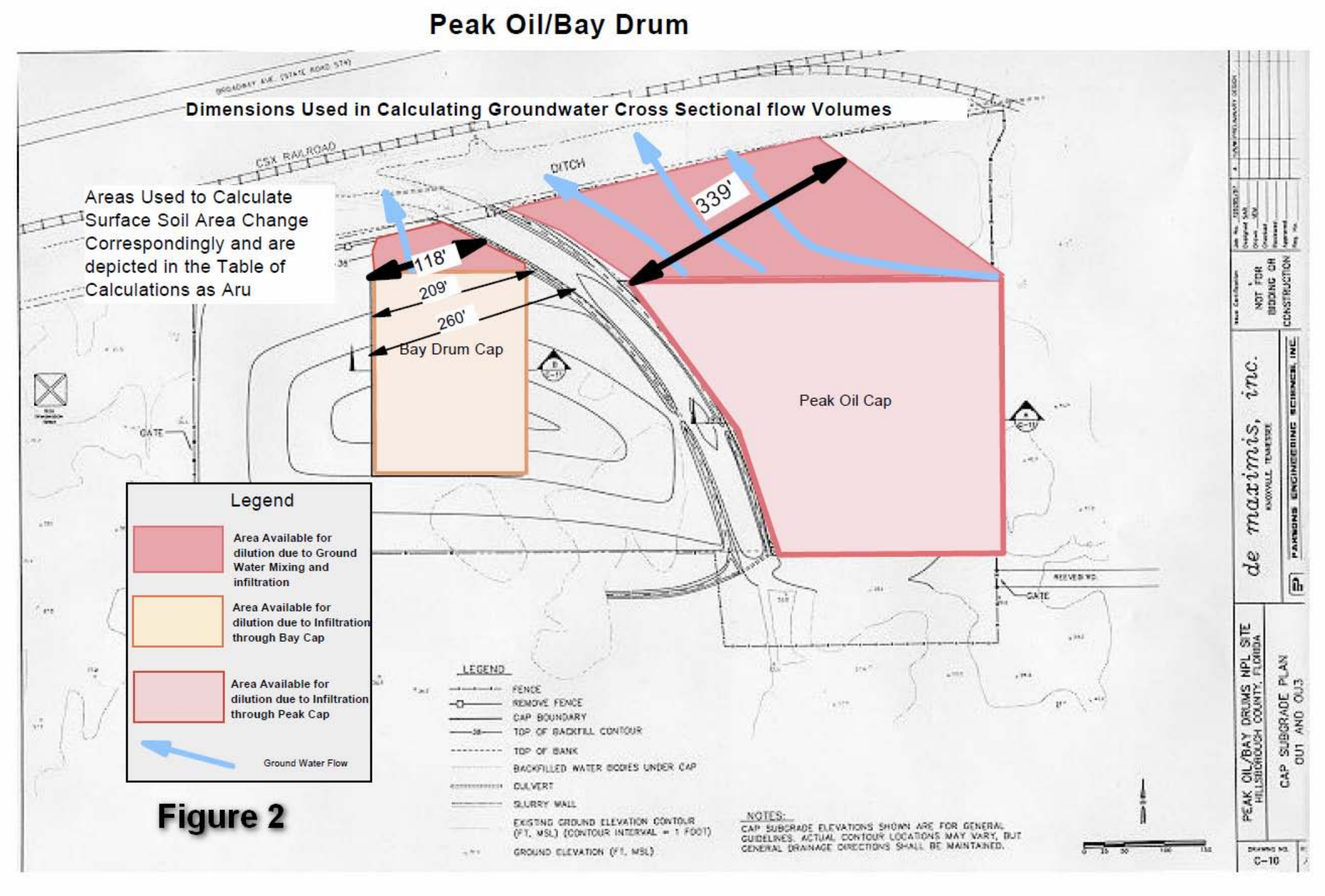
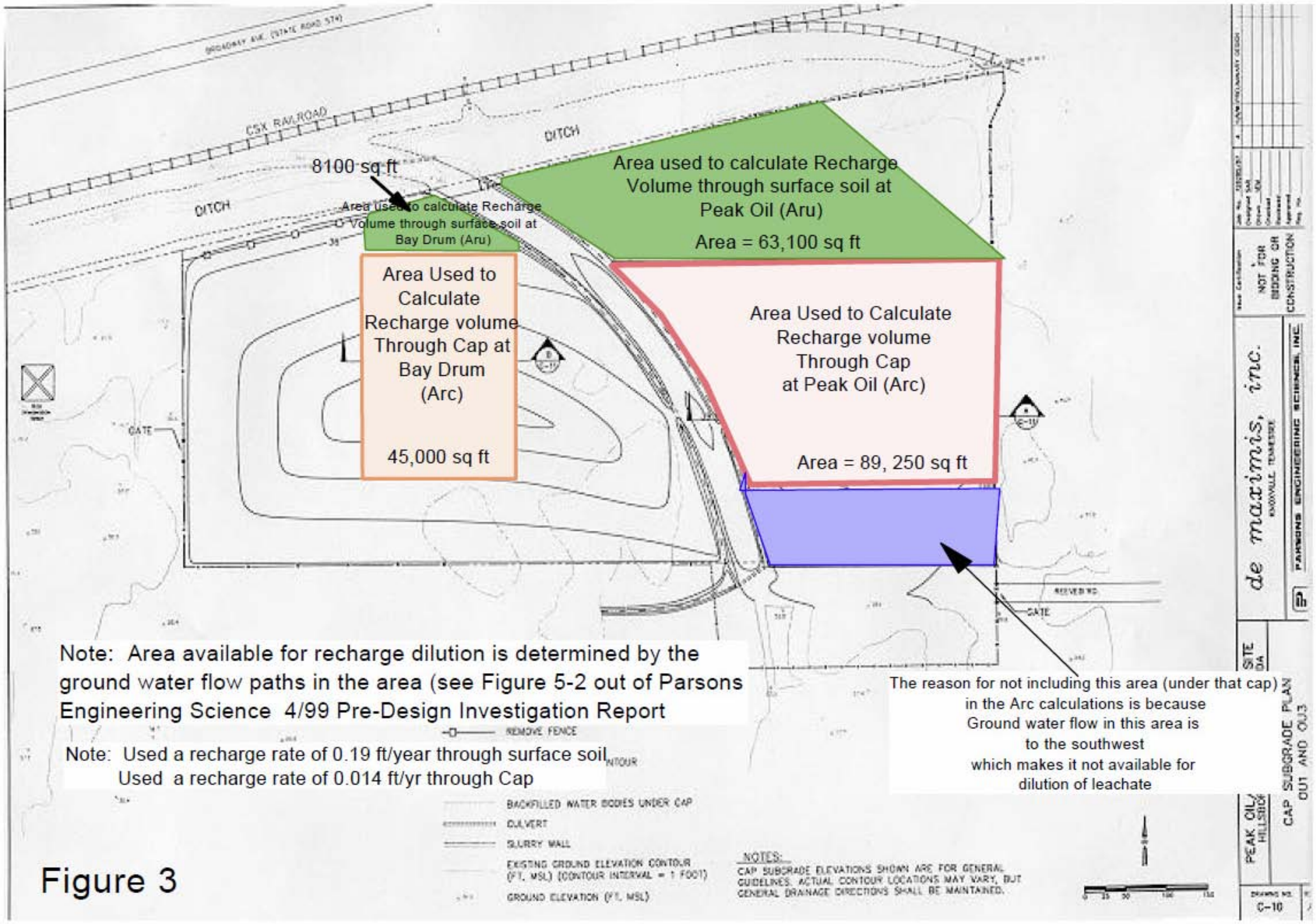


