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CHEMICAL SPECIATION AND FLYASH STABILIZATION OF ARSENIC, BARIUM, CHROMIUM, AND LEAD IN DRILLING FLUID WASTES

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CHEMICAL SPECIATION AND FLYASH STABILIZATION OF ARSENIC, BARIUM, CHROMIUM, AND LEAD IN DRILLING FLUID WASTES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment for the requirements for the

degree of

DOCTOR OF PHILOSOPHY

By

GEORGE M. DEELEY

Norman, Oklahoma

1984

CHEMICAL SPECIATION AND FLYASH STABILIZATION OF ARSENIC, BARIUM, CHROMIUM, AND LEAD IN DRILLING FLUID WASTES

A DISSERTATION

APPROVED FOR THE SCHOOL OF

CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

By

Larry Canter

Edwin Klehr

Gary D. Miller

Dissertation Committee

ABSTRACT

A laboratory study was conducted to determine the influence of pH and ionic strength on the distribution of arsenic, barium, chromium and lead in three different drilling fluid wastes. Samples were obtained in the field and equilibrated in the laboratory under controlled conditions. A sequential extraction procedure was then used to fractionate the heavy metals into the designated forms of exchangeable, adsorbed, organically bound, carbonate, and residual phases, thus providing insight into the potential availability of the heavy metals for possible release into ground waters and/or surface waters. The majority of each of the metals studied was found in the organically bound, carbonate, or residual forms, with the relative distribution among these forms depending on the pH and type of drilling fluid. Generally, decreasing pH caused a shift from the more stable (residual) form toward less stable (carbonate, organic) forms of the heavy metals. Changes in the ionic strength of the equilibrating solution, by diluting to 0.5 and 0.1 times field strength, had no significant influence on the distribution of the heavy metals within the solid phase. The occurrence of the metals in the more stable organic, carbonate, and residual forms in the waste drilling fluids, coupled with no significant release to the aqueous phase upon varying pH and/or ionic strength, indicated the resistance of these waste metals to remobilization from waste drilling fluids.

Another laboratory study was conducted to determine the behavior of metals within drilling fluid wastes stabilized by the addition of flyash. Drilling fluid wastes were mixed with varying proportions of flyash ranging from 10 to 30 percent. After allowing the mixtures to set for 1 week or 5 weeks, EP Toxicity Extractions were performed and the resultant liquid analyzed for arsenic, barium, chromium, lead, and zinc. The behavior of these elements was not significantly affected in the mixtures, beyond that expected by the physical processes involved. No chemical reactions appear to be taking place which might result in a significant release of metals to the environment. Therefore, with respect to the metals tested, flyash stabilization appears to be an acceptable treatment method for drilling fluid wastes.

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CHAPTER I

INTRODUCTION

Concerns about the environmental fate and effects of toxic metals from drilling fluids (muds) have become pronounced in the last few years. This has been the result of increased drilling activity and the disposal of large volumes of drilling fluids in off-site disposal pits. The issue is a complex one and not easily managed with simple solutions because of the complexity of the chemistry of toxic metals in the environment. Often the basic chemical properties of a metal have been described extensively but little information is available on the actual abundance of different species under varying conditions of pH, oxidation-reduction, and temperature, or the presence of complexing materials or solid surfaces. Such information is essential to truly understand the behavior of a toxic metal under a given set of conditions.

Previous studies have documented the presence of toxic metals in waste drilling fluids (Dames and Moore, 1982; Whitmore, no date; Heitman, 1983; Canter, et al., 1984b). The presence of these toxic metals implicates them as potential ground and surface water pollutants should they escape from their disposal pits in a soluble form. A few studies have explored the mobility of various toxic metals, but all were limited in scope (Campbell and Gray, 1975; Dames and Moore, 1982; and Hulse and Jones, no date). These studies dealt mainly with short-term solubilization of metals under static conditions of pH and ionic strength. Their results generally indicated little metal mobility under the high pH values encountered in drilling muds. This is as would be expected under these conditions.

This study is intended to go one step further by considering the effect of decreased pH and dilution of the liquid phase on the fate of toxic metals. Also, sequential extraction analyses will be performed to categorize the position of the metals within the matrix of the drilling muds. This will give some insight as to the stability of the existing metal species, i.e., are they very close to being released to solution or are they being tightly held within the solid matrix. Previous studies have only examined solubilized metals with no mention of the form of the remaining insoluble portion.

An additional aspect of drilling disposal is the proposed use of flyash to physically stabilize the waste fluid (Musser, 1984). Flyash contains toxic metals of its own as contaminants. While at first appearance this union of wastes appears to be an ideal method of codisposal, the possibility of toxic metal release upon mixing these wastes must be considered.

This study examines the potential for toxic metal release from mixtures of drilling muds and flyash. The two wastes were mixed together at differing proportions for varying times to duplicate what might be encountered in the field. EP Toxicity analyses were performed at the end of each experiment and metals analyzed.

In summary, the following objectives were examined by this study:

a. Determine the effects of pH on the solid phase partitioning of arsenic, barium, chromium and lead in waste drilling fluids.

b. Determine the effects of ionic strength (dilution of liquid phase) on the solid phase partitioning of arsenic, barium, chromium and lead in waste drilling fluids.

c. Relate objectives (a) and (b) to the uptake and release of arsenic, barium, chromium and lead in drilling fluids.

d. Determine the potential for release of arsenic, barium, chromium and lead from mixtures of drilling fluids and flyash.

e. From the data obtained, determine if arsenic, barium, chromium and lead are a primary concern in establishing siting criteria for well drilling fluid pits and codisposal with flyash.

The scope of the study was as follows:

a. Collect field samples of drilling fluid wastes for background analysis and experimental material.

b. For chemical speciation experiments:

    1. Perform leachability experiments in the laboratory under desired conditions of pH and dilution of the liquid phase.

    2. Sequentially extract and analyze the resulting mixtures to determine the partitioning of arsenic, barium, chromium and lead.

    3. Relate the results obtained to the potential for the release of arsenic, barium, chromium and lead to the environment by observing their stability in the solid phase under the tested conditions.

c. For flyash stabilization experiments:

1. Mix the desired proportions of flyash and drilling fluid.
2. After 1 week and 5 weeks, perform EP Toxicity tests on the mixtures and analyze for arsenic, barium, chromium, lead and zinc.
3. From these results, determine if the metals are released, retained, or unchanged in the mixtures relative to EP Toxicity.

The information associated with this study is presented in four chapters in addition to this Introduction chapter. Chapter II contains a review of the literature on drilling fluid wastes; chemistry of arsenic, barium, chromium, and lead; results of previous sequential extraction studies; and stabilization of wastes. Chapter III contains the methods and procedures used in this study. Chapter IV presents the experimental results and their interpretation. Chapter V contains the summary, conclusions, and recommendations of this study. Finally, cited references are included along with appendices.

CHAPTER II

LITERATURE REVIEW

Drilling Fluids -- General Information

Uses

The function of an oil or gas well is to provide a conduit from the petroleum-bearing formation to the surface. To provide this conduit the bore hole is usually drilled by the rotary method. The rotary drilling rig is composed of: (1) machinery to turn the bit, to add sections on the drill pipe as the hole deepens, and to remove the drill pipe and the bit from the hole; and (2) a system for circulating a fluid down through the drill pipe and back to the surface. This fluid or drilling mud removes the particles cut by the bit, cools and lubricates the bit as it cuts, and as the well deepens, controls any pressure that the bit may encounter in its passage through various formations. The fluid also stabilizes the walls of the well bore by lining the hole with an impermeable cake. The drilling fluid also transmits hydraulic horsepower to the bit and holds cuttings in suspension when circulation is interrupted.

Drilling Fluid Makeup

Drilling muds can be classified on the basis of their principal component. These components are (1) water, (2) oil, and (3) gas. Frequently two -- and sometimes all three -- of these fluids are present at the same time, and each contributes to the properties of the drilling fluid. The components and concentrations of three types of drilling muds are given in Table 1 (U.S. Environmental Protection Agency, 1975). The clay-base and polymer muds are water-based muds.

Water was the first drilling fluid to be used and still is the principal component of most drilling fluids. Water-based muds may contain several dissolved substances. These include alkalies, salts, and surfactants; organic polymers in colloidal solution; droplets of emulsified oil; and various insoluble substances (such as barite, clay, and cuttings) in suspension. The mud composition selected for use often depends on the dissolved substances in the most economically available make-up water, or on the soluble or dispersive material in the formations to be drilled.

The basic components of drilling muds include clays to increase viscosity and create a gel; barium sulfate (barite), a weighting agent; and lime and caustic soda to increase the pH and control viscosity (Sittig, 1978). Additional conditioning constituents include polymers, starches, lignitic material, and various other chemicals. The circumstances surrounding the drilling determines the type of water-based drilling fluid that should be used for a given situation. The number of additives, weighting agents, deflocculants and treating chemicals now on the market provide the basis of a trend toward "tailor made" drilling fluids. The annual usage of drilling fluid additives includes 1,400 trade-named additives. Nearly 100,000 tons of common

Table 1: Typical Mud Components and Concentrations (U.S. Environmental Protection Agency, 1975)

COMPONENT	CONCENTRATION, lb/bbl
CLAY-BASE MUD	
Water	200 to 340
Bentonite	15 to 30
Lignite	1 to 6
Lignosulfonate	2 to 10
Sodium Hydroxide	0.5 to 1.5
Barite	0 to 500
POLYMER MUD	
Water	300 to 345
Bentonite	0 to 10
Salt (NaCl, KCl)	10 to 100
Sodium or Potassium Hydroxide	0.1 to 0.3
Polymer (Starch, Polyacrylamide)	0.5 to 5
Bactercide (Paraformaldehyde)	0.1 to 0.5
Barite	0 to 300
OIL MUD	
Diesel Oil	150 to 230
Water	35 to 50
Calcium Chloride	15 to 25
Emulsifier (Soap, Polyamide)	5 to 20
Filtrate Reducer (Amine Lignite)	0 to 10
Gellant (Amine Clay)	2 to 4
Barite	0 to 500

inorganic chemicals are added to drilling muds annually. Table 2 lists common mud additives and their uses (Wright, 1977). The most commonly used drilling muds in Oklahoma are water-based fluids containing bentonite, chromiumlignosulfonates, barite, and salt/or caustic soda. Chemicals used in typical Oklahoma mud systems are shown in Table 3 (Oklahoma Corporation Commission, 1983).

Handling and Disposal

Within recent years a growing practice for disposal of drilling fluids has involved the use of off-site pits. Off-site pits are larger than on-site pits, and they may serve the drilling fluids disposal needs for multiple wells over large geographical areas. The design volume for an off-site pit location is generally a function of land availability and topography, and business-related estimates of drilling fluid volumes likely to be generated within the potential geographical service area.

Every off-site pit, when properly designed, constructed and operated, relies on the atmosphere to concentrate drilling fluids by removal of water vapor through evaporation. The presence of high concentrations of dissolved solids and oil films lowers evaporation rates. Other variables which influence the rate include the air and fluid temperature, relative humidity, and wind speed (Reid, et al., 1974). The evaporation rate for a waste at a specific locale can be approximated by applying a salt correction to freshwater evaporation expressions. Methods of increasing evaporation rates include addition of dyes and the use of spray systems.

Table 2: Drilling Mud Additives and Uses (Wright, 1977)

Usage	Additives
alkalinity, pH control	lime, caustic soda, bicarbonate of soda
bactericides	paraformaldehyde, caustic soda, lime, starch preservatives
calcium removers	caustic soda, soda ash, bicarbonate of soda, polyphosphates
corrosion inhibitors	hydrated lime, amine salts
defoamers	not listed
emulsifiers	modified lignosulfonates, certain surface active agents, anionic, non ionic products
filtrate reducers	bentonite clays, CMC (sodium carboxymethyl cellulose), pre-gelatinized starch
flocculants	salt and/or brine, hydrated lime, gypsum, sodium tetraphosphates
foaming agents	not listed
lost circulation materials	not listed
shale control inhibitors	gypsum, sodium silicate, calcium, lignosulfonates, lime, salt
lubricants	certain oils, graphite powder, soaps
surface active agents	not listed
thinners, dispersants	tannins, various polyphosphates lignite materials
viscosifiers	bentonite, CMC, attapulgite, clays, subbentonites
weighting materials	barite, lead compounds, iron oxides

Table 3: Typical Oklahoma Mud Systems (Oklahoma Corporation Commission, 1983)

Area	Chemicals	Chemical Name
Northeastern Oklahoma	Gel	Bentonite (Clay)
	Caustic Soda	Sodium Hydroxide
	Soda Ash	Sodium Carbonate
	Lignite	Mined Lignite (Coal)
	CLS	Chromiumlignosulfonates
Southeastern Oklahoma	Gel	Bentonite (Clay)
	Caustic Soda	Sodium Hydroxide
	Soda Ash	Sodium Carbonate
	Lignite	Mined Lignite (Coal)
	CLS	Chromiumlignosulfonates
	CMS	Sodium Carboxymethyl Cellulose
	WL-100	Sodium Polyacrylate
	Drispac	Polyanionic Cellulose Polymer
Southwestern Oklahoma	Gel	Bentonite (Clay)
	Bar	Barite
	Caustic Soda	Sodium Hydroxide
	Soda Ash	Sodium Carbonate
	Lignite	Mined Lignite (Coal)
	CLS	Chromiumlignosulfonates
	Drispac	Polyanionic Cellulosic Polymer
	Desco	Modified Tannin
Northwestern Oklahoma	Gel	Bentonite (Clay)
	Salt Gel	Attapulgite (Clay)
	Bar	Barite
	Caustic Soda	Sodium Hydroxide
	Soda Ash	Sodium Carbonate
	Lignite	Mined Lignite (Coal)
	CLS	Chromiumlignosulfonates
	Drispac	Polyanionic Cellulosic Polymer
	Starch	Pregelatinized Starch
	Soltex	Processed Hydrocarbons
	Preservative	Paraformaldehyde
	Lime	Calcium Hydroxide

Off-site pits need to be sited, designed, constructed and operated to minimize their potential for surface and ground water pollution. Off-site pits should be close to productive petroleum-rich areas to be cost-effective, yet they should be located in environmentally-safe areas. For example, a site removed from well-defined drainage basins will minimize the potential for surface water pollution from heavy runoff. Major oil and gas-producing states are viewing brine water evaporation pits with growing disfavor because of their history of faulty location, design and operation. Pits which are improperly located, designed, constructed, and operated may only serve as "seepage" pits; they result in the formation of pockets of pollutants in the underlying strata, and these pollutants can slowly migrate to ground water via leaching and percolation. Off-site pits can be lined (sealed) to minimize bottom seepage. The liner could be formed from the natural sealing properties of the drilling muds, natural clays, or man-made materials. In addition, berms should be constructed to prevent berm seepage, or breakage which results in release to surface waters.

Drilling Fluids -- Pollution Potential

Potential ground water pollutants from off-site disposal pits include any harmful constituents present in the disposed mud as additives or trace contaminants. These would be sodium, sulfate, chloride, arsenic, barium, cadmium, chromium, lead, zinc, and total organic carbon. The transport and fate of these constituents in the subsurface environment may involve several processes (adsorption, microbial degradation, ion exchange, chemical precipitation, particulate transport, and others) and is influenced by several variables, including type of constituent, type of soil, oxidation-reduction conditions, pH, and other environmental factors.

Dames and Moore (1982) concluded that subsurface soils, surface soil and vegetation samples at sites in their study showed elevated levels of heavy metals, sodium and chloride in pits and/or downgradient locations. However, apparent rates of migration are slow, based on the observation that contaminated subsurface layers are found in relatively narrow, shallow bands close to the point of origin.

Whitmore (no date) in a study dealing with land spreading of drilling muds concluded that even at the highest level of drilling mud application studied no heavy metal problems were found. However, the levels of total chromium in the soil increased from approximately 7 to 13 parts per million to 23 to 49 parts per million as a result of the mud application. No leachability tests were performed to determine the availability of the chromium under changing environmental conditions.

Aqueous Portion of Disposal Pits

A summary of the chemical analyses for the aqueous portion of 31 disposal pits is presented in Table 4 (Canter, et al., 1984b). Table 4 also lists discharge water standards set by the Oklahoma Corporation Commission (OCC) for comparison with the data. When comparing the mean values with the OCC discharge standards, the data reveal high pH values, conductivity, chloride, chemical oxygen demand (COD), total dissolved solid (TDS), chromium, lead, and sodium. Several parameters for which there are no OCC discharge standards

Table 4: Statistical Analyses of Chemical Data from Pit Aqueous Phase (Canter, et al., 1984b)

Parameter	Minimum Value	Maximum Value	Mean	Median	Standard Deviation	OCC Discharge Standard
pH (std. units)	7.16	11.3	8.55	8.19	1.10	6.5-8.5
Conductivity (umhos/cm)	105	26000	4713	3000	6155	2300
Salinity (%)	0	30	4.6	2.9	6.6	--
Alkalinity (pH 8.3)	0	213	14.6	0	41.6	--
Alkalinity (pH 4.5)	24	743	210	149	171	--
Nitrate (mg/l)	0	0.54	0.10	0.04	0.13	10
Chloride (mg/l)	120	18600	2842	1620	3985	1500
TOC (mg/l)	7.5	522	119.9	41	152.1	--
COD (mg/l)	15	4750	621.9	175	1002.7	250
Phosphorus (mg/l)	0.04	1.07	0.28	0.19	0.28	1.0
Sulfate (mg/l)	0	2420	336	122	552	--
TDS (mg/l)	148	33726	5370	3272	7481	1500
Iron (mg/l)	0	117	17.3	4.1	26.7	--
Chromium (mg/l)	0	8.6	1.3	0.13	2.3	0.2
Arsenic (mg/l)	0.0003	0.2919	0.0224	0.0097	0.0530	0.2
Barium (mg/l)	0.18	23.5	3.80	1	6.39	5.0
Lead (mg/l)	0.01	1.9	0.40	0.08	0.62	0.1
Zinc (mg/l)	0	1.65	0.20	0.046	0.378	5.0
Cadmium (mg/l)	0	0.011	0.0023	0	0.0035	0.03
Calcium (mg/l)	31.6	2330	399	311	484	--
Magnesium (mg/l)	0.591	310.8	50.88	14.05	84.1	--
Sodium (mg/l)	17.7	22630	3784	2000	5164	1000

exhibited high concentrations, including salinity, total organic carbon (TOC), sulfate, and iron. It should be noted that the pit wastes are not discharges and, therefore, not legally subject to the OCC standards. However, if a pit's contents are released to ground or surface water the standards would apply, thus the standards can be used to assess the pollution potential of the pits. Total dissolved solids, conductivity, sodium, and chloride are the constituents most frequently found at high concentrations in the aqueous phase, especially in older or drier pits. This is as expected if a pit is performing its evaporative function properly. Concentrations of metals are generally low in the aqueous portion because they are being retained in the sediments.

The concentrations of the parameters vary greatly with time, primarily in response to natural precipitation and evaporation patterns. During hot dry periods, the pit contents become more concentrated as the water evaporates. Conversely, the dissolved constituents are diluted during periods of heavy precipitation. Figure 1 illustrates this point by comparing the results of sampling the same pits on two different dates from a previous study (Canter, et al., 1984a). Between these two sampling dates there was considerable precipitation and the concentration of dissolved components decreased due to dilution. In addition, less evaporation was occurring in the November time frame. While there was no liquid in some pits on September 26, the aqueous phase of these pits on November 14 had high levels of some constituents because of redissolution with the addition of direct precipitation.

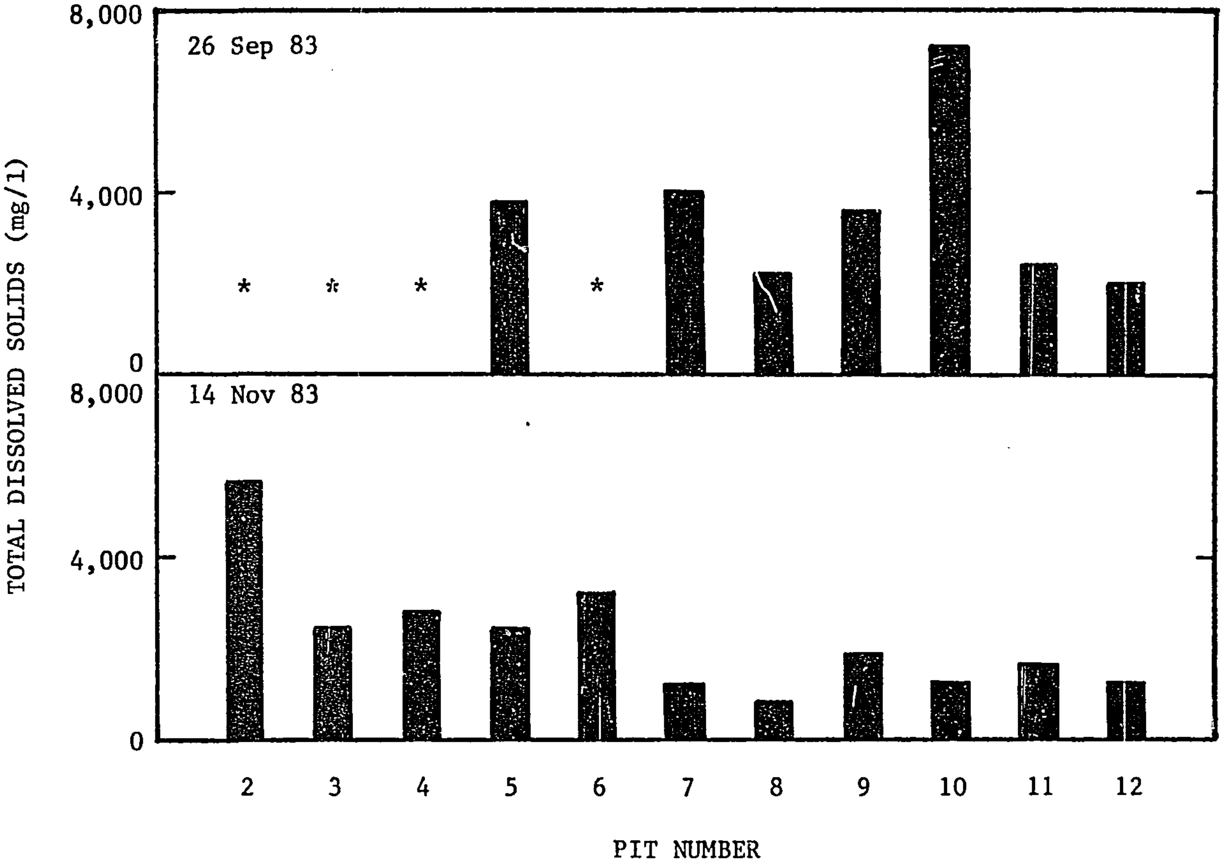


Figure 1: Comparison of Total Dissolved Solids Concentrations in Pits at One Location between 26 Sep 83 and 14 Nov 83 (Canter, et al., 1984a) (*No liquid in pit)

Sediment Portion of Disposal Pits

In a recent study sediments were collected and composited from 4 locations in each of 31 pits (Canter, et al., 1984b). In cases where pits contained liquid or had physically unstable bottoms, 3 locations were composited. This sampling procedure was designed to obtain a composite representative of the pit by including locations from the intake, center, perimeter, and outfall (if any) to other pits. A summary of the metals analyses for pit sediments is reported in Table 5 along with the OCC Screen Analysis Potential (SAP). In general, the mean concentrations in the sediments are high, but do not exceed the SAP except for barium. However, the metals do not represent an immediate threat to the environment because of their insoluble nature. Table 6 illustrates that greater than 99% of the pit concentrations of the metals of concern are retained in the sediments as residual, complexed, adsorbed or exchanged metals. These metals should remain within the pits unless released as particulate overflow or through breaks in the berms. However, from the high levels of metals present, it is clear that the sediments represent a repository for these potential pollutants. Variations in chemical conditions within the pits could make the metals available to solution and subsequently mobile in the subsurface environment. Total sediment analyses, as were performed here, cannot be related to the mobility of sediment-contained constituents. Total analyses only indicate the presence of potential pollutants. Therefore, laboratory experiments (leachability tests) were performed to test this potential.

Table 5: Statistical Analyses of Chemical Data from Pit Sediments (Canter, et al., 1984b)

Parameter	Minimum Value	Maximum Value	Mean	Median	Standard Deviation	OCC Screen Analysis Potential (mg/kg)
Iron (mg/kg)	7090	42000	21474	22500	8706	--
Chromium (mg/kg)	2	264	58	36	64	100
Arsenic (mg/kg)	4.3	41.2	18.2	15	10.4	100
Barium (mg/kg)	18	19970	3789	1124	5924	2000
Lead (mg/kg)	5	281	76.9	52	71.5	100
Zinc (mg/kg)	0	880	134	95	158	--
Cadmium (mg/kg)	0	0.5	0.06	0	0.13	20
Calcium (mg/kg)	280	93400	28380	28500	21220	--
Magnesium (mg/kg)	399	16030	5248	5488	3560	--
Sodium (mg/kg)	74	32400	5214	3750	6482	--

Table 6: Comparison of Average Metal Concentrations in Pit Sediment and Aqueous Phases (Canter, et al., 1984b)

Parameter	Ⓐ Average Sediment Concentration (mg/kg)	Ⓑ Average Liquid Concentration (mg/l)	Percent Retained by Sediment* ((A-B)/B x 100)
Iron	22500	4.1	99.98%
Chromium	36	0.13	99.64%
Arsenic	15	0.0097	99.93%
Barium	1124	1	99.91%
Lead	52	0.08	99.85%
Zinc	95	0.046	99.95%
Cadmium	0	0	--
Calcium	28500	311	98.91%
Magnesium	5488	14.05	99.72%
Sodium	3750	2000	46.67%

*Assumes 1 kg ≃ 1 ℓ in volume.

Sediment Leaching Potential

Leachability tests provide a measure of the potential for metals to be released from the pit sediments to the aqueous phase. In a recent study the first laboratory test conducted followed the procedure of the U.S. Army Corps of Engineers elutriate test (1981). This is a relatively moderate extraction procedure which measures the release of pollutants from sediment when exposed to liquid taken from the same pits under vigorous shaking conditions for 30 minutes. The second laboratory test followed the U.S. Environmental Protection Agency extraction procedure designed to simulate the leaching that waste will undergo if disposed of in a sanitary landfill (U.S. Environmental Protection Agency, 1983). This procedure exposes the sediment to stronger leaching conditions than the elutriate test.

A summary of the metals analyses from the elutriate test are shown in Table 7. Only low levels of arsenic, barium, cadmium, chromium, lead, and zinc were found in the resultant liquid portion under conditions of this test. Therefore, if contents of the pits are not changed, the pits are not altered, and only mixing with the sediments occurs, then the concentration of these metals in leachates from the pits are not likely to pose a significant immediate threat to the subsurface environment and local ground water quality. Calcium, magnesium and sodium were easily leached from the sediments and, therefore, are of more immediate concern to ground water quality (Canter, et al., 1984b).

The results of the extraction procedure are reported in Table 8. Under this more rigorous extraction procedure higher concentrations

Table 7: Statistical Analyses of Elutriate Test Results (Canter, et al., 1984b)

Parameter	Minimum Value	Maximum Value	Mean Value	Standard Deviation
Iron (mg/l)	0.00	55.4	8.2	18.3
Chromium (mg/l)	0.00	2.91	0.48	0.82
Arsenic (μg/l)	0.00	6.00	2.4	2.2
Barium (mg/l)	0.00	3.3	0.9	1.1
Lead (mg/l)	0.00	0.14	0.05	0.04
Zinc (mg/l)	0.00	5.15	0.54	1.41
Cadmium (mg/l)	0.000	0.009	0.004	0.003
Calcium (mg/l)	31	1061	254	278
Magnesium (mg/l)	4.5	116.9	30.5	33.3
Sodium (mg/l)	7	3451	982	882

Table 8: Statistical Analyses of Extraction Procedure Results (Canter, et al., 1984b)

Parameter	Minimum Value	Maximum Value	Mean Value	Standard Deviation
Iron (mg/kg)	0.3	423.3	56.0	114.4
Chromium (mg/kg)	0.00	1.56	0.39	0.40
Arsenic (μg/kg)	0.00	87.21	22.84	27.24
Barium (mg/kg)	0.37	80.38	30.89	21.96
Lead (mg/kg)	0.00	9.26	1.22	2.52
Zinc (mg/kg)	0.00	52.51	14.05	18.44
Cadmium (mg/kg)	0.02	0.38	0.064	0.098
Calcium (mg/kg)	84	19,930	9009	6490
Magnesium (mg/kg)	13	629	293	153
Sodium (mg/kg)	39	3,114	1310	923

were found in the supernatant than in the supernatant from the elutriate test (Canter, et al., 1984b).

Pollution Potential -- Summary

The data presented indicates the pollution potential of the contained wastes in off-site pits. The aqueous phase of the pits were found to contain high levels of dissolved solids such as sodium, chloride, sulfate, and organics. The settled solids contained toxic metals such as arsenic, chromium, barium, and lead as insoluble constituents.

Although leachability studies show these toxic metals to be tightly bound under the conditions of the test, there are still some questions as to the long term fate of these constituents. The sediments represent a repository for these potential pollutants and variations in chemical conditions within the pits could make the metals available to solution and subsequently mobile in the environment.

This study is designed to look not only at leachable metals under various conditions but also at the positional changes of the remaining metals in the solid matrix. These analytical results can then be interpreted from a chemical viewpoint to obtain a more definitive picture of the ultimate fate of toxic metals in disposed drilling muds.

Chemical and Physical Aspects of Toxic Metals in Wastes

In order to better understand and interpret the results of this study, it is necessary to have some general knowledge regarding the chemical and physical aspects of toxic metals and how they react in soil/waste systems. The following discussion is intended to provide a brief background on general factors which affect the uptake and release of toxic metals. Specific chemical properties and a review of pertinent research is then presented specifically for arsenic, barium, chromium and lead.

Toxic metals in soils/wastes are distributed between solid, solution, and gaseous phases. These major components exist in an intimately mixed condition with the proportion of water and air fluctuating under natural conditions depending on climatic and other factors.

The solid phase consists of mineral and organic portions. The mineral (inorganic) portion is composed of small rock fragments and a wide variety of crystalline and noncrystalline materials (Table 9) of varying particle size (Table 10). The organic portion includes the soil biomass, partially degraded plant, animal and microbial components and soil humic constituents (Paul and Huang, 1980). Characteristics of some soil organic fractions are summarized in Table 11. Anthropogenic inputs may provide inorganic or organic components not normally found in nature, such as large concentrations of strong acids or halogenated organic compounds.

The solution phase is held within pores and can be divided into three types of physical classes, gravitational, capillary, and hygroscopic water depending upon the nature of the soil particles and the amount of water present. Gravitational water is that which is in excess of the field capacity and occupies the larger pores. Capillary

Table 9: The Average Amounts of the Elements in Crustal Rocks (Paul and Huang, 1980)

Element[a]	Geochemical Classification[b]	$\mu g\ g^{-1}$	Element	Geochemical Classification	$\mu g\ g^{-1}$
O	At, Bi, Li	466,000	Hf	Li	5
Si	Li	277,200	Dy	Li	5
Al	Li	81,300	Sn	Si	3
Fe	Ch, Si	50,000	B	Li	3
Ca	Li	36,300	Yb	Li	3
Na	Li	28,300	Er	Li	3
K	Li	25,900	Br	Li	3
Mg	Li	20,900	Ge	Si	2
Ti	Li	4,400	Be	Li	2
H	At, Bi, Li	1,400	As	Ch	2
P	Bi, Li, Si	1,180	U	Li	2
Mn	Li	1,000	Ta	Li	2
F	Li	700	W	Li	1
S	Ch	520	Mo	Si	1
Sr	Li	450	Cs	Li	1
Ba	Li	400	Ho	Li	1
C	At, Bi, Li, Si	320	Eu	Li	1
Cl	Li	200	Tl	Ch	1
Cr	Li	200	Tb	Li	0.9
Zr	Li	160	Lu	Li	0.8
Rb	Li	120	Hg	At, Ch	0.5
V	Li	110	I	At, Li	0.3
Ni	Si	80	Sb	Ch	0.2
Zn	Ch	65	Bi	Ch	0.2
N	At, Bi	46	Tm	Li	0.2
Ce	Li	46	Cd	Ch	0.2
Cu	Ch	45	Ag	Ch	0.1

Table 9: (continued)

Element[a]	Geochemical Classification[b]	$\mu g\ g^{-1}$	Element	Geochemical Classification	$\mu g\ g^{-1}$
Y	Li	40	In	Ch	0.1
Li	Li	30	Se	Ch	0.09
Nd	Li	24	A	At	0.04
Nb	Li	24	Pd	Si	0.01
Co	Si	23	Pt	Si	0.005
La	Li	18	Au	Si	0.005
Pb	Ch	16	He	At	0.003
Ga	Ch, Li	15	Te	Ch	0.002
Th	Li	7	Rh	Si	0.001
Sm	Li	7	Re	Si	0.001
Gd	Li	6	Ir	Si	0.001
Pr	Li	6	Os	Si	0.001
Sc	Li	5	Ru	Si	0.001

[a] Omitting those present in less than 0.001 $\mu g\ g^{-1}$; Ne, Kr, Xe and the short-lived radioactive elements

[b] At = Atmosphile: present mainly as atmospheric gases.
Bi = Biophile: tend to be associated with organisms and thus accumulate in the horizons most affected by organisms in soils.
Ch = Chalcophile: not easily ionized and tend to form sulphides and covalent compounds with Se and Te.
Li = Lithophile: ionize readily or form stable oxyanions and occur mainly in oxygen compounds.
Si = Siderophile: do not readily form compounds with O and S and occur mainly as native elements.

Table 10: Classification of Soil Particles According to Size (Paul and Huang, 1980)

Name of Separate	Size Range (mm)
Clay	< 0.002
Silt	0.002-0.02
Fine Sand	0.02-0.2
Coarse Sand	0.2-2.0
Gravel	> 2.0

Table 11: Characteristics of Soil Organic Fractions Extracted from a Wide Range of Soil Types (Includes the Range of Values Measured) (Schnitzer, 1972)

	Humic Acids	Fulvic Acids
Element (%)		
C	56.2 ± 2.6	45.7 ± 5.0
H	4.7 ± 1.5	5.4 ± 1.6
N	3.2 ± 2.4	2.1 ± 1.2
S	0.8 ± 0.7	1.9 ± 1.8
O	35.5 ± 2.8	44.8 ± 5.1
Functional Groups (meq/g)		
Total acidity	6.7 ± 1.1	10.3 ± 3.9
CO_2H	3.6 ± 2.1	8.2 ± 3.0
Phenolic OH	3.9 ± 1.8	3.0 ± 2.7
Alcoholic OH	2.6 ± 2.4	6.1 ± 3.4
Quinonoid C = O and ketonic C = O	2.9 ± 2.8	2.7 ± 1.5
OCH_3	0.6 ± 0.3	0.8 ± 0.5

water is held in pores of capillary size. Hygroscopic water moves primarily in vapor form (Paul and Huang, 1980).

Gaseous Phase

The content and composition of the gaseous phase is determined by the following factors: (1) the soil-water relationships, (2) the rate of production and consumption of the various gases in the soil, and (3) the rate of exchange between the soil air and atmospheric air. Changes in the gaseous phase have significant effects on the physical environment.

The gaseous phase of toxic metals are generally the methylated forms. However, data regarding the concentrations of methylated toxic metals in soil air is sparse and conflicting. It has been reported by O'Hare (1977) that lead undergoes biomethylation under natural conditions; however, Wood (1974) states that lead will not be methylated in the environment. Arsenic has been shown to be reduced and methylated by anaerobes to give dimethylarsine and trimethylarsine as volatile products of extreme toxicity which are readily oxidized to less toxic products (Wood, 1974). Laboratory studies indicate that the concentrations of lead in air within the soil constitute an insignificant part of total lead present in soils (O'Hare, 1977). No evidence was found to indicate that barium or chromium are released to the gaseous phase. Therefore, for all practical purposes, toxic metals in wastes are partitioned between solid and solution phases.

Liquid Phase

The liquid phase of drilling muds may contain contaminants already in soluble form. Contaminants present in interstitial water of drilling muds may originate in two ways: (1) from water trapped within the accumulating solids, and (2) by liberation into solution from the sediment solid phase through diagenetic mobilization processes such as solubilization, ion exchange, and desorption.

Toxic metals in the soluble phase exist in free aquo forms as well as complexes with various organic and inorganic ligands in the soil/waste solution environment. Soil and waste systems are highly complex electrolyte solutions containing a variety of inorganic and organic compounds. The major parameters controlling the solubility of trace metals are the pH and redox of the solution, the type and concentration of complexing inorganic and organic ligands and chelating agents, and the oxidation state of the components (Eichenberger and Chen, 1982). A mass balance for a heavy metal in solution can be expressed as (Mattigod, 1981):

$$M_T = M^{z+} + \sum_{i=1}^{c} a(M_a L_{ib}) + \sum_{i,j=1}^{c,\ (m-1)} (MM_j{}'L_i) + \sum_{i,k=1}^{c,\ (c-1)} (ML_i L'_k)$$

M_T = Total concentration of a metal,

M^{z+} = free ion concentration with valence z+,

$M_a L_{ib}$ = conc. of complex involving a metal with ith ligand,

c and m = total number of ligands and metals, respectively.

a and b = stoichiometric coefficients,

$MM'_j L_i$ = concentration of mixed metal complex involving metal M, jth metal and ith ligand, and

$ML_i L'_k$ = concentration of mixed ligand complex, involving metal M, ith ligand and kth ligand.

The behavior of a heavy metal in a soil/waste liquid phase depends not only on the total concentration of that particular metal in solution but also more directly on speciation. Therefore, the common procedure of measuring total concentration of a particular metal in a water sample may be misleading because of the chemical form of the metal in solution. A water with a high total metal concentration may in fact be less deleterious than another with a lower metal concentration (Emmerich, 1980).

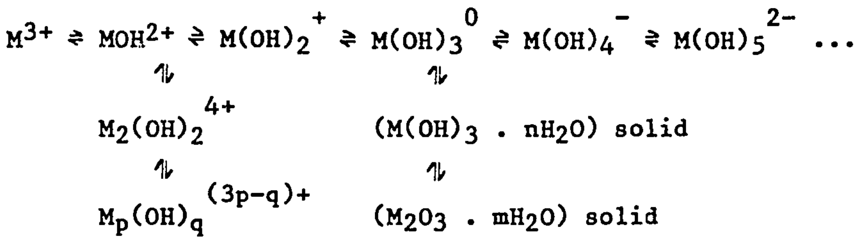
Measuring the trace metal concentrations in soil/waste solutions is analytically difficult, because of the low concentrations encountered and the interrelationship between the various chemical forms. This problem is being approached through the use of computer models based on chemical equilibrium on a thermodynamic basis (Nordstrom, et al., 1979).

The most common interactions between metallic species and other solution species are as follows:

Hydrolysis reactions. Soluble hydrolysis products are particularly important in aqueous systems containing trace concentrations of metal ions. Hydroxo and oxo complexes can significantly affect the chemical behavior of trace metals over a wide range of concentration and pH. The formation of hydrolysis products can control many aspects of chemical behavior such as (1) the adsorption of soluble species on particulates, (2) the tendency of the metal species to coagulate colloidal particles and to form precipitates, (3) the solubility of the controlling solid phase, (4) the extent to which the ions can be complexed in solution, and (5) the oxidation or reduction of the metal species to another valence state (Eichenberger and Chen, 1982).

Two general rules for the hydrolysis of cations have been established (Stumm and Morgan, 1981): (1) the tendency of metal ion solutions to hydrolyze increases with dilution and with increasing pH, and (2) the fraction of polynuclear complexes in a solution decreases on dilution.

The reaction scheme for hydroxide formation is summarized below, the metal is assumed to be trivalent, M^{3+}:



$$\begin{tikzcd}
M^{3+} \arrow[r, leftrightharpoons] & MOH^{2+} \arrow[r, leftrightharpoons] \arrow[d, leftrightharpoons] & M(OH)_2^{+} \arrow[r, leftrightharpoons] & M(OH)_3^{0} \arrow[r, leftrightharpoons] \arrow[d, leftrightharpoons] & M(OH)_4^{-} \arrow[r, leftrightharpoons] & M(OH)_5^{2-} \; \ldots \\
 & M_2(OH)_2^{4+} \arrow[d, leftrightharpoons] & & (M(OH)_3 \, . \, nH_2O) \text{ solid} \arrow[d, leftrightharpoons] & & \\
 & M_p(OH)_q^{(3p-q)+} & & (M_2O_3 \, . \, mH_2O) \text{ solid} & &
\end{tikzcd}$$

The system has two independent variables; the concentrations of the various species depend on both the total concentration of M and the pH. By establishing the total concentration of M, only one degree of freedom remains and a relationship exists between the metal-ion concentration and pH (Kragten, 1978). A curve can be drawn reflecting the defined system (Figure 2).

Hydrolysis equilibria is quickly established with simple hydrolysis products and more slowly with the formation of polynuclear species. Many of these polynuclear species may be considered as kinetic intermediates in the formation of insoluble metal oxides and are thus thermodynamically unstable. Slow kinetics is one of the

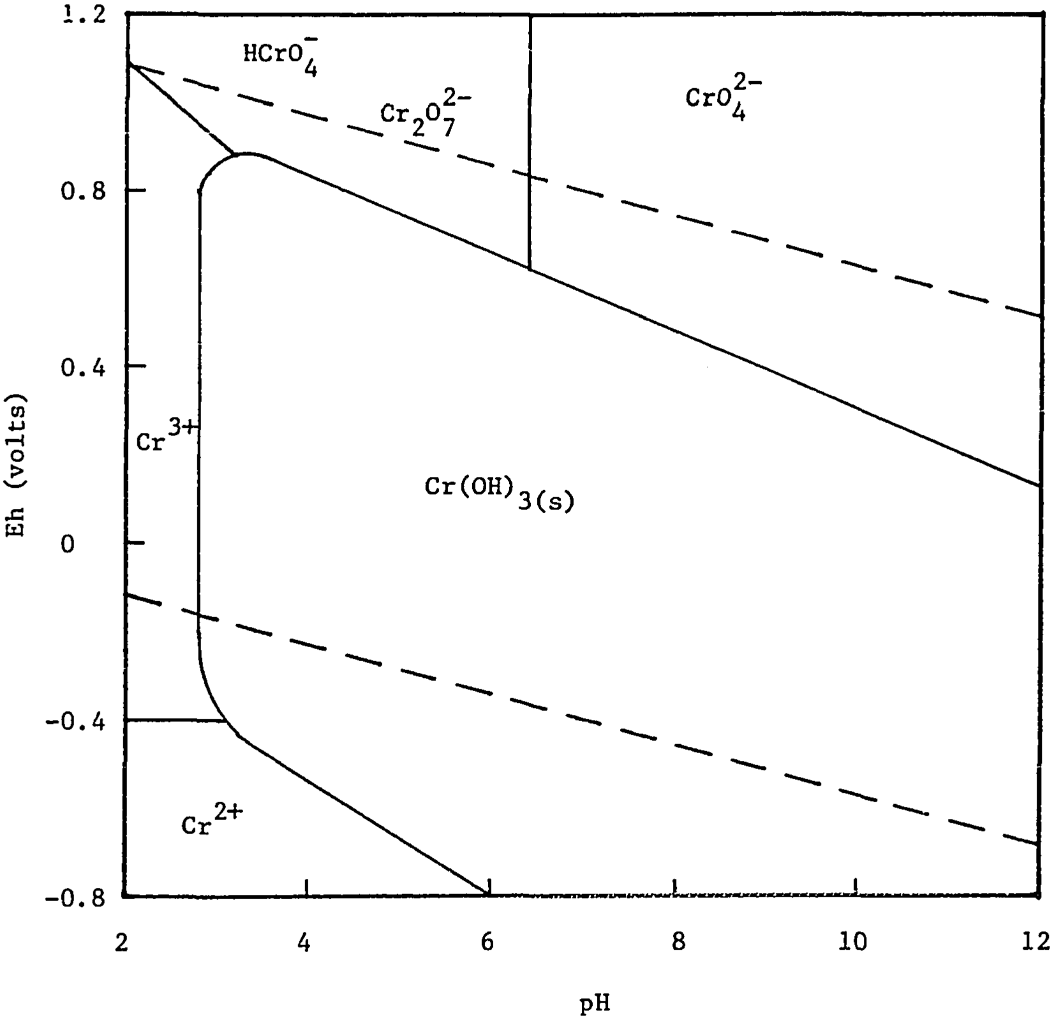


Figure 2: Eh-pH Diagram for the System Chromium-Water at 25°C (Cr)$_t$=10^{-4} M (Faust, et al., 1981)

reasons for the wide variance in the literature of the reported values of hydrolysis constants (Eichenberger and Chen, 1982).

Complexation with inorganic ligands. The most important inorganic complexing agents are bicarbonate, chloride, fluoride, hydroxide, sulfate and sulfide, and phosphate. Complexation of trace metals occurs when the concentrations of these species in water are sufficient to replace coordinated water from aquo complexes. Various soluble and insoluble species can form from the reactions between metal ions and inorganic ligands depending on the metal concentration, ligand concentration, and pH.

Inorganic ligands can be present in liquids at concentrations many orders of magnitude greater than the trace metal ions they tend to complex. The speciation of any metal ion in aqueous solution is dependent upon the stability of the hydrolysis products and the tendency of the metal ion to form complexes with other inorganic ligands. This may include the formation of insoluble complexes which would affect the distribution of metals between the solid and aqueous phases.

The affects of complexation on an aqueous solution are apparent in a study by Griffen, et al. (1977) examining the attenuation of pollutants in municipal landfill leachate by clay minerals (Figure 3). With a solution containing Pb with no complexing agents, more Pb is adsorbed to the clay than when the Pb is present in a solution containing Cl^-, a complexing agent. The difference is due to a significant portion of the soluble lead being complexed with the Cl^- and thus not available in a form susceptible to adsorption onto the clay.

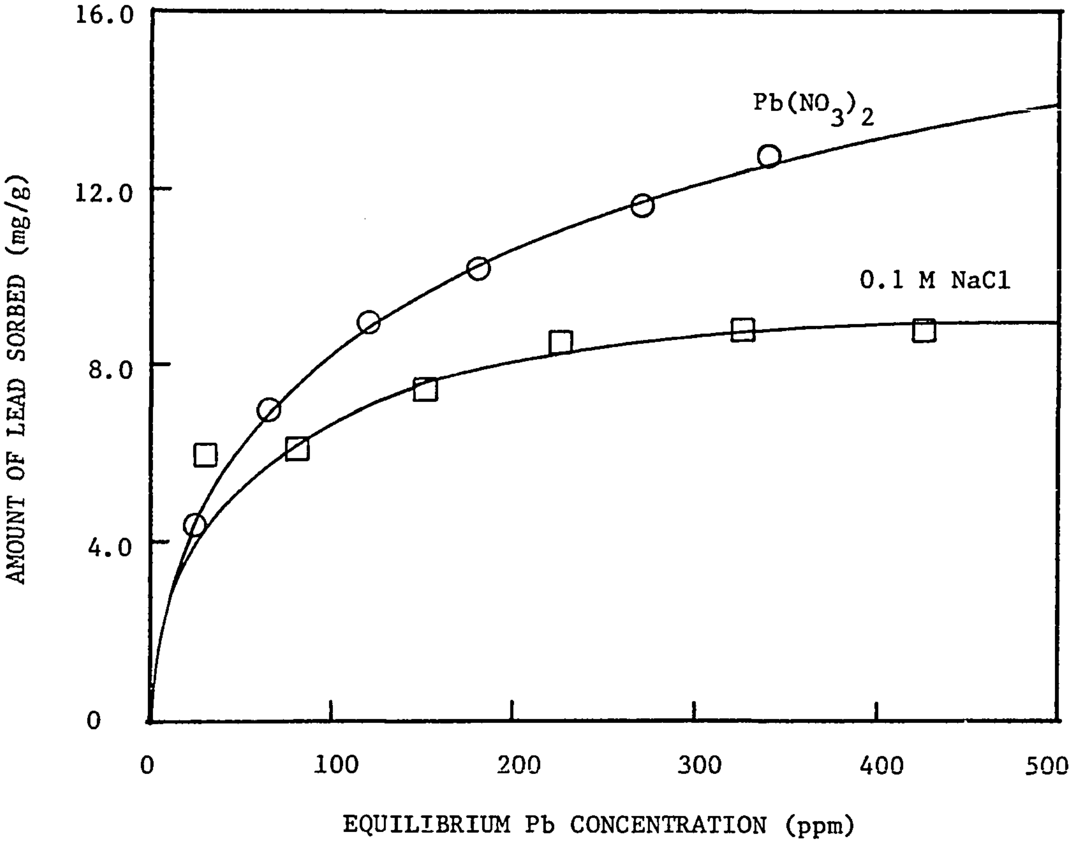


Figure 3: Amount of Lead Sorbed per Gram of Kaolinite at pH 5.0 and 25°C, Plotted as a Function of the Equilibrium Pb Concentration (Griffin, et al., 1977)

Complexation with organic ligands. Organic matter in natural systems can include both natural and synthetic compounds, such as amino acids, humic acid, fulvic acid, fatty acids, citric acid, polysaccharides, organic phosphorous compounds, aromatic compounds containing alcohol and carboxyl functional groups, and porphyrins which contain donor atoms suitable for complex formation.

Metals can be bonded to organic matter by way of (1) carbon atoms yielding organometallic compounds, (2) carboxyl groups producing salts of organic acids, (3) electron-donating atoms, O, N, S, P, etc., forming coordination complexes, or (4) π-electron-donating arrangements (Eichenberger and Chen, 1982). The nature and extent of metal ion complexation by natural or synthetic organics is not well known, because of the poorly defined nature of these organic compounds and also because of the staggering complexity of these multimetal, multiligand systems.

One synthetic organic compound which has caused concern is nitrilotriacetic acid (NTA). It was thought that NTA introduced into detergents would find its way into domestic sewage and keep toxic heavy metals in solution, because of its strong complexing nature. This would prevent the heavy metals from being removed by precipitation as hydroxides, carbonates, phosphates, and sulfides. In the course of time the NTA complexes may be biodegraded, releasing the complexed heavy metal that could cause toxicity in receiving waters. Table 12 lists some calculated percentages of metals complexed by NTA at various concentrations (Snoeyink and Jenkins, 1980). Although it is a strong complexing agent, NTA appears to be biodegradable in secondary,

Table 12: Variation of Metal Complexation by NTA with NTA Concentration at pH 8 (Snoeyink and Jenkins, 1980)

			Percentage of Total Metal Present as Indicated Complex at Stated NTA Concentration		
Total Concentration $C_{T,x}$ M	Complex Species	Log Formation Constant	NTA = 10^{-7}M	NTA = $3\text{x}10^{-6}$M	NTA = $2\text{x}10^{-4}$M
Cu(II)=$2\text{x}10^{-6}$	$CuNTA^{-}$	13	4	82	100
Pb(II)=$3\text{x}10^{-7}$	$PbNTA^{-}$	11.8	2	80	100
Ni(II)=10^{-7}	$NiNTA^{-}$	11.3	1	60	100
Fe(III)=$2\text{x}10^{-6}$	$Fe(OH)NTA^{-}$ $Fe(OH)_2NTA^{2-}$	$\left.\begin{matrix}10.9\\3.1\end{matrix}\right\}$	0.4	34	100
Zn(II)=$1.5\text{x}10^{-6}$	$ZnNTA^{-}$	10.4	0.2	20	100
H=10^{-8}	$HNTA^{2-}$	10.3	0	0	9
Mn(II)=$2\text{x}10^{-6}$	$MnNTA^{-}$	7.4	0	0	100
Ca(II)=10^{-3}	$CaNTA^{-}$	6.4	0	<0.1	17
Mg(II)=$2.5\text{x}10^{-4}$	$MgNTA^{-}$	5.4	0	0	2
Sr(II)=$2\text{x}10^{-6}$	$SrNTA^{-}$	5.0	0	0	0
Ba(II)=$1.5\text{x}10^{-7}$	$BaNTA^{-}$	4.8	0	0	0
Na(I)=$5\text{x}10^{-4}$	$NaNTA^{2-}$	2.2	0	0	0

biological waste treatment processes, hence it should not reach receiving waters.

Fulvic acid appears to be the soluble portion of humic substances that may complex metals and retain them in solution. Table 13 lists the formation constants of various metal ion fulvic acid complexes (Snoeyink and Jenkins, 1980). The high concentrations of some metals in highly organic soils and deposits (such as peat and coal) may arise from the association of metals with natural organics in these materials.

pH-Eh effects. The pH and Eh of a system can control its solution equilibria in terms of species present. These parameters control many aspects of pollutant behavior.

The pH influences adsorption and ion exchange because hydrogen ions compete for active sites. Decreases in pH diminish surface charges releasing metal ions sorbed to hydrous oxides, and clay minerals and hydrous oxides become anion exchangers and will no longer hold cations but will bond complex metal ions with a negative charge. Also, a change in pH can change the degree of complexation of a metal in solution because many ligands are also weak acids or bases (Eichenberger and Chen, 1982). Redox (Eh) exerts similar effects and others in addition to those caused by pH. A change in Eh can cause a direct change in the oxidation state of the metal, and cause changes in available and competing ligands.

Diagrams of pH vs. Eh are often constructed to show the relationship between these two parameters under defined conditions. These diagrams can only reflect the system as calculated for the

Table 13: Formation Constants of Various Metal Ion Fulvic Acid Complexes (Ionic Strength = 0.1 M) (Snoeyink and Jenkins, 1980)

Metal Ion	pH of Measurement	Log K for Metal Ion-Fulvic Acid Complex[a]
Fe^{3+}	1.7	6.1
Al^{3+}	2.35	3.7
Cu^{2+}	3.0	3.3
Ni^{2+}	3.0	3.1
Co^{2+}	3.0	2.9
Pb^{2+}	3.0	2.6
Zn^{2+}	3.0	2.4
Mn^{2+}	3.0	2.1
Mg^{2+}	3.0	1.9

[a] Formation constants, K, are for the reaction
$M + \text{fulvic acid} \longrightarrow M \cdot \text{fulvic acid}$

species considered under given conditions of temperature, pressure, and concentration. Also, the kinetics of the system are not taken into account. However, if used with a knowledge of their limitations these diagrams can provide much insight into the behavior of elements in aqueous solution. Figures 4 and 5 contain diagrams for many elements of interest (Campbell and Whiteker, 1969). For example, by examining these diagrams, it can be determined under what conditions lead would be soluble in the absence of complexing agents. A detailed explanation of these diagrams is contained in Garrels and Christ (1965).

Solid Phase Chemical Forms of Metals

Toxic metals in the solid phase of soils or wastes may occur in many different chemical forms which are not equally active chemically and biologically. The chemical form of a metal can greatly influence its fate in terms of dissolution, migration, and biological uptake. Therefore, it is desirable to know the physico-chemical states in which the metals exist in solid phases.

Metals in wastes are usually expressed in terms of total concentrations. Use of total concentration as a criteria to assess the potential effects of contamination implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable, because a material may be present in a form that makes it completely unavailable chemically and biologically. In fact, the background level of most metals in soils seem high when measured on a total basis (Table 14), but are usually of no concern because of

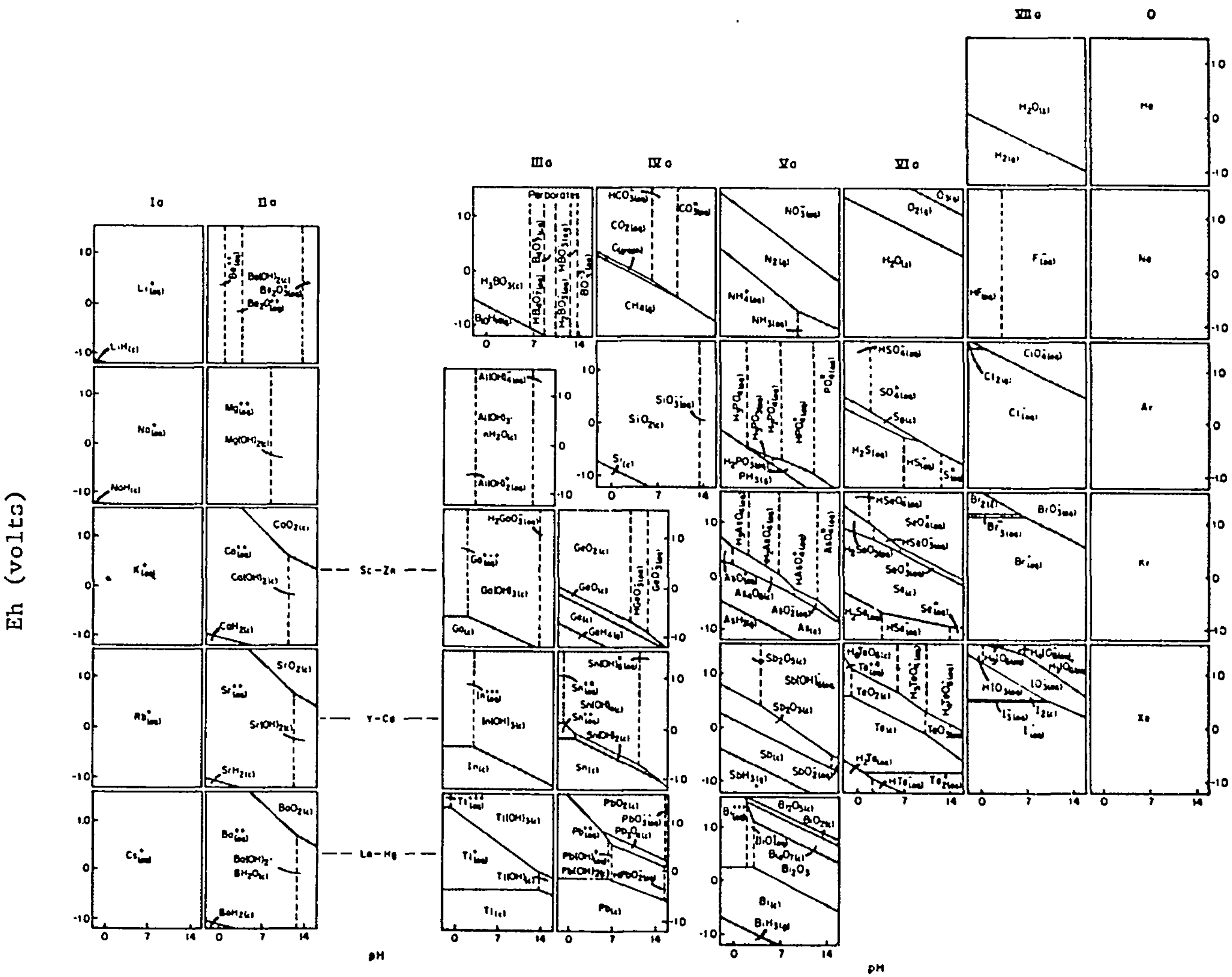


Figure 4: Eh-pH Diagrams for Most of the Group A Metals and the Nonmetals (Campbell and Whiteker, 1969)

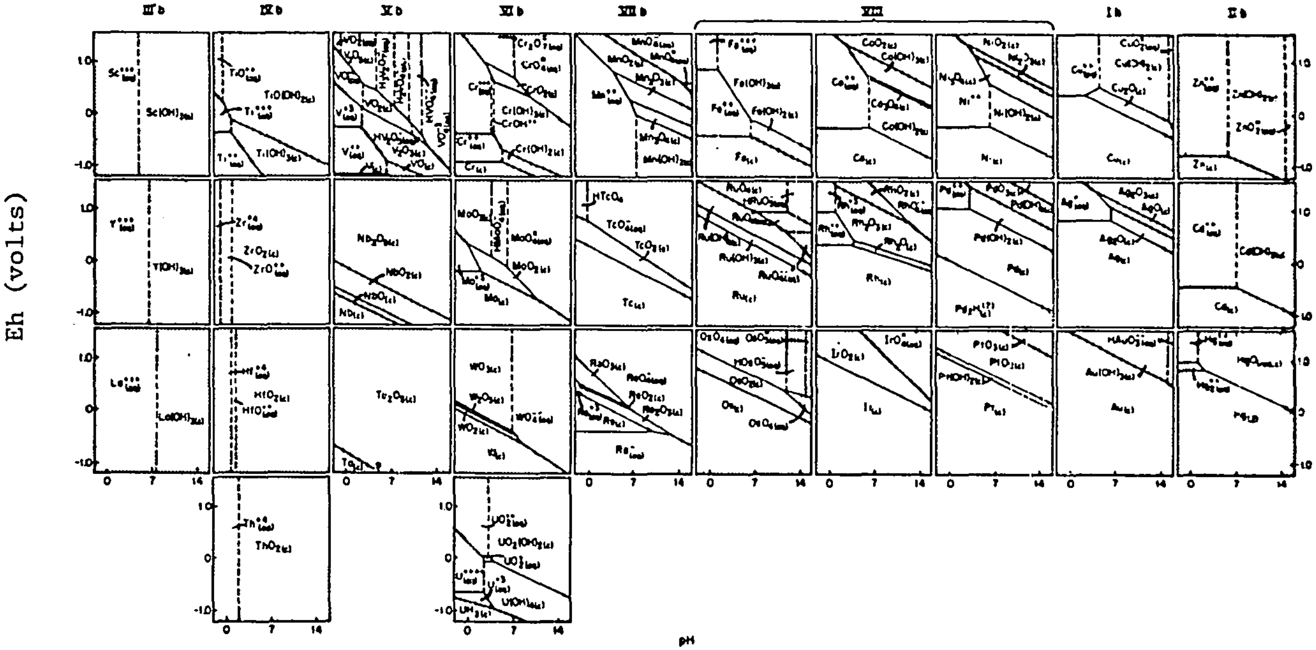


Figure 5: Eh-pH Diagrams for the Transition Metals (Campbell and Whiteker, 1969)

Table 14: The Content of Metals in Soils (Lindsay, 1979)

Element	Common Range for Soils (ppm)
As	1 - 50
Ba	100 - 3000
Cr	1 - 100
Pb	2 - 200

their presence in the mineral phase. Mineral phase metals are not normally mobile in the natural environment.

