Copper, zinc, silver, and lead concentrations and distributions in mine waste ore at Keystone near Ely, Nevada

Joseph B Wright
University of Nevada, Las Vegas

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COPPER, ZINC, SILVER, AND LEAD CONCENTRATIONS
AND DISTRIBUTIONS IN MINE WASTE ORE AT
KEYSTONE NEAR ELY, NEVADA

by

Joseph B. Wright

A thesis submitted in partial fulfilment
of the requirements for the degree of

Master of Science

in

Chemistry

Department of Chemistry
University of Nevada, Las Vegas
August, 1997
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ABSTRACT

This paper investigates the concentrations and distributions of copper (Cu), zinc (Zn), silver (Ag), and lead (Pb) in the Keystone mining waste rock mound. This study employs flame atomic absorption spectrometry for the analysis of ore samples that were totally dissolved, water leaches of ore samples, and dissolved plant material. This study suggests that the Keystone mound contains low grade ore of about 0.08%, or approximately one fifth of the 0.4% established by the mining operations during the 1930s as unprofitable ore. The data show that Cu, Zn and Ag concentrations increase from the top of the mound to the bottom of the mound. The average concentrations are as follows (top and bottom, respectively): Cu - 590 ppm and 920 ppm, Zn - 25 ppm and 75 ppm, Ag - 1.8 ppm and 2.8 ppm. Lead, however, is fairly constant throughout the mound, around 48 ppm.. The change in concentration levels for Cu, Zn, and Ag are probably due to natural leaching and past heap leaching during mining activities. The soil pH is acidic with a pH level of 3 to 4 throughout the mound. This low pH has mediated the transport of Cu, Zn, and Ag down the mound. The data for the plants show that the concentration of Cu, Zn, and Ag are elevated in plants growing on the mound.
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**PHOTOGRAPHS**

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ABBREVIATIONS

vol = volume
mL = milliliter
L = liter
% = percent
° = degrees
C = Celsius; centigrade
g = gram
mg = milligram
kg = kilogram
* = base of the mound
in = inch
ft = foot; feet
rt = right
lt = left
yd = yard
M = molarity
nm = nanometer
ppm = parts per million
W = west
S = south
E = east
N = north
ICV = initial calibration verification
ICB = initial calibration blank
CCV = continuing calibration verification
CCB = continuing calibration blank
LCS = solid laboratory control sample
IDL = instrument detection limit
PB = preparation blank
σ = standard deviation
ICP = inductively coupled plasma spectroscopy
AAS = flame atomic absorption spectroscopy
UNLV = University of Nevada Las Vegas
UNR = University of Nevada Reno
US = United States
EPA = Environmental Protection Agency
%R = percent recovery
RPD = relative percent difference
CAD = computer aided design
For my loving and supporting wife, Michele, and children, Kyra and Toby
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Magma Mining Co, NV.

EPA Laboratories

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Chapter 1 Introduction

This research was motivated by the author's interest in whether or not the concentration and distribution of specific metals in a mining waste rock mound were altered by natural leaching processes. The four metals chosen for study were copper (Cu), zinc (Zn), lead (Pb), and silver (Ag). The research process generated interest also in the effects of the target metals on surrounding plants. The focus of this study is the waste rock mound at the Broken Hills Propriety (BHP) Mine in the Robinson Mining District.

Robinson Mining District History:
The Robinson Mining District, also referred to as the Ruth or Ely District, is located in eastern Nevada and is one of the major porphyry copper districts in the world. A porphyry copper district is a mining district in which the copper mineral is located in layers of porous, metamorphosed sedimentary rock (Sorrell, 1973). Mining began in the area when a Native American named John led a group of miners from Egan Canyon in the Cherry Creek District to the Robinson District resulting in the district's first claim staked December 27, 1867. The Robinson District was named after Thomas Robinson who was an assayer from the Pahranagat District, 120 miles south of Ely. Robinson became a leading rancher in the Ely area and the operator of the Trench mine in the Robinson District (Seedorff and Friehauf, 1991).
"Between 1868 and 1908 the Robinson District consisted mostly of small unprofitable gold and silver mines" (Seedorff and Friehauf, 1991). However, early in the twentieth century many people decided that mining copper may be more profitable than mining gold or silver. Production from 1908 through 1962 totaled nearly 250 million tons of ore averaging a little over one percent copper with a total metal value of nearly one billion dollars. The ores were removed from six major disseminated-type deposits with the Liberty Pit deposit accounting for 70% of the total district production. During this time between 1900 and 1930, waste rock from the Liberty Pit and the Keystone Shaft created the Keystone Mound (Bateman, 1935). According to Richard W. Hasler, a geologist with the Robinson Mining Project, the waste rock that is present at the Keystone dump site is approximately 68 million tons of rock and containing an overall average low grade ore of 0.3% copper (Hasler, 1997).

Approximately 20% of the district’s production came from underground mining operations; the pit ore was mined with shovels and removed by train haulage, truck-train haulage combinations, truck haulage, and by a combination truck-skip system (Bateman, 1935). Many of the ore deposits formerly worked by underground methods used between 1900 and 1930 have been subsequently exploited by open pit methods from 1930 to 1978 (Bauer, et al., 1960). These open pit operations in the Robinson Mining District as of 1976 are depicted on Figure 1.1 and Figure 1.2. Figure 1.1 shows the principle open pit mines of the base and precious metal production. Figure 1.1 indicates the Liberty Pit primarily produced Ag, Pb, and Cu.
FIGURE 1.1 ROBINSON MINING DISTRICT
PRINCIPAL MINES: 1930s-1970s

This map has been modified from (Bauer, et al., 1960) and used with permission from E. Seedorff, 1991.
On Figure 1.1 the chemical symbols depict the location of the metal production.

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FIGURE 1.2  THE ROBINSON MINING DISTRICT
List of Mining Commodities Produced in Order of Total Value
When Sold
(Cu, Au, Ag, Zn, Pb, Mo, Pt, Mn, Fe)

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The Liberty Pit provided the waste rock material for the Keystone dump site. This waste material was less than 0.4% grade ore, and was the source of material used in this study. This 0.4% grade ore would yield approximately 8 pounds of copper metal per ton of ore which during the 1930 to 1978 time period was profitable.

From 1908 to 1978, two companies, Kennecott Copper Corporation and Nevada Consolidated Copper Company, produced the vast majority of the copper from the Robinson District. In 1958 Kennecott Copper Corporation acquired the district assets of Consolidated Coppermines Corporation, and was sole ore producer in the district until 1978 when the mines shut down (Bauer, et. al., 1960).

During the district's operation under Kennecott Copper Corporation, operations were mainly confined to the Liberty Pit where 22,500 tons of ore averaging a little less than 0.8% copper was mined per day. The cutoff grade was 0.4% copper, and the stripping ratio was three to one (Bauer, et. al., 1960). The stripping ratio is the amount of the ore deposit removed versus the amount of the accepted percent grade of copper ore needed for production. The ore was hauled by rail 23 miles to the McGill Reduction Plant where it was concentrated to about 20% copper. Molybdenite was recovered as a by-product in the mill. The copper concentrates were smelted in McGill, and the dore' bars were shipped for refinement at Baltimore where the copper, gold, silver, platinum, and palladium were separated and recovered. The author has been told by many miners, including Dennis Thomas of Kennecott, that the gold, silver, and platinum recovered actually paid the bills for
the companies operations. The district also produced small amounts of iron, manganese and magnetite as shown on Table 1.1. On Table 1.1, a w is used to indicate that the information is withheld to avoid disclosing individual company confidential figures. Also, a zero represents that no production of that particular metal occurred during that particular time period. A blank depicts that production information is not available for that metal during that time period.

Historically, copper and its by-products have been used in the production of goods for over 6000 years. Due to its aesthetic value, chemical stability and electrical conductivity, copper has been used in the production of jewelry, pigments, wire and electrical equipment, pipes and tubes, roofing, brake components, aerospace equipment, ammunition, watches, etc. (Harris and Harben, 1992).

The Robinson Mining District copper mines closed in 1978 due to drop in copper prices on the global market and the outdated operations in the district. These firms were unable to compete with their level of technology. The foreign mining competition implemented the most efficient technology using government subsidies and trade protection in order assume much of the market share. However, the Robinson District mining activity did not completely cease. The gold production continues and currently with new technology and new owners, the copper production is being reactivated. The continual mining activity within the Robinson District makes a vital monetary contribution to the White Pine County and the U.S. economy by reducing dependency on foreign supplies of metals (Howard, 1991).
<table>
<thead>
<tr>
<th>years</th>
<th>ore, old tailings, 1000 short tons</th>
<th>total value when sold</th>
<th>gold in 1000 oz</th>
<th>silver in 1000 oz</th>
<th>copper in 1000 lbs</th>
<th>lead in 1000 lbs</th>
<th>zinc in 1000 lbs</th>
<th>iron ore 40% Fe long tons</th>
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<td>1867-1875</td>
<td>&lt;1</td>
<td>178</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1876-1885</td>
<td></td>
<td>few tons</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>1886-1899</td>
<td>17</td>
<td>178</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
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<tr>
<td>1900-1904</td>
<td>&lt;1</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
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<tr>
<td>1907</td>
<td>&lt;1</td>
<td>2</td>
<td>12</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>1908-1941</td>
<td>116276</td>
<td>402442</td>
<td>1199</td>
<td>5644</td>
<td>2572619</td>
<td>546</td>
<td>6408</td>
<td>9578</td>
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<td>1942</td>
<td>7693</td>
<td>21048</td>
<td>75</td>
<td>274</td>
<td>50126</td>
<td>80</td>
<td>768</td>
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<td>1943-1956</td>
<td>87348</td>
<td>353171</td>
<td>662</td>
<td>2548</td>
<td>1415487</td>
<td>2800</td>
<td>7150</td>
<td>0</td>
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<tr>
<td>1957-1968</td>
<td>w</td>
<td>w w w w w w w w w w w</td>
<td>1936</td>
<td>8466</td>
<td>4138244</td>
<td>8343</td>
<td>14326</td>
<td>9578</td>
</tr>
<tr>
<td>totals</td>
<td>211337</td>
<td>777033</td>
<td>1936</td>
<td>8466</td>
<td>4138244</td>
<td>8343</td>
<td>14326</td>
<td>9578</td>
</tr>
</tbody>
</table>

1 excluding iron
2 includes 9 ounces placer production
w represents information withheld
Table modified from Bauer, et al., 1964.
In 1985 Alta Gold Company obtained the rights to mine gold in the Robinson District and began production in 1986. In late 1990, Magma Copper Company, a company based in Arizona that has other copper mines and processing facilities, joined forces with Alta Gold Company. Magma and Alta planned to mine copper from the Robinson District beginning in mid-1994, by using new reprocessing methods and facilities. However, in 1995 Magma Nevada Mining Company took over the mining operations of the Robinson Mining Project and began mining operations in July, 1996 and milling operations at the beginning of January 1996 with the new facilities. As of the end of January 1996, Magma merged with Broken Hills Proprietary (BHP) and continue operations today (Hasler, 1997).

