IN-SITU CONTAINMENT AND STABILIZATION OF BURIED WASTE

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SUMMARY

Formulations for advanced grouting materials to be used for in-situ containment and stabilization of buried chemical waste in an arid environment were optimized and characterized. The major placement techniques considered were jet grouting (by replacement or penetration), soil mixing or soil sawing. Cementitious grouts with permeabilities of the order of 10^{-11} to 10^{-10} cm/s suitable for monolithic grout subsurface barriers were developed. Permeability after accelerated leaching and repeated wet-dry cycles was of the order of 10^{-10} to 10^{-9} cm/s. The results compare favorably with the EPA permeability limit of 10^{-7} cm/s. Due to the low permeabilities, the dimensions of the barriers can be reduced. The grouts had compressive and flexural strengths in excess of what is required for the landfill. Reinforcement of the grouts with fibrillated polypropylene fibres was demonstrated to reduce crack widths under restrained shrinkage conditions, increase ductility and improve wet-dry cycling durability.

Soil cements were investigated as alternatives to monolithic grout barriers. Mechanical and physical properties for a range of soil/cement ratios were measured to determine the limit of soil content. Permeability of in-situ cured soil cements increased several orders of magnitude from 10^{-10} to 10^{-7} cm/s as soil/cement ratio increased from 1 to 5. Compressive and flexural strengths were adequate at all soil levels. Crack width in restrained shrinkage and wet-dry cycling specimens increased with increasing soil content. At soil/cement ratios of 1 to 2 adequate leach resistance and ability for cracks to heal under wet-dry conditions were exhibited. The best compromise between mechanical and physical properties and durability is achieved at low soil/cement ratios. Shrinkage cracking resistance of soil cements can also be improved by addition of low volume fractions of polypropylene or nylon fibres and the practicality of use of fibres in the field requires investigation. Soil cements are also suitable as low permeability capping materials.

The developed superplasticized grouts and soil cements have significantly superior properties and durability than conventional formulations. The permeabilities are two to five orders of magnitude less than for other materials frequently used as caps and barriers such as clay, soil-bentonite and cement-bentonite slurries.

The estimated material cost of a suitable sanded grout is \$182/m³ and the material cost of soil cement ranges from \$128/m³ to \$89/m³ for soil/cement ratios of 1 to 2. Based on measured values of in-situ cured permeability a sanded grout is more cost effective than soil cements due to the reduced thickness that is required for a given flow rate.

1.0 INTRODUCTION

In FY 1993 research continued on development and testing of grout materials for in-situ containment and stabilization of buried waste. Specifically, the work was aimed at remediation of the Chemical Waste Landfill (CWL) at Sandia National Laboratories (SNL) in Albuquerque, New Mexico as part of the Mixed Waste Landfill Integrated Demonstration (MWLID). The work on grouting materials was initiated in FY 1992 and the accomplishments for that year are documented in the previous annual report (Allan, Kukacka and Heiser, 1992).

The remediation plan involves stabilization of the chromium plume, placement of impermeable vertical and horizontal barriers to isolate the landfill and installation of a surface cap. The required depth of subsurface barriers is approximately 33 m (100 ft). A schematic diagram of the proposed closure is shown in Figure 1.

In FY 1992 it was established that if cement based grouts are mixed in with the chromium contaminated soil, effective stabilization would be achieved provided that any hexavalent chromium is first converted to the trivalent oxidation state. An alternative to grout stabilization is reduction of Cr^{6+} with a ferrous solution followed by treatment with a calcium hydroxide solution to produce insoluble chromium hydroxide. Treatment of chromium contaminated soil and water and use of cement to stabilize chromium has been reported elsewhere (Zamorani et. al., 1988; Corbitt, 1990; Adaska et. al. 1991; Davis and Cocke, 1991; Puls, 1993; Macphee and Glasser, 1993)

Also in FY 1992, polymer and cementitious grouts suitable for in-situ subsurface containment barriers and caps were identified. The materials demonstrated high strength and low permeability. The research identified cementitious grouts as giving the most cost effective and highest overall performance. Grouts that contained fly ash were determined to be inferior to plain or silica fume modified grouts. Latex modified cementitious grouts were found to undergo strength reduction in the expected service environment and use of polyester or vinyl ester resins to treat soil was prohibitively expensive. Other chemical grouts such as acrylates and sodium silicates were discounted due to either toxicity problems or inadequate long term durability in arid environments.

The work performed in FY 1993 concentrated on optimization of grout formulations for use as grout and soil cement barriers and caps. The durability of such materials was investigated, in addition to shrinkage cracking resistance, compressive and flexural strength and permeability. The potential for using fibres in grouts to control cracking was studied. Small scale field trials were conducted to test the practicality of using the identified formulations and to measure the long term performance. Large scale trials were conducted at Sandia as part of the Subsurface Barrier

Chemical Waste Landfill Proposed Closure

Perimeter fence

Surface

480' to Water Table

Figure 1. Proposed Closure and Stabilization of Chemical Waste Landfill.

Emplacement Technology Program. Since it was already determined in FY 1992 that cementitious grouts could effectively stabilize the chromium plume at the CWL after pre-treatment is performed, the majority of the work was devoted to the containment aspect.

As discussed in the FY 1992 annual report, containment barriers must meet certain criteria for adequate performance in the service environment. The major requirements are long term durability, maintenance of permeability less than 10^{-7} cm/s throughout service, resistance to shrinkage, cracking and any forms of deterioration, and acceptable strength for the purpose. Other important requirements of the materials are compatibility with currently available placement techniques and cost effectiveness.

The placement techniques originally under consideration for containment of the CWL included permeation grouting, jet grouting and soil mixing. Jet grouting, either by penetration where a soil cement barrier is produced, or by replacement where grout is pumped into a cavity created by jetting, and soil mixing were considered the placement techniques of greatest promise. Deep soil mixing is suitable for vertical barriers and jet grouting is appropriate for both horizontal and vertical barriers. Another technique that appears suitable for horizontal and vertical barriers is soil sawing where a beam mounted with jets through which grout is pumped at high pressure is pulled through soil to form a soil cement barrier. This technique is expected to produce a similar material to that resultant from jet grouting. Shallow soil mixing could be used to produce a soil cement cap. In FY 1992 it was determined that permeation grouting with ordinary Portland cement based grout was not feasible due to the fine particle size of the site soil. Therefore, the possibility of using a microfine cement grout for permeation grouting was investigated in FY 1993.

2.0 EXPERIMENTAL WORK

2.1 Materials

Grouts based on Type I cement (ordinary Portland, Lone Star) were studied for both production of grout and soil cement barriers. For large scale use Type IV or V cement may be more suitable due to reduced heat of hydration. The grouts were designed to be fluid so as to be compatible with the relevant placement techniques. Neat cement grouts were considered for deep or shallow soil mixing, jet grouting by penetration and soil sawing since sand is incompatible with jetting and inefficient for soil mixing due to strength reduction (Allan, Kukacka and Heiser, 1992). Sanded grouts were designed for jet grouting by replacement and the measured properties were compared with those for neat cement grouts.

Microfine cement grout was investigated for permeation grouting. The microfine cement used was MC 500 supplied by Geochemical Corporation and had a particle size distribution

between 1 and 12 microns. The microfine cement was a blend of Portland cement and blast furnace slag.

All the grout formulations included Wyoming bentonite as this was necessary to prevent excessive bleeding and settling of any sand. The bentonite was comprised mainly of sodium montmorillonite. The superplasticizer used was a sodium salt of sulphonated naphthalene formaldehyde condensate with a solids content of 42% by mass.

For jet grouting by replacement, a sanded grout is desirable to reduce shrinkage. Two grades of silica sand were used to study the effect of sand particle size on grout properties. The finer sand had 98% of particles between sieve sizes 200 and 40 (74 to 420 micron) and the coarser sand had a narrower size distribution with 98% of particles between sieve sizes 60 and 30 (250 to 595 micron). For some grouts the sand/cement ratio by mass was 1. One grout had 0.5 parts fine sand and 0.7 parts coarse sand to 1 part cement by mass. Blending the two sand grades allowed a greater volume fraction of sand to be incorporated in the grout without resorting to a high water/cement ratio (w/c).

Condensed silica fume was added to selected grouts as a partial cement replacement. The purpose of the pozzolanic additive was to study the potential improvements in permeability and leach resistance.

Fibres were added to grouts for use with deep or shallow soil mixing and jet grouting by replacement primarily as a means of adding toughness, reducing shrinkage cracking tendency and reducing crack width. It was necessary that the fibre reinforced grouts remained pumpable. Therefore, polypropylene and nylon fibres were chosen in preference to steel, although superior properties could be expected from steel fibre reinforcement. Two types of fibres were considered. These were collated fibrillated and monofilament fibres. The tested fibrillated fibres were polypropylene and the monofilament fibres were either polypropylene or nylon. Both types of fibres were 19 mm in length. The polypropylene fibres were supplied by Forta Corporation and the nylon fibres were supplied by Kapejo Inc. and are aimed primarily at the concrete construction industry for use as secondary and plastic shrinkage reinforcement.

Relatively low fibre volume fractions of 0.1 and 0.2 % were used so as not to interfere with the pumpability of the grouts. Trial mixes with fibrillated fibre volume fractions of 0.5 and 1% had reduced fluidity that led to excessive entrapment of air voids when grouts were poured into moulds. Vibration would have been necessary to remove the air voids. Higher volume fractions of monofilament fibres than 0.2% appeared possible.

Soil cements were produced using site soil from Sandia. The soil was alluvial with silty to gravelly sand type texture. The Unified Classification of this soil as described in ASTM D 2488-84 is generally SC-SM and SP-SC. The pH of the soil is around 8.4 and

the soil moisture content is typically 2 to 8% by mass, thus reducing the risk of attack due to aggressive soil water. Data supplied to BNL by C.Stein of SNI indicated that water soluble sulphate levels in uncontaminated soil are 10 to 590 ppm which is not considered hazardous for cement based materials. Another potential source of sulphates in the soil is sulphate producing bacteria, although this may not be a problem at large depths if aeration is reduced. Sieve analysis has shown that 60% of particles are typically in the size range of 0.15 to 0.19 mm. The original soil used to produce the soil cements had a moisture content of 8% by mass. This was taken into account in the mix formulations. When further shipments of soil were received, the moisture content was measured and the water content of mixes adjusted so that the total amount of water in a given soil cement remained constant.

The mix proportions of the grouts are given in Table 1. The letters "f" and "c" refer to fine and coarse sand respectively. The grouts were designed to be fluid and have relatively low water/cementitious (cement + silica fume) ratios (w/cm) to optimize durability, permeability and mechanical properties while maintaining required flow properties. For the silica fume modified grout (No. 67) increased w/cm was necessary to improve fluidity. Less bentonite was required when silica fume was added due to reduction of bleeding and settling. The letter "m" refers to microfine cement and the grout produced from this cement required a high w/c because of the high surface area of cement particles. Grout No. 47 was used to produce soil cements at ratios of soil to cement ranging from 1 to 5 by mass since work in FY 1992 identified this grout as the most suitable compared with sanded, silica fume modified and latex modified grouts.

Table 1. Mix Proportions of Plain Grouts

Mix Code	Cement (kg/m ³)	Water (kg/m ³)	Sand (kg/m ³)	Bentonite (kg/m ³)	Silica Fume (kg/m ³)	SP* (ml/kg cm)
9	795	437	795 (f)	22	0	20
47	1361	544	0	12	0	20
60	1435	545	0	10	0	15
67	746	414	830 (c)	16	84	20
68	832	399	832 (c)	20	0	20
70	769	384	538 (c) 384 (f)	19	0	20
M1	703 (m)	703	0	14	0	20

* SP = superplasticizer in ml per kg (cement + silica fume)

Mix proportions for the soil cements are presented in Table 2. The number that follows the Mix Code refers to the soil/cement ratio (s/c) by mass. Additional mixing water was added so that the soil cements would be fluid. The water content includes contributions from the parent grout, additional mixing water and water present in the soil. The consistency required in practice may differ with placement technique. Hence, it may be possible to reduce the water content if adequate consolidation of stiffer mixes can be achieved.

Table 2. Mix Proportions of Plain Soil Cements

Mix Code	Cement (kg/m ³)	Water (kg/m ³)	Bentonite (kg/m ³)	SP (ml/kg cement)	Soil (kg/m ³)
47S1	816	391	7	20	816
47S2	528	428	4	20	1055
47S3	391	451	3	20	1175
47S4	315	434	3	20	1260
47S5	263	422	2	20	1316

Tables 3 and 4 document the type and volume fraction of fibres used in the grouts and the soil cements. The number after the Mix Code refers to the volume fraction of fibres as indicated.

Table 3. Fibre Reinforced Grouts Studied

Mix Code	Volume Fraction and Fibre Type
9 0.1F	0.1% fibrillated polypropylene
9 0.2F	0.2% fibrillated polypropylene
60 0.2F	0.2% fibrillated polypropylene
68 0.1F	0.1% fibrillated polypropylene
68 0.2F	0.2% fibrillated polypropylene
70 0.1F	0.1% fibrillated polypropylene
70 0.2F	0.2% fibrillated polypropylene
70 1.0F	1.0% fibrillated polypropylene
70 0.2MF	0.2% monofilament polypropylene
70 0.2NF	0.2% monofilament nylon

Table 4. Fibre Reinforced Soil Cements Studied

Mix Code	Volume Fraction and Fibre Type
47S1 0.1F	0.1% fibrillated polypropylene
47S1 0.2F	0.2% fibrillated polypropylene
47S1 0.2MF	0.2% monofilament polypropylene
47S1 0.2NF	0.2% monofilament nylon
47S2 0.2MF	0.2% monofilament polypropylene
47S2 0.2NF	0.2% monofilament nylon

2.2 Mixing Procedure

2.2.1 Cementitious Grouts

Preparation of small volumes of grouts was performed using a Waring blender. Small volumes were required for viscosity measurements and preparation of specimens for permeability tests. The order of addition was water, superplasticizer, bentonite, silica fume (if any), cement and sand (if any). The superplasticizer was mixed with water for 15 seconds. Bentonite was added and mixed for 1 minute to ensure complete dispersion. Any silica fume was added and mixed for 15 seconds, followed by addition of cement and any sand, and further mixed for 1 minute.

