MODELLING OF BACTERIAL LEACHING IN HEAP
WITH FORCED AERATION

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My deepest gratitude goes to all my family for their continuous support, love and confidence.
SUMMARY

Transient models for bioleaching of sulphide minerals of copper in heaps/dumps were developed for a bed with forced aeration and a heap formed by three particles sizes. 1-D transient model was developed for describing the impact of the different parameters on the performance of the bioleaching. Equations for the transport de oxygen, mass balance for copper and ferric ions, and heat transport were considered. The reaction in the particles was described by the shrinking core model and one equation for each particle size was required, which describes the variation of the unreacted core radius with time. 2-D model was developed to determine the air flow distribution in the heap.

The main purpose of this research is to show the impact of the different parameters on the leach process and to identify the zones where the aeration is not appropriate and to generate new aeration configurations for optimising the heap performance. In addition that the possibility to find some “average radius” that represents a heap with a distribution of particle size also was studied.

Different configurations of the aeration channels were studied. For the 10 m-high heaps, three distances were tested: 20, 10, and 5 m. When the aeration channels are quite separate, the oxygen concentration between them is low, because the air flow is poor in these zones. The objective of the aeration system is to obtain the same reaction rate at a same height. This may be obtained by increasing the gas flow or by designing an appropriate channel distribution. At the end, the aeration system is an economical decision, which has to consider several factors, such as particle size, type of mineral, number and type of bacteria, heap dimension, and equipment cost.

The possibility of finding some average particle size, such that simulations using this average radius had a performance similar to that of the heap with the particle size distribution was addressed. Two average radii were tested. Three different sizes with a given distribution function were considered. The first one is the “weight average radius” where the weight fraction for each size is used as weighting factor. The second one is the “surface average radius” where the specific surface fraction for each size is
used as weighting factor. The simulations show that it is not possible to find such average radii. This means that the performance of the heap can not be determined using an “average radius”, therefore a distribution of particle sizes has to be used.
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<thead>
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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Constant of Antoine’s equation</td>
<td>(-)</td>
</tr>
<tr>
<td>B</td>
<td>Constant of Antoine’s equation</td>
<td>(-)</td>
</tr>
<tr>
<td>C</td>
<td>Constant of Antoine’s equation</td>
<td>(-)</td>
</tr>
<tr>
<td>$C_{N_2}$</td>
<td>Nitrogen concentration in the gaseous phase</td>
<td>( \text{kg} \cdot \text{m}^{-3} )</td>
</tr>
<tr>
<td>$C_{p,B}$</td>
<td>Average specific heat of bed</td>
<td>( \text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} )</td>
</tr>
<tr>
<td>$C_{p,L}$</td>
<td>Average specific heat of liquid</td>
<td>( \text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} )</td>
</tr>
<tr>
<td>$C_{p,g}$</td>
<td>Average specific heat of gas</td>
<td>( \text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} )</td>
</tr>
<tr>
<td>$C_{p,vap}$</td>
<td>Specific heat of the water vapour</td>
<td>( \text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} )</td>
</tr>
<tr>
<td>$D_l$</td>
<td>Dispersivity</td>
<td>( \text{m}^2 \cdot \text{s}^{-1} )</td>
</tr>
<tr>
<td>FPY</td>
<td>pyrite/chalcocite Ratio</td>
<td>(-)</td>
</tr>
<tr>
<td>$F_{N_2}$</td>
<td>Specific flow of nitrogen</td>
<td>( \text{m} \cdot \text{s}^{-1} )</td>
</tr>
<tr>
<td>$F_{O_2}$</td>
<td>Specific flow of oxygen</td>
<td>( \text{m} \cdot \text{s}^{-1} )</td>
</tr>
<tr>
<td>$F_{H_2O}$</td>
<td>Specific flow of water vapour</td>
<td>( \text{m} \cdot \text{s}^{-1} )</td>
</tr>
<tr>
<td>$f_{31}$</td>
<td>Weight fraction for the average size 1</td>
<td>(-)</td>
</tr>
<tr>
<td>$f_{32}$</td>
<td>Weight fraction for the average size 2</td>
<td>(-)</td>
</tr>
<tr>
<td>$f_{33}$</td>
<td>Weight fraction for the average size 3</td>
<td>(-)</td>
</tr>
<tr>
<td>$G$</td>
<td>Ore grade</td>
<td>(-)</td>
</tr>
<tr>
<td>$H_2O_{vap}$</td>
<td>Concentration of water vapour in the gas</td>
<td>( \text{kmol} \cdot \text{m}^{-3} )</td>
</tr>
<tr>
<td>He</td>
<td>Henry’s Constant</td>
<td>( \text{m}^2 \cdot \text{kg} \cdot \text{kmol}^{-1} \cdot \text{s}^{-2} )</td>
</tr>
<tr>
<td>$H_L$</td>
<td>Enthalpy of the liquid</td>
<td>( \text{kJ} \cdot \text{kg}^{-1} )</td>
</tr>
<tr>
<td>$H_R$</td>
<td>Enthalpy of the gas</td>
<td>( \text{kJ} \cdot \text{kg}^{-1} )</td>
</tr>
<tr>
<td>$\Delta H_R$</td>
<td>Enthalpy Reaction</td>
<td>( \text{kJ} \cdot \text{kmol}^{-1} )</td>
</tr>
</tbody>
</table>
\( \Delta H_S \)  Heat of solution of the reaction products \((kJ \cdot kmol^{-1})\)

