STUDIES ON THE CURING AND LEACHING KINETICS OF MIXED COPPER ORES

by

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Abstract

Heap leaching is a metal extraction process from low grade ores where crushed ore is stacked on an impermeable pad and irrigated from the top with a solution of chemical reagents. An enriched solution containing the targeted metal is collected at the bottom. This technique involves complex chemical/electrochemical reactions and transport processes. Among the main features of this method of extraction include low capital and operative cost, modularity, and relatively high inventory of solutions.

The need to optimize a heap operation has led to research studies in order to understand and interpret the chemistry and transport involved in a heap leach. These scientific investigations are focused on mathematical expressions of the reactions and transport phenomena of the minerals and reagents from the particle scale to the bulk scale. However, it was envisaged that pretreatment of these minerals are not accounted for in existing mathematical models of heap leaching. Sulfuric acid curing is a pretreatment to accelerate the extraction kinetics of copper ores and is widely used in copper operations. The curing process involves the addition of a highly concentrated sulfuric acid to the copper ore during agglomeration. Then, chemical reactions already begin prior to irrigation of the heap, transforming the initial copper species into new copper species which are easier to solubilize once the leach solution is provided to top of the heap.

The present study aims to provide a means for the systematic integration of the curing pretreatment and the subsequent leaching process. The numerical implementation of the model is done using the Matlab programming language. The focus of this curing and leaching model is to represent the leaching kinetics of each mineral species, which involves solution of a system of ordinary differential equations. The numerical parameters of the proposed curing and leaching kinetic model were found from a set of laboratory experiments. Additionally, novel methods for determining the optimum agglomeration moisture, the optimum sulfuric acid dose for acid curing, and the relevant solute transport parameters were employed. The resulting model can be applied for design, scale-up, and optimization of a new or existing commercial heap leach operation.
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Chapter 1

Introduction

Rapid depletion of low grade copper oxide ores has forced the mineral industry to treat secondary copper sulfides using the facilities already in use for oxides. Copper is typically recovered from copper oxides by heap leaching followed by solvent extraction and electro-winning (SX-EW). Additional changes to treat secondary copper sulfides include:

- Tertiary crushing to obtain smaller particle sizes than for copper oxides ores
- High permeability of heaps to allow the flow of air as well as leach solution (the air provides oxygen to oxidize secondary copper sulfide minerals such as chalcocite and covellite)
- Changes in the dose of sulfuric acid for curing pretreatment.
- Use of additional sources of ferric iron such as pregnant leach solution (PLS) from dump leaching to irrigate heaps
- Increased residence time, resulting in large solution inventories (Scheffel, 2006)
- Irrigation rinse-rest cycles and systematic reduction of irrigation flow rates to maintain a high concentration of dissolved copper in solution

Over the last two decades, these advances have been made with isolated efforts by several mining operations around the world. For instance, some operations have adopted forced aeration without previous testing. However, forced aeration of heaps has shown no statistically significant improvement in leach kinetics for ore grades less than 1.5% copper as chalcocite (Scheffel, 2006).
1.1 Problem Definition

According to the literature, there is no well established method for controlling the quality of heap permeability (Velarde 2003). The agglomeration process is practiced with no control. However, it is well known that increasing the volumetric void space of a heap enhances air flow, thus making available the large amounts of oxygen necessary for oxidative leaching, as in the case of chalcocite dissolution (Bouffard 2008).

Another important aspect of the economics of copper heap leaching is the consumption of sulfuric acid. Sulfuric acid curing is a well-established part of the heap leaching process for copper oxide ores and secondary copper sulfide ores. However, a literature survey indicates that none of the current heap leaching models considers the chemical reactions that happen during the curing process.

There is uncertainty concerning the effect of the ferric/ferrous ratio on copper solubilization during the curing process. The proper dosing of sulfuric acid during curing and the minimum rest time for adequate curing are dependent on the gangue mineralogy of each particular ore and should be determined for every particular deposit (Baum 1999).

In order to understand the heap leach chemistry of secondary copper sulfides it is necessary to study the effect of ferric/ferrous ratio applied as leaching reagent. Usually, the acidic leaching of chalcocite is conducted in the presence of ferric, which is a common oxidant in hydrometallurgical processes.

Modeling heap hydrology, solute transport and chemical kinetics depend on the particular ore properties; size distribution (particularly, the presence of fines), leaching reagent concentration, flow rate, and heap height, are among the main variables.

In summary, there is no well established method to control the agglomerate quality, the constant evaluation of sulfuric acid addition for curing process is not a common practice to optimize the consumption of this reagent, and the effect of the ferric/ferrous ratio on curing and leaching of mixed copper ores is uncertain. All these aspects play a key role in the economics and recovery of copper from mixed copper ores.
1.2 General Objective

The aim of this study is the development of an integrated mathematical model of curing and leaching of mixed copper ores in heaps based on chemical kinetics and transport phenomena (solute and fluid transport in unsaturated porous media), which could be used to improve copper extraction by optimizing the agglomerate quality (thereby maximizing heap void space) and the sulfuric acid dose for acid curing. In addition, the effect of the ferric/ferrous ratio on both curing and leaching of mixed copper ores is delineated.

1.3 Project Scope

The present study is focused on sulfuric acid curing and column leaching modeling and validation including agglomeration moisture and effects of the ferric/ferrous ratio on copper extraction from mixed copper ores. Chapter 2 presents the state of art on copper heap leaching. Chapters 3 and 4 discuss the development of the curing model and heap leach model, respectively. Chapter 5 presents the experimental methods used in this study. Chapter 6 presents the experimental results and Chapter 7 complements these results by presenting and discussing the parameters of the curing and leaching model. Finally, Chapter 8 outlines the conclusions of this study.

The first step in evaluating the leachability of an ore is chemical and physical characterization. Note that the ore provided by Barrick Zaldivar is the product of a tertiary crusher. Therefore, the present study is limited to this (relatively fine) particle size distribution. On the other hand, ore mineralogy determines the efficacy of sulfuric acid addition during agglomeration. The particle size distribution and initial moisture of the ore will determine the conditions for agglomeration and curing.

Next, the optimum agglomeration moisture is determined. The bulk density of agglomerates is measured by adding different amounts of water to the crushed ore with the objective to find the maximum void space at a certain level of compression. This compression is related to the natural decrease in height of the stacked agglomerated ore following irrigation of the heap. A maximum void space guarantees the presence of air throughout the heap and the even distribution of irrigation solution to transport the
reagents and dissolved metals. Air within the heap is necessary to provide oxygen for oxidation of secondary copper sulfides contained in the ore.

A test of water retention on agglomerated and unagglomerated ore was performed with a constant flow of 8 L/h/m² to determine the final availability of void space when leach solution occupies some of the total void space.

Once the optimum agglomeration moisture was obtained, then the optimum sulfuric acid addition for curing pretreatment could be determined. This was evaluated by adding sulfuric acid at different concentrations to the ore during agglomeration. After 7 days of rest (i.e. no irrigation) the extraction of copper during curing was evaluated by soaking the cured agglomerate in a known quantity of weakly acidic solution and measuring the dissolved copper. After that, the minimum rest time was evaluated for the curing process to fully occur. Finally, the effect of ferric during curing was determined. This was intended to promote the oxidation of secondary sulfides during curing and thereby to enhance copper extraction during curing.

Having found the optimum agglomeration moisture and the best conditions for curing pretreatment, column leaching of the pretreated ore was begun. Columns were irrigated with a constant flow of sulfuric acid solution at different ferric/ferrous ratios to evaluate the best conditions for copper recovery. In addition to the copper concentration, the ORP, pH, and the concentrations of sulfate, ferrous and ferric in the PLS were evaluated as well. These data aided the interpretation of the best conditions for leaching.

A set of agitated leaching tests at constant pH and different ferric/ferrous ratios was performed to evaluate the copper recovery and consumption of sulfuric acid at room temperature during two hours. The objective of this procedure was to corroborate the effects of the ferric/ferrous ratio on copper recovery from the column tests.

The parameters for solute transport were found experimentally from a conductivity tracer test using an inert KCl tracer solution at two different concentrations. The first solution, at a low concentration of 0.01 g/L KCl was fed to the column to obscure background conductivity noise and to remove some soluble ions. Then, a sudden change of KCl
concentration to 2.5 g/L was done to evaluate a step response in the column containing the agglomerate ore. This step response at the outlet of the column, the length of the column and different irrigating flows were used to find the longitudinal dispersivity and diffusivity parameters of this particular ore. The solution involved numerical methods for inverse modeling of the solute transport equation. These parameters are important to scale up large leaching columns or heaps.

Next, the fluid flow transport parameters were determined. Assuming the popular van Genuchten model for flow through unsaturated porous media (van Genuchten 1980), fitting parameters were found by irrigating the column at different flow rates and measuring the retained moisture in the column. Knowing the curing chemistry and the chemical kinetics of leaching, understanding the solute transport and fluid flow in unsaturated porous media is key to simulating a large scale heap.

Appendix A outlines the numerical methods employed to solve the transport equations proposed for solute transport and fluid flow in unsaturated porous media. Appendix B provides the source code used to solve the kinetics and transport equations applied to heap leach modeling. Finally, Appendix C describes the analytical chemistry procedures applied in the present study.
Chapter 2

Literature Review

This chapter presents a review of copper deposits and mineralogy as well as extraction methods with an emphasis on heap leaching of mixed copper ores. The chemistry of copper oxide and secondary copper sulfide leaching are presented. For a review of copper extraction methods, see Davenport (2004). Finally, a brief review on solute transport and fluid flow transport through unsaturated porous media is presented.

2.1 Copper Geology

2.1.1 Mineralogy

Primary copper minerals occur predominantly in veins and include chalcopyrite accompanied by pyrite. Secondary copper minerals such as chalcocite and covellite are found in the weathered zones of primary deposits. The oxide enrichment zone is located above the water table and contains copper oxides and basic copper salts.

Mixed copper ores are found in between the oxide enrichment zone and the secondary sulfide enrichment zone. Typical copper ores of this transition zone include mainly chalcocite, covellite, chrysocolla and malachite. The oxide enrichment zone includes copper oxide minerals such as cuprite and tenorite, basic copper carbonates and hydroxides such as malachite, copper silicates such as chrysocolla, and basic copper chlorides such as atacamite. Table 2.1 shows a classification of copper species (after Davenport, 2002) according to location in a vein orebody, where the mineral is disseminated within definite boundaries.

Figure 2.1 illustrates how the oxide enrichment and secondary enrichment zones are located relative to the water table (Moon et al, 2006).
Figure 2.1  Copper minerals formed by weathering of a copper sulfide vein, after Moon et al, 2006.

Table 2.1  Main mineralogical copper species by location in orebodies (Davenport 2006)

<table>
<thead>
<tr>
<th>Mineralized zone</th>
<th>Species</th>
<th>Composition</th>
<th>Copper (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary oxidized zone</td>
<td>Native copper</td>
<td>Cu</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Malachite</td>
<td>CuCO$_3$·Cu(OH)$_2$</td>
<td>57.75</td>
</tr>
<tr>
<td></td>
<td>Azurite</td>
<td>2CuCO$_3$·Cu(OH)$_2$</td>
<td>55.3</td>
</tr>
<tr>
<td></td>
<td>Chalcanthite</td>
<td>CuSO$_4$·5H$_2$O</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>Brochantite</td>
<td>CuSO$_4$·3Cu(OH)$_2$</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>Antlerite</td>
<td>CuSO$_4$·2Cu(OH)$_2$</td>
<td>53.7</td>
</tr>
<tr>
<td></td>
<td>Atacamite</td>
<td>3CuO·CuCl·3H$_2$O</td>
<td>59.5</td>
</tr>
<tr>
<td></td>
<td>Chrysocolla</td>
<td>CuO·SiO$_2$·H$_2$O</td>
<td>36.2</td>
</tr>
<tr>
<td></td>
<td>Cuprite</td>
<td>Cu$_2$O</td>
<td>88.8</td>
</tr>
<tr>
<td></td>
<td>Tenorite</td>
<td>CuO</td>
<td>79.9</td>
</tr>
<tr>
<td>Secondary enrichment zone</td>
<td>Chalcocite</td>
<td>Cu$_2$S</td>
<td>79.9</td>
</tr>
<tr>
<td></td>
<td>Digenite</td>
<td>Cu$_9$S$_5$</td>
<td>78.1</td>
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<td></td>
<td>Djurleite</td>
<td>Cu$_{1-0.95}S$</td>
<td>Variable</td>
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<tr>
<td></td>
<td>Covellite</td>
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<td>66.5</td>
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<tr>
<td>Primary enrichment zone</td>
<td>Chalcopirite</td>
<td>CuFeS$_2$</td>
<td>34.6</td>
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<td></td>
<td>Bornite</td>
<td>Cu$_5$FeS$_4$</td>
<td>63.3</td>
</tr>
<tr>
<td></td>
<td>Enargite</td>
<td>Cu$_3$AsS$_4$</td>
<td>48.4</td>
</tr>
<tr>
<td></td>
<td>Tennantite</td>
<td>Cu$_{12}$As$_4$S$_3$</td>
<td>51.6</td>
</tr>
<tr>
<td></td>
<td>Tetrahedrite</td>
<td>Cu$_{12}$Sb$<em>4$S$</em>{13}$</td>
<td>45.8</td>
</tr>
</tbody>
</table>
2.2 Copper Extraction

Approximately 80% of today’s primary copper production involves ore concentration, smelting and electrorefining to convert primary copper sulfides into high purity copper cathodes. The remaining 20% of copper production involves hydrometallurgical processing of copper oxides and secondary copper sulfides, primarily in the form of dump and heap leaching (Davenport et al., 2002).

Copper heap and dump leaching can take place over a period of months to years. Copper leaching from low grade minerals and mine waste has become an important process in the mining industry. The large quantity of mining waste and low grade copper minerals represents a valuable resource. Copper ore grades are often too low to support the high cost of grinding and agitated leaching as indicated in Figure 2.2.

![Figure 2.2 Characteristics of different leaching techniques (Kinnunen 2004)](image)

Heap leaching is applied to low grade copper oxides and secondary copper sulfides. The process typically involves mining, size reduction, agglomeration and sulfuric acid curing, raffinate irrigation on top of the heap, pregnant leach solution (PLS) collection at the bottom of the heap, solvent extraction and stripping, and electrowinning of pure copper cathodes.

The leaching of secondary copper sulfide ores has received considerable attention in recent years as a result of the general transition from oxidized to supergene mineralization. Many copper heap leaching operations began production primarily treating copper oxides. Then, as their mining pits grew deeper these operations encountered supergene enrichment zones with copper mineralization consisting primarily of secondary copper sulfides.
2.3 Selection of the Leaching Method

Heap leaching was developed for low grade dumps or waste rock and flotation tailings (Dresher, 2004). As the technology has progressed, more amenable processes have been developed. Such is the case of heap leaching or agitated leaching. Each of these methods varies in treatment cost. Therefore, as shown in figure 2.3, the mineral grade and particle size are the controlling factors in the selection of leaching process (Dresher, 2004).

![Figure 2.3 Leaching process vs. ore grade and particle size.](image)

2.4 Copper Heap Leaching

Leaching is the heart of any hydrometallurgical operation. A major factor influencing heap leaching is mineral liberation, which is related to size reduction. The presence of fine material from over-crushing of soft or friable ores adversely affects the permeability of the heap. This permeability problem is reduced by ore agglomeration. When the ore is leached without previous pretreatment the consumption of sulfuric acid is rapid and high at the beginning of the leaching process producing undesirable changes on the leach solution pH; as a consequence, basic iron salts are easily precipitated. These precipitates, predominantly jarosites, may create impermeable zones inside the heap, possibly resulting in zones where the leach solution is not able to dissolve the targeted metal. This issue is managed with acid curing.
2.4.1 Curing Chemistry

Curing is a pretreatment in which concentrated sulfuric acid is added to a crushed ore either on a belt conveyor or in an agglomerating drum to start reactions with acid soluble copper and gangue minerals. If done in rotating drums consolidates the fine material with larger particles ensuring acidification and wetting of the ore prior to stacking (Watlin 2006).

The first patent on curing was related to the cleaning of molybdenum ores from copper sulfides by adding sulfuric acid at its boiling point (Morgan, 1930). Another publication was related to the curing of uranium minerals (Smith and Garret, 1972) using 10% acid solution at 95°C. The thin layer leaching method includes acid curing prior to leaching (Johnson, 1977). This patent mentions several beneficial effects of curing, including generation of metal salt crystals that enhance bed permeability, crack generation which enhances diffusion of solutes within the ore particles and accelerates leaching, and dehydration and carbon dioxide evolution.

Farlas and co-workers (1995) have shown that copper oxides such as malachite and chrysocolla react with concentrated sulfuric acid to form copper sulfate crystals:

\[
\text{CuCO}_3 \cdot \text{Cu(OH)}_2(s) + 2\text{H}_2\text{SO}_4 + 7\text{H}_2\text{O} \rightarrow 2\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_s + \text{CO}_2(g) \quad (R2.1)
\]

\[
\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}_s + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}_s + \text{SiO}_2(s) \quad (R2.2)
\]

After the curing period, subsequent leaching with raffinate easily dissolves the copper sulfate.

The current practice of industrial heap leaching has demonstrated the advantage of acid curing. A process for ferric curing of copper sulfdides was patented by Fountain (1997) and used at Inspiration Consolidated Copper Company. The process includes the current method of leaching a heap with PLS from an associated dump leaching operation. The use of dump PLS ensures high ferric concentrations. According to Fountain, ferric curing can be conducted using more than 10 g/L of ferric.
2.4.2 Heap Leach Chemistry and Phenomena

Heap leaching of copper sulfide ore is a complex process involving several sub-processes (Dixon and Petersen, 2003). The process at the macro-scale is governed by mass and energy transport through the stacked mineral, including the flows of solution, gas and heat.

The meso-scale of heap leaching is represented by particle clusters, and involves three processes: gaseous mass transfer which is a function of temperature, bacterial growth and iron/sulfur oxidation, and intra/inter-particle diffusion.

At the scale of individual ore particles, one must consider ore particle topology, valuable metal distribution, host rock composition and pores. In low grade ores the ore matrix can interfere with chemical and biological phenomena. For instance, Petersen and Dixon (2007) had observed negative effects on the kinetics of microbial oxidation of copper secondary sulfides due to high magnesium and aluminum ions in leach solution.

Finally, at the micro-scale of a single mineral grain, metal dissolution is the product of chemical and electrochemical reactions at grain surfaces. A detailed pictorial summary of the various scales of heap leaching is shown in Table 2.2 below.

Figure 2.4 shows the effect of the copper mineralogy on the rate of copper extraction, which ranges from weeks for copper oxides to years for primary copper sulfides (Lasillo and Schlitt, 1996).
Figure 2.4  Column leaching on mineral with particle size -10 millimeters irrigated with a solution of 10 g/L H₂SO₄ and 3 g/L Fe³⁺ (Iasillo and Schlittt 1996)

Tables 2.3, 2.4 and 2.5 show the chemical reactions of the copper species and main gangue reactions (adapted from Watling, 2006 and Jansen and Taylor, 2003).
Table 2.2  Representation of the process and sub-processes involved in heap bioleaching (Dixon and Petersen 2003)

<table>
<thead>
<tr>
<th>Level</th>
<th>Sub-processes</th>
<th>Illustration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Scale</td>
<td>• Ferric/ferrous reduction&lt;br&gt;• Mineral oxidation&lt;br&gt;• Sulfur oxidation&lt;br&gt;• Surface processes</td>
<td><img src="image" alt="Grain Scale Illustration" /></td>
</tr>
<tr>
<td>Particle Scale</td>
<td>• Topological effects&lt;br&gt;• Intra-particle diffusion&lt;br&gt;• Particle and grain size distribution</td>
<td><img src="image" alt="Particle Scale Illustration" /></td>
</tr>
<tr>
<td>Cluster Scale</td>
<td>• Gas adsorption&lt;br&gt;• Particle diffusion&lt;br&gt;• Microbial growth&lt;br&gt;• Microbial attachment&lt;br&gt;• Microbial oxidation</td>
<td><img src="image" alt="Cluster Scale Illustration" /></td>
</tr>
<tr>
<td>Heap Scale</td>
<td>• Solution flow through packed bed&lt;br&gt;• Gas advection&lt;br&gt;• Water vapor transport</td>
<td><img src="image" alt="Heap Scale Illustration" /></td>
</tr>
</tbody>
</table>
### Table 2.3 Copper oxide leaching reactions (Watlin 2006)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenorite</td>
<td>( \text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Cuprite</td>
<td>( \text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{Cu} + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Copper</td>
<td>( \text{Cu} + \text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 )</td>
</tr>
<tr>
<td>Azurite</td>
<td>( \text{Cu}_2\left(\text{CO}_3\right)_2 \cdot \text{Cu}\left(\text{OH}\right)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{CuSO}_4 + 2\text{CO}_2 + 4\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Malachite</td>
<td>( \text{CuCO}_3 \cdot \text{Cu}\left(\text{OH}\right)_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{CuSO}_4 + \text{CO}_2 + 3\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>( \text{CuSiO}_3 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SiO}_2 + 3\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Atacamite</td>
<td>( 2\text{Cu}_2\left(\text{OH}\right)_3\text{Cl} + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{CuSO}_4 + \text{CuCl}_2 + 6\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Brochantite</td>
<td>( \text{CuSO}_4 \cdot 3\text{Cu}\left(\text{OH}\right)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 4\text{CuSO}_4 + 3\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Antlerite</td>
<td>( \text{CuSO}_4 \cdot 2\text{Cu}\left(\text{OH}\right)_2 + 2\text{H}_2\text{SO}_4 \rightarrow 3\text{CuSO}_4 + 4\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Chalcanthite</td>
<td>( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 5\text{H}_2\text{O} )</td>
</tr>
</tbody>
</table>

### Table 2.4 Copper sulfide leaching reactions (Watlin 2006)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcocite</td>
<td>( 5\text{Cu}_2\text{S} + 4\text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow 4\text{CuSO}_4 + 8\text{FeSO}_4 + \text{Cu}_8\text{S}_5 )</td>
</tr>
<tr>
<td>Blaubleibender</td>
<td>( \text{Cu}_6\text{S}_3 + 6\text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow 6\text{CuSO}_4 + 12\text{FeSO}_4 + 5\text{S}^\circ )</td>
</tr>
<tr>
<td>Covellite</td>
<td>( \text{CuS} + \text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow \text{CuSO}_4 + 2\text{FeSO}_4 + \text{S}^\circ )</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>( \text{CuFeS}_2 + 2\text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{S}^\circ )</td>
</tr>
</tbody>
</table>

### Table 2.5 Important gangue leaching reactions in copper heap leaching (Jansen and Taylor 2003)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>( \text{FeS}_2 + (1 - 6\beta)\text{Fe}_2\left(\text{SO}_4\right)_3 + 8\beta\text{H}_2\text{O} \rightarrow (3 - 12\beta)\text{FeSO}_4 + 8\beta\text{H}_2\text{SO}_4 + (2 - 2\beta)\text{S}^\circ )</td>
</tr>
<tr>
<td>Calcite</td>
<td>( \text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2 )</td>
</tr>
<tr>
<td>Siderite</td>
<td>( \text{FeCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{CO}_2 + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Limonite</td>
<td>( \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2\left(\text{SO}_4\right)_3 + 6\text{H}_2\text{O} )</td>
</tr>
</tbody>
</table>
2.4.3 Competitive Reactions in Copper Leaching – Gangue Leaching

When working with low grade copper minerals the reagent consumption depends mostly on gangue mineralogy. Sulfuric acid and ferric ions are consumed by gangue. The presence of pyrite and other iron sulfides in a heap generate heat and these rising temperatures during leaching helps to dissolve valuable sulfides as well (Baum, 1999).