**General Geology:**

The Robinson Mining District is an east-trending zone of altered porphyry, metamorphosed sedimentary rocks. The sedimentary layer is more than 11,000 feet thick and includes the Devonian Guilmette Formation limestone upward through the Permian Arcturus Formation siltstone, sandstone and limestone (Seedorf and Friehauf, 1991, and Smith, 1976). The sedimentary rocks have been folded, faulted and invaded by middle Cretaceous age quartz monzonite porphyry. Close to the porphyry, the sedimentary rocks were metamorphosed. Local mineralization occurred as parts of the porphyry and metamorphic rocks were shattered and hydrothermally altered. During the late Cretaceous or early Tertiary period, the altered mineralized rock was exposed by erosion. As a result, Oligocene or Eocene age extrusive rhyolite partially covered the porphyry and surrounding rocks. Rhyolite
is an extrusive igneous rock which is a fine grained acid lava rock that resembles granite (Sorrell, 1973). Also, rhyolite dikes of the same age cut the porphyry and rocks (Smith, 1976). Kennecott Copper Corporation defined these Robinson Mining District formations and their thicknesses as shown on Table 1.2. The profile used in Table 1.2 is relative geologic time based on the time period in which the different layers of rock formed, and the thickness of the relative rock layer is cited in feet. Table 1.2 begins with the Quaternary time period in which the Alluvium layer formed. This is the most recent deposit of rock material. Prior to the Quaternary time period was the Tertiary time period in which the Sheep Pass Formation. The earliest formation occurred during the Ordovician time period and is represented by four distinct layers.
### STRATIGRAPHIC SECTION OF THE ROBINSON MINING DISTRICT

#### TABLE 1.2

<table>
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<tr>
<th>Era</th>
<th>Formation/Unit</th>
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<tr>
<td><strong>Quaternary</strong></td>
<td>Alluvium</td>
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<tr>
<td><strong>Tertiary</strong></td>
<td>Sheep Pass Formation</td>
<td>1,000</td>
</tr>
<tr>
<td><strong>Permian</strong></td>
<td>Kaibab Limestone</td>
<td>90-150</td>
</tr>
<tr>
<td></td>
<td>Lory Formation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>upper member</td>
<td>1,280</td>
</tr>
<tr>
<td></td>
<td>lower member</td>
<td>1,600</td>
</tr>
<tr>
<td></td>
<td>Rib Hill Sandstone</td>
<td>1,100</td>
</tr>
<tr>
<td></td>
<td>Riepe Springs (Ruth) Limestone</td>
<td>250</td>
</tr>
<tr>
<td><strong>Pennsylvanian</strong></td>
<td>Ely Limestone</td>
<td>2,300</td>
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<tr>
<td><strong>Mississippian</strong></td>
<td>Chainman Shale</td>
<td>400-1,500</td>
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<tr>
<td></td>
<td>Joana Limestone</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>Pilot Shale</td>
<td>350</td>
</tr>
<tr>
<td><strong>Devonian</strong></td>
<td>Guilmette Limestone</td>
<td>2,500</td>
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<td></td>
<td>Simonson Dolomite</td>
<td>850-1,200</td>
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<tr>
<td></td>
<td>Sevy Dolomite</td>
<td>450-650</td>
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<tr>
<td><strong>Silurian</strong></td>
<td>Laketown Dolomite</td>
<td>1,900</td>
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<tr>
<td><strong>Ordovician</strong></td>
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<td></td>
<td>Eureka Quartzite</td>
<td>500</td>
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<td>Lehman Formation</td>
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<tr>
<td></td>
<td>Kanosh Shale</td>
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</tbody>
</table>

This table was modified and used as public domain information from the Geology Department, Nevada Mines Division, Kennecott Copper Corporation, 1969, in Nevada Bureau of Mines and Geology Bulletin 85, by Roscoe M. Smith, 1976, p.69.
Concerning the tectonic characteristics of the Robinson Mining District, the porphyry has been displaced into disconnected segments by post-intrusive faults. The segments' eastward alignment suggests that there exists a deep-seated, east-striking pre-intrusive fault (Smith, 1976). These faults have created strong extensional forces that greatly extended the Robinson District. The normal faulting associated with numerous sets of normal faults created the geological complexities of the district. The district's copper and gold deposits were formed approximately 110 million years ago about a mile below the surface. During more recent geologic time, fault-induced intrusions, erosion and coverings resulted in the copper deposits approaching the surface in its present day locations (Sedorff and Friehauf, 1991).

The Robinson District's metal zoning pattern appears to have a central zone near the porphyry intrusions. These porphyry intrusions contain copper plus molybdenum with gold. Other possible zones contain minor to trace abundances of silver, lead, zinc, tellurium, and mercury. Determining the Robinson's zoning pattern is difficult due to the disruptions of the ore bodies after the ore deposits formed. The metals were dissolved in the hot molten rock and water solution. The temperature of this material ranged on the order of 350-500°C inside the earth's crust (Hasler, 1997). As the crust underwent tectonic disruptions, the hot metal solution moved up through the crust into cracks. The precipitation of the metals from the solution could have been caused by several factors acting independently or in combination with each other. One factor could be when the water solution cooled, the metal compounds precipitated out of the solution forming hydrothermal ore deposits. Another factor could been when the acidic molten material was neutralized
as it intruded into the basic limestone rock layers depositing the metals in the cracks creating ore veins. This process that created the ore deposits in the Robinson Mining District took several million years. The metal ions, which are electrically charged particles of the metal, dissolved in the water as they attracted water molecules around them like layers of an anion. This process is depicted in Figure 1.3 (Seedorff and Friehauf, 1991). Metals without an electric charge do not attract water molecules, and therefore, do not dissolve in water.

Metals dissolved in water precipitate out when the metal ions lose their attraction for the water molecules. This loss of attraction manifests either when the metal ions become atoms or when the metal combines with other elements to form neutrally charged mineral compounds. As an atom, the precipitated metal forms into one of the native metals such as iron, copper, silver, gold, or platinum. By combining with other elements, the precipitated metal forms one of the many possible minerals depending on the particular chemical environment of the solution and elements. For example, copper ions mix with other elements to form any of the following minerals: tenorite which is CuO, black; cuprite which is Cu₂O, bronze; chalcocite which is Cu₂S, black; bomite which is Cu₃FeS₄; chalcopyrite which is CuFeS₂; malachite which is Cu₂(CO₃)(OH)₂, green; azurite which is Cu₃(CO₃)₂(OH)₂, blue; chrysocolla which is [(Cu, Al)₂H₂Si₂O₅(OH)₄], blue-green (Seedorff and Friehauf, 1991). Figure 1.4 depicts the crystalline structures of chalcocite and cuprite.
FIGURE 1.3  METAL ION DISSOLVES IN WATER

This figure was modified and used with permission from Seedorff and Friehaur, 1991.
FIGURE 1.4 CRYSTALLINE STRUCTURES

Chalcocite, Cu₂S (copper(I) sulfide), is a major ore of copper, and is found most abundantly in the enriched zone of sulfur deposits. It is formed in these enriched zones of sulfur deposits when percolating water dissolves copper minerals near the surface and redeposits them below the water table, thereby enriching the vein in that area. Chalcocite is recognized by its dark gray color, its sectility (it is not cut as easily with a knife as argentite, however), and its association with other copper sulfides (Sorrell, 1973).

Cuprite, Cu₂O (copper(I) oxide), has a crystal structure different from zincite-group oxides. Each copper atom is surrounded by only two oxygen atoms. Ruby copper, as cuprite is often called, is a common mineral found as an oxidation product of copper sulfides in the upper zones of veins. It is usually associated with iron oxides, clays, malachite, azurite, and chalcocite. This and its color, crystal form, luster, and streak distinguish it from other minerals. It oxidizes to CuO in air. Cuprite crystallizes in cubic system as cubes, octahedra, dodecahedra, and combinations of them (Sorrell, 1973).

Figure 1.4 was modified from website http://cst-ww.nrl.navy.mil/lattice/truk/c3.html, and from Dana’s A Text-book of Mineralogy, 1898.
Minerals precipitate due to the processes of reduction-oxidation commonly referred to as redox reactions. Reduction occurs when an atom or ion gains one or more electrons and oxidation occurs when an atom or ion gives away one or more electrons. Since an ion gaining an extra electron must receive it from another ion, the reduction and oxidation processes always occur together, never separately, (Seedorff and Friehauf, 1991).

A good example of a redox reaction is demonstrated by the test used by old time prospectors. This test determines if a brownish black mineral contains copper or just iron. The test involves the use of some tenorite, weak hydrochloric acid and an iron nail. Tenorite is a mineral cupric oxide (CuO). It is rarely found in the form of crystals and usually occurs in massive earthy deposits. Its color ranges from steel gray to iron black (Americana, 1980). The process begins with pouring a little of the weak hydrochloric acid on the tenorite so that a small drop or puddle is created. Next, stir the acid drop or puddle with the iron nail. The tip of the iron nail becomes copper colored because a thin layer of native copper metal precipitates on the surface of the iron nail. The copper precipitation will occur because the acid dissolved some of tenorite releasing some positively charged copper ions. The copper ions attract electrons from other metals such as iron resulting in the following redox reaction:

\[
\begin{align*}
    \text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu}^0 & \text{reduction} \\
    \text{Fe}^0 & \rightarrow \text{Fe}^{3+} + 3e^- & \text{oxidation}
\end{align*}
\]
Ore Leaching:

Ore can be leached from large ore rock piles by in situ or heap leaching. The ore can also be leached in large concrete tanks called vats. These processes are usually employed on low grade ore material. Heap leaching is a process of hydrometallurgy. Hydrometallurgy can recover copper from oxide ores or from ores too low in grade for treatment in a concentrator. In the process, the copper ore in the form of copper oxide is made soluble by sulfuric acid from which it is recovered in elemental form, and the stripped leach solution is recycled for further leaching. If vat leaching is employed, a problem of solid waste transport may be encountered due to residue left in the vats. This problem does not occur when the other two methods are used since the solid waste is left in place.

In heap leaching, piles of predominantly oxide ore are leached with circulating dilute acidic solutions depicted in Figure 1.5. During the leaching process, the heap should be carefully prepared to insure that the leach solution is recovered in order to prevent the leach from infiltrating into the ground where it may be lost or contaminate the ground water. Preparation involves placing large, heavy plastic sheets (generally a polyurethane) on the ground as protective cover, then laying perforated pipes on the plastic sheets. The perforations enable collection of the leach solution from the ore material that is placed on top of the pipes. The acid leach solution is sprayed onto the mound and allowed to percolate through the ore body. The leached solution (pregnant leach solution), containing several grams per liter of copper as copper (II) sulfate is then treated by either cementation or solvent extraction. In situ leaching is the same as heap leaching except it employs blasting.
to the heap mound to create the necessary permeability within the mound for the leach solution.

