



**DRAFT ANNUAL REPORT
LEACHING TESTS FOR EVALUATING RISK IN SOLID WASTE
MANAGEMENT DECISION MAKING: Year 1**

September 2001

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Report #

**Leaching Tests for Evaluating Risk in
Solid Waste Management Decision Making**

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EXECUTIVE SUMMARY

PROJECT TITLE: Leaching Tests for Evaluating Risk in Solid Waste Management Decision Making: Year 1

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COMPLETION DATE: May 2001

This report is an annual report of activities on a two-year study and presents preliminary results. The final project report will present the complete set of results and interpretation.

OBJECTIVES

The objective of the project is to conduct a scientifically sound investigation of the use of leaching tests for risk-based decision-making in solid waste management. Several factors that impact leaching will be addressed, and the results of the leaching tests will be examined for use in risk-based decision-making process.

METHODOLOGY

Several different solid wastes were collected and characterized for selected heavy metal leachability. Every sample was leached using the Toxicity Characteristics Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP). A total recoverable metal analysis was also performed on every sample. Additional leachability tests were performed on the following three waste samples: spent abrasive blasting media, CCA-contaminated soils, and wood and tire ash. The additional leaching tests included experiments to evaluate the role of leaching time, pH, and liquid-to-solid ratio (L/S ratio). Finally, the wood and tire ash sample was leached using laboratory leaching columns and field leaching vaults to simulate actual leaching in a beneficial reuse scenario.

RESULTS AND DISCUSSION

Preliminary results indicate that in most cases heavy metals leached less under SPLP than TCLP. This was not universally true; the bulk of the interpretation of this data will be presented in the final project report.

1.0 INTRODUCTION

1.1 BACKGROUND

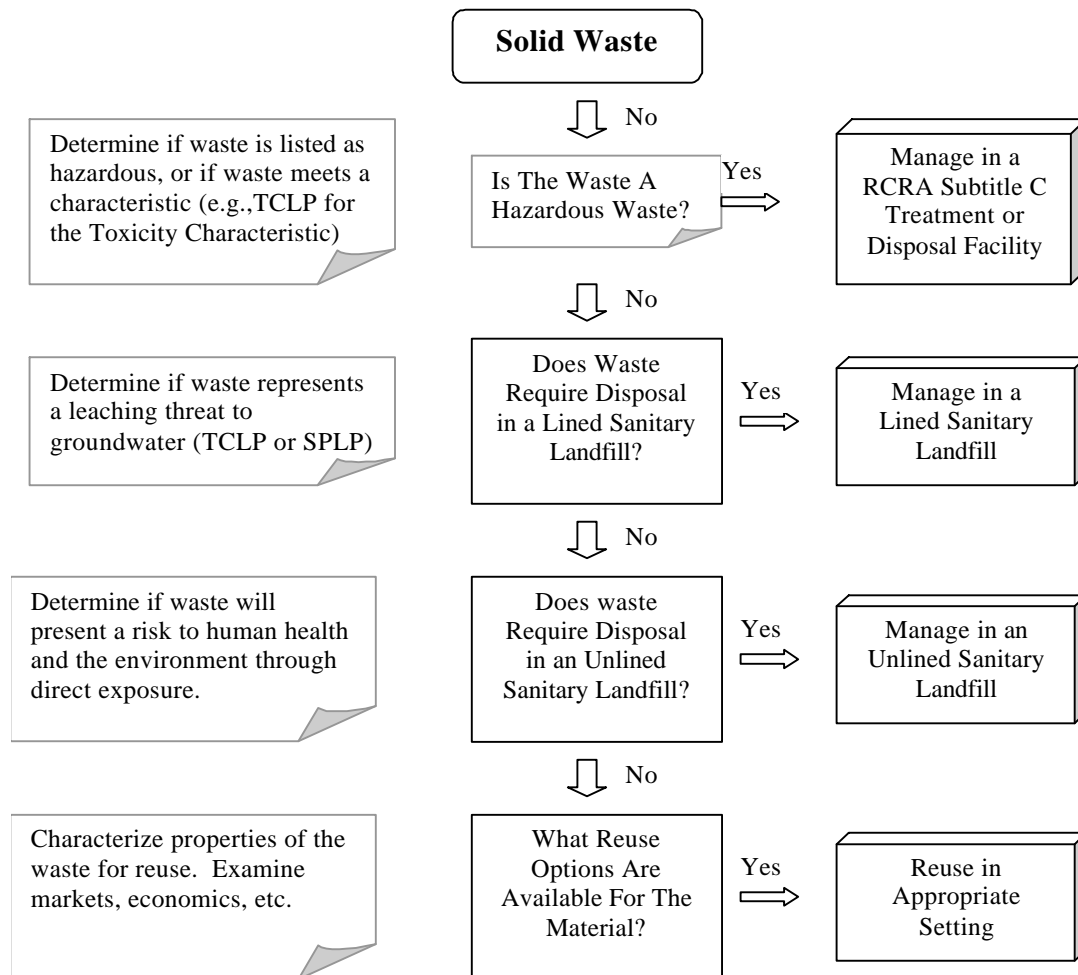
As with other decision-making areas of environmental engineering and management, the use of risk assessment methodologies has been introduced to the solid waste management field. The need to clean up a great number of contaminated sites has led to the use of risk assessments for determining which sites represented the greatest threat (i.e., which sites should be allocated resources first) and to what level should these sites be remediated. The concept of assessing risk incorporates a number of factors, including but not limited to, the targets at risk (e.g., humans, wildlife), the routes of exposure (e.g., water, air), the duration of exposure, and the specific mechanism of hazard (e.g., acutely toxic, carcinogenic).

A growing use of risk-based decision-making in the solid waste field is determining management options for wastes not currently defined or characterized under the Resource Conservation and Recovery Act (RCRA) other than being defined as solid waste. These include such wastes as coal ash, foundry sand, abrasive blasting media, sewage sludge, drinking water sludge, street sweepings, residues from air pollution control systems, and materials derived from the processing or treatment of waste, such as compost from the aerobic treatment of organic solid wastes and screened soil fines produced at construction waste recycling facilities. These materials rarely would be characterized as hazardous, but they may contain chemicals that may be of concern under certain management scenarios. Often, the most desirable management option for these materials is recycling to the environment (i.e., outside of a landfill). The use of compost in agriculture and of coal ash for road building are two such examples.

The quality a waste must possess before it can be managed in an environmentally sound manner must be addressed. If a waste is not hazardous as defined by RCRA, then it can be disposed of in a lined sanitary landfill. Landfill disposal is an expensive option, especially for waste materials with no previous required management steps. This expense and the desire to recycle the materials back to the environment have led generators to find reuse options for their wastes outside landfills; hence the possible risk to human health and the environment must be considered. As with contaminated waste sites, a site-specific risk assessment may be performed. Since the recycled waste materials are often used in many different areas (e.g., compost products distributed to multiple markets), a common approach currently used by many states is the use of soil cleanup target levels (e.g., Florida's Soil Cleanup Target Levels [SCTLs]). These levels were established for contaminated site cleanup. When the concentration of a pollutant in a waste material is below the appropriate target level, it is considered "clean" for a given reuse scenario. Typical risk assessment elements with generic assumptions (i.e., exposure and toxicity) are included in these target levels.

Two routes of exposure typically considered in risk assessment procedures for a waste-derived material are as (1) direct exposure to humans via inhalation, dermal contact, and ingestion; and (2) human exposure through drinking water. In most cases, ecological risk is not considered. If direct human contact is possible when a waste is land applied, the concentrations of pollutants in the material (measured as mg/kg) are compared to the appropriate generic SCTLs. If the concentration is greater than the SCTL, the material may not be land applied where direct human contact occurs. The evaluation of the risk from drinking contaminated groundwater is somewhat more complicated. Since the material is not consumed directly, the amount of a pollutant that leaches or washes off the material must be predicted. This leaching risk may be evaluated by theoretical calculations from the total concentration of a pollutant of concern or preferably by

conducting leaching tests (e.g., TCLP, SPLP). In the end, the leaching concentration (mg/L) is compared to a risk-based water quality standard or guideline, with appropriate consideration of dilution that may occur in groundwater.



The TCLP is the most widely used leaching test in the United States and was developed specifically to address the co-disposal of hazardous waste in an organic waste landfill. As a result, the TCLP may not allow for extrapolation of long-term environmental effects or address different leaching mechanisms. Leaching behavior of heavy metals is well documented as being more complex than can be determined by a single extraction test. The use of the TCLP has been questioned as being too broadly applied, which has been expressed by a number of researchers (van der Sloot et al., 1999, Selim et al., 1997) and recently by the U.S. Environmental Protection Agency (U.S. EPA) science advisory board's Environmental Engineering Committee, SAB EEC (U.S. EPA SAB 1999). In a February 26, 1999, letter to Carol Browner, the SAB EEC cited a number of cases in which the requirement of using the TCLP had been successfully challenged in court. Industry groups successfully argued in these cases that other more appropriate leaching tests should be used.

A number of potential shortcomings of the TCLP test can be cited. The TCLP is a batch test with an arbitrary liquid-to-solid ratio, which may not be representative of actual conditions. The role of kinetics is minimized as the test is performed for a standard 18 hours. The pH of the leaching fluid does not necessarily represent the pH of the leaching environment. The pH of the leachate during the TCLP is highly dependent on the buffering capacity of the waste materials, which may lead to inaccurate determination of waste behavior in the environment. The continued leaching of chemicals into the environment over time is not addressed. The application of a dilution factor to the TCLP test results when conducting a risk-based management evaluation is also not defined. Many of the same questions that are raised regarding the TCLP also are relevant to the application of the SPLP. The SAB EEC cited as its single most important recommendation that U.S. EPA needed to "improve leach test procedures, validate them in the field, and then implement them." The U.S. EPA has taken the steps to address this issue, including a public meeting on July 22 and 23, 1999, to begin discussions of revisiting the TCLP and its application.

1.2 OBJECTIVE

The objective of the project is to conduct a scientifically sound investigation of the use of leaching tests for risk-based decision-making in solid waste management. Several factors that impact leaching will be addressed, and the results of the leaching tests will be examined for use in risk-based decision-making process.

1.3 RESEARCH APPROACH FORMAT

The experimental methodology involved the following steps:

1. Collection of waste materials. Solid wastes and contaminated soils were collected from a number of sources around the state. The decisions of what types of samples collected were made in consultation with the project technical advisory group (TAG).
2. Performing the TCLP and the SPLP. Each waste sample was tested for waste leachability using both the TCLP and the SPLP.
3. Examination of factors impacting leaching. A series of leaching experiments were conducted to better determine the impact of factors such as pH, particle size, liquid-to-solid ratio, and others on waste leachability.
4. Column studies. Once the waste or contaminated soil was characterized, representative samples were tested via column studies to examine more realistic leaching conditions such as might occur in the field (e.g., land application, landfill).

5. Examination of risk. The results of the leaching tests will be examined and critiqued for the use in risk-based decision-making process. Again, the TAG will play a useful role in this review.

All sampling and testing procedures will be performed using standardized U.S. EPA methods (SW 846) where available, following the standard operating procedures outlined in the investigator's comprehensive quality assurance plan with the Florida Department of Environmental Protection. Leaching tests are currently approved as part of this plan.

1.4 REPORT DESCRIPTION

This report is an annual report of activities completed on a two-year study and presents a literature review, description of methods, and preliminary results. The reader is cautioned that the data presented are preliminary and the final project report should be consulted for an interpretation of the data.

2.0 LITERATURE REVIEW

2.1 LEACHABILITY AS A CHARACTERISTIC OF SOLID WASTE

The most commonly employed leaching test used in the United States is the Toxicity Characteristic Leaching Procedure (TCLP), which is the assay required to determine the toxicity characteristic. The TCLP replaced the EP TOX test, which was included in the first promulgation of the RCRA regulations. The TCLP was designed to simulate conditions in an anaerobic landfill and is therefore supposed to represent worse-case leaching conditions in a landfill where organic wastes are co-disposed. The TCLP is a batch test (i.e., a single batch of waste is leached with a defined amount of leaching solution) and involves leaching a size-reduced mass of waste material with an acetic acid solution. A 20-to-1 liquid-to-solid ratio (L/S ratio) is employed, and the mixture is rotated for 18 hours. TCLP pollutant concentrations are also used to determine whether a hazardous waste has met the requirements of the land disposal restrictions and also may be used to determine whether a waste may be disposed in an unlined landfill that contains co-disposed organic wastes.

To better simulate leaching in the environment, the U.S. EPA also developed the Synthetic Precipitation Leaching Procedure (SPLP), which is performed in the same manner as the TCLP except a simulated acid rainfall is employed (U.S. EPA, 1996). The SPLP uses a slightly acidic solution ($\text{pH} = 4.20 \pm 0.05$) by adding the 60/40 weight percent mixture of sulfuric and nitric acids without any buffer systems. Conditions in which this test might apply include disposal of an inorganic waste in a mono-fill or waste pile and land application of a recycled waste material such as ash or compost. U.S. EPA illustrated its interpretation of the different applications of these two tests in its recent proposed lead-based paint (LBP) debris rule. Since test results indicated that LBP debris leached at a greater amount in the TCLP relative to the SPLP, the proposal was made to allow LBP debris to be disposed in C&D landfills but not municipal solid waste (MSW) landfills.

While the TCLP and the SPLP are the leaching tests most commonly used by the U.S. EPA in waste management decision-making, many other different leaching tests exist. California employs the waste extraction test (WET), which utilizes citric acid. The European Union is currently undergoing an effort to “harmonize” leaching methods for waste characterization (van der Sloot et al., 1997). Other leaching tests are also recommended as being better indicators of leaching conditions in the environment. Alternative tests include many varieties of laboratory tests (e.g., tank tests), column studies, and field tests. However, no accepted standardized protocol is currently available for these test methods in the United States.

