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The Evaluation of Silicate Grout Curtains Behaviour for the Protection of
Coastal Aquifers

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ABSTRACT

The Evaluation of Silicate Grout Curtains Behaviour for the Protection of
Coastal Aquifers

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In many coastal areas, groundwater quality has been seriously affected by seawater intrusion. Therefore, the objective of this thesis is to evaluate the effectiveness of barriers for the protection of local groundwater supplies in coastal aquifers. Hydraulic and subsurface barriers are currently used to control groundwater contamination in coastal aquifers. Hydraulic barriers are unsuitable because they may produce water unfit for public water supply systems. Little information is available on the performance of subsurface barriers to control the deterioration of coastal aquifers caused by seawater. Consequently, it is proposed to study grout curtains formed with sodium silicate grouts as a means for intercepting the progressive contamination of groundwater.

To evaluate the behaviour of silicate grout curtains, two silicate grout reagents (ethyl acetate-formamide and calcium chloride), two soil samples, and simulated freshwater and saltwater were used. The results from a series of tests showed that sodium silicate with ethyl acetate-formamide (SA) exhibited a large increase in permeability when subjected to both freshwater and saltwater. Sodium silicate with calcium chloride (SC) showed no change in permeability when subjected to both freshwater and saltwater. A

periodic analysis of water demonstrated that silica gel was less susceptible to dissolution in the presence of saltwater. SA grout leads to a continuous increase in freshwater pH. Contrastingly, a decrease in water pH towards its initial values was determined when SC grout was used.

It is concluded that SC grouted specimens are less vulnerable to the action of freshwater and saltwater than specimens grouted with SA.

ACKNOWLEDGMENTS

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CHAPTER 1

Introduction

1.1 Problem Statement

In many countries, groundwater is the primary source of drinking water. In recent years, due to a tremendous increase in the withdraw of groundwater, saltwater intrusions from upconing and seawater have produced water quality unfit for the public as well as many agricultural and industrial supplies.

Saltwater upconing occurs in a groundwater aquifer when freshwater overlies or is close to saline water. In response to excessive pumping in the freshwater zone, the saltwater and freshwater interface moves upward towards the pumping well. Under some conditions, when the pumping rate is less than the upward movement of saltwater, a stable cone develops at a depth below the bottom of the well, and freshwater will continue to be discharged (Reilly et al, 1987). A successive increase in the pumping rate of the well (beyond the critical pumping rate) induces a greater upconing of saline water, resulting in the well discharge becoming saline (Reilly et al, 1987; Motz, 1992). Saltwater upconing problems have been experienced in many parts of the United States including Michigan,
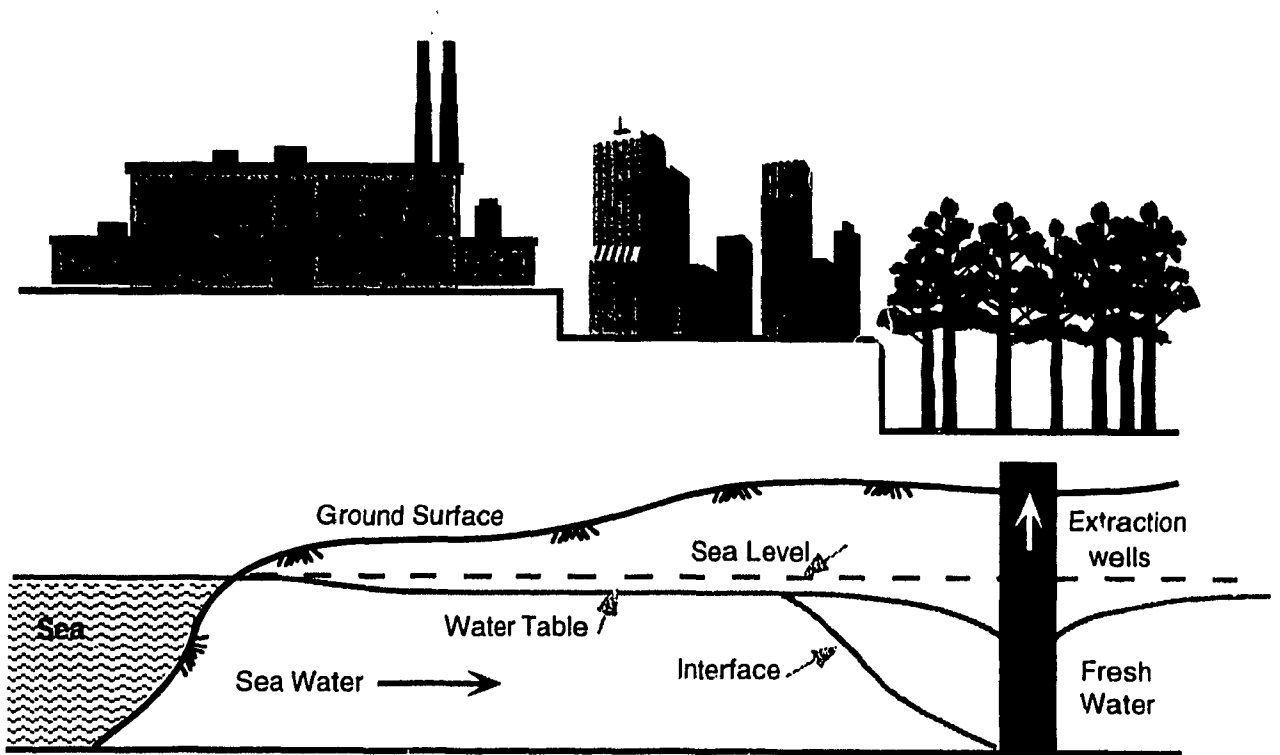
Figure 1.1 Schematic Diagram of Sea-Water Intrusion Due to Pumping from Extraction Wells In Unconfined Coastal Aquifer

New Mexico, Massachusetts, Florida and Texas.(Atkinson, et al, 1986; Reilly, et al, 1987; Motz, 1992).

In a coastal aquifer, the freshwater head is higher than the seawater head. When freshwater is pumped at an excessive rate from an aquifer, the water table level will decline to such an extent that the freshwater head will become lower than the adjacent sea level (Fig. 1.1). Thus, the flow of saltwater will be induced from the sea towards the well. The migration of saltwater into freshwater aquifers is known as seawater intrusion.

The problem of seawater in a pumping well has been widely recognized in groundwater utilization for many aquifers around the world. For example, seawater intrusion has seriously affected freshwater aquifers for most coastal areas including the United States (e.g., California) , China (e.g., Laizhou Bay region), Poland (e.g., Gdansk), and to a greater extent in western parts of Libya (e.g., Tripoli). Due to the extent of contamination by seawater (up to 15,000 ppm of NaCl), some water supplying wells were closed in the Tripoli region.

It is expected that seawater intrusion will slowly rise to the groundwater level. Subsequently, physico-chemical reactions between porous fluid and soil clay particles can affect soil properties. The eventual result will be a decrease in the buffer capacity and an increase in the hydraulic conductivity of the soil (Appendix B). Consequently, groundwater can be contaminated with an increase in leachability of chemical compounds through the soil. Consequently, saltwater intrusion will have a major impact in the whole area rather than contaminating only the aquifer.

As awareness of the importance and the potential threat to natural resources grows, the focus should be on preventive measures rather than only the clean-up of contaminated aquifers. The most logical solution in preventing seawater from reaching the well is to intercept the it with the help of a constructed barrier.

1.2 Research Objective

The main objective of this thesis is to evaluate the effectiveness of a hydraulic or grout curtain barriers in restricting the movement of seawater in coastal aquifers, thus, protect local groundwater supplies. To do this, one needs:

1-to evaluate methods applicable to prevent groundwater contamination in order to chose a viable solution to the problem of seawater intrusion.

2- to conduct a series of laboratory tests that clearly reveal the vulnerability of barriers to freshwater and saltwater chemistry.

1.3 Thesis Organization

This thesis consists of seven chapters and three appendices described as follows:

Chapter 1- presents the problem and the objectives of the study.

Chapter 2- presents methods applicable to increase freshwater yield and restrict seawater intrusion in unconfined coastal aquifers through the use of hydraulic and impermeable

subsurface barriers. Hydraulic barriers are usually created by recharging wells while subsurface barriers are developed by using grouting techniques, in particular chemical grouts.

Chapter 3- discusses the characteristics of chemicals grouts to uncover the most effective grout formula for this study. Chemical, physical, and economic factors are taken in to consideration to determine which grout properties are critical for specific program.

Chapter 4- reviews the literature related to the behaviour of sodium silicate grouted soils including the important factors which have been found to influence the behaviour of grouted specimens.

Chapter 5- describes the experimental program; the tested material and the procedure used for preparing and curing specimens to evaluate the effectiveness of grout curtains using sodium silicate.

Chapter 6- presents the tests results.

Chapter 7- presents conclusive statements deduced from the study and recommendations for further works.

References

Appendix A- describes inorganic and organic components of soil.

Appendix B- discusses the effect of salt composition and concentration on soil behaviour.

Appendix C- presents the testing procedures.

CHAPTER 2

Methods For Controlling Seawater Intrusion

2.1 Hydraulic Barriers

Hydraulic barriers are built by injection freshwater along the coast or by pumping seawater from the ground, or by a combination of both methods. To increase the natural supply and to prevent groundwater contamination, the artificial recharge of groundwater by surface spreading area or recharge well is becoming increasingly important in groundwater management. Particularly, where surface water and ground- water resources are used in conjunction. Surface recharge is much easier than well recharge. Surface recharge requires a large area and it is suitable for recharging unconfined aquifers only. In confined aquifers or when a low permeability layer exists near the ground surface, well injection is the only solution.

When freshwater is injected into a saline aquifer, its subsequent mixing and the cationic exchange produce water with low freshwater ionic strength and a high salinewater sodium absorption value. The combination of these two processes will strongly reduce electrostatic bonding and produce the swelling and dispersion of clay particles (Huisman et

al, 1983).

Hamlin (1987) states that the injection of freshwater or reclaimed wastewater into the San Francisco Bay saline aquifer containing clay minerals resulted in some expansion of the clay minerals and reduced the vertical permeability due to a decrease in ionic strength. However, the replacement of Na^+ by Ca^+ in ion exchange reactions with clay particles in an aquifer will have the effect of reducing expansion during injection and prevent clogging by clay dispersion. The presence of calcite could potentially reduce aquifer permeability by clogging the pore spaces of soil. Thus, it is important that a candidate recharge well be located at a site where calcite precipitation would not adversely affect the pumping well (Katzer et al., 1989).

Subsurface injection of treated sewage, with chloride concentration of 190 mg/l and total solids of 466 mg/l, into the Floridan saline aquifers have indicated that a significant volume of treated sewage did not recover from the injection zone either during or after injection. In addition, water from wells produced water unsuitable for drinking as well as irrigation (Hickey et al., 1984; Fuqua et al, 1992).

The simplest method of intercepting saltwater is by pumping it out from the lower part of the aquifer to be protected. An example of using this method was found on Oxnard plain of Venture County, California (Custodio et al 1978). The pumping wells take saltwater and freshwater from the aquifer, thus impairing the freshwater balance. A pumping barrier is seldom justified as a permanent situation but it is a very effective method for reducing an existing seawater intrusion or depleting the intruded seawater.

Sheahan (1977) claimed that using the pumping method in conjunction with recharge wells will avoid degradation of water supply aquifers from the injected water, and allow reuse of the reclaimed wastewater. In this method, a series of injection wells is used to inject reclaimed water into a shallow aquifer. The injected water is subsequently removed by a similar system of extraction wells to avoid any possible degradation of the water supply aquifer from this source, and to allow reuse of the reclaimed wastewater. An example of using such a method was found at Palo Alto, California. However, it is obvious that such a combination will result in waste of a substantial amount of freshwater as well as increase cost.

Since groundwater serves as an eventual source for drinking water, groundwater recharge with reclaimed municipal wastewater presents a wide spectrum of health concerns that have been under investigation in the United States, particularly in California since the 1970's (Asano, 1992). To ensure that the aquifer for domestic water supply is not impaired, the California Department of Health service has limited the total organic carbon (TOC) and total nitrogen in the injected water to 1 mg/l and 10 mg/l respectively (Asano, 1992; Wehner, 1992). The basis for the proposed TOC limit was the concern of unidentified traces of organic compounds that could pose a health risk. Table 2.1 shows the maximum TOC concentration that may be allowed in reclaimed wastewater. Table 2.2 shows proposed criteria to maintain a microbiologically and chemically safe groundwater for a given reclaimed wastewater contribution.

Groundwater recharge with reclaimed municipal wastewater is not well developed

Table 2.1. Maximum Allowable TOC Concentration in Reclaimed Waste water where Organic Removal to Achieve 1 mg/l TOC in Extracted Water is Required (after Asano, 1992)

Percent Reclaimed Waste water in Extracted Water	Maximum Allowable TOC in mg/l	
	Surface Spreading (Category I)	Direct Injection (Category V)
0-20	20	5
21-25	16	4
26-30	12	3
31-35	10	3
36-45	8	2
46-50	6	2

Table 2.2. Proposed Requirement for Artificial Recharge of Groundwater with Reclaimed Wastewater (after State of California 1990 as cited by Asano, 1992)

Treatment and Recharge Site Requirements	Project Category				
	Surface Spreading			Direct Injection	
	I	II	III	IV	V
Level of Waste Water Treatment					
Primary/Secondary	X	X	X	X	X
Filtration	X	X			X
Organic Removal	X				X
Disinfication	X	X	X		X
Maximum Allowable Reclaimed Wastewater in Extracted well water (%)	50	20	20	20	50
Depth to Groundwater (m) at Initial Percolation Rate of:					
50 mm/min.	3	3	6	15	NA[1]
80 mm/min.	6	6	15	30	NA[1]
Retention Time					
Underground (Months)	6	6	12	12	12
Horizontal Separation[2] (m)	150	150	300	300	300

[1] Not Applicable

[2] From the edge of the groundwater recharge operation to nearest potable water supply well

to get ensure no health risk. Also, clogging problems and drilling costs are expected to be prohibitive. Though the problem of well clogging can be avoided by using 100 percent reclaimed water, the cost of water reclamation is relatively high. Long experience exists in southern California, the US Geological Survey determined that groundwater recharge by injection may be a feasible means of reclaiming aquifers containing water unfit for domestic use (Hamlin, 1987).

2.2 Physical Barriers

Due to a growing demand for freshwater supplies, excessive abstraction can upset the dynamic balance that exists between the freshwater and the outflow to the sea. Thus, increasing freshwater yield and stemming seawater intrusion can be achieved by inserting, across the flow direction, an impervious barrier into the aquifer to modify the flow field.

A physical barrier (subsurface barrier) should be constructed near the coast at an optimum design depth using relatively impervious material. Impervious long curtains such as sheet piles, coffer dams, or grout curtains formed by injecting grout (cement grout or chemical such as sodium silicate) may be used (Atkinson et al, 1986).

Sugio et al (1987) observed that the construction of semi-impervious subsurface barriers (10^5 cm/s) in an unconfined coastal aquifer of Japan using cement grout was able to delay seawater intrusion in an unconfined coastal aquifer for 2 months under continual pumping of the aquifer without recharge. The protection period can be extended for a long

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period of time, depending on the change in barrier permeability, barrier thickness, and pumping rate of groundwater.

The construction of grout curtain barriers by injection of suspension grouts such as cement, bentonite and cement-bentonite are less expensive than chemical grouts. However, suspension grouts are limited to soil deposits coarser than medium sand, for example gravel. The presence of clays, silts and fine sands are the most difficult materials to grout successfully. Chemical grouts such as sodium silicate, acrylamide and acrylate have advantages over bentonite clay or cement grout. Chemical grouts can be formulated to have very low viscosity and can be injected into fine-grained soil to reduce its permeability (Elektorowicz, 1979, 1980; Malone, 1984; Bodocsi et al 1987).

2.3 Summary

This chapter presented a review of the current literature on the application of different types of barriers used to control groundwater quantity and the quality of coastal aquifers. The applications of hydraulic and physical barriers are methods that could restrict the movement of seawater into coastal aquifers.

Hydraulic barriers can be formed through injection of reclaimed wastewater, extraction of saltwater or by a combination of both methods. The formation of a hydraulic barrier through the injection of reclaimed water has been extensively used as the only available option to combat the deterioration of groundwater supplies in coastal areas. Groundwater recharge with reclaimed water may carry trace amounts of toxic chemicals or microbial pathogens jeopardizing the public water supply system. Therefore, the recharge of reclaimed water in groundwater supply is considered an unsuitable technique to stem seawater intrusion.

Physical barriers usually take one of three forms: slurry walls, grout curtains and sheet piles. Very little information has been found on the performance of subsurface barriers as applied to control groundwater contamination by seawater. Therefore, grout curtains formed by chemical grouts are proposed as a means of controlling the progressive contamination of fresh groundwater by seawater. Consequently, the following chapters

CHAPTER 3

Chemical Grouts Materials

3.1 General

Chemical grouting has been used for many years for stabilizing soils to provide a grout curtain below construction projects. Chemical grouting to stabilize loose, cohesionless soil was accomplished successfully through the injection of different chemical solutions. The solution consists of two or more chemicals that permeate into the soil to form a soil-grout matrix that reduce the permeability and/or increase the carrying capacity of the injected soil to some extent (Borden, 1980; Baker, 1982; Nonveiller 1989). Because the purpose of a grout curtain is to increase shear strength and/or decrease permeability, the major applications of chemical grouting are related to geotechnical constructions such as dams, tunnels, and foundation support. Recently, the use of chemical grouting for tunneling seepage control for the New York subway system, and the tunnel excavation support for the Los Angeles metro rail were reported in the literature (La Penta et al, 1992; Gularte at el, 1992).

As advances continue in chemical grouting techniques, a wide range of chemical

materials have become commercially available. Among a number of products, Karol (1990) has suggested that the most common used grouts are lignosulfites, acrylamides, phenoplasts, aminoplasts and sodium silicate grouts. Due to the variety of chemical grout types for soil stabilization, it is necessary that chemical, physical and economic factors are taken in to consideration in order to determine which grout properties are critical for a specific project.

3.2 Lignosulfite Grouts

Lignosulfite grouts principal ingredients are lignosulfonate and a hexavalent chromium salt which form a gel through the action of a catalysts. In an acid environment, the chromium ion changes its valence from plus 6 to plus 3 oxidizing the lignosulfite to form a gel (Tallard et al, 1977; Karol, 1990). Since the oxidation reaction requires an acid medium, a strong acid such as sulfuric acid or acid salt such as calcium chloride should be added (Tallard et al, 1977).

Lignochrome grouts are good products for waterproofing in fine sand having particle size in the range of 0.02- 0.5 mm and a permeability between 10^{-1} cm/s and 10^{-3} cm/s (Tallard et al, 1977). Lignochrome grouts are stable if it is in contact with the water table (Nonveiller, 1989; Karol, 1990). Lignosulfite grouts are considered impermanent under alternate dry or freeze-thaw cycle (Tallard et al, 1977; Karol, 1990). Although hexavalent chromium is reduced to a non-toxic trivalent chromine once the grout has polymerized, a high pH and long setting time may lead to the incomplete reduction of

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chromium (Tallard et al, 1977; Karol, 1990). Thus, gel may leach toxic materials into the surrounding environment. The US Public Health Services has established 0.05 ppm of hexavalent chromium as a permissible limit in drinking water. As a result, no lignosulfite grout are currently in domestic use (Karol, 1990).

3.3 Acrylamide Grouts

Acrylamide grouts are a mixture of two organic monomers: 90-95% acrylamide which could be polymerized at ambient temperature into a long molecular chains, and 5-10% methylene-bis-acrylamide which links the acrylamide chains together (Tallard et al, 1977; Karol, 1990). It gained a widespread use in the United States for grouting sand to make soil impervious to water (Karol, 1990; Moseley, 1993).

A acrylamide solution has a viscosity and density close to water. Both these properties remain constant from the start of mixing until gelation. The presence of sodium chloride and calcium chloride with high pH will lower the setting time (Berry, 1982). Acrylamide grouts shows no loss in strength when stored in moist environment and underwater (Nonveiller, 1989; Karol, 1990). Therefore, acrylamide grouts are considered permanent. However, in very alkaline conditions, which are not naturally found in soil, part of the grout even if it is polymerized can hydrolyze and become soluble in water, thus disturbing the properties of the treated ground (Tallard et al, 1977; Karol, 1990). Furthermore, when it is exposed to dry or freezing cycles, it is subjected to chemical deterioration (Karol, 1990). This problem can be overcome by adding antifreeze additives

such as glycerin and calcium chloride (Haji-Bakar, 1990).

Because several cases of acrylamide water poisoning were reported (Japan 1974), all chemical grouting materials except silicate based grouts not containing toxic additives were banned in Japan. Acrylamide production was also stopped in the United States in 1979 (Karol, 1990; Krizek et al., 1992).

In response to an industrial need for a less toxic substitute for acrylamide, acrylamide grout was replaced in the early 1980's by polyacrylamide (I-80) and acrylate (AC-400) polymer grouts.

Polyacrylamide (I-80) is a low molecular weight linear polymer of acrylamide cross-linked directly with itself using a totally different catalyst system consisting of active chloride (. That solution has a standard viscosity of around 300 $kN.s/m^2$ or centipoises (cP). In running or moving water, the 10-50 $kN.s/m^2$ I-80 provides considerable advantages. I-80 is inert to most substances contained in groundwater, seawater, municipal and industrial waste (Berry, 1982).

Acrylate (AC-400) consists of a mixture of acrylate monomers that are catalyzed with triethanolamine (TEA) and ammonium persulfate (AP) and cross-linked with methylenebis-acrylamide. Acrylate grouts have : 1) very low viscosity 2 $kN.s / m^2$ 2) low solubility in water, 3) excellent gel time control ranging from minutes to several hours 4), abrupt gelation characteristic even when agitated, 5) low toxicity of approximately 5000 mg/kg, and 6) ability to treat fine silts and decrease its permeability to about 5 $X10^{-9}cm/s$

allowing them to be effective in underground water control (Clarke, 1982; Nonveiller, 1989; La penta, et al., 1992; Moseley, 1993).