**FIGURE 1.5  ORE LEACHING OPERATION**

Figure 1.5 has been modified and used with permission from Biotechnology Progress, Vol. 2, No.1, March 1986. Drawn by Jeremy Murray.
In heap leaching the copper oxide dissolves in the leach solution according to the reaction:

\[ \text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} \]

The dissolution of sulfide ores in the rock pile are slower and indirect requiring oxidation by the entry of air into the heap pile during the leaching process as shown by:

\[ \text{CuS} + 2\text{O}_2 \rightarrow \text{CuSO}_4 \] (Williams, 1975)

Ferric sulfate within the heap mound also promotes the oxidation of copper sulfide by a reaction similar to the following:

\[ 4\text{Fe}_2(\text{SO}_4)_3 + \text{CuS} + 4\text{H}_2\text{O} \rightarrow 8\text{FeSO}_4 + \text{CuSO}_4 + 4\text{H}_2\text{SO}_4 \]

Bacteria that may occur in the rock or ore can aid in the leaching of metals from low-grade waste rock mounds as the lixiviant, the acid solution, percolates through the low-grade ore and waste material. The minerals leached by these organisms and the types of bacteria involved in the process are shown in Table 1.3 and Figure 1.6. Since the acid solution carries oxygen and carbon dioxide, it creates an environment conducive to the proliferation of acidophilic, meaning acid-loving, thiobacilli. These thiobacilli are ubiquitous in sulfidic rocks (Higgins, 1985). The principal microbes involved in copper extraction are *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. These rod-shaped, aerobic bacteria that thrive in an acidic environment, having a pH between 1.5 and 3.0, use CO₂ as a carbon source. They function within a temperature range of 18° to 40°C (64° to 104°F) (Levin, et al., 1983). *Thiobacillus ferrooxidans* may number in excess of $10^8$ per gram of rock.
material and per milliliter of leach solution in some zones of the leach dump. By actively oxidizing soluble ferrous iron and attacking the matrices of sulfur-bearing and iron-bearing minerals, the *Thiobacillus ferrooxidans*’ activity is indispensable for optimum leaching activity. At a pH of less than 3.5, the oxidation of iron become independent of pH:

$$-d(Fe^{2+}) = K'(Fe^{2+})(O_2)$$

(Levin, et al., 1983)

In the above equation $K' = 1.0 \times 10^{-7}$ atm$^{-1}$ min$^{-1}$ at 25°C. Therefore, even at the necessary acid pH values required for dump leaching, without the presence of the *Thiobacillus ferrooxidans* the iron would remain in the ferrous state and copper extraction from sulfide minerals would be minimal. The bacteria accelerate the oxidation of ferrous iron by a factor of $10^6$. These leaching bacteria assist in the dissolution of metals in several ways. These methods are either direct and indirect.

Oxidations catalyzed directly by bacteria include the oxidation of iron as follows:

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

The oxidation of sulphur is:

$$S_8 + 12O_2 + 8H_2O \rightarrow 8H_2SO_4$$

Some leaching organisms directly oxidize certain minerals such as pyrite as shown by the following:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4$$

(Levin, et al., 1983).
TABLE 1.3 MINERALS READILY LEACHED BY BACTERIAL ACTION

<table>
<thead>
<tr>
<th>MINERAL</th>
<th>FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu₅S</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>AsFeS</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>MoS₂</td>
</tr>
<tr>
<td>Stibnite</td>
<td>Sb₂S₃</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>NiFeS₂</td>
</tr>
<tr>
<td>Zincblende</td>
<td>ZnS</td>
</tr>
</tbody>
</table>

Table 1.3 modified from Bull, A.T. 1979.

FIGURE 1.6 LEACHING BACTERIA: ORGANISMS AND BASIC METABOLISM

Organisms

- Thiobacillus ferrooxidans
- Leptospirillum ferrooxidans
- Sulfobolus substances
- Thermophilic thiobacilli

- T. ferrooxidans
- Thermophilic thiobacilli
- Sulfobolus
- Mixed cultures

- T. thiooxidans
- T. ferrooxidans
- T. thermosulfidooxidans

- Sulfobolus
- Some heterotrophs
- Other thiobacilli

Energy

- Metal sulfides (FeS₂ or CuFeS₂)
- Metal + sulfate
- Elemental sulfur
- Soluble inorganic sulfur compounds

CO₂ &/or organic

Cellular carbon biosynthesis

Figure 1.6 modified from Bull, A.T. 1979.
Ferric iron is an effective oxidizing agent for solubilizing many minerals such as the solubilization of chalcocite:

$$\text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S}^0$$

Elemental sulphur will frequently form during oxidation of copper sulphide minerals by ferric iron. The sulphur essentially acts as a blind by passivating the mineral particle, thereby, limiting the attack by ferric iron. *Thiobacillus thiooxidans*, numbering between $10^3$ and $10^5$ per gram of rock material and per milliliter of leach solution, oxidize some soluble sulphur compounds and elemental sulphur. The organism's attack on the sulphur removes the passivating sulphur layer surrounding some of the mineral particles and enhances the leaching process. *Thiobacillus ferricooxidans* and *Thiobacillus thiooxidans* degrade sulphide minerals, provide a powerful oxidizing agent for solubilization of copper sulphide minerals, and generate sulfuric acid which provides adequate microbial activity maintains cupric ions in solution (Bull, 1979).

Vat leaching consists of passing the leaching solution through vats of ore that have been crushed to a size ranging between 1.00 cm. and 1.25 cm. (3/8 to ½ inch) (Williams, 1975). These vats may hold up to as much as 20,000 tons of ore. The floors of leach vats are filters that facilitate the upflow or down flow of leach solutions and wash solutions. After the copper oxides are converted to soluble copper (II) sulfate, the ore is washed free of soluble copper by a counter current process in which fresh wash water is added to the vat. The pregnant solution may comprise both the leach and wash solutions. This is why the solutions generated in these
cases are considerably diluted. They are treated by cementation or solvent extraction because they are too dilute for recovery by electrolysis.

Cementation precipitates copper from solution as a finely metallic product by replacement with some more active metal (iron). Historically, scrap tin cans were commonly used as the cementation material; however, today scrap iron is used due to the lack of tin can production. The iron is placed in channels called launders and the copper-rich solution flows on them. Copper is washed out of a launder through screens into settling basins by high-pressure water sprays. After recovery of copper precipitate (called cement copper) (Williams, 1975), the stripped solution containing iron (II) is returned to leaching with or without adding more sulfuric acid. Impure sources of iron can produce some solid waste. This waste is discarded in landfills, tailings ponds, or with low grade ore from open pit operations.

Solvent extraction of pregnant leach solution consists of stripping the dilute leach solution with an organic solvent which is selective of copper into the organic layer. The organic solution is then exposed to an acid stripping solution causing the copper to leave the organic phase and enter an aqueous phase. The aqueous solution is then treated by electrolysis (Williams, 1975).

Electrolytic refining is conducted in rectangular-shaped tanks that are usually constructed of concrete lined with lead or a compound known to contain lead. Then anodes are hung in the tank. The anodes are usually made of lead and the cathodes are made of thin sheets of electrolytically refined copper. The immersed anodes in the electrolyte are supplied with a current that causes the attraction of the aqueous copper (II) ions onto the cathode. The copper oxide is the major impurity
in the anode. It reacts with the sulfuric acid, and one-half precipitates and one-half dissolves according to:

$$\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{Cu}^+ + \text{H}_2\text{O}$$

The current traverses the electrolyte to the cathode where reduction and deposition of copper occurs. The cathodes are removed and washed. The anodes are recycled by melting and casting where the cathodes are melted in a furnace and formed into a bar of copper for further use in manufacturing.

**Chemistry:**

**Zinc:** Relatively insoluble mineral forms account for more than ninety percent of the zinc in soils. Zinc minerals that may occur in soil include: sphalerite (ZnS), smithsonite (ZnCO₃), and hemimorphite [Zn₄(OH)₂Si₂O₇·H₂O]. Zinc is present in the soil in only the divalent form. Organic matter forms coordination complexes with zinc; they may be present in both the soil organic matter and soluble organic complexes in soil solution (Hodgson, 1966). Zinc that may become available for plant uptake is present as Zn²⁺ in the soil solution. The organically complexed zinc in solution or in the soil solid phase is available for plant uptake on the cation-exchange sites.

McBride and Blasiak (1979) equilibrated 10g samples of a soil with 80 ml of solutions containing from 10-70 ppm Zn²⁺. They observed that the proportion of the zinc complexed in solution increased as the pH of the soil increased. The soil solution (supernatants) were passed through cation-exchange columns and the zinc
passing through the column was considered as complexed. Figure 1.7 shows the relationship between pH and the fraction of the metal remaining in solution after passage through the cation-exchange column.

**Copper**: The most common mineral form of copper is the sulfide such that sulfur has combined with Cu$^{2+}$ resulting in minerals such as chalcopyrite (CuFeS$_2$). Under oxidizing conditions, the copper is oxidized to the divalent form as the mineral is dissolved by weathering (McBride and Blasiak, 1979). In general, soils contain a total of 1.0 to 50.0 mg. of copper per kilogram. This relatively small amount of copper could be present as substitutions in noncupric minerals or absorbed copper on mineral surfaces and in organic matter. Copper in the soil can also occur in soil solution, both ionic and complexed; as an exchangeable cation; as a specifically absorbed (nonexchangeable) ion; in organic matter; in occluded oxides; and in minerals. The proportion of copper ion (Cu$^{2+}$) present depends on the total copper level of a solution. Copper remaining in ionic form is affected by pH.
Figure 1.7 was reproduced with permission from the Soil Science Society of America as used in McBride and Blasiak, 1979. This figure shows the fraction of copper and zinc in the soil solution that passed a cation-exchange column as a function of solution pH.

Copper, nickel and zinc are essential nutrients for plants and animals. Plants exhibit toxicity symptoms for copper when the copper level in the plant tissue rises above 20 ppm. However, zinc is necessary for several enzyme systems; therefore, problems associated with zinc application are generally related to deficiency rather than toxicity. High levels of zinc appear to reduce the toxicity of other metals such as cadmium and copper (Bidwell and Dowdy, 1987).
Lead: Relative to copper and zinc, lead is more of a cumulative poison. It is relatively insoluble in soil matrices and quickly immobilized by adsorption and precipitation soon after it is released into the environment (Baird and Gabrielian, 1988). A significant amount of lead has accumulated in the soil, particularly on land near public roadways due to the use of leaded gasoline for fuel in automobiles for several decades. Although lead is relatively insoluble in soil, crops grown in leaded soil contain traces of the element (Outwater, 1994).
Chapter 2  Experimental

The Sample Site

The study site for this research was originally going to be the tailings mound in McGill, Nevada owned by Kennecott Copper Corporation. However, the author was unsuccessful in obtaining permission to use the tailings mound for this study. The author subsequently then drove up to the Robinson Mining District in Ruth, Nevada, and noticed a large waste rock mound. The question arose as to what metals were present in this mound and what was their distribution within the mound. The author talked to the new owners of the mining facilities, the Magma Mining Company, about the research of the Keystone waste rock mound. The Magma Mining Company gave their permission to conduct the research reported in this thesis. Thus, the author was able to obtain the necessary samples and other professional assistance in completing this research.