Figure C-8. Groundwater flow directions, cap area, and groundwater flow cross-sectional lengths.



Note: Area available for recharge dilution is determined by the ground water flow paths in the area (see Figure 5-2 out of Parsons Engineering Science 4/99 Pre-Design Investigation Report

Note: Used a recharge rate of 0.19 ft/year through surface soil
Used a recharge rate of 0.014 ft/yr through Cap

The reason for not including this area (under that cap) in the Arc calculations is because Ground water flow in this area is to the southwest which makes it not available for dilution of leachate

NOTES:
CAP SUBGRADE ELEVATIONS SHOWN ARE FOR GENERAL GUIDELINES. ACTUAL CONTOUR LOCATIONS MAY VARY, BUT GENERAL DRAINAGE DIRECTIONS SHALL BE MAINTAINED.

Figure C-9. Area designations for computation of dilution to leachate coming from the solidified material.

C.2.6 Modeling Results and Conclusions

The results of the HELP3 modeling provided a site dilution factor which was used to calculate allowable leachate concentrations for lead and chlordane for the S/S-treated material. Chlordane was eliminated as a COC for Peak Oil based on its low rate of detection in soil. Table C-2 summarizes the modeling results.

Table C-2. Allowable leachate concentrations for lead and chlordane in S/S-treated material

Chemical	Groundwater protection standard (µg/L)	Allowable leachate concentration (µg/L)	
		Peak Oil	Bay Drum
Lead	15	282	179
Chlordane	2	NA	24

Groundwater modeling results for the site (allowable leachate concentrations) were used as performance criteria for treatability studies to evaluate and develop potential S/S design formulations that would not exceed the calculated maximum leachate concentration. The treatability study identified the most effective formula for the S/S treatment that would be able to meet remediation goals at the compliance point. For example, concentrations of lead in leachate below the performance criteria (or allowable leachate concentration) of 282 µg/L would be expected to meet the remediation goal of 15 µg/L at the POC.

An initial five-year review of the completed site remedy was conducted in 2005 and a second in 2010. The 2010 review (www.epa.gov/superfund/sites/fiveyear/f2010040003559.pdf) indicates that the S/S treatment is adequately containing contaminated soil and materials and is performing as designed. Groundwater monitoring at the site confirms that there are no exceedances of site COCs in groundwater.

The approach in this case study is reflected in the S/S treatment design process discussed in Sections 4–6 of this guidance document. S/S treatment design begins with identified site remediation goals that are represented by performance criteria. The design of the actual S/S formulation is accomplished through treatability testing to identify effective formulations that can achieve the performance criteria.

C.2.7 Case Study #2 References

EPA. 1993a. *Superfund Record of Decision: Peak Oil Co./Bay Drum Co. Operable Unit 1*. EPA/ROD/R04-93/146.

EPA. 1993b. *Superfund Record of Decision: Peak Oil Co./Bay Drum Co. Operable Unit 3*. EPA/ROD/R04-93/148.

EPA. 2000. *Recalculation of SPLP Levels for Peak/Bay*. EPA Memorandum, March 28.

EPA. 2005. *Final Amendment to the 1993 Record of Decision (ROD) for Operable Unit 2, Peak Oil/Bay Drum Site, Tampa, Hillsborough County, Florida*. Region 4, Atlanta, Ga.

EPA. 2009. *Potential for Future Use, Tampa Former Industrial Property*. EPA Reuse Fact Sheet.

EPA. 2010. *Second Five-Year Review Report for Peak Oil Company/Bay Drum Company*. EPA Region 4.

Schroeder, P. R., C. M. Lloyd, P. A. Zappi, and N. M. Aziz. 1994. *The Hydrologic Evaluation of Landfill Performance (HELP) Model*. EPA/600/R-94/168a. U.S. Army Corps of Engineers Waterways Experiment Station and Clemson University Department of Civil Engineering, under contract to U.S. EPA Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati.

C.3 GRADED MODELING APPROACH

Modeling calculations typically consider three phases in the life cycle of an S/S remedy to enable comparison of the relative efficacy of alternative remedies and, on occasion, the likely times required to achieve defined RAOs: preremediation, to describe current site conditions; mid-remediation, to estimate expected conditions during active remediation; and post-remediation, to describe expected conditions after active remediation is completed.

A common modeling objective at sites implementing S/S remedies is to estimate the possible impact to an underlying aquifer of various S/S remediation strategies, typically in terms of possible impacts on groundwater conditions immediately below a source zone and at some distance downgradient of the impacted area where one or more receptors may exist. A variety of calculation techniques can be used to evaluate the efficacy of an identified remedy or to compare the relative efficacy of different remedies, with these design considerations in mind.

