

3 S/S PROCESS PERFORMANCE TESTS

Many different tests can be applied to measure the performance of S/S processes. Some of these tests are mandated by federal, state, or local regulations, whereas others can be employed to provide additional assurance that a given S/S process is appropriate for its intended use. Testing can be expensive, especially when applied to a large number of samples and replicates to ensure statistical validity. On the other hand, only adequate testing can ensure attaining the data quality objectives (DQO). Less than necessary testing may lead to an unacceptable S/S-treated waste in a difficult form to reprocess.

This chapter provides a comprehensive review of the types of tests applied to S/S-treated waste. A given test program normally would use only a small subset of the tests mentioned here, depending on the specific performance goals of that test program (Section 2.3).

The purpose of this section is not to describe all possible tests in detail but rather to present an overview of example tests organized by type of test: physical, leaching/extraction, chemical, biological, and microcharacterization. For each category of test, a table lists and briefly describes the representative tests. Where possible, reference has been made to one possible example method. Some of the tests are most applicable to untreated soil or sludge samples, S/S-treated waste, or liquid samples. These material applications are denoted as U, S, or L in the column titled material application. The test may be required by regulation, provide general information about S/S processing, or support an experimental program. These testing applications are noted as R, I, or E in the column titled testing application. Both columns provide general guidance but specific uses will vary depending on testing program design.

U.S. EPA (1989g and 1990b) provides two sources of additional information on performance tests. The test descriptions offered in Sections 3.1 through 3.5 are taken primarily from U.S. EPA (1990b).

3.1 PHYSICAL TESTS

For the testing of S/S-treated waste, many existing physical and construction tests were adapted. Thus, caution should be exercised when using them to evaluate stabilized wastes. Such tests can be used to differentiate

among the attributes of different binders, to determine compliance with performance objectives, to establish material handling characteristics, and to select large-scale equipment. Table 3-1 gives an overview of physical tests, described below. The testing program should select appropriate tests based on the waste and site conditions and test program objectives (Section 2.7).

3.1.1 General Property Tests

General property tests provide information relating physical characteristics of treated and untreated waste to various process and operational parameters. These tests are often performed to determine the suitability of the wastes to stabilization, to help select binders, or to help design treatability studies.

3.1.1.1 Moisture Content

Moisture content refers to "free" or "pore" water, not water of hydration. On untreated wastes, moisture content is used to determine the materials handling properties and to determine whether pretreatment (e.g., drying, dewatering) is needed. Moisture content is also used to estimate the need to add water to the S/S binder and to convert waste weights to a dry basis to improve reporting consistency. Moisture content may include some volatiles lost under the conditions of the test.

3.1.1.2 Particle Size Analysis

The size distribution of the particles in the waste or soil often indicates the potential for water movement through the material and the compressibility. Also, very fine-grained materials have been shown to produce poorly stabilized materials (U.S. EPA, 1986c). Presence of large particles may require the use of size reduction equipment. The best material for forming a strong interlocking matrix is well graded, with few particles in extreme sizes.

3.1.1.3 Specific Gravity

Specific gravity is the ratio of the mass of the dry solid portion of the waste to the mass of an equivalent volume of water. Specific gravity data are necessary to understand the weight-to-volume (e.g., tons to cubic

TABLE 3-1. PHYSICAL TESTS

Test Procedure	Method	Material Application (a)			Purpose	Testing Application (b)
		U	S	L		
<u>General Property Tests</u>						
Moisture (water content)	ASTM D 2216-85	X	X		To determine the percentage of free water in a material.	X
Particle-size analysis (grain size)	ASTM D 422-63	X	X		To determine the particle-size distribution of material.	X
Specific gravity	ASTM D 854-83	X	X	X	To determine the specific gravity of waste material or S/S-treated waste.	X
Suspended solids	Standard Method 2540D			X	To determine the amount of solids that do not settle from a column of liquids.	X
Paint Filter Test	EPA SW-846 Method 9095		X		To determine the presence of free liquids.	X X
Liquid Release Test	51 FR 46828		X		To determine the presence of free liquids released under pressure.	X X
Atterberg limits (liquid limit, plastic limit, and plasticity index)	ASTM D 4318-84	X	X		To define the bearing capacity and critical slope of a material as a function of its water content.	X
Visual Observation	U.S. EPA, 1990d		X		To define general condition of the S/S-treated waste.	X

TABLE 3-1. PHYSICAL TESTS (Continued)

Test Procedure	Method	Material Application (a)		Purpose	Testing Application (b)
		U	S L		
<u>Bulk Density Tests</u>					
Bulk density by drive-cylinder method	ASTM D 2937-83	X		To determine in-place density and moisture content.	X
Bulk density by sand cone method	ASTM D 1556-90	X		To determine bulk density.	X
Bulk density by nuclear method	ASTM D 2922-81	X		To determine total, in-place wet density.	X
<u>Compaction Tests</u>					
Moisture-density relationship of soils and soil-aggregate mixtures (Proctor test)	ASTM D 698-78 ASTM D 558-82 ASTM D 1557-78	X		To determine the relation between moisture content and density of a material.	X
<u>Permeability Tests</u>					
Constant-head permeability	EPA SW-846 Method 9100	X	X	To measure the rate at which water will pass through a soil-like material.	X
Falling-head permeability	EPA SW-846 Method 9100	X	X	To measure the rate at which water will pass through a soil-like material.	X

TABLE 3-1. PHYSICAL TESTS (Continued)

Test Procedure	Method	Material Application ^(a)		Purpose	Testing Application ^(b)
		U	S L		
<u>Porosity</u>					
Mercury intrusion	ASTM C 493-86	X	X	To measure total porosity and pore distribution.	X
Water or mineral spirit displacement	ASTM C 830-88	X	X	To measure apparent porosity and apparent specific gravity.	X
Helium displacement	Hannak and Liem, 1986	X	X	To measure porosity.	X
<u>Strength Tests</u>					
Unconfined compressive strength of cohesive soils	ASTM D 2166-85	X	X	To evaluate how cohesive soil-like materials behave under mechanical stress.	X X
Immersion compressive strength test	Kasten et al., 1989, p. 22	X	X	To evaluate a material's strength when wet.	X X
Unconfined compressive strength of cylindrical cement specimen	ASTM D 1633-84	X	X	To evaluate how cement-like materials behave under mechanical stress.	X X
Compressive strength of hydraulic cement mortars	ASTM C 109-90	X	X	To measure the compressive strength of hydraulic cement mortars.	X X

TABLE 3-1. PHYSICAL TESTS (Continued)

Test Procedure	Method	Material Application ^(a)		Purpose	Testing Application ^(b)	
		U	S L		R	I E
Triaxial compressive strength	ASTM D 2850-87	X	X	To measure strength of an unconsolidated laterally-confined material.		X
Flexural strength	ASTM D 1635-87		X	To evaluate a material's elastic deformation under stress.		X X
Cone index	ASTM D 3441-86	X	X	To evaluate a material's hardness and setting.		X
<u>General Concrete/Soil-Cement Tests</u>						
Heat of hydration	ASTM C 186-86		X	To measure temperature changes during mixing in order to predict VOC emissions.		X
Making and curing concrete test specimens in the field	ASTM C 31-90		X	To prepare S/S-treated waste under field conditions.		X X
Making and curing concrete specimens in the laboratory	ASTM C 192-90		X	To prepare S/S-treated waste under laboratory conditions.		X X
Bulk density of S/S-treated waste	Stegemann and Côté, 1991		X	To determine bulk density of a monolithic S/S-treated waste.		X X

TABLE 3-1. PHYSICAL TESTS (Continued)

Test Procedure	Method	Material Application (a)		Purpose	Testing Application (b)		
		U	S L		R	I	E
<u>Durability Tests</u>							
Wet/dry weathering (WDW)	ASTM D 4843-88	X		To determine how materials behave or degrade after repeated wet-dry cycles.			X X
Freezing and thawing of soil-cement mixtures	ASTM D 4842-90	X		To determine how materials behave or degrade after repeated freeze-thaw cycles.			X X
Thermal cycling	ASTM B 553-79	X		To determine the effect of thermal cycling.			X X

(a) Material Application Guide:
 U = Untreated sample
 S = S/S-treated sample
 L = Liquid sample

(b) Testing Application Guide:
 R = Regulatory requirement
 I = Information for S/S process
 E = Experimental program

yards) conversion factor for the waste. Specific gravity measurements on waste before and after treatment can be used to calculate the extent of waste volume expansion due to treatment. Specific gravity of insoluble materials can be determined by a water displacement method in which the volume of a waste sample is determined by water displacement in a volumetric flask.

3.1.1.4 Suspended Solids

The quantity of suspended solids in a mixture is one factor in determining the pumpability of liquid wastes. The decrease in volume of the waste that can be achieved by dewatering also can be estimated based on the suspended solids content.

3.1.1.5 Paint Filter Test

The Paint Filter Test is mentioned under RCRA in 40 CFR 264.314 and 265.314. This test is used to determine the presence of free liquids in the waste. The Paint Filter Test can be performed before treatment to help determine the degree of treatment needed or after stabilization to determine if the waste may be disposed of in a RCRA-authorized landfill. If the material fails the test, further treatment is required.

3.1.1.6 Liquid Release Test (LRT)

The Liquid Release Test is also devised to measure free water content. This method uses gas pressure to force a piston against a sample to squeeze any releasable liquid from the material. A special liquid release test apparatus or the zero headspace extraction apparatus, also used in the TCLP test (Section 3.2.1), may be used for the LRT. The U.S. EPA has proposed the LRT as a supplement to the Paint Filter Test (51 FR 46833, December 24, 1986).

3.1.1.7 Atterberg Limits

Atterberg limits are the boundaries of liquid and plastic consistency states for a soil-like material. Another parameter is the plasticity index, which is the difference in the moisture contents at the liquid and plastic limits. The Atterberg limits indicate general civil engineering

properties of a soil-like material and are used to estimate handling and storage characteristics.

3.1.1.8 Visual Observation

Careful observation and recording of the general condition of S/S-treated waste give a good indication of the performance of the S/S process. Characteristics to check include surface spalling, grain exfoliation, crack development, color, salt efflorescence, and surface pore size and condition.

3.1.2 Bulk Density Tests

In situ unit weight, void ratio, and degree of saturation are soil parameters used in most phase relationship, soil pressure, settlement, and stability problems. These parameters help to define the condition or physical makeup of a soil. The unit weight, defined as the ratio of the weight of the mass to the volume of the mass, may be expressed as either a dry, moist, or saturated unit weight. The void ratio equals the ratio of the volume of voids to the volume of solid materials. The porosity of a material, discussed in Section 3.1.5, is related to bulk density. The degree of saturation equals the ratio of the volume of water to the volume of voids, also expressed as a percent.

3.1.3 Compaction Tests

Moisture-density relationships define the compaction characteristics of a soil. The laboratory compaction test, generally referred to as the Proctor test, identifies the maximum dry unit weight that is achieved by using a specified compactive energy. Compaction tests also identify the optimum moisture content to achieve the maximum dry unit weight.

3.1.4 Permeability (Hydraulic Conductivity) Tests

Permeability is a measure of flow of a fluid through the tortuous pore structure of the waste or S/S-treated waste. Typical values of stabilized wastes range from 10^{-6} to 10^{-8} cm/s (U.S. EPA, 1989g). This can be compared to clay (used for liners), which is typically less than 10^{-6} cm/s. A value of $<10^{-5}$ cm/s is recommended for stabilized wastes planned for land burial (U.S. EPA, 1986c). However, high permeability is not as great a

problem if the contaminants in the waste do not easily leach to water. High permeability can also be addressed through engineering solutions (U.S. EPA, 1989g). It may be advisable in some cases to perform a permeability test on samples that have already undergone durability testing to determine whether this property changes under environmental stresses.

3.1.5 Porosity Tests

The porosity indicates the void space in the solid that may or may not be available to retain liquids. The methods available for measuring porosity are based on determining the volume of fluid that can be forced into the pores. Each fluid has unique strengths and weaknesses. Mercury (ASTM C 493) is unlikely to dissolve the solid, but high pressure is needed to push mercury into the pores, possibly altering the pore size. Water- or mineral oil-based methods (ASTM C 830) use lower pressure, but the fluid may dissolve part of the solid. Using helium as the displacement fluid (Hannak and Liem, 1986) avoids both high pressure and dissolution. However, helium is a more penetrating fluid than water, so helium intrusion can overestimate the effective water porosity.

3.1.6 Strength Tests

Strength testing indicates how well a material will hold up under mechanical stresses caused by overburden or earth-moving equipment. Strength testing is usually done on the stabilized waste, although testing the untreated waste can provide a baseline. A common mistake in S/S is to equate treated waste strength with the degree of contaminant stabilization. A correlation between strength testing and contaminant leachability has not been established. However, in general, better strength provides better physical barriers for the containment of contaminants.

3.1.6.1 Unconfined Compressive Strength (UCS)

The UCS test measures the shear strength of a material without lateral confinement. It is applicable to cohesive soil-like materials that do not release water during loading (ASTM D 2166) or to molded cylinders (ASTM D 1633 or C 109). It is not applicable to crumbly or fissured materials. The

ASTM D 1633 or C 109 tests for various binder mixes can also indicate the optimum water/additive ratios and curing times for the setting reaction.

For ASTM D 2166, the U.S. EPA generally considers a stabilized material as satisfactory if it has a compressive strength of at least 50 psi. However, the minimum required strength should be determined from the design loads to which the material may be subjected. Overburden pressures are generally around 1 psi per foot of depth.

Variations of these methods, such as the one-dimensional stability test (ASTM D 2435) and compressive strength of hydraulic cement mortars (ASTM C 109), are sometimes used.

3.1.6.2 Immersion Compressive Strength

Soil and soil-like materials can exhibit good strength when dry and yet become unconsolidated when saturated with liquid. In the immersion compressive strength test, a sample is soaked in water prior to compressive loading to simulate performance in a saturated disposal environment (Kasten et al., 1989, p. 22).

3.1.6.3 Triaxial Compression

The triaxial compression test determines the strength of a specimen encased in an impervious membrane and axially loaded to failure in compression. Triaxial compression testing is applied to unconsolidated soil and granular S/S-treated waste.

3.1.6.4 Flexural Strength

In contrast to the UCS, in the flexural strength test, loads are applied on the short axis of the sample. This test gives a measure of a material's ability to withstand tension or its resistance to cracking due either to settlement of the underlying fill or to surface loads (U.S. EPA, 1989g).

3.1.6.5 Cone Index

The cone index test is a quick screening evaluation for compressive strength (Myers, 1986). This test involves forcing a standard cone- or needle-shaped device into the stabilized waste and measuring the penetration

resistance. Three types of cones are available: the U.S. Army, pocket, or ASTM. Selection depends on the strength of the material and the application. The cone index test can be used instead of the UCS sometimes, but not exclusively, if results are required quickly. This test indicates the stability and load-bearing capacity of the stabilized waste (Cullinane and Jones, 1992). It can be used to determine the kind of earth-moving equipment needed to move the stabilized waste and the curing time required before other construction equipment can move over the stabilized waste (U.S. EPA, 1989g).

3.1.7 General Concrete/Soil-Cement Tests

The test methods used to determine the heat of hydration and other factors involved in making and curing concrete test specimens can be used to evaluate the performance of cement/waste mixtures. Heat of hydration can be a useful measurement, particularly when the waste contains volatile organic compounds (VOCs). Although the standard test intervals for industrial applications are 7 and 28 days, it is recommended that the heat of hydration be measured at more frequent intervals for S/S testing.

In addition to the heat of hydration procedure, it also can be useful to prepare and cure samples of the S/S-treated waste under both field and laboratory conditions. In this way, the S/S-treated waste can be measured for physical parameters after having been subjected to realistic environmental variables. In the laboratory, process variables can be varied and controlled to simulate a wide variety of environmental conditions. Preparing and curing S/S specimens under a variety of potential environmental conditions makes it possible to apply the durability tests described in Section 3.1.8 and to assess the effects of both the curing process and the environmental factors in relation to the ultimate integrity of the S/S waste.

3.1.8 Durability Testing

Durability testing evaluates the ability of a material to withstand environmental stresses such as freezing and thawing (ASTM D 4842) or wetting and drying (ASTM D 4843). Weight loss or the number of such cycles that the material can withstand without failing is an indication of its physical stability. Other performance tests such as UCS, flexural strength, and permeability can be conducted on the material after each cycle to determine

the change in performance due to climatic stresses. No standards have been established for determining acceptance after durability testing, in part because the tests are accelerated and calibration to real disposal environments has not yet been achieved. Hence, the test is more useful for comparing one stabilization process with another (U.S. EPA, 1989g). Engineering design can be used to address stabilized wastes with poor durability.

3.2 LEACHING/EXTRACTION TESTS

The performance of stabilized wastes is generally measured in terms of leaching and extraction tests. A number of different leaching tests are available, and one or more may be required for regulatory approval. However, no single test program would use more than two or three of the leaching/extraction tests described below.

Leaching tests measure the potential of a stabilized waste to release contaminants to the environment. In all tests, the waste is exposed to a leachant and the amount of contaminant in the leachate (or extract) is measured and compared to a previously established standard, which may be a regulatory standard of baseline leaching data for the untreated waste. When using leaching tests to evaluate immobilization performance of S/S-treatment, potential effects of the reduction in contaminant concentration per unit mass of waste due to binder addition should be considered. The treated waste may give reduced contaminant concentration in the leachate due to waste dilution independent of any immobilization mechanism. Table 3-2 lists a number of the leaching tests that can be done to evaluate stabilization, along with information about the standard method, regulatory requirement, and purpose of each test. The extraction conditions of the leaching/extraction tests are summarized in Table 3-3 and Sections 3.2.1 through 3.2.16. Note that none of the tests described in this section have actually been field validated to verify the prediction of contaminant release.

As illustrated in Figure 4-1, the physical strength of cement-based S/S-treated waste develops over a period of several days. Many of the chemical reactions that cause immobilization occur more rapidly. Therefore, curing a sample for 28 days is not as critical for leaching tests, particularly those that require sample size reduction.

Many leaching tests require sample size reduction. The major issues in selecting a size reduction approach are (1) avoid contamination of the

TABLE 3-2. LEACHING/EXTRACTION TESTS

Test Procedure	Method	Material Application ^(*)			Purpose	Testing Application			
		U	S	L		R	I	E	
Toxicity Characteristic Leaching Procedure (TCLP)	EPA SW-846 Method 1311	X	X	X	To compare toxicity data with regulatory level. Includes VOCs. RCRA requirement.			X	X
Extraction Procedure Toxicity (EP Tox) Test	EPA SW-846 Method 1310	X	X	X	To evaluate leachate concentrations. RCRA requirement.			X	X
TCLP "Cage" Modification	53 FR 18792			X	Adds qualitative evaluation of stability to TCLP test. Proposed RCRA requirement.				X
California Waste Extraction Test (Cal Wet)	California Code Title 22, Article 11, pp. 1800.75-1800.82	X	X	X	To provide a more stringent leaching test for metals than TCLP. California requirement.			X	X
Multiple Extraction Procedure (MEP)	EPA SW-846 Method 1320	X	X	X	To evaluate waste leaching under acid conditions.			X	X
Synthetic Acid Precipitation Leach Test	EPA SW-846 Method 1312	X	X		For waste exposed to acid rain. For comment as RCRA requirement.			X	X
Monofilled Waste Extraction Procedure (MWEPP)	SW-924			X	For waste disposed in low-velocity saturated zone.			X	X
American Nuclear Society Leach Test	ANSI/ANS/16.1			X	To establish a diffusion coefficient for comparison of S/S-treated waste. NRC requirement.			X	X

TABLE 3-2. LEACHING/EXTRACTION TESTS (Continued)

Test Procedure	Method	Material Application ^(a)			Purpose	Testing Application			
		U	S	L		R	I	E	
Dynamic Leach Test	WTC, 1991, p. 17		X		To estimate diffusion coefficient for an S/S-treated waste.			X	X
Shake Extraction Test	ASTM D 3987-85		X	X	To provide a rapid means of obtaining an aqueous extract.			X	X
Equilibrium Leach Test (ELT)	WTC, 1991, p. 16		X	X	To evaluate maximum leachate concentrations.			X	X
Sequential Extraction Test (SET)	Bishop, 1986, p. 240		X	X	To evaluate buffering capacity with multiple extractions.			X	X
Sequential Chemical Extraction (SCE)	WTC, 1991, p. 17		X	X	To evaluate bonding nature of metals and organics in the S/S-treated waste.			X	X
Static Leach Test (Ambient or High Temperature)	MCC-1P, MCC-2P		X		To evaluate the leach resistance of a bulk specimen in static fluid.			X	X
Agitated Powder Leach Test	MCC-3S		X	X	To evaluate the leach resistance of a powdered specimen in agitated fluid.			X	X
Soxhlet Leach Test	MCC-5S		X		To evaluate the leach resistance of a bulk specimen in constantly refreshed pure leachant, typically at elevated temperature.			X	X

(a) Material Application Guide:
 U = Untreated samples
 S = S/S-treated sample
 L = Aqueous sample

(b) Testing Application Guide:
 R = Regulatory requirement
 I = Information for S/S process
 E = Experimental program

TABLE 3-3. EXTRACTION CONDITIONS

Test Method	Leaching Medium	Liquid:Solid Ratio	Particle Size	Number of Extractions	Time of Extractions
TCLP	Acetate buffer ^(a)	20:1	< 9.5 mm	1	18 hours
EP Toxicity	0.04 M acetic acid (pH = 5.0)	20:1	< 9.5 mm	1	24 hours
TCLP "Cage" Modification	Acetate buffer ^(a)	20:1	(b)	1	18 hours
Cal WET	0.2 M sodium citrate (pH = 5.0) or water for hexavalent chromium	10:1	< 2.0 mm	1	48 hours
Multiple Extraction Procedure	Same as EP Tox, then with sulfuric acid; nitric acid in 60:40 weight ratio adjusted to pH 3.0	20:1	< 9.5 mm	9 (or more)	24 hours per extraction
Synthetic acid precipitation leach test	^(c)	20:1	< 9.5 mm	1	18 hours
Monofilled Waste Extraction Procedure	Deionized water or other for specific site	10:1 per extraction	< 9.5 mm or monolith	4	18 hours per extraction
ANSI/ANS/16.1	Deionized water	Volume-to-surface ratio of 10 cm	Monolith length-to-diameter ratio between 0.2 and 5.0	12	Leachant renewed at 2.7 hours; 1, 2, 3, 4, 5, 14, 28, 43, and 90 days

TABLE 3-3. EXTRACTION CONDITIONS (Continued)

Test Method	Leaching Medium	Liquid:Solid Ratio	Particle Size	Number of Extractions	Time of Extractions
Dynamic leach test	Deionized water	(d)	Monolith length-to-diameter ratio between 0.2 and 5.0	(d)	Leachant renewed at 0, 1, 4, 7, 24, 31, 48, 72, 79, and 100 hours; or for more immobile species, at 0, 4, 24, 31, 72, 104, 168, and 196 hours
Shake extraction test ASTM D 3987-85	Deionized water	20:1	Particulate or monolith as received	1	18 hours
Equilibrium leach test	Deionized water	4:1	< 150 μm	1	7 days
Sequential extraction test	0.04 M acetic acid	50:1	< 9.5 mm	15	24 hours per extraction
Sequential chemical extraction	Five leaching solutions increasing in acidity	Varies from 16:1 to 40:1	< 45 μm	5	Varies from 2 to 24 hours
Static leach test MCC-1P and MCC-2P	(e)	(f)	Monolith	1	Samples for each of 3, 7, 14, 28, 56, 91, 182, and 364 days plus optional 12-month intervals

TABLE 3-3. EXTRACTION CONDITIONS (Continued)

Test Method	Leaching Medium	Liquid:Solid Ratio	Particle Size	Number of Extractions	Time of Extractions
Agitated powder leach test MCC-3S	(e)	10:1	50% <0.044 mm 50% between 0.074 and 0.149 mm	1	Samples for each of 28, 56, 91, 182, 273, and 364 days plus optional 12-month intervals
Soxhlet leach test MCC-55	Deionized water	Continuous flow of redistilled water	Monolith	1	Samples for each of 3, 7, and 14 days

(a) Either an acetate buffered solution with pH \approx 5 or acetic acid with pH \approx 3.0.

(b) Monolith tumbled in wire cage during TCLP type extraction.

(c) Sulfuric acid:nitric acid in 60:40 weight percent mix. pH adjusted with deionized water to 4.2 or 5.0 for site east or west of the Mississippi River, respectively.

(d) The renewal frequencies are selected based on a known diffusion coefficient. The surface-to-volume ratio must be selected to ensure the contaminant is detected. The renewal frequency must be selected to ensure nonequilibrium conditions prevail.

(e) Silicate water, deionized water, brine, or repository water.

(f) The volume of leachant is based on the measured geometric surface area of the sample. The volume-to-surface ratio must be between 10 and 200 cm.

sample, (2) avoid partitioning of contaminants into a specific size fraction, and (3) avoid loss of contaminants, particularly volatile organics. The typical steps in size reduction are sample fragmentation, grinding, and sizing. Fragmentation is best done with a hammer and anvil and should be minimized to avoid metal contamination of the waste. Grinding can be done with agate, dense alumina or tungsten-carbide equipment. Mortar and pestle or mechanical grinder can be selected based on the sample throughput of the laboratory. Sizing should be done with nylon or other nonmetal screens.

3.2.1 Toxicity Characteristic Leaching Procedure (TCLP)

In the TCLP test, waste samples are crushed to particle size less than 9.5 mm and extracted with an acetate buffer solution with a pH of 5 or an acetic acid solution with a pH of 3, depending on the alkalinity of the waste. Note, however, that the TCLP leachate is poorly buffered and that pH of the leachate upon contact with the waste may be much greater, as high as pH 10-11 or more, depending on the initial alkalinity of the waste. The acetate buffer is added only once at the start of the extraction. A liquid-to-solid ratio of 20:1 is used for an extraction period of 18 hours. The leachate is filtered prior to conducting the contaminant analyses. This test is used to evaluate the leaching of metals, volatile and semivolatile organic compounds, and pesticides from wastes that are categorized under RCRA as characteristically toxic and can be used on other wastes as well.