![Lithology & Alteration Diagram]

One of the most critical aspects of copper leaching is the sulfuric acid consumption in the short and long-term. Acid consumption represents 10-25% of the operating cost (Baum 1999). Acid consumption is a function of rock type and alteration, acid consuming

Figure 2.5 Acid consumption model according to Baum (1999)

One of the most critical aspects of copper leaching is the sulfuric acid consumption in the short and long-term. Acid consumption represents 10-25% of the operating cost (Baum 1999). Acid consumption is a function of rock type and alteration, acid consuming
minerals and particle size. As shown in Figure 2.5, a mineralogical acid consumption profile was proposed by Baum (1999) based on rock type and alteration mineralogy.

### 2.4.4 Reaction Rate Control Mechanism

Table 2.6 shows a summary of the reaction rate controlling mechanisms in a general leaching process considering the reaction R2.3. The integral model is widely used in metallurgy where as the differential model has been left behind because of its complexity at the moment of numerical estimation. The main disadvantage of the integral method is that it is solved for one species at a time. The strong advantage of the differential model is that it can treat multiple chemical species at the same time, and these solutions are best for interpreting the all chemical species interactions within a leaching system.

\[
a_{A(s)} + b_{B(aq)} \rightarrow c_{C(aq)} + e_{E(s)} \quad \text{(R2.3)}
\]

**Table 2.6 Summary of reaction rate control mechanism**

<table>
<thead>
<tr>
<th>Model</th>
<th>control</th>
<th>integral</th>
<th>differential</th>
<th>( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrinking core</td>
<td>Mass transport</td>
<td>( 1 - (1 - \alpha_C) = \frac{t}{\tau_l} )</td>
<td>( \frac{d\alpha_C}{dt} = \frac{1}{\tau_l} )</td>
<td>( \tau_l = \frac{R_{p_b}}{3\alpha_{k_i}b_B} )</td>
</tr>
<tr>
<td>Shrinking core</td>
<td>Product layer diffusion</td>
<td>( 3(1 - \alpha_C)^{2/3} - 2(1 - \alpha_C) = 1 - \frac{t}{\tau_d} )</td>
<td>( \frac{d\alpha_C}{dt} = \frac{1}{2\tau_d} \frac{(1 - \alpha_C)^{2/3}}{1 - (1 - \alpha_C)^{2/3}} )</td>
<td>( \tau_d = \frac{R_{p_b}^2}{6\sigma D_{0,B} C_B^{b}} )</td>
</tr>
<tr>
<td>Shrinking core Shrinking sphere</td>
<td>Surface reaction</td>
<td>( 1 - \alpha_C = \left(1 - \frac{t}{\tau_s}\right)^3 )</td>
<td>( \frac{d\alpha_C}{dt} = \frac{3(1 - \alpha_C)^{2/3}}{\tau_s} )</td>
<td>( \tau_s = \frac{R_{p_b}}{\alpha_k f(C_B^b)} )</td>
</tr>
<tr>
<td>Shrinking sphere</td>
<td>Mass transport</td>
<td>( 1 - \alpha_C = \left(1 - \frac{t}{\tau_l}\right)^{3/2} )</td>
<td>( \frac{d\alpha_C}{dt} = \frac{3(1 - \alpha_C)^{1/3}}{2\tau_l} )</td>
<td>( \tau_l = \frac{\rho_{p_b} R^2}{32\sigma D_B C_B^{b}} )</td>
</tr>
</tbody>
</table>

General

\[
\alpha_C = \begin{cases} 
1 - \exp\left(-\frac{t}{\tau}\right) & \text{if } \varphi = 1 \\
1 - \left[1 - (1 - \varphi)\right]^{1/\varphi} & \text{if } \varphi \neq 1
\end{cases}
\]

\[
\frac{d\alpha_C}{dt} = \frac{(1 - \alpha_C)^{\varphi}}{\tau}
\]

\[
\tau = \frac{D}{k(T)f(C)}
\]

Where:

\( \alpha_B \) = mineral conversion

\( t \) = time
\[ \tau = \text{inverse temporal component} \]
\[ R = \text{radii of the grain particle} \]
\[ \rho_b = \text{bulk density} \]
\[ \sigma = \text{stoichiometric coefficient} \]
\[ k_l = \text{mass transfer constant} \]
\[ C_B = \text{leaching reagent concentration} \]
\[ D_0 = \text{effective diffusion} \]
\[ D = \text{diameter of the particle} \]
\[ K(T) = \text{Arrhenius term} \]
\[ f(C) = \text{function of concentration} \]
\[ \varphi = \text{variable exponent} \]

2.4.5 Oxidation-Reduction Potential (ORP)

Redox potential can be used to explain the stabilities of metals and other species in aqueous solutions. Each line on the Eh-pH diagram represents the condition where the activities of reactants and products of the considered reaction are in equilibrium. Figure 2.6 illustrates the Eh-pH conditions applied in industrial copper leaching.

The Pourbaix diagram is also able to explain the role of other minerals competing with copper in sulfate media. This diagram explains that copper can be dissolved from chalcocite to aqueous sulfate solution by working at pH below 4 in an oxidative media. In practice the presence of iron limits the range of pH below 2. Otherwise, at pH higher than 2 iron will precipitate. One negative effect of oxidative potential is that ferric iron precipitates as jarosite at pH higher than 2 (Watling, 2006).
2.5 Heap Leach Transport Phenomena

The characterization of large scale heap leaching process is necessary to understand not only the chemistry but also the transport of solutes along the heap height.

2.5.1 Solute Transport in Porous Media

The flow through porous media has been widely studied and many equations have been proposed. These mathematical relationships do not allow one to predict the permeability of a stacked bed of ore but delineate the factors influencing heap permeability. The advective flow through porous media is well represented by Darcy’s equation (Domenico and Schwartz 1998):

![Pourbaix diagram for the Cu-S system at 25°C, where the copper ion activity is 0.01 mol/L and other species at unity activity (Bolorunduro 1990) Fig 2.6](image)
\[ v_s = \frac{q}{A} = k \left( \frac{\Delta h}{\Delta L} \right) \]  

(2.1)

Where:

- \( v_s \) = superficial velocity
- \( q/A \) = volumetric flow / area unit
- \( \Delta h \) = head pressure differential
- \( \Delta L \) = heap height
- \( \theta \) = water content for unsaturated media, porosity for saturated media
- \( k \) = specific permeability

Another important mathematical relationship is the Kozeny-Carman equation which is valid for laminar flow regime (Re \( \leq 20 \)).

\[ v_s = \frac{q}{A} = \frac{1}{170} \frac{\Delta h \varepsilon^3}{\Delta L (1-\varepsilon)^2} \frac{(\rho_s d_p)^2}{\mu} \]  

(2.2)

Where:

- \( \varepsilon \) = superficial velocity
- \( \rho_s \) = sphericity
- \( d_p \) = particle size

\[ k \propto \frac{\varepsilon^3}{(1-\varepsilon)^2} (\rho_s d_p)^2 \]  

(2.3)

The Kozeny-Carman equation shows the importance of grain size and particle size distribution. If the particle size distribution contains a major amount of fine material, the bed permeability will decrease because the interstitial space of coarse particles will be filled with fine particles. As a consequence, the porosity \( \varepsilon \) of the bed will be small. On the other hand, if we minimize the amount of fine material the interstitial area will increase; in consequence, the porosity will be high. A way to reduce the amount of fines particle size is by agglomeration (Watling 2006).
Another phenomenon is *dispersion flow*, which is the effect of spreading some of the solution mass beyond the region it would occupy due to advection alone. There are two types of dispersion: longitudinal and transverse dispersion. Longitudinal dispersion refers to the spreading ahead of the advective front and the transverse dispersion laterally into the adjacent flow pattern (Domenico and Schwartz 1998). Figure 2.7 shows the effect of advection alone and the synergistic effect of advection and dispersion. Figure 2.8 shows longitudinal and transverse dispersion viewed at microscopic scale and includes the mathematical relationship of both types of dispersion (Appelo and Postma 2009).
A method to determine the dispersivity consists of continuously feeding a known concentration of inert tracer solution into a column of porous media and reading the concentration at the outlet of the column as shown in Figure 2.9. A tracer commonly used is potassium chloride, KCl (Appelo and Postma 2009).

Figure 2.9 Longitudinal dispersion of a tracer passing through a column of porous medium. Step-function-type tracer test and relative tracer concentration at the column exit (from Appelo and Postma 2009)
Figure 2.10  Typical dynamic heap leach operation for low grade copper oxides and secondary sulfides
Figure 2.11  Typical permanent heap leach operation for low grade copper oxides and secondary sulfides with minor amounts of primary copper sulfides
2.6 Variables Affecting Copper Heap Leaching

To understand the application of the chemical and physical principles used in a standard heap leach operation we can review two types of process. The first step is size reduction followed by agglomeration and curing. Figure 2.10 shows a flow diagram of a typical dynamic heap leach operation. This type of heap leaching method comprises two stage leaching or irrigation and uses only one lift. Figure 2.11 shows a flow diagram of a permanent heap leach operation where the ore is stacked to a determined height. After leaching, fresh ore is stacked on top of the previously irrigated lift. After solution is collected in a PLS (pregnant leach solution) pond the two processes are the same: purification by solvent extraction and copper recovery by electrowinning.

2.6.1 Mineral Liberation and Size Reduction

In general, ores are broken by blasting, crushing and grinding to give the valuable mineral gain access to the surface of the host rock. High surface exposure of the valuable mineral is positive in metal extraction processes because the extraction rate is a function of the exposed surface area. A high mineral exposure to the external surface is achieved by grinding. However, the main constraint is the energy cost of size reduction.

Leaching performance depends on the interaction of the solid, which contains the targeted metal, the associated gangue species, and the leach solution and gas phase. If we consider a bed constituted of a combination of boulders and medium-sized rocks (blasting product less than 60 cm), the aeration in this bed is probably adequate because the space caused by the heterogeneous material allows natural ventilation. At the beginning of the reaction oxygen will be consumed at the surface for oxidative processes. After some time a porous sulfur product layer on secondary copper sulfides oxidation will increase; as a result, the diffusion process will become more important. This is the case for dump leaching.

In the case of heap leaching the particles have a certain maximum size but are very small compared to dump leaching. The consequence of working with small particle sizes is the
low permeability of the bed. The heap leach optimum particle size is determined experimentally from column tests. Usually, the sizes evaluated range from 10 to 40 mm. Generally a $P_{80}$ of 6 mm or less is unacceptable because the bed permeability becomes poor (Brierley and Brierley, 1999).

The permeability of an ore bed is a critical factor for leach solution mobility. The permeability depends on particle size, grain size distribution, and stacking method. The permeability of a heap changes during the leaching process and depends on the operating conditions such as irrigation flow rate and irrigation method. For instance, “wobbler” sprinkler systems do not distribute the irrigation solution uniformly. A better approach is the use of drip lines where it is possible to ensure uniformity of irrigation by reducing the distance between emitters, and where high flow rates could saturate the heap.

2.6.2 Agglomeration and Sulfuric Acid Curing

In the early days of heap leaching where the main minerals were copper oxides, the permeability of a heap was not critical. First of all, the ore in copper oxide heaps is usually the product of a secondary crusher. This means that the maximum particle size is typically about 50 mm. This particle size does not compromise the permeability of the heap, so the heap can be operated at high flow rates to accelerate metal extraction. Since copper oxides only require sulfuric acid to be dissolved without the necessity of oxygen, oxide heaps can be more highly saturated with leach solution.

Once the oxidized copper orebody is depleted, subsequent transitional zones contain secondary copper sulfides. The dissolution of these mineral requires oxidative leaching and a small particle size because overall copper recovery in secondary sulfides is impacted by particle size (Scheffel 2006). In practice, this means the installation of a tertiary crushing stage where the maximum particle size is about 10mm. As a consequence, the generation of fine material increases thus necessitating an agglomeration stage.
Another requirement of leaching secondary copper sulfides is the presence of air to supply some oxygen to create oxidizing conditions in the leach solution. Oxygen is required by bacteria such as *acidithiobacillus ferrooxidans* to oxidize ferrous to ferric.

These two requirements of secondary copper sulfide leaching are achieved by agglomerating the tertiary crushing product. The objective of the agglomeration stage must be to maximize the porosity or void space of the heap in order to create sufficient pore space for the flow of leach solution and air. However, many industrial operations ignore this concept.

Industrial agglomeration comprises the addition of concentrated sulfuric acid and raffinate to the crushed ore in an agglomeration drum (Bouffard 2008). The addition of these two components serves to bind the finer material to the coarser particles. In addition, the highly concentrated sulfuric acid serves as a curing agent.

The addition of concentrated sulfuric acid during the agglomeration stage controls the rapid consumption of sulfuric acid typical of the first day of leaching a heap. In addition, the concentrated sulfuric acid solubilizes copper oxides exposed to the surface of the particle. However, it is not yet clear if secondary copper sulfides also dissolve during this curing stage.

Copper dissolution begins during the curing stage; the copper oxides are transformed into chalcanthite (copper sulfate pentahydrate, CuSO₄·5H₂O) by the addition of concentrated sulfuric acid. Then, during the leaching stage, the chalcanthite is easily dissolved by irrigating the heap with an acidic solution. As a consequence, the extraction kinetics are high during the first few days of leaching. This means that the curing process accelerates the leaching rate of copper ores.

2.6.3 Reagent Consumption

The major reagent consumed in heap leach operations is sulfuric acid. The consumption of this reagent depends on the host rock type, the alteration of acid consuming minerals and crushing size, as reviewed in section 2.2.3.
2.6.4 Heap Leach Aeration

Production underperformance of Girilambone Copper Company (GCC) in Australia and Compañía Minera Quebrada Blanca (CMQB) in Chile was the breaking point to adopt forced aeration to leach secondary copper sulfides. These operations recognized the role of oxygen as a critical component for leaching chalcocite. In 1996 GCC began to use forced aeration, followed by CMQB later that year as well.

GCC studied stocks of 25,000 tons with and without aeration. The grade of the mineral was 3.4% total copper as chalcocite. The results showed a dramatic increase in the conversion of ferrous to ferric and the kinetics of copper extraction. As a consequence, GCC began to install low-pressure blowers delivering 1.5 to 2 m³/h/m².

On the other hand, CMQB conducted a series of experiments, based on chemical stoichiometry including partial pyrite oxidation, to determine the amount of air necessary to create an oxidative environment in heaps. The range of aeration was estimated to be between 0.15 and 0.2 m³/h/m² for minerals containing about 1.5% total copper as chalcocite. The heap height to leach the mineral was 6 meters.

At the same time, most of these operations began to face the problem of too little leach volume and/or leaching cycle. These volumes and leach cycles based on pilot test were not accurate. As a result, nearly all operations began to double the leach solution volume and leaching time as well.

Chalcocite heap leach operations, through fear of underperformance, started employing forced-aeration without consideration of bed porosity that naturally could exist to create a convective air flow and copper grade as chalcocite.

A review of the historic production records at CMQB made by Scheffel (2006) reveals that the actual forced aeration and increment of the leach volume were done at the same time; as a consequence, it is unclear whether the forced aeration alone improved production.
Scheffel (2006) suggests that the forced aeration may be beneficial in operations where the gaseous porosity (as opposed to the liquid porosity) is marginal or when the copper grade is over 1.5% as chalcocite. For detailed information on aeration in heap leaching of secondary copper sulfides it is recommended to review the recent work of Scheffel (2006).

2.6.5 Heap Leaching Irrigation

The appropriate irrigation rate in heap leach operations depends on the mineral type. The irrigation rate for leaching secondary copper sulfides is limited essentially by the permeability of the heap. Since the dissolution of secondary sulfides is predominantly oxidative, flow is necessary to ensure the presence of oxidants such as oxygen in the gaseous phase and ferric in the aqueous phase.

The leaching of secondary sulfides is primarily oxidative, so ferric ions are essential to dissolve copper from these minerals as shown by the reactions in Table 2.4. The copper industry has adopted several methods to create an oxidative environment. Some operations use low-pressure air blowers in the bottom of the heap (Watling 2006), while others use, in addition to the above mentioned, on-off irrigation and others yet rely solely on the natural action of bacteria; all with the same purpose in mind, to create an oxidative environment.

2.7 Copper Solubility as Analysis Tool for Low Grade Copper Ores

The mineralogical analyses of low grade copper ores has certain complications. X-ray diffractometry (XRD) techniques have some technical limitations as well as costly sample preparation and equipment. As an alternative, Parkinson and Bhappu (1995) proposed a diagnostic or sequential leaching method to characterize with certain accuracy the possible copper mineralogy of a sample. This method is currently used in commercial heap leach operations to determine their possible mineralogy. Although the sequential leaching is not completely reliable, according to Baum (1999), it is unlikely that a series of lixiviants will provide a selective speciation of copper. According to Iasillo and
Schlitt (1999), the sequential leach analysis is the best approach to quantify copper oxides, secondary and primary copper sulfides when done in a sequential manner. Table 2.7 expresses the solubility of several copper species at room temperature. We can notice that not all oxides are readily soluble in sulfuric acid solutions. Secondary and primary copper sulfides are partially soluble in acid. According to Iasillo and Schlitt (1999), the sequential leach analysis is the best approach to quantify copper oxides, secondary and primary copper sulfides.

Table 2.7 Dissolution of various copper minerals in sulfuric acid and sodium cyanide solutions (adapted from Parkinson and Bhappu 1995)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Approximate Dissolution in Sulfuric Acid Solution</th>
<th>Approximate Dissolution Sodium Cyanide Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atacamite</td>
<td>Cu₂Cl(OH)₃</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Azurite</td>
<td>2CuCO₃·Cu(OH)₂</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cuprite</td>
<td>Cu₂O</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>CuSiO₃·2H₂O</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>Malachite</td>
<td>CuCO₃·Cu(OH)₂</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Native copper</td>
<td>Cu</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>Tenorite</td>
<td>CuO</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td><strong>Secondary Sulfides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu₂S</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td><strong>Primary Sulfides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu₃FeS₄</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₃</td>
<td>2</td>
<td>7</td>
</tr>
</tbody>
</table>
Chapter 3

Curing Model Development

This section presents the development of a mathematical model applied to a curing process of mixed copper ores.

3.1 General Model Assumptions

- For practical application, it is assumed that copper soluble in sulphuric acid is chrysocolla. Copper soluble in cyanide is chalcocite and the insoluble copper is chalcopyrite.

- The present model considers the curing of a mixed copper ore, where the components are as follows: chrysocolla, chalcocite, chalcopyrite, pyrite and a generalized gangue for simplification purposes.

- Sulphuric acid is consumed by copper oxides and the generalized acid-consuming gangue.

3.2 Curing Model Reactions

In the present model of acidic mixed copper ore curing the following reactions are considered:

\[
\text{CuSiO}_3 \cdot 2\text{H}_2\text{O} (s) + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O} (s) + \text{SiO}_2 (s) \quad (R3.1)
\]

\[
5\text{Cu}_2\text{S} + 4\text{Fe}_2\left(\text{SO}_4\right)_3 + 76\text{H}_2\text{O} \rightarrow 4\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 8\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{Cu}_6\text{S}_5 \quad (R3.2)
\]

\[
\text{MO} + \text{H}_2\text{SO}_4 \rightarrow \text{MSO}_4 \cdot \text{H}_2\text{O} \quad (R3.3)
\]

Where:
M = generic gangue metal ion

Reaction R3.1 represents the conversion of chrysocolla to chalcanthite by reaction with sulfuric acid. This reaction is limited by the amount of sulfuric acid which is shared with the gangue reaction R3.3. Conversion of chalcocite to chalcanthite is represented in reaction R3.2. Oxidation of other species such as second stage chalcocite or “bluableibender” Cu$_6$S$_5$ (Bb), chalcopyrite and pyrite are very slow so we are assuming that they do not occur during curing.

