The Transport and Fate of Chromium(VI) in Deep Well Disposal Zone.

Jaehyuk Hyun

Louisiana State University and Agricultural & Mechanical College

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The transport and fate of Cr(VI) in deep well disposal zone

Hyun, Jaehyuk, Ph.D.

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The Transport and Fate of Cr(VI) in Deep Well Disposal Zone

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Civil Engineering

by

Jaehyuk Hyun
B.S., Sung Kyun Kwan University, 1979
M.S., Texas Tech University, 1985

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ABSTRACT

Several parameters affecting the behavior of Chromium(+VI) in deep well injection zones were studied. Temperature, pH, concentration of inorganic salt in wastewater, and organic chemicals co-injected with wastewater were considered as they affect the adsorption and reduction rates of Cr(VI). Water content, bulk density of shale and sand, and temperature were examined for their effect on the diffusion rate of Cr(VI) in porous media.

Adsorption and reduction of Cr(VI) were investigated using three clays, Na-Montmorillonite, Illite, and Kaolinite, and sand from an injection well formation in southern Louisiana, and a confining layer shale obtained from a second Louisiana injection well. Diffusion rates of Cr(VI) in the confining layer shale and sand were measured using a radioactive tracer ($^{51}$Cr). A transport and fate model of Cr(VI) wastes was developed by incorporating the effects of reduction and adsorption in the governing equations for the injection zone sand and shale confining layers. Advection and dispersion were the driving forces in the sand layer; diffusion was the driving force in the confining shale.

Experimental and modeling results demonstrate that temperature and pH affected the adsorption, and reduction significantly. The amount of inorganic salt did not affect the
above reactions significantly. Diffusion was affected by temperature, water content, and bulk density to a great extent. The simulation of Cr(VI) transport demonstrated the excellent capability of deep well injection zones to confine Cr(VI) wastes in that area safely without posing a threat to other groundwaters. After 500 years of continuous injection, Cr(VI) was predicted to move just a few meters vertically and less than a hundred meters horizontally at low temperature and high pH (2.0), which was the worst condition evaluated. Higher temperature and lower pH were found to reduce Cr(VI) waste transport.

These results indicate that deep well injection may be used for treatment of Cr(VI) wastes with due attention paid to the favorable environmental factors such as pH, temperature, and organic compounds for the attenuation mechanisms such as adsorption and reduction, and for the retardation of Cr(VI) waste transport.
CHAPTER 1
INTRODUCTION

The disposal of hazardous wastes by deep well injection has been practiced for more than thirty years. This method of disposal is favored over other disposal methods, because of its relatively low cost. However, much of the doubt regarding deep well injection arises from the lack of information available on the transportation and ultimate fate of hazardous materials after injection (Gordon and Bloom, 1986).

The United States Congress has passed legislation aimed at controlling all forms of hazardous waste disposal. These measures include the Federal Clean Air Act, Toxic Substances Control Act, Safe Drinking Water Act, Clean Water Act, and most important to this study, the Resource Conservation and Recovery Act of 1976 (Public Law 94-580). This law, among other provisions, gives the Environmental Protection Agency (EPA) the authority to list and identify hazardous wastes, and to regulate their disposal. Additionally, section 3000.4(f) and (g) allows for the banning of well disposal by August, 1988 unless it can be demonstrated that waste injection is not harmful to the environment or to public health. An EPA memorandum, dated June 12, 1987, proposes that deep well disposal may be allowed to continue if it can be shown that the waste will either be rendered non-hazardous in the
disposal zone or that the waste will remain confined for at least 10,000 years.

Louisiana has also passed legislation directed towards controlling the production and disposal of hazardous wastes. Included among these measures are LA Act 334 of 1978, LA Act 449 of 1979, and LA Acts 795 and 803 of 1984. LA Act 803 prohibits well disposal of hazardous wastes after January 1, 1991 unless the waste cannot be reduced by current technology, the waste cannot be reclaimed, well disposal is not hazardous to the environment or human health, and no other reasonable method of disposal exists (Aubert, 1986).

1.1 Scope of Study

The environmental conditions of deep well disposal zones are quite different from those of other shallow subsurface areas. Many investigators have studied the interactions of hazardous municipal and industrial wastes with surface soils and shallow aquifers under moderate environmental conditions, i.e., ambient temperature, pH near 7, and dilute inorganic salt concentration). Deep well disposal zones are typically characterized by high temperatures (50 - 80 °C), low pH (<2) resulting from acid injection fluids, high inorganic salt concentrations (> 10,000 mg/L) and uniform geologic formations (sandstones for aquifers, and shales for aquitards). Little information is available on the interactions between hazardous wastes and soils under extreme
environmental conditions commonly faced in deep well disposal zones.

Part of the justification for this study is the possibility of providing information which may be beneficial in developing guide lines for deep well disposal of chromium(VI) contaminated wastewater. Twenty percent of all injected wastes in LA are classified as wastewater containing more than five percent chromium. This study will quantitatively examine interaction of a specific hazardous waste having potassium chromate at a concentration below 100 mg/L, with disposal reservoir rocks and assess the characteristics of transport of this hazardous waste after well injection.

This research describes interactions, such as adsorption, reduction and diffusion, involving Cr(VI) solution and sandstone matrices and shale matrices. This information is used to simulate the transport of Cr(VI) wastewater in deep well disposal zones. A mathematical model for the processes will be solved numerically using the Stehfest's approximate inverse Laplace transform method.

1.2 Objectives

The ultimate goal of this research is to determine the fate and transport of Cr(VI) as it may be affected by adsorption and reduction in deep well disposal zone. The proposed research will investigate those parameters affecting
the fate of Cr(VI) in deep well disposal zone, and will simulate the transport of Cr(VI) into the confining layers and through the sand formations.

Those important parameters to be studied are: (1) temperature, pH, NaCl concentration and organic chemicals co-injected for the adsorption process, (2) temperature, pH, soil organic material and NaCl concentration for the reduction process, (3) temperature, bulk density, water content, Cr(VI) concentration, and NaCl concentration for the diffusion process, and (4) combining these effects to simulate the fate and transport of Cr(VI) for given injection periods ranging from 50 to 500 years.

The adsorption process is investigated using actual formations (shale and sandstone obtained from a deep well in St. Charles Parish, LA and St. Bernard Parish, LA, respectively), and three types of purified clay. Actual formations are used for the reduction, diffusion, and transport simulation.
CHAPTER 2
BACKGROUND

2.1 History of Injection Wells

Deep well injection of liquids began about 50 years ago in the petroleum industry to increase oil production. In the 1930s, it became common practice to dispose of saltwater (brines) which usually accompanied oil and gas production by injection into underground formations. Deep well disposal of chemical wastes at greater depths began in 1950s.

According to the report provided by Jacobus et al. (1985), Louisiana wells accounted for more than 21 percent of the approximately 12.5 billion gallons of hazardous waste disposed of during 1983. Industries within seven Louisiana parishes between Baton Rouge and New Orleans produced 13.5 million tons of hazardous wastes during 1983. More than 98% of these wastes were retained on site and were then handled by injection well technique (73%) or surface impoundment (26%) prior to treatment. Over 60% of the net wastes produced in Louisiana in 1983 was water containing small concentrations of hazardous materials under EPA designator codes D002(Corrosive), D003(Reactive), and D007(Chromium>5.0 mg/L) (Figure 2-1).

The apparent popularity in Louisiana of waste disposal by deep well injection can be attributed in no small part to the extreme cost advantage enjoyed by well disposal relative to other methods of waste disposal (Jacobus et al., 1985). As
Figure 2-1: Wastes Produced in Louisiana in 1983

EPA Wastes (Jacobus, et al., 1985)

- Unknown (15.3%)
- Corrosive (17.7%)
- Mixed (19.5%)
- Reactive (22.1%)
- Chromium (19.0%)
- Others (4.1%)
- Generic (2.1%)
indicated in Table 2-1, average disposal cost per ton for injection well disposal in Louisiana is $0.54, cost per ton for landfill is $24.00, and cost per ton for incineration is $136.00, EPA estimates for average waste disposal costs are $8.00 per ton for well injection, $28.00 per ton for surface impoundment, and $50.00 per ton for landfiling (Gordon and Bloom, 1986). Moreover, some treatment methods like incineration can produce an eventual greater waste volume. Some waste compounds are not biologically degradable or are difficult to decompose and are possibly better suited for underground disposal.

There are other types of injection wells in use today (CMA, 1984). One type of well is used for the injection of natural gas in geologically suitable underground formations to store it for future use. More recently, another type of injection well known as a barrier well, has been used to prevent the intrusion of saltwater into usable groundwater. Disposal wells also are used by municipalities for sewage disposal and paper, mining, automotive, and food processing industries for waste disposal.

2.2 Disposal Well Design

The main concern in planning hazardous waste disposal wells is protection of fresh water sources from contamination by the wastes (Galley, 1968; Martinez, 1979; Pojasek, 1980; Reeder, 1977; Smith, 1979; Warner, 1968). Hazardous wastes,
Table 2-1: Estimated Cost for Waste Disposal/Ton on Site

<table>
<thead>
<tr>
<th>METHOD</th>
<th>LOW 10%</th>
<th>HIGH 10%</th>
<th>AVERAGE</th>
</tr>
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<tbody>
<tr>
<td>Injection</td>
<td>$0.06</td>
<td>$1.72</td>
<td>$0.54</td>
</tr>
<tr>
<td>Welling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfill/</td>
<td>$3.00</td>
<td>$94.00</td>
<td>$24.00</td>
</tr>
<tr>
<td>Impoundment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incineration</td>
<td>$20.00</td>
<td>$8,000</td>
<td>$136.00</td>
</tr>
</tbody>
</table>

Note: The low 10% of incineration cost is positive, indicating energy recovery.

Source: Jacobus et al., 1985
usually in aqueous form, are injected under pressure into wells penetrating porous and permeable sedimentary rock formations such as sandstone and limestone. The Resource Conservation and Recovery Act (RCRA) identifies hazardous wastes by low pH(<2.0), high pH(>12.5), materials containing cyanides, phenols, sulfides, non-halogenated hydrocarbons in certain concentrations, and materials containing specified concentrations of heavy metals. The rock formations are separated from each other and from the surface by impermeable confining layers, such as shales. The disposal formations are located from about 1000 feet below from the surface to more than 10,000 feet below the surface.

Waste streams must usually be pretreated before injection to prevent damage to surface equipment and subsurface tubulars, and to prevent plugging of the injection zone. Pretreatment includes filtration to remove solids and chemical treatment to prevent formation of precipitates in the disposal zone. Salinity of injected fluid must sometimes be adjusted, as many disposal formations are sensitive to the introduction of wastewater. Mungan (1965) found that formation damage in the form of permeability decrease occurred due to the injection of fresh water in formations containing the clays illite and kaolinite. The decrease in permeability resulted from small pore channels in the formations being blocked by fine particles such as dispersed clays and cementation material. Particles became dislodged due to changes in
EPA criteria for deep well disposal wells address all aspects of the wells from design to operational monitoring (Smith, 1979). Disposal wells must be designed to prevent the escape of wastes via 1) inadequate confining beds, 2) unplanned hydraulic fracturing of confining layers, 3) displacement of saline water into a potable aquifer, 4) migration of injection liquid into a potable water source, 5) upward migration of waste liquid from the injection zone along the outside of well casing, 6) escape into a potable aquifer due to wellbore failure, and 7) vertical migration and leakage through abandoned or closed wells in the vicinity. Additionally, leaks in the confining layers due to dissolution channels and shrinkage cracks induced by geochemical reactions of wastes must also be avoided.

The Underground Injection Control portion of the Federal Safe Drinking Water Act provides the measure of protection for present and future sources of drinking water. Whiteside and Raef (1986) interpreted the UIC regulations as follows: Disposal formations must be saline aquifers containing at least one percent (10,000 mg/L) total dissolved solids. This criterion may be waived if 1) the aquifer contains greater than 3,000 mg/L TDS and less than 10,000 mg/L TDS, 2) the aquifer is not currently a source of potable water, and 3) the aquifer cannot in the future serve as a source of potable water. A candidate aquifer must have adequate volume and
petrophysical properties such as porosity and permeability. There must be adequate confining layers which restrict fluid movement into drinking water zones or into hydrocarbon zones. The area of the injection site should have minimal faulting and risk of seismic activity, and should contain no unplugged wells.

The UIC regulations require disposal well to be completed with three casing strings, such as conductor pipe, surface casing, and protection casing. The largest diameter casing, conductor casing may either be driven into the ground, or cemented in a drilled hole. The purpose of this casing is to seal shallow water zones and protect against loss of circulation during subsequent drilling operations. The second casing string, the surface casing, is set in the well at a depth corresponding to the 3,000 mg/L TDS water. The surface casing should be cemented up to the surface and should be pressure tested upon curing. The smallest diameter casing, the protection casing, must be set to at least the 10,000 mg/L TDS water depth. This casing also is cemented up to the surface, and provides some redundancy in protection of drinking water zones. George and Thomas (1986) compiled a comprehensive cementing technique for use in disposal wells. Injection tubing is installed inside the protection casing. Injection tubing may terminate at a packer, which provides a physical pressure resistant barrier to the movement of injected fluids into the case-tubing annulus. Figure 2-2 is a diagram of a
Figure 2-2: Schematic of a Disposal Well Utilizing a Packer Seal

Source: Gordon and Bloom, 1986
disposal well which utilizes a packer seal. Some disposal wells utilize a fluid seal to provide the barrier to movement of injected fluids into the casing-tubing annulus (Figure 2-3). Before injection begins, completion techniques such as sand screen installation or gravel packing may be used to prevent the migration of formation solids into the disposal wellbore.

The UIC regulations provide also the section of monitoring of disposal wells. Continuous recordings must be made of injection pressure, flow rate, volume injected, and casing-tubing annulus pressure. Maximum allowable injection pressure is determined by fracture leak-off tests or by the use of fracture pressure correlations. Annulus pressure can be maintained above injection pressure, so that any leaks occur from the annulus into the injection tubing rather than vice versa. Most disposal well installations use sacrificial corrosion-monitoring plugs in the injected stream to predict tubing replacement time and evaluate replacement materials.

Mechanical integrity of waste disposal wells must be demonstrated initially and every five years for the working life of the well. UIC mechanical integrity includes 1) no leaks in the casing, tubing, or packer and 2) no vertical fluid movement into a source of drinking water. Leak detection can be accomplished by pressure tests on the annulus. Vertical migration can be detected or inferred by logging techniques such as acoustic cement bond logging, temperature logging of
Figure 2-3: Schematic of a Disposal Well Utilizing a Fluid Seal

Source: Gordon and Bloom, 1986
deviations from an area's geothermal gradient due to fluid flow, and noise logging to detect casing leaks. One of the most common logging techniques for leak detection is the radioactive tracer log, although this method is not mentioned in the UIC regulations.

EPA conducted a survey of the hazardous waste injection industry and the results were reported by Brasier (1986). Salient statistics revealed by the EPA report are that the average disposal well depth is 4,000 feet, the average separation of the disposal zone from aquifers containing less than one percent TDS is 2,800 feet and sixty six percent of injection zones are sand or sandstone with a shale confining layer. All disposal wells contain tubing and at least two casing strings. Most of the wells utilize a packer. The packer-less wells rely on a fluid seal to separate the casing-tubing annulus and the injection fluid.

2.3 Gulf Coast Geology

Virtually, all types of hazardous wastes are being disposed of by deep well disposal in the Gulf Coast area. Some general classes of compounds are organic acids, alcohol, solvents, inorganic acids, bases and salts (Ciaccio, 1971; Green, 1983; Mackay et al., 1985).

60% of the 195 deep waste injection wells active in the United States during 1983, were located in Louisiana and Texas. Most of the 195 disposal wells were located on sites
where the wastes were generated (Jacobus et al., 1985).

Subsurface geology of the Gulf Coast is characterized by alternating layers of sedimentary deposits (Eardley, 1981). These deposits are relatively young, geologically. The principal geological structure underlying the area, the Gulf coast geosyncline, consists of more than twenty thousand feet of Tertiary and Quaternary sediments. Rocks in this area range in age from recent to about 65 million years old, and are frequently unconsolidated. Another common geologic structure in the Gulf coast region is subsurface salt domes. Salt domes exist in various sizes and shapes, and are often a basis of geologic traps for petroleum, as the salt has pierced and deformed near-by fluid bearing sedimentary strata.

In the Gulf Coast region, zones suitable for waste disposal are composed primarily of sandstone, which typically exhibits the necessary permeability and porosity such that large quantities of fluid can be injected (Latil, 1980). Often, these reservoirs are not pure sandstone, and may be streaked with another sedimentary rock, such as shale, or the sandstone matrix may contain some concentration of impurities, such as clays. Van der Marel and Beutelspacher (1976) presented a detailed study of these materials. Some of the common clays and related minerals indigenous to Gulf Coast sand stone formations are listed in Table 2-2.

Some of the clays present in sandstone formations are active clays and react preferentially with certain ions and
Table 2-2: Clays and Related Minerals Common to Sandstones

- Kaolins - Kaolinite
- Smectites - Montmorillonite
- Micas - Illite, Potassium Bentonite, Vermiculite
- Chlorites - Hydrated Chlorite
- Irons - Hematite
- Silicas - Quartz
- Carbonates - Ca, Dolomite
- Sulphurs - Sulfide, Sulfate
- Feldspars - Na, Ca
- Organic Matters - Lignin, Coke

Source: Van der Marel and Beutelspacher, 1976
other molecules (Bourgoyne et al., 1986). Typically, Na-
Montmorillonite, the major mineral in bentonite, reacts with
water, a polar molecule, as follows: When bentonite is brought
into contact with fresh water, the water molecules hydrate the
sodium ions and displace the ions from the surface or
interlayers of the crystals in bentonite. The hydrated ions
and water molecules are physically much larger and cause the
bentonite structure to expand about 10 to 12 times its
unreacted size. This hydration is reversible and responds
differently to varied ions in solution, thus explaining why
some sandstone formations are sensitive to the introduction of
freshwater. Expansion or swelling of clays in the presence of
fresh water inside a sandstone matrix can result in a drastic
reduction in the permeability of the sandstone, as the
physically larger clay molecules take up more space in the
pore channels within the sandstone. Other reactions can cause
the clay to become a 'migratable fine' and physically plug
pore throats. Inorganic ions which react to change the volume
of bentonite are sodium, potassium, calcium, and some acids
and bases. Organic molecules may produce similar effects
depending on the magnitude of their dielectric constant. Waste
streams can contain all of these ionic species, various
organic compounds, and heavy metal wastes.

2.4 Clay Minerals

The clay minerals are defined as fine grained,
crystalline, hydrous silicates with structures of the layer lattice type. They are most common products of water-rock interaction under earth-surface conditions. The term clay is also used in geology to denote a grain size of less than 2 μm. The clay fraction of soils and sediments usually contains quartz, feldspars, iron oxides and carbonates in addition to clay minerals. Naturally occurring clay minerals are classified based on chemical composition or physical structure (Beutelspacher and Van der Marel, 1968).

The most prevalent clay minerals are the layered aluminosilicates. Their crystals are composed of two basic structural units (Grim, 1963; Marshall, 1964; Hillel, 1980), namely: a tetrahedron of oxygen atoms surrounding a central cation, usually Si$^{4+}$, and an octahedron of oxygen atoms or hydroxyl groups surrounding a larger cation, usually Al$^{3+}$ or Mg$^{2+}$. The tetrahedra are joined at their basal corners and the octahedra are joined along their edges by means of shared oxygen atoms. Thus, tetrahedral and octahedral layers are formed (Figure 2-4).

The layered aluminosilicate clay minerals are of two main types, depending on the ratios of tetrahedral to octahedral layers, whether 1:1 or 2:1. In the 1:1 minerals like kaolinite, an octahedral is attached by the sharing of oxygens to a single tetrahedral layer. In 2:1 minerals like montmorillonite or illite, it is attached in the same way to two tetrahedral layers, one on each side. A clay particle is
Figure 2-4: Structures of Tetrahedra and Octahedra Clays

The basic structural units of aluminosilicate clay minerals: a tetrahedron of oxygen atoms surrounding a silicon ion (left), and an octahedron of oxygens or hydroxyls enclosing an aluminum ion (right).

Hexagonal network of tetrahedra forming a silica sheet.

Structural network of octahedra forming an alumina sheet.

Source: Hillel, 1980
composed of multiply stacked composite layers of this sort, called lamellae. The specific surface area of clay minerals, which governs many soil properties, varies from one mineral to another. It is $700-800 \text{ m}^2/\text{g}$ for montmorillonite, $100-300 \text{ m}^2/\text{g}$ for illite, and $5-100 \text{ m}^2/\text{g}$ for kaolinite (Koorevarr et al., 1983). The thickness of clay minerals varies from mineral to mineral. It is about $1.7 \text{ nm}$ for montmorillonite, $1.0 \text{ nm}$ for illite, and $0.7 \text{ nm}$ for kaolinite (Drever, 1988).

Three types of clay which represent various configurations of aluminosilicate structure are smectites, micas, and kaolins. Common examples of each clay are montmorillonite, illite, and kaolinite respectively. Each clay has structure features which contribute to its ion exchange characteristics.

2.4.1 Smectite (montmorillonite)

The term "smectite" is used to describe any clay whose basal spacing (the thickness of the 2:1 sheet plus the interlayer space) expands to $1.7 \text{ nm}$ on treatment with ethylene glycol (Dixon and Weed, 1977). Expansion by ethylene glycol is indicative of a structure in which the number of cations in the interlayer positions corresponds to about 0.2 to 0.5 unit per formula unit $[\text{O}_{10}(\text{OH})_2]$. In montmorillonite, the charge is derived by substitution of $\text{Mg}^{2+}$ for $\text{Al}^{3+}$ in the octahedral layer of pyrophyllite($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$). The compositional variations in the smectite group are enormous, resulting from substitution
of different amounts of Mg$^{2+}$, Al$^{3+}$, Fe$^{2+}$, Fe$^{3+}$, Li$^+$, and other cations in the octahedral layer and substitution of Al$^{3+}$ and probably Fe$^{3+}$ for Si$^{4+}$ in the tetrahedral layer. Smectites normally occur as extremely small crystals (less than 1 μm), so identification is usually based on x-ray diffraction. Figure 2-5 is a schematic of one configuration of smectite.

When Al$^{3+}$ and surface Na$^+$ ions replace Si$^{4+}$ in the tetrahedral layer, or Mg$^{2+}$ and surface Na$^+$ ions replace Al$^{3+}$ in the octahedral layer, other ionic species and water can readily penetrate between the sheets. This penetration causes a change in the relative positions of the layers, which is also referred as "slippage". If water penetrates between the tetrahedral and octahedral layers, the water molecules interact with sodium ions and remove them from their positions as "replacement". Removal of monovalent Na$^+$ ions results in a net negative charge on the sheets from which sodium is removed. Therefore, the entire structure is easily dispersed or expanded as the similarly charged layers repel each other (Iler, 1979). The unit layer formula of montmorillonite is Al$_{1.5}$Mg$_{0.5}$Si$_6$O$_{20}$(OH)$_4$.

The amount of water in the interlayer space is determined by the nature of the interlayer cation, the net charge on the 2:1 layer, and the humidity of the environment to which the clay is exposed. When the interlayer cation is divalent (Mg$^{2+}$ or Ca$^{2+}$), two layers of water molecules are normally present. This gives a basal spacing of about 1.4 nm. When the
Figure 2-5: Basic Structure of Montmorillonite

Source: Drever, 1988
interlayer cation is Na⁺, the amount of interlayer water may increase almost indefinitely, causing the grains to expand or swell. If the clays in an aquifer become sodium saturated, permeability is likely to decrease (Drever, 1988).

2.4.2 Mica (illite)

Mica also exhibits tetrahedral-octahedral-tetrahedral (2:1) structure. In mica, most of the tetrahedral silicon is replaced by aluminum and introduction of one K⁺ ion into the interlayer position. The layers in the micas are held together by relatively strong electrostatic forces between the negatively charged silicate layers and the K⁺ ions. Thus, no water is present in the interlayer space, and the K⁺ ions are not exchangeable under normal conditions. The basal spacing of the micas is about 1 nm. Naturally abundant from of mica is muscovite[KAl₂(Si₃Al)O₁₀(OH)₂].