One method of evaluating the forms of metals in wastes is to determine the recovery of metals by using selective extractants. A number of single extractant methods using reagents including acids, bases, salts, and complexing agents have been employed to extract metals from specific phases or under desired environmental conditions (Stover, et al., 1976). A well known example of a single extractant method is the Extraction Procedure Toxicity Test (EP Toxicity) which is intended to evaluate the potential of an industrial waste to release metal and organic constituents in a municipal landfill (U.S. Environmental Protection Agency, 1980). The extractant is sufficient 0.5 N acetic acid to maintain a pH of between 4.8 and 5.2. The EP Toxicity Test, by maintaining a pH of 5.0 ± 0.2, is intended to represent the initial stages of municipal waste decomposition, when acidic conditions exist. However, it does not attempt to control or simulate the oxidation-reduction potential, ionic activity coefficient, complexation, and other factors in municipal leachate that influence the solubility of waste constituents (Perket, 1982). While it does have its shortcomings, the EP Toxicity Test does go one step further than a total metals analysis towards evaluating the pollution potential of a waste. It does not define in which solid form a metal exists, but it does give an indication of possible metal release upon disposal of a waste.

To make the most of chemical analysis in determining the long- and short-term potential of metals in a waste to be released into the environment, it is necessary to be able to accurately measure their absolute concentrations and chemical forms. The determination of the chemical phases in which a metal can exist is a very difficult problem. It is complicated by the numerous phases found in wastes. These phases include exchanged metal ions, weakly and strongly adsorbed metals, metal carbonates, sulfates, sulfides, oxides, hydroxides, phosphates and organometallic compounds, natural or man-made. The use of sequential extractions rather than single extractants may, therefore, be of greater value in determining metal distribution in wastes. Although more time consuming, sequential extractions can furnish detailed information about the origin, mode of occurrence, biological and physiochemical availability, mobilization, and transport of metals (Tessler, et al., 1979).

A number of procedures have been developed to fractionate specific solids into various homogenous groups or to extract a component of specific chemical property using suitable reagents. The extraction schemes often vary between investigators because of development for a specific purpose, personal preference, or a lack of exchange of information. This makes intercomparison of results difficult, while providing new investigators with a wealth of methods to choose from. Types of solids studied include estuarine sediments (Boust and Saas, 1981; Badri and Aston, 1981), river sediments (Tessler, et al., 1979), marine sediments (Van Valin and Morse, 1982), wastewater sludges (Stover, et al., 1976), sludge amended soils (Schalscha, et al., 1982; Cheng, et al., 1984; Emmerich, 1980; Emmerich, et al., 1982; Sposito, et al., 1982), soils (Sims and Patrick, 1978), and dredged material (Brannon, et al., 1976).

All of these methods have the same basic aim: to determine the physico-chemical forms of trace metals bound to support particles in order to evaluate potential mobility or to define fate, whether it be for environmental or geological purposes. The methods are based on the same principle: extraction by successive attacks of certain solid fractions from the most mobile to those strongly bound to the support mineral. An extraction sequence should be reproducible -- the extracted fraction should always be the same, and selective -- the chosen reagents should be specific of a form or of a group of well-defined constituants (Boust and Saas, 1981).

Because of the physico-chemical complexity of any soil or waste system and extraction scheme, the concept of an operationally defined metal reactivity is generally used rather than attempting to individually characterize each solid phase. The relative reactivity has been defined by the type of chemical leaching necessary to liberate a fraction of a particular metal. This is assumed to be largely dependent on the original phase from which the metal was liberated. Distinct chemical phases that respond similarly are treated as equivalent phases. Since the use of chemical reagents to extract a specific form of a metal is not exact, it is probably more appropriate to say that the extractants extract chemically similar forms with some overlap of other forms. Therefore, it is common practice to report the fractionation of trace metals according to the extracting reagent employed (e.g., KNO_3) instead of the expected solid phase fraction (e.g., exchangeable). Note, however, that sequential extractions can frequently be closely correlated with individual phases (Van Valin and Morse, 1982).

The effective ranges of five extraction procedures are listed in Table 15 based on the initial intent described by the authors. Each extraction procedure was developed for a specific purpose, which accounts for their differences.

Brannon, et al. (1976) explored the possibility that large amounts of some chemicals in sediments could be released into the aqueous phase when sediments are agitated by dredging and subsequent resuspension in water by discharge operations. A selective sediment extraction procedure was developed to study long- and short-term effects of sediment resuspension on water quality (Table 15). Results of the sediment partitioning fractionation scheme showed that the operationally defined phases in a sediment could be isolated with good elemental mass balance and precision among the phases. The physiochemical form of sediment-bound metals (Fe, Mn, Cu, Zn, Ni, Cd, and As) was found to be a much greater factor than the total metal concentration in determining the mobility of metals. In no case were trace metal concentrations in the more mobile sediment partition phases correlated with total metal concentrations in the sediment. However, correlation between a sediment elutriate (leachability) test metal concentrations and their concentrations in the various selective extraction phases revealed that the elutriate test concentrations represented the sediment phases thought to be most mobile and biologically available in the aquatic environment.

Table 15: Sequential Extraction Methods and Defined Forms Separated

Reference	Form*	Reagent
Tessler, et al. (1979)	Exchangeable	$MgCl_2$
	Carbonate	NaOAc
	Fe-Mn Oxides	$NH_2OH \cdot HCl$
	Organic	H_2O_2/HNO_3
	Residual	$HF-HClO_4$
Stover, et al. (1976)	Exchangeable	KNO_3
	Adsorbed	KF
	Organic	$Na_2P_2O_7$
	Carbonate	EDTA
	Residual	HNO_3
Emmerich (1980)	Exchangeable	KNO_3
	Adsorbed	H_2O
	Organic	NaOH
	Carbonate	Na_2EDTA
	Residual	HNO_3
Brannon, et al. (1976)	Exchangeable	NH_4OAc
	Easily Reduced	$NH_4OH \cdot HCl$
	Organic Sulfide	H_2O_2
	Moderately Reducible	$Na_2S_2O_4$
	Residual	$HF-HNO_3$

Table 15: (continued)

Reference	Form*	Reagent
Forstner, et al. (1981)	Exchangeable	NH_4OAc
	Easily Reduced	$NH_2OH \cdot HCl$
	Moderately Reducible	NH_4^+ Oxalate/ Oxalic Acid
	Organic	H_2O_2/HNO_3
	Residual	HNO_3

*It is not meant that the metal is necessarily present in this "form", but extractable with the indicated reagent. The terminology is consistent with the literature.

An analytical procedure involving sequential chemical extractions was developed by Tessler, et al. (1979) for the partitioning of particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn) into the five fractions listed in Table 15. Experimental results obtained on replicate samples of fluvial bottom sediments demonstrate that the relative standard deviation of the sequential extraction procedures was generally better than ± 10%. The accuracy, evaluated by comparing total trace metal concentrations with the sum of the five individual fractions, proved to be satisfactory. A limiting factor was the inherent heterogeneity of the sediment, which could be improved with better sampling methods. A major advantage of the sequential extraction was the simulation to a certain extent of various environmental conditions to which the sediment may be subjected; deductions can then be made about the trace metal levels likely to be observed under these conditions in the environment.

Sequential extraction techniques were used by Forstner, et al. (1981) to determine the chemical associations of heavy metals with specific solid phases (Table 15), whereby the potential availability of toxic compounds in waste materials for biological uptake and possible remobilization effects into the aqueous phase were estimated. In addition to providing information on availability, chemical speciation data also indicated the source of metal enrichments in sediments.

The method of Stover, et al. (1976) was designed to evaluate metals in wastewater sludge. Based on the results obtained from extraction of pure metal precipitates, a fractionation procedure was designed to separate metals into exchangeable, sorbed, organically bound, carbonate, and residual fractions (Table 15). This procedure was evaluated by Schalscha, et al. (1982) and found superior to the others tested because it divides the metal into more defined fractions.

This method as modified by Emmerich (1980) has been used in a number of studies investigating the movement of heavy metals in sewage sludge-treated soils (Emmerich, et al., 1982; Chang, et al., 1984; and Sposito, et al., 1982). Fractions extracted are similar to Stover, et al. (1976): exchangeable, adsorbed, organically bound, carbonate, and residual forms (Table 15), however, H_2O has replaced KF and NaOH has replaced $Na_2P_2O_7$ as extraction reagents.

The properties of the fractions extracted can be summarized as follows:

Exchanged. The KNO_3 was chosen as an initial extractant for metals bound at exchange sites. When the sample is saturated with K^+, the exchangeable metals are displaced from exchange sites located on inorganic and organic components.

The mechanism which results in cation exchange is based on the sorptive properties of negatively charged anionic sites -- $SiOH^-$, $AlOH_2^-$, and $AlOH^-$ groups in clay minerals, $FeOH^-$ groups in iron hydroxides, carboxyl and phenolic OH^- groups in organic substances -- towards positively charged cations. The balancing of negative charges of the lattice is a selective process which accounts for preferential uptake of specific cations and the release of equivalent charges associated with other species (Forstner and Wittmann, 1979).

Surface phenomena of this kind can best be explained by the electric double layer model. One layer of the double layer is envisaged as a fixed charge attached to the solid surface, while the outer layer is distributed more or less diffusely in the liquid in contact. This layer contains an excess of counter ions, opposite in sign to the fixed charge and usually a deficit of coions of the same sign as the fixed charge. If a negative surface with one type of cations as counter ions is considered, the counter ions (1) are electrostatically attracted by the surface (while anions are depleted from the surface); (2) tend, because of thermal motion, to become more evenly distributed through the solution; and (3) may be attracted to the surface by other than electrostatic forces (Stumm and Morgan, 1981). Various models have been developed to describe the spatial distribution of charges at the surface (Figure 6). In the Helmholtz model the electrified surface consists of two charge sheets, one on the surface and one in the solution (Figure 6a). The Guoy-Chapman diffuse charge model exposes the solution charges to the forces of thermal motion and a balance between electrostatic and thermal forces is attained (Figure 6b). The next model divides the solution near the surface into two parts (1) the Stern layer which is subject to both electrostatic and specific interaction and a Guoy layer which is a diffuse layer subject to electrostatic forces (Figure 6c). If the specific interaction is stronger than the electrostatic forces, the charge of the Stern layer may become more positive than that of the surface (Figure 6d). The sum of the charges must be zero to maintain electroneutrality (Stumm and Morgan, 1981):

$\sigma_o + \sigma_s + \sigma_d = 0$

σ_o = surface charge density,

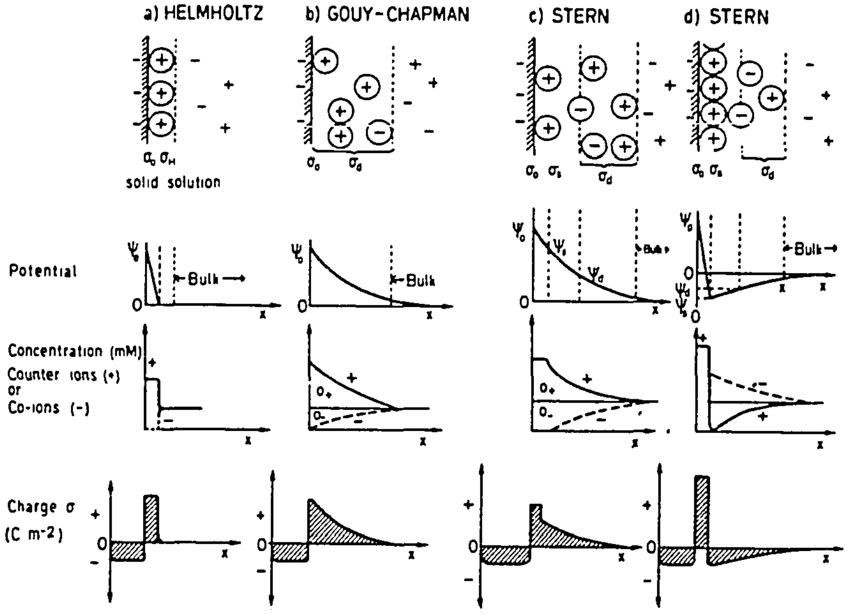


Figure 6: Distribution of Charge, Ions, and Potential at a Solid Solution Interface (Stumm and Morgan, 1981)

σ_s = stern layer charge density, and

σ_d = diffuse (Guoy) layer charge density.

With clay minerals, of which bentonite is common in drilling fluids, the exchange capacity increases markedly in the order of kaolinite < chlorite < illite < montmorillonite(bentonite). This increase corresponds with the reduction of particle size and the related increase of surface area (Table 16).

Clays (layered silicates) are formed from two basic units: a tetrahedron of four oxygen atoms surrounding a central cation, which is usually Si^{4+}, but is occasionally Al^{3+}, and an octahedron of six oxygens or hydroxides around a larger cation which is usually Al^{3+}. Layers of the silicon tetrahedra and the aluminum octahedral systems interact in various combinations to give characteristic layered structures of clay minerals (Figure 7). Ions of similar radii may be substituted for the Al^{3+}. Layers of the silicon tetrahedra and the aluminum octahedral systems interact in various combinations to give characteristic layered structures of clay minerals (Figure 7). Ions of similar radii may be substituted for the Al^{3+} or Si^{4+}. Ions of lower valence result in a residual negative charge which must be balanced by a cation located external to the layered structure (Tinsley, 1979).

Therefore, the layered silicates would have a planar geometry, a very large surface area, and can achieve a very high residual negative charge which is neutralized by a large external concentration of cations. Clay surfaces can assume a negative charge, which is pH dependent and results from the ionization of hydroxyl hydrogens. Thus, the ion exchange capabilities of the clays can result from this type of

Table 16: Specific Surface Area and Exchange Capacities of Several Substances (Forstner and Wittmann, 1979)

Material	Surface Area (m^2/g)	Exchange Capacity (meq/100 g)
Kaolinite	10 - 50	3 - 15
Illite	30 - 80	10 - 40
Chlorite	--	20 - 50
Montmorillonite	50 - 150	80 - 120

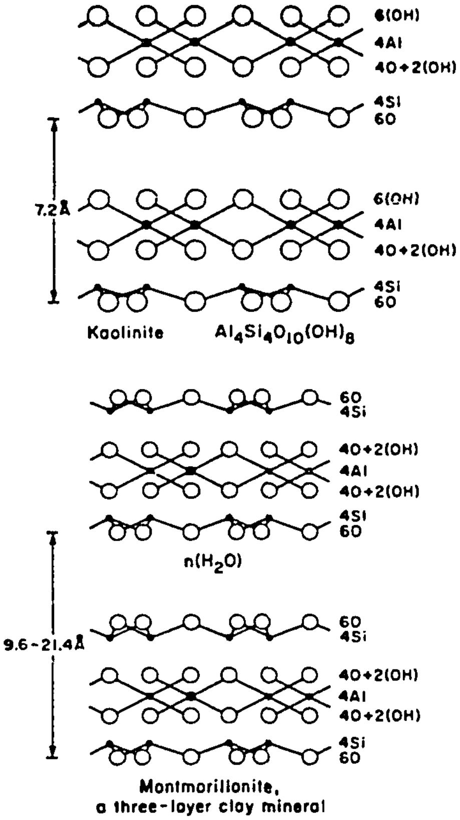


Figure 7: Structure of Kaolinite and Montmorillonite (Tinsley, 1979)

mechanism, as well as the exchange of those metal ions which neutralize the excess charge resulting from the substitution of other cations in the silicon and aluminum structures. A summary of the cation exchange capability is given in Figure 8 (Tinsley, 1979).

Adsorbed. Deionized water was used for the removal of adsorbed metals because of the dependence of the extent of metal adsorption by hydrous oxide surfaces on the ionic strength of the contacting solution. It was found that three washings with deionized water removed between 80 and 100 percent of Cd, Cu, Ni, and Zn mixed with Fe and Al hydrous oxide gels (Emmerich, 1980).

Figure 9 is a cross section of the surface layer of a metal oxide. The metal ions in the surface layer have a reduced coordination number, thus behave as Lewis Acids. In the presence of water, the surface metal ions may first tend to coordinate H_2O molecules followed by dissociation to a hydroxylated surface. It would appear that the surface carries two different types of groups: hydroxyl groups bound to one metal ion and hydroxyl groups bound to two or more metal ions. A number of reactions are suggested to occur at the oxide-water interface (Schlindler, 1981):

(i) acid-base reactions of surface hydroxyl groups,

(ii) deprotonated surface hydroxyls coordinating with dissolved metal ions,

(iii) surface hydroxyls replaced by dissolved ligands,

(iv) a dissolved metal ion coordinating with deprotonated surface hydroxyls and dissolved ligands, and

(v) a dissolved ligand coordinating with a surface metal and a dissolved metal ion.

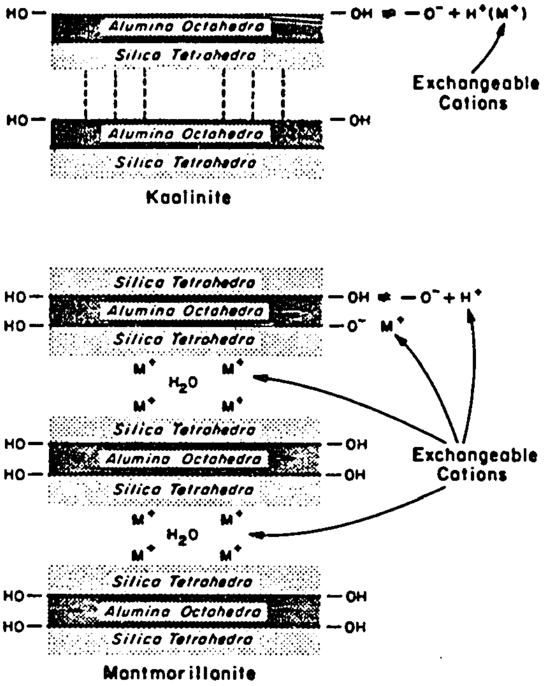


Figure 8: Distribution of Charge and Cation Exchange Potential of a Clay (Tinsley, 1979)

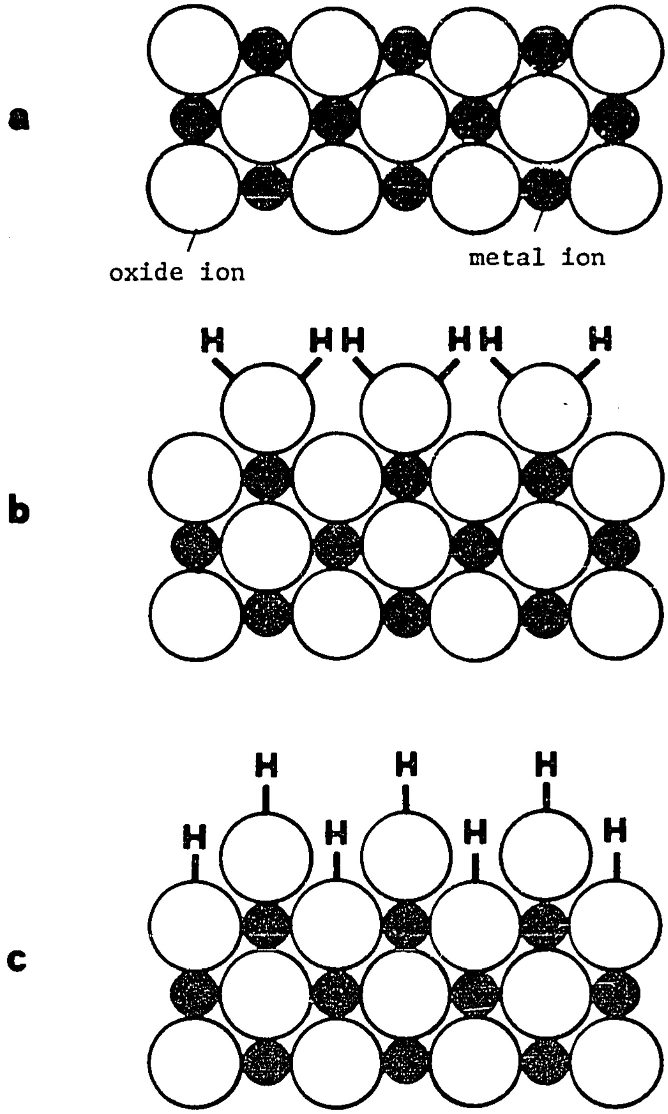


Figure 9: Cross Section of the Surface of a Metal Oxide (Schindler, 1981) (a) Surface ions are coordinatively unsaturated; (b) In the presence of water, the surface metal ions may coordinate H_2O molecules; and (c) Dissociative chemisorption leads to a hydroxylated surface.

These reactions are illustrated in Figure 10.

Organically bound. The organically bound metals have been extracted with 0.5 M NaOH. This solution has been found to remove more of the organically bound metals by removing greater percentages of the organics as well as the complexed metals while extracting little of the carbonate and residual metals (Emmerich, 1980).

Colloidal organic matter has a srong affinity for heavy metal cations, and the retention of added metals is often well correlated with the amount of soil organic matter. Organic matter's strong affinity for heavy metal cations is due to ligands or groups that form chelates and/or complexes with the metals. The functional groups include COOH, phenolic, alcoholic, and carbonyl structures of various types (Jones and Jarvis, 1981). These are also the functional groups that are commonly present in petroleum hydrocarbons and other industrial wastes. Little work has been done on the coincidence of toxic metals with anthropogenic organic wastes other than sewage sludge.

Humic substances are believed to represent a significant fraction of the bulk of organic matter in most soils. Humic substances may be described as polymers containing phenolic OH and carboxylic groups with a lower number of aliphatic OH groups. Based on their solubility in alkaline and acid solutions humic substances are usually divided into three fractions: (1) humic acid, which is soluble in alkaline solution but is precipitated by acidification; (2) fulvic acid, which is the humic fraction that remains in the aqueous acidified solution: that is, it is soluble over the entire pH range; and (3)

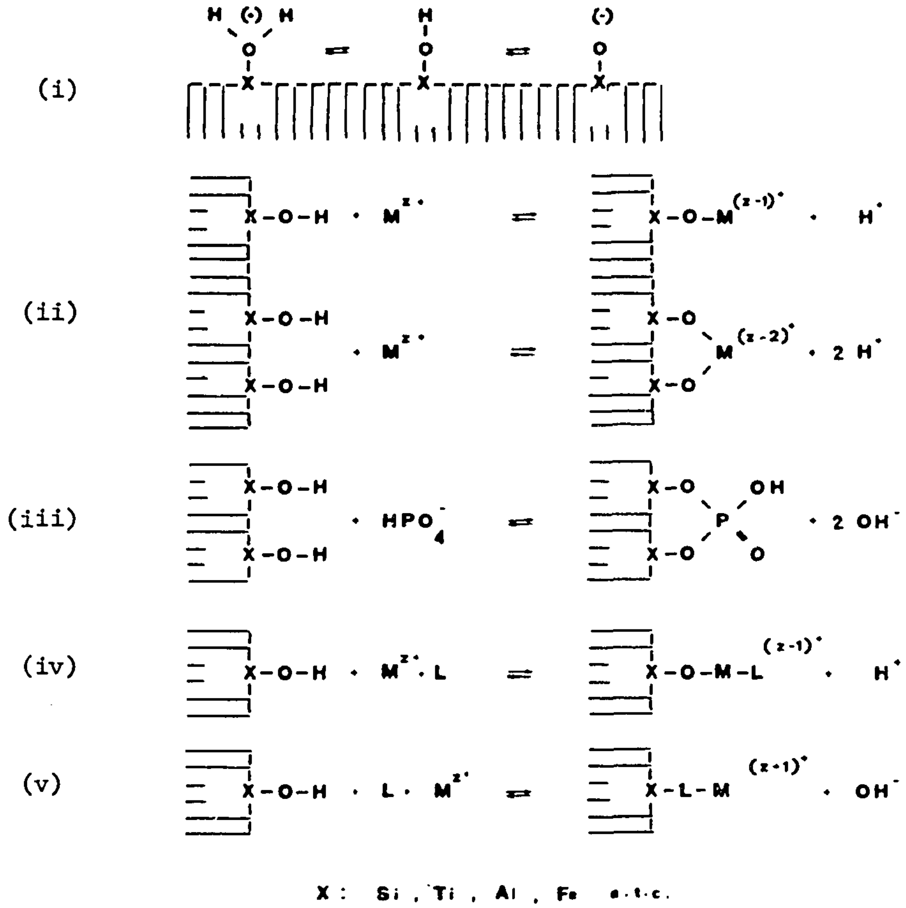


Figure 10: Coordination Phenomena at Oxide-Water Interfaces (Schindler, 1981)

humin, the fraction that cannot be extracted by acid or base. Structurally the three fractions are believed to be similar; they appear to differ in molecular weight and functional group content. Fulvic acid has probably a lower molecular weight but more hydrophilic functional groups than humic acid and humin (Stumm and Morgan, 1981). Fulvic acid may be made up of phenolic and benzene carboxylic acids joined by hydrogen bonds to form a polymeric structure of considerable stability (Figure 11) (Schnitzer and Khan, 1972).

Carbonates. EDTA has been found to be a superior reagent for a complete yet selective extraction of metal carbonates (Stover, et al., 1976). EDTA is commonly used for release of elements bound by organic matter; however, if NaOH is used previously, the metals recovered by the EDTA should be primarily in the carbonate form.

Significant trace metal concentrations can be associated with sediment carbonates; this fraction is expected to be susceptible to changes of pH (Tessler, et al., 1979). Coprecipitation with carbonates, whereby heavy metal cations are sorbed onto the surface becoming part of the crystal lattice, can be an important means of limiting heavy metal concentrations in the environment. Coprecipitation with $CaCO_3$ has been found to enhance the precipitation of heavy metal carbonates of low solubility, such as $PbCO_3$ (Forstner and Wittmann, 1979). The solubility of $PbCO_3$ is apparent when examining solubility products (Table 17).

Residual. Residual forms for metals are extracted with 4.0 M HNO_3. Once the previous fractions have been removed, the remaining solid should contain mainly primary and secondary minerals, which may

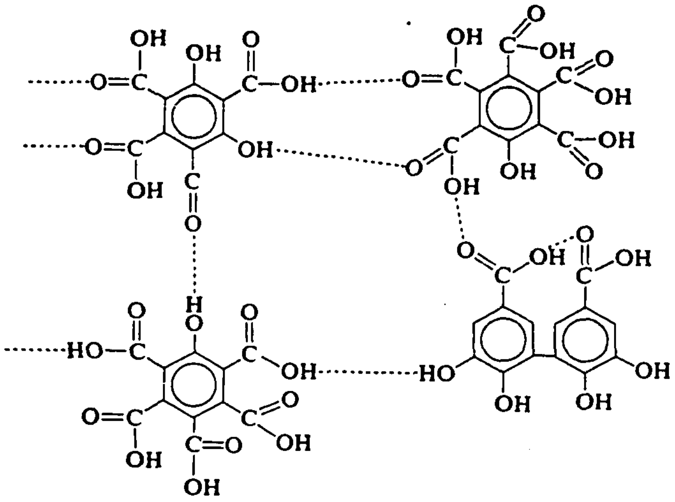


Figure 11: Structure of Fulvic Acid (Stumm and Morgan, 1981)

Table 17: Negative Logarithms of Solubility Products of Heavy Metal Carbonates (pH = 7 at 25°C) (Forstner and Wittmann, 1979)

Carbonate	$-\log K_{sp}$
$MnCO_3$	10.2
$CdCO_3$	11.3
$FeCO_3$	10.5
$PbCO_3$	13.1
$CoCO_3$	12.8
$ZnCO_3$	10.8
$NiCO_3$	6.9
$CuCO_3$	9.6
$Cu_2(OH)_2CO_3$	33.8

hold trace metals within their crystal structure. These metals are not expected to be released over a reasonable time span under the conditions normally encountered in nature. These mineral forms would include precipitates such as metal sulfides and hydroxides. Hydroxide and sulfide solubility products are listed in Table 18. Precipitation of hydroxides, sulfides, and carbonates occurs within a system when the corresponding solubility product is exceeded. The interactions of a variety of factors play an important role in this context with the result that the solubility data, obtained in pure individual systems in distilled water, only represent a guide to the conditions actually found in a natural system (Forstner and Wittmann, 1979).

Summary -- Solid phase. The solid phase is therefore both a complex and diverse environment. The amount of surface area available is extremely large, and the nature of the binding sites variable. The potential exists for hydrophobic interactions, simple ion exchange, all the way on to chemical bonding. The analysis of the solid phase is complicated by the interplay of all these processes; and changes in the system caused by changes in pH, Eh, or ionic strength of the solution. While this discussion attempted to isolate various processes, a more general view of their overlap is given in Table 19. The application of specific equilibrium exchange or adsorption constants to solid-water systems is principally limited by difficulties in quantitatively determining the various phases, and a lack of knowledge concerning (1) chemical and thermodynamic properties of the various solid phases; (2) reaction kinetics, i.e., how nearly equilibrium is approached in a fixed time; and (3) the competitive effect of other cations present.

Table 18: Negative Logarithms of Solubility Products of Heavy Metal Hydroxides and Sulfides (pH = 7 at 25°C) (Forstner and Wittmann, 1979)

Hydroxides	-log K_+	Sulfide	-log K_{sp}
$Cd(OH)_2$	14.4	CdS	27.8
$Fe(OH)_2$	15.1	FeS	17.2
$PbO+H_2O$	15.3	PbS	27.5
$Zn(OH)_2$	15.5	ZnS	21.6
$Ni(OH)_2$	14.7	NiS	18.5
$HgO+H_2O$	25.4	HgS	52.4
$Cr(OH)_2$	37.4		
$Fe(OH)_3$	39.1		

Table 19: Trace Element Sinks and Their Respective Uptake and Release Processes (Jenne and Luoma, 1975)

Sinks	Processes	Reaction Parameter*
Oxides (hydrous and (amorphic)	Surface exchange	K_{eq}
	Diffusion exchange	K_{eq}, R_{ex}
	Co-Precipitation	P, R_{ppt}
Organic substances	Exchange	K_{eq}
	Complexation	K_{eq}
	Chelation	K_{eq}
Biota	"Passive" uptake	R_{gr}
	Exchange, complexation, chelation	K_{eq}
	"Active" uptake	K_{eq}
Carbonates, phosphates sulfides, sulfate and chloride salts	Precipitation	R_{ppt}
	Co-Precipitation	P
	Surface exchange	K_{eq}

*K_{eq} = mass action equilibrium constant; R_{ex} = rate of exchange; P = partitioning coefficient; R_{ppt} = rate of precipitation; and R_{gr} = rate of growth.

Results of Previous Sequential Extraction Studies

The results obtained by Stover, et al. (1976) from the fractionation of Pb, Cu, Zn, Cd, and Ni in wastewater sludge indicate that sludges contain a wide variety of sites capable of metal retention. Retention mechanisms include ion exchange, sorption, chelation, and precipitation. The ranking for different forms of the metals in wastewater sludge were found to be:

- Cu: sulfides (residual) > carbonates > organic bound = adsorbed > exchangeable.
- Zn: organic bound > carbonates > sulfides (residual) > adsorbed > exchangeable.
- Pb: carbonates > organic bound > sulfides (residual) > adsorbed > exchangeable.
- Ni: carbonates > organic bound > exchangeable > adsorbed > sulfides (residual)
- Cd: carbonates > sulfides (residual) > organic bound > adsorbed = exchangeable.

Approximately 80 percent of these metals in wastewater sludges were present in forms that require conversion to water soluble, exchangeable or sorbed forms by chemical or microbial processes in soils before uptake by plants. Metal retention was found to be highly variable, depending on the chemical properties of the sludge and on the nature of the metal.

Emmerich (1980) investigated the possible movement of heavy metals (Cd, Cu, Ni, and Zn) from surface-applied sewage sludge through the use of soil columns. Analysis of the soils in the columns indicated the metals had not moved out of the layer of incorporation. The solid phase forms of the metals in the sludge-soil layers were found to be almost exclusively in the stable organically bound, carbonate, and residual forms. The movement of metals out of the sludge-soil layers was probably prevented by metals being in the stable solid phase forms. The influence of the stable solid phase forms of the metals on movement was evident by their control of the total metal concentrations in the soil solutions. The total metal concentrations in the soil solutions were extremely low and could not significantly contribute to movement of metals in soil profiles.

The implication of the study was that soils seem to be able to retain and prevent ground water contamination from heavy metals added by soil surface applications of sewage sludges, under the conditions of the study. Further studies were recommended to evaluate more diverse soil types and different management conditions.

Schalscha, et al. (1982) demonstrated the adsorbed and exchangeable fractions were not significant chemical forms of heavy metals in the soil. Although considerable amounts of metals were added into the soil in the soluble and exchangeable forms during waste water irrigation, they were converted into the chemically less active forms (organically bonded and inorganic precipitates).

The lack of heavy metals in the soluble and exchangeable forms would greatly reduce the leaching potential of the heavy metals deposited in the soil. However, the accumulation of waste water originated metals in organic complexes and inorganic precipitates may enable them to become reactive whenever the chemical equilibrium in the soil shifts. These results also indicate the need for additional studies examining the affect of changing soil chemistry on the chemical equilbrium in soils.

Sposito, et al. (1982) studied the fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases of soils amended with sewage sludge. The percentage of the total metal content in exchangeable and sorbed forms was very low, averaging between 1.1 and 3.7% for all of the metals regardless of the type of soil, the form of sludge applied, or the sludge application rate. The application of sludge tended to reduce the residual fraction and to increase the organic and carbonate fractions of all five trace metals. At the highest rate of sludge application, the predominant forms of the metals were: Ni, residual; Cu, organic; and Zn, Cd, and Pb, carbonate.

Emmerich, et al. (1982a) mixed anaerobically digested sewage sludge in either liquid or air-dried form into reconstructed soil profiles and leached for 25 months with river water. The metals (Cd, Cu, Ni, and Zn) added into the soil had not moved out of the sludge-soil layers during the course of leaching. Most of each of the metals were found in the organically bound, carbonate, or residual forms, with the relative distribution among these forms depending on whether samples were taken in or below the sludge-soil layer. A shift toward the more stable residual form after soil incorporation was also detected.

The sewage sludge applied to the soils seemed to be controlling the chemical forms of the metals. The percentage of any metal in a certain chemical form in the sludge-soil layers was essentially independent of soil type and for all soils did not differ by more than 10%. The almost constant percentage of a metal indicated that soil properties did not influence the chemical forms of the metals in the sludge-soil layers. The physical condition of the applied sludge (i.e., wet or dry) also did not affect the chemical forms of the metals present at the termination of leaching.

In another report dealing with the same study, Emmerich, et al. (1982b), stated that although no metal movement was observed, situations conducive to metal movement are conceivable. Physical mechanisms of heavy metal movement could include colloidal precipitates and clay particles moving with the soil solution carrying the metals, or sludge moving through cracks in the soil created by repeated wetting and drying cycles. Also, a pH reduction in the sludge-soil layer could increase the solubilization of the metals and induce movement in soil profiles.

Two soils treated with a composted sludge and two liquid sludges annually for 7 consecutive years and cropped to barley each year were sampled at 4-week intervals following planting (Chang, et al., 1984). Barley tissue samples were also obtained at the time of each soil sampling. In untreated soils, essentially all of the heavy metals were present in either the residual form (Cr, Cu, Ni, and Zn) or the carbonate form (Cd and Pb). With sludge treatment, every extracted fraction showed increases in the amounts of heavy metals. However, the most significant increases occurred in the carbonate fraction and, sometimes, in organically bonded fractions as well. There was little indication that the distribution pattern of the solid phase heavy metals in the sludge treated soils changed with time from planting to harvesting. The Cd and Zn concentrations in barley grown in the sludge treated soil were consistently higher than those in the non-sludged control, and the rate of uptake of Cd and Zn by barley progressively decreased with plant development. Since the percentage of Cd and Zn in each extracted fraction did not change appreciably throughout the growing season, the differential Cd and Zn uptake by barley with plant development cannot be related to the chemical transformation of solid phase heavy metals in the soil during the growing season.

These investigations which explored metals in sewage sludge amended soils all employed the sequential extraction method used in the present study dealing with drilling muds. The results from these past studies indicate the following, regarding sludge-amended soils:

(1) solid phase forms of metals were found to be almost exclusively in the stable organically bound, carbonate, and residual forms,

(2) a shift toward more stable forms after soil incorporation was detected, and

(3) additional studies are needed to examine the effect of changing soil chemistry on the fate of metals.

While these studies dealt with sewage sludge and not drilling muds, clearly the problems encountered are similar. Drilling mud study results which correlate with these sewage studies will make it possible to extend the results of previous studies to a further understanding of drilling muds, especially in the area of landfarming of drilling fluid wastes. Also, this drilling mud study is designed to explore the area of changing soil chemistry on metal fate by varying solution pH and ionic strength.

Chemical Properties of Arsenic, Barium, Chromium and Lead

Arsenic, barium, chromium and lead were chosen as toxic metals to be studied because of their prevalence in drilling muds (Canter, et al., 1984b). It does not appear that any arsenic compounds are added directly to drilling fluids but they occur as trace constituents in the clay or other additives. Barium is added directly as barite ($BaSO_4$) and acts primarily as a weighting agent. Chromium is added as a lignosulfonate or to a lesser extent as chromate salts. Lead compounds may also be added as weighting agents (Ranney, 1979).

Arsenic

Arsenic exists in nature in the 3-, 0, 3+ and 5+ oxidation states, however, it is normally found as an anion with acid characteristics in only the trivalent (arsenite) and pentavalent (arsenate) forms. The valence and the species are dependent on oxidation-reduction conditions and the pH of the water. Arsenite is more likely to be found in anaerobic ground waters and arsenate in aerobic surface waters (Sorg and Logsdon, 1978). The rate of oxidation of arsenic (III) to arsenic (V) with oxygen was found to be very slow at neutral pH values but faster in strong alkaline or acid solutions (Fergusen and Gavis, 1972).

Trivalent As exists primarily as the mononuclear species as $As(OH)_3$, $As(OH)_4^-$, AsO_2OH^{2-}, and AsO^{3-}. Polymeric species may include $As_2(OH)_7^-$, $As_2(OH)_8^{2-}$, and $As_3(OH)_{10}^-$, however, they are not expected to be significant in very dilute solutions (Eichenberger and Chen, 1982). The stability diagram (Eh-pH) for the hydrolysis species of inorganic arsenic can be used to thermodynamically predict predominant species (Figure 12).

Pentavalent As is found primarily as the species $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. Many cations form insoluble arsenate salts (Eichenberger and Chen, 1982). Figure 13 shows the solubility relationships of various arsenate minerals (Sadiq, et al., 1983). This diagram is strictly theoretical and based on thermodynamic information. Arsenate species have been shown to adsorb to hydrous iron oxide, aluminum hydroxide and clays (Osishi and Sunell, 1975; LaPointre, 1954).

Both As (III) and As (V) form methylated compounds by microbial conversion. Trivalent As forms dimethylarsenic acid, $(CH_3)_2AsO(OH)$, which ionizes to $(CH_3)_2AsO^{2-}$. Pentavalent As forms methylarsenic acid, $CH_3AsO(OH)_2$, which dissociates to form $CH_3AsO_2OH^-$ and $CH_3AsO_3^{2-}$ (Eichenberger and Chen, 1982).

These species possess different chemical properties which affect the mobility of arsenic in natural systems. Transformations between the different oxidation states and species of arsenic may occur as a result of chemical or biochemical reactions.

Arsenic may form insoluble precipitates with calcium, sulfur, iron, aluminum and barium compounds in natural waters (Wagemann, 1978). Figure 14 includes the effects of barium which was found capable of holding total dissolved arsenic to rather low concentrations (Wagemann, 1978). These precipitates are slow in nucleating and exhibit slow growth rates. Arsenic species are more likely to be adsorbed on the surface of organic and inorganic substrates than as crystalline

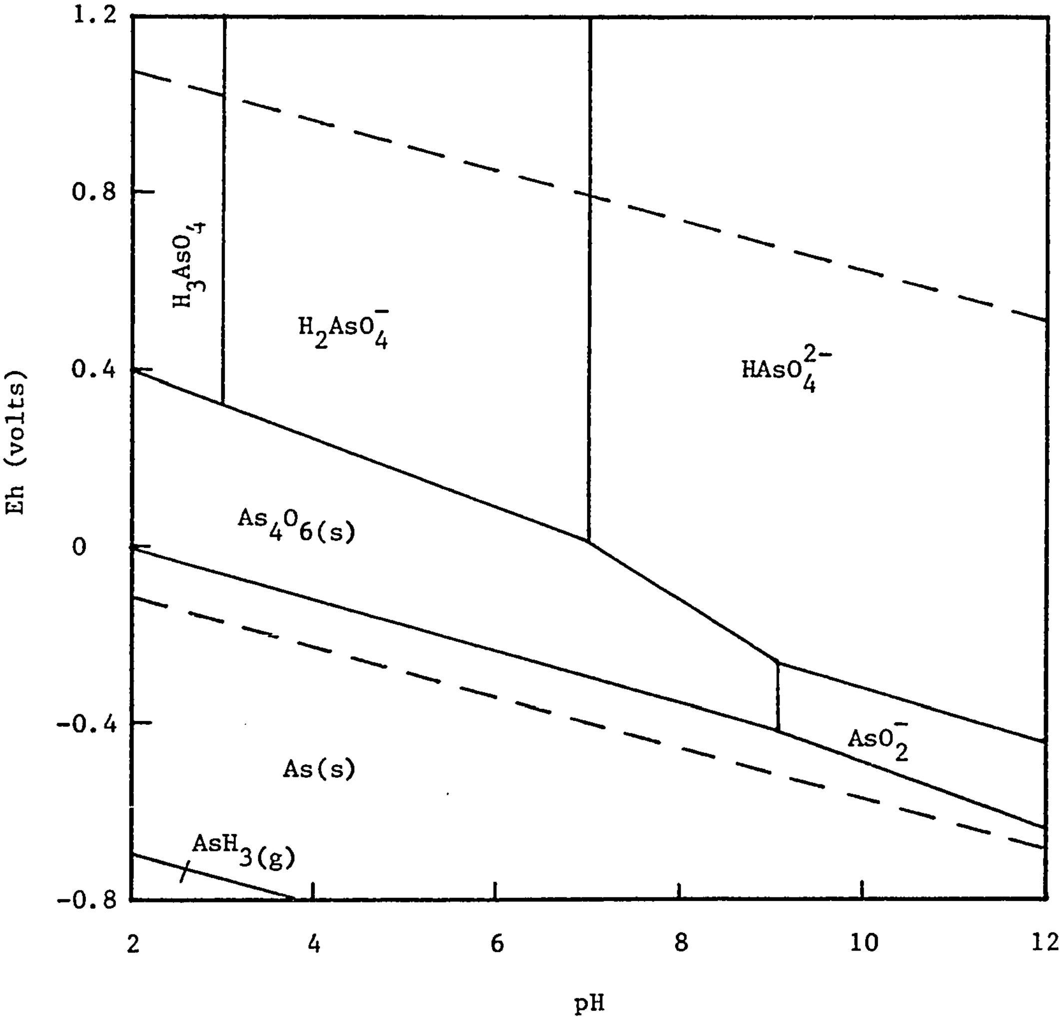


Figure 12: Eh-pH Diagram of Arsenic Hydrolysis Species (Campbell and Whiteker, 1969)

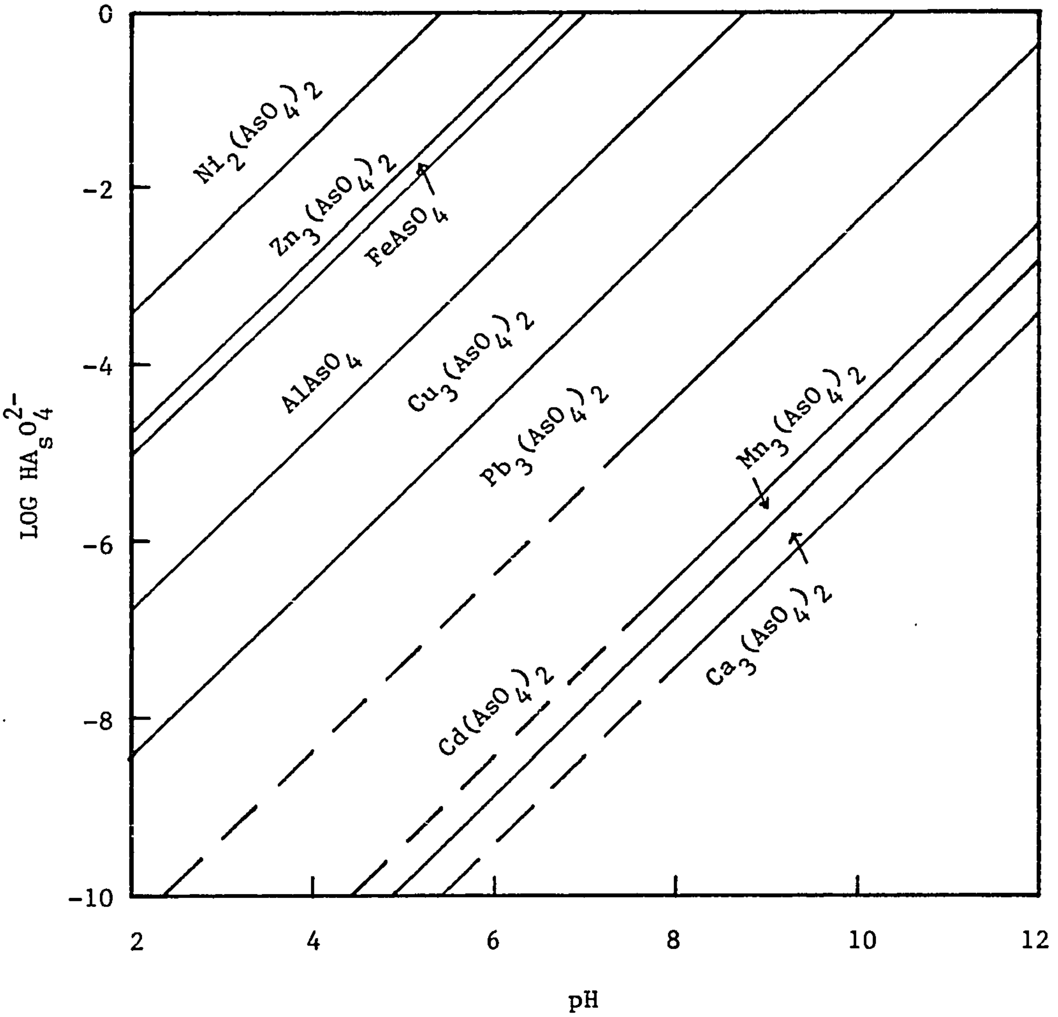


Figure 13: The Stability of Metal Arsenate, $CO_{2(g)}$=0.003 atm (Sadiq, et al., 1983)

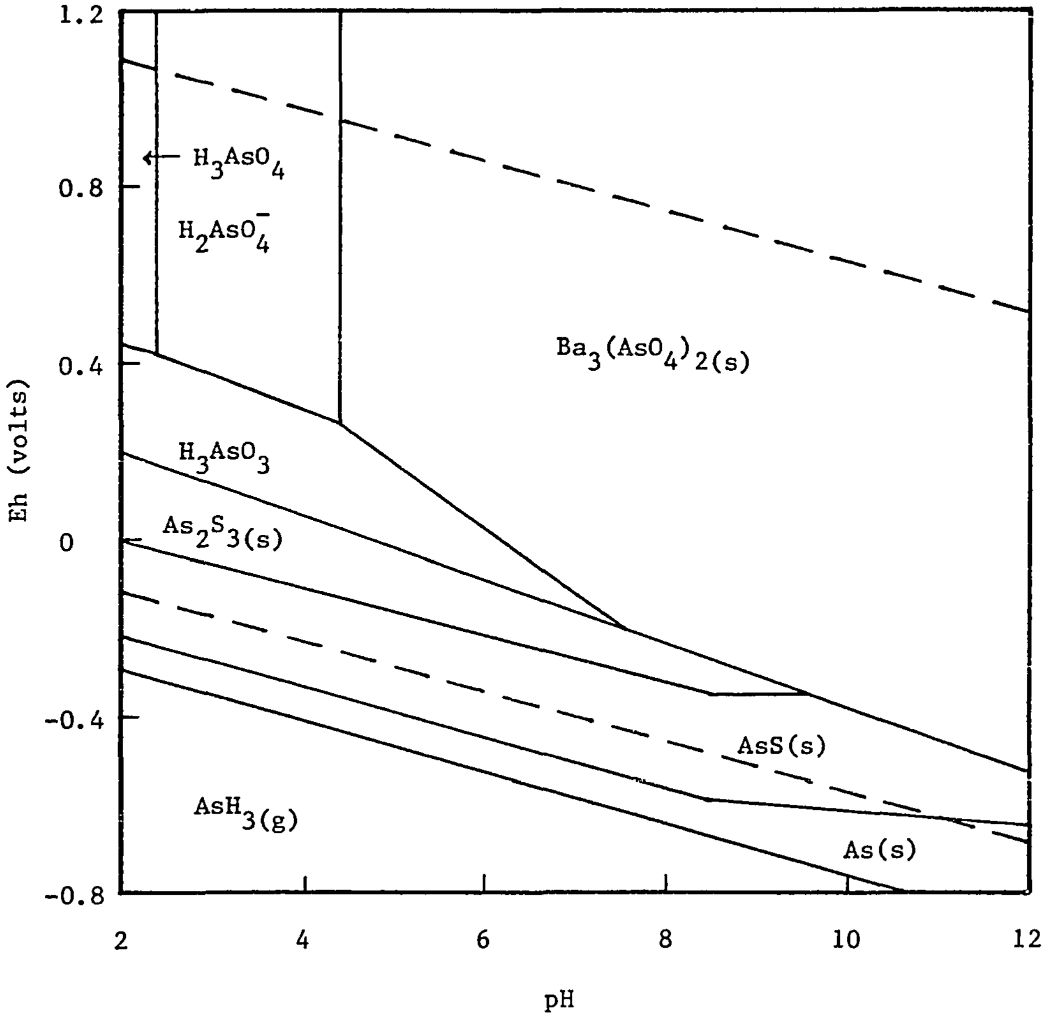


Figure 14: Eh-pH Diagram for Arsenic at 25°C and 1 atm Pressure (Wagemann, 1978) $(As)_t=10^{-5}M$, $(S)_t=10^{-3}M$, and $(Ba)_t=2.2 \times 10^{-7}M$

precipitates. Arsenic was found to be distributed among operationally defined fractions of sediment solids in the order of abundance OH^- (Fe and Al) $>$ oxalate (amorphous or occluded) $>>$ Cl^- (exchangeable) $>>$ H^+ (Ca or arsenopatite) (Holm, et al., 1979).

Arsenate, in municipal landfill leachate, was found to be more effectively adsorbed to clays than arsenite (Figure 15). This same study found that pH has a pronounced effect on the amounts adsorbed (Figure 16) and that the principal adsorption mechanism was anion exchange (Griffin, et al., 1977).

It is clear that much arsenic chemistry is unknown and much of the information that is available is strictly theoretical. The evidence indicates that arsenic under conditions encountered in drilling muds with high clay and barium content might be expected to exist as an insoluble barium species at pH $>$ 4 and as a clay adsorbed ion at lower pH values.

Barium

Barium occurs in only one major form, as a divalent cation (+2). Barium is rare in natural waters because its carbonate ($BaCO_3$) and sulfate ($BaSO_4$) forms are highly insoluble. Also, barium is only slightly soluble in the hydroxide ($Ba(OH)_2$) form. It is therefore expected that any barium ions from soluble salts discharged to natural waters will be precipitated and removed by sedimentation. However, the chloride form of barium is very soluble and could result in a high solubility of barium (Sorg and Logsdon, 1980). Stability diagrams (Eh-

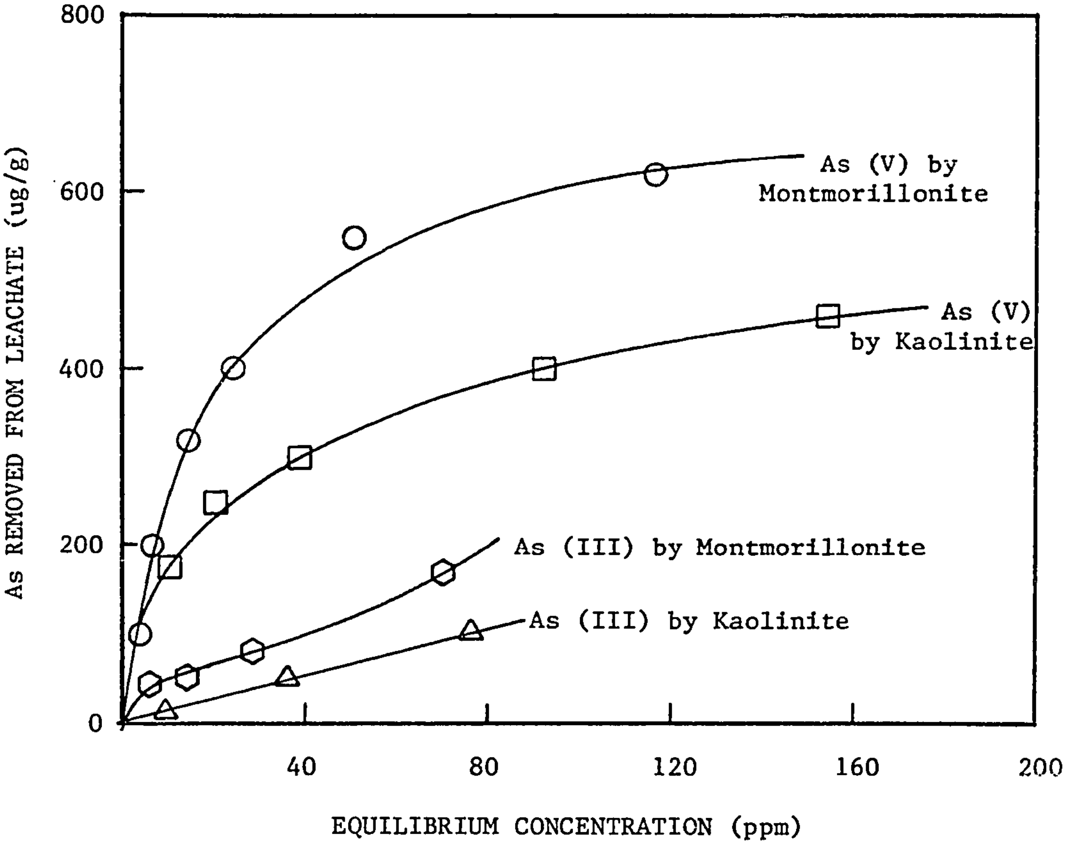


Figure 15: Amount of As (V) or As (III) Removed from Leachate Solutions at pH 5.0 and 25°C per Gram of Clay, Plotted as a Function of the Equilibrium Arsenic Concentration (Griffin, et al., 1977)

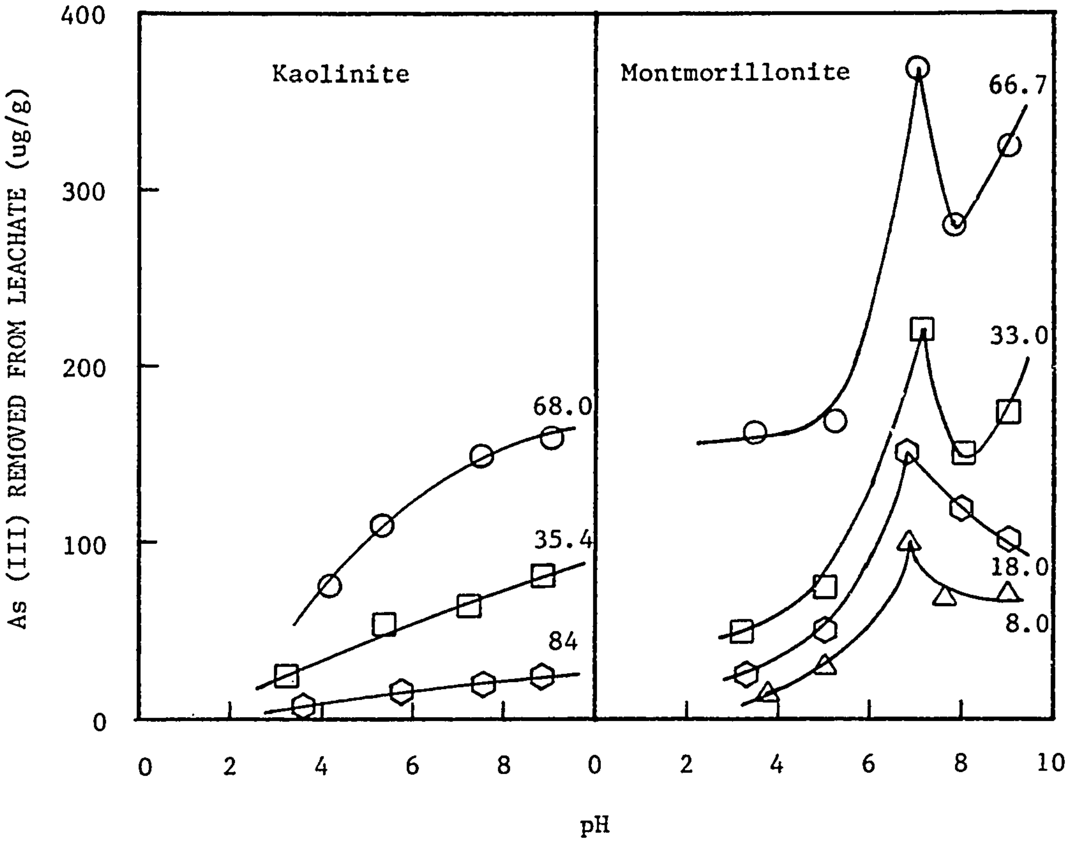


Figure 16: Amount of As (III) Removed from Leachate Solutions by Kaolinite and Montmorillonite at 25°C, Plotted as a Function of pH. Numbers on Curves Gives the Initial Solution Concentration of As (III) in ppm (Griffin, et al., 1977)

pH) for some barium species indicates some of this expected behavior (Figures 17, 18 and 19).

Barium may also be removed from solution by adsorption on clay minerals, a process favored by its large size and low ionic potential (Eichenberger and Chen, 1982). Barium has been reported to form some poorly characterized β-diketone complexes and unstable amines (Heslop and Robinson, 1967). Barium may also form insoluble constituents in the presence of arsenate as has been mentioned in the review of arsenic behavior.

In summary, barium would be expected to be present in either its sulfate or carbonate form in drilling muds. However, should the chloride levels be greatly elevated there may be some solubilization as barium chloride. Barium is generally added to drilling muds as the sulfate (barite) which is very insoluble at any pH greater than 2 and would be expected to remain in this state.

Chromium

Chromium has several oxidation states, but only the trivalent and hexavalent forms are significant in aqueous systems (Figure 20). Trivalent chromium occurs as a cation and the hydroxide complex is very insoluble (Sorg, 1979). Hexavalent chromium occurs as an anion as either chromate ($HCrO_4^-/CrO_4^=$) or dichromate ($Cr_2O_7^{2-}$) (Tandon, et al., 1984).