Larger volumes of grout were required for preparation of compressive strength, flexural strength, wet-dry cycle, restrained shrinkage and freeze-thaw cycle specimens. Mixing was performed in a Blakeslee planetary type mixer. The same order of addition was maintained. Bentonite was mixed with water and superplasticizer for 5 minutes. Any silica fume was then mixed for 1 minute. Cement and any sand were added and mixed for 5 minutes.

For small-scale field trials grouts were mixed using a ChemGrout paddle mixer. The mixing time was increased to ensure uniform distribution of cement and sand.

2.2.2 Soil Cements

Large quantities of soil cements were prepared by adding the required amount of soil to the previously mixed parent grout in the Blakeslee mixer. When additional mixing water was necessary, the water was added after the soil. Mixing was then performed for 5 minutes. For small quantities of soil cements the parent grout was prepared in the Waring blender and transferred to a stainless steel

beaker. Soil and any additional mixing water was added and mixed by hand.

Soil cements for the small-scale field trials were prepared using a Muller mortar mixer. Grout was mixed first, followed by addition of soil and any required extra mixing water.

2.2.3 Fibre Reinforced Grouts and Soil Cements

Fibres were added to grouts after cement and any sand were thoroughly mixed. The fibres were added in increments in an attempt to prevent clumping and mixing continued for 2 minutes. The grouts remained self-levelling when the fibre volume fraction was 0.1 or 0.2%. At high volume fractions of fibres ($>0.2\%$) clumping occurred and fibres tended to cling to the mixer paddle, rather than form a uniform distribution throughout the grout. Any clumps were separated by hand. Clumping and tangling was particularly prevalent with the collated fibrillated fibres, and less problems were encountered with volume fractions of 0.1% and with monofilament fibres.

Fibre reinforced soil cements were prepared by adding the fibres to the prepared grout, followed by addition of soil and any mixing water. The volume fraction of fibres was calculated by the volume of soil cement. Therefore, relatively high concentrations of fibres were added to the parent grout to give volume fractions of 0.1 and 0.2% in the final product. For this reason, the addition of fibrillated fibres was limited to the soil cement with a soil/cement ratio of 1. A pumpable fibrillated fibre reinforced grout that would give soil cements with fibre volume fractions of 0.1 and 0.2% could not be produced due to non-uniform mixing of the fibres. Since the monofilament fibres showed improved mixing behavior, soil cements with a soil/cement ratio of 2 could be reinforced with these fibres at a volume fraction of 0.2%.

2.3 Curing

All materials were covered with plastic sheet after casting to prevent evaporation and plastic shrinkage cracking. Grouts and soil cements were demoulded 24 hours after casting and cured for 28 days for permeability, compressive strength, flexural strength and wet-dry cycle tests. Conventional type curing in the form of submersion in water at room temperature was conducted in order to determine the properties when adequate cement hydration occurs. Simulation of the in-situ curing conditions for subsurface barriers was achieved by burying 24 hour old specimens in 200 l containers of site soil.

2.4 Experimental Methods

2.4.1 Viscosity

Viscosity of grouts was measured using a Fann 35A coaxial cylinder viscometer at 300 rpm. Measurements were taken

immediately after mixing in the blender. All viscosity measurements were conducted at room temperature. Grouts that contained relatively large amounts of sand could not be tested due to the risk of damage to the instrument.

2.4.2 Specific Gravity

The specific gravity of grouts and soil cements was measured using a Baroid mud balance following ASTM D 4380-84.

2.4.3 10 Minute Gel Strength

The 10 minute gel strength measures the shear strength of a grout after it has been allowed to sit for 10 minutes. After measuring viscosity of a cementitious or latex modified grout at 300 rpm the shear rate was changed to 3 rpm and the viscometer was turned off. The grout was rested for 10 minutes. The viscometer was then restarted and the maximum scale deflection prior to the gel break was recorded. This value was the direct gel strength in $\text{lb}_f/100 \text{ ft}^2$. The strength was converted to Pa.

2.4.4 Flow Time

The flow, or efflux, time of grouts was measured using the flow cone method given in ASTM C 939-87. The flow time indicates the relative flowability of grouts by measuring the time of efflux of a specific volume of grout through a standardized cone. For water, the flow time through this cone is 8 seconds. Grouts were prepared in the planetary mixer and tested for flow time prior to casting compressive strength cylinders. Three samples of each grout batch were tested. Flow time was also measured as a means of quality assurance during the small-scale field trials.

2.4.5 Permeability Coefficient

The water permeability was measured using either a Ruska Model 1013 Liquid Permeameter (rigid wall) or a Tricon flexible wall permeameter. The Ruska instrument gives uniaxial flow and does not apply a confining pressure. Permeability of wet cured, in-situ cured and leached specimens was measured with the Ruska permeameter. Specimens were cast in glass tubes 26 mm diameter and 50 mm long. The specimens were trimmed to 36 mm long to fit in the specimen holder and to remove laitance from both ends. The diameter of the specimens was slightly oversized in order to achieve a leakproof seal with the rubber gasket. The seal was further ensured by coating the gasket walls with silicone grease. The applied pressure was 2 atm. Three specimens per batch were tested. All specimens were saturated prior to testing.

Permeability of grouts and soil cements before and after wet-dry cycles was measured using the Tricon permeameter. Specimens were cast in 75 mm diameter 150 mm length cylinders and cured for the required time. After curing the specimens were trimmed to 105

mm length in preparation for testing. The Tricon permeameter gives uniaxial flow and permits application of a confining pressure. For the tests the confining pressure was chosen to be 0.4 MPa to simulate the maximum overburden pressure to which the barriers are likely to be exposed. The applied pressure was 2 atm. Permeability coefficient (hydraulic conductivity) was calculated assuming Darcy's Law for flow through porous materials

2.4.6 Leach Test

Grout and soil cements 26 mm diameter and 36 mm long were subjected to semi-dynamic leaching in deionized water for 6 months to determine the change in permeability that occurs with leaching of calcium hydroxide. Leaching commenced when the specimens were 24 hours old so that the process was accelerated. Specimens were maintained in a container of static deionized water. For the first two months the deionized water leachate was replaced daily. After two months the leachate was replaced weekly. The test gives an indication of the comparative leach resistance of the barrier materials to a soft water that is capable of dissolving calcium hydroxide and hydrates produced from cement hydration reactions. For the landfill under consideration where the groundwater table is deep and the environment is arid, the leach test represents a severe acceleration of service conditions. The data obtained from the leach tests may also be of value for comparing response of grouts and soil cements for environments where leaching due to flow of groundwater is expected.

2.4.7 Compressive Strength

Grouts and soil cements were cast into wax coated cardboard cylinders and were subsequently used for unconfined compressive strength measurements following ASTM C 39-86. Strength of grout is usually determined using 50 mm cubes as described in ASTM C 109-90. However, cylinders were used in preference to cubes since it was desired to compare grout strength with that for soil cements for which cylinders were more appropriate. Cubes were only used for compressive strength measurements associated with freeze-thaw tests. The cylinders were 75 mm diameter and 150 mm long. At the completion of the required curing period compressive strength was measured using a Forney compression tester. Measurements were conducted on 6 specimens per batch.

2.4.8 Flexural Strength

Beams 300 mm x 50 mm x 50 mm of the grouts and soil cements were cast and used to measure the flexural strength by test method ASTM D 1635-87. The beams were in-situ cured for 28 days. Third-point loading was conducted on six specimens per batch.

2.4.9 Wet-Dry Cycling

The durability of grouts and soil cements to wet-dry cycles was tested. In the first type of wet-dry cycle tests the specimens

used were cylinders 75 mm diameter and 150 mm length that had been cured in water for 28 days. Three specimens per mix were tested. Initially, the wet-dry cycling test performed followed that for soil cements specified in ASTM D 559-89 in which the drying cycle occurs at 71°C. The high drying temperature may be applicable for cap materials, but is not suitable for barriers in the ground. The test was subsequently modified so that drying occurred at 25°C to give a more realistic simulation of the subsurface temperatures to which the barriers would be exposed in service. The cycles consisted of submersion in water at 25°C for 5 hours followed by drying in air at 25°C and relative humidity of 40-50% for 43 hours. The 48 hour cycle was repeated 12 times. Weight changes and development of surface cracks were monitored throughout the cycles.

Ultrasonic pulse velocity of the grouts and soil cements at the beginning and end of the cycles was measured in accordance with ASTM C 597-83. Both wet and dry conditions were tested so that the influence of moisture could be evaluated. The residual compressive strength and ultrasonic pulse velocity were compared to those after 28 days wet curing.

In the second type of wet-dry cycle test, specimens 75 mm diameter and 105 mm long were tested for initial permeability, subjected to 23 wet-dry cycles at 25°C, and then retested for permeability. This test gave a measure of the change in permeability that may occur due to formation of drying cracks and enabled quantitative comparison between resistance to cracking of plain and fibre reinforced materials. The specimens were wet cured for 28 days in the first series of experiments. Another batch of specimens were cured in-situ for 3 months. The second batch had not been tested at the time of writing due to the length of time taken to measure the wet cured specimens. After the curing period the specimens will be saturated and measured for initial permeability. The specimens will then be allowed to dry in air, re-saturated, and permeability will be re-measured.

2.4.10 Restrained Shrinkage

Shrinkage cracking tendency of the grouts and soil cements was compared by restrained shrinkage (shrinkage ring) tests. Materials were cast in an annular shape around a rigid steel ring. The annulus, or ring, had an inner radius of 82.5 mm, an outer radius of 125 mm and a height of 65 mm. Twenty four hours after casting, the outer mould was removed and the grout or soil cement ring bonded to the inner steel ring was buried in dry soil to simulate the subsurface exposure conditions. Shrinkage was restrained by the inner steel ring and radial cracks eventuated. Specimens were examined daily for cracking and the time to failure and crack width at failure was noted. After failure, the specimens were removed from the soil and left to dry in air at room temperature and humidity. Crack width versus time was monitored to determine whether fibres were beneficial in controlling crack width and to compare grouts with soil cements.

2.4.11 Linear Plastic Shrinkage

Linear plastic shrinkage and initial drying shrinkage up to an age of 24 hours was measured by the DuPont method. The material was poured into a PTFE lined rectangular tray 135 mm wide and 350 mm long to a thickness of 45 mm. Two angle sections protruded into the material to give a 254 mm gauge length. One angle was permanently fixed and the other was temporarily fixed to a shaft supported above the specimen. After removing the pin securing the movable angle any change in length was continuously monitored by a Proximity probe and recorded by an X-Y plotter as a function of time. The measurements were conducted under normal room air circulation as opposed to forced air movement since the cast in-situ barriers would not be subjected to high winds. The ambient temperature during the tests was 21°C and the relative humidity was 40-50%.

2.4.12 Freeze-Thaw Tests

The durability of selected materials subjected to freeze-thaw cycles was determined. Beams 102 mm wide, 76 mm deep and 406 mm long were cast in accordance with ASTM C 666-90. The beams were cured in water for 14 days. One beam of each material underwent freeze-thaw cycles while a control beam was maintained in water for the same period. The temperature range used in the Logan freeze-thaw cabinet was -18 to 10°C (0 to 50°F). The cycle time was 3 hours and the specimens were tested over a period of 112 cycles (14 days). Instead of measuring the dynamic modulus of elasticity as given in ASTM C 666 for concrete, the compressive strength of 76 mm cubes cut from the cycled beams was measured and compared with that for the control beams. This gave a measure of any strength loss.

2.4.13 Microstructure

The microstructure of grouts and soil cements was examined under optical and scanning electron microscopes. Both wet and in-situ type curing were studied to determine the effect of curing on the microstructure. Particular attention was paid to the effect of fibre reinforcement on the microstructure and to any evidence of deleterious reactions between soil and cement based grout. The microstructure after leaching was also examined to correlate results with leaching mechanisms.

Preparation of specimens for microstructural analysis was the same as that for permeability measurements. After curing, specimens were polished down to 0.3 micron alumina and examined under an optical microscope. Following this, the specimens were carbon coated and viewed under a Jeol JSM 6400 scanning electron microscope equipped with an energy dispersive X-ray analysis system (EDX). Specimens that had been leached were not polished and the leached surface was carbon coated and viewed.

2.4.14 Small-Scale Field Tests

Excavations approximately 0.5 m deep x 0.5 m long x 0.2 m wide were dug in soil at Brookhaven National Laboratory and filled with either grout or soil cement. The trials were used to test the pumpability of grouts and to simulate subsurface barrier exposure. The subsurface environment was less arid than that at the CWL. Plain and fibre reinforced versions of Mix No. 70 and plain versions of Mix No's. 47S1 and 47S2 were studied. The grout was pumped using a ChemGrout piston displacement type pump and the soil cements were poured into the excavation directly from the mixer. Samples of the freshly mixed materials were taken for subsequent compressive strength tests after 28 days curing in a water bath. The properties of the final products may vary with placement technique, so that some variations with barriers produced with full scale equipment can be expected. However, the information from the tests gives an indication of field performance.