The TCLP test has been most commonly used by U.S. EPA and state agencies to evaluate the leaching potential of stabilized wastes, and TCLP is the test required by RCRA implementing regulations (40 CFR Part 261) for determining toxicity. Measurement of pH in the extract can help elucidate the pH-dependence of contaminant leaching.

The TCLP does not provide data on long-term stability (see Section 4.7). In fact, recent studies show a significant effect of curing time on both TCLP results and the chemical structure of the stabilized waste, as evidenced by spectroscopic analyses (Akhter and Cartledge, 1971; Cartledge, 1992). These observations underline the limitations of the TCLP test as an indicator of the long-term leaching of stabilized waste and emphasize the need for other types of leaching data.

3.2.2 Extraction Procedure Toxicity (EP Tox) Test

The EP Tox test is the precursor of and is similar to the TCLP. Only one concentration of acetic acid solution (pH of 5) is used. The liquid-to-solid ratio starts at 16:1 and may increase as additional acid solution is added as needed to adjust the pH during the 24-hour test duration. Results of the EP Tox test are generally comparable to results of TCLP tests at pH 5 but may differ significantly at pH 3. As with the TCLP, the measurement of pH in the extract can help determine the pH-dependence of contaminant leaching. EP Tox cannot be used to assess volatiles.

3.2.3 TCLP "Cage" Modification

The standard TCLP (Section 3.2.1) requires that all samples be passed through a 9.5-mm screen (or meet surface area requirements) before leaching. However, this requirement may not be appropriate for S/S-treated wastes that have been solidified to withstand the environmental stresses encountered in a landfill. Studies in 1988 (53 FR 18792) using a modification wherein the S/S-treated waste was tumbled in a cage indicated that well-stabilized wastes may remain more or less intact, whereas poorly stabilized wastes are significantly degraded. TCLP "cage" modification, proposed as a modified TCLP, requires no preliminary size reduction of samples. The resulting leachate can be used for analytical determinations of organics and metals.

The TCLP "cage" modification is still under development and currently has no regulatory status.

3.2.4 California Waste Extraction Test (Cal WET)

The Cal WET is used by the State of California to classify hazardous wastes. The leachate is a sodium citrate buffer, the liquid-to-solids ratio is 10:1, and testing lasts 48 hours. The Cal WET test applies a soluble threshold limit concentration (STLC) as the regulatory standard. STLC standards for metal concentrations in the leachate are similar to those for the TCLP. However, California regulates several additional metals, such as copper, beryllium, nickel, and zinc, and a number of organic compounds, such as PCBs and pesticides. The Cal WET test also develops a Total Threshold Limit Concentration (TTLC) which is equivalent to a Total Waste Analysis

(TWA). The TWA gives the concentration of priority pollutants, organics, metals, and other substances of interest in the waste.

The Cal WET is a much more aggressive test than either the TCLP or EP Tox and almost always extracts higher levels of contaminants. This aggressive characteristic of the Cal WET has led to the development of a category of hazardous waste specific to the State of California, referred to as "California-only" hazardous waste. This specifically refers to a waste that fails the Cal WET but passes the TCLP. If the waste fails both the Cal WET and the TCLP, then the requirements of both California and the U.S. EPA must be met.

3.2.5 Multiple Extraction Procedure (MEP)

Like the EP Tox, the MEP involves a first extraction with acetic acid, followed by at least eight extractions with a synthetic acid rain solution (sulfuric/nitric acid adjusted to pH 3). The MEP is intended to simulate leaching in an improperly designed landfill where the waste could come into contact with large volumes of acidic leachate. One advantage of the MEP over the TCLP is that the MEP gradually removes excess alkalinity in the waste over time. Thus, the leaching behavior of the contaminants (particularly metal contaminants) can be evaluated as a function of decreasing pH, where the solubility of most metals increases.

The MEP has been used in the regulatory environment for delisting U.S. EPA-listed wastes.

3.2.6 Synthetic Acid Precipitation Leach Test

The TCLP (Section 3.2.1) and the EP Tox test (Section 3.2.2) apply to disposal in a sanitary or municipal landfill, a scenario that does not match the disposal setting of many S/S-treated wastes. A sanitary landfill environment is characterized by large concentrations of low-molecular-weight organic acids, such as acetic acid, that result from anaerobic fermentation of organic waste. The Synthetic Acid Precipitation Leach Test is similar to the TCLP, but the initial liquid-solid separation step has been eliminated and the acetate buffer extraction fluid has been replaced by a dilute nitric acid/sulfuric acid mixture. The Synthetic Acid Precipitation Test simulates acid rain as opposed to simulating a leachate in a sanitary or municipal landfill.

3.2.7 Monofilled Waste Extraction Procedure (MWEP)

The MWEP involves multiple extractions of a monolith or of crushed waste with distilled/deionized water. The sample is crushed to less than 9.5 mm, or it can be left intact if it passes the U.S. EPA SW-846 Structural Integrity Test. The liquid-to-solid ratio is 10:1, and the sample is extracted with water four times at 18 hours per extraction. The MWEP is intended to derive leachate compositions in monofilled disposal facilities or to obtain leachate for testing the compatibility of lining materials with the leachate. Note that this procedure has not yet been approved by EPA.

3.2.8 American Nuclear Society Leach Test (ANSI/ANS/16.1)

The ANSI/ANS/16.1 leaching test is intended mainly to develop a figure-of-merit for comparing the leaching resistance of S/S-treated waste. The results of the leaching tests are recorded in terms of cumulative fraction leached relative to the total mass of the waste sample. Then, results can be used to derive an effective diffusion coefficient and a leachability index, or figure-of-merit. The ANSI/ANS/16.1 is conducted over a period of 90 days and is intended to indicate contaminant release rate, unlike the batch tests described in preceding sections. Typically, the leachant is distilled water, but other solutions, such as simulated groundwater, may also be used.

3.2.9 Dynamic Leach Test (DLT)

The DLT is a modified version of the ANSI/ANS/16.1 test (Section 3.2.8). The renewal frequency of the leaching solution and the leaching volume-to-solid ratio are adjusted based on an estimated or calculated diffusion coefficient and results from batch extraction tests such as the Equilibrium Leach Test (ELT) (Section 3.2.11). The solution renewal frequency is chosen to ensure that equilibrium has not been reached. The leaching volume-to-solid ratio is chosen to ensure that the contaminant can be detected. Data from the DLT can be used to determine a diffusion coefficient that can be used to predict long-term leaching performance (Stegemann and Côté, 1991). Like all the tests described in this section, field validation has not yet been done to verify the leaching prediction.

3.2.10 Shake Extraction Test

The shake extraction test is applicable only to inorganic compounds. It involves the extraction of a solid waste with Type IV reagent water in a rotary agitator for 18 hours. The procedure is intended as a rapid means of obtaining an aqueous extract and is not intended to simulate site-specific leaching conditions.

3.2.11 Equilibrium Leach Test (ELT)

The ELT involves static leaching of hazardous constituents by distilled water. The particle size of the crushed sample ($\leq 150 \mu\text{m}$) is much smaller than that for TCLP and EP Tox to allow greater contact surface area and to reduce the time needed to achieve equilibrium. Water is added once at a liquid-to-solid ratio of 4:1, and the sample is agitated for 7 days. Like MWEF (Section 3.2.7), ELT can be used to determine equilibrium leachate concentrations under mild leaching conditions.

3.2.12 Sequential Extraction Test (SET)

The SET is used to evaluate the waste buffering capacity and alkalinity of cement-based S/S-treated waste. Unlike acid neutralization capacity (Section 3.3.7), the SET involves 15 sequential extractions of one sample of crushed waste with particle sizes between 2.0 and 9.5 mm. Each extraction is performed on a shaker table for 24 hours with the same type of extraction solution (0.04 M acetic acid solution) and liquid-to-solid ratio of 50:1. With each extraction, 2 meq/g of acid is added to the ground waste. The pH is measured and the leaching solution is filtered. After the fifteenth extraction, the remaining solids are digested with three more extractions in which more concentrated acid solutions are used. These last three extractions are combined for analysis.

3.2.13 Sequential Chemical Extraction (SCE)

The objective of the SCE test is to evaluate the nature and bonding strength of metals and organics in S/S-treated waste. This test was originally developed for sediments and adapted to evaluate inorganic waste constituents in a stabilized matrix. Like SET, the test involves sequential extraction of a sample. Unlike SET, however, the leaching solution increases in

acidity from neutral to very acidic with each sequential extraction. The particle size of the sample is also very small (less than 45 μm).

3.2.14 Static Leach Test Method (Ambient- and High-Temperature)

The Materials Characterization Center (MCC) at Pacific Northwest Laboratory (PNL), under a project for the United States Department of Energy (U.S. DOE) developed the static ambient- and high-temperature leach tests as part of a series of standard methods designed to evaluate the chemical durability of S/S-treated nuclear waste. The static leach tests use representative, monolithic specimens of the S/S-treated waste. Specimens of known geometric surface area are immersed in a reference leachant held at a specified temperature. The immersion period can vary from 3 days to many years. Temperatures ranging from 40°C to 190°C are used. The leachant is not agitated during the immersion period. This test is used to evaluate the leach resistance of monolithic S/S-treated waste.

3.2.15 Agitated Powder Leach Test Method

The MCC also developed the agitated powder leach test as part of a series of standard methods designed to evaluate the chemical durability of nuclear waste forms. The agitated leach test uses representative powdered waste specimens of the waste form. The powder is immersed in a reference leachant at a constant ratio of leachant volume to specimen mass of 10 ml/g. Test temperatures range from 40°C to 190°C. The powder and leachant are agitated by constant rolling of the specimen holder. The test is used to determine the maximum concentration of chemical elements in solution from the waste form under steady-state conditions, in closed, agitated systems.

3.2.16 Soxhlet Leach Test Method

The MCC developed the Soxhlet leach test as part of a series of standard methods designed to evaluate the chemical durability of S/S-treated nuclear waste. Although designed primarily for glass and ceramic waste forms, the Soxhlet leach test is applicable to any monolithic S/S-treated waste and the individual components of macroscale physical composite S/S-treated waste. Monolithic specimens of known geometric surface area are suspended in a continuously flowing stream of redistilled water. The precise test temperature

is determined by the barometric pressure in the laboratory but is near 100°C. The test measures the normalized mass losses from the specimen due to a constant flow of redistilled water at its boiling point under local conditions.

3.3 CHEMICAL TESTS AND ANALYSES

Treatability testing usually involves collecting chemical data to define waste compositions and to assess binder performance. Table 3-4 describes a number of these chemical parameters and their applicability to evaluating untreated waste, S/S-treated waste, and aqueous samples. Total waste analyses of metals, VOCs, and BNAs can be applied to characterize untreated waste, S/S-treated waste, or leachate. Other chemical tests may be needed for optional information or to support research. For example, it may be necessary to screen for chemicals that interfere with S/S treatment, if historical information or other sources of information indicate that such chemicals may be present. The chemical test program should be developed based on specific waste and site characteristics.

3.3.1 pH

The pH is a measure of the hydrogen ion activity and indicates the acid-to-base balance of a material. The pH of untreated and S/S-treated wastes, waste leachates, or soils from the intended disposal site can be analyzed by U.S. EPA SW-846 Method 9045. Equal weights of soils/solids and deionized water are mixed and allowed to settle for 1 hour. The pH of the supernatant liquid is then measured electrometrically. The leachability of many metals is a function of the pH. The pH may also affect the leachability of some base, neutral, and acid (BNA) fraction compounds.

3.3.2 Oxidation/Reduction Potential (Eh)

The oxidation/reduction potential, Eh, characterizes the electrochemical state of the media being measured. Data on the Eh of the untreated or treated waste, waste leachates, or soils from the intended disposal site can be very useful. The Eh can be determined by ASTM D 1498. Numerous metals can exist in multiple oxidation states. For example, chromium can exist as Cr(III) or Cr(VI) and arsenic as As(III) or As(V). The leachability of these

TABLE 3-4. CHEMICAL TESTS

Test Procedure	Method	Material Application			Purpose	Testing Application		
		U	S	L		R	I	E
pH (liquid)	EPA SW-846 Method 9040			X	To determine solution pH. pH of leachate and aqueous phase of disposal environment can help estimate metal leaching tendency.	X	X	X
pH (solid)	EPA SW-846 Method 9045	X	X		Leachability of hazardous constituents (e.g., metals) may be governed by the pH. RCRA corrosivity limits are pH 2 and 12.5.	X	X	X
Oxidation/reduction potential (Eh)	ASTM D 1498-76			X	Leachate Eh can indicate potential stability of chemical species. Eh of leachate and aqueous phase of disposal environment can help estimate metal leaching tendency.			X
Major oxide components	ASTM C 114-88			X	Mineralogy of the stabilized/solidified waste may aid in interpretation of leach test results.			X X
Total organic carbon (TOC)	EPA SW-846 Method 9060	X	X	X	Used to approximate the nonpurgeable organic carbon in wastes and treated solids. Useful in approximating interference levels.	X	X	X
Oil and grease - sludge	EPA SW-846 Method 9071			X	May be used to compare the leachable oil and grease from the treated and untreated wastes. Also a possible interference.	X		X
- fluids	EPA SW-846 Method 9070			X				

TABLE 3-4. CHEMICAL TESTS (Continued)

Test Procedure	Method	Material Application			Purpose	Testing Application		
		U	S	L		R	I	E
Electrical conductivity	EPA Method 120.1 EPA SW-846 Method 9050		X	X	To compare ion concentrations in leachate to ion concentrations in receiving waters.			X
Acid neutralization capacity (ANC)	WTC, 1991, p. 16	X	X		To determine pH buffering capacity of S/S-treated waste.			X
Generalized Acid Neutralization Capacity (GANC)	Isenburg and Moore, 1990	X	X		To determine pH buffering capacity of S/S treated waste.			X
Alkalinity	EPA Method 403			X	To indicate the ability of a solution to neutralize acid.			X X
Total dissolved solids (TDS)	EPA Method 209B			X	To measure dissolve solids content of leachate.			X X
Reactive cyanide	EPA SW-846 Section 7.3.3.2	X	X	X	To determine potential for generation of hazardous fumes. RCRA regulatory requirement, 250 mg HCN/kg guideline.			X X X
Reactive sulfide	EPA SW-846 Section 7.3.4.1	X	X	X	To determine potential for generation of hazardous fumes. RCRA regulatory requirement, 500 mg/H ₂ S/kg guideline.			X X X
Reactivity of silica aggregates	ASTM C 289-87			X	To evaluate potential alkali-silica reaction in aggregates.			X X
Metals analysis	EPA SW-846 (Methods 3010, 3020, 3050, and 6010 or 7000)	X	X	X	Used to define metals content of untreated and treated wastes or TCLP leachates of such wastes for numerous specific metals.			X X X

TABLE 3-4. CHEMICAL TESTS (Continued)

Test Procedure	Method	Material Application			Purpose	Testing Application		
		U	S	L		R	I	E
Volatile organic compounds (VOCs)	EPA SW-846 Methods 5030 and 8240	X	X	X	Used to define VOC concentrations in S/S-treated wastes and untreated wastes or in waste extracts.	X	X	X
Base, neutral and acid (BNA) organic compounds	EPA SW-846 Methods 3510, 3520, 3540, and 8270	X	X	X	Used to define BNA concentrations of wastes or waste leachates or extracts from treated or untreated wastes.	X	X	X
Polychlorinated biphenyls (PCBs)	EPA SW-846 Methods 3540, 3520, and 8080; EPA Method 608	X	X	X	Used to define PCB concentrations of wastes or waste extracts in treated or untreated wastes.	X	X	X
Mercury	EPA SW-846 Method 7470		X		Determine Hg content in waste or waste leachates.		X	X
Pesticides	EPA SW-846 Methods 3510 and 8080 or 8081		X		Determine pesticide content in waste or waste leachates.		X	X
Herbicides	EPA SW-846 Method 8150 or 8151		X		Determine herbicide content in waste or waste leachates.		X	X
Ion measurements	Std. Method No. 4110		X		Used to determine leachate anionic species concentrations in aqueous solutions.			X

TABLE 3-4. CHEMICAL TESTS (Continued)

Test Procedure	Method	Material Application			Testing Application		
		U	S	L	R	I	E
<u>Interferants Screen</u>							
Oil and Grease	EPA SW-846 Method 9071	X	X	X			X X
Potassium	EPA SW-846 Method 3050, and 6010	X	X	X			
Sodium	EPA SW-846 Method 3050 and 6010	X	X	X			
Fluoride	EPA Method 300.0	(a)	(a)	X			
Chloride	EPA Method 300.0	(a)	(a)	X			
Orthophosphate	EPA Method 365.1	(a)	(a)	X			
Ammonia	EPA Method 350.2	(a)	(a)	X			
Nitrate	EPA Method 300.0	(a)	(a)	X			
Sulfate	EPA Method 300.0	(a)	(a)	X			

Used to screen for the presence of elements that could adversely affect S/S process or performance.

(a) Extraction or digestion required.

Material Application Guide:
 U = Untreated Samples
 S = S/S-treated Samples
 L = Liquid Samples

Testing Application Guide:
 R = Regulatory Requirement
 I = Information for S/S Process
 E = Experimental Program

metals depends on their oxidation state. Therefore, Eh can indicate the stability of various chemical species in the waste's chemical environment.

3.3.3 Major Oxide Components

The major oxide components can be used to characterize the mineralogy of the S/S-treated waste. Analytical techniques for determining SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , MgO , and loss on ignition are described in ASTM C 114. Between 10 and 30% of cementitious solids will be in the form of oxides.

3.3.4 Total Organic Carbon (TOC)

The TOC analysis measures the overall level of organic compounds present in a liquid, sludge, or solid sample. TOC is measured by U.S. EPA SW-846 Method 9060. This method uses combustion with infrared, thermoconductivity, or other detection. The TOC results can be used to approximate the levels of nonpurgeable organic carbon and to estimate the potential for organic interference in the S/S process.

3.3.5 Oil and Grease

Oil and grease analysis determines the total content of oil and grease in a sample. This analysis can be done by U.S. EPA SW-846 Method 9070 or 9071. The determination before and after treatment provides a method of assessing the effectiveness of the S/S process in immobilizing oil and grease in the waste. Oil and grease analysis of asphaltic solid leachates is important for determining whether the S/S process aids in stabilizing oil and grease or whether the asphalt increases oil and grease leachability. In addition, oil and grease interfere with cement or pozzolan-based S/S treatment.

3.3.6 Electrical Conductivity

The electrical conductivity of a solution is a measure of its ability to carry current. Conductivity varies with the concentration and type of ions present. Solution conductivity can be measured by U.S. EPA Method 120.1 or U.S. EPA SW-846 Method 9050. Conductivity of leachates from untreated and S/S-treated wastes can be compared to find the relative ionic concentrations in the two solutions. In addition, test results from untreated and S/S-treated waste leachates can be compared with conductivities of natural

surface and subsurface waters in the vicinity of the demonstration site and/or potential disposal site. Wide differences in the conductivity of leachate and natural waters create the potential for the waste leachate to cause conductivity fluctuations in adjacent receiving waters.

3.3.7 Acid Neutralization Capacity (ANC and GANC)

These buffering capacity tests indicate the capacity of the S/S-treated waste to maintain an elevated pH when exposed to acidic solutions. The ANC test involves separate extraction of S/S-treated waste samples with leaching solutions of varying levels of acidity. Ten waste samples are predried and crushed to a particle size of -100 mesh. Each sample is extracted for 24 hours in one of 10 nitric acid solutions. The acid equivalents per gram of solid increases incrementally from sample 1 to sample 10. Following the extraction, the pH of each solution is measured. The amount of decrease in pH of the leach solutions with each increase in acid concentration indicates the buffering capacity of the S/S-treated waste. Smaller decreases indicate higher buffering capacity. The higher the buffering capacity, the greater the possibility of maintaining alkaline conditions conducive to metal retention. The GANC is a similar test developed to be consistent with the TCLP test (Isenburg and Moore, 1992).

3.3.8 Alkalinity

Alkalinity indicates the capacity of a solution such as a leachate to neutralize acid solutions to specific pH levels. It can be measured by U.S. EPA Method 403.

3.3.9 Total Dissolved Solids (TDS)

The TDS analysis indicates the total quantity of solid material dissolved in a solution. It can be measured by U.S. EPA Method 209B. The TDS levels in leaching solutions can be used to track the degradation of S/S-treated waste solid or leaching of constituents from the sample. TDS is also a drinking water standard.

3.3.10 Reactive Cyanide and Sulfide

The analyses for reactive cyanide and sulfide apply to waste containing cyanide- or sulfide-bearing material. Sulfide can be present in the waste either as a natural waste constituent or as a binder additive. If waste exposed to a pH in the range of 2 to 12.5 can generate toxic gases, vapors, or fumes in sufficient quantity to present a danger to human health or the environment, it is deemed to contain reactive cyanide or sulfide. The tests for reactive cyanide and sulfide are described in U.S. EPA SW-846 (1986c) Section 7.3. Testing for reactive cyanide and sulfide may be required for some RCRA wastes under regulation 40 CFR 261.23-(a)(5).

3.3.11 Reactivity of Silica Aggregates

The test for reactivity of silica aggregates measures the propensity of silica in the waste to react with alkaline components of Portland cement/ concrete mixtures or similar S/S binders. The potential for silica in suspect aggregates to react with alkaline compounds is determined by ASTM C 289. Reactive silica and alkaline compounds combine to form silicate-alkali gels that expand to cause internal stress in the S/S-treated waste. The internal stress can result in cracking or spalling.

3.3.12 Metal Analysis

Metal analyses can be applied to aqueous leach solutions to determine the concentrations of metals leached from the S/S-treated waste. Metal analysis tests can also be used, following a suitable strong acid digestion step, to measure the total metal concentrations in the untreated or S/S-treated waste. Metals can be determined in accordance with U.S. EPA SW-846 Methods 6010 (analysis by inductively coupled plasma atomic emission spectroscopy [ICP]) or 7000 and associated 7000 series methods (analysis by atomic absorption spectroscopy [AA]). The material should be pretreated with the appropriate digestion procedure (U.S. EPA SW-846 Methods 3005, 3010, 3020, 3040, and 3050).

3.3.13 Volatile Organic Compounds

The VOC test evaluates the types and concentrations of low-boiling-point organic materials present in a sample. U.S. EPA SW-846 Method 8240

describes the extraction and analysis of VOCs by gas chromatography/mass spectrometry (GC/MS) techniques. This method will quantify most organic compounds with a boiling point below 200° C. Concentrations of VOCs in solvent extracts of untreated and S/S-treated wastes can be used to indicate if the compounds have been stabilized during the S/S process, provided measures were taken to account for volatilization or degradation. Concentrations of VOCs in TCLP extracts can indicate the aqueous leachability of the VOCs from S/S-treated wastes. Extreme caution must be paid to the possible release of VOCs during waste sampling, handling, storage, treatability testing, or analysis. The potential for volatilization of the organic contaminants is so great that a mass balance is generally needed to demonstrate that a reduction in volatile organic content after treatment is truly due to immobilization as opposed to volatilization. Although organic leaching may be low in aqueous leaching tests, this may also be a result of low solubility of the organic in water rather than immobilization of the organic.

3.3.14 Base, Neutral, and Acid (BNA) Organic Compounds

The analyses for basic, neutral, and acidic organic compounds are performed by extraction (U.S. EPA SW-846 Method 3510, 3520, or 3540) followed by GC/MS analysis (U.S. EPA SW-846 Method 8270). Certain BNAs can be target contaminants for S/S. Measurements of BNAs in solvent extracts of untreated and treated wastes can determine the fate of organics during the S/S process, provided measures were taken to account for volatilization or degradation. Data on concentrations of BNAs in aqueous extracts can be used to assess the effectiveness of the S/S process in reducing the amount of aqueous leachable BNAs. However, like VOCs, certain BNAs have low aqueous solubility. Thus, the immobilization of such compounds should be evaluated in organic solvent extracts of appropriate polarity.

3.3.15 Polychlorinated Biphenyls (PCBs)

The PCB analysis measures the concentration of polychlorinated biphenyls. PCBs are determined by extraction (U.S. EPA SW-846 Method 3540 or 3520), followed by GC/MS analysis (U.S. EPA SW-846 Method 8080) or by U.S. EPA Method 608. Quantities of PCBs in solvent extracts of untreated and S/S-treated wastes can determine the fate of the PCBs during the S/S process,

provided that measures were taken to conduct mass balances and account for any PCB volatilization during the treatability study. Conducting aqueous leaching tests on PCB-contaminated wastes is generally fruitless because of the low aqueous solubilities of PCB compounds.

3.3.16 Other Contaminant Analyses

Several of the more common waste contaminants not specifically included in Sections 3.3.1 through 3.3.15 are mercury, pesticides, and herbicides. Analytical methods are available for measuring such constituents in either aqueous or organic solvent extracts (see Table 3-4).

3.3.17 Anion Measurements

Anions can be measured by ion chromatography, as described by Water and Wastewater Standard Method 4110 or by U.S. EPA Method 300. This analysis is used to determine the concentration of anions in leach solutions.

3.3.18 Interferants Screen

Interferants screening tests involve a series of analyses for concentrations of materials that can interfere with S/S treatment. The waste is tested for oil and grease, potassium, sodium, fluoride, chloride, ortho-phosphate, ammonia, nitrate, and sulfate.

3.4 BIOLOGICAL TESTS

Biological tests applicable to S/S processes include biodegradation tests and bioassays. Table 3-5 shows some representative biological tests and presents information about the standard methods for each. Biological tests are typically conducted only in special circumstances such as testing the potential biodegradability of organic binders or the aquatic toxicity of the treated waste.

