

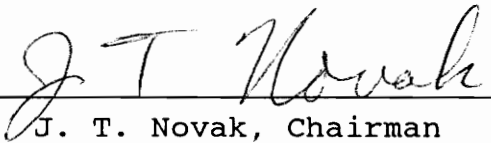
TREATMENT OF INORGANIC HAZARDOUS WASTE CONSTITUENTS
FOUND IN ELECTRIC ARC FURNACE DUST BY
SOLIDIFICATION\STABILIZATION

by

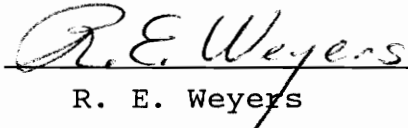
Tiffany Len Moore

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in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Environmental Engineering

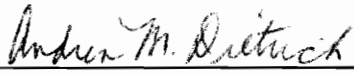
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Committee Chairman: John T. Novak
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(ABSTRACT)

In this study, solidification and stabilization processes were evaluated for use as a treatment method for electric arc furnace dust. Specific objectives were (1) to develop a solidified material capable of meeting EPA requirements for heavy metal leaching, and (2) to develop a solidified material that could be used for construction.

Results from the studies of the untreated electric arc furnace dust showed that the solubility of cadmium is controlled by the hydroxide species. Lead solubility is more complex because its solubility is controlled by a species other than hydroxide and therefore it is more difficult to predict. Studies also indicated that approximately 1.9% of the composition of the electric arc furnace dust is made up of lead.

This study demonstrated that solidification and stabilization is a viable treatment process for electric arc furnace dust. Success in treating the electric arc furnace dust by this method, however, depends upon such factors as the

compressive strength of the solidified waste, the amount of electric arc furnace dust incorporated in the concrete, and the ability of the solidified waste to remain intact during the Toxicity Characteristic Leaching Procedure (TCLP). Based on these factors, approximately 165 lb dust/cu yd concrete was determined to be the upper limit on the amount of electric arc furnace dust that can be incorporated in such a system. Efforts to improve the quality of the concrete by the addition of a chelating agent was moderately successful; however, the addition of salts to speed the concrete set times was not successful.

A model was developed which predicts the required compressive strength of the solidified dust based upon the amount of electric arc furnace dust that is incorporated in the concrete. The model effectively predicts, without performing the TCLP test, whether the solidified material will meet limits for heavy metal required by the EPA.

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CHAPTER 1

INTRODUCTION

Lead, cadmium, and zinc are common hazardous constituents in certain industrial wastes and are typically found at concentrations exceeding regulatory standards. These heavy metals are known toxins to both aquatic organisms and humans. Lead, used in vessels during Roman times, was known to cause gout, mental retardation, and personality changes in the Roman aristocracy and their offspring. Cadmium is a presumed carcinogen and studies have shown that it can concentrate in shellfish and other aquatic organisms as the result of discharging untreated cadmium-bearing wastes. Although not toxic to humans, zinc has been determined to be an aquatic toxin in high concentrations (Conner, 1990).

One method which has been proposed by the Environmental Protection Agency (EPA) to effectively immobilize and render heavy metal wastes nonhazardous is solidification and stabilization technology. The use of portland cement has been proven beneficial as a cementitious additive for the solidification and stabilization of hazardous wastes because it is highly uniform, relatively inexpensive, and widely available. Cement is commonly used because it acts as a binding agent, binding hazardous constituents physically as well as chemically into the cement matrix. Solidification and

stabilization is among one of the four recognized applicable technologies for steel waste (EPA, 1988).

This study was designed to evaluate cement-based solidification and stabilization systems for the immobilization of heavy metals contained in the dust generated from an electric arc furnace. Specific objectives of this study under laboratory conditions were:

1. to develop a cement-based solidification and stabilization system incorporating the electric arc furnace dust that would be adequate in terms of strength to permit utilization of the concrete as a product;
2. to minimize heavy metal leaching from the solidified matrix, particularly lead, so that the regulatory standards are not exceeded;
3. to determine the effects of cement additives and certain salts on the fixation of heavy metals solidified in the cement.

CHAPTER 2
LITERATURE REVIEW

Environmental Concerns with Electric Arc Furnace Dust

In the United States, over 57 million metric wet tons of hazardous wastes are generated annually and this figure is estimated to double by the year 2000 (Bishop et al., 1982). The Toxicity Characteristic Leaching Procedure (TCLP) which recently replaced the Extraction Procedure Toxicity test (EP Tox) was conceived in order to characterize hazardous waste components and to determine if toxic substances are present in the waste. It serves as the basis for environmental acceptability of a hazardous waste for land disposal (Conner, 1990). Untreated electric arc furnace dust generally exceeds the Environmental Protection Agency's (EPA) TCLP test for lead and cadmium by as much as 20 times the maximum allowable concentration. The maximum allowable concentrations for lead and cadmium as defined by the TCLP test are 5.0 mg/L and 1.0 mg/L, respectively (Pirages, 1990). Zinc, also a hazardous constituent of electric arc furnace dust, is currently not regulated by the TCLP test.

Much of the hazardous waste generated by electric arc furnace facilities is land disposed, raising the concern of toxic metals penetrating into groundwater and entering public water supplies. Leaching is one of the most important

mechanisms of mass transport for metals through the soil. The heavy metals in the electric arc furnace dust could cause severe environmental problems if leached in high concentrations. For instance, lead is a cumulative poison with a reputation dating back to the Roman Aristocracy. Lead has been known to interact with fulvic acids in the soil as well as speciate to form numerous compounds such as oxides, silicates, carbonates, and sulfates. Likewise, cadmium is a highly toxic metal and a suspected carcinogen known to be deadly towards fish and other aquatic organisms. Also, the outbreak of Itai Itai disease in Japan which has been linked to cadmium in the environment due to ingestion suggests that cadmium is toxic to humans. Although zinc is an important nutrient in plant and animal life, the EPA has determined that it is an aquatic toxin at high concentrations (Conner, 1990).

Characteristic Properties of Electric Arc Furnace Dust

Steel is an alloy of iron and other metals and nonmetals which aid in strength, durability, and corrosion resistance (Ullmann, 1969). A series of steps are required to produce a finished product from scrap metal. During the meltdown of scrap, hazardous waste in the form of a dust is generated during the primary production of steel in electric furnaces. At Roanoke Electric Steel Corporation (RESCO), the scrap metal is loaded into one of the two electric arc furnaces where temperatures can reach 2800 degrees Fahrenheit for complete

meltdown (RESCO, 1989). The particulate emissions from the electric arc furnaces, which are collected in baghouses, contain many of the hazardous inorganic constituents that are present in the raw materials (EPA, 1988). The metals present in the dust in the greatest proportions include zinc, lead, cadmium, and chromium; however, concentrations vary widely from sample to sample (RESCO, 1989). Olver Incorporated reported that approximately 60 percent by weight of the dust at RESCO is made up of metals. The other 40 percent consists of oxides and carbonates. Table 1 shows the average composition of electric arc furnace dust produced from a typical electric arc furnace. The dust is a fine brown powder with a fairly homogeneous composition and size. The dust can pass through a number 200 sieve (0.074 mm) which is slightly larger than cement particles (VPI&SU, 1989). Overall, the composition of the emission control dust varies depending on the scrap metal used and the grade of steel produced.

Solidification and Stabilization Systems

Previous Roanoke Electric Steel Research

Roanoke Electric Steel Corporation produces almost 6,000 tons of electric arc furnace dust annually. This material is a major problem because of costs associated with handling, transportation and disposal. In light of this, Roanoke Electric Steel Corporation contracted with Virginia Polytechnic Institute and State University in 1987 to study

Table 1. Major constituent composition of untreated electric arc furnace dust (K061) based on EPA's review of chemical analysis (from USEPA, 1988)

Major Constituents of EAF Dust	Concentration (%)
Iron	26
Oxygen (in metal oxides)	18
Zinc	16
Water	12
Calcium	7
Other Elements (C,N,H)	4
Fluorides	3
Manganese	3
Lead	2
Magnesium	2
Alkali Metals (Na,K)	2
Silica	2
Chlorides	2
Other BDAT Metals (Cd,Cr,Cu,As,etc.)	<.5
Total	100%

methods of solidifying and stabilizing the electric arc furnace dust using preliminary data provided by Olver Incorporated. The objectives of that study were to render the waste nonhazardous using solidification and stabilization techniques and to develop a useful construction material incorporating the dust as an additive. The findings of this study indicated that solidification and stabilization may be applicable for electric arc furnace dust but more research was needed to perfect the processes (VPI&SU, 1989). Currently, Roanoke Electric Steel Corporation utilizes solidification and stabilization to prepare the electric arc furnace dust for landfilling. This research is aimed at improving the process so that the product can be used as a construction material.

Definition of Solidification and Stabilization Systems

Only in the last few years has the EPA supported and conducted research in the area of solidification and stabilization. Interest in solidification and stabilization on the part of the solid waste disposal companies, government agencies, waste generators, and engineering firms began about 1975 in anticipation of the coming of the Resource Conservation and Recovery Act (RCRA). This has, in effect, created a boom in this technology and, currently, many solidification and stabilization systems are available or under development for a variety of wastes.

Solidification and stabilization technology, known also

as chemical fixation and solidification (CFS), is an effective method of tying up the heavy metals contained in a hazardous waste (Benson et al., 1985). Chemical fixation and solidification (CFS) systems chemically solidify the waste as well as "insolubilize, immobilize, encapsulate, destroy, absorb, or otherwise interact with selected waste components which are toxic or hazardous" (Conner, 1991). The ultimate goal of CFS is to produce a non-hazardous waste, or at least a less hazardous waste, than the original, untreated waste (Conner, 1991). The solidified waste may or may not be hazardous as defined by the TCLP test or other leaching tests. In addition, solidification and stabilization technology has become increasingly important for industries to assist in delisting a waste. Delisting occurs when it has been shown to the EPA that a specific waste stream is no longer hazardous and not capable of threat to the environment or to human health. Subsequently, CFS systems have become very valuable to waste generators (EPA, 1980).

Feasibility of Solidification and Stabilization on Electric Arc Furnace Dust

The EPA, whenever possible, sets treatment standards for electric arc furnace dust according to the Best Demonstrated Available Technology (BDAT) rather than to designate the use of a specific technology. By denoting performance standards, the EPA encourages flexibility and gives industries an

incentive to develop innovative technologies. Solidification and stabilization is among one of the four recognized applicable technologies for electric arc furnace dust (EPA, 1988). Solidification and stabilization methods are applicable for electric arc furnace dust because the dust is inorganic in nature and, in general, inorganic wastes are more amenable to solidification and stabilization processes than organics. This is because organics tend to interfere with the physical and chemical processes that bind the waste materials together (EPA, 1980). Also, this technology is more applicable to wastes with a high filterable solids content, low-to-moderate water content, and low total organic carbon (TOC) and grease content. The EPA proposed that electric arc furnace dust could be stabilized using either portland cement-based systems or lime/pozzolan-based systems. Although these processes have been implemented for electric arc furnace dust and they have been shown to effectively immobilize the hazardous heavy metals, a solidification/stabilization process developed for a particular waste is not applicable for other types of waste (EPA, 1988). Thus, new mix designs must be formulated for each waste type.

The applicability and use of stabilization and solidification techniques on Roanoke Electric Steel's furnace dust is also governed by its cost effectiveness. This technology is applied to hazardous waste for the reduction in the leaching ability of hazardous metal constituents but does

not destroy, recover, or change the waste constituents (EPA, 1988). Chemical fixation and solidification processes increase the size and weight of the waste, therefore, the handling costs, shipping costs, and disposal costs increase. Stabilization and solidification processes are usually recommended for electric arc furnace dust as long as practical and economically feasible disposal methods are selected.

Metal Fixation and Leaching Mechanisms

Overview

Many factors and mechanisms affect the degree of fixation or immobilization of constituents in the waste. In addition, several mechanisms cause or control the leaching of constituents from a waste. This section explains the most pertinent of these mechanisms in detail as well as discusses leachability and fixation of metals in the environment.

Measurement of Leachability

Leaching is defined as the rate of dissolution that can be measured when water penetrates through a material. The contaminated water that has passed through the solidified material is known as leachate. The rate is often measured in terms of concentration (mg/L) of the constituent in the leachate. Before choosing an appropriate CFS technology, the leachability of the hazardous constituents in the leachate is determined by the TCLP test rather than by actual testing at

the disposal site for long periods of time. Although the TCLP test does not actually simulate any real world set of conditions, arguably, it creates a worst-case scenario for leaching. More specifically, it simulates the leaching potential of a waste in a "mismanaged" landfill (Conner, 1990).

Fixation of Metals

Since they cannot be chemically or thermally destroyed, the most effective method of preventing the release of hazardous metals into the environment is by conversion into their most insoluble form. Likewise, metals can be fixed and effectively contained in a CFS system by several other mechanisms that may or may not operate simultaneously. Some of these mechanisms are chemisorption, redox potential control, adsorption, ion exchange, and precipitation (Conner, 1990). Chemical precipitation of metals as low-solubility species is probably the most effective fixation mechanism, according to researchers in this field. CFS systems can be developed such that metals can be precipitated as hydroxides, inorganic sulfides, silicates, carbonates, and even phosphates. For example, lead and cadmium carbonates are less soluble than their corresponding hydroxides. Patterson et al. (1977) found that lead and cadmium solubilities were controlled by carbonate precipitates over a small pH range. However, even with this in mind, the addition of carbonates to

CFS processes is not widely practiced because carbonates decompose irreversibly under the acidic conditions that the TCLP invokes and thus, the final speciation of the metal will be as the hydroxide (Conner, 1990).

pH Control

The control of pH was once thought to be the only important factor in metal fixation; however, recent studies have not only disproved this idea, but also concluded that several factors may control the rate of metal fixation (Conner, 1990). Nevertheless, CFS systems heavily depend on pH control for metal containment. In general, the minimum hydroxide solubility for metals is in the high pH range of 7.5-11; however, not all metals behave in the same manner and do not reach their minimum solubilities at the same pH. For example, lead hydroxide reaches its minimum solubility at about a pH 9.3 while cadmium has a minimum hydroxide solubility at a pH 11.2. Figure 1 shows solubility curves for several metal hydroxides that were obtained experimentally or calculated from stability constants (Conner, 1990). The lead solubility as carbonates and hydroxides are shown in Figure 2. The leachability of a hazardous constituent is determined by the solubility of the metal compounds. Obviously then, the final pH at the end of the TCLP test is important for controlling metal leachability since most metal hydroxides are sensitive to changing pH conditions.

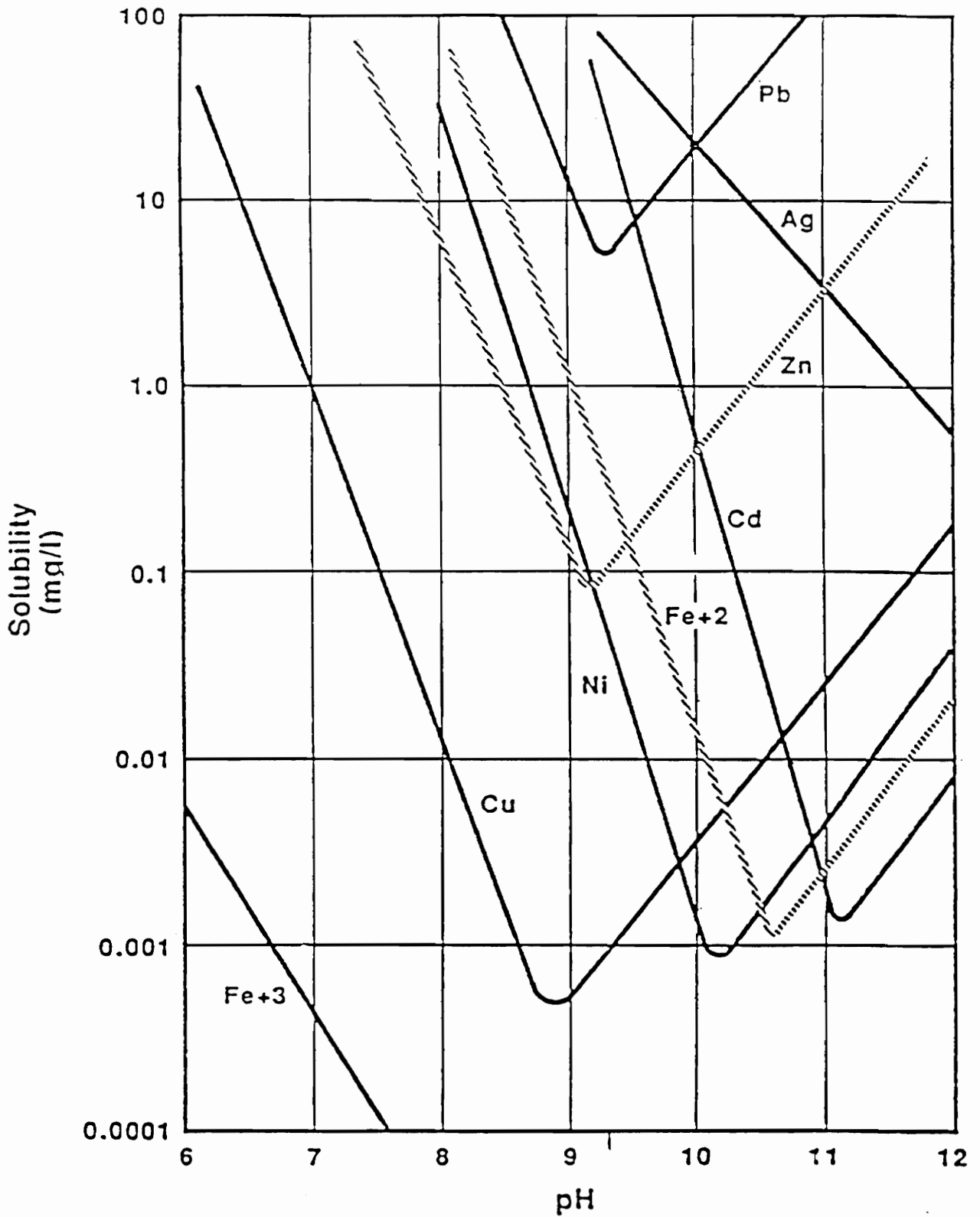


Figure 1. Solubilities of metal hydroxides as a function of pH (from EPA, in Conner, 1990)

