PAHS AND NICKEL CONTAMINATED SOIL CONTAINMENT AND STABILIZATION WITH SILICA GROUT

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ABSTRACT

PAHs and Nickel Contaminated Soil Containment and Stabilization with Silica Grout

Md Mehedi Hasan Emon

The migration of contaminants from a site in the soil represents a real threat to the environment and to human health because contaminants might leach to groundwater and humans could be affected directly and indirectly. Therefore, the objective of this research was to evaluate the vulnerability of silica based chemical grout barriers to protect leaching of contaminants to groundwater. Thirty five experiments were done using calcium chloride (SC), formamide (SF) and combined reagents (SFC) with sodium silicate, along with three different types of soil. Sand, silty sand and sandy silt soils were contaminated with nickel (1000 ppm) or phenanthrene (600 ppm) or mixture of both contaminants. A resistance-based methodology was developed to find out the internal grout changes of grouted specimens. Grouted specimens were submerged in water which was simulated low-mineralized and high-mineralized groundwater. The results show that soil resistivity went up in all specimens. The highest coefficient of stability was found to be 6% in mixed (nickel-phenanthrene) contaminated soil grouted with SF. There was no phenanthrene release from grouted contaminated soil. The nickel release was as low as 4~5 ppm. Furthermore, a complex of sodium formate was found in water based on FT-IR analysis. Lastly, the values of pH and redOx confirmed the stabilization process. This research showed that to reduce contamination with heavy metal, silica formamide (SF) grout should be used. Contamination with phenanthrene was best treated with formamide (SF grout) and a combined (SFC grout) reagent. It was also found that a combination of both reagents made setting faster and created more stable conditions. A model was developed for prediction of contaminant stability. The results of this research can be applied to stabilize any kind of soil with particle size from 1.0 mm to 0.053 mm, contaminated with PAHs and heavy metals.

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CHAPTER 1 INTRODUCTION

1.1 Background

Care of the environment is a serious concern for everyone in the world. A lot of attention is paid to maintaining air and water quality, but this study focuses on the maintenance of soil quality. Such a study is important because the migration of contaminants within the soil from a site represents a real threat to the environment and to human health (Fadel et al., 1997a; 1997b). Contaminants might leach into the groundwater, and human beings are affected directly and indirectly.

The pollutants that are most often found in soil can be categorized in three broad ways (1) heavy metals – nickel, lead, cadmium, aluminium, arsenic, bromide, etc., and their sources are manufacturing plants, fuel and chemical storage facilities, and vehicle depots; (2) hydrocarbon – PAHs, PCE, PCB, pesticides, and aliphatic and aromatic hydrocarbons, and their sources which might be petroleum refineries, gasoline service stations and vehicle depots; and (3) mixtures of contaminants: heavy metals and hydrocarbons and their sources are industrial and manufacturing areas.

Sixty nine percent of soil contamination in Quebec comes from petroleum products (Environment Quebec, 1994). Innovation in the area of hydrocarbon remediation has been significant in the last decade due to implementation of biotechnology. Unfortunately, metals may be only mobilized or immobilized. These limitations are some of the reasons why innovative remediation technologies have not been developed for soils contaminated with mixtures of metals and hydrocarbons. Therefore, there is a need to develop a technology dealing with mixed contaminated soil problems.

In these cases stabilization of soil or formation of containment would be a solution that can protect groundwater. A formation of containment using a grouting technique seems to be the fastest technique for protection groundwater against leaching from contaminated areas. Generally, the routing is the injection of a fluidized material into the soil or rock to enhance its strength and density, or to reduce its permeability (http://www3.interscience.wiley.com). Chemical grouting could be used as a barrier/containment or as a stabilizer. Though grouting is not a permanent remediation process, it can reduce contaminant mobility and toxicity. It can be used before the application of any remediation in mixed contaminated soil that promises to be an effective in-situ treatment process. Grouting has several advantages:

- It reduces water leakage
- It stabilizes and strengthen soil or rock masses
- It isolates waste disposals.

Source: Karol, 2003

1.2 Objective

The main objective of this thesis is to evaluate the stability of silica based chemical grouts containments to protect leaching of contaminants to groundwater. The secondary objectives are:

1. to assess the durability of grouted containments in simulated subsurface conditions in terms of leachibility, coefficients of stability, and porosity of the soil.

2. to describe the best formulation of grout which can be used in all three situations: contamination with heavy metals, with hydrocarbons, and with a mixture of both.

CHAPTER 2 REVIEW OF THE LITERATURE

2.1 Soil Constituents

Soils are complex assemblies of solid (soil matrix), liquid (pore water spaces) and gaseous (air spaces). They can be divided into inorganic and organic types. Based on this, a soil constituent's flow chart can be illustrated in Figure 2-1.

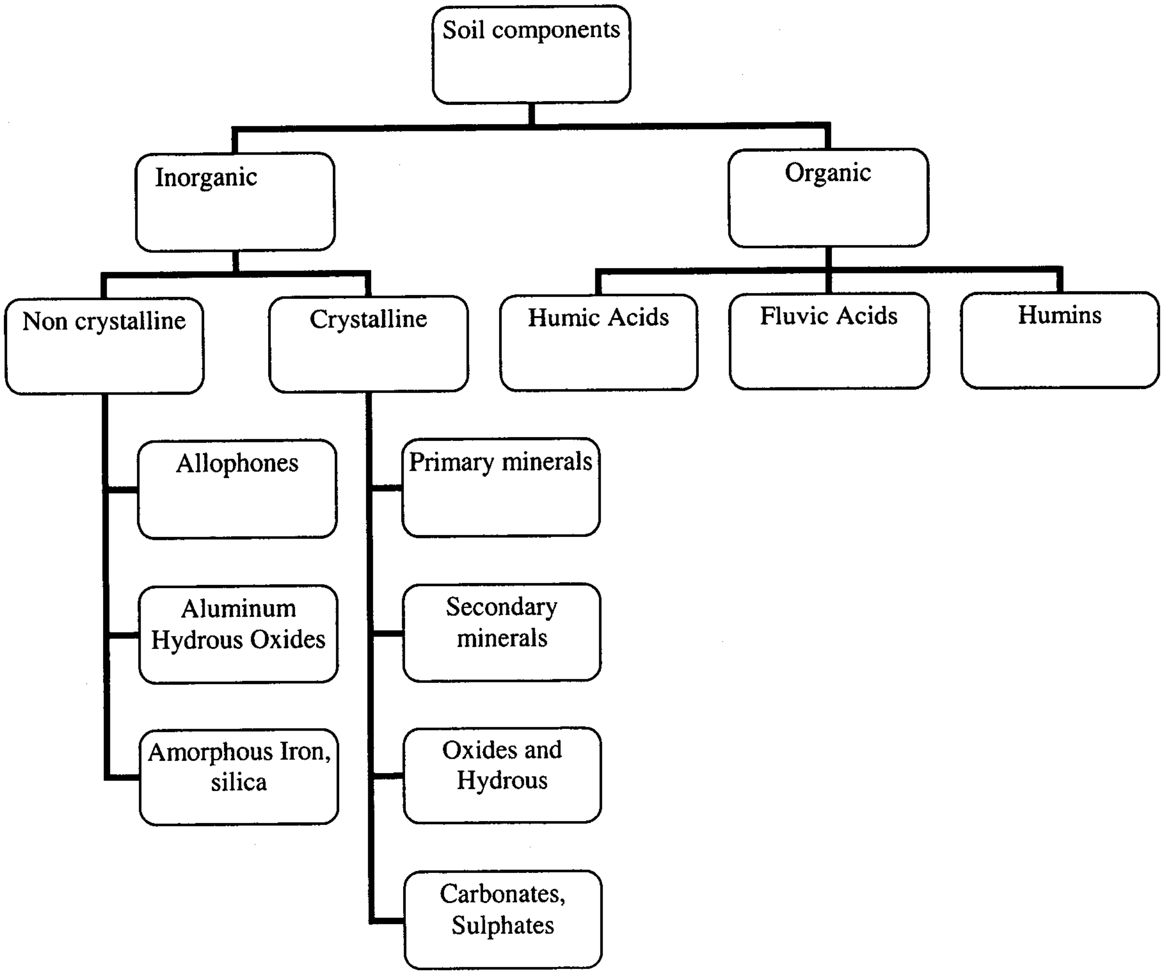

Figure 2-1: Soil Constituents

2.2 Inorganic Soil Components

Oxygen, silica, aluminium, iron, carbon, calcium, potassium, sodium and magnesium are the highest elements found in soils. These elements are also found in the Earth's crust and in sediments. Oxygen is the major element in soils that comprise around 47% of the earth's crust by weight and over 90% by volume (Donald, 2003).

90% of the solid components of soil might be represented by inorganic soil components. They are sub-divided into crystalline and non-crystalline types and are dominated by alumino-silicates. Actually, 60% of inorganic rocks are found in feldspar minerals (Hamblin, 1992), which are altered chemically by its deposition and crystallization from lava. Their properties such as size, surface area, and charge behaviour affect kinetic reactions and in soil processes.

The inorganic crystalline soil components are divided as primary and secondary minerals, which range in size (particle diameter). They are again defined with definite physical, chemical, and crystalline properties. Sand and silt fractions are the major portion of primary minerals and appear less in weathered clay-sized fractions. They are important in geo-environmental engineering for contamination and attenuation processes because of low cation exchange capacities, low surface areas, and high particle sizes.

Secondary minerals are formed from the weathering of primary minerals either by an alternation in the structure or from precipitation of the products by weathering (dissolution).

2.3 Soil Organic Matter (SOM)

Soil organic matter (SOM) is the total organic matter in soils, excluding undecayed plant, animal tissues, their partial decomposition products and their biomass. Soil organic matter is also known as humus. SOM is a "mixture of plant and animal residues in different stages of decomposition, substances synthesized from bodies of live and dead micro-organisms and their decomposing remains" (Donald, 2003). Humus is comprised of humic substances and resynthesis products of micro organism that are stable in soil. SOM consists of non humic and humic substances. The non humic substances have polysaccharides, proteins, fats, and low molecular weight organic acids. Based on different solubility in acid or base of SOM, humic substances are sub devided into fluvic acids, humic acids, and humines (Ruggiero, 1999). Because of SOM's pH dependent charge, they play a vital role in the fate of organic and inorganic soil contaminants. They ultimately influence the condition and constitution of sub-soil. SOM comprises 0.5%-5% (w/w) of most mineral surface soils except peat (Yong, et al., 1992). Soil organic matter also provides sites for absorption of non-polar organic contaminants, such as PAH's. SOM's hydrophobicity, and their octanol-water coefficients are related to the organic colloids sorption (Ruggiero, 1999).

2.4 Soil Engineering Classification

Various systems have been used to classify soils according to the proportion of different sizes of soil particles. Soils are generally called gravel, sand, silt or clay, depending on the predominant size of particles within the soil. However, the unified soil classification system is now accepted worldwide and has been adopted by the American Society for Testing and Materials (ASTM). Following table has been accepted according to ASTM classification.

Table 2-1 Particle size distribution

Gravel (mm)	Sand (mm)	Silt (mm)	Clay (mm)
76.2 to 4.75	4.75 to 0.075	Fines <0.075	

2.4.1 Mechanical Analysis of Soil

Soil particle size ranges that present in the soil are determined by mechanical analysis of soil. It is subdivided into two methods.

1. Sieve Analysis: for particle size larger than 0.075 mm in diameter, and determine by ASTM E-11 sieve analysis.
2. Hydrometer Analysis: for particle size smaller than 0.075 mm in diameter, and determined by settling process described in ASTM soil specification.

➢ **Sieve Analysis According to ASTM E-11 Specification**

The mass of soil retained on each sieve (i.e. M_1, M_2,............M_n) and in the pan (i.e. M_p)

- The total mass of the soil: $M_1 + M_2 + \ldots\ldots M_n + M_p) = \sum M$
- The cumulative mass of soil retained above each sieve. For example, for the i^{th} sieve, it is $M_1+M_2+\ldots+M_i$
- The mass of the soil passing the i^{th} sieve is $\sum M - (M_1+M_2+\ldots+M_i)$
- Percent finer (percent of soil passing) (f) in i^{th} sieve is

$$f = \sum M - (M_1+M_2+\ldots+M_i) \times 100/\sum M$$

Source: Das, 2002

After that, f could be plotted in arithmetic scale and particle size as the logarithmic scale.

2.5 Soil Stability and Soil Internal Erosion

Soil stability of a granular material results from its ability to prevent loss of its finer particles because of seepage forces. The magnitude of the consequent seepage force controls the soil stability by the inter particle force, the weight of the particle, and the drag force due to the percolating water. These forces are dependent on the soil type, particle compaction, and water flow direction. Particle compaction is always dependent on particle size distribution and particle shape, which is described earlier.

The reason for the studying of soil stability and soil internal erosion is that the soil movement, migration and erosion could be possible when water seeps through the soil. This phenomenon might be illustrated by piping and suffusion mechanisms.

2.5.1 Piping

Piping, or internal erosion, means the loss of smaller particles that often represent a higher proportion of the total mass. This erosion can create a big void in the soil where water flow is less restrained and more turbulent.

2.5.2 Suffusion

Suffusion is the migration of finer particles to the rest of the soil matrix. This is not a serious problem like piping. It is easy to determine in a soil matrix either by Isomina or Kenny and Lau method. Isomina (1992) stated that suffusion is liable if the pore diameter (d) is smaller than the smallest grain diameter (D_{min}). He also said that

- No suffusion if uniformity coefficient (CU)<10
- A condition of transition if 10<CU<20
- Suffusion, if CU>20 (quoted by Kovacs, 1981)

According to Kenney and Lau (1985), all soil particles have a primary fabric of particles that support loads and transfer stresses where weak particle bonding can not be fixed in one place. As a result, no transfer stresses, and finer particles can move through pore spaces by water flow if the limitations in the pore space of the primary fabric are larger than loose particles. For a material to show an unstable grading requires loose particles that can be moved from the pore network. The authors describe a method of analyzing the shape of the grading curve measured between particle size D and 4D. The shape of the curve is independent of the grain size and is dependent only on the geometrical form of the grading curve that falls on the line H+f = 1.

Where,

f = the mass fraction smaller than

D = the particle diameter

H = the mass fraction

➢ **Rule of Grading Curve by Kenney and Lau**

- The line H = 1.3 f (Loebotsjkov's 1969, limiting grading for stable materials) is the boundary line of stable and unstable shape.
- Particles are initially stable, and the filter volume will preserve its initial grain size characteristic if the travel distances of the mobile particles are short.
- Finer particles can be lost from anywhere in the filter if potential travel distances of filter thickness are smaller than certain sizes of loose particles. The grain size criteria can be changed and the filter grading will be judged as unstable.

A hydraulic test could confirm the method for determining whether a granular material is unstable or not.

2.6 Soil Resistivity

Resistivity is widely applied in geophysical fields, and, now it is highly accepted in civil engineering fields because of its accurate, easy and quick method. The objective of the use of this parameter is to see internal changes during the grouting aging time. It is an indirect method to find the leachibility of chemical grouting. However, almost no literature review was found on resistivity in chemical grouting. Various studies show that resistivity and permeability are inversely related. Therefore, by measuring soil resistivity, the soil permeability in the grouted specimen can be determined.

2.6.1 True Resistivity

The basic principle of true resistivity is defined by side length through which a current is passed in an electrically uniform dice structure. The materials inside the dice structure resist the conduction of electricity through conductor, and the electrical current drops between opposite sides of the dice structure. The resistance (R) is inversely proportional to the cross-sectional area and proportional to the length of the resistive material. Finally, true resistivity is defined by the constant of proportionality. Also, the resistance is also defined by the ratio of potential drop to the applied current, states Ohm's law. By combining these two expressions (resistance, and distance) the resistivity is measured and the unit is Ω.m (Reynolds, 1997).

Basically, electric current can be conducted through a rock in three different ways. They are:

1. **Electrolytic conduction**: Relatively slow movement of ions within an electrolyte occurs in electrolytic conduction. It depends on type, ionic concentration and mobility.

2. **Electronic conduction**: It is a process by which metals, for instance, move rapidly, resulting carrying in an electronic charge.
3. **Dielectric conduction**: This type of conduction occurs in poorly conducting materials where an external current is applied, and as a result, electrons moves slowly in relation to their nuclei.

   Source: Reynolds, 1997

2.6.2 Mathematical Relationship between True Resistivity, Ohms' law and Resistivity

According to the discussion in 2.6.1, true resistivity is:

$R \infty L/A$

$R = \rho L/A$ ....(2.1)

Again, Ohm's law is

$R = V/I$ ....(2.2)

By combining equations 2.1, and 2.2

$\rho = VA/IL$ (Ω.m) ....(2.3)

Where,

R = Resistance

L= side length

A= cross sectional area

ρ = true resistivity

V and I = potential difference across a resistor and the current passing through it

Archie (1942) built up an empirical formula for the resistivity calculation, which is

$\rho = a\, \Phi^{-m} S^{-n}\, \rho_w$ ....(2.4)

Where,

ρ = effective rock resistivity

ρ_w = effective resistivity of the pore water

Φ = porosity

S= volume fraction of pores with water

a, m, n = constants ($0.5 \leq a \leq 2.5$, $1.3 \leq m \leq 2.5$ and $n \approx 2$) and

Source: Reynolds, 1997

2.6.3 Electrode Configuration

There are mainly three types of electrode configuration methods used. They are:

1. **Wenner Array:** In this method, the last electrode is the main input current electrode (C_2) is installed at the end and an output ground current electrode is installed at the beginning (C_1). The potential current (P_1, P_2) electrodes are also insert at equal distances between C_1 and C_2. Wenner array has only one parameter, which is the dipole length "*a*".

Resistivity defines in this method by

$$R = 2\,\pi.\,a\,\Delta\Phi/I \quad \text{……(2.5)}$$

R = apparent resistivity

a = distance between dipoles

$\Delta\phi$= Amplitude differences between potential dipoles [amplitude = (Max-Min)]

I = current= $\Delta\phi/r$ = Amplitude difference between current electrode [Max-Min] / default resistor

r = default resistor

2. **Schlumberger (differential) array:** In this array, there are three parameters the current dipole length "$2L$", the potential dipole length "2ℓ" and the distance between mid points of the current and potential dipoles "x". Geometrical factor of the Wenner array is $k=2.\pi.a$ and for the Schlumberger-differential array it expressed as:

$$k = 2\pi\left[\left\{\frac{1}{(L-x)-\ell} - \frac{1}{(L+x)+\ell}\right\} - \left\{\frac{1}{(L-x)+\ell} - \frac{1}{(L+x)-\ell}\right\}\right]^{-1} \quad \text{……(2.6)}$$

3. **Dipole-dipole array:** In this array, input and output current electrodes are installed one by one at a known distance (*a*). Again at (*na*) distance two potential current electrodes are installed at a distance.

2.6.4 Electrical Setup for Resistivity Measurement

After choosing a proper array from section 2.4.3, accessories must be connected for resistivity measurement. The Wenner method developed later where it was used a common ground connection for all of the electrodes (C_1, C_2, P_1, P_2) with a known resistor. Finally, all of the electrodes are connected to Data Acquisition Board (DAQ), usually a laptop computer for voltage measurement.

The resistivity was an important parameter of this thesis because all standard tests for grouting can not be applied in contaminated soil containment since impact on environment (groundwater) has to be assessed. Resistivity measurement is much more adequate than standard permeability method. In the setting period, resistivity can also monitor internal changes in the specimens.

2.7 Fate of Inorganic and Organic Contaminants

2.7.1 Inorganic Contaminant Transport

The inorganic contaminant fate and transport largely depend on the secondary mineral and organic material in the soil. This is due to heavy metal cationic exchange and adsorption of organic substances. Existing inorganic contaminants in soil are transported by soil pore space (liquid media) through advection, dispersion, diffusion and suction. Because of clay's low permeability, molecular diffusion is also a transport mechanism of clay soils. Retardation takes place when a contaminant is transporting in a media that helps in immobilizing the contaminants.

Inorganic chemicals transported in soil through a complex medium that is divided in two processes namely (1) transformation and (2) transport. Different types of environmental factors also influence the soil abiotic transformation rate that controls the types and rates of the chemical reactions. They are (1) moisture content, (2) pH, (3) redOx, (4) temperature, (5) adsorption, and (6) surface binding. Besides these environmental factors, transformation is also related to (1) chemical structure, (2) molecular size, (3) functional group, (4) polarity, and (5) charge.

2.7.2 Fate of Inorganic Contaminants

2.7.2.1 Cation Exchange

Five properties of cation exchange are responsible for cationic exchange of secondary minerals (Choudhury, 1998). They are (1) ionic charge (valence), (2) atomic size, (3) concentration of cations (4) pH of soil, and (5) cations type of solution. Basically, the valence of the ion and the atomic size are proportionally related to cationic exchange. Moreover, the shape of the cationic solution reduce soil's cationic exchange rate. For instance, the gap of the two silica sheets is similar to potassium's atomic shape that can easily fit on that gap. Based on the factors above, sequential cation exchange is

$Li^+<Na^+<H^+<K^+<NH_4^+<<Mg^{2+}<Ca^{2+}<Ni^{2+}<Pb^{2+}<<Al^{3+}$ (Chudhury, 1998)

2.7.2.2 Sorption

Sorption is the retardation of a substance which takes place between solid and liquid phases. This retardation can happen at the adsorption, absorption or ion exchange levels. The properties of a metal and its physico-chemical properties determine how much metal will adsorb to the soil. Based on above conditions, the decreasing steps of ion exchange is expressed by

$Cu^{2+}>Pb^{2+}>Zn^{2+}>Cd^{2+}>Ni^{2+}>Mn^{2+}$ (Chudhury, 1998)

with increasing pH condition. Generally, the soil sorption capacity of most metal ions increases but the mobility of the cations is decreased (Merian, 1991).

2.7.2.3 Organic Complexation

In addition to being involved in cation exchange reactions, solid-phase humic substances such as humic acids also adsorb metals by forming chelate complexes. Low-molecular-weight organic ligands, not necessarily humic in original, can form soluble complexes with metals and prevent them from being adsorbed or precipitated. Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids. The maximum amount of any given metal that can be bound is found to be approximately equal to the number of carboxyl groups (Alloway, 1990).

2.7.2.4 Precipitation

Precipitation of a given metal species depends on the Eh (reduction-oxidation potential) and pH of the soil/ground water system, as well as the presence of anions and competing cations that exceed the solubility product constant. pH is a measure of the hydrogen ion concentration in the soil/ground water system, expressed as the negative log of the hydrogen ion concentration. When used together, an Eh/pH diagram can be developed for a given metal, which indicates the species that a given metal will exist as under various Eh and pH conditions. Metal precipitation is also dependent on the presence of anions that cause the metal to form insoluble inorganic compounds. For example, based on the Eh/pH diagram for barium, one could assume that barium is soluble at all pHs and all Ehs. However, the presence of sulfate or phosphate ions will cause the barium to form insoluble barium sulfate or barium phosphate, and therefore be removed from solution and become immobile. Solubility product constants are indicators of the tendency of a given compound to form in solution on the basis of the concentrations of the individual cation and anion of a product. Other cations may also be present in the system which competes for the anions by precipitating at lower concentrations (Merian, 1991, Alloway, 1990).

- **Metals in the Environment**

Metals in the environment endure precipitation, complexation, dissolution, and their oxidation states. Metals react with organic and inorganic substances both in liquid and solid phase. Therefore, it is important to understand the fate of metals in the soil for proper soil containment techniques. The mobility of the metal is influenced by pH, RedOx potential, cation exchange capacity of the solid phase, competition with other metal ions, complex metal and soil composition and concentration in the soil solution (Merian, 1991).

- **Nickel**

The oxidation state of nickel (+2) is usually present in liquid form in different water soluble chemical forms that are acetate, bromide, chloride, floride, iodide, nitrate, sulfamate, and sulfate salts. Highly soluble nickel increases the mobility in the water and that increases contamination rate. Nickel in aqueous solutions has a green hexaquonickel ion, Ni $(H_2O)_6^{+2}$ that living organisms can uptake (Merian, 1991). The contamination of nickel in a typical waste is 24 (mg/kg.ms) in unaltered sites, 1360 (mg/kg.ms) in spiked waste sites, 2.7 (mg/L) in inter stitial water, 877 (mg) in metal stockpiles and (mg/kg.ms) in waste (Lerel and Raimbault, 1991).

Nickel is often bound in soil or sediment particles. The concentration of nickel in unpolluted waters is typically low (Encyclopaedia, 1997). Although most lab analyses for nickel are for total nickel, the hazard presented by nickel, and its exact fate characteristics depend upon chemical speciation (Encyclopaedia, 1997). Nickel is moderately accumulated in many food chain organisms. The bioaccumulation or bioconcentration of nickel is moderate for the following biota: mammals, birds, and fish; while the potential for bioaccumulation appears to be highest for mollusks, crustacea, lower animals, mosses, lichens, algae, and higher plants (Encyclopaedia, 1997). Nickel may be released to the environment from the stacks of large furnaces used to make alloys, or from power plants, and trash incinerators. The nickel that comes out of the stacks of the power plants is attached to small particles of dust that settle to the ground or are taken out of the air in rain. It will usually take many days for nickel to be removed from the air. If the nickel is attached to very small particles, removal can take longer than a month. Nickel cannot be destroyed in the environment. It can only move around, change its form, or become attached to or separated from particles. Most nickel will end up in the soil or sediment where it is strongly attached to particles containing iron or manganese. Under acidic conditions, nickel is more mobile in soil and may seep into groundwater.

2.7.3 Fate on Organic Substances

Soil Organic Matter (SOM) significantly influences the fate of contaminants in subsurface environment. SOM in the soil is affected greatly or barely by the existence of different soil processes such as adsorption, partitioning, solubilization, hydraulic degradation, volatilization, and photo decomposition (Senesi et al., 1995). Humic substances also have impact on adsorption process in soil that absorbs low molecular weight organic compounds. This adsorption process take place in soil via different soil mechanisms that include (1) ionic bonding (2) hydrogen and covalent bonding (3) electron door or acceptor mechanisms (4) cation bridge (5) van der walls forces, and (6) water bridging (Petruzzeli and Helfferich, 1993).

- **Polycyclic Aromatic Hydrocarbons (PAHs)**

Hydrocarbons are characterized by high molecular weight, low solubility and hydrophobicity which play a role in the soil sorption process. Polycyclic Aromatic Hydrocarbons (PAH) is one of the complex organic groups that have multiple benzene rings. The source of PAH is diesel fuel originating from gasoline and diesel engines, chemical manufacturing plants, and disposal areas, disposal wells and leach fields, landfills and leaking storage tanks. Phenanthrene, flurene and pyrene are the most complicated PAHs in the environment. The fate of PAHs is a consequence of hydrolysis, volatilization, chemical oxidation, and adsorption to soil particles and leaching (Hakimpour, 2001).

2.7.4 Conclusion

Secondary minerals and soil organic matter are the prime substances in the soil that control the fate of contaminants. As a result, it is very important to know about different soil components and contaminants and their possible behavior in a soil and water environment so that how contaminants behave with different soil matrices can be predicted. However, the fate of contaminants in the soil is radically influenced by the presence of clay particles, organic matter and amorphous inorganic materials. In this thesis the fate of inorganic and organic contaminants in subsurface were studied to acquire knowledge so that fast prevention measures could be applied in an accidental spill.

2.8 Site Remediation Method

Soil remediation technologies were briefly discussed in this section to see how grouting could be used as a stabilizer in soil remediation. From this discussion, it is easy to see grouting is important in site remediation. All soil remediation technologies are divided into two main groups: (1) inorganic compounds removal, and (2) organic compounds removal. These two main groups are again subdivided in two major approaches that are (1) ex-situ and 92) in-situ processes. Short descriptions of these technologies are given in Chapter 2.8.

2.8.1 Remediation Technologies Used for Inorganic Compounds Removal from Soil

- **Ex-Situ**

1. *Soil Washing:* It is an aqueous based process that deals with chemical and physical extraction and separation processes for the removal of organic and inorganic compounds. This process uses mechanical and/or solubility characteristics of contaminants to separate them from excavated soil. However, this process is problematic for mainly silt and clay contaminated soil. A mix contaminated site creates difficulties for a suitable soil washing and it is unable to remove all types of contaminants (USEPA, 1997). It is also costly to use.

- **In-situ**

1. *Vitrification*: Vitrification is a soil-melting technique that involves the melting and fusion of material in temperatures of 1600-2000^{0}C, followed by rapid cooling into crystalline amorphous form. It is good for both organic and inorganic materials. In this technique, at first the crystalline amorphous vaporizes, than pyrolyses inorganic materials, and then by extracts gases and treatment. Second, an inorganic compound

decomposes or reacts with the melt (N_2, O_2). The process has a very high cost (US EPA, 1997).

2. *Electrokinetic:* Electrokinetic technique involves using a low-density direct current between electrodes placed in the soil to mobilize contaminants in the form of charged ions. This process allows the extraction of metals and radionuclides but is it not useful for organic compounds.

2.8.2 Remediation Technologies Used for Organic Compounds Removal from Soil

- **Ex-Situ**

1. *Incineration*: This technology involves burning soil organic compounds. It reduces the volume and toxicity of the soil. However, burning inorganic compounds in soil is not possible. It is possible to incinerate soil having a low organic content. This is costly (USEPA, 1997).

2. *Chemical Extraction:* This remediation technology uses leaching and solid / liquid contactors (Ram et al, 1993) and is used for polycyclic aromatic hydrocarbon (PAHs) treatment.

3. *Composting:* This technology decomposes organic materials in humic substances. The compost can be used as a soil conditioner. It is later mixed with an organic bulking agent. It is dependent on aeration, pH, moisture, and nutrient level control. However, this method has a low success rate (Wilson and Jones, 1993).

- **In-Situ**

1. *Thermal technique:* This technique allows for the exchange of heat to vaporize, to desorbs and to separate organic compounds. It is used for any form of petroleum contaminated soil treatment such as volatile, semi volatile and PCB contaminated soil. However, it is an expensive method and has medium efficiency. Clay soils are also difficult to treat with this method (USEPA, 1998).

2. *Soil Flushing:* Soil flushing extracts the contaminants from soil in aqueous form and is mostly used for organic compounds. It removes contaminants by dissolving and/or

by mobilizing them so that they can be extracted. The success rate is very limited for clay soil (USEPA 1998).

3. *Soil Vapour Extraction (SVE):* The injection of high air flow into the contaminated soil, causes the movement of vapours containing volatile organic compounds (VOCs). These components are collected for treatment. This movement of VOCs in the soil media can be described by two processes, advection and diffusion. This technology is not useful for clay soils and cannot be applied in saturated zones (USEPA 1998).

4. *Phytoremediation:* This technology uses certain plants that accumulate contaminants through these roots. It also enhances the rate and extent of degradation of PAHs (Johns et al, 1996).

5. *Bioremediation:* This remediation technology motivates microbial populations by adding oxygen or limiting nutrients or adding exotic microbial species. This technology uses biodegradation to degrade organic contaminants into simple forms of reduced toxicity. Bioremediation needs liquid movement and is avoided in clay particles due to low oxygen transfer rate. Also it needs a lot of time to be effective (USEPA, 1998).

6. *Bioventing:* Bioventing is a combined technology of bioremediation and soil vapour extraction (SVE). First, the SVE method is applied to the soil to remove the volatile portion of hydrocarbons and at the same time the bioremediation process biologically degrades heavier hydrocarbons such as diesel fuel.

7. *Solidification/ Stabilization (S/S):* Stabilization is a process that minimizes the migration rate and / or reduces toxicity by converting the waste into another form with the help of an added reagent. Next, solidification is carried out by adding solidifying material (e.g. cement) to the waste to make a solidified mass. Basically, solidification/solidification processes are closely related, because both of them use physical, chemical and thermal processes to decontaminate the soil. Though this process is not a remediation technology, it may alter or change any type of contaminants. Therefore,

- It reduces water leakage,
- It stabilizes and strengthen soil or rock masses,
- It isolates of waste disposals,
- It prevents settling problems.

2.9 Contaminant Mobility and Persistence

Mobility refers to a biological or chemical contaminant's ability to move within soil or ground water over time. A contaminant may move under the influence of gravity, as with light or dense non-aqueous phase liquids, or under the influence of ground water flow, as with dissolved constituents. As the contaminant moves through a porous medium, condition within the medium tend to resist the mobility of the contaminant. For example, molecules (e.g., cations and pesticides) tend to adsorb particles of the porous medium in proportion to their concentration in ground water. Adsorption also depends on the physical and chemical characteristics of the medium, characteristics such as carbon content and pH. Dissolved contaminants also exhibit the tendency to diffuse within the solute, although diffusivity is a minor mechanism of mobility in the case of rapid ground water flow as found, for example, in injection wells (Fadel 2000).

In addition to chemical factors affecting adsorption, physical factors such as ground water hydraulic gradient, hydraulic conductivity, porosity, and bulk density also affect mobility. Constituents may travel significant distances when there are extensive formation voids and/or fractures. In other settings where the receiving formation contains substantial clay or silt content, and does not include solution cavities or fractures, the mobility of some constituents may be "retarded." This is especially true for many metals, which, depending on pH and other site-specific factors, can undergo fixation and adsorption processes that decrease mobility within the soil-ground water system (Fadel, 2000).

Persistence is the ability of a biological or chemical contaminant to remain unchanged in composition, chemical state, and physical state over time. Persistence depends on chemical structure, conditions in the aquifer conducive to degradation conditions such as microbial population, nutrients available to support microbial growth, and the type and quantity of ions in the background ground water. In some cases, the degradation of one constituent occurs along with a chemical change in another, as when electrons are accepted by manganese ions in the breakdown of petroleum hydrocarbon. In this case, the relatively immobile Mg (III) becomes mobile Mg (II).

Persistence can be expressed in terms of half-lives, or the time it takes for a chemical to change one-half of its mass to a different form or compound. The half-life is an empirical, global measurement that encompasses all of the operable degradation mechanisms (Hemond, 2000).

2.10 Groundwater Quality

Ground water is an important factor in forming grout gel (when chemicals mix with water, the chemicals hydrate, and silica particles join together to form a solid bond). Among various kinds of ground water parameters, pH has driven the formation of silica gel in water. In uncontrolled high pH environment, soil mass will be liquid instead of solid (Siwula and Krizek, 1992). Moreover, high pH stops geletion if water comes from a local environment (Baker, 1982). According to Siwula and Krizek (1992), the pH can cause an effect on sodium silicate grouting where a combination ethyl acetate-formamide is used as a reagent. The researchers observed the samples in a less than one hour curing time environment. They found that grouts are more permanent in a lower pH condition. However, more than nine hours curing time caused some effects in a low and high pH environment. They said that usually pH in ground water ranges from 3.2 to 12.2 and high pH could destabilize the entire zone and destroy the permanence.

Many documents describe how a curing environment, a curing time and a hydraulic gradient can affect the permanence of the sodium silicate grouts. Different grout solutions require different curing times to develop initial strength to reach maximum strength. Water removal or higher preparation time would not be feasible after grouting. A significant amount of leaching from a zone can generate high hydraulic gradients which can harm the entire grouting zone. Moreover, all classes of chemicals cannot be identified before a remediation process take place because some chemicals can escape to the surrounding environment (Hesnawi, 1996).

2.11 Conclusion

All of the technologies that were described earlier have limitations such as

1. All of the ex-situ technologies are highly expensive,
2. Silt and clay make remediation complicated and it takes a long time to clean up the contaminants, due to their low hydraulic conductivity, high cation exchange capacity, and high specific surface area,
3. There are no technologies that can be applied efficiently in mix contaminants.

As a result, it is crucial to develop technologies that can be used for mix contaminants and any type of soil, especially silt and clay, in a short time and at a reasonable cost. In this regard, only the soil containment method (grout barrier) can be combined with other remediation technologies to get the highest results in decontaminating the soil. Alhough it is not a permanent solution, the stabilization process will stop the contaminants from migrating into groundwater first, and could be treated with other technology later.

2.12 Containment Practice

There are many innovative technologies currently used in site remediation. Many different technologies can be applied to protect the environment. These have been described earlier. After summarizing these technologies, it is clear that only containment technologies can efficiently reduce cost and risk simultaneously. As an environmental cleanup solution, containment removes the carrying cost and the risks related with it. Most of them are simple, efficient, reliable, sophisticated, and offer short and long term solutions. They are cheaper than other conventional methods if applied properly. Soil containment is a successful technology that is efficient in remediating soil and groundwater to acceptable levels without being excessively costly and / or complex. It can be used a temporary measure or as a permanent solution (Malone, 1996).

There are many different types of containment technologies available and they are divided into two main categories; hydraulic barriers, and physical barriers. Both of them are inexpensive to install, and are effective, but hydraulic barriers are applicable only for groundwater application. Physical barrier technology can be combined with in-situ treatment to get higher achievement quickly. These containment technologies are mainly used to control contaminant migration. For example, a sodium silicate grout barrier may be installed to control the movement of ground water flow. At the same time, an in-situ treatment (e.g. soil stabilization) can be introduced on site to minimize leaching to the ground. One of the popular and proven ways is to impede or redirect the groundwater flow by using passive physical barriers such as a soil-bentonite slurry wall. This is not very effective, considering cost, longevity, and strength. Another recent approach combines soil containment technology using an in-situ treatment zone with a conventional barrier wall system. This technology has the combined effect of controlling groundwater flow and achieving some measure of groundwater cleanup (Karol, 2003).

In many studies, containment technologies were indicated as an ultimate solution, especially in risk-based cases where mitigation is focused on exposure to groundwater contamination by the elimination of exposure pathways. Horizontal or vertical barrier walls represent an even safer control in the form of a barrier.

2.12.1 Physical / Subsurface Barrier

Physical barriers are constructed in the subsurface at the required depth, depending on soil horizon and type of contaminants. Usually, the materials used are (1) slurry trench cutoff walls made of soil-bentonite, cement bentonite, or concrete, or (2) grout barrier made of cement grout or chemical grout, or (3) steel sheet piling. All are impervious to water (Hesnawi, 1996).

A vertical barrier wall around the site slows the rate of contaminants flow, particularly in isotropic aquifers. The formation of a horizontal hydraulic barrier has a much higher rate of conductivity than the vertical hydraulic barrier (Sugio et al., 1987).

Although the construction of grout barriers such as cement, bentonite, and cement – bentonite are cheaper than chemical grouts, they are limited to sand and gravel. It is very difficult to grout sand, silts and gravel in these grout barriers. Different chemical grouts such as acrylate, urethane, lignin, and sodium silicate grouts are successful to grout most soil types except clay. To reduce permeability and for low viscosity, chemical grouts can be injected into fine grained soil (Elektorowicz, 1979, 1980; Malone, 1984; Bodocsi et al., 1991, Hesnawi, 1996).

2.13 Grouting

Grouting is the injection of a fluidised material into the soil or rock to enhance its strength and density, or to reduce its permeability (http://www3.interscience.wiley.com). There are several ways to classify grouting, e.g. mechanical grouting versus chemical grouting. In this study, only chemical grouting was studied.

2.13.1 Chemical Grouting

According to The Grouting Committee, Geotechnical Engineering Division of the American Society of Civil Engineers, chemical grouting is a material that alters the physical characteristics of the structure when injected into a soil or rock. This grout becomes solid or semi solid after a specific period of time, called curing time. The grout stabilizes the soil by changing geotechnical parameters such as permeability, shear stress, and strength, etc. The precise objective of this chemical grouting is to fill up the pore spaces with silica and other reagents and make the contaminated soil impermeable. Chemical grouting can treat soil particles until 10 nm in diameter. (US Army Corps of Engineers Manual, 1973).

There are many types of chemical grouts available and each of them has its own characteristics, depending on the nature of the problem. The most common chemical grouts are acrylate, lignin, urethane, resins, and silicate grouts (US Army Corps of Engineers Manual, 1973; Hesnawi, 1996; FSU, 2001; Karol, 2003).

2.13.1.1 Acrylate grout

Acrylates were introduced from acrylamide compounds that are no longer available as grout. Acrylate grout is a gel formed by the polymerization of acrylates. The addition of triethanolamine and ammonium or sodium persulfate to a metal acrylate is a catalysis form the gelling reaction. Methylene-bis-acrylamide is used as a cross linking agent and potassium ferricyamide is used as an inhibitor when long setting time is required (Karol, 1990).

This type of grout is used to stop water around sewage systems. In wetting, drying and freezing-thawing areas, acrylate grout is not applied. Though its strength is as high as 1.5 MPa and its viscosity is as low as 1 cP (US Army Corps of Engineers Manual, 1973), it is useful only for fine sediments. Moreover, this grout requires a two-part injection technique and the grout do not exist as an impermeable material, only decrease the coefficient of permeability (k) (Barry 1989, Hesnawi, 1996).

2.13.1.2 Urethane grout

Urethane grouts were developed in many different forms, depending on the isocyanate reaction. First, the reaction joins components by forming urethane linkage. This cross-linking reaction forms a rubbery polymer. Polyurethane grouts formed by reacting with unreacted isocyanate group, called prepolymers. Polymerization will be completed as a gel or foam depending on the water quantity. It has a viscosity from 50 to 100 cP. It is used for stopping groundwater flow and for sealing openings as small as 0.01 mm (US Army Corps of Engineers Manual, 1973). It can be applied directly to soil and groundwater. However, isocyanates are toxic. Table 2-2 shows the application of different types of grout and their uses.

Table 2-2 Characteristics of Major Grout Properties

Type	Penetration	Durability	Ease of application	Potential toxicity	Flammability of materials	Relative costs
Portland cement based grout	L^1	H	M	L	N	L
Silicates	H	M	H	L	N	L
Acrylates	H	M	H	M	L	H
Lignins	H	M	H	H	L	H
Urethane	M	H	M	H	H	H
Resins	L	H	M	H	M	H

N= Non flammable; L^1= very low; L= Low; M= Moderate; H= High

Source: US Army Corps of Engineers Manual, 1973

The Table 2-3 is the comparison table that shows silica based chemical grout is efficient to work in almost every case that is pointed below.

Table 2-3 Application of Chemical Grouts

Application	Sodium silicate	Acrylate	Lignin	Urethane	Resins
Adding strength	C^1	C	C	R	R
Reducing water flow	C	C	C	U	R
Concrete repair	U	U	U	C	C
Sewer repair	U	U	U	C	C
Load transfer and support	U	U	U	C	U
Installation of anchors	R	R	R	U	C

C^1= Commonly used; U= Used; R= Rarely used

Source: US Army Corps of Engineers Manual, 1973

2.13.1.3 Lignins

Sodium dichromate and commercially available lignins are by-products of a sulfite process that forms an insoluble (does not dissolve in liquid) gel after a short time. Lignin can be used for fine sands and coarse silts because of low viscosities range. That makes the lignin capable of being injected into void spaces. Basically, there are single and two component lignin based grouts available.

In a single component system, the reactant(s) is premixed in the lignin based material. By changing the water quantity, the gel time of precatalyzed lignosulfonate system can adjust. This precatalyzed lignosulfonate is very dry and is known as chrome lignin. Next, the two component system is prepared individually and than mixed together just before injection. It has a wide range of setting times, and lignin can control setting time but it has high risk of premature gelling. All of the chemicals in the lignin grout are soluble in water and are permanent. It has plastic consistency and has a low permeability. It will not deteriorate in a short term (<3 years) (US Army Corps of Engineers Manual, 1973).

Lignin grouts are used basically on fine materials to decrease soil permeability or to increase load capacity. It is also used to seal fine fissures in fractured rock. Its use is limited to materials finer than 75 μm. This degree of fineness does not allow satisfactory penetration. Moreover, the injection pressure may affect fine material, and some of the reactants such as bichromate are also considered as grout-water pollutants (Barry, 1989).

2.13.1.4 Resins

Resin grouts are formed when resin solutions and a hardener or a catalyst react and ultimately form a hard resin. Resins grouts are either water based or water soluble. Epoxy and polyester are two common forms of resins. They have low viscosity. However, other chemical grouts might have lower viscosities than the above mentioned during curing time. Resins have a short gel stage, which can be adjusted before they become hard. Next, epoxy grouts have two organic chemical components and they are resin based and a catalyst. Sometimes a flexibilizer is added to the epoxy to increase its ability to become hardened grout. Epoxy resin grouts are resistant to acids, alkalis, and organic chemicals. They accept many filling components, such as silica, bentonite, mica, and fibers (Karol, 1990).

Usually, epoxy resins are easier to use than polyesters. They have less shrinkage, tighter bonds, and they are tougher and stronger than polyesters. Therefore, once they have hardened, they will not again liquefy even when heated, but they may soften. These types of grouts have been used for repairs of cracked concrete.

Besides these, there are some other resins available. Most of these resin solutions have a viscosity thirteen times higher than water (US Army Corps of Engineers Manual, 1973). They are moderately toxic and have a high durability. The initial costs are higher than other chemical grouts such as sodium silicate grout. However, some of the materials in the resins are flammable. This decreases interest in applying them in the field (US Army Corps of Engineers Manual, 1973).

2.13.1.5 Silicate grout

Silicate grouting solution consists of aqueous sodium silicate, water and a reagent. Various types of reagent are available for sodium silicate grouts and they can be categorized as inorganic and organic compounds.

2.13.1.5.1 Inorganic Reagent

Inorganic reagents are non toxic and are effective for chemical grouting for better control in a grouting environment. Calcium chloride and sodium aluminate chemicals are common inorganic reagents that were used in the field until 60's (Zielinski, 1956).

2.13.1.5.2 Organic Reagent

For better control of the silica grout, organic reagents are very often used. There are three very common organic chemicals and they are categorized by their detailed evaluations in widespread field applications. They are known as DBE (dibasic ester combination), formamide and ethyl acetate (Malone 1996).