Because of its low viscosity and a more constant viscosity-time behavior than other grouts, acrylate grouts are more susceptible to dilution during and after the injection process (Krizek al et, 1985).

The high price of AC-400 and I-80 make them generally noncompetitive with silica gel, which is more economical and offers a broad range of performance (Tallard et al, 1977).

3.4 Phenoplast Grouts

Phenoplast grouts are polycondensates resulting from the reaction of phenol on an aldehyde. The reaction for most phenols requires an acid or an acid catalysts to produce gel (Shroff et al, 1992). There are several materials which will react with formaldehyde, such as resorcinol, sodium hydroxide, sodium carbonate and hydrochloric acid without requiring an acid medium (Karol, 1990). However, if the soil contains limestone, the catalysts will react immediately with the calcareous particles in the soil and thus lose all effectiveness (Tallard et al, 1977).

The viscosity of grout remains constant until gelation starts. The low viscosity of the phenoplast grouts (1.5 to 3 kN. s/m^2) and the fact that they can easily be used to regulate the strength of treated ground, make it injectable grout for treatment of fine sand,

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silt and silty clay (Tallard et al, 1977; Elektorowicz 1979; Karol, 1990). Phenoplasts always contain a phenol, a formaldehyde and an alkaline base. All these components in the vadose zone can hydrolyze and release the free formaldehyde which may cause potential environmental risk when it forces itself into groundwater or air (Tallard et al, 1977; Elektorowicz, 1979).

3.5 Aminoplast Grouts

Aminoplasts is grout in which the major ingredients are urea and formaldehyde. They have controlled low viscosity. The aminoplasts also require an acid environment to complete the reaction, and since most soils contain carbonates, the use of an acid catalysts is destroyed before it can affect the grout. In addition, pre-injection of an acid for destroying carbonates is costly. Preinjection increases the size of voids and hence increases the permeability of the soil to the point where chemical grouting is no longer necessary (Tallard et al, 1977). However, they should be injected only into ground where pH of soil and groundwater is below 7 (Nonveiller 1989; Karol, 1990).

Most products from aminoplast grout as well as pre-injection processes are all expensive. The cost production of modified urea-formaldehyde grout is 1.5 times higher than cement grout (Elektorowicz, 1980). Aminoplast grouts using urea solution and formaldehyde are considered toxic (Karol, 1990).

Because of the increased concern over groundwater contamination, the choice of

a chemical grout for a specific grouting job depends not only on its durability but also on its toxicity as well as cost. Table 3.1a and 3.1b illustrate the toxicity of the most chemical grouts. Table 3.2 shows the relative cost of grout formulations.

Table 3.1a. Relative Ranking of Solution Grouts as to Their Toxicity Viscosity, and Strength (after Karol, 1990)

Grouts	Symbol	Corrosivity or Toxicity	Viscosity	Strength
Silicates	Joosten process	Low	High	High
	Siroc	Medium	Medium	Medium
	Silicate-bicarbonate	Low	Medium	Low
Lignosulfates	Terra Firma	High	Medium	Low
	Blox-all	High	Medium	Low
Phenoplasts	Terranier	Medium	Low	Low
	Geoseal	Medium	Medium	Low
Aminoplasts	Herculox	Medium	Low	High
	Cyanalog	Medium	Medium	High
Acrylamides	AV-100	High	High/Low	Low
	Rocagel BT	High	Low	Low
	Nitto-SS	High	Low	Low
Polyacrylamide	Inejctite 80	Low	High	Low
Acrylate	AC-400	Low	Low	Low
Polyurethane	CR-250	High	High	High

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Table 3.1b. Selected Properties of Commonly Used Grouts(after Gnatowski et al, 1976; Tallard et al 1977; Karol; 1990; Yan, 1991)

Grout Material	Catalyst Material	Unconfined Strength kN/m^2	Viscosity $kN. s/m^2$	Setting Time (Minutes)	Pollutant *
Silicate Base					
Low Conc.	Bicarbonate	68 - 342	1.5	0.1 - 300	No
Low to High Conc.	Siroc	68 - 3424	4 - 40	5 - 300	No
Low to High Conc.	Joosten Process	68 - 6848	30 - 50	0	No
Low to High Conc.	Ethyl Acetate	68 - 3424	4 - 40	5 - 300	No
Low to High Conc.	Geloc - 3x	68 - 1712	4 - 25	0.5 - 120	No
Lignin Base					
Blox-All	Halliburton Co.	34 - 616	8 - 15	3 - 90	Yes
Terra-Firma	Intrusion Co.	68 - 342	2 - 5	10 - 300	Yes
Lignosol	Lignosol Co.	68 - 342	50	10 - 1000	Yes
Acrylamide Base					
AM -9	American Cyanamide	342-3424	1.2 - 1.6	0.1 - 1000	Yes
Formaldehyde Base					
Urea-Formaldehyde	Halliburton Co.	>6848	10	4 - 60	Yes
Urea-Formaldehyde	American Cyanamid Co.	>3424	13	1 - 60	Yes
Resorcinol Formaldehyde	Cementation Co.	>3424	3.5	----	Yes
MS-10	WMRA	10,000 - 14,000	9-20	60	Yes

* Pollutant to fresh water supplies contacted

Table 3.2. Relative Material Costs of Grout Formulations (after Moseley, 1993)

Formulation	Relative Cost of Materials
Cement-bentonite	
w/c =3.5% bentonite by wt. of water	1.0
w/c =2.1% bentonite by wt. of water	1.3
w/c =1.1% bentonite by wt. of water	2.3
Cement	
w/c = 0.5	3.4
Silicate-bentonite	
20% bentonite, 7% silicate (by wt. of water)	1.3
Silicate-chloride (Joosten)	4.0
Silicate-ester	
37% silicate, 4.4% ester (by volume)	5.0
47% silicate, 5.6% ester (by volume)	6.5
Silicate-aluminate	
46% silicate, 1.4% aluminate (by weight)	5.0
Phenol-formaldehyde	
13% (by volume)	10.5
19% (by volume)	15.3
Acrylate	
10% (by weight)	18.5
Resorcinol-formaldehyde	
21% (by volume)	23.0
28% (by volume)	31.0
Polyacrylamide	
5% (by volume)	20.0
10% (by volume)	40.0

3.6 Summary

This chapter presented review of the characteristics of the most effective grouting materials used for soil stabilization. The most dependable grout formulations are acrylamide, acrylate, and polyacrylamide grouts. The available literature revealed th acrylate grouts are more effective as waterproofing agents, but their low viscosity and high miscibility make them more susceptible to mixing with water. Furthermore, their high cost makes them non competitive with silica gels. Sodium silicate is generally considered less susceptible to dilution by flowing groundwater and is relatively less expensive. Consequently, literature pertinent to the development and understanding of silicate base grouts was subsequently reviewed in order to use it in the test program.

CHAPTER 4

Sodium Silicate Based Grouts

4.1 Background

Sodium silicate based grouts are being used to solve a multitude of geotechnical engineering problems. Field applications of silicate grouts to geotechnical problems including bridge piers, dam structures, foundations, etc., are documented in the literature. Today, over 85% of chemical grouting uses sodium silicate with various reagents to either strengthen the soil mass, reduce its permeability or both. (Baker, 1982 and 1983; Karol, 1990). Sodium silicate $n-SiO_2.Na_2O$ with a silica/alkali ratios between 3 and 4 is commonly used to form gel suitable for grouting (Noveiller, 1989; Karol 1990).

To obtain a single fluid grout with low viscosity and to allow for better mixing of the components, dilute sodium silicate with various reagents were mixed before they were injected into the ground. Most sodium silicate grouting operations use one-solution where sodium silicate is mixed with a setting agent such as sodium aluminate, calcium chloride, formamide, or ethyl acetate. Salts of weak acids such as sodium aluminate, bisulfite, sodium borate and potassium oxalate have also been used as setting agents (Tallard et al,

1977). The weak acid salt setting agents maintain an alkaline condition in the injected soils and are generally favored for water control in grouting (Malone, 1984). In general, inorganic reagents produce soft gels and have a relatively short setting time. They are mostly used for water cut off grouting. Organic reagents have adjustable setting time and a wide range of stabilized soil strength (Tallard et al, 1977; Baker, 1983; Karol, 1990).

4.2 Mechanism of Soil Stabilization

Sodium silicate is initially made up of long silica chains to which sodium is bonded. When liquid silicate is mixed with certain setting agents, the silica ion is released from the dissolved solids of the alkaline solution, hence lowering pH. Subsequently, an insoluble metal silicate is precipitated as a gelatinous amorphous mass (Hurley et al, 1971). For instance, in combining ethyl acetate and formamide with sodium silicate, ethyl acetate is hydrolyzed into acetic acid and ethanol while formamide is slowly converted to formic acid. The produced acids neutralize the sodium silicate and release silica and thus induces gelation by allowing the silicate particles to link together (Tallard et al, 1977). Ethanol contributes to coagulation by dehydrating the medium (Siwula et al, 1992). When a solution of a polyvalent metal salt, for example calcium chloride, is mixed with sodium silicate, an ion exchange reaction causes the formation of calcium silicate and releases sodium ions i.e, the calcium ions replace the sodium on these chains and form rigid gel that solidifies rapidly (Iller, 1955; Huaser,1955).

When sodium silicate is mixed with soil, a strong gel is formed. The two reactions

which form gel are polymerization and/or precipitation (Murray, 1952; Progress Report on Chemical Grouting, 1957). Polymerization reaction is reaction of silicate with organic compounds. In polymer reactions, a physical bond.is formed. In precipitation, an ionic or polar bond is formed between the soil and stabilizers (Murray, 1952). Wooltorton (1955) postulates that the process involved in soil stabilization is an anionic exchange resulting in the formation of insoluble silicate sheats around the soil particles accompanied by a cementation effect. In general, sodium silicate in the voids of soil behave as a glue which bonds soil particles together or a filler which reduces the void volume of the soil (Polivka et al , 1957; Baker, 1982).

4.3 Variables Influencing Silicate Stabilized Soil

In conjunction with the development of grouting technology, numerous laboratory studies have been performed to address the factors influencing the mechanical and physical properties of both the gel and soils stabilized with sodium silicate grouts. The most important variables influencing the behavior of silicate stabilized soil are: 1) silica and reagent content, 2) density and grain size, and 3) curing environment.

4.3.1 Influence of Silica and Reagent Contents on Strength

The unconfined compressive strength of similar density specimens increase as the silicate content of the grout mix increase (Fig. 4.1). However, this increase is strongly dependent on the amount and the type of reagents used in the mix (Clough el. at, 1979;
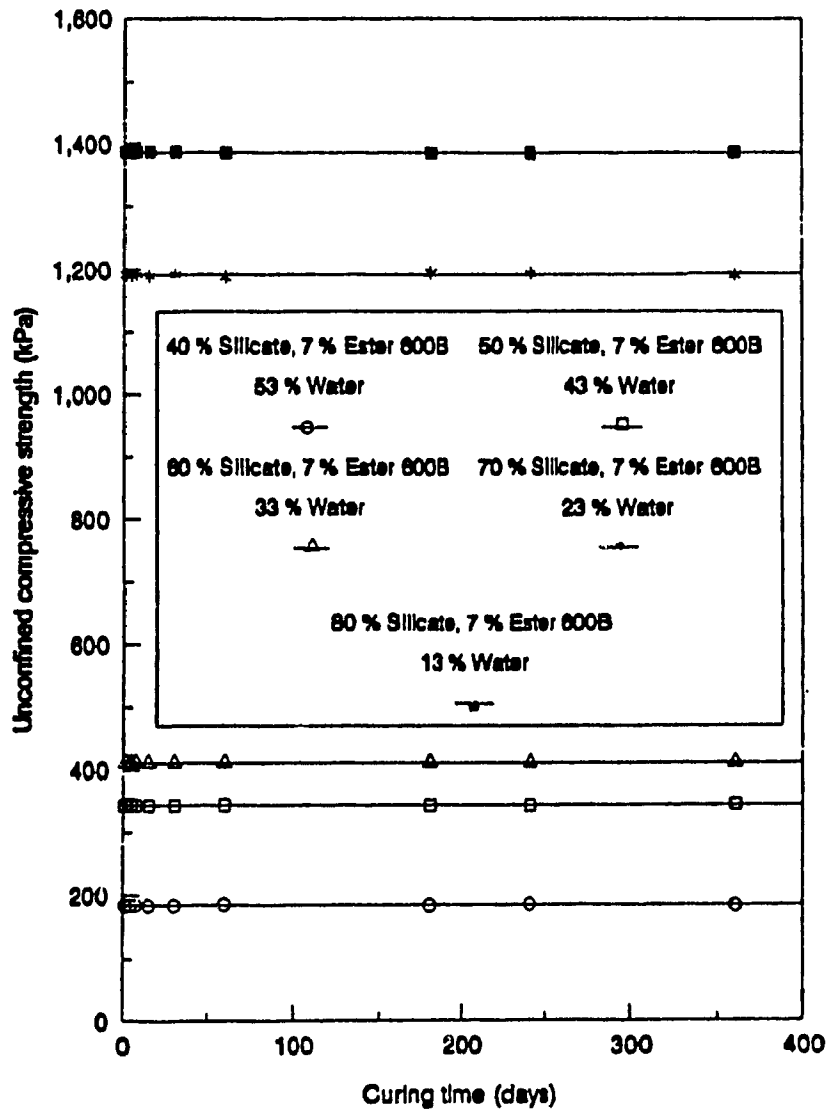
Figure 4.1. Influence of Silicate Content on Unconfined Strength
(after Littlejohn et al, 1992)

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Tallard el. at, 1977). For instance, soil stabilized by sodium silicate and organic reagents showed a compressive strength greater than silicate grouted specimens with inorganic reagents (Krizek et al, 1985; Vipulanandan et al, 1992).

Unconfined compressive strength apparently decreases with increasing distance from the injection point. Bader et al, (1982) suggested that this is attributed to the dilution occuring in the grout as the front advances and the incomplete replacement of water in soil voids. However, the higher compressive strength near the injection point is because the injection of the grout near the end of the process was restricted in its movement and remained undiluted because the ambient flow was stopped (Krizek et al 1985). Yan (1991) stated that it is related to high reagent concentrations absorbed from the grout mix onto soil particles near into the injection point.

4.3.2 Influence of Density and Grain Size on Stabilized Soil Strength

A slight decrease in the strength of stabilized samples, as initial density increased, confirmed that the unconfined strength is developed exclusively by the grout, consequently, less grout can be injected into denser samples (Clough et al, 1979). Increasing the initial density of a sand from loose to dense produced less than a 10% increase in compressive strength (Siwula et al, 1992).

Warner (1972) concluded that the grain size did not exert a significant influence on grouted soil behavior. Clough et al (1979) observed that the strength of stabilized soil increases significantly for finer sands as compared to coarser sands (Fig. 4.2).
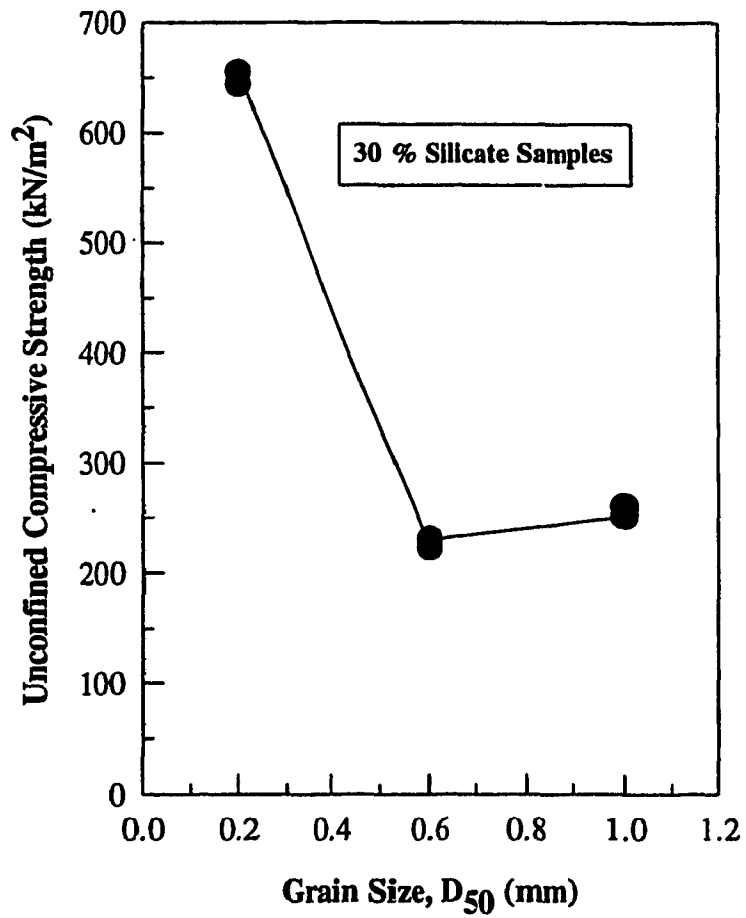
Figure 4.2. Influence of Grain Size on Unconfined Compressive Strength
(after Clough et al, 1977)

Most fine grained soil contain large quantities of crystalline silica, feldspar, colloidal clay minerals, oxides of iron and silica, and organic matter (Appendix A). The presence of clay minerals, organic matter and amorphous materials in soil enhance its the sorption capacity to solute materials (Yong et al, 1992). Thus, efficiency of grout reagents decrease and grouting encounter some difficulties by delaying or preventing grouts setting time (Murray, 1952; Wooltorton, 1955; Sherwood, 1961; Wooltorton; Hurley et. al, 1971).

4.3.3 Influence of Curing Environment on Permanence of Grouted Sand

The permanence of a grout depends on its strength and durability after injection. These are functions of its chemical composition, curing conditions as well as the chemistry of the environment into which it has been injected. As chemical grout is injected into soil and permeated by water, some dilution will occur and some grout will be dissolved by the action of groundwater. The dilution that occurs during injection is highly dependent on the type of grout, grain size, and setting time. Grouts with a high initial viscosity and lower miscibility, such as sodium silicate with ethyl acetate-formamide and sodium aluminate, are less susceptible to dilution than grouts with low viscosity such as acrylate (Krizek et al, 1985). However, the dilution of the grout increases as the effective grain size of the soil increases (Krizek et al, 1985).

Curing time has been shown to exert a substantial influence on the strength and permeability of grouted sand. However, in this area the greatest inconsistencies between investigators are found. For example, one study shows that the maximum strength for soil injected with silicate gels is in excess of seven days and possibly as long as 200 days

(Clough et. al 1979). Another study indicates that the maximum strength of specimens stored in humid environment is achieved in less than four days (Borden, 1980). However, it has been suggested that the maximum strength of soil injected with silicate gels can be accomplished by allowing long curing times of up to several weeks (Baker, 1983; Karol, 1990). In evaluating the permanence of grout by changing the permeability of the grouted specimens, Krizek et al (1985) and Siwula et al (1992) indicated that specimens cured for less than one hour and then subjected to a hydraulic gradient showed an increase in permeability while samples cured for more than one hour exhibited decrease in permeability.

The effect of ambient water with different chemistries such as hardness and pH on the permanence of sodium silicate grouts were also reported. Reidel (1952), Leonard (1963), and Stetanide (1990) state that sodium silicate and calcium solutions formed reliable gel that is not affected by brine or brackish water. Krizek and Madden (1985) observed that silicate grouted sand exposed to tap water exhibited an increase of permeability soon after a gradient was applied, but the permeability stabilized after several weeks and grout remained intact. The increase in permeability was significantly higher when sodium silicate with ethyl acetate was used. Baker (1982) reported that high groundwater pH can be detrimental to sodium silicate based grouts, either by preventing setting of the grout or by promoting deterioration with time. Siwula et al, (1992) reported that the coefficient of permeability of a specimen injected by sodium silicate-ethyl acetate-formamide increased with an increase in water pH from 4 to 10. However, the specimen injected with sodium silicate-sodium aluminate grout, regardless of curing time, exhibited

fairly stable permeability values when it was brought in contact with pH.

Silica leaching and syneresis of the gel could be the most important factors affecting the permanence of grout (Graf et al, 1982; Krizek et al, 1985; Yonekura et al 1992). Syneresis is the process in which water is forced out of the gel (Krizek et al, 1985; Karol, 1990). Shrinkage of the gel due to syneresis will result in the formation of large voids within the grouted soil matrix and increase permeability (Krizek et al 1985, Karol, 1990). Syneresis values less than 10% were determined when organic reagents were used with sodium silicate while less than 2 % synersis was observed with inorganic reagents (Vipulanandan et al, 1992; Yonekura et al, 1992). Generally, the total loss of water decreased as silicate content and reagent concentration increased (Karol, 1990; Vipulanandan et al, 1992).

4.4 Summary

The effectiveness of grouting depends not only on the injection of the desired grout but also on its behavior in-situ. This chapter presented a literature review on the behavior of chemically grouted soils. General information on silicate based grout mixtures were outlined and a discussion of the most important factors affecting the behaviour of silicate grouted sands including the grout composition, grain size and initial density as well curing and environment condition on the permanence of grouted soils followed.

The presented literature indicated that specimens injected with organic reagents, (ethyl acetate-formamide grout) produced gel with a high strength but with a sharp increase in permeability when it was subjected to high water pH. Contrastingly, specimens injected with inorganic reagents, such as sodium aluminate, showed low gel strength and were able to withstand the effects of water pH.

The majority of the work documented in the literature was directed towards improving the behaviour of sand having no silt or clay. Soil materials such as clay, silt or fine sand beyond 200 mesh is generally considered unsuitable for the stabilization process. Moreover, no work has been developed concerning grout behaviour to saltwater, though sodium silicate with calcium chloride was quoted by some investigators for its behaviour to saltwater.

CHAPTER 5

Experimental Program

The experimental program was designed to evaluate the behaviour of grout curtains under natural site conditions. Consequently, laboratory experiments were conducted at both the macroscale and microscale levels of observation. The macroscale study investigated the effects of curing time, environment, grout contents and groundwater quality on the behaviour of silicate grouted specimens. The microscale study investigated the gel formation process and the behaviour of grout curtain materials.

