THE STABILITY OF IN SITU CHEMICALLY REDUCED AND STABILIZED SOILS CONTAMINATED WITH HEXAVALENT CHROMIUM AS AFFECTED BY pH, CO-SOLVENTS AND FREEZE-THAW/WET-DRY CYCLES

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TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

Since the industrial revolution the traditional paradigm of addressing spills of hazardous substances on the Earth has been essentially two-fold. Before the advent of the Environmental Protection Agency (EPA), industry would simply leave the spill on the ground or cover the spill using some form of mechanical means. Prior to the enactment of the Resource Conservation and Recovery Act (RCRA), there was minimal regulatory control over the management of hazardous waste spills. Given this permissive climate, hazardous waste generators had little, if any, incentive to expend resources on more costly management practices. After the promulgation of RCRA, the contaminated soils/debris from industrial spills were removed by the use of front-end loaders, placed in dump trucks and disposed into a "secure" and often times permitted landfill. Generators of hazardous waste fully expected that by properly and legally disposing of these wastes into a "secure and permitted" landfill they would no longer be liable for these waste that had been "permanently" disposed. Unfortunately, this has not been the case. Rather, the legal fees of being named a Potentially Responsible Party (PRP) and the remediation cost of Superfund sites have driven many formerly profitable industries into bankruptcy. In addition, the introduction of "Joint and Several Liability", in which every generator who ever contributed to that landfill may be liable for the remediation and legal fees for the entire Superfund site, has further served to diminish and degrade America's industries and their faith in secure landfills. In the future there are many dependent factors which will continue to diminish the use of hazardous waste landfills for the disposal of spills, these are; there will be a continuation of highly publicized catastrophic failures at a number of landfill facilities, which will further intensify the opposition to siting new and expanded hazardous waste landfill facilities which will continue to exasperate the existing shortage of hazardous waste landfill space.

However, the major problem with spills of hazardous substances that cannot be completely "eliminated" by biological treatment or incineration techniques is that they must still be disposed of on the land. Two ultimate disposal options for these wastes are secured landfills or in situ chemical stabilization/solidification and left in place. Hazardous waste disposal on land, even in a "secure" landfill, has often led to serious ground water pollution problems. Even engineering and design safeguards such as liners, impervious covers and monitoring wells have not been adequate enough to guard against unforeseen natural or human-related conditions that may allow escape of constituents of wastes. As a result, interest in the development of processes to render these wastes less dangerous or to use these materials as a useful product has increased greatly. One process which should receive attention in the future is in situ stabilization/solidification of hazardous substances. In this process, waste sludges and soils are combined with various additives that both chemically bind and physically solidify the hazardous materials making them less susceptible to leaching. This technology involves converting hazardous and toxic waste into an inert, environmentally safe synthetic rock which is suitable for land reclamation material. Stabilized/solidified waste may still leach, but the rate of contaminant leaching should be very low so that the pollutants will disperse harmlessly into the environment.

This study will document empirically the remediation technique used on a 1989 spill of sulfuric/hexavalent chromic acid waste that occurred at a tenant of the Tulsa Airport Authority in Tulsa, Oklahoma. The sulfuric/hexavalent chromic acid spill was caused by a malfunction in a pump truck during an inter-plant transfer. The pump truck, after receiving the waste, rapidly began to overheat and to leak the waste from several seals. The pump truck was escorted to an earthen spill control dike, and a fire truck was used to cool the truck and dilute the spilled acid until the pump truck could be unloaded into a tank truck. During the event, an estimated 500 gallons of the sulfuric/

chromic acid mixture was spilled on the ground. The waste was diluted with approximately 2000 gallons of water which eventually spread and sorbed into the top few inches of soil over an approximate area of 20,000 square feet. The designated 20,000 square feet spill area includes a 5 to 8 foot buffer zone between the actual perimeter of the spill and the line of hazard markers set up to secure the spill area. (See Figure 1)

The purpose of this study is to evaluate and review the applicability of in situ remediation of soils contaminated with hexavalent chromium by the use of chemical reduction, stabilization and solidification and to chemically study the factors that could potentially result in the breakdown of the stabilized materials, such as changes in pH, co-solvents, wet-dry/freeze cycles and the combination synergistic affects of these. This study will also address the in situ remediation techniques which were implemented and subsequent chemical analysis of the remediated soil. The overall goal of this study is consistent with the remedial objectives of the spill remediation, that is, to study and ensure the protection of human health and the environment by the prevention of future releases of chromium from the soil/waste that could result in groundwater contamination.

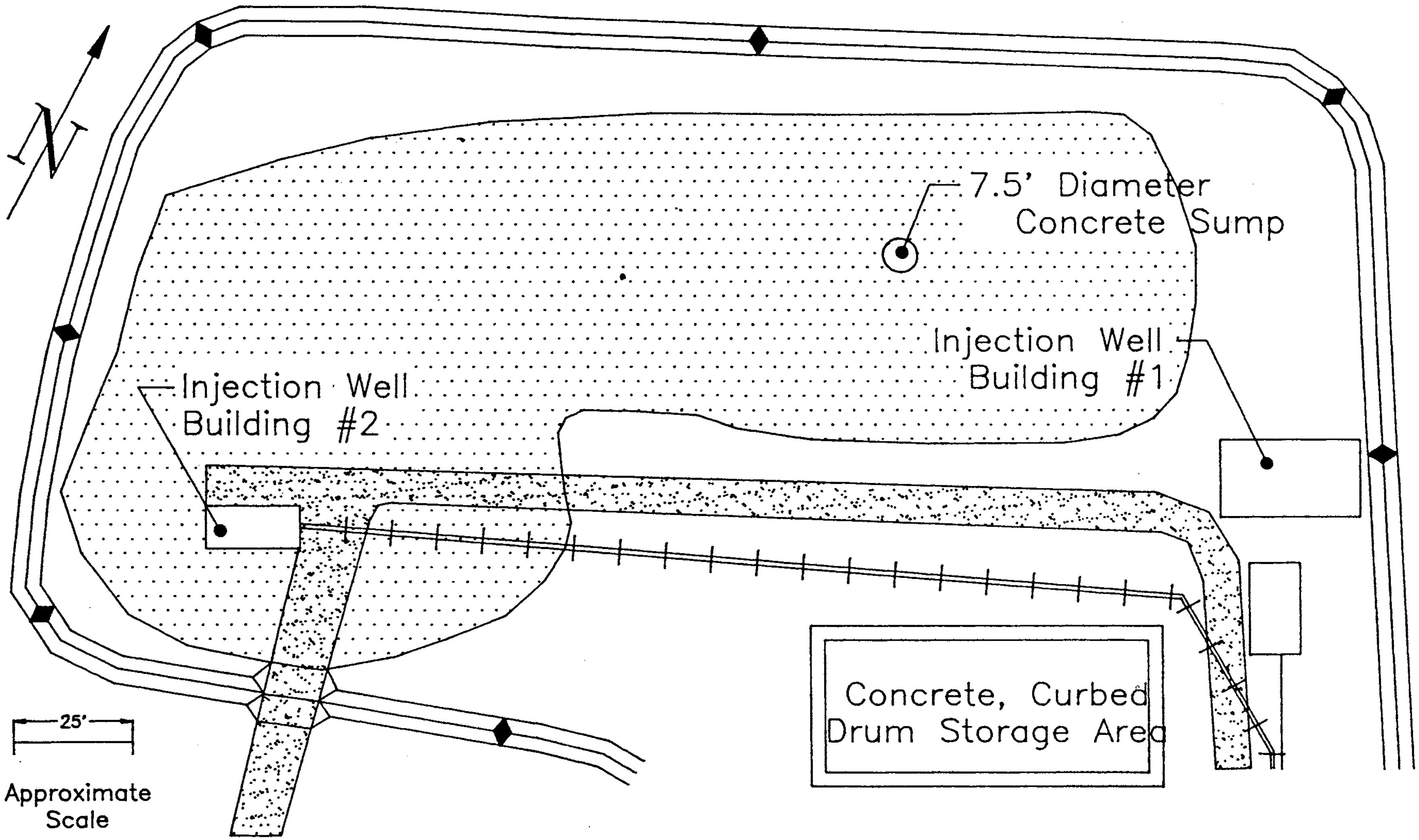

Figure 1. Chromic Acid Spill Site

CHAPTER II

REVIEW OF THE LITERATURE

Introduction

The process of investigating the use of in situ chemical reduction, stabilization and solidification for hexavalent chromium spills should be accomplished using an interdisciplinary approach. The review of the literature will not only examine the science involved for in situ chemical stabilization but also important issues such as: applicable federal regulations, financial impact, chemical and physical analysis of the waste/soil.

Terminology and Definitions

Many terms in the field of chemical stabilization/ solidification using pozzolanic binders have been borrowed from other technical areas. Often, though they have been given new and specific meanings. Unfortunately, there is no "official" set of definitions, so the American Society for Testing and Materials (ASTM, 1980) and the U.S. Environmental Protection Agency (Malone, et al, 1980) have independently promulgated their own different definitions. In this study, the meanings of the terms "stabilization", "solidification" and "pozzolans" are similar to those defined in the EPA publication "Guide to the Disposal of Chemically Stabilized and Solidified Waste" (Malone, et al, 1980). The definitions used in this study are the following:

Chemical Stabilization

Chemical stabilization refers to those techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization. The process involves, but is not limited to, the chemical treatment of waste to insolublize, immobilize, encapsulate, destroy or otherwise interact with selected waste components. Therefore, the overall purpose of chemical stabilization is to produce substances that are nonhazardous, or less hazardous, than the original waste. The measurement of the degree of hazard for these kinds of materials and systems is usually defined by leaching tests (Cote and Hamilton, 1982).

Chemical Solidification

Chemical solidification changes the physical properties of the waste to promote ease in handling and landfilling. This process, which utilizes chemically reactive formulations that, together with water and other components in sludges and other aqueous wastes, form stable solids.

Stable in the sense that the solids are physically stable under expected environmental conditions and will not revert to the original liquid, semiliquids, or unstable solid state. The process of eliminating the free water in the waste is by hydration with setting agent(s). Some solidification techniques encapsulate the waste into a solid of high structural integrity with a nominal load-bearing strength (compacted) in excess of one ton per square foot (Pojasek, 1978). The encapsulation may be of fine waste particles (microencapsulation) or of a large block or container of wastes (macroencapsulation). The microencapsulation chemicals are a mixture of compounds such as silicon dioxide (silica), calcium silicate, calcium aluminate, and aluminum oxide. It is a high pH (11-12), polymerizing material which first precipitates any metals as their hydroxides, then disperses and traps them by a "crystal-capture" mechanism. The result is a high strength, impermeable material (Bricka, 1988). During the course of the reaction, the polymer-forming, cementitious compounds become hydrated with as many as 32 waters of hydration (Bishop, et al, 1983). It is, therefore, necessary to add water in addition to the free water available within the wastes themselves.

Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents, but may mechanically bind or lock with the waste in the solidified matrix (Thompson, et al, 1979). Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the wastes with an impervious capsule "microencapsulation". For some applications, in situ solidification describes the product as a solid, monolithic mass. This would tend to reduce the potential infiltration of leaching of precipitation. But in this study the term solidification will mean the conversion of liquids or semiliquids into solids, but without the requirement of a monolith.

Pozzolans

The terms "pozzolanic" and "pozzolans" comes from Pouzzoles, a city near Naples where volcanic silico-aluminate calcium ash is found. Romans learned that if they mixed lime, sand and stone and volcanic silica ash or lava deposits they could make concrete or synthetic stone (Pojasek, 1979). In this study the term "pozzolans" will refer to Portland cement reactions. Examples of common pozzolans are fly ash, pumice, cement kiln dust, and blast furnace slag. Pozzolans are siliceous or alumina-siliceous materials, and in the presence of water, will chemically react with alkali and alkaline earth hydroxides to form cementitious compounds which aid in the processing of metal containment through the formation of silicate gels (Bougue, 1955). It is this chemical process in which cement and/or cement kiln dust or other pozzolans are combined to produce a relatively high strength waste matrix. The final product can vary from a soft fine-grained material to a hard cohesive material similar in appearance to cement. Pozzolanic reactions are however generally much slower that cement reactions. Waste materials that have been stabilized/ solidified with pozzolans include oil sludges, plating sludges containing various metals (aluminum, nickel, copper, lead, chromium, and arsenic), waste acids and creosote (Christensen and Wakramiya, 1980).

Cement Kiln Dust-Based Stabilization/ Solidification

Cement Kiln Dust (CKD) based stabilization/solidification is a process in which the waste materials are mixed with cement kiln dust. Water is added to the mixture, if it is not already present in the waste material, to ensure the proper hydration reactions necessary for bonding the cement kiln dust to the soil. The wastes are incorporated into the cement kiln dust matrix and, in some cases, undergo physical-chemical changes that further reduce their mobility in the waste-CKD matrix. Typically, silicates and hydroxides of metals are formed, which are much less soluble than other ionic species of the metals (Davis and Hooks, 1975). Small amounts of fly ash, sodium silicate, bentonite or proprietary additives are sometimes added to the CKD to enhance processing. The final product may vary from a granular, soil-like material to a cohesive solid, depending on the amount of reagent added and the types and amounts of waste stabilized/solidified.

CKD-based stabilization/solidification has been applied to plating wastes containing various metals such as cadmium, chromium, copper, lead, nickel and zinc (Assche and Uyttebroeck, 1980). CKD has also been used with complex wastes containing PCBs, oils, and oil sludges (Clark, et al, 1982). This technology has also been applied in Japan to bottom sediments containing toxic substances (Kita and Kubo 1983, Nakamura, 1983, Otsuki and Shima, 1982) and in the United States to industrial wastes (Pojased, 1979, Malone, et al, 1980, Cullinane, et al, 1986). Although stabilization/solidification is not the solution of every disposal problem, consideration of this alternative with other viable technologies will ensure that cost-effective technology is used to maximize environmental protection.

Therefore, stabilization and solidification using a pozzolanic material like cement kiln dust refers to treatment processes that are designed to accomplish one or more of the following:

1) Improve the handling and physical characteristics of the waste, as in the sorption/removal of free liquids.
2) Decrease the surface area of the waste mass across which transfer or loss of contaminants can occur, and/or limit the solubility (reduction in leaching potential) of any hazardous constituents of the waste, e.g., by pH adjustment or sorption phenomena.

3) Development of structural integrity.

The elimination of free liquid before disposal is a regulatory requirement. (USEPA, 1986d). Structural integrity is important because the waste must have sufficient bearing capacity to support the overburden and final cover material. Reduction of leaching potential provides direct benefits in terms of reduced environmental risks associated with particular waste (Roberts, 1977). Many stabilization/solidification processes have been developed, including cement-based, lime-based, thermoplastic, organic polymer, encapsulation, glassification and self-cementing techniques. These processes vary widely in their applicability to different waste types, but most are suitable only for primary inorganic wastes with organic content of less than 25 percent (Bishop and Gress, 1982).

In Situ Treatment

The term "in situ" is a Latin term meaning "in a natural or original position." The term "in place" is often used interchangeably with "in situ". In situ treatment describes treatment of waste that has not been excavated. The existing spill or lagoon is used as both the mixing vessel and the final disposal site for the treated waste so that the waste materials are not removed. This in situ treatment is in contrast to "staged" treatment, in which the application of in situ techniques are applied to wastes that have first been excavated. In practice, treatment may not be feasible or cost-effective unless the waste is first excavated, moved or consolidated, prior to redeposition in a location specifically designed for "staged" treatment. Although technically the staged treatment is not treatment in place, the same techniques could be used such as the application of a stabilization/ solidification agent using a roto-tiller or an auger.

The major problem with staged treatment is that it may trigger regulatory requirements additional to those that apply to treatment of waste that has not been excavated. For this reason, this research and dissertation distinguishes between in situ treatment and staged treatment. Therefore, in situ treatment refers only to the treatment of waste in place, without prior excavation.

For in situ treatment the reagents (like cement kiln dust) are added to the spill or lagoon directly by pneumatic or mechanical means. Pneumatic addition uses blowers to distribute reagent over the entire spill or lagoon. Mechanical addition simply means using dump trucks, front-end loaders or clamshells, depending on the size of the spill/lagoon and the general site topography.

In Situ Chemical Stabilization of Waste/Soil

One remedial action option available to mitigate the leaching potential of contaminant metals into ground water and their subsequent transport through underground aquifers is in immobilization, by the use of in situ chemical stabilization/solidification. The advantages of in situ treatment using this technique include:

1. Because of excavation problems, in situ treatment by stabilization/ solidification maybe the only viable management technique.
2. Alternate hazardous waste treatment and disposal techniques are often economically prohibitive.
3. Selection of stabilization/solidification as a remediation technology is also supported by recent developments in the environmental regulations.
4. In certain wastes, chemical stabilization can convert a "characteristic hazardous waste" into a non-hazardous waste. This benefit can greatly reduce the amount of regulatory oversight in the disposal and/or in transportation of a generator's waste for staged treatment.

In situ techniques can be carried out by introducing treatment chemicals (e.g., CKD) into the ground by various means. If soluble chemicals are used, they can be applied by saturating the soil with the chemicals in solution. This fluid application may be carried out at a high rate by surface flooding the site or more gradually by spraying thus allowing the solution to drain freely into the soil (Cullinane, et al, 1986). Insoluble treatment chemicals, such as cement kiln dust or fly ash, can by introduced into the ground by spreading, filling, forced injection, suspension transport, or by placing it in a low permeability encapsulation barrier. Spreading may suffice as a means of treating metals if the soil has a high moisture content and the metal contaminants lie very close to the surface. This may be most applicable to soils with high organic content. Tilling is the most common method of introducing a soil treatment chemical into the ground. Roto-tilling can mix dry chemical additives into the soil to a depth of one to two feet. Fine insoluble chemicals can be transported short distances through soil voids by placing them in suspension in water. The suspended material is then injected in a fashion similar to chemical grouting or through nozzles in close spaced probes. Typically, fine material can be transported several feet from the nozzle in this fashion.

Chemicals other than soluble silicates have been used in several instances to decontaminate soils. The chemical is injected into the soil and allowed to react with the contaminant to immobilize or destroy it. This approach could be used to destroy cyanide with dilute hypochlorite solution in decontamination project. One caution in such treatment is that the reagent used must either be non-toxic, such as sodium silicate, or unstable in the soil environment, so that any excess does not cause secondary pollution. Also, potential reaction products must be determined so that they will not cause pollution. For shallow soil applications, in situ fixation/destruction may be accomplished simply by spray or trickle irrigation of the reagent solution at the surface, allowing it to permeate the contaminated area by gravity flow. Soil permeability, groundwater conditions, and rainfall are all factors that must be considered when designing such a system.

Recent interest in in situ soil washing systems will probably enhance the use of in situ treatment as well. If the soil can be washed and the permeate recovered for treatment, then in situ treatment could be even easier. Also, if the permeate can be recovered, than a wider range of chemical systems can be used, since excess chemical can be recycled for both economic and environmental reasons, and any toxic reaction products recovered for separate treatment. As a general rule, in situ treatment using cement kiln dust or other pozzolanic reagents as discussed to this point are less costly than removing the waste for treatment and replacement. The primary question is whether the in situ method accomplishes the requirements of the project.

Equipment required for in situ solidification/ stabilization varies with the specific site. Generally, an average site would require equipment in the following categories: dump trucks, front-end loaders, excavator or backhoe, and on site chemical storage and handling facilities. The size and amount of equipment depends on the location and topography of the remedial action site as well as the quantity of material to be treated.

The cost of in situ solidification/stabilization techniques using cement kiln dust is based primarily on the production rate achieved by the equipment mix selection for the specific remedial action project. Field data for the cost of in situ mixing alternative applied to remedial action sites are not available at the present time. However, according to Barth, (1990), the production rates for two RCRA sites using the backhoe-mixing pit technique were the following. A daily (8-hour shift) production rate ranged from 1,000 to 1,200 cubic yards (approximately 1000 cubic meters) of waste could be solidified/stabilized. This rate was dependent on the mixing of less than 5-feet in depth, with a 40 to 50 feet diameter site. This specific site used a backhoe (Caterpillar 225) for all mixing.

Cement Kiln Dust

During the process of manufacturing Portland cement, vast quantities of kiln dust are collected. Typically, 10 to 20 percent of the raw material leaves the kiln as dust, which must be collected to prevent air pollution (Davis, 1975). There is, in general, no value in returning the dust to the kiln, as it is too fine and tends to pass directly back into the air pollution control collectors (cyclones, electrostatic precipitators, and baghouses). Cement kiln dust (CKD) originates when fine-ground raw materials become airborne in the stream of combustion gases traveling up the cement kiln. Carbon dioxide, released from the decomposition of calcium carbonate to calcium oxide or unreacted lime, enhances agitation of the materials and affects the amount of airborne dust. Exposed to the high temperatures of the kiln, the mineralogical structure of the raw materials is altered, allowing a portion of the alkali content to volatilize (Davis and Hooks, 1974). Fine dust particles entrained in the combustion gases are nucleation sites for condensation of alkali oxides as the gases cool. This dust then becomes a mixture of kiln raw materials, which have been partially calcined, including finely divided cement clinker, alkali compounds and others. The composition of CKD varies widely depending on cement kiln operation, type of kiln, type of fuel, and several other factors (Bye, 1983). Dusts coming from zones of higher temperature in the cement kiln often contain dicalcium silicate (one of the primary compounds of Portland cement), in addition to lime. A CKD that contains calcium silicate compounds, i.e., dicalcium silicate and lime, is the most desirable for use in stabilization/ solidification systems. This type of CKD will result in a cementitious binder and is the best candidate for use (Davis and Hooks, 1975).

The Chemistry of Cement Kiln Dust Stabilization/Solidification

Cement kiln-pozzolan solidification involves the reaction of cement kiln dust (a pozzolanic material) in the presence of water with a waste material to form a compound possessing cementitious properties. The liquid waste or fluid in the sludge becomes the mix water for hydration of the cement. As this mixture hydrates, a calcium-silicate-hydrate gel forms, followed by the hardening of the material as thin, densely-packed, silicate fibrils grow and interlace. In the presence of lime, associated with cement kiln dust, heavy metals in the waste are converted to insoluble metal hydroxides and silicates due to the highly alkaline environment of this paste and are trapped within the pores of the paste matrix gel. Along with this gel formation comes the formation of various crystalline hydration products such as calcium hydroxide and various heavy metal hydroxides. These products form in the interstices of the "cement" matrix. During the final stages of hydration the gel swells to the point where particle overlap occurs and silica fibrils develop. At that point all of the hydration by-product crystals are grown to their maximum size and are either overlapped by fibrils or have grown into the particle gel itself (Jones, et al, 1982). "Crystal capture" is the mechanism describing this process in which two interdependent reactions occur (Palmer and Wittbrodt, 1991). Chemical bonds are formed initially between the process chemicals and pollutant ions in solution, then insoluble pollutants are dispersed and trapped within the lattice. This interlocking of the fibrils and formation of various hydration products binds the pozzolan and other components of the mix into a rigid mass. Unreactive materials that are blended with the cement prior to gel formation and setting can become encased in the solid matrix (Cartledge, 1988). It is this pozzolanic microencapsulation which entraps the waste material, particle by particle, resulting in reduced solubility due to lock-up waste constituents within the crystalline matrix (Palmer and Wittbrodt, 1991). The large amount of free alkalinity (e.g., calcium hydroxide) in the fixed waste form is beneficial as it counters or neutralizes the effects of acids which may be present in waste or in the leachates. Over a period of time the cement kiln dust/waste mixture hardens into a rock-like matrix as fibrils grow from the pozzolanic particles. The setting time, rate of hardening, and final strength of pozzolanic reactions are affected by temperature, humidity, water/CKD ratio, porosity, CKD particle size, and the chemical composition of the CKD. Important chemical composition factors include the amount of calcium, the ratio of silica to the sum of alumina and ferric oxide, the ratio of alumina to ferric oxide, and additives or impurities (Lubowitz and Wiles, 1979).

It is only recently that stabilization/solidification techniques have been viewed as a way of accelerating geochemical processes that normally take centuries to accomplish, the formation of sedimentary rocks. Since the constituents of most inorganic (metal) waste originated from the earth in rocks, generally associated with silicate, we have reformed the waste into a silicate soil in the form of a silicate sedimentary rock.

Chemical Stabilization/Solidification of Chromium

In general, most heavy metals in the waste are converted to insoluble metal hydroxides in the highly alkaline environment of the cement kiln dust paste and are trapped within the pores of the cement paste matrix. But chromium (in the trivalent oxidation state) is believed to be bound to the silica matrix itself, rather than being in the pores (Anderson and Benjamin, 1985). This is due to chromium being present in the relatively insoluble silicate form, rather than hydroxide form, the form in which chromium was originally added. This would explain why the leachability of chromium appears to be dependent on the dissolution of the silicate matrix (Cartledge, 1988). Chromium should not leach to any great extent until the silica matrix is broken down, indicating the chromium is strongly complexed in the matrix and is only released when the silica matrix is destroyed (Bishop, 1988).

Chromium

Chromium is a naturally occurring element that is found in soil, volcanic dust and gases and belongs to Group VIB of the periodic table. (Darin, 1956). Chromium is usually found in three major states: chromium (0), chromium (III) also called trivalent chromium and chromium (VI) also called hexavalent chromium. Chromium (III) occurs naturally in the environment, while chromium (VI) and chromium (0) are generally produced by industrial processes (Blair, 1973). Chromium is found in nature only in the combined iron chromate state ($FeO*Cr_2O_3$) and not as the element (Forster, 1979). Under reduction conditions, trivalent chromium is the most thermodynamically stable form of the oxidation states, however, hexavalent chromium can remain metastable for long periods of time. Hexavalent chromium (Cr+6) is acidic, forming chromates $(CrO_4)^{-2}$ and dichromates $(Cr_2O_7)^{-2}$ while the other valence states are basic. The chromium ion in metal finishing wastewaters is found predominately in the hexavalent, or plus six (6) state (Darin, 1956). Chromium in the hexavalent state behaves as an anion and cannot form an insoluble hydroxide or sulfide. This anionic behavior results due to the hexavalent chromium ion becoming tightly bound with oxygen ions to form a tetrahedral radical called chromate. Therefore, materials containing hexavalent chromium must be pretreated before the waste can be solidified. The hexavalent chromium (Cr+6) must be reduced to the trivalent state (Cr+3) in order to be effectively precipitated as an insoluble hydroxide (Cote and Webster, 1987).

Chromium is a widespread contaminant in the environment primarily as the result of increasing urbanization and industrial activities (Doyle, 1979). Focusing on toxicity and exposure potential, the U.S. Environmental Protection

Agency recently designated Chromium as one of the 17 chemicals posing the greatest threats to human health (USEPA, 1985b). The presence of hexavalent chromium is of particular importance because in this oxidation state, chromium is extremely toxic, carcinogenic and water soluble (Forrest, 1987).

Sources of Chromium Pollution

The most significant anthropogenic point sources of chromium are industrial operations including plating and metal finishing, pigments, leather tanning, corrosion control agents, textile dyeing and mordants, wood preservation, photography, catalysts, etc. (Davis and Leiber, 1981). All of these industrial applications present a potential source of waste materials which have the potential to create a spill which could require treatment or remediation. For example, 27 Superfund sites for which the Records of Decision had been signed before 1987, report chromium as being a potential problem (Palmer, et al, 1988). One of most widely known cases of ground water contamination by chromium is the Nassau County site on Long Island, New York. The source of the chromium contamination was a recharge basin used for the disposal of solutions from an aircraft plant. Discharge of untreated wastes occurred between 1941 and 1949. Today, there is a thin elongated plume of hexavalent chromium which has migrated 1300 meters down gradient. The chromium appears to be migrating with the same velocity as the ground water (Ku, 1978).

The extent of treatment or remediation required depends upon the specific industrial process used and the particular chromium chemical which is to be treated (hexavalent or trivalent).

Treatment systems for chromium bearing wastes have been commercially developed and include both destructive and recovery systems. Although the systems have been developed primarily for the metal finishing industry, the application is essentially the same for any source of chromium waste, such as in spill remediation.

Chromates such as CrO_3, $(CrO_4)^{-2}$ or $(Cr_2O_7)^{-2}$ are used in chromium electroplating baths, brass bright dips and chromate conversion coatings for zinc and aluminum (Pickering, 1981).

Hexavalent Chromium

Hexavalent chromium (Cr^{+6}) is the highest oxidation state of chromium. The common chromium chemicals which are composed of hexavalent chromium are chromic acid (or chromium trioxide) CrO_3; the dichromates, $Cr_2O_7^{-2}$ and chromates, CrO_4^{-2} (Cotton and Wilkerson, 1980). The basic building block of all hexavalent chromium chemical is sodium dichromate dihydrate, $Na_2Cr_2O_7*2H_2O$, or technically sodium dichromate, dihydrate. All other common hexavalent chromium chemicals; chromic acid, sodium chromate, the potassium bichromate are derived from sodium dichromate. Solutions of chromic acid, sodium bichromate, potassium bichromate and sodium chromate, contain hexavalent chromium, which, in a diluted solution, is essentially the same regardless of the source (Palmer and Wittbrodt, 1981). Chemical differences are only pronounced in concentrated solution. For example, concentrated chromic acid solutions have a low pH (2.0 or less) and are very strong oxidizing agents. Sodium bichromate solutions with a pH value greater than 4.0 are not as strong oxidizing agents unless the pH is lowered with some mineral acid. Sodium chromate solutions have a nominal pH of 8.6 and show the least oxidizing characteristics. All of the common commercial hexavalent salts are quite soluble at any pH, consequently the chromium cannot be precipitated out of solution as the hydroxide without conversion to trivalent chromium (Nriagu, 1988).