- **DiBasic Esters (DBE)**

Dimethyl adipate, dimethyl glutarate, and dimethyl succinate are three neutralization organic dibasic esters. They are combinely known as DBE. These ester reagents are widely used on the commercial grouts GELOC-4 and Estasol DBE. Table 2.4 shows the percent of each ester in the GELOC reagent along with other relevant chemical data. The total solubility of the DBE mix is approximately 5.3% by weight at 20° Celsius (DuPont, 1990, Malone 1996).

Table 2-4 Components of DBE reagent

Compound	**% of DBE (% wt.)**	**Chemical Formula**	**M.W. (g/mol)**	**Density (g/ml)**
dimethyl glutarate	66	$C_7H_{19}O_4$	160	1.087
dimethyl adipate	17	$C_8H_{14}O_4$	174.2	1.063
dimethyl succinate	16.5	$C_6H_{10}O_4$	146	1.117
Total	99.5		159.3	1.09

Reference: Aldrich, 1991.

The aqueous of sodium silicate solution is a basic compound. After mixing this solution with a dibasic ester, a reaction takes place and forms dicarboxylic anions, adipate, glutarate, and succinate. In addition, methanol is released as a by product. After forming sodium hydroxide, pH reduces and forms silica gel. The following are formed (Malone, 1996):

Step 1: Sodium silicate and water reacts and form sodium hydroxide and silica at approximately pH 11.

$SiO_2{*}Na_2O + H_2O = 2NaOH + SiO_2$ .... (2.4)

Sodium silicate + water = sodium hydroxide + silica

Step 2: NaOH is react and the ester is hydrolyzed to dicarboxylate anion, and finally sodium dicarboxylate forms in an irreversible base-promoted ester hydrolysis (saponification) condition. n[1]= 2, 3, and 4 are denoted by dimethyl succinate and sodium succinate, dimethyl glutarate and sodium glutarate, and dimethyl adipate and sodium adipate respectively.

$H_3COOC(CH_2)_nCOOCH_3 + 2NaOH =$ $NaOOC(CH_2)_nCOONa + 2CH_3OH$ ..... (2.5)
dibasic ester + sodium hydroxide sodium dicarboxylate + 2 methanol
$(C_n+4H_{2n}+6O_4)$ $(Na_2C_{n+2}H_{2n}O_4)$ (CH_3OH)
Source: Malone 1996

Silica gel formed because of a base reaction in step 2. In this equation, the pH reduces below 10.5 and NaOH is consumed by ester hydrolysis. In these conditions, silica is no longer soluble and forms polymeric groups of silicic acid, which is presented in step 3.

Step 3: When pH of the reaction decreases, silicic acid (SiOH)4 is formed, which concentrates subsequently to form the dimer of silicic acid, and finally forms a trimmer of silicic acid. The reaction prolongs until larger silicic acid polymers are formed. These polymers form polymer aggregates and then polymer spheres. The polymer spheres develop continuously when the hydroxyl group joins their nearby spheres of the surface silicon atoms to each other with the water removal. At this stage, the solution is more concentrated and it helps the spheres to stick to one another to form gel (Malone, 1996).

a) $H_20 + SiO_2 = Si(OH)_4$ ....(2.6)
b) $Si(OH)_4 + Si(OH)_4 = Si(OH)_3OSi(OH)_3 + H_20$..(2.7)
c) $Si(OH)_3OSi(OH)_3 + Si(OH)_4 = Si(OH)_3OSi(OH)_3OSi(OH)_3 + H_20$....................(2.8)

The silica gel which is formed holds all the soil particles together, so the soil mass is stabilized. The function of sodium dicarboxylate in the reaction is unclear. Moreover, in the final gel the dicarboxylate is not present. Specialists (Malone, 1996) say that

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[1] 2= dimethyl succinate and sodium succinate, 3= dimethyl glutarate and sodium glutarate, and 4= dimethyl adipate and sodium adipate

polymer silicic acid discharges dicarboxylate (sodium adipate, sodium glutarate, and sodium succinate), methanol and water into the environment.

Ester neutralized NaOH in step 2. By neutralizing the reagent from 40% to 60%, silica gel could get the maximum strength where neutralization means moles of reagent per moles of NaOH (base) x 100%. As a result, a portion of NaOH could be neutralized and discharged in to the environment with toxic substances because of high pH. Therefore, it could be another environmental threat of sodium silicate grouting in spite of the types of reagents. The DBE is completely transformed to sodium dicarboxylate when the neutralization condition is below 100%.

- **Ethyl acetate**

Ethyl acetate is another type of organic reagent. Ethyl acetate was used widely in the late 1950's in sodium silicate grouting (Karol, 1982). Ethyl acetate is a monoester that has similar reactions to DBE (dibasic esters) and the mechanism follows the NaOH consumption. The reaction consists of sodium acetate and ethanol. In this reaction ethyl acetate neutralizes one mole of base but the dibasic esters neutralize two moles of NaOH. The following table shows the properties of ethyl acetate and reacted products of sodium silicate with ethyl acetate reagent in Table 2-5.

$H_3CCOOCH_2CH_3$ + NaOH = CH_3COONa + CH_3CH_2OH..........(2.9)
ethyl acetate + sodium hydroxide = sodium acetate + ethanol
$C_4H_8O_2$) ($NaC_2H_3O_2$) (CH_3CH_2OH)
Source: Malone, 1996

Table 2-5 Ethyl acetate (Reagent) components

Compound	Chemical Formula	M.W. (g/mol)	Density[1] (g/ml)
ethyl acetate	$C_4H_8O_7$	88.11	0.894

Reference: Aldrich, 1991.

Table 2-6 Properties of 10% ethyl acetate and 50% sodium silicate (% by Volume) per liter grout solution

Compound	moles/liter	grams/liter	Solubility (s/L)	pKa
acetate	1.015	60.0	total	4.74
ethanol	1.015	46.7	total	n/a

Reference: Montgomery, 1991

- **Formamide**

Formamide is another type of organic reagent which is studied in this thesis because of its potential application in the field. In the 1960's and 1970's, formamide was extensively used in combination with ethyl acetate as a reagent for sodium silicate grouts (Karol, 1982). In recent years, the use of formamide has decreased because of potential carcinogen effects noticed with the beginning of the organic ester-based commercial grouts such as GELOC, and Estasol DBE. The chemical reaction (2.10) shows the functions of formamide as a neutralizing reagent of the NaOH that forms silica gel. Sodium formate and ammonia are the final products of the formamide reaction. The saponification reaction is described in the step 5 and properties of formamide in table 2-7. In addition, the components of a typical sodium silicate grouting solution along with formamide reagent are presented in Table 2-8.

Step 5: $[Si_2O_5]^{-2}$ $2Na^+$ + $2H_2O$ + 2O = $COC_2H_5CH_3$ → $[Si_2O_5]^{-2}$...$2Na^+$...2O [intermediate complex] = $COC_2H_5CH_3$+H_2O → $[Si_2O_5]^{-2}$ $2H^+$ + 2Na-$OCOCH_3$ + $2C_2H_5OH$ ....(2.10)

$HCONH_2$ + NaOH = HCOONa + NH_3.............................(2.11)

formamide + sodium hydroxide = sodium formate + ammonia

Source: Malone, 1996; Elektorowicz et al., 1997

Table 2-7 Properties of formamide

Compound	Chemical Formula	M.W. (g/mol)	Density 1 (Stall)
formamide	CNH_3O	45.04	1.128

Reference: Aldrich, 1991.

Table 2-8 Properties per liter of grouting solution
(4% formamide reagent and 50% sodium silicate (% by volume))

Compound	moles/liter	grams/liter	Solubility (g/l)	pKa
Sodium formate	1.002	45.0	total	3.75
ammonia	1.002	46.1	total	n/a

Reference: Montgomery, 1991

2.14 Physical Properties of Grouted Soil

From the grout chemistry of formamide, it is clear that ammonia and sodium hydroxide are not integral parts of a formamide reaction. Therefore they gather in liquid form in a porous or soil-grout matrix. The mechanism of this liquid destroys the permanence of the grout mass by the fluid contained within that mass. The contaminants can leach groundwater from the surrounding environment if the grout mass is less resistant because of weaker grout bonds. Based on the review of the literature, it seems that previously practical investigation was done mainly to evaluate the strength and permanence of the grout. It can be said that parameters (pH, hydraulic gradient, etc.) influence grout permanence in terms of strength and permeability. It has been observed that more strength and less permeability are generally found in an environment grouted with sodium silicate.

Krizek and Madden (1985) assume that the capability of the grout to maintain its permanence (the materials and processes used to build structures should last as long as the structures themselves) is directly related to the protection of grout bonds of the soil-grout matrix. Therefore, the conditions that lead to a reduction in strength and an increase in permeability are in fact reducing grout bond strength and could possibly result in an increased leaching potential of the grout chemicals from the stabilized mass. Soil grout mass can crack under adverse situations if it is in a porous permeable soil.

Almost all previous research indicates that soil type (grain size and porosity), hydraulic gradient and groundwater quality have a direct influence on the permanence of a grouted mass in field conditions (Baker, 1982; Caron, 1982; Krizek and Madden, 1985; Barry et al., 1989, Siwula and Krizek, 1992). However, in laboratory conditions, curing time, the curing environment and sineresis (the expulsion of fluid from the grout as the sample shrinks) influence the permanence of sodium silicate grouts (Warner, 1972; Clough et al., 1979; Krizek and Madden, 1985; Barry et al., 1989, Borden, 1990). Some other physical properties of the grout such as penetrability, viscosity, gel time, and silicate and reagent content also affect the permanence of the grouted soil (Warner, 1972; Clough et al., 1979; Borden et al., 1982, Davidson et al., 1982).

Soil deposits, grout viscosity and grout gel time were controllable by proper grouting design. Moreover, different soil types influence the penetrability of the grout. A proper chemical grout design can be built in different soil types based on grout viscosity and soil grain size (Baker, 1982). Sineresis has been identified as largely a laboratory effect, significantly influenced by the volume of unconstrained grout as opposed to a fundamental property of the material (Borden, 1992). A soil mass in a beaker under laboratory-conditions is more important than the size of sineresis in the small pores (Malone, 1996). Thus, curing time, curing environment, hydraulic gradient, and groundwater quality dominate to cause leaching of grout chemicals from the stabilized soil mass. Additionally, silicate and reagent might cause the soil to leach.

Curing time and curing environment have a vital effect on deterioration of the grout barrier, but these parameters cannot represent the entire grouting zone. Only the outer portion is affected by these parameters, and the interior portion remains unaffected due to less water contact. Therefore, the bulk of the grouted mass may remain intact. The outer layer of the grouted zone may be subject to adverse conditions, particularly during the initial stages of curing when there may not be complete bond development. According to Borden (1992), curing conditions may influence the chemical grouting directly in the laboratory but the nature of the conditions is unthinkable when a grout zone is several feet thick. However, outer layer bonds play an important role in the grout barrier in leachibility. A portion of grout in the laboratory is exposed to water, whereas a portion is affected by ground water in the field. Moreover, hydraulic gradient and ground water quality also affect the grout barrier; as a result, leaching happens (Elektorowicz, 1997). A brief discussion on possible effects of curing time, curing environment, hydraulic gradient, and groundwater quality on leaching are presented below.

2.14.1 Curing Time

Barry et al. (1989) calculated the higher grout strength and curing time between one to seven days when a 50% sodium silicate grout and a 10% formamide-ethyl acetate combination reagent are used under laboratory conditions. He stated that samples of one-day curing time were humid and had unconfined compressive strengths of 588 to 608 kPa, while samples of seven days curing time had unconfined strengths of 1325 to 1340 kPa which is twice the value. It ranged from 83 to 93 MPa and 397 to 432 MPa for one and seven day cured specimens respectively.

A comparison has been done with Clough et al., (1979) and Barry et al., (1989) studies. Clough et al. (1979) used 200 days curing time for two different grout solutions composed of different ratios of sodium silicate and formamide e.g. (30%: 6%), (50%, 10%). He achieved 260 kPa, whereas in the Barry et al. (1989) study, curing time was 1 hour with an inorganic reagent ($CaCl_2$) and 12 hours with an organic reagent (formamide) respectively. It means that organic reagents require longer curing time to reach their maximum strength. In the field, longer curing time is required for reaching the grouted region. It is very important to find out the required curing time for its maximum strength, as grouting is vulnerable to leaching due to incomplete curing. In a study of Krizek and Madden (1985) the effect of curing time on permeability using sodium silicate grouts with seven different reagents was investigated. Their results showed that samples cured up to 10 days increased in permeability under an applied gradient. The authors suggested that, in the short term, because of enough strength within grout mass, the permeability increases. In the long term, cavities may form within the soil mass of syneresis. This cavitation causes the erosion and permeability to increase. Consequently, small pores of granular soils have an important effect on syneresis in in-situ grouting.

2.14.2 Curing environment

Warner (1972), Clough et al. (1979), and Barry et al. (1989) documented that the harmful effects of immerse grouted specimen during an initial period of curing should be understood properly. The curing environment means the conditions applied in the grout specimen (e.g. temperature, type of submerge water, etc) have been cured and is the greatest factor influencing the strength of a grouted specimens (Warner, 1972; Clough et al., 1979; Barry et al., 1989). A grout can be dissolved, diluted or washed off incompletely from bonded components, leading to settling and unsuccessful sealing.

Barry et al. (1989) reported that samples that have less then 1 hour open-air curing time collapse completely after being submerged for 1-2 hours. The authors stated that an ineffective strength improvement may result if the gelled grout slowly dissolved into the surrounding water.

2.14.3 Hydraulic gradient

The hydraulic gradient affects the permeability (the ability, or measurement of a rock's ability to transmit fluids) of grouted specimens. The leachibility and permeability were monitored in sodium silicate with sodium aluminates (reagent) in three algonite grouted specimens (Einstein and Schnitter, 1970). They stated that at first permeability increases, but disintegration of the grout was also observed and then permeability increased again, but a decrease in the concentration of leached sodium was observed because of gradient rise from 50 to 110 and then to 160. The authors suggested that this was because the permeate (representing water that had diffused through a reverse osmosis membrane) and the grout lacked contact time.

An applied gradient has two major effects on the grout system: (1) high gradients can wash off the grout and (2) bulk mass can be diffused from grouted mass. Then the gradient size (110 to 160) affects the permeability rate (Malone, 1996). The USEPA (1989) stated that molecular diffusion controls the transport rate of absorbed and chemically bonded components where permeability ranges from 10^{-4} to 10^{-6} cm/s for stabilized solid waste. As a result, permeability can be changed due to flushing or erosion from the grout, the way to eliminate grout products from the stabilized mass is slower, there is limited diffusion and leaching, if the initial gradient is high. Again USEPA 1989 described a link between solid waste and chemical grouts. A typical permeability rate of sodium silicate grout ranges from 10^{-5} to 10^{-6} cm/s.

2.15 Conclusion

Basically hydraulic and physical barriers are used to trap the contaminants before site remediation so that contaminants can not pollute the subsurface and groundwater further.

Slurry walls, grout barriers and sheet piles are three main forms of physical barriers. Of these three, silica based grout barrier was found effective and inexpensive, so it has been projected as a means of trapping the contamination of fresh water.

Acrylate, acrylamide, urethane, lignins, and resins are the most reliable grouts. However, except for silica-based grouting, all other grouting is good as waterproofing agents, for repairing and changing water flow direction. Their low viscosities and high miscibility make them more vulnerable to mixing with water. Compared to silica gel, they have high costs. Sodium silicate is less vulnerable to dilution by flowing groundwater and is less expensive.

The most important factors that influence the silica grouts are grout composition, reagent type, soil grain size, and chemicals densities. Curing time, the curing environment, and the hydraulic gradient also play a vital role.

A review of the literature indicates that specimens injected with inorganic reagents (calcium hydroxide, calcium chloride, sodium aluminate) form low gel strength and are able to endure the effects of water pH and specimens with organic reagents (DBE, ethyl acetate, formamide). They had high strength and high permeability, especially when specimens were subjected to high water pH (Zielinski, 1956; Malone, 1996; Hesnawi, 1996; Karol, 2003).

Most of the papers reviewed for this study dealt with organic reagents. Researchers always recommended improving the behavior of sand (no silt and clay). Soil particles less than 270 meshes (0.053 mm) are not suitable for the stabilization process (Hesnawi, 1996). Therefore, a stabilization process, silica-based grouting using organic and inorganic reagents, is required to develop optimum mobilization and to transport a mix contaminant from sand and silty sand soil (ranges 1.0 mm to 0.053 mm).

CHAPTER 3 EXPERIMENTAL METHODOLOGY

3.1 Theoretical Background

A review of the literature revealed that many researchers have done their research with chemical grouting. Their results are tabulated below:

Table 3-1 Researches have done on grouting

Type of grouting	Research have done	Limitations
Acrylate	To stop water around sewerage system Adding strength	- Long setting time -not useful for fine sediments - requires two-part injection
Urethane	To stop groundwater flow Sealing opening Decrease permeability	- depend on water quality - isocyanates are toxic
Lignins	For fine materials to slow groundwater flow To increase a load capacity Concrete repair	- Wide range of setting time - high risk of premature gelling
Resins	To repairs of cracked concrete Sewer repair Installation of anchors	They are permanent even when heated.
Silica based grout	Adding strength Reducing water flow Concrete repair Isolation of sandy soil	Started to disintegrate after 15 years

It has been found that all types of chemical grout have limitations and none of them are suitable for silty and sandy silt soil stabilization. This is a serious concern. Moreover, it was also found that researchers always did permeability, concentration, and organic content tests to see the longevity and durability of the grout barrier. However, now researchers are being urged to develop some tools which are easy to use, accurate and reliable and inexpensive. Therefore, in this thesis, silica based chemical grout was studied further with two different reagents in three different kinds of soil: sandy, silty sand and sandy silt. Coefficients of stability, soil porosity, soil resistivity measurement were introduced in this thesis, factors which had not previously been studied. From an environmental point of view, once the grout formulation is make, it is not possible to check how grout behaves in soil and how affect groundwater. All standard tests for grouting can not be applied in contaminated soil containment since the impact on the environment (groundwater) has to be assessed. Therefore, to assess the groundwater quality , the following methodology that requires a series of various tests was developed. These are tests for:

i) Internal changes (porosity and indirect monitoring)
ii) Erosion (grout and soil)
iii) Release of contaminants (Ni, PAHs) from contaminated sites.
iv) Release of chemicals which are part of grout formulation (formamide)
v) Chemical changes.

In this thesis, experiments were designed to check the durability of silica based chemical grout in terms of leachability and vulnerability of the grout. Consequently, a series of laboratory tests were performed on a small-scale level. Before going to a direct experiment, several preliminary tests were done to find out the actual chemical ratio, durability, and strength of silica grout composed of three different types of reagents:

Type A: Sodium silicate (50%) + 50% inorganic reagents (calcium hydroxide or calcium chloride).

Type B: Sodium silicate (50%) + 8% organic reagent (formamide) + 42% tap water.

Type C: 70% of [Sodium silicate (50%) + 8% organic reagent (formamide) + 42% tap water] grout mix + 30% of calcium chloride (50g/L) solution.

3.2 Objectives to Initial Experiments

Based on a review of the literature (excluding international patents), it was concluded that grouting in contaminated soil has not received enough attention. Therefore, an extended experimental approach was needed to assess the best recipe of chemicals for containment of contaminated soil. Subsequently, a series of experiment were conducted. The objective of these experiments is presented in Table 3-2 and the description is in the Chapter 3.

3.3 Methodology at a Glance

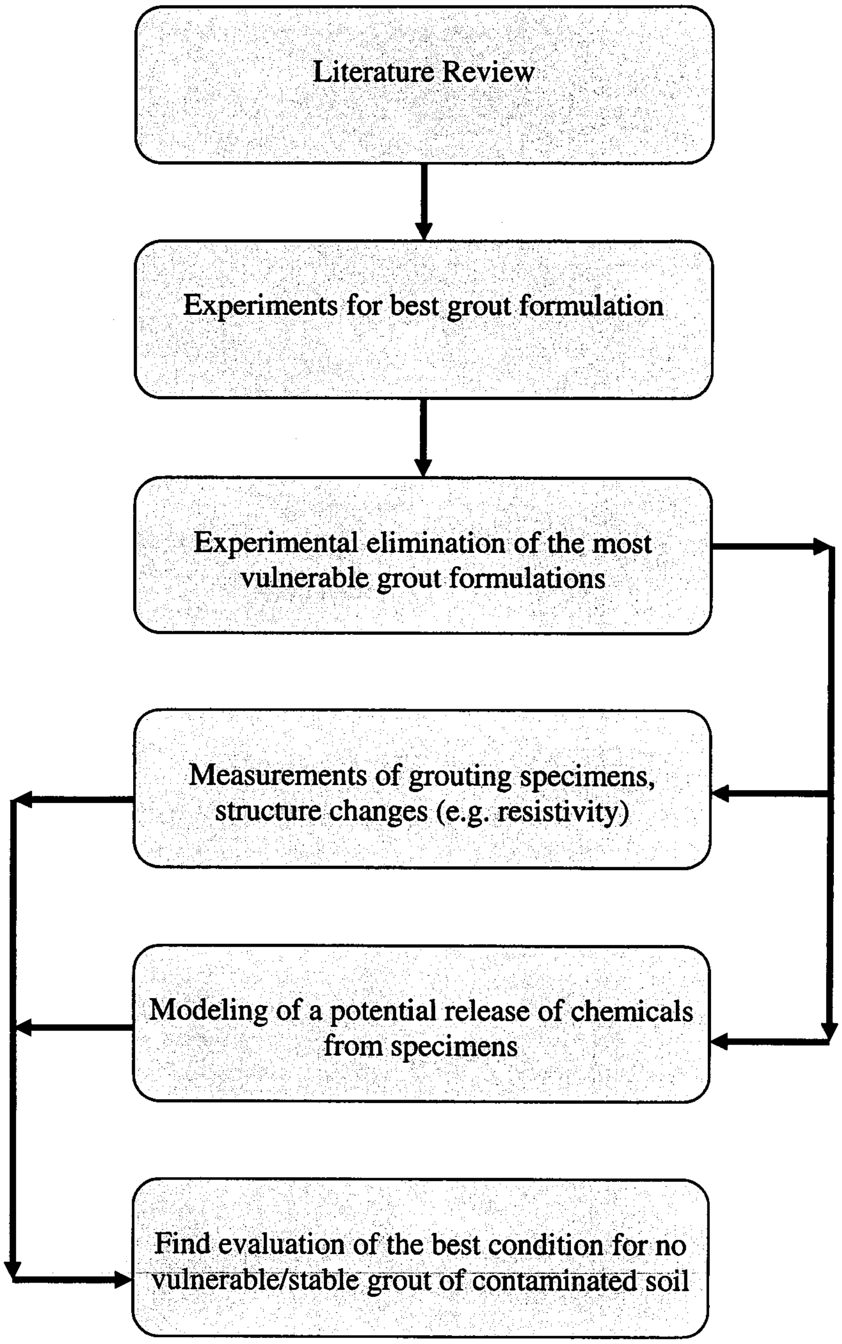


Figure 3-1 Methodology at a glance

Table 3-2 Objectives of the experiments to find optimum conditions for use of silica grout

Objectives	Related experiments
Inorganic reagent ratio	4.5.2, 4.5.3, 4.5.5, 4.5.6, 4.5.7, 4.7.5, 4.7.8, 4.7.13
Vulnerability to groundwater (low mineralized)	4.7.3, 4.7.13, 4.9
Soil component impact	4.7.8, 4.7.9, 4.9
Type of reagent	4.5.1, 4.5.2, 4.5.3, 4.5.4, 4.5.5, 4.7.4, 4.7.8, 4.7.11,4.7.12, 4.8
Setting time	4.5.1, 4.7.10
Curing of inorganic contaminated soil	4.5.1, 4.5.4, 4.7.1, 4.7.9
Curing of organic contaminated soil	4.7.2, 4.7.6, 4.7.9
Curing of mix (organic & inorganic) contaminated soil	4.7.3, 4.7.7

3.4 Initial Experiments

3.4.1 Experiment- 1

- *Procedure*

Based on previous tests (Hesnawi, 1996), an amount of 1 mg dehydrated Ca $(OH)_2$ was mixed in 50 mL of distilled water to maintain 20 mg/L ratio, and was stirred for 5 minutes using a magnetic stirrer. When the calcium hydroxide powder was diluted properly in distilled water, a 50 mL of sodium silicate was added to the solution to prepare an equal component grout solution. The grout solution was stirred for 10 minutes. Then, the grout mix was put in a horizontal plastic box (10.80×5.30×3 cm) using a pipette. Two samples were prepared at this stage. Setting time observed for this grout solution was 78 minutes. Samples were left for five days in open air for maximum curing and then put in low mineralized (tap) water.

- *Results and discussion*

The property change of specimens was observed for once a week. After 7 days the grout had crumbled in the water and no specimen was strong enough to be used in the barriers. Subsequently, two other grout ratios were prepared to verify if these grout formulations could be applied in underground barriers.

3.4.2 Experiment- 2

- *Procedure*

Experiment-2 was prepared without using any soil but to check the grout formulation in 70:30 ratio. The purpose of this test was to expose this grout formulation to a water environment. Subsequently, 17 mL of calcium hydroxide solution (20g/L) was mixed with 26 mL sodium silicate to maintain 70:30 ratios. Then, 23 mL of grout mix was poured into a box (10.80×5.30×3) cm and left in open air for curing. Samples were left for seven days to reach maximum setting time. Then they were submerged in tap water (Simulate ground water).

- *Result and discussion*

It was observed that the disintegration rate of the grout was faster in the first 3 days compared to the next days, and after one week the grout completely disintegrated in tap water.

3.4.3 Experiment- 3

- *Procedure*

The objective of the Experiment-3 was to find out the best grout formulation for containment. 10 mL of calcium hydroxide solution (20g/L) was added to 14 mL sodium silicate to reach 60:40 ratios. Afterwards, it was poured into a plastic container and left in open air at room temperature. From information given in an article by Malone (1996) seven days was chosen as curing time.Then grout formulation was put into the low mineralized (tap) water.

- *Results and discussion*

After three days, it was found that Experiment-2 grout was harder than the Experiment-3 grout, although both of them felt like rock before being put into the tap water environment. After 5 days, the samples had disintegrated in the water. Based on these results, it was decided to do a test with dehydrated calcium hydroxide instead of a solution of calcium hydroxide.

3.4.4 Experiment- 4

- *Procedure*

A preliminary test was done using dehydrated calcium hydroxide to verify the aging period of the grout mix and also to see the permanence of the grout in the tap water. Based on Experiments-1, 2, and 3, it was decided to use 50:50 ratios of the grout components. Subsequently, an amount of 14 mg dehydrated calcium hydroxide was mixed with 14 mL sodium silicate solution. Samples were left for seven days for curing in air environment at room temperature. Afterwards, they were submerged in tap water.

- *Results and discussion*

It seems that this grout mix was harder than the grout mix of Experiments 1, 2, and 3 for unspecified reasons. These specimens crumbled in the tap water after 8 days.

Since the use of the inorganic reagents was not fully satisfactory, three subsequent tests, Experiments 5 to 7 were done using organic reagent formamide. The objectives of these tests were to find out the exact ratio of the chemicals in relation to the vulnerability and strength of specimens.

3.4.5 Experiment- 5

- *Procedure*

Based on literature review an article by Malone, (1996), 25 mL (50%) sodium silicate was poured in a beaker and 22.5 mL (45%) tap water added. A magnetic stirrer was used to mix the solution for one minute. Then a 2.5 mL (5%) formamide was added to that solution and mixed for one minute. A total of 50 mL grout mix for 30 seconds was put in a small plastic box (10.80×5.30×3)cm and left for seven days to reach its maximum curing. Afterwards, specimens were put in tap water for three weeks to check the permanence of the grout formulation.

3.4.6 Experiment- 6

- *Procedure*

In Experiment-6, 50 mL grout mix was prepared using different ratios of chemicals. Here 21 mL (42%) tap water was mixed with 25 mL (50%) of sodium silicate solution and 4 mL (8%) formamide was then added to the solution and stirred for one minute. The mixture was left for seven days in open air, at room temperature, and then put in tap water for three weeks.

3.4.7 Experiment- 7

- *Procedure*

A 25 mL (50%) sodium silicate and 20 mL (40%) tap water was mixed for one minute and later 5 mL (10%) formamide was added to that solution and mixed for one minute. The Specimen was left for seven days in open air at room temperature, for curing in the same container as described in Experiment-6 . Then, it was placed in tap water for three weeks for checking the grout stability.

- *Results and discussion*

It was observed that the specimens of Experiment- 5 to 7 were becoming harder in the tap water with time. Based on the most strength and least amounts of chemical used, the formula of grout used in experiment - 6 was chosen for further experiments. After the above mentioned preliminary experiments, it was decided to carry out a series of laboratory experiments with soil using calcium hydroxide solution (20g/L) and sodium silicate (at the ratio1:1) and the organic reagent to check the grout behaviour in soil environments. First, eleven specimens with the inorganic reagent were prepared since they are less toxic, cheaper, and less time consuming for gel formation.

3.5 Test Procedures

The purpose of this test procedure was to prepare specimens for silica based grouting.

3.5.1 Soil Preparation

Commercially available sand and silt were chosen to simulate a representative sample of soil. The diameter of particle size distribution of the soil ranged from 1 to 0.053 millimetres. However Ottawa 20-30 sand as the media for silicate grouting is well documented in the literature (Diefenthal et al., 1979; Christopher et al., 1989; Siwula and Krizek, 1992). Amounts of 75% sand and 25% silt were chosen for this experiment, then, soil was analysed using ASTM E-II specifications. The soil sieve distributions are shown in Table 3-3, and particle size distributions in Figure 3-2.

Table 3-3 Soil size distribution for silty sand soil

Particle size	ASTM E-11 sieve no.	Mass of soil retained on each sieve g/kg (M)	Percent of soil passing (f) = (Σ M –Col. 3)*100/ 1000
1.000	18	0	100.00
0.850	20	40.57	95.94
0.500	35	190.10	76.93
0.300	50	99.40	66.99
0.250	60	52.27	61.77
0.090	140	363.36	25.43
0.075	200	82.20	17.21
0.053	270	172.10	0.00

Based on above soil grading data, the particle size distribution curve was drawn on the following on logarithm scale.

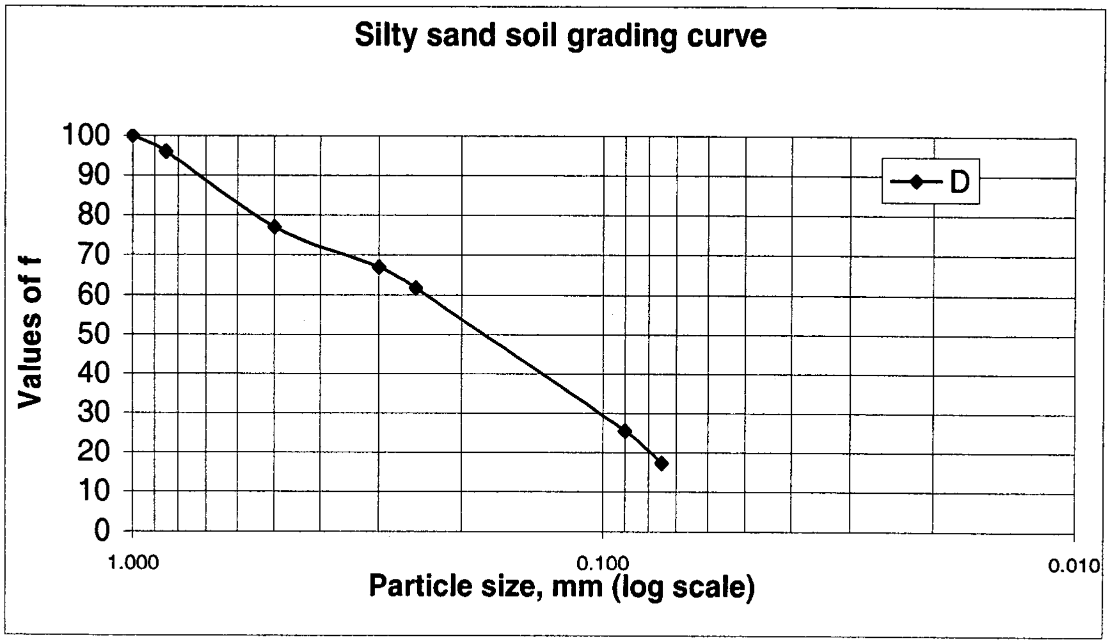


Figure 3-2: Particle size distribution curve for silty sand soil

Three-kilogram soil was prepared, where 73.5% sand (1 to 0.090 mm) and 26.5% silt (0.075 to 0.053 mm) was prepared separately. Soil components washed separately three times in 4 M HCL acid to clean impurities, and finally washed in distilled water. Soils were placed in the oven for 7 hours at 75^{0}C and one more hour at 105^{0}C to completely dry the soil. Once it was dried properly, it was transferred to a desecator. Again, 150 g of dry soil (sand 112.5 g and silt 37.5 g) was taken in an aluminium tray for cross mixing sand and silt.

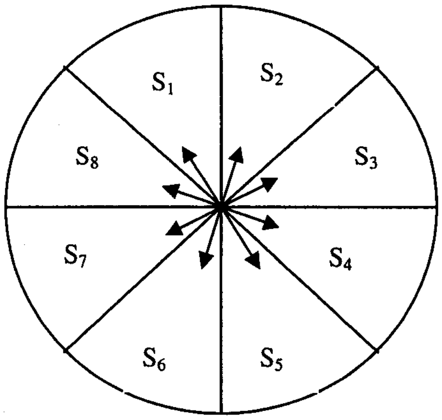


Figure 3-3 Soil cross mixing method

Eight equal amounts of soil were put in an aluminium tray and were cross mixed according to Figure 3-4. From that cross mixing, four new samples were formed and they were again cross-mixed properly. From four samples, two samples were formed and they were cross-mixed to each other. The purpose of the method was to mix the sand and silt uniformly and maintain as close as possible an equal distribution of soil particles.

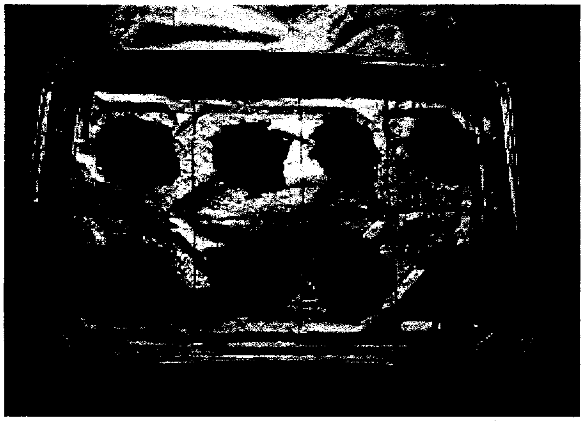


Figure 3-4 Implementation of cross mixing method into 8 samples

Figure 3-5 After cross mixing of 8 divisions

After that, the total volume of the soil was put into a cylindrical plastic mold (8.50x3 cm), and eleven samples were prepared. After all the samples were prepared, they were again put in the desecrator.

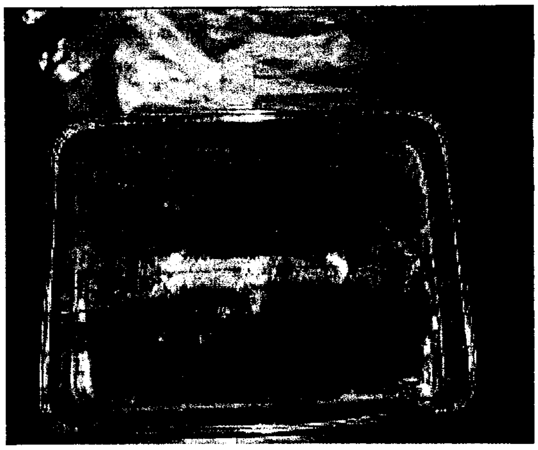


Figure 3-6 Third step of a cross mixing
after four divisions

3.5.2 Contaminated Soil Preparation

Once the soil was washed, a total amount of 900 g soil was divided in portions and subjected to contamination with two different types of chemicals, namely nickel chloride and phenanthrene (in methanol solution). A green deliquescent crystal and odourless nickel chloride was bought from Anachemia Ltd. where six moles of water had been added. The molecular weight of $NiCl_2.6H_2O$ is 237.71, so it was calculated that a total of 3.643 g $NiCl_2.6H_2O$ is necessary to contaminate 900 g soil to get 1000 mg nickel per kg of dry soil. The nickel concentration was chosen after a review of the literature provided the information that the maximum nickel concentration was 900 ppm in a commercial site. The above mentioned amount of nickel chloride was diluted in one litre of distilled water and later added to the 900 g soil. After mixing the nickel contaminated soil (described in 3.6.1), soil samples were placed into the oven for overnight drying at 60^0C. Three cylindrical plastic molds (8.50x3 cm) were filled with contaminated soil (150g each) and placed in the desiccator. After 30 minutes, in order to have a phenanthrene concentration of 600 ppm, 270 mL of phenanthrene-methanol solution was added to 450 g of soil contaminated with nickel and left in the fumehood for 48 hours for methanol evaporation and a uniform diffusion of contaminants across the soil media. The Poly Aromatic Hydrocarbon (PAHs) group was chosen for this research. As a result, phenanthrene was chosen as a PAH component.

3.5.3 Grout Preparation

The "Puddling method" was used in this experiment. The method was introduced by Warner (1972), and updated by Sansalone (1992). This technique is repeatable and has more accuracy in measuring all chemicals and components in the grout (Sansalone, 1992). The puddling method involves pouring contaminated sandy silt, sodium silicate, reagent, and water in a mold(8.50×3)cm . After the samples set (or after reaching their maximum strength) the grout was removed from the mold and tested. Two reagents were used with sodium silicate to prepare two different grout materials for the grouted barrier. Based on a review of the literature and preliminary Experiments 1 to 7, two types of grout material were chosen for a new series of experiments: (1) sodium silicate and calcium hydroxide (SC grout), and (2) sodium silicate and formamide (SF grout). A preliminary test was conducted to prepare the grout mixture in the laboratory using tap water. It was found that solvent could influence the setting time of silicate grouts. This was also confirmed by Connor et al, 1998; Elektorowicz et al., 1997; and Karol, 1990.

As was suggested by Sansalone (1992) and Hesnawi (1996), specimens were designed with 50% sodium silicate, 50% calcium hydroxide solution for SC grout and 8% formamide plus 42% of tap water and 50% sodium silicate for SF grout in a 8.5 cm (height) x 3.0 cm (radius) cylindrical plastic container. An amount of 150 g of artificially contaminated sandy silt (described in 3.6.2) was put into the mold and the average sandy silt density was calculated as 1.60 g/cm^3 and the specific gravity as 2.65. The required components of the grout mix were measured on a volumetric basis. However, it was determined by Hesnawi (1996), 100 grams of sand should be grouted with 25 mL of total grout mix.

3.5.4 Sodium Silicate Grout

Sodium silicate, supplied by the Anachemia Ltd Company, is a viscous liquid, slightly hazy and odourless. The 1% solution in water has the of pH 11.3 and specific gravity of 1.394 (MSDS, Anachemia). Then it is slightly heavier than water and it is also miscible in water. Sodium silicate is the primary chemical to make the above mentioned two types of grouts.

Table 3-4 Grout formulation for Experiments 8-10

Name of grout components	Sodium silicate/ calcium hydroxide (SC)	Sodium silicate / formamide (SF)
Basic Chemical	50% sodium silicate	50% sodium silicate
Reagent	50% calcium hydroxide (50g/L)	8% formamide
Dilution	-	42% tap water
Setting time (observed)	60 minutes	78 minutes

3.6 Batch Experiments 8 to 10

The objective of Experiments 8, 9 and 10 was to assess curing time and leachibility. Experiments 8, 9 and 10 consisted of grouting tests applied to organic, inorganic and mix soil contamination. Triplicate specimens were prepared for each of these tests to obtain higher accuracy. Two controls (uncontaminated samples) were made to compare the results of the grouting.

Figure 3-7 All grout specimen preparation was applied layer by layer method

3.6.1 Experiment- 8

- *Procedure*

Three samples were prepared with only nickel chloride contamination (described in section 3.6.2). SC grout formulation was prepared according to 3.6.3. Afterwards, 16 mL grout mix was poured into a plastic mold (8.5x3) cm first followed by 75 g contaminated soil. After the grout was mix properly, a flat wooden hammer (approximately the same diameter as the plastic mold) was dropped to the specimen from approximately 150 mm height for ten times for better compaction.

3.6.2 Experiment- 9

- *Procedure*

Three samples were prepared with soil previously contaminated with phenanthrene (described in section 3.6.2). The SC grout mix (described in section 3.6.3) was used to stabilize the samples. The compaction method described in section 3.4.1 was also applied in Experiment 9.

3.6.3 Experiment- 10

- *Procedure*

Three soil samples were prepared with mix (nickel and phenanthrene) contamination. Grouts were mixed in the mold layer by layer. The total amount of the contaminated soil

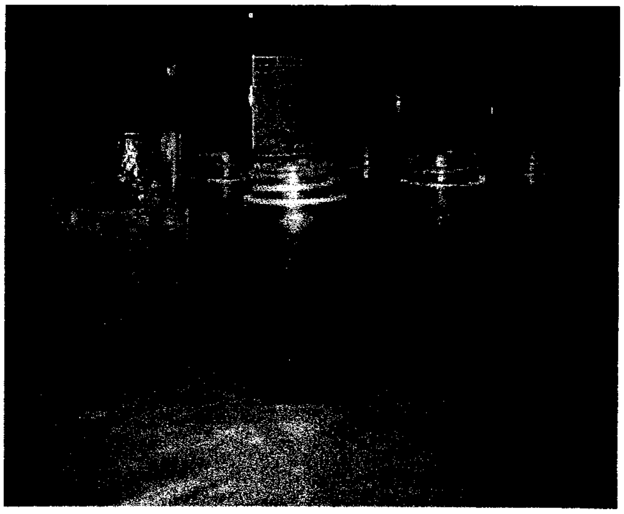


Figure 3-8 Three nickel contaminated soil specimens and two control specimens

(150g each specimen) was divided equally and the total grout mixture (28 mL) was also divided into two equal volumes so that the solution could reach every corner as well as the bottom of the mold. Each layer was compacted in a way described in section 3.4.1.

Eleven of the above mentioned samples (including 2 control specimens of grouted soil without contamination) were left at a room temperature of 21^0C for 7 days for curing. After 7 days, samples were taken from the mold and placed in a plastic container (15x15x10 cm) filled with tap water to simulate groundwater (low mineralized) conditions. Specimens were submerged in tap water up to 2 cm below water level and left for 21 days. Observation notes were taken every day to see if there were any visible changes due to the aging process of the grout barrier. In addition, every alternate day pH, and redOx, were measured.

- *Results and discussion*

Although the samples were very hard after 7 days of their curing time in air, all of them partially disintegrated in the tap water after 7 days. Several reasons were assumed to cause the disintegration of these grouted specimens in water. Initially the following three reasons were suspected:

1. Soil composition;
2. Use of calcium hydroxide as a reagent;
3. Tap water quality.

To find out the real reason for the disintegration of the grouted specimens, the above three assumptions were tested separately. Subsequently, eleven additional samples were prepared.

3.6.4 Experiment- 11

In this test, new parameters were used in a series of tests. Calcium chloride was used as an inorganic reagent instead of calcium hydroxide. All other components (including silty soil) remained the same as described in section 3.4.1. Two different grout formulations of sodium silicate and calcium chloride were prepared, namely 1:1 and 2:1 ratio. All other conditions are summarized on Table 3-5.

Table 3-5 Chemical composition of silica/ calcium chloride grout

Component	^{0}Bé	Specific gravity	Temp. (^{0}C)
Na_2SiO_3	35	1.320	22
$CaCl_2$	15	1.095	22

Reference: Zielinski, 1956

To make $CaCl_2$ solution, the following equation was used according to Zielinski (1956).

$W = X.\ (\gamma_{n.sz} - \gamma_{r.sz}) / (\gamma_{r.sz} - \gamma_w)$ ....(3.1)

Where,

W= Amount of calcium chloride solution needed (L)

$\gamma_{n.sz}$ = Initial specific gravity of sodium silicate

$\gamma_{r.sz}$ = Working solution specific gravity of sodium silicate

γ_w = Specific gravity of water

X = Amount of sodium silicate (L).

Two grout compositions were prepared using a solution (with above mentioned specific gravities) based on 1:1 and 2:1 ratio of sodium silicate to calcium chloride solution. The same preparation technique was followed as was described in Exp-8. After seven curing days, specimens were placed in the tap water to check the vulnerability of the grout specimens. Although all specimens partially disintegrated in tap water after 12 days, it was decided to make nine more specimens using silty sand.

The following equation was used to determine the amount of grout mixture.

$V_{grout} = a\ .\ n.\ V_{soil}$ ....(3.2)

Where,

V_{grout} = volume of grout mixture

a = grain size = 0.75

n = soil porosity

V_{soil} = volume of soil

And soil porosity was calculated from the equation 3.3

$n = 1- \{(\gamma_a^x) / (\gamma_s(1+W^x))\}$ ....(3.3)

Where,

γ_a^x =Amount of natural soil by weight or by volume (g or mL)

γ_s = Amount of dry soil by weight or by volume (g or mL)

W^x = moisture content in fraction

n = soil porosity

Moisture content in the soil was determine from

$W^x = (M_w - M_s) / M_s \times 100$ ....(3.4)

Where,

M_w = mass of wet soil

M_s = mass of dry soil

By using all the above equations, it was calculated that 27~29 mL SC grout mixture is needed to prepare a specimen.

All specimens were prepared following experiment- 8 and using the puddling method. An amount of 1260 g soil was taken where 75% sand (1.0 to 0.090 mm) and 25% silt (<0.090 to 0.053 mm) was washed with 4M HCl acid and dried in the oven at 75^0C for 6 hours and at 105^0C for one hour for completely dried up soil.