2.2 FACTORS IMPACTING WASTE LEACHABILITY

The use of the TCLP as the only acceptable test for most risk-based waste management decisions has been questioned (U.S. EPA SAB 1999). This is due in part to the many complicated factors that control the leaching of chemicals from wastes. Research (Yong et al., 1992) has investigated these factors, which can be divided into two main categories: physical and chemical factors. Physical factors include but are not limited to particle size, homogeneity, flow rate, contact time, porosity, and geometrical shape. Some of the chemical factors include kinetics, pH, redox conditions, complexation with organic or inorganic chemicals, and chemical speciation of pollutants of interest.

2.2.1 Physical Properties

The physical properties of a solid medium controls leaching. Dissolution occurs at the solid-liquid interface. This interface is governed by the solid's surface area, which is controlled by particle size and internal pore structure (Environmental Canada, 1990). A study conducted by Peters (1999) noted that when a soil is fractionated into separate fractions according to size, the finest soil would contain the highest concentration of contaminants. Another physical parameter that influences the leaching of metals is permeability of the solid phase. If the permeability of a waste is low, the leaching fluid will not be transmitted as rapidly and the contaminant may be higher concentration (van der Sloot et al., 1997).

2.2.2 Kinetics

Reaction kinetics are defined as the rate of appearance of solute in solution from a slowly dissolving solid, which is a function of parameters such as pH, oxidation-reduction potential (ORP), and temperature. Quantifying the mass of pollutant in solution in relation to the mass of the constituent remaining in the solid phase is only possible at equilibrium. Depending on the reaction, equilibrium concentration may not be reached for days and even years (van der Sloot et al., 1997). Since the extraction time for both the TCLP and the SPLP was arbitrarily chosen (18 hours \pm 2 hours), these tests might not give sufficient time for equilibrium to be reached. Therefore, these tests may in some circumstances misestimate the amount of pollutants released over a long period of time. Computer modeling can only be used after equilibrium concentrations have been reached (Kersten, 1996).

2.2.3 pH

Research (van der Sloot et al. 1997) has shown that some metals (e.g., lead) have the tendency to leach more at low and high pH values, as in Figure 2.1. Since metals exhibit different solubilities at different pH values, logic dictates addressing this issue when discussing leaching. Since the pH is uncontrolled during both the TCLP and the SPLP extraction, it is governed by the material subjected to the test (van der Sloot et al., 1997, Yong et al., 1992). This is illustrated when comparing the TCLP and SPLP tests; while the pH in the SPLP (4.2) may be lower than the TCLP (4.9), its strong acid is rapidly neutralized by a well-buffered waste, resulting in an overall higher pH of the leaching solution. Some humic and mineral soils carry hydroxyl and other functional groups, which contribute an electric charge at the soil surface. The solution's pH therefore influences the acid base equilibrium reactions of these surface groups and as a result impacts the leachability of heavy metals (Peters, 1999).

2.2.4 Liquid to Solid Ratio

The L/S ratio is defined as the amount of leaching solution that at any given time has been in contact with the amount of waste tested. Since reuse options for waste vary, the L/S ratio varies with the amount of waste used. For example, waste being used as a road base may require one meter of material to be placed, whereas hand waste tilled into the soil as an amendment may only be placed to a depth of a few centimeters. The L/S ratio is quite different between batch tests and what occurs in the environment. For instance, a batch test may overestimate leaching because of the aggressive nature of the test, particle size reduction, and dilution that occurs because of the larger L/S ratio that occurs. The more realistic L/S ratio is why field tests and column tests have been used.

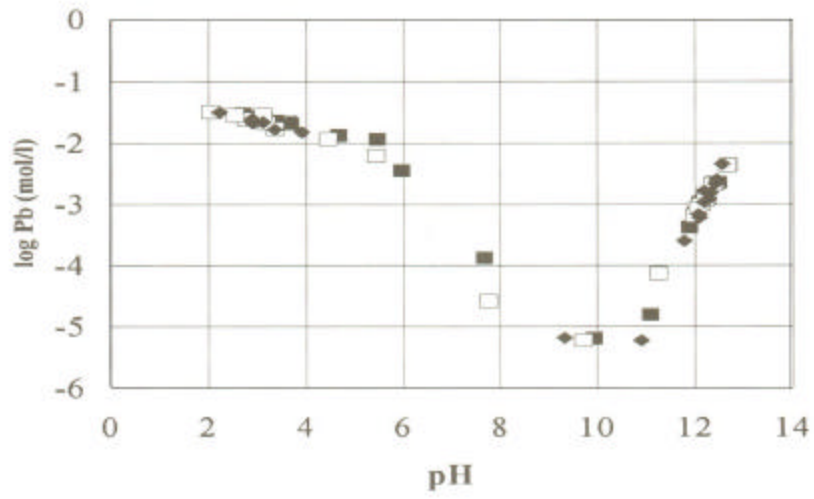


Figure 2.1 Relationship between Lead Leaching and pH for a Waste (van der Sloot et al. 1997).

3.0 METHODOLOGY

3.1 RESEARCH APPROACH

Although factors affecting leachability have been discussed in detail, researchers failed to address how these factors relate to one another. When a solid waste is land applied, these factors collectively impact metal leachability. Therefore, research was conducted on solid wastes with the potential to be land applied. Selected solid wastes were subjected to a battery of leaching tests addressing these factors.

3.2 SAMPLE DESCRIPTION

Table 3.1 presents the different types of wastes used and the sources and preparation of the wastes. The Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) batch tests were employed to determine metal leachability of all the wastes. For three different types of wastes—abrasive blasting media (ABM), CCA-contaminated soil, and wood and tire ash—as well as others, additional batch leaching tests were carried out to examine metal behavior according to factors affecting leachability, pH, liquid to solid ratio, and leaching time.

Table 3.1 Wastes Used in Batch Studies

Waste	Source	Sample preparation
Computer circuit board	Local recycling store	Less than 2 in by 2 in.
Ground circuit board	Computer recycling company	Less than 0.25 in.
Lead fishing weight	Commercial fishing store (1 g)	No size reduction
Mulch	Home improvement store	Less than 1.5 in.
Ni-Cd Battery	AA size, Radio shack D size	Less than 2 in. by 2 in.
Cathode ray tube	Computer and TV from local recycling store	Less than 0.25 in.
Abrasive blasting media	Ship yards, and private contractors	No size reduction
CCA contaminated soil	CCA wood treating facility	No size reduction
Wood and tire ash	Cogeneration Plant	No size reduction

3.3 SAMPLE COLLECTION

Abrasive blasting media (ABM) was sampled from two ABM stockpiles in Tampa. The piles were sectioned into quarters; samples were collected from each quarter and mixed in two 9-gallons containers. The containers were transported to and stored in Solid and Hazardous Waste Laboratory at the University of Florida.

The study focused on CCA-contaminated soil samples because of the documented presence of CCA-solution in the soils. Soil samples were collected from a contaminated site in Archer, approximately 40 miles west of Gainesville. Samples were placed in five 19-liter plastic containers, transported to the laboratory, and stored in the Solid and Hazardous Waste Laboratory.

The wood ash for this study was sampled from a cogeneration power plant that burns wood and tires as a source of energy. The ash is hauled to a local landfill and co-disposed with municipal solid waste (MSW). Elevated heavy metal concentrations, especially arsenic, were detected in the leachate generated from the landfill. Samples were collected from eight truckloads of ash from the cogeneration plant throughout one day. The trucks emptied their load near the working face of landfill, where a front-end loader mixed the ash and a composite sample was collected from its bucket. Samples were collected in 10-gallon PVC containers and transported to the University of Florida laboratories.

3.4 TOTAL METAL CONCENTRATION

Total metal concentration could give an indication of the percent of bioavailable metals in the soil sample. U.S. EPA SW 846 Method 3050B determines the amount of metals that become available under worst-case environment conditions (Link et. al., 1998). Method 3050B is an open vessel method requiring the use of oxidizing agents and refluxing the sample on a hot plate for 2-8 hours.

Total metal digestion requires 2.0 g of sample to be placed in an Erlenmeyer flask. Ten ml of 1:1 nitric acid is added, and the flask is covered with a watch glass. The flask is then heated on a hot plate without boiling. After 15 min, the flask is removed from the hot plate, and an additional 5 ml of concentrated nitric acid is added. The flask is then placed back onto the hotplate for 30 minutes. If brown fumes are generated, 5 ml of concentrated nitric acid are added in a sequential format, until no more fumes are formed. When brown fumes cease, the flask is heated for an additional 2 hours or until the final volume of the mixture is 5 ml.

The flask is then removed from the hotplate, 30% H₂O₂ is added, and the solution is placed on the hotplate for 2 hours. Ten ml of concentrated HCl is added, and then the digestate is filtered through Whatman 51 filters into a 100-ml volumetric flask. The volumetric flask is then filled to 100 ml with additional deionized water. The samples are analyzed using either Inductively Coupled Plasma (ICP) or Flame atomic absorption spectroscopy. For Graphite Furnace Atomic Absorption spectroscopy analysis, no concentrated HCl is added to the last step.

3.5 BATCH LEACHING TESTS

3.5.1 SPLP (SW-846 Method 1312)

U.S. EPA-SW 846 Method 1312, the SPLP, is used to evaluate the potential for metal leaching into ground and surface waters. This method provides a more realistic assessment of metal mobility under field conditions, (e.g., when it rains). The extraction fluid is intended to simulate rainfall (pH 4.20). SPLP is the method of choice when evaluating fate and transport of metals in properly engineered waste land disposal facilities from which MSW is excluded.

A representative 100-g sample was weighed and placed in a 2-L high density polyethylene (HDPE) plastic container. Two liters of SPLP extraction fluid was added to the sample in the vessel. The sample was placed in the extractor and rotated at 30 rpm for 18 hours (\pm 2 hours). The sample was removed from the extractor and filtered with glass fiber filter (pore size 0.7 μ m). An acid-rinsed 1-L plastic bottle is placed under the vessel to collect the filtered sample. The extract was then preserved by adding enough nitric acid to lower the pH to below 2 pH units. The extract was stored in a cold room (below 4 °C) before metal digestion. The digestion is performed by using either U.S. EPA SW-846 Method 3010A or 3020A, depending on metal concentrations in the sample.

3.5.2 TCLP (SW-846 Method 1311)

Method 1311, TCLP is designed to simulate the leaching of metals and organics from contaminated waste materials co-disposed with an MSW landfill. The primary extraction fluid is a buffered organic acid solution at pH 4.98. If the waste is highly alkaline, a different extraction fluid at pH 2.88 is used without pH buffer. The leaching procedure of TCLP is the same as described in the SPLP test with an exception of the leaching fluid.

3.5.3 pH Static Test

The pH of leaching fluids used in the TCLP and the SPLP does not necessarily represent the pH of the leaching environment; the pH of the leachate during the TCLP or the SPLP is highly dependent on the buffering capacity of the waste materials, which leads to inaccurate determination of waste behavior in the environment. To evaluate pH effects on metal leaching, three wastes were tested over a broad pH range (from 2 to 13). In this study, nitric acid was used as the acid to lower the sample/extract pH to the level desired. This choice of acid was selected because nitric acid, as compared with other acids such as hydrochloric acid, demonstrates lower affinity to complex heavy metals in a way that would result in either increased leachability or precipitation of the metals. Diluted sodium hydroxide was used for high pH static tests. As with nitric acid, sodium hydroxide also does not complex heavy metals.

The pH static test was carried out at an L/S ratio of 20 with a leaching duration of 18 hours. A 10-g (each) sample was weighed and placed in 250-ml HDPE plastic containers, and 150 ml of deionized water was added to the sample. The amount of deionized water initially added was adjusted in order to achieve an approximate L/S of 20 after addition of diluted nitric acid needed at the specific pH. The pH was continually monitored and adjusted to ± 0.1 with either 0.1 N – 1 N nitric acid or 0.1 N – 1 N sodium hydroxide. The mixing was performed in a TCLP extractor with the plastic bottle. The sample was filtered with a Gelman glass fiber filter with a pore size of 1.0 μm and analyzed after metal digestion. Triplicate samples were run during pH static tests.

3.5.4 Liquid to Solid (L/S) Study

The L/S ratio is generally defined as the amount of a leaching solution in contact with the amount of waste tested (e.g., liter/kg). The following L/S ratios of the SPLP test were used: 200:1, 100:1, 40:1, 20:1, 10:1, and 5:1. The volume of the SPLP leaching solution was two liters for the entire L/S ratio leaching tests. Only the amount of the contaminated soil was varied to achieve the L/S ratios selected. For example, for L/S ratio 100:1, 20 g of contaminated soil was added to two liters of the SPLP leaching solution in an extraction vessel. The remaining extraction procedures were the same as the SPLP test. Table 3.2 shows the mass of solids and the volume of liquid added to achieve the desired L/S ratios.

Table 3.2 Liquid to Solid Ratios

Liquid / Solid (L³/M)	Volume of Liquid (L)	Mass of Solid (g)
5/1	2.0	400
10/1	2.0	200
20/1	2.0	100
100/1	2.0	20
200/1	2.0	10

3.5.5 Leaching Kinetics

The amount of time a leaching solution is in contact with a waste material may influence the quantity of contaminant leached unless equilibrium conditions are established. The standard SPLP protocol was followed with a L/S ratio of 20:1. Table 3.3 presents the leaching time for the three different samples evaluated. Following removal, samples were filtered as described earlier with the TCLP and the SPLP tests.