Chromium (III) complexes borate, fluorate, ammonia, cyanide, thiocyanate, oxalate, sulfate, citric acid, serine, and a great many organic ligands (Eichenberger and Chen, 1982). Chromium (III)

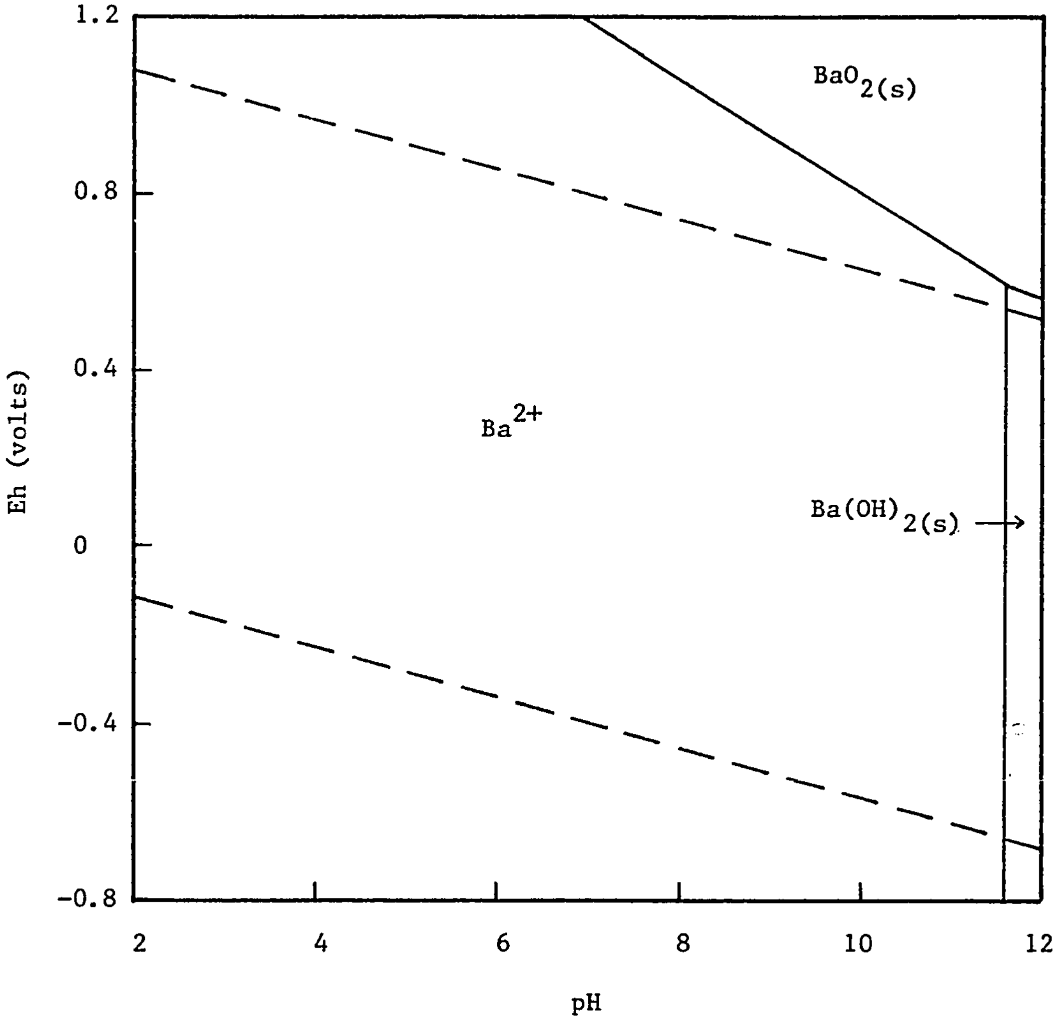


Figure 17: Eh-pH Diagram of Barium Hydrolysis Species (Campbell and Whiteker, 1969)

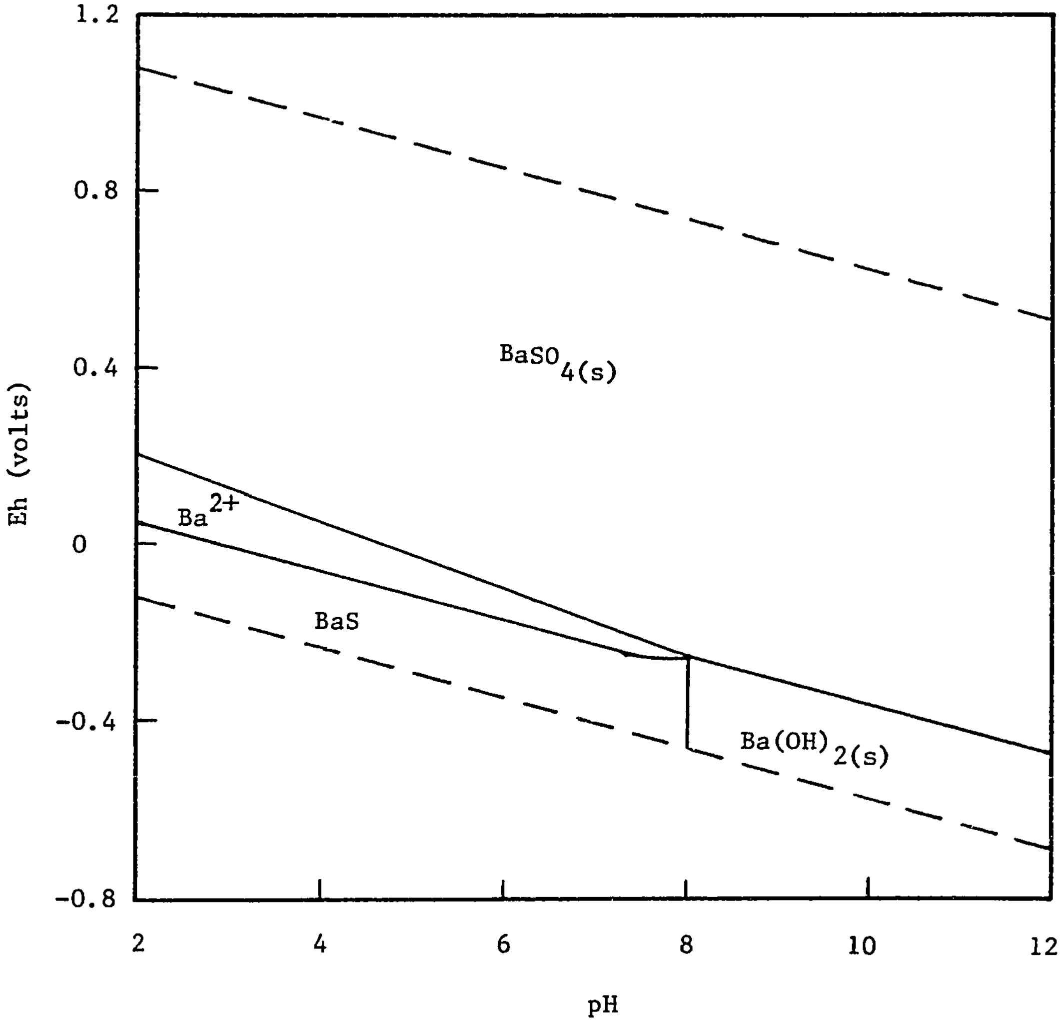


Figure 18: Eh-pH Diagram for Barium at 25°C and 1 atm Pressure (Schmitt, 1962) $(S)_t=10^{-1}$

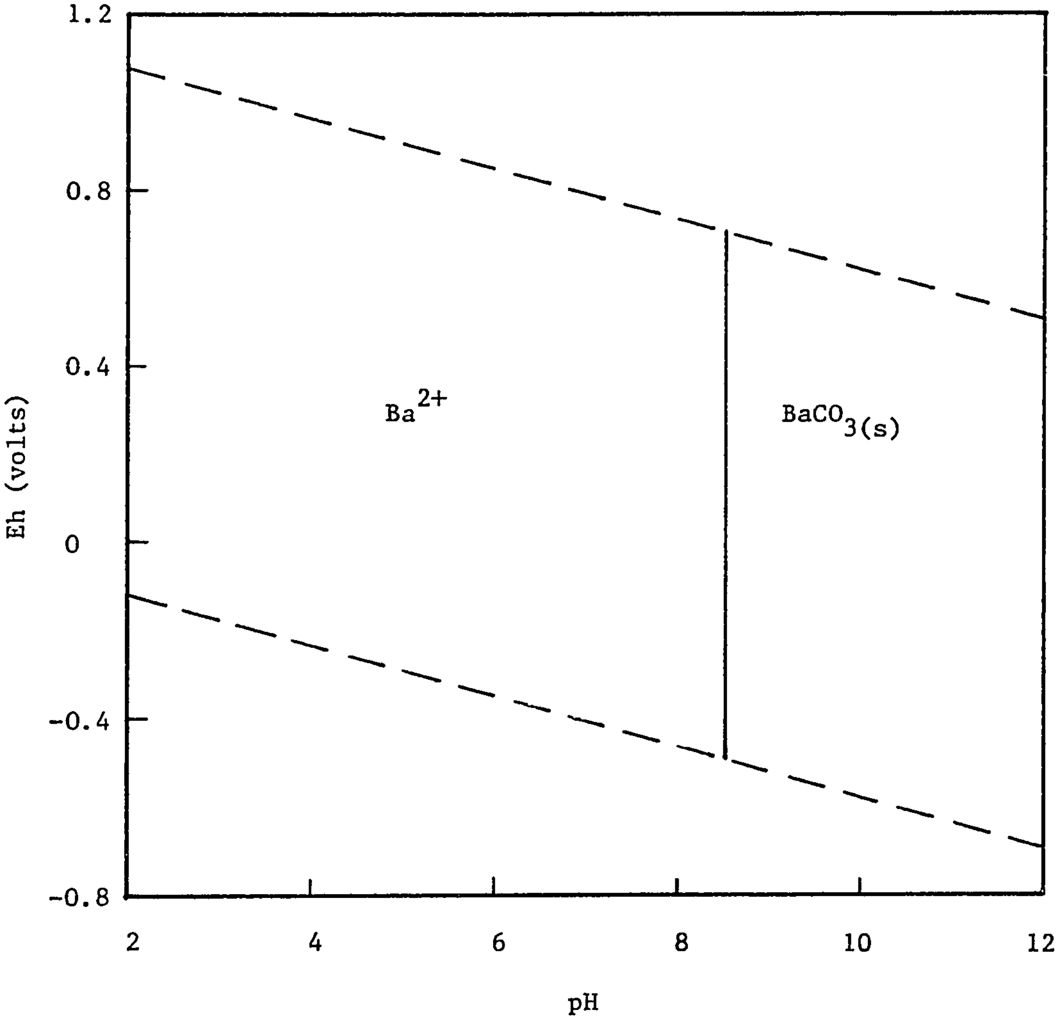


Figure 19: Eh-pH Diagram for Barium at 25°C and 1 atm Pressure (Schmitt, 1962) $(CO_3)_t = 10^{-3}$

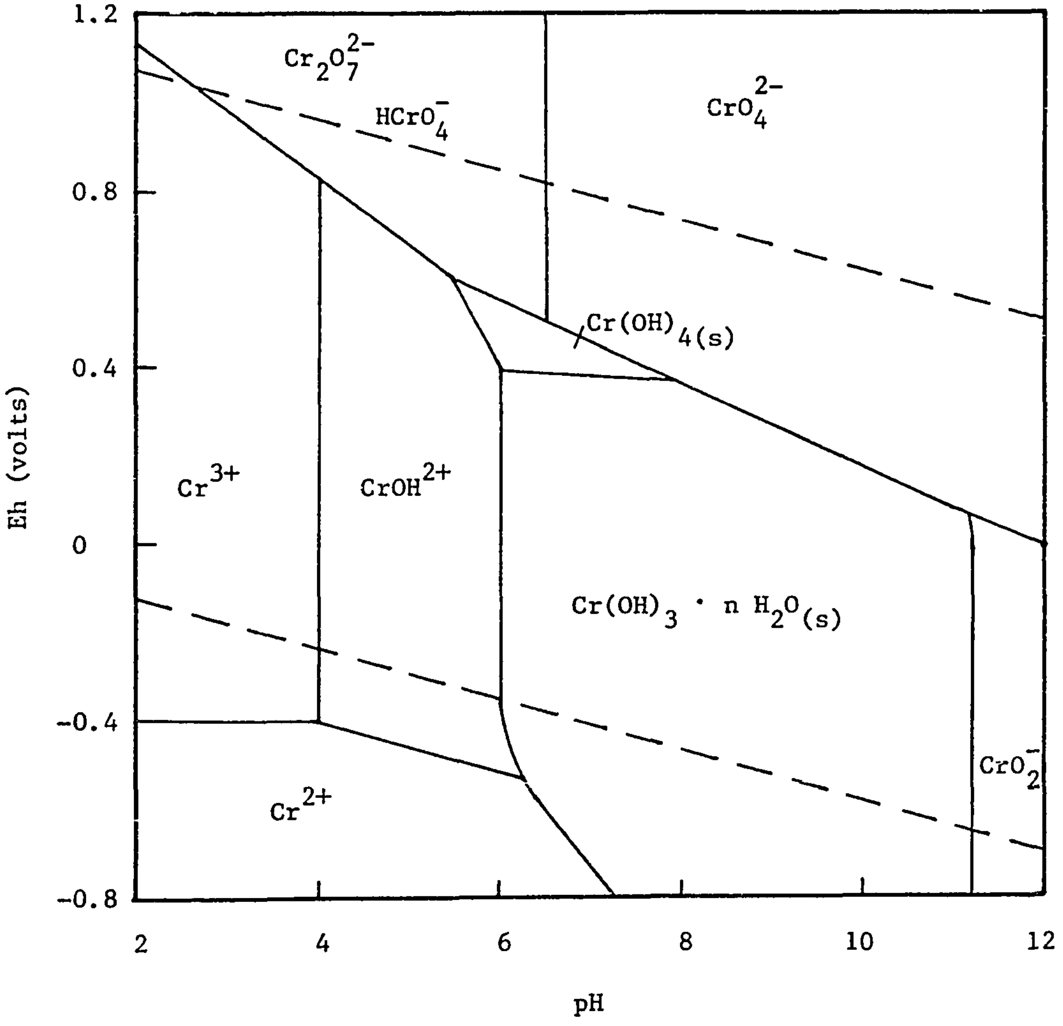


Figure 20: Eh-pH Diagram for the System Chromium-Water at 25°C in Solutions Containing Chlorides $(Cr)_t=10^{-4}$ (Faust, et al., 1981)

mononuclear hydrolysis reactions occur rapidly to yield the species $CrOH^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_4^{-}$, and the neutral species $Cr(OH)_3$. Possible polynuclear species are $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$. Chromium hydroxide, $Cr(OH)_3$, is very insoluble and easily adsorbed onto natural solids.

The hexavalent form is more likely to be found in solution because chromate ($HCrO_4^{-}$) and dichromate (CrO_4^{2-}) are very soluble. At pH 6.5-8.5 under oxygenated conditions, chromium (VI) is the thermodynamically stable species, however, chromium (III) could also be kinetically stable under these conditions (Shroeder and Lee, 1975).

The oxidation of chromium (III) to chromium (VI) by oxygen is slow because other reactions such as adsorption may occur before it can be oxidized. Sulfides and ferrous iron will reduce chromium (VI) to chromium (III) dependent on pH and concentration. Below pH 4, chromium (III) species have been found to be strongly adsorbed by clays (Griffin, et al., 1977). Chromium (VI) removal by clays is much less than that for chromium (III) (Griffin, et al., 1977).

In summary, under most conditions chromium (III) will be present as an insoluble precipitate or adsorbed to clays at lower pH values while chromium (VI) will exist in a soluble state. However, chromium (III) is not likely to be transformed to chromium (VI), and chromium (VI) is easily reduced to chromium (III). Therefore, unless chromium enters the environment in the hexavalent state it is not likely to be present in a soluble form.

Lead

Lead occurs in nature in the 0, 2+, and 4+ oxidation states.

Lead (II) is the most common form and exhibits complex hydrolysis behavior (Figure 21). Lead (II) also forms complexes with carbonate and sulfur (Figure 22). Additional complexes include soluble chloride complexes, methyllead ion $(CH_3)_2Pb^{2+}$ and methyllead hydrolysis species.

The solubility of lead is greatly influenced by pH and the carbonate ion concentration. The most significant insoluble complexes include the carbonate ($PbCO_3$), hydroxide ($Pb(OH)_2$), and hydroxycarbonate ($Pb(OH)_2(CO_3)_2$). The carbonate form occurs in the 5-8 pH range, the hydroxycarbonate form in the 7.5-8.5 pH range, and the hydroxide above pH 8.5 (Sorg, et al., 1978).

Lead (II) has been reported adsorbed by clays at $pH > 6$ (Griffin, et al., 1977). However, at $pH < 6$ the low Pb sorption is apparently due to increased competition for sorption sites (Figure 23).

In summary, under most conditions to be encountered in the environment lead would be present as insoluble carbonates, sulfate, or hydroxide. However, in low pH or high chloride ion waters, lead may be present as soluble Pb^{2+} or $PbCl^+$, respectively.

Flyash Stabilization of Drilling Fluid Wastes

Stabilization/Solidification -- Background

A land-based disposal alternative to simple direct pit disposal of drilling fluids is to structurally isolate the waste material in a solid matrix so that the solid mass can be safely disposed of by conventional techniques, a process known as stabilization/solidification.

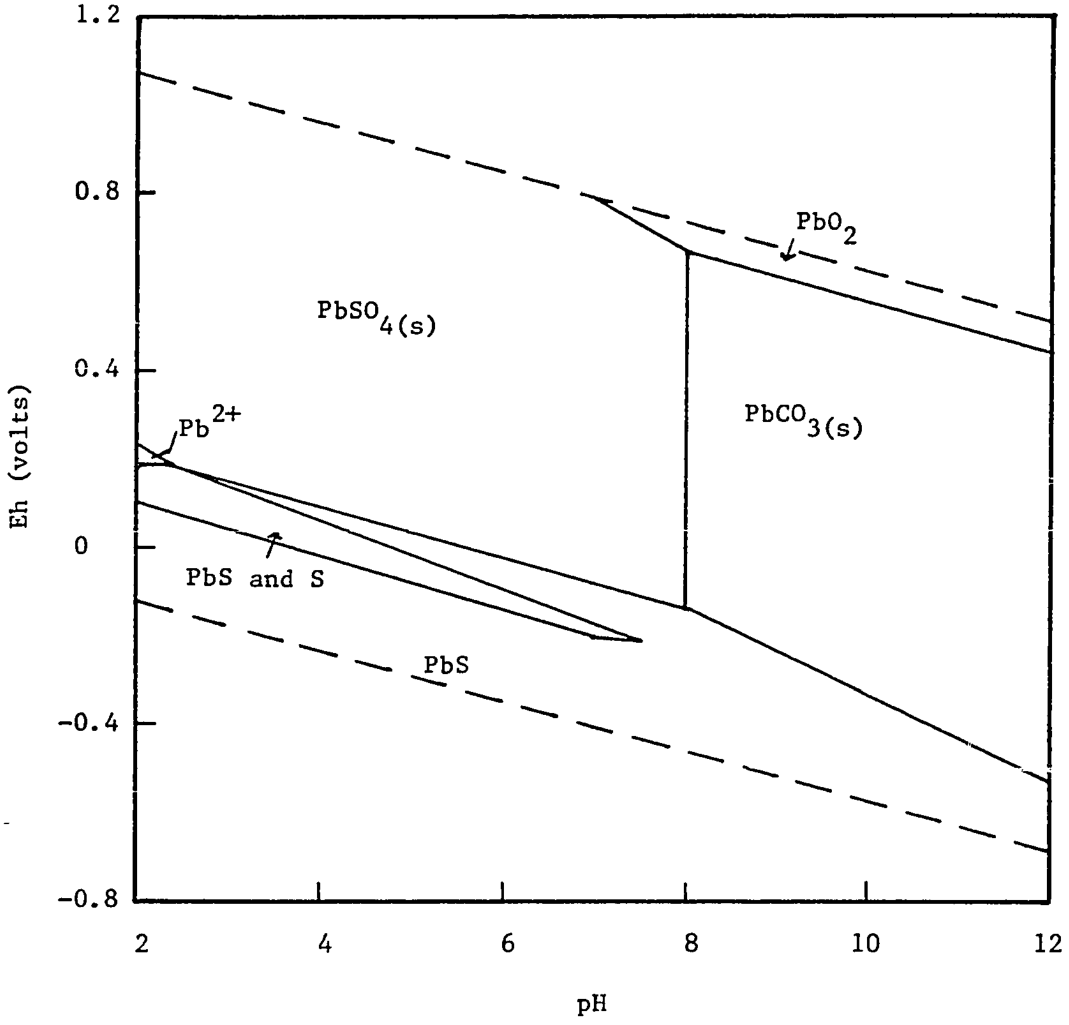


Figure 21: Eh-pH Diagram for Lead in Solutions Containing Sulfates and Carbonates (Garrells and Christ, 1965)

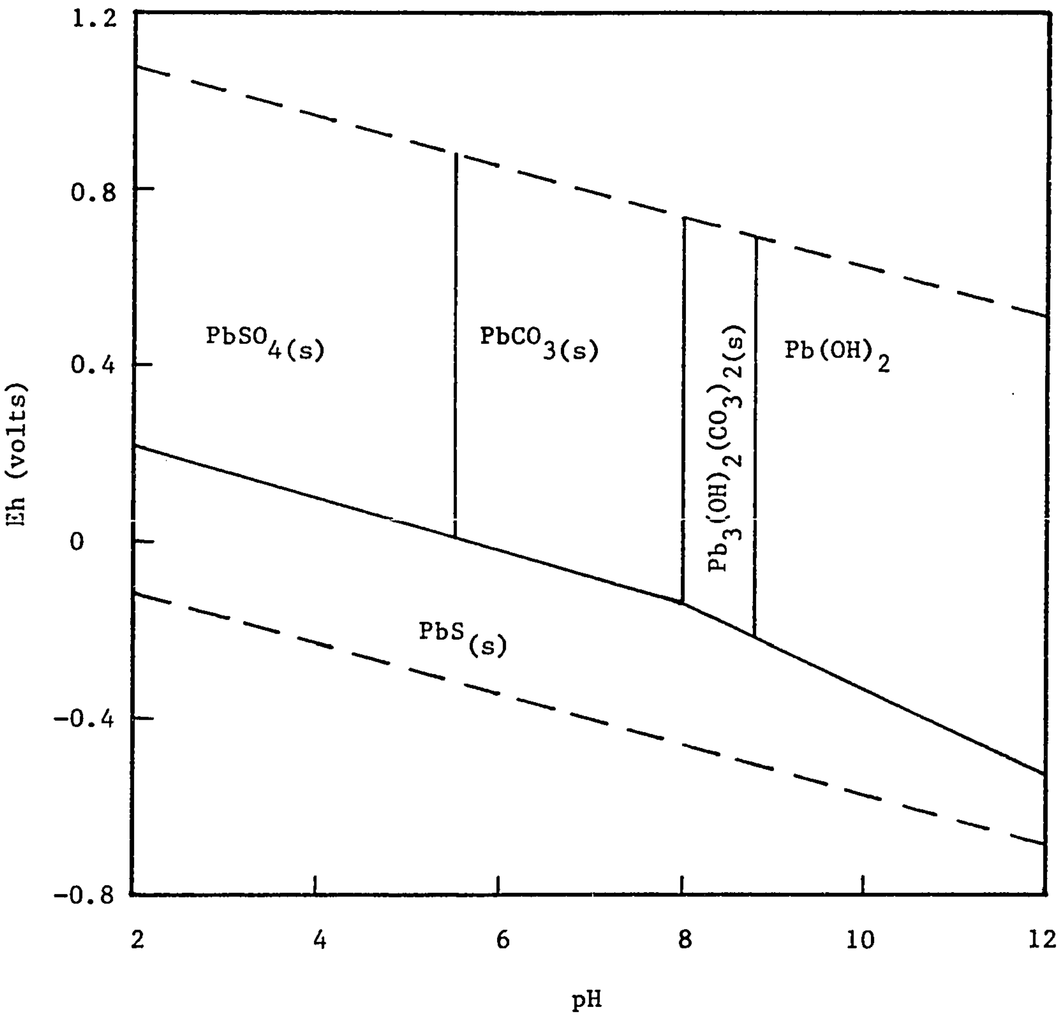


Figure 22: Eh-pH Diagram for Lead in Solutions at 25°C and 1 atm Containing Sulfates, Carbonates and Considering Hydrolysis Species (Hem and Durum, 1973)

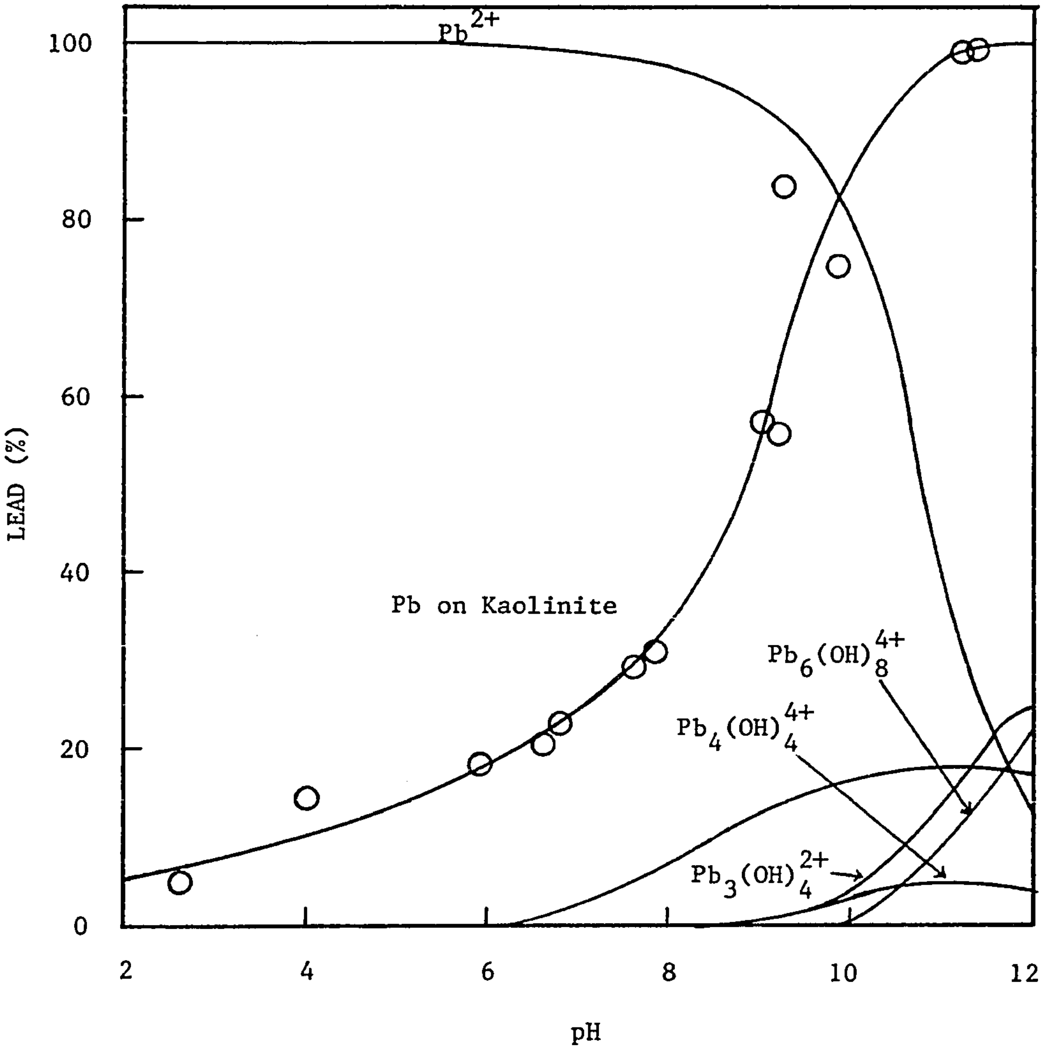


Figure 23: Distribution of Lead (II) Species in 4×10^{-4} M $Pb(NO_3)_2$ and Uptake by 0.1 g Kaolinite from 60 ml of Solution (Griffin, et al., 1977)

The objective of solidification/stabilization processes is to chemically fix the waste in a solid matrix. This reduces the exposed surface area and minimizes leaching of toxic constituents. Effective immobilization includes reacting toxic components chemically to form compounds immobile in the environment and/or by entrapping the toxic material in an inert stable solid. Thus stabilization and solidification have different meanings although the terms are often used interchangeably (Pojasek, 1978):

(1) Stabilization -- immobilization by chemical reaction or entrapping (watertight inert polymer or crystal lattice).

(2) Solidification -- production of a solid, monolithic mass with sufficient integrity to be easily transported.

These processes may overlap or take place within one operation. An example is cementation where the process both stabilizes by producing insoluble heavy metal compounds and solidifies into a formed mass while entrapping the pollutants.

Chemical stabilization is designed to provide a substance which is more resistant to leaching and also more amenable to the solidification process. By chemically fixing the hazardous waste constituents, their release will be minimized in the event of a breakdown of the solid matrix.

Probably the simplest stabilization process is pH adjustment. In most industrial sludges, toxic metals are precipitated as amorphous hydroxides that are insoluble at an elevated pH. By carefully selecting a stabilization system of suitable pH, the solubility of any metal hydroxide can be minimized. Certain metals can also be stabilized by forming insoluble carbonates or sulfides. Care should be taken to ensure that these metals are not remobilized because of changes in pH or redox conditions after they have been introduced into the environment. Where possible, it is desirable to co-dispose of wastes which stabilize without the addition of extraneous chemicals.

The stabilized waste is solidified into a solid mass by microencapsulation or macroencapsulation. Microencapsulation is the dispersion and chemical reaction of the toxic materials within a solid matrix. Therefore, any breakdown of the solid material only exposes material at the surface to potential release to the environment. Macroencapsulation is the sealing of the waste in a thick, relatively impermeable coating layer. Plastic and asphalt coatings or secured land disposal are considered macroencapsulation methods. Breakdown of the protective layer with macroencapsulation could result in a significant release of toxic material to the environment.

Stabilization techniques have concentrated on the containment of toxic inorganic compounds. This is because many of the techniques originated as methods for treating radioactive wastes which consist primarily of inorganic isotopes. Also organic compounds may interfere with the stabilization/solidification process, although small amounts may be mixed in under tested conditions. Chemical oxidation or incineration have been found to be the most successful treatment methods for the majority of dangerous organic chemicals.

Inorganic elements cannot be destroyed and must be disposed of in a manner that limits their migration to the environment. Total immobilization of a contaminant is not normally possible, but the rate of release can be slowed to the point that no serious stresses are exerted on the environment.

Stabilization/solidification processes should produce a material whose physical placement will not render the land on which it is disposed unusable for other purposes. The material should be impervious, with good dimensional stability and load bearing characteristics. It should also have satisfactory wet-dry and freeze-thaw weathering resistance. These properties plus optimum size and shape will make them easily transportable under U.S. Department of Transportation (DOT) regulations, when compared with the precautions necessary when shipping wet wastes or sludges.

There is no optimum stabilization/solidification process which is applicable to every type of hazardous waste. Each individual waste must be characterized and bench tests and pilot studies performed to determine the suitability of a disposal process. Present solidification/stabilization systems can be grouped into seven classes of processes (U.S. Environmental Protection Agency, 1979):

(1) Solidification through cement addition.

(2) Solidification through the addition of lime and other pozzolonic materials.

(3) Techniques involving embedding wastes in thermoplastic materials such as bitumen, parafin, or polyethylene.

(4) Solidification by addition of an organic polymer.

(5) Encapsulation of wastes in an inert coating.

(6) Treatment of the wastes to produce a cementitious product with major additions of other constituents.

(7) The formation of a glass by fusion of wastes with silica.

Effect of Flyash Stabilization of Drilling Fluids on Toxic Metal Availability

The stabilization/solidification of drilling fluids by using flyash has been suggested and attempted (Musser, 1984). The process consists of injecting a suitable amount of flyash into a pit containing drilling fluids to change the physical nature of the waste. Drilling muds retain moisture and are physically unstable because they are primarily wet clays. They dry slowly and are unsafe to walk upon. By mixing flyash with the muds they become more physically stable, less likely to pour out of a pit should a berm break, and can be worked with conventional heavy equipment.

The process would primarily work by dilution of one solid with the other, with some solidification because of calcium carbonates in the drilling fluid acting as a cementing agent. This is a desirable type of treatment since it provides for co-disposal of wastes (flyash and drilling mud) as long as the treatment itself does not result in some threat to the environment.

One possible effect of mixing the two wastes is the release of toxic metals. Since both flyash (Table 20) and drilling muds (Table 21) contain metals, there is cause for some concern. For this reason, studies were performed to test the uptake or release of toxic metals by mixtures of flyash and drilling muds.

Table 20: Typical Flyash Physical and Chemical Properties (Musser, 1984)

Physical:			
Surface Area cm^2/gm			4007.2
Mean Particle Diameter Size			5.65 micron
Percent Retained on 325 Mesh			8.08
Specific Gravity			2.65
Mineralogical:			
Quartz			23%
Hematite			9%
Chemical:			
SiO_2	35.5%	As	20.0 ppm
CaO	30.0%	Ba	5400.0 ppm
Al_2O_3	20.1%	B	210.0 ppm
Fe_2O_3	6.7%	Cd	< 20.0 ppm
MgO	4.5%	Cu	210.0 ppm
		Cr	470.0 ppm
TiO_2	1.8%	Pb	<40.0 ppm
SO_3	2.1%	Mn	550.0 ppm
P_2O_5	1.1%	Hg	< 2.5 ppm
		Ni	140.0 ppm
		Se	60.0 ppm
		Ag	<150.0 ppm
		Zn	170.0 ppm

Table 21: Mean Values of Metals Present in Drilling Fluids (Canter, et al., 1984b)

Metal	Mean Value (mg/kg)
Arsenic	18.2
Barium	3789
Cadmium	0.06
Calcium	28380
Chromium	58
Iron	21474
Lead	76.9
Magnesium	5248
Sodium	5214
Zinc	134

CHAPTER III

METHODS AND PROCEDURES

Sample Collection

Disposal Pit Location and Sampling Sites

Three active drilling fluid disposal sites located in central Oklahoma were sampled to obtain material for chemical analysis and laboratory experimentation (Figure 24). Observations were made at each of the three sites of physical features and maintenance practices. Schematic diagrams of each site accompanied by brief descriptions of site characteristics with the sampling location are presented in Figures 25 to 27.

Sampling for Background Chemical Analysis

All water and sediment samples were collected and analyzed in accordance with the procedures recommended by the U.S. Environmental Protection Agency or set forth by Standard Methods as listed in Table 22. Pit liquids were collected as grab samples in 1 liter narrow-mouth and 500 ml wide-mouth Nalgene bottles. After collection, the 1 liter samples were stored on ice and refrigerated upon arrival at the laboratory. The 500 ml samples were preserved by adding 3 milliliters of concentrated nitric acid. Sediment samples were collected using a

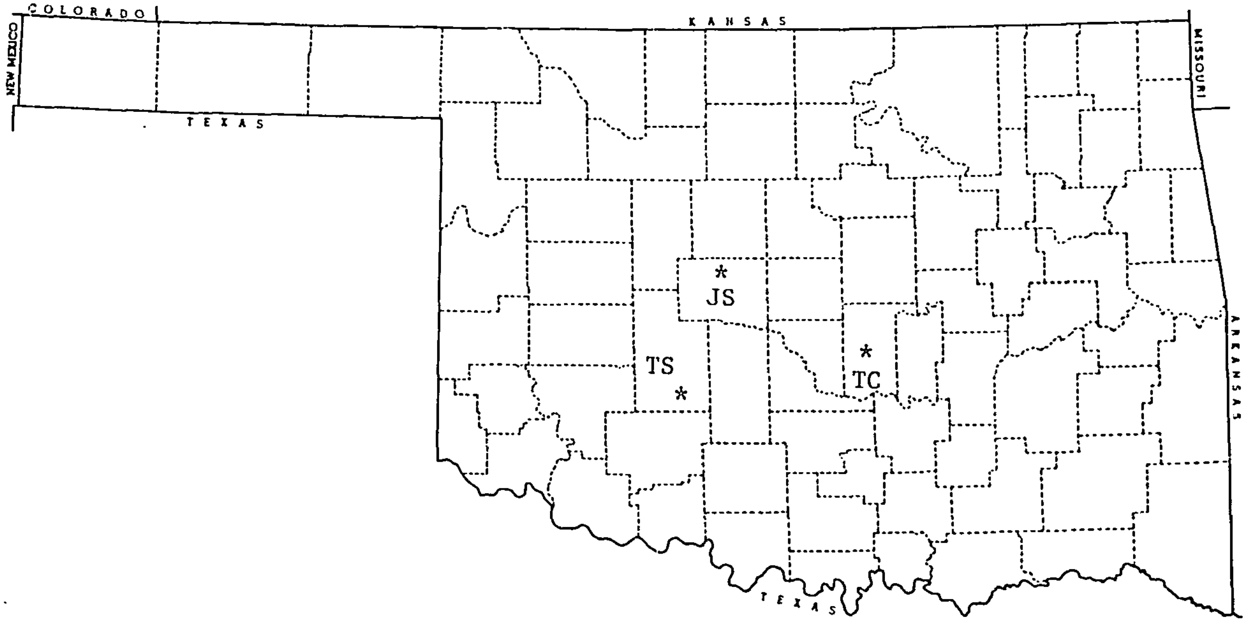
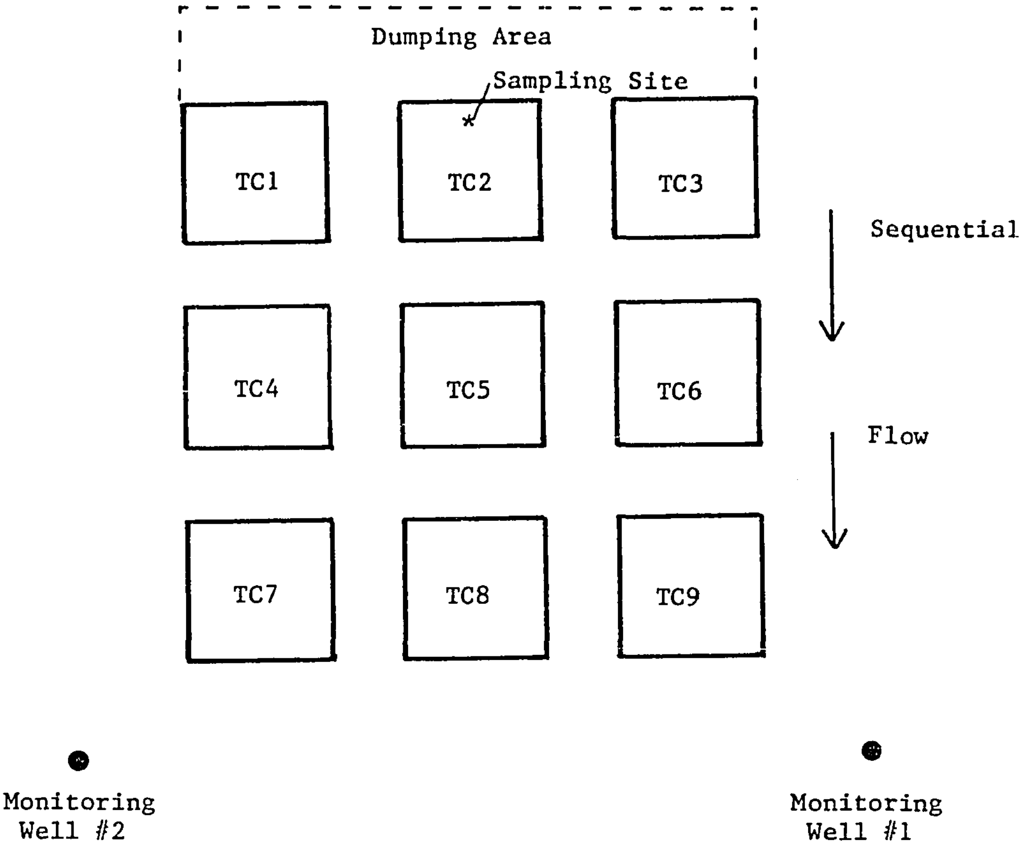
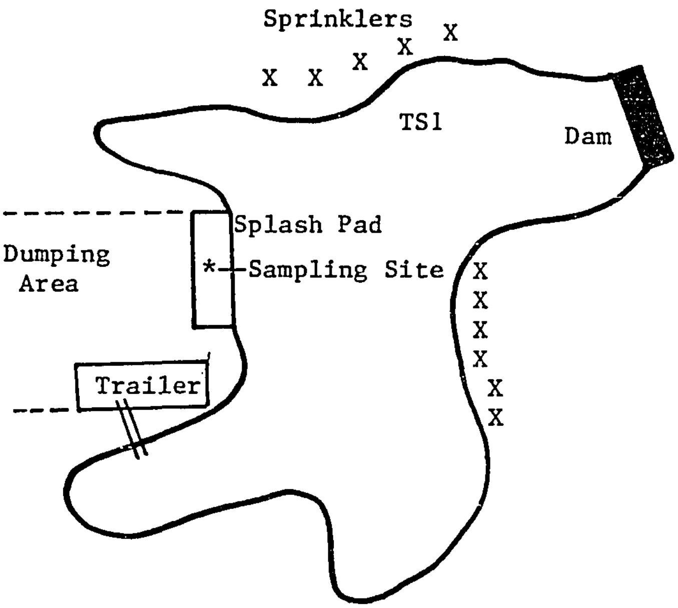


Figure 24: Location of Off-Site Drilling Fluid Disposal Pits which were Sampled for this Study



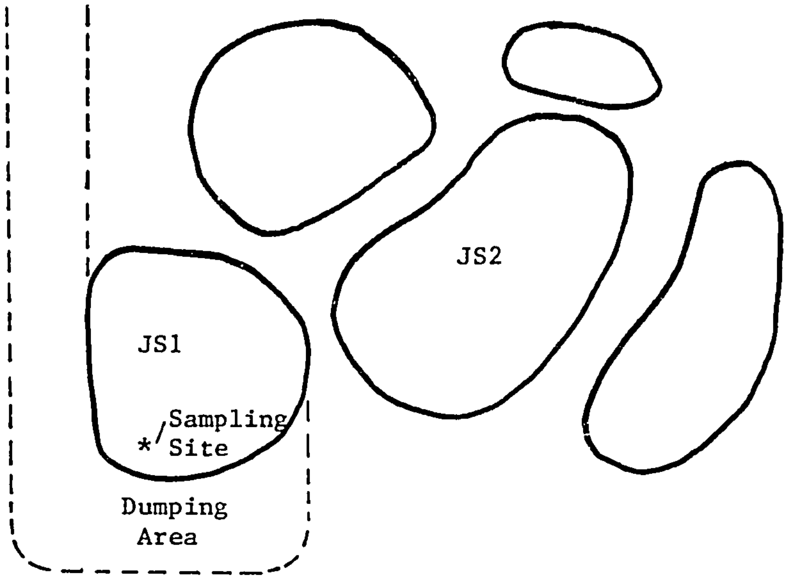
Disposal Site TC. This site was located 5 miles southeast of Tecumseh, Oklahoma in Pottawatomie County (SW NW Section 7-8N-4E). The site consisted of three tiers of 3 pits each, totaling 9 pits. Except for some short-circuiting in the eastern most pits, flow was sequential from the upper pits to the lower pits. The site was easily accessed but continuously monitored and controlled by personnel at the site. Additionally, the owner/operator has provided two ground water monitoring wells and a disposal hose in lieu of a splash pad. Erosion of pit berms was evident, but no seepage from the pits was visible.

Figure 25: Disposal Site TC



Disposal Site TS. This site was located about 2 miles south of Cement, Oklahoma in Caddo County (NE Section 22-5N-9W). The disposal operations consisted of 1 very large, irregularly shaped pit. The dam of this pit was 50 to 60 feet above the drainage basin. The site had lawn sprinklers which had been used to spray liquid into the air to increase evaporation. The site had a concrete splash pad guarded by a large diameter (10 inch) steel pipe. Access to the site was easy and disposal operations were controlled and monitored by personnel on-site 24 hours a day. Effluent from the small trailer housing on-site personnel was allowed to discharge directly to the pit. The site also had an unknown number of ground water monitoring wells which have been routinely sampled and analyzed.

Figure 26: Disposal Site TS



Disposal Site JS. This site was located about 10 miles north of El Reno, Oklahoma in Canadian County (SW Section 16-13N-7W). The site consisted of 5 pits of seemingly irregular construction and irregular placement. Sequential flow was not observable. The pits are situated on an area of local maximum relief which would mean rapid and total loss of fluids in the event of a berm break. Field inspector indicated that one of the berms had recently failed. Access to the site was very easy, but control and monitoring efforts were not known.

Figure 27: Disposal Site JS

Table 22: Methods of Water and Sediment/Solid Analysis

Parameter	Method	Reference
pH	Ion specific electrode	Standard Methods[1], pp. 402-409
Conductivity	Wheatstone bridge; conductance cell	Standard Methods, pp. 70-73
Chloride	Ion specific electrode	Orion Research Inc.[2], pp. 1-26
Alkalinity	Electrometric titration; glass electrode	Standard Methods, pp. 253-257
Salinity	Electrical Conductivity	Standard Methods, pp. 99-106
Total Dissolved Solids	Gravimetric	Standard Methods, pp. 93-94
Total Solids	Gravimetric	Standard Methods, pp. 92-93
Total Phosphorus	Stannous chloride; colorimetric	Standard Methods, pp. 409-421
Sulfate	Turbidimetric	Standard Methods, pp. 439-440
Nitrate	Brucine; colorimetric	U.S. EPA[3] (1979), pp. 352.1-1 to 352.1-3
Total Organic Carbon	Combustion-Infrared	Standard Methods, pp. 471-475
Chemical Oxygen Demand	Colorimetric; microdigestion	Hach Chemical Co.[4], pp. A2-A3
Sodium	Atomic Absorption Spectrophotometry	U.S. EPA (1979), pp. 273.1-1 to 273.1-2
Calcium	Atomic Absorption Spectrophotometry	U.S. EPA (1979), pp. 215.1-1 to 215.1-2

Table 22: (continued)

Parameter	Method	Reference
Magnesium	Atomic Absorption Spectrophotometry	U.S. EPA (1979), pp. 242.1-1 to 242.1-2
Lead	Atomic Absorption Spectrophotometry	U.S. EPA (1982)[5], 7420
Arsenic	Atomic Absorption Spectrophotometry	U.S. EPA (1982), 7060
Chromium	Atomic Absorption Spectrophotometry	U.S. EPA (1982), 7190
Barium	Atomic Absorption Spectrophotometry	U.S. EPA (1982), 7080
Zinc	Atomic Absorption Spectrophotometry	U.S. EPA (1982), 7950
Iron	Atomic Absorption Spectrophotometry	U.S. EPA (1979), pp. 236.1-1 to 236.1-2
Strontium	Atomic Absorption Spectrophotometry	Standard Methods, pp. 234-236
Cadmium	Atomic Absorption Spectrophotometry	U.S. EPA (1982), 7130

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[1] Standard Methods for the Examination of Water and Wastewater, 15th Edition, APHA-AWWA-WPCF, Washington, D.C., 1981

[2] Orion Research Incorporated, Chloride-Specific Ion Electrode Instruction Sheet, 840 Memorial Drive, Cambridge, Massachusetts, 02139, 1979.

[3] U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio, Mar. 1979.

Table 22: (continued)

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[4] Hach Chemical Company, Introduction to Chemical Oxygen Demand, Technical Information Series-Booklet No. 8, Loveland, Colorado, 1979.

[5] U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, SW-846, 2nd Ed., Office of Solid Waste and Emergency Response, Washington, D.C., July 1982.

sediment grab sampler. After collection, sediment samples were placed in 500 ml Nalgene bottles and stored on ice/refrigerated. Some duplicate water and sediment samples were collected to assure quality control of the collection and analysis procedures.

Sampling for Experimental Material

Samples collected for experimental work were collected whole (liquid and solid together) at the point of disposal. By collecting samples at this point, it was assumed they would be representative of the incoming waste. Samples were placed in 20 liter Nalgene containers and stored in the laboratory, where they were prepared for the laboratory experiments.

Flyash Sample

A class C flyash sample was obtained from David Musser, ENRECO, Inc., Amarillo, Texas. The flyash was used in the experiments as received. Total metals analyses and EP Toxicity Tests were performed on the sample prior to experimentation.

Chemical Analyses

The general methods used in all of the analyses for this study are summarized in Table 22. All results are reported as mg/l or ug/l for aqueous samples and mg/kg for sediment/solids other than parameters which are reported in other standard units (pH, salinity, conductivity, and temperature). These methods were used both to analyze samples for background data and to analyze samples generated from laboratory experiments.

Experimental Design and Experiments -- pH and Ionic Strength Variations with Sequential Extraction Analysis for Metals

Laboratory experiments were performed to determine the effects of changing environmental conditions on the uptake and release of trace metals from well drilling fluids. Equilibrium studies were performed in the laboratory to simulate these changes, using the liquid and solid phases from the drilling fluid waste pits. The liquid phase was diluted to simulate ionic strength changes, and the pH was adjusted to monitor its effects on the system. Partitioning analysis of trace metals was performed at the completion of each experiment to determine the response of arsenic, barium, chromium, and lead to changing environmental conditions.

Sample Preparation

The liquid and solid phases of the collected drilling muds were separated. The separation was accomplished by centrifugation in 250 ml polyethylene containers for 30 minutes at 5000 rpm using a Sorvall SS-3 automatic superspeed centrifuge. Following centrifugation the liquid portion was pressure filtered under nitrogen through a 0.45 um millipore filter. A total of 2 liters of liquid and 1 liter of solid for each waste was prepared. Percent solids and percent volatile solids was determined for the drilling fluid solid phase (Table 23). These values were used to determine the dry weight of the material to be used in the experiments.

Equilibrium Experiments

The experimental procedure is outlined below. The raw data,

Table 23: Percent Solids and Volatile Solids in Drilling Fluid Sediment Portion

Sample	% Solid (180°C)	% Volatile Solids (550°C)
JS	41.2	4.3
TS	41.3	7.5
TC	60.6	3.7

calculated results and the computer program used to perform the calculations are contained in Appendix A.

1. A known weight (4 g wet ≃ 2 g dry weight) of the solid portion of the waste from one of the pits was placed in a pre-weighted 50 ml centrifuge tube (polyethylene with screw cap). The solid was well mixed prior to adding and a sample was collected for total and volatile solids analysis.

2. The ionic strength of the added liquid phase from the waste was varied by dilution with deionized water (full strength, 0.5 strength, or 0.1 strength). Twenty-five (25) ml of the desired solution was added to the centrifuge tube.

3. The pH of the mixture was adjusted with 4 M HNO_3 to the desired value (original pH, pH ≃ 5.6, or pH ≃ 4.0). The volume of acid added was recorded and accounted for when calculating results of the experiments.

4. The resulting liquid to solid ratio in the centrifuge tubes is about 27:2.

5. The capped tubes were shaken at room temperature (25°C) for 5 days after the pH stabilized to ensure equilibration.

6. Each experiment was conducted in duplicate. A liquid phase control and distilled water blank were utilized.

7. At the end of the equilibrium period, the suspension was separated by centrifugation at 5,000 rpm for 30 minutes.

8. The liquid phase was saved for analysis of dissolved metals (As, Ba, Cr, and Pb).

9. A selective extraction of the remaining solid phase was then performed and analyzed for metals (As, Ba, Cr, and Pb).

10. The design for the equilibrium experiments are summarized by Figures 28 to 30.

Sequential Extraction (Table 24)

According to Chang, et al. (1984):

1. Shake remaining solid with 25 ml of 0.5 M KNO_3 for 16

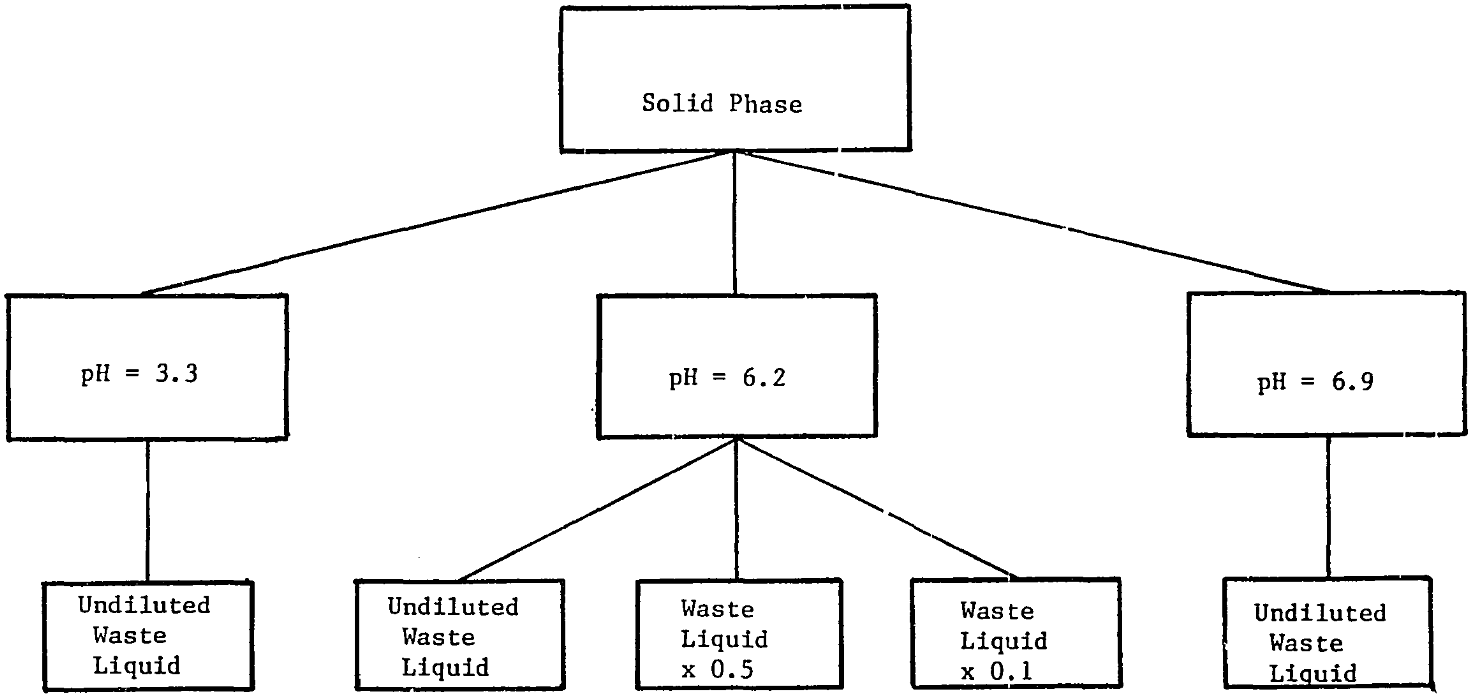

Figure 28: Experiments Performed with Drilling Fluid JS

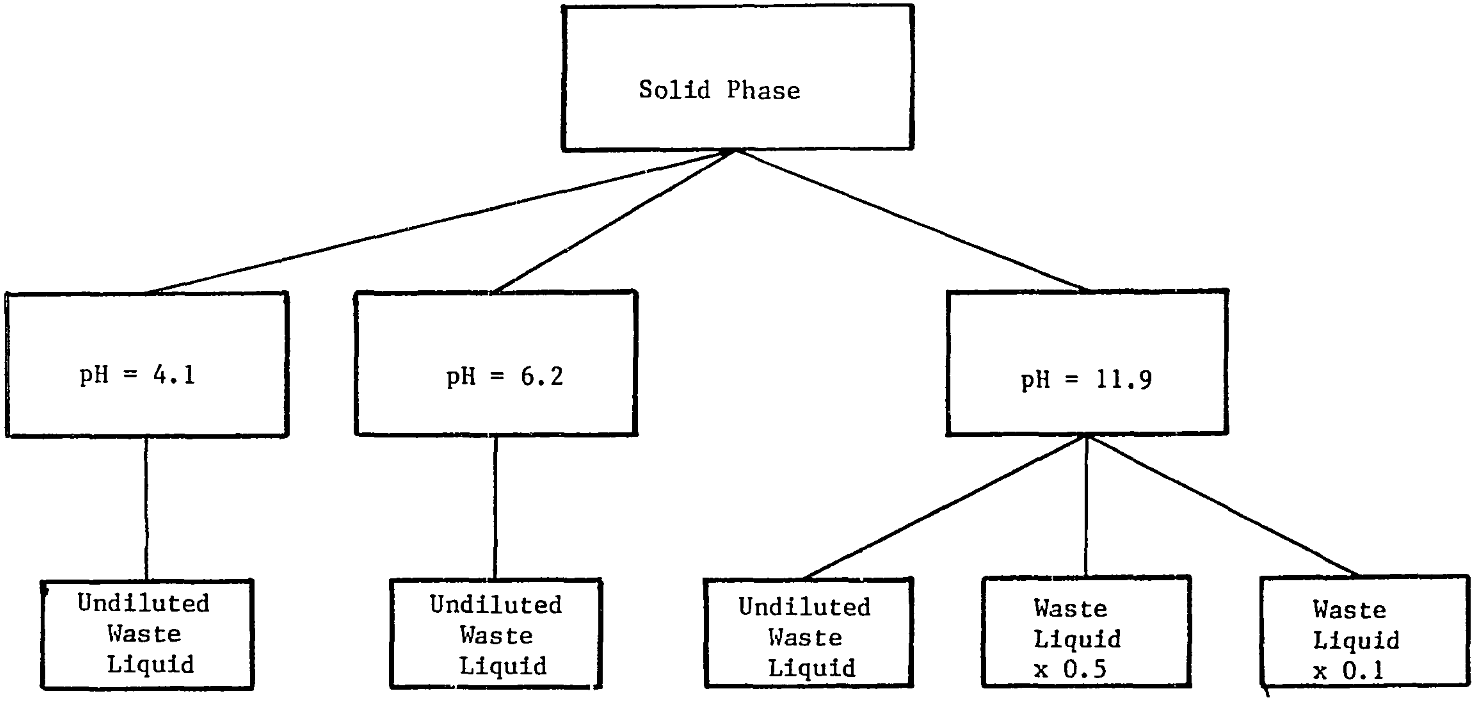

Figure 29: Experiments Performed with Drilling Fluid TS

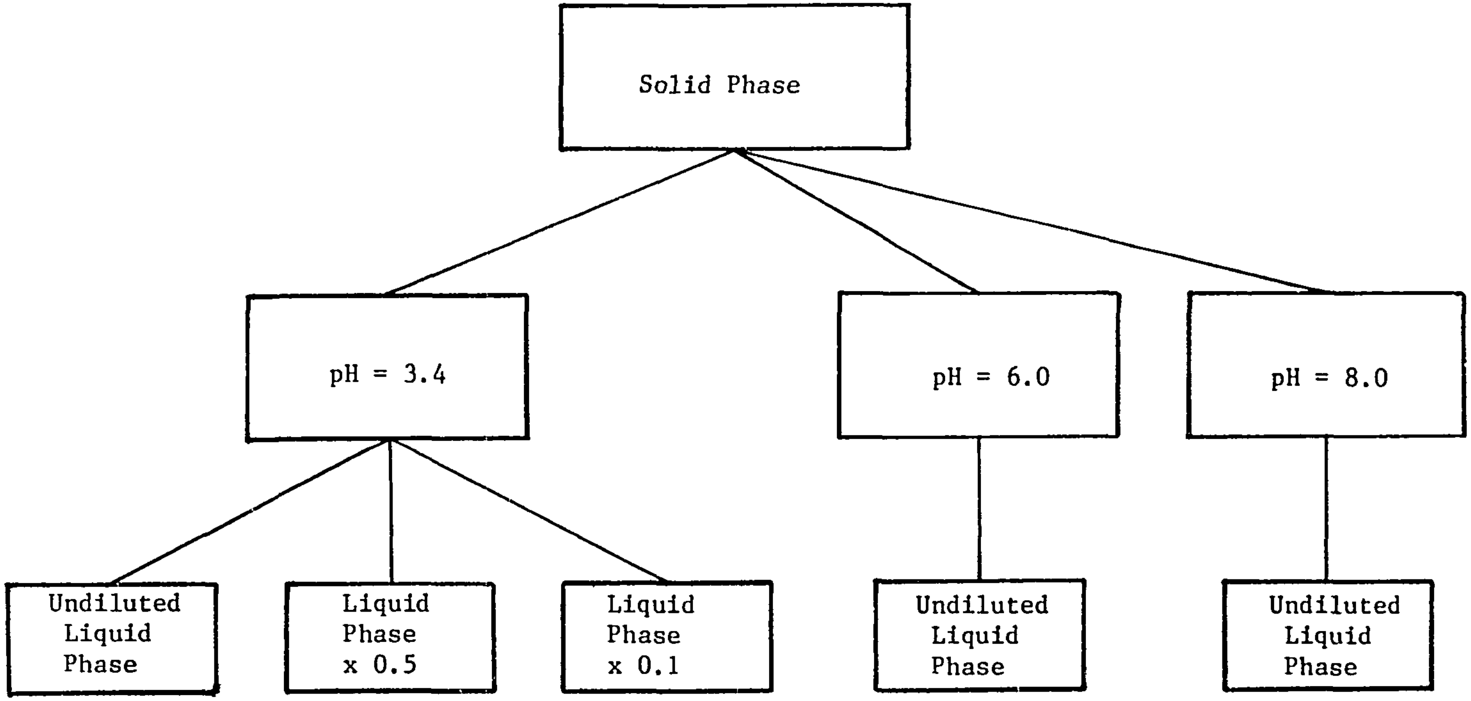

Figure 30: Experiments Performed with Drilling Fluid TC

Table 24: Order of Sequential Extraction Sequence and Designated Chemical Form Extracted (Chang, et al., 1984)

Extractant	Concentration of Extractant (M)	Density (g/ml)	Equilibrating Time on Shaker (hours)	Designated[1] Chemical Form Extracted
KNO_3	0.5	1.03	16	Exchangeable
$X-H_2O$[2]	55.5	1.00	2	Adsorbed
NaOH	0.5	1.02	16	Organically Bound
Na_2-EDTA	0.05	1.00	6	Carbonate
HNO_3 (70-80°C)	4.0	1.12	16[3]	Residual

[1] The terminology, "chemical form extracted", is not meant to imply that the metal is in only adsorbed, carbonate, etc., form, but extractable with that reagent. The terminology is used to be consistent with the literature.