5.1 Macroscale Study

In this study, two different soils and silicate grouts were used to perform grout curtains for the protection of groundwater. Sodium silicate and reagents consisting of an ethyl acetate-formamide mixture and a calcium chloride solution were used in the experimental program. The two soil samples consisted of: sample-I) a mixture of sand, silt and clay, and sample-II) white silica sand, were used to observe the influence of soil minerals on silicate grouting systems. Two simulated waters including freshwater (groundwater) and saltwater (seawater) were used as permeate.

The experimental program at the macroscale level was divided into two major series of tests. The purpose of the first series was to study the durability of a grout curtain. The second series investigated the possible water condition changes after the grout curtain performance.

Constant head permeability tests were performed on the specimens grouted with two silicates grouts. The permeability test was the simplest and the most effective method to demonstrate the applicability of the particular grout in groundwater protection against saltwater intrusion.

5.1.1 Soil Preparation

Preparation of Soil Sample-I

Based on data collected from Libya on the type of soil existing in the Suani region (located in the western part of Tripoli and in 7 km from the sea), an attempt was made to simulate this soil. Commercially available white silica sand and natural clay were chosen to simulate a representative sample of the soil of the given site. The particle size distribution of the soil consisted of 60 % fine sand (0.05-0.25 mm), 25 % coarse sand (0.25-1 mm) and 15% silt and clay (0.001-0.028 mm). The hydrometer method (ASTM D-422-63) was used to obtain the approximate particle size distribution of soil particles passing through sieve # 200.

X-ray mineralogical analysis showed that the clay minerals in the soil consisted of

22 % illite, 5 % chlorite, and 4 % kaolinite. Among the primary minerals, quartz and feldspars (orthoclase $KAlSi_3O_8$), were the dominate minerals present in the soil sample-I. The total composition of this soil is presented in Table 5.1.

Table 5.1. Mineralogical Analysis (%)

Dominate minerals	Soil sample-I %
Quartz	46
Feldspars	12
Dolomite	1
Calcite	2
Clay minerals	
Illite	22
Chlorite	5
Kaolinite	4
Other: Mica Hematite Amphibole	5

Organic matter content, using both ignition at high temperature (800-900 °C) and oxidizable methods (Hesse, 1971), was estimated to be less than 1 % as organic carbon. Calcium carbonate content, using the rapid titration method (Hesse, 1971), was estimated to be 1.2 %.

The cations in the soil sample-I were determined by digesting the soil with an acid (Hesse, 1971). The content of metals were determined using Atomic Absorption Spectroscopy. The content of metals were characterized with the following values: iron 70 mg/kg, sodium 4 mg/kg, potassium 22 mg/kg, calcium 19 mg/kg, magnesium 33mg/kg,

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copper 0.45 mg/kg of dry soil. The amount of sodium and calcium was 30% less in the simulated soil than the representative soil from Libya. Also, magnesium and potassium were 50% higher in the simulated soil.

The presence of amorphous materials in soil may govern the interaction processes in the soil matrix. Amorphous materials in the sample-I were determined by sequential removal with acid and base. To remove Fe_2O_3, the sample-I was washed with 8N HCl eight times followed by eight washings with 0.5N NaOH to remove SiO_2. The presence of amorphous iron oxide and silica oxide in the extracted liquid were determined by using the Perkin-Elmer Lambda 2 UV/VIS Spectrometer according to the method of Voinovitch 1966. The content of Fe_2O_3 and SiO_2 was estimated to be 6.2 mg/g and 40 mg/g of dry soil respectively. The content of metals and amorphous materials in the sample-I is illustrated in Table 5.2.

Table 5.2. Soil Chemical Composition

Cations metals	Concentration (mg/kg)
Fe	70
Na	4
K	22
Ca	19
Mg	33
Zn	Nil
Cu	0.45
Pb	Nil
Amorphous materials	Concentration(mg/g)
Fe_2O_3	6.2
SiO_2	40

The cation exchange capacity (CEC) of the sample-I was determined by following the methodology described in Appendix C. Consequently, the CEC of soil was found to be 25 meq/100 g of soil.

The description of methods used for the determination of the organic matter, calcium carbonate, chemical compositions, amorphous materials, and cationic exchange capacity in the sample-I are all illustrated in Appendix C.

Preparation of Soil Sample II

Pure silica sand, with particle diameters ranging from 0.3 mm to 0.42 mm, was used in this investigation for comparison with soil sample-I. The physico-chemical properties for both the soil samples are summarized in Table 5.3.

Table 5.3. Physico-chemical Properties of Soils

Properties	Sample-I	Sample-II
specific gravity [g/cm^3]	2.65	2.64
void ratio	0.42-0.63	0.74 - 0.9
dry unit weigth [kN./m^3]	18	14
permeability [cm/s]	1.86 x 10^{-4}	7.2 x 10^{-2}
pH	7.9	7.5
cation exchange capacity [meq/100g]	25	-----

5.1.2 Groundwater Preparation

Freshwater and saltwater were simulated in the laboratory based on the chemical analysis of groundwater in the southern region of Tripoli (Libya).

The composition of the synthetic waters was chosen with regard to major ions found in 1977 and 1993 in the groundwater uptake in Tripoli. The preparation of those waters consisted of adding the proper amounts of chemicals to distilled water and mixing the solution to ensure homogeneity. Appropriate amounts of calcium chloride $(CaCl_2.2H_2O)$, sodium chloride (NaCl), sodium bicarbonate $(NaHCO_3)$, potassium chloride (KCl), and magnesium sulfate $(MgSO_4.7H_2O)$ were added to attain the desired composition and hardness. Table 5.4 shows the chemical composition of freshwater and saltwater.

Table 5.4. Composition of Synthetic Waters

Result	Freshwater	Saltwater
pH	8.0	7.7
E.C. [micromhos/cm]	550	16050
Total hardness as $CaCO_3$ [mg/l]	194.0	2640
Calcium as Ca [mg/l]	43	384
Magnesium as Mg [mg/l]	21	408
Sodium as Na [mg/l]	66	3552
Potassium as K [mg/l]	2	40
Bicarbonates as HCO_3 [mg/l]	175	140
Sulfates [mg/l]	40	1612
Chloride [mg/l]	675	6000

5.1.3 Grout Preparation

Two reagents were used with sodium silicate to prepare two different grout materials for the grout curtains. Based on the bibliographic research and the specific necessity of the chosen site, two types of grout materials were chosen for tests, namely: 1) sodium silicate and calcium chloride $(CaCl_2)$; 2) sodium silicate and ethyl acetate

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$(CH_3COOC_2H_5)$ and formamide $(HCONH_2)$.

The variation in water chemistry may influence the setting time of silicate grouts (Connor et al, 1978; Karol, 1990). A preliminary test-1 was conducted to prepare the grout mixture in the laboratory using: 1) distilled water, 2) tap water, 2) freshwater, and 4) saltwater. The chemical analysis of tap water is given in Table 5.5, whereas the chemical analysis of freshwater and saltwater is given in Table. 5.4. The test results showed a large difference in setting time. This can be attributed to the variation in the water chemistry (Tab. 5.6). Setting time decreases with increasing complexity of chemical water composition. Consequently, the dilution of grout that may occur where saltwater exists appears not to influence setting time. In this study, tap water represented average setting time and was chosen to prepare the grout mixture.

Table 5.5. The Chemical Compositions of Tap Water

Result	Tap water
pH	7.5
E.C. [micromh/cm]	276
Total Hardness as CaCo3 [mg/l]	44.5
Calcium as Ca [mg/l]	14.75
Magnesium as Mg [mg/l]	1.83
Sodium as Na [mg/l]	5.18

Sodium Silicate

The sodium silicate for both grouts was supplied by the Fisher Limited Company. This activated component consists of 28.9% SiO_2 and 9.8% Na_2O by weight; 62.4% water by weight, resulting in a SiO_2/Na_2O weight ratio of 3.22. At 20 °C, the sodium silicate

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Table 5.6. Preliminary Test-1: Effect of Water Chemical Composition on Setting Time of Sodium Silicate and Ethyl Acetate-Formamide Grout

Type of water	Setting time (min.)
Distilled Water	70
Tap Water	24
Fresh Water	21
Salt Water	Gelled immediately

solution had a density of 1.38 g/cm^3, a viscosity of 180 kN. s/m^2 and a pH of 11.3. This solution was used to prepare two types of grouts: 1) grout SC where sodium silicate was mixed with calcium chloride, and 2) grout SA where sodium silicate was mixed with ethyl acetate and formamide (Tab. 5.7).

Table 5.7. Grout Formulations

Grout	Active component	Water	Reagents	Setting time
SA	50% Sodium Silicate	40% Tap	5% Ethyl Acetate and 5% Formamide	24 minutes
SC	50% Sodium Silicate	____	50% Calcium Chloride (20g/l)	1 hour

Grout SC: Sodium Silicate-Calcium Chloride

To obtain silicate grout (SC), 50 % of sodium silicate was mixed with 50 % of calcium chloride using a magnetic stirrer until the solution was homogenized.

Grout SA: Sodium Silicate-Ethyl Acetate-Formamide

To obtain silicate grout (SA), 5 % of ethyl acetate and 5 % of formamide was

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diluted with 40 % tap water. The mixture was mixed thoroughly and was combined with 50 % sodium silicate and remixed for five minutes with a magnetic stirrer.

Both SA and SC grouts were used for preparing laboratory grout curtain specimens. The basic components of the silicate grout curtains are shown in Figure 5.1.

5.1.4 Specimen Preparation Techniques

The literature review shows various techniques that have been used to prepare grouted specimens. The specimen preparation techniques at the laboratory scale range from 1) pouring soil into a mold with the desired densities which are obtained by: pressing, tamping or vibration in mold, and 2) injection of grout into precompacted soil specimens.

Molding of the specimen on a vibrating table has proven to be easier as well as faster, with no change in the final quality (Warner, 1972). Since a change in density caused minor variations on the properties of soil grouted specimens with silicate, the pressing technique was chosen for the preparation of specimens in this study.

Warner (1972) and Yan (1991) have found that specimens grouted by the pluviating process, in which soil is slowly poured into a mold containing a premixed grout, and a vibrating table applied to achieve the desired density, is efficient and reliable. In this method; individual grains are believed to be completely coated with grout which may reduce their frictional resistance and result in lower strength (Haji-Bakar, 1990).

The puddling method in which soil is mixed with premixed grout specimens and is
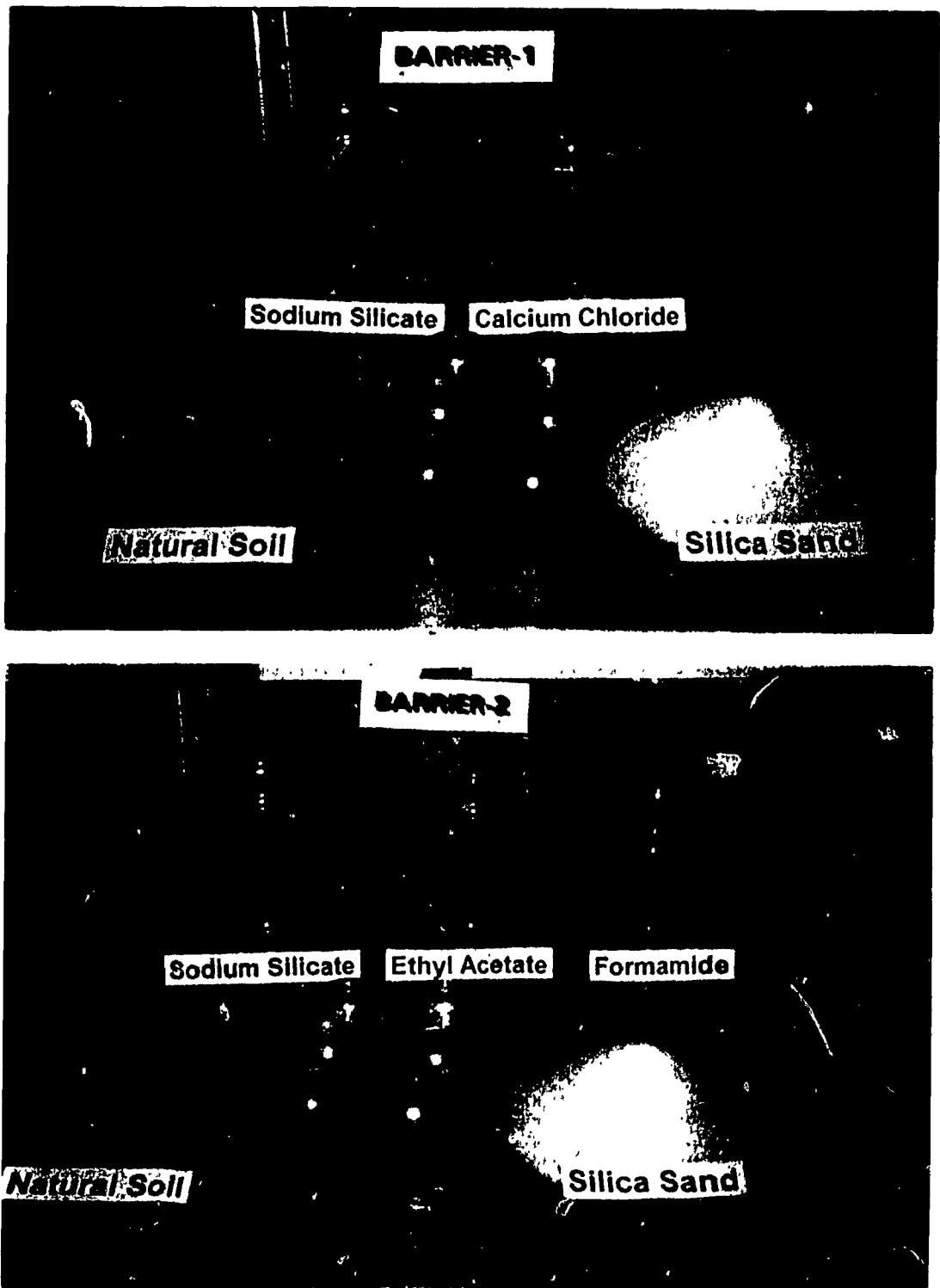
Figure 5.1. Basic Components of Grout Curtain

later compacted into a mold, may lack reproductivity as a result of mixing in open air, especially when grout contains volatile elements (Haji-Bakar, 1990).

To generate the desired information on the behavior of silicate grouted specimens, a series of preliminary tests-2 were conducted on sample-I specimens prepared by using pluviating and puddling methods. The test results showed that the permeability of specimens grouted with the puddling method and cured at room temperature were up to one order of magnitude less than the permeability of specimens grouted by the pluviating method (Tab. 5.8). Hence, the "puddling method" was adopted in the following experiments.

Table 5.8. Preliminary Tests-2: Grouting Techniques

Grout Type	Grouting Method	Permeability (cm/s)
SA	Puddling	1.77×10^{-7}
	Pluviating	2.8×10^{-6}
SC	Puddling	1.49×10^{-6}
	Pluviating	6.2×10^{-6}

To determine the amount of grout required in each specimen, a series of preliminary tests-3 were performed. An estimated volume of 30 ml and 40 ml of grout mixture was used to grout 100 grams of dry soil samples (sample-I and sample-II). The test results (Fig. 5.2) showed that there is a substantial decrease in permeability with increasing grout volume. Consequently, 40 ml of a grout mixture was used to stabilize 100 grams of dry soil in the following experiments.

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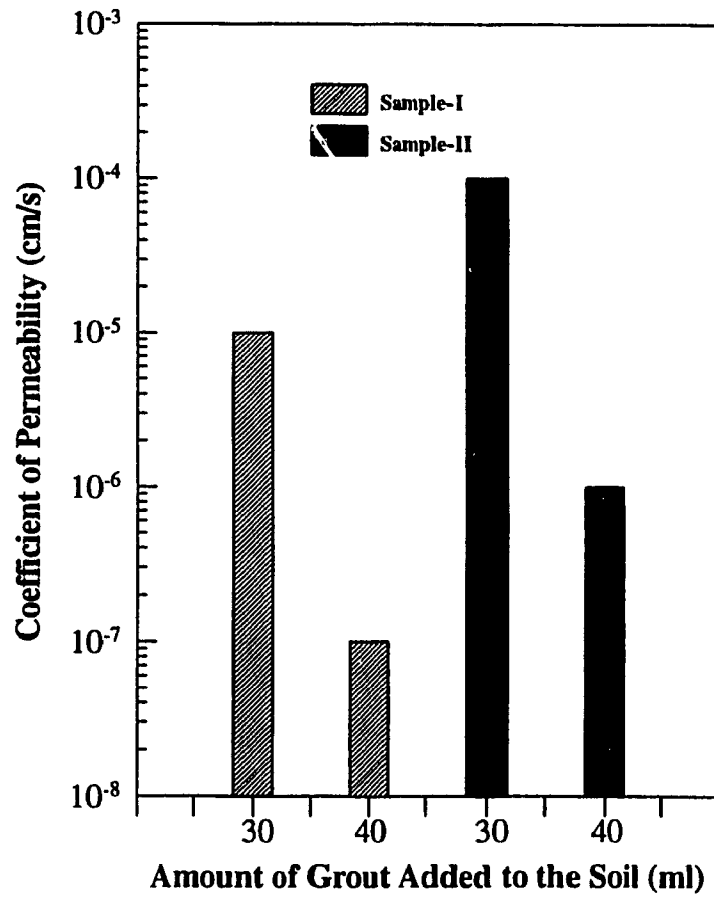
Figure 5.2. Preliminary Test-3: Permeability Versus Amount of Grout For Soil
Samples Grouted With Sodium Silicate & Ethyl Acetate-Formamide

A known volume of grout mixture and soil were mixed in a container using a hand stirrer. Then, the grout-soil mixture was poured and pressed into aluminum cylinder molds with 7.2 cm length and 3.22 cm diameter. Both ends of the mold were covered with plastic wrap and an O ring to prevent leaking as well as to prevent any change in moisture content during the settlement period.

5.1.5 Test Procedures

The macroscale study was divided into two major tests (Fig. 5.3). The first test was to evaluate the durability of grout curtain components under different conditions. The second test was to investigate the change in groundwater quality after performing the grout curtain.

The first test

The first test is divided into three phases for the investigation of: 1) the effect of curing time and environment on the permeability of silicate grouted specimens, 2) the effect of grout ratios on the permeability of specimens, 3) the effect of water chemical composition on the permanence specimens.

In phase 1, approximately 65 specimens were prepared using SA and SC grouts. Both sample-I and sample-II were grouted and left in different curing environments: open air at room temperature (22-25 °C); constant low temperature (5 °C); and submerged in distilled water (21-23 °C), to simulate the curing process below and above the water table.
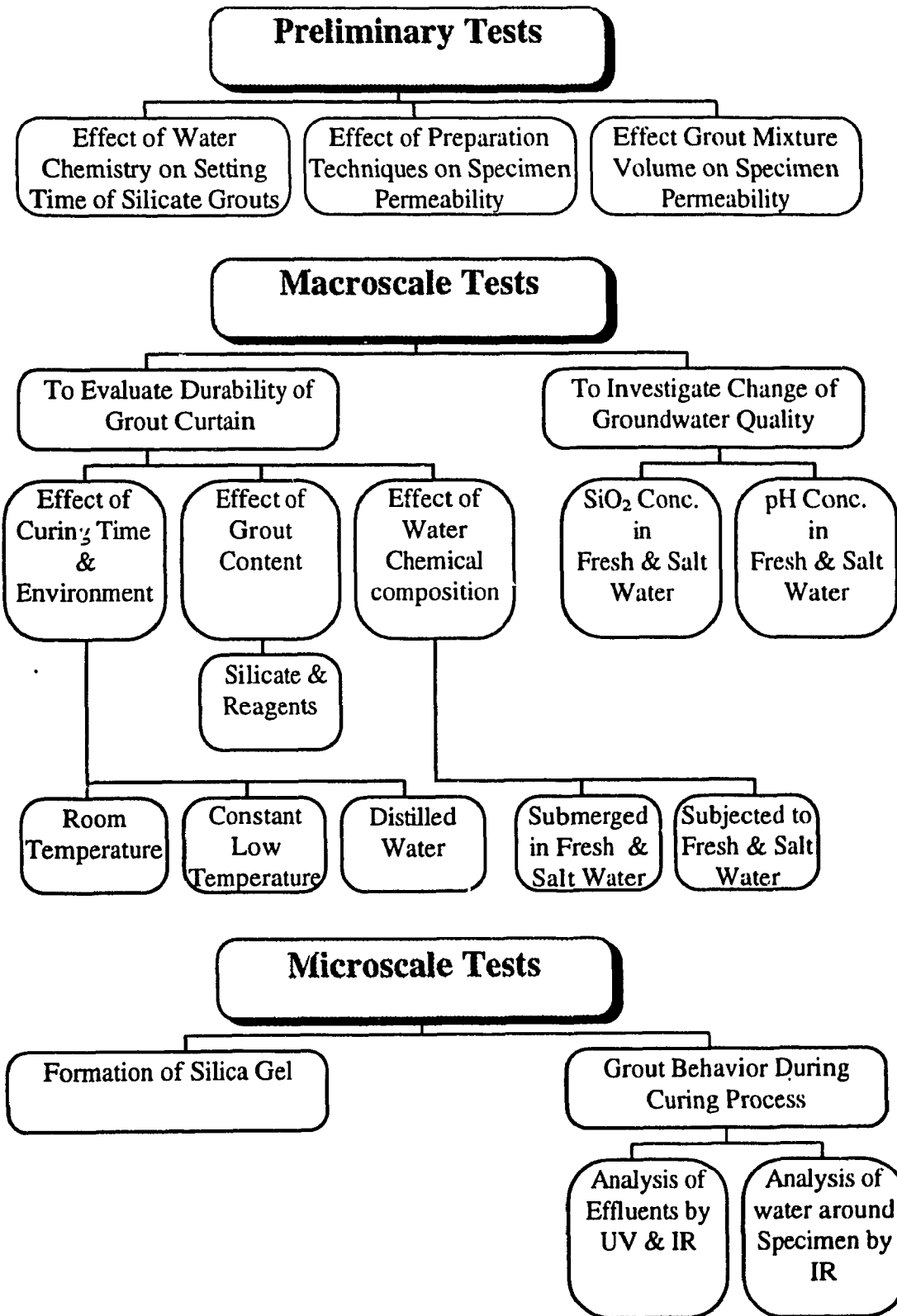
Figure 5.3. Schematic Diagram For Experimental Program

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After an appropriate curing time (from 1-day to 7-days) had elapsed, the specimens were specimens were subjected to the constant head permeability test without removing them from the mold. The laboratory standard apparatus of the permeability test was adopted to measure the permeability of grouted specimens. The permeability test was performed using tap water under hydraulic gradient of approximately 18.