The waste rock mound Keystone consists of low grade ore (<0.4% copper) and is located east of Ruth, Nevada @ 114° 57' W longitude by 39° 18' N latitude—between route 44B and 44A as shown in Figure 2.1 (see also Figure 1.1). The base of the mound is 6822 ft. above mean sea level and the top is 7000 ft. above mean sea level as shown on Figure 2.1. This makes the height of the mound from base to top 178 ft. As shown on Figure 2.2, the base of the mound where the first bore soil samples were taken (J1, J2, & J3) were designated as the zero foot level position. This became the reference point for all other samples. The material at the site varied in size from fine grained particles to large rocks. The mound exhibited signs

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of long term weathering and some erosion. The control site was located approximately 4 to 5 miles southeast from the target site near Highway 6 in an area undisturbed by mining. The control site was also at the same elevation from sea level as the target site and therefore was subject to similar weather characteristics of the area. The plants as shown on Photographs 2.1, 2.2, and 2.3 became a focus of attention for the determination of metal distribution when it was noted that very few species in very few numbers were present on the target mound or in its immediate vicinity. More vegetation existed at the edge of the pond than at the top of the mound. Importantly, no plants grew on the steep-sloped section of the mound. All of the plant samples taken were from plants that were representative of the average size of the particular species found at each site. The control site was used for plant sample collect only.
Figure 2.1 has been used and modified as public domain material from the U.S. Geological Survey, field check 1958, UTM grid, and 1979 magnetic north.
Figure 2.2 originally developed and drawn by Joe Wright, 1996. Redrawn using computer aided design (CAD) by Jeremy Murray.

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Photographs 2.1 and 2.2 taken by Joe Wright, 1996.
Photograph 2.3 taken by Joe Wright, 1996.

Sample Collection

Equipment for Soil Samples:

1. an auger that was borrowed from the UNLV Geoscience laboratory, courtesy of Dr. Eugene Smith is shown in Photograph 2.1 and Figure 2.3.
2. plastic zip-loc bags, one gallon size
3. screwdriver
4. cooler
5. marker
6. tape measure
Soil Material:

The auger bore will take a core sample of soil eight inches in depth and 3.25 inch in diameter. To obtain the samples, the auger bore was screwed into the ground at the sample site, see Photograph 2.4 and Figure 2.3. Three bore samples where taken at most of the sample sites (in the same hole), however at some of the sample sites only two bores of soil were obtained do to the hardness of the waste rock or because there was a large rock in the path. Each soil sample was knocked out of the bore by the screw driver and placed into its own plastic zip-loc bag. The bag was sealed and labeled. Next, the bags were placed in a cooler and transported to the UNLV Chemistry laboratory. At the laboratory, the samples were stored in a refrigerator at 4°C.
The following photograph shows the auger next to sample bags on the small terrace. In the background are sample bags of the another bore hole that is 20 ft. away. Photograph taken in 1990 by Joe Wright.
The bucket auger's dimensions: 8 in. bore length; 3.25 in. diameter opening; 3 ft. auging depth without extensions. The auger has strong carbon steel bails and a hard-drawn stainless steel cylinder welded to bits forged of high-carbon alloy steel. Handle extensions in 2 ft. to 5 ft. lengths are available.

Figure 2.3 has been modified and redrawn from the Baker Hughes Mining Tools, Inc. catalog for 1996. Redrawn by Kay Wall using Adobe.
**Equipment for Plant Samples:**

1. Buck knife with 8 inch stainless steel blade
2. Plastic zip-loc bags, one gallon size
3. Permanent marker
4. Cooler

**Plant Material:**

To obtain the plant samples from both the target and control sites, branches or blades were torn or cut off from the sample plant. These samples were then placed in sealable plastic bags, i.e., Zip-loc bags. The bags were sealed and labeled with the location and identified by its scientific and common name. The samples included: chrysothamnus nauseosus, commonly known as rabbit brush; medicago, commonly known as medic (an alfalfa-type species); and, hordeum jubatum, commonly known as foxtail barley grass. The samples were placed in a cooler for transport to the UNLV where they were transferred to a refrigerator, ensuring sample integrity, until the preparation for analysis occurred.

**Sample Preparation: Procedures for Soil Samples:**

1st option:

Initially, the samples were prepared for option one analysis that uses the x-ray fluorescence instrument, Rigaku 3030 made in Japan. This is a lengthy process of sample preparation. To remove moisture in each sample, the samples were dried at a temperature between 103°C to 105°C for a twenty-four hour time period.
Drying was necessary to determine the moisture content of the soil samples. The US EPA procedure SOW No. 788, 1988-89 was used.

Next, the samples were pulverized to a size of 400-mesh. All of the dried samples were pulverized at the UNLV Geoscience laboratory using the LC-68 pulverizer shown in Photograph 2.5. As suggested by UNLV chemistry laboratory technician Roger Smid, after obtaining the 400-mesh size for the sample material, the samples were rolled one hundred times using a rolling cloth. The rolling cloth which was made of rubberized cloth was 16 in. by 18 in. According to Bill Olsen of Selo Incorporated Assayers, this option remains a reliable and proven method for homogenizing small soil samples.

The rolling process is as follows: The crushed 400-mesh sample was placed in the middle of the rolling cloth, then the right top cover was pulled over to the left bottom corner and the left bottom corner was pulled to the right top corner. Next, right bottom corner was pulled toward the left top corner and the left top corner is pulled toward the right bottom corner. One cycle of this movement in the rolling cloth equals four rolls of the sample. The motion was repeated twenty-five times to equal the required one hundred rolls of the sample.
Photograph 2.5 was taken at the BHP Assaying Laboratory by Joe Wright, 1997.
X-ray fluorescence spectroscopy required the formation of a sample pellet for instrumental analysis. The following procedure was used:

The Pressed Pellet preparation for trace element analyses as provided by the UNLV Geoscience laboratory.

1. Weigh out 3.0000 gm. of sample, 0.6000 gm. of methyl cellulose +/- 0.0002 gm.
2. Mix the powders very well with a spatula.
3. Put about ¼ inch of methyl cellulose in the Angstrom hydraulic press first for a backing then add sample mixture, press pellet for 90 seconds @ 25,000 lbs.
4. Remove pellet and label its underside. The top is the analytical surface and should not be handled.

***Note*** All samples, fused disks and pellets, should be stored in desiccators.

X-ray fluorescence provided a good qualitative analysis of the target elements; however, the lack of available quantitative standards and the persistent instrument equipment failure doomed this approach. As a result, this method was abandoned in favor of induced coupled plasma spectroscopy (ICP) or flame atomic absorption spectrometry (AA). The ICP method was abandoned due to instrument failure. The flame AA became the method of sample analysis. Two sample preparation methods were tried, a hydrofluoric acid (HF) method, and a modified HF soil digestion method that was used for the AA results reported in this thesis. Most methods use HF in conjunction with other acids to digest soil. Dawn M. Boyer of Lockheed Analytical Laboratory, Las Vegas, Nv., provided the following method.
HYDROFLUORIC/NITRIC ACID
HOT PLATE DIGESTION FOR SOIL AND DUST

1.0 Equipment:
1.1 Teflon beakers
1.2 Teflon watch glasses
1.3 Plastic funnels
1.4 Whatman #1 filter paper
1.5 Analytical balance
1.6 200 mL Nalgene volumetric flasks
1.7 Hot plate
1.8 Pipettes
1.9 Plastic 10 mL graduated
1.10 10 mL graduated

2.0 Reagents:
2.1 Concentrated nitric acid (ACS Reagent grade) 16M
2.2 Hydrofluoric acid (48% high purity)
2.3 Reagent water (ASTM type II)
2.4 7M nitric acid

3.0 Procedure:
***NOTE*** Hydrofluoric acid etches glass, only use Teflonware or Plasticware!

3.1 Add 1.000 g. of soil or 0.25 - 1 g. of dust into a clean 250 mL Teflon beaker and weigh to the nearest 0.0001 g. Record data on the bench sheet.

3.2 Working in a laminar flow hood add 4 mL HF and 9 mL of concentrated HNO₃ to the beaker. Record any changes on the sample tracking sheet after the acid is added eg., color change, bubbling, etc.). Add 25 mL of reagent water to each beaker. Cover the beaker with a teflon watch glass and heat gently at 50°C overnight.

3.3 Include in each batch or every twenty samples a Quality Control (QC) digest, Laboratory Control Sample (LCS), Matrix Spike (S), Preparation Blank (PB), and Duplicate (D).

3.4 Repeat steps 3.1 & 3.2 until all samples have been prepared.

3.5 After digesting, cool the samples to room temperature. Rinse the teflon watch glass with D.D.I. water into the teflon beaker. Rinse the teflon beaker with D.D.I. water and filter through Whatman No. 1 filter paper into a 200 mL nalgene volumetric flask.

3.6 Repeat step 3.4 until all the samples have been filtered diluted to volume.

3.7 Transfer digested into a clean plastic bottle, label, and submit for analysis.

3.8 Complete digestion bench sheet and make sure all data has been recorded.
However, this “total” matrix digestion method was not effective in the total destruction of the soil matrix. To correct this problem, the Lockheed method was modified. The modified procedure follows:

**MODIFIED HF SOIL DIGESTION METHOD**

**Reagents:**
- Nitric acid (HNO₃) concentrated 16 M, reagent grade
- Perchloric acid (HClO₄) concentrated, reagent grade
- Acid mixture - made from 1 to 3 ratio concentrated perchloric acid and concentrated nitric acid
- Hydrochloric acid (HCl) - concentrated, reagent grade
- Hydrofluoric acid (HF) - concentrated, reagent grade
- Hydrochloric acid - 6 M
- Deionized H₂O

**Equipment:**
- Hot plates
- Teflon beakers and covers (150 mL.)
- Centrifuge
- Centrifuge test tubes
- Balance
- Automatic pipette (5 - 10 mL.)
- Storage bottles (10 - 20 mL.)

**Procedure:**
1. Place 1.00 g. dried rolled sample in teflon beaker (150 mL.) and cover sample with HNO₃ approximately 10-15 mL., let stand for 2 hours.
2. Heat until volume of 5 mL. and reflux with 10-15 mL. of HNO₃ until a pale yellow solution appears.
3. Add 10 mL. of HNO₃ and HClO₄ (3:1 ratio), heat to dryness.
4. Leach with 5 mL. of hot 6 M HCl, transfer to centrifuge tube and separate insoluble material, save the decant solution.
5. Transfer insoluble material to teflon beaker with 6 M HCl (5-10 mL).
6. Add equal volume of concentrated HF to beaker and heat at 50°C to dryness overnight.
7. Add 5 mL of concentrated HNO₃ and evaporate.
8. Rinse into 60 mL nalgene bottles with 2% HNO₃ and dilute to volume.

Sample Preparation: Procedures for Water Mobility:

The water mobility procedure is used to test the leachability of the target metals from soil samples. This method was used to establish possible pH levels of the soil solutions. The soil samples used for the water mobility method were from the same soil collected for the adjusted HF method.

