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**LABORATORY EVALUATION OF PERFORMANCE AND
DURABILITY OF POLYMER GROUTS FOR SUBSURFACE
HYDRAULIC/DIFFUSION BARRIERS**

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ABSTRACT

Contaminated soils, buried waste and leaking underground storage tanks pose a threat to the environment through contaminant transport. One of the options for control of contaminant migration from buried waste sites is the construction of a subsurface barrier. Subsurface barriers increase the performance of waste disposal sites by providing a low permeability layer that can reduce percolation water migration into the waste site, minimize surface transport of contaminants, and reduce migration of volatile species. Also, a barrier can be constructed to envelop the site or plume completely, thereby containing the contaminants and the potential leakage.

Portland cement grout curtains have been used for barriers around waste sites. However, large castings of hydraulic cements result invariably in cracking due to shrinkage, thermal stresses induced by the hydration reactions, and wet-dry cycling prevalent at arid sites. Therefore, improved, low permeability, high integrity materials are under investigation by the Department of Energy's (DOE) Office of Technology Development, Integrated Demonstrations and Programs.

A series of binders were chosen based upon experience with polymer/waste interactions and compatibilities. These binders cover the broad range of conditions expected throughout the DOE complex. Environmentally, conditions vary from the arid sites at Hanford and Sandia, to the more humid sites at Savannah River and Fernald. BNL has attempted to provide DOE Environmental Management personnel with the flexibility to choose a barrier material that best suits their site. The binders chosen for characterization include: an acrylic, a vinyl ester styrene, bitumen, a polyester styrene, furfuryl alcohol, and sulfur polymer cement. These materials cover broad ranges of chemical and physical durability, performance, viscosity, and cost.

This report details the results of laboratory formulation, testing, and characterization of several innovative polymer grouts. An appendix containing a database of the barrier materials is at the end of this report. There is a data sheet for each binder type which summarizes the results of the laboratory testing. The sheets list aggregate compatibility, strengths attained using different aggregate/binder combinations, and chemical compatibility. Chemical compatibilities are broadly categorized as a percent of baseline value. The sheets are meant to guide the choice of barrier material and to assist in determining what site specific investigations might be required. They are not meant as final recommendations on the use of the material.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
LIST OF FIGURES	vii
LIST OF TABLES	ix
 1.0 INTRODUCTION	 1
1.1 Grout Placement Technologies	3
1.1.1 Permeation Grouting	4
1.1.2 Trenching	7
1.1.3 Jet Grouting	8
1.1.4 Displacement/Replacement Methods	10
1.1.5 Other Technologies	11
 2.0 MATERIALS	 12
2.1 Methacrylate	14
2.2 Vinylester Styrene	15
2.3 Polyester Styrene	15
2.4 Furfuryl Alcohol	15
2.5 Sulfur Polymer Cement	16
2.6 Bitumen	16
2.7 Aggregates	17
 3.0 SAMPLE FORMULATION/FABRICATION	 20
3.1 Soil Mortars	20
3.2 Mortars	21
3.3 Concretes	22
3.4 Glass Concretes	23
3.5 Portland Cement Concrete	23
 4.0 TESTING AND RESULTS	 25
4.1 Hydraulic Conductivity	25
4.2 Compressive Strength	30
4.3 Flexural Strength	31
4.4 Splitting Tensile Strength	32
4.5 Water Immersion	35
4.6 Acid Resistance	38
4.7 Base Resistance	42
4.8 Solvent Resistance	45
4.9 Wet-Dry Cycling	49
4.10 Chloride Diffusivity	54

TABLE OF CONTENTS (Cont.)

	<u>Page</u>
4.11 Hot Nitrate Brine Resistance	56
4.12 Thermal Cycling	60
4.13 Irradiation Stability	61
5.0 ECONOMIC CONSIDERATIONS	63
6.0 SUMMARY AND CONCLUSIONS	70
REFERENCES	73
APPENDIX A	A1

LIST OF FIGURES

	<u>Page</u>
Figure 1	Subsurface Barrier Surrounding Buried Waste 5
Figure 2	Interim Containment Barrier for Underground Storage Tanks 6
Figure 3	Subsurface Barrier Installation by Permeation Grouting 7
Figure 4	Conventional Column Jet Grouting 9
Figure 5	SoilSaw™ Barrier Installation System 11
Figure 6	Blended sand aggregate used to produce polymer mortars 18
Figure 7	Hanford soil from near the 200 series tank farm used in soil mortars . . . 19
Figure 8	Quartz stone aggregate used to produce polymer concretes 19
Figure 9	Recycled glass used to produce polymer glass concretes 20
Figure 10	Unit weight of sand/stone aggregate blend 22
Figure 11	Unit weight of sand/glass aggregate blend 23
Figure 12	Typical Binder Requirements for Polymer Composites 24
Figure 13	Flexible wall permeameter used to measure hydraulic conductivities 28
Figure 14	Permeameter cell showing a polymer concrete specimen sealed with a latex membrane 29
Figure 15	Polymer concrete beam specimen loaded in flexure attachment to determine tensile strength in flexure 34
Figure 16	Alignment jig used to center samples for testing 34
Figure 17	Sulfur polymer cement soil mortars before and after immersion in water for 90 days 37
Figure 18	Effects of immersion in water for 90 days on the compressive strength of polymer composites 37
Figure 19	Effects of immersion in nitric acid (pH = 2) on the compressive strength of polymer concretes 39
Figure 20	Effects of immersion in nitric acid (pH = 2) on the compressive strength of polymer mortars 40
Figure 21	Effects of immersion in nitric acid (pH = 2) on the compressive strength of polymer glass concretes 40
Figure 22	Effect of immersion in sodium hydroxide (pH = 12.5) on the compressive strength of concretes 43
Figure 23	Effect of immersion in sodium hydroxide (pH = 12.5) on the compressive strength of polymer mortars 43
Figure 24	Effect of immersion in sodium hydroxide (pH = 12.5) on the compressive strength of polymer glass concretes 44
Figure 25	Bitumen specimen after immersion in a saturated solution of trichloroethylene, showing widening at the base of the sample 45
Figure 26	Polyester styrene concrete specimen showing binder dissolution after immersion in a saturated solution of trichloroethylene 46

LIST OF FIGURES (Cont.)

		<u>Page</u>
Figure 27	Acrylic glass concrete specimen showing binder dissolution after immersion in a saturated solution of trichloroethylene	47
Figure 28	Effect of immersion in a saturated solution of trichlorethylene on the compressive strength of concretes	47
Figure 29	Effect of immersion in a saturated solution of trichlorethylene on the compressive strength of polymer glass concretes	48
Figure 30	Effect of immersion in a saturated solution of trichlorethylene on the compressive strength of polymer glass concretes	48
Figure 31	Weight changes of polymer concretes and hydraulic cement concrete during wet-dry cycling	51
Figure 32	Weight changes of polymer mortars during wet-dry cycling	52
Figure 33	Weight changes of polymer glass concretes during wet-dry cycling	52
Figure 34	Weight changes of polymer soil mortars during wet-dry cycling	53
Figure 35	Conductance cell for rapid chloride penetration determinations	55
Figure 36	Soil mortars after immersion in hot nitrate brine surrogate	58
Figure 37	The Effect of Hot Nitrate Brine on Strength of Polymer Soil Mortars . . .	58
Figure 38	Cross section of an acrylic soil mortar after 120 days immersion in a hot sodium nitrate brine surrogate	59
Figure 39	Temperature conditions for one cycle of ASTM B-552	60
Figure 40	Effect of thermal cycling on the compressive strength of soil mortars . . .	62
Figure 41	Effect of gamma irradiation of 10^8 rads on the compressive strength of soil mortars	62

LIST OF TABLES

	<u>Page</u>
Table 1	Properties of candidate binder materials for subterranean barrier for USTs ^a 14
Table 2	Size distribution of Morie TC-4727-81 blended sand aggregate (taken from manufacturers analysis sheet) 18
Table 3	Formulations - Aggregate: Binder Ratios (by weight) 24
Table 4	Densities of Polymer Composites (g/cm ³) 25
Table 5	Permeabilities of Polymer Barrier Composites (cm/sec x 10 ⁻¹⁰) 27
Table 6	Compressive Strength of Polymer Barrier Composites (MPa ± standard deviation) 31
Table 7	Flexural Strength of Polymer Barrier Composites (MPa ± standard deviation) 32
Table 8	Splitting Tensile Strength of Polymer Barrier Composites (MPa ± standard deviation) 33
Table 9	Compressive Strength of Polymer Barrier Composites After Immersion in Water for 90 days (MPa ± standard deviation) 36
Table 10	Percent water uptake for polymer composites after water immersion 36
Table 11	Compressive Strength of Polymer Barrier Composites After Chemical Immersion (MPa ± standard deviation) 41
Table 12	Compressive Strength of Polymer Composites after Solvent Immersion (MPa ± standard deviation) 49
Table 13	Compressive Strength of Polymer Barrier Composites Wet-Dry Cycling (MPa ± standard deviation) 51
Table 14	Chloride ion penetrability based on charge passed 55
Table 15	Chloride penetrability of polymer composites based on total charge passed 56
Table 16	Compressive Strengths of Soil Mortars after Nitrate Brine Immersion (MPa ± standard deviation) 57
Table 17	Compressive Strengths of Soil Mortars after Thermal Cycling (MPa ± standard deviation) 61
Table 18	Compressive Strengths of Soil Mortars after Gamma Irradiation (MPa ± standard deviation) 63
Table 19	Unit Price of barrier grout components 66
Table 20	Cost of grouts per cubic meter 67
Table 21	Barrier materials cost, and cost per equivalent permeability unit, for jet based placement technologies 68
Table 22	Barrier materials cost, and cost per equivalent unit, for replacement/displacement technologies 69

1.0 INTRODUCTION

Contaminated soils, buried waste and leaking underground storage tanks (UST) pose a threat to the environment through contaminant transport. One of the options for control of contaminant migration from buried waste sites is the construction of a subsurface barrier. Subsurface barriers increase the performance of waste disposal sites (Figure 1) by providing a low permeability layer that can reduce percolation water migration into the waste site, minimize surface transport of contaminants, and reduce migration of volatile species. Also, a barrier can be constructed to envelop the site or plume completely, thereby containing the contaminants and the potential leakage. A subsurface barrier could be used to contain contaminant plumes during remediation, or could be used to enhance remediation such as limiting the affected field of vacuum extraction. In the case of underground storage tanks, it has been proposed that interim containment barriers be placed around the tanks (Figure 2). This would minimize, or prevent, future contamination of soil and groundwater in the event that further tank leakages occur before, or during, remediation. Use of interim subterranean barriers can provide sufficient time to evaluate and select appropriate remediation alternatives as well.

Portland cement grout curtains have been used for barriers around waste sites. However, large castings of hydraulic cements result invariably in cracking due to shrinkage, thermal stresses induced by the hydration reactions, and wet-dry cycling prevalent at arid sites. Therefore, improved, low permeability, high integrity materials are under investigation by the Department of Energy's (DOE) Office of Technology Development, Integrated Demonstrations and Programs.

This report details the results of laboratory formulation, testing, and characterization of several innovative polymer grouts. This work is funded by the Office of Technology Development, within the Department of Energy's Office of Environmental Management, under the In Situ Remediation Integrated Program. The Environmental and Waste Technology Center at Brookhaven National Laboratory (BNL) has been developing and characterizing polymers for waste management uses for several decades. BNL has developed and characterized polymers for encapsulation of hazardous, mixed, and radioactive waste, and for container materials. A series of binders were chosen based upon experience with polymer/waste interactions and compatibilities. These binders would cover the broad range of conditions expected throughout the DOE complex. Environmentally, conditions vary from the arid sites at Hanford and Sandia, to the more humid sites at Savannah River and Fernald. The geotechnical variability ranges from coarse sand with hydraulic conductivities of 10^{-3} cm/sec and greater, to sandy clays with hydraulic conductivities of 10^{-7} cm/sec or less. Waste types are as varied as the sites. There are hazardous materials such as acids, solvents and chromium sludges, mixed waste such as the nitrate brines at Hanford, Rocky Flats and Savannah River, and radioactive contaminants including strontium, cobalt, cesium, and tritium. It is difficult, if not impossible, for any one barrier material to be compatible with all of these conditions. The host of placement technologies/methods for installing the barrier at the waste site compounds the problem. Each method may have specific requirements of the grout (i.e. viscosity, density, gel time). These requirements may change with environmental, geochemical, and geotechnical variations.

However, it is possible to develop specific barrier materials for specific sites. BNL has attempted to provide DOE Environmental Management personnel with the flexibility to choose a barrier material that best suits their site. The binders chosen for characterization include: an acrylic, a vinyl ester styrene, bitumen, a polyester styrene, furfuryl alcohol, and sulfur polymer cement. These materials cover broad ranges of chemical and physical durability, performance, viscosity, and cost.

Acceptability of these materials by the USEPA for use at hazardous waste sites was confirmed prior to laboratory characterization of the polymer systems.¹ EPA guidance documents describe several kinds of subsurface barriers for controlling the movement of groundwater and/or contaminants at inactive waste disposal sites. We infer from this that EPA considers subsurface barrier technology to be an acceptable method of achieving such control. The selection of subsurface barriers for any given site which needs remediation, and the selection of a particular barrier technology must be done, however, by means of the Superfund Process, with special emphasis on the remedial investigation and feasibility study portions. The chemical compatibility of the material with the wastes, leachates, and geology with which it is likely to come in contact is of particular importance for barriers constructed from fluids which are supposed to set *in-situ*. EPA emphasizes this compatibility in its guidance documents, noting that thorough characterization of the waste, leachate, barrier material chemistry, site geochemistry, and compatibility testing of the barrier material with the likely disposal site chemical environment are all required. Furthermore, EPA requires that the potential release of toxic barrier material constituents be addressed as part of the characterization and testing. This requirement for characterization and testing applies to both traditional, and non-traditional, materials.

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

Generally, improved chemical and/or physical durability and performance increases the cost of the barrier grout. Choosing a grout must be done on a site and job specific basis, while balancing cost and performance. Most likely, the driving force behind grout choice will be determined by environmental and geotechnical parameters at sites like the Sandia Chemical Waste Landfill where contaminants are not highly mobile and/or reactive. A less expensive barrier material might be appropriate and, yet, still provide sufficient environmental protection. Other DOE facilities have harsher contaminant environments. The Hanford tank farm has 149 Underground Storage Tanks (USTs) containing nitrate brines, of which 11 are considered high heat (>40,000 Btu/hr) tanks. Heating is due to radionuclide decay. The average temperature

^aTelephone conversation between B. Siskind, Brookhaven National Laboratory, and R. Steimle, Federal Technology Users' Group, Technology Innovation Office, EPA, on February 10, 1993.

of the tanks is 70°C. Gamma radiation is up to 1000 rad/hr, which results in 25 year (interim containment lifetime) doses of 10^8 rads. The tank waste is a corrosive ($\text{pH} \geq 12.5$) nitrate brine. Cost may be overshadowed by performance requirements, placement technology, and/or stakeholder concerns for such extreme conditions.

Soil and waste chemistry will also affect grout choice. Zeolite clays can dry and shrink when heated for mixing with thermoplastic grouts. The zeolites will swell and induce tensile stresses that can crack the barrier when re-wetted by percolation waters or waste leakage. Alkali soils can react with, and neutralize, acid catalysts that are required for some thermosetting polymers. Complexing agents like EDTA will interfere with, and can prevent, the curing of portland cement based grouts.

An appendix containing a database of the barrier materials is at the end of this report. There is a data sheet for each binder type which summarizes the results of the laboratory testing. The sheets list aggregate compatibility, strengths attained using different aggregate/binder combinations, and chemical compatibility. Chemical compatibilities are broadly categorized as a percent of baseline value. The sheets are meant to guide the choice of barrier material and to assist in determining what site specific investigations might be required. They are not meant as final recommendations on the use of the material. If a specific barrier is for short term use but requires very low permeability then the hydraulic conductivity will be most important. The chemical compatibility may be of little or no value. On the other hand if a barrier is meant to contain aggressive chemicals for long periods then chemical compatibility will be extremely important. The feasibility of using a particular material must be a site specific decision based on performance, cost, placement methods, etc. It should also be noted that the results reported in this document and the data sheets contain information from a previous investigation completed by BNL. The work was done for the Underground Storage Tank Integrated Demonstration under TTP CH321001 and investigated polymers for barriers surrounding the Hanford tanks. While the project specifically targeted Hanford soil as aggregate the results are of importance to this program and therefore have been included to broaden the database. All data and testing pertaining to Hanford soil mortars were completed under TTP CH321001.

