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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

[Signatures]

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.
ACKNOWLEDGEMENT

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<td>Percent of Sequentially Extracted Barium from Drilling Mud TS after Equilibrating at the Indicated pH</td>
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CHEMICAL SPECIATION AND FLYASH STABILIZATION OF ARSENIC, BARIUM, CHROMIUM, AND LEAD IN DRILLING FLUID WASTES

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)

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>CLAY-BASE MUD</th>
<th>POLYMER MUD</th>
<th>OIL MUD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>200 to 340</td>
<td>300 to 345</td>
<td>150 to 230</td>
</tr>
<tr>
<td>Bentonite</td>
<td>15 to 30</td>
<td>0 to 10</td>
<td>35 to 50</td>
</tr>
<tr>
<td>Lignite</td>
<td>1 to 6</td>
<td>10 to 100</td>
<td>15 to 25</td>
</tr>
<tr>
<td>Lignosulfonate</td>
<td>2 to 10</td>
<td>0.1 to 0.3</td>
<td>5 to 20</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>0.5 to 1.5</td>
<td>0.5 to 5</td>
<td>0 to 10</td>
</tr>
<tr>
<td>Barite</td>
<td>0 to 500</td>
<td>0.1 to 0.5</td>
<td>2 to 4</td>
</tr>
</tbody>
</table>

-7-
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, chromium-lignosulfonates, 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)

<table>
<thead>
<tr>
<th>Usage</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkalinity, pH control</td>
<td>lime, caustic soda, bicarbonate of soda</td>
</tr>
<tr>
<td>bactericides</td>
<td>paraformaldehyde, caustic soda, lime, starch preservatives</td>
</tr>
<tr>
<td>calcium removers</td>
<td>caustic soda, soda ash, bicarbonate of soda, polyphosphates</td>
</tr>
<tr>
<td>corrosion inhibitors</td>
<td>hydrated lime, amine salts</td>
</tr>
<tr>
<td>defoamers</td>
<td>not listed</td>
</tr>
<tr>
<td>emulsifiers</td>
<td>modified lignosulfonates, certain surface active agents, anionic, non ionic products</td>
</tr>
<tr>
<td>filtrate reducers</td>
<td>bentonite clays, CMC (sodium carboxymethyl cellulose), pre-gelatinized starch</td>
</tr>
<tr>
<td>flocculants</td>
<td>salt and/or brine, hydrated lime, gypsum, sodium tetraphosphates</td>
</tr>
<tr>
<td>foaming agents</td>
<td>not listed</td>
</tr>
<tr>
<td>lost circulation materials</td>
<td>not listed</td>
</tr>
<tr>
<td>shale control inhibitors</td>
<td>gypsum, sodium silicate, calcium, lignosulfonates, lime, salt</td>
</tr>
<tr>
<td>lubricants</td>
<td>certain oils, graphite powder, soaps</td>
</tr>
<tr>
<td>surface active agents</td>
<td>not listed</td>
</tr>
<tr>
<td>thinners, dispersants</td>
<td>tannins, various polyphosphates lignite materials</td>
</tr>
<tr>
<td>viscosifiers</td>
<td>bentonite, CMC, attapulgite, clays, sub-bentonites</td>
</tr>
<tr>
<td>weighting materials</td>
<td>barite, lead compounds, iron oxides</td>
</tr>
</tbody>
</table>
Table 3: Typical Oklahoma Mud Systems (Oklahoma Corporation Commission, 1983)

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

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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)

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum Value</th>
<th>Maximum Value</th>
<th>Mean</th>
<th>Median</th>
<th>Standard Deviation</th>
<th>OCC Screen Analysis Potential (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (mg/kg)</td>
<td>7090</td>
<td>42000</td>
<td>21474</td>
<td>22500</td>
<td>8706</td>
<td>--</td>
</tr>
<tr>
<td>Chromium (mg/kg)</td>
<td>2</td>
<td>264</td>
<td>58</td>
<td>36</td>
<td>64</td>
<td>100</td>
</tr>
<tr>
<td>Arsenic (mg/kg)</td>
<td>4.3</td>
<td>41.2</td>
<td>18.2</td>
<td>15</td>
<td>10.4</td>
<td>100</td>
</tr>
<tr>
<td>Barium (mg/kg)</td>
<td>18</td>
<td>19970</td>
<td>3789</td>
<td>1124</td>
<td>5924</td>
<td>2000</td>
</tr>
<tr>
<td>Lead (mg/kg)</td>
<td>5</td>
<td>281</td>
<td>76.9</td>
<td>52</td>
<td>71.5</td>
<td>100</td>
</tr>
<tr>
<td>Zinc (mg/kg)</td>
<td>0</td>
<td>880</td>
<td>134</td>
<td>95</td>
<td>158</td>
<td>--</td>
</tr>
<tr>
<td>Cadmium (mg/kg)</td>
<td>0</td>
<td>0.5</td>
<td>0.06</td>
<td>0</td>
<td>0.13</td>
<td>20</td>
</tr>
<tr>
<td>Calcium (mg/kg)</td>
<td>280</td>
<td>93400</td>
<td>28380</td>
<td>28500</td>
<td>21220</td>
<td>--</td>
</tr>
<tr>
<td>Magnesium (mg/kg)</td>
<td>399</td>
<td>16030</td>
<td>5248</td>
<td>5488</td>
<td>3560</td>
<td>--</td>
</tr>
<tr>
<td>Sodium (mg/kg)</td>
<td>74</td>
<td>32400</td>
<td>5214</td>
<td>3750</td>
<td>6482</td>
<td>--</td>
</tr>
</tbody>
</table>
### Table 6: Comparison of Average Metal Concentrations in Pit Sediment and Aqueous Phases (Canter, et al., 1984b)

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

*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)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum Value</th>
<th>Maximum Value</th>
<th>Mean Value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (mg/l)</td>
<td>0.00</td>
<td>55.4</td>
<td>8.2</td>
<td>18.3</td>
</tr>
<tr>
<td>Chromium (mg/l)</td>
<td>0.00</td>
<td>2.91</td>
<td>0.48</td>
<td>0.82</td>
</tr>
<tr>
<td>Arsenic (µg/l)</td>
<td>0.00</td>
<td>6.00</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Barium (mg/l)</td>
<td>0.00</td>
<td>3.3</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Lead (mg/l)</td>
<td>0.00</td>
<td>0.14</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Zinc (mg/l)</td>
<td>0.00</td>
<td>5.15</td>
<td>0.54</td>
<td>1.41</td>
</tr>
<tr>
<td>Cadmium (mg/l)</td>
<td>0.000</td>
<td>0.009</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>Calcium (mg/l)</td>
<td>31</td>
<td>1061</td>
<td>254</td>
<td>278</td>
</tr>
<tr>
<td>Magnesium (mg/l)</td>
<td>4.5</td>
<td>116.9</td>
<td>30.5</td>
<td>33.3</td>
</tr>
<tr>
<td>Sodium (mg/l)</td>
<td>7</td>
<td>3451</td>
<td>982</td>
<td>882</td>
</tr>
</tbody>
</table>
Table 8: Statistical Analyses of Extraction Procedure Results (Canter, et al., 1984b)

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Geochemical Classification&lt;sup&gt;a&lt;/sup&gt;</th>
<th>µg g&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Element</th>
<th>Geochemical Classification&lt;sup&gt;b&lt;/sup&gt;</th>
<th>µg g&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>At, Bi, Li</td>
<td>466,000</td>
<td>Hf</td>
<td>Li</td>
<td>5</td>
</tr>
<tr>
<td>Si</td>
<td>Li</td>
<td>277,200</td>
<td>Dy</td>
<td>Li</td>
<td>5</td>
</tr>
<tr>
<td>Al</td>
<td>Li</td>
<td>81,300</td>
<td>Sn</td>
<td>Si</td>
<td>3</td>
</tr>
<tr>
<td>Fe</td>
<td>Ch, Si</td>
<td>50,000</td>
<td>B</td>
<td>Li</td>
<td>3</td>
</tr>
<tr>
<td>Ca</td>
<td>Li</td>
<td>36,300</td>
<td>Yb</td>
<td>Li</td>
<td>3</td>
</tr>
<tr>
<td>Na</td>
<td>Li</td>
<td>28,300</td>
<td>Er</td>
<td>Li</td>
<td>3</td>
</tr>
<tr>
<td>K</td>
<td>Li</td>
<td>25,900</td>
<td>Br</td>
<td>Li</td>
<td>3</td>
</tr>
<tr>
<td>Mg</td>
<td>Li</td>
<td>20,900</td>
<td>Ge</td>
<td>Si</td>
<td>2</td>
</tr>
<tr>
<td>Ti</td>
<td>Li</td>
<td>4,400</td>
<td>Be</td>
<td>Li</td>
<td>2</td>
</tr>
<tr>
<td>H</td>
<td>At, Bi, Li</td>
<td>1,400</td>
<td>As</td>
<td>Ch</td>
<td>2</td>
</tr>
<tr>
<td>P</td>
<td>Bi, Li, Si</td>
<td>1,180</td>
<td>U</td>
<td>Li</td>
<td>2</td>
</tr>
<tr>
<td>Mn</td>
<td>Li</td>
<td>1,000</td>
<td>Ta</td>
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</tr>
<tr>
<td>F</td>
<td>Li</td>
<td>700</td>
<td>W</td>
<td>Li</td>
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</tr>
<tr>
<td>S</td>
<td>Ch</td>
<td>520</td>
<td>Mo</td>
<td>Si</td>
<td>1</td>
</tr>
<tr>
<td>Sr</td>
<td>Li</td>
<td>450</td>
<td>Cs</td>
<td>Li</td>
<td>1</td>
</tr>
<tr>
<td>Ba</td>
<td>Li</td>
<td>400</td>
<td>Ho</td>
<td>Li</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>At, Bi, Li, Si</td>
<td>320</td>
<td>Eu</td>
<td>Li</td>
<td>1</td>
</tr>
<tr>
<td>Cl</td>
<td>Li</td>
<td>200</td>
<td>Tl</td>
<td>Ch</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>Li</td>
<td>200</td>
<td>Tb</td>
<td>Li</td>
<td>0.9</td>
</tr>
<tr>
<td>Zr</td>
<td>Li</td>
<td>160</td>
<td>Lu</td>
<td>Li</td>
<td>0.8</td>
</tr>
<tr>
<td>Rb</td>
<td>Li</td>
<td>120</td>
<td>Hg</td>
<td>At, Ch</td>
<td>0.5</td>
</tr>
<tr>
<td>V</td>
<td>Li</td>
<td>110</td>
<td>I</td>
<td>At, Li</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni</td>
<td>Si</td>
<td>80</td>
<td>Sb</td>
<td>Ch</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>Ch</td>
<td>65</td>
<td>Bi</td>
<td>Ch</td>
<td>0.2</td>
</tr>
<tr>
<td>N</td>
<td>At, Bi</td>
<td>46</td>
<td>Tm</td>
<td>Li</td>
<td>0.2</td>
</tr>
<tr>
<td>Ce</td>
<td>Li</td>
<td>46</td>
<td>Cd</td>
<td>Ch</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>Ch</td>
<td>45</td>
<td>Ag</td>
<td>Ch</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Table 9: (continued)

<table>
<thead>
<tr>
<th>Element</th>
<th>Geochemical Classification</th>
<th>µg g(^{-1})</th>
<th>Element</th>
<th>Geochemical Classification</th>
<th>µg g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Li</td>
<td>49</td>
<td>In</td>
<td>Ch</td>
<td>0.1</td>
</tr>
<tr>
<td>Li</td>
<td>Li</td>
<td>30</td>
<td>Se</td>
<td>Ch</td>
<td>0.09</td>
</tr>
<tr>
<td>Nd</td>
<td>Li</td>
<td>24</td>
<td>A</td>
<td>At</td>
<td>0.04</td>
</tr>
<tr>
<td>Nb</td>
<td>Li</td>
<td>24</td>
<td>Pd</td>
<td>Si</td>
<td>0.01</td>
</tr>
<tr>
<td>Co</td>
<td>Si</td>
<td>23</td>
<td>Pt</td>
<td>Si</td>
<td>0.005</td>
</tr>
<tr>
<td>La</td>
<td>Li</td>
<td>18</td>
<td>Au</td>
<td>Si</td>
<td>0.005</td>
</tr>
<tr>
<td>Pb</td>
<td>Ch</td>
<td>16</td>
<td>He</td>
<td>At</td>
<td>0.003</td>
</tr>
<tr>
<td>Ga</td>
<td>Ch, Li</td>
<td>15</td>
<td>Te</td>
<td>Ch</td>
<td>0.002</td>
</tr>
<tr>
<td>Th</td>
<td>Li</td>
<td>7</td>
<td>Rh</td>
<td>Si</td>
<td>0.001</td>
</tr>
<tr>
<td>Sm</td>
<td>Li</td>
<td>7</td>
<td>Re</td>
<td>Si</td>
<td>0.001</td>
</tr>
<tr>
<td>Gd</td>
<td>Li</td>
<td>6</td>
<td>Ir</td>
<td>Si</td>
<td>0.001</td>
</tr>
<tr>
<td>Pr</td>
<td>Li</td>
<td>6</td>
<td>Os</td>
<td>Si</td>
<td>0.001</td>
</tr>
<tr>
<td>Sc</td>
<td>Li</td>
<td>5</td>
<td>Ru</td>
<td>Si</td>
<td>0.001</td>
</tr>
</tbody>
</table>

\(^a\)Omitting those present in less than 0.001 µg g\(^{-1}\); Ne, Kr, Xe and the short-lived radioactive elements.