In phase 2, approximately 25 specimens were prepared with various ratios of SA and SC grouts in order to achieve a noticeable permeability decrease. Both sample-I and sample-II were grouted and cured in open air at room temperature (22-25 °C) for one day. Then, the constant head permeability test was conducted. The test was performed under the same conditions described in phase 1.

Phase 3 was divided into two series of tests. In the first series, 8 samples-I, grouted with SA and SC grouts and cured for one day in open air at room temperature, were consequently subjected to the constant head permeability test. This test was performed with the application of freshwater and saltwater until the permeability values stabilized or reached the ungrouted permeability of soil. The gradient was maintained at a value of approximately 18 during the test program.

In the second series of phase 3, 24 specimens were prepared using SA and SC grouts. Both sample-I and sample-II grouted with SA and SC, cured for one day in open air, were removed from the mold and placed in two plastic containers filled with freshwater (groundwater) and saltwater (seawater) for up to 60 days. Both containers were under a constant pressure of 69 kN/m^2 (10 psi). During several weeks of curing, any

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visible change due to the aging process of the grout curtains structure was monitored. An illustration of the curing equipment is shown in Figure 5.4.

Second test

Two stages were recorded during phase 3 testing: 1) characterization of the effluent during the permeability tests and 2) evaluation of the effect of freshwater and saltwater on submerged specimens. This test was directed towards an analysis of pH, and possible leaching of grout components. The pH of 24 cured water samples was measured using a pH meter (Accumet series 1003). Periodic analysis of 24 cured water samples were executed to investigate the possible leaching of grout components into freshwater and saltwater. In this case, the Perkin Elmer UV-VIS Spectrophotometer using the Voinovitch method (1966) was adopted to estimate silicate (SiO_2) in both freshwater and saltwater. A detailed description of this method is presented in Appendix C.

5.2 Microscale Study

The experimental program at the microscale level was divided into two series of tests (Fig. 5.3). The objective of the first test was to investigate the bond formation process during the setting time of SA grout. Special investigations were performed on sodium silicate with organic reagents because of their complex formation as well as their possible impact on the environment. The objective of the second test was to confirm grout curtains behaviour during the aging processes.

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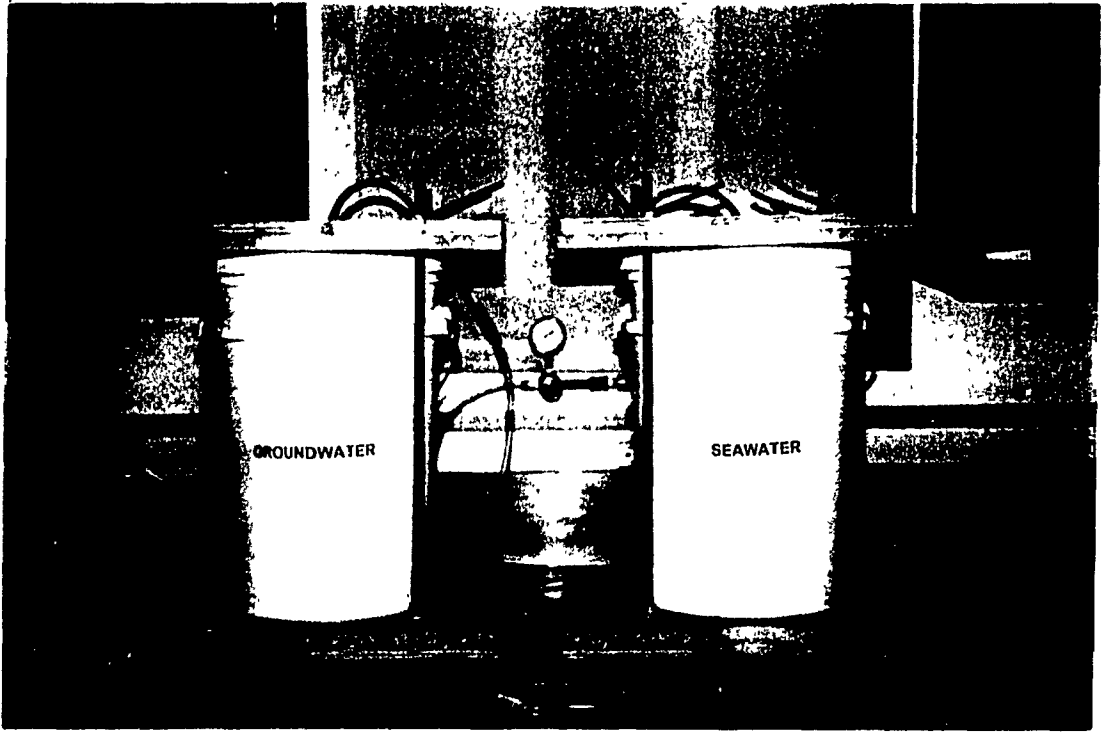
Figure 5.4. Illustration of Cured Equipment for Phase-3, Test-2

Accordingly, the Perkin Elmer UV-VIS spectrophotometer and Perkin Elmer Infra-Red (IR) spectrophotometer 599B were used for analysis in this study.

5.2.1 Test Procedures

<u>First Test</u>

In the first test, two samples of SA grout containing 50% and 60% sodium silicate and 10% organic reagents were prepared by following the procedure shown in section 5.1.3. The grout mixtures were kept until gel formed. Then, a small fraction of initial gel was removed and kept to dry in air for 1 day before being subjected to IR analysis. Preliminary tests demonstrated no change in the spectra when some samples were re-examined after 2 and 3 days. The method of sample preparation for IR analysis is given in Appendix C.

<u>Second test</u>

To investigate the behaviour of grout curtains during the aging process, this test was divided into two phases in order to detect the possible removal of grout components into the freshwater and saltwater environment due to physico-chemical processes.

In phase 1, the effluent collected during the permeability tests (Test 1/Phase 3-1) were allowed to settle. After settling, two layers were observed: 1) transparent upper layer, 2) precipitate lower layer. The upper layer was examined by UV-VIS Spectrophotometer. An air-dried precipitate was examined using IR Spectra.

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In phase 2, the collected freshwater and saltwater samples around the grouted sample-I and sample-II (Test 1/Phase 3-2) were subjected to IR analysis.

The analyses of both tests were conducted in the Environmental Engineering Laboratory of the Civil Engineering Department at Concordia University. The methods used for the preparation of the samples for UV and IR analysis are given in Appendix C.

CHAPTER 6

Results And Discussions

The results from the macroscale and microscale studies were used to evaluate the applicability of silicate grouts in performing grout curtains against saltwater intrusion in groundwater uptakes.

6.1 Macroscale Study Results

The results from approximately 100 Constant-Head Permeability Tests on chemically grouted soils (sample-I, sample-II) were used to analyze waterproofing characteristics of silicate grouts. The results are presented and evaluated in terms of curing time and environments, ratios of sodium silicate and reagents, and various employed water qualities. Also, the results of the periodic analysis of water quality are presented.

6.1.1 Effect of Curing Time and Environment

In this experimental investigation, the major concern was the effect of curing time and environment on the grout curtains performance with: i) sodium silicate and ethyl

acetate-formamide (SA) and, ii) sodium silicate and calcium chloride (SC).

Sodium Silicate-Ethyl Acetate-Formamide Grout (SA)

Soil sample-I grouted with SA and cured for 1 day in open air at room temperature (22-25 ^{0}C) showed permeability (10^{-7}cm/s) three orders of magnitude less than ungrouted sample (Fig. 6.1). For some specimens with 1-day curing time, grout was displaced as a viscous fluid and a complete elutriation occurred within an hour, resulting in the same permeability of ungrouted sample (10^{-4}cm/s). For soil sample-II grouted with SA and cured for 1-day at room temperature, permeability decreased (10^{-6}cm/s) four orders of magnitude compared to ungrouted samples (Fig. 6.2). When both grouted sample-I and sample-II were cured for 3-days, a slight increase (< half order of magnitude) in permeability was observed. Grouted sample-I cured for 7-days exhibited a large increase in permeability (10^{-4}cm/s) like ungrouted samples (Fig. 6.1). Grouted sample-II cured for 7-days showed an increase in permeability (10^{-4}cm/s) of two orders of magnitude less than ungrouted sample (Fig. 6.2).

To further evaluate the effects of the curing environment on SA grouted specimens, grouted samples-I were cured at a low constant room temperature (5 ^{0}C) for 1-day, 3-days and 7-days. The permeability test results showed that these specimens exhibited no increase in permeability (Fig. 6.1).

When soil samples-I grouted with SA were cured submerged in distilled water (21-23 °C) for 1-day, 3-days, and 7-days, no increase in permeability resulted (Fig 6.1).

Figure 6.1. Influence of Environment on Permeability of Soil Sample-I
Grouted with Sodium Silicate & Ethyl Acetate-Formamide

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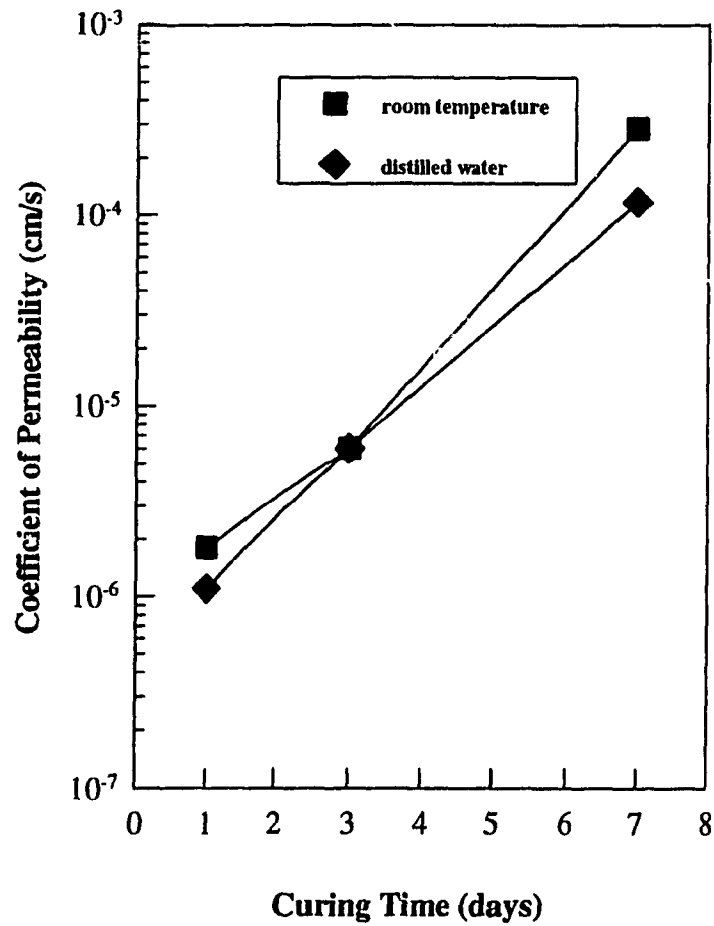
Figure 6.2. Influence of Environment on Permeability of Soil Sample-II
Grouted with Sodium Silicate & Ethyl Acetate-Formamide

Soil sample-II grouted with SA and cured submerged in distilled water showed considerable increase in permeability with increasing curing time. Grouted sample-II cured for 1-day showed a permeability of the order of 1.1 x 0^{-6}cm/s. Grouted sample-II cured for 3-days exhibited a slight increase in permeability of the order of 7.4 : 10^{-6}cm/s. On the other hand, specimens cured for 7-days exhibited an increase in permeability of the orders of 1.17 x 10^{-4}cm/s (Fig. 6.2).

Sodium Silicate-Calcium Chloride Grout (SC)

Soil sample-I grouted with SC and cured for 1-day and 3-days at room temperature (22-25 °C) exhibited a permeability (10^{-6}cm/s) of two orders of magnitude less than that of the ungrouted sample (Fig. 6.3). Soil sample-II cured for 1-day and 3-days at room temperature (22-25 °C), showed a permeability of 10^{-6}cm/s and 10^{-4}cm/s respectively (Fig. 6.4). The permeability of both grouted sample-I and sample-II cured for 7-days were 10^{-4}cm/s and 10^{-3}cm/s respectively.

Soil sample-I grouted with SC showed a permeability of 10^{-6}cm/s (Fig. 6.3) when cured at low constant room temperature (5 °C) for 1-day, 3-days and 7-days.

When soil samples-I grouted with SC were submerged in distilled water for 1-day, 3-days and 7-days, a permeability (10^{-6} cm/s) of the same order of magnitude resulted. Soil samples-II grouted with SC and cured for 1-day, 3-days and 7-days also showed a permeability (10^{-6}cm/s) of the same order of magnitude. The results showed that curing time had no effect on permeability when both grouted sample-I and sample-II were cured
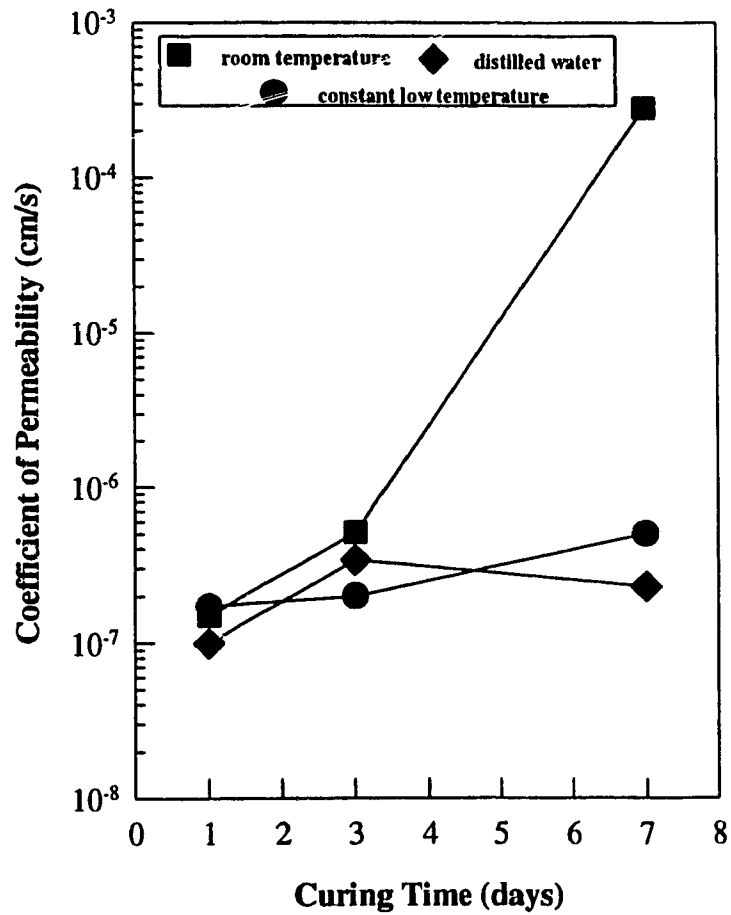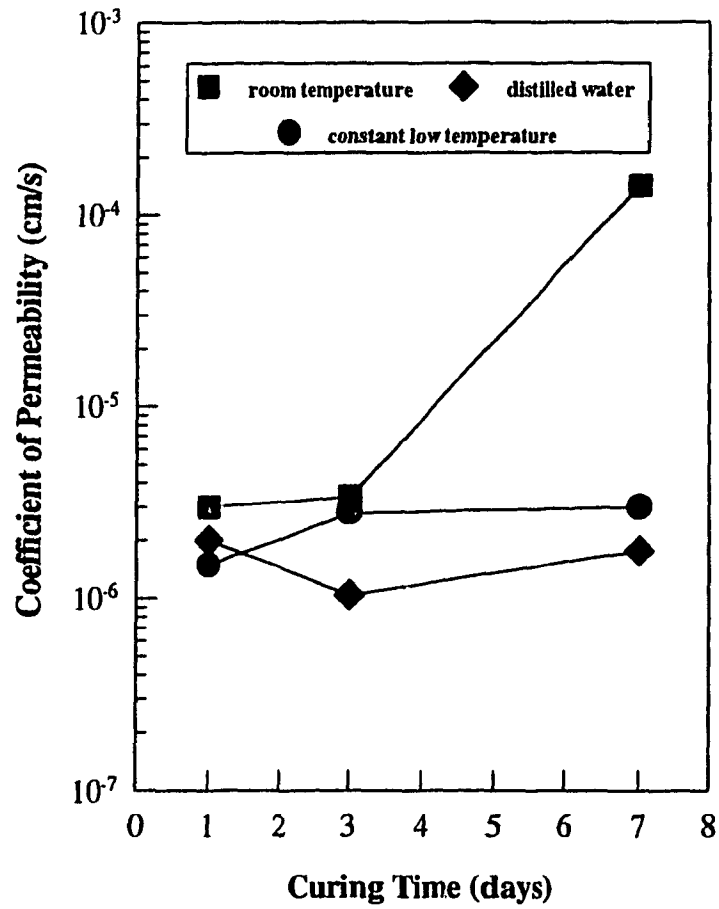
Figure 6.3. Influence of Environment on Permeability of Soil Sample-I
Grouted With Sodium Silicate & Calcium Chloride
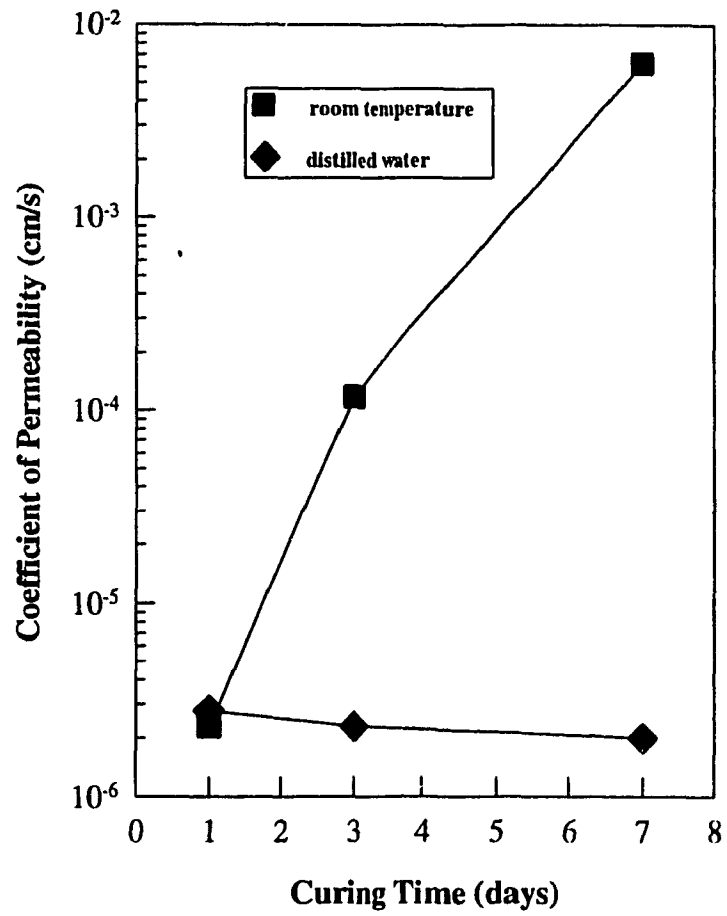
Figure 6.4. Influence of Environment on Permeability of Soil Sample-II
Grouted With Sodium Silicate & Calcium Chloride

submerged in distilled water (Fig. 6.3 and 6.4).

Generally, samples-I grouted with SC showed permeability (10^{-6}cm/s) of one order of magnitude more than the permeability (10^{-7}cm/s) of samples-I grouted with SA. Contrastingly, the permeability (10^{-6}cm/s) of samples-II grouted with both SA and SC was approximately the same order of magnitude (Fig. 6.5). The results from a series of permeability tests with both SA and SC grouts are illustrated in Table 6.1.

Table 6.1. Effect of Curing Time & Environment on Coefficient of Permeability of Silicate Grouted Specimens

Curing Environment	Grout Type	Coefficient of permeability *(cm/s)					
		Soil sample-I			Soil sample-II		
		1 day	3 days	7 days	1 day	3 days	7 days
room tempt.	SA	1.80×10^{-7}	5.1×10^{-7}	1.84×10^{-4}	1.6×10^{-6}	6×10^{-6}	2.8×10^{-4}
(22- 25 °C)	SC	2.99×10^{-6}	3.4×10^{-6}	1.42×10^{-4}	5.59×10^{-6}	1.17×10^{-4}	6.3×10^{-3}
constant low	SA	2.30×10^{-7}	2.1×10^{-7}	5.0×10^{-7}	-----	-----	----
tempt. (5 °C)	SC	1.49×10^{-6}	2.4×10^{-6}	3.1×10^{-6}	-----	-----	----
distilled water	SA	1.55×10^{-7}	3.4×10^{-7}	1.10×10^{-7}	1.1×10^{-6}	7.4×10^{-6}	1.17×10^{-4}
(21-23 °C)	SC	1.5×10^{-6}	1.0×10^{-6}	1.77×10^{-6}	2.78×10^{-6}	2.3×10^{-6}	1.57×10^{-6}

* Average of three samples

6.1.2 Effects of Grout Contents

This experimental program was intended to decrease the permeability of grout curtains. The effects of various ratios of sodium silicate and reagents contents on the
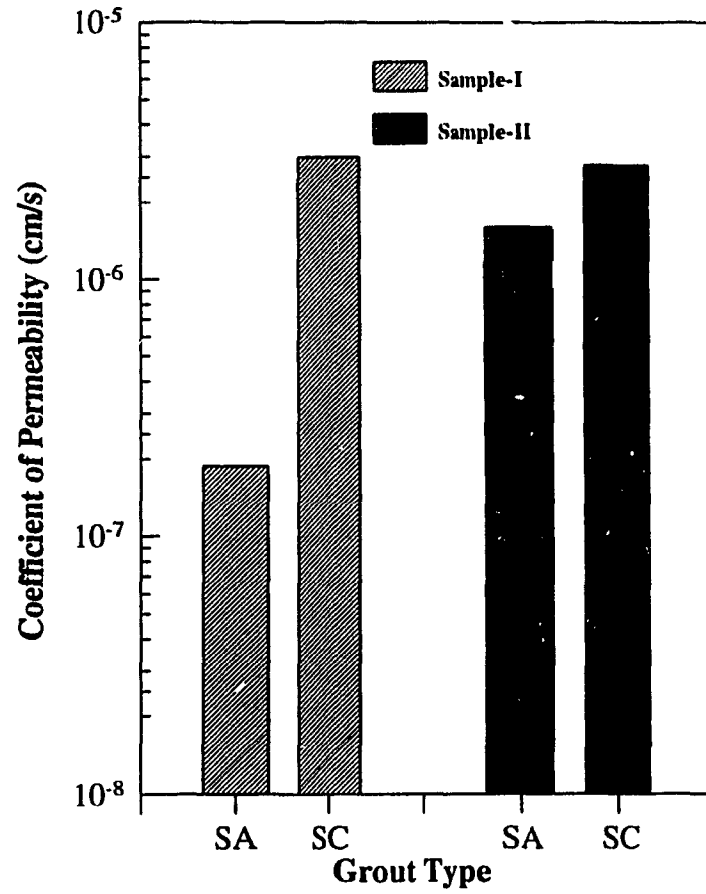
Figure 6.5. Effect of Grout Type on Permeability of Silicate Grouted Specimens

permeability of grouted sample-I and samnple-II cured for one day in open air at room temperature are presented in Table 6.3 and Table 6.4.