1.1 Grout Placement Technologies

Placement technologies must consider many grout characteristics. It is necessary to understand some of the basic placement techniques and their fundamental differences in order to realize how placement technology affects the grout choice. The following sections describe some of the grouting techniques, as well as the binder requirements associated with each technique.

Placement technologies can be divided into several categories. Grouting will be classified as permeation grouting, jet grouting, displacement grouting, or trenching for this report. Each of these classes has numerous variations and perturbations.

1.1.1 Permeation Grouting

A grouting material of low viscosity (typically <300 cps) is injected into the ground through a series of injection wells. The grout penetrates the soil where it then sets, forming the barrier in-situ (see figure 3). The barrier is made continuous by overlapping the injection zones. Permeation is advantageous because it has little spoils, produces low stresses, and can produce low permeable barriers when used in conjunction with advanced polymer systems. Permeation grouting is the principle method of employing acrylates, such as AC-400, for construction industries.

Construction of a subterranean barrier by permeation injection requires the grout material to penetrate the soil completely, and remain in place until solidification is complete. Then, the solidified monolith must provide an impermeable and durable barrier. The ability of the grout to penetrate the soil is dependent on the grout viscosity and the permeability of the soil. A coarse sandy soil can be injected with a higher viscosity binder at low to moderate pressures. A fine sand might require a near water viscosity resin applied at higher pressures. It is generally accepted that permeation grouting is limited to soils having hydraulic conductivities of $\sim 10^{-4}$ cm/sec or greater, if control of grout location and prevention of hydrofracturing is to be accomplished. Also, the viscosity of the injection grout and the "curing time" will determine whether the binder remains in place, or percolates away from the injection zone, prior to hardening. A low viscosity material applied to a coarse sand may "run out", leaving a more permeable barrier after solidifying. The soil types encountered throughout the DOE complex vary from clays (e.g., Savannah River) to coarse sands and gravel (e.g., Hanford). In general, it is desirable to develop several durable binders over a wide range of viscosities (~ 1 to 300 cps) in order to accommodate soil conditions at the various DOE sites.

Figure 1. Subsurface barrier surrounding buried waste.

Figure 2. Interim containment barrier for underground storage tanks.

1.1.2 Trenching

Trenching is the most obvious and simple placement technique. A trench is dug and the

Figure 3. Subsurface barrier installation by permeation grouting

barrier grout is poured into the trench where it hardens and forms the barrier. Trenching is limited to vertical walls only, but allows the greatest flexibility in grout choice. Grouts having high viscosities and large aggregates can be used in trenches. This has both performance and cost benefits. Instead of using soil for an aggregate, clean non-reactive aggregates such as stone, sand, and glass can be mixed with the binder. The aggregate is impermeable, inert, inexpensive, and reduces the amount of binder required to form the barrier. A typical soil-binder polymer grout would require 25% wt/wt of binder. Replacing the soil with graded stone and sand aggregate can reduce the binder to 9%.

Slurry walls are included in trenching techniques and are the most commonly installed barrier type. It is doubtful that polymers will be placed by this method but it is included here for completeness. A vertical trench is excavated to form a slurry wall. The trench is filled with a suspension grout slurry in order to form an engineered panel. The most common slurries are water/soil/bentonite and Portland cement/bentonite. Typically, a bentonite slurry is used to hydraulically shore up the trench during construction, and also to seal the pores in the trench walls. Overlapping is insured by cutting into adjacent panels so the wall is "keyed". Slurry

walls are generally 20 to 80 feet long, and 2 to 3 feet wide. Advantages of slurry walls include: the formation of continuous unbroken barriers, cost effectiveness for massive structures, proven successful technology, ability to be used to ~400 feet depth, and the development of minimal stresses. The disadvantages include: low chemical resistance, large amounts of excavated soils which must be treated if contaminated, limitations to vertical walls, and the walls must be 2-3 feet thick.

Deep soil auger mixing is included in trenching for simplicity. This method bores a large hole as opposed to a trench. The holes are overlapped to form a continuous wall. Several large augers are used to bore into the soil for deep soil mixing, followed by introduction of a grouting material at low pressure (e.g., 300 psi). The augers mix the soil and grout, and are retrieved from the ground gradually. The resultant panel generally has more favorable properties (e.g., permeability) as compared to jet grouted curtains, and has fewer breaks and more consistent dimensions. Deep soil mixing is a proven technology, but is limited to ~100 feet depth. It results in a much larger quantity of spoils as compared to jet grouting.

1.1.3 Jet Grouting

Conventional jet grout curtains are constructed by injecting the grout through tubes into the strata to be waterproofed. The tubes are rotated while injecting at high pressures (e.g. 5000 psi) and slowly withdrawn from the ground. The high velocity jet masticates and mixes the soil and grout which results in a column ~1 meter in diameter that resembles a pancake stack (Figure 4). After the grout pumped into the primary holes has gelled, grout is injected into secondary holes to fill gaps in the primary grout injection. This results in a barrier 1½ to 2 meters thick.. There are often problems in forming a continuous grout barrier despite grouting via the secondary holes. Overall low permeability may be compromised. Also, cobble and other large buried objects will interfere with the continuity of a jet grouted column by blocking the pathway for the jet, and preventing grout from reaching the downstream side of the cobble. The technique requires a pumpable grout that can be injected at pressures greater than 5000 psi through a small orifice, typically 1 mm. This limits any aggregate additions to fine particle sizes. Most often, the jet grouting uses a low viscosity grout (~5 cps), and incorporates only the existing soils for aggregate. Jet grout curtains can be vertical using conventional drilling, or may be angled, or horizontal, using directional drilling.

Figure 4. Conventional column jet grouting.

Jet grouting is the most widely adapted or modified placement method. Several promising jet based grouting technologies that have been developed or are under development, include panel jet grouting such as SoilSaw™ from Halliburton NUS, and ultra-high pressure grouting from Quest Integrated Inc. or Superjet™.

Panel jet grouting is a simple refinement to conventional jet grouting. The tool is turned back and forth only a few degrees, rather than rotating the jetting tool 360° and forming a cylindrical column. This forms a thin panel, typically 12-15 inches wide. Panels are laid side by side with a slight overlap in order to form a continuous barrier. The advantage is greatly reduced grout resulting from thin panels, rather than thick columns.

SoilSaw™ is a modification of panel jet grouting. The system consists of a long beam with multiple jets at regular intervals along the beam (Figure 5). The beam is connected to a modified tracked excavator that is equipped with high pressure pumps to deliver the grout to the jetting nozzles of the beam. The beam reciprocates while the grout is jetted. The combination of jetting action and sawing of the beam liquifies the soil, and cuts a pathway into the ground. The tracked excavator pulls the beam along the course intended for the barrier as soon as the beam has reached the proper depth and cutting angle. The barrier is typically 12-15 inches wide, but the tool can be modified to form 4-6 inch wide walls. Grout requirements are similar to jet grouting, although the manufacturer suggests densifying the grout in order to have a density greater than the surrounding soils. This can be done by adding fine iron oxide.

Pretesting of the grout would be required in order to assure compatibility with the iron oxide. This method uses more grout per cubic foot because the jetting bar must sink into the liquified soil. This may not be a great disadvantage, since the tool can make thin barriers and has a positive placement. SoilSaw™ is limited to vertical barriers. Halliburton, NUS is developing a horizontal tool.

Ultra high pressure grouting uses pressures in excess of 25,000 psi. This greatly increases the affected field. This technique would be used to make thin disks. The high pressure results in an affected area of up to 25 feet in diameter. The method relies on overlapping disks to form continuous barriers. Advantages include: less bore holes to be drilled, high pressure which can cut through cobble and buried objects, and thin barriers which conserve grout requirements. However, disadvantages exist as well. It may be difficult to align thin disks for proper overlap at depths of 100 feet, or more, below grade. Also, grouts would be limited to low viscosity, low solids content.

1.1.4 Displacement/Replacement Methods

Displacement grouting uses some method of pushing the soil away from an area in order to form a void. The void is then filled, or replaced, by a grout. There are several displacement techniques including hydrofracture and vibrating beam. Hydrofracture uses a high pressure liquid (i.e., water or grout) to fracture the soil layer, but has not proven to be reliable in directing the fracture in a controlled manner. Vibrating beam cutoff walls involves vibrating a specifically designed beam into the ground. The barrier material is injected into the ground through a tremmé pipe in the beam, as the beam is slowly extracted from the ground. Panels produced are thin, typically 6-8 inches. A continuous wall is created by repeating the process adjacent to the just formed panel. This technique has been used in conventional construction and has been demonstrated, on a limited basis using emulsified bitumen, for remedial applications. Vibrating beam produced barriers can generate low permeability walls in tight spaces with little or no spoils. This method allows the use of any grout/aggregate combination that can be delivered through the tremmé pipe. Disadvantages include: uncertainty in the alignment of beams which may produce a barrier with gaps, and the limitation of the method to soils that can be penetrated by the vibrating beam.

Figure 5. SoilSaw™ barrier installation system. Photo courtesy of Halliburton, NUS.

1.1.5 Other technologies

There are other methods for placing a subsurface barrier which are seldomly used, or recently developed, for remedial operations. Diaphragm walls are precast panels which are usually reinforced concrete, but could be polymer concrete. They are placed by slurry trench techniques. Diaphragm walls can produce a quality vertical barrier with proper attention to joint construction. Diaphragm walls are seldomly used due to their prohibitive expense.

Rock grouting may be used for sealing fractures, fissures, solution cavities, or other voids in rock. The authors of the EPA's Remedial Action Handbook² could find no applications of this technique in the literature, but consider it "One of the greatest potential uses for grouting in hazardous waste site remediation..."

2.0 MATERIALS

Originally, this program focused on trench emplaced barriers, while considering binders which might be used in some form of jet or permeation grouting. It was apparent that the newer jet technologies were more appropriate for in-situ barrier installation as the project developed. The need to use these binders with jet grouting is most obvious when complete containment of a site is desirable. The horizontal portion of the barrier will have to be placed using an in-situ grouting method, most likely a perturbation of jet grouting. This report deals with a variety of binders and three aggregate types. The aggregate combinations would be used most likely in trench or displacement/replacement technologies. The performance, durability, and resistivity of the binders is generic to any placement method. Results from studies for the Underground Storage Tank Integrated Demonstration (USTID) are presented as well.³ BNL studied some of the same binders using a more site specific basis. The binders were mixed with Hanford soil to produce soil mortars. Then, these mortars were subjected to a series of generic and site specific tests. The placement technology for the USTID was assumed to be jet or permeation grouting. The addition of that data enhances the database available to EM personnel.

BNL selected several polymer grout systems for development and characterization as barrier materials based upon geochemical and geophysical characteristics, waste types, and performance requirements expected for the DOE complex as a whole. The binders chosen for characterization include: an acrylic, a vinylester styrene, bitumen, a polyester styrene, furfuryl alcohol, and sulfur polymer cement.

The polymers can be classified as either thermosetting or thermoplastic. Thermosetting polymers produce a barrier material through chemical reaction. Polymer concrete is an aggregate mixed with a liquid monomer or resin (binder) which is converted in place in order to form a hard polymer monolith. This material can be mixed and cast in the field. Once formed, a thermosetting polymer cannot be reformed. Thermoplastics are melted and mixed with aggregate to form the barrier material. Thermoplastics can be reformed by re-heating to the melt temperature. The thermoplastics grouts used were bitumen and sulfur polymer cement. Bitumen was included due to low cost and widespread use in construction.

The polymers selected are innovative materials with desirable properties in both their fluid, and solid, states. This makes them suitable for applications where impermeability, high strength, and long-term durability are required. These materials have been used extensively in many commercial applications such as sewage and brine handling systems and electrolytic baths. They have been used also by the Corps of Engineers to repair dams and canal locks, and by the Federal Highway Administration for bridge deck and highway repairs. Polymer grouts are candidates for high quality barrier materials due to their impermeability to gases and liquids, combined with their resistance to radiation, acidic, and alkaline environments .

Candidate thermosetting binders were selected based on durability of the polymer, and chemical and physical characteristics of the resin (i.e., viscosity). These included methacrylates,

vinyl-ester styrene, polyester styrene, furfuryl alcohol, and polyacrylic acids. Some properties of the candidate binders are given in Table 1.

The polymerization of unsaturated monomers such as methacrylates and polyester-styrene is typically a chain reaction. Polymerization can be initiated by the action of a free radical on a monomer molecule, which leads to polymer chains consisting of thousands of monomer molecules. Free radicals can be formed by the decomposition of a relatively unstable material called an initiator or a catalyst. Benzoyl peroxide is a commonly used initiator. The peroxide molecule splits at the O-O bond and when subjected to heat or in the presence of a promoter, forms two free radicals that have unpaired electrons and, thus, are very reactive.

Promoters can be used instead of temperature for ambient temperature curing of catalyzed monomer systems. Promoters (also called accelerators) are chemical compounds that induce the decomposition of a peroxide catalyst by breaking the O-O bond. This reaction can take place at a wide temperature range, depending on the promoter-catalyst system used. This is the preferred method for in-situ applications.

Cure time is dependent upon temperature, promoter-catalyst combination and concentration, and admixtures (or contaminants) that may retard or enhance the set. Gel times (the time after which the resin viscosity increases rapidly and can no longer be poured or worked) were set at 1 hour for this study. Each placement technology may require a specific gel time. The environmental conditions (e.g., temperature) will affect the gel time. Gel times can be manipulated easily by the resin manufacturer or the catalyst-promoter supplier. The reaction is exothermic and results in an autoaccelerating reaction that must be properly controlled. Thermosetting polymers have been developed to solidify radioactive, mixed, and hazardous waste.^{4,5,6,7}

Sulfur concrete consists of an aggregate bound with sulfur polymer cement (SPC). SPC is a thermoplastic polymer. Thermoplastic materials become liquid when heated above their melting points and can be mixed with an aggregate filler such as sand or soil. The mix re-solidifies to form a solid monolith upon cooling. No chemical reaction is required for setting (as in hydraulic cements). Thus, incompatibilities between binder and aggregate are minimized. Thermoplastics such as polyethylene and SPC have been used for chemically resistant flooring and reactor vats⁸ and have been developed for solidification of various wastes.^{9,10,11}

The following sections give a brief description of the polymer grouts investigated and the aggregates used.

Table 1 Properties of candidate binder materials for subterranean barriers for USTs^a

	Sulfur Polymer Cement	Polyester Styrene	Vinylester Styrene	Acrylic	Bitumen	Furan
Manufacturer	Martin Chemicals	Riechhold Chemicals	DOW Chemicals	3M Company	Ziegler Chemical and Mineral Corp.	QO Chemicals
Trade Name	Chement 2000	Atlac 4010A	Derakane 470-45	3M Concrete Restorer	Zeco-AA1900 Type III roofing asphalt	FA-Rok 913
Viscosity, cps	28 @ 135°C	300 @ 25°C	100 @ 25°C	10 @ 25°C	90 cps @ 227°C	8.5 @ 20°C
Specific gravity (g/cm ³)	2.07	1.03	1.048	1.025	1.02	1.13
Flashpoint (°C)	191	32	21-32	105	288	77

^a Information obtained from various manufacturers' Material Safety Data Sheets.

2.1 Methacrylate

Methacrylate monomers (acrylic) are a low viscosity, commonly used, family of polymers. The methacrylate chosen is manufactured by the 3M company using the tradename 3M 4R Concrete Restorer. It is a modified high molecular weight methacrylate (viscosity = 5-10 cps). The system consists of dicyclopentadienyl methacrylate and isooctyl acrylate. It is polymerized using a cobalt octoate promoter (reducing agent) and cumene hydroperoxide initiator (oxidative catalyst). The system came prepromoted (1%) and required 3 parts catalyst to 100 parts resin.

3M manufactures two distinctly different types of methacrylates using the name 3M 4R Concrete Restorer. There is a low modulus product called 3M 4R 5742, and a high modulus product called 3M 4R 5740 or 5741 (low odor). The low modulus product is elastic, while the high modulus product is brittle, in the cured state. Both materials will form a polymer concrete that is brittle (due to the aggregate). The high modulus polymer will result in higher strengths than the low modulus polymer. The high modulus material was used originally for the Hanford soil mortars. Then, the manufacturer re-formulated the resin by prepromoting and by adding a solvent inhibitor to increase shelf life. The solvent evaporates out at the time of application. Then, the promoter works efficiently. BNL determined that this solvent addition would not evaporate out at a rapid enough rate when making a polymer concrete that was thick and/or buried. The low modulus material was employed for the present study. This resulted in lower

strengths. Resistance testing proved both materials to be durable and useful for subsurface barriers in the DOE complex.