\(^b\)At = Atmosophile: 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)

<table>
<thead>
<tr>
<th>Name of Separate</th>
<th>Size Range (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td>Silt</td>
<td>0.002-0.02</td>
</tr>
<tr>
<td>Fine Sand</td>
<td>0.02-0.2</td>
</tr>
<tr>
<td>Coarse Sand</td>
<td>0.2-2.0</td>
</tr>
<tr>
<td>Gravel</td>
<td>&gt; 2.0</td>
</tr>
</tbody>
</table>
Table 11: Characteristics of Soil Organic Fractions Extracted from a Wide Range of Soil Types (Includes the Range of Values Measured) (Schnitzer, 1972)

<table>
<thead>
<tr>
<th></th>
<th>Humic Acids</th>
<th>Fulvic Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element (%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>56.2 ± 2.6</td>
<td>45.7 ± 5.0</td>
</tr>
<tr>
<td>H</td>
<td>4.7 ± 1.5</td>
<td>5.4 ± 1.6</td>
</tr>
<tr>
<td>N</td>
<td>3.2 ± 2.4</td>
<td>2.1 ± 1.2</td>
</tr>
<tr>
<td>S</td>
<td>0.8 ± 0.7</td>
<td>1.9 ± 1.8</td>
</tr>
<tr>
<td>O</td>
<td>35.5 ± 2.8</td>
<td>44.8 ± 5.1</td>
</tr>
<tr>
<td><strong>Functional Groups (meq/g)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total acidity</td>
<td>6.7 ± 1.1</td>
<td>10.3 ± 3.9</td>
</tr>
<tr>
<td>CO₂H</td>
<td>3.6 ± 2.1</td>
<td>8.2 ± 3.0</td>
</tr>
<tr>
<td>Phenolic OH</td>
<td>3.9 ± 1.8</td>
<td>3.0 ± 2.7</td>
</tr>
<tr>
<td>Alcoholic OH</td>
<td>2.6 ± 2.4</td>
<td>6.1 ± 3.4</td>
</tr>
<tr>
<td>Quinonoid C = O</td>
<td>2.9 ± 2.8</td>
<td>2.7 ± 1.5</td>
</tr>
<tr>
<td>ketonic C = O</td>
<td>0.6 ± 0.3</td>
<td>0.8 ± 0.5</td>
</tr>
<tr>
<td>OCH₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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):

\[
M_T = M^{z+} + \sum_{i=1}^{c} a(M_aL_i^b) + \sum_{i,j=1}^{c,(m-1)} (MM_j^i'L_i^l) + \sum_{i,k=1}^{c,(c-1)} (ML_i^lL'_k)
\]

\[
M_T = \text{Total concentration of a metal},
\]

\[
M^{z+} = \text{free ion concentration with valence } z+,
\]

\[
M_aL_i^b = \text{conc. of complex involving a metal with } i\text{th ligand},
\]

\[
c \text{ and } m = \text{total number of ligands and metals, respectively.}
\]

\[
a \text{ and } b = \text{stoichiometric coefficients},
\]

\[
MM_j^i'L_i^l = \text{concentration of mixed metal complex involving metal } M, \text{ } j\text{th metal and } i\text{th ligand, and}
\]

\[
ML_i^lL'_k = \text{concentration of mixed ligand complex, involving metal } M, \text{ } ith \text{ ligand and } kth \text{ ligand.}
\]
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, $M^{3+}$:

$$
\begin{align*}
M^{3+} + MOH^{2+} &\rightleftharpoons M(OH)_2^+ \rightleftharpoons M(OH)_3^0 \rightleftharpoons M(OH)_4^- \rightleftharpoons M(OH)_5^{2-} \ldots \\
&\vdots \\
M_2(OH)_2^{4+} &\rightarrow (M(OH)_3 \cdot nH_2O) \text{ solid} \\
M_p(OH)_q^{(3p-q)+} &\rightarrow (M_2O_3 \cdot mH_2O) \text{ solid}
\end{align*}
$$

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
\( (Cr) = 10^{-4} \text{ M} \) (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)

<table>
<thead>
<tr>
<th>Total Concentration ( C_{T,x} ) M</th>
<th>Complex Species</th>
<th>Log Formation Constant</th>
<th>NTA = 10^{-7} M</th>
<th>NTA = 3 \times 10^{-6} M</th>
<th>NTA = 2 \times 10^{-4} M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II) = 2 \times 10^{-6}</td>
<td>CuNTA^-</td>
<td>13</td>
<td>4</td>
<td>82</td>
<td>100</td>
</tr>
<tr>
<td>Pb(II) = 3 \times 10^{-7}</td>
<td>PbNTA^-</td>
<td>11.8</td>
<td>2</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>Ni(II) = 10^{-7}</td>
<td>NiNTA^-</td>
<td>11.3</td>
<td>1</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Fe(III) = 2 \times 10^{-6}</td>
<td>{Fe(OH)NTA^-}</td>
<td>10.9; 3.1</td>
<td>0.4</td>
<td>34</td>
<td>100</td>
</tr>
<tr>
<td>Zn(II) = 1.5 \times 10^{-6}</td>
<td>ZnNTA^-</td>
<td>10.4</td>
<td>0.2</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>H = 10^{-8}</td>
<td>HNTA^2^-</td>
<td>10.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mn(II) = 2 \times 10^{-6}</td>
<td>MnNTA^-</td>
<td>7.4</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Ca(II) = 10^{-3}</td>
<td>CaNTA^-</td>
<td>6.4</td>
<td>0</td>
<td>&lt;0.1</td>
<td>17</td>
</tr>
<tr>
<td>Mg(II) = 2.5 \times 10^{-4}</td>
<td>MgNTA^-</td>
<td>5.4</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Sr(II) = 2 \times 10^{-6}</td>
<td>SrNTA^-</td>
<td>5.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ba(II) = 1.5 \times 10^{-7}</td>
<td>BaNTA^-</td>
<td>4.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na(I) = 5 \times 10^{-4}</td>
<td>NaNTA^2^-</td>
<td>2.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
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

-37-
### Table 13: Formation Constants of Various Metal Ion Fulvic Acid Complexes (Ionic Strength = 0.1 M) (Snoeyink and Jenkins, 1980)

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>pH of Measurement</th>
<th>Log K for Metal Ion-Fulvic Acid Complex&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1.7</td>
<td>6.1</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>2.35</td>
<td>3.7</td>
</tr>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>3.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>3.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Co&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Pb&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>3.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>3.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>3.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

<sup>a</sup>Formation constants, K, are for the reaction $M + \text{fulvic acid} \rightarrow M \cdot \text{fulvic acid}$
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)

<table>
<thead>
<tr>
<th>Element</th>
<th>Common Range for Soils (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1 - 50</td>
</tr>
<tr>
<td>Ba</td>
<td>100 - 3000</td>
</tr>
<tr>
<td>Cr</td>
<td>1 - 100</td>
</tr>
<tr>
<td>Pb</td>
<td>2 - 200</td>
</tr>
</tbody>
</table>
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 constituents (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., KNO₃) 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>
<thead>
<tr>
<th>Reference</th>
<th>Form*</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tessler, et al. (1979)</td>
<td>Exchangeable</td>
<td>MgCl₂</td>
</tr>
<tr>
<td></td>
<td>Carbonate</td>
<td>NaOAc</td>
</tr>
<tr>
<td></td>
<td>Fe–Mn Oxides</td>
<td>NH₂OH•HCl</td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td>H₂O₂/HNO₃</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>HF–HClO₄</td>
</tr>
<tr>
<td>Stover, et al. (1976)</td>
<td>Exchangeable</td>
<td>KNO₃</td>
</tr>
<tr>
<td></td>
<td>Adsorbed</td>
<td>KF</td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td>Na₂P₂O₇</td>
</tr>
<tr>
<td></td>
<td>Carbonate</td>
<td>EDTA</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>HNO₃</td>
</tr>
<tr>
<td>Emmerich (1980)</td>
<td>Exchangeable</td>
<td>KNO₃</td>
</tr>
<tr>
<td></td>
<td>Adsorbed</td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td>NaOH</td>
</tr>
<tr>
<td></td>
<td>Carbonate</td>
<td>Na₂EDTA</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>HNO₃</td>
</tr>
<tr>
<td>Brannon, et al. (1976)</td>
<td>Exchangeable</td>
<td>NH₄OAc</td>
</tr>
<tr>
<td></td>
<td>Easily Reduced</td>
<td>NH₄OH•HCl</td>
</tr>
<tr>
<td></td>
<td>Organic Sulfide</td>
<td>H₂O₂</td>
</tr>
<tr>
<td></td>
<td>Moderately Reducible</td>
<td>Na₂S₂O₄</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>HF–HNO₃</td>
</tr>
</tbody>
</table>
Table 15: (continued)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Form*</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forstner, et al. (1981)</td>
<td>Exchangeable</td>
<td>NH$_4$OAc</td>
</tr>
<tr>
<td></td>
<td>Easily Reduced</td>
<td>NH$_2$OH·HCl</td>
</tr>
<tr>
<td></td>
<td>Moderately Reducible</td>
<td>NH$_4$ Oxalate/ Oxalic Acid</td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td>H$_2$O$_2$/HNO$_3$</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>HNO$_3$</td>
</tr>
</tbody>
</table>

*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, H₂O has replaced KF and NaOH has replaced Na₂P₂O₇ as extraction reagents.

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

**Exchanged.** The KNO₃ 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⁻, A1OH₂⁻, and A1OH⁻ 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
envisioned 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):

\[ \sigma_o + \sigma_s + \sigma_d = 0 \]

\[ \sigma_o = \text{surface charge density,} \]
Figure 6: Distribution of Charge, Ions, and Potential at a Solid Solution Interface (Stumm and Morgan, 1981)
\( \sigma_s \) = stern layer charge density, and
\( \sigma_d \) = 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 \( \text{Si}^{4+} \), but is occasionally \( \text{Al}^{3+} \), and an octahedron of six oxygens or hydroxides around a larger cation which is usually \( \text{Al}^{3+} \). 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 \( \text{Al}^{3+} \). 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 \( \text{Al}^{3+} \) or \( \text{Si}^{4+} \). 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)

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m²/g)</th>
<th>Exchange Capacity (meq/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>10 - 50</td>
<td>3 - 15</td>
</tr>
<tr>
<td>Illite</td>
<td>30 - 80</td>
<td>10 - 40</td>
</tr>
<tr>
<td>Chlorite</td>
<td>--</td>
<td>20 - 50</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>50 - 150</td>
<td>80 - 120</td>
</tr>
</tbody>
</table>
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 H₂O 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 strong 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 CaCO₃ has been found to enhance the precipitation of heavy metal carbonates of low solubility, such as PbCO₃ (Forstner and Wittmann, 1979). The solubility of PbCO₃ is apparent when examining solubility products (Table 17).

**Residual.** Residual forms for metals are extracted with 4.0 M HNO₃. 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)

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>$-\log K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCO$_3$</td>
<td>10.2</td>
</tr>
<tr>
<td>CdCO$_3$</td>
<td>11.3</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>10.5</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>13.1</td>
</tr>
<tr>
<td>CoCO$_3$</td>
<td>12.8</td>
</tr>
<tr>
<td>ZnCO$_3$</td>
<td>10.8</td>
</tr>
<tr>
<td>NiCO$_3$</td>
<td>6.9</td>
</tr>
<tr>
<td>CuCO$_3$</td>
<td>9.6</td>
</tr>
<tr>
<td>Cu$_2$(OH)$_2$CO$_3$</td>
<td>33.8</td>
</tr>
</tbody>
</table>
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)

<table>
<thead>
<tr>
<th>Hydroxides</th>
<th>-log K⁺</th>
<th>Sulfide</th>
<th>-log K_{sp}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(OH)₂</td>
<td>14.4</td>
<td>CdS</td>
<td>27.8</td>
</tr>
<tr>
<td>Fe(OH)₂</td>
<td>15.1</td>
<td>FeS</td>
<td>17.2</td>
</tr>
<tr>
<td>PbO+H₂O</td>
<td>15.3</td>
<td>PbS</td>
<td>27.5</td>
</tr>
<tr>
<td>Zn(OH)₂</td>
<td>15.5</td>
<td>ZnS</td>
<td>21.6</td>
</tr>
<tr>
<td>Ni(OH)₂</td>
<td>14.7</td>
<td>NiS</td>
<td>18.5</td>
</tr>
<tr>
<td>HgO+H₂O</td>
<td>25.4</td>
<td>HgS</td>
<td>52.4</td>
</tr>
<tr>
<td>Cr(OH)₂</td>
<td>37.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>39.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 19: Trace Element Sinks and Their Respective Uptake and Release Processes (Jenne and Luoma, 1975)

<table>
<thead>
<tr>
<th>Sinks</th>
<th>Processes</th>
<th>Reaction Parameter*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides (hydrous and (amorphic)</td>
<td>Surface exchange</td>
<td>$K_{eq}$</td>
</tr>
<tr>
<td></td>
<td>Diffusion exchange</td>
<td>$K_{eq}$, $R_{ex}$</td>
</tr>
<tr>
<td></td>
<td>Co-Precipitation</td>
<td>$P$, $R_{ppt}$</td>
</tr>
<tr>
<td>Organic substances</td>
<td>Exchange</td>
<td>$K_{eq}$</td>
</tr>
<tr>
<td></td>
<td>Complexation</td>
<td>$K_{eq}$</td>
</tr>
<tr>
<td></td>
<td>Chelation</td>
<td>$K_{eq}$</td>
</tr>
<tr>
<td>Biota</td>
<td>&quot;Passive&quot; uptake</td>
<td>$R_{gr}$</td>
</tr>
<tr>
<td></td>
<td>Exchange, complexation, chelation</td>
<td>$K_{eq}$</td>
</tr>
<tr>
<td></td>
<td>&quot;Active&quot; uptake</td>
<td>$K_{eq}$</td>
</tr>
<tr>
<td>Carbonates, phosphates sulfides, sulfate and chloride salts</td>
<td>Precipitation</td>
<td>$R_{ppt}$</td>
</tr>
<tr>
<td></td>
<td>Co-Precipitation</td>
<td>$P$</td>
</tr>
<tr>
<td></td>
<td>Surface exchange</td>
<td>$K_{eq}$</td>
</tr>
</tbody>
</table>