After placement, a hook was embedded in the fresh barrier to facilitate exhumation. The barrier was then covered with a 50 mm layer of soil and left in place from June to September. At the completion of the exposure period, the barriers were removed and 75 mm diameter core samples were taken. The barriers were examined for evidence of cracking or other forms of deterioration and cores were tested for compressive strength and ultrasonic pulse velocity.

2.4.15 Permeation Grouting Tests

The possibility of permeation grouting of site soil was investigated despite reservations that the soil pore structure was too fine for adequate permeation of a cementitious grout. A Moyno pump was used to transfer previously mixed microfine cement grout from a hopper to a perforated steel injection tube embedded in a cylinder of site soil 100 mm in diameter and 200 mm long. In initial tests grout was injected into hand compacted soil and the injection pressure was monitored. Experiments were repeated in soil that had been compacted using the Forney compression tester to simulate an overburden pressure of 0.4 MPa. The grouted soils were allowed to cure overnight and then dissected using a cut-off saw to examine the penetration of grout.

2.4.16 Field Trials at Sandia

The field trials to demonstrate grouting technologies at a clean site adjacent to the CWL were delayed and the results were unavailable at the time of writing. It is assumed that the results will be documented by the Subsurface Barrier Emplacement Program.

3.0 RESULTS AND DISCUSSION

3.1 Rheology

The properties of the unhardened grouts are presented in Table 5. Mix 67 (silica fume modified) was thixotropic and would not flow through the flow cone. The viscosity and gel strength of Mix 70 was not measured due to the high sand content.

Table 5. Properties of Unhardened Grouts

Mix	Viscosity (cP)		10 min. Gel Strength (Pa)		Flow Time (s)		Specific Gravity
	Mean	SD*	Mean	SD	Mean	SD	
9	216	2	36	1	28.3	1.0	2.06
47	50	2	72	1	17.4	1.0	1.95
60	66	1	50	1	24.4	1.1	1.99
67	230	2	110	2	-	-	2.09
68	285	2	140	1	24.9	0.9	2.15
70	-	-	-	-	31.2	1.2	2.11
M1	9	0	15	0	9.4	0.1	1.47

* SD = standard deviation

The rheological behavior of the grouts may be influenced by the mixer type, and different properties may result if the grouts are mixed in a full scale paddle or colloidal mixer. Grouts mixed in the planetary mixer were less viscous and less thixotropic than those mixed in the blender. Addition of a further 10 ml superplasticizer per kg cement after mixing maintained fluidity in hot weather or long pumping times.

The results in Table 5 show the dependence of flow properties on mix proportions when grouts are prepared in laboratory scale mixers. As expected, the viscosity and flow time decrease with increasing w/c for a given grout type. Increasing the coarseness of sand leads to reduction of w/c necessary for similar flow times. Use of a smoother sand may improve the flow properties and reduce the necessary water content compared with the sands used in this work. The silica fume modified grout was thixotropic and may require re-formulation for field use, depending on pumping equipment available. Addition of further superplasticizer did not significantly improve the silica fume grout and increase of fluidity probably requires an increase in w/c. Such an increase would reduce strength and durability and raise permeability.

For fibre reinforced grouts it is imperative that clumps of fibres do not enter the pump and this may necessitate modification of grout mixing equipment to ensure adequate fibre distribution. Monofilament fibres were less susceptible to clumping and may be more suitable if problems are encountered with mixing of fibrillated fibres. As discussed below, the fibrillated fibres give superior crack width reduction performance compared with monofilament fibres. Therefore, a compromise between pumpability and performance must be achieved if fibre reinforced grouts are used.

3.2 Permeability Coefficient

3.2.1 Plain and Fibre Reinforced Grouts

The permeability coefficients of the plain and fibre reinforced grouts for wet and in-situ cured conditions and after 6 months of leaching in deionized water are given in Tables 6 and 7.

Table 6. Permeability of Plain Grouts

Mix	Permeability ($\times 10^{-10}$ cm/s)					
	Wet Cured		In-Situ Cured		Post-Leaching	
	Mean	SD	Mean	SD	Mean	SD
9	0.53	0.03	1.5	0.4	39	2
47	0.90	0.1	-	-	-	-
60	0.63	0.1	0.72	0.04	7.7	0.5
67	0.40	0.03	-	-	2.2	0.6
68	0.44	0.03	0.57	0.03	7.8	0.4
70	0.40	0.1	0.66	0.1	12	2

Table 7. Permeability of Fibre Reinforced Grouts

Mix	Permeability ($\times 10^{-10}$ cm/s)			
	Wet Cured		In-Situ Cured	
	Mean	SD	Mean	SD
9 0.1F	0.43	0.04	1.3	0.3
9 0.2F	0.52	0.2	1.1	0.3
68 0.1F	0.66	0.2	0.77	0.2
68 0.2F	0.64	0.2	0.70	0.1
70 0.2F	0.34	0.09	0.65	0.1
70 0.2MF	2.7	0.3	-	-

The U.S. Environmental Protection Agency states that landfill barrier materials must have a permeability coefficient not exceeding 10^{-7} cm/s, hence the grouts and some of the soil cements studied fulfill this requirement. Permeability coefficient of plain and fibre reinforced grouts is sensitive to w/c and curing conditions as indicated in Tables 6 and 7. For Mix 70 the increase in sand content and increase in w/c did not lead to a significant increase in permeability coefficient compared with Mix 68. The initial permeability of the silica fume modified grout is not significantly lower than that for the equivalent unmodified grout due to the slightly higher water/cementitious material ratio used.

The relationship between mix proportions and permeability is strongly influenced by the curing conditions. Predictably, the permeability coefficient increased when the grouts were cured in-situ due to the reduced hydration of cement compared with that for wet curing conditions. The degree of permeability increase was dependent on w/c. Thus, for the highest w/c, the percentage increase in permeability coefficient was greatest. This is due to the incomplete closure of continuous capillary pores associated with high w/c and compounded by the non-ideal curing conditions that reduce the degree of hydration (Neville, 1981; Bentz and Garboczi, 1991).

The negligible effect of increasing sand content on permeability coefficient is not readily explained by previous studies. It has been suggested that permeability increases when aggregate is incorporated in cement paste due to formation of porous zones and shrinkage microcracks at the aggregate-cement paste interface that give rise to flow paths for water (Young, 1988). For mortars and concretes where interfacial zones of 15-20 micron thickness overlap, transport through such zones will be favored over transport through bulk paste (Snyder et. al., 1992). For the grouts studied, the shortest distance between adjacent sand grains is typically 20-100 micron based on a two dimensional slice. The three dimensional grout structure could be expected to have some degree of overlap and interconnection between proposed porous interfacial zones. However, this is not reflected in the permeability test results. Thus, the introduction of impermeable sand at the levels used does not appear to result in a favorable flow path through interconnected porous interfacial zones. This was confirmed by the examination of the microstructure discussed below.

The effect of fibrillated fibres on the permeability coefficient was relatively small and not consistent. For Mix 68 permeability appeared to increase slightly, while for Mix 70 permeability was the same with and without fibres. Mix 9 showed an increase in permeability at 0.2% fibres. The coefficient of variation in permeability tended to increase when fibres were added and this is attributed to increased heterogeneity. The permeabilities remain of the same order of magnitude and fibres are not detrimental. Hence, at the rate of fibrillated fibre addition used there is no evidence of linkage between porous zones at the fibre interface to cause flow paths for water.

The findings for fibrillated fibre reinforced grouts concur with other research on low volume fraction addition of polypropylene fibres on cementitious materials. A negligible effect on permeability by addition of 0.2% volume fraction of polypropylene fibres to concrete (Al-Tayyib and Al-Zahrani, 1990) and reduction in air permeability of mortar on addition of polypropylene fibres (Sanjuan et. al., 1991) have been reported.

In contrast to the fibrillated fibres, the monofilament fibres caused a definite and significant increase in permeability. Increased permeability was also found when the same grout was tested in the flexible wall permeameter. Therefore, the monofilament fibres must induce favorable pathways for the transport of water. For monofilament fibres there is a greater number of individual fibres and this may result in some degree of interconnection.

3.2.2 Soil Cements

The permeability results for soil cements are given in Table 8.

Table 8. Permeability of Plain and Fibre Reinforced Soil Cements

Mix	Permeability ($\times 10^{-10}$ cm/s)					
	Wet Cured		In-Situ Cured		Post-Leaching	
	Mean	SD	Mean	SD	Mean	SD
47S1	1.2	0.2	1.2	0.3	4.7	1.0
47S2	2.5	0.1	3.9	0.5	20	1.0
47S3	2.9	0.2	95	10	-	-
47S4	3.5	0.4	220	30	-	-
47S5	3.9	0.4	1600	200	-	-
47S1 0.2MF	1.3	0.3			-	-
47S2 0.2MF					-	-

The permeability coefficients of the wet cured soil cements with soil/cement ratio (s/c) less than or equal to 5 were up to three orders of magnitude lower than the EPA limit of 10^{-7} cm/s and thus, are suitable barrier and cap materials if curing is adequate. The relationship between permeability coefficient and s/c for the wet cured soil cements is shown in Figure 2. The results can be compared with those from jet grouted columns produced from grout with w/c = 4 and cement content of 534 kg/m^3 of 10^{-7} to 10^{-5} cm/s (depending on the sampling method) reported by Adaska et. al. (1992). Although the laboratory prepared soil cements will differ from those produced by jet grouting, the results suggest that use

Figure 2. Permeability Coefficient versus Soil/Cement Ratio for Wet Curing.

of superplasticized grouts can enhance impermeability significantly.

The relationship between permeability coefficient and s/c for in-situ cured soil cements is shown in Figure 3. The reduced degree of hydration has a negligible effect on permeability when s/c = 1, and becomes significant when s/c exceeds 2. At this point, the degree of capillary pore continuity probably increases due to the high w/c ratio. It is also possible that there is increased microcracking associated with in-situ curing, resulting in higher permeabilities if microcracks are interconnected. The results suggest that s/c = 4 is the maximum soil content that can be used for in-situ cured soil cements of this type to comply with the permeability limit of 10^{-7} cm/s. Based on permeability coefficient alone, soil cements with s/c = 1 and 2 would be the preferred materials since they give a reasonable safety margin.

An increase in permeability of the soil cements when monofilament fibres were added was observed. The degree of increase was not as high as that for the Mix 70 grout.

The permeability coefficients for the soil cements can be compared with materials commonly used for cutoff walls. Permeability coefficients of soil-bentonite slurries vary from 10^{-7} to 10^{-8} cm/s, and the values for cement-bentonite slurries range from 10^{-5} to 10^{-6} cm/s (Evans, 1993). Thus, the low soil/cement ratio soil cements have permeabilities two to five orders of magnitude lower than typical materials.

Under field conditions the barrier will be subjected to stresses arising from overburden pressure and lateral pressures. Therefore, barriers may exhibit a lower permeability coefficient when subjected to service stresses than that measured in the uniaxial test cell.

3.2.3 Permeability After Leaching

After six months semi-dynamic leaching in deionized water the permeability increased by a factor ranging from 4 for Mix 67 to 30 for Mix 70. Thus, the lowest percentage increase is associated with the silica fume modified grout. The leach resistance can be attributed to the pozzolanic reaction between silica fume and calcium hydroxide during cement hydration to form calcium silicate hydrate. Since the grout containing silica fume effectively contains less calcium hydroxide to be leached, the relative increase in permeability that occurs with dissolution of calcium hydroxide from hardened cement paste is reduced. The greatest percentage increase in permeability coefficient occurred for Mix 70 and this is probably due to the higher water/cement ratio compared with 68 and the absence of silica fume. The leaching resistance is explained further in terms of microstructure in Section 3.8.3.

The two soil cements, 47S1 and 47S2, have higher initial permeability coefficients and higher final values after leaching compared with the grouts. However, the degree of increase in permeability coefficient for the soil cements is relatively low.

Figure 3. Permeability Coefficient versus Soil/Cement Ratio for In-Situ Curing.

After leaching, the permeability coefficient is 4 times greater for 47S1 and 8 times greater for 47S2. Thus, there appears to be a direct correlation between leach resistance and soil/cement ratio and also water/cement ratio.

The relative increase in permeability of 47S1 was similar to that for the silica fume modified grout. The low water/cement ratio of 47S1 is probably a contributing factor to the measured leach resistance. The leach resistance of 47S2 is also good compared with the grouts without silica fume, especially considering the high water/cement ratio of 0.81. The resistance is discussed further in Section 3.8.3.

Although the grouts and soil cements did show an increase in permeability after leaching, the final values remain below the required 10^{-7} cm/s limit. Therefore, adequate performance can be expected, particularly in an arid environment where exposure to water will be occasional and significantly less severe than the leach test. In environments where the barriers are continuously exposed to soft water or groundwater with high soluble sulphate levels, addition of silica fume to grouts is recommended provided that acceptable fluidity and pumpability can be ensured. Silica fume modified grouts can also be used to produce soil cements and properties of such materials were reported in the FY 1992 report.

3.2.4 Permeability After Wet-Dry Cycles

The permeabilities before and after wet-dry cycles and after drying that were measured in the flexible wall permeameter are given in Tables 9 to 12.