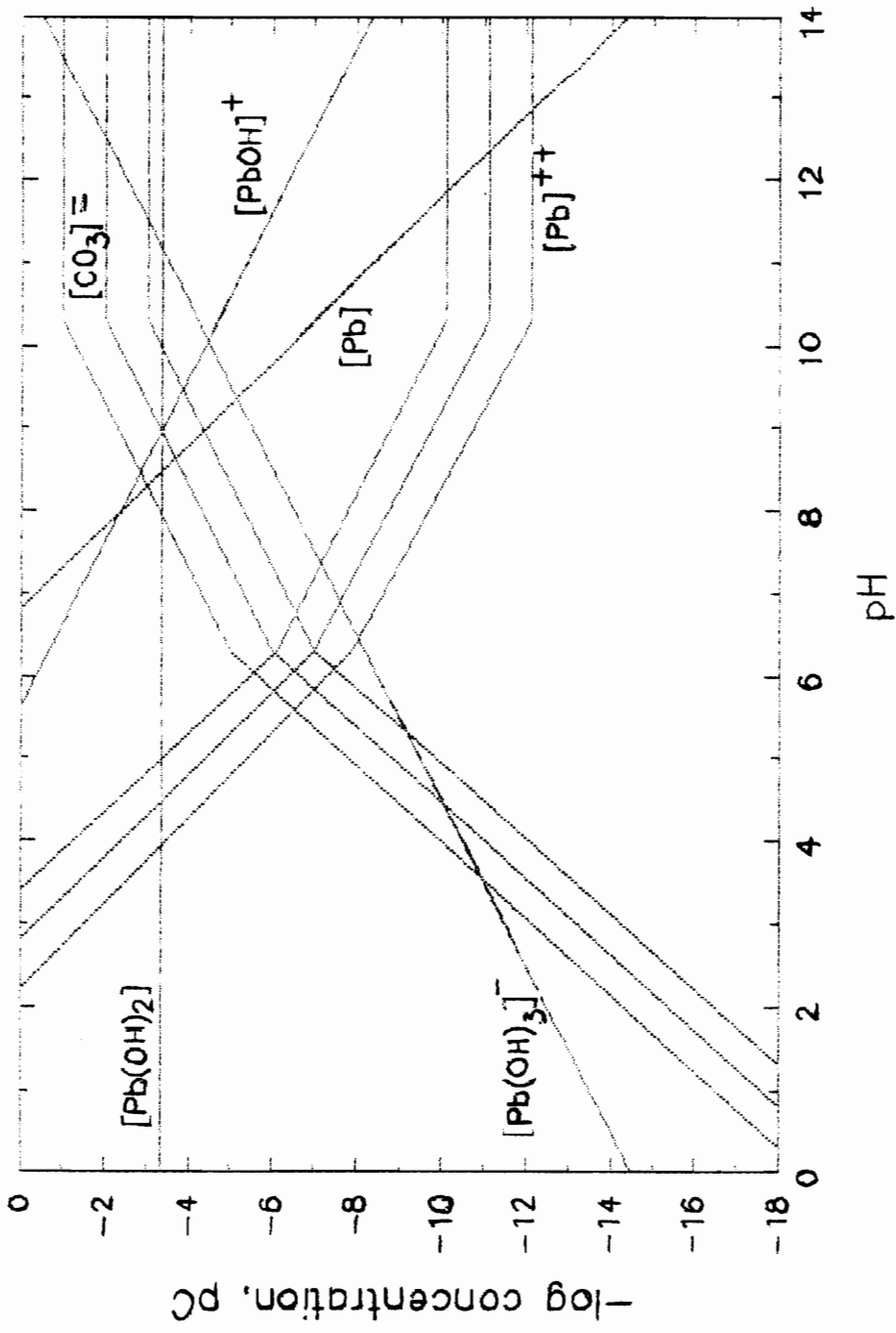


Figure 2. Lead solubility as carbonates and hydroxides

Most CFS systems are quite alkaline with a pH above 11; therefore, the solubility of the metal hydroxide in the CFS treated waste may be higher than the untreated hazardous waste. Moreover, the actual solubility of metals in wastes may vary widely from the hydroxide solubility curves that are shown in Figure 1 and the lead solubility curves as carbonates and hydroxides in Figure 2. This is because the wastes may contain a variety of soluble species such that the solubility of metals also depends on common ion effects, complexation, total ionic strength, and redox potential. Thus, in a complex system such as a CFS system, it is not easy to determine which metal species governs solubility so that predicting leachabilities of metal constituents is difficult (Conner, 1990).

Surface Area of the Waste

Particle size is also a key factor in the immobilization of hazardous constituents. Altering the waste before incorporation into a CFS system can affect the fixation of metals within the waste form. In some cases, reducing the particle size allows the waste to react better with the reagents in the CFS system. This results in an increase in metal fixation of the contaminants (Conner, 1990). Bishop et al. (1988) looked at the metal leachability of CFS systems and demonstrated that particle size is indeed related to the metal fixation of hazardous waste forms. From their experimental

work, it was determined that as the particle size decreased, metal leachability decreased. One mechanism thought to contribute to this behavior was the increased surface area formed by decreasing the particle size. The overall increase in surface area increases sorption of the waste to the cement particles and thus fixes the metals within the CFS system.

Solubilization into the Pore Water

Solubilization is an important factor in the leaching of constituents from a CFS system. A solidified waste is near or at equilibrium and is made up of a porous solid with one or more solid phases and a liquid phase known as the pore solution. Equilibrium is disturbed when the solidified waste is introduced to leaching conditions. This creates concentration gradients that induce bulk diffusion in the solid as a result of a difference in chemical potential between the solidified material and the leaching solution (Conner, 1990). Figure 3 schematically illustrates these main leaching mechanisms proposed by Cote et al., (1985) and are also more fully described in the literature (Conner, 1990, Cote et al., 1985)

In order for hazardous constituents from a CFS process to leach, the solid matrix must first dissolve into the pore water solution contained within the solid matrix or in the leachant (Conner, 1990). The pore water fluid pH is generally

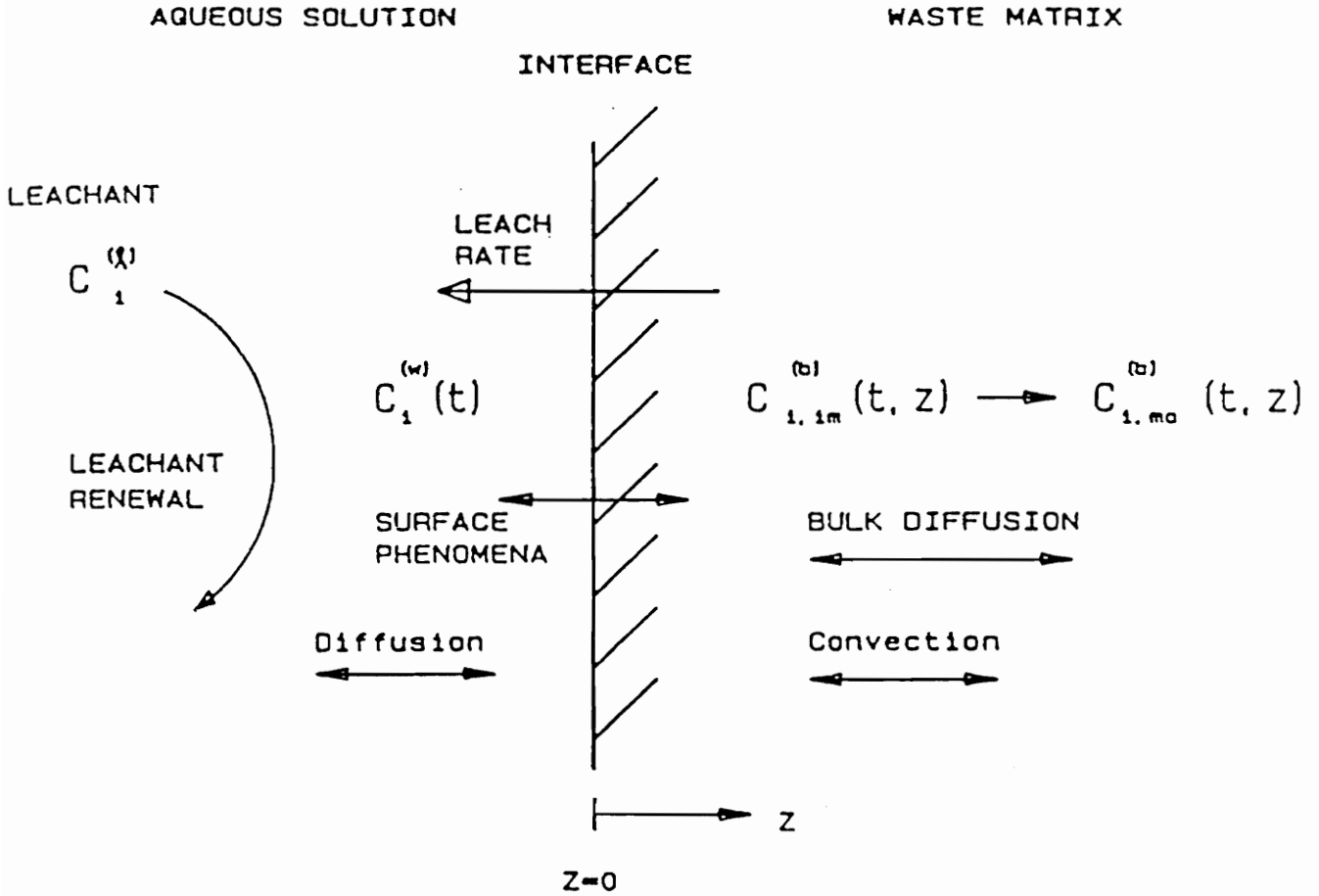


Figure 3. Leaching mechanisms (from Cote et al., in Conner, 1990)

between 12.5 and 13.5 due to the high concentration of hydroxide ions in the pore water solution. In an acidic, aggressive environment such as the TCLP test, solubilization of the solid cementitious particles creates a loss of equilibrium within the CFS system because of a reduction of alkalinity in the pore fluid. Therefore, deterioration of the CFS system by chemical reactions is related to the pH of the leachant and the buffering capacity of the pore fluid (Jones, 1990).

Effects of Concrete Admixtures to CFS Systems

Chemistry of Concrete

The most commonly used cementitious additive for the solidification and stabilization of hazardous wastes is portland cement because it produces products with highly predictable characteristics and can be used even by the unskilled laborer (Jones, 1990). Although a wide variety of standard types of portland cement are commercially available, the main constituents are: calcium oxide, magnesium oxide, silicon dioxide, aluminum oxide, ferric oxide, and small traces of ferrous oxide. portland cement is obtained by burning each of these compounds at a clinkering temperature and then grinding the resulting clinker . The resulting compounds that constitute the make-up of portland cement are essentially, Ca_3SiO_5 (C_3S), Ca_2SiO_4 (C_2S), $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A), and

$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ (C_4AF), magnesium oxide (MgO), and a little free calcium oxide (CaO) (Lea, 1971). Other compounds exist in portland cement but normally in nominal amounts.

The hydration of portland cement is a series of simultaneous and consecutive reactions that leads to the setting and hardening of the cement and occurs when water interacts with the previously mentioned cementitious constituents. The main compounds present in the portland cement clinker (C_3S , C_2S , C_3A , and C_4AF) are anhydrous but when reacted with water, they decompose and form hydrated compounds. At the instant of this reaction, C_3A and C_3S are among the quickest to react, followed by C_2S which reacts more slowly. The C_4AF reacts even more slowly than the C_3A (Lea, 1971). Although these hydration reactions are extremely complex, the rate of setting and hardening of portland cement is altered if any of the hydration reactions are retarded or accelerated. Many concrete admixtures that are incorporated into CFS systems can act as retarders or accelerators such as water-reducing admixtures, and air-entraining surfactants (Jones, 1990). The following sections discuss some of the portland cement admixtures used in CFS systems and explain their role in portland cement-based chemistry.

Water-Reducing Admixtures

Water-reducing admixtures, such as citric acid, gluconic

acid, and lignosulfonic acid, are added to cement-based systems to improve the consistency and workability of cement at a given water-to-cement ratio as well as to increase the strength and lower the permeability at a lower water-to-cement ratio than a concrete containing no admixture. Water-reducing agents act by adsorbing to the surface charges of cement particles such that they become hydrophilic and no longer are attracted to other cement particles (Jones, 1990). Many types of water-reducing admixtures are available depending upon the mix design requirements of the concrete. All water-reducing agents possess properties that can affect the compressive strength and durability of concrete. Also, because the incorporation of water-reducing agents results in a reduction of the water-to-cement ratio, they ensure that the permeability of the concrete is at a minimum. This is especially important in terms of leachability of hazardous constituents in a CFS system (Rixom and Mailvaganam, 1986).

Accelerating Admixtures

Concrete accelerating admixtures such as calcium chloride and triethanolamine increase the rate of hardening of cement and concrete mixes. Although the mechanisms of accelerators are not fully understood, it is clear that they accelerate the hydration of the C_2S and C_3S compounds. Accelerating admixtures not only reduce the set times of concrete, but they

are beneficial in terms of compressive strength. The incorporation of accelerators in concrete mixes will yield a higher 28-day compressive strength than a similar concrete mix with no accelerating admixture. Further, studies with calcium chloride as the accelerating agent demonstrate that concrete containing calcium chloride is more resistant to freeze-thaw conditions (Rixom and Mailvaganam, 1986).

Effects of Hazardous Waste Constituents on CFS Systems

Introduction

Hazardous wastes, when incorporated in CFS systems, can be severely detrimental to the chemical and physical characteristics of the portland cement. Retardation, inhibition, and acceleration of cement setting and curing of CFS systems can occur with the addition of a particular waste. Also, the compressive strength of the concrete, the hydration of cement, permeability, and overall stability can be affected by the addition of hazardous wastes. Heavy metal cations, in particular, can be detrimental to the characteristics of CFS systems (Conner, 1990). This section will encompass the problems encountered when heavy metal constituents of electric arc furnace dust are incorporated into CFS systems.

Detrimental Effects of Lead on CFS Systems

Most researchers in the field of solidification and stabilization are well aware of the detrimental effects that

lead has on CFS systems. So naturally, when Ortega et al. (1989) found that lead acts as a retarder to concrete setting and compressive strength, it was consistent with most previous studies. However, the researchers also wanted to answer the questions of how and why lead interfered with the strength and setting of concrete. In their attempt to understand the nature of chemical binding (fixation) of heavy metals in concrete, a CFS system was prepared by doping cement with a 10 percent by weight aqueous solution of lead nitrate and allowed to cure for 28 days. After studying these samples on a molecular level, it was discovered that lead is predominantly located at the surfaces of the cementitious material. This is very important in terms of cement hydration mechanisms. Lead salts interfered with the hydration processes of two of the clinker compounds, specifically C_3S and C_2S , by forming a "barrier to water interaction". These clinker compounds account for most of the strength acquired in the beginning stages of concrete curing. The fact that lead coats mainly the surface of the clinker serves to severely retard initial concrete setting by removing the surfaces where hydration occurs. The two clinker compounds contain "envelopes" of water under normal hydration conditions. However, in the presence of lead salts, hydration processes are hindered and the areas of water become supersaturated, thus promoting crystal growth. The increase in set times caused by the lead

promote crystal growth in these pockets and probably account for the decrease in overall strength (Ortega et al., 1980).

In another study, Shively et al. (1986) also found that lead as a nitrate salt was a concrete set retarder; however, the compressive strength was found not to be affected (EPA, 1990). Likewise, a study by Campbell et al. (1987) where cadmium and lead sludges were solidified in portland cement paste, suggested that the incorporation of lead or lead hydroxide in a CFS system had no detrimental affect on the system in terms of overall strength. However, Campbell stresses that these results are inconclusive and cannot be verified due to some physical and chemical interferences associated with their analysis.

The effects of lead as a nitrate salt on the hydration of cement was also thoroughly studied by Thomas et al. (1981). It was found by electron microscopic analyses that a colloidal gel containing lead formed around the cement particles when lead waste was added, similar to previous work by Ortega et al. (1980). This behavior of lead decreased the early strength gain; however, the authors note that the decrease in early strength did not affect the long-term strength and no significant effects on the hydration processes were reported. It was concluded that other metals such as zinc and copper would affect concrete in a similar manner.

Bishop et al. (1988) later theorized that lead (and chromium as well) are bound into the silica matrix itself

rather than remaining trapped in the pores of the concrete. This was discovered when, after much testing, lead did not leach at a fast rate compared with other metals thought to reside in the pores. It appeared that lead remained soluble throughout the cement process due to the high pH of the cement at the time of cement-waste mixing. Consequently, this lead was available to react with the silicates in the paste formation rather than becoming trapped in the pores of the concrete. They found that even after sequential extractions of the solidified waste, when all of the alkalinity was leached and 50 to 70 percent of the original sample was dissolved, 75 percent of the lead remained bound to the concrete and did not leach. Therefore, the lead was bound to the silicates which were not solubilized instead of precipitating as hydroxides. Thus, the leachability of lead was found to be dependent on the dissolution of the silicate matrix, and very strongly complexed in the matrix, releasing only after the silica matrix was destroyed.

Effects of Cadmium on CFS Systems

Shively et al. (1986) also studied the impact of cadmium salts, specifically cadmium nitrate, incorporated in cement paste samples to determine the consequences on compressive strength of concrete. They found that cadmium acted as a retarder and consequently reduced the 14 day compressive strength. It was concluded that this phenomenon occurred

because cadmium interfered with the hydration and formation of the cement matrix compounds.

Campbell et al. (1987) revealed an even more impressive detrimental property of cadmium in CFS systems. They found that the presence of cadmium and its release into the leachant is directly related to the physical dissolution of Portland cement paste. After testing the leachability of solidified cadmium sludges using a synthetic seawater leachant, large macroscopic cracks were noted within the solidified samples. The cracks brought about a significant increase in cadmium released into the leachant. Also noted was an increase in porosity, and a greater abundance of crystals in the cadmium paste samples. Based on these results, it has been concluded by the authors that the incorporation of cadmium interferes with the solidification and stabilization process such that the structural integrity of the concrete is decreased and more cadmium is released into the environment.

Lead and cadmium-based paint residue known in the industry as "glass bead waste" was solidified in Portland cement by Benson et al. (1985) in order to determine the effects of strength and leachability. They found that the addition of glass bead waste resulted in a decrease in concrete strength. Also, the cement paste failures increased as more of the glass bead waste was added to the CFS system. The authors believed that these trends occurred because the glass bead waste is made up of very fine particles which have

a large surface area. The large surface area evidently reduced the amount of cement available for binding and stabilizing and allowed more cadmium to be released into the environment.