*$K_{eq}$ = 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 (BaSO₄) 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⁻, AsO₂OH₂⁻, and AsO₃⁻. Polymeric species may include As₂(OH)₇⁻, As₂(OH)₈₂⁻, and As₃(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

-72-
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) \((\text{As})_t=10^{-5}\text{M}, (\text{S})_t=10^{-3}\text{M}, \text{and } (\text{Ba})_t=2.2 \times 10^{-7}\text{M}\)
precipitates. Arsenic was found to be distributed among operationally defined fractions of sediment solids in the order of abundance $\text{OH}^-$ (Fe and Al) $> \text{oxalate (amorphous or occluded)}$ $> \text{Cl}^-$ (exchangeable) $> \text{H}^+$ (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 ($\text{HCrO}_4^-\text{/CrO}_4^{2-}$) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) (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) \((\text{CO}_3)_t = 10^{-3}\)
Figure 20: Eh-pH Diagram for the System Chromium-Water at 25°C in Solutions Containing Chlorides (Cr) = 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 \((\text{CH}_3)_2\text{Pb}^{2+}\) 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 \((\text{PbCO}_3)\), hydroxide \((\text{Pb(OH)}_2)\), and hydroxy-carbonate \((\text{Pb(OH)}_2(\text{CO}_3)_2)\). 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 \(\text{Pb}^{2+}\) or \(\text{PbCl}^+\), 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-\(\text{pH}\) Diagram for Lead in Solutions Containing Sulfates and Carbonates (Garrels 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 $4 \times 10^{-4}$ 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)

<table>
<thead>
<tr>
<th>Physical:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area cm²/gm</td>
<td>4007.2</td>
</tr>
<tr>
<td>Mean Particle Diameter Size</td>
<td>5.65 micron</td>
</tr>
<tr>
<td>Percent Retained on 325 Mesh</td>
<td>8.08</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.65</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Mineralogical:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>23%</td>
</tr>
<tr>
<td>Hematite</td>
<td>9%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35.5%</td>
</tr>
<tr>
<td>CaO</td>
<td>30.0%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.1%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.7%</td>
</tr>
<tr>
<td>MgO</td>
<td>4.5%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.8%</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.1%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.1%</td>
</tr>
<tr>
<td>As</td>
<td>20.0 ppm</td>
</tr>
<tr>
<td>Ba</td>
<td>5400.0 ppm</td>
</tr>
<tr>
<td>B</td>
<td>210.0 ppm</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 20.0 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>210.0 ppm</td>
</tr>
<tr>
<td>Cr</td>
<td>470.0 ppm</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; 40.0 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>550.0 ppm</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt; 2.5 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>140.0 ppm</td>
</tr>
<tr>
<td>Se</td>
<td>60.0 ppm</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt; 150.0 ppm</td>
</tr>
<tr>
<td>Zn</td>
<td>170.0 ppm</td>
</tr>
</tbody>
</table>
Table 21: Mean Values of Metals Present in Drilling Fluids (Canter, et al., 1984b)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Mean Value (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>18.2</td>
</tr>
<tr>
<td>Barium</td>
<td>3789</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.06</td>
</tr>
<tr>
<td>Calcium</td>
<td>28380</td>
</tr>
<tr>
<td>Chromium</td>
<td>58</td>
</tr>
<tr>
<td>Iron</td>
<td>21474</td>
</tr>
<tr>
<td>Lead</td>
<td>76.9</td>
</tr>
<tr>
<td>Magnesium</td>
<td>5248</td>
</tr>
<tr>
<td>Sodium</td>
<td>5214</td>
</tr>
<tr>
<td>Zinc</td>
<td>134</td>
</tr>
</tbody>
</table>
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 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>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Ion specific electrode</td>
<td>Standard Methods¹, pp. 402-409</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Wheatstone bridge; conductance cell</td>
<td>Standard Methods, pp. 70-73</td>
</tr>
<tr>
<td>Chloride</td>
<td>Ion specific electrode</td>
<td>Orion Research Inc.², pp. 1-26</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>Electrometric titration; glass electrode</td>
<td>Standard Methods, pp. 253-257</td>
</tr>
<tr>
<td>Salinity</td>
<td>Electrical Conductivity</td>
<td>Standard Methods, pp. 99-106</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>Gravimetric</td>
<td>Standard Methods, pp. 93-94</td>
</tr>
<tr>
<td>Total Solids</td>
<td>Gravimetric</td>
<td>Standard Methods, pp. 92-93</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>Stannous chloride; colorimetric</td>
<td>Standard Methods, pp. 409-421</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Turbidimetric</td>
<td>Standard Methods, pp. 439-440</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Brucine; colorimetric</td>
<td>U.S. EPA³ (1979), pp. 352.1-1 to 352.1-3</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>Combustion-Infrared</td>
<td>Standard Methods, pp. 471-475</td>
</tr>
<tr>
<td>Chemical Oxygen Demand</td>
<td>Colorimetric; microdigestion</td>
<td>Hach Chemical Co.⁴, pp. A2-A3</td>
</tr>
</tbody>
</table>
Table 22: (continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>Atomic Absorption Spectrophotometry</td>
<td>U.S. EPA (1982)(^5), 7420</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Atomic Absorption Spectrophotometry</td>
<td>U.S. EPA (1982), 7060</td>
</tr>
<tr>
<td>Chromium</td>
<td>Atomic Absorption Spectrophotometry</td>
<td>U.S. EPA (1982), 7190</td>
</tr>
<tr>
<td>Barium</td>
<td>Atomic Absorption Spectrophotometry</td>
<td>U.S. EPA (1982), 7080</td>
</tr>
<tr>
<td>Zinc</td>
<td>Atomic Absorption Spectrophotometry</td>
<td>U.S. EPA (1982), 7950</td>
</tr>
<tr>
<td>Strontium</td>
<td>Atomic Absorption Spectrophotometry</td>
<td>Standard Methods, pp. 234-236</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Atomic Absorption Spectrophotometry</td>
<td>U.S. EPA (1982), 7130</td>
</tr>
</tbody>
</table>


\(^2\)Orion Research Incorporated, Chloride-Specific Ion Electrode Instruction Sheet, 840 Memorial Drive, Cambridge, Massachusetts, 02139, 1979.

Table 22: (continued)


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

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Solid (180°C)</th>
<th>% Volatile Solids (550°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JS</td>
<td>41.2</td>
<td>4.3</td>
</tr>
<tr>
<td>TS</td>
<td>41.3</td>
<td>7.5</td>
</tr>
<tr>
<td>TC</td>
<td>60.6</td>
<td>3.7</td>
</tr>
</tbody>
</table>
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)

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Concentration of Extractant (M)</th>
<th>Density (g/ml)</th>
<th>Equilibrating Time on Shaker (hours)</th>
<th>Designated Chemical Form Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃</td>
<td>0.5</td>
<td>1.03</td>
<td>16</td>
<td>Exchangeable</td>
</tr>
<tr>
<td>X-H₂O²</td>
<td>55.5</td>
<td>1.00</td>
<td>2</td>
<td>Adsorbed</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.5</td>
<td>1.02</td>
<td>16</td>
<td>Organically Bound</td>
</tr>
<tr>
<td>Na₂-EDTA</td>
<td>0.05</td>
<td>1.00</td>
<td>6</td>
<td>Carbonate</td>
</tr>
<tr>
<td>HNO₃ (70-80°C)</td>
<td>4.0</td>
<td>1.12</td>
<td>16³</td>
<td>Residual</td>
</tr>
</tbody>
</table>

¹The 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.

²Ion exchange water, extracted three times.

³Extracted 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$_2$EDTA 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Solid (180°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flyash</td>
<td>99.9</td>
</tr>
<tr>
<td>JS</td>
<td>11.5</td>
</tr>
<tr>
<td>TS</td>
<td>17.6</td>
</tr>
<tr>
<td>TC</td>
<td>26.5</td>
</tr>
</tbody>
</table>
Table 26: Drilling Fluid-Flyash Stabilization Experiments

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Description</th>
<th>Duration of Experiment (wk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI-A</td>
<td>Deionized H₂O Blank</td>
<td>1</td>
</tr>
<tr>
<td>FA-A</td>
<td>Flyash Control</td>
<td>1</td>
</tr>
<tr>
<td>TS-A</td>
<td>TS Control</td>
<td>1</td>
</tr>
<tr>
<td>TS10-A</td>
<td>TS + 10% Flyash</td>
<td>1</td>
</tr>
<tr>
<td>TS30-A</td>
<td>TS + 30% Flyash</td>
<td>1</td>
</tr>
<tr>
<td>TC-A</td>
<td>TC Control</td>
<td>1</td>
</tr>
<tr>
<td>TC10-A</td>
<td>TC + 10% Flyash</td>
<td>1</td>
</tr>
<tr>
<td>TC20-A</td>
<td>TC + 20% Flyash</td>
<td>1</td>
</tr>
<tr>
<td>TC30-A</td>
<td>TC + 30% Flyash</td>
<td>1</td>
</tr>
<tr>
<td>JS-A</td>
<td>JS Control</td>
<td>1</td>
</tr>
<tr>
<td>JS10-A</td>
<td>JS + 10% Flyash</td>
<td>1</td>
</tr>
<tr>
<td>JS30-A</td>
<td>JS + 30% Flyash</td>
<td>1</td>
</tr>
<tr>
<td>DI-B</td>
<td>Deionized H₂O Blank</td>
<td>5</td>
</tr>
<tr>
<td>FA-B</td>
<td>Flyash Control</td>
<td>5</td>
</tr>
<tr>
<td>TS-B</td>
<td>TS Control</td>
<td>5</td>
</tr>
<tr>
<td>TS10-B</td>
<td>TS + 10% Flyash</td>
<td>5</td>
</tr>
<tr>
<td>TS20-B</td>
<td>TS + 20% Flyash</td>
<td>5</td>
</tr>
<tr>
<td>TC-B</td>
<td>TC Control</td>
<td>5</td>
</tr>
<tr>
<td>TC10-B</td>
<td>TC + 10% Flyash</td>
<td>5</td>
</tr>
<tr>
<td>TC20-B</td>
<td>TC + 20% Flyash</td>
<td>5</td>
</tr>
<tr>
<td>TC30-B</td>
<td>TC + 30% Flyash</td>
<td>5</td>
</tr>
<tr>
<td>JS-B</td>
<td>JS Control</td>
<td>5</td>
</tr>
<tr>
<td>JS10-B</td>
<td>JS + 10% Flyash</td>
<td>5</td>
</tr>
<tr>
<td>JS30-B</td>
<td>JS + 30% Flyash</td>
<td>5</td>
</tr>
</tbody>
</table>
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 H\textsubscript{3}NO\textsubscript{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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>JS</th>
<th>TS</th>
<th>TC</th>
<th>OCC Discharge Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (Std. units)</td>
<td>7.45</td>
<td>7.53</td>
<td>11.30</td>
<td>6.5-8.5</td>
</tr>
<tr>
<td>Conductivity (μmhos/cm)</td>
<td>3550</td>
<td>4000</td>
<td>6300</td>
<td>2300</td>
</tr>
<tr>
<td>Salinity (%)</td>
<td>3.5</td>
<td>3.0</td>
<td>6.2</td>
<td>--</td>
</tr>
<tr>
<td>Alkalinity to pH 8.3 (mg CaCO₃/l)</td>
<td>0</td>
<td>0</td>
<td>213</td>
<td>--</td>
</tr>
<tr>
<td>Alkalinity to pH 4.5 (mg CaCO₃/l)</td>
<td>372</td>
<td>300</td>
<td>255</td>
<td>--</td>
</tr>
<tr>
<td>Nitrate (mg/l)</td>
<td>0.02</td>
<td>ND (0.01)</td>
<td>ND (0.01)</td>
<td>10</td>
</tr>
<tr>
<td>Chloride (mg/l)</td>
<td>1680</td>
<td>2880</td>
<td>2900</td>
<td>1500</td>
</tr>
<tr>
<td>Total Phosphate (mg P/l)</td>
<td>0.840</td>
<td>--</td>
<td>0.054</td>
<td>0.2</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>115</td>
<td>640</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>TOC (mg/l)</td>
<td>44</td>
<td>231</td>
<td>37</td>
<td>--</td>
</tr>
<tr>
<td>Sulfate (mg/l)</td>
<td>520</td>
<td>420</td>
<td>237</td>
<td>--</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>4064</td>
<td>4526</td>
<td>5982</td>
<td>1500</td>
</tr>
<tr>
<td>Iron (mg/l)</td>
<td>7.50</td>
<td>2.29</td>
<td>18.9</td>
<td>--</td>
</tr>
<tr>
<td>Chromium (mg/l)</td>
<td>0.50</td>
<td>2.2</td>
<td>0.11</td>
<td>0.2</td>
</tr>
<tr>
<td>Arsenic (mg/l)</td>
<td>0.0049</td>
<td>0.0132</td>
<td>0.0122</td>
<td>0.2</td>
</tr>
<tr>
<td>Barium (mg/l)</td>
<td>0.81</td>
<td>6.0</td>
<td>0.52</td>
<td>5.0</td>
</tr>
<tr>
<td>Lead (mg/l)</td>
<td>0.08</td>
<td>1.80</td>
<td>0.03</td>
<td>0.1</td>
</tr>
<tr>
<td>Zinc (mg/l)</td>
<td>ND (0.001)</td>
<td>0.040</td>
<td>0.910</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Table 27: (continued)

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

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

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

-123-
Table 30: Percent Total Solids and Volatile Solids in the Solid Portion of Drilling Fluid Wastes Used in Laboratory Experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Total Solid (180°C)</th>
<th>% Volatile Solids (550°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JS</td>
<td>33.0</td>
<td>5.7</td>
</tr>
<tr>
<td>TS</td>
<td>45.0</td>
<td>7.5</td>
</tr>
<tr>
<td>TC</td>
<td>63.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Table 31: Amounts of Acid Required to Obtain the Desired pH During Equilibration Studies

