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# Immobilization of Volatile Organic Compounds in Commercial Cement-Based Waste Forms

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Chemical Technology Division

IMMOBILIZATION OF VOLATILE ORGANIC COMPOUNDS  
IN COMMERCIAL CEMENT-BASED WASTE FORMS

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## EXECUTIVE SUMMARY

The use of cementitious grouts is the most widely used method for the treatment and ultimate disposal of both radioactive and chemically hazardous inorganic waste because of their low processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements. Versatile and inexpensive processes to solidify large quantities of liquids, sludges, and fine solids into cementitious waste forms have been developed at Oak Ridge National Laboratory (ORNL). Recent successes in immobilizing more mobile species in grouts encourage the belief that commercial cementitious waste forms may be considered a viable source-control option for waste containing trace quantities of volatile organic compounds (VOCs), such as the waste contained in the sludge lagoon located in Zone 1, Landfill No. 4, on the Robins Air Force Base (RAFB), which is located near Warner-Robins, Georgia.

Field studies at the RAFB Landfill No. 4 and sludge lagoon indicated that chemical contamination of soils and groundwater beneath the landfill and lagoon had occurred. The need for source-control remedial actions was partially based on the assumption that the sites are contributing to off-site groundwater contamination, which presents a potential risk to public health and the environment. The nature, extent, and magnitude of contamination in the landfill and sludge lagoon area were studied in detail in a field sampling investigation. Principal contaminants were determined previously to be metals and, to a lesser extent, organics, with the lagoon being a major, and perhaps the principal, source. Thus, permanent remediation of the source of contaminants must address the lagoon.

A previous study performed by CH2M Hill evaluated several source-control options for the sludge lagoon. Cement-based stabilization/solidification (i.e., grouting technology) was not evaluated by this study because of the lack of significant literature data on retention of organics in a cement-based matrix. Consequently, in 1988, the U.S. Air Force (USAF) initiated a study at ORNL through the U.S. Department of Energy's (DOE's) Hazardous Waste Remedial Actions Program (HAZWRAP) to evaluate the technical feasibility of grouting technology as a source-control option for wastes containing trace quantities of organics such as those contained in the sludge lagoon.

The main objective of this project is to establish whether continued consideration of grouting technology as a remedial action option for the RAFB sludge lagoon was justified from the standpoint of technical performance of the cementitious waste forms, current regulatory guidelines, and estimated economics of implementing this approach at the site. Few regulatory guidelines are available for this study, although the regulatory agencies reserve the right to accept or reject a chosen alternative. Grouting technology is a recognized remedial action alternative and has been approved for use in the past. It is the method

of choice for metals contamination and was used for remediation of soil contaminated with organics at the Pepper Steel site closure in EPA Region IV. The EP-Toxicity and Toxicity Characteristic Leaching Procedure (TCLP) tests provide the only specific regulatory criteria with which to evaluate this option. Only one compound - TCE - proved troublesome in the TCLP test; but one vendor unequivocally passed this test, proving that cementitious waste forms are capable of passing this regulatory test, despite the required destruction of the waste-form physical integrity (i.e., the necessary size reduction). This option is also attractive economically because the cost of implementation is estimated to be about \$3 million for the out-of-ground implementation and approximately \$5 million for a true in situ implementation.

Although some physical properties of the waste forms were measured and reported, the technical performance was evaluated mainly from the standpoint of the VOC-immobilization potential of the waste form. Immobilization in this sense means retention of VOCs or retardation of release to a leachant. Cementitious waste forms provide immobilization by a combination of a physical barrier to diffusion and a chemical affinity for the species. The distribution coefficient is a measure of the chemical affinity of a species in the waste form in question. This chemical affinity combines with the physical barrier of a waste form to give an overall mass-transfer resistance to leaching. The diffusion coefficient is a measure of the mass-transfer resistance of a waste form to the species in question. Some vendors concentrated on immobilizing through a chemical means (i.e., using additives with a known affinity for organics), as evidenced by some of the high distribution coefficients measured. Using this approach allows them to attempt high waste loadings to reduce the volume increases experienced in adding their ingredients. This approach risks the integrity of the physical barrier and may result in a remediated site more like a packed bed than a monolith, with the entire volume accessible for leaching (i.e., the resulting diffusion coefficient may be lower than a physically superior waste form with little or no affinity for the species). On the other hand, concentrating strictly on the physical barrier with little regard for the chemical affinity may lead to high releases if the physical integrity fails (e.g., the size reduction required in the TCLP test removes the advantages of a strong physical barrier since it is designed as a test of the level of contamination and the affinity of the waste or waste form for the contamination). A balanced approach seems best (i.e., improving the chemical affinity of the waste form but ensuring that it is physically sound and relatively impervious to bulk water flow). One of the advantages of cementitious waste forms is their flexibility in formulations and resulting physical properties. Thus, once a vendor has selected the most appropriate additive for a particular application, the blend of ingredients and waste loading can be adjusted to obtain a desired physical property (i.e., some of the diffusion coefficients measured may be improved by simple changes in the recipe such as lower waste loadings). These improvements must be weighed against conflicting criteria or objectives such as maximum waste loading or minimum volume increase.

Although no EPA criteria exist for the leachability index (the negative logarithm of the diffusion coefficient), past experience has demonstrated what indexes are technically achievable for cementitious waste forms for other applications and species. In general, an index less than 6 is considered unacceptable. The porous cementitious waste forms can usually be formulated to provide enough of a physical barrier to give an index of 7. To achieve an index of 8 or higher is more difficult and usually depends on utilizing some sort of chemical approach, such as conversion of metallic ions into relatively insoluble hydroxide species. Achieving indexes as high as 12 is rare and depend on chemically fixing the species by chemical conversion into an "insoluble" species or "irreversibly" sorbing the species into some solid sorbent. The indexes measured in this study conform to these observations, with a few between 6 and 7, most of the values being between 7 and 8, some between 8 and 9, and a few above 9. Three out of the four vendors had quite respectable indexes of close to 8 (7.7 to 7.9) for the key component, TCE.

One of the major criticisms in the past of studies evaluating the immobilization of VOC in cementitious waste forms was that most or all of the VOC escapes during mixing of the grout. One of the major efforts in this study was estimating the amount of VOC each sample retained after mixing and curing. A secondary conclusion from this effort was that a significant fraction of the VOC was retained during mixing, despite the exothermic hydration reactions and the open-top mixing used.



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ABSTRACT

This report assesses the applicability of cement-based solidification/stabilization technology as a remediation action option for wastes containing trace quantities of volatile organic compounds (VOCs). Leach studies were performed to obtain pertinent mass-transfer parameters. Estimates of VOC retention during sample preparation were made in order to quantify the source term used in the interpretation of leach data obtained.

1. INTRODUCTION

The use of cement-based grouts is the most widely used method for the treatment and ultimate disposal of both radioactive and chemically hazardous inorganic waste because of their low processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements. Versatile and inexpensive processes to solidify large quantities of liquids, sludges, and fine solids (< 0.6 mm in diam) in cement-based grouts have been developed at the Oak Ridge National Laboratory (ORNL). Grouts that meet all applicable regulatory requirements for the disposal of heavy metals, selected organics, and radionuclides have been developed.<sup>1-11</sup>

Grouts, particularly neat, cement-paste grouts, have proven less successful in sequestering species such as volatile organic compounds (VOCs) and readily soluble anions (e.g., pertechnetate and nitrate). Recent studies have shown that grouting technology can be successfully applied to the disposal of waste containing technetium and nitrates by

altering both the waste stream chemistry and physical properties of the grout matrix.<sup>12,13</sup> Based on the success with technetium and nitrates, research efforts have been expanded to address the use of grouting technology as a remediation option for wastes containing trace quantities of VOCs. Results of a recently completed study on the immobilization of VOCs are presented in this report.

## 2. BACKGROUND

The U.S. Air Force (USAF), as part of its Installation Restoration Program (IRP), is performing a Phase IV-A study at Robins Air Force Base (RAFB) near Warner Robins, Georgia. This study included Zone 1, Landfill No. 4, and the sludge lagoon and provided most of the following background material.<sup>14</sup>

Landfill No. 4 and the sludge lagoon are contiguous sites located adjacent to a swampy area on the east side of RAFB. The landfill was operated from 1965 to 1978 and was used for disposal of general refuse and occasional disposal of industrial wastes. The landfill occupies approximately 45 acres. The sludge lagoon, located adjacent to the north side of the landfill, was used for disposal of industrial wastewater treatment plant sludges and occasional disposal of other liquid industrial wastes from 1968 until 1978. The lagoon was unlined and bordered by an elevated earthen dike. The lagoon surface area was approximately 1.5 acres, and the depth was approximately 6 ft (1.8 m).

The sludge lagoon and landfill lie in a swampy area, and the surface of the landfill rises about 10 ft (3.05 m) above the swamp. Surface water at the site generally drains from west to east, with much of the surface drainage from adjacent RAFB areas flowing over the landfill and into the

lower-lying swamp. The water level in the swamp is maintained by drainage-control structures and the Hannah Road embankment. At the northern edge of the sludge lagoon and landfill, surface waters flow into a channelized, eastward-flowing drain located just north of the lagoon.

Immediately under the landfill and the swampy area surrounding it are alluvial deposits that form a low-depositional terrace of the Ocmulgee River. The alluvial deposits are composed of sand, gravel, peat, and clay beds, with a total thickness of more than 25 ft (7.62 m). Throughout most of the site, the alluvial deposits are divided into two distinct layers: a lower sand and gravel zone and an upper peat and clay bed. Waste and artificial fill overlie the peat and clay bed in the vicinity of the landfill. Relative depths of the site components are summarized in Fig. 1.

Groundwater flow in the vicinity of Zone 1 generally parallels the surface water flow. Groundwater seems to flow radially away from the landfill, eastward toward and beneath Hannah Road, as well as north toward the channelized drainage. Lateral groundwater flow just beneath the peat and clay bed was estimated at a rate between 100 and 800 ft/year (30.5 and 244 m/year). The vertical groundwater gradient is predominantly upward from deep to intermediate zones. There is little or no upward gradient in the intermediate to shallow zones.

The peat and clay bed directly underlying the wastes consists of interbedded clay and peat constituting a total thickness of 5 to 14 ft (1.52 to 4.27 m). Inspection of recovered split-spoon samples of the clay generally showed it to be a plastic material with roots and channels.

# RAFB ZONE 1

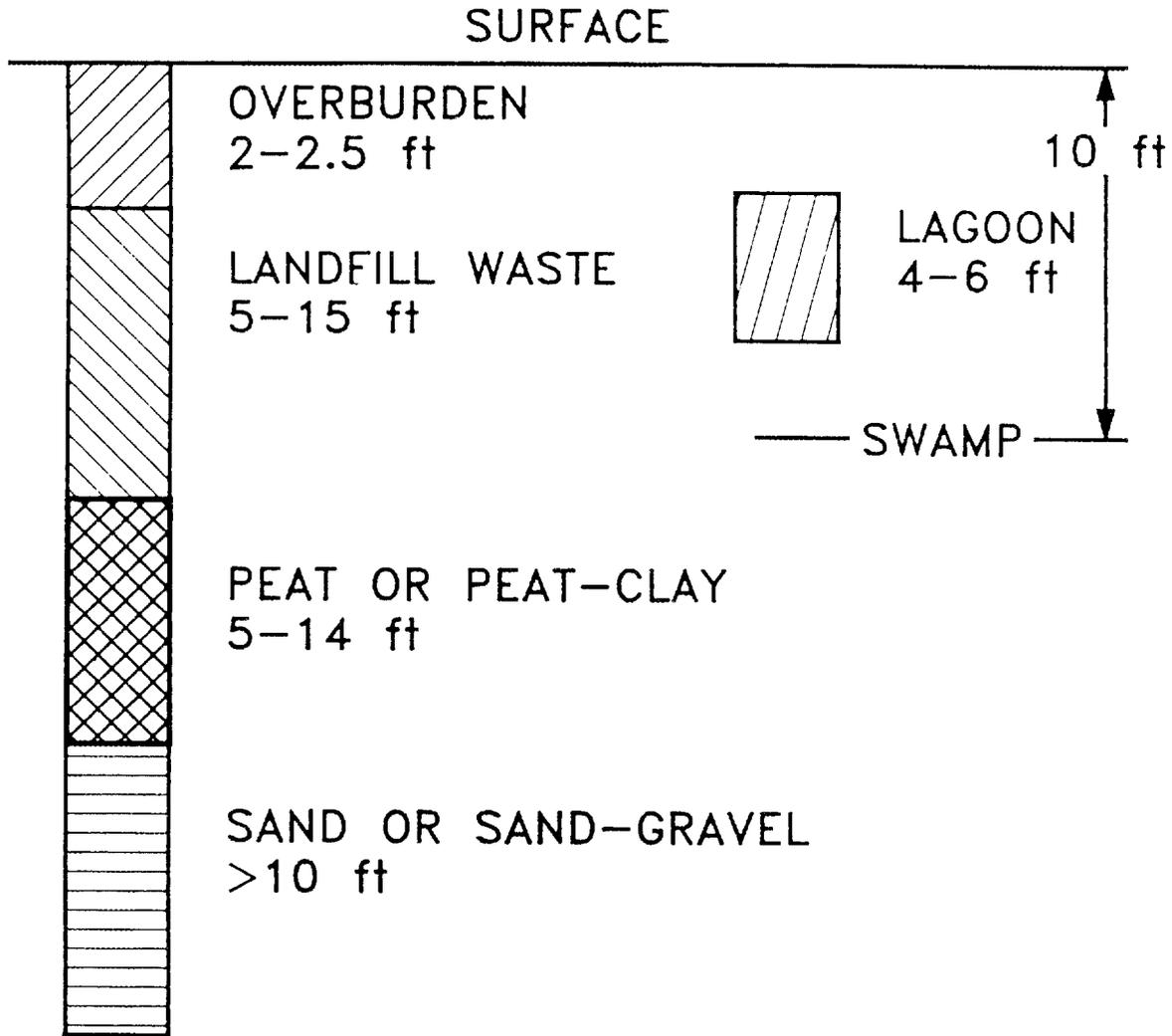


Fig. 1. Relative depths of site components.

Laboratory permeability tests of samples from this bed were approximately  $10^{-8}$  cm/s, while earlier field permeability studies indicated that values averaged approximately  $10^{-4}$  cm/s.<sup>15</sup> Differences between laboratory and field-test results are attributed to larger-scale discontinuities in the stratum (e.g., seams, joints, and root holes) not measured by laboratory methods. Thus, higher permeabilities indicated from field tests are believed to be more representative of the actual permeability in the peat and clay bed.

The peat and clay bed appears to be continuous and may retard flow between the upper perched zone and the underlying sand aquifer. However, field investigations indicated that contaminants have migrated downward into the underlying sands. Furthermore, observed groundwater elevations and gradients indicated that, at best, the peat and clay bed acts to create semiconfining aquifer conditions in the zone underlying the bed.

Although no special testing to assess strength or compressibility characteristics of the peat and clay stratum was performed, the relatively soft nature of the material indicated that remedial activities involving dikes or trenches through the peat and clay, or fills on the top of the peat and clay, could be compromised by soil instability. Significant settlement may be expected for activities such as capping or filling.

Sands underlying the peat and clay bed constitute the most significant groundwater aquifer at the site, extending to depths of several hundred feet. Field investigations using slug tests and observation of shallow-well pumping indicated a hydraulic conductivity in the underlying sands of  $10^{-2}$  to  $10^{-3}$  cm/s. Laboratory permeability values varied between  $6 \times 10^{-4}$  and  $9 \times 10^{-3}$  cm/s for relative densities of 60 and 90%, respectively.

The soil cap overlying the landfill waste is typically 2 to 2.5 ft (1.64 to 1.21 m) thick. The material is a nonplastic, silty, or clayey sand having less than 25% silt or clay. Average field permeability of this layer was measured as  $3 \times 10^{-4}$  cm/s with a laboratory permeability of  $2 \times 10^{-5}$  to  $5 \times 10^{-6}$  cm/s.

Field studies at Landfill No. 4 and the sludge lagoon<sup>15-17</sup> indicated that chemical contamination of soils and groundwater beneath the landfill and lagoon has occurred. The need for source-control remedial actions was partially based on the assumption that the sites are contributing to off-site groundwater contamination, which presents a potential risk to public health and the environment. The presence of odors at the sites and the observation of gas bubbling in ponded water indicated that gas production and migrations through the surface cover were occurring at the landfill and lagoon.<sup>17</sup> Air monitoring performed at the sites indicated that methane and nonmethane organic gaseous compounds were present.

Preliminary data analyses and field observations suggested that the primary pathways for contaminant migration are dissolved contaminant migration in groundwater and atmospheric dispersion of volatile contaminants. Surface water runoff and windblown dusts do not appear to be significant pathways for contaminant migration. The nature, extent, and magnitude of contamination in the landfill and sludge lagoon area were studied in detail in a field-sampling investigation.<sup>17</sup> The maximum concentrations observed in the field studies are shown in Table 1. Principal contaminants were determined to be metals and VOCs, with the lagoon being a major source and perhaps the principal source. Thus,

Table 1. Maximum concentration of each species reported<sup>17</sup>

Species	Concentration (ppb) <sup>a</sup>			Maximum
	Groundwater	Soil borings	Soil leachate	
Volatiles				
Trichloroethylene	14,000	5,500	130,000	130,000
<i>trans</i> -1,2-Dichloroethene	19,000	100,000	36,000	100,000
Tetrachloroethene	290	59,000	1,100	59,000
Toluene	540	20,000	2,200	20,000
Chlorobenzene	810	20,000	8,800	20,000
Chloroform	600	17,000	1,200	17,000
Vinyl chloride	6,700	<	12,000	12,000
Acetone	9,000	630	4,300	9,000
2-Butanone (MEK)	3,700	3,100	930	3,700
Benzene	91	2,800	1,000	2,800
1,2-Dichloroethane	470	-	-	470
4-Methyl-2-pentanone	420	-	-	420
Xylenes	220	-	-	220
Trichlorofluoromethane	170	-	-	170
1,1-Dichloroethane	91	-	-	91
1,1-Dichloroethene	49	-	-	49
Carbon disulfide	29	-	-	29
Ethyl benzene	27	-	-	27
Carbon tetrachloride	5	-	-	5
Bromodichloromethane	5	-	-	5
Dibromochloromethane	5	-	-	5
Subtotal	56,222	228,030	197,530	374,991
Pesticides and PCB				
Chlordane	0.05	8,500	<	8,500
4,4'-DDT	0.01	240	8	240
Dieldrin	0.01	<	<	0.01
PCB-1254	0.04	2,500	0.07	2,500
Subtotal	0.11	11,240	8.07	11,240.01
Base neutrals				
1,4-Dichlorobenzene	2,600	690,000	13,000	690,000
Naphthalene	100	38,000	560	38,000
Fluoranthene	100	4,800	<	4,800
Bis(2-ethylhexyl) phthalate	100	3,600	-	3,600
Pyrene	100	-	-	100
1,2-Dichlorobenzene	5,200	-	-	5,200
1,3-Dichlorobenzene	2,100	-	-	5,200
Subtotal	10,300	736,400	13,560	743,800

Table 1. (continued)

Species	Concentrations (ppb) <sup>a</sup>			Maximum
	Groundwater	Soil borings	Soil leachate	
<b>Acids</b>				
Phenol	1,700	18,000	48,000	48,000
M/P-Cresol	4,200	50,000	7,900	50,000
O-Cresol	940	-	-	940
Pentachlorophenol	100	<	3	100
2,4-Dimethyl phenol	2,200	120,000	11,000	120,000
Subtotal	9,140	188,000	66,903	219,040
<b>Metals</b>				
Arsenic	65	-	-	65
Barium	470	-	-	470
Cadmium	6	599,000	34,800	599,000
Chromium	73	6,419,000	173,000	6,419,000
Copper	40	-	-	40
Lead	120	813,000	27,400	813,000
Nickel	50	-	-	50
Zinc	160	-	-	160
Subtotal	984	7,831,000	235,200	7,831,785
Total cyanide	5	970	400	970
Total	76,651.11	8,995,640	513,607.07	9,181,826.01
Water (or water + soil)	999,923,348	991,004,360	999,486,398	990,818,173

<sup>a</sup>Less than (<) refers to "below detectable limits," and a dash (-) refers to "no measurement."

permanent remediation of the source of contaminants must address the lagoon.

A previous study evaluated several options for the permanent remediation of this site.<sup>18</sup> The study presented only one permanent solution to close this site: exhumation and incineration of the sludges and peat and clay layer that are contaminated with VOCs and heavy metals, with the resulting ash being disposed of off-site. The estimated capital cost for this option was \$20 million.

Seeking a lower-cost option, the study recommended a pump and treat scenario, where a line of wells intercepts the groundwater flowing off the site and the VOCs are subsequently air stripped from the groundwater. While this option has an estimated initial capital investment of only \$500,000, the operational phase, with its estimated annual operating costs of \$610,000, is indeterminate because this option does not permanently control the contaminant source. Thus, RAFB personnel immediately recognized that this option was useful only as an intermediate step or as a means to clean contaminated soil in the landfill and that this should be performed in conjunction with a separate remediation on the lagoon.

In July 1987, ORNL evaluated the study and recommended that grouting technology be considered as an alternative remediation. This recommendation was based on a March 1987 precedent set in the Environmental Protection Agency's (EPA's) Region IV at the Pepper Steel and Alloy Superfund site near Miami, Florida, which established in situ immobilization in a cement-based grout as a permanent remedy for soils contaminated with heavy metals and PCBs.<sup>19</sup> The cost of this option as a permanent remedy for the Zone 1 sludge lagoon was estimated to be on the

order of \$5 million based on costs at the Pepper Steel and Alloy Superfund site.

In addition to a substantial costs savings over the exhumation and incineration option, in situ grouting offers several other potential advantages: (1) complete disposal on-site, thus reducing risk of both exposure and liability by eliminating the need to transport the waste or its ash off-site; (2) no additional landfill space required, as it is anticipated that the resulting solidified material can be accommodated within the existing Zone 1 area; and (3) ultimately, if the solidification can be performed without significant disturbance of the overburden (which is true in situ), then it would reduce the risk of contaminant exposure to area personnel during treatment operations, as well as reduce the hazards associated with soil instability during site exhumation. Consequently, in 1988, a study to evaluate the technical feasibility of grouting technology as a potential remediation option for the Zone 1 sludge lagoon was initiated at ORNL through the Hazardous Waste Remedial Actions Program (HAZWRAP) and the Waste Management Technology Center (WMTC).

The objective of the study was to establish the technical and regulatory credibility of grouting technology as it would be applied to the lagoon at the RAFB Zone 1 site. Grout formulas and materials were obtained from four vendors believed to be representative of available commercial technology. It should be noted that the specific proprietary additives were not disclosed in order to eliminate the need for proprietary agreements and, hence, avoid restricting the distribution of this report. These four vendors were:

Vendor A

RMC Company  
214 West Main Plaza  
West Plains, Missouri 65775  
(417) 256-1101  
Contact: Dr. R. Soundararajan

Vendor B

Wastech, Inc.  
P. O. Box 1213  
Oak Ridge, Tennessee 37831-1213  
(615) 483-6515  
Contact: Mr. E. B. Peacock

Vendor C

International Waste Technologies  
150 North Main, Suite 910  
Wichita, Kansas 67202  
(316) 269-2660  
Contact: Mr. J. P. Newton

Vendor D

Silicate Technology Corporation  
Pegler and Welch Consultants, Inc.  
14455 North Haden, Suite 218  
Scottsdale, Arizona 85260  
Contact: Mr. Greg Maupin

These four vendors are referred to as Vendor A, Vendor B, Vendor C, and Vendor D in this document.

Grout products were then prepared and evaluated as to their suitability for retaining VOCs. The results of the evaluation, presented in this report, involved several subtasks: (1) a screening study to provide guidance to the final experimental design, (2) the development of laboratory quality assurance and quality control procedures to quantify the VOC retention during sample handling and preparation, (3) the evaluation of grout product performance with regard to leachability and

selected physical integrity criteria, and (4) the evaluation of the compatibility of commercially available processing equipment with regard to site regulatory criteria and cost.

### 3. TEST PROCEDURES AND EQUIPMENT

It is important to note that although this study focused on the sludge lagoon, it was also, by necessity, a generic study. Only select VOCs were evaluated, and, in many cases, the concentrations used in this study are not representative of actual site conditions. That is, the site concentrations were used for guidance purposes only; and the actual concentrations used in this study were chosen more to facilitate analytical detection limits and experimental constraints, such as solubility and original estimates of assumed losses during sample preparation. In most cases, this resulted in VOC concentrations in the waste form significantly above those expected at the site.

The waste used for grout preparation was sludge that was obtained from the RAFB Zone 1 sludge lagoon. A large sample was taken from the lagoon, sieved through a 0.25-in. screen for removal of debris, and, finally, homogenized in a Littleford high-shear mixer (Fig. 2). The resulting material provided the basic waste matrix for all testing described in this report. During the homogenization, the waste material lost much of its original VOC content. Spiking the sludge provided the VOC content needed for the leaching and extraction tests (Sect. 3.2). None of the grout samples subjected to the physical testing presented in this section were spiked with VOCs.

After homogenization, the sludge was collected in a stainless steel (SS) 55-gal drum. This drum was rotated on a drum roller for 30 min, and

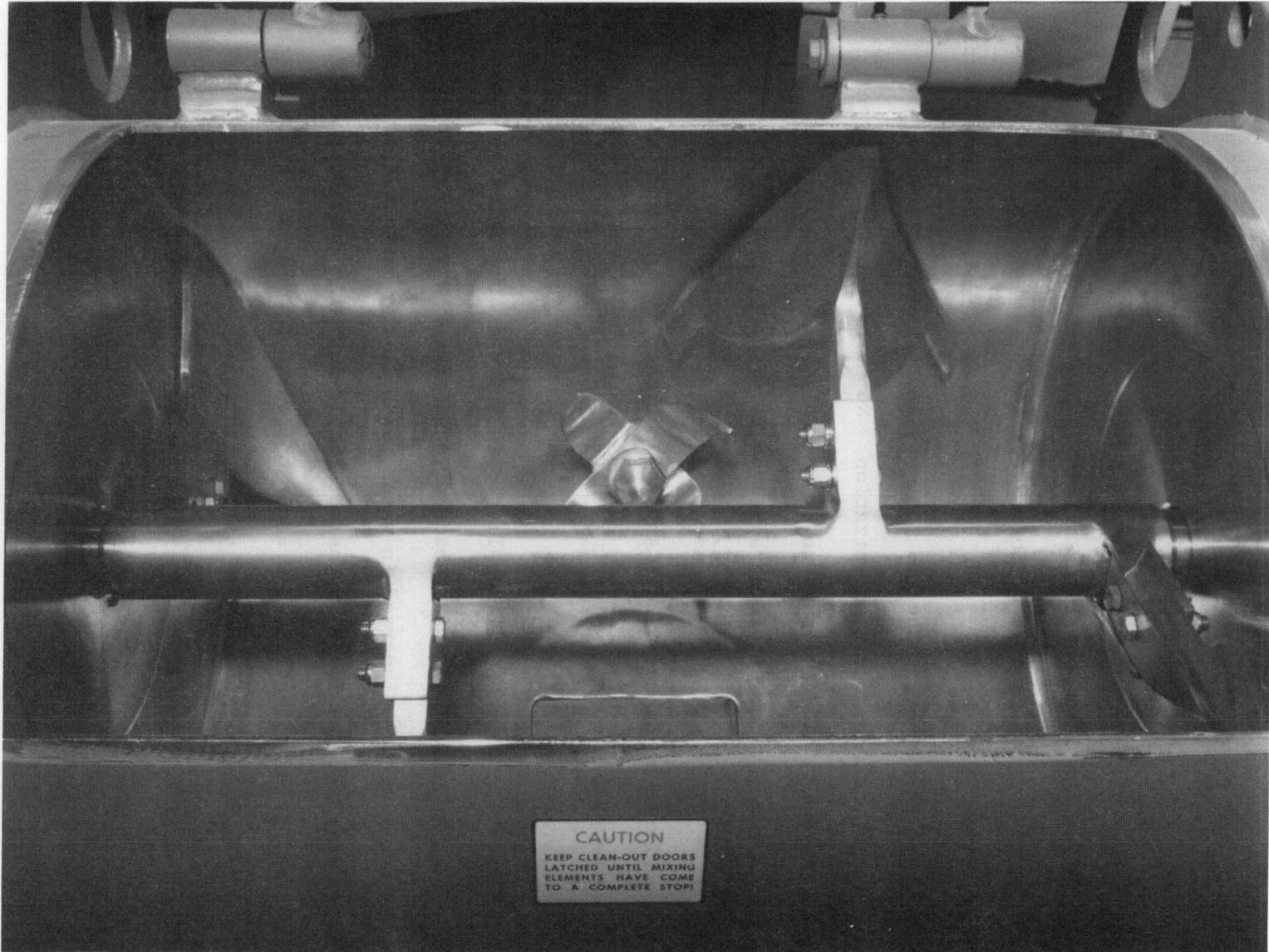


Fig. 2. Mixer used to homogenize sludge sample received from RAFB.

samples were collected from five separate areas within the drum to make a composite sample. The composite was characterized according to EPA protocols, with the results listed in Table 2. Two split-spoon samples were taken from the sludge lagoon at the same location that was later excavated for the large sample used in this project. These samples were submitted to two separate laboratories for characterization. Table 2 also includes these two analyses. The VOC content of these split-spoon samples can be taken to represent the VOC content of the sludge prior to excavation, handling, and homogenization. No herbicide analyses were performed for the sludge composite or one split-spoon sample because of failure to recover the herbicide spike as required by EPA. Thus, the herbicide analysis, reported in Table 2, was performed on a split-spoon sample analyzed by Enseco, Inc., Arvada, Colorado. No herbicide was detected in this sample, indicating that the sludge is not contaminated with herbicides.

In addition to the analyses listed in Table 2, the chloride content of the homogenized sludge was measured to be approximately 1.9 mg/kg, and the pH of the sludge dispersed in water for both the Extraction Procedure (EP)-Toxicity and the Toxicity Characteristic Leaching Procedure (TCLP) extraction, prior to acetic acid addition, was 6.8. The chloride content was considered important because of the corrosive nature observed for the sludge. The cementitious waste forms caused pitting of some of the 304 SS molds used to prepare the 2-in. cubes. It is suspected that the high pH environment of the grout combined with the presence of the chloride ion led to this pitting. The sludge alone has proven corrosive to 5-gal drums of carbon steel. These observations imply that remedial

Table 2. Characterization of sludge samples

Species	Concentration (ppm)		
	Homogenized sludge	Split spoon 1	Split spoon 2
<u>Volatile organic compounds</u>			
Acetone	1.7	12	<250
1,2-Dichloroethene	0.02	< 0.081	< 50
Chloroform	1.7	1.1	< 50
Methylethyl ketone	5.6	3.8	<250
Trichloroethene	15.0	51	280
Benzene	0.55	0.56	< 50
Perchloroethene	7.5	27	< 50
Chlorobenzene	3.9	22	< 50
Vinyl chloride	0.059	< 0.16	<100
Methylene chloride	1.8	0.13	NR <sup>a</sup>
Carbon disulfide	< 0.025	0.26	< 50
1,1-Dichloroethene	0.08	< 0.081	< 50
1,1-Dichloroethane	0.031	< 0.081	< 50
1,2-Dichloroethane	1.1	2.1	< 50
1,1,1-Trichloroethane	0.65	0.34	< 50
Carbon tetrachloride	0.025	0.033	< 50
Vinyl acetate	0.48	0.36	<100
1,1,2-Trichloroethane	0.38	1.2	< 50
4-Methyl-2-pentanone	1.6	14	<100
2-Hexanone	0.52	6.3	<100
1,1,2,2-Tetrachloroethane	0.21	0.57	< 50
Toluene	3.9	18	< 50
Ethyl benzene	3.2	20	< 50
Xylene	2.6	14	< 50

Table 2. (continued)

Species	Concentration (ppm)		
	Homogenized sludge	Split spoon 1	Split spoon 2
	<u>Base/neutral/acid organic compounds</u>		
Phenol	3.7	<10	<470
1,3-Dichlorobenzene	130	<10	<470
1,4-Dichlorobenzene	120	<10	620
1,2-Dichlorobenzene	<6.1	3,100	1,100
2-Methylphenol	10	7.7	NR <sup>a</sup>
4-Methylphenol	47	63	NR <sup>a</sup>
Isophorone	30	<10	<470
2,4-Dimethylphenol	110	210	<470
1,2,4-Trichlorobenzene	100	160	<470
Naphthalene	79	93	<470
2-Methylnaphthalene	190	140	<470
Dibenzofuran	15	17	<470
Fluorene	2.7	4.3	<470
Phenanthrene	2.2	7.4	<470
Anthracene	0.18	<10	<470
Di-n-butylphthalate	160	83	<470
Fluoranthene	2.8	8.9	<470
Pyrene	1.6	5	<470
Butylbenzylphthalate	10	15	<470
Bis(2-ethylhexyl)phthalate	190	1,200	<470
Di-n-octylphthalate	3	6.3	<470
	<u>PCBs/pesticides</u>		
(None detected)			
	<u>Herbicides</u>		
(None detected)			

Table 2. (continued)

Species	Concentration (ppm)		
	Homogenized sludge	Split spoon 1	Split spoon 2
Metals			
Arsenic	NM <sup>b</sup>	NM <sup>b</sup>	1.3
Barium	140	200	60
Cadmium	560	690	850
Chromium	6,200	12,000	6,300
Lead	760	550	140
Mercury	NM <sup>b</sup>	NM <sup>b</sup>	0.32
Selenium	NM <sup>b</sup>	NM <sup>b</sup>	<2
Silver	4.7	1.2	41
Aluminum	28,000	51,000	NR <sup>a</sup>
Beryllium	0.14	0.43	0.2
Boron	47	46	NR <sup>a</sup>
Calcium	3,000	8,200	NR <sup>a</sup>
Cobalt	15	25	11
Copper	270	330	300
Iron	82,000	77,000	NR <sup>a</sup>
Lithium	2.7	1.9	NR <sup>a</sup>
Magnesium	350	340	NR <sup>a</sup>
Manganese	690	2,100	NR <sup>a</sup>
Molybdenum	14	21	NR <sup>a</sup>
Nickel	210	180	230
Phosphorus	5,400	7,300	NR <sup>a</sup>
Potassium	320	460	NR <sup>a</sup>
Silicon	1,500	690	NR <sup>a</sup>
Sodium	200	370	NR <sup>a</sup>
Strontium	67	200	NR <sup>a</sup>
Tin	NR <sup>a</sup>	NR <sup>a</sup>	10
Titanium	680	1,400	NR <sup>a</sup>
Vanadium	20	25	<2
Zinc	630	1,200	640
Zirconium	9	13	NR <sup>a</sup>

<sup>a</sup>Not reported.<sup>b</sup>Not measured.

options that excavate the sludge and store it in drums may experience problems with corrosion.

### 3.1 PHYSICAL PROPERTIES

The main objective of this project was to establish the VOC retention capability of commercially available cement-based waste forms. Thus, the grout physical properties were of secondary concern; no criteria, except VOC retention, were identified to the vendors supplying the grout recipes. Grout products made from these recipes were evaluated as to

(1) rheology, (2) unconfined compressive strength, (3) freeze-thaw resistance, (4) 90-d immersion resistance, (5) bleed water, and (6) penetration resistance.

It should be noted that most of these properties can be tailored to meet specific criteria if a precise application or implementation technique requires a property different from those observed for these recipes. For example, it may be desirable to consider the application of in situ grouting technology to the RAFB site such that the ground cover is not removed from the filled-in sludge lagoon nor is the sludge excavated. None of the recipes were designed to optimize fluid properties. Thus, collaboration would be required between the supplier of the grout formula and the operator of the implementation technique to ensure compatibility between emplacement and product performance criteria.

#### 3.1.1 Sample Preparation

All of the grout samples prepared for physical testing were 2-in. cubes. The grouts were mixed according to vendor instructions using materials supplied by the vendor, the homogenized sludge, and deionized water. The mixing was done in a Model N-50 Hobart mixer (Fig. 3), using a



Fig. 3. Hobart mixer used in grout preparation mixing steps.

flat blade beater. After mixing, the grout was packed into 2-in. SS molds (Fig. 4) that had previously had all surfaces treated with a mold release agent. The grout was cured at room temperature in a saturated humidity environment (Fig. 5) for 28 d. After curing, the cubes were measured, weighed, and photographed. For photographing, three samples, which represented the range of sample conditions from best to worst, were selected. Next, three samples were submitted for measurement of their unconfined compressive strengths, three were subjected to freeze-thaw testing and then submitted for measurement of their unconfined compressive strengths, and three were immersed in deionized water for the 90-d immersion test.

The recipes supplied by the vendors and used to make the 2-in. cubes tested in this phase of the project follow. The fixed masses given in each recipe below total 1000 g, but some recipes allowed addition of more water in order to achieve a smooth homogeneous paste.

#### 3.1.1.1 Vendor A

1. Rotate the sludge drum for 30 min before sampling.
2. Weigh out 450 g of sludge in the Hobart mixing bowl.
3. Add 50 g of deionized water over 15 s while mixing at low speed, approximately 140 rpm (simulation of VOC spike).
4. Add 500 g of Vendor A's dry blend over a 30-s period while mixing at low speed.
5. Mix for 30 s on medium speed (~285 rpm).
6. If this mix does not form a smooth homogeneous paste, add the minimum amount of deionized water to make it so. Record the amounts of each ingredient including water. (Step 6 only applies the first time this

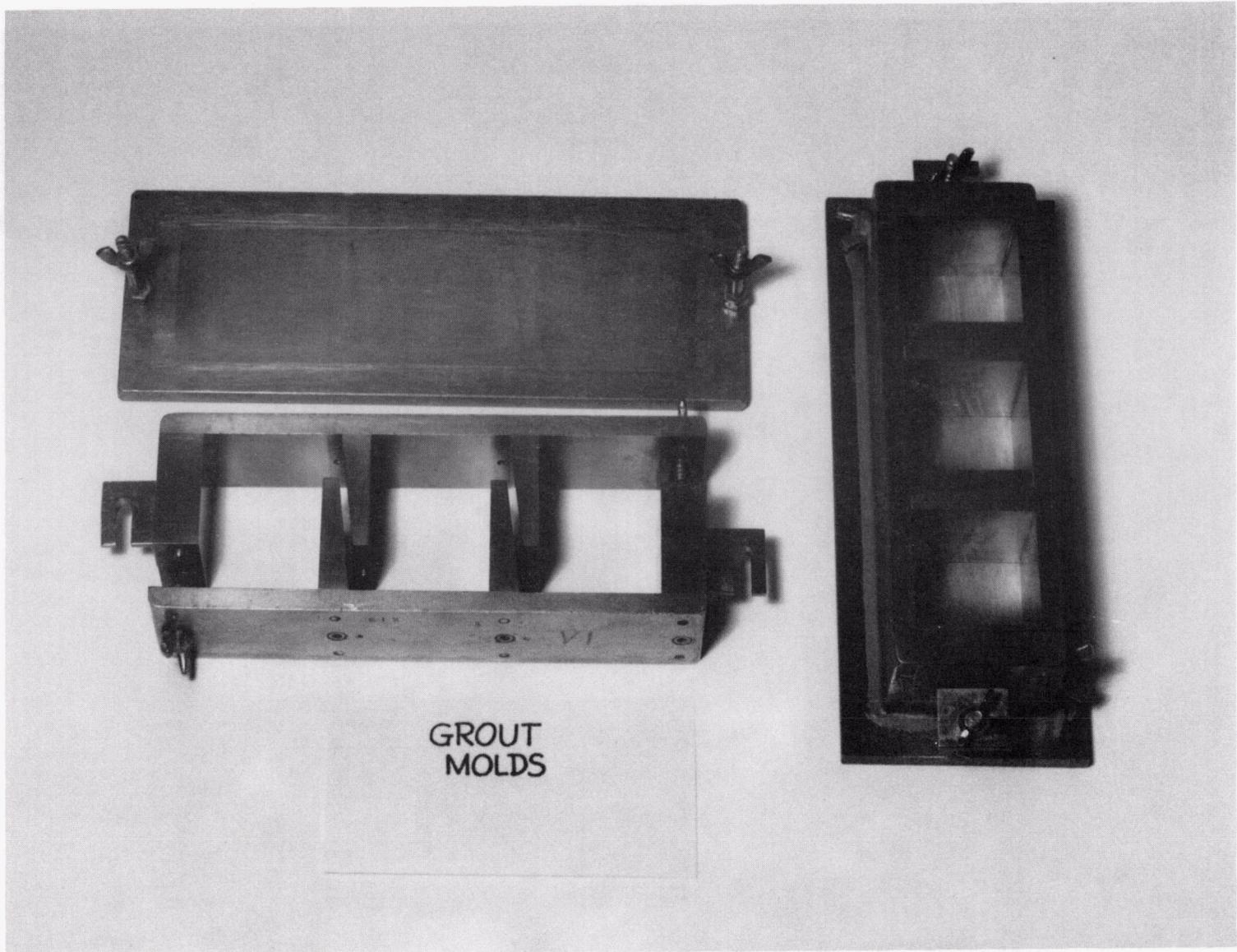


Fig. 4. Two-in. cube molds used for physical property test specimens.