Table 9. Effects of Wet-Dry Cycles on Plain Grouts

Mix	Permeability ($\times 10^{-10}$ cm/s)			
	Initial		Final	
	Mean	SD	Mean	SD
70	6.0	0.5	14	4

Table 10. Effects of Wet-Dry Cycles on Fibre Reinforced Grouts

Mix	Permeability ($\times 10^{-10}$ cm/s)			
	Initial		Final	
	Mean	SD	Mean	SD
70 0.1F	5.6	1.2	6.8	1.7
70 0.2F	7.0	0.6	6.9	1.0
70 1F	2.3	0.1	4.1	0.1
70 0.2MF	67	7	92	11

The values of permeability coefficient of the grouts and soil cements were higher when measured in the flexible wall permeameter, despite the confining pressures. This is possibly due to differences in specimen properties when prepared in the planetary mixer compared with the blender. However, the permeability coefficients show the same trends. The initial permeability of the wet cured version of Mix 70 with 1% fibres was lower than the other versions of Mix 70 and may be due to batch variation. Mix 70 with 0.2% monofilament fibres had an initial permeability coefficient higher than the plain and fibrillated fibre reinforced mixes as was found when measurements were made in the rigid wall permeameter. The tests on in-situ cured specimens are in progress and the full results will be reported in the future.

All wet cured mixes showed some degree of crack healing after several cycles of wetting and drying. Thus, cracks that formed eventually decreased in crack width thereby reducing the change in permeability. The extent of visible surface crack healing was least for 70 0.2MF. The permeability coefficients of Mixes 70 and 70 1F after wet-dry cycles was approximately double the initial 28 day value but remained acceptable for subsurface barriers. The lowest change in permeability coefficient was measured on the grouts with 0.1 and 0.2% fibrillated fibres demonstrating improved resistance to cracking that results in increased flow of water. The monofilament fibre reinforced grout showed the poorest absolute performance with high initial and final permeabilities. The relative increase in permeability was a factor of around 1.4, which is lower than that for the plain and 1% fibrillated fibre mixes. The final permeability is higher than that for the plain mix, hence use of monofilament fibres is inadvisable.

The healing of surface cracks appeared to be due to formation of calcium carbonated deposits. Calcium hydroxide probably leached into the cracks during the wetting cycle and this was converted to calcium carbonate by reaction with atmospheric carbon dioxide during the drying cycle. Such autogenous healing is frequently observed on concrete and has been reported in grout (Onofrei et. al., 1992).

Sealing or partial sealing of cracks by this process would reduce permeability. For the proposed subsurface service conditions of the grouts it is uncertain as to whether crack healing would occur in the same manner as that during the wet-dry tests. This is because the availability of moisture for leaching of Ca(OH)_2 and of CO_2 , either as a gas or dissolved in soil water, for reacting with Ca(OH)_2 to form CaCO_3 would be reduced in comparison. Thus, crack healing by this mechanism may be slower and less extensive.

The reduced degree of surface crack healing on 70 0.2MF is possibly due to loss of Ca(OH)_2 during curing in tap water as a result of initial high permeability. The reduced amount of Ca(OH)_2 would lead to a decrease in the extent of CaCO_3 produced to seal cracks.

In addition to the effect of crack healing on reducing the permeability of wet-dry cycled specimens, it is also possible that there is some ongoing hydration, albeit interrupted, during the wetting cycle. This hydration would reduce permeability. It is also possible that cracks may become blocked with debris formed during the fracture process. The application of a confining pressure may also close cracks and reduce permeability.

Table 11. Effects of Wet-Dry Cycles on Plain Soil Cements

Mix	Permeability ($\times 10^{-10}$ cm/s)			
	Initial		Final	
	Mean	SD	Mean	SD
47S1	6.0	0.5	5.4	0.5
47S2	7.5	0.8	9.0	1.0

Table 12. Effects of Wet-Dry Cycles and Drying on Fibre Reinforced Soil Cements

Mix	Permeability ($\times 10^{-10}$ cm/s)			
	Initial		Final	
	Mean	SD	Mean	SD
47S1 0.2F	5.6	0.8	3.1	0.5

At a soil/cement ratio of 1, the permeability coefficient of the wet-dry cycled specimens was similar, or slightly lower than the initial value. Surface cracks on the specimens were not visible at the conclusion of the cycles and cracking seemed less severe than on cylinders used for measuring residual compressive strength after wetting and drying. The results suggest effective sealing of cracks. The specimens reinforced with fibrillated fibres had lower permeabilities than the initial readings.

When the soil/cement ratio was increased to 2, the initial and final permeability coefficients increased, but remained within the required limits. The permeability after wet-dry cycling was less than that for the plain and monofilament fibre reinforced versions of Mix 70. These results do not correlate with the residual strength measurements as discussed in Section 3.4.2.

It is expected that the in-situ cured specimens will show a higher initial permeability coefficient and that the resistance to cracking as a result of drying in air will be reduced due to lower toughness. The specimens will indicate the increase in permeability that occurs when water is unavailable for leaching of Ca(OH)_2 and subsequent crack healing. The effect of fibres on crack control and reduction of the increase in permeability associated with cracking may be more detectable on the air dried specimens.

3.3 Compressive and Flexural Strength

3.3.1 Plain and Fibre Reinforced Grouts

Table 13 presents the compressive and flexural strengths of the grouts. The results are also shown graphically in Figures 4 to 6. The microfine cement grout (M1) was not tested due to difficulty in producing acceptable specimens as a result of excessive bleeding.

Table 13. Mechanical Properties of Plain Grouts

Mix	Compressive Strength (MPa)				Flexural Strength (MPa)	
	Wet Cured		In-Situ Cured			
	Mean	SD	Mean	SD	Mean	SD
9	35.2	2.6	30.9	2.3	2.3	0.7
47	39.4	2.3	29.2	1.9	-	-
60	40.3	2.9	31.8	3.3	2.1	0.8
67	32.3	4.0	-	-	-	-
68	32.8	2.4	31.3	2.5	2.8	0.3
70	35.8	4.2	29.4	3.5	3.9	0.4

The plain grouts have similar compressive strengths when wet cured as indicated in Figure 4. The neat cement grout (Mix 60) shows the highest strength and this is a reflection of the low water/cement ratio (w/c). Comparison between Figures 4 and 5 shows the expected decrease in compressive strength associated with reduction of hydration for in-situ curing. The strengths are adequate for the landfill application.

The measured mechanical properties of the fibre reinforced grouts are given in Table 14. Figures 4 and 5 compare the compressive strengths of the plain and fibre reinforced grouts and Figure 6 shows the flexural strengths.

In general, addition of fibres did not significantly effect compressive strength as shown in Figures 4 and 5. A two-tailed t-test was conducted at the 5% significance level to compare the sample means of the plain and fibre reinforced grout compressive strengths. It was assumed that the strengths were normally distributed with equal variances. The only significant differences were a decrease in strength for the wet cured fibre reinforced version of Mix 60 and an increase in strength for the wet cured fibre reinforced version of Mix 68. These differences are possibly due to batch variations. Fibre reinforcement did not significantly effect the compressive strength of the in-situ cured grouts. The fibre reinforced grouts hung together after maximum compressive load was achieved due to fibre bridging across cracks whereas the unreinforced grouts fractured completely.

Figure 4. Compressive Strength of Plain and Fibre Reinforced Grouts for Wet Curing.

Figure 5. Compressive Strength of Plain and Fibre Reinforced Grouts for In-Situ Curing.

Figure 6. Flexural Strength of Plain and Fibre Reinforced Grouts for In-Situ Curing.

Table 14. Compressive and Flexural Strength of Fibre Reinforced Grouts.

Mix	Compressive Strength (MPa)				Flexural Strength (MPa)	
	Wet Cured		In-Situ Cured		Mean	SD
	Mean	SD	Mean	SD		
9 0.1F	34.0	2.6	28.3	2.8	3.3	0.5
9 0.2F	34.8	1.1	29.5	2.8	4.2	0.5
60 0.2F	35.2	1.0	31.3	2.2	2.1	0.7
68 0.1F	38.7	4.2	31.5	3.9	3.2	0.2
68 0.2F	37.0	4.4	32.8	1.2	3.7	0.3
70 0.1F	-	-	-	-	3.9	0.3
70 0.2F	35.0	3.4	29.5	2.6	3.7	0.3
70 0.2MF	32.5	1.5	-	-	-	-

The mean flexural strength of Mix 9 was increased at the 5% significance level by incorporation of polypropylene fibres for both 0.1 and 0.2% volume fraction, as indicated in Figure 6. Mix 68 showed an increase in mean flexural strength at the 5% significance level for 0.2% volume fraction of fibres. For the other grouts, flexural strength was not significantly altered by fibres. It was not obvious why Mix 9 should show greater improvement in flexural strength when fibres were added compared with the other grouts. It is possible that the fine sand in Mix 9 results in better distribution of fibres throughout the grout matrix. The high standard deviation associated with flexural strengths for the plain and fibre reinforced neat cement grout (Mix 60) is possibly due to presence of shrinkage cracks within the beams and non-uniform fibre distribution in the fibre reinforced specimens.

The fibre reinforced grouts were more ductile in flexure than their plain counterparts. As was the case for the compressive strength tests, the fibre reinforced beams tested in flexure hung together after failure and the unreinforced beams split into two halves. At the point of failure some fibre pullout occurred, but enough fibres remained bonded to prevent total separation. Such behavior could be advantageous if the grout barriers were inadvertently subjected to mechanical overload since fluid flow through a failed reinforced section would be less than that for an unreinforced section.

3.3.2 Plain and Fibre Reinforced Soil Cements

The compressive and flexural strengths of the plain soil cements are presented in Table 15. These results are also illustrated in Figures 7 to 9.

Figure 7. Compressive Strength versus Soil/Cement Ratio for Wet Curing.

Figure 8. Compressive Strength versus Soil/Cement Ratio for In-Situ Curing.

Figure 9. Flexural Strength versus Soil/Cement Ratio for In-Situ Curing.

Table 15. Mechanical Properties of Plain Soil Cements

Mix	Compressive Strength (MPa)				Flexural Strength (MPa)	
	Wet Cured		In-Situ Cured			
	Mean	SD	Mean	SD	Mean	SD
47S1	32.9	2.8	27.0	3.0	2.9	0.5
47S2	25.3	0.3	20.9	2.3	2.2	0.4
47S3	12.7	1.2	9.0	2.1	2.0	0.2
47S4	8.0	1.4	6.6	0.5	1.6	0.5
47S5	6.5	0.7	6.1	0.3	-	-

The strengths of the soil cements are adequate for the low strength requirement of approximately 1 MPa for the landfill barrier system under consideration. Comparison between Figures 7 and 8 shows the reduction of strength when the soil cements were cured in soil. Strength decrease can be attributed to the reduced availability of water for hydration of cement. The effect of curing conditions on compressive strength diminished as s/c increased and was not significant at s/c = 5. This observation contrasts with the effect of curing on permeability.

The compressive and flexural strengths of fibre reinforced soil cements are presented in Table 16. The effect of fibres on the strengths are illustrated in Figures 10 to 12.

Table 16. Mechanical Properties of Fibre Reinforced Soil Cements

Mix	Compressive Strength (MPa)				Flexural Strength (MPa)	
	Wet Cured		In-Situ Cured			
	Mean	SD	Mean	SD	Mean	SD
47S1 0.1F	29.2	2.1	20.6	1.2	3.8	0.3
47S1 0.2F	24.8	2.9	23.4	2.9	4.3	0.3
47S1 0.2MF	27.4	0.9	-	-	-	-
47S2 0.2MF	23.4	1.1	21.0	1.6	-	-

The influence of fibre reinforcement on compressive and flexural strength of soil cements was assessed by performing a two-tailed t-test on the data. For wet curing conditions, the mean compressive strengths of the fibrillated fibre reinforced soil cements are lower than for plain soil cement at the 5% significance level. When the soil cements were cured in soil the mean compressive strength of the 0.1% fibrillated fibre reinforced material was lower than for plain soil cement at the 5% significance level. The in-situ cured 0.2% volume fraction fibrillated fibre reinforced soil cement did not have a

Figure 10. Compressive Strength versus Soil/Cement Ratio for Wet Cured Fibre Reinforced Soil Cements.

Figure 11. Compressive Strength versus Volume Fraction of Fibrillated Fibres for Soil/Cement Ratio = 1 Cured In-Situ.

Figure 12. Flexural Strength versus Volume Fraction of Fibrillated Fibres for Soil/Cement Ratio = 1 Cured In-Situ.

significantly different mean compressive strength. Addition of monofilament fibres to 47S1 reduced compressive strength. For 47S2, monofilament fibres did not significantly alter strength. The observed reductions in compressive strength are possibly due to batch variation or introduction of flaws through non-uniform distribution of fibres.

The mean flexural strength of the soil cement containing 0.2% fibrillated fibres is significantly higher than the plain soil cement. Addition of 0.1% fibres did not significantly alter the mean flexural strength. The fibre reinforced soil cements were more ductile than the plain versions. Some fibre pullout occurred, but failed halves of the specimens remained attached, whereas the unreinforced specimens completely separated. This indicates that crack width may be reduced by fibres if the soil cements were subjected to mechanical overload.

The mechanical properties of fibre reinforced cement stabilized soil suitable for pavements have been studied by Craig et. al. (1987) and Shrader et. al. (1993). A reduction in compressive strength on addition of 0.75 and 1.5% 38 mm long polypropylene fibres was observed by Craig et. al. (1987). Shrader et. al. (1993) found that addition of 0.5% fibrillated fibres to soil cement improved ductility. These results are similar to the observations for the soil cement barrier materials.

3.4 Wet-Dry Durability

3.4.1 Plain and Fibre Reinforced Grouts

The residual compressive strength and initial and residual ultrasonic pulse velocities (UPV) of grouts subjected to 12 wet-dry cycles are given in Table 17. The temperature at which drying was performed is indicated. The percentage changes in strength and UPV are based on the calculated mean value.

All of the grout and soil cement specimens subjected to wet-dry cycling developed visible surface cracks by the second drying cycle. The neat cement grout, Mix 60, had the greatest tendency of all the tested grouts to crack and the crack widths were approximately 100 micron. The sanded grouts had crack widths lower than 100 micron and a lower visible crack density. The poor performance of the neat cement grout demonstrates the necessity to incorporate sand in grout formulations for barriers to reduce shrinkage and improve durability. Increasing the drying temperature resulted in more extensive cracking and greater strength loss.