[2] Ion exchange water, extracted three times.

[3] Extracted on hot plate, not on shaker.

hours, centrifuge, and decant (exchangeable fraction).

2. Shake residue with 25 ml of deionized water for 2 hours, centrifuge and decant. Repeat 3 times and combine supernatants (adsorbed fraction).

3. Twenty-five (25) ml of a 0.5 M NaOH are added to the residue and shaken for 16 hours, centrifuged, and decanted (organic fraction).

4. Twenty-five (25) ml of 0.05 M Na_2EDTA are added to the residue, shaken 6 hours, centrifuged and decanted (carbonate fraction).

5. Thirteen (13) ml of 4 M HNO_3 are added to the residue and heated at 80°C for 16 hours with an additional 12 ml of 4 M HNO_3 added after heating. The mixture is centrifuged and decanted (sulfide/residual fraction).

The weight of the centrifuge tube was recorded at each step to aid in mass balance determinations. The supernatant liquids were analyzed by atomic absorption spectrophotometry for arsenic, barium, chromium and lead using standards prepared with applicable extractant to compensate for the background matrix. A computer program (Appendix A) was used to calculate the amounts of metals extracted by each extractant. The calculation included a correction for mass changes between extractions and differences in densities of extracting solutions.

Experimental Design and Experiments -- Flyash Stabilization of Heavy Metals in Drilling Fluids

Laboratory experiments were performed to determine the effects of mixing flyash and drilling fluids upon the fate of heavy metals from the mixture. Mixtures containing various proportions of flyash and drilling fluid were prepared and allowed to stand for either 1 week or 5 weeks to measure the effects of both concentration and time. EP

Toxicity Tests were performed on the mixtures, flyash, and drilling fluids as a measure of metal release or uptake.

Sample Preparation

The drilling fluids (TS, TC, and JS) and flyash were well mixed. This was done to provide representative samples of each for the experiments. Percent solids were determined for each individual material (Table 25).

Stabilization Experiments

Flyash and drilling fluid were added together by weight for a total of 400 g in 500 ml wide-mouth Nalgene bottles. The bottles were shaken until well mixed. The mixtures were then allowed to sit at room temperature to allow time for any solidification or stabilization to occur. One set of experiments was allowed to stabilize for 1 week and another identical set for 5 weeks to determine short-term time effects. In addition each mixture was prepared in duplicate along with blanks and controls for flyash and each drilling fluid. Each experiment is summarized in Table 26.

At the completion of a set of experiments (1 week or 5 weeks) a modified EP Toxicity analysis was performed on each sample as follows (raw data is presented in Appendix B):

1. Approximately 5 g of sample was added to a 500 ml Erlenmeyer flask and the weight recorded.
2. Sixteen (16) times the sample weight of deionized water was also added followed by 10 ml of 0.5 N glacial acetic acid.
3. The samples were then shaken for 24 hours.

Table 25: Percent Solids in Drilling Fluid and Flyash Used in Stabilization Study

Sample	% Solid (180°C)
Flyash	99.9
JS	11.5
TS	17.6
TC	26.5

Table 26: Drilling Fluid-Flyash Stabilization Experiments

Sample No.	Description	Duration of Experiment (wk)
DI-A	Deionized H_2O Blank	1
FA-A	Flyash Control	1
TS-A	TS Control	1
TS10-A	TS + 10% Flyash	1
TS30-A	TS + 30% Flyash	1
TC-A	TC Control	1
TC10-A	TC + 10% Flyash	1
TC20-A	TC + 20% Flyash	1
TC30-A	TC + 30% Flyash	1
JS-A	JS Control	1
JS10-A	JS + 10% Flyash	1
JS30-A	JS + 30% Flyash	1
DI-B	Deionized H_2O Blank	5
FA-B	Flyash Control	5
TS-B	TS Control	5
TS10-B	TS + 10% Flyash	5
TS20-B	TS + 20% Flyash	5
TC-B	TC Control	5
TC10-B	TC + 10% Flyash	5
TC20-B	TC + 20% Flyash	5
TC30-B	TC + 30% Flyash	5
JS-B	JS Control	5
JS10-B	JS + 10% Flyash	5
JS30-B	JS + 30% Flyash	5

4. After shaking, the sample volumes were adjusted by adding water according to the following formula:

   $$V = (20)(W) - 16(W) - A$$

   V = ml deionized water to be added,

   W = weight in grams of solid, and

   A = ml of 0.5 N acetic acid added.

5. The samples were then filtered through a 0.45 millipore membrane. Fifty (50) ml of liquid were digested on a hot plate after the addition of 3 ml concentrated HNO_3.

6. The samples were analyzed for arsenic, chromium, barium, lead and zinc after digestion and dilution to 100 ml.

CHAPTER IV

PRESENTATION AND ANALYSIS OF RESULTS

Background Analysis

Aqueous Portion of Disposal Pits

The results of chemical analyses of the aqueous (liquid) portion of the 3 pits are reported in Table 27, along with Oklahoma Corporation Commission (OCC) discharge water standards. The OCC discharge limits are provided only as a base for comparisons. The off-site pits are not discharging to surface water; therefore, the standards are not directly applicable. In fact, elevated levels of dissolved solids in an off-site pit would be an indication that the pit is properly functioning in its evaporative capacity. On the other hand, elevated dissolved solids reflect the need for proper pit design to minimize leaching to ground water, seepage through berms, or berm failure at which time discharge standards would be more applicable.

The data indicates high levels of major dissolved constituents (chlorides, sodium, sulfate and alkalinity) which could contribute to a decrease in surface water or ground water quality if there is seepage, overflow, or breaks in the pit berms. However, at a properly designed site this is desirable because it indicates a properly functioning pit.

Table 27: Chemical Analysis Results for the Aqueous (Liquid) Portion of Disposal Pits Used in this Study

Parameter	JS	TS	TC	OCC Discharge Standard
pH (Std. units)	7.45	7.53	11.30	6.5-8.5
Conductivity (μmhos/cm)	3550	4000	6300	2300
Salinity (%)	3.5	3.0	6.2	--
Alkalinity to pH 8.3 (mg $CaCO_3$/l)	0	0	213	--
Alkalinity to pH 4.5 (mg $CaCO_3$/l)	372	300	255	--
Nitrate (mg/l)	0.02	ND (0.01)	ND (0.01)	10
Chloride (mg/l)	1680	2880	2900	1500
Total Phosphate (mg P/l)	0.840	--	0.054	0.2
COD (mg/l)	115	640	250	250
TOC (mg/l)	44	231	37	--
Sulfate (mg/l)	520	420	237	--
TDS (mg/l)	4064	4526	5982	1500
Iron (mg/l)	7.50	2.29	18.9	--
Chromium (mg/l)	0.50	2.2	0.11	0.2
Arsenic (mg/l)	0.0049	0.0132	0.0122	0.2
Barium (mg/l)	0.81	6.0	0.52	5.0
Lead (mg/l)	0.08	1.80	0.03	0.1
Zinc (mg/l)	ND (0.001)	0.040	0.910	5.0

Table 27: (continued)

Parameter	JS	TS	TC	OCC Discharge Standard
Cadmium (mg/l)	ND (0.001)	0.006	0.010	0.03
Calcium (mg/l)	442	340	551	--
Magnesium (mg/l)	13.55	150.5	12.45	--
Sodium (mg/l)	10,050	1834	2550	1000

Also, values for chromium, barium and lead in the aqueous phase were greater than the OCC discharge standards in some cases. Therefore, these metals would be considered a threat if released from the pits to ground or surface waters relative to these standards. Prevailing physical or chemical conditions outside of the pits could quickly eliminate the threat through attenuation processes or dilution.

Sediment Portion of Disposal Pits

Results for the metals analysis of the sediment portion of the 3 pits are reported in Table 28. From the high levels of metals present it is clear that the sediments are a repository for these potential pollutants. However, at present the chemical environment strongly retains the metals in the sediments as is reflected in the much lower aqueous phase metal concentrations. These metals are held very strongly within the sediments due to the existence of high pH and alkalinity within the wastes. The high calcium and magnesium levels would also indicate a resistance to pH change.

However, it is possible that changing chemical conditions within the pits could make the metals available to solution and subsequently mobile in a surface or subsurface environment. The two most likely chemical changes are pH change (rain or acid rain) and changing ionic strength (dilution). These were the two variables in the experiments designed to test the potential for release.

Waste Drilling Fluids Collected for Experiments

Total metals were determined for the waste drilling fluid collected for experimental materials. These tests were performed and

Table 28: Chemical Analysis Results for the Solid (Sediment) Portion of Disposal Pits Used in this Study

Parameter	JS	TS	TC
Iron (mg/kg)	25920	30340	22820
Chromium (mg/kg)	36	183	28
Arsenic (mg/kg)	10.1	24.2	8.1
Barium (mg/kg)	2856	16210	53
Lead (mg/kg)	75	127	25
Zinc (mg/kg)	95	222	169
Cadmium (mg/kg)	0.1	0.1	ND (0.1)
Calcium (mg/kg)	9440	31100	47000
Magnesium (mg/kg)	3991	5488	9300
Sodium (mg/kg)	13200	3940	3920

are used in determining mass balance after the extraction tests. The results are compared here (Table 29) with the previously determined sediment metals concentrations from Table 28. These results illustrate the variation which occurs by different sampling methods and locations. Experimental material samples were collected at the point of waste dumping while sediment samples were composited from various locations within the pit. It is clear that metal concentrations can vary within a pit. However, in no case is the difference extreme and for most of the samples they are comparable, considering the different methods of sampling.

After separation of the liquid and solid phase as described in the methods section, percent solids and volatile solids tests were performed on the solid phase (Table 30). These results were used in calculating experimental results. Again, these values are comparable to those obtained for sediment samples as reported in Table 23.

Effects of pH Variation on Metal Speciation

pH Adjustment

The amount of HNO_3 required to obtain a stable desired pH during the experiments is reported in Table 31. The amounts of acid required are indicative of the neutralizing capacity of the drilling muds tested. They also reflect the fact that these experiments are probably worst case tests since these amounts of acid are unlikely to be encountered in the environment.

Table 29: Total Metal Analysis Results of Experimental Materials Compared with Sediment Sample Analysis

Metal	Pit	Experimental Material	Sediment Samples from Table 28
As (μg/kg)	JS	18600	10,100
	TS	4150	24,200
	TC	30,400	8,100
Ba (mg/kg)	JS	1730	2856
	TS	4060	16210
	TC	197	53
Cr (mg/kg)	JS	49.9	36
	TS	236	183
	TC	79.6	28
Pb (mg/kg)	JS	68.2	75
	TS	206	127
	TC	24.2	25

Table 30: Percent Total Solids and Volatile Solids in the Solid Portion of Drilling Fluid Wastes Used in Laboratory Experiments

Sample	% Total Solid (180°C)	% Volatile Solids (550°C)
JS	33.0	5.7
TS	45.0	7.5
TC	63.6	1.3

Table 31: Amounts of Acid Required to Obtain the Desired pH During Equilibration Studies

Fluid	Solid Wt.	Final pH	ml of 4 M HNO_3	$\frac{\text{Moles } HNO_3}{\text{kg Solid}}$
JS	1.32	6.9	0	0
	1.32	6.5	0.24	0.73
	1.32	3.6	0.30	0.91
TS	1.85	11.8	0	0
	1.85	6.2	1.38	2.98
	1.85	4.1	1.60	3.56
TC	2.58	8.0	0	0
	2.60	6.0	0.30	0.46
	2.48	4.8	0.50	0.81

General Comments on Sequential Extraction Results

The results from the sequential extractions of fluids equilibrated under conditions of varying pH are presented as percent recovered from each extractant and actual concentration per unit solid or liquid. Percent recovered allows for comparison between different drilling muds while actual concentrations permit comparison with water quality standards and are used for mass balance calculations.

A mass balance was performed by taking the sum of the metals for each extracted fraction within a sample and comparing that with results of a total metals analysis (Table 32). The random differences present are probably caused by errors in the multistep extraction procedure used or by analytical interferences with the prepared samples. It is likely that interferences resulted from the high levels of dissolved constituents present in the wastes.

Of more interest than mass balance with total metals analysis is the mass balance between experiments for each fluid, because comparisons between these experiments will determine the results of this study. Table 33 contains the percent standard deviation within experiments for each metal and fluid. The percent standard deviation ranges from 5.0 percent to 40.9 percent.

Metal Speciation with Varying pH

Arsenic. Results for the sequential extraction of arsenic in drilling fluids JS, TS, and TC are reported in Tables 34 and 35 and Figures 31 to 33. All values are reported as the average of duplicate experiments. At the higher pH values which existed in the pits at the

Table 32: Comparison of Total Metals Analysis with the Sum of Extracted Metal Fractions within Each Sample

Sample	A Sum of Extracted Fractions	B Total Metal	Percent Difference (A-B/A) x 100
	Arsenic (g/kg)		
JS	17600 ± 2900*	18600	-5.6
TS	21500 ± 8800	4150	+420
TC	15100 ± 5600	30,400	-50
	Barium (mg/kg)		
JS	4110 ± 860	1730	+58
TS	3880 ± 860	4060	-4.4
TC	254 ± 32	197	+22
	Chromium (mg/kg)		
JS	89.6 ± 4.5	49.9	+44
TS	317 ± 29	236	+25
TC	39.0 ± 4.9	79.6	-51
	Lead (mg/kg)		
JS	80.6 ± 18.2	68.2	+15
TS	211 ± 19	206.4	+2.2
TC	22.1 ± 4.1	24.2	-8.7

*Standard deviation of measurements on 10 different samples.

Table 33: Percent Standard Deviation within Experiments for Each Metal and Fluid

Sample	Sum of Extracted Fractions	Percent Standard Deviation (S.D.)
	Arsenic (μg/kg)	
JS	17600 ± 2900*	16.5
TS	21500 ± 8800	40.9
TC	15100 ± 5600	37.0
	Barium (mg/kg)	
JS	4110 ± 860	20.9
TS	3880 ± 860	22.2
TC	254 ± 32	12.6
	Chromium (mg/kg)	
JS	89.6 ± 4.5	5.0
TS	317 ± 29	9.1
TC	39.0 ± 4.9	12.5
	Lead (mg/kg)	
JS	80.6 ± 18.2	22.5
TS	211 ± 19	9.0
TC	22.1 ± 4.1	18.5

*Standard deviation of measurements on 10 different samples.

Table 34: Percent Arsenic Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (%)	Extractant KNO_3 (%)	 H_2O (%)	 NaOH (%)	 EDTA (%)	 HNO_3 (%)
			Drilling Fluid JS			
6.9	0.3	0.1	1.4	1.8	0.6	95.6
6.5	0.5	< 0.1	1.3	0.2	17.7	80.3
3.6	0.9	3.1	1.0	2.6	1.1	91.2
			Drilling Fluid TS			
11.8	0.4	0.4	0.1	1.6	9.3	88.2
6.2	1.0	2.3	2.5	38.1	3.7	52.0
4.1	1.7	1.9	1.0	44.4	4.3	46.6
			Drilling Fluid TC			
8.0	2.2	1.3	0.3	3.1	0.2	92.8
6.0	< 0.1	1.3	0.3	3.3	0.1	95.0
4.8	1.3	2.1	0.3	23.8	13.8	58.7

Table 35: Concentration of Arsenic Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (μg/l)	Extractant KNO_3 (μg/kg)	H_2O (μg/kg)	NaOH (μg/kg)	EDTA (μg/kg)	HNO_3 (μg/kg)
		Drilling Fluid JS				
6.9	3.3	27.1	256	339	112	17300
6.5	4.8	< 0.1	229	32.9	3560	16100
3.6	6.9	454	154	397	170	13700
		Drilling Fluid TS				
11.8	13.9	153	48.7	588	3510	33400
6.2	13.6	412	448	6770	664	9190
4.1	21.6	325	176	7650	756	8130
		Drilling Fluid TC				
8.0	46.7	244	64.9	563	30.7	17000
6.0	< 0.1	228	44.5	570	28.7	16400
4.8	8.9	141	18.6	1270	606	3760

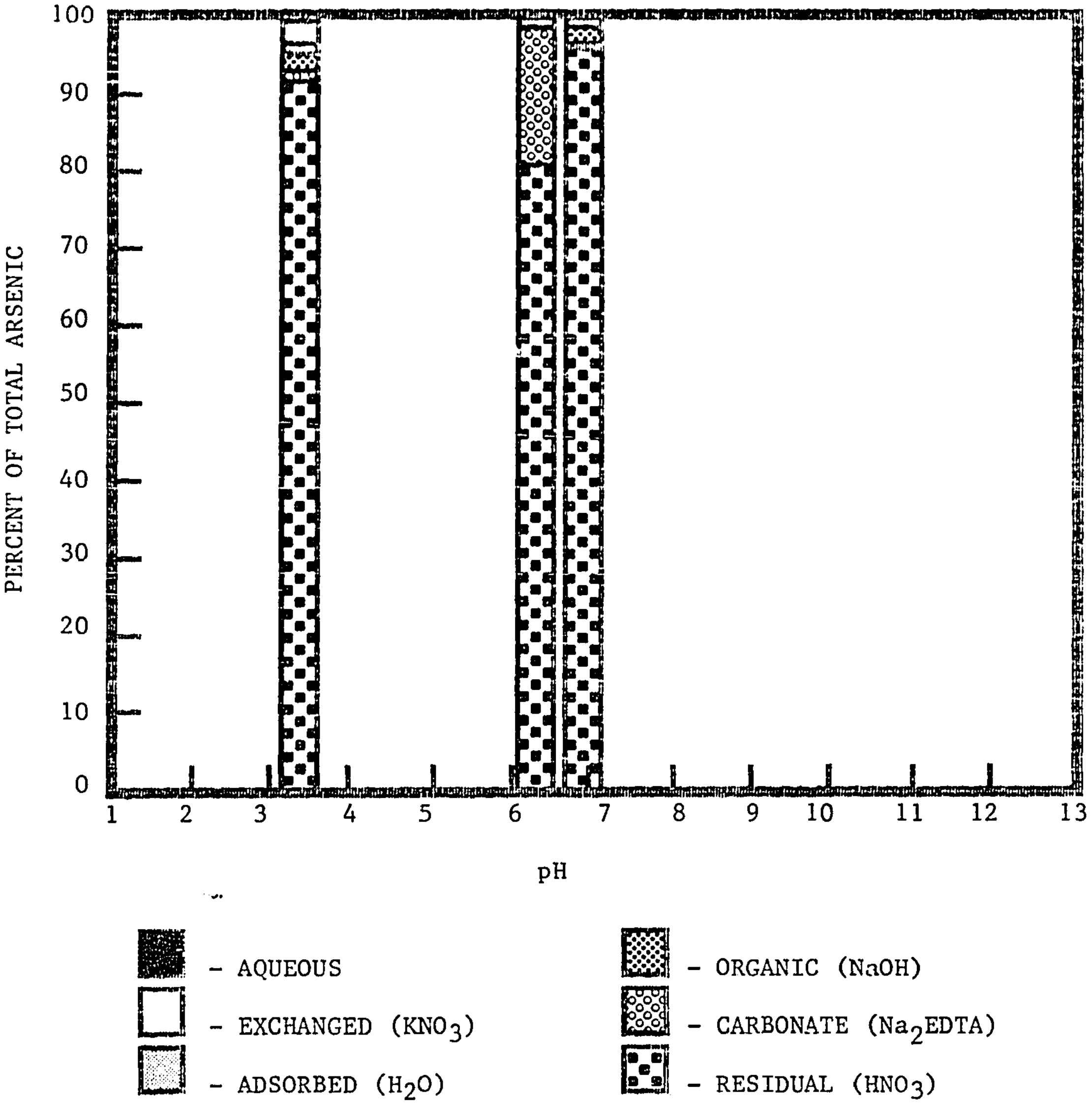

Figure 31: Percent of Sequentially Extracted Arsenic from Drilling Mud JS after Equilibrating at the Indicated pH

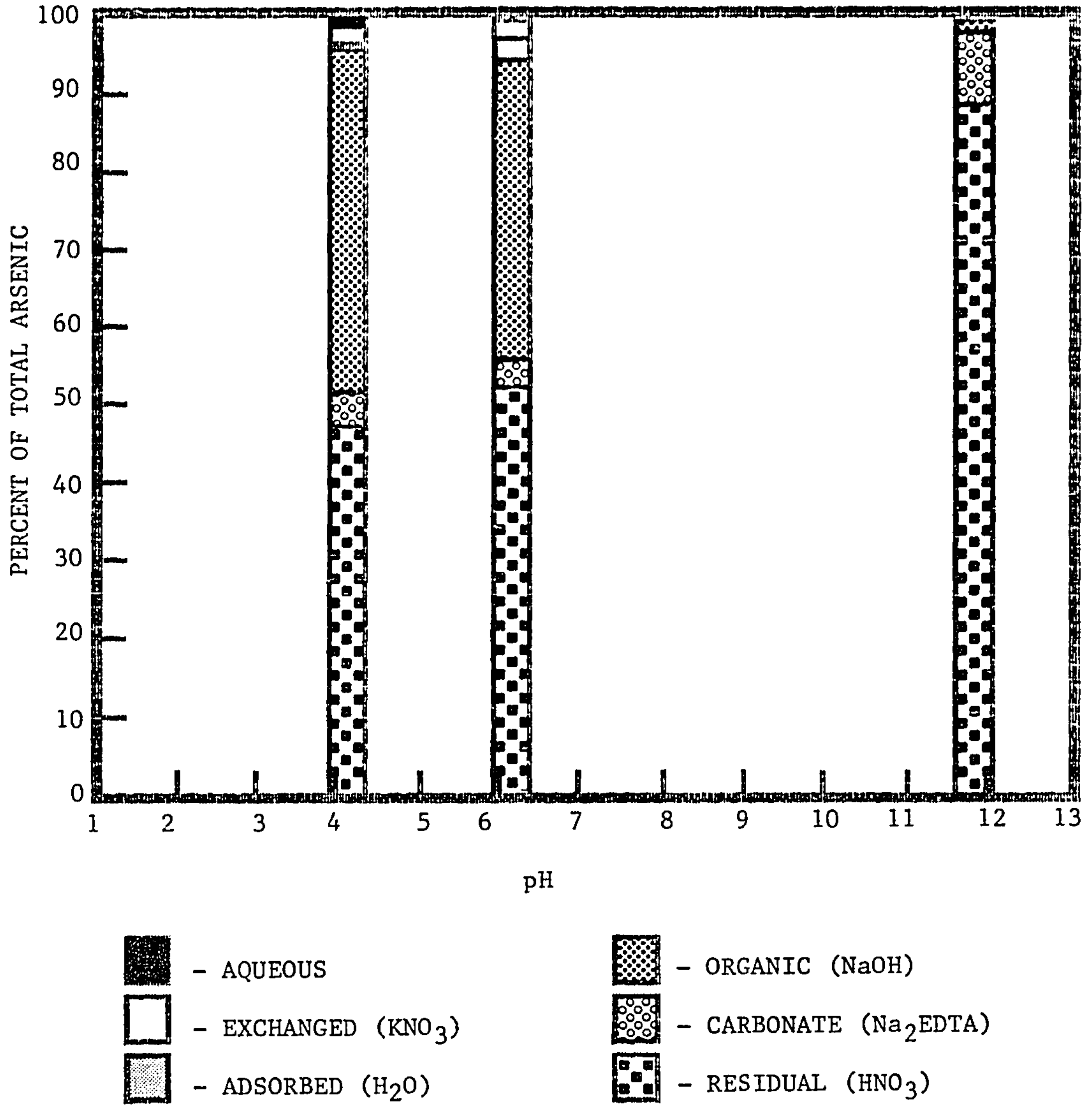

Figure 32: Percent of Sequentially Extracted Arsenic from Drilling Mud TS after Equilibrating at the Indicated pH

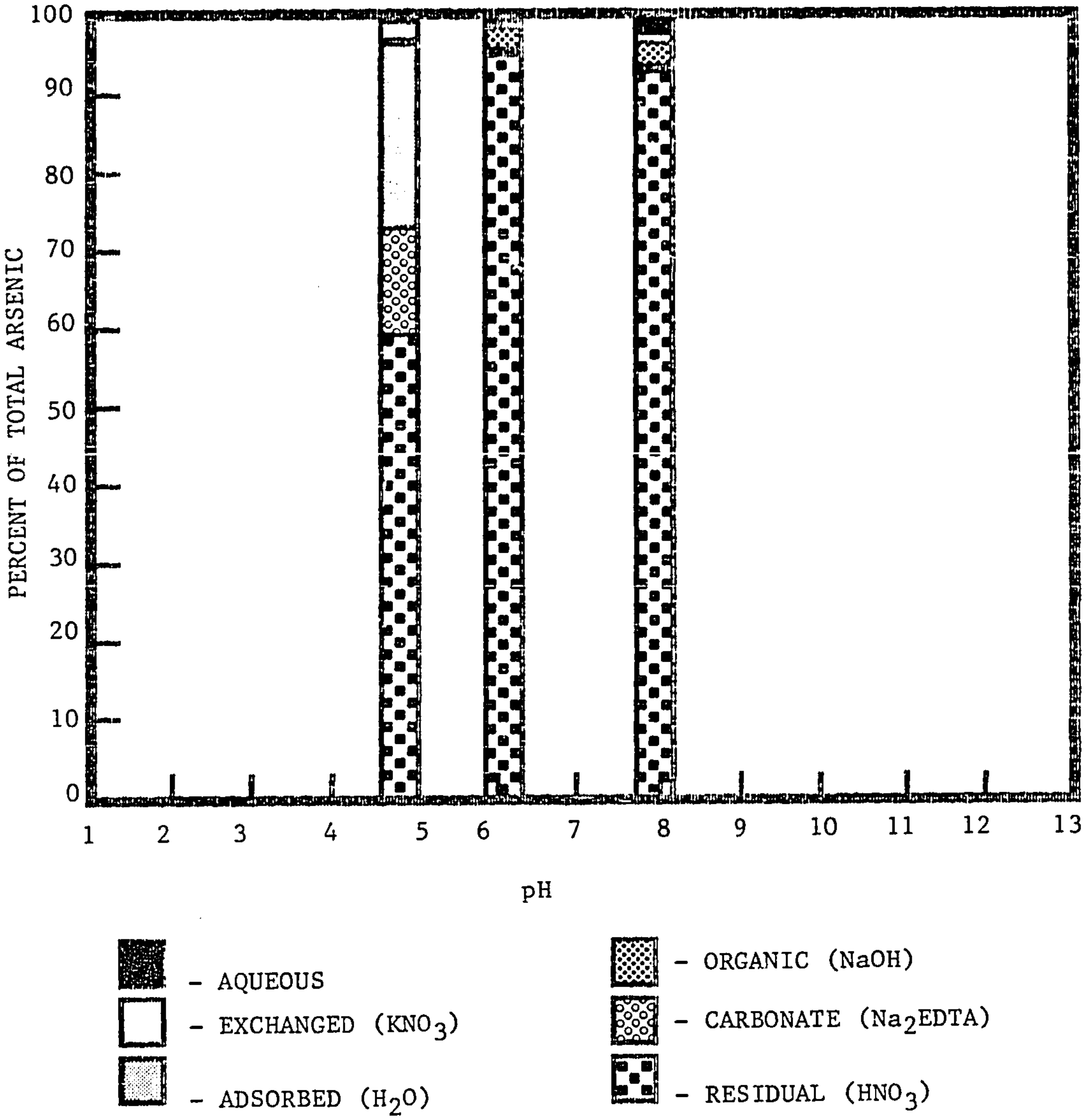

Figure 33: Percent of Sequentially Extracted Arsenic from Drilling Mud TC after Equilibrating at the Indicated pH

time of sampling more than 88 percent of the arsenic in each fluid is present in the residual fraction. This is consistent with evidence that arsenic forms insoluble inorganic complexes at high pH values, perhaps insoluble barium complexes.

As the pH decreases to approximately pH=6, the residual fraction continues to predominate in fluids JS and TC while there are significant levels (38.1 percent) of arsenic in the organic fraction of fluid TS. Fluid JS shows some shift of arsenic from the residual to the carbonate phase. With further decrease to between pH 3 and pH 5, arsenic remains primarily in the residual form in fluid JS, the organic and residual forms in fluid TS while some residual arsenic shifts to carbonate and adsorbed fractions in fluid TC. The shift to the organic fraction in fluid TS is probably due to the type of organic additives present, perhaps surfactants of some type. The shift to the adsorbed phase in fluid TC probably reflects adsorption to clay particles.

The percent of arsenic in the aqueous or exchanged fractions at no time exceeded 2.2 or 3.1 percent, respectively. This reflects the stability of arsenic with these three fluids. The drinking water limit for arsenic is 50 ug/l. This value is only approached by the aqueous phase concentration in fluid TC at pH=8 (46.7 ug/l). Therefore, arsenic does not appear to be a threat, even under drinking water standards, for these fluids if the pH changes are within the limits examined in this study.

Barium. Results for the sequential extraction of barium in drilling fluids JS, TS, and TC are reported in Tables 36 and 37 and Figures 34 to 36. All values are reported as the average of duplicate

Table 36: Percent Barium Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (%)	Extractant				
		KNO_3 (%)	H_2O (%)	NaOH (%)	EDTA (%)	HNO_3 (%)
		Drilling Fluid JS				
6.9	0.2	5.3	1.0	2.2	20.5	70.9
6.5	2.4	7.4	1.7	1.5	16.5	70.6
3.6	2.2	8.9	2.6	1.6	17.8	66.9
		Drilling Fluid TS				
11.8	0.6	2.4	0.3	1.6	4.4	90.6
6.2	1.3	3.5	0.8	0.4	30.4	63.7
4.1	0.5	2.2	0.8	0.7	86.6	9.2
		Drilling Fluid TC				
8.0	< 0.1	57.0	0.6	< 0.1	17.6	14.1
6.0	5.0	66.3	0.7	< 0.1	17.4	10.5
4.8	5.1	72.4	1.4	0.2	11.9	8.9

Table 37: Concentration of Barium Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (mg/l)	Extractant				
		KNO_3 (mg/kg)	H_2O (mg/kg)	NaOH (mg/kg)	EDTA (mg/kg)	HNO_3 (mg/kg)
			Drilling Fluid JS			
6.9	0.4	238	45.3	99.1	932	3250
6.5	4.8	286	66.3	60.8	670	2790
3.6	3.8	294	88.1	52.5	648	2210
			Drilling Fluid TS			
11.8	1.7	81.2	11.8	60.0	152	3120
6.2	3.9	142	34.0	20.3	1430	3030
4.1	1.2	79.2	29.5	26.4	3180	340
			Drilling Fluid TC			
8.0	$<$ 0.1	172	1.7	$<$ 0.1	85.5	42.1
6.0	1.4	167	1.6	$<$ 0.1	43.6	26.3
4.8	1.4	174	3.3	0.4	28.6	21.2

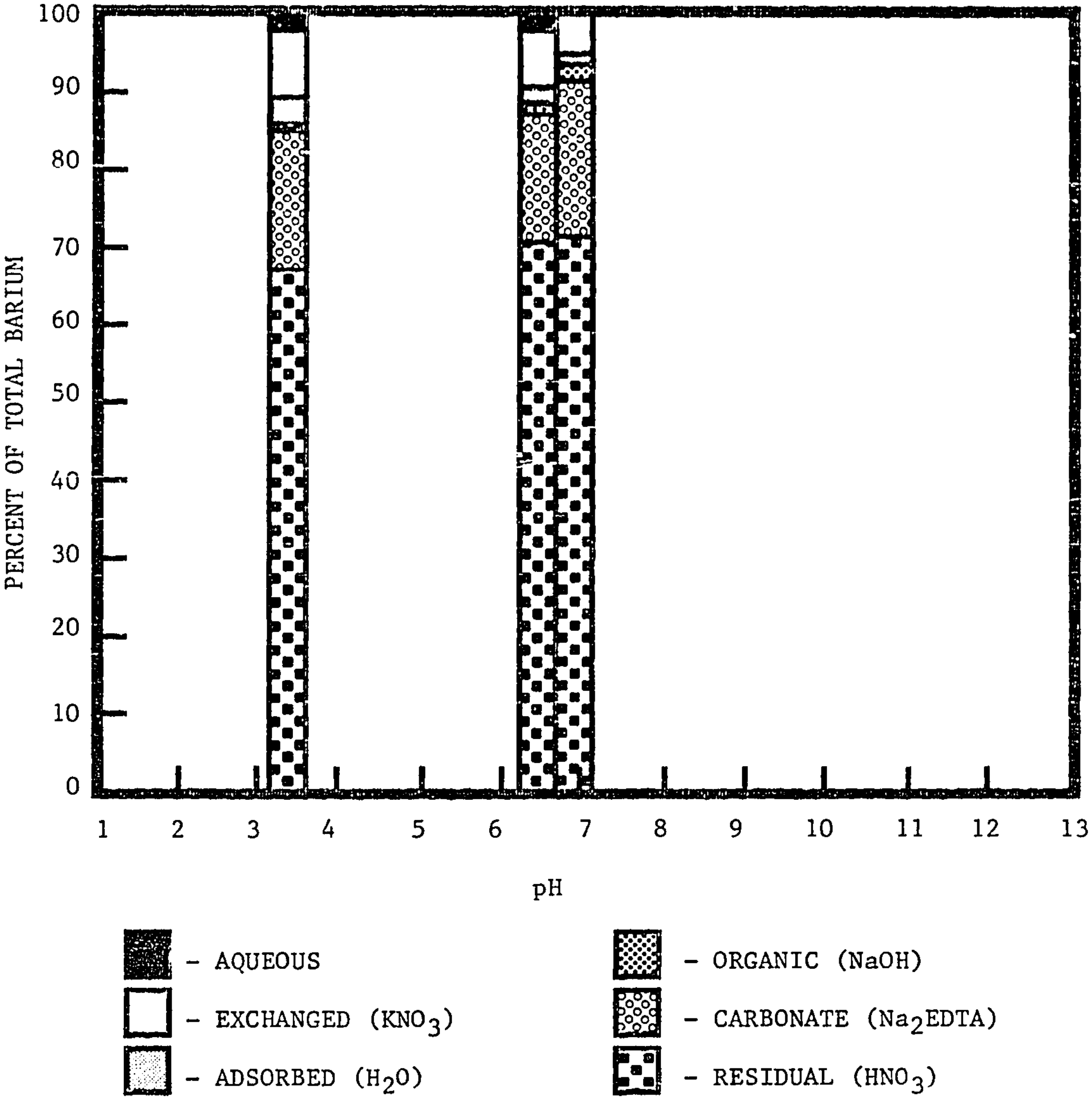

Figure 34: Percent of Sequentially Extracted Barium from Drilling Mud JS after Equilibrating at the Indicated pH

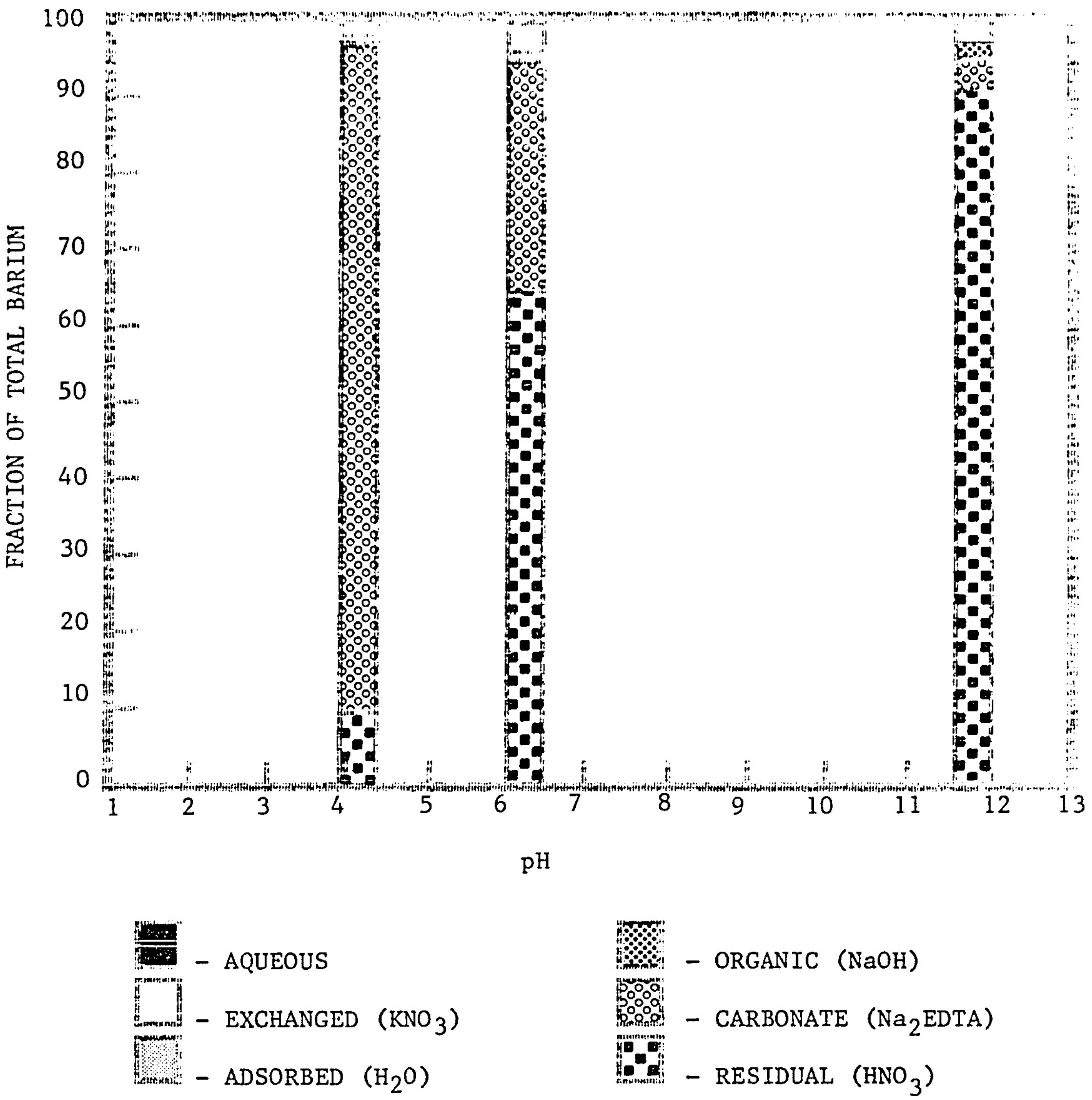

Figure 35: Percent of Sequentially Extracted Barium from Drilling Mud TS after Equilibrating at the Indicated pH

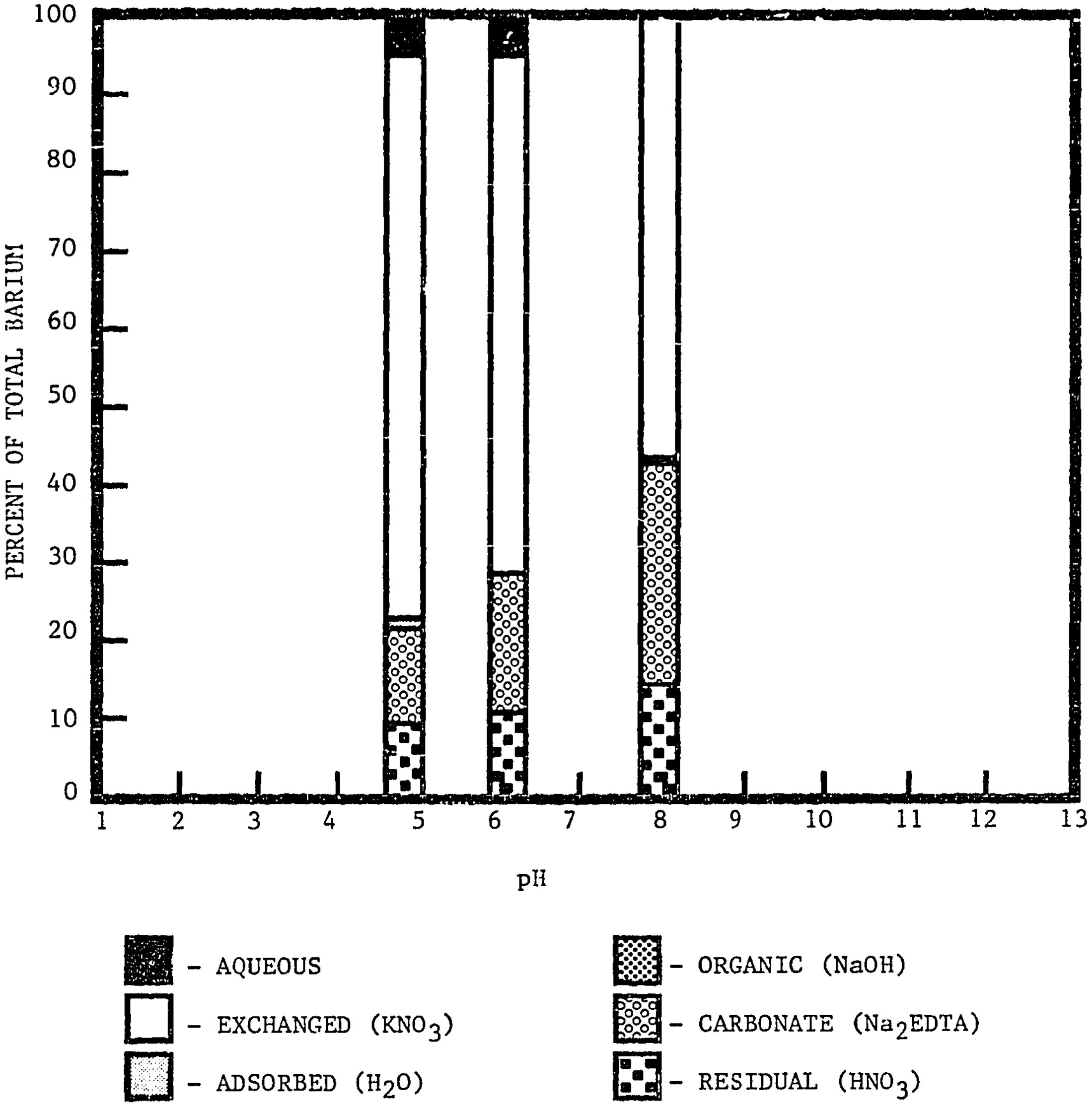

Figure 36: Percent of Sequentially Extracted Barium from Drilling Mud TC after Equilibrating at the Indicated pH

experiments. For drilling fluids JS and TS, the residual and carbonate forms of barium predominate at all pH values tested. This is consistent with the formation of stable, insoluble sulfate and carbonate compounds by barium over a wide range of pH values.

Drilling fluid TC exhibited decreasing levels of carbonate and residual barium with decreasing pH. The exchanged fraction predominated at pH=8 (57 percent) and increased to 72 percent at pH=4.8. This indicates the wide variation between fluids. In this case conditions were present for adsorption of most of the barium. This is environmentally unfavorable in that it made more barium immediately available to the aqueous phase which subsequently contained significant levels of barium. The barium drinking water limit of 1 mg/l was exceeded in most cases, although by no great amount. The EP Toxicity limit (100 mg/l) was not even approached.

Chromium. Results for the sequential extraction of chromium from drilling fluids JS, TS, and TC are reported in Tables 38 and 39 and Figures 37 to 39. All values are reported as the average of duplicate experiments. In all three fluids the residual and carbonate phases predominated. This probably reflects the presence of stable, insoluble hydroxides of chromium and stable chromium additives. The chromium present is likely in the trivalent state, otherwise, more would be expected in the aqueous phase.

At the lower pH values in fluids JS and TS the aqueous phase contains 7.4 and 4.1 percent chromium, respectively. In actual concentrations this is 0.3 and 0.9 mg/l, which is well above the

Table 38: Percent Chromium Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (%)	Extractant KNO_3 (%)	 H_2O (%)	 NaOH (%)	 EDTA (%)	 HNO_3 (%)
			Drilling Fluid JS			
6.9	0.4	< 0.1	3.4	1.6	32.4	62.2
6.5	0.8	< 0.1	2.7	3.0	28.8	64.7
3.6	7.4	6.2	2.1	5.8	24.4	54.0
			Drilling Fluid TS			
11.8	0.9	1.8	< 0.1	0.5	0.7	96.1
6.2	0.6	0.6	1.1	0.9	5.0	91.8
4.1	4.1	1.6	0.8	1.2	6.8	85.5
			Drilling Fluid TC			
8.0	0.4	< 0.1	6.2	< 0.1	4.2	89.2
6.0	< 0.1	< 0.1	< 0.1	< 0.1	5.6	94.4
4.8	0.5	< 0.1	< 0.1	< 0.1	6.5	92.9

Table 39: Concentration of Chromium Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (mg/l)	Extractant KNO_3 (mg/kg)	 H_2O (mg/kg)	 NaOH (mg/kg)	 EDTA (mg/kg)	 HNO_3 (mg/kg)
			Drilling Fluid JS			
6.9	< 0.1	< 0.1	3.1	1.4	30.1	57.8
6.5	< 0.1	< 0.1	2.4	2.7	25.8	58.1
3.6	0.3	6.0	1.9	5.1	21.4	46.9
			Drilling Fluid TS			
11.8	0.3	6.1	0.2	1.6	2.3	332
6.2	0.1	1.7	3.1	2.7	13.9	257
4.1	0.9	5.3	2.3	3.5	20.2	255
			Drilling Fluid TC			
8.0	< 0.1	< 0.1	2.8	< 0.1	1.9	40.7
6.0	< 0.1	< 0.1	< 0.1	< 0.1	2.3	34.3
4.8	< 0.1	< 0.1	< 0.1	< 0.1	2.0	34.6

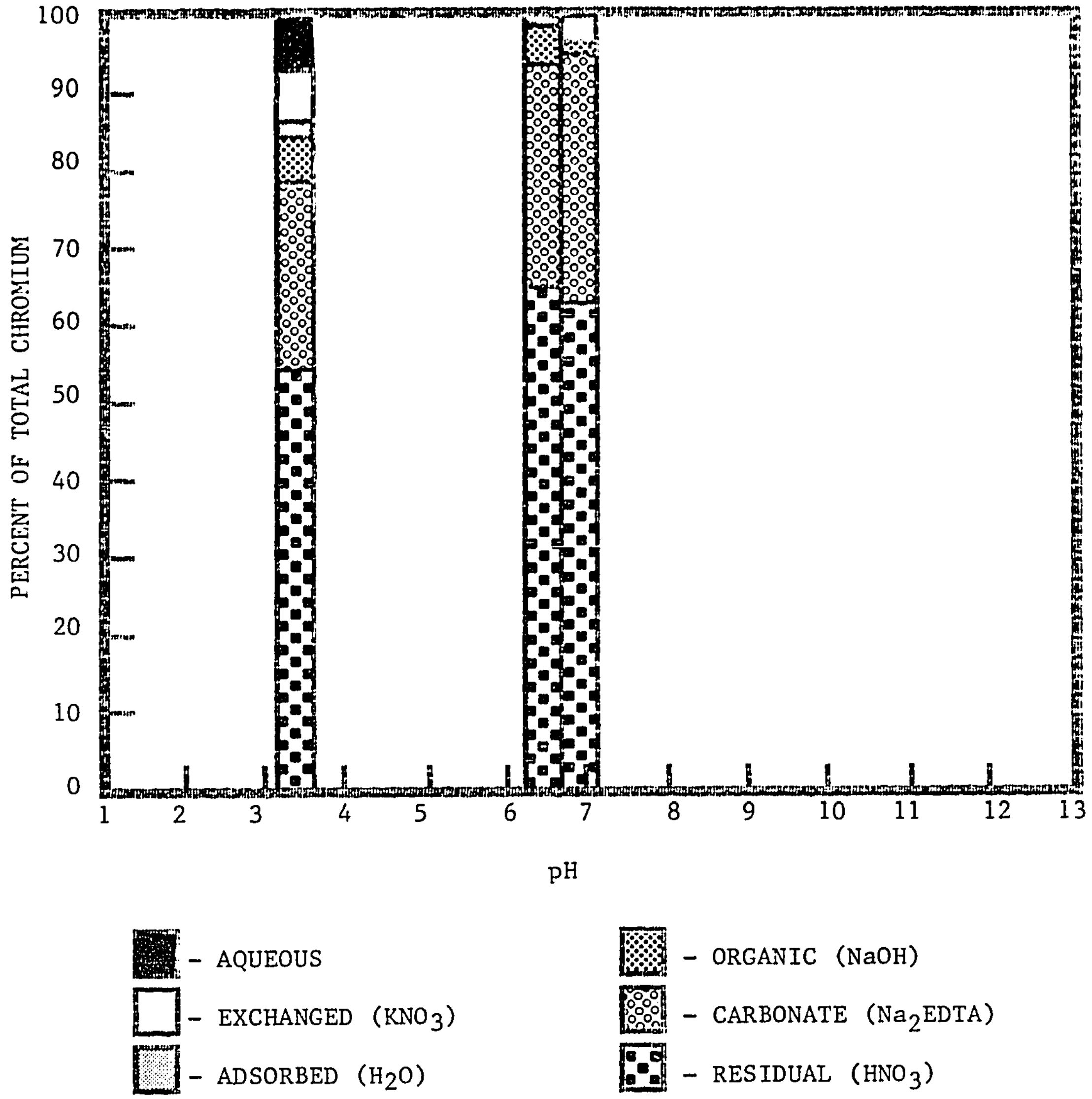

Figure 37: Percent of Sequentially Extracted Chromium from Drilling Mud JS after Equilibrating at the Indicated pH

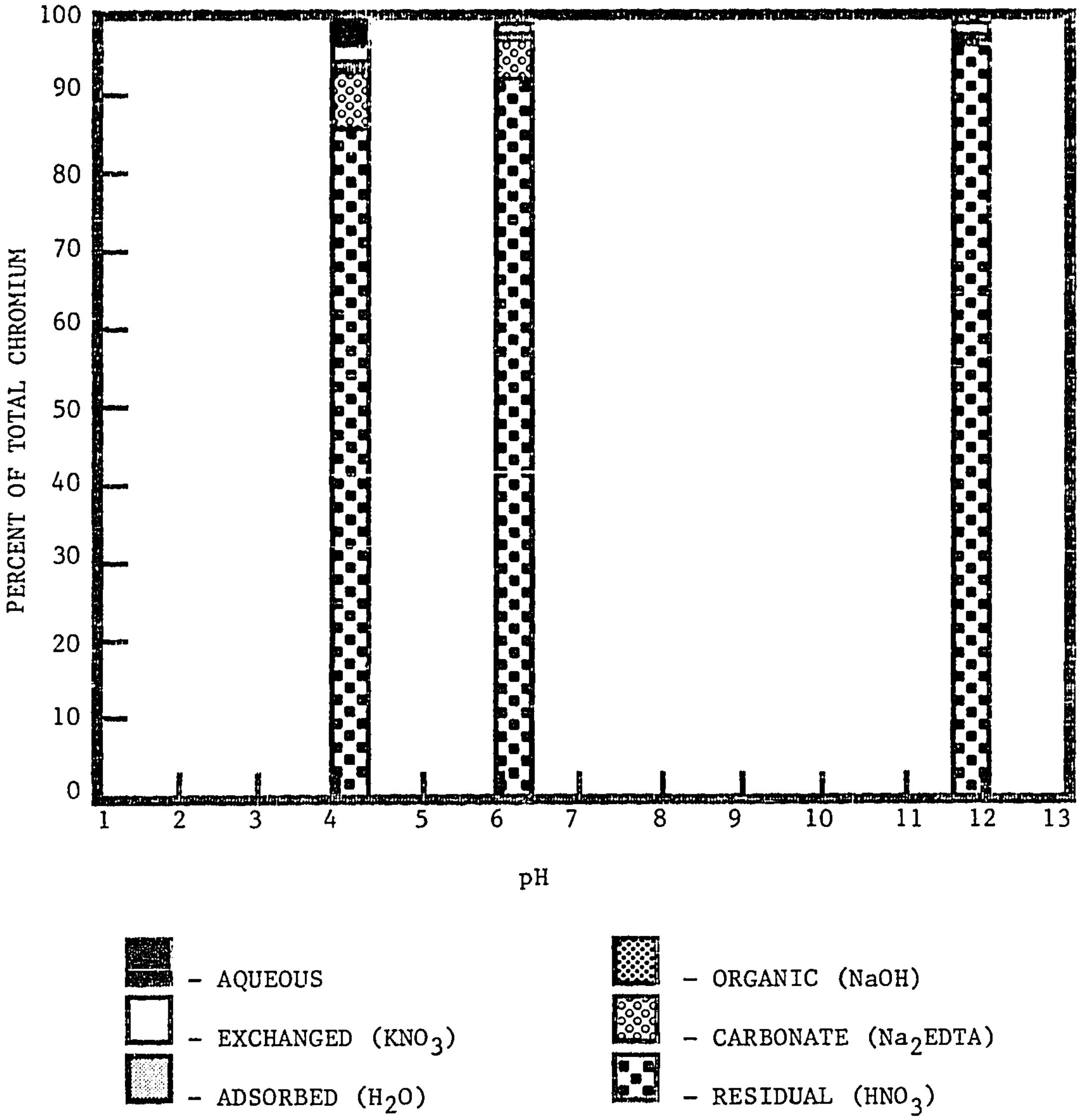

Figure 38: Fraction of Sequentially Extracted Chromium from Drilling Mud TS after Equilibrating at the Indicated pH

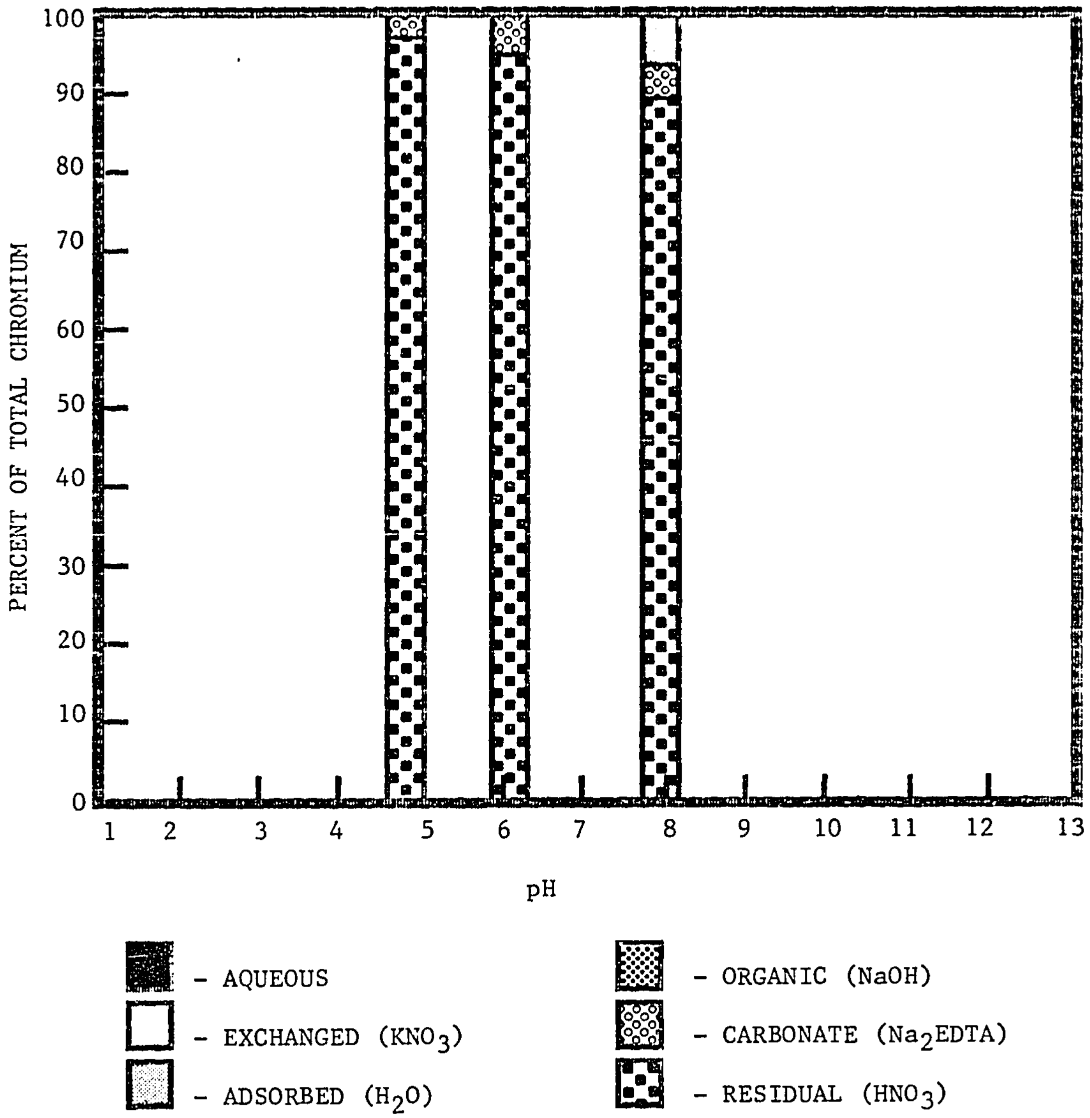

Figure 39: Percent of Sequentially Extracted Chromium from Drilling Mud TC after Equilibrating at the Indicated pH

drinking water limit of 0.05 mg/l, but below the EP Toxicity limit of 5 mg/l.

The sequential extraction percentages obtained are similar to those found by Chang, et al. (1984) in sewage amended soils (Table 40). In this study and that of Chang the residual and carbonate fractions were the predominant forms of chromium.

Lead. Results for the sequential extraction of lead in drilling fluids JS, TS, and TC are reported in Tables 41 and 42 and Figures 40 to 42. All values are reported as the average of duplicate experiments. At the two high pH values for each fluid the residual and carbonate forms predominate. This is as would be expected since lead forms stable, insoluble complexes with hydroxide and carbonate. At the lower pH values ($<$ 6) there is a shift towards the exchanged and aqueous phases, especially with drilling mud JS. This reflects the greater availability of lead, probably as the chloride complex, and subsequently increased pollution potential. The aqueous phase concentrations of lead for fluids JS (0.9 mg/l) and TS (0.8 mg/l) exceed the drinking water standard of 0.05 mg/l at the low pH.

The sequential extraction percentages obtained are similar to those found by Sposito, et al. (1982) and Chang, et al. (1984) in sewage amended soils and Stover, et al. (1976) in waste water sludge (Table 43). Similar processes are likely occurring in all studies, as indicated by the fact that the residual, carbonate and organic extracts predominate over the adsorbed, exchanged and aqueous extracts.

