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**POLYMERS FOR SUBTERRANEAN CONTAINMENT
BARRIERS FOR UNDERGROUND STORAGE TANKS (USTs)**

Letter Report on FY 1992 Activities

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1. INTRODUCTION

The U.S. Department of Energy (DOE) set up the Underground Storage Tank Integrated Demonstration Program (USTID) to demonstrate technologies for the retrieval and treatment of tank waste, and closure of underground storage tanks (USTs). There are more than 250 underground storage tanks throughout the DOE complex. These tanks contain a wide variety of wastes including high level, low level, transuranic, mixed and hazardous wastes. Many of the tanks have performed beyond the designed lifetime resulting in leakage and contamination of the local geologic media and groundwater. To mitigate this problem it has been proposed that an interim subterranean containment barrier be placed around the tanks (Figure 1). 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 also provide sufficient time to evaluate and select appropriate remediation alternatives.

The DOE Hanford site was chosen as the demonstration site for containment barrier technologies. The demonstration site is located in a semi-arid region of southeastern Washington state. Annual precipitation is 15.9cm (6.25") with the largest percent falling during the cooler months from November to February. Evaporation exceeds precipitation by 5-9 times with annual groundwater recharge rates of 0-10cm (0-4"). The groundwater aquifer is 60-75 m (200-250 ft.) below surface. Typical soil moisture ranges from 1.5 to 3.5% (surface 5-10ft = 5-10%).^[1]

The tank chosen for the subterranean containment barrier demonstration is Tank 106-C located in the 241-C Tank Farm Area. This tank comes under the control of the *Hanford Federal Facility Agreement and Consent Order* of 1989 which calls for interim stabilization by September 1996. Interim stabilization includes physical isolation of the tank. Tank 106-C is a single shell storage facility, 75 ft in diameter, has a capacity of 533,000 gals., and first received waste in 1947. The designed lifetime of the barrier is conservatively set at 25 years.

A panel of experts for the USTID was convened in February, 1992, to identify technologies for placement of subterranean barriers. The selection was based on the ability of candidate grouts to withstand high radiation doses, high temperatures and aggressive tank waste leachates. The group identified and ranked nine grouting technologies that have potential to place vertical barriers and five for horizontal barriers around the tank (Table 1).^[2] The panel also endorsed placement technologies that require minimal excavation of soil surrounding the tanks. The two placement methods given high ratings were jet grouting (Figure 2) and permeation grouting (Figure 3).

Design Features of Hanford SST 241-C-106

Figure 1 Schematic of proposed confinement barrier for underground storage tanks.

Barrier Placement by Jet Grouting

Figure 2 Placement of a confinement barrier using jet grouting.

Barrier Placement by Permeation Grouting

Figure 3 Placement of a confinement barrier using permeation grouting.

Table 1 Potential Placement Technologies for Subterranean Containment Barriers[2]

Placement Technology	Rating for Vertical Barrier Placement	Rating for Horizontal Barrier Placement
Cement Slurry Wall	High	NA
Deep Soil Mixing	Medium	NA
In Situ Vitrification	Low	Low
Jet Grout Curtain	High	High
Ground Freeze Barriers	Medium	Medium
Modified Sulfur Cement	Medium	Medium
Permeation Grouting	High	High
Polymer Impregnated Concrete	Low	NA
Sheet Metal Pilings	High	NA

NA = not applicable

Construction of a subterranean barrier by injection requires the grout material to completely penetrate the soil and remain in place until solidification is complete. The solidified monolith must then provide an impermeable and durable barrier. The ability of the grout to penetrate the soil is dependent on the liquid binder viscosity and the permeability of the soil. A coarse sandy soil can be injected with a higher viscosity binder at low to moderate pressures while a fine sand might require a near water viscosity resin applied at higher pressures. The viscosity of the injection grout and the "curing time" will also 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 involved in the USTID 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) to accommodate soil conditions at the various DOE sites. The most commonly used grout materials (i.e., suspension grouts) for cutoff curtains achieve permeabilities of 1×10^{-9} M/sec under the best conditions. The goal for polymer-soil composite barriers is to achieve high durability barriers with permeabilities of 1×10^{-11} M/sec or less.

In March, 1992, Brookhaven National Laboratory began a program to define, develop, and characterize advanced polymer systems for *in situ* applications at the Hanford UST site.

The scope of this program is to investigate polymer materials that can be used with the high rated placement technologies. It is recognized that some modifications to the placement technologies may be required to meet the characteristics of individual polymer systems. However, this is not within the scope of this program and will be considered as the technology progresses. This report describes the initial work performed on several polymer-soil composites.