Modeling calculations can become complex, involving sophisticated three-dimensional (3D) numerical models of flow and transport that require a large computational burden to execute. While sophisticated methods provide valuable insight, complexity is not always warranted, particularly when comparing the relative benefits of different approaches or when conducting screening-level analyses aimed at ranking sites or remedial technologies. For this reason, methods and codes that can be used to make defensible screening-level calculations using site-specific parameters prior to undertaking rigorous and sophisticated numerical analyses can be beneficial. The existence of different methods that span a wide range of sophistication and complexity naturally lends itself to the development and application of a graded approach to undertaking calculations in support of remedy design and evaluation.

The following sections describe some important considerations when undertaking modeling analyses of S/S remedies and outline one example of a graded approach that could be considered at a many sites for which S/S remedies are under consideration or already implemented. The specific elements of the graded approach described are not always suitable or applicable to a particular site; however, the concepts and terms have broad-ranging applicability. The demonstrative examples that are presented focus on impacts to groundwater although the concepts are also applicable to evaluating impacts to other media, such as soil and air.

C.3.1 Definitions

The following terms are used throughout the discussion of remedy design calculations and the graded approach:

- *method*—One or more mass-balance or constitutive relationships, described using one or a sequence of equation(s) that enable the method to be quantified. Examples of methods range from a simple three-phase partitioning equation to finite-difference numerical models that require computers to evaluate.
- *code*—An executable program or a spreadsheet that implements a method or a sequence of methods and produces outputs. An example of a code is the program VS2DT, which simulates flow and transport in variably saturated media in two dimensions.
- *model*—A code that implements one or more methods and that, together with the assignment of parameter values, can be used to make site-specific calculations.
- *parameter*—A value that is fundamental to a method and that must be assigned as an input to a model implemented via a specific code. An example of a parameter is the distribution coefficient (K_d) that describes the relative affinity of a contaminant to partition from the dissolved phase on to adjacent soils.

The graded modeling approach presented here includes the following:

- a description of methods that can be used to evaluate the likely fate of contaminants in the subsurface
- some example codes that implement these methods
- the role that some parameters play in determining when to progress from simpler to more sophisticated calculations

It is not the intent here to be prescriptive regarding the use of codes that implement specific methods. Although generic implementations of some codes using default parameter values may occasionally be used, on most occasions a site-specific model is developed and parameterized using site-specific information and data.

C.3.2 Requirements of a Graded Modeling Approach

A graded modeling approach includes methods and codes that enable the development of cleanup levels enabling decisions regarding remedial actions to be reached within the context of CERCLA, RCRA, and/or other applicable standards. It should ideally do the following:

- integrate with the exposure/risk assessment process
- guide the selection and engineering of appropriate remedies
- support the development of long-term performance monitoring
- support the development of ICs

The principal requirements of a graded modeling approach, as outlined below, encompass methods and codes that enable relatively simple (“abstract”) to relatively complex (“realistic”) calculations. Such a graded approach accomplishes the following:

- Encompasses both (a) “look-up” analyses based upon previously compiled results obtained using generic or reasonably representative assumptions and parameters and (b) site-specific analyses that generate new results specific to an individual waste site or group of waste sites sharing characteristics using parameters more site specific than those used for the “look-up” type of analyses.
- Encompasses methods, models, and codes that enable calculations ranging from relatively simple to relatively complex to be completed.
- Incorporates inherent conservatism in the simpler methods and models. As the complexity of the methods, codes and models increase and conservatism decreases. As a result, calculations become increasingly realistic and less conservative as the complexity increases.
- Avoids overly conservative methods; methods that are simple but not necessarily conservative; and unnecessarily complex methods, codes, and models.
- Includes identifiable, communicable, and verifiable justification for progressing from simpler methods and codes to more complex methods and codes. Justification for progressing from simpler (abstract) methods and codes to complex (realistic) methods and codes should be consistent with applicable regulations.
- Uses fully documented and verified (benchmarked) codes that can be made available for review by third parties.
- Ensures that calculations completed using any method or code are documented and independently verifiable, enabling independent reproduction and verification of results.

Use of a graded calculation approach should proceed in a stepwise manner commencing with simple, conservative calculations (i.e., using methods that overpredict likely impacts to the environment) and progress to more complex calculations more representative and inclusive of the conditions likely to be encountered (i.e., rigorous or “realistic” calculations). Progression between calculation levels occurs under the following conditions:

- The current calculation step suggests that the soil or other concentrations required to be protective of groundwater are overly conservative.
- The next calculation step incorporates one or more features, events, and/or processes (FEPs) that
    - are necessary and appropriate
    - are verifiable
    - can be reasonably expected to significantly impact the calculated impact to groundwater

Implementation of any method and code to a specific site in the form of a site-specific model should be accompanied by description of the CSM, documentation of the basis for the values assigned to parameters, a discussion of assumptions and the level of conservativeness associated with the analysis, and a discussion of reducible and irreducible uncertainties.

C.3.3 Key Features, Events, and Processes of a Conceptual Site Model

Completion of calculations requires the development of a site-specific CSM. This in turn requires the identification, documentation, and understanding of key FEPs that govern(ed) the release, migration, and fate of contaminants in the subsurface as well as the risk to potential receptors. FEPs are site specific and must be identified and documented as part of the development of the site-specific CSM prior to determining appropriate methods, applicable codes, and site-specific parameters for inclusion in the modeling analysis. Table C-3 shows some example FEPs that are commonly encountered at sites considered for S/S remedies.

Table C-3. Example features, events, and processes of a CSM

Category	Examples
Features	• distribution of residual contamination within a discrete soil block of specified dimensions • vertical variation of soil media (heterogeneity)
Events	• implementation of a soil removal action • implementation of a capping action, considering an effective life cycle for the capping action
Processes	• transient depletion and partitioning of a finite mass of contaminant from a discrete soil block of specified dimensions • transient vadose zone transport of water and dissolved solutes • transient mixing of water and contaminants from the vadose zone with lateral groundwater flux • saturated zone migration of water and advective-dispersive-reactive transport of the dissolved solute

By way of example, an instantaneous multiphase partitioning equation might be used to assess the likely partitioning of contaminants from an emplaced waste. However, progression from the use of an instantaneous partitioning equation that uses site-specific parameters to the use of an integrated treatment of flow and contaminant transport enables the inclusion of several FEPs pertinent at many sites, such as the following:

- site-specific geometry, including a significant vadose zone
- a finite, depleting source of contaminants
- variably saturated flow and transport through the vadose zone
- convolution of the contaminant flux calculated at the base of the vadose zone
- advection, retardation, degradation, and dispersion of dissolved contaminants within the vadose and saturated zones

C.3.4 Example Methods of Calculation

Calculation methods range from simple to complex and differ with respect to their ability to include common FEPs and the level of expertise required to design and execute calculations. Most sites contain common elements, although the extent to which each element is included in a calculation depends on the objective of the analysis and the complexity of the methods and codes employed. These common elements are as follows:

- *source zone*—The area in which the contaminants are known or believed to exist and from which they are hypothesized as emanating in the predictive calculations.
- *vadose zone*—The path from the source zone to the water table below.