Table 3.3 Leaching Time of Waste

Waste	ABM	CCA-contaminated soil	Ash
Leaching Time	30 min., 1hr., 2hr., 4 hr., 8 hr., 12 hr., 18 hr., 24 hr., 48 hr., 4 days, 8 days, 16 days, and 30 days.	30 min., 1hr., 2hr., 4 hr., 8 hr., 12 hr., 18 hr., 24 hr., 48 hr., 4 days, 8 days, 16 days, and 30 days.	15min, 30 min, 1 hr , 2 hrs, 4 hrs, 8 hrs, 12 hrs, 18 hrs, 24 hrs, 2 days, 3 days, 4 days, 5 days, 6 days, and 7 days.

3.6 COLUMN TEST

In order to provide adequate tools for assessing the environmental impact of solid waste land application, column studies are carried out. Column tests simulate to a greater degree the leaching conditions at an actual site (Hjemlar, 1990). Unlike batch tests, column tests take into account the neutralizing effects of CO₂ and address low L/S ratios that are not attainable under batch tests conditions.

The testing apparatus consists of sixteen stainless steel leaching columns (also known as lysimeters). The lysimeters are constructed with 6" diameter Type 316 stainless steel, Teflon O-Rings, and stainless steel filter screens. A diagram of a lysimeter is provided in Figure 3.1. The entire column apparatus is shown in Figure 3.2. Deionized water solution is pumped from a 16-gallon stainless steel reservoir, using a peristaltic pump at a flow rate of 225 ml/day.

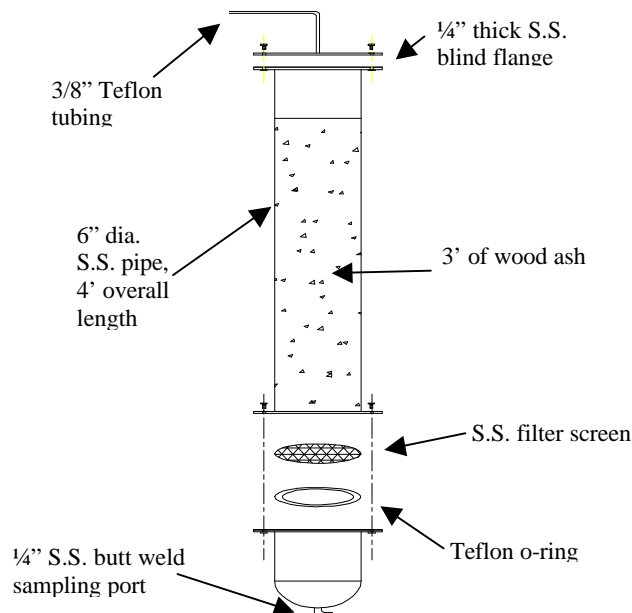


Figure 3.1 Apparatus of stainless Steel Column



Figure 3.2 Stainless steel column setup

3.7 VAULT EXPERIMENT

Four PVC-lined (2.5' by 7.5' by 2') concrete vaults were used (Figure 3.3). Three drainage holes were drilled at the bottom of the vaults, which were constructed in a way to facilitate leachate sample collection from each of the three drainage layers or a composite sample. The bottom of the vaults were lined with geotextile and covered with 10 inches of coars sand. Approximately 12 inches of wood ash (i.e., combination of wood and car tires) were placed on top of the sand drainage layer, and 2 inches of sand was placed on top. The vaults were placed at the Alachua County Southwest Landfill (ACSWL), and rain water was allowed to percolate through the waste. Leachate samples collected over time were analyzed for heavy metals. The results of this experiment will be compared to the batch tests and the column tests that were conducted during year 1.



Figure 3.3 Leaching Vaults in Field Loaded with Wood/Tire Ash

4.0 RESULTS AND DISCUSSIONS

This chapter presents the major results from the analyses. First, total metal concentrations of three different wastes with detailed leaching tests are reported. After the presentation of the total concentrations, the Toxicity Characteristics Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP) results from eight different types of waste are compared. The results of additional leaching tests for the three different wastes are presented to demonstrate that several factors, especially pH, influence the release of metals from wastes.

4.1 TOTAL CONCENTRATIONS

A measure of total metal concentrations in waste samples is useful to compare the concentrations from leaching tests for the samples. A total concentration analysis was conducted on three different wastes (abrasive blasting media [ABM], CCA-contaminated soil, and wood ash) in comparison with the results of leaching tests. Total metal concentrations were measured by the U.S. EPA SW-846 acid-soluble methods (3050). In some matrixes, acid-soluble metal concentrations fell short of absolute total concentrations (often measured by instrumental neutron activation analysis).

4.1.1 Abrasive blasting media

Analytical results of total metal concentrations in ABM by Inductively Coupled Plasma (ICP) are presented in Table 4.1. Relatively high concentrations of iron and zinc, followed by copper and chromium, were found in ABM samples.

Table 4.1 Average Heavy Metal Concentrations (dry weight) in ABM in mg/kg

Element	Concentration (standard deviation)
As	6.7
Cd	< 5.0
Cu	414 (67)
Cr	145 (19)
Fe	35,450 (7,630)
Ni	32.6 (7.0)
Pb	67 (4.7)
Zn	731 (219)

4.1.2 Contaminated soil

The mean concentrations of heavy metals (As, Cu, and Cr) determined in CCA-contaminated soil are presented in Table 4.2. The highest heavy metal content of the contaminated soil was arsenic followed by chromium. A relatively small amount of copper was present in the soil.

Table 4.2 Average Heavy Metal Concentrations (dry weight) in Contaminated Soil in mg/kg

Element	Concentration (standard deviation)
As	100 (14.2)
Cr	75.2 (10.4)
Cu	10.4 (1.8)

4.1.3 Wood ash

Analytical results of total metal concentrations by ICP, flame, or furnace are presented in Table 4.3. Concentrations of metals (lead, arsenic, zinc, iron, copper) found above detection limits in the ash samples are presented.

Table 4.3 Heavy Metal Concentrations in Wood Ash in mg/kg

Sample Number	Pb	As	Zn	Fe	Cu
1	200	80.0	45,600	52,600	368
2	175	61.0	44,400	39,200	376
3	195	55.0	49,900	59,800	355
4	232	85.0	52,600	40,900	394
5	227	87.0	47,200	34,100	410
6	192	60.0	47,800	31,900	332
7	178	95.0	44,700	32,200	360
8	163	58.0	40,700	35,100	302
9	211	59.0	58,700	44,800	407
10	237	57.0	59,900	97,600	533
11	192	63.0	53,600	37,800	363
12	154	55.0	38,100	35,300	258
13	170	62.0	44,200	40,800	302
Average	194	67.0	48,300	44,500	366

4.2 SPLP AND TCLP RESULTS

The results of the SPLP and TCLP batch tests for eight different solid wastes are summarized in Table 4.4. TCLP extracted much more lead from the computer circuit boards, cathode ray tube, and fishing weight than SPLP. For the Ni-Cd battery, the cadmium concentrations in TCLP were higher than those in SPLP. The TCLP nickel concentration of the small size battery was higher than the SPLP concentration, whereas the opposite results were found in the large size battery (i.e., D size). Metals (As and Cu) from the mulch samples leached more in TCLP than SPLP.

Table 4.4 Summary of SPLP and TCLP Results (mg/L)

Waste	SPLP							
	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
ABM	< 0.05	< 0.05	< 0.05	0.14	1.01	< 0.05	< 0.05	0.33
Contaminated soil ¹	253	-	24.3	< 5.0	-	-	-	-
Mulch ¹	38.3	-	-	< 5.0	-	-	< 5.0	-
Ni-Cd Battery Type A ²	-	5.5	-	-	-	4.5	-	-
Ni-Cd Battery Type B ³	-	< 0.1	-	-	-	< 0.1	-	-
Fishing Weight	-	-	-	-	-	-	243	-
Cathode Ray Tube	-	-	-	-	-	-	2.18	-
Shredded Cir. Board #1	-	-	-	-	-	-	3.8	-
Shredded Cir. Board #2	-	-	-	-	-	-	1.0	-
Shredded Cir. Board #3	-	-	-	-	-	-	9.9	-
Shredded Cir. Board #4	-	-	-	-	-	-	5.6	-
Ground Cir. Board #1	-	-	-	-	-	-	< 0.1	-
Ground Cir. Board #2	-	-	-	-	-	-	< 0.1	-
Wood Ash ¹	-	-	-	-	-	-	133	-
Waste	TCLP							
	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
ABM	< 0.05	< 0.05	< 0.05	4.66	1.23	< 0.05	0.18	26.6
Contaminated soil ¹	867	-	19.3	< 5.0	-	-	-	-
Mulch ¹	58.9	-	-	22	-	-	< 5.0	-
Ni-Cd Battery Type A ²	-	244	-	-	-	0.8	-	-
Ni-Cd Battery Type B ³	-	229	-	-	-	33.4	-	-
Fishing Weight	-	-	-	-	-	-	933	-
Cathode Ray Tube	-	-	-	-	-	-	413	-
Shredded Cir. Board #1	-	-	-	-	-	-	175	-
Shredded Cir. Board #2	-	-	-	-	-	-	193	-
Shredded Cir. Board #3	-	-	-	-	-	-	205	-
Shredded Cir. Board #4	-	-	-	-	-	-	157	-
Ground Cir. Board #1	-	-	-	-	-	-	641	-
Ground Cir. Board #2	-	-	-	-	-	-	675	-
Wood Ash ¹	-	-	-	-	-	-	77.7	-

¹ Unit: ug/L, ² D size Ni-Cd battery, ³ AA size Ni-Cd battery

The concentrations of copper and zinc leached from ABM using the TCLP test were much greater than those from the SPLP test. Iron leached from TCLP (1.23 mg/L) was close to the iron concentration of SPLP (1.01 mg/L). No arsenic, cadmium, chromium, and nickel leached in both leaching tests. The concentration of arsenic leached from the CCA-contaminated soil using the TCLP was greater than that using the SPLP. Chromium leached from TCLP (19.3 $\mu\text{g/L}$) was not much different from the SPLP concentration (24.3 $\mu\text{g/L}$). Copper never leached in both batch tests. The SPLP lead concentration of the wood ash was higher than the TCLP concentration, partly because the final pH of the SPLP wood ash was higher than the TCLP final pH.

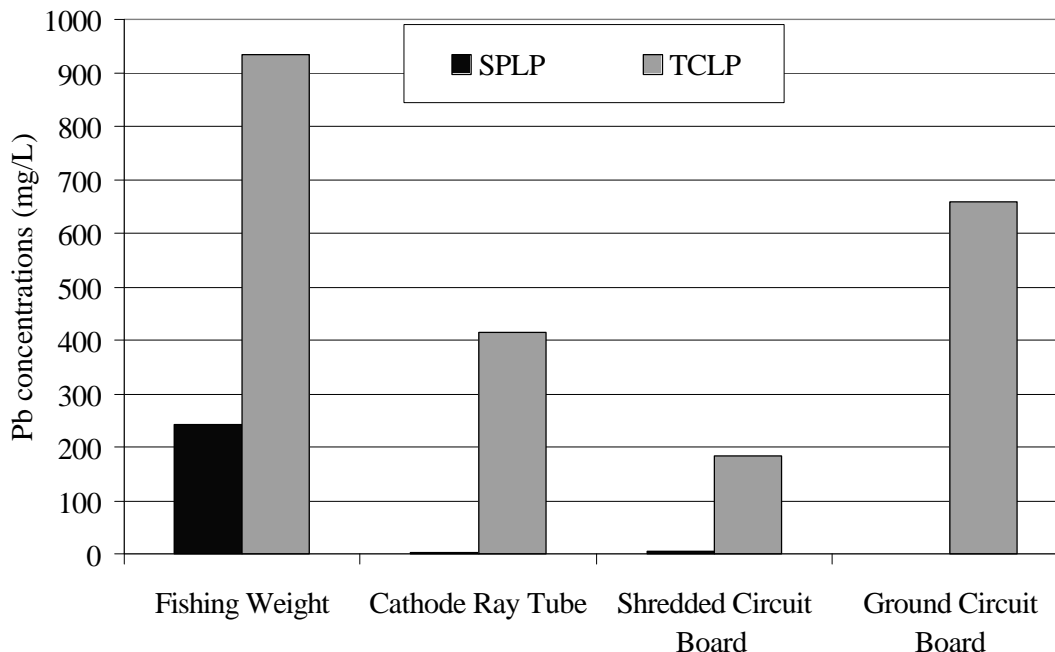


Figure 4.1 SPLP and TCLP lead results of fishing weight, cathode ray tube, and circuit board

The lead results of the SPLP and TCLP extractions of fishing weight, cathode ray tube, and circuit board are presented in Figure 4.1. The pH value of the TCLP extraction fluid typically did not vary significantly from the initial pH value of TCLP, whereas the SPLP final pH value was higher than the initial pH of SPLP (data not shown). TCLP was buffered at $\text{pH } 4.93 \pm 0.05$ and contained the monodentate ligand acetate. The SPLP extraction fluid was not buffered at $\text{pH } 4.20 \pm 0.05$ and contained nitrate and sulfate. In most cases, TCLP extracted more metals from the wastes evaluated than SPLP. The higher metal concentrations in TCLP can be explained by the affinity of acetate ion for the metal complexation. The use of SPLP resulted in the neutralization of the acid during waste mixing and, as a result, minimized the release of metals. Most metals are known to leach less into the aqueous phase under neutral pH conditions. Figure 4.2 presents the lead results of the SPLP and the TCLP for the wood ash samples (8 truckloads). In all samples, SPLP extracted more lead than TCLP. For arsenic leaching, TCLP extracted more arsenic from the contaminated soil and mulch samples than SPLP (Figure 4.3).