In another study by Bishop et al. (1988), cadmium as a hydroxide was incorporated into a Portland cement based system where leachability characteristics and buffering capacity were analyzed in an attempt to understand how cadmium is bound in CFS processes. At the high pH (12 to 13) of the cement paste when it is being mixed with the waste and begins to set, cadmium hydroxide is not soluble and it remains a solid, thus it is trapped into the pores as the cement paste matrix is formed. It was determined that cadmium is significantly leached out of the pores only when the alkalinity is leached from the pores which was measured by performing sequential extractions of the stabilized material. The final pH after the fourth extraction of the leachant acid was below 6 and at this time, cadmium leached significantly. Thus, cadmium leachability was found to be dependent on the release of alkalinity and subsequent lowering of the pH of the leachant acid.

Effects of Zinc on CFS Systems

The effect of zinc on the hydration of two principal portland cement compounds, C_3S and C_3A , was examined by

Arlinguie et al. (1982). Using x-ray diffraction, it was determined that zinc acted as a retarder by interfering with the hydration processes when incorporated into cement. The researchers concluded that the hydration of the clinker compound C_3S was retarded to a greater degree than C_3A . The reason why zinc acts as a retarder is because it precipitates an amorphous layer of zinc hydroxide around the C_3S grains. This prevents the hydration of the clinker compounds from occurring.

Tashiro et al. (1980) found somewhat different results in that they determined zinc retarded the early hydration of C_3A to a greater degree than C_3S . Tashiro also determined that zinc is detrimental to the compressive strength of concrete.

A study by Shin et al. (1988) investigated the cement-based solidification process for hazardous sludge from an electroplating industry. Leaching characteristics and compressive strengths were evaluated. They found that the compressive strength decreased when the water-to-cement (W/C) ratio increased. Likewise, the compressive strength decreased as the amount of wet sludge incorporated in the cement increased. The precipitator had no affect on compressive strength. The leaching characteristics were determined by the EP Toxicity test and this study found that as W/C and S/C ratios increased from 2.0 to 2.5, zinc leached more from the solidified waste; however, there was no significant difference

from 1.5 to 2.0. The increased W/C ratios created poor solidification of hazardous sludges because the "degree of hydration and crystallization becomes greater". As curing time passes, the water evaporates from the cavities in the cement leaving large pores. The pores and thus the increased permeability cause more leaching of zinc. The zinc also leached out more as the amount of sludge and sand incorporated in the cement was increased. The precipitator had some affect on the leaching characteristics by reducing the zinc in the leachant acid by 20 percent.

Utilizing powder X-ray diffraction, leaching tests, and electron microscopy, Poon et al. (1985) analyzed the mechanisms of zinc leaching from CFS processes. A simulated industrial waste containing 2000 ppm of zinc (and mercury) was prepared and fixed in portland cement and allowed to cure for 28 days. The leaching test was used to simulate the long-term leaching potential. They found that initial zinc concentrations were low in the leachate, but increased dramatically after several elutions. This increase in released zinc correlated with the amount of calcium released from the cement matrix. The release of calcium after a number of elutions was an indication that there had been a massive breakdown of the cement matrix. Once the matrix was destroyed, zinc concentrations in the leachate increased because the ability of the matrix to effectively "fix" the metals had been broken down.

CHAPTER 3

EXPERIMENTAL METHODS AND MATERIALS

Overview

This chapter describes the process used by Roanoke Electric Steel Corporation where all of the samples for this study were taken. Also, the experimental design, preliminary experiments, solidification and stabilization of the waste, and the sample analysis are outlined in this section. Samples were collected on-site from atop a transport truck which had taken the dust from large collection silos on-site. The samples were solidified and stabilized and subsequently subjected to compression tests and the TCLP test for eventual determination of compressive strength, leaching characteristics and the ability to withstand acidic environments.

Roanoke Electric Steel Corporation

The Roanoke Electric Steel Corporation, located in Roanoke, Virginia, was founded in 1955 to provide steel products to manufactures and distributors in the metals industry. Roanoke Electric uses scrap metal to produce over 440,000 tons of carbon steel a year. Of this, about 5,600 tons of electric arc furnace dust is generated from the

electric furnace and must be disposed according to federal regulations because of its hazardous nature (RESCO, 1989). The waste is coded as K061 according to the Code of Federal Register, Part 261.32 wherein it is defined as "emission control dust/sludge from the primary production of steel in electric furnaces". At the time of this writing, the hazardous dust was transported off-site for zinc recovery and the remaining waste was solidified and disposed in an industrial landfill.

Experimental Design

The experimental portion of this thesis consisted of two major parts. First, various cement mixes incorporating the electric arc furnace dust were prepared and tested to determine the compressive strength, air entrainment, slump, and other concrete properties. This step was undertaken in the Structures and Materials Laboratory on the Virginia Tech campus. Second, the various samples were subjected to the TCLP test in order to determine the leaching characteristics of the various solidified and stabilized materials.

The main thrust of the study was to evaluate the effect of the electric arc furnace dust content on the concrete properties. The mix included four electric arc furnace dust variations: 528 lb, 264 lb, 132 lb, and 53 lb/cu yd concrete. Within each of the four concrete mixes, the cement remained relatively the same; however, the admixtures were varied so

that these effects on leachability and strength could be studied.

Treatment effectiveness was measured by the TCLP test which utilized a dilute acetic acid solution as the leachant to simulate the effects of landfill conditions on the waste once it is land impounded. This extraction procedure, which very recently replaced the Extraction Procedure Toxicity Test, was designed to address the mobility of a broad range of both organic and inorganic compounds as well as improve and expand upon the EPTox protocol (Esposito, 1989). All industries generating hazardous waste constituents must meet standards defined by the TCLP or else risk violations and face tough fines. Therefore, this research implemented the TCLP test to determine the heavy metals in the leachate from the prepared mixes.

The TCLP extraction process consists of two stages: the agitation period which provided the necessary acidic, harsh environment and the filtration period where the sample was fractionated into its soluble portion known as the leachate. An end-over-end rotary agitator was used which rotated at 30 ± 2 rpm. Figure 4 shows the Rotary Agitator, Model DC-18, built by Analytical Testing and Consulting Services, Inc. and used for this study. Eight extraction vessels made of high density polyethylene capable of containing 2.5 liters of fluid was attached to the rotary device. For filtration, borosilicate glass microanalysis filter and 320 ml glass filter holder was

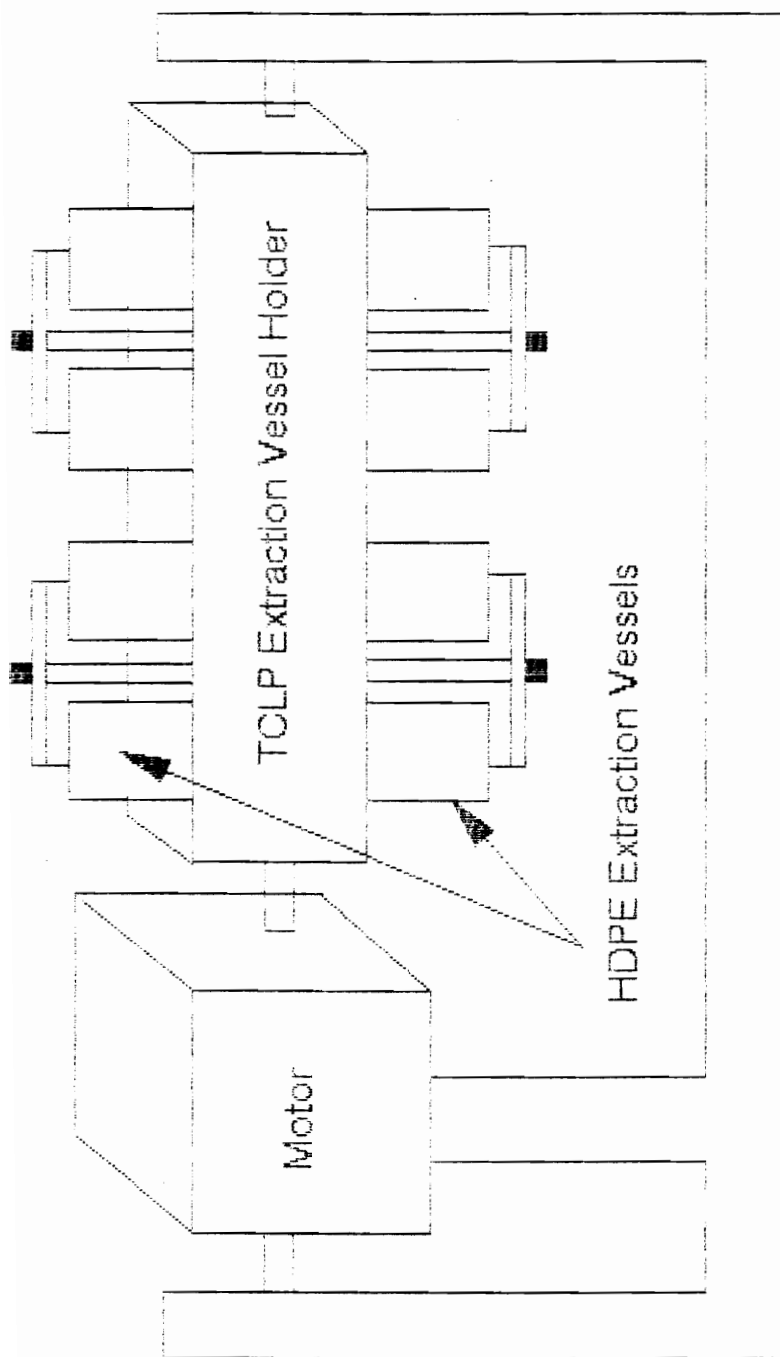


Figure 4. Schematic of a rotary agitator used in the TCLP test

connected by a rubber hose to a vacuum pump as shown in Figure 5. A Whatman Type GF\F Binder-free glass microfiber filters (particle retention, 0.7 microns) were used to filter the liquid into a 1-liter Erlenmeyer flask with sidearm.

Before agitation, an appropriate extraction fluid was prepared daily which depended upon the pH of the sample. Since the pH of the samples were greater than 5, then according to the Federal Register (40 CFR Part 260 et al.), extraction fluid #2 was used. Extraction fluid #2 was prepared by diluting 5.7 ml of glacial acetic acid (HOAc) with reagent water, ASTM Type II water or equivalent (Milli-Q Reagent Water System was used) to a final volume of 1 liter. When correctly prepared, the pH of this extraction fluid should be $2.88 \pm .05$.

A minimum 100 gram sample of the solidified and stabilized material was obtained and placed in the extraction vessel with an amount of extraction fluid equal to 20 times the volume by weight of the sample (2 Liters). With the lids of the vessels secured with teflon tape and mounted on the rotary agitator, the vessels were rotated overnight for 18 ± 2 hours. After this time period, the pH of the liquid in the vessel was measured again and values were found to be typically between 4.5 and 5.0. Weight losses of each sample, due to the aggressive nature of the extraction fluid, were also recorded.

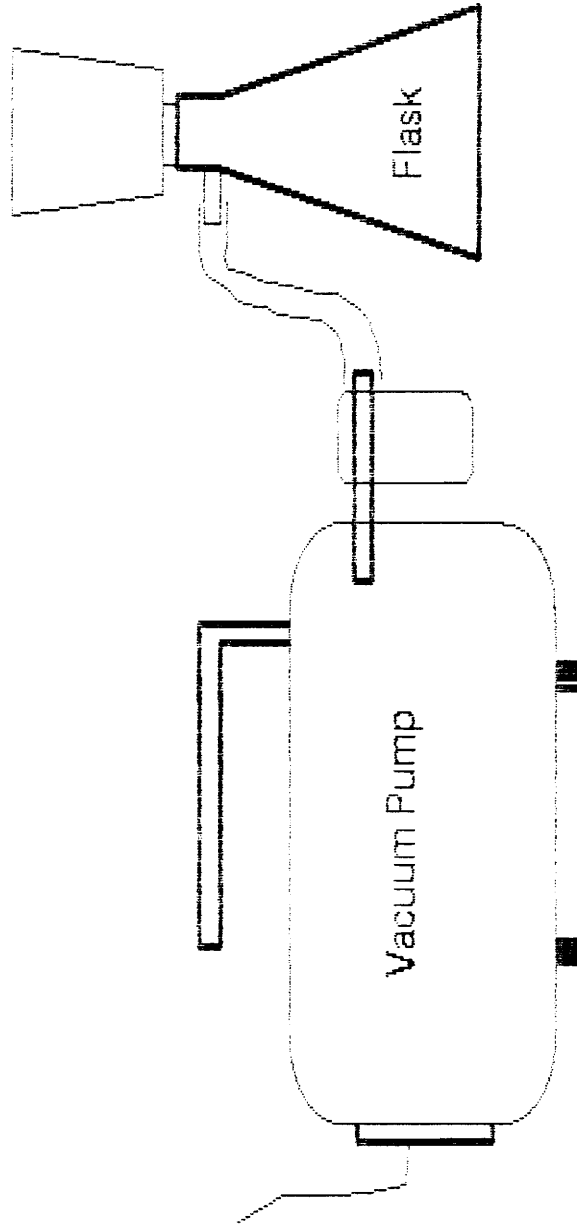


Figure 5. Schematic of a filtration device used in the TCLP test

Sample Analysis

The prepared solidified and stabilized samples were stored in a moisture room suitable for the curing of concrete samples until the time of extraction. A borosilicate glass filtration device was used to separate the suspended from the soluble fractions of the samples. Only the soluble fraction known as the leachate was quantified. For each extracted sample, approximately 300 ml was filtered through a 0.7 micron binderless Whatman filter. All of the samples to be analyzed for dissolved metals were acidified with concentrated nitric acid to a pH<2 immediately after filtration. These samples were digested prior to analysis. The samples to be analyzed for anions were not acidified but were analyzed directly.

Digestion Method

According to the EPA (1985), since the leachate obtained from the TCLP method was in the aqueous phase and contained dissolved metals, digestion was required (Method 3005). This method is an acid digestion procedure which is used to prepare surface water and ground water samples for analysis by flame atomic adsorption spectroscopy (FAA). This method is also appropriate for TCLP extracts. Immediately following filtration and collection of a representative sample of the leachate, 100 ml was transferred to a beaker. Two ml of concentrated nitric acid and 5 ml of concentrated hydrochloric acid were added to the sample, covered with a ribbed watch

glass, and heated to 95 degrees Celsius on a hot plate until the volume was reduced to 15-20 ml. After the liquid was allowed to cool, the walls of the beaker were rinsed with Milli-Q water and the final volume was adjusted to 100 ml. The samples were then ready for analysis.

Experimental Analysis

All digested samples were measured with a Model 703 Perkin-Elmer Atomic Adsorption Spectrophotometer for metals determination. Anions were determined with a Dionex Ion Chromatograph. A Fisher Accumet pH meter was used to quantify pH before and after TCLP extractions. Initial and final weights of the solidified and stabilized samples were determined by a Mettler PM 4000 scale.

Preliminary Experimental Procedures

Dust Variability

The Roanoke Electric Steel Corporation generates all of its steel from scrap; therefore, the issue of dust variability in day-to-day operations was given full consideration. To check diversity, freshly generated waste samples were collected at RESCO at once a week intervals for a total period of 6 weeks. Six samples from each week were extracted using the TCLP method in preparation for determination of metals and anions. All of the samples were left unsolidified for the TCLP test. The pH before and after the extraction, the lead

and cadmium concentrations in solution, and anions in solution were determined.

Metal Solubility

Solubility data found in the literature, calculated from stability constants for individual species or for simple combinations, may exhibit completely different solubilities than those measured for actual materials. According to Conner (1990), factors other than hydroxide solubility may control the metal solubility of CFS systems. This is especially true for lead because lead forms complexes with many species. With this realization, a solubility experiment was performed to determine the solubility of heavy metals in the dust as a function of pH and to reveal the total concentration of metals in the electric arc furnace dust.

This experiment utilized 42 acid-washed 150 ml glass beakers arranged in three rows of 14 each. To each of the beakers in the first row, 25.1 grams of electric arc furnace dust was added. In a similar fashion, 12.5 grams and 6.3 grams of electric arc furnace dust were added to the beakers in the second and third rows, respectively. The electric arc furnace dust was weighed by an electronic scale. By conversion, the amounts of electric arc furnace dust added to the beakers in each row (25.1 gm, 12.5 gm, and 6.3 gm) corresponded to 528 lb, 264 lb, and 132 lb/cu yd concrete. Next, 80 ml of Milli-Q reagent water were added to each of the

beakers containing the electric arc furnace dust and stirred thoroughly with a glass stirring rod. So that the entire pH range (0-14) could be explored, nitric acid and sodium hydroxide were added in a dropwise manner for pH adjustment. The pH of each solution was checked every hour for 24 hours and, if necessary, adjusted. The solutions were also stirred every hour to aid in the dissolution of metals. After 24 hours, equilibrium was assumed in each of the beakers because the pH no longer changed. The result of pH adjustments was that each row contained a wide range of pH values. Samples were filtered with a 0.45 micron filter and immediately analyzed for metals and anions.

Lead in Electric Arc Furnace Dust

The previous experiment failed to determine the exact concentration of lead present in the electric arc furnace dust even at the lowest pH because not all of the lead was dissolved. Therefore, an experiment was designed to address the problems of the incomplete dissolution of lead. Five acid-washed 150 ml glass beakers were used for this experiment. The electric arc furnace dust was weighed out in varying amounts by electronic scale and placed in each beaker. The weighed samples of electric arc furnace dust were as follows: 6.0 gm, 3.0 gm, 1.5 gm, 1.0 gm, and 0.5 gm. Eighty milliliters of Milli-Q reagent water was added to each sample and stirred with a glass stirring rod until completely mixed.

Each sample was pH adjusted every hour with concentrated nitric acid to maintain a pH near zero. After 24 hours, when equilibrium was reached, the samples were filtered with a 0.45 micron borosilicate glass Whatman filter and syringe and were analyzed for lead by atomic adsorption.

Cement Paste Samples

Pore water is the solution contained within the pores of concrete and usually has a high pH. According to Weyers (1991), the pore water solution in the matrix of concrete is made up of 0.3 M NaOH, 0.6 M KOH, and 0.06 M Ca(OH)₂. An experiment was devised to study the potential for leaching of metals by the pore water solution.

The leachability of heavy metals from the pore water solution in concrete was evaluated by developing several cement paste samples. Specifically, the effects of incorporating varying amounts of chelator and varying amounts of electric arc furnace dust were studied. Cement paste is essentially the same as concrete except that sand and aggregates are not included.