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Solid Wt.</th>
<th>Final pH</th>
<th>ml of 4 M HNO₃</th>
<th>Moles HNO₃ kg Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>JS</td>
<td>1.32</td>
<td>6.9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.32</td>
<td>6.5</td>
<td>0.24</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>1.32</td>
<td>3.6</td>
<td>0.30</td>
<td>0.91</td>
</tr>
<tr>
<td>TS</td>
<td>1.85</td>
<td>11.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.85</td>
<td>6.2</td>
<td>1.38</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>1.85</td>
<td>4.1</td>
<td>1.60</td>
<td>3.56</td>
</tr>
<tr>
<td>TC</td>
<td>2.58</td>
<td>8.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2.60</td>
<td>6.0</td>
<td>0.30</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>2.48</td>
<td>4.8</td>
<td>0.50</td>
<td>0.81</td>
</tr>
</tbody>
</table>
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

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

*Standard deviation of measurements on 10 different samples.
Table 33: Percent Standard Deviation within Experiments for Each Metal and Fluid

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

*Standard deviation of measurements on 10 different samples.*

-128-
Table 34: Percent Arsenic Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (%)</th>
<th>Extractant</th>
<th>KNO₃ (%)</th>
<th>H₂O (%)</th>
<th>NaOH (%)</th>
<th>EDTA (%)</th>
<th>HNO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid JS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>0.3</td>
<td>0.1</td>
<td>1.4</td>
<td>1.8</td>
<td>0.6</td>
<td>95.6</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>0.5</td>
<td>&lt; 0.1</td>
<td>1.3</td>
<td>0.2</td>
<td>17.7</td>
<td>80.3</td>
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</tr>
<tr>
<td>3.6</td>
<td>0.9</td>
<td>3.1</td>
<td>1.0</td>
<td>2.6</td>
<td>1.1</td>
<td>91.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid TS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.8</td>
<td>0.4</td>
<td>0.4</td>
<td>0.1</td>
<td>1.6</td>
<td>9.3</td>
<td>88.2</td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>1.0</td>
<td>2.3</td>
<td>2.5</td>
<td>38.1</td>
<td>3.7</td>
<td>52.0</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>1.7</td>
<td>1.9</td>
<td>1.0</td>
<td>44.4</td>
<td>4.3</td>
<td>46.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid TC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>2.2</td>
<td>1.3</td>
<td>0.3</td>
<td>3.1</td>
<td>0.2</td>
<td>92.8</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>&lt; 0.1</td>
<td>1.3</td>
<td>0.3</td>
<td>3.3</td>
<td>0.1</td>
<td>95.0</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>1.3</td>
<td>2.1</td>
<td>0.3</td>
<td>23.8</td>
<td>13.8</td>
<td>58.7</td>
<td></td>
</tr>
</tbody>
</table>
Table 35: Concentration of Arsenic Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (μg/l)</th>
<th>KNO₃ (μg/kg)</th>
<th>H₂O (μg/kg)</th>
<th>NaOH (μg/kg)</th>
<th>EDTA (μg/kg)</th>
<th>HNO₃ (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>3.3</td>
<td>27.1</td>
<td>256</td>
<td>339</td>
<td>112</td>
<td>17300</td>
</tr>
<tr>
<td>6.5</td>
<td>4.8</td>
<td>&lt;0.1</td>
<td>229</td>
<td>32.9</td>
<td>3560</td>
<td>16100</td>
</tr>
<tr>
<td>3.6</td>
<td>6.9</td>
<td>454</td>
<td>154</td>
<td>397</td>
<td>170</td>
<td>13700</td>
</tr>
</tbody>
</table>

Drilling Fluid JS

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (μg/l)</th>
<th>KNO₃ (μg/kg)</th>
<th>H₂O (μg/kg)</th>
<th>NaOH (μg/kg)</th>
<th>EDTA (μg/kg)</th>
<th>HNO₃ (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.8</td>
<td>13.9</td>
<td>153</td>
<td>48.7</td>
<td>588</td>
<td>3510</td>
<td>33400</td>
</tr>
<tr>
<td>6.2</td>
<td>13.6</td>
<td>412</td>
<td>448</td>
<td>6770</td>
<td>664</td>
<td>9190</td>
</tr>
<tr>
<td>4.1</td>
<td>21.6</td>
<td>325</td>
<td>176</td>
<td>7650</td>
<td>756</td>
<td>8130</td>
</tr>
</tbody>
</table>

Drilling Fluid TS

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (μg/l)</th>
<th>KNO₃ (μg/kg)</th>
<th>H₂O (μg/kg)</th>
<th>NaOH (μg/kg)</th>
<th>EDTA (μg/kg)</th>
<th>HNO₃ (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>46.7</td>
<td>244</td>
<td>64.9</td>
<td>563</td>
<td>30.7</td>
<td>17000</td>
</tr>
<tr>
<td>6.0</td>
<td>&lt;0.1</td>
<td>228</td>
<td>44.5</td>
<td>570</td>
<td>28.7</td>
<td>16400</td>
</tr>
<tr>
<td>4.8</td>
<td>8.9</td>
<td>141</td>
<td>18.6</td>
<td>1270</td>
<td>606</td>
<td>3760</td>
</tr>
</tbody>
</table>

Drilling Fluid TC
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

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (%)</th>
<th>Extractant</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KNO₃ (%)</td>
<td>H₂O (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>0.2</td>
<td>5.3</td>
<td>1.0</td>
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<tr>
<td>6.5</td>
<td>2.4</td>
<td>7.4</td>
<td>1.7</td>
</tr>
<tr>
<td>3.6</td>
<td>2.2</td>
<td>8.9</td>
<td>2.6</td>
</tr>
<tr>
<td>11.8</td>
<td>0.6</td>
<td>2.4</td>
<td>0.3</td>
</tr>
<tr>
<td>6.2</td>
<td>1.3</td>
<td>3.5</td>
<td>0.8</td>
</tr>
<tr>
<td>4.1</td>
<td>0.5</td>
<td>2.2</td>
<td>0.8</td>
</tr>
<tr>
<td>8.0</td>
<td>&lt; 0.1</td>
<td>57.0</td>
<td>0.6</td>
</tr>
<tr>
<td>6.0</td>
<td>5.0</td>
<td>66.3</td>
<td>0.7</td>
</tr>
<tr>
<td>4.8</td>
<td>5.1</td>
<td>72.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Table 37: Concentration of Barium Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (mg/l)</th>
<th>Extractant</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KNO₃ (mg/kg)</td>
<td>H₂O (mg/kg)</td>
<td>NaOH (mg/kg)</td>
<td>EDTA (mg/kg)</td>
<td>HNO₃ (mg/kg)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
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</tr>
</tbody>
</table>

**Drilling Fluid JS**

<table>
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<tr>
<th>pH</th>
<th>Aqueous Phase (mg/l)</th>
<th>Extractant</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>0.4</td>
<td>238</td>
<td>45.3</td>
<td>99.1</td>
<td>932</td>
<td>3250</td>
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<tr>
<td>6.5</td>
<td>4.8</td>
<td>286</td>
<td>66.3</td>
<td>60.8</td>
<td>670</td>
<td>2790</td>
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<tr>
<td>3.6</td>
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<td>294</td>
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<td>648</td>
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**Drilling Fluid TS**

<table>
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<th>Aqueous Phase (mg/l)</th>
<th>Extractant</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>11.8</td>
<td>1.7</td>
<td>81.2</td>
<td>11.8</td>
<td>60.0</td>
<td>152</td>
<td>3120</td>
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</tr>
<tr>
<td>6.2</td>
<td>3.9</td>
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<td>34.0</td>
<td>20.3</td>
<td>1430</td>
<td>3030</td>
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</tr>
<tr>
<td>4.1</td>
<td>1.2</td>
<td>79.2</td>
<td>29.5</td>
<td>26.4</td>
<td>3180</td>
<td>340</td>
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</tbody>
</table>

**Drilling Fluid TC**

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (mg/l)</th>
<th>Extractant</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>&lt; 0.1</td>
<td>172</td>
<td>1.7</td>
<td>&lt; 0.1</td>
<td>85.5</td>
<td>42.1</td>
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</tr>
<tr>
<td>6.0</td>
<td>1.4</td>
<td>167</td>
<td>1.6</td>
<td>&lt; 0.1</td>
<td>43.6</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>1.4</td>
<td>174</td>
<td>3.3</td>
<td>0.4</td>
<td>28.6</td>
<td>21.2</td>
<td></td>
</tr>
</tbody>
</table>
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

- AQUEOUS
- EXCHANGED (KNO₃)
- ADSORBED (H₂O)
- ORGANIC (NaOH)
- CARBONATE (Na₂EDTA)
- RESIDUAL (HNO₃)
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

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (%)</th>
<th>KNO₃ (%)</th>
<th>H₂O (%)</th>
<th>NaOH (%)</th>
<th>EDTA (%)</th>
<th>HNO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drilling Fluid JS</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>0.4</td>
<td>&lt; 0.1</td>
<td>3.4</td>
<td>1.6</td>
<td>32.4</td>
<td>62.2</td>
</tr>
<tr>
<td>6.5</td>
<td>0.8</td>
<td>&lt; 0.1</td>
<td>2.7</td>
<td>3.0</td>
<td>28.8</td>
<td>64.7</td>
</tr>
<tr>
<td>3.6</td>
<td>7.4</td>
<td>6.2</td>
<td>2.1</td>
<td>5.8</td>
<td>24.4</td>
<td>54.0</td>
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<td>Drilling Fluid TS</td>
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<td></td>
</tr>
<tr>
<td>11.8</td>
<td>0.9</td>
<td>1.8</td>
<td>&lt; 0.1</td>
<td>0.5</td>
<td>0.7</td>
<td>96.1</td>
</tr>
<tr>
<td>6.2</td>
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<td>0.6</td>
<td>1.1</td>
<td>0.9</td>
<td>5.0</td>
<td>91.8</td>
</tr>
<tr>
<td>4.1</td>
<td>4.1</td>
<td>1.6</td>
<td>0.8</td>
<td>1.2</td>
<td>6.8</td>
<td>85.5</td>
</tr>
<tr>
<td></td>
<td>Drilling Fluid TC</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.4</td>
<td>&lt; 0.1</td>
<td>6.2</td>
<td>&lt; 0.1</td>
<td>4.2</td>
<td>89.2</td>
</tr>
<tr>
<td>6.0</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>5.6</td>
<td>94.4</td>
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<td>4.8</td>
<td>0.5</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>6.5</td>
<td>92.9</td>
</tr>
</tbody>
</table>
Table 39: Concentration of Chromium Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (mg/l)</th>
<th>Extractant</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>KNO₃ (mg/kg)</td>
<td>H₂O (mg/kg)</td>
<td>NaOH (mg/kg)</td>
<td>EDTA (mg/kg)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid JS</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>3.1</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid TS</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid TC</td>
<td>0.3</td>
<td>0.3</td>
<td>6.0</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>11.8</td>
<td>0.3</td>
<td>6.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.2</td>
<td>0.1</td>
<td>1.7</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.1</td>
<td>0.9</td>
<td>5.3</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.0</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
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<td>6.0</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.8</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Chang, et al. (1984)</th>
<th>JS pH=6.9</th>
<th>TS pH=6.2</th>
<th>TC pH=8.0</th>
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<tr>
<td>KNO₃ + H₂O</td>
<td>&lt; 1</td>
<td>3.4</td>
<td>1.7</td>
<td>6.2</td>
</tr>
<tr>
<td>NaOH</td>
<td>3</td>
<td>1.6</td>
<td>0.9</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>EDTA</td>
<td>17</td>
<td>32.4</td>
<td>5.0</td>
<td>4.2</td>
</tr>
<tr>
<td>HNO₃</td>
<td>80</td>
<td>62.2</td>
<td>91.8</td>
<td>89.2</td>
</tr>
</tbody>
</table>
Table 41: Percent Lead Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (%)</th>
<th>KNO₃ (%)</th>
<th>H₂O (%)</th>
<th>NaOH (%)</th>
<th>EDTA (%)</th>
<th>HNO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drillling Fluid JS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>0.6</td>
<td>0.5</td>
<td>5.1</td>
<td>6.6</td>
<td>72.7</td>
<td>14.7</td>
</tr>
<tr>
<td>6.5</td>
<td>0.5</td>
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<td>4.0</td>
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<td>74.8</td>
<td>14.1</td>
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<tr>
<td>3.6</td>
<td>15.8</td>
<td>49.7</td>
<td>2.4</td>
<td>2.3</td>
<td>24.1</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>Drillling Fluid TS</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>11.8</td>
<td>&lt; 0.1</td>
<td>0.4</td>
<td>0.2</td>
<td>2.9</td>
<td>4.2</td>
<td>92.4</td>
</tr>
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<td>6.2</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>1.5</td>
<td>2.7</td>
<td>59.9</td>
<td>35.8</td>
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<td>0.9</td>
<td>1.9</td>
<td>45.8</td>
<td>39.4</td>
</tr>
<tr>
<td></td>
<td>Drillling Fluid TC</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.92</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>1.7</td>
<td>58.0</td>
<td>39.4</td>
</tr>
<tr>
<td>6.0</td>
<td>2.4</td>
<td>&lt; 0.1</td>
<td>0.2</td>
<td>2.8</td>
<td>62.8</td>
<td>31.8</td>
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<tr>
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<td>&lt; 0.1</td>
<td>15.9</td>
<td>0.1</td>
<td>0.7</td>
<td>50.9</td>
<td>64.8</td>
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</table>
Table 42: Concentration of Lead Recovered in Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Aqueous Phase (mg/l)</th>
<th>Extractant</th>
<th>KNO₃ (mg/kg)</th>
<th>H₂O (mg/kg)</th>
<th>NaOH (mg/kg)</th>
<th>EDTA (mg/kg)</th>
<th>HNO₃ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Drilling Fluid JS</td>
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<td></td>
<td></td>
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<td>10.6</td>
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<td>&lt; 0.1</td>
<td>3.0</td>
<td>5.0</td>
<td>55.5</td>
<td>10.5</td>
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</tr>
<tr>
<td>3.6</td>
<td>0.9</td>
<td>56.0</td>
<td>2.7</td>
<td>2.6</td>
<td>26.8</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid TS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.8</td>
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<td>0.8</td>
<td>0.4</td>
<td>6.4</td>
<td>9.2</td>
<td>202</td>
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<td>4.4</td>
<td>106</td>
<td>92.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drilling Fluid TC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
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<td>&lt; 0.1</td>
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<td>12.8</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>&lt; 0.1</td>
<td>2.4</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>8.5</td>
<td>5.3</td>
<td></td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃ + H₂O</td>
<td>&lt; 1</td>
<td>2.1</td>
<td>8.8</td>
<td>5.6</td>
<td>1.5</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>NaOH</td>
<td>2</td>
<td>5.2</td>
<td>29.1</td>
<td>6.6</td>
<td>2.7</td>
<td>1.7</td>
</tr>
<tr>
<td>EDTA</td>
<td>82</td>
<td>68.6</td>
<td>61.4</td>
<td>72.7</td>
<td>59.9</td>
<td>58.0</td>
</tr>
<tr>
<td>HNO₃</td>
<td>16</td>
<td>23.8</td>
<td>4.4</td>
<td>14.7</td>
<td>35.8</td>
<td>39.4</td>
</tr>
</tbody>
</table>
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.

