BNL--48252

DE93 008563

IN SITU CONTAINMENT AND STABILIZATION OF BURIED WASTE

ANNUAL REPORT

M.L. ALLAN*, L.E. KUKACKA* AND J.H. HEISER**

*DEPARTMENT OF APPLIED SCIENCE

**DEPARTMENT OF NUCLEAR ENERGY

NOVEMBER 1992

Report of FY 1992 Work Performed Under
TTP No. CH3211-01

Prepared for the
Mixed Waste Landfill Integrated Demonstration
Office of Technology Development
U.S. Department of Energy
Washington, DC 20585

Energy Efficiency and Conservation Division
Department of Applied Science
Brookhaven National Laboratory
Associated Universities, Inc.

This work was performed under the auspices of the U.S. Department of Energy, Washington, DC under Contract No. DE-AC02-76CH00016.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

LIST OF TABLES

LIST OF TABLES (CONT.)

LIST OF FIGURES

LIST OF FIGURES (CONT.)

SUMMARY

Advanced grouting materials were developed and tested for use as subsurface barriers and caps for in-situ containment of buried waste and as stabilizing agents for chromium contaminated soil. Cementitious and polymer grouts were investigated for use as solid barriers and as binders for soil. Cementitious grouts with varying amounts of silica fume, latex and sand were all found to have permeability coefficients of the order of 10^{-10} cm/s. This is three orders of magnitude below the EPA limit of 10^{-7} cm/s. The grouts were used to produce soil cements with varying soil contents. Permeability coefficients of the soil cements ranged from 1.0 to $3.9\text{x}10^{-10}$ cm/s for soil/cementitious material ratios of 1 to 5. Soil cements made from conventional high water/cement ratio grouts without superplasticizers or other admixtures had permeability coefficients of $4.4\text{x}10^{-9}$ to $3.1\text{x}10^{-6}$ cm/s for the same range of soil/cement ratios.

An EPA acceptable polymer grout was produced from vinyl ester resin and sand. This grout had a very low permeability coefficient of $2.9\text{x}10^{-11}$ cm/s. Polymer-soil composites were produced by mixing vinyl ester and polyester resins with site soil. These materials had strengths and permeability coefficients similar to cementitious grouts.

The material costs of the advanced cementitious grouts were \$162 to \$280 per cubic meter depending on mix proportions. Addition of latex to grouts raised the cost to \$431 to \$699 per cubic meter. Soil cements are less expensive, ranging from \$48 to \$180 per cubic meter depending on the grout used and the soil content. Polymer grouts and polymer-soil composites are significantly more expensive than cement based materials ranging from \$1097 to \$1463 per cubic meter.

By comparing the permeability coefficient with the volumetric cost, the most cost effective materials were identified. The most cost effective grouts were those that do not contain any silica fume. The soil cements based on grout with no silica fume or sand are the most cost effective, and a soil/cement ratio of 1 has the best ratio of permeability to cost. The soil cements produced from advanced grouts are significantly more cost effective than conventional soil cements. In addition to permeability, durability should be considered in evaluation of the most cost effective and suitable materials and this will be the focus of future work.

Cement grouts successfully stabilized site soil contaminated with chromium provided that Cr^{6+} was first converted to Cr^{3+} with a reductant such as Fe^{2+}. An alternative to stabilization by grouting is chemical treatment with Fe^{2+} followed by $Ca(OH)_2$ to produce insoluble chromium hydroxide.

1.0 INTRODUCTION

The objective of the project was to develop, demonstrate and implement advanced grouting materials for the <u>in-situ</u> installation of impermeable, durable subsurface barriers and caps around waste sites and for the <u>in-situ</u> stabilization of contaminated soils. Specifically, the work was aimed at remediation of the Chemical Waste (CWL) and Mixed Waste Landfills (MWL) at Sandia National Laboratories (SNL) as part of the Mixed Waste Landfill Integrated Demonstration (MWLID).

Between 1962 and 1985 waste solutions containing heavy metals were disposed in the CWL. The site is approximately 450 feet (135 m) by 200 feet (60 m) and located 480 feet (144 m) above the water table in an arid environment. The major concern is the presence of a chromium plume that has migrated to a depth of 75 ft (23 m) originating from disposal of chromic acid and chromic sulphuric acid. High levels of trichloroethylene and other organics are also present. The MWL is 1.6 acres in area and also located 480 feet above the water table. The MWL received hazardous, radioactive and mixed waste and a tritium plume has reached a depth of 50 ft (15 m).

The work was conducted in two subtasks. These were (1) Capping and Barrier Grouts, and (2) <u>In-situ</u> Stabilization of Contaminated Soils. Subtask 1 examined materials and placement methods for <u>in-situ</u> containment of contaminated sites by subsurface barriers and surface caps. In Subtask 2 materials and techniques were evaluated for <u>in-situ</u> chemical stabilization of chromium in soil.

2.0 IN-SITU CONTAINMENT OF BURIED WASTE

2.1 Introduction

The objective of Subtask 1 was to develop and test advanced grouting materials suitable for <u>in-situ</u> placement of subsurface barriers and surface caps to contain buried waste. The required depth of subsurface barriers,or curtains, is approximately 100 ft (33 m). A schematic diagram of the proposed closure of the CWL is shown in Figure 1 indicating subsurface vertical and horizontal barriers and a surface cap. The same concept is proposed for the MWL. The actual extent of stabilization may vary with that drawn subject to further characterization of the chromium plume and economic studies. In particular, it may be found that the chromium plume has migrated further by the final remediation stage and that deeper stabilization is necessary.

Candidate materials compatible with available placement techniques were selected and tested for critical performance parameters such as permeability and strength. The materials investigated can be divided into two categories. These were inorganic cement based grouts and organic based grouts.

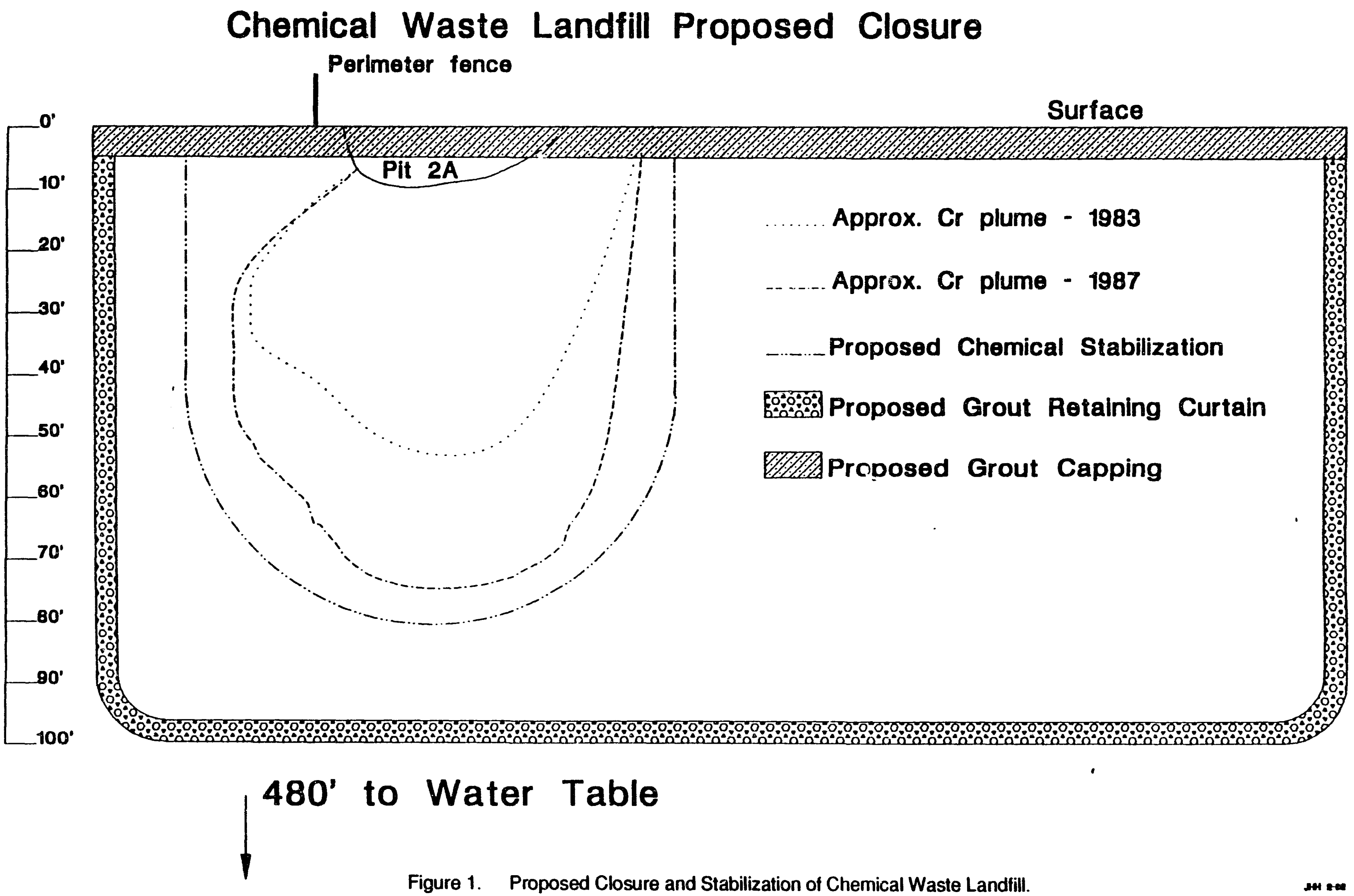

Figure 1. Proposed Closure and Stabilization of Chemical Waste Landfill.

2.2 Performance Criteria

Materials used as barriers and caps to contain buried waste must meet certain performance criteria both in the cured and uncured states. The criteria are outlined below:

2.2.1 EPA Acceptability

The EPA acceptability of grouts used to produce barriers and caps was critical. Further contamination of the sites through use of toxic cured or uncured grouts was not permitted. All materials were required to comply with EPA 40 Code of Federal Regulations Part 261 Subpart D which lists hazardous materials. As a result, several commercially available chemical grouts were excluded from evaluation. These included polyacrylamide, polyacrylic acid, phenol-formaldehyde and urea-formaldehyde.

Portland cement based grouts and benzoyl peroxide catalyzed vinyl ester and polyester resins are not EPA listed wastes and were therefore considered suitable on a lack of toxicity basis. However, both vinyl ester and polyester resins contain styrene monomer and their use must comply with the Clean Air Act.

2.2.2 Hydraulic Conductivity (Permeability)

Barriers and caps are required to have low hydraulic conductivity (permeability) in order to limit the migration of hazardous species out of the contained site. Hydraulic properties of core samples taken from the site were conducted and reported by Daniel B. Stephens and Associates, Inc. (1990). The hydraulic conductivities measured range from 10^{-5} to 10^{-3} cm/s. Hence, it is necessary to reduce this hydraulic conductivity by several orders of magnitude to significantly decrease the current rate of migration. EPA 40 Code of Federal Regulations Part 264 Subpart N (landfills) stipulates that liners for waste impoundments must have a hydraulic conductivity less than 10^{-7} cm/s. Therefore, barrier and cap materials were developed to meet this criterion.

2.2.3 Compatibility with Placement Techniques

The materials were required to be compatible with currently available placement techniques. A range of techniques exist and the choice of technique depends on the properties of site soil, grout and final product. For this project the possible placement techniques considered for vertical and horizontal barriers were permeation grouting, jet grouting and displacement grouting. Deep soil mixing was considered for vertical barriers. For surface caps the alternative methods were covering the landfill with a layer of grout and shallow soil mixing. Another MWLID project examined the placement techniques and therefore, this project concentrated on material aspects.

2.2.3.1 Permeation Grouting

Permeation grouting involves pumping low viscosity grout through an injection pipe into soil. The grout permeates the pores and voids within the soil and hardens to give a final product with improved strength and resistance to water. Reduction of groundwater flow and stabilization of foundations are typical applications. A variation of permeation grouting is vacuum injection in which grout permeates pores due to a pressure differential created by a vacuum. The feasibility of permeation grouting for containment of buried low-level and TRU waste and bottom sealing of hazardous waste landfill has been reported by Tallent et al (1986) and May et al (1986) respectively.

Detailed descriptions of the technique have been documented (Kosmatka, 1990, Nonveiller, 1989). Injection pipes, 25 to 50 mm diameter, are inserted and sealed into pre-drilled holes, 0.6 to 3 m apart, depending on the soil permeability. Grout injection commences at the lowest level and progresses upwards and laterally so that air and water can be displaced. During permeation grouting the soil is not disrupted. Construction of a continuous barrier using this technique requires successive injections of grout, possibly with more than one row of holes.

The type of grout that can be used for permeation grouting is controlled by the pore size and grain size of the soil. Kosmatka (1990) recommends that soil permeability should be greater than 0.5 cm/sec for portland cement grout and this value is not exceeded by the site soil. Sieve analysis of site soils conducted by Stephens and Associates (1990) showed that the soils ranged from sands to silt with the median grain size usually 0.1 - 0.2 mm. The grain size distribution varied with depth and location. In addition, use of a suspension type grout such as portland cement would probably lead to bridging between soil particles by cement particles with resultant sedimentation of the grout and incomplete permeation of the soil. Therefore, low viscosity (<10cP) solution and resin grouts or microfine cement grout would be necessary for permeation grouting of the site.

Microfine (also known as ultrafine) cement or reground cement that have smaller particle sizes would be required. Both of these cements are more expensive and less readily available than ordinary portland cement. For example, microfine cement is around $1.10 to $1.50 per kilogram depending on the quantity ordered whereas the cost of bulk ordinary portland cement is around $0.11 per kilogram. Owing to high costs and less ready availability microfine and reground cements were not evaluated in this project.

A disadvantage of the permeation grouting technique is that the penetration of grout cannot be accurately controlled due to soil inhomogeneity. Hence, it is difficult to construct a continuous barrier. This is a major concern for the landfill remediation project particularly at large depths where testing of barrier continuity is expected to be complex. Consequently, other placement techniques may be more suitable than permeation grouting.

2.2.3.2 Jet Grouting

Jet grouting can be performed in two different ways to produce in-situ subsurface barriers. The first method is termed jet grouting by penetration and firstly involves placement of a jetting pipe inside a drilled hole at the bottom of the soil to be treated. Portland cement based grout is pressurized and forced out laterally from jet ports in the rotating pipe. The resultant high velocity grout breaks up and intimately mixes with the soil to form soil cement or "soilcrete". The pipe progresses upwards and columns 0.6 to 0.75 m in diameter can be produced. Vertical barriers are produced by overlapped rows of columns.

The second method is termed jet grouting by excavation and is sometimes referred to as replacement grouting. In this method a columnar cavity is produced by a high pressure fluid jet such as water that is blasted out of a rotating jet pipe. The soil cuttings are removed to the surface. The cavity is prevented from collapsing by water or air pressure. Grout is then introduced to the cavity and allowed to harden. Columns 1.8 m in diameter can be produced by this technique. Use of cement-sand and chemical grouts with jet grouting is feasible in addition to conventional cement grouts.

Further details are available from Andromalos and Pettit (1986), May et al (1986), Guatteri et al (1988), Andromalos and Gazaway (1989) and Kosmatka (1990). In addition to vertical columns, pancake shapes can be produced and used for bottom sealing (May et al, 1986 and Brunsing, 1987). The portland cement grouts used typically have water/cement ratios ranging from 1 to 3. Soil cements produced by jet grouting have been reported to have permeabilities of the order of 10^{-7} cm/s (Guatteri et al, 1988).

2.2.3.3 Displacement Grouting

Displacement grouting involves pressure grouting of thick cementitious grouts which disturb the soil structure rather than permeate the pores. Compaction grouting is a form of this principle and consists of controlled injection to compact and hence densify and strengthen soil. This is described by Kosmatka (1990) and Borden and Groome (1984). Another form of displacement grouting uses pressure injection of stiff grouts to cause hydraulic fracture of soil. The fractures created are then filled with the grout thus reducing permeability. Displacement grouting by hydraulic fracture is a possible method for constructing subsurface vertical barriers. Brunsing (1987) reported use of displacement grouting to produce a bottom seal by injecting grout to cause horizontal fractures and subsequently filling the fractures with grout. This has been demonstrated to a depth of 7.5 m.

Grouts used for the displacement method are usually pumpable cement-sand-bentonite slurries with possible addition of fly ash (Borden and Groome, 1984). Use of resins should also be feasible with this method.

2.2.3.4 Deep Soil Mixing

Soil cement vertical subsurface barriers can be constructed in-situ by the deep soil mixing (DSM) technique. Multiple hollow mixing shafts/augers attached to a crane are inserted into the ground and rotated and a grout is injected into the soil at the tip of the augers. The intimate mixing produces soil cement columns 1 m in diameter and up to 45 m deep. Further details of the technique are given by Ryan (1987) and Jasperse and Miller (1990).

Cementitious grouts are typically used with this technique. However, it may be feasible to use low viscosity resins and produce soil-resin composites which may have improved permeability compared with soil cement.

2.2.3.5 Shallow Soil Mixing

Shallow soil mixing (SSM) uses the same basic principles as DSM. A single crane mounted hollow mixing shaft/auger is used to mix grout with soil. The auger is 1 to 3.7 m in diameter and can be used to a depth of 9 m (Broomhead and Jasperse, 1992). SSM could be used to produce a surface cap of soil cement. A soil-resin composite cap may also be feasible.

2.2.4 Grout Rheology

The grouts must have a viscosity compatible with the placement technique employed. It is preferable that grouts are self-levelling and do not become thixotropic before placement is completed otherwise specialized equipment may be required. For a solid grout barrier or cap the grout should flow to completely fill the required cavity. Immediate thixotropy on the removal of stress may cause air pockets within the final mass due to inadequate consolidation.

2.2.5 Uncured Grout Stability

All grouts to be used should exhibit stability in the uncured form. For cementitious grouts bleeding of water and settling of particles should not occur. Similarly, any physical separation of chemical or resin grout components is unacceptable.

2.2.6 Set Time

The minimum set time of the grouts should be long enough to permit placement and equipment clean up. The maximum set time is not as critical unless continuation of work depends on setting of a previously treated area. A period of 12-24 hours is probably acceptable.

2.2.7 Durability

Long-term durability of the barrier and cap materials with minimum maintenance is required. Therefore, the materials must be stable and retain mechanical and physical properties in the exposure environment. Resistance to weather, ultraviolet rays (for caps), soil bacteria and any deleterious species in the soil is necessary. In particular, a permeability less than 10^{-7} cm/s must be maintained throughout the service life. The actual service life has not yet been defined, but a few hundred to a thousand years may be reasonable.

The landfills are located in a region where temperature ranges from -5°C to 11°C in winter and 14°C to 33°C in summer. The average annual precipitation and relative humidity are 200 mm and 46% respectively. Hence, the environment can be regarded as arid with moderate temperatures. The soil consists of alluvial deposits and is mostly sand with some silt and clay. The subsurface moisture content is 2-8%. Analysis of the soil in locations nearby the landfill conducted by the Geochemistry Division of Sandia National Laboratory showed soil pH of 8.4 and water soluble sulphate levels ranging from 10.1 to 586 ppm (1×10^{-3} to 0.058%).

Since temperatures below freezing point do occur the surface caps should exhibit freeze-thaw durability. Freezing of the subsurface barriers is not likely.

2.2.8 Strength

The subsurface barriers must be able to withstand compressive and flexural forces encountered in service without cracking. The horizontal subsurface barrier, or bottom seal, must withstand the uniform overburden pressure due to the weight of the soil and the weight of the cap. Assuming a soil density of 1800 kg/m^3 (typical value measured by Daniel B. Stephens and Associates), the vertical overburden pressure would be approximately (1800 x 36 x 9.8) = 0.63 MPa (91 psi) at a depth of 36 m (120 feet). The load due to the cap will depend on the thickness and type of material. As an example, consider a 1 m thick cap with a density of 2000 kg/m^3. This would give a uniform pressure on the horizontal barrier of approximately (2000 x 1 x 9.8) = 0.02 MPa (3 psi). Hence, the total pressure would be 0.65 MPa.

The vertical subsurface barriers must withstand lateral soil pressures which should be approximately equal on both sides. Therefore, the strength requirement of the vertical barriers is minimal. The design thickness of the barriers will be controlled by impermeability requirements rather than strength.

For the surface cap, the material should support occasional heavy vehicle movement. The maximum load likely to be encountered from a heavy vehicle would be approximately 10000-30000 kg over an area of approximately 1.8 m by 2 m. This gives a pressure of 0.03 to 0.08 MPa (4 to 12 psi).

The above calculations indicate that low strengths are required for integrity. Since durability correlates with strength for cement based materials it is proposed that the strength criteria be based on durability requirements rather than load.