BNL has been in contact with the manufacturer about these modifications since the investigation began. 3M is quite willing to manufacture the resins at whatever specification is required. They can produce resins with no solvent additions and can regulate promoter/catalyst quantities (hence cure times).

2.2 Vinylester Styrene

Vinylester styrene (VES) polymers are extremely durable both chemically and physically. These polymers have been used to encapsulate radioactive waste, and in a wide variety of applications calling for resistance to harsh chemicals.^{12,13} The VES system used in this study is manufactured by DOW Chemicals using the tradename Derakane 470-45. It is an epoxy novolac-based vinyl ester resin dissolved in styrene. This particular Derakane was formulated to exhibit good chemical resistance (including solvents), retention of properties at high temperatures, and low viscosity (~100 cps). The polymerization occurs using an oxidation-reduction reaction. Dimethylaniline (DMA) promoter was used in conjunction with a 40% benzoyl peroxide (BPO) catalyst solution. The following ratios were used: 0.1 parts DMA, 2.5 parts BPO, and 100 parts resin for this study.

2.3 Polyester Styrene

Polyester styrenes (PES) are among the most widely used thermosetting resins. The basic components of a PES polymer are a mixture of a linear polyester resin and styrene monomer. Chemical and physical characteristics of the final polymer depend on the ratios of polyester resin to styrene. Resistance to the strong alkali supernatants in the tanks is probably the most critical factor in choosing a PES system for the Hanford UST containment barrier. Therefore, BNL selected a modified bisphenol fumarate resin distributed by Reichhold Chemicals using the tradename Atlac 4010A. This resin is formulated especially for alkali resistance. A 6% solution of cobalt naphthenate (CON6) was used as the promoter. Methyl ethyl ketone peroxide (MEKP) was added as the initiator. The manufacturers recommended ratios were: 2.4 parts of CON6, 100 parts resin, and 1 part MEKP. The viscosity of the polyester styrene solution is approximately 300 cps.

2.4 Furfuryl Alcohol

A commercial, furfuryl alcohol (FA) based furan polymer, FA-Rok 913 manufactured by QO Chemicals, was used for this study. FA-Rok has a low viscosity (~3-8 cps), low vapor pressure, low flammability, and is soluble in water. This material produces a very resistant polymer using inexpensive and environmentally innocuous components. Furfuryl alcohol based polymers (furans) have been used: in the fabrication of polymer concrete pipes, as an organic cementing and sand consolidating material in oil wells, as floor coatings, and as chemically resistant containers. Polymerization of furfuryl alcohol occurs through a condensation reaction

using a strong acid catalyst. Basic reagents tend to inhibit the polymerization.¹⁴ Set times and exotherms cannot be as tightly controlled as in the other polymer systems. The catalyst used for this study was a mix of FA-Rok catalysts: 2 parts 6301:1 part 6300, in a ratio of 1:10 catalyst:resin. Free floating resin will polymerize very quickly without the heat sink that the aggregates provide. Care should be taken to avoid free standing catalyzed resin in order to prevent localized excessive exotherms.

2.5 Sulfur Polymer Cement

Sulfur polymer cement (SPC) was developed by the U.S. Bureau of Mines to utilize surplus sulfur.¹⁵ Sulfur concretes offer excellent chemical resistance to strong acids and salts, and are relatively inexpensive. SPC is used for construction of chemical vats, road repairs, and is a candidate for encapsulating radioactive, hazardous, and mixed wastes^{8,16}. SPC is a thermoplastic material that is formed by reacting elemental sulfur with dicyclopentadiene and oligomers of cyclopentadiene. This modification to elemental sulfur suppresses a crystalline phase change that occurs as sulfur cools below 95.6°C. The monoclinic form of sulfur changes to the orthorhombic form in unmodified sulfur, with a resultant density increase and an introduction of stresses. Such residual stresses make sulfur susceptible to shock damage by impact or thermal changes. The sulfur cement used in this study was manufactured by Martin Chemicals using the trade name Chement 2000 (viscosity = 28 cps @ 135°C). SPC can be mixed with aggregate, soil, waste, etc., when heated above its melting point (119°C). A hard monolithic solid is formed upon cooling. Processing was done at 124°C in this study. SPC can be processed up to 150-160°C. A phase change occurs above this temperature. This results in a severe viscosity increase and a decrease in workability. Full strength is achieved in hours, rather than weeks, as compared with hydraulic cements.

2.6 Bitumen

Bitumen is a common thermoplastic construction material used mainly for roofing, paving and sealing. Bitumen was included in this study for completeness, although it is not new. This study used a roofing grade type III asphalt, manufactured by Ziegler Chemical and Mineral Corp using the tradename Zeco-AA1900. A high temperature system is required in order to utilize the bitumen in its bulk form. BNL processed samples at 200°C. It may be possible for trench placement to simply modify construction equipment to feed the heated grout. Modifications would be required for other placement techniques that allow heating of the grout, the injection pipes, and possibly the soil to be grouted. There is another form of bitumen that may be better utilized in jet or permeation grouting. Emulsified bitumen consists of microspheres of bitumen suspended in water. The water is used as a carrier fluid for the bitumen. The emulsion breaks when injected into soil, either by additives put in the grouting fluid, or by bentonites/zeolites in the soil. The bitumen microspheres begin to agglomerate and "clog" the porosity of the soil when the emulsion breaks.

The two forms of bitumen are quite different physically, but should behave the same chemically. The emulsified form will not produce hydraulic conductivities as low as the bulk material, or other fluid polymer binders. The bulk form will act as a glue and consolidate the soils, whereas the emulsified form adds no structural integrity to the soil. The data for durability and resistance obtained in this report for the bulk bitumen can also be applied to the emulsified form. The strength measurements for the bulk form are meaningless to the emulsified bitumen.

2.7 Aggregates

The aggregate additions of stone, sand, or recycled glass were developed for use in trenching or displacement/replacement barrier formation technologies. Other methods will use the natural soils of the waste site as aggregate. A site specific compatibility study must be performed and should address the compatibility of the resins and polymers with site soil, if this has not already been addressed. BNL has determined the compatibility of the polymers studied with Hanford soil.

BNL utilized a round quartz stone that passed through a $\frac{3}{8}$ inch sieve. The blended sand was a 99+ % SiO_2 , size-graded mix obtained from Morie Co., Inc. The grain size distribution is given in Table 2. The recycled glass was obtained from the Brookhaven Town Recycle Center, NY. It is a typical, residential, mixed-color waste, sodium glass. The recycle center crushed the glass. BNL used the fraction that passed through a $\frac{3}{8}$ inch sieve (95+ %). The Hanford soil was clean sand taken from about 15 feet below grade, near the 200 series tank farm. The soil is a coarse brown sand with a measured soil pH of 9.0 (ASTM D-4972).¹⁷ Porosity is estimated to be 35-45% from the single mode size distribution. Hydraulic conductivity is estimated to be 10^{-3} cm/sec or greater, based on particle size. Moisture content is reported to be 1-3% in the areas around the demonstration tank, although the soil sample received contained 5.6% moisture. Figures 6 - 9 are photographs of the various aggregates.

Table 2 Size distribution of Morie TC-4727-81 blended sand aggregate (as in the manufacturers analysis sheet).

Sieve	Cumulative	% Retained
12	0.2	0.2
20	40.3	40.1
30	51.9	11.6
40	71.6	19.7
50	73.8	2.2
70	84.3	10.5
100	96.3	12.0
140	99.0	2.7
200	99.8	0.8
270	100.0	0.2

Figure 6. Blended sand aggregate used to produce polymer mortars.

Figure 7. Hanford soil used in soil mortars from near the 200 series tank farm.

Figure 8. Quartz stone aggregate used to produce polymer concretes.

Figure 9. Recycled glass used to produce polymer glass concretes.

3.0 SAMPLE FORMULATION/FABRICATION

The terms concrete, glass concrete, mortar and soil mortar will be used to label the barrier material composites in this report. A concrete consists of the polymer binder with a coarse stone aggregate and a blended sand aggregate. Glass concretes have the polymer binder and blended sand, but the coarse stone is replaced by re-cycled glass chips. Mortars are a mix of the polymer binder and blended sand. Soil mortars contain the polymers binder with natural site soil as the aggregate. The term "clean aggregate" samples includes all composites except the soil mortars. Concrete samples were made using Portland Type II hydraulic cement (PC) in addition to the polymer composites. The PC concrete samples are used as an engineering baseline. Ordinary PC concrete has been well characterized. BNL used this database as a check of the quality of the data obtained during testing. Values of strength or expected result obtained for the PC concrete should not deviate severely from literature values. Composite formulations are given in Table 3 and average sample densities in Table 4.

3.1 Soil Mortars

The polymer systems chosen were optimized to the chemical and physical properties of the Hanford soil. The first set of experiments were designed to determine the effect of soil aggregate on the resin gel times. Samples of monomer were allowed to cure with and without soil aggregate, choosing 1-2 hours as a reasonable working time prior to polymer gelling. The

furfuryl alcohol failed to gel with added Hanford soil because of the neutralizing effect of the high pH soil on the acid catalyst. All other systems followed expected gel times, both with and without Hanford soil. This initial trial eliminated furfuryl alcohol as a candidate material for Hanford soil mortar barrier technologies. However, displacement/replacement might still use furfuryl alcohol with neutral aggregates.

Sample fabrication techniques were refined after confirmation of catalyst-promoter quantities to achieve reasonable gel times. Porosity of the soil surrounding the tanks was estimated to be 35-45%, based on the coarseness of the soil sample received from Hanford. This would correspond to approximately 20-25% by weight monomer required to fill the void volume of the soil. The soil samples received were unconfined. Attempts to replicate the density of the confined soils would be difficult and unnecessary at this time, since an exact placement technology has not yet been chosen. The interaction of the monomer/soil composite and its durability properties are of primary importance. BNL attempted to balance the requirement of achieving a near 20-25 wt% monomer, while creating laboratory samples that were reproducible and homogeneous.

Soil mortar samples were fabricated by mixing together (in order) resin, promoter, catalyst, and the soil as received, in a Hobart mixer. The only exception to this is with the FA system. FA requires the catalyst to be mixed first with the aggregate, and to be evenly dispersed through the aggregate. This is to prevent the extremely reactive conditions (e.g. explosive) that could occur by adding the catalyst directly to the resin. The mixtures were poured into 3.5 foot long x 1.5" (38mm) diameter PVC pipe. The pipe was cut into 3" (76mm) lengths after polymerization was completed. The samples were removed from the mold and were measured and weighed to check for homogeneity within each lot.

The SPC samples were made by mixing SPC and aggregate in a heated double action planetary mixer. The lot was mixed until the temperature reached 124°C. Then, the mixture was poured into 2" (51mm) diameter polyvinylchloride (PVC) pipe, which was used as a casting mold. The lot was allowed to cool for several hours. The pipe was cut into 4" (102mm) lengths after solidification of the mix. The samples were removed from the PVC casing, measured, and weighed.

3.2 Mortars

Mortar samples were made in an identical fashion as the soil mortars, except a blended sand was used as aggregate, and the binder quantity was reduced for better economics. The blended sand packed better than the uniform particle size soil, which resulted in a lower porosity and reduced binder requirements. Binder quantity for soil mortars are influenced greatly by the soil porosity. Displacement/replacement grouts can be formulated with greater economic consideration. Trial samples at various binder/aggregate ratios were made for each binder type. Final formulation selection was based on forming a flowable grout that had as little free standing binder as reasonable, after pouring the mix and allowing for settling. Bitumen samples were made in a heated mix pot in a similar way to the SPC. The processing temperature was 200°C.

All samples were cast in 2" (51mm) x 30" cylindrical molds which were cut to 4" (102mm) lengths for testing after solidification.

3.3 Concretes

Concrete samples were made in an identical fashion to the mortars, except the aggregate was a 50-50 by weight mix of a blended silica sand and coarse silica stone. The aggregate composition was determined by measuring the maximum compact unit weight of various sand/stone combination. Figure 10 shows a plot of unit weight of the sand/stone blend versus percent sand. The maximum density or "best" packing occurs at 50% sand. Generally, the maximum density combination leads to increased strength, lower binder requirements, and increased performance (e.g. lower permeability). A graph of aggregate type versus average binder requirements is given in figure 12. Mixing had to be transferred for the SPC sample to the ordinary heated mix pot, since the stone aggregate would interfere with the close tolerance spacing of mixing blades in the planetary mixer. Sample cylinders measured were 2" (51mm) x 4" (102mm).

Figure 10. Unit weight of sand/stone aggregate blend.

3.4 Glass concretes

Glass concretes contain a 60-40 by weight mix of a blended silica sand, and a recycled glass aggregate. Figure 11 shows the plot of unit weight of the sand/glass mix versus percent sand. The maximum density combination occurs at 60% sand.. Recycle glass was chosen as an aggregate in order to reduce the binder requirements (compared to mortars), and to utilize a waste product. The glass is generally inert to geological, geochemical, and waste conditions, within the DOE complex. Sample cylinders measured 2" (51mm) x 4" (102mm) .

Figure 11. Unit weight of sand/glass aggregate blend.

3.5 Portland Cement Concrete

The formulation for the PC concrete was 17.9 % type II portland cement, 7.1 % water, 30.0 % blended sand, and 45.0 % coarse stone aggregate. The resultant water to cement ratio was 0.4. This was a typical construction concrete with no additives (e.g., superplasticizer). The concrete was made by adding all the ingredients into a portable, ¼ cubic yard, cement mixer. The cement was mixed for 5-10 minutes and poured into 2" (51mm) diameter x 30" cylindrical PVC molds. The tubes were cut to 4" (102mm) lengths for testing after solidification.

Table 3 Formulations - aggregate:binder ratios (by weight)

Binder	soil mortar	mortar	concrete	glass
VES	75:25	85:15	90:10	88.5:11.5
PES	73:27	82:18	88:12	85.5:14.5
Acrylic	77:23	87:13	91:9	89:11
FA	n.a.	86:14	90:10	88:12
SPC	70:30	75:25	84:16	82:18
Bitumen	n.a.	82:18	89:11	87:13

n.a. = not applicable

Figure 12. Typical Binder Requirements for Polymer Composites.

Table 4. Densities of polymer composites (g/cm³).

Binder	soil mortar	mortar	glass	concrete
VES	1.96	2.20	2.26	2.32
PES	1.85	1.93	2.17	2.28
Acrylic	1.95	2.17	2.19	2.29
FA	n.a.	2.23	2.19	2.34
SPC	n.a.	2.12	2.18	2.32
Bitumen	n.a.	1.95	2.09	2.20
Portland	n.a.	n.a.	n.a.	2.43

n.a. = not applicable

4.0 TESTING AND RESULTS

Representative samples of the various binder/aggregate combinations were subjected to a series of performance tests in order to determine if the materials were capable of meeting the requirements of a subterranean barrier for USTs. Soil mortars were part of an initial comparative study directed at the USTID. They were conditioned to about 50% humidity for seven days after durability tests were complete, but prior to destructive strength testing. The "clean" aggregate samples were tested at about 100% humidity with the exception of the baseline compressive strengths which were measured at "room humidity" of ~30%, in accordance with the ASTM procedure. Samples were "cured" 30 days at room temperature and humidity (except PC concrete which was moist cured), prior to any testing.

4.1 Hydraulic Conductivity

One of the most important performance considerations for a containment barrier is the rate that liquids will penetrate the barrier. Hydraulic conductivity is a direct measure of the ability of the barrier to prevent leakage or exclude percolation waters. Hydraulic conductivities were measured using a flexible wall permeameter after the issue of ASTM D-5084¹⁸. A photograph of the permeameter panel showing the water level, burettes, pressure regulators, gauges and sample cell is given in figure 13 with a closeup of the sample cell in figure 14. The permeant was deaired tap water which had an electrical conductivity of 120 μ mhos. Test sample cylinders measured 3.8 cm diameter by 3.0 cm for soil mortars, and 5.1 cm diameter by 5 cm for clean aggregate samples. Samples were preconditioned by placing them in a vacuum desiccator and evacuating (< 1 mm Hg) for 3 hours. Deaired water was introduced into the desiccator at the end of three hours without losing the vacuum. The vacuum was applied for an additional hour after the samples were covered by water. Then, the vacuum was

disconnected and air was allowed to enter the desiccator. The samples were left in the deaired water for up to 1 month in order to induce saturation. The water in the desiccator was deaired periodically by applying a vacuum to the desiccator for 1-2 hours.

