3.0 POTENTIALLY SUITABLE MATERIALS, DELIVERY SYSTEMS AND MODELING TECHNIQUES

A literature review was performed to identify materials suitable for stabilizing liquefiable sands and to determine if techniques developed for contaminated site remediation could be adapted for use in passive site remediation. The stabilizer candidates include organic and inorganic materials such as iron, bacteria, and several types of grouts. Potential delivery systems and groundwater modeling programs were also identified. The candidate stabilizers are identified and described in this chapter. The evaluation of stabilizer candidates, delivery systems and modeling codes is done in Chapter 4.

3.1 Rheology of Potential Stabilizers

Potential stabilizers are likely to be introduced into the liquefiable formation as either solutions or particulate suspensions. For solutions, the viscosity of the stabilizer is the primary rheological parameter that determines penetrability into a soil formation (Karol 1990). For particulate suspensions, the particle size of the suspension is the controlling factor determining penetrability, although the rheological properties are also important (DePaoli et al. 1992).

The important rheologic properties of a suspension include the viscosity and cohesion. The viscosity is the proportionality constant that relates the shear resistance in a fluid to the velocity gradient, as shown in Figure 3-1. Solutions behave like Newtonian fluids, so their rheological characteristics can be described completely using the viscosity. Suspensions have more complex behavior, so an additional term is needed to describe it. Before a suspension will start to deform, there is a yield stress that must be exceeded, as shown in Figure 3-1. This yield stress is called cohesion. A fluid that has both viscosity and cohesion is called a Bingham fluid. The viscosity and cohesion can be lumped together into a term called apparent viscosity (Lombardi 1985), as shown in Figure 3-1.

An important consideration with particulate suspensions is the stability of the suspension. The term stability refers to the tendency of the particles in suspension to settle. In cement grouting technology, the stability of a suspension is measured in terms of "bleed." Bleed is a measure of the free water at the top of a column of a particulate suspension as the particles settle. A cement grout that has less than 5 percent bleed in two hours is considered stable. A stable suspension will behave like a Bingham fluid. If a mix is unstable, it will separate into components and its behavior will be unpredictable. In determining the penetrability of a particulate grout, Lombardi (1985) found that cohesion determines the maximum distance a grout can penetrate, while the viscosity determines the flow rate and the time necessary to complete the injection. When particulate grouts are injected under pressure, another parameter that needs to be considered is the stability under pressure. A stable particulate grout under atmospheric pressure may become unstable when injected under higher pressures. The pressure filtration coefficient is a measure of how well the stability is maintained under high pressures. A low pressure filtration coefficient is an indication that a grout is stable under high pressure.

Pure solutions, such as resins, maintain a constant viscosity until just prior to gelling. These solutions are termed non-evolutive. Colloidal solutions, such as colloidal silica or sodium silicate grouts, increase in viscosity gradually over time and are termed evolutive solutions. The change in viscosity of these solutions with time is depicted in Figure 3-2 (Mongilardi and Tornaghi 1986). The behavior of particulate suspensions, such as cement grouts, depends upon the stability of the suspension. The evolution of viscosity of stable grouts is shown in Figure 3-2.

3.2 Penetrability of Cement Grout

The factors controlling the ability of a cement grout to penetrate a formation include the pore size of the formation and the grain size of the cement particles, the hydraulic gradient and the rheology and stability of the grout. The rheology and stability of the grout were discussed above.

Groutability ratios (Mitchell 1981) are often used to determine if cement grouts can be successfully injected into soil formations. The groutability ratio is a measure of a characteristic grain size of a soil formation in relation to a characteristic grain size of a particular cement. Both the grain size of the cement and the pore size of the formation are important in determining the ability of a cement grout to permeate a formation. Two commonly used groutability ratios follow:

$$N = (D_{15})_{soil}/(D_{85})_{grout} \qquad (3\text{-}1)$$

where D_{15} = grain size of soil for which 15% by weight is finer
D_{85} = grain size of cement for which 85% by weight is finer

If N is greater than 24, grouting is consistently possible. If N is less than 11, grouting is not possible. In the range of 11 to 24, grouting may be possible but field tests should be done to determine the groutability of the formation.

$$N_c = (D_{10})_{soil}/(D_{95})_{grout} \qquad (3\text{-}2)$$

where D_{10} = grain size of soil for which 10% by weight is finer
D_{95} = grain size of cement for which 95% by weight is finer

If N_c is greater than 11, grouting is consistently possible. If N_c is less than 6, grouting is not possible. In the range of 6 to 11, field tests should be done to determine the penetrability of the grout. For the grain size distribution of most liquefiable soils (Figure 2-1), the grouting ratios calculated for ordinary Portland cement grout and for microfine cement grouts are shown in the table below.

Table 3.1 Grouting Ratios for Most Liquefiable Soils

Type of Cement	N	N_c
Ordinary Portland Cement	1-9	1-5
Microfine Cement	15-113	8-71

Based on groutability ratios, ordinary Portland cement grouts would not be able to penetrate most liquefiable sands, but microfine cement grouts should be able to be injected into many of these formations.

Cement grouts are usually injected under pressure, so the hydraulic gradient is not usually considered to be of concern when considering the penetrability of the grout. However, in passive site remediation, the natural groundwater flow will be used to deliver the stabilizer to the target area. Therefore, the groundwater flow regime will be important in determining the penetrability of the grout. The hydraulic gradient in the treatment area will need to be high enough to maintain the particles in suspension.

3.3 Microfine Cement Grouts

The main distinction between microfine cement and ordinary cement is the particle size distribution. Microfine cements typically have an average particle size of around 3 to 4 microns, while ordinary Portland cement has an average particle size of about 20 microns (Clarke 1987). There are several brands of microfine cement available. Most are mixtures of Portland cement, slag, and dispersant, although some contain pumice as well. The main advantage of microfine cement is the small particle size, which allows it to penetrate formations with smaller pore sizes than can be penetrated with ordinary cement grouts. However, the small particle size presents certain difficulties as well.

Microfine cements have a large specific surface area, so the particles tend to flocculate when mixed with water. Therefore, dispersants are required to prevent particle aggregation. Dispersants act by coating the cement particles and putting a negative charge on them so the particles repel each other and cannot agglomerate. The use of dispersants actually causes a decrease in the apparent viscosity of a neat cement grout. Additionally, microfine cement grouts need to be mixed with high-speed shear mixers. High-speed shear mixers create a vortex and a strong shearing motion, which create an ideal mixing environment for the microfine cements. The high-speed mixer separates the individual cement particles and allows thorough wetting of each particle, facilitating hydration (Houlsby 1982).

The factors that control the stability and rheology of microfine cement grouts are the water to cement ratio of the mix, the composition and specific surface area of the cement, and the additives used. Neat cement grouts will typically have low apparent viscosity but will bleed significantly. Adding more water will decrease the apparent viscosity of the grout but reduce the stability. Another way to reduce the apparent viscosity is to use special consistency control admixtures that enhance penetrability without compromising stability (Gause and Bruce 1997, DePaoli et al. 1992, Naudts 1996). These additives can be long-chain polymers or sodium metacrylates. These additives work to reduce the attraction between single solid particles, which reduces grain agglomeration; to reduce apparent viscosity and cohesion; and, to increase mix stability.

Additives that are commonly used to improve mix stability include bentonite, welan gum, silica fume, fly ash and anti-washout admixtures. Bentonite is one of the best additives for improving stability, but it increases the viscosity and cohesion dramatically. Welan gum is a starch-based additive that reduces the pressure filtration coefficient although it raises the cohesion slightly (Bruce et al. 1997). Silica fume and fly ash improve the stability somewhat without much detrimental effect on the apparent viscosity (Ata and Vipulanandan 1997). Anti-washout additives such as cellulose derivatives can enhance the stability, pressure filtration and washout resistance of grouts. These water-soluble polymers increase the viscosity of the mix water by forming bonds with some of the mix water and absorbing additional water molecules (Gause and Bruce 1997).

There is generally a tradeoff between improving stability and affecting rheological properties. For example, bentonite reduces bleed but increases the viscosity and cohesion of a mix. The goal in designing microfine cement grouts is to find a combination of additives that improves the stability but has a minimal effect on the viscosity and cohesion. The best penetrability will be achieved using a stable mix with low apparent viscosity.

DePaoli et al. (1992) tested several properties of ordinary and microfine cement grouts, including viscosity and cohesion, bleed, stability under pressure, strength and permeability. The test results showed that a stable mix with a consistency control additive had a lower apparent viscosity than an ordinary stable mix. In addition, the rheological properties of all stable mixes were strongly influenced by the fineness of the cement. When equal cement and bentonite contents were used, the finer cement caused a sharp increase in cohesion and viscosity of the grout, which is expected because the specific surface area of microfine cement is so much larger than that of ordinary Portland cement.

Microfine cement grouts would cost in the range of $100 to $200 per cubic meter of treated ground.

3.4 Set-Retarding Admixtures

Cement grouts typically set in a few hours. For passive site remediation, the set time would have to be delayed using set-retarding admixtures. Set retarding admixtures delay the hydration of tricalcium silicate (C_3S), which is one of the major components of Portland cement. C_3S reacts to produce the amorphous calcium silicate hydrates that give concrete its strength.

The list of materials that retard the setting of cement is long. The list of organic compounds includes carbohydrates, lignosulfates, hydroxycarboxylic acids and phosphonates. Carbohydrates used for retardation include sugars and certain polymers obtained from polysaccharides (Collepardi 1995). Lignosulfates are a waste product from the paper industry and are widely used in the production of set retarding admixtures. Salts of hydroxycarboxylic acids were developed as set-retarding admixtures in the 1950's and include gluconic acid, citric acid, and heptonic acid, among others. Hydroxylated carbosilicic acid and certain phosphonates show promise as extended set retarders. More recently, antiwashout admixtures used for concrete placed underwater have been found to have set-retarding properties (Khayat 1995). The list of inorganic compounds is shorter but includes phosphates, borates, lead or zinc oxides, and copper or magnesium salts (Collepardi 1995).

Sugars are well known for their set retarding abilities, but not all sugars have the same capacity to delay setting. Sucrose and glucose have been found to be effective retarders. Bruere (1966) found that sucrose delayed the initial setting of cement pastes up to 133 hours. Milestone (1979) found that glucose delayed the setting time of tricalcium silicate (C_3S) cement by about 11 days. Studies on different types of sugar have shown that sucrose and raffinose are the most effective retarders (Thomas and Birchall 1983)

Lignosulfate contains a mixture of lignin sulfonation products of lignin, cellulose and lignin decomposition products, carbohydrates, free sulfurous acid and sulfates. Lignosulfates have a widely varying composition, which depends on the type and age of wood used for papermaking, as well as the successive processes used, such as neutralization, precipitation or fermentation. Milestone (1979) studied the effect of different lignosulfates on the setting time of tricalcium silicate cement. Lignosulfates high in sugars were found to be better set retarders than lignosulfates high in salts of lignosulfonic acids. The lignosulfates high in sugar delayed the setting of the cement paste by more than 7 days.