2.2.9 Shrinkage

Although the barriers and caps are not precision elements, shrinkage during curing and service should be minimized. Shrinkage cracking is unacceptable.

2.3 Materials Selection

The main focus of the work described within was materials for use with jet grouting, deep soil mixing and shallow soil mixing techniques. Capping grouts placed by pumping were also investigated. For displacement grouting polymer grouts were considered. The material property relationships determined from low viscosity cementitious grouts may be used to predict the properties for more viscous grouts with lower water/cement ratios suitable for displacement grouting.

2.3.1 Cementitious and Polymer Modified Cementitious Materials

Cements, mortars and concrete exhibit long term durability in excess of hundreds of years in suitable environments. The arid environment and high soil pH conditions are ideal for cement based materials since these conditions reduce or eliminate concerns about excessive wet-dry cycling, carbonation and acid attack. The water soluble sulphate levels in the soil are much less than the critical level of 0.1 to 0.2% at which deleterious sulphate attack of cement can occur (Kosmatka et al 1991). Therefore, it is not necessary to use sulphate resistant cement. No information on bacteria types and levels in the site soil was available at the time of writing. However, deterioration of cement based materials as a result of bacteria is only usually of concern in sewer systems or exposure to weathered black shale (Ramachandran et al, 1981). Owing to the proven durability of cementitious materials and relatively benign environment, cementitious grouts were a major focus of this work.

In addition to durability, ordinary portland cement based materials are readily available, non-hazardous and inexpensive. Thus, they are suitable candidates for landfill caps and barriers. Type I cement supplied by Norval was used in this project.

Several admixtures can be used to improve the physical and mechanical properties of grouts. The typical grouts currently used in the field have water/cement ratios greater than 1 and do not use admixtures. Water/cementitious material ratio (w/cm) is the primary controlling factor for durability, strength and permeability. Significant improvement in these properties can be achieved without detrimental effect on flow properties through use of superplasticizers to reduce the w/cm ratio. Superplasticizers have been used in grouts investigated for high performance applications such as caps for solidified low-level waste (Wakeley and Ernzen, 1991) and sealing nuclear waste disposal vaults in granite (Onofrei _et al_ 1989, Hooton and Konecny, 1990 and Al-Manaseer _et al_, 1991). A superplasticizer containing 42% naphthalene sulphonate formaldehyde condensate was chosen for the MWLID project to reduce the amount of water in cementitious grout formulations.

Pozzolanic admixtures to partially replace cement such as fly ash and silica fume can also be used to improve grout properties. Class F (low calcium) fly ash has been reported to improve flow behavior (Rattanussorn, Roy and Malek, 1987, ACI Committee 304, 1991) and reduce permeability (Kosmatka _et al_, 1991 and Mehta, 1984). Silica fume also improves grout properties by reducing bleeding and permeability (Kosmatka _et al_, 1991, Mehta, 1984, Aitcin _et al_, 1984 and Al-Manaseer _et al_, 1991). Permeability is reduced by the pore refinement that results from addition of silica fume. An example of use of fly ash in high performance grouts is described by Wakeley and Ernzen (1991) and examples of use of silica fume are given by Hooton and Konecny (1990), Onofrei _et al_ (1989) and Al-Manaseer _et al_ (1991). Hooton and Konecny (1990) reported that silica fume was more effective in reducing permeability than fly ash. A Class F fly ash supplied by Detroit Edison and condensed silica fume supplied by Norcem Concrete Products were selected for study in barrier and cap formulations.

Latex has been used as an admixture to improve properties of mortars and concretes. Improvements include flexural behavior, carbonation resistance and permeability. Latex is an emulsion of fine organic polymer particles dispersed in water. When incorporated in concrete or mortar the latex particles form a continuous polymer film around hydrated cement paste and within air voids. The most commonly used latexes are styrene butadiene, polyvinyl acetate, polychloroprene, poly(ethylene-vinyl acetate), polyacrylic ester and styrene acrylic. Further details on the influence of latex and applications of latex-modified concrete and mortar are given by ACI Subcommittee 548A (1990), Ohama (1984), and Walters (1990). In studies comparing physical and mechanical properties such as strength, rapid chloride permeability, weathering resistance and freeze-thaw resistance of mortars modified with different latexes, a carboxylated styrene butadiene copolymer showed the best all-round performance (Walters, 1990). For this work a carboxylated styrene butadiene latex was selected for addition to grouts to improve performance. Tylac 68009-00 containing 46-48% polymer solids and an antifoaming agent produced by Reichold Chemicals was used.

A fine silica sand was chosen for use in some of the grout formulations. The sand used had 98% of the particles between sieve sizes 200 and 40 (74 to 420 um) and was from the Morie

Company. The fine particle size was chosen so as to minimize settling and give low permeability.

Bentonite is commonly used in cementitious grouts to prevent bleeding and segregation. Loss of strength due to inclusion of bentonite can occur (Hooton and Konecny, 1990) and the proportion of bentonite should not exceed 5% by weight of water (Long, 1990). In this work Wyoming bentonite (sodium type) supplied by NL Baroid Industries was used.

2.3.2 Chemical Grouts

A number of EPA acceptable chemical grouts are commercially available. Of these, sodium silicate and acrylate have often been used to reduce the permeability of soil. Sodium silicate is unsuitable for the long term performance required due to possible dehydration and leaching. Acrylate grouts undergo dehydration in dry conditions (Clarke, 1982) which is a concern for the arid environment of the landfills. In addition, the long term durability of acrylate grouts is uncertain and unproven. Therefore, acrylate and sodium silicate grouts were not considered further.

Vinyl ester and polyester resins show excellent stability, low permeability and high strength (Updegraff, 1990, Messick and White, 1990). The resins were predicted to perform well in the subsurface exposure conditions. The vinyl ester chosen for investigation was Derakane 470-36 (Dow Chemicals) which has a relatively low styrene monomer content of 36% and a viscosity of 250 cP. The low styrene content was desirable to minimize the styrene vapor given off and to minimize any unreacted monomer in the final product. Some experiments were also conducted with Derakane 470-45 which had a styrene content of 45% and a viscosity of 100 cP. A polyester resin supplied by Alpha Corporation was used. The supplied sample was not the low viscosity resin requested.

The fine aggregates used in production of vinyl ester-sand grouts were graded silica sand (TC 4727-81) and silica flour (Morie Company).

Another chemical selected for investigation was furfuryl alcohol which can be polymerized by acidic catalysts. It has a low viscosity (5 cP at 25°C), is not an EPA listed waste and has been used to produce polymer concrete (Sugama, Kukacka and Horn, 1981).A sample of furfuryl alcohol was supplied by QO Chemicals for experimental evaluation.

2.3.3 Soil Cements and Polymer-Soil Composites

Soil cements usually consist of cement, soil, water and possibly aggregate. The primary uses of soil cement are pavement bases, low permeability liners, slope protection and foundation stabilization. The mix design and properties of soil cement are described by Johnson et al (1960) and ACI Committee 230 (1990). Adequate performance of low permeability soil cement liners for over 30 years has been reported (ACI Committee 230, 1990). Durability is related to strength and a compressive strength of 5.5 MPa (800 psi) is a conservative estimate of compressive strength required for freeze-thaw durability (ACI Committee 230, 1990).

Soil cements are usually compacted to high density. For soil cement subsurface barriers produced by in-situ techniques such as jet grouting or soil mixing, compaction is not convenient. Therefore, it is necessary to produce a fluid, self-levelling soil cement that will harden to a dense material. This requires more water to produce a fluid mix and more cement to meet strength and durability requirements. Such soil cement mixtures are often termed plastic soil cement or controlled low strength material (CLSM).

The possibility of producing a low permeability material by mixing a polymer resin with the site soil was also investigated. Such material would be expected to have similar properties to resins containing inactive fillers.

Two 200 liter drums of uncontaminated soil were received from Sandia. The soil moisture content was determined by oven drying to be 8 % by weight. The soil was maintained in sealed containers so that moisture content would not decrease throughout the course of the project. No drying of soil was conducted prior to use in soil cements or polymer-soil composites so that site conditions were simulated.

2.4 Experimental Procedure

Experiments were conducted to evaluate candidate barrier and cap materials. Cement based grouts and soil cements produced from mixing grout and soil were prepared and tested. Resin-sand and resin-soil mixes were also tested. Furfuryl alcohol was investigated as a potential permeation grout.

2.4.1 Mix Proportions

2.4.1.1 Cementitious Grouts

Cementitious grouts of different mix proportions were prepared in order to select which mixes were suitable for further evaluation as barrier and cap materials. Superplasticized Type I cement-bentonite grout was used as the basic mix. Variations on this included 10-20% replacement of cement with Class F fly ash, 5-10% replacement with silica fume and cement:sand ratios of 1:1 and 1:3.

The objective was to produce flowable, low viscosity, low permeability, low shrinkage, durable grouts that were not thixotropic immediately on the cessation of stress. Water/cementitious material ratios were kept as low as possible to optimize permeability, strength and durability. The maximum amount of superplasticizer that could be added without detrimental strength reduction and no further reduction of viscosity was determined. The minimum bentonite content that would aid dispersion of cement and sand particles and eliminate bleeding was used.

In the preliminary grout formulations it was found that bentonite was definitely necessary to prevent bleeding. Less bentonite was required for silica fume modified grouts due to the bleed reduction behavior of the silica fume particles. Higher levels of bentonite were required for grouts that contained sand. Cement:sand ratios of 1:3 had unacceptably high viscosity unless a w/cm in excess of 1 was used and this defeated the purpose of producing a high performance grout. For grouts without sand the minimum w/cm to give a viscosity less than 100 cP was 0.4.

The superplasticizer dosage recommended for concrete by the manufacturer was 5 to 20 ml/kg of cementitious material. This translates to 0.25 to 1% active superplasticizer by weight of cement. For cement grouts 20 ml/kg cement was used. Silica fume grouts were more viscous and thixotropic due to the very fine particle sizes and required higher dosages of superplasticizer if a low water content was to be maintained. A dosage of 30 ml/kg cement plus silica fume (1.5%) was found to be the maximum level at which no further reduction of viscosity occurred and no strength reduction was observed.

Several different grout mixes with 10 and 20% replacement of cement by fly ash were prepared. The fly ash modified grouts tended to be more viscous and required higher water/cementitious material ratios than unmodified grouts. The higher water content led to bleeding and segregation despite addition of bentonite. In addition, the fly ash tended to retard the set and grouts were still soft and weak 24 hours after casting. Materials superior to the fly ash grouts were produced from unmodified and silica fume modified grouts. As a result, fly ash modified grouts were discontinued from the project.

The mix proportions of the cementitious grouts selected for evaluation from the preliminary tests are given in Table 1. The amount of active superplasticizer solids used is given.

2.4.1.2 Latex Modified Grouts

Selected grouts were modified with a carboxylated styrene butadiene copolymer latex. The latex contained 46-48% solids and was added to give an active polymer:cement ratio of 0.2. Since the latex contained water, the added mixing water could be reduced. Viscosities of the grouts were increased due to the stickiness of latex. Grouts required less bentonite when latex was added due to reduction of bleeding and segregation. The required superplasticizer dosage for the silica fume modified grouts was reduced. The mix proportions of the latex modified grouts are given in Table 2. When the water content of the latex is included the

TABLE 1. Mix Proportions of Cementitious Grouts by Weight

Mix	Cement	Water	Sand	Bentonite	Silica Fume	SP*
1	1.00	0.40	0	8×10^{-3}	0.00	0.01
2	1.00	0.66	1	0.033	0.00	0.01
3	0.95	0.40	0	6×10^{-3}	0.05	0.015
4	0.95	0.66	1	0.033	0.05	0.015
5	0.90	0.42	0	4×10^{-3}	0.10	0.015
6	0.90	0.68	1	0.033	0.10	0.015

* SP = Superplasticizer

actual w/cm for Mixes 1L and 5L was 0.42 and 0.68 for Mix 6L. Superplasticizer and latex proportions are expressed as active solids.

Table 2. Mix Proportions of Latex Modified Grouts by Weight

Mix	Cement	Water	Sand	Bentonite	Silica Fume	SP	Latex
1L	1.0	0.20	0	0.00	0.0	0.01	0.2
5L	0.9	0.20	0	0.00	0.1	0.01	0.2
6L	0.9	0.46	1	0.01	0.1	0.01	0.2

2.4.1.3 Soil Cements

Soil cements were produced by mixing the specialized grouts developed in Section 2.4.1.1 with site soil. The initial soil/cementitious material ratios (s/cm) studied were 1, 2 and 5. A mix with a s/cm of 6 was also evaluated after testing the initial mixes. For a s/cm of 1 it was found that no additional mixing water was required to make the soil cement self-levelling. Mixes with higher s/cm required extra water. The amount of water added to the soil-grout mix was minimized in order to optimize permeability, durability and strength. The effect of added water on properties was investigated by increasing the water content of one of the soil cements with a s/cm of 5.

In addition to the mixes produced using the specialized grouts, conventional grouts without admixtures and high water/cement ratios typical of what are currently used in the field were used to make soil cements. These conventional materials were compared with the developed soil cements. The mix proportions of the soil cements tested are given in Table 3. For the specialized grouts the first digit of the mix number refers to the parent grout in Table 1. The conventional grouts are denoted by the letter "C". The last digit indicates the soil/cementitious material ratio.

2.4.1.4 Latex Modified Soil Cements

Latex modified grouts developed in Section 2.4.1.2 were used to produce soil cements. The mix proportions are given in Table 4. Again, the first digit of the mix number refers to the parent grout and the last digit refers to the soil/cementitious material ratio.

Table 3. Mix Proportions of Soil Cements by Weight

Mix	Cement	Water	Sand	Bentonite	Silica Fume	SP	Soil
1S1	1.00	0.40	0	$8x10^{-3}$	0.00	0.01	1
2S1	1.00	0.66	1	0.033	0.00	0.01	1
3S1	0.95	0.40	0	$6x10^{-3}$	0.05	0.015	1
4S1	0.95	0.66	1	0.033	0.05	0.015	1
5S1	0.90	0.42	0	$4x10^{-3}$	0.10	0.015	1
6S1	0.90	0.68	1	0.033	0.10	0.015	1
1S2	1.00	0.65	0	$8x10^{-3}$	0.00	0.01	2
5S2	0.90	0.62	0	$4x10^{-3}$	0.10	0.015	2
6S2	0.90	0.93	1	0.033	0.10	0.015	2
1S5	1.00	1.20	0	$8x10^{-3}$	0.00	0.01	5
5S5	0.90	1.20	0	$4x10^{-3}$	0.10	0.015	5
6S5	0.90	1.60	1	0.033	0.10	0.015	5
1S5F	1.00	1.34	0	$8x10^{-3}$	0.00	0.01	5
1S6	1.00	1.60	0	$8x10^{-3}$	0.00	0.01	6
C1S1	1.00	1.00	0	0.02	0.00	0.00	1
C1S2	1.00	1.00	0	0.02	0.00	0.00	2
C2S5	1.00	2.00	0	0.04	0.00	0.00	5

Table 4. Mix Proportions of Latex Modified Soil Cements

Mix	Cement	Water	Sand	Bentonite	SF	SP	Latex	Soil
1LS1	1.0	0.20	0	0.00	0.0	0.01	0.2	1
5LS1	0.9	0.20	0	0.00	0.1	0.01	0.2	1
6LS1	0.9	0.46	1	0.01	0.1	0.01	0.2	1
1LS2	1.0	0.26	0	0.00	0.0	0.01	0.2	2
5LS2	0.9	0.28	0	0.00	0.1	0.01	0.2	2
6LS2	0.9	0.46	1	0.01	0.1	0.01	0.2	2
1LS5	1.0	1.20	0	0.00	0.0	0.01	0.2	5

2.4.1.5 Polymer-Soil Composites and Polymer-Sand Grouts

Grouts comprised of Derakane 470-36 vinyl ester resin and sand were prepared with the object of optimizing the proportion of sand so that a resin-rich top layer would not form. In all experiments the resin was catalyzed by adding 4% by weight of 50% active benzoyl peroxide (BFF-50) and promoted by 0.1% by weight dimethyl aniline. This gave a set time of approximately 20 minutes. For field applications where a longer set time would be required the amounts of catalyst and promoter could be reduced. A surfactant S440 was used at a rate of 0.5% by weight of resin to promote sand dispersal. The mix proportions of the vinyl ester-sand grouts are given in Table 5.

Table 5. Mix Proportions of Vinyl Ester-Sand Grouts by Weight

Mix	Vinyl Ester	Graded Sand	Silica Flour
V3	1	3	0
V5	1	3	1
V6	1	4	1
V7	1	5	1

The vinyl ester resin was mixed with as-received site soil and allowed to cure at room temperature. The proportions of catalyst and promoter were the same as for the resin-sand grouts. The proportion of soil was varied in order to optimize the soil content and maintain self-levelling properties. The mix proportions studied are given in Table 6.

Table 6. Mix Proportions of Vinyl Ester-Soil Composites by Weight

Mix	Vinyl Ester	Soil
V10	1	3.5
V11	1	3.0
V12	1	3.3

Polyester resin was also mixed with site soil. The resin was catalyzed with 2% by weight of 50% active benzoyl peroxide and promoted with 0.2% by weight dimethyl aniline. The set time was approximately 20 minutes and this could be increased by reducing the amounts of catalyst and promoter. The amount of soil that could be incorporated in the polyester resin while maintaining self-levelling properties was the same as for the vinyl ester resin tested. The optimum soil:polyester resin ratio was 3.3.

Furfuryl alcohol was catalyzed with p-toluenesulphonic acid. The proportion of catalyst used was 0.5 to 1% by weight for soil permeation mixes and 0.5 to 10% for direct mixing with soil.

2.4.2 Mixing Procedure

2.4.2.1 Cementitious and Latex Modified 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, latex (if any), bentonite, silica fume (if any), cement and sand (if any). The superplasticizer was mixed with water and any latex 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 specimens. Mixing was performed in a Blakeslee planetary type mixer. The same order of addition was maintained. Bentonite was mixed with water, superplasticizer and any latex for 5 minutes. Any silica fume was then mixed for 1 minute. Cement and any sand were added and mixed for 5 minutes.

2.4.2.2 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.

2.4.2.3 Polymer-Soil Composites and Polymer-Sand Grouts

For resins used to make polymer-soil composites and polymer-sand grouts, the promoter was added to the resin and stirred by hand. The promoted resin was transferred to the bowl of a planetary type mixer and the catalyst was added and mixed for 1 minute. Soil or sand was then mixed into the resin for 2 minutes. Surfactant was mixed in with sand prior to adding to resin.

Different mixing procedures were used with furfuryl alcohol. In order to simulate permeation grouting a catalyzed mix of furfuryl alcohol was poured over loosely compacted soil and allowed to seep in. Simulation of direct mixing with soil was performed in two ways. In the first method catalyzed furfuryl alcohol was mixed with soil and in the second method p-toluenesulphonic acid was first mixed with soil and furfuryl alcohol was then added and mixed.

2.4.3 Curing

All cementitious materials were covered with plastic sheet after casting to prevent evaporation. This was found to be of great importance since grouts and soil cements, particularly those containing silica fume and/or latex, would undergo plastic shrinkage cracking if not protected from excessive evaporation. Cementitious materials were demoulded 24 hours after casting and cured for 28 days for compressive strength tests. Some selected cementitious materials were also tested for 7 day strength. Two forms of curing were used for cementitious materials. Conventional curing in the form of submersing in water at room temperature was conducted in order to determine the 28 day strength when adequate cement hydration occurs. Simulation of the in-situ curing conditions for subsurface barriers was achieved by burying 24 hour old specimens in the received 200 l containers of site soil. For strength tests the specimens were maintained in soil until testing at 28 days after casting.

Resin based materials were demoulded 2 hours after casting and cured in air at room temperature. Compressive strength tests were performed at 24 hours age. One batch of vinyl ester-soil was buried in soil for 28 days prior to compressive strength testing in order to determine if there was any effect of in-situ curing.

For permeability tests it was necessary that specimens be saturated with water. Cementitious grouts and soil cements were maintained in water at room temperature until testing at 56 days age. This curing period and method was selected to ensure that adequate hydration had occurred and that the measurements would not be significantly affected by ongoing hydration reactions. Latex modified materials were cured in soil for 49 days and then placed in water for 7 days prior to testing at 56 days. Soil curing was adequate for the latex modified materials and prevented degradation of latex that can occur during water curing. Resin based materials for permeability tests were placed in a water bath 24 hours after casting and tested at 7 days.

2.4.4 Viscosity

Viscosity of cementitious and latex modified grouts was measured using a Fann 35A coaxial cylinder viscometer at 300 rpm. Measurements were taken immediately after mixing in the blender. A Brookfield viscometer was used to measure viscosity of uncatalyzed resins following the procedure given in ASTM D 2393-86. All viscosity measurements were conducted at room temperature.