The test specimens were placed in the permeameter cell and sealed using a latex membrane and a 35 kPa differential cell pressure. Back pressuring was used to accomplish full saturation of the samples. Full saturation was determined by measuring the compression B value according to ASTM D-4767-(88).¹⁹ The B value was 0.95-0.96 for most, but not all samples. The B value may not reach the specified 0.95 or better for brittle incompressible materials like polymer concrete. The B value is measured at two different pressure differentials in this case to see that it does not change. After full saturation was achieved, the cell pressure was set to 450-480 kPa, the lower cap pressure to 410 kPa, and the upper cap pressure to 210 kPa. This resulted in a pressure differential across the specimen of 210 kPa (21m H₂O). The hydraulic conductivities of the first few samples were measured at three different pressure differentials in order to make certain that Darcy's law was still valid at these pressures. The measured conductivities were the same at ΔP of 70, 140, and 210 kPa. This shows laminar flow is obeyed to 210 kPa ΔP for these binder/aggregate combinations. The water flow in and out of the sample was measured at about 24 hour intervals. The hydraulic conductivity was calculated according to:

$$k = QL/At h$$

where:

k = hydraulic conductivity, cm/sec

Q = water quantity through the sample, taken as the average of inflow and out flow, cm³

L = length of the specimen, cm

A = cross sectional area of the sample, cm²

t = time interval, s over which Q was measured

h = pressure differential across the sample, cm of water

Permeabilities are given in table 5 (average of two samples). The instrument limits were determined to be 2×10^{-11} cm/sec. Most of the hydraulic conductivities are in the range expected for polymer concretes. The exceptions were FA and acrylic mortars which resulted in conductivities higher than expected. The FA mortars were ~ 100 times higher than the FA concretes and glass concretes. The acrylic mortars were ~ 10 times higher than the respective concretes and glass concretes. The values should have fallen between those for the concretes and glass concretes, based on trends seen with the other binders. Both of these binders are low viscosity and required the lowest binder to aggregate ratios. There may have been insufficient binder to adequately fill the voids between aggregate particles. The volume percent of binder can be calculated using the binder weight percentages from table 3, the average specimen density from table 4 and the binder density from table 1. The FA and acrylic mortars used 27.6% and 27.5% binder respectively. The PES and VES mortars required 31.5% and 33.7% binder respectively to obtain the same slump as the FA and acrylic mortars. Increasing the binder

percentage in the FA and acrylic mortar grouts should decrease the hydraulic conductivities if greater resistance to water flow is required.

Ignoring the anomalies for the mortars, the order of hydraulic conductivities based on binder type is: bitumen < low modulus acrylic < furan < sulfur polymer cement < vinylester styrene $\equiv$ polyester styrene < high modulus acrylic. The order based on aggregate type follows the porosity order expected for each aggregate type. The concrete aggregate is formulated for best packing and minimal void space. The blended sand used for mortars is size graded, and is trimodal in particle size to reduce voids and porosity. Glass particles from the glass concretes are long irregular shaped chips and do not pack as well as round aggregate. The Hanford soil is basically unimodal coarse sand and has a large void volume. The order of conductivities based on aggregate type is: concrete < mortar < glass concrete < soil mortar.

Table 5 Hydraulic conductivities of polymer barrier composites (cm/sec $\times 10^{-10}$).

Polymer	Concrete	Mortar	Glass Concrete	Soil Mortar
Vinylester Styrene	1.5	3.0	4.2	6.7
Polyester Styrene	1.6	2.5	6.6	2.2
Acrylic	<0.2	7.0	0.35	40.0
Furan	0.45	340	0.48	n.a.
Sulfur Polymer Cement	0.63	0.54	0.67	n.a.
Bitumen	<0.2	<0.2	<0.2	n.a.
Portland Type II Cement	0.38	n.a.	n.a.	n.a.

n.a. = not applicable

Figure 13. Flexible wall permeameter used to measure hydraulic conductivities.

Figure 14. Permeameter cell showing a polymer concrete specimen sealed with a latex membrane.

4.2 Compressive Strength

Replicate (10 for soil mortars, 5 for all others) samples of each binder/aggregate combination were tested for unconfined compressive strength (ASTM C-39)²⁰ in order to determine baseline strength. Compressive strength by itself is not a very important parameter for subsurface barriers because of low (50-100 psi) overburden forces. However, compressive strength is measured easily and is a good barometer for the integrity of a sample. It can be used to gauge effects of testing on the barrier material. Compressive strength is used throughout this report as an indicator of the loss of integrity after resistance and durability testing.

Baseline values for polymer concretes showed low scatter which is evidence of good homogeneity. SPC samples showed larger standard deviations. Examination of the fractured samples indicated the presence of entrained air within the samples which is typical of SPC. It is postulated that the amount and size of these air bubbles is dependent upon mix viscosity, soil loading, mix speed, and mix time. The effect of these parameters may explain the variability.

Initially, it was thought that the compressive strength of bitumen samples would best be measured using ASTM D-1074²¹. This test calls for a constant rate of deformation and utilizes a test specimen having equal diameter and height. The bitumen samples made for this study were not meant for paving, and are to be compared to the other polymer composites. Therefore, the test method was modified to provide better comparative results. The bitumen samples were compression tested adhering to ASTM C-39 where the sample aspect ratio is 2:1, but the load rate was taken from ASTM D-1074. The load at 10% deformation was recorded in case the sample did not fail in a brittle manner. All of the specimens had a distinct maximum load and the compressive strength was calculated directly. Results are given in table 6. It is known that bitumen stiffens with aging and this could change the compressive strength value over the course of resistance testing. To be certain that aging was not a problem archived samples (stored during the resistance tests) were tested for compressive strength at the conclusion of the resistance tests. The strength values of these "aged" samples were identical to initial baseline samples so aging effects are not a concern for the short term testing that was performed.

Comparing the compressive strengths of the various polymer composites based on binder type elicits the following order: vinylester styrene > polyester styrene > sulfur polymer cement > furan > acrylic > bitumen. The strengths were highest for the round size graded aggregate types. The concretes and mortars had the highest strength. The unimodal Hanford soil was next in strength. The sharp edged glass aggregate were the lowest in strength.

Table 6 Compressive strength of polymer barrier composites
(MPa $\pm$ standard deviation).

Polymer	Concrete	Mortar	Glass Concrete	Soil Mortar
Vinylester Styrene	72.9 $\pm$ 2.5	82.4 $\pm$ 3.2	33.6 $\pm$ 1.4	47.6 $\pm$ 2.6
Polyester Styrene	59.6 $\pm$ 1.4	50.0 $\pm$ 12.2	39.5 $\pm$ 3.0	49.1 $\pm$ 3.6
Acrylic	14.0 $\pm$ 2.9	12.8 $\pm$ 1.5	9.7 $\pm$ 1.1	^a 25.7 $\pm$ 2.6
Furan	31.3 $\pm$ 2.0	35.6 $\pm$ 4.5	29.3 $\pm$ 3.2	n.a.
Sulfur Polymer Cement	34.1 $\pm$ 5.3	38.1 $\pm$ 6.1	27.4 $\pm$ 3.9	30.6 $\pm$ 5.8
Bitumen	3.0 $\pm$ 0.2	2.3 $\pm$ 0.2	3.1 $\pm$ 0.1	n.a.
Portland Type II Cement	45.2 $\pm$ 13.7	n.a.	n.a.	n.a.

a = high modulus resin; n.a. = not applicable

4.3 Flexural Strength

The method adhered to for determining the tensile strength of the candidate polymer composites in flexure was ASTM C-78, "Flexural Strength of Concrete (Using Simple Beam With Third-Point Loading)." ²² A concrete or polymer beam is placed between the load-applying and support blocks of the flexure apparatus in this test. The flexural strength is determined when bending under third-point loading results in sample failure.

Flexural strength tests were performed on five replicate samples of the clean aggregate polymer composites and PC concrete. A total of ninety-five specimens were prepared using two gang, prism molds which resulted in cured or polymerized specimens measuring 2 in. wide x 2 in. deep x 10 in. length (51mm x 51mm x 254mm). All samples were conditioned in a chamber at about 100% humidity for seven days before testing. The flexural strength testing was performed on a Soiltest Versa-Tester compression testing machine that was converted to a beam testing machine by the addition of a Soiltest flexure attachment (this arrangement meets ASTM specifications). Figure 15 shows a VES concrete beam positioned in the Versa-Tester/flexure attachment which is ready to be tested.

The moment in which the prism (beam) fails during flexure testing is usually the value of maximum tensile stress. It is defined as the modulus of rupture. Since all the prism fractures in our testing occurred in the tension surface located within the middle third of the span length, the following formula was used to determine the modulus of rupture: ²²

$$R = Pl/bd^2$$

where:

R = modulus of rupture, psi, (MPa)

P = maximum applied load indicated by the testing machine, lbf, (or N)

l = span length, in., (or mm)

b = average width of specimen, in., (or mm)

d = average depth of specimen, in., (or mm)

Bitumen samples proved to be too elastic to obtain a flexural strength measurement. The samples bowed in the center without failing. Results for all polymer composites are given in table 7.

The order of flexural strength based on binder type was: vinylester styrene > polyester styrene > furan > sulfur polymer cement > acrylic. The order based on aggregate type was the same as for compressive strength: concretes $\equiv$ mortars > glass concretes.

Table 7 Flexural strength of polymer barrier composites
(MPa $\pm$ standard deviation).

Polymer	Concrete	Mortar	Glass Concrete
Vinylester Styrene	15.0 $\pm$ 0.4	18.1 $\pm$ 2.4	9.3 $\pm$ 0.6
Polyester Styrene	17.2 $\pm$ 0.5	15.9 $\pm$ 0.6	7.1 $\pm$ 0.3
Acrylic	4.3 $\pm$ 0.2	3.4 $\pm$ 0.1	4.7 $\pm$ 0.1
Furan	9.0 $\pm$ 0.6	11.1 $\pm$ 0.4	9.2 $\pm$ 0.6
Sulfur Polymer Cement	7.9 $\pm$ 1.4	6.1 $\pm$ 0.4	4.9 $\pm$ 0.4
Portland Type II Cement	6.6 $\pm$ 0.3	n.a.	n.a.
Bitumen	n.m.	n.m.	n.m.

n.a. = not applicable

n.m. = not measurable, samples too elastic and bowed without failure.

4.4 Splitting Tensile Strength

A second method for determining the tensile strength of concrete and polymer concretes is the splitting tensile test. The method used by BNL was ASTM C-496, "Splitting Tensile Strength of Cylindrical Concrete Specimen."²³ The samples in this test had a standard cylindrical shape and measured 2 in. diameter x 4 in. length (51mm x 102mm). Replicates (5) of clean aggregate samples were tested destructively to determine the splitting tensile strength. Testing was performed on the same Soiltest Versa-Tester compression tester used to measure the flexural strength.

This test requires each cylindrical sample to be positioned with its horizontal axis between the loading plates of the compression test machine. However, the cylindrical test specimens were first placed in an aligning jig (See Figure 16) in order to ensure proper centering

and positioning during testing. Note that 1/8 in. thick plywood bearing strips are positioned between the two horizontal surfaces of the sample and the aligning jig bearing blocks. These bearing strips are used to eliminate the compressive stresses that would develop directly under the applied load. In addition, the placement of these bearing strips induces "a system of biaxial compression to exist and, therefore, failure in compression does not take place."²⁴ As a result, "the vertical mid-section of the cylinder is subject to horizontal tensile stress under this loading arrangement."²⁵

Five replicate, cylindrical samples of the clean aggregate composites and PC concrete were prepared for splitting tensile testing. All specimens were conditioned before testing in a about 100% humidity environment for seven days. Finally, the maximum applied load at failure for each sample was recorded, and the splitting tensile strength calculated, using the following formula:²³

$$T = 2P / \pi ld$$

where:

T = splitting tensile strength, in pounds per square inch (or kilopascals)

P = maximum applied load indicated by the testing machine, in pounds-force (or kilonewtons)

l = length, in inches (or meters)

d = diameter, in inches (or meters).

All the cylindrical composites tested fractured at the vertical diameter and along the horizontal axis. In addition, most specimens fractured into two, relatively equal, pieces. However, sometimes the failure resulted in the generation of 3 or 4 pieces. Results are presented in table 8.

The tensile strengths followed the order: vinylester styrene > polyester styrene > furan > sulfur polymer cement > acrylic > bitumen. Aggregate to strength relationships found in compressive and flexural strengths remained the same for tensile strength.

Table 8 Splitting tensile strength of polymer barrier composites (MPa $\pm$ standard deviation).

Polymer	Concrete	Mortar	Glass Concrete
Vinylester Styrene	11.7 $\pm$ 0.3	13.9 $\pm$ 0.5	7.7 $\pm$ 0.9
Polyester Styrene	10.3 $\pm$ 0.2	9.2 $\pm$ 1.9	8.0 $\pm$ 0.3
Acrylic	2.6 $\pm$ 0.2	2.9 $\pm$ 0.5	2.2 $\pm$ 0.1
Furan	6.5 $\pm$ 0.5	7.6 $\pm$ 0.5	6.3 $\pm$ 0.4
Sulfur Polymer Cement	6.3 $\pm$ 0.8	5.1 $\pm$ 0.2	5.0 $\pm$ 0.4
Bitumen	0.94 $\pm$ 0.04	0.89 $\pm$ 0.02	0.89 $\pm$ 0.07
Portland Type II Cement	8.7 $\pm$ 1.0	n.a.	n.a.

n.a. = not applicable

Figure 15. Polymer concrete beam specimen loaded in the flexure attachment to determine tensile strength in flexure.

Figure 16. Alignment jig used to center samples for testing.

4.5 Water Immersion

It is expected that a subterranean containment barrier will be exposed to aqueous environments from either leakage of the supernatant contained in a UST, waste site container leakage, or percolate water. Exposure of barrier materials to aqueous solutions can result in swelling, cracking, or dissolution. Also the soils used as aggregate may also interact with the water through swelling (i.e., expansive clays) or dissolution of mineral components. Aggregate interactions can cause internal stresses with resultant cracking and strength losses in the barrier. Replicate (5) samples of each binder/aggregate combination were immersed in deionized water for a period of 90 days. The samples were inspected visually for cracking and swelling periodically, during the course of the test. The samples were weighed, measured, and destructively tested for compressive strength (ASTM D-695 for soil mortars and ASTM C-39 for clean aggregate samples) at the end of the test period. Compressive strength data after immersion is given in Table 9 and shown in Figure 18. There was minimal water uptake by the polymer composites. Table 10 lists the percent weight change (water uptake) for the various binder/aggregate combinations.

SPC soil mortars cracked after three to five days exposure to ionized water (see figure 17). Probably, this effect is due to small expansive clay portions in the Hanford soils, which would induce tensile stresses in the sample when exposed to water. The effect of such expansive clays is accentuated with SPC since temperatures in excess of 120°C are required to melt the binder during the fabrication of SPC samples. The residual soil moisture is driven off at these temperatures, and the clays shrink to their minimum volume. The clays expand with resultant internal stresses when they are re-wetted. The soil was used as received for all the other soil mortars, with approximately 5.6% moisture content, and without showing detrimental effects.

Results were mixed for the clean aggregate samples. The FA, bitumen, acrylic concrete, and acrylic mortar samples showed no strength changes for any of the aggregate types after 90 days. The acrylic glass composite showed strength loss averaging 40%, which may indicate some reactivity between the polymer and the glass. SPC samples showed no statistical change in strengths. However, there is a large amount of scatter in the results. This is most pronounced for the glass concrete. The error bands just overlap but the magnitude is about 50% of the baseline strength. There is a chance that water immersion has an adverse effect of water immersion on SPC glass concrete. This was substantiated further by acid and base resistance testing which is detailed latter in this report. The PES samples showed losses averaging 17%, while the VES averaged 26% losses. PC concrete samples showed no strength change after 90 days.