Fig. 5. Humidity cabinet used to cure physical test specimens.

grout is made. Use the same recipe for subsequent batches and add any water needed in step 3.)

An extra 109 g of water was added in step 6 for the first batch of this grout. Subsequent batches added 159 g of water in step 3.

#### 3.1.1.2 Vendor B

1. Rotate the sludge drum for 30 min before sampling.
2. Weigh out 90.5 g of sludge in the Hobart mixing bowl.
3. Add 10 g of deionized water over 15 s while mixing at low speed (simulation of VOC spike). The amount added in this step is not important as long as the total water-VOC from this step and water from step 6 add up to 185.3 g (i.e., adjust step 6 if 10 g is not added in this step).
4. Add 90.5 g of Vendor B's liquid additive over a 30-s period while mixing at low speed.
5. Mix for 30 s at medium speed.
6. Add 175.3 g of deionized water while mixing at low speed for 30 s.
7. Mix for 30 s at medium speed.
8. Add 633.8 g of Vendor B's dry blend while mixing at low speed for 30 s.

#### 3.1.1.3 Vendor C

1. Rotate the sludge drum for 30 min before sampling.
2. Weigh out 625 g of sludge in one Hobart mixing bowl and 139 g of Vendor C's dry blend in another Hobart mixing bowl.
3. Add 69 g of deionized water to the sludge over 15 s while mixing at low speed (simulation of VOC spike).

4. Add 69 g of Vendor C's liquid additive to the sludge over a 30-s period while mixing at low speed.
5. Mix for 30 s at medium speed.
6. Slurry Vendor C's dry blend with 98 g of Vendor C's liquid additive and add to the sludge over a 30-s period while mixing at low speed.
7. Mix for 30 s at medium speed.

At the time this grout was mixed, the liquid additive was in short supply. Vendor C indicated this additive was a water solution of an agent intended to interact with the VOC components to be spiked during performance testing. Since no VOC was spiked for the physical testing, Vendor C substituted deionized water for the liquid additive in steps 4 and 6 to make the 2-in. cubes.

#### 3.1.1.4 Vendor D

1. Rotate the sludge drum for 30 min before sampling.
2. Weigh out 735 g of sludge in the Hobart mixing bowl.
3. Add 81 g of deionized water over 15 s while mixing at low speed (simulation of VOC spike).
4. Add 184 g of Vendor D's dry blend over a 30-s period while mixing at low speed.
5. Mix for 30 s on medium speed.
6. If this mix does not form a smooth homogeneous paste, add the minimum amount of deionized water to make it so. Record the amounts of each ingredient including water. (Step 6 only applies the first time this grout is made. Use the same recipe for subsequent batches and add any water needed in step 3.)

No extra water was required in step 6 for this grout.

### 3.1.2 Unconfined Compressive Strength

Unconfined compressive strength is a measure of the ability of the waste form to withstand applied loads such as those that would occur from disposal site overburden or stacked drums (or containers) during interim storage. Thus, unconfined compressive strength is an important parameter that addresses the concern of overburden subsidence and maintenance of structural integrity during interim storage or disposal. In general, the host matrix supplies the strength of the waste form. Hence, improved strength usually incurs the penalty of decreased waste loading and increased disposal volumes (versus the original waste volume). Therefore, it is desired to have only the sufficient strength necessary to support the anticipated loads.

In this study, freshly prepared grouts were poured or spooned into 2-in. cube molds conforming to American Society for Testing and Materials (ASTM) C 109-80, "Compressive Strength of Hydraulic Cement Mortars (using 2-in. or 50-mm cube specimens)," specifications. The grouts are then placed in a humidity cabinet maintained at 27°C and 98% relative humidity. Twenty-eight days after being placed in the molds, the cured grouts were removed and the unconfined compressive strength determined using a Tinius Olsen Super L Universal Testing Machine (Fig. 6). In this method, a uniaxial compressive load is applied along the specimen axis perpendicular to the specimen's flat parallel surfaces until the specimen fails. The maximum load is divided by the exposed cross-sectional area of the specimen surface to determine the unconfined compressive strength.

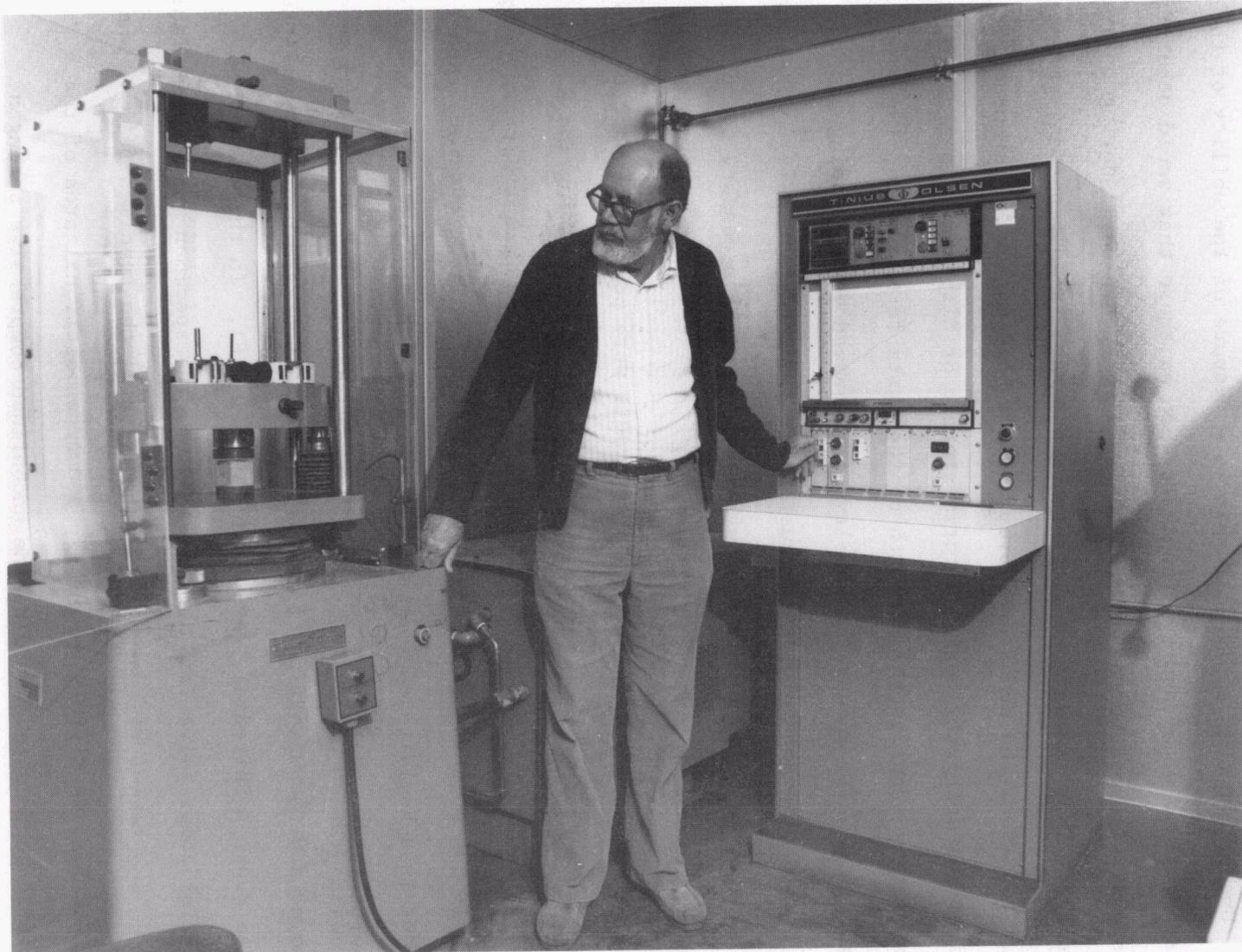


Fig. 6. Instrumentation used to determine unconfined compressive strength.

### 3.1.3 Penetration Resistance

Penetration resistance is a measure of set, or stiffening, of the grout (ASTM C 403-85, "Time of Setting of Concrete Mixtures by Penetration Resistance"). Initial set is the elapsed time, after initial contact of the dry-solids blend and waste, required to reach a penetration resistance of 500 psi. Final set is the elapsed time, after initial contact of the dry-solids blend and waste, required to reach a penetration resistance of 4000 psi. Although no substitute for calorimetry data, penetration resistance does provide a quick and easy method for assessing the extent to which the cementitious reactions have occurred, as well as a means of comparing the effects of differing grout recipes.

In this study, freshly prepared grouts were poured into 2-in. cube molds and then stored in a humidity cabinet at 27°C with a relative humidity of 98%. The cured grout samples were removed after 28 d, and the penetration resistance measurements were obtained. Penetration resistance data were obtained using an Acme Penetrometer (Fig. 7) with a needle having an 0.11-in.<sup>2</sup> surface area at the point of penetration. A vertical force downward on the apparatus is applied until the needle penetrated the grout to a depth of 1 in. Penetration resistance is determined by dividing the force required to penetrate the grout to a depth of 1 in. by the surface area of the needle at the point of contact with the grout.

### 3.1.4 Thermal Cycling

Resistance to freeze-thaw cycles is a measure of the capability of a waste form to withstand the natural temperature variation at a disposal or storage site. This resistance is particularly important during interim

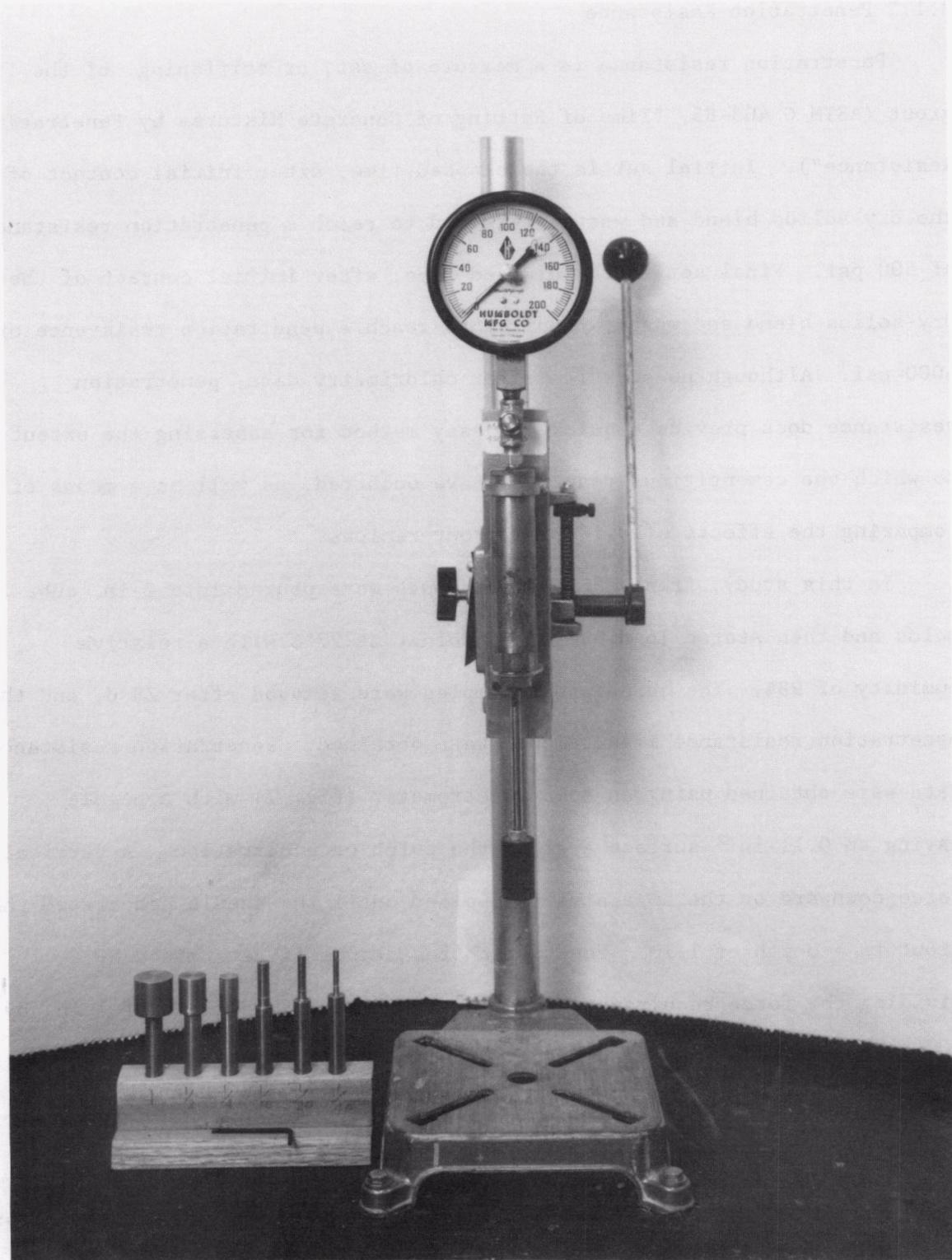


Fig. 7. Instrumentation used to determine penetration resistance.

storage or for waste disposal above ground. Temperature variations experienced by waste disposed below the frost line should be minor.

In this study, freshly prepared grouts were poured into 2-in. cube molds and then stored in a humidity cabinet at 27°C with a relative humidity of 98%. The cured grout samples were removed after 28 d and subjected to thermal cycling using a test method involving modifications to ASTM B553, "Standard Test Method for Thermal Cycling for Electroplated Plastics." For this test, 2-in. cube samples were sealed inside Teflon® PFA jars. The cubes were placed on platforms to raise them above any water that condensed during testing. The jars were placed in a Ransco Environmental Chamber (Fig. 8) and subjected to 30 thermal cycles between temperature extremes of +50°C and -30°C. The high and low temperatures used were based on temperature extremes recorded during the last 39 years by the National Weather Bureau for the Macon, Georgia, area. Each thermal cycle consists of:

1. Ramp from 20 to 50°C.
2. Hold at 50°C for 1 h.
3. Ramp from 50 to 20°C.
4. Hold at 20°C for 1 h.
5. Ramp from 20 to -30°C.
6. Hold at -30°C for 1 h.
7. Ramp from -30 to 20°C.
8. Hold at 20°C for 1 h.

Figure 9 illustrates one temperature cycle used in the freeze-thaw testing. A ramp time of 45 min. was used for Vendors B and D and 1 h for Vendors A and C. After being subjected to this thermal cycling, the

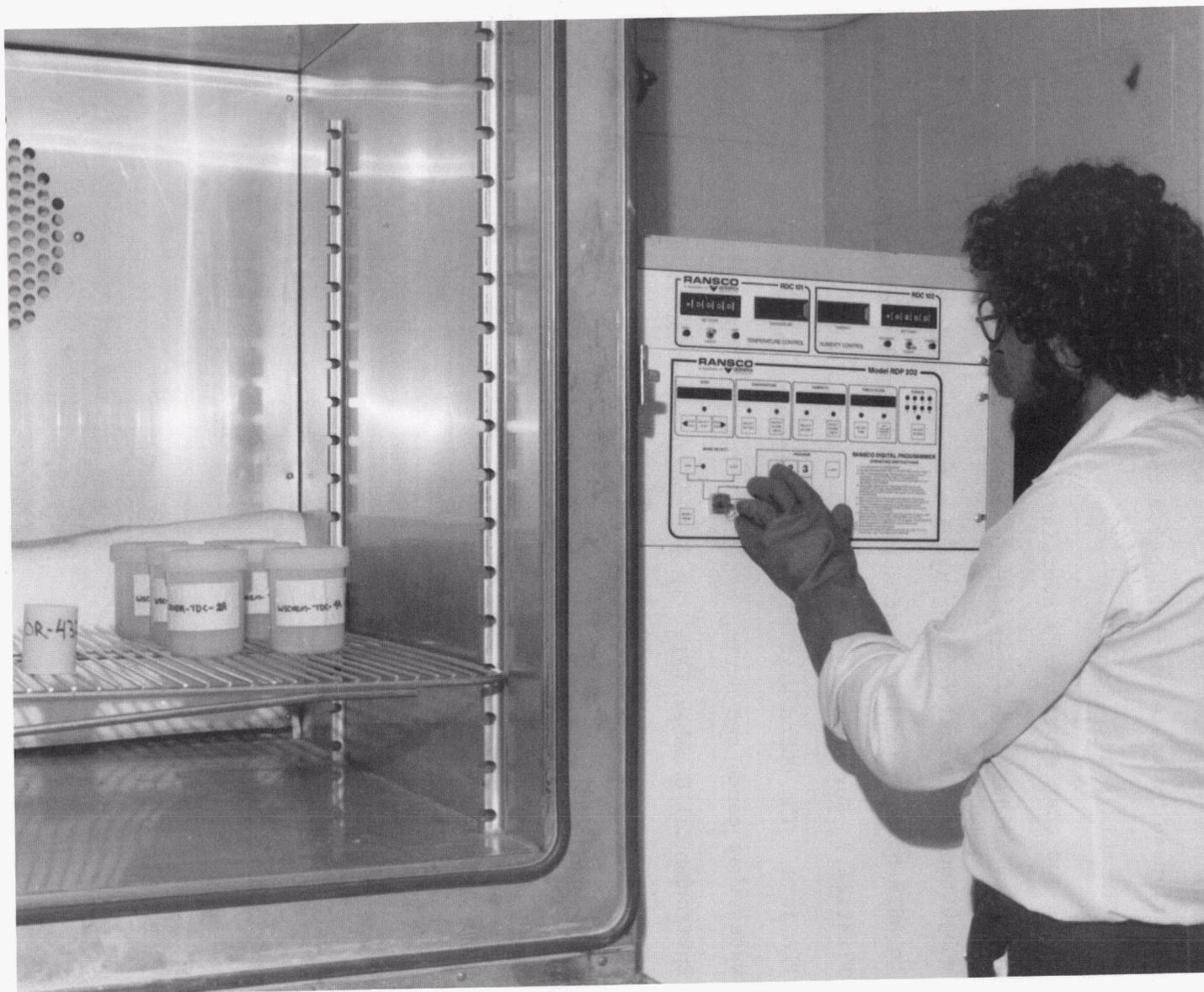


Fig. 8. Instrumentation used to control temperature during freeze-thaw cycles.

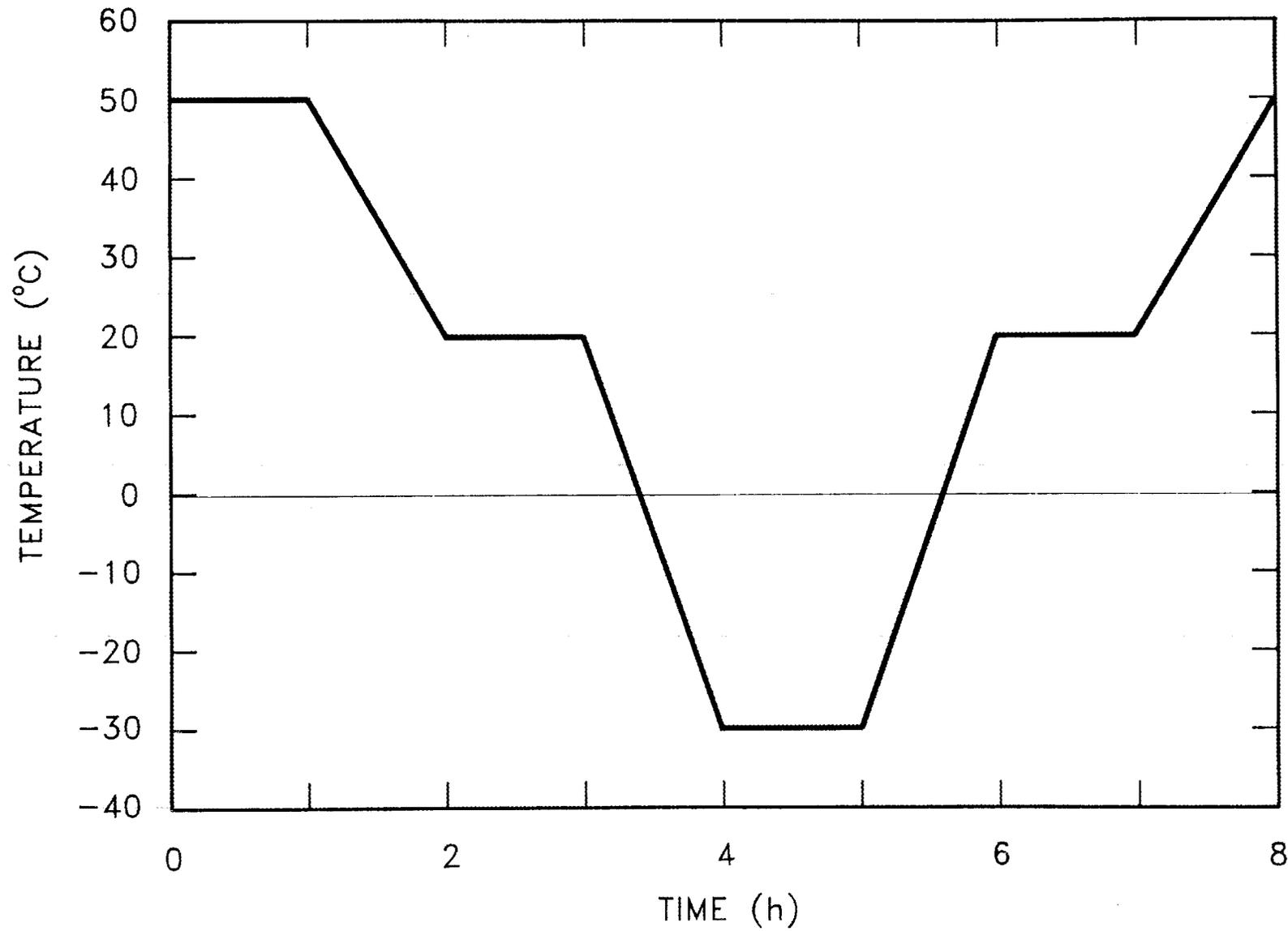


Fig. 9. Typical temperature profile in environmental chamber during one freeze-thaw cycle.

samples were subjectively evaluated for degradation and were submitted for measurement of their unconfined compressive strengths. These values would then be compared with the values obtained after a 28-d cure (before freeze-thaw testing).

### 3.1.5 Immersion Resistance

Immersion resistance is an indication of the waste form's ability to withstand prolonged exposure to water, such as would be experienced upon water intrusion into a storage container or a raising of the water table during a rainy period. For this study, freshly prepared grouts were poured into 2-in. cube molds and then stored in a humidity cabinet at 27°C and at a relative humidity of 98%. The cured grout samples were removed after 28 d and immersed in deionized water (nominally 1500 mL) contained in plastic jars. The cubes were placed on platforms so that the water had access to all sides of the sample. The jars were sealed and allowed to remain static for 90 d. After immersion for 90 d, the cubes were removed from the water, subjectively observed for signs of physical deterioration, and the unconfined compressive strength was measured for each cube. These values would then be compared with the values obtained after a 28-d cure (before immersion testing).

### 3.2 LEACHABILITY

The release of the VOCs from the waste form to the environment (i.e., its leachability) is, perhaps, the major factor in determining the acceptability of grout technology as a potential remedial action option for the RAFB Zone 1 sludge lagoon. Performance specifications related to leachability are limited. Regulatory-related tests such as the EP-Toxicity<sup>20</sup> and the TCLP<sup>20</sup> deal more with the classification of the waste

form and do not supply data that can be used in modeling VOC release from the waste form. In addition, the specified procedures associated with these tests do not adequately address the potential loss of VOCs during sample handling, nor are all of the VOCs of potential concern assigned a threshold concentration by the EPA.

In reality, the leaching process, which is the release of the species from the waste form into the surrounding solution, is complex. The chemical potential of the species in the aqueous phase is different from that on the waste-form surface. Thus, the immersion of the waste form in a liquid (such as groundwater) leads to a flux of mass between the solid surface and the solution. The release of surface molecules into the solution establishes a concentration gradient in the solid adjacent to the surface. This leads to the movement of species from the interior of the waste form toward the surface and their subsequent release into the solution. The instantaneous rate of release of a species from the solid surface into the liquid is proportional to this concentration gradient, which is the difference in chemical potentials of the solid at the surface and the liquid at any given moment of time. In mathematical terms, this concept is represented by the following equation for slab geometries, known as Fick's first law:<sup>21,22</sup>

$$J = -D (dC/dX), \quad (1)$$

where,

J = Instantaneous flux at time t of a given species from the surface of a slab of the porous solid body,  $g \cdot cm^{-2} \cdot s^{-1}$ ;

D = Diffusion coefficient for the species in the porous, solid body soaked in an aqueous environment,  $cm^2/s$ ;

$C$  = Concentration of the species in the overall volume of the porous solid body at time  $t$  and position  $X$ ,  $\text{g}/\text{cm}^3$ ;

$X$  = Distance from the slab centerline toward the slab surface,  $\text{cm}$ ;

$dC/dX$  = Instantaneous concentration gradient at time  $t$  and position  $X$ ,  $\text{g} \cdot \text{cm}^{-3} \cdot \text{cm}^{-1}$ .

In a static environment, with no leachate replacement, the waste species in the liquid will eventually equilibrate with the waste species remaining in the waste form. When equilibrium is reached, the net transfer of species from the solid to the liquid will cease. The relationship between the liquid concentration at equilibrium with the remaining waste-form concentration is described by the distribution coefficient.

Thus, in this study, tests were conducted to supply both (1) information related to the concentrations resulting from EP-Toxicity and TCLP testing (regulatory-related tests) and (2) the diffusion and distribution coefficients (mass-transfer parameters). Standard testing protocols were used for the EP-Toxicity and TCLP tests,<sup>20</sup> while testing to obtain the desired mass-transfer parameters required significant development.

### 3.2.1 Waste-Form VOC Content

One difficulty in dealing with VOCs is in knowing how much is contained in a given sample at a given time. Even if an accurate VOC analysis is performed, the concentration may change with time, particularly if the sample is handled or exposed to air. Soil or water contaminated with VOCs tends to lose a significant fraction of its VOC content to the environment, whether small samples are being handled in

the laboratory or large sites are being excavated for remedial action (e.g., incineration), unless steps are taken to control or reverse this VOC flow. This point is illustrated by comparing the VOC content of the split-spoon samples taken at the site with the analysis of the homogenized waste (shown in Table 2).

If cement-based waste forms are made using standard equipment and procedures, the VOC content of the final waste form must be considered unknown, even if the VOC content of the original waste material is accurately known. This is not surprising in light of the fact that standard waste-form preparation procedures involve vigorous mixing in open-faced equipment, coupled with the evolution of heat during hydration. The determination of the waste-form VOC content is critical to the interpretation of the leach test results. This can be illustrated by considering the TCLP test, which provides no criteria for the preparation of a cement-based sample. In this test, a waste that had been determined to be of environmental concern due to its VOC content may well meet the TCLP leachate threshold concentrations after solidification/stabilization. However, the question becomes, "Did the waste form retard the release of the VOCs sufficiently to be an environmentally acceptable treatment option, or did the waste form lose sufficient VOCs during sample preparation such that the leach results are misleading?" Since the principal objective of this study was to assess the ability of commercially available waste forms to retard the release of VOCs, the determination of the waste-form VOC content became an integral part of the leach studies.

One approach to this problem is to try to directly measure the VOC content of the waste form. Due to the complexity of the waste-form matrix and the relatively low VOC concentrations contained therein, the analytical technique for direct measurement requires grinding of the waste form followed by solvent extraction. Existing techniques would require a major development effort to control and quantify VOC releases during the grinding step. In addition, the waste form may retard the release of VOCs by providing a physical barrier around the waste or chemically altering the VOCs to a nonextractable or low-solubility form. Thus, solvent extraction would only measure the extractable VOCs remaining in the waste form and would not identify VOCs lost during sample preparation or nonextractable VOCs remaining in the waste form. Thus, the technique would not differentiate between a commercially available waste form that rendered the VOCs nonextractable and one which simply lost significant VOCs during sample preparation. Consequently, the approach taken in this project was to do both: that is, to measure the VOC loss to the environment during sample preparation and to measure the extractable VOC content of the final waste-form sample.

### 3.2.2 Selection of Individual VOCs

As discussed previously, the loss of VOCs during sample preparation and handling was a major concern to the experimental work in support of this project. Consequently, the decision was made to control the VOC content of the waste used in this study by spiking the homogenized waste sample (Sect. 3) with a known quantity of VOCs. This section provides the rationale for the selection of the VOCs used in the experimental work.

The maximum reported concentrations found in the site groundwater, soil, and soil leachate samples for each constituent of potential interest are shown in Table 1. Because this study is principally concerned with the immobilization of VOCs, the constituents from Table 1 are of interest here.

In order to identify the key VOCs of concern, the VOCs from Table 1 were weighted by multiplying the species mole fraction by the species vapor pressure and ranking the resulting product in decreasing order. The results are listed in Table 3. (Although this product is essentially Raoult's law, it is recognized that significant deviation from ideality will occur for these organic species in water; that is, this product is not an estimate of the species vapor pressure above the sludge.) Vinyl chloride and trichlorofluoromethane, which are normally gases at room temperature and, hence, require the development of special sampling procedures, were excluded from consideration. Toluene and benzene are expected to behave similarly in the grout product. Consequently, benzene was chosen over toluene because of higher solubility in aqueous solutions, in an effort to both simplify the analytical requirements and facilitate analytical detection limits. 1,2-dichloroethane was also excluded due to the fact that it interfered with the analysis of 2-butanone, a constituent present at the site in significantly higher concentrations. The following eight were selected as the main species of interest: *t*-1,2-dichloroethene, trichloroethylene (TCE), acetone, chloroform, tetrachloroethene (PERC), 2-butanone (MEK), benzene, and chlorobenzene.

Table 3. Estimation of the product of the mole fraction and vapor pressure of each VOC species

Species	Maxium concentration (ppb)	Vapor pressure at 25°C (nm Hg)	Product of the mole fraction and vapor pressure (nm Hg)
<i>trans</i> -1,2-Dichloroethene	100,000	344,000,000	6,038.065
Vinyl chloride	12,000	984,000,000	3,214.687
Trichloroethylene	130,000	80,000,000	1,346.832
Acetone	9,000	263,000,000	693.448
Chloroform	17,000	236,000,000	571.836
Tetrachloroethene	59,000	23,000,000	139,238
Toluene	20,000	32,000,000	118.175
2-Butanone (MEK)	3,700	100,000,000	87.295
Benzene	2,800	96,000,000	58.548
Chlorobenzene	20,000	13,000,000	39.304
Trichlorofluoromethane	170	808,000,000	17.014
1,2-Dichloroethane	470	86,000,000	6.950
1,1-Dichloroethene	49	617,000,000	5.307
1,1-Dichloroethane	91	264,000,000	4.131
Carbon disulfide	29	373,000,000	2.417
4-Methyl-2-pentanone	420	9,000,000	0.642
Xylenes	220	10,000,000	0.353
Carbon tetrachloride	5	117,000,000	0.065
Bromodichloromethane	5	100,000,000	0.052
Ethyl benzene	27	10,000,000	0.043
Dibromochloromethane	5	20,000,000	0.008
Total	374,991		
Water	999,625,009		

### 3.2.3 Preliminary Procedural Evaluation

As discussed previously, it can be assumed that significant VOC losses will occur during the preparation of VOC-containing grout samples for subsequent evaluation in the leach testing. It is, therefore, desirable that the initial VOC content of the waste used at the beginning of the sample preparation step be as high as possible so that the VOC content of the final product (after sample handling losses) will be sufficient to provide measurable quantities in the leachates that result from leach testing. In response to this need, a preliminary screening study was performed to provide guidance to the project on the effects of these excessive original VOC concentrations on subsequent leachate analyses, as well as to provide a preliminary estimate of the VOC losses that might occur during sample preparation.

In the screening study, a water-VOC surrogate was substituted for the waste. All of the VOC constituents of interest (from Table 3) except acetone have solubility limits in water. Based on some simplistic assumptions, it was calculated that a 10 wt % acetone solution should result in leachate concentrations in subsequent leach testing that would be quantifiable by the analytical equipment then available for the screening study. Consequently, a 10 wt % acetone solution became the primary material used in this preliminary procedural screening effort. Although not technically necessary, it was desired that this solution be of relative composition similar to the lagoon waste. As such, one would desire to add the other components at relative (to acetone) concentrations similar to those shown in Table 3. However, with the exception of 2-butanone, solubility limits precluded this. Thus, the initial surrogate

started with a solution of 10 wt % acetone, 4 wt % 2-butanone, and the other six components added at their reported solubility limits. Adding these remaining six constituents at their reported solubility limits resulted in the formation of two phases. This was not unexpected because the reported solubilities (listed in Table 4) are for each constituent alone with water; hence, the multicomponent surrogate should lower these reported limits. This initial VOC-water solution was diluted with a ketone-water mix until the formation of two phases was no longer observed. In addition, methanol was added to aid in the solubilization of the hydrophobic compounds. The resulting solution had a faintly cloudy appearance and was used as the surrogate in the screening study. Its composition, as calculated from the mass of each constituent added, is shown in Table 4.

This surrogate was then used with the vendor-supplied formulas to prepare grout samples that were subsequently subjected to leach testing. In the sample preparation, the surrogate was placed in a Model N-50 Hobart mixer and the stirrer turned on a low setting (~139 rpm). The dry-solids-blend components (supplied by the vendors) were then added to the water according to the vendors' instructions. After addition of the solids, the Hobart was set to a medium setting (~285 rpm) to facilitate blending. Total mixing time varied from 1 to 4 min. After mixing, the fresh grout was poured or packed into Teflon curing molds. Each mold makes 12 grout cylinders; each cylinder is nominally 2.52 cm in diam and 4.65 cm long. The curing mold was sealed between two Teflon slabs and two SS slabs using four nuts and bolts. This entire assembly was placed inside plastic bags during curing to help maintain saturated conditions inside the sealed

Table 4. Aqueous VOC-surrogate waste solution composition

Species	Maximum site concentration (ppm)	Solubility (ppm)	Surrogate concentration (ppm)
Acetone	9	<sup>a</sup>	100,100
2-Butanone	4	240,000	45,348
<i>trans</i> -1,2-Dichloroethene	100	8,100	1,997
Chloroform	17	8,200	1,991
Trichloroethylene	130	1,000	277
Benzene	3	700	197
Chlorobenzene	20	490	160
Perchloroethylene	59	400	80
Methanol	<sup>b</sup>	<sup>a</sup>	122,608

<sup>a</sup>Miscible.<sup>b</sup>Not applicable.

molds. The grouts were cured inside these molds for 28 d. Each cylinder was pushed from the mold and then subjected to the leaching protocol.

The leaching containers were nominally 16-fl. oz. (0.473-L) amber jars with Teflon seals inside the screw-on lids. The jars were partially filled with deionized water, and the grout sample was placed atop a small SS screen in the jar to raise the sample off the bottom and maintain a position along the jar centerline. Then, the jar was topped with deionized water and the lid was screwed on tight. Each jar was allowed to remain static for specified time intervals before the jar was unsealed and two 40-mL samples were taken for analyses. These analyses became the leachate concentrations used in mass-transfer parameter determination.

In order to determine the VOC content of the grout leach samples, mass balance tests were conducted on the VOC-water solution, which had been subjected to the same preparation steps as the grout leach samples; that is, the VOC-water solution was subjected to the identical mixing and curing steps as the grout samples, and the solution was analyzed before and after each of the preparation steps. Tables 5 and 6 show the retentions of each constituent in the VOC-water solution at each preparation step (i.e., mixing and curing). These data indicate that, on a percentage basis, the magnitude of the loss is similar at each step. The cumulative losses for the VOC-water solution (Tables 5 and 6) were then assumed to be representative of the VOC losses which occurred during the actual preparation of the grout samples. Table 7 lists the initial concentration of the surrogate used to prepare the grout samples, the assumed percent retention of the VOCs (from Tables 5 and 6), and the

Table 5. VOC retained during mixing of a VOC-water solution in the screening study

Species	Concentration (ppm)			Retained <sup>a</sup> (%)
	Before mixing		Measured after mixing	
	Calculated	Measured		
Acetone	100,100	93,311	93,808	100
2-Butanone	45,348	47,617	44,408	93.3
<i>trans</i> -1,2-Dichloroethene	1,997	1,411	120	8.5
Chloroform	1,991	1,610	247	5.3
Trichloroethylene	277	222	152	68.5
Benzene	197	183	95	51.9
Chlorobenzene	160	<i>b</i>	<i>b</i>	<i>b</i>
Perchloroethylene	80	<i>b</i>	<i>b</i>	<i>b</i>

<sup>a</sup>Based on the measured quantities.

<sup>b</sup>The quantitative analysis using the FID was too inconsistent for chlorobenzene and perchloroethylene.

Table 6. VOC retained in a VOC-water solution held in the curing mold for 28 d in the screening study

Species	Concentration (ppm)			Retained <sup>a</sup> (%)
	Initial		Measured after 28 d	
	Calculated	Measured		
Acetone	100,100	93,311	88,842	95.2
2-Butanone	45,348	47,617	46,623	97.9
<i>trans</i> -1,2-Dichloroethene	1,997	1,411	<2	<0.1
Chloroform	1,991	1,610	403	25
Trichloroethylene	277	222	34	15.3
Benzene	197	183	36	19.7
Chlorobenzene	160	<i>b</i>	23	14.4
Perchloroethylene	80	<i>b</i>	<2	<2.5

<sup>a</sup>Based on measured quantities.

<sup>b</sup>The quantitative analysis using the FID was too inconsistent for chlorobenzene and perchloroethylene.

Table 7. Surrogate VOC concentrations and retentions used in the screening study

Species	Initial concentration (ppm)	Retained (%)	Final concentration (ppm)
Acetone	93,000	95	88,000
2-Butanone	48,000	90	43,000
<i>trans</i> -1,2-Dichloroethene	1,400	0	0
Chloroform	1,600	5	80
Trichloroethylene	220	10	22
Benzene	180	10	18
Chlorobenzene	160	10	16
Perchloroethylene	80	10	8

calculated concentration of the surrogate contained in the grout samples used in the leach tests.

The assumed waste-form concentration (i.e., source term) was combined with the leachate analyses (i.e., release) to obtain the species' fractional release rate as a function of time in an attempt to determine mass-transfer parameters. Not surprisingly, the predominant species in the leachate were the two ketones (acetone and 2-butanone). The actual leachate samples required significant dilution to prevent the ketone content from overloading the analytical detector. This required dilution had a deleterious effect on the analysis of the constituents present in the leachate in concentrations less than the ketones (the majority of the constituents studied). Indeed, the majority of the constituents were below analytical detection limits, which precluded the determination of the desired mass-transfer parameters.

In summary, this screening study provided procedural guidance to the project in two important areas: (1) waste concentration and (2) VOC loss during sample preparation. The difficulties discovered in analyzing leachates and the subsequent inability to obtain mass-transfer parameters on a majority of the constituents (a major objective of this project) clearly indicated that the original starting waste should not have excessive relative concentrations of any individual constituent. That is, in order to facilitate the analyses of leach solutions, the starting waste material should have similar individual VOC concentrations. In addition, the screening study clearly indicated that VOC losses during sample preparation were potentially significant. That is, VOC losses during preparation of the grout leach specimens must be determined in order to

allow a technically defensible interpretation of the subsequent leach data. Both of these findings were incorporated into the grout sample preparation procedures discussed in the next section.

It is emphasized that the VOC-water solution VOC retentions were only used to correct the screening study data. The leaching data that are the main subject of this report (detailed in subsequent sections) were not corrected in this manner. Rather, the actual VOC losses during grout preparation were measured as described in the following sections.

#### 3.2.4 Procedure for Preparation of Grout Samples

The screening study indicated that there was a need to control the VOC concentrations of the starting waste and that VOC losses needed to be determined at each of the grout-sample preparation steps. The approach taken in the sample preparation procedures described here utilized a VOC-water spike to control the VOC content of the starting waste and attempted to perform each of the preparation steps in a contained environment. The philosophy behind the preparation step procedures was to (1) attempt to minimize head space and (2) measure the VOC losses to that headspace. The losses to the headspace were then subtracted from the starting VOC content to obtain the VOC content remaining in the final grout product utilized in the subsequent leaching procedures.

##### 3.2.4.1 Waste spiking

The homogenized sludge described in Sect. 3 was the basic waste matrix used in these procedures. Throughout the remainder of this section, the homogenized sludge is referred to as simply *sludge*. The VOC content of the waste material used in the subsequent grout preparation steps was controlled by spiking the sludge with a VOC-water cocktail.

Throughout the remainder of this section, the sludge containing the VOC-water cocktail is referred to as *spiked sludge*.