Sodium Silicate and Ethyl Acetate-Formamide Grout (SA)

The test results demonstrated that permeability decreased from 10^{-5} cm/s to 10^{-7} cm/s for soil sample-I and 10^{-4} cm/s to 10^{-6} cm/s for soil sample-II when the content of silicate increased from 5.98 g/100g to 7.98 g/100 g of soil (Tab. 6.2). No decrease in permeability was observed when silicate content was increased from 7.98 g/100g to 9.57 g/100 g of soil. When silicate content was kept constant and the quantity of organic reagents was increased, no decrease in permeability was noticed.

Table 6.2. Effect of Silicate and Organic Contents on Coefficient of Permeability

Wt.[1] of Reagent	Wt[1] of SiO_2	Wt.[1] of Na_2O	Permeability (cm/s)	
[1]g / 100 g of soil			soil sample-I	soil sample-II
3	5.98	1.84	5.6×10^{-5}	1.55×10^{-4}
4.8	5.98	1.84	1.8×10^{-5}	-----
4	7.98	2.46	1.88×10^{-7}	1.14×10^{-6}
4	9.57	2.95	1.4×10^{-7}	1.6×10^{-6}
4.8	9.57	2.95	1.33×10^{-7}	-----

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Sodium Silicate and Calcium Chloride Grout (SC)

For soil sample-I, when the silicate content was increased from 7.98g/100g to 10.63 g/100 g of soil, the permeability decreased by approximately a half order of magnitude. However, when sodium silicate was kept constant and calcium chloride was increased from 0.27g/100g to 0.53g/100g of soil, no noticeable decrease of permeability was observed (Tab. 6.3).

Table 6.3. Effect of Silicate & Calcium Chloride Contents on Coefficient of Permeability

Wt % [1] of Na₂O	Wt [1] of SiO₂	Wt %[1] of CaCl₂	Permeability (cm/s)	
[1] g / 100 g of soil			soil sample-I	soil sample-II
3.28	10.63	0.27	9.7×10^{-7}	-----
3.28	10.63	0.4	8.8×10^{-7}	-----
3.28	10.63	0.53	9.5×10^{-7}	-----
2.46	7.98	0.2	1.45×10^{-6}	1.45×10^{6}
2.46	7.98	0.4	2.93×10^{-6}	1.57×10^{6}

6.1.3 Effect of Water Chemical Composition

This experimental program was directed toward evaluating the effect of water chemical composition on the behavior of grout curtain performed with different silicate

grouts. The performance of a grout curtain herein was reflected by: 1) changes in permeability, 2) visible changes in structure of silicate grouted specimens.

6.1.3.1 Effect of Freshwater and Saltwater on Grout Curtain Permeability

Sodium Silicate-Ethyl Acetate-Formamide Grout (SA)

The permeability (10^{-7} cm/s) of samples-I grouted with SA and cured for 1-day at room temperature remained relatively constant for 4-days when subjected to freshwater. After 4-days, a slight decrease in permeability of one order of magnitude was observed (Fig. 6.6). Subsequently, the gradual rise in permeability occurred and finally ended within 20-days when the permeability approached its initial value (10^{-4}cm/s).

When samples-I grouted with SA cured for 1-day at room temperature and were subjected to saltwater, a high increase in permeability (10^{-5}cm/sec) occurred within 4-days (Fig. 6.6). In the case of specimens cured for 3 days, a one order increase in permeability was found after 4-days of saltwater actions. Then, specimens exhibited a constant permeability (10^{-6}cm/sec) throughout the remaining 20 days of the test (Fig. 6.7). A gradual increase in permeability with SA grout is evidence of changes in the structure occurring due to the hydraulic gradient and physico-chemical processes.

Sodium Silicate-Calcium Chloride Grout (SC)

Soil samples-I grouted with SC and subjected to freshwater and saltwater, showed a somewhat constant permeability throughout the period of the test (Fig. 6.8). Since the
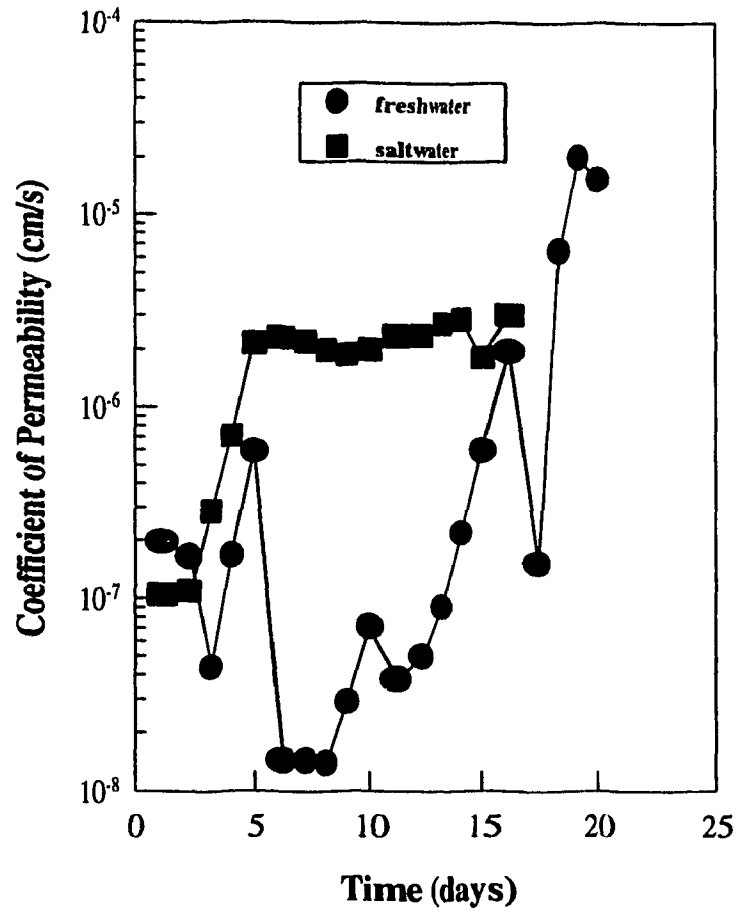
Figure 6.6. Effect of Water Chemical Composition on Permeability of Soil Sample-1
Grouted with Sodium Silicate & Ethyl Acetate-Formamide
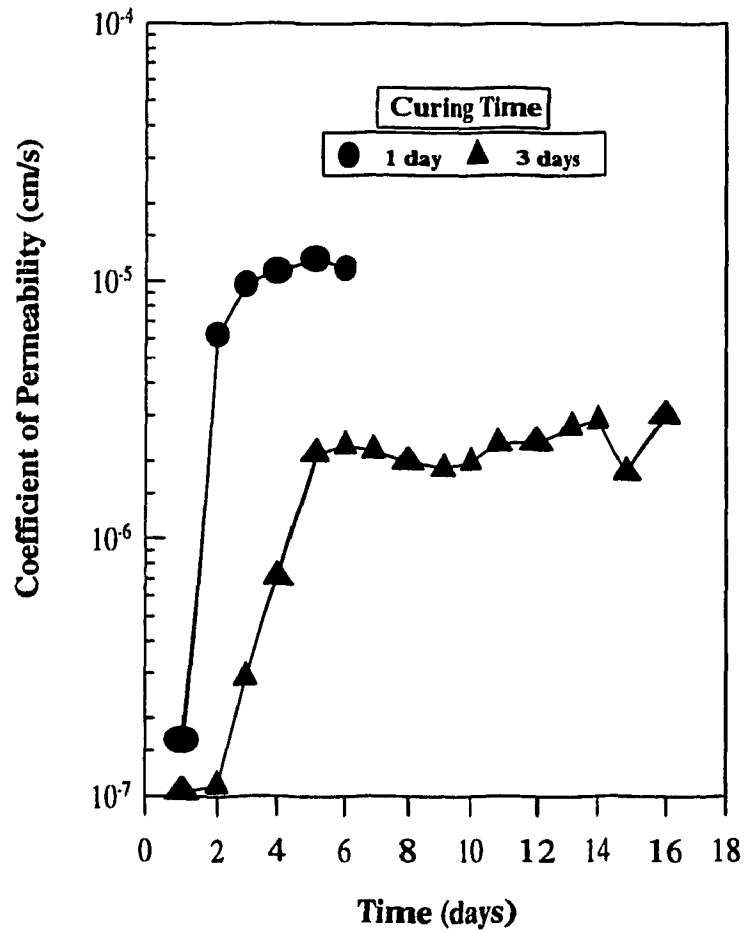
Figure 6.7. Effect of Saltwater on Permeability of Soil Sample-I Grouted With Sodium Silicate & Ethyl Acetate-Formamide
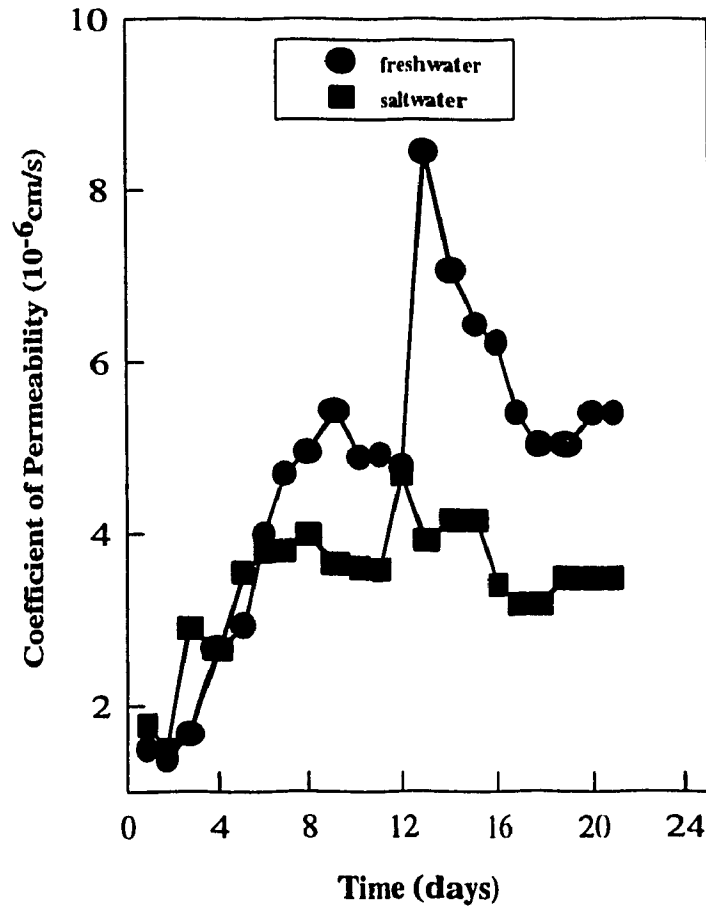
Figure 6.8. Effect of Water Chemical Composition on Permeability of Soil Sample-I
Grouted With Sodium Silicate & Calcium Chloride

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permeability (10^{-6}cm/s) remained fairly constant, SC grout was not susceptible to deterioration by the hydraulic gradient and water chemical compositions. This is probably due to the fact that calcium ions and magnesium ions in waters tend to form strong calcium and magnesium silicate.

6.1.3.2 Effect of Freshwater and Saltwater on Grout Curtain Structure

Sodium silicate-Ethyl Acetate-Formamide Grout (SA)

For grouted samples-I submerged in freshwater, deterioration of the specimens was observed after approximately 13-days (Fig 6.9a). When grouted samples-II were submerged in freshwater, they were destroyed after 4-days (Fig. 6.9b). These observations are consistent with the results of the permeability tests, and probably indicate that the SA grout structure was elutriated from specimens by the physico-chemical action of freshwater.

When grouted samples-I and samples-II were cured submerged in saltwater, no visible changes in the structure were observed for 60-days (Fig. 6.9a and 6.9b).

Sodium Silicate-Calcium Chloride Grout (SC)

When sample-I and sample-II grouted with sodium silicate and calcium chloride solution, the grout delayed the deteriorating effects of freshwater to 60 days for grouted samples-I and 30 days for grouted samples-II. When grouted sample-I and sample-II cured submerged in saltwater for 60 days, no visible structure changes were observed

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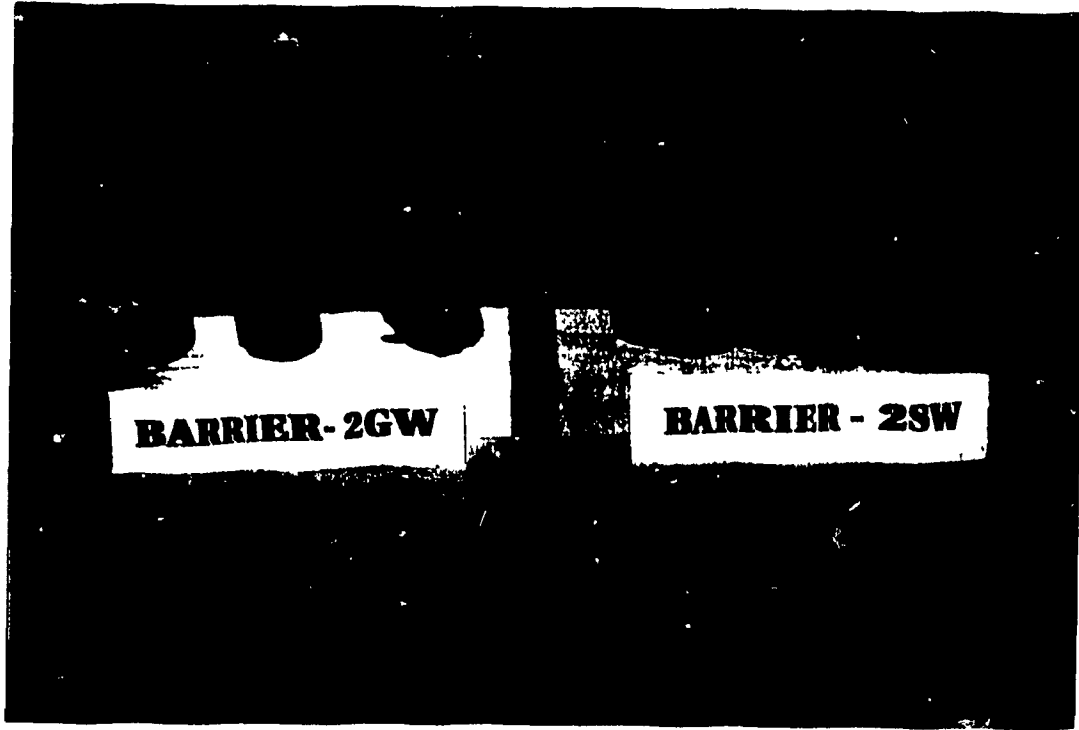
Figure 6.9. Effect of Water Chemical Composition on Sample-I (a) and Sample-II (b)
Grouted with Sodium Silicate & Ethyl Acetate-Formamide
GW: Freshwater SW: Saltwater
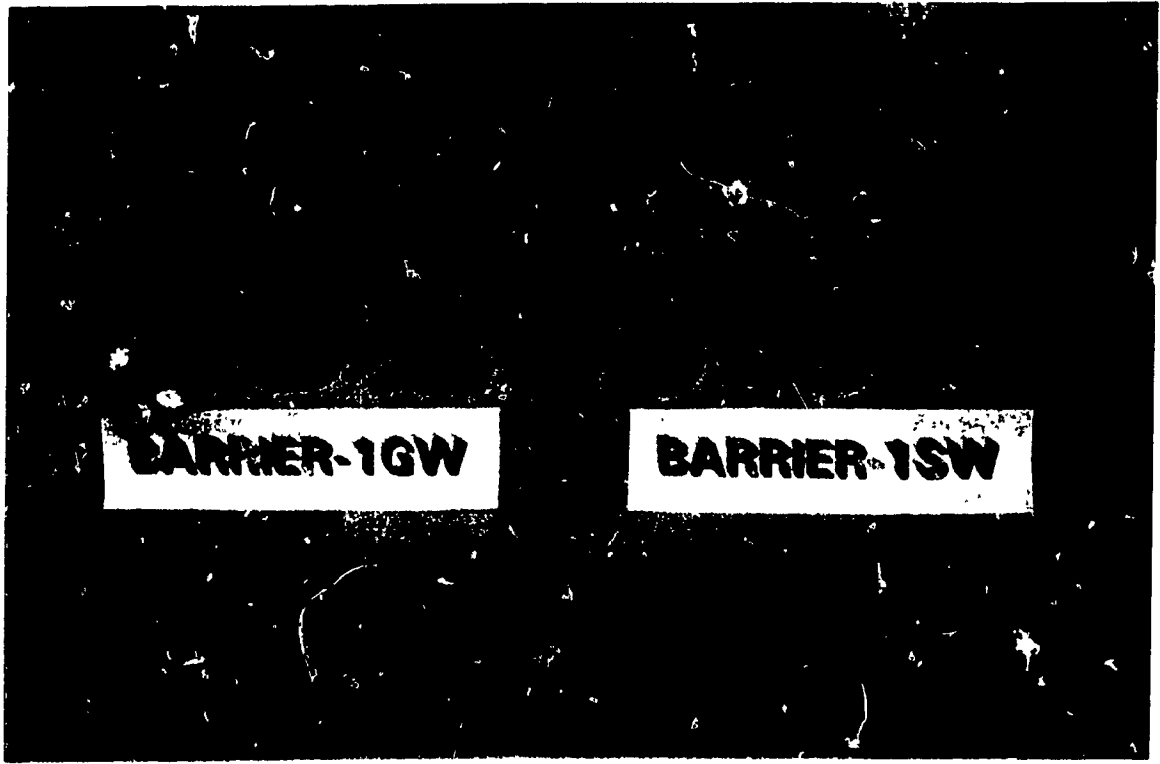
Figure 6.10. Effect of Water Chemical Composition on Sample-I (a) and Sample-II (b)
Grouted with Sodium Silicate & Calcium Chloride
GW: Freshwater   SW: Saltwater

(Figure 6.10a and 6.10b).

Generally, both SA and SC specimens were found not to be affected by saltwater. This can be a result of the thin layer observed on the surface structure of the grouted specimens. It was found by using IR Spectroscopy that this layer resulted mostly from carbonates.

6.1.4 Investigation of Water Quality

Periodic water analyses of collected samples during the second series of tests from phase 3 were performed to determine: 1) possible leaching of sodium silicate from grouted specimens and, 2) change in water pH.

Sodium Silicate-Ethyl Acetate-Formamide Grout (SA)

Silicate leaching from SA grout was high. An increase of silicate leaching was in progress with continued immersion of grouted specimens in freshwater. However, it was found that silicate concentration in saltwater was less than that in freshwater. The silicate concentrations after 5 weeks were 3.6 mg/l and 0.72 mg/l in freshwater and saltwater respectively (Fig. 6.11).