2. MATERIALS

Based upon site geochemical and geophysical characteristics, and UST performance requirements, BNL's two candidate polymer grout systems were selected for development and characterization as barrier materials. The two grouts are polymer concrete and sulfur concrete. Both polymer concrete and sulfur concrete are innovative materials with desirable properties in both their fluid and solid states which make them suitable for applications where impermeability, high strengths, and long-term durability are required. These materials have been extensively used in many commercial applications such as in sewage and brine handling systems, and electrolytic baths. They have also been used by the Corps of Engineers to repair dams and canal locks, and by the Federal Highway Administration for bridge deck and highway repairs. Their impermeability to gases and liquids, combined with resistance to radiation, acidic and alkaline environments, make polymer grouts candidates for high quality barrier materials.

Polymer concrete is defined as an aggregate mixed with a liquid monomer or resin (binder) which is converted in place, to form a hard polymer monolith. This material can be mixed and cast in the field. Candidate 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 2. These binders are classified as thermosets. Thermosetting polymers require a chemical reaction to convert monomer to polymer. Once formed they cannot be reformed or remelted.

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. When subjected to heat or in the presence of a promoter, the peroxide molecule splits at the O-O bond to form two free radicals that have unpaired electrons and are thus 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 over 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 that may retard or enhance the set. 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.[3,4,5,6]

Table 2 Properties of candidate binder materials for subterranean barriers for USTs^a

Property	Modified Sulfur Cement (MSC) Chement 2000	Polyester-Styrene (PES) Atlac	Vinyl Ester Styrene (VES) Derakane 470-45	Methacrylate 3M 4R	Acrylate AC-400	Furfuryl Alcohol
Viscosity, cps	28 @ 135°C	300 @ 25°C	100 @ 25°C	5 @ 25°C	3 @ 25°C	3 @ 20°C
Specific gravity	2.07	1.03	1.048	1.025	1.18	1.14
Flashpoint (°C)	191	32	21-32	105	NF	77

^a Information taken from manufacturers Material Safety Data Sheets.
 NF = non flammable

Sulfur concrete consists of an aggregate bound with modified sulfur cement (MSC). MSC is a thermoplastic polymer. Thermoplastic materials when heated above their melting points become liquid and can be mixed with an aggregate filler such as sand or soil. Upon cooling the mix re-solidifies to form a solid monolith. No chemical reaction is required for setting (as in hydraulic cements), thus minimizing incompatibilities between binder and aggregate. Thermoplastics such as polyethylene and MSC have been used for chemically resistant flooring and reactor vats[7] and have been developed for solidification of various wastes.[8,9,10]

For the Hanford demonstration it is desirable to have a placement technology that does not require excavation of potentially contaminated soils. The aggregate is the natural soil as it exists around the tanks. For this report, the grouting materials are defined as "mortars" or "soil mortars" and consist of the polymer binders mixed with Hanford soil. A description of the binder materials follows.

2.1 Methacrylates

Methacrylate monomers are a low viscosity, inexpensive, and commonly used family of polymers. The methacrylate chosen is manufactured by the 3M company under the

tradename 3M 4R Concrete Restorer and is a modified high molecular weight methacrylate. The system consists of dicyclopentadienyl methacrylate and isooctyl acrylate and is polymerized using a cobalt octoate promoter (reducing agent) and cumene hydroperoxide initiator (oxidative catalyst).

2.2 Polyester Styrene

Polyester styrenes (PES) are among the most widely used thermosetting resins. The basic components of a PES polymer consist of a mixture of a linear polyester resin and styrene monomer. Chemical and physical characteristics of the final polymer are dependent on the choice of polyester resin and styrene content. For the Hanford UST containment barrier, resistance to the strong alkali supernatants in the tanks is probably the most critical factor in choosing a PES system. For this reason BNL selected a modified bisphenol fumarate resin distributed by Reichhold Chemicals, under the tradename Atlac 4010A. This resin is especially formulated for alkali resistance. The Atlac PES requires a 6% cobalt naphthenate (CoN6) solution as the promoter and methylethyl ketone peroxide (MEKP) as the initiator. The viscosity of the polyester-styrene solution is approximately 300 cps.

2.3 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.[4,11,12] The VES system used in this study is manufactured by DOW Chemicals under the tradename Derakane 470-45 and is an epoxy novolac-based vinyl ester resin dissolved in styrene. This particular Derakane was formulated for good chemical resistance (including solvents), retention of properties at high temperatures and has a low viscosity. The polymerization occurs using an oxidation-reduction reaction. Dimethylaniline (DMA) promoter was used in conjunction with a 40% benzoyl peroxide (BPO) catalyst solution.