Biological testing can be used to measure either the degradation of the matrix leading to release of contaminants or the alteration of contaminant properties to increase their mobility or toxicity. Standard tests for matrix degradation exist, but none are available for biologically induced changes in the contaminants.

TABLE 3-5. BIOLOGICAL TESTS

Test Procedure	Method	Material Application			Purpose ^(e)
		U	S	L	
<u>Biodegradation Tests</u>					
Biodegradability of plastics	ASTM G 21-90, G 22-76		X		To determine whether biodegradation may decrease long-term stability of S/S wastes.
Biodegradability of paints	ASTM D 3273-86, D 3274-82, D 3456-86		X		To determine whether biodegradation may decrease long-term stability of S/S wastes.
Biodegradability of alkylbenzene sulfonates			X		To determine whether biodegradation may decrease long-term stability of S/S wastes.
<u>Bioassays</u>					
Assessing the hazard of a material to aquatic organisms	ASTM E 1023-84	X	X	X	To evaluate acute aquatic toxicity at a point source discharge, e.g., a leachate collection system. May be required by state or federal ARARs.

^(e) Testing Application: Biological testing is normally applied as part of an experimental program.

Material Application Guide:

- U = Untreated Samples
- S = S/S-treated Sample
- L = Liquid Sample

Biodegradation tests are used to measure the biodegradability of various waste materials, almost exclusively organic binders such as asphalt or plastic. Biodegradation is one possible degradation mechanism for such binders. At present, the U.S. EPA recommends no particular methods for evaluating the biodegradation of S/S-treated wastes. In general, binders that produce an alkaline environment (e.g., Portland cement-based processes) are not favorable for microbial activity; however, this may not be true for proprietary binders and processes that are tailored to treat organic wastes.

Bioassays are performed only when the proximity of the treated waste disposal site poses a threat to an aquatic community. If a site undergoing S/S treatment has a point source discharge, such as from a leachate collection system, bioassays may be required to meet federal or state ARARs. However, note that the alkaline nature of many S/S binders may elicit a toxic response during the bioassay, which may far outweigh any acute toxic response from the contaminants in the waste.

Although the results of bioassays may provide evidence of reduced toxicity after S/S treatment, predictions of toxicity from bioassays are highly site-specific and must be combined with data on exposure pathways for a specific site. Acute bioassays may be performed rapidly and at low cost, but they do not predict the response of the test organism to chronic, low-level contamination. The bioassay techniques that most accurately predict long-term environmental effects are expensive and time-consuming.

3.5 MICROCHARACTERIZATION

Special methods developed for mineralogic and materials science testing are applicable to specialized, detailed characterization of materials for S/S treatment (Hannak and Liem, 1986). These nonroutine tests can be applied for detailed analysis of the structure of S/S-treated waste or to better understand the physicochemical form of the target contaminants. Table 3-6 lists a few of the many tests that can be applied to microcharacterization. However, note also that microcharacterization tests provide special research and problem-solving tools that would not be used in the vast majority of S/S treatability studies.

TABLE 3-6. MICROCHARACTERIZATION TESTS

Test Procedure	Method	Purpose ^(a)
X-Ray Powder Diffraction		To identify crystalline matrix and contaminant phases
Fourier Transform Infrared (FTIR) Spectroscopy	ASTM E 1252-88 ASTM E 168-88	To identify the presence or absence of functional groups in a molecule
Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Analysis (EDAX)		To examine the physical structure and chemical makeup of the surface of a material on the microscopic scale
Nuclear Magnetic Resonance (NMR) Spectroscopy		To identify and characterize molecules
Optical Microscopy Transmitted Light, Reflected Light, and Polarized Light	ASTM C 856-83 ASTM C 295-90	To study microstructure of S/S-treated waste

^(a) Microcharacterization tests are typically applied to treated waste as part of an experimental program.

3.5.1 X-Ray Diffraction

X-ray diffraction examines the crystal structure of a material. X-rays are scattered and diffracted by the lattice structure of crystals, yielding patterns characteristic to various crystals based on the lattice spacing. The crystalline components of a mixture, including crystalline phases of the contaminant or contaminants, in amounts of 1% or more can be identified individually by the X-ray diffraction patterns produced. However, noncrystalline components are not detected.

3.5.2 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectroscopy analytical technique can identify the presence or absence of functional groups within a molecule. The class or type of compound can be deduced, although positive identification of the exact

composition of the unknown is not always possible. This technique can be useful in determining the physicochemical form of the contaminant in either treated or untreated waste.

3.5.3 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDXA)

SEM is a technique for examining the surfaces of solid materials. The method provides a large depth of field, so it is frequently possible to observe three-dimensional structures in a sample. By adding an EDXA detector to the SEM, it is possible to obtain simultaneous, multi-element analysis. This technique can be useful in determining the physicochemical form of the contaminant in either treated or untreated waste.

3.5.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy identifies and characterizes molecules. Data from NMR analysis delineate complete sequences of groups or arrangements of atoms in a molecule. This technique has been used successfully to characterize the physicochemical form of the contaminant in the treated waste and to help elucidate the mechanism of contaminant immobilization.

3.5.5 Optical Microscopy

The arrangement of phase structures in a solid sample can be observed and measured by thin section transmission microscopy or reflected light microscopy. Optical properties, such as refractive index, also can be measured. Additional petrographic information can be obtained by using polarized light microscopy. This is another possible analytical tool for characterizing contaminant speciation and physicochemical form.

4 STATUS OF SOLIDIFICATION/STABILIZATION TECHNOLOGY

This chapter of the TRD reviews and summarizes existing literature on a wide variety of subjects and issues pertaining to S/S technology. A number of books and summary reports on various aspects of S/S are available. These resource documents include the following:

- ASTM (1989), STP 1033, *Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes*, American Society for Testing and Materials.
- ASTM (1992), STP 1123. *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, American Society for Testing and Materials.
- Conner, J.R. (1990), *Chemical Fixation and Solidification of Hazardous Waste*, Van Nostrand Reinhold.
- Czupyrna, G., et al. (1989), *In Situ Immobilization of Heavy-Metal-Contaminated Soils*, Noyes Data Corporation
- Pojasek, R. (1979), *Toxic and Hazardous Waste Disposal, Options for Solidification/Stabilization*, Ann Arbor Science Publishers
- U.S. EPA (1990e), *Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils*
- U.S. EPA (1989b), *Immobilization Technology Seminar, Speaker Slide Copies and Supporting Information*
- U.S. EPA (1986c), *Handbook for Solidification/Stabilization of Hazardous Wastes*
- U.S. EPA (1983), *Feasibility of In Situ Solidification/Stabilization of Landfilled Hazardous Wastes*
- U.S. EPA (1980), *Guide to the Disposal of Chemically Stabilized and Solidified Waste.*

Overview-type information on specific S/S issues can be found in Sections 4.1 through 4.10. Sections 4.1 and 4.2 describe the types of S/S binders and their binding mechanisms. Applicable waste and contaminant types are discussed in Section 2.2.3.2. Section 4.3 outlines the interferences to S/S that

arise from waste constituents. Section 4.4 deals with S/S treatment of organic contaminants. Section 4.5 discusses air emissions from organic constituents, particulates, and other emissions. Sections 4.6 and 4.7 describe leaching mechanisms and long-term stability. Sections 4.8 and 4.9 discuss reuse and disposal issues. Section 4.10 gives cost estimates for S/S testing, materials, and processes. The publications referenced in Chapter 7 provide additional technical details.

4.1 S/S PROCESSES AND BINDERS

Solidification/stabilization processes are "nondestructive" methods to immobilize the hazardous constituents in a waste. S/S processes are nondestructive in the sense that they do not remove or reduce the quantities of these constituents. Typically, S/S processes physically sorb, encapsulate, or change the physicochemical form of the pollutant in the waste, resulting in a less leachable product. Concentrations of contaminants in the treated waste are often lower than in the untreated waste, primarily because of incidental dilution by the binder rather than by destruction or removal of the contaminants.

S/S processes can generally be grouped into inorganic processes (cement and pozzolanic) and organic processes (thermoplastic and thermosetting polymers). In addition to the individual use of inorganic and organic binders, some systems combine organic with inorganic binders. For example:

- Diatomaceous earth with cement and polystyrene
- Polyurethane with cement
- Polymer gels with silicate and lime cement

The basic S/S processes are generic, and many of the basic materials are readily available. A variety of additives are used to promote the development of specific chemical or physical properties. Pretreatment may also be used to better prepare the waste for treatment by an S/S process.

S/S technology is offered commercially by a large number of vendors. The specifics of vendor technology are in most cases protected as proprietary and are not disclosed to the potential user except under agreement of confidentiality. The majority of vendors use conventional S/S technology supple-

mented by a variety of additives and know-how from previous experience in applying this technology.

4.1.1 Inorganic Binders

The two principal types of inorganic binders are cement binders and pozzolanic binders (lime, kiln dust, fly ash). A pozzolan is a material containing silica or silica and alumina that has little or no cementation value itself but, under some conditions, can react with lime to produce cementitious material. Cement-based and pozzolanic processes or a combination of cement and pozzolans are the methods of choice in the S/S industry today. This probably is attributable to the low cost of the materials, their applicability to a wide variety of waste types, and the ease of operation in the field. The most common inorganic binders are:

- Portland cement
- Lime/fly ash
- Kiln dust (lime and cement)
- Portland cement/fly ash
- Portland cement/lime
- Portland cement/sodium silicate

These binders are routinely used to solidify water-based waste liquids, sludges, and filter cakes. The lime/fly ash process probably has been used most extensively in the United States, in terms of the total volume of waste treated. The treatment of flue gas desulfurization (FGD) sludges from coal-fired power plants accounts for much of the lime/fly ash process application. Specifications are available for a wide variety of cement and pozzolanic materials. ASTM standards for these materials include:

- C311: *Method for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete*
- C400: *Test Methods of Testing Quicklime and Hydrated Lime for Neutralization of Waste Acid*

- C593: *Specification for Fly Ash and Other Pozzolans for Use with Lime*
- C618: *Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete*
- C821: *Specification for Lime for Use with Pozzolans*
- C911: *Specification for Quicklime, Hydrated Lime, and Limestone for Chemical Uses*
- C977: *Specification for Quicklime and Hydrated Lime for Soil Stabilization*

Most concentrated industrial or Superfund wastes contain complex mixtures of contaminants, and a generic inorganic binder will frequently stabilize one contaminant to a greater extent than another. Certain constituents, such as oils and anions, can retard or prevent the setting of the binder. Chemicals that interfere with cement- and pozzolan-based processes are discussed in greater detail in Section 4.3. Complications in the stabilization of certain types of contaminants are discussed in Sections 4.2 and 4.4.

4.1.1.1 Cement Processes

Of the inorganic binders, Portland cement has probably had the greatest diversity of application to a wide range of hazardous wastes, especially combined with fly ash. Because cement is a common construction material, the materials and equipment are mass-produced and generally inexpensive compared with energy-intensive treatment processes such as vitrification and incineration (McDaniel et al., 1990). Many types of cement have been used for a variety of purposes, but only those classified as Portland cement, which is primarily composed of anhydrous calcium silicate, have seen substantial use in S/S technology (Conner, 1990). Other types of cement, such as alumina or Sorel cement, have not been used extensively for S/S, primarily because of their high cost.

Advantages of cement-based processes include (McDaniel et al., 1990 and Conner, 1990):

- Availability of materials locally on a worldwide basis
- Low cost of materials and mixing equipment

- Use of naturally occurring minerals as raw materials for the matrix
- Ability to make a strong physical barrier under adverse conditions
- Flexibility of tailoring the properties for different applications
- Low variability in composition
- Well-known setting and hardening reactions and some existing data on the immobilization of metals

The disadvantages of cement-based processes include:

- Sensitivity of product quality to presence of impurities at high enough concentrations. (Specific examples of impurities are discussed in detail in Section 4.3.)
- Porosity of the S/S-treated waste.
- Waste volume typically increases due to binder addition, although not necessarily more than with other inorganic binders.
- Expertise needed for successful application, although process appears deceptively simple.

The major performance objectives of S/S treatment are to reduce the mobility of contaminants, minimize free liquids, and, occasionally, to increase the strength of the waste. Cement-based processes accomplish these objectives by forming a granular or monolithic solid that incorporates the waste materials and immobilizes contaminants. The solid matrix forms because of hydration of silicates in the cement, yielding calcium-silicate-hydrate. Sufficient free water may be present in the waste material, or additional water may be needed. In most cases, the bulk of the strength-forming ingredients are provided as an added cement binder.

ASTM provides specifications for eight types of Portland cement. Type I is the least expensive and is the most widely used for S/S treatment. Tricalcium and dicalcium silicates are the major crystalline compounds present in Portland cement, while tricalcium aluminate and a calcium aluminoferrite are present in smaller quantities. The cementation process binds free water,

increases the pH and alters other chemical properties of the mixture, reduces the surface area, and increases strength. All these mechanisms contribute to improved performance characteristics of the treated waste.

Cementation of the waste/binder mixture begins when water is added, either directly or as part of the waste. Once the cement powder contacts water, tricalcium aluminate immediately hydrates, causing the rapid setting which produces a rigid structure. In an idealized setting, the water hydrates the calcium silicates and aluminates in the cement to form calcium-silicate-hydrate. Thin, densely-packed fibrils of silicate grow out from the cement grains and interlace to harden the mixture entrapping inert materials and unreacted grains of cement. Hydration of tricalcium and dicalcium silicates results in the formation of tobermorite and crystalline calcium hydroxide. These compounds account for strength development after the initial setting. The setting rate is controlled by the amount of gypsum added to the cement. If sufficient gypsum is present, sulfates combine with tricalcium aluminate to form calcium aluminate sulfate, which coats the cement particles and retards hydration reactions.

The ratio of free water to cement (W/C) is a major factor controlling the porosity and strength of the final product. With a W/C weight ratio of about 0.48, the cement will fully hydrate, leaving some water adsorbed in the pore spaces. If the W/C ratio increases greatly above 0.48, the porosity increases rapidly and the strength declines. When estimating the required water addition, it is important to note that the total water content of the waste is not always available to hydrate the cement. Water that is held by hydration in the waste material may be unavailable or "bound" and thus not available to hydrate the cement.

In many applications, the binder is supplemented by additives to tailor the S/S process to waste-specific conditions. The additives may be used to modify the characteristics of the fresh mix to improve processing. For example, lignosulfonic or carboxylic acids can reduce the viscosity and retard the set of the mix. Low concentrations of calcium chloride accelerate setting. In other cases, additives may be needed to reduce interferences or improve the performance of the treated waste.

For cementation reagents to react, they must become wetted with water. In general, the higher the surface area of the particles, the more difficult they are to wet. Some additives may even have hydrophobic surfaces

initially. Many wastes, such as fine particulates and oils, may inhibit the setting and curing of the cement by interfering with the wetting process through coating of the reacting surfaces. Addition of surfactants to the waste may aid in the wetting of reagents, allowing thorough mixing of all components. Compounds such as alcohols, amides, and specific surfactants aid in wetting solids and dispersing fine particulates and oil. Flocculants have a similar effect by aggregating fine particles and film-formers.

The waste constituents can exhibit positive, negative, or inert contributions to the strength-forming reactions. Wastes with free calcium hydroxide can contribute to the strength-forming reactions, but excess hydroxide will increase the pH and increase the solubility of amphoteric metals. Alcohols and glycols decrease durability, while aliphatic, aromatic, and chlorinated organics increase set time and often decrease durability. Inorganic compounds such as boric acid, phosphates, iodates, sulfates, and sulfides can slow or prevent setting. Salts of some metals such as manganese, tin, zinc, copper, and lead can increase set time and reduce strength. Fine particulates such as silt, clay, or coal dust can coat cement particles and prevent the growth of calcium-silicate-hydrate crystals from the cement grain. Inerts such as soils or calcium fluoride do not directly participate in the cementation reactions but do become trapped in the solid matrix.

Cement-based solidification and stabilization processes have proven versatile and adaptable. It is possible to form waste/cement composites that have good strength and durability and that retain wastes effectively. Sorbents and/or emulsifiers can be added to reduce contaminant migration through the porous solid matrix, thus improving the leaching resistance of the treated wastes (U.S. EPA, 1986c).

4.1.1.2 Pozzolanic Processes

Pozzolanic processes generally involve siliceous and aluminosilicate materials, which do not display cementing action alone but form cementitious substances when combined with lime or cement and water at ambient temperatures. The primary containment mechanisms are precipitation and physical immobilization of the contaminant in the pozzolan matrix. Common examples of pozzolans are fly ash, pumice, lime kiln dusts, and blast furnace slag. The addition of bentonite can substantially reduce the amount of fly ash required (U.S. EPA, 1986c, p. 2-11). Pozzolans contain significant amounts of sili-

cates, which distinguish them from the lime-based materials (U.S. EPA, 1989g). Typical tests of pozzolanic activity with lime and the strength of lime/pozzolan mixtures use hydrated lime-to-pozzolan ratios in the range of 1:2 to 1:6 on a weight basis (ASTM C 311 and ASTM C 593). Typically, pozzolanic reactions occur more slowly than do cement reactions.

Standard testing systems (ASTM C 311) and standard specifications (ASTM C 593 and ASTM C 618) exist for pozzolanic materials, especially for fly ash. The specifications take into account the chemical composition (percent SiO_2 , percent SO_3), moisture content, and physical properties (fineness, pozzolanic activity with lime, and specific gravity). Pozzolanic activity greater than a specified minimum can be expected if the material used meets the specification for fly ash normally produced from burning either anthracite or bituminous coal (Type F) or lignite or sub-bituminous coal (Type C). Some Type C fly ashes have enough lime to be not only pozzolanic but also self-cementing (U.S. EPA, 1986c).

Lime/fly ash treatment is relatively inexpensive and, with careful selection of materials, can reliably convert waste to a solid material. In general, lime/fly ash-solidified wastes are not considered as durable as Portland cement-treated wastes.

Common problems with lime/pozzolan reactions involve interference with the cementitious reaction that prevents bonding of materials. The bonds in pozzolan reactions depend on the formation of calcium silicate and aluminate hydrates. Therefore, the interferences are broadly the same as for cement-based processes (Sections 4.1.1.1 and 4.3).

4.1.1.3 Ettringite Formation Effects

Formation of a calcium aluminate sulfate hydrate (i.e., ettringite) is typically required early in the curing process to control setting rate. However, the ettringite then dissolves and reprecipitates as calcium sulfate. Due to the high content of water of hydration, ettringite increases the volume of solids when it forms.

If the ettringite is formed while the S/S-treated waste is still plastic, the material can accommodate the expansive salt. However, if the ettringite forms after the grout has become rigid, cracking can occur and will reduce the strength of the product. The formation of this salt, with its large amount of water of crystallization and consequently large increase in

volume, can be destructive to the S/S-treated product. Figure 4-1 is an idealized representation of the progress of cementation reactions.

4.1.2 Organic Binders

Application of organic binders is usually limited to special waste types. Inorganic binders are used much more frequently and are generally favored over organic binders because of cost and ease of application. The primary niche of organic S/S processes in the commercial sector is to solidify radioactive wastes or hazardous organics that cannot be destroyed thermally.

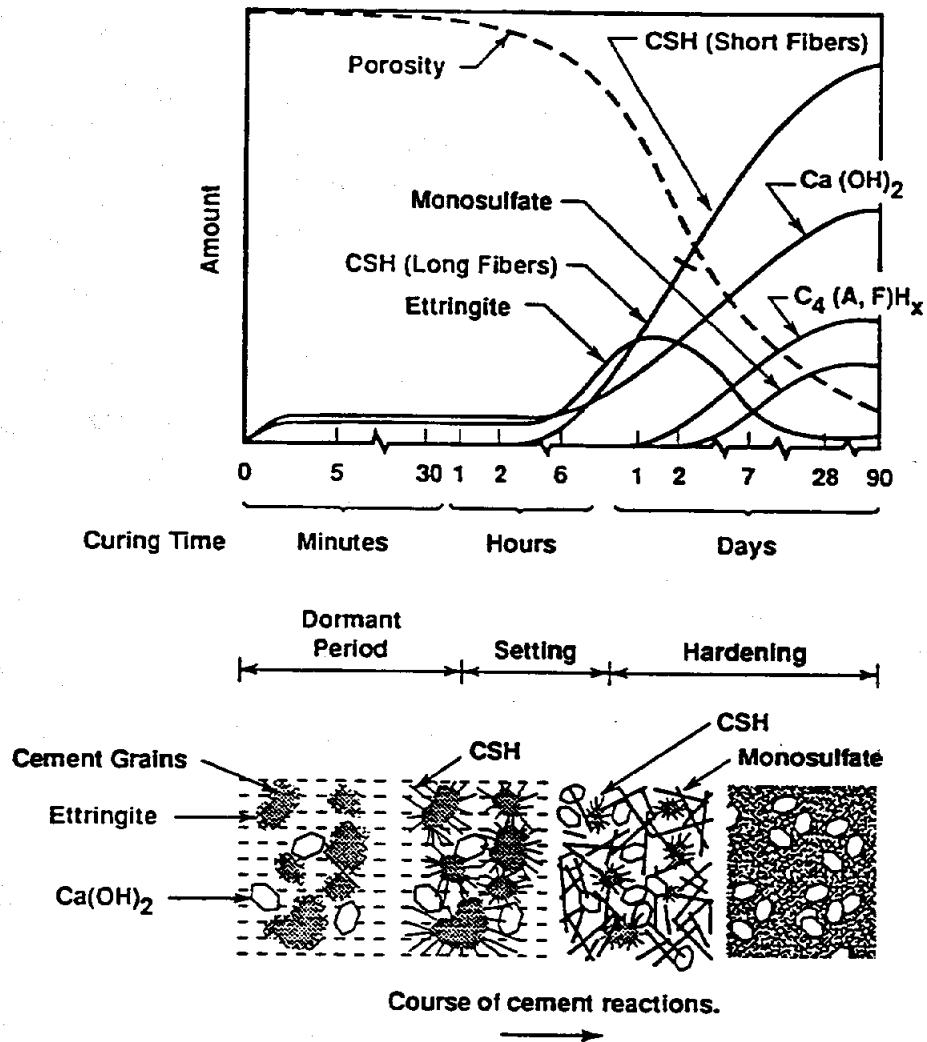
Organic binders that have been tested or used for S/S include the following:

- Asphalt (bitumen)
- Polyethylene
- Polyesters
- Polybutadiene
- Epoxide
- Urea formaldehyde
- Acrylamide gel
- Polyolefin encapsulations

The basic types of organic S/S processes are: (1) thermoplastic and (2) thermosetting with organic polymers. Thermoplastic processes involve blending waste with melted asphalt, polyethylene, or other thermoplastic binders. Liquid and volatile phases associated with the waste are driven off, and the waste is contained in a mass of cooled, hardened thermoplastic (U.S. EPA, 1986c).

Immobilization in thermosetting polymers involves mixing waste with reactive monomers, which join to form a solid incorporating the waste. Urea formaldehyde is one thermosetting resin that has been used for S/S processes.

One problem with organic processes is that many use hydrophobic binders, which are not compatible with water-based wastes unless the waste is first converted to an emulsion or a solid. Many hazardous wastes are



Legend:

CSH = Calcium Silicate Hydrate
 C₄(A, F)H_x = Ferrite Solid Solution

Source: Dole, 1985; figure used with permission of author and symposium proceedings publisher, WM Symposia, Inc., Tuscon, Arizona.

FIGURE 4-1 PROGRESS OF CEMENTATION REACTIONS

water-based and require special pretreatment to form an emulsion prior to treatment by an organic binder.

Organic binders are also subject to deterioration from environmental factors such as biological action or exposure to ultraviolet light. Therefore, the long-term stability of organic binders for S/S processes will depend on the physicochemical characteristics of the disposal or reuse environment (as in the case of asphalt cement for roadways).

4.1.2.1 Thermoplastic Processes

Thermoplastic processes are used in nuclear waste disposal and can be adapted to special industrial wastes. The thermoplastic technique for S/S treatment of waste involves drying and dispersing waste through a plastic matrix. The waste is mixed into a hot plastic mass which then cools, incorporating the waste in a rigid but deformable solid. In most cases, the hot waste/thermoplastic mix is extruded into a container, such as a fiber or metal drum, to give the final waste form a convenient shape for transport. The most common thermoplastic material used for waste incorporation is asphalt. When cost is not a limiting factor, other materials such as polyethylene, polypropylene, or wax can be employed for specific wastes to provide containment in an impermeable medium (U.S. EPA, 1986c).

One advantage of thermoplastic processes is their ability to treat soluble, toxic materials. For example, thermoplastic processing is one of the few alternatives applicable to S/S treatment of spray-dried salt (U.S. EPA, 1986c).

However, compatibility of the waste with the matrix is a limiting factor in using thermoplastic processes. Most thermoplastic S/S binders are chemically reduced materials (e.g., solid hydrocarbons) that can react (combust) when mixed with an oxidizer at elevated temperatures. The reaction can be self-sustaining or even explosive with perchlorates or nitrates (U.S. EPA, 1986c).

Other compatibility problems relate to softening or hardening of the waste/binder mix. Some solvents and greases can prevent asphalt hardening. Borate salts can initiate hardening at high temperatures, leading to stalled or clogged mixing equipment. Xylene and toluene can diffuse through asphalt (U.S. EPA, 1986c). Other interferences have been documented for salts that dehydrate at elevated temperature and for chelating and complexing agents.

Unlike inorganic S/S processes, thermoplastic processes require more complex, specialized melting and extrusion equipment. Both organic and inorganic processes require a trained operations staff to ensure safe, consistent operation. The power consumption for organic processes is higher than that for inorganic processes because of the need to dry the waste and melt the matrix material (U.S. EPA, 1986c).