The residual compressive strengths and ultrasonic pulse velocities of the fibre reinforced grouts after 12 wet-dry cycles at 25°C are presented in Table 18.

Table 17. Residual Strength and Ultrasonic Pulse Velocity of Grouts after Wet-Dry Cycles.

Mix	Temp (°C)	Residual Strength (MPa)		% Change	Initial UPV (km/s)		Residual UPV (km/s)		% Change
		Mean	SD		Mean	SD	Mean	SD	
9	71	21.6	1.4	-38.6	-	-	-	-	-
60	71	16.0	3.6	-59.6	-	-	-	-	-
68	71	27.2	5.3	-17.1	-	-	-	-	-
9	25	31.4	2.1	-10.8	3.45	0.05	3.45	0.03	0
60	25	18.1	3.2	-55.1	3.43	0.09	3.34	0.06	-2.6
67	25	37.0	9.3	+15.6	3.50	0.08	3.53	0.04	+0.8
68	25	37.2	2.2	+13.4	3.58	0.05	3.57	0.10	-0.3
70	25	38.6	4.1	+7.8	3.45	0.04	3.59	0.01	+4.0

Table 18. Residual Strength and Ultrasonic Pulse Velocity of Fibre Reinforced Grouts after Wet-Dry Cycles.

Mix	Residual Strength (MPa)		% Change	Initial UPV (km/s)		Residual UPV (km/s)		% Change
	Mean	SD		Mean	SD	Mean	SD	
9 0.1F	32.9	1.9	-3.2	3.29	0.06	3.42	0.02	+3.9
9 0.2F	33.7	1.3	-3.2	3.33	0.03	3.35	0.19	+0.6
60 0.2F	26.2	1.0	-25.5	3.14	0.10	3.4	0.04	+8.2
68 0.1F	35.3	1.7	-8.8	3.46	0.11	3.48	0.21	+0.6
68 0.2F	34.5	2.0	-6.7	3.49	0.15	3.33	0.10	-4.6
70 0.2F	40.0	4.8	+14.3	3.63	0.05	3.69	0.00	+1.6
70 0.2MF	32.3	1.5	-0.6	-	-	-	-	-

Addition of fibres did not eliminate the appearance of surface cracks, but generally reduced the number and width of cracks. The greatest improvement by addition of fibres was observed for Mix 60 for which both the crack density and crack widths were significantly reduced.

For all grouts except Mixes 60 and 60 0.2 F, a decrease in visible crack width was observed several cycles after initial cracks had formed. Crack healing was attributed to formation of CaCO_3 deposits within cracks as discussed in the section on permeability coefficient after wet-dry cycling. The failure of the neat cement grout to exhibit crack sealing is probably due to the

greater crack widths which could not be completely filled with deposits in the test period.

The residual compressive strength data did not always reflect the degree of visible surface cracking in the wet-dry specimens. The measured value of strength depended on the orientation of the cracks with respect to direction of loading. The greatest strength losses were measured for Mixes 60 and 60 0.2 F which corresponded with the visual observations of the highest degree of cracking. Fibres did reduce the strength loss for Mix 60. For the other mixes, the relative degree of surface cracking was not reflected in the residual strength data. Some mixes showed an increase in strength over that measured at 28 days, and this is probably due to ongoing hydration. The overall effect of fibres on the residual strength was masked by the increases in strength. It is also possible that an error is introduced by comparing 28 day and residual strength data from different batches. Thus, small changes in strength are probably negligible.

The measurement of ultrasonic pulse velocity was unable to distinguish the degree of cracking in the grouts as indicated in Tables 17 and 18. This is because the hairline cracks did not cause a significant increase in transit time for ultrasonic pulses. Addition of fibres did not result in a significant change in initial pulse velocity of specimens

3.4.2 Plain and Fibre Reinforced Soil Cements

The residual strengths and ultrasonic pulse velocities of soil cements after 12 wet-dry cycles are given in Table 19. The temperature at which the drying cycle was performed is indicated.

Table 19. Residual Strength and Ultrasonic Pulse Velocity of Plain Soil Cements After Wet-Dry Cycles

Mix	Temp (°C)	Residual Strength (MPa)		% Change	Initial UPV (km/s)		Residual UPV (km/s)		% Change
		Mean	SD		Mean	SD	Mean	SD	
47S1	71	24.5	4.2	-25.5	-	-	-	-	-
47S2	71	13.5	1.7	-46.6	-	-	-	-	-
47S3	71	11.9	0.1	-6.3	-	-	-	-	-
47S4	71	7.3	0.6	-8.7	-	-	-	-	-
47S5	71	6.1	0.2	-6.1	-	-	-	-	-
47S1	25	26.6	3.1	-19.1	3.52	0.05	3.36	0.09	-4.5
47S2	25	16.2	3.0	-36.0	3.12	0.04	2.72	0.15	-12.8
47S3	25	11.7	0.7	-7.9	2.82	0.03	2.64	0.13	-6.4
47S4	25	9.0	0.8	+12.5	2.74	0.09	2.38	0.17	-13.1
47S5	25	6.0	1.1	-7.7	2.60	0.00	2.33	0.03	-10.4

For soil cements, the width of surface cracks increased with increasing soil content. Mixes 47S1 and 47S2 showed greater extent of surface cracking than the soil cements with higher s/c. This is probably due to higher cement content. Cracking was more extensive when drying was performed at 71°C. Healing of cracks in a manner similar to that which occurred for the grouts was evident for soil cements with s/c = 1 and 2. However, at higher soil contents cracks did not heal. This suggests that under repeated wet-dry cycles cracks that form in soil cements with low soil contents may seal, whereas cracks in materials with high soil contents will remain open and possibly result in higher permeability.

Table 20 shows the residual compressive strength and ultrasonic pulse velocity of the fibre reinforced soil cements after 12 wet-dry cycles.

Table 20. Residual Compressive Strength and Ultrasonic Pulse Velocity for Fibre Reinforced Soil Cements After Wet-Dry Cycles

Mix	Residual Strength (MPa)		% Change	Initial UPV (km/s)		Residual UPV (km/s)		% Change
	Mean	SD		Mean	SD	Mean	SD	
47S1 0.1F	29.5	2.7	+1.0	3.46	0.04	3.29	0.01	-4.9
47S1 0.2F	34.6	4.1	+19.3	3.45	0.07	3.29	0.01	-4.6
47S1 0.2MF	20.5	3.9	-25.2	3.50	0.03	3.46	0.04	-1.1
47S2 0.2MF	14.4	0.5	-38.5	3.07	0.04	2.92	0.01	-4.9

The extent of cracking was possibly reduced by addition of fibres, but this was difficult to quantify. The plain version of 47S1 showed a significant decrease in compressive strength at the 5% level after 12 wet-dry cycles at 25°C. The residual compressive strengths of the fibrillated fibre reinforced soil cements were somewhat anomalous in that strength was greater than that measured after 28 days wet curing despite the presence of cracks. The monofilament fibre reinforced version of 47S1 showed a greater decrease in residual compressive strength than either the plain or fibrillated fibre reinforced mixes. Similarly, monofilament fibres did not improve resistance to loss of strength for 47S2.

The value of ultrasonic pulse velocity measured prior to the wet-dry cycles corresponded with compressive strength. As soil/cement ratio increased, the ultrasonic pulse velocity decreased. Addition of fibres did not result in a significant change in initial pulse velocity of specimens. For all soil cements, the ultrasonic pulse velocity decreased after the wet-dry cycles reflecting an increase in transit time due to presence of cracks. The percentage change in velocity did not correlate with the change in compressive strength. This is possibly because of

the different effect of crack orientation on strength and on velocity. Residual compressive strength is more likely to be influenced by longitudinal and inclined cracks, whereas changes ultrasonic pulse velocity would be more readily detected if cracks transverse to the specimen's longitudinal axis are present since cracks perpendicular to the direction of ultrasonic pulses result in a decrease in velocity. The ultrasonic pulse velocity data suggested that mixes with soil/cement ratios of 2,3 and 4 had the greatest degree of cracking. This is in contrast with the observed relationship between visible surface cracks and s/c, indicating that surface cracking may not give a true measure of deterioration caused by wet-dry cycling.

The wet-dry cycling tests can be considered as an aggressive acceleration of the likely exposure conditions for the barriers at the CWL. Therefore, cracking in the test specimens does not necessarily imply that the barriers will also crack. The rainfall at the site is low and the barriers are protected from rapid drying by surrounding soil. Thus, soil with low moisture content gives better protection than direct exposure to air.

The tendency of the grouts and soil cements to crack when exposed to high temperatures suggests that caps made from these materials must be protected with soil and vegetation as is used with clay caps. A fibre reinforced concrete or fibre reinforced shotcrete liner may prove superior to grout or soil cement caps since improved toughness, shrinkage resistance and durability can be expected. Pozzolan additives could be used with concrete or shotcrete.

3.5 Restrained Shrinkage Tests

3.5.1 Plain and Fibre Reinforced Grouts

The times to failure of restrained shrinkage rings made from plain and fibre reinforced grouts are presented in Tables 21 and 22. Figure 13 compares the crack width versus time for plain and fibre reinforced versions of Mix 70.

Table 21. Time to Failure for Plain Grout Shrinkage Rings.

Mix	Time to Failure (days)
9	26
68	11
70	9

Figure 13. Crack Width versus Time After Failure for Plain and Fibre Reinforced Grouts.

Table 22. Time to Failure for Fibre Reinforced Grout Shrinkage Rings.

Mix	Time to Failure (days)
9 0.2F	9
68 0.2F	21
70 0.1F	14, 27
70 0.2F	10
70 0.1MF	15
70 0.2MF	11
70 0.2NF	13

The results in Tables 21 and 22 suggest that the time to appearance of the first crack is highly variable for nominally identical specimens and that there is no definite increase in failure time due to addition of fibres. All specimens showed one radial crack at failure, except for Mix 68 which had two radial cracks. The crack width at failure was typically 100 to 150 micron for unreinforced grouts and was approximately 100 micron when fibres were present. Crack widths increased with time when the shrinkage rings were removed from soil and left to dry and shrink in air as depicted in Figure 13. Reduced crack widths would be expected if the specimens were maintained in soil instead of air.

An important potential benefit of fibres is the reduction of plastic and drying shrinkage cracking and the reduction of any crack widths. This would be due to toughening and increased tensile strain capacity. Although toughness was not measured, the restrained shrinkage test can be used to compare the restrained shrinkage cracking resistance of the grouts.

Fibres did not prevent drying shrinkage cracking, but did reduce the width of the shrinkage crack, as illustrated in Figure 13. At a given time after failure the crack width of the fibre reinforced grout was less than the companion plain grout due to fibre bridging. It was also evident that the crack width at a given time decreased as the volume fraction of fibres increased. The final crack widths of the polypropylene monofilament, nylon monofilament and 0.1% fibrillated fibre reinforced grouts were similar.

The reduction of crack width in shrinkage rings by fibres has also been demonstrated for carbon fibres in cement composites (Soroushian et. al., 1993) and for cellulose and polypropylene fibres in concrete (Sarigaphuti et. al., 1993). Al-Tayyib, et. al. (1988) observed that addition of 0.2% 20 mm fibrillated polypropylene fibres eliminated plastic shrinkage cracking in concrete slabs.

3.5.2 Plain and Fibre Reinforced Soil Cements

The times to failure of restrained shrinkage rings made from plain and fibre reinforced soil cements are presented in Tables 23 and 24. Figures 14 and 15 show the effect of fibre reinforcement on crack width versus time for $s/c = 1$ and 2.

Table 23. Time to Failure for Plain Soil Cement Shrinkage Rings.

Mix	Time to Failure (days)
47S1	7
47S2	8,8

Table 24. Time to Failure for Fibre Reinforced Soil Cement Shrinkage Rings.

Mix	Time to Failure (days)
47S1 0.2F	6
47S1 0.2MF	22
47S1 0.2NF	8
47S2 0.2MF	13
47S2 0.2NF	12

Soil cements have greater crack widths than grouts and increasing the soil content increases the crack width. Fibre reinforcement reduces crack width at a given time after failure. The final crack widths for reinforced 47S1 were similar for fibrillated and monofilament fibres, and the rate of crack growth was lower for the monofilament materials. The fact that the polypropylene monofilament fibre reinforced specimen failed at later age than the fibrillated fibre specimen may have resulted in reduced crack width due to a longer curing period. The stepwise increase in crack width for the fibre reinforced soil cements was due to successive pull out of fibres. Plain specimens tended to reach a steady crack width in a shorter time.

The degree of crack width reduction by fibres is greater for the material with higher soil content. As was the case for 47S1, the polypropylene and nylon fibre reinforced versions of 47S2 had similar final crack widths.

The formation of cracks under restrained shrinkage conditions of the tests does not necessarily imply that the grout or soil cements will fail in service since the stresses developed in the rings may be higher than those experienced by the barriers. In practice, the barriers will be subjected to internal restraint arising from thermal gradients and drying shrinkage associated with moisture variations from the surface to the interior. External restraint will arise from the surrounding soil and any adjacent barriers that have set. Self-desiccation will occur over an

Figure 14. Effect of Fibres on Crack Width versus Time After Failure for Soil/Cement Ratio = 1.

Figure 15. Effect of Fibres on Crack Width versus Time After Failure for Soil/Cement Ratio = 2.

extended period. Susceptibility to early thermal cracking could be reduced by use of low heat or blended cement, reducing cement content as much as possible without detriment to the other properties and minimization of the barrier thickness. Restraint of the barriers may be lowered by inclusion of joints, thereby reducing the risk of cracking.