At concentrations less than 10 mM or at neutral pH, Cr+6 exits as $H_2CrO_4^o$, $HCrO_4^-$ and CrO_4^{-2} which are involved in the acid dissociation reactions:

$$H_2CrO_4^o \longleftrightarrow H^+ + HCrO_4^- \qquad ;K1$$

$$HCrO_4^- \longleftrightarrow H^+ + CrO_4^{-2} \qquad ;K2$$

The pK values are 0.86 and 6.52 respectively (Beattie and Haight, 1972). Therefore, CrO_4^{-2} is predominant above pH 6.5, $H_2CrO_4^o$ predominates only if the pH is below 0.9, and $HCrO_4^-$ predominates in the pH range of 0.9 to 6.5. Although these boundaries shift with ionic strength and temperature, they are reasonable demarcations between the dominant aqueous forms. Under acid conditions and for total concentrations of Cr+6 greater than 10 mM, $HCrO4^-$

polymerized to form dichromate, $Cr_2O_7^{-2}$.

$$HCrO_4^- + HCrO_4^- \longleftrightarrow Cr_2O_7^{-2} + H_2O$$

with a pK of -1.54 (Beattie and Haight, 1972). The dominance of the chromate ions ($HCrO_4^-$ and CrO_4^{-2}) in chromium-contaminated waters is recognized by the yellow color imparted to the water in concentrations above 1 mg/l. The presence of dichromate is seen as an orange color in contaminated water.

Trivalent Chromium

Chromium in soil is present as the insoluble oxide, trivalent chromium (Cr_2O_3), which is a lower oxidation state of chromium. Therefore, it is not very mobile in soil. Trivalent chromium compounds do not exhibit the strong oxidizing characteristics of hexavalent compounds and are soluble only at low or very high pH levels. At a pH of 8.6, trivalent chromium is essentially insoluble (Blair, 1973). Trivalent chromium chemicals such as chromic chloride, chromic acetate, and chrome alums are trivalent salts. These salts are soluble since water solutions are acidic (Blair, 1973). Treatment of trivalent chromium in waste spills can be accomplished using precipitation of the chromium salts by a simple pH adjustment. Chromium (III) hydroxide can be precipitated from solutions containing chromium (III) ions by aqueous ammonia, alkalies, and carbonates. The hydrolysis of trivalent chromium with increasing pH has been studied by Rai, et al, (1985). Their data suggest that the most important species are $CrOH^{+2}$,

$Cr(OH)_3^o$ and $Cr(OH)_4^-$ with $Cr(OH)2^{-2}$ occurring in a very narrow pH band between 6.27 and 6.84.

The Reduction of Hexavalent Chromium

The reduction of hexavalent chromium is required as a pretreatment step because the valence of chromium must be changed from plus six (6) to plus three (3) before the metal can precipitated into the hydroxide. The chemical treatment of hexavalent chromium waste spills is a two-step process. The first treatment insures the reduction of the hexavalent chromium to trivalent chromium by the introduction of a reducing agent. The second step brings about the removal of the trivalent chromium from solution by precipitation using lime to the highly insoluble chromic hydroxide (USEPA, 1986b).

The most common reducing agents used in the reduction of hexavalent chromium in industrial waste waters are sulfur dioxide, or its salts; sodium metabisulfite, sodium bisulfite, or sodium sulfite. But in spill remediation, a good alternative to sulfur compounds for the reduction process is divalent iron (Fe^{+2}), either ferrous sulfate, $FeSO_4*7H_2O$ (as used in this study and remediation) or ferrous chloride. Both ferrous sulfate and ferrous chloride are exceptionally good reducing agents (Conner, 1990) in place of the SO_2 or the sulfites. The distinct advantages or ferrous salts are:

1. They are inexpensive and readily available.

2. There is no need for ventilation or cartridge type respirators as with the sulfite or sulfur dioxide reduction agents.
3. The pH of the reaction is not as critical as with the sulfite or sulfur dioxide reduction agents.

Ferrous sulfate (copperas) is an effective reducing agent for hexavalent chromium over a relatively wide pH range and is readily available as a dry crystalline material at a relatively low cost. Ferrous sulfate can be obtained very inexpensively at some locations because it is a waste material from spent pickle liquor (hydrochloric or sulfuric acid which has been used to descale or remove rust from steel). Spent pickle liquor also contains some free acid thereby reducing the acid requirement when ferrous sulfate is used. The major disadvantage of ferrous sulfate is that it creates a substantial amount of sludge. For this reason its application as a chromium reducing agent is largely confined to land applications such as in situ treatment (Wiles, 1987).

The reduction of hexavalent chromium using ferrous sulfate can be illustrated as follows (Cotton and Wilkerson, 1980):

$$6FeSO_4{*}7H_2O + 2H_2CrO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 15H_2O$$

The ferrous ion is converted to ferric by the loss one electron, but hexavalent chromium required three electrons to reach the trivalent state. Consequently, it takes three ferrous ions to yield the electrons to reduce one chromium ion. Therefore, the stoichiometry shows that 3.84 grams of ferrous sulfate are required to reduce 1 gram of hexavalent chromium.

Although the equation shows a requirement for acid, it is not necessary to carry out the reduction since the reduction will proceed at near neutral pH values according to the equation:

$H_2CrO_4 + 8H_2O + 3FeSO_4 \text{ --> } Cr(OH)_3! + Fe(OH)_3 + 3H_2SO_4$

Similar equations may be written for ferrous chloride. This reaction is only slightly less favorable thermodynamically than the reaction which takes place under acidic conditions. Consequently, the acid requirements are of little importance. This is extremely important in a spill of dilute chromic acid in which the alkalinity of the indigenous soil has buffered the spill to about a pH of 4. Therefore, the ferrous salts are excellent reducing agents in both acid and neutral solutions (Weizman, et al, 1988).

In practice, most chromium bearing solutions will be acidic except for certain chromate solutions. Additionally ferrous sulfate, when hydrolyzed, will provide hydrogen ions, which will lower the pH of the solution being treated. Under these conditions the only alkali required would be the amount necessary to precipitate the reduced chromium and iron.

The two half cell reactions for the reduction of hexavalent chromium are:

$$6Fe^{+2} \text{ ---> } 6Fe^{-3} + 6e- \qquad E^{o} \quad -0.77v$$

$$\underline{Cr_2O_7^{-2} + 14H^{+} + 6e- \text{ ---> } 2Cr^{+3} + 7H_2O \qquad E^{o} \quad +1.33v}$$

$$6Fe^{+2} + Cr_2O_7^{-2} + 14H^{+} \text{ ---> } 6Fe^{-3} + 2Cr^{+3} + 7H_2O \quad E^{o} \quad +0.56v$$

The summation of the two half cell reactions gives a positive E^{o} value, therefore the reaction will occur spontaneously in the direction in which it is written; if negative, it proceeds spontaneously in the reverse direction (Peters, 1971). According to thermodynamics Gibb's free energy charge is given by:

$$G = -nfE^{o}$$

where n is the number of electrons involved in the redox reaction, f is the Faraday constant (96,487 coulombs) and E^{o} is the sum of the two half cell reactions. In this case:

$$G = -1 \text{ x } 96,487 \text{ x } + 0.56 \text{ v}$$

$$G = -54,032 \text{ cal}$$

Since G is a large negative value, the reactions has to be spontaneous.

To determine the equilibrium constant (K) for this reaction we use the Nernst equation:

$$E^{o} = \frac{0.0592}{n} \log K$$

Therefore:

$$+0.56v = \frac{0.0592}{1} \log K$$

$$\log K = 9.459$$

$$K = 2.88 \text{ E+09}$$

While the trivalent and hexavalent chromium are the most commonly encountered in the environment, Cr^{+5} and Cr^{+4} are important intermediate states that influence the rate of reduction of the hexavalent form (Eary and Rai, 1988). Hexavalent chromium does not always convert directly to trivalent chromium but may be initially reduced to either Cr^{+5} or Cr^{+4}. Many reduction experiments follow a rate law for one-equivalent reduction agent that assumes that the concentration of Cr^{+5} is a steady-state value, that rate of oxidation of Cr^{+4} to Cr^{+5} is negligible, and the reduction of Cr^{+5} to Cr^{+4} is the rate-limiting step . For two-equivalent reducing agents, the reduction of Cr^{+6} to Cr^{+5} is often the initial and rate-limiting step. Unfortunately, most of these rate laws have been developed for very high concentrations and extreme pH concentrations, and their applicability to environmental conditions has yet to be explored.

The Adsorption of Chromium on Soil

According to Griffin, et al, (1977) the amount of hexavalent chromium adsorbed by soils is dependent upon the concentration of CrO_4^{-2} ions in solution. Conversely, the lack of adsorption at pH values above 8.5 indicates that the CrO_4^{-2} ion does not favor adsorption. The preferential adsorption of $HCrO_4^{-1}$ to CrO_4^{-2} species is probably related to the number of negative charges per adsorbing ion. The two adjacently located negative charges of the tetrahedral CrO_4^{-2} ion cause it to be repelled by the net negative charge on the clay surface. The positive charge on clays and hydrous oxides increase as the pH is lowered. Therefore, in the low pH range the positive charge of the clay minerals and hydrous oxide impurities on the clays probably increased, thus allowing increased hexavalent chromium adsorption to occur. Below pH of 2, the $HCrO_4^-$ ion concentration in solution decreased in favor of the neutral H_2CrO_4 species and hence the hexavalent chromium adsorption gradually decreased (Ainsworth, et al, 1989).

Chromate is adsorbed by soils, including Fe and Al oxides (MacNaughton, 1977), kaolinites and to a lesser extent montmorillonites (Griffin, et al, 1977). Chromate adsorption increases with decreasing pH as a result of protonation of surface hydroxyl site (increasing positive charge on the sorbents) and aqueous speciation of CrO_4^{-2} (increasing concentration of dichromate);

$$HCrO_4^- \longleftrightarrow CrO_4^- + H^+ \qquad pKa = 6.5$$

Outer-sphere surface complexation models have shown the dichromate ion preferentially sorbs on pure oxide and kaolinites surfaces (Davis and Leiber, 1980). Solids bind chromate via surface coordination, although the nature of the surface complex (inner or outer sphere) has not been resolved. Indirect evidence suggests that the complex is in the outer sphere (Hayes, 1987). Chromate adsorption on oxide sorbents over ranges in pH, ionic strength, and competing ions have been described using the Triple Layer Model (TLM) and outer-sphere surface complexation reactions (Davis and Leiber, 1980).

The Toxicity of Chromium

Chromium can enter the body via oral, inhalation and dermal exposure. Generally, the gastrointestinal tract has been the primary route of entry, although entry through the airways can be significant near industrial sources.

Hexavalent Chromium. Hexavalent chromium can be a poison by subcutaneous route, a very powerful oxidizer, a powerful irritant and corrosive to skin, eyes and mucous membranes (Baruthio, 1992). Hexavalent chromium is a confirmed human carcinogen producing tumors of the lungs, nasal cavity and paranasal sinus (Lewis, 1991). It is a poison by ingestion, intraperitonaeal and subcutaneous routes. The U.S. Dispensatory characterizes potassium dichromate as a violent irritative and corrosive poison, which can be fatal. Hexavalent chromium is approximately 1,000 times more toxic than trivalent chromium and has more strictly controlled discharge limits.

Hexavalent chromium is irritating, and short-term exposure can result in adverse effects at the site of contact, such as ulcers of the skin, irritation of the nasal mucosa and perforation of the nasal septum. Hexavalent chromium compounds have also the potential via inhalation to induce lung tumors in humans and experimental animals. Oral ingestion can produce gastrointestinal corrosion, testicular atrophy and acute multisystem shock, followed by renal failure, and hepatic injury within several days (De Flora, et al, 1989).

Once absorbed into the body, hexavalent chromium can cross the cell membranes easily and is reduced to trivalent chromium inside the cells, forming chromium protein complexes during the reduction. Once complexed with protein, chromium cannot leave the cell (Braver, et al, 1985). It is during the chemical reduction process that hexavalent chromium interacts with the DNA molecule, which can lead to the induction of cancer, in addition to teratogenic and reproductive mutations (Bianchi and Lewis, 1987).

Hexavalent chromium salts will impart a yellow color to water at very low concentration, 1.5 ppm, and is easily detected in water solutions. The same concentration is near the taste threshold. For domestic water supplies the U.S. Public Health Service set a mandatory limit, in 1946, of 0.05 ppm hexavalent chromium. The World Health Organization (WHO) International Drinking Water Standards prescribed the 0.05 ppm limit. The 0.05 ppm limit was the lower limit of detectability at the time.

In plant life, hexavalent chromium interferes with uptake of essential nutrients for proper root and leaf development (De Flora, et al, 1989).

Trivalent Chromium. Generally, salts of trivalent chromium are not considered to be physiologically harmful. Administered orally, the chromium salts are not retained by the body, but are rapidly and completely eliminated (De Flora and Wetterhahn, 1989). There is no evidence at the present time that trivalent chromium compounds have any toxic effects. In fact, Mertz, (1988) has concluded that trivalent chromium is considered an essential nutrient that helps to maintain normal metabolization of glucose, cholesterol, and fat in humans. Trivalent chromium is considered essential for the maintenance of vascular integrity by stabilizing biological proteins in their proper configurations. A deficiency of trivalent chromium in mammals results in elevated serum cholesterol levels and an increase of atherosclerotic aortic plaques (De Flora and Wetterhahn, 1989).

Signs of trivalent chromium deficiency in humans include weight loss and impairment of the body's ability to remove glucose from the blood. Trivalent chromium assists in binding insulin to fat cell membranes stimulating them to absorb glucose. The minimum human daily requirement of chromium for optimal health is not known, but a daily ingestion of 50 to 200 micrograms per day has been estimated to be adequate (Gross and Heller, 1946).

The less toxic nature of trivalent chromium was reflected in the 1962 Drinking Water Standards set by the U.S. Department of Health, Education, and Welfare which placed a limit of 1.0 ppm trivalent chromium. The 0.05 limit was retained on hexavalent chromium.

Waste Streams Not Conducive to Stabilization

There are many different waste types which are not suitable for stabilization, or do not require it, such as:

1. Solid, non-hazardous waste require no treatment.
2. Non-aqueous hazardous wastes and solvents are best treated by other means such as recovery, recycling, or incineration.
3. Hazardous and non-hazardous solid, semi-solid waste, or liquid wastes with high metal constituents (e.g. 30% Nickel) should be sent to a recycler through a metals recovery program.
4. The presence of high concentrations of soluble or insoluble organic compounds (greater than 25%) may adversely affect the curing of the solidified product.

Therefore, chemical stabilization/solidification could be used for waste that are aqueous (or less than 25% organic) and whose metal concentration is insufficient for recycling. When these wastes cannot be feasibly reused in any beneficial way, there is no other recourse but land disposal. Even when other techniques are used, they usually generate residues that are themselves hazardous. One example is the ash produced for the incineration of hazardous wastes (Jones, et al, 1982). Also, in the cleanup of abandoned sites under the Superfund program and the remediation of other old disposal practices by private entities, on-site or in situ treatment and disposal often remain the safest and least expensive alternatives.

Rational for Land Disposal

Land disposal of hazardous wastes is not the method of choice from an environmental standpoint. In fact, land disposal occupies the lowest position in the EPA's hierarchy of methods (Jones, et al, 1982). Nevertheless, land disposal is developing an increasing important place in the overall waste management scheme of the future for several reasons. For example, there are many hazardous wastes that are simply not amenable to techniques such as thermal, chemical, or biological destruction. When these wastes cannot be feasibly reused in any beneficial way, there is no other recourse but land disposal. Even when other disposal treatment techniques are used, these techniques usually generate residues that are themselves hazardous. One example is the ash produced from the incineration of hazardous wastes. Another example is the cleanup of abandoned sites under the Superfund program and remediation of other old disposal practices by private entities. Therefore, land disposal of certain types of wastes remains a safe and one of the least expensive alternatives. A good example is a spill of a metal plating solution onto the Earth, the concentration of chromium is simply too small to reclaim economically (Landreth and Mahloch, 1977).

CONCERNS WITH LAND DISPOSAL

A major concern with landfilling is the potential release of contaminants and the consequent contamination of ground and surface waters. Past experiences have shown us that unless precautionary measures are taken, long-term adverse environmental impacts could result and remedial actions are very costly, if not impossible. It is important that even if the physical integrity of the treated waste is not maintained the waste should not leach contaminants into the soil or groundwater. Disintegration, resulting in the generation of small particulates, or the formation of cracks, would increase the apparent permeability of the solid matrix. Such deterioration in physical integrity could be caused by adverse climatic conditions, such as changes in temperature which cause repeated freeze-thaw or wet-dry cycles (Bokkan, 1978). Even if the treated wastes are eventually buried under soil layers, which would minimize such effects, there is still an intermediate period during which these wastes are exposed to such adverse conditions. Therefore, at locations where freeze-thaw/wet-dry cycles occur, measurements of ability to withstand these conditions are an important and integral part of the stabilization/ solidification process evaluation. Unfortunately, at the present time there are no standard test parameters for the simultaneous analysis of physical integrity (freeze/thaw, etc.) and leachability of contaminants (Lindsey, 1975).

Alternative Remedial Options

Available technologies for treating soils contaminated with hazardous levels of heavy metals are expensive and include:

A. Excavation, transportation and disposal of the contaminated soil/waste in a hazardous waste landfill.

B. Excavation, treatment (ex situ), transportation and disposal of the contaminated soil/waste in a hazardous or a non-hazardous waste landfill, depending on the classification of the waste.

C. Soil washing: The treatment could include washing of the soil with a dilute acid to leach the heavy metal contamination into groundwater. A pump and treat system would be necessary to bring the ground water to the surface for subsequent pH adjustment and lime precipitation.

In situ chemical reduction and stabilization of the contaminated soils, which when completed, could be left in place (Malone and Larson, 1983).

Environmental Regulations Pertinent to Stabilization/Solidification

Most of the impetus for chemical stabilization/ solidification has been provided by the Resource Conservation and Recovery Act (RCRA) of 1976, including the subsequent 1984 HSWA (Hazardous Solid Waste Amendment), and the Comprehensive Environmental Response,, Compensation and Liability Act (CERCLA), otherwise known as Superfund.

Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) included provisions for developing criteria to determine which wastes are hazardous, and to establish standards for design and operation of disposal facilities. The HSWA reauthorized RCRA and made changes, including the establishment of more specific criteria and strict deadlines for regulator action and compliance. Regulations promulgated under both RCRA and HSWA direct in detail the generation, handling, treatment and disposal of wastes.

The disposal of hazardous liquid, sludge, or semi-solid waste has been a controversial issue since the passage of the Resource Conservation and Recovery Act (RCRA) in 1976. Prior to RCRA the disposal of liquid waste, other than by underground injection, was regulated under the authority of the Clean Water Act or controlled through State laws. In the first liquid-waste-disposal regulations proposed under RCRA in December 1979, EPA believed that bulk liquids, sludge, and semi-solid wastes could be placed in a landfill under certain controlled conditions, such as with a secure liner and a system for the collection and removal of leachate (USEPA, 1986d). If these measures were not available, EPA required treatment by mixing the waste with materials such as fly ash, or cement kiln dust to stabilize or solidify the waste to ensure that free liquids were no longer present. EPA defined free liquids as those that will readily separate from the solid portion of a waste under ambient temperature and pressure.

Hazardous Solid Waste Amendment (HSWA)

The HSWA landbans were designed to prevent environmental degradation when the residuals are disposed of in uncontrolled landfills, or in the event that all the protective measures of a secure landfill at TSD facilities fail. In the promulgation of the various landbans, specific technologies are specified as "best demonstrated available technology" (BDAT). Chemical stabilization/solidification treatment is one of the most important BDATs, and will continue to be in the future (USEPA, 1988b, 1989).

Comprehensive Environmental Response, Compensation and Liability Act

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980, as amended by the Superfund Amendments and Reauthorization Act (SARA) of 1986 provides for federal authority to respond to releases of hazardous substances to air, water and the land. CERCLA authorized EPA to revise the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) to include responses to hazardous substance releases. The NCP defines methods and criteria for determining the appropriate extent of removal, remedial, and other measures. Specific techniques mentioned in the NCP for remedial action at hazardous waste sites include solidification/stabilization techniques for handling contaminated soil, sediment and waste. In fact, solidification/stabilization has been designated a "best demonstrated available technology" (BDAT) under SARA, and to the present-date is the second most frequently selected method for source control at Superfund sites. (Weisman, et al, 1988a, 1988b). Although it has been applied mainly to inorganic contaminants, recent experiences with organic materials show promise as well.

Environmental Regulations Concerning In Situ Treatment

In situ stabilization/solidification of hazardous waste is considered treatment under RCRA because it changes the chemical and/or physical characteristics of the waste in order to render it non-hazardous or less hazardous, or easier to manage (USEPA, 1980).

If in situ treatment is used to treat hazardous waste in a RCRA-regulated unit, unit-specific standards would be pertinent. However, in many cases in situ treatment will be used as part of a RCRA Corrective Action or CERCLA cleanup to treat wastes that have breached any unit boundaries that may have existed, and unit-specific standards would not apply. In these cases, because the waste treated in situ will remain in place over the long term, in situ treatment is usually governed by site-specific cleanup standards, which are often risk based.

If contaminated soil is a "characteristic waste" (40 CFR 261), the cleanup standards would be the regulatory levels in the leachate of the EP Toxicity or TCLP test, independent of treatment of the contaminated soil, in situ or ex situ.

Since hazardous wastes treated in situ will be left in place, provisions regulating closure and post-closure of disposal facilities may apply. Disposal or landfill closure requires capping and post-closure care, including groundwater monitoring for at least 30 years. "Clean" closure of a RCRA unit requires removal and/or decontamination that would allow the site to remain without care or supervision after closure. At the present time, draft guidance defining performance standards for clean closure are health-based standards for constituent concentrations determined by total waste analysis.

Therefore, because in situ treatment does not involve excavation or placement of the waste to be treated, it appears that RCRA requirements would be applicable only if: 1. the waste to be treated in situ was found to be a RCRA hazardous waste, and the hazardous waste was disposed after the effective date of the RCRA requirements and 2. the waste contained free liquids.

EPA Hazardous Wastes

The treatment standards and disposal options for all hazardous wastes are dependent upon how the U.S. Environmental Protection Agency has defined that waste. Basically, EPA has two broad classifications of wastes, "Listed" and "Characteristic" wastes.

Characteristic Wastes. A "characteristic" hazardous waste is a RCRA solid waste which meets one or more of the characteristics of hazardous waste presented in Title 40 CFR Part 261-Subpart C (Sections 261.20 through 261.24). These waste are generally referred to as "D" wastes. All characteristic wastes fall in the following four (4) general categories:

Ignitability: Wastes which have a flash point less than 140 F,

Corrosivity: Wastes which have a pH of 2.0 or less or a pH of 12.5 or greater,

Reactive: Wastes which react violently with water or are unstable or generate toxic gases (sulfide or cyanide) when mixed with water or acid, and

Toxicity: (Extraction Procedure (EP) Toxicity or TCLP): Wastes which fail the leaching test for hazardous waste. In 1989, the eight heavy metals were As (D004), Ba (D005), Cd (D006), Cr (D007), Pb (D008), Hg (D009), Se (D010), and Ag (D011). In addition, there were six (6) pesticides and herbicides.

Characteristic hazardous wastes can be treated so that they no longer exhibit any characteristics of hazardous waste. At such time, they are no longer regulated as hazardous waste and can be sent to a non-hazardous waste disposal facility using a general transporter and without requiring a waste manifest. In certain instances these treated non-hazardous wastes may also be left in place.

However, as long as a "Characteristic" hazardous waste continues to exhibit any of the characteristics of a hazardous waste, they are regulated as hazardous waste and must be transported, manifested and disposed of in the same manner as "listed" hazardous waste.

Listed Wastes. A "listed" hazardous waste is a RCRA solid waste which is listed as a hazardous waste in the tables within Title 40 part 261, Subpart D, Sections 261.31, 261.32, or 261.33. Under current law, all "Listed" hazardous waste and mixtures of "Listed" hazardous waste and non-hazardous waste are forever regulated as hazardous waste irrespective of their subsequent treatment. They must be manifested as hazardous wastes and shipped via licensed hazardous waste transporters to licensed hazardous waste disposal facilities. Deliberate mixtures of any of these "listed" wastes with any volume of non-hazardous waste are also considered to be listed hazardous waste in their entirety.

Contained-In Rule

The Environmental Protection Agency's "contained-in" rule states that environmental media (ground water, soil and sediment) are not considered solid wastes in the sense of being abandoned, recycled, or inherently waste-like as those terms defined in 40 CFR 261. Therefore, a remediation of a characteristic waste, rather than a listed waste, the soil/waste mixture are not considered a hazardous waste via the "mixture" rule or the "derived-from" rule. Therefore, once the RCRA characteristics of this waste have been removed it no longer needs to be managed as a hazardous waste.

Free Liquid Determination

During the early 1980's, EPA proposed additional regulations to control the disposal of liquid waste. These included the use of a paint filter test to determine the presence of free liquids in sludges, semisolids, slurries, and other wastes. USEPA was particularly concerned with the disposal of containerized liquid wastes because of possible leachate generation and subsidence of the final landfill cover as a result of container degradation (USEPA 1986d). On November 8, 1984, the Hazardous and Solid Waste Amendments (HSWA) to RCRA were signed into law. These amendments significantly expanded both the scope and requirements of RCRA and specifically addressed the issue of liquid waste disposal. Section 3004(c)(1) of HSWA states:

> "Effective 6 months after the date of enactment of the Hazardous Solid Waste Amendments of 1984, the placement of bulk or noncontainerized liquid hazardous waste or free liquids contained in hazardous waste (whether or not absorbents have been added) in any landfill is prohibited."

This Congressionally mandated, absolutely banned the placement of bulk liquids in a landfill for any purpose or length of time, regardless of the presence of liners or leachate collection systems. This ruling was effective on May 8, 1985.

Section 3004(c)(2) of HSWA further requires EPA to promulgate regulations within 15 months that will:

> "Minimize the disposal of containerized liquid hazardous waste in landfills, and minimize the presence of free liquids in containerized hazardous waste to be disposed of in landfills. Such regulation shall also prohibit the disposal in landfills of liquids that have been absorbed in materials that biodegrade or that release liquids when compressed as might occur during routine landfill operations."

This legislative history of these amendments reveals that Congress considered prohibiting entirely the placement of all liquids, containerized or not, in a landfill, but later reconsidered containerized liquids, particularly those designed to hold small quantities, such as ampules or lab packs (U.S. EPA 1986d).

To comply with Section 3004(c)(1), an owner or operator must first use the Paint Filter Liquids Test (U.S. EPA 1986b) to determine whether a waste is liquid or contains free liquids. If the sample passes the test, the waste is not subject to the ban. If it does not pass, the waste must be chemically, thermally, or biologically treated prior to landfilling by the application of a technology that does not involve the use of a material that functions primarily as a sorbent (including both absorbents and adsorbents). The purpose of this congressional ban on sorbents is to force the use of treatment technologies that are not reversible, such as chemical stabilization/solidification. An absorbent may release the absorbed liquid back into the landfill but chemical stabilization/solidification renders liquids permanently unavailable to the environment. It was EPA's intention or emphasis to address a permanent solution, not a temporary alternative (U.S. EPA 1986d)

The use of a sorbent as part of the chemical stabilization process can make it difficult to determine whether true stabilization has taken place. If there is any doubt, the EPA guidance document "Prohibition on the Disposal of Bulk Liquid Hazardous Waste in Landfills-Statutory Interpretive Guidance" recommends the use of an unconfined compressive strength test as an indirect method for determining the extent to which the waste has been chemically transformed into a solid state (USEPA, 1986d). The test should be modeled on ASTM D2166-85, Unconfined Strength of Cohesive Soil. This test is applicable to a wide range of stabilized wastes, regardless of the specific waste type or stabilization process used. A minimum strength of 50 psi is recommended as a measure of adequate bonding. The rationale for selecting this value is an attempt to require a bonding level in excess of that achieved with sorbents. A minimum compressive strength limit of 50 psi should assure that the treated waste has at least as much strength as the soil surrounding the disposal site. The 50 psi was based on a 100 ft landfill depth and an overlying material bulk density of 70 lbs/cu ft. (U.S. EPA 1986c).