Illites are the most common clay minerals in nature, making up the bulk of ancient shales. The illites in ancient shales are not ideal muscovite. Compared to muscovite, they contain less K⁺ and Al³⁺ and more Si⁴⁺. They also contain some Mg²⁺ and Fe³⁺. It appears that most natural illites have a mixed layer structure; in any crystallite, about 80 % of the layers are similar to muscovite, and 20 % are similar to smectite (Hower and Mowatt, 1966; Srodon et al., 1986). It appears that clay minerals intermediate in composition between vermiculite (smectite) and the micas do not form layers of a single type, but form mixed layer structures with some low charged
layers (smectite type) interspersed among high-charged (mica type) layers. Figure 2-6 presents the structure of illite. The unit layer formula of illite is $\text{Al}_2\text{O}_5(\text{OH})_4\text{K}_{0.8}$.

2.4.3 Kaolin (kaolinite)

Kaolinite consists of an octahedrally coordinated layer of aluminum ions and a layer of tetrahedrally coordinated silicon atoms (1:1) (Figure 2-7). These are stacked in alternating fashion and held together by hydrogen bonding in a rigid, multilayered lattice which often forms an hexagonal platelet. Since water and ions cannot enter between the basic layers, these cannot ordinarily be split or separated. Moreover, since only the outer faces and edges of the platelets are exposed, kaolinite has a rather low specific surface. Kaolinite crystals generally range in planar diameter from 0.1 to 2 μm with a variable thickness in the range of about 0.02-0.05 μm (Hillel, 1980). Owing to its relatively large particles and low specific surface, kaolinite exhibits less plasticity, cohesion, and swelling than most other clay minerals. The unit formula of kaolinite is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$.

2.4.4 Surface Charge of Clay Minerals

During the formation of clay minerals, the tetrahedral and octahedral sheets do not meet as already finished sheets. Rather they grow together unit by unit. During growth, $\text{Si}^{4+}$, $\text{Al}^{3+}$, and $\text{Mg}^{2+}$ are hardly present in the ideal ratios required for the clay mineral. Thus, if $\text{Al}^{3+}$ ions are present in excess,
Figure 2-6: Basic Structure of Illite

Source: Drever, 1988
Figure 2-7: Basic Structure of Kaolinite

Source: Drever, 1988
they may occupy Si⁺⁴ sites in the crystal lattice. Similarly, Mg⁺² ions may occupy sites of Al⁺³ ion if there is a shortage of Al⁺³ ions. This process which leads to an excess negative charge in the crystal lattice is called "isomorphous replacement" (Hillel, 1982). This is named isomorphous because these replacements hardly affect the shape of the crystal lattice. Another source of unbalanced charge on clay minerals is the incomplete charge neutralization of terminal atoms on lattice edges. These charges are balanced externally by exchangeable ions (mostly cations), which concentrate near the external surfaces of the particle and occasionally penetrate into interlamellar spaces. These cations are not an integral part of the lattice structure, and can be replaced, or exchanged, by other cations.

2.4.5 Colloid Properties

When a clay particle such as a montmorillonite is suspended in water, some of the interlayer cations pass into solution, resulting in a negatively charged silicate framework surrounded by a diffuse cloud of cations (Figure 2-8). The charged surface and diffuse cloud of positively charged ion are called a double layer. A double layer may also consist of a positively charged surface surrounded by a cloud of anions. The stability of colloidal suspensions and the ion exchange properties of solids are closely related to the behavior of the double layer.

In montmorillonite, the surface charge results from
Figure 2-8: Simple Structure of the Electric Double Layer

Source: Hillel, 1980
substitutions in the silicate framework, so the charge is more or less independent of pH. In most other natural colloids, for instance oxides of silicon, aluminum, iron, and magnesium; colloidal organic matter, the surface charge results from ionization of, or adsorption on, the surface of the solid. The surface of oxides (and the edges of clay particles) have chemical groups such as

\[ \geq \text{Si} - \text{OH} \quad \text{and} \quad \geq \text{Al} - \text{OH} \]

In strongly acid solution, these groups will accept a proton and become

\[ \geq \text{Si} - \text{O}^+ \text{H}_2 \quad \text{and} \quad \geq \text{Al} - \text{O}^+ \text{H}_2 \]

In strongly alkaline solutions, they will lose a proton and become

\[ \geq \text{Si} - \text{O}^- \quad \text{and} \quad \geq \text{Al} - \text{O}^- \]

The net charge on a surface containing such hydroxyl groups will therefore vary with pH. In acid solutions, the surface will be positively charged; its cation exchange capacity will be small and it will have a significant anion exchange capacity (Drever, 1988).

The pH at which the net charge on the surface is zero is called the "isoelectric point" (James and MacNaughton, 1977). Many transition metals, and some anions such as phosphate, are strongly adsorbed at oxide surfaces. When such species are adsorbed, the balance of electric charge at the surface is altered, and the zero point of charge will differ from the isoelectric point, which is the zero point of charge when the only reactions affecting surface charge are adsorption and desorption of protons.
2.4.6 Electric Double Layer

Because of the presence of an electron negative charge, clay in suspension can attract cations. These positively charged ions are not distributed uniformly throughout the dispersion medium. They are held on or near the clay surface. Some are free to exchange with other cations. The negative charge of the clay surface is thus screened by an equivalent swarm of counter ions that are positive. The negative charge on the clay surface and the swarm of positive counter ions are called the "electric double layer" (Tan, 1982). In general terms, the double layer consists of ions more or less attached to the solid surface (the fixed or Stern layer) and outside that a diffuse (or Gouy) layer in which the ions are free to move (Figure 2-9). In the Gouy layer, the concentration of cations not balanced by anions decreases exponentially away from the boundary with the fixed layer. The ions in the Stern layer may be held by purely electrostatic forces or by formation of complexes with groups on the surface of the solid.

The stability of a colloidal suspension depends on the thickness of the Gouy layer, which depends on the potential at the outside of the fixed layer and, approximately on the ionic strength of the solution (Table 2-3). High concentrations of electrolyte usually result in suppression of the Gouy layer. When this happens, the electrostatic repulsion that tends to keep the particle apart is not sufficient to counteract the
Figure 2-9: Schematic Picture of the Fixed and Diffuse Layer

Source: Tan, 1982
Table 2-3: Effect of Concentration and Valences of Ions on Thickness of the Diffuse Double Layer

<table>
<thead>
<tr>
<th>Electrolyte Concentration (mol/L)</th>
<th>Thickness of Diffuse Double Layer (1/K), cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 * 10^{-5}</td>
<td>1 * 10^{-5} 0.5 * 10^{-5}</td>
</tr>
<tr>
<td>1 * 10^{-3}</td>
<td>1 * 10^{-6} 0.5 * 10^{-6}</td>
</tr>
<tr>
<td>1 * 10^{-1}</td>
<td>1 * 10^{-7} 0.5 * 10^{-7}</td>
</tr>
</tbody>
</table>

Source: Tan, 1982
Van der Waals' force, which attracts the particle toward each other, and the suspension is no longer stable. This is why clay minerals commonly form stable suspensions in fresh water, but flocculate in more saline solutions such as seawater (Drever, 1988).

The thickness of the diffusive double layer is also affected by the valency of the exchangeable cations. Generally, it has been reported that at equivalent electrolyte concentrations, monovalent cations in exchange position yield thicker diffuse double layers than divalent cations (Table 2-3). Trivalent ions will decrease the thickness of the double layer more strongly than divalent ions. This phenomenon is due to the tendency of ions to diffuse away from the colloidal surface being in the following decreasing order: Monovalent ions > Divalent ions > trivalent ions. For example, sodium and potassium ions are reported to be responsible for relatively thicker double layer than calcium and magnesium ions, whereas double layer formed by aluminum ions are comparatively the thinnest. For this reason, polyvalent cations are often used in water treatment to cause flocculation (Tan, 1982).

2.5 Chromium

Chromium, a transition element, is a steel gray, lustrous, hard metal, which melts at 1857 °C, boils at 2672 °C, and has a specific gravity of 7.18 to 7.20 at 20 °C
with an atomic weight of 51.99 g/M (Weast, 1974). Chromium has economic importance in industry for the production of stainless steels, tool steels, cast iron and steel, super alloys, pigments and paints, leather tanning chemicals, metal finishing chemicals, and an anti-corrosive and anti-algal agent in cooling towers (Sitling, 1981). The radio-isotope commonly used in tracer work is $^{51}$Cr.

Chromium, the 24th element of the periodic chart, belongs to the first series of transition elements. The electronic configuration of this element is \{Ar\}3d$^5$4s$^1$. Oxidation states of chromium range from -2 to +6, but it most commonly occurs in the trivalent and hexavalent forms. Chemically, the most stable and important state is Cr(III). In this species, chromium has a strong tendency to form octahedral complexes of coordination number six with ligands such as water, ammonia, urea, ethylene-diamine, halides, sulfate, and organic acids (Weast, 1974).

Each $t_{2g}$ level in these complexes is strongly occupied, which produces a sort of half-filled shell stability (Cotton and Wilkinson, 1988). This arrangement results in extremely slow ligand exchange rates and imparts a pseudo-stability to the complex, even under conditions in which these complexes are thermodynamically very unstable. Oxidation states lower than Cr(III) are strongly reducing; in aqueous solutions only the divalent state is known. Cr(V) and Cr(IV) are formed as transient intermediates in the reduction of Cr(VI) solutions.
The highest oxidation state, Cr(VI), corresponds to the loss of the total number of 3d and 4s electrons. Stable compounds of this state exist only in the oxy species, such as CrO$_3$, CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$, and CrO$_2$Cl$_2$, which are strongly oxidizing.

2.5.1 Divalent Chromium

Chromium forms divalent compounds with oxygen, the halogens, sulfur, organic acids, and a number of complexing agents. In aqueous solution and in many of its salts, the chromous ion, Cr(II), is bright blue. Its chemical behavior is similar to that of the ferrous ion, except that the tendency to pass from the divalent to the trivalent state is much stronger with chromium than with iron. In fact, chromous ions are among the strongest known reducing agents in aqueous solution; the standard reduction potential for the Cr(II)/Cr(III) couple is -0.4 V (Weast, 1974). Due to this tendency to oxidize, chromous compounds are not found in nature (NAS, 1974).

2.5.2 Trivalent Chromium

The trivalent state of chromium is the most stable oxidation state of the element and the most important chemically. The unique characteristic of this state is the strong tendency to form kinetically inert hexa-coordinate complexes. Because of the very slow ligand exchange rate, many of these complexes can be isolated as solids, even though they are quite unstable thermodynamically. In acid solutions, the
sample ion is coordinated with the solvent as \([\text{Cr(OH}_2\text{)}_6]^{3-}\). The tendency to coordinate is as marked in the trivalent chromium species as in any other known element and extends to all kinds of ligands; it is especially strong with nitrogen compounds such as amines (Sidgwick, 1950).

2.5.3 Hexavalent Chromium

Hexavalent chromium is the highest oxidation state and the second most stable valency, next to that of \text{Cr(III)}. All stable \text{Cr(VI)} compounds are exclusively oxy molecules and potent oxidizing agents (Cotton and Wilkinson, 1988). Hexavalent chromium occurs rarely in nature, apart from man's invention, because it is readily reduced in the presence of organic matter. Hexavalent chromium occurs most commonly in the form of chromate, or dichromate, both of which are high-tonnage industrial products (NAS, 1974).

Chromium trioxide(\text{CrO}_3) is readily precipitated in the form of bright red needles by the addition of sulfuric acid to aqueous solutions of sodium or potassium dichromates. The trioxide melts at 197 °C, but it is unstable at high temperatures, gradually losing oxygen until \text{Cr}_2\text{O}_3 is formed. Its solubility in water as a function of temperature is given in Table 2-4. The trioxide is a very powerful oxidizing agent. Hydrogen, ammonia, and hydrogen sulfide are oxidized in the gaseous state. Certain organic materials such an alcohol or paper are ignited on brief contact with \text{CrO}_3 (Udy, 1956). Chromic acid(\text{H}_2\text{CrO}_4 or \text{CrO}_3\cdot\text{H}_2\text{O}), the hydrated form of chromium
Table 2-4: Solubility of Chromium Trioxide and Selected Chromates in Water

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>CrO₃</th>
<th>Na₂CrO₄</th>
<th>K₂CrO₄</th>
<th>Na₂Cr₂O₇</th>
<th>K₂Cr₂O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61.70</td>
<td>24.21</td>
<td>37.14</td>
<td>70.60</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>62.08</td>
<td>32.11</td>
<td>38.05</td>
<td>71.67</td>
<td>7.8</td>
</tr>
<tr>
<td>20</td>
<td>62.49</td>
<td>44.36</td>
<td>38.96</td>
<td>73.16</td>
<td>11.7</td>
</tr>
<tr>
<td>30</td>
<td>62.91</td>
<td>46.84</td>
<td>39.80</td>
<td>75.00</td>
<td>16.1</td>
</tr>
<tr>
<td>40</td>
<td>63.39</td>
<td>48.84</td>
<td>40.61</td>
<td>77.09</td>
<td>20.9</td>
</tr>
<tr>
<td>50</td>
<td>63.90</td>
<td>51.04</td>
<td>41.40</td>
<td>79.46</td>
<td>26.0</td>
</tr>
<tr>
<td>60</td>
<td>64.46</td>
<td>53.54</td>
<td>42.15</td>
<td>82.04</td>
<td>31.3</td>
</tr>
<tr>
<td>70</td>
<td>65.08</td>
<td>55.20</td>
<td>42.88</td>
<td>84.98</td>
<td>36.6</td>
</tr>
<tr>
<td>80</td>
<td>65.79</td>
<td>55.50</td>
<td>43.60</td>
<td>88.39</td>
<td>42.0</td>
</tr>
<tr>
<td>90</td>
<td>66.59</td>
<td>55.80</td>
<td>44.31</td>
<td>90.60</td>
<td>46.50</td>
</tr>
<tr>
<td>100</td>
<td>67.46</td>
<td>56.10</td>
<td>45.00</td>
<td>91.43</td>
<td>50.20</td>
</tr>
</tbody>
</table>

Source: Udy, 1956
trioxide, does not occur in the free state, but it is readily formed in solution. It is widely used in chrome plating and other metal finishing operations and in recirculating water systems, and cooling towers as a corrosion inhibitor for ferrous alloys (IARC, 1973).

Sodium chromate and sodium dichromate, primary products of the chemical industry, are produced by roasting chromite ore in the presence of soda ash. The soluble chromates are removed by leaching with water and are converted to sodium dichromate by treatment with sulfuric acid.

All of the metallic chromates, except those alkalies and the light alkaline earths, are insoluble in water (Cotton and Wilkinson, 1988). As the pH is lowered, solutions of chromate ions turn orange, because of the formation of dichromate ion:

\[
2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \quad K = 4.2 \times 10^{-14}
\]

Acid solutions of dichromate are powerful oxidizing agents:

\[
\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E = 1.33 \text{ V}.
\]

Basic solutions of the chromate ion are much less oxidizing:

\[
\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3^{(aq)} + 5 \text{OH}^- \quad E = -0.13 \text{ V}.
\]

The solubilities of the most important chromates and dichromates are given as a function of temperature in Table 2-4.

Potassium dichromate, once the leading commercial form of chromium, has been now largely replaced by the less costly sodium dichromate, from which almost all other chromium chemicals are prepared. In view of the ubiquity of sodium
dichromate, this compound is probably responsible for the pollution of waterways with hexavalent chromium (Weast, 1974).

2.5.4 Effect on Human and Aquatic Life

Chromium is essential to life. A deficiency (in rats and monkeys) has been shown to impair glucose tolerance, decrease glycogen reserve, and inhibit the utilization of amino acids (Saner, 1980). It has also been found that inclusion of chromium in the diet of humans sometimes improves glucose tolerance. Certain Cr(III) compounds enhance the action of insulin.

On the other hand, chromates and dichromates are severe irritants to the skin and mucous membranes, so workers who handle large amount of these materials must be protected against dusts and mists. Continued breathing of the dusts finally leads to serious ulceration and perforation of the nasal septum (Burrows, 1983). Contact of cuts or abrasions with chromate may lead to serious ulceration. Even on normal skin, dermatitis frequently results (Langard, 1982). Cases of lung cancer and asthma also have been observed in plants where chrome pigments and chromates are produced (Burrows, 1983).

The toxicity to aquatic life varies widely with the species, temperature, pH, valence of chromium, and synergistic and antagonistic effects, particularly that of hardness (NASE, 1972). The 96 hour LC$_{50}$ and safe concentrations for hexavalent chromium were reported to be 33 and 1 mg/L respectively for fathead minnows in hard water; 50 and 0.6 mg/L in soft water.
for brook trout; and 69 and 0.3 mg/L for rainbow trout in soft water (NAS, 1974). A hexavalent chromium concentration of 5 mg/L reduced photosynthesis on giant kelp by 50 % during 4 days of exposure (Clendennig, 1960). Because of the sensitivity of lower forms of aquatic life to chromium and its accumulation at all trophic levels, the maximum concentration of 0.05 mg/L has been recommended for fresh water aquatic life (AFS, 1979).

The toxicity of chromium toward bacteria is controlled by the valence of chromium, the type of organism and the amount of organic matter present. Hexavalent chromium has been reported to lower the 5 day biochemical oxygen demand (BOD₅) by 50 %, at a level of 100 mg/L (McKee and Wolf, 1963). Due to chromium's toxicity, strict E.P.A. guide lines for effluent limitations have been set for chromium as shown in Table 2-5 (U.S. General Service Admin., 1979).

2.6 Adsorption

Adsorption is the process through which a net accumulation of a substance occurs at the common boundary of two contiguous phases, such as liquid-solid phases (Everett, 1972). The study of adsorption in soils is characterized by three laboratory operations that define the net accumulation of a substance at the interface between solid particles and a contiguous fluid: 1) reaction of the soil with a fluid of prescribed composition for a prescribed period of time, 2) isolation of the soil from the reactant fluid phase, and 3)
<table>
<thead>
<tr>
<th>Industry</th>
<th>Maximum for any 1 day</th>
<th>Average Daily Chromium Values for 30 Days Shall Not Exceed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textile</td>
<td>0.04-0.14 kg/kkg Wool or Product</td>
<td>0.02-0.07 kg/kkg Wool or Product</td>
</tr>
<tr>
<td>Electroplating</td>
<td>Total Cr 80-160 mg/m² of Oper. Cr(VI) 8-16 mg/m² of Oper.</td>
<td>40-80 mg/m² of Oper. 4-8 mg/m² of Oper.</td>
</tr>
<tr>
<td>Inorganic Chemicals</td>
<td>Total Cr 0.0088 mg/L Cr(VI) 0.009 mg/L</td>
<td>0.004 mg/L 0.005 mg/L</td>
</tr>
<tr>
<td>Iron &amp; Steel Manufact.</td>
<td>Total Cr 0.0225 kg/kkg of Prod. Cr(VI) 0.00015-0.0009 kg/kkg of Product</td>
<td>0.0075 kg/kkg of Prod. 0.0005-0.0003 kg/kkg of Product</td>
</tr>
<tr>
<td>Ferroalloy Manufact.</td>
<td>Total Cr 0.0006-0.008 kg/MWh Cr(VI) 0.0006-0.0008 kg/MWh</td>
<td>0.0003-0.004 kg/MWh 0.0003-0.0004 kg/MWh</td>
</tr>
<tr>
<td>Leather Tanning &amp; Finishing</td>
<td>0.1-0.24 kg/kkg Raw Product</td>
<td>0.06-0.12 kg/kkg Raw Product</td>
</tr>
</tbody>
</table>

Source: U.S. General Service Admin., 1979
chemical analysis of the soil and/or the reactant fluid phase. Step 1) can take place either with the fluid phase at rest relative to the soil particles (batch process) or with the fluid phase in uniform motion relative to the soil particles (flow-through process). The reaction time should be long enough to permit a close approach to thermodynamic equilibrium but short enough to prevent unwanted side reactions. Step 2) is usually carried out in batch processes through the application of centrifugal or gravitational force. It is understood that some of the reactant fluid phase is always entrained with the soil in this kind of separation (Burchill et al., 1978).

Adsorption is an important process governing the fate of chemicals injected into deep well disposal areas. Model of the transport of such substances must therefore incorporate mathematical description of the chemical process of adsorption as well as the physical processes of advection and diffusion. Sorption processes that happen during reactive solute movement through porous media can be modeled using either an equilibrium or a kinetic approach. A more precise definition of an equilibrium situation is one in which the rate of sorption between the soil solution and the soil phase is much greater than the rate of change in concentration of solute in the soil solution because of any other cause. A kinetic situation can then be defined as one for which an equilibrium sorption isotherm cannot be used, because the equilibrium is
James and Rubin (1979) performed laboratory column experiments over a range of seepage velocities ($1.7 \times 10^{-5}$ to $1.7 \times 10^{-2}$ cm/s) and found that the equilibrium theory failed at the higher fluxes. They concluded the local equilibrium assumption was possible only when the ratio of the hydrodynamic dispersion coefficient to the molecular diffusion coefficient was near unity. However, several other investigations (Table 2-6) indicated equilibrium models were successful even under conditions where hydrodynamic dispersion was significantly greater than molecular diffusion. Valocchi (1985) recognized that the local equilibrium assumption was valid when the rate of change of solute mass due to the sorption process is much greater than that due to the bulk flow process and that this validity depends on seepage velocity, hydrodynamic dispersion, mass transfer coefficient, and aggregate size.

2.6.1 Equilibrium Model

It is common practice to carry out the reaction between a soil and an aqueous solution at a controlled temperature and applied pressure. The resulting adsorption data are $S$ (concentration of solute attached to soil) that can be plotted with $C$ (concentration of solute remaining in solution) as a dependent variable. This kind of graph is called an adsorption isotherm.

The simplest and most widely used equilibrium adsorption
### Table 2-6: Experiments with Local Equilibrium Assumption

<table>
<thead>
<tr>
<th>Reference</th>
<th>Porous Medium</th>
<th>Solute</th>
<th>Seepage Velocity (cm/s)</th>
<th>Dispersion Coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gupta and Greenkorn</td>
<td>Otawa Sand and 5 % Clay</td>
<td>Po₄</td>
<td>2.5E-2</td>
<td>3.7E-2</td>
</tr>
<tr>
<td>Hill and Lake</td>
<td>Berea Sandstone</td>
<td>Na, Ca</td>
<td>3.5E-4 ~ 6.4E-5</td>
<td>2E-4</td>
</tr>
<tr>
<td>Van Beek and Pal</td>
<td>Synthetic Resin</td>
<td>Na, Ca</td>
<td>2.9E-4</td>
<td>1E-5</td>
</tr>
<tr>
<td>Persaud and Wieregna</td>
<td>Synthetic Resin</td>
<td>Na, Li</td>
<td>4.2E-4 ~ 2.2E-5</td>
<td>1.6E-4</td>
</tr>
</tbody>
</table>

Source: Valocchi, 1985
isotherm is that given by a linear relationship. That is, it is assumed that S and C are related by the linear relationship such as

\[ S = K_d \times C \quad (2.6-1) \]

where \( K_d \): partition coefficient (L/g), is a measure of retention of solute by the soil matrix. This linear model has been used frequently to describe the transport of solutes through porous media. Selim et al. (1977) used the above equation to develop a model for transport of the herbicide 2,4-D through a two layer soil column. They found that the order in which the soil layers were stratified in a water saturated profile did not influence the effluent solute concentration distribution. Based on this result, a layered soil profile could be regarded as homogeneous with an average retardation factor "\( R_a \)" for n-layered soil, which can simply be obtained from:

\[ R_a = \frac{1}{L} \left( \sum_{i=1}^{n} R_i L_i \right) \quad (2.6-2) \]

where \( L_i \): depth of \( i \)th soil layer. Lai et al. (1978) used a linear isotherm for the adsorption of sodium and magnesium ions on soils. The adsorption isotherms for magnesium on calcium saturated loam showed that the adsorption was not affected by the total concentration of magnesium applied.