The meteoric water mobility procedure used was provided by the Nevada Division of Environmental Protection Bureau of Mining Regulation and Reclamation. The procedure involved the following:

Collect a representative sample of the material. The minimum sample size for this procedure is 5 Kg.; however, to accommodate the necessary sample size for this project instead of 5 Kg., a soil sample size of 500 g. plus 500 mL. of water. This classified sample is placed in a rotation device, as shown in Figure 2.4, which allows the sample to be continuously wetted by circulation of the synthetic meteoric water (lixiviant). The volume of the synthetic meteoric water must be equal in weight to the weight of the classified sample plus the additional volume necessary to saturate the sample. The lixiviant is circulated, agitated, or mixed for 24 hours, continuously wetting the full surface of the sample. For this procedure, the lixiviant (extracting solvent) is distilled water whose hydrogen ion activity (pH) has been
adjusted to between pH 5.5 and 6.5 with reagent grade nitric acid after it has been added to the soil, and before placing it into the extraction device. No further adjustment of the pH during extraction is required. If the pH is acidic below the 5.5 pH no adjustment was required. One hour after ceasing to circulate, a sample of the lixiviant is decanted and prepared for analysis. Analysis shall be performed for the constituents listed at the end of this procedure. The extraction device can be a packed column with small recycle reservoir or bottle roll or large barrel fitted with internal circulation/agitation or equivalent (Procedure used and modified with permission from Nevada Division of Environmental Protection Bureau of Mining Regulation and Reclamation).

The information to be recorded and reported is:

1. The procedure used to collect a representative sample.
2. The adjusted pH of original lixiviant.
3. The final pH of fluid after mixing.
4. Percentage of sample passing 200 mesh.
5. Total weight of solid sample.
6. Moisture required to saturate sample.
7. Time of contact in extraction device.
8. Synopsis of technique and equipment used to leach sample, i.e., column, batch, etc.
9. Results of the analysis of the lixiviant after ending the extraction.
This procedure is used to detect the following:

- Alkalinity
- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Bismuth
- Cadmium
- Calcium
- Chloride
- Chromium
- Cobalt
- Copper
- Fluoride
- Gallium
- Iron
- Lanthanum
- Lead
- Lithium
- Magnesium
- Manganese
- Mercury
- Molybdenum
- Nickel
- Nitrate
- ph.
- Phosphorus
- Potassium
- Scandium
- Selenium
- Silver
- Sodium
- Strontium
- Sulfate
- Thallium
- Tin
- Titanium
- Tot. dissolved solid
- Vanadium
- *WAD CN
- Zinc

**FIGURE 2.4 ROTARY EXTRACTOR**

1/15 - Horsepower Electric Motor

2-Liter Plastic Bottles

Screws for Holding Bottles

---

Figure 2.4 redrawn from EPA document 1310-3 by Jeremy Murray using CAD, 1997.

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Sample Preparation: Procedure for Plant Method:

An Atomic Absorption newsletter provided the sample preparation procedure (Ganje and Page, 1974). The following reagents, equipment and procedures were used to prepare the plant material for analysis:

Reagents:
- nitric acid (HNO₃) - concentrated reagent grade
- perchloric acid (HClO₃) - 70% reagent grade
- acid mixture - made from a 2:1 ratio of concentrated nitric acid to 70% perchloric acid

Materials:
- hot plate
- beakers - 100 mL capacity
- pipette automatic (5 mL) for dispersing acid
- thermometer - with range of 0 to 100 degrees Celsius (0 - 100°C)

Procedure:

The plant tissue was dried for 48 hours in a forced-draft oven that was set at 70°C. Then, the plant material was ground in a porcelain mortar and pestle. The plant tissue was rolled one hundred times to achieve a homogenous mixture. This is the same process used on the soils as previously discussed in Chapter 2. The procedure required a 100 mg. plant tissue sample with 1 mL. of acid mixture. In order to be consistent with the soil samples of 1 g., the plant tissue sample was increased to one gram of plant tissue to 10 mL. of acid solution. The combined mixture of 1 g. of plant tissue and 10 g. of acid mixture was placed into a 100 mL. beaker, covered with a watch glass, and then placed on the hot plate. The beaker
contents were pre-heated at 60°C for fifteen minutes, or until the reaction had subsided. Then the contents were heated at 120°C until complete dissolution of the sample occurred. The sample took about 60 to 75 minutes at 120°C for dissolution to take place.

Digestion, as required, was conducted in a stainless steel perchloric acid fume hood to minimize the hazards associated with the powerful oxidizing capacity of perchloric acid. Once the digestion process was completed and cooled, deionized water was added to obtain the desired volume of 10 mL. Upon reaching the desired volume, the sample was transferred to storage bottles or test tubes and placed in the refrigerator until analysis on the flame AA for copper (Cu), lead (Pb), and zinc (Zn). The plant material was not tested for silver.

**Preparation and Storage of Standard Solutions for Flame AA Analysis:**

Standard Solutions were prepared by the dilution of 1000 ppm. atomic absorption stock solutions obtained from UNLV chemical storage laboratory. Standards are stored in pyrex volumetric flasks 100 mL. at 4°C in a refrigerator.

\[
\text{Calibration Standard (ppm)} = \frac{\text{# mL Standard (1000 ppm)}}{\text{# mL Dilution Volume of Standard}}
\]

**Example:**

\[
\begin{align*}
&0.50 \text{ mL (1000 ppm)} \quad \frac{100 \text{ mL dilution volume}}{5.0 \text{ ppm}}
\end{align*}
\]

The calibration standards for each metal were used to establish instrumental calibration curves for the flame AA as shown in Appendix B, and the instrument detection limits are shown on Table 2.1.
Instrumental Parameters:

1. Hollow cathode lamp Cu, Zn, Pb, and Ag
2. Fuel: Acetylene
3. Oxidant: Air
4. Type of flame: Oxidizing
5. Wavelength: Cu - 324.7 nm, Zn - 213.9 nm, Pb - 283.3 nm, Ag - 328.1 nm

**TABLE 2.1 INSTRUMENT DETECTION LIMITS (IDL)**

<table>
<thead>
<tr>
<th></th>
<th>IDL (ppm)</th>
<th>MDL (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.06</td>
<td>14</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.025</td>
<td>1.5</td>
</tr>
<tr>
<td>Lead</td>
<td>0.2</td>
<td>12</td>
</tr>
<tr>
<td>Silver</td>
<td>0.04</td>
<td>2.4</td>
</tr>
</tbody>
</table>

The instrumental detection limit for the flame AA was established from the data documented during analysis.

DL = 3σ = 3 x σ avg.
Chapter 3 Results and Discussion

As mentioned in Chapter 2, the first analytical method using x-ray fluorescence was abandoned because of continued mechanical failures and the lack of obtaining quantitative standards for the target metals. The ICP analysis method was also abandoned due to instrument failure thus, the flame AA became the analytical method for the target metals (Cu, Zn, Ag, and Pb) due to this machine’s reliability and continued use in the mining industry today. All concentrations obtained from the flame AA had an uncertainty equal to or less than 10%. The quality assurance plan developed and used for the analysis of all digests of soil and plant samples analyzed on the flame AA is in Appendix C.

Sample Data:

A second aliquot of several samples was treated the same as its original sample in order to determine the precision of the methods, total destruction, water mobility and total destruction of plants. The precision of the methods was determined by calculating the relative percent difference. The figures for the relative percent difference in duplicate sample analysis for the various methods are shown on Table 3.1.
### TABLE 3.1 RELATIVE PERCENT DIFFERENCE

<table>
<thead>
<tr>
<th></th>
<th>Cu ppm</th>
<th>RPD</th>
<th>Zn ppm</th>
<th>RPD</th>
<th>Pb ppm</th>
<th>RPD</th>
<th>Ag ppm</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>J10</td>
<td>434</td>
<td>2</td>
<td>30</td>
<td>18</td>
<td>48</td>
<td>1</td>
<td>1.4</td>
<td>4.4</td>
</tr>
<tr>
<td>J10D</td>
<td>427</td>
<td></td>
<td>36</td>
<td>49</td>
<td></td>
<td></td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>J22</td>
<td>790</td>
<td>3</td>
<td>78</td>
<td>5</td>
<td>47</td>
<td>0</td>
<td>2.9</td>
<td>23.3</td>
</tr>
<tr>
<td>J22D</td>
<td>766</td>
<td></td>
<td>82</td>
<td>47</td>
<td></td>
<td></td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>J34</td>
<td>2035</td>
<td>4</td>
<td>261</td>
<td>2</td>
<td>106</td>
<td>0</td>
<td>3.9</td>
<td>18.2</td>
</tr>
<tr>
<td>J34D</td>
<td>2126</td>
<td></td>
<td>267</td>
<td>106</td>
<td></td>
<td></td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>J45</td>
<td>458</td>
<td>1</td>
<td>117</td>
<td>8</td>
<td>102</td>
<td>7</td>
<td>2.7</td>
<td>8.5</td>
</tr>
<tr>
<td>J45D</td>
<td>454</td>
<td></td>
<td>108</td>
<td>95</td>
<td></td>
<td></td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>JT9</td>
<td>1410</td>
<td>10</td>
<td>76</td>
<td>4</td>
<td>67</td>
<td>8</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>JT9D</td>
<td>1565</td>
<td></td>
<td>79</td>
<td>62</td>
<td></td>
<td></td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>115</td>
<td>3</td>
<td>68</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>P1D</td>
<td>118</td>
<td></td>
<td>69</td>
<td>30</td>
<td></td>
<td></td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>P5</td>
<td>80</td>
<td>3</td>
<td>203</td>
<td>3</td>
<td>34</td>
<td>6</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>P5D</td>
<td>78</td>
<td></td>
<td>209</td>
<td>32</td>
<td></td>
<td></td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>P8</td>
<td>17</td>
<td>6</td>
<td>50</td>
<td>10</td>
<td>22</td>
<td>27</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>P8D</td>
<td>18</td>
<td></td>
<td>45</td>
<td>29</td>
<td></td>
<td></td>
<td>na</td>
<td></td>
</tr>
</tbody>
</table>

The relative percent difference (RPD) for each component are calculated as follows:

\[
\text{RPD} = \left( \frac{S - D}{S + D} \right) \times 100
\]

Where:
- **RPD** = Relative Percent Difference
- **S** = First sample value (original)
- **D** = Second sample value (duplicate)

**J** = soil, total destruction  
**JT** = soil, water mobility  
**P** = plants, total destruction
The solid laboratory control sample, LCS (0287) were prepared by the UNLV Quality Assurance Laboratory, and distributed by ICF Technology, Inc., under contract with the EPA. The “True Value” concentrations were derived from results of an EPA multi-laboratory analysis. The “True Values” were determined by EPA method 6010. This method is a leaching process involving nitric and hydrochloric acids and is not a total dissolution method. The values for total dissolution of the LCS samples would be higher than the “True Values” from metals that are not readily leached by acids. Comparing the LCS average to the “control limits” on Table 3.2 the author found that lead is outside of the acceptable leaching range and therefore the least leachable of the four metals tested.

**TABLE 3.2 LCS RECOVERY**

**SOLID LABORATORY CONTROL SAMPLE ANALYSIS**

<table>
<thead>
<tr>
<th></th>
<th>LCS avg. ppm</th>
<th>True Value ppm</th>
<th>Control Limits ppm</th>
<th>% Error</th>
<th>%R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>6383 Low</td>
<td>6910</td>
<td>6006-7820</td>
<td>-7.6</td>
<td>92.4</td>
</tr>
<tr>
<td>Zinc</td>
<td>212 High</td>
<td>187</td>
<td>138-236</td>
<td>+13.3</td>
<td>113</td>
</tr>
<tr>
<td>Lead</td>
<td>293 High</td>
<td>236</td>
<td>188-195</td>
<td>+24.4</td>
<td>124</td>
</tr>
<tr>
<td>Silver</td>
<td>15.6 Low</td>
<td>22.2</td>
<td>15.5-29.0</td>
<td>-29.5</td>
<td>70.5</td>
</tr>
</tbody>
</table>

\[
\text{% Error} = \frac{\text{True Value} - \text{LCS (avg.)}}{\text{True Value}} \times 100
\]

\[
\text{% Recovery} = 100 \times \frac{C_L}{C_T}
\]

\[
C_L = \text{LCS concentration avg. (ppm)}
\]

\[
C_T = \text{true value (ppm)}
\]

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The value concentrations per dry weight (ppm) of Cu, Zn, Pb, and Ag were determined from the flame AA analysis of the soil samples. The dry weight concentrations are shown in Table 3.3.