2.4.5 Specific Gravity

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

2.4.6 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 $lb_f/100\ ft^2$. The strength was converted to Pa.

2.4.7 Flow Time

The flow, or efflux, time of cementitious and latex modified 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. 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.

2.4.8 Compressive Strength

Barrier and capping materials 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 C109-90. However, cylinders were used in preference to cubes since it was desired to compare grout strength with that for soil cements and resin materials for which cylinders were more appropriate. Cubes were only used for compressive strength measurements associated with freeze-thaw tests. The cylinders were 65 mm diameter and 150 mm long. After demoulding the cylinders were trimmed to 130 mm long using a cut-off saw. At the completion of the required curing period compressive strength was measured using a Forney compression tester. Measurements were conducted on 4 to 6 specimens per batch.

2.4.9 Flexural Strength

Flexural strength was not measured directly and was estimated using reported relationships between compressive strength. The estimates should be regarded as approximate only. Only the flexural strength of the soil cements was of concern as the mechanical properties of the developed cementitious grouts and polymer based materials far exceeded the requirements. The flexural strength of soil cements is approximately one-fifth to one-third of the unconfined compressive strength and can be estimated from Equation 1 (ACI Committee 230, 1990).

$$R = 0.51 \ (f_c)^{0.88} \qquad (1)$$

where R = flexural strength in psi
f_c = unconfined compressive strength in psi

2.4.10 Permeability

The water permeability was measured using a Ruska Model 1013 Liquid Permeameter. This gives uniaxial flow and does not apply a confining pressure. 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.

Preliminary measurements showed that the same value of permeability was determined whether tests were run over 24 hours or 1 week. Therefore, the chosen test time for the low permeability materials was 24 hours. Some tests were run for 72 hours. The initial readings were not taken until equilibrium flow was achieved. This usually took 0.5 to 1 hour to establish. For high permeability materials the test time was reduced to a few hours.

Permeability was calculated assuming D'arcy's Law for flow through porous materials as given in Equation 2.

$$K = uVL/APt \qquad (2)$$

where K = permeability (darcys)
u = viscosity of liquid (cP)
V = volume (cm^3)

L = length of specimen (cm)
A = cross-sectional area of specimen (cm^2)
P = pressure gradient across specimen (atm)
t = time (s)

Hydraulic conductivity, or permeability coefficient, is given by Equation 3.

$$K_H = Kdg/u \quad (3)$$

where K_H = hydraulic conductivity or permeability coefficient (cm/s)
u = viscosity of liquid (cP)
d = density of liquid (g/cm^3)
g = gravitational constant (cm/s^2)

2.4.11 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 Reeves Motodrive pump was used to transfer previously mixed grout (Mix 1) 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.

2.4.12 Freeze-Thaw Tests

The durability of candidate cap materials subjected to freeze-thaw cycles was determined. Grout Mix 1 and soil cement 1S5 were selected for testing. Beams 102 mm wide, 76 mm deep and 406 mm long were cast in accordance with ASTM C666-90. 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 C666 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.

2.5 Experimental Results

2.5.1 Cementitious Grouts

Properties of the unhardened cementitious grouts are presented in Table 7. Included in this table are the conventional cementitious grouts C1 and C2 used to make soil cements.

Table 7. Properties of Unhardened Cementitious Grouts

Mix	Viscosity (cP)		10 min. Gel Strength (Pa)		Flow Time (s)		Specific Gravity
	Mean	SD*	Mean	SD	Mean	SD	
1	50	2	72	1	17.4	1.0	1.95
2	71	2	31	1	13.6	0.3	1.96
3	36	1	53	1	27.5	1.3	1.91
4	73	2	31	1	17.6	0.2	1.95
5	40	2	100	1	21.9	1.6	1.90
6	65	1	45	1	17.5	1.2	1.94
C1	40	2	0	0	-	-	1.49
C2	12	1	0	0	-	-	1.25

* SD = standard deviation

Table 8 gives the measured properties of the hardened cementitious grouts. The 7 day strength was only measured on Mix 1 and this was wet cured.

Table 8. Properties of Hardened Cementitious Grouts

Mix	28 Day Strength (MPa)				7 Day Strength (MPa)		Permeability (10^{-10} cm/s)	
	Wet Cured		Soil Cured					
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	39.4	2.3	29.2	1.9	21.4	0.8	0.9	0.1
2	31.4	1.4	27.4	2.7	-	-	1.2	0.1
3	39.6	1.9	31.7	0.9	-	-	1.1	0.3
4	33.1	2.6	25.4	1.7	-	-	1.0	0.2
5	39.2	1.2	30.5	3.0	-	-	1.1	0.2
6	34.3	1.9	30.7	2.0	-	-	1.2	0.3

2.5.2 Latex Modified Grouts

Table 9 gives the measured properties of the unhardened latex grouts. The properties of the hardened grouts are given in Table 10.

Table 9. Properties of Unhardened Latex Modified Grouts

Mix	Viscosity (cP)		10 min. Gel Strength (Pa)		Flow Time (s)		Specific Gravity
	Mean	SD	Mean	SD	Mean	SD	
1L	94	2	48	1	16.2	0.7	1.63
5L	89	2	52	1	18.6	0.3	1.53
6L	60	1	31	1	14.2	0.1	1.54

Table 10. Properties of Hardened Latex Modified Grouts

Mix	28 Day Strength (MPa)				Permeability (10^{-10} cm/s)	
	Wet Cure		Soil Cure			
	Mean	SD	Mean	SD	Mean	SD
1L	11.0	0.7	11.4	0.6	0.63	0.05
5L	15.2	0.3	14.9	0.3	0.65	0.07
6L	9.9	0.5	8.7	0.4	0.81	0.03

2.5.3 Soil Cements

The properties of the soil cements containing specialized admixtures are given in Table 11. Specific gravity measurements were conducted on the unhardened material. The specimens for the 7 day strength tests were soil cured.

Table 11. Properties of Soil Cements

Mix	28 Day Strength (MPa)				7 Day Strength (MPa)		Specific Gravity	Permeability (10^{-10} cm/s)	
	Wet Cure		Soil Cure						
	Mean	SD	Mean	SD	Mean	SD		Mean	SD
1S1	32.9	2.8	27.0	3.0	14.6	1.3	2.05	1.2	0.2
2S1	24.4	1.5	21.2	2.2	-	-	-	1.7	0.2
3S1	25.1	0.8	25.0	3.0	-	-	-	1.0	0.3
4S1	20.8	0.4	18.4	1.5	-	-	-	1.7	0.2
5S1	31.7	1.7	26.7	1.4	-	-	2.04	1.3	0.4
6S1	26.6	0.7	21.4	1.2	-	-	2.00	1.5	0.4
1S2	25.3	0.3	20.9	2.3	5.4	0.1	2.03	2.5	0.1
5S2	23.4	2.2	22.1	1.3	-	-	2.00	2.1	0.3
6S2	19.5	1.4	14.7	0.4	-	-	1.99	2.4	0.3
1S5	6.5	0.7	6.1	0.3	2.6	0.3	2.01	3.9	0.4
5S5	8.8	0.9	6.8	0.8	-	-	1.98	3.7	0.4
6S5	7.3	0.3	5.4	0.2	-	-	1.99	3.4	0.1
1S5F	-	-	4.6	0.5	-	-	1.95	22	2.0
1S6	-	-	3.8	0.2	-	-	1.96	4700	800

Table 12 gives the properties of the conventional soil cements tested. Specimens for the 28 day strength tests were soil cured.

Table 12. Properties of Conventional Soil Cements

Mix	**28 Day Strength (MPa)**		**Specific Gravity**	**Permeability (10^{-10} cm/s)**	
	Mean	SD		Mean	SD
C1S1	7.8	0.3	1.74	44	4
C1S2	7.0	0.2	1.94	51	7
C2S5	2.9	0.1	1.92	31000	6000

2.5.4 Latex Modified Soil Cements

Data for the latex modified soil cements is given in Table 13.

Table 13. Properties of Latex Modified Soil Cements

Mix	28 Day Strength (MPa)				Specific Gravity	Permeability (10^{-10} cm/s)	
	Wet Cure		Soil Cure				
	Mean	SD	Mean	SD		Mean	SD
1LS1	13.8	0.7	13.5	1.2	1.82	1.5	0.2
5LS1	17.7	0.8	16.3	1.6	1.80	0.55	0.04
6LS1	18.1	0.4	16.8	0.9	1.73	2.5	0.4
1LS2	15.3	1.5	15.6	1.5	1.92	1.2	0.1
5LS2	14.9	1.2	14.5	0.9	1.84	1.2	0.2
6LS2	16.0	0.3	15.5	0.9	1.86	0.56	0.07
1LS5	-	-	1.0	0.1	-	-	-

2.5.5 Vinyl Ester-Sand Grouts

The results of 24 hour compressive strength and permeability measurements on the vinyl ester-sand grouts studied are given in Table 14. The optimum mix was V6 which had self-levelling properties without excess resin. The viscosity of this uncatalyzed mix was measured and found to be so high that the pumpability is questionable with conventional equipment.

Table 14. Properties of Vinyl Ester-Sand Grouts

Mix	24 Hour Strength (MPa)		Viscosity (cP)	Permeability (10^{-10} cm/s)	
	Mean	SD		Mean	SD
V3	78.9	2.9	-	-	-
V5	111.7	1.5	-	-	-
V6	101.9	2.6	24800	0.29	0.02
V7	93.7	2.4	-	-	-

2.5.6 Vinyl Ester and Polyester-Soil Composites

For both the vinyl ester and polyester resins the optimum soil:resin ratio which maintained self-levelling properties was found to be 3.3. The results of strength and permeability measurements on the resin-soil composites are presented in Table 15. "V" denotes vinyl ester and "P" denotes polyester. Specimens for 28 day strength tests were maintained in soil.

Table 15. Properties of Resin-Soil Composites

Mix	**24 Hour Strength (MPa)**		**28 Day Strength (MPa)**		**Permeability (10^{-10} cm/s)**	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**
V10	26.8	0.6	-	-	-	-
V11	33.5	0.8	32.5	1.0	0.94	0.1
V12	31.3	1.0	-	-	1.3	0.3
P1	25.8	2.7	-	-	1.1	0.07

2.5.7 Furfuryl Alcohol

Experiments showed that furfuryl alcohol would not cure when in the presence of soil. Catalyzed solutions that were poured over soil to simulate permeation grouting did not cure where seepage had occurred, but cured above the soil layer. Curing did not occur when catalyzed furfuryl alcohol was mixed with soil or when uncatalyzed furfuryl alcohol was mixed with soil containing various proportions of catalyst that usually caused polymerization. The failure of the furfuryl alcohol to cure was attributed to the high pH of the soil which interferes with the acidic conditions required for polymerization. As a result, work with furfuryl alcohol was discontinued.

2.5.8 Permeation Grouting Tests

Grouting tests performed in hand compacted soil showed that the grout displaced the soil to form a dense grout bulb. No penetration of the soil was observed. Injection pressures up to 1 MPa were measured. For tests in soil compacted to a pressure of 0.4 MPa some displacement and fracture of soil occurred. Uplifting of the entire cylinder of soil was also observed. Pressures were in excess of 1 MPa. The grouting tests confirmed that permeation grouting of the site soil with ordinary portland cement based grouts was not feasible. Displacement grouting did appear feasible.

2.5.9 Freeze-Thaw Tests

The soil cement 1S5 began to crack after 24 freeze-thaw cycles and by the end of 112 cycles had swollen and disintegrated. Failure was manifested as exfoliation of thin layers of soil cement. Grout Mix 1 showed pop-outs on the top surface as cast and a longitudinal shear type failure of the beam. Due to the failure cube compressive strength measurements of the beam could not be made. The surface degradation of the grout was probably due to formation of a weaker, more porous and permeable surface layer as a result of cement particle settling, although excessive bleeding was not observed. The observed longitudinal split in the grout beam was possibly due to propagation of shrinkage microcracks caused by the expansion of ice within the cracks.

The 28 day compressive strengths of cubes sawn from the control beams were measured and are presented in Table 16.

Table 16. Results of Freeze-Thaw Tests

Mix	Control Cube Strength (MPa)		Freeze-Thaw Cube Strength (MPa)		% Change
	Mean	SD	Mean	SD	
1	56.2	6.1	0	0	100
1S5	6.3	0.4	0	0	100

2.6 Discussion

2.6.1 Cementitious Grouts

The developed grouts showed suitable rheological properties and stability. The relatively low flow times suggest that further reduction of w/cm may be possible while maintaining a flow time less than 30 seconds. Conventional grouts (C1 and C2) showed excessive bleeding, segregation and shrinkage despite the addition of bentonite. Specimens for strength and permeability measurements could not be prepared from these grouts due to phase separation.

The viscosities of the developed grouts were strongly dependent on the proportions of bentonite, silica fume, superplasticizer, sand and w/cm. Addition of silica fume without alteration of other proportions causes an increase in viscosity. Through use of additional mixing water, higher dosages of superplasticizer and reduction of bentonite, the viscosities of silica fume modified grouts can be reduced. Grouts with sand had higher viscosities than those without and required significantly higher w/cm to produce low viscosities. The viscosities of the silica fume modified grouts are similar to those reported by

Al-Manaseer and Keil (1992) and Domone and Tank (1986) for similar mix proportions. The flow times of the grouts were less than 30 seconds which indicates good flowability. Flow time was also controlled by proportions of silica fume, superplasticizer, bentonite and w/cm. Viscosity and flow time cannot be correlated because different mixing procedures were used in the measurement of the two properties.

The rheological properties of the grouts could easily be further tailored to the end use through modification of mix proportions. For the grouts studied the maximum superplasticizer dosage was used. Therefore, further reduction of viscosity would require an increase in w/cm. Reduction of superplasticizer content for the silica fume modified grouts increased the thixotropic tendencies.

Gel strengths of the grouts were controlled by proportions of silica fume, bentonite, superplasticizer and w/cm. For displacement grouting gel strength and specific gravity are important parameters. Different stages of the displacement grouting process require different grout properties and mix proportions can be altered to suit (Nonveiller, 1989).

The 28 day wet cured compressive strengths of the grouts far exceed the minimum required for barriers or caps. The results showed that silica fume did not have a significant effect for grouts without sand with strengths being virtually identical for 0,5 and 10% replacement. The increase in w/cm from 0.40 for 0 and 5% silica fume grouts to 0.42 for 10% silica fume was not detrimental to strength, possibly indicating some compensation effect. High levels of superplasticizer in the silica fume grouts did not have an adverse effect on strength. Addition of sand and corresponding increase in w/cm lowered compressive strengths. The effect of silica fume on 28 day strength of cement-sand grouts was not statistically significant and the increase in w/cm required for 10% silica fume was not detrimental. For longer curing periods the influence of silica fume on strength may be more significant since silica fume content effects the rate of strength gain (Al-Manaseer and Keil, 1992, Mehta, 1984).

The compressive strength was strongly dependent on the specimen geometry. The mean 28 day wet cured strength measured on 75 mm cubes sawn from the control freeze-thaw beams for grout Mix 1 was 56.2 MPa compared with 39.4 MPa for cylinders.

Curing had a significant effect on 28 day strength. The water necessary for cement hydration is not as readily available in soil and the reduced water availability causes a decrease in strength for <u>in-situ</u> curing. The strength loss for grouts without sand was 20 to 26% and 11 to 23% for grouts with sand. No consistent trend between strength loss and silica fume content was observed. The least decrease in strength of 11% occurred for Mix 6 with 10% silica fume and w/cm = 0.68. The greatest decrease of 26% was for Mix 1 with no silica fume and w/cm = 0.40. For barrier grouts which cannot be readily water cured once placed, the strength loss associated with in-situ curing is an important consideration. If the site soil has a lower moisture content than the 8% used in the experiments the percentage strength loss can be expected to increase. However, the strengths are not likely to drop below the minimum value of 1-2 MPa required.

The 7 day strength of Mix 1 was 54% of the 28 day strength and indicated that early strength is also adequate.

The permeability coefficients measured for the six grouts were similar and three orders of magnitude below the EPA limit for barrier materials of 10^{-7} cm/s. The relatively high standard deviations calculated can be attributed to heterogeneity of the grout. High variability of replicate permeability tests is typical for concrete (Bisaillon and Malhotra, 1988, Whiting, 1988, and Hooton, 1989) and can be expected for cementitious grouts. The high w/cm used for the grouts with sand did not adversely affect permeability. This is probably due to the introduction of a tortuous path created by the distribution of fine sand particles throughout the cement paste matrix and results in a decrease in permeability. The high degree of moist curing experienced by the cement-sand grouts is also conducive to low permeability as measured since higher w/cm materials require longer curing periods in order to close continuous capillary pores that give rise to permeability (Neville, 1981).

The effect of silica fume on the permeability of the grouts studied was not significant. The increased w/cm used in conjunction with silica fume may have masked any permeability benefit. It is possible that the levels of permeability reduction associated with silica fume modified concrete are not observed for the grout formulations due to the much higher cement contents used.

Direct comparison of the results obtained with reported grout permeabilities is limited due to the large variation in materials, mix proportions, curing periods, test periods and test equipment used. The permeabilities were lower than those reported for fly ash modified grouts which had higher w/cm but similar viscosities (Tallent et al, 1986).

Water curing for 56 days was used to reduce the effect of hydration reactions on permeability measurements. However, the vertical and bottom barriers are unlikely to receive this form of curing and subsequent degree of hydration. Hence, the permeabilities of in-situ cured materials is likely to be greater than those measured on water cured specimens. In order to determine a quantitative indication of the effect of in-situ curing on permeability specimens from Mix 1 were buried in site soil for 56 days and tested. The mean permeability coefficient increased to 1.5×10^{-10} cm/s compared with 9.0×10^{-11} cm/s for water curing. Despite the increase, the permeability is still acceptably low.

The freeze-thaw test conducted on Mix 1 indicated that this grout had insufficient long term resistance to freezing and thawing cycles. The observed surface pop-out failure suggested that a weaker, more porous surface layer forms on the grout and that a reduction in bleeding is required, although free water was not observed on this grout mix. The failure of the entire beam suggested the possibility of shrinkage microcracks. If long term freeze-thaw resistance is deemed necessary for the caps, the grouts probably require addition of an air entraining agent as well as improvement of shrinkage and bleeding behavior. Further mix optimization and addition of an air entraining agent is required for freeze-thaw durability.

All of the six grouts have suitable strength and permeability for use as barriers. However, it was noticed that Grout 1 cracked if allowed to dry out in air after curing in water whereas Grout 2 did not crack under the same conditions. It is possible that this form of cracking may also occur for silica fume grouts without sand since silica fume increases the risk of plastic shrinkage cracks. This observation indicates poor wet-dry cycle durability of grouts without sand which probably results from high cement content and associated shrinkage stresses and microcracks. Therefore, grouts without sand are probably not suitable as solid caps or barriers.

Based on the strength and permeability results, silica fume does not produce a significant improvement in strength and permeability of the hardened grout. It is possible that the durability of silica fume modified grout is superior to ordinary grout due to reduced free $Ca(OH)_2$ that occurs as a result of the pozzolanic reaction between silica fume and $Ca(OH)_2$ from cement hydration to form calcium silicate hydrate. The reduction of free $Ca(OH)_2$ improves resistance to chemical attack from aggressive species such as sulphates, carbon dioxide and acids. In the relatively benign exposure environment for the barriers and caps it is uncertain as to whether increased durability that may result from inclusion of silica fume is necessary.

The results indicate that Mix 2 is an appropriate grout and that use of silica fume modified grout is only justified if durability improvements are required and can be demonstrated. Further work on refinement of mix proportions for the applications could lead to improvement in properties. For example, it may be possible that grouts with reduced w/cm and slightly higher viscosities and flow times can be used with the placement techniques. This would improve strength, permeability and durability. In addition, properties not investigated in this project, such as shrinkage, require optimization. This is particularly important for grouts without sand since the high cement content will predispose the grout to shrinkage and possible shrinkage cracking. Possible means of controlling shrinkage are use of expansive agents such as calcium sulphoaluminate or use of fibers.

2.6.2 Latex Modified Grouts

Suitable self-levelling grouts that included latex could be formulated. Compared to the original cementitious grouts, the latex modified grouts had higher viscosities and slightly lower flow times. The low flow times indicated good flowability. Gel strength was reduced by addition of latex.

The wet cured 28 day strength of latex modified grouts was significantly lower than that for corresponding unmodified grouts. The percentage losses of strength were 72, 61 and 71% for Mixes 1L, 5L and 6L respectively. Loss of strength of latex modified mortar and concrete subjected to prolonged wet curing or wet exposure conditions has been reported previously (Ohama, 1984, Popovics, 1987). As a result, it is important that latex modified grouts are not continuously wet cured. Optimum curing of latex modified grout involves wet curing for 1 to 3 days to promote cement hydration followed by drying at ambient temperature (Ohama, 1984). Strength loss is reversible by drying (Ohama, 1984).