The Freundlich isotherm is defined by the nonlinear relationship

\[ S = K \times C^N \quad (2.6-3) \]

where \( K \) and \( N \) are constants. This isotherm is the oldest of
the nonlinear isotherms and has been widely used to describe the sorption of solutes by soils. Numerous examples exist in the literature where the Freundlich isotherm has been used to describe the adsorption of solutes by the soil matrix. Charbeneau (1981) used it for groundwater contaminant transport modeling. Sidle et al. (1977) used the Freundlich isotherm to describe sorption of zinc, copper and cadmium ions by a forest soil for the study of these heavy metals transport in a sludge treated soil.

The Langmuir adsorption isotherm was developed by Langmuir to describe the adsorption of gases by solids. Langmuir assumed that the surface of a solid phase has a finite number of adsorption sites. The standard form of this isotherm is

\[
C/S = \frac{1}{Kb} + \frac{C}{b} \quad - - - (2.6-4)
\]

where \( K \) is a measure of the bond strength holding the sorbed solute on the soil surface, and \( b \) is the maximum amount of solute that can be adsorbed on the soil matrix. The Langmuir isotherm has been extensively used to describe sorption of solute by the soil. Harter (1979) used this isotherm to describe the sorption of copper and lead ion by 30 soils in the north eastern U.S.. He derived soil adsorption maxima from the reciprocal of the slope obtained by a least squares fit of Langmuir plot for each soil and found that, in subsurface horizons, the adsorption of both copper and lead ions was significantly related to vermiculite content. Singh and Sekhon
(1977) investigated the adsorption, desorption and solubility relationship of lead and cadmium species in alkaline soils and analyzed the results by the Langmuir equation. They concluded that both metals were retained by soil by adsorption on mineral interfaces and interaction with organic matter. At high concentration, mechanisms other than adsorption were also involved in retention of lead in alkaline soils, such as precipitation. Enfield and Bledsoe (1975) used this isotherm to model the movement of phosphate in soils resulting from the renovation of wastewater by a land application treatment system.

2.6.2 Kinetic Model

The most commonly used first order kinetic sorption model is

\[
\frac{dS}{dt} = K_1 \theta \frac{C}{\rho} - K_2 S \quad (2.6-5)
\]

where \( \theta \) : volumetric soil water content, \( \rho \) : soil bulk density, \( K_1 \) and \( K_2 \): kinetic coefficients. This equation has been frequently used to describe the sorption kinetics of chemicals by soil (Hornsby and Davidson, 1973; Leistra and Dekker, 1977). According to Hornsby and Davidson (1973), the distribution of the sorbed and solution phases of the pesticide were well described at high flow rates (5.5 cm/hr). At low flow rates, where equilibrium conditions exists, the kinetics of the adsorption process was not so important and
the process was described equally well using the linear adsorption isotherm.

Another first order kinetic equation to describe the sorption is the nonlinear kinetic equation

$$\frac{ds}{dt} = \frac{K_1 \cdot \theta \cdot C^N}{\rho} - K_2 \cdot S \quad - - - (2.6-6)$$

This equation describes adsorption as nonlinear, while desorption is linear. If N=1, then it reduces to the reversible linear equation described previously. Enfield and Bledsoe (1975) have used this equation with a value of N less than unity to model the sorption of herbicides by soil. Enfield et al. (1976) found that phosphate movement in soil could be described with equation using a value of N less than unity. Fiskel et al. (1979) compared experimental data with results calculated using the two-site sorption model and found that, for contact time > 1 hour, the observed phosphate ion sorption could be described by assuming rapid and slow reversible reactions to occur simultaneously at two separate types of sorption sites. However, for shorter time, the two-site model did not describe the phosphate ion sorption adequately. The orders of the adsorption reactions at the rapid and slow sorption sites were fractional and first order, respectively, with regard to the phosphate ion concentration in solution.

A model proposed by Enfield (1974) to describe the kinetics of P species sorption by soil is the equation
where $a$, $b$, and $d$ are constants. This equation was empirically derived. He compared the results of using this equation with those obtained using the reversible linear kinetic model for five selected soils. Even though the five soils had widely varying physical/chemical properties, in every case this equation gave a better fit to the experimental data than the reversible linear kinetic equation.

2.7 Redox Reactions

Redox reactions play an important role in many of reactions occurring in natural waters and in water and wastewater treatment processes. The behavior of compounds containing carbon, nitrogen, sulfur, iron, and manganese in natural waters and treatment processes is largely influenced by redox reactions. These reactions are encountered in many of the analyses conducted on water and wastewater; for example, the BOD and the COD tests and the analysis of dissolved oxygen are based on them (APHA et al., 1985). Many of the chemicals employed in water and wastewater processes are used to alter the chemical nature of water and wastewater constituents by redox reactions, such as chlorine, chlorine dioxide, permanganate, hydrogen peroxide, oxygen, ozone, and sulfur dioxide (Metcalf and Eddy, 1979). Redox reactions catalyzed by enzymes form the basis for wastewater treatment processes like
activated sludge, biological filtration, and anaerobic digestion. Such microbially mediated redox reactions are also significant in transformation of nutrients, metals, and other chemical species in natural waters (Drever, 1988).

Redox reactions involve a net change in the formal oxidation state of the elements involved in the reaction. There is a conceptual analogy between acid-base and redox reactions. In a same way that acids and bases have been interpreted as proton donors and acceptors, reductants and oxidants are defined as electron donors and acceptors (Stumm and Morgan, 1981). It follows that an oxidizing agent is the chemical species that gains electrons, that is, becomes reduced and a reducing agent is the chemical species that loses electrons, that is, becomes oxidized.

The "electron levels" of elements in various chemical species are given a formal and conventional value called the "oxidation state" of the element and symbolized by a roman numeral, with a sign, in a parentheses following the element: Fe(+III), C(0), C(+IV), and so on. The oxidation state of any element in a compound with oxygen, hydrogen, and electrons is simply equal to minus the stoichiometric coefficient of the electron, normalized per atom of the element, in the formula of the compound (Tan, 1982). For a general chemical formula involving the element A,

$$A_a O_b H_n^{2-n} = (A)_{a} (H_2O)_{b} (H)_{b-2b} (e^-)_{2b-2b+n}$$

This translates into the equation
Oxidation State = \( \frac{(2b-h-n)}{a} \)

The oxidation state of elements does not change due to coordination reactions among metal and ligands.

The reaction of Fe\(^{3+}\) with Sn\(^{2+}\) to form Fe\(^{2+}\) and Sn\(^{4+}\) demonstrates electron transfer:

\[
2\text{Fe}^{3+} + \text{Sn}^{2+} \leftrightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+} \quad (2.7-1)
\]

In the forward reaction, Fe\(^{3+}\) is the oxidizing agent and Sn\(^{2+}\) is the reducing agent; Fe\(^{3+}\) is reduced and Sn\(^{2+}\) is oxidized. For the reverse reaction, Fe\(^{2+}\) is the reducing agent and Sn\(^{4+}\) is the oxidizing agent.

The reaction shown in eq. 2.7-1 is composed of two half reactions:

\[
\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad - \quad (2.7-2)
\]

and

\[
\text{Sn}^{2+} \leftrightarrow \text{Sn}^{4+} + 2\, e^- \quad - \quad (2.7-3)
\]

When the redox reactions are divided into two half reactions, the rules for balancing half reactions are the same as those for ordinary reactions, namely, the number of atoms of each element as well as the net charge on each side of the reaction must be equal.

Redox reactions may result from the direct transfer of electrons from the donor to the acceptor. For example, when zinc metal is immersed in a copper(II) sulfate solution, the Cu\(^{2+}\) ions migrate to the surface of the zinc and are reduced:

\[
\text{Zn}_{(s)} + \text{Cu}^{2+} \leftrightarrow \text{Cu}_{(s)} + \text{Zn}^{2+} \quad - \quad (2.7-4)
\]

This reaction also may be accomplished when the reactants are
not in contact. Such an arrangement is shown in Figure 2-10. Direct contact between \( \text{Zn}_\text{(s)} \) and \( \text{Cu}^{2+} \) is not possible; however, electrons are transferred by means of the external circuit. The transfer is through a wire connecting the two electrode (Benefield et al., 1982).

By definition, oxidation occurs at the anode and reduction at the cathode. In this example, \( \text{Zn}_\text{(s)} \) is the anode and \( \text{Cu}_\text{(s)} \) is the cathode. As the redox reaction proceeds, the concentration of \( \text{Zn}^{2+} \) will increase and that of \( \text{Cu}^{2+} \) will decrease. These solutions have to maintain electrical neutrality and thus, there has to be a net migration of anions from the copper solution through the salt bridge to the zinc solution. The redox reaction continues until equilibrium is achieved and there is no net additional transfer of electrons.

2.7.1 Free Energy and Electromotive Force

The schematic diagram in Figure 2-10 represents an electrochemical cell, which is capable of producing electrical energy because the system is not at equilibrium. Since the temperature and pressure can be kept constant within an electrochemical cell, it is possible to equate the electrical work done in a reversible cell to the free energy change for the reaction.

The free energy change \( \Delta G^\circ \) is related to the electromotive force(emf) by

\[
\Delta G^\circ = -nF E^\circ
\]  

(2.7-5)

where \( n \) is the number of equivalents of electrons transferred
Figure 2-10: Galvanic Cell Measuring Cell Potential

Source: Benefield et al., 1982
and \( F \) is the Faraday constant (96,487 coulombs/mole). A galvanic cell has a positive potential and therefore a negative free energy.

When the reaction is at equilibrium,

\[
\Delta G = \Delta G^\circ + RT \ln K = 0 \quad \ldots \quad (2.7-6)
\]

Thus, \( \Delta G^\circ = -RT \ln K \quad \ldots \quad (2.7-7) \)

Substituting in eq. 2.7-5 yields

\[
E^\circ = \frac{RT}{nF} \ln K \quad \ldots \quad (2.7-8)
\]

Equation 2.7-8 is widely used since it enables equilibrium constants to be evaluated from electrochemical data (Benefield et al., 1982).

The redox reaction is temperature dependent. In acid solution, the following reduction is possible (Snoeyink and Jenkins, 1980).

\[
6 \text{ e}^- + 14 \text{ H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \quad \ldots \quad (2.7-9)
\]

If the chloride ions exist in the solution, the oxidation of \( \text{Cl}^- \) to \( \text{Cl}_2 \) will occur also with the reduction of \( \text{Cr(VI)} \) to \( \text{Cr(III)} \) (APHA et al., 1985). The overall redox reaction can be written as follows:

\[
\begin{align*}
6 \text{ e}^- + 14 \text{ H}^+ + \text{Cr}_2\text{O}_7^{2-} & \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \\
3 \times (2 \text{Cl}^- & \rightarrow \text{Cl}_2(\text{aq}) + 2 \text{ e}^-) \\
\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{Cl}^- & \rightarrow 2 \text{Cr}^{3+} + 3 \text{Cl}_2 + 7 \text{H}_2\text{O} \quad \ldots \quad (2.7-10)
\end{align*}
\]

This unwanted reaction in COD analysis leads to the reading of greater COD than actual value. To suppress the interference of
chloride ion in COD analysis, some treatments (Burns and Marshall, 1965; Baumann, 1974) were suggested. The basic principle was to complex the chloride ion with a metallic ion, such as mercury. To study if the redox reactions such as eq. 2.7-10 can take place at standard state (25 °C, 1 Atm.), Gibb's free energy at standard state is calculated as follows:

\[
6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \quad E^o = +1.33 \text{ V}
\]

\[
3 \times (2Cl^- \rightarrow Cl_2(aq) + 2e^-) \quad E^o = -1.39 \text{ V}
\]

\[
Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O \quad \Delta G^o = -0.06 \text{ V}
\]

Then from eq. 2.7-5, \( \Delta G^o \) is calculated to be positive and the reaction does not take place from left to right spontaneously. Therefore, it can be concluded that the redox reactions which are possible at one temperature may not be possible at another temperature. The possibility of above redox reactions at different temperatures between 25 °C and 100 °C is studied in next chapter.

### 2.8 Diffusion

Diffusion is the process of the transport of ions or molecules under the influence of their kinetic activity. This is an important process of mass transport in geologic systems. Such a process is irreversible and results from chemical potential.

Diffusion has been used to account for the vertical distribution with depth of various chemical species within the interstitial water of various soils (Sadeghi, 1989; Jansen and
Diffusion is a function of several factors. In free solution, these are temperature, pH, chemical reaction and solution composition (Sadeghi et al., 1988; Mahtab et al., 1971; Place et al., 1968). In a porous medium, these also include the tortuosity, porosity, pore saturation, viscosity variation, and chemical and/or electrical interactions with the walls of the medium (Sadeghi et al., 1988; Warncke and Baker, 1973a; Warncke and Baker, 1973b). All of these factors are generally grouped together in a single variable known as the diffusion coefficient. This coefficient is combined with the concentration to determine the rate of diffusion (eq. 2.8-1).

Practical application of diffusion generally necessitates the use of eq. 2.8-2 to determine a function which describes the change in concentration of a component with time and distance. This function cannot be evaluated unless the diffusion coefficient is known.

For one dimensional diffusion of a component in the solution, diffusion can be ascribed to a driving force such as concentration gradient or chemical potential gradient. Adolf Fick attributed the driving force to be the concentration gradient. Later, Hartley (1931) showed it was actually the chemical potential gradient. A component will diffuse spontaneously from regions of high chemical potential to regions of low chemical potential. However, for convenience,
many studies deal with concentration gradients which are reflections of the chemical potential gradients.

Diffusion can be described mathematically by Fick's first and second laws:

\[
J = -D \frac{\partial C}{\partial x} \quad \text{-- (2.8-1)}
\]

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{-- (1.8-2)}
\]

Here \( J \) is the flux of material, which is the mass of material moving across unit area in unit time; \( C \) is the concentration in mass per unit volume; \( D \) is the diffusion coefficient; \( X \) is linear distance; \( t \) is time. The minus sign in the Fick's first law is simply a result of the fact that the flux is in the opposite direction to the concentration gradient. Fick's first law is used primarily for calculations involving "steady state" systems, that is, systems in which the concentrations at any particular location are not changing with time. Fick's second law is used primarily for systems that are not in a steady state.

The diffusion coefficients of most species in aqueous solution are approximately \( 10^{-6} \) to \( 10^{-5} \) cm²/s (Robinson and Stokes, 1965; Li and Gregory, 1974). Diffusion coefficients in solids are much smaller than this. Diffusion in a water saturated sediment takes place almost entirely through the interstitial water. The rate of diffusion is slower than it would be in pure water, because the porosity of the sediment
is less than 1 and the paths by which a species must diffuse are not straight. These effects can be taken into account by use of an effective diffusion coefficient $"D'"$. Berner (1971) gives the relationship

$$D = \frac{D \phi}{\omega^2} \quad (2.8-3)$$

where $D$ is the molecular diffusion coefficient in solution, $\phi$ is porosity, and $\omega^2$ is tortuosity.

The factor $\omega^2$ is introduced to allow for the fact that the diffusion path is greater than the distance traveled normal to the face, and for varying cross section of the pores, which are not straight, round tubes (Thibodeaux, 1979). This correction factor must normally be obtained experimentally except for materials with exceedingly uniform structure and pore size. Values obtained from experimental data show that the tortuosity varies from unity to more than six (Smith, 1970).

To predict restoration rate of contaminated muds, Greskovich, Pommersheim and Kenner (1975) investigated the diffusion rates through soils and calculated hindrance factors. The hindrance factor is defined as:

$$\hat{D} = \frac{D}{H} \quad (2.8-4)$$

where $H$ is the hindrance factor. Particle shape, tortuosity, and bed void fraction are closely related to the hindrance factor. Because the pore size in the bed is usually much
larger than the molecular diameter of the diffusing species, a hindrance factor based on one diffusing species is also accurate for other species of similar molecular diameter that exhibit the same effects with the muds.

Table 2-7 contains the experimental data for potassium chloride through various test media. The results indicate that the diffusion rates differ greatly for various bed types with different packing characteristics and different particle composition. The hindrance factors shown in Table 2-7 vary from 3.04 for fine sand to 1.58 for loosely packed stream bed silt.

2.8.1 Hydrodynamic Dispersion

Diffusion of ions often occurs simultaneously with mass flow of the soil solution. This may be caused, for example, by drainage or pumping. The movement of water through the soil tends to increase the random displacement of a solute that normally occurs by diffusion, because of the irregular pattern of the flow velocity through its pores, a process known as "eddy" or "hydrodynamic" dispersion (Helfferich, 1962). Consequently, the diffusion coefficient D' should be replaced by a "longitudinal dispersion" coefficient $D_L'$. Frissel and Poelstra (1967) found that the theoretical equation

$$D_L = D + \frac{\lambda d \nu}{f \theta}$$

expressed the dispersion of Sr as it was percolated through columns of resin-sand and clay-sand mixtures. Here, d is the
Table 2-7: Experimental Hindrance Factors and Void Fractions for test Media

<table>
<thead>
<tr>
<th>Medium</th>
<th>Particle Diameter (cm)</th>
<th>Void Fraction</th>
<th>Hindrance Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.0147-0.0208</td>
<td>0.491</td>
<td>2.82</td>
</tr>
<tr>
<td>Sand</td>
<td>0.0208-0.0295</td>
<td>0.507</td>
<td>3.04</td>
</tr>
<tr>
<td>Sand</td>
<td>0.0417-0.0589</td>
<td>0.510</td>
<td>2.7</td>
</tr>
<tr>
<td>Clay-silt soil</td>
<td>~50% &lt;0.0035</td>
<td>-</td>
<td>2.24</td>
</tr>
<tr>
<td>Clay-silt soil</td>
<td>~70% &lt;0.002</td>
<td>-</td>
<td>2.46</td>
</tr>
<tr>
<td>Clay-silt soil</td>
<td>~50% &lt;0.002</td>
<td>-</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Source: Greskovich et al., 1975
particle diameter, $\lambda$ is the packing factor, which is 1 for spheres, but may become as high as 10 when the particle sizes are irregular, $f$ is an impedance factor, $\Theta$ is the fraction of the soil volume occupied by solution and $v$ is the flow velocity. In these experiments, $v$ ranged from $0.2 \times 10^{-7}$ to $200 \times 10^{-7}$ m/s.

In soil, it is not possible to separate $d$ and $\lambda$. Frissel et al. (1970) followed the drainage of tritiated water through undisturbed soil samples and found the product, $d^\lambda$, to be 0.007, 0.008, and 0.06 m in a sandy, clay, and loose loam soil over a range of $v$ from $0.06 \times 10^{-7}$ to $23 \times 10^{-7}$ m/s. These data suggested that in undisturbed soil, dispersion was significant. For example, if a moist soil $\lambda d = 0.01$ m, $v = 10^{-8}$ m/s, $\Theta_f = 0.1$, then in the previous equation, $\lambda dv/\Theta_f = 10^{-9}$ m$^2$/s, which is comparable to $D'$ for most ions. Clearly, for the much greater flow rates that may occur in drainage ($\sim 10^{-7}$ m/s), eddy dispersion will be more important than diffusion.

2.9 Approximate Inverse Laplace Transform

In order to predict the fate and transport of the solute, one should solve the governing mass conservation equations, using initial and boundary conditions. Laplace transform has been widely used for the above purposes. The power of the Laplace transform lies in the fact that one of the independent variables of a partial differential equation is eliminated, thus in many instances, simplifying greatly the solution of
the transformed equations and boundary conditions. Once the transform solution has been derived, the solution to the original problem may sometimes be obtained through analytical inversion by means of a table of transforms, if the appropriate function is available, or by use of the inversion theorem for Laplace transform. In many instances, this inversion is difficult or not possible analytically because of the required integration in the complex plane. In these situations, an approximate solution can often be obtained with some form of numerical inversion of the transform solution.

There are many methods for numerical inversion given in the literature. Most are in the form of a polynomial approximation of which the Fourier series is most commonly used because of calculation ease (Dubin, 1973; Crump, 1976). Other investigators have used the Gaussian formula for integration of the inversion integral (Piessens, 1971). In these methods, the coefficients of the series expansions are functions of the transform solution and the number of terms in the approximating polynomial, thus making calculation somewhat complex.

2.9.1 Stehfest's Method

A numerical method developed by Gaver (1966), revised and presented in the form of an algorithm by Stehfest (1970), is extremely simple to use and requires relatively little computation. In this approach, the weighing coefficients depend only on the number of terms used in the computation.
The inverse of a Laplace transform obtained by a formula developed by Stehfest is

\[ F_a = \frac{\ln 2}{T} \sum_{i=1}^{N} V_i P \left( \frac{\ln 2}{T} i \right) - \quad (2.9-1) \]

where \( F_a \) is the approximate value of the inverse \( F(t) \) at \( T \) and \( P(s) \) is the Laplace transformed function to be inverted. \( N \) must be even number. The coefficients \( V_i \) are given by

\[ V_i = (-1)^{\frac{N+i}{2}} \sum_{k=\left(\frac{i+1}{2}\right)}^{\min(\frac{i+N}{2}, N)} \frac{k^{N/2} (2k)!}{(N-k)! k! (k-1)! (i-k)! (2k-i)!} \quad (2.9-2) \]

where \( k \) is computed using integer arithmetic. Two properties of eq. 2.9-2 are that for a given \( N \), the \( V_i \) sum to zero, and as \( N \) increases, \( V_i \) tend to increase in absolute value. Since the \( V_i \) depend on \( N \) only, in case of repeated procedure calls with the same \( N \), the array \( V \) is to be evaluated only once.

The calculation method originates from Gaver (1966), who considered the expectation of \( F(t) \) with respect to the probability density

\[ f_n(a, t) = a \frac{(2n)!}{n! (n-1)!} (1-e^{-at})^n e^{-nat}, \quad a>0 - \quad (2.9-3) \]

\[ F_n = \int_0^\infty F(t) f_n(a, t) \, dt \]

\[ = a \frac{(2n)!}{n! (n-1)!} \sum_{i=0}^{n} \frac{n}{i} (-1)^i P((n+i)a) - \quad (2.9-4) \]

\( f_n(a, t) \) has the following properties
1) \[ \int_0^\infty f_n(a, t) \, dt = 1 \]
2) modal value of \( f_n(a, t) = \frac{\ln 2}{a} \)
3) \[ \text{Var}(t) = \frac{1}{a^2} \sum_{i=0}^{n} \frac{1}{(n+i)^2} \]

They imply that \( F_n \) converges to \( F(\ln 2/a) \) for \( n \to \infty \).

\( F_n \) has the asymptotic expansion

\[ F_n \sim F\left(\frac{\ln 2}{a}\right) + \frac{\alpha_1}{n} + \frac{\alpha_2}{n^2} + \frac{\alpha_3}{n^3} + \ldots \]

For a given number of \( N \) of \( P \) values, a much better approximation to \( F(\ln 2/a) \) than \( F_{n-1} \) is attainable, and that by linear combination of \( F_1, F_2, \ldots, F_{N/2} \): requiring

\[ \sum_{i=1}^{K} x_i(K) \frac{1}{\left(\frac{N}{2} + 1 - i\right)^k} = \delta_{k0} \]

where \( k = 0, 1, \ldots, k-1, k \leq (N/2) \), it is found

\[ x_i(k) = \frac{(-1)^{i-1}}{K!} \binom{K}{i} \left(\frac{N}{2} + 1 - i\right)^{K-1} \]

and thus

\[ \sum_{i=1}^{K} x_i(K) F_{\frac{N}{2} + 1 - i} = F\left(\frac{\ln 2}{a}\right) + (-1)^{(k+1)} \alpha_k \frac{(\frac{N}{2} - K)!}{(\frac{N}{2})!} \]

\[ + o\left(\frac{N}{2} \right) \]

Setting \( k = N/2 \), \( a = \ln 2/T \), and using eq 2.9-1, following expression can be drawn:
\[ F_a = \sum_{i=1}^{N/2} X_i \left( \frac{N}{2} \right) F_{N/2 + 1 - i} = \frac{\ln 2}{T} \sum_{i=1}^{N} V_i P\left( \frac{\ln 2}{T} i \right) \]

Theoretically, \( F_a \) becomes the more accurate the greater \( N \). Practically, however, rounding errors worsen the result if \( N \) becomes too large, because \( V_i \) with greater absolute value occurs. For given \( P(s) \) and \( T \), the value of \( N \) to use for maximum accuracy is approximately proportional to the number of significant figures that the computer in use holds.