4.1.2.2 Thermosetting Processes

Another type of organic S/S processes uses thermosetting resins such as urea formaldehyde. This type of process relies on polymer formation to immobilize the waste (U.S. EPA, 1989g). This technology has been evaluated for stabilizing radioactive wastes and largely abandoned due to problems with excess free water and radiolytic decomposition. Thermosetting processes have also been tested on a limited basis on hazardous wastes such as organic chlorides, phenols, paint sludges, cyanides, and arsenic as well as flue gas desulfurization sludge, electroplating sludges, nickel/cadmium battery wastes, kepone-contaminated sludge, and chlorine product wastes that have been dewatered and dried (U.S. EPA, 1989g).

Usually, there is no direct reaction between the waste constituent and the polymer. That is, thermosetting processes do not usually insolubilize, modify, or destroy the hazardous constituents. Rather, the effect of most thermosetting processes is to microencapsulate the waste, and the process is potentially applicable to a wide variety of waste types (Conner, 1990).

4.1.3 Additives

S/S processes may be used in conjunction with sorbents or other additives to improve immobilization of specific contaminants. Additives can be particularly useful for cement or pozzolan processes to decrease the mobility of contaminants in the porous, solid products. Additives to cement or pozzolan processes can also be incorporated to mitigate the effects of certain inhibitors. Some previously used additives and their applications are as follows:

- Soluble silicates, such as sodium silicate or potassium silicate. These agents will generally "flash set" Portland cement to produce a low-strength concrete.

Soluble silicates can also be beneficial in reducing interferences from metal ions.

- Selected clays to sorb liquid and bind specific anions or cations. Bentonite can reduce the amount of sorbent required in low-solids mixtures.
- Emulsifiers and surfactants to allow the incorporation of immiscible organic liquids. Waste turbine oil and grease can be mixed into cement blends if dispersing agents are used and if the proper mixing system is employed.
- Certain sorbents (e.g., carbon, silicates, zeolitic materials, and cellulosic sorbents) can help retain toxic constituents.
- Activated carbon in particular has been used primarily as a sorbent for organics, although this material will also sorb at least some metal ions and other inorganics.
- Lime (CaO or $\text{Ca}(\text{OH})_2$), soda ash (sodium carbonate, Na_2CO_3), fly ash, sodium hydroxide (NaOH) and, less commonly, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) are added for maintaining alkaline conditions.
- Ferrous sulfate, sodium metabisulfite/bisulfite, sodium hydrosulfite, sulfides, blast furnace slag, sodium borohydride, reductive resins, and hydrazine are added as reducing agents.
- Organophilic clays have been used to increase the immobilization of certain organic contaminants within hydrophobic binders. Organophilic clays are clay minerals, such as montmorillonite, that have been modified by treatment with a quaternary ammonium compound that expands the spacing between clay layers, thus promoting the absorption of organic constituents between these layers. After treatment, the layer spacing is reduced by treatment with an alkaline substance, such as sodium chloride, to immobilize the absorbed organic constituents in the clays.
- Organosilanes have been applied to increase the binding of metals.

This list is not comprehensive but rather provides examples of additives used. Note that many additives may work for one constituent but have the opposite effect for a different constituent. An evaluation of the system performance of the additive needs to be conducted.

4.1.4 Pretreatment

Frequently, the ultimate performance of an S/S process can be improved by pretreating the waste. Improvements can sometimes be made to the physical characteristics of the waste, to alter metal speciation, to improve metal immobilization, or to remove problematic organics.

4.1.4.1 Adjustment of Physical Characteristics

Treatment by S/S involves extensive handling and mixing of the contaminated material. The presence of large pieces of debris or poor handling characteristics of the waste can interfere with sampling, analysis, and S/S processing (Barth, 1991).

Some amount of debris or large solids will be encountered in waste at almost any site. Debris such as wire, broken brick, timbers, tires, scrap metal, or scrap cloth can be encountered at many industrial or waste disposal sites. Other sites may have waste-specific debris, such as wood or bark pieces at a creosote wood preserving site. Large pieces of material present considerable obstacles to obtaining a representative sample and to characterizing the waste as well as to performing the treatment.

The preliminary site characterization should identify the presence of debris. Sample collection should be planned to allow collection of meaningful characterization data of the waste and the debris. The debris can either be removed by screening and processed separately or can be broken down with size-reduction equipment to a size compatible with the S/S processing equipment.

Mixing requires the ability to handle the waste material. Debris can damage the mixing equipment and/or prevent good mixing. Excess free liquid, high viscosity, or caking properties can all present problems in materials handling. Possible pretreatment methods to improve handling are drying, pelletizing, or adding sorbents to control liquids.

4.1.4.2 Pretreatment for Inorganic Constituents

Properly formulated inorganic binders can often incorporate metals and their inorganic salts without extensive pretreatment. In some cases, however, pretreatment can significantly improve the performance of the S/S treatment system. Examples include (Conner, 1990):

- Chemical reduction of hexavalent chromium to the less soluble and toxic trivalent state
- Elimination of problem constituents, for example, destruction of cyanide or stripping of ammonia
- Degrading soluble nickel complexes to ionic nickel
- Removing hygroscopic salts such as sodium sulfate by aqueous extraction.

4.1.4.3 Pretreatment of Organic Constituents

Organic constituents can complicate stabilization in both inorganic and organic-based S/S treatment systems. Volatile organics can make it necessary to use expensive off-gas collection and treatment systems. As described in Section 4.3, organic materials incorporated into the S/S-treated waste can prevent setting or degrade product quality.

A variety of pretreatment options are available to remove volatiles and semivolatiles or to control the effects of the organic material prior to S/S treatment:

- Soil washing
- Thermal removal
- Chemical oxidation
- Extraction
- Biodegradation
- Addition of a sorbent (such as limestone, diatomaceous earth, clays, activated carbon, or fly ash) prior to mixing

A study of RODs for Superfund sites where S/S was one component in the treatment program showed that wastes contaminated with VOCs underwent pre-treatment more often than any other wastes (U.S. EPA, 1989a).

4.1.4.4 Treatment Trains Involving S/S

In many cases, treatment of wastes containing multiple and diverse contaminants becomes so complex that S/S treatment becomes just one step in a

treatment system or a treatment train. For example, the BDAT treatment for several RCRA nonwastewater waste types includes one or more other processes followed by S/S treatment (Table 1-1). The most common BDAT treatments that prepare waste for S/S are incineration and chemical precipitation. In other cases S/S treatment can be the initial step in a treatment train. For example, it can be used to improve materials handling characteristics or to immobilize metals prior to a different type of treatment.

Pretreatment to mitigate one problem may give rise to problems of another nature. For example, oxidation of organic contaminants with permanganate leaves a permanganate residue in the waste, and permanganate will oxidize organic binders such as asphalt. Washing with solvent leaves traces of solvent that must be removed from the waste prior to S/S treatment. Incineration can leave certain metals (e.g., chromium) in the ash in their higher and more mobile oxidation states.

Selection of the appropriate combination of binders, additives, and pretreatment options for a particular waste requires careful consideration of the waste material, the contaminants, and the performance objectives of the project (Sections 2.3 and 2.4).

4.2 IMMOBILIZATION MECHANISMS

Waste stabilization may involve physical mechanisms, chemical mechanisms, or a combination of the two. Physical stabilization (solidification or encapsulation) changes the physical form of the waste but does not necessarily cause chemical binding of the waste constituents. Chemical stabilization changes the chemical states of waste constituents to forms with lower aqueous solubilities. Although the mechanisms of immobilization are discussed separately for convenience, under actual S/S treatment conditions, these mechanisms usually do not work independently.

4.2.1 Physical Mechanisms

Physical mechanisms of S/S operate by confining waste constituents to a certain area or zone in the waste. That is, the waste constituent may or may not occur in a soluble form, but one or more physical barriers prevent its mobilization. Containment by a barrier is a satisfactory method as long as

the barrier remains stable. Encapsulation is the most commonly used method of containment, superseding earlier use of sorbents.

Encapsulation techniques use materials that trap waste constituents in the form of stable solids, preferably as a monolith with high cohesive strength and low leachability. Waste constituents are dispersed throughout an inorganic or organic binder matrix (Section 4.1) that physically isolates them from groundwater and air. The effectiveness of isolation depends on the permeability and long-term stability of the matrix and on the degree of mixing of waste constituents throughout the matrix. In practice, mixing may be less than ideal, resulting in some of the waste material occupying cavities in the matrix. Encapsulation of inorganic wastes is generally accompanied by chemical stabilization, but encapsulation of organic wastes such as oil and grease, PCBs, pesticides, and volatile compounds usually occurs without accompanying chemical interactions (Conner, 1990). Encapsulation can be further described at three levels: microencapsulation, macroencapsulation, and embedment (Conner, 1990).

The term "microencapsulation" describes a process of adsorbing or trapping contaminants in the pore spaces of a cementitious material. The contaminants are fine waste particles that may not be visible to the naked eye. As the system ages, the waste and matrix may eventually become a homogeneous material, although this might occur in a time frame of thousands of years or more (Conner, 1990).

The term "macroencapsulation" describes a process of coating a solid or cemented waste with an impermeable layer, such as bitumen (thermoplastic) or amorphous silica (U.S. EPA, 1990e). The success of this method depends on both effective coating reactions and thorough mixing. "Macroencapsulation" may also refer to the containment of large waste solids, as in a sealed drum.

The term "embedment" describes a process of incorporating large waste masses into a solid matrix before disposal. Examples of such wastes are contaminated debris from remedial actions, laboratory protective equipment, solid medical wastes (e.g. syringes), and radioactive objects (Conner, 1990). Embedment is used in situations where it is impractical to reduce the bulk of the waste but where the waste is hazardous enough to be treated prior to disposal. In addition, special consideration may also have to be given to the strength, water permeability, and long-term stability properties of the matrix.

Finally, sorbents once were used extensively to prevent the loss of liquid wastes and to improve handling characteristics. Materials such as expanding-layer clays and vermiculite were considered attractive for liquid waste disposal because of their low cost and easy handling. However, the use of sorbents has greatly diminished since the 1985 landban on bulk liquids in landfills, although sorbents are currently permitted for certain applications (Conner, 1990). The main problem with sorbents is that they may become highly leachable under certain circumstances, for example, if oversaturation should occur and load levels become too high.

4.2.2 Chemical Mechanisms

Different chemical mechanisms of S/S are operable for inorganic and organic wastes. Also, the aqueous chemistries of most inorganic and organic compounds are fundamentally different, leading to different leaching behaviors.

4.2.2.1 Inorganic Wastes

4.2.2.1.1 Basic Chemical Equilibria. The chemistry of inorganic waste constituents is dominated by hydrolysis reactions. The term "hydrolysis" implies that a substance, usually a metal, reacts with water. Hydrolyzed products can react in the aqueous phase to form new ionic or neutral species, or they can form precipitates of hydroxides, oxides, or salts (commonly carbonates, sulfates, and sulfides).

It is useful to compare the solubilities of different metal compounds. Consider the dissolution reaction of a generic compound M_mA_a :



where M^{n+} is the cation and A^{m-} is the anion. The solubility product constant for this reaction is

$$K_{sp} = [M^{n+}]^m [A^{m-}]^a$$

where square brackets indicate concentration (activity) and K_{sp} depends only on temperature and pressure. The solubility product is therefore a constant

if temperature and pressure of the solid and solution phases remain fixed, for example, at the ambient conditions of a disposal site. Frequently, the solubility product is written as pK_{sp} , where $pX = -\log_{10}(X)$.

Table 4-1 lists solubility product values for the hydroxides, carbonates, sulfates, and sulfides of some regulated metals (higher pK_{sp} means lower solubility). Table 4-1 shows that the following metals salts have very low solubility products: Cr(III) hydroxide and sulfides of Cd(II), Pb(II), Hg(I), and Hg(II). The least soluble barium solid is barium sulfate (barite). This type of information can be important for deciding which form of a given hazardous metal is most stable and which metal compounds may be attainable given specific site conditions and available technology.

Actual concentrations of dissolved species depend on a number of solution parameters, such as pH, redox potential, and solution composition. The simplest and most common method of controlling speciation and precipitation is pH adjustment. To illustrate this process, consider the role of a strong acid in the solubility of a simple metal hydroxide, $M(OH)_n$. According to the equilibrium expression above, the solubility of $M(OH)_n$ is described by the following reaction:

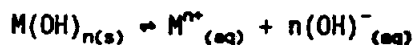


TABLE 4-1. pK_{sp} VALUES FOR SELECTED METAL PRECIPITATES^(a)

Metal	Hydroxide	Carbonate	Sulfate	Sulfide
Ba	2.30	8.09	9.97	--
Cd	14.30	11.60	--	28.44
Cr(III)	30.20	--	0.50	--
Pb	19.90	13.48	7.71	27.47 ^{(b)(c)}
Hg(II)	25.52	--	1.43	48.70
Hg(I)	--	16.05	6.17	51.42

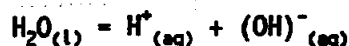
^(a) Data apply to equilibria at 25°C except where otherwise noted.

^(b) Equilibria at 18°C.

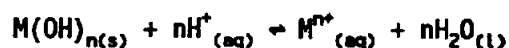
^(c) Galena.

Sources: Means et al. (1991c) and Dragun (1988).

To show the dependence on pH directly, the following equation must be subtracted from the preceding one, n times:



Where $pK_w = 14$ the result is



The solubility constant for this reaction is

$$K_s = [M^{n+}]/[H^+]^n$$

or upon rearranging terms:

$$[M^{n+}] = 10^{-npH} K_s$$

The concentration of M^{n+} ions clearly increases as pH decreases. However, M^{n+} ions are not necessarily the dominant aqueous species of the metal M at all pH values and solution compositions. The total dissolved metal is the sum of all hydrolysis species [$M(OH)^{n-1}$, $M(OH)_2^{n-2}$, etc.] and complex species [MCO_3^{n-2} , MSO_4^{n-2} , etc.] that form in solution. At sufficiently high or low pH, some aqueous species can be hydroxylated or protonated. Therefore, these species are sensitive to pH and they affect the solubilities of the solid phases. The task of determining which species are present and in what concentrations is often time consuming and expensive. As an alternative, speciation calculations can be made if bulk solution compositions are known. Compilations of thermochemical data that are needed to perform these calculations are available in the chemistry literature (Means et al., 1991c).

An investigation of immobilization mechanisms for S/S of cadmium and lead (U.S. EPA, 1990f) found that, even though $Cd(OH)_2$ and $Pb(OH)_2$ have comparable and very low solubilities, the degree of leaching from cement treated wastes differed for the two metals. In leaching tests, cadmium concentrations were very low, whereas lead concentrations were considerably higher and could potentially pose a threat to groundwater. The differences were attributed to the fact that the Cd/cement system involves early formation

of $\text{Cd}(\text{OH})_2$ which provides nucleation sites for precipitation of C-S-H and calcium hydroxide and results in Cd being in the form of an insoluble hydroxide with an impervious coating. The Pb/cement system was more complicated in terms of precipitation reactions. Mixed salts containing hydroxide, sulfate, and nitrate ions were precipitated. These salts retard the cement hydration reactions by forming an impervious coating around the cement clinker grains. Also, as pH in the cement pore water fluctuated during hydration, the Pb salts undergo solubilization and reprecipitation, resulting in Pb salts on the surface of cement minerals that are readily accessible to leach water and apparently are more soluble under basic conditions than a pure lead hydroxide.

4.2.2.1.2 Effect of Alkaline Conditions. Numerous compatible ionic species form solids by coprecipitation. Therefore, the application of chemical equilibria based on pure end-members may not be completely valid. Ferric iron has long been recognized for its ability to flocculate and coprecipitate toxic metals from solution (Sittig, 1973; Legendre and Runnells, 1975; Swallow et al., 1980). Coprecipitated metals may have solubilities that are substantially lower than those of either of the pure end-member phases. For example, the Cr(III) concentrations are many times lower in solutions that are in equilibrium with coprecipitated $\text{Cr}(\text{OH})_3$ - $\text{Fe}(\text{OH})_3$ than those that are in equilibrium with pure chromium hydroxide (Sass and Rai, 1987).

The minimum solubility of most metal hydroxides occurs within the approximate pH range of 7.5 to 11. This implies that solubility increases under extremely alkaline conditions as well as under acidic conditions (amphoteric behavior). When the waste material under consideration for S/S contains a number of different metals, it is possible that their solubility minima may not entirely overlap. In cases where pH values at these solubility minima are not too different, it may be sufficient to choose an average pH, but in cases where pH values are very different, the best recourse may be to attempt to precipitate the contaminants in a phase or phases other than a hydroxide.

As an example, suppose that Cd and Cr(III) are the predominant hazardous constituents in a waste system. Solubility minima occur at pH ~ 11 to 11.5 for $\text{Cd}(\text{OH})_2$ (Brookins, 1988) and pH ~ 8.5 for $\text{Cr}(\text{OH})_3$ (Baes and Mesmer, 1976). In this situation, one might elect to precipitate highly insoluble CdS by adding a soluble sulfide, such as Na_2S , and to precipitate

$\text{Cr}(\text{OH})_3$ by adjusting the pH to 8.5. Note, however, that if barium is present in the same waste, it has a high solubility in the presence of sulfide. This example illustrates the need for understanding the waste chemistry as well as the pertinent chemical equilibria in order to achieve a maximum degree of chemical stabilization.

Any alkali may be used to control pH, but the common choices are lime [either CaO or $\text{Ca}(\text{OH})_2$], sodium carbonate, or sodium hydroxide. Most solidification reagents are alkaline and can substitute in part or entirely for traditional alkalies, acting both as pH controls and as binding agents. Alkaline binders include Portland cement, cement and lime kiln dusts, Type C fly ash, and sodium silicate (Conner, 1990).

Buffers provide resistance to rapid changes in pH upon exposure to acid or base. The presence of pH buffers in stabilized waste is desirable to maintain the pH at the target value for the long term, thus promoting long-term stability. Limestone (primarily CaCO_3) is used to buffer waste acidity; Na-montmorillonite is also used for this purpose.

4.2.2.1.3 Effect of Redox Potential. Redox potential is another important solution parameter in S/S technology. An oxidation-reduction, or redox reaction, is one that involves the transfer of electrons between products and reactants. Experimentally, the redox potential of a half-cell reaction is measured by a quantity called "Eh." High Eh voltages indicate that the solution is oxidizing and low Eh voltages indicate that the solution is reducing. The redox potential of a waste form can be controlled to convert the valence states of hazardous metals to valence states that are more favorable for precipitation.

Among the regulated metals listed in Table 4-1, Cr and Hg have more than one common oxidation state. The table shows that trivalent chromium species precipitate as a low-solubility hydroxide. However, Cr(VI) forms mainly chromate and dichromate species, such as CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, which do not form precipitates with low solubility (Eary and Rai, 1987). The table also shows that mercury in both oxidation states forms very-low-solubility sulfides. Redox potential has particularly important effects on the regulated semimetals, such as As and Se, which exhibit a number of different oxidation states.

Table 4-2 lists selected stable solids of As and Se for reference. A literature review by Means et al. (1991c) shows that calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$ is the most stable metal arsenate [As(V)] in oxidizing alkaline conditions. Under acidic conditions, calcium arsenate becomes unstable because its calcium source (calcite) is leached away. Another potentially stable phase for the immobilization of As(V) appears to be basic ferric arsenate $\text{FeAsO}_4 \cdot x\text{Fe}(\text{OH})_3$, which forms readily in the presence of ferric hydroxide. However, basic ferric arsenate is most stable at lower pH.

Under highly oxidizing conditions the selenate ion SeO_4^{2-} [Se(VI)] predominates in both acidic and basic solutions (Means et al., 1991c). Barium selenate appears to be the most stable solid (Elrashidi et al., 1987) but is fairly soluble (4mM activity). Other metal selenates are even more soluble. In moderately oxidizing conditions, manganese selenite, MnSeO_3 [Se(IV)], is the most stable solid that persists in both neutral and acidic environments (Elrashidi et al., 1987); at pH 5 the activity of the dominant species HSeO_3^- is 2.5 μM . According to (Elrashidi et al., 1987), PbSeO_3 has a solubility minimum near pH 8. Under highly reducing conditions, selenide [Se(II)] species predominate (Elrashidi et al., 1987); lead selenide PbSe and tin selenide SnSe are the most stable solids in both neutral and alkaline conditions. Elemental Se also has a stability region, but it is more soluble than most of the metal selenides (Elrashidi et al., 1987).

The major reducing agents and their attributes are described by Conner (1990). The most common agents are ferrous sulfate, Na-metabisulfite/bisulfite, Na-hydrosulfite, sulfides, Na-borohydride, hydrazine, and reductive resins. The most widely used reducing agent in S/S technology is ferrous sulfate, which is used primarily to reduce hexavalent chromium. Its main disadvantage is that pH must be adjusted below 3 in order for the chromium reduction reaction to go to completion. The amount of acid needed can therefore be quite large, particularly if the waste material contains appreciable amounts of alkaline buffers. Na-metabisulfite/bisulfite and soluble sulfides, such as Na_2S , work similarly to ferrous sulfate but require less acid and alkali to complete a reduction/precipitation process. However, Na-metabisulfite/bisulfite is expensive, and Na_2S is unsafe to use at very low pH because of the possible evolution of toxic H_2S . Na-hydrosulfite, Na-borohydride, hydrazine, and freshly precipitated FeS (the Sulfex™ process) work under alkaline conditions, which may be more convenient for pretreated wastes.

TABLE 4-2. pK_{sp} VALUES FOR SELECTED As AND Se PRECIPITATES^(a)

Element	Compound	pK_{sp}
As(V)	(arsenates)	
	$Ba_3(AsO_4)_2$	50.11
	$Ca_3(AsO_4)_2$	18.17
	$Cd_3(AsO_4)_2$	32.66
	$Mg_3(AsO_4)_2$	19.7
	$Pb_3(AsO_4)_2$	35.39
	$FeAsO_4 \cdot xFe(OH)_3$	20.24
As(III)	As_2S_3	29.6
As(II)	AsS	12.3
Se(VI)	(selenates)	
	$BaSeO_4$	7.46
	$CaSeO_4 \cdot 2H_2O$	3.09
	$CdSeO_4$	2.27
	$PbSeO_4$	6.84
Se(IV)	(selenites)	
	$BaSeO_3$	6.57
	$CaSeO_3 \cdot H_2O$	5.44
	$CdSeO_3$	8.84
	$HgSeO_3$	13.90
	Hg_2SeO_3	14.23
	$MnSeO_3$	7.27
	$PbSeO_3$	12.12
Se(-II)	(selenides)	
	BaSe	21.86
	CaSe	10.87
	CdSe	35.20
	CuSe	48.10
	FeSe	26.00
	HgSe	64.50
	PbSe	42.10
SnSe	38.40	

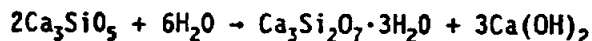
^(a) Data apply to equilibria at 25°C.
Source: Means et al. (1991c).

Reductive resins (e.g., Amborane™) are selective for certain metals and are used for precious metal recovery. They have potential uses for recovering hazardous metals such as silver, arsenic, mercury, and antimony (Conner, 1990). Blast furnace slag, a common binder, can serve as a reducing agent.

While adjustment of the redox-sensitive contaminant to its least soluble oxidation state is an important aspect of chemical stabilization, this objective eventually will be defeated if the treated waste is placed in a disposal or reuse environment having a very different oxidation state. Long-term stability can only be ensured if the oxidation states of the treated waste and the disposal or reuse environment are similar.

4.2.2.1.4 Metal Silicates. The behavior of hazardous metals in the silicate system is critical to cement-based S/S technology. However, full understanding of the chemical processes involved may be difficult to achieve because the waste constituents are often heterogeneous mixtures of solutions, suspended solids, and immiscible liquids. Reactions between metal salts in solution and soluble silicates have been studied extensively, but their insoluble products usually have not been well characterized. Metal silicates are generally nonstoichiometric and poorly crystallized. In fact, their chemical and physical properties depend considerably upon the conditions under which they are formed, for example, temperature, concentration, addition rate, and ionic speciation. The pH is also very important because it affects how readily soluble silicate (or colloidal silica) adsorbs metal ions. It has been found that adsorption occurs when the pH is 1 to 2 units below the hydroxide precipitation point (Iler, 1979).

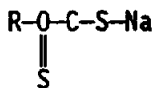
Just how the metal ions are incorporated into the cement structure is still a matter of debate. Using Portland cement as an example, the cementitious phase of calcium silicate hydrate, or CSH, forms by a hydration reaction that takes from 28 days to 1 year to complete (Kantro et al., 1962):



It is believed that CSH incorporates metal ions into the silicate matrix during the hydration reaction (Bhatty and Greening, 1978). The number of metal ions retained decreases as the CaO:SiO₂ ratio in CSH increases (Bhatty, 1987).

If metals have already been precipitated as low-solubility solids, they may gradually react with the silicate (if such a reaction is favorable) as long as free silicate is available; i.e., before it reacts with other ions in the system, such as calcium. The probable result is that the cementitious matrix will encapsulate the metal solids as hydroxides, sulfides, carbonates, etc. (see Section 4.2.1 on physical mechanisms). Continued reaction of metal ions with silicate will only occur if a continuous source of soluble silica can be created within the matrix or if the waste is pretreated to dissolve the metal hydroxides.

4.2.2.1.5 Other Low-Solubility Phases. Another alternative to precipitating metals as hydroxides is to bind them using insoluble substrates. Insoluble starch xanthates have been widely used for this purpose since they became commercially available in 1980 (Conner, 1990). Xanthates are produced by reacting an organic hydroxyl-containing substrate (R-OH), such as starch, cellulose, or alcohol with carbon disulfide in the presence of a strong base such as NaOH (Bricka and Hill, 1987). The structure of a Na-xanthate is represented by



Xanthates remove metals from solution by exchanging the base metal (Na) for generally heavier metals, which are bound more strongly. The selectivity for metal removal increases in the following order (Flynn et al., 1980):



Wastes stabilized by xanthates are less sensitive to pH and have better sludge dewatering properties than metal hydroxides. However, the xanthates produce large quantities of sludge that must be handled like any RCRA material (Bricka and Hill, 1987).