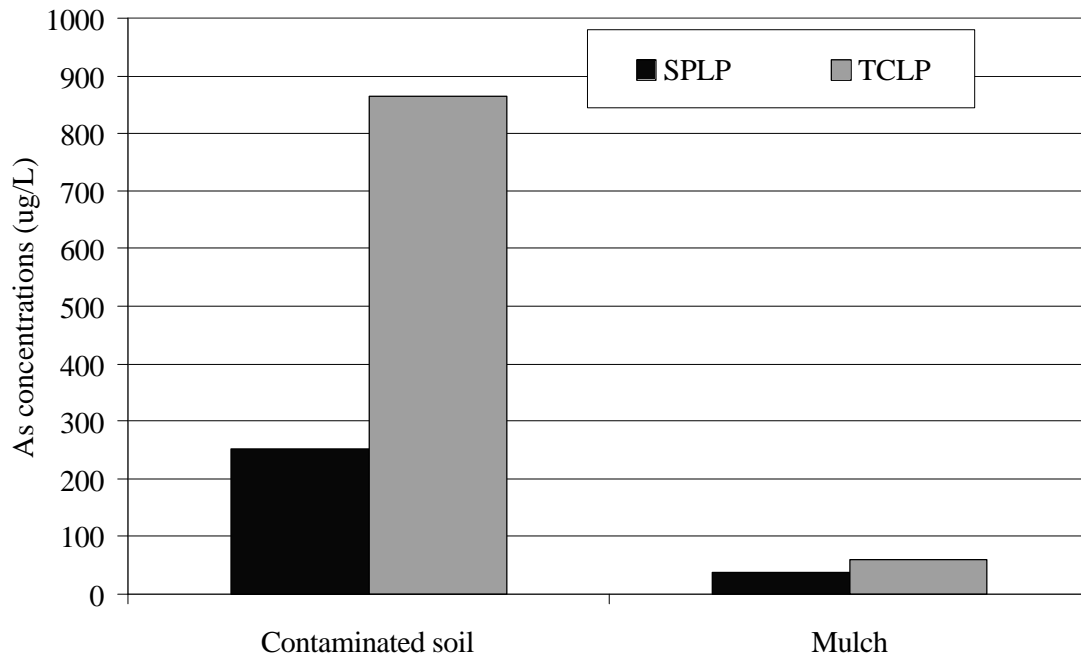


Figure 4.2 SPLP and TCLP lead results of wood ash

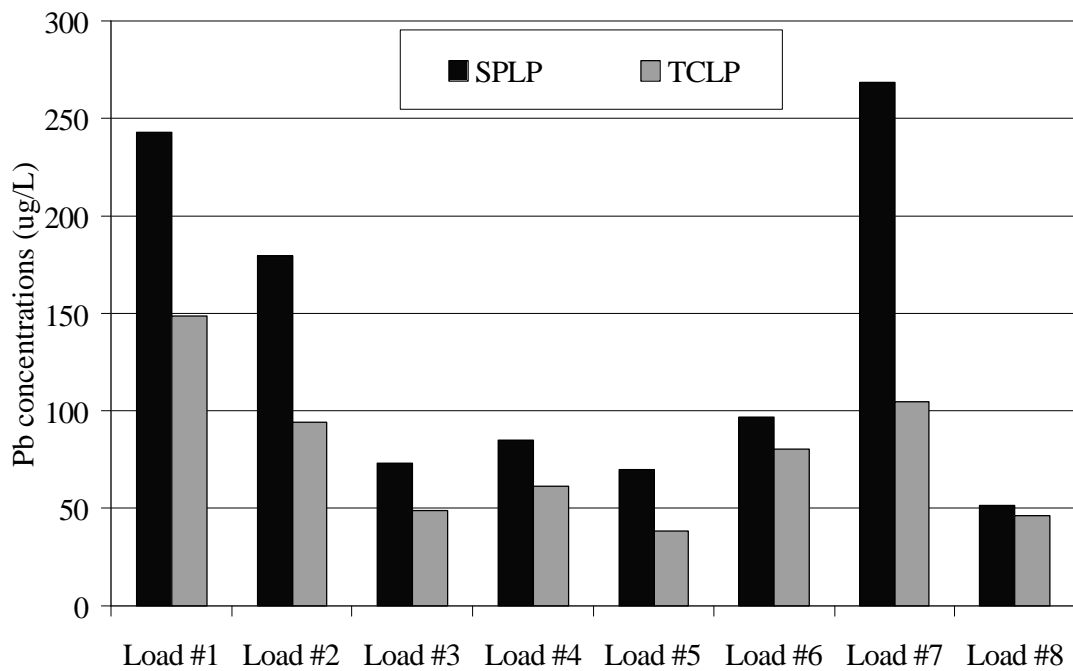


Figure 4.3 SPLP and TCLP arsenic results of contaminated soil and mulch

Table 4.5 shows the percentage leaching of the metals from both leaching tests, comparing the total metal content in ABM. The percentage of metal extracted from ABM averaged less than 1% of iron, and 1.0% of copper, and 1.1% of zinc using the SPLP extraction procedure. For the TCLP leaching test, high leaching percentage of zinc (92.1%) was observed followed by copper (28.5%) and lead (6.9%). No arsenic, cadmium, chromium, and nickel leached in both leaching tests.

Table 4.5 Percent Leaching of Metal Extracted from ABM Using SPLP and TCLP

Element	SPLP		TCLP	
	Ave. Leaching Concentration (mg/kg of dry weight)	% Leaching	Leaching Concentration (mg/kg of dry weight)	% Leaching
As	< 1.3	-	< 1.3	-
Cd	< 1.3	-	< 1.3	-
Cu	4.5	1.0 (0.6) ¹	118	28.5 (0.6)
Cr	< 1.3	-	< 1.3	-
Fe	25.6	< 1.0	31.2	< 1.0
Ni	< 1.3	-	< 1.3	-
Pb	< 1.3	-	4.6	6.9 (3.9)
Zn	8.4	1.1 (0.5)	673	92.1 (6.7)

¹ The value in parenthesis is standard deviation.

Table 4.6 compares the percent leaching of metal extracted from the contaminated soil using the SPLP and TCLP tests. The percentage of metal extracted from the soil averaged less than 1% of chromium and copper and 6.5% of arsenic using the SPLP extraction procedure. For the TCLP leaching test, the percent leaching of chromium and copper was also less than 1%, but higher leaching percentage of arsenic (22.2%) was observed. These results suggest that most chromium and copper were bound to the resistant sites and would not be expected to leach readily, whereas arsenic resulted in high leachability from the soil using the TCLP extraction procedure.

Table 4.6 Percent Leaching of Metal Extracted from Contaminated Soil

Element	SPLP		TCLP	
	Ave. Leaching Concentration (mg/kg of dry weight)	% Leaching (standard deviation)	Leaching Concentration (mg/kg of dry weight)	% Leaching (standard deviation)
As	6.5	6.5 (1.1)	22.2	22.2 (2.6)
Cr	0.62	< 0.1	0.5	< 0.1
Cu	< 0.13	< 0.1	< 0.13	< 0.1

4.3 LEACHING TIME

Leaching time is a factor influencing metal concentration in a batch extraction test. A leaching time study was conducted as described earlier. The batch extraction process of the CCA-

contaminated soil and ABM was carried out by shaking the mixture for different periods of time ranging from 30 minutes to 30 days. Figures 4.4 and 4.5 represent the change of arsenic and chromium concentrations in CCA-contaminated soils as a function of leaching time. Arsenic increased from approximately 170 $\mu\text{g/L}$ to 510 $\mu\text{g/L}$, while the range of chromium was from approximately 20 $\mu\text{g/L}$ to 130 $\mu\text{g/L}$.

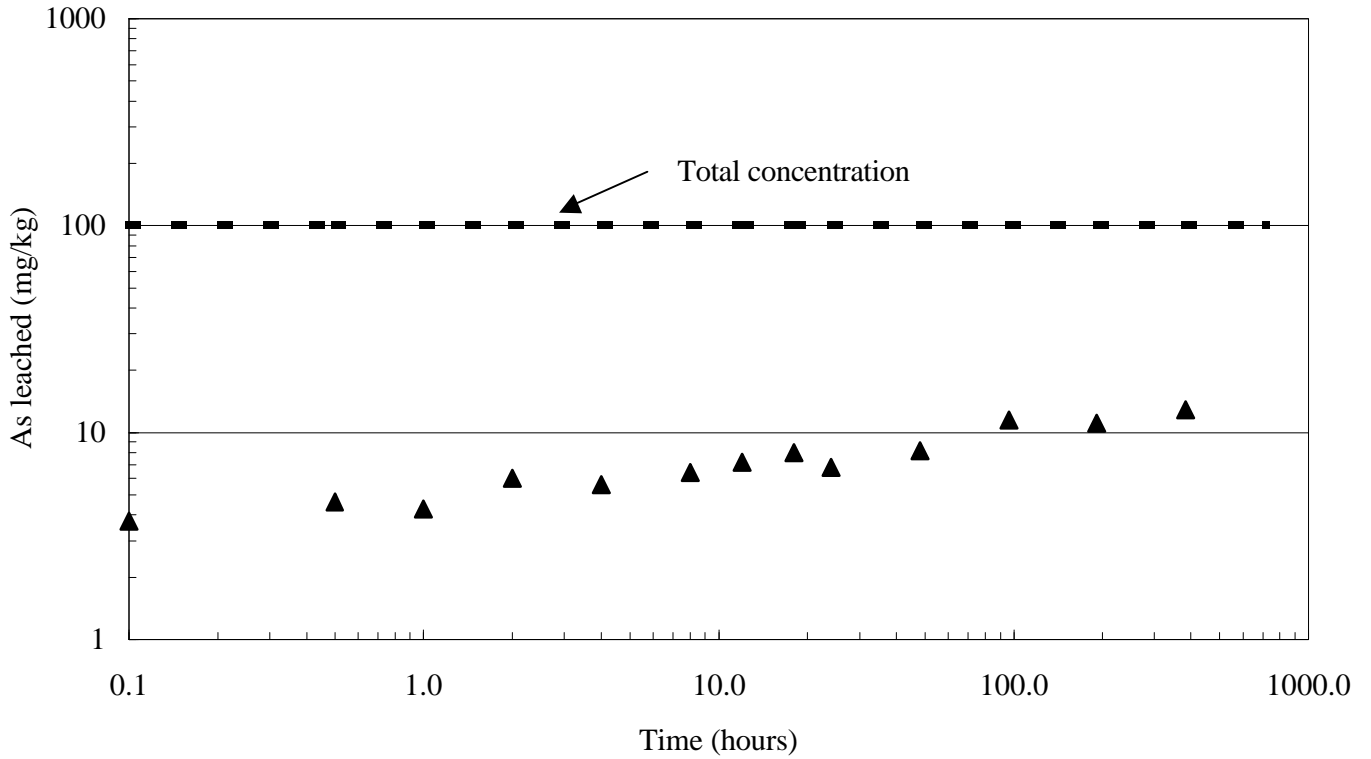


Figure 4.4 Arsenic leaching of CCA-contaminated soil as a function of time

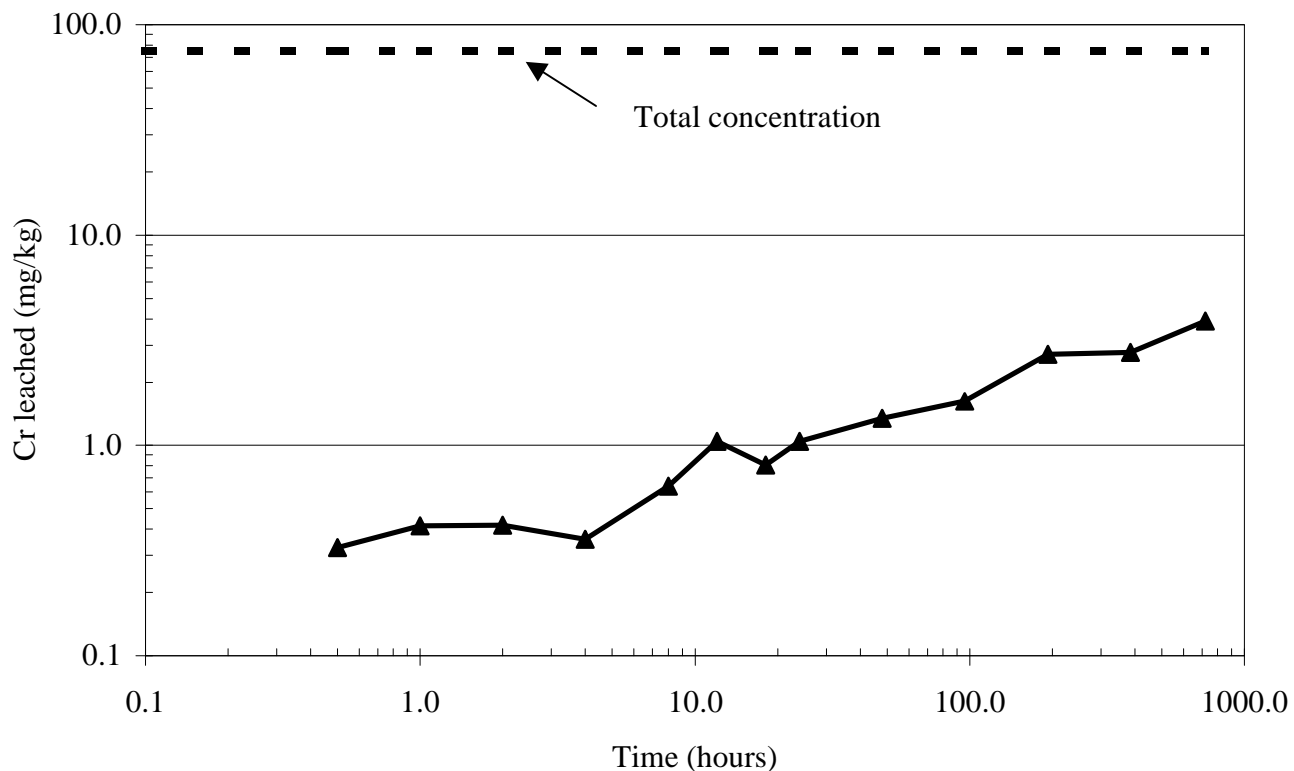


Figure 4.5 Chromium leaching of CCA-contaminated soil as a function of time

The interval and range of leaching time was the same as the contaminated soil time study described previously. The results of three metals (Cu, Zn and Fe) are presented in Figures 4.6 through 4.8. All three metals increased slightly as a function of time, while other target metals (As, Pb, Cd, Ni, and Cr) did not constantly leach into the SPLP extraction fluid above the detection limit of 0.05 mg/L).