Paint Filter Test

Stabilization/solidification technology has long been used at land disposal sites for attaining the "no free liquids" requirement of the Hazardous and Solid Wastes Amendments of 1984 in the Resource Conservation and Recovery Act (RCRA). The regulations do not permit the use of a material that functions primarily as an absorbent. It must be demonstrated that the individual material irreversibly binds a particular liquid through a chemical reaction (chemisorption) rather than through the weak forces of absorption or adsorption (USEPA, 1989).

Since chemisorption reactions are specific to the chemical structure of the sorbent and waste material, the irreversible binding must be demonstrated for each particular reagent/waste combination, (Bishop, 1986). EPA suggests (USEPA, 1986c) that this be accomplished by the indirect chemical stabilization test (ICST) based on the unconfined compressive strength of the treated material. EPA has interpreted the statutory language as banning the placement of treated bulk liquid hazardous wastes in a landfill prior to the treated material passing the paint filter test (PFT), (50 FR 18370).

The Paint Filter Test (USEPA Method 9095-SW846) is used to determine the presence of free liquids in a representative sample of bulk (or noncontainerized) waste. The test is required by RCRA 40 CFR 264.314 and 265.314 and is used to determine if a material releases free liquids. In addition, EPA recommended cement kiln dust as a nonbiodegradable sorbent to be used for the removal of water.

The American Nuclear Society has a test similar to the Paint Filter Test, the Allowable Drainable Liquid Test (ANS 55.4). The EPA's Office of Solid Waste and Emergency Response is proposing that the Liquid Release Test be used in conjunction with the Paint Filter Test. In the December 24, 1986, Federal Register, the EPA proposed the use of the Liquid Release Test to test for release of liquids from nonbiodegradable absorbent mixtures when a waste is under compressive forces of a landfill. The proposed Liquid Release Test calls for the application of 50 psi pressure to the waste sample to determine if liquids will be released under compressive forces.

Financial Impact

In 1989 the cost for the remediation of 10,000 cubic feet of hexavalent chromium-contaminated soil, which includes in situ chemical reduction of hexavalent chromium and the subsequent chemical stabilization/solidification, was about $29,000.00 as compared to the traditional remediation technique of excavation and landfilling which would have cost about $88,000.00. In 1991 the cost of in situ treatment rose about 8% per year to about $34,000 but the traditional technique (excavation and landfilling) increased 132 percent to about $201,000.00

There are numerous reasons for the significant cost savings in the use of in situ stabilization/solidification using cement kiln dust (CKD) as compared to the traditional remediation technique of transport and disposal. These reasons are: 1) cement kiln dust is a waste product, therefore it is relatively inexpensive compared to Portland cement or other virgin materials, 2) it is significantly more cost effective to treat a waste on-site (in situ). In many instances the waste needs to be handled only once, and 3) it is significantly more cost effective to leave the treated waste onsite rather than offsite which requires transportation and disposal.

Scope of Impact

According to EPA estimates, (USEPA, 1984), of the approximately 5,700 non-federal Treatment, Storage or Disposal (TSD) facilities in the United States, about 62% of these facilities have suspected releases of hazardous constituents. Therefore, EPA estimates the total national costs of implementing the remedial action would be for non-federal facilities between $7 billion and $42 billion dollars. The modeling indicated that the proposed rule will require cleanups lasting more than 75 years at nearly 50% of the facilities, even assuming that the cleanup goals will be based on health-based standards, not background levels.

Economics of In Situ Treatment

Selection of on-site disposal is rapidly becoming one viable economic option, with the limited sites available for industrial waste disposal. The costs associated with hauling and disposal are in many cases prohibitive, and if deemed to be the only available option, would sharply curtail the rate that waste sites are remediated. When it is determined that waste materials are to remain on-site, stabilization and solidification is in many cases the only option available.

An example of the potential application of the in situ chemical stabilization/solidification for the remediation of spills of hazardous substances can be found in the New England area. The New England states of Massachusetts, Rhode Island, Connecticut, Vermont, New Hampshire and Maine constitute an area where hazardous waste disposal has been a significant problem. No secure hazardous waste (Class C) landfills are found in all of New England. All hazardous waste must be transported (often at great expense) to the nearest secured landfills in either western New York State or in New Jersey. Because of the expense involved, spills of hazardous substances are commonly disposed of illegally in municipal, unsecured landfills or in other illegal ways (blending with home heating oils). Such practices have been documented in Massachusetts by Fennelly, et al, (1977). These authors suggest that up to 44% of all hazardous wastes are disposed of illegally in Massachusetts.

Economic Utilization of Cement Kiln Dust

One of the most comprehensive reviews of applications for cement kiln dusts has been completed by Davis and Hooks, (1974, 1975). Although only a small portion of this dust is presently being utilized, its high potassium and lime content make waste kiln dust potentially valuable in acid neutralizing capacity for the treatment of acid wastes and chemical stabilization/solidification. Its high pH tends to keep metals in their most-insoluble forms (i.e., as hydroxides, silicates and carbonates), which helps minimize subsequent leaching. Unfortunately, the United States has the lowest rate of cement kiln dust utilization of any industrialized country in the world, but interest is growing in marketing opportunities for the product. The wasted dust represents about 10 million dollars worth of lost materials per year, in addition to the amount of energy expended to grind and partially calcine it. It is estimated that an excess of 20 to 24 million tons of fresh kiln dust is generated annually by cement and lime manufacturers. In addition to fresh kiln dust, there is well in excess of 200 million tons of kiln dusts in stockpiles throughout the country (Davis and Hooks, 1974, 1975). Utilization of this dust would alleviate costly pollution control measures that are required to prevent degradation of air, land and water in the vicinity of dust disposal sites. In spite of the efforts of many in the cement and lime industries, about half of the kiln dust collected each year must still be disposed. At many plants, virtually all dust produced (100,000 tons per year) is wasted due to lack of available markets (Mullen, et al, 1978). Kiln dust disposal is thus an increasing financial and environmental burden to cement and lime producers.

Beneficial Reuse of Waste-Product

In the future, as available landfill space becomes depleted, one goal of chemical stabilization using CKD should be the utilization of the waste product as a commercial construction material. This goal has not been universally accepted due to the lack of available field data on the suitability of stabilized material for construction and an inherent fear of the toxic nature of certain industrial sludges (Patterson, 1985). The major consideration in sludge treatment has usually been economics. As long as doubts exist as to the safety of using "toxic wastes" in construction, there is little incentive for expending the money and effort to produce a stabilized sludge with specific physical properties used in construction (Collins, et al, 1983). In 1980, EPA published their research on this matter which demonstrated the enormous economic, environmental and energy conservation advantages of using pozzolanic stabilized pavements such as cement kiln dust in lieu of traditional pavement materials. In 1982, pozzolanic pavements would have resulted in savings, compared to comparable asphalt pavements, of over $30,000.00 per mile, in addition to the conservation of over 100,000 gallons of oil. Nationally, that is almost one billion dollars in cost savings, 20,000 tons of recycled materials, and over 35,000,000 barrels of oil conserved.

EPA'S Current Analysis for Leaching

The environmental acceptability of a hazardous waste for land disposal in the United States is largely based on the leachability results obtained from performing the U.S. Environmental Protection Agency Extraction Procedure (EP) test or Toxicity Characteristic Leaching Procedure (TCLP) test (USEPA, 1986a). In the EP test, the waste is contacted with a mild acetic acid leachate for 24 hours, after which the leachate is analyzed for specific metals which may have leached. The TCLP test expanded the EP test procedure and adds additional compounds to be tested for. Both leaching tests are designed to address the mobility of both organic and inorganic compounds and to apply compound-specific dilution/attenuation factors generated by a groundwater transport model. The purpose of both tests is to simulate the potential for leaching which would occur if the waste was disposed in a municipal landfill along with other general refuse (USEPA, 1986c). These EPA approved test procedures may be valid for general solid waste testing, but they are not suitable for solidified/stabilized wastes because the alkalinity in the waste should neutralize the acid present in the leaching solution (Barth, 1990). The newer TCLP test should improve testing of general solid wastes, but it still does not address the unique problems associated with testing of stabilized/solidified wastes, (e.g.) high alkalinity. In addition, neither leaching protocol adequately addresses the potential effects of acid pH values, freeze-thaw/wet-dry, co-solvents or the combined (synergistic) effects and the differences concerning the liquids-to-solids ratio on leaching from waste forms. Both leaching tests were intended to observe only short-term leaching potential of the waste, and are not suitable for long-term studies where the waste alkalinity may eventually become depleted so that leaching will occur under acidic conditions. Therefore, the technical problems with the EP-Toxicity (or the newer Toxicity Characteristic Leaching Procedure-TCLP) are that both were designed for a specific regulatory purpose, not for chemical stabilization/ solidification of wastes. In addition, both leachate tests are allowed to go to equilibrium. No information can be deduced on the rate of release or its dependence on time. In a dynamic leaching "fresh" leaching agents are used after certain periods of liquid-solid contact have elapsed and the solid and leachate are separate. Hence time-related behavior could be deduced and used for long-term prediction of leaching rates.

Conditions in a Landfill

The conditions of the landfill will have a strong correlation on the landfill failing and allowing pollutants to leach into the subsurface and/or groundwater. Such conditions include amount and acidity of rainfall, organic co-solvents, permeation rate into the landfill, temperature variations, freeze-thaw cycles, exposure to ultraviolet light, effects of biological organisms in both aerobic and anaerobic situations, and amount and quality of infiltration groundwater.

Mobility of Heavy Metals

The mobility of heavy metals in the soil and groundwater environment is affected by the soil organic matter content, hydrous metal oxides, cation exchange capacity, pH, oxidation-reduction potential, particle size and permeability (Geraghty and Miller, 1985). Surface soils typically retain the heavy metal cations in the upper few feet of strata, which contain the highest organic matter. The various heavy metal species have different mobilities under different pH conditions. For example, under alkaline conditions, divalent cadmium has low mobility but hexavalent chromium has much higher mobility. These variations of mobility under different pH conditions have considerable impact under multiple metal contamination conditions. Once the toxic metals reach the saturated zone, their transport in the ground water is an environmental and health hazard. Contaminant metals in the soil/water can be removed by adsorption and/or precipitation. Adsorption in soils is defined as the adhesion of dissolved substances to the surface of soil solids with which they are in contact. Precipitation involves the formation of a solid phase which has low solubility in soil water (Hatton and Pickering, 1980). Different mechanisms can be operative for the removal of the metal ion from the soil/water onto a solid surface: physical adsorption and penetration onto a solid surface. Physical adsorption occurs through weak atomic and molecular attractive forces (Van der Waal forces). This process is important for metal retention in soils because it can lead to other stronger attractions, such as chemical adsorption. Chemical adsorption occurs when chemical bonds form that are more ionic in nature between an ion in the soil solid phase and an ion that was formerly in the soil solution. Insertion or penetration of an ion into the solid mineral phase may occur as a consequence of chemical adsorption. This reaction is frequently irreversible and time-dependent (Van Der Sloot and Wijkstra, 1987).

Most heavy metals become less mobile in soils with an increase of pH. This observation can be explained by the precipitation of heavy metal hydroxides, changes in the carbonate and phosphate concentrations in the soil water, adsorption and desorption of metals by hydrous oxides and organic matter, and the formation and dissolution of the effect of Fe and Mn oxides. The heavy metals Cd and Zn are illustrative of the effect of pH of mobility. Cadmium exists in the divalent form to pH 7.8 and only 50 percent is converted to the precipitate $Cd(OH)_2$ at pH 11. On the other hand, 50 percent of zinc is in the $Zn(OH)_2$ form at pH 7.5. This comparison suggests that a given pH, zinc will be less mobile that cadmium in a soil system (USEPA, 1984).

<u>Interaction of Soil and Contaminant Metals</u>. Heavy metals which are added to soils react with the soil components in a variety of ways. These reactions can be generally classified as ion exchange, adsorption, precipitation and complexation. The reaction mechanisms and rates are dependent upon the type and amount of the organic matter, clay and hydrous oxides present in the soil. Additional factors are the exchangeable cations, soil reaction, oxidation-reduction potential (Eh), soil water composition, and concentration (Geraghty and Miller, 1985). These additional factors are dynamically affected by the physical and biological properties of the soil and any investigation of soil-heavy metal interactions must consider the whole soil continuum. Metal ions may be bound to soil particulates by a combination of forces ranging from electrostatic to covalent forces. When stronger covalent bonding dominates, certain cations are specifically bound

and the reversiblity of exchange decreases. This type of bonding occurs in organic matter, clay and hydrous oxides.

Void Structure. The void structure within the soil has a major impact on both the transport and immobilization potential of the contaminant metals. The void structure is highly dependent on the distribution of grain size and degree of compaction, which is a function of soil history (Barto and Palermo, 1977). The size and continuity of voids determine the migration paths through the soil. The resistance of the migration paths to soil water flow is called the permea-bility of the soil. The migration of the heavy metal ions (such as chromium) and the treatment chemicals (such as cement kiln dust) is dependent on the transport paths. These voids can be categorized as connected macro voids, micro voids and isolated voids. Solution and gases within the soil move easily through connected macro voids but require a disruption in the soil and/or a driving force to enter or pass through micro voids or isolated voids. Variation in the soil environments and weathering with time can liberate potentially mobile constituents trapped in these isolated voids, such as cations, which are temporarily in solution (Cote and Hamilton, 1982).

The several types of voids in hydrated cement/CKD paste have great influence on its final properties of strength, durability, and permeability. The smallest voids, which occur within the hydrated calcium silicate gel structure, are 0.5 to 2.5 nm in diameter. They account for about 28 percent of the porosity in solid hydrated calcium silicate. These small voids have little effect on the strength and permeability of the final product but appear to be important in drying shrinkage and creep.

Capillary voids account for the larger spaces which are not filled with solid components. In well-hydrated, low water/CKD ratio mixes, capillary voids range from 10 to 50 nm. It is generally held that pore size distribution, and not simply total capillary porosity, is a better criterion for evaluating the characteristics of a stabilized product. Capillary voids larger than about 50 nm are thought to be detrimental to strength and permeability, while voids smaller than 50 nm are more important to drying shrinkage and creep. Capillary voids limit the strength of concrete by acting as "stress concentrators" (Davis and Hooks, 1974).

The third type of voids, usually called "air voids," are generally spherical and usually range from 0.05 to 0.2 mm but may range up to 3 mm. Air voids are usually introduced intentionally into the hydrated CKD paste to increase the resistance of the final product to freeze-thaw (frost) damage even through they typically adversely affect its strength and permeability.

Depending on the environmental conditions, the voids are capable of holding large amounts of water. Capillary water (in voids 5 nm or larger) is bulk water that is largely free from attractive surface forces. Water in voids greater than about 50 nm is considered free-water since its loss causes no shrinkage in the final product, while loss of water held by capillary tension in voids from about 5 to 50 nm may cause some shrinkage.

Leaching Properties. From an environmental standpoint, the most important standard to be applied to chemical stabilization/ solidification methods is concerned with the leachate. Leachate is the fluid resulting from percolation or permeation of rainwater or ground water through, around or over a landfilled waste. Downward-infiltration precipitation often moves into and through the hazardous wastes, thereby dissolving certain constituents and leaching them. Surface runoff may eventually remove some constituents of the hazardous waste at some sites. Finally, gaseous by-products of decay or sublimation may move upward through evaporation and/or transpiration and eventually be released in the atmosphere (Conner, 1977). It is known that many "insoluble" metal hydroxides such as chromium produced in neutralization systems are solubilized quite easily under acid conditions, due to their amphoteric nature. This means that the hydroxides can act as acids or bases. If the metal hydroxides encounter pH conditions other than 7.5 to 9.0, the metals can quickly redissolve and re-enter the ground water or surface water (Geraghty and Miller, 1985). It is the lack of amphoteric nature that makes silicates a preferred material for reaction with metal ions that must be placed in ground water conditions.

Previous researchers have determined that, under mild leaching conditions, diffusion within the solid matrix usually controls the transfer of contaminants from the solid to the surrounding liquid phase (Cote and Webster, 1987). It is assumed that before immersion of the solid in water, the solid is in chemical equilibrium and the chemical potential of any given species is the same anywhere in the solid. When the solid is placed in water, however, the chemical potential of the species in the water phase is less than that on the solid surface, which leads to a flux of mass between the surface and the solution (Bishop, 1988). This in turn creates a gradient in chemical potential in the solid adjacent to the surface, and migration of the species from the interior of the particle toward the surface, a bulk diffusion process. The flux of the species at some position inside the solid can be described by concentration gradient diffusion according to Fick's first law. This model assumes continual renewal of the leachate so that contaminant concentrations do not increase in the leachate, which would lead to a change in surface flux. Therefore, the model is best used with continuous flow or multiple batch leaching test, rather than static single batch leaching procedures.

The most widely accepted model for leaching from stabilized/solidified wastes is that proposed by Joy (1988). This model assumes that leaching is controlled by diffusion through the solid, a uniform initial contaminant concentration in the solid, and a zero surface concentration (contaminant dissolves into the bulk liquid from the surface immediately). The model takes the form:

$$\frac{(a_n)}{A_o} \times \frac{(V)}{S} = 2 \, \frac{(D_e^{0.5})}{} \; t_n^{0.5}$$

where:

a_n = contaminant loss during leaching period n, mg

A_o = initial amount of a contaminate present in the specimen, mg

V = volume of the specimen, cm3

S = surface area of the specimen, cm2

t_n = time to the end of leaching period n, seconds

D_e = effective diffusion coefficient cm2/sec.

The American Nuclear Society (33) recommends use of this model for evaluation of leaching from solidified radioactive wastes. They suggest that the results be presented as a leachability index, LX, equal to the negative logarithm of the effective diffusivity:

$$LX = \frac{1}{7} \, \mathrm{LOG} \, \frac{1}{De}$$

This index can be used to compare the relative mobility of different contaminants on a uniform scale that varies from 5 (De = 1 E-5 cm2/sec, very mobile) to 15 (De = 1E-15 CM2/SEC, immobile).

The leaching model presented above can be modified to include the leachability index :

$$\frac{a_n}{A_o} = 1.128 \, (10^{-.5LX}) \, (t_n^{0.5}) \, \frac{(S)}{V}$$

This model accounts for most of the variables discussed earlier which can have an effect on heavy metal leaching from stabilized/solidified hazardous wastes, namely waste speciation (De), particle size (V and S), and initial contaminate concentration (Ao). When used with the results from a multiple extraction or continuous flow leaching procedure, rates of leaching can be determined.

External Forces/Leachability Relationship

The stabilized waste product will be exposed to many external forces once landfilled or left in place. Each of these external forces may cause it to leach contaminants into the subsurface which could eventually pollute ground water. Examples of these external forces are: acid rain, wet-dry/freeze-thaw cycles, co-solvents and the different combinations of these forces (synergistic effects).

Rainfall Activity

The acidity of rainfall can have a significant impact on the solubility of metals because the solubility of most metals is directly dependent upon pH. Acidic pHs tend to solubilize metals into the leachate. Once these metals are solubilized they can easily move through the subsurface soils and into groundwater (Forster and Wittman, 1979). Normally, high pH is desirable because metal hydroxides have minimum solubility in the range of pH 7.5-11. In principle, any environment where the pH is less than about 12.5 could be considered an aggressive one because any reduction of alkalinity in pore fluid will eventually lead to destabilization of the principal cementitious hydration product. The rate of chemical attack on the stabilized/solidified waste product is a function of the pH of the external fluid, its buffering capacity, and the permeability of the stabilized/solidified waste product (Jones and Malone, 1982). In general, pH levels above 6 cause such a slow reaction that they can be neglected. However, natural CO_2, sulfates, and chlorides common in ground and rain waters may result in aggressive solutions below pH 6, which can be detrimental to the stabilized/solidified waste product.

Theoretically, a pH of 7 should be the pH value of pure water. Water droplets formed by condensation in the atmosphere normally have a pH close to a value of 7 before being acidified by CO^2 and either sulfates or nitrates.

Acid Rain

Most rainwater is acidified by at least 2 processes (Glass and Glass, 1979):

1. The dissolution of atmospheric CO2 in rainwater produces equal concentrations of H^+ and HCO_3^-:

   $$CO_2 + H_2O \text{ ---> } H^+ + HCO_3^-$$

   The carbonic acid dissolved in the rainwater tends to lower the pH. This acid is very weak, and at equilibrium with CO2 the pH of rainwater would be about 5.67.

2. Much of the sulfur oxides entering the atmosphere are converted to sulfuric acid. Data from the eastern United States indicates that approximately 60-70 percent of the acidity in acid rain is due to sulfuric acid (Shaw, 1979). A typical reaction is:

$$2SO_2 + O_2 \;\text{-->}\; 2SO_3$$

$$SO_3 + H_2O \;\text{-->}\; 2H^+ + SO_4^{2-}$$

Sulfuric Acid is the main culprit in the acid-rain problem and is now a major pollution problem in some areas. By the early 1970's, individual pH values from 2 to 6 were measured in various part of the world, with yearly averages between 4 and 5. Acid rain can have severe detrimental effects on aquatic life, forest and crop productivity, and may leach heavy metals from soils, rocks and the sediments of lakes and streams.

Freeze-Thaw/Wet-Dry Cyclical Effects

Long-term durability of the stabilized/solidified waste product is a prime consideration in designing and specifying a waste stabilization/solidification system. Predicting the long-term integrity of the final waste form requires considering all possible modes of failure. For cementitious stabilized/solidified products, water is generally involved in every form of deterioration; and in porous solids, permeability of the material to water usually determines the rate of deterioration. Internal movement and changes in the structure of water are known to cause disruptive volume changes of many types of products. Examples are water freezing into ice, formation of ordered structure of water inside fine pores, development of osmotic pressures because of different ionic concentrations and hydrostatic pressure buildup by differential vapor pressures (American Nuclear Society, 1986). All of these can lead to large internal stresses within a moist solid and to its ultimate failure.

In porous solids, water also acts as a vehicle for transport of solutes through the material, both aggressive ions into and waste materials out. Permeability of a stabilized product depends primarily on the water/CKD ratio (which determines the size, volume, and continuity of capillary voids) and the development of micro-cracks that occur between the CKD paste and the surface of included solids (such as aggregates or waste solids). The suspended particulates in waste sludges (acting as small aggregate) are typically very small (Forrest, 1987). In general, the smaller the suspended particles, the fewer the micro-cracks at their surface, and the lower the overall permeability of the final product. The primary consideration of permeability of the stabilized/solidified waste sludges of small particle then, is the water/CKD ratio.

<u>Freeze-Thaw Cycling</u>. Although there is generally a direct relationship between strength and durability, this does not hold in the case of frost damage. The freezing of water increases its volume by approximately 9 percent. When freezing in a capillary void, the added volume produces

large stresses on the stabilized/solidified waste structure unless the excess water can flow into larger voids as the specimen freezes. In a manner analogous to salt crystals, ice crystals forming at subfreezing temperatures can rapidly deteriorate water saturated stabilization/solidification waste products. The hydraulic pressure generated by the freezing pore water depends on the permeability of the material, the distance from the surface (escape boundary), and the rate at which ice is formed (Carter, 1983). Durability of the stabilized/ solidified waste products to freeze-thaw cycles can be provided by entraining small air bubbles into the CKD/waste paste which provides water escape boundaries. Small amounts of certain air-entraining agents added to the CKD paste (e.g., 0.05 weight percent of CKD) will bring about the incorporation of stable, 0.05 to 1 mm bubbles in the voids, the number of voids, and the void spacings. The degree of protection against freezing damage can vary a great deal.

The degree of water saturation also affects freeze-thaw damage. There is a critical degree of saturation above which stabilized material is likely to crack and spall when exposed to very low temperatures, usually between 80 and 90 percent saturation. Below the critical degree of saturation, freeze-thaw damage does not usually occur. A stabilized/solidified waste product may fall below the critical degree of saturation after adequate curing, but depending on the permeability, it may again reach or exceed the critical degree of saturation in a short time when exposed to a moist environment. In general, the higher the water/CKD ratio, or the lower the degree of hydration, the greater the amount of freeze-able water that will be present at any given temperature and humidity.

The freeze/thaw mechanism is of great concern to EPA, and was the primary reason in the change of EPA's protocol in sample size between the EP-Toxicity and TCLP. EPA feels that if a monolith is landfilled it will soon be broken down into smaller and smaller pieces, by the freeze/thaw cycle, creating a larger surface area and a greater chance for leaching.

Wet-Dry Cycling. There are two major mechanisms in which wet-dry cycles can effect the mechanical integrity of the stabilized waste products, these are:

1. Most stabilized waste products contain substantial amounts of salts and/or organic molecules with appreciable water solubilities. Concentrations of these materials at or below the surface of the solid where evaporation of pore water is occurring can cause the development of supersaturated solutions and the formation of salt crystals in the pores of the stabilized/solidified product. Damage to stabilized/solidified products due to wet-dry cycles may be to a large extent due to the cyclic dissolution and crystallization of contained salt. Crystallization occurs only when the concentration of the solute (C) exceeds the saturation concentration (Cs) at a given temperature.

Generally, the higher the degree of super-saturation (the ratio of C/Cs), the greater the crystallization pressure exerted on the solid structure. Values were calculated by Winkler (1975) in an effort to understand the rapid deterioration of stone and concrete monuments by smog and high-sulfate acidic rain. For example, at C/Cs = 2, Halite (NaCl) at 25 degrees centigrade produces 605 ATM (61 MPa) of pressure, and at C/Cs = 10, 2,020 ATM (205 MPa). These pressures are strong enough to disrupt the structure of the stabilized waste products which contain these constituents. Damage typical to this effect is the powdering or spalling of the subsurface of the solid materials which progressively deepens into the material as its porosity increases. Jones and Malone (1982) reported rapid deterioration of stabilized /solidified inorganic waste products produced by commercial stabilization/solidification vendors using ASTM standard test procedure D559-57 for compacted soil-cement mixtures (ASTM, 1976), and

2. Absorbed water is close to the surface (probably within 1.5 nm of the surface) and held by hydrogen bonding and Van de Wal forces. Loss of absorbed water, even in air of 30-percent relative humidity, is mainly responsible for the shrinkage and cracking of the solidifying mass. The water more tightly bound in the interlayers of the hydrated calcium silicate structure will be lost only in air if the relative humidities fall below 10 percent. The loss of water from the hydrated calcium silicate structure will cause considerable drying shrinkage.

Current Testing Methodology. The existing methods for measuring freeze-thaw/wet dry resistance do not address permeability of the waste, rather they were designed and developed as a Civil Engineering protocol for concrete and soil-cement mixtures.

The wet/dry durability test is used to evaluate the resistance of soil-cement mixtures to the naturally weathering stress of wetting and drying. The cured specimens are subjected to 12 test cycles, each consisting of 5 hr. of submergence in water, 42 hr. of oven dry, and 2 firm strokes on all surface areas with a wire scratch brush. Test results are generally expressed as weight loss after 12 cycles (ASTM, 1976).

The freeze/thaw durability test is used to evaluate the resistance of soil-cement mixtures to the natural weathering stress of freezing and thawing. The test specimen is subjected to 12 test cycles, each consisting of freezing for 24 hr., thawing for 23 hr. and 2 firm strokes with a wire scratch brush on all surface areas. Performance is evaluated by determining the weight loss after 12 cycles or the number of cycles to cause disintegration, whichever occurs first (ASTM, 1986). Therefore, both of these physical examinations may be appropriate to evaluate mechanical integrity of the soil/waste by measuring weight loss as an evaluation of freeze-thaw/wet-dry resistance, but do not address leachability of the contaminant from the stabilized waste product.

Co-Solvent Effects

Co-solvents, such as 1,1,1-Trichloroethane, have been shown to cause large increases in hydraulic conductivity of soil samples and slurry wall backfill materials. Organic solvents can change the hydraulic conductivity of clay particles, in general, by altering the electrical double layer that surrounds them which contracts the double layer which caused shrinkage of the soil, flocculation of soil particles, formation of cracks or macropores and a higher hydraulic conductivity (Brown, 1983). The thickness of the electrical double layer, based on the Gouy-Chapman theory for suspensions, is controlled by the dielectric constant, electrolyte concentration, and valence of the electrolytes in the pore liquid. The single most important characteristic of organic solvents is the dielectric constant (Fernandez and Quigley, 1985). Water has a dielectric constant of 83, while 1,1,1-Trichloroethane has a dielectric constant of only 3. A reduction of dielectric constant tends to cause a reduction in the thickness of the diffuse double layer which can lead to shrinkage and an increase of the hydraulic conductivity. This mechanism is thought to both be responsible for the large increase in conductivity and the destruction of the plasticity of soil (Forman and Daniel, 1986).

In addition, some co-solvents replace the water of hydration in the clay while others compete with water for the clay sites (Green, et al, 1981). These mechanisms could increase the amount of free heavy metals, such as hexavalent chromium, that are not sorbed by the clay particles. This increase of free heavy metals should increase the probability that these metals will leach into groundwater (Gibbons and Soundararajan, 1988).

Synergistic Effects

Synergistic effects, such as external forces like changes in pH, wet/dry-freeze/thaw, and co-solvents, may have a greater total effect than the sum of the individual effects. Unfortunately, very little, if any, synergistic research has been performed on stabilized waste/soil.