- *mixing zone*—The volume at the top of the unconfined aquifer beneath the source zone, within which infiltrating water containing contaminants mixes with through-flowing groundwater.
- *saturated zone*—The (unconfined) aquifer beneath the source zone, within which contaminants migrate.
- *receptor*—A water body, well, faucet, or other location at which exposure to contamination occurs.

Calculation outputs vary depending on the sophistication of the method and the complexity of the site, as follows:

- *Simple* methods may include a concentration independent of time and space.
- *Intermediate* methods may include a groundwater concentration over time at a given distance from the contaminant release.
- *Sophisticated* methods may include maps of contaminant concentration over time and space and/or concentrations to which potential receptors may be exposed.

Depending on the transport properties of the contaminant, release scenario, and site geometry, a significant difference may exist between groundwater concentrations calculated immediately beneath a site versus concentrations calculated some distance downgradient, such as at the site boundary. For this reason, either the points of calculation and/or POCs should be agreed on prior to making decisions on the basis of calculations, or the method should be able to provide outputs describing concentrations versus time at various distances from the release to ensure that the location of peak impacts is identified.

C.3.4.1 Look-Up Type Analyses

Look-up type analyses typically comprise tabulated values published in guidance documents and/or regulations. These values are sometimes used as cleanup levels, but the decision on whether a look-up value can be relied on for this purpose depends on the pertinent state and federal regulations and/or other site-specific requirements. Look-up type analyses are easy to implement and require relatively little expertise. However, their applicability to site-specific decisions can be questionable since the underlying assumptions may not be valid. Since little or no site-specific information is required to use look-up type analyses, they are by design very conservative (protective), and as a result, the outputs of look-up type analyses usually indicate that very low concentrations of contaminants remaining in source zones may contaminate groundwater.

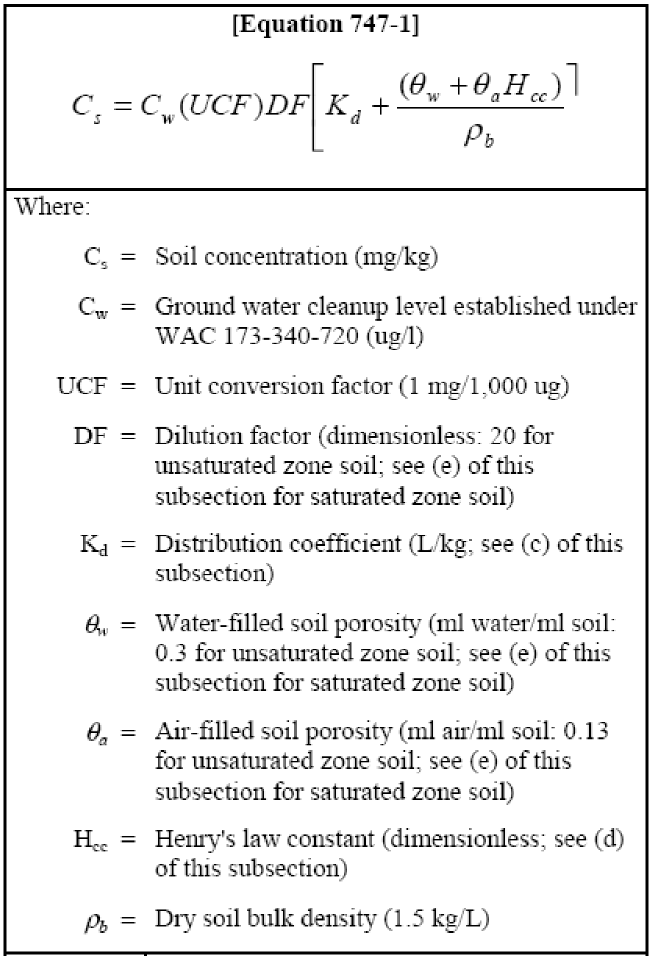
C.3.4.2 Site-Specific Analyses

Calculations are typically made using site-specific parameters, particularly when evaluating the likely efficacy of an existing remedy or attempting to determine whether a remedy has been sufficiently effective as to warrant consideration for site closure. The use of site-specific parameters is conditional on meeting a reasonable burden of proof that the information used in the analysis is appropriate; that site-specific parameters are defensible; and that any new scientific information, method, or code is reliable. Site-specific analyses can themselves include a wide variety of simple to sophisticated calculations, some examples of which are described in the following subsections.

Batch or "flash" calculations

Batch or flash calculations are usually based on partitioning of a contaminant between two or more phases, such as from a soil into the air and/or groundwater. Partitioning equations typically assume that partitioning is instantaneous (i.e., they do not explicitly consider time or space) and that the target media—in this case, groundwater—is adjacent to the source zone. These calculations allow the use of some site-specific parameters, such as the distribution coefficient.

On some occasions, these calculations may be combined with other calculations, such as infiltration rates or groundwater flow rates, enabling dilution factors and approximate concentrations in groundwater to be determined. For example, the State of Washington Administrative Code (WAC) 173-340-747, "Deriving Soil Concentrations for Ground Water Protection," presents methods for establishing soil concentrations that will not contaminate groundwater above levels established under WAC 173-340-720. [NOTE: References for Section C.3 are in Section C.3.8, beginning on p. C-31.] In particular, WAC 173-340-747(3) lists several methods for deriving soil concentrations, including the use of a variable-parameter, three-phase partitioning model and the use of an alternate fate-and-transport model.