2.4 Furfuryl Alcohol

A commercial grade furfuryl alcohol (FA) was used for this study. FA has a low viscosity, low vapor pressure, low flammability, and is soluble in water. This material produces a very resistant polymer using cheap and environmentally innocuous components. FA has been used in the fabrication of polymer concrete pipes, as an organic cementing and sand consolidating material in oil wells, floor coatings, and chemically resistant containers. Polymerization of furfuryl alcohol occurs through a condensation reaction using a strong acid catalyst. Basic reagents tend to inhibit the polymerization.[13] Set times and exotherms cannot be as tightly controlled as in the other polymer systems. For this study the catalyst used was p-toluene sulfonic acid.

2.5 Polyacrylic Acid

Polyacrylic acid, under the tradename AC-400 (Geochemical Corporation) is among the most widely used hydraulic barrier materials for construction applications in the United States. This material, a magnesium acrylate, produces a soft gel rather than a hard solid with typical compressive strengths of 50 psi. AC-400 is commonly used to seal sewer pipe leaks and to stop water infiltration at construction sites. Acrylate grouts have been shown to have low water permeabilities and to be resistant to a large number of chemicals.[14] Acrylate grout gels typically contain 80-90% water and are extremely sensitive to wet-dry and freeze-thaw cycling. Such high water content gels work best in 100% humidity or water submerged conditions. The soft gels are also prone to creep fatigue failures and can fail with loadings as low as 20% of the unconfined compressive strength (UCS).[15] Acrylate grouts behave similarly to the acrylamide grouts and have quickly replaced the latter due to lower toxicities (1/100th of acrylamide grouts). Polymerization occurs using triethanolamine (TEA) catalyst and ammonium persulfate (AP) initiator. Gel time is variable from 5 seconds to 1 hour and can be adjusted by adding potassium ferricyanide ($\text{KFe}[\text{CN}]_6$), an inhibiting agent. AC-400 was investigated due to the high use in construction, existing placement technologies, and interest from several outside parties.

2.6 Modified Sulfur Cement

Modified sulfur cement is a sulfur polymer developed by the U.S. Bureau of Mines to utilize surplus sulfur.[16] Sulfur concretes offer excellent chemical resistance to strong acids and salts and are relatively inexpensive. MSC is used for construction of chemical vats, road repairs, and is a candidate for encapsulating radioactive, hazardous, and mixed wastes.[7,17] MSC 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. In unmodified sulfur, the monoclinic form of sulfur changes to the orthorhombic form 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 under the trade name Chement 2000. MSC is a thermoplastic material that melts at 119°C. When heated above its melting point MSC can be mixed with aggregate, soil, waste, etc., and upon cooling forms a hard monolithic solid. Full strength is achieved in hours rather than weeks as compared to hydraulic cements.

3. FORMULATIONS

The polymer systems chosen had to be optimized to the chemical and physical properties of the Hanford soil. A sample of soil was obtained from a clean area of the Hanford 200 series tank farm. The soil is a coarse brown sand with a measured soil pH of 9.0 (ASTM D-4972).[18] Moisture content is reported to be 1-3% in the areas around the demonstration tank, although the soil sample received from PNL contained 5.8% moisture. The first set of experiments were designed to determine the effect of soil aggregate on the resin gel times. Because of the alkali nature of the soil it was postulated that problems would occur using furfuryl alcohol due to the acidic characteristics of the catalyst. This is the only system where difficulties in solidifying the soils were predicted. Choosing 1-2 hours as a reasonable working time prior to polymer gelling, samples of monomer were allowed to cure with and without soil aggregate. 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, with and without Hanford soil. This initial trial eliminated furfuryl alcohol as a candidate material for Hanford soil grout barrier technologies. However, placement technologies that rely on displacement/replace-ment methods where the subterranean soils are "pushed away" (displaced) by the barrier material or removed and replaced by the barrier material might still use furfuryl alcohol with a neutral silica aggregate.

After confirmation of catalyst-promoter quantities to achieve reasonable gel times sample fabrication techniques were refined. 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 and 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. Of primary importance is the interaction of the monomer/soil composite and its durability properties. BNL attempted to balance the requirement of staying near 20-25 wt% monomer and produced laboratory samples that were reproducible and homogeneous.