For this experiment, portland cement, electric arc furnace dust, and several admixtures were weighed on a dry basis by an electronic scale and combined with Milli-Q water. The various mix designs are outlined in Table 2 where 528 lb, 264 lb, and 132 lb/cu yd concrete of electric arc furnace dust were incorporated into the concrete. The amounts of each

Table 2. Cement paste mixes with 528 lb, 264 lb, and 132 lb dust/cu yd concrete

Paste Ingredients lb/cu yd concrete	Experiment #			
	1	2	3	4
EAF Dust	528	528	528	528
Portland Cement	517	517	517	517
Milli-Q Water	902.8	902.8	902.8	902.8
Chelator Sodium Citrate	0.0	4.8	10.7	20.8
Solubility Reducer Ferrous Sulfate	7.1	7.1	7.1	7.1
EAF Dust	264	264	264	264
Portland cement	517	517	517	517
Milli-Q water	889.7	889.7	889.7	889.7
Chelator	0.0	5.1	10.3	20.8
Solubility Reducer	7.1	7.1	7.1	7.1
EAF Dust	132	132	132	132
Portland cement	517	517	517	517
Milli-Q water	916.5	916.5	916.5	916.5
Chelator	0.0	5.1	10.3	20.8
Solubility Reducer	2.1	2.1	2.1	2.1

ingredient were scaled down drastically for the experiment because of the size of the available equipment. After the ingredients were combined, they were mixed at high speed for approximately two minutes with a lab-scale cement mixer until a homogeneous paste formed. The paste was then filtered as in the setup shown previously in Figure 5 and the filtrate was analyzed for heavy metals and anions.

Solidification and Stabilization of Electric Arc Furnace Dust

Each of the solidified and stabilized samples weighed at least 100 grams according to the protocol of the TCLP test. To ensure that every sample was 100 grams or more, freshly mixed concrete batches were poured into a PVC pipe and allowed to set. Then, two-inch pieces were cut by an electric saw and the PVC pipe was removed from each sample. The solidified samples were then placed in a steam room. All of the concrete batches are described in Tables 3-6. The samples were subjected to the TCLP after being allowed to cure for 1, 7, 28, and 56 days. At these cure times, the compressive strength, weight loss of the sample due to the TCLP test, the pH before and after the TCLP test, the concentration of lead, cadmium, and zinc in the leachate, and the concentration of anions in the leachate were determined.

In Table 3, the control concrete mix formulas to which no electric arc furnace dust was added are provided. These were used as a basis for comparison to concrete mixes which

Table 3. Concrete contents for control mixes (no dust)

Concrete Contents (lb/cu yd concrete)	Values			
	Control 1	Control 2	Control 3	Control 4
Cement	515	611	515	611
Water	326	306	326	306
Coarse Aggregate	1101	1101	1101	1101
Fine Aggregate	1897	1692	1789	1586
Flyash	0	0	100	100
Chelator Sodium Citrate	0	0	0	0
Solubility Reducer Ferrous Sulfate	0	0	0	0

Table 4. Concrete contents for mixes containing electric furnace dust

Concrete Contents (lb/cu yd concrete)	Values			
	Batch 1	Batch 2	Batch 3	Batch 4
EAF Dust	528	264	132	53
Cement	517	517	517	517
Water	308	295	322	323
Coarse Aggregate	1101	1101	1101	1101
Fine Aggregate	1659	1743	1820	1866
Flyash	0	0	0	0
Chelator Sodium Citrate	20.57	10.29	5.14	2.06
Solubility Reducer Ferrous Sulfate	12.56	6.28	3.13	1.26

Table 5. Concrete contents for mixes containing with electric arc furnace dust (chelator is varied)

Concrete Contents lb/cu yd concrete	Values				
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
EAF Dust	264	264	264	264	132
Cement	517	517	517	517	517
Water	384	322	312	284	316
Coarse Aggregate	1101	1101	1101	1101	1101
Fine Aggregate	1743	1743	1743	1743	1820
Flyash	0	0	0	0	0
Chelator Sodium Citrate	0	10.29	20.57	41.16	20.56
Solubility Reducer Ferrous Sulfate	6.2	6.28	6.28	6.28	3.14

Table 6. Concrete contents for mixes with electric arc furnace dust and salts (NaCl and Na₂SO₄)

Concrete Contents (lb/cu yd concrete)	Values			
	Batch 5	Batch 6	Batch 7	Batch 8
EAF Dust	264	264	132	132
Cement	517	517	517	517
Water	295	295	326	336
Coarse Aggregate	1101	1101	1101	1101
Fine Aggregate	1743	1743	1820	1820
Flyash	0	0	0	0
Chelator Sodium Citrate	10.29	10.29	5.14	5.14
Solubility Reducer Ferrous Sulfate	6.28	6.28	3.14	3.14
Sodium Sulfate Na ₂ SO ₄	10.8	2.7	16.2	4.15
Sodium Chloride NaCl	0	8.1	0	12.15

contained dust. The amount of water and coarse and fine aggregate remained relatively the same for each control mix, but experiments 1 and 3 used 515 lb cement/cu yd concrete while 2 and 4 used 611 lb cement/cu yd concrete. The formulas for the batches with varying amounts of electric arc furnace dust are described in Tables 4 and 6. Chelating agents and solubility reducers were added based on the amount of electric arc furnace dust to be incorporated in the concrete mix. For the mixes listed in Table 5, the amount of chelator between each sample was varied from no chelator to 41.2 lb/cu yd concrete. The amount of electric arc furnace dust in the mixes was 264 lb/cu yd concrete except for the last batch mix. Lastly, salts, specifically sodium sulfate and sodium chloride, were added to some of the batches as outlined in Table 6. The amount of salts added was determined from the leachability results of the solidified dust samples.

Quality Control and Assurance

Glassware Preparation

All glassware was acid washed in 10 percent nitric acid for 24 hours or more, rinsed thoroughly with distilled water, and allowed to dry completely before each use. The extraction vessels were disposable and therefore used only once so that contamination from one sample to the next was avoided.

Analytical Testing

Quality assurance was maintained during all analytical testing by periodic checking of standards for the Atomic Adsorption Spectrophotometer and the Ion Chromatograph. In addition, the analytical equipment was standardized every 6 or 7 samples during sample runs.

All experiments were duplicated and some were conducted in triplicate to ensure reliability in testing procedures and equipment. The filters were also prerinsed with concentrated nitric acid before use to remove any contaminants. Blanks were run through the entire TCLP test and digestion process periodically to ensure that contamination had not occurred.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

Introduction

This chapter presents the experimental results and a discussion. Included in this section is a compilation of the data collected during the study and a discussion of the hazardous constituents in the electric arc furnace dust, the behavior of metals with pH, the effects of electric arc furnace dust when incorporated in concrete, and the effects of concrete additives on concrete properties. The focus of this chapter will be on the fate of lead because this metal appeared to be the most critical with regard to meeting the TCLP limits.

Dust Variability at Roanoke Electric Steel

Untreated electric arc furnace dust was examined in order to determine variations in dust metal levels in the week-to-week operations at the Roanoke Electric Steel Corporation Plant. The soluble concentrations of lead, silver, and cadmium in the electric arc furnace dust measured over a six-week time period are shown in Table 7. A substantial variation in the metal content of the dust over time is evident. The data show that soluble lead ranges from 30 to

Table 7. Metals concentrations of the electric arc furnace dust over a six-week sampling period

Date of Batch		Lead (mg/L)	Silver (mg/L)	Cadmium (mg/L)
June 14	#1	67	1.3	13.6
	#2	68	0.7	11.5
	#3	72	1.1	12.2
	#4	72	1.2	12.6
	#5	80	0.7	12.3
	#6	96	1.0	12.0
June 21	#1	30	ND	5.8
	#2	54	0.3	11.5
	#3	59	0.3	12.4
	#4	64	0.3	13.2
	#5	74	0.8	15.1
	#6	84	1.0	18.2
June 28	#1	99	3.5	17.9
	#2	101	4.8	16.8
	#3	104	3.5	20.5
	#4	115	4.8	15.6
	#5	117	5.2	16.3
	#6	129	2.3	16.9
July 5	#1	70	0.8	18.2
	#2	70	1.6	18.9
	#3	73	0.8	17.3
	#4	75	1.5	18.5
	#5	76	1.3	16.4
	#6	76	1.2	17.3
July 12	#1	35	2.9	19.2
	#2	55	2.9	18.5
	#3	60	2.6	17.2
	#4	60	3.6	17.1
	#5	80	2.2	18.2

129 mg/L depending on the time of dust collection. The highest content of soluble metals is the batch dated June 28; however, the hazardous constituents vary not only between batches but also vary considerably within a batch.

The values in Table 7 do not reflect the total concentration of heavy metals in the untreated electric arc furnace dust. Instead, they represent the concentrations of heavy metals that leach into solution and remain soluble at a pH of 6.2 and 6.8 since this was the pH at the completion of the TCLP test. However, these values are still useful for demonstrating that variability of the dust exists. Because lead is a known retarder to the setting of concrete, variations in lead are especially important in determining concrete properties in CFS systems.

Total Lead in the Electric Arc Furnace Dust

Figure 6 shows the amount of lead in solution as a function of the amount of electric arc furnace dust in the acid solution. The data in this figure were generated by adjusting the pH of the dust and water to near zero so that the maximum solubility of lead could be achieved.

In this test, it was assumed that all of the lead in the electric arc furnace dust was soluble. Thus, a linear relationship should exist between the concentration of lead in solution and the amount of electric arc furnace dust used in the test. However, the data deviates from the linear

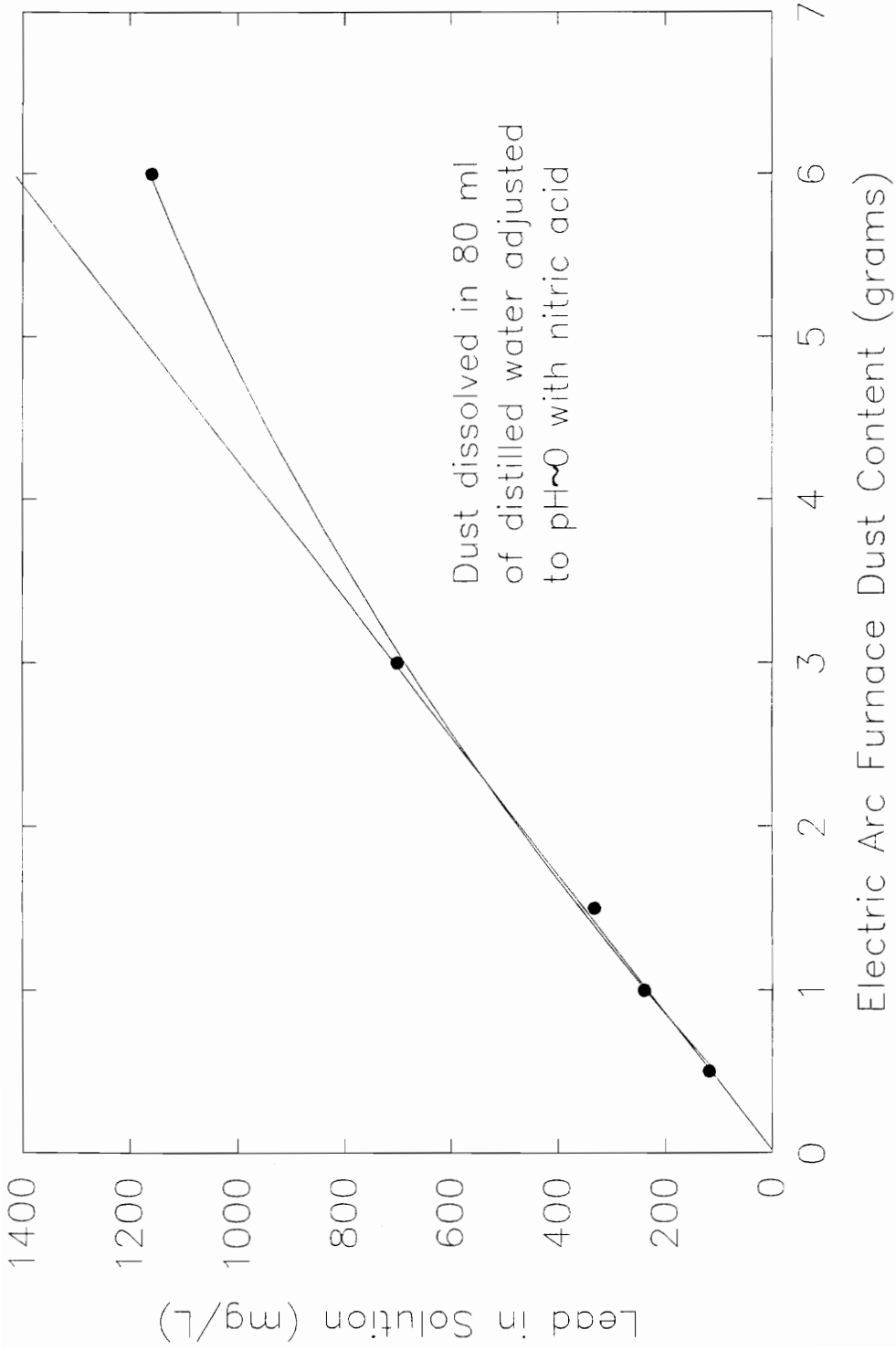


Figure 6. Concentration of dissolved lead in the electric arc furnace dust as a function of the amount of dust at a pH=0

indicating that, when more than 3 grams of dust is used in the test, not all of the lead is solubilized. From the linear relationship, it was determined that approximately 1.9% of the composition of the electric arc furnace dust is lead. This is similar to the results found by the EPA who found that approximately 2% of the electric arc furnace dust is made up of lead (Table 1).

Behavior of Lead and Cadmium with pH

The solubility curves for lead in the dust are important for determining the concentration of soluble lead at the pH that exists upon completion of the TCLP test. From these solubility curves, it has been shown that, at the pH at the end of the TCLP test (approximately 4.5), only a fraction of the 1.9% lead is solubilized.

Figure 7 shows the solubility of lead for the untreated electric arc furnace dust. The amount of untreated electric arc furnace dust used in this experiment, 156.8 gm/L, is equivalent by weight on a dry-basis to the solidified waste mixes that incorporated 264 lb dust/cu yd concrete. At a pH of 4.5, only 200 mg/L lead, or 6.5% of the total lead in the dust, is solubilized. Therefore, in order for a CFS system that incorporates 264 lb dust/cu yd concrete to pass the TCLP test for lead, it must retain, by physical or chemical means, at least 195 mg/L of the lead in the concrete. Figure 7 also shows that not all of the lead in the dust is solubilized at

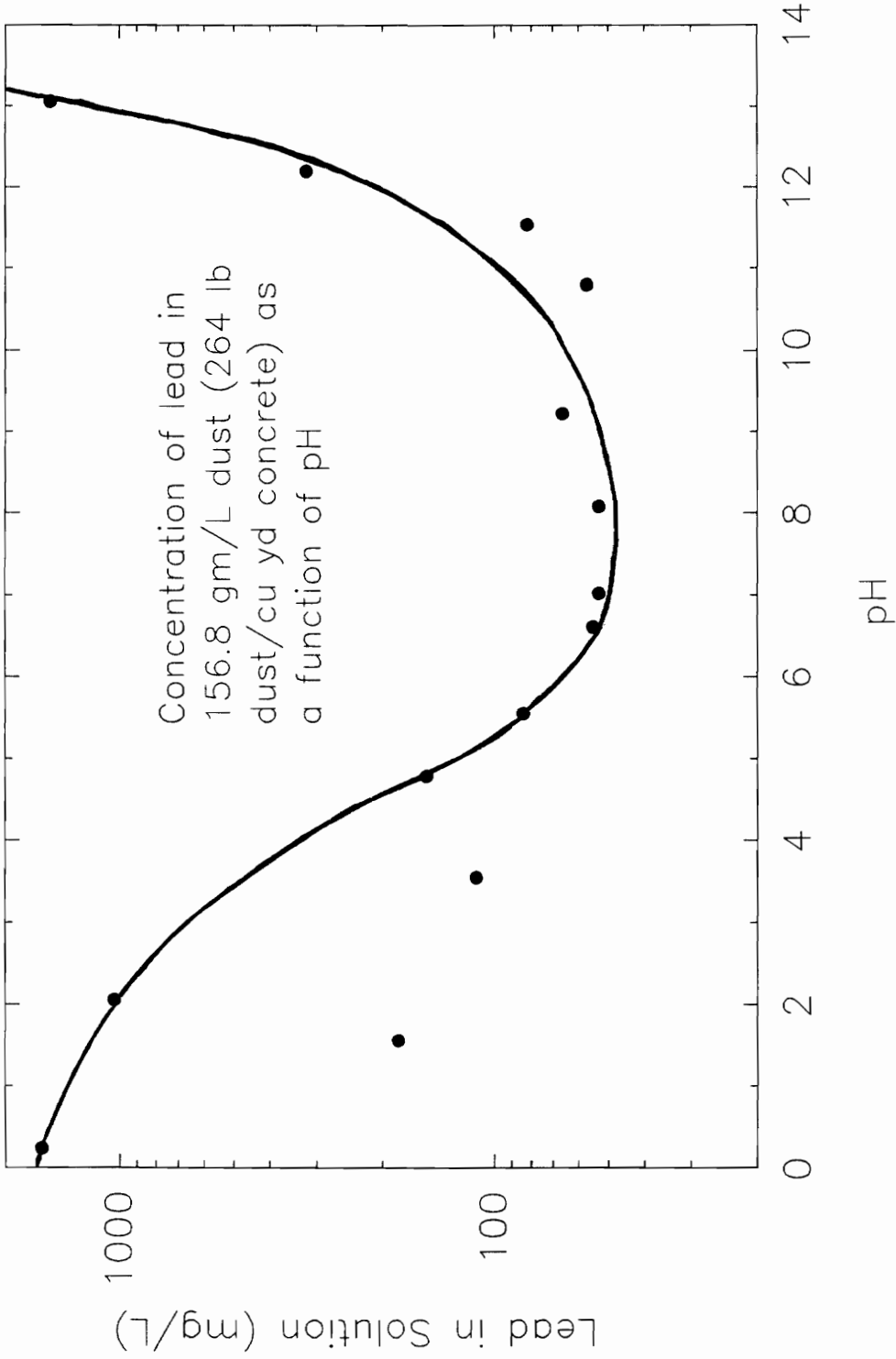


Figure 7. Solubility of lead in the dust as a function of pH
(264 lb dust/cu yd concrete)

the lowest pH. Only 65% of the total lead in the dust was soluble at this low pH. This was because of the larger amount of electric arc furnace dust used in this solubility experiment (156.8 gm/L).