Milestone (1979) studied the effect of sodium gluconate on the setting time of cement composed only of tricalcium silicate (C_3S). Adding 0.1% sodium gluconate inhibited hydration for the duration of the test, which lasted 50 days. Ramachandran et al. (1993) tested three phosphonic acids and their corresponding sodium salts to determine their effect on the hydration of Portland cement. Of the phosphonates tested, methylenephosphonic acid (DTPMP) and its corresponding sodium salt, Na_6DTPMP were the most effective retarders. At high concentrations, the sodium salt Na_6DTPMP increased the induction period from 2 hours to 72 hours.

As part of a feasibility study for concrete bridge protection and rehabilitation, Dillard et al. (1993) tested sodium tetraborate and zinc borate as corrosion abatement treatments. Part of the study considered the treatment effects on the compressive strength of mortar. Both sodium tetraborate and zinc borate were found to retard the setting time of the mortar at very low concentrations. Zinc, lead, and copper salts also retard the hydration of Portland cement. For example, as little as

0.15% by weight of lead compounds has a significant retarding effect on hydration of Portland cement (Thomas et al. 1981)

3.5 Extended Set Control Admixtures

Gause and Bruce (1997) discuss the use of hydration control using a two-component, liquid, chloride-free system. The system consists of a stabilizer and an activator. The stabilizer base is hydoxylated carbosilicic acid, which can arrest hydration for up to 72 hours by forming a barrier around the cement particles. The barrier is dissolved when the inorganic alkaline activator is added. Test results show that the hydration control additives do not affect the final grout properties. The cost of this extended set control admixture would add about $10 to the cost of microfine cement grout for each cubic meter of treated ground if used at a rate of 5 weight percent by weight of cement.

Ramachandran and Lowery (1992) tested several potential retarders for extended set control. Calcium gluconate, sodium heptonate and sucrose were found to be the most efficient retarders because less than 0.15% by weight were required to extend the induction period to 40 hours. There was generally a linear relationship between the dosage of retarder added and the increase in induction period.

3.6 Colloidal Silica

Colloidal silica is an aqueous suspension of microscopic silica particles produced from saturated solutions of silicic acid (Iler 1979). The particles can range in size from 2 to 100 nanometers, although the particle size is fairly constant in a given suspension. In dilute solutions, colloidal silica has a density and viscosity similar to water. Gel times of up to 49 days have been reported by Noll et al. (1992). Colloidal silica is attractive as a potential grouting material because it has long, controllable gel times and excellent durability characteristics. It is also chemically and biologically inert and nontoxic.

Colloidal silica particles form when H_4SiO_4 molecules interact to form siloxane (Si-O-Si) bonds with other molecules. The surfaces of the particles contain uncombined silanol (SiOH) groups (Iler 1979). When the particles interact with other particles, they form interparticle siloxane bonds, as shown in Figure 3-3. When the particles grow to the desired size, the solution is stabilized to prevent further particle growth. The solution is stabilized by increasing the pH, which causes the particles to ionize and repel each other. Gelation can be induced by reducing the repulsive forces in a controlled manner. This allows the colloidal particles to coagulate. The gel time is determined by the rate of particle-to-particle interaction.

Colloidal silica solutions are often stabilized to prevent gelling using alkaline solutions such as sodium hydroxide. The alkali reacts with the surfaces of the particles, creating a negative charge on the particles and causing them to repel each other. This process is shown in Figure 3-4(a). The hydroxyl ions added by the alkaline solution actually catalyze gel formation, but at high pH the colloidal silica is stable because of high particle charge. At lower pH's, the particle charge decreases in proportion to the concentration of hydroxyl ions in solution. Therefore, the particles can interact and form siloxane bonds as depicted in Figure 3-4(b). The result is that the minimum gel time occurs between pH 5 and 6. As the pH continues to drop below 5, the hydroxyl ions disappear and the particles become uncharged, as shown in Figure 3-4(c). Therefore, the rate of siloxane bond formation decreases and there is a corresponding increase in gel time.

3.6.1 Gel Time Control

The gel time of colloidal silica depends on several variables, including the silica solids content, the size or surface area of the silica particles, the pH, the charge on the particles, and the salt concentration. Gel time increases as the silica solids content is decreased and as the size of the silica particles increases. As noted above, minimum gel times tend to occur between pH 5 and 6. Substantially higher gel times can be achieved if the pH is either above or below this range. Gel time is also affected by temperature; however, in the range anticipated in this project, temperature will likely have a negligible effect on the gel time.

The addition of salt to the stabilized colloidal silica solution shrinks the double layer around the particles, increasing the probability of interparticle collisions and reducing gel time. Higher concentrations of salt will have larger effects on gel time. Typically, sodium chloride or ammonium chloride is used for salt-induced gelation. Polyvalent cations have more of an effect on the double layer than monovalent cations so they reduce the gel time more than monovalent cations.

Noll et al. (1992) performed a series of bench-scale tests to determine the factors affecting the gel time of Du Pont's Ludox colloidal silica. The tests were conducted using a concentrated colloidal silica sol diluted with a salt-water solution to the desired concentrations of silica and salt. Hydrochloric acid was used to adjust the pH. The factors considered included the concentration of colloidal silica, pH, salinity, and the effects of various salts.

Solution pH was found to have the most significant effect on gel time. Minimum gel times were found to occur in the pH range of 6 to 7. However, a wide range of gel times can be obtained by varying the pH, the sol concentration, and the salt concentration. Noll et al. (1992) report that gel times from 20 minutes to more than 49 days can be obtained using 5-weight-percent Ludox sol in the pH range of 5 to 9.5. Longer gel times occur at lower sol concentrations, lower salt concentrations and at higher pH's.

Most of the tests to determine gel time were conducted using sodium chloride as the added salt. However, since other cations are likely to be present in groundwater, the effects of calcium and aluminum on gel time were also considered. The addition of aluminum caused a rapid agglomeration and sedimentation of the silica particles, resulting in a detrimental effect on gel formation. Calcium had little effect in the acid pH range, but decreased the gel time in the basic pH range. The effects of low levels of dissolved organic chemicals and aqueous metals were also considered and found to have no detrimental effect on gel time.

Persoff et al. (1994) did experiments using soils with significant concentrations of exchangeable calcium ions. They found that chemical interactions between the calcium cations and the colloidal silica grout caused rapid, uncontrolled gelation of the grout. Divalent cations decrease gel time because they increase the ionic strength and collapse the double layer. Replacement of 2 Na^+ by one Ca^{2+} increases ionic strength because ionic strength is proportional to the square of the charge. Persoff et al. (1994) propose three methods to prevent premature gelation, including preflushing with brine, starting the grout injection with a dilute grout, or formulation of the grout with NaF rather than NaCl. Preflushing with brine displaces the divalent cations away from the grout. A disadvantage of this method is that it could mobilize contaminants. Dilute colloidal silica suspensions will displace the cations away from the grout that follows, but will eventually gel, so contaminants should not be mobilized. Formulation of the grout with NaF will cause precipitation and complexation of divalent cations in the following manner: the Na^+ ions cause displacement of divalent cations, while F^- ions cause the cations to precipitate or complex. However, NaF is a toxic material and may not be suitable for use in this application.

3.6.2 Strength, Hydraulic Conductivity and Durability Characteristics

Yonekura and Miwa (1993) did strength, syneresis, leaching and hydraulic conductivity tests on sands stabilized with colloidal silica. Sands were grouted with a 32 percent colloidal silica solution. The unconfined compressive strength of the grouted sands was about 7 kips per square foot (ksf) at the start of the test and increased continuously over 1000 days to a final strength of more than 25 ksf. Samples of colloidal silica gel were kept saturated for more than 1000 days and tested for syneresis and leaching of silica. Syneresis is shrinkage of a gel accompanied by exudation of liquid. In this study, syneresis was calculated by dividing the measured volume of gel at a particular time by the initial volume of the gel. The silica leaching ratio is the quantity of silica leached into the water divided by the quantity of silica in the initial gel. There was virtually no leaching or syneresis during these tests. Samples of colloidal silica gel were also submerged in alkaline and acidic water for 100 days and showed virtually no syneresis. No pH values were reported for the acidic and alkaline solutions. Yonekura and Miwa (1993) report decreased permeability in grouted samples for periods up to about 5 years, although no specific hydraulic conductivity values are reported.

Noll et al. (1992) performed hydraulic conductivity tests on sandpacks before and after treatment with a 5-weight-percent Ludox sol. They report a 3 to 4 order of magnitude reduction in hydraulic conductivity with final values in the range of 10^{-7} to 10^{-8} cm/s. They also found that the gel adsorbs metals from solution and that effluent from gelled sandpacks has lower leachable metal than effluent from untreated sandpacks. Noll et al. (1992) state that for colloidal silica grout to be stable for long periods the grouted materials need to be kept saturated and the pH must be between 3 and 9.

Persoff et al. (1997) conducted tests to determine the effect of dilution and contaminants on the strength and hydraulic conductivity of sand grouted with colloidal silica gel. They found that unconfined compressive strength increased and hydraulic conductivity decreased with increasing concentration of colloidal silica in the grout. There was a linear relationship between the silica concentration and the unconfined compressive strength, up to a maximum strength of about 9 ksf at a silica concentration of 20 percent. The strength continued to increase over the course of a year. A sample with 20 percent colloidal silica had strength of about 14 ksf at 349 days. The hydraulic conductivity decreased from about 10^{-7} cm/s at 7.4% silica to about 10^{-9} cm/s at 27% silica. Samples were immersed for 95 days in test liquids containing different non-aqueous phase liquids (NAPL's), water saturated with different NAPL's, HCl diluted to pH 3, and aniline. Only the sample immersed in aniline was weaker after immersion.

Whang (1995) reports that in wet-dry cycling, colloidal silica crumbles when dried quickly. However, when colloidal silica is kept saturated, Whang (1995) concluded that is should be stable for more than 25 years. The cost of colloidal silica depends on the dilution. Assuming a porosity of 35 percent, the cost of colloidal silica in dilutions of 5, 10 and 15 percent would be about \$60, \$120, and \$180 per cubic meter of treated soil.

3.6.3 Pilot and Field Testing Using Colloidal Silica Grouts

Noll et al. (1992) did a pilot test in a model scale sandbox to compare colloidal silica grout flow behavior with modeling predictions. The sandbox was 12 feet by 6 feet by 4 feet deep. Twelve injection and monitoring wells were installed. Pump and tracer tests were done to determine the hydraulic conductivity and dispersivity for design of the grouting program. The groundwater modeling programs MODFLOW and MT3D were used to model the flow regime and chemical transport simulations, respectively. The grout was injected through 4 wells in a row in the center of the sandbox while water was withdrawn from 3 wells on each side of the injection wells, as shown in Figure 3-5. The simulation results indicated that the area between the injection wells and the withdrawal wells could be saturated with the Ludox sol in about 12 hours. During the pilot test, CS grout with a 16-hour gel time was injected for 14 hours as described above. Excavation of the grouted area after the test showed that the actual grout distribution in area between the injection wells and the withdrawal wells was "remarkably similar" to what was predicted based on the MODFLOW and MT3D simulations.