[Equation 747-1]

$$C_s = C_w(UCF)DF\left[K_d + \frac{(\theta_w + \theta_a H_{cc})}{\rho_b}\right]$$

Where:

C_s = Soil concentration (mg/kg)

C_w = Ground water cleanup level established under WAC 173-340-720 (ug/l)

UCF = Unit conversion factor (1 mg/1,000 ug)

DF = Dilution factor (dimensionless: 20 for unsaturated zone soil; see (e) of this subsection for saturated zone soil)

K_d = Distribution coefficient (L/kg; see (c) of this subsection)

θ_w = Water-filled soil porosity (ml water/ml soil: 0.3 for unsaturated zone soil; see (e) of this subsection for saturated zone soil)

θ_a = Air-filled soil porosity (ml air/ml soil: 0.13 for unsaturated zone soil; see (e) of this subsection for saturated zone soil)

H_{cc} = Henry's law constant (dimensionless; see (d) of this subsection)

ρ_b = Dry soil bulk density (1.5 kg/L)

The box to the right presents the basic three-phase partitioning equation provided in WAC 173-340-747 (equation 747-1). Use of the three-phase partitioning equation is generally accompanied by the use of equations to estimate the K_d, groundwater Darcy flux, infiltration rate, and groundwater dilution factor. Site-specific leaching tests may also be used as a basis for establishing an appropriate K_d. The three-phase partitioning equation provides simple, though relatively abstract, estimates of the likely impact of residual contamination on the concentration of contaminants at the water table. The use of this and similar equations is usually most appropriate for only screening-level calculations, since the method does not readily accommodate site-specific geometry and other potentially important FEPs.

Analytical models

Analytical models are mathematical models that have a closed-form solution; i.e., the solution to the equations used to describe changes in a system can be expressed as an analytic function of one or more parameters. Analytical models typically provide fairly concise representations of the principal FEPs at a site in a way that is more readily available than when using numerical models. Nonetheless, although analytical models for simple systems are themselves simple, analytical solutions to equations that describe complex systems can become complicated.

The use of analytic models can be justifiable at sites where the groundwater flow field is fairly uniform; source area, vadose zone, and aquifer geometries are fairly regular; and key parameters can be reasonably approximated using single (usually average but at other times bounding) values. Because of their relative simplicity and the requirement that an analytical equation has a closed solution, analytical methods usually simulate source, vadose, mixing, and saturated zones separately using a series of process-specific models. Therefore, it is necessary to combine the results of several process-specific analytical models to obtain results that encompass all principal FEPs at a site. Example analytical codes that are used to evaluate the fate and transport of contaminants include BIOSCREEN and BIOSCREEN-AT, screening models that simulate contaminant transport in groundwater.

Analytical models require more expertise to use than simple partitioning equations; however, the expertise required is generally significantly less than that required to use numerical models.

Numerical models

Numerical models typically solve large systems of simultaneous (coupled) partial-differential equations that describe flow and transport processes using a discretized (i.e., grid) representation of the real-world site. Numerical models have been developed using finite difference, finite element, and finite volume techniques. Numerical models are theoretically capable of incorporating all relevant FEPs and simulating these relevant FEPs on any spatial or temporal scale. Because of their theoretically unlimited capability, numerical methods can integrate source, vadose, mixing, and saturated zones within a single site-specific model and can even integrate calculations to estimate likely impacts at receptors.

The use of numerical models is often justified for sites at which the groundwater flow field is nonuniform; the source area, vadose zone, and aquifer geometries are irregular; or key parameters cannot be reasonably approximated using single (usually average) values. Example numerical codes that are used to simulate the fate and transport of contaminants include MT3DMS, a finite difference code that considers only saturated transport and reactions, and STOMP (Subsurface Transport Over Multiple Phases), an integrated-volume finite-difference code that solves partial-differential equations that describe the conservation of mass or energy throughout one to four phases (i.e., aqueous, gaseous, NAPL, ice, and solid phases).

Numerical codes and models require significant expertise to use, and as a result, justification for their use must consider the implications of selecting or designing a code or model that can be used by only a small number of subject-matter experts.

C.3.5 An Intermediate Method: Integrated Analytical Solutions

While the three-phase partitioning equation is a fundamental calculation that provides basic information regarding partitioning of chemicals in the immediate vicinity of contaminated soil, it generally neglects common FEPs that are encountered at many sites. On the opposite end of the spectrum, numerical simulators are sophisticated and essentially fully capable codes with the potential to realistically simulate the widely ranging conditions and contaminants encountered at any site. However, their technical and computational requirements, coupled with the level of expertise required to complete such calculations, renders the use of complex numerical simulators at every site a demanding undertaking that is less readily verifiable and transparent to independent review than simpler calculations.

Integrated analytical solutions (IASs) offer an intermediate level of sophistication that can consider many of the FEPs that are usually incorporated in numerical models but retain the relative simplicity of analytical methods. An IAS essentially comprises a sequence of compatible analytical solutions whose inputs and outputs are designed to enable sequential or simultaneous execution with outputs from some analytical equations providing inputs to other analytical equations. Due to the relative simplicity of each analytical equation, integrated analytical solutions can be readily implemented within one or more simple programs or spreadsheets that describe source, vadose, mixing, and saturated zone flow and contaminant FEPs. Thus, the use of IASs as an intermediate method lies comfortably between the use of simple partitioning equations and analytical solutions and the use of sophisticated numerical models.

Bedekar, Neville, and Tonkin (2010, in press) describe an IAS implemented within an EXCEL spreadsheet for wide accessibility and transparency that comprises analytical equations describing the following:

- partitioning of contaminants from a source zone
- migration of contaminants vertically through a vadose zone
- mixing of contaminants with actively flowing groundwater at an underlying water table
- migration of the dissolved contaminants in the underlying aquifer

The vadose zone and saturated capabilities of this intermediate IAS method above can incorporate time-varying conditions to consider the implementation of soil remedial actions, such as soil removal and capping. The IAS method can therefore evaluate, through the use of appropriate infiltration rates, (a) current conditions for a specified number of years; (b) capped conditions, with assumed cap life cycle and effective depth, for a specified number of years; and (c) post-cap conditions for a specified number of years. While the method is not as

The conceptual model for the source screening analyses is shown schematically in Figure 1. Three sequential calculations are performed as follows.
1. Conversion from soil concentrations to pore water concentrations in the source area;
2. Transport across the vadose zone; and
3. Transport in the saturated zone to a potential receptor.