CHAPTER III

SPILL REMEDIATION

Introduction

On February 17, 1989 a waste spill occurred at a tenant of the Tulsa Airport Authority in Tulsa, Oklahoma. A sulfuric/chromic acid mixture was being removed from a plating tank by the use of a pump truck. The pump truck, after receiving the waste, rapidly began to overheat and to leak the waste from several seals. The pump truck was escorted to an earthen spill control dike, and a fire truck was used to cool the truck and dilute the spilled acid until the pump truck could be unloaded into a tank truck. During the event, an estimated 500 gallons of the sulfuric/chromic acid mixture was spilled on the ground. The waste was diluted with approximately 2000 gallons of water which eventually spread and sorbed into the top few inches of soil over an approximate area of 20,000 square feet. The designated 20,000 square feet spill area includes a 5 to 8 foot buffer zone between the actual perimeter of the spill and the line of hazard markers set up to secure the spill area.

This study investigates the in-place treatment (in situ chemical reduction of hexavalent chromium, neutralization and stabilization/solidification) of the top 6 inches of waste/soil of this spilled "characteristic" hazardous waste (D002 and D007) so that it no longer exhibits any characteristics of hazardous wastes (40 CFR 261.39). The treated/stabilized soil/waste was tested and permission was requested and received from the Oklahoma State Department of Health (OSDH) to leave the stabilized soil in place. Before any form of treatment, a composite soil/waste sample from the top six inches of the spill-site was analyzed and revealed a EP-Toxicity chromium of 6.36 mg/l which classifies the soil as a D007 hazardous waste (40 CFR 261). Therefore, by considering the entire top 6 inches of topsoil to have been contaminated, the top 6 inches would be treated and removed. The second 6 inches would then be analyzed to see if this layer had been contaminated. If this second layer was determined to have been contaminated, then this second 6-inch layer would be treated and removed with the third layer being tested. This testing and removal would be continued until the next 6-inch layer was found not to have been contaminated by the spill.

Treatability Study

Unfortunately, the stabilized/solidified process design was primarily empirical. The state of the art is not sufficiently developed for a process formulation to be designed on the basis of chemical characterization of the material to be solidified/stabilized alone. Stabilization processes must usually be adapted to a particular sludge. A trial and error method of process development is generally used due to the many complex chemical reactions involved that cannot be predicted in advance. In this method of process development, samples are prepared using different amounts and/or types of additives. A series of tests, which may include determination of both chemical and physical properties, is then conducted on the samples. In addition to determining the proper mix ratios between CKD, ferrous sulfate and the soil, the following information is also secured before the project can begin:

1. Safety problems in handling the waste. Safety problems with in situ chemical stabilization/solidification may involve fuming, heat development and volatilization of organic materials. Allowances may have to be made to adapt equipment for vapor control or cooling of reaction areas. Rapid addition of a reactive solidification/ stabilization agents (such as unhydrated lime) can cause rapid volatilization of organic compounds having low boiling points, with the possibility of a flash fire occurring. Heat transfer characteristics may be very different as a treatment or reaction system is scaled up and dimensions increases. With lower heat losses, temperatures can rise, causing reaction rates to accelerate and the treatment process to become self-promoting.
2. Waste uniformity and mixing properties. Mixing or

pumping problems can arise from variations in the consistency of the waste or soil. Mixing can also become a problem if the solidifying waste changes viscosity rapidly during setting.

3. Development of the in situ processing parameters and analytical techniques to measure treatment effectiveness. Processing parameters include items such as mix ratios, mix times, set times, and conditions of treated waste curing.
4. Volume increase associated with processing. All solidification procedures result in some increase in waste volume. This could affect the grade of land after an in situ project has been completed.

This treatability study should help to determine the minimum of additives required to produce a suitable product. Representative samples of the cement kiln dust, ferrous sulfate, etc. are obtained from the various sources of supply, and a purchase price is established for delivery to the waste site.

Sample Collection and Preservation

Samples of soil/waste were obtained with the use of a hand-auger. The samples were collected and preserved as per EPA protocol 7196A, Section 6. Soil/waste samples were obtained on a 50-foot grid basis (8 samples from the actual spill area) using a 3-in stainless steel hand auger. All sampling devices and tools were cleaned and decontaminated between bore-holes and sampling intervals. The contents of each waste/soil container (5-gallon plastic buckets) were stored at 0^{o} C until used and mixed immediately before use. The samples were subsequently transported to the laboratory for further testing using appropriate chain-of-custody and sample documentation procedures. No other processing (e.g., dewatering) was applied prior to the application of the various stabilization/solidification additives.

Regulatory Factors Affecting Mix Design

Regulatory factors can be expected to play a greater role in the use of stabilization/solidification technologies for managing hazardous waste in the future. But at the present time the only regulatory requirements that are specified by U.S. EPA are EP-Toxicity (40 CFR 261) and the Paint Filter Test (EPA Method 9095-SW 846).

Stabilization Mix Design

Stoichiometrically, a total of approximately 22,102,500 mg (absolute) of hexavalent chromium spilled, therefore the minimum amount of Ferrous Sulfate (reducing agent) that could be used for reduction is 383 pounds. To compensate for interfering reactions a 1.4 safety multiplier was used, therefore a total of 430 pounds of ferrous sulfate was used. Previous laboratory studies and experience in soil remediation has shown that a mixture of soil/waste to cement kiln dust at a ratio of 3:1 by volume provided the best mix.

The bench-scale laboratory sludge stabilization studies were then performed by compositing equal amounts of the eight (8) soil/waste samples obtained from the actual spill area into one sample. This sample was then pretreated with Ferrous Sulfate and Cement Kiln Dust. The ratio used for the soil to CKD was 3:1 by volume. The sample was allowed to set for 48 hours at room temperature. The sample-mix was then analyzed to determine if the treatment removed all hazardous waste characteristics as per 40 CFR 261.

Table 1 shows the analysis performed:

TABLE 1

CHEMICAL ANALYSIS OF TREATABILITY WASTE
BENCH-SCALE TESTING

EP-Toxicity	Result*	MCL
Arsenic	<0.001	5.0
Barium	<0.14	100.0
Cadmium	<0.006	1.0
Chromium	<0.05	5.0
Lead	<0.05	5.0
Mercury	0.0002	0.2
Selenium	<0.002	1.0
Silver	<0.02	5.0

*In mg/l in the extract
MCL: Maximum Concentration Limit (40 CFR 261)

Flashpoint (^{o}F)	= >140	>140
pH (10% w/v)	= 8.51	2>X<12.5
Reactivity Cyanide (mg/l)	= <1.0	
Reactivity Sulfide (mg/l)	= <0.1	

The chemical analysis clearly shows that the treatability study was successful in the removal/treatment of this characteristic waste, therefore task analyses were developed.

Task Steps for Remediation

1. Flagging and staking of spill area to designate area for soil treatment, as well as elevations which will result in the removal of the top 6 inches of soil. After the remediation of the first six inches of soil, the second six inches (6 to 12 inches deep) would then be analyzed to see if this layer had been contaminated.

Results: Completed with client and approved with a written contract for remediation.

2. Mix and apply the ferrous sulfate solution. This will result in the conversion of the highly soluble and toxic hexavalent chromium to a much less soluble less toxic trivalent chromium.

Results: A ferrous sulfate solution was produced by dissolving the ferrous sulfate solid in water into new open-topped 55-gallon drums. It was then sprayed onto the waste spill using a 25% aqueous solution of ferrous sulfate. After the ferrous sulfate solution has had sufficient time to soak the soil thoroughly, (about 24 hours), water was applied to ensure a saturated condition and to create a small hydraulic head, attempting to push the ferrous sulfate solution downward.

3. Mix the top six inches of spill site.

Results: The top six inches of the spill site was rototilled for two days and mixed well using a disk every four hours. Water was applied between mixing occasions to facilitate treatment of the soil.

4. Re-spray spill site with Ferrous Sulfate.

Results: The spill area was sprayed again using a 25% aqueous solution of ferrous sulfate a second time. The total amount of Ferrous Sulfate applied was 530 pounds for both applications. This is to ensure that all the hexavalent chromium has been converted to trivalent chromium. This solution is again allowed to soak in for about 24 hours.

5. Re-mix the top six inches of spill site.

Results: The top six inches of the spill site was rototilled for two days and mixed well using a disk every four hours. Water was applied between mixing occasions as to facilitate treatment of the soil.

6. Check to determine if all hexavalent chromium from the spill has been converted to trivalent chromium.

Results: To ensure that all hexavalent chromium has been reduced to trivalent chromium, sampling was completed and analyzed before the introduction of the stabilization chemicals. Testing was performed of the contaminated soils on a 100 foot grid basis (4 samples for entire spill area).

7. If all hexavalent chromium analyses are below the detection limit of the analysis, task #8 will start.

If hexavalent chromium is detected, task #2 will be completed again until hexavalent chromium is not detected. Results: The chemical analysis (See Table 2) revealed the soil samples hexavalent chromium levels all were less than 0.05 mg/l. This would indicate that all the hexavalent chromium had been converted to trivalent chromium. Therefore, task #8 was started.

TABLE 2

HEXAVALENT CHROMIUM ANALYSIS OF
PRE-TREATED WASTE/SOIL

Sample Number	Hexavalent Chromium (MG/L)
1	<0.01
2	<0.01
3	<0.01
4	<0.01
5	<0.01

8. Order cement kiln dust and have delivered.

Results: Approximately 96 tons of cement kiln dust was delivered to the site. A light water spray over the pile will develop a surface crust, minimizing dusting during subsequent handling. The cement kiln dust was spread by a front end loader over the entire spill area. The contaminated area was covered with approximately 2 to 3 inches of kiln dust.

9. Mix the cement kiln dust into the soil.

Results: Over the next 2 days the cement kiln dust was rototilled into the top six inches of soil. Every four hours a small disc was also used to help facilitate the mixing of the soil, cement kiln dust. Water was constantly added between mixing occasions so as to facilitate treatment of the soil. This treatment process will result in the precipitation of all heavy metals as insoluble hydroxides and/or silicates.

10. Collect representative samples.

Results: Representative samples were collected of treated soil on a 50 foot grid (8 samples). These samples were analyzed for pH, EP-Toxicity (8 metals), and reactivity (H2S and HCN).

11. If task #10 is successful, (chemical analysis shows no leaching of heavy metals), the stabilized soils will be removed and stockpiled in 6 inch lifts. The soils underlying the previously excavated materials will be sampled and tested for comparison to "background" levels of indicator contaminants. Once the underlying soils have been shown to be at or near "background" levels and the stabilized soils have been shown to be non-hazardous, the stabilized soils will be re-compacted into the previously excavated area and left as an improved liner material on the floor of the area

enclosed by the clay retention dikes. These re-compacted, treated soils would be alkaline (pH 9 to 11), with extremely low permeability. When left in place, these soils would provide an excellent buffer material, should a future acid spill occur within the retention dike area.

Results: Chemical analysis (see Tables 3 through 5) of the final treated soils were all below RCRA standards for EP-Toxicity, pH and reactivity (H2S and HCN). The spill area was then divided into thirds (1/3). First the eastern third (E/3) of the spill was removed and stockpiled on the center third (C/3). The soil under the material just removed would then be tested to see if the layer (6-12 inches deep) had been contaminated by the spill. While waiting for test results on the eastern third (E/3), the western third (W/3) was also removed and also stockpiled on the center third (C/3). After the eastern third (E/3) had been tested and the results known, the eastern third (E/3) stockpile was spread and recompacted over the eastern third (E/3) of the spill area. The same would be applicable for (W/3) and (C/3).

12. Analyze representative samples of background and subsurface soils from all three areas (W/3, E/3 and C/3).

Results: Following the treated soil (6") removal, the underlying soil was tested for comparison to "background" values of potential contaminants to document efficiency of site cleanup. Tables 6 though 8 shows the chemical analysis. All samples were within RCRA (40 CFR 261) limits.

13. Re-compact soil.

Results: Soils were recompacted to 90% Proctor. In addition, 17 tons of crushed 1-inch rock was purchased and placed around the existing sump to form a french drain system to the sump. Approximately 240 cubic yards of sandy loam was delivered and spread over the entire spill site. After spreading this clean sandy loam over the spill area, approximately 23,000 square feet of Bermuda sod was placed and gently rolled on top of the sandy loam.

14. Submittal of the cleanup certification report to the Oklahoma State Department of Heath on behalf of client.

Results: Submitted and approved by OSDH.

TABLE 3

CHEMICAL ANALYSIS OF EAST THIRD (E/3) TREATED WASTE/SOIL

EP-Toxicity*	1A	1B	1C	MCL
Arsenic	<0.10	<0.10	<0.10	5.0
Barium	0.15	0.22	0.14	100.0
Cadmium	<0.01	<0.01	<0.01	1.0
Chromium	0.03	0.01	0.03	5.0
Lead	0.26	0.19	0.25	5.0
Mercury	<0.0005	<0.0005	<0.0005	0.2
Selenium	<0.10	<0.10	<0.10	1.0
Silver	<0.01	<0.01	<0.01	5.0

*In mg/l in the extract
MCL: Maximum Concentration Limit (40 CFR 261)

pH (10% w/v)	8.10	6.6	7.5	2>X<12.5
HCN (mg/l)	<1.0	<1.0	<1.0	
H2S (mg/l)	<1.0	<1.0	<1.0	

TABLE 4

CHEMICAL ANALYSIS OF WEST THIRD (W/3) TREATED WASTE/SOIL

EP-Toxicity*	1H	1G	1F	MCL
Arsenic	<0.10	<0.10	<0.10	5.0
Barium	0.09	0.05	0.05	100.0
Cadmium	<0.01	<0.01	<0.01	1.0
Chromium	<0.01	<0.01	<0.01	5.0
Lead	<0.04	<0.04	<0.04	5.0
Mercury	<0.0005	<0.0005	<0.0005	0.2
Selenium	<0.10	<0.10	<0.10	1.0
Silver	<0.01	<0.01	<0.01	5.0
*In mg/l in the extract				
MCL: Maximum Concentration Limit (40 CFR 261)				
pH (10% w/v)	8.10	7.7	7.9	2>X<12.5
HCN (mg/l)	<1.0	<1.0	<1.0	
H2S (mg/l)	<1.0	<1.0	<1.0	

TABLE 5

CHEMICAL ANALYSIS OF CENTER THIRD (C/3) TREATED WASTE/SOIL

EP-Toxicity*	1C	1D	1E	MCL
Arsenic	<0.10	<0.10	<0.10	5.0
Barium	0.06	0.31	0.12	100.0
Cadmium	<0.01	<0.01	<0.01	1.0
Chromium	<0.01	<0.01	<0.01	5.0
Lead	<0.04	0.13	<0.04	5.0
Mercury	<0.0005	<0.0005	<0.0005	0.2
Selenium	<0.10	<0.10	<0.10	1.0
Silver	<0.01	<0.01	<0.01	5.0

*In mg/l in the extract
MCL: Maximum Concentration Limit (40 CFR 261)

pH (10% w/v)	7.5	7.9	8.2	2>X<12.5
HCN (mg/l)	<1.0	<1.0	<1.0	
H2S (mg/l)	<1.0	<1.0	<1.0	

TABLE 6

CHEMICAL ANALYSIS OF WEST THIRD (W/3) BACKGROUND AND SUBGRADE SOILS

EP-Toxicity*	Background Soil	Subgrade Soil	MCL
Arsenic	<0.10	<0.10	5.0
Barium	0.21	0.24	100.0
Cadmium	<0.01	<0.01	1.0
Chromium	0.01	<0.01	5.0
Lead	0.22	0.52	5.0
Mercury	<0.0005	<0.0005	0.2
Selenium	<0.10	<0.10	1.0
Silver	<0.01	<0.01	5.0
*In mg/l in the extract MCL: Maximum Concentration Limit (40 CFR 261)			
pH (10% w/v)	8.0	9.6	2>X<12.5
HCN (mg/l)	<1.0	<1.0	
H2S (mg/l)	<1.0	<1.0	

TABLE 7

CHEMICAL ANALYSIS OF EAST THIRD (E/3) BACKGROUND AND SUBGRADE SOILS

EP-Toxicity*	Background Soil	Subgrade Soil	MCL
Arsenic	<0.10	<0.10	5.0
Barium	0.21	0.16	100.0
Cadmium	<0.01	<0.01	1.0
Chromium	0.01	0.01	5.0
Lead	0.22	0.22	5.0
Mercury	<0.0005	<0.0005	0.2
Selenium	<0.10	<0.10	1.0
Silver	<0.01	<0.01	5.0

*In mg/l in the extract

MCL: Maximum Concentration Limit (40 CFR 261)

pH (10% w/v)	8.0	7.9	2>X<12.5
HCN (mg/l)	<1.0	<1.0	
H2S (mg/l)	<1.0	<1.0	

TABLE 8

CHEMICAL ANALYSIS OF CENTER THIRD (C/3) BACKGROUND AND SUBGRADE SOILS

EP-Toxicity*	Background Soil	Subgrade Soil	MCL
Arsenic	<0.10	<0.10	5.0
Barium	0.21	0.44	100.0
Cadmium	<0.01	0.05	1.0
Chromium	0.01	<0.01	5.0
Lead	0.22	0.74	5.0
Mercury	<0.0005	<0.0005	0.2
Selenium	<0.10	<0.10	1.0
Silver	<0.01	<0.01	5.0

*In mg/l in the extract
MCL: Maximum Concentration Limit (40 CFR 261)

pH (10% w/v)	8.0	9.8	2>X<12.5
HCN (mg/l)	<1.0	<1.0	
H2S (mg/l)	<1.0	<1.0	

CHAPTER IV

MATERIALS AND METHODS

Introduction

This study will investigate the conditions that could occur at a site in which the soil/waste contaminated with hexavalent chromium had been treated in situ and left in place or had not been treated and left in place. Specifically, the study will investigate the effects of: differences in pH, freeze-thaw/wet-dry cycles, co-solvents, and synergistic effects on the leachability of the treated stabilized waste/soil. This will be accomplished in two phases, physical and chemical analysis. It should be pointed out that the results of these tests should not be directly used for prediction of contaminant release under field conditions. For example, the importance of freeze-thaw resistance could obviously depend on local climatic conditions.

Soil Types

Soil samples in this study are classified into four groups:

1. Treated waste/soils: These are soils which were contaminated with the hexavalent chromium spill and

have been chemically reduced and stabilized/solidified in situ. Soil samples were removed approximately 24 hours after the remediation project was completed.

2. Untreated waste/soils: These are soils samples which were also contaminated with the hexavalent chromium spill but have <u>not</u> been treated. Soil/waste samples were removed approximately 18 hours after the spill occurred. During the hand-augering it was noted that there was two distinct layers. The top 2.5 to 3.8 cm was reddish-brown in color followed by a grayish-brown soil. It was assumed that the reddish-brown color was indicative of the chromic acid. This top "contaminated" soil/waste layer was place in a separate bucket from the bottom "uncontaminated" underlying soils.
3. Background soils: These are soil samples taken at the fence line in which it appeared no industrial activity had taken place (north of spill site). These should represent background samples that have not been exposed to pollutants.
4. Stabilized waste/soils that have not been pre-treated: These are soils that were contaminated with the hexavalent chromium spill (top layer) and have been stabilized/solidified ex situ without chemically reducing the hexavalent chromium to trivalent chromium. Contaminated soil samples were removed approximately 18 hours after the spill occurred and

frozen at 0° C until ex situ stabilization/solidification was performed without the addition or use of a reducing agent (ferrous sulfate).

Leachability Study

The leachability study was accomplished by the use of multiple columns (27) packed with background soils (uncontaminated), untreated soils (contaminated), treated soils (reduced and stabilized) and soils that have been treated but not chemically reduced (no pre-treatment). This testing procedure and research should answer four important questions concerning the in situ chemical reduction and stabilization of hexavalent chromium waste:

1. Can hexavalent chromium be reduced to trivalent chromium in situ?
2. How do changes in pH, freeze-thaw/wet-dry cycles, co-solvents and combinations of these affect the leachability of hexavalent and total chromium from the waste/soil samples?
3. Is pre-treatment (chemical reduction) of hexavalent chromium necessary in stabilization/solidification or can the cementious matrix entrain the hexavalent chromium and preclude leaching?
4. How does the in situ treated waste/soil compare in chromium leachability versus the background (uncontaminated) soils?

Test Equipment and Operation of Columns

A total of twenty-seven leachate columns (nine sets of three columns) were set up in parallel with a leachate collection system on the bottom. Each column contained equal masses (1000.0 grams) of either the stabilized soil/waste mixture, the untreated contaminated soils or the background uncontaminated soils respectively, compacted into equal volumes of 333 cm^3. Therefore, one column volume is equal to 333 ml.

With the exception of the wet-dry/freeze-thaw samples and the untreated "contaminated soils", all other soils (treated) were pulverized using a non-metallic mortar and pestle to the same consistency. This will ensure that each column will have nearly the same exposed soil surface area. The wet-dry/freeze-thaw samples were tested without pulverizing, to determine if the wet-dry/freeze-thaw cycles will break the soil down by natural weathering, which should increase the surface area of the waste/soil. The increase of surface area of the waste soil may increase the leachability of chromium.

The untreated soil layers were mixed separately; the top "reddish-brown" contaminated layers were mixed together separately from the bottom grayish-brown (uncontaminated) soils. The untreated soils were packed in the column similar to as they were collected. The bottom grayish-brown soils were packed first with the reddish-brown (contaminated) soils on top.

The acid/water or acid/water/solvent mixtures were pumped to the top of each respective column and allowed to trickle through each column by gravity. Sulfuric acid was used to create the "acid rain" for this study. The sulfuric acid strengths used were: 0.10 N (pH = 1), 0.0001 N (pH = 4) and 1 E-07 N (pH = 7). Glass wool, which has been acid-washed, was placed on the top of each column to disperse the influent equally. This precluded channelization within the column. Acid-washed glass wool was also placed at the base of each column to prevent the loss of soil/waste during the tests. The columns were constructed of polyvinyl chloride (PVC), had an inside diameter of 2.0 inches (5.1 cm) and were 24 inches (60.9 cm) in length. The apparatus was constructed without any metal components contacting the fluid or samples. Leachates from the columns were collected in Erlenmeyer flasks, filtered and analyzed for pH, hexavalent chromium and total chromium. Thirty-five column volumes were drawn off for each sample and analyzed independently. Table 9 describes the identification of column set, the pH value of influent and the description of the column condition.

TABLE 9

COLUMN CONDITIONS FOR LEACHABILITY STUDY

Column Number	pH Value of Influent	Conditions*
1-1, 1-4, 1-7	1, 4, 7	Treated (In Situ) Waste/Soil
2-1, 2-4, 2-7	1, 4, 7	Background (Control)
3-1, 3-4, 3-7	1, 4, 7	Untreated Waste/Soil (Spill)
4-1, 4-4, 4-7	1, 4, 7	Freeze-Thaw/Wet-Dry
5-1, 5-4, 5-7	1, 4, 7	Co-Solvent (0.1% TCA)
6-1, 6-4, 6-7	1, 4, 7	Co-Solvent (1.0% TCA)
7-1, 7-4, 7-7	1, 4, 7	Synergistic (Freeze-Thaw/Wet-Dry, 0.1% TCA)
8-1, 8-4, 8-7	1, 4, 7	Synergistic (Freeze-Thaw/Wet-Dry, 1.0% TCA)
9-1, 9-4, 9-7	1, 4, 7	No Pretreatment (Chemical Reduction of Cr+6 -> Cr+3) Before Stabilization

* Column Numbers 1, 4, 5, 6, 7 & 8 are in situ treated waste/soils.
Column Numbers 2 & 3 were not treated.
Column Number 9 was treated ex situ.

Column Set 1: pH Effects

The first set of three columns was filled with the actual in situ stabilized waste/soil after treatment (treated samples). The treated soils were divided into three columns and subjected to a pH of 1.0, 4.0 and 7.0 respectively. Sulfuric acid or sodium hydroxide and deionized water was used to create the specific pH values. This set of downflow columns simulated the possible effects of acidic or neutral rain on an unsaturated treated waste/soil system.

Column Set 2: Background Soils

Column Set #2 is the background control for column set #1. These background soils were also exposed to pH values of 1.0, 4.0, and 7.0 in a downflow unsaturated configuration. This column set determined if background soils contained any leachable hexavalent "indigenous" chromium and at what point (column volume) will uncontaminated soils leach indigenous chromium.

Column Set 3: Untreated Waste/Soil

Column Set #3 contained the untreated soil/waste. This examined what would have happened if no remediation had occurred and the chromic acid plating solution was allowed to remain in place without any form of treatment. These soil/wastes samples were also exposed to pH values of 1.0, 4.0, and 7.0 in a downflow unsaturated configuration.

Column Set 4: Wet-Dry/Freeze-Thaw Cycle Effects

The fourth set of columns was filled with the treated stabilized waste/soil and also exposed to pH values of 1.0, 4.0, and 7.0. The difference was that after each column was saturated, the column was frozen for 24 hours in a freezer at 15 F (-10 C) and then allowed to thaw. Once thawed, each column volume was allowed to drain fully and allowed to desiccate for 48 hours. Thirty-five wet-dry/freeze-thaw cycles were performed. Following each freeze-thaw/wet-dry cycle, the leachate from each column was collected in Erlenmeyer flasks, filtered and analyzed. This column set examined the effects that wet-dry/freeze-thaw cycles have on the leachability of stabilized chromium.

Column Set 5: Co-Solvent Effects (0.1% v/v)

The fifth set of columns was filled with the treated stabilized waste/soil and also exposed to a pH of 1.0, 4.0, and 7.0, but a co-solvent (0.1% by volume of 1,1,1-Trichloroethane) was added to each solution to determine if this co-solvent affects leachability of chromium in a stabilized form.

Column Set 6: Co-Solvent Effects (1.0% v/v)

The sixth set of columns was filled with the treated stabilized waste/soil and also exposed to pH values of 1.0, 4.0, and 7.0. But instead of a 0.1% v/v co-solvent as in column set #5, this set contained a 1.0% v/v co-solvent of 1,1,1-Trichloroethane to determine if the concentration of the co-solvent combined with different pH affects the leachability of hexavalent or total chromium.

Column Set 7: Synergistic Effects (0.1% v/v)

Column set number 7 was filled with the treated stabilized waste/soil and saturated with pH values of 1.0, 4.0, and 7.0, each of which contained 0.1% v/v 1,1,1-Trichloroethane. After each column was saturated, the column was frozen for 24 hours in a freezer at 15 F (-10 C) and then allowed to thaw. Following each freeze/thaw cycle, the leachate from each column was collected in Erlenmeyer flasks, filtered and analyzed.

Column Set 8: Synergistic Effects (1.0% v/v)

Column set number 8 was filled with the treated stabilized waste/soil and also exposed to pH values of 1.0, 4.0, and 7.0. Each column was then filled with "acid or neutral rain" and a 1.0% by volume TCA and was frozen and then allowed to thaw. This experiment examined the synergistic effects of a 1.0% v/v co-solvent and the freeze/thaw mechanism.

Column Set 9: Stabilized Waste/Soils Without Pre-Treatment

These are soils that were contaminated with the hexavalent chromium spill and have been stabilized-solidified ex situ without chemically reducing the hexavalent chromium to trivalent chromium. Contaminated soil samples were removed approximately 18 hours after the spill occurred and frozen at 0^{o} C until ex situ stabilization-solidification was performed without the addition or use of a reducing agent (ferrous sulfate).

Chemical Analysis

Chemical analysis was performed on the leachate of each column. The analysis consisted of total chromium, hexavalent chromium and pH. The data was evaluated to determine if the metal-binding properties of the stabilization of the waste/soil would be adequate to minimize the adverse effects of the environment after landfilling in place. This project will help to demonstrate the ability of in situ chemical stabilization in the remediation of hexavalent chromic acid spills. This data will also show the affects of a pH, co-solvent, freeze/thaw cycles, combinations of these and the affects on the environment if no remediation was accomplished.

Hexavalent Chromium Analysis

Hexavalent chromium was determined according to U.S.

EPA test method 7196A. This test method was used to determine the concentration of hexavalent chromium (Cr+6) in extracts and water and is also applicable to domestic and industrial wastes. The hexavalent chromium was determined using Beers Law by the addition of 1,5-Diphenylcarbohydrazide, which reacts to give a purple color when hexavalent chromium is present. This reaction is very sensitive, the absorbency index per gram atom of chromium being about 40,000 at 540 nm. The colorimetric equipment that was used is a Sequoia-Turner Model 340 spectrophotometer at 540 nm with a path length of 1 cm.

Reagents. The following reagents were used in this study:

Reagent Water: Deionized water with a conductivity of less that 1 umho/cm.

Potassium Dichromate Stock Solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1 liter (1 ml = 50 ug Cr).

Potassium Dichromate Standard Solution: Dilute 10.00 ml potassium dichromate stock solution to 100 ml (1 ml = 5 ug Cr).

Sulfuric Acid, 10% (v/v): Dilute 10 ml of reagent grade sulfuric acid, H_2SO_4, to 100 ml with reagent water.