Noll et al. (1993) discuss the results of a field-scale injection using colloidal silica grout. A subsurface investigation was done to characterize the site and included soil borings and aquifer pumping and recovery tests. Computer modeling using MODFLOW and MODPATH was done to design the test grouting program. Tracer tests were done before the grouting to confirm model predictions. One injection well and six withdrawal wells were used to place the grout. The withdrawal wells were placed 10 feet from the injection well in a hexagonal array. A gel time of 40 hours was selected. Ground penetrating radar and a hand boring were used to confirm placement of the grout. The field results were good, but there were discrepancies between the field results and the computer models. Noll et al. (1993) concluded that they need to develop an attenuation factor to use in the model to achieve proper gel times and pumping rates.

Moridis et al. (1996) did a field test using colloidal silica to grout heterogeneous, unsaturated deposits of sand, silt and gravel. The purposes of the demonstration were to use standard permeation grouting equipment to inject the colloidal silica, to control gel time under field conditions, to create a uniform grout plume in heterogeneous deposits, to reduce the permeability and to create intersecting grout bulbs. All of the test objectives were achieved. Excavation of the grout bulbs showed that fairly uniform bulbs were formed. The colloidal silica bulbs "did not have substantial cohesiveness or strength, but allowed vertical sections of the soil to be exposed" (Moridis et al. 1996).

3.7 Chemical Grouts

The primary chemical grouts used in the United States from the 1970's onward have been sodium silicates and acrylamides, although acrylamides are being replaced by acrylates (Karol 1990). More recently, many innovative grouts have been researched for use in environmental applications. Colloidal silica is an experimental grout that has already been discussed. Other experimental grouts with low viscosities and controllable gel times include iron precipitation grouts, epoxy and polysiloxane (Whang 1995).

3.7.1 Sodium Silicate

Sodium silicate is made by burning silica sand and sodium carbonate at high temperatures and then dissolving the product in water to get "water glass" (Iler 1979). A typical sodium silicate solution for grouting comprises 20-30% SiO_2, 5-15% Na_2O, and 60-70% water (Karol 1990). The silica to alkali ratio is between 3 and 4. Dilute sodium silicate solutions can be made to gel by the addition of a catalyst. The best known combination is a mixture of sodium silicate and bicarbonate. The bicarbonate neutralizes the solution, causing silica to precipitate and form a weak gel. Stronger gels can be formed when higher concentrations of silica or organic catalysts are used. The organic catalysts react with the silicate-water mixture to form an acid, which in turn cause precipitation of the silica. Setting time is controlled by the rate of acid formation, which is controlled by the quantity of organic compound added rather than the dilution of the sodium silicate solution. The main catalysts used today are glyoxal, mixtures di-basic esters and organic compounds, ethyl acetate and formamide (Naudts 1996, Whang 1995). Formamide is very toxic.

Sodium silicate grout solutions typically range in viscosity from 3 to 10 cP. Higher concentration solutions have higher viscosity. The viscosity approximately doubles in the first three-quarters of the induction period (Karol 1990). The induction period (or gel time) is the time lag that occurs between mixing the grout and gel formation. The gel time is easily controlled for gel times of a few minutes, but is not easily controllable for longer gel times.

Although most silicate formulations are considered to be permanent, the gel is subjected to two phenomena that cause doubts about longevity. First, a newly made silica gel undergoes syneresis, which is shrinkage due to the expulsion of water. Yonekura and Miwa (1993) report that sodium silicate specimens catalyzed with glyoxal and stored under water experienced from 4 to 6 percent syneresis in 1200 days. In addition, more than 30 percent of the silica in the initial gel leached into the water during that time. The second phenomenon that causes concern about permanence is the reversal of neutralization of the sodium silicate. If there is any unreacted soda ash in the sodium silicate, the neutralization of the sodium silicate will be reversed and the gel will deteriorate. Grouts with long setting times are likely to have unreacted soda ash since there will be low reactant concentrations in the grout. Karol (1990) reports "stabilized sand cylinders stored under water for a period of time show loss of strength which varies from negligible to total (complete falling apart of the grains) depending on the grout chemistry." According to Whang (1995), the expected lifetime of sodium silicate grouts is 10 to 20 years.

Yonekura and Miwa (1993) did long-term strength tests on sands stabilized with sodium silicate grouts. Two grout formulations were used. Grouts A and B had 20 and 15 percent sodium silicate, respectively. Both were catalyzed with glyoxal. The initial strength of Grout A was about 33 ksf, which decreased gradually to about 20 ksf after 1200 days. The initial strength of Grout B was about 18 ksf. The strength decreased to about 11 ksf after 100 days and remained constant for the remainder of the 1200-day test period.

The cost of sodium silicate is about $180 per cubic meter of treated soil assuming a porosity of 35 percent (Whang 1995).

3.7.2 Acrylamide

Acrylamide is a mixture of organic monomers that can be polymerized at ambient temperatures using a catalyst (Karol 1990). Acrylamide grouts have many advantages, including a density and viscosity similar to water, easily controlled gel times and the possibility of extended set times with the use of retarders. Acrylamide is a non-evolutive grout, so the viscosity remains almost constant during the induction period and is followed by rapid gelation. Additionally, acrylamide is considered to be permanent (Naudts 1996). Unfortunately, acrylamide is a neurotoxin in powdered form and in solution. Although the hazards are likely to be negligible when acrylamide is used appropriately, acrylamide grouts should not be used in areas where there is any chance they can be diluted excessively or get into public or recreational water supplies.

The gels that form from acrylamide grouts are about 8-12 % solids in the form of long molecular chains that are randomly cross-linked. The remainder of the grout is water molecules trapped between the molecular chains. The structure of the grout has been described as a “brush-heap” (Karol 1990). Acrylamide grouts are catalyzed with a two-part redox system consisting of a catalyst and an accelerator. The catalyst or initiator is a peroxide or persalt and the accelerator or activator is an organic compound such as triethanolamine. Gel times can be extended with the use of potassium ferricyanide, which acts as an inhibitor. The gel time depends the concentrations of catalyst, accelerator and inhibitor in the solution, as well as temperature. The gel time is independent of the concentration of acrylamide in the grout. Naudts (1996) reports that acrylamide is a very durable grout. Karol considers acrylamide grout to be permanent (Karol 1990). It is chemically stable and is expected to be mechanically stable unless it is subjected to wet/dry or freeze/thaw cycles. The cost of acrylamide grout is about $500 per cubic meter of treated soil assuming a porosity of 35 percent (Avanti International 1999).

3.7.3 Acrylate

Acrylate gels were originally used as a less toxic substitute for acrylamides and are currently used for seepage control in the sewer industry. Acrylates are similar in many respects to acrylamides, although the viscosity is slightly higher, the gel time is not as easily controlled and the strength is somewhat lower. Acrylates are also far less toxic, which has led to acrylates replacing acrylamides in many applications. The viscosity of acrylates remains constant for most of the induction period. Although the composition of acrylate grouts is considered proprietary, Karol (1990) states that acrylate grouts are believed to be mixtures of acrylate salts. All acrylate grouts require a cross-linking agent such as methylene-bis-acrylamide, a redox catalyst system (triethanolamine and ammonium persulfate) and potassium ferricyanide as an inhibitor. Retarders can be used to obtain gel times up to 6 hours. Acrylates are chemically stable and mechanically stable unless subjected to freeze/thaw and wet/dry cycles. The expected lifetime of acrylate grouts is 10 to 20 years (Whang 1995). The cost of acrylate grout is about $325 per cubic meter of treated soil assuming a porosity of 35 percent (Whang 1995).

3.7.4 Iron Precipitation Grouts

Hapka and Whang (1996) and Whang (1995) discuss the development of iron hydroxide precipitation grouts for use in environmental applications. The grouts were developed to utilize concentrated iron solutions from low-pH waste streams. The iron can be precipitated from the waste stream by increasing the pH. To stabilize the waste stream material for transport, the pH of the waste stream is increased to about 3 and citric acid is added as a chelating agent to keep the iron in solution. When precipitation is desired, urea and urease are added to cause the pH of the solution to rise and the iron to precipitate. Urease causes urea to breakdown. When urea breaks down it generates ammonia, causing the pH to rise. Set times of up to 5 hours were measured in laboratory tests and longer set times may be possible. The viscosity of the grout is about 1 centipoise (cP). Long-term tests have not been done, but the grout is expected to be very durable in certain environments. The cost of iron precipitation grout is estimated to be about $250 per cubic meter of treated soil assuming a porosity of 35 percent (Whang 1995).

3.7.5 Epoxy

One new type of epoxy may have applications for grouting (Whang 1995). It is an alcohol-based, two-component epoxy originally designed to encapsulate radioactive waste. The viscosity, which ranges from 5 to 20 cP, is very low compared to other epoxies. The epoxy hardens to a flexible material resembling polyurethane. When extended with water, the epoxy forms a gel similar to polyacrylamide gel polymers. Although originally designed for jet grouting, the material can also be used for permeation grouting due to the low viscosity. The maximum gel time of the grout is about 8 hours. The lifetime is estimated to be greater than 25 years. The epoxy is nontoxic, so it presents minimal safety, handling and environmental concerns. It is also expected to be chemically and mechanically stable. Assuming a porosity of 35 percent, the cost of epoxy grout is about $2200 per cubic meter of treated soil (Whang 1995).

3.7.6 Polysiloxane

Polysiloxane is a silicon-based chain polymer that is chemically and biologically inert and nontoxic (Whang 1995). It consists of two types of polymers, a cross-linker, a catalyst, and an inhibitor. The inhibitor can be used to control cross-linking after the catalyst is added. The viscosity can range from 10 to 35 cP depending on the lengths of the polymer chains. The set time can be varied by changing the amount of catalyst; however, there is a minimum amount of catalyst which must be added or a gel will not form. Extended set times can be obtained using retarders. Durability is expected to be very good, with predicted lifetimes of more than 25 years. The cost of polysiloxane is estimated to be about $1400 per cubic meter of treated soil assuming a porosity of 35 percent (Whang 1995).

3.8 Permeable Reactive Barriers for Controlling Groundwater Contamination

Permeable reactive barriers are a recent innovation for remediation of contaminated groundwater at polluted sites. A typical permeable reactive barrier consists of a trench filled with reactive material that intercepts the flow of contaminated groundwater. Impermeable walls are sometimes used to direct the flow of groundwater through the barrier. Types of reactive barriers include sorption barriers and precipitation barriers. Sorption barriers extract dissolved contaminants by adsorption, absorption, or chelation with the barrier materials. Precipitation barriers cause dissolved contaminants to be extracted from the groundwater by precipitation of newly formed minerals.