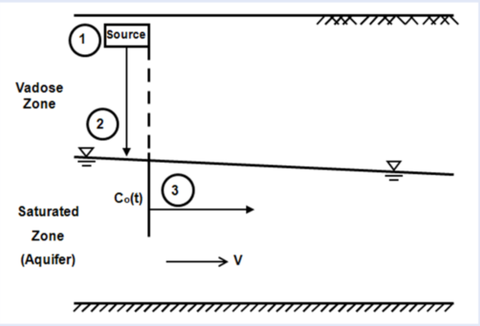


Figure 1 Conceptual model for source screening analysis

realistic as the use of sophisticated numerical models, the level of expertise and the computational burden required are also substantially less. For this reason, the use of the intermediate IAS method will often be appropriate when sufficient site-specific information is available to undertake more rigorous calculations than are offered by simple partitioning equations but when there is insufficient justification to warrant the use of sophisticated numerical models. The IAS method described by Bedekar, Neville, and Tonkin (2010, in press) is freely available for use and possesses similar capabilities to the GWSCREEN program developed by Idaho National Engineering and Environmental Laboratory (INEEL 1998).

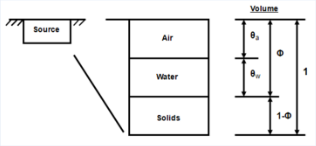


Figure 2 Idealization of the material in the source area

Source Area Concentration

Field measurements reported as soil concentration or total concentration are converted to dissolved concentration by partitioning the total mass of the species in the source area between the water (dissolved), solids (sorbed), and vapor (air) phases (Figure 2).

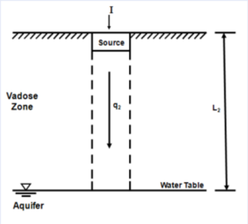


Figure 3 Conceptual model for transport across the vadose zone

Vadose Zone

The analysis considers one-dimensional flow across the vadose zone, with one-dimensional dispersion, equilibrium sorption, and first-order transformation reactions (Figure 3). Three general source histories can be simulated:

1. Constant source;
2. Leaching source; and
3. User-defined source.

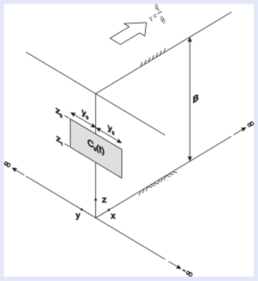


Figure 4 Conceptual model for transport in the saturated zone

Saturated Zone

The analysis considers one-dimensional flow in the aquifer, with three-dimensional dispersion, equilibrium sorption, and first-order transformation reactions. In the analysis the source is represented as a "patch" along the inflow boundary as shown in Figure 4. The concentration for the patch is specified as the output from the vadose zone.

C.3.6 Summary—A Graded Modeling Approach

The graded calculation approach discussion has three principal methods that enable the construction of models of varying complexity from simple to realistic. Table C-4 briefly describes these levels of the proposed graded approach. In developing a graded calculation approach, incorporating levels such as those that are illustrated in Table C-4, it is assumed that evaluation of a site for each COC proceeds in a stepwise manner and that the appropriate calculation level incorporates relevant processes while acknowledging that the calculations represent simplifications of the actual conditions. Accordingly, the graded approach commences with simple calculations that by their nature and design are conservative (i.e., overpredict likely impacts to groundwater) and progresses to more complex calculations more representative/ inclusive of the conditions likely to be encountered. For example the progression from the three-phase partitioning equation using site-specific parameters to the vertically integrated analytical treatment of steady-state variably saturated flow and transient contaminant transport enables the inclusion of several FEPs, including the following:

- site-specific geometry, including discrete extents for the contaminated soil and a thick vadose zone
- a finite, depleting source of contaminants
- variably saturated flow and transport through the thick vadose zone
- convolution of the contaminant flux calculated at the base of the vadose zone

- advection, retardation, degradation, and dispersion of dissolved contaminants within the vadose and saturated zones

Table C-4. Graded modeling approach description

Description	Format	Notes
Level 1		
Partitioning equation with site-specific dilution factor and parameters	Spreadsheet	• Lumped parameter analytical partitioning • Considers bulk properties and conditions • Uses site-specific parameters and dilution factor(s) • Can help to screen, rank, or identify drivers for unacceptable risk • Unlikely that this method/code can demonstrate compliance under anything other than the simplest of conditions
Level 2		
IAS for flow and transport	Spreadsheet	• Relatively sophisticated but simple to implement • Vertically integrated site properties • Considers depletion of the source over time, 1D mass-conserved partially saturated transport through the vadose zone, mixing at the water table, and 2D advective-dispersive-reactive transport in the aquifer to a POC and/or receptor • Can demonstrate compliance and/or identify drivers for unacceptable risk under specific remedial alternatives and guide refinement of potential remedies
Level 3		
Integrated numerical solutions for subsurface flow and transport	Command prompt or graphical user interface (GUI)	• Sophisticated and relatively complex to implement • Spatially variable properties in 1D, 2D, or 3D • Considers depletion of the source over time; variably saturated flow and advective-dispersive-reactive transport in 1D, 2D, or 3D using finite-difference/finite-volume/finite-element solution techniques • Can complete realistic evaluations of future impacts under a variety of remedial alternatives when more conservative methods/ models lead to outcomes that are impractical to implement • Can demonstrate compliance and/or identify drivers for unacceptable risk under specific remedial alternatives and guide refinement of potential remedies

C.3.7 Quality Assurance and Other Implementation Considerations

As described earlier, there are numerous other considerations for implementing any calculations at a site, whether or not the graded approach that is described here is employed, another graded approach is used, a single deterministic calculation is made, or multiple stochastic-type calculations are made. These additional considerations include, but are certainly not limited to, the following:

- How will the burden of proof on parameter values used in the calculations be met?

- How will parameters used in the calculations be defined—as point values, as distributions? Or will bounding values be used? Hence, will "best-estimate" calculations be provided, or will an effort to consider bounding values be made?
- How will (a) variability and (b) uncertainty be considered in the calculations? These are important and distinct concepts.

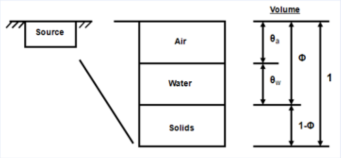


Figure 2 Idealization of the material in the source area

Source Area Concentration
Field measurements reported as soil concentration or total concentration are converted to dissolved concentration by partitioning the total mass of the species in the source area between the water (dissolved), solids (sorbed), and vapor (air) phases (Figure 2).