1,5-Diphenylcarbohydrazide Solution: Dissolve 250 mg 1,5-Diphenylcarbazide in 50 ml acetone. Store in a brown bottle.

Acetone: Analytical reagent grade

<u>Color Development</u>. Transfer 95 ml of the leachate to be tested to 100 ml volumetric flask. Add 2.0 ml of 1,5-diphenylcarbazide solution and mix. Add the H_2SO_4 solution to give a pH about 2, dilute to 100 ml with reagent water, and let stand 5 to 10 minutes for full color development. Transfer an appropriate portion of the solution to a 1 cm adsorption cell and measure its absorbance at 540 nm. Use reagent water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method. An aliquot of the sample containing all reagents except 1,5-diphenylcarbazide should be prepared and used to correct the sample for turbidity. From the corrected absorbance, determine the mg/l of chromium present by reference to the calibration curve. A calibration curve was developed by plotting absorbance values against known concentrations of hexavalent chromium (ug/l of Cr+6).

<u>Interferences</u>. The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violent intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble. Iron in concentrations

greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered, if the absorbency is measured photometrically at the appropriate wavelength.

Total Chromium Analysis

Total chromium was analyzed by the use of a Jarrell Ash flame atomic absorption spectrometer. All samples were acid/heat digested in a fume-hood according to U.S. EPA test method 3005 and analyzed in accordance to U.S. EPA test method 6010. Metal concentrations in liquid samples above the linear range of the instrument were appropriately diluted before measurement. The Atomic Absorption unit was calibrated with each sample batch. A calibration curve was prepared with a minimum of a calibration blank and two standards and then verified with a standard from a certified source near the action levels for the project requirements. The calibration was verified on an ongoing basis with a QC check standard. The standards met established criteria or the system was recalibrated and all samples analyzed since the last acceptable calibration check were re-analyzed.

pH Analysis

The hydrogen ion activity (pH) of solutions used in this study was measured using Standard Methods protocol 4500. A Corning pH meter equipped with a combination electrode probe was used. This meter is accurate and reproducible to 0.1 pH units with a range of 0 to 14 and is equipped with a temperature compensation adjustment. Buffer (pH) standards were purchased and used to calibrate the meter/probe before each set of analysis.

Physical Analysis

In addition to the chemical analysis of the leachate, this study also examined physical properties of the soil and waste/soil. The physical constants of these soils or waste/soils were investigated to determine the effects chemical stabilization has on soil properties, such as, permeability, strength, density, etc.

Moisture Content

Water content (or percent moisture) is defined as the ratio of the weight of water to the weight of solids and is expressed as percentage. The percent moisture or water content is used to develop requirements for pretreatment and for designing solidification procedures for the treated materials. ASTM Standard Method D2216-80, "Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures," was used to measure waste content (ASTM 1987b). Replicate samples were dried to a constant weight at 60° C. The change in mass corresponded to the water content.

Grain Size

The Grain-size distribution of an industrial waste becomes important in designing remedial actions. Fine-grain wastes generally present more handling problems and are subject to wind dispersion. Fine-grained wastes also present problems in producing high-strength solidified waste. Large percentages of fines lower the ultimate strength developed in concrete/waste composites. ASTM Method D422 was used to determine grain size distribution.

Compacted Density

The compaction test for optimum moisture-density (ASTM Standard D698-70) measures the effect of solids moisture content on density, but it also indicates the point where maximum strength is expected. The point at which compacted solids or sludge is compacted to the maximum density is where maximum shear strength and minimum permeability are likely.

Bulk Density

The bulk density is the ratio of the total weight (solids and water) to the total volume. These basic data are needed to convert weight to volume in material handling calculations. ASTM Method D-698 was used to determine dry and wet bulk density of the soils.

Unconfined Compressive Strength (UCS)

Among the physical properties of a solidified waste, an important requirement is its ability to withstand compaction by equipment when left on site. This strength is generally expressed as unconfined compressive strength (psi) which indicates load-bearing capacity. Unconfined compressive strength tests are used to determine bearing capacity and shear strength of cohesive materials. Shear strength is an important factor in determining the ultimate bearing capacity of the material, embankment stabilities, and pressures on retaining walls holding the material in place. In addition, a policy directive issued by the USEPA Office of Solid Waste and Emergency Response (OSWER) (USEPA 1986) established a minimum UCS of 50 psi (344 kPa) as indicative of satisfactory solidification of hazardous liquids. The 50 psi UCS is used to determine if the processing of hazardous liquids prior to landfilling involves primarily "sorbents" (materials that hold liquids by surface and capillary tension) or solidification/stabilization reagents (materials that chemically react with aqueous liquids to produce a hardened mass). The test method used to measure unconfined compressive strengths of the soils and the treated waste/soils was ASTM Standard Method D2166-85. Unfortunately, no correlation has been demonstrated between UCS and leachability (Cote et al., 1984)

Permeability

Permeability (also called hydraulic conductivity) indicates the degree to which the material permits the passage of water, and is therefore one measure of potential for contaminants to be released to the environment. It would also be a factor in estimating the potential for long-term durability of the treated waste. Permeability depends on the solidified/stabilized material's density, degree of saturation, and particle size distribution, as well as pore size, void ratio, interconnecting channels and the liquid pressure. The rate of water passing through a sample of solids of a given cross section is proportional to the gradient applied, according to Darcy's law:

$$q = KAi$$

where q = rate of flow, cm3/sec
K = coefficient of permeability, cm/sec
A = cross section area to flow, cm2
i = flow gradient, cm/cm

The proportionality constant, K, is the coefficient of permeability, which indicates the degree of permeability of the solids under consideration. Permeability of a material depends on various parameters including density, degree of saturation, and particle size distribution.

Permeability was measured by a falling head test with a triaxial cell (ASTM STP 479). In this test, a cylindrical specimen surrounded by a thin flexible rubber membrane is placed in a triaxial cell. The permeability of a specimen can affect the rate at which contaminants can be leached by convective transport (flow of water through the matrix).

CHAPTER V

RESULTS AND DISCUSSION

Chemical Analysis

The results of the chemical analyses of the column leachate to determine the stability of these soil or soil/waste samples are described in Figures 2 through 28.

Leachate Analyses

Figure 2 (column 1-1) describes the affect acid rain of a pH value of 1.0 would have on the treated waste/soil. Only after 26 column volumes could total chromium be detected. No hexavalent chromium was detected through-out the 35 column volumes. The buffering capacity of the column changed the greatest between the 26th and 27th column volume, and this also corresponds to the first detection of chromium. It appears that between the the 26th and 27th column volume the buffering capacity became depleted allowing the chromium to be solubilized. Figure 2 (column 1-1) also describes the relationship between pH, total chromium (mg/l) and column volumes but also solubilized silicon (mg/l). An attempt was made to investigate the theory of silicate entrainment of chromium. Chromium (in the trivalent oxidation state) is believed to be bound to

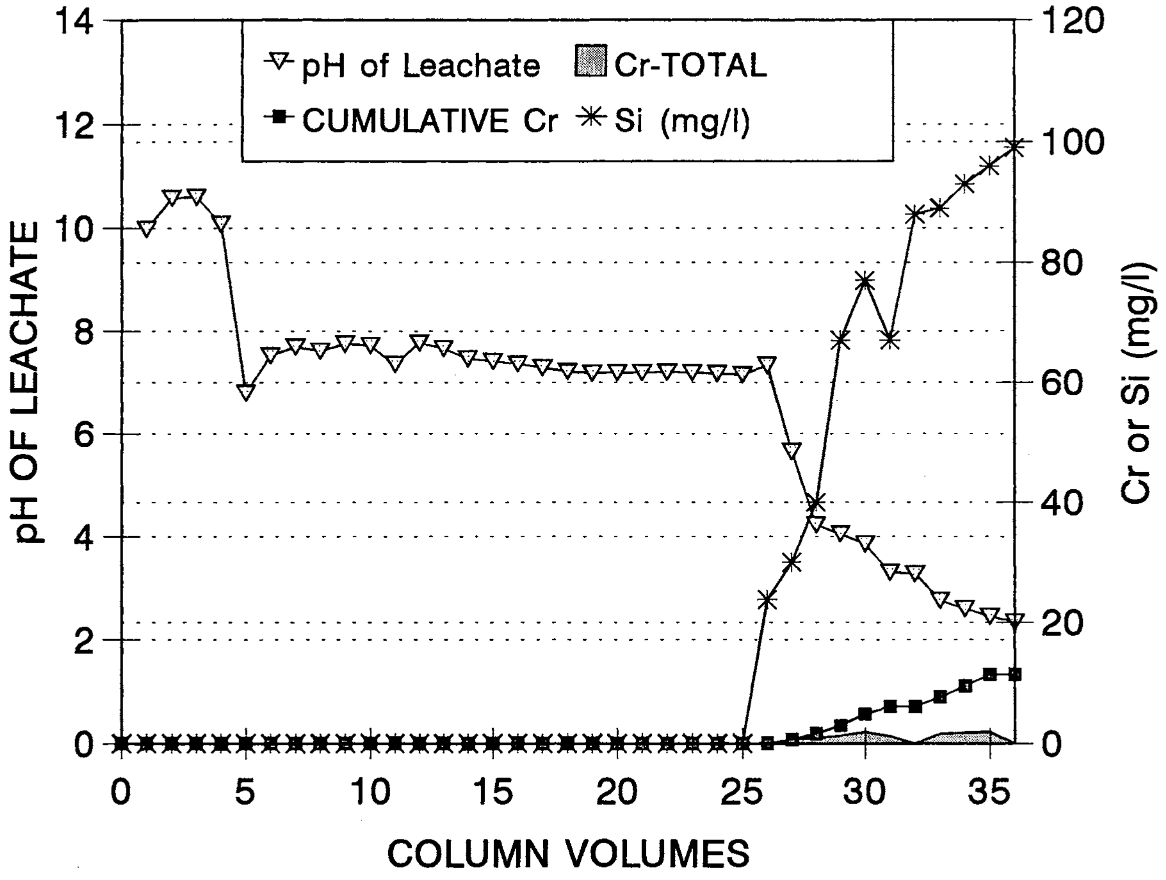

FIGURE 2: (COLUMN 1-1) EFFLUENT LEACHATE OF TREATED WASTE/SOIL.
INFLUENT pH EQUALS 1.0

the silica matrix itself, rather than being in the pores, therefore soluble silicon should be an indicator parameter, and should be detected before chromium (Barth, 1990). No silicon was detected until the 26 column volume at that point silicon values increase dramatically, indicating the silicate matrix became solubilized. The next column volume chromium was detected. Again, possibly indicating the chromium had been entrained in the silicate matrix.

Figure 3 (column 1-4) describes the affect acid rain at a pH value of 4.0 would have on the treated waste/soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium (hexavalent or total) was detected.

Figure 4 (column 1-7) describes the affect neutral rain of a pH value of 7.0 would have on the treated waste/soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium (hexavalent or total) was detected.

Figure 5 (column 2-1) describes the affect acid rain of a pH value of 1.0 would have on background soil. The pH of the effluent changed the greatest between the 4th and the 5th column volume. Total chromium was detected on the 21st column volume, and continued from the 21st to the 35th column volume. No hexavalent chromium was detected. This represents the solubilization of indigenous chromium using an acid of a pH of 1.0. This column set represents one of the most significant issues in this study. The indigenous

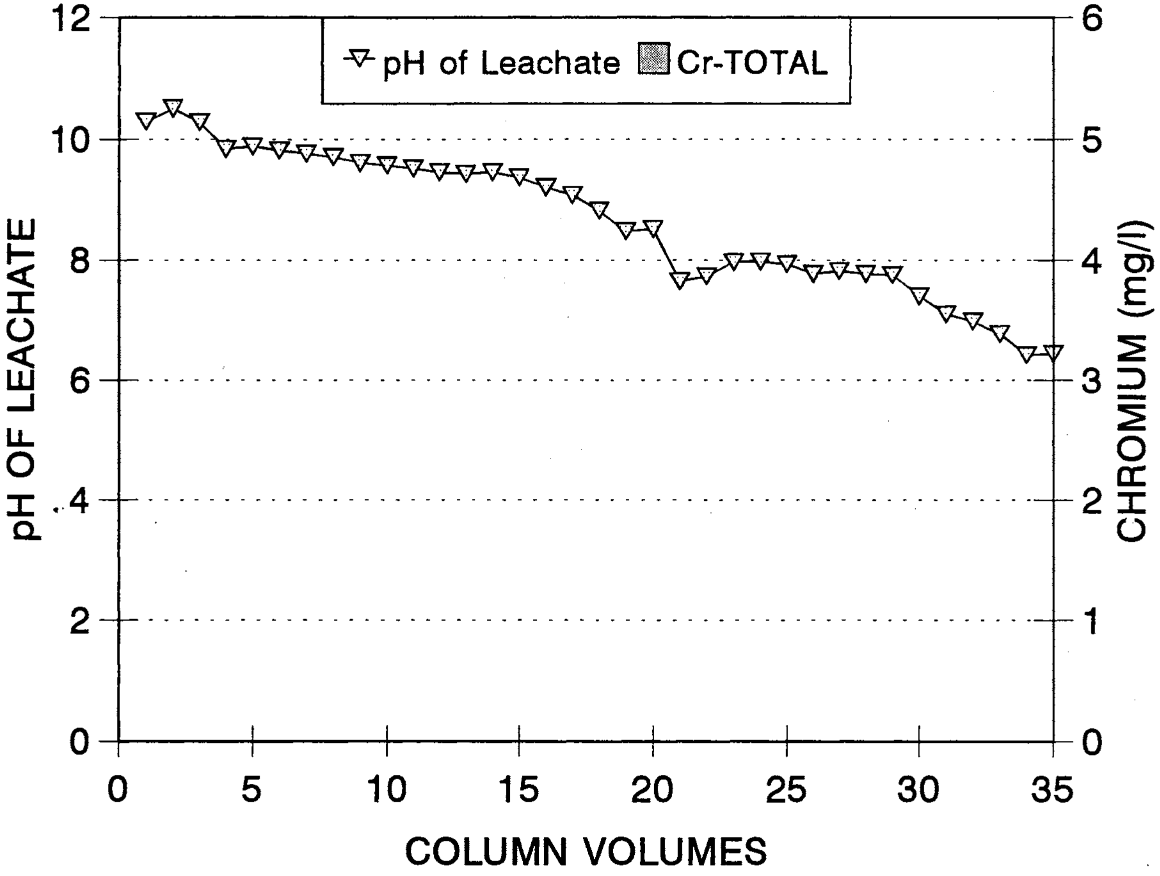

FIGURE 3: (COLUMN 1-4) EFFLUENT LEACHATE OF TREATED WASTE/SOIL
INFLUENT pH EQUALS 4.0

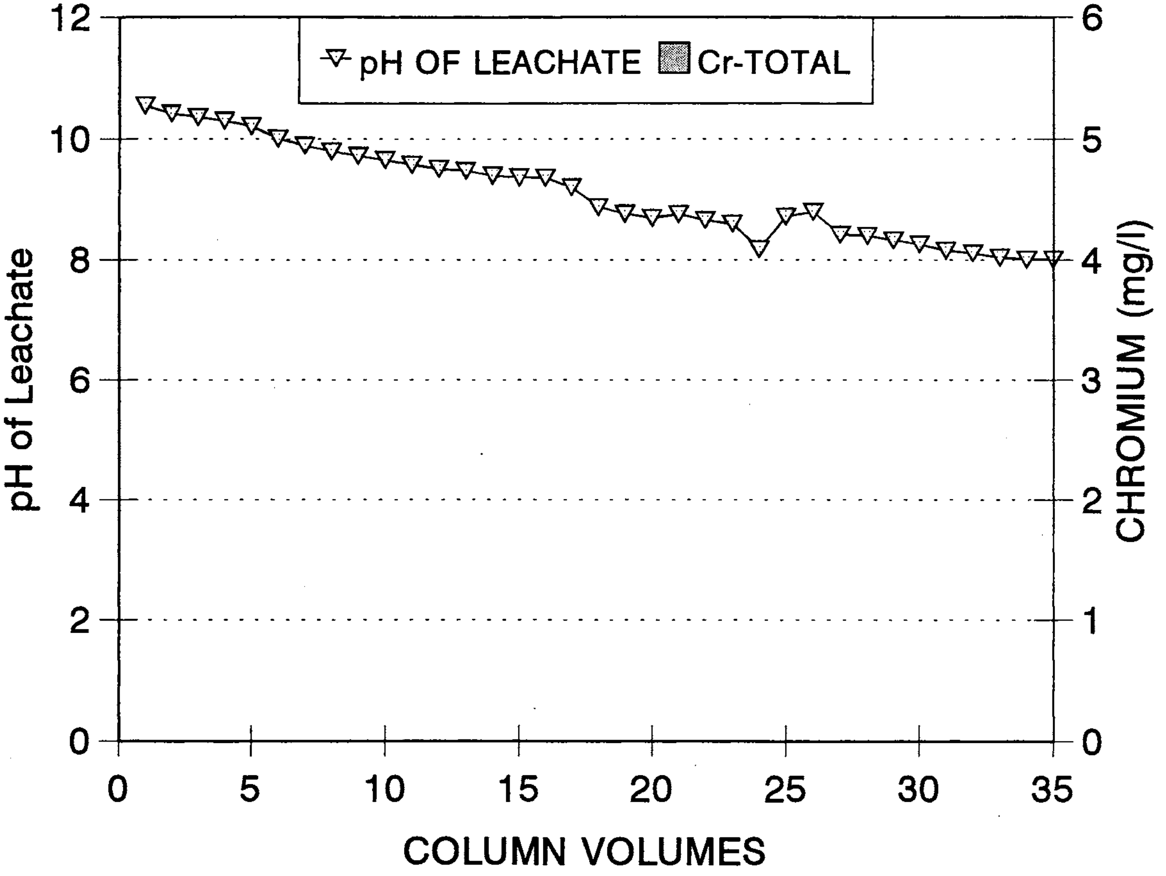

Figure 4: (Column 1-7) EFFLUENT LEACHATE OF TREATED WASTE/SOIL.
INFLUENT pH EQUALS 7.0

background soil starting releasing chromium on the 21st column volume and continued to release chromium from column volume 21 through 35, with a total chromium release of 16 mg. The treated waste/soil started releasing chromium on column volume 27 and continued through column volume 35 with a total release of less than 12 mg/l. Therefore, the treated waste withstood this harsh acidic solution better than the naturally occurring soil. This can be attributed to two factors. The first being that lime-based CKD has significant buffering capacity, preventing the suppression of pH, which can solubilize heavy metals. The other being the theory that chromium is entrained into the silicate matrix once stabilized, which would prevent solubilization until such time the silicate matrix is solubilized.

Figure 6 (column 2-4) describes the affect acid rain of a pH value of 4.0 would have on background soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium (hexavalent or total) was detected.

Figure 7 (column 2-7) describes the affect neutral rain of a pH of 7.0 would have on the background soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium (hexavalent or total) was detected.

Figure 8 (column 3-1) describes the affect acid rain of a pH value of 1.0 would have on the untreated waste/soil. This column set represents what may have happened if the

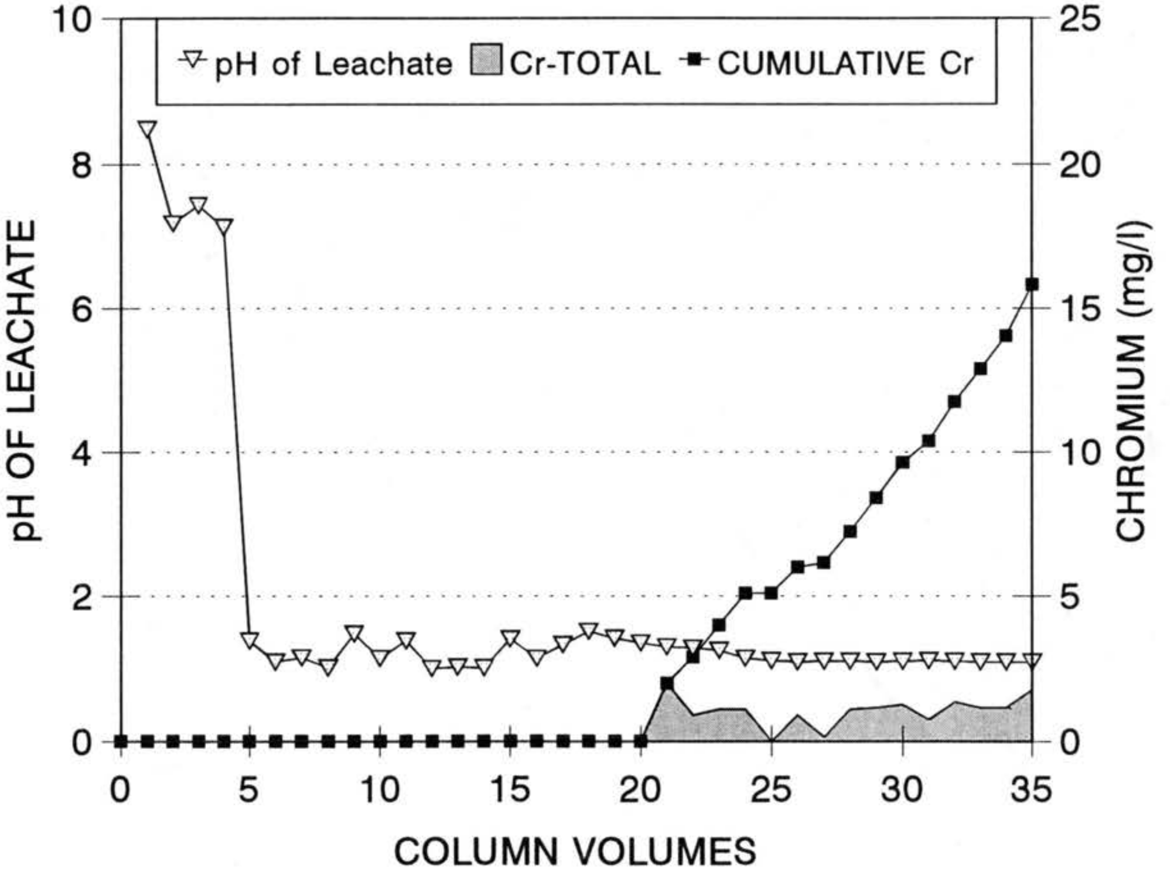

FIGURE 5: (COLUMN 2-1) EFFLUENT LEACHATE OF BACKGROUND SOIL.
INFLUENT pH EQUALS 1.0

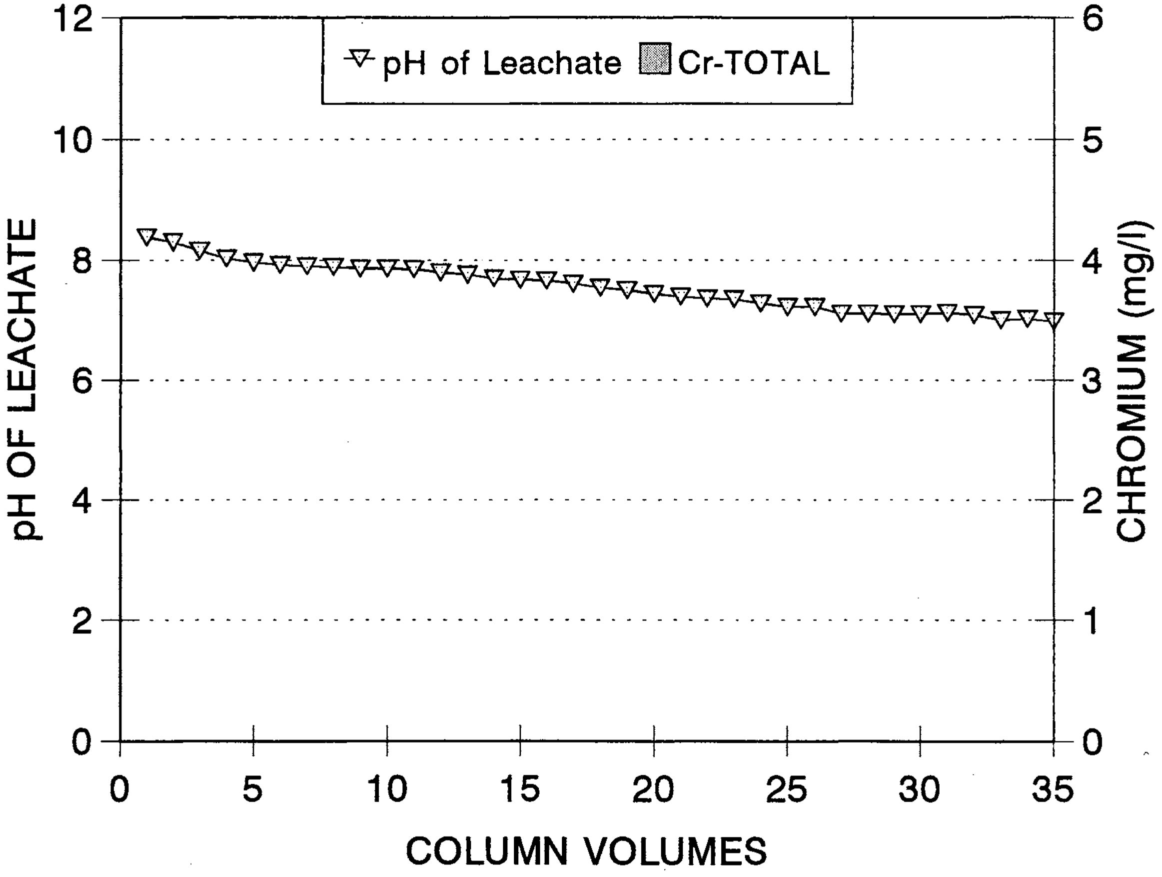

FIGURE 6: (COLUMN 2-4) EFFLUENT LEACHATE OF BACKGROUND SOIL.
INFLUENT pH EQUALS 4.0

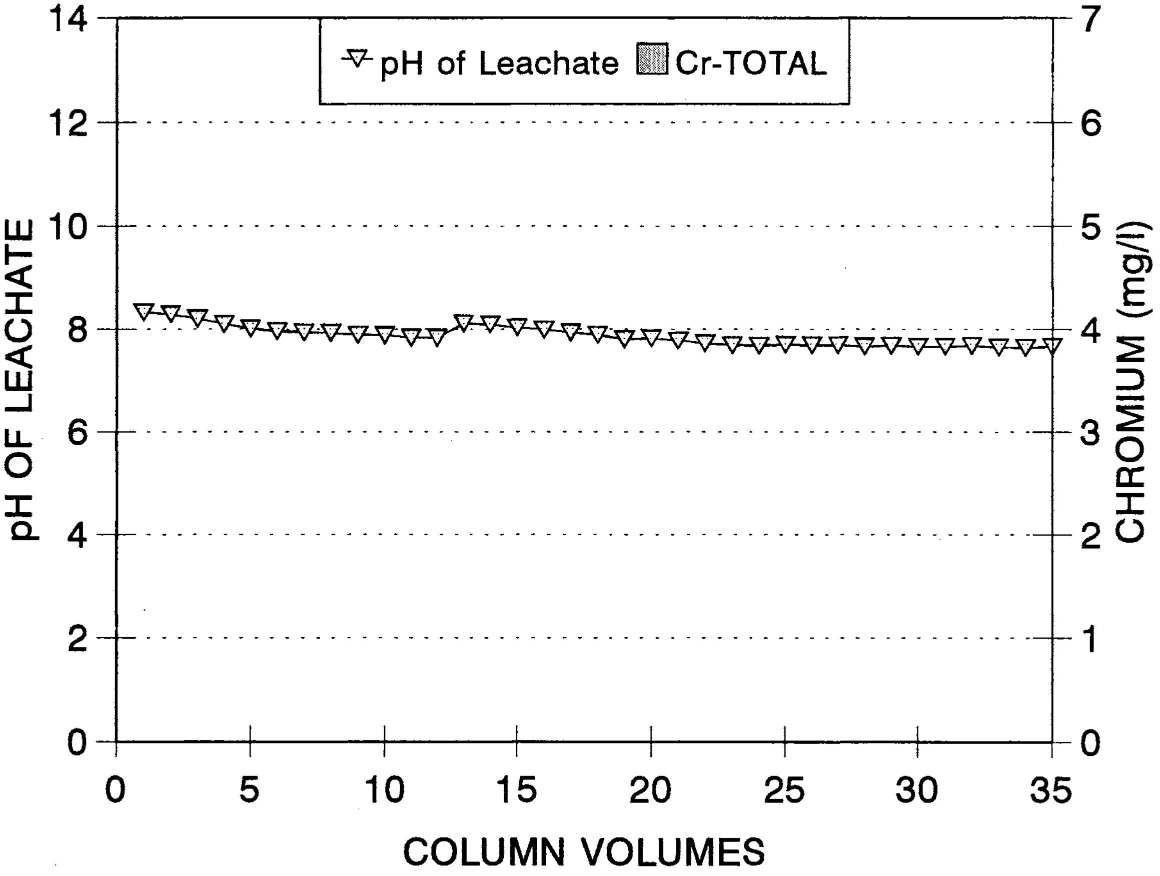

FIGURE 7: (COLUMN 2-7) EFFLUENT LEACHATE OF BACKGROUND SOIL.
INFLUENT pH EQUALS 7.0.

waste spill was allowed to remain on the ground. The buffering capacity of the column appears to have been spent after the forth column volume. On the fifth column volume a slug of chromium was detected with a large decrease in pH. What could be theorized is that the chromate bonded with the free hydrogen of the influent sulfuric acid. This slug appeared to pass through the column with little retention. After this slug passed through the pH increased again and chromium levels decreased. The predominate chromium species detected (about 80%) was hexavalent chromium.