The effects of typical S/S techniques for binding heavy metals using cellulose and starch xanthates were investigated by Bricka (1988) and Bricka and Hill (1987), who found:

1. Xanthates of Cd, Cr, Hg, and Ni effectively immobilize these metals when bound with Portland cement.
2. Mercury precipitated by starch xanthate has lower leachability than mercury precipitated by hydroxide, even after solidification.
3. Starch xanthate binds mercury better than cellulose xanthate.
4. Cd-, Cr-, and Ni-xanthates alone do not have sufficiently low solubilities for direct disposal; thus solidification is necessary to achieve acceptable leachability levels.

4.2.2.2 Organic Wastes

Aqueous wastestreams containing small amounts (10 to 1000 ppm) of organic hazardous contaminants are the most treatable organic waste forms under S/S technology (Conner, 1990). With regard to normal cement-based methods, containment will be most effective for immiscible liquids and least effective for soluble liquids (Conner, 1990). It is unclear, however, whether appreciable chemical reactions take place in the matrix. Losses may be caused by other factors, such as volatilization, which may be especially important in S/S processes that involve elevated temperatures (Weitzman et al., 1987).

As with inorganic wastes, organic constituents can undergo reactions including hydrolysis, change of oxidation state, and precipitation as some form of salt. Hydrolysis normally involves the loss of a hydroxyl group (-OH) in exchange for another functional group. Reactions must be catalyzed by a strong base to proceed at reasonable rates. Oxidation and reduction reactions can occur naturally in soils, with clays performing the role as catalysts (Warren et al., 1986). Many substituted aromatics undergo free radical oxidation. According to Dragun and Helling (1985), this group includes benzene, benzidine, ethyl benzene, naphthalene, and phenol. On the other hand, chlorinated aromatics and polynuclear organics are unlikely to be oxidized under natural conditions (Conner, 1990). Of course, oxidation can be made to occur by treating the waste with strong oxidizing agents such as potassium permanganate. However, the possible disadvantages of using such additives, such as the mobility or toxicity of the additive itself, must be weighed against the advantages. The mechanism of salt formation by organics will apply only to the ionized or ionizable organic fraction; it is not

directly applicable to nonpolar species. The formation of organic salts in S/S technology is a possible significant mechanism, but it has not been studied extensively.

One additional area of recent research is the S/S binding mechanisms of nonpolar organics in organophilic additives such as modified clays and activated carbon. Modified clays are clays that have been modified by ion exchange with selected organic compounds that have a positive charged site hence rendering the clay/organo complex hydrophilic. The binding capacity for such materials with certain types of organics has been well demonstrated. For example, Sell et al. (1992) found that sodium bentonite clay, modified with dimethyl di(hydrogenated tallow) ammonium chloride (LOCKIT®) can be used to remove phenol and chlorinated phenols from aqueous solutions. The question for organophilic additives, however, centers on whether the binding mechanism entails simple absorption or adsorption, or whether the formation of stronger covalent bonds between the additive and the contaminant is occurring. Additional evaluation is necessary.

4.2.3 Concept of Surface Sealing

The concept of "surface sealing" pertains to the situation where the surfaces of stabilized waste products are sealed, limiting the release of contaminants and the uptake of matrix-unfriendly components such as salts. Hockley and van der Sloot (1991) found that "self-sealing" may occur in some stabilized wastes. They examined the precipitation and dissolution processes in waste blocks formed from stabilization of coal combustion wastes with Portland cement and lime that had been exposed to seawater for up to 8 years. Results indicated that dissolution of calcium hydroxide, calcium sulfite, and ettringite began at the block surface and proceeded as a moving boundary toward the interior. Some calcium released by dissolution was reprecipitated as a carbonate phase, and the remainder was lost to the surrounding seawater. Magnesium ions infiltrating from the seawater were precipitated, apparently as a hydroxide phase. Concentration profiles of As, Sb, and B showed that minor elements also exhibit moving boundary effects, perhaps through association with the mineral phases. These alteration and leaching processes were confined to within 10 to 20 mm of the block surface, and many concentration profiles showed sharp discontinuities at the 10- to 20-mm region.

These discontinuities could not be explained by the simple diffusion-based models currently used to interpret leaching data. The sharp discontinuities in the concentration profiles of nonreactive sea salts led to the hypothesis that the precipitation of small crystals in pores near the block's surface restricted diffusion, a process similar to the concept of "pore refinement" previously identified in the literature on concrete durability. This process causes a slowing of all diffusion-controlled processes, including the degradation of the block matrix and the leaching of contaminants.

Similar phenomena have been observed in borosilicate glasses. Upon leaching, these glasses develop an alteration layer at the glass/water interface. The alteration layer consists of numerous growths (grouts) that precipitate and impede glass dissolution and diffusion of glass constituents into the aqueous phase (Doremus, 1979).

4.3 POTENTIAL INTERFERENCES

S/S processes can be affected by the chemical constituents present in the waste being treated and by many other factors (e.g., binder-to-waste ratio, water content, or ambient temperature). The interferences caused by the chemical constituents of the waste can affect the solidification processes and/or the chemical stabilization of the treated product as discussed in Sections 4.3.1 and 4.3.2. Waste-specific treatability studies are needed to identify and overcome such interferences. General types of interference caused by the chemical constituents include (U.S. EPA, 1990g):

- Inhibition of bonding of the waste material to the S/S material
- Retardation of setting
- Reduction of stability of the matrix resulting in increased potential for leachability of the waste
- Reduction of physical strength of the final product

The exact mechanisms for interference are not known, and because different wastes respond differently to various types of interferences, limits on

various interfering agents cannot be set. More study is needed to establish acceptable levels for interfering agents, both singly and in combination.

4.3.1 Interferences with Solidification

The contaminated materials usually treated by S/S processes are widely fluctuating, complex mixtures. Even with one waste source, the concentrations can vary by a factor of ten or more from batch to batch. Many waste constituents affect cementation chemistry by altering the setting rate or the properties of S/S-treated waste. Depending on the contaminant type and concentration, setting rate may be increased or decreased. As an example of concentration effects, mild accelerators such as chloride or nitrate anions can slow setting at higher concentrations. Treated waste properties such as porosity or flexural and compressive strength may be reduced by contaminants.

There is typically a threshold below which the contaminant has no measurable effect. Because S/S treatment performance is influenced by complex interactions of waste material and binder, it is usually not possible to quantify the threshold. Treatability studies are required to determine the feasibility of treating a specific waste.

Table 4-3 lists substances found to affect cement reactions. Many of these substances can reduce the ultimate mechanical strength of the waste form by producing cracking and spalling. Table 4-4 compiles the characteristics reported to interfere with solidification/stabilization processes and indicates their potential impacts.

4.3.2 Interferences with Stabilization

Table 4-5 summarizes some typical waste characteristics found to interfere with the stabilization processes. This table focuses on the effects of waste constituents on immobilization mechanisms, in contrast to Table 4-4, which addresses the effects on formation of a solid product. Interferences with stabilization include chemical incompatibilities and undesirable reactions. Generally, the types of effects reported in Table 4-5 are releases of noxious gases or effects resulting in the increased leaching potential of the contaminants.

**TABLE 4-3. SUBSTANCES THAT MAY AFFECT CEMENT REACTIONS:
INHIBITION AND PROPERTY ALTERATION**

Substance or Factor	Inhibition	Property Alteration
Fine particulates	X	X
Clay	X	
Silt	X	
Ion exchange materials	X	
Metal lattice substitution	X	
Gelling agents	X	X
Organics, general	X	X
Acids, acid chlorides		X
Alcohols, glycols	X	X
Aldehydes, ketones		X
Carbonyls	X	
Carboxylates	X	
Chlorinated hydrocarbons	X	X
Grease	X	X
Heterocyclics		X
Hydrocarbons, general		X
Lignins	X	
Oil	X	X
Starches	X	
Sulfonates	X	
Sugars	X	
Tannins	X	
Organics, specific		
Ethylene glycol		X
Hexachlorobenzene		X
Phenols	X	X
Trichloroethylene		X
Inorganics, general		
Acids		X
Bases		X
Borates	X	
Chlorides	X	X
Copper compounds	X	
Lead compounds	X	
Magnesium compounds	X	
Metal salts	X	X
Phosphates	X	
Salts, general	X	X

TABLE 4-3. SUBSTANCES THAT MAY AFFECT CEMENT REACTIONS:
INHIBITION AND PROPERTY ALTERATION (Continued)

Substance or Factor	Inhibition	Property Alteration
Inorganics, general (cont'd)		
Silicas	X	
Sodium compounds	X	
Sulfates	X	X
Sulfides	X	
Tin compounds	X	
Zinc compounds	X	
Inorganics, specific:		
Calcium chloride	X	
Copper hydroxide	X	
Copper nitrate		X
Gypsum, hydrate	X	
Lead hydroxide	X	
Lead nitrate	X	X
Sodium arsenate	X	
Sodium borate	X	
Sodium hydroxide		X
Sodium iodate	X	
Sodium sulfate		X
Sulfur	X	
Tin		
Zinc nitrate		X
Zinc oxide/hydroxide	X	

Adapted from: Conner, J. R. 1990. *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York. pp. 349-350. Used with permission of Van Nostrand Reinhold.

TABLE 4-4. SUMMARY OF FACTORS THAT MAY INTERFERE WITH SOLIDIFICATION/STABILIZATION PROCESSES

Possible Interfering Characteristics	Potential Interference Mechanism	Reference
Semivolatatile organics or PAHs	Organics interfere with bonding of waste materials.	U.S. EPA, 1988c
Oil and grease	Weaken bonds between waste particles and cement by coating the particles. Decrease in unconfined compressive strength with increased concentrations of oil and grease.	U.S. EPA, 1988c; Cullinane and Bricka, 1989.
Phenols	Marked decrease in compressive strength.	U.S. EPA, 1988c; Cullinane and Bricka, 1989.
Nonpolar organics (oil, grease, aromatic hydrocarbons, PCBs)	May impede setting of cement, pozzolan, or organic-polymer S/S. May decrease long-term durability and allow escape of volatiles during mixing. With thermoplastic S/S, organics may vaporize from heat.	U.S. EPA, 1989g
Polar organics (alcohols, phenols, organic acids, glycols)	With cement or pozzolan S/S, phenol retards setting and may decrease short-term durability; all may decrease long-term durability. With thermoplastic S/S, organics may vaporize. Alcohols may retard setting of pozzolans.	U.S. EPA, 1989g
Solid organics (plastics, tars, resins)	Ineffective with urea formaldehyde polymers, may retard setting of other polymers.	U.S. EPA, 1989g; Wiles, 1987

TABLE 4-4. SUMMARY OF FACTORS THAT INTERFERE WITH SOLIDIFICATION/STABILIZATION PROCESSES (Continued)

Possible Interfering Characteristics	Potential Interference Mechanism	Reference
Aliphatic & aromatic hydrocarbons	Increase set time for cement.	U.S. EPA, 1989b
Chlorinated organics	Increase set time and decrease durability of cement.	U.S. EPA, 1989b
Complexing organics (hydroxycarboxylic acid, citric acid, tartaric acid, benzoic acid, EDTA)	Retard setting rate.	Dole, 1985
Presence of phenols and nitrates	Cannot be immobilized with lime/fly ash, cement, and soluble silicates; fly ash and cement; or bentonite and cement.	Stegemann et al., 1988
Metals (lead, chromium, cadmium, arsenic, mercury)	May increase setting time of cements.	U.S. EPA, 1989g
Metal salts and complexes	Increase set time and decrease durability for cement or clay/cement.	U.S. EPA, 1989b
Copper, lead, and zinc	Detrimental effect on physical properties of cement-treated waste.	U.S. Army, 1990
Halides	May retard setting, easily leached from cement and pozzolan S/S-treated waste. May dehydrate thermoplastics.	U.S. EPA, 1988c

TABLE 4-4. SUMMARY OF FACTORS THAT INTERFERE WITH SOLIDIFICATION/STABILIZATION PROCESSES (Continued)

Possible Interfering Characteristics	Potential Interference Mechanism	Reference
Soluble salts of manganese, tin, zinc, copper, and lead	Reduce physical strength of final product; cause large variations in setting time; reduce dimensional stability of the cured matrix, thereby increasing leachability potential.	U.S. EPA, 1988c
Cyanides	Cyanides interfere with bonding of waste materials.	U.S. EPA, 1988c
Arsenates, borates, phosphates, iodates, sulfides, and carbohydrates	Retard setting and curing and weaken strength of final product.	U.S. EPA, 1988c
Sulfates	Retard setting and cause swelling and spalling in cement S/S. With thermoplastic solidification may dehydrate and rehydrate causing splitting.	U.S. EPA, 1988c
Presence of coal or lignite	Coals and lignites can cause problems with setting, curing, and strength of the end product.	U.S. EPA, 1988c
Sodium borate, calcium sulfate, potassium dichromate, and carbohydrates	Interferes with pozzolanic reactions that depend on formation of calcium silicate and aluminates hydrates.	U.S. EPA, 1986c

TABLE 4-4. SUMMARY OF FACTORS THAT INTERFERE WITH SOLIDIFICATION/STABILIZATION PROCESSES (Continued)

Possible Interfering Characteristics	Potential Interference Mechanism	Reference
Oxidizers (sodium hypochlorite, potassium permanganate, nitric acid, or potassium dichromate)	May cause matrix breakdown or fire with thermoplastic or organic polymer S/S.	U.S. EPA, 1989g
Nitrates, cyanides	Increase setting time, decrease durability for cement-based.	Colonna et al., 1990
Soluble salts of magnesium, tin, zinc, copper, and lead	May cause swelling and cracking within inorganic matrix, exposing more surface area to leaching.	Colonna et al., 1990
Flocculants (e.g., ferric chloride)	Interference with setting of cements and pozzolans.	Colonna et al., 1990 p. 407
Soluble sulfates >0.1% in soil or 150 mg/L in water	Endangerment of cement products due to sulfur attack.	Jones, 1990
Soluble sulfates >0.5% in soil or 2000 mg/L in water	Serious effects on cement products from sulfur attack.	Jones, 1990
Inorganic acids	Decrease durability for cement (Portland Type I) or clay/cement.	U.S. EPA, 1989b
Inorganic bases	Decrease durability for clay/cement; KOH and NaOH decrease durability for Portland cement Type II & IV.	U.S. EPA, 1989b

TABLE 4-4. SUMMARY OF FACTORS THAT INTERFERE WITH SOLIDIFICATION/STABILIZATION PROCESSES (Continued)

Possible Interfering Characteristics	Potential Interference Mechanism	Reference
Sodium hydroxide	Increase early strength at 2 to 5% concentration but decreased early strength at 8% level.	U.S. Army, 1990
Presence of anions in acidic solutions that form soluble calcium salts (e.g., calcium chloride, acetate, and bicarbonate)	Cation exchange reactions — leach calcium from solidified/stabilized product, increases permeability of concrete; increases rate of exchange reactions.	Jones, 1990
Low-solids wastes	Large volumes of cement or other reagents required, greatly increasing the volume and weight of the end product. Waste may require reconstitution with water to prepare waste/reagent mix.	U.S. EPA, 1988c
Fine particle size	Insoluble material passing through a No. 200 mesh sieve can delay setting and curing. Small particles can also coat larger particles, weakening bonds between particles and cement or other reagents. Particle size >1/4 inch in diameter not suitable.	U.S. EPA, 1988c
Environmental/waste conditions that lower the pH of matrix	Eventual matrix deterioration.	Colonna et al., 1990 p. 407

TABLE 4-5. POTENTIAL CHEMICAL INCOMPATIBILITIES BETWEEN BINDER AND WASTE CONSTITUENTS

Characteristics Affecting Process Feasibility	Potential Incompatibilities	Reference
Volatile organics	Volatiles not effectively immobilized; driven off by heat of reaction.	U.S. EPA, 1988c
Use of acidic sorbent with metal hydroxide wastes	Solubilizes metal.	U.S. EPA, 1986c
Use of acidic sorbent with cyanide wastes	Releases hydrogen cyanide.	U.S. EPA, 1986c
Use of acidic sorbent with sulfide wastes	Releases hydrogen sulfide.	U.S. EPA, 1986c
Use of alkaline sorbent with waste-containing ammonium compounds	Releases ammonia gas.	U.S. EPA, 1986c
Use of alkaline sorbent (containing carbonates such as calcite or dolomite) with acid wastes	Releases carbon dioxide which can cause frothing.	U.S. EPA, 1986c
Use of carbonaceous sorbent (carbon, cellulose) with oily waste	May create pyrophoric waste.	U.S. EPA, 1986c
Use of siliceous sorbent (soil, fly ash) with hydrofluoric acid waste	May produce soluble fluorosilicates.	U.S. EPA, 1986c

4.4 ISSUES DEALING WITH THE STABILIZATION OF ORGANIC WASTES AND OF MIXED ORGANIC AND INORGANIC WASTES

4.4.1 Introduction

This section focuses on issues related to S/S processing of wastes in which the primary contaminants are organics or where significant quantities of organic contaminants are mixed with other types of waste, such as inorganics. Issues relating to interferences caused by low levels of organics are discussed in Section 4.3.

Threshold levels for organic interference with S/S processes exist. However, the actual level depends on the nature of the organic, the waste matrix, and the binder. Different types of interferences and some guidance on threshold levels are discussed in greater detail in Section 4.3.

Organic contaminants are more difficult to treat with inorganic S/S processes than are inorganics such as metals and metal compounds. Organics generally do not react with an inorganic matrix but instead are sorbed or encapsulated within pores. The reason organic contaminants do not react is that many of them are nonpolar and hydrophobic, whereas inorganic S/S binders are polar and hydrophilic. Therefore, additives with hydrophobic functional groups are sometimes added to binders to increase the binding affinity for the organic contaminants. Inorganics may be either entrapped or incorporated into the chemical structure, depending on the treatment process.

Wastes with very high concentrations of hazardous organic compounds are generally better suited for treatment by destructive processes such as incineration, biodegradation, chemical oxidation, and dechlorination. Another problem with organic contaminants is volatilization. Releases of volatile organics to the air during S/S treatment will occur whenever volatiles are present. Both the mixing required in treatment and the heat input (from exothermic reactions in inorganic processes or external heat input in thermoplastic processes) will contribute to the loss of volatile organics. Section 4.5 discusses air emissions in greater detail.

However, many industrial wastes and contaminated materials contain organics at low concentrations, mixed with inorganics, or in a viscous waste matrix. Application of treatment processes to destroy the organics in such wastes may be very expensive compared to the benefits and may, in some cases, be ineffective (Conner, 1990). S/S can be a very viable option. S/S processes that have been tested on or applied to various organic constituents are

listed in Table 4-6. Note, however, that an entry in this table indicates only that the binder has been successfully applied at least once in the stabilization of the indicated contaminant. The degree of stabilization and the long-term stability of the product are not indicated. Also, an entry in this table does not imply that the issue of volatilization (as opposed to immobilization) of the air emissions was properly addressed.

Mechanisms that stabilize organics are not well understood (Section 4.2.2). Some stabilization of the organics appears to occur in cementitious systems. However, it has been difficult to determine whether apparent decreased contaminant mobility is caused by sorption effects, dilution by reagent additions, sample heterogeneity, or volatilization.

Quantifying the degree of immobilization of organic contaminants in S/S-treated waste is not as straightforward as for inorganic contaminants. Aqueous leach tests may provide an estimate of the propensity for the organic contaminant to be transported in groundwater as a solute, but they do not provide a good measure of organic immobilization for nonpolar organics that have low solubility in water. For nonpolar organics, the use of nonpolar solvent extraction (e.g., the Total Waste Analysis, or TWA) has been recommended. However, this recommendation is still under consideration by EPA because it is unclear how the results of a solvent extraction relate to the environmental mobility of a contaminant in groundwater. Also, there are few if any data that demonstrate that the chemical interaction between an S/S binder and an organic contaminant is strong enough to resist leaching by an aggressive nonpolar extractant. Therefore, one of the potential pitfalls of using S/S technology to treat waste with significant nonpolar organic contaminants is the inability to adequately assess the extent of contaminant immobilization attributable to S/S treatment.

4.4.2 S/S Additives Compatible with Organics

Testing of additives to improve immobilization of organic compounds with inorganic binders has shown promising results. These additives include activated carbon, charcoal, modified clays, and condensed silica fumes (fine silica particulate prepared by condensing silica fumes).

Ontario Waste Management Corporation's Wastewater Technology Centre (WTC, 1989, p. 3) investigated the use of S/S systems with the addition of activated carbon and condensed silica fumes. The S/S process was based on

TABLE 4-6. S/S PROCESSES TESTED ON OR APPLIED TO ORGANIC-CONTAINING WASTES

Binder	Organic Contaminant	Physical Form of Waste	Reference
Bitumen	Oil and gasoline	Soil	U.S. EPA, 1989g
Chemfix ^a	Oil	Sludge	U.S. EPA, 1989g
Fly ash	Phenol	Sludge	Côté and Hamilton, 1984
Kiln dust	Oil	Sludge	U.S. EPA, 1989g
	Creosote	Sludge	U.S. EPA, 1989g
Lime and fly ash	Phenol	Sludge	Côté and Hamilton, 1984
	Organics	Sludge	U.S. EPA, 1989g
Lime and kiln dust	PCBs and dioxins	Sludge	U.S. EPA, 1989g
Lime and nucleophilic reagents	PCB	Soil	HazTech News, 1991
Organic	Kepon	Sediment	Conner, 1990
Portland cement	Latex	Waste caulk	Conner, 1990
	Phenol	Sludge	Côté and Hamilton, 1984
Portland cement and clay	Phenol	Sludge	Côté and Hamilton, 1984
	Substituted phenol	Solution	Sheriff et al., 1989

TABLE 4-6. S/S PROCESSES TESTED ON OR APPLIED TO ORGANIC-CONTAINING WASTES (Continued)

Binder	Organic Contaminant	Physical Form of Waste	Reference
Portland cement and fly ash	Phenol	Sludge	Côté and Hamilton, 1984
Portland cement, kiln dust, and a proprietary agent	Pesticides	Sludge	U.S. EPA, 1989g
Portland cement and polymer	Kepone	Soil	U.S. EPA, 1989g
Portland cement and a proprietary agent	Oil	Sludge	U.S. EPA, 1989g
	Vinyl chloride and ethylene chloride	Sludge	U.S. EPA, 1989g
	API separator sludge	Sludge	U.S. EPA, 1989g
	PCBs	Soil	U.S. EPA, 1989g
Portland cement and soluble silicate	Kepone	Sediment	Conner, 1990
	Phenol	Sludge	Côté and Hamilton, 1984
Pozzolan and proprietary agent	Oil	Soil	U.S. EPA, 1989g
Sulfur-based	Kepone	Sediment	Conner, 1990

TABLE 4-6. S/S PROCESSES TESTED ON OR APPLIED TO ORGANIC-CONTAINING WASTES (Continued)

Binder	Organic Contaminant	Physical Form of Waste	Reference
Bentonite clay modified with dimethyl di(hydrogenated tallow) ammonium chloride and mixed with Type I Portland cement	Phenol and chlorinated phenols	Soil	Sell et al., 1992

* Proprietary binder formulation.

Note: An entry in this table does not mean that the binder will work under all conditions or that it necessarily worked under the conditions of the reported study. In addition, the degree of solidification/stabilization achieved was not reported in all references, nor was the extent of contaminant volatilization uniformly addressed.

Portland cement and proprietary additives. The waste was metal-finishing sludge spiked with 500 mg/kg each of acenaphthene, aniline, bis(2-chloroethyl) ether, phenol, benzene, and trichloroethylene. WTC found both physical and chemical mechanisms to be important in containing the contaminants. Activated carbon was found to be the best additive for immobilizing organic contaminants. With the exception of phenol, none of the contaminants tested in this study were detected in the aqueous leachate. Condensed silica fumes were the best additive to entrap organic contaminants physically, and the formulation tested resulted in small increases in waste mass and volume. The physical containment factor was about ten times better than that of the other cement-based processes. Further investigation of both additives is needed to define dosages, applicability to various waste constituents, and long-term stability.

Modified clays can be added with inorganic processes to reduce the mobility of organic wastes. Investigations by Lagoutte et al. (1990) indicated that S/S processes using modified clays show promise as an effective treatment for hazardous waste containing such organic contaminants as pentachlorophenol. Some clays, such as bentonite, can be modified by introducing quaternary ammonium compounds into the spaces between the alumina and silica layers. These aqueous spaces in the clay are normally hydrophilic and polar, but they can be made more hydrophobic and less polar by introducing quaternary ammonium compounds with long-chain alkyl groups or aromatic groups attached.

One common S/S formulation combines Portland cement, treated clay, and coal fly ash. The addition of coal fly ash produces a high-strength solid, although the combination generally requires longer curing times than with Portland cement alone. The residual carbon content of the coal fly ash has been shown to have an ability comparable to that of activated carbon for adsorption of organics (Lagoutte et al., 1990). Thus, both the modified clays and the coal fly ash act to immobilize the organics.

Sheriff et al. (1989) investigated the use of activated charcoal and tetra-alkylammonium-substituted clays as prestabilization adsorbents for phenols and chlorinated phenols prior to application of cement-based S/S processes. Charcoal is a well-known adsorbent, whereas the use of the substituted clays exploits the hydrophobic properties of the alkyl groups to fix organic materials within the clay matrix. Wyoming bentonite substituted with hexadecyltrimethylammonium bromide and benzyldimethyltetradecylammonium chloride (Chemical Abstracts Registry Number 139-08-2) was found to be very

effective in adsorbing chlorinated phenols with adsorption capacities of ~150 mg of chlorinated phenol per gram of clay. The results indicated a clear relationship between the chain length of the alkyl ammonium ion in the exchanged clay and the ability of the clay to adsorb a particular phenolic compound. Activated charcoal was found to adsorb effectively 180 mg of phenol or chlorinated phenols per gram of charcoal.