Table 40: Comparison of Percent Chromium in Sequentially Extracted Drilling Fluids with the Results of Chang, et al. (1984) for Sewage

Extractant	Chang, et al. (1984)	JS pH=6.9	TS pH=6.2	TC pH=8.0
$KNO_3 + H_2O$	< 1	3.4	1.7	6.2
NaOH	3	1.6	0.9	< 0.1
EDTA	17	32.4	5.0	4.2
HNO_3	80	62.2	91.8	89.2

Table 41: Percent Lead Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (%)	Extractant				
		KNO_3 (%)	H_2O (%)	NaOH (%)	EDTA (%)	HNO_3 (%)
			Drilling Fluid JS			
6.9	0.6	0.5	5.1	6.6	72.7	14.7
6.5	0.5	< 0.1	4.0	6.6	74.8	14.1
3.6	15.8	49.7	2.4	2.3	24.1	5.7
			Drilling Fluid TS			
11.8	< 0.1	0.4	0.2	2.9	4.2	92.4
6.2	< 0.1	< 0.1	1.5	2.7	59.9	35.8
4.1	4.7	7.2	0.9	1.9	45.8	39.4
			Drilling Fluid TC			
8.0	0.92	< 0.1	< 0.1	1.7	58.0	39.4
6.0	2.4	< 0.1	0.2	2.8	62.8	31.8
4.8	< 0.1	15.9	0.1	0.7	50.9	64.8

Table 42: Concentration of Lead Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

pH	Aqueous Phase (mg/l)	Extractant KNO_3 (mg/kg)	 H_2O (mg/kg)	 NaOH (mg/kg)	 EDTA (mg/kg)	 HNO_3 (mg/kg)
		Drilling Fluid JS				
6.9	< 0.1	0.3	3.6	4.7	52.1	10.6
6.5	< 0.1	< 0.1	3.0	5.0	55.5	10.5
3.6	0.9	56.0	2.7	2.6	26.8	6.4
		Drilling Fluid TS				
11.8	< 0.1	0.8	0.4	6.4	9.2	202
6.2	< 0.1	< 0.1	3.2	5.6	126	75.6
4.1	0.8	17.7	2.0	4.4	106	92.2
		Drilling Fluid TC				
8.0	< 0.1	< 0.1	< 0.1	0.4	13.4	8.9
6.0	< 0.1	< 0.1	< 0.1	0.6	12.8	6.5
4.8	< 0.1	2.4	< 0.1	0.1	8.5	5.3

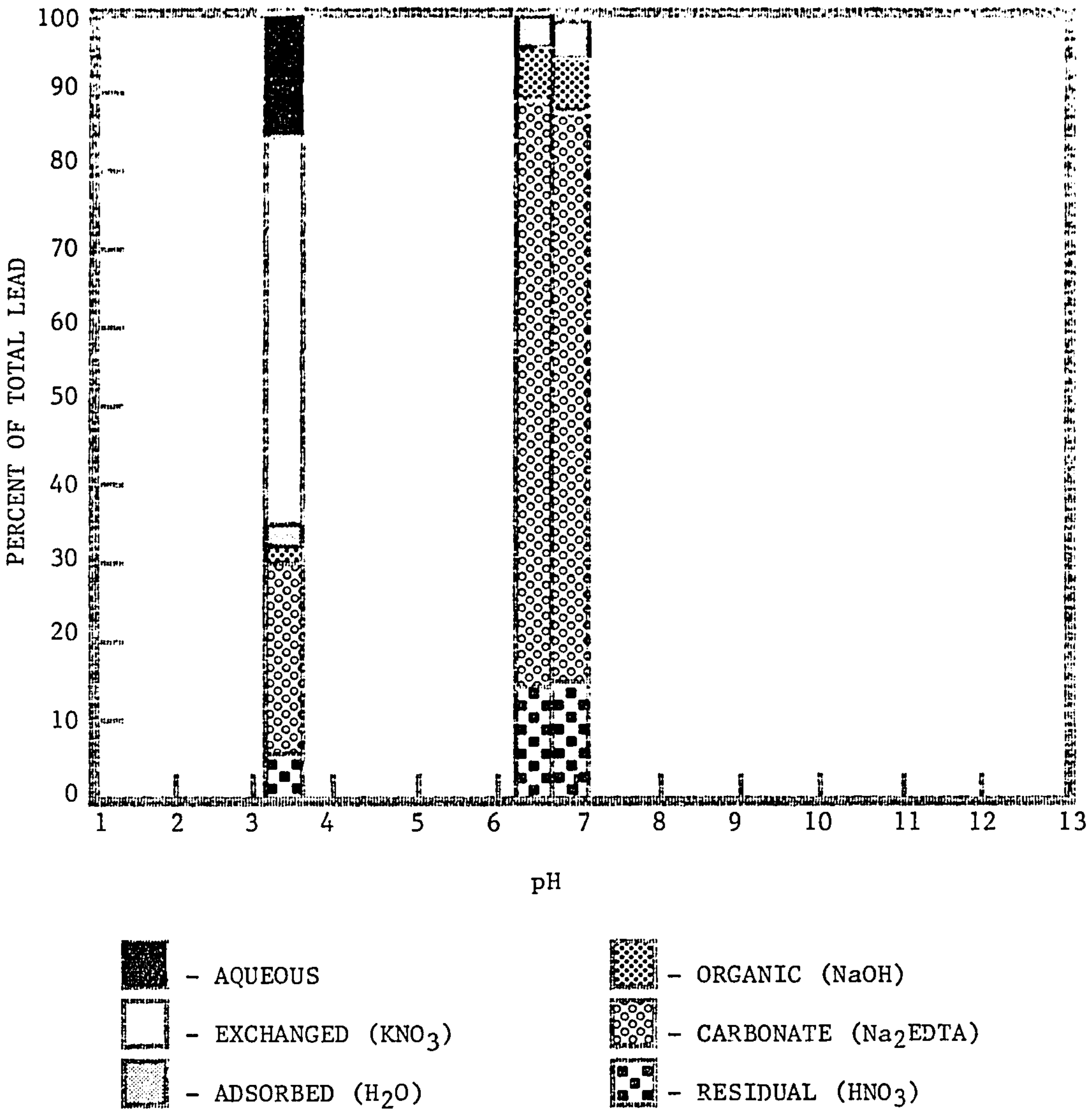

Figure 40: Percent of Sequentially Extracted Lead from Drilling Mud JS after Equilibrating at the Indicated pH

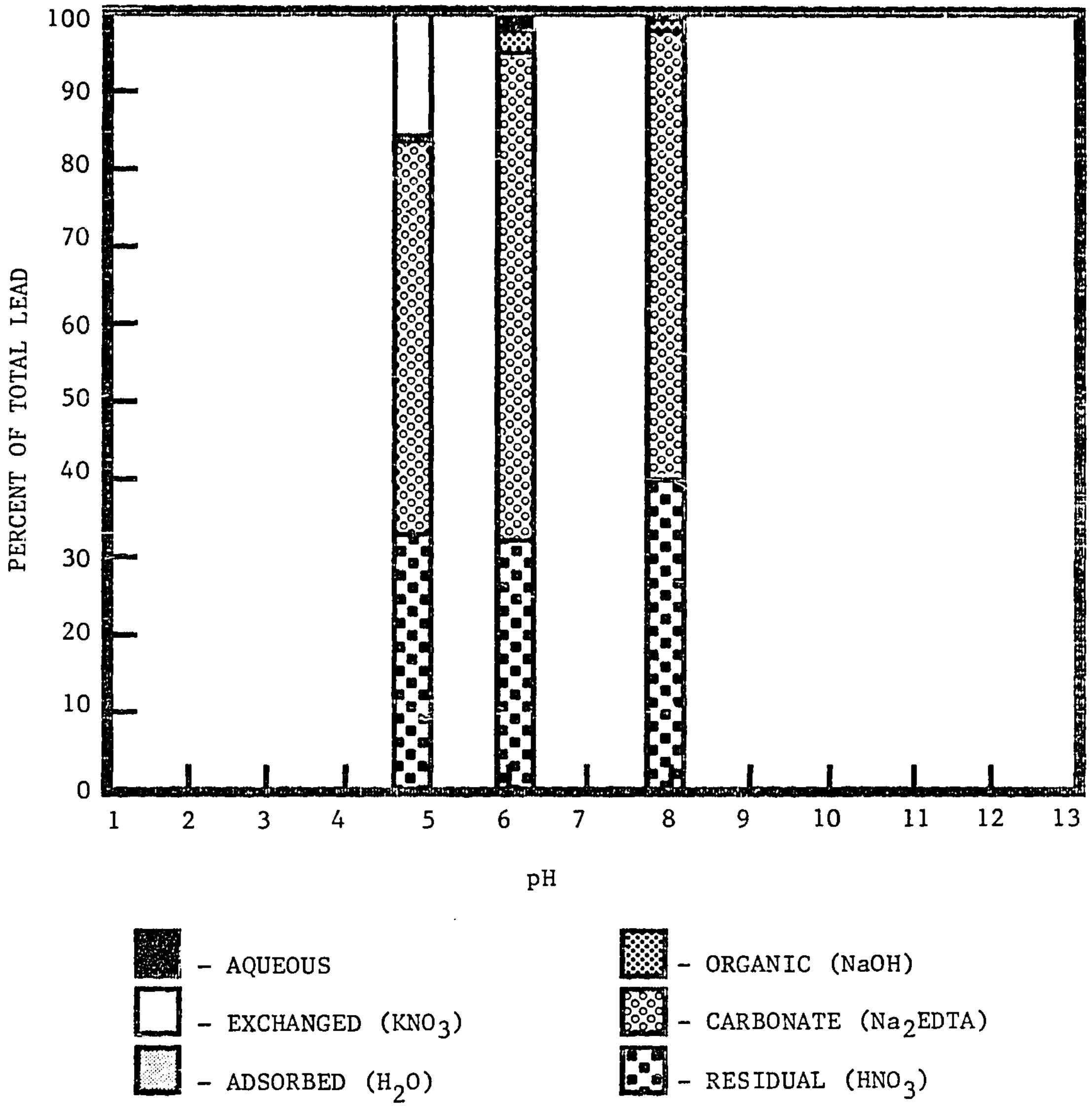

Figure 41: Percent of Sequentially Extracted Lead from Drilling Mud TC after Equilibrating at the Indicated pH

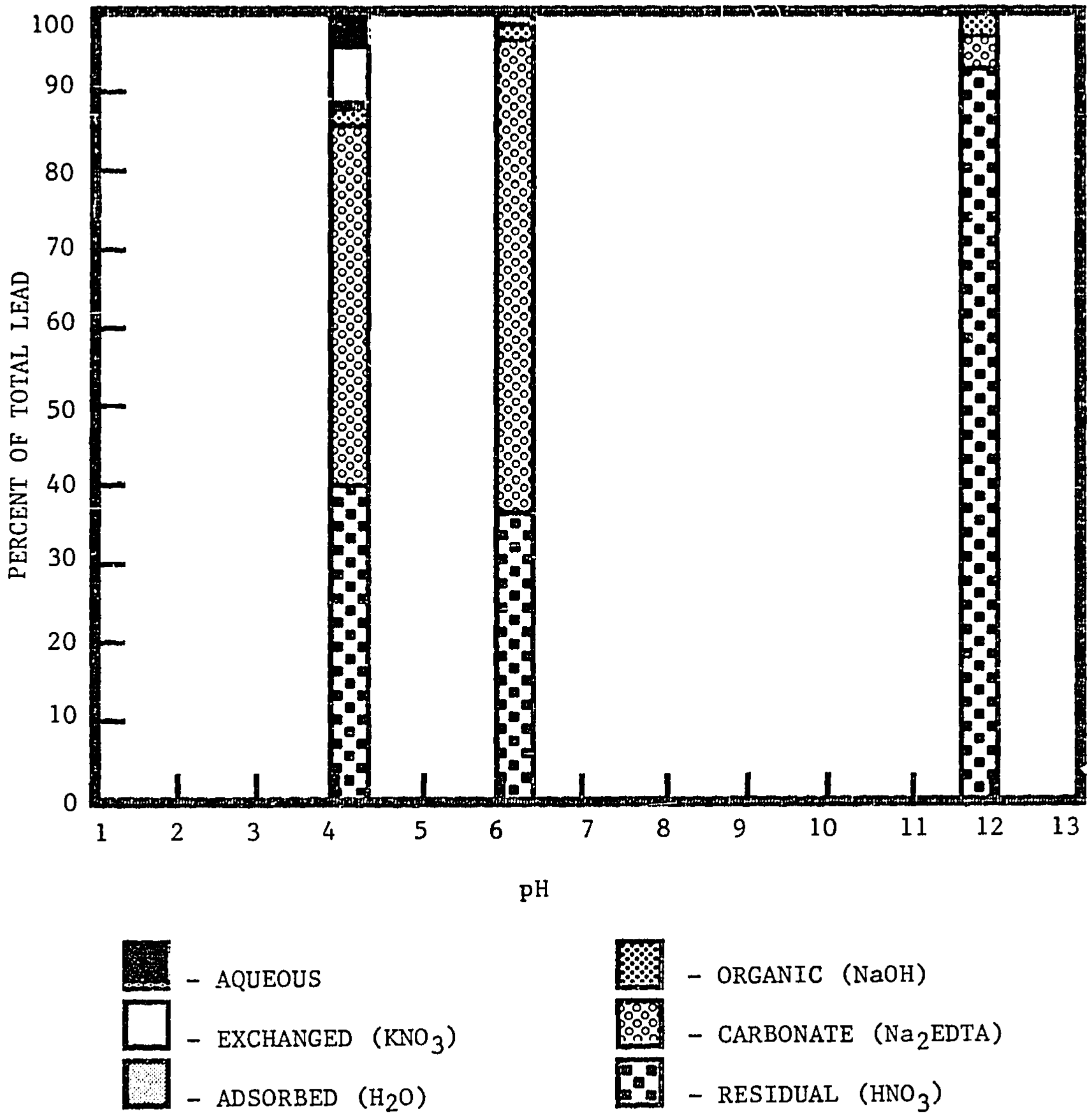

Figure 42: Percent of Sequentially Extracted Lead from Drilling Mud TS after Equilibrating at the Indicated pH

Table 43: Comparison of Percent Lead in Sequentially Extracted Drilling Fluids with the Results of Previous Studies

Extractant	Chang, et al. (1984)	Sposito, et al. (1982) pH=7.1	Stover, et al. (1976)	JS pH=6.9	TS pH=6.2	TC pH=8.0
$KNO_3 + H_2O$	< 1	2.1	8.8	5.6	1.5	< 0.1
NaOH	2	5.2	29.1	6.6	2.7	1.7
EDTA	82	68.6	61.4	72.7	59.9	58.0
HNO_3	16	23.8	4.4	14.7	35.8	39.4

Summary -- pH Variation of Drilling Fluids

The important observation to be made from the percentages of metal in each extracted fraction is associated with the very high percentages of the metals that were in the residual, carbonate, and organic forms for most metals at the pH values tested. Only lead in sample JS at low pH, and barium in sample TC at all pH values tested, showed significant percentages present in the exchanged or soluble form.

In no case was there a substantial release to the soluble phase with changing pH. There were primarily shifts from the residual to the carbonate, organic, or exchanged forms. However, some metals in aqueous solution did exceed drinking water standards (Figures 43 to 46). Arsenic did not exceed the standards in any of the tests. Barium exceeded the standards in most cases regardless of pH, probably because of the large levels of barium in the waste and the formation of soluble chloride complexes. Chromium exceeds the standard in all cases for fluid TS and at $pH < 4$ for fluid JS. Lead in samples TS and JS exceed the drinking water standard at low pH, probably because of the formation of soluble chloride complexes. Although the standards are exceeded it is not by a great amount and these metals would probably quickly precipitate out of solution if they were released from the pits. In no instance did the levels of metals in the aqueous solution exceed the EP Toxicity Limits.

The significance of these results is that with pH changes to be expected in the natural environment there is not likely to be a significant release of metals from drilling fluid disposal pits. The

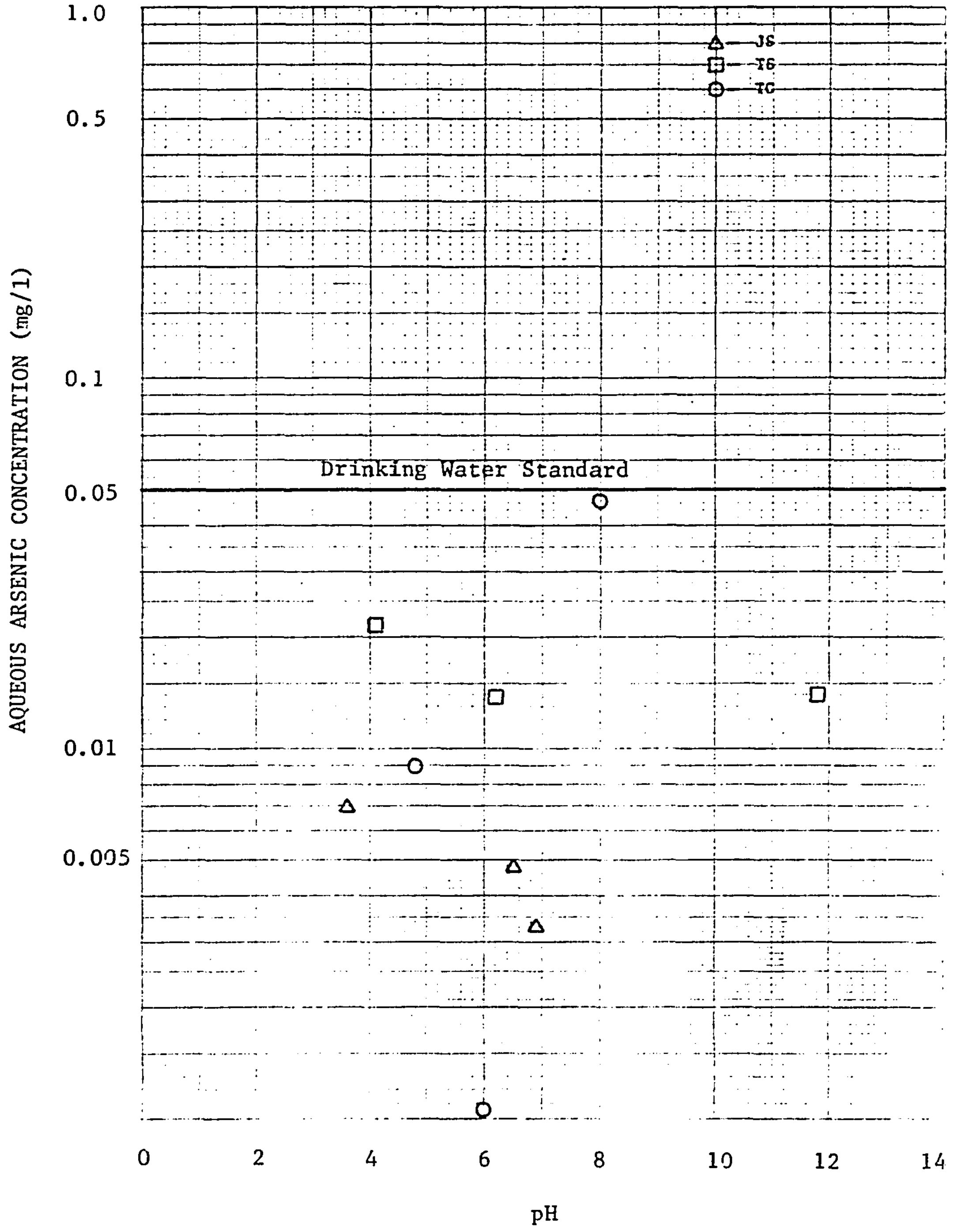

Figure 43: Comparison of Aqueous Arsenic Concentrations and Drinking Water Standard (0.05 mg/l)

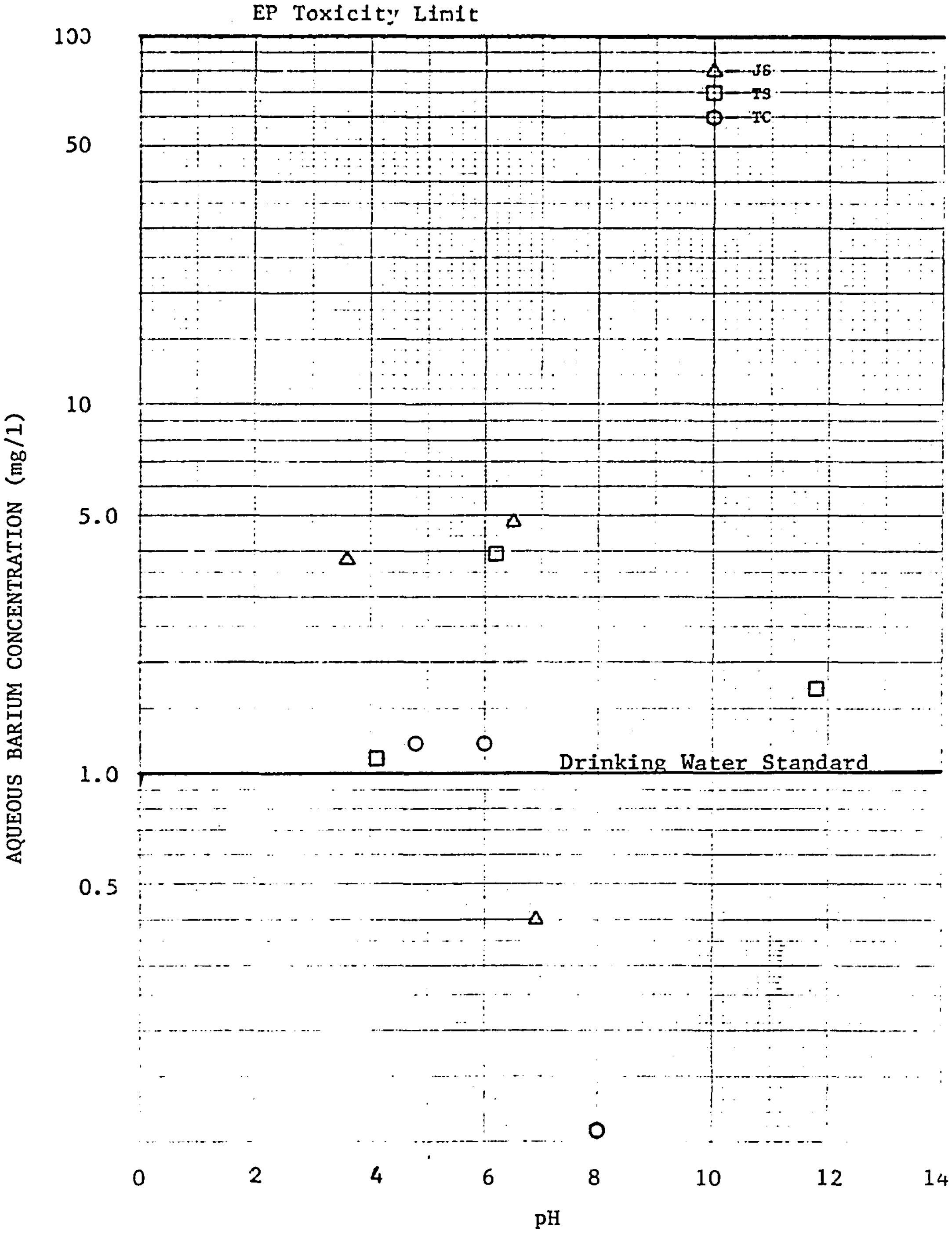

Figure 44: Comparison of Aqueous Barium Concentrations with Drinking Water Standard (mg/l) and EP Toxicity Limit (mg/l)

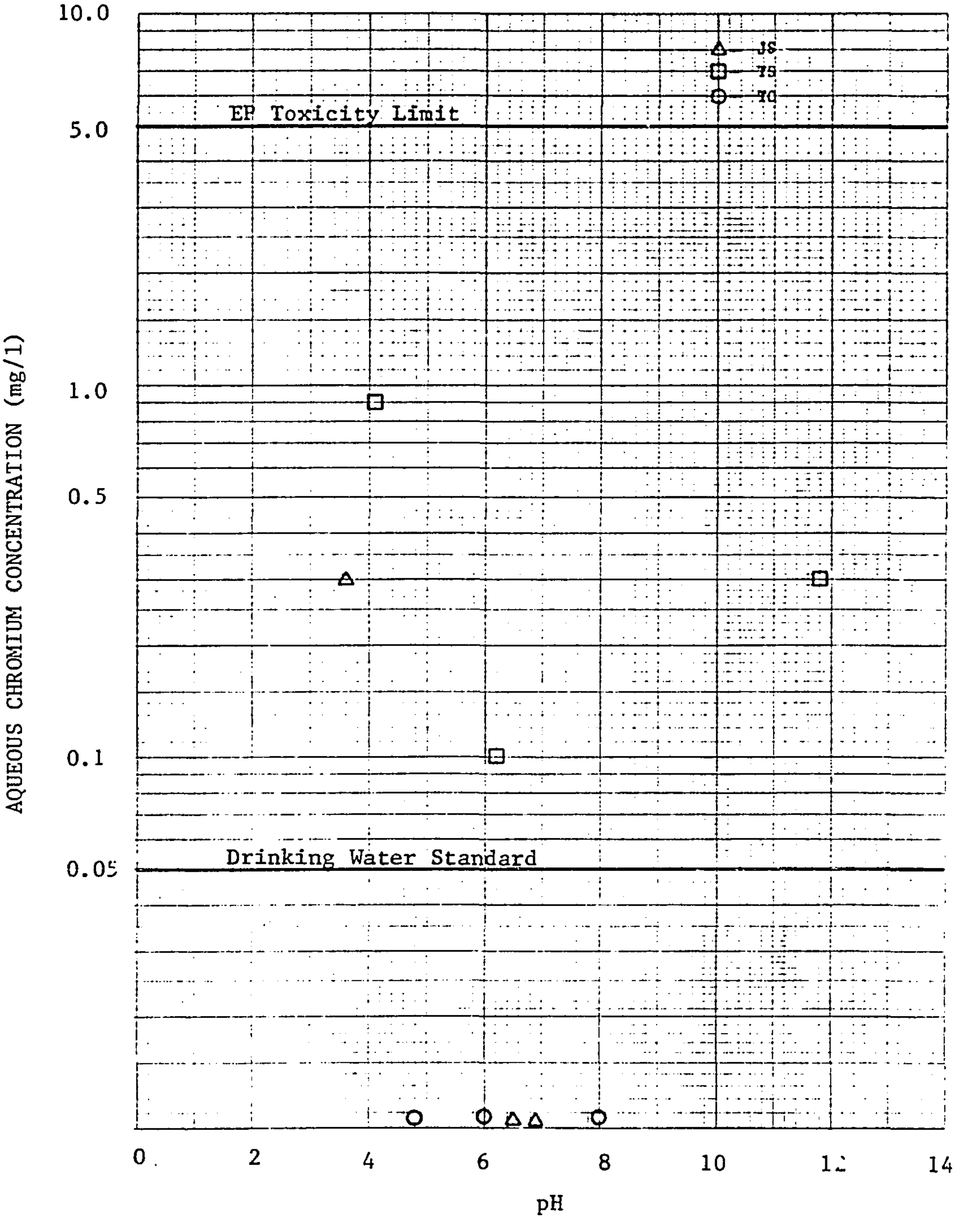

Figure 45: Comparison of Aqueous Chromium Concentrations with Drinking Water Standard (mg/l) and EP Toxicity Limit (mg/l)

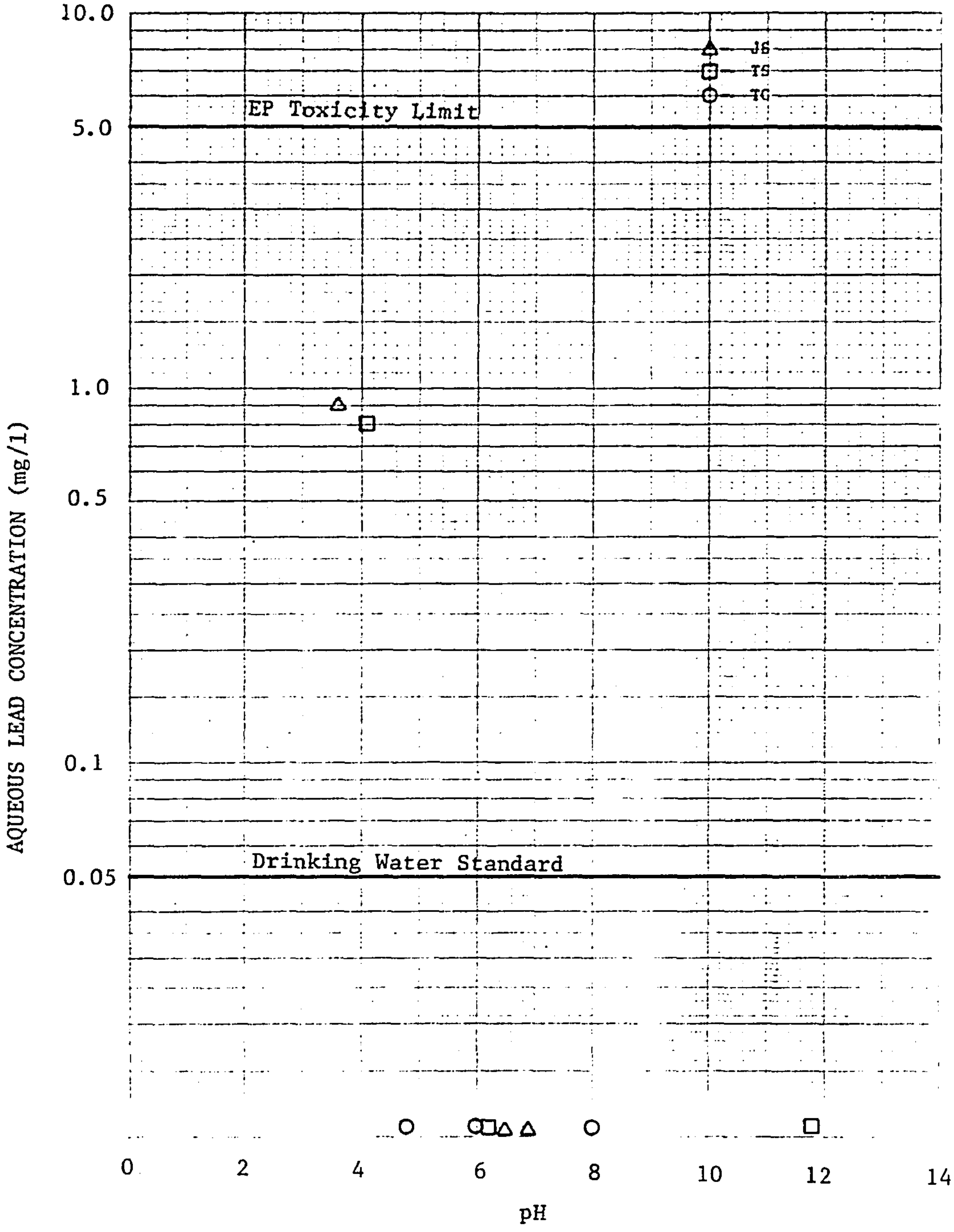

Figure 46: Comparison of Aqueous Lead Concentrations with Drinking Water Standard (mg/l) and EP Toxicity Limit (mg/l)

lower pH values (< 4) which might produce some environmental impact are unlikely to occur in the environment, especially when considering the alkalinity of these wastes.

Also, the similarity of these results with those obtained by other investigators (Chang, et al., 1984; Sposito, et al., 1982; and Stover, et al., 1976) indicates that their results in the area of amending soils with wastes may be applicable to the landfarming of drilling fluid wastes with regards to metals.

This study indicates the applicability of sequential extraction methods to waste studies while changing pH. The consistency of the method is shown by the similar results obtained from repeat experiments (Appendix A). By using this method, much more information has been obtained than is possible from a total metals analysis or an EP Toxicity Test. Actual shifts in the chemical nature of the pollutants with changing pH have been observed and predictions can be made regarding behavior of metals in the environment.

The results are summarized for each metal in Figures 47 to 50. The figures were obtained by grouping the results of all three fluids tested for each metal and determining the first order regression line for each fraction. Overall the metals shift, with decreasing pH, from the residual fraction to the carbonate, organic or exchangeable fraction. Barium and lead seem the most likely to be released to solution because of the large exchanged fraction present at low pH. However, there is no evidence of significant release to the aqueous phase, even at very low pH values. In the worst case (pH=2) about 7 percent of total lead is in the aqueous phase.

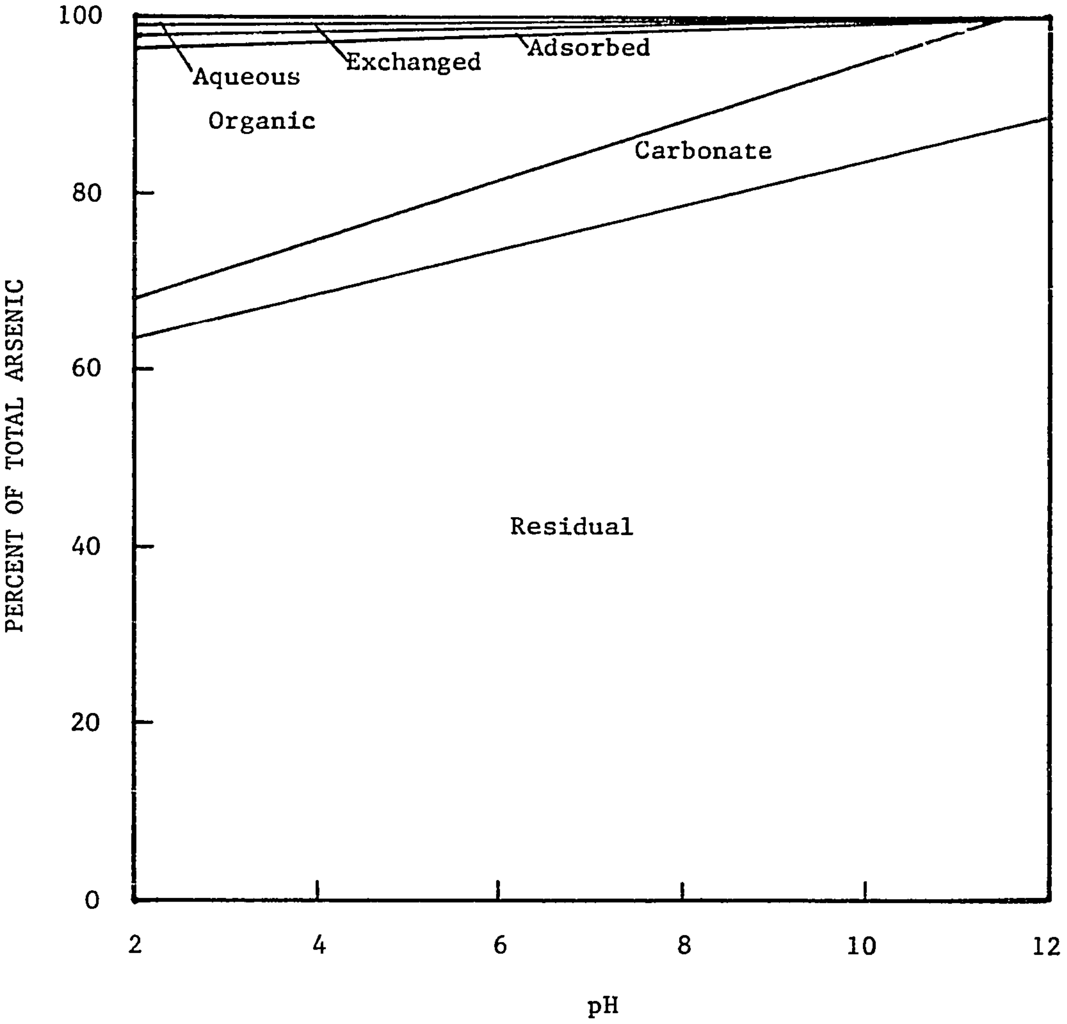

Figure 47: Summary of Arsenic Behavior with pH for the Drilling Fluids Tested

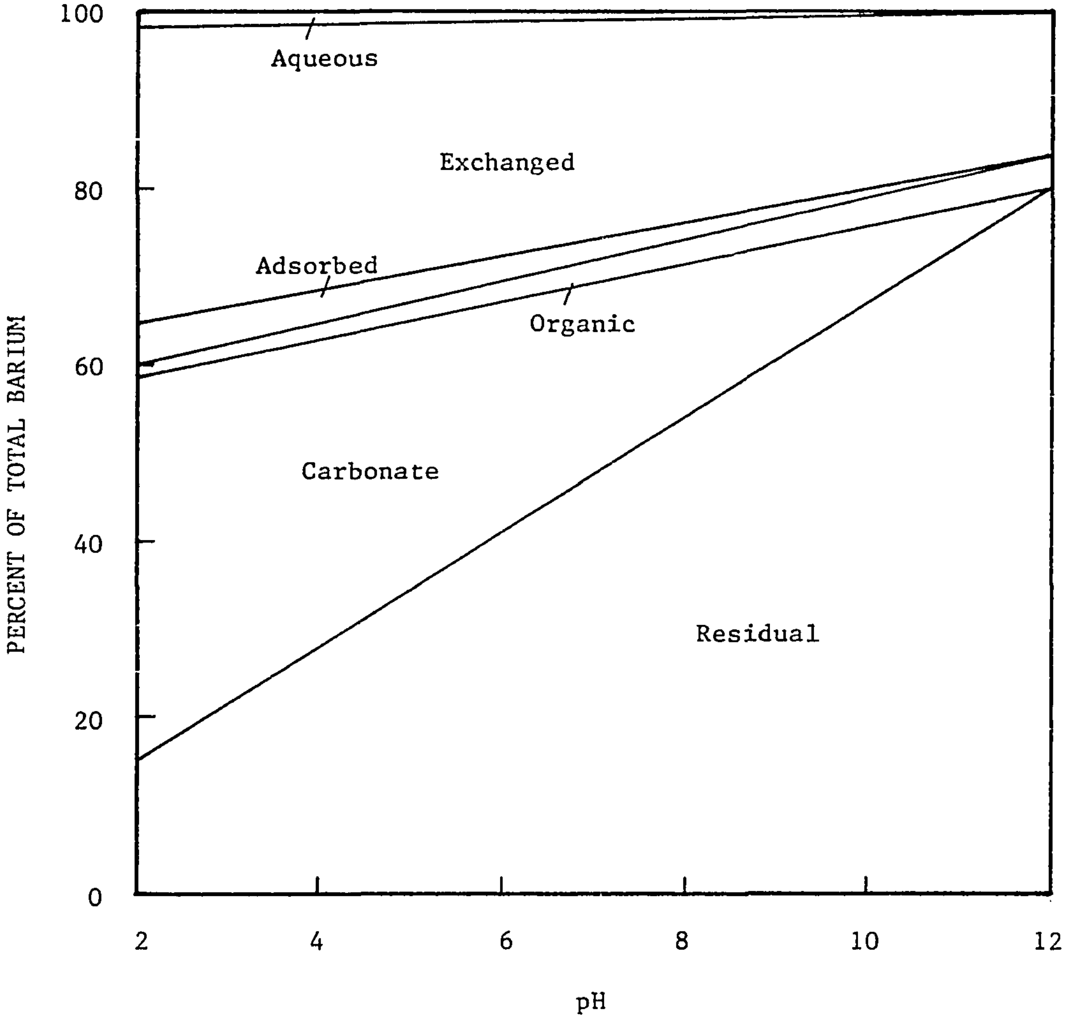

Figure 48: Summary of Barium Behavior with pH for the Drilling Fluids Tested

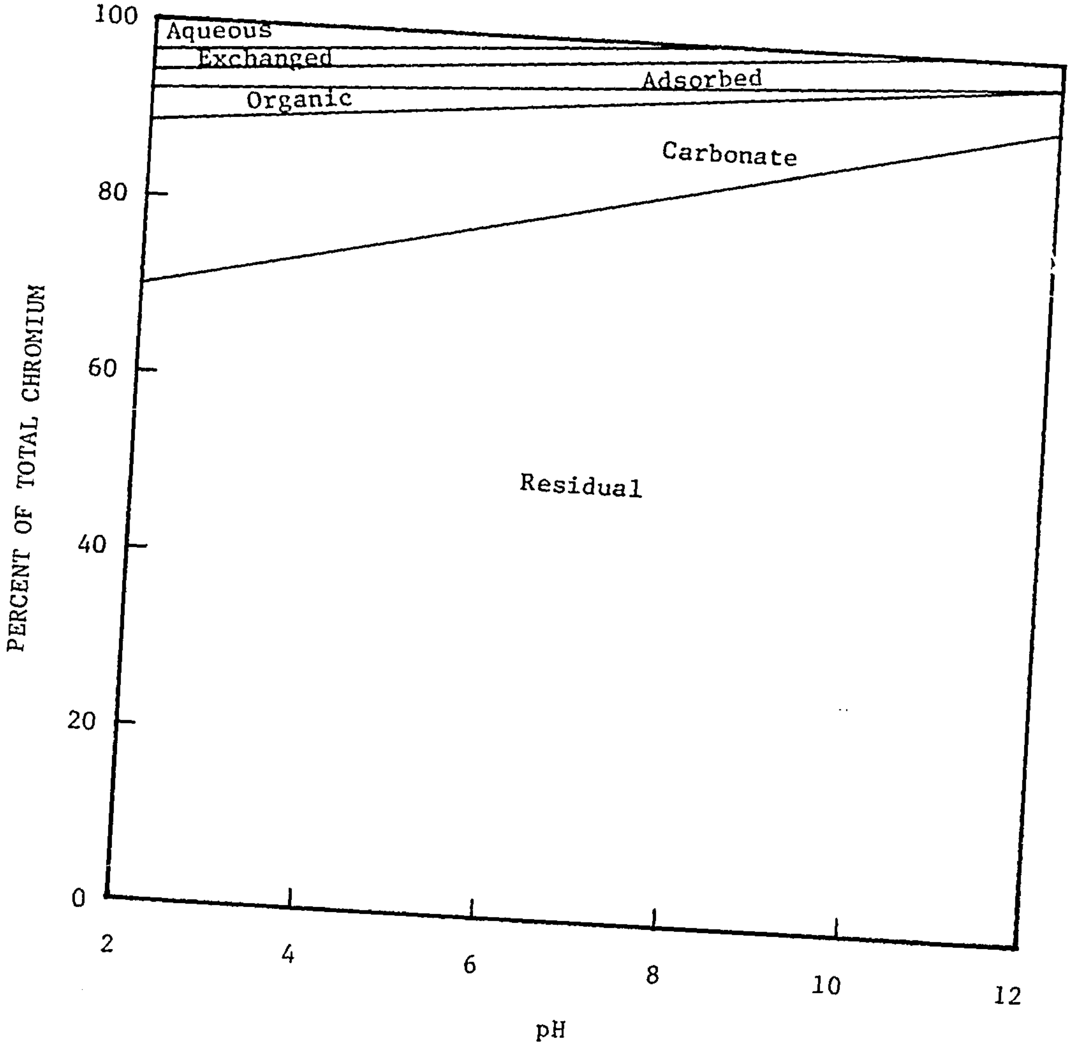

Figure 49: Summary of Chromium Behavior with pH for the Drilling Fluids Tested

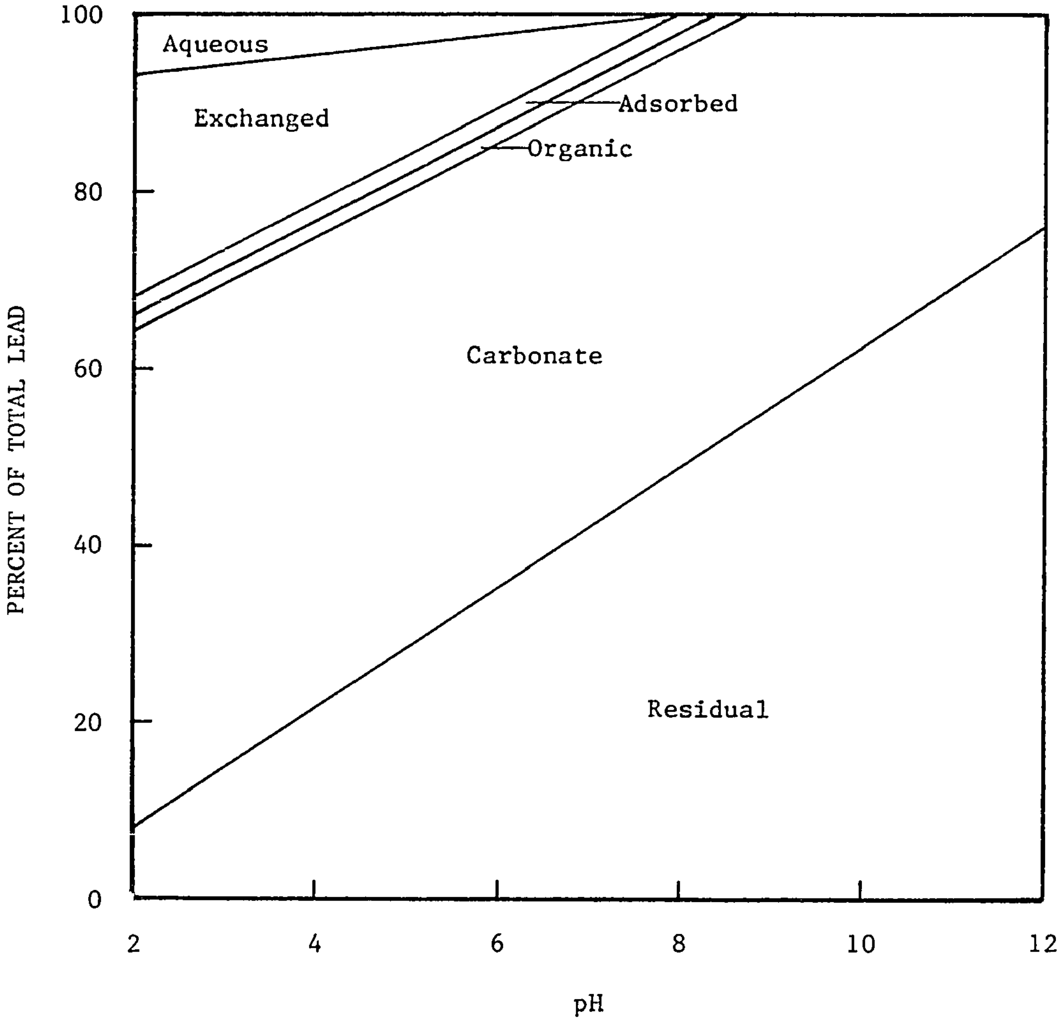

Figure 50: Summary of Lead Behavior with pH for the Drilling Fluids Tested

Effects of Ionic Strength Variation (Dilution of Aqueous Phase) on Metal Speciation

General Comments on Sequential Extraction Results

The results of the sequential extractions of fluids equilibrated under conditions of varying ionic strength are presented as percent recovered for each extractant and actual concentration per unit solid or liquid. Percent recovered allows for comparison between the different drilling fluids while actual concentrations permit comparison with water quality standards.

Metal Speciation with Varying Ionic Strength

The results for arsenic, barium, chromium, and lead are reported in Tables 44 to 51 and Figures 51 to 62. Ionic strengths were changed by diluting the drilling fluid liquid to 0.5 and 0.1 of field strength, and also testing at field strength. These tests were performed to determine the effect that dilution might have on the nature of metals within the fluids. Any major changes in equilibrium would indicate potential metal release during periods of heavy rainfall or perhaps if the wastes are landfarmed.

Arsenic. In all of the experiments arsenic remained predominantly in the residual fraction with the remaining distributed between the carbonate and organic fractions. Fluids JS and TC showed an increase in residual arsenic with dilution of the aqueous phase -- this may have resulted from the dissolution of carbonate compounds containing trapped arsenic compounds. This could result in the distribution of the associated arsenic to the organic and residual

Table 44: Percent Arsenic Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

Dilution of Aqueous Phase	pH	Aqueous Phase (%)	Extractant KNO_3 (%)	 H_2O (%)	 NaOH (%)	 EDTA (%)	 HNO_3 (%)
			Drilling Fluid JS				
1.0	6.5	0.5	< 0.1	1.3	0.2	17.7	80.3
0.5	6.3	0.4	< 0.1	1.4	8.3	7.2	82.6
0.1	6.0	0.1	0.4	1.0	9.6	1.7	87.2
			Drilling Fluid TS				
1.0	11.8	0.4	0.4	0.1	1.6	9.3	88.2
0.5	11.9	0.9	1.3	0.2	3.9	11.9	81.8
0.1	11.9	0.6	1.9	0.3	4.9	12.0	80.2
			Drilling Fluid TC				
1.0	4.8	1.3	2.1	0.3	23.8	13.8	58.7
0.5	3.1	2.6	2.6	0.1	8.6	0.2	85.8
0.1	3.0	1.8	1.6	< 0.1	6.2	0.5	89.8

Table 45: Concentration of Arsenic Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

Dilution of Aqueous Phase	pH	Aqueous Phase (μg/l)	Extractant				
			KNO_3 (μg/kg)	H_2O (μg/kg)	NaOH (μg/kg)	EDTA (μg/kg)	HNO_3 (μg/kg)
			Drilling Fluid JS				
1.0	6.5	4.8	< 0.1	229	32.9	3560	16100
0.5	6.3	3.1	6.4	216	1500	1380	13400
0.1	6.0	0.1	70.1	172	1610	289	15800
			Drilling Fluid TS				
1.0	11.8	13.9	153	48.7	588	3510	33400
0.5	11.9	12.9	217	38.1	626	1920	13300
0.1	11.9	9.3	351	51.7	891	2200	14600
			Drilling Fluid TC				
1.0	4.8	8.9	141	18.6	1270	606	3760
0.5	3.1	34.4	325	20.6	1160	22.9	12800
0.1	3.0	35.3	299	12.5	1170	93.7	17400

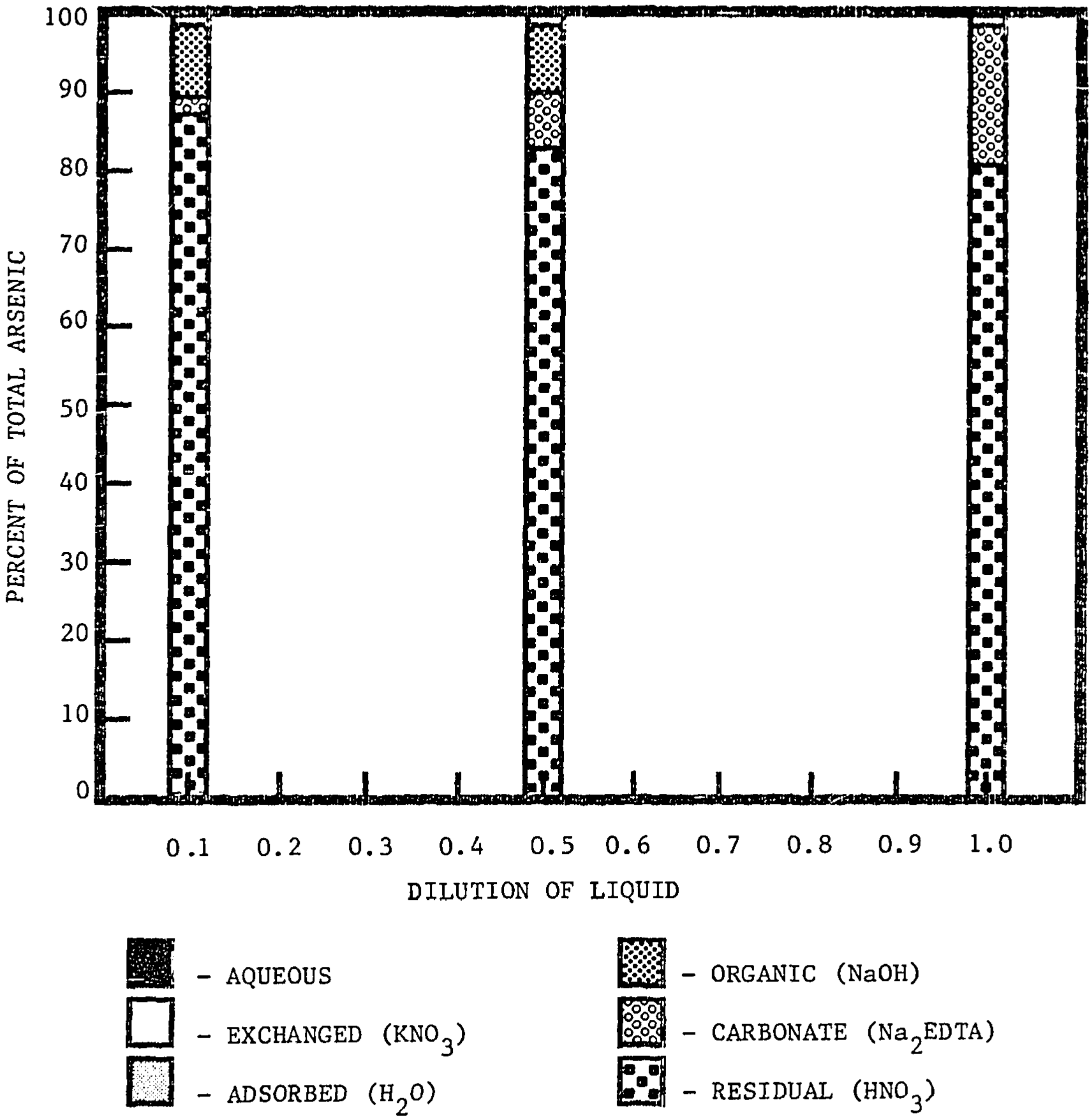

Figure 51: Percent of Sequentially Extracted Arsenic from Drilling Mud JS after Equilibrating at Varying Dilutions of Original Liquid

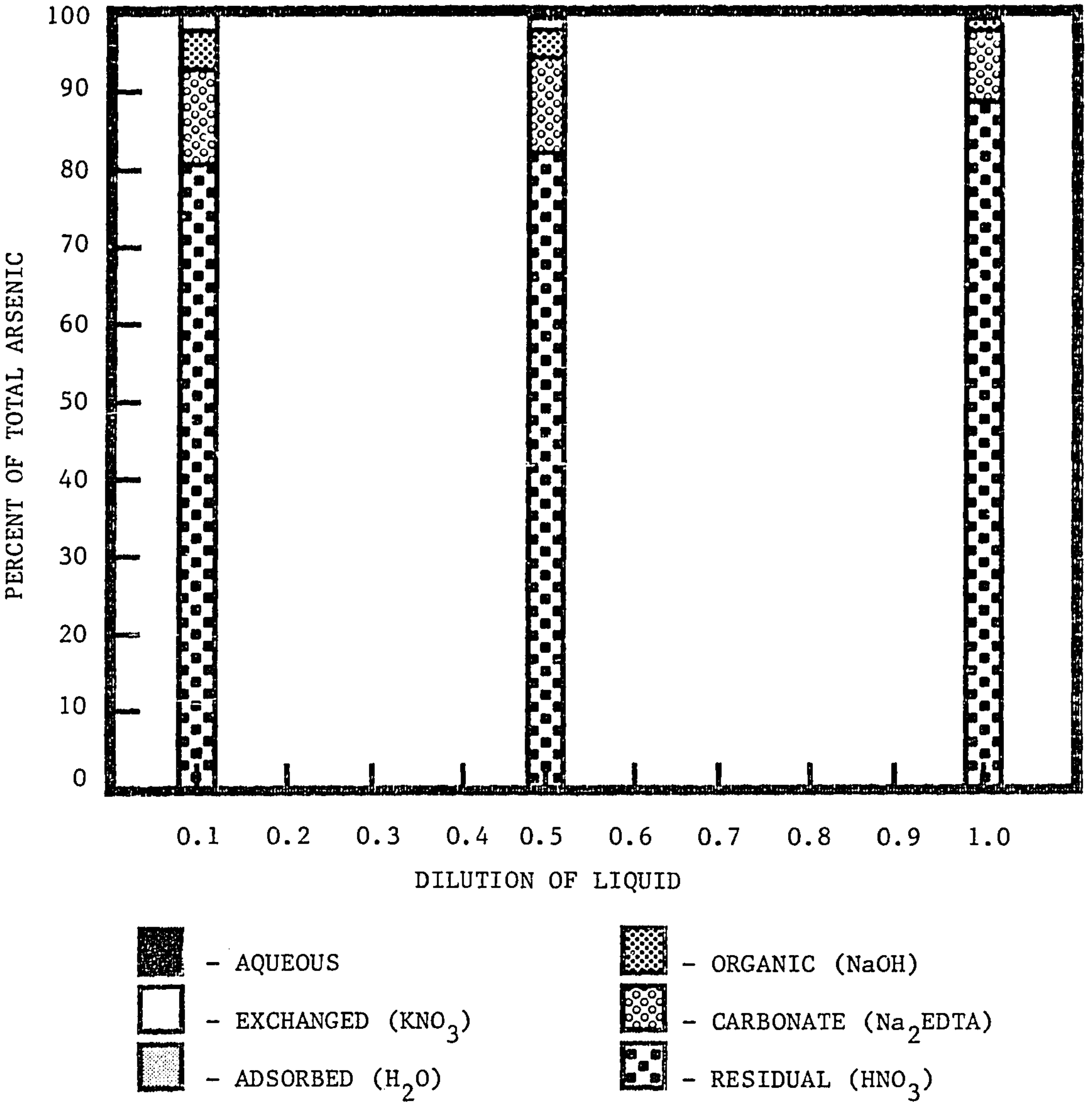

Figure 52: Percent of Sequentially Extracted Arsenic from Drilling Mud TS after Equilibrating at Varying Dilutions of Original Liquid

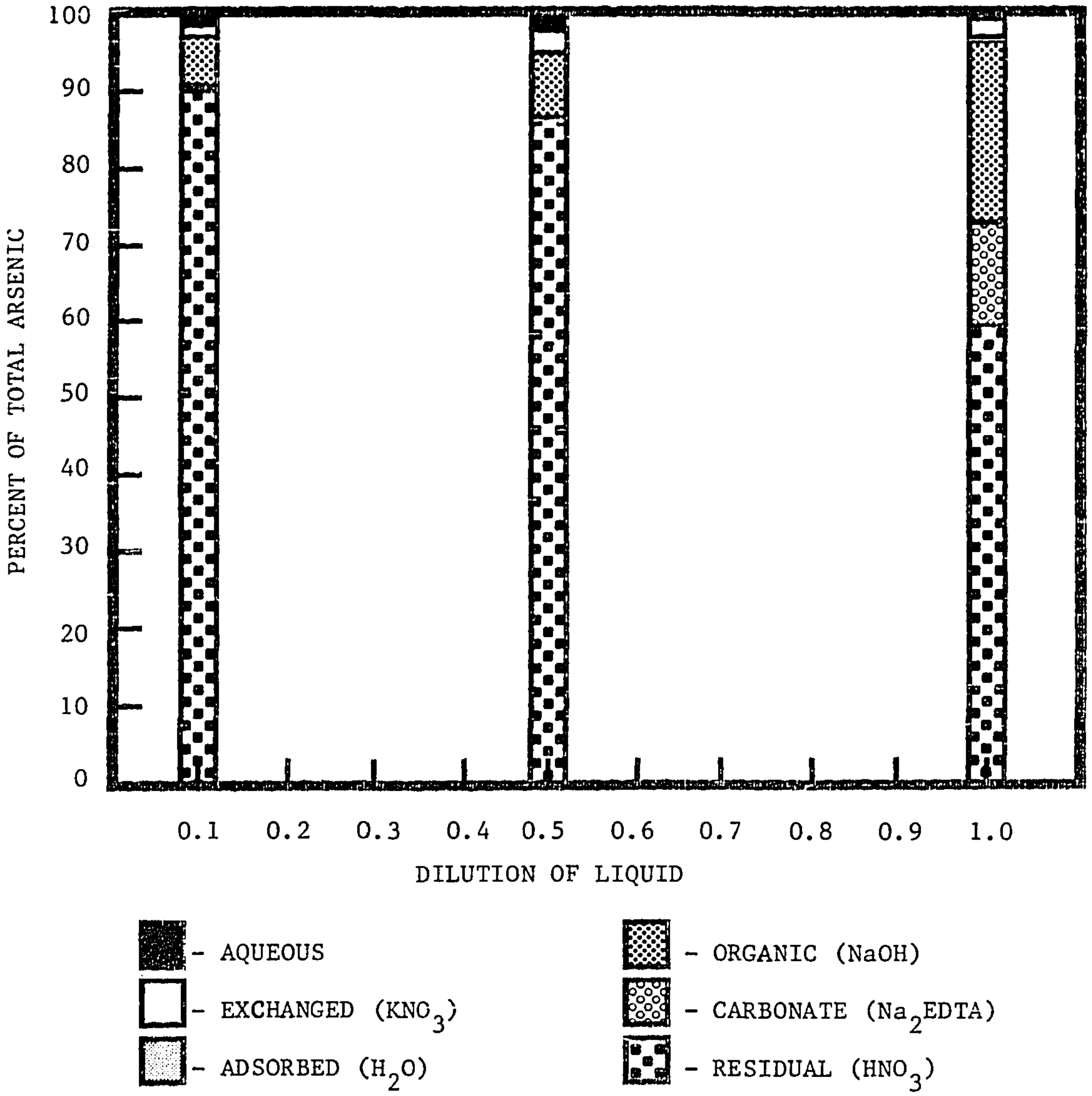

Figure 53: Percent of Sequentially Extracted Arsenic from Drilling Mud TC after Equilibrating at Varying Dilutions of Original Liquid