3.6.5 Experiment- 12

- *Procedure*

An amount of 420 g dry soil contaminated with nickel chloride (1000 ppm) was used to prepare 3 specimens. Sodium silicate (^{0}Bé 35, specific gravity 1.320) and calcium chloride (^{0}Bé 15, specific gravity 1.095) were prepared according to Zielinski (1956) to make a grout mix. At first, an amount of 16 mL sodium silicate solution was poured in a plastic mold (8.5x3) cm. Then, 140 g of soil were placed and mix properly. Finally, 16 mL calcium chloride was poured into the mold and mixed at the same time. After that, a wooden flat hammer was used to make the specimen compacted and left the sample in open air at room temperature for 7 days for curing. The procedure was repeated for two other specimens. After that, specimens were submerged in tap water for 2 weeks.

- *Results*

After 8 days of aging, all specimens had disintegrated in the tap water.

3.6.6 Experiment- 13

- *Procedure*

An amount of 420 g dry soil contaminated with phenanthrene (600 ppm) was used to prepare three specimens. The procedure was the same as described in section 4.4.5 (Experiment- 12).

- *Results and discussion*

After 8 days of aging, all specimens had disintegrated in the tap water.

3.6.7 Experiment- 14

- *Procedure*

An amount of 420 g dry soil was contaminated with nickel (1000 ppm), and phenanthrene (600 ppm) was used to prepare three specimens. Then, 16 mL sodium silicate solutions (^{0}Bé 35, specific gravity 1.320) was taken in the plastic mold (8.5x3 cm) and poured into 140 g dry soil from a height of 150 mm. The soil was mixed with sodium silicate. After that, the same amount of calcium chloride solution (16 mL) was poured into the mold and mixed (^{0}Bé 15, specific gravity 1.095). Subsequently, each specimen was pressed ten times with a wooden hammer (described in 4.4.1) for better compaction. Specimens were left to settle in the open air at room temperature for 7 days. After 7 days, a piece of each mold was cut off and put in tap water (at pH = 7.3) for 21 days for aging.

- *Results*

  After 10 days of aging, most of the samples had disintegrated in water.

3.6.8 Experiment- 15

- *Procedure*

  In this experiment, the procedure of experiment- 12 was followed to make 3 specimens contaminated with nickel. However, the chemical ratio of sodium silicate and calcium chloride was 2:1.

- *Results*

  Specimens had disintegrated in water after 10 days.

3.6.9 Experiment- 16

- *Procedure*

  Experiment- 13 was followed in this experiment to make 3 specimens contaminated with phenanthrene; but the sodium silicate and calcium chloride mixing ratio was 2:1 in this experiment.

- *Results*

  Specimens had disintegrated in water after 9 days.

3.6.10 Experiment- 17

- *Procedure*

  The procedure described in Experiment- 14 was used with 3 additional specimens. However, at this time the sodium silicate and calcium chloride mixing ratio was 2:1. In Experiment- 17, the soil was contaminated with both nickel and phenanthrene.

- *Results*

In this case, all samples had disintegrated in water after 9 days.

It was assumed that soil components, i.e. silt, could be responsible for disintegration of grouted specimens.

Subsequently, a new series of experiments was prepared with coarse, medium, and fine (33.33% of each) sand (1.0 to 0.090 mm). The particle size distribution is presented in Table 3-6 and the soil grading curve is in Figure 3-9. Since it was suspected that silica colloids disturb gel formation, calcium chloride was chosen as a reagent. Following Hesnawi, (1996), a 20 mg/L calcium chloride solution was used to formulate the grout with sodium silicate (41 ^{0} Bé) and specific gravity is 1.394 (MSDS, Anacemia Ltd.) was used. A new plastic mold (PVC of 8.50 cm diameter and 4.60 cm height) was used to get an exact cylindrical shape.

Table 3-6 Particle size distribution for sandy soil

Particle size	**ASTM E-11 sieve no.**	**Mass of soil retained on each sieve (M) g/kg**	**Percentage of soil passing (f) = (Σ M[2] – m)*100/ 1000**
1.000	18	0	100.00
0.850	20	168.25	83.18
0.500	35	155.47	67.63
0.300	50	175.42	50.09
0.250	60	168.54	33.23
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

---

[2] M = Initial amount of soil for sieving =1000 kg

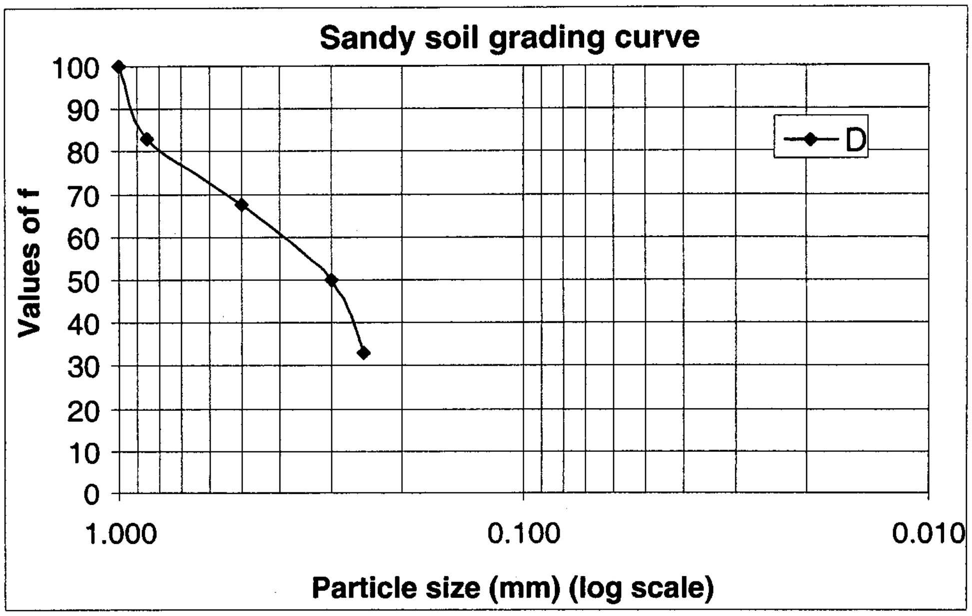


Figure 3-9 Particle size distribution curve for sandy soil

At this stage, the methodology was modified further. It was decided to use: 1) sodium silicate and an inorganic reagent for nickel and phenanthrene contaminated soil 2) sodium silicate and an organic reagent for phenanthrene contaminated soil; and 3) sodium silicate and both inorganic and organic reagents for mix contaminated (nickel & phenanthrene), combining previous experience (Malone, 1996, Hesnawi, 1996 and Zielinski, 1956). They agreed that the inorganic reagent accelerates the whole process and it takes less time for stabilization in comparison with other reagents. Again, these previous experiments also showed that organic reagents are more durable, inexpensive, and more viable. Although no literature was found which described using both (combined) reagents, it was decided to compare the performance of the combined reagent application. Therefore, three different samples were formulated using combined grout mix (SCF) to see their response to mixed contamination of nickel and phenanthrene.

3.6.11 Experiment- 18

- **Materials used in Experiments 18 and 19**

Inorganic grout mix consists of the following components:

- Sodium silicate (41 ^{0} Bé) (50%) .... 16 mL
- Calcium chloride (20 g/L) (50%) .... 16 mL

- *Procedure*

In this experiment, calcium chloride (20 g/L) solution, an inorganic reagent, was used with sodium silicate in nickel contaminated sandy soil. The chemical ratio was 1:1. Three specimens were prepared at this stage and an amount of 32 ml grout mix was required for each specimen to saturate 160 g dry sandy soil. Specimens were left in an open air environment for 7 days for curing. After that, they were submerged in the tap water for 4 weeks.

3.6.12 Experiment-19

- *Procedure*

In this experiment, calcium chloride (20 g/L) solution, an inorganic reagent, was used with sodium silicate in phenanthrene contaminated sandy soil. The chemical ratio was 1:1. Three specimens were prepared at this stage and an amount of 33~34 ml grout mix was required for each specimen to saturate 160 g dry sandy soil. Specimens were left in an open air environment for 7 days for curing. After that, they were submerged in the tap water for 4 weeks.

- *Results and discussion*

The results of both experiments (18 & 19) showed that the grout mixes were unchanged in the tap water at 12 days but disintegrated after 2 weeks. This means neither silty sand soil nor type of contamination were responsible for grout disintegration in tap water.

3.6.13 Experiment- 20

- *Procedure*

An organic reagent grout mix consists of the following components for phenanthrene contaminated soil (method experimented in 3.5.5, 3.5.6, 3.5.7) and Experiments- 5, 6 & 7.

- Sodium silicate (50%)........................... 16 mL
- Formamide (8%).............................. 2.56 mL
- Distilled water (42%)........................... 13.44 mL

Sandy soil (1.0 mm to 0.090 mm) was taken for the experiment that was contaminated with phenanthrene (600 ppm). After preparing the grout mix according to Experiment- 6, an amount of 16 mL grout mix was poured into the mold followed by 75 g dry phenanthrene contaminated sandy soil. After being mixed properly, 17 mL grout mix was again poured into the mold and then 75 g dry sandy soil was added to the mold and mixed properly. After that, the wooden hammer was used for compaction and the grout mix was left for 7 days in the open air at room temperature for 7 days for curing. Afterwards, specimens were submerged in tap water for 4 weeks.

- *Results and discussion*

All of the specimens hardened over time and remained unchanged, even after four weeks. A negligible amount of disintegration was noticed. Effluent was taken for testing every 10 days for further analysis.

3.6.14 Experiment- 21

- *Procedure*

Grout with combined (Inorganic and organic) reagents consists of the following components for mix (nickel & phenanthrene) contaminated soil:

- Sodium silicate (50%)..........................16 mL
- Formamide (8%)..............................2.56 mL
- Distilled water (42%)........................13.44 mL
- Calcium chloride (30%)........................10 mL

In this test, chemicals were injected into soil in two phases. First of all, the total amount of grout mix was calculated from equation 3.2. Then 70% of that calculated grout mix (pre-prepared organic grout) was poured into the mold followed by 160 g mixed (nickel and phenanthrene) contaminated dry sandy soil. This was mixed thoroughly.

Later on, 10mL, 30% of the total required grout, calcium chloride solution (20g/L) was added to the mold and again mixed to ensure calcium chloride reached ever corner of the mold. Then the rest of the organic grout mix was poured into the specimen. Three specimens were prepared for this experiment. After that a wooden hammer was used for better compaction of the soil.

- *Results and discussion*

Some changes were noticed during the aging period of the specimens in 30 days. In the first week, a big disintegration took place and after that there were no changes observed. However, at the beginning of the third week, again partial disintegration took place. Therefore, the grout used in the Experiment- 20 was used for further experiments. The summary of 12 specimens tested in Experiment 18-21 are summarized in Table 3-7.

Table 3-7 Summary of the experiments

Experiment no.	Sand composition	No. of specimens	Grout components	Grout mixing percentage	Contamination	Curing time (days)
18	Coarse 33% Medium 33% Fine 33%	3	Na_2SiO_3 + $CaCl_2$	50%, 50%	$NiCl_2$	7
19	Coarse 33% Medium 33% Fine 33%	3	Na_2SiO_3 + $CaCl_2$	50%, 50%	Phenanthrene	7
20	Coarse 33% Medium 33% Fine 33%	3	Na_2SiO_3 + H_2O + formamide	50%, 42%, 8%	Phenanthrene	7
21	Coarse 33% Medium 33% Fine 33%	3	Na_2SiO_3 + H_2O + formamide + $CaCl_2$	70%(50%, 42%, 8%), & 30%	$NiCl_2$ + Phenanthrene	7

3.6.15 Experiment- 22

The Experiments 22 and 23 are summarized on the following Table 3-8.

Table 3-8 Properties of grout mix

Grout Mix	Amount of chemical (mL)	Calcium chloride preparation	Percentage /Ratio
Na_2SiO_3+$CaCl_2$	10 +10	20g/L	50%, 50%
Na_2SiO_3+$CaCl_2$	10 +10	50g/L	50%, 50%
Na_2SiO_3+$CaCl_2$	10 +10	75g/L	50%, 50%
Na_2SiO_3+$CaCl_2$	13.20 +6.80	20g/L	66%, 34%
Na_2SiO_3+$CaCl_2$	13.20 +6.80	50g/L	66%, 34%
Na_2SiO_3+$CaCl_2$	13.20 +6.80	75g/L	66%, 34%

- *Procedure*

The object of this experiment was to check the bonding between a sodium silicate and a calcium chloride solution. Therefore, 3 samples were prepared where the concentration of the calcium chloride solution was 20 g /L, 50 g/L, and 75 g/L. Afterwards, a 10 mL sodium silicate solution was mixed with a 10 mL of calcium chloride solution in each concentration. A 1:1 ratio of sodium silicate and calcium chloride was maintained in the entire experiment. The solutions were left for 7 days for curing in the open air at room temperature. After that, all of the samples were submerged in low mineralized (tap) water.

3.6.16 Experiment- 23

- *Procedure*

In this test, 3 grout mixes were prepared, each using sodium silicate and calcium chloride solutions. Calcium chloride solutions were prepared with the following concentrations: 20 g/L, 50 g/L and 75 g/L. These grout mixes were prepared with a ratio of 2:1 (sodium silicate: calcium chloride). After that, samples were left for 7 days for curing in the open air at room temperature. After that, all of the samples were submerged in high-mineralized (salt) water, following to Hesnawi (1996). The high-mineralized water was prepared in the laboratory and the chemical composition of salt water shows in Tab. 3-9 (Hesnawi, 1996).

Table 3-9 Composition of mineralized water

Characteristics	Design values
pH	7.7
$CaCO_3$ (mg/L)	2640
Ca (mg/L)	384
Mg (mg/L)	408
Na (mg/L)	3552
K (mg/L)	40
HCO_3 (mg/L)	140
Sulfate (mg/L)	1612
Chloride (mg/L)	6000

Hesnawi, 1996

- *Results and discussion*

All of the samples sheared in the tap water disintegrated after 5 days. However, samples of those sheared in the salt water remained during the first week without changes. In the second week, 20 g/L and 75 g/L with both ratios disintegrated. It was observed that only the sample containing 50 g/L calcium chloride solution (both ratios) sheared without visible changes until the end of second week and then they finally crumbled. Subsequently, experiments were performed using only organic and combined grout reagents.

3.7 Conclusion and a Subsequent Series of Experiments

Based on results from Experiments 1-23, it was decided to use organic and combined reagents with sodium silicate. In order to assess the impact of fine particles, it was decided to use different compositions of silt and sand. In total, three different types of soil compositions, sandy soil, silty sand soil and sandy silt, were used in the next series of experiments involving nickel, phenanthrene, and mix (nickel and phenanthrene) contamination. In order to evaluate the vulnerability of grouted specimens, a number of direct and indirect assessment methods namely resistivity of specimens, porosity changes of specimens, and coefficient of stability were applied. In addition, when specimens were submerged in water was controlled every alternate day and measurements of, pH, RedOx and temperature were taken (described in section 3.4). The summary of this experimental methodology is given in Table 3-10 and shown in Fig. 3-10.

Table 3-10 Summery of specimen preparation for experiments 24 to 35

Experiment/No. of sample	Contamination	Grout Mixture	Soil Composition
Exp. 24/3	Nickel	Sodium silicate + Formamide + tap water (SF grout)	Sand (100%)
Exp. 25/3	Nickel	Sodium silicate + Formamide + tap water (SF grout)	Sand (75%) Silt (25%)
Exp.26/3	Nickel	Sodium silicate + Formamide +tap water (SF grout)	Sand (50%) Silt (50%)
Exp. 27/3	Phenanthrene	Sodium silicate + Formamide +tap water (SF grout)	Sand (100%)
Exp. 28/3	Phenanthrene	Sodium silicate + Formamide +tap water (SF grout)	Sand (75%) Silt (25%)
Exp. 29/3	Phenanthrene	Sodium silicate + Formamide + tap water (SF grout)	Sand (50%) Silt (50%)
Exp. 30/3	Nickel + Phenanthrene	Sodium silicate + Formamide + tap water (SF grout)	Sand (100%)
Exp. 31/3	Nickel + Phenanthrene	Sodium silicate +Formamide + tap water (SF grout)	Sand (75%) Silt (25%)
Exp. 32/3	Nickel+ Phenanthrene	Sodium silicate + Formamide + tap water (SF grout)	Sand (50%) Silt (50%)
Exp. 33/3	Nickel + Phenanthrene	Sodium silicate + Formamide + tap water + calcium chloride(SFC grout)	Sand (100%)
Exp. 34/3	Nickel + Phenanthrene	Sodium silicate + Formamide + tap water + calcium chloride (SFC grout)	Sand (75%) Silt (25%)
Exp. 35/3	Nickel + Phenanthrene	Sodium silicate + Formamide + tap water +calcium chloride (SFC grout)	Sand (50%) Silt (50%)

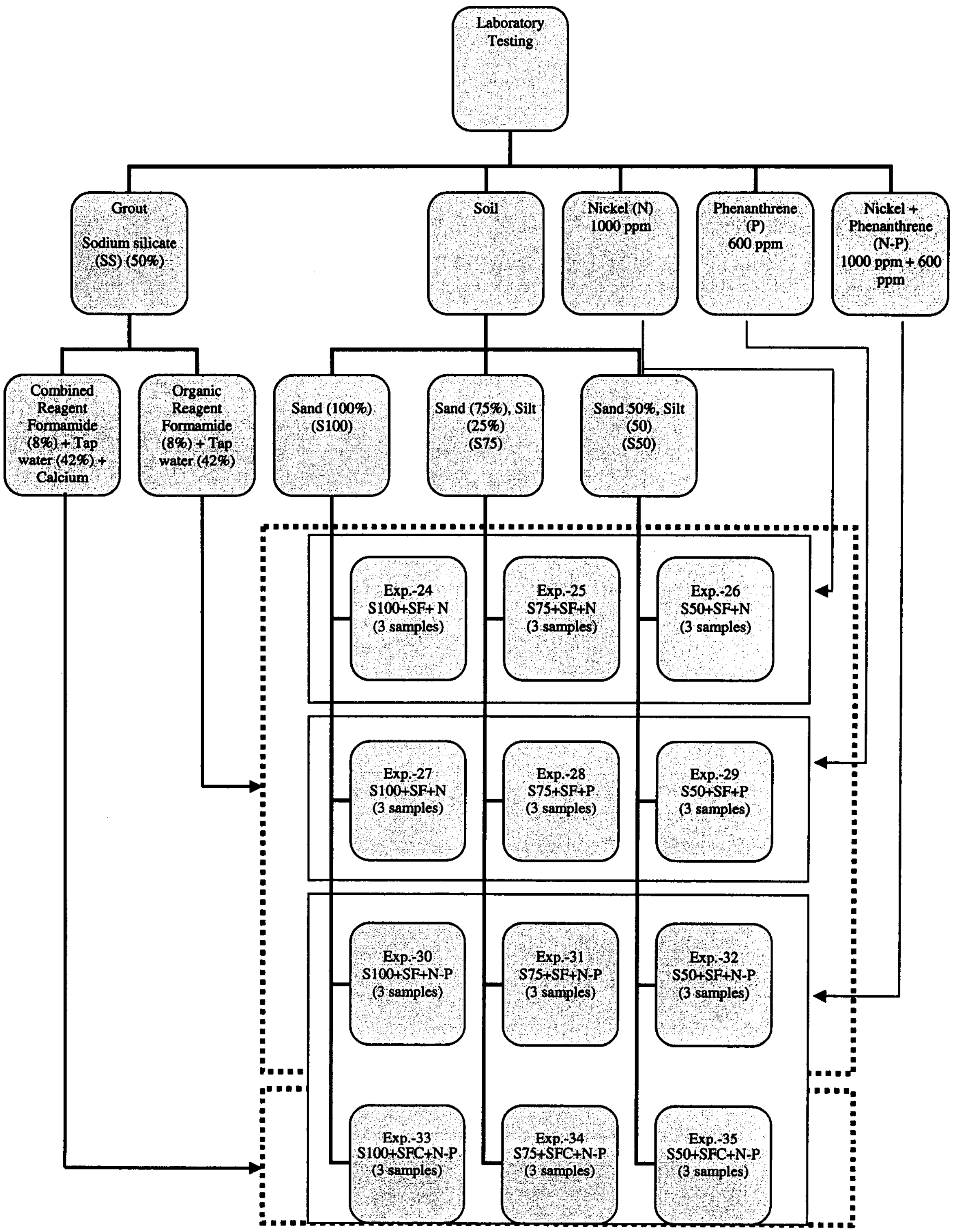
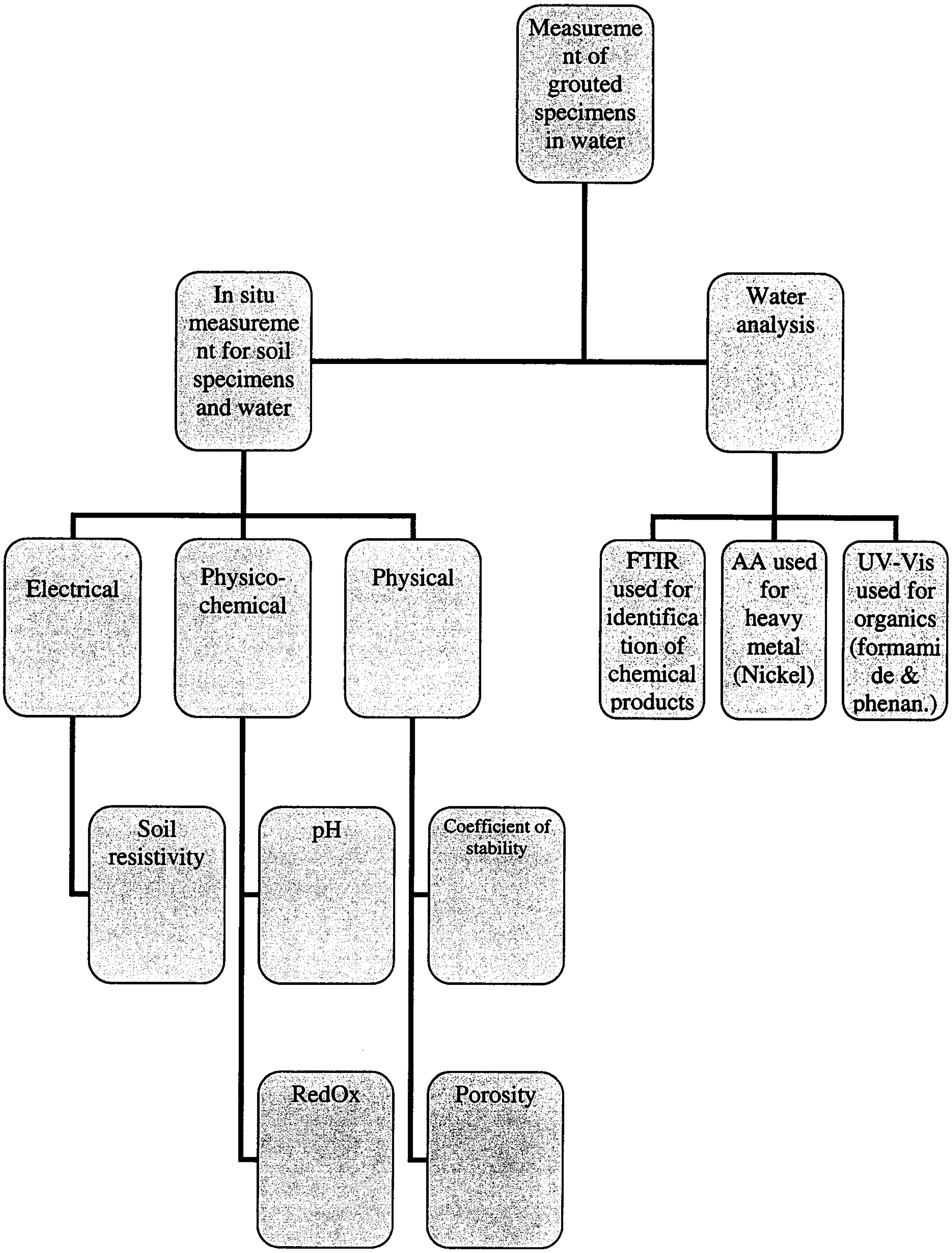


Figure 3-10 Methodology flowchart for Experiments 24 to 35

3.8 Flowchart of Experimental Measurements and Analyses of Silica Based Grout



3.9 Final Experimental Phase (Experiments 24 to 35)

3.9.1 Soil Composition

Detailed procedures for soil (grain size analysis), soil contamination of nickel and phenanthrene, and grout mixture were discussed earlier in sections 3.6.1, 3.6.2, 3.6.3, and 3.6.4 respectively. However, at this stage, a new soil composition was introduced and was discussed in section 3.8. After grain size analysis, soil grading Table 3-11 and particle size distribution curve Figure 3-11 were prepared as follows.

Table 3-11 Sandy silt soil size distribution

Particle size	ASTM E-11 sieve no.	Mass of soil retained on each sieve (M) g/kg	Percentage of soil passing (f) = (Σ M[3] – m)*100/ 1000
1.180	16	0	100.00
1.000	18	29.68	97.03
0.850	20	26.67	94.37
0.500	35	142.58	80.11
0.300	50	101.65	69.94
0.250	60	96.54	60.29
0.090	140	103.41	49.95
0.075	200	240.65	25.88
0.053	270	258.82	0.00

---

[3] M = Initial amount of soil for sieving =1000 kg

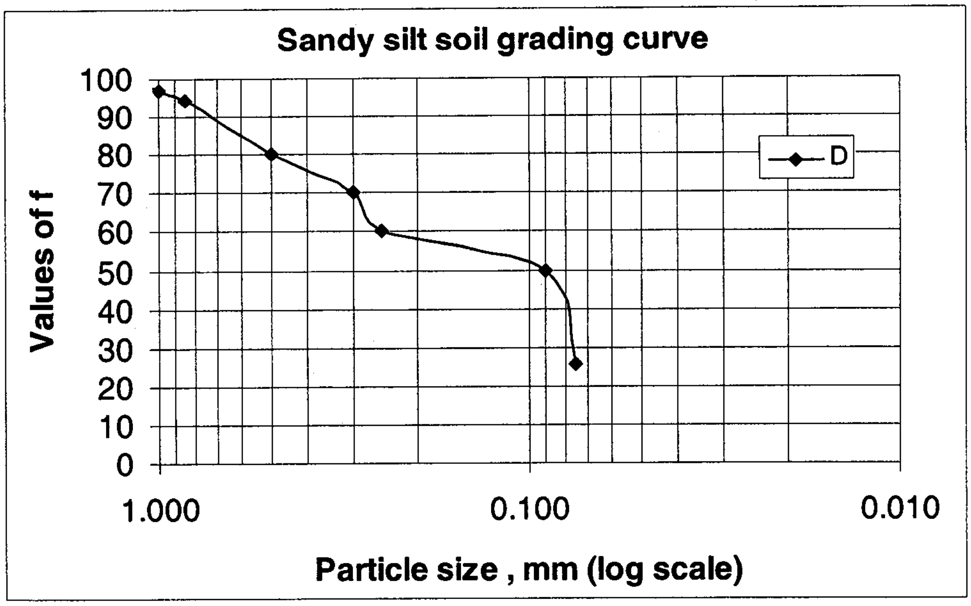


Figure 3-11 Particle size distribution curve for sandy silt soil

Three different soil compositions were chosen for the final experimentation, they are:

a) Sand (100%)
b) Sand (75%), Silt (25%)
c) Sand (50%), Silt (50%)

Tables 3-6, 3-3, 3-11, and Figures 3-9, 3-2, 3-11 are representing above three kinds of soil's particle size distribution and their soil grading curve respectively.

3.9.2 Grout Mixture

A one litre of silica based grouting solution contains 500 ml of sodium silicate, 420 ml of tap water and 80 ml of formamide (elaborated in section 3.6.3).

3.9.3 Electrodes Installation

Four silver (99% pure) electrode-probes (0.8 mm diameter and 1 cm height each) were used to measure the soil resistivity for each specimen. They were inserted in a plastic mold and a distance of 1 cm between electrodes was maintained. Outside of the mold, electrodes were fixed in the plastic sheet by using glue. In total 36, plastic plates were prepared.

3.9.4 PVC Mold Preparation

A PVC pipe was cut into 36 equal pieces. The height was 8.50 cm and the diameter 4.60 cm. In each mold, four holes were drilled with a 1 mm bit and the in-between distance was 1 cm for electrode-probe installations.

3.9.5 Specimen Preparation Techniques for SF Grout

The puddling method (section 3.6.3) was used in this test because this method is repeatable and provides greater accuracy in measuring grout components. In this method, a premixed known volume of grout was poured into a cylindrical mold and a specific amount of dry soil was poured into the mold. Once the soil was saturated with grout, it reacted after a specific time and made an encapsulation that lead to a stable soil mass (Sansalone, 1992). This technique was introduced for a 50% sodium silicate, 42% tap water and 8% formamide formulation in (height 8.50 cm and diameter 4.60 cm) PVC molds.

1) 160 g dry soil poured into the mold. Nine different specimens were made with triplication of the samples. However, these 27 samples were made with different soil compositions that were tabulated in Table 3-10.

2) The total required grout mix was calculated from the equation 3.2, 3.3, and 3.4. Here the calculated specific gravity of the soil was 2.65 and the soil dry density was 1.68 g/cm^3.

3) The approximate required grout mix for each specimen was measured by volume and by percentage.

- Liquid sodium silicate (50%)............. 16.00 mL
- Tap water (42%) .... 13.44 mL
- Liquid formamide (8%) .... 2.56 mL

4) One litre of grout mix was prepared in a beaker. Liquid sodium silicate was taken into a 1000 mL beaker using a 100 mL pipette. Later, tap water was measured using another 100 mL pipette and poured into the beaker and blended for 10 minutes using a magnetic stirrer. While they were blending, formamide was taken with a 50 mL glass pipette and added to the beaker. The grouting mixture was blended continually to obtain a consistent mix.

5) Approximately, 16 mL of grout was taken into an empty PVC mold by closing one end of the mold with parafilm. Half (80 g) of the soil was poured into the mold from a height of 900 mm and the grout was mixed thoroughly. After that, soil was pressed 10 times with a wooden hammer for uniform compaction.

6) Step 5 was repeated for the rest of 80 g soil. This procedure was applied for SF grouted 27 specimens which means from experiment 24 to experiment - 32.

After sample preparation, a plate with four electrode-probes was installed in each specimen to measure resistivity changes of the specimens. Eventually, all of the 27 samples were again pressed softly with the wooden hammer for better compaction of the soil in grout mix.

Samples were cured for 7 days and then put individually in a small plastic container (height 18 cm and diameter 9 cm) with water, once the parafilm was removed from the other side of the mold.

3.9.6 Specimen Preparation Techniques for SFC Grout

Nine specimens (Experiments 33-35) were prepared using combined grout mix that is briefly described, step by step, in the following.

1) First of all, SF grout mix was prepared following section 3.9.5 (steps 1-4).

2) After that a 20 g/L calcium chloride solution was prepared.

3) Approximately 11.50 mL of grout was taken into an empty PVC mold by closing one end of the mold with parafilm. Half (80 g) of the soil was poured into the mold from a height of 900 mm and mixed with the grout and soil thoroughly.

4) After that, 15% (5 ml) of calcium chloride was added to the sample. They were mixed thoroughly and pressed 10 times with a wooden hammer for uniform compaction.

5) Step 3 & 4 were repeated for the rest of the 80 g soil (total dry soil was 160 g). This procedure was applied for SFC grouted 9 specimens, which means from experiment 33 to experiment- 35.

After sample preparation, a plate with four electrode-probes was installed in each specimen to measure resistivity changes of the specimens. Eventually, all of the 9 samples were again pressed softly with the wooden hammer for better compaction of the soil in grout mix.

Samples were cured for 7 days and then put individually in a small plastic container (height 18 cm and diameter 9 cm) with water, once the parafilm was removed from the other side of the mold.

3.10 Set-Up for Experiments 24-35

- **Apparatus, and Equipment Used in the Experiment**
    - 144 Silver probe electrodes (D = 0.8 mm)
    - 36 PVC pipes (8.50 X 4.60) cm
    - Wooden hammer
    - 144 centrifuge tubes for effluent collection
    - Digital multimeter (Mastercraft)
    - Microsis R6 (Data Acquisition System)
    - 4 special data cables to connect electrodes and microsis machine
    - 2 pieces of 50 Ω resistors
    - 1 specula
    - 1 micro balance

- pH meter (Promet)
- RedOx meter (Promet)
- Standard balance
- UV/Vis spectrometer (Perkin Elmer, Lambda 40)
- FTIR spectrometer (Nicolet Nexus 470)
- Atomic Absorption spectrometer (Perkin Elmer, Analyst 100)

- **Chemicals used in the experiment**

  Soil Contaminants

  - 1000 ppm solution of $NiCl_2$ (prepared from $NiCl_2.6H_2O$)
  - 600 ppm solution of phenanthrene (dissolve in methanol);
    (3.6 g of phenanthrene-methanol solution for 6 kilogram of dry soil)

  Basic chemical grout

  - Sodium silicate solution (41 ^{0}Bé)

  Reagents

  - Formamide
  - Calcium chloride solution (20 g/L)

3.11 Analytical Testing Procedure and Measurement

3.11.1 Fourier Transform-Infrared (FT-IR) Spectrometer Analysis

Nicolet 470 Nexus FT-IR spectrometer was used to analyse the water samples' residues coming from potential disintegration of specimens.

- **Scope of FT-IR Method**

The method describes a general procedure for the identification of chemical (complex form) that might be released to groundwater from soil specimens which are grouted with sodium formamide (SF) and sodium formamide-calcium chloride (SFC).

Water samples were collected in glass vials on four different days (1^{st}, 10^{th}, 20^{th} and 30^{th} day) and preserved in the refrigerator at 4^0C.

- **Sample Preparation**
    - 5 ml of water was collected in four different days from each vial by a pipette and put it in 2 cm diameter plastic petri dish. Petri dishes were left in the fumehood for complete evaporation.
    - All of the samples were completely dried up after 64 hours.
    - All the solid residues were collected precisely, using a spatula.
    - Agate mortar was used to grind the residues to make them powder. It was observed that some residues were partially wet because silica was in white gel form that is hard to dry at room temperature.
- **Experimental Procedure**
    - Smart miracle AMTIR crystal accessory was installed in FTIR spectrometer.
    - Run OMNIC Custom software on the computer
    - Background was collected on the machine before the sample was placed on the machine for analysis.
    - Approximately 1 mg of powdered sample was placed on the smart miracle accessory's designated place.
    - Then "collect sample" was pressed on the software and the machine started to analyse the sample
    - After 3 scans, Omnic started to give spectra, and the spectra became smoother and more accurate after 64 scans that were defined before.
    - The spectra were printed (Appendix- E)
- **Analysis of Spectra**

After getting spectra, several parameters were adjusted for accuracy.

- Limit X, Y axis of spectra instead of high range.
- Picks values were described
- Display setup was defined
- Pick height was calculated for different days for the same sample and compared with the day one sample in order to know the changes in spectra.
- Data were presented in Microsoft excel for graphical presentation

- **FT-IR Instrument Setup Parameters**
  - Selection of method: Smart endurance
  - Resolution: 4
  - Spectral range: 4000 to 400 nm
  - Source: InfraRed (IR)

- **Quality Control Procedure Followed**
  - Ran the system validation of the instrument, using polystyrene standards 1.5 mil. The system passed the validation test.
  - Collected a new background every 10 minutes.

3.11.2 UltraViolet-Visible (UV/Vis) Spectrometer Analysis

UV-Vis Lambda 40 (Perkin Elmer) spectrometer was used in the experiment to analyse the water sample.

- **Measurement of Formamide Content**

Effluent was analyzed on four different days to determine the concentration of formamide using UV spectrometer where a 10 mm quartz cuvette was used. A filtration process took place before analysis.

- **Scope of UV /Vis Method**

The scope of UV-Vis spectrometer determines the molecular composition of a wide range of organic liquid complex samples. It provides a molecular footprint for quantitative and qualitative analysis.

- **Experimental Procedure**
  - Preserved liquid samples (section 3.12.1) were directly used in UV-Vis spectrometer.
  - 10 mm long crystal cuvette were used for analysis.
  - After initializing the instrument, parameters (described later) were input.

- Reference and sample cell, both with the solvent (formamide in water) were used for the sample analysis.
- The cuvettes were matched to ensure the quality of the measurement.
- "Start" was pressed and waited until it stopped.
- The same procedure was repeated for phenanthrene in hexane
- At this point, a calibration curve and data were printed for both cases. It was observed that formamide in water has one and phenanthrene in hexane has two intensive bands.
- The instrument was ready to analyse the unknown water samples absorbance.
- The cell with solvent from sample position that was on the edge was taken out and replaced with an unknown sample by taking the same volume of effluent from the upper layer of the vials.
- "Start" was pressed again and the instrument detected the sample absorbance in 5 seconds
- When "Stop" (after finishing analysing the samples) was pressed, data were printed.

- **Procedure for Graphs Analysis**
  - From the graph, absorbance 250 nm was picked for analysis.
  - The value of X axis was found on the graph where the curve crossed the edge of Y axis (250 nm line).
  - Data was presented in Excel.

- **UV-Vis Set-Up Parameters**

  Slit: 2.0 nm
  Wave max: 700.0 nm
  Wave min: 190.0 nm
  Speed: 960 nm/min
  Cycle time: 0.1 min
  Lamp: UV+Vis

- **Quality Control Procedure**
  - "Autozero" was pressed each time before measurement with the solvent cell in the sample position to ensure that the reading was the true value.

3.11.3 Atomic Absorption (AA) Analysis

The total nickel that was released to the water was evaluated by measuring nickel concentration in the water and in the soil that degraded to the water.

- **Scope of AA Method**

The basis of the atomic absorption spectrometer is the absorption of discrete wavelengths of light by liquid and gas phase free atoms. Free atoms are formed from the sample by an "atomizer" at high temperature.

- **Measurement of Nickel Content in the Water**

Nickel content was evaluated in the effluent by measuring the concentration of nickel in the effluent.

- **Experimental Procedure**
  - 5 ml of water was taken from each sample after the filtration process.
  - The liquids collected from the filtration were analysed using an Atomic Absorption spectrometer (Perkin Elmer , Analyst 100)

- **Measurement of Nickel Content in the Released Soil Particles**

The nickel content was evaluated in the soil particles that were released in the tap water by digestion process (in hydrochloric acid).

- **Experimental Procedure**
  - Solid particles that were in the water were oven dried at 75^0C
  - The water residue was crushed and 0.50 g of each sample was collected by the metal extraction procedure.

- Crushed soil was placed in a 50 ml centrifuge tube.
- Then, 5 ml of 4M hydrochloric (HCL) acid was added to the crushed soil.
- The suspension was shaken overnight in an orbital shaker followed by 1 hour settling.
- Supernatant was filtered in 100 nm filter paper and analysed with an atomic absorption spectrometer.

- **Analysis of Atomic Absorption (AA) Spectrometer**

The supernatants were analysed for nickel concentration in water. Nickel concentrations were determined with AA flame analysis with the wavelength of 232.0 nm. Three standard nickel solutions of 5ml/L, 10ml/L, and 25mL/L in water defined the standard curve for nickel.

- **Flame Parameters**
    - Wavelength: 232.0 nm
    - Signal: AA
    - Integration time: 1.0 sec
    - Calibration type: Linear
    - Standards: 5 mg/L, 10 mg/L, and 25 mg/L
    - Slit: 0.2 H
    - Lampe current: 20 mA
    - Technique: Flame.

- **Quality Control Procedure**
    - "Autozero" was pressed each time before measurement of each sample to ensure that the reading was the true value.
    - After measuring every 5 samples, standards were checked to ensure the values were correct.

3.11.4 Measurement of pH and RedOx

- *Procedure*

First of all, pH/RedOx meter was calibrated in buffer solution of 7.0, 4.0, and 10.0 with an electrode probe. After removing the specimens from the container for porosity calculation, water was stirred. Afterwards, an electrode was inserted in each plastic container for taking the reading of pH and redOx. pH and redOx of the water were measured on every alternate day for 4 weeks during the aging time of the specimens, using an Promet 25 pH meter.

3.11.5 Moisture Content

The moisture content was calculated according to the ASTM standard method (No. ASTM 2216-90, vol. 4.08). First, soil samples were weighted, and then they were washed and dried at 75^0 C. After that, soil were left in desiccator for 15 minutes for cooling and weighted (at 75^0 C). Soils were left in the oven for 24 hours at a temperature of 105^0C for further complete drying. After that, samples were put in a desiccator for 15 minutes to cool properly. The samples were weighed again and the moisture content was calculated according to the following calculation.

$$w\% = \left\{ \frac{(w_2 - w_3)}{(w_3 - w_4)} \right\} \times 100 \quad \text{(3.5)}$$

Where,

w^x = Moisture content

$w_2 = S_2 + C_2$ @ 75^0 C

$w_3 = S_3 + C_3$ @ 105^0 C

$w_4 = C_2 = C_3 = C_4$

S = Sample, C = Container

3.11.6 Measurement of Resistivity

Soil resistivity was calculated every alternate day during the experiment for four weeks. Resistivity was calculated by generating an electrical field (5 Volts) in the soil by Microsis and electrical parameters were measured (voltage, ohms) in each electrode. Finally, Wenner array (described in section 2.6.3) was used to calculate the resistivity (Ω.m).

CHAPTER 4 RESULTS AND DISCUSSIONS

The vulnerability/durability of grouted soil specimens was analysed based on a series of measurements and analyses. Every alternate day electrical parameters (resistivity) measurements permitted the assessment of continuous changes within the mass of grouted specimen. Analysis of water samples allowed definition of the type of water quality change due to differences in composition of different specimens. A combination of these results permitted the assessment of the durability of the silica grout and its potential implementation.

4.1 Experimental Results

4.1.1 Assessment of Soil Specimens

4.1.1.1 Resistivity in Different Grouted Soil Specimens

Generated results allowed the definition of soil resistivity of grouted specimens over time. Soil resistivity was introduced to assess the internal changes of various grouts in various conditions. It is much more adequate than the standard permeability method. In setting period, resistivity can monitor internal changes in the specimens during the aging period. Soil resistivity was defined as follows:

To calculate the soil resistivity, the Wenner resistivity method was used following Renoylds, 1997 (described in section 2.6.3). Therefore, soil resistivity

$R = 2 \times \pi \times a \times (\Delta\phi / I)$ Ω.m ....(4.1)

Where,

R = apparent resistivity

a = distance between dipoles

$\Delta\phi$ = Amplitude differences between potential dipoles [amplitude = (Max-Min)]

I = current $= \Delta\phi / r =$ Amplitude difference between current electrode [Max-Min] / default resistor

r = default resistor

- *Procedure to Calculate Soil Resistivity*

First of all, a set of four electrodes was permanently installed in each specimen where the distance between each electrode was one cm. The reason for permanent installation of these electrodes was to not disturb the specimens while measuring resistivity and to check the internal changes of the complex environment during the aging period of the specimen.

- *Setup of Microsis*

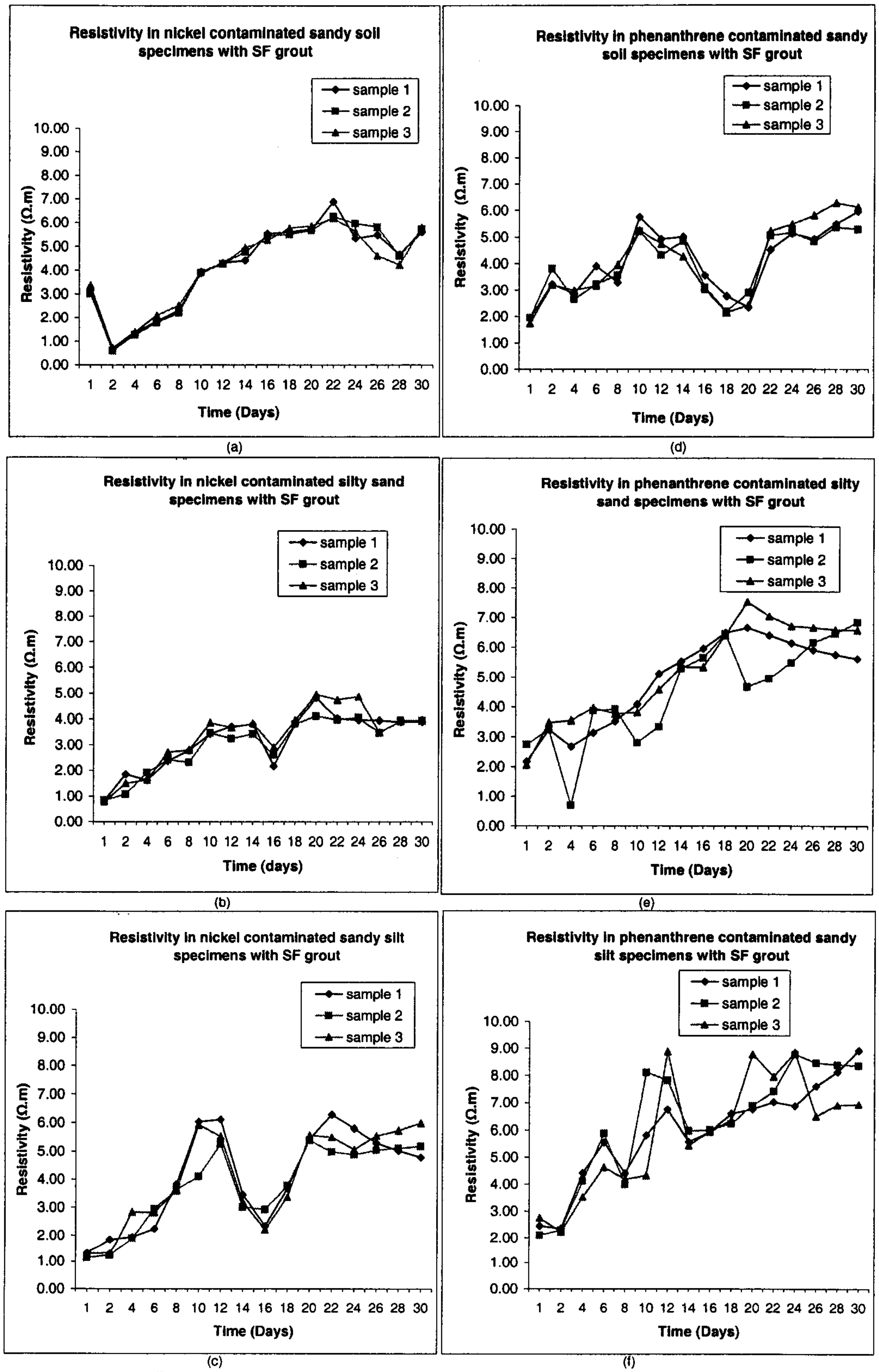
Sampling rate: 20
Frequency: 4096 Hz
Wave platform: Continuous
Input: 5 Volts.