Cost is an important consideration in using additives such as modified clays and activated charcoal. Most additives are more expensive than binders such as cement. If a large quantity of additive is needed, the cost can be prohibitive. However, the additives frequently are effective in low concentrations. Costs of S/S processes are discussed in greater detail in Section 4.10.

Many of the additives used to reduce organic mobility in inorganic binders rely on sorption mechanisms. Sorption, especially with activated carbon, is at least partially reversible. The long-term performance of any S/S-treated waste is an important issue that is not fully resolved (Section 4.7). Long-term performance of binders that rely on sorption should be examined with particular attention.

4.4.3 Approach to Evaluating Feasibility of S/S for Wastes Containing Organics

Figure 4-2 presents a proposed approach in the form of a decision tree for evaluating the feasibility of S/S for treating organic-bearing wastes. This decision tree provides guidance for determining whether S/S is an acceptable alternative for treating a particular waste containing organics. At the outset of the process, the following information is needed (Wiles and Barth, 1992):

- The quantity of organic material relative to inorganic contaminants and other materials, including information on chemical and physical characteristics.
- The type and amount of inorganic compounds that would remain if all organics were destroyed or removed.
- The chemical and physical characteristics of residuals from the destroyed or removed organics.

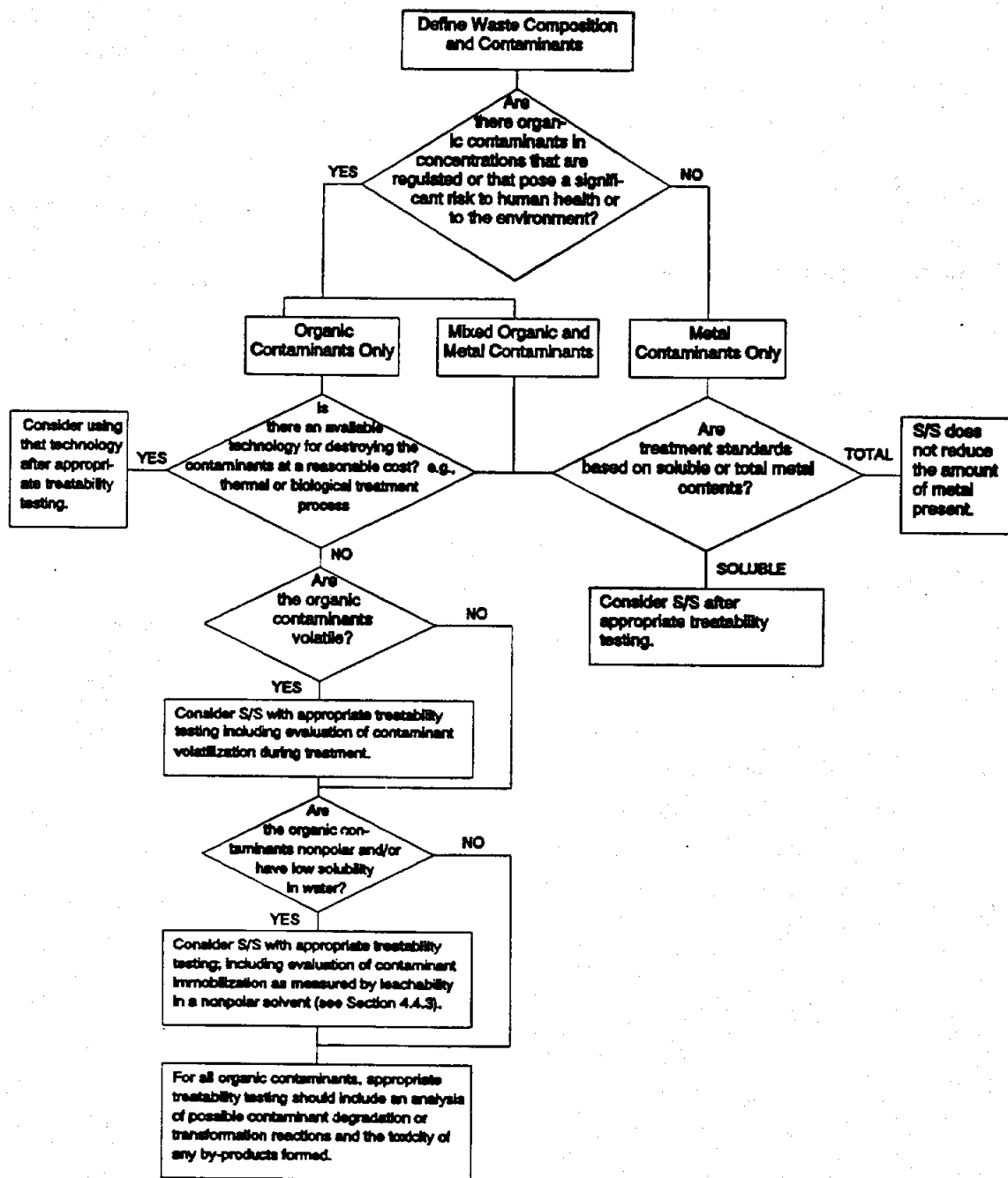


FIGURE 4-2. GENERAL DECISION TREE FOR S/S APPLIED TO ORGANIC CONTAMINANTS

The first step in the decision tree is to evaluate whether the organic contaminants present in the waste pose a significant hazard or threat to human health or the environment. This evaluation is carried out as follows:

- Determine whether the waste is either a listed or characteristic RCRA hazardous waste. If the waste is not RCRA hazardous, then the following conservative risk-based approach assuming no containment of the waste by the S/S process is proposed.
- Determine the concentration of the organic present in the waste to be treated. Determine the compound that poses the highest health or environment risk (quantity and toxicity). Then, determine the level and/or concentration of the highest risk compound that can be allowed without creating a health or environmental risk at the given site.

This conservative approach assumes that:

- The S/S process will not treat or contain the selected compound. Therefore, all of it will be released from the solidified waste; and/or
- All of the compound will be released as air emissions during the S/S process (Wiles and Barth, 1992).

If the concentration of the highest-risk compound is above the level determined to pose a health or environmental risk at the given site, then pretreatment to remove or destroy the organic(s) will be required and/or air emission controls and treatment will be needed on the S/S treatment train.

After determining that the waste contains organic contaminants that require treatment, then the decision tree in Figure 4-2 addresses the following four important issues pertaining to the feasibility and practicality of using an S/S treatment approach on the organic-bearing waste:

1. Is there an applicable technology that will either destroy or remove the organic contaminants?
2. Are the organic contaminants volatile and likely to be released as air emissions during S/S treatment?
3. Do the organic contaminants have low solubility in water? If so, the inherent potential for migration

in groundwater is low and will invalidate the meaningfulness of aqueous leach tests.

4. Will S/S treatment cause the organic contaminants to degrade or transform into toxic by-products?

These four issues are discussed further below.

4.4.3.1 Destructive or Removal Technologies Versus S/S

The concern over the use of S/S versus a destructive or removal technology for treating organic-bearing wastes relates to the hierarchy of waste treatment — that is, all other factors being equal, technologies that destroy or reduce the amount of contaminants are preferred over technologies that simply immobilize the contaminants (see Section 1.1.2). Technologies that are capable of degrading organic constituents to innocuous components such as CO₂ and H₂O, or of separating organic contaminants from inorganic constituents based on thermal or chemical properties, are preferred over immobilization technologies. Degradation and separation-based remedies are permanent, whereas immobilization may lose its effectiveness over time (see Section 4.7 on Long-Term Performance).

Consequently, S/S treatment typically is not used at sites heavily contaminated with organic wastes (Wiles and Barth, 1992). Alternative technologies (e.g., incineration, steam stripping, vacuum extraction, bioremediation) should be considered first. However, S/S treatment is frequently appropriate for the residues remaining after the use of one of these other technologies, or for soils or sludges containing low concentrations of organics. A well-designed and controlled treatability study should be conducted to assess S/S effectiveness and to select and design a proper S/S process (see Section 2).

4.4.3.2 Volatile Organic Contaminants

A wide variety of organic constituents in hazardous waste are volatile to varying degrees. As indicated in Figure 4-2, when volatiles comprise the dominant constituents, a destructive or removal technology is usually preferred. However, there are many cases where volatiles are present as a relatively minor contaminant, but in concentrations high enough to pose a potential health or environmental risk. For example, some volatiles, mixed

with metals, salts, or semivolatile organics, may respond to S/S without pretreating to remove the organics. Pretreatment or treatment trains can add significantly to the cost and the time needed to complete the cleanup. The difficulty is that volatile contaminants are not always effectively treated using S/S.

Demonstration that the volatile organic contaminants are being immobilized during treatability studies greatly complicates the treatability study. Special precautions have to be made during treatability testing to assess volatile organic emissions. This means that proper controls must be used to perform a complete mass balance, in which all organic air emissions are collected and analyzed during the treatability study, from the point of waste compositing and mixing through the curing of the treated waste specimen. The required containment, sampling, and analysis equipment and activities can more than triple the cost of the treatability study. The testing should be structured to allow a closed mass balance to fully account for the organic materials.

Unfortunately, air emissions monitoring during treatability testing is infrequently carried out as needed, and numerous studies have reported the apparent immobilization of volatile contaminants when the post-treatment reduction in contaminant concentration was, in actuality, caused by volatilization. Nevertheless, volatile contaminants in low concentrations can be and have been successfully treated using S/S when precautions are taken to minimize volatilization. Well-designed treatability studies using technology that can be implemented in the field are needed.

4.4.3.3 Nonpolar Organic Contaminants

The third issue pertains to the low aqueous solubilities of numerous organic contaminants, both volatile and nonvolatile. Polar organic contaminants such as carboxylic acids, alcohols, and phenols are typically very soluble in water. Accordingly, the TCLP aqueous leaching test defines standards for selected organic contaminants with adequate solubility in water.

However, nonpolar organics such as polyaromatics, benzene, tetrachloroethane, and hydrocarbons are generally insoluble in water. Hence, for this latter group of compounds, an aqueous leach test is a meaningless indicator of the degree of immobilization caused by S/S. Therefore, the use of a nonpolar solvent extraction (e.g., the TWA) has been recommended.

However, this recommendation is still under consideration by EPA because it is unclear how the results of a solvent extraction relate to the environmental mobility of a contaminant in groundwater. Also, there are few if any data that demonstrate that the chemical interaction between an S/S binder and an organic contaminant is strong enough to resist leaching by an aggressive nonpolar extractant. Therefore, one of the potential pitfalls of using S/S technology to treat waste with significant nonpolar organic contaminants is the inability to adequately assess the extent of contaminant immobilization attributable to S/S treatment.

4.4.3.4 Degradation and By-Product Formation

The final issue in Figure 4-2 pertaining to the immobilization of organic contaminants applies to all types of organic contaminants — volatile and nonvolatile, polar and nonpolar — in all ranges of concentrations. Because organic constituents readily undergo chemical transformation reactions and S/S binders are associated with fairly aggressive chemical environments (such as increased temperature and alkaline pH), the potential for chemical transformation or degradation always exists; and a post-treatment reduction in the concentration of an organic contaminant may be erroneously interpreted as evidence for immobilization when it, in actuality, may be attributable to contaminant transformation. Moreover, chemical transformation or degradation may result in the formation of by-products which can be more or less toxic than the parent compound. Therefore, it is not sufficient to demonstrate the extent to which transformation is occurring. The identities of the by-products and their toxicities must also be characterized. Unfortunately, the process of detecting and analyzing by-products can be extremely expensive and can therefore be a deterrent to considering S/S as an option for the treatment of organics-bearing wastes.

4.5 AIR EMISSIONS AND CONTROL

In considering S/S options, the possibility of air emissions must be taken into account. Many wastes contain VOCs that can escape into the atmosphere. Even compounds not generally considered volatile can be released by the mixing and heating operations involved in S/S. In addition to volatilization, other forms of air emissions, such as fugitive dust or particulates,

must be taken into account. The cost of installing and operating equipment to prevent air emissions can be significant. The local air board or other cognizant regulatory agency should be consulted to define air emissions issues.

4.5.1 Volatile Organic Compounds

Volatile organic compounds can escape into the atmosphere during the mixing and heating steps of the S/S process, and even during sampling, sample handling, and sample preparation prior to analysis. For example, one study of volatilization during S/S processing found that an average of 0.11% of the feed into the process was emitted to the air (Ponder and Schmitt, 1991). As a general rule, sites contaminated with only volatile contaminants should not be considered as candidates for S/S (Wiles and Barth, 1992) (see also Sections 4.4 and 2.4). However, volatile and/or semivolatile organic compounds are frequently present as secondary components in wastes that contain mostly metallic or other inorganic contaminants.

In wastes containing VOCs, significant VOC losses to the atmosphere will occur with remediation activities that involve exhumation of the waste. In situ S/S technology that produces a monolithic product is capable of reducing VOC losses but not of eliminating them (Spence et al., 1990). Also, volatiles can continue to escape from a solidified waste form, regardless of the reduction in pore space and increase in tortuosity.

The quantities of VOCs acceptable for S/S should be based on a risk assessment for the given site and/or on the result of a treatability study that includes a mass balance of the organics before, during, and after treatment. As a worst-case scenario, the risk assessment should assume that none of the highest risk compounds will be retained by the S/S process and/or that all the compounds will be lost via air emissions during S/S processing (Section 4.4).

A system for measuring the emissions of organic compounds from mixing processes such as those used in S/S activities is currently under development. This "modified headspace" sampling system, having been demonstrated at VOC emission rates ranging from less than 1 milligram per minute up to tens of grams per minute, can be used at the laboratory scale to measure organic emissions both from the S/S process and from the S/S-treated waste during curing. Such equipment can also be used in conjunction with a full-scale

remediation effort by testing samples of the treated waste from the field in the laboratory (Weitzman et al., 1990).

4.5.2 Particulates and Other Emissions

In addition to gaseous emissions from volatile organics, particulate releases to the atmosphere from operations associated with S/S treatment can also be a concern. Possible sources of air pollutants and fugitive dust in a field S/S project include excavation, the movement of trucks and other heavy equipment, and the loading and processing of waste and binder materials in the mixing device. In the study cited in Section 4.5.1 for VOC volatilization, it was also found that an average of more than 0.01% of the waste feed being processed was released as particulate emissions (Ponder and Schmitt, 1991). Care must frequently be taken to reduce the escape of both contaminated particulates and fugitive dust during treatment. Typical engineering controls include scrubbers for certain types of air pollutants and wetting the waste or ground to reduce dust.

Various guidelines exist for determining maximum air emissions of contaminants and fugitive dust during remediation projects. For example, *Toxic Air Pollutant Source Assessment Manual for California Air Pollution Control Districts and Applicants for Air Pollution Control District Permits* specifies a risk-screening methodology for evaluating air emissions and a fugitive dust concentration limit for remediation projects in California (Interagency Working Group, 1987). The risk-screening methodology is a simple, conservative estimation of the maximum possible health impacts associated with air emissions during the duration of the project. If the project fails the initial risk screening calculation, then a much more detailed risk assessment may have to be conducted prior to initiating field treatment.

4.5.3 Controlling Air Emissions

Depending on the nature of the anticipated air emissions, it may be necessary to adopt control measures to ensure that volatile and particulate emissions are within acceptable levels. Equipment such as air scrubbers or large enclosures around the treatment area may have to be employed as an adjunct to the S/S treatment process, thus increasing the complexity and costs associated with S/S. The U.S. EPA's Office of Air Quality Planning and

Standards (OAQPS) is developing guidance for controlling air emissions at RCRA treatment, storage, and disposal facilities (TSDs). This guidance will require many S/S processes to incorporate capture and control mechanisms for volatile constituents. Even those projects involving relatively low levels of volatile constituents may be affected (Wiles and Barth, 1992). However, apart from this guidance for TSD facilities, air emissions and controls are currently assessed on a project-by-project basis.

4.5.4 Significance of the Amended Clean Air Act

The purpose of the Clean Air Act (CAA) is to:

- protect and enhance the quality of the nation's air resources so as to promote the public health and welfare and the productive capacity of its population
- initiate and accelerate a national research and development program to achieve the prevention and control of air pollution
- provide technical and financial assistance to state and local governments in connection with the development and execution of their air pollution prevention and control programs
- encourage and assist the development and operation of regional air pollution control programs

Within these purposes, waste minimization or pollution prevention is encouraged but, in most cases, is not mandated. Under the CAA, regulations have been promulgated that give industry the choice of either preventing or controlling air emissions. These regulations include the National Ambient Air Quality Standards (NAAQS); National Emission Standards for Hazardous Air Pollutants (NESHAP), which control emission of specific pollutants for specific industries; and permitting requirements.

Just as the forthcoming RCRA-related guidelines for TSD facilities will affect S/S operations, the amended Clean Air Act portends increased use of capture and control mechanisms. Stricter regulations will require more careful screening of candidate sites for the application of S/S technology. This screening will be based on the potential to achieve regulatory compliance and the cost of achieving regulatory compliance.

4.6 LEACHING MECHANISMS

After disposal, the S/S-treated waste may eventually come into contact with water. The S/S processes are aimed at either reducing the mobility of the contaminants or reducing access of water to the contaminant, or both. However well the S/S waste is stabilized and isolated from the hydrosphere in disposal, some transport of contamination from the S/S-treated waste into the groundwater will eventually occur. Complete immobilization of contaminants is not a realistic expectation (Bishop, 1988).

This process of slow extraction of contaminants from the S/S-treated waste by water or some other solvent is called "leaching." Leaching tests are discussed in Section 3.2. Leaching can occur when the S/S-treated waste is exposed to stagnant leachant or to a flow of leachant through or around the waste. Leaching is the general term for complex physical and chemical mechanisms. These mechanisms mobilize a contaminant and transport it away from the waste.

In a disposal scenario, the solvent will usually be groundwater. Leaching occurs when the contaminants in the S/S-treated waste come into contact with the groundwater. The leachant flow and composition are determined by the physical properties of the disposal area and any engineered barriers at the disposal site. Leaching tests may use water, aqueous solutions of acids or salts, or organic liquids to model various disposal scenarios, determine waste composition, measure diffusion coefficients, or for other specific test purposes.

There is significant experimental evidence that, when waste stabilized by cement or similar pozzolanic materials is exposed to acidic water, significant matrix dissolution occurs. Thus, the leaching rates of contaminants from stabilized waste will be a function of both the dissolution rate as well as the diffusion rate of contaminants into the leachate.

In the Netherlands, a database has been developed to collate, organize, and analyze information about the leaching of contaminants from waste and waste-containing materials (de Groot and van der Sloot, 1992). Organization of the information into a database is intended to assist identification of systematic trends in leaching behavior and mechanisms.

4.6.1 Leaching Associated with Inorganic S/S Processes

The typical S/S-treated waste resulting from use of an inorganic binder is a porous solid. The pore space contains some mixture of water and gas, so many different phases can be present. There may be several different solid phases, each containing contaminants. For example, contaminants may be present in the cement mineral phases because of substitution in the crystal structure or as a separate phase, such as a precipitated solid. There can also be one or more aqueous phases such as an adsorbed layer of fluid as well as the bulk pore fluid. The sorbed layer may have a different contaminant composition than the bulk fluid. There can also be one or more nonaqueous phases if organic contaminants are present (WTC, 1990a).

Prior to introduction of the leachant, the pore system will have approached equilibrium conditions with the surrounding solid phase. That is, the contaminants are associated with a specific phase, and there is no net transfer between the phases. The leachant changes the composition of the system and disrupts the chemical equilibrium, resulting in the mobilization of contaminants. The new system may evolve towards a new equilibrium if sufficient time passes with no leachant renewal.

The two basic mechanisms in the leaching process are mobilization and transport of the contaminant. The leachant mobilizes contaminants within the pores by dissolving the contaminant. Dissolution results from a combination of chemical and physical mechanisms. Examples include bulk dissolution of mineral phases in the S/S-treated waste, washoff of surface contaminants, changing chemical parameters such as pH or Eh dissolving a formerly insoluble phase, desorption of contaminants, or other mechanisms (deGroot and van der Sloot, 1992). Factors that affect the extent of equilibrium concentrations include the solubility of the constituent and the chemical makeup of the pore water. Under neutral conditions, the leaching rate is controlled by molecular diffusion of the solubilized species. However, if the leachant induces acid conditions, the rate will also depend on the rate of back diffusion of the hydrogen ion because the pH determines the chemical speciation within the S/S-treated waste (Cheng, et al, 1992).

As more soluble constituents are leached from a relatively insoluble solid matrix, a layer deficient in the leached constituents develops. Under low pH conditions, both H^+ and the leachable constituents must diffuse through this layer in opposite directions. The leaching rate in the leached layer

should eventually be limited by diffusion of constituents, because H^+ diffuses much faster than other species. However, this layer may not be rate-limiting in the overall process (Cheng and Bishop, 1990). As constituents leach, the layer may become more porous compared to the unleached solid, so that molecular diffusion in the pore water and boundary layer phenomena become the limiting factors (Conner, 1990).

Transport of the mobilized contaminants occurs by bulk advective flow or diffusion. If water flows within the S/S-treated waste, advective transport causes contaminants that have been mobilized by reactions in the pores to flow through the waste. The velocity of leachant moving through the pores will vary considerably in both magnitude and direction due to the small size and the tortuosity of the pores (WTC, 1990b). In most S/S-treated waste, the pores are small and tortuous, so the advective transport is small. However, contaminant movement still occurs by molecular diffusion (Crank, 1967).

Only a fraction of the pores within the S/S-treated waste are linked to each other and to the outside to form what is referred to as "connected porosity." The pores that are not linked to this network are referred to as "closed porosity." Also, large pore spaces may be connected by small-diameter pathways, resulting in "occluded porosity." The micromorphology of the matrix - including the number, size, and degree of connection of the pores - will determine how quickly water can permeate through an S/S waste (i.e., hydraulic conductivity) and will influence the leaching process. As might be expected, leaching occurs most quickly through the connected pores.

In most cases, cement-based monoliths have low hydraulic conductivity, which limits the amount of leaching water contacting the matrix. However, it has been shown that the hydraulic conductivity of S/S waste may vary over several orders of magnitude, from low values typical of compacted clay to higher values typical of silty soils (Côté et al., 1986). Hydraulic conductivity of the waste determines whether leaching rates will be controlled by advection or by molecular diffusion. Advection is more important than diffusion when hydraulic conductivity is larger than 10^{-7} cm/s. On the other hand, slow diffusion limits transport rates when hydraulic conductivity is lower than 10^{-7} cm/s. If the hydraulic conductivity of the waste is much lower than that of the surrounding material, infiltrating water such as rainwater or groundwater follows the path of least resistance and flows around

the waste. In this case, leaching is limited by molecular diffusion in the connected porosity of the S/S waste matrix because, when contaminants reach the interface of the S/S waste and surrounding material, they are carried away by the groundwater. If, on the other hand, the hydraulic conductivity of the solidified waste is on the same order of magnitude or higher than that of the surrounding material, water flows around and through the waste. In that case, the pore water solution is displaced, and leaching takes place largely by advection (Côté and Bridle, 1987, p. 60).

The surface-area-to-volume ratio (SA/V) of a waste product greatly influences the release of potentially harmful elements to the environment. A smaller SA/V results in a lower rate of release. The leaching percentage relative to the total amount of an element present in a waste form is related to the SA/V, for a given exposure time. Therefore, all measures leading to products with a smaller SA/V lead to a proportional decrease in leaching percentage but the long-term quantities released are not decreased (van der Sloot et al., 1989).

Chemical speciation also influences leaching. Van der Sloot et al. (1989) found that elements leached from cement-based waste products are mainly anionic species such as MoO_4^{2-} , BO_3^{3-} , VO_4^{3-} , F^- , and SO_4^{2-} . These anions are associated with cationic species typical of cement-based waste forms such as calcium. Leaching of metals such as copper, cadmium, zinc, and lead typically is limited when the pH in the pore solution remains above 8 or 9, but can increase at very high pH (above 11.5 or 12). Van der Sloot et al. (1989) concluded that chemical speciation of potentially hazardous elements within a waste product and the interaction of these elements with matrix components within the pore system are crucial for determining the release rate to the environment. Also, they suggested that more information on different ways of contact with water is needed, particularly in relation to pH, to allow utilization of intrinsic leach parameters in a wide range of environmental conditions.

For cement-based S/S processes, sulfate can increase leaching rate. The onset of the leaching rate increase may be delayed, however, so test results immediately after setting may be misleading. Sulfate either in the cement or present in the waste causes formation of ettringite, which slowly hydrates and expands, causing an increase in porosity and possible breakdown of the waste form. Sulfites and sulfides are also a problem because they may

slowly oxidize to sulfate, increasing the solid volume and causing the waste to crack.

Poon et al. (1985) found that the microstructure of the solidified waste was important in leaching metals from the cementitious matrix. They assessed mechanisms of zinc and mercury leaching from cement/silicate stabilization processes using extended leaching tests, scanning electron microscopy, and powder X-ray diffraction. After an extended leaching period, massive breakdown of the matrix occurred with a subsequent dramatic increase in leachate concentration. Once the structural integrity of the stabilized waste was removed, massive leaching of zinc and mercury occurred.

4.6.2 Leaching Associated with Organic S/S Binders

The thermoplastic and thermosetting resin binder processes operate mainly by encapsulating the waste. The S/S-treated waste is, therefore, less porous than the material resulting from S/S processes using inorganic binders. The leaching process requires the same two fundamental mechanisms discussed in Section 4.6.1, mobilization and transport. However, the organic binder systems rely more on denying the leachant access to the contaminant than on immobilization.

4.6.3 Leaching Models

Several models of leaching mechanisms have been developed to predict the rate of release from the stabilized waste matrix. Modeling is the only existing method for predicting long-term performance because it is impractical to conduct empirical leaching tests for hundreds or thousands of years and because accelerated tests are not well developed.