Table 46: Percent Barium Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

Dilution of Aqueous Phase	pH	Aqueous Phase (%)	Extractant KNO_3 (%)	H_2O (%)	NaOH (%)	EDTA (%)	HNO_3 (%)
			Drilling Fluid JS				
1.0	6.5	2.4	7.4	1.7	1.5	16.5	70.6
0.5	6.3	2.2	10.1	2.1	1.6	12.9	71.0
0.1	6.0	1.9	9.6	1.6	1.3	15.3	70.3
			Drilling Fluid TS				
1.0	11.8	0.6	2.4	0.3	1.6	4.4	90.6
0.5	11.9	0.2	1.4	0.3	1.6	4.5	92.0
0.1	11.9	0.3	2.1	0.4	1.4	5.3	90.5
			Drilling Fluid TC				
1.0	4.8	5.1	72.4	1.4	0.2	11.9	8.9
0.5	3.1	7.3	61.5	2.6	<0.1	15.7	12.9
0.1	3.0	19.1	44.7	2.3	<0.1	20.4	13.4

Table 47: Concentration of Barium Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of the Aqueous Phase

Dilution of Aqueous Phase	pH	Aqueous Phase (mg/l)	Extractant				
			KNO_3 (mg/kg)	H_2O (mg/kg)	NaOH (mg/kg)	EDTA (mg/kg)	HNO_3 (mg/kg)
			Drilling Fluid JS				
1.0	6.5	4.8	286	66.3	60.8	670	2790
0.5	6.3	3.9	355	74.9	57.4	472	2500
0.1	6.0	5.2	486	83.0	63.3	774	3630
			Drilling Fluid TS				
1.0	11.8	1.7	81.2	11.8	60.0	152	3120
0.5	11.9	0.5	51.6	11.3	54.5	143	3390
0.1	11.9	0.9	77.3	13.5	52.1	206	3560
			Drilling Fluid TC				
1.0	4.8	1.4	174	3.3	0.4	28.6	21.2
0.5	3.1	1.9	157	6.6	0.1	39.8	33.4
0.1	3.0	4.5	98.7	5.2	0.1	45.5	29.8

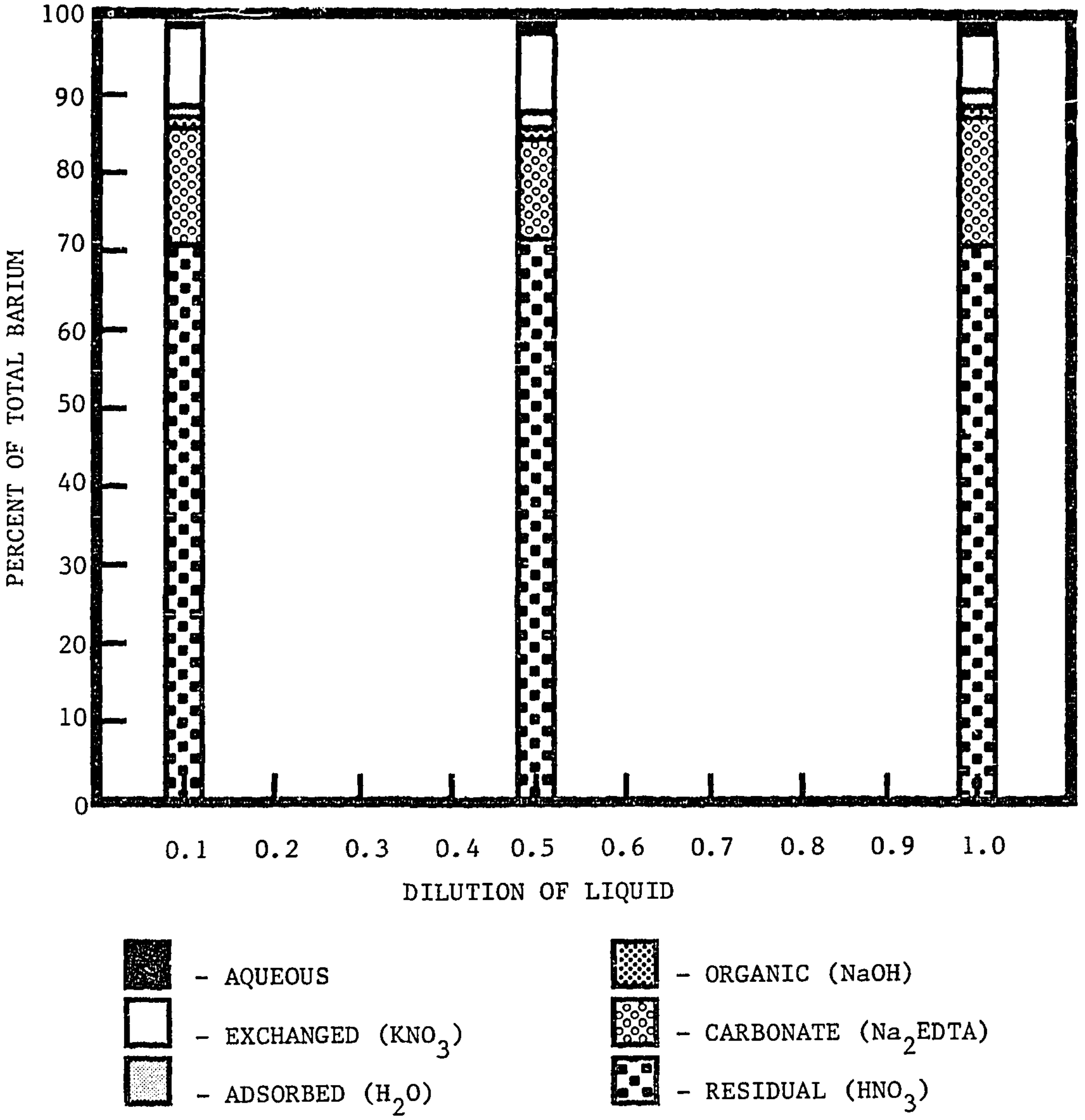

Figure 54: Percent of Sequentially Extracted Barium from Drilling Mud JS after Equilibrating at Varying Dilutions of Original Liquid

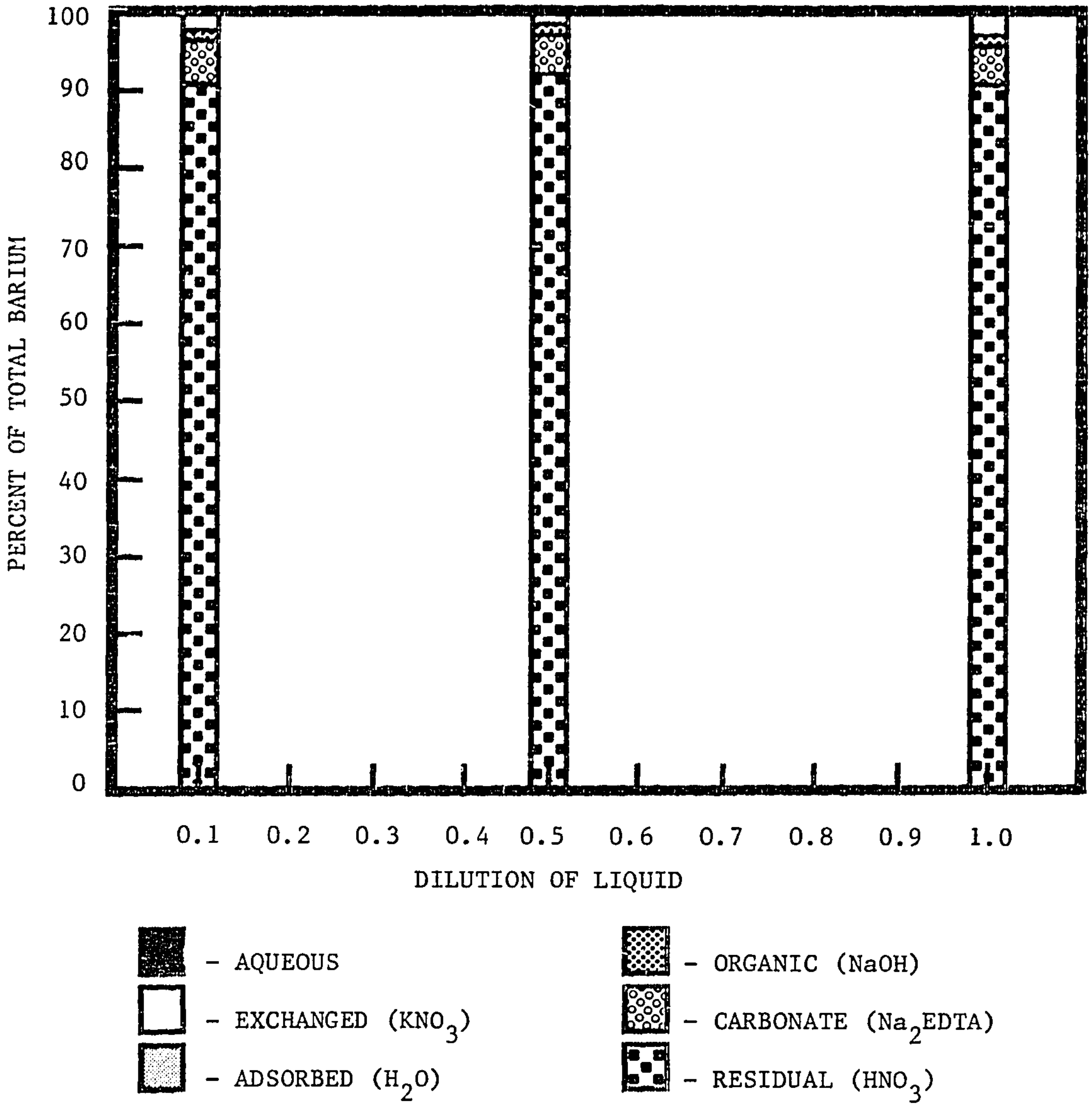

Figure 55: Percent of Sequentially Extracted Barium from Drilling Mud TS after Equilibrating at Varying Dilutions of Original Liquid

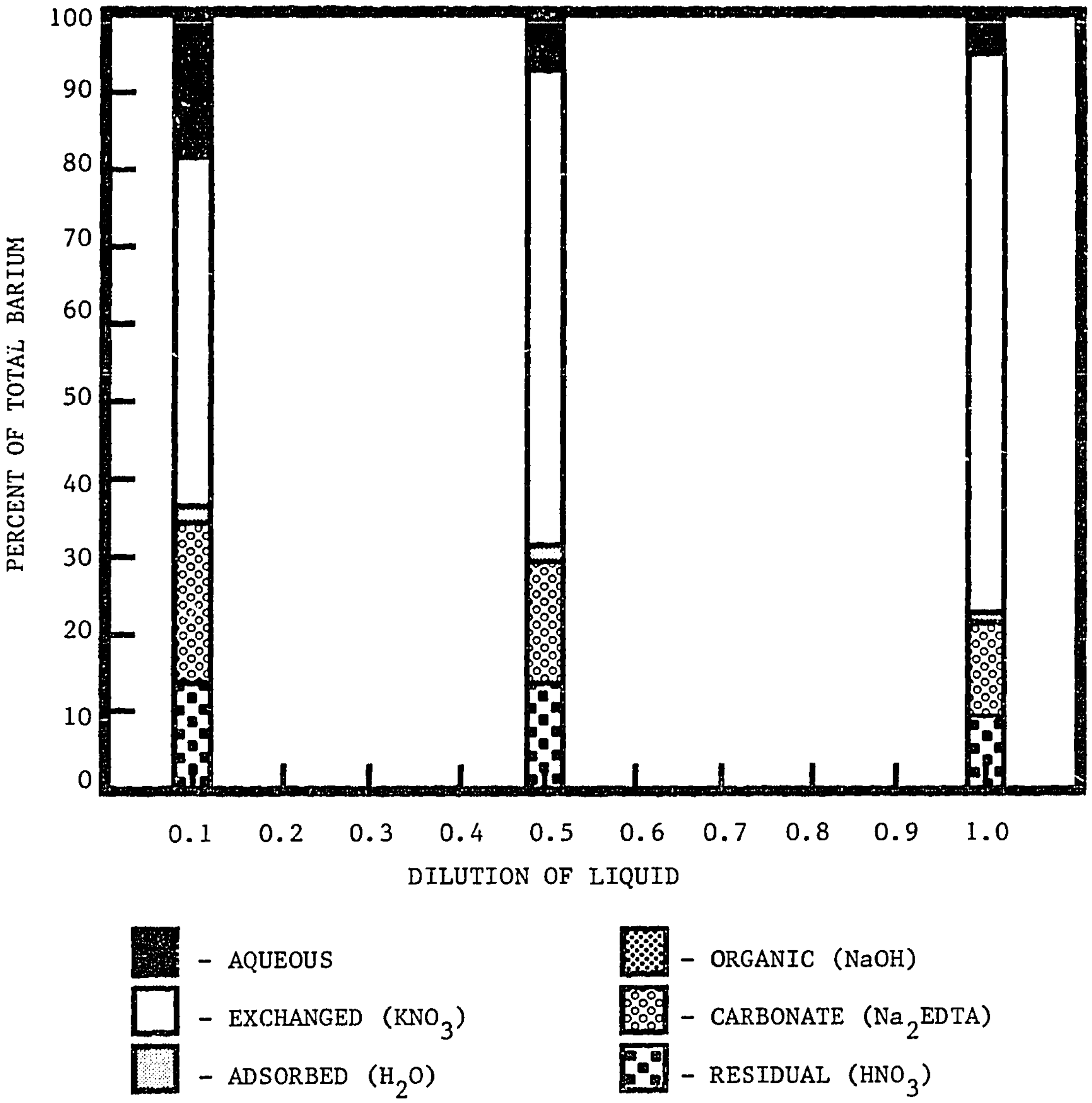

Figure 56: Percent of Sequentially Extracted Barium from Drilling Mud TC after Equilibrating at Varying Dilutions of Original Liquid

Table 48: Percent Chromium Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

Dilution of Aqueous Phase	pH	Aqueous Phase (%)	Extractant KNO_3 (%)	H_2O (%)	NaOH (%)	EDTA (%)	HNO_3 (%)
			Drilling Fluid JS				
1.0	6.5	0.8	< 0.1	2.7	3.0	28.8	64.7
0.5	6.3	0.1	< 0.1	2.2	3.0	30.0	67.6
0.1	6.0	< 0.1	< 0.1	2.8	5.2	26.0	66.0
			Drilling Fluid TS				
1.0	11.8	0.9	1.8	< 0.1	0.5	0.7	96.1
0.5	11.9	1.2	1.2	< 0.1	0.3	0.6	96.8
0.1	11.9	0.9	1.4	0.1	0.4	0.7	96.5
			Drilling Fluid TC				
1.0	4.8	0.5	< 0.1	< 0.1	< 0.1	6.5	92.9
0.5	3.1	2.2	< 0.1	< 0.1	< 0.1	5.5	92.2
0.1	3.0	0.7	< 0.1	< 0.1	< 0.1	5.9	93.4

Table 49: Concentration of Chromium Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

			Extractant				
Dilution of Aqueous Phase	pH	Aqueous Phase (mg/l)	KNO_3 (mg/kg)	H_2O (mg/kg)	NaOH (mg/kg)	EDTA (mg/kg)	HNO_3 (mg/kg)
			Drilling Fluid JS				
1.0	6.5	< 0.1	< 0.1	2.4	2.7	25.8	58.1
0.5	6.3	< 0.1	< 0.1	2.0	2.7	24.1	60.5
0.1	6.0	< 0.1	< 0.1	2.5	4.6	22.8	58.0
			Drilling Fluid TS				
1.0	11.8	0.3	6.1	0.2	1.6	2.3	332
0.5	11.9	0.4	3.8	< 0.1	1.1	1.8	322
0.1	11.9	0.2	4.7	0.3	1.3	2.3	319
			Drilling Fluid TC				
1.0	4.8	< 0.1	< 0.1	< 0.1	< 0.1	2.0	34.6
0.5	3.1	0.1	< 0.1	< 0.1	< 0.1	1.9	32.2
0.5	3.0	< 0.1	< 0.1	< 0.1	< 0.1	2.3	37.7

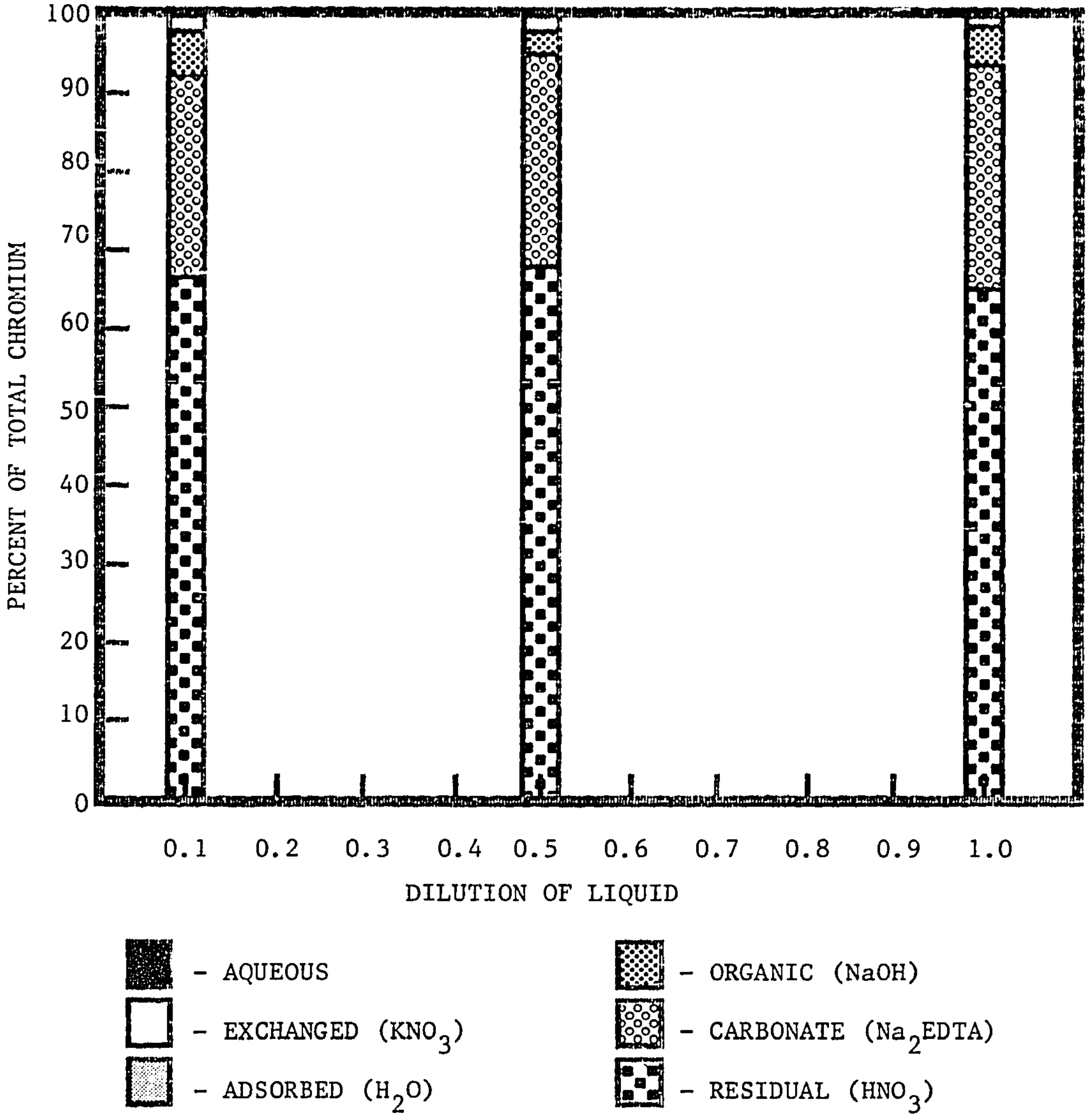

Figure 57: Percent of Sequentially Extracted Chromium from Drilling Mud JS after Equilibrating at Varying Dilutions of Original Liquid

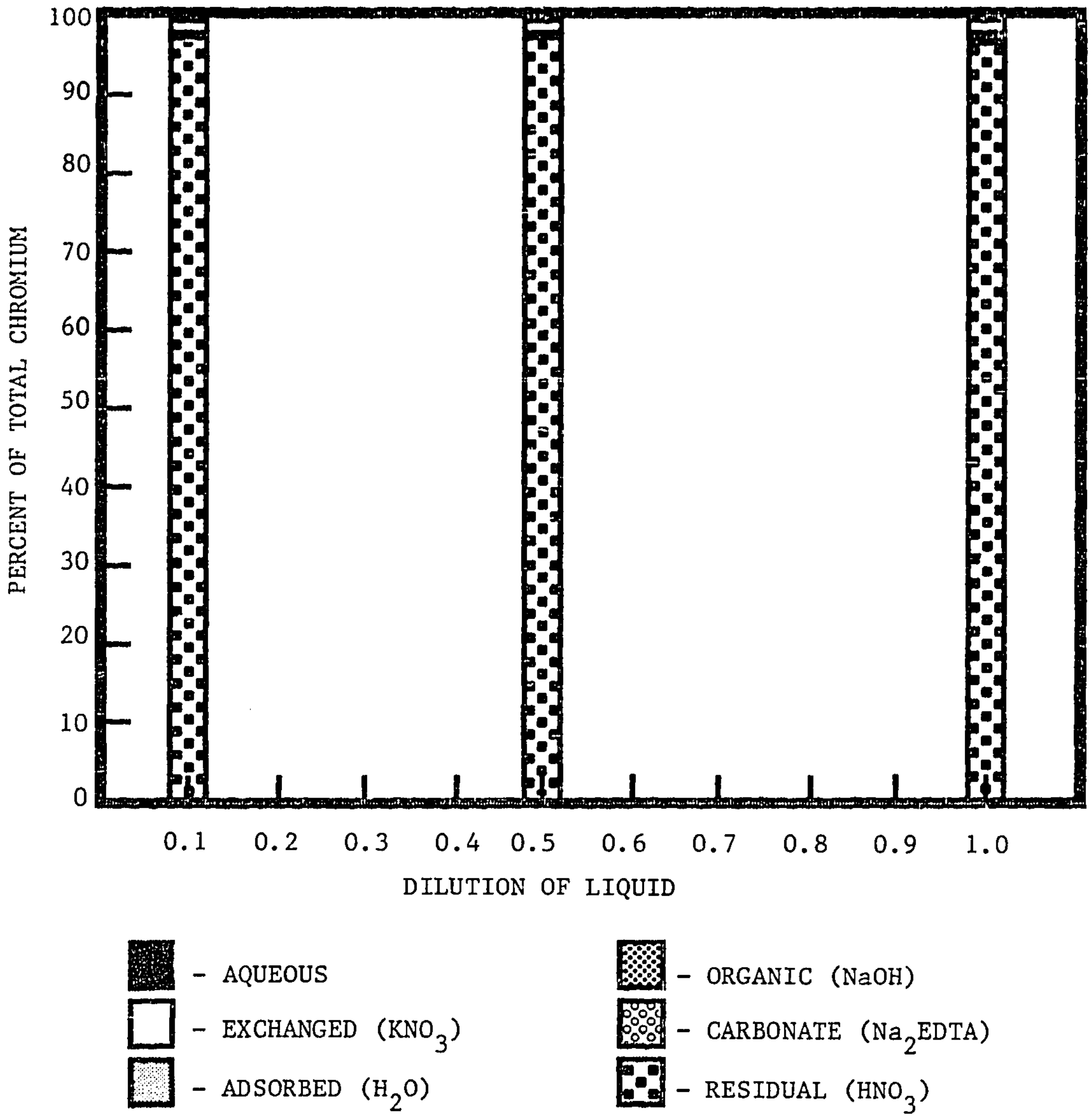

Figure 58: Percent of Sequentially Extracted Chromium from Drilling Mud TS after Equilibrating at Varying Dilutions of Original Liquid

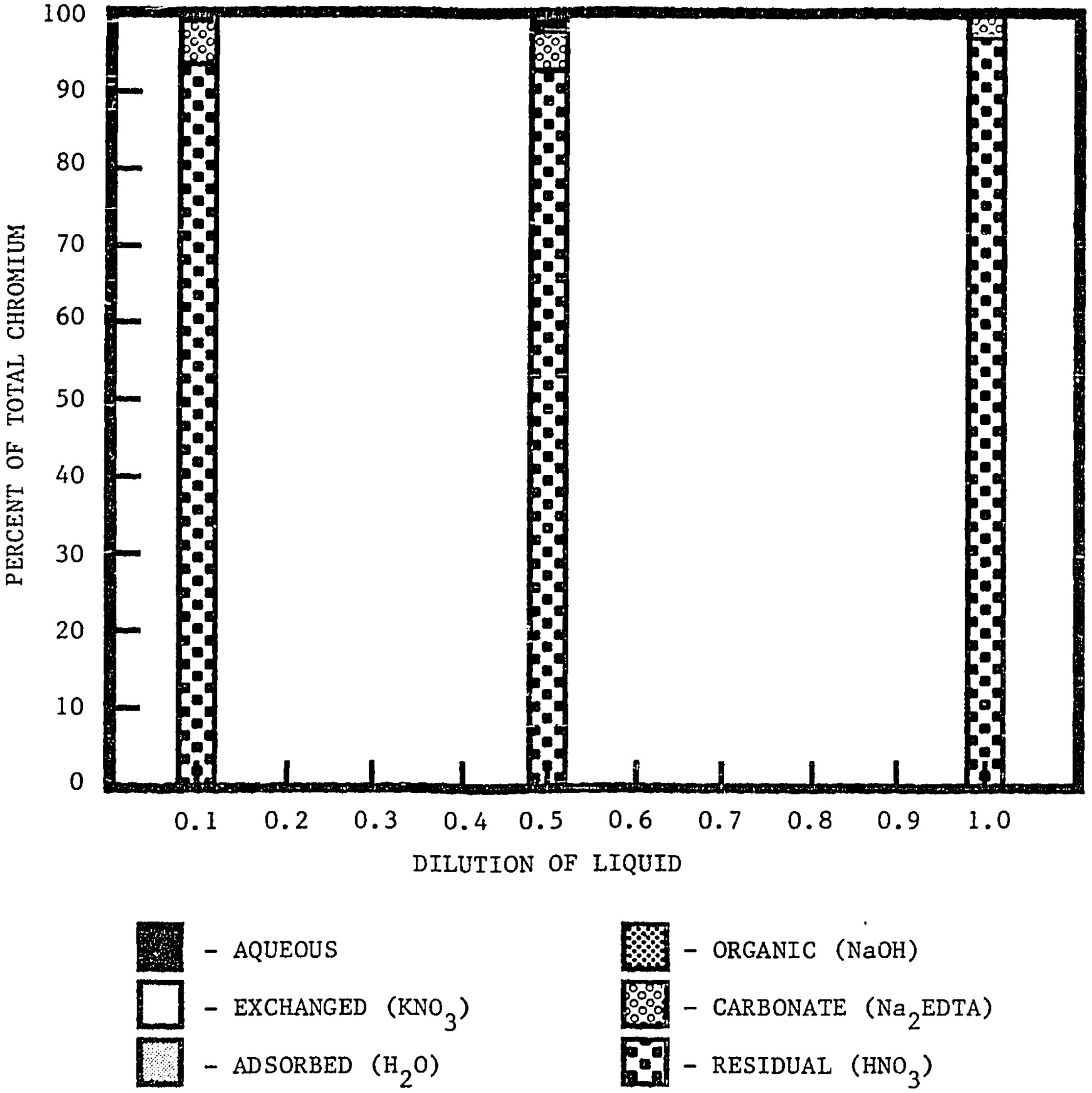

Figure 59: Percent of Sequentially Extracted Chromium from Drilling Mud TC after Equilibrating at Varying Dilutions of Original Liquid

Table 50: Percent Lead Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

Dilution of Aqueous Phase	pH	Aqueous Phase (%)	Extractant KNO_3 (%)	 H_2O (%)	 NaOH (%)	 EDTA (%)	 HNO_3 (%)
Drilling Fluid JS							
1.0	6.5	0.5	< 0.1	4.0	6.6	74.8	14.1
0.5	6.3	0.2	0.7	4.9	8.1	72.7	13.4
0.1	6.0	< 0.1	2.2	6.2	11.0	69.9	10.7
Drilling Fluid TS							
1.0	11.8	< 0.1	0.4	0.2	2.9	4.2	92.4
0.5	11.9	0.2	0.2	0.2	3.0	3.9	92.4
0.1	11.9	0.2	< 0.1	0.1	3.3	6.2	90.2
Drilling Fluid TC							
1.0	4.8	< 0.1	15.9	0.1	0.7	50.9	64.8
0.5	3.1	7.6	35.1	0.2	0.5	32.5	24.2
0.1	3.0	9.7	36.4	< 0.1	0.3	31.1	22.4

Table 51: Concentration of Lead Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

Dilution of Aqueous Phase	pH	Aqueous Phase (mg/l)	Extractant				
			KNO_3 (mg/kg)	H_2O (mg/kg)	NaOH (mg/kg)	EDTA (mg/kg)	HNO_3 (mg/kg)
			Drilling Fluid JS				
1.0	6.5	< 0.1	< 0.1	3.0	5.0	55.5	10.5
0.5	6.3	< 0.1	0.5	3.3	5.5	49.6	9.2
0.1	6.0	< 0.1	2.2	6.2	11.0	69.9	10.7
			Drilling Fluid TS				
1.0	11.8	< 0.1	0.8	0.4	6.4	9.2	202
0.5	11.9	< 0.1	0.5	0.4	5.9	7.6	180
0.1	11.9	< 0.1	0.1	0.3	6.3	11.8	176
			Drilling Fluid TC				
1.0	4.8	< 0.1	2.4	< 0.1	0.1	8.5	5.3
0.5	3.1	0.2	8.3	< 0.1	0.1	7.7	6.8
0.1	3.0	0.3	9.9	< 0.1	0.1	8.4	6.1

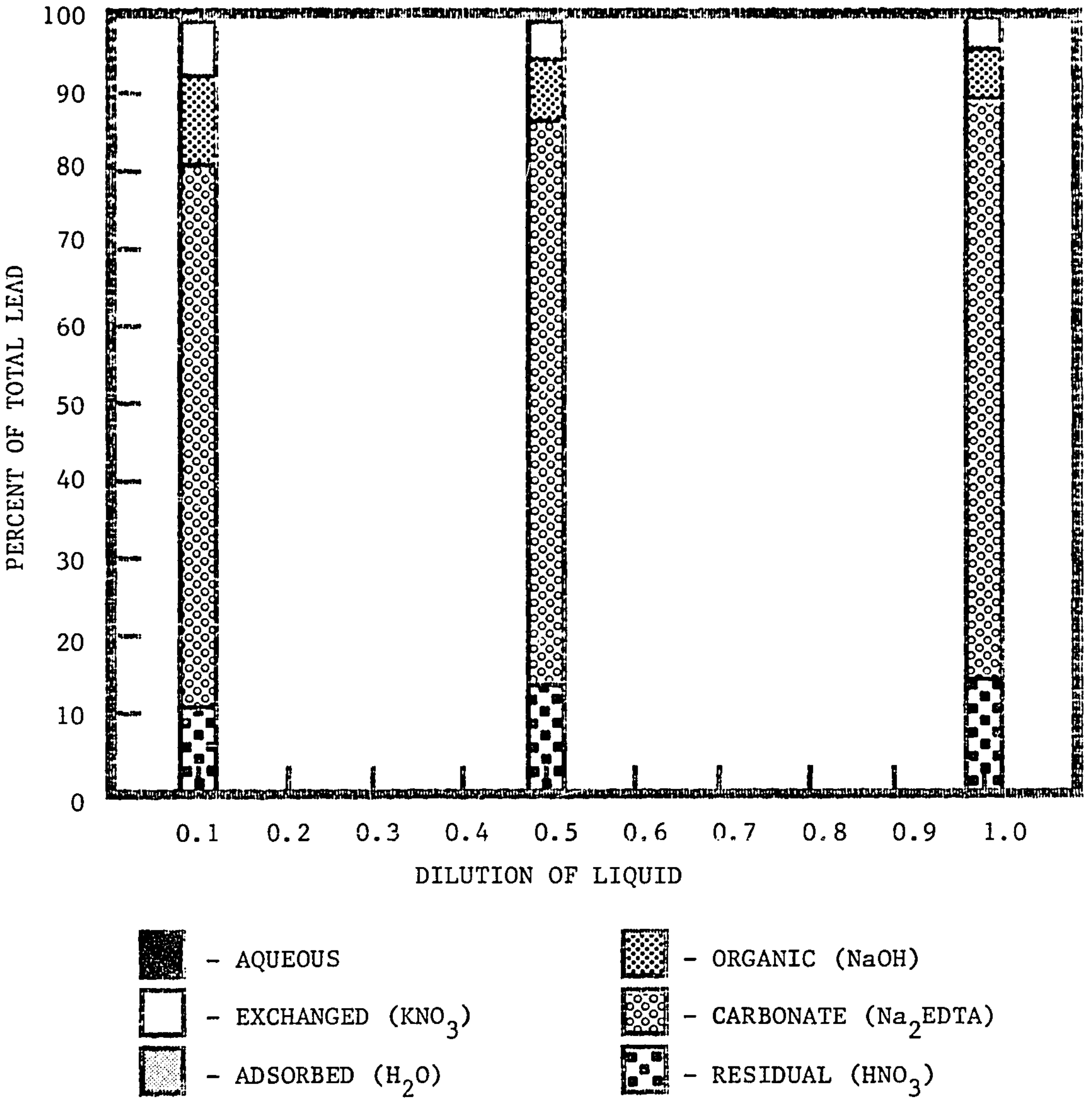

Figure 60: Percent of Sequentially Extracted Lead from Drilling Mud JS after Equilibrating at Varying Dilutions of Original Liquid

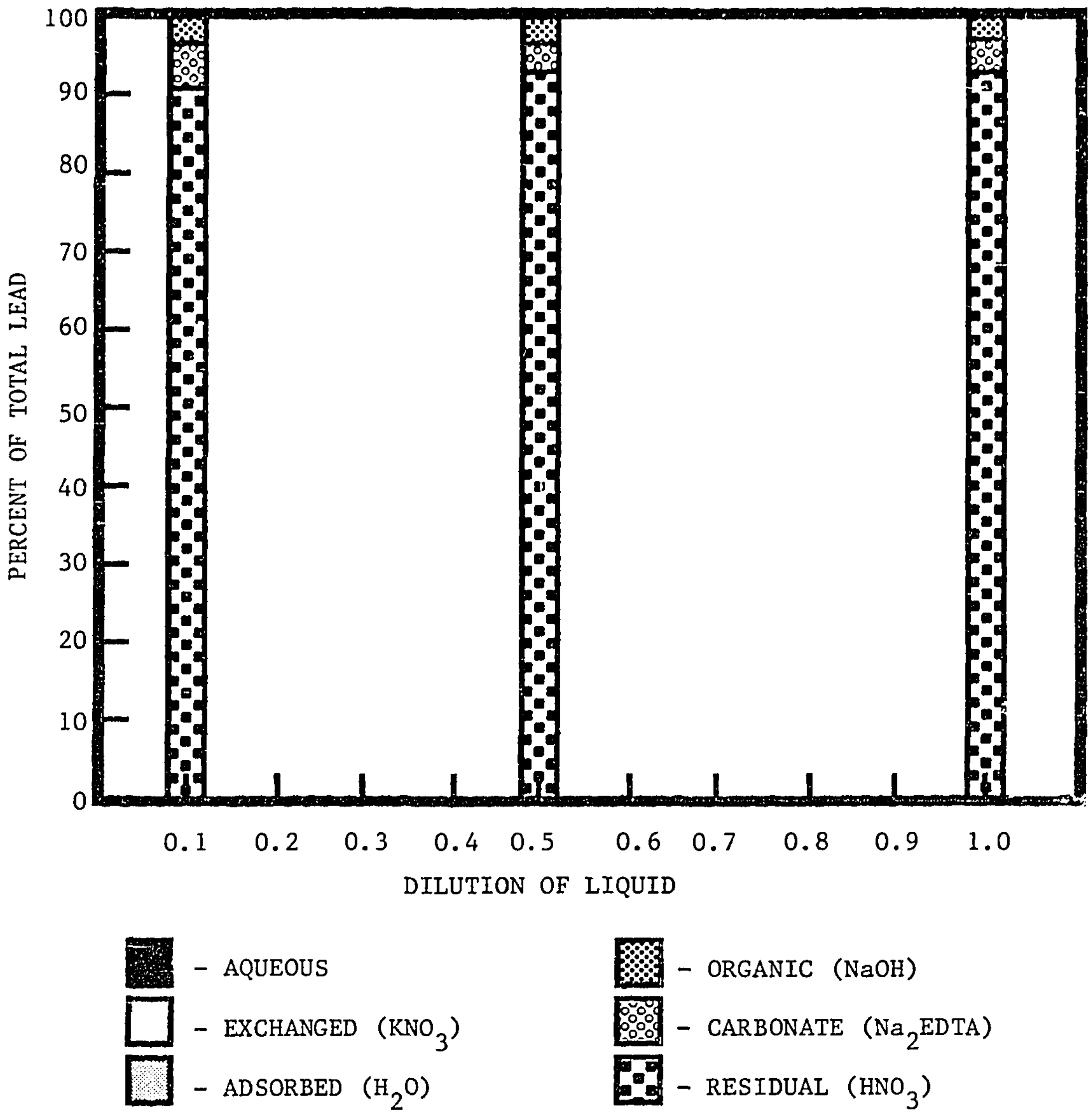

Figure 61: Percent of Sequentially Extracted Lead from Drilling Mud TS after Equilibrating at Varying Dilutions of Original Liquid

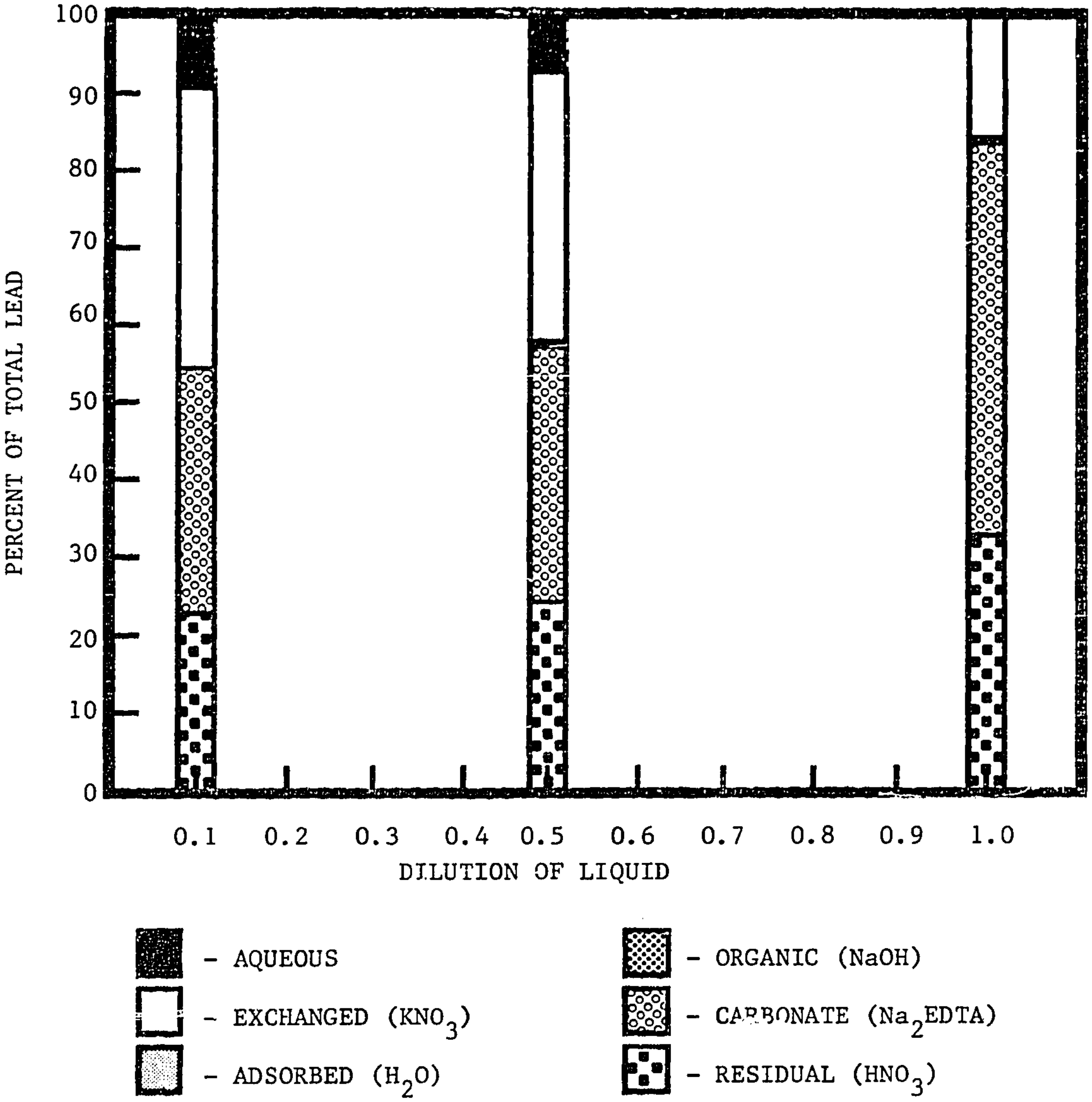

Figure 62: Percent of Sequentially Extracted Lead from Drilling Mud TC after Equilibrating at Varying Dilutions of Original Liquid

phases. This is especially likely because these experiments were conducted at pH values of approximately 6 for fluid JS and approximately 3.5 for fluid TC. This is in contrast to fluid TS which was subjected to a pH of approximately 11.6, and showed a slight decrease in the residual fraction with dilution. The associated increase in the carbonate, organic and exchanged fractions may reflect arsenic leaving the residual fraction to occupy sites left vacant by other anions reestablishing equilibrium in the aqueous phase.

Barium. Barium experienced no significant changes with dilution in fluids JS and TS. However, in fluid TC there was an increase in residual, carbonate, and aqueous forms of barium at the expense of exchanged forms with dilution. This reflects the potential of exchanged forms to move into the aqueous phase. With the aqueous phase diluted and fewer competing cations the barium became more soluble at the low pH (3.5) of these tests. With more barium in solution from the exchanged fraction, equilibrium may subsequently have shifted to precipitate some additional barium into the residual and carbonate fractions.

Chromium. In all dilution experiments chromium remained primarily in the residual and carbonate fractions with only minor changes in its relative distributions. This is an indication of the stability of chromium within well drilling fluid wastes.

Lead. There was no significant redistribution of lead in fluids JS and TS with dilution of the aqueous phase. However in fluid TC there was an increase in exchanged and aqueous forms of lead with a decrease in residual and carbonate forms. This is similar to the behavior of barium under the same conditions and illustrates the potential for movement to more available forms. With the aqueous phase diluted and fewer competing cations the lead became more soluble at the low pH (3.5) of these tests.

Summary -- Ionic Strength Variation

The tests indicated little change in the distribution of arsenic and chromium with dilution of the initial aqueous phase. More significant changes were observed with barium and lead, with some of these metals being released to the aqueous phase in one of the wastes (TC). This may be the result of the tendency of barium and lead to form soluble chloride complexes. Conditions may be favorable with dilution of the liquid in fluid TC for the complex to form and be stable in the aqueous phase.

A possible explanation for the majority of the wastes is that after dilution the original equilibrium is again established in the waste. Since the amounts of metal in the aqueous phase are minimal to begin with, the shifts within the solid phase required to equilibrate the system are not apparent with this short term test. A longer term experiment might reveal a slow, but continuous, release of metal into solution with a subsequent depletion of the solid phase metals inventory. This slow release would probably be of little concern if it were to enter ground or surface waters. In fact, the released metals would probably again become associated with the solid phase after leaving the pit because of the new equilibrium conditions encountered.

Flyash Stabilization of Metals in Drilling Fluids

General Comments on Stabilization Results

Table 52 and Figures 63 to 67 summarize the results of the experiments which investigated the effect of mixing flyash and drilling fluid wastes on the release or uptake of arsenic, barium, chromium, lead and zinc. These results are reported as the average of multiple experiments and EP Toxicity Tests. The raw data is contained in Appendix B.

The graphs (Figures 63 to 67) contain a line which illustrates the analysis results expected if combining the two wastes results in no release or uptake of metals, i.e., a simple physical mixing with no chemical reaction affecting the metals. The experimental results are represented by the points on the graphs, with the effects of flyash solidification on the metal behavior illustrated by the location of the experimental results relative to the line representing the drilling fluid used in the experiment. It is apparent that three possible effects can be illustrated:

(1) experimental points fall above the line, indicating release of metal upon mixing fluid and flyash, or

(2) experimental points fall on the line, indicating only physical mixing of fluid and flyash,

(3) experimental points fall below the line, indicating uptake of metal by the mixture.

Case (1) is not desirable since it reflects the potential for enhanced release of metals into the environment. Case (2) is acceptable since the release of metals is not adversely affected by the solidification process. Case (3) is a desired situation because it

Table 52: EP Toxicity Analysis Results from Drilling Fluids, Flyash, and Mixtures of Drilling Fluid and Flyash (The Mixtures were Allowed to Stand for 1 Week or 5 Weeks Prior to EP Toxicity Testing)

Sample	Percent Flyash	Arsenic (μg/l)	Barium (mg/l)	Chromium (mg/l)	Lead (mg/l)	Zinc (mg/l)
Flyash*	100	836.2	10.91	3.074	0.221	2.438
TS*	0	16.27	0.718	1.586	0.835	2.626
TC*	0	14.83	1.918	0.058	0.077	1.030
JS*	0	4.54	1.019	0.216	0.020	0.366
			1 Week			
TS**	10	110.2	2.267	1.524	0.538	2.422
	30	266.3	6.830	2.080	0.212	2.280
TC**	10	61.78	1.063	0.301	< 0.001	0.908
	20	276.5	3.406	0.751	0.069	1.195
	30	490.5	--	1.014	0.036	1.516
JS**	10	62.58	1.679	0.422	< 0.001	0.610
	30	170.0	3.335	1.059	0.005	1.007
			5 Weeks			
TS**	10		0.864	1.625	0.490	2.751
	30		4.810	1.890	0.401	2.369
TC**	10		1.351	0.266	0.132	1.119
	20		3.211	0.533	0.159	1.464
	30		4.070	0.849	0.207	1.356
JS**	10		1.986	0.390	0.044	0.573
	20		1.217	0.965	0.181	1.149
		EP Toxicity Test Limits				
		5,000	100	5.0	5.0	--

*Average of quadruplicate analyses.

**Average of duplicate experiments.

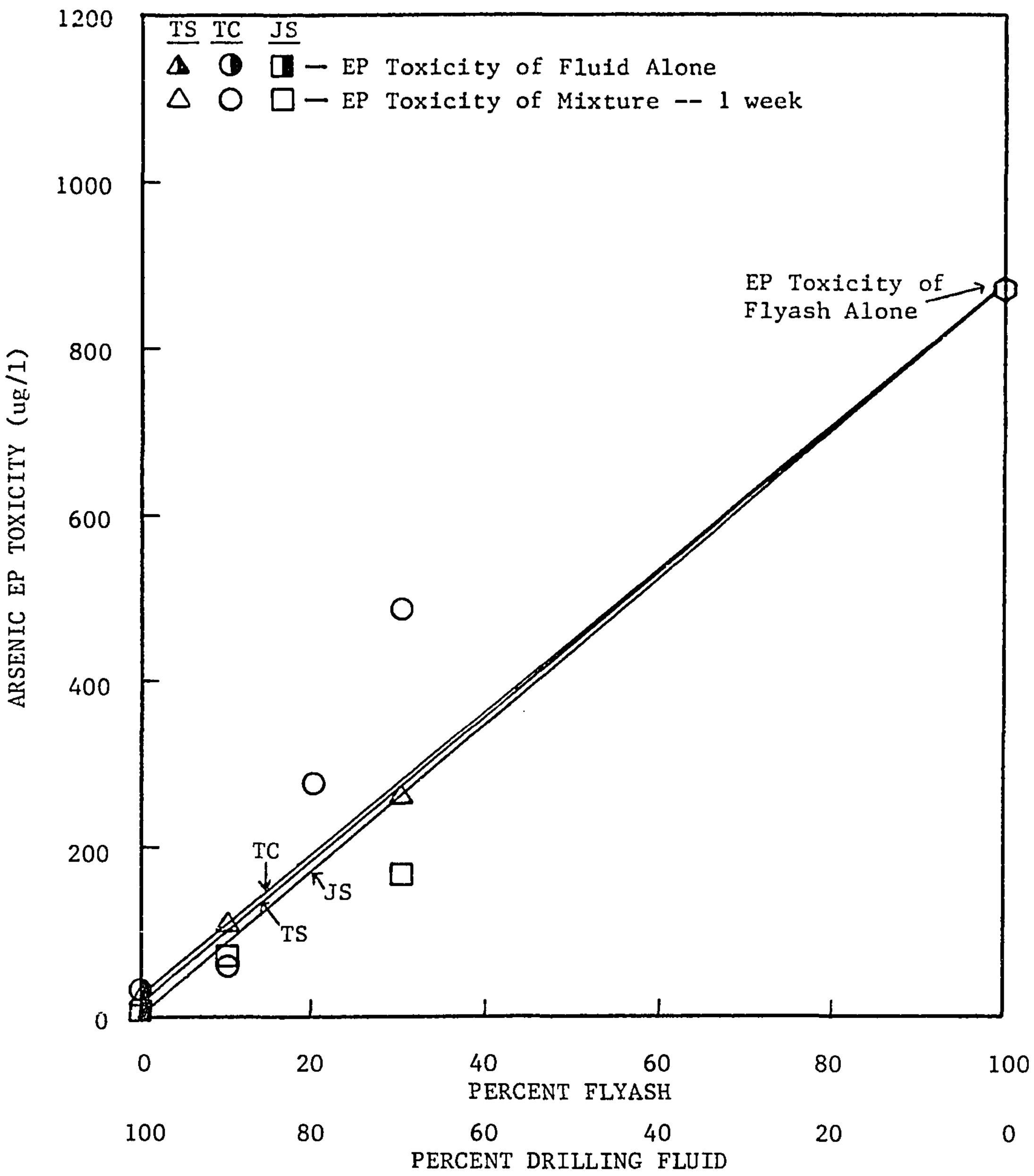

Figure 63: EP Toxicity Results for Arsenic in Mixtures of Flyash and Drilling Fluids

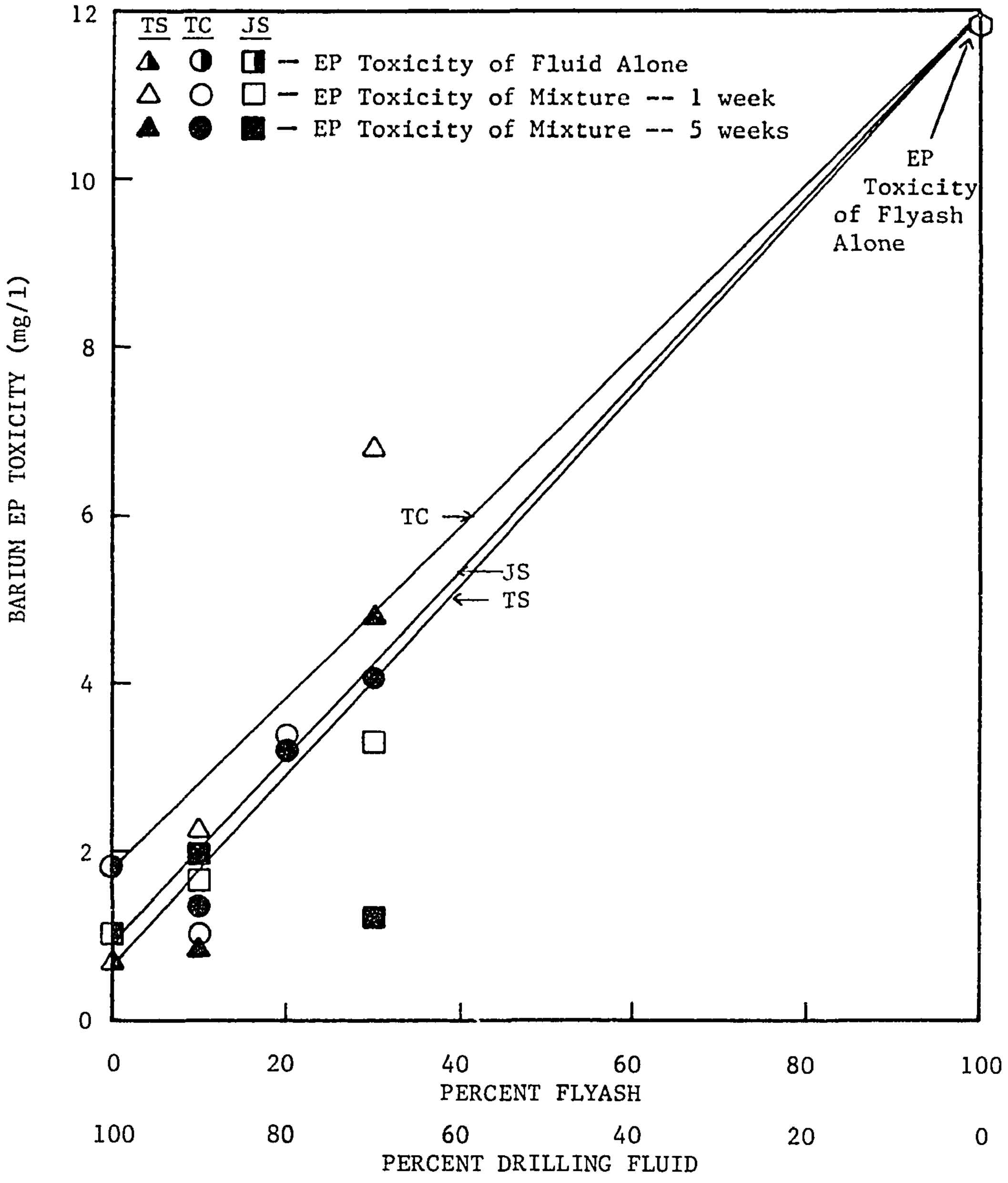

Figure 64: EP Toxicity Results for Barium in Mixtures of Flyash and Drilling Fluids

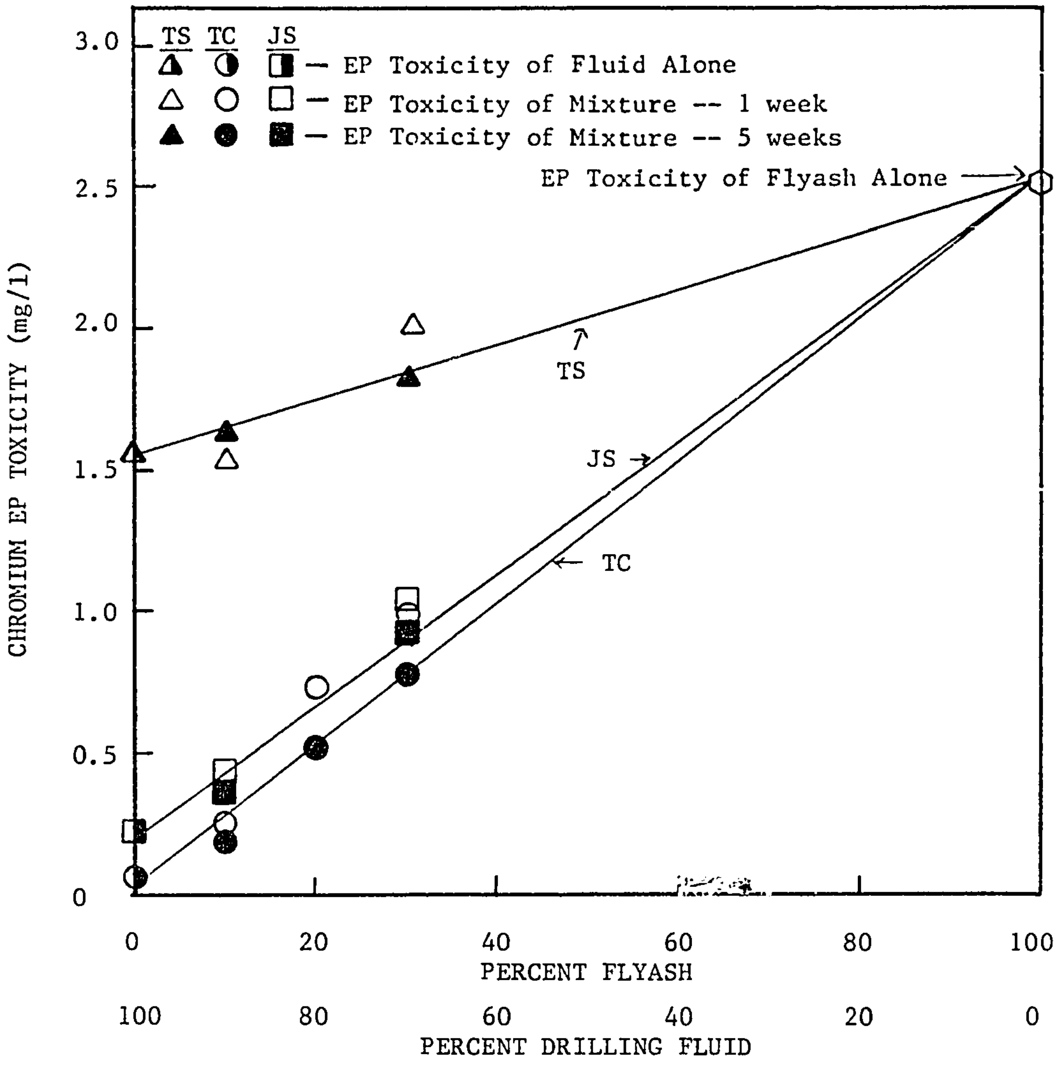

Figure 65: EP Toxicity Results for Chromium in Mixtures of Flyash and Drilling Fluids

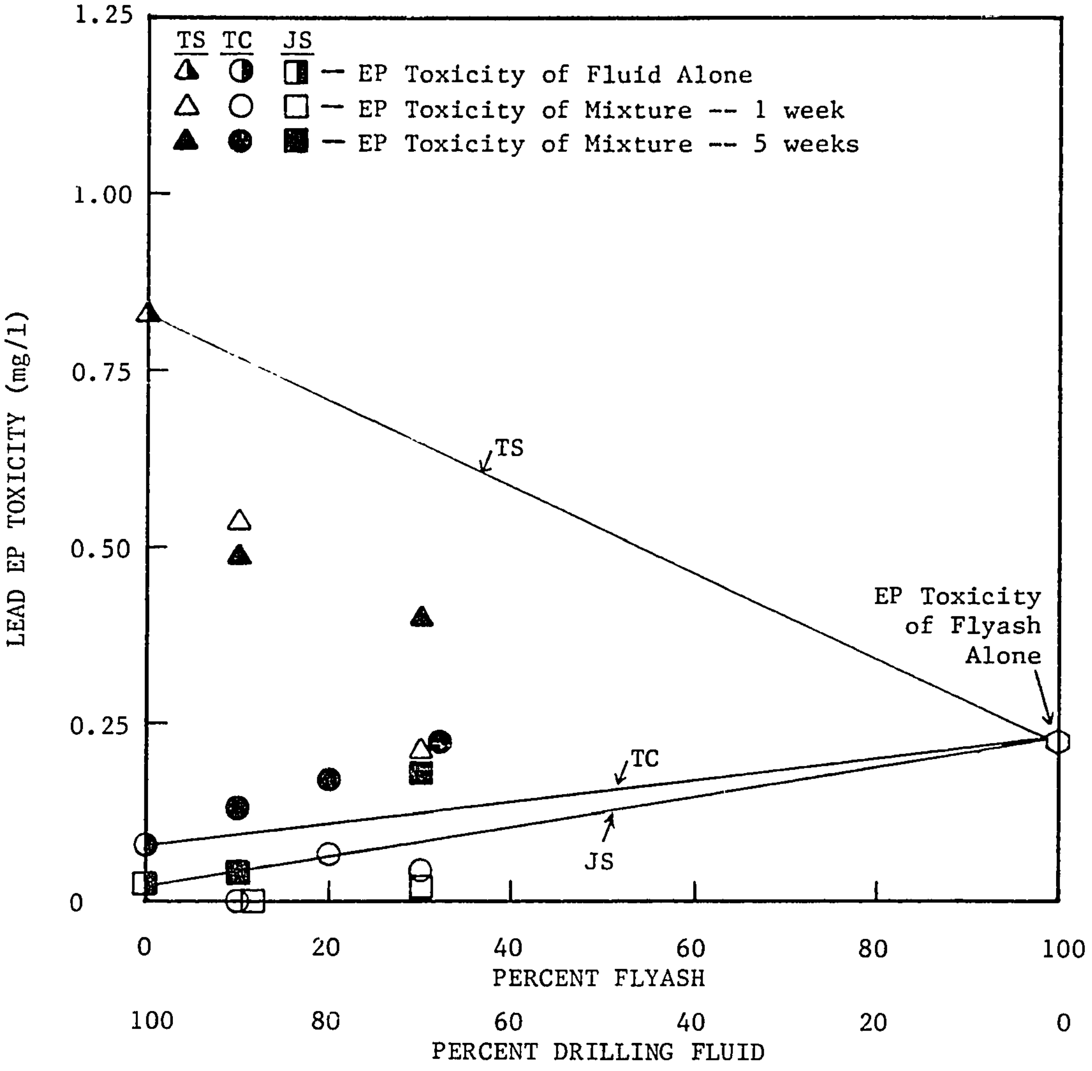

Figure 66: EP Toxicity Results for Lead in Mixtures of Flyash and Drilling Fluids

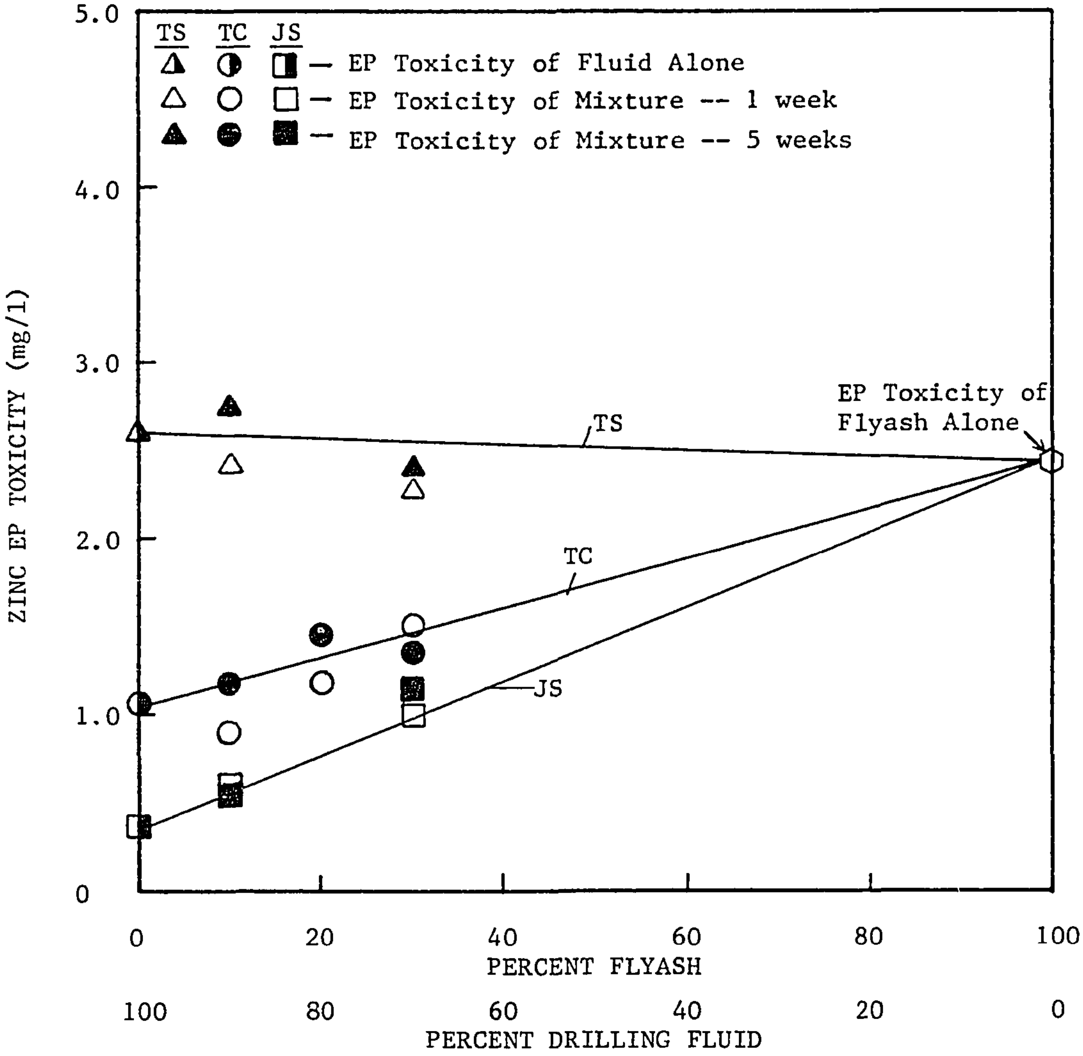

Figure 67: EP Toxicity Results for Zinc in Mixtures of Flyash and Drilling Fluids

indicates that flyash addition not only solidifies the drilling fluid but also chemically treats it relative to the particular metal being examined.