The reaction rate is generally expressed as the product of functions of temperature and conversion of the mineral species for integrated methods. The present model will use species concentration instead of conversion. Since the method used in the present model considers the kinetics for every species; that means solving a system of differential equations. The metal recovery will be obtained by accumulating the partial concentrations related to the initial metal.

Equation 3.1 represents the reaction rate of each individual reaction $i$ and was taken from the generalization summarized in table 2.6 (Dixon 2001) and modified to use concentrations instead of recoveries. Equation 3.2 represents the influence of the temperature of each component $i$ on the reaction rate expressed as the Arrhenius expression. Equations 3.3 to 3.5 represents the individual reaction rates of chrysocolla, chalcocite and gangue as a function of temperature and concentrations of reagents and minerals.

$$r_i = k_i(T) \cdot f_i(c_{\text{reagents}}) \cdot f_i(c_{\text{minerals}})$$  \hspace{1cm} (3.1)

$$k_i = k_{0,i} \exp \left[-\frac{E_i}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref},i}}\right)\right]$$  \hspace{1cm} (3.2)

$$r_{Cy} = k_{Cy}(T) \frac{c_{\text{Acid}}}{A_{\text{Acid}} + c_{\text{Acid}}} c_{Cy}^{\phi_{Cy}}$$  \hspace{1cm} (3.3)

$$r_{Cc} = k_{Cc}(T) \frac{c_{Fe3}}{F_{\text{Acid}} + c_{Fe2}} c_{Cc}^{\phi_{Cc}}$$  \hspace{1cm} (3.4)
\[ r_M = k_M(T) c_{\text{Acid}} \]  

(3.5)

Where:

- \( r_i \) = reaction rate of the mineral species \( i \)
- \( k_i \) = kinetic constant of the species \( i \) as a function of temperature
- \( k_{0,i} \) = kinetic constant of the species \( i \)
- \( E_i \) = activation energy of the species \( i \)
- \( R \) = ideal gas constant
- \( T_{\text{ref},i} \) = reference temperature at which \( E_i \) is given
- \( T \) = working temperature
- \( c_i \) = molar concentration of the species \( i \)

where the subscripts are:

- \( Cy \) = chrysocolla
- \( Cc \) = chalcocite
- \( \text{Acid} \) = sulfuric acid
- \( M \) = gangue
- \( \text{Fe3} \) = ferric
- \( \text{Fe2} \) = ferrous

The reaction rate proposed for chrysocolla, \( r_{Cy} \) in equation 3.3, is limited by the sulfuric acid concentration and a shrinking core exponent \( \varphi_{Cy} \). In the case of the reaction rate of chalcocite, \( r_{Cc} \), the rate is limited by the ferric/ferrous redox couple and the shrinking core exponent \( \varphi_{Cc} \). Finally the gangue reaction rate is considered to be first order with respect to acid concentration (Dixon and Petersen 2003).

### 3.3 Curing Model Speciation

The molar balances of the chemical reactions are expressed in a differential manner. The present model considers the main species in a curing reaction. Those exist in two phases: an aqueous phase and a solid phase. The aqueous phase includes sulphuric acid, ferric sulphate and ferrous sulphate. The solid species are the generated chalcanthite, and the chrysocolla, chalcocite, second stage chalcocite (or *blaubleibender*) (Bb) and gangue
present in the ore. We have chosen to ignore the gaseous phase in this model because in this work the oxidant is added in the form of ferric, and no bacteria have been added, so re-oxidation of ferrous is not expected to occur. However, in an actual bioleaching heap, accounting for the gas phase mole balances would also be necessary.

**Figure 3.1** Acid curing of mixed copper ores is a batch process

The present model attempts to model the curing process of a mixed copper ores for posterior heap leach modeling. The main product of the curing process is chalcanthite. This hydrated copper sulfate will be easily dissolved during the heap leaching stage. Once the results of the curing model are obtained, the new species can be easily incorporated into a heap leaching model, which is the subject of the next chapter.
\[
\begin{align*}
\frac{d}{dt} c_{H_2SO_4} &= -r_{Cy} - r_M \\
\frac{d}{dt} c_{Fe_2(SO_4)_3} &= -4r_{Ce} \\
\frac{d}{dt} c_{FeSO_4} &= 8r_{Ce} \\
\frac{d}{dt} c_{Ch} &= 4r_{Ce} + 4r_{Cc} \\
\frac{d}{dt} c_{Cy} &= -r_{Cy} \\
\frac{d}{dt} c_{Cc} &= -5r_{Cy} \\
\frac{d}{dt} c_{Bb} &= r_{Ce} \\
\frac{d}{dt} c_{M} &= -r_{M}
\end{align*}
\]

(3.6)

Where

- \( c_{Ch} \) = molar concentration of chalcanthite
- \( c_{Bb} \) = molar concentration of second stage chalcocite (blaubleibender)

The component rates of equation 3.6 were developed based on the stoichiometry of the chemical reactions considered for chrysocolla, chalcocite and gangue. The species of interest considered are sulfuric acid, ferric sulphate, ferrous sulfate, chrysocolla chalcanthite, chalcocite, second stage chalcocite (Bb) and gangue. The system of differential equations was solved using Matlab. The section numerical results (Table 7.5) shows the parameters found from experimental data.
Chapter 4

Leaching Model Development

This section presents the development of a column leach model for mixed copper ores including solute transport and fluid flow transport.

4.1 General Model Assumptions

The present heap leach model includes several assumptions that are explained in this chapter. First, the main assumptions are reviewed to systematically develop a heap leach model considering the species of interest for leaching mixed copper ores in heaps. Then, the chemical reactions involved in a heap leaching process containing chrysocolla, chalcanthite, chalcocite, second stage chalcocite, chalcopyrite, pyrite and gangue including aqueous oxygen are considered.

- The model considers three phases: aqueous, solid and gas. The aqueous phase contains sulfuric acid, ferric and ferrous sulfate, copper sulfate and some other metal sulfates that will not be considered because they are assumed to have little or no effect on the leaching process such as magnesium, aluminum, and other gangue metal ions.
- This model will only be considering chrysocolla which is soluble in sulphuric acid and chalcocite which is soluble in cyanide.
- This model does not consider bacterial activity. It is accepted that bacteria assist the leaching of secondary sulphides. However, the present work will consider ferrous oxidation for any future specific ore.
- The model will take the new concentrations of minerals produced in the curing model. For instance, the new amount of chalcanthite will be plugged into the leaching model as an initial value.
- The host rock is considered as one chemical species, when in reality the host rock contains several species such as silica, plagioclase, muscovite, feldspars and
biotite among the important ones (Table 6.2) The host rock, in some cases, may be a major consumer of acid.

4.2 Heap Leach Model Reactions

In the present model of heap leaching mixed copper ores the following reactions are considered:

**Copper Oxides**

\[
\text{CuSiO}_3 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SiO}_2 + 3\text{H}_2\text{O} \quad \text{(R4.1)}
\]

\[
\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 5\text{H}_2\text{O} \quad \text{(R4.2)}
\]

**Secondary Copper Sulfide**

\[
5\text{Cu}_2\text{S} + 4\text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow 4\text{CuSO}_4 + 8\text{FeSO}_4 + \text{Cu}_6\text{S}_5 \quad \text{(R4.3)}
\]

\[
\text{Cu}_6\text{S}_5 + 6\text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow 6\text{CuSO}_4 + 12\text{FeSO}_4 + 5\text{S}^\circ \quad \text{(R4.4)}
\]

**Primary Copper sulfides**

\[
\text{CuFeS}_2 + 2\text{Fe}_2\left(\text{SO}_4\right)_3 \rightarrow \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{S}^\circ \quad \text{(R4.5)}
\]

**Competitive Reactions in Copper Leaching – Gangue Leaching**

\[
\text{FeS}_2 + (1 - 6\beta)\text{Fe}_2\left(\text{SO}_4\right)_3 + 8\beta\text{H}_2\text{O} \rightarrow (3 - 12\beta)\text{FeSO}_4 + 8\beta\text{H}_2\text{SO}_4 + (2 - 2\beta)\text{S}^\circ \quad \text{(R4.6)}
\]

\[
\text{MO} + \text{H}_2\text{SO}_4 \rightarrow \text{MSO}_4 + \text{H}_2\text{O} \quad \text{(R4.7)}
\]

**Ferrous Oxidation**

\[
4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{O}_{2(\text{aq})} \rightarrow 2\text{Fe}_2\left(\text{SO}_4\right)_3 + 2\text{H}_2\text{O} \quad \text{(R4.8)}
\]

**Oxygen Dissolution**

\[
\text{O}_{2(g)} \rightarrow \text{O}_{2(\text{aq})} \quad \text{(R4.9)}
\]
4.3 Heap Leach Modeling by Species

In this section, the development of the kinetics of the reactions R4.1 to R4.9 are considered. Equation 4.1 is the expression of the chemical kinetics as a function of temperature $k_i(T)$ and concentration of minerals and reagents $f_i(c)$. Expression 4.2 is the Arrhenius equation for the activation energy. Equations 4.3 to 4.10 present the kinetic functions of concentration of the reactions considered in section 4.2. For purposes of species interaction the model is developed in a differential manner instead of the popular integral method. For this case, a shrinking core model corresponds a value of $\phi_i$ equal to 0.667.

$$r_i = k_i(T) \cdot f_i(c_{\text{reagents}}) \cdot f_i(c_{\text{minerals}})$$

(4.1)

$$k_i = k_{0,i} \exp \left[ -\frac{E_i}{R} \left( 1 - \frac{1}{T_0,i} \right) \right]$$

(4.2)

**Copper oxides: chrysocolla and chalcanthite**

$$r_{Cy} = k_{Cy}(T) \cdot \frac{c_{\text{Acid}}}{A_{Cy} + C_{\text{Acid}}} \cdot c_{Cy}^{\phi_{Cy}}$$

(4.3)

$$r_{Ch} = k_{Ch}(T) \cdot c_{Ch}^{\phi_{Ch}}$$

(4.4)

**Secondary copper sulfides: chalcocite and blaubleibender**

$$r_{Cc} = k_{Cc}(T) \cdot \frac{c_{Fe3}}{F_{Cc} + c_{Fe2}} \cdot c_{Cc}^{\phi_{Cc}}$$

(4.5)

$$r_{Bb} = k_{Bb}(T) \left( \frac{c_{Fe3}}{F_{Bb} + c_{Fe2}} \right)^{n_{Bb}} \cdot c_{Bb}^{\phi_{Bb}}$$

(4.6)

**Primary copper sulfide: chalcopyrite**

$$r_{Cpy} = k_{Cpy}(T) \left( \frac{c_{Fe3}^{n_{Cpy}}}{c_{Fe2}^{n_{Cpy}}} \right) \cdot c_{Cpy}^{\phi_{Cpy}}$$

(4.7)
Gangue: pyrite and generic gangue

\[ r_{p} = k_{p}(T) \left( \frac{c_{Fe^{3+}}}{A_{p} + c_{\text{Acid}}} \right) \left( F_{p} + c_{Fe^{2+}} \right)^{n_{p}} c_{p} \]  
\[ r_{M} = k_{M}(T) c_{\text{Acid}}^{n_{M}} c_{M}^{\phi_{M}} \]  

Ferrous oxidation due to aqueous oxygen

\[ r_{FO} = k_{FO}(T) \left( \frac{c_{\text{Acid}}}{F_{FO} + c_{\text{Acid}}} \right) c_{Fe}^{2} \cdot c_{Ox} \]  

The secondary and primary copper sulfides must be oxidized. Hence, it is necessary to consider the dissolution of oxygen gas. This is well represented by linear mass transfer and Henry’s law; Henry’s law constants are calculated using Tromans’s equation for oxygen solubility (Tromans, 2000).

Oxygen solubilization

\[ r_{Ox} = k_{L} a(\text{c}_{\text{Ox}}^{\text{sat}} - c_{Ox}) \]  
\[ c_{Ox}^{\text{sat}} = H_{Ox}(T) \cdot c_{Ox} \]  
\[ H_{Ox}(T) = \exp \left( \frac{A_{Ox} + B_{Ox}T + C_{Ox}T^{2} + D_{Ox}T \ln T}{RT} \right) \]  

Table 4.1 Constants for the solubility model of the Tromans equation (Tromans 2000)

<table>
<thead>
<tr>
<th>Gas</th>
<th>(A_{i}) [J/mol]</th>
<th>(B_{i}) [J/mol/K]</th>
<th>(C_{i}) [J/mol/K(^2)]</th>
<th>(D_{i}) [J/mol/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O_{2})</td>
<td>68,623</td>
<td>-1,430.4</td>
<td>-0.046000</td>
<td>203.35</td>
</tr>
<tr>
<td>(CO_{2})</td>
<td>72,681</td>
<td>-1,295.7</td>
<td>-0.009167</td>
<td>180.17</td>
</tr>
</tbody>
</table>
The development of the chemical kinetics for leaching mixed copper ores considers three phases: a liquid phase in continuous movement, a static solid phase, and a flowing gaseous phase. Appendix A1 demonstrates the development of the differential kinetic model. Next, the set of equations 4.14 represents the flowing aqueous phase kinetics. Then, the set of equations 4.15 expresses the dissolution or formation of solid species. Finally the equation 4.16 represents the dissolution of gaseous oxygen into the aqueous phase.

The system of equations 4.14 to 4.16 are solved using Matlab. In Chapter 7 the parameters found from experimental studies of column leaching are presented.

**Reaction rates of the aqueous phase:**

\[
\begin{align*}
    s_{\text{CuSO}_4} &= \lambda \left( e_{\text{CuSO}_4,\text{in}} - e_{\text{CuSO}_4} \right) + r_{\text{Cy}} + 4r_{\text{Cc}} + 6r_{\text{Bb}} + r_{\text{Ch}} + r_{\text{Cpy}} \\
    s_{\text{H}_2\text{SO}_4} &= \lambda \left( e_{\text{H}_2\text{SO}_4,\text{in}} - e_{\text{H}_2\text{SO}_4} \right) - r_{\text{Cy}} + 8\beta r_{\text{Py}} - r_{\text{M}} - 2r_{\text{FO}} \\
    s_{\text{Fe}_2(\text{SO}_4)_3} &= \lambda \left( e_{\text{Fe}_2(\text{SO}_4)_3,\text{in}} - e_{\text{Fe}_2(\text{SO}_4)_3} \right) - 4r_{\text{Cc}} - 6r_{\text{Bb}} - 2r_{\text{Cpy}} - (1 + 6\beta)r_{\text{Py}} + 2r_{\text{FO}} \\
    s_{\text{FeSO}_4} &= \lambda \left( e_{\text{FeSO}_4,\text{in}} - e_{\text{FeSO}_4} \right) + 8r_{\text{Cc}} + 12r_{\text{Bb}} + 5r_{\text{Cpy}} + (3 + 12\beta)r_{\text{Py}} - 4r_{\text{FO}}
\end{align*}
\] (4.14)
Reaction rates of the solid phase:

\[ s_{Cy} = -r_{Cy} \]
\[ s_{Cc} = -5r_{Cy} \]
\[ s_{Bb} = r_{Ce} - r_{Bb} \]
\[ s_{Ch} = -r_{Ch} \]
\[ s_{Cpy} = -r_{Cpy} \]
\[ s_{Py} = -r_{Py} \]
\[ s_{M} = -r_{M} \]

\( (4.15) \)

Reaction rates of the gaseous phase:

\[ s_{Ox} = \lambda (c_{Ox,in} - c_{Ox}) + r_{Ox} \]

Where the source term is the reaction rate of each species \( i \) (Ogbonna et al 2005):

\[ s_i = \frac{dc_i}{dt} \]

\( (4.17) \)

4.4 Heap Leach Solute Transport

Heap leaching is a process where a porous ore bed is unsaturated in leach solution and the irrigation flow is applied to the top of the heap and collected from the bottom of the heap. This led us to the use of the solute transport equation for unsaturated porous media (Smith 2009, Ogbonna et al. 2005).

\[ \frac{\partial}{\partial t} (\theta c_i) = \frac{\partial}{\partial z} \left[ \theta D_L \frac{\partial}{\partial z} c_i - \theta v c_i \right] - s_i \]

\( (4.18) \)

Where:

\[ c_i = \text{concentration of the species } i \]
\[ \theta = \text{water content} \]
\[ v = \text{superficial velocity} \]
\[ D_L = \text{dispersion-diffusion term} \]
\[ z = \text{spatial component} \]
\[ t = \text{temporal expression} \]
\[ s_i = \text{source term of the species} \ i \]

This 1D solute transport equation considers the advective flow and the dispersion diffusion effect. Appendix A2 presents the origin of the transport equation and the numerical solution using the method of finite volume. Appendix A2 also provides with complete detail the application of the power law schema (Patankar 1980) with central dispersion and forward advection. The temporal term is solved using the implicit schema where the solution is found by solving an equation involving both the current state of the system \( y(t) \) and the later one \( y(t+\Delta t) \) and have a better convergence for stiff problems (Versteeg and Malalasekera 1995).

The source term \( s_i \) is the concentration of each species \( i \) considered in the reaction rate. The irrigation rate is related to superficial velocity \( \upsilon \). For scaling-up purposes a tracer test is fundamental to determine the dispersivity of the specific mineral at certain condition of agglomeration. This tracer test is discussed in chapter 7.

According to Bear (1972), the dispersivity value may be represented with a linear function of superficial velocity \( \upsilon \):

\[ D_L = \alpha_L \upsilon + D_0 \]  \hspace{1cm} (4.19)

Where:

\[ D_L = \text{longitudinal dispersion term} \]
\[ \alpha_L = \text{longitudinal dispersivity} \]
\[ \upsilon = \text{superficial velocity} \]
\[ D_0 = \text{bulk diffusivity} \]

### 4.5 Heap Leach Fluid Transport

The dynamic equation of fluid transport in unsaturated porous media is presented in Equation 4.18. This equation represents the flow of solutions through a heap of agglomerated ore, which contains aqueous, solid and gaseous phases. The Richards
equation expressed as a function of pressure head is presented in Equation 4.19, and relates the local water content of a porous medium to the local gravitational and capillary pressure head.

\[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[ k \frac{\partial}{\partial z} h \right] \quad (4.20)
\]

\[
S(p)\frac{\partial}{\partial t} p = \frac{\partial}{\partial z} \left[ k \left( 1 + \frac{\partial}{\partial z} p \right) \right] \quad (4.21)
\]

The water content is calculated using the equation proposed by van Genuchten (1980). Equations 4.20 to 4.23 are necessary to compute the fluid flow at the beginning of irrigation. Once a steady state is attained the water content is constant.

The pressure head value is positive for saturated porous media, and negative for unsaturated porous media.

\[
\theta = \begin{cases} 
\varepsilon & p \geq 0 \\
\theta_r + (\varepsilon - \theta_r)S_e & p < 0 
\end{cases} \quad (4.22)
\]

\[
S_e = \frac{\theta - \theta_r}{\varepsilon - \theta_r} = \frac{1}{1 + (-\alpha p)^a} \quad (4.23)
\]

\[
\frac{\partial \theta}{\partial p} = S(p) \equiv \begin{cases} 
10^{-20} & p \geq 0 \\
\frac{(\varepsilon - \theta) n \cdot m \cdot a (-\alpha p)^a}{1 + (-\alpha p)^a} & p < 0 
\end{cases} \quad (4.24)
\]

\[
k = \begin{cases} 
k_s & p \geq 0 \\
k_s \sqrt{S_e} \left[ 1 - \left( 1 - S_e^{1/m} \right)^{m+1} \right]^2 & p < 0 
\end{cases} \quad (4.25)
\]

Where:

\[
h = \text{hydraulic head [m]}
\]

\[
p = \text{pressure head [m]}
\]
\( \varepsilon = \) porosity \([\text{m}^3\text{void/m}^3\text{soil}]\)

\( \theta = \) water content or volume liquid fraction \([\text{m}^3\text{liq/m}^3\text{soil}]\)

\( \theta_r = \) residual water content \([\text{m}^3\text{liq/m}^3\text{soil}]\)

\( a, m, n = \) fitting parameters

\( k = \) hydraulic conductivity \([\text{m/h}]\)

\( k_s = \) saturated hydraulic conductivity \([\text{m/h}]\)

\( k_r = \) relative unsaturated hydraulic conductivity

\( S_e = \) effective saturation

\( S = \) water capacity storage \([\text{1/m}^3]\)
Chapter 5

Experimental

This chapter explains the laboratory techniques used to obtain the necessary data for every stage of the present research. The various test procedures were systematically designed to determine optimum values and recognize the effects of reagents and their consumption.