Comparing Figure 7 to the lead hydroxide solubility curves in Figure 1, it appears that lead hydroxide is not the controlling species for lead solubility (Conner, 1990). The theoretical curves for lead hydroxide reach a minimum solubility at 9.3 while the lead solubility curve for the electric arc furnace dust had a wider range of minimum solubility. This is similar to the findings by Conner (1990) who determined that the lead solubility can not only be remarkably different for different types of wastes but can also be different from the theoretical solubility curves.

Figure 8 shows the lead solubility versus the pH data for three different amounts of untreated electric arc furnace dust: 313.5 gm/L (528 lb dust/cu yd concrete), 156.8 gm/L (264 lb dust/cu yd concrete) and 78.4 gm/L (132 lb dust/cu yd concrete). This solubility study shows that the amount of dust incorporated in a CFS system as well as the pH dictates the concentration of soluble lead in solution. As the amount of electric arc furnace dust incorporated in the concrete mix is increased, the concentration of lead in solution will also increase such that it becomes increasingly more difficult to meet the TCLP limits for lead. However, the concentration of soluble lead is approximately the same for the three amounts

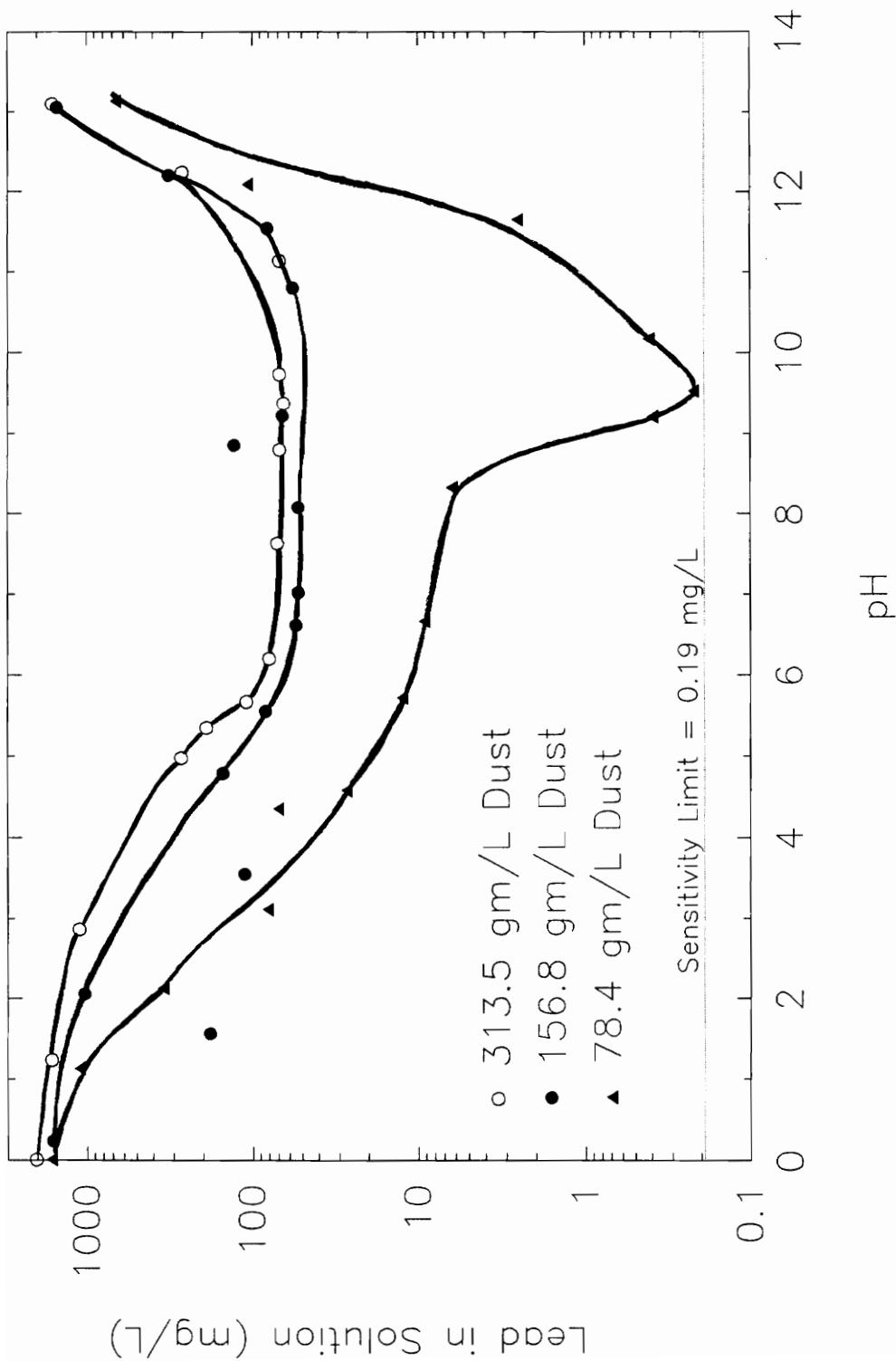


Figure 8. Solubility of lead in the dust as a function of pH (528 lb dust, 264 lb dust, and 132 lb dust/cu yd concrete)

of electric arc furnace dust at the lowest pH because not all of the lead in this test was solubilized.

Figure 9 shows a cadmium solubility versus pH plot for 156.8 gm/L of untreated electric arc furnace dust. This is equivalent to 264 lb dust/cu yd concrete. The theoretical cadmium hydroxide solubility curve is also shown for comparison. The point of minimum solubility is in the pH range of 10 to 12. This is very similar to the minimum solubility of the theoretical calculated cadmium hydroxide curves shown in Figure 1. Because the theoretical cadmium solubility curve nearly matches the experimental curve for the untreated dust, it appears that cadmium solubility is probably controlled by the hydroxide species.

The concentration of soluble cadmium is about 40 mg/L at pH 4.5; therefore, a CFS system incorporating 264 lb dust/cu yd concrete would have bind 39 mg/L cadmium into the concrete in order to meet the TCLP standard of 1 mg/L set by the EPA.

Figure 10 shows the cadmium solubility curves for the three different amounts of electric arc furnace dust. The theoretical cadmium hydroxide solubility curve is also shown in the figure. It is clear from this figure that as the amount of dust incorporated in the concrete mix is increased, the concentration of soluble cadmium is increased over the pH range found for the TCLP test. Figure 10 also reveals that at pH levels less than 5, cadmium is completely dissolved.

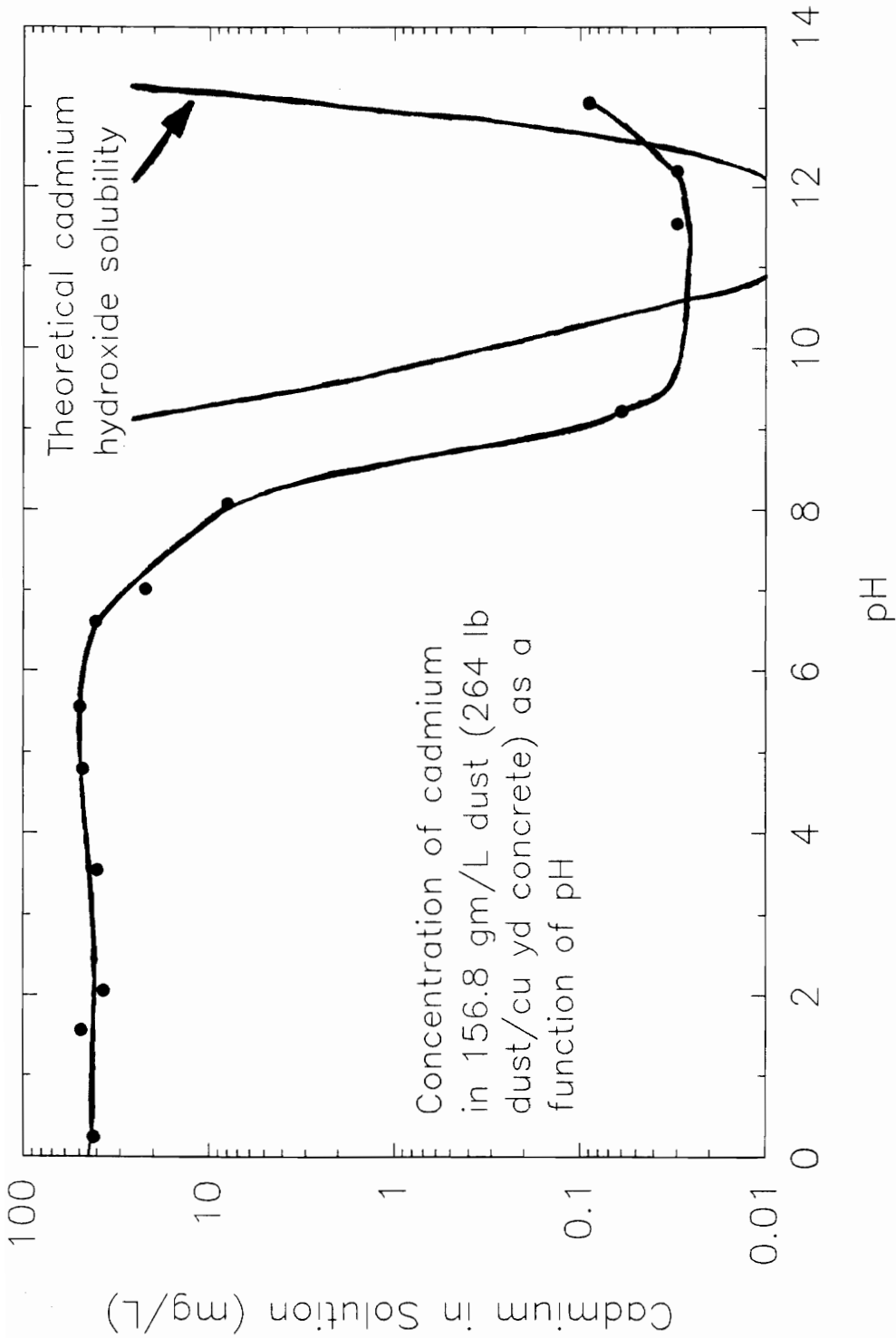


Figure 9. Solubility of cadmium in the dust as a function of pH and theoretical cadmium hydroxide solubility (264 lb dust/cu yd concrete)

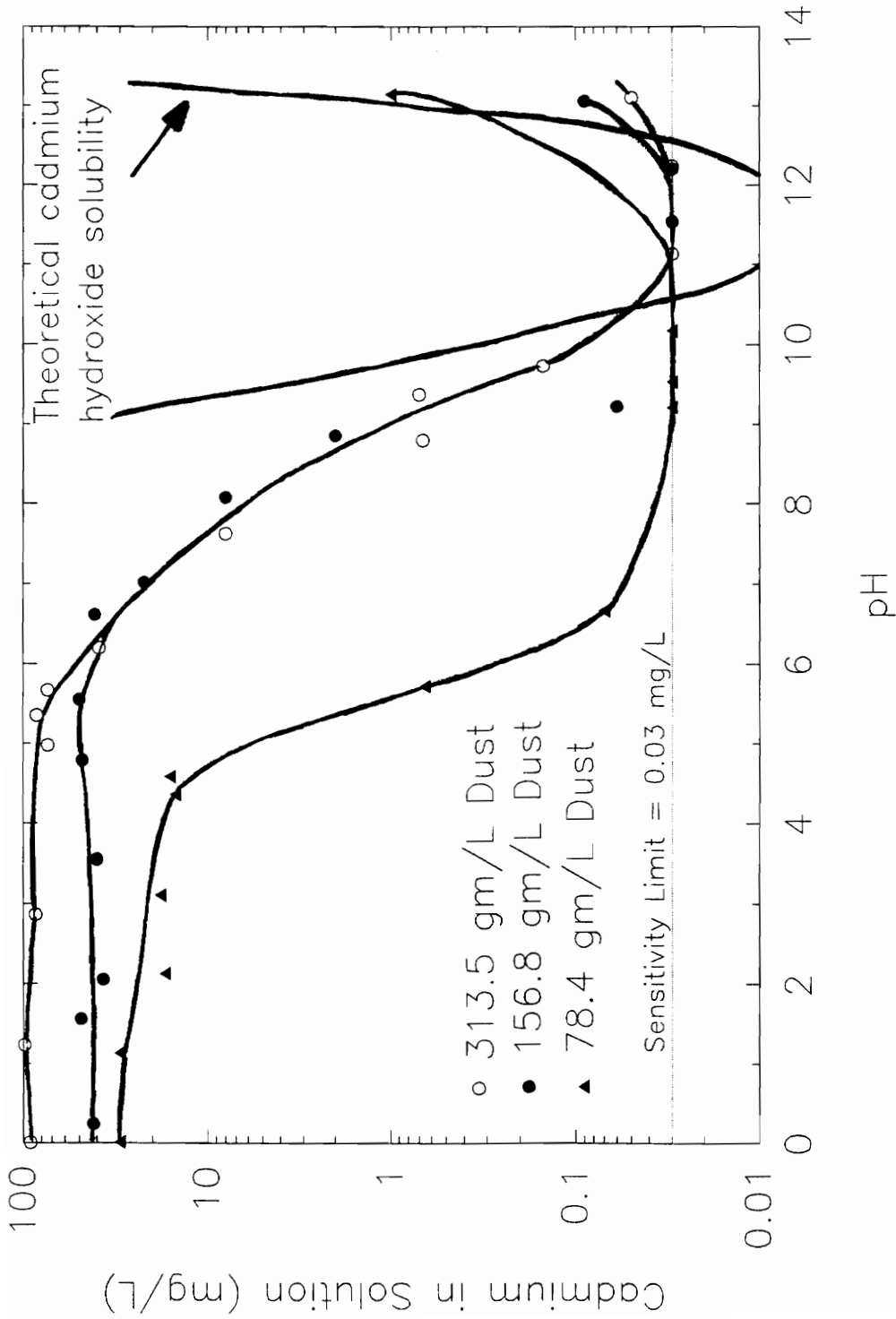


Figure 10. Solubility of cadmium in the dust as a function of pH and theoretical cadmium hydroxide solubility (528 lb dust, 264 lb dust, and 132 lb dust/cu yd concrete)

Metal Leaching from the Pore Water Solution

In order for heavy metals to leach from a solidified material, the metal must first solubilize into the pore water solution. When a solidified mass comes into contact with an acid, a disturbance in the equilibrium of the pore water solution occurs. Due to the acidic environment, the pH of the pore water solution decreases, the concrete matrix breaks down, and the heavy metals leach out of the material. Bishop (1988), who theorized that lead is bound into the silica matrix instead of in the pores, suggested that when the matrix is broken down, the lead will solubilize into the pore water solution and then leach. Thus, the question arises as to how much of the hazardous constituents will leach into the pore water solution as a function of the amount of electric arc furnace dust contained in the concrete.

Figure 11 shows the lead content in the pore water for different dust additions. This figure shows a linear relationship between the concentration of lead in solution and the amount of electric arc furnace dust added. Further, Figure 11 shows the concentration of lead that has been solubilized into the pore water solution due to a disturbance of the solution by contact with an acid. Although the pH controls solubility once the lead enters the pore water solution, the amount of lead entering the solution depends upon the amount of dust added.

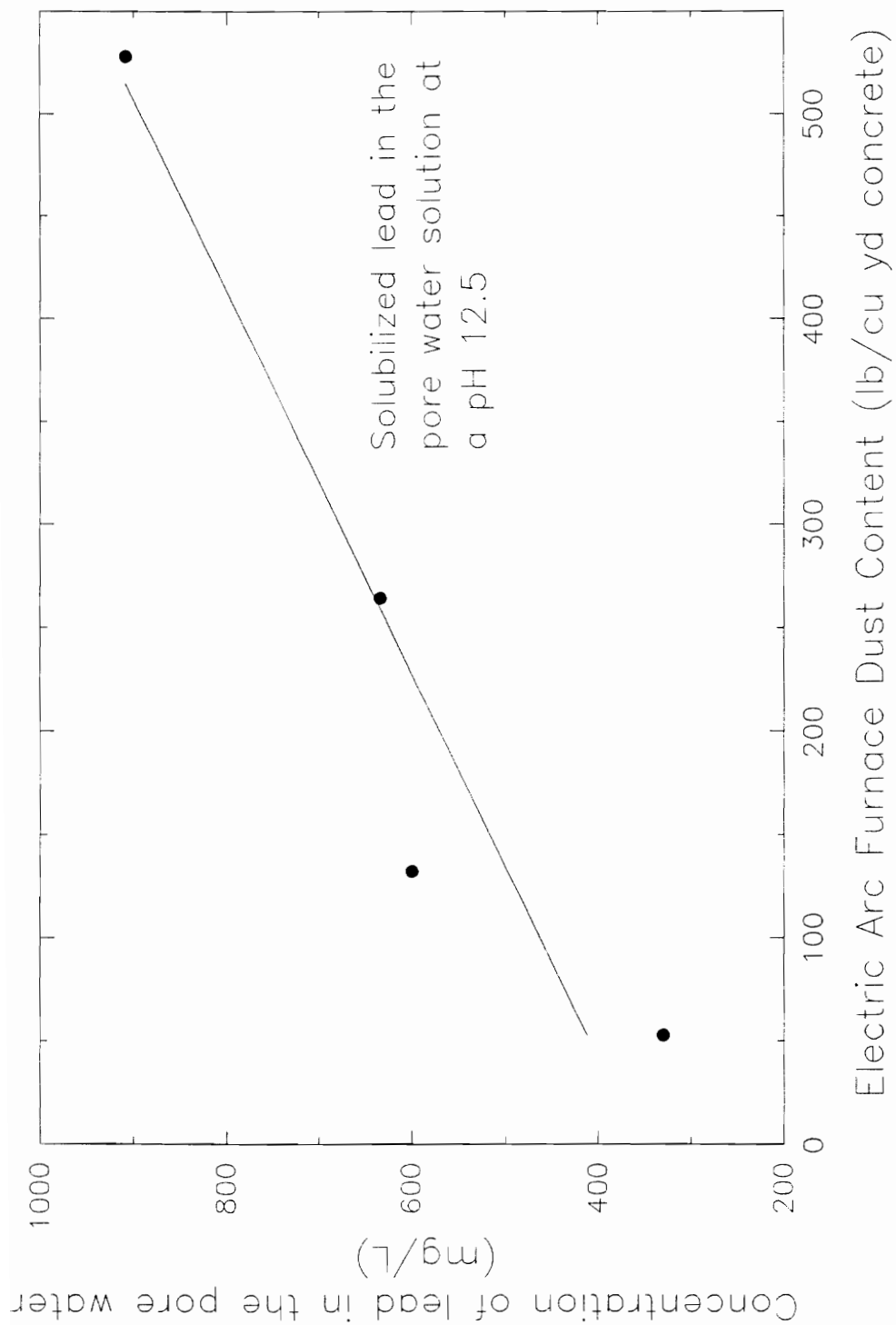


Figure 11. Soluble lead in a simulated pore water solution as a function of the amount of electric arc furnace dust

Figure 12 shows the behavior of chloride and sulfate as a function of the amount of electric arc furnace dust in the cement paste mix. Soluble chloride is directly proportional to the amount of electric arc furnace dust and increases as the amount of dust increases. On the other hand, the sulfate in solution is not dependent on the amount of electric arc furnace dust.