4.6.3.1 Dissolution/Diffusion Kinetics

The problem of kinetics, with regard to the aqueous dissolution of a solid or to the preferential dissolution of a chemical species from a solid, has long been studied. Several factors may be involved. For example, if more than one kinetic process takes place, it must be determined which (if any) of the processes controls the overall reaction rate. The shape of the solid, the existence of any surface-connected porosity, the charge state of the dissolv-

ing species, and the chemistry of the aqueous medium into which the solid is dissolving are also considered.

The discussion that follows considers two kinetic processes from a largely qualitative point of view: the dissolution reaction itself, which consists of mass transport across the solid/liquid interface, and chemical diffusion away from this interface into the surrounding aqueous medium. It is assumed for this specific example that the rate of supply of dissolving material from the bulk of the solid to this interface occurs quickly. It is also assumed that the solution is quiescent, so that convective flow does not contribute to the mass transport. Two fundamentally different types of systems are considered within this context: a nonporous solid dissolving into an essentially infinite aqueous medium and a porous solid for which dissolution takes place principally into the interconnected solution-containing pores, coupled with diffusive transport through the pores to the solution outside the material. Idealized models of these two systems are described in Sections 4.6.3.1.1 and 4.6.3.1.2 to illustrate the concepts in leaching models.

If the dissolving chemical species is electrically charged, considerations of charge neutrality in the solution become important, as does mass transport in the solution by electromigration. The species also may react chemically with other species within the aqueous medium. Diffusing ions may also react with the matrix in the leaching zone, adsorbing or precipitating, which can slow their release. Diffusing ions may also react with the matrix in the leaching zone, adsorbing or precipitating, which can slow their release. These factors are not considered here. However, a general treatment of ionic transport within a crevice-like region, which could be applied to dissolution and diffusive transport in a porous solid, has been presented by Markworth and Kahn (1985).

4.6.3.1.1 Nonporous Solid. For a nonporous solid, the two kinetic processes, i.e., dissolution at the solid/liquid interface and chemical diffusion of the dissolved species away from the interface, occur sequentially. For this case, the interface may be regarded as a spatially localized "source" of the dissolving species.

At the solid/liquid interface, the flux of matter due to the dissolution reaction must be equal, point by point, to the diffusive flux in

the solution to avoid a nonphysical accumulation or depletion of matter at the interface. Consequently, the slower of the two processes is the one that dominates the overall kinetics.

Three characteristic values for the aqueous concentration of the dissolved species are important in describing the overall kinetics for this case:

1. C_e , the concentration that would exist at the interface under conditions of thermodynamic equilibrium.
2. C_i , the actual, instantaneous concentration at the interface.
3. C_∞ , the far-field concentration, i.e., the value at distances far from the interface.

The "driving force" for the dissolution reaction depends upon the difference $C_e - C_i$. If $C_i < C_e$, the net transport of matter across the interface occurs from solid to liquid as the solid dissolves, while the opposite is true for $C_i > C_e$. If these two concentrations are equal, there is no net transport across the interface. Likewise, the driving force for chemical diffusion is the difference $C_i - C_\infty$, assuming monotonic variation of the concentration from the interface to the far field. If $C_i > C_\infty$, matter diffuses away from the solid/liquid interface, the converse is true for $C_i < C_\infty$.

Two limiting or extreme cases exist for the overall kinetics; one or the other of these cases is often satisfied in nature.

1. In the dissolution-controlled case, diffusion occurs rapidly compared to the dissolution reaction so the driving force required to maintain the diffusive flow is very small and $C_i \cong C_e$.
2. In the diffusion-controlled case, diffusion occurs slowly compared to the dissolution rate. For this case, dissolution is rapid but a concentration gradient is needed to drive the diffusion process so $C_i \cong C_e$.

For dissolution-controlled kinetics, dependence on diffusion-related rate constants is virtually nonexistent, whereas for diffusion-controlled kinetics, dependence on dissolution-related rate constants similarly vanishes.

The intermediate case is that for which neither of the two mass transport processes controls the overall kinetics. For example, the solid is dissolving when $C_{\infty} < C_i < C_s$, but it is growing by supply of dissolved species from solution when $C_s < C_i < C_{\infty}$.

Figure 4-3 illustrates the two limiting cases and the intermediate case. The actual concentration profile of the dissolved species in the aqueous medium would generally be a complex function of position and time as well as of the geometry of the dissolving solid.

It should be noted that this view of the dissolution process, which is widely applied in practice, must be used carefully or be modified in some cases. One such case, considered by McCoy and Markworth (1987), involved the dissolution of glasses containing high-level nuclear waste. One question there concerned how these "impure" materials actually do dissolve. In their work, McCoy and Markworth assumed that the material dissolves congruently. To describe this process, they assumed first-order, dissolution-controlled kinetics, with transport of silicon across the surface/solution interface being the rate-limiting factor. As another case, consider a dissolving material which consists of two different, distinct phases, with one phase tending to dissolve into the surrounding aqueous medium much more rapidly than the other. The more soluble phase will be preferentially dissolved (i.e., leached), leaving behind a material that is enriched in the less soluble phase. Of course, the microstructure of the material left behind will depend on the morphology of the two phases prior to dissolution. If, for example, the more soluble phase exists as an interconnected network, then the leached portion of the material will consist of a porous structure that likewise contains a network of interconnected porosity, assuming that the solution can penetrate into the porous structure as it is being created. This process could be inhibited if transport of dissolved species through the solution, within the porous structure or away from the external surface, occurs slowly.

4.6.3.1.2 Porous Solid. The situation differs for a porous solid, with liquid penetrating and filling the porous structure, where dissolution can occur along the entire length of the pores. The distinctly sequential

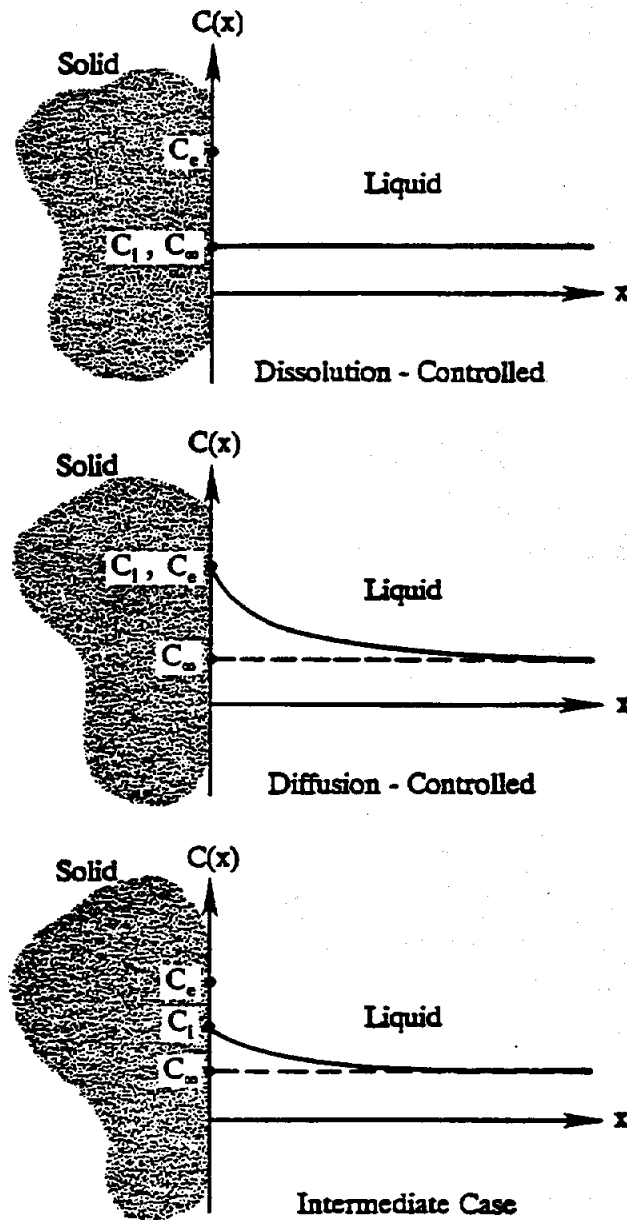


FIGURE 4-3. SCHEMATIC ILLUSTRATION OF CONCENTRATION PROFILES, $C(x)$, CHARACTERISTIC OF SPECIES DISSOLVING FROM A NONPOROUS SOLID INTO AN AQUEOUS MEDIUM, WITH x BEING THE DISTANCE INTO THE SOLUTION MEASURED FROM THE SOLID/LIQUID INTERFACE. THE TWO RATE-LIMITING CASES AND AN INTERMEDIATE CASE ARE SHOWN.

coupling between the two processes, characteristic of nonporous solids, does not exist. The "source" of dissolving species, considered to exist at the pore/solution interface, is *not* spatially localized as it is for a nonporous solid. Instead, dissolution can take place along the entire length of the pores within which the dissolved species is diffusing, the pore walls acting as a spatially extended "source" of this species to the solution within. Diffusion of the species takes place within the network of pores until release occurs at the intersection of the pores with the external surface. Figure 4-4 shows this type of mass-transport kinetics.

4.6.3.2 Examples of Existing Models

The complex relationship between dissolution and diffusion for a porous solid means that the overall rate of release of dissolved species to the external surface depends on both dissolution-related and diffusion-related rate constants, even if one occurs faster than the other.

Godbee and Joy's widely used empirical model (Godbee et al., 1980) assumes that leaching is controlled by diffusion through the solid, and that a zero surface concentration exists (i.e., contaminant dissolves into the bulk liquid from the surface immediately). The equation takes the form:

$$\left[\frac{\sum a_n}{A_0} \right] \left[\frac{V}{S} \right] = 2 \left[\frac{D_e}{\pi} \right]^{0.5} t_n^{0.5} \quad (1)$$

where

- a_n = contaminant loss during leaching period n (mg)
- A_0 = initial amount of contaminant present in the specimen (mg)
- V = volume of specimen (cm^3)
- S = surface area of specimen (cm^2)
- t_n = time to end of leaching period n (sec)
- D_e = effective diffusion coefficient (cm^2/sec)

Models have also been developed to account for other factors and conditions in the leaching process. For example, where Godbee and Joy's model assumes leaching from an infinite depth, leaching in cementitious waste forms occurs in a narrow, but inwardly-moving, leaching zone. A model that addresses this is discussed in Section 4.6.3.3.

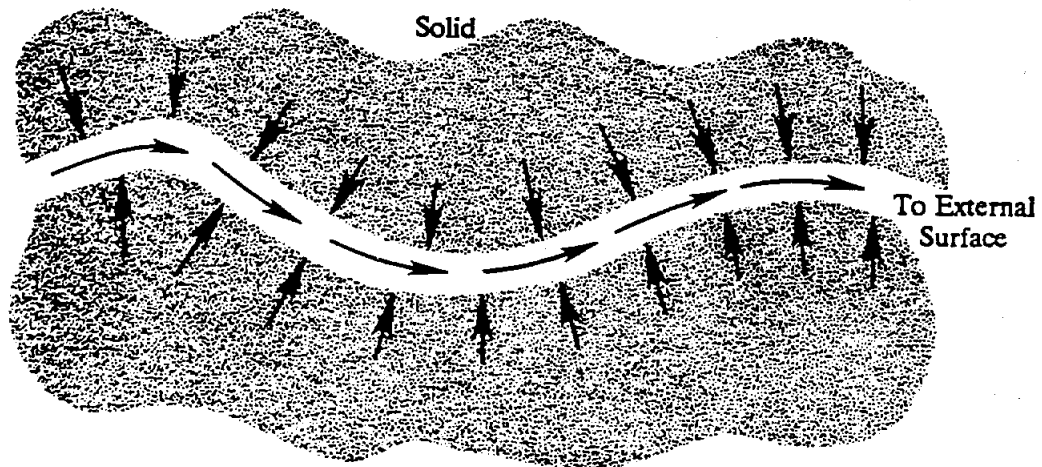


FIGURE 4-4. ILLUSTRATION OF SPECIES DISSOLUTION WITHIN A POROUS SOLID. DISSOLUTION ACROSS A PORE WALL IS SHOWN, COUPLED WITH TRANSPORT THROUGH THE SOLUTION-FILLED PORE TO THE EXTERNAL SURFACE.

Batchelor (1990) reviewed the theory and application of leaching models. His results indicate that a variety of mechanistic leaching models can be developed to describe leaching and predict the effects of process variables on the performance of solidified wastes. These models are distinguished by the assumptions made about the leaching environment and the chemical and physical mechanisms at work.

Several simple leaching models predict that the fraction of contaminant leached is proportional to the square root of leaching time. The different models assume that contaminants either do not react or react by linear sorption, by precipitation, or by an undefined mechanism that results in complete immobilization of part of the contaminant. The observed diffusivity is the parameter in these models that describes the extent of immobilization, and it can be determined by conducting a leaching test. However, these leach tests cannot themselves describe the type of immobilization occurring. Each model results in a relationship that shows that the observed diffusivity is proportional to the effective diffusivity. The effective diffusivity is the parameter that describes diffusive transport by Fick's law and therefore describes only physical immobilization. The proportionality coefficient depends on parameters that describe the particular chemical immobilization mechanisms assumed for that model.

Batchelor applied mechanistic leach models to describe performance of solidified wastes in the TCLP test by modifying a simple model to describe the effect of inward diffusion of acetic acid from the leaching solution. However, the model did not incorporate changes in the acetic acid concentration that would be observed over time as pH rises. Batchelor further notes that mechanistic leach models could also be applied to predict long-term leaching, to quantify the relative importance of chemical and physical immobilization mechanisms, to correlate and extrapolate leaching data for various contaminants and binders, and to predict ultimate performance from early characteristics of the solidified waste.

Numerous other leaching models have been developed, with a variety of intended applications. Many of these models are sophisticated and require an experienced user. For S/S remediation projects requiring application of a leaching model to evaluate long-term performance, the use of a technical expert with experience in leaching modeling is strongly recommended.

4.6.3.3 The Moving Boundary or Shrinking Core Model

A qualitative model of the leaching of cement-based waste forms, in contact with an acidic leachant, has recently been developed by Cheng et al. (1992) based on experimental observations. According to this model, acids in the leachant are thermodynamically favored to be driven into the waste form. Once inside, they cause the waste form to decompose, leaving a residue (the leached layer) that is both porous and rich in silica. The unleached core of the waste form is separated from the leached portion by a very thin boundary which gradually moves into the core and thus reduces its volume. The thickness of this boundary is only about 100 μm , but the pH varies from less than 6 on the leached side to greater than 12 within the 100 μm distance.

What is needed is for this general physical model to be quantified, that is, to be expressed in mathematical form. Then it could be used as a predictive tool as well as an aid in the interpretation of experimental data. One way to begin would be to determine the applicability to this problem of certain mathematical models that have already been developed to describe the leaching of glasses that contain high-level nuclear waste. Although the materials, solution chemistry, distance scales, and even the associated physical processes may not be the same as for S/S wastes, the mathematical approaches may be applicable, to some extent, to the model of Cheng et al. (1992). For example, Banba et al. (1985) have developed a one-dimensional mathematical treatment of a "moving boundary" model for the leaching of nuclear-waste-containing glasses. This treatment involves a surface layer that moves into the bulk glass. Also, Harvey et al. (1984) have developed some diffusion-based mathematical models for leaching of glassy nuclear waste forms. In this latter work, they described a depleted layer in the waste-form matrix which is situated between the matrix/leachant interface and a so-called depletion front. This front is the interface between the depleted and undepleted matrix and advances into the matrix as leaching progresses. Again, the mathematical structure of these various models may have some applicability to the moving boundary model of Cheng et al. (1992).

4.7 LONG-TERM PERFORMANCE

A significant unresolved S/S technology issue is how well the S/S-treated waste maintains its immobilization properties over time. Although the

long-term durability of cement is well proved in conventional construction, some amount of release is virtually inevitable. S/S materials can be deposited in landfills to provide secondary barriers between natural waters and the wastes. Contaminant release begins when these secondary barriers permit natural waters to come into contact with the waste forms (Côté and Bridle, 1987). The question is not whether S/S wastes eventually release contaminants into the environment, but whether the rate of release is environmentally acceptable. S/S technologies for waste treatment have been in use for only a few decades, so the number and duration of studies on field-disposed S/S wastes are limited. Decisions about the acceptability of particular S/S products must be based on the available shorter-term field data, laboratory tests, and models of leaching behavior.

There is evidence that elements can be fixed in cementitious materials for millennia in a variety of geochemical settings (Dole, 1985). Ancient grouts from Cyprus and Greece that are 3500 to 2300 years old have held their trace metal fingerprints, allowing their constituents to be traced to nearby pits from which they had been mined. These ancient grouts are composed largely of undifferentiated, amorphous hydrosilicates, even after thousands of years. The in situ performance of these ancient grouts demonstrates the effectiveness of these metastable amorphous hydrosilicates in sequestering a wide range of elements. However, these observations are not directly applicable to S/S wastes because of differences in the physicochemical forms of the trace metals in ancient grouts versus modern waste and differences in the disposal environments in a Mediterranean climate versus the wetter climate that dominates most of the United States.

4.7.1 Field Studies

There have been only a few studies of the effects of several years' duration of environmental exposure on S/S-treated waste. The Coal Waste Artificial Reef Program (CWARP) studied the environmental consequences of using stabilized coal combustion wastes as construction material for artificial fishing reefs. On September 12, 1980, some 16,000 blocks of stabilized waste were released from a hopper barge to form an artificial reef in the New York Bight. The blocks consisted of coal fly ash and flue gas desulfurization residues stabilized with lime and Portland cement additives. Blocks recovered and tested in 1988 indicated little deterioration and no decrease in compres-

sive strength. Chemical analyses and surveys of biological communities established on the reef indicated contaminants were successfully immobilized (Hockley and van der Sloot, 1991).

A Superfund Innovative Technology Evaluation (SITE) field evaluation examined the long-term performance of S/S treatment of lead and other metals, oil and grease, and mixed volatile and semivolatile organic compounds using Portland cement and a proprietary additive. Durability was tested with weathering tests, by wet-dry and freeze-thaw cycling, and by sampling S/S-treated waste after 9 and 18 months of burial. The testing showed that lead and other metals remained highly immobilized, the physical properties of the S/S-treated waste deteriorated only slightly, and the porosity decreased. The organic contaminants, however, were not effectively immobilized (de Percin and Sawyer, 1991).

The demonstrated long-term durability of concrete structures may help in the analysis of the long-term durability of S/S waste forms. Structures made with cement have lasted hundreds and even thousands of years. Long-term durability of a structure is not directly analogous to immobilization of contaminants in S/S-treated waste. However, it does indicate the ability of inorganic binders to resist gross structural degradation from exposure to the natural environment. Natural mineral deposits occurring in the environment are another possible analog to certain S/S waste forms. Metal sulfide deposits, for example, have remained stable for many millions of years in subsurface geologic formations. In general, mineral leach rates in nature do not approach those in the laboratory. The same processes that inhibit the leaching of natural substances also may apply to S/S wastes disposed in subsurface environments (Conner, 1990), provided that the chemical speciation of the materials disposed and the disposal environment are the same.

4.7.2 Laboratory Studies

At present, the environmental acceptability of a hazardous waste in the United States is based primarily upon the EPA's Extraction Procedure Toxicity Test (EP Tox) or the Toxicity Characteristic Leaching Procedure (TCLP). Neither test, however, simulates real-world, long-term conditions, although they may constitute a fairly severe set of conditions for single-exposure leaching.

Perry et al. (1992) used TCLP to examine long-term leaching performance of four types of wastes contaminated with metals or inorganics. Each waste was treated with six different commercial stabilization processes. TCLP was performed on raw waste and at 28, 90, 200, 470 and 650 days after treatment. Results indicated that the effect of time on the TCLP results was highly waste-dependent. Leachate values for some wastes remained stable over time while leachate concentrations for other wastes increased over time. In some wastes, changes in TCLP concentrations did not occur until 90-200 days after stabilizations. Similar results have been obtained by Akhter and Cartledge (1991) and Cartledge (1992), except that both increases and decreases in metals leachability as measured by the TCLP have been observed with aging. In some cases, these changes in TCLP data have been associated with changes in the chemical structure of the stabilized waste, as measured by spectroscopic analyses. These results suggest that additional evaluation of stabilization is required to ensure confidence in long-term leaching performance.

The U.S. EPA's Multiple Extraction Procedure (MEP) or other tests that expose the waste to repeated, sequential leaching can give information on leach resistance over time. Other sequential or flow-through leaching tests such as ANSI/ANS/16.1 (see Section 3.2 and Table 3-3) can give information to support prediction of long-term leach resistance.

By and large, however, attempts to correlate laboratory leaching tests with field data have not been successful. The EP Tox test, for example, can be used only to predict the potential for leaching; it cannot predict the rate of leaching over time (Bishop, 1986). Deviations between the laboratory and field are sometimes caused by testing materials under oxidized conditions (open contact with air), while the groundwater in contact with the waste may be chemically reducing. Laboratory leaching tests use continuous wetting of the waste with a leachant at controlled temperature. In situ conditions typically involve periodic contact with water and fluctuations in temperature.

4.7.3 Modeling

Numerical modeling (Section 4.6.3) is another approach to predicting the long-term performance of S/S-treated waste. Parameters based on the physical and chemical properties of a waste form can be used in conjunction with mathematical models to infer long-term leachability, based on assumptions about the leaching mechanisms and environment (Côté et al., 1986).

Mathematical models have also been combined with accelerated dynamic leaching tests to assess the long-term stability of S/S waste forms containing arsenic, cadmium, chromium, and lead.

Other recent research also indicates that metal leaching follows diffusion theory and that mathematical models combined with various leaching tests allow some predictions about metal leaching over time, with particle size, leachant velocity, and leachant acidity being key variables (Bishop, 1990). Although these models suggest good long-term stability for several S/S approaches, a test or model that simulates field conditions to a degree that would allow for confident predictions of long-term stability is lacking.

4.8 USE/REUSE VERSUS DISPOSAL

One of the principal aims of S/S processes is to produce an end product that is less environmentally threatening than the original waste. There is an added benefit if the stabilized waste can be put to some practical end use. The ability to use S/S end products eases the burden of disposing of the waste and provides obvious economic and environmental advantages over hazardous waste disposal practices. However, concerns about the long-term performance of the S/S product and the possible exposure of human or ecological receptors to contaminants released from it greatly restrict use/reuse options, and in practice relatively few S/S-treated wastes have been reused or recycled to date.

4.8.1 Alternatives

The purpose of use/reuse is to ease the burden on land disposal. Therefore, use/reuse alternatives, when deemed environmentally safe, can be a productive alternative to disposal. Possible use/reuse alternatives for stabilized/solidified waste include construction material for use in concrete, Portland cement, asphalt, road base material, landfill cover, or agricultural additives. In addition, some solidified waste may be used in direct water contact applications, such as for diking material and for forming new land from lakes, streams, marine waterways, or low-lying swamp areas. Another potential application is to help solve shoreline erosion problems by installing support structures made from incinerator ash and cement. These structures are being studied by the State University of New York not only for their

potential to reuse S/S products, but also for their ecological benefit in controlling erosion and offering a marine habitat for some species. Another potential application for S/S products is to construct artificial reefs from stabilized drilling muds from offshore drilling rigs (Kelley, 1988). In Europe, there is an emphasis on combining wastes from incineration plants with fly ash, water, and plaster to form a solid material that can be used to create sealed landfill reservoirs (Lukas and Saxer, 1990).

Until the long-term performance of S/S-treated waste in such applications is clearly demonstrated, most S/S products in the United States will still have to be disposed of in a more cautious manner, which generally means disposal in a landfill. Environment Canada (WTC, 1990b) has suggested an overall classification system for S/S waste. Classifications are based on batch extraction tests to estimate the amount of contaminant available for leaching and an evaluation of monolithic waste form leaching performance. Analysis of leaching performance uses mathematical models derived from the S/S literature with input from a database on S/S waste properties. For the purpose of this classification system, two utilization and two disposal scenarios have been selected that require different degrees of contaminant containment in a S/S waste. The scenarios are briefly described below, in order of decreasing performance requirements for S/S waste.

S/S wastes that do not qualify for utilization or disposal according to one of these scenarios would need to be disposed in a secure landfill or subjected to a more effective treatment process. In a secure landfill, containment is more a function of engineered barriers and the host geological setting than of the waste properties. Space in a secure landfill is at a premium and waste treatment that results in volume increase is usually undesirable. The performance requirements for S/S wastes disposed in secure landfills are not addressed here.

- **Unrestricted Utilization** – In an unrestricted utilization scenario, the S/S waste has a negligible leaching potential and may be used in any way that a natural material might be used, on land or in water (e.g., as a construction material). Once a given wastestream and S/S process have been approved, the resulting product becomes exempt from waste management regulations.

- **Controlled Utilization** – In this scenario, the leaching potential of the S/S waste is acceptable for a specific utilization (e.g., quarry rehabilitation, lagoon closure, road-base material). The environmental impact of S/S waste leachability measured by this classification should be assessed and utilization approved on a site-specific basis.
- **Segregated Landfill** – The S/S waste is not acceptable for utilization, or utilization is not possible or practical. The S/S waste is isolated from other wastes in a segregated landfill which does not necessarily have an engineered barrier or a leachate collection system.
- **Sanitary Landfill** – The S/S waste is not acceptable for utilization and is not acceptable for disposal in a segregated landfill without special engineered protection of the environment. Disposal with municipal garbage in a sanitary landfill is permitted (WTC, 1990b).

Use/reuse of waste materials was the subject of a recent conference on *Waste Materials in Construction, the Proceedings of the International Conference on Environmental Implications of Construction with Waste Materials* (eds., Goumans et al., 1991). The focus of this conference was on use/reuse of waste materials in general. However, several of the studies addressed wastes treated with S/S technologies. For example, the U.S. EPA Risk Reduction Engineering Laboratory (RREL) is investigating use of S/S-treated residues from combustion of municipal solid waste (fly ash, bottom ash, and combined residues). Wiles et al. (1991a and b) reported that the type of S/S treatment had little effect on the species of metals found in the municipal waste combustion residues. Instead, attenuation of metals was attributed to pH and dilution effects. In another part of this study, Holmes et al. (1991) investigated the physical properties of S/S-treated municipal waste combustion residues (bottom ash, air pollution control residue and combined ash). Results indicated that wastes treated with Portland cement only, that is, with no proprietary additives, generally produced the most durable test specimens. Of the three types of residues, the air pollution control residues produced the least durable test specimens. Kosson et al. (1991) researched the leaching properties of S/S-treated municipal waste combustion residues using a variety of leaching tests.