5.1 Experimental Objectives

- Determine the optimum agglomeration moisture
- Determine the optimum sulfuric acid curing dose
- Determine the effect of the raffinate ferric/ferrous ratio on the curing process
- Determine the effect of the raffinate ferric/ferrous ratio on leaching kinetics

The experimental program developed for this study can be divided into five phases:

- Physical and chemical characterization of the mineral sample
- Optimum agglomeration moisture
- Optimum sulfuric acid curing dose
- Ferric effect on acid curing
- Acid consumption test for different ferric/ferrous ratios
- Column leaching

5.2 Sequential Leaching Analysis

A sequential leaching analysis was conducted according to Parkinson and Bhappu (1995) to determine the amount of copper soluble in acid and copper soluble in cyanide. From these results, one can roughly estimate the amount of copper oxide and secondary copper sulfide present in the mineral.
Figure 5.1  Schematic representation for the copper solubilization test: Copper soluble in acid and copper soluble in cyanide

For the copper soluble in acid test, 0.5 gram of sample ground to −150 mesh was used. This sample was leached at 25°C for one hour in a 250 mL shake flask with 15 mL of sulfuric acid 5%. Then, the filtered solution was diluted to 500 mL and analyzed for copper by atomic absorption spectroscopy.
The washed residue was used for the copper soluble in cyanide test. The residue was leached with 50 mL of sodium cyanide 5% for 30 minutes at 25°C. Finally, the filtered solution was diluted to 100 mL and analyzed for copper.

5.3 Agglomeration Moisture

The objective of the agglomeration stage is to improve the permeability of the ore bed. In other words, to increase the amount of void space in the stacked ore in order to improve the flow of irrigating solutions and air for oxidation.

Figure 5.2 Flow and circuit diagram to measure the current through agglomerate.
The natural moisture of the ore was obtained by taking three representative samples of 1 kg each. These were dried for 24 hours in an oven at 100°C. The average moisture was found to be 3.09% by difference.

On the other hand, the ore specific gravity was calculated in a graduated cylinder by adding 250 mL of deionized water and 300 g of ore. From the mineral weight and the water displacement the ore density was found to be 2.53 g/cm³.

Agglomeration was achieved by rolling the ore sample on a flexible plastic sheet. First, a determined amount of ore is weighed and placed on a square of plastic sheet. Then, raffinate and concentrated sulfuric acid are spread on the ore and finally a total of 20 rolling movements are done: 10 rolling east-west and 10 north-south.

A modified bulk density measurement was used to find the optimum moisture for agglomeration. This method measures the bulk density after compression of the agglomerate, and then the void space is calculated by difference assuming the specific gravity of the ore is known.

Different amounts of water (to obtain 6, 8, 9, 10, 11 and 13 % water content) were added independently to 300 g of ore. Then, the sample was agglomerated and poured into a plastic tube of 6 cm of diameter and 10 cm height. Next, each agglomerate sample was compressed with a pressure of 0.41 kg/cm² and finally the volume was measured to estimate the modified bulk density. The sample compression attempts to simulate the compaction of the heap when irrigation is applied. It is clear that this value of pressure is relative to a specific ore. The value applied here was taken from previous work of Velarde (2003).

Additionally, the tube was equipped with two electrodes of stainless steel 316. These electrodes were used to measure the current passing through the compressed agglomerate by applying 5 volts DC in all cases. This current can be used to estimate indirectly the moisture of the agglomerate industrially in heap leach operations. It should be clarified that the relationship of void space to current measured across the agglomerated ore in this
study is relative to the dimensions of the container and the electrodes as well as the pressure applied.

This modified bulk density (since the sample is compacted) was used to estimate the void space of the agglomerate. The water content (by addition) that creates the larger void space is the optimum agglomeration moisture as shown in Figure 6.4.

Figure 5.3    Experimental setup to measure the agglomerate quality

5.4    Water Content or Dynamic Moisture Retention

Moisture retention is an important parameter especially for oxidative heap leaching processes. Moisture retention is the amount of water retained at a certain irrigation rate when flow reaches steady state. The water content during irrigation is used to estimate the optimum irrigation rate of a leach solution. This water retention especially for oxidative leach processes is very important for the proper distribution of leach solution and air flow through the porous media.
Water retention is a function of agglomerate quality; in other words, the higher the void space in the agglomerate, the lower the water retention. As a result, the rest of the void space is filled with air which is favorable for oxidative processes.

Two tests were designed to demonstrate the effect of agglomeration on the water retention of the packed bed. These tests were done at a constant irrigation rate of 8 L/h/m². In the first case, the sample was not agglomerated and in the second case it was, with the optimum agglomerate moisture determined as described in section 5.3 and showed in Figure 6.4. In each test 1 kg of representative ore was used.

![Diagram](image)

**Figure 5.4** Experimental setup to measure the dynamic moisture of the mineral
The experimental set up (Figure 5.4) included a column of 10 cm diameter mounted on a scale connected to a data acquisition system to register the variation in weight. Each test was run for 50 hours.

### 5.5 Optimum Sulfuric Acid Curing Dose

Since the mineral sample contains primarily copper oxides and secondary copper sulfides, it is common industrial practice to accelerate copper dissolution by adding concentrated sulfuric acid to the ore during agglomeration. The resulting agglomerates are stacked in heaps and allowed to rest so that the curing process can occur. Figure 5.5 shows the agglomerates obtained from the Zaldivar ore on the left side, and the right side shows the soaking of the agglomerates in 1 g/L of sulfuric acid solution for later filtering and washing.

![Figure 5.5](image.png)

**Figure 5.5** Zaldivar’s mixed copper agglomerate cured for 7 days and soaked for 30 minutes then washed, producing a filtrate for chemical analysis.

Figure 5.6 shows the flow diagram of the agglomeration evaluation method. This experiment was done using 500 g of representative sample. Then, different acid doses
were added to reach: 5.5, 11.0, 16.5, 22.0, 27.5 and 33.0 kg of sulfuric acid per ton of ore. Next, the sample was rolled on a flexible plastic sheet as described in section 5.3 to obtain agglomerates of each sample. Synthetic raffinate was used to complete the optimum agglomerate moisture found as described in section 5.4. The synthetic raffinate was prepared with a chemical composition of 5 g/L of sulfuric acid and 2.5 g/L of total iron with a ferric/ferrous ratio of 1/1. The curing time was fixed to seven days.

After curing, each sample was washed with 750 mL (1.5 times the ore weight) of solution containing 1 g/L of sulfuric acid for 30 minutes. Next, a final wash was done with 250 mL solution 1 g/L sulfuric acid. The total wash solution was analyzed for copper, total iron, ferrous iron and sulfuric acid concentration, and the pH and ORP were measured.

The optimum sulfuric acid curing dose is determined using a graph showing the dose of H₂SO₄ per ton of mineral vs. copper extraction after soaking and washing the cured agglomerate. Figure 6.6 shows that there is no significant influence of acid dose on copper extraction when applying more than 15 kg/t of sulfuric acid.
Figure 5.6  Agglomeration evaluation method

5.6 Ferric Effect on the Curing Stage

Since the mineral sample in this study contains secondary sulfides it was decided to run a test to evaluate the oxidative effect of ferric ion on the curing process. It is well known that chalcocite and covellite are readily dissolved in oxidative media.
Five 500-g samples were agglomerated with the optimum curing dose of sulfuric acid (16.49 kg/t) and different amounts of ferric sulfate dissolved in the synthetic raffinate. The amount of synthetic raffinate was calculated from the optimum agglomeration moisture taking into account the volume of the optimum sulfuric acid added to the ore samples.

The synthetic raffinate was prepared with 5 g/L sulfuric acid and 1.25 g/L ferrous. The amount of ferric was varied from 5 to 133 g/L.

After seven days the agglomerate samples were washed for 30 min in a solution of 750 mL with 1 g/L of sulfuric acid concentration. Then, a final washing of the samples was done during filtering with 250 mL of solution containing 1 g/L of sulfuric acid. The total amount of solution was analyzed for copper, total iron, ferrous and sulfuric acid concentrations.

5.7 Curing Kinetics

The curing kinetics test was done to estimate the time necessary to rest the agglomerate to complete the curing reactions. The test was done by using several 500-g samples of ore agglomerated with the “optimum curing dose” of 16.49 kg/ton sulfuric acid. The optimum agglomerate moisture of 10 % was completed with synthetic raffinate described in section 5.5 above.

The samples were washed as described in section 5.5 above, then analyzed for copper, total iron, ferrous and sulfuric acid concentrations.

5.8 Acid Consumption Test and Ferric/Ferrous Effect on Copper Extraction

An acid consumption test at constant pH and different ferric/ferrous ratios was designed to study the potential sulfuric acid consumption and influence of the ferric/ferrous ratio on copper extraction.
A 300-mL jacketed reactor equipped with pH and ORP probes was used. For pH regulation, a loop control was established using an Applikon controller ADI-130 and a peristaltic pump to provide sulfuric acid to keep a constant pH. In addition, a data acquisition system was used to register the pH, ORP, temperature and weight of the scale containing the sulfuric acid solution.

The procedure for this test started with pouring 100 mL of deionized water into the jacketed reactor. Once the desired temperature was reached (in all the cases 25°C), the pH was then maintained to the desired level and the ferric and ferrous sulfate were added to the reactor. After complete dissolution of the ferric and ferrous sulfate, 50 g (33% solid content) of ore ground to −150 mesh was poured into the reactor.

After three hours of agitated leaching, the pulp was filtered and washed with deionized water. Then, the entire solution was diluted to 250 mL and analyzed for copper, total iron, ferrous and sulfuric acid concentrations.

Figure 5.7 shows the piping and instrument diagram (P&ID) of the experimental setup for determining the influence of acid addition and the ferric/ferrous ratio on copper extraction where TI stands for temperature indicator, AI analysis indicator which in this case is ORP, AIC stands for analysis indicator and controller of pH where the set point SP in entered in the instrument. All this is installed in a panel box which is indicated by the square box. The TE temperature element, AE analysis element (ORP) and AE (pH) are installed in the reactor. A PC is used to acquire the data from the controller via serial RS232 port. The acid consumption is measured by a scale using the differential weight and recorded via serial port in a PC. A water bath equipped with a temperature indicator controller (TIC) was used as well to keep the jacketed reactor at the desired temperature.
Figure 5.7  Experimental set up for acid consumption and ferric/ferrous influence in copper extraction of the Zaldivar ore grounded 100% −150 mesh maintaining constant pH of 1 and 2 with ferric/ferrous ratios of 1/9, 1/3, 1/1, 3/1, 9/1 at room temperature and agitated at 500 rpm for 3 hours
5.9 Column Leaching Test

Once the optimum agglomeration moisture (section 5.3), the optimum sulfuric acid curing dose (section 5.5) and the minimum resting time for curing were determined, a set of nine experiments were designed to evaluate the effect of the ferric/ferrous ratio of the synthetic raffinate on the kinetics of copper extraction and later validation of the proposed mathematical model of curing and leaching in Chapters 3 and 4, respectively.

Figure 5.8 shows the experimental set up of the column test to evaluate the ferric/ferrous iron effect on copper recovery and validate the proposed curing-leaching model on this study. Figure 5.9 presents the flow diagram used to implement the column leach test showing the conditions used in the present study.
Figure 5.9  Column test leaching procedure and set up.

1.2 kg of sample was agglomerate in each case with sulfuric acid according to Table 5.1 and adjusted to the optimum agglomeration moisture (10%) with synthetic raffinate containing 10 g/L of sulfuric acid and 5 g/L of total iron with ferric/ferrous ratios as shown in Table 5.1.
The feed ore was 100% −1 cm. The irrigation rate was fixed at 8 L/h/m² by using peristaltic pumps. The agglomerate was cured for five days in each column of 6 cm diameter and 20 cm height.

The pregnant leach solution (PLS) was collected in the bottom of each column and analyzed for copper, total iron, ferrous and sulfuric acid concentrations, and the pH and ORP were measured.

### Table 5.1  Experimental conditions

<table>
<thead>
<tr>
<th>Column</th>
<th>Curing H₂SO₄ (kg/t)</th>
<th>Raffinate Fe³⁺/Fe²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>12.37</td>
<td>1/3</td>
</tr>
<tr>
<td>C2</td>
<td>12.37</td>
<td>3/1</td>
</tr>
<tr>
<td>C3</td>
<td>15.11</td>
<td>1/9</td>
</tr>
<tr>
<td>C4</td>
<td>15.11</td>
<td>1/3</td>
</tr>
<tr>
<td>C5</td>
<td>15.11</td>
<td>1/1</td>
</tr>
<tr>
<td>C6</td>
<td>15.11</td>
<td>3/1</td>
</tr>
<tr>
<td>C7</td>
<td>15.11</td>
<td>9/1</td>
</tr>
<tr>
<td>C8</td>
<td>18.32</td>
<td>1/3</td>
</tr>
<tr>
<td>C9</td>
<td>18.32</td>
<td>3/1</td>
</tr>
</tbody>
</table>

### 5.10 Tracer Test

A tracer test was necessary to determine the dispersion coefficients of this particular sample of Zaldivar ore after optimum agglomeration. The main objective of this test was to determine the longitudinal dispersivity and van Genuchten parameters for fluid flow transport, simultaneously.
Figure 5.10  Tracer test leaching procedure

Figure 5.10 describes the procedure used to trace the solute transport using KCl. The test was done using 8 kg of ore with about 3% humidity and agglomerated with water reaching the optimum agglomeration moisture of 10%. The agglomerate was placed in column of 8.6 cm diameter and 1 m height on top of a digital scale.

A solution of 0.1 g/L KCl was used to provide the background electrical conductivity of the agglomerate sample. Once a constant conductivity was reached at the outlet of the column the solution was changed to 2.5 g/L KCl thus creating the step change source for the study of the dispersivity by registering the outlet concentration.
KCl solution was used because it is conductive and relatively non-reactive. The outlet conductivity was measured with a flow-through conductivity probe and registered in a data acquisition system (Campbell Scientific CR1000). At the same time, the weight of the column was registered in a custom made spreadsheet programmed to acquire the weight from an Ohaus digital scale via serial port in order to track the water content.

The test was developed for three different irrigation rates: 6, 8 and 12 L/h/m². The variation in fluid flow means a variation in the advection or superficial velocity to calculate an accurate longitudinal dispersion factor. Figure 5.11 shows the elements used for the solute transport tracer test. Note the column is on top of a scale to measure the amount of retained solution at different irrigation rates for fluid flow studies.

Figure 5.11  Tracer test leaching setup
Chapter 6

Results and Discussion

This section describes and discusses the results of the curing and leaching experiments on mixed copper ores for later numerical analyses.

6.1 Physical and Chemical Characterization

After coning and quartering the whole ore sample, 8 kg was sieved and the results are presented in the Table 6.1 and a plot of the partial and cumulative fraction is shown in Figure 6.1. The Rosin Rammler cumulative distribution and probability density functions are defined in Equations 6.1 and 6.2, respectively.

\[
F(\xi) = 1 - \exp\left(-\xi^m\right) \quad (6.1)
\]

\[
f(\xi) = m\xi^{m-1}\exp\left(-\xi^m\right) \quad (6.2)
\]

With \( \xi = \frac{D}{D^*} \) \quad (6.3)

Where \( m \) is a dimensionless parameter and \( D^* \) is the normalizing size.

The P80 was found to be 4.12 mm. The mean was \( \mu = 2.56 \) mm, the variance \( \sigma^2 = 8.01 \), the \( CV^2 = 1.22 \), \( m = 0.907 \), and \( D^* = 2.45 \) mm. Figure 6.1 reveals that this particular sample has a relatively high amount of fines. As a result, this ore may have very low permeability without pretreatment. An agglomeration stage would be necessary to treat this ore in heaps.
Table 6.1  Particle size distribution (PSD) of the Zaldivar ore sample

<table>
<thead>
<tr>
<th>Passing (g)</th>
<th>D (mm)</th>
<th>data $F(D)$</th>
<th>$\Delta \mu$</th>
<th>$(D-\mu)^2$</th>
<th>$\Delta CV^2$</th>
<th>Rosin $F(D)$</th>
<th>Rosin $f(D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>151.4</td>
<td>0.000</td>
<td>0.0185</td>
<td>0.00</td>
<td>6.57</td>
<td>0.52</td>
<td>0.000</td>
<td>0.5133</td>
</tr>
<tr>
<td>658.4</td>
<td>0.053</td>
<td>0.099</td>
<td>0.01</td>
<td>6.30</td>
<td>0.82</td>
<td>0.030</td>
<td>0.4914</td>
</tr>
<tr>
<td>1077.6</td>
<td>0.075</td>
<td>0.231</td>
<td>0.01</td>
<td>6.19</td>
<td>0.36</td>
<td>0.042</td>
<td>0.3882</td>
</tr>
<tr>
<td>523.7</td>
<td>0.300</td>
<td>0.295</td>
<td>0.03</td>
<td>5.12</td>
<td>0.30</td>
<td>0.138</td>
<td>0.3195</td>
</tr>
<tr>
<td>551.0</td>
<td>0.600</td>
<td>0.362</td>
<td>0.09</td>
<td>3.85</td>
<td>0.28</td>
<td>0.244</td>
<td>0.2368</td>
</tr>
<tr>
<td>796.3</td>
<td>1.180</td>
<td>0.460</td>
<td>0.20</td>
<td>1.91</td>
<td>0.11</td>
<td>0.403</td>
<td>0.1402</td>
</tr>
<tr>
<td>931.5</td>
<td>2.380</td>
<td>0.574</td>
<td>0.35</td>
<td>0.03</td>
<td>0.04</td>
<td>0.623</td>
<td>0.0949</td>
</tr>
<tr>
<td>994.6</td>
<td>3.360</td>
<td>0.695</td>
<td>0.26</td>
<td>0.63</td>
<td>0.18</td>
<td>0.736</td>
<td>0.0562</td>
</tr>
<tr>
<td>531.2</td>
<td>4.750</td>
<td>0.760</td>
<td>0.61</td>
<td>4.78</td>
<td>0.82</td>
<td>0.839</td>
<td>0.0412</td>
</tr>
<tr>
<td>961.1</td>
<td>5.600</td>
<td>0.878</td>
<td>0.55</td>
<td>9.22</td>
<td>1.56</td>
<td>0.880</td>
<td>0.0177</td>
</tr>
<tr>
<td>655.9</td>
<td>8.000</td>
<td>0.958</td>
<td>0.21</td>
<td>29.56</td>
<td>1.15</td>
<td>0.947</td>
<td>0.0060</td>
</tr>
<tr>
<td>179.8</td>
<td>11.200</td>
<td>0.980</td>
<td>0.24</td>
<td>74.59</td>
<td>1.87</td>
<td>0.981</td>
<td>0.0031</td>
</tr>
<tr>
<td>162.9</td>
<td>13.200</td>
<td>1.000</td>
<td>113.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.1  Cumulative particle size distribution of the Zaldivar ore sample
6.1.1 XRD Analysis

X-ray diffraction analysis of the ore sample shows that this mixed copper ore contains around 0.5% of chalcopyrite. Chalcocite, covellite and copper oxide concentrations were not detected during this analysis. A summary of the mineralogy is shown in Table 6.2 where the major gangue mineral is quartz. Another important mineral is pyrite which is a potential ferric iron consumer and source of sulfuric acid.

Table 6.2  XRD analysis of the Zaldivar ore sample.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>28</td>
</tr>
<tr>
<td>Clinohlore</td>
<td>(Mg,Fe$^{2+}$)$_5$Al(Si$<em>3$Al)O$</em>{10}$(OH)$_8$</td>
<td>6.2</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl$_2$(AlSi$<em>3$O$</em>{10}$)(OH)$_2$</td>
<td>20.2</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg,Fe)$_3$(AlSi$<em>3$O$</em>{10}$)(OH)$_2$</td>
<td>3.3</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>NaAlSi$_3$O$_8$ – CaAl$_2$Si$_2$O$_8$</td>
<td>25</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>KAlSi$_3$O$_8$</td>
<td>9.1</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO$_4$·2H$_2$O</td>
<td>3</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>0.6</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
<td>4.1</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS$_2$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

6.1.2 Copper Distribution According to Particle Size Distribution

From the sieved sample a chemical analysis was performed for every fraction retained and the results are shown in Table 6.3 and Figure 6.2. The weighted average copper grade was estimated to be 0.88% Cu. The major amount of copper was found to be between the particle sizes of 75 and 300 μm corresponding to 23% of the total copper contained in this ore.
Table 6.3  Copper distribution of the Zaldivar sample.

<table>
<thead>
<tr>
<th>D (mm)</th>
<th>Mass (g)</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>151.40</td>
<td>1.26%</td>
</tr>
<tr>
<td>0.053</td>
<td>658.40</td>
<td>1.36%</td>
</tr>
<tr>
<td>0.075</td>
<td>1077.60</td>
<td>1.56%</td>
</tr>
<tr>
<td>0.300</td>
<td>523.70</td>
<td>1.26%</td>
</tr>
<tr>
<td>0.600</td>
<td>551.00</td>
<td>0.90%</td>
</tr>
<tr>
<td>1.180</td>
<td>796.30</td>
<td>0.76%</td>
</tr>
<tr>
<td>2.380</td>
<td>931.50</td>
<td>0.78%</td>
</tr>
<tr>
<td>3.360</td>
<td>994.60</td>
<td>0.62%</td>
</tr>
<tr>
<td>4.750</td>
<td>531.20</td>
<td>0.62%</td>
</tr>
<tr>
<td>5.600</td>
<td>961.10</td>
<td>0.55%</td>
</tr>
<tr>
<td>8.000</td>
<td>655.90</td>
<td>0.38%</td>
</tr>
<tr>
<td>11.200</td>
<td>179.80</td>
<td>0.41%</td>
</tr>
<tr>
<td>13.200</td>
<td>162.90</td>
<td>0.79%</td>
</tr>
<tr>
<td>Total</td>
<td>8175.40</td>
<td>0.88%</td>
</tr>
</tbody>
</table>

Figure 6.2  Copper distribution according to particle size
6.1.3 Sequential Copper Solubility Analysis

The sequential copper solubility test performed to the head sample shows that 55% of the copper is soluble in cyanide which suggest a high content of copper as secondary sulfides. 30% of the copper in this ore is insoluble, suggesting the presence of primary sulfides. Finally, 15% copper is soluble is acid which suggest the presence of copper oxides.