VES and PES soil mortar samples were fabricated by mixing together the as received soil with resin, promoters and catalysts in a Hobart mixer. The mixture was poured into 3.5 foot long x 1.5 inch diameter PVC pipe. After polymerization was completed, the pipe was cut into 3 inch lengths, the samples were removed from the mold and the samples were measured and weighed to check for homogeneity within each lot. Multiple lots of each binder-combination were fabricated, cut to length and allowed to set in this manner. Three samples (top, middle, and bottom) from each lot were tested for unconfined compressive strength (ASTM D-695)[19] to determine baseline strength and for homogeneity within each lot and between lots. Resultant values showed low scatter and no lot to lot variation which is evidence of good homogeneity. Formulations and baseline strengths are given in Tables 3 and 4. Photographs of VES and PES soil mortars are shown in Figures 4 and 5, respectively.

Table 3 Soil Mortar Formulations

Polymer	Soil (by wt.)	Binder (by wt.)	Catalyst phr (%)	Promoter phr (%)
Methacrylate	76	23	3	1
Polyester-Styrene	72	27	2.4	1
Vinylester-Styrene	75	25	2.5	0.1
Sulfur Cement	70	30	N.A.	N.A.
Acrylate ^a	82	18	1	1
Furfuryl Alcohol	N.A.	N.A.	0.5-2.0	-

N.A. = not applicable

phr (%) = per hundred parts of resin by weight

^a = 12% solids

Table 4 Unconfined Compressive Strengths of Polymer-Soil Mortars

Material	Strength, psi [MPa]	Standard deviation
VES	6910 [47.6]	385 [2.65]
PES	7120 [49.1]	522 [3.60]
Methacrylate	3730 [25.7]	383 [2.64]
Sulfur Cement	4440 [30.6]	838 [5.78]
MSC lot #1	5760 [39.7]	136 [0.94]
MSC lot #2	5180 [35.7]	309 [2.13]
MSC lot #3	4500 [31.0]	364 [2.51]
MSC lot #4	3560 [24.5]	226 [1.56]
MSC lot #5	3470 [23.9]	157 [1.08]
MSC lot #6	4240 [29.2]	37 [0.26]

Figure 4 Vinyl ester styrene soil mortars made using Hanford soil.

Figure 5 Polyester styrene soil mortars made using Hanford soil.

The MSC samples were made by mixing MSC and soil in a heated double action planetary mixer (Figure 6). The lot was mixed until the temperature reached 124°C at which time the mixture was poured into two inch diameter PVC pipe, which was used as a casting mold. The lot was allowed to cool for several hours. After solidification of the mix, the pipe was cut into 4" lengths and the samples were removed from the PVC casing, measured, and weighed. The unconfined compressive strengths were measured (ASTM D-695) for three samples from each lot. The samples showed very low scatter (UCS = 4440 psi, avg. std. dev. = 206) within each lot but much larger variation (std. dev. = 838) between lots. Examination of the fractured samples indicated the presence of entrained air within the samples, possibly due to the high viscosity of the melt. 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 variables may explain the lot to lot variability. For durability testing each sample of MSC was compared to the lot it came from. Formulation and baseline compressive strengths for total samples and individual lots are given in Tables 3 and 4. Figure 7 shows a photograph of a MSC soil mortar sample.

Soil mortar samples made with 3M 4R methacrylate were fabricated by mixing the resin and catalyst together, followed by the addition of the promoter. The prepared binder was then poured into a PVC mold followed by slowly adding a preweighed lot of soil. After solidification, the lot was cut into 3 inch lengths, the samples were removed from the mold and they were measured and weighed. Three samples were tested for unconfined compressive strength (ASTM D-695) and checked for homogeneity. No variations either within a lot or between lots resulted. Sample weights in any given lot typically ranged from 186 to 205 g. There was a slight vertical weight variation within a given lot, amounting to 3-5% of the average. These differences, however, did not manifest as differences in UCS. The formulations and UCS are given in Tables 3 and 4. A photograph is shown in Figure 8.

Initial samples made with AC-400 immediately showed problems. Samples were prepared utilizing a manufacturers recommended formulation. The binder was made up in two parts; solution one was 49 parts water and 1 part AP, solution two was 30 parts AC-400 resin (40% solids), 19 parts water (containing .02% $\text{KFe}[\text{CN}]_6$), and 1 part TEA. The two solutions were then mixed, as needed, to form the final binder and induce polymerization. Samples were fabricated by filling a container with soil and subsequently flooding the soil, from the bottom, with the AC-400 binder. The gel formed was soft and produced a final composite with a compressive strength estimated to be less than 100 psi. The samples showed measurable dimensional changes after sitting for one hour at room temperature at 40% relative humidity. The observed behavior of AC-400 gels is as expected for extremely high water content gels and has been reported in the literature. However, the Hanford site is arid and as such, dry conditions will prevail. A barrier made using AC-400 would in time be prone to shrinkage and cracking. This conclusion is enforced by Karol¹⁷ who writes that "Long term tests ...indicate that grouts gain their full strengths immediately upon gelation and retain that strength (as long as freeze-thaw and wet-dry conditions do not exist)." The Manufacturer states "Under conditions that allow water to evaporate, AC-400 chemical grout will gradually dehydrate." [20] Based upon observations and literature reports, AC-400 was eliminated as a candidate binder for PNL site specific polymer-soil mortar.