To do resistivity analysis, a microsis machine was used. In setting up the microsis, the first current electrode (C_1) was connected by a special cable to the input channel of microsis while the last electrode (C_2) was connected by a special cable to a common ground (r = 100 ohms) resistor that came from the current electrode. After that, another cable was connected on the output channel of the microsis to measure the voltage in each electrode. Data acquisition was activated for 5 seconds and than stopped to obtain the measurement from the statistics of microsis. Voltages were measured in one current and two potential electrodes. After that, values were put on the above equation to estimate soil resistivity. The procedure was repeated every alternate day for a month to observe soil internal changes in silica grout.

By using the above formula, soil resistivity was calculated. An example of resistivity measurement is presented in Appendix-A. Figures 4-1 (a, b, c) show the resistivity (Ω.m) distribution vs. time in nickel contaminated sandy soil, silty sand, and sandy silt grouted with sodium silicate- formamide (SF). The resistivity of all 9 specimens increased until around day 20 when it stabilized (considering an average value). This is probably due to probably due to the accomplishment solidification/stabilization (S/S) process and lack of obvious symptoms of specimen vulnerability. The highest resistivity scores observed at day 20 in Experiment 24 (Fig.4-1 a), Experiment 25 (Fig. 4-1b), and Exp 26 (Fig. 4-1c) were 6.19, 4.95, and 6.29 Ω.m respectively.

Figures 4-1 (d, e, f) represent the resistivity (Ω.m) vs. time in phenanthrene-contaminated sandy soil, silty sand, and sandy silt soil grouted with SF. In all Experiments 27-29, resistivity continuously increased over time. In these cases stabilization was not finalised and needed more time compared to time for contamination with heavy metals (see Figure 4-1 a,b,c). However, after day 26, all of the specimens were stabilized, which indicates that phenanthrene contaminated soil (particle size ranges 1.00 mm – 0.053 mm) was good for silica based chemical grouting. The highest resistivity scores observed at day 20 in Experiment 27 (Fig.4-1d), at day 20 in Experiment 28 (Fig. 4-2e), and at day 12 in Exp 29 (Fig. 4-2f) were 6.28, 7.53, 8.88 Ω.m respectively.

Figures 4-2 (a, b, c) indicates that there was an internal changes taking place in mixed (nickel-phenanthrene) contaminated sandy soil, silty sand, and sandy silt grouted with sodium silicate- formamide (SF). The resistivity of all 9 specimens increases until around day 18 when it stabilizes (considering an average value). It is probably due to accomplishment solidification/stabilization (S/S) process and lack of obvious symptoms of specimen vulnerability. The highest resistivity scores observed at day 20 in Experiment 30 (Fig.4-2 a), at day 22 in Experiment 31 (Fig. 4-2b), and at day 22 in Exp 32 (Fig. 4-2c) were 5.19, 6.31, 6.03 Ω.m respectively. It seems from Figure 4-2 (a, b, c) that resistivity scores always increases over time, and they started to stabilize at day 16, earlier than sole organic or inorganic contaminated specimen scores.



Resistivity in nickel contaminated sandy soil specimens with SF grout

(a)

Resistivity in nickel contaminated silty sand specimens with SF grout

(b)

Resistivity in nickel contaminated sandy silt specimens with SF grout

(c)

Resistivity in phenanthrene contaminated sandy soil specimens with SF grout

(d)

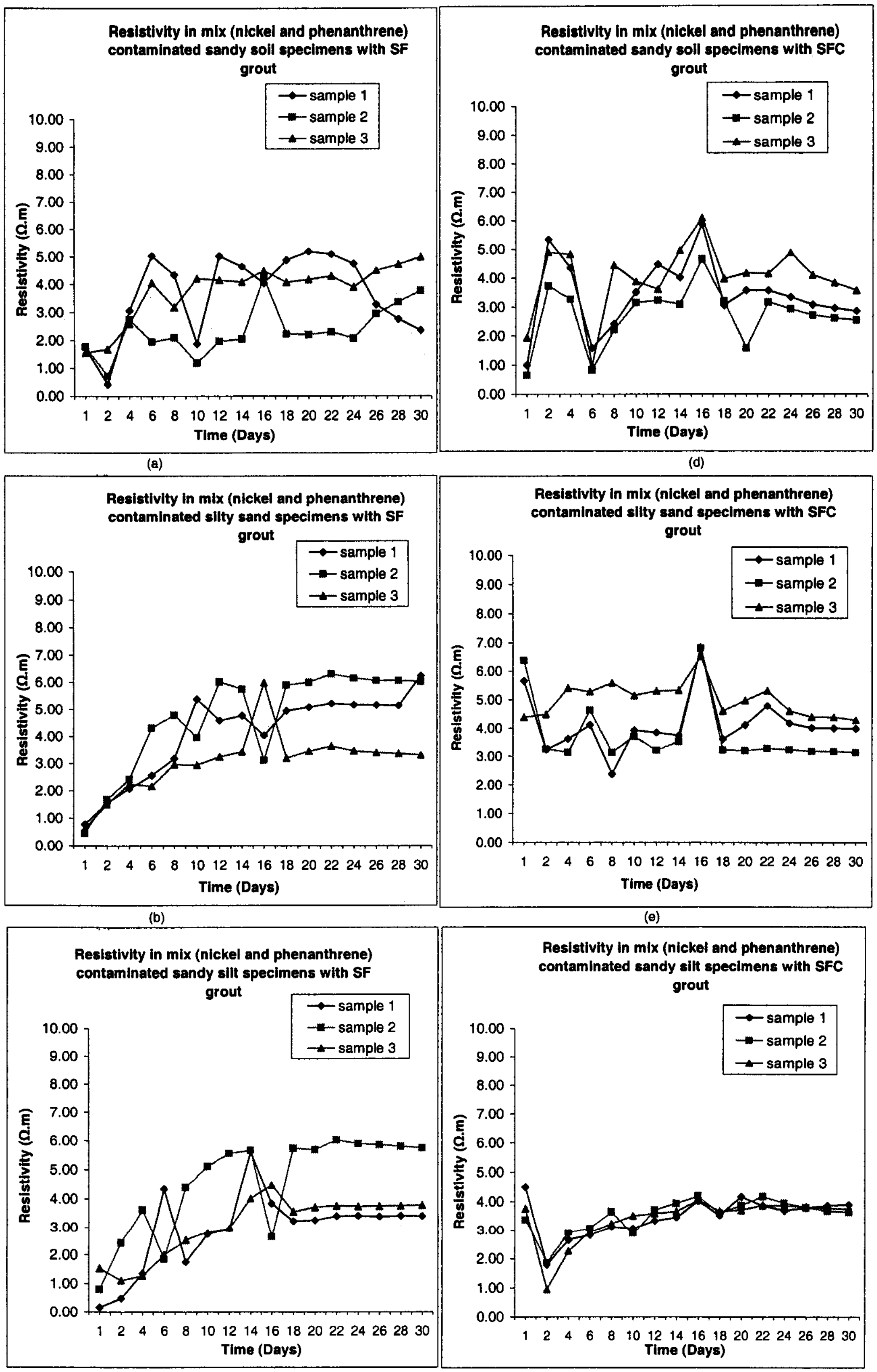
Resistivity in phenanthrene contaminated silty sand specimens with SF grout

(e)

Resistivity in phenanthrene contaminated sandy silt specimens with SF grout

(f)

Figure 4-1 Resistivity in nickel and phenanthrene contaminated specimens with SF grout



Resistivity in mix (nickel and phenanthrene) contaminated sandy soil specimens with SF grout

(a)

Resistivity in mix (nickel and phenanthrene) contaminated sandy soil specimens with SFC grout

(d)

Resistivity in mix (nickel and phenanthrene) contaminated silty sand specimens with SF grout

(b)

Resistivity in mix (nickel and phenanthrene) contaminated silty sand specimens with SFC grout

(e)

Resistivity in mix (nickel and phenanthrene) contaminated sandy silt specimens with SF grout

(c)

Resistivity in mix (nickel and phenanthrene) contaminated sandy silt specimens with SFC grout

(f)

Figure 4-2 Resistivity in mix contaminated specimens with SF or SFC grout

Figures 4-2 (d, e, f) represent the resistivity (Ω.m) vs. time in mixed (Nickel-Phenanthrene) contaminated sandy soil, silty sand, and sandy silt soil grouted with SFC. In all Experiments 33-35, resistivity continuously increased over time. In these cases stabilization was not finalised and needed more time compared to contamination with heavy metals (see Figure 4-1 a,b,c). However, after day 18, all of the specimens were stabilized, which indicates longer setting time was required for SFC grout. However, any type of soil ranging from 1.0 to 0.053 mm was good for silica based chemical grouting. The highest resistivity scores observed at day 16 in Experiment 33 (Fig.4-2 d), at day 22 in Experiment 34 (Fig. 4-2e), and at day 22 in Exp 35 (Fig. 4-2f) were 6.10, 6.81, 4.18 Ω.m respectively. It seems that sandy silt is good soil for this type of grout because it has already started to stabilize from day 14. However, two other types of specimens (Figure 4-2 d, e) started to stabilize from day 18.

4.1.2 Soil Porosity in Different Soil Composition

Generated results permitted the assessment of soil porosity of grouted specimens over time. Soil porosity was introduced to assess the response of various grouts to water conditions. Soil porosity was described as follows:

- *Procedure to Calculate Soil Porosity*

Soil porosity was calculated on different days and compared with the soil porosity of the dry condition specimens (before submerging). Therefore, initial soil porosity with dry conditions and soil porosity over time were calculated to see the relative changes of porosity. The following two equations were developed following Budhu (2002).

At dry condition (i.e. initial condition) soil porosity is defined as:

$$n_0 = 1 - \frac{(\gamma_d)_0}{G_s \times \gamma_w} \qquad \text{(4.2)}$$

After submerging the specimens at time *t* soil porosity is defined as:

$$n_t = 1 - \frac{(\gamma_d)_t}{G_s \times \gamma_w} \quad \text{...} (4.3)$$

Where,

n_0 = Initial soil porosity

$(\gamma_d)_0$ = Soil density at dry condition (g/cm^3)

$(\gamma_d)_t$ = Total bulk density of the soil in dry condition (g/cm^3)

G_s = Specific gravity

γ_w = Water density (g/cm^3)

- *Calculation of Initial (dry) Soil Porosity Based on Equation 4.2*

$$(\gamma_d)_0 = \frac{M_0}{V_0} \text{ g/cm}^3 \text{..} (4.4)$$

Where,

M_0 = Mass of soil after mixing contamination and grout (g)

V_0 = Total volume of a sample after mixing contamination and grout (mL)

And, $M_0 = M''_0 - P$ (g)..(4.5)

Where,

M''_0 = Mass of soil after mixing contamination and grout including mold and electrode (g)

P = mold + electrode (g)

Again, $V_0 = \pi \times r^2 \times h$ ....(4.6)

Where

r = Radius of the specimen (cm)

h = Height of the specimen (cm)

By combining the equations 4.4, 4.5, 4.6 in equation 4.2, it was obtained that

$$n_0 = 1 - \left(\frac{M''_0 - P}{\pi \times r^2 \times h \times G_s \times \gamma_w} \right) \quad \text{.....(4.7)}$$

The initial soil porosity of the specimens was tabulated in Appendix-B.

Specimens consumed water over time once they were submerged in water. Therefore, equation 4.3 must be used to calculate soil porosity over time according to Budhu (2002), because water content must be taken into consideration. Therefore,

$$(\gamma_d)_t = \frac{\gamma_h}{(1+W)} \quad \text{.....(4.8)}$$

Where,

$(\gamma_d)_t$ = Total bulk density of the soil in dry condition (g/cm^3)

γ_h = Sample density after submerging into water (g/cm^3)

W =Total water absorbed

Again,

$$W = \frac{(M_1 - M_0)}{M_0} \quad \text{.....(4.9)}$$

Where,

M_1 = Mass of soil sample after submerging into water (g)

M_0 = Mass of soil sample after mixing contamination and grout including mold and electrode (g)

And $\gamma_h = \frac{M_1}{V_1}$ g/cm^3.....(4.10)

Where,

V_1 = Volume of soil sample after submerging into water (mL)

Again, $M_1 = M''_1 - P$ (g)…………………………………………………………………(4.11)

Where,

M''_1 = Mass of soil sample after submerging for time t including mold and electrode (g)

P = Mass (mold + electrode) (g)

And $V_1 = \pi \times r^2 \times h$ ……………………………………………………………(4.12)

Where,

r = Radius of the sample (cm)

h = Height of the sample (cm)

By combining the equations 4.3, 4.8, 4.9, 4.10, 4.11 and 4.12, it was found that

$$n_t = 1 - \left[\frac{(M''_1 - P)}{(\pi \times r^2 \times h)(1 + W)(G_s \times \gamma_w)} \right] \quad \text{……………………………………………}(4.13)$$

Soil porosity for each specimen was estimated and their comparison was tabulated in Appendix-B.

Using the above formulas, soil porosity in nickel contaminated sandy soil, silty sand, and sandy silt soil was estimated on different days over time. Figure 4-3 (a, b, c) shows that initially porosity decreased rapidly until day 6 but became almost constant in the remaining time. It was observed that just after being submerged into tap water, the specimen shrank, and became stable once the reaction was completed. Furthermore, the porosity varied a little even when the curing process was completed. The reason may be the release of chemicals from specimens to the surrounding water, since there were negligible amounts of soil erosion observed. The highest porosity was noted on day 1 in Experiment 24 is 0.376, but after day 6 (4-3, a) the value decreased to 0.300 in sandy soil. In silty sand soil, the highest porosity was observed in Experiment 25 was 0.377 at day one, but the constant value fluctuated from 0.299 to 0.303 from day 6 to day 30 (4-3 b), and in sandy silt, the constant value varied between 0.296 and 0.301 in Experiment 26.

Figure 4-3 (d, e, f) shows that phenanthrene contaminated sandy soil, silty sand, and sandy silt soil porosity grouted with SF also remained constant after day 6. The constant value was 0.304 in sandy soil and the constant value varied between 0.286 and 0.292, and between 0.287 and 0.294 in silty sand, and sandy silt soil. The difference was considered negligible.

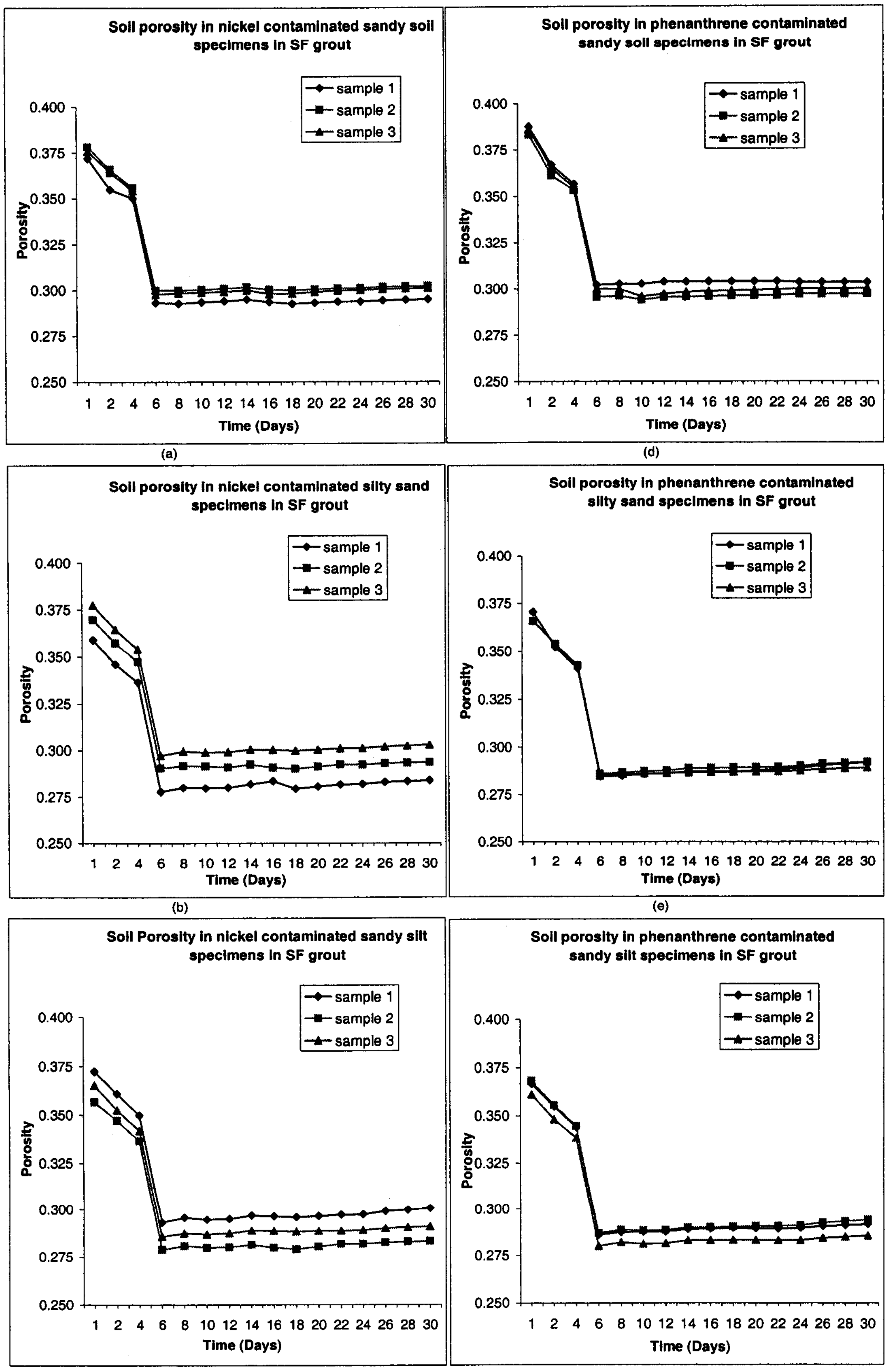
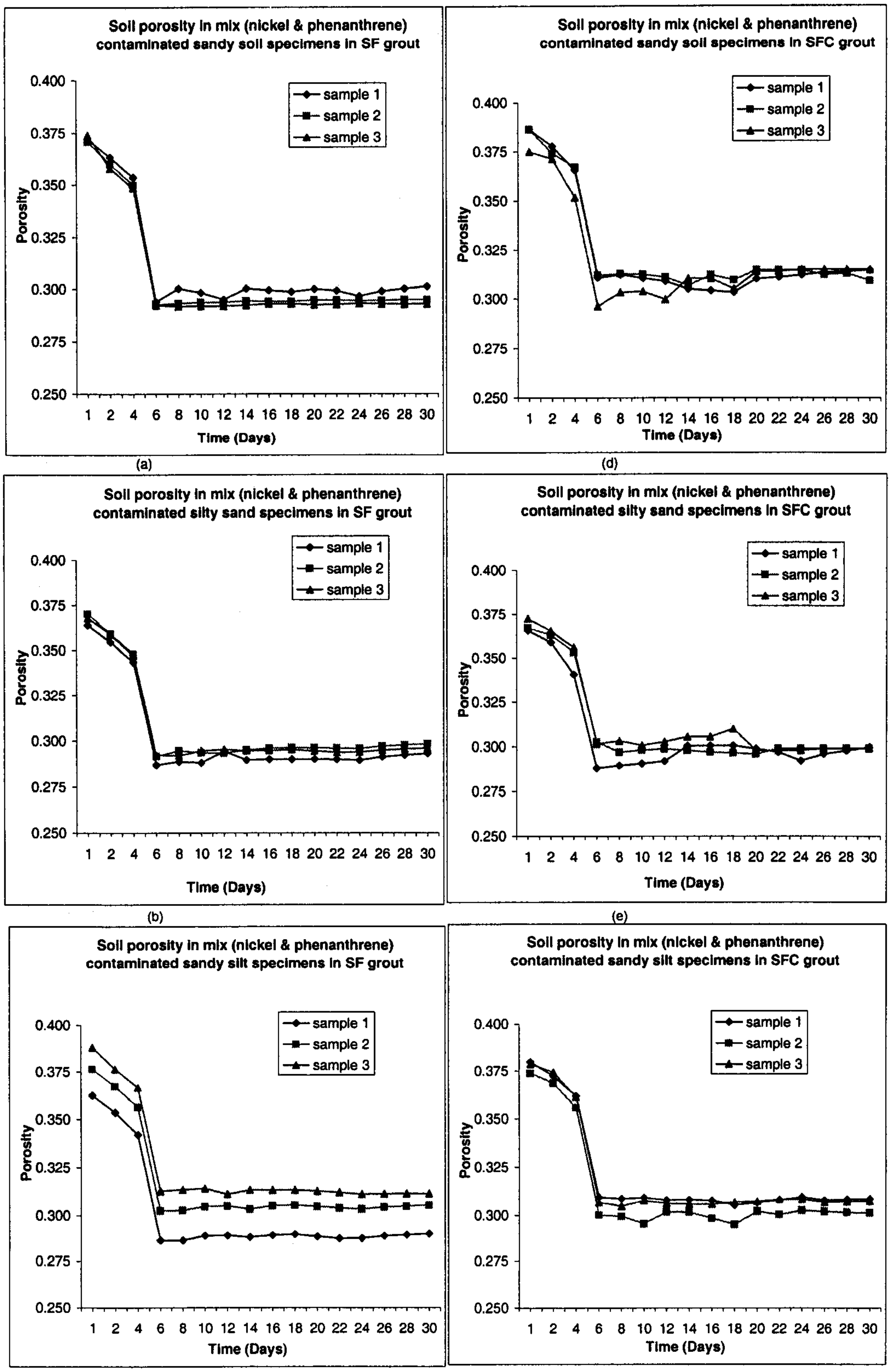


Figure 4-3 Soil porosity in nickel and phenanthrene contaminated specimens


Soil porosity in mix (nickel & phenanthrene) contaminated sandy soil specimens in SF grout

Soil porosity in mix (nickel & phenanthrene) contaminated sandy soil specimens in SFC grout

Soil porosity in mix (nickel & phenanthrene) contaminated silty sand specimens in SF grout

Soil porosity in mix (nickel & phenanthrene) contaminated silty sand specimens in SFC grout

Soil porosity in mix (nickel & phenanthrene) contaminated sandy silt specimens in SF grout

Soil porosity in mix (nickel & phenanthrene) contaminated sandy silt specimens in SFC grout

(a) (d)

(b) (e)

(c) (f)

Figure 4-4 Soil porosity in mixed contaminated SF or SFC grout specimens

Figure 4-4 (a, b, c) indicates that the porosities of mixed (Nickel-Phenanthrene) contaminated sandy soil, silty sand, and sandy silt became constant after day 6. The average constant values were 0.296, 0.295, and 0.300 respectively. Figure 4-4 (d, e, f) shows that mix (Nickel-Phenanthrene) contaminated sodium silicate-formamide-calcium chloride (SFC) grouted specimens were not constant after day 6. Although all of the porosities of the specimens decreased initially, only sandy and silty sand specimens remained constant after day 20, with average values of 0.314 and 0.299 respectively. However, sandy silt specimens became constant after day 6, with an average value of 0.309. It seems that specimens in Experiments 33-35 (Figure 4-4 d, e, f) consumed more water and at the same time they had a high release of soil grain and chemicals from the specimens.

4.1.3 Coefficient of Stability (CS) in Different Soil Composition

Generated results permitted the definition of stability of grouted specimens. A novel coefficient of stability (CS) was introduced to assess the response of various grouts to various conditions. The coefficient of stability was defined as follow:

- *Procedure to Calculate Coefficient of Stability (CS)*

According to AFNOR-Geotechnique (1995), the coefficient of stability (*CS*) can be estimated by initial D_{10} from soil particle distribution over D_{10} of released soil particles on specific time that can be expressed by

$$CS = \frac{(D_{10})_i}{(D_{10})_t} \quad \text{...(4.14)}$$

Therefore, the D_{10} of released particles was calculated every alternate day for one month by developing new soil particle size distribution. First of all, released soil particles from the specimens were filtered on 100 nm filter paper and oven dried at 60^0C for an hour. After that, soil particles were weighed and data were tabulated. From visual observation, it was found that released particles were very fine. The sizes of released particles determined for sandy soil specimens were 0.250 mm for silty sand and sandy silt 0.075 mm. A new particle size distribution was developed by deducting the released amount from the initial soil mass corresponding to its particle size (mentioned above) on every alternate day for a month for 36 specimens (Appendix- C). After that, by using the values of percentages of soil passing (f) and particle size, a new particle size distribution graph was made to find out the new D_{10} (Appendix- H). The new D_{10} value and initial D_{10} value were put in equation 4.14 to estimate the coefficient of stability (*CS*).

The above data in Figure 4-5 (a) shows that SF grouted nickel contaminated sandy soil specimens were 96% stable in tap water after day 16. Only 5.4 % soil disintegrated into tap water in the first 15 days. This means that stabilization finalized after 2 weeks. Figure 4-5 (b) indicates that 91% of specimens were stabilized in tap water from day 16 in SF grouted nickel contaminated silty sand. However, all specimens started to stabilize from day 14. During the first 2 weeks, 9% of disintegration took place, which was bigger than in Experiment- 24 (Figure 4-5 a). However, specimens in SF grouted nickel contaminated sandy silt were 88% stable in water after day 18, which indicates they have more degradation than specimens in Experiments 24-25 (Figure 4-5 a & b). Sandy silt started to degrade from day 2 and stopped at day 16. The highest degradation took place between days 8 and 10. It was about 4.4%, while the total degradation was 12%. This means that more than 50% of degradation took place between days 8 and 10. The reason could be that in this case the stabilization process was not finalized before day 10.

Figure 4-5 (d, e, f) indicates that the coefficients of stabilities for specimens of phenanthrene contaminated SF grouted sand, silty sand, and sandy silt were 93.8%, 92.5% and 90% respectively in tap water (Figure 4-5 a). Stabilization was finalized in phenanthrene contaminated specimens at day 16 in sand, and silty sand, while in sandy silt it was day 18.

Figure (4-6 a) shows that in Experiment- 30, 94.2% of soil specimens was stabilized in day 16 in mixed (Nickel-Phenanthrene) contaminated sandy soil specimens grouted with SF. Figure (4-6 b) specimens were stabilized at day 18 in Experiment- 31 with

93.6% of soil and, more than 95% of soil in the specimens was stabilized in day 16 in Experiment- 32 and in Figure (4-6 c). This means that, on average, a peak of 5.5% soil disintegrated in tap water in the first 2 weeks in all 9 specimens.

Figure 4-6 (d, e, f) represents SFC grouted mix (Nickel-Phenanthrene) contaminated sandy soil, silty sand, and sandy silt respectively. In Experiment- 33 (Figure 4-6 d), there was 12.9% disintegration in the first 10 days and it seems continuous degradation was taking place. However, specimens became 87.1% stable after day 12. Experiment- 34 (Figure 4-6 e) shows 81.2% soil in the specimens (silty sand) were stabilized in tap water after day 20, and 83.2% of sandy silt specimens were stable at day 22 (Figure 4-6 f). A rapid degradation took place from day 1 to day 20, which made the specimens more vulnerable to groundwater than SF grouted specimens.

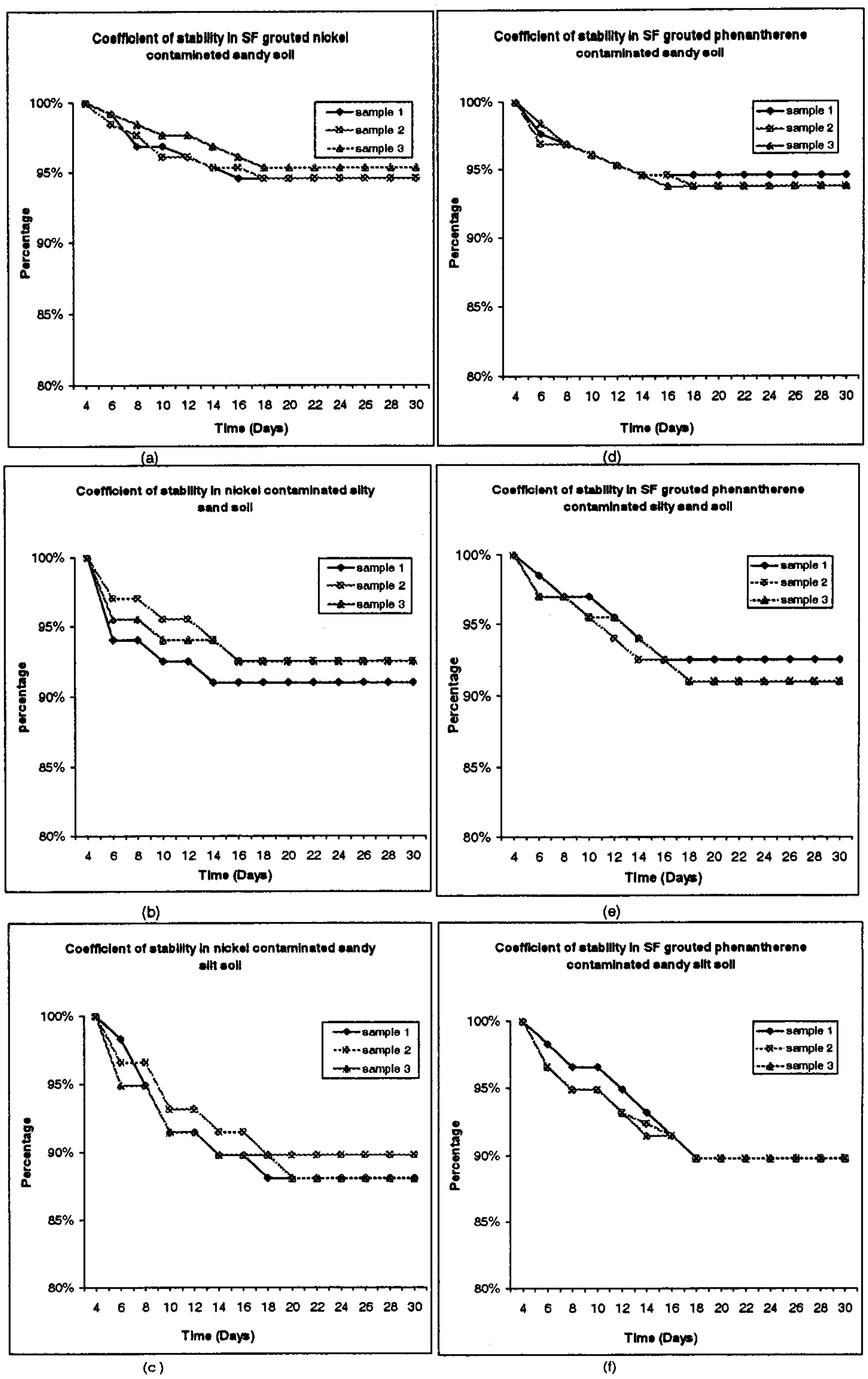


Figure 4-5 Coefficient of soil stability in nickel and phenanthrene contaminated soil

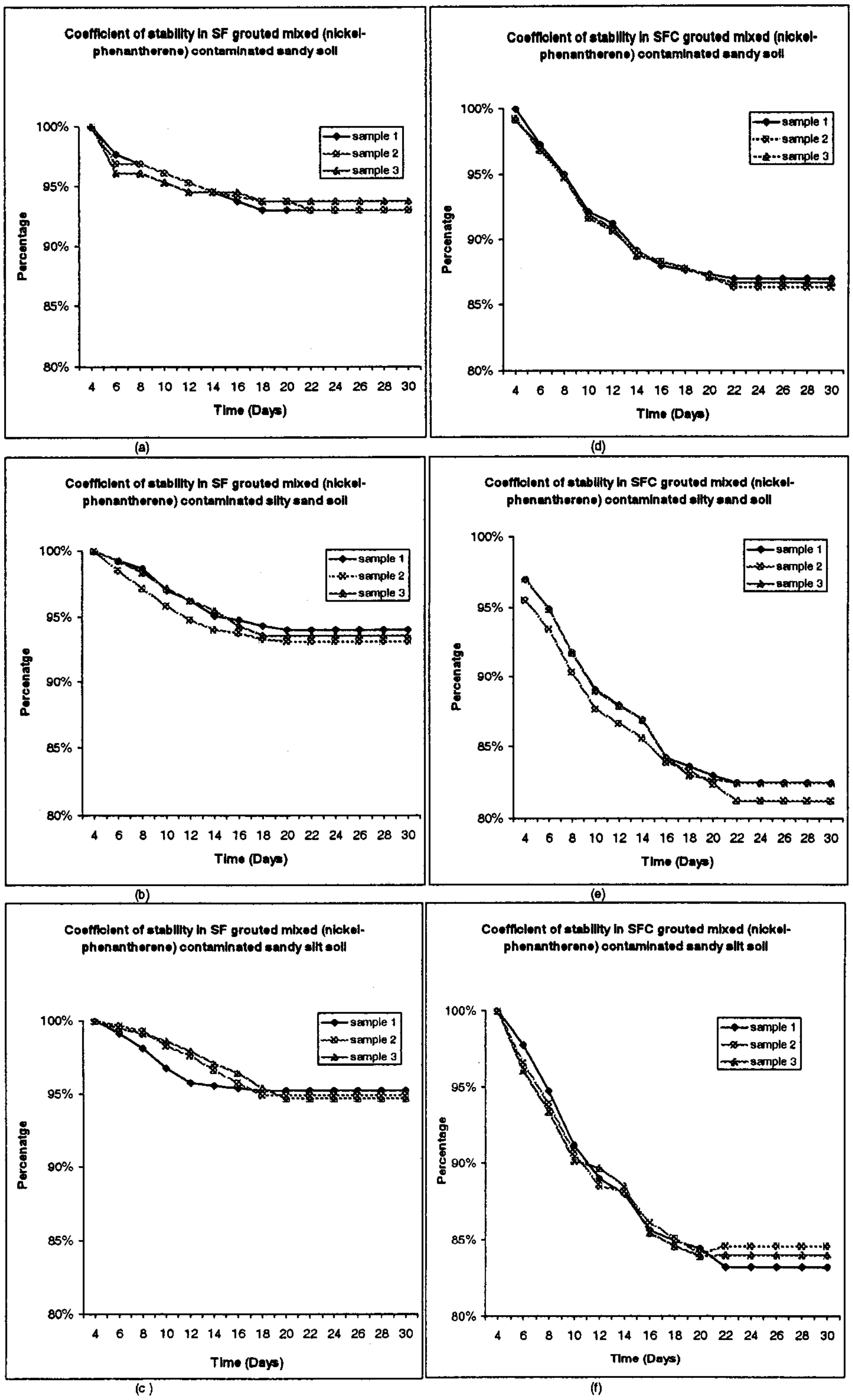


Figure 4-6 Coefficient of stability in mixed contaminated SF or SFC grouted soil

4.2 Assessment of Water Quality

A water sample from each Experiment 24, 26, 27, 29, 30, 32, 33, and 35 sandy soils and sandy silt specimens were analysed in four days of the exposure of the specimens (Day 1, Day 10, Day 20, and Day 30). Fourier Transform Infrared (FTIR), Ultra Violet and Visible light (UV-Vis), and Atomic Absorption (AA) spectrometers (described in 4.2.1.1) were used to obtain additional information about a potential release of specimen components into groundwater.

4.2.1 Fourier Transform Infrared Spectrometer (FT-IR) Analysis

FT-IR was mainly used to evaluate the eroded solid parts found in water samples. Minerals, inorganic grout (calcium chloride) and organic grout (formamide) with sodium silicate were evaluated in Experiments 24, 26, 27, 29, 30, 32, 33, and 35. The presence of an organic reagent (formamide) leads to a curing process with subsequent complex reactions. The curing with formamide is not fast because the grout forms intermediate complexes in the reactions (a similar chemical reaction is presented in equation 2.10). When the complex reacts with sodium silicate, it forms sodium formate (HCOONa). Therefore, it is expected that sodium formate spectra in FT-IR will be caused if formamide is release into water. At this point, all samples were analyzed for the presence of HCOONa (sodium formate) except those of Experiment- 33 where calcium chloride and mix (Nickel-Phenanthrene) contaminated the sandy soil specimens.

In spectra (Appendix F), a modified spectrum of sodium formate was observed, which means the original band shifted to a band closer to the original. Generally, 1605 cm^{-1} is the band of sodium formate but all the samples had a band of 1580 cm^{-1} and a band of 1347.22 cm^{-1}. This was a modified sodium formate. Three reasons were identified for band shifting: (1) not original sodium formate, (2) already included complex, (3) mixture of chemicals.

The results concerning water samples were compared by initial day and last day to see the extreme changes. Therefore, nickel & phenanthrene (mixed) contaminated sandy silt soil specimens in SFC grout were compared (Appendix F) and bands 1578, 1350, 1228, 1093, 790, and 668 cm^{-1} were examined. It was found that usually the 1738 cm^{-1} (formic acid) band and the 1683 cm^{-1} (formamide) band are undisturbed. However, 1578 cm^{-1} was also observed in the spectra and which was a disturbed formamide. The band for the sodium formate is 1350 cm^{-1}. The reason of the modified formamide was the influence of other chemicals, especially by sodium silicate because bands 1228 and 1093 cm^{-1} are related to silica and 790 and 668 cm^{-1} are related to formic acid, which was found in the FTIR spectra analysis.

It was speculated that during the first day of submerging, by-products of the reaction (formic acid) and free formamide (which had not reacted yet) were found in the specimens. It could be concluded that two reagents (formamide and calcium chloride) had "competed" at the beginning of the curing process. Calcium chloride reacted first, although it was mixed with sodium silicate after a formamide reagent. It is certain that they were not releasing to ground water but waited for a reaction because there was no free formamide found in FT-IR analysis.

The same situation was observed in a nickel & phenanthrene (mixed) contaminated sandy soil specimen in SFC grout. However, noise of the spectra was less visible. Both sodium formate and disturbed formamide were found in these spectra, indicating a not finalized stabilization process.

Phenanthrene contaminated sandy soil in SF grout has the highest release of formamide into the water but no release of sodium formate. In order to assess a potential release of phenanthrene, additional analyses were performed using UV/Vis.

Analysis of spectra peak heights were done for all specimens so as to find out the ratios of both sodium formate bands (1578 cm^{-1} and 1350 cm^{-1}). They were calculated and presented in Figure 4-7 for peak height comparison and another Figure 4-8 is represented the comparison of spectra in different contaminated soil.

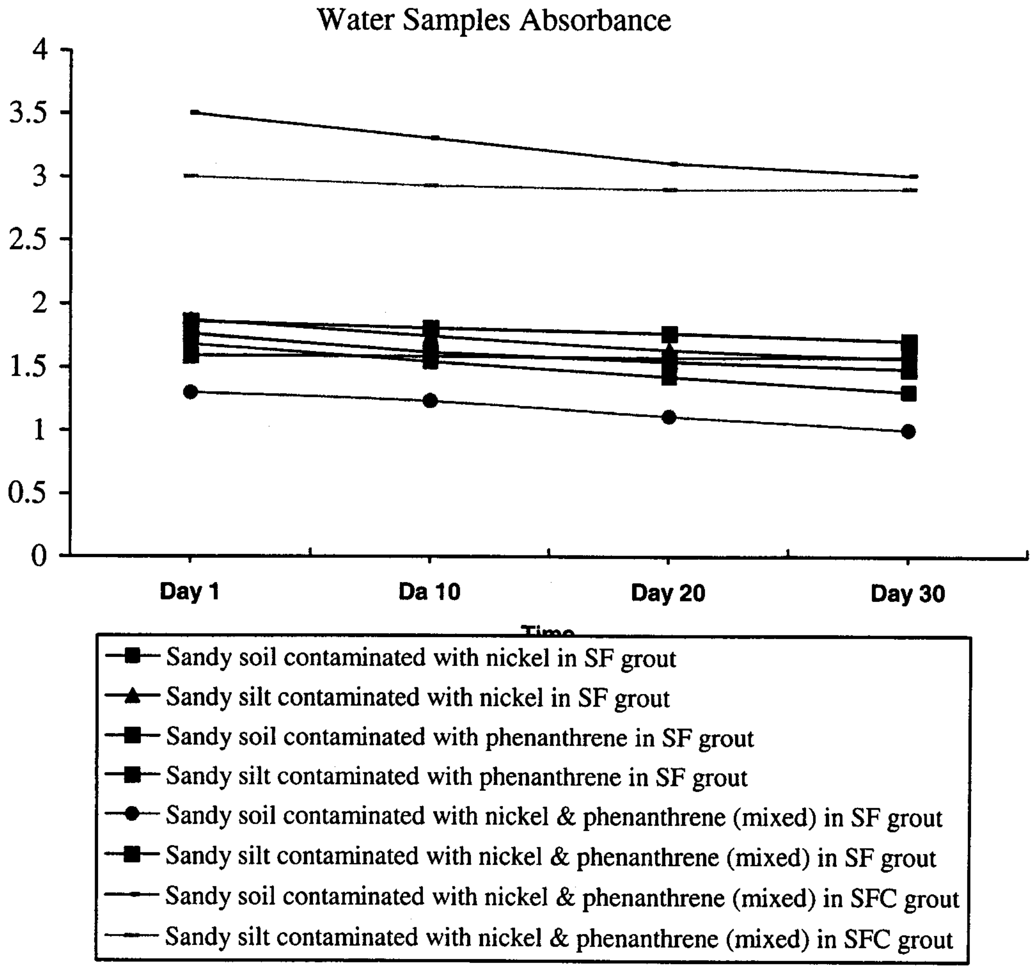


Figure 4-7 Comparison of peak heights of nickel, phenanthrene and mixed (Nickel-Phenanthrene) contaminated sandy and sandy silt soil spectra

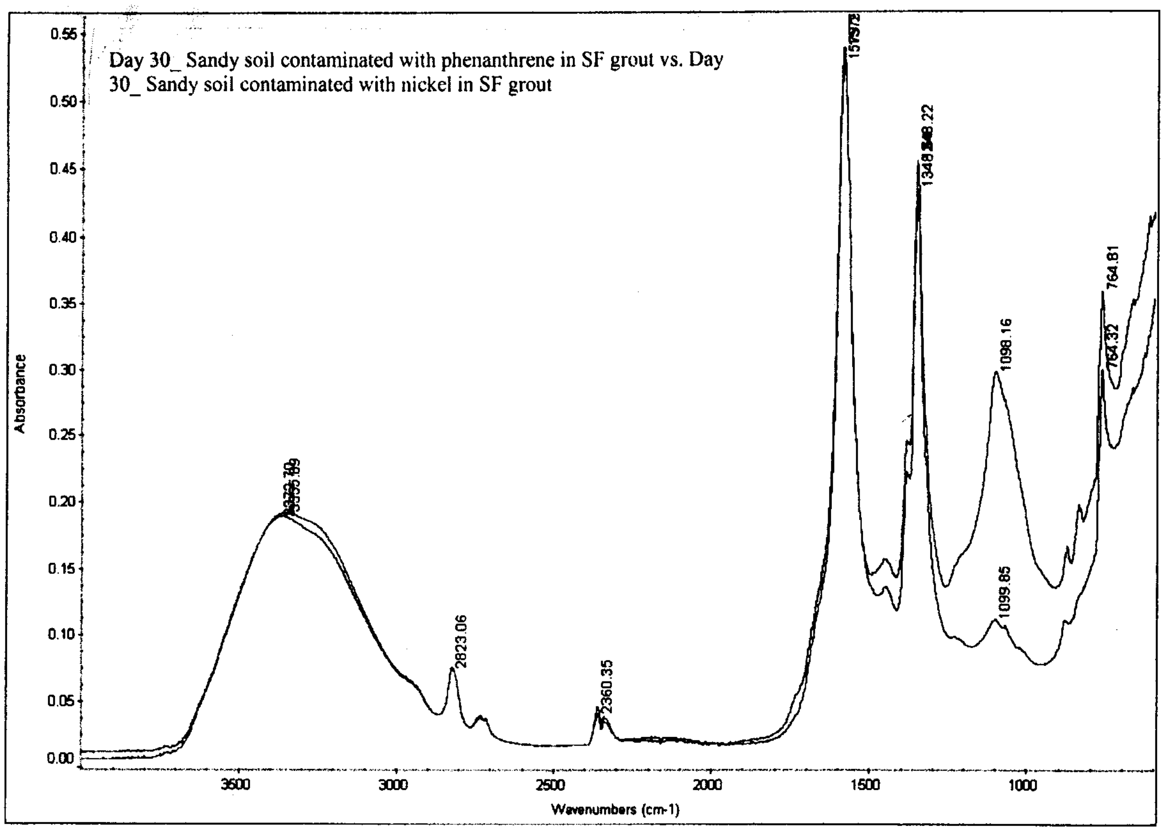


Figure 4-8 Comparison of spectra of SF grouted nickel contaminated sandy soil vs. SF grouted phenanthrene contaminated sandy soil

4.2.2 UV-Vis Analyses

Thirty two water samples, one sample from each Experiment – 24, 26, 27, 29, 30, 32, 33, and 35 were analysed using UV-Vis (Lambda 40) to detect organic substances (formamide and phenanthrene) in water environment. A standard solution of phenanthrene in hexane (Appendix-G) was used to analyse two strong bands, nearly 236.00 and 214.80 nm. Formamide in water (Appendix- G) showed a single band about 205.60 nm. The amount of formamide in water were almost stable condition over time (10, 20, 30 days) at 250 nm wavelength.