Arsenic (Figure 63). After one week, drilling fluid TC apears to be releasing arsenic while drilling fluids TS and JS show concentrations as expected from simple mixing with flyash. However, all EP Toxicity Test results are far below EP Toxicity Limits (Table 52).

Barium (Figure 64). In drilling fluid TS, barium appears to be released after one week at both 10 percent and 30 percent flyash. After 5 weeks, barium is being taken up at 10 percent flyash and only slightly released at 30 percent flyash. For drilling fluids TC and JS, barium is being stabilized by the flyash as indicated by all points falling on or below the mixture line.

The results indicate a possibility of early release of barium, followed by stabilization with time. However, the release of barium found under the conditions of the experiment was minimal when compared with EP Toxicity Limits (Table 52) or the total amount of barium found in the drilling fluids or flyash (Table 53).

Chromium (Figure 65). In all three drilling fluids, the amount of chromium found by EP Toxicity Testing could be attributed to simple physical mixing of the wastes. No significant release or uptake of chromium was apparent in any of the experiments. This is representative of the stability of the chromium compounds present in the wastes. All measured amounts of chromium were below the EP

Table 53: Comparison of Total Metals Analyzed for Drilling Fluids and Flyash in this Study

Metal	TS	TC	JS	Flyash
Arsenic (mg/kg)	4.15	30.4	18.6	--
Barium (mg/kg)	4,060	197	1,730	895
Chromium (mg/kg)	236	79.6	49.9	81.3
Lead (mg/kg)	206	24.2	68.2	14.6
Zinc (mg/kg)	222	169	95	87.0

Toxicity Limits (Table 52) and only a fraction of the total chromium concentrations (Table 53).

Lead (Figure 66). Lead appeared to be slightly released from drilling fluids TC and JS after 5 weeks of being combined with flyash. However, the amount of release is not significant when compared with EP Toxicity Limits. Drilling fluid TS appeared to very strongly take up lead and thereby stabilize it within the fluid-flyash matrix.

Zinc (Figure 67). Zinc was similar in behavior to chromium in that no uptake or release seems to have occurred as a result of stabilizing the drilling fluids with flyash.

Summary of Flyash Stabilization of Metals in Drilling Fluids

In most of the cases tested, all of the metals were either taken up or unaffected when drilling fluids were mixed with flyash. Additional barium was released in one case after one week but was readsorbed by 5 weeks time. Lead was slightly released by two fluid-flyash mixtures but strongly taken up by another. Arsenic was slightly released by one drilling fluid. Chromium and zinc behaved as if the combination of drilling fluids and flyash were a simple physical mixture with no chemical effects.

In no case were EP Toxicity Limits exceeded. Also the amount of metal released did not approach the total amounts present in drilling fluids or flyash (Table 53).

Flyash solidification/stabilization of drilling fluids appears to be a valid method of treatment in regards to metal behavior. In general, no significant uptake or release of metals can be expected during treatment. The processes occurring are those of mixing and solidification with no chemical effects contributing to the fate of the metals tested.

CHAPTER V

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary

With off-site disposal of drilling fluids in open pits, significant amounts of heavy metal elements may be introduced into the environment. Chemical forms of the deposited metals are essential to determine their reactivity and pollution potential in the environment. This potential must be explored in light of the dynamic conditions encountered (changing pH and ionic strength) and any proposed treatment schemes (flyash solidification). In this study, attempts were made to fractionate heavy metals in three drilling fluids after equilibrating in the laboratory under controlled conditions of pH and ionic strength. Also, drilling fluid-flyash mixtures were analyzed by EP Toxicity Methods to determine if there was any significant release or uptake of heavy metals with solidification treatment. The following was found:

1. The predominant chemical fractions of arsenic, barium, chromium, and lead were the stable residual, carbonate, and organically bound forms.
2. In no case was there a substantial release of these metals to the soluble phase with changing pH.
3. There were primarily shifts of the metals from the residual to the carbonate, organic, or exchanged forms with changing pH.

4. Barium, chromium, and lead slightly exceeded drinking water standards in some of the tests, but no metals approached EP Toxicity Limits.

5. Barium and lead seem the most likely to be released to solution because of the large exchanged fraction present at low pH. However, there is no evidence of actual significant release to the aqueous phase, even at very low pH values.

6. Drilling muds are capable of neutralizing significant amounts of acid and thereby resist changes in pH.

7. There is little change in the distribution of arsenic and chromium with dilution of the aqueous phase (decreasing ionic strength).

8. Barium and lead were also stable with the exception of one waste where significant levels were released to the aqueous phase.

9. There was no significant release of heavy metals with flyash treatment of drilling fluids. Some tests indicated minor release or uptake potential but, generally, no change in chemical form was observed.

Conclusions

1. With the pH changes to be expected in the natural environment, there is not likely to be a significant release of arsenic, barium, chromium or lead from drilling fluid disposal pits.

2. Dilution (ionic strength decrease) of drilling fluid wastes are also unlikely to result in significant release of arsenic, barium, chromium, or lead in the natural environment.

3. The lower pH values (< 4) which might produce some environmental impact are unlikely to occur in the environment, especially when considering the alkalinity of these wastes.

4. The similarity of these results with those obtained by other investigators indicates that their results in the area of amending soils with wastes may be applicable to the landfarming of drilling fluid wastes with regards to metals.

5. This study indicates the applicability of sequential extraction methods to waste studies while changing environmental parameters (pH and ionic strength). By using this method, more information has been obtained than is possible from a total metals analysis or an EP Toxicity Test. Actual shifts in the chemical nature of the pollutants have been observed and predictions made regarding behavior of metals in the environment.

6. Flyash solidification/stabilization of drilling fluids appears to be a valid method of treatment in regards to metal behavior. In general, no significant uptake or release of metals can be expected during treatment. The processes occurring are those of mixing and solidification with no chemical effects contributing to the fate of the metals tested.

7. These results should not be considered valid for all drilling fluids under all conditions. For example: if chromium were present as the chromate, different results would be expected.

Recommendations

1. Before metal concentrations measured in a particular fraction can be ascribed with reasonable certainty to well defined solid forms the following is suggested:

    a. Spiking experiments involving the addition of known forms of metals to sediment matrices to obtain information concerning the selectivity of the sequential extraction procedure.

    b. Further characterization of the solid matrix being examined to include the determination of cation exchange capacity, mineral constituency (x-ray diffraction), pH, percent organic matter, and type of organic matter.

    c. By measuring the major chemical and physical parameters of the solid and liquid phases a correlation may be obtained with the measured amounts of metals in the sequentially extracted fractions.

When sufficient information is obtained it may be possible to determine equilibrium relationships by using certain key parameters. This could prove to be an important tool for dealing with chemical behavior in the presence of a solid phase.

2. Landfarming studies with drilling fluids should include sequential extraction of the amended soils throughout the project period, along with the analysis of flora to determine metal behavior. Of special interest would be any preferential uptake of a given extracted fraction by plants.

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APPENDIX A

RAW DATA AND CALCULATION RESULTS FOR PH AND IONIC STRENGTH VARIATION EXPERIMENTS

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100 'THIS PROGRAM CALCULATES CONCENTRATIONS AND PERCENTAGES OF METALS IN
FRACTIONS OF SEQUENTIALLY EXTRACTED SAMPLES.
105 'THE WEIGHT OF THE SAMPLE HAS BEEN RECORDED AT EACH STEP OF THE EXTRACTION
SO THAT ANY WEIGHT LOSS OR GAIN IS CONSIDERED IN THE CALCULATIONS.
110 'THE DENSITIES OF ALL EXTRACTING SOLUTIONS IS ALSO ACCOUNTED FOR IN THE
CALCULATIONS.
115 'INPUT HOW MANY METALS WERE ANALYSED.
120 CLS
125 PRINT"NUMBER OF METALS ANALYZED?":INPUT NM
130 'INPUT SAMPLE NUMBER.
135 PRINT"SAMPLE NUMBER?":INPUTA$
140 'INPUT DILUTION FOR IONIC STRENGTH EXPERIMENTS.
145 PRINT"DILUTION OF LIQUID PHASE USED?":INPUT D
150 'INPUT DRIPS OF ACID REQUIRED TO REACH THE DESIRED PH.
155 PRINT"DROPS OF ACID ADDED?":INPUT DA
160 'DROPS OF ACID CONVERTED TO VOLUME.
165 VA=DA/50:VA=INT(VA*100):VA=VA/100
170 'INPUT FINAL PH.
175 PRINT"FINAL PH?":INPUT PH
180 'DENSITIES OF EXTRACTING SOLUTIONS.
185 D(1)=1:D(2)=1.03:D(3)=1:D(4)=1.02:D(5)=1:D(6)=1.12
190 'TOTAL VOLUME OF EACH EXTRACTING SOLUTION ADDED.
195 L(1)=25+VA:L(2)=75:L(3)=25:L(4)=25:L(5)=25:L(6)=100
200 'INPUT INITIAL VIAL WEIGHT.
205 PRINT "EMPTY WEIGHT OF VIAL?":INPUT E
210 SS=S
215 'INPUT WEIGHT OF VIAL WITH WET SEDIMENT.
220 PRINT"WEIGHT OF VIAL WITH WET SEDIMENT?":INPUT S
225 SS=S
230 'INPUT THE PERCENT SOLID DETERMINED FOR THE SEDIMENT.
235 PRINT"PERCENT SOLID OF SEDIMENT?":INPUT P
240 'CALCULATES DRY WEIGHT OF SEDIMENT.
245 DW=INT(((S-E)*P)*100):DW=DW/100
250 DIM F(6),WF(6),VF(6),MC(6),M(6),P(6),PT(7)
255 FOR X=1TO6
260 'INPUT VIAL WEIGHT AFTER EXTRACTANT IS REMOVED.
265 PRINT"WEIGHT OF VIAL CONTENTS WITHOUT EXTRACTANT";X;"?":INPUT WF(X)
270 F(X)=S+(L(X)*D(X))
275 VF(X)=(F(X)-WF(X))/D(X):VF(X)=INT(VF(X)*100):VF(X)=VF(X)/100
280 S=WF(X)
285 NEXT X
290 FOR Y=1 TO NM
295 'INPUT NAME OF METAL ANALYZED.
300 PRINT"METAL ANALYZED?":INPUT M$
305 MT=0
310 FOR X=1TO6
315 'INPUT RESULT OF METAL ANALYSIS (mg/l).
320 PRINT"RESULT OF METAL ANALYSIS IN MG/L?":INPUT MC(X)
325 'CALCULATES CONCENTRATION OF METAL PER UNIT WEIGHT OF SEDIMENT (mg/kg).
330 M(X)=(MC(X)*VF(X))/DW:M(X)=INT(M(X)*100):M(X)=M(X)/100
335 'CALCULATES TOTAL METAL IN SEDIMENT SAMPLE (SUM OF INDIVIDUAL FRACTIONS).
340 MT=MT+M(X)
345 NEXT X
350 PT(7)=0
355 FOR X=6 TO 1 STEP -1
360 'CALCULATES PERCENT OF TOTAL METAL IN EACH EXTRACTED FRACTION.
365 P(X)=(M(X)/MT)*100:P(X)=INT(P(X)*100):P(X)=P(X)/100
370 'CALCULATES CUMULATIVE PERCENT OF METAL IN EXTRACTED FRACTIONS.
375 PT(X)=(PT(X+1))+(P(X)):PT(X)=INT(PT(X)*100):PT(X)=PT(X)/100
380 NEXT X
385 'OUTPUT OF RESULTS IN TABULAR FORM.
390 PRINT#-2,"METAL:";M$;:PRINT#-2,CHR$(16);"40";"SAMPLE NO.:";A$:PRINT#-2
395 PRINT#-2,"PH=";PH;:PRINT#-2,CHR$(16);"40";"VIAL WEIGHT=";E;"GRAMS":PRINT#-2
400 PRINT#-2,"LIQUID DILUTION:";D;:PRINT#-2,CHR$(16);"40";"VIAL + SEDIMENT WEIGH
T=";SS;"GRAMS":PRINT#-2
405 PRINT#-2,"SOLID FRACTION=";P;:PRINT#-2,CHR$(16);"40";"DRY WEIGHT=";DW;"GRAMS
":PRINT#-2:PRINT#-2
410 PRINT#-2,"NO.    ";"INITIAL";CHR$(16);"16";"FINAL";CHR$(16);"27";"EXTRACT";CH
R$(16);"39";"MG/L";CHR$(16);"50";"MG/KG";CHR$(16);"60";"PERCENT";CHR$(16);"70";"
CUMULATIVE"
415 PRINT#-2,"        WEIGHT";CHR$(16);"16";"WEIGHT";CHR$(16);"27";"VOLUME";CHR$(1
6);"61";"TOTAL";CHR$(16);"71";"PERCENT"
420 FOR T=1TO79:PRINT#-2,"-";:NEXTT:PRINT#-2
425 FOR X=1 TO 6
430 PRINT#-2,X;:PRINT #-2,USING"####.###    ";F(X);WF(X);VF(X);MC(X);M(X);P(X);PT
(X):PRINT#-2
435 NEXT X
440 PRINT#-2,"TOTAL METAL=";MT;"MG/KG":PRINT#-2:PRINT#-2:PRINT#-2
445 NEXT Y
```

```
METAL:ARSENIC                           SAMPLE NO.:JS1

PH= 6.61                                VIAL WEIGHT= 14.14 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 18.14 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.  INITIAL  FINAL    EXTRACT    µG/L        µG/KG     PERCENT   CUMULATIVE
     WEIGHT   WEIGHT   VOLUME                             TOTAL    PERCENT
-----------------------------------------------------------------------------
 1   44.080   18.510   25.560     6.620     128.180     0.650     99.970

 2   95.760   19.080   74.440     0.000       0.000     0.000     99.320

 3   44.080   17.440   26.640    14.300     288.600     1.460     99.320

 4   42.940   17.190   25.240     0.000       0.000     0.000     97.860

 5   42.190   17.420   24.770   172.200    3231.350    16.390     97.860

 6  129.420   17.420  100.000   211.980   %16059.090    81.480     81.470

TOTAL METAL= 19707.22 µG/KG
```

```
METAL:ARSENIC                           SAMPLE NO.:JS2

PH= 6.28                                VIAL WEIGHT= 13.6 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 17.61 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.  INITIAL  FINAL    EXTRACT    µG/L        µG/KG     PERCENT   CUMULATIVE
     WEIGHT   WEIGHT   VOLUME                             TOTAL    PERCENT
-----------------------------------------------------------------------------
 1   43.550   18.010   25.530     3.070      59.370     0.290     99.980

 2   95.260   18.370   74.650     0.000       0.000     0.000     99.700

 3   43.370   16.900   26.470    11.440     229.400     1.120     99.700

 4   42.400   16.300   25.580     3.400      65.880     0.320     98.580

 5   41.300   16.870   24.430   210.400    3893.990    19.060     98.260

 6  128.870   16.870  100.000   213.300   %16159.090    79.180     79.180

TOTAL METAL= 20407.73 µG/KG
```

```
METAL:ARSENIC                           SAMPLE NO.:JS3

PH= 6.42                                VIAL WEIGHT= 14.02 GRAMS

LIQUID DILUTION: .5                     VIAL + SEDIMENT WEIGHT= 18.04 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     µG/L        µG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
-----------------------------------------------------------------------------------
 1    43.980    18.530    25.450      2.860      55.140      0.440     99.980

 2    95.780    18.920    74.620      0.000       0.000      0.000     99.540

 3    43.920    17.360    26.560     10.860     216.510      1.750     99.540

 4    42.860    17.060    25.290     36.670     702.560      5.640     97.790

 5    42.060    17.170    24.890     18.200     343.160      2.750     92.150

 6   129.170    17.170   100.000    147.000   %11136.360     89.400     89.400

TOTAL METAL= 12455.75 µG/KG
```

```
METAL:ARSENIC                           SAMPLE NO.:JS4

PH= 6.11                                VIAL WEIGHT= 13.33 GRAMS

LIQUID DILUTION: .5                     VIAL + SEDIMENT WEIGHT= 17.37 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.33 GRAMS

NO.   INITIAL   FINAL     EXTRACT     µG/L        µG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
-----------------------------------------------------------------------------------
 1    43.310    17.790    25.520      3.280      62.930      0.300     99.980

 2    95.040    18.240    74.560      0.230      12.890      0.060     99.680

 3    43.240    16.640    26.590     10.650     212.910      1.020     99.620

 4    42.140    16.330    25.300    120.520    2292.590     11.050     98.600

 5    41.330    18.540    22.790    141.600    2426.360     11.700     87.550

 6   130.540    18.540   100.000    209.200   %15729.320     75.850     75.850

TOTAL METAL= 20737 µG/KG
```

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METAL:ARSENIC                               SAMPLE NO.:JS5

PH= 5.8                                     VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .1                         VIAL + SEDIMENT WEIGHT= 17.64 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.33 GRAMS

NO.  INITIAL  FINAL     EXTRACT      µG/L        µG/KG      PERCENT  CUMULATIVE
     WEIGHT   WEIGHT    VOLUME                              TOTAL     PERCENT
---------------------------------------------------------------------------------
 1   43.580   18.180    25.400      1.050      20.050      0.120     99.960

 2   95.430   18.590    74.600      2.500     140.220      0.880     99.840

 3   43.590   17.000    26.590      7.930     158.540      1.000     98.960

 4   42.500   16.470    25.510    127.320    2442.050     15.460     97.960

 5   41.470   16.820    24.650     20.000     370.670      2.340     82.500

 6  128.820   16.820   100.000    168.400   %12661.650     80.170      80.160

TOTAL METAL= 15793.18 µG/KG
```

```
METAL:ARSENIC                               SAMPLE NO.:JS6

PH= 6.17                                    VIAL WEIGHT= 13.29 GRAMS

LIQUID DILUTION: .1                         VIAL + SEDIMENT WEIGHT= 17.26 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.31 GRAMS

NO.  INITIAL  FINAL     EXTRACT      µG/L        µG/KG      PERCENT  CUMULATIVE
     WEIGHT   WEIGHT    VOLUME                              TOTAL     PERCENT
---------------------------------------------------------------------------------
 1   43.200   17.800    25.400      0.940      18.220      0.090     99.980

 2   95.050   18.170    74.640      0.000       0.000      0.000     99.890

 3   43.170   17.300    25.870      9.350     184.640      0.910     99.890

 4   42.800   16.220    26.050     38.920     773.940      3.630     98.980

 5   41.220   16.930    24.290     11.190     207.460      1.020     95.150

 6  128.930   16.930   100.000    248.900   %19000.000     94.130      94.130

TOTAL METAL= 20184.28 µG/KG
```

METAL:ARSENIC
PH= 3.5
LIQUID DILUTION: 1
SOLID FRACTION= .33

SAMPLE NO.:JS7
VIAL WEIGHT= 13.53 GRAMS
VIAL + SEDIMENT WEIGHT= 17.55 GRAMS
DRY WEIGHT= 1.32 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µ G/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.750	18.090	25.660	6.280	122.070	0.740	99.980
2	95.340	18.670	74.430	6.810	383.990	2.330	99.240
3	43.670	18.260	25.410	8.200	157.840	0.960	96.910
4	43.760	17.020	26.210	22.170	440.200	2.680	95.950
5	42.020	17.200	24.810	11.540	216.890	1.320	93.270
6	129.200	17.200	100.000	199.300	%15098.480	91.950	91.950

TOTAL METAL= 16419.47 µG/KG

METAL:ARSENIC
PH= 3.7
LIQUID DILUTION: 1
SOLID FRACTION= .33

SAMPLE NO.:JS8
VIAL WEIGHT= 13.85 GRAMS
VIAL + SEDIMENT WEIGHT= 17.85 GRAMS
DRY WEIGHT= 1.32 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.050	18.430	25.620	7.600	147.500	1.060	99.970
2	95.680	18.770	74.660	9.280	524.880	3.860	98.890
3	43.770	18.310	25.450	7.800	150.380	1.100	95.030
4	43.810	17.100	26.180	17.870	354.420	2.600	93.930
5	42.100	16.580	25.520	6.350	122.760	0.900	91.330
6	128.580	16.580	100.000	162.300	%12295.450	90.430	90.430

TOTAL METAL= 13595.39 µG/KG

```
METAL:ARSENIC                               SAMPLE NO.:JS9

PH= 6.84                                    VIAL WEIGHT= 13.99 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     µG/L        µG/KG       PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                              TOTAL     PERCENT
-----------------------------------------------------------------------------------
 1    43.000    18.430    24.570      3.900       72.590      0.410     99.980

 2    95.680    19.130    74.320      0.000        0.000      0.000     99.570

 3    44.130    17.440    26.690     12.000      242.630      1.370     99.570

 4    42.940    17.540    24.900      8.070      152.220      0.860     98.200

 5    42.540    17.920    24.620      5.930      110.600      0.620     97.340

 6   129.920    17.920   100.000    225.200    %17060.600      96.720     96.720

TOTAL METAL= 17638.64 µG/KG
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METAL:ARSENIC                               SAMPLE NO.:JS10

PH= 6.97                                    VIAL WEIGHT= 14.06 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 18.06 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     µG/L        µG/KG       PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                              TOTAL     PERCENT
-----------------------------------------------------------------------------------
 1    43.060    18.620    24.440      2.620       48.500      0.260     99.950

 2    95.870    19.160    74.470      0.960       54.160      0.290     99.700

 3    44.160    17.330    26.830     13.230      268.900      1.440     99.420

 4    42.830    17.480    24.850     27.970      526.550      2.830     97.980

 5    42.480    17.030    25.450      5.860      113.360      0.600     95.150

 6   129.030    17.030   100.000    232.000    %17575.750      94.550     94.550

TOTAL METAL= 18587.22 µG/KG
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METAL:BARIUM                                  SAMPLE NO.:JS1

PH= 6.61                                      VIAL WEIGHT= 14.14 GRAMS

LIQUID DILUTION: 1                            VIAL + SEDIMENT WEIGHT= 18.14 GRAMS

SOLID FRACTION= .33                           DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL    FINAL      EXTRACT      MG/L        MG/KG     PERCENT     CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                             TOTAL       PERCENT
-------------------------------------------------------------------------------------
 1    44.080     18.510     25.560      4.928       95.420      2.090       99.960

 2    95.760     19.080     74.440      5.171      291.610      6.400       97.870

 3    44.080     17.440     26.640      3.060       61.750      1.350       91.470

 4    42.940     17.190     25.240      4.251       81.280      1.780       90.120

 5    42.190     17.420     24.770     47.310      887.770     19.510       88.340

 6   129.420     17.420    100.000     41.340     3131.810     68.830       68.830

TOTAL METAL= 4549.64 MG/KG
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METAL:BARIUM                                  SAMPLE NO.:JS2

PH= 6.28                                      VIAL WEIGHT= 13.6 GRAMS

LIGUID DILUTION: 1                            VIAL + SEDIMENT WEIGHT= 17.61 GRAMS

SOLID FRACTION= .33                           DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL    FINAL      EXTRACT      MG/L        MG/KG     PERCENT     CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                             TOTAL       PERCENT
-------------------------------------------------------------------------------------
 1    43.550     18.010     25.530      4.637       89.680      2.650       99.970

 2    95.260     18.370     74.650      4.966      280.840      8.320       97.320

 3    43.370     16.900     26.470      3.534       70.860      2.090       89.000

 4    42.400     16.300     25.580      2.080       40.300      1.190       86.910

 5    41.300     16.870     24.430     24.440      452.320     13.400       85.720

 6   128.870     16.870    100.000     32.214     2440.450     72.320       72.320

TOTAL METAL= 3374.45 MG/KG
```

METAL:BARIUM

PH= 6.42

LIQUID DILUTION: .5

SOLID FRACTION= .33

SAMPLE NO.:JS3

VIAL WEIGHT= 14.02 GRAMS

VIAL + SEDIMENT WEIGHT= 18.04 GRAMS

DRY WEIGHT= 1.32 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.980	18.530	25.450	1.609	31.020	0.840	99.980
2	95.780	18.920	74.620	5.602	316.680	8.580	99.140
3	43.920	17.360	26.560	3.648	73.400	1.990	90.560
4	42.860	17.060	25.290	4.010	76.820	2.080	88.570
5	42.060	17.170	24.890	43.390	818.160	22.180	86.490
6	129.170	17.170	100.000	31.304	2371.510	64.310	64.310

TOTAL METAL= 3687.59 MG/KG

METAL:BARIUM

PH= 6.11

LIQUID DILUTION: .5

SOLID FRACTION= .33

SAMPLE NO.:JS4

VIAL WEIGHT= 13.33 GRAMS

VIAL + SEDIMENT WEIGHT= 17.37 GRAMS

DRY WEIGHT= 1.33 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.310	17.790	25.520	6.151	118.020	3.490	99.960
2	95.040	18.240	74.560	7.030	394.100	11.680	96.470
3	43.240	16.640	26.590	3.818	76.330	2.260	84.790
4	42.140	16.330	25.300	1.995	37.950	1.120	82.530
5	41.330	18.540	22.790	7.300	125.080	3.700	81.410
6	130.540	18.540	100.000	34.866	2621.500	77.720	77.720

TOTAL METAL= 3372.98 MG/KG

METAL:BARIUM

PH= 5.8

LIQUID DILUTION: .1

SOLID FRACTION= .33

SAMPLE NO.:JS5

VIAL WEIGHT= 13.58 GRAMS

VIAL + SEDIMENT WEIGHT= 17.64 GRAMS

DRY WEIGHT= 1.33 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.580	18.180	25.400	7.645	146.000	2.530	99.960
2	95.430	18.590	74.600	8.660	485.740	8.420	97.430
3	43.590	17.000	26.590	4.235	84.660	1.460	89.010
4	42.580	16.470	25.510	2.520	48.330	0.830	87.550
5	41.470	16.820	24.650	42.410	786.010	13.640	86.720
6	128.820	6.820	108.920	51.428	4211.680	73.080	73.080

TOTAL METAL= 5762.42 MG/KG

METAL:BARIUM

PH= 6.17

LIQUID DILUTION: .1

SOLID FRACTION= .33

SAMPLE NO.:JS6

VIAL WEIGHT= 13.29 GRAMS

VIAL + SEDIMENT WEIGHT= 17.26 GRAMS

DRY WEIGHT= 1.31 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.200	17.800	25.400	2.872	55.680	1.230	99.970
2	95.050	18.170	74.640	8.546	486.920	10.810	98.740
3	43.170	17.300	25.870	4.116	81.280	1.800	87.930
4	42.800	16.220	26.050	3.941	78.360	1.730	86.130
5	41.220	16.950	24.270	41.170	762.740	16.930	84.400
6	128.950	16.950	100.000	39.806	3038.620	67.470	67.470

TOTAL METAL= 4503.6 MG/KG

METAL:BARIUM
SAMPLE NO.:JS7
PH= 3.5
VIAL WEIGHT= 13.53 GRAMS
LIQUID DILUTION: 1
VIAL + SEDIMENT WEIGHT= 17.55 GRAMS
SOLID FRACTION= .33
DRY WEIGHT= 1.32 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.750	18.090	25.660	3.623	70.420	1.860	99.960
2	95.340	18.670	74.430	5.225	294.610	7.790	98.100
3	43.670	18.260	25.410	4.783	92.070	2.430	90.310
4	43.760	17.020	26.210	2.736	54.320	1.430	87.880
5	42.020	17.200	24.810	59.470	1117.760	29.580	86.450
6	129.200	17.200	100.000	28.366	2148.930	56.870	56.870

TOTAL METAL= 3778.11 MG/KG

METAL:BARIUM
SAMPLE NO.:JS8
PH= 3.17
VIAL WEIGHT= 13.85 GRAMS
LIQUID DILUTION: 1
VIAL + SEDIMENT WEIGHT= 17.85 GRAMS
SOLID FRACTION= .33
DRY WEIGHT= 1.32 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.050	18.430	25.620	3.931	76.290	2.570	99.980
2	95.680	18.770	74.660	5.201	294.170	9.930	97.410
3	43.770	18.310	25.450	4.369	84.230	2.840	87.480
4	43.810	17.100	26.180	2.556	50.690	1.710	84.640
5	42.100	16.580	25.520	9.270	179.220	6.050	82.930
6	128.580	16.580	100.000	30.056	2276.960	76.880	76.880

TOTAL METAL= 2961.56 MG/KG

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METAL:BARIUM                               SAMPLE NO.:JS9

PH= 6.84                                   VIAL WEIGHT= 13.99 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .33                        DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT    CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
-------------------------------------------------------------------------------
 1    43.000    18.430    24.570      0.801      14.900      0.360      99.980

 2    95.680    19.130    74.320      4.221     237.650      5.770      99.620

 3    44.130    17.440    26.690      2.189      44.260      1.070      93.850

 4    42.940    17.540    24.900      5.141      96.970      2.350      92.780

 5    42.540    17.920    24.620     46.830     873.450     21.210      90.430

 6   129.920    17.920   100.000     37.622    2850.150     69.220      69.220

TOTAL METAL= 4117.38 MG/KG
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METAL:BARIUM                               SAMPLE NO.:JS10

PH= 6.97                                   VIAL WEIGHT= 14.06 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 18.06 GRAMS

SOLID FRACTION= .33                        DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT    CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
-------------------------------------------------------------------------------
 1    43.060    18.620    24.440      0.000       0.000      0.000      99.950

 2    95.870    19.160    74.470      4.231     238.690      4.750      99.950

 3    44.160    17.330    26.830      2.284      46.420      0.920      95.200

 4    42.830    17.480    24.850      5.271      99.230      1.970      94.290

 5    42.480    17.030    25.450     51.400     991.000     19.750      92.320

 6   129.030    17.030   100.000     48.048    3640.000     72.570      72.570

TOTAL METAL= 5015.34 MG/KG
```

```
METAL:CHROMIUM                          SAMPLE NO.:JS1

PH= 6.61                                VIAL WEIGHT= 14.14 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 18.14 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
------------------------------------------------------------------------------
 1   44.080    18.510     25.560     0.077       1.490      1.600     99.980

 2   95.760    19.080     74.440     0.000       0.000      0.000     98.380

 3   44.080    17.440     26.640     0.108       2.170      2.330     98.380

 4   42.940    17.190     25.240     0.197       3.760      4.040     96.050

 5   42.190    17.420     24.770     1.391      26.100     28.070     92.010

 6  129.420    17.420    100.000     0.785      59.460     63.940     63.940

TOTAL METAL= 92.98 MG/KG
```

```
METAL:CHROMIUM                          SAMPLE NO.:JS2

PH= 6.28                                VIAL WEIGHT= 13.6 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 17.61 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
------------------------------------------------------------------------------
 1   43.550    18.010     25.530     0.000       0.000      0.000     99.980

 2   95.260    18.370     74.650     0.000       0.000      0.000     99.980

 3   43.370    16.900     26.470     0.136       2.720      3.130     99.980

 4   42.400    16.300     25.580     0.089       1.720      1.980     96.850

 5   41.300    16.870     24.430     1.384      25.610     29.500     94.870

 6  128.870    16.870    100.000     0.749      56.740     65.370     65.370

TOTAL METAL= 86.79 MG/KG
```

```
METAL:CHROMIUM                          SAMPLE NO.:JS3

PH= 6.42                                VIAL WEIGHT= 14.02 GRAMS

LIQUID DILUTION: .5                     VIAL + SEDIMENT WEIGHT= 18.04 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
-----------------------------------------------------------------------------------
 1    43.980    18.530    25.450      0.000       0.000     0.000     99.980

 2    95.780    18.920    74.620      0.000       0.000     0.000     99.980

 3    43.920    17.360    26.560      0.153       3.070     3.440     99.980

 4    42.860    17.060    25.290      0.137       2.620     2.940     96.540

 5    42.060    17.170    24.890      1.348      25.410    28.530     93.600

 6   129.170    17.170   100.000      0.765      57.950    65.070     65.070

TOTAL METAL= 89.05 MG/KG
```

```
METAL:CHROMIUM                          SAMPLE NO.:JS4

PH= 6.11                                VIAL WEIGHT= 13.33 GRAMS

LIQUID DILUTION: .5                     VIAL + SEDIMENT WEIGHT= 17.37 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.33 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
-----------------------------------------------------------------------------------
 1    43.310    17.790    25.520      0.012       0.230     0.250     99.970

 2    95.040    18.240    74.560      0.000       0.000     0.000     99.720

 3    43.240    16.640    26.590      0.045       0.890     0.990     99.720

 4    42.140    16.330    25.300      0.146       2.770     3.080     98.730

 5    41.330    18.540    22.790      1.336      22.890    25.490     95.650

 6   130.540    18.540   100.000      0.838      63.000    70.170     70.160

TOTAL METAL= 89.78 MG/KG
```

```
METAL:CHROMIUM                              SAMPLE NO.:JS5

PH= 5.8                                     VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .1                         VIAL + SEDIMENT WEIGHT= 17.64 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.33 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
------------------------------------------------------------------------------
 1    43.580    18.180    25.400      0.000       0.000      0.000     99.970

 2    95.430    18.590    74.600      0.000       0.000      0.000     99.970

 3    43.590    17.000    26.590      0.135       2.690      3.000     99.970

 4    42.500    16.470    25.510      0.265       5.080      5.670     96.970

 5    41.470    16.820    24.650      1.301      22.250     24.860     91.300

 6   128.820    16.820   100.000      0.791      59.470     66.450     66.440

TOTAL METAL= 89.49 MG/KG
```

```
METAL:CHROMIUM                              SAMPLE NO.:JS6

PH= 6.17                                    VIAL WEIGHT= 13.29 GRAMS

LIQUID DILUTION: .1                         VIAL + SEDIMENT WEIGHT= 17.26 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.31 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
------------------------------------------------------------------------------
 1    43.200    17.800    25.400      0.000       0.000      0.000     99.980

 2    95.050    18.170    74.640      0.000       0.000      0.000     99.980

 3    43.170    17.300    25.870      0.117       2.310      2.670     99.980

 4    42.800    16.220    26.050      0.208       4.130      4.780     97.320

 5    41.220    16.930    24.290      1.262      23.390     27.070     92.540

 6   128.930    16.930   100.000      0.741      56.560     65.470     65.470

TOTAL METAL= 86.39 MG/KG
```

```
METAL:CHROMIUM                                SAMPLE NO.:JS7

PH= 3.5                                       VIAL WEIGHT= 13.53 GRAMS

LIQUID DILUTION  1                            VIAL + SEDIMENT WEIGHT= 17.55 GRAMS

SOLID FRACTION= .33                           DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT      MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                              TOTAL      PERCENT
----------------------------------------------------------------------------------
 1    43.750    18.090    25.660      0.187        3.630       4.530     99.980

 2    95.340    18.670    74.430      0.000        0.000       0.000     95.450

 3    43.670    18.260    25.410      0.062        1.190       1.480     95.450

 4    43.760    17.020    26.210      0.241        4.780       5.960     93.970

 5    42.020    17.200    24.810      1.076       20.220      25.230     88.010

 6   129.200    17.200   100.000      0.664       50.300      62.780     62.780

TOTAL METAL= 80.12 MG/KG
```

```
METAL:CHROMIUM                                SAMPLE NO.:JS8

PH= 3.17                                      VIAL WEIGHT= 13.85 GRAMS

LIQUID DILUTION: 1                            VIAL + SEDIMENT WEIGHT= 17.85 GRAMS

SOLID FRACTION= .33                           DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT      MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                              TOTAL      PERCENT
----------------------------------------------------------------------------------
 1    44.050    18.430    25.620      0.510        9.890      10.310     99.960

 2    95.680    18.770    74.660      0.211       11.930      12.440     89.650

 3    43.770    18.310    25.450      0.135        2.600       2.710     77.210

 4    43.810    17.100    26.180      0.276        5.470       5.700     74.500

 5    42.100    16.580    25.520      1.167       22.560      23.530     68.800

 6   128.580    16.580   100.000      0.573       43.400      45.270     45.270

TOTAL METAL= 95.85 MG/KG
```

```
METAL:CHROMIUM                              SAMPLE NO.:JS9

PH= 6.84                                    VIAL WEIGHT= 13.99 GRAMS

LIQUID DILUTION  1                          VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
---------------------------------------------------------------------------------
 1    43.000    18.430    24.570      0.005       0.090     0.090     99.980

 2    95.680    19.130    74.320      0.000       0.000     0.000     99.890

 3    44.130    17.440    26.690      0.163       3.290     3.490     99.890

 4    42.940    17.540    24.900      0.086       1.620     1.720     96.400

 5    42.540    17.920    24.620      1.593      29.710    31.540     94.680

 6   129.920    17.920   100.000      0.785      59.460    63.140     63.140

TOTAL METAL= 94.17 MG/KG
```

```
METAL:CHROMIUM                              SAMPLE NO.:JS10

PH= 6.97                                    VIAL WEIGHT= 14.06 GRAMS

LIQUID DILUTION  1                          VIAL + SEDIMENT WEIGHT= 18.06 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
---------------------------------------------------------------------------------
 1    43.060    18.620    24.440      0.036       0.660     0.720     99.980

 2    95.870    19.160    74.470      0.000       0.000     0.000     99.260

 3    44.160    17.330    26.830      0.146       2.960     3.230     99.260

 4    42.830    17.480    24.850      0.069       1.290     1.400     96.030

 5    42.480    17.030    25.450      1.583      30.520    33.300     94.630

 6   129.030    17.030   100.000      0.742      56.210    61.330     61.330

TOTAL METAL= 91.64 MG/KG
```

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METAL:LEAD                                  SAMPLE NO.:JS1

PH= 6.61                                    VIAL WEIGHT= 14.14 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 18.14 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL      EXTRACT      MG/L        MG/KG      PERCENT    CUMULATIVE
      WEIGHT    WEIGHT     VOLUME                              TOTAL      PERCENT
----------------------------------------------------------------------------------
 1    44.080    18.510     25.560      0.020        0.380      0.490     99.970

 2    95.760    19.080     74.440      0.000        0.000      0.000     99.480

 3    44.080    17.440     26.640      0.141        2.840      3.730     99.480

 4    42.940    17.190     25.240      0.332        6.340      8.340     95.750

 5    42.190    17.420     24.770      2.928       54.940     72.270     87.410

 6   129.420    17.420    100.000      0.152       11.510     15.140     15.140

TOTAL METAL= 76.01 MG/KG
```

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METAL:LEAD                                  SAMPLE NO.:JS2

PH= 6.28                                    VIAL WEIGHT= 13.6 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 17.61 GRAMS

SOLID FRACTION= .33                         DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL      EXTRACT      MG/L        MG/KG      PERCENT    CUMULATIVE
      WEIGHT    WEIGHT     VOLUME                              TOTAL      PERCENT
----------------------------------------------------------------------------------
 1    43.550    18.010     25.530      0.018        0.340      0.460     99.970

 2    95.260    18.370     74.650      0.000        0.000      0.000     99.510

 3    43.370    16.900     26.470      0.157        3.140      4.320     99.510

 4    42.400    16.300     25.580      0.185        3.580      4.930     95.190

 5    41.300    16.870     24.430      3.029       56.050     77.230     90.260

 6   128.870    16.870    100.000      0.125        9.460     13.030     13.030

TOTAL METAL= 72.57 MG/KG
```

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METAL LEAD                                    SAMPLE NO. JS3

PH= 6.42                                      VIAL WEIGHT= 14.02 GRAMS

LIQUID DILUTION= .5                           VIAL + SEDIMENT WEIGHT= 18.04 GRAMS

SOLID FRACTION= .33                           DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL    FINAL      EXTRACT      MG/L         MG/KG       PERCENT    CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                                TOTAL      PERCENT
-------------------------------------------------------------------------------------
 1   43.980     18.530     25.450      0.001        0.010       0.010      99.950

 2   95.780     18.920     74.620      0.002        0.110       0.170      99.950

 3   43.920     17.360     26.560      0.151        3.030       4.910      99.790

 4   42.860     17.060     25.290      0.275        5.260       6.530      94.880

 5   42.060     17.170     24.890      2.398       45.210      73.330      86.350

 6  129.170     17.170    100.000      0.106        8.030      13.020      13.020

TOTAL METAL= 61.65 MG/KG
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METAL LEAD                                    SAMPLE NO. JS4

PH= 6.11                                      VIAL WEIGHT= 13.33 GRAMS

LIQUID DILUTION= .5                           VIAL + SEDIMENT WEIGHT= 17.37 GRAMS

SOLID FRACTION= .33                           DRY WEIGHT= 1.33 GRAMS

NO.   INITIAL    FINAL      EXTRACT      MG/L         MG/KG       PERCENT    CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                                TOTAL      PERCENT
-------------------------------------------------------------------------------------
 1   43.310     17.790     25.520      0.013        0.240       0.320      99.980

 2   95.040     18.240     74.560      0.017        0.950       1.270      99.660

 3   43.240     16.640     26.590      0.180        3.590       4.790      98.390

 4   42.140     16.330     25.300      0.304        5.780       7.720      93.600

 5   41.330     18.540     22.790      3.148       53.940      72.110      85.880

 6  130.540     18.540    100.000      0.137       10.300      13.770      13.770

TOTAL METAL= 74.8 MG/KG
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METAL:LEAD                                 SAMPLE NO.:JS5

PH= 5.8                                    VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .1                        VIAL + SEDIMENT WEIGHT= 17.64 GRAMS

SOLID FRACTION= .33                        DRY WEIGHT= 1.33 GRAMS

NO.   INITIAL    FINAL      EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                             TOTAL      PERCENT
-------------------------------------------------------------------------------------
 1    43.580     18.180     25.400      0.002       0.030      0.040      99.970

 2    95.430     18.590     74.600      0.047       2.630      3.650      99.930

 3    43.590     17.000     26.590      0.239       4.770      6.620      96.280

 4    42.500     16.470     25.510      0.493       9.450     13.120      89.660

 5    41.470     16.820     24.650      2.593      48.050     66.740      76.540

 6   128.820     16.820    100.000      0.094       7.060      9.800       9.800

TOTAL METAL= 71.99 MG/KG
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METAL:LEAD                                 SAMPLE NO.:JS6

PH= 6.17                                   VIAL WEIGHT= 13.29 GRAMS

LIQUID DILUTION: .1                        VIAL + SEDIMENT WEIGHT= 17.26 GRAMS

SOLID FRACTION= .33                        DRY WEIGHT= 1.31 GRAMS

NO.   INITIAL    FINAL      EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                             TOTAL      PERCENT
-------------------------------------------------------------------------------------
 1    43.200     17.800     25.400      0.000       0.000      0.000      99.970

 2    95.050     18.170     74.640      0.010       0.560      0.690      99.970

 3    43.170     17.300     25.870      0.236       4.660      5.790      99.280

 4    42.800     16.220     26.050      0.360       7.150      8.890      93.490

 5    41.220     16.930     24.290      3.166      58.700     73.020      84.600

 6   128.930     16.930    100.000      0.122       9.310     11.590      11.580

TOTAL METAL= 80.38 MG/KG
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METAL:LEAD                                   SAMPLE NO.:JS7

PH= 3.5                                      VIAL WEIGHT= 13.53 GRAMS

LIQUID DILUTION: 1                           VIAL + SEDIMENT WEIGHT= 17.55 GRAMS

SOLID FRACTION= .33                          DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL      PERCENT
--------------------------------------------------------------------------------
 1    43.750    18.090    25.660      0.780      15.160     14.950     99.970

 2    95.340    18.670    74.430      0.851      47.980     47.340     85.020

 3    43.670    18.260    25.410      0.144       2.770      2.730     37.680

 4    43.760    17.020    26.210      0.124       2.460      2.420     34.950

 5    42.020    17.200    24.810      1.421      26.700     26.340     32.530

 6   129.200    17.200   100.000      0.083       6.280      6.190      6.190

TOTAL METAL= 101.35 MG/KG
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METAL:LEAD                                   SAMPLE NO.:JS8

PH= 3.17                                     VIAL WEIGHT= 13.85 GRAMS

LIQUID DILUTION: 1                           VIAL + SEDIMENT WEIGHT= 17.85 GRAMS

SOLID FRACTION= .33                          DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL      PERCENT
--------------------------------------------------------------------------------
 1    44.050    18.430    25.620      1.055      20.470     16.640     99.970

 2    95.680    18.770    74.660      1.131      63.970     52.020     83.330

 3    43.770    18.310    25.450      0.132       2.540      2.060     31.310

 4    43.810    17.100    26.180      0.138       2.730      2.220     29.250

 5    42.100    16.580    25.520      1.368      26.830     21.810     27.030

 6   128.580    16.580   100.000      0.085       6.430      5.220      5.220

TOTAL METAL= 122.97 MG/KG
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METAL:LEAD                              SAMPLE NO.:JS9

PH= 6.84                                VIAL WEIGHT= 13.99 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    43.000    18.430    24.570     0.018      0.330      0.490     99.970

 2    95.680    19.130    74.320     0.011      0.610      0.910     99.480

 3    44.130    17.440    26.690     0.172      3.470      5.180     98.570

 4    42.940    17.540    24.900     0.245      4.620      6.890     93.390

 5    42.540    17.920    24.620     2.611     48.690     72.710     86.500

 6   129.920    17.920   100.000     0.122      9.240     13.790     13.790

TOTAL METAL= 66.96 MG/KG
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METAL:LEAD                              SAMPLE NO.:JS10

PH= 6.97                                VIAL WEIGHT= 14.06 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 18.06 GRAMS

SOLID FRACTION= .33                     DRY WEIGHT= 1.32 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    43.060    18.620    24.440     0.026      0.480      0.620     99.970

 2    95.870    19.160    74.470     0.000      0.000      0.000     99.350

 3    44.160    17.330    26.830     0.187      3.800      4.960     99.350

 4    42.830    17.480    24.850     0.253      4.760      6.210     94.390

 5    42.480    17.030    25.450     2.884     55.600     72.650     88.180

 6   129.030    17.030   100.000     0.157     11.890     15.530     15.530

TOTAL METAL= 76.53 MG/KG
```

METAL:ARSENIC

SAMPLE NO.:TS1

PH= 11.83

VIAL WEIGHT= 13.46 GRAMS

LIQUID DILUTION: 1

VIAL + SEDIMENT WEIGHT= 17.65 GRAMS

SOLID FRACTION= .45

DRY WEIGHT= 1.88 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.650	19.960	22.690	15.270	184.290	0.460	99.960
2	97.210	20.020	74.940	3.330	132.730	0.330	99.500
3	45.020	19.110	25.910	4.090	56.360	0.140	99.170
4	44.610	21.690	22.470	46.610	557.080	1.400	99.040
5	46.690	20.450	26.230	251.950	3515.230	8.870	97.640
6	132.450	20.450	100.000	661.200	%35170.210	88.770	88.770

TOTAL METAL= 39615.9 µG/KG

METAL:ARSENIC

SAMPLE NO.:TS2

PH= 11.89

VIAL WEIGHT= 13.12 GRAMS

LIQUID DILUTION: 1

VIAL + SEDIMENT WEIGHT= 17.2 GRAMS

SOLID FRACTION= .45

DRY WEIGHT= 1.83 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.200	19.690	22.510	12.580	154.740	0.420	99.970
2	96.940	19.580	75.100	4.200	172.360	0.470	99.550
3	44.580	18.750	25.830	2.910	41.070	0.110	99.080
4	44.250	21.090	22.700	49.940	619.470	1.710	98.970
5	46.090	19.970	26.120	245.750	3507.640	9.690	97.260
6	131.970	19.970	100.000	579.600	%31672.130	87.570	87.570

TOTAL METAL= 36167.41 µG/KG

METAL:ARSENIC

SAMPLE NO.:TS3

PH= 11.93

VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .5

VIAL + SEDIMENT WEIGHT= 17.97 GRAMS

SOLID FRACTION= .45

DRY WEIGHT= 1.97 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.970	20.370	22.600	12.220	140.180	0.820	99.980
2	97.620	20.300	75.060	6.300	240.030	1.400	99.160
3	45.300	19.670	25.630	3.290	42.800	0.250	97.760
4	45.170	21.940	22.770	43.230	499.660	2.920	97.510
5	46.940	20.770	26.170	138.350	1837.870	10.750	94.590
6	132.770	20.770	100.000	282.150	%14322.330	83.840	83.840

TOTAL METAL= 17082.87 µG/KG

METAL:ARSENIC

SAMPLE NO.:TS4

PH= 11.98

VIAL WEIGHT= 13.62 GRAMS

LIQUID DILUTION: .5

VIAL + SEDIMENT WEIGHT= 18.16 GRAMS

SOLID FRACTION= .45

DRY WEIGHT= 2.04 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.160	20.820	22.340	13.550	148.380	0.950	99.950
2	98.070	20.690	75.120	5.290	194.790	1.250	99.010
3	45.690	19.740	25.950	2.630	33.450	0.210	97.760
4	45.240	22.550	22.240	68.950	751.690	4.850	97.550
5	47.550	21.140	26.410	155.250	2009.870	12.980	92.700
6	133.140	21.140	100.000	251.800	%12343.130	79.720	79.720

TOTAL METAL= 15481.31 µG/KG

```
METAL:ARSENIC                                SAMPLE NO.:TS5

PH= 11.94                                    VIAL WEIGHT= 14.23 GRAMS

LIQUID DILUTION: .1                          VIAL + SEDIMENT WEIGHT= 18.58 GRAMS

SOLID FRACTION= .45                          DRY WEIGHT= 1.95 GRAMS

NO.   INITIAL    FINAL      EXTRACT     µG/L        µG/KG      PERCENT   CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                             TOTAL     PERCENT
-------------------------------------------------------------------------------------
 1    43.580     20.810     22.770     11.390     133.000      0.770     99.970

 2    98.060     20.860     74.950      8.110     311.710      1.800     99.200

 3    45.860     19.940     25.920      4.110      54.630      0.310     97.400

 4    45.440     21.990     22.990     69.800     822.920      4.770     97.090

 5    46.990     21.250     25.730    146.300    1930.400     11.190     92.320

 6   133.250     21.250    100.000    272.800   %13989.740     81.130     81.130

TOTAL METAL= 17242.4 µG/KG
```

```
METAL:ARSENIC                                SAMPLE NO.:TS6

PH= 11.97                                    VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .1                          VIAL + SEDIMENT WEIGHT= 17.64 GRAMS

SOLID FRACTION= .45                          DRY WEIGHT= 1.82 GRAMS

NO.   INITIAL    FINAL      EXTRACT     µG/L        µG/KG      PERCENT   CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                             TOTAL     PERCENT
-------------------------------------------------------------------------------------
 1    42.640     19.700     22.940      7.180      90.490      0.470     99.980

 2    96.950     22.050     72.710      9.790     391.110      2.030     99.510

 3    47.050     19.180     27.870      3.190      48.840      0.250     97.480

 4    44.680     20.690     23.510     74.230     958.870      4.980     97.230

 5    45.690     20.310     25.380    177.700    2478.030     12.890     92.250

 6   132.310     20.310    100.000    277.650   %15255.490     79.360     79.360

TOTAL METAL= 19222.83 µG/KG
```

METAL:ARSENIC

PH= 6.07

LIQUID DILUTION: 1

SOLID FRACTION= .45

SAMPLE NO.:TS7

VIAL WEIGHT= 13.27 GRAMS

VIAL + SEDIMENT WEIGHT= 17.25 GRAMS

DRY WEIGHT= 1.79 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.630	18.580	25.050	14.040	196.480	1.120	99.970
2	95.830	18.810	74.770	7.530	314.530	1.800	98.850
3	43.810	17.540	26.270	26.420	387.730	2.220	97.050
4	43.040	19.570	23.000	565.100	7518.040	43.120	94.830
5	44.570	17.650	26.920	12.400	186.480	1.060	51.710
6	129.650	17.650	99.990	158.100	8831.510	50.650	50.650

TOTAL METAL= 17434.77 µG/KG

METAL:ARSENIC

PH= 6.24

LIQUID DILUTION: 1

SOLID FRACTION= .45

SAMPLE NO.:TS8

VIAL WEIGHT= 13.48 GRAMS

VIAL + SEDIMENT WEIGHT= 17.72 GRAMS

DRY WEIGHT= 1.9 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.100	18.590	25.510	13.180	176.950	0.980	99.970
2	95.840	18.910	74.680	12.940	508.610	2.840	98.990
3	43.910	17.470	26.440	36.580	509.030	2.840	96.150
4	42.970	19.610	22.900	493.200	6016.670	33.600	93.310
5	44.610	17.830	26.780	81.050	1142.370	6.370	59.710
6	129.830	17.830	100.000	181.500	9552.630	53.340	53.340

TOTAL METAL= 17906.26 µG/KG

METAL:ARSENIC

PH= 4.41

LIQUID DILUTION: 1

SOLID FRACTION= .45

SAMPLE NO.:TS9

VIAL WEIGHT= 13.48 GRAMS

VIAL + SEDIMENT WEIGHT= 17.54 GRAMS

DRY WEIGHT= 1.82 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.160	18.750	25.410	12.420	173.400	1.080	99.970
2	96.000	18.740	75.000	8.050	331.730	2.080	98.890
3	43.740	17.300	26.440	15.130	219.600	1.380	96.810
4	42.800	19.310	23.020	603.300	7630.750	47.900	95.430
5	44.310	18.070	26.240	43.650	629.320	3.950	47.530
6	130.070	18.070	100.000	126.350	6942.300	43.580	43.580

TOTAL METAL= 15927.3 µG/KG

METAL:ARSENIC

PH= 3.7

LIQUID DILUTION: 1

SOLID FRACTION= .45

SAMPLE NO.:TS10

VIAL WEIGHT= 13.89 GRAMS

VIAL + SEDIMENT WEIGHT= 17.81 GRAMS

DRY WEIGHT= 1.76 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.370	19.320	25.050	30.780	438.090	2.330	99.970
2	96.570	19.410	74.910	7.470	317.940	1.690	97.640
3	44.410	17.890	26.520	8.770	132.140	0.700	95.950
4	43.390	19.820	23.100	585.100	7679.430	40.910	95.250
5	44.820	17.430	27.390	56.800	863.950	4.700	54.340
6	129.430	17.430	100.000	164.000	9318.180	49.640	49.640

TOTAL METAL= 18769.73 µG/KG

```
METAL:BARIUM                                  SAMPLE NO.:TS1

PH= 11.83                                     VIAL WEIGHT= 13.46 GRAMS

LIQUID DILUTION: 1                            VIAL + SEDIMENT WEIGHT= 17.65 GRAMS

SOLID FRACTION= .45                           DRY WEIGHT= 1.88 GRAMS

NO.   INITIAL    FINAL      EXTRACT       MG/L        MG/KG      PERCENT    CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                               TOTAL      PERCENT
--------------------------------------------------------------------------------------
 1    42.650     19.960     22.690       3.033       36.600      1.070      99.950

 2    97.210     20.020     74.940       2.723      108.540      3.190      98.890

 3    45.020     19.110     25.910       0.945       13.020      0.380      95.700

 4    44.610     21.690     22.470       5.160       61.670      1.810      95.320

 5    46.690     20.450     26.230      11.680      162.960      4.790      93.510

 6   132.450     20.450    100.000      56.650     3013.290     88.720      88.720

TOTAL METAL= 3396.08 MG/KG
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METAL:BARIUM                                  SAMPLE NO.:TS2

PH= 11.89                                     VIAL WEIGHT= 13.12 GRAMS

LIQUID DILUTION: 1                            VIAL + SEDIMENT WEIGHT= 17.2 GRAMS

SOLID FRACTION= .45                           DRY WEIGHT= 1.83 GRAMS

NO.   INITIAL    FINAL      EXTRACT       MG/L        MG/KG      PERCENT    CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                               TOTAL      PERCENT
--------------------------------------------------------------------------------------
 1    42.200     19.690     22.510       0.399        4.900      0.140      99.970

 2    96.940     19.580     75.100       1.314       53.920      1.540      99.830

 3    44.580     18.750     25.830       0.753       10.620      0.300      98.290

 4    44.250     21.090     22.700       4.055       50.290      1.440      97.990

 5    46.090     19.970     26.120       9.890      141.160      4.040      96.550

 6   131.970     19.970    100.000      59.020     3225.130     92.510      92.510

TOTAL METAL= 3486.02 MG/KG
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METAL:BARIUM                                SAMPLE NO.:TS3

PH= 11.93                                   VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .5                         VIAL + SEDIMENT WEIGHT= 17.97 GRAMS

SOLID FRACTION= .45                         DRY WEIGHT= 1.97 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
--------------------------------------------------------------------------------
 1    42.970    20.370    22.600     0.982     11.260      0.400     99.970

 2    97.620    20.300    75.050     1.103     42.020      1.510     99.570

 3    45.300    19.670    25.630     0.885     11.510      0.410     98.060

 4    45.170    21.940    22.770     4.705     54.380      1.960     97.650

 5    46.940    20.770    26.170    14.240    189.160      6.830     95.690

 6   132.770    20.770   100.000    48.470   2460.400     88.860     88.860

TOTAL METAL= 2768.73 MG/KG
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METAL:BARIUM                                SAMPLE NO.:TS4

PH= 11.98                                   VIAL WEIGHT= 13.62 GRAMS

LIQUID DILUTION: .5                         VIAL + SEDIMENT WEIGHT= 18.16 GRAMS

SOLID FRACTION= .45                         DRY WEIGHT= 2.04 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
--------------------------------------------------------------------------------
 1    43.160    20.820    22.340     0.000      0.000      0.000     99.980

 2    98.070    20.690    75.120     1.664     61.270      1.350     99.980

 3    45.690    19.740    25.950     0.865     11.000      0.240     98.630

 4    45.240    22.550    22.240     5.015     54.670      1.200     98.390

 5    47.550    21.140    26.410     7.490     96.960      2.130     97.190

 6   133.140    21.140   100.000    87.950   4311.270     95.060     95.060

TOTAL METAL= 4535.17 MG/KG
```