In addition to the U.S. EPA studies, the conference proceedings included two other investigations on the use of S/S-treated waste. Wahlstrom et al. (1991) investigated the properties of S/S-treated soils contaminated with wood preserving chemicals (As, Cr, Cu) or lead for potential use in construction of roads or storage areas in landfills. Dijkink et al. (1991) investigated the potential use of S/S-treated river sediments as building material in the Netherlands.

4.8.2 Limitations

Although there are many potential ways to use or reuse S/S-treated waste, there are many nontechnical factors to consider when evaluating any specific application. Certainly, a key question will be that of liability, which is related to political, public, and legal questions that are becoming increasingly sensitive issues of public concern.

Associated with the liability question is the lack of knowledge about the long-term performance and environmental impacts of S/S waste. The environmental consequences of the utilization of waste products or materials containing waste products on the basis of a single type of test (e.g., an extraction test) is impossible in view of the wide range of scenarios that will occur in actual use/reuse situations. Test methods to better determine the leaching mechanisms and characteristics of S/S-treated waste have been studied by van der Sloot et al. (1989), but much research remains. In addition, *Waste Materials in Construction* (eds., Goumans et al., 1991) contained numerous studies on leaching procedures for evaluating waste materials proposed for use in construction. In any event, demand will increase both for beneficial use/reuse of S/S products because of increasing constraints on land disposal and for technologies that can produce materials that are environmentally benign. However, the regulatory community is likely to be unwilling to encourage or permit reuse options unless environmental risks are clearly and confidently defined.

4.8.3 Compatibility With the Disposal Environment

In evaluating the performance of S/S technologies, the focus is often on the S/S process itself. What is often overlooked is the fact that the stabilized waste still must be evaluated in terms of its performance in

the environment into which it is placed, regardless of whether that environment is a landfill, a roadbed, or the ocean floor. Often, the interaction of the stabilized waste and its surroundings is hardly addressed, but the fact remains that both mobilization and immobilization may occur at the stabilized waste/soil or stabilized waste/water interface. The stabilized waste and the site should be evaluated together as a system to realistically assess the compatibility of the S/S product with the disposal environment. The forces and elements to which a treated waste is exposed would vary significantly, for example, depending on whether disposal occurred at the surface, in deep excavations, or in the ocean.

Environmental compatibility is a major issue at CERCLA sites, although past studies have generally not considered this factor. Compatibility with the disposal environment should have a bearing on the design and conduct of the treatability study as well as what tests are performed.

Hockley and van der Sloot (1991) have modelled the interactions occurring at the waste-soil interface. They noted that the interactions between the waste and soil phases lead to phenomena that are not predicted by consideration of either phase separately, as is the case with most of the tests currently used to assess the acceptability of a waste for placement in the environment.

Another possible option to improve environmental compatibility is to codispose with the S/S waste material to modify certain physicochemical characteristics of the disposal environment. Such material could be placed between the waste and its disposal environment to improve the long-term performance of the S/S-treated waste. Environment modifiers might include bentonite or other clays to reduce groundwater infiltration; surface-reactive materials to adsorb migrating contaminants; or substances to buffer the pH or redox potential of the disposal environment. With or without the use of modifiers, however, one message clearly communicated by studies of environmental compatibility is that, to be successful, S/S process selection and design must consider the S/S product as part of a system that includes the disposal environment.

4.9 COST INFORMATION

The two major cost categories in remediation by S/S are (a) the treatability study (laboratory screening and bench-scale study), and (b) full-

scale remediation. The costs associated with these two efforts are discussed in this section. Because each project is different, it is very difficult to generalize the costs of S/S treatment. Hence the costs mentioned in this section should be regarded as estimates.

4.9.1 Treatability Study Costs

The major cost elements of a treatability study for S/S include (a) waste and site characterization (Section 2.2); and (b) bench-scale treatability screening and performance testing and associated chemical analyses (Sections 2.6 and 2.7). Since these studies are expensive, it is important to strike a balance between collection of enough data to provide statistically sound results and the available budget. Also, it is important to remember that the regulators drive the testing and that their requirements must be met before the treatability study can be accepted and full-scale remediation can proceed.

4.9.1.1 Waste Characterization and Establishing Performance Objectives

Waste sampling and characterization is conducted to determine the type, levels, and spatial distributions of the contaminants, presence of possible interferants, and for other purposes (Section 2.2). Sampling often requires the use of drill rings depending on depths to be sampled. Analyses of waste properties must be conducted in sufficient replication to permit determination of data quality by statistical methods. Refer to Section 2.2 for guidance. Some of the analytical tests conducted and their estimated costs are given in Table 4-7. Not all these analyses are necessary for every waste type.

4.9.1.2 Bench-Scale Testing and Analysis

The level of effort will depend on the number of candidate binder systems selected for testing, the number of tests performed based on the design study (or statistical design), and the types of chemical analyses to be performed, with organic analyses being significantly more expensive than inorganic analyses (Table 4-7).

TABLE 4-7. COSTS OF TYPICAL ANALYTICAL TESTS OF UNTREATED AND TREATED WASTES

Analysis	Method	Unit Cost ^(a) , \$
Physical		
Particle size analysis	ASTM D 422	30-160
Suspended solids	Standard Method 2092	20
Density	Various	40-240
Permeability	EPA 9100	350-450
Unconfined compressive strength (UCS) of cohesive soils	ASTM D 2166	25
Unconfined compressive strength of cylindrical cement specimens	ASTM D 1633	20-130
Cone index	ASTM D 3441	20
Flexural strength	ASTM D 1635	25
Heat of hydration	ASTM C 186	30-75
Wet/dry weathering	ASTM D 4843	530
Freeze/thaw weathering	ASTM D 4842	530
Paint filter test	EPA 9095	10-25
Atterberg limits	ASTM D 4318	40-100
Moisture	Various	10-20
Chemical		
pH	EPA 9045	10-20
Oxidation reduction potential	ASTM D 1498	75
Total organic carbon (TOC)	EPA 9060	50
Oil and grease	EPA 413.2	60-80
Alkalinity	EPA 403	35
Volatile organic compounds (VOCs)	EPA 5030, 8240	300-400
Semivolatile organics	EPA 3510, 8270	600-800
Base, neutral, and acidic compounds (BNA)	EPA 3540, 3520, 8270	600-1400
Polychlorinated biphenyl (PCB)	EPA 3540, 3520, 8080	150-2001
As	EPA 3050, 7060	25-30 ea ^(b)
Se	EPA 3050, 7740	25-30/ea ^(b)
Hg	EPA 7470	20-25
As, Ag, Ba, Cd, Cr, Pb, or Se	EPA 3010, 6010	10-20/ea ^(c)
Leach Tests		
- Extraction	EPA 1311 TCLP Metals	70-90
- Extraction	EPA 1311 TCLP ZHE	100-140
- Volatile organic compounds	EPA 8240	150-175
- Semivolatile organic compounds	EPA 3510, 8270	600-800
- Pesticides	EPA 3510, 8080	125-175
- Herbicides	EPA 8150	125-175
- As	EPA 3050, 7060	25-30 ea ^(b)
- Se	EPA 3050, 7740	25-30/ea ^(b)
- Hg	EPA 7470	20-25
- As, Ag, Ba, Cd, Cr, Pb, or Se	EPA 3010, 6010	10-20/ea ^(c)

^(a) 1991 costs. May vary considerably among various laboratories. Approximate ranges are given based on quoted prices. There may be some savings of scale if a large number of samples are being analyzed.

^(b) Furnace atomic absorption spectroscopy.

^(c) Inductively coupled plasma atomic emission spectroscopy.

The total analytical cost will depend on the number of samples and should always include quality assurance samples. Analytical costs are the major element in treatability testing (usually $\geq 50\%$ of the cost). Typical total costs of bench-scale treatability studies for S/S range from \$10K to \$100K, depending on process complexity, number of samples, types of analyses, and the need to capture and test air emissions. A number of different treatability laboratories are available that will conduct bench-scale treatability testing for S/S on a service basis.

4.9.2 Full-Scale Remediation Costs

The costs involved in full-scale S/S treatment fall into four major categories—planning, mobilization and demobilization, treatment, and disposal.

4.9.2.1 Planning

The planning costs are the administrative and engineering planning costs associated with the remediation. Waste and site characterization activities and the treatability study are assumed to have been completed before project planning starts. Planning costs may include permitting, engineering design (scale-up), equipment and materials procurement, and preparation of a work plan, quality assurance plan, and/or a health and safety plan. Permitting can take weeks or months, and costs can be substantial, especially for uncommon contaminants or complex sites.

Engineering costs involve designing and engineering for full-scale operation based on bench-scale (treatability testing) data. A pilot- or field-scale demonstration may be necessary, either to establish scale-up factors or to satisfy potentially responsible parties (PRPs) and/or regulators of the feasibility of the cleanup. The actual price of equipment or raw materials is not included in this category, but the labor involved in procurement is. If the remediation is to be performed through a contractor, contract procurement costs are also involved.

A site-specific work plan, quality assurance plan, and/or a health and safety plan are almost always required, and review comments from regulatory agencies and other parties must be addressed. Depending on the magnitude of the project, planning costs can range from \$25K to several hundred thousand dollars.

4.9.2.2 Mobilization and Demobilization

Mobilization costs involve transportation of personnel, equipment, and raw materials to the site, site preparation, and equipment installation and start-up. Demobilization costs include equipment shut-down and disassembly, and transportation of personnel and equipment from the site. Mobilization and demobilization (mob/demob) costs vary depending on type of equipment, facilities available at the site, decontamination requirements, and the location of the site. When large-scale equipment is necessary, mob/demob costs will range from \$25K to \$50K or more if extensive site preparation is involved.

4.9.2.3 Treatment

Treatment costs typically include costs for excavation (if treatment is ex situ), chemicals, equipment, utilities, labor, and sampling and analysis. Full-scale S/S treatment services are offered by a variety of firms, including S/S vendors, remediation companies, and construction companies certified to conduct hazardous waste remediation. Full-scale treatment should not be undertaken by anyone not fully qualified and certified, including OSHA safety certifications.

Excavation applies to sites containing contaminated materials that are to be stabilized by plant mixing. Excavation equipment consists of typical earth-moving equipment, which can be rented along with an operator at most sites. Cost for excavation ranges from about \$0.85/yd³ to \$4.09/yd³ (U.S. EPA, 1987b).

Chemical costs depend on the type of chemicals required for the binder system and the amounts as determined by the waste-to-binder ratio. Table 4-8 shows the costs of some typical stabilization chemicals. If chemicals are transported for large distances, the transportation costs may equal or exceed the chemical costs.

Equipment costs other than for excavation are based on the type of equipment selected for materials handling and processing. Qualified S/S vendors and remediation firms will own the necessary equipment and charge a use-rate based on the time it is used. Equipment can also be purchased (for large and long-term projects), in which case depreciation costs should be considered, or rented (for smaller sites). Customary equipment includes

TABLE 4-8. COSTS OF TYPICAL STABILIZATION CHEMICALS

Chemicals	Costs \$/Ton ^(a)
Portland cement	\$55 - 70 (bulk)
Quick lime	\$45 - 75 (bulk)
Hydrated lime	\$55 - 80 (bulk)
Kiln dust	\$10 - 40 (bulk)
Fly ash	\$ 1 - 40 (bulk)
Sodium silicate	\$160 - 239 (bulk)
Chloranan ^(b)	\$600
IWT-HWT 20M ^(c)	\$300
Concrete admixtures	\$ 2 - 12/gallon

^(a) 1991 Costs obtained from suppliers. Costs may vary based on suppliers and the location of the site.

^(b) Proprietary additive

^(c) Proprietary modified clay binder

backhoes, front-end loaders, storage tanks, mixers, conveyors, etc. Sometimes equipment and its operators are available for an hourly, weekly, or monthly charge. The purchase costs of different types and sizes of equipment, and estimates of their rental costs are mentioned in the *Handbook for Stabilization/Solidification of Hazardous Waste* (U.S. EPA, 1986c).

Table 4-9 shows the major unit cost elements for S/S treatment with cement by typical stabilization techniques (in-drum mixing, in situ mixing, plant mixing, and area mixing as defined in Section 2.8.2). These are the unit costs for mixing only and exclude the numerous other cost elements such as mobilization and demobilization, engineering and administration, and health and safety. In addition to processing equipment, personal protective equipment may be needed, including Tyvek suits, respirators, decontamination equipment, etc.

TABLE 4-9. COMPARISON OF MAJOR COST ELEMENTS OF SOLIDIFICATION/STABILIZATION WITH CEMENT

Category	Cost, \$/Cubic Yard			
	In-Drum Mixing	In Situ	Plant Mixing	Area Mixing
Labor, overhead, and profit	216.30	1.40	1.10	3.00
Equipment and metering	65.40	1.60	0.70	3.00
Conveyance	NA	NA	1.40	
Pretreatment	NA	NA	0.50	NA
Monitoring and testing ^(a)	115.40	4.00	3.10	5.10
Reagents and mixing materials	31.10	31.10	31.10	31.10
Offsite disposal (nonhazardous waste)	NA	NA	3.10	NA
Supplies	84.60	0.60	0.80	1.30
TOTAL	512.80	38.70	41.80	43.50

^(a) Monitoring and testing costs assume that in-drum wastes require sampling of each drum, while the other approaches require representative samples of a large, relatively uniform body of waste. Source: Arniella and Blythe, 1990, p. 101. Excerpted by special permission from *Chemical Engineering*, February 1990, © 1990 by McGraw-Hill, Inc., New York, NY 10020.

NOTES:

1. NA = not applicable
2. Not included are costs for mobilization and demobilization, engineering and administration, and health and safety.
3. All mixes are based on 30% Portland cement and 2% sodium silicate.
4. Cost for delivering reagent is not included.
5. Approximate production rates assumed are: in-drum mixing, 5 drums/h; in situ, 500 yd³/d; plant mixing, 650 yd³/d; area mixing, 400 yd³/d.

Utilities normally include water and electricity. Sometimes the remediation may have to provide its own energy supply, such as diesel generators. If pretreatment is necessary, other sources of heat, such as oil, gas, or steam may be needed.

Labor costs are based on the number of equipment operators, supervisory personnel, and managers, as well as the number of hours of operation. An important factor in remediation can be the stand-by time. If operations are not scheduled appropriately or if unanticipated delays such as stop work orders are incurred, equipment or personnel will go unutilized. For example, if the operation runs short of a chemical, or if a piece of equipment breaks down, the entire operation may have to be temporarily halted. Another type of work stoppage is when sampling and analysis of treated waste show that the stabilization is ineffective. Clearly, some types of work stoppages can be avoided or minimized by effective planning. Other types of stoppages are less controllable, such as stop work orders issued by regulators so that they can review preliminary data.

Sampling and analysis are conducted during full-scale remediation to determine whether the treated process is achieving the performance goals for chemical and physical properties. A sampling and analysis and/or quality assurance plan will be prepared during planning. Implementation of the plans may be a significant part of the remediation cost. Particularly during the early stages of full-scale treatment, it may be necessary to have samples analyzed on a rush basis, in order to minimize standby time while waiting for data. Note that with rush fees, analysis costs can be 2 or 3 times higher than fees for normal turnaround-time analyses.

If a full-scale demonstration precedes full-scale cleanup, regulatory approval for the full-scale cleanup may be contingent on results of the demonstration. If the initial demonstration shows deficiencies in the process, then process modifications followed by additional demonstration runs will have to be conducted until the process is working satisfactorily. As discussed in Section 2.8, demonstration runs prior to full-scale processing are highly recommended for refining the process and verifying that process scale-up in the field has been accomplished satisfactorily. However, this step has potentially significant cost impact on the project, particularly if several demonstration runs need to be conducted prior to full-scale treatment.

4.9.2.4 Final Disposal

When field treatment is completed, the S/S-treated waste has to be disposed of as planned. In some cases, depending on the characteristics of the treated waste and on regulatory approval, the S/S-treated waste can be returned to its original location. Some final steps such as compacting or capping (with the associated costs) may be required.

However in other cases, the treated waste cannot be disposed of on site. Then arrangements have to be made to transport the treated waste to a sanitary or secure landfill, again depending on waste characteristics and regulatory policy. Tipping fees at sanitary landfills typically range from approximately \$10 to \$50/ton and for secure (RCRA-permitted) landfills range from \$100 to \$300/ton. Added to this is the cost of waste transport to the landfill. The cost for transportation by covered bed dump truck or roll off box carrier typically ranges from \$0.15/yd³-mile to \$0.60/yd³-mile. Costs include the actual charge for hauling; demurrage (charge for truck waiting time); and training, licensing, and protective clothing for the truck operator (if required) (U.S. EPA, 1987b). Because there are far fewer secure landfills than sanitary landfills, the transportation distance to secure landfills will generally be much greater.

4.9.3 Estimates of Stabilization Costs

Table 4-10 lists the estimated costs registered in the records of decision (RODs) for CERCLA sites. Because costs in this table are estimates, there is no indication whether or not the remediation was actually accomplished for that cost. Total costs vary according to type of contaminants and amount of wastes. Missing from this table is information on necessary pretreatment steps and other project-specific requirements that may significantly impact total cost. In general, a relatively straightforward S/S project involving more than 5,000 to 10,000 tons of waste should cost in the range of \$100 to \$150/ton of waste processed. Below this amount, unit costs can increase because of fixed costs; above 10,000 tons, unit costs can decrease because of economics of scale. Therefore, the higher unit costs in Table 4-10, some of which greatly exceed the \$100 to \$150/ton range, are almost certainly inflated by pretreatment requirements or other factors.

TABLE 4-10. ESTIMATED TREATMENT PROJECT COSTS MENTIONED IN THE RODS FOR SUPERFUND SITES WHERE STABILIZATION HAS BEEN SELECTED AS A COMPONENT OF THE REMEDIAL ACTION

Site	Media	Volume	Contaminants	Project Cost, \$	Unit Cost, \$/cy ^(a)
Love Canal, NY	Soil	7,500 cy	dioxin	3,675,000	490
Marathon Battery, NY	Sediment/soil	23,700 cy	Cd, Co, Ni,	16,640,000	702
Alladin Plating, PA	Soil	12,000 cy	Cr	4,461,000	372
Amnicola Dump, TN	Soil	400	As, Cd, Cr, cyanide, Pb, Hg, PAH, pesticides, VOC	256,000	640
Davie Landfill, FL	Soil/sludge	75,000 cy	As, Cd, Cr, cyanide, Pb, Hg, sulfides	3,700,000	49
Independent Nail, SC	Sediment/soil	6,200 cy	Cd, Cr, cyanide, Ni, Zn	1,132,000	183
Burrows Sanitation, MI	Sludge/soil	250 cy	Cr, Cu, Pb, Zn	237,700	951
Outboard Marine	Sediment	5,700 cy	PCB	3,150,000	553

^(a) Includes planning, sampling, and pretreatment costs as well as direct S/S process costs. Source: Based on data contained in U.S. EPA (1989a).

4.9.4 Case Study

A treatability study and field demonstration/cleanup of 1800 cubic yards of lead-contaminated soil conducted by Battelle (Means et al., 1991b) at Port Hueneme, California, demonstrates the various aspects of an S/S field project and the associated costs. To establish a baseline concentration on the amount of lead in the soil before treatment, 18 grab samples (and two blind replicates) of the untreated soil were collected and analyzed for total and soluble lead. Because the levels of lead in these samples varied greatly, seven additional samples were collected. Total lead levels averaged 178 (± 162) mg/kg in the soil. The EP Tox average of 0.9 mg/L lead was lower than the U.S. EPA standard (5 mg/L lead). Previous data on the Cal WET test, however, showed that the average of 11.7 mg/L lead exceeded the STLC established by California (5 mg/L). (See Section 3.2 for further discussion of leaching tests.)

The bench-scale treatability study involved evaluating two stabilization techniques, a sulfide-based process and a silicate-based process. Eleven samples were treated with the sulfide process, which involved adding a hydrated sodium sulfide solution in water, low-alkaline Portland cement, and a small amount of detergent. Ten samples were treated with the silicate process, which involved adding sodium silicate instead of the sulfide. The sulfide process was used in this instance as an alternative to the silicate process to determine the relative attributes of the two processes. Although the sulfide process produced slightly lower soluble lead values than the silicate, the silicate process was concluded to be the preferable based on ease of application in the field.

The stabilization formulation used in the field was the same as that used during bench-scale testing; no additional testing to determine optimum ratio was done in this case. During the field demonstration, eight sets each of pre- and post-stabilization samples were collected and analyzed for pH, total lead, and Cal WET test. The average Cal WET test results were reduced from 11.7 mg/L before stabilization to 2.7 mg/L after stabilization. After a number of discussions with cognizant regulatory agencies, the treated soil was released for placement in a sanitary landfill.

Table 4-11 provides cost details for this project. A pug mill was rented for the mixing of soil, cement, silicate, and bicarbonate. Most of the

TABLE 4-11. STABILIZATION COSTS FOR AN 1800-CUBIC-YARD SITE
CONTAMINATED WITH LEAD

1.	<u>Bench-Scale Treatability Study/Planning</u>	
	• Chemist, 8 hrs @ \$50/Hr.	\$ 400
	• Chemical Analysis, 12 samples each TTL, STL, and pH	3,240
	• Project Manager, 16 hrs. @ \$95/hr	<u>1,520</u>
	Subtotal	\$5,160
2.	<u>Move Soil from Storage Hut to Work Area</u>	
	• End-dump trucks, 2 trucks x 1 day each x \$55/hr	\$ 880
	• Field supervision, 8 hrs @ \$78/hr	624
	• Laborers, 2 x 8 hrs each @ \$30/hr	480
	• Plastic sheeting, 10 rolls @ \$120/roll	<u>1,200</u>
	Subtotal	\$3,184
3.	<u>Steam Clean Storage Hut (Subcontracted)</u>	\$4,000
4.	<u>Power Sieving</u>	
	• Power screen @ \$4,000/wk including mobilization/demobilization	\$4,000
	• Front-end loaders, 2 loaders x 1 day each @ \$90/hr	1,440
	• Field supervision, 8 hrs @ \$78/hr	624
	• Laborers, 2 x 8 hrs each @ \$30/hr	<u>480</u>
	Subtotal	\$6,544
5.	<u>Debris Disposal</u>	
	• Front-end loader, 1 loader x 1 day @ \$90/hr	\$ 720
	• End-dump trucks, 2 trucks x 10 trips each x 1 hr/round-trip @ \$55/hr	1,100
	• Field supervision, 10 hrs @ \$78/hr	780
	• Laborers, 2 x 10 hrs each @ \$30/hr	600
	• Tipping at landfill, 300 tons @ \$18.70/ton	<u>5,610</u>
	Subtotal	\$8,810

**TABLE 4-11. STABILIZATION COSTS FOR AN 1800-CUBIC-YARD SITE
CONTAMINATED WITH LEAD (Continued)**

6. <u>Stabilization</u> (approximately 4 working days and 10 hour-days, including mobilization/demobilization)		
• Cement, 150 tons @ \$0.04/lb		\$12,000
• Sodium silicate solution, 150 tons @ \$0.08/lb		24,000
• Sodium bicarbonate, 15 tons @ \$0.10/lb		3,000
• Freight for chemical deliveries		3,000
• Plastic sheeting, 5 rolls @ \$120/roll		600
• Pugmill and components, including mobilization/demobilization		29,000
• Front-end loaders, 2 loaders x 40 hrs each @ \$90/hr		7,200
• End-dump trucks, 1 truck x 40 hrs @ \$55/hr		2,200
• Baker tank, 1 month @ \$30/day		900
• Field supervision, 40 hrs @ \$78/hr		3,120
• Project Manager, 24 hrs @ \$95/hr		2,280
• Chemist, 32 hrs @ \$50/hr		1,600
• Laborers, 2 laborers x 40 hrs each @ \$30/hr		2,400
• Travel and subsistence for contractor staff, 5 persons x 7 days each @ \$100/day		3,500
• Industrial hygiene monitoring and oversight		2,000
• Analytical fees, rush basis (100% surcharge)		1,080
	Subtotal	<u>\$97,880</u>

TABLE 4-11. STABILIZATION COSTS FOR AN 1800-CUBIC-YARD SITE
CONTAMINATED WITH LEAD (Continued)

7. <u>Post-Treatment at Project Closure Activities</u>	
• Chemical analysis, TTLC, STLC, and pH on 12 samples, normal turnaround	\$3,240
• Regulator meetings concerning disposal options, Project Manager 20 hrs @ \$95/hr	1,900
• End-dump trucks, 4 trucks x 25 trips each x 1 hr/round trip @ \$55/hr	5,500
• Front-end loader, 1 truck x 25 hrs @ \$90/hr	2,250
• Reporting and documentation, Project Manager, 16 hrs @ \$95/hr and secretary, 16 hrs @ \$40/hr	2,160
Subtotal	<u>\$15,050</u>
Grand Total - Expenses	\$140,628
Contractor Fee	<u>9,372</u>
Total Cost	<u>\$150,000</u>

other equipment, such as dump trucks, power screen, and front-end loaders, was also rented. A number of other cost elements are itemized to provide the reader with the variety of typical cost elements for an S/S treatment project and the stages of the project in which they were incurred. Note, however, that the unit costs associated with this project were fairly modest compared to those for other larger-scale S/S projects (e.g., Table 4-9). The total cost of the cleanup of 1800 cubic yards (approximately 2,430 tons) was \$150,000, for an average of \$83/cu yd or \$62/ton.