**TABLE 3.3 CONCENTRATIONS (in ppm) of COPPER, ZINC, LEAD and SILVER in the SOIL SAMPLES (ppm, dry weight)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Cu (ppm)</th>
<th>Zn (ppm)</th>
<th>Pb (ppm)</th>
<th>Ag (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>base of mound 0 ft. Level*</td>
<td>1562</td>
<td>98</td>
<td>64</td>
<td>2.9</td>
</tr>
<tr>
<td>J2</td>
<td>base*</td>
<td>792</td>
<td>65</td>
<td>50</td>
<td>2.2</td>
</tr>
<tr>
<td>J3</td>
<td>small terrace 20 ft. Level</td>
<td>967</td>
<td>68</td>
<td>67</td>
<td>1.8</td>
</tr>
<tr>
<td>J4</td>
<td>small terrace 20 ft. Level</td>
<td>1260</td>
<td>70</td>
<td>61</td>
<td>2.2</td>
</tr>
<tr>
<td>J5</td>
<td>small terrace 20 ft. Level</td>
<td>838</td>
<td>77</td>
<td>63</td>
<td>2.0</td>
</tr>
<tr>
<td>J6</td>
<td>slope 89 ft. Level</td>
<td>722</td>
<td>69</td>
<td>53</td>
<td>1.9</td>
</tr>
<tr>
<td>J7</td>
<td>slope 89 ft. Level</td>
<td>619</td>
<td>67</td>
<td>58</td>
<td>2.0</td>
</tr>
<tr>
<td>J8</td>
<td>slope 89 ft. Level</td>
<td>629</td>
<td>105</td>
<td>64</td>
<td>2.0</td>
</tr>
<tr>
<td>J9</td>
<td>top 178 ft. Level</td>
<td>379</td>
<td>47</td>
<td>41</td>
<td>1.7</td>
</tr>
<tr>
<td>J10</td>
<td>top 178 ft. Level</td>
<td>434</td>
<td>30</td>
<td>48</td>
<td>1.4</td>
</tr>
<tr>
<td>J10D</td>
<td>top 178 ft. Level</td>
<td>427</td>
<td>36</td>
<td>47</td>
<td>1.3</td>
</tr>
<tr>
<td>J11</td>
<td>top 178 ft. Level</td>
<td>794</td>
<td>55</td>
<td>48</td>
<td>2.0</td>
</tr>
<tr>
<td>J12</td>
<td>base 20 ft. to rt.</td>
<td>744</td>
<td>69</td>
<td>26</td>
<td>3.3</td>
</tr>
<tr>
<td>J13</td>
<td>base 20 ft. to rt.</td>
<td>799</td>
<td>68</td>
<td>38</td>
<td>3.2</td>
</tr>
<tr>
<td>Bore</td>
<td>Location</td>
<td>Depth</td>
<td>Width</td>
<td>Thickness</td>
<td>Slope</td>
</tr>
<tr>
<td>------</td>
<td>----------------</td>
<td>-------</td>
<td>-------</td>
<td>-----------</td>
<td>-------</td>
</tr>
<tr>
<td>J14</td>
<td>small terrace</td>
<td>768</td>
<td>71</td>
<td>44</td>
<td>2.2</td>
</tr>
<tr>
<td>J15</td>
<td>small terrace</td>
<td>708</td>
<td>58</td>
<td>45</td>
<td>2.3</td>
</tr>
<tr>
<td>J16</td>
<td>slope</td>
<td>773</td>
<td>58</td>
<td>48</td>
<td>na</td>
</tr>
<tr>
<td>J17</td>
<td>slope</td>
<td>962</td>
<td>73</td>
<td>51</td>
<td>na</td>
</tr>
<tr>
<td>J18</td>
<td>slope</td>
<td>691</td>
<td>76</td>
<td>54</td>
<td>na</td>
</tr>
<tr>
<td>J19</td>
<td>top</td>
<td>499</td>
<td>27</td>
<td>50</td>
<td>na</td>
</tr>
<tr>
<td>J20</td>
<td>top</td>
<td>638</td>
<td>22</td>
<td>40</td>
<td>na</td>
</tr>
<tr>
<td>J21</td>
<td>top</td>
<td>595</td>
<td>22</td>
<td>54</td>
<td>na</td>
</tr>
<tr>
<td>J22</td>
<td>base</td>
<td>790</td>
<td>78</td>
<td>47</td>
<td>2.9</td>
</tr>
<tr>
<td>J22D</td>
<td>base</td>
<td>766</td>
<td>82</td>
<td>47</td>
<td>2.3</td>
</tr>
<tr>
<td>J23</td>
<td>base</td>
<td>794</td>
<td>104</td>
<td>46</td>
<td>2.9</td>
</tr>
<tr>
<td>J24</td>
<td>small terrace</td>
<td>643</td>
<td>69</td>
<td>37</td>
<td>2.7</td>
</tr>
<tr>
<td>J25</td>
<td>small terrace</td>
<td>588</td>
<td>76</td>
<td>38</td>
<td>2.3</td>
</tr>
<tr>
<td>J26</td>
<td>slope</td>
<td>622</td>
<td>58</td>
<td>32</td>
<td>2.6</td>
</tr>
<tr>
<td>J27</td>
<td>slope</td>
<td>1087</td>
<td>43</td>
<td>54</td>
<td>3.4</td>
</tr>
<tr>
<td>J28</td>
<td>slope</td>
<td>535</td>
<td>41</td>
<td>76</td>
<td>3.1</td>
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<tr>
<td>J29</td>
<td>top</td>
<td>540</td>
<td>29</td>
<td>50</td>
<td>na</td>
</tr>
<tr>
<td>J30</td>
<td>top</td>
<td>910</td>
<td>25</td>
<td>38</td>
<td>na</td>
</tr>
<tr>
<td>J31</td>
<td>top</td>
<td>538</td>
<td>30</td>
<td>40</td>
<td>na</td>
</tr>
<tr>
<td>Bore</td>
<td>Description</td>
<td>X-Location</td>
<td>Y-Location</td>
<td>Z-Location</td>
<td>Interval</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>----------</td>
</tr>
<tr>
<td>J32</td>
<td>base 70 ft. to rt.</td>
<td>657</td>
<td>39</td>
<td>107</td>
<td>2.6</td>
</tr>
<tr>
<td>J33</td>
<td>base wash 70 ft. to rt.</td>
<td>367</td>
<td>57</td>
<td>68</td>
<td>2.6</td>
</tr>
<tr>
<td>J34</td>
<td>base 20 ft. to lt.</td>
<td>2035</td>
<td>261</td>
<td>106</td>
<td>3.9</td>
</tr>
<tr>
<td>J34D</td>
<td>base 20 ft. to lt.</td>
<td>2126</td>
<td>111</td>
<td>106</td>
<td>4.7</td>
</tr>
<tr>
<td>J35</td>
<td>base 100 yd. to lt.</td>
<td>1262</td>
<td>129</td>
<td>108</td>
<td>3.2</td>
</tr>
<tr>
<td>J36</td>
<td>base wash 100 yd. to lt.</td>
<td>833</td>
<td>92</td>
<td>74</td>
<td>4.0</td>
</tr>
<tr>
<td>J37</td>
<td>base to pond in wash 20 ft. from base</td>
<td>602</td>
<td>107</td>
<td>66</td>
<td>2.0</td>
</tr>
<tr>
<td>J37D</td>
<td>base to pond in wash 20 ft. from base</td>
<td>895</td>
<td>111</td>
<td>53</td>
<td>1.7</td>
</tr>
<tr>
<td>J38</td>
<td>base to pond in wash 20 ft. from base</td>
<td>578</td>
<td>95</td>
<td>69</td>
<td>1.7</td>
</tr>
<tr>
<td>J39</td>
<td>wash mouth at edge of pond 40 ft. from base</td>
<td>1128</td>
<td>201</td>
<td>20</td>
<td>2.1</td>
</tr>
<tr>
<td>J40</td>
<td>wash mouth at edge of pond 40 ft. from base</td>
<td>1068</td>
<td>209</td>
<td>85</td>
<td>2.3</td>
</tr>
<tr>
<td>J41</td>
<td>pond surface 1 to 2 inches</td>
<td>350</td>
<td>85</td>
<td>100</td>
<td>2.9</td>
</tr>
<tr>
<td>J42</td>
<td>pond 1 bore length</td>
<td>406</td>
<td>91</td>
<td>120</td>
<td>4.5</td>
</tr>
<tr>
<td>J43</td>
<td>pond 1 bore length</td>
<td>353</td>
<td>73</td>
<td>56</td>
<td>5.2</td>
</tr>
<tr>
<td>J44</td>
<td>pond 13 to 18 inches</td>
<td>492</td>
<td>123</td>
<td>111</td>
<td>2.6</td>
</tr>
<tr>
<td>J45</td>
<td>pond 20 to 30 inches</td>
<td>458</td>
<td>117</td>
<td>102</td>
<td>2.7</td>
</tr>
<tr>
<td>J45D</td>
<td>pond 20 to 30 inches</td>
<td>454</td>
<td>108</td>
<td>95</td>
<td>2.9</td>
</tr>
<tr>
<td>J46</td>
<td>on mine rd. 200 yd. SE of base</td>
<td>914</td>
<td>58</td>
<td>48</td>
<td>2.5</td>
</tr>
<tr>
<td>J47</td>
<td>on mine rd. 200 yd. SE of base</td>
<td>1080</td>
<td>80</td>
<td>81</td>
<td>2.9</td>
</tr>
</tbody>
</table>
The data from each bore collected at each sample location was averaged to develop a graphical representation of the three separate zones. For example: J1 and J2 concentrations of each metal were averaged to obtain the metal concentration at the 0 ft. level of zone #1. A zone represents all the soil samples collected from the bottom to the top of the mound. Zone #1 is represented by samples J1-J11, zone #2 is represented by samples J12-J21, and zone #3 is represented by samples J22-J31 as shown in Figure 3.1. The concentrations of each metal at the various heights in the three zones are shown in Figures 3.2 to 3.4. The data for the zones does not include the metals in the wash or pond. In Figure 3.2 (copper) and Figure 3.3 (zinc) the concentration of each metal increases in samples from the top, 178 ft., to the base, 0 ft. However at zone #2 and zone #3 for copper and zone #2 for zinc show that there are some variables present that may be affecting the movement of the metals at the 89 ft. level and the small terrace at 40 ft. After discussing the data with P. E. Paul Liebendorfer, some of these variables may include soil material size, fracturing, pH, type of soil, mineral, dispersement, metal solubility, slope grade of the mound or action of bacteria. The average of all the three zones of copper and zinc show that the concentration of the metal is inversely proportional to the height of the sample. Lead, however, shows very little concentration variation throughout the mound at the various zones. Therefore, the above variables have the least effect on lead's concentration. This could be due to the chemical nature of lead. Lead is a more stable metal and not effected by the leaching action of acids or bacteria to the degree that copper and zinc can be. Silver was omitted from the zone category because the concentration rarely exceeded the MDL.
Figure 3.1 originally developed and drawn by Joe Wright, 1996. Redrawn using computer-aided design (CAD) by Jeremy Murry.