The concentration of soluble lead in the pore water solution is not only affected by the amount of electric arc furnace dust, but is also affected by the addition of chelator. Table 8 shows the soluble concentrations of the heavy metals and anions that leached from the pore water solution. Table 2 shows the paste ingredients used for this experiment. The final pH for all three pore water solution mixes was approximately 12.5. In experiment 1 (Table 8), no chelator was used and experiments 2, 3, and 4 incorporated increasing amounts of chelator.

When no chelating agent is added, the soluble lead in the pore water solution increases as the dust levels increase. As increasing amounts of chelator is added to the cement paste, the lead in solution decreases. However, an excess of chelator causes the lead in solution to increase. For the dust used in this study, 10.3 lb/cu yd concrete appeared to be a sufficient chelator concentration to bind the lead, but at 20.8 lb/cu yd concrete, lead levels increased in the pore water. Conner (1990) stated that chelating agents can keep a

Table 8. Soluble cation and anion concentrations (mg/L) in the pore water solution obtained from the cement paste studies

lb dust/ cu yd concrete	Cations and Anions in Solution (mg/L)	Experiment #			
		1	2	3	4
528	Lead	1875	762	703	908
	Zinc	231	44	65	79
	Chloride	12840	14520	14050	15520
	Sulfate	10300	14130	11150	19380
264	Lead	1000	966	634	750
	Zinc	51	109	45	90
	Chloride	42830	36710	34115	35090
	Sulfate	14820	10300	13340	11890
132	Lead	850	600	355	450
	Zinc	82	88	74	99
	Chloride	3495	4200	3730	3350
	Sulfate	9850	10320	14490	17180

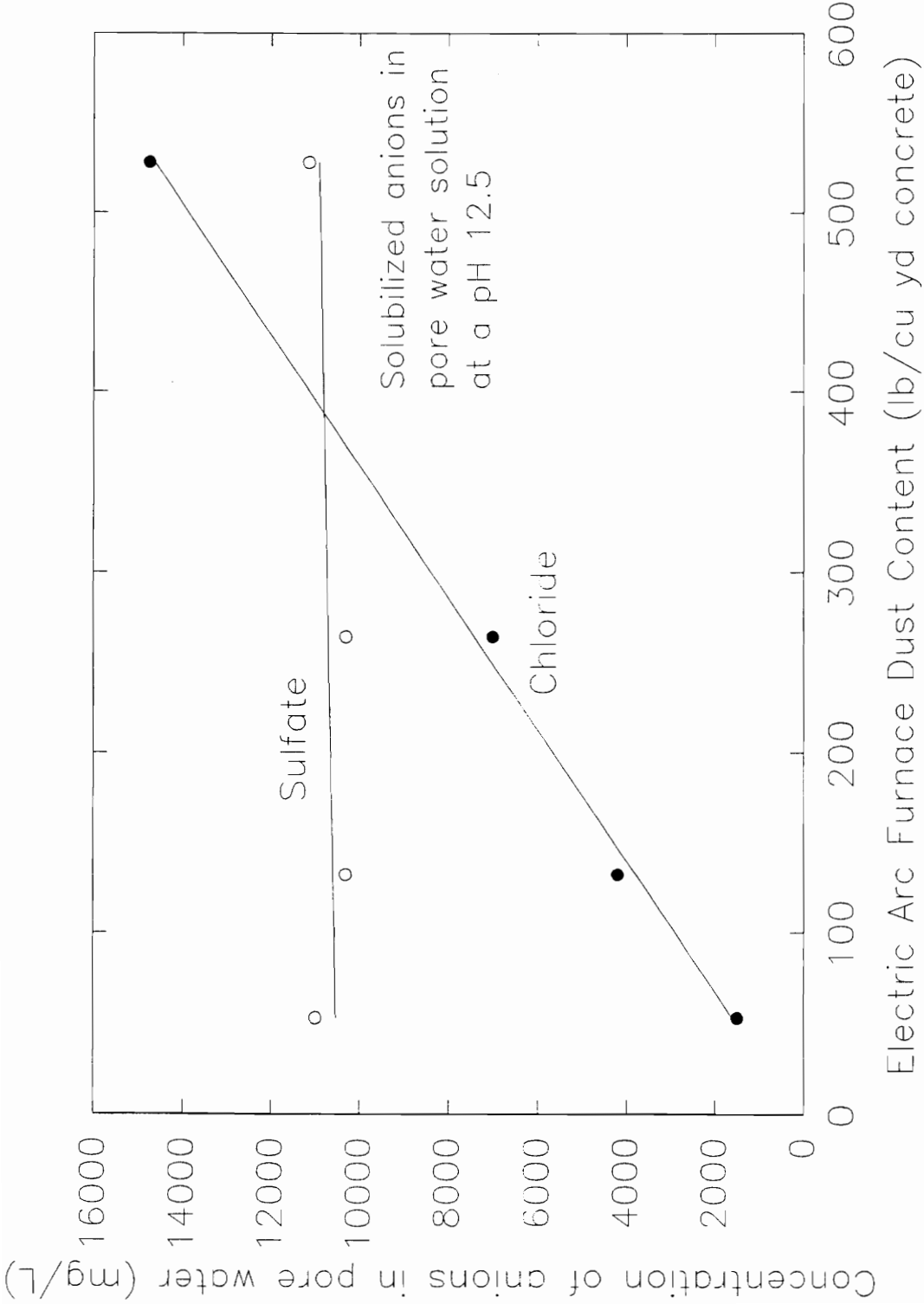


Figure 12. Soluble chloride and sulfate in a simulated pore water solution as a function of the amount of electric arc furnace dust

metal in solution as well as dissolve insoluble metal species. Evidently, the chelator contributes to lead leaching when too much is added.

Soluble zinc, chloride, and sulfate concentrations, shown in Table 8, remain fairly constant as the amount of chelator is increased or exhibit an irregular pattern, suggesting that chelator has little effect on these ions.

Solidified/Stabilized Electric Arc Furnace Dust

Developing High-Strength Concrete

Ortega et al. (1989), Campbell et al. (1987), Arlinguie et al. (1982), and other researchers in the solidification and stabilization field have concluded that lead, cadmium, and zinc, contained in the electric arc furnace dust can be detrimental when incorporated into concrete. Further, because these constituents decrease the compressive strength and decrease the overall durability of a solidified waste, the hazardous constituents are more likely to be released into the environment. For example, Campbell et al. (1987) determined that the presence of cadmium and its release into the leachant is directly proportional the physical dissolution of cement. Therefore, a solidified waste with a high compressive strength is thought to allow less of the concrete to dissolve. Thus, the first protocol in the study of solidification and stabilization was to produce a strong and durable concrete.

Figure 13 shows the weight loss properties of the four control or non-dust containing concrete mixes when subjected to the TCLP test. These data can be used for comparisons to mixes that incorporated electric arc furnace dust in place of sand. Two mixes used 515 lb concrete (5.5 bag mix), one with and without flyash. Two other mixes used 611 lb concrete (6.5 bag mix), with and without flyash. Specimens were subjected to the TCLP test after the concrete was allowed to cure for 1, 7, 28, and 56 days. Weight loss is defined as the amount of the concrete sample that is dissolved in an 18 hour period as a result of the TCLP test.

The concrete mix that used 611 lb concrete with flyash had the least weight loss. The concrete mix with no flyash and 515 lb concrete had the highest weight loss. For all of the samples, the lowest weight loss occurred after a 56 day cure period. After a 56 day cure period, the hydration reactions in the concrete are nearly complete and little additional strength will be gained after this time. Based upon these findings, it was determined that the most durable concrete yielded approximately a 10 gram or 10% weight loss of the concrete in the TCLP test. The 515 lb cement mix with no flyash was chosen as the mix for comparative tests with dust because this mix was the most economical.

Relationship Between Compressive Strength and Weight Loss

A comparison of weight loss occurring in the TCLP test

Weight Loss of Concrete after TCLP test (gm)

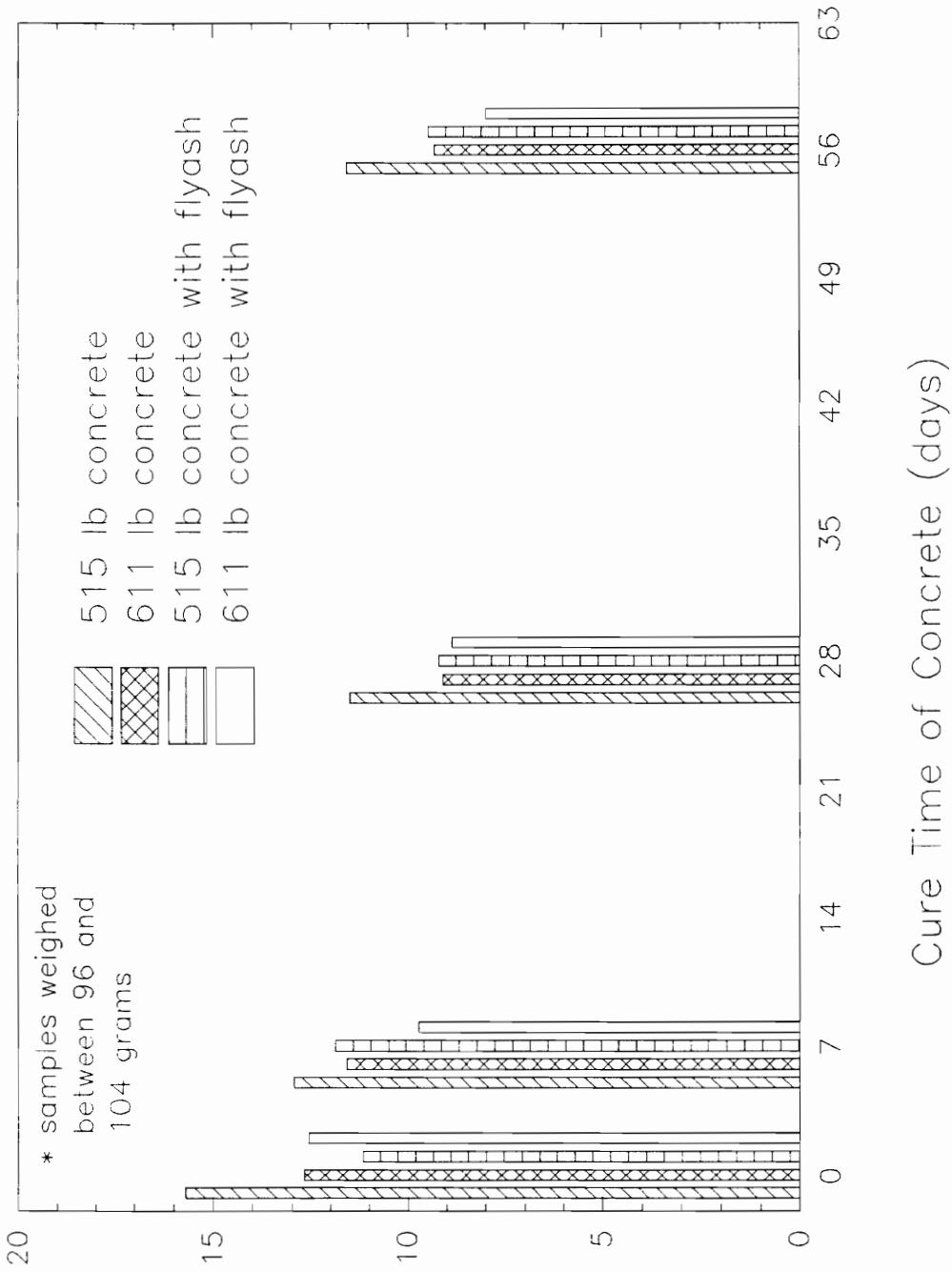


Figure 13. Weight loss of concrete without dust as a function of cure time

with compressive strength indicated that the strongest concrete has the lowest weight loss. This relationship is shown in Figure 14. This graph was generated using solidified mixes that incorporated 528 lb, 264 lb, and 132 lb dust/cu yd concrete. Figure 14 shows that most of the solidified mixes lost between 8 and 15 grams of material as a result of the TCLP test over a range of compressive strengths from 1000 psi to nearly 8000 psi. A relatively durable solidified material, one that will lose less than 10 grams of waste material, requires a compressive strength greater than 4500 psi. According to Weyers (1991), the required compressive strength range in order for a concrete to be used for construction is between 4000 and 5000 psi. Also, the required range of compressive strengths of a concrete to be used for decorative purposes is between 3500 and 4000 psi. Therefore, decorative concrete may lose about 12% of its mass in the TCLP test while construction grade concrete may only lose 10% or less.

Compressive Strength and Weight Loss Properties Over Time

Changes in the compressive strength of the solidified electric arc furnace dust over a curing period of 28 days is shown in Figure 15. The compressive strength of concrete without the addition of electric arc furnace dust is also included. The data indicate that, while all of the solidified samples increased in compressive strength over time, each displayed different patterns of strength gain over time. The

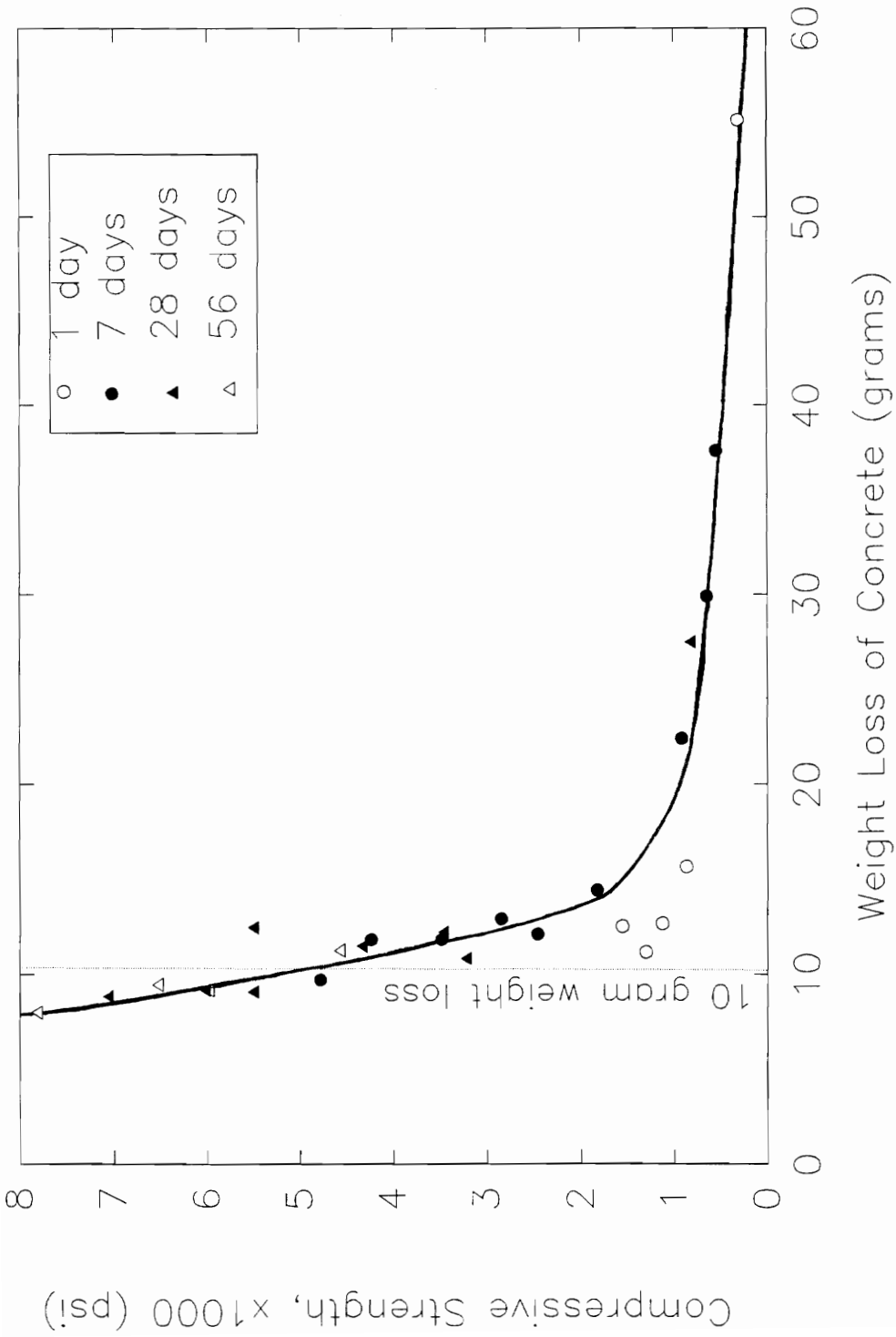


Figure 14. Relationship between compressive strength and weight loss of the solidified dust samples in the TCLP test