The results for PES and VES were unexpected, based on the results previously obtained where no losses occurred for soil mortars. This can be explained by pretest conditioning. The soil mortar immersion samples were returned to 50% humidity environments for 7 days after immersion, but prior to destructive strength testing. This study was for comparative losses. And all samples were conditioned to the ASTM conditions outlined in D-695, "Compressive Properties of Rigid Plastics". The clean aggregate samples (used in an engineering study)

adhered to ASTM C-39 standard conditions for the baseline strengths, and followed the Nuclear Regulatory Commissions (NRC) recommendations for the immersion test²⁶. The NRC test calls for strength testing of the immersed samples immediately after removal from the water. This would keep the samples at 100 % humidity. This water content difference may result in the strength differences between the PES and VES samples.

All of these materials are to be used underground. The soil gases will be at 100% humidity. Therefore, it was decided that all future strength testing of the barrier materials (e.g., acid resistance, base resistance, wet-dry cycling) would be performed after conditioning the samples to about 100% humidity for seven days.

Table 9. Compressive strength of polymer barrier composites after immersion in water for 90 days (MPa $\pm$ standard deviation).

Polymer	Concrete	Mortar	Glass Concrete	Soil Mortar
Vinylester Styrene	49.2 $\pm$ 1.8	55.5 $\pm$ 3.9	29.4 $\pm$ 1.7	51.1 $\pm$ 1.2
Polyester Styrene	45.8 $\pm$ 0.9	43.8 $\pm$ 3.9	34.4 $\pm$ 1.2	47.4 $\pm$ 1.3
Acrylic	11.3 $\pm$ 1.2	11.2 $\pm$ 2.1	5.8 $\pm$ 1.6	^a 23.1 $\pm$ 3.8
Furan	35.9 $\pm$ 1.0	38.4 $\pm$ 5.4	29.9 $\pm$ 1.3	n.a.
Sulfur Polymer Cement	25.8 $\pm$ 4.2	36.2 $\pm$ 7.0	18.9 $\pm$ 7.5	failed
Bitumen	3.0 $\pm$ 0.2	2.3 $\pm$ 0.2	3.1 $\pm$ 0.1	n.a.
Portland Type II Cement	42.8 $\pm$ 9.2	n.a.	n.a.	n.a.

a = high modulus resin; n.a. = not applicable

Table 10. Percent water uptake for polymer composites after water immersion.

Binder Type	Percent Weight Change		
	Mortar	Glass Concrete	Concrete
Vinylester styrene	0.46	0.42	0.37
Polyester styrene	1.76	0.79	0.51
Acrylic	0.18	0.27	0.13
Furan	0.29	0.29	0.22
Sulfur polymer cement	0.18	0.25	0.21
Bitumen	0.04	0.04	0.02
Portland cement	n.a.	n.a.	1.70

n.a. = not applicable

Figure 17. Sulfur polymer cement soil mortars before and after immersion in water for 90 days.

Figure 18. Effects of immersion in water for 90 days on the compressive strength of polymer composites.

4.6 Acid Resistance

Clean aggregate samples were immersed in an aqueous nitric acid solution at pH 2 for 90 days. Nitric acid was chosen as representative of conditions within the DOE complex. The pH values are based upon the EPA characteristic corrosivity criteria for hazardous waste. The samples were visually inspected during the 90 days on a daily basis for cracking, swelling, or spalling. The pH was checked daily, and adjusted back to 2 if it changed by 0.5 units or more. Only the PC concrete specimens required pH adjustment during the 90 days. The excess hydroxide from the cement neutralized the acid at a fairly rapid rate in the first 14 days. Acid additions were required daily at first, then every other day. The acid consumption dropped off rapidly after two weeks, and pH adjustments were infrequent. Triplicate samples were removed from the media, rinsed, measured, weighed and subjected to compressive strength testing every 30 days, adhering to ASTM-C39. No visual or dimensional changes were observed for any samples. No significant weight losses or gains were recorded for any of the polymer composites. Compressive strengths after testing are given in Table 11. Results were similar to the immersion test. PES, VES, and acrylic\glass showed similar strength losses which were observed after water immersion. Bitumen mortar samples remained relatively unchanged. The average strength of the bitumen glass samples show a slight increase in strength over the 90 days, but still fall within one standard deviation of the baseline. Bitumen concrete samples increased steadily in strength as time progressed. This may indicate slight attack on the bitumen binder by the acid. Bitumen is highly plastic, as compared to the other polymer materials which are brittle. Bitumen stiffens, and loses some of its plasticity when degradation such as oxidation occurs. This translates to a slight increase in ultimate compressive strength. All other composites remained unchanged except the SPC/glass composite, which showed continual loss of strength after 30, 60, and 90 day intervals. This suggests a binder/aggregate interaction. The SPC mortars and concretes show downward trends in the average strength, but the strengths fall within one standard deviation of the baseline. PC Concrete showed continual losses as expected, as time progressed. PC is hydroxide based. The excess hydroxide is attacked readily by acid. The strengths are depicted graphically, as percent of immersion test strengths in figures 19-21. The immersion test was used as a baseline for this plot based on the humidity effects which were seen for the VES and PES.

Figure 19. Effects of immersion in nitric acid ($\text{pH} = 2$) on the compressive strength of polymer concretes (baseline in post water immersion strength).

Figure 20. Effects of immersion in nitric acid (pH = 2) on the compressive strength of polymer mortars (baseline in post water immersion strength).

Figure 21. Effects of immersion in nitric acid (pH = 2) on the compressive strength of polymer glass concretes (baseline in post water immersion strength).

Table 11 Compressive strength of polymer barrier composites after chemical immersion (MPa $\pm$ standard deviation).

Binder	Mixture Type	Base Resistance			Acid Resistance		
		30 days	60 days	90 days	30 days	60 days	90 days
VES	mortar	75.3 $\pm$ 9.6	61.6 $\pm$ 0.4	52.8 $\pm$ 2.6	66.1 $\pm$ 4.6	62.9 $\pm$ 8.2	67.0 $\pm$ 12
	concrete	54.2 $\pm$ 0.9	48.5 $\pm$ 1.2	43.7 $\pm$ 1.9	51.2 $\pm$ 1.4	49.1 $\pm$ 2.3	47.2 $\pm$ 0.7
	glass	25.0 $\pm$ 1.7	25.1 $\pm$ 1.4	27.0 $\pm$ 1.8	27.5 $\pm$ 1.1	27.7 $\pm$ 2.0	28.9 $\pm$ 3.0
PES	mortar	46.5 $\pm$ 4.5	39.7 $\pm$ 3.5	39.6 $\pm$ 3.8	43.1 $\pm$ 6.6	43.7 $\pm$ 1.6	43.9 $\pm$ 3.7
	concrete	43.5 $\pm$ 2.0	38.8 $\pm$ 0.0	44.4 $\pm$ 2.9	42.2 $\pm$ 0.9	40.9 $\pm$ 2.6	42.0 $\pm$ 2.7
	glass	30.7 $\pm$ 2.2	33.7 $\pm$ 2.7	30.4 $\pm$ 1.6	32.3 $\pm$ 1.1	33.2 $\pm$ 2.4	33.6 $\pm$ 0.5
Acrylic	mortar	9.2 $\pm$ 2.1	11.4 $\pm$ 0.3	10.0 $\pm$ 0.4	10.8 $\pm$ 3.8	11.3 $\pm$ 3.1	12.1 $\pm$ 1.8
	concrete	8.4 $\pm$ 1.6	10.7 $\pm$ 0.9	10.0 $\pm$ 0.8	10.0 $\pm$ 2.8	8.1 $\pm$ 0.1	10.9 $\pm$ 0.9
	glass	3.7 $\pm$ 0.5	5.6 $\pm$ 0.2	4.6 $\pm$ 0.7	4.6 $\pm$ 0.8	5.0 $\pm$ 0.9	6.4 $\pm$ 0.6
FA	mortar	37.4 $\pm$ 4.6	46.1 $\pm$ 1.6	36.8 $\pm$ 3.8	32.9 $\pm$ 3.6	37.7 $\pm$ 2.1	35.3 $\pm$ 2.4
	concrete	29.5 $\pm$ 1.9	31.3 $\pm$ 2.3	33.2 $\pm$ 3.9	29.6 $\pm$ 1.4	30.5 $\pm$ 1.2	33.4 $\pm$ 2.9
	glass	29.5 $\pm$ 0.0	28.5 $\pm$ 2.1	28.0 $\pm$ 1.8	27.3 $\pm$ 1.8	28.9 $\pm$ 1.8	30.9 $\pm$ 3.0
SPC	mortar	36.5 $\pm$ 2.2	28.6 $\pm$ 8.6	28.6 $\pm$ 1.6	35.0 $\pm$ 1.8	31.5 $\pm$ 1.6	26.0 $\pm$ 7.4
	concrete	29.5 $\pm$ 3.3	19.8 $\pm$ 3.7	18.1 $\pm$ 5.7	32.8 $\pm$ 4.6	25.2 $\pm$ 4.8	21.1 $\pm$ 3.5
	glass	19.6 $\pm$ 6.3	9.5 $\pm$ 1.4	8.7 $\pm$ 2.1	26.0 $\pm$ 0.4	16.7 $\pm$ 2.4	7.3 $\pm$ 0.4
Bitumen	mortar	2.1 $\pm$ 0.2	2.6 $\pm$ 0.2	3.1 $\pm$ 0.2	2.5 $\pm$ 0.3	2.8 $\pm$ 0.4	2.6 $\pm$ 0.4
	concrete	3.3 $\pm$ 0.3	3.6 $\pm$ 0.2	4.5 $\pm$ 0.1	3.5 $\pm$ 0.4	3.8 $\pm$ 0.2	4.2 $\pm$ 0.2
	glass	3.0 $\pm$ 0.1	3.0 $\pm$ 0.1	3.4 $\pm$ 0.1	2.9 $\pm$ 0.2	3.3 $\pm$ 0.2	3.5 $\pm$ 0.3
PC	concrete	39.4 $\pm$ 7.5	39.6 $\pm$ 3.5	26.6 $\pm$ 3.8	43.7 $\pm$ 6.0	36.3 $\pm$ 0.9	26.8 $\pm$ 5.7

4.7 Base Resistance

Clean aggregate samples were immersed in an aqueous, sodium hydroxide solution at pH 12.5 for 90 days. Sodium hydroxide was chosen as representative of conditions within the DOE complex. The pH values are based upon the EPA characteristic corrosive for hazardous waste. The samples were visually inspected on a daily basis during the 90 days for cracking, swelling, or spalling. The pH was checked daily and adjusted back to 12.5 if it changed by 0.5 units or more. Triplicate samples were removed from the media, inspected and subjected to compressive strength testing every 30 days adhering to ASTM-C39. No visual or dimensional changes were observed for any samples. All weight changes were the same as seen in the immersion testing. Compressive strengths after testing are given in table 11. Results for PES, VES, and acrylic were similar to the immersion and acid resistance tests. FA composites remained unchanged after 90 days. All SPC composites showed some loss of strength with the glass aggregate showing continual losses after 30, 60, and 90 day intervals. SPC is known to be attacked by base and the results are as expected. All bitumen composites showed strength increases after 90 days immersion. The increases averaged 28% and are indicative of binder degradation. The PC concretes are within a single standard deviation for 30 and 60 days exposure. The strength lies just below one standard deviation after 90 days, which indicates some loss of integrity. PC should not be affected by sodium hydroxide, since the material is hydroxide based. The strength loss is probably a sign of aggregate-base interaction. Results for 30, 60, and 90 days are graphically depicted in figures 22-24.

Figure 22. Effect of immersion in sodium hydroxide ($\text{pH} = 12.5$) on the compressive strength of concretes (baseline in post water immersion strength).

Figure 23. Effect of immersion in sodium hydroxide ($\text{pH} = 12.5$) on the compressive strength of polymer mortars (baseline in post water immersion strength).

Figure 24. Effect of immersion in sodium hydroxide (pH= 12.5) on the compressive strength of polymer glass concretes (baseline in post water immersion strength).

4.8 Solvent Resistance

Nine replicate samples of each aggregate/binder combination for VES, PES, SPC, 3M acrylic polymer, furfuryl alcohol, bitumen, and Portland cement were immersed in water saturated with trichloroethylene (TCE) at room temperature for immersion periods of 30, 60, and 90 days. TCE was chosen as the candidate media for VOC solvent testing because it appears to be the predominate contaminant found at many DOE facilities. Three replicates from each composite type were placed in one of three containers which were sealed to zero head space in order to avoid evaporative losses. In addition, each container had a reservoir of excess TCE to keep the solution saturated, and a clear lexan lid to allow visual inspection of the samples. Bitumen samples were placed in different containers because of the strong possibility of binder dissolution. At each sampling interval, triplicate samples were removed from one container, rinsed, measured, visually inspected and placed in a chamber at 100% humidity for seven days. Samples were then subjected to compressive strength testing in accordance with ASTM Method C-39.

The magnitude of the physical condition of each composite never changed throughout the 90 day test period in every case, regardless of the condition of each composite after 30 days of immersion. Portland cement, VES, furfuryl alcohol, and SPC composites showed no visible evidence of surface deterioration. However, the surface of the SPC samples did show a "drip-like"

Figure 25. Bitumen specimen after immersion in a saturated solution of trichloroethylene, showing widening at the base of the sample.

pattern, as well as a blotchy discoloration. The bitumen samples revealed a surface texture after 30 days of TCE immersion which was both randomly pitted and granular. In addition, the surface color changed from glossy to dull black except where the "drip-like" surface patterns were visible once again. A slight widening at the base of many of the bitumen samples was observed, as shown in Figure 25. This is the partial dissolution of the bitumen by the TCE (and was further evidenced by the discoloration of the solution from clear to tinted). Both the 3M acrylic polymer and PES composites showed moderate surface degradation, irrespective of the composition. This deterioration was characterized by surface blistering, flaking, small depressions, discoloration (blotchy or "drip-like" patterns), granular texture, and binder dissolution. Although this "attack" occurred on the entire sample surface, the most severe damage was concentrated on the top or bottom surfaces, and at the lower lateral/base interface. Figure 26 shows the magnitude of binder dissolution observed on the bottom surface of a PES concrete. The top surface of a 3M Glass sample is shown in figure 27.

Figure 26. Polyester styrene concrete specimen showing binder dissolution after immersion in a saturated solution of trichloroethylene.

Results for VES composites were the same as in the immersion test. FA composites remained unchanged after 90 days. Bitumen and PC specimens show losses just under 10% with standard deviations close to this difference. PES and acrylic samples had slight losses after 30 days but, the losses then remained at a constant level up to 90 day immersion. Acrylic glass concretes show larger losses than the mortars or concretes. This is attributed to the aggregate/binder/water interactions seen earlier in the water immersion testing. SPC composites all showed some loss of strength after 90 days immersion, with the glass aggregate showing continual losses after 30, 60 and 90 day intervals. Results are given in table 12 and figures 28-30.

Figure 27. Acrylic glass concrete specimen showing binder dissolution after immersion in a saturated solution of trichloroethylene.

Figure 28. Effect of immersion in a saturated solution of trichloroethylene on the compressive strength of concretes (baseline in post water immersion strength).

Figure 29. Effect of immersion in a saturated solution of trichlorethylene on the compressive strength of polymer mortars (baseline in post water immersion strength).

Figure 30. Effect of immersion in a saturated solution of trichlorethylene on the compressive strength of polymer glass concretes (baseline in post water immersion strength).