#### 3.2.4.2 Waste spiking procedure

The spike procedure follows:

1. Label and tare a 40-mL glass vial with a Teflon-lined septum and containing a small Teflon-coated stirring bar.
2. Add about 0.5 g of liquid surfactant and reweigh so later mass additions will be accurately known.
3. Fill the vial with deionized water and seal.
4. Using a needle and syringe, withdraw a volume of water from the vial (via the septum) about equivalent to the volume of VOC to be added later.
5. Reweigh the vial and record the mass of water added.
6. Inject the predetermined amounts of each VOC into the vial, weighing after each addition. Inject benzene last, as it is the only hydrophobic (i.e., insoluble) VOC with a density less than water.
7. The vial can be used immediately or stored at 4°C for a short time period (e.g., a few hours).
8. Weigh out the required amount of sludge (minimum of 360 g for a 40-mL spike) in a Hobart mixing bowl.
9. Prior to use, disperse or emulsify the organic phase in the water in the vial. (The magnetic stirring bar and an ultrasonic bath are used.)
10. Add the contents of the vial while mixing the sludge on low speed with the Hobart mixer (inside a hood) for about 15 s.

11. Rinse the vial with the preweighed deionized water from another vial, and mix this rinse with the sludge as well.
12. Quickly take three spiked sludge samples from separate areas within the bowl and submit for analysis.
13. Quickly transfer the bowl containing the spiked sludge into the glovebox (Fig. 10) and seal the glovebox.

The analyses of the three sludge samples determine the quantity of VOC entering the mixing step.

#### 3.2.4.3 Mixing procedure

The mixing procedure follows:

1. Quickly weigh the bowl after taking the three spiked samples and record the amount of spiked sludge remaining for mixing into grout (Fig. 11).
2. Quickly place the bowl with the spiked sludge into the glovebox.
3. Mix the sludge into a grout using the vendor materials and vendor instructions (see Sect. 3.1.1).
4. Pack the grout into curing molds, eliminating air voids as much as possible.
5. Seal the curing mold (Fig. 12).
6. Clean up and seal all potential sources of VOC.
7. Remove curing molds from glovebox.
8. Take gas samples immediately and analyze on the GC-FID.

These analyses are used to determine the quantity of VOC entering the curing step. Verification tests using a VOC-water solution in place of the sludge and grout were able to account for 60% to 100% of the VOC used in the system.



Fig. 10. Chamber containing spiked sludge.



Fig. 11. Mixing steps in preparation of static leach test specimens.

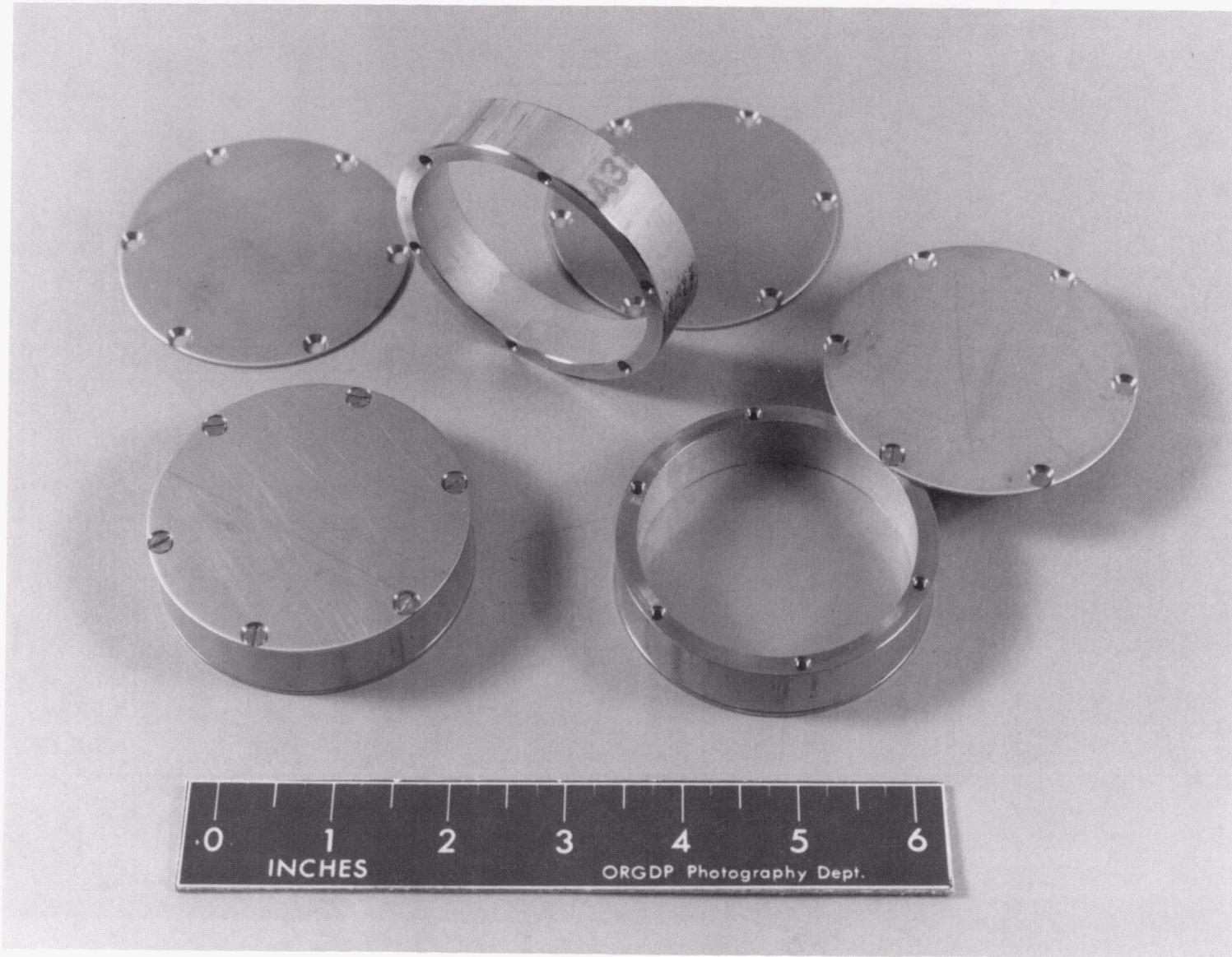


Fig. 12. Molds used in preparation of static leach test specimens.

#### 3.2.4.4 Curing procedure

1. The sealed sample molds from the glovebox are placed in the curing pipe shown in Fig. 13.
2. After the pipe is filled with molds (10), the top is screwed on and tightened.
3. The pipe is allowed to remain static for a curing period of 28 d.
4. At the end of the curing period, a sample of the air contained in the pipe headspace is taken and analyzed.

This analysis determines the VOC loss during the curing step.

5. The pipe is opened, and the sample molds are removed.
6. The mold end plates are removed.

The resulting grout disk inside the SS ring (see Fig. 13) becomes the static leach test specimen. Verification tests using a VOC-water solution was able to account for 70% to 115% of the VOC used in the system.

#### 3.2.4.5 Static leach test procedure

1. Each disk from the curing step is suspended in 603 g of deionized water in a zero-headspace extraction vessel (described in ref. 20 and shown in Fig. 14) by SS wires attached to the ring surrounding the grout disk.
2. After sealing the vessel, air is pushed through the top valve using the vessel piston, leaving no headspace inside the vessel.

At this point, the leach test begins. At selected time intervals, leachate samples are withdrawn from the leach vessel for analyses.

It is important to note that two types of leachate samples were generated in these studies: semicontinuous and batch. Semicontinuous samples were obtained in the following manner:



Fig. 13. Curing pipe used in preparation of static leach test specimens with four resulting test specimens.



Fig. 14. Zero-headspace extraction vessel used during static leach test.

1. The leachate was homogenized by withdrawal into a large SS syringe (see Fig. 15) and reinjection into the vessel without exposing the leachate to air or introducing air into the vessel. This process was done twice to ensure that a representative sample could be obtained at the top of the vessel.
2. A small aliquot was withdrawn from the leachate.
3. The aliquot was analyzed by a dedicated liquid sample concentrator -gas chromatograph-ion trap detector(LSC-GC-ITD).
4. Leaching is allowed to continue.

Batch samples were obtained in the following manner:

1. The entire leachate was withdrawn.
2. The leachate analyses were performed by the K-25 Analytical Department, using a LSC-GC-MS with EPA-approved contract laboratory program (CLP) procedures.
3. In this case, leaching stops and requires one test specimen per analysis.

### 3.3 CHEMICAL ANALYSIS

The chemical analyses were performed utilizing a gas chromatograph dedicated to the project and an EPA contract laboratory. The dedicated gas chromatograph was a Perkin-Elmer model 8500 GC with both a flame ionization detector (FID) and an ECD. The GC was also coupled to a Perkin-Elmer ITD and a Tekmar liquid sample concentrator (LSC 2000). The ITD measures the mass of fragments generated from the chemical species passing through the ITD and generates this mass spectrum every 2 s. Thus, a detailed mass spectrum with time is generated as a sample is separated into its individual molecular constituents in the GC prior to being

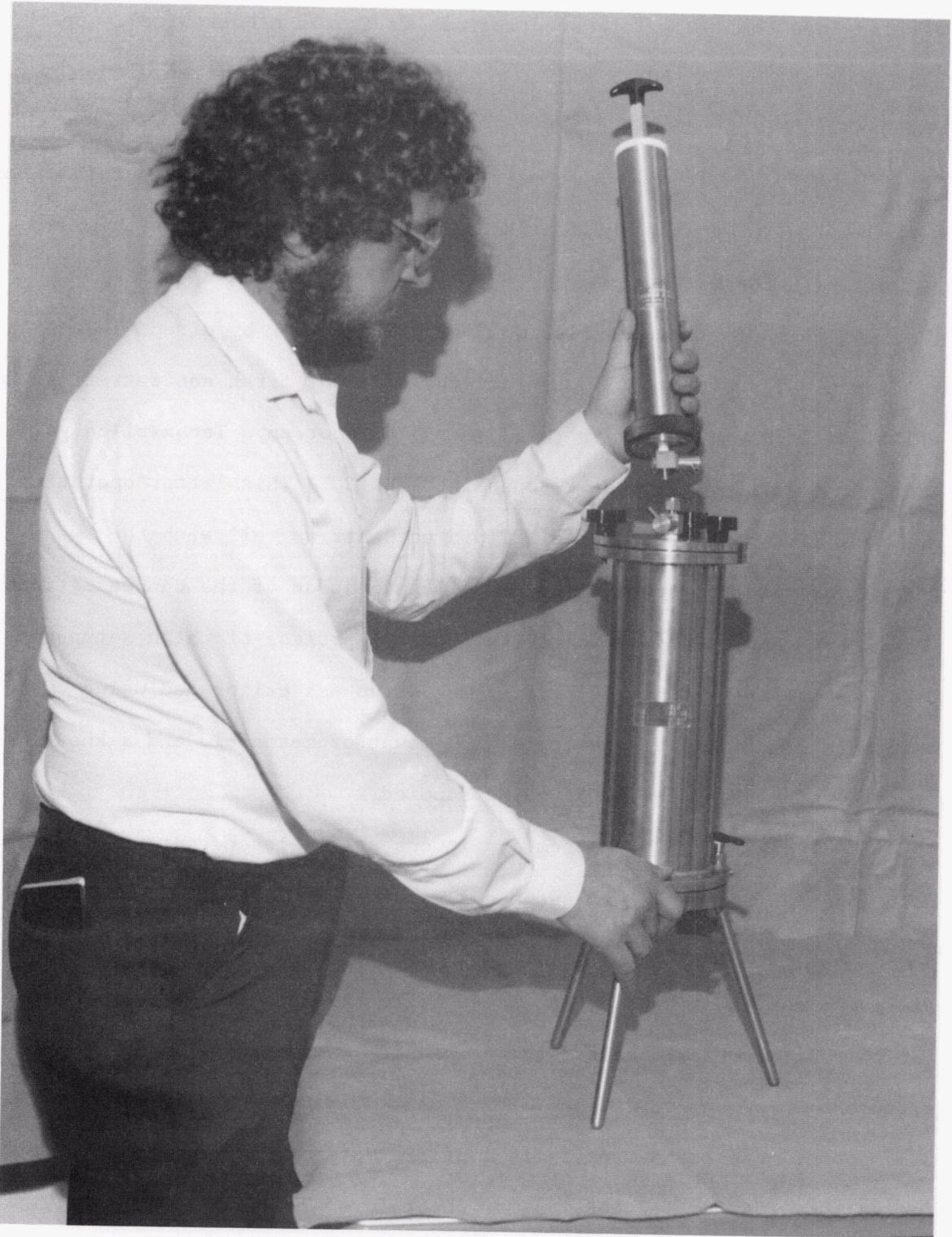


Fig. 15. Technician preparing to sample leachate.

carried into the ITD. This spectrograph is stored electronically on the hard disk of the IBM-PC-XT slaved to the ITD. The GC column used throughout this study was a 1/8-in.-OD by 8-ft-long SS tube packed with 1% SP-1000 on 60/80 Carbopak B, consistent with EPA Method 8010. This column works well with benzene and the halogenated compounds used in this study but not with the two ketones.

Analysis of liquid samples was performed either by direct injection of a small aliquot (e.g., 3  $\mu$ L) into the GC or by first concentrating the volatiles from a much larger (e.g., 5 mL) aliquot on a Tenax/silica gel trap and injecting what was trapped into the GC. This latter operation was performed by the LSC. The LSC did not work as well with the two ketones as with the other compounds. Quantitation of the concentrations in unknown samples was basically the same regardless of which setup was used, though the details differed. The setup was calibrated using solutions of deionized water, a small amount of methanol, and a known amount of the eight compounds being studied.

The leachates from the semicontinuous static leach test were analyzed using the LSC-GC-ITD. This setup has a detection limit of approximately 2  $\mu$ g/L for the two ketones and equal to or less than 1  $\mu$ g/L for the other six compounds. Calibration was accomplished by measuring the peak areas for the characteristic mass fragment of each compound for at least four different known concentrations. (The characteristic masses used for these 8 compounds were taken from Table 1 of EPA Method 8240 and consisted of 43 for acetone, 96 for 1,2-DCE, 83 for chloroform, 72 for MEK, 130 for TCE, 78 for benzene, 164 for PERC, and 112 for chlorobenzene.) Linear regression of the peak areas and known concentrations gave the necessary

correlation for interpolating an unknown concentration from the measured peak area. These regressions typically had correlation coefficients of 0.99. One of the advantages of using the ITD was that electronic storage of the spectra of the unknown concentration allowed calibration after measuring the unknown, if this was desired.

The setup used for gas analysis was direct injection into the GC-FID. This setup was calibrated with direct injection of 3  $\mu$ L of a liquid standard. In this case, the peak area generated at the retention time characteristic for the compound was divided by the total mass of the compound (typically 50 ng) in the injection to give the proportionality constant used to determine the unknown. This calibration was tested by injecting a second standard and comparing the measured amount against the known amount. If any of the eight compounds differed more than 15%, then the setup was recalibrated. PERC and chlorobenzene often gave variable results with this setup and required recalibration. Once the calibration was satisfactory, a much larger gas volume (0.5 to 5 mL) was injected directly into the GC. Since the setup was calibrated for mass, the mass was measured in the sample and the concentration calculated from the volume injected. The gas volume was selected to give a mass reasonably close to the calibration mass (~50 ng), though the different concentrations of the eight compounds in the gas prevented an ideal matchup.

An EPA contract laboratory is one that is qualified for analysis. The laboratory in question was the Analytical Chemistry Department within the Quality and Technical Services Division of the Oak Ridge Gaseous Diffusion Plant located at the K-25 Facility in Oak Ridge, Tennessee (and referred

to hereafter in this document as Analytical). Analytical was CLP qualified for both organic and inorganic analyses. The sludge samples, batch leachate samples, and EP-Toxicity and TCLP samples were submitted to Analytical for analysis by CLP and with accompanying chain-of-custody cards. Chain-of-custody was established for the large sample excavated at the RAFB site for delivery at Oak Ridge and finally for the subsamples taken for testing and analysis and to those samples submitted to Analytical.

In addition to normal CLP, arrangements were also made for (1) the spike recovery and matrix spike analyses to be performed using the batch leachate samples from this study (rather than some other samples also being analyzed as is allowed), (2) the batch leachates to be removed directly from the ZHE vessel to a SS syringe to a glass syringe and injected directly into Analytical's LSC without the leachate ever being exposed to air, and (3) batch leachate analysis to be performed quickly with a target of analysis on the same day as the sample is received. Aliquots of the semicontinuous leachates were transferred directly into glass syringes from the ZHE vessel and hence directly into the dedicated LSC-GC-ITD, also without exposure to air. Unlike the batch leachates, not all of the leachate was removed for analysis, only a small aliquot was removed for analysis and later replaced with fresh deionized water as leaching continued. The leachate was withdrawn and reinjected prior to subsampling to ensure that the leachate was mixed and that a representative aliquot was taken for analysis.

Although reanalysis was sometimes required for the CLP analysis of the batch leachates, especially the leachates for Vendor B's product, the

spike recovery and matrix spike analyses were usually within the prescribed limits for the leachates. Similarly, spike recoveries indicated no masking in the analysis of the semicontinuous leachates for Vendors A, C, and D by the dedicated LSC-GC-ITD. Spike recovery was a problem for the leachate from Vendor B's product on the dedicated LSC-GC-ITD. Although this problem was eventually solved, the first 3 weeks of data for this vendor were questionable and are not reported.

However, it was not unusual for the CLP-spike recovery to be out of compliance on the sludge analysis by Analytical. This is a common occurrence for soils and sludges, in general. Whenever this happens, the CLP procedure is to repeat the analysis, and if the problem reoccurs, the best of the two analyses is the one reported (best being defined as the one most in compliance with CLP).

The blanks (a ZHE vessel filled with deionized water at the beginning of leaching and being analyzed after 28 d) indicated that some cross contamination was occurring when the vessels were reused. This cross contamination had a negligible effect on the observed leachate concentrations and subsequent data interpretation due to the fact that the leachate concentrations were at least two orders of magnitude greater than the indicated contamination. This contamination would have to be controlled if waste forms with slower releases (e.g., a leachability index of 10 or higher) are tested using these procedures.

#### 4. RESULTS

Data obtained from the testing protocols described in Sect. 3 are presented. Interpretation and discussion of the data are contained in

this section, with the exception of the static leach test data, which are contained in Sect. 5.

#### 4.1 PHYSICAL PROPERTIES

Grout composition and selected physical property data are summarized in Tables 8 through 10. Given the flexibility of grout formulations, these properties, summarized in Table 11, can likely be adjusted to desired field-performance specifications, while retaining the immobilization potential of the waste forms. Each of the recipes formed cohesive monoliths, but the products of Vendors C and D contained high waste loadings and were physically weak, as compared with products of Vendors A and B. These physically weak waste forms are much more likely to crumble and flake than the stronger products of Vendors A and B. Thermal cycling of the waste forms in the freeze-thaw test had little noticeable effect on the products except for the loss of some surface material for Vendors C and D. Immersion of the waste forms in water for 90 d also had little noticeable effect. In general, the sludge can be formed into strong, seemingly impervious solids; but, as the sludge loading increases, the strength decreases and the physical appearance of the final waste form approaches that of the sludge.

##### 4.1.1 Rheology

All of the grouts were thick, sticky, and viscous. The shear stresses were much higher than usual for the shear rates tested in the Fann viscometer. These grouts could not be packed into the viscometer to give reproducible, usable rheology curves. Normally, such data are most useful for fluid grouts that will be pumped through closed conduits. Since grouts are non-Newtonian fluids, the shear rate/shear stress curve

Table 8. Grout compositions and properties for 2-in. cubes

	Vendor A	Vendor B	Vendor C	Vendor D
<u>Composition, wt %</u>				
Sludge	39.8	9.1	62.5	73.5
Water added	15.9	18.5	6.9	8.1
Dry blend	44.3	63.3	13.9	18.4
Liquid additive	n/a <sup>a</sup>	9.1	16.7 <sup>b</sup>	
<u>Properties over 28-d cure</u>				
Shrinkage, vol %	0.0	0.0	12.7	4.6
Density, g/cm <sup>3</sup>				
freshly mixed	1.61	1.62	1.22	1.39
after 28 d	1.61	1.62	1.40	1.46
Bleed water at 28 d	0	0	0	0
Penetration resistance after 28 d (psi)	>4000	>4000	0	490

<sup>a</sup>n/a = not applicable.

<sup>b</sup>Deionized water was substituted for Vendor C's liquid additive.

Table 9. Unconfined compressive strength results for the 28-d cures and freeze-thaw testing

Vendor	Unconfined compressive strength (psi)		Mass loss (%)
	28-d cure	After freeze-thaw	
A	881	830	1.6
	829	1207	1.6
	1095	1160	1.5
	av	935	1066
	std dev	115	168
B	2176	2694	0.4
	1856	2154	0.3
	1537	2789	0.3
	av	1856	2546
	std dev	261	280
C	4	0	16.0
	16	5	17.0
	16	17	7.3
	av	12	7
	std dev	6	7
D	62	55	1.5
	58	54	2.5
	60	64	3.5
	av	60	58
	std dev	2	4

Table 10. Unconfined compressive strengths after immersion for 90 d

Vendor	Unconfined compressive strength (psi)				SD <sup>a</sup>
	1	2	3	Average	
A	1534	2081	2025	1880	246
B	3685	3508	4019	3737	212
C	10	9	17	12	4
D	59	51	45	52	6

<sup>a</sup>SD = one standard deviation.

Table 11. Comparison of the unconfined compressive strengths for the 28-d cure, freeze-thaw test, and 90-d immersion test

Vendor	After 28-d cure	After freeze-thaw	After 90-d immersion
A	935	1066	1880
B	1856	2546	3737
C	12	7	12
D	60	58	52

generated by the Fann viscometer is required to give as much information as a single viscosity value for a Newtonian fluid (e.g., water). This rheology information can be used to estimate the energy required to pump the grout or the energy required to restart pumping if the grout is allowed to set idle inside pipes or conduits for a few minutes during process interruptions. The grouts used in this study are much too thick to be handled in this manner. The strong mechanical systems (e.g., screw mixer/conveyors, backhoes) used for mixing and transporting sludges and solids must be used with these types of grouts rather than, for example, pumps, pipes, or slurry mixers. As mentioned earlier, these grouts probably can be tailored to be more fluid while retaining their primary immobilization capability, but no rheology criteria have been established for the grout formulations as yet. Once an implementation technique has been selected, then the importance of rheology criteria and the need for tailoring will be known.

#### 4.1.2 Shrinkage

Products from two of the vendors, C and D, were observed to shrink inside the 2-in. curing molds. This shrinkage is speculated to be caused by the high sludge loading (62.5 wt % and 73.5 wt %, respectively) and low water content of these grouts. The cement powders apparently dehydrated the sludge, possibly causing the observed shrinkage. After curing for 28 d, the dimensions of the cubes were measured and compared with the mold dimensions (taken to be the initial dimensions of the grout) to obtain the volume shrinkages listed in Table 8. Such shrinkage was not observed for the leach/extraction samples prepared using the same formulations, but cured in covered SS molds sealed inside a SS pipe. Apparently, the

shrinkage observed in the 2-in. cubes was a combination of the high sludge loading and the exposed surface during cure (although curing was done inside a high-humidity cabinet).

#### 4.1.3 Density

The grout densities are usually measured with a mud balance, but these grouts were too thick to use with this technique. The densities were obtained by weighing the 2-in. cubes after curing for 28 d and using the mold volume (freshly mixed density) and the measured dimensions after 28 d.

In the past, some grouts have lost as much as 10 wt % during a 28-d cure, even in the humid curing environment. These were fluid grouts (i.e., excess water), and having more water than needed for the cement reactions may explain the weight loss (i.e., the exothermic reactions may have driven off some water which was not replaced, even in the humid environment). The observed shrinkage of these grouts may mean that they had enough affinity for water that they gained water during the 28-d cure (i.e., the density may have increased over 28 d not only from volume shrinkage, but also from mass gain). In other words, the mass of the cubes may have changed over 28 d, but the densities listed in Table 8 are accurate for a 28-d cure and are representative for the freshly mixed grouts.

#### 4.1.4 Bleed Water

Although some of the grouts looked moist for a day or so after mixing, none had any problems with bleed water (Table 8). A typical criterion for even a watery grout is 0 vol % bleed water after 28 d. None of the current recipes for these four vendors will have any trouble

meeting this or more stringent criteria. Tailoring the grouts to make them pumpable for in situ implementation may cause bleed water, so this property must be checked again if the grouts are to be fluid.

#### 4.1.5 Penetration Resistance

The penetration resistance is roughly 10 to 20 times the compressive strength of the grouts and is used as an objective measure of when the grout sets. Initial set is defined as a penetration resistance of 500 psi (usually achieved in a few days) and final set as greater than 4000 psi (usually achieved in a week or two). Some of the waste loadings were so high that set as defined above was doubtful, even after 28 d. As suspected, the two weaker products with high waste loadings (from Vendors C and D) did not achieve the defined initial set, much less the final set (Table 8). If this property is deemed important, set, as defined above, can likely be achieved for these two products by a lower waste loading, higher blend content, and/or more water.

#### 4.1.6 28-d Compressive Strength

The unconfined compressive strength of the grouts is a measure of its load-bearing capabilities. Generally, waste products do not have to bear heavy loads, so compressive strengths too weak for construction concretes may be acceptable for waste products. Regulatory agencies tend to have little or no criteria for compressive strengths (e.g., the NRC has a requirement of only 60 psi for solidified low-level radioactive waste).<sup>20</sup> Usually, if the cementitious waste forms set (i.e., harden) and form a monolith, the compressive strength is about an order of magnitude above this value (i.e., ~500 psi). The recipes supplied by three of the

four vendors do not emphasize the physical properties of the final product, and no criteria were placed on these properties. The purpose of this phase of the project was to measure the physical properties of recipes the vendors supplied for controlling VOC release from the RAFB sludge. Any of these grouts can be tailored to meet physical property criteria, including fluid properties, if they can be demonstrated to control VOC release. The high waste loadings for Vendors C and D resulted in the low compressive strengths reported in Table 9; Vendors A and B's products had compressive strengths of equal to or greater than 900 psi.

#### 4.1.7 Freeze-Thaw

Freeze-thaw testing is a measure of the capability of a waste form to withstand the natural temperature variation at a site. The high and low temperatures used (50°C and -30°C) were based on the 39-year records for Macon, Georgia. These records were for aboveground air temperatures, so the results are a measure of the durability of the waste forms for aboveground storage. Temperatures below ground will not vary over as wide a range; thus, using 50°C and -30°C was conservative for in situ stabilization/solidification or final disposal underground. After being subjected to this thermal cycling, the samples were subjectively evaluated for degradation and were submitted for measurement of their unconfined compressive strengths. A significant decrease in compressive strengths from those measured after curing 28 d would have indicated a potential problem in the long-term durability of these products. Since cementitious products continue to cure after 28 d, an increase during the 8- to 10-d freeze-thaw testing would not have been surprising.

Little difference was noted by visual examination or for the compressive strengths listed in Table 9 before and after the freeze-thaw test for any of the samples. Of course, Vendors C and D's samples were weak both before and after, but the samples did hold together and did not crumble during the freeze-thaw cycling. However, the results for Vendor C are suspect due to the sample's low initial strength and the data scatter in measurements taken after the freeze-thaw cycle. Products from Vendors A and B experienced little weight loss during the test, and the weight loss reported for products from Vendors C and D may be explained by the loss of some surface material (some loose material was noted in the bottom of the container after the test). The cube dimensions were essentially the same before and after the test, indicating no shrinkage occurred for any products. Also, no free water was observed in the containers after testing. Similar behavior was observed for the immersion resistance test (Table 10). Table 11 summarizes all of the measured compressive strengths.

#### 4.2 LEACHABILITY

Standard deviations of 10 to 20% are normal for remeasurement of organic concentrations at low concentrations in clean water. The errors involved in measuring sludge concentrations, gas concentrations, and water concentrations on different days and then comparing these to each other are even higher. Taken in this context, a mass balance of 60 to 114%, as was the case in the verification tests on the preparation of grout samples, was acceptable using these analytical techniques. Basically, these analytical techniques have been pushed to their limit in trying to measure mass-transfer parameters using standard procedures. These

techniques are typically used to ascertain the rough level of contamination at a site, and such large standard deviations are acceptable. However, for deducing mass-transfer parameters, it is necessary to detect the changes in a leachate concentration over a relatively (i.e., relative to the times for site closure and risk assessment) short time interval.

For the most part, the masses estimated for the static leach test were fairly self-consistent in comparing the known amount spiked, the measured amount spiked, the amount estimated remaining after mixing into a grout and curing, and the amount extracted or estimated extractable (in static leaching). The samples prepared for the EP-Toxicity and TCLP tests were not as self-consistent, in that, the amounts measured in the spiked sludge exceeded the amount added in the spike in many cases. Nevertheless, the sludge analyses were reported and used as the basis for estimating the VOC retained in the grout samples, just as was done for the static leach samples.

With this level of uncertainty, it is not surprising that, in a few cases, more was leached than was estimated retained in the sample. Nevertheless, the trend of leaching was apparent in most cases.

#### 4.2.1 Sample Preparation

Samples for use in the static leach testing were prepared as described in Sect. 3.2.4. The VOC content of the spiked waste used in the sample preparation step is shown in Table 12, as an average from three analyses. Note that these concentrations are significantly above the reported site maximums shown in Table 1. Data on the VOC losses (assuming the average starting concentration shown in Table 12), measured at each of

Table 12. Measured concentrations of the sludge spiked  
for the static leaching tests

Component	Samples			Average (ppm)	Standard deviation (ppm)	Standard deviation (%)
	1 (ppm)	2 (ppm)	3 (ppm)			
<b>Vendor A</b>						
Acetone	7.9	10	26	15	8	55
1,2-DCE	920	760	1100	927	139	15
Chloroform	1000	900	1200	1033	125	12
MEK	350	220	190	253	69	27
TCE	600	570	700	623	56	9
Benzene	780	670	910	787	98	12
PERC	1100	810	980	963	119	12
Chlorobenzene	530	500	620	550	51	9
<b>Vendor B</b>						
Acetone	90	150	130	123	25	20
1,2-DCE	170	150	190	170	16	10
Chloroform	190	170	210	190	16	9
MEK	130	130	150	137	9	7
TCE	210	180	190	193	12	6
Benzene	180	150	190	173	17	10
PERC	670	550	390	537	115	21
Chlorobenzene	620	510	510	547	52	9
<b>Vendor C</b>						
Acetone	210	230	230	223	9	4
1,2-DCE	55	710	690	485	304	63
Chloroform	58	430	450	313	180	58
MEK	410	370	510	430	59	14
TCE	51	260	240	184	94	51
Benzene	62	460	460	327	188	57
PERC	510	1000	790	767	201	26
Chlorobenzene	130	260	270	220	64	29
<b>Vendor D</b>						
Acetone	350	220	60	210	119	56
1,2-DCE	1000	1100	760	953	143	15
Chloroform	1300	1200	950	1150	147	13
MEK	190	360	220	257	74	29
TCE	680	560	480	573	82	14
Benzene	920	840	700	820	91	11
PERC	1200	860	600	887	246	28
Chlorobenzene	520	480	430	477	37	8

Table 13. Summary of VOC retention during mixing and curing of the static leach samples reduced to the same basis (per gram of grout)

Component	Reduced mass ( $\mu\text{g/g}$ grout)				Calculated retained (%)
	Spiked sludge	Glove box air	Curing pipe air	Calculated retained	
<b>Vendor A</b>					
Acetone	7	12	0.02	-5	-80
1,2-DCE	415	137	1.26	277	67
Chloroform	463	111	0.02	352	76
MEK	114	31	0.03	83	73
TCE	279	53	0.22	226	81
Benzene	353	82	0.40	270	77
PERC	432	20	0.07	412	95
Chlorobenzene	247	13	0.03	233	95
<b>Vendor B</b>					
Acetone	13	3	0.0025	9	75
1,2-DCE	17	10	0.0007	8	44
Chloroform	19	6	0.0021	13	66
MEK	14	3	0.0002	11	76
TCE	20	7	0.0023	13	64
Benzene	18	6	0.0026	12	67
PERC	54	15	0.0048	39	72
Chlorobenzene	55	5	0.0011	50	90
<b>Vendor C</b>					
Acetone	151	3	0.001	148	98
1,2-DCE	329	83	0.061	245	75
Chloroform	212	67	0.053	144	68
MEK	291	5	0.001	286	98
TCE	124	24	0.011	101	81
Benzene	222	47	0.038	174	79
PERC	519	9	0.003	510	98
Chlorobenzene	149	27	0.005	122	82
<b>Vendor D</b>					
Acetone	171	63	0.03	108	63
1,2-DCE	775	292	1.61	482	62
Chloroform	935	225	0.38	710	76
MEK	209	63	0.03	146	70
TCE	466	74	0.21	392	84
Benzene	667	187	0.48	480	72
PERC	721	19	0.07	702	97
Chlorobenzene	388	18	0.12	370	95

the subsequent sample preparation steps (i.e., mixing and curing) on a per-gram-of-grout-product basis, are shown in Table 13. The source term, or mass, of individual VOCs contained in the grout leach samples was determined by subtracting the measured losses from the mass of the VOC measured in the spiked waste and is also shown in Table 13. These source-term values were used in the subsequent data reduction on the leach tests (see Sect. 5.5) with the exception of acetone for Vendor A (which had a calculated retention of less than 0%). In this case, the source term was considered unknown and was subsequently calculated by the computer program used in the data reduction.

Applying the calculated VOC retentions to the spiked waste concentrations allows the calculation of the VOC content of the waste contained in the grout samples. A comparison between these calculated concentrations and the reported site maximums is shown in Table 14.

#### 4.2.2 Static Leach Data

Tables 15 through 18 list the mass measured in the leachate with time for each VOC of interest for Vendors A, B, C, and D, respectively. These analyses were generated from the semicontinuous leach testing analysis described in Sect. 3.2.4.8. It is noted that there is significant variability with respect to these data. For example, cumulative mass leached should continuously increase until saturation or equilibrium is achieved, at which point it will remain constant. As seen in Tables 15 through 18, this is not always the case. This variability is believed to be because of the inadequacies of the standard analytical protocols upon application to this complex matrix.

Table 14. Comparison of the equivalent sludge VOC content inside the cured grout to the site maximum VOC content and estimation of the mass available for leaching from the static leach samples

Component	Cured grout (ppm)	Calculated concentration in sludge (ppm)	Maximum site concentration (ppm)	Mass in sample (mg)
Vendor A	Average cured grout sample mass = 87.02 g Estimated sludge content of cured grout = 41 wt %			
Acetone	a	a	9	a
1,2-DCE	277	680	100	24.1
Chloroform	352	865	17	30.6
MEK	83	204	4	7.2
TCE	226	555	130	19.7
Benzene	270	663	3	23.5
PERC	412	1012	59	35.9
Chlorobenzene	233	572	20	20.3
Vendor B	Average cured grout sample mass = 85.68 g Estimated sludge content of cured grout = 10.2 wt %			
Acetone	9	89	9	0.8
1,2-DCE	8	79	100	0.7
Chloroform	13	128	17	1.1
MEK	11	108	4	0.9
TCE	13	128	130	1.1
Benzene	12	118	3	1.0
PERC	39	384	59	3.3
Chlorobenzene	50	492	20	4.3
Vendor C	Average cured grout sample mass = 68.14 g Estimated sludge content of cured grout = 62 wt %			
Acetone	148	240	9	10
1,2-DCE	245	397	100	17
Chloroform	144	233	17	10
MEK	286	464	4	19
TCE	101	164	130	7
Benzene	174	282	3	12
PERC	510	827	59	35
Chlorobenzene	122	198	20	8

Table 14. (continued)

Component	Cured grout (ppm)	Calculated concentration in sludge (ppm)	Maximum site concentration (ppm)	Mass in sample (mg)
Vendor D	Average cured grout sample mass = 75.72 g Estimated sludge content of cured grout = 75 wt %			
Acetone	108	144	9	8
1,2-DCE	482	644	100	36
Chloroform	710	948	17	54
MEK	146	195	4	11
TGE	392	524	130	30
Benzene	480	641	3	36
PERC	702	938	59	53
Chlorobenzene	370	494	20	28

<sup>a</sup>The amount measured in the spiked sludge was less than that estimated lost during mixing and curing. Consequently, the amount retained in the cured grout is unknown.

Table 15. Mass measured in leachate for the samples monitored with time in the static leach test for Vendor A

Component	Mass measured in leachate at the indicated nominal time intervals (mg)					
	1 d	3 d	7 d	14 d	28 d	51 d
A1						
Acetone	1.0	0.5	4.0	3.1	14.9	4.5
1,2-DCE	2.8	0.5	6.3	8.0	22.6	9.7
Chloroform	0.2	0.1	0.0	0.2	4.1	0.6
MEK	2.0	0.5	5.2	7.6	12.6	4.2
TCE	1.2	0.2	2.3	2.5	7.0	4.1
Benzene	2.6	0.4	5.2	6.6	17.3	9.3
PERC	0.4	0.6	0.4	0.6	2.6	1.2
Chlorobenzene	0.5	1.1	1.0	1.2	4.0	2.0
A2						
Acetone	0.6	4.2	4.3	2.7	10.2	5.2
1,2-DCE	2.3	5.4	6.8	12.4	20.0	10.1
Chloroform	0.2	0.1	0.0	0.2	4.4	0.6
MEK	1.5	5.2	5.4	9.3	9.0	5.0
TCE	1.0	2.1	2.7	4.0	6.6	4.2
Benzene	2.2	4.6	5.9	10.6	15.4	9.7
PERC	0.4	0.7	0.6	1.0	2.6	1.2
Chlorobenzene	0.5	1.2	1.3	1.9	3.8	2.0
A3						
Acetone	0.3	4.6	4.2	2.7	15.0	4.5
1,2-DCE	2.1	6.6	7.0	12.3	21.6	9.6
Chloroform	0.3	0.1	0.0	0.2	4.4	0.6
MEK	1.3	5.8	5.0	9.1	13.1	4.3
TCE	0.0	2.6	2.8	4.0	6.7	3.8
Benzene	2.1	5.5	5.8	10.4	16.1	8.8
PERC	0.3	0.6	0.6	1.0	2.6	1.2
Chlorobenzene	0.4	1.0	1.3	1.9	3.8	1.9

Table 16. Mass measured in leachate for the samples monitored with time in the static leach test for Vendor B

Component	Mass measured in leachate at the indicated nominal time intervals (mg)			
	21 d	27 d	35 d	63 d
B1				
Acetone	0.11	0.37	6.02	0.50
1,2-DCE	0.13	0.30	1.88	0.89
Chloroform	0.00	0.27	1.71	0.69
MEK	0.21	0.37	2.06	0.47
TCE	0.05	0.22	1.04	0.72
Benzene	0.13	0.28	1.56	0.77
PERC	0.14	0.28	0.70	0.67
Chlorobenzene	0.27	0.26	1.77	0.45
B2				
Acetone	0.41	0.73	1.79	0.68
1,2-DCE	0.15	0.38	1.88	0.89
Chloroform	0.02	0.35	1.72	0.69
MEK	0.71	0.32	1.76	0.52
TCE	0.13	0.29	1.06	0.72
Benzene	0.35	0.37	1.58	0.79
PERC	0.16	0.41	0.74	0.67
Chlorobenzene	0.31	0.41	1.82	0.45
B3				
Acetone	0.44	0.60	1.73	0.95
1,2-DCE	0.05	0.37	1.88	0.89
Chloroform	0.00	0.34	1.71	0.69
MEK	0.26	0.20	2.06	0.64
TCE	0.04	0.27	1.05	0.72
Benzene	0.09	0.35	1.57	0.78
PERC	0.12	0.33	0.88	0.71
Chlorobenzene	0.21	0.36	1.87	0.46

Table 17. Mass measured in leachate for the samples monitored with time in the static leach test for Vendor C

Component	Mass measured in leachate at the indicated nominal time intervals (mg)					
	1 d	3 d	7 d	14 d	28 d	35 d
C1						
Acetone	0.5	0.0	1.0	0.0	0.0	0.2
1,2-DCE	4.7	8.0	10.0	9.4	4.5	9.1
Chloroform	3.9	4.9	6.1	6.4	2.9	3.2
MEK	0.0	0.0	1.5	2.9	2.8	0.5
TCE	1.1	2.6	3.4	4.0	1.4	3.4
Benzene	2.6	5.3	7.3	6.9	3.0	7.0
PERC	0.2	1.4	0.8	1.8	2.4	0.9
Chlorobenzene	0.5	1.5	2.3	4.4	3.3	1.5
C2						
Acetone	0.0	0.0	1.0	0.0	0.0	0.2
1,2-DCE	1.8	4.5	5.6	6.2	5.6	5.1
Chloroform	2.1	3.0	3.9	5.4	3.1	2.0
MEK	0.0	0.0	1.4	2.8	2.3	0.5
TCE	0.5	1.8	2.6	3.4	2.7	2.8
Benzene	1.3	3.5	5.3	5.1	5.3	5.1
PERC	0.1	1.3	0.8	1.7	1.1	1.0
Chlorobenzene	0.3	1.2	2.2	4.3	3.5	1.5
C3						
Acetone	0.0	0.0	1.3	0.0	0.0	0.2
1,2-DCE	5.8	6.8	7.6	16.6	7.3	6.6
Chloroform	5.8	4.8	5.5	9.9	4.2	3.1
MEK	0.0	0.0	1.5	2.9	2.9	0.8
TCE	1.7	2.5	3.0	7.2	2.8	2.9
Benzene	3.7	4.9	6.2	13.9	6.1	5.7
PERC	0.4	1.4	0.8	2.3	1.3	0.9
Chlorobenzene	0.7	1.5	2.3	5.3	3.4	1.4

Table 18. Mass measured in leachate for the samples monitored with time in the static leach test for Vendor D

Component	Mass measured in leachate at the indicated nominal time intervals (mg)					
	1 d	3 d	7 d	14 d	28 d	60 d
D1						
Acetone	4.0	6.1	1.3	9.2	21.9	16.7
1,2-DCE	3.7	16.5	11.3	17.8	29.0	19.1
Chloroform	2.1	10.6	5.1	5.7	5.2	1.5
MEK	7.2	5.8	4.4	9.6	24.2	11.5
TCE	1.4	8.2	3.3	4.5	8.1	7.5
Benzene	2.9	14.2	9.2	13.2	23.3	16.7
PERC	0.5	5.3	0.9	0.1	1.6	1.4
Chlorobenzene	0.7	6.3	1.1	1.9	4.2	2.8
D2						
Acetone	3.9	3.4	1.3	7.8	18.1	12.8
1,2-DCE	4.0	9.4	11.4	17.3	25.4	19.8
Chloroform	2.3	5.1	5.6	6.6	5.6	1.9
MEK	4.1	5.4	3.8	8.1	19.1	8.7
TCE	1.2	2.9	3.5	4.8	7.3	8.1
Benzene	3.0	7.1	0.1	12.8	20.3	17.1
PERC	0.3	0.6	1.1	0.2	1.6	1.5
Chlorobenzene	0.5	1.1	0.0	2.2	3.9	2.8
D3						
Acetone	4.4	6.2	0.1	9.1	22.7	15.5
1,2-DCE	5.0	11.2	5.6	20.4	29.2	21.5
Chloroform	2.7	5.5	2.8	7.4	5.7	1.9
MEK	4.8	6.5	0.4	9.3	24.3	11.1
TCE	1.5	3.2	2.0	5.7	7.7	7.9
Benzene	3.7	8.0	4.7	14.6	21.8	18.1
PERC	0.3	0.6	0.8	0.4	1.5	1.4
Chlorobenzene	0.5	1.1	0.7	2.4	3.9	2.9

Table 19 lists the pH and electrical conductivities measured for the leachates that had a separate sample for each time interval (batch analysis described in Sect. 3.2.4.8). The samples referred to as BLK are blanks that were allowed to remain static for 28 d with no grout sample contained in the deionized water. Table 20 lists the mass measured in the leachate with times for each VOC of interest for this same set of samples. Discussion and interpretation of these data are presented in Sect. 5.