![Image of copper solubility analysis]

Figure 6.3 Average copper solubility with sulfuric acid and sodium cyanide

6.2 Agglomeration Moisture

According to Figure 6.4, the optimum agglomerate moisture was found to be about 10% with a maximum void space of 43.5%. The values are shown in Table 6.4. In addition, electrical conductivity was measured to demonstrate that in the field it would be of benefit just to measure the conductivity instead of the bulk volume (Velarde 2003).
Table 6.4  Moisture and porosity of the Zaldivar sample.

<table>
<thead>
<tr>
<th>moisture (%)</th>
<th>bulk density (g/cm³)</th>
<th>current (mA)</th>
<th>void space</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.19%</td>
<td>1.80</td>
<td></td>
<td>28.64%</td>
</tr>
<tr>
<td>6.00%</td>
<td>1.61</td>
<td>0.13</td>
<td>36.45%</td>
</tr>
<tr>
<td>8.00%</td>
<td>1.51</td>
<td>0.28</td>
<td>40.19%</td>
</tr>
<tr>
<td>9.00%</td>
<td>1.47</td>
<td>0.44</td>
<td>41.90%</td>
</tr>
<tr>
<td>10.00%</td>
<td>1.43</td>
<td>0.93</td>
<td>43.51%</td>
</tr>
<tr>
<td>11.00%</td>
<td>1.56</td>
<td>1.40</td>
<td>38.37%</td>
</tr>
<tr>
<td>13.00%</td>
<td>1.63</td>
<td>2.30</td>
<td>35.44%</td>
</tr>
</tbody>
</table>

Figure 6.4  The void space reaches its highest value at 10% of water content in the agglomerate.
The moisture retention or water content for the agglomerate case was 13.01% which gives us a value of 30.50% of void space for air flow at a solution flow rate of at 8 L/h/m². For the non-agglomerate case 15.30% was the moisture retention with 13.34% of void space at the same flow rate. Clearly, the agglomeration helps to create more free void space for air flow.

6.3 Sulfuric Acid Curing Dose

The curing process was studied under experimental conditions presented in section 5.5; 500 g of ore were agglomerated to reach a total water content of 10% (the natural water content was 3%, Table 6.4) including the synthetic raffinate and concentrated sulfuric
acid. The synthetic raffinate contained 10 g/L sulfuric acid and 5 g/L total iron with a ferric/ferrous ratio of 1/1.

![Figure 6.6](image)

**Figure 6.6** Copper recovery as a function of sulfuric acid curing dose at 10% water content (total moisture), 5 g/L total iron with ferric/ferrous ratio 1, after 7 days curing.

Figure 6.6 shows us that the optimum sulfuric acid curing dose is about 15 kg/ton. After this point, additional copper recovery from curing is insignificant. The wash solution of each cured sample with different sulfuric curing doses confirms that after 15 kg/ton of sulfuric acid there is no appreciable consumption of this reagent, as shown in Figure 6.7.

Figure 6.7 shows the copper species distribution as copper soluble in acid, copper soluble in cyanide, and insoluble copper in the feed, and the cured and washed agglomerates. About 7.4% of the copper originally soluble in cyanide in the feed became soluble in acid after curing. Furthermore, about 8% of the insoluble copper in the feed became soluble in acid after curing, rendering a total of about 31% of the total copper soluble in acid after acid curing. After the agglomerate was washed, about 25% of the total copper content
was removed and the resulting copper distribution is similar to the cured agglomerate in terms of insoluble copper and copper soluble in cyanide.

![Copper distribution chart](image)

**Figure 6.7 Copper solubility comparison on feed, agglomerate and residue**

### 6.4 Ferric Effect on the Curing Stage

Figure 6.8 suggests the ferric iron concentration has only a minor effect on copper dissolution during the curing process. About 23% of copper extraction is due to the concentrated sulfuric acid addition with 2.5 g/L of ferric iron. Even 70 g/L of ferric in the raffinate solution for curing increase copper recovery by only 3%.

In summary, the oxidant effect of the ferric is relative unimportant during the curing process for mixed copper ores. The cause of this low dissolution of secondary copper sulfides is the short duration of the curing process.
Figure 6.8  Ferric effect on curing mixed copper ores

6.5  Curing Kinetics

According to the results shown in Figure 6.9, after the second day (48 hours) the copper recovery does not show a significant change. Hence, minimum curing time is around 48 hours. This is within the usual time employed for the deployment of the irrigation system for leaching cells of 10,000 m² in commercial operations (personal experience).

The condition for the development of the curing kinetics was 500 g of ore, 16.5 kg/ton of sulfuric acid, 5 g/L sulfuric acid, 5 g/L of total iron with a ferric/ferrous ratio of 1/1. The total moisture applied was 10%. More details are given in Chapter 5.
Figure 6.9  Sulfuric acid curing kinetics at the following conditions: 500 g of ore, 10% initial total water content, 16.5 kg/t of concentrated sulfuric acid and synthetic raffinate with 10 g/L sulfuric acid and 5 g/L total iron with in a ferric/ferrous iron ratio of 1/1.

6.6  Acid Consumption

For the purposes of the present study, before further leach testing, a reagent consumption test was done to appreciate the tendencies of acid and ferric consumption and the effects on the copper recovery from this particular mixed copper ore.

Table 6.5 summarizes the conditions applied and the results for copper recovery and sulfuric acid consumption. The leach solution contained 5 g/L of total iron distributed according to Table 6.5, and sulfuric acid was pumped accordingly to maintain the desired pH.
Table 6.5 Copper recovery and acid consumption at constant pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;/Fe&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>ORP (mV)</th>
<th>Cu Recovery</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/3</td>
<td>326.2</td>
<td>23.98%</td>
<td>26.75</td>
</tr>
<tr>
<td>1</td>
<td>1/1</td>
<td>373.7</td>
<td>26.67%</td>
<td>26.94</td>
</tr>
<tr>
<td>1</td>
<td>3/1</td>
<td>421.1</td>
<td>29.53%</td>
<td>24.65</td>
</tr>
<tr>
<td>1</td>
<td>9/1</td>
<td>438.5</td>
<td>30.93%</td>
<td>17.77</td>
</tr>
<tr>
<td>2</td>
<td>1/9</td>
<td>281.5</td>
<td>15.02%</td>
<td>8.98</td>
</tr>
<tr>
<td>2</td>
<td>1/3</td>
<td>299.5</td>
<td>22.16%</td>
<td>8.98</td>
</tr>
<tr>
<td>2</td>
<td>1/1</td>
<td>365.5</td>
<td>29.67%</td>
<td>8.98</td>
</tr>
<tr>
<td>2</td>
<td>3/1</td>
<td>420.2</td>
<td>30.02%</td>
<td>7.45</td>
</tr>
<tr>
<td>2</td>
<td>9/1</td>
<td>428.7</td>
<td>29.63%</td>
<td>6.12</td>
</tr>
</tbody>
</table>

Figure 6.10 Copper recovery for different ferric/ferrous ratios at pH 1 and pH 2 and 33% solids after 3 hrs leaching at 25°C.
According to Figure 6.10, at pH 1 the copper recovery is influenced positively by the higher ferric/ferrous ratio. However, at pH 2 beyond a ferric/ferrous ratio of 1/1 the copper recovery does not increase.

![Graph showing acid consumption for different ferric/ferrous iron ratio at pH=1 and pH=2 after 3 hrs leaching at 25 °C with 33% solids.]

**Figure 6.11** Acid consumption for different ferric/ferrous iron ratio at pH=1 and pH=2 after 3 hrs leaching at 25 °C with 33% solids.

From Figure 6.11, one may infer that a high ferric concentration reduces the amount of sulfuric acid consumption because the pyrite in the ore is oxidized and generates some sulfuric acid.

The data obtained from this set of experiments was plugged into an empirical linear regression model according to Equation 6.4 for copper recovery and Equation 6.5 for sulfuric acid consumption.

\[
R_{Cu} = b_0 + b_1 \cdot \text{pH} + b_2 \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} + b_3 \cdot \text{pH} \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}
\]  

(6.4)
\[ A_{\text{Cu}} = c_0 + c_1 \cdot \text{pH} + c_2 \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} + c_{12} \cdot \text{pH} \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \]  

(6.5)

Table 6.6  Coefficients of Equation 6.4 for copper recovery as a function of pH and ferric/ferrous ratio

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>( b_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_0 )</td>
<td>0.286</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>-0.030</td>
</tr>
<tr>
<td>( b_2 )</td>
<td>0.003</td>
</tr>
<tr>
<td>( b_{12} )</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 6.7  Coefficients of Equation 6.5 for sulfuric acid consumption as a function of pH and ferric/ferrous ratio

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>( c_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_0 )</td>
<td>46.285</td>
</tr>
<tr>
<td>( c_1 )</td>
<td>-18.637</td>
</tr>
<tr>
<td>( c_2 )</td>
<td>-1.833</td>
</tr>
<tr>
<td>( c_{12} )</td>
<td>0.747</td>
</tr>
</tbody>
</table>

Figure 6.12 shows the surface plot for the experimental model of copper recovery as a function of pH and ferric/ferrous ratio. The graph shows a slight effect of the ferric/ferrous ratio on the copper recovery and no appreciable effect of pH.

The acid consumption surface tendency is shown in Figure 6.13 as a function of pH and ferric/ferrous ratio. A major effect is shown in both variables. Acidic pH gives higher sulfuric acid consumption but has no benefit for copper recovery. Evidently, a pH of 2 would be a good choice for leaching this ore sample.
Figure 6.12 Copper recovery as a function of pH and ferric/ferrous ratio.

Figure 6.13 Sulfuric acid consumption as a function of pH and ferric/ferrous ratio.

6.7 Column Leaching Test

A final series of column leaching tests were designed to evaluate the effect of the ferric/ferrous ratio on the leaching performance of Zaldivar mixed copper ore. The
conditions applied are shown in Table 6.8 as well as a summary of the results on sulfuric acid consumption and final copper recovery after 220 days of continuous leaching.

The columns were irrigated at the same flow rate of 8 L/h/m², 12, 15, and 18 kg/ton of sulfuric acid were applied during agglomeration with a synthetic raffinate containing 5 g/L of sulfuric acid and 5 g/L of total iron distributed according to Table 6.8.

### Table 6.8 Copper recovery and acid consumption

<table>
<thead>
<tr>
<th>Column test</th>
<th>Curing H₂SO₄ (kg/t)</th>
<th>Raffinate Fe³⁺/Fe²⁺</th>
<th>Consumed H₂SO₄ (kg/t)</th>
<th>Copper recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>12</td>
<td>1/3</td>
<td>43.76</td>
<td>82.70%</td>
</tr>
<tr>
<td>C2</td>
<td>12</td>
<td>3/1</td>
<td>19.63</td>
<td>82.07%</td>
</tr>
<tr>
<td>C3</td>
<td>15</td>
<td>1/9</td>
<td>43.35</td>
<td>79.04%</td>
</tr>
<tr>
<td>C4</td>
<td>15</td>
<td>1/3</td>
<td>43.97</td>
<td>80.45%</td>
</tr>
<tr>
<td>C5</td>
<td>15</td>
<td>1/1</td>
<td>37.56</td>
<td>83.90%</td>
</tr>
<tr>
<td>C6</td>
<td>15</td>
<td>3/1</td>
<td>6.94</td>
<td>81.48%</td>
</tr>
<tr>
<td>C7</td>
<td>15</td>
<td>9/1</td>
<td>4.71</td>
<td>81.77%</td>
</tr>
<tr>
<td>C8</td>
<td>18</td>
<td>1/3</td>
<td>43.21</td>
<td>83.45%</td>
</tr>
<tr>
<td>C9</td>
<td>18</td>
<td>3/1</td>
<td>2.61</td>
<td>82.49%</td>
</tr>
</tbody>
</table>

As shown in Figure 6.14, increasing the ferric/ferrous ratio above 1/1 had little effect on copper recovery. These results show an agreement with the stirred leaching results at constant pH in section 6.4, as shown in Figure 6.10.

Another interesting point from these results is the clear effect of the acidic curing on accelerating the copper dissolution during the first few days of leaching. In every case, the copper recovery is about 25% from the very first day of leaching. Of course in a full-scale heap this would be further subject to solute transport across the height of the heap.

Figure 6.15 shows the ferric/ferrous ratio at the outlet of the five columns after irrigating with fixed ferric/ferrous ratio of 9/1, 3/1, 1/1, 1/3 and 1/9. The behaviour of this ratio is noticeable after 40 days in all the cases where this ratio drops as the ratio applied is
higher in ferrous. This explains that the ferric consumption starts about 30 days consuming all ferric in the cases of ferric/ferrous ratio fed 1/9 and 1/3. This might explain the slow copper kinetics recovery for the columns with ferric/ferrous ratios less than 1. Another outcome for higher ferric/ferrous ratios fed could be the ferric precipitation as a basic sulfate like jarosite hindering the complete dissolution of chalcopyrite (Petersen et al 2001) which would explain low copper recoveries for higher ferric/ferrous ratios fed at the column leaching.
Figure 6.14 Copper recovery kinetics for 15 kg/ton of sulfuric acid curing dose at five different ferric/ferrous ratios.
Figure 6.15  Ferric/ferrous ratio in the effluent for 15 kg/ton of sulfuric acid curing dose at five different ferric/ferrous ratios
Chapter 7

Numerical Estimations

In this section, the curing model is applied to study Zaldivar mixed copper ore with chrysocolla, chalcocite, chalcopyrite and pyrite as major components. The experimental copper conversion as a function of sulfuric acid addition was studied. Then, the results of the curing process are plugged into a column leach model to find the multi-species kinetic parameters. After that, the solute transport parameters are determined from an inert tracer test. Finally, the parameters for fluid flow in unsaturated media are estimated.

7.1  Curing Modeling

The copper ore feed, coming from the Zaldivar mine in Chile, was determined to have 0.84% total copper. Then, the sample was subjected to sequential leaching tests (section 5.2). To simplify the data input of copper species, it is assumed that the portion of insoluble copper is the amount of copper contained in chalcopyrite, the copper soluble in cyanide in chalcocite. Next, the initial amount of chalcanthite was assumed to be the portion coming from the curing test with 0 kg/t H$_2$SO$_4$ (Figure 6.6). Finally, from the above assumption, the amount of copper as chrysocolla is deducted from copper soluble in acid and chalcanthite. A summary of these assumed values is presented in Table 7.1.

<table>
<thead>
<tr>
<th>Species</th>
<th>Cu (%)</th>
<th>Cu distribution</th>
<th>Deduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>chalcanthite</td>
<td>0.036%</td>
<td>4%</td>
<td>curing washing at 0 kg/t H$_2$SO$_4$</td>
</tr>
<tr>
<td>chrysocolla</td>
<td>0.088%</td>
<td>11%</td>
<td>copper soluble in acid – chalcanthite</td>
</tr>
<tr>
<td>chalcocite</td>
<td>0.462%</td>
<td>55%</td>
<td>copper soluble in cyanide</td>
</tr>
<tr>
<td>chalcopyrite</td>
<td>0.250%</td>
<td>30%</td>
<td>non-soluble copper</td>
</tr>
<tr>
<td>Total</td>
<td>0.836%</td>
<td>100%</td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions for the curing tests are presented in Table 7.2. The grain size of the ore was kept uniform with a maximum size of 10 mm.
Table 7.2  Experimental conditions of the curing process to locate the optimum sulfuric acid curing dose

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ore sample weight</td>
<td>500 g</td>
</tr>
<tr>
<td>particle size</td>
<td>100% −10 mm</td>
</tr>
<tr>
<td>initial ore moisture</td>
<td>3.09%</td>
</tr>
<tr>
<td>volumetric water content of curing</td>
<td>10%</td>
</tr>
<tr>
<td>maximum curing time</td>
<td>7 days</td>
</tr>
<tr>
<td>sulfuric acid curing dose</td>
<td>0, 5.5, 10.99, 16.49, 21.98, 27.48, and 32.98 kg/t</td>
</tr>
<tr>
<td>sulfuric acid curing dose kinetics</td>
<td>16.49 kg/t</td>
</tr>
<tr>
<td>sulfuric acid in synthetic raffinate</td>
<td>10 g/L</td>
</tr>
<tr>
<td>ferric in synthetic raffinate</td>
<td>2.5 g/L</td>
</tr>
<tr>
<td>ferrous in synthetic raffinate</td>
<td>2.5 g/L</td>
</tr>
</tbody>
</table>

Table 7.3  Copper extraction from the cured agglomerate at different sulfuric acid curing dosages

<table>
<thead>
<tr>
<th>H₂SO₄ (kg/t)</th>
<th>Cu Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>4.2%</td>
</tr>
<tr>
<td>5.50</td>
<td>20.4%</td>
</tr>
<tr>
<td>10.99</td>
<td>24.5%</td>
</tr>
<tr>
<td>16.49</td>
<td>25.7%</td>
</tr>
<tr>
<td>21.98</td>
<td>26.3%</td>
</tr>
<tr>
<td>27.48</td>
<td>26.5%</td>
</tr>
<tr>
<td>32.98</td>
<td>27.0%</td>
</tr>
</tbody>
</table>

Table 7.4  Parameters for the sulfuric acid curing model proposed in Chapter 3 applied to the Zaldivar mixed copper ore

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Chrysocolla</th>
<th>Chalcocite</th>
<th>Gangue</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ</td>
<td>—</td>
<td>0.667</td>
<td>0.667</td>
<td>—</td>
</tr>
<tr>
<td>k₀</td>
<td>1/ hr</td>
<td>0.0140</td>
<td>0.0120</td>
<td>0.0065</td>
</tr>
<tr>
<td>T₀</td>
<td>K</td>
<td>298</td>
<td>298</td>
<td>298</td>
</tr>
<tr>
<td>E</td>
<td>kJ/mol</td>
<td>60.0</td>
<td>22.0</td>
<td>25.0</td>
</tr>
<tr>
<td>A</td>
<td>mol/kg</td>
<td>0.6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>F</td>
<td>mol/kg</td>
<td>—</td>
<td>0.9</td>
<td>—</td>
</tr>
</tbody>
</table>
Figure 7.1  Curing modeling of the Zaldivar mixed copper ores where figures (a) and (b) show the concentration profiles of the aqueous and solid phases, and figures (c) and (d) show the copper recovery kinetics and sulfuric acid curing dose where the solid curves are model output and the circular points are experimental data.

7.2 Heap Leaching Model

In this section, the column leach experimental data are used to find kinetic parameters for the leaching rate equations presented in Chapter 4. Some of the parameters were taken from previous studies on chalcocite, chalcopyrite (Dixon 2012) and pyrite leaching (Bouffard 2006).
At this point, after curing has taken place, the curing model of the preceding section indicates changes in the amounts of existing minerals, and the appearance of new minerals by chemical reaction: chalcanthite and blaubleibender. For the curing process, it was assumed that copper soluble in acid is chrysocolla, copper soluble in cyanide is chalcocite and the insoluble copper is chalcopyrite. After the curing simulation, Table 6.6 shows the new grades of the copper species present in the curing product which are the initial grades for the following leaching stage.

Table 7.5  Calculated mineral grades in the Zaldivar ore for leach modeling

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>chalcanthite</td>
<td>0.036% Cu</td>
</tr>
<tr>
<td>chrysocolla</td>
<td>0.088% Cu</td>
</tr>
<tr>
<td>chalcocite</td>
<td>0.462% Cu</td>
</tr>
<tr>
<td>chalcopyrite</td>
<td>0.250% Cu</td>
</tr>
</tbody>
</table>
Table 7.6  Parameters of the leaching model proposed in chapter 4 applied to the Zaldivar mixed copper ore sample

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>chrysocolla</th>
<th>chalcocite</th>
<th>blaubleinder</th>
<th>chalcanthite</th>
<th>*chalcopyrite</th>
<th>pyrite</th>
<th>ferrous oxidizer</th>
<th>oxygen</th>
<th>Gangue</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi$</td>
<td>—</td>
<td>0.667</td>
<td>0.667</td>
<td>1.2</td>
<td>1</td>
<td>0.333</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$k_0$</td>
<td>1/hr</td>
<td>$5 \times 10^{-3}$</td>
<td>$3.75 \times 10^{-2}$</td>
<td>$6.2 \times 10^{-3}$</td>
<td>$5.2 \times 10^{-2}$</td>
<td>$1.76 \times 10^{-4}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$5 \times 10^{-2}$</td>
<td>—</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>K</td>
<td>298</td>
<td>298</td>
<td>298</td>
<td>298</td>
<td>298</td>
<td>298</td>
<td>298</td>
<td>—</td>
<td>298</td>
</tr>
<tr>
<td>$E$</td>
<td>kJ/mol</td>
<td>5,000</td>
<td>50,000</td>
<td>50,000</td>
<td>25,000</td>
<td>25,000</td>
<td>2,500</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$A$</td>
<td>mol/kg</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$F$</td>
<td>mol/kg</td>
<td>0.1</td>
<td>0.9</td>
<td>0.08</td>
<td>—</td>
<td>—</td>
<td>0.01</td>
<td>0.01</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$n_1$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$n_2$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.17</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.93</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$k_La$</td>
<td>1/hr</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>10</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Notes:

* The kinetic expression for chalcopyrite was taken from Dixon (2012).