Latex modified grouts that were cured in site soil for 28 days also showed significant strength loss and the final strengths were almost identical to the 28 day wet cured values. The percentage losses of strength compared with unmodified soil cured grouts were 61, 51 and 72% for Mixes 1L, 5L and 6L respectively. The results indicate that significant strength loss can be expected for in-situ curing when surrounding soil is moist. The percentage loss of strength may decrease if the soil contains less moisture than the 8% by weight used in the experiments. The strength of latex modified grouts exposed to wet soil would probably be similar to that measured for wet curing. It is evident that incorporation of latex in grouts does not overcome strength loss due to insufficient hydration of unmodified grouts cured in-situ. The compressive strength of latex modified grouts remains above the minimum required for barriers and caps despite the observed decrease.

Use of latex in the grouts decreased the permeability coefficient compared to the corresponding water cured unmodified grouts which had equal or slightly higher w/cm. Permeability coefficients were similar for Mixes 1L and 5L. Mix 6L had a higher permeability and this can be attributed to the higher w/cm. The permeability coefficient of Mix 1L was more than half that measured for Mix 1 which was cured in soil. Specimens were examined under an optical microscope and the pore blocking behavior of latex film was clearly evident. Thus, latex is effective at reducing permeability.

Partial replacement of cement by silica fume in Mix 5L improved compressive strength but did not reduce permeability for the curing conditions studied. Therefore, if improved strength is required for subsurface barriers then silica fume is useful. For latex modified caps further study of optimization of mix proportions for combined wet and dry curing is necessary before recommendations can be made.

Shrinkage was not measured quantitatively, but it was visually observed that latex modified grouts shrunk less than those without latex. In addition, latex modified grouts without sand did not crack on drying out as did Grout 1.

In summary, addition of latex is beneficial for permeability reduction but adversely affects compressive strength for the likely in-situ curing and prolonged exposure conditions of subsurface barriers. Popovics (1987) has reported that strength loss of latex modified concrete under wet conditions can be counterbalanced through use of a carboxylic acid type accelerator and this could be a possible means of compensating strength loss observed for in-situ curing. If latex modified grouts are considered for subsurface barriers some means of controlling strength loss should be investigated. The latex modified grouts appear to be more suited to use as surface caps where suitable curing conditions can be applied and exposure conditions are predominantly dry in the arid environment. Lower latex/cement ratios of 0.05 to 0.15 may be more suitable.

2.6.3 Soil Cements

The soil cements made using the grouts containing admixtures showed low shrinkage, no bleeding and few air voids. Strength decreased with increase in soil and water content. The greatest decrease in 28 day wet cured strength for s/cm = 1 was observed for the two mixes which contained 5% cement replacement by silica fume. At s/cm = 1 and 2 soil cements with sand and higher w/cm had lower strengths. The presence of silica fume in soil cements with s/cm = 5 led to a slight increase in wet cured strength. The relationship between strength and s/cm for wet curing is shown in Figures 2 and 3.

The in-situ cured 28 day strengths of the soil cements were lower than the wet cured strengths. However, the proportional decrease was less than that for grouts. At s/cm = 5 the in-situ cured strengths of the three soil cements were virtually the same indicating that the mix proportions of the parent grout have reduced effect. The high w/cm for Mix 6S5 appeared to be compensated by the higher grout:soil ratio necessary to maintain s/cm = 5. Figures 4 and 5 depict the effect of s/cm on strength for in-situ curing. The effect of curing conditions diminished as s/cm increased and was not significant at s/cm = 5. This is shown graphically in Figures 6 to 8. Silica fume did not appear to play an important role in strength for in-situ curing at any s/cm. For both forms of curing the 28 day compressive strengths were adequate for the applications even at s/cm = 5. The 7 day strengths were also adequate.

When s/cm was increased to 6 a further decrease in compressive strength was observed. The low strength measured raised doubts concerning the durability of a soil cement with this high proportion of soil. The effect of adding extra mixing water on soil cement with s/cm was illustrated by Mix 1S5F which showed a

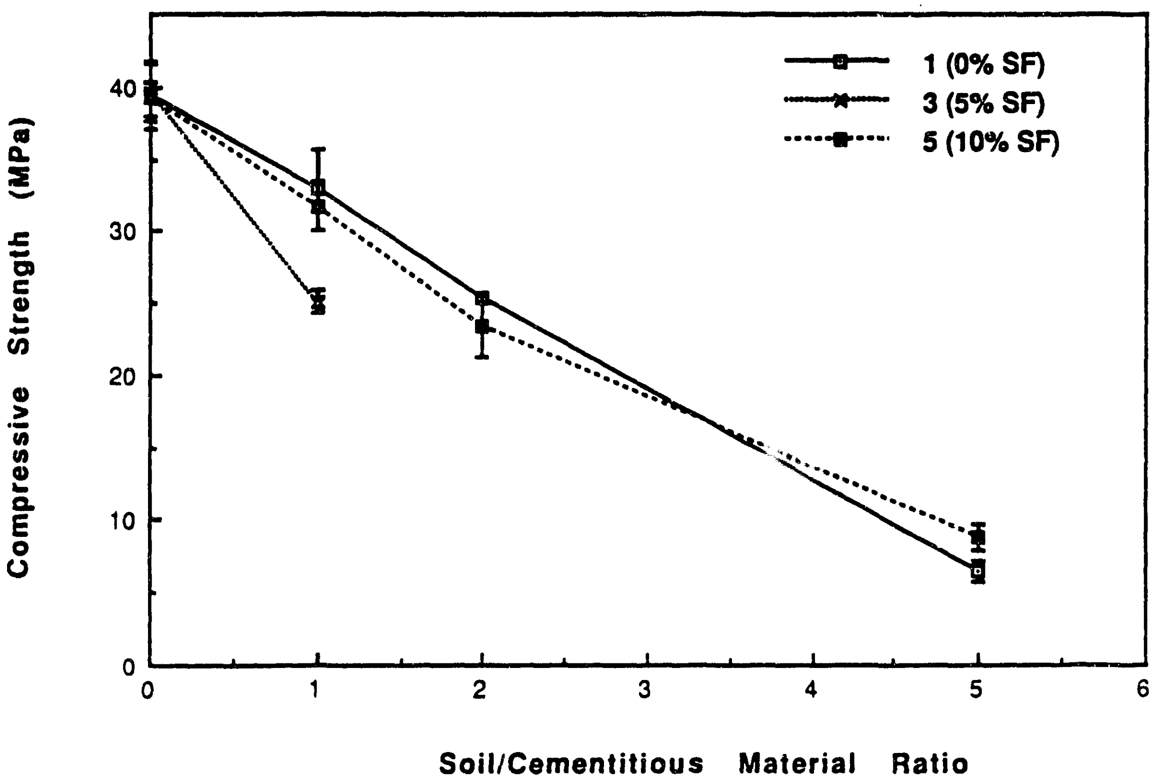

Figure 2. Strength versus Soil/Cementitious Material Ratio for Wet Cured Grouts Without Sand.

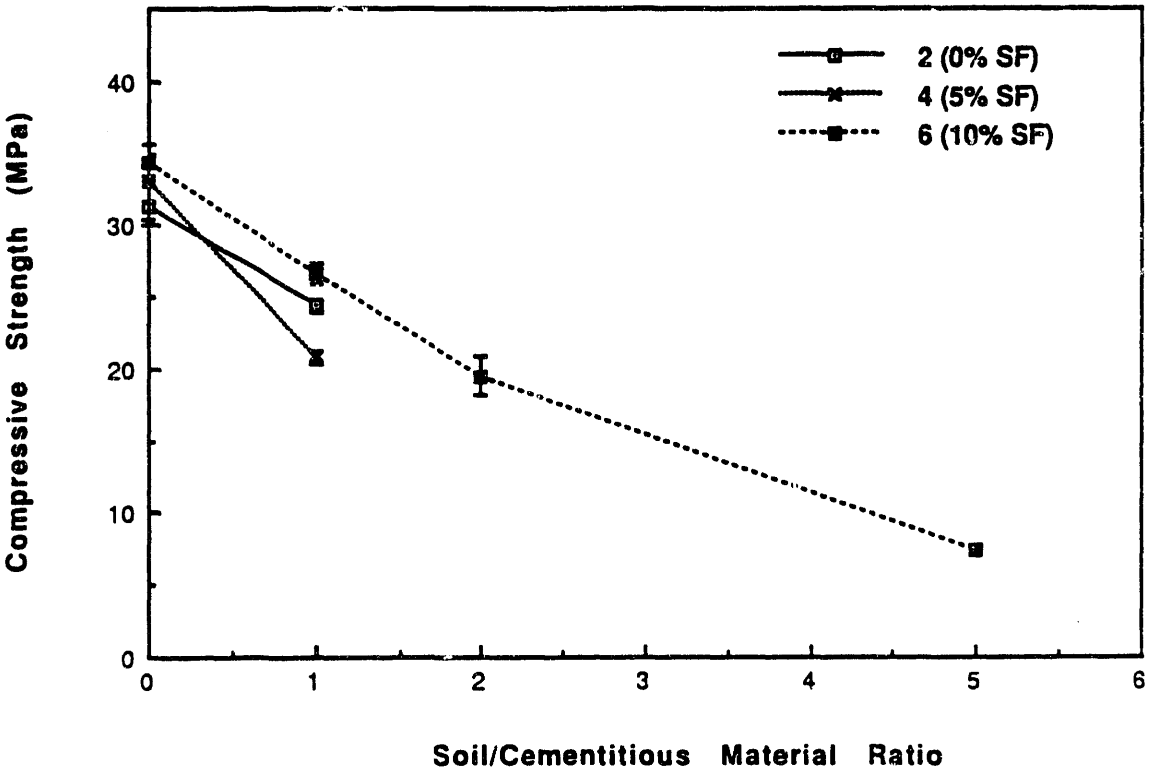

Figure 3. Strength versus Soil/Cementitious Material Ratio for Wet Cured Grouts With Sand.

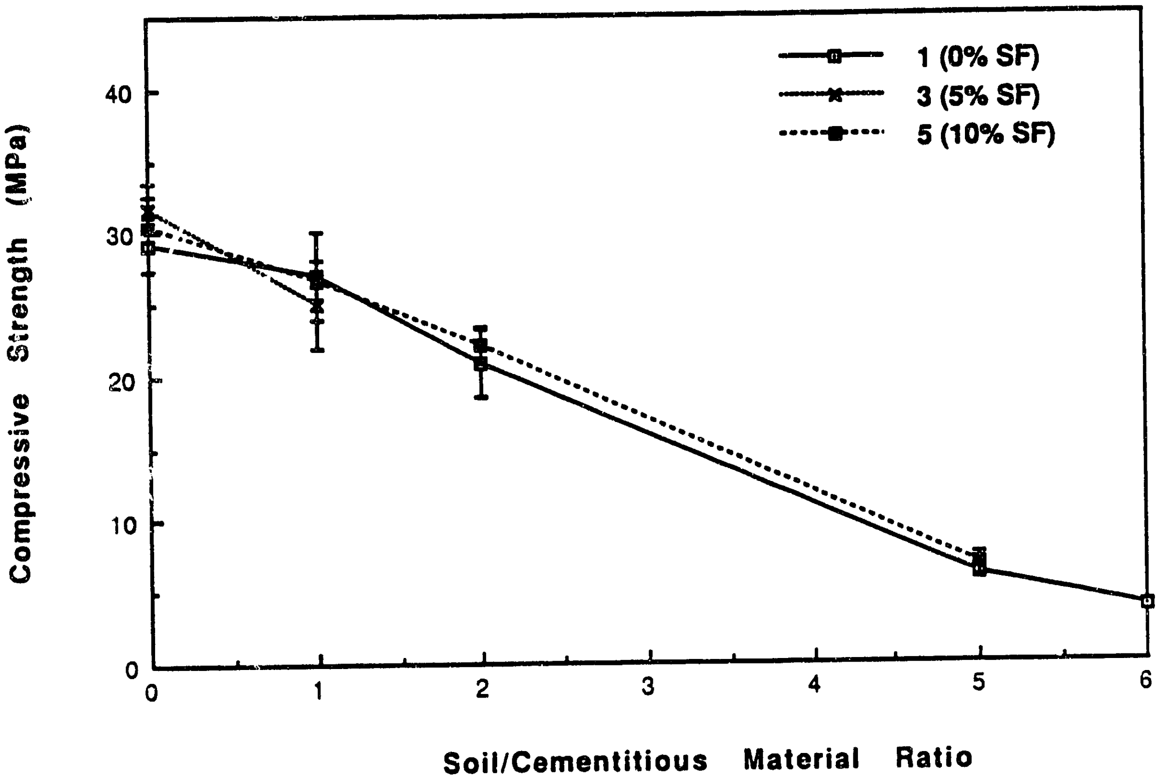

Figure 4. Strength versus Soil/Cementitious Material Ratio for In-Situ Cured Grouts Without Sand.

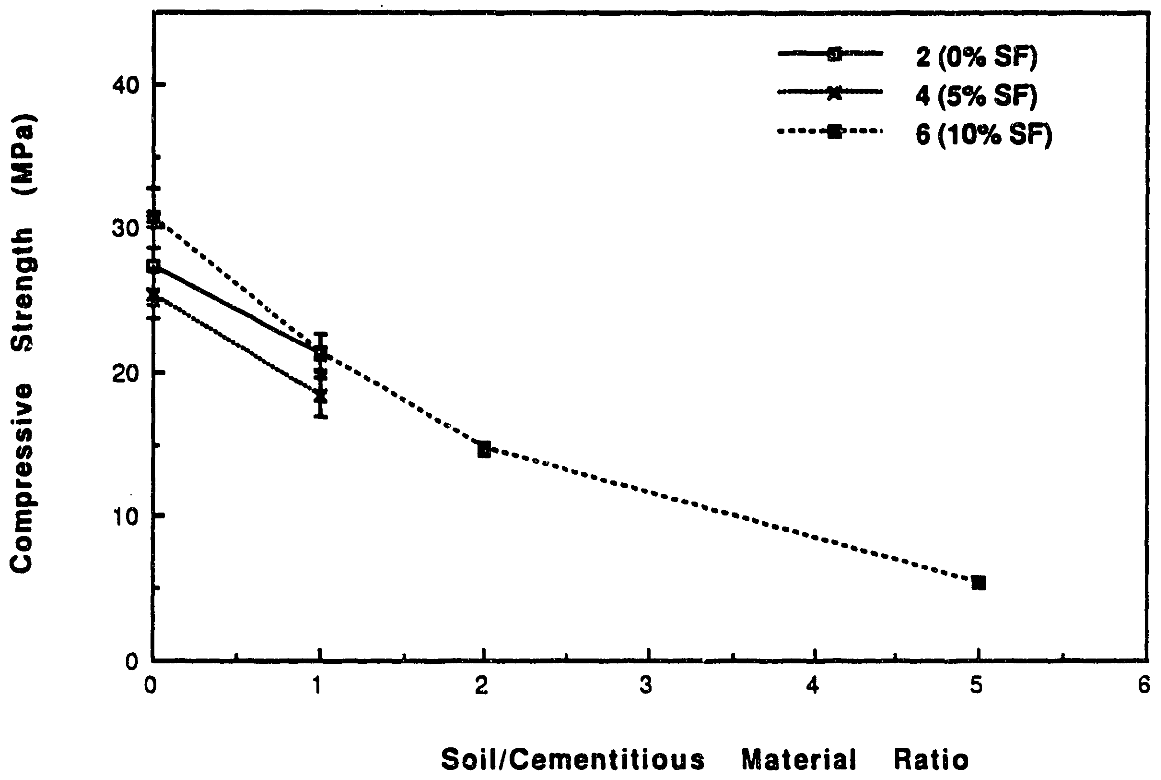

Figure 5. Strength versus Soil/Cementitious Material Ratio for In-Situ Cured Grouts With Sand.

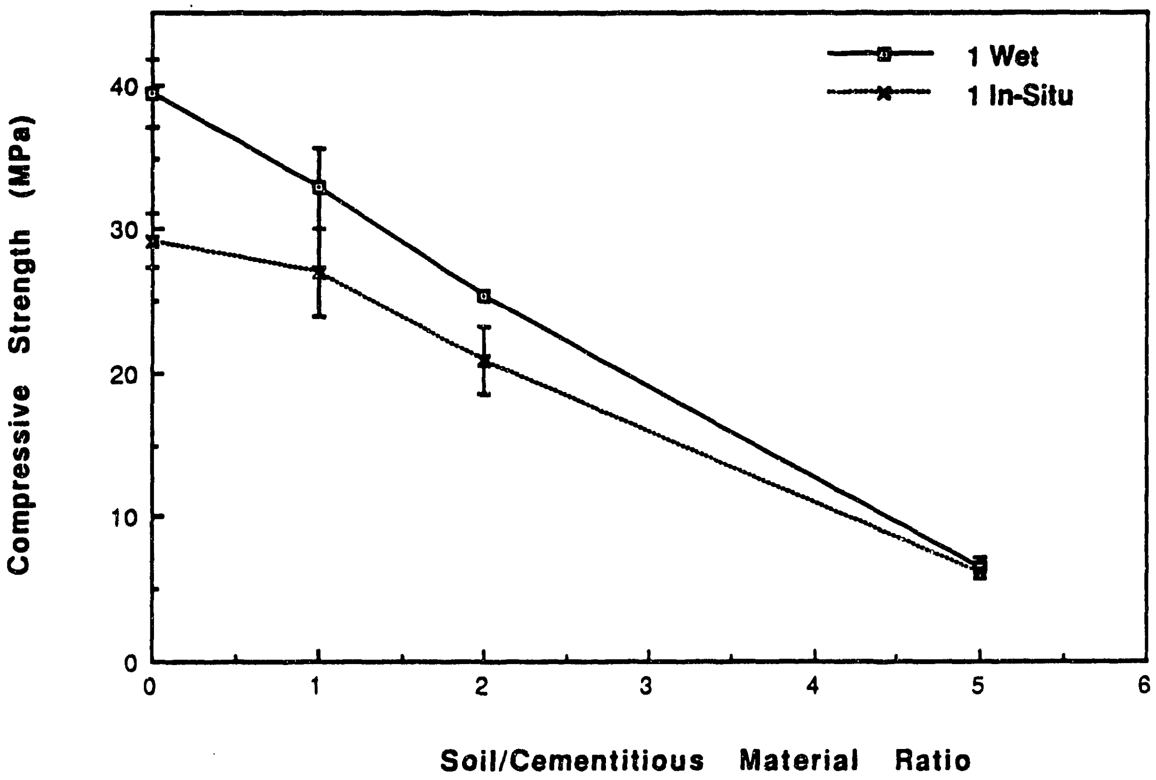

Figure 6. Effect of Curing on Strength for Mix 1 Grouts and Soil Cements.

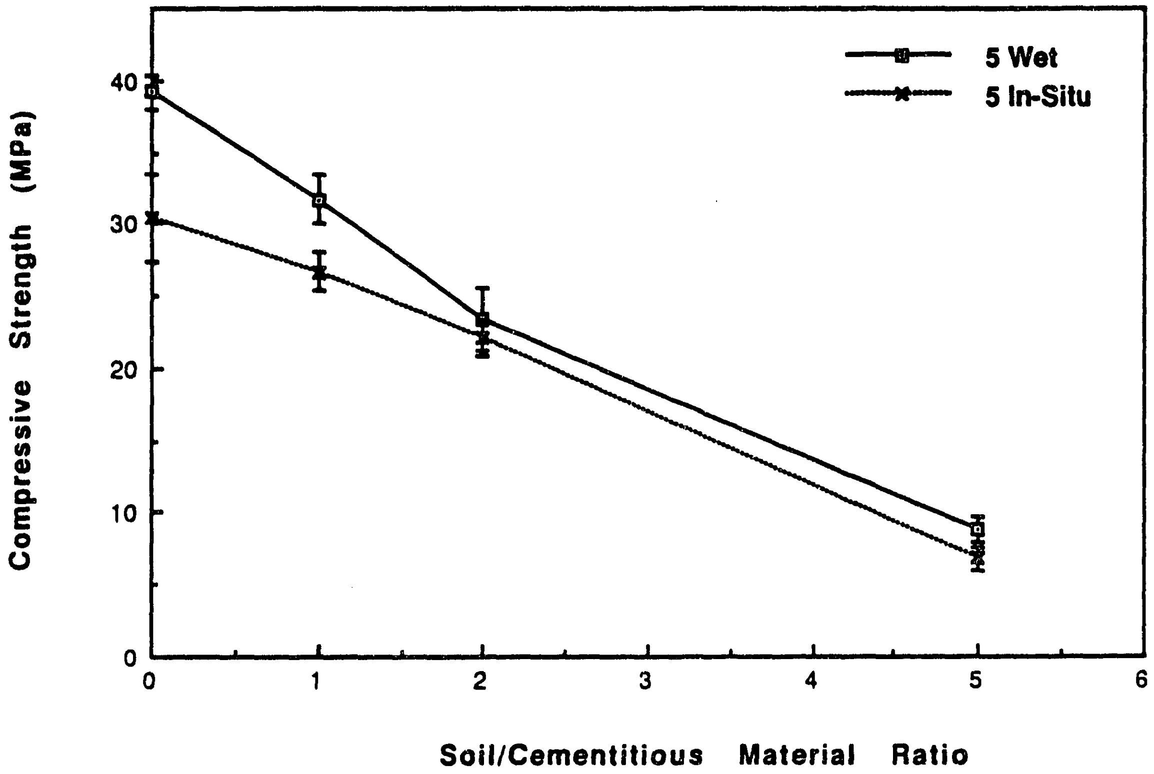

Figure 7. Effect of Curing on Strength for Mix 5 Grouts and Soil Cements.