#### 4.3 REGULATORY LEACH TESTING

##### 4.3.1 Sample Preparation

Grout samples submitted for EP-Toxicity and TCLP testing were prepared as described in Sect. 3.2.4. Whereas, the static leach samples were cast as flat disks (6.2-cm diam x 1.6-cm ht) inside of SS rings, these samples were cast as cylinders (3.3-cm diam x 7.1-cm ht) as prescribed in the EP-Toxicity procedures.<sup>20, 23</sup> Table 21 lists the VOC concentrations analyzed in the spiked sludge used to prepare these samples. The target spike for these samples was quite different than for the static leach samples. Whereas, the spike for static leaching was intended to ensure detectable VOC concentrations at about the same level in the leachates, the spike for these samples was intended to be representative of the maximum site concentration for each species.

Table 22 summarizes the VOC losses during preparation of these samples and the quantity calculated left in the samples (by difference between average quantity measured in the spiked sludge and the quantity measured in the glovebox gas and curing pipe gas). The VOC quantities listed in this table were reduced to the same basis (per gram of grout) for ease of comparison.

Table 19. Leachate pH and conductivity for the samples leached using the batch analyses (separate sample for each time interval)

ID	Nominal leach interval (d)	Leachate pH	Leachate electrical conductivity ( $\mu\text{mho/cm}$ )
<b>Vendor A</b>			
A4	1	11.3	870
A5	3	11.6	1617
A6	7	11.8	2390
A7	14	12.1	2680
A8	28	11.9	2290
A9	BLK <sup>a</sup>	8.4	17
<b>Vendor B</b>			
B4	1	11.6	1079
B5	3	11.6	1770
B6	7	11.9	3070
B7	14	12.0	3530
B8	28	12.1	3930
B9	BLK	8.8	17
<b>Vendor C</b>			
C4	1	11.0	790
C5	3	11.3	1074
C6	7	11.5	1259
C7	14	11.6	1504
C8	28	11.4	1535
C9	BLK	8.4	16
<b>Vendor D</b>			
D4	1	11.0	594
D5	3	11.3	1207
D6	7	11.6	1970
D7	14	11.7	2250
D8	28	11.8	2090
D9	BLK	8.7	21

<sup>a</sup>BLK = blanks that were allowed to remain static for 28 d with no grout sample contained in the deionized water.

Table 20. Mass measured in the leachate with time in the batch leach test

Component	Sample time	Mass measured in the leachate ( $\mu\text{g}$ )				
		No. 4 1 d	No. 5 3 d	No. 6 7 d	No. 7 14 d	No. 8 28 d
<b>Vendor A</b>						
Acetone		1930	0	6633	4342	3317
1,2-DCE		2291	157	14472	9045	13266
Chloroform		27	55	157	157	45
MEK		2472	10	5186	4583	4100
TCE		844	1447	3497	3075	5005
Benzene		2231	3015	10854	7839	12060
PERC		271	458	844	905	1266
Chlorobenzene		537	917	1628	1508	2533
<b>Vendor B</b>						
Acetone		37	78	235	1085	1025
1,2-DCE		2	4	26	0	39
Chloroform		5	6	20	17	21
MEK		10	16	53	0	0
TCE		12	17	49	84	78
Benzene		17	27	84	157	121
PERC		25	29	90	139	145
Chlorobenzene		36	48	127	199	169
<b>Vendor C</b>						
Acetone		519	223	392	235	259
1,2-DCE		3618	7839	9045	10251	8442
Chloroform		2171	5548	5608	5427	4703
MEK		295	259	428	0	223
TCE		1206	2774	3256	4161	3256
Benzene		2412	6030	6633	8442	7839
PERC		295	573	603	784	663
Chlorobenzene		603	1327	1447	1869	1749
<b>Vendor D</b>						
Acetone		2714	11457	10251	10854	6633
1,2-DCE		2111	5367	18090	24120	22914
Chloroform		1085	3256	5789	7236	4945
MEK		3377	7236	10251	10854	5427
TCE		1085	1990	3075	6633	8442
Benzene		1628	4221	13869	19899	18090
PERC		247	905	488	1749	1869
Chlorobenzene		603	1387	1568	3075	3980

Table 21. Measured concentrations of the sludge spiked for the EP-Toxicity/TCLP tests

Component	Samples			Average (ppm)	Standard deviation (ppm)	Standard deviation (%)
	1 (ppm)	2 (ppm)	3 (ppm)			
<b>Vendor A</b>						
Acetone	43	210	190	148	74	50
1,2-DCE	280	570	520	457	127	28
Chloroform	30	31	33	31	1	4
MEK	800	760	730	763	29	4
TCE	13	160	130	101	63	63
Benzene	3.7	8	5.5	6	2	31
PERC	280	280	140	233	66	28
Chlorobenzene	46	53	44	48	4	8
<b>Vendor B</b>						
Acetone	140	200	200	180	28	16
1,2-DCE	340	300	300	313	19	6
Chloroform	31	28	27	29	2	6
MEK	25	240	330	198	128	65
TCE	210	180	150	180	24	14
Benzene	5.7	5.8	5.2	6	0	5
PERC	190	220	180	197	17	9
Chlorobenzene	38	43	33	38	4	11
<b>Vendor C</b>						
Acetone	200	200	150	183	24	13
1,2-DCE	270	370	270	303	47	16
Chloroform	27	29	26	27	1	5
MEK	25	580	25	210	262	125
TCE	160	210	180	183	21	11
Benzene	4.9	5.7	5.6	5	0	7
PERC	110	79	130	106	21	20
Chlorobenzene	30	37	40	36	4	12
<b>Vendor D</b>						
Acetone	140	200	150	163	26	16
1,2-DCE	370	370	350	363	9	3
Chloroform	31	26	25	27	3	10
MEK	370	860	680	637	202	32
TCE	98	120	92	103	12	12
Benzene	8.6	7.9	7.4	8	0	6
PERC	200	190	120	170	36	21
Chlorobenzene	41	43	36	40	3	7

Table 22. Summary of VOC retention during mixing and curing of the EP-Toxicity/TCLP samples, reduced to the same basis (per gram of grout)

Component	Reduced mass (mg/kg grout)				
	Spiked sludge	Glovebox air	Curing pipe air	Calculated retained	Calculated retained
<b>Vendor A</b>					
Acetone	70	2	0.02	68	98%
1,2-DCE	216	69	1.26	146	68%
Chloroform	15	2	0.02	13	85%
MEK	361	1	0.03	360	100%
TCE	48	20	0.22	28	58%
Benzene	3	0	0.40	2	67%
PERC	110	4	0.07	107	97%
Chlorobenzene	23	1	0.03	21	94%
<b>Vendor B</b>					
Acetone	20	2	0.02	18	92%
1,2-DCE	35	8	1.26	25	73%
Chloroform	3	1	0.02	2	74%
MEK	22	0	0.03	22	99%
TCE	20	9	0.22	10	52%
Benzene	1	0	0.40	0	36%
PERC	22	3	0.07	19	88%
Chlorobenzene	4	0	0.03	4	93%
<b>Vendor C</b>					
Acetone	124	1	0.02	124	99%
1,2-DCE	206	45	1.26	160	78%
Chloroform	19	2	0.02	16	89%
MEK	142	0	0.03	142	100%
TCE	124	26	0.22	98	79%
Benzene	4	0	0.40	3	76%
PERC	72	5	0.07	67	93%
Chlorobenzene	24	2	0.03	23	93%
<b>Vendor D</b>					
Acetone	134	3	0.02	131	98%
1,2-DCE	298	84	1.26	212	71%
Chloroform	22	3	0.02	19	87%
MEK	522	2	0.03	520	100%
TCE	85	29	0.22	56	66%
Benzene	7	1	0.40	5	83%
PERC	139	4	0.07	135	97%
Chlorobenzene	33	2	0.03	31	95%

Finally, Table 23 compares the equivalent VOC concentration of the sludge inside the cured grout with the reported site maximums. The equivalent VOC concentration of the sludge inside the cured grout was calculated by dividing the estimated VOC concentration retained in the grout by the estimated weight fraction of spiked sludge in the grout. The logic behind this comparison is to note what sludge concentration, corrected for preparation losses, led to the observed extract concentrations (Tables 24 and 25) and how this concentration compares to the reported site maximums. Note that only TCE for Vendors A, B, and D does not exceed the reported site maximum in Table 23. In addition, Table 23 lists the estimated masses retained in the grout samples prior to extraction.

#### 4.3.2 Regulatory Leach Data

Table 24 lists the EP-Toxicity extract concentrations. The EP-Toxicity procedure identifies eight metals and six pesticides/herbicides as the constituents to be analyzed in the extract for classification of whether a waste is hazardous. Since the sludge characterization (Table 2) indicated the six pesticides/herbicides were not present, the extracts were analyzed for the metals but not the pesticides/herbicides. Although the EP-Toxicity procedure does not call for any further organic analysis, the base, neutral, and acid organic compounds (BNAs) were analyzed in the extracts, and these results were also listed in Table 24 and compared to the TCLP limits for these compounds. Neither the EP-Toxicity limits for metals nor the TCLP limits for BNAs were exceeded in the EP-Toxicity extracts.

Table 23. Comparison of the equivalent sludge VOC content inside the cured grout to the site maximum VOC content and estimation of the mass available for extracting from the EP-Toxicity/TCLP samples

Component	Cured grout (ppm)	Calculated concentration in sludge (ppm)	Maximum site concentration (ppm)	Mass in sample (mg)
Vendor A	Average cured grout sample mass = 110.2 g Estimated sludge content of cured grout = 41 wt %			
Acetone	68	167	9	7.5
1,2-DCE	146	358	100	16.1
Chloroform	13	32	17	1.4
MEK	360	882	4	39.7
TCE	28	69	130	3.1
Benzene	2	5	3	0.2
PERC	107	262	59	11.8
Chlorobenzene	21	51	20	2.3
Vendor B	Average cured grout sample mass = 111.25 g Estimated sludge content of cured grout = 9.2 wt %			
Acetone	18	195	9	2.0
1,2-DCE	25	271	100	2.8
Chloroform	2	22	17	0.2
MEK	22	238	4	2.4
TCE	10	108	130	1.1
Benzene	0.4	4	3	0.0
PERC	19	206	59	2.1
Chlorobenzene	4	43	20	0.4
Vendor C	Average cured grout sample mass = 69.12 g Estimated sludge content of cured grout = 60 wt %			
Acetone	124	207	9	8.6
1,2-DCE	160	268	100	11.1
Chloroform	16	27	17	1.1
MEK	142	238	4	9.8
TCE	98	164	130	6.8
Benzene	3	5	3	0.2
PERC	67	112	59	4.6
Chlorobenzene	23	38	20	1.6

Table 23. (continued)

Component	Cured grout (ppm)	Calculated concentration in sludge (ppm)	Maximum site concentration (ppm)	Mass in sample (mg)
Vendor D	Average cured grout sample mass = 95.22 g Estimated sludge content of cured grout = 72 wt %			
Acetone	131	181	9	12.5
1,2-DCE	212	293	100	20.2
Chloroform	19	26	17	1.8
MEK	520	719	4	49.5
TCE	56	77	130	5.3
Benzene	5	7	3	0.5
PERC	135	187	59	12.9
Chlorobenzene	31	43	20	3.0

Table 24. Concentrations measured in the extracts for the EP-Toxicity test (mg/L)

Component	Vendor A	Vendor B	Vendor C	Vendor D	TCLP Limit
<u>Metals</u>					
Arsenic	<0.0025	<0.0025	<0.0025	<0.0025	5.0
Barium	0.088	0.113	0.244	0.128	100.
Cadmium	<0.0044	<0.0044	<0.0044	0.0056	1.0
Chromium	0.025	0.012	0.088	0.027	5.0
Lead	0.018	0.011	0.011	0.013	5.0
Mercury	<0.0002	<0.0002	<0.0002	<0.0002	0.2
Nickel	0.135	<0.0093	0.086	0.049	<i>a</i>
Selenium	<0.0021	<0.0021	<0.0021	<0.0021	1.0
Silver	<0.0044	<0.0044	<0.0044	<0.0044	5.0
<u>Base organic, neutral organic, and acid organic compounds</u>					
1,2,4-Trichlorobenzene	<0.010	<0.010	<0.010	<0.010	<i>a</i>
1,2-Dichlorobenzene	0.13	0.026	0.11	0.002	4.3
1,3-Dichlorobenzene	0.003	<0.010	0.006	0.006	<i>a</i>
1,4-Dichlorobenzene	0.043	0.004	0.059	0.066	10.8
2,4,5-Trichlorophenol	<0.050	<0.050	<0.050	<0.050	5.8
2,4,6-Trichlorophenol	<0.010	<0.010	<0.010	<0.010	0.3
2,4-Dimethylphenol	<0.010	<0.010	0.20	0.29	<i>a</i>
2,4-Dinitrotoluene	<0.010	<0.010	<0.010	<0.010	0.13
2-Methylnaphthalene	0.002	<0.010	0.007	0.004	<i>a</i>
2-Methylphenol	<0.010	<0.010	0.025	0.23	<i>a</i>
4-Methylphenol	0.016	<0.010	0.16	<0.010	<i>a</i>
Benzyl alcohol	<0.010	<0.010	0.006	<0.010	<i>a</i>
Di- <i>n</i> -butylphthalate	<0.010	<0.010	0.013	<0.010	<i>a</i>
Hexachlorobenzene	<0.010	<0.010	<0.010	<0.010	0.13
Hexachlorobutadiene	<0.010	<0.010	<0.010	<0.010	0.72
Hexachloroethane	<0.010	<0.010	<0.010	<0.010	4.3
Naphthalene	<0.010	<0.010	0.006	0.005	<i>a</i>
Nitrobenzene	<0.010	<0.010	<0.010	<0.010	0.13
Pentachlorophenol	<0.050	<0.050	<0.050	<0.050	3.6
Phenol	0.011	<0.010	0.055	0.037	14.4
Bis(2-chloroethyl)ether	<0.010	<0.010	<0.010	<0.010	0.05
Bis(2-ethylhexyl)phth.	0.009	0.37	0.007	0.048	<i>a</i>
Di- <i>n</i> -octylphthalate	0.035	<0.010	<0.010	<0.010	<i>a</i>
Bis(2-chl. isopro.)ether	<0.010	<0.010	<0.010	0.036	<i>a</i>
Benzoic acid	<0.050	<0.050	0.033	0.020	<i>a</i>
<i>n</i> -Nitroso-di- <i>n</i> -propylam	<0.010	<0.010	<0.010	0.23	<i>a</i>

<sup>a</sup>No limit has been promulgated for this species.

Table 25 lists the TCLP extract concentrations and the TCLP limits. The extracts were analyzed for the VOCs, BNAs, and metals present based on what was measured in the unspiked sludge. Unlike the EP-Toxicity extraction, the cylindrical grout samples had to be reduced in size (crushed or ground) prior to extraction according to TCLP protocol, with the extraction being performed inside a zero-headspace extraction (ZHE) vessel for VOC analysis. The results listed in Table 25 are from two separate extracts: (1) a ZHE for VOC and (2) a standard extract for BNAs and metals. None of the unspiked compounds exceeded the TCLP limits.

TCE for Vendors B, C, and D and PERC for Vendor C exceeded the TCLP limit in the extract. If the measured PERC concentration for Vendor C is multiplied by the ratio of the site maximum concentration to the equivalent sludge concentration in Table 23 (i.e., correcting for the variance from site conditions), the product does not exceed the TCLP limit. It must be noted that this "correction" and conclusions drawn constitute an assumption. However, EPA has allowed use of this "correction" at other sites. Also, the concentration of 1,2-DCE for Vendors A, C, and D equals or exceeds the limit set for 1,1-DCE (no TCLP limit is given for 1,2-DCE, so, the limit for 1,1-DCE was applied). Once again, correcting for the excessive spike predicts that maximum site concentrations would not give extract concentrations for 1,2-DCE above the limit for 1,1-DCE. The only spiked compound contained in the grout specimens at levels below the reported site maximum was TCE for Vendors A, B, and D. The other spiked compounds contained in the grout specimens were at levels which exceeded the reported site maximums and resulted in TCLP extracts below the threshold limits and, thus, would not have caused

Table 25. Concentrations measured in the extracts for the TCLP test (mg/L)

Component	Vendor A	Vendor B	Vendor C	Vendor D	TCLP limit
<u>Volatile organic compounds</u>					
Spiked Compounds					
Acetone	0.15	0.18	0.25	0.18	0.59
1,2-DCE	0.13	0.08	0.10	0.19	a
Chloroform	0.005	0.004	0.009	0.004	0.07
MEK	0.014	0.008	0.048	0.032	7.2
TCE	0.025	0.071	0.30	0.19	0.07
Benzene	0.002	0.009	0.005	0.007	0.07
PERC	0.026	0.028	0.11	0.083	0.1
Chlorobenzene	0.074	0.027	0.11	0.14	1.4
Unspiked compounds					
Methylene chloride	0.008	0.012	0.009	0.009	8.6
Toluene	0.016	0.008	0.030	0.038	14.4
Xylene	0.046	0.021	0.069	0.090	a
Ethyl benzene	0.007	0.004	0.013	0.016	a
1,1,1-Trichloroethane	<0.005	<0.005	<0.010	<0.005	30.0
1,1,2,2-Tetrachloroet.	<0.005	<0.005	<0.010	<0.005	1.3
1,1,2-Trichloroethane	<0.005	<0.005	<0.010	<0.005	1.2
1,1-Dichloroethene	<0.005	<0.005	<0.010	<0.005	0.1
1,2-Dichloroethane	<0.005	<0.005	<0.010	<0.005	0.4
Carbon disulfide	<0.005	<0.005	<0.010	<0.005	14.4
Carbon tetrachloride	<0.005	<0.005	<0.010	<0.005	0.07
Vinyl chloride	<0.010	<0.010	<0.020	<0.010	0.05
<u>Base organic, neutral organic, and acid organic compounds</u>					
1,2,4-Trichlorobenzene	0.008	<0.010	0.002	0.010	a
1,2-Dichlorobenzene	0.91	0.36	0.82	0.27	4.3
1,3-Dichlorobenzene	0.16	0.004	0.022	0.047	a
1,4-Dichlorobenzene	0.28	0.077	0.20	0.22	10.8
2,4,5-Trichlorophenol	<0.050	<0.050	<0.050	<0.050	5.8
2,4,6-Trichlorophenol	<0.010	<0.010	<0.010	<0.010	0.3
2,4-Dimethylphenol	0.10	<0.010	0.22	0.38	a
2,4-Dinitrotoluene	<0.010	<0.010	<0.010	<0.010	0.13
2-Methylnaphthalene	0.008	<0.010	0.011	0.018	a
2-Methylphenol	0.028	<0.010	0.030	0.047	a
4-Methylphenol	0.19	<0.010	0.19	0.28	a
Benzyl Alcohol	<0.010	<0.010	0.016	0.031	a
Di-2n-butylphthalate	<0.010	<0.010	<0.010	0.002	a
Hexachlorobenzene	<0.010	<0.010	<0.010	<0.010	0.13
Hexachlorobutadiene	<0.010	<0.010	<0.010	<0.010	0.72
Hexachloroethane	<0.010	<0.010	<0.010	<0.010	4.3

Table 25. (continued)

Component	Vendor A	Vendor B	Vendor C	Vendor D	TCLP limit
Naphthalene	0.021	<0.010	0.026	0.040	<sup>a</sup>
Nitrobenzene	<0.010	<0.010	<0.010	<0.010	0.13
Pentachlorophenol	<0.050	<0.050	<0.050	<0.050	3.6
Phenol	0.32	<0.010	0.14	0.11	14.4
Bis(2-chloroethyl)ether	<0.010	<0.010	<0.010	<0.010	0.05
Bis(2-ethylhexyl)phth.	<0.010	0.19	0.011	0.13	<sup>a</sup>
Di- <i>n</i> -octylphthalate	<0.010	0.003	<0.010	0.003	<sup>a</sup>
<u>Metals</u>					
Arsenic	<0.0025	<0.0025	0.009	<0.0025	5.0
Barium	0.423	0.964	0.383	0.515	100.
Cadmium	<0.022	<0.022	<0.022	<0.022	1.0
Chromium	0.050	<0.039	<0.039	<0.039	5.0
Lead	0.0013	0.008	0.0025	0.0037	5.0
Mercury	<0.0002	<0.0002	<0.0002	<0.0002	0.2
Nickel	<0.047	<0.047	<0.047	<0.047	<sup>a</sup>
Selenium	<0.0021	<0.0021	<0.0021	<0.0021	1.0
Silver	<0.022	<0.022	<0.022	<0.022	5.0

<sup>a</sup>No limit has been promulgated for this species.

the waste forms to be classed hazardous. Table 26 lists the correction to site conditions for those compounds and vendors for which the correction was important. None of the extract concentrations for Vendor A exceeded the TCLP limits. For the other vendors, only TCE exceeded its limit.

However, the threshold limit for TCE is not exceeded if the quantity contained in the grout specimens is corrected to the TCE concentration (5.8 mg/L) obtained by averaging all of the TCE concentrations reported for samples from the sludge lagoon. Thus, all grouts studied are assumed to result in TCLP extract concentrations below the threshold limits for waste at the calculated average site concentrations. Significantly, grouts containing VOCs at levels above reported site maximums resulted in TCLP extract concentrations below threshold limits for all VOCs studied with the exception of TCE.

For comparative purposes, Table 27 lists the EP-Toxicity and TCLP extract concentrations for the unspiked sludge. Neither the EP-Toxicity nor the TCLP limits were exceeded, although the cadmium concentration in the EP-Toxicity extract was measured to be equal to the threshold limit (1 mg/L). The EP-Toxicity procedure does not require BNA or VOC analysis, but the EP-Toxicity extract was measured for these compounds, and the results are listed in Table 27. Not surprisingly, the VOC detected in the TCLP-ZHE was not detected in the EP-Toxicity extract (since organics can be easily vaporized from the open, stirred vessel specified for the EP-Toxicity extractions).

##### 5. INTERPRETATION OF THE STATIC LEACH RESULTS

As discussed previously, the leaching process, which is the release of the species from the waste form into the surrounding solution, is complex.

Table 26. Correction of the observed TCLP extract concentration to site concentrations for selected compounds and vendors

Component	Observed extract concentration (mg/L)	Ratio site to actual	Corrected extract concentration (mg/L)	TCLP limit (mg/L)
<b>1,2-DCE</b>				0.1 <sup>a</sup>
Vendor A	0.13	0.28	0.04	
Vendor B	0.08	0.37	0.03	
Vendor C	0.10	0.37	0.04	
Vendor D	0.19	0.34	0.06	
<b>PERC</b>				0.1
Vendor A	0.026	0.23	0.006	
Vendor B	0.028	0.29	0.008	
Vendor C	0.11	0.53	0.058	
Vendor D	0.083	0.32	0.026	
<b>TCE</b>				0.07
<u>Site maximum</u>				
Vendor A	0.025	1.88	0.047	
Vendor B	0.071	1.20	0.086	
Vendor C	0.30	0.79	0.24	
Vendor D	0.19	1.69	0.32	
<u>Lagoon average<sup>b</sup></u>				
Vendor A	0.025	0.08	0.002	
Vendor B	0.071	0.05	0.004	
Vendor C	0.30	0.04	0.011	
Vendor D	0.19	0.08	0.014	

<sup>a</sup>Limit for 1,1-DCE; no TCLP limit is given for 1,2-DCE.

<sup>b</sup>The average of the TCE analyses reported for the lagoon was 5.8 mg/L compared to the site maximum of 130 mg/L. The site maximums were used for the other two compounds.

Table 27. The EP-Toxicity and TCLP extract concentrations for the unspiked sludge

Component	EP-Toxicity (mg/L)	TCLP (mg/L)	Regulatory limit (mg/L)
<u>Volatile organic compounds</u>			
Acetone	<0.010	0.11	0.59
1,2-DCE	<0.005	0.52	a
Chloroform	0.001	0.012	0.07
MEK	<0.010	<0.010	7.2
TCE	<0.005	0.005	0.07
Benzene	<0.005	0.005	0.07
PERC	<0.005	0.015	0.1
Chlorobenzene	<0.005	0.052	1.4
Methylene chloride	<0.005	<0.005	8.6
Toluene	<0.005	0.059	14.4
Xylene	0.005	0.088	a
Ethyl benzene	0.001	0.018	a
1,1,1-Trichloroethane	<0.005	<0.005	30.0
1,1,2,2-Tetrachloroethane	<0.005	0.004	1.3
1,1,2-Trichloroethane	<0.005	0.006	1.2
1,1-Dichloroethene	<0.005	<0.005	0.1
1,2-Dichloroethane	<0.005	0.003	0.4
Carbon disulfide	<0.005	<0.005	14.4
Carbon tetrachloride	<0.005	<0.005	0.07
Vinyl chloride	<0.010	<0.010	0.05
Bromodichloromethane	<0.005	0.001	a
<u>Base organic, neutral organic, and acid organic compounds</u>			
1,2,4-Trichlorobenzene	0.003	0.005	a
1,2-Dichlorobenzene	0.046	0.65	4.3
1,3-Dichlorobenzene	0.002	0.042	a
1,4-Dichlorobenzene	0.022	0.40	10.8
2,4,5-Trichlorophenol	<0.025	<0.025	5.8
2,4,6-Trichlorophenol	<0.005	<0.005	0.3
2,4-Dimethylphenol	0.28	0.19	a
2,4-Dinitrotoluene	<0.005	<0.005	0.13
2-Methylnaphthalene	0.020	0.018	a
2-Methylphenol	0.012	0.008	a
4-Methylphenol	0.031	0.021	a
Benzyl Alcohol	<0.005	<0.005	a
Di-n-butylphthalate	0.003	0.003	a
Hexachlorobenzene	<0.005	<0.005	0.13
Hexachlorobutadiene	<0.005	<0.005	0.72
Hexachloroethane	<0.005	<0.005	4.3
Naphthalene	0.010	0.027	a
Nitrobenzene	<0.005	<0.005	0.13

Table 27. (continued)

Component	EP-Toxicity (mg/L)	TCLP (mg/L)	Regulatory limit (mg/L)
Pentachlorophenol	<0.025	<0.025	3.6
Phenol	<0.005	<0.005	14.4
Bis(2-chloroethyl)ether	<0.005	<0.005	0.05
Bis(2-ethylhexyl)phth.	0.094	0.059	<sup>a</sup>
Di-n-octylphthalate	0.005	0.003	<sup>a</sup>
2,4-Dichlorophenol	0.028	0.027	<sup>a</sup>
Dibenzofuran	0.0003	<0.005	<sup>a</sup>
Diethylphthalate	0.002	0.001	<sup>a</sup>
<u>Metals</u>			
Arsenic	<0.005	<0.005	5.0
Barium	1.3	0.94	100.
Cadmium	1.0	0.67	1.0
Chromium	0.41	0.29	5.0
Lead	0.16	0.10	5.0
Mercury	<0.0002	<0.0002	0.2
Nickel	0.69	0.56	<sup>a</sup>
Selenium	<0.005	<0.005	1.0
Silver	<0.010	<0.010	5.0

<sup>a</sup>No limit has been promulgated for this species.

The chemical potential of the species in the aqueous phase is different from that on the waste-form surface. Thus, the immersion of the waste form in a liquid leads to a flux of mass between the solid surface and the solution. The release of surface molecules into the solution establishes a concentration gradient in the solid phase adjacent to the surface. This leads to the movement of species from the interior of the waste form toward the surface and their subsequent release into the solution. The instantaneous rate of release of a species from the solid surface into the liquid is proportional to this concentration gradient, with the proportionality constant being defined as the diffusion coefficient. In general, release of the species from a monolithic waste form into a surrounding liquid (such as groundwater) is diffusion controlled, as long as the volume of liquid is sufficiently large (as compared to the volume of waste form) so that the species concentration at the waste-form surface is maintained at zero, such as would be maintained by a waste form suspended in a free flowing river. In a static environment, such as a waste form in a trench that remains filled with rainwater for an extended period of time, the waste species in the liquid will eventually equilibrate with the waste species remaining in the waste form. When equilibrium is reached, the net transfer of species from the solid to the liquid will cease. The relationship between the liquid concentration at equilibrium with the remaining waste-form concentration is described by the distribution coefficient. Ideally, the species contained in a waste form would be characterized by a low diffusion coefficient, indicating a slow rate of release from the waste form into the surrounding liquid, and a high distribution coefficient, indicating that equilibrium is achieved

between the waste form and the surrounding liquid at a low liquid concentration.

This section describes the methodology used to obtain diffusion and distribution coefficients from the static leach data presented in Sect. 4. The coefficients were estimated using NEWBOX, a sophisticated computer program developed at ORNL for interpretation of leach data.

### 5.1 ESTIMATION OF THE MASS-TRANSFER PARAMETERS

The static leach test results were analyzed using NEWBOX, a program that combines several analytical solutions of Fick's second law (a second order partial differential equation) with an optimization procedure to select the best estimate of parameters (e.g., diffusion coefficient) to fit a given set of data.<sup>24,25</sup> The data presented in Tables 15, 16, 17, 18, and 20 were averaged and used as input to the program, along with the sample geometry and the initial amount estimated (see Table 14). Table 28 lists the average mass leached with time and the estimated initial mass used as input. In general, the program output was an estimate of the diffusion coefficient (D) and the mass remaining in the sample at equilibrium ( $A_f$ ). The distribution coefficient (K) was calculated from  $A_f$  using the following equation:

$$K = A_f V_1 / (A_0 - A_f) V_s, \quad (2)$$

where

K = Distribution coefficient, mg species/L sample per mg species/L leachate;

$A_f$  = Mass of species remaining in sample at equilibrium, mg;

$A_0$  = Mass of species initially in sample, mg;

$V_1$  = Volume of leachate, L;

$V_s$  = Geometric volume of sample, including void volume, L.

Table 28. Average total mass leached in the static leach tests  
(both semicontinuous and batch) at the given times

Component	Average total mass leached (mg)						Estimated initial mass (mg)		
	1	3	6	14	28	51			
Vendor A									
Time, d =	1	3	6	14	28	51			
Acetone	0.962	2.347	4.784	3.216	10.850	4.739	<sup>a</sup>		
1,2-DCE	2.342	3.177	8.638	10.427	19.369	9.783	24.083		
Chloroform	0.178	0.084	0.042	0.175	3.227	0.565	30.619		
MEK	1.845	2.877	5.188	7.636	9.702	4.486	7.222		
TCE	0.993	1.575	2.831	3.380	6.355	4.055	19.693		
Benzene	2.273	3.392	6.959	8.866	15.194	9.255	23.476		
PERC	0.343	0.571	0.583	0.872	2.255	1.207	35.839		
Chlorobenzene	0.466	1.053	1.317	1.632	3.528	1.961	20.288		
Vendor B									
Time, d =	1	3	7	14	21	27	35	63	
Acetone	0.037	0.078	0.235	1.085	0.321	0.682	3.182	0.709	0.801
1,2-DCE	0.002	0.004	0.026	0.000	0.110	0.271	1.877	0.888	0.656
Chloroform	0.005	0.006	0.020	0.017	0.006	0.245	1.714	0.690	1.099
MEK	0.010	0.016	0.053	0.000	0.395	0.223	1.960	0.542	0.906
TCE	0.012	0.017	0.049	0.084	0.072	0.215	1.048	0.723	1.079
Benzene	0.017	0.027	0.084	0.157	0.191	0.279	1.568	0.781	1.003
PERC	0.025	0.029	0.090	0.139	0.139	0.291	0.773	0.686	3.373
Chlorobenzene	0.036	0.048	0.127	0.199	0.259	0.302	1.820	0.451	4.290
Vendor C									
Time, d =	1	3	7	14	28	35			
Acetone	0.266	0.056	0.938	0.060	0.066	0.196			7.200
1,2-DCE	3.954	6.765	8.060	10.624	6.470	6.943			11.885
Chloroform	3.500	4.570	5.262	6.766	3.721	2.757			7.000
MEK	0.074	0.065	1.206	2.187	2.057	0.591			13.865
TCE	1.140	2.414	3.047	4.692	2.565	3.035			4.885
Benzene	2.489	4.924	6.351	8.601	5.547	5.942			8.455
PERC	0.271	1.155	0.755	1.639	1.389	0.926			24.734
Chlorobenzene	0.532	1.384	2.059	3.964	2.998	1.435			5.917

Table 28. (continued)

Component	Average total mass leached (mg)						Estimated initial mass (mg)
	1	3	9	14	28	60	
Vendor D							
Time, d =	1	3	9	14	28	60	
Acetone	3.738	6.774	3.234	9.251	17.335	15.001	8.180
1,2-DCE	3.708	10.619	11.612	19.912	26.624	20.125	36.497
Chloroform	2.038	6.117	4.807	6.742	5.343	1.783	53.782
MEK	4.861	6.209	4.724	9.472	18.245	10.426	11.054
TCE	1.309	4.083	2.999	5.399	7.888	7.851	29.700
Benzene	2.817	8.366	6.967	15.133	20.871	17.283	36.334
PERC	0.350	1.851	0.834	0.621	1.646	1.443	53.162
Chlorobenzene	0.575	2.472	0.838	2.385	3.973	2.860	28.009

<sup>a</sup>The sludge concentration measured for acetone was low for Vendor A and more was vaporized than was originally present according to this sludge analysis. Consequently, for Vendor A the acetone present in the grout sample prior to leaching was unknown.

Scatter was obvious in the data (see Table 28 and Fig. 16). As discussed previously, the scatter is thought to be due primarily to the inadequacies of the standard analytical procedures. The effect of deleting individual data points and inputting selected data sets was tested in an attempt to determine the most representative parameters for a given species and vendor. The parameters that resulted in the model prediction closest to the observed performance were selected as being most representative for that combination of species and vendor. Figure 16 illustrates one of the better fits using this approach. Such fits were typical for Vendors A, C, and D with 1,2-DCE, TCE, benzene, PERC, and chlorobenzene. Table 29 lists the parameters selected as being most reasonable and representative for the data generated in this study. The leachability index (LI) listed in Table 29 is defined as follows:

$$LI = \text{Log}(b/D), \quad (3)$$

where

$$b = 1.0 \text{ cm}^2/\text{s},$$

$$D = \text{diffusion coefficient, cm}^2/\text{s}.$$

In general, the two ketones--acetone and MEK--suffered from more scatter in the data than the other compounds. This problem may have been caused by the low sensitivity of the analytical technique to these two compounds. As a consequence, these two were subject to masking by other compounds, leading to erroneously low measurements in some instances. Chloroform gave seemingly contradictory results, with some data (for Vendors C and D) suggesting that the concentration increased to a maximum and then started declining. This result may have been caused by an error in analysis or may have been real. If real, it is not clear what caused

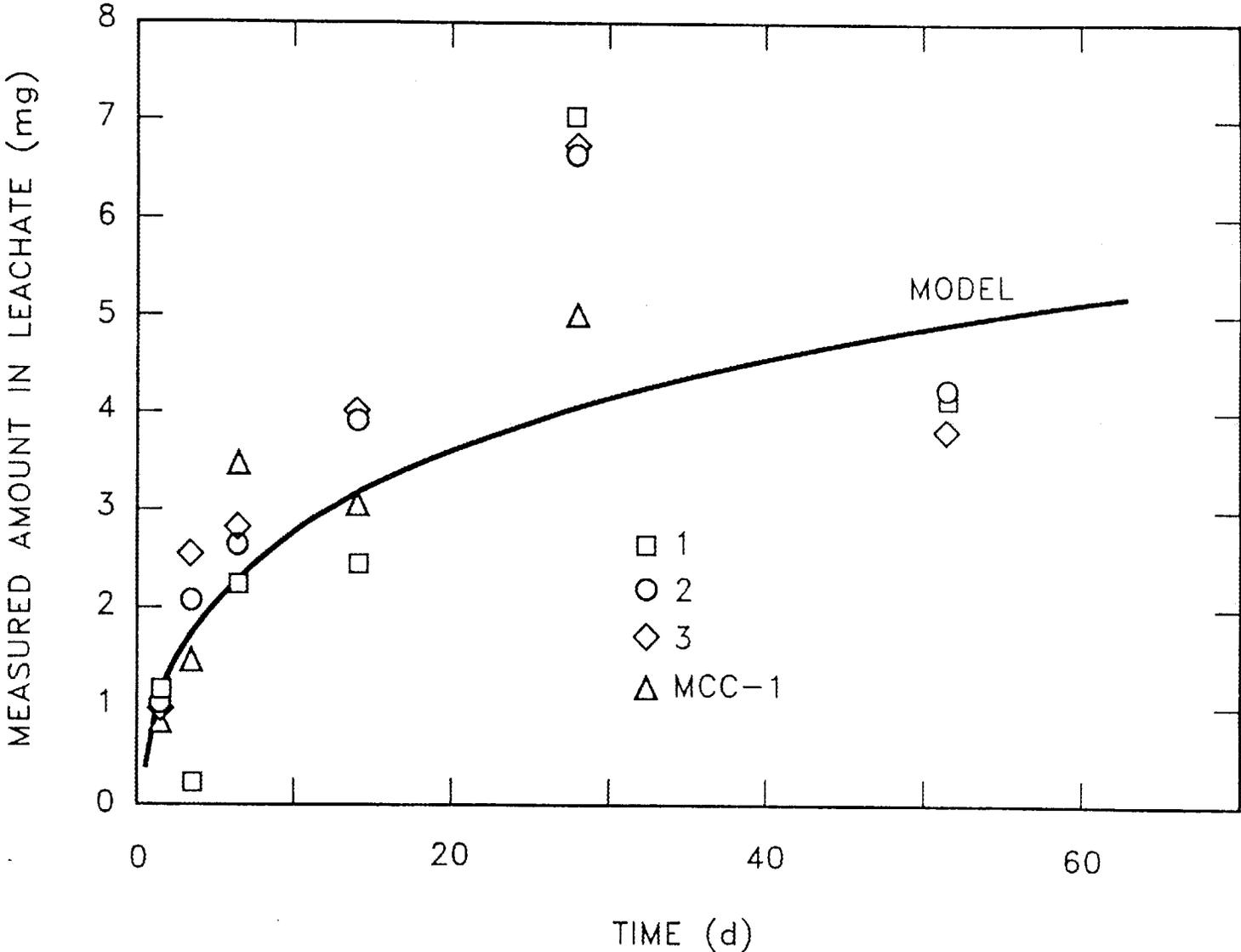


Fig. 16. Static leaching of TCE from Vendor A's product (1, 2, and 3 are the samples leached semicontinuously; MCC-1 are the samples leached batchwise).