Requirements for use of eqs 2.9-1 and 2.9-2 are that the function \( F(t) \) have no discontinuities or rapid oscillations. Stehfest recommends that the accuracy be checked by employing different values of \( N \) and other inversion techniques.
REFERENCES


CHAPTER 3
Adsorption of Cr(VI)

3.1 INTRODUCTION

According to the Resource Conservation and Recovery Act of 1976, EPA will ban the deep well disposal of hazardous wastes, unless the EPA can determine that deep well disposal is not detrimental to environmental quality and to human health. Deep well disposal may be permitted to continue, if it can be shown that the waste will either be rendered non-hazardous in the disposal zone or that the waste will remain confined for at least 10,000 years. Louisiana Acts 795 and 803 of 1984 prohibit new deep well disposal after Jan. 1, 1991, unless the hazardous nature of the waste cannot be reduced by current technology, the waste cannot be reclaimed, well disposal is not hazardous to the environment or human health, and no other proper alternative exists. Nevertheless, this technique is very attractive among the various hazardous waste treatments due to its low cost and easy handling (Table 3-1). As indicated in Table 3-1, average disposal cost per ton of wastes for injection well disposal in Louisiana is approximately only 1/45 of that for land fill and is only 1/250 of that for incineration.

In 1983, Louisiana injected three million tons of chromium contaminated wastewater, which represented 20% of total hazardous wastes injected [Jacobus et al., 1985]. Acute
Table 3-1: Estimated Cost for Waste Disposal/Ton on Site

<table>
<thead>
<tr>
<th>METHOD</th>
<th>LOW 10%</th>
<th>HIGH 10%</th>
<th>AVERAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection</td>
<td>$0.06</td>
<td>$1.72</td>
<td>$0.54</td>
</tr>
<tr>
<td>Welling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfill/Impoundment</td>
<td>$3.00</td>
<td>$94.00</td>
<td>$24.00</td>
</tr>
<tr>
<td>Incineration</td>
<td>$20.00</td>
<td>$8,000</td>
<td>$136.00</td>
</tr>
</tbody>
</table>

Note: The low 10% of incineration cost is positive, indicating energy recovery.
Source: Jacobus et al., 1985
and chronic toxicity of chromium to human life are not known yet. EPA adopted a limit of 0.05 mg/L as a maximum allowable concentration in public water supplies [EPA, 1976]. Among the chromium species, Cr(VI) is known to be hazardous to human and aquatic life. In light of EPA's proposed actions, the fate of Cr(VI) upon deep well disposal needs to be addressed to continue the practice of injecting chromium-contaminated wastewaters.

The major mechanisms controlling the transport and fate of Cr(VI) in the deep well disposal zone are adsorption and reduction. Most adsorption phenomena occur in clay components of a soil because of the clay's high surface area to volume ratio and the charge potential to attract electrolytes from the liquid phase [Hillel, 1980; Drever, 1988]. Previous research has demonstrated the adsorption and reduction of Cr(VI) by clay or humic substances [Griffin et al., 1977; Stollenwerk and Grove, 1985; Bartlett and Kimble, 1976; James and Bartlett, 1983; Grove and Ellis, 1980; Rose et al., 1981]. The results of these studies include: 1) the adsorption of Cr(VI) is generally anion dependent, 2) more adsorption at lower pH results from the greater positive net surface charge due to increased H⁺ ion concentration, 3) available oxidizing materials such as organic substances (humic substances) can reduce Cr(VI) to Cr(III), and 4) the rate of this reaction increases with decreasing pH. All of these studies were performed at ambient temperature, which is far from the
temperature in deep well disposal zones (100 to 180 °F). The role of organic substances in the disposal zone has not been addressed.

The objective of this research is to investigate how environmental factors such as clay type, pH, temperature, inorganic salt concentration in wastewater, and organic compounds coinjected can affect the attenuation mechanisms of Cr(VI).

3.2 RESEARCH METHODS

A. Sample Treatment

Samples of Wyoming montmorillonite, well crystallized Georgia kaolinite, and Montana illite were obtained from the Clay Mineral Repository, Dept. of Geology, Columbia, MO. The colloidal fraction (< 2 μm in diameter) was separated from the bulk clay minerals by dispersion and sedimentation techniques. Colloidal samples were sodium (Na\(^+\)) saturated by washing with 1 N NaCl. The clays were then washed with 0.1 N NaCl followed by washing with distilled deionized water to remove entrained salts.

B. Adsorption and Reduction

pH Effect

For the equilibrium adsorption study, 0.75 g of NaCl was added to 50 ml of Cr(VI) solution having 100 mg/L of Cr(VI). Then 1 g of clay was added to the solution and shaken for 48
hours at 50 °C under nitrogen gas. Each reactor had a different pH, ranging 1.5 to 8. The pH was checked every 6 hours and adjusted if necessary with 1 N and 0.1 N of HNO₃ and NaOH. At the end of the reaction, the clay suspension was centrifuged at 13,000 g force for 25 minutes with an Eppendorf Centrifuge 5415. The supernatant was used to determine the concentration of Cr(VI). The amount of Cr(VI) adsorbed was determined from the difference between the concentration reduced and removed from the solution.

Temperature Effect

At the pH which yielded maximum adsorption, 1 g of clay was reacted with 50 ml of Cr(VI) solution having various concentrations (12 to 100 mg/L) of Cr(VI) and shaken for 48 hours at three different temperature (23 °C, 50 °C, and 70 °C). The NaCl concentration in the solution was 15,000 mg/L.

NaCl Effect

Three different concentrations (0, 15000, and 30000 mg/L) were added to determine if chloride ions would hamper the adsorption of Cr(VI) onto the surface of Na-Montmorillonite. The procedures were the same as the one used in the temperature effect experiment.

Organic Compounds Effect

1) 10 μL of organic chemical was added to 42 mL vial, containing 20 mg/L Cr(VI) solution without Na-Montmorillonite. The organic chemical concentration was 238 mg/L. Then, the
vial was placed in 50 °C and 70 °C water bath for 48 hours and shaken for 20 minutes every 6 hours. Four different kinds of organic chemicals (NN- Dimethyl-aniline, 3-chloro-1-butene, ethyl-alcohol, and ethylene-dichloride) were used.

2) Step 1) was repeated with 1 g of Na-Montmorillonite.

3) After centrifugation, supernatants from steps 1) and 2) were analyzed for total chromium and hexavalent chromium determination.

C. Analyses

Cr(VI) was analyzed by the pink color complex developed between 1,5-diphenylcarbazide and chromium(VI) ion in an acidified solution (APHA et al., 1985). Absorbance was measured at 540 nm with a Perkin Elmer Lambda 4 Spectrophotometer using a 1 cm cuvette. The minimum detectable concentration was 0.005 mg/L. The amount of Cr(VI) reduced was determined from the difference between total chromium and hexavalent chromium. Total chromium was determined by oxidizing the chromium with permanganate followed by analysis of hexavalent chromium (APHA et al., 1985). In order to determine clay organic content, the clay samples were ignited in a muffle furnace at a temperature of 550 +/- 50 °C until weight loss is less than 4 % of previous weight (APHA et al., 1985). All experiments were run in duplicate.

3.3 RESULTS AND DISCUSSION

Figure 3-1 shows the time to reach equilibrium in
Figure 3–1: Time to Reach an Equilibrium
adsorption of Cr(VI) with Na-Montmorillonite. At any
temperature, 48 hours were enough to reach equilibrium. Huang
and Wu (1977) used 24 hours to reach an equilibrium for the
adsorption of Cr(VI) by activated carbon at 25 °C. According
to Amacher et al. (1988), the adsorption of Cr(VI) required 5
to 144 hours depending on the soil types and temperature. The
time to reach equilibrium is closely related to the type of
adsorbent and temperature which the adsorption occurs. Illite
and Kaolinite showed similar behavior over time, with 48 hours
of reaction time adequate for reaching equilibrium.

Figures 3-2, 3-3 and 3-4 show the effect of pH on
adsorption and reduction of Cr(VI) reacted at 50 ºC for
Na-Montmorillonite, Na-Illite and Na-Kaolinite, respectively.
All of three clay types demonstrate an increase in adsorption
of Cr(VI) with decreasing pH from 8 down to 2, after which
adsorption decreases. The speciation of Cr(VI) at different pH
values accounts for this dependency of adsorption on pH.
According to Butler (1964) and Parfitt (1978), bichromate
(HCrO₄⁻) is predominant in the pH range 1.5 to 6.5 and as pH
decreases in this range, the increased positive surface charge
of the clay attracts more anions. At pH less than 1.5, chromic
acid (H₂CrO₄) is predominant and is less preferentially
adsorbed relative to bichromate. In the range of pH greater
than 6.5, chromate (CrO₄²⁻) is dominant, and is also less
preferentially adsorbed than bichromate, accounting for the
reduced adsorption with increased pH in the higher pH range.
Figure 3-2: Cr(VI) Removal by Adsorption and By Reduction on Na-Montmorillonite at 50 °C
Figure 3-3: Cr(VI) Removal by Adsorption and by Reduction on Na-Illite at 50 °C
Figure 3-4: Cr(VI) Removal by Adsorption and by Reduction on Na-Kaolinite at 50 °C

Cr(VI) Removed (mg/g)

- △ Ads.+ Red.
- □ Adsorption
- * Reduction

pH

Cr(VI) Removed (mg/g)
Comparing the adsorption curves of Figures 3-2, 3-3 and 3-4 reveals that Cr(VI) is adsorbed in similar amounts for Na-Montmorillonite and Na-Illite (0.33 and 0.3 mg/g respectively), whereas Na-Kaolinite adsorbs roughly 1/3 of this amount (0.1 mg/g). This is most likely due to the fact that the specific surface area of Kaolinite (5-100 m²/g) is much less than the specific surface area of Na-Illite (300-500 m²/g) and Na-Montmorillonite (700-800 m²/g). Though the surface area of Na-Illite is only one half of the Na-Montmorillonite, adsorption is approximately the same at pH < 3; at higher pH, Na-Illite adsorbs slightly more than Na-Montmorillonite. This greater adsorption capacity by Na-Illite is attributable to the greater organic content of the Na-Illite (4.8 % vs <1% by weight). The effect of the attendant organic matter is evident at higher pH where adsorption in clay surface is lessened. The reduction of Cr(VI) is pH dependent at pH < 5 for Na-Illite and Na-Montmorillonite; for both clays, reduction increases as pH decreases. Above pH 5, no reduction was found for Na-Illite and Na-Montmorillonite. No reduction of Cr(VI) was found for Na-Kaolinite at any pH.

Figures 3-5, 3-6, 3-7, 3-8 and 3-9 show the temperature effect on Cr(VI) removal for Na-Montmorillonite, Na-Illite, and Na-Kaolinite, respectively. For all clays, adsorption of Cr(VI) was found to decrease with increasing temperature, demonstrating that the adsorption of Cr(VI) is an exothermic reaction. At room temperature (23 °C), no evidence of
Figure 3-5: Cr(VI) Total Removal by Adsorption and Reduction on Na-Mont. at Different Temperature
Figure 3-6: Cr(VI) Removal by Adsorption and by Reduction on Na-Mont. at Different Temperature
Figure 3-7: Cr(VI) Total Removal by Adsorption and Reduction on Na-Illite at Different Temperature
Figure 3-8: Cr(VI) Removal by Adsorption and by Reduction on Na-Illite at Different Temperature
Figure 3-9: Cr(VI) Total Removal by Adsorption on Na-Kaolinite at Different Temperature
reduction is found for all three clays. This can be proven thermodynamically through the redox reaction between chloride ion and Cr(VI). The overall electric potential at 25 °C is -30 mV; consequently the Gibbs Free Energy at standard state is positive, indicating the nonspontaneity of the reaction. As the temperature increases to 50 °C and 70 °C, however, increased reduction occurs for Na-Illite and Na-Montmorillonite. In this case, the chloride ion can serve as reducing reagent, being oxidized to Cl\(_2\)(aq). Similar reference to Cl\(^-\) participation as a reducing agent can be found in a wastewater analysis manual (i.e., Chemical Oxygen Demand, [APHA et al., 1985]).

For Na-Montmorillonite, total amount of Cr(VI) removed by adsorption and reduction at 23 °C is larger than that by adsorption and reduction at 50 °C and 70 °C. This is demonstrated in Figure 3-5. As seen in Figure 3-6, when temperature increases from 23 °C to 50 °C, the increase in Cr(VI) removal by reduction is less than the decrease in Cr(VI) removal by adsorption. This is the same, when temperature increases from 50 °C to 70 °C. However, this is not the same for Na-Illite containing a considerable amount of organic material. As seen in Figure 3-7, the total removal of Cr(VI) by adsorption and reduction increases as the temperature increases from 23 °C to 50 °C. However, total removal by adsorption and reduction at 50 °C is larger than that at 70 °C. From Figure 3-8, the increase in Cr(VI) removal
by reduction is much larger than decrease in Cr(VI) removal by adsorption, when temperature increases from 23 °C to 50 °C. However, as the temperature increases from 50 °C to 70 °C, the increase in Cr(VI) removal by reduction is less than decrease in Cr(VI) removal by adsorption. Comparing Figures 3-6 and 3-8, the Cr(VI) removed by reduction on Na-Illite is more than double that amount removed by reduction on Na-Montmorillonite when temperature increases from 23 °C to 50 °C. This fact indicates the importance of the role of organic matter contained in Na-Illite as a reducing agent.

The reduction of Cr(VI) is suspected to be independent of clay type, in direct contrast to the results presented. The difference in reduction between Na-Illite and Na-Montmorillonite can be explained by the higher organic content of the Na-Illite, which would account for an increased electron donor source providing for an accelerated reduction. No reduction was found in Na-Kaolinite solution at any temperature (Figure 3-9). However, the lack of reduction in the Na-Kaolinite tests is not readily explainable.

If an adsorption can be described with Langmuir isotherm, the following equation should be satisfied, denoting a linear relationship.

\[
\frac{C}{S} = \frac{1}{b \cdot C} + \frac{1}{ab}
\]

where 'C' is the equilibrium concentration, 'S' is the
concentration adsorbed, 'b' is the adsorption maximum, and 'a'
is a constant which represents bonding strength. Data
presented in Figures 3-6, 3-8, and 3-9 are applied to this
equation, and adsorption maxima and bonding strengths are
presented in Table 3-2. At any temperature, Na-Montmorillonite
has greater adsorption maxima than Na-Illite. However, the
total removal by adsorption and reduction by Na-Illite is
greater than that by Na-Montmorillonite at the elevated
temperature which is common in deep well disposal zones, due
to the reduction occurring with the presence of soil organic
matter.

Figure 3-10 shows the effect of inorganic salt
concentration on the adsorption of Cr(VI) from the solution.
As the concentration of NaCl increases, the amount of Cr(VI)
removed from the solution decreases. According to Davis and
Leckie (1980), a decrease in electrostatic potential near the
surface of a charged particle may be found due to an increase
in solution of an electrolyte such as NO₃⁻ or Cl⁻. This fact
may result in less adsorption of anions such as HCrO₄⁻.
Stollenwerk and Grove (1985) attributed the decrease in the
activity of a fixed concentration of Cr(VI) to the decrease in
adsorption of Cr(VI) as the ionic strength of a solution
increased.

The effect of inorganic salt concentration on the
reduction of Cr(VI) is shown in Figure 3-11. As the
concentration of NaCl increases, the amount of Cr(VI) reduced
### Table 3-2: Adsorption Maxima and Bonding Strength on Various Clay at Different Temperature (pH = 2)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>23 °C</td>
<td>0.581</td>
<td>0.332</td>
<td>0.15</td>
</tr>
<tr>
<td>50 °C</td>
<td>0.354</td>
<td>0.284</td>
<td>0.124</td>
</tr>
<tr>
<td>70 °C</td>
<td>0.252</td>
<td>0.185</td>
<td>0.078</td>
</tr>
<tr>
<td>23 °C</td>
<td>0.179</td>
<td>0.165</td>
<td>0.202</td>
</tr>
<tr>
<td>50 °C</td>
<td>0.118</td>
<td>0.129</td>
<td>0.041</td>
</tr>
<tr>
<td>70 °C</td>
<td>0.079</td>
<td>0.075</td>
<td>0.026</td>
</tr>
</tbody>
</table>
Figure 3-10: Effect of NaCl Addition on Adsorption of Cr(VI)

Amount Removed (mg/L)

I: 0 mg/L
II: 15,000 mg/L
III: 30,000 mg/L

NaCl Conc.
Cr(VI) Conc.
Figure 3-11: Effect of NaCl Addition on Reduction of Cr(VI)

I : 0 mg/L
II : 15,000 mg/L
III: 30,000 mg/L

Amount Removed (mg/L)
increases slightly, and without NaCl addition, only the soil organic matter is reducing agent. From this figure it is apparent that the chloride ion works as a reducing agent, i.e., electron donor. The overall effect of NaCl addition on total removal is shown in Figure 3-12. At any Cr(VI) concentration, the decrease in the adsorption compensates for the increase in the reduction. Consequently, the total removal is not significantly affected by the addition of NaCl at pH 2.

The effect of different organic compounds on the removal of Cr(VI) at 50 °C and 70 °C are presented in Figures 3-13 and 3-14, respectively. In Figures 3-13 and 3-14, 6.54 and 5.22 mg/L represent total amounts of Cr(VI) removed by adsorption and reduction at 50 °C and 70 °C, respectively. The four different organic compounds were selected for their different characteristics, as noted in Table 3-3, and their likelihood for co-disposal with chromium bearing wastes via deep well injection. The effect of the organics were examined using 20 mg/L of Cr(VI) in the presence and absence of Na-Montmorillonite, and compared to total chromium removal (adsorption and reduction) in the presence of Na-Montmorillonite without organic compound present.

NN-dimethyl-aniline is found to be a strong reducing agent at both 50 °C and 70 °C, reducing all the Cr(VI) present in each experimental condition. This is consistent with dimethyl-aniline's known incompatibility with strong oxidizers and strong acids. Ethyl-alcohol removes approximately one
Figure 3-12: Effect of NaCl Addition on Total Removal of Cr(VI)

I : 0 mg/L
II : 15,000 mg/L
III : 30,000 mg/L

Cr(VI) Conc.

NaCl Conc.
Figure 3-13: Effect of Organic Compounds Addition on Adsorption and Reduction at 50 °C

A: NN Dimethyl-aniline
B: Ethyl-alcohol
C: 3 Chloro-1 butene
D: Ethylene-dichloride
Figure 3-14: Effect of Organic Compounds Addition on Adsorption and Reduction at 70 °C

A: NN Dimethyl-aniline
B: Ethyl-alcohol
C: 3 Chloro-1 butene
D: Ethylene-dichloride
Table 3-3: Characteristics of Organic Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN Dimethyl-aniline</td>
<td>C₆H₅N(CH₃)₂</td>
<td>Substituted Amine</td>
</tr>
<tr>
<td>Ethyl-alcohol</td>
<td>C₂H₅OH</td>
<td>Alcohol</td>
</tr>
<tr>
<td>3 chloro-1 butene</td>
<td>CH₃CHClCH=CH₂</td>
<td>Unsaturated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Halogenated Alkene</td>
</tr>
<tr>
<td>Ethylene-dichloride</td>
<td>CH₂ClCH₂Cl</td>
<td>Saturated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Halogenated Alkane</td>
</tr>
</tbody>
</table>
third of the Cr(VI) from solution when no Na-Montmorillonite is present, slight increases in Cr(VI) removal are affected with the presence of Na-Montmorillonite. Increased temperature results in slightly increased removal (~1 mg/L). In all cases, the Cr(VI) concentrations were decreased by ethyl-alcohol slightly more than exposure to Na-Montmorillonite alone. It is suspected that reduction is the primary method of Cr(VI) removal by ethyl-alcohol since sensitivity to temperature is minor, and removals increase with increasing temperature. Ethyl-alcohol reactions appear to be competitive with that of the Na-Montmorillonite as indicated by their combined effects being far less than the sum of individual reactions.

The reduction of Cr(VI) produced by 3-chloro-1-butene without Na-Montmorillonite is approximately one half that produced by ethyl-alcohol; the reduction produced by ethylene-dichloride is less than 10% of that produced by ethyl-alcohol. Both the reduction produced by 3-chloro-1-butene and ethylene-dichloride increase with increasing temperature. The decrease in reduction of Cr(VI) with the unsaturated alkenes and saturated alkanes is supported by their decrease in reactivity and their difficulty in being oxidized [Sawyer and McCarty, 1978]. Unlike ethyl-alcohol, both 3-chloro-1-butene and ethylene-dichloride do not compete with the reactions of Na-Montmorillonite as evidenced by the cumulative effects of clays and organic compounds equaling the
combined clay and organic effects. Thus, the technique of superposition may be an adequate method of quantifying the effects of adsorption and reduction for alkane and alkene series organic compounds, but is not appropriate for alcohols.

The adsorption behavior of Cr(VI) on shale was studied and used in the transport simulation study in Chapter VI. Shale from a deep well injection zone in St. Charles Parish, LA. was used instead of clay. The adsorption behavior of Cr(VI) on shale followed the Langmuir isotherm in the same manner as the adsorption on clay. The adsorption maximum was between that of Na-Montmorillonite and Na-Illite (i.e., lower than that of Na-Montmorillonite, but higher than that of Na-Illite). Figure 3-15 shows the adsorption behavior at different temperatures at a pH of 2.0.

3.4 CONCLUSION

Adsorption and reduction of Cr(VI) are dependent on the type and amount of clay in the shale confining layers and sand aquifer zones. In soils containing a large portion of kaolinite clay, less adsorption and no reduction are expected, as compared to soils containing montmorillonite and illite, which demonstrate significant adsorption and reduction capacity. This capacity is both pH and temperature dependent. The pH of a deep well injection zone is usually extremely high (>12) or extremely low (<2) [EPA, 1988]. In case of a high pH environment, we can hardly expect the Cr(VI) removal
Figure 3-15: Cr(VI) Removal by Adsorption on Shale at pH 2.0
by adsorption and reduction. However, in low pH environment, deep well injection is an excellent technique to remove Cr(VI) by reduction and adsorption. Increased temperature in deep well injection zones can decrease adsorption, but it can increase reduction. Overall Cr(VI) removal decreases as temperature increases, when significant amount of soil organic matter is not present. The concentration of chloride found commonly in deep well injection zones serves as a good agent for Cr(VI) reduction to Cr(III) in association with elevated temperature. The reduction of Cr(VI) by the oxidation of chloride is not possible in ambient temperature but possible in elevated temperature which is typical in deep well injection zones. The co-injected organic compounds provide another good source of Cr(VI) reduction. Depending on organic wastes present, such as NN Dimethyl-aniline, even 100 % removal of Cr(VI) by reduction can be expected. Consequently, the deep well injection technique may provide favorable methodology to remove Cr(VI) from the wastewater injected, as the above mentioned environmental conditions are commonly found in deep well injection zones.
REFERENCES


CHAPTER 4

Diffusion of Cr(VI)

4.1 INTRODUCTION

In the Gulf Coast region, almost 90% of industrial wastewaters are disposed via the deep well injection techniques. The liquid wastes are injected into brackish and saline aquifers which typically are sand bodies of 50 to 100 ft thickness and are bound by clay or shale aquitards. The interstitial solution within the confining aquitards is not in chemical equilibrium with the fresh injected wastewater. In addition, wastewater velocities in the aquitards are very slow, because of the low permeabilities ($k \sim 10^{-4} - 10^{-5}$ md) (Constant, 1989). Consequently, the movement of hazardous solutes in the aquitard is controlled by diffusion. The key to the success of the geologic repository is how fast hazardous solutes are released into the accessible environment. To predict the physical transport rates of solutes in deep well injection zones, bench scale tests were performed with aquitard and aquifer soils, obtained from deep well injection zones in Louisiana.