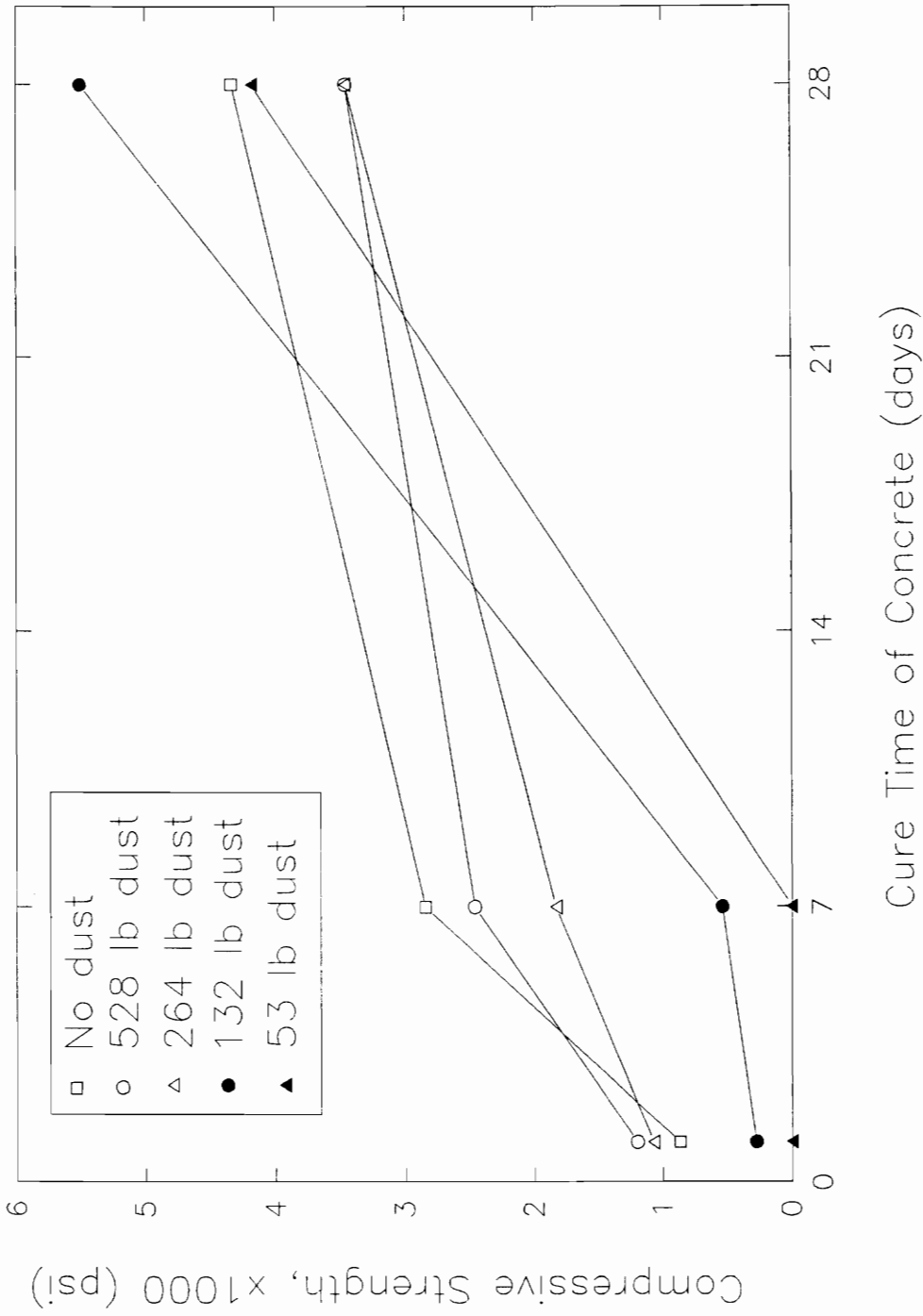


Figure 15. Compressive strengths of the solidified dust samples as a function of cure time

"path" of increased compressive strength depended upon the amount of electric arc furnace dust that was incorporated in the concrete samples. For example, the concrete sample that contained 53 lb dust/cu yd concrete had no measurable strength until 7 days; however, the strength increased to over 4000 psi at 28 days. The solidified samples that incorporated 264 lb and 528 lb dust/cu yd concrete had similar paths of compressive strengths over the 28 day time period but had a lower 28 day compressive strength than the solidified sample with no dust. These results conflict with the findings by Ortega et al. (1980) who found that, although the lead in the waste retarded early compressive strength, lead did not affect the final compressive strength of the concrete. Overall, the 132 lb dust/cu yd water sample was best because it had the highest final strength and also some initial strength.

The solidified samples containing 264 lb and 528 lb dust/cu yd concrete had consistently lower compressive strengths after 28 days probably because of the retarding effects of lead, cadmium, and zinc. Several researchers have tried to find an explanation for this phenomenon. Ortega et al. (1980) suggested that the increased crystal growth, created because lead hinders the hydration processes of concrete, accounts for an overall decrease in compressive strength. As the lead content is increased, more of the lead coats the surface of the clinker compounds and hinders the hydration reactions. Thus, the final or long term compressive

strength is reduced only in the solidified samples that contain the higher amounts of electric arc furnace dust (264 lb and 526 lb dust/cu yd concrete). Tashiro et al. (1980) believe that zinc acts a retarder in concrete and decreases the compressive strength by precipitating an amorphous layer of zinc hydroxide around particular clinker compounds. Perhaps, all of these factors contributed to the overall decrease in compressive strength of the solidified samples that incorporated 264 lb and 528 lb dust/cu yd concrete.

The weight loss properties of the solidified electric arc furnace dust at three cure times are shown in Figure 16. At 7 days, the solidified dust that contained 132 lb dust/cu yd concrete lost approximately 37 grams of material in the TCLP test. However, after 56 days, this sample had the lowest weight loss. The solidified electric arc furnace dust samples that contained 264 lb and 528 lb dust/cu yd concrete also improved over time. At 56 days, all of the solidified electric arc furnace dust samples had weight losses at or below 10 grams. The concrete products produced under these conditions should be acceptable for most uses.

The data in Figures 15 and 16 can be compared because the compressive strength and weight loss properties of the solidified electric arc furnace dust are related. At 56 days, the solidified samples that incorporated 132 lb dust/cu yd concrete had a weight loss of approximately 8 grams and a compressive strength of approximately 5500 psi. The weight

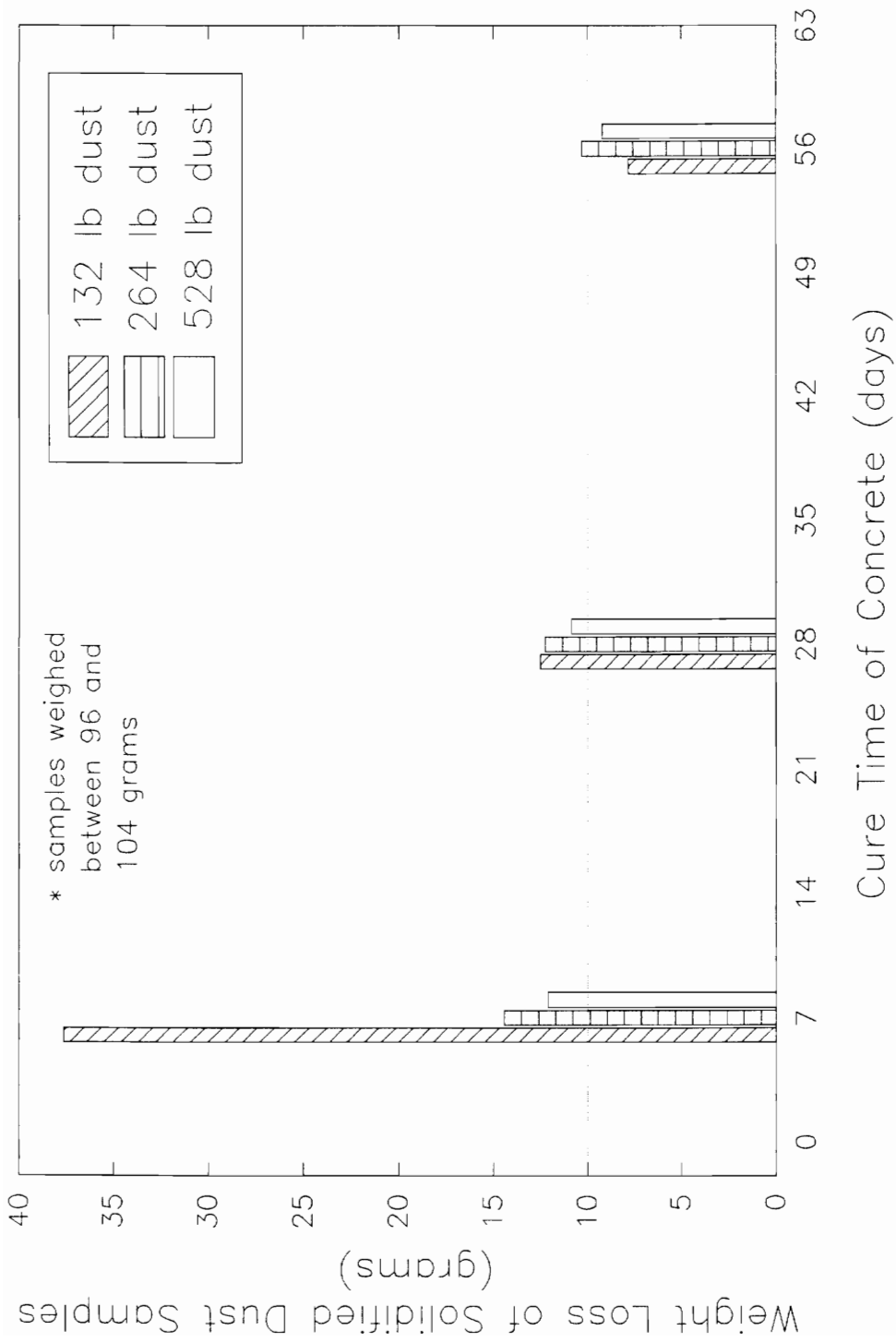


Figure 16. Weight loss of the solidified dust samples as a function of cure time and dust content

losses for the solidified samples that contained 264 lb and 528 lb dust/cu yd concrete were only slightly higher than the solidified samples containing 132 lb dust/cu yd concrete, yet the compressive strengths were much lower (approximately 3400 psi). Therefore, it is possible to develop a CFS process with moderate compressive strengths and still maintain acceptable weight losses (10 grams or less) as long as curing times of 56 days are used.

Leaching Considerations

The amount of lead that will be present in the TCLP solution depends upon the solubility of the solidified waste as a function of pH, the amount of electric arc furnace dust in the concrete, and the amount of concrete that dissolves during the TCLP test. These are not independent because the amount of concrete that dissolves in the TCLP test will dictate the final pH of the TCLP solution and the amount of concrete that dissolves depends on the dust content and curing time of the concrete.

Figure 17 shows the weight loss properties of the electric arc furnace dust and the corresponding concentrations of lead that will leach, assuming that all of the lead in the concrete that dissolves will be found in the TCLP solution. Figure 18 shows the weight loss properties of the solidified electric arc furnace dust as a function of the concentration of leachable lead. Figure 17 and 18 are similar even though

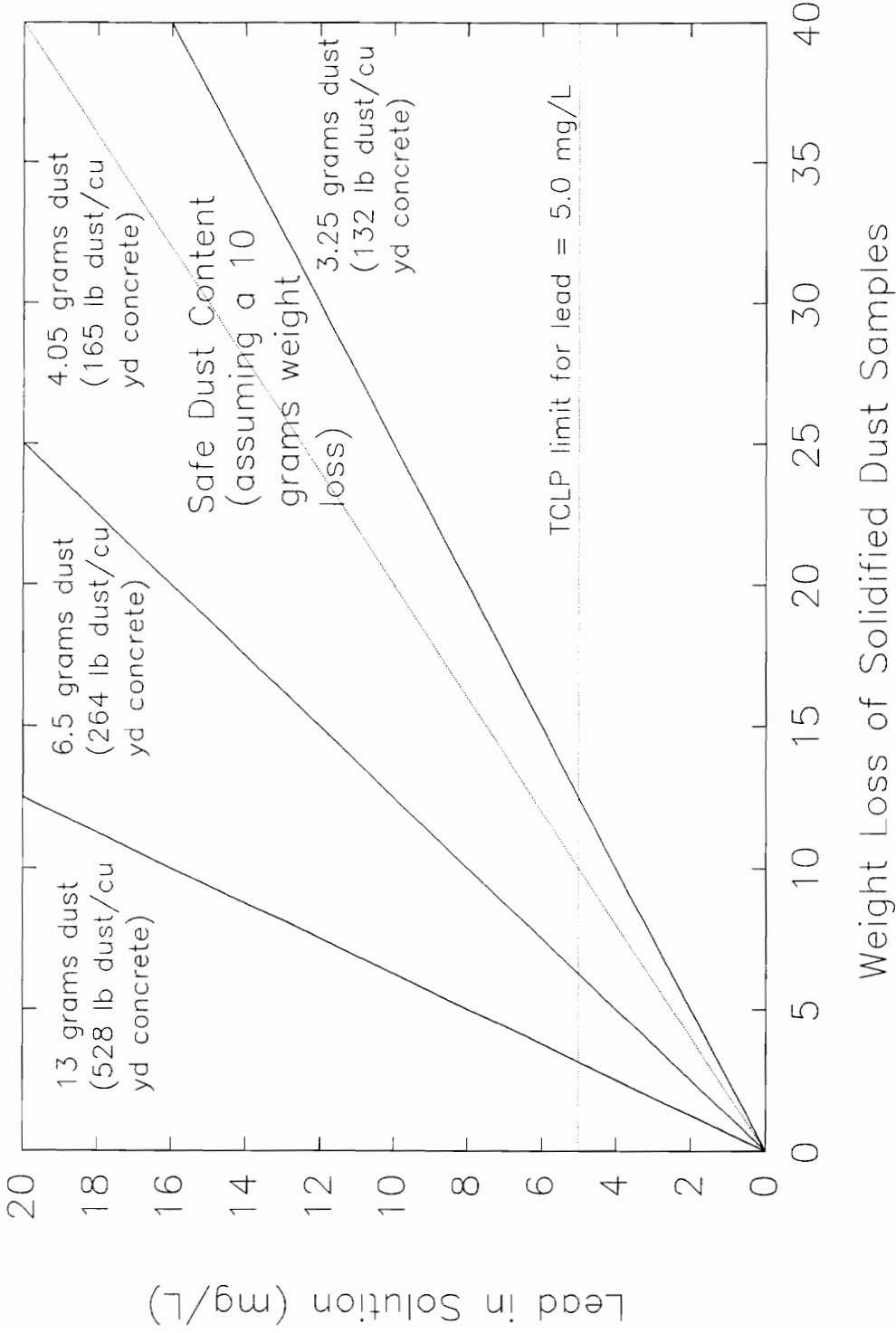


Figure 17. Soluble lead as a function of weight loss of the electric arc furnace dust

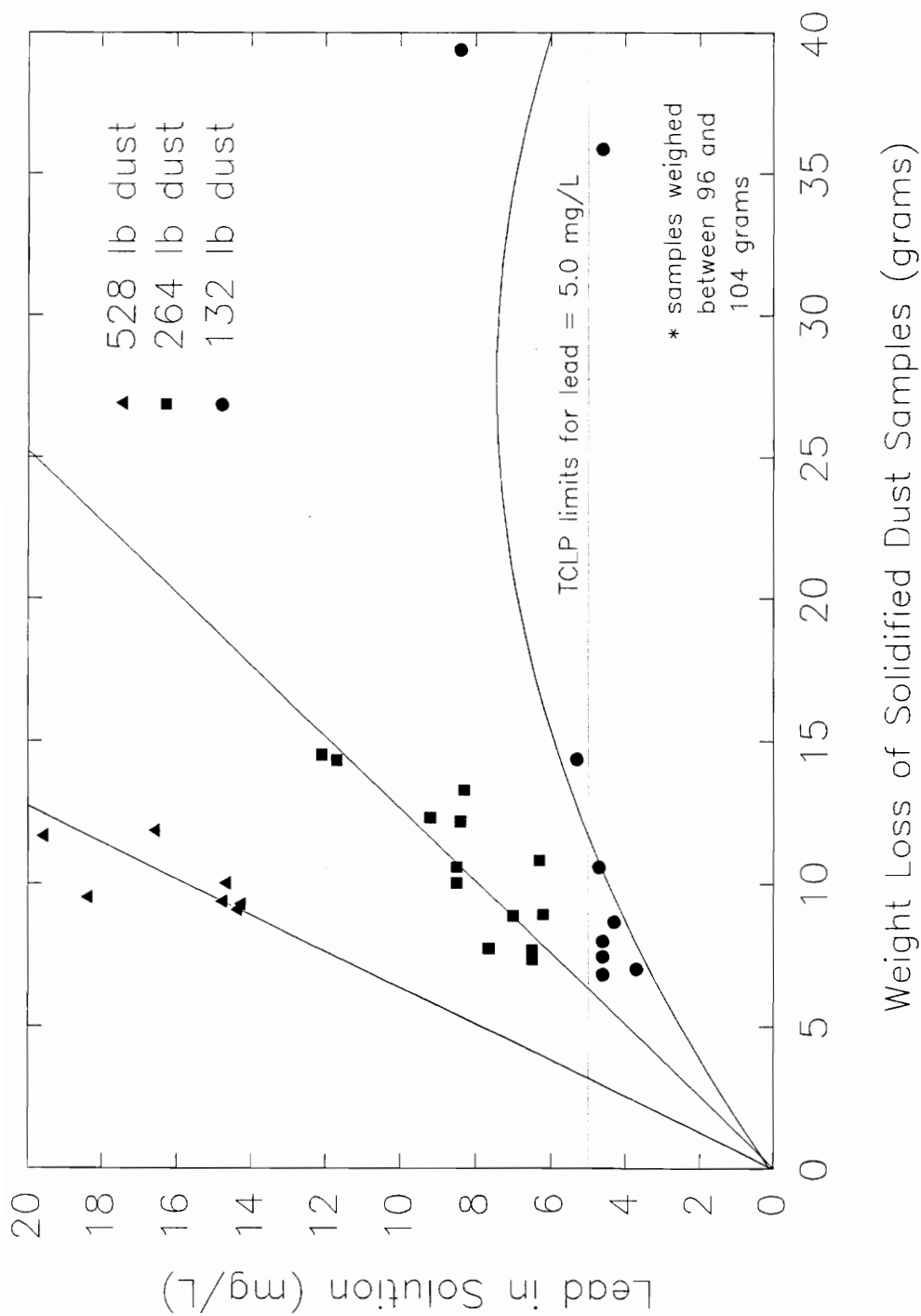


Figure 18. Soluble lead as a function of weight loss of the solidified dust samples and dust content

Figure 17 was based on calculations and assumptions and Figure 18 was formulated from the data and includes most of the solidified electric arc furnace dust samples that were tested. This figure was based on a conservative assumption that approximately 2.5% of the electric arc furnace dust is made up of lead, although 1.9% was the measured value. Dust amounts of 13 grams, 6.5 grams, and 3.25 grams of dust were used because these are the amounts of electric arc furnace dust in a representative 100 gram solidified sample (for the TCLP test) and correspond to concrete containing 528 lb, 264 lb, and 132 lb dust/cu yd concrete, respectively. The "Safe Dust Content" line corresponds to a 10% weight loss of the solidified electric arc furnace dust and the TCLP limit for lead, 5 mg/L.