Table 29. NEWBOX estimates of the mass-transfer parameters

	D (cm <sup>2</sup> /s)	A <sub>f</sub> (mg)	A <sub>o</sub> (mg)	Leachability index	$\left( \frac{K}{\text{mg/L water}} \right)$ mg/L grout per
Acetone					
Vendor A	3.0E-07	0.00 <sup>a</sup>	5.0 <sup>a</sup>	6.5	0.0 <sup>a</sup>
Vendor B	3.5E-08	0.00	0.8	7.5	0.0
Delay 17.6 d	3.5E-08	0.06	0.8	7.5	1.0
Vendor C	<sup>b</sup>	7.00	7.2	<sup>b</sup>	439.7
Vendor D	3.0E-07	0.00 <sup>a</sup>	16.0 <sup>a</sup>	6.5	0.0 <sup>a</sup>
1,2-Dichloroethene					
Vendor A	7.0E-08	10.00	24.0	7.2	9.0
Vendor B	1.0E-08	0.00	0.7	8.0	0.0
Delay 16.7 d	6.0E-08	0.00	0.7	7.2	0.0
Vendor C	1.0E-06	4.00	12.0	6.0	6.3
Vendor D	1.0E-07	13.00	36.0	7.0	7.1
Chloroform					
Vendor A	<sup>c</sup>	30.00 <sup>d</sup>	30.6	<sup>c</sup>	628.1 <sup>d</sup>
Vendor B	1.5E-08	0.00	1.1	7.8	0.0
Delay 18.8 d	4.0E-08	0.00	1.1	7.4	0.0
Vendor C	1.0E-06	0.70 <sup>e</sup>	7.0	6.0	1.4 <sup>e</sup>
Vendor D	2.0E-08	46.00	54.0	7.7	75.0
Methyl ethyl ketone					
Vendor A	4.0E-07	1.30	7.2	6.4	2.8
Vendor B	3.0E-08	0.00	0.9	7.5	0.0
Delay 12.2 d	4.0E-08	0.55	0.9	7.4	19.7
Vendor C	1.0E-08	8.00	14.0	8.0	16.8
Vendor D	1.0E-06	1.25	11.0	6.0	1.6
Trichloroethene					
Vendor A	2.0E-08	13.00	20.0	7.7	23.3
Vendor B	1.0E-09	0.00	1.1	9.0	0.0
Delay 17.4 d	1.3E-08	0.00	1.1	7.9	0.0
Vendor C	5.0E-07	1.70	4.9	6.3	6.7
Vendor D	1.5E-08	17.00	30.0	7.8	16.4

Table 29. (continued)

	D (cm <sup>2</sup> /s)	A <sub>f</sub> (mg)	A <sub>o</sub> (mg)	Leachability index	K (mg/L grout per mg/L water)
Benzene					
Vendor A	7.0E-08	11.00	23.0	7.2	11.5
Vendor B	1.0E-08	0.00	1.0	8.0	0.0
Delay 12.9 d	3.5E-08	0.00	1.0	7.5	0.0
Vendor C	8.0E-07	1.40	8.5	6.1	2.5
Vendor D	9.0E-08	14.00	36.0	7.0	8.0
Perchloroethene					
Vendor A	6.0E-10	33.50	36.0	9.2	168.3
Vendor B	4.0E-10	0.00	3.4	9.4	0.0
Delay 12.8 d	2.0E-09	0.00	3.4	8.7	0.0
Vendor C	1.0E-09	22.00	25.0	9.0	92.1
Vendor D	4.0E-10	51.50	53.0	9.4	431.3
Chlorobenzene					
Vendor A	4.8E-09	16.50	20.0	8.3	59.2
Vendor B	6.0E-10	0.00	4.3	9.2	0.0
Delay 0.5 d	1.0E-09	0.90	4.3	9.0	3.3
Vendor C	6.0E-08	0.00	5.9	7.2	0.0
Vendor D	1.8E-09	21.00	28.0	8.7	37.7

<sup>a</sup>The amount leached exceeded the estimated A<sub>o</sub>; thus, A<sub>f</sub> was set as negligible and NEWBOX estimated A<sub>o</sub> and D. The low acetone concentration measured in the sludge used to prepare Vendor A's samples was suspected of being erroneous.

<sup>b</sup>This data set was particularly poor for evaluating D. Using all the data, NEWBOX selected a D of 1E-5, which is not realistic, especially combined with the high K. This value is left unknown until a more thorough analysis will hopefully yield a defensible value.

<sup>c</sup>NEWBOX estimated a suspiciously high D of 1E-11 using the graphical estimate for A<sub>f</sub>, but NEWBOX's estimate for both (a D of 1E-12 and a negligible A<sub>f</sub>) was considered even worse.

<sup>d</sup>This A<sub>f</sub> was estimated graphically and used as input for NEWBOX to estimate a D.

<sup>e</sup>Parameters estimated using only the data from the first 14 d of leaching.

the decline. Some possibilities are reaction (with the waste form, another compound, or the vessel), sorption (by the waste form again or the vessel O-rings), vaporization (through some leak in the vessel), or decomposition. Some of these possibilities do not seem likely considering the behavior of the other compounds in these leachates and the behavior of chloroform observed in blank tests. Basically, a definitive conclusion cannot be reached about the behavior of chloroform, and diffusion-controlled release was assumed to prevail for the purposes of this study. The chloroform parameters suggested in Table 29 for Vendors C and D were estimated by NEWBOX without the data for the last two sample intervals (when the leachate concentration decreased according to the reported results). The point being made is that the parameters for these three compounds—acetone, MEK, and chloroform—are more questionable than for the other five, making extrapolation to other conditions more questionable for these three.

The data for Vendor B presented a different problem in that most of the data indicated little or no early release, but later release at a much greater rate than expected (based on the early behavior). The optimization procedure used by NEWBOX did not make reasonable parameter estimates using this data. The slow early release led NEWBOX to suggest leachability indexes as high as 12. Most of the parameters listed in Table 29 for Vendor B were estimated by NEWBOX without any of the early data. Even then the predicted release sometimes fell far short of the observed release (see Fig. 17). Better predictions (see Fig. 17) were obtained by a simple change in the model, that is, assuming that no release occurs for a finite time greater than zero followed by standard

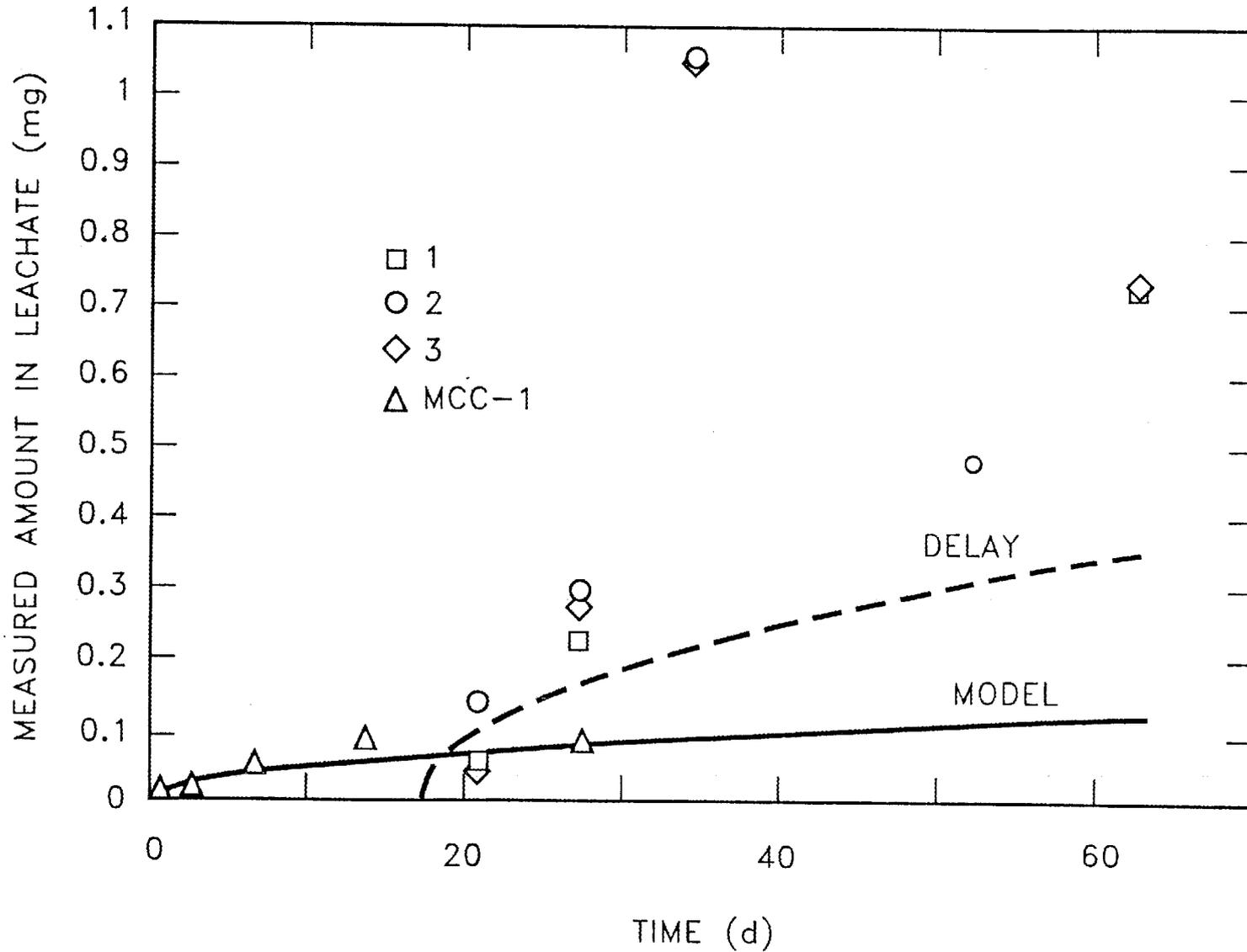


Fig. 17. Static leaching of TCE from Vendor B's product (1, 2, and 3 are the samples leached semicontinuously; MCC-1 are the samples leached batchwise).

diffusion-controlled release. Such behavior might be expected if a film (e.g., a film of the reagent Vendor B uses) covered the waste form, thus hampering release. Later, after the film dissolved or eroded, standard release might be expected. If this explanation were the main cause of the observed behavior, then the time delays estimated for each compound should have been approximately the same. Since this statement was not true, the actual mechanism for release was more complicated; however, such a film may play a part in the true mechanism. Although the time delay currently appears to be a curve-fitting parameter (i.e., it is not clear how to extrapolate it to other conditions), it was judged that the diffusion coefficients estimated using this approach were more representative of the behavior of this waste form at longer times. The parameters estimated by NEWBOX using this approach are listed in Table 29 along with the estimated time delay for each compound below the other parameters estimated for Vendor B. The time delays were estimated by linear regression of the square root of time and the average total mass leached to find the time intercept. The point for Vendor B is that the diffusion model alone does not adequately explain the observed leach behavior for the product. Further analysis may eventually suggest a mechanism more convincing than the one proposed.

The values reported in Table 29 are reasonable for the most part, that is, they predict leaching behavior representative of the trends observed from the leach data. Most of the diffusion coefficients are in the range expected for porous cementitious bodies, and the distribution coefficients are within the range reported for solid sorptive agents. The leachability indexes reported in Table 29 may have an error band as large

as 0.5, but this is not unusual for cementitious porous bodies. On the other hand, there is much greater uncertainty in the estimates for  $A_f$  and, consequently,  $K$ . NEWBOX's ability to accurately estimate  $A_f$  decreases as  $A_f$  approaches either  $A_0$  or zero.

For the case of  $A_f$  approaching zero, both  $A_f$  and  $K$  will always be a finite value greater than zero, although  $K$  can be less than 1. Even if the compound in question does not adsorb on the solid surface, which is highly unlikely, the solution residing in the pores of the solid guarantees the presence of a finite amount of the compound in question being within the geometric boundaries defined for the sample (i.e., some of the compound will always be present in the sample during leaching, even if it is dissolved in the pore solution). In the unlikely case of a noninteractive solid surface,  $K$ , as defined, becomes the ratio of the pore volume to the leachate (external to the pore) volume. Using this logic,  $K$  had a lower bound of 0.02 to 0.04 (depending on the porosity) for the leach test in question. For all practical purposes, such a low  $K$  is insignificantly different from zero. Low  $K$ s had little practical effect on accurately predicting the observed leaching behavior and became more of a curve-fitting parameter rather than an estimate of a fundamental equilibrium value, that is, low interaction (low  $K$ s) with the solid cannot be accurately measured and must essentially be viewed as zero interaction ( $K = 0.0$ ).

The opposite case of strong interaction with the solid (high  $K$ s) is not so easily handled. A small change in either  $A_0$  or  $A_f$  can make a large change in the estimated  $K$ , and, for the cases where only a small fraction of what was present leached, NEWBOX had difficulty distinguishing between

slow leaching (low  $D$ ) and equilibrium (high  $K$ ), especially with the large deviations in experimental data. Unlike the kinetic constant ( $D$ ), the equilibrium constant ( $K$ ) is sensitive to the accuracy of both  $A_0$  and  $A_f$ . The measured quantities are the sludge concentration corrected for losses during preparation and leachate concentration. If the amount leached is small compared to the amount calculated to remain in the sample, the confidence is high in the obvious qualitative conclusion of a strong interaction, but a large error is associated with the quantitative estimate of  $K$ . For example, a strong interaction is implied whether  $K$  is 100 or greater.

Basically, the kinetics (i.e., how fast equilibrium is approached) is dependent on  $D$  and is relatively independent of the final equilibrium value. For a given  $D$ , the model prediction of the amount leached varies little with  $K$  until the equilibrium amount leached for each  $K$  is approached. The experimental data verified this predicted behavior. NEWBOX analysis of the early (i.e., short leach time) data while significant changes were still occurring in the leachate concentration gave a  $D$  insignificantly different from the  $D$  estimated using all of the data, even when equilibrium appeared to have been achieved. Of course, the estimated  $K$ s were totally different, being zero for the early data and dictated by the approach to equilibrium in the latter case. This observation supports diffusion control as the leaching mechanism and lends confidence in the  $D$ s estimated by NEWBOX.

Two values for  $D$  estimated by NEWBOX are suspicious. One is for chloroform for Vendor A and is related to the low release observed in this case and NEWBOX's difficulty in handling such a case. Leaving both

parameters unknown, NEWBOX suggested a leachability index of 12 with a negligible K. Reviewing the data suggested that equilibrium may have occurred at the observed concentration. Using the graphical estimate of equilibrium as input, NEWBOX suggested a leachability index of 11. None of the other data give such a high index. The reported correlation between D and K does suggest a leachability index of 9 for a K of 628, but a leachability index of 11 suggests a K of 10,000 or more.<sup>25, 26</sup> Considering the strange behavior of chloroform for the other products makes these estimates even more suspect. It may be that the estimate for  $A_0$  was erroneous or changing for chloroform, which would lead to incorrect estimates of D and K. Until more is known about what is truly happening with chloroform, the parameter estimates must be viewed with suspicion.

The other suspicious D is that for acetone for Vendor C. In this case, the leachate concentration apparently came immediately to a relatively constant concentration with a large standard deviation. This constant concentration implied an equilibrium with a fairly high K, but the rate at which equilibrium was established implied a leachability index of 5. One reason this value is suspect is that the leachability index for a species in water (i.e., no grout barrier) is about 5. The waste form with its attendant geometric barrier and interaction potential (K) cannot have a leachability index as low as water. Still the observed behavior was an equilibrium established almost immediately. More frequent analysis may have detected a more gradual rise to equilibrium. If the estimates of the leachate and solid concentrations are accepted, then K was accurately estimated for acetone for Vendor C, but D must be left unknown.

The point is that, in general, the estimates of leachability index are considered to be fairly accurate, but that the  $K_s$ , while truly indicating strong or weak interactions, are more inaccurate, especially at the two extremes of high and low.

## 5.2 EXTRAPOLATION OF LEACH DATA

The mass-transfer parameters (i.e., diffusion and distribution coefficients) discussed in the previous section can be used to predict the long-term release of the constituents over time. The diffusion coefficients are used in determining the rate of constituent release from the waste form until it achieves or approaches equilibrium with the liquid medium (e.g., groundwater), while the distribution coefficients are used in determining the equilibrium concentration of the released constituents in the liquid medium. In reality, these parameters would be incorporated into a risk assessment (or equivalent) model deemed representative of the actual site conditions, which, in turn, involves the use of complex hydrogeological models. This type of approach was beyond the scope of this project.

However, in order to provide the reader with an example of how this data can be used, a simplified extrapolation of the data to site conditions is presented in this section. It cannot be overemphasized that this presentation is only an example and is not meant to predict actual site behavior. However, the authors believe that this example provides the reader with a qualitative feel for the type of performance that can be expected if this technology is applied to the site and provides guidance as to which site characteristics can affect the release of constituents of interest.

The leachability indexes in Table 29 range from 6.0 to 9.4 and K ranges from 0 to 628. To bracket the expected performances, two sets of parameters (LI = 6 and K = 0 and LI = 9.4 and K = 628 taken from Table 29) were used in the model to estimate long-term release at the two extremes. A leachability index of 6.0 and K of 0 gave a fast release with no equilibrium to prevent total release, even in stagnant situations. If a limited amount of leachate is assumed, extrapolation to the large dimensions of the site must be carefully checked to ensure that solubility limits are not exceeded. A leachability index of 9.4 and K of 628 gave the slowest release rate and lowest equilibrium release that could be expected.

The dimensions of the leaching waste form are part of the diffusion model, so extrapolating from the small laboratory sample to the dimensions of the sludge lagoon was a relatively straightforward process. The dimensions of the sludge lagoon are reported as 6070.5 m<sup>3</sup> (1.5 acres) with the depth of contamination contained within 4.57 m (15 ft), giving a volume for remedial action of 27,754 m<sup>3</sup>. Table 30 summarizes the volume increase observed by mixing the homogenized RAFB sludge into cementitious

Table 30. Estimated volume increase by mixing the sludge into grout (measured sludge density: 1.46 kg/L)

	Vendor A	Vendor B	Vendor C	Vendor D
Sludge wt % in grout	41	10.2	62	75
Grout density, kg/L	1.61	1.62	1.22	1.39
Grout volume/sludge volume	2.21	8.84	1.93	1.40
Volume increase	121%	784%	93%	40%

waste forms during this study. The volume increased from a low of 40% for the highest sludge loading of 75 wt % for Vendor D to a high of 784% for the low waste loading of 10.2 wt % for Vendor B. Economics and a practical need to minimize this volume increase will likely result in a formulation with a higher sludge loading than 10.2 wt %. On the other hand, the higher sludge loadings resulted in a weak physical product, perhaps so weak that the waste form will not be impervious to bulk water flow. To guard against this possibility, the sludge loading will likely be restricted to 40 or 50 wt %. For the purposes of this extrapolation, a volume increase of 120% was assumed (i.e., a grout volume of 61,059 m<sup>3</sup>). Assuming a proportionate increase in the sides of the square (assumed) enclosing the original 1.5 acres and the depth, the grout monolith dimensions were projected to be an area of 10,300 m<sup>2</sup> (2.5 acres) to a depth of 5.96 m (19.5 ft) to accommodate the assumed volume increase.

The surface area of the proposed monolith is about 23,000 m<sup>2</sup>. Of more importance is how much of this surface area will be in contact with water for leaching. For extrapolating, the entire surface area was assumed immersed and leaching. This is not a realistic assumption for actual field conditions since most, if not all, of the monolith will not likely be immersed in water. However, this assumption allows a model prediction of leaching behavior if the entire sludge lagoon were mixed into a grout monolith and leached in a manner similar to the laboratory leach tests.

Figure 18 illustrates the predicted leaching for a Leachability Index of 6 and 9.4 if a constituent concentration of zero is maintained at the monolith surface, that is, dynamic leaching or the flow of water is

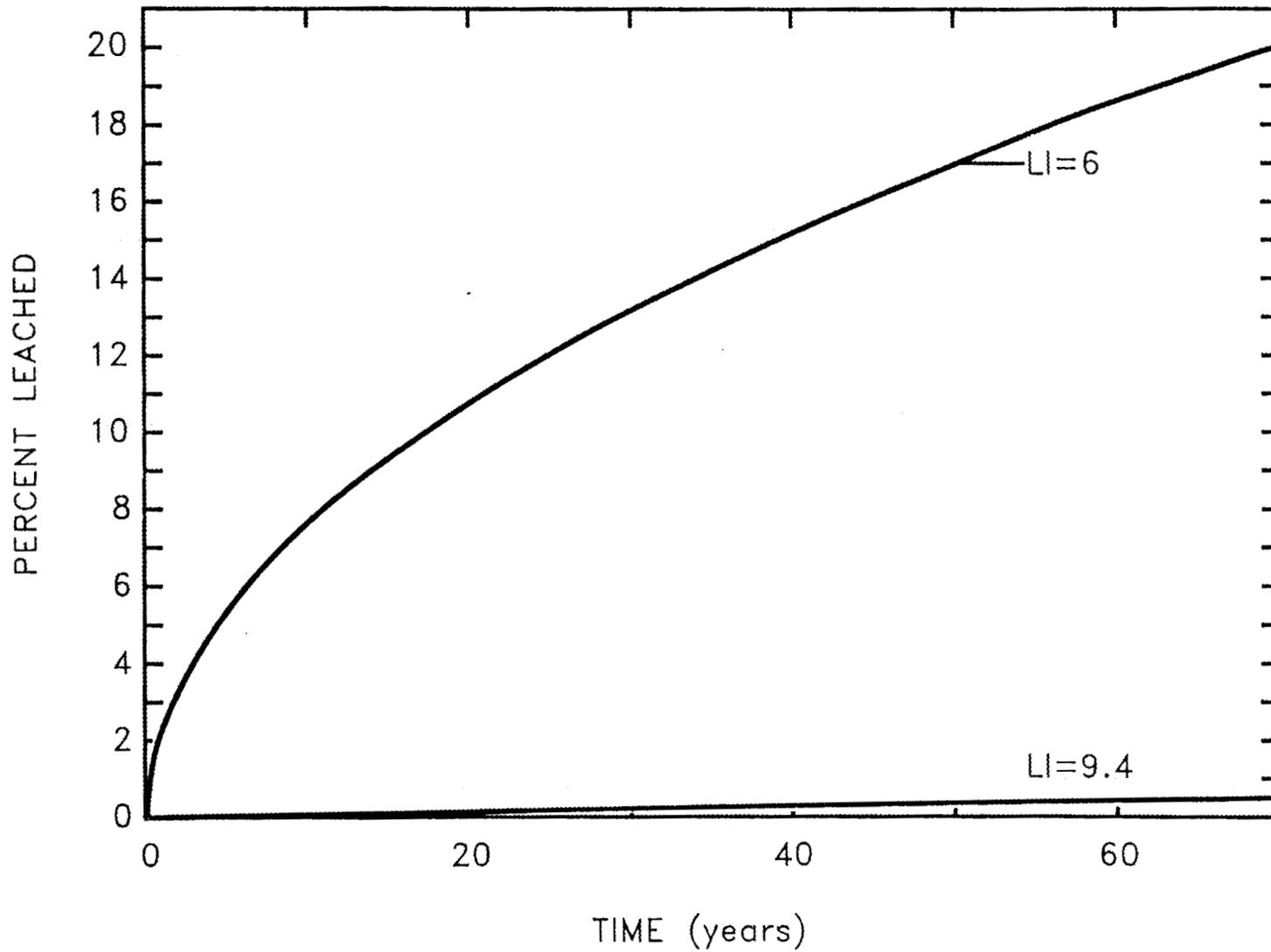


Fig. 18. Predicted dynamic leaching behavior of the sludge lagoon monolith for the indicated leachability indexes.

sufficiently rapid so as to allow no significant accumulation of the constituent in the water. (This is the same behavior predicted for a K of zero for the same indexes.) In this case, leaching is controlled entirely by D and neither K nor  $A_0$  is an important factor, meaning that the fraction leached at any given time will be the same regardless of the starting or equilibrium concentrations. The model assumes all of the contaminant is leachable (i.e., any sorption is reversible). The equilibrium distribution observed in this study would not have distinguished between reversible and irreversible sorption, or disappearance of the species by chemical reaction. Thus, all of the species must be assumed available for eventual release. The time span of 70 years was selected to be consistent with anticipated regulatory extrapolations. The two leachability indexes bracket the values listed in Table 29. For a leachability index of 6, 7 wt % would be leached within 10 years and about 20 wt % after 70 years. Less than 1 wt % would be leached in 70 years for an index of 9.4. The water concentrations during leaching depend on the original mass of the contaminant in the monolith at the start of leaching and the amount of water. Obviously, the higher the index the better, but no regulatory criteria govern this parameter for the VOCs. Listed in Table 29 (counting only the time delay for Vendor B) are 8 indexes between 6 and 6.9, 14 between 7 and 7.9, 4 between 8 and 8.9, and 4 between 9 and 9.4. Thus, indexes between 7 and 7.9 predominated. Among the four vendors, no single compound was limited to a Leachability Index as low as 6 with 1,2-DCE having the lowest collective index of all the compounds at 7.2 (i.e., selecting the highest index listed for each compound and comparing demonstrates that the lowest index for these eight

compounds among the four vendors is 7.2). For this site, some compounds will not be of regulatory concern in a technical sense (e.g., the regulatory limit for MEK is so high and the site concentration so low that a low index for this compound would not be a problem). Thus, a lower index for this compound would be acceptable in order to achieve a higher index for some other compound presenting more of a risk. The VOCs with the highest reported site maximums were TCE at 130 mg/L, 1,2-DCE at 100 mg/L, and PERC at 59 mg/L, with none of the rest being greater than 20 mg/L. PERC has the highest indexes listed in Table 29 (i.e., the most immobilized species of the eight) and no TCLP limits exist for 1,2-DCE, making TCE the compound of most interest for this site. Vendor C's product had an index of 6.3 for TCE, but the other three indexes were close to 8 (7.7, 7.9, and 7.8, respectively, for A, B, and D).

Figure 19 illustrates the importance of the equilibrium distribution coefficient on leaching if the water volume for leaching is limited (static) or the flow of water is sufficiently slow so as to allow significant accumulation (i.e., "high" concentration) of the constituent in the water. Both curves were calculated using an index of 9.4, but the upper curve assumed dynamic leaching just as in Fig. 18 (note the difference in scales for the per cent leached between Figs. 18 and 19). For the static leach calculation, the amount of water was limited to the same basis as the static leach tests—a volume (mL) of water equal to ten times the monolith surface area ( $\text{cm}^2$ ) that is leaching. Thus, the monolith was assumed immersed in  $2300 \text{ m}^3$  of water over the entire time span. This is a direct extrapolation of the laboratory static leach test

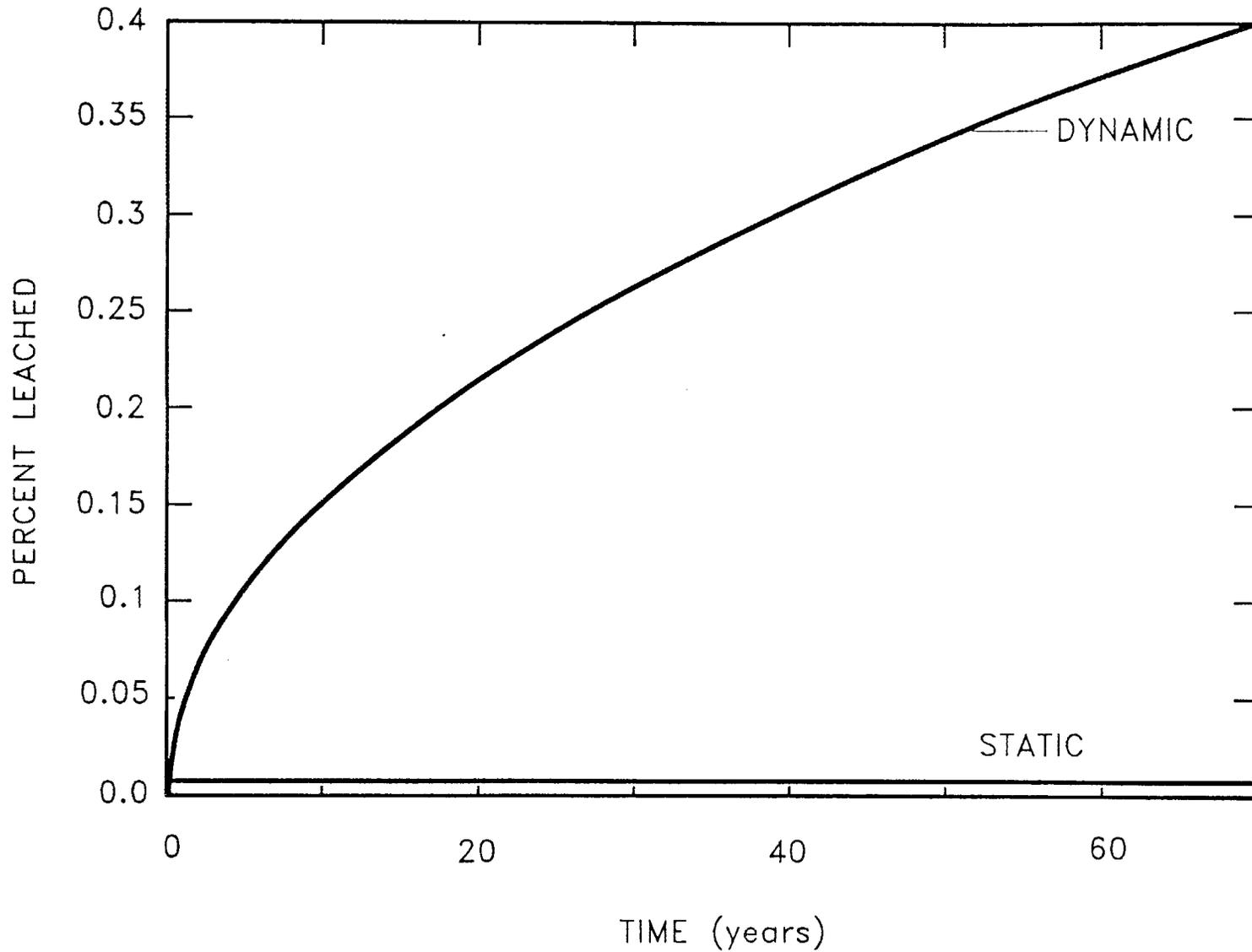


Fig. 19. Comparison of static and dynamic leaching from the sludge lagoon monolith for an LI of 9.4 and K of 628 (water volume of 2300 in.<sup>3</sup> and an initial sludge concentration of 130 mg/L for static leaching).

to site dimensions and longer times. The initial amount of contaminant in the entire volume of the sludge lagoon is important for this extrapolation, since an approach to equilibrium is involved. The original sludge lagoon volume was assumed to be at the highest reported concentration of any of the contaminants (130 mg/L for TCE; see Table 1), giving an  $A_0$  of 3.61 Mg (another extreme assumption compared to actual site conditions). While dynamic leaching continues throughout, leading to 0.4 wt % leached after 70 years, static leaching quickly approaches equilibrium at less than 0.006 wt %. Figure 20 expands the scales for the static leach case, illustrating how the amount leached levels off in less than a year. The shape of the static curve would be similar for different values of  $K$ , but the percent leached at equilibrium would be different. The equilibrium percent leached is defined as:

$$\text{Equilibrium percent leached} = 100(A_0 - A_f)/A_0. \quad (4)$$

Rearranging Eq. (2) and solving for the equilibrium percent leached yields:

$$\text{Equilibrium percent leached} = 100 \left[ 1 - \frac{1}{1 + \frac{V_l}{KV_s}} \right]. \quad (5)$$

Thus, the equilibrium percent leached is a function of only  $K$  and the ratio of the volume of leachate to the volume of the porous solid body

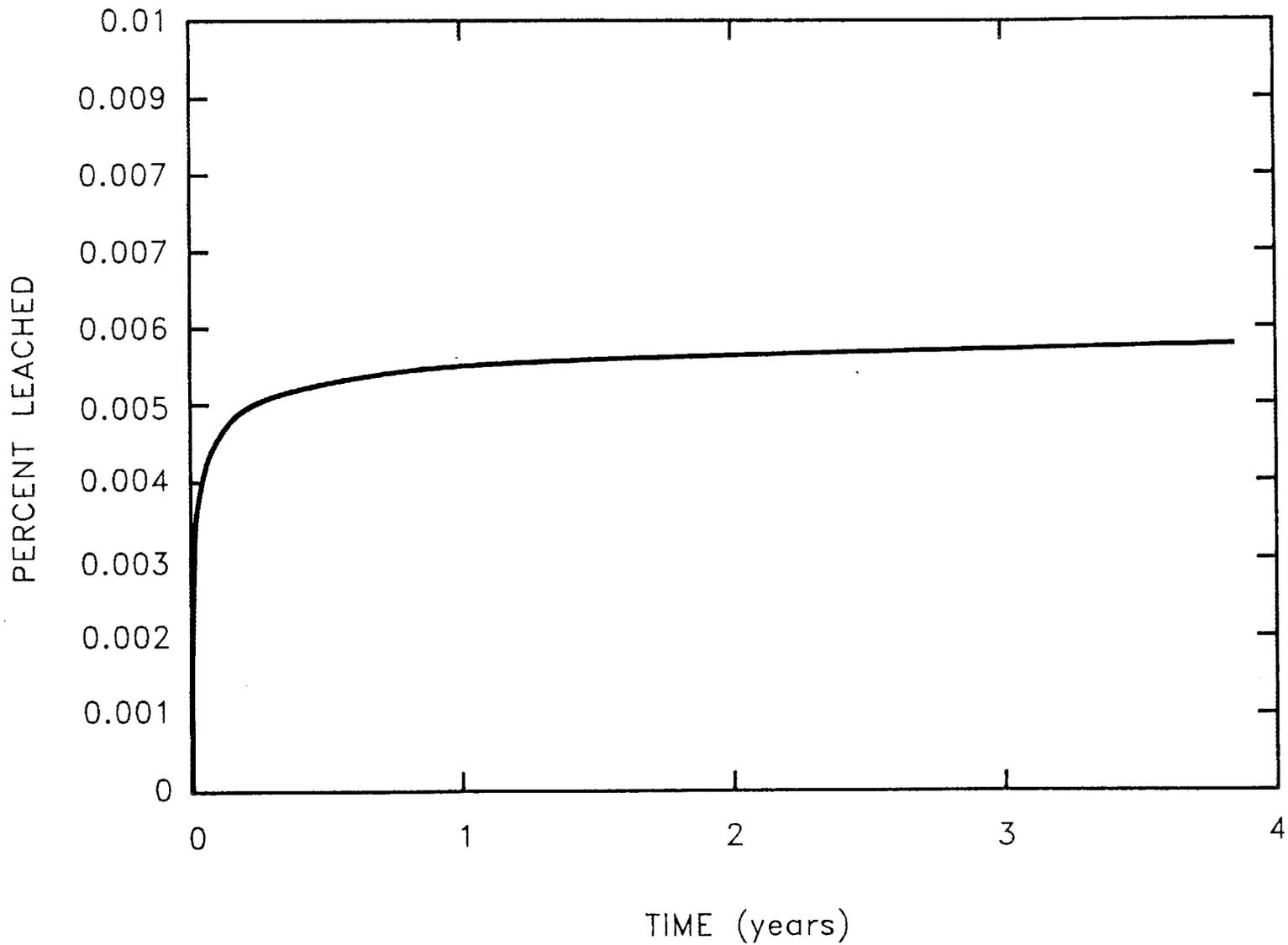


Fig. 20. Predicted static leaching of the sludge lagoon monolith for an LI of 9.4 K of 628, a water volume of 2300 in.<sup>3</sup>, and an initial sludge concentration of 130 mg/L (monolith volume of 61,059 in.<sup>3</sup>).

being leached. Figure 21 illustrates this dependence as a function of  $K$  for constant values of  $V_1/V_S$ . The bottom curve was calculated for the case extrapolated to the site with a  $V_1$  of 2300 m<sup>3</sup> and  $V_S$  of 61,059 m<sup>3</sup>. The static leach test had a  $V_1/V_S$  of 12.6. Note that for a  $V_1/V_S$  ratio of 0.04 the percent leached at equilibrium is relatively insensitive to  $K$ s in the hundreds. Only a few percent would be leached at equilibrium for a  $K$  as low as 1.0. With such a large disparity in volumes, the monolith should retain more of the species dissolved in its pore solution than is dissolved in the external water. Figure 21 does not reflect this realistic limit since 100% leaching was allowed in the calculation. (Realistically, leaching is limited to about 10 wt % for the proposed static leaching of the monolith). Thus, the affinity of a waste form for the species is important not only in helping to retard the rate of release but also in limiting the maximum water concentration in stagnant situations. (Note the difference in scale for each case: 20 wt % for an index of 6 and 0.4 wt % for an index of 9.4 for dynamic leaching, or a  $K$  of zero, and 0.006 wt % for an index of 9.4 and  $K$  of 628.)

Figure 22 illustrates the declining leach rate with time for all three cases. Note the initial rapid decline in rate followed by a fairly constant rate. The static leach rate with the large  $K$  quickly approached a negligible value, orders of magnitude below the other two cases. The two curves for dynamic leaching give the maximum leach rate at any given time for the selected indexes and monolith.

Figure 23 illustrates the effect of breaking the monolith up into 1000 pieces of equal size for dynamic leaching with an index of 9.4. The surface area would increase by an order of magnitude and the amount

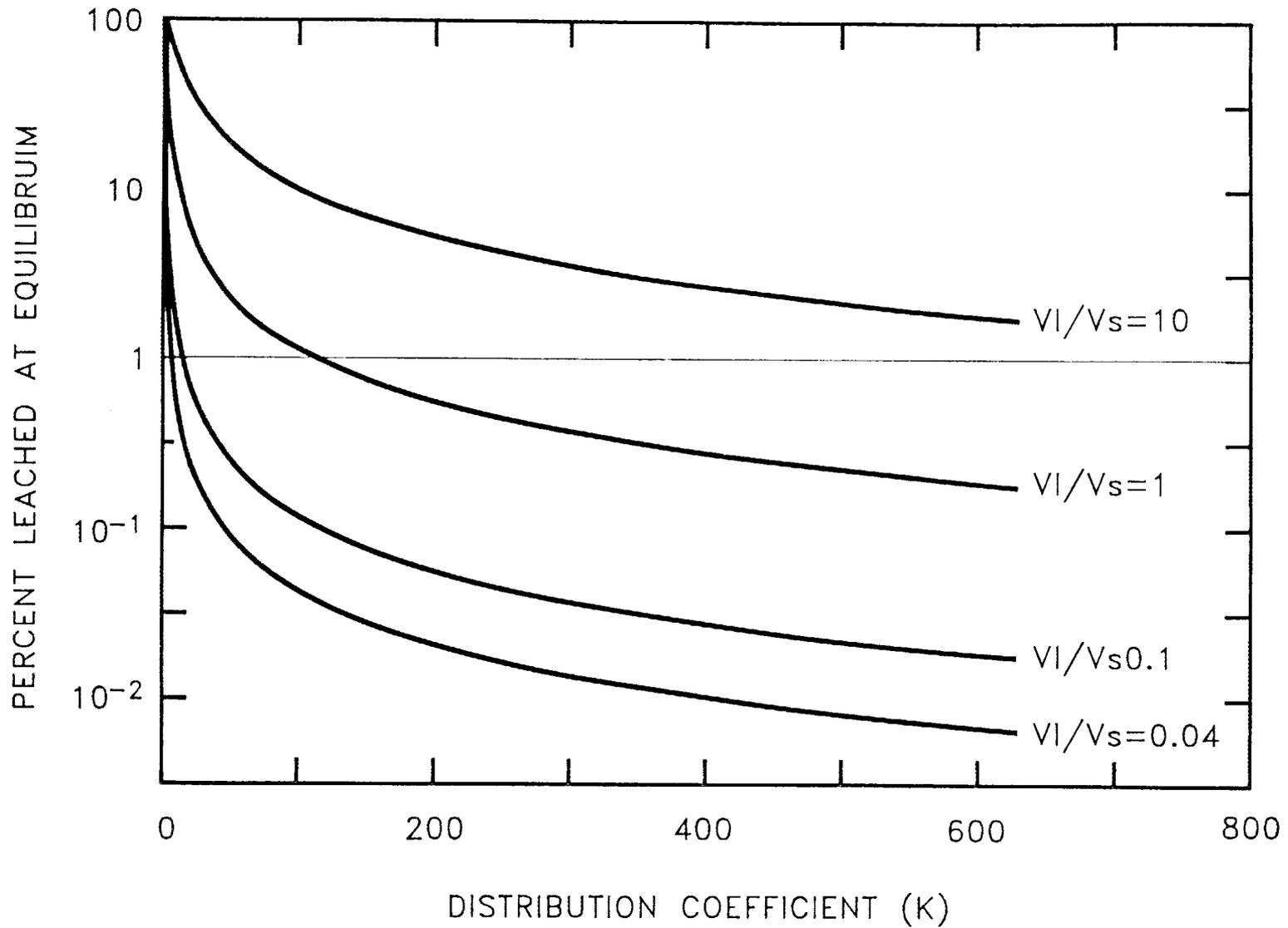


Fig. 21. Percent leached at equilibrium as a function of K and the ratio of the volume of leach water to the volume of monolith (this ratio was 0.04 for the extrapolation to the site and was 12.6 for the static leach test).