Lai and Mortland (1961) found decreases in the diffusion coefficients of exchangeable cations, such as sodium and calcium ions, with increasing clay concentration. They explained the decreases by suggesting that the number of exchange sites present per unit volume affects the diffusion
rate. Increasing the amount of clay per unit volume increases the number of exchange sites, thereby increasing the average number of exchanges an ion had to make in a given distance. Phillips and Brown (1964) compared the molecular diffusion and surface diffusion coefficients and found that the magnitude of molecular diffusion was larger than those for surface diffusion in each of the four soil materials. The rate of rubidium (Rb) molecular and surface diffusion was largest in kaolinite clay and was least in montmorillonite clay. Their findings support the conclusions of Lai and Mortland.

On the contrary, some investigators found that the effect of diffusion was increased by the release of cations from exchange sites on the clay minerals (Komiyama and Smith, 1974). Jahnke and Radke (1987) postulated that some cationic adsorption created a surface diffusion path for enhanced ion transport, and showed that this parallel surface transport mechanism could have a significantly adverse effect on the performance of the packing by reducing or completely eliminating sorption retardation.

Jensen and Radke (1988) investigated the counter ionic migration of Cs$^+$ and Sr$^{2+}$ against Na$^+$ in Na-Montmorillonite. They found both monovalent cation Cs$^+$ and divalent cation Sr$^{2+}$ showed enhanced diffusion through the media. When the temperature increased from 22 °C to 90 °C, the Cs surface diffusivities increased approximately four fold (2.2*10^{-6} to 8*10^{-6} cm$^2$/s). The temperature effects on diffusion were also
studied by Sadeghi et al. (1988) in water at temperatures ranging from 0 to 50 °C. In this study, the diffusion coefficients of urea increased almost three fold (9*10^{-9} to 3.2*10^{-8} m^2/s) as the temperature increased 50 °C.

Some diffusion rates have been shown to be dependent on the concentration of the solute applied and the pH. Phosphorus diffusion in several soils showed a thirty nine fold increase as the rate of added phosphorus increased from 0 to 100 mg/L (Mahtab et al., 1971). The presence of soluble iron and aluminum under very acid conditions or calcium at very high pH values affect the availability of phosphorus and should also affect its movement and rate of diffusion. Place et al. (1968) found that molecular diffusion increased as the water soluble P and Al-P concentration increased and the Fe-P and free iron oxide contents decreased. This relationship between phosphorus availability and pH is closely related to the adsorption capacity of soils. As the pH changed from 8.5 to 4, the diffusion coefficient increased from 3*10^{-9} cm^2 to 1.2*10^{-7} cm^2/s in kaolinite and it increased from 2*10^{-8} cm^2/s to 1.15*10^{-7} cm^2/s in montmorillonite.

The objective of this study is to investigate how environmental factors such as temperature, NaCl concentration, Cr(VI) concentration, soil bulk density, and water content in porous media can affect the diffusion rate of Cr(VI).
4.2 MATERIAL AND METHODS

Two soils, shale and sand, were obtained from deep well injection zones in St. Charles Parish and St. Bernard Parish, La. respectively. Both soils were treated and stored as previously described (Hyun and Field, 1990). The results of X-ray diffraction analysis of both soils are listed in Table 4-1.

Temperature Effect: the temperature effect on the diffusion coefficients was determined by a method described in Lai and Mortland (1961). Pretreated soil samples were ashed at 550 °C for 15 minutes to remove any soil organic matter (APHA et al., 1985). This process prevented Cr(VI) reduction caused by the oxidation of soil organic matter. For same reason, no chloride ion was added into the solution. The diffusion coefficients of Cr(VI) and Cr(III) are different, but the detector cannot distinguish Cr(VI) and Cr(III). These facts may result in the misinterpretation of Cr(VI) diffusion. Shale was mixed with fresh nitric acid of pH - 0.62 to yield 37.5% of water by weight. Then this salt free paste was carefully put in a 10 ml disposable syringe from which the tips on both sides were cut off to make a cylindrical figure with a diameter of 1 cm and a height of 6 cm. Sand was packed every 0.5 cm to yield bulk density of 1.4 g/cm³, and it was saturated with fresh nitric acid of pH - 0.62. Aged nitric acid may produce NO₂ and it may reduce Cr(VI) to Cr(III) (Stollenwerk and Grove, 1985). After covering
Table 4-1: X-Ray Diffraction Results (Weight Percent)

<table>
<thead>
<tr>
<th>Component</th>
<th>Sand</th>
<th>Shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>57</td>
<td>93</td>
</tr>
<tr>
<td>Feldspar</td>
<td>07</td>
<td>06</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>04</td>
<td>02</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>03</td>
<td>04</td>
</tr>
<tr>
<td>Calcite</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Clay Minerals</td>
<td>36</td>
<td>01</td>
</tr>
</tbody>
</table>

100% 100%

**Values in ( ) indicate percent of expandable smectite interlayers**

polyethylene caps on both sides, samples were placed in the water bath for 5 hours to raise the temperature to that of the water bath. Then 100 μL of $^{51}$Cr as Na$_2$CrO$_4$ solution were placed on the top of the soil as a thin film. Total radioactivity was set to 2 μCi in 100 μL. The syringe was capped to prevent evaporation and placed between two plexiglas plates to ensure the prevention of water evaporation (Figure 4-1). The sample syringes were placed in 3 different water baths of 23 °C, 50 °C, and 70 °C. After 30 days, the syringes were removed from the water baths and the shale and sand samples were frozen prior to segmentation by exposing them to liquified nitrogen gas for 15 seconds. The soil plugs were sectioned in even depth increments of 1.25 mm for shale and 2.5 mm for sand. The same volume of the soil plug in each section provided same geometry under the radioactivity detector, minimizing detection errors caused by the variable absorption rates of gamma ray. The radioactivity of each section was determined by the Auto-Gamma Detector in Nuclear Science Department, LSU and was summed up to yield the amount at different depths.

$^{51}$Cr Amount Effect: The $^{51}$Cr amount effect study followed the same procedures as those in the temperature effect study. Three different concentrations were used, 2 μCi, 10 μCi, and 20 μCi per 100 μL. The temperature was set to 70 °C.

NaCl Effect: This experiment was necessary to determine the effect of solution density change on the diffusion rate of $^{51}$Cr in shale. The shale sample was saturated with 1 N NaCl and
Figure 4-1: $^{51}$Cr Diffusion Experiment
washed several times to remove free Na\(^+\) and Cl\(^-\) ions from the shale. Then, the shale was dried in 102 +/- 1 °C, crushed to pass No. 100 sieve and stored in a vacuum desiccator. The other procedures were the same as those in the temperature effect study with the exception of two different NaCl concentrations (15,000 and 30,000 mg/L) and of temperature, 70 °C. The pH was maintained at 8.0 to prevent possible reduction of Cr(VI) at low pH.

Water Content Effect: Three different ratios of water to shale (33.3 %, 37.5 %, and 42.5 % w/w) were used to determine the effect of amount of water on diffusion. The same volume of pastes were placed in each syringe and the same procedures were applied as those in the temperature effect study. In the preliminary study, it was found that 42.5 % ratio of shale to water was the maximum allowable ratio to avoid bleeding of water from shale after 30 days. The solution pH and the temperature were set to -0.62 and 70 °C, respectively.

Bulk Density Effect: Dry bulk densities of 1.3, 1.4, and 1.5 g/cm\(^3\) were obtained by packing the sand every 0.5 cm. The soil packing was performed by tamping with a polyethylene syringe plunger, of which the rubber head was cut off and the outer diameter was slightly smaller than the inside diameter of the syringe. The procedures were the same as those in the \(^{51}\)Cr amount effect study except that one concentration was used, 2 μCi/100 μL.
4.3 DIFFUSION EQUATION

When a Mass "M" of a substance is deposited as a uniform and indefinitely thin layer on a surface area "A" and allowed to diffuse into an infinitely thick medium, this initial condition can be treated as Fick's law for instantaneous sources (Lai and Mortland, 1961).

The mass transport equation by diffusion can be analytically solved by use of the Laplace transform.

Diffusion Equation: \( \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \) \hspace{1cm} (4-1)

with I.C. \( C(x,t) = \frac{M}{A} \delta(x) \text{ when } t=0 \) \hspace{1cm} (4-2a)

B.C. No. 1: \( \lim_{x \to \infty} C(x,t) = 0 \) \hspace{1cm} (4-2b)

B.C. No. 2: \( \frac{\partial C(x,t)}{\partial x} = 0 \text{ when } x=0 \) \hspace{1cm} (4-2c)

Let \( L_x[C(x,t)] = G_1(x,\rho) \), \( L_x[G_1(x,\rho)] = G_2(\rho,\rho) \)

Taking the Laplace transform of eq. 4-1, it becomes

\( \rho G_1(x,\rho) - C(x,0) = D \frac{d^2 G_1(x,\rho)}{dx^2} \) \hspace{1cm} (4.3)

Combining eq. 4-2a to eq. 4-3 results in

\( \frac{d^2 G_1(x,\rho)}{dx^2} - \frac{\rho}{D} G_1(x,\rho) = - \frac{M}{AD} \delta(x) \) \hspace{1cm} (4-4)

Taking the Laplace transforms of eq.s 4-2b and 4-2c produces
Taking the Laplace transform of eq. 4-4, it becomes

\[ \omega^2 G_2(\omega, \varphi) - \omega G_1(0, \varphi) - \frac{dG_1(0, \varphi)}{dx} - \frac{\varphi}{D} G_2(\omega, \varphi) = -\frac{M}{AD} \quad -(4-7) \]

Note that \( \int_0^\infty f(x) \delta(x) \, dx = f(0) \) when \( x > 0 \) (Spiegel, 1965).

Consequently

\[ \int_0^\infty -\frac{M}{AD} \delta(x) e^{-\omega x} \, dx = -\frac{M}{AD} \]

Then eq. 4-7 can be rearranged as

\[ G_2(\omega, \varphi) = \frac{\omega G_1(0, \varphi)}{\omega^2 - \lambda^2} - \frac{M}{AD} \frac{1}{\omega^2 - \lambda^2} \quad -(4.8) \]

\[ = \frac{G_1(0, \varphi)}{2} \frac{1}{\omega - \lambda} + \frac{G_1(0, \varphi)}{2} \frac{1}{\omega + \lambda} - \frac{M}{AD} \frac{1}{2\lambda} \frac{1}{\omega - \lambda} \]

\[ + \frac{M}{AD} \frac{1}{2\lambda} \frac{1}{\omega + \lambda} \quad -(4-9) \]

where \( \lambda = \sqrt{\frac{\varphi}{D}} \)

Taking the inverse Laplace transform of eq. 4-9, it becomes

\[ G_1(x, \varphi) = \left( \frac{G_1(0, \varphi)}{2} - \frac{M}{2\lambda AD} \right) e^{\lambda x} + \left( \frac{G_1(0, \varphi)}{2} + \frac{M}{2\lambda AD} \right) e^{-\lambda x} \quad -(4-10) \]

Using eq. 4-5 into eq. 4-10, it is found that

\[ \frac{G_1(0, \varphi)}{2} = \frac{M}{2\lambda AD} \quad -(4-11) \]

Then eq. 4-10 can be rearranged as
\[ G_1(x, p) = \frac{M}{\lambda \Delta D} e^{-\lambda x} \]
\[ = \frac{M}{\sqrt{DA}} \frac{1}{\sqrt{p}} e^{-\lambda x} \quad -- (4-12) \]

Taking the inverse Laplace transform of eq. 4-12, it becomes

\[ C(x, t) = \frac{M/A}{\sqrt{\pi Dt}} e^{-x^2/(4Dt)} \quad -- (4-13) \]

Note that \( \mathcal{L}^{-1}\left(\frac{e^{-a^2}}{\sqrt{\pi t}}\right) = \frac{e^{-a\sqrt{s}}}{\sqrt{s}} \)

In Figure 4-1, the total amount of radioactivity \( (A_0) \) calculated by the integration of \( C_x \) from the surface to the bottom of the soil plug is

\[ A_0 = \frac{M/A}{\sqrt{\pi Dt}} \int_0^\infty e^{-x^2/(4Dt)} dx \quad -- (4-14) \]

Let \( y^2 = \frac{x^2}{4Dt} \) and \( y = \frac{x}{2\sqrt{Dt}} \)

Then \[ A_0 = \frac{M/A}{\sqrt{\pi Dt}} \int_0^\infty e^{-y^2} d(2\sqrt{Dt}y) \]
\[ = \frac{M/A*2\sqrt{Dt}}{\sqrt{\pi Dt}} \int_0^\infty e^{-y^2} dy \]
Similarly, when the surface of a plug has been sliced down to a depth $x$ below the original surface, the radioactivity in the piece ($A_x$) will be given by

$$A_x = \frac{M/A}{\sqrt{\pi Dt}} \int_0^x e^{-\frac{x^2}{4Dt}} dx$$

$$= \frac{M/A}{\sqrt{\pi Dt}} \int_0^x e^{-y^2} d(2\sqrt{Dt} y)$$

$$= \frac{M/A \cdot 2\sqrt{Dt}}{\sqrt{\pi Dt}} \int_0^y e^{-y^2} dy$$

$$= \frac{M/A \cdot 2\sqrt{Dt}}{\sqrt{\pi Dt}} \left( \frac{\sqrt{\pi}}{2} \text{erf} y \right)$$

$$= \left( \frac{M/A}{A_o} \right) \text{erf} y \quad -(4-16)$$

Combining eq.s 4-15 and 4-16 results in

$$\text{erf} y = \frac{A_x}{A_o} \quad -(4-17)$$

The values of $A_o$ and $A_x$ can be obtained from experiments and the value of $y$ can be found from $\text{erf} y$ in standard probability tables (Abramowitz and Stegun, 1972). A plot of $y$ vs $x$ should result in a straight line passing through the origin. Then, the diffusion coefficient "$D$" can be evaluated from the
straight line of slope \(1/(2(Dt)^{0.5})\).

4.4 Results and Discussion

Figures 4-2 and 4-3 show the linearity of the data points obtained from the experiments with sand and shale respectively. In all experiments, the coefficient of correlation 'r' was more than 0.99. This reflects the fact that the experiments followed the theoretical equation 4-17. From eq. 4-17, it is clear that the diffusion coefficient 'D' is inversely proportional to the square of the slope at a fixed time 't'. This means the small slope in Figures 4-2 and 4-3 corresponds to a greater diffusion coefficient. Calculated diffusion coefficients are 5.58*10^{-6}, 2.69*10^{-6}, and 1.49*10^{-5} cm^2/sec for sand and 2.08*10^{-7}, 4.62*10^{-7}, 2.26*10^{-7}, and 7.23*10^{-7} cm^2/sec for shale. Generally, it was found that the magnitude of diffusion coefficients of shale was one tenth of the diffusion coefficients of sand. Theoretically, only two data points were enough to calculate the diffusion coefficient 'D' in eq. 4-17. The extra three data points were used to minimize the error in the data interpretation resulting from the mistake in the count of radioactivity.

Figures 4-4 and 4-5 show the effect of temperature on the diffusion of \(^{51}\text{Cr}\) on sand and shale respectively. When the temperature was increased from 23°C to 50°C, the diffusion coefficient of sand was increased from 1.2*10^{-6} to 2.8*10^{-6} cm^2/sec and when the temperature was increased from 50°C to
Figure 4-2: Linearity of Data (with Sand)

- ○ 1.4 g/cm³, 50 °C, 10 μCi, r: 0.999
- ● 1.4 g/cm³, 50 °C, 5 μCi, r: 0.9998
- △ 1.4 g/cm³, 50 °C, 2 μCi, r: 0.9993

Distance X (Cm)
Figure 4–3: Linearity of Data (with Shale)

- ○ 0.375, 50 °C, 10 μCi,  r: 0.9975
- ● 0.375, 50 °C, 5 μCi,  r: 0.9973
- △ 0.375, 50 °C, 2 μCi,  r: 0.9994
Figure 4-4: Temperature Effect on Diffusion (Sand)

\[ D = -1.1136 \times 10^{-6} + 8.9865 \times 10^{-8} \times (T) \]

\[ r = 0.97289 \]
Figure 4-5: Temperature Effect on Diffusion (Shale)

\[ D = -3.5615 \times 10^{-7} + 2.101 \times 10^{-8} \times T \]

\[ r = 0.93385 \]
70 °C, it was increased from $2.8 \times 10^{-6}$ to $5.45 \times 10^{-6}$ cm$^2$/sec. The bulk density of sand applied was 1.4 g/cm$^3$. In shale, the diffusion coefficients were changed from $2.08 \times 10^{-7}$ to $4.76 \times 10^{-7}$ cm$^2$/sec, when the temperature was increased from 23 °C to 50 °C. When the temperature was increased from 50 °C to 70 °C, it was changed from $4.76 \times 10^{-7}$ to $1.24 \times 10^{-6}$ cm$^2$/sec. The water content applied to shale was 37.5 %. In both soils, diffusion coefficients increased linearly as the temperature was increased. This is attributed to the change in density and viscosity of solution as the temperature changes. A less dense and less viscous solution at higher temperatures, enhances the movement of ions or molecules in solution. Thus, it was possible to linearize the relationship between the diffusion coefficient and temperature. It was found that $D = -1.1136 \times 10^{-6} + 8.9865 \times 10^{-8} \times (T)$ with $'r' = 0.973$ for sand and $D = -3.5615 \times 10^{-7} + 2.101 \times 10^{-8} \times (T)$ with $'r' = 0.934$ for shale. From these equations, the diffusion coefficients at 18 °C for sand and shale could be predicted as $5.04 \times 10^{-7}$ cm$^2$/sec and $2.203 \times 10^{-8}$ cm$^2$/sec respectively. These values were compared with the diffusion coefficients of Cr(VI) in free aqueous solutions without solids. The average diffusion coefficient in free aqueous solution at 18 °C was $1.17 \times 10^{-5}$ cm$^2$/s (Washburn, 1980), which was 20 times greater than that in sand pores and 500 times greater than that in shale pores. Table 4-2 shows the diffusion coefficients calculated using the above equations.

The variation of the diffusion coefficient with
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Sand Diffusion, cm²/sec</th>
<th>Shale Diffusion, cm²/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>6.837×10⁻⁷</td>
<td>6.405×10⁻⁸</td>
</tr>
<tr>
<td>30</td>
<td>1.58×10⁻⁶</td>
<td>2.742×10⁻⁷</td>
</tr>
<tr>
<td>40</td>
<td>2.481×10⁻⁶</td>
<td>4.843×10⁻⁷</td>
</tr>
<tr>
<td>50</td>
<td>3.38×10⁻⁶</td>
<td>6.944×10⁻⁷</td>
</tr>
<tr>
<td>60</td>
<td>4.278×10⁻⁶</td>
<td>9.045×10⁻⁷</td>
</tr>
<tr>
<td>70</td>
<td>5.177×10⁻⁶</td>
<td>1.115×10⁻⁶</td>
</tr>
<tr>
<td>80</td>
<td>6.076×10⁻⁶</td>
<td>1.325×10⁻⁶</td>
</tr>
<tr>
<td>90</td>
<td>6.974×10⁻⁶</td>
<td>1.535×10⁻⁶</td>
</tr>
</tbody>
</table>
temperature can be expressed by the equation

\[ D = A \cdot e^{-\frac{E_a}{RT}} \]

where \( E_a \) is the activation energy, which works as an energy barrier for the diffusion to occur, \( A \) is the activation coefficient, and \( R \) is the gas constant (8.139 J/mole °K). The activation energy can be estimated by determining the diffusion coefficient at different temperatures and plotting the \( \ln D \) versus \( 1/T \). The activation energy \( E_a \) is calculated from the slope of the linear plot. Figure 4-6 shows the Arrhenius plot for the diffusion coefficients of \(^{51}\)Cr in sand and shale. Calculated activation energies for sand and shale are summarized in Table 4-3. The activation energies of 24.88 KJ/mole for sand and 29.15 KJ/mole for shale were much greater than that for ions in free aqueous solutions, which was approximately 17 KJ/mole (Nye, 1979).

The greater activation energy for shale than that for sand shows that the occurrence of diffusion in shale is more difficult than the occurrence in sand, because the greater activation energy implies the greater driving force is required to make the diffusion occur. This explains the cause of smaller diffusion coefficients in shale than the diffusion coefficients in sand.

Figure 4-7 shows the bulk density effect on the diffusion coefficient for sandy soil. Linear regression analysis gave a linear relationship between the bulk density and the diffusion
Figure 4-6: Arrehnius Plot of Diffusion Coefficients

- Sand: Slope = -2.99E3
- Shale: Slope = -3.51E3

\[ \ln D \quad \frac{1}{T} \quad ^{\circ} \text{K}^{-1} \]
Table 4-3: Activation Energy of Diffusion

<table>
<thead>
<tr>
<th>Soil</th>
<th>Diffusion Coefficient cm²/sec</th>
<th>Eₐ, KJ/mole</th>
<th>Bulk Density g/cm³</th>
<th>Water Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>1.2*10⁻⁶ at 23 °C</td>
<td>24.88</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.8*10⁻⁶ at 50 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.45*10⁻⁶ at 70 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shale</td>
<td>2.08*10⁻⁷ at 23 °C</td>
<td>29.15</td>
<td></td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>4.76*10⁻⁷ at 50 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.24*10⁻⁶ at 70 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4–7 : Bulk Density Effect on Diffusion

○ 50 °C \( D = 4.03E-5 - 2.682E-5 \times \text{(B.D.)} \)
\[ r = 0.9998 \]

\( D = 9.237E-5 - 6.05E-5 \times \text{(B.D.)} \)
\[ r = 0.9538 \]

70 °C
coefficient. At 50 °C, it was described as $D = 4.03 \times 10^{-5} - 2.682 \times 10^{-5} \times (B.D.)$, and the correlation coefficient was found to be 0.9998. At 70 °C, it was described as $D = 9.237 \times 10^{-5} - 6.05 \times 10^{-5} \times (B.D.)$, and the correlation coefficient was found to be 0.9538. Even though the value of the correlation coefficient was lower at 70 °C, it still gave a strong linear relationship. In the figure, the diffusion coefficients were increased from $1.41 \times 10^{-7}$ to $2.8 \times 10^{-6}$, and $5.58 \times 10^{-6}$ cm$^2$/sec, when the bulk density was decreased from 1.5 to 1.4 and 1.3 g/cm$^3$ at 50 °C. At 70 °C, it was changed from $2.69 \times 10^{-6}$ to $5.45 \times 10^{-6}$, and $1.49 \times 10^{-5}$ cm$^2$/sec. Here, it should be noted that the diffusion coefficient of $^{51}$Cr at 1.3 g/cm$^3$ and 70 °C in sand media reached the same order of magnitude as the diffusion coefficient in free aqueous solution at room temperature (~ $1.45 \times 10^{-9}$ cm$^2$/sec at 25 °C; Washburn, 1980).

Warncke and Barber (1972) reported that the maximum rate of zinc diffusion did not always occur at a soil bulk density where the diffusion path was least tortuous. This is in contrast to our results, which showed the inverse relationship between bulk density and the diffusion coefficients. This would be expected, since the bulk density changes affect the physical and chemical properties of a soil. Changes in the physical property are reflected in the tortuosity, while the changes in the chemical property are reflected in the interaction of the diffusing ion with the solid phase.

Initially, at low bulk density, compaction can increase
the continuity of the liquid phase by bringing water films in contact. However, the increasing solids per unit volume may increase the tortuosity of the diffusion path. Thus, the net effect of increasing soil bulk density upon the rate of ion diffusion in a soil should be related to the balance between changes in the relative influence of the physical and chemical components. However, the sandy soil in our study was chemically non-reactive and the physical component (tortuosity) was the only one affected. Consequently, while the bulk density was increased, the tortuosity was increased and the diffusion rate was decreased.