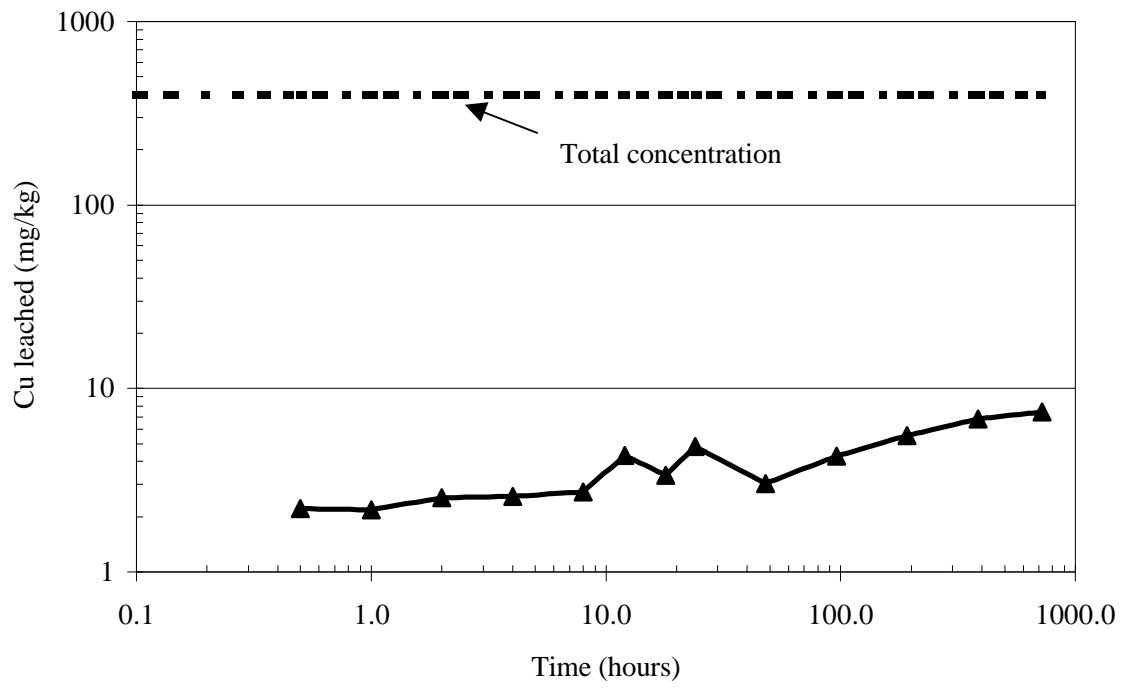


Figure 4.6 Copper leaching of ABM as a function of leaching time

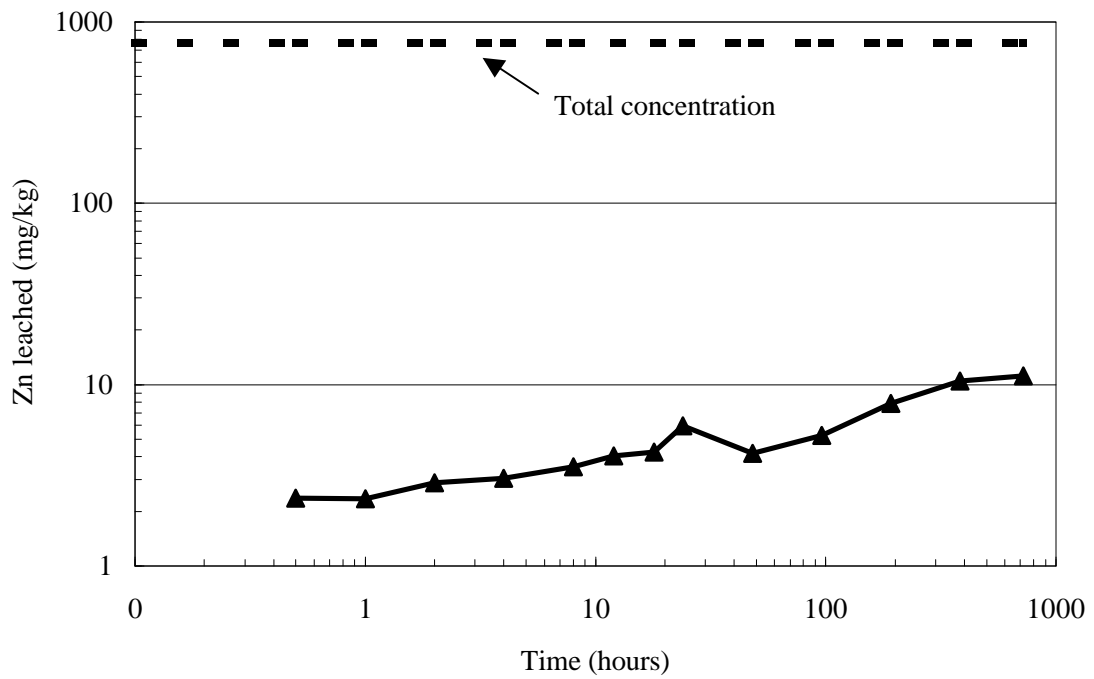


Figure 4.7 Zinc leaching of ABM as a function of leaching time

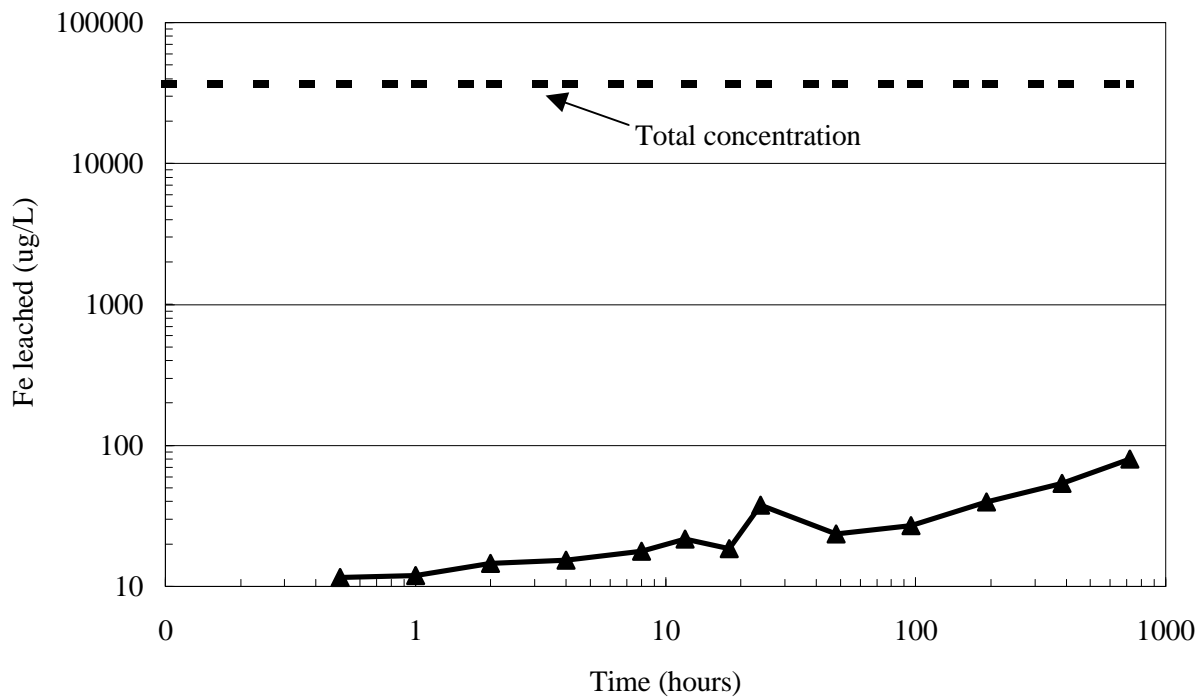


Figure 4.8 Iron leaching of ABM as a function of leaching time

The lead result of the leaching time study on the wood ash samples is presented in Figure 4.9. As shown in the graph, the kinetic equilibrium is reached after 4 hours of contact time. The result indicates that contact time does not play a vital role in the SPLP tests.

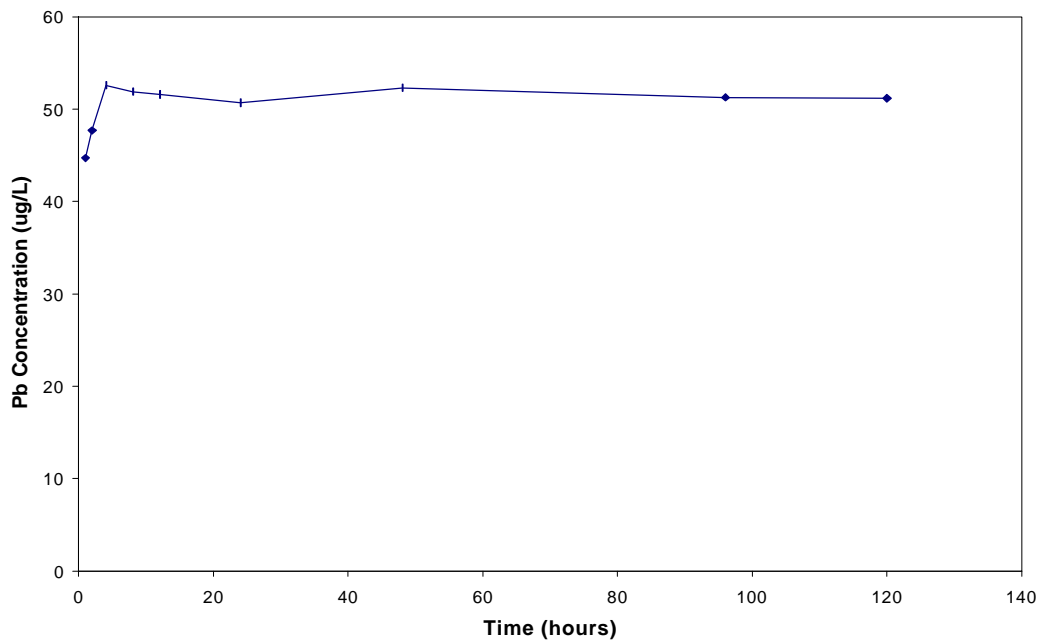


Figure 4.9 Lead leaching of wood ash as a function of leaching time

4.4 LIQUID TO SOLID (L/S) RATIO

In Figure 4.10 and 4.11, the results of batch leaching tests performed on the CCA-contaminated soil are presented in terms of metal concentrations ($\mu\text{g/L}$) as a function of L/S for arsenic and copper. At an L/S ratio of less than 20, arsenic and chromium concentrations did not vary distinctively, whereas the metals at the greater L/S ratios leached much less into the aqueous phase. Copper did not leach from the soil at an L/S ratio of greater than 5.