3.6 Linear Shrinkage Tests

3.6.1 Plain and Fibre Reinforced Grouts

The early change in length of grout specimens is given in Table 25. The total plastic shrinkage was measured at the point where setting commenced which was typically 6 to 8 hours after casting. This value was often positive, and hence, actually an expansion since the grouts typically expanded prior to shrinking after setting. The results for fibre reinforced grouts are presented in Table 26.

Table 25. Results of Linear Shrinkage Tests on Grouts.

Mix	Plastic length change (%)	24 hour shrinkage (%)
9	+0.012	-0.145
60	-3×10^{-3}	-0.163
68	+0.015	-0.146
70	+0.014	-0.123

Table 26. Results of Linear Shrinkage Tests on Fibre Reinforced Grouts.

Mix	Plastic Shrinkage (%)	24 hour Shrinkage (%)
9 0.1F	-1×10^{-3}	-0.090
9 0.2F	-0.015	-0.095
9 0.5F	-3×10^{-3}	-0.085
68 0.1F	-0.01	-0.171
68 0.2F	$+5 \times 10^{-3}$	-0.237

The results of the linear shrinkage tests on plain grouts given in Table 25 demonstrate that shrinkage at 24 hours could be reduced by increasing sand content. The 24 hour linear shrinkage of Mix 9 is similar to that of Mix 68 despite the higher volume fraction of sand. The higher w/c of Mix 9 probably counteracts the aggregate volume. Comparison between Tables 25 and 26 shows a slight decrease in 24 hour shrinkage for Mix 9 and an increase in shrinkage for Mix 68 with increasing fibre content. There was no correlation between fibre content and plastic shrinkage. The

results can be compared with those of Sanjuan et. al. (1990) in which polypropylene fibres at 0.1 and 0.2% were found to reduce plastic shrinkage of cement-sand mortars provided that w/c was less than 0.5. At higher w/c, fibres could not compensate for increased shrinkage.

Addition of an expansive agent such as calcium sulphate or calcium sulphotoaluminate to reduce shrinkage was considered. Expansion is achieved by formation of ettringite which has a greater volume than the reactants from which it is formed. The expansive reaction continues after the plastic stage thereby causing increased porosity and microcracking. This in turn leads to greater permeability. Therefore, expansive additives were not studied and use of Type K (expansive) cement is not recommended. It has been reported that silica fume can reduce the expansive reaction time and therefore reduce the expansion-induced damage (Lobo and Cohen, 1992). Further work to determine the properties and durability of a silica fume modified expansive cement grout would be necessary before it is considered for subsurface barriers.

3.6.2 Soil Cements

Table 27. Results of Linear Shrinkage Tests on Soil Cements

Mix	Plastic Shrinkage (%)	24 hour Shrinkage (%)
47S1	-0.024	-0.098
47S2	+0.016	+5x10 ⁻³
47S3	+2x10 ⁻³	-0.016
47S4	+5x10 ⁻³	-0.050
47S5	-0.025	-0.072

Linear shrinkage tests on soil cements presented in Table 27 indicated that plastic and 24 hour shrinkage decreased from s/c = 1 to 2 and then increased as s/c increased to 5. The high shrinkage of 47S1 is due to the high cement content. Linear shrinkage over the test period was lower for soil cements than grouts. This is possibly due to reaction between any gypsum in the soil and tricalcium aluminate to form ettringite. If the toughness of the soil cements is lower than that for the grouts, resistance to shrinkage induced cracking will be reduced regardless of the amount linear shrinkage.

3.7 Freeze-Thaw Durability

The residual cube strengths after freeze-thaw cycles for plain and fibre reinforced versions of Mix 9 are given in Table 28 and compared with the cube strength of control specimens.

Table 28. Residual Cube Strengths of Plain and Fibre Reinforced Grouts After Freeze-Thaw Cycles.

Mix	Control Strength (MPa)		Residual Strength (MPa)	
	Mean	SD	Mean	SD
9	37.4	3.8	30.3	3.0
9 0.2F	39.1	4.1	34.7	3.5

The freeze-thaw performance of the plain and fibre reinforced Mix 9 grouts was compared using a two-tailed t-test of the residual cube compressive strengths. For the control beams, the mean strengths of the plain and fibre reinforced grouts were not significantly different at the 5% level. For the beams exposed to freeze-thaw cycles, the mean residual strengths for the plain and fibre reinforced grouts were also not significantly different at the 5% level. Therefore, it appears that addition of 0.2% volume fraction of fibres did not significantly improve the residual cube compressive strength. This result also demonstrates the importance of conducting statistical analysis of the data, since comparison of the percentage loss of strength alone would suggest that the fibre reinforced grout (11% strength loss) performed better than the plain grout (19% strength loss).

3.8 Microstructure

3.8.1 Plain and Fibre Reinforced Grouts

The microstructure of grouts and soil cements is shown in Figures 16 to 34. The low magnification bright field optical micrographs in Figures 16 to 20 show the relative particle sizes and spacing between particles for Grouts 9, 68 and 70 and soil cements 47S1 and 47S2. Sand or soil particles appear white under bright field conditions. The micrographs show that Grouts 9 and 70 have a uniform distribution of sand grains throughout the cement paste matrix. For Mix 68 larger areas of the cement paste matrix are free from sand, and this could lead to reduced shrinkage control compared for grouts that contain finer sand provided that the water/cement ratio remains constant. The soil particles in Figures 19 and 20 are relatively fine and the effect of increasing soil content on the microstructure is evident.

Scanning electron micrographs of the plain and fibre reinforced grouts at X1,000 and 10,000 magnification are given in Figures 21 to 28. The micrographs depict the size of capillary pores and the nature of the microstructure at the interface between cement paste and sand and between cement paste and polypropylene fibres. Phases were identified using EDX.

Figures 29 to 34 show the scanning electron micrographs of the soil cements. The microstructure of the soil cements has many different features compared with the grouts such as presence of SiO₂ crystals that appear to have precipitated after mixing and

Figure 16. Bright Field Image of Mix 9 at x32. (Sand grains appear white).

Figure 17. Bright Field Image of Mix 68 at x32.

Figure 18. Bright Field Image of Mix 70 at x32.

Figure 19. Bright Field Image of Mix 47S1 at x32.

Figure 20. Bright Field Image of Mix 47S2 at x32.

Figure 21. Micrograph of Sand/Calcium Silicate Hydrate Interface in Mix 68 at x1,000. Sand indicated by "S".

Figure 22. Micrograph of Mix 70 at x 1,000 Indicating Capillary Pores in Calcium Silicate Hydrate and Interface at Sand Grain.

Figure 23. Sand Grains, Calcium Silicate Hydrate and Capillary Pores in Mix 70 at x 1,000.

Figure 24. Sand/Calcium Silicate Hydrate Interface in Mix 68 at x10,000.

Figure 25. Capillary Pores in Gel in Mix 70 at x10,000.

Figure 26. Capillary Pores in Gel in Mix 70 at x10,000.

Figure 27. Polypropylene Fibre/Calcium Silicate Hydrate Interface in Mix 9 0.2F at x1,000. Fibre indicated by "F".

Figure 28. Porous Region of Polypropylene Fibre/Calcium Silicate Hydrate Interface in Mix 9 0.2F at x10,000. White particle in centre is calcium aluminate hydrate.

Figure 29. Micrograph of Soil Cement (47S1) at x1,000 Illustrating Precipitated Cubic Crystals of SiO_2 on Surface of Cement Paste.

Figure 30. Cement Paste and Capillary Pores with Ettringite Needles in 47S1 at x1,000.

Figure 31. Interface Between Soil Grain (S) and Calcium Silicate Hydrate in 47S1 at x10,000.

Figure 32. Calcium Silicate Hydrate Gel and Cubic SiO_2 Crystals in 47S1 at x10,000.

Figure 33. Ettringite Needles in Capillary Pore in 47S1 at x10,000.

Figure 34. Ettringite Needles in Capillary Pore, Calcium Silicate Hydrate Gel and Cubic SiO_2 Crystals in 47S2 at x10,000.

presence of ettringite needles in capillary pores. The morphology of the calcium silicate hydrate phase also differs and appears more plate-like. The features are discussed further in Section 3.8.2.

The microstructure of the grouts was dominated by amorphous type calcium silicate hydrate gel (CSH). Other phases detected include $\text{Ca}(\text{OH})_2$, monosulphate aluminoferrite and calcium aluminate hydrate. The EDX trace suggested the possibility of Al substitution for Ca in a small proportion of the CSH and this is probably due to reaction with bentonite (Komarneni et. al., 1982). The calcium silicate hydrate gel contained numerous capillary pores typically 1 to 10 micron in diameter. Submicron gel pores were also observed. Some microcracks were observed and it was uncertain as to whether these were an artefact of specimen preparation.

$\text{Ca}(\text{OH})_2$ hexagonal crystals were observed in some capillary pores and air voids in a manner similar to that reported previously (Barker and Barnes, 1984). Increased concentration of $\text{Ca}(\text{OH})_2$ and preferred orientation of these crystals at sand grains was not observed in either secondary or back scattered electron images, which does not necessarily imply that they did not exist. This appears to be in contrast with other work that has shown a film structure of $\text{Ca}(\text{OH})_2$ heterogeneously nucleated and growing around aggregate particles, surrounded by CSH (Barnes et. al., 1979; Diamond, 1987; Breton et. al., 1993).

It is possible that a $\text{Ca}(\text{OH})_2$ layer around sand grains was obscured by the gel phase. In addition, there exists a possibility that a cation exchange reaction between bentonite and $\text{Ca}(\text{OH})_2$ occurs (Milestone et. al., 1987) that results in a decrease in the presence of $\text{Ca}(\text{OH})_2$ at sand interfaces. Since the majority of reported microstructure studies are on pastes, mortars and concretes that do not contain bentonite and usually are not superplasticized, the findings of such studies may not be transferable to grouts if bentonite and superplasticizers are important influences on the bulk and interfacial microstructure. Comparison between the microstructures of grouts with and without bentonite and superplasticizer would be necessary to distinguish the role of these additives.

Pores that result in permeability must form a continuous network to transport water through the material and it is not possible to make definitive conclusions about the effect of mix proportions on the microstructure features that control permeability based on a two dimensional image. However, some general and qualitative observations can be stated. Both fine and coarse pores were concentrated in the cement paste matrix rather than preferentially located at the interface of sand grains. Assuming that at least some of these pores form a continuous path, the tendency for the majority of pores to exist in the cement phase implies that permeability is controlled by the cement paste microstructure rather than the microstructure of the sand/paste interface. This could explain why the increase in volume fraction and surface area of sand grains in Mix 70 compared to Mix 68 did not increase permeability.

Mix 68 appeared to have a greater number and greater size of capillary pores than Mixes 9 and 70, despite the lower w/c ratio. A greater number of round, isolated air voids were present in this grout, although such voids do not result in permeation of water. No distinct differences in the pore structure for Mix 9 with the highest w/c were apparent at high or low magnifications. In addition, the effect of curing on the microstructure was not obvious. Differences may become more apparent after longer curing times. Image analysis techniques could be used to give quantitative information about microstructural features and overcome subjectivity.

The interfacial features of the polypropylene fibres were similar to those for the sand grains. Higher concentrations of Ca(OH)_2 were not observed on the fibre surfaces. The CSH gel was relatively dense around the fibres, with no definite increased occurrence of coarse or fine pores at the interface. The observations correlate with the conclusions from the permeability measurements that low volume fractions of fibres did not result in significantly increased permeability.

3.8.2 Soil Cements

Examination of the soil cement microstructure revealed CSH gel around sand particles from the soil. Other phases detected included calcium aluminate and calcium aluminosilicate. The calcium aluminosilicate is possibly attributable to ion-exchanged bentonite or soil minerals. At high magnification the CSH gel appeared to have a more plate-like structure than was observed for the grouts. Cubic SiO_2 crystals approximately 1 micron in length appeared to have precipitated in-situ as shown in Figures 29, 30, 32 and 34. Capillary pores 1 to 10 micron in diameter and submicron gel pores were evident.

The capillary pores of the soil cements frequently displayed ingrowing Ca(OH)_2 crystals and ettringite needles of submicron width. Ettringite is probably the result of reaction between gypsum in the soil or cement and tricalcium aluminate. This observation concurs with the hypothesis developed from results of the linear shrinkage tests. The preferential growth of ettringite into pores suggests that the risk of cracking due to expansion of the soil cement is reduced since there is ample space for further growth without detriment to the surrounding paste. The presence of ettringite needles and Ca(OH)_2 in the capillary pores may restrict flow of fluid, thereby reducing permeability. Needles were not observed in grout pores. Ca(OH)_2 crystals were not apparent at the interface between soil particles and cement paste and this is possibly due to cation exchange between bentonite and soil minerals and Ca(OH)_2 . Magnesium was evident in some EDX traces and this is probably derived from the soil.

As was the case for the grouts, the differences in microstructure of the soil cements for different curing conditions were not distinct.

3.8.3 Microstructure of Leached Specimens

The leached surfaces of the grouts and soil cements are shown in Figures 35 to 44. The surfaces were visibly etched after leaching due to dissolution of cement paste and sand or soil particles were unattacked. In Figure 34 the relatively clean appearance of sand grains in Mix 70 is evident. Most of the cement paste that covered the grains has been removed and localized spots of CSH and other hydration phases remain. Evidence of $\text{Ca}(\text{OH})_2$ crystals was not found. The EDX trace revealed that the CSH phase between sand grains was depleted in Ca. This indicates that the CSH gel was partially dissolved by deionized water, in addition to attack of $\text{Ca}(\text{OH})_2$. Reduction of the Ca/Si ratio in CSH due to corrosion by deionized water has also been reported by Adenot and Buil (1992). CaCO_3 crystals were detected by the EDX. The interface between cement paste and sand frequently showed loss of paste as illustrated in Figures 35 and 36. The resultant increase in porosity at the interface explains the measured increase in permeability.