Some of the molecules and ions show their dependency of diffusion rate on their concentration in the solution. The effect of $^{51}$Cr amount applied on diffusion rate were shown in Figures 4-8 and 4-9 for sand and shale respectively. For a given temperature and soil type, the diffusion coefficients were not changed significantly. In case of sand at $50^\circ$C, the diffusion coefficients were $2.8*10^{-6}$, $2.73*10^{-6}$, and $2.97*10^{-6}$ cm$^2$/sec for $2 \mu$Ci, $5 \mu$Ci, and $10 \mu$Ci of $^{51}$Cr applied respectively. After taking an average of these diffusion coefficients, the deviations of individual values from the mean value were 1.18 %, 3.65 %, and 4.94 % respectively. The standard deviation was $1.234*10^{-7}$ and the relative standard deviation was 4.34 %. The diffusion coefficients at $70^\circ$C were $5.45*10^{-6}$, $5.49*10^{-6}$, and $5.2*10^{-6}$ cm$^2$/sec for $2 \mu$Ci, $5 \mu$Ci, and $10 \mu$Ci of $^{51}$Cr applied. After taking an average of the
Figure 4–8: $^{51}$Cr Amount Effect on Diffusion (Sand)

Diffusion Coeff. (cm$^2$ S$^{-1}$ 1E8)

$^{51}$Cr Amount Applied ($\mu$Ci)

Soil: Sand

- $70^\circ C$
- $50^\circ C$
Figure 4-9: $^{51}$Cr Amount Effect on Diffusion (Shale)

Diffusion Coeff. (cm$^2$ S$^{-1}$) $\times 10^7$

- $\circ$ 70 °C
- $\bullet$ 50 °C

Soil: Shale

$^{51}$Cr Amount Applied (µCi)
diffusion coefficients the deviations of individual values from the mean value were 3.35 %, 2.04 %, and 1.3 % respectively. The standard deviation was $1.574 \times 10^{-7}$, and the relative standard deviation was 3.1 %.

In case of shale at 50 °C, the diffusion coefficients were $4.76 \times 10^{-7}$, $4.75 \times 10^{-7}$, and $4.52 \times 10^{-7}$ cm$^2$/sec for 2 μCi, 5 μCi, and 10 μCi of $^{51}$Cr applied. The deviation of individual value from the mean value were 1.78 %, 1.57 %, and 3.35 % respectively. The standard deviation was $1.36 \times 10^{-8}$, and the relative standard deviation was 2.9 %. When the temperature was raised to 70 °C, the diffusion coefficients were $1.24 \times 10^{-6}$, $1.26 \times 10^{-6}$, and $1.19 \times 10^{-6}$ cm$^2$/sec. The deviation of individual value from the mean value were 0.81 %, 2.44 %, and 3.25 % respectively. The standard deviation was $3.61 \times 10^{-8}$, and the relative standard deviation was 2.93 %. From the above results, it was found that the deviation of individual values was usually less than the relative standard deviation. Moreover, there is no consistent relationship between the diffusion coefficients and the $^{51}$Cr applied. For example, the diffusion coefficient of shale was largest at 5 μCi, when the temperature was 50 °C. But it was smallest at 5 μCi, when the temperature was 70 °C. The diffusion coefficient of sand was largest at 10 μCi when the temperature was 50 °C, but it was largest at 2 μCi at 70 °C. Therefore, it can be concluded that the diffusion rate of $^{51}$Cr in a porous media is independent of the amount of $^{51}$Cr applied.
Analyzing the diffusion coefficient data in International Critical Tables (Washburn, 1980), it can be said that the diffusion in a free aqueous solution is not concentration dependent either. In a free aqueous solution, as the Cr(VI) concentration was changed from 0.016 to 0.05 mole at 18 °C, it did not show any change in the diffusion coefficient (from $1.17 \times 10^{-5}$ to $1.17 \times 10^{-5} \text{ cm}^2/\text{sec}$). Moreover, when the concentration was changed from 0.05 to 0.15 mole, it showed a decrease in the diffusion coefficient (from $1.17 \times 10^{-5}$ to $1.09 \times 10^{-5} \text{ cm}^2/\text{sec}$, which is a 6.8 % decrease). However, realizing the possible error in the data was 5 %, it was not a significant change in the diffusion coefficients.

Figure 4-10 shows the effect of water content on the diffusion rate of $^{51}$Cr in shale. As the water content was decreased from 42.9 % to 37.5 % and 33.3 %, the diffusion coefficient was gradually decreased from $7.23 \times 10^{-7}$ to $4.76 \times 10^{-7}$, and $2.26 \times 10^{-7} \text{ cm}^2/\text{sec}$, when the temperature was 50 °C. The figure shows a more rapid change in the diffusion coefficient at a temperature of 70 °C. The diffusion coefficients were decreased from $2.49 \times 10^{-6}$ to $1.24 \times 10^{-6}$, and $5.47 \times 10^{-7} \text{ cm}^2/\text{sec}$. These results agree well with those of Warncke and Barber (1972). According to Olsen et al. (1965), as the water content of a soil decreases, the cross-sectional area available for diffusion decreases and the ion should travel a longer distance to reach a given point. Other factors such as viscosity, and desorption also become important as the water
Figure 4-10: Water Content Effect on Diffusion

\[ D = -1.48 \times 10^{-6} + 5.15 \times 10^{-6} \times (\text{W.C.}) \]

\[ D = -6.3 \times 10^{-6} + 2.04 \times 10^{-5} \times (\text{W.C.}) \]

- 50 °C, \( r = 0.998 \)
- 70 °C, \( r = 0.994 \)
content decreases. When the temperature was increased from 50 °C to 70 °C, the slope of the linear regression line was increased from $5.15 \times 10^{-6}$ to $2.04 \times 10^{-5}$ (4 times in magnitude). The relation between the gravimetric water content and the diffusion coefficient are well presented as $D = -1.48 \times 10^{-6} + 5.15 \times 10^{-6} \times (W.C.)$ at 50 °C, and $D = -6.3 \times 10^{-6} + 2.04 \times 10^{-5} \times (W.C.)$ at 70 °C. Calculated values for different water contents are given in Table 4-4. In order to have a certain diffusion rate at 70 °C, the water content at 50 °C must be increased considerably. For example, to have a diffusion coefficient of $7.5 \times 10^{-7}$ cm²/sec, the required water content at 70 °C is 0.35. However, to have same diffusion coefficient at 50 °C, the required water content is increased from 0.35 to 0.43.

In our study, the $^{51}$Cr concentration was maintained constant in various water contents. However, it should be noted that according to Warncke and Barber (1972), when the solution metal (zinc) level dropped as the water content increased, the effect of water content on the diffusion coefficient was almost insignificant.

Figure 4-11 shows the effect of NaCl addition on the diffusion rate. At 50 °C, as the NaCl concentration was increased, the diffusion coefficients was changed from $4.76 \times 10^{-7}$ to $4.74 \times 10^{-7}$, and $4.62 \times 10^{-7}$ cm²/sec/ The changes were only 0.4 % and 2.5 % respectively. At 70 °C, the diffusion coefficients were changed from $1.24 \times 10^{-6}$ to $1.25 \times 10^{-6}$, and
Table 4-4: Diffusion Coefficient as a Function of Water Content in shale

<table>
<thead>
<tr>
<th>Water Content</th>
<th>50 °C</th>
<th>70 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>6.5*10^{-8}</td>
<td>8.2*10^{-8}</td>
</tr>
<tr>
<td>0.35</td>
<td>3.255*10^{-7}</td>
<td>8.4*10^{-7}</td>
</tr>
<tr>
<td>0.4</td>
<td>5.8*10^{-7}</td>
<td>1.86*10^{-6}</td>
</tr>
<tr>
<td>0.45</td>
<td>8.375*10^{-7}</td>
<td>2.88*10^{-6}</td>
</tr>
<tr>
<td>0.5</td>
<td>1.095*10^{-6}</td>
<td>3.9*10^{-6}</td>
</tr>
<tr>
<td>0.55</td>
<td>1.353*10^{-6}</td>
<td>4.92*10^{-6}</td>
</tr>
<tr>
<td>0.6</td>
<td>1.61*10^{-6}</td>
<td>5.94*10^{-6}</td>
</tr>
</tbody>
</table>
Figure 4-11: NaCl Effect on Diffusion

- NaCl Free
- NaCl 15,000 mg/L
- NaCl 30,000 mg/L

Diffusion Coefficient (cm² s⁻¹ * 1E7)

50 °C

70 °C
1.21\times 10^{-6} \, \text{cm}^2/\text{sec}. The increases were only 0.8 % and 3.2 % respectively. From these results, it is concluded that the effect of solution density change due to the addition of NaCl does not contribute significantly to the change in the diffusion rate.

4.5 Conclusions

The diffusion experiments with $^{51}$Cr to find the diffusion coefficients under various environments and the data obtained were reliable. The regression lines yielded the correlation coefficient 'r' greater than 0.99 for all trials.

As the temperature increased, the diffusion coefficient also increased. The relationship between the diffusion coefficient and temperature was plotted and calculation of the diffusion coefficients corresponding to different temperature enables the calculation of the activation energy. The activation energies of diffusion in shale and sand (29.15 KJ/mole and 24.88 KJ/mole respectively) were much greater than the activation energy of diffusion in a free aqueous solution (~ 17 KJ/mole). This fact indicates the difficulties of diffusion occurrence in porous media, compared to the diffusion in a free aqueous solution.

As the bulk density of sand was increased, the diffusion coefficient was decreased due to the increase of tortuosity of the sand. The linear regression provided a relationship between the bulk density and the diffusion coefficient. It was
described as \( D = 4.03 \times 10^{-5} - 2.682 \times 10^{-5} \times (\text{B.D.}) \) at 50 °C, and
\( D = 9.237 \times 10^{-5} - 6.05 \times 10^{-5} \times (\text{B.D.}) \) at 70 °C.

The amount of \( ^{51}\text{Cr} \) applied did not affect the diffusion rate significantly either in porous media or in a free aqueous solution. The deviations of the individual value were less than 5 % from the mean value.

As the water content increased, so did the diffusion coefficients. When the temperature was 70 °C, the slope of linear regression line increased up to 4 times the slope of regression line at 50 °C. In order to obtain a certain diffusion coefficient, the higher temperature requires less water content, and the lower temperature requires more water content. The effect of NaCl addition on the diffusion rate was not significant, i.e., the density change in the solution did not contribute significantly to the change of the diffusion rate.

Thus far, several environmental factors have been studied for their effect on the diffusion rate of \( ^{51}\text{Cr} \) in sand and shale. Some factors such as temperature, bulk density, and water content affected the diffusion rate significantly, while others, such as \( ^{51}\text{Cr} \) amount and NaCl concentration in the solution did not significantly affect the diffusion rate. The environments of the deep well disposal zones are too complicated to be characterized by one or two environmental factors. Therefore, more environmental factors such as viscosity, porosity, pH, etc., should be studied to evaluate
the behavior of diffusion in deep well disposal zones more accurately.
References


CHAPTER 5
Equilibria and Kinetics of Reduction

5.1 INTRODUCTION

The fate and transport of deep well injected materials has come under extreme scrutiny with the upcoming ban to be imposed by the United States Environmental Protection Agency (EPA) in January 1991. The Louisiana Department of Natural Resources has shown that chromium contaminated wastewater is a significant portion of the wastes being deep well injected, occupying 20% of total wastewater disposed of through deep well injection practices in Louisiana (Jacobus et al., 1985). As part of an overall study on the fate and transport of chromium upon deep well injection, this paper addresses the kinetics of chromium reduction in deep well injection zones.

Many investigators reported the behavior of Cr(VI) and Cr(III) and removal techniques using different kinds of mechanisms. The two major removal pathways are adsorption and reduction. Zachara et al. (1987) studied chromate (CrO$_4^{2-}$) adsorption on amorphous iron oxyhydroxide. They found that anionic co-solutes such as SO$_4^{2-}$ and H$_4$SiO$_4$ reduced chromate adsorption through a combination of competitive and electrostatic effects, but cations such as K$^+$, Mg$^{2+}$, Ca$^{2+}$ did not show appreciable influence. Stollenwerk and Grove (1985a) showed the quantity of Cr(VI) adsorbed varied with the type and concentration of other anions in solution. They found that
a mixture of 50% $\text{H}_2\text{PO}_4^-$ + $\text{HPO}_4^{2-}$ inhibited adsorption of Cr(VI) to a great extent. Griffin et al. (1977) showed that adsorption of Cr(VI) by two different clays increased with pH decrease in the range of 9 to 1.

James and Bartlett (1983a) investigated the effect of dissolved organic carbon on the reduction of Cr(VI) at different pH and the effect of sulfate and phosphate on Cr(VI) adsorption. Field and Hyun (1989) showed the effect of chloride ion on adsorption and reduction of Cr(VI), temperature effect, and the role of organic chemicals coinjected in the reduction of Cr(VI). The mechanism of Cr(VI) reduction by chloride ion oxidation is similar to the interference caused by chlorides in the chemical oxygen demand (COD) test of a wastewater. The environment in the COD reaction vessel is similar to that in deep well injection zones with respect to high temperature and low pH. Cripps and Jenkins (1964) suggested that an ion pair form with mercury ion ($\text{HgCl}_2^-$) before any chloride reacts with $\text{K}_2\text{Cr}_2\text{O}_7$, prevents the interference by chloride ion.

Stollenwerk and Grove (1985b) investigated the reduction of Cr(VI) in water samples acidified for preservation. They found the occurrence of reduction by dissolved organic matter, even at 4°C. They found also that the rate of reduction of Cr(VI) increased with increase of nitrite produced from aged nitric acid, dissolved organic carbon, hydrogen ion($\text{H}^+$), and temperature. The reduction by inorganic
substances such as ferrous ion is also possible in shallow subsurface environments (Eary and Rai, 1988).

The objective of this study is to investigate how environmental factors such as temperature, pH, soil organic material, and chloride ion can affect the reduction rate of Cr(VI).

5.2 METHODS

Two samples were obtained from injection zone core samples of existing wells in Louisiana. A sample of injection zone shale was obtained from the St. Bernard injection well. Injection zone sand was collected from boring samples obtained during the drilling of the St. Charles injection well. Both well samples were crushed with pestle and mortar and were washed with deionized water until the chloride ion in decanted water was not detected, using the silver nitrate titration technique (APHA et al., 1985). Then the injection zone formation materials (shale and sand) were dried at 102 +/- 1 °C in a drying oven and were ground to pass through a No. 100 sieve. The injection zone formation materials were then stored in a desiccator until use.

In case of the experiment at pH -0.62, 83 mL of deionized water, and 7 mL of concentrated nitric acid (HNO₃) were mixed with 2 grams of dry shale or sand and shaken at 50 °C for 24 hours in 250 mL Erlenmeyer flasks adapted with a septum port. Twenty four hours at 50 °C has been shown to be adequate to
reach a stabilized pH (Fink, 1987). Each flask then received 10 mL of K\textsubscript{2}CrO\textsubscript{4} solution (1 mg/ml of Cr(VI)).

The flasks were purged with purified nitrogen gas to remove all traces of oxygen and then sealed. The flasks were then shaken in a water bath (120 rpm). At various intervals, 2 mL of solution was taken by syringe through the septum port and centrifuged (Eppendorf Microcentrifuge Model # 5415), maintaining 14,000 G force for 20 min. The use of a septum and syringe to withdraw samples from the flasks prevented escape of chlorine gas (Cl\textsubscript{2}), which would consequently trigger the further reduction of Cr(VI). 1 mL of supernatant was used to analyze the Cr(VI) concentration. Fresh nitric acid was used and always kept in a dark cabinet to prevent nitrite reduction of chromium.

Temperature was controlled at 50 °C and 70 °C to observe temperature dependency. Sodium chloride concentrations were maintained at 0, 0.26, and 0.52 M. The pH influence was investigated at four values (2, 0, -0.62, and -0.81). Only at pH 2 was there a slight pH change after 24 hour stabilization. 1 N and 0.1 N HNO\textsubscript{3} or NaOH were added to maintain pH 2 before reduction experiments were initiated. During the experiments pH did not change more than +/- 0.2 from pH 2.

Cr(VI) was analyzed by measuring the pink color complex developed between 1,5-diphenylcarbazide and Cr(VI) ions in an acidified solution (APHA et al., 1985). Absorbance was measured at 540 nm with a Perkin Elmer Lambda 4
Spectrophotometer, using 1 cm cuvette. The minimum detectable concentration was 0.005 mg/L.

The amount of soil organic materials (reducing agents in injection zone formation materials) was determined on separate sample aliquots by weight loss after ashing at 550 °C (APHA et al., 1985). Experimental preparations are summarized in Table 5-1.

5.3 RESULTS AND DISCUSSION

Figure 5-1 shows that injection zone shale containing 1.3 % organic materials produces 100 % reduction at 70 °C in 24 hours \( (k \approx 3.97 \times 10^{-2} \text{ hr}^{-1}) \). In the experiment with injection zone sand containing 0.5 % organic materials, the reaction period to reach 100 % was extended to 48 hours \( (k \approx 2.47 \times 10^{-2} \text{ hr}^{-1}) \). When the temperature was high enough, both experiments showed complete reduction of Cr(VI). When chloride ion was involved in the reduction of Cr(VI), the reactions on both injection zone formation materials showed the same rate of reaction as shown in Figure 5-2 \( (k \approx 2.1 \times 10^{-2} \text{ hr}^{-1}) \). This implies that the chloride ion hinders Cr(VI) reduction by soil organic materials and the reduction rate is governed by the oxidation of chloride ion. Consequently, the amount of soil organic materials is no longer important. James and Bartlett (1983a) reported that among the soil organic materials, compounds such as fulvic acid played an important role in the reduction of Cr(VI).
Table 5-1. Experiment Preparations

<table>
<thead>
<tr>
<th>Experiment</th>
<th>NaCl Effect</th>
<th>Temp.</th>
<th>pH</th>
<th>Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fromation</td>
<td>0 Mole</td>
<td>70 °C</td>
<td>0.62</td>
<td>Shale</td>
</tr>
<tr>
<td>Effect</td>
<td>0.26 Mole</td>
<td></td>
<td></td>
<td>Sand</td>
</tr>
<tr>
<td>Temp. Effect</td>
<td>0.26 Mole</td>
<td>50 °C</td>
<td>0.62</td>
<td>Shale</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70 °C</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>NaCl Effect</td>
<td>0 Mole</td>
<td>50 °C</td>
<td>0.0</td>
<td>Shale</td>
</tr>
<tr>
<td></td>
<td>0.26 Mole</td>
<td>70 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.52 Mole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH Effect</td>
<td>0 Mole</td>
<td>50 °C</td>
<td>2.0</td>
<td>Sand</td>
</tr>
<tr>
<td></td>
<td>0.26 Mole</td>
<td></td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.81</td>
<td></td>
</tr>
</tbody>
</table>
Cr(VI) in Solution (mg/L)

Figure 5-1: Formation Effect on Reduction at 70°C (NaCl: 0 M

NaCl: 0 M
pH: 0.62

Shale
Sand
Figure 5-2: Formation Effect on Reduction of Cr(VI) in Solution (mg/L) at 70 °C. PH = 0.65, NaCl = 0.26 M.
Figure 5-3 shows the pH effect on the adsorption of Cr(VI) by shale and sand injection zone formation materials respectively. Initial concentration of Cr(VI) was 20 mg/L. As seen in the figure, the shale adsorbs Cr(VI) slightly (11%) only at pH 2, but not below pH 2. Mayer and Shick (1981) reported that the adsorption of Cr(III) to clay surface could control the reduction rate of Cr(VI). However, the Cr(III) ion reduced from Cr(VI) is not adsorbed at pH 2 to the surface of clay components in shale, and most of Cr(III) remains in the soil solution (Huang and Wu, 1977; Griffin et al., 1977). Thus, adsorption cannot control the reduction rate at pH 2 in our study, though the adsorption is possible at pH 2. No adsorption is shown at any pH, even at 2, when sand injection zone formation material is used. This is due to the small specific surface area and the small electrostatic potential at the surface of the sand.

Figures 5-4 and 5-5 show the temperature effect on reduction at pH -0.62 and -0.81, respectively. In Figure 5-4, when the temperature was 50 °C, the time to reach equilibrium took more than 100 hours and only 60% of Cr(VI) in solution was reduced. However, at 70 °C, the time to reach equilibrium was reduced to 50 hours and 100% reduction was possible. Once the temperature was high enough, such as 70 °C, even the reduction hindered by the presence of chloride ion could become 100% in 50 hours. The effect of temperature on reduction rate is related to its effect on the reaction rate.
Cr(VI) Restored (%)
Figure 5.4: Temperature Effect on Reduction at pH = 0.62

Cr(VI) in Solution (mg/L)

Time (Hour)

PH: 0.62

NaCl: 0.26 M

70°C

50°C
Cr(VI) in Solution (mg/L) vs. Time (Hour)

- pH: 0.81
- NaCl: 0.26 M

Figure 5-5: Temperature Effect on Reduction at pH = 0.81
constant. In most reactions, collisions between reacting species are necessary for chemical reactions to occur. The number of collisions between reacting species can be increased by increasing the temperature. Amacher and Baker (1982) reported that the rate of reduction could be increased by increasing the temperature, but the most dramatic change was produced by lowering the pH of the solution. They attributed this large rate increase to the protons which were one of the reactants in the reduction rate. However, comparing Figures 5-4 and 5-5, it was found that when pH was changed from -0.62 to -0.81, the equilibrium Cr(VI) concentration changed from 35 mg/L to 20 mg/L. When temperature was changed from 50 °C to 70 °C, that concentration was decreased from 35 mg/L to 0 mg/L. Therefore, the temperature had more dramatic effect in the change of reduction reaction in our study.

The activation energy for this reaction could be calculated from the data on Figures 5-4 and 5-5. The effect of temperature on reaction rate is well presented in Arrhenius empirical rate law (Snoeyink and Jenkins, 1980),

$$k = Ae^{(-E_a/RT)} \quad \text{--- (5-1)}$$

where A: frequency factor, $E_a$: activation energy, $R$: ideal gas constant and $T$: temperature in °K. Equation 5-1 can be linearized as

$$\ln k = \ln A - E_a/(RT) \quad \text{--- (5-2)}$$

Thus, a plot of $\ln k$ versus $1/T$ should give a straight line with a slope of $-E_a/R$ and a intercept on the $1/T$ axis of
ln(A/(E_a/R)). From the calculation, activation energy at pH -0.81 was 17.61 Kcal/mole and at pH -0.62 was 15.12 Kcal/mole. These values imply that the temperature dependence of reduction at lower pH is greater than that at higher pH. These values are comparable to 13.9 Kcal/mole of activation energy for the reduction of Cr(VI) by fulvic acid at pH 5.5 obtained by Amacher and Baker (1982).

Figures 5-6 and 5-7 show the effect of chloride ion on reduction of Cr(VI) to Cr(III). In this experiment, possible reducing agents are only chloride and soil organic materials. The shale from a disposal well in St. Charles Parish contained 1.3 % (w/w) of soil organic materials. In Figure 5-6, at any concentration of NaCl, equilibrium was reached in 100 hours and never yielded 100 % reduction at 50°C. When no NaCl was added, soil organic materials were the only reducing agents for Cr(VI), resulting in about 40 % of the Cr(VI) being reduced. Increased Cr(VI) reduction to about 50 % of Cr(VI) was independent of NaCl amount added. From this result, it is concluded that the reduction rate is not a function of the NaCl amount added. This result contradicts that of Mayer and Shick (1981). They found that Cr(VI) reduced from a 1 μM Cr(VI) solution by a 20 μM gallic acid solution was a function of salinity. However, they believed that Cr(III) reduced from Cr(VI) would become rapidly adsorbed by suspended sediments and this adsorption which was affected by the salinity would control the reduction rate of Cr(VI). pH range in our study
Figure 5-6: NaCl Effect on Reduction at 50 °C

Formation: Shale
pH: 0.0

Cr(VI) in Solution (mg/L) vs. Time (Hour)
was far less than pH 2, and consequently no adsorption was possible. No adsorption at pH 0.0 or less is due to the formation of chromic acid, $\text{H}_2\text{CrO}_4$, which is predominant below pH 1.5 and is not readily adsorbed (Griffin et al., 1977).