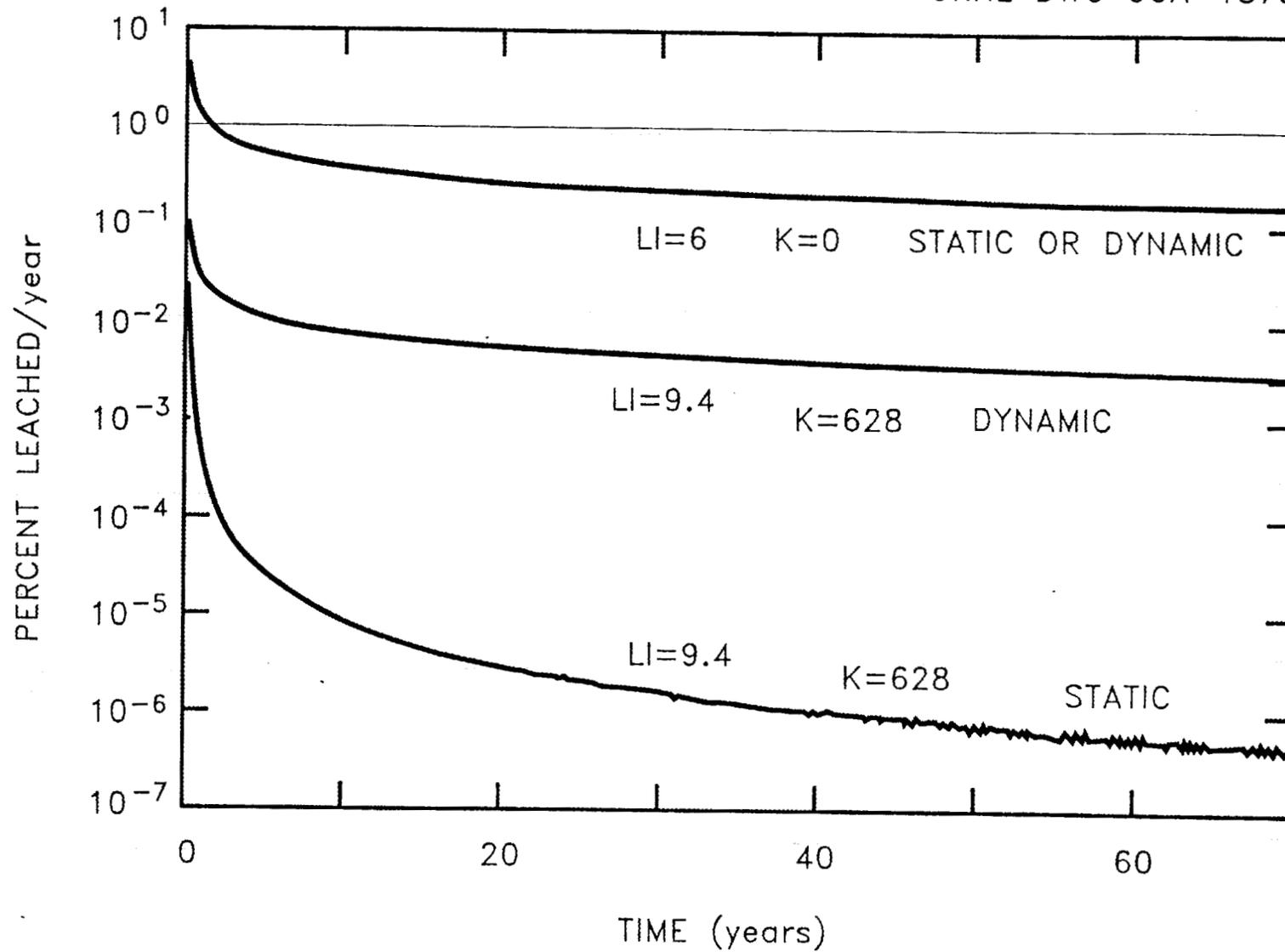


Fig. 22. Predicted leach rates for the sludge lagoon monolith (2300 in.<sup>3</sup> leachate and 130 mg/L in original sludge) for static leaching.

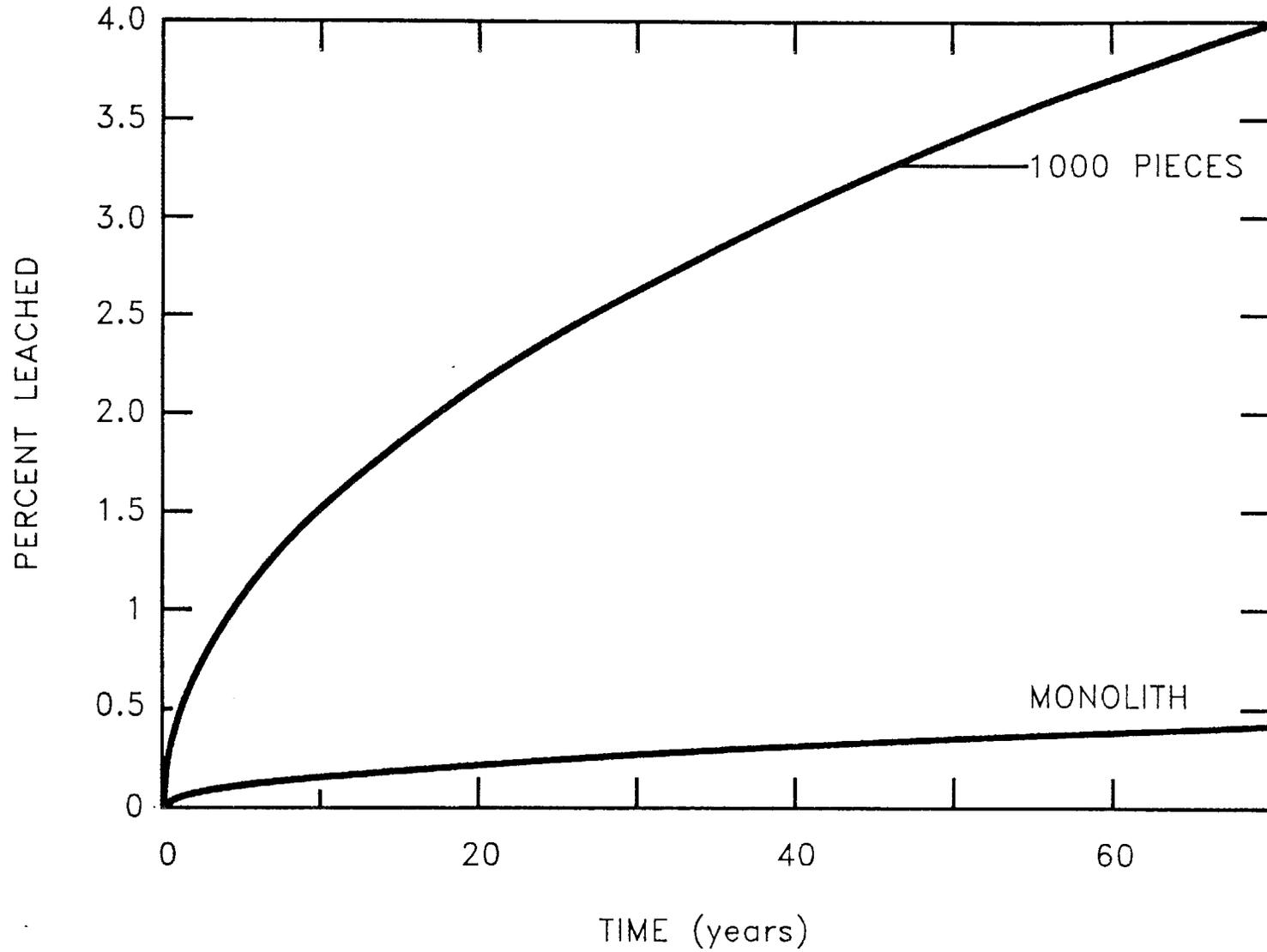


Fig. 23. The predicted dynamic leaching of the monolith compared to the predicted dynamic leaching after breaking the monolith up into 1000 pieces of equal size.

leached in 70 years would increase by an order of magnitude from 0.4 wt % to 4 wt %. In other words, breakup of the monolith will not necessarily lead to unacceptable increases in leaching. For the case calculated, the increase in leaching was proportionate to the increase in area, but the ratio of the number of pieces after breakup to the number before was equal to the ratio of the areas (and amount leached) cubed.

Groundwater velocities were reported for the site, and this information was combined with an extrapolation for dynamic leaching to generate an estimate of the level of groundwater concentrations that might be expected if the monolith were immersed in this groundwater. The velocities were converted into an estimate of volumetric flow rate of water that might reasonably be expected to come into contact with the monolith and disperse the contaminant. The projected underground area of the monolith was assumed to be a reasonable estimate of the amount of water involved (i.e., the amount of water that would have flowed through the lagoon if the monolith was not present and the lagoon was immersed as assumed for the calculation). This simple approach is not intended to replace more sophisticated hydrogeological models but to give a ballpark estimate. The projected area is about 1000 m<sup>2</sup>. The reported velocities of 30.5 to 244 m/year (100 to 800 ft/year) refer to the groundwater velocity through a porous media (soil) (i.e., most of the projected area will be occupied by soil). A reasonable void volume for porous media is 40 vol %; thus, assume 40% of the projected area is water, leading to a volumetric flow rate from about 12,000 to about 100,000 m<sup>3</sup>/year. Dividing the extrapolated leach rate by these two volumetric flow rates and converting to the proper units led to the estimated concentrations with

time downstream of the monolith plotted in Fig. 24. The extrapolated leach rate in this case was generated for a leachability index of 8 and a sludge lagoon concentration of 130 mg/L, both reasonable values for the VOC of most interest, TCE. (Note that the TCLP limit for TCE is 0.07 mg/L.)

The assumptions used to make these extrapolations are summarized below:

1. The leaching behavior for the monolith over 70 years is similar to that observed in the laboratory over several weeks. The laboratory behavior was bracketed with a leachability index and K of 6.0 and 0 to 9.4 and 628.
2. A sludge volume of 27,753 m<sup>3</sup> homogeneously contaminated with 130 mg/L of the given species requiring treatment.
3. A volume increase of 120 vol % during treatment.
4. A time range of 70 years was selected to be consistent with anticipated regulatory extrapolations.
5. The grout monolith was completely immersed in water, and leaching was from the surface only (i.e., no water flow through the monolith).
6. For static leaching, the water was limited to 2300 m<sup>3</sup> and was well stirred.
7. For dynamic leaching, the surface concentration was kept at zero.
8. For Fig. 24:
  - a. Maximum leach rate (by assuming zero surface concentration),
  - b. Water available for leaching limited to the projected area underground of the monolith, and
  - c. A leachability index of 8.

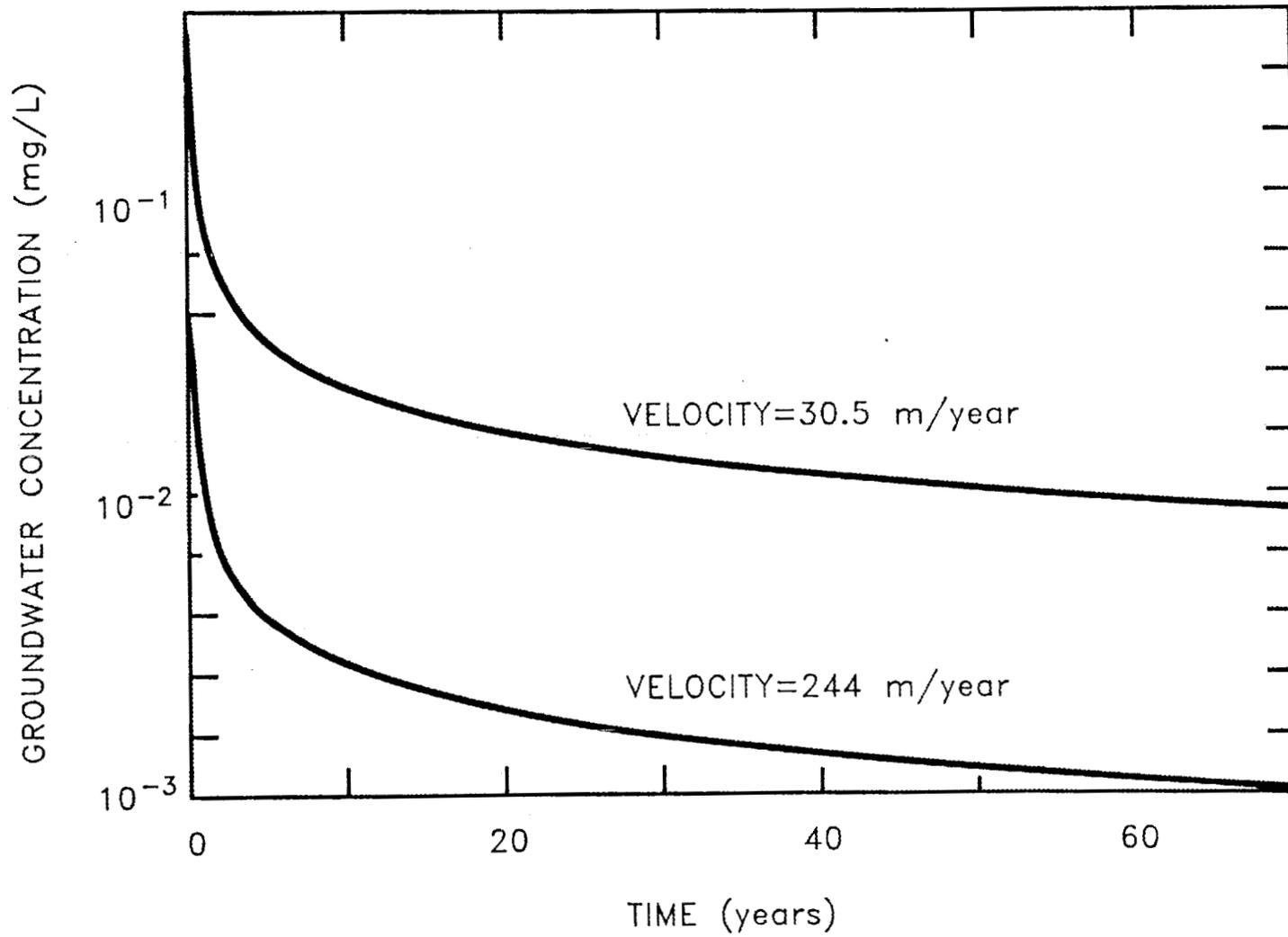


Fig. 24. Predicted groundwater concentrations for the dynamic leaching of the sludge lagoon monolith immersed in groundwater flowing at the reported velocities.

Collectively, this analysis shows that the most desirable grout formula would be characterized by low diffusivities (corresponding to high leachability indexes) and high distribution coefficients. In addition, the analysis indicates that release from a solidified lagoon is dependent on such site-specific parameters as monolith geometry, degree of monolith contact with water, and both the volume and flow rate of the water in contact with the monolith.

## 6. ENGINEERING EVALUATION

Results presented to this point have focused on laboratory-scale studies which addressed the ability of commercially available grout formulas to retard the release of VOC. Ultimately, for successful application to the RAFB site, grouting technology must meet all regulatory and performance criteria applicable to the site. Toward this end, a subcontract was issued to Automated Sciences Group, Inc., and EBASCO Services, Inc., to perform an engineering evaluation which addressed these issues. Specifically, the engineering evaluation was to (1) identify applicable regulations and performance requirements and assess their compatibility with grouting technology, (2) determine the availability of commercial grouting equipment and its compatibility with identified regulations and performance requirements, and (3) provide a preliminary estimate of the cost of implementing the technology at the site. The resulting evaluation is presented in Appendix A. Pertinent highlights of the evaluation are summarized as follows:

The regulatory requirements that govern activities at the RAFB NPL site are those defined by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and its amendments, the Superfund

Amendments and Reauthorization Act (SARA). SARA establishes the use of applicable, relevant, and appropriate regulations (ARARs) to set guidance criteria for cleanup and risk assessment standards at NPL sites. The Resource Conservation and Recovery Act (RCRA) and Clean Air Act (CAA) are possible ARARs that may be used at the RAFB site. CERCLA does not require environmental permits to be issued in order to leave remediated waste on-site. Under existing permits, RAFB is allowed to release up to 100 tons per year of VOCs, and they are currently releasing about 60 tons per year of VOCs. A conservative estimate of the maximum amount of VOCs in the sludge lagoon is less than 15 tons.

There are no standard-performance specifications for solidified or stabilized wastes; however, some typical criteria that can be used are that the treated material should pass the TCLP test and that the permeability of the treated waste should be about  $1 \times 10^{-5}$  to  $1 \times 10^{-7}$  cm/s or less. The use of on-site solidification/stabilization technologies has been accepted by the EPA as viable remedial actions for Superfund sites as well as for sites requiring RCRA closure. The Pepper Steel and Alloy, Inc., Superfund site was remediated using an out-of-ground solidification/stabilization technology. The Superfund Innovative Technology Evaluation (SITE) Program evaluated the use of Hazcon's solidification/stabilization process and concluded that this technology can immobilize heavy metals in a cost-effective manner.

There are in situ processes available for the remediation of the RAFB site. In situ methods vary widely, while the number of commercial vendors offering these services is very limited. Only one of the vendors, ENRECO, has demonstrated extensive experience in stabilization of hazardous wastes

by in situ methods; however, their particular process is potentially the least feasible for the RAFB site. Other in situ vendors either have had no experience remediating hazardous waste sites or have not used their proposed process equipment on a hazardous waste site to date.

Out-of-ground processes have been demonstrated to be the most capable in treating high-solids wastes. Contaminated soils and dry-waste solids are the types of materials found at the RAFB site. Effective out-of-ground process units are widely available from commercial vendors to treat these types of wastes. The lagoon is bordered on two sides by a swamp. Integrity of the excavation and water infiltration could be major concerns. VOC emissions from an out-of-ground process may have to be controlled.

Assuming that a grout can be successfully developed and its cost is reasonable, there is potential for this site to be remediated using in situ solidification/stabilization for less than an estimated \$5 million. If an out-of-ground process can be successfully used at the site with its supporting operations, the cost of remediation could be about \$3 million. Costs for design, procurement, site closeout such as capping and monitoring well installation, and maintenance of the site will add to these above projected costs.

## 7. SUMMARY AND CONCLUSIONS

The main objective of this project was to establish whether continued consideration of grouting technology as a remediation option for the RAFB sludge lagoon was justified from the standpoint of technical performance of the cementitious waste forms, current regulatory guidelines, and estimated economics of implementing this approach at the site. Evaluation

of the waste-form technical performance involved extensive laboratory study, while regulatory requirements and cost estimates were performed by Automated Sciences Group, Inc., and EBASCO through a subcontract.

Few regulatory guidelines and criteria were found that were directly applicable to this evaluation, although regulatory agencies reserve the right to accept or reject a chosen alternative. Grouting technology is a recognized remediation technology and has been approved by regulatory agencies in the past. It is the method of choice for wastes contaminated with metals (which are the predominant contaminants in the sludge lagoon) and is recognized as the best demonstrated available technology (BDAT) for wastes of this type. In addition, this technology received regulatory acceptance for remediation of a soil-waste contaminated with lead and PCB at the Pepper Steel site closure in EPA Region IV. Thus, although specific regulatory guidance applicable to evaluating the technology has not been found, there is a historical precedence to indicate regulatory acceptability.

Although grouting technology is generally accepted for wastes containing metals, the same cannot be said for wastes containing organics. The generally accepted method for dealing with organic wastes is destruction by some technique, such as incineration, which is the BDAT for organic wastes. Standard remediation techniques for wastes containing both metals and organics, such as in the lagoon, represent a nebulous category of wastes from a regulatory point of view, and the BDAT for wastes of this type has not been established. Wastes that are primarily contaminated with metals coupled with trace quantities of organics, such as the lagoon wastes, would, from a technical and economic point of view,

be more amenable to treatment by grouting rather than by incineration. In determining the applicability of grouting technology to such wastes, a critical question is: Does the resulting waste form sufficiently retard the release of the organics to meet protection of human health and environment objectives?

Consequently, the principal focus of this study was to assess the leachability of VOCs from the waste form. Toward this end, grout recipes from four commercial vendors, believed to be representative of the commercially available technologies, were obtained; samples were prepared; and the release of VOCs was evaluated in a series of static and regulatory (EP-Toxicity and TCLP) leach tests. Significantly, this study determined the VOC losses that occurred during the sample preparation procedure and corrected for these losses in determining the VOC content of the final grout product and its subsequent impact on interpretation of resulting leach data. Previous studies have often been deemed inconclusive by not accounting for these losses.

Although definitive regulatory guidance on the definition of acceptable leachability has not been found, a survey of case histories of previous applications of this technology to other sites indicates that meeting the regulatory criteria for a nonhazardous waste based on TCLP leach results may be a requirement. TCLP results have been presented for waste spiked with 1,2-dichloroethene, acetone, 2-butanone, trichloroethylene, tetrachloroethylene, chloroform, benzene, and chlorobenzene. Significantly, one waste form met the criteria for a nonhazardous waste based on TCLP for all constituents, despite spiking to levels approaching or exceeding site maximums. Trichloroethylene and/or

tetrachloroethylene were the two constituents that exceeded the TCLP limits for the other waste forms, and these waste forms would have passed if the TCLP extract concentration was corrected proportionately by the ratio of the maximum, or average, site concentration to the spiked concentration. Consequently, the data indicate that grouting technology can meet these criteria if it is applied to this site. Furthermore, the data also indicate that TCE can be viewed as the key constituent which should be monitored at the site to evaluate the effectiveness of this remediation option.

Evaluation of the VOC losses during grout sample preparation, as well as losses observed during acquisition of the site sample used in this study, clearly indicates that significant VOC losses will occur upon application at the site of any remediation option involving exhumation of the waste (e.g., out-of-ground grouting or incineration). That is, removal of VOCs from the waste and required treatment of these VOCs will predominantly occur during the exhumation step rather than during treatment of the material following exhumation (e.g., grouting or incineration). The authors believe that the concerns associated with this release of VOCs during implementation of the grouting option, both in terms of total amount released to the environment and safety concerns associated with worker exposures, can be minimized by application using in situ grouting techniques rather than the out-of-ground techniques. This belief is based on the fact that in situ application with its associated punching or drilling of holes through the overlying clay layer will facilitate the control of VOC release to the air environment as compared with bulk excavation. Therefore, it is recommended that in situ grouting

be utilized instead of the out-of-ground techniques. Preliminary cost estimates for in situ application to the lagoon are on the order of \$5 million. It must be recognized that, although numerous in situ techniques are commercially available, their application to waste remediation has been extremely limited. Consequently, application of in situ grouting technology to the sludge lagoon must be considered a demonstration of this technology.

In the evaluation of the static leach data, significant data scatter was observed. This data scatter was believed to be due primarily to the inadequacies of standard analytical techniques applied to this complex chemical matrix. These inadequacies will impact the evaluation of any remediation alternative, and the reader should be aware of this. Basically, these analytical techniques were developed specifically for analyses of water contaminated with trace quantities of organics and, in the majority of cases, were not developed to address the case of multiple organics at differing relative concentrations in the presence of waste sludge or grout. However, as these techniques represent standard, approved methods (by regulatory agencies such as EPA), they were used throughout this study.

Although some physical properties of the waste forms were measured and reported (all four formulations tested resulted in a monolithic product), the technical performance was evaluated mainly from the standpoint of the VOC-immobilization potential of the waste form as determined by static leach tests. Immobilization, in this sense, means retention of VOC or retardation of release to the leachant. Cementitious waste forms provide immobilization by a combination of a physical barrier

to diffusion and a chemical affinity for the species. Consequently, the leach data were used to determine both a diffusion coefficient and distribution coefficient for each of the species evaluated. The distribution coefficient is a measure of the chemical affinity of a species for the waste form. The diffusion coefficient is a measure of the mass-transfer resistance to release of the species from the waste form. Diffusion coefficients were reported as leachability indexes, which is the negative logarithm of the diffusion coefficient.

Because of the data scatter, a greater degree of confidence in the diffusion coefficients (leachability indexes) was achieved as compared with the distribution coefficients (see discussion in text). Consequently, the majority of the conclusions derived from the evaluation of the leach data are based on the leachability indexes. Simple diffusion through water of a species would correspond to a leachability index on the order of 5. A leachability index of 6 denotes the presence of a physical barrier that is measurably retarding the movement of the species [note that leachability index utilizes a logarithmic scale, and an increase in the index of one unit (e.g., increasing from 5 to 6) corresponds to a factor-of-10 decrease in the diffusion coefficient]. Although there are no EPA requirements with respect to leachability index, NRC requires a minimum leachability index of 6 for each radionuclide prior to disposal of low-level radioactive waste contained in a waste form. In general, the leachability indexes increase as the effectiveness of the physical barrier is increased up to index values between 7 and 8. Experience suggests that indexes above 8 denote alteration of the species to a less mobile form (e.g., through chemical conversion of the species to a different form or

strong chemical/physical interaction between the species and a constituent in the waste-form matrix), in addition to the presence of a physical barrier. For example, many metals contained in a cement-based waste form routinely exhibit leachability indexes greater than 8 because of the chemical alteration of the metals in the waste-form matrix to a relatively insoluble hydroxide form.

Not surprisingly, the leachability indexes obtained in this study varied from vendor to vendor and from compound to compound. However, the majority of the indexes obtained were between 7 and 8. Significantly, three of the four products tested resulted in a leachability index close to 8 (7.7 to 7.9) for the identified key component, TCE.

The fact that the majority of the indexes obtained were less than 8 (a few were in the range between 6 and 7) suggests that the dominant mechanism for retarding release is the creation of a physical barrier. As such, it is recommended that only grout formulas and implementation techniques that result in a monolithic product be considered. A monolithic product represents a more cohesive physical structure than a granular product and, hence, reduces access to the waste constituents by groundwater (the principal mechanism of contaminant release and transport to the environment).

This study has demonstrated that commercial grout formulations are available for retarding (i.e., controlling) the release of VOCs at the levels present in the sludge lagoon. In some cases, leachability indexes above 8 were obtained. As discussed previously, this would suggest that for some constituents, an alteration of the constituent to a less mobile form, in addition to the creation of a physical barrier, is achievable

with available commercial technology. Improvement over the indexes presented in this report may be possible upon formula optimization necessary to meet all of the sites objectives and constraints.

Although the data presented in this report indicate that grouting technology should receive continued consideration as a remediation option for the RAFB sludge-lagoon waste contaminated primarily with metals and, to a lesser extent, organics, the reader is cautioned against extrapolating these conclusions to other wastes/sites. As discussed previously, retardation of many of the organic constituents appears to be primarily due to the creation of a physical barrier. Assuming that the reported fraction of constituents released remains constant when applied to different waste VOC concentrations (a standard assumption in the absence of confirmation data), one can easily see that, at some higher VOC concentrations in the waste, this fractional release will result in unacceptable leachate concentrations.

#### 8. DOCUMENTATION

This report contains a summary of all data pertinent to the study. Additional raw data are contained in ORNL Technical Notebook Nos.: A-103015, A-103290-G, A-103417-G, A-103418-G, and A-103059-G.

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APPENDIX: ENGINEERING EVALUATION REPORT

This appendix contains a report prepared by Automated Sciences Group, Inc., and EBASCO Services, Inc.



IN SITU STABILIZATION STUDY  
ENGINEERING AND REGULATORY FEASIBILITY  
FOR  
ROBINS AIR FORCE BASE SUPERFUND SITE

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## ACRONYMS

ARARs	Applicable, Relevant, and Appropriate Regulations
ASG	Automated Sciences Group, Inc.
BNA	Base Neutral/Acid (extractable)
CAA	Clean Air Act
Cd	Cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
Cr	chromium
DSM	deep soil mixing
EBASCO	EBASCO Services, Inc.
EM	electromagnetic
EPA	Environmental Protection Agency
FS	Feasibility Study
GAEPD	Georgia Environmental Protection Division
HAZWRAP	Hazardous Waste Remedial Action Program
HCB	hexachlorobutadiene, hexachlorobenzene
MCL	Maximum Contaminant Levels
NPL	National Priority List
ORNL	Oak Ridge National Laboratory
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	lead
PCBs	Polychlorinated Biphenyls
PCE	Tetrachloroethylene (Perchloroethylene)
ppm	parts per million
RAFB	Robins Air Force Base
RCRA	Resource Conservation and Recovery Act
RI	Remedial Investigation
ROD	Record of Decision
SARA	Superfund Amendments and Reauthorization Act
SCO	Support Contractor Office
SITE	Superfund Innovative Technology Evaluation Program
SOW	Statement of Work
SSM	shallow soil mixing
TCE	trichloroethylene
TLV	threshold limit value
TSD	Treatment, Storage, and Disposal
VOC	Volatile Organic Compounds
WWTP	wastewater treatment plant

## EXECUTIVE SUMMARY

The on-site solidification/stabilization of hazardous waste has the potential to provide a regulatory acceptable and cost effective remedy for hazardous waste sites. Oak Ridge National Laboratory (ORNL) is conducting a study for Robins Air Force Base (RAFB) to evaluate the technical feasibility of using on-site solidification/stabilization with commercially available grouts to contain volatile organic compounds (VOCs) and heavy metals at the Zone 1 sludge lagoon adjacent to Landfill No. 4. This site is identified as a Superfund site on the National Priority List (NPL). This portion of the study is to evaluate regulatory issues, engineering feasibility, and prepare estimated costs associated with using this technology at the Sludge Lagoon. This report contains an analysis of in situ and out-of-ground solidification/stabilization technologies.

The regulatory requirements that govern activities at the RAFB NPL site are those defined by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and its amendments, the Superfund Amendments and Reauthorization Act (SARA). SARA establishes the use of applicable, relevant, and appropriate regulations (ARARs) to set guidance criteria for cleanup and risk assessment standards at NPL sites. The Resource Conservation and Recovery Act (RCRA) and Clean Air Act (CAA) are possible ARARs that may be used at the RAFB site. CERCLA does not require environmental permits to be issued in order to leave remediated waste on-site. The release of VOC from the site during remediation does not seem to be a problem from a regulatory standpoint regarding the total amount of VOC that can be released from a facility. RAFB is allowed to release up 100 tons per year of VOC, and they are currently releasing about 60 tons per year of VOC. A conservative estimate of the maximum amount of VOC in the sludge lagoon less than 15 tons.

There are no standard performance specifications for solidified or stabilized wastes; however, some typical criteria that can be used are that the treated material should pass the EP Toxicity test and that the

permeability of the treated waste should be about  $1 \times 10^{-5}$  to  $1 \times 10^{-7}$  cm/s or less. The use of on-site solidification/stabilization technologies have been accepted by the EPA as viable remedial actions for Superfund sites as well as sites requiring RCRA closure. The Pepper Steel & Alloy, Inc. Superfund site was remediated using an out-of-ground solidification/stabilization technology. The Superfund Innovative Technology Evaluation (SITE) Program evaluated the use of Hazcon's solidification/stabilization process and concluded that this technology can immobilize heavy metals in a cost effective manner.

Wastes treated by solidification/stabilization processes must not only contain the waste constituents to an acceptable degree as processed but the product must be able to meet requirements for its long term emplacement. Grout developed in a laboratory environment can meet these needs but this character must be reproducible by full scale hardware in a field setting. Product design parameters such as strength, swell, consolidation, creep potential, etc. must be set as well as leachability or rate of release of toxic species.

There are in situ processes available for the remediation of the RAFB site. In situ methods vary widely while the number of commercial vendors offering these services is very limited. Only one of the vendors, Enreco, has demonstrated extensive experience in stabilization of hazardous wastes by in situ methods; however, their particular process is potentially the least feasible for the RAFB site. Other in situ vendors either have had no experience remediating hazardous waste sites or have not used their proposed process equipment on a hazardous waste site to date.

Out-of-ground processes have been demonstrated to be the most capable in treating high solids wastes. Contaminated soils and dry waste solids are the types of materials found at the RAFB site. Effective out-of-ground process units are widely available from commercial vendors to treat these types of wastes. The Lagoon is bordered on two sides by a swamp. Integrity of the excavation and water infiltration could be major concerns. VOC emissions from an out-of-ground process may have to be controlled.

Assuming that a grout can be successfully developed and its cost is reasonable, there is potential for this site to be remediated using in situ solidification stabilization for less than \$5 million. If an out-of-ground process can be successfully used at the site with its supporting operations, the cost of remediation could be about \$3 million. Costs for design, procurement, site closeout such as capping and monitoring well installation, and maintenance of the site will add to these above projected costs.

## 1. INTRODUCTION

The Landfill 4/Sludge Lagoon at Robins Air Force Base, Georgia, (RAFB) was placed on the Superfund National Priority List (NPL) in August 1987. The sludge lagoon occupies a 1.5 acre corner of the 45-acre landfill site. This shallow sludge lagoon was used by RAFB from 1968 to 1978 for the disposal of various industrial wastes such as chlorinated and aromatic solvents, aircraft paint strippers, and electroplating solutions and sludges. The sludge lagoon, located adjacent to a swamp, has been backfilled for closure. Based on the Remedial Investigation (RI), the original excavated lagoon and the underlying peat layer are contaminated with heavy metals and volatile organic compounds (VOC) with the VOC being concentrated in the peat layer.

CH2M Hill performed the RI in 1986 and also prepared a draft Feasibility Study (FS) to evaluate options for the permanent remediation of the lagoon. The FS identified exhumation, thermal treatment, and off-site disposal of the residuals as the only permanent remediation option available. The cost for this exhumation option was estimated to be \$20 million. As an interim solution, a pump and treat (air stripping) process was proposed for removing VOC from the groundwater. The pump and treat option was estimated at \$500,000 for capital equipment and \$600,000/year for operating costs for an indeterminable number of years.<sup>1,2</sup>

To explore a more cost effective, permanent, remediation option, RAFB contracted Oak Ridge National Laboratory (ORNL) through the Hazardous Waste Remedial Action Program (HAZWRAP) to evaluate the technical feasibility of using an on-site solidification/stabilization technology as a permanent remediation option for the RAFB sludge lagoon site. This action was prompted by the successful application of an on-site solidification/stabilization technology for remediation of the Pepper Steel and Alloy, Inc. Superfund Site in Florida and its acceptance by EPA Region IV.<sup>3</sup>

The objective of the ORNL grout study for RAFB is to establish the technical and regulatory feasibility for applying an on-site solidification/stabilization technology for the permanent remediation of the RAFB sludge lagoon. The program is divided in five subtasks:

1. Perform a screening study to determine if commercial grout recipes are available that potentially will retard the release of VOC and heavy metals at the RAFB sludge lagoon;
2. Develop laboratory quality assurance/quality control (QA/QC) procedures which address the loss of VOC during sample handling and testing;
3. Assess the commercial availability and performance of grouting equipment for delivery of potentially viable grout recipes for waste solidification/stabilization;
4. Determine the likely site performance criteria for remediation of the RAFB sludge lagoon; and
5. Evaluate the overall applicability of grouting equipment/grout recipes for the RAFB sludge lagoon site including cost estimates for the on-site solidification/stabilization options.

Automated Sciences Group, Inc. (ASG), along with its subcontractor, EBASCO Services Inc. (EBASCO), was retained by HAZWRAP to provide support to ORNL for Subtask 3, 4, and 5. The objectives of the ASG/EBASCO project presented in this report are to:

1. Evaluate regulatory and performance requirements for on-site solidification/stabilization of the RAFB sludge lagoon site;
2. Review the application of on-site solidification/stabilization technologies at other Superfund sites;

3. Assess the availability of vendors and process options for performing on-site solidification/stabilization of the RAFB sludge lagoon site; and
4. Determine the approximate costs for on-site solidification /stabilization options at RAFB sludge lagoon site and identify issues that could affect cost and performance of this remedial option.

The information presented in this report was obtained from various publications including vendor literature, personal communication with vendors and regulatory agencies, and general knowledge and experience in waste management, remediation, and on-site solidification/stabilization processes possessed by the authors.

## 2. SITE DESCRIPTION

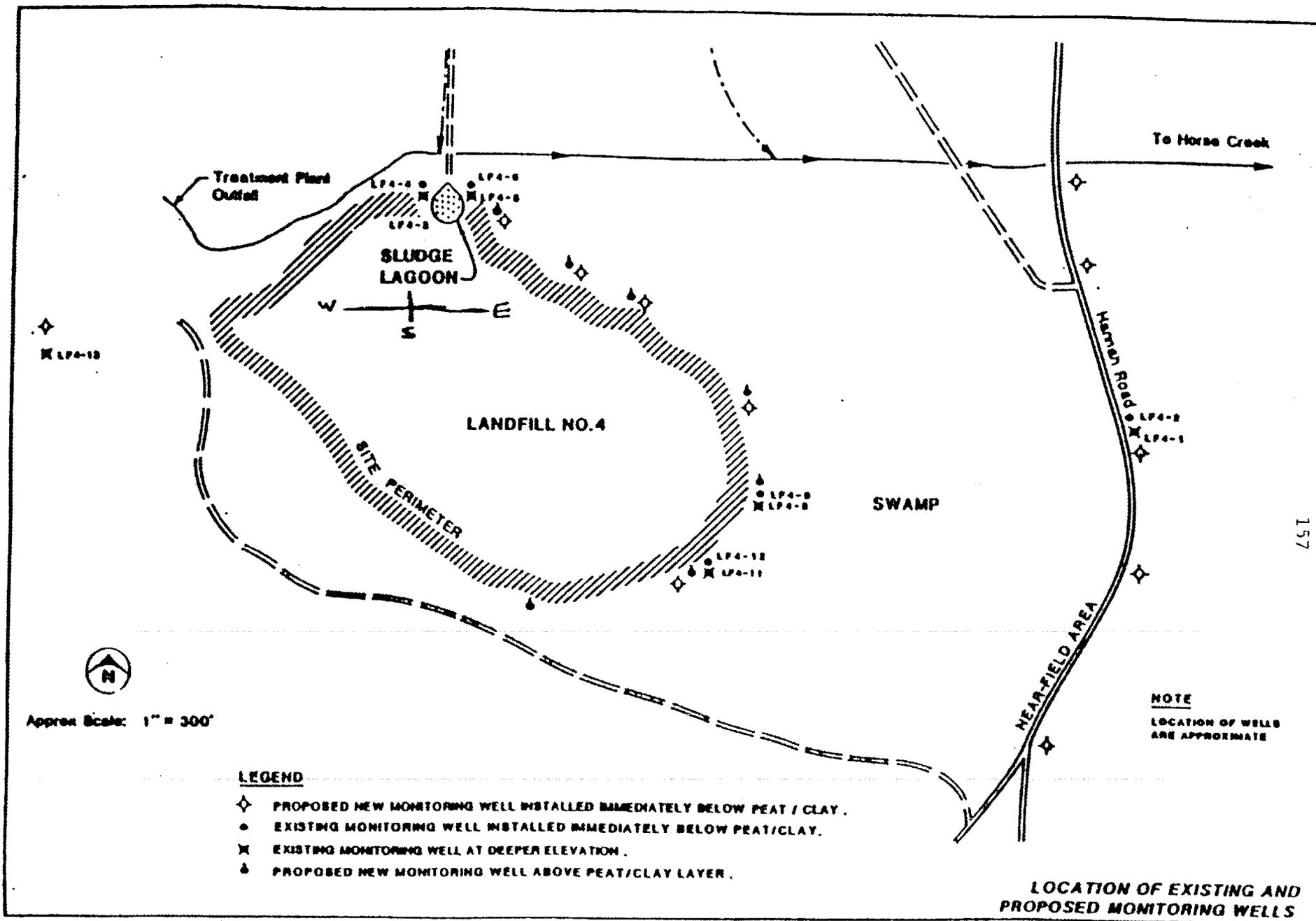
The Sludge Lagoon is a 1.5-acre area located on one corner of the 45-acre landfill site. The general site configuration is shown on Figure 2.1. The sludge lagoon is a 6-ft deep, unlined earthen pit which was formed by excavation, with the excavated soils used to form a berm around the lagoon. The lagoon was used from 1968 to 1978 for disposal of industrial waste primarily from electroplating and paint stripping operations. Upon completion of its intended use, the pit was closed by back filling with soil in 1978. The original berm around the pit is still evident on two sides; however, the berm on the other two sides blends in with the soil cap used to cover the entire landfill. Most of the site description information in this section was obtained from previous studies prepared for RAFB.<sup>1-6</sup>

The boundaries of the sludge lagoon within the landfill site were tentatively determined by an electromagnetic (EM) survey in July, 1986. The landfill was largely formed by the filling of a swampy area and was subsequently used for the disposal of general refuse, construction debris, limited amounts of putrescible waste, and reportedly, some industrial waste.