Table 12 Compressive strengths of polymer composites after solvent immersion.
(MPa $\pm$ standard deviation)

Binder	Aggregate Type	30 days	60 days	90 days
VES	concrete	44.5 $\pm$ 2.9	39.3 $\pm$ 4.3	47.0 $\pm$ 2.9
	mortar	58.2 $\pm$ 10.3	57.8 $\pm$ 0.7	51.6 $\pm$ 0.0
	glass concrete	27.7 $\pm$ 1.0	28.4 $\pm$ 1.1	26.2 $\pm$ 0.9
PES	concrete	30.5 $\pm$ 2.2	44.1 $\pm$ 2.1	41.4 $\pm$ 1.2
	mortar	36.3 $\pm$ 2.8	40.2 $\pm$ 7.3	39.4 $\pm$ 2.2
	glass concrete	30.7 $\pm$ 2.2	32.4 $\pm$ 1.5	32.5 $\pm$ 4.8
Acrylic	concrete	8.7 $\pm$ 2.7	8.7 $\pm$ 0.5	8.9 $\pm$ 2.3
	mortar	8.6 $\pm$ 1.7	11.1 $\pm$ 2.3	10.2 $\pm$ 1.2
	glass concrete	7.0 $\pm$ 0.4	3.7 $\pm$ 0.8	5.7 $\pm$ 0.2
Furan	concrete	24.6 $\pm$ 2.1	34.9 $\pm$ 0.4	33.7 $\pm$ 3.1
	mortar	37.3 $\pm$ 3.0	39.3 $\pm$ 2.1	46.6 $\pm$ 2.1
	glass concrete	25.6 $\pm$ 3.7	24.6 $\pm$ 0.5	27.9 $\pm$ 5.0
SPC	concrete	24.1 $\pm$ 9.7	20.2 $\pm$ 8.4	17.0 $\pm$ 3.1
	mortar	22.2 $\pm$ 0.8	18.0 $\pm$ 1.8	20.6 $\pm$ 3.4
	glass concrete	11.2 $\pm$ 6.4	9.8 $\pm$ 1.8	6.6 $\pm$ 0.6
Bitumen	concrete	3.1 $\pm$ 0.2	3.0 $\pm$ 0.4	2.5 $\pm$ 0.3
	mortar	2.3 $\pm$ 0.3	2.0 $\pm$ 0.2	2.0 $\pm$ 0.3
	glass concrete	2.6 $\pm$ 0.2	2.7 $\pm$ 0.3	2.6 $\pm$ 0.4
Portland Cement	concrete	30.1 $\pm$ 3.8	41.7 $\pm$ 2.9	43.6 $\pm$ 2.3

4.9 Wet-Dry Cycling

The Hanford tank farm is located in a semi-arid region. The soil moisture content is low, ranging between 1 and 3 %. Sometimes precipitation percolates the ground and recharges the aquifer. The barrier will be under saturated conditions during these times. Wet-dry cycling has a severe impact on construction materials such as hydraulic cements. Replicate samples of

the various binder/aggregate combinations were subjected to wet-dry cycling adhering to ASTM D-4843.²⁷ SPC soil mortars were excluded based on water immersion results. Test samples are cycled twelve times, from 60°C dry to 20°C wet. The ASTM test requires the evaporation of the water after each wet cycle, and the weighing of the residue left in the beaker. The samples were wet cycled in the same beaker, for each cycle while reusing the water (additional water was added to replenish losses from evaporation). The water was evaporated and the residue weight recorded at the end of the final cycle. The wet samples were towel dried and weighed after each cycle. The dry cycle samples were weighed directly. In addition, samples were compression tested (ASTM D-695 for soil mortars and ASTM C-39 for clean aggregate samples) after the final cycle in order to determine mechanical integrity.

None of the polymer samples showed any visible degradation after 12 cycles. Weight changes were minimal from beginning to end. The average weight changes for soil mortars were -0.7%, -1.2%, and +1.0% for VES, PES, and acrylic, respectively. PC concrete specimens averaged -0.9%. Weight changes were even lower for the clean aggregate samples, and ranged from a high of 0.23% for FA glass concrete, to a low of 0.004% for PES concrete, with the average at 0.07%. The average weight histories of the materials are given in figures 31-34. Note the difference in magnitude of weight fluctuation between the polymer concretes and the PC concrete in figure 31.

PC concretes showed hairline cracking after 1-2 cycles. The size of cracking remained constant, although the number of cracks increased continually throughout the testing. This hairline cracking did not affect the strength as greatly as might be anticipated. The strength losses averaged 20%. VES and PES specimens showed no strength changes for the soil mortars (conditioned at ~50% humidity). The clean aggregate samples showed similar strength changes, as observed after immersion, acid resistance, and base resistance. Acrylic samples showed slight strength increases for the soil mortar, unchanged for the mortar and concrete, and similar losses for the glass composite, as observed after immersion, acid resistance, and base resistance. FA samples (clean aggregate only) showed significant strength increases, averaging 57% after wet-dry cycling. This may be attributed to further curing induced by the elevated temperature during the dry cycle. All of the SPC samples tested lost strength during the wet-dry cycling. The losses were 47% for mortars, 56% for concretes, and 81% for the glass concrete. The magnitude of the losses for mortars and concretes are similar to those for thermal cycling of the soil mortars, as well as and industry expectations for thermal cycling. If the wet-dry cycling were to occur at nearly constant temperatures, as it does in the subsurface, SPC should not show any losses. The losses for the glass concretes are significantly greater, and may be due to the additive effects of thermal cycling (see soil mortars) and immersion (see immersion for SPC\glass composites). The bitumen mortar samples slowly slumped from the elevated temperature during the dry cycle. Bitumen is well documented for creep. Eventually, the samples were about 2/3 their original height, and could not be used for compressive testing afterwards. The bitumen concrete and glass concrete held their shapes throughout the test. Both showed slight strength increases. Values for compressive strength are given in Table 13.

Table 13 Compressive strength of polymer barrier composites wet-dry cycling (MPa $\pm$ standard deviation).

Polymer	Concrete	Mortar	Glass Concrete	Soil Mortar
Vinylester Styrene	46.3 $\pm$ 3.8	64.3 $\pm$ 3.7	24.1 $\pm$ 1.8	52.6 $\pm$ 2.7
Polyester Styrene	43.7 $\pm$ 2.1	39.2 $\pm$ 6.9	29.6 $\pm$ 2.7	57.8 $\pm$ 5.4
Acrylic	12.9 $\pm$ 0.9	15.3 $\pm$ 3.6	6.7 $\pm$ 1.6	^a 34.0 $\pm$ 5.1
Furan	53.7 $\pm$ 3.8	59.1 $\pm$ 4.0	39.1 $\pm$ 2.8	n.a.
Sulfur Polymer Cement	15.0 $\pm$ 5.4	19.9 $\pm$ 5.8	5.1 $\pm$ 1.5	n.a.
Bitumen	3.8 $\pm$ 0.4	slumped	3.6 $\pm$ 0.4	n.a.
Portland Type II Cement	36.1 $\pm$ 6.5	n.a.	n.a.	n.a.

a = high modulus resin; n.a. = not applicable

Figure 31. Weight changes of polymer concretes and hydraulic cement concrete during wet-dry cycling.

Figure 32. Weight changes of polymer mortars during wet-dry cycling.

Figure 33. Weight changes of polymer glass concretes during wet-dry cycling.

Figure 34. Weight changes of polymer soil mortars during wet-dry cycling.

4.10 Chloride Diffusivity

Resistance to penetration of chloride ions through the polymer composites was determined using AASHTO T277-93, "Electrical Indication of Concretes Ability to Resist Chloride".²⁸ This method measures the electrical conductance across a 51mm thick slice of material in order to provide a rapid indication of resistance to chloride ions.

A cylindrical sample is mounted between two halves of the test cell, as shown in figure 35. One face of the sample is immersed in a 3% by weight aqueous, sodium chloride solution. The other face is immersed in 0.3 N sodium hydroxide solution. The outer surface of the sample was sealed with an epoxy sealant. A potential difference of 50 Vdc is maintained across the sample. The amount of electrical current passing through the sample is monitored for six hours. The total charge in coulombs passed is related to chloride ion penetrability. The current was recorded every 30 minutes. The total charge passed, Q is calculated according to:

$$Q = 900(I_o + 2I_{30} + 2I_{60} + \dots + 2I_{300} + 2I_{330} + I_{360})$$

where Q = charge passed, coulombs
 I_o = current immediately after voltage is applied, amperes
 I_t = current at time t after voltage is applied, amperes

The samples tested were not standard size (95 mm diameter) for the test. The charge passed had to be corrected according to:

$$Q_s = Q_x (95/x)^2$$

where Q_s = charge passed through a 95 mm diameter sample, coulombs
 Q_x = charge passed through x mm diameter sample, coulombs
 x = diameter of the nonstandard sample, mm

Duplicate samples of each polymer/binder combination and PC concrete were tested. Table 14 (which is found in AASHTO T277-93) gives the suggested ratings based on charge passed. The PC concrete passed 1241 coulombs which ranks it as low. This agrees with published values for typical plain concretes which have water to cement ratios of 0.3-0.4.²⁹ The polymer composites ranged from 0 to 26 coulombs which ranks them as very low. This shows the benefit of polymer composites as barriers to ionic species. PC concrete pore waters have a high ionic activity, and ionic transport is enhanced. The polymer composites have low ionic activity in the pore waters and ionic transport is much less. Chloride diffusivity is reversed from water permeability. The PC concrete had a lower hydraulic conductivity than polymer composites, but the ionic diffusivity as measured by electrical conductance was much higher than any polymer matrix. Results are given in table 15.

Table 14. Chloride ion penetrability based on charge passed.

Charge Passed, coulombs	Chloride Penetrability
> 4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
< 100	Negligible

Figure 35. Conductance cell for rapid chloride penetration determinations.

Table 15. Chloride penetrability of polymer composites based on total charge passed.

Material	Coulombs Passed	Ranking
VES glass concrete	15	negligible
VES mortar	24	negligible
VES concrete	23	negligible
PES glass concrete	23	negligible
PES mortar	20	negligible
PES concrete	22	negligible
Acrylic glass concrete	10	negligible
Acrylic mortar	13	negligible
Acrylic concrete	7	negligible
Furan glass concrete	22	negligible
Furan mortar	9	negligible
Furan concrete	15	negligible
SPC glass concrete	26	negligible
SPC mortar	20	negligible
SPC concrete	21	negligible
Bitumen glass concrete	1	negligible
Bitumen mortar	0	negligible
Bitumen concrete	0	negligible
Portland cement concrete	1241	low

4.11 Hot Nitrate Brine Resistance

Presumably, the barrier will be exposed to the supernatant from the tank, in the event of leakage from USTs. The supernatants in most of the USTs are nitrate-nitrite salt solutions. The composition of the supernatant for the USTID demonstration tank in percent is: NaNO_3 , 34.7; NaNO_2 , 26.4; Na_2CO_3 , 1.0; NaOH , 10.4; NaAlO_2 , 20.9; Na_3PO_4 , 3.8; and organic, 2.8.³ Also, the liquid may be at elevated temperature due to the heat production from radionuclide

decay. Soil mortar samples were subjected to immersion in a hot surrogate nitrate brine in order to determine the durability of the polymers in such an environment. The brine was 50% solid using salts in the proportions given above. The temperature of 70°C was the average tank temperature of the 11 high heat (>40,000 Btu/hr) tanks at Hanford. Twelve samples of VES, PES, and acrylic soil mortars were immersed in the brine, and placed in an environmental chamber at 70°C for 120 days. The exclusion of SPC soil mortar was based on water immersion results. The samples were inspected routinely for cracking and/or spalling. Salt crystals formed on the sides of the samples after one week, with no signs of sample degradation. Figure 36 shows a photograph of the samples as they appeared after 30 days.

Three samples of each soil-mortar composite were removed at 30 day intervals for visual and destructive testing in order to determine sample integrity. The samples were scrubbed clean with water and steel wool to remove the crystal formation in order to allow inspection. It should be noted that the crystals were most prevalent on the 3M 4R mortar, followed by the PES and VES. The crystals showed a slight orange to brown coloration, which indicates probable interaction between the iron in the soil and the brine [none of the surrogate brine salts were colored originally]. The samples were inspected for cracking and spalling. All samples were in good condition after cleaning. Then, the specimens were conditioned at about 50% RH for seven days and tested for compressive strength. The results given in Table 16 (see also figure 37) show no loss in integrity for VES and PES soil mortars. The acrylic soil mortars show no strength losses up to the 60 day interval. There is apparent degradation at 90 days, as evidenced by a 40% loss in strength. No further losses occur at 120 days. Figure 38 is a photograph of the cross-section of an acrylic soil mortar (after destructive testing). The picture shows a dark band along the perimeter of the specimen. This is the line of penetration or attack by the brine solution. The attack sealed the sample surface porosity and slowed penetration/attack. Thus, no further strength losses were apparent after 120 days.

Table 16 Compressive strengths of soil mortars after nitrate brine immersion.
(MPa $\pm$ standard deviation)

Binder	30 days	60 days	90 days	120 days
VES	59.3 $\pm$ 1.1	63.7 $\pm$ 1.4	56.4 $\pm$ 4.2	58.6 $\pm$ 1.6
PES	55.4 $\pm$ 2.4	55.8 $\pm$ 3.6	56.1 $\pm$ 1.6	58.3 $\pm$ 3.2
Acrylic ^a	25.4 $\pm$ 2.0	24.5 $\pm$ 2.5	15.3 $\pm$ 3.0	17.8 $\pm$ 4.0

a = high modulus resin

Figure 36. Soil mortars after immersion in hot nitrate brine surrogate.

Effect of Hot Nitrate Brine on the Strength of Soil Mortars

Figure 37. The effect of hot nitrate brine on strength of polymer soil mortars.

Figure 38. Cross section of an acrylic soil mortar after 120 days immersion in a hot sodium nitrate brine surrogate.

4.12 Thermal Cycling

Thermal cycling of materials can be useful to determine durability to temperature changes, as a tool to indicate internal prestressing, and as a comparative measure of quality. Although a subterranean containment barrier for USTs is not expected to see freezing conditions (unless a cryogenic barrier is used as a secondary backup), thermal cycling was used as a qualitative yard stick. Thermal cycling causes expansion and contraction of the material, thus fatiguing the sample. Materials that are highly prestressed or have low strength (especially tensile strength) will be more prone to damage from thermal cycling.

Six replicate samples of VES, PES, SPC, and acrylic soil mortars were tested in accordance to ASTM B-553³⁰, with modifications recommended by the Nuclear Regulatory Commission.⁹ Cycling of the samples was performed using an environmental chamber controlled by a microprocessor, which was capable of temperature ranges between -73 and $+200^{\circ}\text{C} \pm 0.3^{\circ}\text{C}$. The specimen were placed in the chamber, and cycled between -40 and $+60^{\circ}\text{C}$ for a total of 30 cycles. Each cycle lasted approximately 5 hours. Figure 39 is a plot of temperature versus time for one cycle.

Figure 39. Temperature conditions for one cycle of ASTM B-552

The samples were inspected and measured after the cycling was complete. No visible effects were observed, and no dimensional changes recorded, for any of the soil mortars. Then, the samples were subjected to compressive strength testing and compared to baseline values. Compressive strength values for VES and acrylic mortar samples remained basically unchanged. PES samples gained about 26% of their baseline strength after thermal cycling. This increase may be due to further crosslinking reactions induced by the higher temperatures in the thermal cycle. SPC samples were affected adversely by thermal cycling, and lost an average of 51% of their baseline compressive strength. Such behavior is expected for SPC. Freeze-thaw cycling losses are given as 40% in data sheets from National Chempruf Concrete, Inc.³¹ Data for compressive strength is given in Table 17 and shown graphically in figure 40.

Table 17 Compressive strengths of soil mortars after thermal cycling.
(MPa $\pm$ standard deviation)

Binder Type	Compressive Strength
Vinylester Styrene	52.1 $\pm$ 1.6
Polyester Styrene	51.0 $\pm$ 1.8
Acrylic ^a	23.0 $\pm$ 1.9
Sulfur Polymer Cement	12.8 $\pm$ 1.6

a = high modulus resin

4.13 Irradiation Stability

Several of the sites throughout the DOE complex can be expected to see significant radiation doses. The 106-C UST at the USTID demonstration site is a high activity storage facility. The barrier should be expected to receive an appreciable radiation dose during the projected 25 year lifetime for interim containment. The radiation fields in many of the USTs are stated to be in excess of 1000 rad/hr.¹ This translates to slightly more than 2×10^8 rad over 25 years for worst case tanks. The containment barrier will not get the full dose since the tank concrete, steel liner, and surrounding soils will shield the barrier.

Replicate samples of the soil mortars were subjected to irradiation. A total dose of 1×10^8 rads was chosen for testing purposes in order to remain conservative. Irradiation was performed at the Co-60 Gamma Facility at BNL. The dose rates ranged from 1×10^6 to 4×10^6 rad/hr. The samples were visually inspected and measured for dimensional changes after irradiation. The PES samples changed color from a beige to yellow after irradiation. No other visual or dimensional changes were observed. The samples were then destructively tested for compressive strength (ASTM D-695). The results are given in Table 18 (also see figure 41). All three thermoset binders show significant strength increases after irradiation. This is a commonly observed effect attributable to additional cross-linking of the polymer chains. The SPC soil mortars remained unchanged.