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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

<table>
<thead>
<tr>
<th>Dilution of Aqueous Phase</th>
<th>pH</th>
<th>Aqueous Phase (%)</th>
<th>Extractant (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KNO₃</td>
<td>H₂O</td>
</tr>
<tr>
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Table 45: Concentration of Arsenic Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

<table>
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<th>Dilution of Aqueous Phase</th>
<th>Aqueous Phase pH</th>
<th>KNO₃ (μg/kg)</th>
<th>H₂O (μg/kg)</th>
<th>NaOH (μg/kg)</th>
<th>EDTA (μg/kg)</th>
<th>HNO₃ (μg/kg)</th>
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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

<table>
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<th>Aqueous Phase pH</th>
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<th>NaOH (%)</th>
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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

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<th>Dilution of Aqueous Phase</th>
<th>pH</th>
<th>Aqueous Phase (mg/l)</th>
<th>KNO₃ (mg/kg)</th>
<th>H₂O (mg/kg)</th>
<th>NaOH (mg/kg)</th>
<th>EDTA (mg/kg)</th>
<th>HNO₃ (mg/kg)</th>
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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

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<th>pH</th>
<th>Extractant</th>
<th>KNO₃ (%)</th>
<th>H₂O (%)</th>
<th>NaOH (%)</th>
<th>EDTA (%)</th>
<th>HNO₃ (%)</th>
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Table 49: Concentration of Chromium Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

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<th>Aqueous Phase pH</th>
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<th>KNO₃ (mg/kg)</th>
<th>H₂O (mg/kg)</th>
<th>NaOH (mg/kg)</th>
<th>EDTA (mg/kg)</th>
<th>HNO₃ (mg/kg)</th>
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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

<table>
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<th>Dilution of Aqueous Phase</th>
<th>pH</th>
<th>Aqueous Phase (%)</th>
<th>Extractant</th>
<th>KNO₃ (%)</th>
<th>H₂O (%)</th>
<th>NaOH (%)</th>
<th>EDTA (%)</th>
<th>HNO₃ (%)</th>
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<td>69.9</td>
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<td>1.0</td>
<td>11.8</td>
<td>&lt; 0.1</td>
<td>0.4</td>
<td>0.2</td>
<td>2.9</td>
<td>4.2</td>
<td>92.4</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>11.9</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>3.0</td>
<td>3.9</td>
<td>92.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>11.9</td>
<td>0.2</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>3.3</td>
<td>6.2</td>
<td>90.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Drilling Fluid TC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.8</td>
<td>&lt; 0.1</td>
<td>15.9</td>
<td>0.1</td>
<td>0.7</td>
<td>50.9</td>
<td>64.8</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3.1</td>
<td>7.6</td>
<td>35.1</td>
<td>0.2</td>
<td>0.5</td>
<td>32.5</td>
<td>24.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3.0</td>
<td>9.7</td>
<td>36.4</td>
<td>&lt; 0.1</td>
<td>0.3</td>
<td>31.1</td>
<td>22.4</td>
</tr>
</tbody>
</table>
Table 51: Concentration of Lead Recovered from the Aqueous Phase and with Each Extractant for Each Drilling Fluid with Varying Strength of Aqueous Phase

<table>
<thead>
<tr>
<th>Dilution of Aqueous Phase</th>
<th>Aqueous Phase pH</th>
<th>Extractant</th>
<th>KNO$_3$ (mg/kg)</th>
<th>H$_2$O (mg/kg)</th>
<th>NaOH (mg/kg)</th>
<th>EDTA (mg/kg)</th>
<th>HNO$_3$ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drilling Fluid JS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>6.5 &lt; 0.1</td>
<td>&lt; 0.1</td>
<td>3.0</td>
<td>5.0</td>
<td>55.5</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>6.3 &lt; 0.1</td>
<td>0.5</td>
<td>3.3</td>
<td>5.5</td>
<td>49.6</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>6.0 &lt; 0.1</td>
<td>2.2</td>
<td>6.2</td>
<td>11.0</td>
<td>69.9</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>Drilling Fluid TS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>11.8 &lt; 0.1</td>
<td>0.8</td>
<td>0.4</td>
<td>6.4</td>
<td>9.2</td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>11.9 &lt; 0.1</td>
<td>0.5</td>
<td>0.4</td>
<td>5.9</td>
<td>7.6</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>11.9 &lt; 0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>6.3</td>
<td>11.8</td>
<td>176</td>
<td></td>
</tr>
<tr>
<td>Drilling Fluid TC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4.8 &lt; 0.1</td>
<td>2.4</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>8.5</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>3.1 &lt; 0.2</td>
<td>8.3</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>7.7</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>3.0 &lt; 0.3</td>
<td>9.9</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>8.4</td>
<td>6.1</td>
<td></td>
</tr>
</tbody>
</table>
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)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent Flyash</th>
<th>Arsenic (µg/l)</th>
<th>Barium (mg/l)</th>
<th>Chromium (mg/l)</th>
<th>Lead (mg/l)</th>
<th>Zinc (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flyash*</td>
<td>100</td>
<td>836.2</td>
<td>10.91</td>
<td>3.074</td>
<td>0.221</td>
<td>2.438</td>
</tr>
<tr>
<td>TS*</td>
<td>0</td>
<td>16.27</td>
<td>0.718</td>
<td>1.586</td>
<td>0.835</td>
<td>2.626</td>
</tr>
<tr>
<td>TC*</td>
<td>0</td>
<td>14.83</td>
<td>1.918</td>
<td>0.058</td>
<td>0.077</td>
<td>1.030</td>
</tr>
<tr>
<td>JS*</td>
<td>0</td>
<td>4.54</td>
<td>1.019</td>
<td>0.216</td>
<td>0.020</td>
<td>0.366</td>
</tr>
</tbody>
</table>

1 Week

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent Flyash</th>
<th>Arsenic (µg/l)</th>
<th>Barium (mg/l)</th>
<th>Chromium (mg/l)</th>
<th>Lead (mg/l)</th>
<th>Zinc (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS**</td>
<td>10</td>
<td>110.2</td>
<td>2.267</td>
<td>1.524</td>
<td>0.538</td>
<td>2.422</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>266.3</td>
<td>6.830</td>
<td>2.080</td>
<td>0.212</td>
<td>2.280</td>
</tr>
<tr>
<td>TC**</td>
<td>10</td>
<td>61.78</td>
<td>1.063</td>
<td>0.301</td>
<td>&lt; 0.001</td>
<td>0.908</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>276.5</td>
<td>3.406</td>
<td>0.751</td>
<td>0.069</td>
<td>1.195</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>490.5</td>
<td>--</td>
<td>1.014</td>
<td>0.036</td>
<td>1.516</td>
</tr>
<tr>
<td>JS**</td>
<td>10</td>
<td>62.58</td>
<td>1.679</td>
<td>0.422</td>
<td>&lt; 0.001</td>
<td>0.610</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>170.0</td>
<td>3.335</td>
<td>1.059</td>
<td>0.005</td>
<td>1.007</td>
</tr>
</tbody>
</table>

5 Weeks

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent Flyash</th>
<th>Arsenic (µg/l)</th>
<th>Barium (mg/l)</th>
<th>Chromium (mg/l)</th>
<th>Lead (mg/l)</th>
<th>Zinc (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS**</td>
<td>10</td>
<td>0.864</td>
<td>1.625</td>
<td>0.490</td>
<td>2.751</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.810</td>
<td>1.890</td>
<td>0.401</td>
<td>2.369</td>
<td></td>
</tr>
<tr>
<td>TC**</td>
<td>10</td>
<td>1.351</td>
<td>0.266</td>
<td>0.132</td>
<td>1.119</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.211</td>
<td>0.533</td>
<td>0.159</td>
<td>1.464</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.070</td>
<td>0.849</td>
<td>0.207</td>
<td>1.356</td>
<td></td>
</tr>
<tr>
<td>JS**</td>
<td>10</td>
<td>1.986</td>
<td>0.390</td>
<td>0.044</td>
<td>0.573</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.217</td>
<td>0.965</td>
<td>0.181</td>
<td>1.149</td>
<td></td>
</tr>
</tbody>
</table>

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 appears 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

<table>
<thead>
<tr>
<th>Metal</th>
<th>TS (mg/kg)</th>
<th>TC (mg/kg)</th>
<th>JS (mg/kg)</th>
<th>Flyash (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (mg/kg)</td>
<td>4.15</td>
<td>30.4</td>
<td>18.6</td>
<td>--</td>
</tr>
<tr>
<td>Barium (mg/kg)</td>
<td>4,060</td>
<td>197</td>
<td>1,730</td>
<td>895</td>
</tr>
<tr>
<td>Chromium (mg/kg)</td>
<td>236</td>
<td>79.6</td>
<td>49.9</td>
<td>81.3</td>
</tr>
<tr>
<td>Lead (mg/kg)</td>
<td>206</td>
<td>24.2</td>
<td>68.2</td>
<td>14.6</td>
</tr>
<tr>
<td>Zinc (mg/kg)</td>
<td>222</td>
<td>169</td>
<td>95</td>
<td>87.0</td>
</tr>
</tbody>
</table>
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 readorsbed 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.

-198-
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.
BIBLIOGRAPHY


Canter, L.W., et al., "Environmental Implications of Off-Site Drilling Mud Pits in Oklahoma", Environmental and Ground Water Institute, University of Oklahoma, Norman, Oklahoma, May 1984b.


Hulse, M. and Jones, M., "Environmental Fate and Effects of Chromium Derived from Drilling Fluids", Environmental Services, IMCO Services Division, Halliburton Company, Houston, Texas, no date.


Sittig, M., Petroleum Transportation and Production; Oil Spill and Pollution Control, Noyes Data Corporation, Park Ridge, New Jersey,
1978, pp. 3-20.


Whitmore, J.C., "Water Based Drilling Mud Land Spreading and Use as a Site Reclamation and Revegetation Medium", A Study for the American Petroleum Institute, Forsgren-Perkins Engineering, Resburg, Pennsylvania, (no date).


APPENDIX A

RAW DATA AND CALCULATION RESULTS FOR PH AND IONIC STRENGTH VARIATION EXPERIMENTS
100 'THIS PROGRAM CALCULATES CONCENTRATIONS AND PERCENTAGES OF METALS IN FRACTIONS OF SEQUENTIALLY EXTRACTED SAMPLES.
110 '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.
120 'THE DENSITIES OF ALL EXTRACTING SOLUTIONS IS ALSO ACCOUNTED FOR IN THE CALCULATIONS.
130 'INPUT HOW MANY METALS WERE ANALYSED.
150 CLS
160 INPUT "NUMBER OF METALS ANALYZED?": NM
170 INPUT "SAMPLE NUMBER?": X
180 PRINT "DILUTION FOR IONIC STRENGTH EXPERIMENTS."
190 INPUT "DILUTION OF LIQUID PHASE USED?": D
200 PRINT "DROPS OF ACID ADDED?": INPUT DA
210 INPUT "DROPS OF ACID CONVERTED TO VOLUME."
215 VA=DA/50: VAINT(VA=100)
220 INPUT INITIAL VIAL WEIGHT.
225 PRINT "EMPTY WEIGHT OF VIAL?": INPUT E
230 SS=0
235 INPUT WEIGHT OF VIAL WITH WET SEDIMENT.
240 PRINT "WEIGHT OF VIAL WITH WET SEDIMENT?": INPUT S
245 SS=S
250 INPUT THE PERCENT SOLID DETERMINED FOR THE SEDIMENT.
255 PRINT "PERCENT SOLID OF SEDIMENT?": INPUT P
260 CALCULATES DRY WEIGHT OF SEDIMENT.
265 DW= SS*P/100: DW=DW/100
270 DIM F'A).WF'A),VF(6) MC(S).MC6),PCF),PT(7)
280 FOR X=1 TO 6
285 NEXT X
290 FOR V=1 TO NM
295 'INPUT NAME OF METAL ANALYZED.
300 PRINT "METAL ANALYZED?": INPUT M
305 MT=0
310 FOR X=1 TO 6
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): M(X)=INTC M(X)*100: M(X)=M(X)/100
335 FOR X=6 TO 1 STEP -1
340 'CALCULATES PERCENT OF TOTAL METAL IN EACH EXTRACTED FRACTION.
345 PC(X)=(M(X)/MT)*100: PC(X)=INTC PC(X)*100: PC(X)=PC(X)/100
350 FOR X=1 TO 6
355 PRINT#2,X;PC(X);VF(X);VF(X)*100;VF(X)=VF(X)*100
360 PRINT#2,MT;PC(1);VF(1);VF(1)*100;VF(1)=VF(1)*100
370 PRINT#2,MT;PC(6);VF(6);VF(6)*100;VF(6)=VF(6)*100
380 NEXT X
390 NEXT Y
400 PRINT "TOTAL METAL=";MT;"MG/KG"
**METAL:** ARSENIC  
**SAMPLE NO.: JS1**