Precipitation barriers can be designed to manipulate the geochemical environment in several ways, including altering the pH, the chemical composition, or the redox potential of the groundwater. By altering the geochemical environment, the solubility limits of the desired precipitate can be exceeded. Iron is the material most often used in permeable reactive barriers. Different types of iron that have been proposed for use in permeable reactive barriers include granular zero-valent iron, colloidal zero-valent iron, and ferric chloride (Morrison and Spangler 1993, Gillham et al. 1994, Kaplan et al. 1994). The cost of granular iron is about $350 per ton.

If a “reverse” precipitation barrier could be designed, the technology could be applied to passive site remediation. In this scenario, a stabilizer would be placed in the trench. The stabilizer would dissolve as the groundwater flowed through the barrier. The dissolved stabilizer would then be carried into the liquefiable formation and precipitate in the pores to cement the soil particles together. The geochemical behavior of iron as it would apply to passive site remediation is discussed in the following section.

3.8.1 Geochemical Reactions Between Zero-Valent Iron and Groundwater

There are numerous reactions that can occur when zero-valent iron is in contact with groundwater, including aerobic corrosion, anaerobic corrosion, and precipitation. For a passive site remediation application, a combination of corrosion and precipitation would likely be required. Corrosion of iron would cause an increase in the amount of dissolved iron present in the groundwater. If the dissolved iron were to be carried downgradient from the source and precipitated in the pores of the formation, it could serve to bind the particles together and increase the liquefaction resistance. The likely corrosion and precipitation reactions that could occur in groundwater are summarized below.

During the corrosion process, iron metal is oxidized to Fe^{2+} or Fe^{3+} by giving up two or three electrons. If oxygen is present in the groundwater, aerobic corrosion will occur until the dissolved oxygen is depleted. The reaction for corrosion of iron under aerobic conditions is

$$2Fe(s) + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 4H_2O \qquad (3\text{-}3)$$

This reaction can be followed by the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) if further oxygen is available.

$$4Fe^{2+} + O_2 + 4\,H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (3\text{-}4)$$

When oxygen is depleted, anaerobic corrosion will occur according to the reaction

$$Fe(s) + 2\,H^+ \rightarrow Fe^{2+} + H_2 \qquad (3\text{-}5)$$

Groundwater moving through the trench would first corrode iron by aerobic corrosion until the dissolved oxygen in the groundwater was depleted. Further corrosion would occur anaerobically until the groundwater passed completely through the trench. Down gradient from the iron source, the dissolved iron would precipitate. If ferric iron is in solution, precipitation of amorphous ferric oxyhydroxide is expected. The reaction is

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (3\text{-}6)$$

In the long term, amorphous $Fe(OH)_3$ could eventually crystallize to goethite.

If the conditions are reducing and the pH is above 8.5, ferrous hydroxide is expected to precipitate according to the reaction

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (3\text{-}7)$$

Ferrous hydroxide is a metastable phase in low-temperature, anaerobic groundwater environments and will convert to magnetite according to the reaction

$$3Fe(OH)_2(s) \rightarrow Fe_3O_4(s) + H_2(g) + 2H_2O(l) \qquad (3\text{-}8)$$

If the conditions are reducing, the pH is near neutral and the carbonate concentration is high, the expected precipitate is ferrous carbonate (siderite) according to the reaction

$$HCO_3^- + Fe^{2+} \rightarrow FeCO_3 + H^+ \qquad (3\text{-}9)$$

This reaction is fairly uncommon. Iron corrosion rates could be used to predict the flux of Fe^{2+} and OH^- ions into the aqueous phase and determine the impact of iron corrosion on the composition of the groundwater.

If the precipitate forms as a coating on the iron particles, it may prevent further corrosion and reduce the effectiveness of the iron to react with the groundwater. It could also reduce the permeability or porosity of the formation. Under aerobic conditions, the protective layer can consist of precipitates such as ferric oxides (Johnson and Tratnyek, 1994). Under anaerobic conditions, hydrogen gas is produced. This may passivate the iron by forming a surface film on the particles (Johnson and Tratnyek, 1994). If the iron precipitates as colloids, it could be transported out of the soil formation with the groundwater flow.

Schumacher et al. (1997) identified several precipitates that formed on zero-valent iron during column tests. Anaerobic aqueous solutions of calcium carbonate and potassium bromide were pumped through columns containing pure zero-valent ion. Visible precipitates formed on the iron near the influent end of the column treated with $CaCO_3$. These precipitates contained both aragonite($CaCO_3$) and siderite ($FeCO_3$). Although invisible, precipitates identified as magnetite (Fe_3O_4)

formed throughout the rest of the column treated with $CaCO_3$ solution and the column treated with KBr solution.

3.8.2 Colloidal Zero-Valent Iron

An obvious problem with zero-valent iron is its extreme sensitivity to oxidation and reduction. Because of this problem, it will be difficult to keep iron in solution for the entire length of the treatment area. An alternative would be to use colloidal suspensions of iron to place iron in all the pores of the formation prior to reactions occurring. Cantrell and Kaplan (1997) discuss the emplacement of reactive barriers by injecting suspensions of colloidal zero-valent iron into porous media. In column tests, they used high flow rates to inject colloidal iron into sand columns and obtained relatively uniform iron concentrations throughout the column. One difficulty in using colloidal iron is that the high density of the colloids makes them prone to gravitational settling, decreasing the distance over which they can be injected. Cantrell et al. (1997) address this issue by using shear-thinning fluids to suspend the colloids. Shear-thinning fluids are more viscous when the shear rate is low. The viscosity decreases with increasing shear rate. Therefore, during injection the viscosity near the suspended iron particles will be high while the viscosity near the porous media surface will be low because the fluid will be experiencing a higher shear stress in this area. The use of shear-thinning fluids should make the suspension viscous enough to deep the particles in suspension without causing a large decrease in the hydraulic conductivity of the formation. After emplacement, the iron would corrode and could cement the matrix material together.

3.8.3 Ferric chloride

Morrison and Spangler (1993) and Morrison et al. (1996) studied dissolved ferric chloride as a potential candidate for injectable barriers to control groundwater contamination. In the presence of carbonate minerals, dissolved ferric chloride ($FeCl_3$) hydrolyzes to form amorphous ferric oxyhydroxide ($Fe(OH)_3$) according to the reaction

$$FeCl_3(aq) + 2CaCO_3 + 3H_2O \rightarrow$$
$$Fe(OH)_3 + 2Ca^{2+} + 3Cl^- + HCO_3^-(l) + CO_2\,(v) \qquad (3\text{-}10)$$

If dissolved ferric chloride were injected into calcite-bearing formations, a barrier of amorphous ferric oxyhydroxide (AFO) could be formed by this reaction. The AFO tends to form high volume flocs and gels. For the barrier to be effective, the AFO would have to spread throughout the aquifer during injection and then remain immobile after emplacement.

Morrison et al. (1996) did column and tank tests in which dissolved ferric chloride was injected into calcite-bearing gravel to form a barrier of AFO. One of the goals of the study was to consider the mobility of AFO in porous media. Low concentrations of iron were observed in the effluent, so the authors concluded that the AFO was immobile. The flow velocities used in the tests were higher than typical groundwater velocities, so if the AFO is immobile in the tests, it should also be immobile under groundwater flow velocities.

One potential drawback of this idea is that carbon dioxide is a secondary reaction product of the reaction between ferric chloride and carbonate-bearing sediment. The production of CO_2 could cause temporary flow restrictions in the formation as it expanded into the pores. This could cause trouble in terms of placing the ferric chloride in the formation. The AFO was successful in adsorbing the target contaminants, but breakthrough occurred much sooner than anticipated. This result was attributed to aquifer heterogeneity. The authors believe that AFO was deposited in a complex flow network with primary, secondary and tertiary channels. The reaction was thought to occur mostly in the primary flow channels, with little occurring in the secondary or tertiary channels.

3.9 Biological Materials

Recently, biopolymers and slime-forming bacteria have been investigated for use in reducing hydraulic conductivity and increasing strength of soils for waste containment applications (Martin et al. 1996, Dennis and Turner 1998). Biopolymers are polymers produced by microorganisms.

Martin et al. (1996) report strength increases of up to 50% and hydraulic conductivity reductions of one to two orders of magnitude in clayey silts amended with biopolymers and slime-forming bacteria. Turner et al. (1997) and Dennis and Turner (1998) measured hydraulic conductivity reductions of one to three orders of magnitude in silty sand samples treated with slime-forming bacteria. Yang et al. (1992) describe strength increases of up to 60% when solutions containing a biopolymer were applied to soil.

Biofilms have been studied extensively by the petroleum industry because of their tendency to clog injection wells used in oil recovery operations. The bacteria present in the injection water can attach to the well screens and form biofilms, effectively plugging the injection face (Shaw et al. 1985). Biofilms consist of a sticky polymer matrix that surrounds the microorganisms. If bacteria can be injected deep into oil-bearing formations where high-permeability channels form during water injection, biofilms could cause clogging of the high-permeability channels. Then the injection water would be directed into low-permeability zones that contain oil (Lappin-Scott et al. 1988, Cusack et al. 1992). This process is called selective plugging.

Shaw et al. (1985) studied the effects of bacterial plugging using cores made of lightly fused glass beads. MacLeod et al. (1988), Lappin-Scott et al. (1988) and Cusack et al. (1992) researched the use of starved bacteria for selective plugging of oil reservoirs to enhance oil recovery. Bacteria in low-nutrient environments can enter a dormant state in which the cells shrink but remain viable (Lappin-Scott and Costerton 1990). Starved bacteria could be injected far into a formation and then stimulated with nutrients to produce a biofilm. Cusack et al. (1992) used a reservoir simulator to test the injection and resuscitation of starved bacteria. After resuscitation, the bacteria formed a uniform biofilm throughout the simulator. Jack et al. (1991) performed a field test to selectively plug a soil formation using bacteria. Unfortunately, the test was unsuccessful because the flow of water through the formation was so high that the bacteria were transported farther than anticipated and did not form a biofilm.

The biofilm properties and the rate of production will depend on both the type of organism and the environment in which the biofilm is produced. Certain bacteria produce biofilms that are more resistant to attack when they are provided with nutrients that have a high carbon-to-nitrogen ratio. The additional resistance to chemical, biological and physical attack is due to the production of exopolysaccharides with glucuronic acid residues (Mitchell and Nevo 1964).

Wu et al. (1997) used nutrient solution to stimulate biomass growth of indigenous microbes in river sands in column tests to study the effect of biomass on hydraulic conductivity. The largest decrease in hydraulic conductivity occurred in the tests where there was a high concentration of nutrients in the nutrient solution. The authors found a high correlation between the amount of attached biomass and the reduction in hydraulic conductivity. The researchers indicate that the biomass appeared to consist of microbial aggregates rather than sticky exopolysaccharides, which may be due to the use of dextrose as a nutrient solution and low carbon to nitrogen (C/N) ratios in the solution.