When grouted specimens were placed into containers filled with freshwater, continuous increase in the pH value was estimated. A slight increase in saltwater pH of up to 8.7 was observed for less than 6 days. Then, pH decreased slowly toward its initial value of 7.7 (Fig. 6.12).
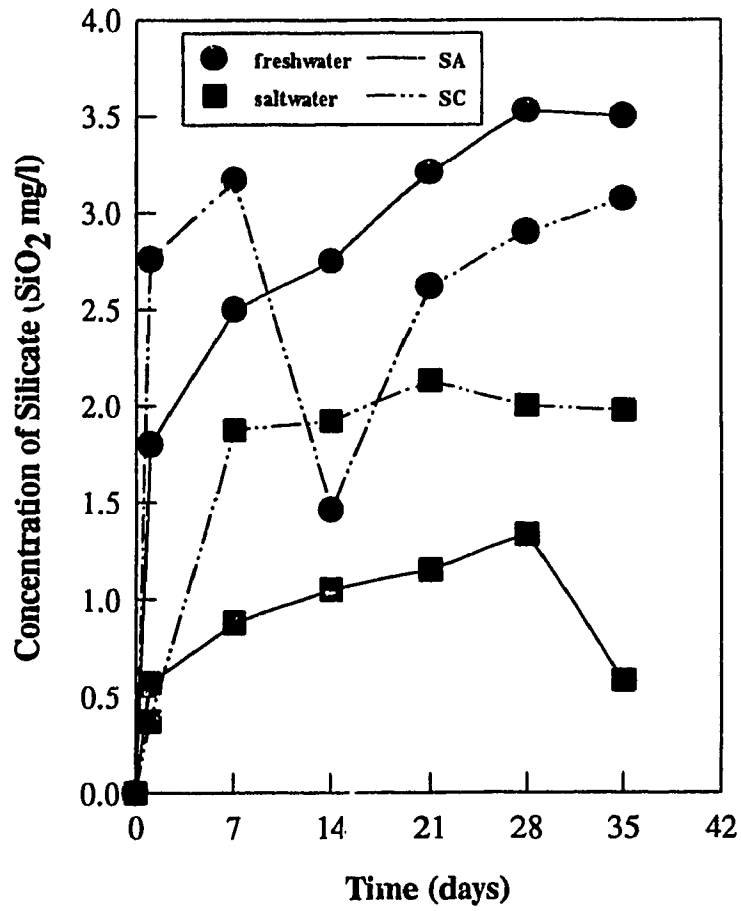
Figure 6.11. Silicate Leaching After Curing Silicate Grouted Specimens
At Different Water Qualities
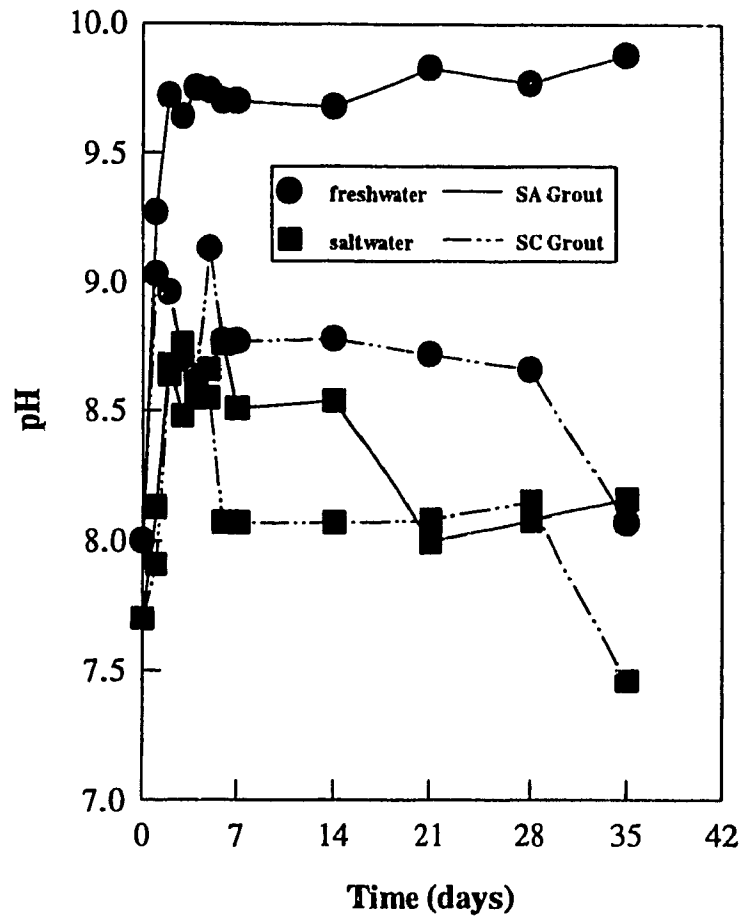
Figure 6.12. pH of Water After Curing Silicate Grouted
Specimens at Different Water Qualities

Sodium Silicate-Calcium Chloride Grout (SC)

Silicate leaching from SC grout was high when specimens were cured submerged in freshwater. On the other hand, less silicate leaching was observed when specimens were cured submerged in saltwater. The silicate concentrations after 5 weeks were 3.27 mg/l and 2.1 mg/l in freshwater and saltwater respectively (Fig. 6.11).

When grouted specimens were placed into containers filled with freshwater, pH value of freshwater was estimated to be approximately 9 for six days. Subsequently, freshwater pH decreased slowly until it reached its initial value of 8. A slight increase in saltwater pH of up to 8.7 was determined for less than 6 days. Then, the pH decreased slowly to approach its initial value of 7.7 (Fig. 6.12).

6.2 Microscale Study Results

The results from IR and UV analyses were used to provide a complementary picture on silica gel formation and its behavior in freshwater and saltwater.

6.2.1 Formation of Silica Gel

In the first test of this study, the bonding group of the gel formed by sodium silicate with organic reagents were examined using IR spectroscopy. IR spectra of the initial ethyl acetate (EA) and formamide (FA) coincided with the spectra reported by Pouchurt (1981) and Keller (1986). IR spectrum of a mixture of these two organic

components showed no reaction between them. i.e. there is no shifting of the band to other regions of the spectrum as well as no change in absorbance when compared with the original spectra of EA and FA.

By comparing, the IR spectra of initial EA and FA with the spectrum of the grout, it was found that the highest changes occurred in the regions 2900-2700, 1750-1600 cm^{-1}. These results and assignment of bands (Tab. 6.4) showed that the low frequency shift of the bands 1750 cm^{-1} of EA and 1680 cm^{-1} of FA was related to the stretching vibration of C=O groups. Therefore, the C=O groups from both organic compounds were involved in the transformations occurring during the gelation process.

Table 6.4. Main IR Absorption Bands of SA Grout Components.

Formula		Assignment	
		C-H stretching cm^{-1}	C= O stretching cm^{-1}
Formamide	HCONH$_2$	2880 m*	1680 vs
Ethyl acetate	CH$_3$COOC2H$_5$	2995 m	1750 s
Sodium silicate	Na$_2$ SiO$_3$	------	------
Grout : 50 % Na$_2$ SiO$_3$ 10 % HCONH$_2$ & CH$_3$COOC$_2$H$_5$, 40 % H$_2$O		2880 m	1660 sh, 1600 vs

* relative intensity of the bands : s- strong, m- medium, sh- shoulder, vs- very strong

Consequently, two reactions resulting in the low-frequency shift of the C=O band can be assumed:

1) the hydrolysis reaction of EA, which forms acetic acid or sodium acetate in the presence of NaOH, was proposed as the main reaction in the gelation process by other investigators. In this process, the band of C=O group in acetic acid usually is located in 1720 cm^{-1} region. Two strong bands related to the C=O group in sodium acetate are

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usually located at 1356 and 1413 cm^{-1} (Nakamoto, 1986). These features do not coincide with the present observations.

2) A complexion reaction between the sodium cations and the carbonyl group was assumed. This reaction may cause bonding between different molecules or groups of sodium silicate molecules in large aggregates. Therefore, the carbonyl group serves like a bridge between the inorganic components. This reaction should be the preliminary stage of silicate gel formation. In the next stage of the gelation process, the hydrolysis reaction of organic bridges (C=O) probably occurs resulting in a regular structure of bonded silicate groups similar to quartz. Hydrolysis causes the transformation of the solution to gel and transfer water, organic compounds and sodium cations in the liquid phase.

In the preparation of samples with various sodium silicate concentrations, an intensity change of the band was observed (Fig. 6.13). The increasing sodium silicate concentration caused changes in the intensity of the bands : 2820, 1600, 1350 and 770 cm^{-1} which are related to organic components.

6.2.2 Grout Behaviour During Curing Processes

In the second test of this study, the collected effluent (precipitated and transparent layers) during the permeability test and from cured water around the grouted specimens were examined using IR and UV spectroscopy.

The IR Spectra of precipitate was similar to the IR spectra of the grouting mixture (Fig. 6.14). Therefore, it can be concluded that part of the grout mixture was dissolved
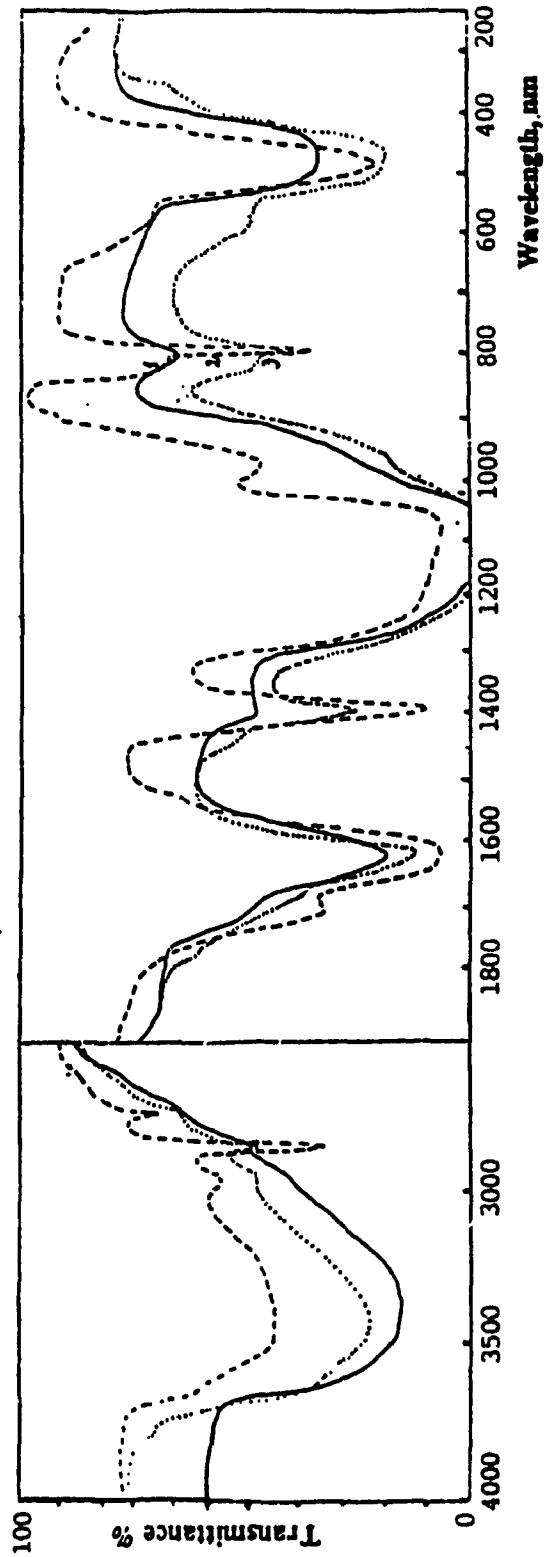
Figure 6.13. The IR Spectra of the Grout Mixture(1) 60 % Sodium Silicate, (2) 50% Sodium Silicate

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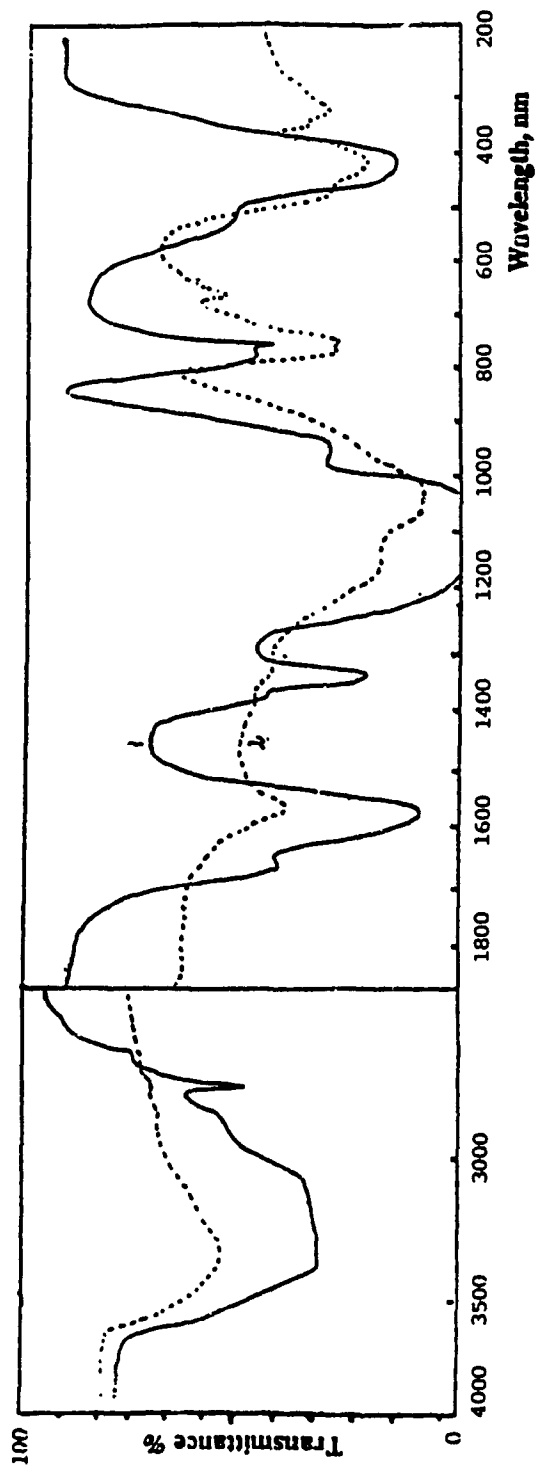
Figure 6.14. The Spectra of Precipitate Part of Effluent (1) and Grouted Soil (2)

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during the permeability tests.

In attempting to detect grout organic components, the transparent parts of the collected effluent were subjected to UV analysis. These transparent parts had no absorbance in the UV region of the spectra. It should be mentioned that the transparent upper layer that was obtained from permeability tests of grouted sample-I had a brown color. The color depended on effluent pH. With decreasing pH (approximately 8.4), the color of freshwater and saltwater effluent disappeared after 7-days and 11-days respectively (Fig. 6.15).

Soil contains humic compounds, including humic acids and fulvic acids (see Appendix B). The solubility of humic acid and fulvic acid can successfully be increased with increasing leachate solution pH (Fig. A-6). Since silicate grout has a high pH, the brown color of the effluent is probably connected with the removal of humic compounds which are included in the composition of sample-I. Moreover, the samples collected during the permeability test (test-1/phase-1) on grouted sample-II were found colorless, this strongly indicates that the brown color was related to humic compounds in sample-I.

The waters in which the grouted sample-I and sample-II were cured for 1, 7, 14, 21, 28, and 35 days were examined by using UV spectra. It was found that the sodium silicate content leached from SA grout is much less in saltwater than in freshwater. In the case of SC grout, the sodium silicate leached in freshwater and saltwater decreased toward equilibrium (Fig. 6.16).

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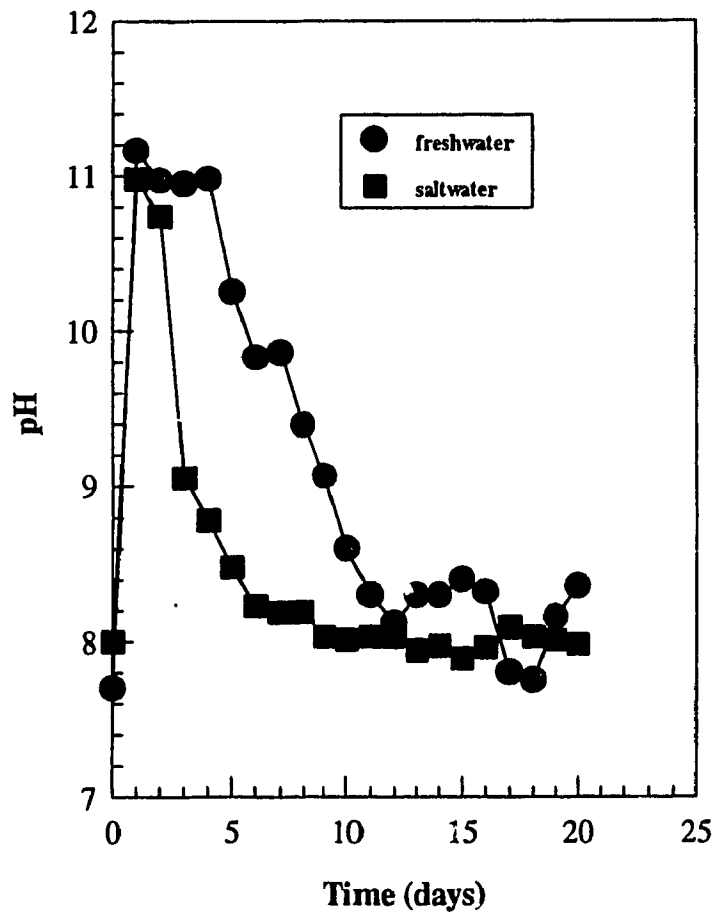
Figure 6.15. pH of Effluent Versus Time
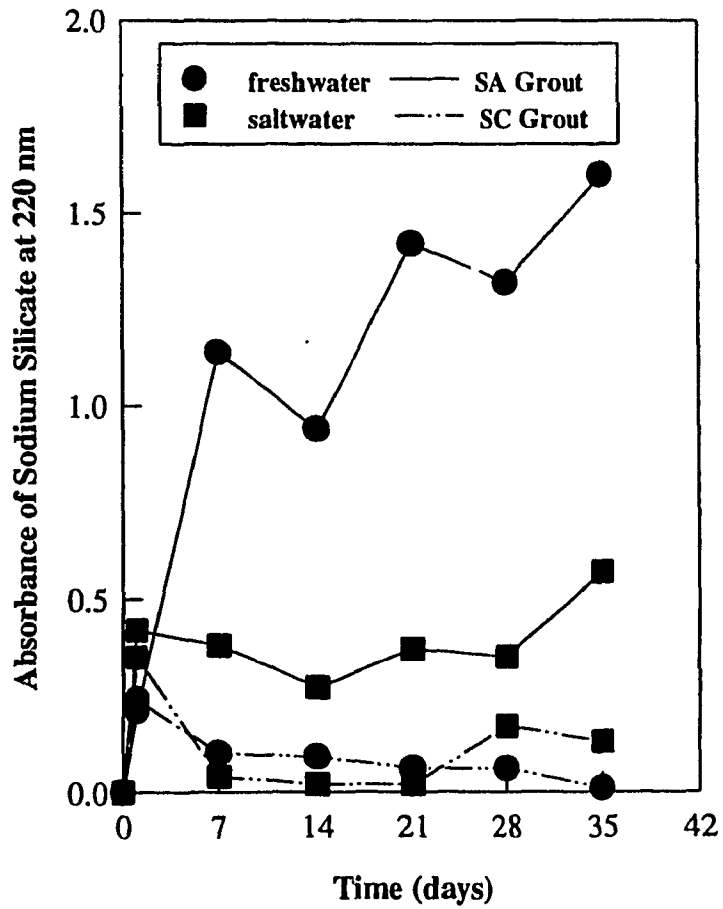
Figure 6.16. Sodium Silicate Leaching After Curing Silicate Grouted
Specimens At Different Water Qualities

CHAPTER 7

Conclusions And Recommendations

7.1 Conclusions

Based on the laboratory tests, the following conclusions can be made:

1. The macroscale laboratory study demonstrated that grout curtains behave differently and depend on the following factors: a), grout type and content, b) curing time and environment and c) water chemical composition

1.a. A decrease in permeability was observed, with both sodium silicate-ethyl acetate-formamide (SA) and sodium silicate-calcium chloride (SC), when silicate was added to sample-I (a mixture of sand, silt and clay) and sample-II (white silica sand).

1.b. The curing time and the environment exerted a substantial effect on the permeability of silicate grouted specimens:

i. Silicate grouted specimens (sample-I and sample-II) submerged in distilled water showed no increase in permeability with curing time. However, sample-II grouted with ethyl acetate-formamide (SA) exhibited an increase in permeability when cured for

more than one day in distilled water.

ii. The curing time did not affect the permeability of both silicate grouted specimens cured at a constant low temperature (5 °C).

iii. Both sodium silicate-ethyl acetate-formamide (SA) and sodium silicate-calcium chloride (SC) grouted specimens, cured in open air at room temperature (22-25 °C), exhibited a substantial increase in permeability with curing time. This is probably due to the shrinkage of soil matrix or silicate grout between soil grains with time.

1.c Silicate based grouts reacted differently when they were subjected to and submerged in freshwater and saltwater:

i. Sodium silicate and calcium chloride (SC) in contact with either freshwater or saltwater showed no increase in permeability during the test. This is due to the fact that calcium or magnesium ions in soil or water form an additional coated sheath of calcium or magnesium silicate around soil particles.

ii. Sodium silicate with ethyl acetate-formamide (SA) subjected to freshwater and salt water exhibited large increases in permeability. Permeability seemed to increase with time.

iii. When both SA and SC grouts were cured submerged in saltwater, the structure of the grouted sample-I and sample-II remained intact during the test.

iv. Both sample-I and sample-II grouted with SA deteriorated rapidly when they were cured submerged in freshwater. The deterioration of specimens grouted with SC was observed after 30-days for sample-I and 60-days for sample-II. This indicates that fine soil particles were capable of retaining grout in their voids for a longer period than

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coarse soil particles. Therefore, the deterioration process does not only depend on reagent types, but also on soil particle size

2. A periodic analysis of water demonstrated that the concentration of silicate leachate from both SA and SC grouts was higher when specimens were cured submerged in freshwater rather than saltwater. This indicated that silica gel was less susceptible to dissolution in the presence of saltwater.

3. SA grout caused a continuous increase in freshwater pH whereas SC grout increased pH of freshwater up to 9 in 6 days. With both SA and SC grouts, the saltwater pH increased slightly up to 8.7 and then decreased towards its initial values of 7.7.

4. Microscale study demonstrated that:

4.a. Silicate leaching was observed when SA and SC grouts were brought in contact with freshwater and saltwater.

4.b. Both SA and SC grouts dissolved the humic substances present in the sample-I. This is probably due to the increase of soil pH value in that environment.

5. Finally, the research determined that SC grouted specimens are less vulnerable to the action of freshwater and saltwater than specimens grouted with SA. Therefore, sodium silicate and calcium chloride may be used to form grout curtains to restrict seawater intrusion into a coastal aquifer.

7.2 Recommendations

Several recommendations for further application of the method are suggested based on the results of this study:

1. Before field applications, a detailed soil analysis is required to determine the particle size distribution as well as the inorganic and organic components of soil which may influence the behaviour of silicate grouted specimens.

2. A compatibility study should be conducted on particular soil samples for different grout component ratios. This will lead to the optimization of the grouts setting time. and avoid the its dilution by groundwater as well as its premature setting in the injector.

3. Field and technological parameters including grout flow rate and injection pressure have to be designed based on information obtained from the soil analysis and the grouts compatibility study. Preliminary test programs may be performed in the field in order to verify the grouting parameters.

4. The compatibility of the grout with the chemicals in groundwater should be examined.

5. When grout injection is limited by the presence of fine minerals in soil (clay or silt), the electrokinetics technique can be used to introduce the grout.