The leached surface of the silica fume modified grout differed significantly from the plain grout. The surface was covered with a reaction layer of hexagonal $\text{Ca}(\text{OH})_2$ stacked plate crystals. A typical example of the crystals is given in Figure 38. Few areas of cement paste or sand grains were visible due to the extensive presence of $\text{Ca}(\text{OH})_2$. The areas of paste that were evident were comprised mainly of CSH and calcium aluminosilicate hydrate. The Ca peaks of these products were stronger than those for Mix 70. There was more cement paste remaining on the sand grains for the silica fume modified grout. An example of this is shown in Figure 37. Comparison between Figures 35 and 37 indicates the reduced leaching around sand grains when silica fume is added. CaCO_3 crystals were also detected.

The presence of $\text{Ca}(\text{OH})_2$ and CaCO_3 crystals on the surface of silica fume modified grout leached statically in distilled deionized water has been observed by Onofrei et. al. (1992). The reaction product layer contained more CaCO_3 than Mix 67. The production of $\text{Ca}(\text{OH})_2$ on the leached surface was explained by Onofrei et. al. (1992) as the result of dissolution of Ca^{2+} in the initial stages of leaching which then precipitates on the grout surface in a more stable form. The dissolution rate of Ca^{2+} decreased with time and this was attributed to the presence of the surface layer.

It is apparent that sufficient concentrations of Ca^{2+} and OH^- were reached in the Mix 67 leachate to exceed the solubility limit and precipitate $\text{Ca}(\text{OH})_2$. Once the reaction layer of $\text{Ca}(\text{OH})_2$ formed, the grout was protected to some degree from further leaching. For Mix 70, which did not have a protective reaction layer, leaching continued with the result that the post-leaching permeability was significantly higher than that for Mix 67.

The scatter in values of post-leaching permeability can be explained by the inhomogeneity observed in the attacked surface of Mix 70 and in the layer of $\text{Ca}(\text{OH})_2$ on Mix 67. The $\text{Ca}(\text{OH})_2$ layer may

Figure 35. Leached Surface of Mix 70 at x1,000 Indicating Attack of Calcium Silicate Hydrate Gel Around Sand Grains.

Figure 36. Pit at Sand/Calcium Silicate Hydrate Interface in Mix 70 at x1,000 Caused by Leaching.

Figure 37. Interfacial Attack and Exposure of Sand in Silica Fume Modified Grout (Mix 67) at x1,000. Degree of attack less severe than Mix 70.

Figure 38. Calcium Hydroxide Crystals on Leached Surface of Mix 67 at x1,000.

Figure 39. Calcium Hydroxide Crystals on Leached Surface of 47S1 at x100.

Figure 40. Calcium Hydroxide Crystals on Leached Surface of 47S1 at x1,000. Note irregular perimeters.

Figure 41. Calcium Hydroxide Crystals on Leached Surface of 47S2 at x100. Surface layer more porous than for 47S1.

Figure 42. Surface Layer of Calcium Hydroxide Crystals on Leached Surface of 47S2 at x500.

Figure 43. Hexagonal Stacked Plate Morphology of $\text{Ca}(\text{OH})_2$ Crystals on Leached Surface of 47S2 at x1,000.

Figure 44. Hexagonal Stacked Plate Morphology of Ca(OH)_2 Crystals on Leached Surface of 47S2 at $\times 1,000$.

also act to reduce permeability of the specimen and the porosity of the layer may be an important factor.

The leached soil cements also exhibited a reaction layer of Ca(OH)_2 . Micrographs of the specimens are shown in Figures 39 to 44. The Ca(OH)_2 crystals tended to obscure the original surface and only isolated areas of CSH, calcium aluminate and calcium aluminosilicate were visible. Figure 39 shows the Ca(OH)_2 crystals growing on the CSH surface of 47S1 at low magnification. The crystals are shown at higher magnification in Figure 37. The edges of the crystals are irregular, possibly indicating impurities or poisoning. At a soil/cement ratio of 2, Ca(OH)_2 crystals were also present on the leached surface as indicated in Figures 41 and 42. The stacked plate morphology of the Ca(OH)_2 crystals is clearly evident in Figures 43 and 44. The surface of 47S2 was less extensively covered with crystals than 47S1 and the reaction layer and visible CSH phase showed greater porosity. Ettringite was not visible in the few surface capillary pores that were not obscured. Smaller crystals of calcium aluminosilicate were often located on Ca(OH)_2 crystals.

3.9 Small Scale Field Tests

Figure 45 shows a typical excavation into which grout or soil cements were placed. Filling of the excavation with grout is shown in Figures 46 and 47 indicating the pumpability of the grout. The grout mixer/pump is illustrated in Figure 48.

Grout Mix 70 was easily pumped and could possibly undergo reduction of water/cement ratio without detriment to pumpability. Fibre reinforced grouts were pumpable provided that the fibres were uniformly distributed in the mix. Any clumps of fibres resulted in blockage of the pump at the ball valves. Fewer problems with pumping of the fibre reinforced grouts were encountered when the volume fraction of fibres was 0.1% compared with 0.2%.

The soil cements were self levelling. The structure and properties of the soil cements prepared in the mortar mixer are expected to differ from that produced by jet grouting or soil mixing.

Cores taken from the cast barriers were free from cracks, excessive voids, or other defects. The strength of cylinders cast at the time of mixing and cured in water for 28 days is compared with the strength of core samples taken from the barriers at 4 months age in Table 29. The compressive strength of cast cylinders maintained in water for 4 months is shown for Mixes 70 and 47S2. The ultrasonic pulse velocity of the cores is given also. The cores and 4 month old cylinders had identical ultrasonic pulse velocities.

Figure 45. Excavation Used in Small Scale Field Trials.

Figure 46. Pumping Grout into Excavation.

Figure 47. Pumping Grout into Excavation.

Figure 48. Grout Mixer and Pump Used in Small Scale Field Trials.

Table 29. Compressive Strength and Ultrasonic Pulse Velocity of Test Barriers

Mix	28 Day Compressive Strength (MPa)		Core Compressive Strength (MPa)		4 Month Compressive Strength (MPa)		UPV (km/s)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
70	30.0	4.4	38.5	4.3	30.0	2.1	3.82	0.07
70 0.1F	31.8	3.9	40.9	5.2	-	-	3.90	0.05
70 0.2F	29.8	3.5	37.0	4.8	-	-	3.87	0.10
47S1	31.9	3.8	33.2	4.3	-	-	3.52	0.12
47S2	15.9	1.8	19.3	3.0	13.3	0.8	3.17	0.05

The compressive strengths of the barriers and the cylinders cast simultaneously were all in excess of that required. The 4 month old cores exhibited an increase in strength compared to the cylinders tested at 28 days. This indicates that hydration was ongoing under subsurface conditions. The increase in strength of the barriers observed in these tests may not necessarily be reproduced under the arid site conditions because of the lower rainfall and humidity. Cylinders maintained in water for 4 months did not increase in strength and had lower ultimate values than the barrier cores. This is possibly due to leaching of $\text{Ca}(\text{OH})_2$ from the cylinders since they were stored in tap water as opposed to saturated $\text{Ca}(\text{OH})_2$ solution. Standard deviations tended to be higher than those for laboratory prepared specimens. The ultrasonic pulse velocity values were relatively high and comparable to the results on 28 day wet cured cylinders given in Tables 17 - 19. The grout barriers showed an increase in UPV as compared with 28 day cylinders used in wet-dry cycling tests.

3.10 Permeation Grouting Tests

Laboratory scale tests of permeation with a microfine cement grout were unsuccessful, despite the finer particle size than Portland cement grout. The microfine cement grout actually performed somewhat worse than the Portland cement grout tested in FY 1992. Due to the very fine particle size of the microfine cement, a filter cake formed and effectively produced a lining between the grout injection tube and the soil, preventing further penetration. The degree of permeation of the microfine cement grout was negligible for the cylinders that ranged from loosely compacted soil to soil compressed to an overburden pressure of 0.4 MPa.

It is possible that the laboratory test was not an accurate simulation of field conditions and equipment. Therefore, specimens were prepared to simulate the injected soil that would be produced if permeation grouting was successful. Microfine cement grout was mixed with site soil at a ratio that assumed pores in the soil

would be fully penetrated. Some differences in the properties of a material produced in this manner compared with a grouted soil are expected.

Grout M1 was mixed with the soil to give a soil/cement ratio of 4.6. Additional mixing water was not added so that the water/cement ratio was the same as that for M1 ($w/c = 1$). The 28 day compressive strength of in-situ cured cylinders was 8.1 MPa $\pm$ 1.3 MPa. The permeability of the material was 1.0×10^{-10} cm/s for wet cured conditions and 1.5×10^{-10} cm/s for in-situ curing.

The inability of the microfine cement grout to penetrate the site soil in the laboratory tests can probably be explained in terms of the particle sizes of the soil and cement. A rule of thumb developed from field experience, termed the "groutability ratio", relates the particle size of the medium to be grouted to the particle size of the grout (e.g. Weaver and Graf, 1993).

The groutability ratio, R_g , is defined as follows:

$$R_g = D_{15}/D_{85}$$

where D_{15} = the 15% passing size of the soil to be grouted (microns)

D_{85} = the 85% passing size of the grout particles (microns)

R_g should be greater than 24 for consistent permeation, and is a guideline only. The site soil typically has a D_{15} value of 70 to 90 microns based on the CWL samples tested by Daniel B. Stephens and Associates. The soil used in the permeation grouting tests at BNL had a D_{15} value of 95 microns. The microfine cement had a D_{85} value of 3 to 4 microns. This gives an R_g value of 24 to 32. Hence, based on the groutability ratio, it is somewhat borderline as to whether the grout would completely penetrate the tested soil. Therefore, it is concluded that the soil was probably too fine to be permeated by the microfine cement grout. For coarser soil permeation may be possible.

The strength and permeability of the specimens prepared to simulate successful permeation of soil with microfine cement grout were adequate for the landfill. The permeability was lower than the soil cements prepared using Portland cement with similar soil/cement ratios due to lower w/c .

4.0 IN-SITU STABILIZATION

As discussed earlier, effort was concentrated on the barrier aspect of the program since effective stabilization of trivalent chromium contaminated soil mixed with Portland cement grout was demonstrated in FY 1992 and alternative technologies exist. If successful permeation grouting using microfine cement grout is demonstrated at the site, it may be feasible to use this grout for stabilization of Cr^{3+} . This will firstly require confirmation that the microfine cement can effectively stabilize Cr^{3+} through precipitation of $Cr(OH)_3$ since the chemistry of microfine cement differs from Portland cement. It is also possible that

stabilization of Cr^{3+} using a lime solution may be more cost effective and practical than permeation with microfine cement grout.

An alternative may be to mix a blast furnace slag cement with the untreated contaminated soil since this may simultaneously reduce Cr^{6+} and immobilize the resultant Cr^{3+} (Macphee and Glasser, 1993; Langton, 1988; Langton and Wong, 1991). This is probably due to the presence of Fe^{2+} and S^{2-} ions in the blast furnace slag.

5.0 COSTS

A cost analysis of barrier and cap materials was conducted. The costs were compared with the measured properties in order to determine which products were the most efficient with respect to economics and performance. Only the material costs were investigated and other expenses such as freight, labor and placement were not considered. The bulk material costs given by manufacturers are given in Table 30 and should be regarded as approximate only. If Type IV or V cement is used, material costs will increase.

Table 30. Estimated Material Costs

Material	Cost per Kilogram (\$/kg)
Type I Portland Cement	0.11
Sand	0.07
Water	0.00
Bentonite	0.07
Silica Fume	0.55
Superplasticizer	1.70
Fibres (fibrillated or mono.)	5.00

Using the relevant densities and mix proportions, the cost per cubic metre of barrier or cap was calculated. The estimated material costs of grouts and soil cements are given in Table 31.

The "value for money" of the various materials studied can be assessed by comparing the material cost against performance parameters such as permeability.

For materials with lower permeability the barrier thickness can be reduced to give the same performance. This in turn leads to cost savings. As an example, a vertical barrier that has a permeability coefficient of 10^{-7} cm/s must be 1000 times thicker than a barrier with a permeability coefficient of 10^{-10} cm/s for the same level of containment. Similarly, the required thickness of caps can be reduced through use of a low permeability, high strength material. The actual thickness used in practice will also be controlled by the placement method. For example, the minimum

Table 31. Estimated Material Costs of Selected Grouts and Soil Cements

Mix	Cost per cubic metre (\$/m ³)
67	218
70	182
70 0.1F	187
70 0.2F	192
70 0.2MF	192
47S1	128
47S1 0.2F	138
47S1 0.2MF	138
47S2	89
47S2 0.2MF	99
47S3	61

thickness of a column shaped vertical barrier produced by jet grouting would be approximately 0.6 m and the minimum thickness of a soil mixed barrier would be approximately 1 m. A panel shaped barrier produced by jet grouting or soil sawing could possibly have a reduced thickness. Decreasing the barrier thickness also has the advantage of reducing the risk of cracking induced by thermal stresses.

In order to quantify the possible cost benefits of using a low permeability material, the required thickness of different grouts and soil cements for equivalent flow rate was compared with an arbitrary standard of 0.6 m thick material with a mean in-situ cured permeability coefficient of 1.0×10^{-10} cm/s. The required thickness to meet the equivalent flow rate criteria was then used to calculate the cost of a 1 m² area of material using the data given in Table 31. The results of this comparison for selected materials are given in Table 32.