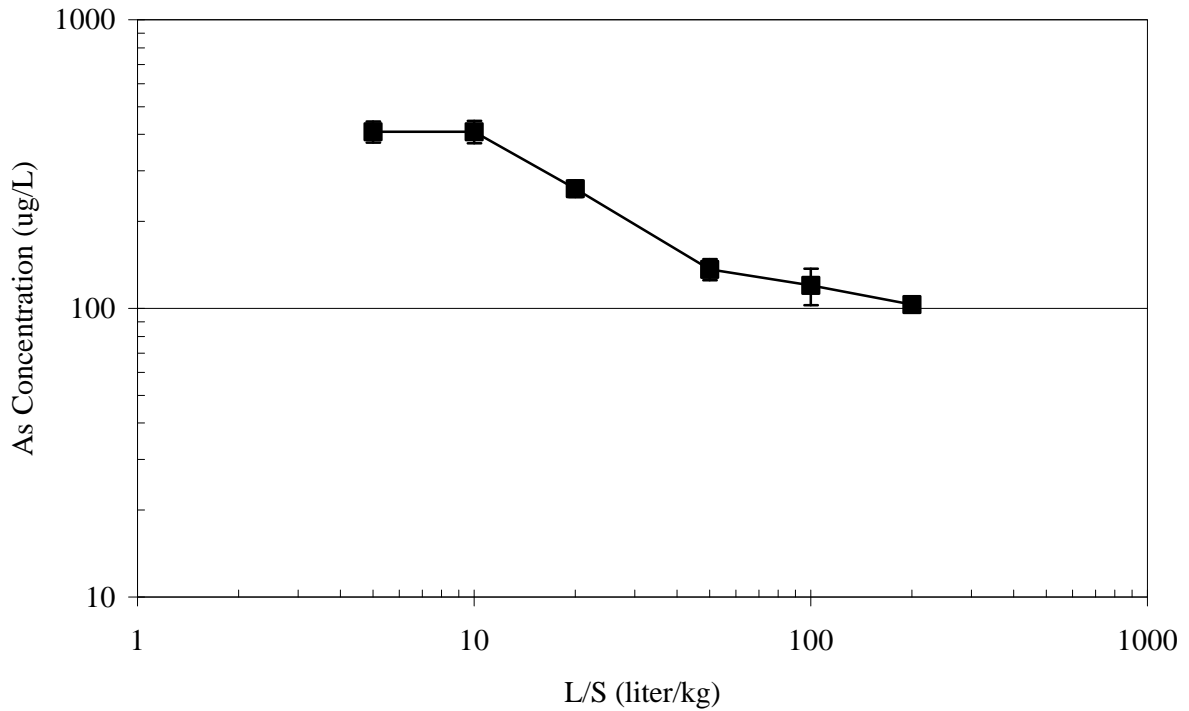


Figure 4.10 Arsenic leaching of contaminated soil as a function of L/S Ratio

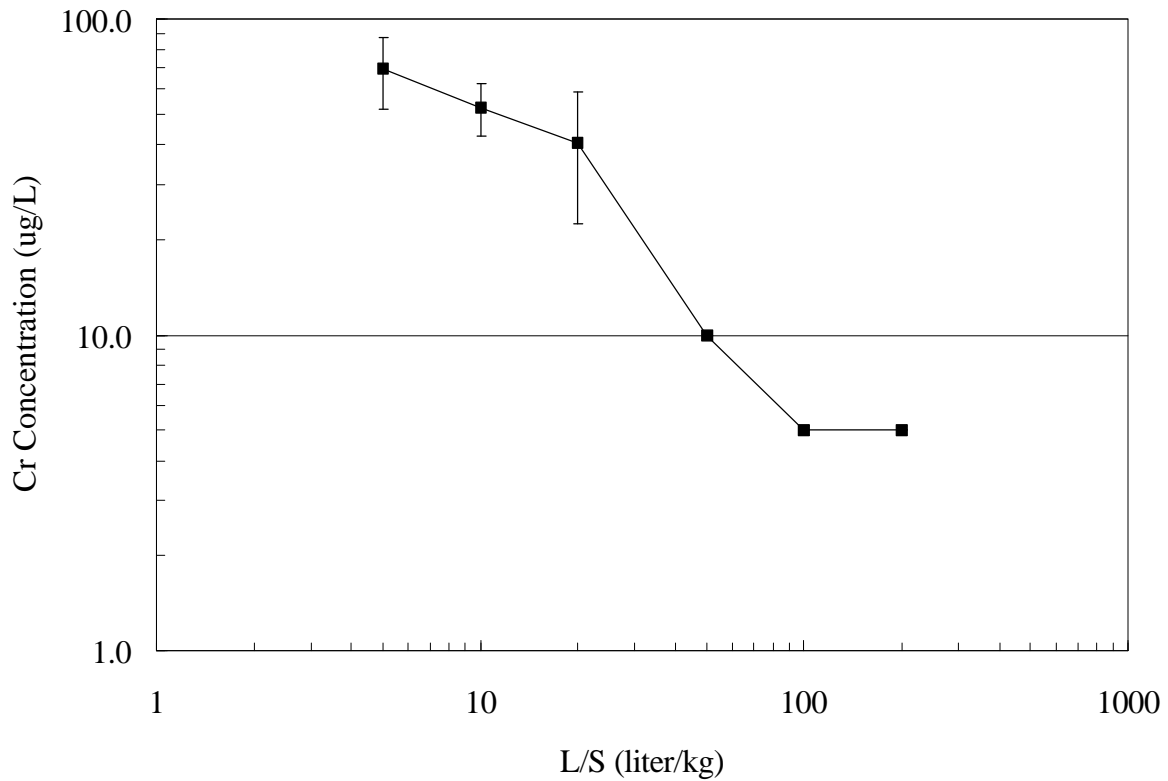


Figure 4.11 Chromium leaching of contaminated soil as a function of L/S Ratio

The results of the SPLP batch test performed on ABM are presented in terms of metal concentrations (ug/L) as a function of L/S for copper, iron, and zinc (Figure 4.12 through 4.14). In general, as the L/S ratio decreased, the higher concentrations of the metals were observed with an exception of an L/S ratio of 5. Since the L/S ratio decreased, more metals present in the ABM samples could have leached into the solution. Other metals (e.g., As, Cd, Cr, Ni, and Pb) did not leach in the range of the L/S ratio selected.

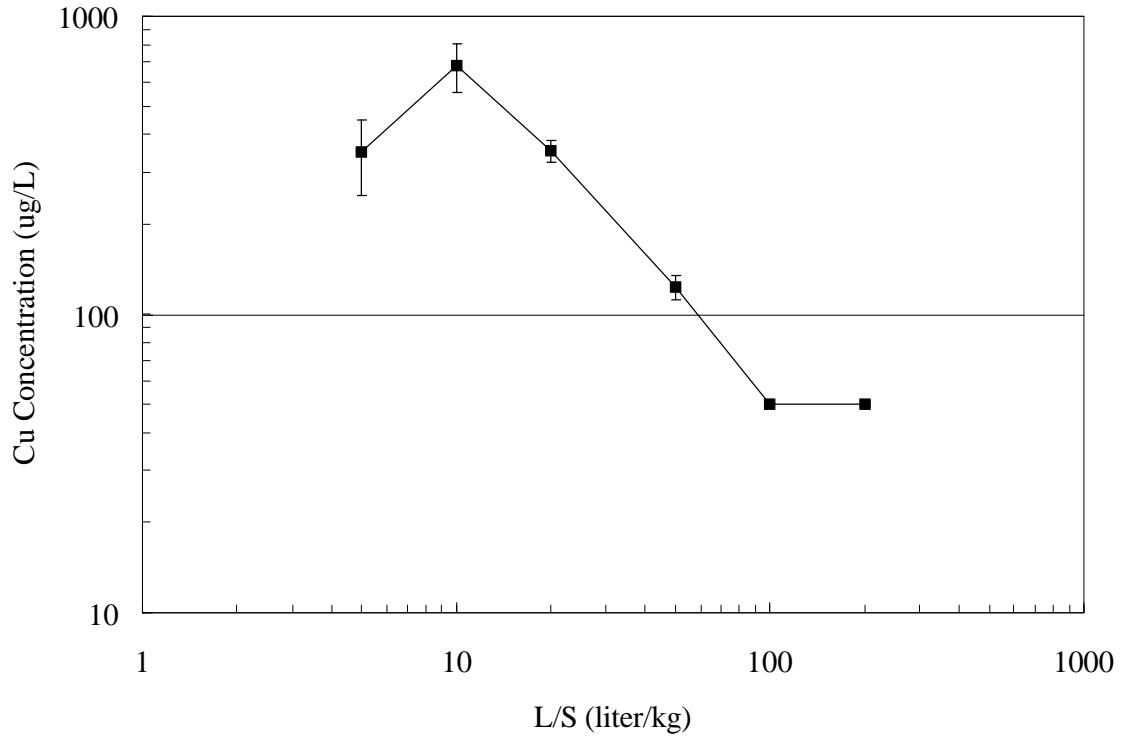


Figure 4.12 Copper leaching of ABM as a function of L/S Ratio

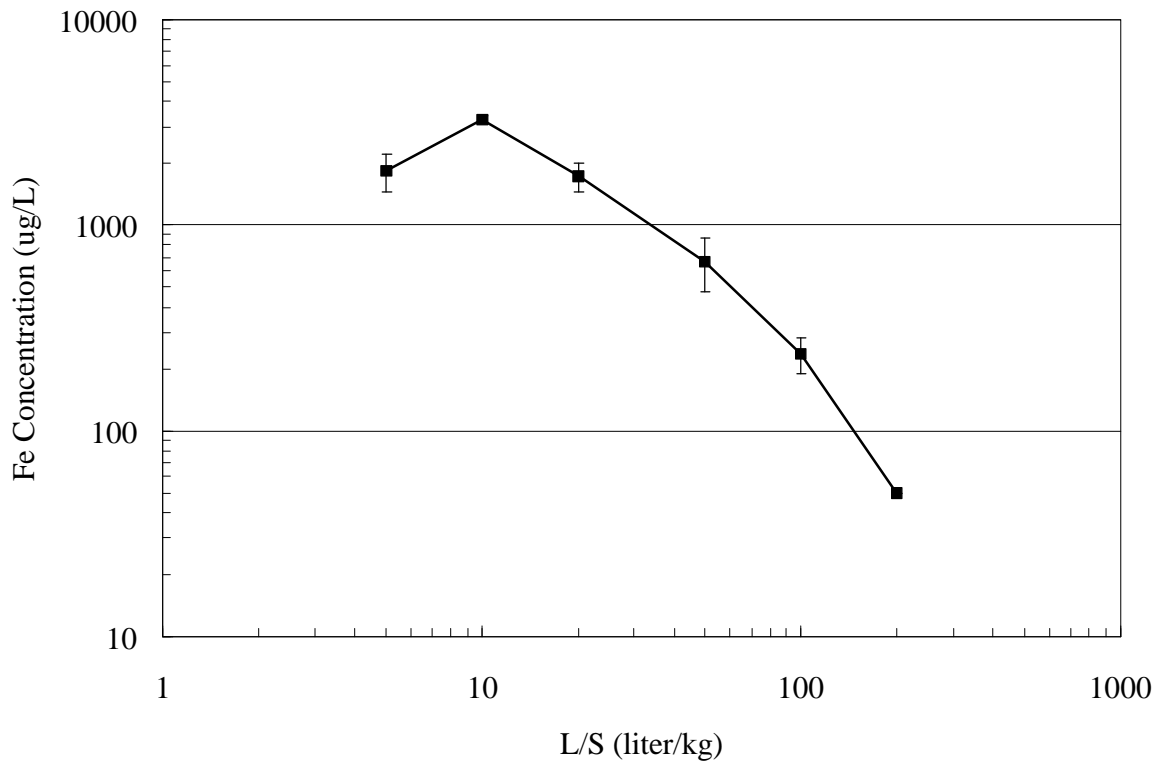


Figure 4.13 Iron leaching of ABM as a function of L/S Ratio

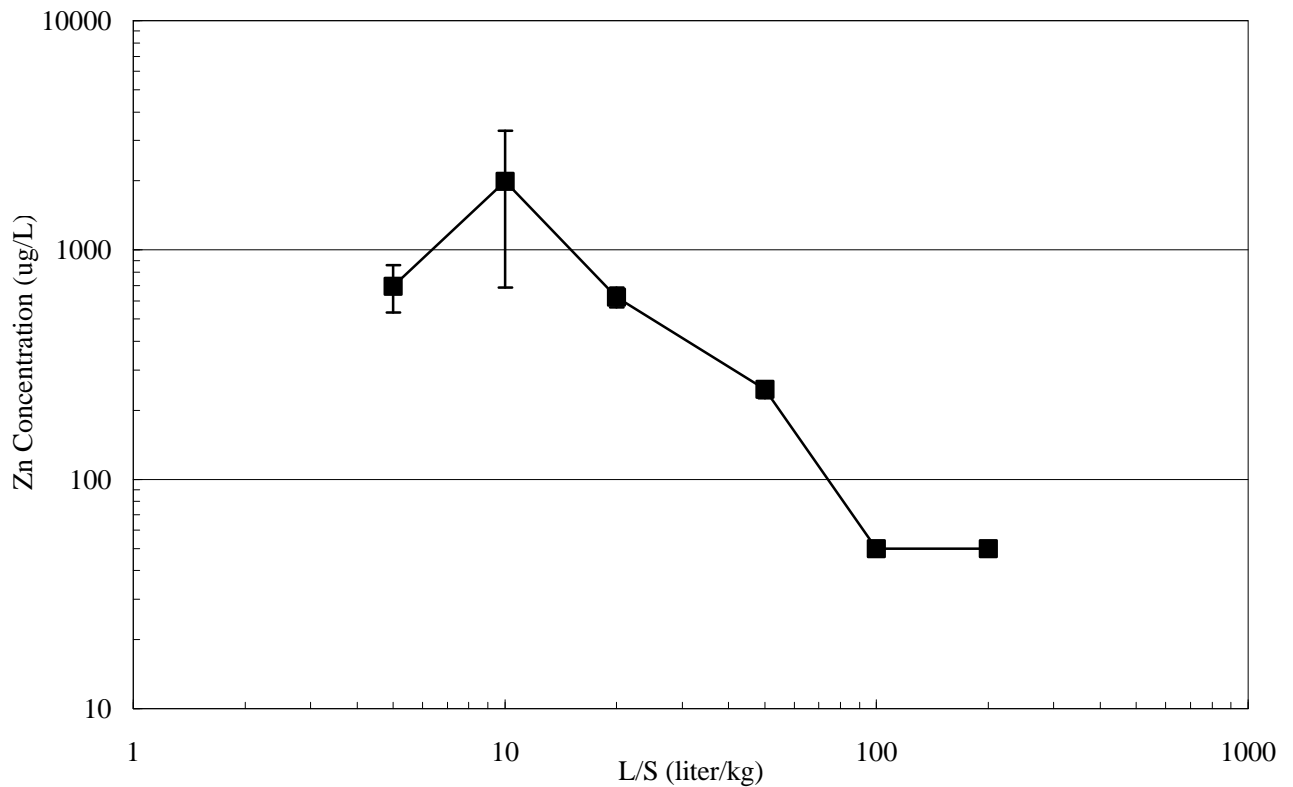


Figure 4.14 Zinc leaching of ABM as a function of L/S ratio

4.5 pH STATIC

One of the significant factors influencing the release of metals from waste materials is pH, which has been shown to be a crucial parameter in determining the solubility of metal. The results of the pH static tests for the CCA-contaminated soil are presented in Figure 4.15, 4.16, and 4.17 for arsenic, chromium, and copper, respectively. All three metals showed strong pH dependence of leaching. In general, the metals exhibited a marked increase in solubility at both low and high pH values, and relatively low leachability of the metals extracted from the contaminated soil was found at neutral pH values. At pH static 2, the arsenic concentration was close to the total concentration of arsenic present in the CCA-contaminated soil.