The close proximity of the landfill/lagoon to the underlying groundwater could enable some interactions between the landfill contaminants and the underlying groundwater. The general subsurface conditions at the landfill/lagoon site are shown in Figure 2.2. The landfill/lagoon apparently lies completely above the peat/clay layer which characterizes typical swamp-type geology of the area. Borings indicate that the peat/clay layer may also be discontinuous. The groundwater flow appears to be slightly upward in an easterly direction. The peat layer and potentially the bottom of the sludge lagoon are below the groundwater table during most of the year.

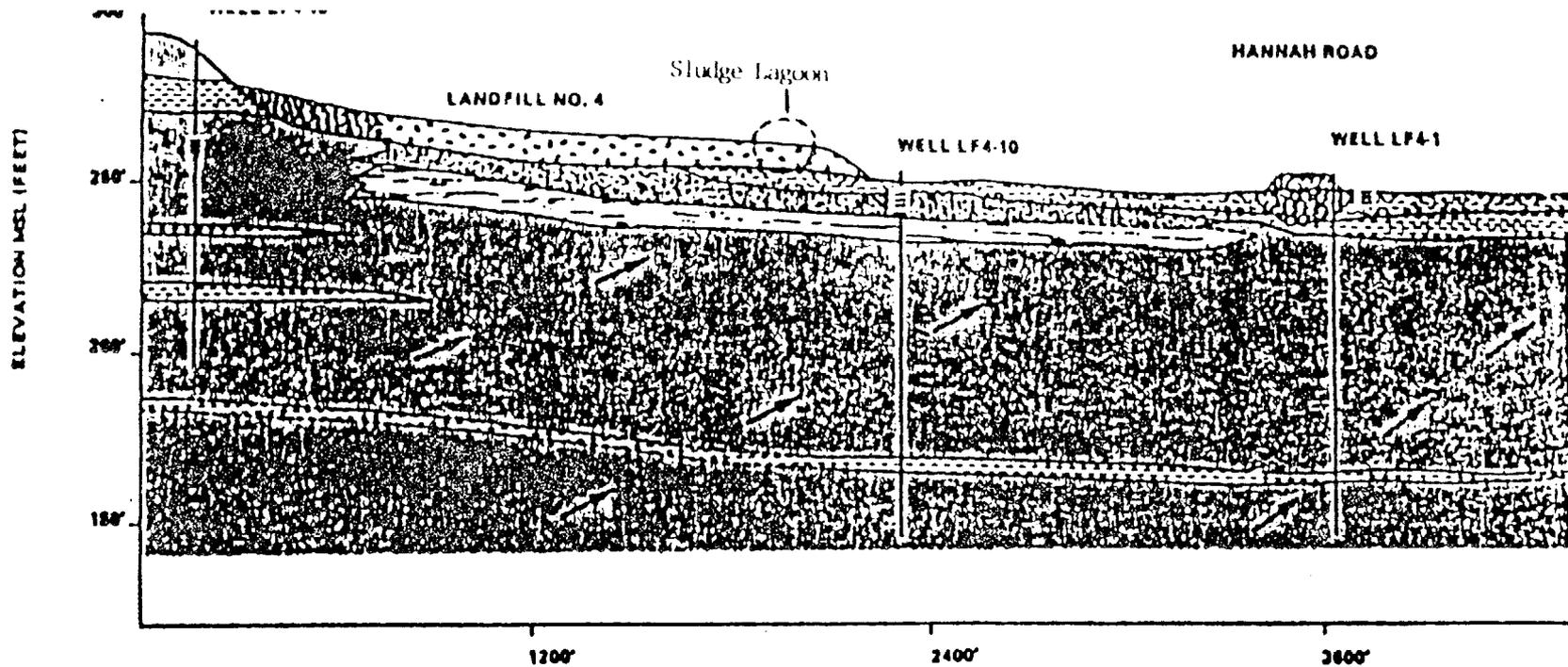
The principle contaminants found in the lagoon consist of heavy metals and VOCs. The VOC consist primarily of trichloroethylene (TCE) and the principle heavy metal contaminant is chromium (Cr). Borings into the peat/clay layer below the lagoon indicate that VOCs are concentrated in the

2-2



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Fig. 2.1. Site Map: Location of existing and proposed monitoring wells, Robins Air Force Base.



GENERALIZED EAST-WEST CROSS SECTION

LEGEND

-  SAND
-  CLAY
-  PRESENT LANDFILL MATERIAL
-  PEAT
-  SANDY CLAY
-  ORGANIC CLAY
-  FILL
-  APPROXIMATE DIRECTION OF GROUNDWATER FLOW

Source; AirForce IRP Phase II Confirmation/Quantification Report WAR 1985

Fig. 2.2. Subsurface conditions at Landfill 4/Sludge Lagoon, 1st bins Air Force Base.

peat layer. The physical properties of two sludge samples taken from the lagoon are shown below:

<u>Parameter</u>	<u>Sample 1</u>	<u>Sample 2</u>
Moisture	40.8%	54.4%
Loss on Ignition	10.2%	8.5%
Ash	49.0%	34.1%
Density	1.44 g/cc	1.28 g/cc
Ash Density	0.91 g/cc	0.86 g/cc
Flammability	Yes	No

## 2.1 REMEDIAL INVESTIGATION CONCLUSIONS

The general conclusions from the CH2M Hill Remedial Investigation which could affect on-site solidification/stabilization remediation are listed below.

1. The descriptions of the Sludge Lagoon depicted in 1968 and 1971 engineering drawings provided by RAFB personnel were consistent with field conditions encountered during this study. Those descriptions can therefore be used to evaluate sludge lagoon remediation criteria (e.g., volumes of material, placement of control systems, etc.).
2. The peat/clay bed underlying the landfill and lagoon appeared to be laterally persistent with a 5- to 14-ft thickness and an estimated permeability of  $10^{-4}$  cm/sec (based on previous field tests).
3. Groundwater flow generally parallels surface water flow (i.e., radially away from the landfill and toward the channelized ditch to the north of the site, east to Hannah Road, or south toward the swampy area).
4. No consistent groundwater gradient was measured across the peat/clay bed. Groundwater level measurements did indicate an upward gradient in

the aquifer zones underlying the peat/clay bed, most notably from the deeper zone to intermediate zone.

5. Groundwater elevations and the observed gradients indicate that, at best, the peat/clay bed acts to create semi-confining aquifer conditions in the zone underlying the bed.
6. The peat/clay stratum samples were compressible. This could result in significant settlement after installation of a cap or additional placement of fill.
7. The underlying sand stratum has a high hydraulic conductivity, measured in the laboratory at  $6 \times 10^{-4}$  to  $9 \times 10^{-3}$  cm/sec and estimated from field tests to be  $10^{-2}$  to  $10^{-3}$  cm/sec.
8. Existing cover materials exhibit laboratory permeability of  $2 \times 10^{-5}$  to  $5 \times 10^{-6}$  cm/sec and a field permeability of  $1 \times 10^{-4}$  to  $3 \times 10^{-4}$  cm/sec.
9. Surface cracks and gas migration (methane and non-methane organic compounds) were observed in the existing cover material.
10. VOCs were the major category of contaminants found throughout the site. Much higher levels of VOCs were observed in the sludge lagoon than in the landfill sediments. The VOCs were most concentrated in the peat bed for both areas.
11. VOCs were found at the landfill and lagoon perimeter in the groundwater zone just underlying the peat/clay bed. The highest levels were found near the sludge lagoon, indicating the sludge lagoon as the major source of VOCs.
12. Metals were found throughout the site but were detected at much higher levels in the sludge lagoon. EP Toxicity test results did not demonstrate leachable metals in soil and sediment samples.

13. Cadmium, chromium, and lead concentrations in groundwater samples above the peat/clay bed exceeded Maximum Contaminant Levels (MCLs) in areas surrounding both the landfill and lagoon. The MCLs for these metals are: cadmium (10 ppb), chromium (50 ppb), and lead (50 ppb).
14. Non-VOC organics were found mainly in the sludge lagoon area but were also prevalent in the landfill. PCBs and pesticides were found at both sites, but pentachlorophenol was found only in the landfill.
15. Cyanide was detected in both the landfill and sludge lagoon borings but only in the perimeter wells adjacent to the sludge lagoon. Cyanide was detected in the deeper upgradient well at the highest reported level and also at Hannah Road in several deeper wells (60 and 100 ft).
16. Based on the groundwater flow patterns indicated in this study and the presence of contaminants in groundwater just beneath the peat/clay layer, a groundwater plume is migrating from the landfill/lagoon area in an eastward direction. No conclusive data exist which demonstrate the plume has reached Hannah Road. A low level of TCE contamination was found in shallow groundwater at Hannah Road (well LF4-18) near the drainage channel, but it is not certain whether or not this originated from the sludge lagoon/landfill source. The cyanide found upgradient of the site, and at several deeper wells at Hannah Road, is not consistent with expected migration pathways based on the current understanding of groundwater flow.
17. Based on groundwater samples for the deeper zone wells, contaminants were present beneath the lagoon area to at least 60 ft but not to 100 ft.
18. Contaminants were detected at the wells considered upgradient of the landfill and sludge lagoon. This could indicate either a separate contaminant source or a groundwater flow pattern influenced by pumping from water supply wells on RAFB.

19. The maximum concentrations observed for the contaminants at the site are:

<u>Contaminants</u>	<u>Concentration (ppm)</u>
VOCs	375
Metals	7,832
Pesticides and PCBs	11
Base Neutral Acids	744
Organic Acids	219
Cyanide	1

## 2.2 SITE VISIT OBSERVATIONS

A site visit at the RAFB Landfill 4/Sludge Lagoon site was conducted on March 21, 1989, in order to better evaluate any factors that might effect the implementation of an on-site solidification/stabilization remedial option. A summary of the observations follow:

- o Access to the sludge lagoon is tightly controlled. The facility lies within a restricted entrance military base. The waste lagoon and landfill are isolated and surrounded by a fence with a locked gate. Much of the lagoon is also bordered by swamp area.
- o The sludge lagoon appears to have been constructed by excavating soil within the lagoon area. Excavated soil was then used as retaining berms for the perimeter of the lagoon. The top of the berm is nearly the same grade of the landfill area but is several feet above the swamp level. The berm appears to form only an immediate buffer between the swamp and the lagoon or the landfill and the lagoon.
- o The capped area and berms are about 1.5 acres in size with the entire cap depressed. Several hours of heavy rain had occurred on the morning of the site visit evidenced by numerous low pocket areas of standing water on the cap. The cap is breached several ft deep in a 10 X 30-ft area near the northern end of the lagoon. An area near the northeast

end of the lagoon the cap is eroded by several 2 X 2-ft channels from surface water drainage to the swamp.

- o The 10 X 30-ft breached area contains a few dozen, small, scrub trees. Otherwise, only scrub grasses exist on the cap.
- o The cap is littered with occasional asphalt chunks (10 X 10-in.) and other debris. A limited excavation in the northwest corner of the lagoon encountered debris such as pipes, hoses, and filters, but no large durable debris. A past EM survey indicated a number of metal objects.
- o Access to utilities such as water and electricity appears to be available from the adjacent wastewater treatment plant (WWTP) and garbage/trash processing areas. Adequate secure areas for processing equipment, storage, and office trailers are available for a solidification/stabilization operation.
- o According to the June 26, 1988, CH2M Hill sampling effort, the fill is stratified. The first 5 ft of fill consists of soil and a grey/white WWTP sludge. Fill at the 5- to 8-ft level consists of a dark, oily/grainy waste. Below the 8 ft levels a peat layer is underlain by a marl clay. Substantial emissions were noticed through measurement by Draeger tubes once the dark, oily/grainy waste was encountered.
- o The current RI for the landfill is now being conducted and will not be available for review until November 1989. The potential impact of the leachate on the treated waste will therefore not be known until then. The swamp area is expected to be naturally acidic. Leachate from the landfill is also likely to be acidic.
- o Excessive water infiltration to the lagoon area could likely result if excavation of the site is necessary.

### 3. REGULATORY ISSUES AND REQUIREMENTS

#### 3.1 GENERAL

The regulatory requirements associated with using on-site solidification/stabilization techniques, either in situ or out-of-ground, for the remediation of hazardous waste sites are very limited. The solidification/stabilization of waste containing heavy metals in a grout matrix is an accepted practice; however, the use of this technique to stabilize organics, including VOC, is still in the developmental stages. Research being conducted by the federal government and private companies to develop admixture grouts that can be used to stabilize materials containing VOC looks promising for minimizing the leaching of the VOCs from the stabilized material. Acceptance by EPA Region IV of an on-site solidification/stabilization remediation technique at the Pepper Steel & Alloy, Inc. Superfund Site in Florida prompted RAFB to consider the possible application of this option for the remediation of the sludge lagoon. There are several advantages to using on-site solidification/stabilization as a remedial action at this site. This technique will allow the waste to remain in place and on-site which will minimize waste handling and worker and public exposure. On-site solidification/stabilization can also provide a cost effective, permanent remedy. Uncertainties associated with the application of on-site solidification/stabilization technologies are the lack of acceptable performance criteria and verification procedures.

This section addresses several regulatory issues that must be considered when on-site solidification/stabilization grouting techniques are proposed for hazardous waste remediation.

#### 3.2 APPLICABLE REGULATIONS

The sludge lagoon is identified as a NPL site in accordance with the requirements of the CERCLA and its amendments, the SARA as defined in 40

Code of Federal Regulations (CFR) 300-302. The site is also identified by the State of Georgia as being subject to corrective action authority under the RCRA. The Environmental Protection Agency (EPA), in a final policy (54 FR 10520) issued March 13, 1989, stated that they would, in most cases, prefer to address sites under CERCLA, with an interagency agreement that may include the state as a party.<sup>7</sup> An interagency agreement is currently being developed by the EPA Region IV and RAFB.

In addition to the requirements of CERCLA that must be addressed when selecting a remedy, this site may require that sections of the CAA be reviewed because of the potential to release VOCs during the implementation of the remedial action.

### 3.2.1 CERCLA Requirements

CERCLA identifies the use of such technologies as grout curtains for groundwater control and solidification/encapsulation for the remediation of soils contaminated with hazardous materials/wastes. These technologies are addressed in 40 CFR 300.70. SARA, a CERCLA amendment, states in Section 121.b. that the remedial action must reduce the mobility of the hazardous constituents. The technology of in situ solidification/stabilization with a grout is designed to reduce the mobility of contaminants along with providing a cost effective remedial option. Section 121.d.4 of SARA allows for the use of technologies that can attain equivalent standards to proven remedial methods.

CERCLA does not require that federal, state, and local environmental permits be issued in order to leave the remediated material on the site. This is identified in 40 CFR 300.68(a)(3). The remedial alternative must meet the requirements that are established in the interagency agreement and the record of decision (ROD).

SARA establishes the use of applicable, relevant, and appropriate regulations (ARARs). It is the establishment of ARARs that may require the

selected remedial action to meet certain requirements that are applicable to RCRA and the CAA.

### 3.2.2 RCRA Requirements

The primary area of RCRA that might apply to this project is the standards in 40 CFR 261.24 that define the leachate concentration levels at which specific heavy metals become a hazardous waste. The EP Toxicity test is used to extract leachates from sludges and solid materials. As discussed previously, the Landfill 4/Sludge Lagoon site is currently being regulated under CERCLA authority, and a RCRA permit is not required in order to leave the remediated waste on-site. Section V of the RAFB Part B Permit, issued by the Georgia Environmental Protection Division (GAEPD) in September, 1988, addresses the NPL site and the need for corrective action.

### 3.2.3 CAA Requirements

No permit will be required to release VOCs during implementation of the remedial action. RAFB indicated in an air permit application filed in 1988 that they were releasing approximately 60 tons of VOCs per year with the allowable limit being 100 tons. This limit was established by the GAEPD for RAFB since the Base is located in an attainment area and no specific emission requirements are available for the operations that are performed at RAFB.<sup>8</sup>

It is anticipated that, during implementation of a solidification/stabilization technique, some amount of VOCs will be released. The amount of VOCs that may be released during remediation can not be realistically estimated. However, an extreme case estimate indicated that the air emission standards at the base would not be exceeded. The extreme case calculations were based on the assumption that 375 ppm of VOCs (the highest observed site concentrations) are evenly dispersed in the entire waste volume of the lagoon. The waste volume calculation assumes that the area of the lagoon is 1.5 acres, remediation to a depth of 15 ft, and a soil density of 80 lbs/cu ft, therefore establishing that there is about 36,000 cu yds of

waste to be remediated. Using this waste volume and assuming the 375 ppm VOC level is uniformly distributed throughout the material, 15 tons of VOCs are calculated to be present. If all 15 tons of VOC were released during remediation RAFB would not exceed the limit of 100 tons per year based on the current release of about 60 tons per year.

### 3.3 PERFORMANCE REQUIREMENTS FOR SOLIDIFICATION/STABILIZATION PROCESSES

No standards for testing stabilized/solidified wastes have been developed.<sup>9</sup> Due to this lack of standards, performance requirements will vary from site to site. Some of the common criteria used to evaluate solidified waste may include the EP Toxicity test for leachate extraction, permeability standards of less than  $1 \times 10^{-7}$  cm/s which are acceptable for soil liners used in landfill construction, and evaluation by a risk assessment that the remedy provides adequate protection of public health, welfare, and environment.<sup>10,11</sup> Based on information in the Enforcement Decision Document for the Pepper's Steel & Alloy, Inc. Superfund Site, the solidification/stabilization agent must undergo a development and testing program that demonstrates that the mixture exhibits satisfactory performance. Satisfactory performance will have to be determined by the EPA on a case by case basis since there are no standards available. Table 3.1 presents some examples of minimum suggested specifications and test procedures for solidified waste that are to be placed in landfills.<sup>9</sup> The suggested permeability specification of  $1 \times 10^{-5}$  cm/s in Table 3.1 is not as stringent as that discussed in the HAZCON SITE Demonstration document, a permeability of  $1 \times 10^{-7}$  to  $1 \times 10^{-5}$  cm/s is thus a range over which performance of solidified waste may be found acceptable; however, it is this kind of requirement that must be determined on a case by case basis.<sup>9,11</sup>

Permeability is a measure of a solids ability to permit the passage of water. The appropriate value will not only be site specific, but dependent on the desired performance specifications. It can be shown that when the permeability of the stabilized/solidified waste is at least two orders of

Table 3.1 Example of Specifications for Solidified Wastes

Characteristic	Recommended Value
Leachability	For Major toxic components leachability is greater than 6 using ANS 16.1. Must pass the EPA extraction procedure test
Risk assessment	Maximum possible concentration test.
Engineering design	Solid waste leaching procedure. Uniform leaching procedure
Free liquid content	No liquid exuded under maximum loading proposed in landfill design.
Reactivity	Nonreactive.
Ignitability	Nonpyrophoric. Flash point above 60°C using ASTM D-91-79 or D3278-78.
Biological activity	No microbial growth observed using ASTM G21 or G22.
Strength	Greater than 50 psi using ASTM D2166-66 or C109.
Permeability	Less than $1 \times 10^{-5}$ cm/s when measured using upflow triaxial procedure.
Durability	As required by site design. Measured using ASTM D560-57 and ASTM D559-57.
Physical stability	Will not allow unacceptable settlement under landfill design conditions.

\*M. John Cullinane, Jr. and Larry Jones, Hazardous Materials Control  
Vol 2, No. 2, 29 (1989).

magnitude less than that of the surrounding host soil, then groundwater preferentially flows around the waste rather than through it. Preliminary field permeability measurements on the peat/clay layer (the least permeable of the lagoon strata, see Section 2.1) indicate a permeability of  $10^{-4}$  cm/s; thus, for groundwater to preferentially flow around the stabilized/solidified waste, the field permeability of the waste would need to be  $10^{-6}$  cm/s. Typically, laboratory permeability measurements are one to two orders of magnitude less than those observed in the field. Consequently, a reasonable permeability specification for application to this site may be  $10^{-6}$  cm/s in the field or  $10^{-8}$  cm/s in the laboratory.<sup>17</sup>

Field QA/QC procedures will need to be developed in order to verify waste solidification/stabilization. The procedures should include guidance on sampling, testing, acceptable tests results, and ways to remedy problems that might occur during an on-site solidification/stabilization remediation, whether it is an in situ or out-of-ground process.

#### 3.4 REGULATORY ACCEPTANCE OF SOLIDIFICATION/STABILIZATION TECHNOLOGIES FOR NPL SITE REMEDIATION

The EPA has accepted the use of out-of-ground solidification/stabilization as a remedial action to be implemented at several Superfund sites. Table 3.2 identifies 16 NPL sites on which technology is the recommended remedial action as defined in the ROD for each of the sites. The Pepper Steel & Alloy, Inc. site is the only site that remedial action has been completed using the out-of-ground solidification/stabilization technology. To date no NPL site has been remediated using in situ solidification/stabilization. Discussion on seven of the NPL sites identified on Table 3.2 are presented in the following sections.

##### 3.4.1 Pepper's Steel & Alloy, Inc.

EPA Region IV accepted the use of a grouting technique to stabilize the waste at the Pepper's Steel & Alloy, Inc. Superfund Site in Dade County, Florida. It was the acceptance of using stabilization at a Superfund site

Table 3.2 Summary of Superfund Sites Using Solidification/Stabilization

Site Name/ Location	EPA <sup>1</sup> Region	ROD <sup>2</sup> Date	Contaminants							Waste Media	Generating Operation
			Pb <sup>3</sup>	Cr <sup>4</sup>	Cd <sup>5</sup>	VOC <sup>6</sup>	PCB <sup>7</sup>	ICE <sup>8</sup>	Other <sup>9</sup>		
Pepper's Steel & Alloy Medley, FL	4	3-12-86	X	X	X		X		X	Soil, Sediment, Groundwater	Manufacturing - Batteries, Fiberglass Boats, and Auto Repairs
Chemical Control Corp. Elizabeth, NJ	2	9-23-87				X	X		X	Soil	Hazardous Waste TSD <sup>10</sup> Facility
Liquid Disposal, Inc. Utica, MI	5	9-30-87	X		X	X			X	Soil, Groundwater	Commercial Liquid Waste Incinerator
Fields Brook Ashtabula, OH	5	9-30-86		X		X	X	X	X	Sediment	Various Industrial Sources
York Oil Company Moir, NY	2	2-9-88				X	X		X	Soil, Sediment	Oil Recycling
Commencement Bay Tacoma, WA	10	12-30-87	X			X	X		X	Soil	Coal Gasification Process
Northern Engraving Corp. Spartan, WI	5	9-28-87						X	X	Soil, Groundwater, Sludge	Metal Finishing Process
Independent Nail Co. Beaufort, SC	4	9-28-87		X	X				X	Soil, Sediment	Manufacturing - Plating
Gold Coast Oil Corp. Miami, FL	4	9-11-87	X			X		X	X	Soil, Groundwater	Solvent Recycling
Gould, Inc. Portland, OR	10	3-31-88	X			X				Soil, Sediment	Battery Manufacturing
Sapp Battery Alford, FL	4	9-26-86	X		X				X	Soil, Sediment, Groundwater	Lead Reclaimer
Geiger (C&M Oil) Site Rantowles, SC	4	6-1-87	X	X			X		X	Soil, Groundwater Surface Water	Waste Oil Incineration

Table 3.2 Summary of Superfund Sites Using Solidification/Stabilization (continued)

Site Name/ Location	EPA <sup>1</sup> Region	ROD <sup>2</sup> Date	Contaminants							Waste Media	Generating Operation
			Pb <sup>3</sup>	Cr <sup>4</sup>	Cd <sup>5</sup>	VOC <sup>6</sup>	PCB <sup>7</sup>	TCE <sup>8</sup>	Other <sup>9</sup>		
Mowbray Engineering Greenville, AL	4	9-25-86					X		X	Soil	Transformer Repair
Sand Springs Petro-Chemical Complex Sand Springs, OK	6	9-29-87		X		X			X	Sludge, Soil, Surface Water	Oil Refinery, Solvent Recycling, Transformer Repair
Marathon Battery Cold Spring, NY	2	9-30-86			X				X	Sediment, Surface Water	Battery Manufacturing
Western Processing Kent, WA	10	9-25-85		X	X	X	X		X	Soil, Sediment, Groundwater, Surface Water	Waste Recycling

1. EPA--Environmental Protection Agency

2. ROD--Record of Decision

3. Pb--Lead

4. Cr--Chromium

5. Cd--Cadmium

6. VOC--Volatile Organic Compounds

7. PCBs--Polychlorinated biphenyls

8. TCE--Trichloroethylene

9. Others: This may include any one or more of the following contaminants: arsenic, copper, manganese, mercury, zinc, antimony, nonspecified organic compounds, pesticides, base-neutral extractables, and non-specified metals.

10. TSD--Treatment, Storage, and Disposal

that influenced RAFB to pursue the study of in situ stabilization as a remedial alternative. This site was contaminated with PCBs and heavy metals. The heavy metal contamination was primary lead with concentrations in the soil as high as 98,000 ppm (9.8%). This is a considerably higher heavy metal contamination than is present at the sludge lagoon on RAFB which has about 7,800 ppm (0.78%) heavy metal concentration with the primary metal being chromium. The Enforcement Decision Document stated the this type of remedy was consistent with CERCLA, the National Contingency Plan, and a cost-effective remedy that provides adequate protection of public health, welfare, and the environment.<sup>10</sup> This site has been remediated using the out-of-ground solidification/stabilization technology.

#### 3.4.2 Chemical Control Corp.

The Chemical Control Corp. Superfund Site, located in Elizabeth, New Jersey, will use fixation (solidification) to treat about 18,000 cu yds of soil contaminated with heavy metals, organics, pesticides, and VOCs. This site is located in EPA Region II and the ROD is dated September 23, 1987.

#### 3.4.3 Liquid Disposal, Inc.

This Superfund site, located in EPA Region V, is in Utica, Michigan. The site is contaminated with barium, lead, cadmium, PCBs, semi-volatile organics, and VOCs. The remedial action will employ the use of solidification/fixation and air stripping of groundwater. The ROD is dated September 30, 1987.

#### 3.4.4 Fields Brook

This site in Ashtabula, Ohio, is contaminated with arsenic, chromium, mercury, PCBs, tetrachloroethylene (PCE), TCE, other VOCs, and zinc. The remediation of this site involves the thermal treatment of 16,000 cu yds of soils and the solidification and on-site disposal of 36,000 cu yds of contaminated soils. The date of the ROD was September 30, 1986.

#### 3.4.5 York Oil Company Site

This site in Moira, New York, is contaminated with metals, PCBs, phenols, and VOCs. The ROD, dated February 9, 1988, identifies this site to be remediated by using on-site solidification of about 30,000 cu yds contaminated soils followed by on-site disposal of the treated residuals.

#### 3.4.6 Commencement Bay--Nearshore/Tide Flats

The ROD, dated December 30, 1987, addresses source control of on-site contamination through excavation of contaminated soils and stabilization of these soils in a polymer/cement matrix. The stabilized matrix will remain on-site and be capped to reduce surface water infiltration. The soils are contaminated with lead, polycyclic aromatic hydrocarbons (PAHs), and VOC. This site, also known as the Tacoma Tar Pit Site, is located in Tacoma, Washington (EPA Region X).

#### 3.4.7 Northern Engraving Corp.

This site in Sparta, Wisconsin, is being remediated by excavation and solidification of soils and sludges contaminated with inorganics, metals, and TCE. The solidified material will be capped with RCRA cover and monitored for proper closure. The waste sludges are from a plating operation and may be similar to the site at RAFB. The ROD is dated September 28, 1987.

### 3.5 SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION (SITE) PROGRAM

The primary purpose of the SITE Program is to enhance the development and demonstration and thereby establish the commercial availability of innovative technologies applicable to Superfund sites. The SITE Program evaluated the use of the HAZCON solidification technology on waste from the Douglassville, Pennsylvania Superfund Site. The HAZCON process mixes the hazardous waste with cement, a proprietary additive called Chloranan, and

water. This process is an out-of-ground solidification/stabilization technique. The Chlororan is claimed to neutralize the inhibiting effect that organics normally have on the hydration of cement. The conclusions drawn from this project indicate that: (1) the process can solidify waste high in organics (25%); (2) heavy metals were immobilized with leachate reductions in excess of a factor of 100 in many instances; (3) organic contaminants, VOCs and BNA (base neutral/acid) were not immobilized for the most part, although instances where immobilization of organics occurred were observed in some studies outside the SITE Program; (4) a large volume increase can be expected where moisture contents of the wastes are low (average of 120% increase during the Demonstration Test); (5) the solidified material shows good structural results with high unconfined compressive strengths and low permeabilities; (6) microstructural results indicate a potential for degradation over the long term; and (7) the process is economical.<sup>11</sup>

### 3.6 RCRA SITES USING ON-SITE SOLIDIFICATION/STABILIZATION

The on-site solidification/stabilization of hazardous wastes at RCRA sites has been accomplished using both in situ and out-of-ground technologies. Table 3.3 identifies several of the sites, along with the major contaminants, that have been remediated using solidification/stabilization. In addition to the data on Table 3.3, brief summaries are provided on three of the sites.

#### 3.6.1 Ciba Geigy—McIntosh, Alabama

Ciba Geigy disposed of herbicide, pesticide, and other chemical and treatment process residuals for more than 30 years into approximately 20 lagoons on-site. In situ solidification/stabilization was chosen as the remediation method for some 450,000 yd<sup>3</sup> of the waste. Dry grout injection units were used to inject and mix the grout. Throughout the operation, perimeter air monitoring alarms were not affected. Spot checking at the solidification/stabilization process equipment revealed airborne contaminant

Table 3.3 Summary of RCRA Sites Using Solidification/Stabilization

Site Name/ Location	EPA <sup>1</sup> Region	Technology	Contaminants							Waste Media	Generating Operation
			Pb <sup>2</sup>	Cr <sup>3</sup>	Cd <sup>4</sup>	VOC <sup>5</sup>	PCB <sup>6</sup>	TCE <sup>7</sup>	Other <sup>8</sup>		
Ciba Geigy/ McIntosh, AL	4	In Situ processing				X				Liquids, Sludges	Chemical manufacturing, pharmaceuticals, pesticides herbicides
Martin Marietta/ Pascagoula, LA	6	In Situ processing				X			X	Sludges	Fuels operation
Chevron Facility/ San Francisco, CA	9	In Situ processing				X			X	Liquids, Sludges	Pesticides and herbicides manufacturing
Amoco/ Wood River IL	5	Out-of-ground processing	X	X	X	X			X	Liquids, Sludges	Petroleum processors
MBI/ Charlotte, NC	4	Out-of-ground processing							X	Sludges	Inorganic materials manufacture
Old/ Vickery, OH	5	In Situ processing	X	X	X	X	X	X	X	Liquids, Sludges	Deep well injection facility
Elger/ Tupelo, MS	4	In Situ processing	X	X	X				X	Sludges/Soils	Ceramic production facility
MBTA/ Boston, MA	1	Out-of-ground	X	X	X				X	Soils	Smelting operation
Marathon Steel/ Colorado	8	Out-of-ground	X	X	X				X	Slag/Soils	Smelting/ore refining
Olin Corp./ Alabama	4	Out-of-ground				X			X	Sludges/Soil	Chemicals manufacture

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1. EPA--Environmental Protection Agency
2. Pb--Lead
3. Cr--Chromium
4. Cd--Cadmium
5. VOC--Volatile Organic Compounds
6. PCBs--Polychlorinated biphenyls
7. TCE--Trichloroethylene
8. Others--This may include any one or more of the following contaminants: arsenic, copper, manganese, mercury, zinc, antimony, nonspecified organic compounds, pesticides, base-neutral extractables, and non-specified metals.

levels requiring OSHA level C personal protection. Those supporting the operation a distance from the process units required only the emergency availability of level C protection.

### 3.6.2 Martin-Marietta Facility--Pascagoula, Louisiana

Emissions at this facility were not considered to be a potential problem from a health and safety standpoint. A slurried grout injection system was used on these organic content process wastes and VOC and odor emissions were not found to be a concern.

### 3.6.3 Chevron Facility--San Francisco, California

The wastes to be processed were high water content petroleum sludges with arsenic contaminants as the principal concern. Quicklime was the major component of the grout reagent used in this in situ stabilization process. A temperature rise to over 200°F was found after reagent injection. The solidified waste was moved to a separate landfill area. However, the waste remained too hot for safe equipment handling purposes for more than eight hours afterward. Off-gassing was not documented but apparently was not a concern.

#### 4. SOLIDIFICATION/STABILIZATION PROCESSES

The general objectives of solidification/stabilization for on-site remediation are to provide for the isolation of the waste from groundwater and the physical and/or chemical entrapment of the waste, to destroy the waste species of concern by reaction, and to provide a stable base for the application of a closure cap. For the RAFB lagoon site, the primary objective of the solidification/stabilization process will be to provide for isolation of the heavy metals and VOC from the groundwater. Because of some concern for the release of VOC during remediation operations it is desirable that the technology provide for the containment of VOC within the waste mass if practical.

The technology of solidification/stabilization for on-site remediation can be divided into two general categories: (1) in situ and (2) out-of-ground. The following sections describe general requirements of solidification/stabilization processes and discuss the technologies applicability to the RAFB lagoon site.

##### 4.1 General Requirements

The successful and cost effective remediation by solidification/stabilization relies on evaluation and design of a successful grout and obtaining a suitable hardware system to blend the grout and waste together. Grout and hardware requirements must be matched with each other.

##### 4.1.1 Binders/Grouts/Reagents

Materials used to solidify and stabilize wastes are variously called binders, grouts, and/or reagents. For this document, the term grout will be used. Development of the grout to be used at the RAFB lagoon site is a task being addressed separately.

Grouts can be cementitious, pozzolanic, thermoplastic, or reactive. Highly specialized equipment able to control the pressure and temperature of waste and grout could be required for some grouts. This is generally not the case. For purposes of this study of solidification/stabilization implementation, hardware, and costs of implementation it will be assumed that the grout will be blended into the waste at site ambient conditions. Grout blends introduced under ambient conditions are dominant in use in the industry and are most cost effective.

The pozzolanic/cementitious grouts will likely be found to be successful in controlling the RAFB site waste. Such grouts are widely available from the construction and utility industries, usually geographically local, and in the high volumes needed.<sup>12</sup> Their costs are relatively low and the methods of delivery and storage well developed.<sup>13</sup>

In solidification/stabilization operations, grouts are delivered in either a slurried or dry form into the hardware's zone of mixing. The method of delivery is grout dependent upon hardware design, but most process units can be modified to accept either a pneumatic system of dry injection or wet injection. Wet injection usually improves the efficiency of blending the waste and grout especially for a high solids content waste.

Some grouts can become highly exothermic once wetted and combined with waste. This temperative effect must be considered in the choice of hardware and handling of the waste and treated residual.

#### 4.1.2 Product Design

The treated waste product must not only contain the waste constituents to an acceptable degree as processed, but the product must be able to meet requirements for long-term emplacement. Grout developed in a laboratory environment can meet these needs. However, hardware systems which blend the waste and grout must be able to reproduce in the field a product with characteristics the same as that produced in the laboratory. These product

design requirements and how they can be affected by the hardware system used are as follows:

Strength: Provide for sufficient compressive strength to support the maximum overburden expected for the landfill cell.<sup>14</sup>

The vendor hardware must achieve a homogenous mix of waste and grout to allow for the reproduction in the field of the strength and character found in the bench laboratory sample. This is especially important if the strength of the bench scale product is only marginal. The grout mix strength may or may not be easily and cost effectively supplemented by the addition of an inexpensive admix.

The water content of the grout/waste mix will also tend to greatly influence final setting strength of the treated product. High water content can leave voids in the treated product resulting in low strength. Low water content can also leave unreacted grout, again resulting in low strength voids in the product.

Free Liquid Content: Should allow no fluid expulsion after curing under the maximum vertical pressures expected in the landfill cell.<sup>14</sup> As with strength, a non-homogenous processing outcome will leave void, weakened areas and a place for pore liquids to accumulate.

pH: A high pH tends to reduce metals solubility in water minimizing the potential for metals migration from the solidification/stabilization mass.

Poor hardware mixing can leave untreated areas of waste with resultant undesirable leachate character.

The raising of the lagoon waste pH from its present pH of 5 to the potential pH 9 to 12 range will not involve the costly pretreatment operations that could occur in more acidic lagoons.

Swell Volume:

The volume of the waste is expected to expand from the grout and water addition as well as from the reaction between the grout and waste which follows. In situ mixing hardware also displaces the compacted waste and soil further expanding the treated volume. Out-of-ground units with the operations of excavation, processing, and replacement can produce a treated product with an even greater swell volume.

Volume swell is desirably minimal especially in an in situ application. For an in situ application a 30% grout load rate can typically produce a low 15% swell volume result. Swell volume results from an out-of-ground unit are typically slightly higher. A low 15% to 20% swell volume is likely acceptable for leaving the waste mass in the lagoon area.

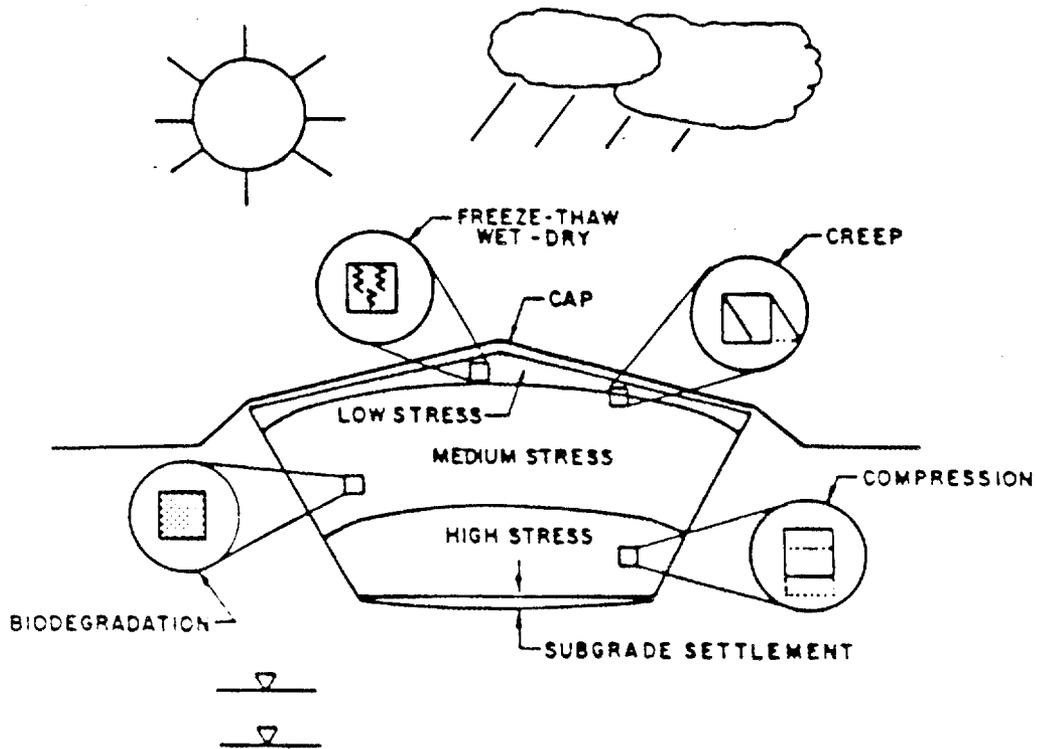
Creep Potential:

Time dependent deformation under stress. The treated product will deform to a degree once emplaced. This deformation potential should be taken into account in the final design to insure the overall integrity of the landfill.<sup>14</sup>

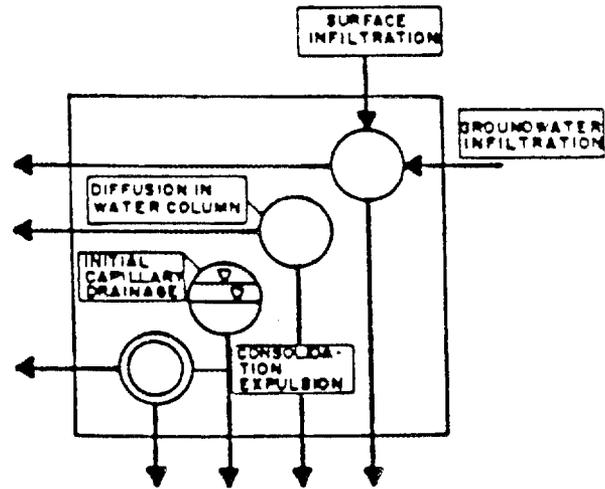
Again, hardware capable of reproducing an acceptable, similar character, bench scale product should be used.

- Consolidation: Expected reduction in volume as the product cures. This is usually a function of the overburden pressure of the landfill. This consolidation should be incorporated into the final design such that the elasticity limits of the landfill cap are not exceeded.
- Compaction Curve: For out-of-ground processing only. A relationship between the dry unit weight and the water content of the treated product.
- This should be established such that during processing an optimal as possible ratio of the two can be produced to allow for the most effective reemplacement of the treated product.
- Permeability, Leaching Potential pH Stability: These are most influenced by grout design. However, the vendor hardware used must be capable of reproducing a product similar in character to the bench scale treated product to stay within these performance parameters.
- Biodegradation: Organic components such as plant roots, sewage sludge, and trash in major proportions could affect the long term stability of the grout.
- Grubbing of the site can remove most near surface debris. A preprocessing separation operation may also be needed if such material is found in major amounts more than a few feet below the surface.