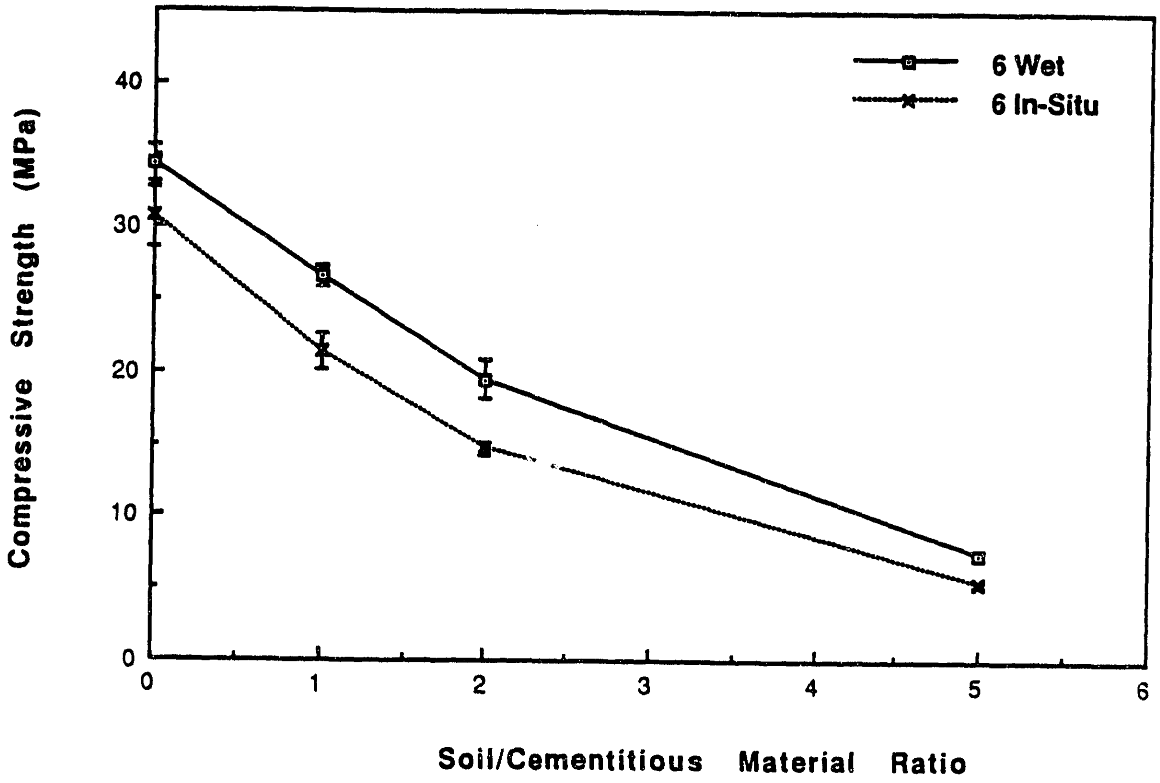

Figure 8. Effect of Curing on Strength for Mix 6 Grouts and Soil Cements.

38% decrease in strength when w/cm was increased from 1.20 to 1.34 to improve flow properties. This indicates that w/cm must be controlled strictly in order to maintain required strength.

The majority of the in-situ cured strengths exceed the durability guideline value of 5.5 MPa. However, Mixes 6S5, 1S5F and 1S6 fall below this value. Mixes 1S5 and 5S5 are just above 5.5 MPa. This suggests that further durability testing of these soil cements is necessary before their use can be recommended. Lower s/cm of 3 or 4 may be required for improved strength and durability.

The role of parameters such as w/cm, cementitious content and grout/soil cement ratio by volume in the control of in-situ cured strength for the developed soil cements is shown in Figures 9 to 11. Compressive strength decreases with increasing w/cm and increases with increasing cementitious content in the same manner for all three parent grouts. Strength increases with increasing grout/soil cement ratio by volume and the curve shifts to the right for the parent grout that contains sand as shown in Figure 11. These curves can be used to predict strength for given mix parameters.

Soil cements prepared with grouts that had water/cement ratios of 1 and 2 showed excessive bleeding. The in-situ cured 28 day strengths of conventional type soil cements were compared with those for the developed materials containing admixtures. For s/cm = 1 the mean strength of the conventional soil cement was 71% lower than that for Mix 1S1. This is a significant decrease. Similarly, at s/cm = 2 the mean strength of the conventional soil cement was 66% lower than that for Mix 1S2, also representing a significant decrease. This indicates that use of admixtures in the parent grout, particularly superplasticizer to reduce w/cm, has a profound effect on in-situ cured strength for s/cm = 1 and 2. The conventional soil cement with s/cm = 5 had a mean strength of 2.9 MPa which is 52% lower than the corresponding Mix 1S5 with admixtures. This low strength suggests that the mix may not have sufficient durability for the purpose.

The developed soil cements have higher strengths than jet grouted soils with similar cement contents reported by Guatteri et al (1988) due to the lower w/cm used in this work. The type and size distribution of the soil used may also influence strength and Guatteri et al (1988) have demonstrated that sandy silt type soils give lower strengths when jet grouted than sand with gravel soils for the same w/cm and cement content. Therefore, some variation in strength with location and depth of jet grouted or deep soil mixed barriers could be expected. Variation in soil moisture content may also alter the added mixing water requirement and the final strength of the soil cement.

The flexural strength of the soil cements was estimated using Equation 1. The results of this calculation are given in Table 17.

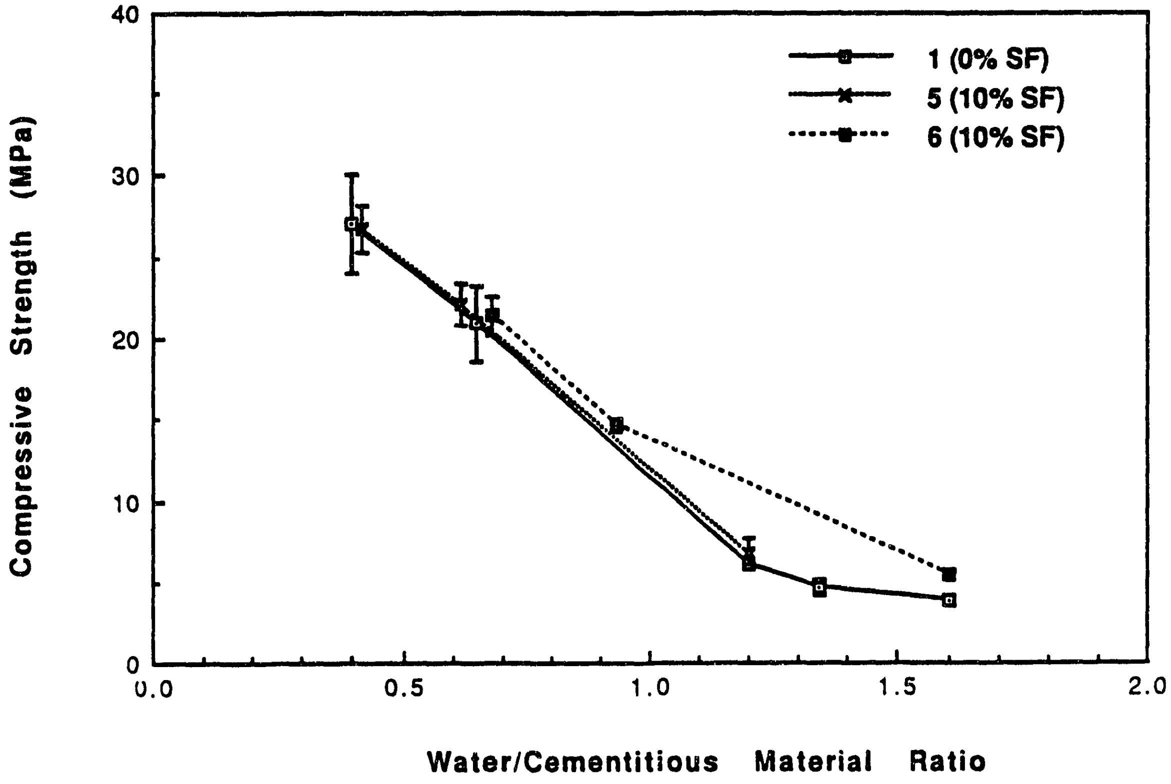

Figure 9. Effect of Water/Cementitious Material Ratio on In-Situ Cured Strength.

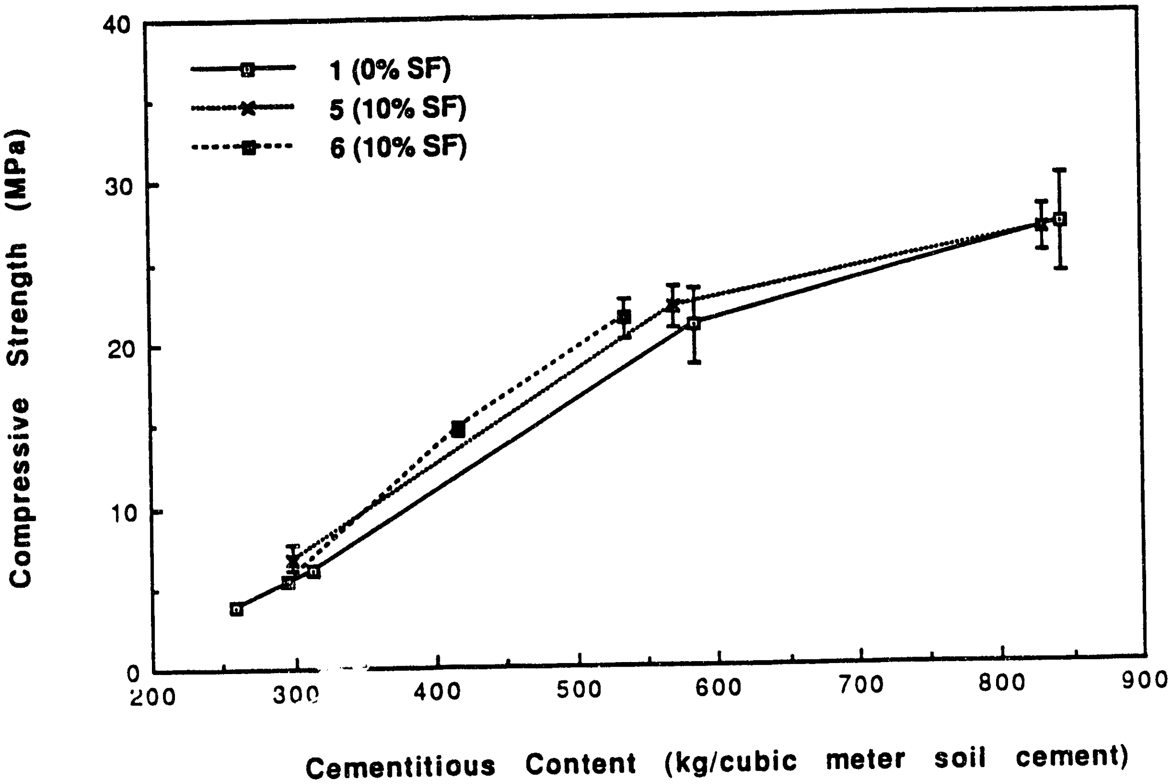

Figure 10. Effect of Cementitious Content on In-Situ Cured Strength.

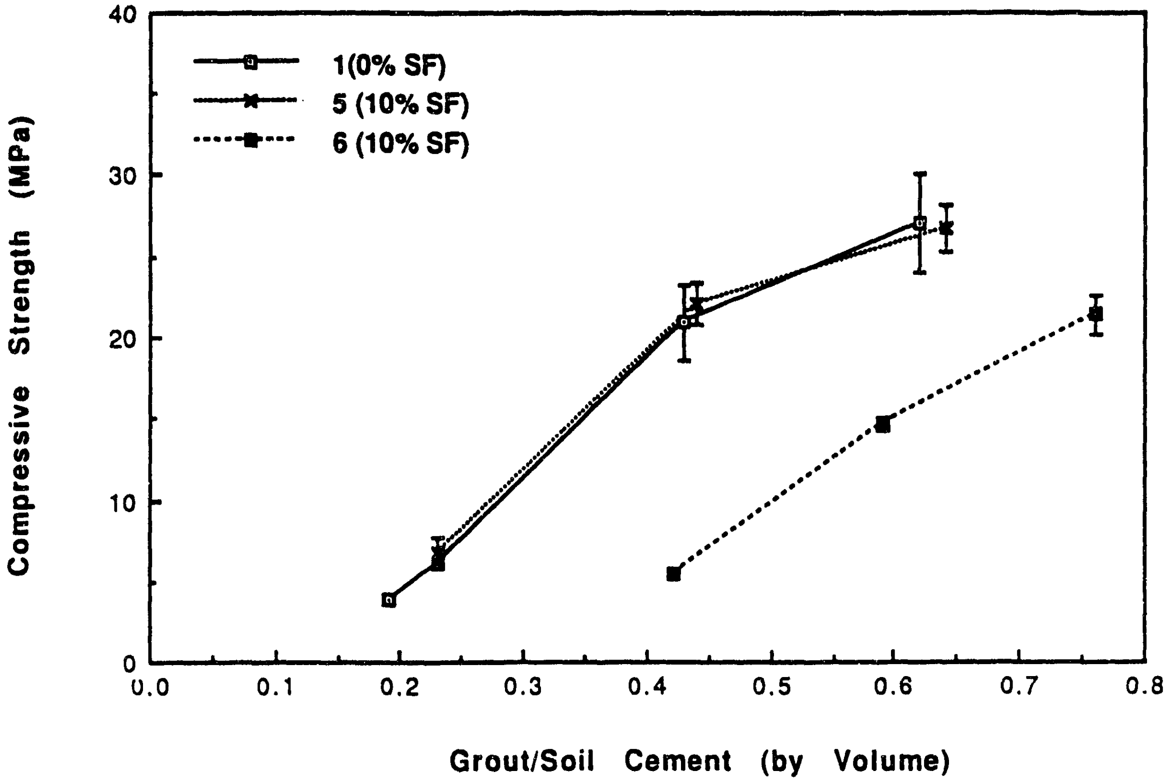

Figure 11. Effect of Grout/Soil Cement Ratio on In-Situ Cured Strength.

Table 17. Estimated Flexural Strengths for Soil Cements

Mix	Estimated Flexural Strength (MPa)
1S1	5.1
5S1	5.0
6S1	4.2
1S2	4.1
5S2	4.3
6S2	3.0
1S5	1.4
5S5	1.5
6S5	1.2
1S5F	1.1
1S6	0.91
C1S1	1.7
C1S2	1.5
C2S5	0.71

The results of the permeability tests for soil cements presented in Table 11 indicate that at s/cm = 1 the permeability coefficient tends to be slightly greater than that for the parent grout. At s/cm = 2 the permeability coefficient was approximately double that of the parent grout. Silica fume did not appear to have a significant effect on permeability. The permeability coefficients for s/cm = 5 were similar. Mix 6S5 had similar values to Mixes 1S5 and 5S5 despite the higher w/cm used. The higher grout: soil ratio may compensate for the high w/cm. Permeability increased dramatically when s/cm was increase to 6 for Mix 1S6. The associated increase in w/cm from 1.2 to 1.6 is another contributing factor to the permeability increase. This soil cement had a permeability over three orders of magnitude greater than that for soil cements with s/cm = 5. It is apparent that s/cm = 5 is the upper limit for a low permeability soil cement for the grout and soil types studied. Raising w/cm from 1.2 to 1.34 for Mix 1S5F increased permeability by a factor of 5 thus indicating the importance of maintaining a minimum w/cm.

The relationship between permeability coefficient and s/cm for the soil cements for s/cm = 0 to 5 is shown in Figure 12. The materials show a similar response to increase in soil content. Figures 13 - 15 show the effect of w/cm, cementitious content and

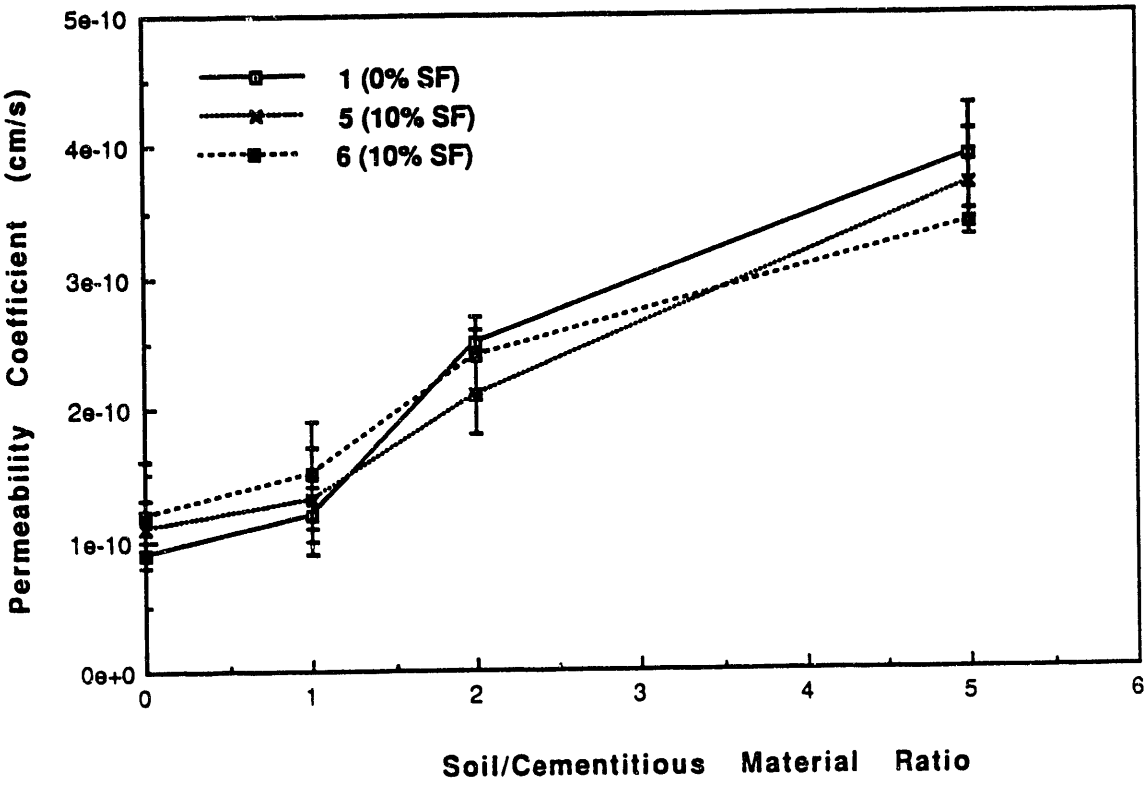

Figure 12. Permeability Coefficient versus Soil/Cementitious Material Ratio.