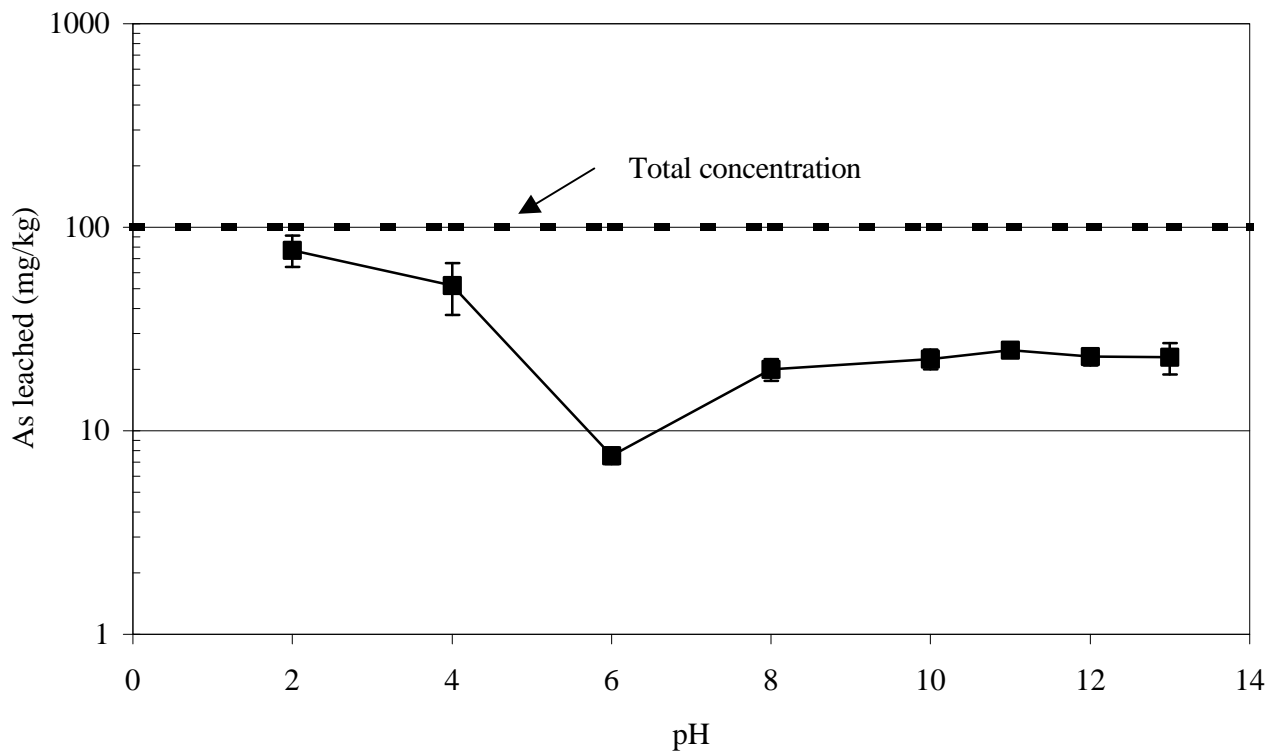


Figure 4.15 Arsenic leaching of CCA-contaminated soil as a function of pH

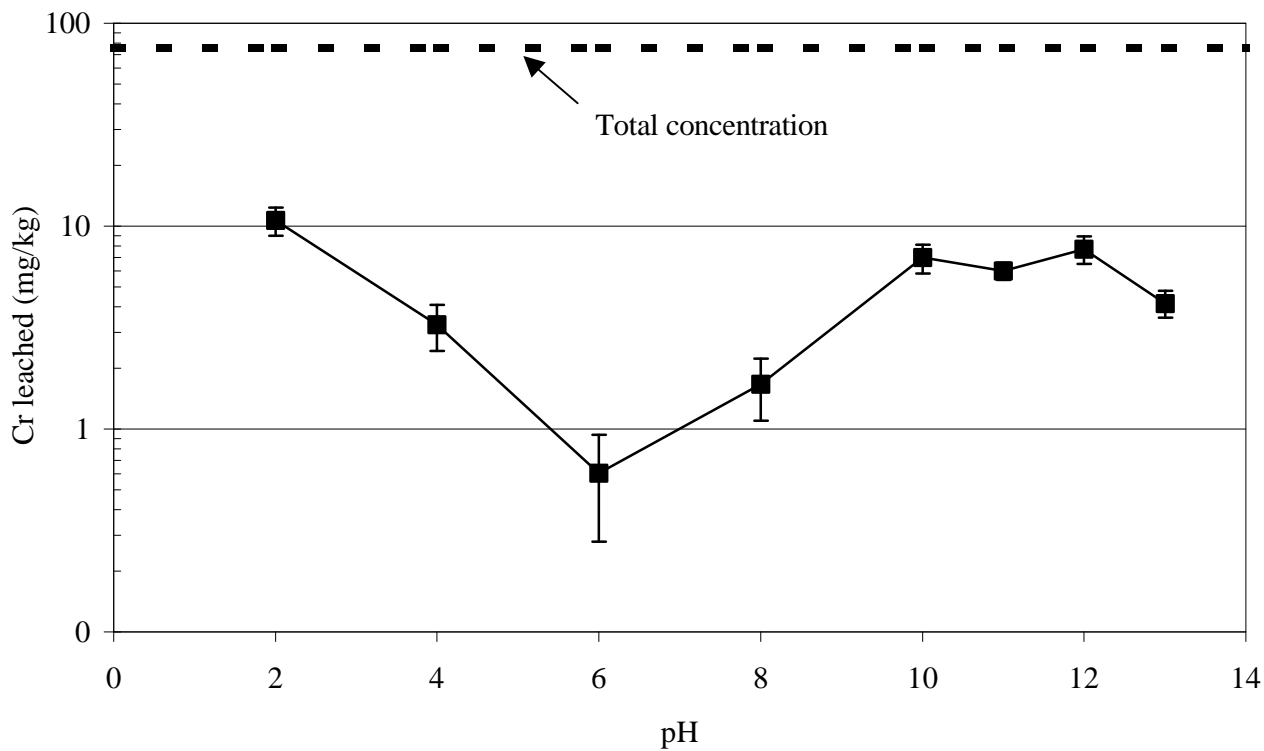


Figure 4.16 Chromium leaching of CCA-contaminated soil as a function of pH

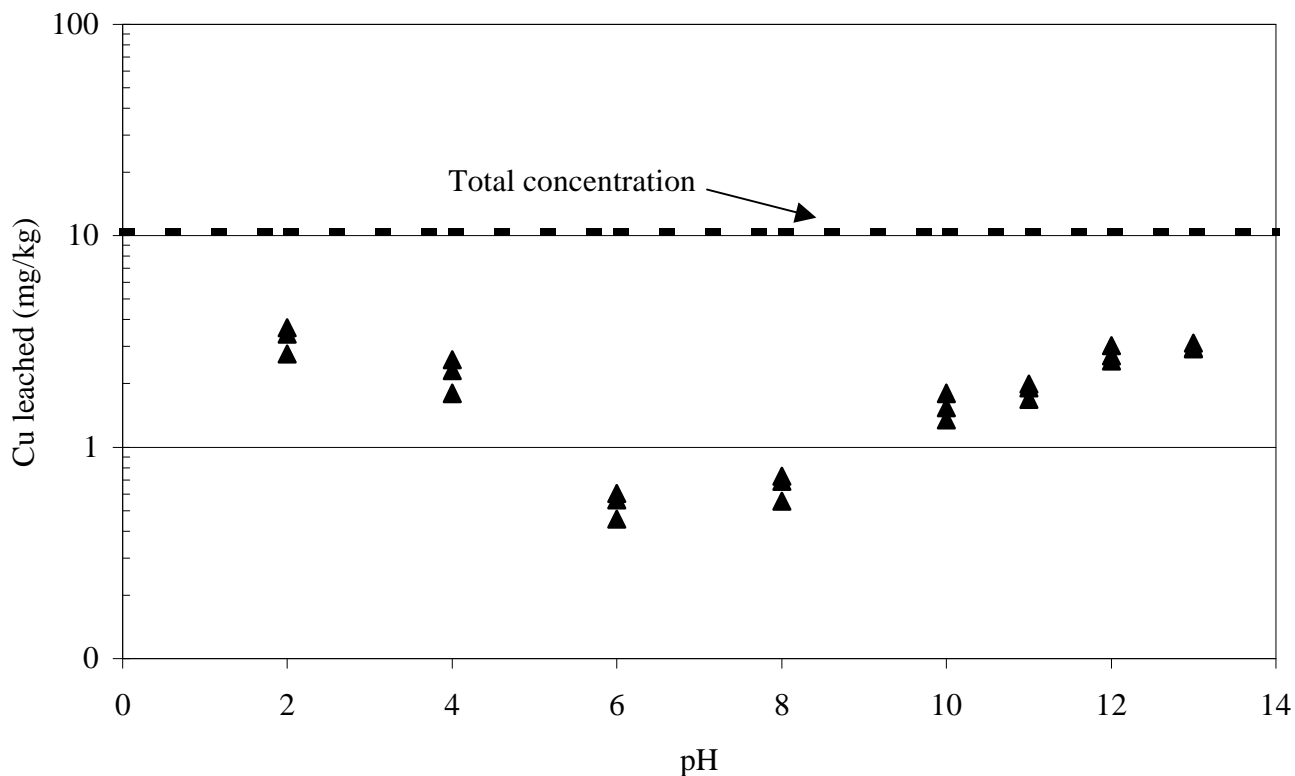


Figure 4.17 Copper leaching of CCA-contaminated soil as a function of pH

The results of the pH static tests of ABM samples are presented in Figure 4.18 through 4.21. In general, all metals leached more into the extracts at low pH values (less than pH 7) than at neutral and high pH values. As pH value increased, the metal concentrations in the extracts of pH static tests either increased slightly (As and Cu) or remained relatively constant (Fe, Zn, and Pb). Arsenic, chromium (figure not shown), and lead leached into the extracts during pH static tests, although they never leached during the other tests (e.g., SPLP, TCLP, L/S ratio tests). This indicates that the pH static test for arsenic and lead in ABM was aggressive compared to the other types of the batch leaching tests. At the pH 2 static test, the concentrations of copper and zinc were close to the total content (digested by acid-soluble method), indicating that the pH 2 static test is as almost aggressive as the total digestion technique.