Figure 6 Heated double action planetary mixer

Figure 7 Modified sulfur cement soil mortars made using Hanford soil.

Figure 8 Methacrylate soil mortars made using Hanford soil.

4. TESTING

The soil mortar samples for VES, PES, MSC, and methacrylate binders were subjected to a series of performance tests to determine if the materials were capable of meeting the requirements of a subterranean barrier for USTs, as follows:

4.1 90-Day Water Immersion Test

A subterranean containment barrier is expected to be exposed to aqueous environments either from leakage of the supernatant contained in the UST or percolate water. Exposure of barrier materials to aqueous solutions can result in swelling, cracking, dissolution, etc. The soils used as aggregate may also interact with the water through swelling (i.e., expansive clays) and dissolution of mineral components. Aggregate interactions can cause internal stresses with resultant cracking and strength losses in the barrier. Six replicate samples of each soil mortar combination were immersed in deionized water for a period of 90 days. Periodically, during the course of the test, the samples were visually inspected for cracking and swelling. At the end of the test period the samples were weighed, measured and destructively tested for compressive strength (ASTM D-695). With the exception of MSC no visual, dimensional, or significant strength changes were observed. Compressive strength data for VES, PES, and 3M 4R are given in Table 5 and Figure 9.

MSC samples cracked after three to five days exposure to ionized water. Figure 10 shows the MSC soil mortar samples before and after immersion. This effect is probably due to a small expansive clay portion in the Hanford soils which would induce tensile stresses in the sample when exposed to water. The effect of such expansive clays is most pronounced with MSC because of its low tensile strength. During the fabrication of MSC samples, temperatures in excess of 120°C are required to melt the binder. At these temperatures the residual soil moisture is driven off and the clays shrink to their minimum volume. When the clays are re-wetted they expand with resultant internal stresses. For all the other binders the soil was used as received, with approximately 5.6% moisture content, without showing detrimental effects. Perhaps the important factor assisting the other binders is their higher tensile strengths.

Table 5 Compressive Strengths of Soil Mortars After 90 days Water Immersion

Material	Post Immersion psi [MPa]	std. dev.	% change
VES	7410 [51.1]	167 [1.15]	+7
PES	6880 [47.4]	186 [1.28]	-3
3M 4R	3340 [23.1]	554 [3.83]	-11

Effects of 90 Day Water Immersion on Soil Mortar Strengths

Figure 9 Change in compressive strengths of Hanford soil mortars after 90 days water immersion.

Figure 10 Photograph modified sulfur cement Hanford soil mortars after 5 days immersion in water.

4.2 Thermal Cycling

Thermal cycling of materials can be useful not only to determine durability to temperature changes but also as a tool to indicated internal prestressing and as a comparative measure of quality. While 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, will be more prone to damage from thermal cycling.

Six replicate samples of VES, PES, MSC, and 3M 4R soil mortars were tested in accordance to ASTM B-553[21] with modifications recommended by the Nuclear Regulatory Commission.[22] Cycling of the samples was performed using a microprocessor controlled environmental chamber capable of temperature ranges between -73 and +200°C $\pm$ 0.3°C. The specimen were placed in the chamber and cycled between -40 and +60°C for a total of 30 cycles, with each cycle lasting approximately 5 hours. A plot of temperature versus time for one cycle is given in Figure 11.

After cycling was complete, the samples were visually checked and measured. No visible effects were observed and no dimensional changes recorded for any of the soil mortars. The samples were then subjected to compressive strength testing and compared to baseline values. UCS values for VES and 3M 4R mortar samples remained basically unchanged. PES samples gained ~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. MSC samples were adversely effected by thermal cycling and lost an average of 51% of their baseline compressive strength. Data for USC is given in Table 6 and a graphical presentation of the results of thermal cycling is shown in Figure 12.