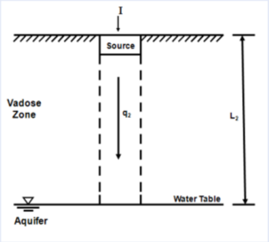


Figure 3 Conceptual model for transport across the vadose zone

Vadose Zone
The analysis considers one-dimensional flow across the vadose zone, with one-dimensional dispersion, equilibrium sorption, and first-order transformation reactions (Figure 3). Three general source histories can be simulated:

1. Constant source;
2. Leaching source; and
3. User-defined source.

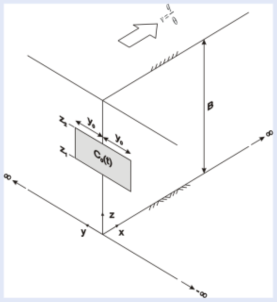


Figure 4 Conceptual model for transport in the saturated zone

Saturated Zone
The analysis considers one-dimensional flow in the aquifer, with three-dimensional dispersion, equilibrium sorption, and first-order transformation reactions. In the analysis the source is represented as a "patch" along the inflow boundary as shown in Figure 4. The concentration for the patch is specified as the output from the vadose zone.

These considerations are outside the scope of this appendix. The reader is therefore referred to other guidance documents that have been published by leading agencies and groups such as EPA, U.S. Geological Survey (USGS), National Research Council (NRC), and ASTM. Recent guidance document released by EPA and ASTM include the following:

- *Guidance for Quality Assurance Project Plans for Modeling* (EPA 2002).
- *Guidance on the Development, Evaluation, and Application of Environmental Models* (EPA 2009). This guidance "recommends best practices to help determine when a model, despite its uncertainties, can be appropriately used to inform a decision." The guidance also identifies model corroboration using independent data as a specific element of the model evaluation step. The guidance states that "[m]odel corroboration includes all quantitative and qualitative methods for evaluating the degree to which a model corresponds to reality."
- *Standard Guide for Application of a Ground-Water Flow Model to a Site-Specific Problem* (ASTM 2010) lists eight primary steps in the application of a groundwater model.

Finally, it is noted that the use of models is accompanied by uncertainty and that although most models are deterministic (i.e., a single set of outputs is produced on the basis of a single set of inputs, and the model performs the same way for a given set of initial conditions), the results should not be misconstrued as the best possible answer. The use of simple methods and codes can be accompanied by more, or less, error and uncertainty than the use of complex methods—oversimplification can result in exclusion of FEPs that impact the fate of contaminants, while overcomplication can lead to the specification of parameter values for which no information is available and therefore are accompanied by great uncertainty. While the degree of uncertainty that accompanies model calculations is method, code, model, and site specific and therefore outside the scope of this appendix, it is common practice to undertake some form of evaluation of the goodness (suitability) of the model for its intended purpose. And, although the subjects of model calibration, verification, validation, and uncertainty analysis are all outside the scope of this appendix, the following paragraph provides some perspective on the use of data to corroborate or otherwise test the representativeness of a model.

In their 1992 book *Applied Groundwater Modeling: Simulation of Flow and Advective Transport*, Drs. M. P. Anderson and W. Woessner state that "continual improvement of the conceptual model by collection of new field data will improve the numerical model." In his 2003 article "From Models to Performance Assessment: The Conceptualization Problem," Dr. J. Bredehoeft states that "[g]ood modeling is an iterative process. As new data are acquired, the model is revisited and adjusted (or recalibrated) so that the model predictions are consistent with all the data, including the new data." Finally, in 2007 the NRC Committee on Models in the Regulatory Decision Process published *Models in Environmental Regulatory Decision*, assessing scientific and technical criteria that should be considered in deciding whether a model and its results could serve as a reasonable basis for environmental regulatory activities. This document states that "[m]odels also can evolve through multiple versions that reflect new scientific findings, acquisition of data, and improved algorithms," and that "[t]he interdependence of models and measurements is complex and iterative for several reasons. Measurements help to provide the conceptual basis of a model and inform model development, including parameter estimation. Measurements are also a critical tool for corroborating model results."

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Appendix E

Glossary

GLOSSARY

additive—A substance added in small amounts to something else to improve, strengthen, or otherwise alter it.

adsorption—Partitioning of a dissolved species onto a solid surface.

cementitious—Of, or relating to, a chemical precipitate, especially of carbonates, having the characteristics of cement.

compliance testing—Tests to evaluate cured material properties for direct comparison to project performance criteria.

consistency testing—Real-time or short-term evaluations of treated material during implementation used to adjust reagent addition rates or mixing procedures to maintain material properties consistent with construction performance specifications.

construction performance specifications—Associated with S/S treatment implementation in the field to verify that the final treated material is consistent with the specifications developed during treatability testing.

contaminated material—Toxic or potentially harmful substances that may be present in soil, groundwater, and/or building materials.

dilution attenuation factor—The ratio of original soil leachate concentration to the receptor point concentration.

eluate—The liquid solution that results from an elution process. In this guidance, “eluate” refers to the liquid phase resulting from laboratory leaching tests. For example, the liquid that elutes through a column of granular material is considered an eluate. The term is similar to “field leachate” and differentiates laboratory test liquids from field leachates.

engineering controls—Barriers or systems that control downward migration, infiltration, or seepage of surface runoff and rain or natural leaching/migration of contaminants through the subsurface over time.

ettringite—The mineralogical name for calcium sulfoaluminates, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$. This mineral commonly precipitates in the pores of cementitious materials when sources of calcium sulfate (e.g., gypsum) are present. Petrographic analysis of ettringite shows the needle-like structure of the mineral. Since the molar volume of ettringite is greater than the sum of the molar volumes of its reactants, precipitation of ettringite is an expansive reaction. Formation of ettringite may occur during hydration, where it is generally considered to be harmless or even beneficial to the cement matrix, or after formation of a rigid mineral structure, where it is considered one form of sulfate attack.

ex situ S/S—Stabilization and solidification technologies that apply S/S treatment to excavated material. Ex situ treated material can be returned to its original location or placed on another part of the project area (e.g., reuse of S/S-treated material as paving base). At some projects, treated material has been excavated and placed at the final location prior to use of in situ mixing equipment to treat the relocated material. Ex situ S/S-treated materials may also be taken off site; however, this kind of ex situ S/S treatment is beyond the scope of this document because of the additional regulatory considerations for this kind of ex situ S/S treatment.