Figure 40. Effect of thermal cycling on the compressive strength of soil mortars.

Figure 41. Effect of gamma irradiation to 10^8 rads on the compressive strength of soil mortars.

Table 18 Compressive strengths of soil mortars after gamma irradiation.
(MPa $\pm$ standard deviation)

Binder Type	Compressive Strength
Vinylester Styrene	62.6 $\pm$ 2.5
Polyester Styrene	54.1 $\pm$ 1.6
Acrylic ^a	40.3 $\pm$ 5.9
Sulfur Polymer Cement	25.3 $\pm$ 3.7

a = high modulus resin

5.0 ECONOMIC CONSIDERATIONS

BNL has investigated the regulatory drivers associated with polymers for subsurface barriers and has found no regulatory problems with their use. The laboratory results just described have shown polymer composites to have many desirable properties in terms of durability and resistance. The economics of the various polymer systems as compared to conventional barriers is an important consideration. Polymers (especially the thermosetting resins such as: VES, PES and acrylics) are more expensive than conventional portland cement. The most important goal of EM is the protection of the environment and public although total waste site management must consider and balance a host of variables including regulatory requirements, public opinion, and cost. The key consideration in choosing a barrier grout is waste site performance goals. Material cost of the barrier becomes secondary, if the contaminants at a site pose a severe threat to the environment. Design criteria (such as no cracking in an arid environment) may preclude the use of cheaper cement based grouts, and require a more expensive specialty grout. Cost alone cannot be the determining factor in grout selection. However, we will proceed with a very simplified cost comparison of polymer barriers to cementitious barriers.

We would neglect the performance capabilities of the polymers, if we compared the bulk costs of materials exclusively. Polymers permit barriers that are much thinner than cement slurry wall barriers, while still yielding better performance and durability. A cost comparison must cover a wide scope of issues, including: site specific performance requirements, placement technology, materials costs, and stakeholder considerations.

The site specific concerns are the most difficult to consider for a generic cost comparison. There are no performance criteria that apply to subsurface containment barriers. The only guidance available is from the USEPA. Credit in the performance assessment will be given if the barrier has a permeability of 10^{-7} cm/sec or less. There are no requirements for thickness, tensile strength, or chemical resistance. The requirements for performance depend on the specific site of installation. A waste site located close to groundwater or a populated area would require a much thicker barrier (assuming equal hydraulic conductivities) than a site

located further away. Any final cost comparison must be done on a site specific basis. Generic comparisons are yard stick measures at best.

A set of performance criteria must be considered; the placement method(s) must be chosen; and the size and configuration of the site must be considered in order to accomplish a generic cost comparison. The most important performance consideration for a containment barrier is hydraulic conductivity. We will use the EPA accepted 10^{-7} cm/sec as the minimum requirement. Most other performance criteria are site specific, and will not be considered for this comparison. The thickness of the barrier must be considered. How thick should the low permeability zone be at 10^{-7} cm/sec ? This report will use cement slurry wall barriers as the baseline case. Cement slurry wall barriers are the most widely used barrier type for waste site improvement. The EPA has approved slurry wall installation at many locations. Such barriers are typically one meter thick. The ultimate comparison of barrier materials is the equivalent flow rate through the containment walls. We will define 1 equivalent permeability unit as the equivalent of a barrier 1 meter thick with a hydraulic conductivity of 10^{-7} cm/sec. Cost will be given in material cost and in cost per equivalent permeability unit.

Also, the size of the barrier is important to overall cost. We will consider a barrier that is 200 meters by 200 meters, 25 meters deep, has vertical walls and a horizontal floor. Estimates for trench placed walls will be for vertical walls only, since trenching is only feasible in the vertical placement. Trenching is still valuable for percolation and diffusion barriers and, as such, does not necessarily require a floor.

The last consideration is placement technology. Several placement methods were discussed briefly earlier in this report. Each of these methods has limitations that will affect the cost of the barrier. Different placement technologies require different wall thicknesses. The polymer composite might be good enough to be used in 2.5 cm thick panels, but the minimum installation thickness may be 1 meter. We will consider four placement techniques in order to broaden this cost comparison : conventional column jet grouting which produces a minimum wall thickness of 2 meters, trenching with a 1 meter thick wall, panel jet grouting with a minimum thickness of 0.3 meters, and a SoilSaw™ barrier type with a minimum wall thickness of 0.15 meters. The two thin wall methods use the existing soils for aggregate and produce a soil mortar. Therefore, we will consider vibrating beam placement that produces a 0.15 meter thick barrier. This is the same thickness as the SoilSaw™ , but allows the introduction of clean aggregate which can be used to increase performance and decrease resin requirements.

Placement cost will not be considered here, since the actual installation should not be highly dependent on the grouting fluid. The number of boreholes and related cost remains constant in jet grouting regardless of which grout is used. We will assume compatibility of the grouts with the placement technology. The thermosetting resins are liquid until polymerization, and should be compatible with any placement technique that uses PC grout. The thermoplastic materials require heating to melting before placement and must be kept hot during placement. Many of the placement methods would require modifications in order to use thermoplastics, but

that is beyond the scope of this program. Most of the systems (with the possible exception of the SoilSaw™) could be modified to meet the needs of the thermoplastic grouts.

The volumes of barrier wall required for the different thicknesses were calculated based on our assumptions. The barrier wall volume is 120,000m³ or 31.7 million gallons for 2 meters, with a floor of equal thickness. The volume is 20,000m³ or 5.28 million gallons for the case of 1 meter thick, but no floor. Reducing the wall thickness to 0.3 and including a floor of equal thickness results in a volume of 18,000m³ or 4.75 million gallons. Using SoilSaw™ technology to produce walls and a floor as thin as 0.15m gives a barrier wall a volume of 9,000m³ or 2.38 million gallons. Horizontal floors would not be feasible for the vibration beam placement method, but the technique can be used at angles. A V-shaped barrier could be placed in order to accomplish full containment. We will assume for simplicity that the volume of the vibration beam containment barrier walls to be the same as the wall volume from SoilSaw™ which has the same wall thickness. Each placement technology uses a different binder to aggregate ratio. The binder requirement for each of these cases must be determined separately.

It can be assumed that 25% by volume binder will be required for jet grouting in order to grout the soils. This applies to conventional column jet grouting and panel jet grouting. If the distance of affected area is increased (larger diameter column), then the binder ratio will also go up (a more liquid soil is needed to penetrate further). We will consider the case of 25% by volume for jet and panel grouting. SoilSaw™ barrier installation requires 1:1 to 1:3 binder to soil by volume, in order to liquify the soil sufficiently. SoilSaw produces a large number of spoils. Up to 1 cubic meter of soil must be displaced for each cubic meter of binder injected into the soil. The displaced soil is mixed with grout, resulting in greater binder requirements. Using a 1:2 binder to soil ratio results in 33% of the volume of the barrier walls being pure polymer. Assumes one third waste results in binder requirements of 43% of the barrier volume. The "grout" can contain clean aggregate for trenching and vibrating beam placement methods. The binder requirements and cost are dependent on the type of aggregate and the binder viscosity. Of the three aggregate mixes; mortar, glass concrete and concrete, we will determine costs only for the concrete blends. The actual cost of the mortars and glass concretes will differ slightly from the concretes. The difference is attributed almost entirely to the differences in percent binder requirements. The aggregate cost is a small percentage of the total cost. The difference between the cost of sand, glass/sand, and stone sand mixes is small also. The relative costs of the various polymer composites will remain the same. The grout and barrier materials cost given (in tables 20 and 22 for trenching and vibrating beam) are for the concrete aggregate. One hundred percent of the barrier wall volume will be filled with the introduced binder/aggregate mix for these replacement/displacement methods. The cost per cubic meter is calculated directly from the binder and aggregate percentages from table 3. The average sample density is calculated from table 4. The unit prices of each component are listed in table 19.

The final variable for cost comparison is the economics of the grout. The grout is made up of several components including; the binder, aggregate (if used), additives such as

superplasticizer for cement, or cure inhibitors for polymers, and a variety of resins in each class of polymer. For instance: specialty polyester resins can cost \$2.00/lb, while the more commonly used resins are as cheap as \$0.60/lb. Table 19 lists the cost of the components of a variety of grouts. Listed are bulk prices of binders, aggregates, and some additives. Bulk prices are tank car quantities for binders, and drum quantities for additives, as of May 1994. Included in the list are some similar resins that were not part of the laboratory studies, but may be useful cost saving substitutes in many cases.

Table 19. Unit prices of barrier grout components (does not include delivery charges).

Material	Unit price per pound
Portland Type II Cement	\$0.03
Sulfur Polymer Cement	\$0.14
Bitumen Type III	\$0.08
FA-Rok 913 (furfurol based)	\$1.02
FA-Rok 6300 (catalyst)	\$1.50
FA-Rok 6301 (catalyst)	\$1.50
Derekane 470-45 Vinylester Styrene	\$1.58
Derekane 411-C-50 Vinylester Styrene	\$1.44
Atlac 4010A Polyester Styrene	\$1.39
Isophthalic Polyester Styrene	\$0.70
Orthophthalic Polyester Styrene	\$0.60
3M 4R Concrete Restorer 5741	\$6.52
3M 4R Concrete Restorer 5742LO	\$4.00
Superplasticizer	\$1.00
Quartz stone aggregate	\$0.01
Blended quartz sand	\$0.02

The composition of the grout must be considered in order to determine the grout cost for each placement method. The polymer binders will be used as is, with no additives, for column jet grouting, panel jet grouting and SoilSaw™ installation. A catalyst will be added for the thermosetting polymers. Since the catalyst is less than 1% of the binder it can be neglected for a simple cost estimate. The only exception is FA-Rok, which uses 10% catalyst. The cost has

been considered in the final grout cost. Portland based grouts will be a mix of cement, water, and superplasticizer and may also have other additives (e.g., to prevent shrinkage). The cost of cement grout was estimated based on discussions with grouting companies. A better grade of grout is required for a waste site containment barrier than for jet grouting for construction, where the only important parameter is soil consolidation. Trench and vibration beam placed barrier grouts will contain a mix of binder and aggregate. The cost is established from the unit price and component composition of each composite type, as mentioned earlier. Numerous combinations are available for portland based grouts with trenching or vibrating beam. Conventional slurry grouts, mortars, and concrete are among the choices. A conventional concrete mix will be considered for trenching and vibrating beam since we will be considering pumpable cement based jet grouts for the other placement methods. This concrete will be the same as the baseline used in the laboratory studies. The cost of aggregate in table 19 does not include delivery charges. A cost of \$0.025/lb was used for all aggregate to be conservative. Table 20 lists the cost per cubic meter of the various grouts for each different placement technology.

Table 20. Cost of grouts per cubic meter.

Grout Type	Grout cost per cubic meter	
	SoilSaw™, Column and Panel Jet Grouting	Trenching or Vibrating Beam
Portland cement - pumpable grout	\$141	\$141
Portland cement - ordinary concrete	--	\$129
Sulfur polymer cement	\$630 ^a	\$219
Bitumen - type III	\$180	\$150
Furan	\$2680 ^a	\$666
Vinylester styrene - Derekane 470-45	\$3650	\$921
Vinylester styrene - Derekane 411-C-50	\$3330	\$850
Polyester styrene - Atlac 4010A	\$3160	\$947
Polyester styrene - Isophthalic	\$1640	\$532
Polyester styrene - Orthophthalic	\$1360	\$472
Acrylic - 3M 4R concrete restorer 5741	\$14800	\$3070
Acrylic - 3M 4R concrete restorer 5742LO	\$9080	\$1930

a = may not be compatible with certain soil types.

We can now determine the cost of materials for each barrier type using the volumes for each barrier and the percent of barrier volume of binder required, as listed in table 20. We can determine the cost per equivalent permeability unit by combining the volumes for each barrier with the hydraulic conductivities of the polymers from the laboratory studies and conductivities of pumpable cement grout from industrial installations. Polymer binder permeabilities for jet based placement are taken from laboratory measurements on soil mortars. Permeabilities for PC jet grouting are typically 1×10^{-7} cm/sec. This value is used for column and panel jet grouting. Literature values for bentonite soil walls made using SoilSaw™ are 1×10^{-8} cm/sec.³² This technology uses greater binder/soil ratios, and should produce less permeable barriers, than column or panel jet grouting. A value of 10^{-8} cm/sec will be used for the permeability of SoilSaw™ PC grout barriers. The permeability of the barrier will be much lower than jet based methods for the trench and vibrating beam placements using a pumpable PC grout. This is because little or no dilution by soil occurs. The permeability for neat PC grout is set at 1×10^{-9} cm/sec. Table 21 lists the materials cost. Table 22 lists the cost per equivalent permeability unit. Furan polymers and the thermoplastic grouts are not listed in table 21, due to the incompatibilities found in laboratory studies. Furfuryl alcohol catalysts are acidic and are not compatible with the alkali soils found at most DOE sites. SPC soil mortars demonstrated that the heating process dries soil particles which causes the particles to shrink. The particles swell and cause cracking when rewetted by percolation waters or leachates. The furan and thermoplastics will be considered only for clean aggregate grouts used in replacement/displacement techniques.

Table 21. Barrier materials cost, and cost per equivalent permeability unit, for jet based placement technologies.

Grout	Cost per equivalent permeability unit	SoilSaw™	Panel jet grouting	Column jet grouting
PC pumpable	\$141 ^a	\$0.55M	ng	\$4.2M
VES 470-45	\$24	\$14.1M	\$16.4M	\$109M
VES 411-C-50	\$22	\$12.9M	\$15.0M	\$99.9M
PES 4010A	\$7	\$12.2M	\$14.2M	\$94.8M
PES isophthalic	\$4	\$6.3M	\$7.4M	\$49.2M
PES orthophthalic	\$3	\$5.3M	\$6.1M	\$40.8M
Acrylic 5741	\$592	\$57.3M	\$66.6M	\$444M
Acrylic 5742LO	\$363	\$35.1M	\$40.9M	\$272M

a = SoilSaw™ will be less per unit equivalent due to lower permeability. Actual cost per equivalent permeability unit is <\$28.

ng = cannot meet the equivalent flow rate requirement at this thickness.

Table 22. Barrier materials cost, and cost per equivalent permeability unit, for replacement/displacement technologies.

Grout	Cost per equivalent permeability unit	Vibrating beam	Trenching
PC - pumpable grout	\$1.41	\$1.3M	\$2.8M
PC - ordinary concrete	\$0.05	\$1.2M	\$2.6M
Sulfur polymer cement	\$0.14	\$2.0M	\$4.4M
Furan	\$0.30	\$6.0M	\$13.3M
VES 470-45	\$1.38	\$8.3M	\$18.4M
VES 411-C-50	\$1.27	\$7.6M	\$17.0M
PES 4010A	\$1.52	\$8.5M	\$18.9M
PES isophthalic	\$0.85	\$4.8M	\$10.6M
PES orthophthalic	\$0.76	\$4.3M	\$9.4M
Acrylic 5741	\$0.61	\$27.6M	\$61.4M
Acrylic 5742LO	\$0.39	\$17.4M	\$38.6M
Bitumen	\$0.03	\$1.35M	\$3.0M

Table 19 displays the wide range of cost of the polymer binders. Notice that the thermosetting resins range from \$0.60/lb to \$6.52/lb. This cost discrepancy becomes even more obvious when considering the grout costs, per cubic meter, in table 20. The cost of grouts for jet based placement technologies is based on pure binder cost, with no aggregate dilution (clean or soil). The acrylic binders are cost prohibitive without aggregate dilution. The expenses are far less restrictive when considering the cost per cubic meter for trench or vibrating beam grouts. Tables 21 and 22 list the cost of materials of the complete barrier, using the various composite types. The polymers are more expensive for a given thickness of wall than the conventional grouts. Geotechnical, geochemical, and contaminant conditions, and regulatory requirements will justify the additional cost in many cases. A portland based cement has not been developed yet that will not crack under wet-dry conditions in a large monolithic structure. Polymers will fill the needs, if no cracking is warranted. Tables 21 and 22 also list the cost per equivalent permeability unit in order to better see the performance advantages of the polymers. The polymers are far superior to the conventional grouts in this case. Polymers cost only a fraction of the cost of conventional grouts, while obtaining the same equivalent flow rate across

the contaminant barrier. The vinylester styrenes and polyester styrenes are extremely cost effective, either as a pure grouting fluid for jet based placement, or as aggregate diluted barrier material. Even the high cost acrylic from 3M has good cost to performance values when used in an aggregate diluted barrier grout (table 22). A site specific basis is necessary to decide whether the extremely high performance of polymer systems is warranted.