SF grouted nickel, phenanthrene and mixed (Nickel-Phenanthrene) contaminated sandy silt are different in nature and it seems organic matter, especially formamide, is absorbed in silt because no phenanthrene was found in UV-Vis analysis. Moreover, formamide increased initially but later practically stabilized. Phenanthrene contaminated sandy soil absorbance continually increased. However, calcium chloride reagent mixed grout samples did not change a lot and were much more stable. Analysis of all water samples using UV-Vis did not demonstrate the presence of phenanthrene (Appendix – G). The Figure 4-8 shows the graphic presentation of UV-Vis analysis of different specimens and Figure 4-9 shows the comparison of UV-Vis absorbance in 4 different days in phenanthrene contaminated SF grouted sandy silt soil specimens.

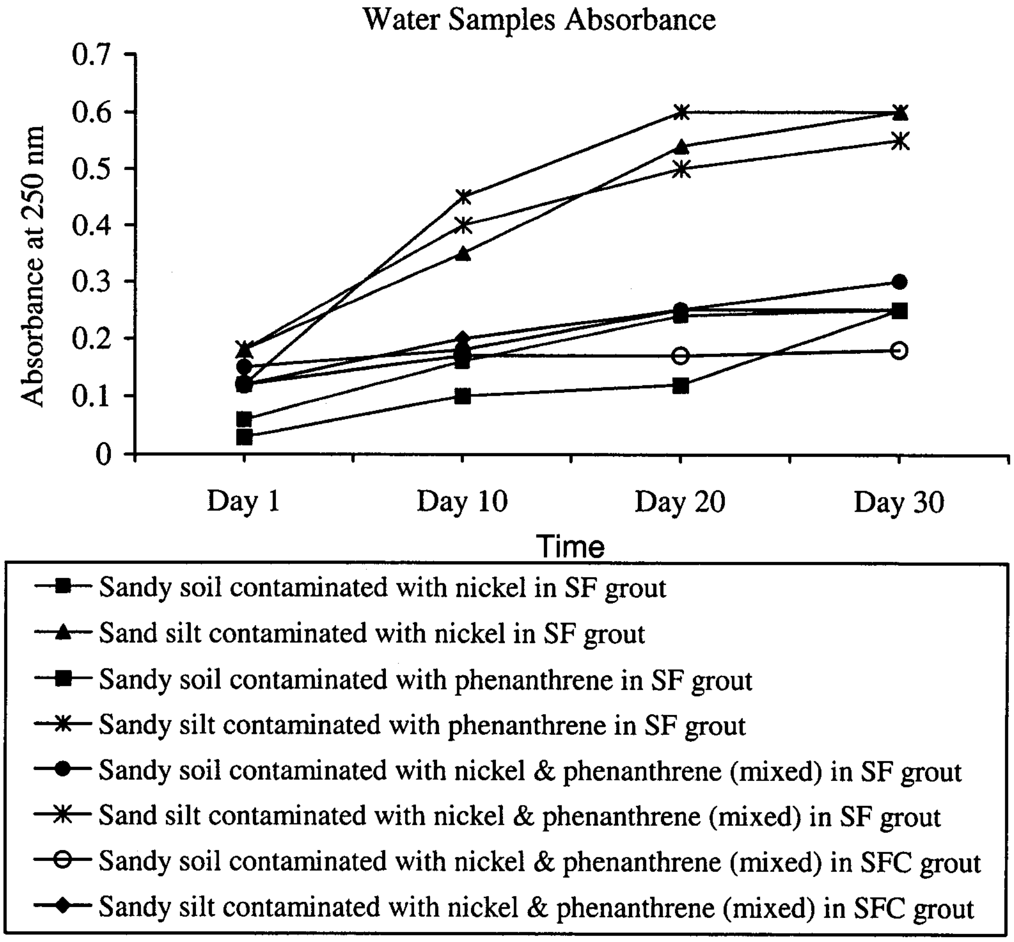
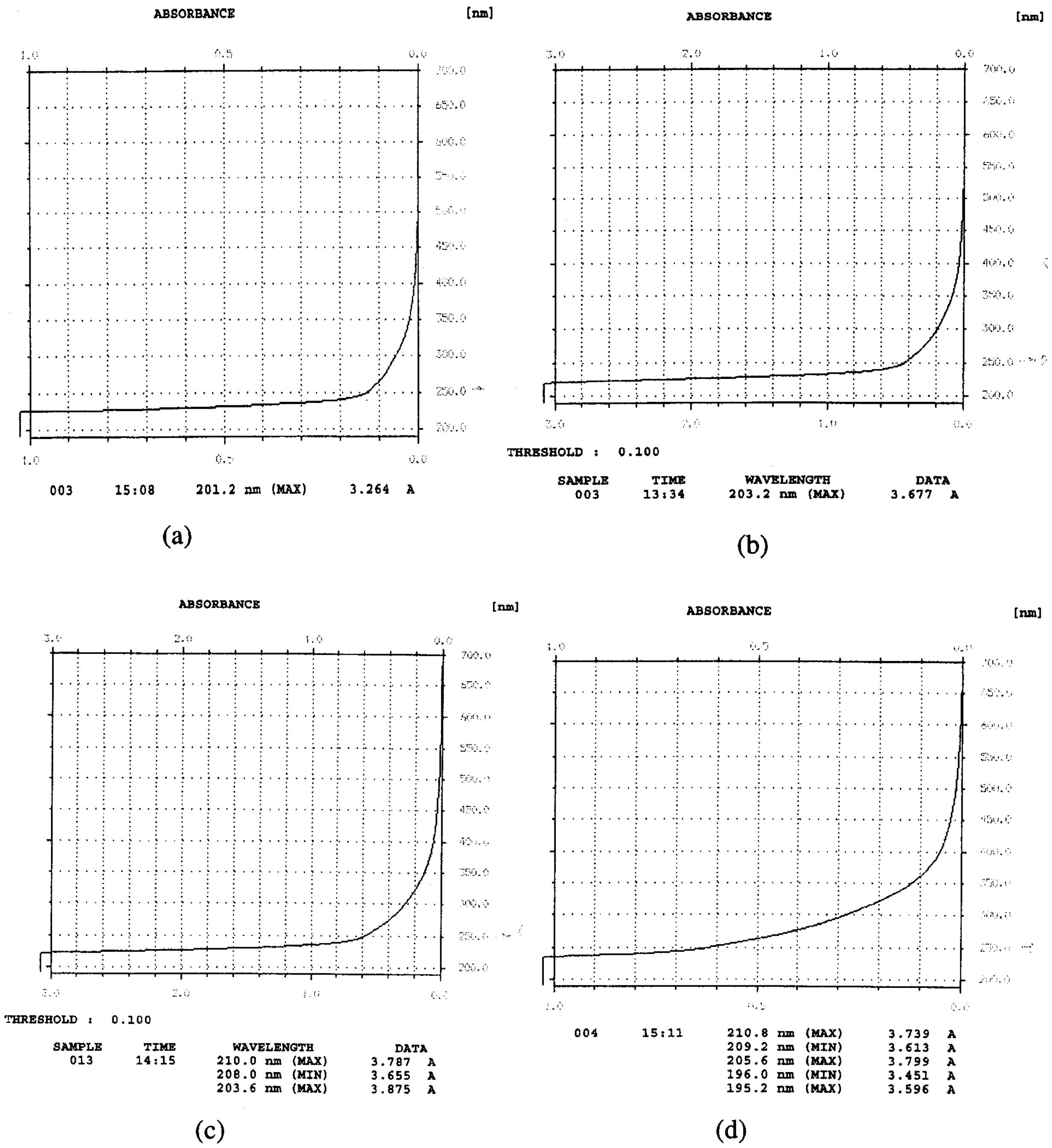


Figure 4-9 UV-Vis analysis of sandy soil and sandy silt soil in different contamination



(a) (b)

(c) (d)

Figure 4-10 Comparison of UV-Vis absorbance in phenanthrene contaminated SF grouted sandy silt soil specimens. (a) Day 1, (b) Day 10, (c) Day 20, and (d) Day 30.

4.2.3 Atomic Absorption (AA) Spectrometer Analysis

A potential nickel release was measured in water using AA. Table 4-1 shows the soluble nickel concentrations that are found in water samples collected every 10 days (from 1 to 30) in Experiments 24, 26, 27, 29, 30, 32, 33, 35 representing sandy and sandy silt grouted with SF and SFC. It was observed in Table 4-1 that on the first day there was a small amount of nickel released into the water and slightly more released in combined reagents (SFC grout). However, there was a sporadic release detected after day one. Table 4-2 shows the nickel concentrations when an entire water column (including suspended matter) was considered. The digesting procedure shows that released nickel was mostly in precipitated or adsorptive forms, demonstrating the low mobility of this heavy metal in subsurface.

Table 4-1 Concentration of nickel (mg/L) dissolved in submerged water

Specimen type	Day 1	Day 10	Day 20	Day 30
Sandy soil contaminated with nickel in SF grout	1	1	ND	1
Sandy silt soil contaminated with nickel in SF grout	2	ND	ND	2
Sandy soil contaminated with nickel-phenanthrene (mixed) in SF grout	3	ND	2	ND
Sandy silt soil contaminated with nickel-phenanthrene (mixed) in SF grout	1	ND	ND	ND
Sandy soil contaminated with nickel-phenanthrene (mixed) in SFC grout	4	1	ND	ND
Sandy silt soil contaminated with nickel-phenanthrene (mixed) in SFC grout	1	2	ND	ND

* ND = Not Detect

Table 4-2 Total concentration of nickel (mg/L) in bulk water samples

Specimen type	Day 1	Day 10	Day 20	Day 30
Sandy soil contaminated with nickel in SF grout	1	3	3	1
Sandy silt soil contaminated with nickel in SF grout	2	4	4	4
Sandy soil contaminated with nickel-phenanthrene (mixed) in SF grout	1	3	3	3
Sandy silt soil contaminated with nickel-phenanthrene (mixed) in SF grout	2	4	4	4
Sandy soil contaminated with nickel-phenanthrene (mixed) in SFC grout	4	5	6	6
Sandy silt soil contaminated with nickel-phenanthrene (mixed) in SFC grout	4	6	8	8

On the first day, the nickel concentration was found to be almost the same as that found in water suspended particles. After that, nickel was released only via soil erosion (piping). This means higher soil stability lowers the contamination in water. It as also observed that after day 20, the nickel concentration was stable in the suspension or in the solid matter of the water samples. This means once the stabilization is finalized in the soil, no nickel is released to the groundwater. It was found that sandy silt had different behaviour in nickel contaminated organic grout (SF grout) because nickel precipitates, leaches and may unite with organic chemicals.

4.2.4 pH of Submerged Water

The pH measurement of water, where SF grouted nickel contaminated sandy soil was submerged, shows stable values until day 18; afterwards, pH decreased slightly. Until day 18, pH varied from 9.75 to 9.92. Then lowest pH (9.51) was observed at day 30 (Appendix H –1)

In the water of the SF grouted nickel contaminated silty sand water pH stabilized after day 26. The initial average pH was 9.78 and it increased until day 26 and then remained almost constant with pH values of 9.69~9.71. However, the pH slightly decreased on day 24 and day 26 (Appendix H-2).

The initial average water pH of SF grouted nickel contaminated sandy silt was 9.80 and increased very slowly until day 16 and then decreased a little bit at day 18 and day 20 and remained almost constant for the rest of the days with an average pH value of 9.67 (Appendix H-3).

Phenanthrene contaminated organic grout mix sandy soil had almost constant water pH from initial day to the final day. The initial water pH was 9.62 and the final water pH at day 30 was 9.64 (Appendix H-4).

The initial water pH of phenanthrene contaminated organic grout mix silty sand soil was 9.77 and the water pH was unstable until day 26. The final water pH was 9.58 (Appendix H-5).

The water pH of phenanthrene contaminated sandy silt soil varied from 9.86 to 9.62. The pH had the same behaviour that was observed in phenanthrene contaminated silty sand soil where pH was almost constant until day 18 but decreased after (Appendix H-6).

Initial water pH in SF grouted mixed (Nickel-Phenanthrene) contaminated sandy soil was 9.85 but it started to decreased very slowly after day 18. The final water pH was 9.61 at day 30 (Appendix H-7).

The water pH of mixed (Nickel-Phenanthrene) contaminated SF grouted silty sand soil varied from 9.79 to 9.65. At day 2, the water pH was 9.79, but it decreased gradually until day 22. After that, the water pH decreased faster than usual (Appendix H-8).

The water pH of SF grouted mixed (Nickel-Phenanthrene) contaminated sandy silt was 9.82 at day 2, but it decreased slowly after day 18. The final water pH at day 30 was 9.70 (Appendix H-9).

The pH in SFC grouted mixed (Nickel-Phenanthrene) contaminated sandy soil was 8.00 at day 2 and 9.80 at day 30. It was observed that water pH increased from day 2 to day 20. After that, water pH decreased and became constant after day 24 (Appendix H-10).

The same situation has been observed in mixed (Nickel-Phenanthrene) contaminated silty sand organic grout. Water pH started to increase from the beginning and was almost stable after day 18. Initially, water pH was 8.22 and pH was 8.86 at day 30 (Appendix H-11).

Water pH in SFC grouted mixed contaminated (Nickel-Phenanthrene) sandy silt soil's water pH varied from 8.59 to 9.03. The pH started to increase from the beginning but became stable after day 18 (Appendix H-12).

4.2.5 RedOx in Submerged Water

The water redOx of SF grouted nickel contaminated sandy soil was not stable. The trend was downward over time, especially after day 18. The initial redOx was -124 mV at day 2 and -114 mV at day 30 (Appendix I-1).

Initially redOx was stable in SF grouted nickel contaminated silty sand soil until day 18. After that redOx decreased rapidly. Initial redOx was -127 mV at day 2 and -115 mV at day 30 (Appendix I-2).

Initial redOx in SF grouted nickel contaminated sandy silt soil was -128 mV at day 2 and -119 mV at day 30. It was observed that redOx was almost constant until day 22 and then it slightly decreased (Appendix I-3).

Phenanthrene contaminated sandy soil redOx in SF grout was much more stable than that of heavy metal specimens. At day 2, redOx was -127 mV and -122 mV at day 30 (Appendix I-4).

The same situation was observed in phenanthrene contaminated SF grouted silty sand soil. It was observed that initial redOx was -123 mV at day 2 and -116 mV at day 30. RedOx was stable until day 18, an afterwards decreased up to -116 mV (Appendix I-5).

Almost the same behaviour was observed in phenanthrene contaminated SF grouted sandy silt soil as was found in phenanthrene contaminated sandy and silty sand soil. RedOx was stable until day 18 and decreased afterwards. The initial redOx was -127 mV at day 2 and almost same value was observed until day 18. The final redOx was -119 mV. (Appendix I-6).

The redOx of SF grouted mixed (Nickel-Phenanthrene) contaminated sandy soil was almost constant from day 2 to day 30. The initial redOx was -127 mV at day 2 and final redOx was -128 mV (Appendix I-7).

RedOx in SF grouted mixed (Nickel-Phenanthrene) contaminated silty sand water redOx was not stable. Initially, it increased, but later on it started to decrease at day 14. The average initial redOx was -126 mV at day 2 and final redOx was -116 mV (Appendix I-8).

In mixed (Nickel-Phenanthrene) contaminated sandy silt water, redOx was stable initially but became unstable after day 18 when redOx dropped rapidly and became unstable. Initial redOx was -126 mV and -112 mV at day 30 (Appendix I-9).

In SFC grout, the situation was completely opposite to that of SF grout. Here, redOx was high initially and after a certain time it became stable. In mixed (Nickel-Phenanthrene) contaminated SFC grouted sandy soil, water redOx was -34 mV at day 2 and -73 at day 30. A constant value was observed after day 18 (Appendix I-10).

The initial redOx of SFC grouted mixed (Nickel-Phenanthrene) contaminated silty sand soil was -39 mV at day 2 and final redOx was -77 mV at day 30. It was practically stable at day 20 with the value of -78 mV (Appendix I-11).

The situation was quite different in sandy silt soil that was mixed (Nickel-Phenanthrene) contaminated in SFC grout. The initial redOx was -72 mV at day 2 and increased until day 12 with the value of -89 mV when it became stable. However, it became unstable after day 20 when the redOx was -90 mV. Although there were some changes afterwards, it became stable again with the value of -88 mV at day 24 (Appendix I-12).

4.3 Discussions

4.3.1 Soil Specimens

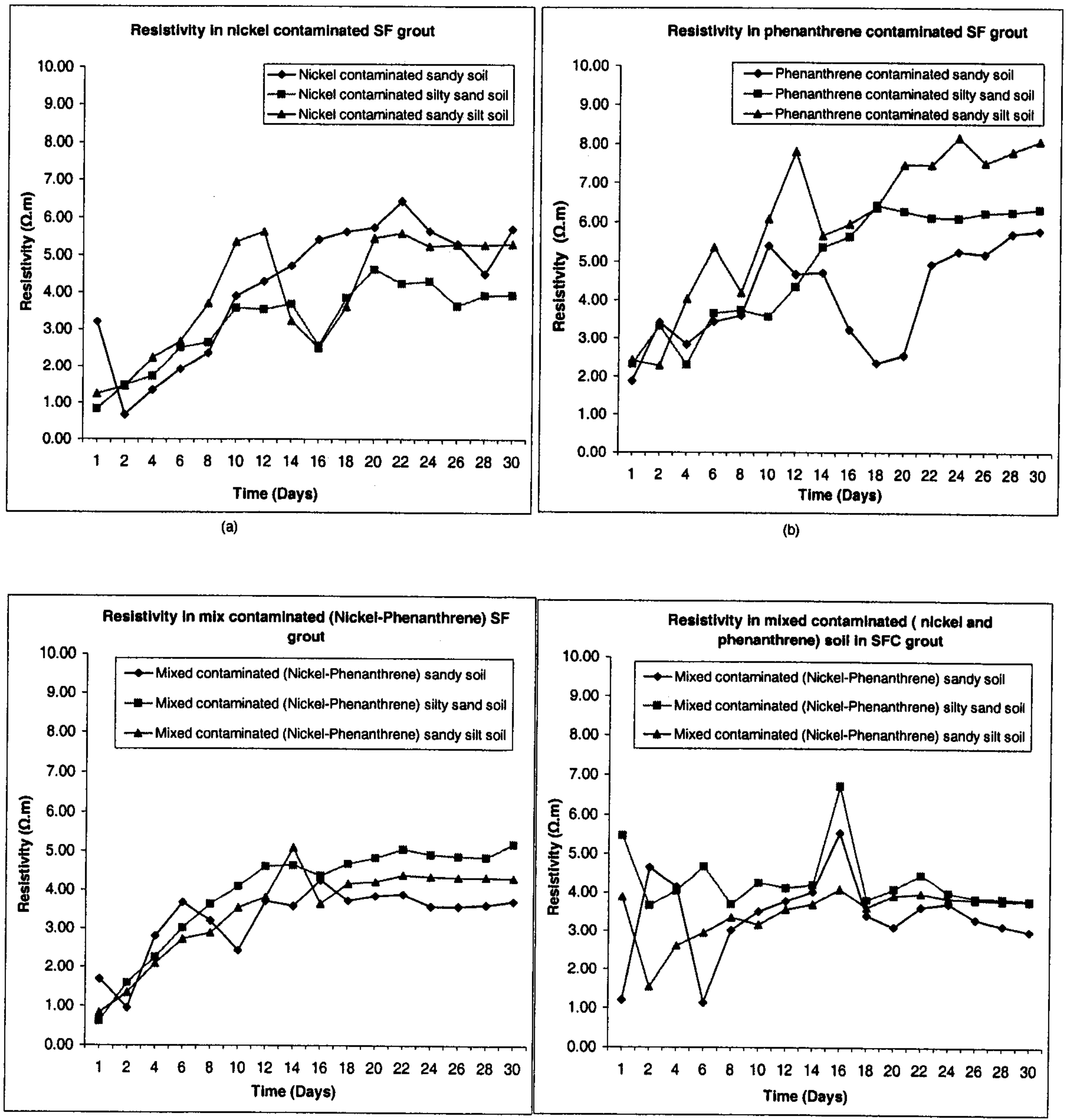
The discussion part of this thesis is organized according to studies of contaminants, type of soil, and grout mixing types. This means that studies of heavy metals in SF grout, organic matters in SF grout, mix contaminants in SF grout, and mix contaminants in SFC grout were discussed separately to discover the behaviour of these variables in sandy, silty sand and sandy silt soil.

4.3.1.1 Effect of Different Soil Compositions on Grouting Specimen Resistivity

Resistivity is a method for monitoring internal changes in soil depending on chemical reactions and water. In other studies this method was used in the geophysical field. In this study it is used for measuring internal changes in grout specimens. Results have showed that for all sandy soil specimens grouted with SF resistivity increased over time, particularly when soil was mix (Nickel-Phenanthrene) contaminated or when it was independent of type of contamination.

Sandy silt specimens grouted with SF showed the highest resistivity (7.83 Ω.m) at day 12. It was 1.41 times higher than that of sandy soil specimens grouted with SF.

The resistivity of nickel contaminated SF grout sandy soil increased over time. It is observed in Figure 4-9 that sandy silt soil has the highest resistivity compared to sandy and silty sand soil. Figure 4-9 shows that internal changes took place mainly between days 2 and day 24. These changes may be because of volume shrinkage, water consumption by the specimens, soil compaction, contaminant release, and rate of internal erosion. Sandy silt soil resistivity decreased on day 12 when sandy soil had maximum resistivity. However, silty sand soil has lower resistivity compared to sandy soil. The behaviour of the soil resistivity in sandy soil is different from that in sandy silt soil when mixed contaminated SF grout is used. Its resistivity increased gradually over time. It was also observed in mixed contaminated SFC grout that massive changes took place internally in the specimens, and the grout took more time to stabilize. This means that SFC grout reacts differently from SF grout.. It can be said that in nickel and phenanthrene contaminated SF grout, sandy silt has the highest resistivity, while sandy soil has less resistivity. And in mixed contaminated SF and SFC grout, less silty soil has higher resistivity than sandy silt soil. Therefore, it can be said that the grouted specimens is less permeable in the water.



(a)

(b)

(c)

(d)

Figure 4-11 Comparison of soil resistivity in different contaminated soil and grout

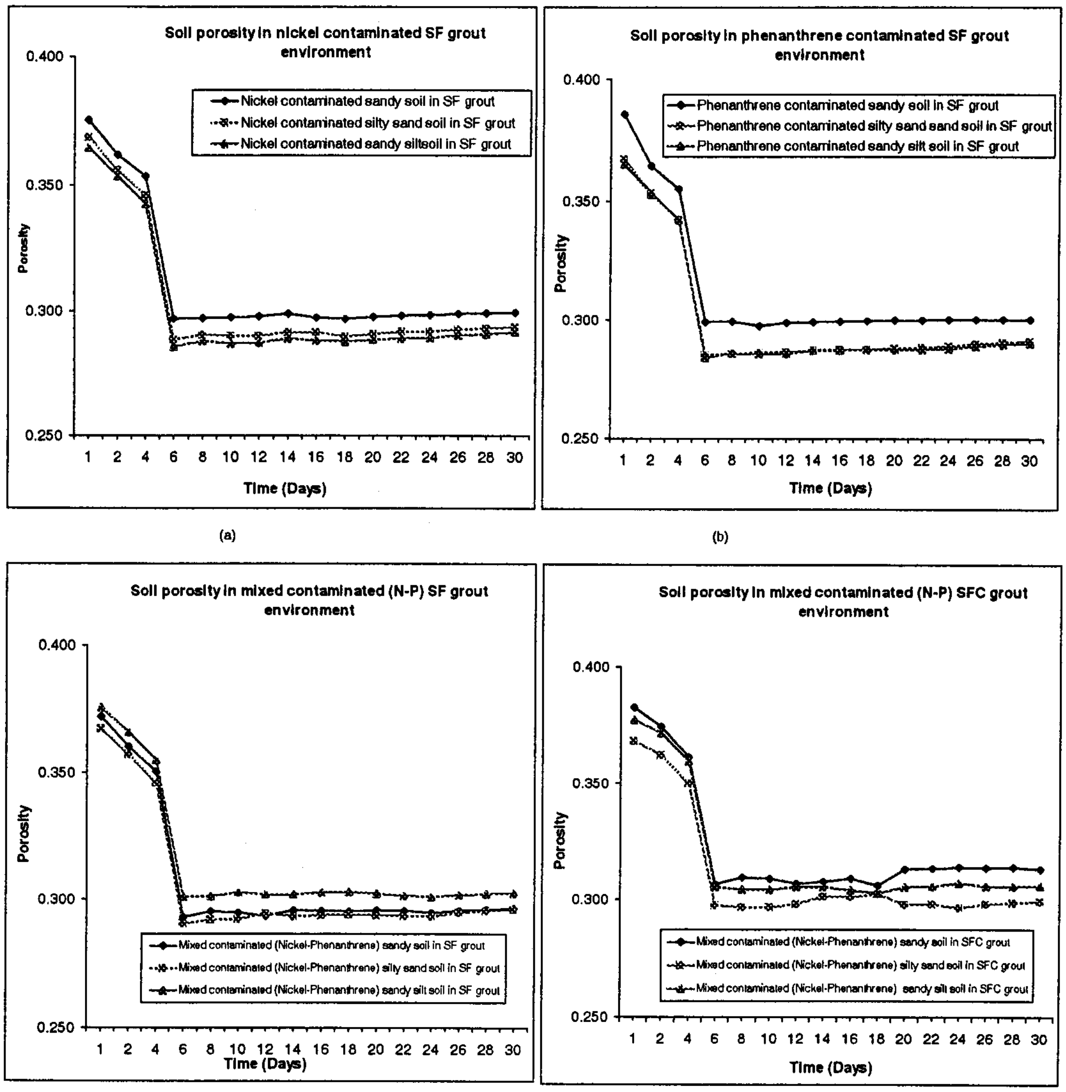
4.3.1.2 Effect of Soil Composition on Porosity

Figure 4-12 (a) represents the porosity of all nine specimens (Experiments 24-26) that were contaminated with nickel chloride at the level of 1000 ppm. Initial porosities of all samples were from 0.365 to 0.375, and for compacted grout, maximum porosity was 0.40 in studies reviewed. However, the porosities decreased rapidly in the first six days after specimens were submerged in tap water because SF grout shrinks in contact with water. Porosities became stable after stabilization took place. Nickel contaminated sandy (100%) soil has higher (0.375) porosity compared to silty sand and sandy silt soils. The reason may be bigger pore spaces in sandy soil.

Figure 4-12 (b) shows three different soil compositions that were contaminated with phenanthrene. The initial porosity of sandy soil was 0.386, of silty sand it was 0.367, and of sandy silt it was 0.365. Porosities decreased in all specimens after they were put in tap water. However, all of the porosities of the samples became stable after one week. It seems that sandy soil has higher porosity than other specimens, but the porosities of silty sand, and sandy silt were almost alike. Bigger pore spaces might be a reason for higher porosity in sandy soil. The initial porosity of sandy soil was 0.386 and the final porosity was 0.300. The initial porosities of silty sand, and sandy silt were 0.367 and 0.365 and their final porosities were 0.291 and 0.290 respectively.

Figure 4-12 (c) indicates that mixed contaminated (Nickel-Phenanthrene) sandy silt has bigger (0.365) porosity than sandy and silty sand soil porosities, which were 0.372 and 0.367 at day 1. The final porosities were 0.299, 0.294, and 0.292 in sandy, silty sand and sandy silt soil. However, the porosities were almost the same in sandy and silty sand soil in SF grout.

Figure 4-12 (d) shows that all of the specimens' porosities were higher than in other specimens described in Figure 4-12 (a, b, c,). The reason could be calcium chloride.



(a) (b)

(c) (d)

Figure 4-12 Comparison of soil porosity in different contaminated soil and grout

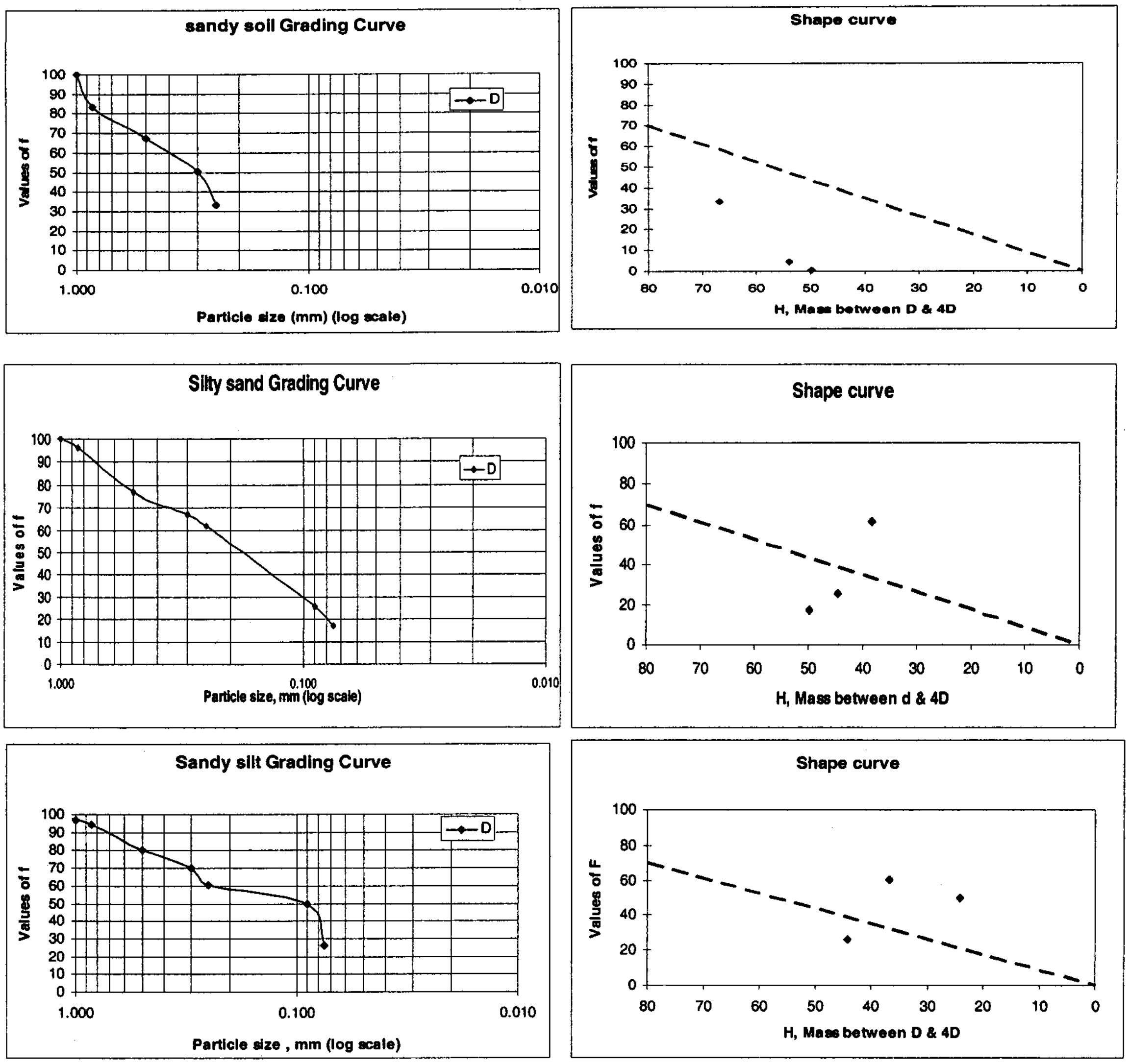


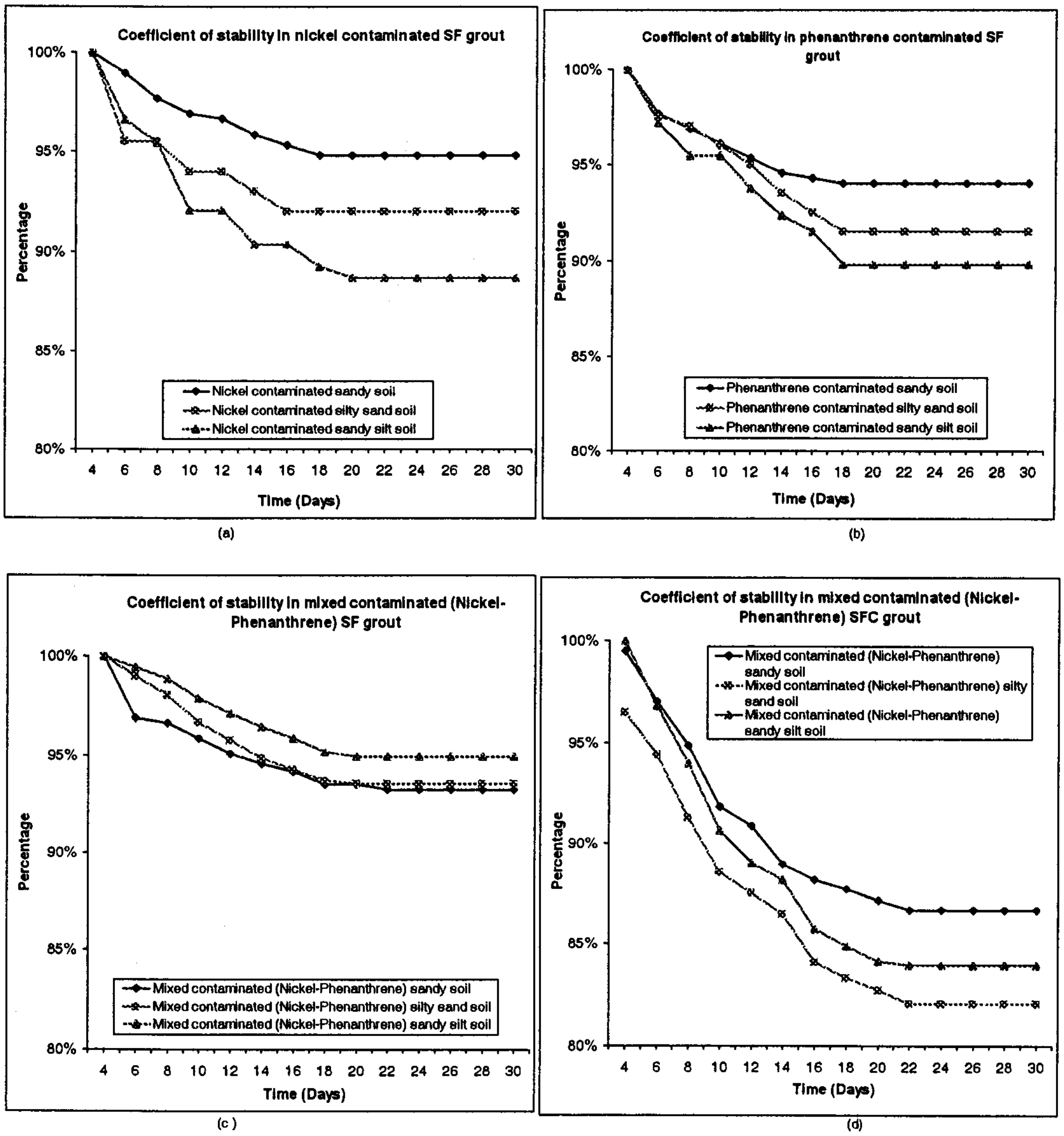
Figure 4-13 Particle size distribution and related shape of grading curve

The grout containing combined reagents (formamide-calcium chloride SFC) was good to stabilize the soil but it was not as strong as the grout with SF. Therefore, the specimens had higher water consumption and more soil degradation. As a result, volume changed and porosity increased.

Considering sections 2.6, 2.6.1, 2.6.2 and related equations (2.3), porosity decreased vs. time in all specimens because resistivity and porosity are inversely related. But Figure 4.3 and 4.4 show almost constant porosity everywhere. Therefore, the soil internal stability was studied in 2.5, 2.5.1 and 2.5.2. Following Kenny and Lau (1985), three different shapes of grading curve were drawn based on the data obtained in sieve analysis. Finally, H = 1.3F boundary line was drawn in each grading curve and showed that soils that were used in the experiment were unstable, so suffusion can take place. As a result, soil internal particles were moving from one soil horizon to other and resistivity was increasing and/or changing for that reason.

4.3.1.3 Coefficient of Stability (CS) for Different Soil Compositions

Figure 4-14 shows the comparison of stability coefficients of stability of soil with nickel, phenanthrene, and mix (Nickel-Phenanthrene) contaminated sand, silty sand, and sandy silt soil in SF and SFC grout. Sandy soil had higher stability than other soils. A 5.2% soil degrade in nickel contaminated SF grout was observed, while silty sand soil and silty sand degraded by 8% and 4.5% respectively. Phenanthrene contaminated sandy, and silty sand degraded by 5.9%, and 8.5% respectively while sandy silt degraded almost half as much (1.72 times) as sand. However, in mix contaminated SF grout, more than 95% of the soil specimen was stable in sandy, 93.7% in silty sand, and 93.5% in sandy silt. However, in SFC grouted mix contaminated soil the degradation rate was much higher than in other grouted specimens, and the total grout environment was different from SF grout. SFC grouted specimens needed more time than SF grout to stabilize. The reason may be the presence of calcium chloride. It was also found from the FT-IR analysis that in combined reagents, calcium chloride reacted first, followed by formamide. Inorganic grout made specimens more vulnerable than organic grout. Specimens SFC were more stable, but initially released a higher amount of chemicals into water. The reason for the degradation may be the curing time and the grout environment. It seems that grout mix needed at least 2 weeks to finalize the stabilization process, so during these 2 weeks specimens had a higher degradation rate.



(a) (b)

(c) (d)

Figure 4-14 Comparison of coefficient of stability in different contaminated soil and grout

The basis of comparison of soil resistivity change and coefficient of stability change can be said to be that the coefficient of stability gave more optimistic values in the case of mixed contamination in both types of grout. The SF and SFC grout showed the agreement between resistivity results and the coefficient of stability. Stable values take place in resistivity. The coefficient of stability in Figure 4-14 (c,d) in day 18 in mixed contaminated with SF and SFC grout. Resistivity and CS stable in mixed contaminated SFC grout (Figure 4-11 c) on the day 22. However, internal changes do not influence the result of contaminant release.

4.3.2 Water Quality

4.3.2.1 Effect of the Type of Grout on Water pH

It is observed (Figure 4-15) that nickel contaminated sandy soil and silty sand, have maintained almost the same water pH. But sandy silt has a bit higher water pH than the water pH of sandy and silty sand soil. Sandy soil has stable water pH in SF grouted phenanthrene contaminated soil. However, the pH in water when silty sand and sandy silt specimens were submerged, increased slightly until day 18 and afterwards decreased. In mix contaminated soil, the average water pH was 9.80 for all kinds of soil. In SFC grouted specimens, water pH increased over time and became practically stable after day 20. Sandy silt has higher water pH than others, while silty sand water pH is in second place. The variation of pH in water directly depends on the released amount of chemicals and the higher degradation of soil into water. It was observed that SFC grouted specimens have the highest release of soil degradation.

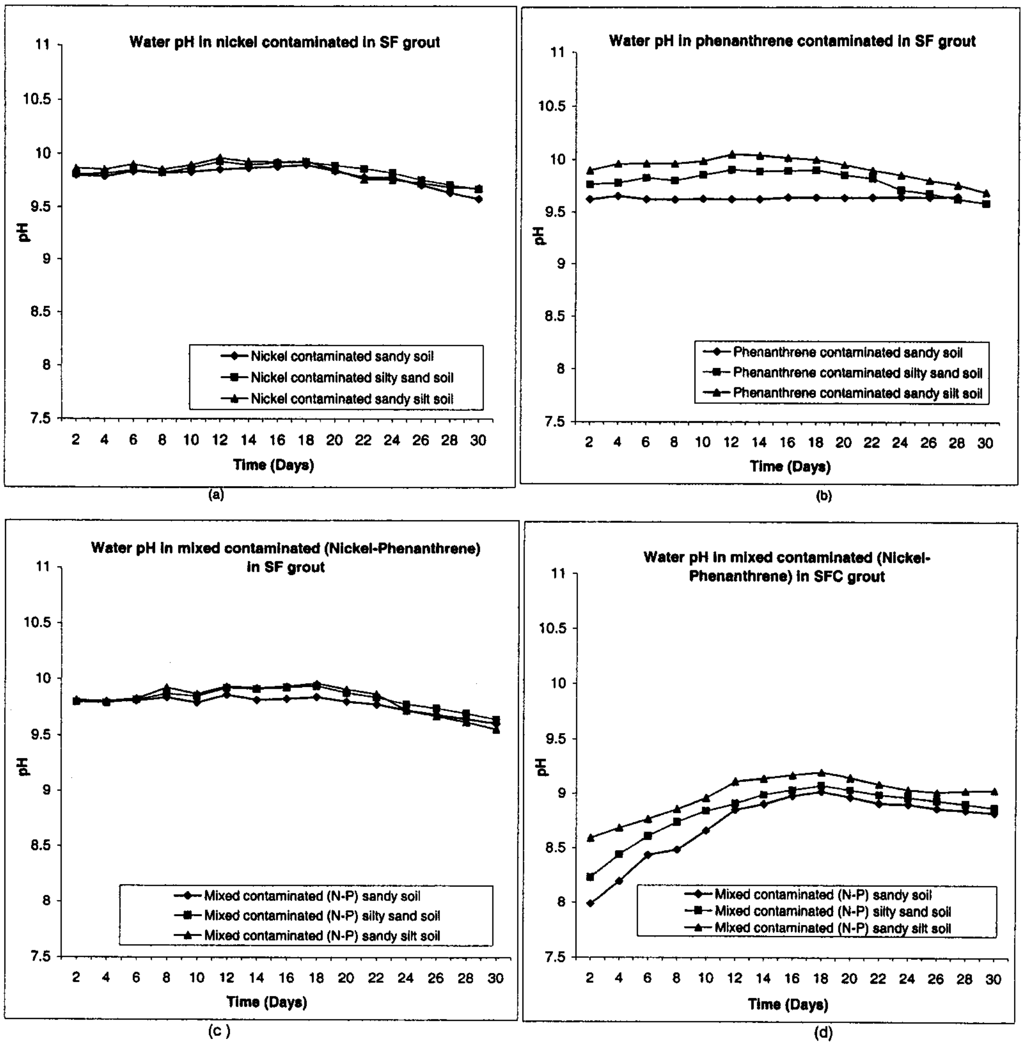
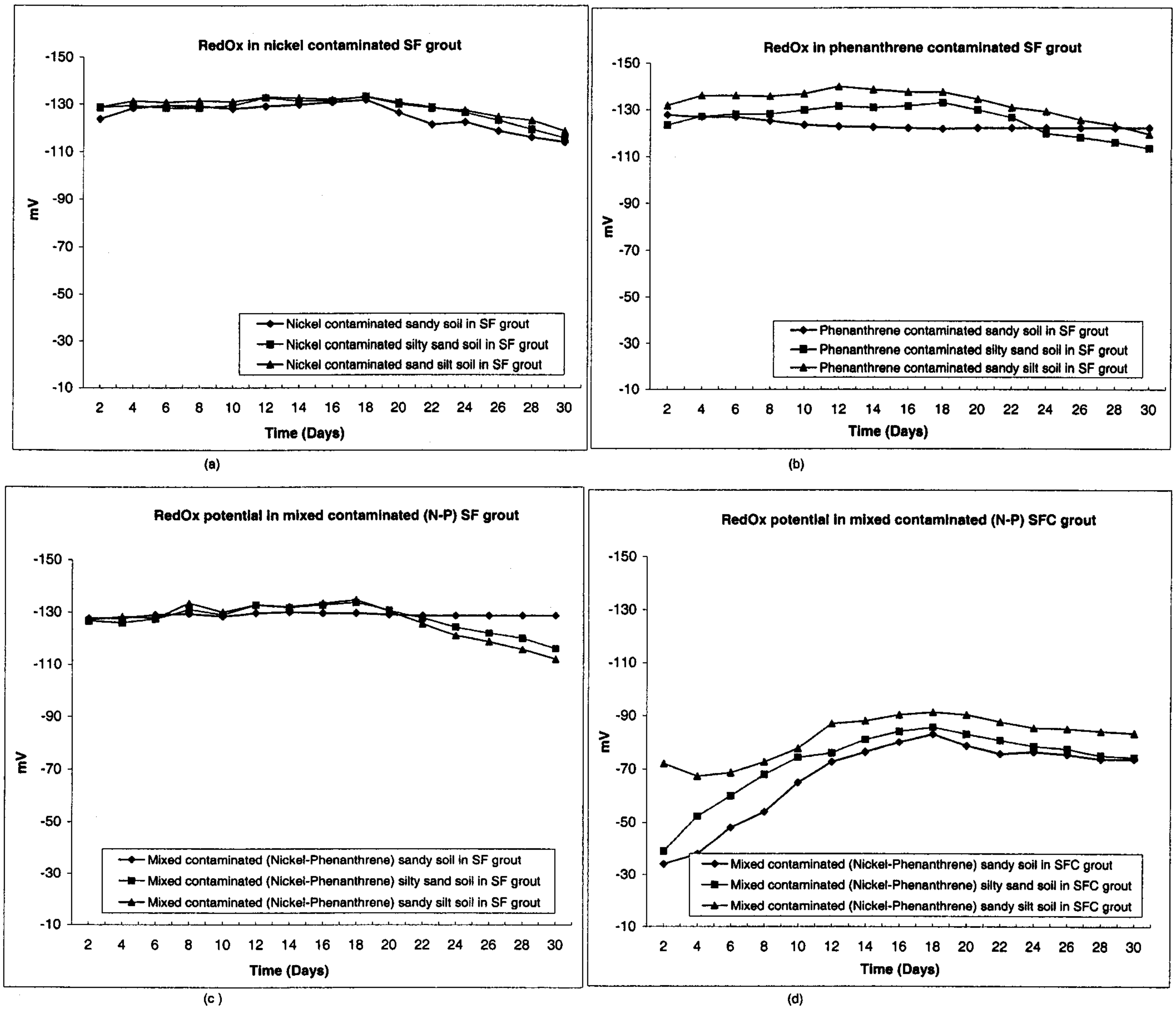


Figure 4-15 Comparison of water pH in different contaminated soil and grout



(a) (b)

(c) (d)

Figure 4-16 Comparison of redOx in different contaminated soil and grout

4.3.2.2 Effect of Different Grouts on redOx

It is observed (Figure 4-16) that sandy silt soil has higher redOx than sandy soil contaminated with nickel and grouted with SF. Until day 18, redOx was stable (-121.67) but it started to decrease slightly after day 20. In phenanthrene contaminated SF, grouted sandy silt soil has the highest redox (-139.67) at day 12. In the case of sandy soil, redOx was stable for 4 weeks. In all mix contaminated SF grout cases, water redox was stable until day 20, and afterwards specimens containing silt decreased gradually, but redOx in the case of sandy soil remained constant. In the case of SFC grout, initial redOx was low and it increased gradually. Sandy silt has a higher redOx than other specimens. Water of other specimens became stable at day 28. The situation in SFC cases is opposite to that in SF cases. It was speculated that higher oxidation could weaken the bonds so that a hard gel of silica could not form.