In all cases, the kinetics expressions were taken from previous work of Dixon (2003) and Ogbonna et al. (2005).
Figure 7.2  Column leaching kinetics experimental and modeled for 15 kg/t of sulfuric acid curing, 8 L/h/m² at 5 different ratios of ferric/ferrous iron: 1/9 (blue), 1/3 (red), 1/1 (black), 3/1 (magenta) and 9/1 (green).
7.3 Solute Transport Model, Tracer Test

In a large scale heap leach operation, effective transport of solution through the heap height is critical. Hence, it is fundamental to study the transport properties of a heap leach ore. The present test was designed to determine the dispersivity parameters for the Zaldivar ore sample. Three tests at three different irrigation rates (6, 8, and 12 L/h/m²) were conducted. The water content was determined by weighing the entire ore column while under irrigation at different flow rates. The agglomeration stage was done using de-ionized water to reach 10% water content. After irrigation and constant concentration on top of the column, the tracer concentration at the outlet was measured, giving three breakthrough curves as shown with symbols in Figure 7.3.

\[
\frac{\partial}{\partial t}(\theta c) = \frac{\partial}{\partial z} \left[ \theta D_L c_i - \theta \phi c_i \right] \tag{7.1}
\]

\[
D_L = a_L v + D_0 \tag{7.2}
\]

Where:

- \( c \) = concentration of the species
- \( \theta \) = water content
- \( v \) = superficial velocity
- \( D_L \) = dispersion-diffusion term
- \( a_L \) = longitudinal dispersivity
- \( D_0 \) = diffusion
- \( z \) = vertical distance
- \( t \) = time

The longitudinal dispersivity was found using the solute transport equation 7.2. The computer code used to achieve these parameters is found in Appendix B3. The longitudinal dispersion and the diffusion values are shown in Table 7.8.
Figure 7.3  Constant input tracer test for three different irrigation rates using the dispersion advection equation 7.1 solved as discussed in Appendix B3
Figure 7.4  Dispersion-diffusion term as a function of superficial velocity. The irrigation rates are 5.58, 7.85 and 12 L/h/m². The water content for each irrigation rate was 14.76, 15.60, and 15.85 respectively.

Table 7.7  Longitudinal dispersivity and diffusion values after regression

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (m²/h)</td>
<td>0.000198</td>
</tr>
<tr>
<td>$\alpha_L$ (m/h)</td>
<td>0.4654</td>
</tr>
</tbody>
</table>
7.4 Heap Hydrology Parameters

Table 7.9 summarizes the conditions and results of the column containing the agglomerated mineral for this study purposes. The agglomeration was made with deionized water to reach the 10% optimum agglomerate water content found during the agglomeration studies (Figure 6.4). The irrigation started with 5.58 L/h/m² with a solution containing KCl 0.1 g/L then changed to 8.16 L/h/m² and KCl 2.5 g/L and finally 12.0 L/h/m² and 0.1 KCl to track at the same time the solute transport as well (section 5.10).

Table 7.8 Column hydrology: conditions and results

<table>
<thead>
<tr>
<th>Irrigation rate</th>
<th>L/h/m²</th>
<th>5.58</th>
<th>8.16</th>
<th>12.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore weight</td>
<td>g</td>
<td>8,000</td>
<td>8,000</td>
<td>8,000</td>
</tr>
<tr>
<td>Natural moisture</td>
<td>%</td>
<td>3.09</td>
<td>3.09</td>
<td>3.09</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>g/cm³</td>
<td>2.53</td>
<td>2.53</td>
<td>2.53</td>
</tr>
<tr>
<td>Dry weight</td>
<td>g</td>
<td>7,753</td>
<td>7,753</td>
<td>7,753</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>cm</td>
<td>8.6</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Ore column height</td>
<td>cm</td>
<td>94.5</td>
<td>93.3</td>
<td>92.5</td>
</tr>
<tr>
<td>Agglomerate water content</td>
<td>%</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Bulk density</td>
<td>g/cm³</td>
<td>1.412</td>
<td>1.430</td>
<td>1.443</td>
</tr>
<tr>
<td>Void space</td>
<td>%</td>
<td>44.13</td>
<td>43.42</td>
<td>42.93</td>
</tr>
<tr>
<td>Irrigation water content</td>
<td>%</td>
<td>14.76</td>
<td>15.60</td>
<td>15.85</td>
</tr>
<tr>
<td>Net void space</td>
<td>%</td>
<td>44.1</td>
<td>43.4</td>
<td>42.9</td>
</tr>
<tr>
<td>Air void space</td>
<td>%</td>
<td>29.4</td>
<td>27.8</td>
<td>27.1</td>
</tr>
<tr>
<td>Residual water content</td>
<td>%</td>
<td>11.06</td>
<td>11.06</td>
<td>11.06</td>
</tr>
<tr>
<td>Superficial velocity</td>
<td>m/h</td>
<td>0.00558</td>
<td>0.00816</td>
<td>0.01200</td>
</tr>
<tr>
<td>Superficial velocity (model)</td>
<td>m/h</td>
<td>0.00542</td>
<td>0.00926</td>
<td>0.01089</td>
</tr>
</tbody>
</table>

Figure 7.5 shows the water content on the column once irrigation started at 5.58 L/h/m². The water content starts at 10% because that was the water content applied at the agglomeration stage. The final water content for 5.58 L/h/m² was of 14.76% in a period of about 13 hours for a column height of 94.5 cm. Figure 7.6 shows water content as
function of irrigation flow indicating that above 8 L/h/m² the increase on water content on the agglomerated mineral is relatively low which indicates an acceptable permeability.

Figure 7.5  Water content variation in a column leach at 5.58 L/h/m² after agglomeration to 10% initial water content

Figure 7.6  Water content of the leaching column as a function of irrigation flow
Figure 7.7  Superficial velocity as a function of effective saturation at 5.58, 8.16, and 12.0 L/h/m² to find the Brooks-Corey parameters

Figure 7.7 shows the superficial velocity as a function of the effective saturation calculated from results obtained in Table 7.9. We obtained the relationship expressed in equation 7.3 used in the past (Afewu 2009) to find the Brooks-Corey parameter $\Psi$. From this parameter, the van Genuchten parameters shown in Table 7.10 are easily calculated using Equations 7.4 and 7.5.

\[ v = k_s S_e^\psi \]  \hspace{1cm} (7.3)

Van Genuchten conversion parameter from Brooks Corey constants

\[ m = \frac{4}{2\psi - 1} \]  \hspace{1cm} (7.4)

\[ n = \frac{1}{1-m} \]  \hspace{1cm} (7.5)

Where:

\[ v = \text{superficial velocity} \]
\[ k_s = \text{saturation constant} \]
\[ S_e = \text{effective saturation} \]
\[ \Psi = \text{Brooks-Corey fitting parameter} \]
\[ m, n = \text{van Genuchten fitting parameters} \]

Table 7.9  Brooks-Corey parameters and van Genuchten parameters estimated from Brooks-Corey

<table>
<thead>
<tr>
<th>Brooks-Corey</th>
<th>van Genuchten</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_s )</td>
<td>( \varphi )</td>
</tr>
<tr>
<td>0.9382</td>
<td>2.3527</td>
</tr>
<tr>
<td>( m )</td>
<td>4.56</td>
</tr>
<tr>
<td>( k_s )</td>
<td>0.0450</td>
</tr>
</tbody>
</table>

The hydraulic and dispersion parameters found in this study can be applied for further studies on scale-up from column leaching to commercial heap leaching. These parameters can be used to describe fluid flow and solute transport through a stacked heap, and to predict the best conditions for heap leaching of this particular mixed copper ore.
Chapter 8

Concluding Remarks

A systematic study of column leaching of mixed copper ores was performed: Optimum agglomeration moisture, best sulfuric acid curing dose and curing kinetics, and the influence of the ferric/ferrous ratio on copper extraction in both agitated and column leaching were determined. Then a model of curing and column leaching was validated with data obtained from experiments. Finally, a fluid flow and solute transport study was conducted.

The kinetic model was based on concentrations rather than recoveries as is widely used in extractive metallurgy. The method used to solve the kinetic model was entirely differential rather than integral. The advantage of the differential method is that it allows the expression of the leaching rates of different contributing copper species by stoichiometry.

Finally, a tracer test was performed to characterize the longitudinal dispersivity from three different irrigation rates. To find this parameter was necessary to solve the 1D solute transport equation. From this test as well was inferred all the parameters necessary for the Richards equation for fluid flow in unsaturated media.

8.1 Conclusions

- Measurement of the generated void space of agglomerates after compression was used successfully as an indicator of agglomerate quality. In addition, current passing through the agglomerate can be used as a practical field tool for measuring the quality of agglomeration in real time. The Zaldivar ore used in this study requires 10% final moisture for maximum void space generation. The current passing through the agglomerate at 10% final moisture was 0.9 mA with a compression of 0.41 kg/cm².
An experimental method of sequentially increasing the amount of sulfuric acid curing dose was successfully used to find the optimum addition of this reagent. The evaluation of the increasing amounts of sulfuric acid was determined by soaking the agglomerate in a solution containing a known quantity of sulfuric acid and analyzed for copper. Then, a plot of copper recovery as a function of sulfuric acid curing dose help us to determine the optimum sulfuric acid addition for curing. The optimum curing dose was found to be about 15 kg/t of sulfuric acid for the Zaldivar ore.

The experimental curing kinetics shows us that the minimum time necessary for curing to occur is at least two days. After this time no significant difference in copper extraction was noted.

Ferric addition to curing was performed resulting in no significant difference in copper recovery as shown in Figure 6.8. In summary, excess ferric addition for curing of this particular mineral is not advantageous.

The effect of the ferric/ferrous ratio was studied both in agitated leaching and column leaching. The final copper extractions for both types of test were similar. A ferric/ferrous ratio of 1/1 was found to be optimal for obtaining maximum copper extraction. Higher ratios did not increase copper extraction, and lower ratios gave lower extractions.

Column test results and subsequent kinetic modeling suggests that the most influential factor for maximum copper recovery from this ore sample is the kinetics of chalcopyrite (Equation 4.7).

The curing kinetic model was developed assuming that copper soluble in acid is from chrysocolla, copper soluble in cyanide is from chalcocite, and insoluble copper is from chalcopyrite. This model considers three basic reactions: chalcanthite generation from chrysocolla, chalcanthite and second stage chalcocite (blaubleibender) generation from chalcocite. Chalcopyrite is considered non-reactive at this stage. The proposed kinetic model solved as a system of differential equations reproduces the experimental curing kinetics and sulfuric acid curing dose in a satisfactory way for
this particular ore. According to Figures 7.1c and d, acid solubilization reaches a maximum of 25% of copper at seven days. The sulfuric acid curing dose versus copper solubilization is well represented by the proposed model. The kinetic expressions used are as follows:

$$r_{Cy} = k_{Cy}(T) \frac{c_{Acid}}{A_{Acid} + C_{Acid}} c_{Cy}^{\phi_{Cy}}$$  
(8.1)

$$r_{Cc} = k_{Cc}(T) \frac{c_{Fe3}}{F_{Acid} + c_{Fe2}} \cdot c_{Cc}^{\phi_{Cc}}$$  
(8.2)

$$r_M = k_M(T)c_{Acid}$$  
(8.3)

$$k_i = k_{0,i} \exp \left[ \frac{-E_i}{R} \left( \frac{1}{T} - \frac{1}{T_{ref,i}} \right) \right]$$  
(8.4)

| Table 8.1 Parameters of the proposed curing model (Equations 8.1 to 8.4) found from experimental sulfuric acid curing of the Zaldivar mixed copper ore |
|-------------------------------|-------------------|-------------------|-------------------|
| **Parameter** | **Unit** | **Chrysocolla** | **Chalcocite** | **Gangue** |
| $\phi$ | — | 0.667 | 0.667 | — |
| $K_0$ | 1/hr | 0.014 | 0.012 | 0.0065 |
| $T_0$ | K | 298 | 298 | 298 |
| $E$ | kJ/mol | 60.0 | 22.0 | 25.0 |
| $A$ | mol/kg | 0.6 | — | — |
| $F$ | mol/kg | — | 0.9 | — |

Five leaching columns were modeled applying the differential kinetic approach with initial conditions resulting from curing modeling. After agglomeration and sulfuric acid curing with 15 kg/t H$_2$SO$_4$, the columns were irrigated at 8 L/h/m$^2$ with 5 g/L H$_2$SO$_4$ and 5g/L total iron. The ferric/ferrous iron ratios were distributed as 1/9, 1/3, 1/1, 3/1 and 9/1. The copper extraction curves are shown in Figure 7.2. There is clear influence of the acidic curing in the copper extraction during the very first day, where the extraction in the 5 leaching columns is close to 25%, and the curing model mimics these results. The present leaching model has a close reproduction of the experimental
part except for ferric/ferrous iron ratio of 1/3 probably due to sampling or chemical analysis errors. Overall, the present model reproduces the influence of the ferric/ferrous ratio on the leaching mixed copper ores from Zaldivar. A higher copper recovery is achieved with a 1/1 ferric/ferrous ratio of the leaching solution. A low ratio is detrimental to copper recovery and very high ratios are not beneficial. The present model suggests that the kinetics of chalcopyrite might be responsible for this behavior. This same copper recovery tendencies were seen in the agitated tests, which proves that the leaching columns were performed with minimum relative error.

- In summary, the present study on agglomeration, sulfuric acid curing and column leaching of mixed copper ores from the Zaldivar mine was successfully modeled both in terms of curing and consequent column leaching. The curing dose reproduces the behavior of the copper recovery at this stage and the influence of the ferric/ferrous ratio is well represented using a differential model which allow us to reproduce the synergistic interaction of all chemical compounds present.

### 8.2 Recommendations and Future Work

- A better kinetic model could be obtained by inverse modeling. The development of an inverse model implicates the collection of data for every chemical species, solid, aqueous, and gaseous, at different times.

- Biological effects were not studied or taken in account in the present study. Subsequent work on the effects of bacterial activity on leaching should be conducted.

- A large scale column leach would be necessary to corroborate the scale-up parameters.

- No particle size studies were done in the present study. A future set of tests should test the influence of particle size on the kinetics of copper extraction.

- Since a laboratory column used was small, no flow segregation was present. In a real heap leaching scenario, however, it is expected that the flow segregation would
contributes to preferential flow. Hence, the hydraulic and transport parameters should be measured in large columns or test heaps to provide a more realistic assessment of fluid flow and solute transport.
References


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Appendices

Appendix A

Concepts and Numerics

C.1 Conception of a Heap Leaching Model

Continuous aqueous phase input

\[ c_{aq,in} \]

Initial solid phase

\[ C_{sol,0} \]

Final solid phase

\[ c_{sol} \]

Continuous aqueous phase PLS

\[ c_{aq} \]

Figure A.1 Heap leaching modeling concept

Solid phase balance:

\[ \text{acc} = \text{in} - \text{out} \pm \text{ss} \]

\[ \frac{d(\theta V \cdot c_{sol})}{dt} = F_{in} c_{sol,in} - F_{c_{sol}} + \theta V \cdot r\left(c_{aq}, c_{sol}\right) \]

\[ F_{in} = F = 0 \text{ and } \theta = \text{constant} \]

\[ \frac{dc_{sol}}{dt} = r\left(c_{aq}, c_{sol}\right) \]
Aqueous phase balance

\[ \text{acc} = \text{in} - \text{out} \pm \text{ss} \]
\[ \frac{d(\theta V \cdot c_{aq})}{dt} = F_{in} c_{aq,in} - F c_{aq} + \theta V \cdot r(c_{aq}, c_{sol}) \]

\( F_{in} = F \) and \( \theta = \text{constant} \)

\[ \frac{dc_{aq}}{dt} = \frac{F}{\theta V} \left( c_{aq,in} - c_{aq} \right) + r(c_{aq}, c_{sol}) \]

\( \rho_b = \frac{M_{Min}}{V} \)

\[ \frac{dc_{aq}}{dt} = \frac{F \rho_b}{\theta M_{Min}} \left( c_{aq,in} - c_{aq} \right) + r(c_{aq}, c_{sol}) \]

\[ \lambda = \frac{F \rho_b}{\theta M_{Min}} \]

\[ \frac{dc_{aq}}{dt} = \lambda \left( c_{aq,in} - c_{aq} \right) + r(c_{aq}, c_{sol}) \]

Where:

\( \theta V \) = effective volume

\( c_{aq} \) = final concentration of the aqueous specie

\( c_{sol} \) = final concentration of the solid specie

\( c_{aq,in} \) = concentration of the aqueous species in the irrigation solution

\( F_{in} \) = irrigation flow

\( \rho_b \) = bulk density

\( M_{Min} \) = mineral mass

\( V \) = mineral volume

\( \theta \) = water content
r = reaction rate

C.2 1D Solute Transport Numerics

![Balance element diagram]

Figure A.2 Balance element

Solute transport considering advection and dispersion in 1D

\[ f = \theta_0 C - \theta D \frac{\delta C}{\delta Z} \]

Introducing the Patankar’s power law schema

\[ f = \theta_0 C - \theta D \cdot \gamma(p) \frac{\delta C}{\delta Z} \]

\[ p_{i-1} = \frac{\nu_{i-1} \delta z}{0.5(D_{i-1} + D_i)} \quad p_i = \frac{\nu_i \delta z}{0.5(D_i + D_{i+1})} \]

\[ \lambda(p) = \begin{cases} 
-p & p < -10 \\
(1 + 0.5p)^5 - p & -10 \leq p < 0 \\
(1 + 0.5p)^5 & 0 \leq p < 10 \\
0 & p \geq 10 
\end{cases} \]

Applying balance in the element figure A.1
input - output ± sink / source = accumulation

\[(Af)_{iw} - (Af)_{ie} + (A\delta zS)_{i} = (A\delta z)_{i} \frac{\delta}{\delta z}(\theta C)\]

\[\frac{1}{(\delta z)_{i}w} \left[ \theta uC - \theta D \frac{\delta C}{\delta z} \right]_{iw} - \frac{1}{(\delta z)_{i}e} \left[ \theta uC - \theta D \frac{\delta C}{\delta z} \right]_{ie} + S_{i} = \frac{\delta}{\delta t}(\theta C)\]

\[U = \theta C\]
\[\delta z = \text{constant}\]

\[(\theta D)_{iw} = 0.5(\theta_{i-1} + \theta_{i})0.5(D_{i-1} - D_{i})\]
\[(\theta D)_{ie} = 0.5(\theta_{i} + \theta_{i+1})0.5(D_{i} - D_{i+1})\]

Upwind advection

\[(\nu U)_{iw} = (\nu U)_{i-1}\]
\[(\nu U)_{ie} = (\nu U)_{i}\]

\[\lambda = \frac{\delta t}{(\delta z)^{2}}\]
\[\phi = \frac{\delta t}{\delta z}\]

General solution

\[-\left[ \phi u_{i-1} + \frac{\lambda(\theta D)_{iw}}{\theta_{i-1}} \right] U_{i-1}^{t+1} + \left[ \frac{\lambda}{\theta_{i}} \left( (\theta D)_{iw} - (\theta D)_{ie} \right) + \phi u_{i} + 1 \right] U_{i}^{t+1} - \left[ \frac{\lambda(\theta D)_{ie}}{\theta_{i+1}} \right] U_{i+1}^{t+1} = U_{i}^{t} + S_{i}\delta t\]

Applying boundary conditions:

\[BC1: \quad C_{0} = \text{constant} @ i = 1\]

\[\frac{\lambda}{\theta_{1}} \left( (\theta D)_{iw} - (\theta D)_{ie} \right) + \phi u_{1} + 1 \quad U_{1}^{t+1} - \left[ \frac{\lambda(\theta D)_{ie}}{\theta_{2}} \right] U_{2}^{t+1} = U_{1}^{t} + S_{1}\delta t + \left[ \phi u_{0} + \frac{\lambda(\theta D)_{ow}}{\theta_{0}} \right] U_{0}^{t+1}\]

\[BC2: \quad \frac{\partial f}{\partial z} = 0 @ i = n\]
- \left[ \phi u_{i-1} + \frac{\lambda(\theta D)_{nW}}{\theta_{n-1}} \right] U_{n-1}^{i+1} + \left[ \frac{\lambda(\theta D)_{nW}}{\theta_n} + 1 \right] U_n^{i+1} = U_n^i + S_n \delta t

C.3 1D Fluid Flow Transport Numerics

![Balance element diagram]

Figure A.3  Balance element

$$
\theta = \begin{cases} 
\epsilon & p \geq 0 \\
\theta_r + (\epsilon - \theta_r) Se & p < 0 
\end{cases}
$$

$$
Se = \frac{\theta - \theta_r}{\epsilon - \theta_r} = \frac{1}{1 + (\alpha p)^n}
$$

$$
\frac{\partial \theta}{\partial p} = S(p) = \begin{cases} 
10 - 20 & p \geq 0 \\
\frac{(\epsilon - \theta)n \cdot m \cdot \alpha (-\alpha p)^n}{\left[1 + (-\alpha p)^n\right]^{m+1}} & p < 0 
\end{cases}
$$

$$
k = \begin{cases} 
k_s & p \geq 0 \\
k_s \sqrt{Se} \left[1 - (1 - Se^{1/m})^m\right]^2 & p < 0 
\end{cases}
$$

$$
h = z + p$$

$$
q = -k \frac{\partial h}{\partial z}
$$

$$
\frac{\partial h}{\partial z} = 1 + \frac{\hat{\rho}}{\hat{\theta} z}
$$
\[ q = -k \left( 1 + \frac{\partial p}{\partial z} \right) \]