hydraulic conductivity—A measureable material property related to ease of movement of water through a porous medium under groundwater flow conditions governed by Darcy's Law (Bear 1972). This term is often used interchangeably with the more general term "permeability," which relates to the ease with which a fluid (e.g., water, oil, air, etc.) will pass through a porous medium.

inorganic compounds—Chemicals that do not contain carbon; for example, metals are inorganic.

in situ S/S—Stabilization and solidification technologies that apply S/S treatment to in situ materials using auger-type and injector-head systems.

institutional controls—"Non-engineering measures, such as administrative and/or legal controls that help to minimize the potential for human exposure to contamination and/or to protect the integrity of a remedy by limiting land or resource use," as defined by EPA.

leachability—The ability of the material to retain contaminants of concern through a combination of chemical and physical mechanisms. May be used to describe either the extent of leaching (e.g., percentage of total content that have leached) or rate of release (e.g., the time-dependent release) from materials.

leaching—The process of constituent movement from the solid when a solid material is contacted with a liquid.

mass flux—A rate measurement specific to a defined area, which is usually a subset of a plume cross section. Mass flux is expressed as mass/time/area (e.g., $g/d/m^2$).

material performance goals—Design targets that describe a treated material that will meet specific site remediation goals.

material performance specifications—Material performance needs to adequately address performance goals and to guide the treatability study phase.

monolith—Solid matrix with high structural integrity.

organic compound—Any compound containing carbon.

performance—Refers to the ability of the material or remedy to maintain its function of minimizing release of contaminants to the environment.

performance criteria—Design values of a performance parameter used for comparison to performance measurements to evaluate whether acceptable performance has been achieved.

performance parameters—The material properties characteristic of the ability of an S/S-treated material to carry out its intended purpose.

performance tests—Protocols or assessments used to characterize a performance parameter of an S/S-treated material and which return one or more values considered representative of performance measurement.

pocket penetrometer—Test instrument used to measure compressive strength of soil or concrete.

point of compliance—The location where the S/S-treated material must comply with site remediation goals.

porewater—The water filling the spaces between grains of sediment.

pozzolanic reagents—Siliceous or siliceous and aluminous material that reacts chemically with an alkali in the presence of water to produce a cementitious material at standard temperatures.

pugmill—A machine in which materials are simultaneously ground and mixed with a liquid.

reagent—A substance or compound used in a chemical reaction to detect, measure, or produce other substances.

slump test—A test used to determine the consistency of fresh concrete and to ensure uniformity for different batches of similar concrete under field conditions.

solidification—The processes that encapsulates contaminated material to form a solid material and restricts contaminant migration by decreasing the surface area exposed to leaching and/or by coating the contaminated material with low-permeability materials. Solidification can be accomplished by mechanical processes that mix the material and one or more reagents. Solidification entraps the contaminated material within a granular or monolithic matrix. (EPA definition)

solubility—The relative capacity of a substance to serve as a solute, usually in reference to water as the solvent.

sorption—The process of being taken up or held by either adsorption or absorption.

stabilization—The processes where chemical reactions occur between the reagents and contaminated material to reduce the leachability of contaminated material into a stable insoluble form. Stabilization chemically binds free liquids and immobilizes contaminated materials or reduces their solubility through a chemical reaction. The physical nature of the contaminated material may or may not be changed significantly by this process. (EPA definition)

stakeholder—May include people in communities living near contaminated sites, site-specific advisory boards, local governments, and a variety of nongovernmental organizations.

stewardship (long-term stewardship)—The physical controls, institutions, information, and other mechanisms needed to ensure protection of people and the environment.

strength—The ability of a material to withstand an applied physical stress without incurring an inelastic strain leading to structural failure.

treatability studies—Tests to characterize the untreated contaminated material and evaluate the technology performance under different operating conditions.

unconfined compressive strength—A common performance parameter in S/S treatment used to ensure that treated material has at least as much bearing strength as surrounding material.

Appendix F

Acronyms

ACRONYMS

ANS	American Nuclear Society
AOC	area of contamination
ASTM	ASTM International, formerly American Society for Testing and Materials
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	contaminant of concern
CQA	construction quality assurance
CSM	conceptual site model
DAF	dilution-attenuation factor
DOC	dissolved organic carbon
DOI	U.S. Department of the Interior
DQO	data quality objective
DSM	deep soil mixing
EC	engineering control
EPA	U.S. Environmental Protection Agency
EPACMTP	EPA Composite Model for Leachate Migration with Transformation Products
EPRI	Electric Power Research Institute
FEP	feature, event, and/or process
HCL	hydrochloride
HSVOCs	halogenated semivolatile chemicals
HSWA	Hazardous and Solid Waste Amendments [to RCRA] of 1984
HVOC	halogenated volatile chemical
IAS	integrated analytical solution
IC	institutional control
ITRC	Interstate Technology & Regulatory Council
KOH	potassium hydroxide
K_{ow}	octanol-water partitioning coefficient
LDR	land disposal restriction
LEAF	Leaching Environmental Assessment Framework
L/S	liquid-solid ratio
LSP	liquid-solid partitioning
MGP	manufactured gas plant
NAPL	nonaqueous-phase liquid
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
N-HSVOC	nonhalogenated semivolatile chemical
N-HVOC	nonhalogenated volatile chemical
NPL	National Priorities List
NRC	National Research Council
N-VOC	nonvolatile organic compound
O&M	operations and maintenance
OU	operating unit
PAH	polycyclic aromatic hydrocarbon
PASSiFy	Performance Assessment of Solidified/Stabilized Waste-Forms

PCB	polychlorinated biphenyl
POC	point of compliance
QA	quality assurance
QC	quality control
RAO	remedial action objective
RCRA	Resource Conservation and Recovery Act
ROD	record of decision
SPLP	Synthetic Precipitation Leaching Procedure
S/S	solidification/stabilization
STARNET	Stabilization/Solidification Treatment and Remediation Network
SVOC	semivolatile organic chemical
TCLP	Toxicity Characteristic Leaching Procedure
UCS	unconfined compressive strength
USACE	U.S. Army Corps of Engineers
USCS	Unified Soil Classification System
VOC	volatile organic chemical
WAC	Washington Administrative Code
WET	[California] Waste Extraction Test