Biofilms are reputed to be persistent in aquatic environments, which was generally confirmed in the study by Shaw et al. (1985). Dennis and Turner (1998) suggest that the permeability reductions caused by biofilms can likely be maintained without continuous nutrient stimulation. Many types of bacteria, especially those found in subsurface environments, can survive for prolonged periods with minimal nutrient supply. Additionally, biofilms appear very resistant to degradation after formation. A study by Shaw et al. (1985) found that a biofilm persisted after the application of a biocide killed the bacteria. However, the same study found that a strong oxidant (5% bleach) killed the bacteria and increased the permeability of the porous media significantly. Additionally, bleach has been used as a treatment for injection wells clogged by biofilms (Clementz et al. 1982). Therefore, the durability of biofilms in porous media remains questionable.

Biofilms could be used to cement the particles of a liquefiable formation. Ultramicrobacteria could be cultured and injected deep into the pores of a liquefiable formation and then resuscitated to form a biofilm. The biofilm might hold the formation together during an earthquake. It would cause a reduction in permeability, so the pore pressure would likely rise more quickly, but the sticky biofilm would hold the formation together and could prevent excessive deformation.

3.10 Delivery Systems

The concept of passive site remediation departs radically from the concepts of traditional grouting techniques in the delivery of the stabilizer. Most grouting is done using high pressures. Permeation grouting involves the use of pressures on the order of 1 psi per foot of depth. Jet grouting employs pressures high enough to erode the soil. The idea behind passive site remediation is to allow the natural groundwater flow to carry the stabilizer from the upgradient edge of the site to the downgradient edge of the site. There are scenarios where the natural groundwater flow regime will be adequate to deliver the stabilizers to the target area. However, there are other situations where the natural groundwater flow regime will be inadequate to deliver the stabilizers in an appropriate timeframe. In these cases, the natural groundwater flow regime could be augmented. Different possibilities for delivery systems include injection or extraction wells, magnetic fluids or electrokinetics.

3.10.1 Injection or Extraction Wells

The use of injection and extraction wells for delivery of colloidal silica grout was discussed in Section 3.6.3. Injection or extraction wells could be used to increase the hydraulic gradient in areas where the natural flow regime is inadequate to deliver the stabilizers in a timely manner. Extraction wells would be especially useful in directing the flow of the stabilizer into the target treatment area. They would also be useful in helping to control the flow of stabilizer beyond the down gradient edge of the treatment area.

3.10.2 Magnetic Fluids

Magnetic fluids, or ferrofluids, consist of microscopic magnetic particles coated with dispersant and suspended in a carrier fluid. Each particle is a permanent magnet that ranges in size from 3 to 15 nanometers (Rosensweig 1985). The suspension is stable because the dispersant prevents particle agglomeration and Brownian motion keeps the particles suspended in the carrier fluid. The behavior of ferrofluids depends on the presence or absence of a magnetic field. When no magnetic field is present, the particles will have a random orientation. If a magnetic field is applied to the fluid, the particles will align themselves within that field. If the magnetic field has a gradient, the ferrofluid will behave as a continuous fluid magnet (Rosensweig 1985).

Researchers at the Lawrence Berkeley National Laboratory (Moridis et al. 1998, Borglis et al. 1998) have experimented with ferrofluids to guide barrier liquids in the subsurface. In the experiments, ferrofluids were injected into vertical and horizontal test beds of sand and subjected to a magnetic field. The magnetic fluids were observed to flow through the soil and collect around the magnet in a predictable shape. When the fluids were close to the magnets, the magnetic forces were stronger than gravitational forces, so in vertical test beds, the ferrofluid collected around the magnets rather than sinking to the bottom of the tank.

Unfortunately, ferrofluids can only be used over a limited distance. The magnetization of the ferrofluid is strongly influenced by the strength of the magnetic field. As the strength of the magnetic field declines rapidly with increasing distance from the source, the technology will only be useful close to the magnetic source, i.e. on the order of 1 meter (Borglis et al. 1998).

3.10.3 Electrokinetic Processing

The use of electrokinetic soil processing to remove contaminants from soil or to add nutrients for bioremediation is emerging as a technology for remediation of contaminated sites. Electrokinetic phenomena in soils result from coupling of electrical and hydraulic flows and gradients (Mitchell 1993). These phenomena involve the movement of charged species in the pore fluid of a soil matrix due to the presence of an electric field. Electroosmosis is the movement of pore water, electrophoresis is the movement of charged particles and electromigration is the movement of ions in response to an electric field. Although electroosmosis only works in fine-grained soils, electromigration might be an effective means of delivering stabilizers to the target area.

3.11 Computer Modeling

Computer modeling for passive site remediation presents numerous challenges. The problem involves modeling the existing groundwater flow regime, predicting the flow regime when a stabilizing material is introduced, and accounting for the specific properties of the stabilizer. For example, the stabilizing material could interact with the aquifer matrix and affect the porosity of the aquifer. It could also have physical properties such as viscosity or density that are different from the groundwater. The analytical techniques developed to solve the problem will need to account for these factors.

Hydrological and contaminant transport codes are widely used in groundwater studies and in modeling the migration of chemical contaminants. A hydrological code could likely be used to model the groundwater flow regime for the passive site remediation scenario. It is also possible that a contaminant transport code could be used to model the introduction of a stabilizing material and predict the concentration of stabilizer that could be delivered to the treatment area. Geochemical codes are also used for contaminant transport modeling and might be useful in modeling the effect of the stabilizer on aquifer porosity.

There are many hydrological and contaminant transport codes available that model various aspects of fluid flow and mass transport in porous media, including flow in strata of different permeability and storativity, anisotropy in porous media, and flow of conservative solutes (Mangold and Tsang 1991). Both steady state and transient processes can be modeled using either finite difference or finite element codes. In these codes, the principles of conservation of mass and momentum are used to model the flow of groundwater, while the principles of conservation of mass, energy, and charge are used to model the chemical processes of solute transport.

Geochemical codes use assumed chemical reactions to predict the concentrations of dissolved species in groundwater (Gavaskar et al. 1998). Some of the reactions that may be modeled include complexation, sorption, dissolution and precipitation, redox, acid-base and mineral alteration (Mangold and Tsang 1991). Three types of models are currently available. Forward models use thermodynamic expressions to model reaction progress and result in an equilibrium prediction. Inverse models calculate probable reactions at different points along a flow path based on the data input at those points. Therefore, the result is not necessarily an equilibrium prediction. Reaction-transport or hydrogeochemical modeling combines hydrological, contaminant transport and geochemical modeling, so it can be used to simulate transport processes as well as geochemical processes.

Until recently, hydrological and contaminant transport codes evolved separately from geochemical codes. Recent research has attempted to couple hydrological, contaminant transport, and geochemical models into reaction-transport models. When reaction-transport models are used, a detailed conceptual model of the flow regime is used in conjunction with chemical data to predict the flowpath of both conservative and non-conservative species. Unfortunately, reaction-transport modeling is a fairly new area of geochemical modeling research, so few highly sophisticated codes are available. Most reaction-transport models consider only steady-state flow in one or two dimensions.

3.11.1 Previous Modeling Studies to Design Colloidal Silica and Permeable Reactive Barriers

As discussed in Section 3.6.3, Noll et al. (1992, 1993) did pilot and field testing using colloidal silica grout. The groundwater and contaminant transport modeling were done using MODFLOW and MT3D, respectively. MODFLOW is a three-dimensional, finite-difference groundwater flow model developed by the United States Geological Survey (USGS) (McDonald and Harbaugh 1988). MT3D is a modular three-dimensional, finite-difference transport model for the simulation of advection, dispersion, and chemical reactions of dissolved constituents in groundwater (Zheng 1990). MT3D is used in conjunction with MODFLOW to simulate contaminant transport in flow regimes modeled with MODFLOW.

The MODFLOW and MT3D simulations for the pilot test were calibrated using pump and tracer test results. The calibrated model was then used to design the location of injection wells and the injection rate of the colloidal silica grout. The numerical modeling for the field-scale test was not as successful as the modeling for the pilot test. Although tracer test results were used to confirm model predictions, there was a discrepancy between model predictions and field results. Noll et al. (1993) discuss the need for developing an attenuation factor to use in the model to achieve proper gel times and pumping rates.

Moridis et al. (1996) designed a colloidal silica barrier to encapsulate radioactive waste for a pilot-scale test at the Savannah River site. The computer modeling was completed using the TOUGH2 simulator, which is a general-purpose, finite-difference numerical simulation code for three-dimensional flow of fluid and heat in porous media. A gelation module has been developed to simulate the behavior of the grout. This module accounts for the increase in grout viscosity as a function of time and gel concentration (Finsterle et al. 1997). The gelation model has been used to simulate lab experiments and field tests in both saturated and unsaturated formations. One simulation involved the injection of colloidal silica grout into the saturated zone and simultaneous extraction of groundwater for control of the flow regime (Finsterle et al. 1997).

For in situ barrier design, groundwater flow modeling is done to determine the location and configuration of the barrier, to estimate the flow velocity through the barrier and to estimate the hydraulic capture zone. The flow velocity is used to determine the thickness of the barrier necessary to achieve the required residence time. The required residence time is the time the water must spend in the reactive cell to achieve adequate treatment. The hydraulic capture zone is the width of the groundwater zone that will flow through the barrier instead of traveling around or beneath it. According to Gavaskar et al. (1998), MODFLOW has been used to model in situ barrier design at numerous sites across the United States. MODFLOW is used in conjunction with the particle tracking code MODPATH (Pollock 1989) to simulate the permeable reactive barrier technology.

Geochemical modeling is not used much for in situ barrier design. Instead, Gavaskar et al. (1998) state that designs often rely on empirical evidence of reactions between groundwater and the reactive medium because of the lack of geochemical models that incorporate reaction kinetics. It is also unclear how the results of geochemical modeling can be used to predict the amount of precipitate that would be generated or correlate that information to porosity losses in the barrier, especially since the precipitates could be colloidal and travel out of the reactive cell with the water. When geochemical modeling is used for barrier design, commercial geochemical models such as PHREEQ (Parkhurst 1995) are usually employed.

Schaeffer (1998) used MODFLOW to model excess pore pressure migration and dissipation in densified sand zones during and after earthquakes. In densified sand zones within otherwise loose soil deposits, there is a risk that the loose soil surrounding the densified zone will liquefy during earthquake shaking and exert pressure on the sides of the densified zone. This could cause migration of excess pore pressure into the densified zone, thereby increasing the risk of instability in the improved zone. Schaeffer (1998) used a series of transient seepage analyses to model the development of excess pore pressure during earthquake shaking, the migration of pore pressure into the densified zone during shaking, and the subsequent dissipation of the pore pressure after the shaking ceased. Cooke (2000) noted that using a series of migration and dissipation analyses to model the interaction of pore water pressures between liquefied and densified zones provided a reasonable approximation of the actual pore water pressure behavior during and after earthquakes.

3.11.2 Codes Considered for Passive Site Remediation

Ideally, the code selected for groundwater modeling should be capable of simulating groundwater flow processes, transport processes, and chemical reactions. Of particular concern is the ability to model the addition of a stabilizing material with different physical properties than water. It is likely that the stabilizing material will have a density or viscosity that are different than those of water. It is also likely that the viscosity will change with time. If the stabilizer will react with the aquifer matrix, it would be ideal if the code could model that process as well. Additionally, the code should be available to practitioners who might apply this technology. Several models were considered for this study, including MODFLOW, MODPATH, MT3DMS, NUFT, SUTRA, TOUGH2, and HYDROGEOCHEM. A brief description of each program is provided below.