6. Further research work should be performed to evaluate the interaction systems of sodium silicate grout agents with components of natural soil such as amorphous materials and humic substances.

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APPENDIX-A

SOIL COMPOSITION

APPENDIX A

Soil Composition

A.1 Introduction

Soil constituents consist of solids, liquid and gas. The solids include inorganic and organic components. The inorganic components can take the form of minerals as well as crystalline and non-crystalline materials. Organic components include primarily partly decomposed humic substances and soil polysaccharides. The liquid contains water with dissolved solutes. The gas is composed of nitrogen, oxygen and carbon dioxide.

The solid components and soil water chemistry control the properties of a soil. Therefore, to obtain a general understanding of soil composition, this chapter briefly describes the structures of important minerals and other solids constituents.

A.2 Primary and Secondary Minerals

Primary minerals are derived in unaltered form from the parent rock. They include quartz, feldspar, micas, amphiboles and pyroxenes. Contrastingly, the secondary minerals are derived as altered products of physical, chemical and/or biological weathering processes. They

exhibit a large specific surface area because of their small particle size.

Secondary minerals are layer silicates (phyllosilicates) and comprise the major portion of clay-sized fraction material in soils. Clay minerals or silicate mineral varies between slightly active mineral of kaolinite up to the highly active minerals of montmorillonite, carrying an intense field of negative charges. Thus, surface structure of the clay minerals characterised by possessing negative charges on the soil particles. The more common layer silicates in soils include kaolinites, illite, and montmorillonites.

Primary minerals in soil posses low specific surface areas and are thus of lesser importance in interaction processes in the soil. On the other hand, the secondary minerals in soil exhibits large specific surface areas and significant surface charge. Thus, secondary minerals are very important in interaction processes in the soils

A.2.1 Kaolinite

Kaolinite is a 1:1 layer clay mineral. Each layer consists of a sheet of silica tetrahedral (Si and 4 O) and sheet of aluminium octahedral (Al and 6 OH). The two sheets share a layer of oxygen atoms forming a single plane (Fig. A-1). Successive layers of the basic structure are held together by Van der Waals force and hydrogen bonds between hydroxyls from the alumina sheet and oxygen from the silica. Since the hydrogen bond is very strong, it prevents penetration of water between successive layers (i.e. no interlayer swelling) and allows many layers to build .
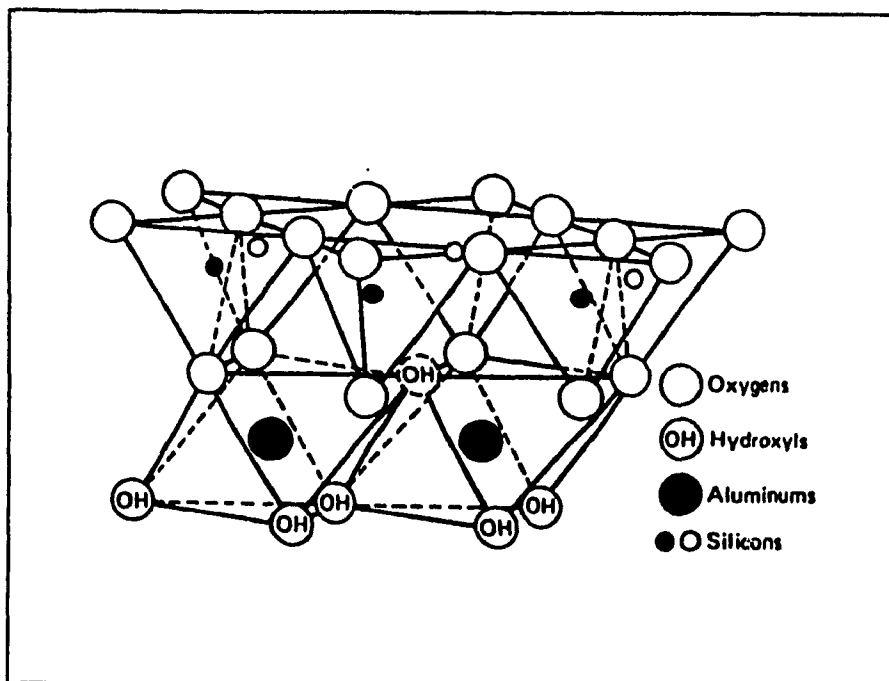
Figure A-1. Kaolinite Structure (after Mitchell, 1976)

A typical kaolinite crystal can be 70 to 100 layers. The height of the kaolinite unit cell is 7.2 A° and the specific surface area is in the order of 10 to 20 m²/g of dry clay. Kaolinite clay mineral have a small net negative charge resulting from the little isomorphous substitution in kaolinite minerals (Yong et al, 1992). Because of low surface activity, kaolinite exhibits low plasticity and swelling potential. The cation exchange capacity (2-15 meq/100g) is attributable primarily to the edges of the particles. When hydrogen ion concentration of pore water decreases, broken bonds will attract an extra hydrogen ion and kaolinite becomes positively charged or neutral.

A.2.2 Illite

Illite consists of a sheet of aluminium octahedral sandwiched between two sheets of silica tetrahedral with shared oxygen to make a unit four oxygen atoms thick. The layers are bonded together by potassium cations arising from the substitution of aluminium for silicon in the silica sheet to balance the negative charge. The potassium atom fits tightly in the hexagonal hole in the silica sheet and it is not exchangeable (Fig. A-2). As a result, a strong bond exists between the layers. Since illite layers are tightly bonded by interlayer potassium bond, it effectively prevents hydration and does not expand. The height of the illite layer ranges from 10A° to 14 A°. The cation exchange capacity (CEC) is about 20-40 meq/100g and the specific surface area for the minerals is about 65-100 m²/g. Because of the lack of interlayer swelling, the cations between the layers are not available for exchange. Therefore, CEC involves only the ions on the exterior surface of the stack.
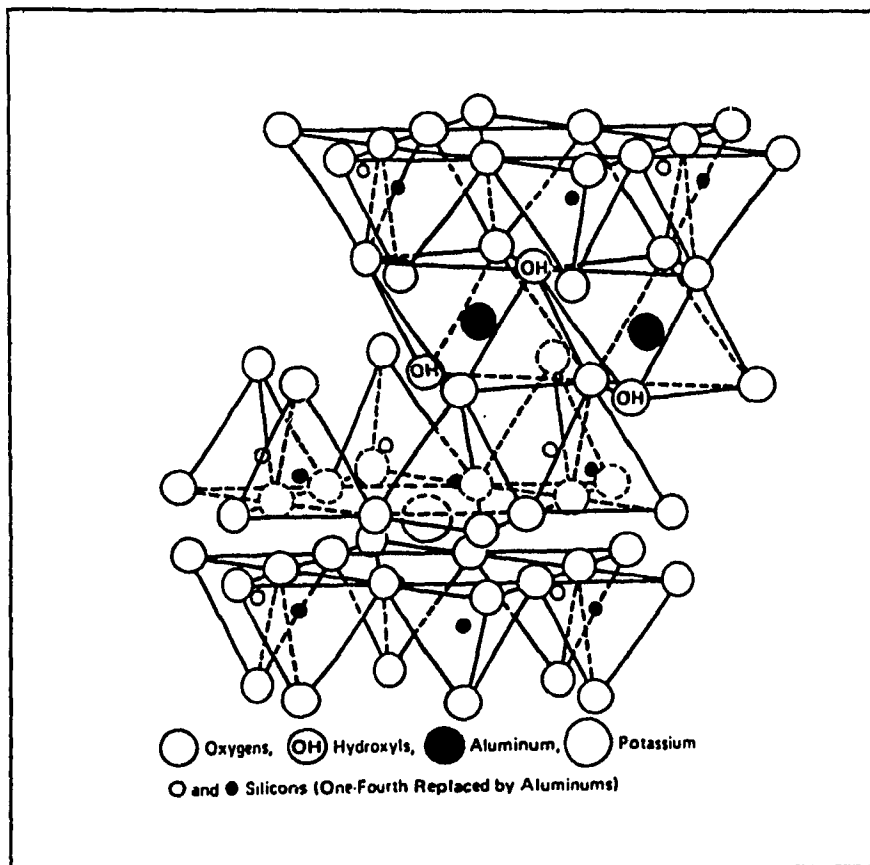
Figure A-2. Illite Structure (after Mitchell, 1976)

A.2.3 Montmorillonite

The montmorillonite minerals have the same layers as illite. However, isomorphous substitution occurs mainly in the alumina sheet, with magnesium or iron substituting for aluminium in the dioctahedral minerals. The substitution of higher positive valence for that of lower valance results a net negative charge on the surface of montmorillonite. This charge deficiency is usually balanced by exchangeable cations that are positioned between the layers and on the surface of particles (Fig. A-3).

Montmorillonite particles usually exist as stacks held together by Van der Waal forces when they are dry. These forces are fairly weak and are easily broken with water. The penetrated water is adsorbed to the clay surface by establishing hydrogen bonds. Since this is a strong bond, water can not be easily separated from the montmorillonite mineral. As a result, montmorillonite particles can be dispersed in sheets of unit layer thickness of 10 A°. This dispersion results in a specific area of 600-800 m²/g. Montmorillonite has high cation exchange capacity (usually around 80 to 150 meq/100g), and large degree of swelling due to the hydration of interlayer cations and to the fact that the large hydration energy involved is able to overcome the attractive forces between the layers. Because of the high specific area, montmorillonite is the most active mineral to react with chemicals.

A.3 Amorphous Materials

They includes allophanes, imogolites, amorphous silica, amorphous iron and aluminum hydrous oxides. In this section only amorphous silica, iron, and alumina oxides will b discussed.
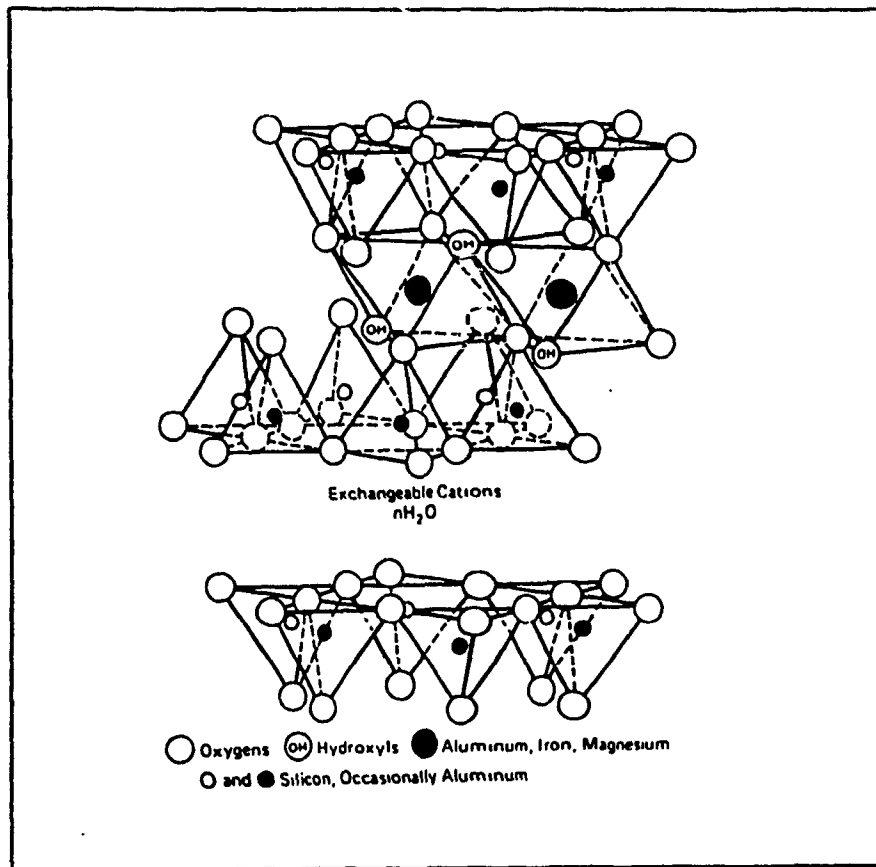
Figure A-3. Montmorillonite Structure (after Mitchell, 1976)

Amorphous material are generally believed to be a weathering product derived primarily from parent minerals, such as amphibole and feldspar. The iron and alumina oxides originate in the octahedral sheet of clay minerals and the silica originate in the tetrahedral sheet of the clay. Amorphous materials have a specific surface area that varies from 790 m^2/g for pure silica (MR = 0) to 670 m^2/g for the pure iron (MR = 1) with a minimum of about 500 m^2/g for mixed iron hydroxide and amorphous silica at MR = 0.4, where MR is amount of amorphous iron to the sum amount of iron and silica in the form of oxides (Young et al, 1992). Therefore, the surface area of amorphous materials can be as high as 500- 800 m^2/g depending on its composition and type. Amorphous materials have a cation exchange capacity ranging from 8.0 mequiv/100g for pure amorphous iron to 55 mequiv /100g for pure amorphous silica (Yong et al, 1992). The surface charges of amorphous materials vary with pH and, hence, amorphous materials are very sensitive to a change in the environment, such as pH, pore fluid chemistry and mechanical disturbance.

Amorphous materials are compounds of the cementation bond in sensitive clay. Amorphous materials provide a coating which surrounds the largest primary minerals and which contribute to the bond mechanism within the soil fabric units and generate a high remoulded shear strength (Yong et al, 1992). The existence of some amorphous material in soils would enhance its sorption of solute materials (Yong et al., 1992). The removal of amorphous materials may change the mechanical properties of sensitive clay. Removing amorphous iron or alumina increases the void and causes a decrease in the strength. The sample from which amorphous silica was removed showed an increase in the remoulded strength after pH decreased to 7. This the shear strength increase was probably due to the

bridging effect of fresh precipitated silica between soil particles (Becker, 1979). Figure A-4 shows the effect of washing on the structure of amorphous materials.

A.4 SOIL ORGANIC MATTER

Soil contains organic compounds, molecules composed of carbon and hydrogen, with carbon as the skeletal structure. Organic materials occur in mineral surface soils in proportions as small as 0.5% to 5% by weight. Peat is exception with proportions as high as 100%. They originate from vegetation and animal sources. The organic constituents in soil are grouped into humic substances, polysaccharides and functional groups. This section will briefly discuss humic substances.

Humic substances including humic acids, fulvic acids and humins, are entirely amorphous (Yong et al 1992). Humic substances are aromatic polymers and recognised for their high functional group content. They are polymers with molecular weights ranging from hundreds to tens of thousands. The high functionality and surface area of humic material appear to account for their high interactive and complexion properties (Kononova et al, 1961; Yong et al, 1992).

Humic acids represent polydisperse systems with a wide range of molecular weights varying from a few 1,000 to more than 100,000 (Mc Laren et al 1971). Humic acids are soluble in base and precipitate in acids. They are formed of the following constituents: 50-65% carbon, 15-40% oxygen, 3-5% hydrogen, 3-5.5% nitrogen (Kononova et al, 1961; Kumada,
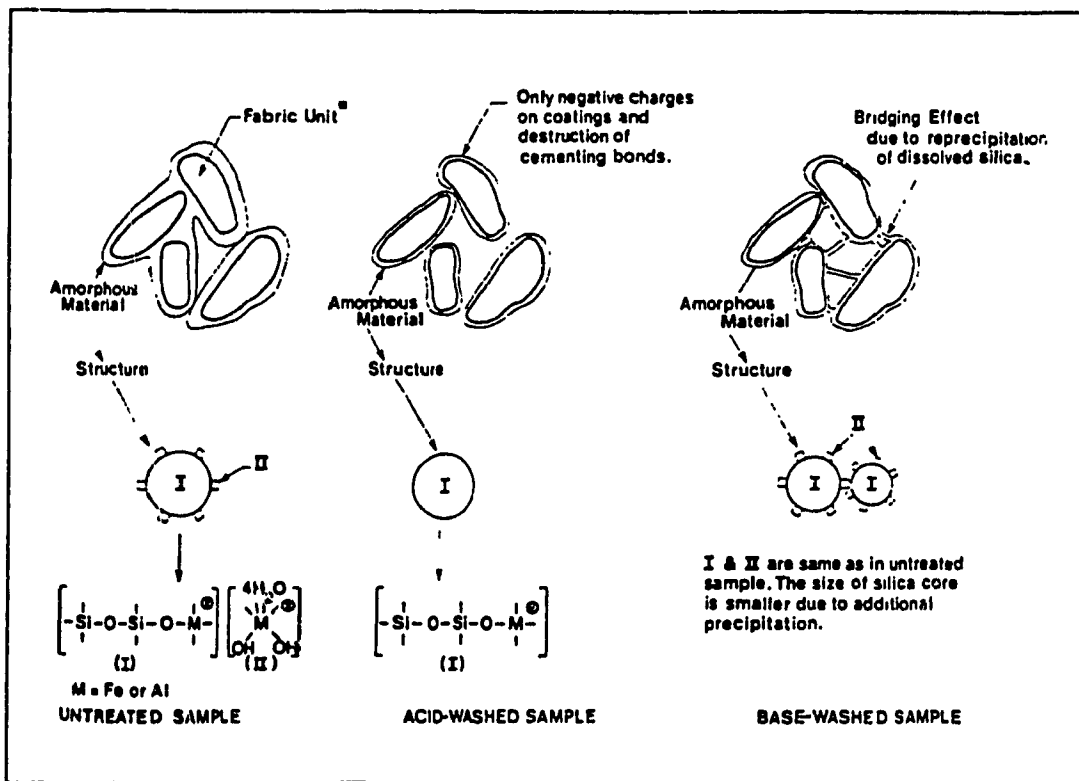
Figure A-4. Effect of Washing with Acids and Bases on the Structure of Amorphous Materials (after Yong et al, 1979)

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1987). Carbon and oxygen may be likely to reflect the difference conditions of soils. Humic acid compositions are significantly higher (>85%) in soil of pH 4-5 than those of soil of pH 8 (<13%) (Kumada, 1987). These humic acids are aromatic polymers with carbon aromaticity values ranging from approximately 35-92 % (Yong et al, 1992). The total functional group of humic acids were reported in wide ranges of the values depend on soil types and partly on the investigation method. The average values reported in the literature are as follows: total OH, 2-7%; carboxyls, 3-10%; phenolic OH, 2-5%; alcoholic OH, 0-2%; carbonyls, 0.5-4%; quinones, 1-2%; and ketonic groups, 1-4%; methoxyl groups, 1-2% (Griffith et al, 1975).

Fulvic acids contain more oxygen and sulphur and less carbon, hydrogen and nitrogen than humic acids. Elementary compositions of fulvic acids have been reported in the literature: carbon, 40-50%; oxygen, 40-50%; hydrogen, 4-7%; nitrogen, 0.7-3% and sulphur 0.25-4 % (Kononova et al, 1961; Kumada, 1987, Yong et al, 1992). The functional groups include: carboxyls, 1.5-6%; phenolic OH, 2-6%; alcoholic OH, 2.5- 4%; quinones, 2.5-4%; ketones, 1.5-2%; and carbonyls, 0.3-5% (Griffith et al, 1975).

Only a small fraction organic matters presented in the soil is free. The major portion is linked with minerals. Humus substances form links with cations of alkaline metals in the form of humuate and fulvates of Ca, Mg, K, Na, Al, Fe, NH_4 (Kononova et al, 1961). The links shape occurs by exchange reactions of humic acids and fulvic acids with soluble alkaline or neutral salt. In this reaction, the hydrogen of functional groups-carboxyl and phenolic hydroxyl-is replaced by a metal. The replacement increases with pH increase (Kononova et al, 1961). Humic acids are soluble in base but precipitate in acid, whereas fulvic acids are soluble in base

and acid (Fig. A-5). However, the interaction of clay with humic acids and exchangeable cations form a type of linkage that is not extracted by alkaline (Kononova, 1961).

Humins are insoluble in both acid and alkali. They are generally considered to be composed of carbon, with minor fractions of nitrogen and polysaccharides. However, not much attention has been paid to the composition of these materials, and much work remains to be done to better understand these materials (Yong et al, 1992).
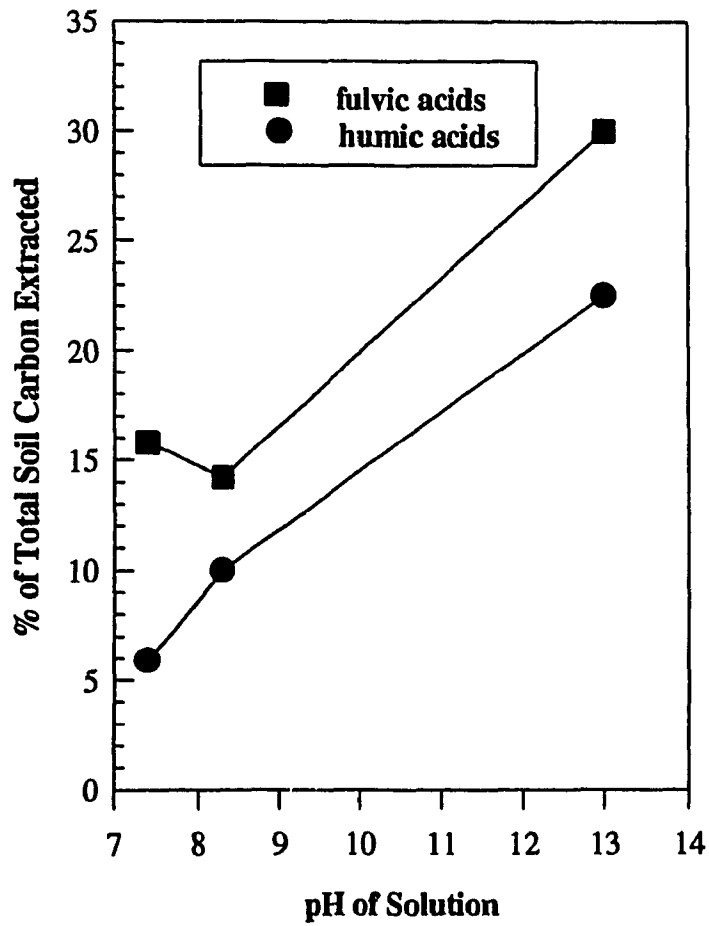
Figure A-5. Effect of pH on Solubility of Humic Substances
(data from Kononova et al, 1961)

APPENDIX-B

EFFECT OF SALT ON PERMEABILITY

OF SOIL

APPENDIX B

Effect of Salt on Permeability of Soils

B-1 Soil-Water interaction

Clay particles carry negative charges on the their surface. These negative charges can absorb cations in the soil solution. The positively charged side of water molecules are also oriented toward the negatively charged clay minerals. Therefore, water molecules will hydrate to clay minerals and exchangeable cations located on the clay minerals surface. The exchangeable cations become much larger once hydrated.