Figure 17 shows that a study using 13 grams of dust cannot meet the TCLP limits for lead if more than 3.1% of the sample is dissolved. Likewise, a 6.5 gram dust sample cannot lose more than approximately 6.2% of its material. However, 3.25 grams dust can lose up to 12.3% of its material and still meet TCLP limits for lead. This is important because this study has determined that a 10% weight loss is the maximum weight loss that can occur for a concrete to be adequate as a construction material.

Figure 18 includes three different amounts of electric arc furnace dust. As predicted from Figure 17, the solidified samples incorporating 528 lb and 264 lb dust/cu yd concrete

exceeded the TCLP standards. The solidified samples with 528 lb dust/cu yd concrete leached an average of 16 mg/L lead, while the solidified samples that contained 264 lb dust/cu yd concrete leached between 6 and 10 mg/L lead. Also as predicted from Figure 17, the solidified samples that incorporated 132 lb dust/cu yd concrete generally leached at or below the TCLP standard for lead. This means that, even though all three of the dust contents are at or below a 10 gram weight loss at 56 days (Figure 16), the TCLP standards can still be exceeded when there is too much dust in the concrete. Therefore, the amount of dust incorporated in a concrete must be less than the level of dust defined by the "Safe Dust Content" line shown in Figure 17. Dust levels exceeding 165 lb dust/cu yd concrete cannot be incorporated in a CFS system without exceeding the TCLP standards (assuming a weight loss of 10%).

The data from the solidified samples that incorporated 132 lb dust/cu yd concrete deviates from the linear due to the effects of solution pH on lead solubility. When a large weight loss occurs, as happened with the 132 lb dust mix, the soluble concentration of lead decreases because the dissolved concrete raises the pH to the point where lead solubility decreases.

pH Effects

The amount of material that is dissolved from a

solidified electric arc furnace dust sample was found to effect the concentration of soluble lead by effecting the final pH of the TCLP test. Figure 19 shows the relationship between the weight loss of the solidified electric arc furnace dust and the final pH of the TCLP test. As the weight loss of the solidified electric arc furnace dust increases, the pH of the TCLP extraction fluid also increases. The increase in pH results in a decrease in the concentration of soluble lead which is the phenomenon that occurred in Figure 18. The cause of the increase in the pH of the TCLP extraction fluid is due to the high pH of the concrete that dissolves into the leachant.

Additives to Improve the Solidified Dust Samples

Chelator was incorporated into the solidified electric arc furnace dust samples in an attempt to increase the compressive strength of the concrete. An increase in the compressive strength of the solidified dust causes a decrease in the weight loss such that more of the electric arc furnace dust could be incorporated in a solidified waste without exceeding the TCLP limits for lead.

Figure 20 shows the effects of chelator on the compressive strength of the solidified electric arc furnace dust. All of the solidified samples incorporated 264 lb dust/cu yd concrete. It was found that the solidified dust sample that incorporated 10.29 lb chelator and the sample with

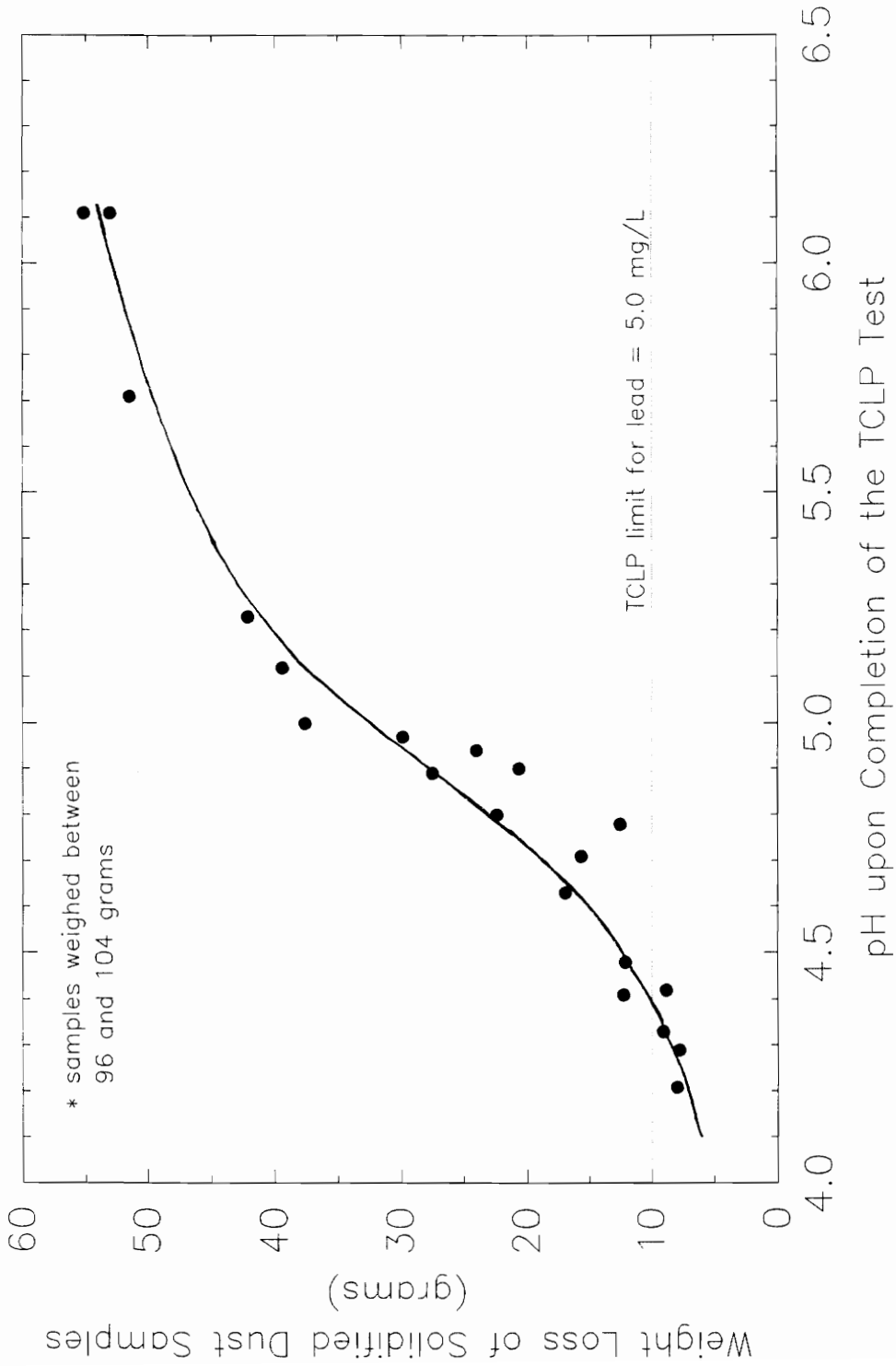


Figure 19. Relationship between the weight loss of the solidified dust samples and the final pH after the TCLP test

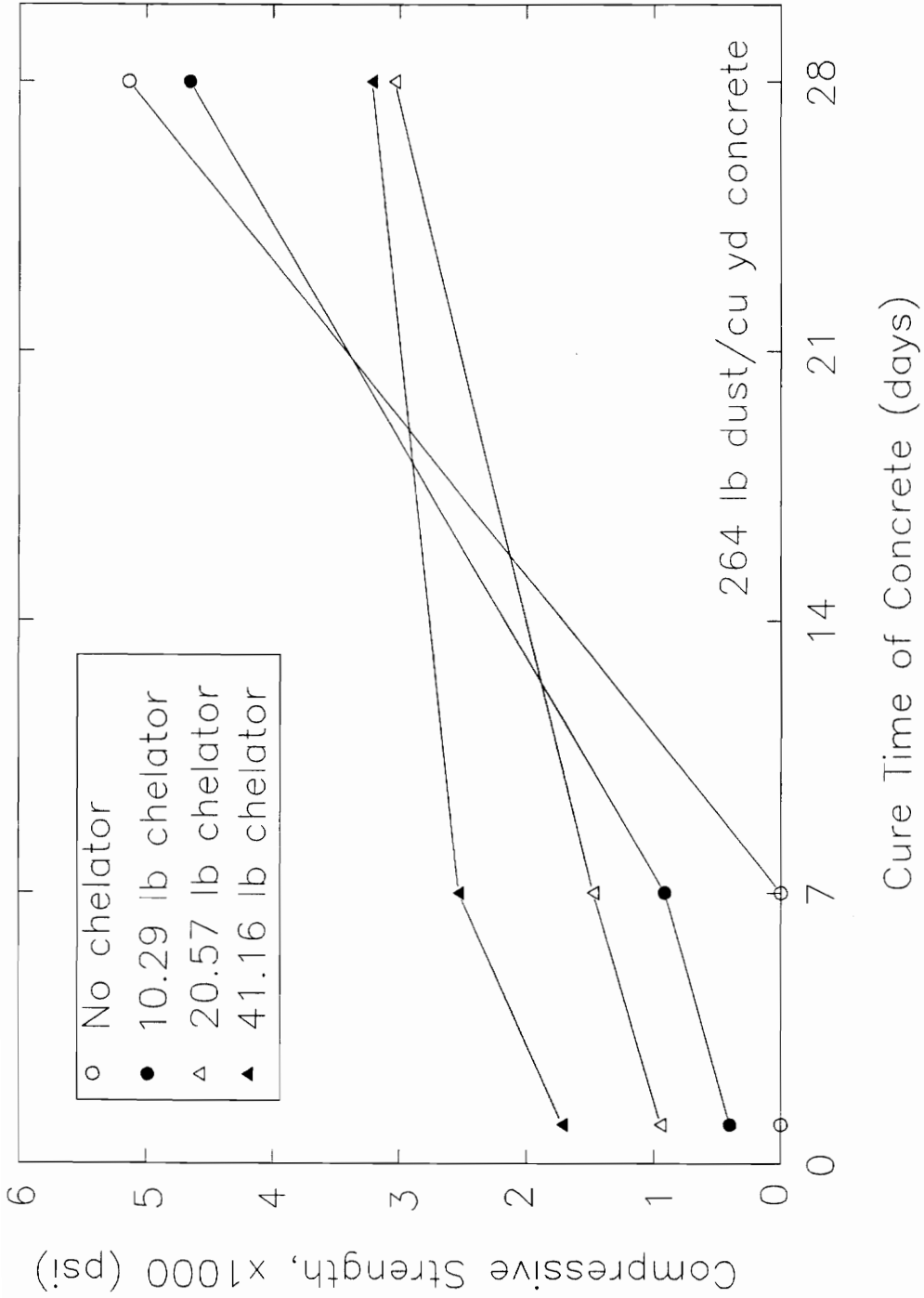


Figure 20. Effects of chelator on the compressive strength of the solidified dust samples as a function of cure time

no chelator had the highest 56 day compressive strength; however, the concrete with 10.29 lb chelator had some initial strength while the non-chelated sample had none.

These compressive strength results correspond to the pore water studies which show that the dust having 10.3 lb chelator leached the least amount of lead. Therefore, it appears from this study that as more lead leaches out of the pore water solution, the compressive strength of the concrete decreases. Chelator can contribute to the leaching of lead if too much is added.

In summary, although the addition of 10.29 lb chelator decreased the 56 day compressive strength, it reduced the soluble lead and helped in early strength. This is important because some initial compressive strength is necessary before the concrete can be removed from the forms.

Salt Addition to Increase Compressive Strength

Chloride is an accelerator in concrete and may offset the retarding effects of lead. The addition of a chloride salt, NaCl, was studied to determine whether chloride could increase the compressive strength of the electric arc furnace dust samples so that more dust could be incorporated. In this study, the concentration of chloride in the solidified sample containing 264 lb dust/cu yd concrete was increased so that it would have the same concentration of chloride as the solidified samples containing 528 lb dust/cu yd concrete.

These calculations were based on the pore water solution studies shown in Figure 12 which shows that the soluble concentration of chloride increased as the amount of electric arc furnace dust increased. Other anions, such as sulfate, were not thought to counteract the effects of the lead because their soluble concentrations did not depend on the amount of electric arc furnace dust.

It was found that the addition of chloride, as NaCl, did not increase the compressive strength of the solidified samples. In fact, most of the solidified electric arc furnace dust samples had no compressive strength even after 28 days. Thus, although chloride was presumed to be an accelerator, it did not accelerate the concrete such that the retardation effects of the lead were counteracted.

Required Compressive Strength

The results of this study have made it possible to determine the required compressive strengths for the solidified electric arc furnace dust. The solidified electric arc furnace dust must meet this requirement in order to pass the TCLP limits. The required compressive strengths for the solidified electric arc furnace dust are shown in Figure 21. The compressive strength curve was derived from selecting weight losses and the corresponding amounts of electric arc furnace dust from Figure 18. Then, using the selected weight loss, the corresponding compressive strength was determined

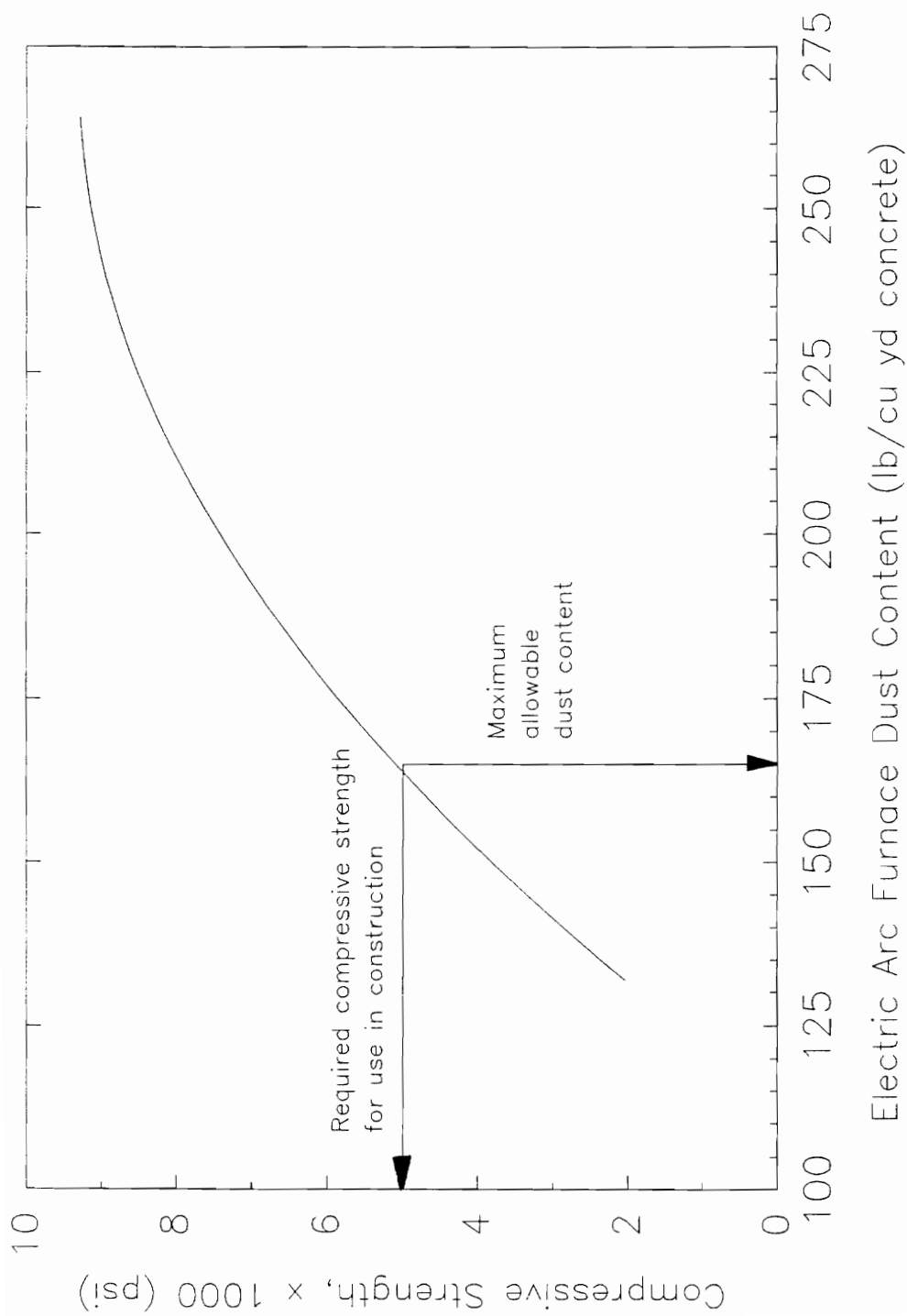


Figure 21. Determination of allowable dust content in the solidified dust samples to provide a suitable construction material

from Figure 14. Figure 21 was based on the ability of the solidified waste to pass the TCLP test for lead. It was determined that if the standards for lead were passed, all other heavy metal standards would be passed.

This figure illustrates that a compressive strength of over 9000 psi is required to pass the TCLP limits for lead if 264 lb dust/cu yd concrete is solidified. From our studies, we have determined that this compressive strength is unobtainable. The compressive strength and weight loss properties of the solidified waste dictate that the maximum amount of electric arc furnace dust that can be incorporated is approximately 165 lb dust/cu yd concrete. This is also known as the "Safe Dust Content" line shown in Figure 17. Therefore, a compressive strength of approximately 4500 psi and a weight loss of approximately 12 grams is required in order to pass the TCLP test for lead. This concrete can be used either as a construction material or for decoration.

CHAPTER 5
CONCLUSIONS

The following conclusions have been reached from this study:

- 1) approximately 1.9% of the electric arc furnace dust is made up of lead,
- 2) the solubility of cadmium in the electric arc furnace dust is controlled by hydroxide, while the solubility of lead is not,
- 3) the weight loss properties of the solidified dust dictate that at least a 10 gram or a 10% weight loss of the material will occur,
- 4) based on the compressive strength and weight loss properties of the solidified electric arc furnace dust, 165 lb dust/cu yd concrete is the maximum amount of dust that can be incorporated into concrete without exceeding TCLP standards,
- 5) the addition of 10.29 lb chelator/cu yd concrete increased the initial strength and decreased soluble lead of the solidified electric arc furnace dust; however, the addition of salts did not strengthen the solidified dust samples.

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VITA

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In the fall of 1985, Tiffany began college at Virginia Polytechnic Institute and State University. She received her Bachelor of Science degree in Geophysics in the early summer of 1989. She immediately continued her college studies, this time in the Civil Engineering department's Environmental Engineering program. After spending over a year on her research as well as fulfilling some undergraduate engineering requirements, Tiffany completed her Master of Science degree in Environmental Engineering in October, 1991.

After graduate school, Tiffany and her husband, Paul, moved to Newport Beach, California where she found employment with Levine-Fricke.

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