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METAL:BARIUM                          SAMPLE NO.:TS5

PH= 11.94                             VIAL WEIGHT= 14.23 GRAMS

LIQUID DILUTION: .1                   VIAL + SEDIMENT WEIGHT= 18.58 GRAMS

SOLID FRACTION= .45                   DRY WEIGHT= 1.95 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    43.590    20.810    22.770      1.708      19.940     0.620     99.980

 2    98.060    20.860    74.950      2.367      90.970     2.830     99.360

 3    45.860    19.940    25.920      1.057      14.040     0.430     96.530

 4    45.440    21.990    22.990      4.070      47.980     1.490     96.100

 5    46.990    21.250    25.730     13.810     182.220     5.670     94.610

 6   133.250    21.250   100.000     55.730    2857.940    88.940     88.940

TOTAL METAL= 3213.09 MG/KG
```

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METAL:BARIUM                          SAMPLE NO.:TS6

PH= 11.97                             VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .1                   VIAL + SEDIMENT WEIGHT= 17.64 GRAMS

SOLID FRACTION= .45                   DRY WEIGHT= 1.82 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    42.640    19.700    22.940      0.124       1.560     0.030     99.980

 2    96.950    22.050    72.710      1.593      63.640     1.370     99.950

 3    47.050    19.180    27.870      0.850      13.010     0.280     98.580

 4    44.680    20.690    23.510      4.345      56.120     1.210     98.300

 5    45.690    20.310    25.380     16.500     230.090     4.980     97.090

 6   132.310    20.310   100.000     77.450    4255.490    92.110     92.110

TOTAL METAL= 4619.91 MG/KG
```

METAL:BARIUM

PH= 6.07

LIQUID DILUTION: 1

SOLID FRACTION= .45

SAMPLE NO.:TS7

VIAL WEIGHT= 13.27 GRAMS

VIAL + SEDIMENT WEIGHT= 17.25 GRAMS

DRY WEIGHT= 1.79 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.630	18.580	25.050	2.819	39.450	0.680	99.980
2	95.830	18.810	74.770	1.914	79.940	1.390	99.300
3	43.810	17.540	26.270	2.480	36.390	0.630	97.910
4	43.040	19.570	23.000	1.715	22.030	0.380	97.280
5	44.570	17.650	26.920	116.830	1757.010	30.550	96.900
6	129.650	17.650	99.990	68.300	3815.260	66.350	66.350

TOTAL METAL= 5750.08 MG/KG

METAL:BARIUM

PH= 6.24

LIQUID DILUTION: 1

SOLID FRACTION= .45

SAMPLE NO.:TS8

VIAL WEIGHT= 13.48 GRAMS

VIAL + SEDIMENT WEIGHT= 17.72 GRAMS

DRY WEIGHT= 1.9 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.100	18.590	25.510	5.034	67.580	1.840	99.980
2	95.840	18.910	74.680	5.170	203.200	5.530	98.140
3	43.910	17.470	26.440	2.276	31.670	0.860	92.610
4	42.970	19.610	22.900	1.536	18.510	0.500	91.750
5	44.610	17.830	26.780	78.640	1108.410	30.200	91.250
6	129.830	17.830	100.000	42.570	2240.520	61.050	61.050

TOTAL METAL= 3669.89 MG/KG

```
METAL:BARIUM                              SAMPLE NO.:TS9

PH= 4.41                                  VIAL WEIGHT= 13.48 GRAMS

LIQUID DILUTION: 1                        VIAL + SEDIMENT WEIGHT= 17.54 GRAMS

SOLID FRACTION= .45                       DRY WEIGHT= 1.82 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
------------------------------------------------------------------------------
 1    44.160    18.750    25.410      0.962     13.430     0.360     99.970

 2    96.000    18.740    75.000      1.260     51.920     1.410     99.610

 3    43.740    17.300    26.440      2.290     33.260     0.900     98.200

 4    42.800    19.310    23.020      2.360     29.850     0.810     97.300

 5    44.310    18.070    26.240    220.720   3182.240    86.720     96.490

 6   130.070    18.070   100.000      6.529    358.730     9.770      9.770

TOTAL METAL= 3669.43 MG/KG
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METAL:BARIUM                              SAMPLE NO.:TS10

PH= 3.7                                   VIAL WEIGHT= 13.89 GRAMS

LIQUID DILUTION: 1                        VIAL + SEDIMENT WEIGHT= 17.81 GRAMS

SOLID FRACTION= .45                       DRY WEIGHT= 1.76 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
------------------------------------------------------------------------------
 1    44.370    19.320    25.050      1.400     19.920     0.540     99.950

 2    96.570    19.410    74.910      2.504    106.570     2.900     99.420

 3    44.410    17.890    26.520      1.713     25.810     0.700     96.520

 4    43.390    19.820    23.100      1.755     23.030     0.620     95.820

 5    44.820    17.430    27.390    203.920   3173.500    86.470     95.200

 6   129.430    17.430   100.000      5.651    321.070     8.740      8.730

TOTAL METAL= 3669.9 MG/KG
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METAL:CHROMIUM                         SAMPLE NO.:TS1

PH= 11.83                              VIAL WEIGHT= 13.46 GRAMS

LIQUID DILUTION: 1                     VIAL + SEDIMENT WEIGHT= 17.65 GRAMS

SOLID FRACTION= .45                    DRY WEIGHT= 1.88 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL      PERCENT
-------------------------------------------------------------------------------
 1    42.650    19.960    22.690     0.282        3.400     0.970     99.980

 2    97.210    20.020    74.940     0.146        5.810     1.660     99.010

 3    45.020    19.110    25.910     0.000        0.000     0.000     97.350

 4    44.610    21.690    22.470     0.165        1.970     0.560     97.350

 5    46.690    20.450    26.230     0.186        2.590     0.740     96.790

 6   132.450    20.450   100.000     6.297      334.940    96.050     96.050

TOTAL METAL= 348.71 MG/KG
```

```
METAL:CHROMIUM                         SAMPLE NO.:TS2

PH= 11.89                              VIAL WEIGHT= 13.12 GRAMS

LIQUID DILUTION: 1                     VIAL + SEDIMENT WEIGHT= 17.2 GRAMS

SOLID FRACTION= .45                    DRY WEIGHT= 1.83 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL      PERCENT
-------------------------------------------------------------------------------
 1    42.200    19.690    22.510     0.260        3.190     0.920     99.950

 2    96.940    19.580    75.100     0.155        6.360     1.850     99.040

 3    44.580    18.750    25.830     0.029        0.400     0.110     97.190

 4    44.250    21.090    22.700     0.099        1.220     0.350     97.080

 5    46.090    19.970    26.120     0.138        1.960     0.570     96.730

 6   131.970    19.970   100.000     6.039      330.000    96.170     96.170

TOTAL METAL= 343.13 MG/KG
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METAL:CHROMIUM                             SAMPLE NO.:TS3

PH= 11.93                                  VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .5                        VIAL + SEDIMENT WEIGHT= 17.97 GRAMS

SOLID FRACTION= .45                        DRY WEIGHT= 1.97 GRAMS

NO.   INITIAL    FINAL      EXTRACT        MG/L           MG/KG        PERCENT    CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                                     TOTAL      PERCENT
----------------------------------------------------------------------------------------------
 1    42.970     20.370     22.600         0.329          3.770        1.080      99.950

 2    97.620     20.300     75.060         0.101          3.840        1.100      98.870

 3    45.300     19.670     25.630         0.000          0.000        0.000      97.770

 4    45.170     21.940     22.770         0.119          1.370        0.390      97.770

 5    46.940     20.770     26.170         0.126          1.670        0.480      97.390

 6   132.770     20.770    100.000         6.622        336.140       96.920      96.920

TOTAL METAL= 346.79 MG/KG
```

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METAL:CHROMIUM                             SAMPLE NO.:TS4

PH= 11.98                                  VIAL WEIGHT= 13.62 GRAMS

LIQUID DILUTION: .5                        VIAL + SEDIMENT WEIGHT= 18.16 GRAMS

SOLID FRACTION= .45                        DRY WEIGHT= 2.04 GRAMS

NO.   INITIAL    FINAL      EXTRACT        MG/L           MG/KG        PERCENT    CUMULATIVE
      WEIGHT     WEIGHT     VOLUME                                     TOTAL      PERCENT
----------------------------------------------------------------------------------------------
 1    43.160     20.820     22.340         0.389          4.250        1.330      99.970

 2    98.070     20.690     75.120         0.102          3.750        1.170      98.640

 3    45.690     19.740     25.950         0.000          0.000        0.000      97.480

 4    45.240     22.550     22.240         0.074          0.800        0.250      97.480

 5    47.550     21.140     26.410         0.156          2.010        0.620      97.230

 6   133.140     21.140    100.000         6.291        308.380       96.610      96.610

TOTAL METAL= 319.19 MG/KG
```

METAL:CHROMIUM

PH= 11.94

LIQUID DILUTION: .1

SOLID FRACTION= .45

SAMPLE NO.:TS5

VIAL WEIGHT= 14.23 GRAMS

VIAL + SEDIMENT WEIGHT= 18.58 GRAMS

DRY WEIGHT= 1.95 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.580	20.810	22.770	0.237	2.760	0.800	99.960
2	98.060	20.860	74.950	0.109	4.160	1.210	99.160
3	45.860	19.940	25.920	0.040	0.530	0.150	97.950
4	45.440	21.990	22.990	0.090	1.060	0.300	97.800
5	46.990	21.250	25.730	0.166	2.190	0.630	97.500
6	133.250	21.250	100.000	6.477	332.150	96.870	96.870

TOTAL METAL= 342.87 MG/KG

METAL:CHROMIUM

PH= 11.97

LIQUID DILUTION: .1

SOLID FRACTION= .45

SAMPLE NO.:TS6

VIAL WEIGHT= 13.58 GRAMS

VIAL + SEDIMENT WEIGHT= 17.69 GRAMS

DRY WEIGHT= 1.84 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.690	19.700	22.980	0.223	2.780	0.870	99.980
2	96.950	20.650	74.070	0.132	5.310	1.670	99.110
3	45.650	19.180	26.470	0.005	0.070	0.020	97.440
4	44.680	20.690	23.510	0.126	1.600	0.500	97.420
5	45.690	20.310	25.380	0.172	2.370	0.740	96.920
6	132.310	20.310	100.000	5.622	305.540	96.180	96.180

TOTAL METAL= 317.67 MG/KG

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METAL:CHROMIUM                           SAMPLE NO.:TS7

PH= 6.07                                 VIAL WEIGHT= 13.27 GRAMS

LIQUID DILUTION: 1                       VIAL + SEDIMENT WEIGHT= 17.25 GRAMS

SOLID FRACTION= .45                      DRY WEIGHT= 1.79 GRAMS

NO.  INITIAL  FINAL    EXTRACT   MG/L        MG/KG    PERCENT   CUMULATIVE
     WEIGHT   WEIGHT   VOLUME                         TOTAL     PERCENT
----------------------------------------------------------------------------
 1   43.630   18.580   25.050    0.138       1.930    0.700     99.970

 2   95.830   18.810   74.770    0.050       2.060    0.750     99.270

 3   43.810   17.540   26.270    0.223       3.270    1.180     98.520

 4   43.040   19.370   23.200    0.206       2.660    0.960     97.340

 5   44.370   17.650   26.720    0.969      14.460    5.240     96.380

 6  129.650   17.650   99.990    4.496     251.140   91.140     91.140

TOTAL METAL= 275.54 MG/KG
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METAL:CHROMIUM                           SAMPLE NO.:TS8

PH= 6.24                                 VIAL WEIGHT= 13.48 GRAMS

LIQUID DILUTION: 1                       VIAL + SEDIMENT WEIGHT= 17.72 GRAMS

SOLID FRACTION= .45                      DRY WEIGHT= 1.9 GRAMS

NO.  INITIAL  FINAL    EXTRACT   MG/L        MG/KG    PERCENT   CUMULATIVE
     WEIGHT   WEIGHT   VOLUME                         TOTAL     PERCENT
----------------------------------------------------------------------------
 1   44.100   18.590   25.510    0.110       1.470    0.510     99.950

 2   95.840   18.910   74.680    0.034       1.330    0.460     99.450

 3   43.910   17.470   26.440    0.210       2.920    1.020     98.990

 4   42.970   19.610   22.900    0.221       2.660    0.930     97.970

 5   44.610   17.830   26.780    0.945      13.310    4.680     97.040

 6  129.830   17.830  100.000    4.988     262.520   92.360     92.360

TOTAL METAL= 284.21 MG/KG
```

METAL:CHROMIUM
PH= 4.41
LIQUID DILUTION: 1
SOLID FRACTION= .45

SAMPLE NO.:TS9
VIAL WEIGHT= 13.51 GRAMS
VIAL + SEDIMENT WEIGHT= 17.54 GRAMS
DRY WEIGHT= 1.81 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.160	18.750	25.410	0.513	7.200	2.590	99.960
2	96.000	18.740	75.000	0.102	4.220	1.520	97.370
3	43.740	17.300	26.440	0.232	3.380	1.210	95.850
4	42.800	19.310	23.020	0.249	3.160	1.130	94.640
5	44.310	18.070	26.240	1.328	19.250	6.940	93.510
6	130.070	18.070	100.000	4.345	240.050	86.570	86.570

TOTAL METAL= 277.26 MG/KG

METAL:CHROMIUM
PH= 3.7
LIQUID DILUTION: 1
SOLID FRACTION= .45

SAMPLE NO.:TS10
VIAL WEIGHT= 13.89 GRAMS
VIAL + SEDIMENT WEIGHT= 17.81 GRAMS
DRY WEIGHT= 1.76 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.370	19.320	25.050	1.246	17.730	5.560	99.960
2	96.570	19.410	74.910	0.126	5.360	1.680	94.400
3	44.410	17.890	26.520	0.083	1.250	0.390	92.720
4	43.390	19.820	23.100	0.292	3.830	1.200	92.330
5	44.820	17.430	27.390	1.358	21.130	6.630	91.140
6	129.430	17.430	100.000	4.736	269.090	84.510	84.510

TOTAL METAL= 318.39 MG/KG

```
METAL:LEAD                                SAMPLE NO.:TS1

PH= 11.83                                 VIAL WEIGHT= 13.46 GRAMS

LIQUID DILUTION: 1                        VIAL + SEDIMENT WEIGHT= 17.65 GRAMS

SOLID FRACTION= .45                       DRY WEIGHT= 1.88 GRAMS

NO.   INITIAL    FINAL     EXTRACT     MG/L        MG/KG     PERCENT    CUMULATIVE
      WEIGHT     WEIGHT    VOLUME                            TOTAL       PERCENT
------------------------------------------------------------------------------------
 1    42.650     19.960     22.690     0.000       0.000      0.000      99.950

 2    97.210     20.020     74.940     0.013       0.510      0.230      99.950

 3    45.020     19.110     25.910     0.013       0.170      0.070      99.730

 4    44.610     21.690     22.470     0.511       6.100      2.800      99.660

 5    46.690     20.450     26.230     0.583       8.130      3.730      96.860

 6   132.450     20.450    100.000     3.807     202.500     93.140      93.140

TOTAL METAL= 217.41 MG/KG
```

```
METAL:LEAD                                SAMPLE NO.:TS2

PH= 11.89                                 VIAL WEIGHT= 13.12 GRAMS

LIQUID DILUTION: 1                        VIAL + SEDIMENT WEIGHT= 17.2 GRAMS

SOLID FRACTION= .45                       DRY WEIGHT= 1.83 GRAMS

NO.   INITIAL    FINAL     EXTRACT     MG/L        MG/KG     PERCENT    CUMULATIVE
      WEIGHT     WEIGHT    VOLUME                            TOTAL       PERCENT
------------------------------------------------------------------------------------
 1    42.200     19.690     22.510     0.000       0.000      0.000      99.960

 2    96.940     19.580     75.100     0.027       1.100      0.490      99.960

 3    44.580     18.750     25.830     0.040       0.560      0.250      99.470

 4    44.250     21.090     22.700     0.541       6.710      3.040      99.220

 5    46.090     19.970     26.120     0.714      10.190      4.620      96.180

 6   131.970     19.970    100.000     3.688     201.530     91.560      91.560

TOTAL METAL= 220.09 MG/KG
```

METAL:LEAD

PH= 11.93

LIQUID DILUTION: .5

SOLID FRACTION= .45

SAMPLE NO.:TS3

VIAL WEIGHT= 13.58 GRAMS

VIAL + SEDIMENT WEIGHT= 17.97 GRAMS

DRY WEIGHT= 1.97 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.970	20.370	22.600	0.031	0.350	0.170	99.980
2	97.620	20.300	75.060	0.013	0.490	0.230	99.810
3	45.300	19.670	25.630	0.023	0.290	0.140	99.580
4	45.170	21.940	22.770	0.540	6.240	3.050	99.440
5	46.940	20.770	26.170	0.657	8.720	4.260	96.390
6	132.770	20.770	100.000	3.713	188.470	92.130	92.130

TOTAL METAL= 204.56 MG/KG

METAL:LEAD

PH= 11.98

LIQUID DILUTION: .5

SOLID FRACTION= .45

SAMPLE NO.:TS4

VIAL WEIGHT= 13.62 GRAMS

VIAL + SEDIMENT WEIGHT= 18.16 GRAMS

DRY WEIGHT= 2.04 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.160	20.820	22.340	0.033	0.360	0.190	99.970
2	98.070	20.690	75.120	0.012	0.440	0.230	99.780
3	45.690	19.740	25.950	0.038	0.480	0.250	99.550
4	45.240	22.550	22.240	0.519	5.650	3.030	99.300
5	47.550	21.140	26.410	0.506	6.550	3.520	96.270
6	133.140	21.140	100.000	3.519	172.500	92.750	92.750

TOTAL METAL= 185.98 MG/KG

```
METAL:LEAD                                 SAMPLE NO.:TS5

PH= 11.94                                  VIAL WEIGHT= 14.23 GRAMS

LIQUID DILUTION: .1                        VIAL + SEDIMENT WEIGHT= 18.58 GRAMS

SOLID FRACTION= .45                        DRY WEIGHT= 1.95 GRAMS

NO.   INITIAL   FINAL     EXTRACT    MG/L      MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                         TOTAL      PERCENT
-------------------------------------------------------------------------------
 1   43.580    20.810    22.770     0.037      0.430     0.200     99.970

 2   98.060    20.860    74.950     0.000      0.000     0.000     99.770

 3   45.860    19.940    25.920     0.025      0.330     0.150     99.770

 4   45.440    21.990    22.990     0.523      6.160     2.960     99.620

 5   46.990    21.250    25.730     0.741      9.770     4.690     96.660

 6  133.250    21.250   100.000     3.729    191.230    91.970     91.970

TOTAL METAL= 207.92 MG/KG
```

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METAL:LEAD                                 SAMPLE NO.:TS6

PH= 11.97                                  VIAL WEIGHT= 13.58 GRAMS

LIQUID DILUTION: .1                        VIAL + SEDIMENT WEIGHT= 17.69 GRAMS

SOLID FRACTION= .45                        DRY WEIGHT= 1.84 GRAMS

NO.   INITIAL   FINAL     EXTRACT    MG/L      MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                         TOTAL      PERCENT
-------------------------------------------------------------------------------
 1   42.690    19.700    22.980     0.017      0.210     0.110     99.970

 2   96.950    20.650    74.070     0.005      0.200     0.100     99.860

 3   45.650    19.180    26.470     0.018      0.250     0.130     99.760

 4   44.680    20.690    23.510     0.508      6.490     3.560     99.630

 5   45.690    20.310    25.380     1.008     13.900     7.630     96.070

 6  132.310    20.310   100.000     2.964    161.080    88.440     88.440

TOTAL METAL= 182.13 MG/KG
```

```
METAL:LEAD                                  SAMPLE NO.:TS7

PH= 6.07                                    VIAL WEIGHT= 13.27 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 17.25 GRAMS

SOLID FRACTION= .45                         DRY WEIGHT= 1.79 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                              TOTAL     PERCENT
-----------------------------------------------------------------------------------
 1    43.630    18.580    25.050      0.000       0.000       0.000     99.970

 2    95.830    18.810    74.770      0.000       0.000       0.000     99.970

 3    43.810    17.540    26.270      0.234       3.430       1.680     99.970

 4    43.040    19.370    23.200      0.465       6.020       2.950     98.290

 5    44.370    17.650    26.720      8.274     123.500      60.680     95.340

 6   129.650    17.650    99.990      1.263      70.550      34.660     34.660

TOTAL METAL= 203.5 MG/KG
```

```
METAL:LEAD                                  SAMPLE NO.:TS8

PH= 6.24                                    VIAL WEIGHT= 13.48 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 17.72 GRAMS

SOLID FRACTION= .45                         DRY WEIGHT= 1.9 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                              TOTAL     PERCENT
-----------------------------------------------------------------------------------
 1    44.100    18.590    25.510      0.000       0.000       0.000     99.970

 2    95.840    18.910    74.680      0.003       0.110       0.050     99.970

 3    43.910    17.470    26.440      0.217       3.010       1.370     99.920

 4    42.970    19.610    22.900      0.429       5.170       2.360     98.550

 5    44.610    17.830    26.780      9.162     129.130      59.190     96.190

 6   129.830    17.830   100.000      1.534      80.730      37.000     37.000

TOTAL METAL= 218.15 MG/KG
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METAL:LEAD                               SAMPLE NO.:TS9

PH= 4.41                                 VIAL WEIGHT= 13.51 GRAMS

LIQUID DILUTION: 1                       VIAL + SEDIMENT WEIGHT= 17.54 GRAMS

SOLID FRACTION= .45                      DRY WEIGHT= 1.81 GRAMS

NO.   INITIAL   FINAL      EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT     VOLUME                              TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    44.160    18.750     25.410      0.271        3.800       1.760     99.970

 2    96.000    18.740     75.000      0.114        4.720       2.180     98.210

 3    43.740    17.300     26.440      0.162        2.360       1.090     96.030

 4    42.800    19.310     23.020      0.432        5.490       2.540     94.940

 5    44.310    18.070     26.240      7.962      115.420      53.470     92.400

 6   130.070    18.070    100.000      1.521       84.030      38.930     38.930

TOTAL METAL= 215.82 MG/KG
```

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METAL:LEAD                               SAMPLE NO.:TS10

PH= 3.7                                  VIAL WEIGHT= 13.89 GRAMS

LIQUID DILUTION: 1                       VIAL + SEDIMENT WEIGHT= 17.81 GRAMS

SOLID FRACTION= .45                      DRY WEIGHT= 1.76 GRAMS

NO.   INITIAL   FINAL      EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT     VOLUME                              TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    44.370    19.320     25.050      1.351       19.220       7.640     99.950

 2    96.570    19.410     74.910      0.723       30.770      12.240     92.310

 3    44.410    17.890     26.520      0.109        1.640       0.650     80.070

 4    43.390    19.820     23.100      0.249        3.260       1.290     79.420

 5    44.820    17.430     27.390      6.168       95.980      38.190     78.140

 6   129.430    17.430    100.000      1.768      100.450      39.960     39.950

TOTAL METAL= 251.32 MG/KG
```

METAL:ARSENIC
SAMPLE NO.:TC1

PH= 5.12
VIAL WEIGHT= 13.81 GRAMS

LIQUID DILUTION: 1
VIAL + SEDIMENT WEIGHT= 17.72 GRAMS

SOLID FRACTION= .636
DRY WEIGHT= 2.48 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µ G/L	µ G/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.220	18.720	24.500	2.020	19.950	0.490	99.960
2	95.970	19.880	73.870	1.530	45.570	1.120	99.470
3	44.880	18.470	26.410	1.700	18.100	0.440	98.350
4	43.970	18.560	24.910	124.390	1249.410	30.960	97.910
5	43.560	18.350	25.210	96.730	983.290	24.360	66.950
6	130.350	18.350	100.000	42.630	1718.950	42.590	42.590

TOTAL METAL= 4035.27 µG/KG

METAL:ARSENIC
SAMPLE NO.:TC2

PH= 3.23
VIAL WEIGHT= 14.89 GRAMS

LIQUID DILUTION: 1
VIAL + SEDIMENT WEIGHT= 18.81 GRAMS

SOLID FRACTION= .636
DRY WEIGHT= 2.49 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µ G/L	µ G/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.310	18.720	25.590	15.820	162.580	2.090	99.970
2	95.970	19.740	74.000	7.940	235.960	3.030	97.880
3	44.740	18.330	26.410	1.800	19.090	0.240	94.850
4	43.830	18.690	24.640	130.340	1289.790	16.600	94.610
5	43.690	18.500	25.190	24.610	248.960	3.200	78.010
6	130.500	18.500	100.000	144.740	5812.850	74.810	74.810

TOTAL METAL= 7769.23 µG/KG

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METAL ARSENIC                                SAMPLE NO.:TC3

PH= 2.9                                      VIAL WEIGHT= 13.5 GRAMS

LIQUID DILUTION: .5                          VIAL + SEDIMENT WEIGHT= 17.44 GRAMS

SOLID FRACTION= .636                         DRY WEIGHT= 2.5 GRAMS

NO.  INITIAL   FINAL     EXTRACT     µG/L        µG/KG      PERCENT   CUMULATIVE
     WEIGHT    WEIGHT    VOLUME                              TOTAL     PERCENT
--------------------------------------------------------------------------------
 1    42.940   18.590     24.350     46.820    456.020      4.130      99.970

 2    95.840   19.590     74.020     15.590    461.580      4.180      95.840

 3    44.590   18.400     26.190      1.900     19.900      0.180      91.660

 4    43.900   18.220     25.170    123.640   1244.800     11.290      91.480

 5    43.220   18.100     25.120      4.570     45.910      0.410      80.190

 6   130.100   18.100    100.000    219.870   8794.800     79.780      79.780

TOTAL METAL= 11023.01 µG/KG
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METAL:ARSENIC                                SAMPLE NO.:TC4

PH= 3.25                                     VIAL WEIGHT= 14.06 GRAMS

LIQUID DILUTION: .5                          VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .636                         DRY WEIGHT= 2.5 GRAMS

NO.  INITIAL   FINAL     EXTRACT     µ G/L       µG/KG      PERCENT   CUMULATIVE
     WEIGHT    WEIGHT    VOLUME                              TOTAL     PERCENT
--------------------------------------------------------------------------------
 1    43.500   19.170     24.330     22.030    214.390      1.170      99.970

 2    96.420   20.140     74.050      6.390    189.270      1.030      98.800

 3    45.140   18.960     26.180      2.030     21.250      0.110      97.770

 4    44.460   19.160     24.800    109.390   1085.140      5.940      97.660

 5    44.160   18.710     25.450      0.000      0.000      0.000      91.720

 6   130.710   18.710     99.990    418.500   %16738.320     91.720      91.720

TOTAL METAL= 18248.37 µG/KG
```

METAL:ARSENIC

PH= 3.04

LIQUID DILUTION: .1

SOLID FRACTION= .636

SAMPLE NO.:TC5

VIAL WEIGHT= 13.25 GRAMS

VIAL + SEDIMENT WEIGHT= 17.4 GRAMS

DRY WEIGHT= 2.63 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µ G/L	µ G/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.900	18.560	24.340	47.740	441.620	2.580	99.980
2	95.810	19.610	73.980	12.340	347.110	2.030	97.400
3	44.610	18.380	26.230	0.600	5.980	0.030	95.370
4	43.880	18.370	25.000	140.140	1332.120	7.790	95.340
5	43.370	18.460	24.910	18.490	175.120	1.020	87.550
6	130.460	18.460	99.990	389.100	%14793.190	86.530	86.530

TOTAL METAL= 17095.34 µG/KG

METAL:ARSENIC

PH= 2.97

LIQUID DILUTION: .1

SOLID FRACTION= .636

SAMPLE NO.:TC6

VIAL WEIGHT= 13.64 GRAMS

VIAL + SEDIMENT WEIGHT= 17.7 GRAMS

DRY WEIGHT= 2.58 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µ G/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.200	19.050	24.150	22.940	214.720	0.990	99.960
2	96.300	19.770	74.300	8.750	251.980	1.160	98.970
3	44.770	18.670	26.090	1.890	19.110	0.080	97.810
4	44.170	19.050	24.620	105.140	1003.310	4.640	97.730
5	44.050	18.860	25.190	1.260	12.300	0.050	93.090
6	130.860	18.860	100.000	518.100	%20081.390	93.040	93.040

TOTAL METAL= 21582.81 µG/KG

```
METAL:ARSENIC                               SAMPLE NO.:TC7

PH= 6.04                                    VIAL WEIGHT= 13.79 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 17.88 GRAMS

SOLID FRACTION= .636                        DRY WEIGHT= 2.6 GRAMS

NO.   INITIAL   FINAL     EXTRACT     µG/L        µG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
---------------------------------------------------------------------------------
 1    43.180    19.010    24.170     0.000       0.000      0.000      99.970

 2    96.260    20.150    73.890     7.980     226.780      1.400      99.970

 3    45.150    18.560    26.590     3.370      34.460      0.210      98.570

 4    44.060    18.940    24.620    50.340     476.680      2.960      98.360

 5    43.940    18.700    25.230     0.490       4.750      0.020      95.400

 6   130.700    18.700   100.000   399.200  %15353.840      95.380      95.380

TOTAL METAL= 16096.51 µG/KG




METAL:ARSENIC                               SAMPLE NO.:TC8

PH= 6.02                                    VIAL WEIGHT= 13.91 GRAMS

LIQUID DILUTION: 1                          VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .636                        DRY WEIGHT= 2.6 GRAMS

NO.   INITIAL   FINAL     EXTRACT     µG/L        µG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
---------------------------------------------------------------------------------
 1    43.300    19.070    24.230     0.180       1.670      0.000      99.950

 2    96.320    20.170    73.930     8.060     229.160      1.230      99.950

 3    45.170    18.480    26.690     5.320      54.610      0.290      98.730

 4    43.980    19.180    24.310    70.840     662.350      3.570      98.440

 5    44.180    18.310    25.870     5.300      52.730      0.280      94.870

 6   130.310    18.310   100.000   455.600  %17523.070      94.590      94.590

TOTAL METAL= 18523.61 µG/KG
```

METAL:ARSENIC

SAMPLE NO.:TC9

PH= 8.18

VIAL WEIGHT= 13.61 GRAMS

LIQUID DILUTION: 1

VIAL + SEDIMENT WEIGHT= 17.75 GRAMS

SOLID FRACTION= .636

DRY WEIGHT= 2.63 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.750	20.540	22.210	33.300	281.210	1.530	99.950
2	97.790	20.760	74.780	7.110	202.160	1.100	98.420
3	45.760	18.710	27.050	7.140	73.430	0.400	97.320
4	44.210	19.210	24.500	61.690	574.670	3.140	96.920
5	44.210	18.330	25.880	3.520	34.630	0.180	93.790
6	130.330	18.330	100.000	449.900	%17106.460	93.610	93.610

TOTAL METAL= 18272.56 µG/KG

METAL:ARSENIC

SAMPLE NO.:TC10

PH= 7.76

VIAL WEIGHT= 14.28 GRAMS

LIQUID DILUTION: 1

VIAL + SEDIMENT WEIGHT= 18.27 GRAMS

SOLID FRACTION= .636

DRY WEIGHT= 2.53 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	µG/L	µG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.270	20.630	22.630	60.010	536.760	2.920	99.970
2	97.880	21.230	74.410	9.730	286.160	1.560	97.050
3	46.230	19.270	26.960	5.290	56.370	0.300	95.490
4	44.770	19.880	24.400	57.090	550.590	3.000	95.190
5	44.880	18.750	26.130	2.590	26.740	0.140	92.190
6	130.750	18.750	100.000	427.000	%16877.470	92.050	92.050

TOTAL METAL= 18334.09 µG/KG

```
METAL:BARIUM                            SAMPLE NO.:TC1

PH= 5.12                                VIAL WEIGHT= 13.81 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 18.81 GRAMS

SOLID FRACTION= .636                    DRY WEIGHT= 3.18 GRAMS

NO.  INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    44.310    18.720    25.590     1.814     14.590      6.670     99.950

 2    95.970    19.880    73.870     6.710    155.870     71.280     93.280

 3    44.880    18.470    26.410     0.290      2.400      1.090     22.000

 4    43.970    18.560    24.910     0.107      0.830      0.370     20.910

 5    43.560    18.350    25.210     3.229     25.590     11.700     20.550

 6   130.350    18.350   100.000     0.616     19.370      8.850      8.850

TOTAL METAL= 218.65 MG/KG
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METAL:BARIUM                            SAMPLE NO.:TC2

PH= 3.23                                VIAL WEIGHT= 14.89 GRAMS

LIQUID DILUTION: 1                      VIAL + SEDIMENT WEIGHT= 18.81 GRAMS

SOLID FRACTION= .636                    DRY WEIGHT= 2.49 GRAMS

NO.  INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    44.310    18.720    25.590     0.910      9.350      3.600     99.960

 2    95.970    19.740    74.000     6.437    191.300     73.680     96.360

 3    44.740    18.330    26.410     0.401      4.250      1.630     22.680

 4    43.830    18.690    24.640     0.000      0.000      0.000     21.050

 5    43.690    18.500    25.190     3.122     31.580     12.160     21.050

 6   130.500    18.500   100.000     0.576     23.130      8.900      8.890

TOTAL METAL= 259.61 MG/KG
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METAL:BARIUM                                SAMPLE NO.:TC3

PH= 2.9                                     VIAL WEIGHT= 13.5 GRAMS

LIQUID DILUTION: .5                         VIAL + SEDIMENT WEIGHT= 17.44 GRAMS

SOLID FRACTION= .636                        DRY WEIGHT= 2.5 GRAMS

NO.  INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT    WEIGHT    VOLUME                           TOTAL      PERCENT
-------------------------------------------------------------------------------
 1   42.940    18.590    24.350      1.809     17.610      7.400     99.970

 2   95.640    19.590    74.020      4.972    147.210     61.910     92.570

 3   44.590    18.400    26.190      0.614      6.430      2.700     30.660

 4   43.900    18.220    25.170      0.000      0.000      0.000     27.960

 5   43.220    18.100    25.120      4.125     41.440     17.420     27.960

 6  130.100    18.100   100.000      0.627     25.080     10.540     10.540

TOTAL METAL= 237.77 MG/KG
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METAL:BARIUM                                SAMPLE NO.:TC4

PH= 3.25                                    VIAL WEIGHT= 14.06 GRAMS

LIQUID DILUTION: .5                         VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .636                        DRY WEIGHT= 2.5 GRAMS

NO.  INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT    WEIGHT    VOLUME                           TOTAL      PERCENT
-------------------------------------------------------------------------------
 1   43.500    19.170    24.330      2.032     19.770      7.220     99.970

 2   96.420    20.140    74.050      5.650    167.350     61.120     92.750

 3   45.140    18.960    26.180      0.638      6.680      2.430     31.630

 4   44.460    19.160    24.800      0.016      0.150      0.050     29.200

 5   44.160    18.710    25.450      3.739     38.060     13.900     29.160

 6  130.710    18.710    99.990      1.045     41.790     15.260     15.260

TOTAL METAL= 273.8 MG/KG
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METAL:BARIUM                            SAMPLE NO.:TC5

PH= 3.04                                VIAL WEIGHT= 13.25 GRAMS

LIQUID DILUTION: .1                     VIAL + SEDIMENT WEIGHT= 17.4 GRAMS

SOLID FRACTION= .636                    DRY WEIGHT= 2.63 GRAMS

NO.  INITIAL   FINAL    EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT    WEIGHT   VOLUME                            TOTAL     PERCENT
-----------------------------------------------------------------------------
 1   42.900    18.560   24.340     5.447      50.410     24.460     99.970

 2   95.810    19.610   73.980     3.235      90.990     44.160     75.510

 3   44.610    18.380   26.230     0.463       4.610      2.230     31.350

 4   43.880    18.370   25.000     0.000       0.000      0.000     29.120

 5   43.370    18.460   24.910     3.642      34.490     16.730     29.120

 6  130.460    18.460   99.990     0.672      25.540     12.390     12.390

TOTAL METAL= 206.04 MG/KG
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METAL:BARIUM                            SAMPLE NO.:TC6

PH= 2.97                                VIAL WEIGHT= 13.64 GRAMS

LIQUID DILUTION: .1                     VIAL + SEDIMENT WEIGHT= 17.7 GRAMS

SOLID FRACTION= .636                    DRY WEIGHT= 2.58 GRAMS

NO.  INITIAL   FINAL    EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT    WEIGHT   VOLUME                            TOTAL     PERCENT
-----------------------------------------------------------------------------
 1   43.200    19.050   24.150     3.465      32.430     13.760     99.950

 2   96.300    19.770   74.300     3.696     106.430     45.180     86.200

 3   44.770    18.670   26.090     0.568       5.740      2.430     41.020

 4   44.170    19.050   24.620     0.028       0.260      0.110     38.590

 5   44.050    18.860   25.190     5.797      56.590     24.020     38.490

 6  130.860    18.860  100.000     0.880      34.100     14.470     14.470

TOTAL METAL= 235.55 MG/KG
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METAL:BARIUM                             SAMPLE NO.:TC7

PH= 6.04                                 VIAL WEIGHT= 13.79 GRAMS

LIQUID DILUTION: 1                       VIAL + SEDIMENT WEIGHT= 17.88 GRAMS

SOLID FRACTION= .636                     DRY WEIGHT= 2.6 GRAMS

NO.  INITIAL  FINAL    EXTRACT    MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT   WEIGHT   VOLUME                          TOTAL     PERCENT
-----------------------------------------------------------------------------
 1   43.180   19.010   24.170     1.252     11.630     4.490     99.980

 2   96.260   20.150   73.890     6.133    174.290    67.330     95.490

 3   45.150   18.560   26.590     0.153      1.560     0.600     28.160

 4   44.060   18.940   24.620     0.000      0.000     0.000     27.560

 5   43.940   18.700   25.230     4.629     44.910    17.340     27.560

 6  130.700   18.700  100.000     0.688     26.460    10.220     10.220

TOTAL METAL= 258.85 MG/KG
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METAL:BARIUM                             SAMPLE NO.:TC8

PH= 6.02                                 VIAL WEIGHT= 13.91 GRAMS

LIQUID DILUTION: 1                       VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .636                     DRY WEIGHT= 2.6 GRAMS

NO.  INITIAL  FINAL    EXTRACT    MG/L       MG/KG     PERCENT   CUMULATIVE
     WEIGHT   WEIGHT   VOLUME                          TOTAL     PERCENT
-----------------------------------------------------------------------------
 1   43.300   20.540   22.760     1.528     13.370     5.500     99.980

 2   97.790   20.760   74.780     5.548    159.560    65.630     94.480

 3   45.760   18.710   27.050     0.166      1.720     0.700     28.850

 4   44.210   19.210   24.500     0.000      0.000     0.000     28.150

 5   44.210   18.330   25.880     4.253     42.330    17.410     28.150

 6  130.330   18.330  100.000     0.679     26.110    10.740     10.740

TOTAL METAL= 243.09 MG/KG
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METAL:BARIUM                               SAMPLE NO.:TC9

PH= 8.18                                   VIAL WEIGHT= 13.61 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 17.75 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.63 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    42.750    20.540    22.210     0.000       0.000     0.000     99.980

 2    97.790    20.760    74.780     5.961     169.490    57.310     99.960

 3    45.760    18.710    27.050     0.183       1.880     0.630     42.670

 4    44.210    19.210    24.500     0.000       0.000     0.000     42.040

 5    44.210    18.330    25.880     6.498      63.940    21.620     42.040

 6   130.330    18.330   100.000     1.589      60.410    20.420     20.420

TOTAL METAL= 295.72 MG/KG
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METAL:BARIUM                               SAMPLE NO.:TC10

PH= 7.76                                   VIAL WEIGHT= 14.28 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 18.27 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.53 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                           TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    43.270    20.630    22.630     0.014       0.120     0.030     99.970

 2    97.880    21.230    74.410     5.901     173.550    56.690     99.940

 3    46.230    19.270    26.960     0.150       1.590     0.510     43.250

 4    44.770    19.880    24.400     0.000       0.000     0.000     42.740

 5    44.880    18.750    26.130    10.360     106.990    34.950     42.740

 6   130.750    18.750   100.000     0.604      23.870     7.790      7.790

TOTAL METAL= 306.12 MG/KG
```

METAL:CHROMIUM　　SAMPLE NO.:TC1

PH= 5.12　　VIAL WEIGHT= 13.81 GRAMS

LIQUID DILUTION: 1　　VIAL + SEDIMENT WEIGHT= 17.72 GRAMS

SOLID FRACTION= .636　　DRY WEIGHT= 2.48 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.220	18.720	24.500	0.000	0.000	0.000	99.990
2	95.970	19.880	73.870	0.000	0.000	0.000	99.990
3	44.880	18.470	26.410	0.000	0.000	0.000	99.990
4	43.970	18.560	24.910	0.000	0.000	0.000	99.990
5	43.560	18.350	25.210	0.117	1.180	3.520	99.990
6	130.350	18.350	100.000	0.800	32.250	96.470	96.470

TOTAL METAL= 33.43 MG/KG

METAL:CHROMIUM　　SAMPLE NO.:TC2

PH= 3.23　　VIAL WEIGHT= 14.89 GRAMS

LIQUID DILUTION: 1　　VIAL + SEDIMENT WEIGHT= 18.81 GRAMS

SOLID FRACTION= .636　　DRY WEIGHT= 2.49 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	44.310	18.720	25.590	0.044	0.450	1.080	99.980
2	95.970	19.740	74.000	0.000	0.000	0.000	98.900
3	44.740	18.330	26.410	0.000	0.000	0.000	98.900
4	43.830	18.690	24.640	0.000	0.000	0.000	98.900
5	43.690	18.500	25.190	0.392	3.960	9.570	98.900
6	130.500	18.500	100.000	0.920	36.940	89.330	89.330

TOTAL METAL= 41.35 MG/KG

METAL:CHROMIUM

PH= 2.9

LIQUID DILUTION: .5

SOLID FRACTION= .636

SAMPLE NO.:TC3

VIAL WEIGHT= 13.5 GRAMS

VIAL + SEDIMENT WEIGHT= 17.44 GRAMS

DRY WEIGHT= 2.5 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.940	18.590	24.350	0.152	1.480	4.510	99.980
2	95.840	19.590	74.020	0.000	0.000	0.000	95.480
3	44.590	18.400	26.190	0.000	0.000	0.000	95.480
4	43.900	18.220	25.170	0.000	0.000	0.000	95.480
5	43.220	18.100	25.120	0.192	1.920	5.860	95.480
6	130.100	18.100	100.000	0.734	29.360	89.620	89.620

TOTAL METAL= 32.76 MG/KG

METAL:CHROMIUM

PH= 3.25

LIQUID DILUTION: .5

SOLID FRACTION= .636

SAMPLE NO.:TC4

VIAL WEIGHT= 14.06 GRAMS

VIAL + SEDIMENT WEIGHT= 18 GRAMS

DRY WEIGHT= 2.5 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.500	19.170	24.330	0.000	0.000	0.000	99.990
2	96.420	20.140	74.050	0.000	0.000	0.000	99.990
3	45.140	18.960	26.180	0.000	0.000	0.000	99.990
4	44.460	19.160	24.800	0.000	0.000	0.000	99.990
5	44.160	18.710	25.450	0.187	1.900	5.120	99.990
6	130.710	18.710	99.990	0.879	35.150	94.870	94.870

TOTAL METAL= 37.05 MG/KG

METAL:CHROMIUM
PH= 3.04
LIQUID DILUTION: .1
SOLID FRACTION= .636

SAMPLE NO.:TC5
VIAL WEIGHT= 13.25 GRAMS
VIAL + SEDIMENT WEIGHT= 17.4 GRAMS
DRY WEIGHT= 2.63 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.900	18.560	24.340	0.014	0.120	0.300	99.990
2	95.810	19.610	73.980	0.000	0.000	0.000	99.690
3	44.610	18.380	26.230	0.000	0.000	0.000	99.690
4	43.880	18.370	25.000	0.000	0.000	0.000	99.690
5	43.370	18.460	24.910	0.378	3.580	9.050	99.690
6	130.460	18.460	99.990	0.943	35.850	90.640	90.640

TOTAL METAL= 39.55 MG/KG

METAL:CHROMIUM
PH= 2.97
LIQUID DILUTION: .1
SOLID FRACTION= .636

SAMPLE NO.:TC6
VIAL WEIGHT= 13.64 GRAMS
VIAL + SEDIMENT WEIGHT= 17.7 GRAMS
DRY WEIGHT= 2.58 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.200	19.050	24.150	0.052	0.480	1.160	99.990
2	96.300	19.770	74.300	0.000	0.000	0.000	98.830
3	44.770	18.670	26.090	0.000	0.000	0.000	98.830
4	44.170	19.050	24.620	0.000	0.000	0.000	98.830
5	44.050	18.860	25.190	0.114	1.110	2.690	98.830
6	130.860	18.860	100.000	1.023	39.650	96.140	96.140

TOTAL METAL= 41.24 MG/KG

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METAL:CHROMIUM                             SAMPLE NO.:TC7

PH= 6.04                                   VIAL WEIGHT= 13.79 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 17.88 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.6 GRAMS

NO.   INITIAL   FINAL     EXTRACT    MG/L        MG/KG       PERCENT    CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
-------------------------------------------------------------------------------------
 1    43.180    19.010    24.170     0.000       0.000       0.000      100.000

 2    96.260    20.150    73.890     0.000       0.000       0.000      100.000

 3    45.150    18.560    26.590     0.000       0.000       0.000      100.000

 4    44.060    18.940    24.620     0.000       0.000       0.000      100.000

 5    43.940    18.700    25.230     0.000       0.000       0.000      100.000

 6   130.700    18.700   100.000     0.855      32.880     100.000      100.000

TOTAL METAL= 32.88 MG/KG
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METAL:CHROMIUM                             SAMPLE NO.:TC8

PH= 6.02                                   VIAL WEIGHT= 13.91 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.6 GRAMS

NO.   INITIAL   FINAL     EXTRACT    MG/L        MG/KG       PERCENT    CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL      PERCENT
-------------------------------------------------------------------------------------
 1    43.300    19.070    24.230     0.000       0.000       0.000       99.990

 2    96.320    20.170    73.930     0.000       0.000       0.000       99.990

 3    45.170    18.480    26.690     0.000       0.000       0.000       99.990

 4    43.980    19.180    24.310     0.000       0.000       0.000       99.990

 5    44.180    18.310    25.870     0.454       4.510      11.190       99.990

 6   130.310    18.310   100.000     0.930      35.760      88.800       88.800

TOTAL METAL= 40.27 MG/KG
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METAL:CHROMIUM

PH= 8.18

LIQUID DILUTION: 1

SOLID FRACTION= .636

SAMPLE NO.:TC9

VIAL WEIGHT= 13.61 GRAMS

VIAL + SEDIMENT WEIGHT= 17.75 GRAMS

DRY WEIGHT= 2.63 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.750	20.540	22.210	0.045	0.380	0.830	99.980
2	97.790	20.760	74.780	0.000	0.000	0.000	99.150
3	45.760	18.710	27.050	0.418	4.290	9.430	99.150
4	44.210	19.210	24.500	0.000	0.000	0.000	89.720
5	44.210	18.330	25.880	0.250	2.460	5.400	89.720
6	130.330	18.330	100.000	1.009	38.360	84.320	84.320

TOTAL METAL= 45.49 MG/KG

METAL:CHROMIUM

PH= 7.76

LIQUID DILUTION: 1

SOLID FRACTION= .636

SAMPLE NO.:TC10

VIAL WEIGHT= 14.28 GRAMS

VIAL + SEDIMENT WEIGHT= 18.27 GRAMS

DRY WEIGHT= 2.53 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.270	20.630	22.630	0.000	0.000	0.000	99.990
2	97.860	21.230	74.410	0.000	0.000	0.000	99.990
3	46.230	19.270	26.960	0.129	1.370	2.990	99.990
4	44.770	19.880	24.400	0.000	0.000	0.000	97.000
5	44.880	18.750	26.130	0.134	1.380	3.010	97.000
6	130.750	18.750	100.000	1.089	43.040	93.990	93.990

TOTAL METAL= 45.79 MG/KG

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METAL:LEAD                                 SAMPLE NO.:TC1

PH= 5.12                                   VIAL WEIGHT= 13.81 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 17.72 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.48 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL      PERCENT
---------------------------------------------------------------------------------
 1   43.220    18.720    24.500      0.000      0.000       0.000     99.980

 2   95.970    19.880    73.870      0.000      0.000       0.000     99.980

 3   44.880    18.470    26.410      0.004      0.040       0.220     99.980

 4   43.970    18.560    24.910      0.026      0.260       1.470     99.760

 5   43.560    18.350    25.210      1.110     11.280      63.870     98.290

 6  130.350    18.350   100.000      0.151      6.080      34.420     34.420

TOTAL METAL= 17.66 MG/KG
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METAL:LEAD                                 SAMPLE NO.:TC2

PH= 3.23                                   VIAL WEIGHT= 14.89 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 18.81 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.49 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L       MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                            TOTAL      PERCENT
---------------------------------------------------------------------------------
 1   44.310    18.720    25.590      0.000      0.000       0.000     99.980

 2   95.970    19.740    74.000      0.162      4.810      31.720     99.980

 3   44.740    18.330    26.410      0.000      0.000       0.000     68.260

 4   43.830    18.690    24.640      0.000      0.000       0.000     68.260

 5   43.690    18.500    25.190      0.568      5.740      37.860     68.260

 6  130.500    18.500   100.000      0.115      4.610      30.400     30.400

TOTAL METAL= 15.16 MG/KG
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METAL:LEAD                                  SAMPLE NO.:TC3

PH= 2.9                                     VIAL WEIGHT= 13.5 GRAMS

LIQUID DILUTION: .5                         VIAL + SEDIMENT WEIGHT= 17.44 GRAMS

SOLID FRACTION= .636                        DRY WEIGHT= 2.5 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L      MG/KG     PERCENT    CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                          TOTAL      PERCENT
------------------------------------------------------------------------------
 1    42.940    18.590     24.350     0.220     2.140      9.260     99.980

 2    95.840    19.590     74.020     0.287     6.490     36.760     90.720

 3    44.590    18.400     26.190     0.000     0.000      0.000     53.960

 4    43.900    18.220     25.170     0.000     0.000      0.000     53.960

 5    43.220    18.100     25.120     0.708     7.110     30.790     53.960

 6   130.100    18.100    100.000     0.134     5.350     23.170     23.170

TOTAL METAL= 23.09 MG/KG
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METAL:LEAD                                  SAMPLE NO.:TC4

PH= 3.25                                    VIAL WEIGHT= 14.06 GRAMS

LIQUID DILUTION: .5                         VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .636                        DRY WEIGHT= 2.5 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L      MG/KG     PERCENT    CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                          TOTAL      PERCENT
------------------------------------------------------------------------------
 1    43.500    19.170     24.330     0.147     1.430      5.860     99.980

 2    96.420    20.140     74.050     0.275     8.140     33.360     94.120

 3    45.140    18.960     26.180     0.010     0.100      0.400     60.760

 4    44.460    19.160     24.800     0.024     0.230      0.940     60.360

 5    44.160    18.710     25.450     0.821     8.350     34.220     59.420

 6   130.710    18.710     99.990     0.154     6.150     25.200     25.200

TOTAL METAL= 24.4 MG/KG
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METAL:LEAD                               SAMPLE NO.:TC5

PH= 3.04                                 VIAL WEIGHT= 13.25 GRAMS

LIQUID DILUTION: .1                      VIAL + SEDIMENT WEIGHT= 17.4 GRAMS

SOLID FRACTION= .636                     DRY WEIGHT= 2.63 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    42.900    18.560    24.340      0.238       2.200       8.670    99.970

 2    95.810    19.610    73.980      0.302       8.490      33.490    91.300

 3    44.610    18.380    26.230      0.000       0.000       0.000    57.810

 4    43.880    18.370    25.000      0.015       0.140       0.550    57.810

 5    43.370    18.460    24.910      0.920       8.710      34.350    57.260

 6   130.460    18.460    99.990      0.153       5.810      22.910    22.910

TOTAL METAL= 25.35 MG/KG
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METAL:LEAD                               SAMPLE NO.:TC6

PH= 2.97                                 VIAL WEIGHT= 13.64 GRAMS

LIQUID DILUTION: .1                      VIAL + SEDIMENT WEIGHT= 17.7 GRAMS

SOLID FRACTION= .636                     DRY WEIGHT= 2.58 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG      PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    43.200    19.050    24.150      0.332       3.100      10.710    99.990

 2    96.300    19.770    74.300      0.396      11.400      39.390    89.280

 3    44.770    18.670    26.090      0.000       0.000       0.000    49.890

 4    44.170    19.050    24.620      0.000       0.000       0.000    49.890

 5    44.050    18.860    25.190      0.829       8.090      27.950    49.890

 6   130.860    18.860   100.000      0.164       6.350      21.940    21.940

TOTAL METAL= 28.94 MG/KG
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METAL:LEAD                                 SAMPLE NO.:TC7

PH= 6.04                                   VIAL WEIGHT= 13.79 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 17.88 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.6 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    43.180    19.010    24.170     0.000       0.000      0.000     99.990

 2    96.260    20.150    73.890     0.000       0.000      0.000     99.990

 3    45.150    18.560    26.590     0.000       0.000      0.000     99.990

 4    44.060    18.940    24.620     0.067       0.630      3.110     99.990

 5    43.940    18.700    25.230     1.384      13.430     66.450     96.880

 6   130.700    18.700   100.000     0.160       6.150     30.430     30.430

TOTAL METAL= 20.21 MG/KG
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METAL:LEAD                                 SAMPLE NO.:TC8

PH= 6.02                                   VIAL WEIGHT= 13.91 GRAMS

LIQUID DILUTION: 1                         VIAL + SEDIMENT WEIGHT= 18 GRAMS

SOLID FRACTION= .636                       DRY WEIGHT= 2.6 GRAMS

NO.   INITIAL   FINAL     EXTRACT     MG/L        MG/KG     PERCENT   CUMULATIVE
      WEIGHT    WEIGHT    VOLUME                             TOTAL     PERCENT
-------------------------------------------------------------------------------
 1    43.300    19.070    24.230     0.106       0.980      4.750     99.970

 2    96.320    20.170    73.930     0.000       0.000      0.000     95.220

 3    45.170    18.480    26.690     0.008       0.080      0.380     95.220

 4    43.960    19.180    24.310     0.056       0.520      2.520     94.840

 5    44.180    18.310    25.870     1.226      12.190     59.140     92.320

 6   130.310    18.310   100.000     0.178       6.840     33.180     33.180

TOTAL METAL= 20.61 MG/KG
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METAL:LEAD

PH= 8.18

LIQUID DILUTION: 1

SOLID FRACTION= .636

SAMPLE NO.:TC9

VIAL WEIGHT= 13.61 GRAMS

VIAL + SEDIMENT WEIGHT= 17.75 GRAMS

DRY WEIGHT= 2.63 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	42.750	20.540	22.210	0.026	0.230	0.890	99.980
2	97.790	20.760	74.780	0.000	0.000	0.000	99.090
3	45.760	18.710	27.050	0.000	0.000	0.000	99.090
4	44.210	19.210	24.500	0.059	0.540	2.110	99.090
5	44.210	18.330	25.880	1.625	15.990	62.500	96.980
6	130.330	18.330	100.000	0.232	8.820	34.480	34.480

TOTAL METAL= 25.58 MG/KG

METAL:LEAD

PH= 7.76

LIQUID DILUTION: 1

SOLID FRACTION= .636

SAMPLE NO.:TC10

VIAL WEIGHT= 14.28 GRAMS

VIAL + SEDIMENT WEIGHT= 18.27 GRAMS

DRY WEIGHT= 2.53 GRAMS

NO.	INITIAL WEIGHT	FINAL WEIGHT	EXTRACT VOLUME	MG/L	MG/KG	PERCENT TOTAL	CUMULATIVE PERCENT
1	43.270	20.630	22.630	0.022	0.190	0.940	99.970
2	97.880	21.230	74.410	0.000	0.000	0.000	99.030
3	46.230	19.270	26.960	0.000	0.000	0.000	99.030
4	44.770	19.860	24.400	0.025	0.240	1.190	99.030
5	44.880	18.750	26.130	1.040	10.740	53.530	97.840
6	130.750	18.750	100.000	0.225	8.890	44.310	44.310

TOTAL METAL= 20.06 MG/KG

APPENDIX B

RAW DATA FOR STABILIZATION EXPERIMENTS

Sample	As (μg/l)	Ba (mg/l)		Cr (mg/l)		Pb (mg/l)		Zn (mg/l)	
	1 wk	1 wk	5 wk	1 wk	5 wk	1 wk	5 wk	1 wk	5 wk
Distilled H_2O	4.68	0	0.07	0	0	0	0	0.09	0.08
Distilled H_2O	--	--	0.02	--	0.04	--	0	--	0.01
100% Flyash (FA)	1,031.0	7.56	15.36	2.46	--	0.17	--	2.05	--
100% Flyash	641.4	13.29	7.46	2.90	3.64	0	0.25	2.13	3.13
100% TS	16.12	1.14	0.58	1.50	1.60	0.74	0.80	2.44	2.65
100% TS	16.42	0.61	0.55	1.45	1.80	0.84	0.97	2.46	2.95
90% TS/10% FA	110.2	2.27	0.85	1.52	1.59	0.54	0.40	2.42	2.52
90% TS/10% FA	--	--	0.88	--	1.66	--	0.58	--	2.98
70% TS/30% FA	233.8	--	4.78	2.00	1.87	0.20	0.38	2.42	2.35
70% TS/30% FA	298.8	6.83	4.84	2.16	1.91	0.22	0.42	2.14	2.39
100% TC	20.66	2.90	1.21	0	0.03	0	0.10	1.25	0.72
100% TC	9.00	2.01	1.55	0.14	0.06	0	0.10	1.20	0.95
90% TC/10% FA	40.04	0.97	1.05	0.29	0.25	0	0.25	0.92	1.25
90% TC/10% FA	83.52	1.16	1.65	0.31	0.28	0	0.02	0.90	0.99
80% TC/20% FA	394.0	2.44	2.55	0.63	0.57	0	0.14	1.15	1.55

Sample	As (μg/l)	Ba (mg/l)		Cr (mg/l)		Pb (mg/l)		Zn (mg/l)	
	1 wk	1 wk	5 wk	1 wk	5 wk	1 wk	5 wk	1 wk	5 wk
80% TC/20% FA	159.0	4.37	3.88	0.87	0.54	0.14	0.13	1.24	1.37
70% TC/30% FA	682.2	--	--	1.04	0.73	0.01	0.12	1.40	1.25
70% TC/30% FA	298.8	--	4.07	0.99	0.97	0.06	0.17	1.63	1.46
100% JS	7.84	0.97	1.11	0.25	0.21	0	0.04	0.44	0.37
100% JS	1.24	0.72	1.28	0.17	0.23	0	0.06	0.36	0.29
90% JS/10% FA	64.76	1.80	1.81	0.37	0.38	0	0.01	0.62	0.56
90% JS/10% FA	60.40	1.56	2.16	0.47	0.40	0	0.07	0.60	0.59
70% JS/30% FA	180.2	3.55	0.86	1.16	1.02	0.01	0.15	1.07	1.19
70% JS/30% FA	159.8	3.12	1.57	0.96	0.91	0	0.21	0.95	1.10