MODFLOW, MODPATH, MT3DMS, and NUFT are all run using the Groundwater Modeling System (GMS) platform, which is a graphical interface for performing groundwater simulations. GMS was developed at Brigham Young University by the Engineering Computer Graphics Laboratory in conjunction with the United States Army Waterways Experiment Station. It is commonly used in industry and is readily available to practitioners in the groundwater modeling field.

As discussed previously, MODFLOW is a saturated flow model developed by the USGS (McDonald and Harbaugh 1988). It is a three-dimensional, cell-centered, finite difference flow model capable of both steady state and transient analyses. Many different types of boundary conditions can be modeled. In addition, options are available to model wells, recharge, drains, evapotranspiration, and rivers. Each of these options can be modeled independently using the appropriate stand-alone module in the program. Both confined and unconfined aquifers can be modeled.

The governing differential equation assumes movement of groundwater of constant density and viscosity through porous earth material. It describes non-equilibrium flow in heterogeneous, anisotropic media when the principal axes of hydraulic conductivity match the coordinate directions. The addition of boundary conditions completes the mathematical formulation of the problem. The solution computed by MODFLOW is a time-varying head distribution that accounts for both the energy of flow and the amount of water stored in the aquifer. This solution can be used to calculate the direction and rate of movement of the water.

MODFLOW does not have the capacity to simulate materials with different densities or viscosities. However, the hydraulic conductivity of the porous media can be adjusted to account for a permeant with a different density or viscosity according to the relationship in Equation 2-3. The adjusted hydraulic conductivity remains constant for a given simulation, so the viscosity could not be adjusted progressively within a simulation to account for the flow of the stabilizer through the formation.

MODPATH (Pollock 1989), which was also developed by the USGS, is used in conjunction with MODFLOW to track advective transport of particles through a flow field. The flow field is first computed using MODFLOW. The user then designates a set of particles that are tracked either forward or backward through time using MODPATH. The travel time is also computed, so the length of time it takes a particle to travel through the flow field can be determined.

MODPATH works by computing the average linear groundwater velocity across each face in a cell. The principal flow components for each cell are then computed using linear interpolation, which results in a continuous velocity vector in the cell that satisfies the differential conservation of mass equation (Pollock 1989). The velocity and width of the cell are used to determine the time it takes a particle to cross the cell. The particle's exit point from the cell can be computed using the velocity components and the time. MODPATH is commonly used for delineating recharge or capture zones for wells.

MT3DMS is a multi-species version of MT3D developed by Zheng (1999). Like MODPATH, MT3DMS is used in conjunction with the flow field computed by MODFLOW. MT3DMS uses the flow field to simulate transport of contaminants dissolved in groundwater. Advection, dispersion, and diffusion can be modeled, as well as basic chemical reactions such as sorption and first-order kinetic reactions. The program is written in a modular style similar to MODFLOW, so different types of boundary conditions, sources and sinks can be modeled. The program computes the changes in concentration of contaminants throughout the flow field. The governing equations in MT3DMS describe the mass balance of chemicals entering, leaving, and remaining in the cell at any given time. It cannot account for variable viscosity because it uses the flow field calculated by MODFLOW and is subject to the same restrictions as MODFLOW.

NUFT (<u>N</u>onisothermal <u>U</u>nsaturated-Saturated <u>F</u>low and <u>T</u>ransport Model) is a three-dimensional finite-volume model for non-isothermal, multi-phase flow and transport developed at Lawrence Livermore National Laboratory (Nitao 1998). Up to three phases can be modeled, including a gas phase, an aqueous phase, and a non-aqueous phase liquid (NAPL). NUFT was developed to simulate various remediation strategies in the vadose zone, including air sparging, steam injection, and vapor extraction. The program solves partial differential balance equations “whose specific form depends on the particular NUFT model being used” (Nitao 1998). NUFT has several modules, each of which requires a different balance equation. The partial differential equations are solved using “an integrated, finite-difference, spatial discretization” which results in a nonlinear equation that is solved for each time step using the Newton-Raphson method (Nitao 1998). NUFT was considered for this study because the viscosity of the aqueous phase and the NAPL phase can be specified.

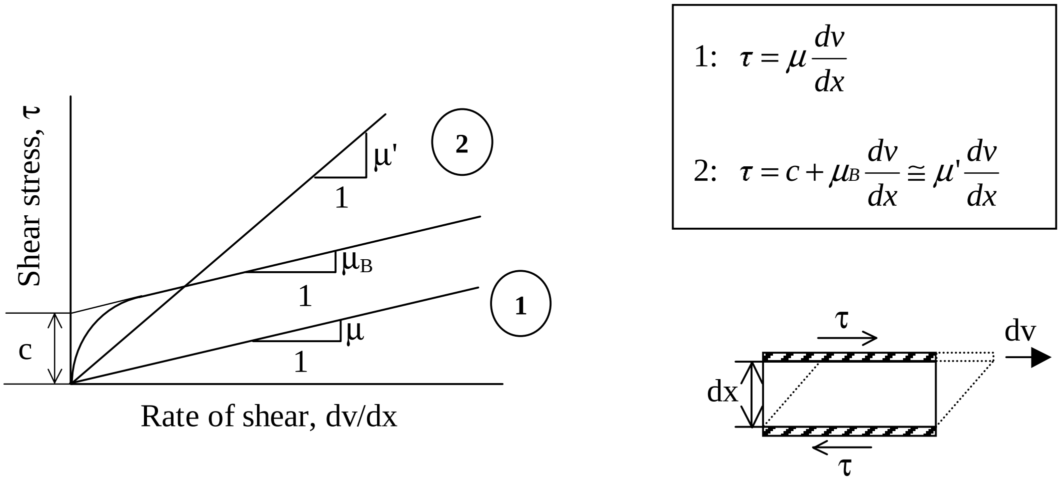
As discussed in the previous section, TOUGH2 (Transport of Unsaturated Groundwater and Heat) is a three-dimensional, general-purpose numerical simulator for coupled transport of heat and fluid flow. Its primary applications are in geothermal reservoir engineering, nuclear disposal and unsaturated zone hydrology. More recently, it has been used to model subsurface barriers for environmental remediation. Multi-phase flow can be modeled using modules that have been developed to handle different fluid mixtures. TOUGH2 is of particular interest for modeling passive site remediation because it has a gelation module to simulate grout injection. This module accounts for the increasing viscosity of a grout as a function of time and grout concentration.

SUTRA (Saturated-Unsaturated Transport Finite-Element Ground-Water Simulation Model) is a United States Geological Survey code known for its ability to model saltwater intrusion in aquifers. It is a two-dimensional finite-element model for simulation of saturated-unsaturated, fluid-density dependent groundwater flow (Voss 1984). It is capable of solute transport of chemically-reactive single species. The code is well verified by comparison with analytical solutions, other codes and a field experiment (Mangold and Tsang 1991). SUTRA was considered for this study because of its ability to model fluids of variable density.

HYDROGEOCHEM2 is a two-dimensional model that couples hydrologic transport and geochemical reactions in saturated or unsaturated porous media (Yeh and Salvage 1997). It has a transport module and a geochemical module. The transport module simulates advection, dispersion, and diffusion of aqueous components and mass balance of adsorbent components and ion-exchange sites. Both transient and steady state transport can be modeled. The geochemical module uses nine types of reactions to compute species distribution of equilibrium-and kinetic-controlled adsorbed, ion-exchanged, and precipitated species. The two modules are solved iteratively to determine the concentrations of chemicals as a function of time and space. Additionally, the chemical speciation is determined at specified nodes. The flow velocity, moisture content and pressure head must be computed using a subsurface flow model and then input into HYDROGEOCHEM.

3.12 Conclusion

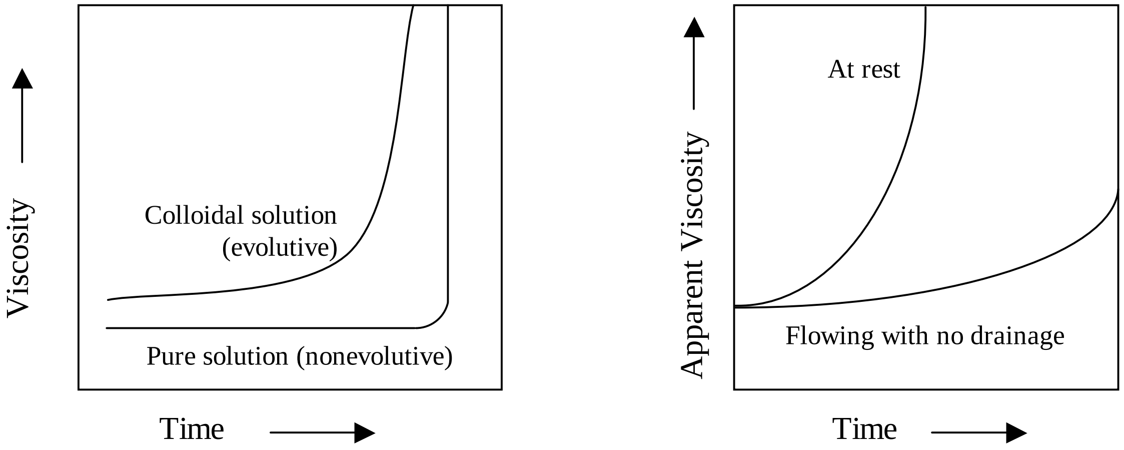
The potentially suitable materials identified for possible use in passive site remediation include several types of grouts, iron, and bacteria. Potential delivery systems include injection and extraction wells, electrokinetics, and magnetic fluids. Numerous groundwater modeling codes were also identified. These materials, delivery systems, and modeling codes are evaluated for use in passive site remediation in Chapter 4.



$$1: \quad \tau = \mu \frac{dv}{dx}$$

$$2: \quad \tau = c + \mu_B \frac{dv}{dx} \cong \mu' \frac{dv}{dx}$$

Figure 3-1 Rheological laws for (1) Newtonian fluid and (2) Bingham body (After Lombardi 1985)



(a) Newtonian Fluids (Solutions)

(b) Bingham Fluids (Stable thixotropic suspensions)

Figure 3-2 Rheological behavior of typical grouts (After Mongilardi and Tornaghi 1986)