4.3.2.3 Impact of Grouts on Groundwater Quality

From table 4-1, it could be predicted that a slight amount of nickel was released in the water on the first day, but after that, there was no contamination found in the water. It is suspected that nickel precipitated or sorbed into another form but was not released into the groundwater. Table 4-2 shows that in soil particles eroded from the specimens the higher concentration of nickel was found. However, release began to be stable after a certain period of time. The Quebec Ground Water Quality standard states that a maximum 1 ppm nickel could be present in groundwater while the contamination is 1000 ppm (Environment Quebec, 1994). The results of this research showed levels could be obtained that criterion, except for the case with SFC grout. But heavy metals especially nickel standards for Groundwater Quality in other places like Australia, and Europe, are much higher than the Quebec standard, and the results of this research could be applied in those places. Furthermore, no traces of phenanthrene were found in the groundwater. This means that the developed grouting is safe for organic contaminated and mixed contaminated sites. Although a higher release of nickel was found in SFC grouted mixed contaminated sandy soil, this grout was more stable than SF grout in sand.

4.3.3 Effect of Silt Content

It was observed that silt is not a problem for this grout application because nickel contaminated sandy and silty soil have almost the same pH in water. At day 20, pH dropped slightly in all soil compositions. However, in SF grouted phenanthrene contaminated soil, initially, silty sand had higher water pH (9.90) than sandy soil. Water pH in silty sand soil dropped to 9.69 at day 26, when sandy soil had 9.58. In mixed contaminated SF grout environment, the situation was almost the same as in nickel contamination. There are no changes found in the presence of silt. The average initial pH (day 1) of sandy soil was 9.80, silty sand soil was 9.81 and final pH at day 30 was 9.61, and 9.56 respectively. The situation was different in a mix contaminated SFC grout environment. Sandy and silty sand soil's initial pH were lower than sandy silt specimens grouted with SF. Silty sand has higher pH (8.59) (like organic contaminated organic grout) and all of the specimens' pH increased until day 18 and remained almost constant for the rest of the days. However, silty sand had a higher pH value until the last day (Appendix-H). This means there is an effect of silt content on the grout. It was observed that redOx behaved in exactly the same way as pH in silty soil (Appendix- I).

The coefficient of stability showed that silty soils are more vulnerable than sandy soil. In nickel contaminated SF grout, 88.7% silty sand specimens were stable; 89.8% were stable in phenanthrene contaminated SF grout; 95.2% silty sand specimens were stable in mixed contaminated SF grout, and 84.1% were stable when SFC grout was applied. It seems that mixed contaminated SF grouted sandy silt is the best solution for this type of application (Figure 4-14).

4.3.4 Effect of the Use of the Combined Reagents

FT-IR analysis showed that in the case of using both reagents, calcium chloride set first with silica. The setting with formamide took time because it had much more complicated chemical reactions. It was speculated that a high groundwater gradient might provoke additional leaching of formamide in these circumstances. This means that pH of groundwater could also increase slightly in the vicinity of vulnerable barriers. However, the application of two reagents provoked, (Experiments 33-35), an increased pH during the first 2 weeks in sandy silt soil from 8.59 to an almost 9.16 falling almost stable to 9.01 on day 24. Sandy soil pH increased up to 9.05 until day 22 and again dropped later on day 26 (8.86).

4.3.5 Effect of the Contaminants Content

It is obvious that phenanthrene was not released in the water with the application of formamide. Any type of contaminated sand and silt did not release phenanthrene (even in the case of mixed contamination). It was also observed in the case of combined reagents that phenanthrene is not released into the water environment. However, the release of nickel was observed. This could be due to higher concentration. The erosion of soil was not high. Therefore this also meant that there was less possibility of contaminants being released into the ground water.

Nickel was found to be released in negligible amounts in all cases. Slightly higher release of nickel was observed in the case of silt samples where combined reagents were applied. The maximum percentage was 0.06%. This low percentage could be attributed to ion exchange with calcium in day 1. On the following days, inconsistence traces of nickel were found. Nickel could probably precipitate with an increase of pH in the water. However, in silty soil, although two reagents were used, an increase of nickel release was observed with time. It is speculated that nickel sorption to fine soil particles or/and more complicated porosity system retarded diffusion of nickel.

4.4 Contaminant Release-Empirical Model Development

4.4.1 Introduction

An empirical model was developed based on laboratory experimental results. The objective of this model was to find a relationship between the release of contaminants and the actual amount of contamination, grouting, and internal erosion so that engineers can predict the total amount of contaminants released (dissolved and sorbed) from a contaminated site. It was observed from the experiments that the release of contaminated specimens was influenced by almost all the factors considered in this experimental investigation, factors such as initial concentration (*C*), soil porosity (*n*), ratios of sodium silicate and reagents (*G*), water qualities (ρ_w), soil type, hydraulic gradient (S_t), pore size, and rate of internal erosion (ε_e). From various literature reviews, it was found that release (*R*) of contaminant is directly proportional to contaminant concentration (*C*), soil porosity (*n*) and inversely proportional to percent of grouting (*G*) and rate of internal erosion (ε_e). Individual relationships between each of the above parameters have been developed and are shown below.

$R \alpha C$ $R = f_1 (C)$ ....(4.15)

$R \alpha n$ $R = f_2 (n)$ ....(4.16)

$R \alpha 1/(G)$ $R = f_3 (1/G)$ ....(4.17)

$R \alpha 1/\acute{\varepsilon}_e$ $R = f_4(1/\acute{\varepsilon}_e)$ ....(4.18)

By combining the effect of the parameters and rearranging them, TERC can be written as:

$$R = \frac{A \times C \times n}{G \times \varepsilon e} \quad \text{..(4.19)}$$

Where,

A is a parameter of proportionality, which depends on time, type of soil, and type of grouting. TERC stand for Tahar-Emon Release of Contaminant model.

4.4.2 Parameters Considered in the Development of the TERC Model

4.4.2.1 Total Contaminant Release

To find out the total release of nickel (R_N) and phenanthrene (R_P) concentration, released water effluents was evaluated for dissolved and sorbed concentration, as was described in 4.2.2 and 4.2.3. However, no phenanthrene was traced in the water. Therefore, in the model, only nickel concentration was used to validate the TERC model.

4.4.2.2 Porosity

Soil porosity is an important parameter in this model. It was determined that soil porosity changed over time due to volume shrinkage of the grout and to water suction by the specimens. Therefore, in the model, percentages of soil porosity on different days were considered for the validation of the model. Furthermore, a detailed porosity calculation is added in the Appendix B. .

4.4.2.3 Percent of Grouting

It was considered that different types of grout mix and their mixing ratios changed the grout strength, durability, and the concentration of contaminants. Therefore, this parameter was used to show that the percent of grout can affect the silica based grouting. The percent of grouting is inversely proportional to the total amount of release of contaminants.

4.4.2.4 Rate of Internal Erosion

Soil erosion testing by a number of researchers has shown an approximately linear relationship between the rate of erosion and the applied hydraulic shear stress. The relationship can be expressed as

$$\varepsilon_e = Ce(\tau_t - \tau_c) \quad \text{.........(4.20)}$$

Where, ε_e = rate of erosion per unit surface area of the hole at time t (kg/s.m^2); Ce = proportionality constant named by the coefficient of soil erosion (s/m); τ_t = hydraulic shear stress along the hole at time t; (N/m^2);, and τ_c = critical shear stress (N/m^2) or D_{50} (%) from soil particle size distribution curve in logarithm scale (Appendix- C).

4.4.2.5 Proportionality Constant (Ce)

It was found that if - log (Ce) is used in correlation analysis and plotting of results. It is easy to use the soil erosion rate index, which is denoted by I. In this model, moderately slow erosion speed was chosen because soils was grouted and compacted. Therefore, I=3 (Table 4-3). The standard erosion rate index described on table 4-3 is defined as

$$I = -\log(Ce) \quad \text{.........(4.21)}$$

Table 4-3 Soil erosion rate index

>6	Extremely slow
5-6	Very slow
3-5	**Moderately slow/rapid**
2-3	Very rapid
<2	Extremely rapid

I has an order of magnitude in the range of 0 to 6.

4.4.2.6 Critical Shear Stress

The critical shear stress can be obtained from a particle size distribution curve (log scale). Usually, D_{50} (m) is considered to be the equivalent of τ_c that is found in literature reviews.

4.4.2.7 Hydraulic Shear Stress

The hydraulic shear stress can be obtained from the following equation that is found from the Hole Erosion Test (HET).

$$\tau_t = \rho_w \times g \times S_t \times \frac{Pe}{4} \quad \text{.........(4.22)}$$

Where, τ_t = Hydraulic shear stress on the surface of the preformed hole at time t (N/m^2); ρ_w = density of the water (considered as eroding fluid) (kg/m^3); g = acceleration due to gravity (9.81 m/s^2); S_t = hydraulic gradient across the soil sample at time t; and De = equivalent particle size (m);

Hydraulic gradient is the water height (H) of the container after submerged the specimen in the water (cm) over the height (h) of the specimen (cm) and that can be expressed as

$$S_t = \frac{H}{h} \quad \text{.........(4.23)}$$

And the *De* is inversely proportional to the summation of $\frac{x_i}{d_i}\alpha_i$.

Where, x_i = corresponding percentage of particle size (f); α_i = shape factor (described in Table 4-4); d_i = diameter of the particle size. These parameters can be expressed as

$$De = \frac{1}{\Sigma(\frac{x_i \times \alpha_i}{d_i})} \quad \text{...(4.24)}$$

A brief calculation of *De* for sandy and silty sand soil is tabulated on table 4-5, and 4-6 following Kovacs, 1981.

Table 4-4 Shape factor for various soil particles

Type of soil particle	**Shape factor, α**	
	Recommended range	Value used to compute data
Na- Montmorillonite	700 – 1000	1000
Kaolinite clay	30 – 70	70
Illite clay	20 – 60	N.A.
Silt (2 to 20μm)	**10 – 50**	**25**
Sand (20 to 2000μm)	**8 – 10**	**8**
Gravel (> 2000μm)	7 - 11	7

However, in this model equivalent pore size is studied further. It is expressed by

$$Pe = \frac{4 \times n \times De}{(1-n)} \quad \text{...(4.25)}$$

Where, *Pe* = equivalent pore size; *n* = soil porosity; *De* = equivalent particle size.

Finally, combining equations 4.15 to 4.25 gives the final complete equation of the TERC model in the form of

$$R = \frac{A \times C \times n}{G \times e^{-I} \times \left[\rho_w \times g \times S_t \times \left(\frac{n}{(1-n) \times \Sigma\left(\frac{x_i \times \alpha_i}{d_i} \right)} \right) - D_{50} \right]} \quad \text{.............................(4.26)}$$

4.4.3 Model Review

An empirical model was developed to estimate total concentration that released to the groundwater from silica based chemical grouting. The model was formulated in the following set of equations

$$\varepsilon_e = Ce(\tau_t - \tau_c) \quad \text{......(4.20)}$$

$$I = -\log(Ce) \quad \text{......(4.21)}$$

$$\tau_t = \rho_w \times g \times S_t \times \frac{Pe}{4} \quad \text{......(4.22)}$$

$$S_t = \frac{H}{h} \quad \text{......(4.23)}$$

$$De = \frac{1}{\Sigma(\frac{x_i \times \alpha_i}{d_i})} \quad \text{......(4.24)}$$

$$Pe = \frac{4 \times n \times De}{(1-n)} \quad \text{......(4.25)}$$

Where,

A = Parameter of proportionality (Detail will be shown on the following section)

C = Initial concentration (mg/L)

n = Percentage of soil porosity

ε_e = Rate of erosion per unit surface area of the hole at time t (kg/s.m^2)

Ce = Proportionality constant named by the coefficient of soil erosion (s/m)

τ_t = Hydraulic shear stress along the hole at time t; (N/m^2)

τ_c = Critical shear stress (N/m^2) or

D_{50} (%) from soil particle size distribution curve in logarithm scale

I = Soil erosion rate index

ρ_w = Density of the water (considered as eroding fluid) (kg/m^3)

g = Acceleration due to gravity (9.81 m/s^2)

S_t = Hydraulic gradient across the soil sample at time t

H = Water height of the container after submerged in the specimens (cm)

h = Specimen height (h) over time (cm)

De = Equivalent particle size (m)

Pe = Equivalent pore size

n = Soil porosity

4.4.4 Parameter of Proportionality (A)

In this section, an attempt is made to determine the parameter of proportionality (A). A back calculation using Equation (4.26) is undertaken to calculate the different values of the parameter (A) at different times. For this purpose, all the parameters obtained experimentally (such as release, R, concentration, C, percentage of grouting, G, and D_{50}) and the calculated values of the porosity, n , the hydraulic gradient across the soil sample at time t, S_t , and the equivalent particle size, De (Tables 4-5 and 4-6) are used.

Table 4-5 Calculation of De for sandy soil

Xi	*di* **(m)**	*ai*	*(Xi*ai)/di* **(m)**	*De = 1/Σ(Xi*ai)/di* **(m)**
1.0000	0.0010	8.00	8000.00	
0.8318	0.0009	8.00	7828.71	
0.6763	0.0005	8.00	10820.80	
0.5009	0.0003	8.00	13357.33	0.0000181
0.3323	0.0003	8.00	10633.60	
0.0419	0.0001	8.00	3724.44	
0.0023	0.0001	25.00	766.67	
			Σ= 55131.55	

Table 4-6 Calculation of De for silty sand soil

Xi	di (m)	αi	$(Xi*\alpha i)/di$ (m)	$De = 1/\Sigma(Xi*\alpha i)/di$ (m)
1.0000	0.0012	8.00	8000.00	
0.9703	0.0010	8.00	9132.24	
0.9437	0.0009	8.00	15099.20	
0.8011	0.0005	8.00	21362.67	0.0000026
0.6994	0.0003	8.00	22380.80	
0.6029	0.0003	8.00	53591.11	
0.4995	0.0001	25.00	166500.00	
0.2588	0.0001	25.00	86266.67	
			Σ= 382332.68	

The parameter of proportionality (*A*) was found for the different soil types and grout mix used in this investigation. The results obtained were plotted in two graphs (Figures 4-17 and 4-18). The best fitting technique was used on the obtained data in order to determine the different formulae giving the parameter *A*. A general formula is defined as follows:

$$A = at^2 + bt + c \quad (4.27)$$

Where, a, b and c can be determined from the following Table 4-7.

Table 4-7 Values of a, b, and c for different types of soil, contamination and grout

Parameter	Nickel and Mix contaminated sandy soil in SF grout	Mix contaminated sandy soil in SFC grout	Nickel and Mix contaminated sandy silt soil in SF grout	Mix contaminated sandy silt soil in SFC grout
a	-5.10^{-8}	-2.10^{-8}	-6.10^{-9}	-7.10^{-9}
b	2.10^{-6}	1.10^{-6}	3.10^{-7}	4.10^{-7}
c	8.10^{-6}	3.10^{-5}	2.10^{-6}	4.10^{-6}

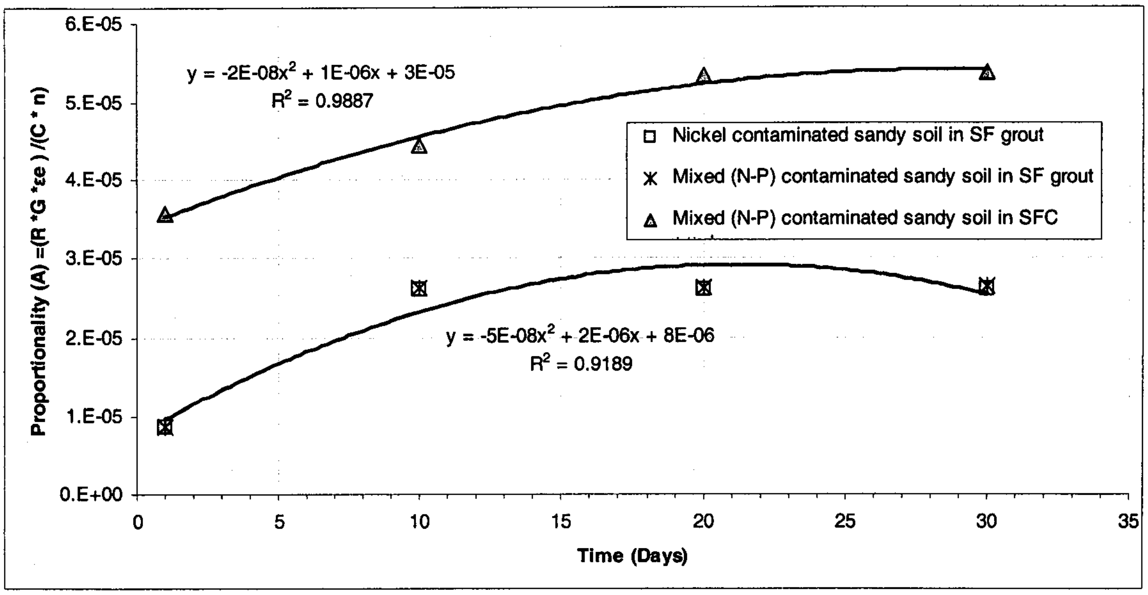


Figure 4-17 Coefficient of proportionality in sandy soil. Symbols are experimental data and lines are best fits

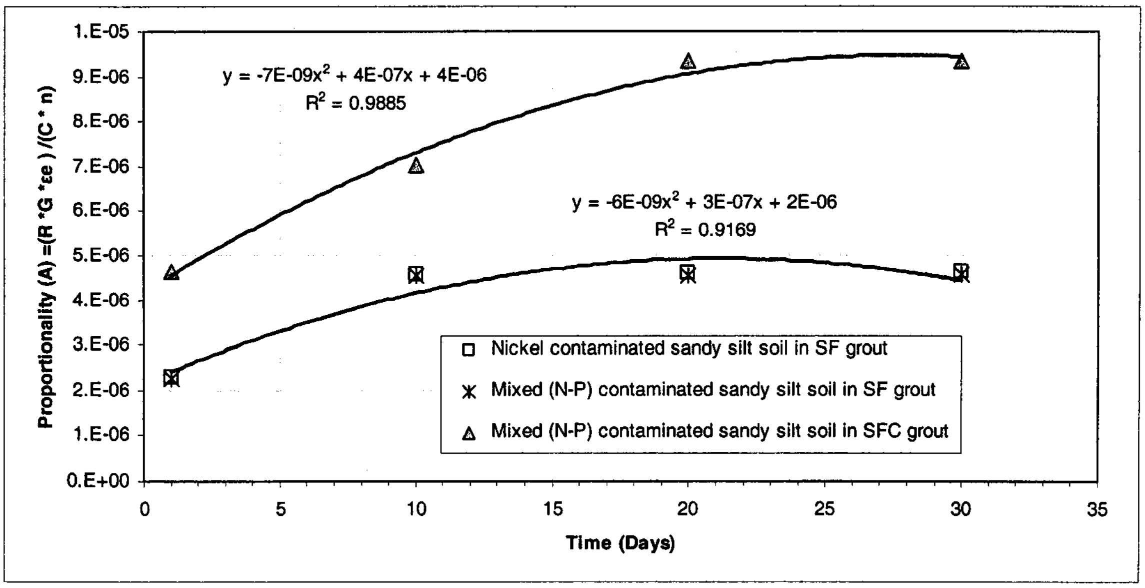


Figure 4-18 Coefficient of proportionality in sandy silt soil. Symbols are experimental data and lines are best fits

It is worth noting that the parameter *A* defined previously depends on time and can be used only with the type of grouts and the type of soils used in this investigation. However, it should be noted that one of them (i.e. SF) is the most used in the field.

Furthermore, the three soils used have different particle size distributions with a big range of coefficient of uniformity, C_u and mean particle size, D_{50}. The value of the parameter A for any soil between these three types of soil can be obtained by linear interpolation. A similar behavioral relationship is expected for different types of soils and higher uniformity coefficients. However, additional data, especially on natural soils, is needed before generalizing from the present findings.

4.4.5 Fitting of TERC Model Results to Experimental Data

In order to assess the viability of the empirical model proposed, the model has to be validated. Unfortunately, no data was found in literature dealing with both release and internal erosion. In these circumstances, the validation or the verification part will be limited only to a comparison between the measured results of this investigation and the predicted results obtained from the present model. The different formulae of the parameter *A*, and the measured or calculated values of all the parameters included in equation (4.26) were used to estimate the different values of the release (*R*) under different conditions. Six different cases were chosen from the experimental program for this purpose:

Case 1: Nickel contaminated sandy soil in SF grout

Table 4-8 Results of Case 1

a) Input data

Input parameter	**Day 1**	**Day 10**	**Day 20**	**Day 30**
C (mg/L)	1000	1000	1000	1000
n (%)	37.1	29.4	29.3	29.5
G (%)	44.16	44.16	44.16	44.16
ε_e (kg/s/m^2)	$7.335.10^{-03}$	$5.779.10^{-03}$	$5.751.10^{-03}$	$5.807.10^{-03}$
A*	$9.950.10^{-06}$	$2.300.10^{-05}$	$2.800.10^{-05}$	$2.300.10^{-05}$

* Parameter A is find out from the graph (Figure 4-17)

b) Output Data & Comparison

Time (Day)	Release, *R* ((mg/L)	
	Predicted results	**Experimental results**
1	1.140	1
10	2.650	3
20	3.230	3
30	2.646	3

Case 2: Nickel contaminated sandy silt soil in SF grout

Table 4-9 Results of Case 2

a) Input Data

Input parameter	Day 1	Day 10	Day 20	Day 30
C (mg/L)	1000	1000	1000	1000
n (%)	37.24	29.5	29.7	30.1
G (%)	40.5	40.5	40.5	40.5
ε_e (kg/s/m^2)	$1.057.10^{-03}$	$8.350.10^{-04}$	$8.431.10^{-04}$	$8.595.10^{-04}$
A*	$2.294.10^{-06}$	$4.400.10^{-06}$	$5.600.10^{-06}$	$5.600.10^{-06}$

* Parameter A is find out from the graph (Figure 4-18)

b) Output Data & Comparison

Time (Day)	Release, *R* ((mg/L)	
	Predicted results	**Experimental results**
1	1.996	2
10	3.838	4
20	4.871	4
30	4.842	4

Case 3: Mixed contaminated sandy soil in SF grout

Table 4-10 Results of Case 3

a) Input Data

Input parameter	**Day 1**	**Day 10**	**Day 20**	**Day 30**
C (mg/L)	1000	1000	1000	1000
n (%)	37.19	29.8	30	30.1
G (%)	44.16	44.16	44.16	44.16
ε_e (kg/s/m^2)	$7.333.10^{-03}$	$5.891.10^{-03}$	$5.948.10^{-03}$	$5.976.10^{-03}$
A*	$9.950.10^{-06}$	$2.300.10^{-05}$	$2.800.10^{-05}$	$2.300.10^{-05}$

* Parameter A is find out from the graph (Figure 4-17)

b) Output Data & Comparison

Time (Day)	**Release, *R* ((mg/L)**	
	Predicted results	**Experimental results**
1	1.143	1
10	2.634	3
20	3.198	3
30	2.623	3

Case 4: Mixed contaminated sandy silt soil in SF grout

Table 4-11 Results of Case 4

a) Input Data

Input parameter	**Day 1**	**Day 10**	**Day 20**	**Day 30**
C (mg/L)	1000	1000	1000	1000
n (%)	36.26	28.9	28.9	29.1
G (%)	40.5	40.5	40.5	40.5
ε_e (kg/s/m^2)	$1.013.10^{-03}$	$8.110.10^{-04}$	$8.110.10^{-04}$	$8.189.10^{-04}$
A*	$2.294.10^{-06}$	$4.400.10^{-06}$	$5.600.10^{-06}$	$5.600.10^{-06}$

* Parameter A is find out from the graph (Figure 4-18)

b) Output Data & Comparison

Time (Day)	**Release, *R* ((mg/L)**	
	Predicted results	**Experimental results**
1	2.027	2
10	3.871	4
20	4.927	4
30	4.913	4

Case 5: Mixed contaminated sandy soil in SFC grout

Table 4-12 Results of Case 5

a) Input Data

Input parameter	**Day 1**	**Day 10**	**Day 20**	**Day 30**
C (mg/L)	1000	1000	1000	1000
n (%)	38.66	31.1	31	31.5
G (%)	44.16	44.16	44.16	44.16
ε_e (kg/s/m^2)	$7.804.10^{-03}$	$6.265.10^{-03}$	$6.236.10^{-03}$	$6.383.10^{-03}$
A*	$3.098.10^{-05}$	$3.800.10^{-05}$	$4.200.10^{-05}$	$4.200.10^{-05}$

* Parameter A is find out from the graph (Figure 4-17)

b) Output Data & Comparison

Time (Day)	**Release, *R* ((mg/L)**	
	Predicted results	**Experimental results**
1	3.475	4
10	4.271	5
20	4.728	6
30	4.693	6

Case 6: Mixed contaminated sandy silt soil in SFC grout

Table 4-13 Results of Case 6

a) Input Data

Input parameter	**Day 1**	**Day 10**	**Day 20**	**Day 30**
C (mg/L)	1000	1000	1000	1000
n (%)	38	30.9	30.7	30.9
G (%)	40.5	40.5	40.5	40.5
ε_e (kg/s/m^2)	$1.092.10^{-03}$	$8.927.10^{-04}$	$8.843.10^{-04}$	$8.927.10^{-04}$
A *	$4.393.10^{-06}$	$7.300.10^{-06}$	$9.200.10^{-06}$	$9.700.10^{-06}$

* Parameter A is find out from the graph (Figure 4-18)

b) Output Data & Comparison

Time (Day)	**Release, *R* ((mg/L)**	
	Predicted results	**Experimental results**
1	3.774	4
10	6.239	6
20	7.886	8
30	8.290	8

It can be noted from Tables 4-7 to 4-12 that, in general, the predicted values slightly underestimate the values of the release by 0.2% to 21% with a mean value of 0.3%. This may be attributed to the fact that the calculated values of the parameter *A* are smaller than values used to plot Figures 4.15 and 4.16. The model permitted the assessment of the highest contaminant release based on internal erosion of grouted soil. The output from the model shows the same tendency observed during experiments. Water analyses also showed the same trends. The values of nickel concentrations in submerged water were lower than predicted, since during the 30 days period of the experiment some of the released nickel was able to diffuse into the environment from the mass of grouted soil. Finally, it can be stated that, although the validation is good, further research is required to validate the suggested model.

4.4.6 Design Procedure

An empirical model for predicting the potential release of contaminants from soil specimen to groundwater was proposed. A step-by-step procedure is provided for the design of grouts for contaminated soil, as follows:

1. Determine the initial value of concentration of contaminants (C),
2. Determine the particle size distribution and the porosity (n), and D_{50} of the soil,
3. Calculate the equivalent particle size, De,
4. Know the hydraulic gradient across the soil sample at time t (S_t) and the soil erosion rate index (I),
5. Know the percent of grouting (G),
6. Deduce the parameter A from Figures 4.15 and 4.16 or calculate it using the different proposed formulae,
7. Finally, estimate the total release of contaminants using Equation (4.26).

In cases where the release if above certain fixed limits, the type or the percentage of grouting can be changed and steps 7 and 8 are repeated.

4.4.7 Conclusion from the Model

It is visualized from the data that the model has the potential of regenerating experimental results, and could, therefore, be applicable to predict the rate of release of contaminants such as heavy metal, PAH, and their mixtures in groundwater. This model could, consequently, improve the ability to forecast and to assess environmental threats to groundwater quality. Data were taken from SF and SFC grout environment where internal rate erosion was one of the prime concerns. However, no real field data related to grouting were found to validate the model. Additional data, especially on natural soils, is needed before generalizing from the present findings.

CHAPTER 5 CONCLUSIONS AND RECOMMMENDATIONS

5.1 Summary

The purpose of this thesis was to formulate an optimal recipe for the composition of silica-formamide (SF) and silica-formamide-calcium chloride (SFC) grout gel to be used in preventing contamination from leaching into groundwater.

The investigation described in this study (Chapter 3) permitted the finding of grouts which can be successfully used for stabilization of contaminated areas or for containment of contaminated sites making them available to further cleaning.

The experimentation with organic and inorganic contaminated soils showed successful application of SF and SFC grouts. The results of using SF and SFC grout in these experiments are given in Chapter 4.

Recommendations for the best conditions for use of SF, and SFC grout and suggestions for further testing are given in Chapter 5.

5.2 Conclusions

Based on the experiments, the following conclusions can be made:

1. Silica grout with formamide reagent was satisfactorily used for formation of containments in contaminated sand, silty sand, and sandy silt.
2. Silica/formamide grout (SF) was satisfactorily applied to contamination with heavy metal (nickel), and mix contamination (nickel and phenanthrene).
3. Both formulations, formamide reagent (SF) and combined reagents (formamide and calcium chloride SFC), were able to be applied to soil contaminated with organics (phenanthrene).

4. Only traces of nickel were found in water. No release of phenanthrene was observed.
5. Release of by-products of organic reagent reactions was observed in water.
6. The grouted soil was vulnerable to water where inorganic reagent (calcium chloride) was used. However, vulnerability might be decreased by applying organic reagents.
7. Different concentration of inorganic reagents does not affect grout stability.
8. Silica based grout reacted differently when it was formulated with an inorganic reagent, organic reagent, and combined reagents.
9. It was found that the combination of both reagents makes faster setting and more stable conditions.
10. The overall vulnerability of the SFC grout in contaminated soil is much better for the environment than other formulations.
11. Predictions of grouted soil vulnerability based on the developed model (TERC) can be made.
12. The proposed TERC model was validated using results of experimental investigation.
13. Application of indirect measurement using an electrical device and Microsis permitted for close continuous monitoring of the changes within the mass of grouted contaminated soil.
14. It was showed that soil resistivity could indirectly define the internal changes within the mass of a specimen. This also confirms the vulnerability of the grouted specimens.
15. The development of the above described method permits to solve the problem of mixed contaminated sites.
16. The results from the research can be applied for containments formulation in any site that is contaminated with heavy metal or organic products, or mixed contamination, before site remediation takes place.

5.3 Contribution

1. The first successful stabilization of soil contaminated with metal and PAHs were performed.
2. First successful application of combine (Sodium-Formamide-Calcium chloride) reagent in silica grout was introduced into contaminated soil.
3. Coefficient of Stability (CS) was introduced for the first time to assess grout performance.
4. Electrical measurement (resistivity) was introduced to assess indirectly the grouting process and stability of grout.
5. New method of calculation for grouted soil porosity was developed.

5.4 Recommendations for Using of Grouted Containments in Contaminated Soil

Several recommendations for further applications of the grouting method for contaminated soil are suggested based on the results:

1. Due to simultaneous applications of both reagents, the vulnerability of the barrier is lower. It is recommend using combination of both reagents.
2. It is suggested to use developed TERC model to assess potential release of contaminants and contaminants concentrations before grouting in the field. As well, organic, and inorganic components of soil should be determined because they may influence the behaviour of silica grouted specimens.
3. Preliminary tests should be carried out in the field in order to confirm the grouting parameters.
4. The formation of the grouted containment can be served the further soil remediation including bioremediation (Figure 5-1), pump and treat method, and soil washing.

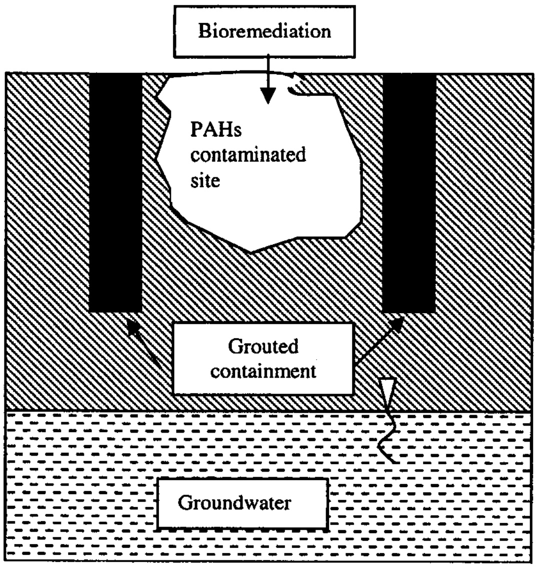


Figure 5-2 Application of grouted containment to protect groundwater and proceed with bioremediation (cross-section)

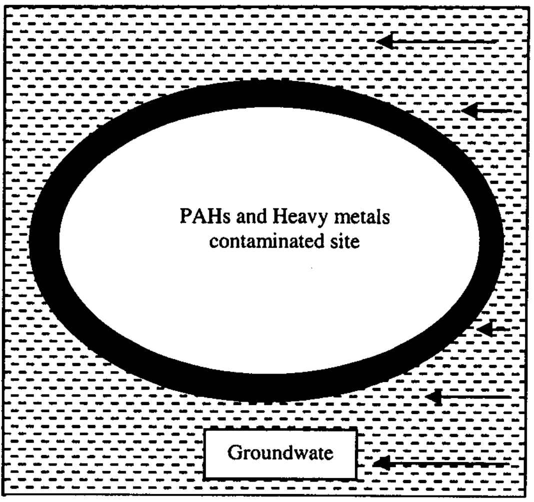


Figure 5-2 Application of containments to protect groundwater against spills (plan)

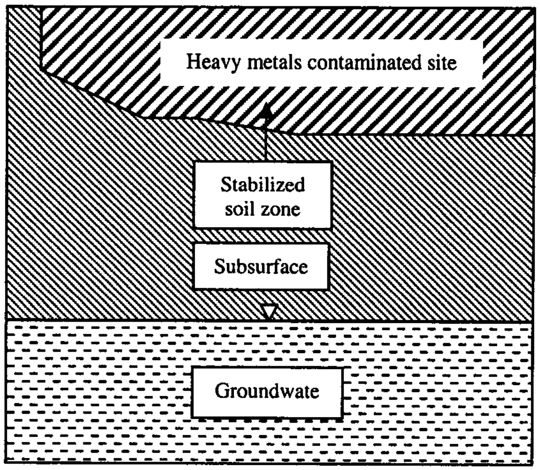


Figure 5-3 Application of grouted stabilization for contaminated site (cross-section)

5. Grouted containment (Figure 5-2) can be also use as a physical barrier to protect groundwater against accidental spills, liquids generated due to extinguishing of fire, and leachate from damaged landfill liners.
6. Grouting can also be used for stabilization of contaminated soils (Figure 5-3).

5.5 Future Research

1. The interaction of the grout with the chemicals reagent in groundwater should be investigated.
2. Research on grouting, the contaminated soil containing a high fraction of clay might be carried out.
3. The development and use of electrical resistivity devises for field measurement is recommended.
4. Validation of the TERC model using data from natural soil in field conditions.

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APPENDIX- A

CALCULATION OF SOIL RESISTIVITY IN DIFFERENT DAYS

Soil resistivity in mixed contaminated (nickel-phenanthrene) sandy soil in SF grout- An example of resistivity measurement

Day	**Current electrode**		**Potential electrode 1**		**Potential electrode 2**		**($\Delta\Phi$/I)**	**R = (2* π*a).($\Delta\Phi$/I) Ω.m**
	$U_{i\,max}$	$U_{i\,min}$	U_2S_{max}	U_2S_{min}	U_3S_{max}	U_3S_{min}		
1	1.11	-1.08	3.25	-3.15	3.55	-3.45	0.27	1.72
2	0.80	-0.80	2.25	-2.30	2.33	-2.33	0.07	0.43
4	0.81	-0.81	2.29	-2.26	2.67	-2.67	0.49	3.06
6	0.63	-0.63	2.20	-2.18	2.73	-2.66	0.80	5.03
8	0.73	-0.73	2.57	-2.45	3.08	-2.95	0.69	4.34
10	0.68	-0.69	2.67	-2.58	2.91	-2.75	0.30	1.87
12	0.43	-0.43	2.03	-1.94	2.41	-2.25	0.80	5.02
14	0.70	-0.69	2.62	-2.49	3.16	-2.98	0.74	4.64
16	0.56	-0.59	2.42	-2.51	2.82	-2.85	0.64	4.04
18	0.65	-0.67	2.66	-2.47	3.19	-2.97	0.78	4.88
20	0.63	-0.64	2.69	-2.57	3.27	-3.04	0.83	5.19
22	0.61	-0.62	2.75	-2.66	3.29	-3.12	0.81	5.09
24	0.65	-0.65	2.91	-2.81	3.45	-3.24	0.76	4.75
26	0.87	-0.87	2.84	-2.76	3.36	-3.15	0.52	3.28
28	0.98	-0.98	2.81	-2.74	3.31	-3.10	0.44	2.75
30	1.08	-1.09	2.78	-2.72	3.26	-3.05	0.37	2.35

APPENDIX- B

CALCULATION OF SOIL POROSITY IN DIFFERENT DAYS

Soil porosity in mixed contaminated (nickel-phenanthrene) sandy soil in SF grout- An example of tabulated calculation

Day	P (g)	M"$_0$ (g)	M_0 (g)	V0 $=\pi.r^2.h$ (cm^3)	$\delta_0 = M_0/V_0$ g/cm^3	G_s	$n_0 = 1 - (\delta_d)_o/(G_s.\delta_w)$	M"$_1$ (g)	M_1 (g)	V_1 $=\pi.r^2.h$ (cm^3)	δ_1	$W = (M_1 - M_o)/M_0$	$(\delta_d)_t = \delta_t/(1+W)$	$n_1 = 1 - (\delta_d)_t/(G_s.\delta_w)$	%n = (n_0- n1)/n0
1	40.00	215.82	175.82	107.37	1.64	2.65	0.382	226.92	186.92	101.09	1.85	0.11	1.66	0.372	0.03
2	40.00	215.82	175.82	107.37	1.64	2.65	0.38	227.62	187.62	99.47	1.89	0.12	1.69	0.363	0.05
4	40.00	215.82	175.82	107.37	1.64	2.65	0.38	227.98	187.98	97.85	1.92	0.12	1.71	0.354	0.07
6	40.00	215.82	175.82	107.37	1.64	2.65	0.38	226.23	186.23	90.15	2.07	0.10	1.87	0.294	0.23
8	40.00	215.82	175.82	107.37	1.64	2.65	0.38	228.67	188.67	90.15	2.09	0.13	1.85	0.300	0.21
10	40.00	215.82	175.82	107.37	1.64	2.65	0.38	227.91	187.91	90.15	2.08	0.12	1.86	0.298	0.22
12	40.00	215.82	175.82	107.37	1.638	2.65	0.382	226.62	186.62	90.15	2.070	0.108	1.868	0.295	0.228
14	40.00	215.82	175.82	107.37	1.638	2.65	0.382	228.67	188.67	90.15	2.093	0.1285	1.855	0.300	0.214
16	40.00	215.82	175.82	107.37	1.638	2.65	0.382	228.36	188.36	90.15	2.089	0.1254	1.857	0.299	0.216
18	40.00	215.82	175.82	107.37	1.638	2.65	0.382	228.08	188.08	90.15	2.086	0.1226	1.858	0.299	0.218
20	40.00	215.82	175.82	107.37	1.638	2.65	0.382	228.6	188.6	90.15	2.092	0.1278	1.855	0.300	0.215
22	40.00	215.82	175.82	107.37	1.638	2.65	0.382	228.26	188.26	90.15	2.088	0.1244	1.857	0.299	0.217
24	40.00	215.82	175.82	107.37	1.638	2.65	0.382	227.25	187.25	90.15	2.077	0.1143	1.864	0.297	0.224
26	40.00	215.82	175.82	107.37	1.638	2.65	0.382	228.16	188.16	90.15	2.087	0.1234	1.858	0.299	0.218
28	40.00	215.82	175.82	107.37	1.638	2.65	0.382	228.62	188.62	90.15	2.092	0.128	1.855	0.300	0.215
30	40.00	215.82	175.82	107.37	1.638	2.65	0.382	229.07	189.07	90.15	2.097	0.1325	1.852	0.301	0.212

APPENDIX- C

CALCULATION OF COEFFICIENT OF STABILITY IN DIFFERENT DAYS

Soil grading for SF grouted mixed contaminated sandy soil based on released soil particles- An example of tabulated data for CS

Day 6

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.17
0.500	35	155.47	67.62
0.300	50	175.42	50.07
0.250	60	168.286	33.24
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 8

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.17
0.500	35	155.47	67.62
0.300	50	175.42	50.07
0.250	60	168.218	33.24
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 10

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.17
0.500	35	155.47	67.62
0.300	50	175.42	50.07
0.250	60	168.185	33.24
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 12

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.17
0.500	35	155.47	67.61
0.300	50	175.42	50.06
0.250	60	167.974	33.25
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 14

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.59
0.300	50	175.42	50.03
0.250	60	167.833	33.23
0.090	140	290.44	4.15
0.075	200	39.56	0.19
0.053	270	1.919	0.00

Day 16

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.60
0.300	50	175.42	50.04
0.250	60	167.648	33.26
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 18

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.60
0.300	50	175.42	50.04
0.250	60	167.59	33.26
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 20

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.60
0.300	50	175.42	50.04
0.250	60	167.523	33.27
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 22

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.15
0.500	35	155.47	67.57
0.300	50	175.42	50.00
0.250	60	167.479	33.23
0.090	140	290.44	4.13
0.075	200	39.56	0.17
0.053	270	1.718	0.00

Day 24

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.59
0.300	50	175.42	50.03
0.250	60	167.443	33.27
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 26

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.59
0.300	50	175.42	50.03
0.250	60	167.409	33.27
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 28

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.59
0.300	50	175.42	50.03
0.250	60	167.396	33.27
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

Day 30

Particle size (mm)	ASTM E-11 selve no.	Mass retained on the selve (g)	f
1.000	18	0	100.00
0.850	20	168.25	83.16
0.500	35	155.47	67.59
0.300	50	175.42	50.03
0.250	60	167.385	33.27
0.090	140	290.44	4.19
0.075	200	39.56	0.23
0.053	270	2.32	0.00

APPENDIX- D

REDOX MEASUREMENT

RedOx measurement in different days

Sample no	Day 2 mV	Day 4 mV	Day 6 mV	Day 8 mV	Day 10 mV	Day 12 mV	Day 14 mV	Day 16 mV	Day 18 mV	Day 20 mV	Day 22 mV	Day 24 mV	Day 26 mV	Day 28 mV	Day 30 mV
1	-125	-128	-128	-129	-130	-129	-129	-130	-131	-125	-117	-120	-118	-113	-111
2	-123	-129	-130	-129	-125	-126	-128	-130	-131	-124	-119	-121	-117	-115	-113
3	-123	-128	-130	-129	-129	-132	-132	-132	-133	-130	-128	-126	-121	-120	-118
4	-132	-132	-133	-131	-133	-136	-135	-136	-138	-133	-130	-130	-125	-121	-119
5	-123	-123	-121	-120	-121	-127	-129	-130	-132	-131	-129	-125	-122	-118	-112
6	-131	-133	-131	-134	-134	-135	-130	-128	130	-128	-127	-124	-122	-119	-116
7	-124	-133	-130	-134	-133	-133	-134	-132	-132	-125	-121	-125	-123	-121	-117
8	-130	-131	-131	-133	-133	-135	-134	-133	-133	-132	-132	-125	-121	-122	-117
9	-132	-130	-131	-127	-127	-131	-130	-131	-134	-133	-132	-132	-130	-126	-122
10	-128	-119	-110	-89	-86	-85	-86	-90	-93	-97	-98	-98	-95	-105	-110
11	-127	-120	-109	-90	-87	-86	-86	-91	-93	-98	-98	-97	-96	-104	-104
12	-128	-119	-109	-88	-88	-87	-87	-90	-92	-97	-97	-98	-98	-106	-107
13	-126	-126	-127	-127	-129	-131	-130	-131	-131	-127	-123	-117	-115	-113	-111
14	-122	-128	-129	-129	-129	-130	-129	-130	-133	-131	-128	-122	-120	-118	-115
15	-122	-127	-128	-128	-131	-133	-133	-133	-134	-131	-128	-120	-119	-117	-114
16	-130	-136	-137	-138	-139	-140	-137	-136	-135	-129	-126	-121	-119	-118	-116
17	-131	-135	-133	-134	-134	-138	-138	-139	-142	-136	-127	-127	-123	-120	-117
18	-134	-137	-138	-135	-137	-141	-140	-137	-135	-138	-139	-139	-134	-131	-125
19	-128	-127	-128	-131	-129	-132	-130	-129	-127	-128	-129	-120	-119	-119	-119
20	-127	-120	-121	-126	-120	-131	-118	-125	-130	-127	-124	-121	-120	-117	-115
21	-128	-128	-130	-129	-128	-132	-131	-131	-132	-128	-125	-123	-121	-118	-111
22	-128	-124	-124	-130	-126	-130	-130	-129	-128	-126	-123	-121	-119	-118	-114
23	-127	-128	-128	-130	-130	-133	-134	-136	-138	-133	-130	-130	-127	-123	-120
24	-125	-126	-130	-133	-131	-135	-131	-133	-135	-133	-130	-122	-120	-119	-116
25	-127	-128	-130	-134	-130	-133	-132	-135	-136	-134	-130	-126	-124	-121	-119
26	-128	-125	-123	-130	-127	-130	-129	-130	-130	-129	-126	-123	-120	-115	-109
27	-126	-132	-130	-136	-133	-135	-135	-135	-138	-128	-121	-114	-112	-111	-108
28	-25	-40	-93	-48	-62	-73	-77	-82	-86	-84	-80	-79	-76	-72	-68
29	-21	-34	-47	-55	-63	-67	-70	-73	-75	-74	-73	-74	-75	-74	-75
30	-25	-40	-54	-59	-70	-78	-82	-85	-88	-78	-74	-76	-75	-74	-75
31	-38	-53	-64	-73	-79	-82	-84	-86	-87	-85	-83	-85	-80	-76	-75
32	-39	-52	-56	-63	-68	-76	-80	-85	-88	-86	-85	-81	-80	-79	-79
33	-43	-52	-60	-68	-76	-70	-79	-81	-82	-78	-74	-69	-72	-70	-69
34	-70	-59	-62	-73	-77	-87	-86	-89	-94	-89	-85	-82	-83	-84	-85
35	-82	-69	-72	-81	-86	-91	-93	-96	-98	-92	-89	-74	-76	-78	-79
36	-66	-51	-62	-70	-77	-85	-88	-90	-93	-90	-89	-83	-82	-80	-79