Figure 9 (column 3-4) describes the affect acid rain of a pH value of 4.0 would have on untreated waste/soil. The buffering capacity of the column did not appear to have become spent through out the 35 column volumes. Chromium was detected in column volume 17 and continued through out column volume 35, with a total chromium value of less than 8 mg/l. The predominate chromium species detected (about 82%) was hexavalent chromium.

Figure 10 (column 3-7) describes the affect neutral rain of a pH of 7.0 would have on the untreated waste/soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes. Chromium was detected from column volume 18 through 35, with a total chromium released of less than 4 mg/l. The predominate chromium species detected (about 80%) was hexavalent chromium.

Figure 11 (column 4-1) describes the affect acid rain of a pH value of 1.0 would have on treated waste that has

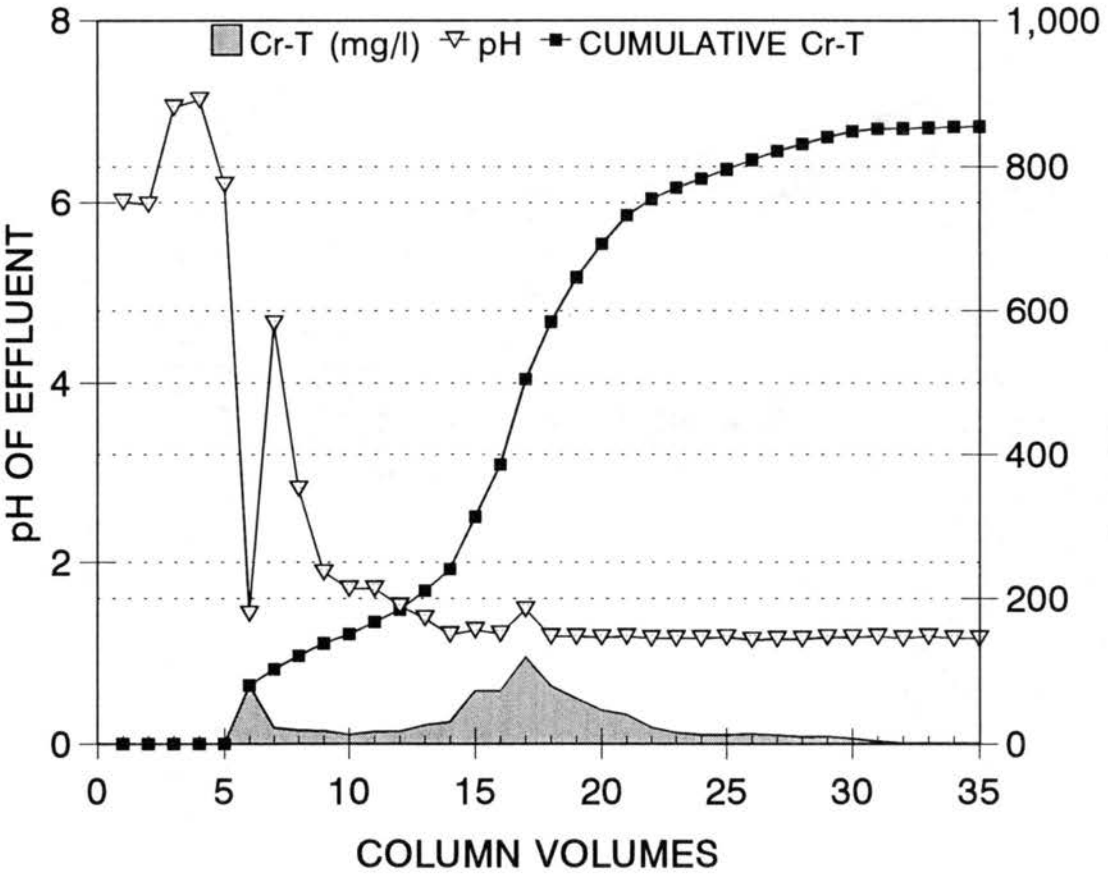

FIGURE 8:(COLUMN 3-1) EFFLUENT LEACHATE OF UNTREATED WASTE.
INFLUENT pH EQUALS 1.0

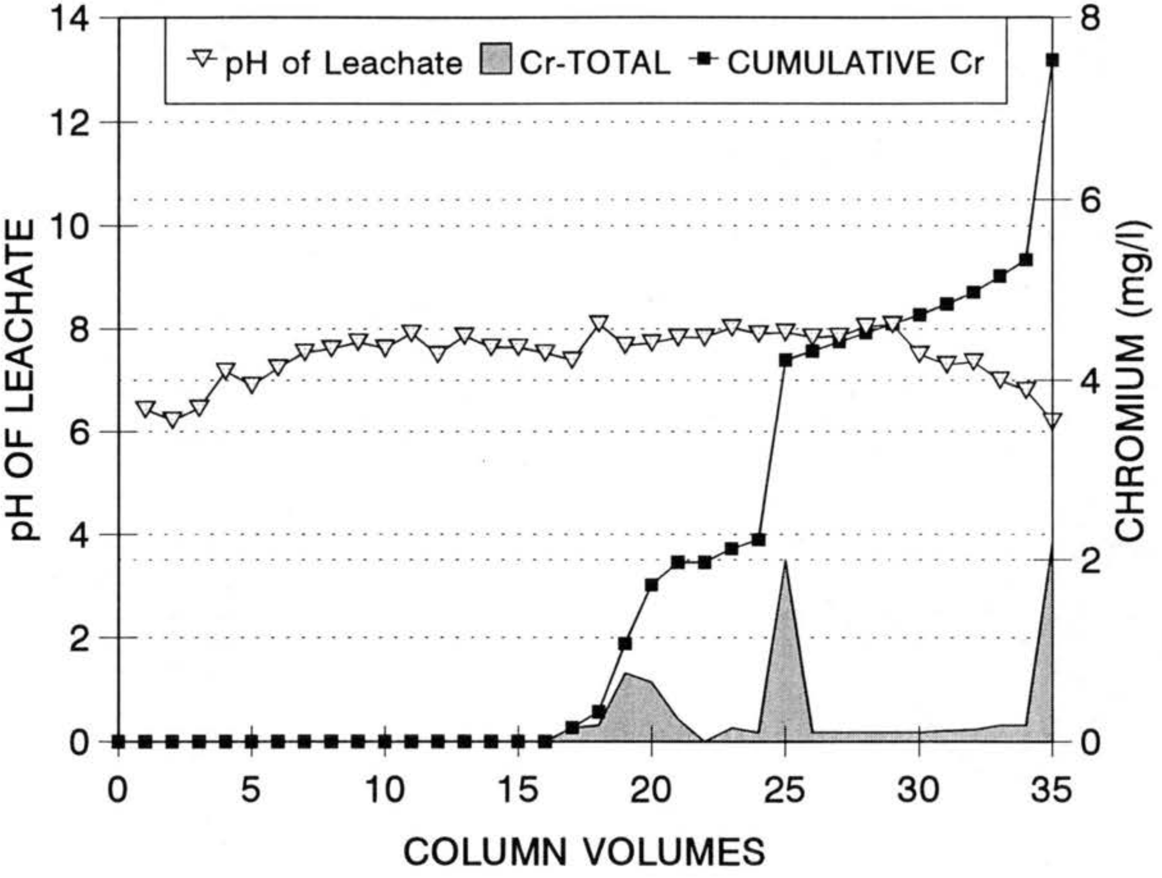

FIGURE 9: (COLUMN 3-4) EFFLUENT LEACHATE OF UNTREATED WASTE.
INFLUENT pH EQUALS 4.0

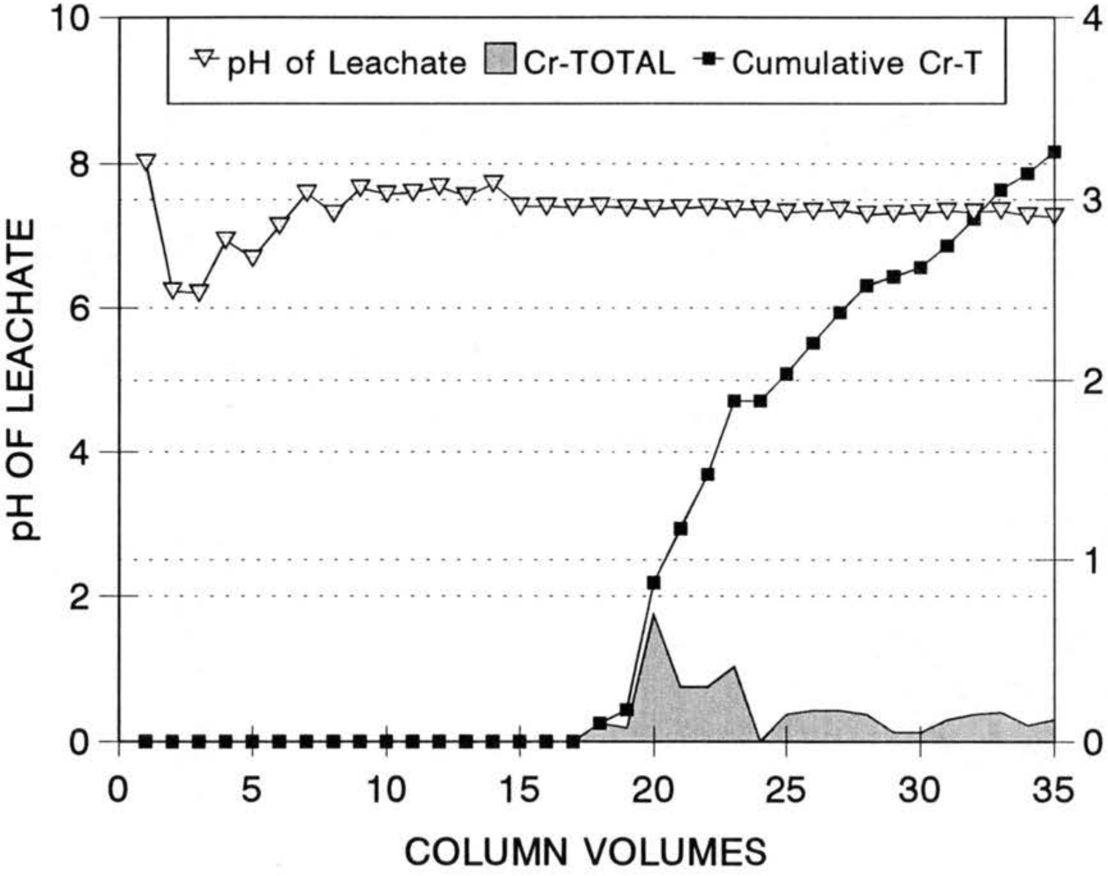

FIGURE 10: (COLUMN 3-7) EFFLUENT LEACHATE OF UNTREATED WASTE.
INFLUENT pH EQUALS 7.0

been exposed to freeze-thaw/wet-dry cycles. Chromium was detected from column volume 27 through 35, with a total chromium release of 8.3 mg/l. No hexavalent chromium was detected. These results appear to be very similar to column 1-1, therefore, it does not appear that the wet-dry/freeze-thaw cycles affects leachability of chromium. It appears that leachability is pH dependent and independent of wet-dry/freeze-thaw cycles.

Figure 12 (column 4-4) describes the affect acid rain of a pH value of 4.0 would have on the treated waste/soil that has been exposed to freeze-thaw/wet-dry cycles. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium (hexavalent or total) was detected. The results appears to be similar to column 1-4, therefore, it does not appear that the wet-dry/freeze-thaw cycles affect the leachability of chromium.

Figure 13 (column 4-7) describes the affect neutral rain of a pH value of 7.0 would have on the treated waste/soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium (hexavalent or total) was detected. The results appears to be similar to column 1-7, therefore, it does not appear that the wet-dry/freeze-thaw cycles affect the leachability of chromium.

Figure 14 (column 5-1) describes the affect acid rain of a pH value of 1.0 would have on treated waste/soil that has also been exposed to a co-solvent (0.1% v/v, 1,1,1 -Trichloroethane). Chromium was detected from column volume

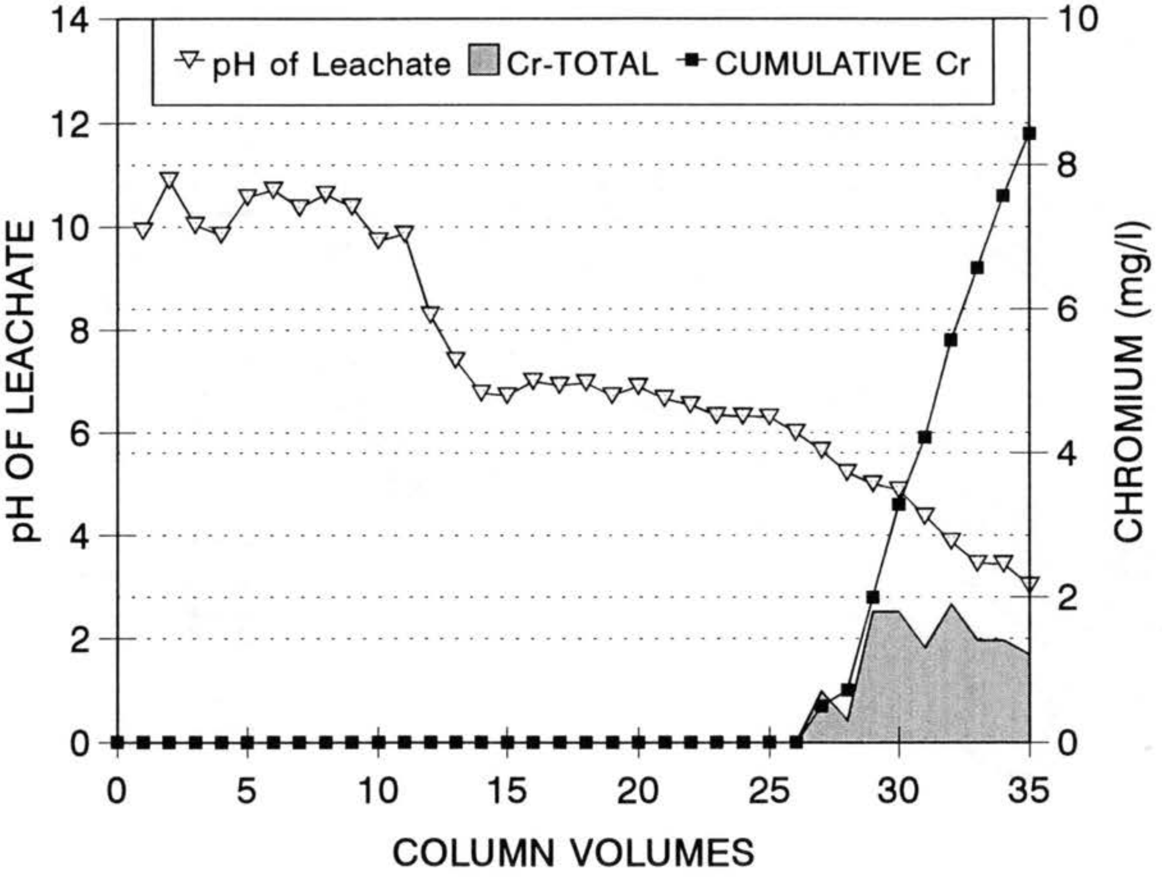

FIGURE 11: (COLUMN 4-1) EFFLUENT LEACHATE OF TREATED WASTE
INFLUENT pH EQUALS 1.0: FREEZE-THAW/WET-DRY CYCLES

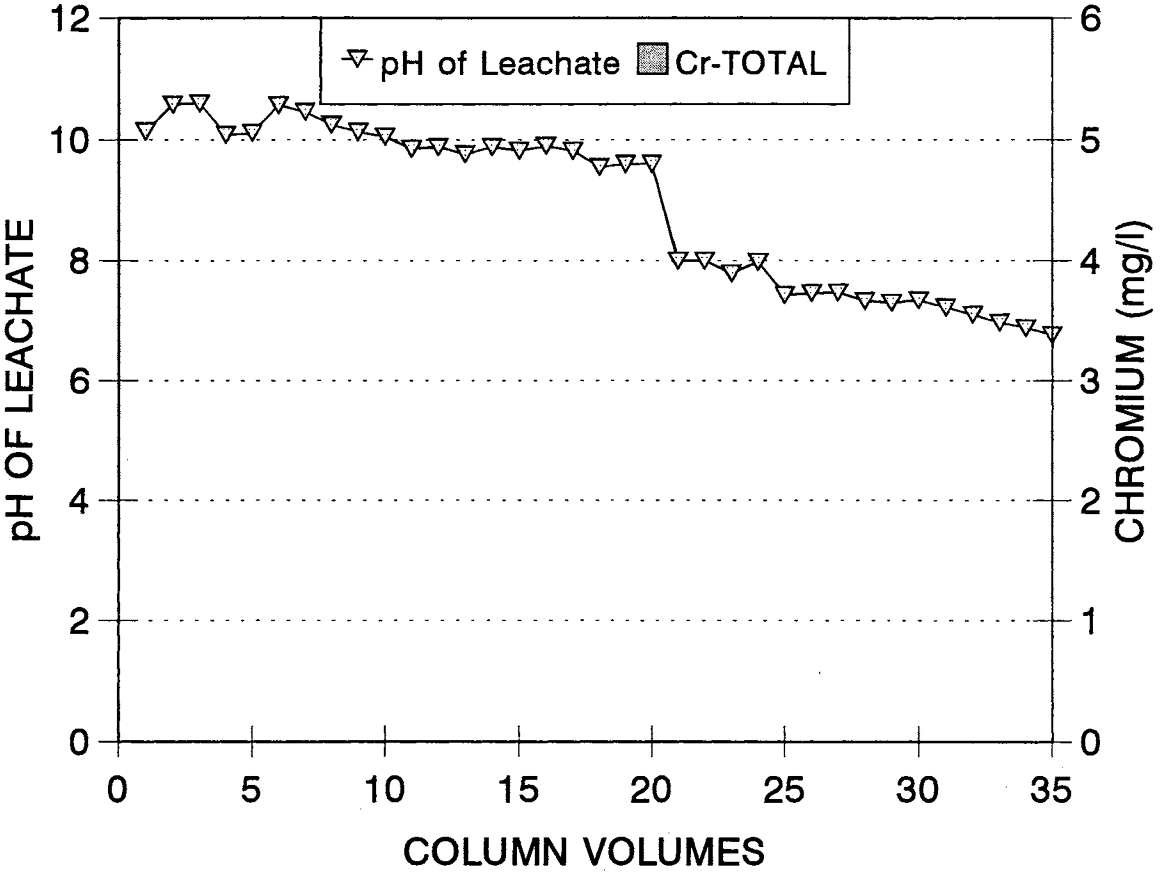

FIGURE 12: (COLUMN 4-4) EFFLUENT LEACHATE OF TREATED WASTE.
INFLUENT pH EQUALS 4.0: FREEZE-THAW/WET-DRY CYCLES

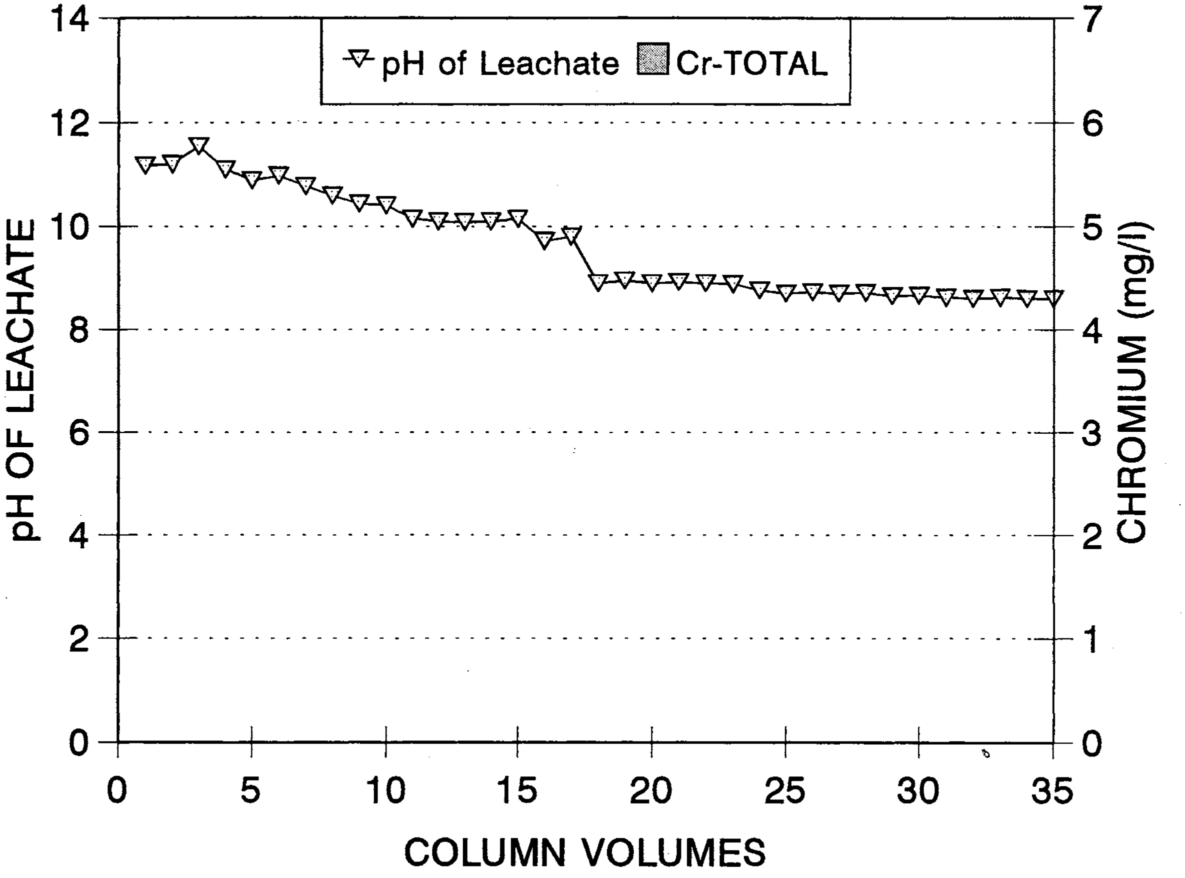

FIGURE 13: (COLUMN 4-7) EFFLUENT LEACHATE OF TREATED WASTE.
INFLUENT pH EQUALS 7.0: FREEZE-THAW/WET-DRY CYCLES

27 through 35, with a total chromium release of less than 12 mg/l. No hexavalent chromium was detected. These results appear to be very similar to column 1-1, therefore, it does not appear that the this co-solvent at this concentration affected leachability of chromium. It appears that for these treated waste/soils, chromium leachability is pH dependent and independent of a 0.1 % v/v, 1,1,1-Trichloroethane.

Figure 15 (column 5-4) describes the affect acid rain of a pH value of 4.0 would have on the treated waste/soil that have also been exposed to a co-solvent (0.1% v/v, 1,1,1-Trichloroethane). The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appears to be similar to column 1-4, therefore, it does not appear that the this co-solvent at this concentration affects the leachability of chromium in the treated waste/soil.

Figure 16 (column 5-7) describes the affect a neutral rain of a pH value of 7.0 would have on the treated waste/soil that have also been exposed to a co-solvent (0.1% v/v, 1,1,1-Trichloroethane). The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appears to be similar to column 1-7, therefore, this this co-solvent at this concentration affects the leachability of chromium in the treated waste/soil.

Figure 17 (column 6-1) describes the affect the

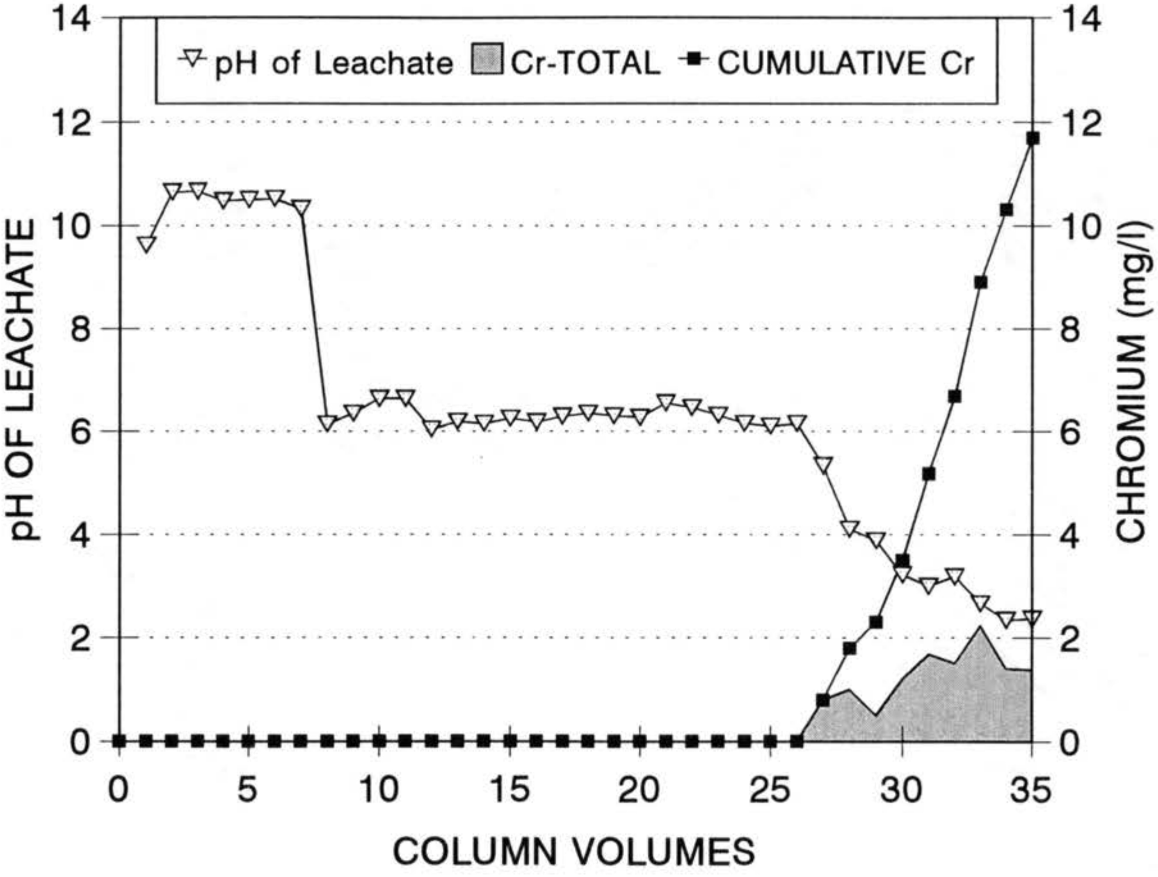

FIGURE 14: (COLUMN 5-1) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 1.0.
CO-SOLVENT (0.1% v/v) 1,1,1-TRICHLOROETHANE