Table 32. Estimated Costs for Equivalent Flow Rate

Mix	Thickness (m)	Cost per Square Metre (\$/m ²)
70	0.40	73
70 0.2F	0.39	75
47S1	0.72	92
47S2	2.34	208
47S3	57	3477

The results in Table 32 compare the cost effectiveness of the different materials based on measured values of in-situ cured permeability. It is seen that an unrealistic thickness of 47S3 is required for a flow rate equivalent to the others. This is because of the steep increase in in-situ cured permeability that occurs when soil/cement ratio passes 2. The permeabilities achieved in the field are expected to differ somewhat from the laboratory values. However, the rankings in Table 32 should remain similar. The analysis suggests that a sanded grout gives more value for money than the soil cements. This conclusion may differ if the costs of placement are included in the calculations. The material costs of cement based grouts and soil cements may be insignificant compared with the cost of placement, in which case the best material should be used.

The above calculations of cost per square meter for equivalent flow rate rank the materials for permeability performance but should not be the only deciding factor. Durability and safety are of greater importance than material costs. In addition, if a design flow rate higher than that for a 0.6 m thick wall with a permeability coefficient of 10^{-10} cm/s is acceptable then it may be cheaper to use a material with a higher permeability that has a lower unit cost at the same thickness.

6.0 RECOMMENDATIONS

The choice of barrier or cap material depends on the properties that can be achieved in-situ. Consequently, the placement technique must be considered in addition to the material behavior. The primary concerns are production of durable, low permeability barriers and caps in a cost effective manner and verification of material integrity. Thus, a material that exhibits excellent attributes in the laboratory is not useful if it cannot be placed in-situ to form a defect free barrier or cap that meets durability, permeability and mechanical criteria.

For caps, it is apparent that soil cements produced in-situ by soil mixing may be adequate if the exposed surface can be protected from excessive drying and from high temperatures. Soil cement permeabilities lower than the values of 10^{-9} to 10^{-6} cm/s typical for compacted soil and clay liners (Devinny et. al., 1990) can be achieved. Use of a superplasticized neat cement grout such as Mix 47 is necessary.

Fibre reinforcement would improve the performance of the caps provided that the fibres can be mixed satisfactorily into the matrix. Monofilament fibre reinforced parent grouts have improved mixing and pumpability compared with fibrillated fibres. However, monofilament fibres tend to reduce resistance to loss of strength due to wetting and drying and increase permeability. Fibrillated fibres can only be used when the soil/cement ratio is low so that the fibres can be uniformly mixed in the parent grout and pumped at the volume fraction required for the soil cement. If the fibrillated fibres could be mechanically mixed into the surface soil prior to mixing the grout with the soil, it may be possible to produce a fibrillated fibre reinforced soil cement. The

practicality of using fibres in field scale equipment requires verification.

Since surface caps can be wet cured, a higher proportion of soil can be incorporated in the soil cement without loss of permeability. However, increasing the soil content reduces the long term durability and shrinkage cracking resistance. A soil/cement ratio less than 4 would be recommended, with a value of 2 favored and fibre reinforcement preferred.

It is necessary to use isolation or construction joints in a soil cement cap to control drying shrinkage and thermal cracking. The joints should be sealed to ensure low permeability. The risk of thermal cracking of a large mass of soil cement could be reduced by using Type IV or Type V cement which have lower heats of hydration than ordinary Portland (Type I) cement. Addition of pozzolans such as blast furnace slag may also reduce heat of hydration and provide sulphate resistance. Although the properties of soil cements produced from Type IV or Type V cement were not measured, significant differences in mechanical and physical properties are not expected. Grout produced from these cements may require minor re-formulation to ensure suitable viscosity and pumpability.

Alternatives to a soil cement cap include properly designed fibre (steel or polymer) reinforced concrete or fibre reinforced shotcrete. These materials could be modified with silica fume or fly ash.

The choice of subsurface barrier material will depend on the placement technique. Preferably, the combination of material and technique that will give the best overall performance should be selected.

Permeation grouting with microfine cement requires successful field demonstration at the site before consideration. Some reservations remain even if permeation is successful. This is because the suspension grout will take the path of least resistance and permeation of coarse soil will occur in preference to a less coarse soil. Blockage of pores in soils by cement particles is also possible. Therefore, it will be difficult to control the permeation process and a inhomogeneous barrier may result. In addition, extensive verification testing will be necessary since it cannot be guaranteed that the grout penetrated where intended. A further problem that may be encountered is repair of areas that are found to be insufficiently grouted.

It is suggested that jet grouting, soil mixing or soil sawing may be superior alternatives to permeation grouting for production of subsurface barriers at the CWL. For jet grouting by replacement, a grout based on the Mix 70 proportions is recommended. A low heat cement or partial replacement of cement with a low heat pozzolan such as blast furnace slag would improve resistance to thermal cracking. It may be possible to reduce the w/c from 0.5 to approximately 0.48 while maintaining pumpability. Addition of silica fume to improve leach resistance is probably not necessary for the expected site conditions. If use of silica fume

is deemed necessary, a mix that is self-levelling and has a low w/c would be required. Consideration to the reported increased risk of shrinkage (Sellekvold, 1992) and shrinkage cracking associated with silica fume (Struble et. al., 1992) should be given before using a silica fume modified grout for the landfill remediation.

Fibre reinforcement with fibrillated fibres at a volume fraction of 0.2% is desirable for crack control provided that the fibres can be mixed to give a uniform distribution. Despite the improved mixing and pumpability of monofilament fibres and reduction of restrained shrinkage crack widths, the increase in permeability makes these fibres unsuitable for grout reinforcement.

As was the case for soil cement caps, Type IV or Type V cement is recommended for large masses of grout. Joints to control shrinkage cracking are desirable if it can be ensured that the joints can be sealed and are not a potential source of leakage due to localized high permeability.

Since a grout barrier produced from Mix 70 is predicted to have low permeability, a low thickness can be used. In addition, a panel shape is preferred for vertical barriers since smaller thickness would be possible, thereby reducing risk of shrinkage cracking and reducing material costs.

It is imperative that further testing of site soils for soluble sulphates be performed before placing subsurface barriers. Initial tests performed by C. Stein at SNL indicated acceptably low sulphate levels in uncontaminated soil. Since grouts made from Type I cement are susceptible to sulphate attack the sulphate levels must be confirmed before the cement type can be specified. The possibility of the presence of sulphate producing bacteria in the soil should also be investigated. If excessive sulphates are found, Type II or Type V cement must be used for either grout or soil cement barriers.

Verification of barrier or cap integrity by non-destructive techniques is of prime importance and a plan for achieving this quality assurance must be developed before full scale implementation. The experimental results showed that ultrasonic pulse velocity can indicate compressive strength, but cannot consistently detect hairline cracks. Larger cracks and voids may be detectable with ultrasonic methods. Alternative techniques that require investigation include sonic logging and seismic tomography.

7.0 CONCLUSIONS

Cement based grouts can be used to produce low permeability, high strength and high durability subsurface barriers suitable for in-situ containment of buried chemical waste. Either a monolithic grout barrier or soil cement barrier appear feasible. A sanded grout is necessary for a grout barrier in order to reduce shrinkage and reduce the risk of shrinkage cracking. Use of a blend of sand grades can increase the volume fraction of sand, thereby reducing shrinkage. By adding a superplasticizer to the grout, a relatively low water/cement ratio can be achieved without reducing

pumpability. Addition of silica fume to sanded grouts increases thixotropy thereby making grouts more difficult to pump.

The optimum grout barrier formulation developed for jet grouting by replacement (Mix 70) was found to have a wet cured mean compressive strength of 35.8 MPa and an in-situ cured strength of 29.4 MPa. The flexural strength under in-situ curing conditions was 3.9 MPa. Permeability measured in a rigid wall permeameter was 4.0×10^{-11} cm/s for wet curing and 6.6×10^{-11} cm/s for in-situ curing. When measured under a confining pressure of 0.4 MPa (60 psi) in a flexible wall permeameter the wet cured permeability was 6.0×10^{-10} cm/s. After six months leaching in deionized water the permeability measured in the rigid wall permeameter increased to 1.2×10^{-9} cm/s. This was significantly higher than for a silica fume modified grout. However, subsurface exposure conditions are not expected to be as aggressive as those in the leach test and use of silica fume is probably not necessary unless information indicating groundwater flow or high soluble sulphate levels is uncovered. The grout formulation could possibly be improved further by replacement of Type I cement for Type IV or V, or partial replacement with blast furnace slag.

Wet-dry cycling caused surface cracking of the grout and these cracks underwent self healing due to production of CaCO_3 . It is uncertain as to whether such crack healing will occur under the arid subsurface exposure conditions. Wet cured grout subjected to 23 wet-dry cycles approximately doubled in permeability, but remained below the 10^{-7} cm/s requirement.

The grout demonstrated good pumpability and could possibly undergo a further reduction in water/cement ratio depending on the type of full scale mixing equipment employed. Small scale field trials demonstrated that this grout could be pumped into an excavation and exhibited excellent properties after 4 months subsurface exposure, including absence of cracks or other deterioration.

Addition of collated fibrillated polypropylene fibres to grouts at volume fractions of 0.1 and 0.2% was found to be beneficial in reducing widths of cracks induced by restrained shrinkage. Fibrillated fibres did not significantly or consistently alter microstructure, compressive strength or permeability. Flexural strength was improved by fibrillated fibres for some, not all, grouts. The major benefit of fibres on mechanical properties was an increase in ductility and prevention of complete separation, thereby reducing crack width in the case of mechanical overload. Fibrillated fibres improved resistance of grouts to cracking, decreased loss of strength and reduced the amount of increase in permeability under wet-dry cycling conditions. A problem encountered with fibrillated fibres was clumping of mats of fibres during mixing. This interferes with pumpability and feasibility of using fibres with grouts with full scale placement equipment requires confirmation.

Monofilament fibres produce a more uniform distribution of fibres throughout the grout matrix and have improved pumpability.

However, reduction of crack widths with monofilament fibres is not as great as for fibrillated fibres and permeability is significantly increased. Thus, monofilament fibres appear unsuitable.

Soil cements were studied as alternatives to monolithic grout barriers. The materials were designed to be compatible with jet grouting, soil sawing or soil mixing. A superplasticized neat cement grout (i.e. Mix 47) is suitable for in-situ mixing with soil by either of these techniques. It was determined that high soil contents result in excessive permeability when the soil cements are cured in-situ. Compressive and flexural strength decrease with increasing soil content, but remain adequate up to a soil/cement ratio of 5. Crack widths under restrained shrinkage conditions increase with increasing soil/cement ratio. Percentage loss of compressive strength after wet-dry cycles is higher at low soil contents. However, crack widths are smaller and undergo self healing after repeated wetting and drying, whereas soil cements with high soil/cement ratios do not.

The best compromise of mechanical and physical properties and durability appears to be achieved with low soil/cement ratios of 1 to 3. The permeabilities of these materials range from 1.2×10^{-10} to 2.9×10^{-10} cm/s under wet curing and 1.2×10^{-10} to 9.5×10^{-9} cm/s under in-situ curing. Compressive strength ranges from 32.9 to 12.7 MPa for wet curing and 27.0 to 9.0 MPa for in-situ curing. Flexural strength for s/c = 1 to 3 varies from 2.9 to 2.0 MPa. These values may vary for materials placed in the field. However, the observed trends should still be valid.

Scanning electron microscopy investigation of soil cements revealed calcium silicate hydrate gel, other hydrates, precipitated cubic crystals of SiO_2 and ettringite needles growing into capillary pores. Soil/cement ratios of 1 and 2 demonstrated resistance to leaching in deionized water due to formation of a surface layer of $\text{Ca}(\text{OH})_2$ and the difference between initial and post-leaching permeability increases with increasing soil content. The increase in permeability due to cracking induced by wet-dry cycles is low for s/c = 1 to 2 due to crack healing.

Soil cement barriers produced in small scale field tests by direct mixing had high compressive strengths and did not crack or deteriorate in any obvious manner.

Polypropylene fibres were added to parent grouts designed for producing soil cements by soil mixing. Flexural strength and ductility were improved by addition of 0.2% volume fraction fibrillated fibres. Fibres reduced restrained shrinkage crack widths, with the two types of fibres demonstrating similar performances for a soil/cement ratio of 1 and volume fraction of 0.2%. Wet-dry cycling resistance was improved by fibrillated fibres but not by monofilament fibres.

As was the case for the grout barrier materials, problems were encountered with the mixing equipment used in obtaining a uniform distribution of fibrillated fibres in the parent grout for

the soil cements. This is particularly evident because higher amounts of fibres must be mixed into the grout to give a volume fraction of 0.2% in the final soil cement. Thus, use of fibrillated fibres at high soil/cement ratios requires investigation of the practicality for field applications. From a practical standpoint, monofilament fibres are more suited to soil cements produced by mixing a fibre reinforced grout with soil in-situ. However, the reduction in wet-dry resistance and increase in permeability requires further investigation before these fibres can be recommended.

Soil cements also appear suitable for caps if protection against excessive drying is provided. Fibre reinforcement would improve the performance of caps if adequate distribution can be achieved. Concrete or shotcrete may be suitable alternatives.

The estimated material cost of a suitable sanded grout is \$182/m³ and the cost of soil cement ranges from \$128/m³ to \$89/m³ for soil/cement ratios of 1 to 2. Based on measured values of in-situ cured permeability, a sanded grout is more cost effective than soil cements. However, placement costs may change the comparative ratings of candidate materials.

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