Table 6 Compressive Strengths of Soil Mortars After Thermal Cycling

Material	Post Cycling	std. dev.	% change
VES	7560 [52.1]	239 [1.65]	+9
3M 4R	3340 [23.0]	274 [1.89]	-11
PES	7390 [51.0]	262 [1.81]	+4
MSC lot 5	2030 [14.0]	188 [1.30]	-42
MSC lot 6	1700 [11.7]	120 [0.83]	-60

Temperature Conditions for One Cycle Following ASTM B-533

Figure 11 Temperature history for one cycle of the thermal cycling test of Hanford soil mortars.

Effects of Thermal Cycling on Soil Mortar Strengths

Figure 12 Change in compressive strengths of Hanford soil mortars after thermal cycling.

4.3 Irradiation Stability

The 106-C UST at the demonstration site is a high activity storage facility. The containment barrier should be expected to receive an appreciable radiation dose during the projected 25 year lifetime. The radiation fields in many of the USTs are stated to be in excess of 1000 rad/hr.[1,20,21] This translates to slightly more than 2×10^8 rad over 25 years for worst case tanks. The containment barrier will not see the full dose since the UST concrete and steel liner and surrounding soils will shield the barrier. In order to remain conservative, a total dose of 1×10^8 rads was chosen for testing purposes. Irradiation was performed in a Co-60 gamma facility at BNL. The dose rates ranged from 1×10^6 to 4×10^6 rad/hr. After irradiation, the samples were visually inspected and measured for dimensional changes. The PES samples changed color from a white tinting to 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 7 and shown graphically in Figure 13. The three thermoset binders all show significant strength increases after irradiation. This is a commonly observed phenomena attributable to additional cross-linking of the polymer chains. The polymers will continue to crosslink due to the energy input of the irradiation. This will continue only to a point and then the energy from irradiation will begin to break bonds and a gradual decrease will be observed. The MSC showed mixed inconclusive results. Lot 3 (5 samples) shows a 20 percent strength loss with a baseline standard deviation of 8 percent. Lot 4 (3 samples) showed a 6% increase that is within one standard deviation for the lot.

Table 7 Compressive Strength of Irradiated Soil Mortar Composites

Material	Post Irradiation ^a psi [MPa]	std. dev.	% change
VES	9080 [62.6]	357 [2.46]	+31
3M 4R	5840 [40.3]	860 [5.93]	+57
PES	7840 [54.1]	239 [1.65]	+10
MSC lot 3	3600 [24.8]	505 [3.48]	-20
MSC lot 4	3760 [25.9]	572 [3.94]	+6

^atotal dose of 10^8 rads.

Effects of Irradiation on Soil Mortar Strengths

total dose = 108 rads

Figure 13 Change in compressive strengths of Hanford soil mortars after gamma irradiation to 10^8 rad.

4.4 Wet-Dry Cycling

The Hanford tank farm is located in a semi-arid region. The soil moisture content is fairly dry and as stated earlier ranges between 1 and 3 %. Assuming little or no tank leakage, the barrier will be under dry conditions most of the time. There are times when precipitation percolates the ground and recharges the aquifer. During these times the barrier will be under saturated conditions. Wet-dry cycling is known to have a severe impact on construction materials such as hydraulic cements. Replicate samples of VES, 3M 4R, and PES soil mortars were subjected to wet-dry cycling following ASTM D-4843.[23] [MSC was excluded based on water immersion results.] The test cycle samples from 60°C dry to 20°C wet, twelve times. The ASTM test calls for evaporating the water after each wet cycle and weighing the residue left in the beaker. The samples were wet cycled in the same beaker for each cycle reusing the water (additional water was added to replenish losses from evaporation). At the end of the final cycle the water was evaporated and the residue weight recorded. The wet samples were towel dried and weighed after each cycle. The dry cycle samples were weighed directly (Table 8). The weight histories of each sample are plotted in Figures 14, 16, and 18. The "end" weight represents the weight of the samples after the seven day 40% humidity conditioning. In addition to the test method, samples were compression tested after the final cycle to determine mechanical integrity. Upon completion of wet-dry cycling the samples were conditioned at 40% relative humidity for seven days and then tested for UCS (ASTM D-695).

None of the samples showed any visible degradation after 12 cycles. Final weight changes were minimal and the averages are given in Table 8. The table also gives values for the average fluctuation in weight going from the saturated to the dry condition. To illustrate the small weight changes observed for all the polymer mortars, the dry cycle weights have been plotted as percent of initial dry weight versus cycle number (Figures 15, 17, and 19). The scale spans less than 1.5% for all polymer soil mortars tested. The polymers proved to be extremely resistant to wet-dry cycling. This was substantiated by performing compressive strength testing of the cycled samples. The values of UCS given in Table 9 show no strength losses for any binder system. Instead, all the binders showed slight strength increases (see also Figure 20).