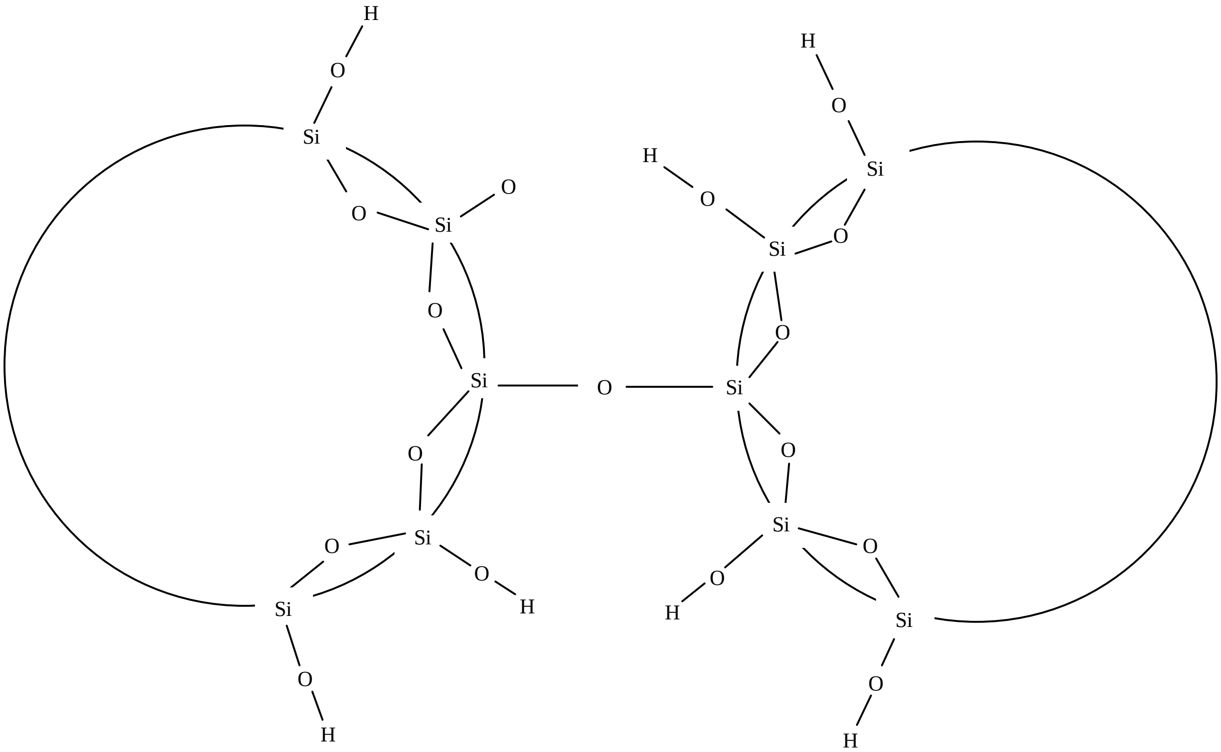
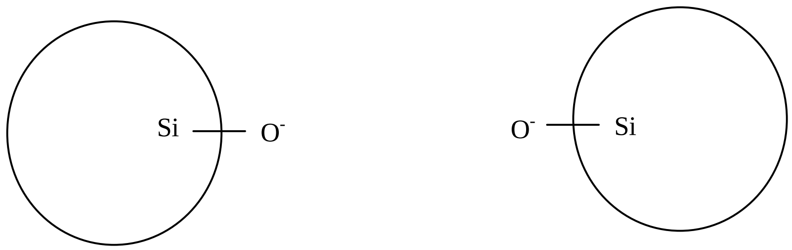
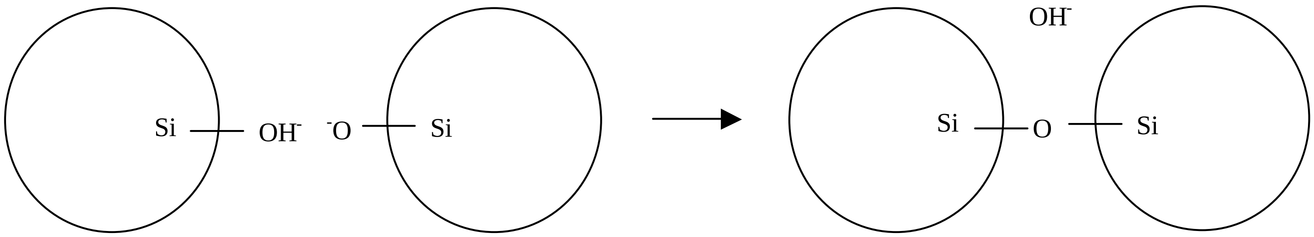


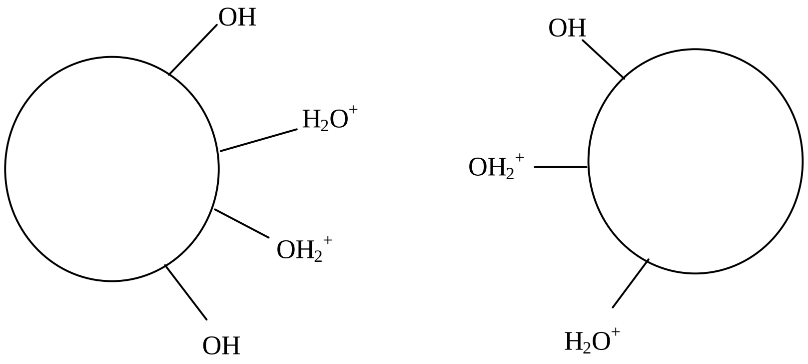
Figure 3-3 Formation of siloxane bonds as colloidal silica particles gel (After Moridis et al. 1995)



(a) pH ≥ 8: O^- on surface causes particles to repel each other



(b) 5 < pH < 8: O^- on surface of one particle forms bond with H on other particle, Si-O-Si bond forms between molecules



(c) pH < 5: particles are neutral or repel each other

Figure 3-4 Behavior of colloidal silica particles at different pH's

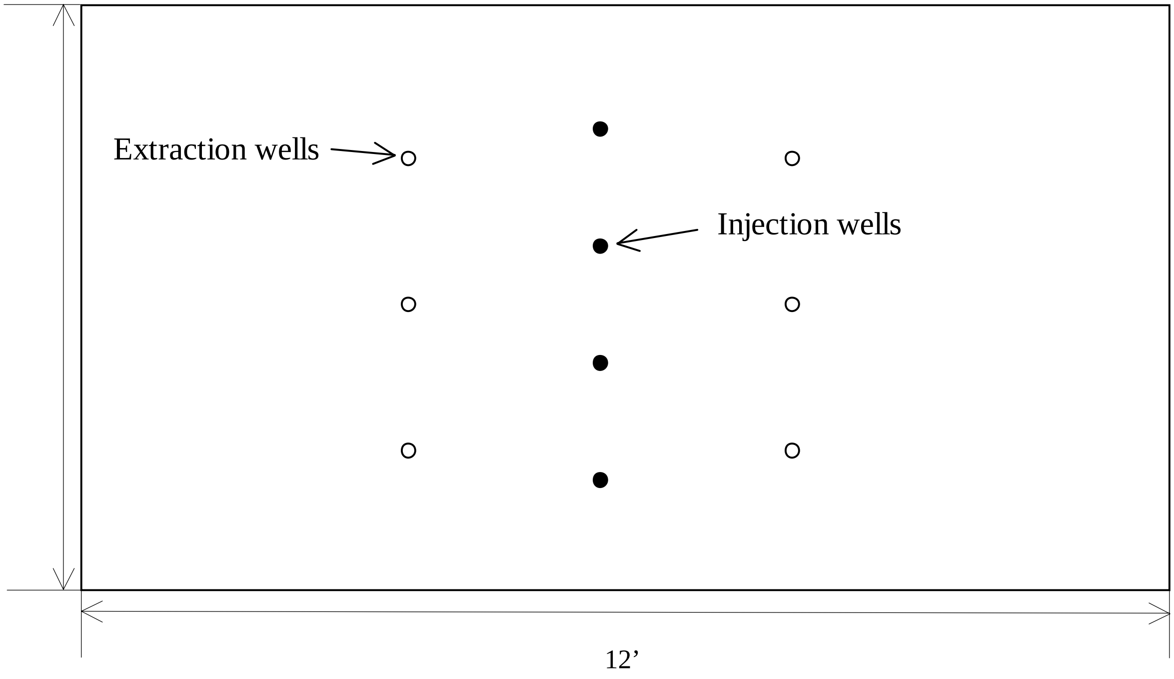


Figure 3-5 Layout of injection and extraction wells in sandbox experiment (After Noll et al. 1992)

4.0 EVALUATION BASED ON PERFORMANCE CRITERIA

Based on the literature review, potentially suitable materials were evaluated for use in passive site remediation. The characteristics of the materials were evaluated to see how closely they matched the performance criteria. The ability of the grout candidates to meet the performance criteria is summarized in Table 4-1. Depending on the results of the evaluation, the materials were either selected for laboratory testing or eliminated from further consideration. Delivery systems and modeling techniques were also evaluated.

4.1 Cement-based grouts

Microfine cement grouts are expected to be good candidates for passive site remediation because they should be able to penetrate liquefiable sand formations. Extended set times may be possible given the availability of new set-retarding admixtures that can retard hydration for up to 72 hours. Higher doses of these admixtures may result in extended set times. Microfine cement grouts are likely to be the most economical stabilizers available. Cement grouts have a long history of use in grouting applications. They are expected to be chemically and mechanically stable and to have excellent durability characteristics. In addition, safety, handling and environmental concerns are expected to be minimal.

The main concerns with respect to microfine cement grouts are the typical values of viscosity, cohesion and stability. Low-viscosity grout formulations tend to be unstable while stable formulations tend to have high values of viscosity and cohesion. Laboratory testing was done to determine if a stable grout with a low viscosity and cohesion as well as an extended set time could be formulated.

4.2 Colloidal silica

Colloidal silica is expected to be an excellent candidate for use in passive site remediation. In low concentrations, colloidal silica has a viscosity and density similar to water. The gel time is controllable and reproducible and long gel times are possible. The material has minimal safety, handling and environmental concerns. It is also expected to be cost-competitive with other technologies. Colloidal silica gels are expected to be chemically stable and have excellent durability characteristics. Based on these considerations, colloidal silica was selected for laboratory testing.

The main concern with respect to most chemical grouts, including colloidal silica, is the mechanical stability. Most chemical grouts will gradually disintegrate when subjected to wet/dry or freeze/thaw cycles, but this should not be a problem for this application. It is possible that repeated earthquake cycles could cause the grout bonds to break as well. In most cases, once the bonds are destroyed they do not heal. However, is unlikely that all of the bonds in the entire treatment area would be destroyed in a single earthquake event. It is likely that the destruction of bonds would be partial and the bulk of the treated area would remain intact.

4.3 Chemical grouts

4.3.1 Sodium Silicate

Sodium silicate has a long history of use in the United States and is one of the primary chemical grouts in use today. It meets the performance criteria in terms of viscosity and is expected to be cost-competitive. The toxicity depends on the catalyst used to formulate the grout. For example, formamide and ethyl acetate are both toxic, so there would be safety, handling and environmental concerns if these catalysts were used.