**Input – Output ± Sink / Source = Accumulation**

\[
(Aq)_{NW} - (Aq)_{IE} + (Aq)_i = (S \cdot A \delta z)_i \frac{\partial p}{\partial z} \\
- \frac{k_{iw}}{(\delta z)_i} \left( 1 + \frac{p_i - p_{i+1}}{(\delta z)_{iw}} \right) + \frac{k_{ie}}{(\delta z)_i} \left( 1 + \frac{p_{i+1} - p_i}{(\delta z)_{iw}} \right) + \frac{q_{si}}{S_i} = S_i \frac{\partial p}{\partial z} \\
\frac{1}{S_i(\delta z)^2} \left[ k_{iw} p_{i-1} - (k_{iw} + k_{ie}) p_i + k_{ie} p_{i+1} \right] + \frac{1}{S_i(\delta z)} [k_{ie} - k_{iw} + q_{si}] = \frac{\partial p}{\partial z}
\]

\[ \lambda = \frac{\Delta t}{(\Delta z)^2} \phi = \frac{\Delta t}{\Delta z} \quad k_{iw} = 0.5(k_{i-1} + k_i) \quad k_{ie} = 0.5(k_i + k_{i+1}) \\
- \lambda k_{iw} p_{i-1}^{t+1} + [S_i + \lambda(k_{iw} + k_{ie})] p_i^{t+1} - \lambda k_{ie} p_{i+1}^{t+1} = S_i p_i^{t+1} + \phi(k_{ie} - k_{iw} + q_{si})
\]

**BC1**: infiltration \( k_{iw} = 0 \) at \( i = 1 \) \( q_{si} \) = constant and \( q_{si} = 0 \) with \( i \geq 0 \)

\[ [S_i + \lambda k_{ie}] p_i^{t+1} - \lambda k_{ie} p_{i+1}^{t+1} = S_i p_i^{t+1} + \phi(k_{ie} - k_{iw} + q_{si}) \]

**BC2**: \( p_{n+1} \) = constant

\[- \lambda k_{iw} p_{i-1}^{t+1} + [S_i + \lambda(k_{iw} + k_{ie})] p_i^{t+1} = S_i p_i^{t+1} + \phi(k_{ie} - k_{iw} + q_{si}) + \lambda k_{ie} p_{i+1}^{t+1} \]

\[
\begin{bmatrix}
S_i + \lambda k_{1E} & -\lambda k_{1E} \\
-\lambda k_{2E} & S_i + \lambda(k_{2w} + k_{2E}) & -\lambda k_{2E} \\
-\lambda k_{3w} & S_i + \lambda(k_{3w} + k_{3E}) & -\lambda k_{3w} \\
-\lambda k_{4w} & S_i + \lambda(k_{4w} + k_{4E}) & -\lambda k_{4w} \\
\end{bmatrix}
\begin{bmatrix}
p_1^{t+1} \\
p_2^{t+1} \\
p_3^{t+1} \\
p_4^{t+1} \\
\end{bmatrix} =
\begin{bmatrix}
S_i p_i' + \phi(k_{1E} + q_{si}) \\
S_2 p_i' + \phi(k_{2E} - k_{2w}) \\
S_3 p_i' + \phi(k_{2E} - k_{2w}) \\
S_4 p_i' + \phi(k_{4E} - k_{4w}) + \lambda k_{4E} p_5^{t+1} \\
\end{bmatrix}
\]

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Appendix B

Code Listing

B.1  Curing of Mixed Copper Ores

```matlab
function Heap_curing_mixed
    clear all; close all; clc;
    global Cy; global Cc; global M;
mCu=63.5; mS=32; mO=16; mH=1; mM=40; mSi=28; mFe=56;
mCy=mCu+mSi+3*mO+2*(2*mH+mO);
mM=mM+mO;
mCh=mCu+mS+4*mO+5*(2*mH+mO);
mCc=2*mCu+mS;
mAcid=2*mH+mS+4*mO;
mMin=1200; % g_min
    diam=0.1; % m
dbulk=1680; % g_min/L_heap
    theta=0.1; % L_sol/L_heap
    moist=0.01; % g_sol/g_min
    tMax = 7; % days
    tf = tMax*24; %hrs
    tData=[0 0.458 1 2 4 7]';
    RData=[0.0424 0.0634 0.1121 0.1475 0.2022 0.2532]';
    Cy.K=0.014; Cy.E=60000; Cy.T=298; Cy.F=0.6;
    Cc.K=0.0012; Cc.E=22000; Cc.T=298; Cc.F=0.9;
    M.K=0.0001; M.E=25000; M.T=298;
    % Initial conditions
    AcidDose=[0 5.5 10.99 16.49 21.98 27.48 32.98]';
    cFe3Dose=[0 2.5 2.5 2.5 2.5 2.5 2.5]';
    cFe2Dose=[0 2.5 2.5 2.5 2.5 2.5 2.5]';
    RCuDose=[.042 .204 .245 .257 .263 .265 .270]';
    cAcid_i = AcidDose;   % g_Acid/Kg_min
    cFe3_i = cFe3Dose;   % g_Fe3+/L_sol
    cFe2_i = cFe2Dose;   % g_Fe2+/L_sol
    gCu_Cy=0.000884;  % g_Cu/gMin as Chrysocolla
    gCu_Cc=0.004616;  % g_Cu/gMin as Chalcocite
    gCu_Cpy=0.002499;  % g_Cu/gMin as Chalcopyrite
    gCu_Bb=0.00000;   % g_Cu/gMin as Bb
    gCu_Ch=0.000364;  % g_Ch/gMin as Chalcanthite
    gM=0.033;        % g_Ca/gMin
    cAcid0 = cAcid_i/mAcid;    % mol_Acid/Kg_min
    cFe30 = cFe3_i/(2*mFe)*moist*dbulk;    % mol_Fe2(SO4)3/Kg_min
    cFe20 = cFe2_i/mFe*moist*dbulk;     % mol_FeSO4/Kg_min
    cCy0 = gCu_Cy/mCu*1000;    % mol_Cy/Kg_min
    cCc0 = gCu_Cc/(2*mCu)*1000;    % molCc/Kg_min
```
cBb0 = gCu_Bb/mCu*1000;       % mol_Bb/Kg_min
cCh0 = gCu_Ch/mCu*1000;       % mol_Ch/Kg_min
cM0 = gM/mM*1000;              % mol_M/Kg_min

for i=1:size(AcidDose)
C_0 = [cAcid0(i); cFe30(i); cFe20(i); cCy0; cCc0; cBb0; cCh0; cM0];
%initial conditions
options = odeset('NonNegative',[1 2 3 4 5 6 7 8]);
[th, Cp] = ode45(@LeachReactions, [0 tf], C_0, options);
RCu=Cp(:,7)*mCu/1000/(gCu_Cy+gCu_Cc+gCu_Bb+gCu_Cpy+gCu_Ch);
td=th./24;
subplot(2,2,1); plot(td,Cp(:,1),td,Cp(:,2),td,Cp(:,3),'-');hold on;
xlabel('days'); ylabel('mol/kg min');legend('Acid','Fe2(SO4)3','FeSO4','Location','Best');
subplot(2,2,2); plot(td,Cp(:,4),td,Cp(:,5),td,Cp(:,6),td,Cp(:,7));hold on;
xlabel('days'); ylabel('mol/kg min');legend('Cy','Cc','Bb','Ch','Location','Best');
subplot(2,2,3); plot(td,RCu,tData,RData,'o'); hold on;
xlabel('days'); ylabel('Cu Recovery');
recovery(i)=RCu(size(RCu,1)-1);
end
subplot(2,2,4);
plot(AcidDose,recovery,AcidDose,RCuDose,'o'); hold on;
xlabel('H2SO4 kg/t'); ylabel('Cu Recovery');

function f = LeachReactions(t, C)
global Cy; global Cc; global M;
f = zeros(size(C));
T=300;
cAcid=C(1); cFe3=C(2); cFe2=C(3); cCy=C(4); cCc=C(5); cBb=C(6);
cCh=C(7); cM=C(8);
rCy = km(Cy.K,Cy.E,Cy.T,T)*cAcid/(Cy.F+cAcid)*cCy^0.667;
rCc = km(Cc.K,Cc.E,Cc.T,T)*cCc^0.667*cFe3/(Cc.F+cFe2);
rM = km(M.K,M.E,M.T,T)*cAcid;

f(1) = - rCy - rM;
f(2) = - 4*rCc;
f(3) = 8*rCc;
f(4) = - rCy;
f(5) = - 5*rCc;
f(6) = rCc;
f(7) = rCy + 4*rCc;
f(8) = -rM;

function Km_r=km(k,Ea,Tr,T)
R=8314;
Km_r=k*exp(-Ea/R*(1/T-1/Tr));
B.2 Column Leach Model of Mixed Copper Ores

function Heap_mixed_5columns_model
clear all; close all; clc;
global Cy; global Cc; global Bb; global Ch; global Cpy; global Py;
global M; global FO;
global T; global in; global lambda; global pOx; global beta
color = [ 'b', 'r', 'k', 'm', 'g' ];

mCu=63.5; mS=32; mO=16; mH=1; mM=40; mSi=28; mFe=56;
mCy=mCu+mSi+3*mO+2*(2*mH+mO);
mCc=2*mCu+mS;
mBb=6*mCu+5*mS;
mCh=mCu+mSi+4*mO+5*(2*mH+mO);
mAcid=2*mH+mSi+mO;
mFe3=2*mFe+3*(mS+4*mO);
mFe2=mFe+mSi+4*mO;
mM=mM+mO;
mPy=mFe+2*mS;
%-----------------
[filename, pathname] = uigetfile('*.*');
inputfile = fopen([pathname, filename]);
values = textscan(inputfile, '%f%f%f%f%f%f%f%f%f%f', 'delimiter','/t');
close(inputfile);
t1Data=values{1}; R1Data=values{2}; t2Data=values{3}; R2Data=values{4};
t3Data=values{5}; R3Data=values{6}; t4Data=values{7}; R4Data=values{8}; t5Data=values{9}; RxData=values{10};

T=300;       % (K) Temp
pOx=0.21;     % (atm) oxygen pressure partial
TMax=250;     % (days) Max time simulation
tf = TMax*24; % (hrs)
mMin=1200;    % (g_min) Mass of mineral
diam=0.1;     % (m) column diameter
dbulk=1680;   % (g_min/L_heap)
theta=0.1;    % (L_sol/L_heap)WATER CONTENT
beta=0.7;     % sulfur/acid conv from pyrite after S.Bouffard

Cy.K=5e-3; Cy.E=5000; Cy.T=298; Cy.F=0.1;
Cc.K=3.75e-2; Cc.E=500000; Cc.T=298; Cc.F=0.9; Cc.phi=0.667;
Bb.K=0.62e-2; Bb.E=50000; Bb.T=298; Bb.n1=0.333; Bb.n2=1;
Bb.gamma=0.82; Bb.phi=1.2;     Bb.F=0.08;
Ch.K=0.052; Ch.E=25000; Ch.T=298;
Cpy.K=1.76e-4; Cpy.E=5000; Cpy.T=298; Cpy.n1=0.5; Cpy.n2=1.17;
Cpy.gamma=0.93; Cpy.phi=0.333;
Py.K=1e-5; Py.E=25000; Py.T=298; Py.F=0.01; Py.A=0.01; Py.n=0.5;
Py.phi=0.5;
M.K=1e-3; M.E=2500; M.T=298;
FO.K=0.05; FO.E=2500; FO.T=298; FO.F=0.01;
%Input
irri=8;       % L_sol/h/m2
flow=irri*3.14*(diam^2)/4; % L_sol/h
\[
\lambda = \frac{\text{flow} \times \text{dbulk}}{(\theta \times \text{mMin})};
\]

cAcid\_i = 10; % g\_Acid/L\_sol

cFe3\_i = [0.5 1.25 2.5 3.75 4.5]; % g\_Fe3+/L\_sol

cFe2\_i = [4.5 3.75 2.5 1.25 0.5]; % g\_Fe2+/L\_sol

% for some reason doesn't converge 1.25 / 3.75

for \( k = 1:5 \)
    in.cAcid = cAcid\_i/mAcid; % mol\_Acid/L\_sol
    in.cFe3 = cFe3\_i(k)/(2*\text{mFe}); % mol\_Fe2(SO4)3/L\_sol
    in.cFe2 = cFe2\_i(k)/\text{mFe}; % mol\_FeSO4/L\_sol
    in.cCu = 0; % mol\_Cu/L\_sol
    in.cOx = kOx(T)\times pOx;

    \%
    \% Initial conditions
    gCu\_Cy = 0.0005588; % g\_Cu/g\_Min as Chrysocolla
    gCu\_Cc = 0.0011303; % g\_Cu/g\_Min as Chalcocite
    gCu\_Cpy = 0.0025; % g\_Cu/g\_Min as Chalcopyrite
    gCu\_Bb = 0.0020955; % g\_Cu/g\_Min as Bb
    gCu\_Ch = 0.00020828; % g\_Cu/g\_Min as Chalcantite

    gPy = 0.0041; % g\_Py/g\_Min
    gM = 0.033; % g\_M/g\_Min
    cCu\_0 = 0; % mol\_Acid/L\_sol
    cAcid\_0 = 0; % mol\_Acid/L\_sol
    cFe3\_0 = 0; % mol\_Acid/L\_sol
    cFe2\_0 = 0.000001; % mol\_Acid/L\_sol

    cCy\_0 = gCu\_Cy/\text{mCu}\times \text{dbulk}/\theta; % mol\_Cy/L\_sol
    cCc\_0 = gCu\_Cc/(2\times \text{mCu})\times \text{dbulk}/\theta; % mol\_Cy/L\_sol
    cBb\_0 = gCu\_Bb/(6\times \text{mCu})\times \text{dbulk}/\theta; % mol\_Ch/L\_sol
    cCh\_0 = gCu\_Ch/\text{mCu}\times \text{dbulk}/\theta; % mol\_Ch/L\_sol
    cCpy\_0 = gCu\_Cpy/\text{mCu}\times \text{dbulk}/\theta; % mol\_Cpy/L\_sol

    cPy\_0 = gPy/\text{mPy}\times \text{dbulk}/\theta; % mol\_Py/L\_sol
    cM\_0 = gM/\text{mM}\times \text{dbulk}/\theta; % mol\_M/L\_sol
    cOx\_0 = kOx(T)\times pOx;

    C\_0 = [cCu\_0;cAcid\_0; cFe3\_0; cFe2\_0; cCy\_0; cCc\_0; cBb\_0; cCh\_0; cCpy\_0; cPy\_0; cM\_0; cOx\_0]; % initial conditions

    options = odeset('NonNegative',[1 2 3 4 5 6 7 8 9 10 11 12], 'RelTol', 1e-5);
    [th,Cp] = ode45(@LeachReactions, [0 tf], C\_0, options);

    \%
    \% Recovery time-stepping
    n = size(Cp);
    xCu = zeros(n,1);

    xCu(1) = Cp(1) * mCu * flow * (th(2) - th(1)) / ((gCu\_Cy + gCu\_Cc + gCu\_Bb + gCu\_Ch + gCu\_Cpy) \times m\_Min);

    for \( i = 2:n \)
        xCu(i) = xCu(i-1) + Cp(i) \times mCu \times flow \times (th(i) - th(i-1)) / ((gCu\_Cy + gCu\_Cc + gCu\_Bb + gCu\_Ch + gCu\_Cpy) \times m\_Min);
    end

    \%
    \% Plot data
    plot(th./24, xCu, color(k), t1Data, R1Data, 'ob', t2Data, R2Data, 'or', t3Data, R3Data, 'ok', t4Data, R4Data, 'om', t5Data, R5Data, 'og'); hold on; % axis([0 tMax 0 1]);
    legend('model', 'data', 'Location', 'Best'); xlabel('days'); ylabel('Cu recovery');
end
function f = LeachReactions(t,C)
global T; global in; global lambda; global pOx; global beta;
global Cy; global Cc; global Bb; global Ch; global Cpy; global Py;
global M; global FO;
f = zeros(size(C));
cCu=C(1); cAcid=C(2); cFe3=C(3); cFe2=C(4); cCy=C(5); cCc=C(6);
cBb=C(7); cCh=C(8); cCpy=C(9); cPy=C(10); cM=C(11); cOx=C(12);

rCy = km(Cy.K,Cy.E,Cy.T,T)*cAcid/(Cy.F + cAcid)*cCy^0.667;
rCc = km(Cc.K,Cc.E,Cc.T,T)*cFe3/(Cc.F + cFe2)*cCc^Cc.phi;
rBb = km(Bb.K,Bb.E,Bb.T,T)*(cFe3/cFe2)^Bb.n1/(1+Bb.gamma*(cFe3/cFe2)^Bb.n2)*cBb^Bb.phi;% (cFe3/(Bb.F + cFe2))^0.333
rch = km(Ch.K,Ch.E,Ch.T,T)*cCh;
rCpy = km(Cpy.K,Cpy.E,Cpy.T,T)*(cFe3/cFe2)^Cpy.n1/(1+Cpy.gamma*(cFe3/cFe2)^Cpy.n2)*cCpy^Cpy.phi;
rPy = km(Py.K,Py.E,Py.T,T)*(cFe3/((Py.A+cAcid)*(Py.F+cFe2)))^Py.n*cPy^Py.phi;
rM = km(M.K,M.E,M.T,T)*cAcid;
rFO = km(FO.K,FO.E,FO.T,T)*cAcid/(FO.F+cAcid)*cFe2^2*cOx;
rSO = 0;

cOx_sat=kOx(T)*pOx;%Henry's law
kLa=20; % 1/hr oxygen mass transfer constant
rOx = kLa*(cOx_sat-cOx);

f(1) = lambda*(in.cCu - cCu) + rCy + 4*rCc + 6*rBb + rCh + rCpy;
f(2) = lambda*(in.cAcid - cAcid) - rCy - rM - 2*rFO + 2*rSO;
f(3) = lambda*(in.cFe3 - cFe3) - 4*rCc - 6*rBb - 2*rCpy - (1+6*beta)*rPy + 2*rFO;
f(4) = lambda*(in.cFe2 - cFe2) + 8*rCc + 12*rBb + 5*rCpy + (3+12*beta)*rPy - 4*rFO;
f(5) = -rCy;
f(6) = -5*rCc;
f(7) = rCc-rBb;
f(8) = -rCh;
f(9) = -rCpy;
f(10) = -rPy;
f(11) = -rM;
f(12) = lambda*(in.cOx-cOx) - rOx;

function Km_r=km(k,Ea,Tr,T)
R=8314;
Km_r=k*exp(-Ea/R*(1/T-1/Tr));

function K_Ox=kOx(T)
R=8.314;  \bar{A}=68623;  B=-1430.4;  C=-0.046;  D=203.35;
K_Ox=exp((A+B*T+C*T^2+D*T*log(T))/(R*T));
function solute_transport_integrated
  clear all; close all; clc;
  %-----------------
  [filename, pathnamen] = uigetfile('*.txt');
  inputfile = fopen([pathname, filename]);
  values = textscan(inputfile, '%f%f%f%f', 'delimiter','/t');
  fclose(inputfile);
  tdata=values{1}; c1data=values{2}; c2data=values{3}; c3data=values{4};
  %-----------------
  tmax = 360;                % maximum time [h]
  lmax = 0.93;               % column length [m]
  diam = 0.086;                 % column diameter [m]
  rhob = 1412;                  % bulk density [kg/m3]
  irri = [5.58 7.85 12];         % Irrigation rate [L/h/m2]
  theta = [0.1456 0.1560 0.1585];  % water content [-]
  c0 = 0;                    % initial condition [kg/m3]
  cin = 1;                   % boundary condition [kg/m3]
  nt = 40;                   % number of timesteps
  nl = 40;                   % number of nodes
  t = linspace(tmax/nt,tmax,nt);    % time discretization
  x = linspace(0,lmax,nl);      % space discretization
  v=irri/1000;   % sup velocity [m/h]
  Diff = 0.000198 + 0.4654*v; % [m2/h]
  for i=1:3
    options = odeset; if (c0 == 0) c0 = 1.e-20; end
    c = pdepe(0,@eqn,@initial,@bc,x,[0 t],options,Diff(i),v,c0,cin);
    %figure; surf (x,[0 t],c);
    %xlabel ('space'); ylabel ('time'); zlabel('concentration');
    for j=1:nt
      ct(i,j)=c(j,nt);
    end
  end
  figure; plot (t,ct,tdata,c1data,'o',tdata,c2data,'o',tdata,c3data,'o');
  hold on;
  xlabel('Time (hours)'); ylabel('C/Co');
  legend('6L/h/m2 model','8L/h/m2 model','12L/h/m2 model','6L/h/m2 data','8L/h/m2 data','12L/h/m2 data')

function [c,f,s] = eqn(x,t,u,DuDx,Diff,v,c0,cin)
c = 1;
f = Diff*DuDx;
s = -v*DuDx;

function u0 = initial(x,D,v,c0,cin)
u0 = c0;

function [pl,q1,pr,qr] = bc(xl,u1,xr,ur,t,Diff,v,c0,cin)
pl = ul-cin;
ql = 0;
pr = 0;
qr = 1;
Appendix C

Procedures

C.1 Ferrous Iron Titration with Potassium Permanganate

C.1.1 Preparing Potassium Permanganate KMnO₄ 0.02M

1. Dissolve about 3.2 g of KMnO₄ in 1L of deionized water using a large beaker.
2. Cover that beaker with a watch-glass and heat to boiling using a hot plate in the hood.
3. Keep the solution at a gentle boil for about 1 hr. Let the solution stand overnight.
4. Remove MnO₂ by filtering through a filter crucible.
5. Transfer the solution to a clean amber glass-stoppered bottle; store in the dark when not in use.