Table 8 Weight Changes of Samples Subjected to Wet-Dry Cycling^a

Material	VES	3M 4R	PES
Weight Before ^b	193.68	192.22	182.28
Weight After ^b	192.33	194.14	180.00
% Change ^b	-0.7	+1.0	-1.2
Initial Dry ^c Weight	192.12	190.20	179.68
Final Dry ^d Weight	190.55	191.14	178.41
% Change	-0.8	+0.5	-0.7
Initial Wet ^c Weight	195.32	194.51	182.73
Final Wet ^d Weight	194.35	197.46	181.75
% Change	-0.5	+1.5	-0.5
avg. fluctuation per cycle	3.52	5.36	3.28
residue	0.15	0.15	0.06

- (a) values are in grams and are composites of six replicates
(b) measured at 40 % RH,
(c) from first cycle,
(d) from last cycle

Table 9 Compressive Strengths of Soil Mortar Samples After Wet-Dry Cycling

Materials	UCS after wet-dry cycling , psi [MPa]	std. dev.	% change
VES	7630 [52.6]	388 [2.68]	+10
3M 4R	4930 [34.0]	744 [5.13]	+32
PES	8390 [57.8]	787 [5.43]	+18

Vinylester-Styrene Soil Mortar Samples Wet-Dry Cycling (ASTM D 4843)

Figure 14 Weight history of vinylester styrene Hanford soil mortars subjected to wet-dry cycling.

Wet-Dry Cycling of Vinylester Styrene

Figure 15 Weight changes of vinylester styrene Hanford soil mortars subjected to wet-dry cycling.

Methacrylate Soil Mortar Samples Wet-Dry Cycling (ASTM D 4843)

Figure 16 Weight history of methacrylate Hanford soil mortars subjected to wet-dry cycling.

Wet-Dry Cycling of Methacrylate Soil Mortar

Figure 17 Weight changes of methacrylate Hanford soil mortars subjected to wet-dry cycling.

Polyester-Styrene Soil Mortar Samples **Wet-Dry Cycling (ASTM D 4843)**

Figure 18 Weight history of polyester styrene Hanford soil mortars subjected to wet-dry cycling.

Wet-Dry Cycling of Polyester Styrene

Figure 19 Weight changes of polyester styrene Hanford soil mortars subjected to wet-dry cycling.

Effects of Wet-Dry Cycling on Soil Mortar Strengths

Figure 20 Change in compressive strengths of Hanford soil mortars after wet-dry cycling.

4.5 Hot Nitrate Brine Immersion

In the event of leakage from USTs, the barrier will presumably be exposed to the supernatant from the tank. The supernatants in most of the USTs are nitrate-nitrite salt solutions. For the demonstration tank, the composition of the supernatant is given in Table 10.[2] The liquid may also be at elevated temperature due to the heat production from radionuclide decay. To determine the durability of the soil-polymer composites, in this environment, samples were subjected to immersion in a hot surrogate nitrate brine. The brine was 50% solids using salts in the proportions taken from Table 10. The temperature of 70°C was taken as the average tank temperature of the 11 high heat (>40,000 Btu/hr) tanks at Hanford.[1] Twelve samples of VES, 3M 4R, and PES soil mortars were immersed in the brine and placed in an environmental chamber at 70°C. [MSC was excluded based on water immersion results.] The samples were inspected routinely for cracking and/or spalling. At 30 day intervals three samples of each soil-mortar composite were removed for visual and destructive testing to determine sample integrity. Salt crystals formed on the sides of the samples after ~1 week with no signs of degradation. Figure 21 shows photographs of the samples as they were removed from the brine (30 days). The samples were scrubbed clean with water and steel wool to remove the crystal formations. It should be noted that the crystals were most heavy 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 originally colored.] After cleaning, the samples were inspected for cracking and spalling. All samples appeared sound. The specimens were then conditioned at 40% RH for seven days and tested for compressive strength. The results for up to 60 days exposure, given in Table 11 (also Figure 22), show no loss in integrity for any of the composites.

Table 10 Estimated Chemical Composition of Supernatant for Single-Shell Tanks[1]

Chemical	Dry Weight %
NaNO ₃	34.7
NaNO ₂	26.4
Na ₂ CO ₃	1.0
NaOH	10.4
NaAlO ₂	20.9
Na ₃ PO ₄	3.8
Organic	2.8

Figure 21 Photographs of Hanford soil mortars after 30 days exposure to 70°C nitrate brine.