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Copper Concentration at Keystone (ppm)
FIGURE 3.3

Zinc Concentration at Keystone (ppm)
FIGURE 3.4

Lead Concentration at Keystone (ppm)

- Zone #1
- Zone #2
- Zone #3
- Avg.

- 178 ft.
- 89 ft.
- 40 ft.
- 0 ft.
Figures 3.5 to 3.12 are graphs of the concentrations of each metal in the bores from the top of Keystone to the pond below. These graphs represent the metal concentrations from the level described as the 178 ft., top level of the mound, to the 0 ft. level, base of the mound and beyond to the pond at the -50 ft. level. The base sample zone#1 is the reference point for all heights and distances reported.

Starting at the top of the mound, at the 178 ft. level, the deeper into the mound, the greater the concentration of copper. At the 89 ft. level, the first bore sample taken was slightly higher in concentration at 722 ppm than the second and third bores at 619 and 629, respectively. The higher concentration of copper in the first bore can be attributed to the steepness of the mound, approximately 60 to 65° to the horizontal, due to the natural leaching process. This steep grade and height of the mound increases the flow of solution and soil material down through the mound naturally due to gravity. The concentrations of the bores at the various heights for zinc and silver, however, are very consistent. This could be attributed to the lack of these metals present in the mound compared to copper which is the main metal in the ore body. The lead concentrations of bores throughout the entire mound stay very consistent, approximately 50 ppm.

However, at the 40 ft. level where the small terrace occurs, the concentration of copper increases. The second bore at this level has the highest copper concentration possibly due to the fact that the metals in solution flow onto the terrace and then they are re-absorbed into the soil at a slower rate and accumulate.
FIGURE 3.5

Distribution of Copper at Keystone

Copper Concentration (ppm)  O Bore#1 ▲ Bore#2 □ Avg.

FIGURE 3.6

Distribution of Zinc at Keystone

Zinc Concentration (ppm)  O Bore#1 ▲ Bore#2 □ Avg.
FIGURE 3.7
Distribution of Lead at Keystone

![Graph showing the distribution of lead at Keystone. The graph plots Lead Concentration (ppm) against Keystone Mound Height (ft) with data points for Bore#1, Bore#2, and Avg.]

FIGURE 3.8
Distribution of Silver at Keystone

![Graph showing the distribution of silver at Keystone. The graph plots Silver Concentration (ppm) against Keystone Mound Height (ft) with data points for Bore#1, Bore#2, and Avg.]

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FIGURE 3.9

Sample Average Concentration (ppm)
FIGURE 3.10

Sample Average Concentration (ppm)

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Sample Average Concentration (ppm)
Sample Average Concentration (ppm)
The third bore’s copper concentration at this level is less than the first two bores possibly due to the natural steepness throughout the mound above and below the terrace as previously discussed.

The first bore at the base of the mound, the zero foot level, has the highest concentration value for Cu, Zn, and Ag. At the base, the mound’s steepness subsides and one would assume that the leaching process halts beyond the base of the mound. This appears to be due to the dispersion of the solubilized metals into a miniature alluvial fan at the mound’s base before reaching a wash which leads to the pond. Due to the flow to the pond, the concentration of copper and silver are lower in the wash than at the mound’s base or in the pond. Figures 3.7 and 3.11 show the first bore concentration of lead in the wash is slightly higher than the mound indicating the small amounts of lead leached over time will settle and accumulate in the soil. Figure 3.6 and 3.10 show zinc concentrations continue to increase in the wash. This could be due to the sample collected or the presence of zinc compounds in the non-mined soil found in the washed. At the mouth of the pond, the concentration of all four metals increase. The accumulation of metal concentrations could have been caused by evaporation. At the mouth of the pond there is a small dike that the drainage from the mound must overcome before entering the pond. With the low precipitation 10 in/yr (arid climate), often the run-off from the mound is not sufficient in amount to overcome this dike and the evaporated solution leaves behind its soluble contents and fine grain particles.

The concentration of copper decreases in the pond samples. This decrease may be caused by the distribution of the solution into the pond. Zinc concentrations
of the pond samples are very close to the concentrations in the wash indicating that the zinc leached from the mound ends up in the pond soil. Lead, unlike the other target metals, does not appear to be naturally leached for the mound or affected by acidic solutions (see Figures 3.4 and 3.7). Lead's concentration appears to stay constant throughout the mound, however, its concentration tends to increase slightly in the wash and pond areas. Figures 3.7 and 3.11 show that the concentration of lead in the wash and the pond are elevated slightly above the level throughout the mound. The fairly constant distribution of lead may be caused by its chemical properties of being reasonably unreactive.

As previously discussed in Chapter 1, the Keystone waste rock mound was formed between the years of 1900 and 1930. During its formation, the waste rock copper levels were 0.4% or less than 0.4%. New mining tests on the Keystone have revealed that the average per cent copper in the mound is 0.3%. The average concentration of copper from the data in Table 3.3 is approximately 800 ppm or 0.08%. This low value average may be due to the fact that the samples are surface related. The metals may have been leached out or leached into deeper levels within the mound. As discussed in Chapter 2, in the water mobility procedure, the soil samples were screened to measure soil particle size as shown on Table 3.4 and Figure 3.13. Figure 3.13 shows that at higher elevations the majority of the soil particle sizes are relatively larger than at lower elevations on the mound. This is apparently due to the fact that smaller particles were carried by rain water or heap leaching processes down the mound. The greatest mass of the soil samples at Keystone is in the range between 20 to 100 mesh. Mesh size can affect the
solubility of certain metals. The smaller the mesh the greater the surface area of the matrix, which may accelerate leaching.

Ralph Orgallo a security guard for Kennecott Copper Corporation confirmed that an ongoing heap leaching process occurred at the Keystone mound between 1950 and 1960 (Williams, 1975). This heap leaching process involved setting up a pipe system with sprinklers on the Keystone mound. The mound was then sprinkled with a leach solution containing sulfuric acid. The pregnant solution drained off the mound into ponds at its base. The pond in this study is the remains of one such pond. The pregnant solution was the treated to remove the leached metals. As shown on Table 3.4, the pH of the target site soil has been altered by this leaching process. The pH of the soils was determined from measuring the pH of the distilled water after it was added to the soil samples for the water mobility experiment. The pH levels of soils tested were acidic except for sample JT39 as shown on Table 3.7. Sample JT39 is from the mouth of the wash at the edge of the pond. It is possible that the soil at this location has not been disturbed by mining activity, and is typical native soil. The native soil consists of mainly limestone. Limestones consist of carbonated compounds which have a basic pH. Further evidence on Figure 3.14 shows that the pH level within the mound has an approximate average of 3.05. The wash contains mostly natural or natural unmined material from the area which has a pH of 7.08; however, the mound and the pond containing mostly imported material have pH levels averaging 3.05 and 2.15, respectively.
### Table 3.4  MASS DISTRIBUTION AND pH

<table>
<thead>
<tr>
<th>Sample</th>
<th>20 mesh (g)</th>
<th>100 mesh (g)</th>
<th>150 mesh (g)</th>
<th>200 mesh (g)</th>
<th>+200 mesh (g)</th>
<th>Total (g)</th>
<th>pH Before</th>
<th>pH After</th>
</tr>
</thead>
<tbody>
<tr>
<td>JT9</td>
<td>169.54</td>
<td>141.09</td>
<td>72.65</td>
<td>56.32</td>
<td>59.89</td>
<td>499.49</td>
<td>2.99</td>
<td>3.50</td>
</tr>
<tr>
<td>JT9D</td>
<td>161.99</td>
<td>141.58</td>
<td>75.95</td>
<td>60.96</td>
<td>59.96</td>
<td>500.44</td>
<td>4.00</td>
<td>3.61</td>
</tr>
<tr>
<td>JT6</td>
<td>170.68</td>
<td>187.59</td>
<td>60.70</td>
<td>38.61</td>
<td>42.22</td>
<td>499.89</td>
<td>2.60</td>
<td>2.33</td>
</tr>
<tr>
<td>JT1</td>
<td>187.62</td>
<td>146.13</td>
<td>67.89</td>
<td>54.30</td>
<td>44.86</td>
<td>500.80</td>
<td>2.60</td>
<td>3.48</td>
</tr>
<tr>
<td>JT39</td>
<td>227.21</td>
<td>143.29</td>
<td>55.22</td>
<td>42.14</td>
<td>34.14</td>
<td>500.00</td>
<td>7.08 adj. 6.08</td>
<td>7.64</td>
</tr>
<tr>
<td>JT42</td>
<td>74.11</td>
<td>163.52</td>
<td>99.46</td>
<td>99.32</td>
<td>62.11</td>
<td>498.52</td>
<td>3.01</td>
<td>2.55</td>
</tr>
<tr>
<td>Natural surface H₂O (runoff)</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>2.15</td>
<td>na</td>
</tr>
<tr>
<td>JTPB</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>6.07</td>
<td>6.82</td>
</tr>
<tr>
<td>ph. (4.0) Meter Std.</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>4.06</td>
<td>4.06</td>
</tr>
</tbody>
</table>

Before represents the pH of the soil after adding the distilled water and before tumbling the sample.

After represents the pH of the soil after adding the distilled water and tumbling the sample for 24 hours.

Each soil sample was a 500 g aliquot of the original soil samples from the mound and mixed with 500 ml of distilled water.

If the pH of the soil sample was below 5.5 pH no adjustment in the samples pH was required, the only sample requiring adjustment was JT39.
FIGURE 3.13

Mass Distribution
Grams per Mesh

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The circles on Figure 3.14 represent the soil pH at various heights in the target area. The pH of the mound samples become more acidic at the bottom.
The pH data is summarized in Table 3.5. The mining activity (heap leaching) has resulted in soil pH values (by this method) from pH 2.60 to pH 4.00. The past heap leaching activities are more than likely responsible for the acid pH of 2.15 of the natural surface water (runoff) as shown on Table 3.6. The natural surface water was the drainage solution from the mound after a rain storm. It was collected directly by placing a collection bottle into the solution that accumulated in the pond after a rain storm. This acidic pH value will increase the natural extraction of most metals from the waste ore rock. However, lead does not appear to be affected by pH. The JT label represents soil samples prepared for analysis by the water mobility method.