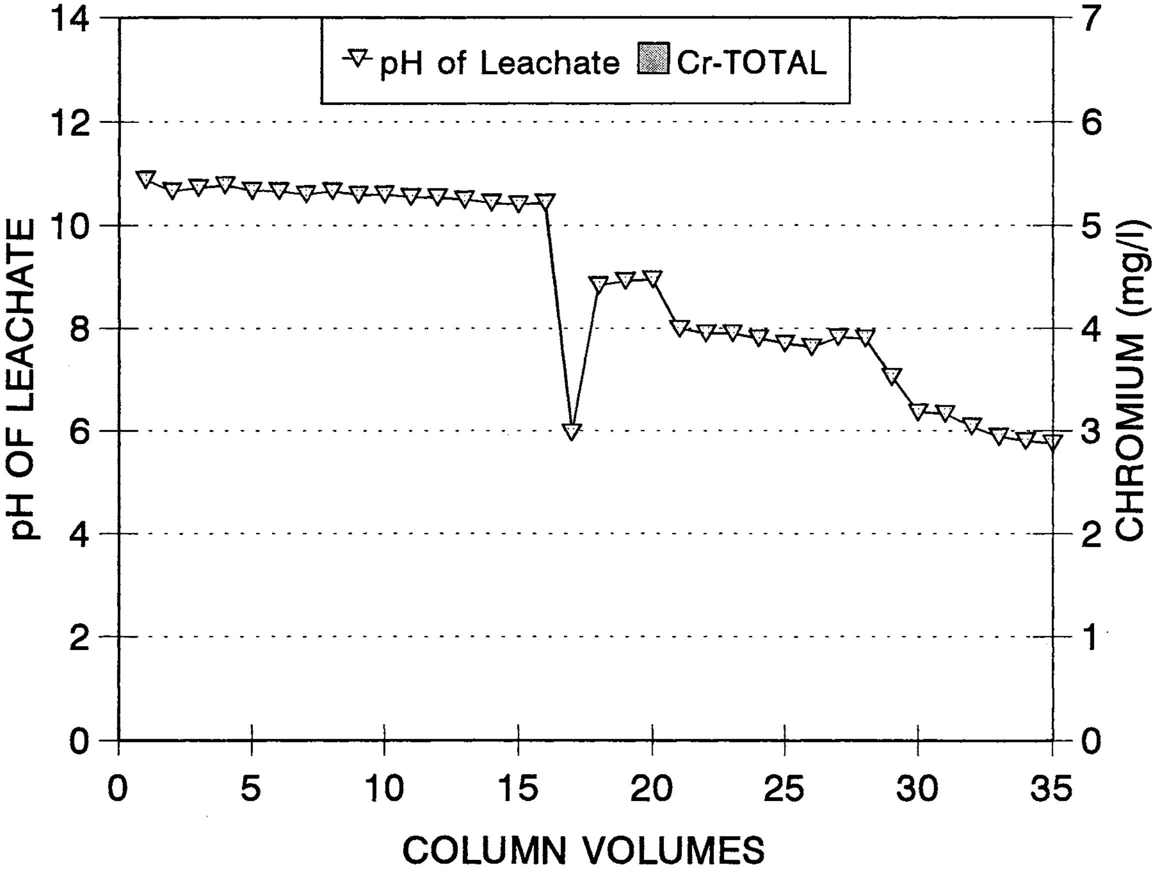

FIGURE 15: (COLUMN 5-4) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 4.0.
CO-SOLVENT (0.1% v/v) 1,1,1-TRICHLOROETHANE

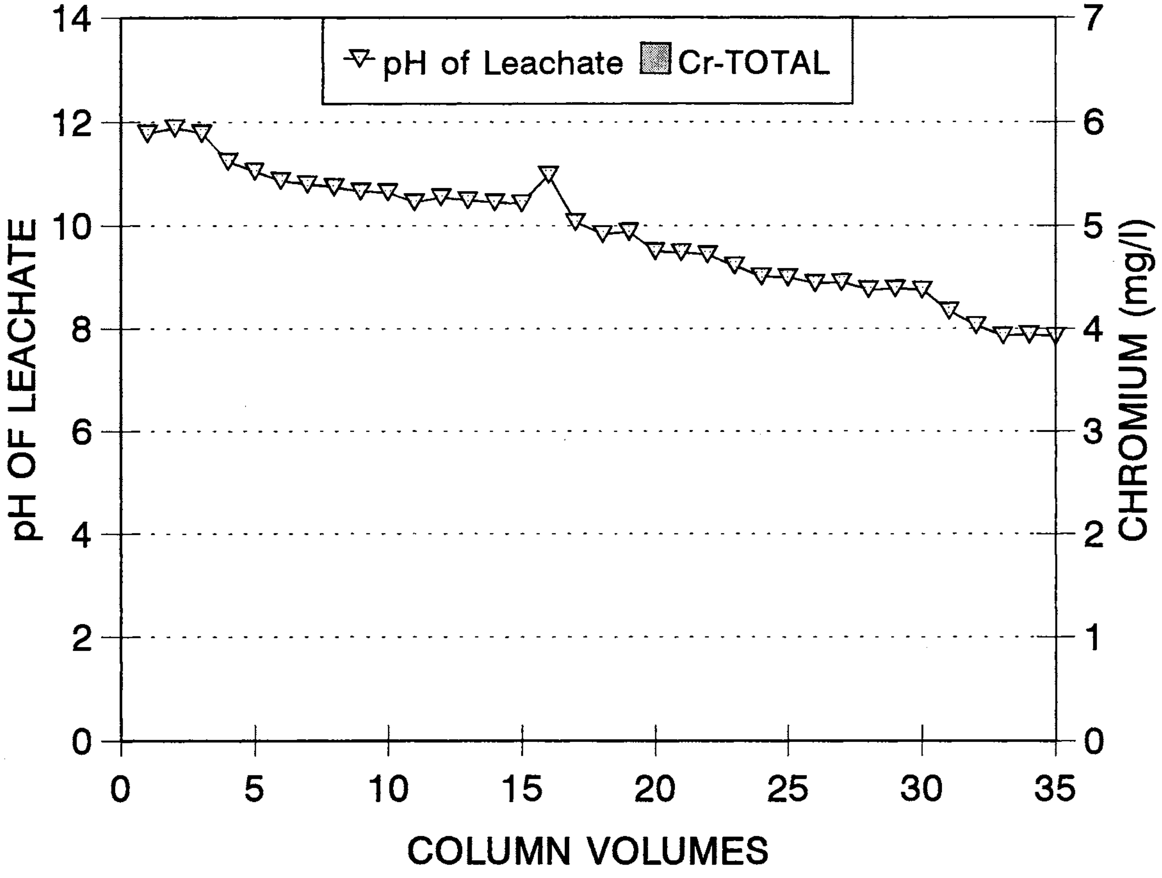

FIGURE 16: (COLUMN 5-7) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 7.0.
CO-SOLVENT (0.1 % v/v) 1,1,1-TRICHLOROETHANE

leachability of chromium affect acid rain of a pH value of 1.0 would have on treated waste/soil that has also been exposed to a co-solvent (1.0% v/v, 1,1,1-Trichloroethane). This represents a 10 fold increase of co-solvent as compared to column 5-1 with the same pH value of 1.0. Chromium was detected from column volume 27 through 35, with a total chromium release of less than 12 mg/l. No hexavalent chromium was detected. These results appear to be very similar to column 1-1, therefore, it does not appear that by increasing this co-solvent by 10 fold affected leachability of chromium. It appears that for these treated waste/soils chromium leachability is pH dependent and independent of a 1.0 % v/v, 1,1,1-Trichloroethane co-solvent.

Figure 18 (column 6-4) describes the affect the leachability of chromium affect acid rain of a pH value of 4.0 would have on treated waste/soil that has also been exposed to a co-solvent (1.0% v/v, 1,1,1-Trichloroethane). This represents a 10 fold increase of co-solvent as compared to column 5-4 with the same pH value of 4.0. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appears to be similar to column 1-4, therefore, it does not appear that increasing the co-solvent by 10 fold at this pH affected the leachability of chromium in the treated waste/soil.

Figure 19 (column 6-7) describes the affect a neutral rain of a pH value of 7.0 would have on the treated

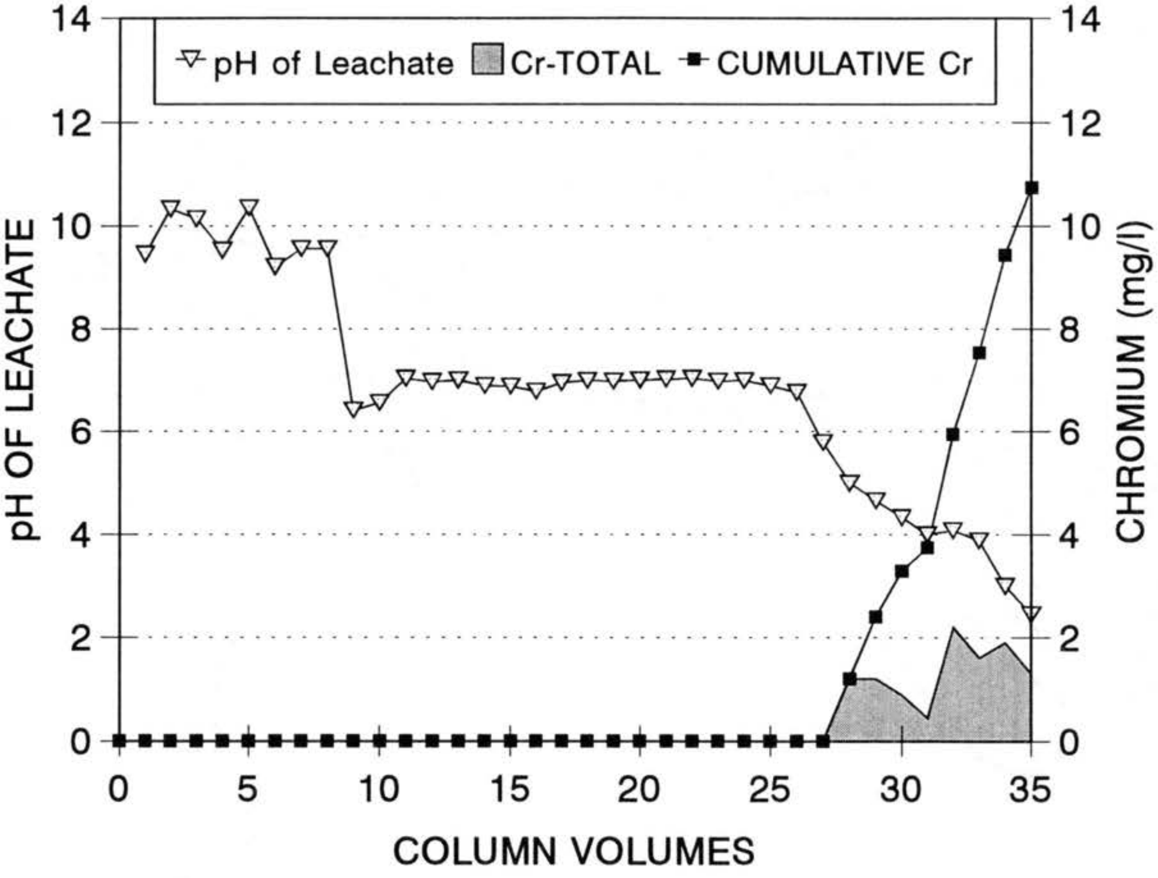

FIGURE 17: (COLUMN 6-1) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 1.0. CO-SOLVENT (1.0 % v/v) 1,1,1-TRICHLOROETHANE

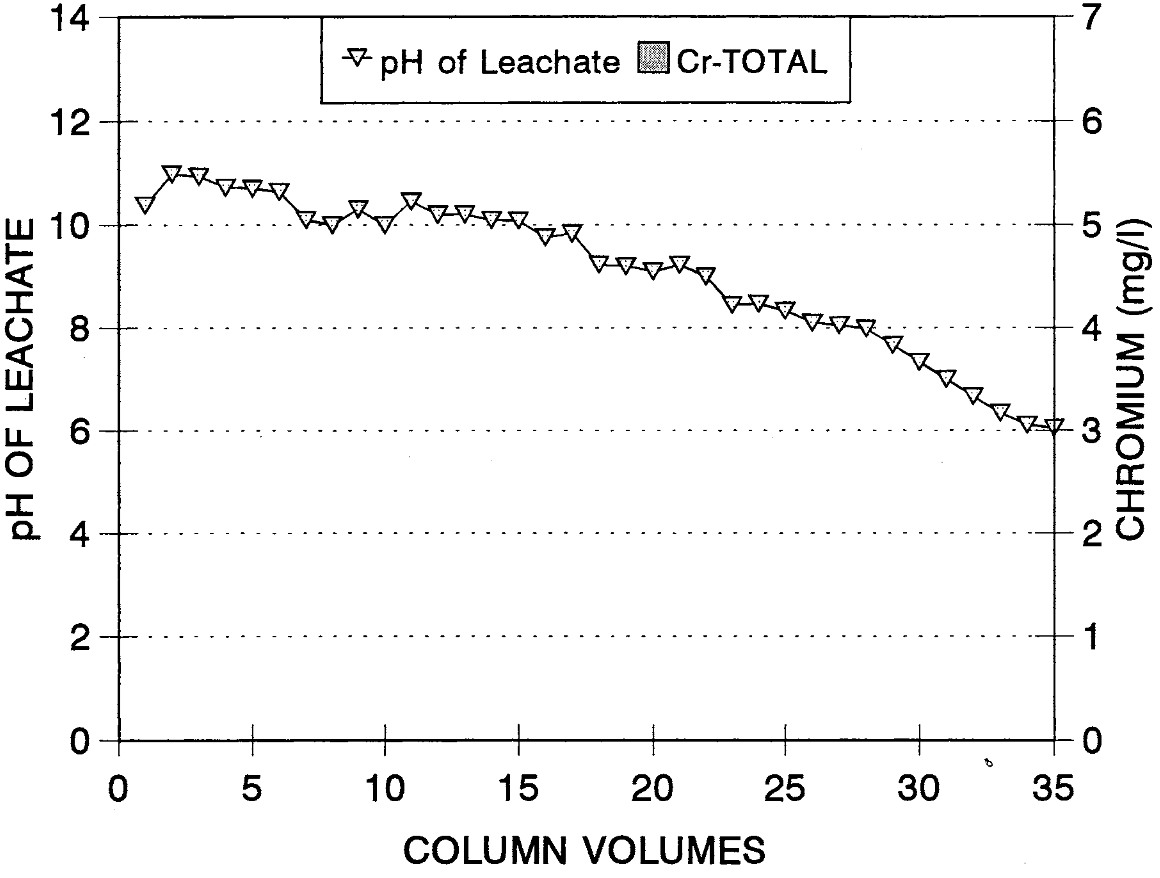

FIGURE 18: (COLUMN 6-4) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 4.0.
CO-SOLVENT (1.0 %) 1,1,1-TRICHLOROETHANE

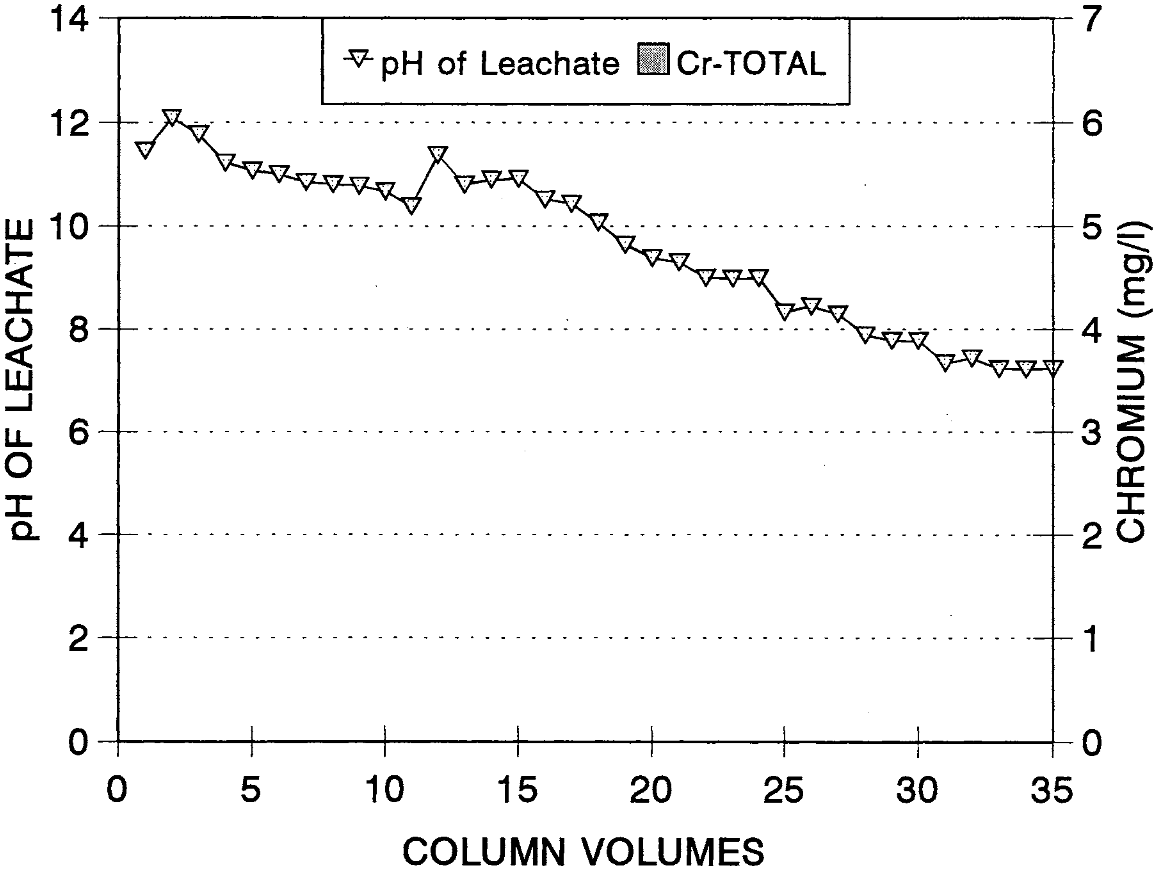

FIGURE 19: (COLUMN 6-7) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 7.0. CO-SOLVENT (1.0 %) 1,1,1-TRICHLOROETHANE

waste/soil that have also been exposed to a co-solvent (1.0% v/v, 1,1,1-Trichloroethane). The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appears to be similar to column 1-7, therefore, it does not appeared that by increasing this co-solvent by 10 fold affects the leachability of chromium in the treated waste/soil.

Figure 20 (column 7-1) describes the synergistic affects of an acid rain of pH value of 1.0, wet-dry/freeze thaw cycles and a co-solvent (0.1 % v/v, 1,1,1-Trichloroethane) of treated waste/soil. Chromium was detected from column volume 27 through 35, with a total chromium release of 10 mg/l. No hexavalent chromium was detected. These results appear to be very similar to column 1-1, therefore, it does not appear that these synergistic interactions affected the leachability of chromium. It appears that for these treated waste/soils chromium leachability is pH dependent and independent of these synergistic affects.

Figure 21 (column 7-4) describes the synergistic affects of an acid rain of pH value of 4.0, wet-dry/freeze thaw cycles and a co-solvent (0.1 % v/v, 1,1,1-Trichloroethane) of treated waste/soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appears to be similar to column 1-7, therefore, it does not appear that these synergistic interactions affected

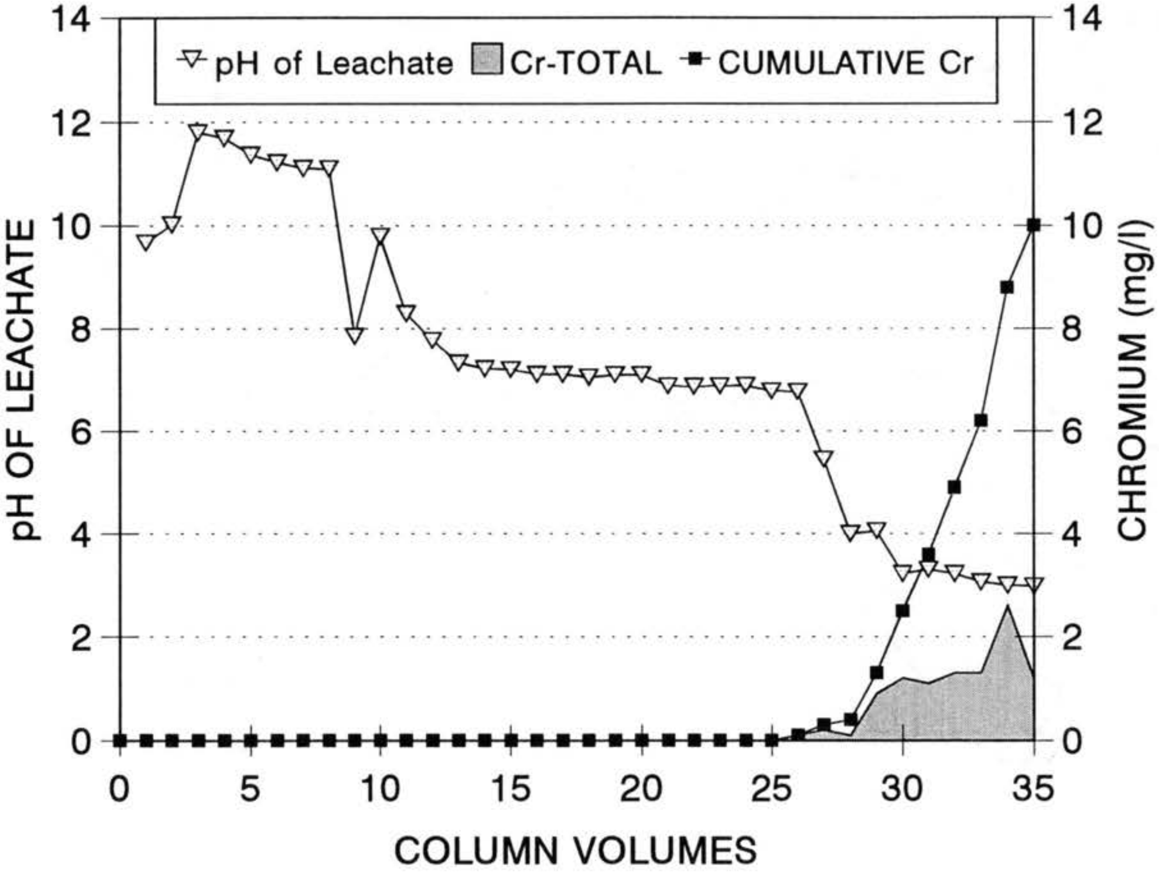

FIGURE 20: (COLUMN 7-1) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 1.0
SYNERGISTIC EFFECTS (FREEZE-THAW/WET-DRY, (0.1 % v/v) 1,1,1-TRICHLOROETHANE.

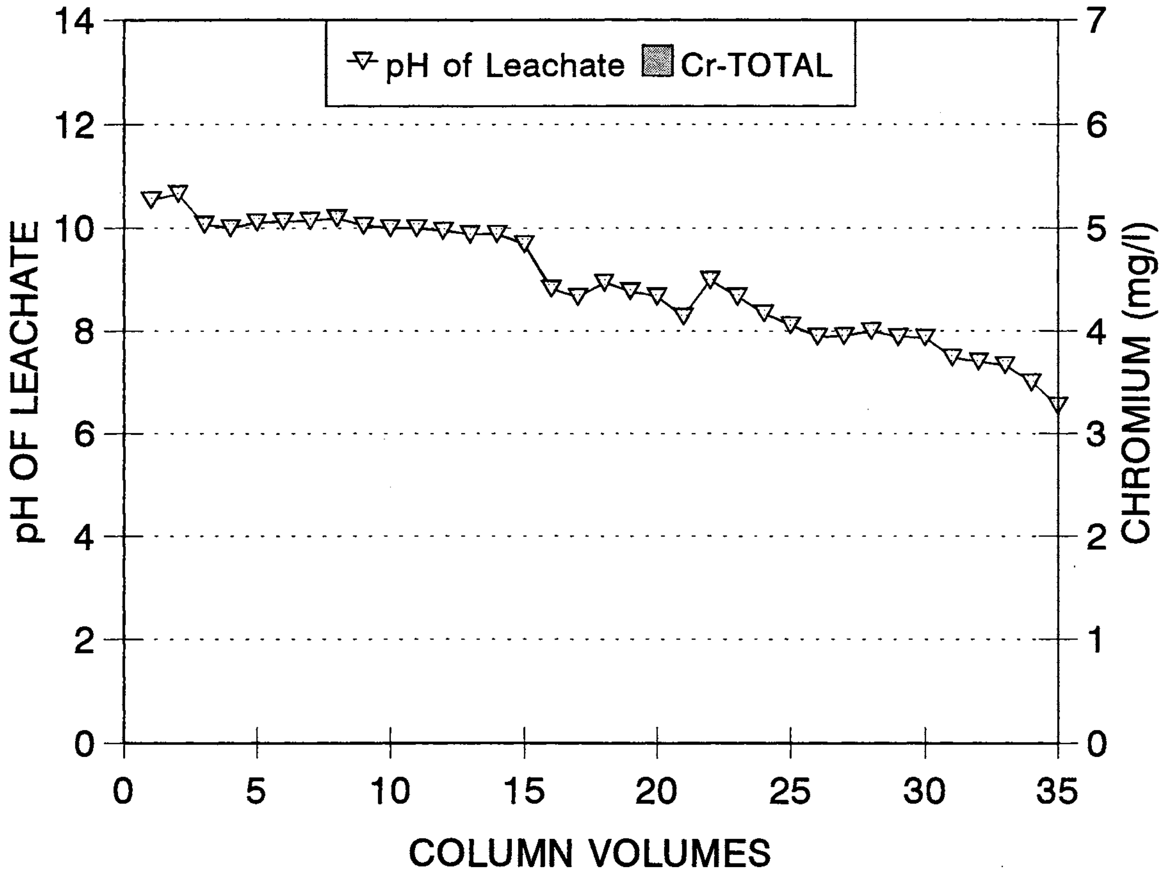

FIGURE 21: (COLUMN 7-4) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 4.0 SYNERGISTIC EFFECTS (FREEZE-THAW/WET-DRY, (0.1 % v/v) 1,1,1-TRICHLOROETHANE.

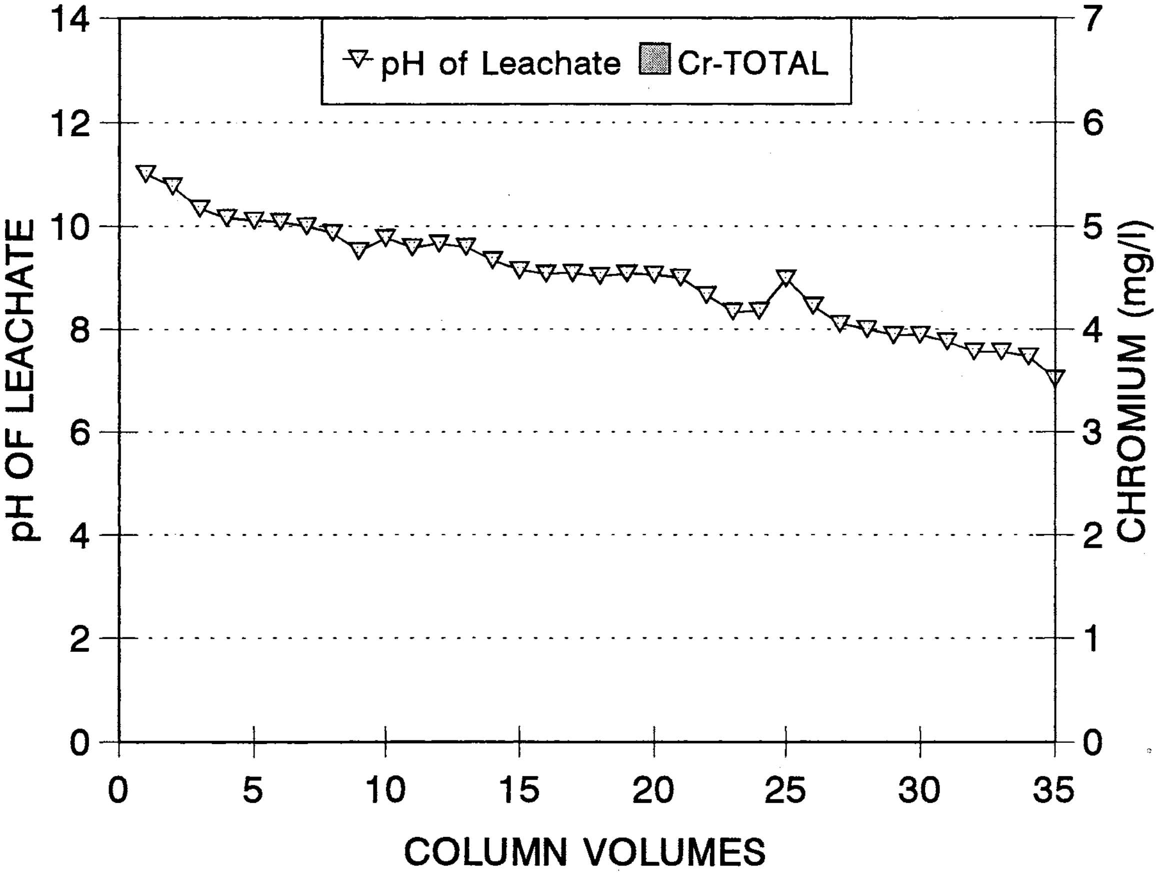

FIGURE 22: (COLUMN 7-7) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 7.0 SYNERGISTIC EFFECTS (FREEZE-THAW/WET/DRY, (0.1 % v/v) 1,1,1-TRICHLOROETHANE.

the leachability of chromium.

Figure 22 (column 7-7) describes the synergistic affects of a neutral rain of pH value of 7.0, wet-dry/freeze thaw cycles and a co-solvent (0.1 % v/v 1,1,1-Trichloroethane) of treated waste/soil. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appear to be similar to column 1-4, therefore, it does not appear that these synergistic interactions affected the leachability of chromium.

Figure 23 (column 8-1) describes the synergistic affects of an acid rain of pH value of 1.0, wet-dry/freeze thaw cycles and a co-solvent (1.0 % v/v, 1,1,1-Trichloroethane) of treated waste/soil. This represents a 10 fold increase of co-solvent as compared to column 7-1 with the same pH value of 1.0. Chromium was detected from column volume 27 through 35, with a total chromium release of 9.0 mg/l. No hexavalent chromium was detected. These results appear to be very similar to column 1-1, therefore, it does not appear that these synergistic interactions affected the leachability of chromium. It appears that for these treated waste/soils chromium leachability is pH dependent and independent of these synergistic affects.