Effects of Hot Nitrate Brine Immersion on Soil Mortar Strengths

Figure 22 Change in compressive strengths of Hanford soil mortars after 60 days exposure to 70°C nitrate brine.

Table 11 Compressive Strengths of Soil Mortars After Exposure to 70°C Nitrate Brine

Material	Exposure Time (d)	UCS (ASTM D-695)	std. dev.	% change
VES	30	8600 [59.3]	162 [1.12]	+24
PES		8040 [55.4]	345 [2.38]	+13
3M 4R		3690 [25.4]	291 [2.01]	-2
VES	60	9240 [63.7]	211 [1.45]	+34
PES		8090 [55.8]	515 [3.55]	+14
3M 4R		3550 [24.5]	362 [2.50]	-5

4.6 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 retain leakage from the UST. The hydraulic conductivities of samples of VES, PES, and 3M 4R soil mortars were measured following ASTM D-5084.[24] Measurements were made using a flexible wall permeameter. The permeant was deaired tap water having an electrical conductivity of 120 μ mhos. Test samples were 3.8 cm diameter cylinders with a height of 3.0 cm. Samples were preconditioned in tap water for several days to induce saturation. The test specimens were then placed in the permeameter cell and sealed using a latex membrane and a 10 psi differential cell pressure. Back pressuring was used to accomplish full saturation of the samples. Full saturation was determined by measuring the compression B value using ASTM D-4767-(88).[25] The pressure required to bring about a compression B value of .95 or greater varied with the mortars, VES samples required 10 psi, PES samples 30 psi, and 3M 4R mortars 20 psi. Measurements were made at three different pressure differentials to assure that Darcy's Law behavior was obeyed. After allowing for stabilization, permeabilities were calculated for three consecutive 24 hour readings. The results are given in Table 12.

Table 12 Hydraulic Conductivity of Hanford Soil Mortars

Hydraulic Conductivity of Polymer Soil Mortars (M/s x 10 ⁻¹²)				
ΔP, psi	interval	VES	PES	3M 4R
30	1	8.3	2.8	48
	2	8.0	2.7	37
	3	6.7	2.8	37
20	1	5.8	1.7	36
	2	6.2	1.5	47
	3	5.8	1.5	38
10	1	6.2	1.5	37
	2	5.5	3.0	42
	3	7.8	2.4	40
Average	--	6.7	2.2	40

5. CONCLUSIONS

Polymer concrete soil composites appear to be well suited to conditions expected to be prevalent at the Hanford UST site. Short term testing in severe conditions have shown soil mortars made with vinylester styrene, polyester styrene, and a high molecular weight methacrylate to be extremely durable. From laboratory testing the following observations were made:

1. Sufficient strengths are easily achieved with polymer-soil composites. The order of strengths were PES > VES > MSC > 3M 4R.
2. VES, PES, and 3M 4R have surpassed 90 days water immersion with no loss in integrity.
3. MSC failed in water immersion after 3-5 days exposure. This is attributed to some expansive quality of the Hanford soil.
4. VES and PES samples survived thermal cycling with no strength losses. 3M 4R soil mortars showed an 11% strength loss against a baseline standard deviation of 10%. MSC failed to retain a reasonable amount of strength, showing losses of 40-60% of original strength.
5. The thermosetting 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. Results from MSC were inconclusive. One lot of three samples showed a 6% strength gain with a baseline standard deviation of 6%. The second lot (5 samples) had a 20% loss with a baseline standard deviation of 8%.
6. VES, PES, and 3M 4R soil mortars were subjected to wet-dry cycling with no detrimental effects. The average weight changes were -0.7, -1.2, and +1.0 % for VES, PES, and 3M 4R respectively. No strength loss occurred for any binder, with 3M 4R and PES soil mortars showing modest strength gains.
7. VES, PES, and 3M 4R withstood 60 days immersion 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. No strength losses were recorded with modest strength increases for VES and PES samples.

8. Soil mortar hydraulic conductivities on the order of 5×10^{-12} M/s are achievable. VES samples averaged 6.7×10^{-12} M/s, PES averaged 2.2×10^{-12} M/s, and 3M 4R samples averaged 40×10^{-12} M/s.
9. Polymer grouts having a wide range of viscosities (300, 100, and 3 cps for PES, VES, and 3M 4R, respectively) have been demonstrated to have desirable qualities for a subterranean containment barrier. The resin characteristics should allow these materials to be used in a wide range of soil types and conditions.

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