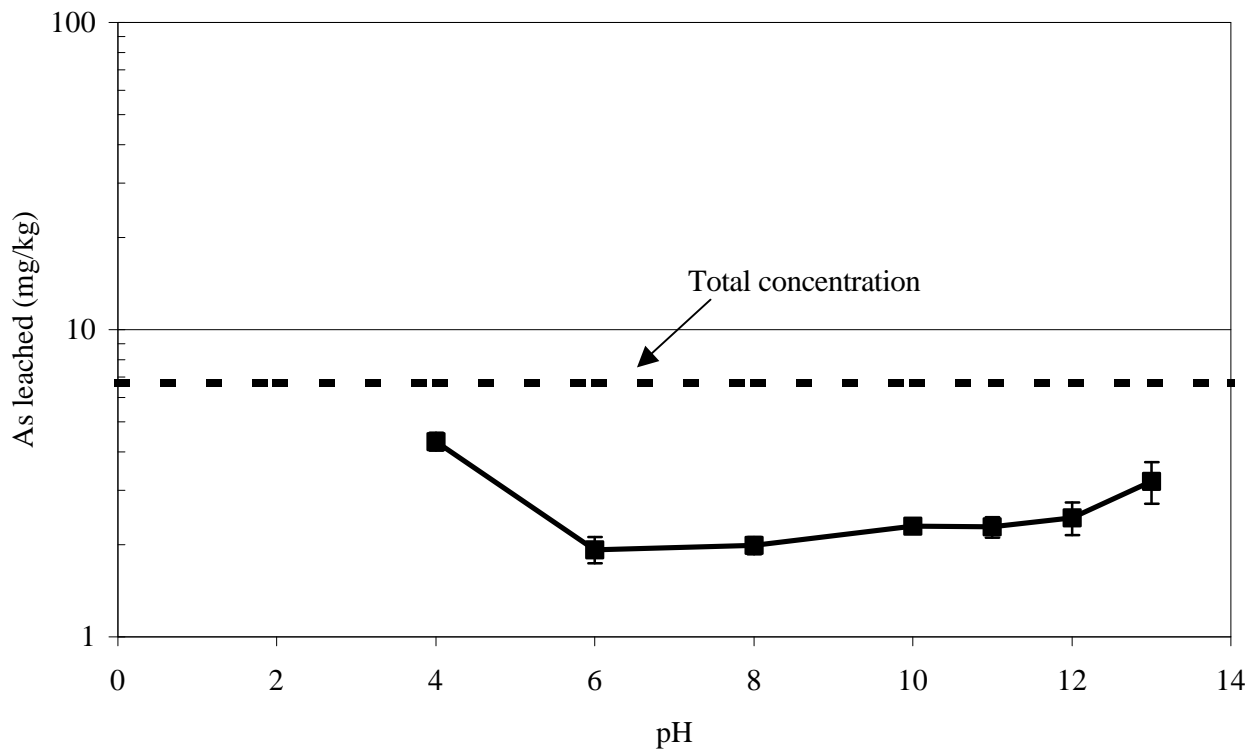


Figure 4.18 pH static test results of arsenic in ABM Figure

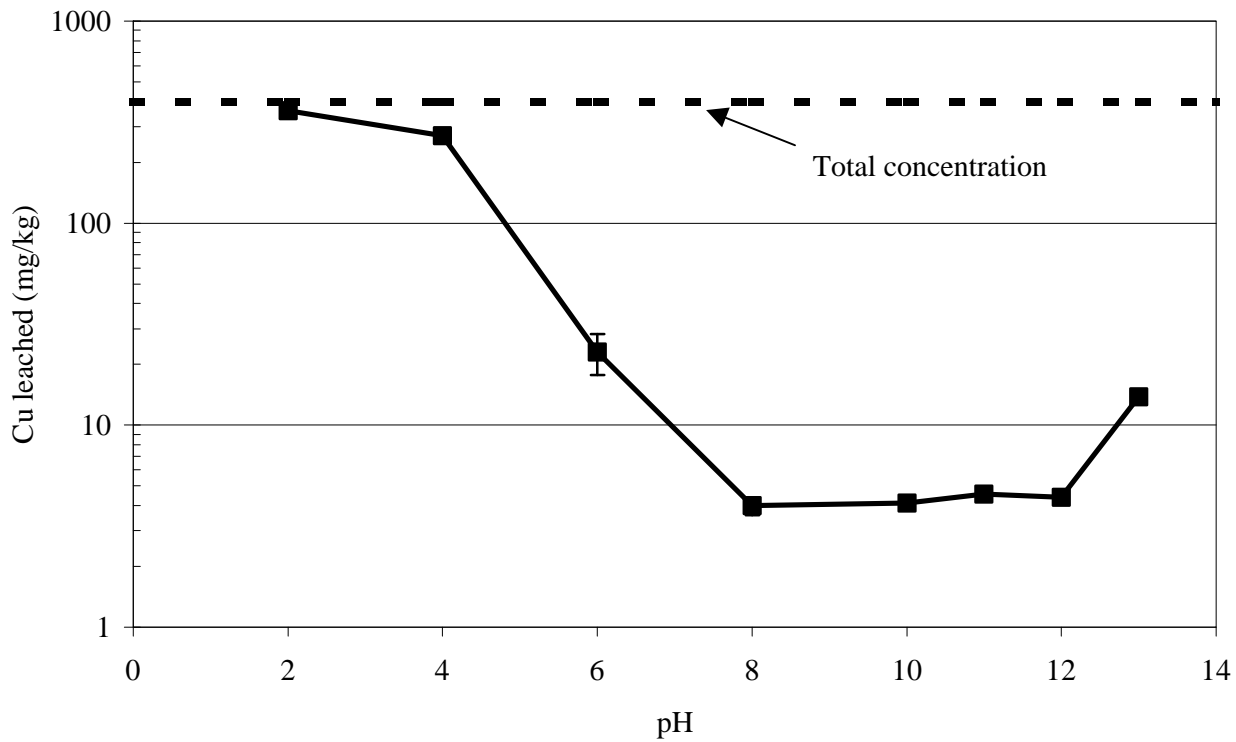


Figure 4.19 pH static test results of copper in ABM

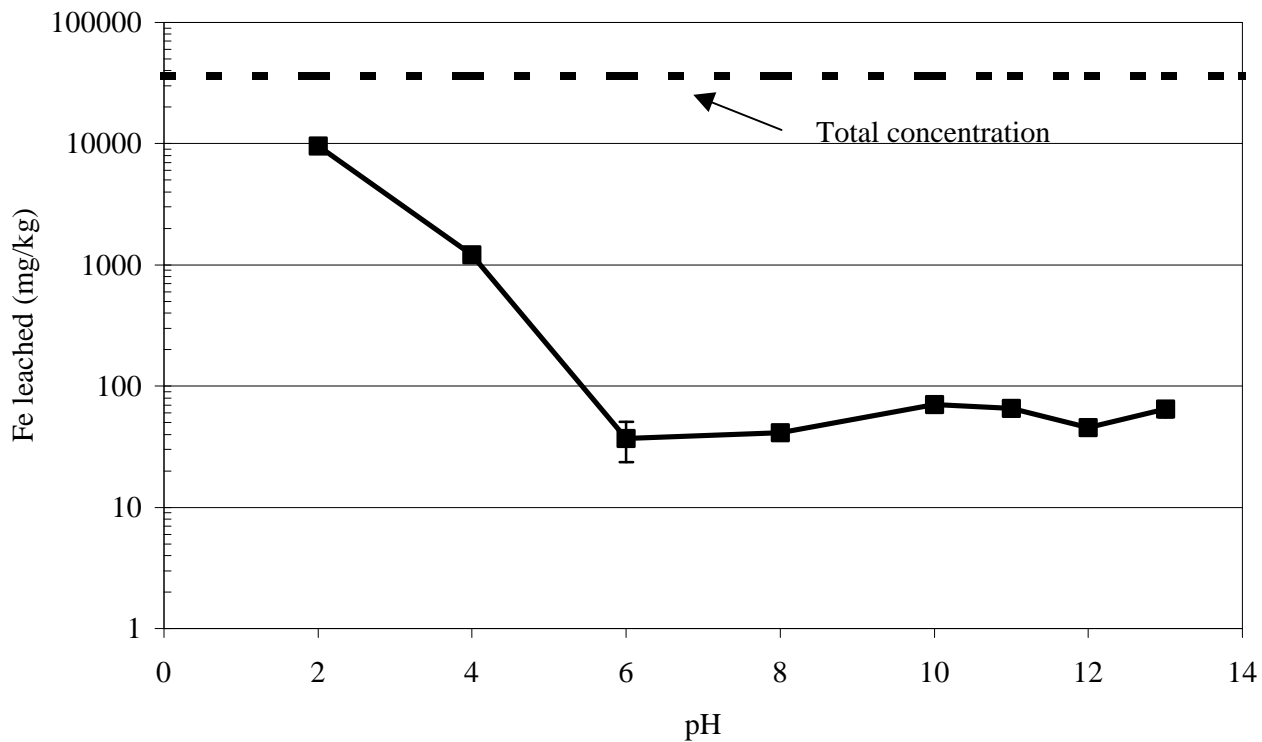


Figure 4.20 pH static test results of iron in ABM

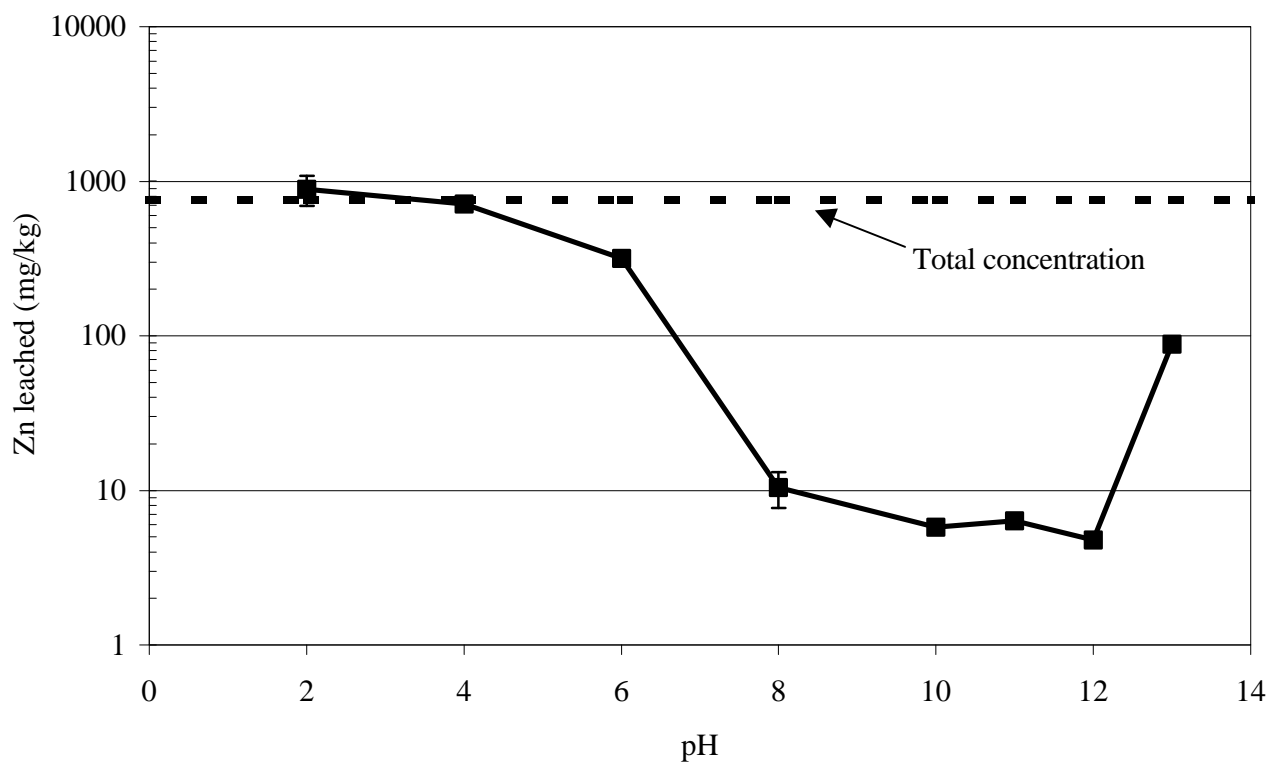


Figure 4.21 pH static test results of zinc in ABM

In pH static tests for wood and tire ash, only lead results are presented in Figure 4.22. As shown in Figure 4.22, lead leached most at lower pH values, while the lowest lead leaching occurred at neutral pH values. The pH static test supports the previous hypothesis that the difference in pH is the reason that TCLP extracted less Pb than the SPLP. The difference of the final extraction pH between TCLP and SPLP was 0.5 pH unit. At high pH values, a slight increase resulted in high levels of lead concentrations.

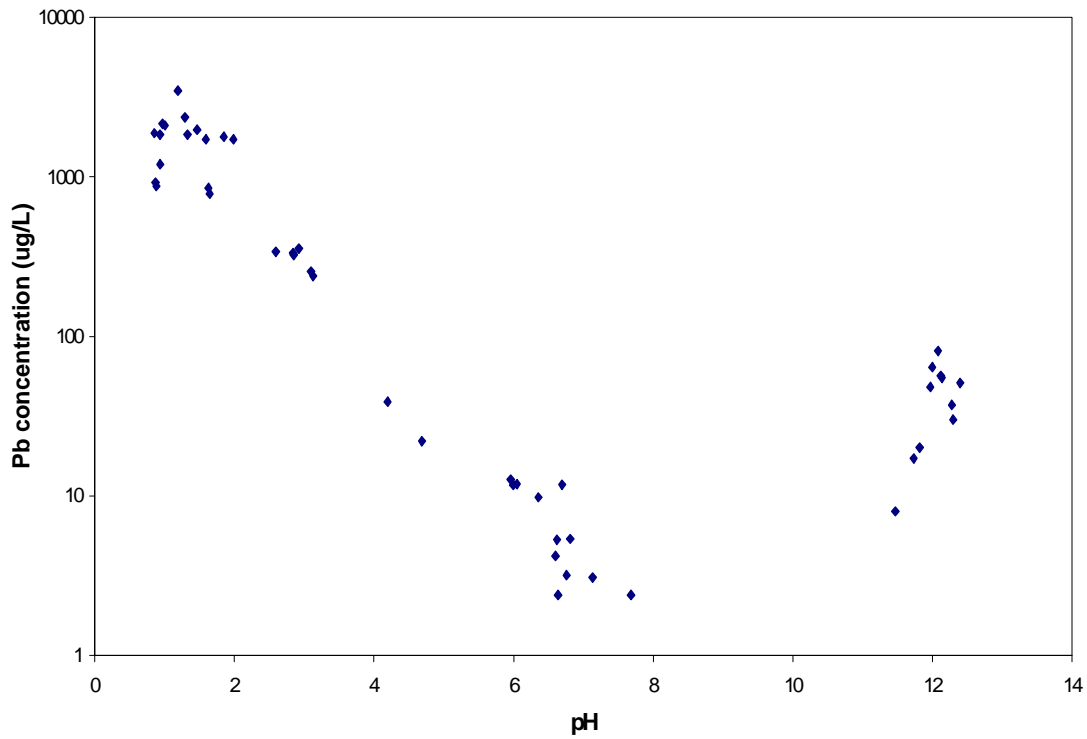


Figure 4.22 pH static test results for lead in wood/tire ash

5.0 SUMMARY

This report is an annual report of activities on a two-year study examining leaching tests for evaluating risk in solid waste management decision making. This report presented preliminary results. The final project report will present the complete set of results and interpretation along with conclusions. The first year of research consisted of collecting different types of solid wastes to perform leachability tests on. The total recoverable metal content of every sample was found as well as every sample was leached using the Toxicity Characteristics Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP). Additional leachability tests were performed on three specific waste samples: spent abrasive blasting media, CCA-contaminated soils, and wood and tire ash. The additional leaching tests performed included experiments to evaluate the role of leaching time, pH, and liquid-to-solid ratio (L/S ratio). The wood and tire ash sample was leached using laboratory leaching columns and field leaching vaults to simulate actual leaching in a beneficial reuse scenario. Research continues; however, preliminary results indicate that in most cases heavy metals leached less under SPLP than TCLP. This was not universally true and the bulk of the interpretation of this data (along with the second year of data) will be presented in the final project report.

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