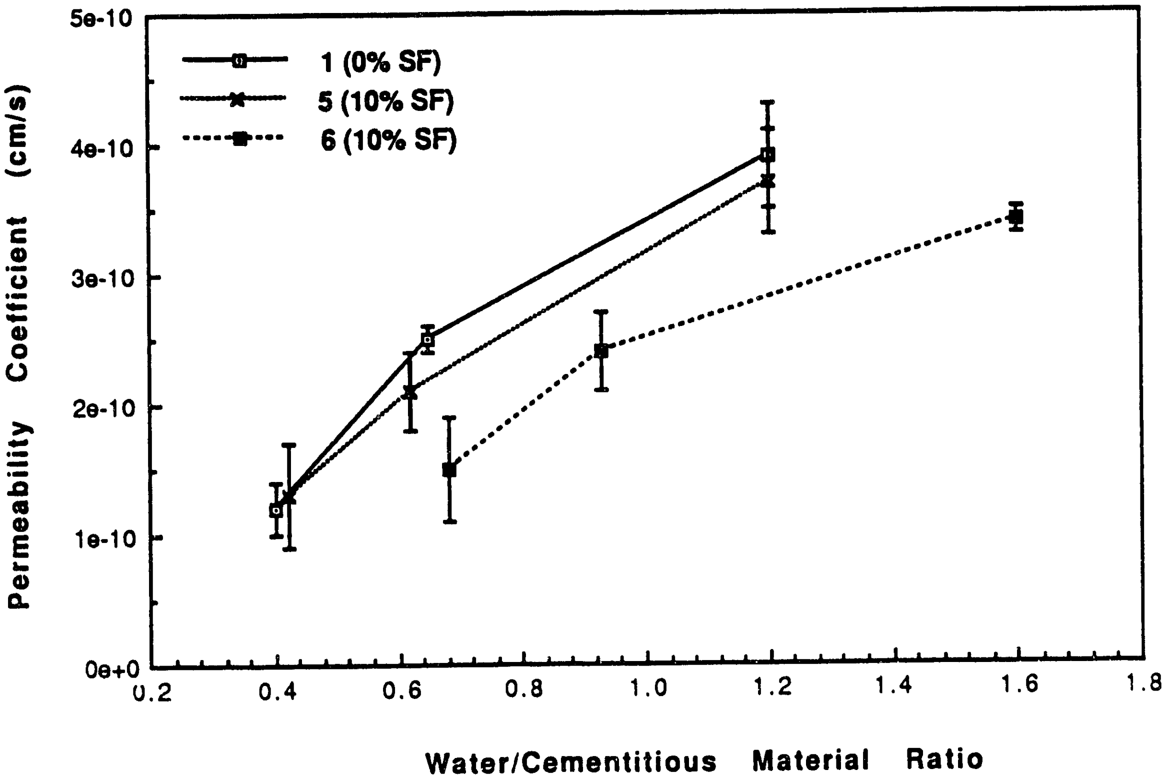

Figure 13. Effect of Water/Cementitious Material Ratio on Permeability Coefficient.

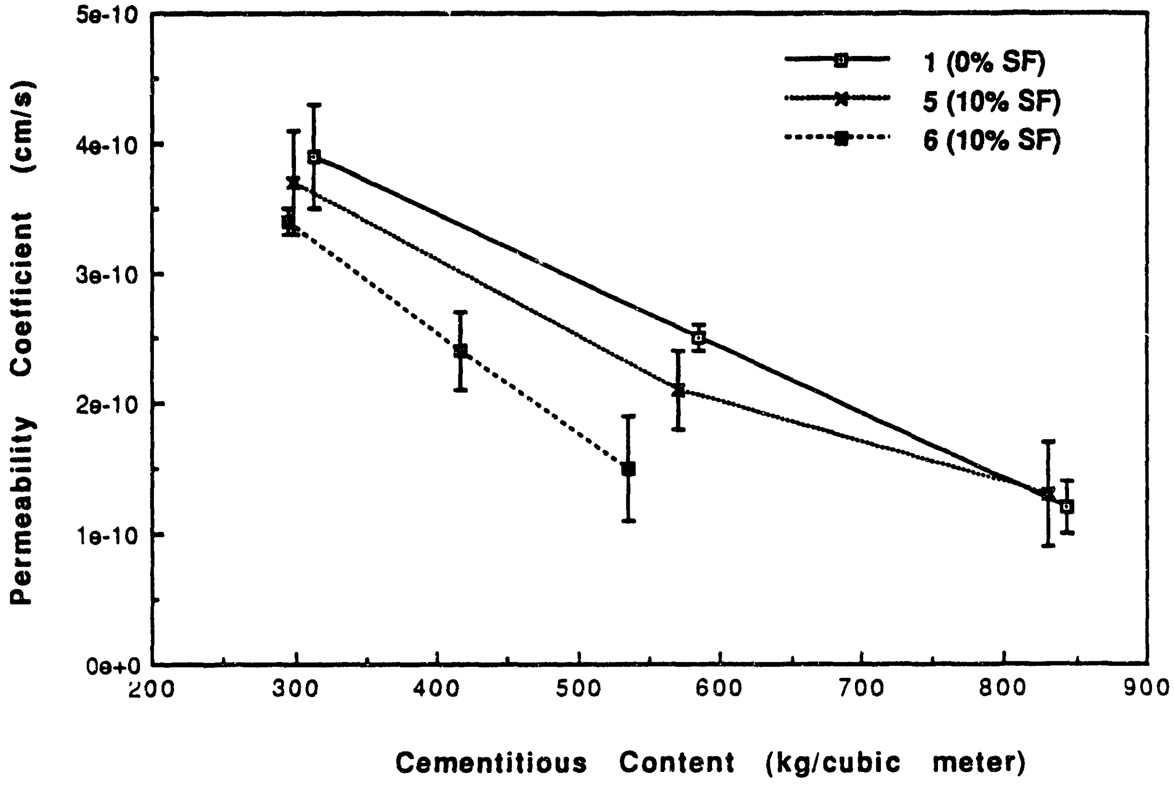

Figure 14. Effect of Cementitious Content on Permeability Coefficient.

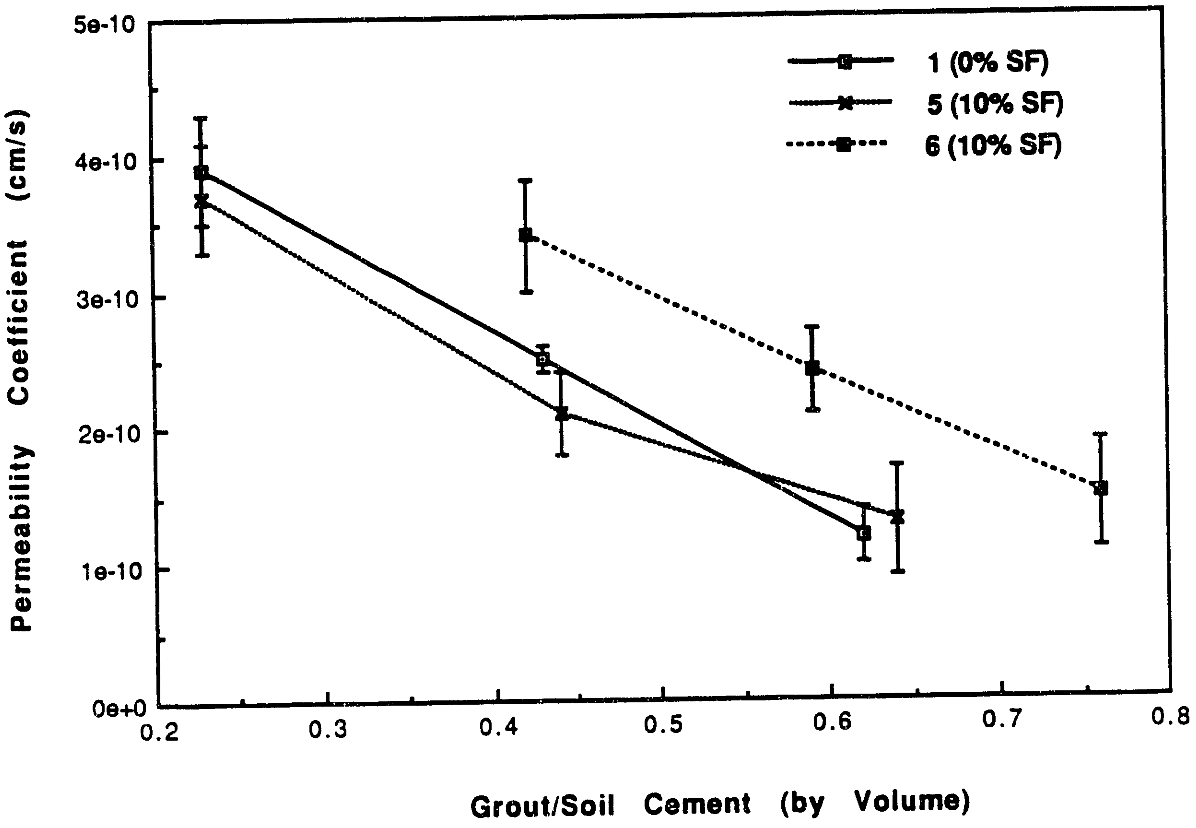

Figure 15. Effect of Grout/Soil Cement Ratio on Permeability Coefficient.

grout/soil cement ratio on permeability coefficient for s/cm = 1 to 5. In Figure 13 it is observed that the plot of permeability coefficient against w/cm shifts to the right for soil cements based on Mix 6, whereas the two parent grouts without sand show similar behavior. For the relationship between permeability coefficient and cementitious content in Figure 14, the soil cement based on Mix 6 has lower permeability at a given cementitious content than those based on Mixes 1 and 5. Figure 15 shows that for a given grout/soil cement ratio soil cements based on Mix 6 have higher permeability coefficients.

The permeability coefficients of the soil cements containing admixtures with s/cm less than or equal to 5 were all far less than the limit of 10^{-7} cm/s and thus, are suitable barrier and cap materials. Higher soil contents and associated higher w/cm give soil cements with unacceptably high permeability. The use of grouts containing sand for deep and shallow soil mixing and jet grouting by penetration may require investigation of the practical aspects since sand particles of unsuitable size could cause nozzle blockage.

The conventional soil cements with water/cement ratios of 1 and 2 had significantly higher permeabilities than those prepared from grouts containing admixtures. For s/cm = 1 the mean permeability coefficient of the conventional soil cement was 4.4×10^{-9} cm/s which is 38 times higher than Mix 1S1. When s/cm was increased to 2 the mean permeability coefficient increased to 5.1×10^{-9} cm/s and this represented a 20 fold increase over the comparable Mix 1S2. At s/cm = 1 and 2 the permeabilities of the conventional soil cements were still acceptable. However, when s/cm was increased to 5 and w/cm was increased to 2 for Mix C2S5 the mean permeability coefficient showed a dramatic increase to 3.1×10^{-6} cm/s. Such a high permeability is unacceptable for cap or barrier materials. The permeability coefficient was approximately 4 orders of magnitude greater than that for Mix 1S5. The results indicate that significant improvement in reducing permeability can be achieved through use of superplasticizers to reduce the w/cm ratio of the grout and using the minimum amount of added water necessary for self-levelling.

The permeability results can be compared with other published results for workable soil cements. Kunito et al (1989) found that the permeability coefficient of soil cements suitable for use with soil mixing techniques ranged from 2×10^{-8} to 10^{-5} cm/s after 28 days curing. The high permeabilities can be attributed to the high w/cm used of 1.5 to 2.5. Similar results were obtained for the conventional soil cements produced in this project. Permeability increased with increasing sand:clay ratio, increasing w/cm and decreasing curing time. The relationship between grouting ratio and permeability was not definite. Tallent et al (1987) measured permeability coefficients of 10^{-10} to 10^{-9} cm/s for soil mixed with cement-fly ash grouts with s/cm 0.47 to 1.1 and w/cm 0.53 to 0.71.

As was the case for strength, the permeability coefficient of soil cement can be expected to change with soil type, moisture content, particle size and amount of added mixing water.

The freeze-thaw test conducted on Mix 1S5 indicated that this material is unsuitable for any application that involves freeze-thaw cycling. Soil cements with lower soil contents require freeze-thaw testing in order to determine whether they are suitable as caps that might undergo such exposure.

2.6.4 Latex Modified Soil Cements

Soil cements which were modified with latex in an attempt to reduce permeability showed a decrease in compressive strength. For s/cm = 1 the 28 day wet cured strengths were 32 to 58% lower than the unmodified soil cements. The decrease in strength was 18 to 39% for s/cm = 2. The 28 day in-situ cured strengths of the latex modified soil cements were virtually identical to the wet cured strengths for s/cm = 1 and 2, as was the case for latex modified grouts.

When s/cm was increased to 5 for Mix 1LS5 the in-situ cured strength showed a dramatic decrease to 1.0 MPa. The material was also extremely soft. The low strength is inadequate for caps or barriers and indicates that latex is not a suitable admixture at high s/cm and high w/cm. The decrease in strength is possibly due degradation of the latex by salts within the soil. Such degradation may have also occurred to a lesser extent in soil cements with lower s/cm but was not as profound. Therefore, the long term behavior of latex modified soil cements is of concern if there is a possibility of destructive interaction between latex and soil.

The strengths of Mixes 1LS1,1LS2, 6LS1 and 6LS2 were higher than the corresponding parent grouts while the variations on Mix 5L showed similar strengths at different s/cm. This is depicted in Figures 16 - 18. The relationship between strength and s/cm for latex modified materials does not show the almost linear decrease observed for unmodified materials. A possible reason for the strength behavior is that latex causes a decrease in strength and the amount of decrease is proportional to the latex content of the material. Thus, as s/cm and soil:grout increase the latex content decreases and the influence on strength diminishes. Changes in parameters such as w/cm and cement content that accompany the decrease in latex with increasing s/cm counterbalance any benefits of reduced latex on strength. Possible degradation of latex at higher s/cm and w/cm as was observed for Mix 1LS5 would alter this relationship.

Latex had a mixed effect on permeability of soil cements as shown in Figure 19. For s/cm = 1 the latex modified soil cement with Mix 1L parent grout had similar permeability to the corresponding unmodified soil cement. However, for Mix 5L the permeability at s/cm = 1 was lower than the equivalent unmodified

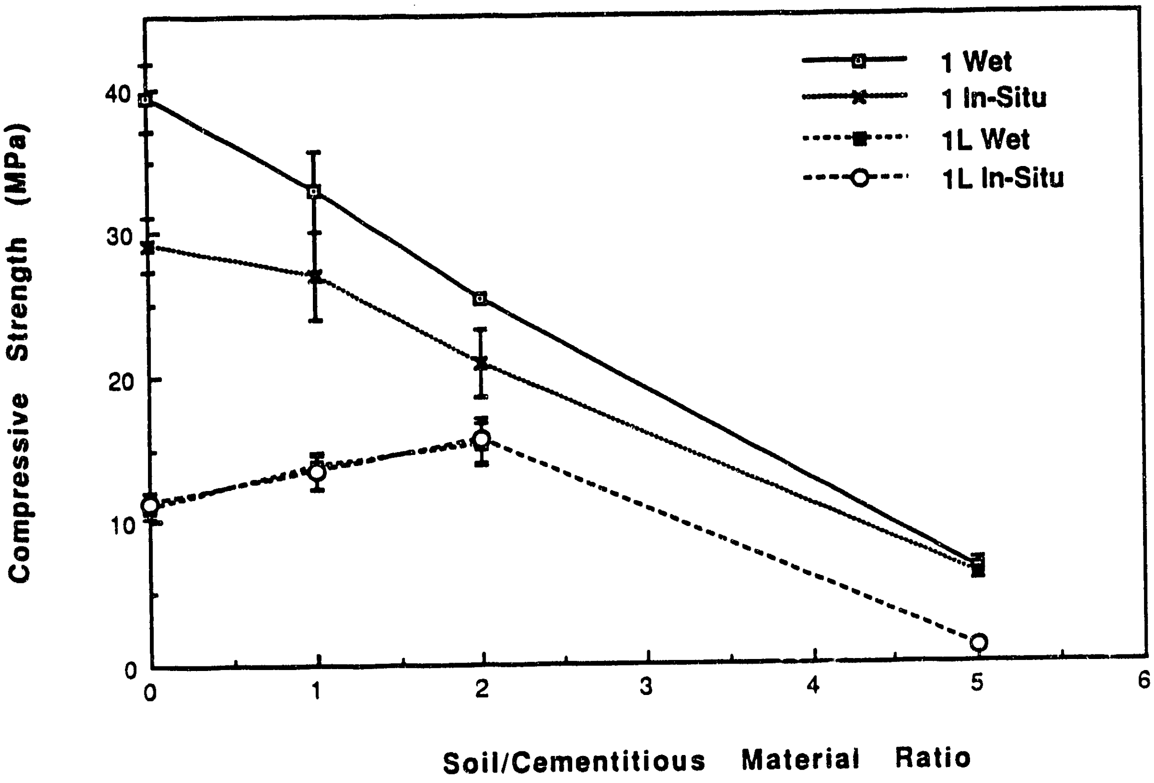

Figure 16. Effect of Curing Conditions and Latex on Strength of Mix 1 Grouts and Soil Cements.

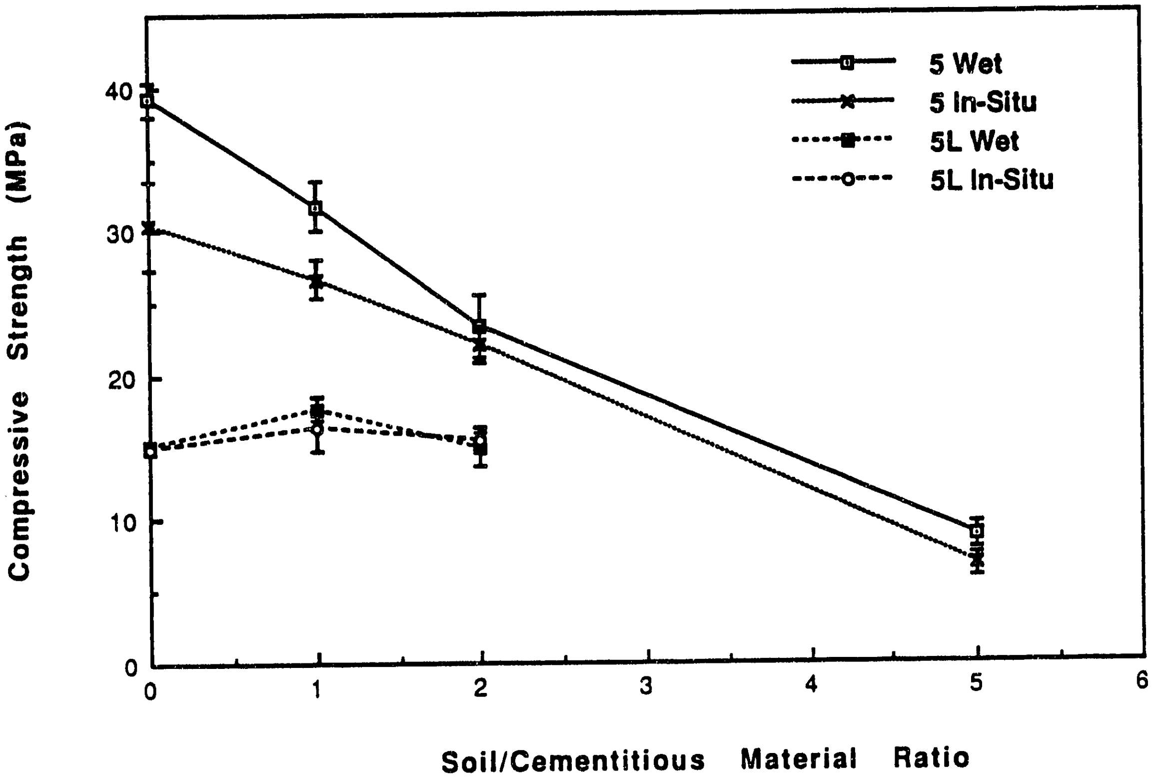

Figure 17. Effect of Curing Conditions and Latex on Strength of Mix 5 Grouts and Soil Cements.

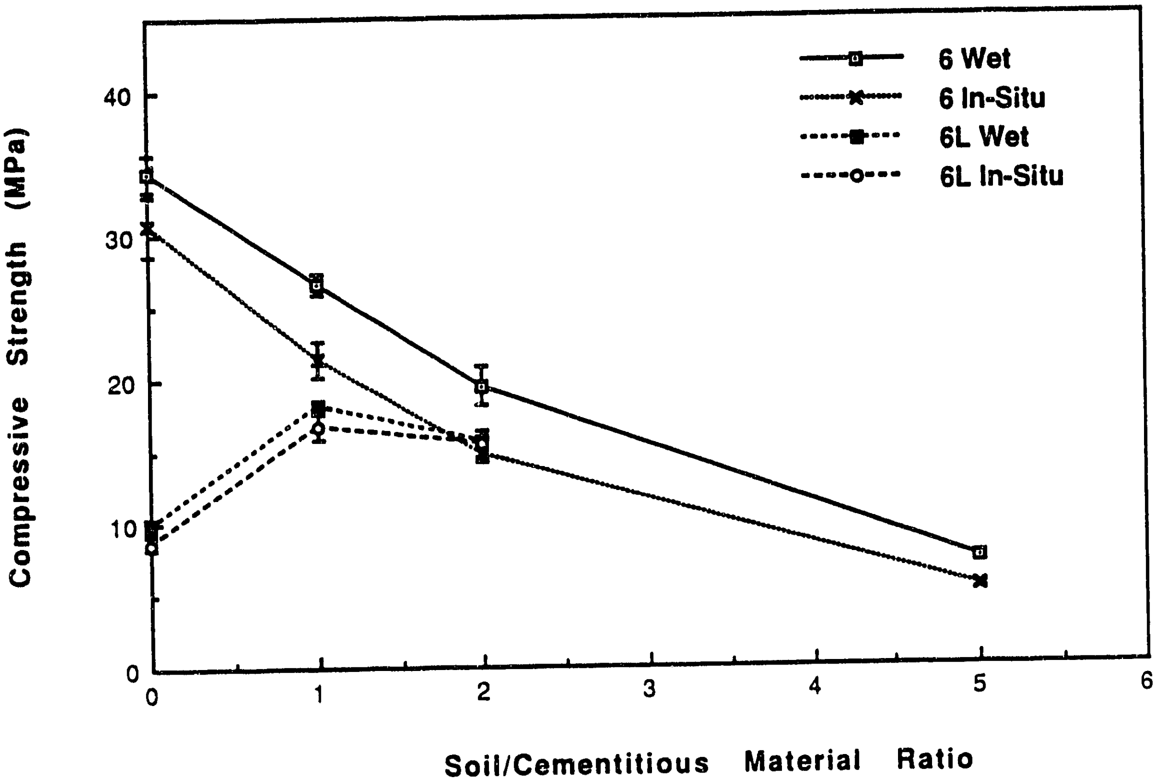

Figure 18. Effect of Curing Conditions and Latex on Strength of Mix 6 Grouts and Soil Cements.