   Important: clean the filter and beakers using a solution of sodium bisulfite (use about 1g in 400 mL of water)

\[
\begin{align*}
158g \text{KMnO}_4 & \leftrightarrow 1M \leftrightarrow 1000mL \\
Xg \text{KMnO}_4 & \leftrightarrow 0.02M \leftrightarrow 1000mL \\
X = 3.16g \text{KMnO}_4 \left( \frac{1g \text{KPerm}}{0.995g \text{KMnO}_4} \right) = 3.17g \text{KPerm} @ 99.5%
\end{align*}
\]

C.1.2 1L of Sulfo-Phosphoric Solution (0.5M H₃PO₄ and 1.5M H₂SO₄)

1. Add 150 grams of sulfuric acid 98% into 500 mL of water while cooling the flask.
2. Once cooled the flask, add 57.64 grams of concentrated H₃PO₄ (85%)
3. Complete to 1000 mL.

\[
\begin{align*}
98g \text{H}_2\text{SO}_4 & \leftrightarrow 1M \leftrightarrow 1000mL \\
Xg \text{H}_2\text{SO}_4 & \leftrightarrow 1.5M \leftrightarrow 1000mL \\
X = 147g \text{H}_2\text{SO}_4 \left( \frac{1g \text{SulfAc}}{0.98g \text{H}_2\text{SO}_4} \right) = 150g \text{SulfAc} @ 98%
\end{align*}
\]

\[
\begin{align*}
98g \text{H}_3\text{PO}_4 & \leftrightarrow 1M \leftrightarrow 1000mL \\
Xg \text{H}_3\text{PO}_4 & \leftrightarrow 0.5M \leftrightarrow 1000mL \\
X = 49g \text{H}_3\text{PO}_4 \left( \frac{1g \text{PhosAc}}{0.85g \text{H}_3\text{PO}_4} \right) = 57.64g \text{PhosAc} @ 85%
\end{align*}
\]
C.1.3  Ferrous Iron Determination with Potassium Permanganate in 0.15M H₂SO₄ and 0.05M H₃PO₄ Media

1. In a 250 mL shaking flask add 10 mL of the sulfo-phosphoric solution.
2. Add 25 mL of the sample solution.
3. Complete the volume flask up to 100 mL.
4. With the flask in agitation titrate with 0.02M potassium permanganate solution until a stable pink endpoint is reached.
5. Calculate the ferrous Iron concentration according to:

\[
\text{V}_{\text{KMnO}_4} = 19.8\text{mL} \cdot 0.02\text{M} \\
\text{V}_{\text{Fe}^{2+}} = 25\text{mL} \cdot C_{\text{Fe}^{2+}} \\
\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}
\]

\[
(19.8\text{mL}) \left( \frac{0.02 \text{ mol MnO}_4^-}{L} \cdot \frac{1\text{L}}{1000\text{mL}} \right) \left[ \frac{5\text{ mol Fe}^{2+}}{1\text{ mol MnO}_4^-} \right] = 1.98 \times 10^{-3} \text{ mol Fe}^{2+}
\]

\[
C_{\text{Fe}^{2+}} = \left( \frac{1.98 \times 10^{-3} \text{ mol Fe}^{2+}}{25\text{mL} \cdot \text{Fe}^{2+}} \cdot \frac{1\text{L}}{1000\text{mL}} \right) \left[ \frac{56\text{ g Fe}^{2+}}{1\text{ mol Fe}^{2+}} \right] = 4.44 \text{ g Fe}^{2+} \cdot \frac{1}{L}
\]

C.2  Sulfuric Acid Titration Using Sodium Hydroxide and Methyl Orange as Indicator

C.2.1  Preparation of 1L sodium hydroxide 0.1

1. Dissolve about 4.04 g of NaOH in 700mL of deionized water
2. Dilute to 1 L in a volumetric with distilled water.

\[
40\text{g NaOH} \leftrightarrow 1\text{M} \leftrightarrow 1000\text{mL} \\
x\text{g NaOH} \leftrightarrow 0.1\text{M} \leftrightarrow 1000\text{mL} \\
X = 4\text{g NaOH} \left( \frac{1}{0.99} \right) = 4.04\text{g NaOH @ 99%}
\]

C.2.2  Preparation of Methyl orange indicator for pH change

1. Add 0.025 grams of methyl orange into 70 mL of ethyl alcohol
2. Stir the solution for 30 minutes.
3. Dilute to 100 mL with ethyl alcohol.

**C.2.3 Free Sulfuric Acid Determination with Sodium Hydroxide and Methyl Orange Indicator**

Methyl orange is **red in acidic solutions** and **orange in basic solutions**. Not appropriate if you have iron in solution which precipitates as orange at high pH.

1. Add 50 mL of distilled water in a 250 mL Erlenmeyer flask.
2. Add 5 drops of methyl orange, the initial color will be orange.
3. Add 2 mL of the sample solution in the Erlenmeyer flask. The solution will change to red color.
4. Titrate with 0.1M NaOH solution until a stable orange endpoint is reached.

\[ V_{NaOH} = 2.1 \text{mL} @ 0.1 \text{M} \]

\[ V_{H^+} = 2 \text{mL} @ C_{H^+} \]

\[ \text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

\[
(2.1 \text{mL}) \left[ 0.1 \text{ moleOH}^- \right] \left[ \frac{1 \text{L}}{1000 \text{mL}} \right] \left[ \frac{1 \text{ moleH}_2\text{SO}_4}{2 \text{ moleNaOH}} \right] = 1.05 \times 10^{-4} \text{ moleH}_2\text{SO}_4
\]

\[
C_{H_2SO_4} = \left[ \frac{1.05 \times 10^{-4} \text{ moleH}^+}{2 \text{ moleH}^+} \right] \left[ \frac{1000 \text{ mL}}{1 \text{ L}} \right] \left[ \frac{98 \text{ gH}_2\text{SO}_4}{1 \text{ moleH}_2\text{SO}_4} \right] = 5.14 \frac{\text{gH}_2\text{SO}_4}{\text{L}}
\]

**C.3 Sulfuric Acid Titration Using Sodium Hydroxide and Bromothymol Blue**

**C.3.1 Bromothymol Blue (~0.0064M NaOH) indicator for pH change**

1. Add 0.1g Bromthymol blue into 16ml of 0.1M NaOH
2. Add 4mL of ethyl alcohol.
3. Dilute to 250ml with distilled water. The solution should be deep blue
4. If it is green, add sodium hydroxide solution drop by drop until the solution turns blue.

**C.3.2 Free Sulfuric Acid Determination With Sodium Hydroxide and Bromothymol Blue as Indicator**

Bromothymol blue is yellow in acidic solutions and blue in basic solutions.
If you have iron in solution which precipitates as orange at high pH the change color will be around green. Make sure the change in color is stable.

1. Add 50 mL of distilled water in a 250 mL Erlenmeyer flask.
2. Add 5 drops of bromothymol blue, the initial color will be blue.
3. Add 2 mL of the sample solution in the Erlenmeyer flask, the color will change to yellow.
4. Titrate with 0.1M NaOH solution until a stable blue color endpoint is reached.

\[ V_{\text{NaOH}} = 2.1\text{mL @ 0.1M} \]
\[ V_{H^+} = 2\text{mL @ } C_{H^+} \]
\[ H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \]

\[
(2.1\text{mL}) \left( 0.1 \frac{\text{molOH}^-}{\text{L} \times 1000\text{mL}} \right) \left( \frac{1\text{molH}_2\text{SO}_4}{2\text{molNaOH}} \right) = 1.05 \times 10^{-4}\text{molH}_2\text{SO}_4
\]

\[
C_{H_2SO_4} = \left( \frac{1.05 \times 10^{-4}\text{molH}^+}{2\text{mLH}^+} \right) \left( \frac{1000\text{mL}}{1\text{L}} \right) \left( \frac{98\text{gH}_2\text{SO}_4}{1\text{molH}_2\text{SO}_4} \right) = 5.14\text{gH}_2\text{SO}_4/\text{L}
\]

**C.4 Aqua Regia Digestion for Solid Sample Analysis**

1. Add 0.5g dried ore sample into 20ml of concentrated Aqua-Regia
2. Leach at 80°C for 30 minutes.
3. Filter, dilute to 1000mL and read on atomic absorption.

\[ \text{HNO}_3(\text{aq}) + 3\text{HCl(}aq) \rightarrow \text{NOCl(g)} + 2\text{H}_2\text{O(}aq) \]

\[
63\text{gHNO}_3 \left( \frac{1\text{g NitricA}}{0.68\text{g} \text{HNO}_3} \right) \left( \frac{1\text{mL NitricA}}{1.42\text{gNitricA}} \right) = 65.2\text{mL NitricA}
\]

\[
3 \times 35.5\text{gHCl} \left( \frac{1\text{g ChlorA}}{0.37\text{g HCl}} \right) \left( \frac{1\text{mL ChlorA}}{1.19\text{gChlorA}} \right) = 247.9\text{mL ChlorA}
\]

\[
x(65.2 + 247.9) = 20\text{mL}
\]

\[
x_{20} = 0.064 \quad x_{100} = 0.319
\]

4.17mL NitricA 20.79mL NitricA

15.86mL ChlorA 79.08mL ChlorA
Method 1: guess 1% Cu

\[ C_{Sample} \frac{V_{Sample}}{V_{AA}} = C_{AA} \frac{V_{AA}}{V_{AA}} \]

\[0.5g Min \left( \frac{1g Cu}{100g Min} \right) V_{AA} = 0.005 \frac{g Cu}{L} V_{AA} \]

\[ V_{AA} = 1L \]

Dilute to 1L and read on AA

Method 2: guess 1% Cu

\[ C_{Sample} \frac{V_{Sample}}{V_{Sample}} = C_{AA} \frac{V_{AA}}{V_{Sample}} \]

\[ 0.5g Min \left( \frac{1g Cu}{100g Min} \right) \frac{0.1L}{V_{Sample}} = 0.005 \frac{g Cu}{L} [50mL] \]

\[ V_{Sample} = 5mL \]

Dilute to 0.1L and take 5mL on 50mL volumetric flask then, read on AA

C.5 Dynamic Moisture Determination

Hardware and Software

2. Plexiglas column with 10 cm internal diameter and 20 cm height equipped with a radial screen at the bottom of the column with at least 1 cm of separation between the screen and the drain outlet.
4. PC Windows XP and Microsoft Excel.
5. VBA Excel code for data acquisition using Chapcomm™.

2L synthetic raffinate solution containing 5g/L H₂SO₄ and Fe⁴⁺=2.5g/l with Fe³⁺/Fe²⁺=1/1
\[
5 \frac{\text{gH}_2\text{SO}_4}{\text{L}} \cdot \{2\text{L}\} \left( \frac{1\text{gSulfAcid}}{0.98\text{gH}_2\text{SO}_4} \right) = 10.20\text{g SulfAcid}
\]
\[
5 \frac{\text{gH}_2\text{SO}_4}{\text{L}} \cdot \{2\text{L}\} \left( \frac{1\text{mL SulfAcid}}{0.98\text{gH}_2\text{SO}_4} \right) = 5.55\text{mL SulfAcid}
\]
\[
1.25 \frac{\text{gFe}^{3+}}{\text{L}} \cdot \{2\text{L}\} \left( \frac{490\text{gFe}_2\text{(SO}_4)_3 \cdot 5\text{H}_2\text{O}}{2 \cdot 56\text{gFe}^{3+}} \right) \left( \frac{1\text{gFerricSulf}}{0.97\text{gFe}_2\text{(SO}_4)_3 \cdot 5\text{H}_2\text{O}} \right) = 11.28\text{g FerricSulf}
\]
\[
1.25 \frac{\text{gFe}^{2+}}{\text{L}} \cdot \{2\text{L}\} \left( \frac{278\text{gFeSO}_4 \cdot 7\text{H}_2\text{O}}{56\text{gFe}^{2+}} \right) \left( \frac{1\text{gFerrousSulf}}{0.98\text{gFeSO}_4 \cdot 7\text{H}_2\text{O}} \right) = 12.66\text{g FerrousSulf}
\]

Irrigation rate

\[
\left( \frac{8 \text{L}}{\text{h} \cdot \text{m}^2} \right) \pi \left( \frac{10\text{cm}}{2} \right) \left( \frac{1\text{m}}{100\text{cm}} \right)^2 \left( \frac{1\text{h}}{60\text{min}} \right) \left( \frac{1000\text{mL}}{1\text{L}} \right) = 1.047 \frac{\text{mL}}{\text{min}}
\]

Dynamic moisture retention

\[
w_{\text{max}} = \text{Maximum weight during stable irrigation}
\]
\[
w_{\text{dry}} = \text{weight of dry mineral}
\]
\[
H_d = \frac{w_{\text{max}}}{w_{\text{dry}}}
\]

Procedure

1. Take a representative sample of 1kg of Mineral.
2. Add raffinate to get the optimum moisture agglomeration (10% in this case), agglomerate and rest for 7 days.
3. Start registering weight and irrigate the column at 8L/h/m² for two days.
4. Stop irrigating then, after a day stop registering the weight.
C.6 Sulfuric acid consumption test

1. In a jacketed reactor at 25°C equipped with pH and ORP probe, add 100mL of distilled water (33% of solids).
2. Start the pH control at pH to 1.0 (1.5 and 2.0) with 100g/L sulfuric acid using a burette (or scale).
3. Add Fe$_2$(SO$_4$)$_3$•5H$_2$O and FeSO$_4$•7H$_2$O (look the calculation below).
4. Once dissolved reach the desired pH and dissolved the ferric and ferrous iron add 50 g of mineral (33% of solids).
5. Leach for 3 hours then,
6. Filter and wash with distilled water the solution.
7. Dry, weight and analyze the solid residue for copper and total ferrous iron.
8. Pour the total solution in a 250 mL volumetric flask and complete it with distilled water up to 250.
Figure C.2  Sulfuric acid consumption test set up

Solids percentage

\[ V_{\text{liq}} = \frac{M_{\text{solid}}}{\rho_{\text{liq}}} \left( \frac{1}{f_{\text{solid}}} - 1 \right) \]

\[ V_{\text{liq}} = \frac{50 \text{g}}{1 \text{g/mL} \left( \frac{1}{0.33} - 1 \right)} = 100 \text{mL} \]
Ferric iron and ferrous iron addition $Fe^{3+}/Fe^{2+}=1/1$ with $Fe^T=5g/l$

$$
2.5 \frac{gFe^{3+}}{L} \cdot 0.1L \left( \frac{490gFe_2(SO_4)_3 \cdot 5H_2O}{2*56gFe^{3+}} \right) \left( \frac{lgFerricSulf}{0.97gFe_2(SO_4)_3 \cdot 5H_2O} \right) = 1.12gFe_2(SO_4)_3 \cdot 5H_2O
$$

$$
2.5 \frac{gFe^{2+}}{L} \cdot 0.1L \left( \frac{278gFeSO_4 \cdot 7H_2O}{56gFe^{2+}} \right) \left( \frac{lgFerrousSulf}{0.98gFeSO_4 \cdot 7H_2O} \right) = 1.26gFeSO_4 \cdot 7H_2O
$$

Ferric iron and ferrous iron addition $Fe^{3+}/Fe^{2+}=1/3$ with $Fe^T=5g/l$

$$
1.25 \frac{gFe^{3+}}{L} \cdot 0.1L \left( \frac{490gFe_2(SO_4)_3 \cdot 5H_2O}{2*56gFe^{3+}} \right) \left( \frac{lgFerricSulf}{0.97gFe_2(SO_4)_3 \cdot 5H_2O} \right) = 0.56gFe_2(SO_4)_3 \cdot 5H_2O
$$

$$
3.75 \frac{gFe^{2+}}{L} \cdot 0.1L \left( \frac{278gFeSO_4 \cdot 7H_2O}{56gFe^{2+}} \right) \left( \frac{lgFerrousSulf}{0.98gFeSO_4 \cdot 7H_2O} \right) = 1.89gFeSO_4 \cdot 7H_2O
$$

Ferric iron and ferrous iron addition $Fe^{3+}/Fe^{2+}=3/1$ with $Fe^T=5g/l$

$$
3.75 \frac{gFe^{3+}}{L} \cdot 0.1L \left( \frac{490gFe_2(SO_4)_3 \cdot 5H_2O}{2*56gFe^{3+}} \right) \left( \frac{lgFerricSulf}{0.97gFe_2(SO_4)_3 \cdot 5H_2O} \right) = 1.69gFe_2(SO_4)_3 \cdot 5H_2O
$$

$$
1.25 \frac{gFe^{2+}}{L} \cdot 0.1L \left( \frac{278gFeSO_4 \cdot 7H_2O}{56gFe^{2+}} \right) \left( \frac{lgFerrousSulf}{0.98gFeSO_4 \cdot 7H_2O} \right) = 0.63gFeSO_4 \cdot 7H_2O
$$

Sulfuric acid consumption

$$
5mLH_2SO_4 \left( \frac{100gH_2SO_4}{1000mL} \right) \left( \frac{1}{0.05kg_{\text{Mineral}}} \right) = 10 KgH_2SO_4 \text{ton}_{\text{Mineral}}
$$

Dilution

$$
C_i V_i + C_w V_w = C_f V_f \quad C_w = 0
$$

$$
C_i = C_f \left( \frac{V_f}{V_i} \right) = C_f \left( \frac{100mL_{\text{vol.flask}}}{\text{ImL}_{\text{sample}}} \right) = 100C_f
$$

Recovery

$$
\text{w}_{Cu} \text{g}_{\text{PLS+wash}} = \left( \frac{C_{Cu-PLS-Wash}}{L} \right) [\text{IL}]
$$

$$
\text{w}_{Cu} \text{g}_{\text{Sol.Residue}} = \left( \frac{C_{Cu-Mineral}}{ton_{\text{Mineral}}} \right) \left( \frac{1\text{ton}_{\text{Mineral}}}{10^6 \text{g}_{\text{Mineral}}} \right) \left( \text{wg}_{\text{Sol.Residue}} \right)
$$

$$
R_{Cu} = \frac{\text{w}_{Cu} \text{g}_{\text{PLS+wash}}}{\text{w}_{Cu} \text{g}_{\text{PLS+wash}} + \text{w}_{Cu} \text{g}_{\text{Sol.Residue}}}
$$
C.7 Galvanox Chalcopyrite-Pyrite / Enargite-Activated Carbon Leaching

1. Tare a flask and add 1000 mL of distilled water.
2. Add 30 g of sulfuric acid and complete till 1500 g of solution.
3. Pour the solution in the jacketed reactor and turn-on the water bath to 80 ºC.
4. Start stirring at low speed (500 rpm) and pour X g of Fe₂(SO₄)₃·5H₂O and Y g of FeSO₄·7H₂O.
5. Calibrate the pH and ORP electrodes and insert them in the reactor.
6. Once dissolved the sulfate salts and reached 80 ºC, start the data logger and control of oxygen at the desired ORP set-point.
7. Pour the concentrate and pyrite into the reactor.
8. For kinetic study, take a sample of 4 mL every determined time, centrifuge it and just keep 2 mL of solution free of solids for analysis. Agitated the rest of the sample and pour it into the reactor.
9. Finally, filter the pulp and take a sample of 2 mL. Then, wash the solid with 500 g of water and take another sample of 2 mL.

\[
f_{\text{solid}} = \frac{M_{\text{solid}}}{M_{\text{solid}} + V_{\text{liq}} \rho_{\text{liq}}}
\]

\[
C_{\text{py}} + P_{\text{y}} = M_{\text{solid}} = \frac{V_{\text{liq}} \rho_{\text{liq}}}{1 - \frac{1}{f_{\text{solid}}}} - 1
\]

\[
r_{\text{py}} = \frac{C_{\text{py}}}{P_{\text{y}}}
\]

\[
C_{\text{py}} = \left(\frac{V_{\text{liq}} \rho_{\text{liq}}}{1 - \frac{1}{f_{\text{solid}}}}\right) \left(\frac{1}{1 + \frac{1}{r_{\text{py}}}}\right)
\]

\[
P_{\text{y}} = \left(\frac{V_{\text{liq}} \rho_{\text{liq}}}{1 - \frac{1}{f_{\text{solid}}}}\right) \left(\frac{1}{1 + r_{\text{py}}/P_{\text{y}}}\right)
\]

1.5L solution containing 20g/L H₂SO₄ and Fe⁺=1.6g/l with Fe³⁺/Fe²⁺=1/1

\[
20 \frac{\text{gH}_2\text{SO}_4}{\text{L}} \{1.5\text{L}\} \left(\frac{1\text{gSulfAcid}}{0.98\text{gH}_2\text{SO}_4}\right) = 30.60\text{g SulfAcid}
\]

\[
0.8 \frac{\text{gFe}^{3+}}{\text{L}} \{1.5\text{L}\} \left(\frac{490\text{gFe}_2(\text{SO}_4)_3\cdot5\text{H}_2\text{O}}{2\times56\text{gFe}^{3+}}\right) \left(\frac{\text{lgFerricSulf}}{0.97\text{gFe}_2(\text{SO}_4)_3\cdot5\text{H}_2\text{O}}\right) = 5.34\text{g FerricSulf}
\]

\[
0.8 \frac{\text{gFe}^{2+}}{\text{L}} \{1.5\text{L}\} \left(\frac{278\text{gFeSO}_4\cdot7\text{H}_2\text{O}}{56\text{gFe}^{2+}}\right) \left(\frac{\text{lgFerrousSulf}}{0.98\text{gFeSO}_4\cdot7\text{H}_2\text{O}}\right) = 6.00\text{g FerrousSulf}
\]