The distribution of cations on the clay surface after hydration is caused by an electrostatic force. This force tends to attract some cations to the clay surface and repel anions from the negatively charged surface. Other cations can diffuse away from the clay surface in order to equal their concentration in solution. The diffusion tendence and the electrostatic attraction can generate an diffuse double layer. The attraction and repulsion forces determine the thickness of the diffuse double layer. The diffuse double layer is compressed or extended with changes on the clay particle concentration and chemical composition of the soil-water system as well as the mode of particle interaction and the distance between particles.

The type of exchangeable cations and the ionic concentration are the most important factors affecting the thickness of the diffuse double layer, i.e, cross linking force between particle (Fig. B-1). Consequently, the introduction of a salt solution into soil tends to change the activity of the surface forces. This alteration may cause corresponding changes in the thickness of water layers held to clay soil particles. Moreover, a change in porous fluid composition may bring substantial alterations in the soil particles arrangement. Flocculation and dispersion are the most important type of particle rearrangement (Fig. B-2). Maximum flocculation of clay particles (face to face structure) occurs when the valence of counter ions and salt concentration increases, and pH decreases, whereas maximum dispersion occurs at low salt concentration, low valence, and high pH.

From the above discussion, it clear that the hydraulic properties of soil will not only depend on soil type but also on the solution. Therefore, the following section will discuss the effect of salt water on the permeability of different clay minerals groups.

B.2 Effect of Salt Concentration and Composition of Pore Fluid on Permeability

Soil composition, salt type and concentration have a great influence on the permeability of soils. Fine-grained soil typically contains a substantial clay fraction that possesses electrochemical forces capable of acting between the particles and the solution. Upon introducing the solution, the soil-water system changes the double layer thickness, which in turn causes clay particles to flocculate or disperse in electrolyte solution. On the other hand, sand and silt particles are generally inert to solution passing the porous medium. Hydraulic
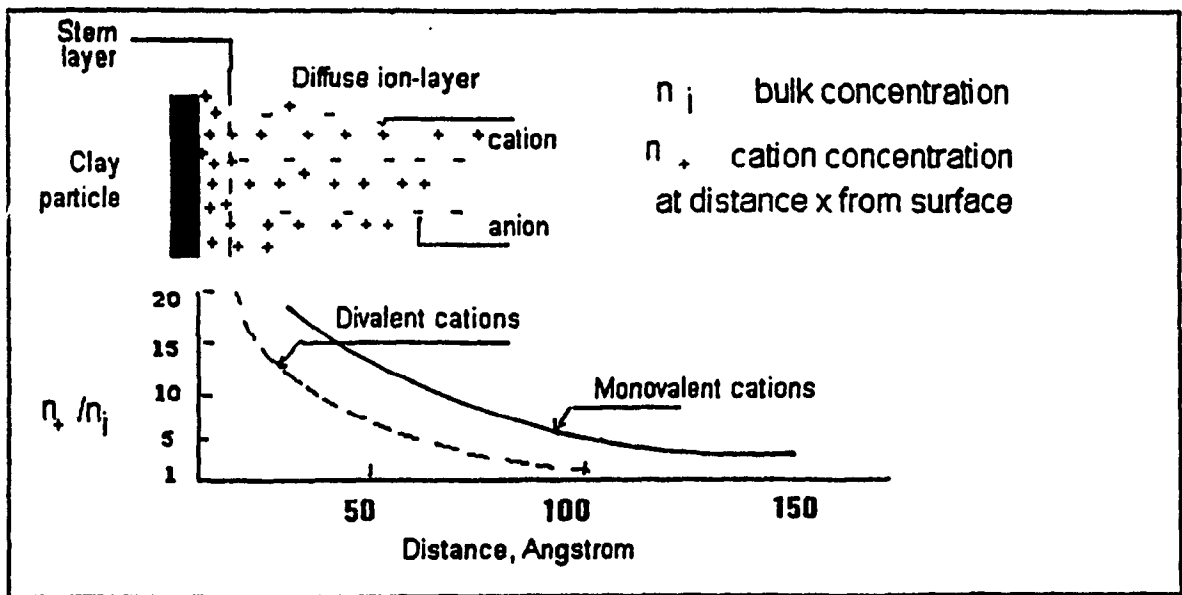
Figure B-1. The Theoretical Distribution of Ions Adjacent to a Charged Surface
Showing Influence of Valence on Thickness of Diffuse Ion-Layer
(after Yong et al, 1992)

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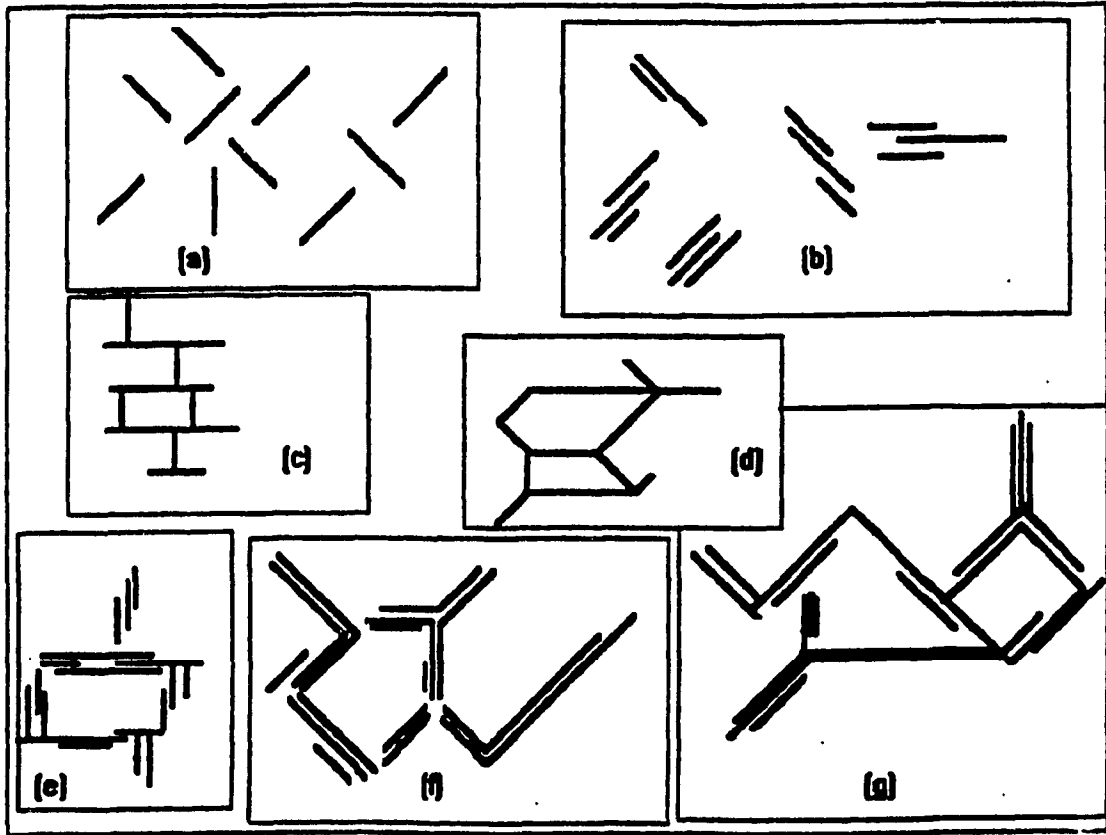Figure B-2. Modes of particle Association in Clay Suspension   (after Van Olphen, 1977)

(a) "Dispersed" and "deflocculation"; (b) aggregated but "deflocculated" (face-to-face); (c) edge-to-face flocculated but "dispersed"; (d) edge-to-edge flocculated but "dispersed"; (e) edge-to-face flocculated but aggregated; (f) edge-to-edge flocculated but "aggregated"; (g) edge-to-face and edge-to-edge flocculated "aggregated"

conductivity of fine-grained soil mainly depends salt type and concentration.

B.2.1 Effect of Salt Concentration

At dilute ion concentrations, the adsorbed water layers expand and repulsive forces become dominant over attractive forces. The expansion of adsorbed water layers will reduce the effective flow path, decreasing permeability. Decreasing salt concentration of percolating solution induces a more pronounced decrease in permeability of soil containing expandable layers 2:1 of silicates such as montomorillonite. Natural clay soil composed predominantly of illite shows a decrease with distilled water (Chang, 1987). On the other hand, soil containing considerable amounts of kaolinite shows no variation in permeability with salt concentrations (Mc Neal et al, 1966; Mouradian, 1993).

The reduction in permeability was probably due to the clogging of conducting pores either by the dispersion of minerals or by the translocation of clay particles. They accumulate and decrease the pore size, specifically, for soils containing a smaller quatity of expandable minerals (Mc Neal et al, 1966; Pupisky et al, 1979; Chang, 1980). On the other hand, swelling is a possible mechanism for the permeability decrease upon percolating low salt concentration solution through the soil containing significant proportions of montmorillonite or in compacted or confined soil. This is due to the fact that the constraints would prevent soil particles from moving sufficiently far apart to permit dispersion and translocation (Mc Neal et al, 1966; Shainberg et al, 1971).

he increase in porewater salt concentration can attribute to a significant decrease in

repulsive forces by reducing the water thickness around the clay particle (Yong et al, 1992). Hence, permeability increases as compared to distilled water (Fig. B-3). Upon introduction of saline water, containing 1500 mg/l as total dissolved salt, into a soil rich in illite (26 %) the permeability is relatively increased (Chang, 1980). For a soil containing a considerable amount of kaolinite, the permeability is almost not affected by the salinity of water (Yong, et al 1992, Mouradian, 1993). For montmorillonite, an increase in salt concentration results in an increase in permeability (Mouradian, 1993).

B.2.2. Effect of Salt Type

The presence of monovalent ions as Na^+ in percolating liquid will frequently decrease soil permeability, particularly at low salt concentration because of its dispersive effects. Meanwhile, the presence of divalent ions as Ca^{++} generally stabilizes or increase soil permeability by flocculating soil particles (Yong et al, 1985). Change of water composition from NaCl to CaCl increased permeability of montmorillonite (Fig. B-4), while for illite and kaolinite a change of salt type exhibited no significant variation at higher concentration. Ridley et al (1983) found that soil high in montmorillonite produced a high increase in permeability when it is percolated with 30 % NaCl brine solution.

The increase of salt concentration and the change of water composition brings about change in the permeability of soils. Soils high in either kaolinite or illite appear to be quite stable under such conditions. Soils contain montmorillonite exhibit a large increase in permeability.
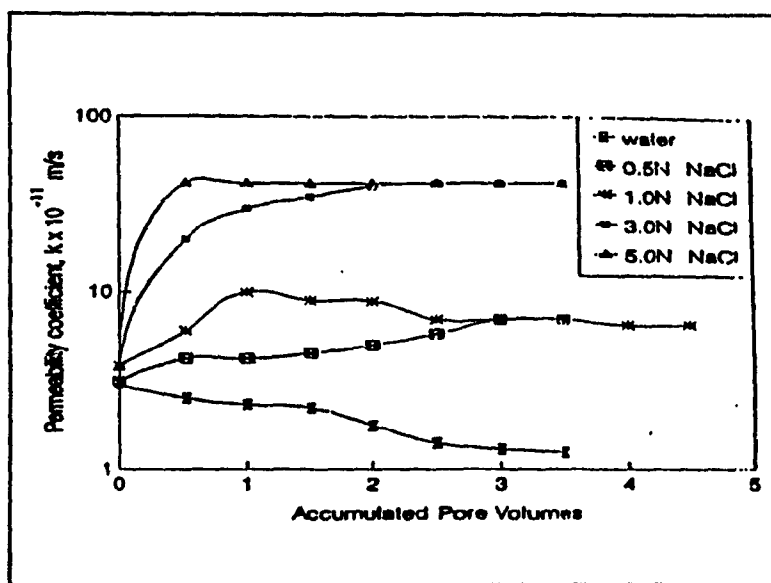
120

Figure B-3. Influence of Salt Concentration on Permeability of a Natural Soil
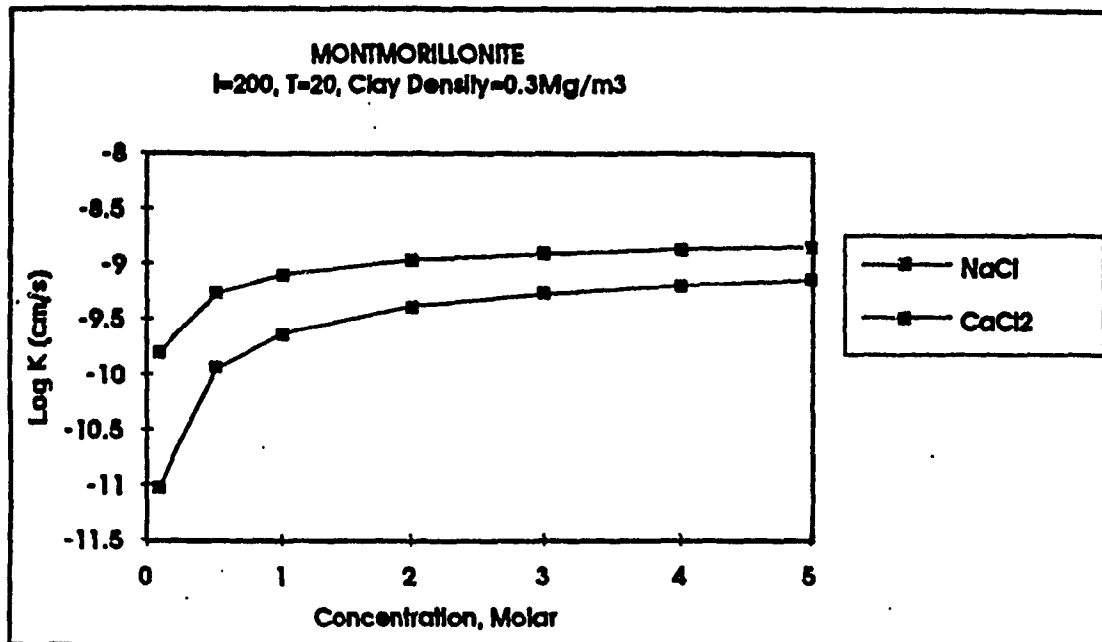(after Yong et al, 1992)

Figure B-4. Influence of Salt Type and Concentration on Permeability of
Montmorillonite (after Mouradian, 1993)

APPENDIX-C

DETAILED DESCRIPTION OF TESTING

PROCEDURES

APPENDIX C

Detailed Description of Testing Procedures

C.1 Grain Size Analysis

Hydrometer Methods (ASTM D-422-63)

Hydrometer analysis is a widely used method for obtaining an estimate of the distribution ion of soil particle sizes from 0.075 mm (No. 200 sieve) to 0.001 mm. The particle diameter was obtained by following these steps:

1. 50 g of dry soil were mixed with 125 ml of 4% sodium metaphosphate $NaPO_3$ solution in a small evaporating dish. Then, the mixture was allowed to settle for 16 hrs.

2. Malt mixer was used to mix the mixture for one minute. The suspension was transfered from malt mixer to the sedimentation cylinder. The cylinder was filled to 1000 ml mark with temperature-stabilized water.

3. The mixture was rotating the cylinder 60 times. Then, hydrometer type (152H) and a thermometer were inserted and a reading was taken at interval of 2, 4, 8, 16, 30, 60 min. and then 2, 8, 24, 32, 48, 56, 72 hrs.

4. Based on hydrometer readings, the particle diameter at each elapsed time was computed

C.2 Determination of Amorphous Materials

C.2.1 Procedure (Segalin Method)

0.5 g of an air dried sample was mixed with 40 ml of 8N HCl and shaked for 30 minutes in a shaker to remove amorphous iron and alumina. The suspension was centrifuged for 4 and 5 minutes and the supernatant liquid was collected for analysis. The sample was then mixed with 40 ml of 0.5N NaOH and placed in a steaming water bath for 5 minutes to remove amorphous silica and alumina compounds. The suspension was centrifuged for 5 minutes, and the supernatant liquid was collected.

This procedure was repeated 8 times in order to remove amorphous content in the sample. SiO_2, and Fe_2O_3 contents were determined using the Perkin-Elmer Lambda 2 UV/VIS Spectrometer. The determination methods of the amount of silica content and iron content are described below.

C.2.2 Identification of Amorphous Iron (Voinovitch Mehod)

1. 5 ml of supernatant liquid (see C.2.1) was transferred into a 100 ml volumetric flask

2. 5 ml of ammonium chloride and 5 ml of sulfosalicylic acid were added.

3. Ammonium hydroxide was added until the color changed from pink to bright yellow.

4. The content was mixed and distilled water was added to make 100 ml.

5. The absorbance of the samples at wavelength 420 nm was measured and the amount of Fe_2O_3 was determined using a standard curve.

6. Once the total contents of washing have been determined, the cumulative amounts of Fe_2O_3 were plotted versus the number of washings. Then, Fe_2O_3 was determined by extrapolating the straight portion of the graph back to the X-axis.

C.2.3 Identification of Amorphous Silica (Voinovitch Mehod)

1. 3 ml of supernatant liquid (see C.2.1) was transferred to a 100 ml volumetric flask.

2. 1 ml of ammonium molybdate (10 %) was added. After 10 minutes 4 ml of tartaric acid (10%) solution was added while stirring the contents of the flask.

3. 1 ml of reducing solution was added. Distilled water was added to make the volume up to 100 ml. The solution was allowed to stand for 30 minutes.

4. The absorbance of the samples at wavelength 730 nm was measured and the amount of SiO_2 was determined using a standard curve.

5. Once the total contents of washing were determined the cumulative amounts of SiO_2 were plotted versus the number of washings. SiO_2 content was determined by extrapolating the straight portion of the graph back to the X-axis.

C.3 Identification of Cations

Acid Digestion Method (Hesse, 1971)

1. 1 g of soil sample was mixed with 10 ml of concentrated nitric acid (HNO_3) in a conical beaker. The sample was covered with a watch glass and heated to 95 °C for 15 minutes

without boiling. Then, the sample was allowed to cool.

2. 5 ml of HNO_3 were added and heated for 30 minutes to ensure complete oxidation. A Ribbed watch glass was used to allow the solution to evaporate to 5 ml without boiling.

3. After the sample had cooled, 2 ml of distilled water and 3 ml of hydrogen peroxide (30 % H_2O_2) were added. The sample was then returned to the hot plate to start the peroxide reaction.

4. 5 ml of concentrated hydrochloric acid (HCl) and 10 ml of distilled water were added. The sample was heated for 10 minutes without boiling. After cooling, the sample was filtered through filter paper and diluted to 100 ml with distilled water.

5. Flame Atomic Absorption was used to determine the metals in the collected samples.

C.4 Determination of Total Organic Content

C.4.1 Ignition Technique at High Temperature (Hesse, 1971)

1. 10 g of an oven dry sample were ignited at 900 °C for 30 minutes. The sample was allowed to cool partially in the air.

2. The sample was weighed and weight loss was expressed as percent organic matter.

C.4.2 Oxidation Technique (Hesse, 1971)

1. 0.5 g of air-dried soil was mixed gently with 10 ml of potassium dichromate solution into 500 ml conical flask.

2. 20 ml of sulphuric acid were added into flask. The Flask was swirled for 20 seconds and allowed to stand on the hot plate for 30 minutes.

3. After the solution was allowed to cool, 250 ml of distilled water and 10 ml of phosphoric acid were added.

4. 0.5 ml of barium diphenylamine sulphonate solution was added. The mixture was then titrated with ferric ammonium sulphate until bright green was observed.

5. Percent organic matter was calculated based on blank titration.

C.5 Determination of Carbonate Content

Rapid Titration Method (Hesse, 1971)

1. 5 g of air-dried soil was mixed with 100 ml of 1.0 M hydrochloric acid (HCl) into 250 ml conical flask.

2. The flask was placed on a shaker for 1 hour, then the soil was allowed to settle.

3. 20 ml of the supernatant was transferred into a 100 ml Erlenmeyer flask and titrated with 1.0 M sodium hydroxide.

4. Percent of carbonate as $CaCO_3$ was calculated based on blank titration.

C.6 Determination of Cation Exchange Capacity (Hesse, 1971)

1. 10 g of air dried soil was shaken for 2 hours with 200 ml of 0.04 M hydrochloric acid (HCl). After standing for one day, 100 ml of supernatant liquid was titrated with 0.1M

sodium hydroxide (NaOH).

2. 10 g of air-dried soil were mixed with 20 ml of 2.5 % barium chloride solution and 12 drops of 2 % phenolphthalein solution. The suspension was titrated with 0.1M NaOH solution until, with repeated shaking, the foam remained pink.

3. The difference between the two titration was taken as a measure of exchange capacity.

C.7 Preparation of Samples For UV Analysis

For UV measurements of the liquid samples (ethyl acetate, formamide, sodium silicate, and their mixture) and supernatants of the leachate, a 10 mm quartz cuvette was used. Since the analysis of all components no have band maximums in the observed region of spectra, the absorbance at 220 nm, on the edge of the analysed band, were chosen for measurement. Reproducibility of this measurements was ± 0.02 %.

C.8 Preparation of Samples For IR analysis

Air dried samples of precipitate or initial gel (SA grout) were grinded to obtain good quality spectra. These samples were mixed with potassium bromide (KBr) to obtain a homogeneous mixture. The matrix should be pure and dry to avoid any effect of miosture on the band. Then, the mixture was pressed into a disk to form a pellet. For some liquid samples, the IR spectra was measured using barium fluoride plated (BaF_2). The reproducibility of the peak location was found to be ±10 cm^{-1} in the region of 4000-2000 and ± 5 cm^{-1} in the region of 2000-200 cm-1.