The NaCl effect experiment was repeated at higher temperature (70 °C). The results are shown in Figure 5-7. Equilibrium was reached in 60 hours. However, in contrast to the experiment performed at 50 °C, 100 % reduction occurred in the absence of NaCl and only 70 % reduction occurred when 0.26 M of NaCl was added. It resulted from the hindrance of chloride ion on the reduction of Cr(VI) to Cr(III) by the soil organic materials. As the temperature increased, the reactivity of chloride ion as a reducing agent became predominant in the solution and the chloride ion controlled the reaction rate of reduction. If it is assumed that chloride ion and soil organic materials work independently of each other, the reduction with the addition of NaCl should be larger than that without NaCl as in Figure 5-6. Therefore, at low temperatures, both soil organic materials and chloride ion were active for the reduction of Cr(VI) and at high temperatures, the reactivity of chloride ion was greater than that of soil organic materials.

Figures 5-8 and 5-9 show the effect of pH on reduction kinetics. In the figures, when pH was 2, the reduction was less than 10 % and was slightly increased when chloride ion was added. However, it was still less than 10 % and the time
Fig. 5-8: pH Effect on Reduction without NaCl

Cr(VI) in Solution (mg/L)

Formation: Sand
Temp.: 50 °C
Fig. 5-9: pH Effect on Reduction with NaCl

Cr(VI) in Solution (mg/L)

Formation: Sand
Temp: 50 °C

Time (Hour)
to reach equilibrium was not changed. Even though the pH was decreased, the time to reach equilibrium did not change significantly. James and Bartlett (1983b) observed that the reduction of Cr(VI) increased as pH decreased. This is shown in Figure 5-8 when pH changes from 2 to 0 and finally to -0.62. Considering the curves at pH -0.81 and pH -0.62, it was postulated that once the pH was lower than a certain value, -0.62 here, the reduction rate by soil organic materials was no longer changed with pH. In Figure 5-9, when NaCl was added, the contribution of NaCl to the reduction of Cr(VI) was very much sensitive to pH. At pH -0.62, the reduction was equilibrated at about 40 mg/L of Cr(VI) and at pH -0.81, about 20 mg/L. Thus, pH change resulted in 20% increase in the reduction of Cr(VI). In Figures 5-8 and 5-9, the reduction rate was determined to be first order, in which the reaction was a function of Cr(VI) amount remaining in the solution. The reduction rate coefficient 'k' and the correlation coefficient 'r^2' were calculated and are shown in Table 5-2. The r^2 values in Table 5-2 support the first order reaction. Amacher and Baker (1982) studied Cr(VI) reduction at the pH range of 1.0 to 5.5, and in all cases, the reduction rate was first order. Their findings support our results. In their study, when pH was changed from 5.5 to 1.0, the reaction rate was increased 100 times in magnitude from 0.037 day^{-1} to 0.15 hr^{-1}. Meanwhile, in our study, when pH was changed from 2 to -0.81, the reduction rate was increased approximately 20 times in
Table 5-2: $k$ and $r^2$ Values at Different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>$k$ (sec$^{-1}$)</th>
<th>$r^2$</th>
<th>$k$ (sec$^{-1}$)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.81</td>
<td>$3.1 \times 10^{-3}$</td>
<td>0.84</td>
<td>$7.2 \times 10^{-3}$</td>
<td>0.82</td>
</tr>
<tr>
<td>-0.62</td>
<td>$2.6 \times 10^{-3}$</td>
<td>0.79</td>
<td>$4.6 \times 10^{-3}$</td>
<td>0.85</td>
</tr>
<tr>
<td>0.0</td>
<td>$1.9 \times 10^{-3}$</td>
<td>0.79</td>
<td>$2.6 \times 10^{-3}$</td>
<td>0.85</td>
</tr>
<tr>
<td>2.0</td>
<td>$1.7 \times 10^{-3}$</td>
<td>0.82</td>
<td>$2.8 \times 10^{-4}$</td>
<td>0.87</td>
</tr>
</tbody>
</table>
magnitude. Our study showed a change 5 times lower in the reduction rate. This results from the fact that their study was performed at high pH ranges where the reduction rate was more sensitive.

Figure 5-10 shows the linearity of the reduction reaction at different pH values. When the reaction is first order, the plot of log Cr(VI) concentration versus time shows a linear relationship. At low pH values (less than 0), the correlation coefficient, $r^2$, was higher than 0.9 and at relatively high pH such as 2, the $r^2$ was slightly less than 0.9. Therefore, overall reaction rate can be concluded to be first order over the pH values examined here. Though the equilibrium Cr(VI) concentration at different pH was not shown on Figure 5-10, it is important to note that not all reactions showed a 100 % reduction (some reactions showed less than a 10 % reduction).

5.4 CONCLUSIONS

When temperature is moderate, such as 50 °C, both soil organic materials and chloride ion contribute to the reduction of Cr(VI). However as the temperature increases, the reactivity of chloride ion for Cr(VI) reduction becomes predominant, and chloride ion controls the reduction rate, which is slower than that by soil organic materials. Temperature affects both time and extent of the reduction. When temperature is high enough, such as 70 °C, 100 % reduction happens in just half the time of reduction at 50 °C.
Fig. 5-10: Linear Regression for Sand Formation at 70 °C

Cr(VI) in Solution (mg/L) vs. Time (Hour)

- pH: -0.81, $r^2 = 0.85$
- pH: -0.62, $r^2 = 0.95$
- pH: 0.0, $r^2 = 0.91$
- pH: 2.0, $r^2 = 0.99$
- NaCl: 0 M
Using the Arrehnius' Law, the activation energy can be calculated, when the reduction rate constants are determined at more than two different temperature.

As the pH decreases, more Cr(VI) is reduced from the soil solution. However, 100% reduction is not obtained at low temperatures, no matter what pH the deep well injection zones commonly have. In the pH range of this study, all the reduction reactions were found to be first order.

When no chloride ion is present, the amount of soil organic materials plays an important role in the reduction of Cr(VI). When the soil organic materials increase from one to another injection zone formation material, the reaction time is reduced and the rate constant also increases. However, when chloride ion is present, the role of soil organic materials is suppressed by chloride ion and this ion controls the reduction rate.
REFERENCES


CHAPTER 6
Transport Simulation

6.1 INTRODUCTION

Problems of solute transport through aquifers subject to wastewater injection have been extensively studied and a number of solutions have been obtained in terms of analytical functions (analytical solutions). Tang and Babu (1979) gave exact solutions in integral forms to radial dispersion in a diverging flow field caused by a single injection well. They also developed an approximate solution producing satisfactory results only for relatively large time periods. Al-Niami and Rushton (1978) presented analytical expressions for dispersion toward an extraction well using a constant dispersion coefficient even for the converging flow condition. Both solutions are based on the common assumption that the aquifer being considered does not allow any leakage of contaminants into adjacent strata.

In field conditions, however, many aquifers are surrounded by formations that are not completely impervious. In this system, solute can be transmitted into those strata as well as through the aquifer. For the cases of uniform groundwater flow fields, Tang et al. (1981), Sudicky and Frind (1982), and Rasmuson (1984) gave transient and steady state analytical solutions for various conditions.

Analytical solutions for radial flow problems were given
by Stan Feenstra et al. (1984), who neglected longitudinal dispersion, and by Chen (1985), who included longitudinal dispersion. However, both did not consider the adsorption and the chemical reactions of solutes. By examining the analytical solution given by Tang and Babu (1979), it becomes clear that the solution contains rather complicated functions which are difficult to evaluate. Their solution was developed for a radial flow in a completely confined aquifer using the Laplace transform, and involves three consecutive integrals in each of which the integrand consists of a number of different Bessel functions of order of 1/3.

Because of this difficulty, the applicability of exact inversion of the Laplace transform is limited. In this situation, often an approximate solution was obtained with some form of numerical inversion of the transform solution. A numerical method presented in the form of an algorithm by Stehfest (1970), is extremely simple to use and requires relatively little computation. Moench and Ogata (1981) have successfully applied this technique. The computations were carried out using double precision for all real numbers. They reported the limiting factor in the accuracy of the mathematical results, which is the number of significant figures that the computer is capable of holding. Applying Stehfest's method, they used N=18, which yielded maximum accuracy. Theoretically, the accuracy can always be improved by increasing N. However, roundoff error limits the value of
N that can be used. They calculated the results which agreed closely with Hoopes and Harleman, who presented the numerical solution to this same problem using a finite difference method.

6.2 Approximate Solution

The development of a solute transport model described in eq.s 6-1 and 6-2 below uses the following assumptions: (1) Sand aquifer is horizontally located between the shale aquitards with a uniform width; that is, overburden pressure or the injected wastewater pressure does not close or widen the width. (2) A constant flow rate 'Q' is discharged into the sand aquifer from an injection well with a radius of r_sorted. (3) Wastes are transported through the sand aquifer by radial advection and longitudinal dispersion; the molecular diffusion is neglected (Fig. 6-1). (4) Wastes are transported into the shale aquitard by molecular diffusion. (5) These transports through the sand aquifer and within the shale aquitard are retarded by adsorption and reduction (Chen, 1986).

The governing equations are given as follows:
\[
D_m \frac{\partial^2 C_2}{\partial x^2} - \lambda_2 R_2 C_2 = R_2 \frac{\partial C_2}{\partial t} \quad -(6-1)
\]

\[
\frac{dA}{r} \frac{\partial^2 C_1}{\partial r^2} - \frac{A}{r} \frac{\partial C_1}{\partial r} + \frac{n_2 D_m}{b} \frac{\partial C_2}{\partial x} \bigg|_{x=0} - \lambda_1 R_1 C_1 = R_1 \frac{\partial C_1}{\partial t} \quad -(6-2)
\]

where \( R_1 \) and \( R_2 \) are the retardation factors. The initial and
Figure 6-1: Schematic Diagram of Cr(VI) Transport in Deep Well Disposal Zone
boundary conditions are given as follows:

I.C. \( C_1(r, 0) = C_2(x, 0) = 0 \) \( --(6-3) \)

B.C. No. 1: \( C_1(\infty, t) = C_2(\infty, t) = 0 \) \( --(6-4) \)

B.C. No. 2: \( C_1(r, t) = C_2(0, t) \) \( --(6-5) \)

B.C. No. 3 \( C_1(r_o, t) = 1 \) \( --(6-6) \)

The initial condition states that no wastes exist in the shale aquitard and in the sand aquifer prior to injection. The boundary condition for 'r' and 'x' of infinity is given by eq. 6-4. Eq. 6-5 describes the condition of continuity of wastes concentration at the interface of the sand aquifer and the shale aquitard. The concentration of wastes at the injection well bore remains constant (eq. 6-6).

Writing eq.s 6-1 through 6-6 in dimensionless form yields

\[
\frac{\partial^2 C_2}{\partial \xi^2} - \alpha_2 C_2 = \frac{\partial C_2}{\partial \tau} \quad --(6-7)
\]

\[
\frac{1}{\rho} \frac{\partial x^2 C_1}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial C_1}{\partial \rho} + \alpha \frac{\partial C_2}{\partial \xi} \bigg|_{\xi = 0} - \alpha_1 C_1 = \frac{\partial C_1}{\partial \tau} \quad --(6-8)
\]

\( C_1(\rho, 0) = C_2(\xi, 0) = 0 \) \( --(6-9) \)

\( C_1(\rho, \tau) = C_2(0, \tau) \) \( --(6-10) \)

\( C_1(\infty, \tau) = C_2(\infty, \tau) = 0 \) \( --(6-11) \)

\( C_1(\rho_o, \tau) = 1 \) \( --(6-12) \)

where \( \rho, \rho_o, \xi \) and \( \tau \) are the dimensionless terms for radial
distance, well radius, vertical distance, and time respectively.

Applying the Laplace transformation with respect to \( \tau \) to eq.s 6-7 through 6-12 results in

\[
\frac{d^2 P_2}{d \xi^2} - (\phi + \alpha_2) P_2 = 0 \quad (6-13)
\]

\[
\frac{1}{\rho} \frac{d^2 P_1}{d \rho^2} - \frac{1}{\rho} \frac{d P_1}{d \rho} + \alpha \frac{d P_2}{d \xi} \bigg|_{\xi=0} - (\phi + \alpha_1) P_1 = 0 \quad (6-14)
\]

with

\[
P_1(\rho, \phi) = P_2(\xi, \phi) = 0 \quad (6-15)
\]

\[
P_1(\infty, \phi) = P_2(\infty, \phi) = 0 \quad (6-16)
\]

\[
P_1(\rho, \phi) = P_2(0, \phi) \quad (6-17)
\]

and

\[
P_1(\rho_0, \phi) = \frac{1}{\rho} \quad (6-18)
\]

where

\[
P_1(\rho, \phi) = \int_0^\infty e^{-\rho \tau} C_1(\phi, \tau) \, d\tau
\]

\[
P_2(\xi, \phi) = \int_0^\infty e^{-\phi \tau} C_2(\xi, \tau) \, d\tau
\]

The solution of eq. 6-13 subject to eq.s 6-16 and 6-17 is

\[
G_2(\xi, \phi) = G_1 \exp\left(-\xi (\phi + \alpha_2)^{\frac{1}{2}}\right) \quad (6-19)
\]

From eq.6-19, \( \frac{d G_2}{d \xi} = - (\phi + \alpha_2)^{\frac{1}{2}} \) at \( \xi = 0 \) \quad (6-20)

Inserting eq. 6-20 to eq. 6-14 and rearranging the terms, eq.
\[ \frac{1}{\rho} \frac{d^2 G_1}{d \rho^2} - \frac{1}{\rho} \frac{d G_1}{d \rho} - (\rho + \alpha_2) \frac{1}{2} \alpha + \rho + \alpha_1) G_1 = 0 \quad --(6-21) \]

The solution of eq. 6-21 satisfying the conditions of eq.s 6-17 and 6-18 is,

\[ G_1 = \frac{1}{\rho} \exp \left( \frac{\rho - \rho_0}{2} \right) \frac{Ai(\beta^{\frac{1}{3}} y)}{Ai(\beta^{\frac{1}{3}} y_0)} \quad --(6-22) \]

Then, from eq.s 6-19 and 6-22, the solution for \( P_2 \) is

\[ G_2 = \frac{1}{\rho} \exp \left( \frac{\rho - \rho_0}{2} \right) \frac{Ai(\beta^{\frac{1}{3}} y)}{Ai(\beta^{\frac{1}{3}} y_0)} \exp \left( -\xi (\rho + \alpha_2) \frac{1}{2} \right) \quad --(6-23) \]

Using the Stehfest's method, eq.s 6-22 and 6-23 are inverted as follows:

\[ C_1 = \frac{\ln 2}{\tau} \sum_{i=1}^{N} V_i G_1 \left( \frac{\ln 2}{\tau} i \right) \quad --(6-24) \]

\[ C_2 = \frac{\ln 2}{\tau} \sum_{i=1}^{N} V_i G_2 \left( \frac{\ln 2}{\tau} i \right) \quad --(6-25) \]

The computation of the Airy functions in eq.s 6-22 and 6-23 is performed by converting them into appropriate Bessel function \( K_{\frac{1}{3}}(x) \), using the identity (Abramowitz and Stegun, 1970).

\[ Ai(x) = \frac{1}{\pi} \left( \frac{x}{3} \right)^{\frac{1}{2}} K_{\frac{1}{3}} \left( \frac{2}{3} x^{\frac{3}{2}} \right) \quad --(6-26) \]

\( K_{\frac{1}{3}}(x) \) is computed with MMBSK subroutine of the International
Mathematics and Statistics Library (1982). Subroutine MMBSKR is fully detailed in Appendix B. The weighing coefficients, \( V_1 \), are determined by selecting \( N = 18 \). Double precision is used for all computations.

6.3 Model Application

The approximate solution techniques presented in the previous section have been employed as the basis for calculating the mass transfer phenomena. Specific relationship to describe the influences of temperature and pH on the adsorption and reduction processes are described below. Salinity is omitted since its influences was found to be minor, the effects of organics on chromium adsorption and reduction were also omitted to lack of development of fundamental relationship.

From the results of adsorption study in Chapter III, it was found that the adsorption of Cr(VI) to clay and shale followed the Langmuir equilibrium isotherm. When the Langmuir isotherm is involved in the waste transport model, the retardation factor is not constant as in the Linear equilibrium isotherm but a function of waste concentration. Then the solute transport model becomes complicated and the eq.s 6-23 and 6-24 are no longer the solutions for this model. However, simple assumption and modification of the Langmuir isotherm equation makes the current transport model feasible and eq.s 6-23 and 6-24 can still be the solutions of this
The Langmuir isotherm is commonly written as

\[ S = \frac{abC}{1 + aC} \quad (6-27) \]

where \( S \): concentration of solute adsorbed, \( C \): concentration of solute remaining in solution after equilibrium, \( a \) and \( b \): constants. In case when 'aC' in denominator is much less than 1, eq. 6-27 reduced to \( S = abC \), which is the same as linear isotherm. Then 'ab' becomes \( K_d \) in eq.s 6-1 and 6-2. In case when 'aC' is larger than 1 in the denominator, eq. 6-27 reduced to \( S = b \) and \( K_d \) becomes zero. Then the retardation factor 'R' in the transport model remains as 1. Therefore, in either case, retardation factor 'R' remains constant and we can adopt the Langmuir isotherm without altering anything from the Cr(VI) transport model described previously. The critical concentration where \( K_d \) is zero or a certain constant can be determined graphically as shown in Figure 6-2. The values of critical concentration and \( K_d \) were found to be a function of temperature at pH 2. For shale, the critical concentration was 32, 26, and 22 mg/L for 23 °C, 50 °C, and 70 °C respectively. Then the linear regression analysis for the relationship between concentration and temperature yielded

\[ C_c = 36.83 - 0.213^\times(T) : r^2 = 0.99 \quad (6-28) \]

where \( C_c \): critical concentration \( T \): temperature in °C. The \( K_d \) value was found to be 14.69, 11.15, and 8.18 cm³/g for 23°C, 50 °C, and 70 °C respectively. Again, the linear regression
Figure 6–2: Simplified Langmuir Isotherm
analysis for the relationship between $K_d$ and temperature yielded

$$K_d = 17.92 - 0.138*(T) : r^2 = 0.98 --- (6-29)$$

These values were utilized in the main computer program, where the initial retardation factor was zero at the adsorption aspect, because the initial concentration was higher than $C_c$. However when the concentration in shale aquitard or sand aquifer became below $C_c$, the retardation factor calculated using eq 6-29 was substituted for the value of zero in retardation factor. Since no adsorption was found in shale and sand below pH 2.0, the retardation factor was set to zero during the entire injection event.

Depending on the temperature and pH, 100 % or only a partial reduction occurs. When a partial reduction occurs, the equilibrium concentration of wastes becomes more important than the reduction kinetic coefficient, and equilibrium approach ($S = aC$) for the reduction term in the governing equations substitutes for the kinetic approach. In this case, $S$ is equal to $aC$, and $\partial S/\partial t$ becomes $a*\partial C/\partial t$, where $S$ is the concentration of Cr(III), reduced from Cr(VI). Thus, the constant 'a' is added to the retardation factor and the reduction kinetic coefficient can be put zero. At 50 °C, over the pH range 2 to -0.81, all the reduction observations for shale were not 100 %, but partial. The equilibrium concentration ($C$) was found to be 15.21, 32.0, 45.87, and 92.35 mg/L for -0.81, -0.62, 0.0, and 2.0 respectively.
Utilizing the multi-regression analysis, the relationship between $C$ and $[H^+]$ were calculated as
\[ C = 92.99 - 64.28[H^+] + 18.83[H^+]^2 - 1.669[H^+]^3 : r^2 = 1.0 \]
For sand, the equilibrium concentration 'C' was found to be 19.53, 37.35, 49.88 and 96.15 mg/L for pH -0.81, -0.62, 0.0, and 2.0 respectively, and the relationship was
\[ C = 96.79 - 64.26[H^+] + 19.05[H^+]^2 - 1.669[H^+]^3 : r^2 = 1.0 \]
Then $S$ at any pH was calculated from $S = 100 - C$, and thus 'a' became $(100 - C)/C$.

When the temperature was 70 °C, at pH values of 0.0 and 2.0, the reduction in both shale and sand showed partial reduction. At pH 0.0, 'a' was found to be 1.778 and 1.381 for shale and sand respectively. In the main computer program, this 'a' value was added to the retardation factor, because the Cr(III) reduced from Cr(VI) in solution contributes to the attenuation of Cr(VI) in solution such as Cr(VI) adsorbed on the surface of shale and sand.

Diffusion was neglected in the sand aquifer, but was considered in shale aquifer as a transport mechanism of Cr(VI) in solution. Diffusion rate also is a function of temperature. The relationship between diffusion coefficient and temperature was described as
\[ D = -3.5615 \times 10^{-7} + 2.101 \times 10^{-8}(T) : r^2 = 0.87 \]
Thus, the diffusion coefficient at any temperature can be incorporated into the governing equation of transport in shale aquitard.
6.4 Transport Simulation

An imaginary deep well disposal system was used for the simulation, and has the following characteristics:

- Sand aquifer thickness: 30 m
- Porosity of sand aquifer: 0.3
- Porosity of Shale aquitard: 0.1
- Cr(VI) wastes concentration: 100 mg/L of Cr(VI)
- Injection rate: 0.007 m³/min (2 gal/min)
- Injection wastes: Cr(VI) containing acid brine
- Liquid pH: various from 2 to -0.82
- Injection period: various from 50 to 500 years
- Well radius: 0.15 m
- Dispersivity: 0.7 m

Some of the information given above is taken from Aubert (1986), and represent typical injection well characteristics. Injection rate is based on 2 million gallons of Cr(VI) wastes injected in 1983 at two different commercial wells (Jacobus et al., 1985). The pH values are reported to be typical of many injection fluids (Fink, 1986). Computer program for the simulation is shown in Appendix C.

Figure 6-3 shows a plot of dimensionless Cr(VI) concentration versus dimensionless radial distance from the center of the injection well bore. The individual curves on the plot represent time elapsed after the commencement of injection, ranging from 50 to 500 years. The pH of the liquid waste was assumed to be -0.62 and the temperature was 50 °C.
Figure 6-3: Chromium(VI) Transport Through Sand Layer at Various Time
For this simulation, the retardation factor was calculated as 2.677 for sand aquifer, and no adsorption was possible at pH - 0.62. The partial reduction of Cr(VI) at 50 °C resulted in an increase of 'R' by 1.677. When the injection period was 500 years, the concentration became less than 0.99 of the initial concentration at the dimensionless distance of 60.3, which is equivalent to 86.1 m, it became 0.5 of the initial concentration at 76.3 (109 m), and it became less than 0.01 of the initial concentration at the distance of 90.3 (129 m). Table 6-1 shows the distance for the 0.99, 0.5, and 0.01 of the initial concentration at various time periods.

The effect of temperature is demonstrated in Figure 6-4, where the transport of Cr(VI) wastes in sand aquifer at 50 °C and 70 °C is shown. Figure 6-4 is for 100 years of continuous injection at pH -0.62. When the temperature was 70 °C, no adsorption was possible and reduction was 100 % at this pH. Thus, at 70 °C, the reduction kinetic coefficient was adopted, and was found to be 5.8*10^{-6} Sec^{-1} at the sand aquifer. When the temperature was 50 °C, due to the partial reduction, retardation factor became 2.5 in sand aquifer. This factor is determined based on the reduction equilibrium coefficient.

From the Figure 6-4, it was found that even after 100 years injection of wastes, the front of the wastes advanced only 1.9 (2.7 m) of horizontal distance from the well bore, when the temperature was 70 °C. In case of 50 °C, the front advanced to 46.1 m and the concentration of Cr(VI) became less
Table 6-1: Horizontal Distance for Various Cr(VI) Concentration in Sand Aquifer

<table>
<thead>
<tr>
<th>Dimensionless Concentration</th>
<th>Injection</th>
<th>500 Years</th>
<th>250 Years</th>
<th>100 Years</th>
<th>50 Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection</td>
<td>0.99</td>
<td>0.5</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 Years</td>
<td>86.57 m</td>
<td>109 m</td>
<td>129 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 Years</td>
<td>56.14 m</td>
<td>76.14 m</td>
<td>93.29 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 Years</td>
<td>30.43 m</td>
<td>47.57 m</td>
<td>61.86 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 Years</td>
<td>19 m</td>
<td>33.28 m</td>
<td>44.71 m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6-4: Chromium(VI) Transport Through Sand Layer, when pH: -0.62
than 0.99 of the initial concentration after 14.3 m from the well bore. Figure 6-4 explains the significant difference in the attenuation of Cr(VI) front from the wastewater between 100 % reduction and partial reduction.