APPENDIX- E

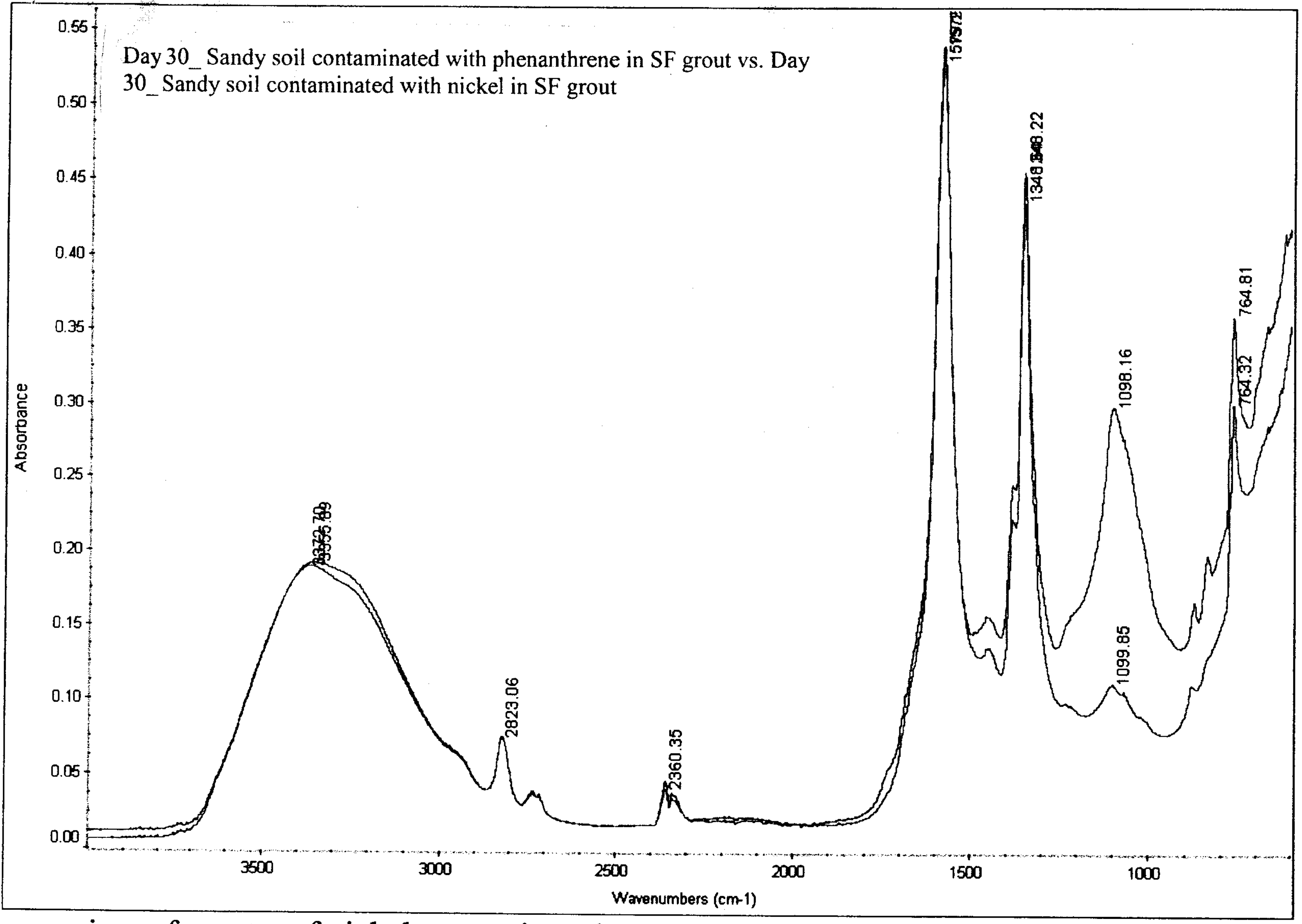
PH MEASUREMENT

pH measurement in different days

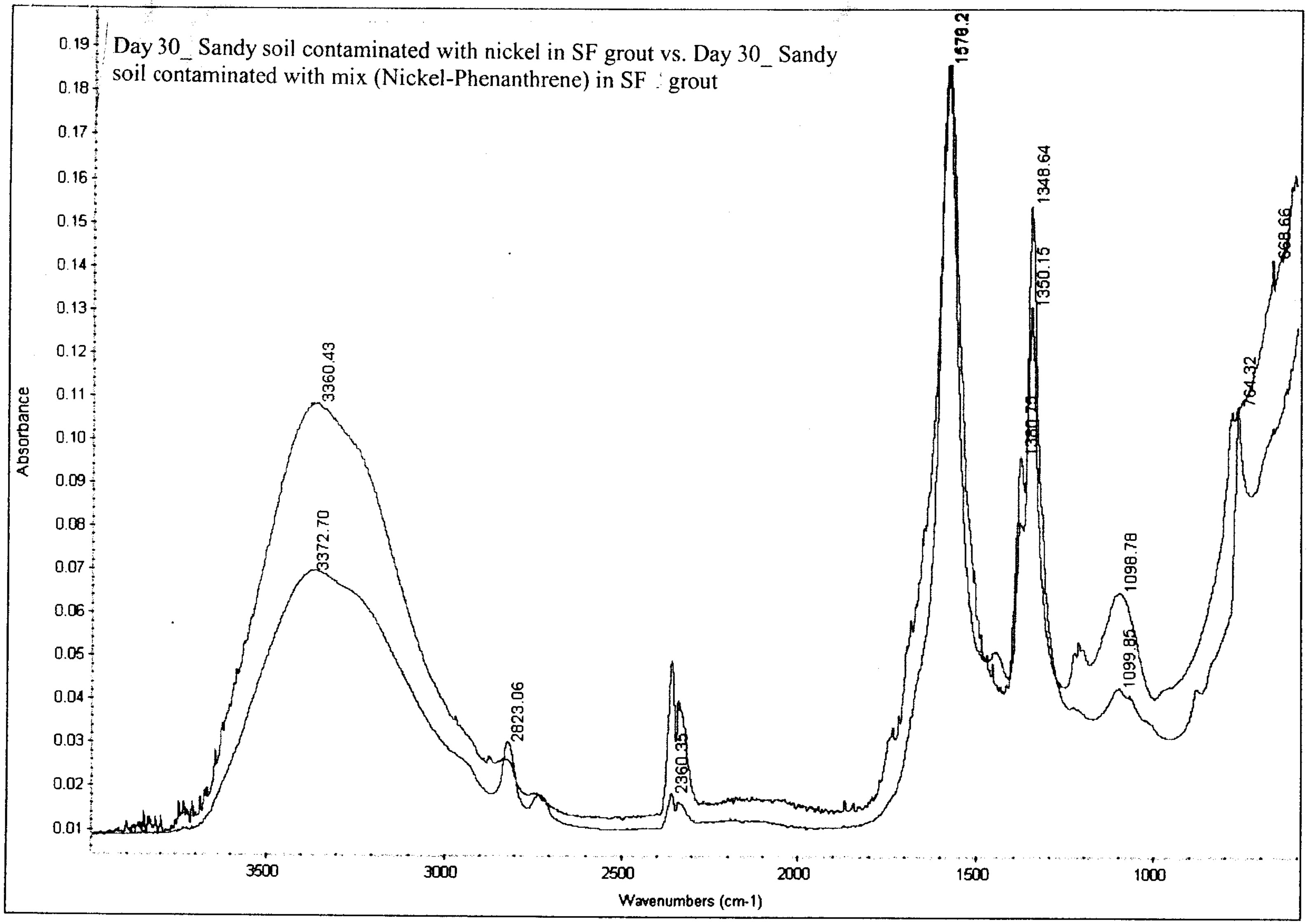
Sample no	Day 2	Day 4	Day 6	Day 8	Day 10	Day 12	Day 14	Day 16	Day 18	Day 20	Day 22	Day 24	Day 26	Day 28	Day 30
	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
1	9.85	9.76	9.78	9.85	9.87	9.85	9.84	9.85	9.87	9.8	9.73	9.77	9.65	9.58	9.51
2	9.8	9.8	9.86	9.81	9.77	9.81	9.84	9.87	9.9	9.85	9.78	9.74	9.71	9.63	9.56
3	9.75	9.8	9.87	9.81	9.85	9.9	9.92	9.92	9.92	9.86	9.83	9.81	9.75	9.69	9.66
4	9.87	9.88	9.94	9.87	9.94	10	9.97	10.01	10.04	9.96	9.9	9.9	9.8	9.72	9.69
5	9.72	9.69	9.71	9.67	9.72	9.81	9.85	9.89	9.91	9.89	9.86	9.79	9.74	9.71	9.68
6	9.84	9.87	9.9	9.93	9.94	9.98	9.87	9.85	9.83	9.82	9.82	9.77	9.72	9.69	9.63
7	9.88	9.88	9.93	9.91	9.94	9.94	9.96	9.92	9.9	9.85	9.72	9.7	9.68	9.64	9.66
8	9.83	9.85	9.89	9.88	9.93	9.97	9.95	9.94	9.92	9.84	9.8	9.75	9.71	9.65	9.63
9	9.89	9.83	9.89	9.77	9.82	9.98	9.88	9.92	9.97	9.86	9.76	9.81	9.78	9.76	9.74
10	9.63	9.66	9.45	9.18	9.06	9.04	9.07	9.14	9.22	9.32	9.25	9.25	9.23	9.47	9.49
11	9.61	9.68	9.43	9.17	9.11	9.1	9.11	9.18	9.23	9.32	9.31	9.31	9.31	9.38	9.41
12	9.63	9.62	9.45	9.21	9.09	9.1	9.09	9.17	9.21	9.29	9.31	9.29	9.29	9.43	9.45
13	9.8	9.75	9.81	9.78	9.84	9.89	9.87	9.83	9.78	9.76	9.75	9.67	9.64	9.6	9.54
14	9.75	9.8	9.85	9.82	9.84	9.88	9.87	9.91	9.95	9.9	9.87	9.74	9.7	9.63	9.61
15	9.74	9.78	9.82	9.8	9.88	9.94	9.92	9.94	9.97	9.9	9.84	9.72	9.69	9.64	9.6
16	9.87	9.94	9.97	10.01	10.03	10.05	10.03	9.99	9.97	9.89	9.82	9.71	9.69	9.66	9.62
17	9.87	9.95	9.91	9.93	9.95	10.03	10.02	10.04	10.01	9.92	9.81	9.85	9.79	9.74	9.64
18	9.95	9.99	10.01	9.95	9.98	10.07	10.07	10.02	10.02	10.04	10.06	10	9.92	9.87	9.8
19	9.8	9.82	9.83	9.85	9.85	9.93	9.88	9.85	9.82	9.83	9.85	9.74	9.72	9.71	9.68
20	9.8	9.72	9.72	9.77	9.69	9.72	9.67	9.72	9.79	9.74	9.69	9.65	9.64	9.62	9.6
21	9.81	9.86	9.87	9.89	9.83	9.93	9.89	9.9	9.91	9.83	9.78	9.78	9.69	9.61	9.54
22	9.8	9.78	9.75	9.85	9.79	9.87	9.9	9.87	9.83	9.79	9.76	9.7	9.67	9.63	9.6
23	9.81	9.84	9.83	9.84	9.87	9.93	9.95	9.97	10	9.93	9.87	9.89	9.84	9.78	9.71
24	9.77	9.74	9.87	9.92	9.88	9.96	9.88	9.93	9.98	9.91	9.88	9.74	9.71	9.68	9.62
25	9.8	9.78	9.87	9.92	9.87	9.94	9.93	9.95	9.99	9.91	9.88	9.82	9.78	9.74	9.69
26	9.83	9.73	9.74	9.86	9.82	9.87	9.85	9.86	9.88	9.84	9.8	9.75	9.66	9.6	9.5
27	9.81	9.9	9.87	9.99	9.91	9.99	9.97	9.99	10.01	9.97	9.92	9.59	9.57	9.52	9.48
28	8	8.24	8.48	8.37	8.6	8.84	8.92	9.02	9.07	9.04	9.01	8.95	8.89	8.84	8.76
29	7.89	8.12	8.35	8.48	8.63	8.77	8.79	8.84	8.88	8.86	8.85	8.86	8.82	8.8	8.82
30	7.92	8.22	8.47	8.55	8.74	8.94	9	9.07	9.1	8.99	8.87	8.89	8.88	8.89	8.88
31	8.19	8.43	8.68	8.82	8.93	9.03	9.05	9.06	9.08	9.06	9.02	9.07	8.99	8.92	8.88
32	8.22	8.43	8.54	8.64	8.72	8.9	8.97	9.05	9.14	9.1	9.07	9.04	9.03	9.01	8.95
33	8.28	8.46	8.6	8.75	8.87	8.79	8.95	8.99	9.01	8.94	8.87	8.77	8.78	8.78	8.78
34	8.81	8.57	8.72	8.82	8.88	9.08	9.08	9.08	9.1	9.08	9.05	9.04	9.02	9.06	9.05
35	9.01	8.74	8.82	8.98	9.08	9.19	9.22	9.25	9.26	9.18	9.08	8.89	8.82	8.78	8.95
36	8.72	8.45	8.65	8.77	8.91	9.06	9.11	9.17	9.22	9.17	9.13	9.02	8.96	8.94	8.96

APPENDIX- F

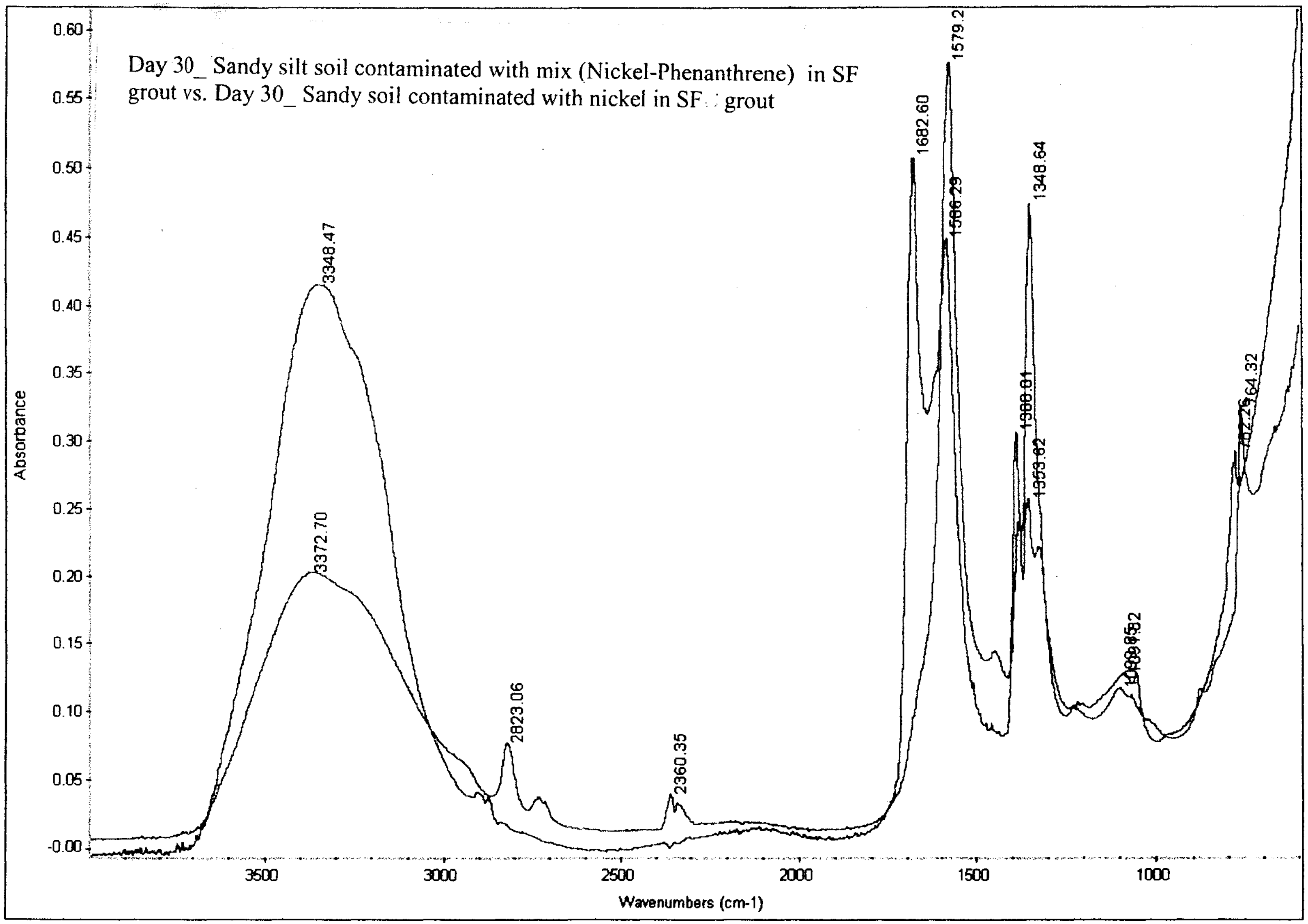
ANALYSIS OF FTIR SPECTRA



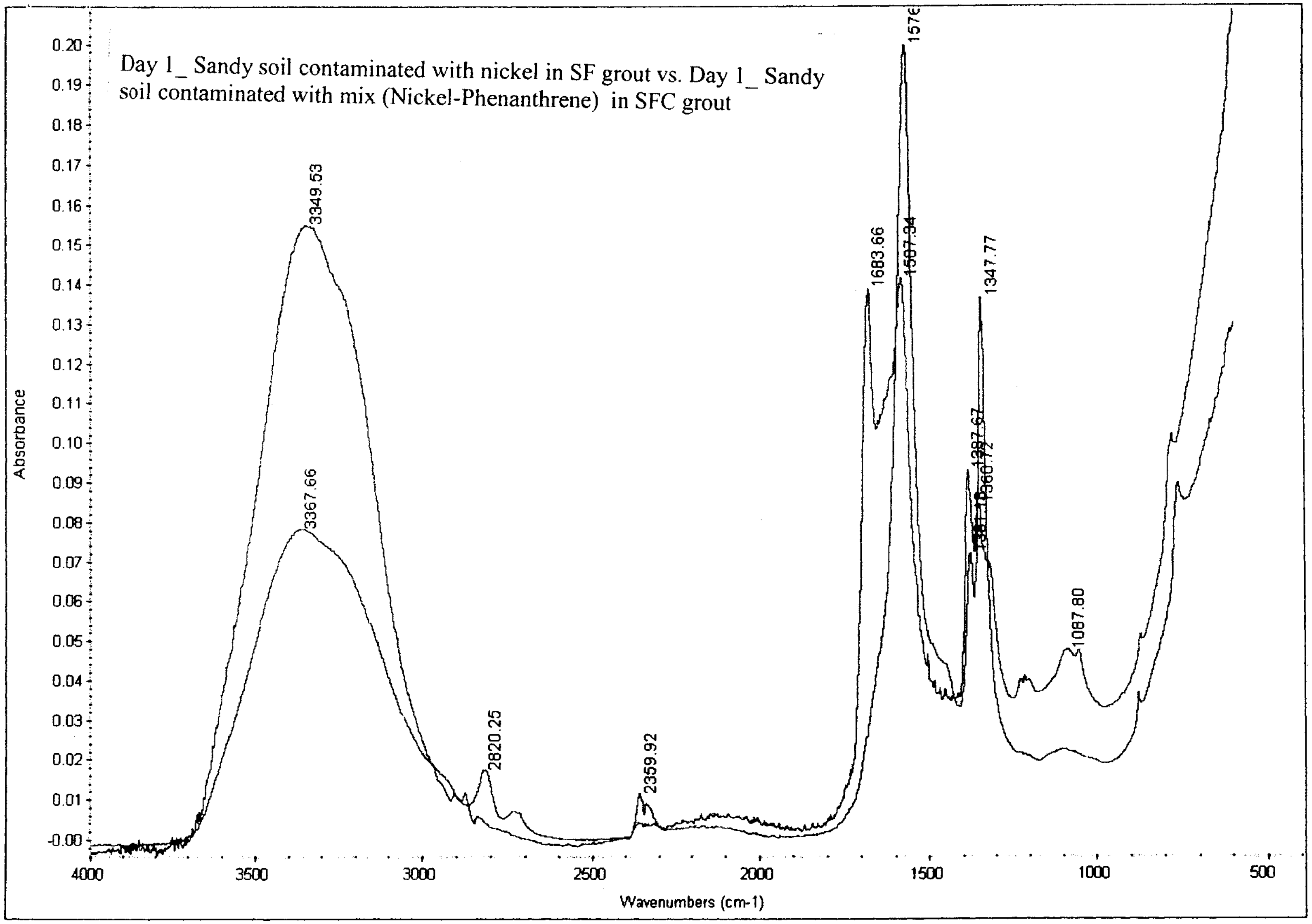
Comparison of spectra of nickel contaminated sandy soil in SF grout at day 30 vs. Phenanthrene contaminated sandy soil in SF grout at Day 30



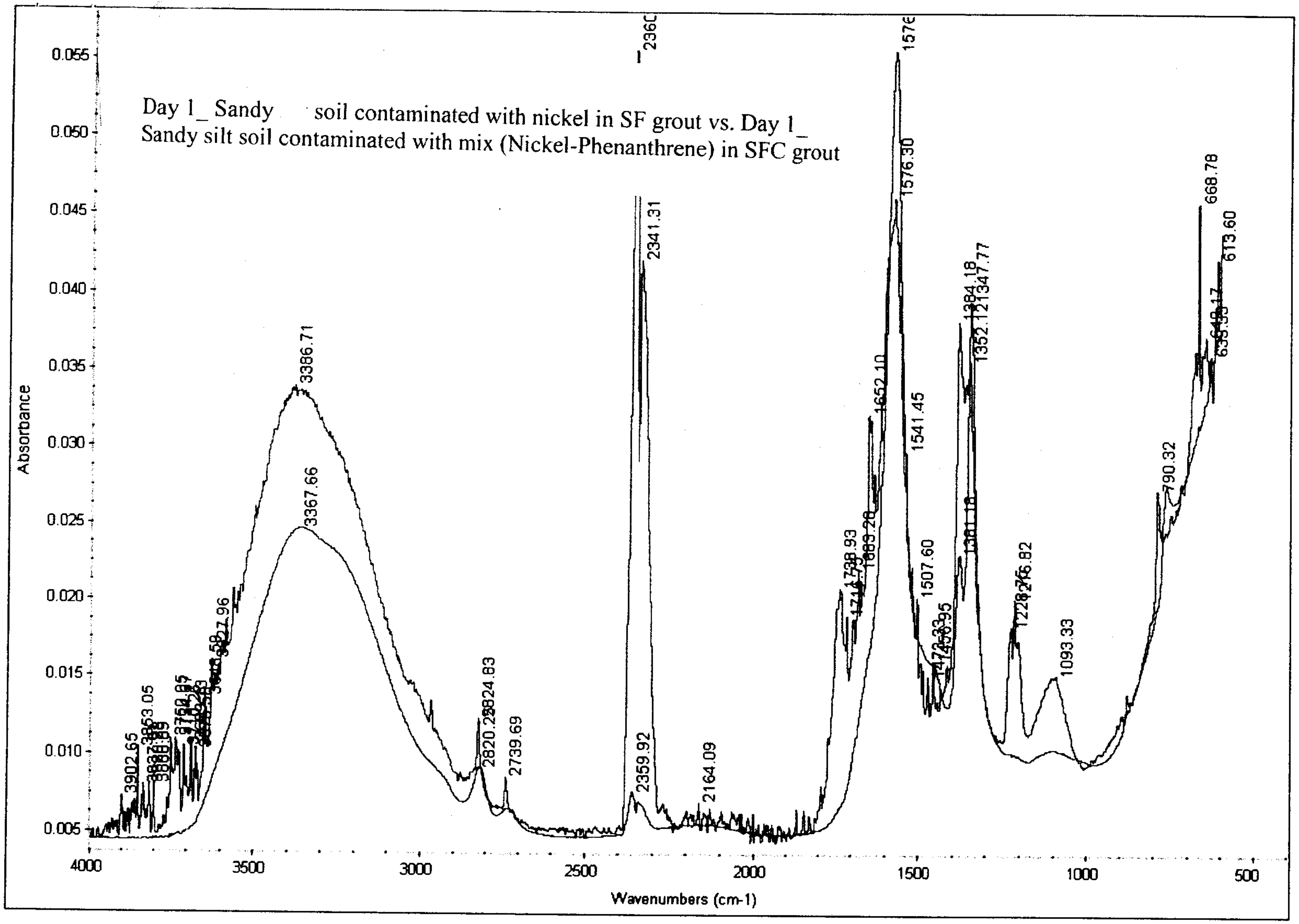
Comparison of spectra of nickel contaminated sandy soil in SF grout at day 30 vs. mix contaminated sandy soil in SF grout at Day 30



Comparison of spectra of nickel contaminated sandy soil in SF grout at day 30 vs. mix contaminated sandy silt soil in SF grout at Day 30



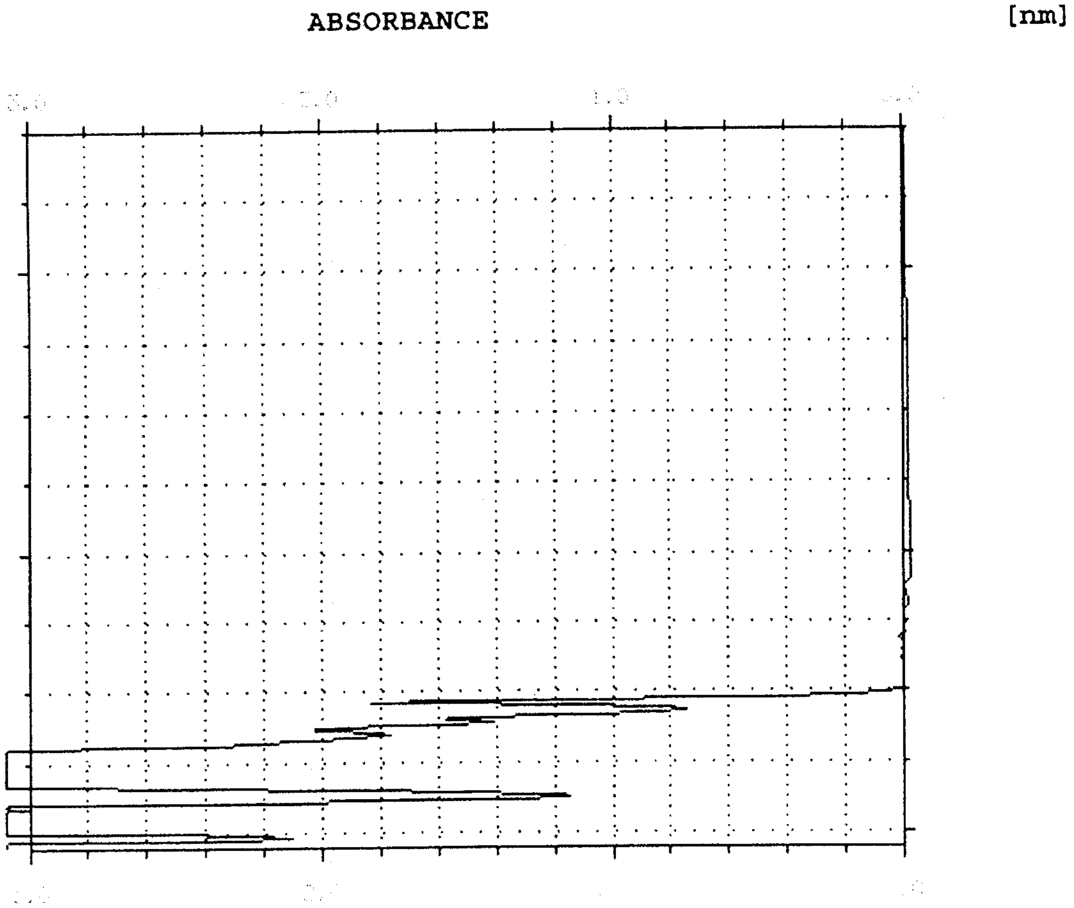
Comparison of spectra of nickel contaminated sandy soil in SF grout at day 30 vs. mix contaminated sandy soil in SFC grout at Day 30



Comparison of spectra of nickel contaminated sandy soil in SF grout at day 30 vs. mix contaminated sandy silt soil in SFC grout at Day 30

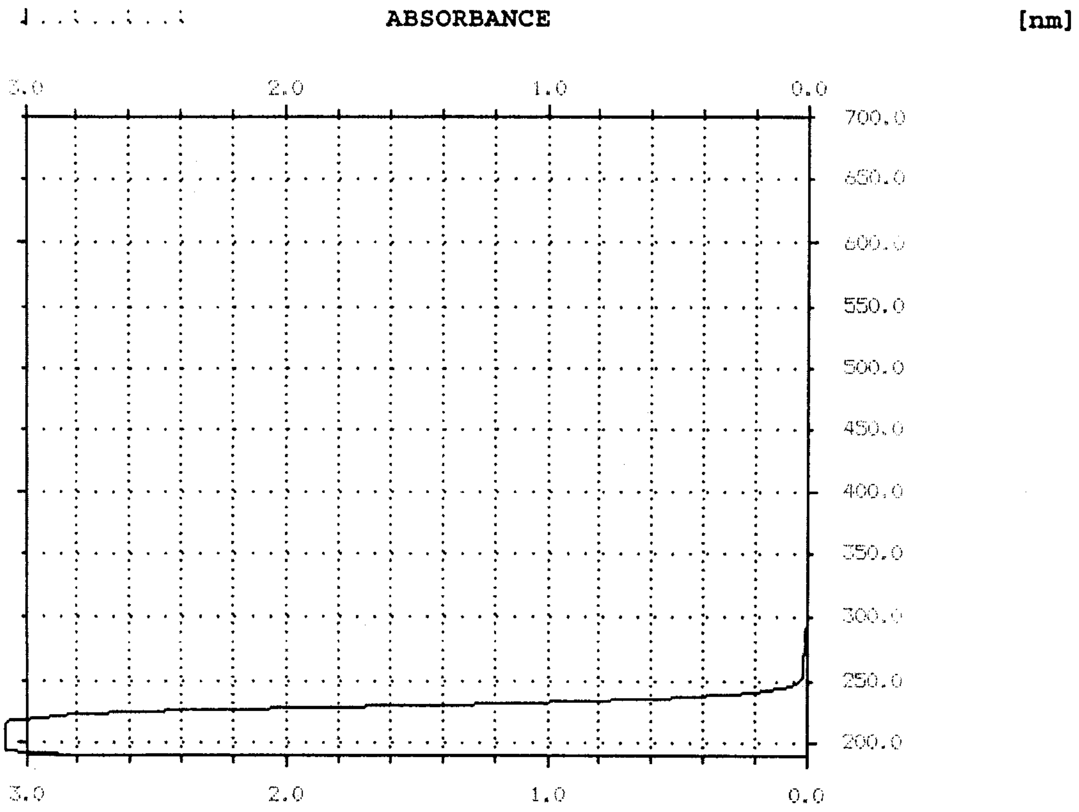
APPENDIX- G

UV-VIS ANALYSIS



```
005        17:50        292.4 nm (MAX)        1.834  A
                        286.8 nm (MIN)        0.748  A
                        280.4 nm (MAX)        1.573  A
                        278.0 nm (MIN)        1.410  A
                        273.6 nm (MAX)        2.038  A
                        269.6 nm (MIN)        1.771  A
                        236.0 nm (MAX)        6.160  A
                        225.2 nm (MIN)        1.150  A
                        220.0 nm (MAX)        3.269  A
                        218.0 nm (MIN)        3.004  A
                        215.2 nm (MAX)        6.163  A
                        214.8 nm (MIN)        6.000  A
                        202.4 nm (MAX)        6.158  A
                        196.8 nm (MIN)        2.104  A
                        193.2 nm (MAX)        6.260  A
```

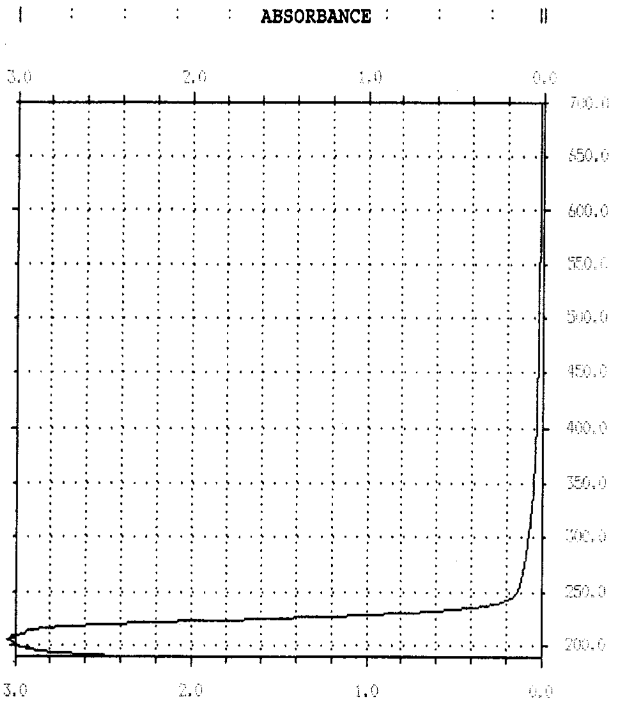
Phenanthrene in Hexene- standard



```
001       16:54       196.8 nm (MAX)       3.361   A
```

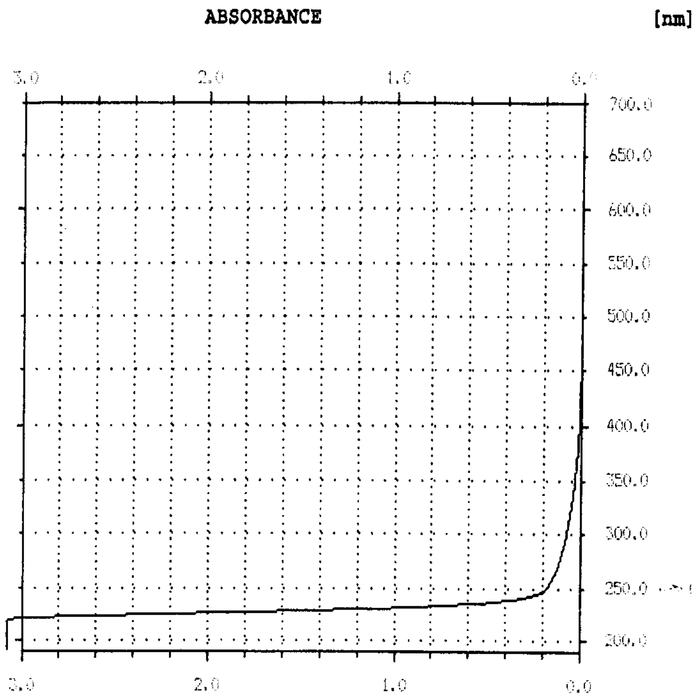
Formamide in water- standard

An example of UV-Vis absorbance of mix contaminated sandy soil specimens at different days



```
001      15:32      206.0 nm (MAX)      3.047  A
```

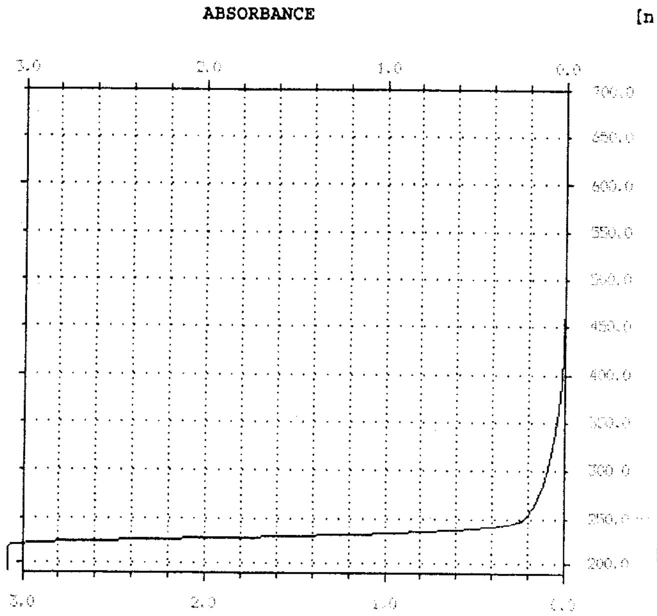
Day 1



```
THRESHOLD :  0.100

  SAMPLE     TIME      WAVELENGTH          DATA
   004      13:39    206.8 nm (MAX)      4.774  A
                     206.0 nm (MIN)      4.347  A
```

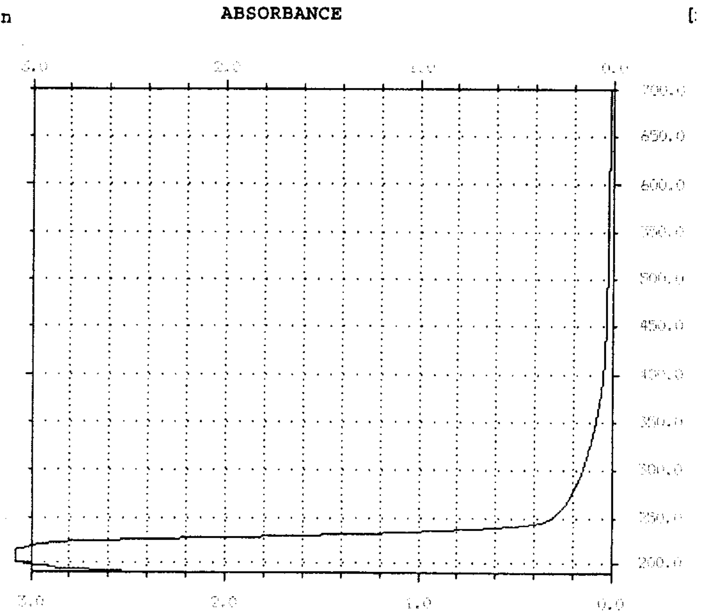
Day 10



```
THRESHOLD :  0.100

  SAMPLE     TIME      WAVELENGTH          DATA
   014      14:17    199.6 nm (MAX)      3.544  A
                     198.0 nm (MIN)      3.440  A
                     196.4 nm (MAX)      3.570  A
```

Day 20

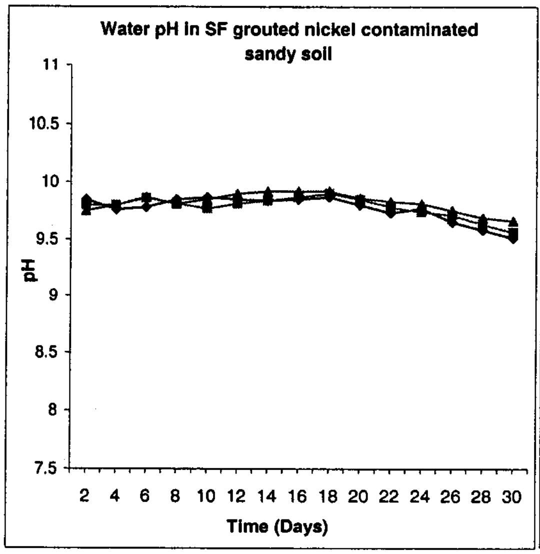


```
002      15:34      206.8 nm (MAX)      3.141  A
```

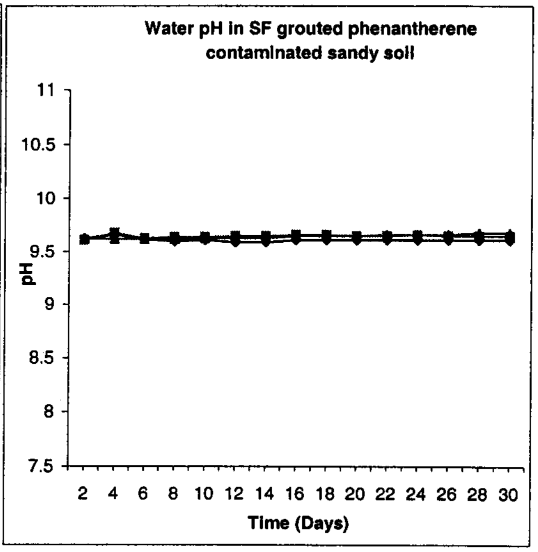
Day 30

APPENDIX- H

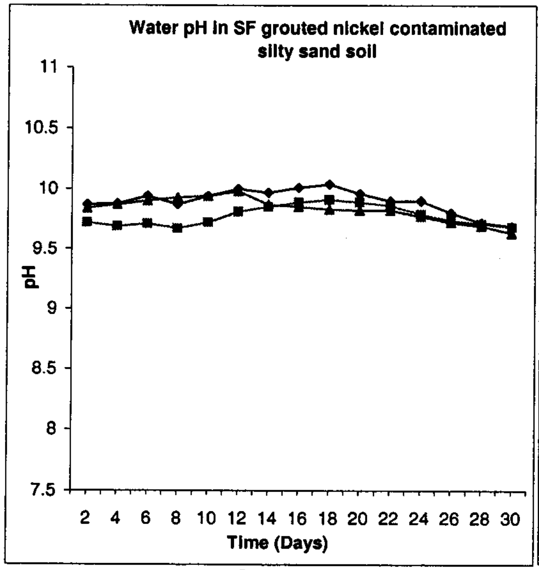
PH GRAPHS


Water pH in SF grouted nickel contaminated sandy soil
pH
11
10.5
10
9.5
9
8.5
8
7.5
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time (Days)

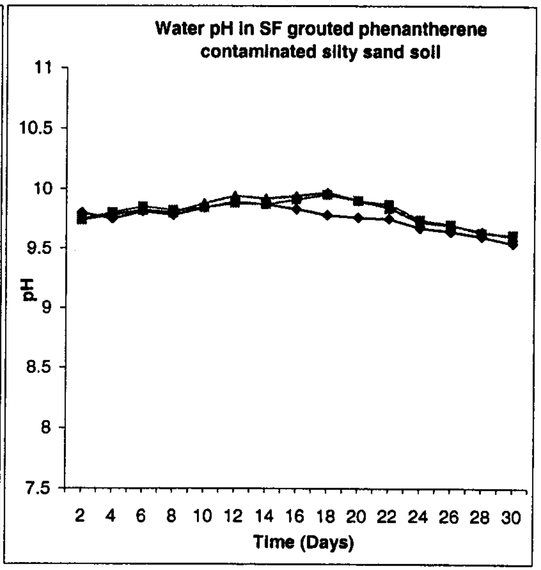
1


Water pH in SF grouted phenantherene contaminated sandy soil
pH
11
10.5
10
9.5
9
8.5
8
7.5
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time (Days)

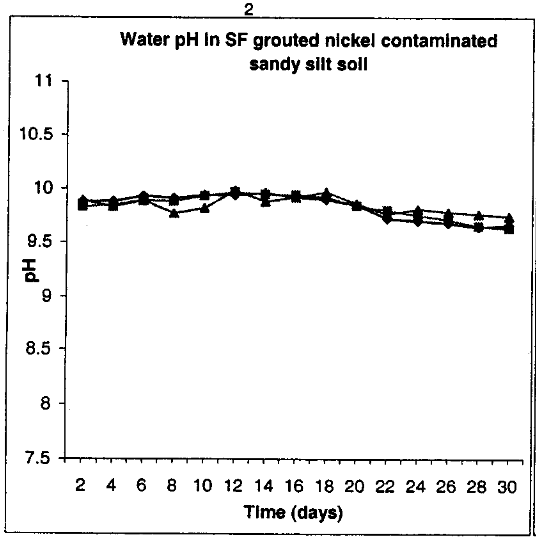
4


Water pH in SF grouted nickel contaminated silty sand soil
pH
11
10.5
10
9.5
9
8.5
8
7.5
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time (Days)