6.0 SUMMARY AND CONCLUSIONS

Polymer grouts with a wide range of viscosities have demonstrated to have desirable qualities for a subterranean barrier. Performance values indicate that polymers can meet the requirements for containment barriers for USTs throughout the DOE complex. Proper choice of binder and aggregate and appropriate site specific compatibility testing will result in a durable, high strength, low permeability barrier.

Hydraulic conductivities were low for all polymer composites. Concretes ranged from 1.6×10^{-10} to $< 2 \times 10^{-11}$ cm/sec, mortars from 3.4×10^{-8} to $< 2 \times 10^{-11}$ cm/sec, glass concretes from 6.6×10^{-10} to $< 2 \times 10^{-11}$ cm/sec, and soil mortars from 4×10^{-9} to 2.2×10^{-10} cm/sec. The order of hydraulic conductivities based on binder type is: bitumen $<$ low modulus acrylic $<$ furan $<$ sulfur polymer cement $<$ vinylester styrene $\equiv$ polyester styrene $<$ high modulus acrylic.

SPC soil mortars failed in water immersion after 3-5 days exposure. This is attributed to the expansive quality of the Hanford soil. Thus, the importance of site specific testing when choosing barrier materials is emphasized. Testing should include compatibility of the binder with: aggregate (especially if using natural soils as in jet grouting), waste constituents, and site geology and geochemistry. The results for acrylic glass concrete shows further evidence of the need of compatibility testing. Glass is a relatively inert matrix and should not cause interactions with the binder or waste. These samples lost an average of 40% of their baseline strength after 90 days immersion in water, whereas the mortars and concretes remained unchanged. This is indicative of a binder/aggregate interaction.

Immersion testing of VES and PES showed the need for further studies on the effect of moisture content on the unconfined, uniaxial, compressive strengths of polymers. There was an apparent loss of strength for VES and PES clean, aggregate specimens which were conditioned at 100% humidity prior to compressive testing, but no loss for soil mortars conditioned at 50% humidity. It is recommended that all barrier material strength measurements be made at 100% humidity, since subsurface soil gases will be at 100 % humidity (even for arid regions where soil moisture content is 1-2%).

Compressive strengths of the polymer composites followed the order: vinylester styrene $>$ polyester styrene $>$ sulfur polymer cement $>$ furan $>$ acrylic $>$ bitumen. The strengths were highest for the round size-graded aggregate types. The concretes and mortars had the

highest strength. The unimodal Hanford soil was next in strength. The sharp edged glass aggregate were the lowest in strength.

The order of flexural strengths was: vinylester styrene > polyester styrene > furan > sulfur polymer cement > acrylic. The order based on aggregate type was the same as for compressive strength: concretes = mortars > glass concretes.

Tensile strengths followed the order: vinylester styrene > polyester styrene > furan > sulfur polymer cement > acrylic > bitumen. Aggregate to strength relationships in compressive and flexural strengths remained the same for tensile strength.

Polymer composites were immersed in an aqueous nitric acid solution at pH 2 for 90 days. Results were similar to the immersion test. PES, VES, and acrylic\glass showed similar strength losses when observed after water immersion. FA, SPC, and acrylic (mortar and concrete) composites remained unchanged, with the marked exception of the SPC\glass composite which showed continual loss of strength after 30, 60, and 90 day intervals.

Clean aggregate samples were immersed in an aqueous sodium hydroxide solution at pH 12.5 for 90 days. Results for PES, VES, and acrylic were similar to the immersion and acid resistance tests. FA composites remained unchanged after 90 days. All SPC composites showed some loss of strength. The glass aggregate showed continual losses after 30, 60, and 90 day intervals. The results are expected since SPC is known to be attacked by the base.

VES composites which were immersed in a saturated solution of trichloroethylene gave results that were the same as in the immersion test. FA composites remained unchanged after 90 days. Bitumen and PC specimens show losses just under 10%, with standard deviations close to this difference. PES and acrylic samples had slight losses after 30 days. Then, the losses remained at a constant level up to 90 days immersion. Acrylic glass concretes showed larger losses than the mortars or concretes. This is attributed to the aggregate/binder/water interactions seen earlier in the water immersion testing. All SPC composites showed some loss of strength after 90 days immersion. The glass aggregate showed continual losses after 30, 60, and 90 day intervals.

Wet-dry cycling of polymer composites resulted in no visual damage and minimal weight changes. VES and PES specimens showed no strength changes for the soil mortars. They showed similar strengths changes as observed after water, acid, base, and solvent resistance for the clean aggregate samples. Acrylic samples show slight strength increases for the soil mortar, unchanged for the mortar and concrete, and similar losses for the glass composite as observed in water, acid, base, and solvent resistance testing. FA samples showed significant strength increases which averaged 57%. The increases are attributed to further polymerization occurring due to the heat of the dry cycle. SPC samples lost 47% of the baseline strength for mortars, 56% for concretes, and 81% for the glass concrete.

Soil mortars made using VES, PES, and acrylics were subjected to additional site specific testing for the Hanford complex. This testing included irradiation, nitrate brine resistance, and thermal cycling. These polymers showed strength gains averaging 32% after 10^8 rads irradiation from a gamma source. The strength gains are attributed to additional crosslinking of the polymer. VES and PES were immersed for 120 days in 70°C concentrated nitrate brine with no detrimental effects. The brine is a surrogate for the Hanford UST supernatant, and is an aggressive media. VES and PES samples showed no loss in strength. The acrylic samples showed 40% strength losses after the 90 day interval. VES, PES, and acrylic samples survived thermal cycling with no strength losses.

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APPENDIX

Material Name	Acrylic			
Discription	High molecular weight methacrylate			
Manufacturer	3M Company, Construction Markets Department			
Product Code	3M 4R concrete restorer - 5740 low mod			
Aggregate Compatibility				
Quartz sand	Quartz sand/stone	Quartz sand/sodium glass	Hanford soil	
☒ Yes ☐ No	☒ Yes ☐ No	☐ Yes ☒ No	☒ Yes ☐ No	
Performance				
	Concrete	Mortar	Glass concrete	Hanford soil ^a
Hydraulic conductivity, m/s	$< 2 \times 10^{-13}$	7.0×10^{-12}	3.5×10^{-13}	4.0×10^{-11}
Density, Kg/m ³	2290	2170	2190	1950
Compressive strength, MPa	14.0 ± 2.9	12.8 ± 1.5	9.7 ± 1.1	25.7 ± 2.6
Tensile strength, MPa	2.6 ± 0.2	2.9 ± 0.5	2.2 ± 0.1	
Flexural strength, MPa	4.3 ± 0.2	3.4 ± 0.1	4.7 ± 0.1	
Chloride diffusivity				
Chemical Compatabiltiy and Durability				
Type	Good	Fair	Poor	NR
Water	☒	☐	☐	☐
Nitric acid, pH = 2	☒	☐	☐	☐
Sodium hydroxide, pH = 12.5	☒	☐	☐	☐
Trichloroethylene, saturated aqueous solution	☐	☐	☒	☐
Wet-dry cycling	☒	☐	☐	☐
70°C nitrate brine surrogate	☐	☐	☐	☒
Irradiation stability, 10 ⁸ rads total dose	☒	☐	☐	☐
Thermal cycling	☒	☐	☐	☐

NR = not recommended, a = high modulus resin, 5742

Material Name	Bitumen			
Discription	Type III roofing asphalt			
Manufacturer	Ziegler Chemical and Mineral Corp.			
Product Code	ZECO-AA1900			
Aggregate Compatibility				
Quartz sand	Quartz sand/stone	Quartz sand/sodium glass	Hanford soil	
☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	☐ Yes ☐ No	
Performance				
	Concrete	Mortar	Glass concrete	Hanford soil
Hydraulic conductivity, m/s	$<2 \times 10^{-13}$	$<2 \times 10^{-13}$	$<2 \times 10^{-13}$	
Density, Kg/m ³	2200	1950	2090	
Compressive strength, MPa	3.0 ± 0.2	2.3 ± 0.2	3.1 ± 0.1	
Tensile strength, MPa	0.94 ± 0.04	0.89 ± 0.02	0.89 ± 0.07	
Flexural strength, MPa				
Chloride diffusivity				
Chemical Compatibilitiy and Durability				
Type	Good	Fair	Poor	NR
Water	☒	☐	☐	☐
Nitric acid, pH = 2	☐	☒	☐	☐
Sodium hydroxide, pH = 12.5	☐	☐	☐	☒
Trichloroethylene, saturated aqueous solution	☐	☒	☐	☐
Wet-dry cycling	☐	☐	☒	☐
70°C nitrate brine surrogate	☐	☐	☐	☐
Irradiation stability, 10 ⁸ rads total dose	☐	☐	☐	☐
Thermal cycling	☐	☐	☐	☐

NR = not recommended

Material Name	Furan			
Discription	Furfuryl alcohol based furan polymer			
Manufacturer	QO Chemicals, Inc.			
Product Code	FA-Rok 913			
Aggregate Compatibility				
Quartz sand	Quartz sand/stone	Quartz sand/sodium glass	Hanford soil	
☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	☐ Yes ☒ No	
Performance				
	Concrete	Mortar	Glass concrete	Hanford soil
Hydraulic conductivity, m/s	4.5×10^{-13}	3.4×10^{-10}	4.8×10^{-13}	
Density, Kg/m ³	2340	2230	2190	
Compressive strength, MPa	31.3 ± 2.0	35.6 ± 4.5	29.3 ± 3.2	
Tensile strength, MPa	6.5 ± 0.5	7.6 ± 0.5	6.3 ± 0.4	
Flexural strength, MPa	9.0 ± 0.6	11.1 ± 0.4	9.2 ± 0.6	
Chloride diffusivity				
Chemical Compatibiltiy and Durability				
Type	Good	Fair	Poor	NR
Water	☒	☐	☐	☐
Nitric acid, pH = 2	☒	☐	☐	☐
Sodium hydroxide, pH = 12.5	☒	☐	☐	☐
Trichloroethylene, saturated aqueous solution	☒	☐	☐	☐
Wet-dry cycling	☒	☐	☐	☐
70°C nitrate brine surrogate	☐	☐	☐	☐
Irradiation stability, 10 ⁸ rads total dose	☐	☐	☐	☐
Thermal cycling	☐	☐	☐	☐

NR = not recommended

Material Name	Polyester styrene			
Discription	Modified bisphenol fumerate resin			
Manufacturer	Reichhold Chemicals, Inc.			
Product Code	Atlac 4010A			
Aggregate Compatibility				
Quartz sand	Quartz sand/stone	Quartz sand/sodium glass	Hanford soil	
☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	
Performance				
	Concrete	Mortar	Glass concrete	Hanford soil
Hydraulic conductivity, m/s	1.6×10^{-12}	2.5×10^{-12}	6.6×10^{-12}	2.2×10^{-12}
Density, Kg/m ³	2280	1930	2170	1850
Compressive strength, MPa	59.6 ± 1.4	50.0 ± 12.2	39.5 ± 3.0	49.1 ± 3.6
Tensile strength, MPa	10.3 ± 0.2	9.2 ± 1.9	8.0 ± 0.3	
Flexural strength, MPa	17.2 ± 0.5	15.9 ± 0.6	7.1 ± 0.3	
Chloride diffusivity				
Chemical Compatibilty and Durability				
Type	Good	Fair	Poor	NR
Water	☒	☐	☐	☐
Nitric acid, pH = 2	☒	☐	☐	☐
Sodium hydroxide, pH = 12.5	☒	☐	☐	☐
Trichloroethylene, saturated aqueous solution	☐	☒	☒	☐
Wet-dry cycling	☒	☐	☐	☐
70°C nitrate brine surrogate	☒	☐	☐	☐
Irradiation stability, 10 ⁸ rads total dose	☒	☐	☐	☐
Thermal cycling	☒	☐	☐	☐

NR = not recommended

Material Name	Sulfur polymer cement			
Discription	Modified sulfur			
Manufacturer	Martin Resources, Inc.			
Product Code	Chement 2000			
Aggregate Compatibility				
Quartz sand	Quartz sand/stone	Quartz sand/sodium glass	Hanford soil	
☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	☐ Yes ☒ No	
Performance				
	Concrete	Mortar	Glass concrete	Hanford soil
Hydraulic conductivity, m/s	6.3×10^{-13}	5.4×10^{-13}	6.7×10^{-13}	
Density, Kg/m ³	2320	2120	2180	
Compressive strength, MPa	34.1 ± 5.3	38.1 ± 6.1	27.4 ± 3.9	30.6 ± 5.8
Tensile strength, MPa	6.3 ± 0.8	5.1 ± 0.2	5.0 ± 0.4	
Flexural strength, MPa	7.9 ± 1.4	6.1 ± 0.4	4.9 ± 0.4	
Chloride diffusivity				
Chemical Compatabiltiy and Durability				
Type	Good	Fair	Poor	NR
Water	☒	☐	☐	☐
Nitric acid, pH = 2	☒	☐	☐	☐
Sodium hydroxide, pH = 12.5	☐	☐	☐	☒
Trichloroethylene, saturated aqueous solution	☐	☐	☐	☒
Wet-dry cycling	☐	☐	☐	☐
70°C nitrate brine surrogate	☐	☐	☐	☐
Irradiation stability, 10 ⁸ rads total dose	☒	☐	☐	☐
Thermal cycling	☐	☐	☐	☒

NR = not recommended

Material Name	Vinylester styrene			
Discription	Epoxy novalac based vinyl ester resin			
Manufacturer	Dow Chemicals, Dow Plastics			
Product Code	Derakane 470-45			
Aggregate Compatibility				
Quartz sand	Quartz sand/stone	Quartz sand/sodium glass	Hanford soil	
☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	
Performance				
	Concrete	Mortar	Glass concrete	Hanford soil
Hydraulic conductivity, m/s	1.5×10^{-12}	3.0×10^{-12}	4.2×10^{-12}	6.7×10^{-12}
Density, Kg/m ³	2320	2200	2260	1960
Compressive strength, MPa	72.9 ± 2.5	82.4 ± 3.2	33.6 ± 1.4	47.6 ± 2.6
Tensile strength, MPa	11.7 ± 0.3	13.9 ± 0.5	7.7 ± 0.9	
Flexural strength, MPa	15.0 ± 0.4	18.1 ± 2.4	9.3 ± 0.6	
Chloride diffusivity				
Chemical Compatibilitiy and Durability				
Type	Good	Fair	Poor	NR
Water	☒	☐	☐	☐
Nitric acid, pH = 2	☒	☐	☐	☐
Sodium hydroxide, pH = 12.5	☒	☐	☐	☐
Trichloroethylene, saturated aqueous solution	☒	☐	☐	☐
Wet-dry cycling	☒	☐	☐	☐
70°C nitrate brine surrogate	☒	☐	☐	☐
Irradiation stability, 10 ⁸ rads total dose	☒	☐	☐	☐
Thermal cycling	☒	☐	☐	☐

NR = not recommended

Material Name	Portland cement			
Discription	Type II			
Manufacturer	3M Company, Construction Markets Department			
Product Code	3M 4R concrete restorer - 5740 low mod			
Aggregate Compatibility				
Quartz sand	Quartz sand/stone	Quartz sand/sodium glass	Hanford soil	
☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	☒ Yes ☐ No	
Performance				
	Concrete	Mortar	Glass concrete	Hanford soil
Hydraulic conductivity, m/s	3.8×10^{-13}			
Density, Kg/m ³	2430			
Compressive strength, MPa	45.2 ± 13.7			
Tensile strength, MPa	8.7 ± 1.0			
Flexural strength, MPa	6.6 ± 0.3			
Chloride diffusivity				
Chemical Compatibilitiy and Durability				
Type	Good	Fair	Poor	NR
Water	☒	☐	☐	☐
Nitric acid, pH = 2	☐	☐	☐	☒
Sodium hydroxide, pH = 12.5	☒ ^b	☐	☐	☐
Trichloroethylene, saturated aqueous solution	☐	☒	☐	☐
Wet-dry cycling	☐	☐	☒	☐
70°C nitrate brine surrogate	☐	☐	☐	☐
Irradiation stability, 10 ⁸ rads total dose	☐	☐	☐	☐
Thermal cycling	☐	☐	☐	☐

NR = not recommended, b = with non-reactive aggregate