See Figure 4.1 for a summation of these product design concerns.<sup>14</sup>



LAND DISPOSAL ENVIRONMENT



LEACHATE GENERATION AND TRANSPORT MECHANISMS

EBASCO

Fig 4.1. Leachate generation and transport mechanisms.

#### 4.1.3 VOC Control

VOC loss may or may not be a concern at the RAFB site. Solidification/stabilization processes involve blending operations where waste and grout are mixed and new waste surfaces are exposed. Exposing the waste surfaces increases the possibility of VOC release. In addition, most grout formulations react exothermally with the liquid and waste being processed. A considerable amount of heat can be generated during the blending operation and for some time after as the mixture cures. A temperature rise to over 200°F, sustained for several hours, has occurred in past operations where highly exothermic blends have been used. This heat rise promotes the release of VOCs.

In the past, the level of VOC losses in a field solidification/stabilization operation have only been marginally addressed and documented. Part of this lack of resource data is a result of the low number of sites containing VOCs that have been remediated by solidification/stabilization. Lack of data is also attributed to the fact that VOCs, while present in the waste, were not measured for during many processing operations.

Protocols to control VOC loss from a sample in the laboratory during solidification/stabilization bench scale testing are not standardized. Thus, either VOC loss has been ignored during testing or methods to control or measure the loss have been different from study to study. Therefore, most bench scale testing data has not been useful for interpretation of VOC losses in field operations.

In situ VOC control during processing has an advantage over out-of-ground processing because it minimizes the exposure of waste surfaces during processing. In in situ processing there is no need for preprocessing operations such as sizing or debris removal either further recycling waste surface exposure and potential VOC emissions. The primary route of VOC loss during in situ solidification/stabilization processing is believed to occur through VOC entrainment in the grout feed stream. If dry grout feed operations are employed, pneumatic systems are used to convey and inject the

grout into the in-place waste. Through the combination of the mixing effect and heat rise, VOCs are mobilized in this injected air. The injected air escapes, carrying with it volatile species to the atmosphere.

Slurrying the grout prior to injection appears to eliminate the problem with air entrainment of VOCs. The ability to inject a slurried rather than a dry grout is within the capabilities of the vendors reviewed for this study. Liquid outflow of the grout/waste mix from the area of processing can then become a problem source of VOCs. The outflow of grout/waste product should be minimized if possible to reduce VOC losses by this route. Past solidification/stabilization projects where VOCs have been monitored for include:

Basin F—Rocky Mountain Arsenal—Denver, Colorado

A 400,000 yd<sup>3</sup> lagoon of wastes was solidified by an out-of-ground process operation. The wastes in the basin were generated over several decades by military operations to produce chemical reagents for battlefield use and by private companies manufacturing herbicides and pesticides. This area has been described as the most polluted square mile on the planet. During the entire operation, an extensive in-place set of air monitoring equipment was operated on the perimeter of the site as well as continual mobile checking within the site. No dangerous levels of contaminants were found to exit the site during this solidification/stabilization operation.

Ciba Geigy—McIntosh, Alabama

Ciba Geigy disposed of herbicide, pesticide, and other chemical and treatment process residuals for more than 30 years into approximately 20 lagoons on-site. In situ solidification/stabilization was chosen as the remediation method for some 450,000 yd<sup>3</sup> of the waste. Dry grout injection units were used to inject and mix the grout. Throughout the operation,

perimeter air monitoring alarms were not affected. Spot checking at the solidification/stabilization process equipment revealed airborne contaminant levels. OSHA level C personal protection was required at the process units. Those supporting the operation a distance from the process units required only the emergency availability of level C protection.

Martin-Marietta Facility--Pascagoula, Louisiana

Emissions at this facility were not considered to be a potential problem from a health and safety standpoint. A slurried grout injection system was used on these organic content process wastes and VOC and odor emissions were not found to be a concern.

Chevron Facility--San Francisco, California

The wastes to be processed were high water content petroleum sludges with arsenic contaminants as the principal concern. Quicklime was the major component of the grout reagent used in this in situ stabilization process. A temperature rise in the waste/grout mix to over 200°F was found after grout injection. The solidified waste was moved to a separate landfill area. However, the waste remained too hot for safe equipment handling purposes for more than eight hours afterward. Off-gassing was not documented but apparently was not a concern.

Petroprocessors--Louisiana

At Petroprocessors, operations had to be ceased due to uncontrollable and unacceptable levels of VOC emissions.

The site was a former solvents reclamation site. Unacceptable levels of HCB's (hexachlorobutadiene, hexachlorobenzene) were released as the material was exposed during excavation. Threshold Limit Values (TLV) on the perimeter alarms that were affected had

been set at a conservative 1/42nd. A foam system was used at the site to control emissions loss but did not effectively solve the emission problem.<sup>15</sup>

In past operations, both solidification/stabilization and other treatment operations, VOC controls have been used. The more successful ones used have been:

Misting/Spraying: Fine water sprays and limewater sprays and slurries have been used to control emissions on a project. The system is relatively easy to set up and inexpensive to operate. The mist or spray effectively "knocks down" emissions at their source. Limewater content sprays also can physically "knock down" emissions, neutralize acidic components of the emission, and coat the source waste thereby reducing the level of further emissions by a physical barrier. The added calcium content of the lime is also of benefit to some grout blends.

Foams: The many VOC foams on the market appear to work effectively. Specifically, the 3M Corporation FX 9161, 9162, 9163 foams and extenders. There are high density foams made especially to VOC organic waste applications. They provide a nearly impermeable barrier to VOCs. Foams are relatively easy to apply and can be mixed with extenders to last over 24 hours per application. Costs can be relatively low compared to the project total cost.

Tenting/Absorption/Flaring: Tenting the process area of the site has been used effectively in the past. The entrapped VOC can be passed through an adsorption media such as activated carbon or through a gas flare for cleaning the air. Costs can be high and workability of the project can be detrimentally affected.

Most literature references VOC controls as objectionable odor control operations undertaken for aesthetic rather than health and safety reasons.

It is therefore not possible to project VOC losses for the RAFB operation on the basis of VOC loss in past operations or from a bench scale study.

Past operations have, however, shown that VOC losses observed, measured as health and safety program data on solidification/stabilization sites, have been very low even with high VOC concentrations in the waste being treated.

#### 4.2 IN SITU PROCESSING

In situ processing of wastes has been widely used in the treatment of low viscous sludge type wastes. High solids content wastes have typically been treated by out-of-ground process systems. The RAFB lagoon waste is primarily a high solids, soil type waste.

The technology to process high solids content waste in situ has been recently developed. In situ grouting for stabilization of clean soils has been done for many years within the construction industry to improve the load bearing properties of soils. This high solids technology has been adapted for use in waste remediation primarily for the construction of cutoff walls around a site. It also appears to be suitable for waste and grout blending at a site.

In situ technologies tend to have the advantage over out-of-ground processing. Little or no waste preprocessing is required to remove debris or to reduce waste particle size. An additional advantage is that the lagoon does not have to be excavated. The disadvantages are a lower mixing effect, difficulty in controlling reagent loading and reducing particle size and the general problems associated with the remote, blind processing of a waste.

Verification of treatment of an in situ treated waste is primarily done by coring the treated mass. Typically a preset grid and required number of samples is determined for examination. Failure of a sample or number of samples can require that the volume be retreated. Considerations for

retreatment such as curing time and analytical turnaround time must be taken into account.

There are four basic processes available to in situ blend waste and grout. These processes and their applicability are discussed in the following sections.

#### 4.2.1 Trenching

Some of the largest operations to date have been done by backhoe type equipment. Primarily the work has involved only the solidification or absorption of liquids and not the true stabilization of the waste. Grouts are typically "dumped" on the waste mass surface or low pressure injected and worked into the waste with a backhoe bucket or specialized rack mounted arms attached to an excavator. Thorough mixing in a high solid waste substrate is difficult to effect. The open pit excavation effect can also lead to a high VOC loss compared to other in situ operations. Examples of this process are Enreco and Envirite.

#### 4.2.2 Low Pressure Injection

Low pressure injection is only viable for low viscous type wastes. It relies on the natural diffusion of grout into the waste with some added benefit due to movement of the injectors. This would not be viable at the RAFB site. An example is Envirite PF-5.

#### 4.2.3 High Pressure Injection

High pressure injection relies on the introduction of grout into the waste at a very high velocity thereby impinging on the soil/waste and shattering it, reducing the particle size of the waste and somewhat uniformly distributing the grout within the waste.

Processing with the Halliburton system is slow and expensive compared to other methods but appears to provide a very good level of mixing. Outflow

of excess grout/waste from the area of mixing a processed with their type unit may be an insurmountable problem also. An example is the Halliburton CCP process.

#### 4.2.4 Auger-Paddle Process

The auger-paddle process has been adapted from the construction industry where it has been used for improving the strength of soils. Grout is low pressure injected into the waste and a series of auger flights breaks the waste/soil in place. Rotating, shaft mounted paddles mix the waste and grout together.

The mixing effect and ability to affect a reduction in particle size are very good. This could be the most viable in situ process for use at the RAFB site. Examples are GEO-CON and SMW.

### 4.3 OUT-OF-GROUND PROCESSING

Out-of-ground solidification/stabilization technology has been widely developed and used for over 15 years. Out-of-ground processing relies on proven technology adapted from the chemical and commodity manufacturing process industry. Processing can be done in either a batch or continuous mode typically using mixing units such as ribbon blenders, shear bar mixers, pug mills and other rugged blending units.<sup>13,16</sup> The out-of-ground solidification/stabilization process market is well developed and highly competitive. Many vendors are able to supply hardware and service capabilities to meet specific process needs.

Out-of-ground processing has the advantage compared to in situ processing of high power input to achieve very efficient mixing, particle size reduction, and homogeneity. Out of ground processing also has high control of grout loading and other process variables that can affect the quality of the final treated product.

#### 4.4.1 Formulation Laboratories

- o Wastech Laboratories - Oak Ridge, Tennessee

To date, the Pepper Steel and Alloy, Inc. Superfund site is the only project Wastech have had known direct involvement with. Wastech is owned by Bellamy Brothers of Atlanta, Georgia. Wastech has no commercial vendor preference.

- o Silicate Technologies Corporation - Scottsdale, Arizona

Silicate Technologies' (STC) major project to date has involved the remediation of the Marathon Steel site for which they provided the grout design. STC utilized a processing system for this project that made use of truck-mounted concrete mixers. While not directly used by them, STC has a preference for in situ work by the low pressure injection/auger-paddle system.

- o IWT - Wichita, Kansas

RMC Laboratories - West Plains, Missouri

Both laboratories work closely together and have been involved in formulation attempts for a number of projects. The Hialeah, Florida, PCB stabilization demonstration is one example. IWT has a preference for low pressure injection/auger-paddle technology for in situ process purposes. RMC appears to have no preference.

Additional information on formulation laboratories and binder/grout/reagent sources is enclosed in Appendix A.

#### 4.4.2 In Situ Technology Vendors

Information is provided for these vendors on the following data forms.

- o Halliburton
- o SMW Seiko
- o Geo-Con
- o Enreco
- o Tone PCW
- o Envirite

IN SITU TECHNOLOGY

VENDOR NAME: Halliburton Industrial Services Division

PROCESSING SYSTEM: High pressure injection

NAME OF TECHNOLOGY: CCP Jet Grouting System  
(Compagnia Consolidament c Pali)

HANDLING CAPACITY/UNIT: 60 yd<sup>3</sup>/day

COSTS: Would not quote directly. Costs believed to be in the \$150/yd<sup>3</sup> range.

## TECHNICAL:

Advantages

- o Very high mixing effect
- o Very high particle size reduction effect

Disadvantages

- o Low processing rate
- o High waste/grout outflow, approaches 100% of volume
- o Relatively high cost
- o Potentially high VOC mobilization due to waste/grout outflow

## GENERAL DESCRIPTION:

There are three basic steps used in the CCP process: drilling, column formation, repetition.

First, a flush drill pipe with a special bit attached to it is used to drill to the desired depth. Drilling is done by the force of drilling fluid forced through the bit cutting and displacing soil and rock.

Next, the bit is closed to flow and grout is forced out laterally through jets immediately above the bit. Grout jetting pressure varies but is typically between 4,000 and 6,000 psi. The drill pipe is rotated continuously and withdrawn at about 1 ft per minute.

The grout slurry exiting the jets at its very high velocity impinges on the soil and shatters it for some distance from the jets. The grout slurry is then uniformly mixed into the waste.

The diameter of area affected is dependent upon factors such as waste and soil type, jetting pressure, jetting time, nozzle diameter, grout density and rotational speed. Typical range of effect is 24 in. to 48 in. diameter areas. Halliburton claims the area of effect is quite predictable so waste of grout is minimized.

There is a disadvantage in the major amount of outflow or overflow loss of grout and waste from the process area. Losses are roughly equal in volume to the volume being treated. This "carryout" or entrainment of grout/waste mix could make this unit unfeasible for use on this site.

#### OPERATING EXPERIENCE:

The CCP unit is a product of an Italian company known as CCP Italia and its Brazilian counterpart, Novatecna. The unit was developed in 1978 and therefore has roughly a 10 year operating history. Its primary use has been in making jet columns for stabilizing footings, tunnels, dams, placing tiebacks, etc.

Halliburton is currently the only licensed U.S. user of this technology. Halliburton will lease this equipment only with operational oversight by their employees.

#### VENDOR CONTACT INFORMATION:

Don McCabe, District Manager  
Houston, TX  
(713) 456-8288  
(409) 336-8191

Lindsey Lee, Sales Coordinator  
1415 Louisiana St., Suite 2300  
Houston, TN 77022  
(713) 552-6073  
(800) 433-5883

The CCP hardware units are warehoused at Halliburton's Houston location.

IN SITU TECHNOLOGY

VENDOR NAME: SMW SEIKO, INC.

PROCESSING SYSTEM: Low pressure injection/auger-paddle mixers

NAME OF TECHNOLOGY: SMW Technique

HANDLING CAPACITY/UNIT: 100 to 300 yd<sup>3</sup>/day

COSTS: Projected \$80 to \$150/yd<sup>3</sup> of waste treated

## TECHNICAL:

Advantages

- o Average process speed
- o Good mixing effect

Disadvantages

- o Moderate particle size reduction effect
- o No present hazardous waste site experience

## GENERAL DESCRIPTION:

The SMW SEIKO hardware unit consists of three to four overlapped auger-paddle shafts mounted on a crane. GEO-CON uses this similar design as their DSM technology unit. Auger-paddle sizes range up to 40 in. in diameter with an equivalent zone of mixing effect by them.

SMW Seiko has, as part of Seiko Kogyo of Japan, been operating in the United States since 1986. The equipment has been proven on over 1,000 construction projects. SMW Seiko equipment has the advantage over the Halliburton equipment in that grout overflow is minimal.

SMW Seiko will allow contractors to lease their equipment but only with operational oversight by one of their engineers on the project.

## OPERATING EXPERIENCE:

Seiko has no operating experience on hazardous waste sites to date.

They have although operated this equipment over a 17 year period on more than 1,000 construction projects.

VENDOR CONTACT INFORMATION:

David Yang, Environmental Project Manager  
Osamu Taki, President  
(415) 591-9646

1000 Martin Parkway, Suite 350  
Redwood City, CA 94065

Hardware system is warehoused (or would originate) from the Los Angeles area.

IN SITU TECHNOLOGY

VENDOR NAME: GEO-CON Inc.

PROCESSING SYSTEM: Low pressure injection/auger-paddle mechanicals

NAME OF TECHNOLOGY: DSM (Deep Soil Mixing) System

HANDLING CAPACITY/UNIT: DSM - 80 to 200 yd<sup>3</sup>/day

COSTS: \$80 to \$150/yd<sup>3</sup> of waste treated on fixed price lump sum contract.

## TECHNICAL:

Advantages

- o Average process speed
- o Good mixing effect

Disadvantages

- o Moderate particle size reduction effect
- o Some waste/grout outflow in area of processing

## GENERAL DESCRIPTION:

DSM System - The deep soil mixing system makes use of a crane supported set of leads which guide a series of hydraulically driven mixing paddles and augers. Grout is fed into the waste to be treated through the center of each shaft. The auger flights break the soil loose and lift it to the mixing paddles which blend the grout with the waste.

As the augers advance to a greater depth, the waste and grout are further mixed by the additional mixing paddles on each shaft. When the desired depth is reached the augers are withdrawn and the mixing process is repeated on the way up to the surface.

## OPERATING EXPERIENCE:

GEO-Con, Inc. has been in operation as a geotechnical construction company for 10 years.

The one large solidification/stabilization project they have accomplished is in Vickery, OH where a 240,000 yd<sup>3</sup> lagoon was treated. This work was done using backhoes as mixing equipment and not by use of their DSM or SSM systems.

The DSM is regularly used on construction projects to shore excavations, foundations, install tiebacks, etc. A pilot scale version of the DSM has been used for demonstration purposes at the Hialeah, Florida, PCB site to solidify/stabilize some of the waste. At least two projects have involved the installation of cutoff walls at waste sites. Treatment of an entire site waste volume has not yet been done with the DSM equipment.

VENDOR CONTACT INFORMATION:

Jeffery J. Goldin, Marketing Manager  
(412) 856-7700

P.O. Box 17380  
Pittsburgh, PA 15235

Offices in Texas, California, and Florida also. Equipment warehoused in the Pittsburgh, Pennsylvania area.

IN SITU TECHNOLOGY

VENDOR NAME: GEO-CON Inc.

PROCESSING SYSTEM: Low pressure injection/auger paddle mechanicals

NAME OF TECHNOLOGY: SSM (Shallow Soil Mixing) System

HANDLING CAPACITY/UNIT: 100 to 300 yd<sup>3</sup>/day

COSTS: \$80 to \$120/yd<sup>3</sup> of waste treated on fixed price lump sum contract.

TECHNICAL:

Advantages

- o Average process speed
- o Potentially very good VOC control
- o Precise grout loading capability

Disadvantages

- o Moderate particle size reduction effect
- o Slow process rate compared to out-of-ground technology

GENERAL DESCRIPTION:

SSM System - The shallow soil mixing system utilizes a crane-mounted mixing system. The auger and paddle mixing head is enclosed in a bottom-opened cylinder to allow for a near closed-system mixing of the waste and grout. Treatment grouts can be introduced dry or in slurry form by an injection system separate from the mixing unit. Due to the closed nature of the system, grout loading rates can be much more precisely controlled than with other in situ systems. Also, because it is a closed system, VOC emissions will likely be less and will be more easily controlled than that of other systems.

OPERATING EXPERIENCE:

GEO-Con has a moderate amount of experience operating on hazardous waste sites. The one large project they were involved in used backhoes as the mixing equipment to solidify a 240,000 yd<sup>3</sup> lagoon. The SSM system is a recently designed piece of equipment which has not been tested full scale on a waste site yet but appear to be promising for the remediation of the RAFB site.

VENDOR CONTACT INFORMATION:

Jeffery J. Goldin, Marketing Manager  
(412) 856-7700

P.O. Box 17380  
Pittsburgh, PA 15235

Offices in Texas, California, and Florida also. Equipment warehoused in the Pittsburgh, Pennsylvania area.

IN SITU TECHNOLOGY

VENDOR NAME: ENRECO Corporation

PROCESSING SYSTEM: Low pressure injection/rack mounted rake arms

NAME OF TECHNOLOGY: In Situ Solidification Unit  
Soil Mixing Unit

HANDLING CAPACITY/UNIT: In Situ Solidification Unit  
500 to 800 yd<sup>3</sup>  
Soil Mixing Unit - 300 to 600 yd<sup>3</sup>

COSTS: Willing to bid projects on a lump sum, fixed price unit basis.  
Costs range from \$40 to \$90 yd<sup>3</sup>.

## TECHNICAL:

Advantages

- o Potential low cost
- o Fast processing
- o No waste/grout outflow

Disadvantages

- o Need for some excavation of site
- o Low mixing effect
- o Negligible particle size reduction effect
- o Likely greatest potential to mobilize VOC's of all in situ processes

## GENERAL DESCRIPTION:

ENRECO uses rack mounted injectors attached to an excavator arm to treat hazardous wastes. Injection of the grout is at the forward end of each series of injector arms. During injection the excavator moves the injector arms in a reciprocating motion to blend the grout and waste together. Zone of mixing is limited to 7 ft or less from the surface.

The Soil Mixing System is a heavy duty version of the above system with shorter, reinforced injector arms. Injection and mixing are accomplished in much the same way, but the effective depth of mixing is limited to 5 ft or less from the surface.

To accomplish in situ solidification/stabilization of impoundments greater than a 5- to 7-ft depth, ENRECO treats wastes in layers. Layers 5- to 7-ft deep of wastes are treated, and the cured waste is pushed to the side. The untreated volume is then treated.

## OPERATING EXPERIENCE:

ENRECO corporation has treated wastes on over 180 projects with 80 of them involving hazardous wastes. ENRECO has been in operation since 1982 and is the largest solidification/stabilization company in terms of revenues.

Work has included projects as large as 200,000 yd<sup>3</sup> of both organic and inorganic species.

IN SITU TECHNOLOGY

VENDOR NAME: Tone Boring Co.

PROCESSING SYSTEM:

NAME OF TECHNOLOGY: Tone PCW System  
Tone BW System  
Tone BWN System

HANDLING CAPACITY/UNIT:

COSTS:

TECHNICAL:

AdvantagesDisadvantages

- o Much literature search has turned up documents on the system but no known U.S. based contacts or equipment.

GENERAL DESCRIPTION:

Innovative boring and in situ machinery of various types. Development has been in Japan. Equipment would not appear to have any advantages for implementation over other currently available equipment from other vendors.

OPERATING EXPERIENCE:

VENDOR CONTACT INFORMATION:

IN SITU TECHNOLOGY

VENDOR NAME: ENVIRITE

PROCESSING SYSTEM: Low Pressure Injection

NAME OF TECHNOLOGY: PF-5 system

HANDLING CAPACITY/UNIT: 100-200 yd<sup>3</sup>/day

COSTS: Treatment costs are \$25 to \$60/yd<sup>3</sup>

## TECHNICAL:

Advantages

- o Low cost
- o Easy to implement process on liquid sludge wastes

Disadvantages

- o Low mixing effect
- o Cannot process high solids/viscous materials

## GENERAL DESCRIPTION:

The Envirite system is a collection of approximately five low pressure injection tubes. Injected grout is dispersed into the waste mostly by diffusion and some movement of the injection tubes by the excavator or backhoe to which they are attached.

The Envirite system is applicable to low viscosity sludges and liquid lagoons. The system would not be effective at the RAFB site.

## OPERATING EXPERIENCE:

N/A

## VENDOR CONTACT INFORMATION:

Edward Shuster, Marketing Manager  
(404) 876-8300

1447 Peachtree St., N.E.  
Suite 810  
Atlanta, GA 30309

#### 4.4.3 Out-of-Ground Process Technology Vendors

Information is provided for these vendors on the following data forms.

- o Aces-Envirosafe
- o Chemfix
- o Chem-Met
- o Stablex
- o Hazcon
- o OHM
- o Qualtec
- o Solidtek
- o SRS

OUT-OF-GROUND TECHNOLOGY

VENDOR NAME: Aces-Envirosafe

PROCESSING SYSTEM: Pugmill

NAME OF TECHNOLOGY: ETI System

HANDLING CAPACITY/UNIT: 300 yd<sup>3</sup> to 1,000 yd<sup>3</sup>/day

COSTS: \$40 to \$80/yd<sup>3</sup> of waste to be treated

TECHNICAL:

Advantages

- o Fair mixing capability
- o Greater than average process speed

Disadvantages

- o Mixing capability lower than most pugmill systems
- o Relatively large unit for the site size
- o Fair grout loading control

GENERAL DESCRIPTION:

Envirosafe uses a pugmill system adapted from a large scale concrete production mill. While production rate may be higher than most, the desired mixing effect may not be as good as other out-of-ground pugmill systems.

OPERATING EXPERIENCE:

The Envirosafe process has existed in one form or another for 13 years. The solidification/stabilization group is backed by an effective hazardous waste service organization with much relevant experience.

VENDOR CONTACT INFORMATION:

John J. Colussi  
(215) 962-0800

900 East 8th Avenue, Suite 200  
King of Prussia, PA 19406-0956

OUT-OF-GROUND TECHNOLOGY

VENDOR NAME: Chemfix Technologies, Inc.

PROCESSING SYSTEM: Pugmill

NAME OF TECHNOLOGY: Chemfix process

HANDLING CAPACITY/UNIT: 300 to 800 yd<sup>3</sup>/day

COSTS: \$50 to \$90/yd<sup>3</sup> for high solids content wastes

## TECHNICAL:

Advantages

- o Excellent mixing effect
- o Precise control of grout loading

Disadvantages

- o Not much experience in using other its own proprietary grout
- o Wastes must be screened of debris greater than 2 in.

## GENERAL DESCRIPTION:

The Chemfix process employs the use of a highly modified, dual-rotor, pugmill to generally achieve an excellent dispersion of grout within the waste and achieve particle size reduction at the same time. Processing needs usually require waste streams to be free of damaging debris and of no greater than a 30% to 40% solids content. This specification would likely require Chemfix to add large amounts of water to the waste to get it into a form suitable for processing.

## OPERATING EXPERIENCE:

Chemfix has operated its equipment for 15 years on a number of waste sites. The largest project to date involved the solidification/stabilization of 400,000 yd<sup>3</sup> of an oily sludge waste at the Wood River, Illinois, site. Chemfix has not routinely processed soils or high solids content materials without amendment of them first by addition of water.

VENDOR CONTACT INFORMATION:

Sonja B. Manuel, Customer Service Rep.  
(800) 334-5953

Suite 610, Metairie Center  
Metairie, LA 20031

OUT-OF-GROUND TECHNOLOGY

VENDOR NAME: Chem-Met

PROCESSING SYSTEM:

NAME OF TECHNOLOGY: Chem-Met Fixation

HANDLING CAPACITY/UNIT: 300 to 800 yd<sup>3</sup>/day

COSTS: \$60 to \$100 yd<sup>3</sup>

TECHNICAL:

Advantages

Disadvantages

- o Process is not portable.  
Cannot be considered for  
RAFB site.

GENERAL DESCRIPTION:

OPERATING EXPERIENCE:

VENDOR CONTACT INFORMATION:

W. R. Hartman  
(313) 282-9250

18550 Allen Road  
Wyandotte, MI 48192

OUT-OF-GROUND TECHNOLOGY

VENDOR NAME: Hazcon

PROCESSING SYSTEM: Batch-enclosed auger

NAME OF TECHNOLOGY: Hazcon Process

HANDLING CAPACITY/UNIT: 200 to 800 yd<sup>3</sup>/day

COSTS: \$40 to \$60 yd<sup>3</sup> of waste processed

TECHNICAL:

Advantages

- o High control of grout loading
- o Good materials handling experience
- o Relatively low cost

Disadvantages

- o Fair mixing effect
- o Fair particle size reduction effect
- o Open system VOC control would have to be added

GENERAL DESCRIPTION:

Hazcon operates a batch process system with enclosed auger flights to mix the grout and waste blend. Since it is a batch system, grout loading can be tightly controlled. It is also an open batch system, so VOC control would be difficult. Hazcon material handling capabilities have been shown to be better than most on past projects.

OPERATING EXPERIENCE:

Hazcon has been in operation for five years and has operated on a number of small to medium sized sites.

Hazcon has demonstrated its ability to handle viscous oily sludges with its equipment as a participant in the Superfund Innovative Technology Evaluation (SITE) program.

VENDOR CONTACT INFORMATION:

Ray Funderburk, President  
 (800) 227-6543  
 P.O. Box 1247  
 Brookshire, TX 77423

OUT-OF-GROUND TECHNOLOGY

VENDOR NAME: Qualtec, Inc.

PROCESSING SYSTEM: Pugmill

NAME OF TECHNOLOGY: Qualtec Solidification/Stabilization Process

HANDLING CAPACITY/UNIT: 300 to 800 yd<sup>3</sup>/day

COSTS: \$40 to \$90 yd<sup>3</sup>/day

TECHNICAL:

Advantages

- o Good mixing effect
- o Fair grout loading control

Disadvantages

- o In present configuration grout is dry fed only
- o Relatively unsealed process system, therefore, little VOC control capability

GENERAL DESCRIPTION:

Qualtec uses a modified road stabilization unit with pugmill mounted on a mobile frame. They also have immediate access to materials processing equipment to screen debris and size waste.

OPERATING EXPERIENCE:

Qualtec's experience is limited to one site in Miami, Florida, where some 100,000 yd<sup>3</sup> of PCB and metal bearing waste was stabilized. The project was the first Superfund site to be treated by a solidification/stabilization process.

VENDOR CONTACT INFORMATION:

Fred G. Mullins, V.P.  
(407) 775-8300

11300 U.S. Highway 1, Suite 500  
Palm Beach Gardens, FL 33408

Qualtec's equipment is located at its South Florida location.

OUT-OF-GROUND TECHNOLOGY

VENDOR NAME: Solidtek Systems, Inc.

PROCESSING SYSTEM:

NAME OF TECHNOLOGY: Solidtek System

HANDLING CAPACITY/UNIT:

COSTS:

TECHNICAL:

AdvantagesDisadvantages

- o System is not portable, therefore, cannot be considered for the RAFB site.

GENERAL DESCRIPTION:

OPERATING EXPERIENCE:

VENDOR CONTACT INFORMATION:

Bill Risch  
(404) 361-6181  
P.O. Box 888  
5731 Cook Road  
Morrow, GA

OUT-OF-GROUND TECHNOLOGY

VENDOR NAME: Separation and Recovery Systems, Inc.

PROCESSING SYSTEM: Enclosed series of pugmills

NAME OF TECHNOLOGY: SRS Oily Sludge Fixation Process

HANDLING CAPACITY/UNIT: 100 to 500 yd<sup>3</sup>/day

COSTS: Treatment costs are \$50 to \$100/yd<sup>3</sup>. SRS will quote on a firm, fixed-price basis of waste to be treated.

## TECHNICAL:

Advantages

- o Excellent VOC control
- o Excellent mixing effect

Disadvantages

- o Higher than usual OOG processing cost

## GENERAL DESCRIPTION:

The process uses two sequential steps to treat the wastes. A transportable treatment unit includes two pugmills and refrigeration/activated carbon units.

If the waste contains volatile organics, a totally enclosed system is used that can recover volatile organics using refrigeration and activated carbon.

The waste is processed in out-of-ground pugmill units. Unlike other systems, the waste is mixed in two separate operations with its grout. One grout is added and mixed with the waste in a pugmill. Then a second grout or preparation is added, and the grout/waste is mixed again in another pugmill. The uncured product can be pumped to its emplacement area for curing.

## OPERATING EXPERIENCE:

The process originated in France and has been commercially available for 10 years.

The process units have been used to treat tarry acid sludges containing 20% to 40% organics. The units have also treated oily sludges of high water content from a refinery surface impoundment.

SRS typically uses their own in-house developed lime based binder. It appears to have been successful in use on the above two operations having

achieved such performance parameters as below detectable limits on TCLP constituents and permeabilities of  $1 \times 10^{-12}$  cm/sec.

VENDOR CONTACT INFORMATION:

Joseph De Franco, President  
(714) 261-8860

16901 Armstrong Avenue  
Irvine, CA 92714-4962

Equipment based in Irvine, California location.

#### 4.5 COST OF IMPLEMENTATION

Table 4.1 summarizes those vendors whose process technology is potentially viable for use at the RAFB site.

A site scenario of a potential of 36,000 yd<sup>3</sup> of waste to be treated to a maximum depth of 15 ft was costed. All treated waste was to be left in the lagoon. Binder/grout/reagent cost was estimated to be \$25 per cu yd of waste to be treated. All support costs such as health and safety, construction management, etc. were estimated and included. The final cost given per technology does not include the project close out costs of capping the site, monitoring well installation, etc. Costs of maintenance of the cap, although necessary, would likely be negligible.

Table 4.1 Summary of Solidification/Stabilization Process Data and Cost Estimates Associated with the RAFB Site

Technology	Vendor	Commercial Name	Depth Limitation (ft)	Processing Capacity (cu yd/10hr day)	Processing Costs (\$ per cu yd)	RAFB Sludge Lagoon		Cost (2) Estimate (\$THOU)
						Remediation Time (days)	Support Costs (1) (\$THOU)	
<u>In Situ</u>								
Low pressure injection/ rack mounted rakes	ENRECO	Soil Mixing Unit	5 to 7 (lifts)	300	\$40 to \$90	140	200	2,600
Low pressure injection/ rack tubes	Envirite	PF-5	11	150	\$25 to \$60	N/A	N/A	N/A
Low pressure injection/ auger-paddle	GEO-COM	SSM	30	150	\$80 to \$120	230	260	3,900
Low pressure injection/ auger-paddle	GEO-COM	DSM	>100	100	\$80 to \$150	380	400	4,600
High pressure injection	Halliburton	CCP JET Grouting	>100	60	\$150	620	660	6,000
Low pressure injection/ auger/paddle	JST	Deep Soil Method	>100	100	\$80 to \$150	380	400	4,600
Low pressure injection	SMW Seiko	SMW Technique	>100	100	\$80 to \$150	380	400	4,600
<u>Out-of-Ground</u>								
Pugmill	ACES Enviro-safe	ETI Solidification System		500	\$40 to \$80	90	170	2,400
Pugmill	Chemfix	CTI System		500	\$50 to \$90	90	170	2,700
Pugmill	Hazcon	Advanced Solidification		500	\$40 to \$60	90	170	2,000
Enclosed auger	OHM	Pugmill		500	\$40 to \$80	90	170	2,400
Pugmill	Qualtec	Pugmill		500	\$40 to \$90	90	170	2,500
Pugmill series	SRS	SRS Process		300	\$50 to \$100	140	280	3,000

\* Includes reagents and processing.

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## Key to Table 4.1

(1) Support Costs

Support costs on a per day basis are projected as follows:

In Situ

Health & Safety	\$ 500
Laboratory Analytical	200
Construction Management	400
Site Security	<u>Existing</u>
	\$1,100/day

Additionally (Enreco) only

Excavation/Backfilling	\$ 300/day
GW Pump & Treat	<u>200/day</u>
	\$1,600/day

Out-of-Ground

Health & Safety	\$ 500
Laboratory Analytical	200
Construction Management	600
Site Security	Existing
Excavation/Backfilling	350
Materials Preprocessing	300
GW Pump & Treat	<u>200</u>
	\$2,150/day

VOC control is not included. A cost of less than \$100,000 for effective VOC control during the project is estimated.

(2) Cost Estimate

- o Mobilization, Demobilization Costs/All Systems \$ 30,000
- o Typical costs of processing for each vendor (\$ per cu yd) is averaged
- o 36,000 cu yds is the estimated volume to be treated
- o Reagent cost is estimated at \$25 cu yd of waste treated
- o Does include all support costs
- o Does not include close-out costs such as capping of the site, monitoring well installation, etc.

NOTE: All costs are study estimates except for "Typical Cost of Processing" ranges which were quoted by vendor representatives.

## 5. ADDITIONAL CONCERNS

This section addresses some additional concerns that were raised during the engineering feasibility and regulatory issues study.

- o The relatively soft nature of the peat/clay stratum beneath the lagoon suggests that remedial solidification/stabilization activities or trenching activities could be compromised by soil instability. In addition, the relative compressibility of the stratum could create significant settling of the final fill due to the greater overburden expected from the treated waste.

The present cap on the lagoon provides adequate support to walk across or drive an automobile across it. The wide load distribution of an in situ unit and the fact that the load is not distributed over the area being processed makes it appear the lagoon area can safely support remediation activity. Standard penetration tests and a limited number of borings should be done to support this assumption.

The peat/clay stratum beneath the lagoon has the potential to be extremely compressible. Additional borings should be taken in the lagoon area to show adequate detailed stratigraphics of composition. Consolidation tests would then be done on these borings. Once the consolidation potential is known, the amount of settlement can be controlled by structurally stabilizing the peat/clay stratum during remediation using the solidification/stabilization process unit and/or by design and construction of the cap to compensate for settlement.

- o The amount of swell volume the site can handle needs to be addressed. Swell volume is the amount of expansion expected of the final treated product. Typical swell volume of a solidified/stabilized waste is less than 20% and the lagoon could accommodate this increase. The actual swell volume cannot be predicted until a grout is formulated for use. Excessive swell volume could make it impractical to place all the

treated product within the lagoon site. The consolidation of the peat/clay lagoon bottom, the design of the fill, and the design of the cap could accommodate some increase. An expansion of the fill could also potentially be needed.

- o Some processing equipment will be crane mounted. The crane height could exceed 50 ft for the duration of the project. This could be a problem due to the proximity of the sludge lagoon to the flightline.
- o The lagoon waste is stratified into distinct zones of widely varying waste character. One grout formula may not be capable of treating each waste character. If this is found to be the case, either solidification/stabilization equipment capable of homogenizing the volume being treated should be selected for use or vendor equipment capable of injecting and mixing different grouts at specific levels should be used. Each of the in situ vendors surveyed can meet the homogeneity requirement or the specific zone grout injection requirement.
- o The use of multiple processing units is feasible and should reduce the length of time needed to remediate the site.
- o Field verification of in situ techniques are limited and would require sufficient core sampling of the monolith for confidence in the homogeneity of the products or demonstrations of other techniques.
- o The use of in situ technologies for waste stabilization has not been widely demonstrated, thus the application of this technology at the RAFB site may need to be considered a demonstration.
- o Out-of-ground process methods would require the excavation of the waste. The rate of water infiltration into the excavation must be determined. The cost of shoring and water treatment may be a significant design consideration and cost.

The rate of water infiltration could be predicted through modeling of the site for the artificial conditions created by excavation. These would be predicted by doing pump tests or slug tests on water wells. Also potentially acceptable but less precise would be using stratigraphic information to predict the hydraulic conductivity of the soils/aquifer.

For shoring needs the excavation would have to be studied as to slope stabilization needs, wall flotation, etc. for design. OSHA regulations would also have to be addressed.

## 6. SUMMARY

An engineering application and regulatory feasibility study was performed to evaluate the use of on-site solidification/stabilization techniques, both in situ and out-of-ground, for permanent remediation of the RAFB sludge lagoon. Potential regulatory issues were addressed concerning the use of this type of remedial technology, along with a background review of Superfund sites where solidification/stabilization is the selected remedial alternative. The technology was also evaluated from an engineering application standpoint to consider the use of in situ or out-of-ground processing at the site.

The regulatory evaluation considered the impact of CERCLA, RCRA, and CAA on the use of solidification/stabilization techniques. CERCLA and its amendments, SARA, allow for the use of innovative technologies and these regulations also discuss the use of such techniques as grout curtains and slurry walls. RCRA and CAA are considered to be ARARs and some of their requirements are applicable as clean-up standards. The release of VOCs during implementation should not present a compliance problem since the estimated maximum concentration of VOCs on the site is no more than 15 tons. The EPA has approved the use of solidification/stabilization as a permanent remedy for a number of Superfund sites. One site, the Pepper's Steel & Alloy site in Miami, Florida, is the first Superfund site to be remediated using this technology.

The engineering evaluation looked at the use of both in situ and out-of-ground solidification/stabilization techniques for use on the RAFB site. Both of these techniques have the potential to successfully process the site's wastes; however, each of the techniques do have some limiting factors. In situ techniques have not been used to date on Superfund sites, thus the use of this technique may have to be considered a demonstration project. An out-of-ground technique has been used on a Superfund sites. Additional information would need to be obtained on the RAFB site in order to determine if soils could be excavated to depths of over 15 ft in this swampy area and what problems if any would arise.

Assuming that a grout can be successfully developed and its costs is reasonable, there is potential for the site to be remediated using an on-site solidification/stabilization technique. While in situ processing is the preferred implementation technique, this is a soil-like, high solids site which may require an out-of-ground processing capability to adequately blend the grout and water together. The estimated cost for using an in situ technique is less than \$5 million and the cost of out-of-ground techniques would be about \$3 million. These costs do not include design, procurement, site closeout such as capping and monitoring well installation, and maintenance of the site.

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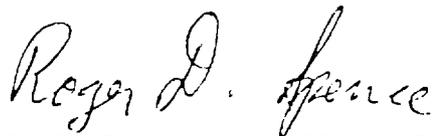
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RDS-89-069  
June 30, 1989

G. E. Kamp

ORNL Study of VOC Immobilization of RAFB Sludge

Enclosed are four copies of the report *Immobilization of Volatile Organic Compounds in Commercial Cement-Based Waste Forms*, which completes the ORNL effort for FY 1989. It is our intention to publish this report as an ORNL/TM. In this context, the report is a DRAFT requiring peer review and editing prior to publication. You are invited to participate in the peer-review process. I would appreciate receiving your comments by July 31, 1989.



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