The primary concerns with respect to sodium silicate are gel time and durability. According to Karol (1990), gel time is not well controlled at long gel times. The issue of mechanical stability was discussed in the previous section. Additionally, the chemical durability of formulations with long gel times is questionable. The neutralization of sodium silicate will be reversed if there is any unreacted soda ash in the grout. Grouts with long gel times have low concentrations of reactant, which results in unreacted soda ash in the gel. Whang (1995) estimates the lifetime of sodium silicate grouts to be in the range of 10 to 20 years. Therefore, sodium silicate grouts have been eliminated for further consideration in the passive site remediation application.

4.3.2 Acrylamide

Acrylamide grouts have low viscosity values and easily controlled gel times. Gel times of several hours have been reported and there is a possibility that gel times could be extended beyond that limit. Acrylamide grouts are also expected to be chemically stable and to have excellent durability characteristics. Mechanical stability presents the same concerns discussed in Section 4.2. Karol (1990) considers acrylamide grouts to be permanent, although a specific lifetime is not reported.

The primary concerns with the use of acrylamide grouts for passive site remediation are the environmental, safety and handling concerns. Acrylamide is a neurotoxin in powdered form and in solution. If formulated and used properly, the toxicity should be minimal; however, Karol (1990) suggests that acrylamide should not be used in areas where there is any potential migration into drinking or recreational water bodies. Another concern is the cost. Acrylamide grouts are very expensive and are not likely to be cost-competitive with other methods of ground improvement. Therefore, acrylamide grout was not considered further for use in this application.

4.3.3 Acrylate

Acrylates meet the performance criteria with respect to viscosity and gel time control. There is also the possibility of extending the gel time by increasing the dosage of retarder used in formulating the grout. It has minimal safety, handling and environmental concerns. Acrylate grouts have fair chemical resistance except in acidic environments and are mechanically stable except under in freeze/thaw or wet/dry cycling. The mechanical stability concerns discussed in Section 4.2 apply to acrylate grouts as well.

Acrylate grouts are not durable enough to be used for passive site remediation. Whang (1995) estimates their lifetimes to be in the range of 10 to 20 years. Additionally, acrylates grouts are expensive. Therefore, they were not considered further.

4.3.4 Iron precipitation grouts

Iron precipitation grout meets the performance criteria in terms of viscosity. The durability and permanence of iron precipitation grout would depend on the geochemical environment. There is a possibility that set times could be extended, but the manufacturer discontinued research on iron precipitation grouts. Therefore, it was ruled out for further consideration for passive site remediation.

4.3.5 Epoxy

The elastomeric epoxy considered here meets the performance criteria with respect to viscosity, durability and permanence. It is nontoxic and presents minimal safety, handling and environmental concerns. However, it is a poor candidate for passive site remediation because it is prohibitively expensive and has a maximum set time of about eight hours.

4.3.6 Polysiloxane

Polysiloxane would be an excellent candidate for passive site remediation if it were not prohibitively expensive. It meets the performance criteria with respect to viscosity, durability and permanence. It has the potential for extended set times. It is nontoxic and presents minimal safety, handling and environmental concerns. However, the cost is so high that it would not be cost-competitive with other technologies. Therefore, it was eliminated for further consideration in this application.

4.4 Zero-valent iron

Zero-valent iron is extremely sensitive to oxidation and reduction, so it is likely that iron minerals precipitated by redox reactions will not be chemically stable or permanent. In addition, iron redox reactions occur very quickly and close to the iron source, so it would be extremely difficult for dissolved iron to travel through the entire treatment zone without reacting.

Johnson and Tratnyek (1994) performed a column study to model the distribution of chemical conditions that would develop through a treatment zone containing iron. They found that aerobic corrosion caused rapid depletion of the dissolved oxygen in the water entering the treatment zone. Anaerobic corrosion then caused the iron concentration and pH to rise throughout the remainder of the treatment zone. The pH and iron concentrations decreased quickly after leaving the treatment zone. The zones of precipitation that formed at each end of the treatment zones were narrow.

For iron to be successful in a passive site remediation application, it would have to be placed in all pores of the formation prior to the occurrence of the redox or cementation reactions. It might be possible to do this using colloidal zero-valent iron or ferric chloride. However, even if it were possible to place iron in all the pores of the formation and cause iron precipitates to form, it is likely that the reactions would reverse when the groundwater regime returned to pretreatment conditions. Therefore, zero-valent iron was eliminated from further consideration in this application.

4.5 Biological Materials

Biofilms are not expected to be good candidates for passive site remediation. While bacteria and biopolymers have been tested successfully in the lab, the biopolymers or bacteria were added to the soil and mixed thoroughly. Experiments in which bacteria were injected into a column or reservoir simulator have been successful, but field trials were unsuccessful. The main concern with respect to biofilms is the long-term durability. Even if biofilms could be maintained for long periods without additional nutrient stimulation, adding oxidants such as bleach to the groundwater could dissolve them. If contaminants were introduced to the treated formation, the biofilm might not be permanent or stable. Therefore, biopolymers and bacteria were eliminated from further consideration.

4.6 Delivery Systems

The goal of passive site remediation is to deliver the stabilizer to the formation while disturbing the site as little as possible. Therefore, the natural groundwater flow regime will be the first candidate for a delivery system. The natural groundwater flow regime may be adequate to deliver the stabilizer in a timely manner if the hydraulic gradient and the hydraulic conductivity of the formation are large enough. In situations where the hydraulic conductivity or the hydraulic gradient is insufficient, low-head injection wells or extraction wells could be used to augment the natural groundwater flow regime.

Both low-head injection wells and extraction wells would increase the hydraulic gradient in the treatment area. Extraction wells have the added advantage of causing the groundwater flow to be directed to the area of interest. A disadvantage of extraction wells is that they could produce large quantities of water, which would need to be handled in some manner. Ideally, the produced water could be used to mix the stabilizer. Another option would be to discharge the water to a surface body or storm sewer, but this scenario would likely require approval from environmental or local officials.

Magnetic fluids are not expected to be suitable for the delivery of the stabilizers to the target area. The magnetization of ferrofluids depends strongly on the strength of the magnetic field. Currently, ferrofluids are used for distances of up to 1 meter from the magnetic source. It would be extremely difficult and costly to set up a magnetic field that would act on the order of a few hundred feet. Therefore, magnetic fluids were not considered further for use as a delivery system.

Electrokinetic processing requires the establishment of an electric potential across the treatment area. The cost of setting up an electric field across the treatment area would likely be prohibitive. Therefore, this delivery method was not considered further. If the opportunity to do passive site remediation were to arise at a power plant and free electricity were available, this method could be reconsidered.

4.7 Groundwater Modeling

MODFLOW, MODPATH and MT3D were considered to be excellent candidates for preliminary modeling of passive site remediation. These models are industry standards and are well verified. MODFLOW is versatile and capable of modeling many different scenarios. MODPATH is useful for determining travel times and could also be used to determine the capture width for injection and extraction wells. The contaminant transport capabilities of MT3D could be used to determine if the appropriate concentration of stabilizer could be delivered to the target area. Additionally, GMS is a powerful pre- and post-processing tool with excellent graphics.

The main difficulty with using MODFLOW is the inability to model the addition of a stabilizer with a viscosity that is different than the viscosity of water. As the higher-viscosity stabilizer is injected and travels through the formation, the hydraulic conductivity of the formation will decrease according to the relationship described by Equation 2-3. This behavior cannot be modeled using MODFLOW. However, if the entire treatment area is assigned the lower hydraulic conductivity associated with the higher-viscosity stabilizer, then an upper bound of travel time can be estimated. If passive site remediation is determined to be a feasible technology, either a MODFLOW module could be written to account for a variable viscosity, or a program such as TOUGH2 or NUFT could be used.

TOUGH2 and NUFT were considered to be good candidates for modeling passive site remediation. They are both capable of modeling aqueous phases with variable viscosities. TOUGH2 is especially attractive because it has a module to simulate grout injection. NUFT is appealing because is will eventually be available for use through the GMS platform. However, neither is commonly used in the groundwater modeling industry, so they are not readily available to practitioners who might be applying this technology. Therefore, MODFLOW, MODPATH, and MT3D were selected for use in the preliminary modeling.

The programs SUTRA and HYDROGEOCHEM 2 were eliminated from further consideration for the following reasons. The idea behind using SUTRA was to consider modeling the stabilizer as a fluid with a variable density. If the viscosity of the stabilizer could be modeled as a variable-density fluid, then SUTRA might be successful in modeling the flow processes of the combined system. However, there was no way to correlate the viscosity of the stabilizer with a variable density. Additionally, the passive site remediation problem is three-dimensional, so it would be difficult to model it accurately with a two-dimensional code. Therefore, SUTRA was eliminated from further consideration.

HYDROGEOCHEM2 was originally considered for use because of the potential for geochemical reactions between the stabilizer, the groundwater and the soil formation. However, none of the stabilizers selected for laboratory testing is expected to interact geochemically. Since the code is two-dimensional and requires that the flow field be modeled independently, it was eliminated from further consideration.

4.8 Selection of Materials for Testing, Delivery Systems, and Modeling Codes

Based on the results of the evaluation, colloidal silica and microfine cement were selected for laboratory testing. Colloidal silica is likely to be able to meet most of the performance criteria required for a stabilizer. Microfine cement is less likely to be able to meet all of the performance criteria, but if it can meet enough to be suitable for passive site remediation, it would likely be the most cost effective material available. The microfine cement testing program and results are presented in Chapter 5. The colloidal silica testing program and results are discussed in Chapter 6.

Injection and extraction wells were selected for further consideration as delivery systems. MODFLOW, MODPATH and MT3D were considered to be the best modeling codes available for a preliminary analysis of the feasibility of passive site remediation. The groundwater and stabilizer transport modeling are presented in Chapter 7.

Table 4-1 Evaluation of Grouts with Respect to Performance Criteria

Criterion	Essential or Desireable (E/D)	Microfine Cement	Colloidal Silica	Sodium Silicate	Acrylamide	Acrylate	Iron Precipitation	Epoxy	Polysiloxane
Low initial viscosity	E	N[1]	Y	Y	Y	Y	Y	Y	Y
Slow evolution of viscosity	E	Y	Y	Y	Y	Y	M	N	Y
Gel or reacts rapidly	D	N	N	N	Y	N	M	Y	Y
Forms firm gel, cement, or precipitate	E	Y	Y	Y	Y	Y	Y	Y	Y
Long induction period	E	M	Y	M	M	M	M	M	M
Controllable and reproducible gel time	E	M	Y	M	M	M	M	M	M
Expected lifetime (years)	E	>25	>25	10-20	>25	10-20	Unknown	>25	>25
Chemically stable	E	Y	Y	N	Y	M	M	Y	Y
Mechanically stable	E	Y	M	M	M	M	M	Y	M
Stabilizer is compatible with formation	E	Y	Y	Y	Y	Y	M	Y	Y
Minimal safety, handling, and mixing concerns	D	Y	Y	M	N	Y	N	Y	Y
Minimal environmental concerns	D	Y	Y	M	N	Y	M	Y	Y
Cost-competitive	D	Y	Y	Y	N	N	Y	N	N

1 - Y – Yes; N – No; M – Maybe