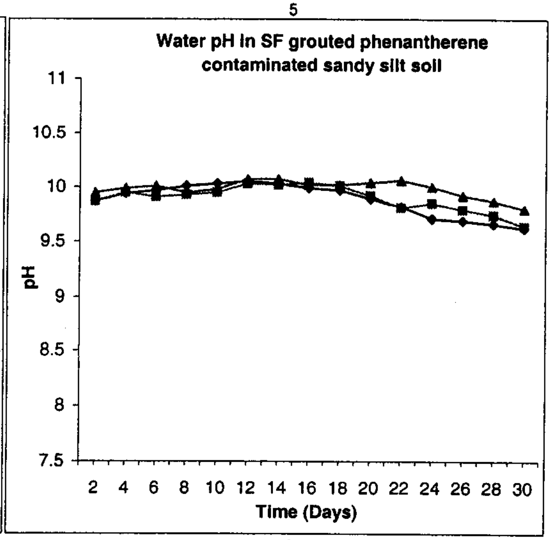
2


Water pH in SF grouted phenantherene contaminated silty sand soil
pH
11
10.5
10
9.5
9
8.5
8
7.5
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time (Days)

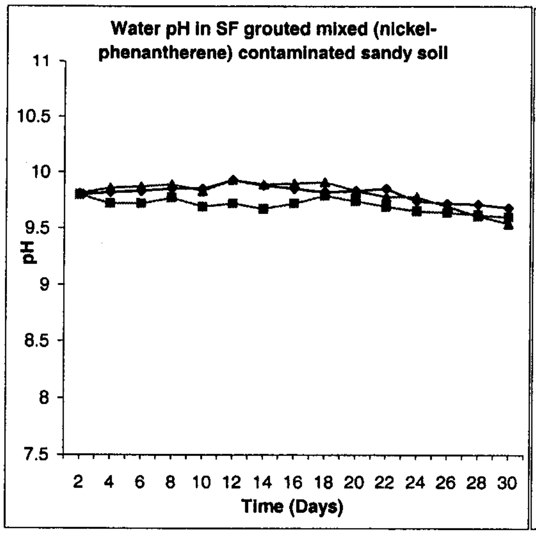
5


Water pH in SF grouted nickel contaminated sandy silt soil
pH
11
10.5
10
9.5
9
8.5
8
7.5
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time (days)

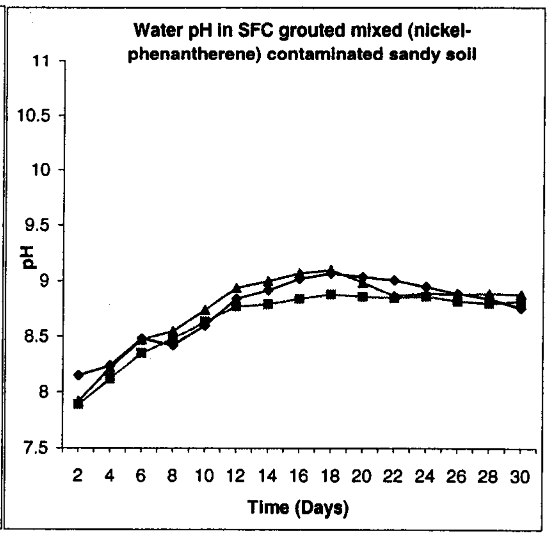
3


Water pH in SF grouted phenantherene contaminated sandy silt soil
pH
11
10.5
10
9.5
9
8.5
8
7.5
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time (Days)

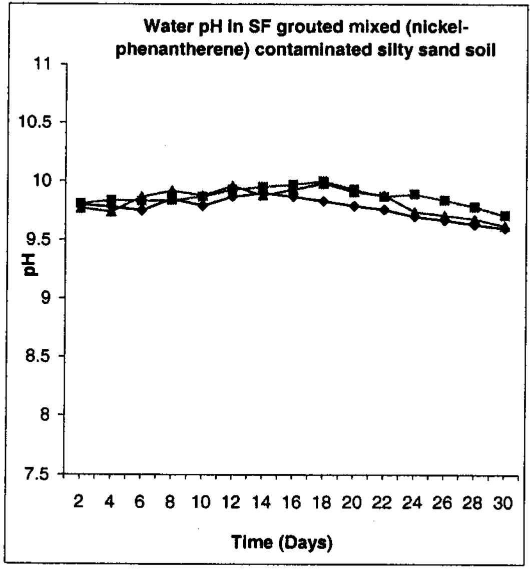
6


Water pH in SF grouted mixed (nickel-phenantherene) contaminated sandy soil

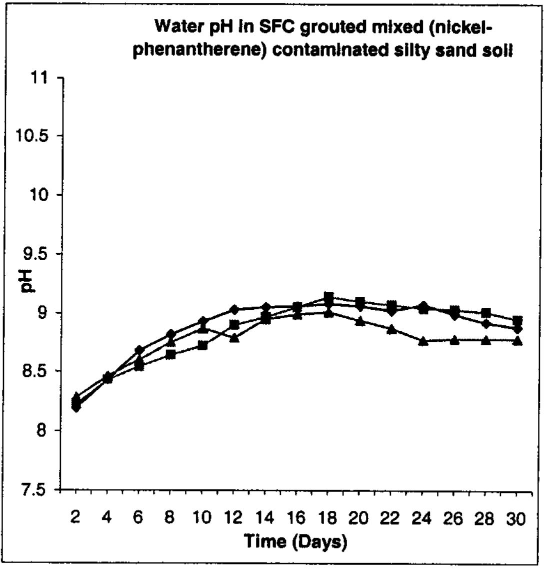
7


Water pH in SFC grouted mixed (nickel-phenantherene) contaminated sandy soil

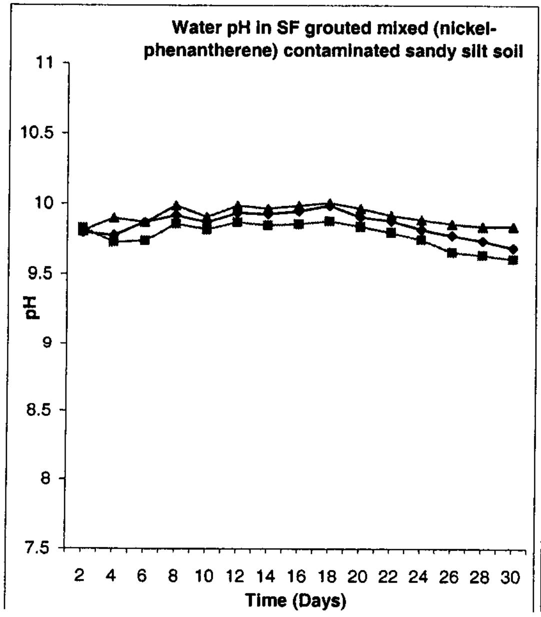
10

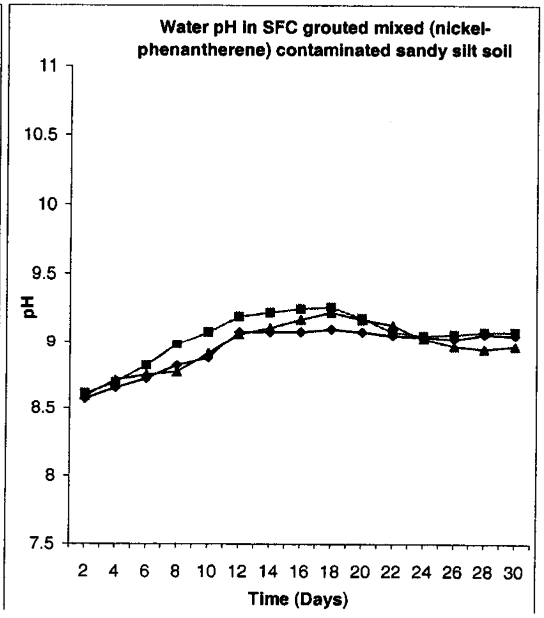

Water pH in SF grouted mixed (nickel-phenantherene) contaminated silty sand soil

8


Water pH in SFC grouted mixed (nickel-phenantherene) contaminated silty sand soil

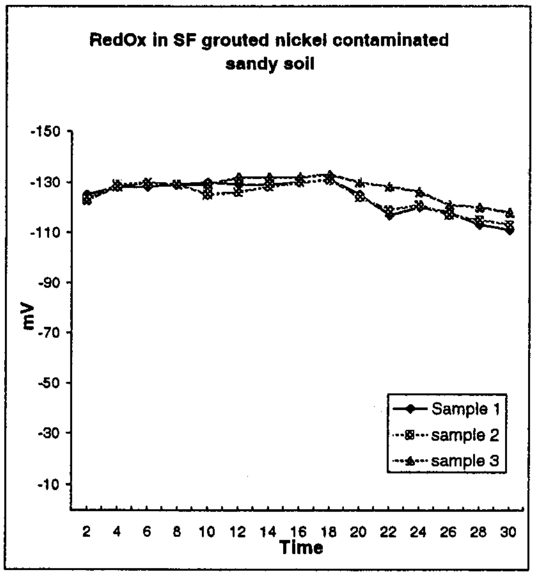
11


Water pH in SF grouted mixed (nickel-phenantherene) contaminated sandy silt soil

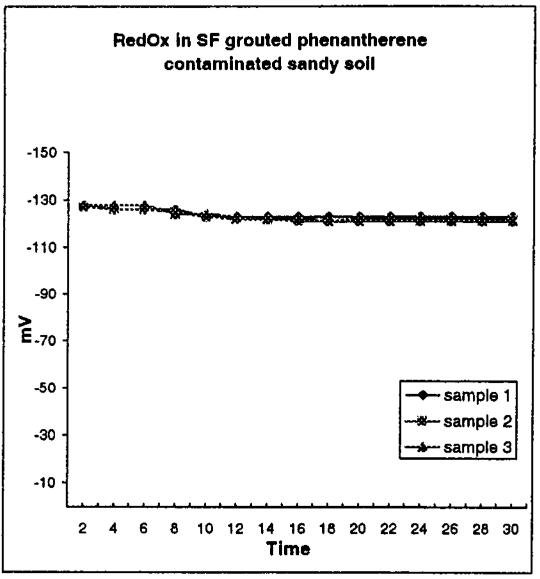

Water pH in SFC grouted mixed (nickel-phenantherene) contaminated sandy silt soil

APPENDIX- I

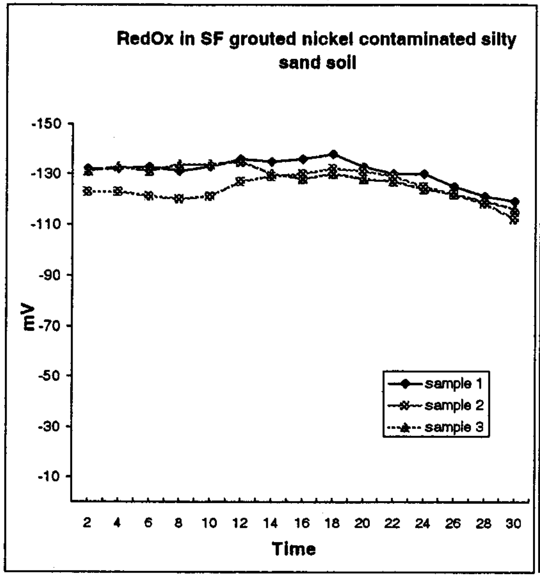
REDOX GRAPHS


RedOx in SF grouted nickel contaminated sandy soil
-150
-130
-110
-90
-70
-50
-30
-10
mV
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
Sample 1
sample 2
sample 3

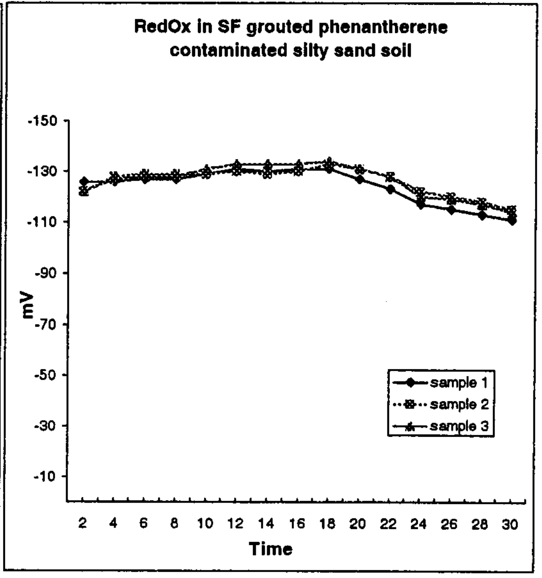
1


RedOx in SF grouted phenantherene contaminated sandy soil
-150
-130
-110
-90
-70
-50
-30
-10
mV
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

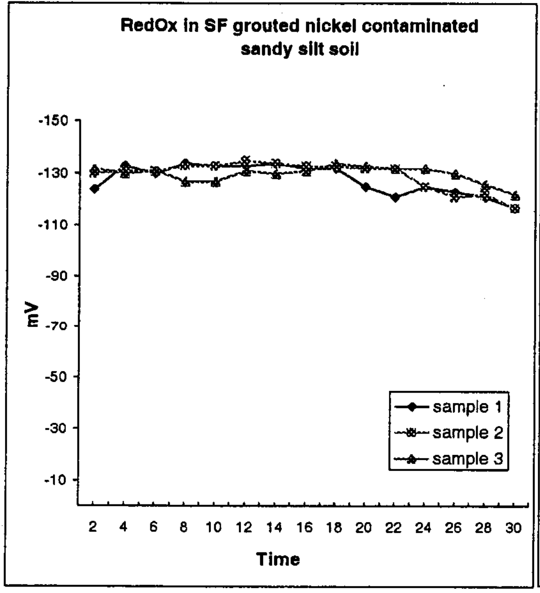
4


RedOx in SF grouted nickel contaminated silty sand soil
-150
-130
-110
-90
-70
-50
-30
-10
mV
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

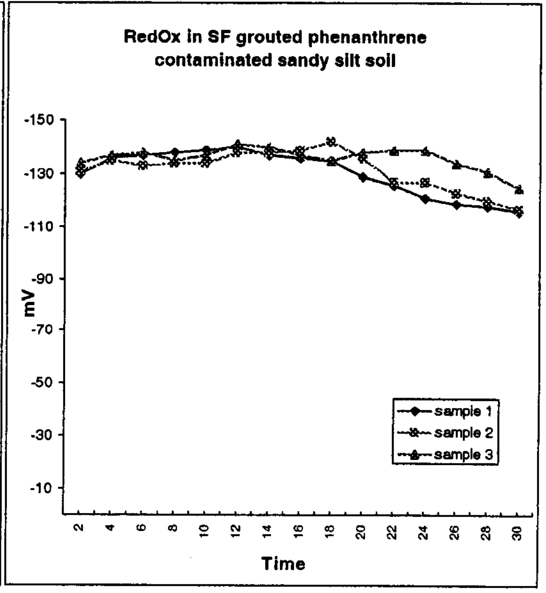
2


RedOx in SF grouted phenantherene contaminated silty sand soil
-150
-130
-110
-90
-70
-50
-30
-10
mV
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

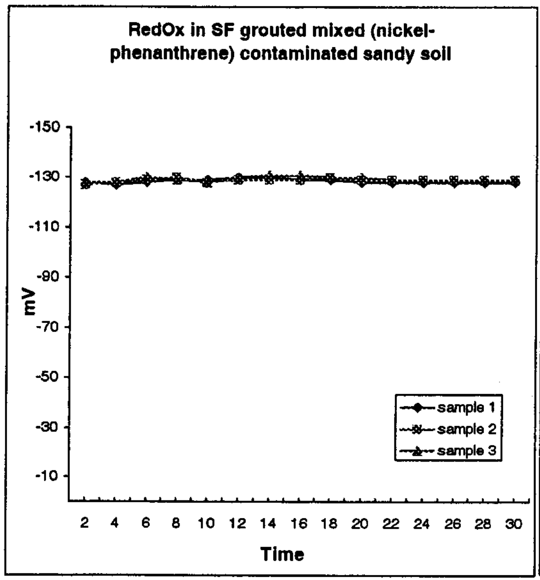
5


RedOx in SF grouted nickel contaminated sandy silt soil
-150
-130
-110
-90
-70
-50
-30
-10
mV
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

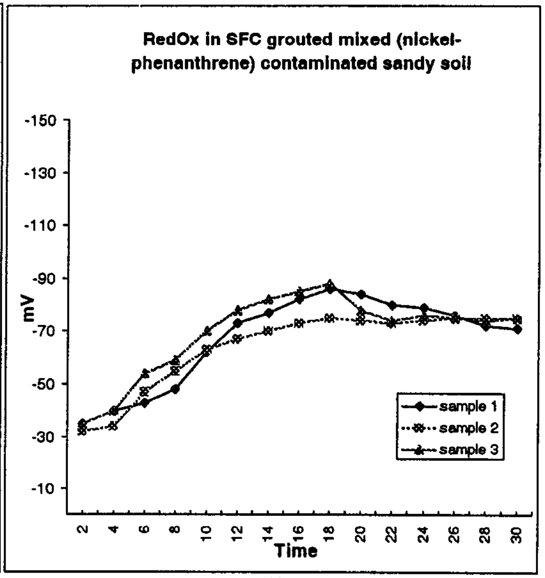
3


RedOx in SF grouted phenanthrene contaminated sandy silt soil
-150
-130
-110
-90
-70
-50
-30
-10
mV
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

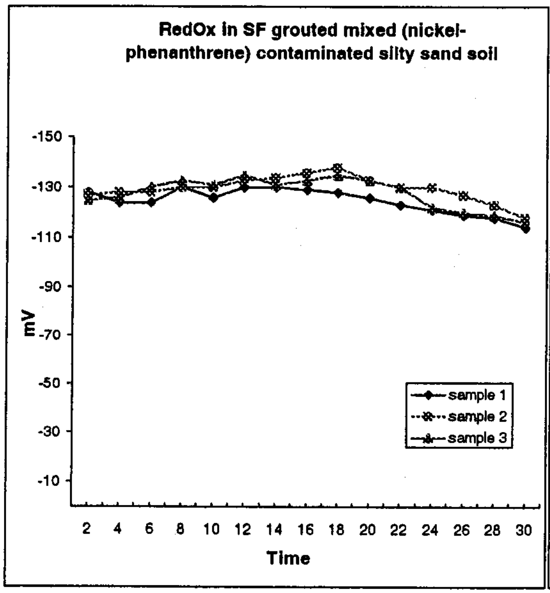
6


RedOx in SF grouted mixed (nickel-phenanthrene) contaminated sandy soil
mV
-150
-130
-110
-90
-70
-50
-30
-10
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

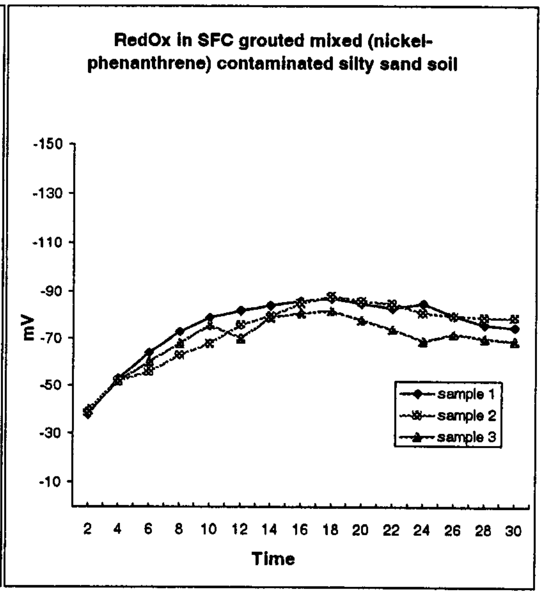
7


RedOx in SFC grouted mixed (nickel-phenanthrene) contaminated sandy soil
mV
-150
-130
-110
-90
-70
-50
-30
-10
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

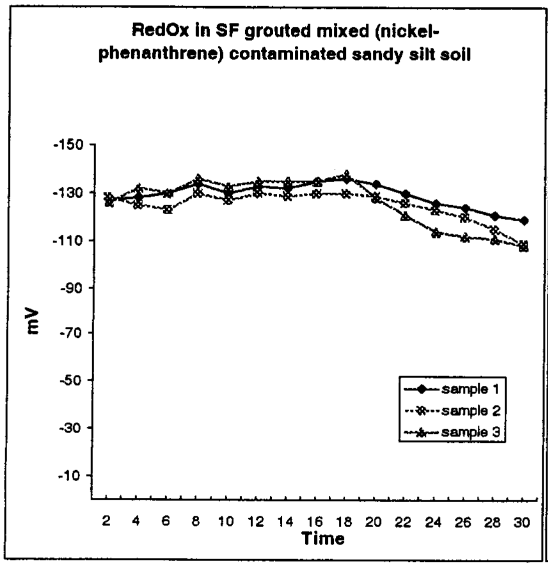
10


RedOx in SF grouted mixed (nickel-phenanthrene) contaminated silty sand soil
mV
-150
-130
-110
-90
-70
-50
-30
-10
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

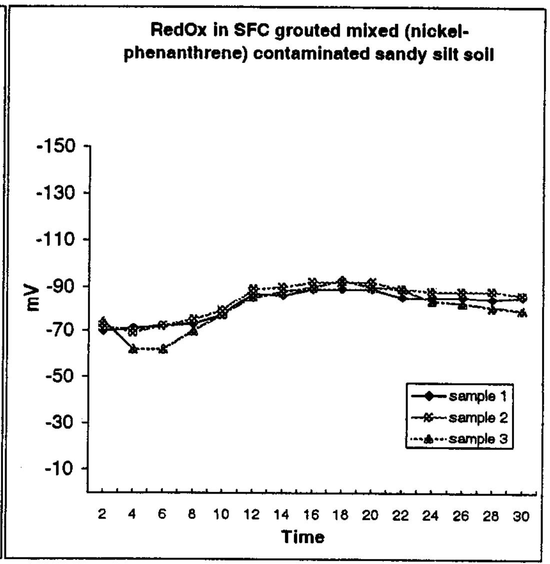
8


RedOx in SFC grouted mixed (nickel-phenanthrene) contaminated silty sand soil
mV
-150
-130
-110
-90
-70
-50
-30
-10
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

11


RedOx in SF grouted mixed (nickel-phenanthrene) contaminated sandy silt soil
mV
-150
-130
-110
-90
-70
-50
-30
-10
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

9


RedOx in SFC grouted mixed (nickel-phenanthrene) contaminated sandy silt soil
mV
-150
-130
-110
-90
-70
-50
-30
-10
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Time
sample 1
sample 2
sample 3

12

APPENDIX- J

CALCULATION OF RELEASE USING TERC MODEL

Calculation of De for sandy soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m)
1.0000	0.0010	8.00	8000.00	
0.8318	0.0009	8.00	7828.71	
0.6763	0.0005	8.00	10820.80	
0.5009	0.0003	8.00	13357.33	**0.0000181**
0.3323	0.0003	8.00	10633.60	
0.0419	0.0001	8.00	3724.44	
0.0023	0.0001	25.00	766.67	
			55131.55	

Calculation of De for sandy silt soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m)
1.0000	0.0012	8.00	8000.00	
0.9703	0.0010	8.00	9132.24	
0.9437	0.0009	8.00	15099.20	
0.8011	0.0005	8.00	21362.67	**0.0000026**
0.6994	0.0003	8.00	22380.80	
0.6029	0.0003	8.00	53591.11	
0.4995	0.0001	25.00	166500.00	
0.2588	0.0001	25.00	86266.67	
			382332.68	

Day 1

sample	R (mg/L)	C (mg/L)	n (%)	G (ml/ml)	Ce (s/m)	ρw (kg/m^3)	g (m/s^2)	St (cm/cm)	De (m)	Pe	ζt (kg/m.s^2)	ζc (kg/m.s^2)	ξe (kg/m^2/s)	A_1 (kg/m^2/s)
Nickel contaminated sandy soil in SF grout	1	1000	37.20	44.16	0.04978	1000.00	9.81	1.40	0.00001814	0.000043	0.1476484	0.00030	0.007335	0.0000087
Nickel contaminated sandy silt soil in SF grout	2	1000	37.24	40.50	0.04978	1000.00	9.81	1.40	0.00000262	0.000006	0.0213243	0.00009	0.001057	0.0000023
Mixed (N-P) contaminated sandy soil in SF grout	1	1000	37.19	44.16	0.04978	1000.00	9.81	1.40	0.00001814	0.000043	0.1476131	0.00030	0.007333	0.0000087
Mixed (N-P) contaminated sandy silt soil in SF grout	2	1000	36.26	40.50	0.04978	1000.00	9.81	1.40	0.00000262	0.000006	0.0204445	0.00009	0.001013	0.0000023
Mixed (N-P) contaminated sandy soil in SFC grout	4	1000	38.66	44.16	0.04978	1000.00	9.81	1.40	0.00001814	0.000046	0.1570682	0.00030	0.007804	0.0000357
Mixed (N-P) contaminated sandy silt soil in SFC grout	4	1000	38.00	40.50	0.04978	1000.00	9.81	1.40	0.00000262	0.000006	0.0220275	0.00009	0.001092	0.0000047

Calculation of De for sandy soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m/%)
1.0000	0.0010	8.00	8000.00	
0.8318	0.0009	8.00	7828.71	
0.6763	0.0005	8.00	10820.80	
0.5009	0.0003	8.00	13357.33	0.0000181
0.3323	0.0003	8.00	10633.60	
0.0419	0.0001	8.00	3724.44	
0.0023	0.0001	25.00	766.67	
			55131.55	

Calculation of De for sandy silt soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m/%)
1.0000	0.0012	8.00	8000.00	
0.9703	0.0010	8.00	9132.24	
0.9437	0.0009	8.00	15099.20	
0.8011	0.0005	8.00	21362.67	0.0000026
0.6994	0.0003	8.00	22380.80	
0.6029	0.0003	8.00	53591.11	
0.4995	0.0001	25.00	166500.00	
0.2588	0.0001	25.00	86266.67	
			382332.68	

Day 10

sample	R (mg/L)	C (mg/L)	n (%)	G (ml/ml)	Ce (s/m)	ρw (kg/m^3)	g (m/s^2)	St (cm/cm)	De (m)	Pe	ζt (kg/m.s^2)	ζc (kg/m.s^2)	ξe (kg/m^2/s)	A_{10} (kg/m^2/s)
Nickel contaminated sandy soil in SF grout	3	1000	29.400	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003021	0.1163935	0.00030	0.005779	0.0000260
Nickel contaminated sandy silt soil in SF grout	4	1000	29.500	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000438	0.0168647	0.00009	0.000835	0.0000046
Mixed (N-P) contaminated sandy soil in SF grout	3	1000	29.800	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003080	0.1186493	0.00030	0.005891	0.0000262
Mixed (N-P) contaminated sandy silt soil in SF grout	4	1000	28.900	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000425	0.0163822	0.00009	0.000811	0.0000045
Mixed (N-P) contaminated sandy soil in SFC grout	5	1000	31.100	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003275	0.1261616	0.00030	0.006265	0.0000445
Mixed (N-P) contaminated sandy silt soil in SFC grout	6	1000	30.900	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000468	0.0180229	0.00009	0.000893	0.0000070

Calculation of De for sandy soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m/%)
1.0000	0.0010	8.00	8000.00	
0.8318	0.0009	8.00	7828.71	
0.6763	0.0005	8.00	10820.80	
0.5009	0.0003	8.00	13357.33	**0.0000181**
0.3323	0.0003	8.00	10633.60	
0.0419	0.0001	8.00	3724.44	
0.0023	0.0001	25.00	766.67	
			55131.55	

Calculation of De for sandy silt soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m/%)
1.0000	0.0012	8.00	8000.00	
0.9703	0.0010	8.00	9132.24	
0.9437	0.0009	8.00	15099.20	
0.8011	0.0005	8.00	21362.67	**0.0000026**
0.6994	0.0003	8.00	22380.80	
0.6029	0.0003	8.00	53591.11	
0.4995	0.0001	25.00	166500.00	
0.2588	0.0001	25.00	86266.67	
			382332.68	

Day 20

sample	R (mg/L)	C (mg/L)	n (%)	G (ml/ml)	Ce (s/m)	ρw (kg/m^3)	g (m/s^2)	St (cm/cm)	De (m)	Pe	ζt (kg/m.s^2)	ζe (kg/m.s^2)	ξe (kg/m^2/s)	A_{20} (kg/m^2/s)
Nickel contaminated sandy soil in SF grout	3	1000	29.300	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003007	0.1158335	0.00030	0.005751	0.0000260
Nickel contaminated sandy silt soil in SF grout	4	1000	29.700	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000442	0.0170273	0.00009	0.000843	0.0000046
Mixed (N-P) contaminated sandy soil in SF grout	3	1000	30.000	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003109	0.1197869	0.00030	0.005948	0.0000263
Mixed (N-P) contaminated sandy silt soil in SF grout	4	1000	28.900	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000425	0.0163822	0.00009	0.000811	0.0000045
Mixed (N-P) contaminated sandy soil in SFC grout	6	1000	31.000	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003260	0.1255737	0.00030	0.006236	0.0000533
Mixed (N-P) contaminated sandy silt soil in SFC grout	8	1000	30.700	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000463	0.0178546	0.00009	0.000884	0.0000093

Calculation of De for sandy soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m/%)
1.0000	0.0010	8.00	8000.00	
0.8318	0.0009	8.00	7828.71	
0.6763	0.0005	8.00	10820.80	
0.5009	0.0003	8.00	13357.33	0.0000181
0.3323	0.0003	8.00	10633.60	
0.0419	0.0001	8.00	3724.44	
0.0023	0.0001	25.00	766.67	
			55131.55	

Calculation of De for sandy silt soil

Xi (%)	di (m)	αi	(Xi*αi)/di (%/m)	De = 1/Σ(Xi*αi)/di (m/%)
1.0000	0.0012	8.00	8000.00	
0.9703	0.0010	8.00	9132.24	
0.9437	0.0009	8.00	15099.20	
0.8011	0.0005	8.00	21362.67	0.0000026
0.6994	0.0003	8.00	22380.80	
0.6029	0.0003	8.00	53591.11	
0.4995	0.0001	25.00	166500.00	
0.2588	0.0001	25.00	86266.67	
			382332.68	

Day 30

sample	R (mg/L)	C (mg/L)	n (%)	G (ml/ml)	Ce (s/m)	ρw (kg/m^3)	g (m/s^2)	St (cm/cm)	De (m)	Pe	ζt (kg/m.s^2)	ζc (kg/m.s^2)	ξe (kg/m^2/s)	A$_{30}$ (kg/m^2/s)
Nickel contaminated sandy soil in SF grout	3	1000	29.500	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003036	0.1169550	0.00030	0.005807	0.0000261
Nickel contaminated sandy silt soil in SF grout	4	1000	30.100	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000451	0.0173554	0.00009	0.000859	0.0000046
Mixed (N-P) contaminated sandy soil in SF grout	3	1000	30.100	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003124	0.1203581	0.00030	0.005976	0.0000263
Mixed (N-P) contaminated sandy silt soil in SF grout	4	1000	29.100	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000429	0.0165421	0.00009	0.000819	0.0000046
Mixed (N-P) contaminated sandy soil in SFC grout	6	1000	31.500	44.16	0.04978	1000.00	9.81	1.57	0.00001814	0.00003336	0.1285304	0.00030	0.006383	0.0000537
Mixed (N-P) contaminated sandy silt soil in SFC grout	8	1000	30.900	40.50	0.04978	1000.00	9.81	1.57	0.00000262	0.00000468	0.0180229	0.00009	0.000893	0.0000094

	DAY 1	DAY 10	DAY 20	DAY 30
	A	**A**	**A**	**A**
Nickel contaminated sandy soil in SF grout	9.950E-06	2.300E-05	2.800E-05	2.300E-05
Nickel contaminated sandy silt soil in SF grout	2.294E-06	4.400E-06	5.600E-06	5.600E-06
Mixed (N-P) contaminated sandy soil in SF grout	9.950E-06	2.300E-05	2.800E-05	2.300E-05
Mixed (N-P) contaminated sandy silt soil in SF grout	2.294E-06	4.400E-06	5.600E-06	5.600E-06
Mixed (N-P) contaminated sandy soil in SFC grout	3.098E-05	3.800E-05	4.200E-05	4.200E-05
Mixed (N-P) contaminated sandy silt soil in SFC grout	4.393E-06	7.300E-06	9.200E-06	9.700E-06

Prediction of contaminants release using TERC Model

Nickel contaminated sandy soil in SF grout

Input parameter	**Day 1**	**Day 10**	**Day 20**	**Day 30**
C (mg/L)	1000	1000	1000	1000
n (%)	37.1	29.4	29.3	29.5
G (%)	44.16	44.16	44.16	44.16
ε_e (kg/s/m^2)	7.335E-03	5.779E-03	5.751E-03	5.807E-03
A*	9.950E-06	2.300E-05	2.800E-05	2.300E-05
R	1.140	2.650	3.230	2.646

Nickel contaminated sandy silt soil in SF grout

Input parameter	**Day 1**	**Day 10**	**Day 20**	**Day 30**
C (mg/L)	1000	1000	1000	1000
n (%)	37.24	29.5	29.7	30.1
G (%)	40.5	40.5	40.5	40.5
ε_e (kg/s/m^2)	1.057E-03	8.350E-04	8.431E-04	8.595E-04
A*	2.294E-06	4.400E-06	5.600E-06	5.600E-06
R	1.996	3.838	4.871	4.842

Mixed (N-P) contaminated sandy soil in SF grout

Input parameter	Day 1	Day 10	Day 20	Day 30
C (mg/L)	1000	1000	1000	1000
n (%)	37.19	29.8	30	30.1
G (%)	44.16	44.16	44.16	44.16
ε_e (kg/s/m^2)	7.333E-03	5.891E-03	5.948E-03	5.976E-03
A*	9.950E-06	2.300E-05	2.800E-05	2.300E-05
R	1.143	2.634	3.198	2.623

Mixed (N-P) contaminated sandy silt soil in SF grout

Input parameter	Day 1	Day 10	Day 20	Day 30
C (mg/L)	1000	1000	1000	1000
n (%)	36.26	28.9	28.9	29.1
G (%)	40.5	40.5	40.5	40.5
ε_e (kg/s/m^2)	1.0132E-03	8.1103E-04	8.1103E-04	8.1899E-04
A*	2.2940E-06	4.4000E-06	5.6000E-06	5.6000E-06
R	2.027	3.871	4.927	4.913

Mixed (N-P) contaminated sandy soil in SFC grout

Input parameter	Day 1	Day 10	Day 20	Day 30
C (mg/L)	1000	1000	1000	1000
n (%)	38.66	31.1	31	31.5
G (%)	44.16	44.16	44.16	44.16
ε_e (kg/s/m^2)	7.804E-03	6.265E-03	6.236E-03	6.383E-03
A*	3.098E-05	3.800E-05	4.200E-05	4.200E-05
R	3.475	4.271	4.728	4.693

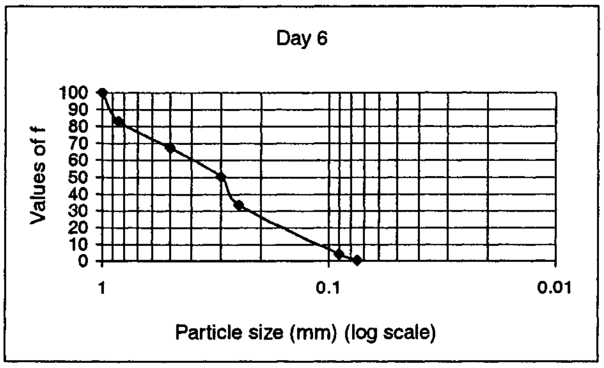
Mixed (N-P) contaminated sandy silt soil in SFC grout

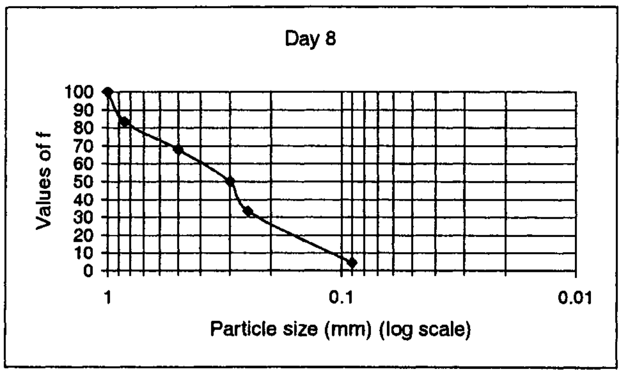
Input parameter	Day 1	Day 10	Day 20	Day 30
C (mg/L)	1000	1000	1000	1000
n (%)	38	30.9	30.7	30.9
G (%)	40.5	40.5	40.5	40.5
ε_e (kg/s/m^2)	1.092E-03	8.927E-04	8.843E-04	8.927E-04
A*	4.393E-06	7.300E-06	9.200E-06	9.700E-06
R	3.774	6.239	7.886	8.290

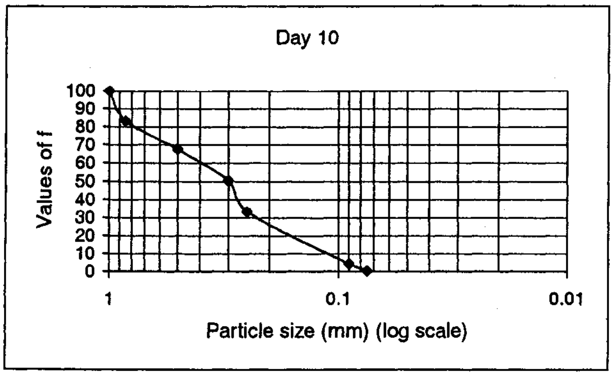
APPENDIX- K

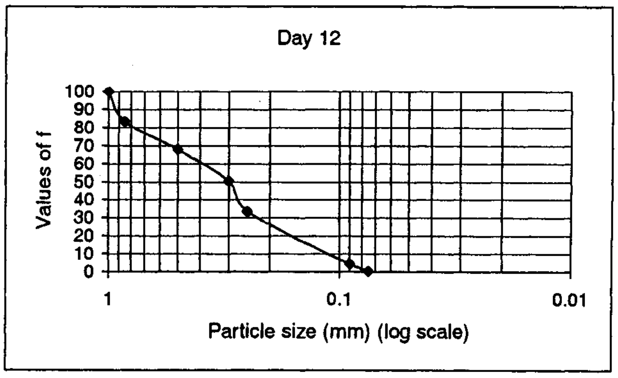
PARTICLE SIZE DISTRIBUTION CURVE

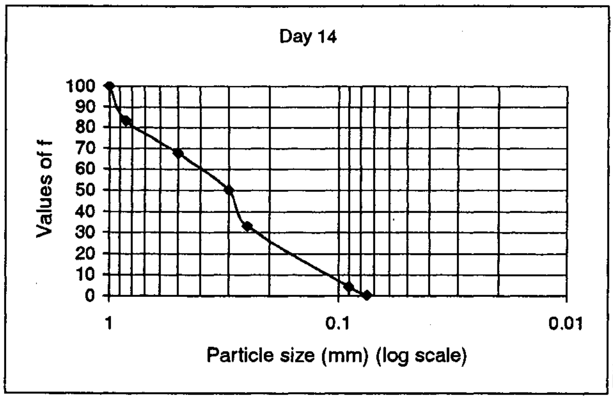
Sandy soil particle size distribution curve at different days for mixed contaminated SF grout

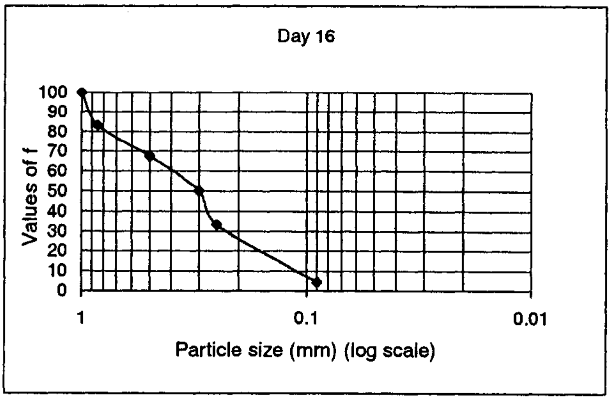


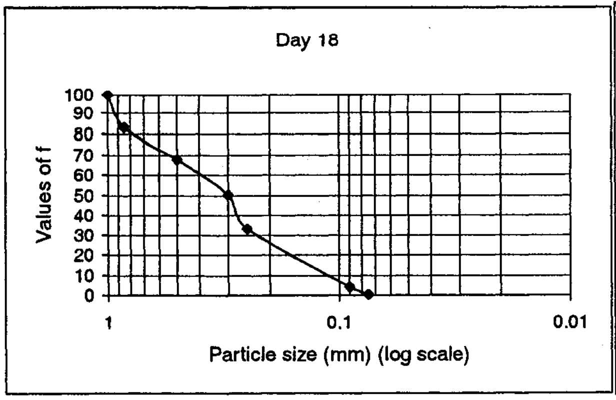








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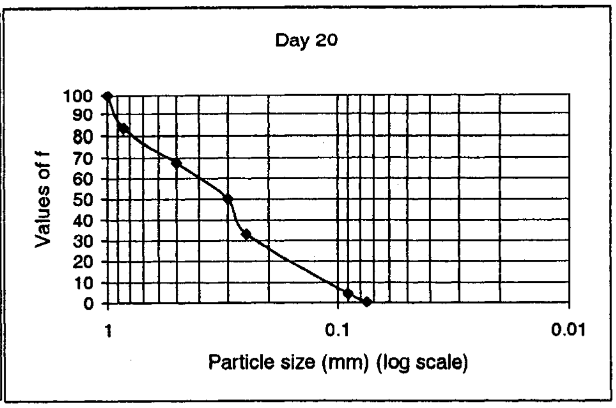
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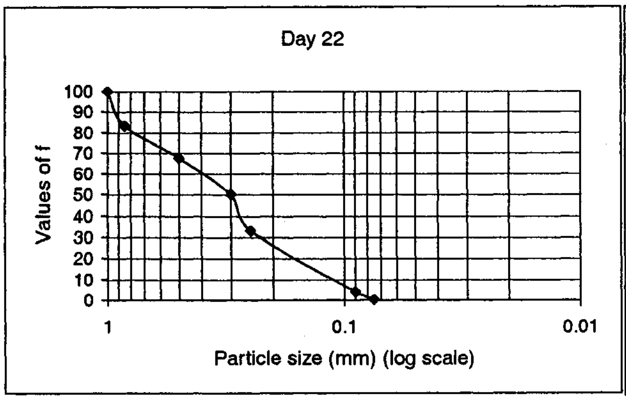
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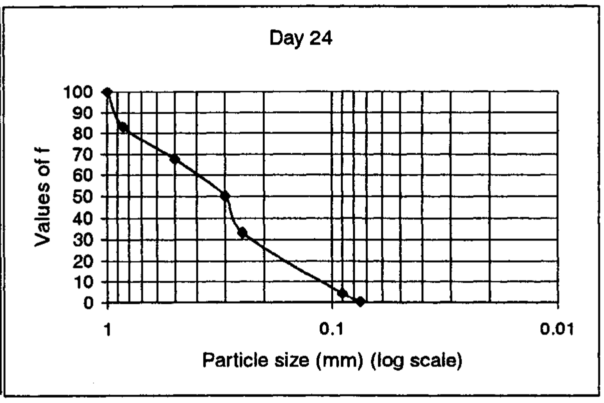
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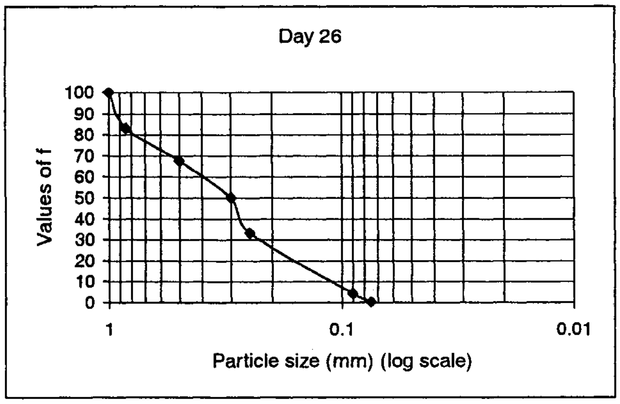
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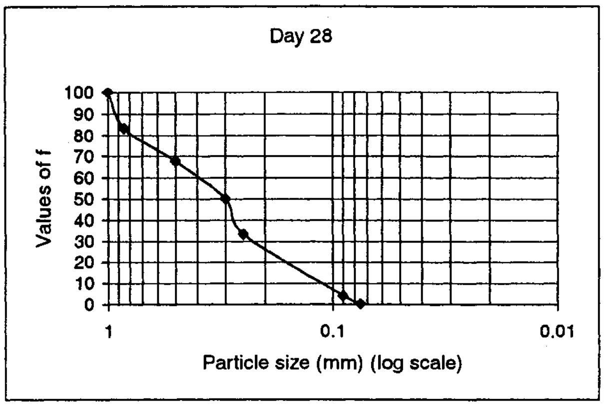
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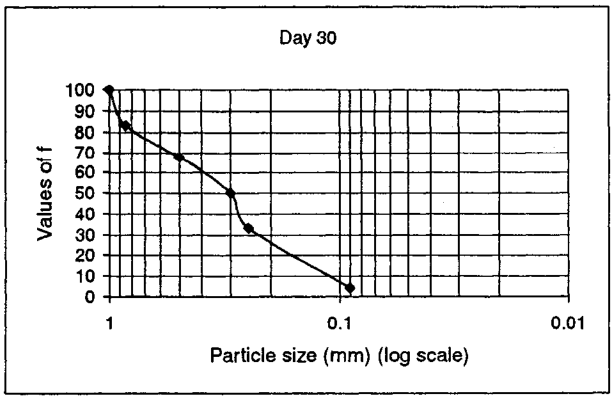
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