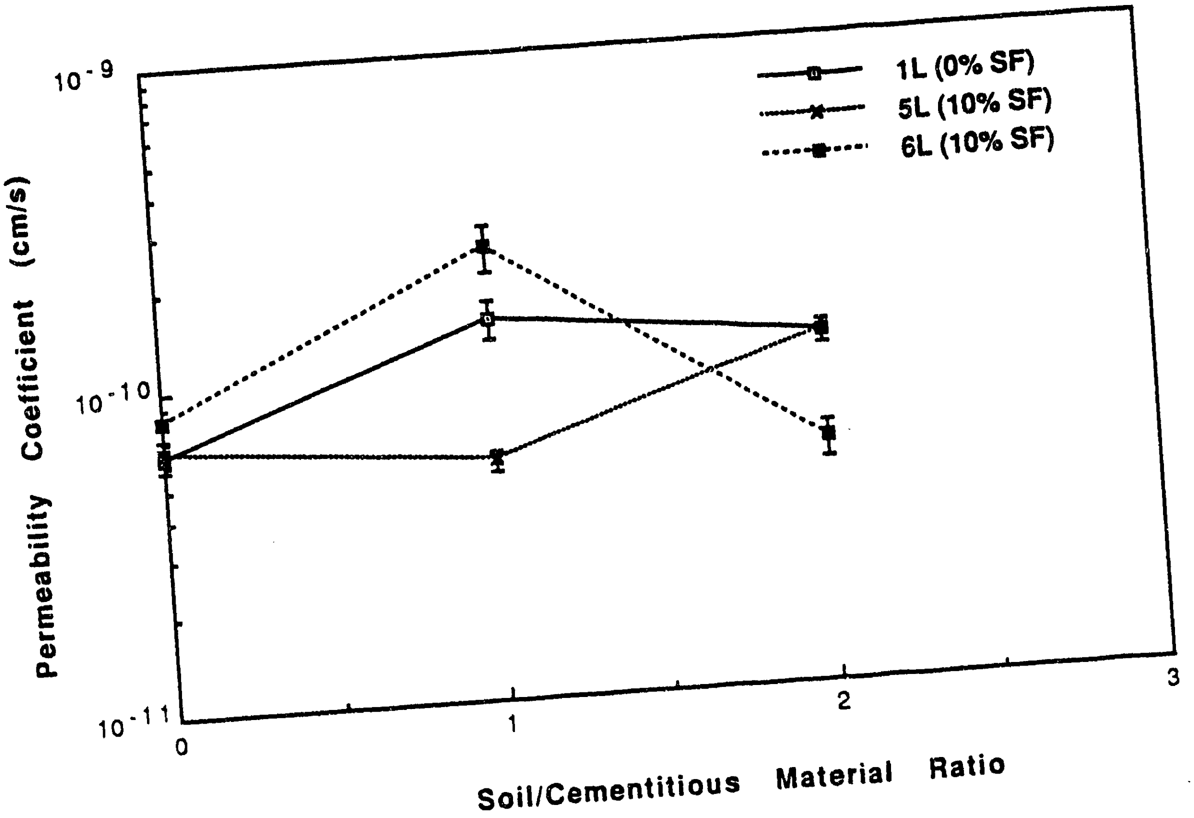

Figure 19. Permeability Coefficient versus Soil/Cementitious Material Ratio for Latex Modified Grouts and Soil Cements.

soil cement while for Mix 6L the permeability was higher. For s/cm = 2 all latex modified soil cements had lower permeabilities than the unmodified soil cements. Comparison between the permeabilities for s/cm = 1 and 2 for latex modified mixes showed a similar results for parent grout Mix 1L, significantly higher permeability for Mix 5L and significantly lower permeability for Mix 6L. The soil cements 5LS1 and 6LS2 had lower permeabilities than the parent grouts. Therefore, there appeared to be no direct relationship between soil content or latex content and permeability.

The inconsistent and unpredictable effect of latex on permeability of soil cements, loss of strength under moist conditions and possibility of latex degradation indicates that further work on long term behavior of these materials is necessary before any recommendations can be made.

2.6.5 Vinyl Ester-Sand Grouts

The vinyl ester-sand grouts showed excellent compressive strength that was greater than that for cementitious materials and far exceeded the requirements as indicated in Table 14. The mix with the best combination of optimum aggregate content and self-levelling properties was V6 with 4 parts graded sand and 1 part flour sand to 1 part resin. Cure time could be increased by reducing catalyst and promoter concentrations. The permeability coefficient of this mix was 2.9×10^{-11} cm/s and was the lowest of all materials studied. The high strength and low permeability of the vinyl ester-sand grout imply that thinner barriers could be used than for cementitious materials. This point is discussed further in Section 2.8. Deterioration due to ultraviolet radiation is a potential problem if the resin grout is used as a cap and not protected from sunlight.

The potential drawbacks associated with the vinyl ester-sand grout are the cost as discussed in Section 2.8 and the high viscosity which could require specialized pumping equipment. The grout is probably most suited to use with the jet grouting by replacement technique in which a cavity produced by jet grouting would be filled with the resin-sand grout.

2.6.6 Polymer-Soil Composites

The vinyl ester and polyester-soil composites showed 24 hour strengths similar to the 28 day strengths for cementitious grouts. The polyester-soil composite had a slightly lower strength than that for vinyl ester. Table 15 shows that strength decreased with increasing soil content for the vinyl ester-soil composites as expected. Strength of one selected mix did not decrease on exposure to soil for 28 days indicating stability over this period. Further long term testing may be required. The optimum soil content to maintain self levelling properties was 3.3 parts to 1 part resin for both vinyl ester and polyester. This content could possibly be increased for resins with significantly lower viscosity (<100 cP).

The permeability coefficient of V12 with 3.3 parts soil to 1 part vinyl ester was 1.3×10^{-10} cm/s which is similar to that for cementitious grouts and soil cements with s/cm = 1. Lower permeabilities could be achieved by decreasing the soil content but this would increase the material cost. The polyester-soil composite had a similar permeability coefficient.

2.7 Cost Analysis

A cost analysis of selected products suitable for use as barriers and caps 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 18 and should be regarded as approximate only.

Table 18. Bulk Material Cost Estimate

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
Latex	1.32
Vinyl Ester Resin	3.50
Polyester Resin	2.60

Using the relevant densities and mix proportions, the cost per cubic meter of barrier or cap material was calculated. The estimated costs of suitable grouts, soil cements and polymer based materials are presented in Tables 19 to 22.

Table 19 indicates that use of a 1:1 cement: sand mix reduces cost and that grouts which contain silica fume are more expensive than those without. The rise in cost of the silica fume grouts is not only due to the silica fume itself, but also the higher levels

Table 19. Estimated Costs of Selected Cementitious Grouts

Grout Mix	Cost per Cubic Meter ($/m^3)
1	207
2	162
5	281
6	201

of superplasticizer used. In order to reduce the cost of Grouts 5 and 6 and maintain the same level of silica fume it would be necessary to decrease the superplasticizer dosage. This would necessitate increasing the water content to maintain low viscosity and result in reduction of strength and increase of permeability. Taking a broader view than the material costs, silica fume requires less energy to produce than cement since it is a byproduct from production of silicon and ferrosilicon alloys. Therefore, a grout which contains silica fume may be more energy efficient.

Table 20. Estimated Costs of Latex Modified Grouts

Grout Mix	Cost per Cubic Meter ($/m^3)
1L	699
5L	697
6L	431

The latex modified grouts are considerably more expensive per unit volume than ordinary grouts despite the lower densities. Any performance advantages tend to be outweighed by the higher costs as discussed in Section 2.8.

The cost analysis of the soil cements given in Table 21 shows the decrease in cost with increase in soil content. Soil cements based on parent grouts with silica fume show higher costs. For grouts with sand the ratio of grout to soil increases to maintain similar strength and permeability as grouts without sand. Therefore, at high soil contents soil cements produced from grouts with sand become more expensive than soil cements with plain grout. The relationship between cost and s/cm for the different mixes is shown in Figure 20. The analysis indicates that at high soil contents it is more economic to use Grout Mix 1 or 2. Performance and economics are compared in Section 2.8. Latex modified soil

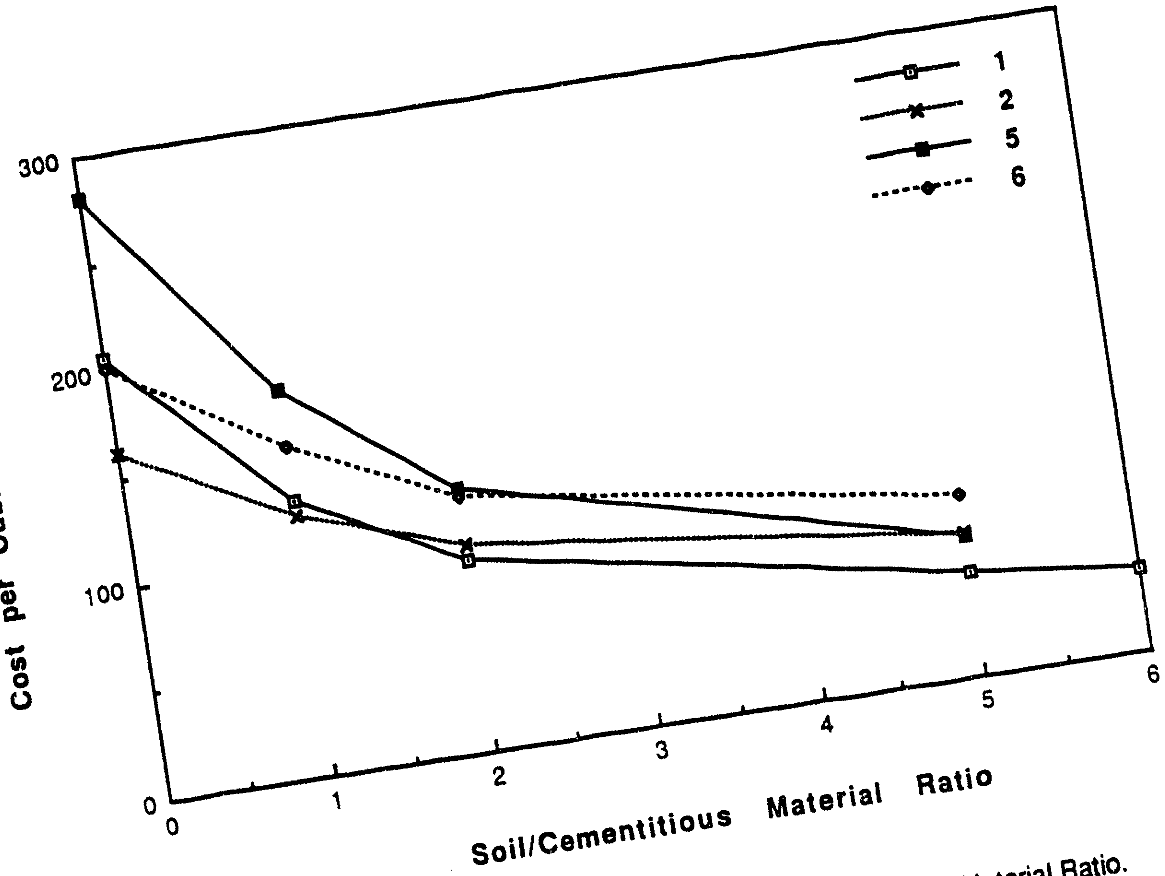

Figure 20. Cost Per Cubic Meter versus Soil/Cementitious Material Ratio.

Table 21. Estimated Costs of Selected Soil Cements

Soil Cement Mix	S/CM	Cost per Cubic Meter ($\$/m^3$)
1S1	1	128
1S2	2	89
1S5	5	48
1S6	6	39
2S1	1	121
2S2	2	96
2S5	5	66
5S1	1	180
5S2	2	123
5S5	5	65
6S1	1	153
6S2	2	119
6S5	5	84

cements would be significantly more expensive than unmodified and were not considered in the cost analysis due to the uncertain performance observed in short term tests.

Table 22. Estimated Cost of Polymer Based Materials

Mix	Cost per Cubic Meter ($\$/m^3$)
V6	1335
V12	1463
P1	1097

The vinyl ester-sand grout and vinyl ester or polyester-soil composites are significantly more expensive than cement based materials. The vinyl ester-sand grout is less expensive than the vinyl ester-soil composite because less vinyl ester is necessary to give the same volume of final material. As a result of the high costs, use of such materials requires demonstration of vastly superior performance and cost savings by reduction of the volume of barrier material necessary. These points are considered in Section 2.8.

2.8 Cost Versus Performance and Design Considerations

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

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 emplacement method. For example the minimum thickness of a vertical barrier produced by jet grouting would be approximately 0.6 m and the minimum thickness of a deep soil mixed barrier would be approximately 1 m.

In order to quantify the possible cost benefits of using a low permeability, high strength cap or barrier, the required thickness for equivalent flow rate and strength of different materials were compared with an arbitrary standard of 0.6 m (2 feet) thick material with a 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 m^2 area of material using the data given in Tables 19 to 22. The results of this comparison for selected materials are given in Tables 23 to 25.

Table 23. Cost of Grouts for Equivalent Flow Rate

Grouts	Thickness (m)	Cost per Square Meter ($/$m^2$)
1	0.54	112
2	0.72	117
5	0.66	185
6	0.72	145
1L	0.38	265

Table 23 indicates that Grouts 1 and 2 have similar costs for a square meter of barrier with equivalent flow rate despite the lower volumetric cost of Grout 2. The latex modified grout is also more expensive even with the reduction in thickness resulting from the low permeability coefficient. Thus, the most cost effective grouts on the basis of permeability are Grouts 1 and 2. However, the resistance to wet-dry cycling of grouts without sand is of concern, and Grouts 2 or 6 are probably preferred materials where a solid grout barrier or cap are required.

Table 24. Cost of Soil Cements for Equivalent Flow Rate

Soil Cement	Thickness (m)	Cost per Square Meter ($\$/m^2$)
1S1	0.72	92
1S2	1.50	134
1S5	2.34	112
5S1	0.90	162
5S2	1.26	155
5S5	2.22	144
6S1	0.90	138
6S2	1.44	171
6S5	2.04	171
C1S1	26.4	1690
C1S2	30.6	1622
C2S5	18600	502200

The cost versus performance analysis indicates that impractical thicknesses of conventional soil cements would be required to give equivalent flow rate to that of 0.6 m thick Mix 1 grout. Soil cements with s/cm = 2 are less cost effective than s/cm = 1 or 5 for parent grouts without sand. For parent grout 6 with sand a mix with s/cm = 1 is more cost effective than higher s/cm due to the associated increase in permeability. The addition of silica fume to the parent grout does not decrease permeability sufficiently to make the soil cement more cost effective than one produced from grout without silica fume.

Table 25. Cost of Polymer Based Materials for Equivalent Flow Rate

Mix	Thickness (m)	Cost per Square Meter ($\$/m^2$)
V6	0.17	227
V12	0.78	1141
P1	0.66	724

The reduction in permeability measured on Mix V6 is not great enough to compensate for the high material cost and therefore is not as cost effective as a cementitious grout or a soil cement. The cost per square meter of resin-soil composites is significantly greater than the grouts or soil cements. If polyester resin was used to produce a resin-sand grout with the same proportion of sand and equivalent permeability coefficient to V6 the approximate cost per square meter would be $200 which is still more expensive that cement based alternatives. From the cost analysis it appears that polymer based grouts or soil composites are not economically viable for barriers or caps.

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 is a prime concern also, although durability should correlate with permeability. 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. 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.

2.9 Barrier and Cap Durability

It is critical that the barriers and caps exhibit long term durability. In order to optimize durability the permeability should be minimized so that penetration of species aggressive to cement is also minimized. The longevity portland cement grout for sealing underground repositories for nuclear waste has been investigated by Alcorn, Coons and Gardiner (1990). It was estimated that for granitic rock environments a Type V (sulphate resistant) cement grout containing 10% silica fume with an initial permeability coefficient of 10^{-10} cm/s may show acceptable performance for tens of thousands to millions of years. In the thermodynamic analysis it was assumed that the silica fume would react with all the free $Ca(OH)_2$ from the hydration of cement and that this would improve durability since deleterious reactions between aggressive species and $Ca(OH)_2$ are reduced. It was also assumed that use of Type V cement will reduce the amount of ettringite formed and this consequently improves stability and durability. The model considered the increase in permeability due to dissolution of phases by movement of ground water.

The low permeability coefficients of around 10^{-10} cm/s measured on the six grouts indicate that any flow through the barrier will be extremely slow. The hydraulic gradient for the operating conditions is likely to be low since the barriers will be located above the water table and the environment is arid. Placement of a low permeability cap will further reduce the hydraulic gradient that the vertical and horizontal barriers are subjected to. As a result, the hydraulic gradients assumed by Alcorn, Coons and Gardiner (1990) of initially 1000 m/m and 1 m/m after 100 years in exposure conditions of initial steep hydraulic gradient are probably higher than that experienced at the CWL and MWL sites. This results in a slower rate of dissolution of cementitious phases than that used in the model of permeability increase with time.

Counterbalancing the slower rate of dissolution is the increased proportion of $Ca(OH)_2$ that can be dissolved for grouts which do not contain silica fume. The solubility of $Ca(OH)_2$ in pure water is around 1.7 g/l and leaching of free $Ca(OH)_2$ causes increase in permeability, decrease in strength and is followed by dissolution of other cement phases such as calcium silicates, aluminates and ferrites (Czernin, 1980). The chemistry of the leachant is an important factor and alkaline waters that contain high levels of calcium are less deleterious than waters with a low pH or low concentration of calcium. The soil chemistry will control the composition of water that leaches from the landfill through the barrier. Provided that the barriers are placed in uncontaminated soil well away from acidic conditions the aggressivity of leachant can be minimized. Further investigation of the likely leachant composition is necessary to determine the likely dissolution rate of cement grouts and the effect of admixtures such as silica fume on this rate.

Grouts with sand have less $Ca(OH)_2$ per unit volume or surface to dissolve but the higher w/cm ratios necessary for a low viscosity mix may increase the dissolution rate of the cement paste matrix. This is because the cement paste has a higher porosity and permeability than the bulk grout.

The degree of curing is another important factor in determination of grout longevity. For <u>in-situ</u> cured conditions the degree of hydration is decreased and this leads to an increase in permeability. The influence of curing on permeability of grouts containing sand will be greater since higher w/cm ratio materials require longer periods of moist curing to achieve closed continuous capillary pores than lower w/cm materials (Neville, 1981).

For soil cements the dissolution rate of the cement matrix phases can be predicted to be higher since the permeability of the bulk material is higher and soil cements with added mixing water will also have a more permeable matrix. Any interaction between soil and cement matrix would be deleterious. The sulphate content of the site soil appears to be below the level likely to cause any degradation. However, this possibility requires further investigation. Scanning electron microscopy and X-ray diffraction analysis of the soil-cement matrix interface could be used to study any interactions.

3.0 IN-SITU STABILIZATION OF BURIED WASTE

Study of <u>in-situ</u> stabilization concentrated on dealing with the chromium plume in the CWL. Chromium ions have the highest levels of the RCRA (Resource Conservation and Recovery Act) metal ions present. After reviewing the characterization report, "Chromium Migration from Pit 2A at the Chemical Waste Landfill", (Phelan, 1989), it was determined that the levels of chromium representative of the vast majority of the plume were 100 - 200 mg/l. The chromium is in the hexavalent (Cr^{6+}) oxidation state.