Figure 6-5 shows the similar effect when the pH was -0.81. At the temperature of 70 °C, the reduction kinetic coefficient was found to be $9.5 \times 10^{-6}$ sec$^{-1}$ in sand aquifer. No adsorption was possible at this pH either. When the temperature was 50 °C, the reduction equilibrium coefficient was used and the retardation factor in sand aquifer became 5.12. Comparing Figures 6-4 and 6-5, the front advanced 15.7 m more at pH -0.62 and temperature 50 °C. This was the result of the small retardation value at pH -0.62 (2.5 vs 5.12). When the temperature was 70 °C, the front advanced 0.6 m more at pH -0.62. This was resulted from the small value of the reduction kinetic coefficient at pH -0.62 ($5.8 \times 10^{-6}$ vs $9.5 \times 10^{-6}$ sec$^{-1}$).

Figure 6-6 shows the Cr(VI) transport in the sand aquifer when the pH was 0.0. At this pH, again no adsorption was possible and partial reduction occurred at 50 °C and 70 °C. The retardation factor became 2.396 and 2.005 at the temperature of 70 °C and 50 °C respectively. The difference of 0.391 in the retardation factor shows 5.7 m advance of the front after 100 years' injection. The 0.99 of the initial concentration appeared at the distance of 33 m and 29 m at the temperature of 50 °C and 70 °C respectively.

In Figure 6-7, the transport of Cr(VI) wastes at pH 2.0
Figure 6–5: Chromium(VI) Transport Through Sand Layer, when pH: −0.81
Figure 6-6: Chromium(VI) Transport Through Sand Layer, when pH: 0.0
Figure 6–7: Chromium(VI) Transport Through Sand Layer, when pH: 2.0
is presented. No significant difference between 50 °C and 70 °C was observed. The adsorption of Cr(VI) on sand was still not possible even at pH 2.0, and the retardation factor was 1.04 and 1.027 respectively for 50 °C and 70 °C. At 41.9 m, the 0.99 of the initial concentration was found and 0.01 of the initial concentration was at found 94.7 m.

Figure 6-8 shows the distribution of Cr(VI) wastes in shale aquitard after 50 years' injection. The pH was assumed to be -0.62, and temperature was 50 °C. Each curve in the Figure 6-8 represents dimensionless Cr(VI) concentration versus dimensionless vertical distance at horizontal distances from the well bore of 0.43, 6.1, 14.7, 20.4, 27.6, 34.7, and 41.9 m respectively. Even at the closest point from the well bore (0.4 m), the Cr(VI) concentration became lower than the Safe Drinking Water Act Limit (0.05 mg/L) after the vertical distance of 1.14 m from the interface of shale aquitard and sand aquifer. When the horizontal distance was 34.7 m from the well bore, Cr(VI) wastes were transported only 0.6 m vertical distance. As can be seen the farther the horizontal distance from the well bore, the less vertical distance Cr(VI) is transported.

Figures 6-9 and 6-10 show the vertical transport of Cr(VI) wastes for 100 years when pH was -0.81 and -0.62 respectively. The temperature affected the distribution of Cr(VI) wastes in shale aquitard significantly, similar to that found in the sand aquifer (cf. Figures 6-4 and 6-5). This is
Figure 6-8: Vertical Cr(VI) Transport Through Shale Layer After 50 Years
Figure 6–9: Vertical Cr(VI) Transport Through Shale Layer, when pH: −0.81
Figure 6-10: Vertical Cr(VI) Transport Through Shale Layer, when pH: -0.62
resulted from the 100% reduction at 70 °C and a partial reduction at 50°C over these pH range. When the pH was -0.81 at 70 °C, Cr(VI) wastes was transported 0.1 m and it became 0.11 m when the pH was -0.62. However, it was extended to 1.1 m and 1.7 m for pH -0.81 and -0.62 respectively at 50°C. The transport distance increased more than 10 times as the temperature decreased from 70°C to 50 °C.

In Figure 6-11, the vertical distance for the Cr(VI) concentration less than 0.05 mg/L was 3.6 m at 50 °C and 2.0 m at 70 °C. At the distance of 0.43 m from the well bore the 0.89 and 0.8 of the initial concentration was found at the temperature of 50 °C and 70 °C respectively. When pH was 0.0, no adsorption was possible in shale aquitard and partial reduction occurred at both 50 °C and 70 °C. The retardation factor became 2.18 and 2.786 for those temperature respectively, adopting the equilibrium reduction approach.

Figure 6-12 shows the vertical transport of Cr(VI) when the pH was 2.0. At pH 2.0, shale adsorbs Cr(VI) and follows the Langmuir isotherm. As explained in the previous section, the retardation factor was changed from 1.04 to 12.233 at 50 °C, and from 1.027 to 9.229 at 70 °C upon attaining the dimensionless critical concentration of 0.26 and 0.22 respectively. In Figure 6-12, both curves show a big change in slope at these concentrations. Due to this slope change, the vertical distance of the Cr(VI) transport decreased from 3.6 m to 2.3 m at 50 °C and also decreased from 2.0 m to 1.1
Figure 6-11: Vertical Cr(VI) Transport Through Shale Layer, when pH: 0.0
Figure 6-12: Vertical Cr(VI) Transport Through Shale Layer, when pH: 2.0
m at 70 °C, though the reduction at pH 2.0 was less than that at pH 0.0. Vertical transport of Cr(VI) in the shale aquitard at different temperature and pH are summarized in Table 6-2.

6.5 Conclusions

The transport of Cr(VI) wastes is closely related to the temperature and pH of the deep well disposal zones. The temperature and pH affect the attenuation mechanisms such as adsorption and reduction. They also affect the diffusion rate in the shale aquitard.

At the range of pH and temperature common in the typical deep well injection zone, the transport of Cr(VI) in both sand aquifer and shale aquitard was not far from the well bore even after 500 years injection. Especially, the vertical transport of Cr(VI) was extremely small due to the relatively fast adsorption and reduction rate as compared to diffusion rate. For example, even at pHs 0.0 and 2.0, the vertical transport was less than 4 m after 100 years injection. When pH was low such as -0.81 and -0.62, if the temperature was 70 °C, the horizontal transport was 1.9 m and 2.5 m respectively from the well bore, and the vertical transport was 0.1 m and 0.11 m respectively after 100 years injection. These values were increased to 46.1 m and 61.8 m in horizontal transport and was increased to 1.1 m and 1.7 m respectively in vertical transport at 50 °C. When pH was relatively high such as 0.0 or 2.0, the horizontal transport was not more than 33 m and 95
Table 6-2: Vertical Transport of Cr(VI) at various pH and Temperature in Shale Aquitard (100 Years Injection)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>pH</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-0.81</td>
<td>-0.62</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>50 °C</td>
<td>1.14 m</td>
<td>1.71 m</td>
<td>3.61 m</td>
<td>2.33 m</td>
</tr>
<tr>
<td>70 °C</td>
<td>0.1 m</td>
<td>0.114 m</td>
<td>2.04 m</td>
<td>1.14 m</td>
</tr>
</tbody>
</table>
m respectively even at 50 °C. Though the horizontal transport was larger at pH 0.0 as compared to that at pH 2.0, the vertical transport was smaller at pH 2.0 due to the adsorption of Cr(VI) on shale at pH 2.0. Therefore, lower pH and higher temperature is preferred for the prevention of Cr(VI) transport horizontally and vertically. Although the effect of the coinjected organic chemical compounds was not reflected in the transport simulation, it should be noted that their effect on the reduction was enormous depending on the chemical species.

From the results shown above, due to the favorable environmental conditions given to the injection zone, the Cr(VI) wastes can be confined in deep well injection zone safely without damaging the source of groundwater. Consequently, deep well injection practice is found to be a good technology to handle the wastes containing Cr(VI).
NOTATION

A: \( Q/(2\pi b) \) [m²/sec]  \hspace{1cm} b: half aquifer thickness [m]
C: concentration of solute [dimensionless]
d: dispersivity [m]  \hspace{1cm} Q: injection flow rate [m³/s]

\( D_m \): effective molecular diffusivity [m²/sec]

\( K_{1/3}(x) \): modified Bessel function of the second kind with order of 1/3

\( R_1, R_2 \): retardation factor [dimensionless]

r: radial distance from well bore [m]

\( r_o \): injection well radius [m]

P: Laplace transform of C with respect to \( \tau \)

x: vertical distance from the interface of aquifer and aquitard

\( y: \rho + (4\theta)^{-1} \)  \hspace{1cm} \( y_o: \rho_o + (4\theta)^{-1} \)

\[ a: (e_2/d) (R_2 D_m/(R_1 A))^\frac{1}{2} \]

\[ a_1: R_1 K_1 d^2/A \]
\[ a_2: R_2 K_2 d^2/A \]

\[ \beta: \rho + a_1 + \alpha (\rho + a_2)^\frac{1}{2} \]

\[ \xi: (x/d) (R_2 A/(R_1 D_m))^{\frac{1}{2}} \]

\( \rho_o: r_o/d \) dimensionless well radius
\( \rho : r/d \)  \textit{dimensionless radial distance}

\( \tau : At/(R_i d^2) \)  \textit{dimensionless time}

\( \varepsilon : \text{porosity} \)

\( \Phi : \text{Laplace transform parameter} \)
REFERENCES


CHAPTER 7
SUMMARY & CONCLUSIONS

The transport and fate of Cr(VI) in deep well disposal zones are quite dependent on the environmental factors such as pH, temperature, and co-injected organic chemicals in the liquid phase. In solid phase, soil bulk density, water content, type of clay and soil organic material play an important role for the attenuation and retardation of Cr(VI) wastes transport.

Cr(VI) showed increased adsorption in the presence of clays down to a pH of 2, after which the adsorption decreased. The adsorption by shale, which contained 30% Montmorillonite and 6% Illite, followed similar behavior as pure clays. However, the amount adsorbed on the shale was higher than pure Illite but less than pure Montmorillonite. At a pH lower than 0.0, no adsorption was found in shale solution, due to the preferential adsorption of bichromate ($\text{HCrO}_4^-$) and lack of adsorption of chromic acid ($\text{H}_2\text{CrO}_4$).

The adsorption and reduction of Cr(VI) in the confining shale were well represented by the pure clay studies. The shale studies indicated little adsorption at a pH of 2 and no adsorption below pH 0.0. Reduction was also similar to that found in the clay studies, increasing continuously with decreasing pH. Reduction in the presence of two pure clays, Na-Montmorillonite and Na-Illite, increased with decreasing pH.
down to a pH of 2; no reduction was apparent in the presence of Kaolinite. The shale showed increasing reduction with decreasing pH to a pH of -0.81, the limit of this study. Sandstone did not adsorb any Cr(VI) from the solution at any pH.

In the shale, as the temperature increased, the adsorption of Cr(VI) decreased, but the reduction and diffusion rate increased. The adsorption of Cr(VI) on clay and shale was an exothermic reaction and followed the Langmuir isotherm. In the study of transport, the Langmuir isotherm was simplified to yield a constant $K_d$ value, which produced constant retardation factor 'R'. Using a constant R, the model could be solved numerically using approximate inverse Laplace transform.

When temperature was 50 °C, both soil organic material and chloride ion contributed to the reduction of Cr(VI). However as the temperature increased, the reduction rate was controlled only by the chloride ion. Depending on the temperature, partial and complete reduction was possible, and the complete reduction showed a significant effect on the transport of Cr(VI), as compared to the partial reduction.

The temperature also affected the diffusion rate. The activation energy calculated by applying Arrehnius' equation illustrated the greater difficulty of diffusion in porous media than in free aqueous solution. Though high temperature increased the diffusion rate, higher temperature was preferred
for reduction which would overall retard the transport of Cr(VI) in deep well disposal zone.

The concentration of chloride ion did not significantly affect the adsorption and diffusion of Cr(VI). The amount of Cr(VI) reduced was not dependent on the chloride ion added. The influence of NaCl was therefore ignored in the transport simulation.

The types of organic chemicals co-injected are very important. 100 % reduction in 48 hours was observed from the aromatic compound, NN Dimethyl-aniline, which had largest reduction capacity among the organic chemicals investigated. In contrast, the alkane series compound, Ethylene-dichloride showed no reduction even at high temperature (70 °C).

Soil bulk density and water content affected the diffusion rate of Cr(VI) in sand pores and shale pores, respectively. Due to the tortuosity, the increase in bulk density provided lower diffusion rate in sand pores. Likewise, as the water content increased, the diffusion rate increased in shale pores. Though the bulk density affected the diffusion in the sand aquifer, the advection and dispersion were much greater than diffusion. Thus, the bulk density effect could be ignored in the transport simulation.

The results from the transport simulation showed the excellent capability of Cr(VI) confinement and removal in the deep well disposal zone. The Cr(VI) waste was transported only 0.4 m into the shale confining layers even after 100 years in
the worst environmental condition. When the temperature was 70 °C and pH was less than 0.0, the vertical transport was less than 0.2 m. Consequently, the higher temperature and low pH common in deep well disposal zones provided good removal conditions for Cr(VI) wastes injected and justify the deep well disposal practice as a viable technology to handle the wastes containing Cr(VI).
THE RECOMMENDATIONS

The recommendations of this research for future study are summarized as:

1. Even though many investigators simplify the retardation factor with the assumption of linear equilibrium isotherm, which makes the retardation constant and the transport model simple, the adsorption process which follows the Freundlich isotherm should be studied. When the Freundlich isotherm is adopted in the transport model for the reflection of retardation factor, the retardation factor is no longer constant but depends on the concentration of the compounds injected. In this case, the transport model becomes quite different from that with the linear equilibrium isotherm assumption.

2. The kinetic approach of the adsorption process should be studied and be compared to the equilibrium approach, because some adsorption processes take a long period of time depending on the chemical compounds. In such cases, local equilibrium assumptions may lead to erroneous results in chemical compound transport.

3. The reduction kinetics and equilibria of Cr(VI) by the oxidation of various organic chemical compounds should be studied and be reflected in the transport model.
(4) Diffusion studies at various pH are required. The physical and chemical characteristics of the shale and sand can be altered by various pH. This can result in different diffusion rate.

(5) Small bench scale experiments should be set up for the verification of the transport simulations.
Appendix A
Langmuir Isotherm for Na-Montmorillonite
Langmuir Isotherm for Na-Illite

Temperature (°C)
- - - 23
- - - 50
- - - 70
Langmuir Isotherm for Na-Kaolinite

Temperature (°C) → 23 → 50 → 70
Appendix B
IMSL ROUTINE NAME - MMBSKR

PURPOSE - MODIFIED BESSEL FUNCTION OF THE SECOND KIND OF NONNEGATIVE REAL FRACTIONAL ORDER FOR REAL POSITIVE ARGUMENTS SCALED BY EXP(ARG)

USAGE - CALL MMBSKR (ARG, ORDER, N , BK, IER)

ARGUMENTS

ARG - INPUT ARGUMENT. ARG MUST BE TYPED APPROPRIATELY IN THE CALLING PROGRAM. (SEE THE PRECISION/HARDWARE SECTION.) ARG MUST BE GREATER THAN ZERO.

ORDER - INPUT VALUE SPECIFYING THE DESIRED ORDER OF THE BESSEL FUNCTION. ORDER MUST BE TYPED APPROPRIATELY IN THE CALLING PROGRAM. (SEE THE PRECISION/HARDWARE SECTION.) ORDER MUST BE GREATER THAN OR EQUAL TO ZERO.

N - INPUT PARAMETER SPECIFYING THE NUMBER OF FUNCTION VALUES TO BE COMPUTED.

BK - OUTPUT VECTOR OF LENGTH N CONTAINING THE COMPUTED FUNCTION VALUES. BK MUST BE TYPED APPROPRIATELY IN THE CALLING PROGRAM. (SEE THE PRECISION/HARDWARE SECTION.) BK(1) WILL CONTAIN THE COMPUTED VALUE FOR THE INPUT ORDER, BK(2) WILL CONTAIN THE COMPUTED FUNCTION VALUE FOR ORDER + 1, BK(3) FOR ORDER + 2, ETC.

IER - ERROR PARAMETER. (OUTPUT)

TERMINAL ERROR

IER = 129 INDICATES THAT ONE OR MORE OF THE INPUT ARGUMENTS, ARG, ORDER, OR N IS OUT OF RANGE. BK(I), I=1,N, IS SET TO MACHINE INFINITY.

IER = 130 INDICATES THAT BK(1) IS GREATER THAN MACHINE INFINITY. BK(I), I=1,N, IS SET TO MACHINE INFINITY.

IER = 131 INDICATES THAT BK(N)/BK(N-1) IS GREATER THAN MACHINE INFINITY, BUT THAT BK(1) IS COMPUTED CORRECTLY. BK(I), I=2,N, IS SET TO MACHINE INFINITY.

IER = 131+J INDICATES THAT BK(J) WOULD HAVE BEEN GREATER THAN MACHINE INFINITY. BK(I), I=J-1,N, IS SET TO MACHINE INFINITY. BK(L), L=1,J-1, IS COMPUTED CORRECTLY.

PRECISION/HARDWARE - DOUBLE/H32,H36 - SINGLE/H48,H60

REQD. IMSL ROUTINES - UERST,UGETIO

NOTATION - INFORMATION ON SPECIAL NOTATION AND CONVENTIONS IS AVAILABLE IN THE MANUAL INTRODUCTION OR THROUGH IMSL ROUTINE UHELP

June, 1982
Algorithm

For $x=\text{ARG}$ and $v=\text{ORDER}$, MMBSKR computes approximate values of $E^v(x)\equiv K_{v+n}(x)$ for $n=0,1,\ldots,N-1$, where $K_{v+n}(x)$ is the modified Bessel function of the second kind of order $v+n$, $v$ is nonnegative and $x$ is positive.

MMBSKR first generates starting values $K_{v+1}(x)$ where $-5 \leq v < 5$. Then the forward recurrence relation

$$K_{v+1}(x) = \frac{2v}{x} K_v(x) + K_{v-1}(x)$$

is used to generate the sequence of modified Bessel functions.

Backward recursion is used for values of $x$ greater than 4, and the Wronskian relation involving the modified Bessel functions of the first kind is used for $x$ between 1 and 4. Miller’s algorithm is used to compute the values of the modified Bessels of the first kind.

MMBSKR is based on a code by J.B. Campbell which uses Temme’s algorithm for the modified Bessel function. Computations are constrained so as not to yield results greater than $10^{75}$, even though on some computers the “machine infinity” is greater than this.

See references:


Example

This example illustrates the use of a single precision version of MMBSKR.

Input:

```fortran
INTEGER N,IER
REAL ARG,ORDER,BK(6)
ARG = 2.
ORDER = 0.5
N = 6
CALL MMBSKR(ARG,ORDER,N,BK,IER)
```

Output:

```fortran
BK(1) = .8862269255
BK(2) = 1.329340388
BK(3) = 2.880237508
BK(4) = 8.529934157
BK(5) = 32.73500706
BK(6) = 155.8374659
IER = 0
```

MMBSKR-2 June, 1982
Appendix C
**LAPLACE TRANSFORM INVERSION FOR RADIAL DISPERSION**

**TIME**: 500 YR  **FIG. 1**

**RHO**: DIMENSIONLESS RADIAL DISTANCE  **RHOO**: DIMENSIONLESS WELL RADIUS  **TAU**: DIMENSIONLESS TIME AT WHICH INVERSION VALUE IS WANTED

**N**: AN EVEN NUMBER THAT GOVERNS ACCURACY OF THE INVERSION

**R1, R2**: RETARDATION FACTOR  **ALAMB**: REDUCTION RATE COEFFICIENT  **DM2**: DIFFUSION COEFFICIENT IN AQUITARD  **DISP**: DISPERSIVITY  **TAU= 3000**: TEMP= 50 C.  **DISP= 0.7, ALAMB= 0.0**

**BHO<  1)= 0.0**  **BHO<J)=BHO(J-1)+0.1**

**DD= 0.5D0**  **ETHA= BHO(J)**

**W RITE**: *(6,*) BHO(J), ETHA **XPONE= 0.0**  **XPTWO= 0.0**
ZERO=0. DO
  DO 30 I=1,N
  PP=XLN2*/TAU
  VALUE= (-ETHA*DSGRTIPP+ALPHA2))
  ZETA=PP+ALPHA1+ALPHA2
  ZETA0=ZETA**ORDER
  CALL MMBSKR(ZETA,ORDER,1.BK,IER)
  CALL MMBSKR(ZETA0,ORDER,1.BKO,IER)
  BESSEL=BESSEL-BK1/BKO1*DEXP(ZETA-ZETA0)
  GIONE=DO/PD*DEXP(DO)*DSGRT(Z/20)*BESSEL
  XPTWO= XZONE+V(*)*GIONE
  XPONE= XZONE+BETA
  Z= BETA**ORDER*Y
  Z0= BETA**ORDER*Y0
  ZETA0=ZETA**ORDER
  CALL MMBSKR(ZETA0,ORDER,1.BKO,IER)
  GIONE1=DO/PD*DEXP(DO)*DSGRT(Z/20)*BESSEL
  XPTWO1= XZONE1+V(1)*GIONE1
  XPONE1= XZONE1+BETA
  ZETAO=ZETA**ORDER
  CALL MMBSKR(ZETAO,ORDER,1.BK,IER)
  CALL MMBSKR(ZETAO,ORDER,1.BKO,IER)
  BESSEL1=BESSEL-BK11/BKO11*DEXP(ZETA-ZETA0)
  GIONE11=DO/PD*DEXP(DO)*DSGRT(Z/20)*BESSEL
  XPTWO11= XZONE11+V(1)*GIONE11
  XPONE11= XZONE11+BETA
  Z1= BETA**ORDER*Y
  Z01= BETA**ORDER*Y0
  ZETA01=ZETA**ORDER
  CALL MMBSKR(ZETA01,ORDER,1.BKO,IER)
  GIONE11=DO/PD*DEXP(DO)*DSGRT(Z/20)*BESSEL
  XPTWO11= XZONE11+V(1)*GIONE11
  XPONE11= XZONE11+BETA
  CONTINUE
  IF (1KM-KM/5*5.) EQ. ZERO) GO TO 32
  IF (C2U) LT. 0.) THEN R2=1B. BDO
  IF (C2J). LT. 0.0005D0) GO TO 37
  END IF
  CONTINUE
  IF (Cl (K-l) LT. 0. C-1D0) GO TO 10
  CONTINUE
  DO 20 L=1,399
  IF (C1 (L). LT. 0.999) GO TO 60
  WRITE(1,100) L, RH01L), CltL)
  FORMAT(' 0X, I  5..10X. F5. 1  .  '  OX, F6 4)
  CONTINUE
  STOP
  END

  SUBROUTINE LIN(V,N)
  IMPLICIT REAL*B (X-M,G-Z)
  DIMENSION Q(50),V(50),H(25)
  DO 1 J=1,N
  DO 1 I=1,J
  G(I)=G(I)+Q(I+J)
  IF (1 EQ NH) GO TO 2
  H(I)=H(I)+Q(NH-I+1)
  DO 3 J=1,NH
  CONTINUE
  WRITE(1,100) H(I), V(I)
  FORMAT(' 0X, I  5..10X. F5. 1  .  '  OX, F6 4)
  CONTINUE
  STOP
  END

C
VITA

Jaehyuk Hyun was born in South Korea on March 1, 1956. He holds a Bachelor and a Master of Science degrees in Civil Engineering from Sung Kyun Kwan University, Seoul, and Texas Tech University, Texas, respectively. He is currently a candidate for the degree of Doctor of Philosophy in the Civil Engineering Department at Louisiana State University.
Candidate: Jaehyuk Hyun

Major Field: Civil Engineering

Title of Dissertation: The Transport and Fate of Cr(VI) in Deep Well Disposal Zone

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Donald Dean Adrian

Debora Roy

Robert J. Gale

[Signature]

Date of Examination:

April 26, 1990