**TABLE 3.5 MOBILITY CONCENTRATION**

(mg/L)

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH before</th>
<th>pH after</th>
<th>Cu (ppm)</th>
<th>Zn (ppm)</th>
<th>Pb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JT9</td>
<td>2.99</td>
<td>3.50</td>
<td>4</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>JT9D</td>
<td>4.00</td>
<td>3.61</td>
<td>5</td>
<td>1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>JT6</td>
<td>2.60</td>
<td>2.33</td>
<td>13</td>
<td>3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>JT1</td>
<td>2.60</td>
<td>3.48</td>
<td>14</td>
<td>3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>JT39</td>
<td>7.08</td>
<td>7.64</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

**TABLE 3.6 NATURAL SURFACE H₂O**

(mg/L)

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Cu (ppm)</th>
<th>Zn (ppm)</th>
<th>Pb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>2.15</td>
<td>978</td>
<td>48</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
Using the concentration data in (Table 3.3) and the data from the mobility experiments (Table 3.5), the amount of each element that would be leached is in Table 3.7. The mobility leach percents are experimental.

**TABLE 3.7 THEORETICAL LEACHABILITY (PERCENT)**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>pH Before</th>
<th>pH After</th>
<th>Cu (ppm)</th>
<th>Zn (ppm)</th>
<th>Pb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J9T</td>
<td>2.99</td>
<td>3.50</td>
<td>2</td>
<td>2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>J9DT</td>
<td>4.00</td>
<td>3.61</td>
<td>2</td>
<td>2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>J6T</td>
<td>2.60</td>
<td>2.33</td>
<td>2</td>
<td>4</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>J1T</td>
<td>2.60</td>
<td>3.48</td>
<td>1</td>
<td>3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>J39T</td>
<td>7.08</td>
<td>7.64</td>
<td>&lt; 1%</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

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Several factors influence the absorption of metals by plants. The significant factor in the absorption of the metals by plants near the pond may be the acidic value of the surface run-off water flowing into the pond. The pond surface run-off water had a pH level of 2.15.

Even though the plant sample size consisted of only 9 samples, several observations are evident. Copper and zinc are evaluated in the target area plants relative to the control site plants as seen on Table 3.8. However, lead concentrations in plants from the target site and the control site show little variation as shown on Table 3.9. The slightly higher concentrations of lead concentrations in the foxtail grass at the control site may be due to the fact that the grass grows relatively close to U.S. Route 6 which is more heavily traveled than the target site roads. The greater traffic flow on U.S. Route 6 relative to the target site roads increases the area's exposure to lead emissions from vehicles. However, the difference in the lead is probably not significant.
### Table 3.8  Metal Concentration in Plants (ppm)

<table>
<thead>
<tr>
<th>PLANT MATERIAL</th>
<th>METAL</th>
<th>NEUTRAL SITE (ppm)</th>
<th>TOP OF MOUND (ppm)</th>
<th>BASE OF MOUND (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>foxtail grass</td>
<td>Cu</td>
<td>5</td>
<td>34</td>
<td>116 118</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>38</td>
<td>21</td>
<td>30 20</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>34</td>
<td>47</td>
<td>68 69</td>
</tr>
<tr>
<td>medic</td>
<td>Cu</td>
<td>12</td>
<td>na</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>33</td>
<td>na</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>31</td>
<td>na</td>
<td>117</td>
</tr>
<tr>
<td>rabbit brush</td>
<td>Cu</td>
<td>17 18</td>
<td>80 78</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>22 28</td>
<td>34 31</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>50 45</td>
<td>203 209</td>
<td>159</td>
</tr>
</tbody>
</table>

### Table 3.9  Lead Concentration in Plants (ppm)

<table>
<thead>
<tr>
<th>plant</th>
<th>neutral site</th>
<th>top of mound</th>
<th>base of mound</th>
</tr>
</thead>
<tbody>
<tr>
<td>foxtail grass</td>
<td>38</td>
<td>21</td>
<td>30 20</td>
</tr>
<tr>
<td>medic</td>
<td>33</td>
<td>na</td>
<td>35</td>
</tr>
<tr>
<td>rabbit brush</td>
<td>22 28</td>
<td>34 31</td>
<td>32</td>
</tr>
</tbody>
</table>
As discussed in Chapter 1, copper, nickel and zinc are essential nutrients for plants and animals. Therefore, plants exhibit greater tolerance to increased concentrations of these aforementioned metals relative to lead. Plants need specific levels of copper, nickel and zinc depending on the species and environment; however, lead is detrimental to plant growth. For example, zinc is necessary for several enzyme systems (Barber, 1985). Problems associated with zinc application are generally related to deficiency rather than toxicity because high levels of zinc appear to reduce the toxicity of other metals such as cadmium and copper (Bidwell and Dowdy, 1987). The data results from Table 3.9 show that copper and zinc concentrations are greater at the target site compared to their concentrations at the control site for all plant species.

Since high levels of metals can be toxic the plant species at the target site may have developed or adapted methods to cope with the elevated metal concentrations. One method appears to be limiting the number of plant species and number of actual plants of each species living on the target site. Those plants existing at the target site may have the ability to restrict the absorption of toxic levels of lead, copper and zinc, or to expunge absorbed toxic levels of lead, copper, and zinc, thereby limiting their accumulation. For example, the plant may strategically store the toxic elements in its root tissue, or in vacuoles of nonessential plant tissue, or in older plant tissue such as leaves. These older plant tissues are eventually lost along with the accumulated toxic elements. This process is similar to the process used by pickle grass which grows on very alkaline soils. The pickle grass stores
salts in a vacuole sack. Once the sack fills with salt, it bursts releasing the salt (Devitt, 1996). Further investigation of this phenomena is needed. The plant data for Cu, Zn, and Pb are presented graphically in Figures 3.15 to 3.20.
Figure 3.15 METAL CONCENTRATION IN FOXTAIL GRASS (ppm)

Metal Concentration in Foxtail Grass (ppm)

- Cu
- Zn
- Pb
Figure 3.16 METAL CONCENTRATION IN RABBIT BRUSH (ppm)

Metal Concentration in Rabbit Brush (ppm)

- Control Site
- Base
- Top

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Figure 3.17 METAL CONCENTRATION IN MEDIC (PPM)

Metal Concentration in Medic (ppm)

- Control Site
- Base
- Top

![Graph showing metal concentration in Medic (ppm)]
Copper Concentrations in Plants (ppm)

Figure 3.18 COPPER CONCENTRATIONS IN PLANTS (ppm)
Figure 3.19  ZINC CONCENTRATION IN PLANTS (ppm)

Zinc Concentrations in Plants (ppm)

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Lead Concentrations in Plants (ppm)
Chapter 4 Conclusion

The concentrations of copper and zinc increase from the top of the Keystone waste mound to it's base. Lead, on the other hand is fairly uniformly distributed in the mound. This result suggests that a small fraction of the copper, zinc and silver have been more effectively leached or washed from the top of the mound. The highest concentration of copper and zinc are found behind a small earthen barrier or dike at the base of the wash leading from the mound to the evaporation pond. The concentrations of lead in this area is very similar to the concentration in the mound, suggesting lead is unaffected by leaching. The highest concentrations of lead and silver are found in the pond. The average concentration of copper in the mound is 800 ppm or 0.08%, considerably lower than the low grade ore value of 0.4% established as unprofitable during the 1930's. However, heap leaching of the mound has occurred since that time. The low average reported suggests that the metals in the surface samples may have been leached out or leached to deeper levels within the mound.

The pH of water contacted with the waste material from the mound and pond is acidic. The pH decreases from the top of the mound (pH=3.5) to the bottom of the mound (pH=2.6) and is lowest in the pond soil (pH=2.15). The overall pH average of the mound is 3.05. This, also suggests a leaching of the Keystone mound overtime.
The water mobility studies indicate that approximately 2% of the copper and 2.5% zinc can be removed from the waste ore by tumbling with distilled water (which becomes acidic on contact with the ore) and less than 1% of the lead is removed.

The plant tissue analysis indicates that copper and zinc are somewhat elevated, up to a factor of 25, over the concentrations found in plants at the control site. Lead is not concentrated in plants at the Keystone site over the control site.

There are many factors in this area that can affect the solubilization of metals. The parameters that may play a role in the movement of these metals in the environment could include: soil grain size, temperature, salts (buffering agents), veins or fracturing, type of mineral, plants, and bacteria. These variables can act independently or in conjunction with each other in some complex way. The techniques and procedures used in this research could be incorporated in further environmental studies of this and other mine sites or related areas in biology, botany, zoology, geology, and hydrology.
APPENDIX A: PHOTOGRAPHS OF THE KEYSSTONE SITE

A.1 Photo of the Keystone mound and sample area.
A.2 The wash at Keystones' Base.

A.3 The wash leading to the pond.
A.4 The wash at the base of the sample site (alluvial fan).

A.5 Base of the Keystone sample site.
A.6 The pond showing its dam.

A.7 The pond and dam.
The pond bore sites.
A.10 View of the pond and mound.

A.11 View of the steepness of the ponds' dam.
APPENDIX B: CALIBRATION CURVES

Calibration curves were established on the flame AA with standards made by above for each metal of interest. Figure B.1 shows copper's calibration curve, Figure B.2 shows zinc's calibration curve, Figure B.3 shows lead's calibration curve, and Figure B.4 shows silver's calibration curve.
Figure B.1

Copper Calibration Curve

Flame AA Absorption

Copper Concentration (ppm)
Figure B.2

Zinc Calibration Curve

Flame AA Absorption

Zinc Concentration (ppm)
Figure B.3

Lead Calibration Curve

Flame AA Absorption

Lead Concentration (ppm)
FIGURE B.4

Silver Calibration Curve
APPENDIX C: Quality Assurance Plan

The following quality assurance/quality control practices were employed during the sample preparations and analytical work. The quality assurance plan in this project was based on the plan for US EPA contractor laboratory program (SOW No. 788, 1988-89).

**Instrument Calibration**

One blank and at least three calibration standards were used for the determination of the calibration curve.

**Initial Calibration Verification (ICV)**

Immediately after instrument was calibrated, the accuracy of the initial calibration was verified and documented. For calibration verification, an independent elemental standard was used.

**Continuing Calibration Verification (CCV)**

To ensure calibration accuracy during each analysis run, approximately every tenth sample calibration standard or every two hours running during analysis run, whichever is more frequent was analyzed for every wavelength used for analysis. The standard was also analyzed and reported after the last analytical sample.

**Initial Calibration Blank (ICB) & Continuing Calibration Blank (CCB)**

A calibration blank was analyzed immediately after every initial and continuing calibration verification.
**Preparation Blank (PB)**

At least one preparation blank, consisting of a clean empty teflon beaker processed through each sample preparation and analysis procedure was prepared and analyzed with each sample group.

**Duplicate Sample Analysis (D)**

At least one duplicate sample was analyzed from each group of samples. The relative percent difference (RPD) of results of the duplicate analysis should have a control limit of 20%.

**Laboratory Control Sample (LCS)**

At least one solid laboratory control sample was prepared and analyzed for every group of samples digested. All laboratory control sample results and percent recovery (%R) shall be reported. The results should fall inside the control limits established by EPA or analysis must be terminated.
### Appendix D: Percent Solid

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<th>Dry Weight (g)</th>
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The figures for the percent solids were obtained using the following calculation:  
\[
\text{% solids} = \frac{\text{sample dry weight}}{\text{sample wet weight}} \times 100
\]

The percent solid measurements were calculated in order to formulate the dry weight metal concentrations of each soil sample.
REFERENCES


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