Two alternative approaches were considered for stabilization of chromium. The first alternative involved use of cement grouts and the second alternative was chemical stabilization.

The grouting approach to stabilization requires pretreatment to reduce Cr^{6+} to Cr^{3+}. A suitable pretreatment is impregnation of the contaminated soil with an iron (II) chloride solution to cause reduction. Once the Cr^{6+} is converted to Cr^{3+} cement grout can be added. The Cr^{3+} forms an insoluble hydroxide on the addition of basic reagents such as cement. The pretreatment to reduce Cr^{6+} is necessary as this does not form an insoluble hydroxide when mixed with cement.

Chemical stabilization of Cr^{6+} follows the same principal of stabilization by cement and involves reduction to Cr^{3+} by $FeCl_2$ or sodium sulphide followed by addition of a basic reagent to form an insoluble hydroxide. A suitable basic reagent is a $Ca(OH)_2$ solution.

3.1 Stabilization by Grouting

Chromium contaminated soils were prepared by doping samples of site soil with Cr^{3+} to a level of 1000 mg/l. The resulting contaminated soil was mixed with 30 weight % Mix 1 grout. The 30% level was chosen to simulate the void volume of the soil that would be penetrated by permeation grouting. This was done before it was concluded that permeation grouting was probably not feasible for the site conditions. Mix 1 grout was selected because it was necessary to have as much free $Ca(OH)_2$ as possible for the production of chromium hydroxide. Therefore, silica fume modified grouts which have reduced free $Ca(OH)_2$ were not appropriate.

The resultant mix of contaminated soil and grout was allowed to cure and subjected to EPA Toxicity Characteristic Leaching Procedure (TCLP) tests. Doped soil without grout was also tested to determine what, if any, fixation the alkali soil could attain. the TCLP tests showed Cr levels of 0.4 mg/l (ppm) for the grouted soil and 6.0 mg/l for the untreated soil. The threshold limit is 5.0 ppm. Therefore, the addition of grout is suitable for stabilization of Cr^{3+} soil. The pH of the TCLP leachates after testing were 11.09 for the grouted soil and 4.38 for the untreated soil. The high pH of the site soil will most likely be beneficial to the final stabilization process.

Since permeation grouting of the contaminated soil is not feasible with cement grouts, an alternative method of mixing grout with soil must be considered. Shallow soil mixing would not penetrate to the proposed stabilization depth of 75 feet (25 m). Therefore, jet grouting or deep soil mixing of the contaminated soil would be suitable methods for blending in cement grout. Stabilization with grout must be preceded by treatment to reduce any Cr^{6+}. Further characterization of the plume with respect to Cr specification is necessary to determine whether reduction of Cr^{6+} is required.

3.2 Chemical Stabilization

An alternative to cement based stabilization is chemical stabilization. This may prove more economic and just as effective as treatment with grout. EPA limits on the production of H_2S complicate the use of sodium sulphide to reduce Cr^{6+}. Therefore, the main focus was on reduction by $FeCl_2$.

Three 100 g samples of site soil were doped with 200 mg/kg (ppm) Cr^{6+}. Two of these samples were washed with a $1.2x10^{-3}$ M Fe^{2+} solution. One was subsequently treated with 1.5 g $Ca(OH)_2$. The third sample was treated with only the $Ca(OH)_2$. After allowing the samples to air dry for three days, TCLP tests were performed. The leachate was analyzed for hexavalent and total chromium.

No Cr^{6+} levels exceeded the 0.003 ppm detection limit even in the sample treated with $Ca(OH)_2$ only. This implies that the natural Fe^{2+} level and alkali conditions in the site soil should be sufficient to reduce Cr^{6+} and this requires confirmation.

The two samples treated with $Ca(OH)_2$ had total Cr levels of 0.1 ppm. The sample treated with Fe^{2+} but no $Ca(OH)_2$ had total Cr levels of 1.9 ppm. Previous samples that were not treated with $Ca(OH)_2$ showed total Cr levels in excess of the 5.0 ppm limit. The variation in results may be due to variability in acid capacity of the relatively small sample size used. The results indicate that the alkali site soil has insufficient acid capacity and that $Ca(OH)_2$ additions are required for stabilization of Cr^{3+}.

Chemical stabilization in conjunction with capping and subsurface barriers should be sufficient to prevent further migration of the chromium plume.

4.0 FUTURE WORK

Future work will involve further optimization of cement grouts and soil cements through variation of mix proportions. For example, lower grout permeabilities could be achieved by lowering w/cm. However, compatibility with the placement techniques for higher viscosity grouts will require study. Soil cements with s/cm = 3 and 4 should also be investigated since these are predicted to have suitable strengths and permeabilities based on the results reported. In particular, the "value for money" of such soil cements should be determined.

Properties not fully investigated to date such as shrinkage, wet-dry cycling resistance and freeze-thaw resistance should be studied. Shrinkage is of concern for large mass placement, particularly with grouts that have high cement contents. Addition of fibers to grout may improve resistance to shrinkage and shrinkage cracking. Expansive agents such as calcium sulphoaluminate, calcium sulphate and calcium oxide could also be investigated for shrinkage control. Type K cement which contains calcium sulphoaluminate may be a suitable alternative to Type I cement.

The effect of in-situ curing on permeability of soil cements which showed promise should be measured. This will give a clearer indication of likely field performance and a better basis for selection of subsurface barriers.

The permeability that can be achieved with soil cements produced at greater depths requires determination since different soil types at different depths may effect the properties of the final product. In addition, different soil moisture contents may result in different permeabilities.

It is also necessary to study the long term durability of the grouts and soil cements. Examination of cement phases and any interaction between soil and cement by scanning electron microscopy and X-ray diffraction methods could be used to predict durability. In particular, silica fume modified grouts should be compared with unmodified grouts in order to determine whether the additional expense is justifiable by the production of more stable phases. Based on the strength and permeability results to date, silica fume is not significantly beneficial and only through improved durability could its use be considered.

Optimization of materials is geared towards field demonstrations in the future at an uncontaminated site, and ultimately, the full scale remediation of the CWL and MWL sites. In addition, the materials and technologies are applicable to other landfill sites and areas such as groundwater control and containment of leaks from underground storage tanks.

For the initial field demonstration in the uncontaminated site it is proposed that a number of promising grouts and soil cements are tested using different placement techniques. The resultant trial caps and barriers should be allowed to cure and then excavated. The monolithic barrier or cap can then be inspected for integrity and continuity. Core samples should be investigated for strength, permeability and any attributes likely to compromise durability and performance such as cracking and heterogeneity. The field trials also represent an opportunity for testing instrumentation to evaluate the integrity of an <u>in-situ</u> barrier such as ultrasonic pulse velocity, impact-echo or other non-destructive techniques.

5.0 CONCLUSIONS

Cement based grouts that contain superplasticizers to reduce viscosity have high cylinder compressive strengths of 25 - 40 MPa depending on curing conditions and very low permeabilities of 10^{-10} cm/s that make them suitable for cap and subsurface barrier materials for <u>in-situ</u> containment of buried waste. The EPA permeability requirement of less than 10^{-7} cm/s is easily achieved. These grouts have superior performance to high water/cement ratio grouts commonly used. Addition of silica fume to cement grouts does not significantly improve strength or permeability for the mix proportions and test conditions studied. The developed grouts appear suitable for use with techniques such as jet grouting, deep soil mixing and shallow soil mixing to produce soil cements. The grouts containing sand also appear suitable as solid materials for caps or barriers produced by jet grouting with replacement. Further mix modification is necessary to optimize shrinkage resistance and durability before these grouts are used.

Silica fume modified grouts are significantly more expensive than unmodified grouts due to the cost of silica fume and higher dosages of superplasticizer required to maintain low viscosity and reduce thixotropy. Lower dosages of superplasticizer would reduce cost but require and increase in water/cementitious material ratio to keep viscosity compatible with placement techniques. On the basis of the strength and permeability measurements the additional expense did not appear justifiable. Unless superior durability of silica fume modified grouts can be demonstrated or predicted with confidence, or costs can be reduced, the use of silica fume for this application appears unwarranted.

Addition of latex to cementitious grouts improves permeability but significantly reduces strength under wet or moist curing and exposure conditions. The additional expense incurred through use of latex does not outweigh the benefits in permeability reduction. Therefore, latex modified grouts are probably not a cost effective choice for cap or barrier materials.

Soil cements produced by mixing the specialized grouts with site soil had moderate compressive strengths of 15 - 33 MPa depending on the curing conditions and low permeabilities of 1.0 - 2.5×10^{-10} cm/s at soil/cement ratios of 1 and 2. These soil cements appeared suitable barrier and cap materials and are predicted to have good durability. Further testing of the freeze-thaw resistance for capping applications and the permeability for *in-situ* curing conditions for barrier applications is warranted. At higher soil/cement ratios of 5 the compressive strength is adequate for the applications but is reduced to a level that raises questions concerning durability. One of the soil cements at this ratio was tested for freeze-thaw resistance and showed unacceptably poor performance. High water/cement ratios at high soil contents also significantly reduce strength and increase durability. Soil/cement ratios of 6 give inadequate performance. Thus, the upper limit of soil/cement ratio appears to be 5. Ratios of 3 and 4 should be investigated as these may show adequate performance and give cost savings.

The soil cements produced from specialized grouts had superior strength and permeability characteristics to those produced from high water/cement ratio grouts. The reductions in permeability achieved were 38, 20 and 8000 fold for soil/cement ratios of 1, 2 and 5 respectively. This demonstrates the vast improvement in performance that can be achieved through use of admixtures such as superplasticizers to reduce water/cement ratio and that through appropriate mix design soil cements can be used for containment.

Silica fume did not demonstrate any significant benefit on the properties of the soil cements studied. Hence, the associated additional costs do not appear justifiable. Use of latex modified grout to produce soil cements gave severe reductions in strength under moist conditions, particularly at high soil/cement ratios, and had an erratic effect on permeability. Therefore, use of latex in soil cements is not recommenced.

Vinyl ester resin-sand grouts and resin-soil composites produced using vinyl ester and polyester showed high strengths of 26 - 102 MPa and low permeability coefficients of 2.9×10^{-11} to 1.3×10^{-10} cm/s. However, the high costs associated with these resins make such materials prohibitively expensive for large scale use when cheaper cementitious grouts and soil cements show adequate performance also.

The six grouts tested range in material cost from $162 to $281 per cubic meter. Addition of silica fume and associated higher dosages of superplasticizer significantly increase costs, while addition of sand can reduce costs and improve resistance to shrinkage. Soil cements range in cost from $48 to $180 per cubic meter depending on the amount of soil and the parent grout used. Soil cements based in Mix 1 and 2 grouts are significantly less expensive than those that contain silica fume.

Soil cements are less expensive per unit volume than the parent grouts but have increased permeability. Therefore, greater thicknesses must be used to achieve equivalent flow rates. The best value for money of the soil cements was Mix 1S1 which used a cement based grout (Mix 1) and a soil/cement ratio of 1. Ranked second by this method was Mix 1S5 produced from the same grout with a soil/cement ratio of 5. However, the durability of this soil cement is expected to be poorer than a cement grout or soil cement with a lower proportion of soil. Soil cements produced from grouts with sand have a lower ranking since a greater amount of grout must be used to achieve adequate properties and this is associated with increased expense.

Further improvements in performance may be achievable by optimization of the best grout and soil cement formulations identified by this work to ensure that durability and cost effectiveness are maximized. Durability comparisons with silica fume modified grout are necessary before silica fume is omitted as a potential admixture.

6.0 REFERENCES

1. ACI Committee 230, State of the Art Report on Soil Cement, American Concrete Institute Materials Journal, V. 87, No. 4, 1990, 395-417.

2. ACI Committee 304, Guide for the Use of Preplaced Aggregate Concrete for Structural and Mass Concrete Applications, American Concrete Institute Materials Journal, V. 88, No. 6, 1991, 650-668.

3. ACI Subcommittee 548A, State of the Art Report on Polymer Modified Concrete, Chapters 1 and 2, Draft 10, April 1990, 1-89.

4. P.-C. Aitcin, G. Ballivy, and R. Parizeau, The Use of Condensed Silica Fume in Grouts, in Innovative Cement Grouting, American Concrete Institute SP 83, J.P. Welsh (Ed), Detroit, 1984, 1-18.

5. S.R. Alcorn, W.E. Coons, and M.A. Gardiner, Estimation of Longevity of Portland Cement Grout Using Chemical Modelling Techniques, in Scientific Basis for Nuclear Waste Management XIII, V.M. Oversby and P.W. Brown (Eds), Materials Research Society Symposium Proceedings, V. 176, 1990, 165-173.

6. A.A. Al-Manaseer and L.D. Keil, Physical Properties of Cement Grout Containing Silica Fume and Superplasticizer, American Concrete Institute Materials Journal, V. 89, No. 2, 1992, 154-160.

7. A.A. Al-Manaseer, M. Onofrei, M.N. Gray and B. Shenton, The Effect of Silica Fume and Water/Cement Ratio on the Hydraulic Conductivity of Cement-Based Grout, in Scientific Basis for Nuclear Waste Management XIV, T. Abrajano and L.H. Johnson (Eds), Materials Research Society Symposium Proceedings, V. 212, 1991, 433-440.

8. K.B. Andromalos and H.N. Gazaway, Jet Grouting to Construct a Soilcrete Wall Using a Twin Stem System, Foundation Engineering Proceedings, ASCE CO Division, Evanston, 1989, 301-312.

9. K.B. Andromalos and P.J. Pettit, Jet Grouting: Snail's Pace of Adoption, Civil Engineering, December 1986, 40-43.

10. A. Bisaillon and V.M. Malhotra, Permeability of Concrete Using a Uniaxial Water-Flow Method, in Permeability of Concrete, American Concrete Institute SP 108, D. Whiting and A. Walitt (Eds), Detroit, 1988, 175-193.

11. R.H. Borden and D.M. Groome, Influence of Bentonite Cement on the Pumpability of Compaction Grouts, in Innovative Cement Grouting, American Concrete Institute SP 83, J.P. Welsh (Ed), Detroit, 1984, 115-128.

12. D. Broomhead and B.H. Jasperse, Shallow Soil Mixing - A Case History, Grouting, Soil Improvement and Geosynthetics, ASCE Geotechnical Division Specialty Conference, New Orleans, 1992.

13. T.P. Brunsing, Block Displacement Method Field Demonstration and Specifications, EPA/600/2-87/023, 1987.

14. W.J. Clarke, Performance Characteristics of Acrylate Polymer Grout, Grouting in Geotechnical Engineering Proceedings, ASCE, New Orleans, 1982, 418-432.

15. W. Czernin, Cement Chemistry and Physics for Civil Engineers, Goodwin Ltd, London, 1980.

16. P.L. Domone and S.B. Tank, Use of Condensed Silica Fume in Portland Cement Grouts, in Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Proceedings of Second International Conference, Volume 2, Madrid, American Concrete Institute SP 91, V.M Malhotra (Ed), 1986, 1231-1260.

17. G. Guatteri, P. Mosiici and V.D. Altan, Jet Grouted Cutoff Walls, Proceedings of REMR Workshop on New Remedial Seepage Control Methods for Embankment-Dams and Soil Foundations, E.B. Perry (Ed), Vicksburg, 1988, 71-105.

18. R.D. Hooton, What is Needed in a Permeability Test for Evaluation of Concrete Quality, in Pore Structure and Permeability of Cementitious Materials, L.R. Roberts and J.P. Skalny, Materials Research Society Symposium Series, Volume 137, 1989, 141-149.

19. R.D. Hooton and L.Konecny, Permeability of Grouted Fractures in Granite, Concrete International, July 1990, 38-52, 56.

20. B.H. Jasperse and A.D. Miller, Installation of Vertical Barriers Using Deep Soil Mixing, HazMat Central '90, Rosemont, 1990.

21. A.W. Johnson, M. Herrin, D.T. Davidson and R.L. Handy, Soil Stabilization, in Highway Engineering Handbook, First Edition, K.B. Woods (Ed), McGraw Hill, New York, 1960, 21-1 - 21-133.

22. S.H. Kosmatka, Cementitious Grouts and Grouting, Portland Cement Association, 1990.

23. S.H. Kosmatka, W.C. Panarese, G.E. Allen and S. Cumming, Design and Control of Concrete Mixtures, Canadian Portland Cement Association, 1991.

24. T. Kunito, A. Honda. M. Mashima and S. Hamasato, A Study of the Relationship Between Pore Structure and Coefficient of Permeability of Soil Stabilized with Cement, in Pore Structure and Permeability of Cementitious Materials, L.R. Roberts and J.P. Skalny, Materials Research Society Symposium Series, Volume 137, 1989, 457-462.

25. W.B. Long, Grouting, in The Maintenance of Brick and Stone Masonry Structures, A.M. Snowdon (Ed), E. and F.N. Spon, Cambridge, 1990, 229-237.

26. J.H. May, R.J. Larson, P.G. Malone, J.A. Boa and D.L. Bean, Grouting Techniques in Bottom Sealing of Hazardous Waste Sites, EPA-600/2-86/020, 1986.

27. P.K. Mehta, Mineral Admixtures, in Concrete Admixtures Handbook, V.S. Ramachandran (Ed), Noyes Publications, Park Ridge, 1984, 303-336.

28. V.B. Messick and M.N. White, Reinforced Plastics, Vinyl Esters, in Handbook of Plastics Materials and Technology, I.I. Rubin (Ed) J. Wiley and Sons, New York, 1990.

29. A.M. Neville, Properties of Concrete, Pitman, London, 1981.

30. E. Nonveiller, Grouting Theory and Practice, Elsevier, Amsterdam, 1989.

31. Y. Ohama, Polymer Modified Mortars and Concretes, in Concrete Admixtures Handbook, V.S. Ramachandran (Ed), Noyes Publications, Park Ridge, 1984, 337-429.

32. M. Onofrei, M.N Gray, L.D. Keil and R. Pusch, Studies of Cement Grouts and Grouting Techniques for Sealing a Nuclear Fuel Waste Disposal Vault, in Pore Structure and Permeability of Cementitious Materials, L.R. Roberts and J.P. Skalny, Materials Research Society Symposium Series, Volume 137, 1989, 349-358.

33. S. Popovics, Strength Losses of Polymer Modified Concretes Under Wet Conditions, in Polymer Modified Concrete, American Concrete Institute SP 99, D. Fowler (Ed), Detroit, 1987, 165-189.

34. V.S. Ramachandran, R.F. Feldman and J.J. Beaudoin, Concrete Science, Heyden, London, 1981.

35. M. Rattanussorn, D.M. Roy and R.I.A. Malek, Effect of Fly Ash Incorporation on Rheology of Cement Pastes, in Fly Ash and Coal Conversion By-Products Characterization, Utilization and Disposal III, G.J. McCarthy, F.P. Glasser, D.M. Roy and S. Diamond (Ed), Materials Research Society Symposium Proceedings V. 86, 1987, 229-237.

36. C.R. Ryan, Vertical Barriers in Soil for Pollution Containment, Geotechnical Practice for Waste Disposal, ASCE-GT Specialty Conference, Ann Arbour, 1987.

37. D.B. Stephens and Associates, Laboratory Analysis of Soil Hydraulic Properties from the MW-4 CWL Monitoring Well, 1990.

38. T. Sugama, L.E. Kukacka and W.Horn, Properties of Water-Compatible Furfuryl Alcohol Polymer Concrete, Cement and Concrete Research, V. 11, 1981, 497-506.

39. O.K. Tallent, T.L. Sams, T.Tamura, T.T. Godsey, C.L. Francis and E.W. McDaniel, Grout Testing and Characterization for Shallow-Land Burial Trenches at the Idaho National Engineering Laboratory, ORNL/TM-9881, 1986.

40. I.H. Updegraff, Reinforced Plastics, Alkyd Polyesters, Vinyl Esters, in Handbook of Plastics Materials and Technology, I.I. Rubin (Ed) J. Wiley and Sons, New York, 1990.

41. L.D. Wakeley and J.J. Ernzen, Cold Cap Grout Formulation for Waste Containment at DOE Site, Hanford, Washington, in Advanced Cementitious Systems: Mechanisms and Properties, Materials Research Society Symposium Proceedings, F.P. Glasser, G.J. McCarthy, J.F. Young, T.O. Mason and P.L. Pratt (Eds), V. 245, 1992, 117-122.

42. D.G. Walters, Comparison of Latex-Modified Portland Cement Mortars, American Concrete Society Materials Journal V. 87, No. 4, 1990, 371-377.

43. D. Whiting, Permeability of Selected Concretes, American Concrete Institute SP 108, D. Whiting and A. Walitt (Eds), Detroit, 1988, 195-222.

END

DATE
FILMED

5/20/93