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
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<th>μG/L</th>
<th>μG/KG</th>
<th>PERCENT TOTAL</th>
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**TOTAL METAL:** 19707.22 μG/KG

---

**METAL:** ARSENIC  
**SAMPLE NO.: JS2**

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**TOTAL METAL:** 20407.73 μG/KG
**METAL: ARSENIC**

**SAMPLE NO.: JS3**

**PH = 6.42**

**LIQUID DILUTION: .5**

**SOLID FRACTION = .33**

**VIAL WEIGHT = 14.02 GRAMS**

**VIAL + SEDIMENT WEIGHT = 18.04 GRAMS**

**DRY WEIGHT = 1.32 GRAMS**

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<th>EXTRACT VOLUME</th>
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**TOTAL METAL = 12455.75 μG/KG**

---

**METAL: ARSENIC**

**SAMPLE NO.: JS4**

**PH = 6.11**

**LIQUID DILUTION: .5**

**SOLID FRACTION = .33**

**VIAL WEIGHT = 13.33 GRAMS**

**VIAL + SEDIMENT WEIGHT = 17.37 GRAMS**

**DRY WEIGHT = 1.33 GRAMS**

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>μG/L</th>
<th>μG/KG</th>
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**TOTAL METAL = 20737 μG/KG**

---

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**METAL: ARSENIC**

**SAMPLE NO.: JS5**

**PH = 5.8**

**LIQUID DILUTION: .1**

**SOLID FRACTION: .33**

<table>
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<th>EXTRACT VOLUME</th>
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<th>µG/KG</th>
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TOTAL METAL = 15793.18 µG/KG

---

**METAL: ARSENIC**

**SAMPLE NO.: JS6**

**PH = 6.17**

**LIQUID DILUTION: .1**

**SOLID FRACTION: .33**

<table>
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<td>0.000</td>
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</table>

TOTAL METAL = 20184.28 µG/KG
### Sample JS7

**Metal:** Arsenic  
**pH:** 3.5  
**Liquid Dilution:** 1  
**Solid Fraction:** 0.33  
**Vial Weight:** 13.53 grams  
**Vial + Sediment Weight:** 17.55 grams  
**Dry Weight:** 1.32 grams

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>μg/L</th>
<th>μg/kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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**Total Metal:** 16419.47 μg/kg

---

### Sample JS8

**Metal:** Arsenic  
**pH:** 3.7  
**Liquid Dilution:** 1  
**Solid Fraction:** 0.33  
**Vial Weight:** 13.85 grams  
**Vial + Sediment Weight:** 17.85 grams  
**Dry Weight:** 1.32 grams

<table>
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<th>Extract Volume</th>
<th>μg/L</th>
<th>μg/kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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**Total Metal:** 13595.39 μg/kg

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-213-
METAL: ARSENIC
SAMPLE NO. J59
PH = 6.84
LIQUID DILUTION: 1
SOLID FRACTION = 0.33

<table>
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<th>µg/Kg</th>
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TOTAL METAL = 17638.64 µg/kg

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METAL: ARSENIC
SAMPLE NO. J510
PH = 6.37
LIQUID DILUTION: 1
SOLID FRACTION = 0.33

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<th>µg/Kg</th>
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TOTAL METAL = 18587.22 µg/kg
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<th>EXTRACT VOLUME</th>
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<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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TOTAL METAL= 5762.42 MG/KG

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TOTAL METAL= 4503.6 MG/KG
**METAL: BARIUM**

**SAMPLE NO.: JS7**

PH= 3.5

LIQUID DILUTION: 1

SOLID FRACTION= .33

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TOTAL METAL= 3778.11 MG/KG

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**METAL: BARIUM**

**SAMPLE NO.: JS8**

PH= 3.17

LIQUID DILUTION: 1

SOLID FRACTION= .33

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TOTAL METAL= 2961.56 MG/KG
METAL: BARIUM
SAMPLE NO. :JS9

PH = 6.84
LIQUID DILUTION: 1
SOLID FRACTION= .33

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TOTAL METAL= 4117.38 MG/KG

METAL: BARIUM
SAMPLE NO. :JS10

PH = 6.97
LIQUID DILUTION: 1
SOLID FRACTION= .33

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TOTAL METAL= 5015.34 MG/KG

-219-
**METAL: CHROMIUM**

**SAMPLE NO.: JS1**

**VIAL WEIGHT: 14.14 GRAMS**

**VIAL + SEDIMENT WEIGHT: 16.14 GRAMS**

**DRY WEIGHT: 1.32 GRAMS**

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**TOTAL METAL: 92.98 MG/KG**

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**METAL: CHROMIUM**

**SAMPLE NO.: JS2**

**VIAL WEIGHT: 13.6 GRAMS**

**VIAL + SEDIMENT WEIGHT: 17.61 GRAMS**

**DRY WEIGHT: 1.32 GRAMS**

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</table>

**TOTAL METAL: 86.79 MG/KG**
**METAL: CHROMIUM**

**SAMPLE NO.: J53**

**PH = 6.42**

**VIAL WEIGHT = 14.02 GRAMS**

**LIQUID DILUTION: .5**

**VIAL + SEDIMENT WEIGHT = 16.04 GRAMS**

**SOLID FRACTION = .33**

**DRY WEIGHT = 1.32 GRAMS**

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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<td>0.000</td>
<td>99.980</td>
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<td>17.170</td>
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<td>1.348</td>
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<td>65.070</td>
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</table>

TOTAL METAL = 83.05 MG/KG

---

**METAL: CHROMIUM**

**SAMPLE NO.: J64**

**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**

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
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<td>0.990</td>
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<td>22.690</td>
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<td>95.650</td>
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TOTAL METAL = 89.78 MG/KG
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<th>mg/L</th>
<th>mg/kg</th>
<th>Percent</th>
<th>Total</th>
<th>Cumulative Percent</th>
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<tr>
<td>2</td>
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<td>18.500</td>
<td>64.600</td>
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<td>0.000</td>
<td>0.000</td>
<td>99.970</td>
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<tr>
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<td>66.450</td>
<td>99.970</td>
<td></td>
</tr>
</tbody>
</table>

**Total Metal = 69.49 mg/kg**

---

**Sample No. J55**

METAL: CHROMIUM

PH = 6.17

VIAL WEIGHT = 15.56 Grams

LIQUID DILUTION = 0.1

VIAL + SEDIMENT WEIGHT = 17.64 Grams

SOLID FRACTION = 0.33

DRY WEIGHT = 1.33 Grams

---

**Sample No. J56**

METAL: CHROMIUM

PH = 6.17

VIAL WEIGHT = 13.29 Grams

LIQUID DILUTION = 0.1

VIAL + SEDIMENT WEIGHT = 17.26 Grams

SOLID FRACTION = 0.33

DRY WEIGHT = 1.31 Grams

---

**Total Metal = 86.39 mg/kg**
## Sample No. J57

**Metal: Chromium**

**pH:** 3.5

**Liquid Dilution:** 1

**Solid Fraction:** 0.33

**Vial Weight:** 13.52 grams

**Vial + Sediment Weight:** 17.55 grams

**Dry Weight:** 1.32 grams

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/Kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.750</td>
<td>16.090</td>
<td>25.660</td>
<td>0.187</td>
<td>3.630</td>
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<td>99.960</td>
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<tr>
<td>2</td>
<td>35.340</td>
<td>18.670</td>
<td>74.430</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>100.000</td>
</tr>
<tr>
<td>3</td>
<td>43.670</td>
<td>16.260</td>
<td>25.410</td>
<td>0.062</td>
<td>1.120</td>
<td>1.480</td>
<td>95.450</td>
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<tr>
<td>4</td>
<td>43.760</td>
<td>17.030</td>
<td>26.210</td>
<td>0.241</td>
<td>4.780</td>
<td>5.960</td>
<td>93.970</td>
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<td>5</td>
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<td>17.200</td>
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<td>28.220</td>
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<tr>
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</table>

**Total Metal:** 80.12 mg/kg

## Sample No. J88

**Metal: Chromium**

**pH:** 3.17

**Liquid Dilution:** 1

**Solid Fraction:** 0.33

**Vial Weight:** 13.52 grams

**Vial + Sediment Weight:** 17.85 grams

**Dry Weight:** 1.32 grams

<table>
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<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/Kg</th>
<th>Percent Total</th>
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<td>2</td>
<td>35.680</td>
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<td>43.770</td>
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**Total Metal:** 95.85 mg/kg
### METAL: CHROMIUM

**SAMPLE NO.: JS9**

**PH = 6.64**

**VIAL WEIGHT: 13.99 GRAMS**

**LIQUID DILUTION: 1**

**VIAL + SEDIMENT WEIGHT: 18 GRAMS**

**SOLID FRACTION: .33**

**DRY WEIGHT: 1.32 GRAMS**

<table>
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<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
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</table>

TOTAL METAL = 54.17 MG/KG

---

### METAL: CHROMIUM

**SAMPLE NO.: JS10**

**PH = 6.97**

**VIAL WEIGHT: 14.06 GRAMS**

**VIAL + SEDIMENT WEIGHT: 18.06 GRAMS**

**SOLID FRACTION: .33**

**DRY WEIGHT: 1.32 GRAMS**

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
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<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
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</table>

TOTAL METAL = 51.64 MG/KG

---
**Sample No. JS1**

Metal: Lead

PH: 6.61

Liquid Dilution: 1

Solid Fraction: 0.33

<table>
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<th>No.</th>
<th>Initial Height</th>
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<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/Kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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<td>0.000</td>
<td>0.000</td>
<td>99.480</td>
</tr>
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</tr>
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</table>

Total Metal: 75.81 Mg/kg

**Sample No. JS2**

Metal: Lead

PH: 6.28

Liquid Dilution: 1

Solid Fraction: 0.33

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Height</th>
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<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/Kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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</tr>
<tr>
<td>3</td>
<td>43.370</td>
<td>16.900</td>
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<td>0.157</td>
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<td>4.320</td>
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</tr>
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<td>95.190</td>
</tr>
<tr>
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<td>41.300</td>
<td>16.670</td>
<td>24.430</td>
<td>3.029</td>
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</tr>
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<td>126.870</td>
<td>16.670</td>
<td>100.000</td>
<td>0.125</td>
<td>9.460</td>
<td>13.030</td>
<td>13.030</td>
</tr>
</tbody>
</table>

Total Metal: 72.57 Mg/kg
### Sample JS3

**Metal Lead**

**PH**: 6.42  
**Liquid Dilution**: 0.5  
**Solid Fraction**: 0.33  

<table>
<thead>
<tr>
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<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.920</td>
<td>18.530</td>
<td>25.450</td>
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<td>0.010</td>
<td>99.990</td>
</tr>
<tr>
<td>2</td>
<td>42.920</td>
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<td>26.560</td>
<td>0.325</td>
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<td>4.940</td>
<td>94.990</td>
</tr>
<tr>
<td>3</td>
<td>42.060</td>
<td>17.060</td>
<td>25.290</td>
<td>0.275</td>
<td>4.560</td>
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<td>99.550</td>
</tr>
<tr>
<td>4</td>
<td>42.010</td>
<td>17.010</td>
<td>25.290</td>
<td>0.304</td>
<td>5.760</td>
<td>5.760</td>
<td>95.310</td>
</tr>
<tr>
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<td>0.106</td>
<td>1.690</td>
<td>1.690</td>
<td>13.020</td>
</tr>
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</table>

**Total Metal**: 61.65 MG/KG

---

### Sample JS4

**Metal Lead**

**PH**: 6.11  
**Liquid Dilution**: 0.5  
**Solid Fraction**: 0.33  

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
</thead>
<tbody>
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</table>

**Total Metal**: 74.8 MG/KG
### METAL: LEAD

**SAMPLE NO.: JS5**

**VIAL WEIGHT**: 13.58 GRAMS

**VIAL + SEDIMENT WEIGHT**: 17.64 GRAMS

**DRY WEIGHT**: 1.33 GRAMS

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
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<tbody>
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**TOTAL METAL**: 71.99 MG/KG

---

### METAL: LEAD

**SAMPLE NO.: JS5**

**VIAL WEIGHT**: 13.29 GRAMS

**VIAL + SEDIMENT WEIGHT**: 17.26 GRAMS

**DRY WEIGHT**: 1.31 GRAMS

<table>
<thead>
<tr>
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<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
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<td>95.050</td>
<td>18.170</td>
<td>74.640</td>
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**TOTAL METAL**: 80.38 MG/KG
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<th>Mg/L</th>
<th>Mg/Kg</th>
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<th>Cumulative Percent</th>
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</table>

Total Metal = 101.35 Mg/Kg

**Metal: Lead**

**Sample No.: J57**

**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

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/Kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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<tbody>
<tr>
<td>1</td>
<td>44.050</td>
<td>18.430</td>
<td>25.620</td>
<td>1.055</td>
<td>20.470</td>
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<td>16.580</td>
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Total Metal = 122.97 Mg/Kg
**METAL: LEAD**

**SAMPLE NO.: J59**

**PH:** 6.84  
**VIAL WEIGHT:** 13.99 GRAMS  
**LIQUID DILUTION:** 1  
**VIAL + SEDIMENT WEIGHT:** 18 GRAMS  
**SOLID FRACTION:** .33  
**DRY WEIGHT:** 1.32 GRAMS

<table>
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<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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</table>

**TOTAL METAL = 66.96 MG/KG**

---

**METAL: LEAD**

**SAMPLE NO.: J510**

**PH:** 6.87  
**VIAL WEIGHT:** 14.06 GRAMS  
**LIQUID DILUTION:** 1  
**VIAL + SEDIMENT WEIGHT:** 18.06 GRAMS  
**SOLID FRACTION:** .33  
**DRY WEIGHT:** 1.32 GRAMS

<table>
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<th>NO.</th>
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<th>EXTRACT VOLUME</th>
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<th>MG/KG</th>
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</table>