Figure 24 (column 8-4) describes the synergistic affects of an acid rain of pH value of 4.0, wet-dry/freeze thaw cycles and a co-solvent (1.0 % v/v, 1,1,1-Trichloroethane) of treated waste/soil. This represents a

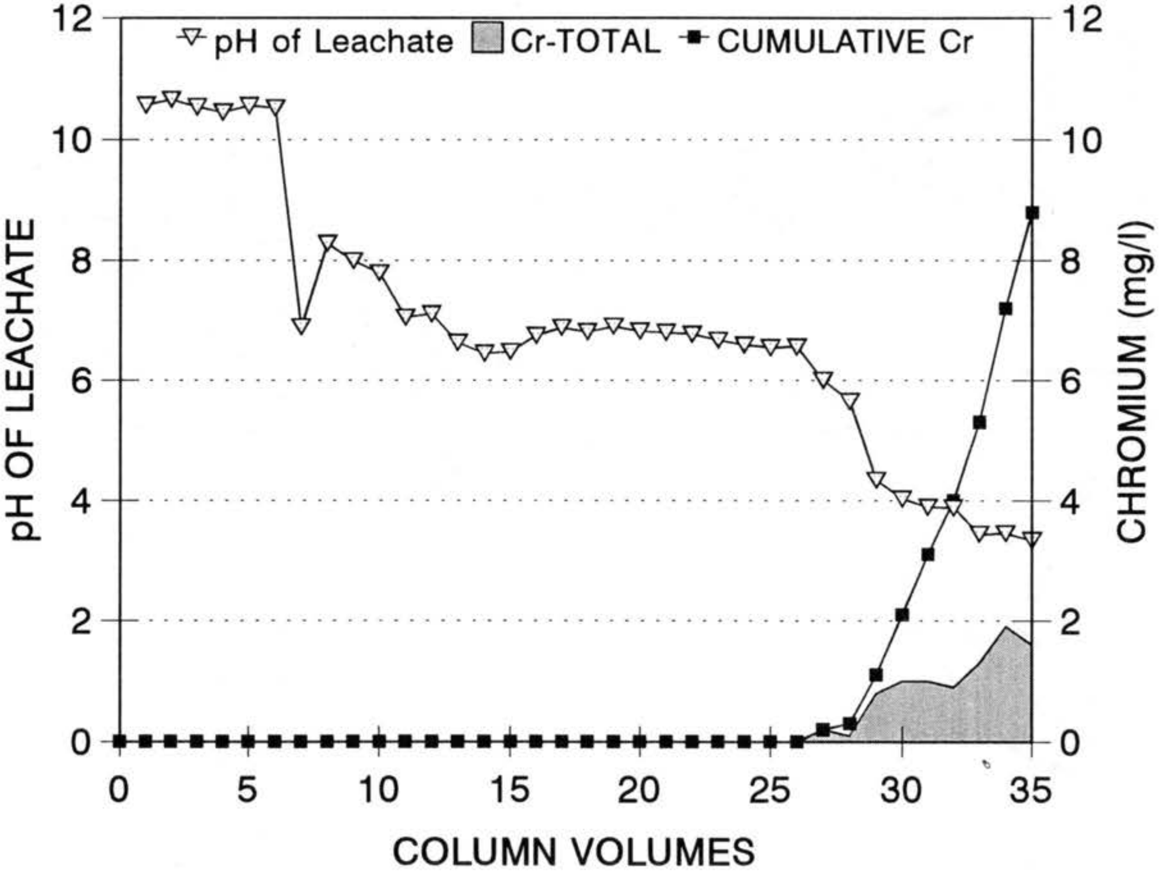

FIGURE 23: (COLUMN 8-1) EFFLUENT LEACHATE OF TREATED WASTE, INFLUENT pH EQUALS 1.0
SYNERGISTIC EFFECTS (FREEZE-THAW/WET-DRY, (1.0 % v/v) 1,1,1-TRICHLOROETHANE

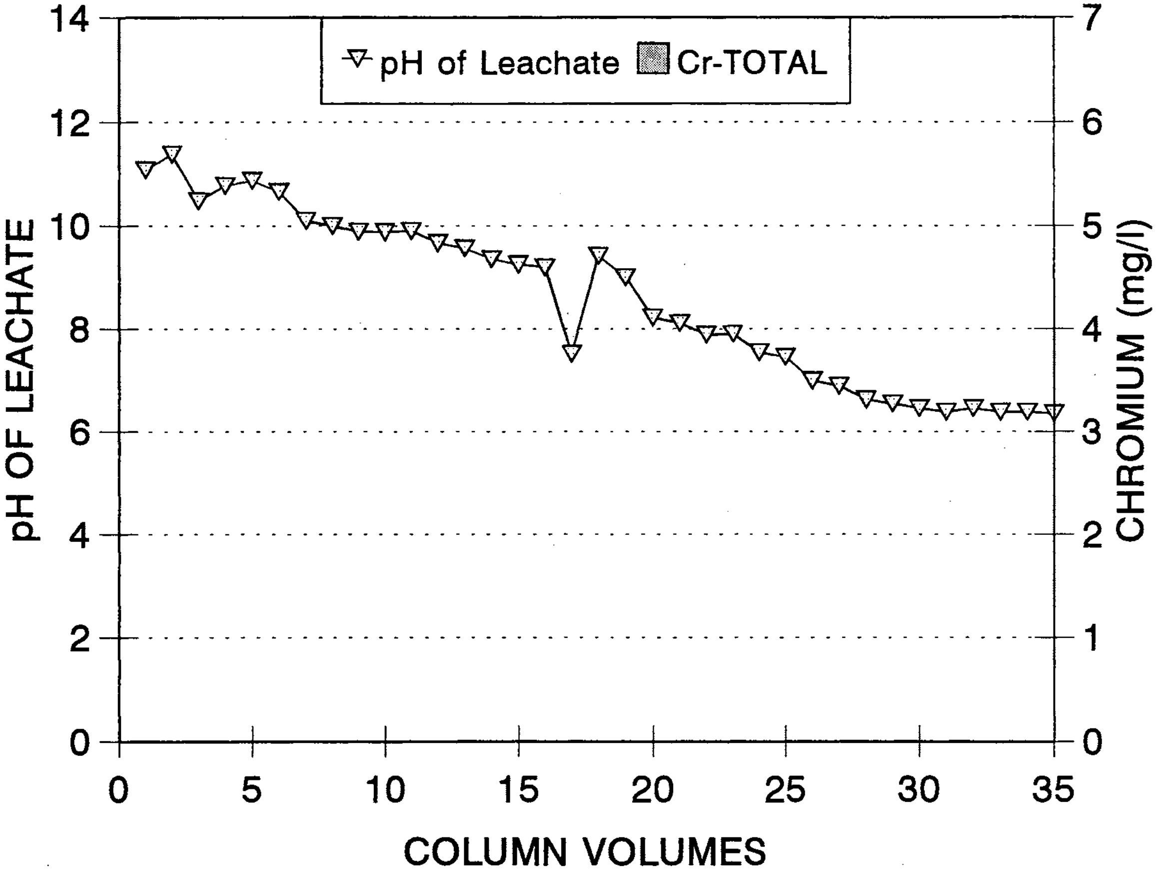

FIGURE 24: (COLUMN 8-4) EFFLUENT LEACHATE OF TREATED WASTE, INFLUENT pH EQUALS 4.0 SYNERGISTIC EFFECTS (FREEZE-THAW/WET-DRY, (1.0 % v/v) 1,1,1-TRICHLOROETHANE.

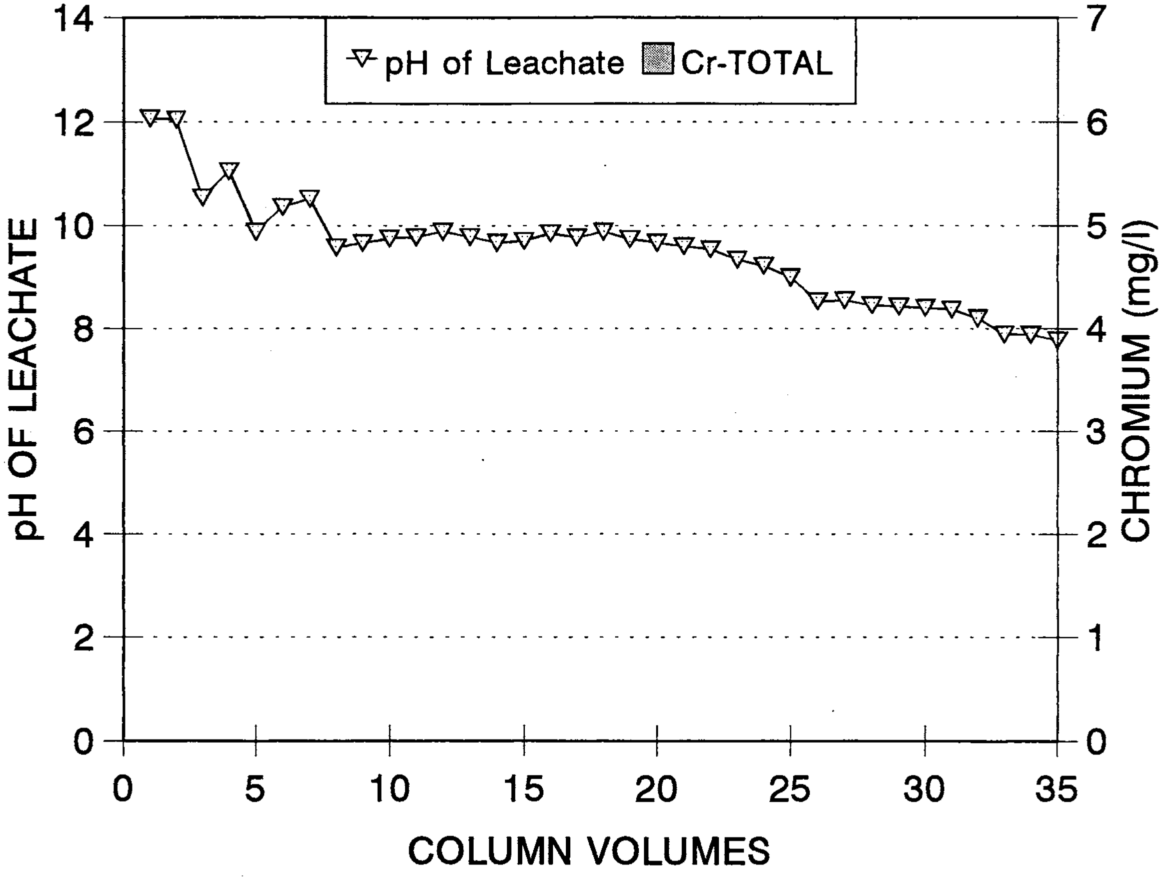

FIGURE 25: (COLUMN 8-7) EFFLUENT LEACHATE OF TREATED WASTE. INFLUENT pH EQUALS 7.0 SYNERGISTIC EFFECTS (FREEZE-THAW/WET-DRY, (1.0 % v/v) 1,1,1-TRICHLOROETHANE.

10 fold increase of co-solvent as compared to column 7-4 with the same pH value of 4.0. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appears to be similar to column 1-4, therefore, it does not appear that these synergistic interactions affected the leachability of chromium.

Figure 25 (column 8-7) describes the synergistic affects of a neutral rain of a pH value of 7.0, wet-dry/freeze-thaw cycles and a co-solvent (1.0 % v/v 1,1,1-Trichloroethane) of treated waste/soil. This represents a 10 fold increase of co-solvent as compared to column 7-7 with the same pH value of 7.0. The buffering capacity of the column did not appear to be spent, even after 35 column volumes, no chromium was detected. The results appears to be similar to column 1-7, therefore, it does not appear that these synergistic interactions affected an increases chromium solubility.

Figures 26 (column 9-1), 27 (column 9-4) and 28 (column 9-7) describe the affects of rain at different pH values, (1.0, 4.0 and 7.0 respectively), would have had on stabilized soil/waste that has not be pre-treated. This pre-treatment is the chemical reduction of hexavalent chromium to trivalent chromium. The data clearly shows that chromium can easily leach from a stabilized material, independent of influent pH values, if the chemical reduction has not taken place prior to stabilization.

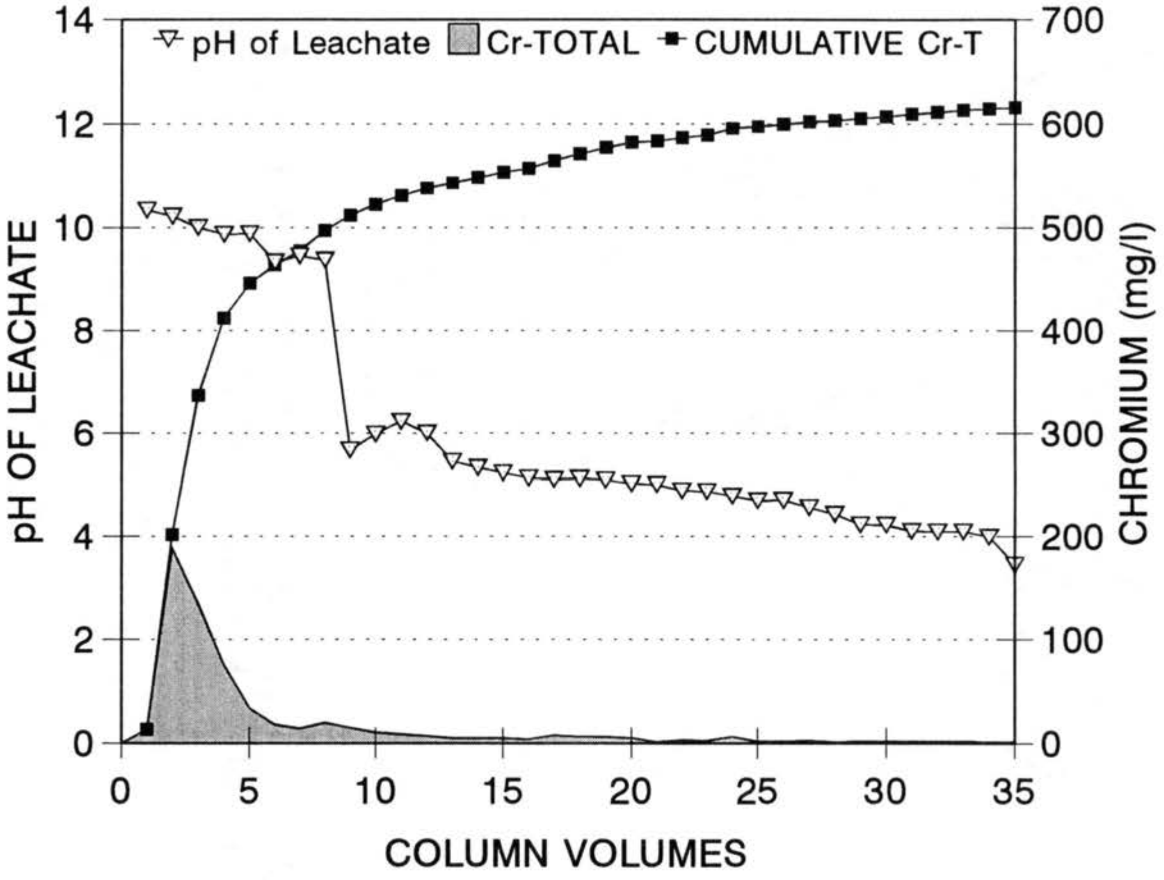

FIGURE 26: (COLUMN 9-1) EFFLUENT LEACHATE OF TREATED WASTE, INFLUENT pH EQUALS 1.0
NO CHEMICAL REDUCTION OF Cr+6 TO Cr+3 BEFORE STABILIZATION

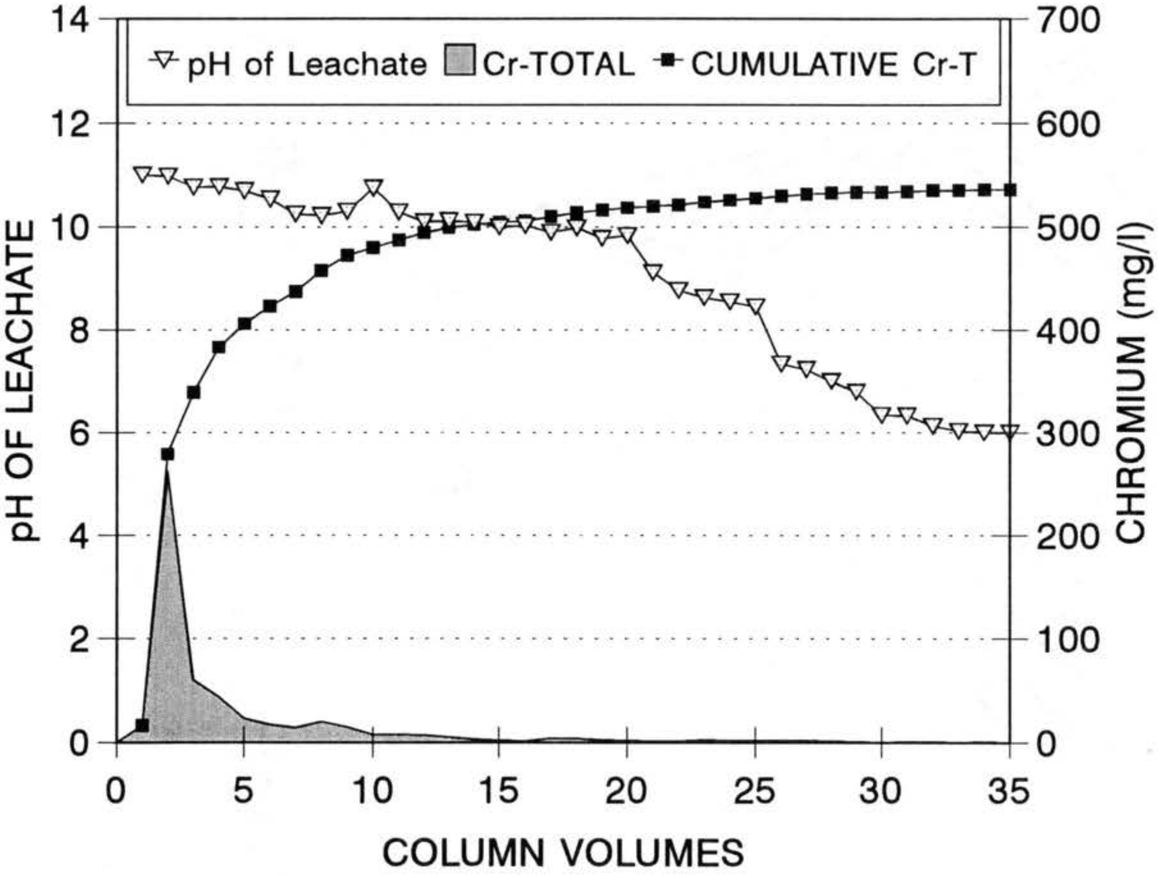

FIGURE 27: (COLUMN 9-4) EFFLUENT LEACHATE OF TREATED WASTE, INFLUENT pH EQUALS 4.0
NO CHEMICAL REDUCTION OF Cr+6 TO Cr+3 BEFORE STABILIZATION

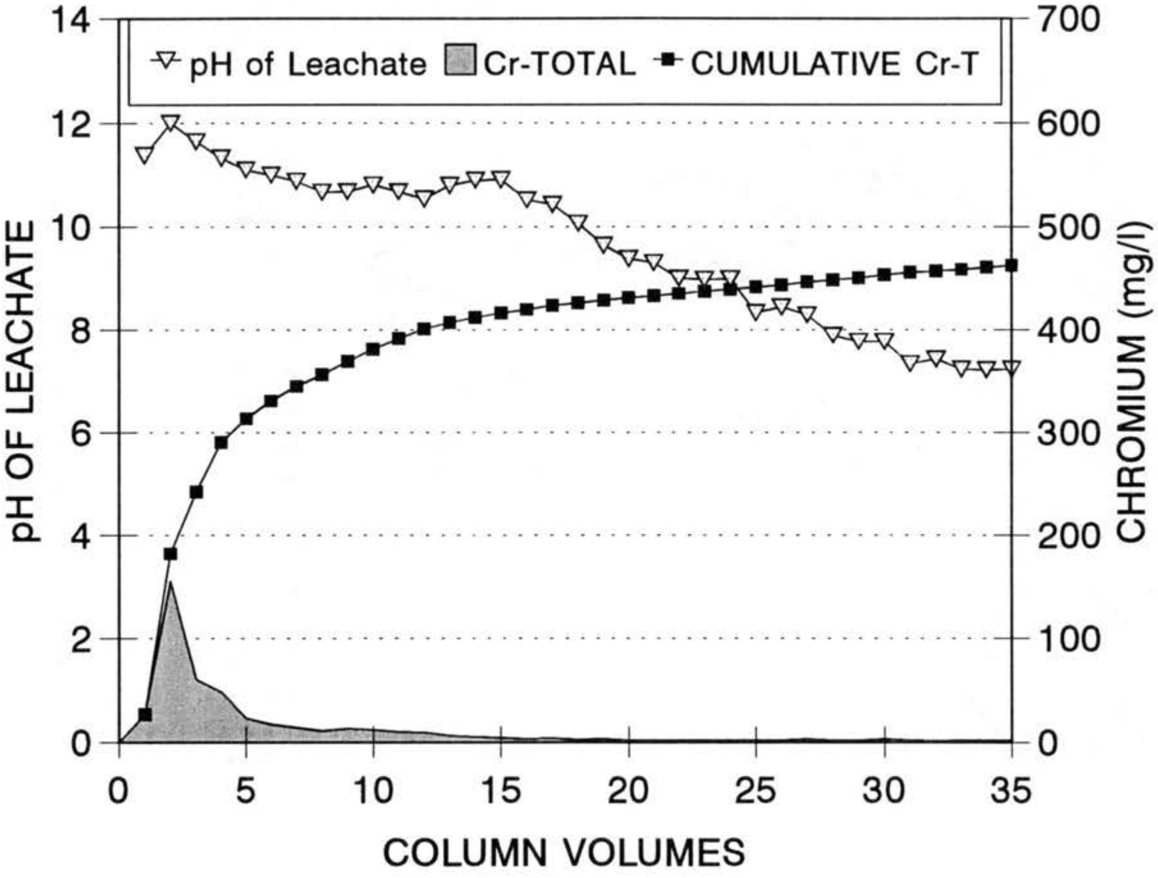

FIGURE 28 (COLUMN 9-7) EFFLUENT LEACHATE OF TREATED WASTE, INFLUENT pH EQUALS 7.0
NO CHEMICAL REDUCTION OF Cr+6 TO Cr+3 BEFORE STABILIZATION

Physical Analysis

Table 10 describes the physical analysis performed on the background soils, the test methods and results. Table 11 describes the physical analysis performed on the in situ treated waste/soils, the test methods and the results.

The physical analyses showed that the density (wet and dry) of the in situ treated waste/soils was less than the background soil. This could be attributed to during the stabilization process, using a roto-tiller may "fluff" the waste/product with air. This entrainment of air is beneficial in prevention of the degradation of the treated waste when exposed to wet-dry/freeze-thaw cycles.

The treated waste/soil also had a decrease in permeability as compared to the background soils. But the in situ treated soils had an increase in the unconfined compressive strength as compared to the background soils. This is typical for stabilized waste/soils. As soil is stabilized with cement kiln dust, the strength of the soil increases with a decrease in permeability.

TABLE 10

PHYSICAL ANALYSIS OF BACKGROUND SOILS

Parameter	Results	Test Protocol
Dry Density (LB/FT3)	131.0	ASTM D2922-81
Wet Density (LB/FT3)	143.9	ASTM D2922-81
Moisture Content (%)	9.1	ASTM D2216-80
Volume of Voids (FT3)	0.205	ASTM 301-88
Volume of Solids (FT3)	0.795	ASTM 301-88
Void Ratio	0.258	ASTM 301-88
Specific Gravity	2.617	ASTM 854-83
Unconfined Compressive Strength (PSI)	10.2	ASTM D2166-85
Grain Size (Percent)		
Sand	40.0	ASTM D422-63
Gravel	34.0	ASTM D422-63
Silt	23.0	ASTM D422-63
Clay	3.0	ASTM D422-63
Permeability (CM/S)	3E-08	ASTM STP 479

TABLE 11

PHYSICAL ANALYSIS OF IN SITU TREATED WASTE/SOILS

Parameter	Results	Test Protocol
Dry Density (LB/FT3)	100.3	ASTM D2922-81
Wet Density (LB/FT3)	118.8	ASTM D2922-81
Moisture Content (%)	18.8	ASTM D2216-80
Specific Gravity	2.179	ASTM 854-83
Unconfined Compressive Strength (PSI)	75.0	ASTM D2166-85
Permeability (CM/S)	5E-09	ASTM STP 479
Paint Filter Test	Passed	EPA 9095-SW846
Optimum Moisture Content	21.6	ASTM D698, M-C
Maximum Dry Density (LB/FT3)	102.2	ASTM D698, M-C

CHAPTER VI

CONCLUSIONS

It should be noted that the following conclusions are based solely upon the data obtained from the 35 column volumes per column set in this study. It would be difficult to correlate these 35 column volumes to a specific time interval.

- No hexavalent chromium was found in any of the indigenous soils (background soils).
- Hexavalent chromium can be chemically reduced and stabilized in situ using ferrous sulfate and cement kiln dust. This in situ process for the treatment of hexavalent chromium is extremely effective in the immobilization of chromium.
- Stabilized waste/soils have a greater buffering capacity than indigenous soils. It appears that the buffering capacity of the cement kiln dust (due to free lime) has a beneficial effect in the immobilization of chromium.
- Stabilized waste/soils have a less chance due to chromium entrainment of leaching chromium than the normal indigenous soils when both are exposed to the same concentrations of sulfuric acid.
- Pre-treatment (chemical reduction) of hexavalent

chromium to trivalent chromium is necessary in the pozzolanic stabilization/solidification of a waste soil contaminated with hexavalent chromium. The pozzolanic matrix does not entrain the hexavalent chromium, which would preclude leaching.

* If the chromic acid plating solution was allowed to remain in place without any form of treatment or remediation, this toxic hexavalent chromium could have leached to ground water.

* The only external effect that appears to increase the leachability of chromium was an acidic pH. Freeze-thaw/wet-dry, co-solvents nor the combinations of these external forces appear to have little effect on the ability of these soils to leach chromium.

* Increasing the co-solvent (1,1,1-Trichloroethane) concentration by 10 fold did not appear to effect the leachability of chromium.

* Silicon was not detected in column 1-1 (treated waste/ soil, influent pH equals 1.0) until the 26th column volume, at which point the silicon concentration increase dramatically, indicating the silicate matrix became solubilized. The very next column volume chromium was detected. Again, indicating the chromium had been entrained into the silicate matrix.

* The chromium that leached from column 3-1 (untreated waste/soil, influent pH of 1.0) did not leach in a linear manner. Rather, it appears that due to the

inability of the soil to adsorb the initial large concentration of chromium a "slug" of chromium passes through the column electrostatically bonded with hydronium ions, which was detected by a decrease in pH.

CHAPTER VII

RECOMMENDATIONS FOR FUTURE WORK

The potential for in situ chemical stabilization/ solidification using a waste material like cement kiln dust for the immobilization of wastes that have been spilled is vast. But the requisite research (treatability studies) will need to be performed prior to actual spill site remediation. In each instance leachability studies should be performed before and after treatment. Therefore, the following recommendations for future research are made.

- Sodium or potassium cyanide spills could be treated in situ by alkaline chlorination, releasing free nitrogen and carbon dioxide.
- Cadmium or chromium cyanide spills could be pre-treated with alkaline chlorination and then stabilized/ solidified with cement kiln dust and left in place.
- Phenolic acids spill could be pre-treated with a oxidizer (potassium permanganate or peroxide) and then stabilized with cement kiln dust.
- Spills of radioactive materials could be in situ stabilized/solidified using cement kiln dust.
- Many waste spills are comprised of mixtures of heavy metals and organics. These spill could be treated in

situ in a two-step process. Bioremediation could be used to treat the organics and cement kiln dust could be used for the treatment of the heavy metals.

* Plastic resins have been used for many years to increase the strength of cements and concrete. This same technique could be utilized in situ during the treatment of heavy metals using cement kiln dust in a waste/soil to enhance the strength of the final waste/product.

* The cement kiln dust used in this study is a waste/product from the bag house of a cement kiln. Therefore, it would contain and introduce other heavy metals such as Cd, Pb, etc., during the stabilization process. Long-term chemical analysis should be performed on a waste-product to determine if these metals are leaching from the waste product.

* On a controlled "spill", that is, by knowing the exact amount of chromic acid spilled, mass balance analysis should be conducted.

* Research should be conducted to determine if weathering has any effect on differences in leachability. A fresh spill should be compared to a one year old spill, to determine haw weathering affects leachability.

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