**TOTAL METAL = 76.53 MG/KG**
### Sample No. TS1

**Metal: Arsenic**

**PH:** 11.83

**Liquid Dilution:** 1

**Solid Fraction:** 0.45

**Sample Weight:** 13.46 grams

**Vial + Sediment Weight:** 17.65 grams

**Dry Weight:** 1.88 grams

<table>
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<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>μG/L</th>
<th>μG/KG</th>
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<th>Cumulative Percent</th>
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</table>

**Total Metal:** 39615.9 μG/KG

### Sample No. TS2

**Metal: Arsenic**

**PH:** 11.89

**Liquid Dilution:** 1

**Solid Fraction:** 0.45

**Sample Weight:** 13.12 grams

**Vial + Sediment Weight:** 17.2 grams

**Dry Weight:** 1.83 grams

<table>
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<th>Extract Volume</th>
<th>μG/L</th>
<th>μG/KG</th>
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<th>Cumulative Percent</th>
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<tr>
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</table>

**Total Metal:** 36167.41 μG/KG

---

Page 230
**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**

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>µG/L</th>
<th>µG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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<td>97.760</td>
</tr>
<tr>
<td>4</td>
<td>45.170</td>
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**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**

<table>
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<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>µG/L</th>
<th>µG/KG</th>
<th>PERCENT TOTAL</th>
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<td>97.760</td>
</tr>
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**TOTAL METAL = 15481.31 µG/KG**
**METAL: ARSENIC**

**SAMPLE NO.: TS5**

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<th>U G/KG</th>
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**TOTAL METAL: 17242.4 µG/KG**

**METAL: ARSENIC**

**SAMPLE NO.: TS6**

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**TOTAL METAL: 19222.83 µG/KG**
### METAL: ARSENIC

**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

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<thead>
<tr>
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**TOTAL METAL:** 17434.77 µG/KG

### METAL: ARSENIC

**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

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<th>EXTRACT VOLUME</th>
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<th>µG/KG</th>
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**TOTAL METAL:** 17906.26 µG/KG
METAL: ARSENIC
PH = 4.41
LIQUID DILUTION: 1
SOLID FRACTION: .45
SAMPLE NO.: TS9
VIAL WEIGHT: 13.46 GRAMS
VIAL + SEDIMENT WEIGHT: 17.54 GRAMS
DRY WEIGHT: 1.62 GRAMS

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TOTAL METAL: 15327.3 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

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TOTAL METAL: 18769.73 µG/KG
### Sample TS1

**Metal: Barium**

**PH:** 11.83

**Liquid Dilution:** 1

**Solid Fraction:** .45

**Sample No.:** TS1

**Vial Weight:** 13.46 grams

**Vial + Sediment Weight:** 17.65 grams

**Dry Weight:** 1.88 grams

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percentage</th>
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**Total Metal:** 3396.08 mg/kg

---

### Sample TS2

**Metal: Barium**

**PH:** 11.89

**Liquid Dilution:** 1

**Solid Fraction:** .45

**Sample No.:** TS2

**Vial Weight:** 13.12 grams

**Vial + Sediment Weight:** 17.2 grams

**Dry Weight:** 1.83 grams

<table>
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<th>MG/KG</th>
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**Total Metal:** 3486.02 mg/kg
**METAL: BARIUM**

PH = 11.93

LIQUID DILUTION = 0.5

SOLID FRACTION = 0.45

SAMPLE NO.: TS3

VIAL WEIGHT = 13.58 GRAMS

VIAL + SEDIMENT WEIGHT = 17.97 GRAMS

DRY WEIGHT = 1.97 GRAMS

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<th>EXTRACT VOLUME</th>
<th>MG/L</th>
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</table>

TOTAL METAL = 2768.73 MG/KG

---

**METAL: BARIUM**

PH = 11.98

LIQUID DILUTION = 0.5

SOLID FRACTION = 0.45

SAMPLE NO.: TS4

VIAL WEIGHT = 13.62 GRAMS

VIAL + SEDIMENT WEIGHT = 18.16 GRAMS

DRY WEIGHT = 2.04 GRAMS

<table>
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<th>MG/L</th>
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TOTAL METAL = 4535.17 MG/KG
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TOTAL METAL: 3213.08 MG/KG

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TOTAL METAL: 4619.91 MG/KG
### Metal: Barium

**PH:** 6.07

**Liquid Dilution:** 1

**Solid Fraction:** .45

**Sample No.: TS7**

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**Total Metal:** 5750.03 Mg/kg

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### Metal: Barium

**PH:** 6.24

**Liquid Dilution:** 1

**Solid Fraction:** .45

**Sample No.: TS8**

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**Total Metal:** 3669.89 Mg/kg

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**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**

**VIAL WEIGHT = 13.88 GRAMS**

**VIAL + SEDIMENT WEIGHT = 17.81 GRAMS**

**DRY WEIGHT = 1.76 GRAMS**

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**TOTAL METAL = 3669.43 MG/KG**

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**METAL: BARIUM**

**SAMPLE NO.: TS10**

**PH = 3.7**

**VIAL WEIGHT = 13.69 GRAMS**

**LIQUID DILUTION: 1**

**VIAL + SEDIMENT WEIGHT = 17.61 GRAMS**

**SOLID FRACTION = .45**

**VIAL WEIGHT = 13.48 GRAMS**

**VIAL + SEDIMENT WEIGHT = 17.54 GRAMS**

**DRY WEIGHT = 1.82 GRAMS**

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**TOTAL METAL = 3669.9 MG/KG**
**METAL: CHROMIUM**

**SAMPLE NO.: TS1**

**PH**: 11.83

**LIQUID DILUTION**: 1

**SOLID FRACTION**: .45

**VIAL WEIGHT**: 13.46 GRAMS

**VIAL + SEDIMENT WEIGHT**: 17.65 GRAMS

**DRY WEIGHT**: 1.88 GRAMS

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**TOTAL METAL**: 348.71 MG/KG

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**METAL: CHROMIUM**

**SAMPLE NO.: TS2**

**PH**: 11.89

**LIQUID DILUTION**: 1

**SOLID FRACTION**: .45

**VIAL WEIGHT**: 13.12 GRAMS

**VIAL + SEDIMENT WEIGHT**: 17.2 GRAMS

**DRY WEIGHT**: 1.63 GRAMS

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**TOTAL METAL**: 343.13 MG/KG

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### METAL: CHROMIUM

**SAMPLE NO.: TS3**

**PH:** 11.93

**LIQUID DILUTION:** .5

**SOLID FRACTION:** .45

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**TOTAL METAL = 346.79 MG/KG**

### METAL: CHROMIUM

**SAMPLE NO.: TS4**

**PH:** 11.98

**LIQUID DILUTION:** .5

**SOLID FRACTION:** .45

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**TOTAL METAL = 319.19 MG/KG**
### METAL: CHROMIUM

**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:** 1.55 GRAMS  

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<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
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<th>PERCENT TOTAL</th>
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<td>96.870</td>
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**TOTAL METAL:** 342.87 MG/KG

---

### METAL: CHROMIUM

**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  

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<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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**TOTAL METAL:** 317.67 MG/KG
### Metal: Chromium

**Sample No. TS7**

**PH = 6.07**

**Liquid Dilution:** 1

**Solid Fraction:** .45

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<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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<td>0.050</td>
<td>2.060</td>
<td>0.750</td>
<td>99.270</td>
</tr>
<tr>
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<td>43.810</td>
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<td>25.270</td>
<td>0.223</td>
<td>3.270</td>
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**Total Metal = 275.54 MG/KG**

### Metal: Chromium

**Sample No. TS8**

**PH = 6.24**

**Liquid Dilution:** 1

**Solid Fraction:** .45

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<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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</table>

**Total Metal = 284.21 MG/KG**

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**METAL: CHROMIUM**

**SAMPLE NO.: TS9**

PH = 4.41

LIQUID DILUTION: 1

SOLID FRACTION = .45

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT</th>
<th>CUMULATIVE PERCENT</th>
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<td>97.370</td>
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TOTAL METAL = 277.26 MG/KG

---

**METAL: CHROMIUM**

**SAMPLE NO.: TS10**

PH = 3.7

LIQUID DILUTION: 1

SOLID FRACTION = .45

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT</th>
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TOTAL METAL = 316.39 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  

<table>
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<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
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<th>Mg/kg</th>
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<th>Cumulative Percent</th>
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<td>0.170</td>
<td>0.070</td>
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<td>2.800</td>
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</tr>
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**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  

<table>
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<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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**Total Metal:** 220.95 mg/kg

---
### METAL: LEAD

**Sample No.: TS3**

**Sample Information:**
- **PH:** 11.93
- **Liquid Dilution:** 0.5
- **Solid Fraction:** 0.45
- **Vial Weight:** 13.58 grams
- **Vial + Sediment Weight:** 17.97 grams
- **Dry Weight:** 1.97 grams

<table>
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<tr>
<th>No.</th>
<th>Initial Weight</th>
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<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
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**Total Metal:** 284.56 mg/kg

### METAL: LEAD

**Sample No.: TS4**

**Sample Information:**
- **PH:** 11.93
- **Liquid Dilution:** 0.5
- **Solid Fraction:** 0.45
- **Vial Weight:** 13.62 grams
- **Vial + Sediment Weight:** 18.16 grams
- **Dry Weight:** 2.04 grams

<table>
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<th>Initial Weight</th>
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<th>Extract Volume</th>
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<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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</thead>
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<tr>
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<td>92.750</td>
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**Total Metal:** 185.98 mg/kg

---

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METAL: LEAD

SAMPLE NO.: TS5

PH = 11.94

LIQUID DILUTION: .1

SOLID FRACTION: .45

<table>
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<tr>
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<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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<tr>
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<td>43.580</td>
<td>20.810</td>
<td>22.770</td>
<td>0.037</td>
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<td>0.200</td>
<td>99.970</td>
</tr>
<tr>
<td>2</td>
<td>98.060</td>
<td>20.860</td>
<td>74.950</td>
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<td>45.860</td>
<td>19.940</td>
<td>25.920</td>
<td>0.025</td>
<td>0.330</td>
<td>0.150</td>
<td>99.770</td>
</tr>
<tr>
<td>4</td>
<td>45.440</td>
<td>21.990</td>
<td>22.950</td>
<td>0.523</td>
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TOTAL METAL = 207.92 MG/KG

METAL: LEAD

SAMPLE NO.: TS6

PH = 11.97

LIQUID DILUTION: .1

SOLID FRACTION: .45

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TOTAL METAL = 182.13 MG/KG
### SAMPLE NO. 'TS7

**METAL: LEAD**  
**PH: 6.07**  
**LIQUID DILUTION: 1**  
**SOLID FRACTION: .45**  
**VIAL WEIGHT: 13.27 GRAMS**  
**VIAL + SEDIMENT WEIGHT: 17.25 GRAMS**  
**DRY WEIGHT: 1.79 GRAMS**

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**TOTAL METAL: 203.5 MG/KG**

### SAMPLE NO. 'TSS

**METAL: LEAD**  
**PH: 6.24**  
**LIQUID DILUTION: 1**  
**SOLID FRACTION: .45**  
**VIAL WEIGHT: 13.48 GRAMS**  
**VIAL + SEDIMENT WEIGHT: 17.72 GRAMS**  
**DRY WEIGHT: 1.9 GRAMS**

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**TOTAL METAL: 218.15 MG/KG**
### Metal: Lead

**Sample No.: TS10**

**PH:** 3.7  
**Vial Weight:** 13.89 grams  
**Vial + Sediment Weight:** 17.81 grams  
**Dry Weight:** 1.76 grams  
**Liquid Dilution:** 1  
**Solid Fraction:** .45

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**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

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<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
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**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

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**TOTAL METAL:** 7769.23 μG/KG

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-250-
**METAL ARSENIC**

SAMPLE NO.: TC3

PH = 2.9

LIQUID DILUTION: .5

SOLID FRACTION: .636

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TOTAL METAL = 11023.01 µG/KG

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**METAL ARSENIC**

SAMPLE NO.: TC4

PH = 3.25

LIQUID DILUTION: .5

SOLID FRACTION: .636

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TOTAL METAL = 18248.37 µG/KG
# METAL: ARSENIC

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**TOTAL METAL = 17095.34 µG/KG**

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# METAL: ARSENIC

## SAMPLE NO.: TC6

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**TOTAL METAL = 21582.81 µG/KG**
**METAL: ARSENIC**

**SAMPLE NO.: TC7**

- **PH= 6.04**
- **LIQUID DILUTION: 1**
- **SOLID FRACTION= .636**
- **VIAL WEIGHT= 13.79 GRAMS**
- **VIAL + SEDIMENT WEIGHT= 17.88 GRAMS**
- **DRY WEIGHT= 2.6 GRAMS**

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>µG/L</th>
<th>µG/KG</th>
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<tbody>
<tr>
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**TOTAL METAL= 16096.51 µG/KG**

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**METAL: ARSENIC**

**SAMPLE NO.: TC8**

- **PH= 6.92**
- **LIQUID DILUTION: 1**
- **SOLID FRACTION= .636**
- **VIAL WEIGHT= 13.91 GRAMS**
- **VIAL + SEDIMENT WEIGHT= 18 GRAMS**
- **DRY WEIGHT= 2.6 GRAMS**

<table>
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<tr>
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<th>EXTRACT VOLUME</th>
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**TOTAL METAL= 18523.61 µG/KG**

---

-253-
**METAL: ARSENIC**

**SAMPLE NO.: TC9**

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**TOTAL METAL= 18272.56 µG/KG**

**METAL: ARSENIC**

**SAMPLE NO.: TC10**

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<th>µG/KG</th>
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**TOTAL METAL= 18334.09 µG/KG**

-254-
**METAL: BARIUM**

**SAMPLE NO. TC1**

**PH = 5.12**

**LIQUID DILUTION: 1**

**SOLID FRACTION = .636**

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<th>NO.</th>
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<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
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TOTAL METAL = 218.65 MG/KG

**METAL: BARIUM**

**SAMPLE NO. TC2**

**PH = 3.23**

**LIQUID DILUTION: 1**

**SOLID FRACTION = .636**

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<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
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TOTAL METAL = 259.61 MG/KG
**METAL: BARIUM**

**SAMPLE NO. TC3**

**PH = 2.9**

**LIQUID DILUTION: .5**

**SOLID FRACTION = .636**

**VIAL WEIGHT = 13.5 GRAMS**

**VIAL + SEDIMENT WEIGHT = 17.44 GRAMS**

**DRY WEIGHT = 2.5 GRAMS**

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<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
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<th>EXTRACT VOLUME</th>
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<th>MG/KG</th>
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<tr>
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</table>

**TOTAL METAL = 237.77 MG/KG**

---

**METAL: BARIUM**

**SAMPLE NO. TC4**

**PH = 3.25**

**LIQUID DILUTION: .5**

**SOLID FRACTION = .636**

**VIAL WEIGHT = 14.06 GRAMS**

**VIAL + SEDIMENT WEIGHT = 18 GRAMS**

**DRY WEIGHT = 2.5 GRAMS**

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<tr>
<th>NO.</th>
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<th>EXTRACT VOLUME</th>
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**TOTAL METAL = 273.8 MG/KG**

---
### Metal: Barium

**Sample No.: TC5**

- **PH:** 3.04
- **Liquid Dilution:** 0.1
- **Solid Fraction:** 0.636
- **Vial Weight:** 13.25 grams
- **Vial + Sediment Weight:** 17.4 grams
- **Dry Weight:** 2.63 grams

<table>
<thead>
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<th>Initial Weight</th>
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<th>Extract Volume</th>
<th>MG/L</th>
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**Total Metal:** 206.04 MG/KG

### Metal: Barium

**Sample No.: TC6**

- **PH:** 2.97
- **Liquid Dilution:** 0.1
- **Solid Fraction:** 0.636
- **Vial Weight:** 13.64 grams
- **Vial + Sediment Weight:** 17.7 grams
- **Dry Weight:** 2.58 grams

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**Total Metal:** 235.55 MG/KG
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

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
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<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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</tr>
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</table>

TOTAL METAL: 258.85 MG/KG

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

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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TOTAL METAL: 243.09 MG/KG
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

<table>
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TOTAL METAL= 295.72 MG/KG

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

<table>
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<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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</table>

TOTAL METAL= 306.12 MG/KG

-259-
METAL: CHROMIUM Sample No.: TC1

PH = 5.12

Liquid Dilution: 1

Solid Fraction: 0.636

<table>
<thead>
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<th>NO.</th>
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<th>Final Weight</th>
<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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<td>95.970</td>
<td>19.880</td>
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</table>

Total Metal = 33.43 MG/KG

---

METAL: CHROMIUM Sample No.: TC2

PH = 3.23

Liquid Dilution: 1

Solid Fraction: 0.636

<table>
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<tr>
<th>NO.</th>
<th>Initial Weight</th>
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<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
</thead>
<tbody>
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<td>0.450</td>
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</tr>
<tr>
<td>2</td>
<td>95.970</td>
<td>19.740</td>
<td>74.000</td>
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<td>0.000</td>
<td>0.000</td>
<td>96.900</td>
</tr>
<tr>
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<td>44.740</td>
<td>18.330</td>
<td>26.410</td>
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<td>0.000</td>
<td>0.000</td>
<td>96.900</td>
</tr>
<tr>
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<td>0.920</td>
<td>36.940</td>
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</tr>
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</table>

Total Metal = 41.35 MG/KG

-260-
### Sample TC3

**Metal:** Chromium  
**Sample No.:** TC3  
**vial weight:** 13.5 grams  
**vial + sediment weight:** 17.44 grams  
**Dry weight:** 2.5 grams  

<table>
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<th>Initial Weight (mg)</th>
<th>Final Weight (mg)</th>
<th>Extract Volume (L)</th>
<th>mg/L</th>
<th>mg/kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
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<td>0.000</td>
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</tr>
<tr>
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<td>44.590</td>
<td>18.400</td>
<td>26.190</td>
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<td>0.000</td>
<td>0.000</td>
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</tr>
<tr>
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</tr>
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</table>

**Total metal content:** 32.76 mg/kg

---

### Sample TC4

**Metal:** Chromium  
**Sample No.:** TC4  
**vial weight:** 14.06 grams  
**vial + sediment weight:** 18 grams  
**Dry weight:** 2.5 grams

<table>
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<th>Initial Weight (mg)</th>
<th>Final Weight (mg)</th>
<th>Extract Volume (L)</th>
<th>mg/L</th>
<th>mg/kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
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<tbody>
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<td>24.330</td>
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<td>0.000</td>
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</tr>
<tr>
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<td>0.000</td>
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</tr>
<tr>
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<td>45.140</td>
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<td>26.180</td>
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<td>0.000</td>
<td>99.990</td>
</tr>
<tr>
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**Total metal content:** 37.05 mg/kg

---

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### METAL: CHROMIUM

**Sample No.: TC5**

**PH:** 3.04  
**Liquid Dilution:** 0.1  
**Solid Fraction:** 0.636  

<table>
<thead>
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<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/kg</th>
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<th>Cumulative Percent</th>
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</tr>
<tr>
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<tr>
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**Total Metal:** 39.35 Mg/kg

---

### METAL: CHROMIUM

**Sample No.: TC6**

**PH:** 2.97  
**Liquid Dilution:** 0.1  
**Solid Fraction:** 0.636  

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<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/kg</th>
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</tr>
<tr>
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<td>99.830</td>
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<td>2.690</td>
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</tr>
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</table>

**Total Metal:** 41.24 Mg/kg
**Metal: Chromium**

**Sample No. 1C7**

**PH = 6.04**

**Vial Weight = 13.79 Grams**

**Liquid Dilution: 1**

**Vial + Sediment Weight = 17.88 Grams**

**Solid Fraction = 0.636**

**Dry Weight = 2.6 Grams**

<table>
<thead>
<tr>
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<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/Kg</th>
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<th>Cumulative Percent</th>
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<tbody>
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<tr>
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<td>45.150</td>
<td>18.500</td>
<td>26.590</td>
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<td>0.000</td>
<td>0.000</td>
<td>100.000</td>
</tr>
<tr>
<td>4</td>
<td>44.060</td>
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<td>0.000</td>
<td>100.000</td>
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<tr>
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<td>0.855</td>
<td>32.880</td>
<td>100.000</td>
<td>100.000</td>
</tr>
</tbody>
</table>

**Total Metal = 32.88 Mg/Kg**

---

**Metal: Chromium**

**Sample No. 1C8**

**PH = 6.02**

**Vial Weight = 13.91 Grams**

**Liquid Dilution: 1**

**Vial + Sediment Weight = 18 Grams**

**Solid Fraction = 0.636**

**Dry Weight = 2.6 Grams**

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>Mg/L</th>
<th>Mg/Kg</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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**Total Metal = 48.27 Mg/Kg**
**METAL: CHROMIUM**

**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

<table>
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**TOTAL METAL:** 45.49 MG/KG

---

**METAL: CHROMIUM**

**SAMPLE NO.: TC10**

**PH:** 7.76

**VIAL WEIGHT:** 14.28 GRAMS

**VIAL + SEDIMENT WEIGHT:** 16.27 GRAMS

**SOLID FRACTION:** .636

**DRY WEIGHT:** 2.53 GRAMS

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**TOTAL METAL:** 45.79 MG/KG
**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

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**TOTAL METAL**: 17.66 MG/KG

---

**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

<table>
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**TOTAL METAL**: 15.16 MG/KG
**METAL: LEAD**

**SAMPLE NO.: TC3**

**PH = 2.9**

**LIQUID DILUTION: .5**

**SOLID FRACTION = .636**

**VIAL WEIGHT = 13.5 GRAMS**

**VIAL + SEDIMENT WEIGHT = 17.44 GRAMS**

**DRY WEIGHT = 2.5 GRAMS**

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</table>

**TOTAL METAL = 23.09 MG/KG**

---

**METAL: LEAD**

**SAMPLE NO.: TC4**

**PH = 3.25**

**LIQUID DILUTION: .5**

**SOLID FRACTION = .636**

**VIAL WEIGHT = 14.06 GRAMS**

**VIAL + SEDIMENT WEIGHT = 18 GRAMS**

**DRY WEIGHT = 2.5 GRAMS**

<table>
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<tr>
<th>NO.</th>
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<th>EXTRACT VOLUME</th>
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<th>MG/KG</th>
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**TOTAL METAL = 24.4 MG/KG**
METAL: LEAD

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

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TOTAL METAL = 25.35 MG/KG

METAL: LEAD

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

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TOTAL METAL = 28.94 MG/KG

-267-
### Sample No. TC7

**Metal: Lead**

**PH:** 6.04

**Liquid Dilution:** 1

**Solid Fraction:** 0.636

<table>
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<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
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**Total Metal:** 20.21 MG/KG

---

### Sample No. TC8

**Metal: Lead**

**PH:** 6.02

**Liquid Dilution:** 1

**Solid Fraction:** 0.636

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Extract Volume</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>Percent Total</th>
<th>Cumulative Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.300</td>
<td>19.070</td>
<td>24.230</td>
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<td>0.900</td>
<td>4.750</td>
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<tr>
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<td>96.320</td>
<td>20.170</td>
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<td>0.000</td>
<td>95.220</td>
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<tr>
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<td>26.690</td>
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<td>0.000</td>
<td>95.220</td>
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<tr>
<td>4</td>
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</table>

**Total Metal:** 20.61 MG/KG

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### METAL: LEAD

**SAMPLE NO.: TC9**

- **PH:** 8.18
- **LIQUID DILUTION:** 1
- **SOLID FRACTION:** 0.636
- **VIAL WEIGHT:** 13.61 Grams
- **VIAL + SEDIMENT WEIGHT:** 17.75 Grams
- **DRY WEIGHT:** 2.63 Grams

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>42.750</td>
<td>20.540</td>
<td>22.210</td>
<td>0.028</td>
<td>0.230</td>
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<td>2</td>
<td>97.750</td>
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<td>15.990</td>
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<td>96.960</td>
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</table>

**TOTAL METAL:** 25.58 MG/KG

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### METAL: LEAD

**SAMPLE NO.: TC10**

- **PH:** 7.76
- **LIQUID DILUTION:** 1
- **SOLID FRACTION:** 0.636
- **VIAL WEIGHT:** 14.28 Grams
- **VIAL + SEDIMENT WEIGHT:** 18.27 Grams
- **DRY WEIGHT:** 2.53 Grams

<table>
<thead>
<tr>
<th>NO.</th>
<th>INITIAL WEIGHT</th>
<th>FINAL WEIGHT</th>
<th>EXTRACT VOLUME</th>
<th>MG/L</th>
<th>MG/KG</th>
<th>PERCENT TOTAL</th>
<th>CUMULATIVE PERCENT</th>
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<td>19.270</td>
<td>26.960</td>
<td>0.000</td>
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<tr>
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<td>0.240</td>
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<tr>
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<td>10.740</td>
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</table>

**TOTAL METAL:** 20.06 MG/KG

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APPENDIX B

RAW DATA FOR STABILIZATION EXPERIMENTS
<table>
<thead>
<tr>
<th>Sample</th>
<th>As (μg/l) 1 wk</th>
<th>Ba (mg/l) 1 wk</th>
<th>Cr (mg/l) 1 wk</th>
<th>Pb (mg/l) 1 wk</th>
<th>Zn (mg/l) 1 wk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distilled H₂O</td>
<td>4.68</td>
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<td>0.07</td>
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<tr>
<td>Distilled H₂O</td>
<td>--</td>
<td>--</td>
<td>0.02</td>
<td>--</td>
<td>0.04</td>
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<tr>
<td>100% Flyash (FA)</td>
<td>1,031.0</td>
<td>7.56</td>
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<td>2.46</td>
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<td>100% Flyash</td>
<td>641.4</td>
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<td>7.46</td>
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<td>3.64</td>
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<tr>
<td>100% TS</td>
<td>16.12</td>
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<td>0.58</td>
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<td>1.60</td>
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<tr>
<td>100% TS</td>
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<td>0.61</td>
<td>0.55</td>
<td>1.45</td>
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<tr>
<td>90% TS/10% FA</td>
<td>110.2</td>
<td>2.27</td>
<td>0.85</td>
<td>1.52</td>
<td>1.59</td>
</tr>
<tr>
<td>90% TS/10% FA</td>
<td>--</td>
<td>--</td>
<td>0.88</td>
<td>--</td>
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<tr>
<td>70% TS/30% FA</td>
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<td>70% TS/30% FA</td>
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<td>2.01</td>
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<td>90% TC/10% FA</td>
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<td>0.97</td>
<td>1.05</td>
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<td>0.25</td>
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<tr>
<td>90% TC/10% FA</td>
<td>83.52</td>
<td>1.16</td>
<td>1.65</td>
<td>0.31</td>
<td>0.28</td>
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<tr>
<td>80% TC/20% FA</td>
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<td>2.55</td>
<td>0.63</td>
<td>0.57</td>
</tr>
<tr>
<td>Sample</td>
<td>As (μg/l) 1 wk</td>
<td>Ba (mg/l) 1 wk</td>
<td>Cr (mg/l) 1 wk</td>
<td>Pb (mg/l) 1 wk</td>
<td>Zn (mg/l) 1 wk</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------------</td>
<td>----------------</td>
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</tr>
<tr>
<td>80% TC/20% FA</td>
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<td>70% TC/30% FA</td>
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<td>70% TC/30% FA</td>
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<td>4.07</td>
<td>0.99</td>
<td>0.06</td>
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<td>100% JS</td>
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<td>100% JS</td>
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<td>1.28</td>
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</tr>
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<td>1.81</td>
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<td>0.07</td>
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<td>0.86</td>
<td>1.16</td>
<td>0.01</td>
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<td>70% JS/30% FA</td>
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<td>3.12</td>
<td>1.57</td>
<td>0.96</td>
<td>0.21</td>
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</table>