\( \Delta H_{Ch} \)  Chalcocite reaction enthalpy \((kJ \cdot kg^{-1})\)

\( \Delta H_{Py} \)  Pyrite reaction enthalpy \((kJ \cdot kg^{-1})\)

\( \Delta H_{CuSO_4} \)  Enthalpy of solution for \( CuSO_4 \) \((kJ \cdot kg^{-1})\)

\( \Delta H_{FeSO_4} \)  Enthalpy of solution for \( FeSO_4 \) \((kJ \cdot kg^{-1})\)

\( k \)  Bed permeability \((m^2)\)

\( k_s \)  Global specific kinetics \((m^2 \cdot s^{-1})\)

\( k_g \)  Mass transfer coefficient in the liquid-solid film \((m \cdot s^{-1})\)

\( k_B \)  Effective thermal conductivity in bed \((kJ \cdot m^{-1} \cdot s^{-1} \cdot K^{-1})\)

\( K_m \)  Michaelis constant \((kg \cdot m^{-3})\)

\( K_{ads} \)  Absorption constants \((m^3 \cdot bacteria^{-1} \cdot s^{-1})\)

\( K_{des} \)  Desorption constants \((s^{-1})\)

\( mFPY \)  Molar pyrite/chalcocite Ratio \((-)\)

\( M_{N_2} \)  Molecular weight of Nitrogen \((kg \cdot kmol^{-1})\)

\( M_{O_2} \)  Molecular weight of Oxygen \((kg \cdot kmol^{-1})\)

\( M_{Cu} \)  Molecular weight of Copper \((kg \cdot kmol^{-1})\)

\( M_{Ch} \)  Molecular weight of chalcocite \((kg \cdot kmol^{-1})\)

\( M_{Fe} \)  Molecular weight of iron \((kg \cdot kmol^{-1})\)

\( M_{Py} \)  Molecular weight of Pyrite \((kg \cdot kmol^{-1})\)

\( n_{N_2} \)  Kilo moles of nitrogen \((kmol)\)

\( n_{O_2} \)  Kilo moles of Oxygen \((kmol)\)

\( n_{H_2O_{vap}} \)  Kilo moles of water vapour \((kmol)\)

\( n_{Ch} \)  Kilo moles of chalcocite \((kmol)\)

\( O_{2L} \)  Oxygen concentration in the liquid solution \((kmol \cdot m^{-3})\)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_{2,g}$</td>
<td>Oxygen concentration in the gas</td>
<td>$(\text{kmol} \cdot \text{m}^{-3})$</td>
</tr>
<tr>
<td>$P$</td>
<td>Total Pressure</td>
<td>$(\text{Pa}) = (\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2})$</td>
</tr>
<tr>
<td>$P_{N_2}$</td>
<td>Partial pressure of nitrogen</td>
<td>$(\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2})$</td>
</tr>
<tr>
<td>$P_{O_2}$</td>
<td>Partial pressure of oxygen</td>
<td>$(\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2})$</td>
</tr>
<tr>
<td>$P_{H_2O}$</td>
<td>Partial pressure of water vapour</td>
<td>$(\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2})$</td>
</tr>
<tr>
<td>$q_L$</td>
<td>Specific flow rate of liquid</td>
<td>$(\text{m} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$q_g$</td>
<td>Specific flow rate of gas</td>
<td>$(\text{m} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$R_{Cu}$</td>
<td>Dissolution rate of copper</td>
<td>$(\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$R_{Fe^{3+}}$</td>
<td>Consumption rate of ferric ions</td>
<td>$(\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$R_{O_2}$</td>
<td>Consumption rate of oxygen</td>
<td>$(\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$R_{Cu}$</td>
<td>Dissolution rate of chalcocite</td>
<td>$(\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$R_{py}$</td>
<td>Dissolution rate of pyrite</td>
<td>$(\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Initial radius of mineral ore particle</td>
<td>$(\text{m})$</td>
</tr>
<tr>
<td>$r_c$</td>
<td>Radius of unreacted core of them particle</td>
<td>$(\text{m})$</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal Gas constant</td>
<td>$(\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1})$</td>
</tr>
<tr>
<td>$r_c$</td>
<td>Unreacted particle core radius</td>
<td>$(\text{m})$</td>
</tr>
<tr>
<td>$S_{ex}$</td>
<td>External surface area</td>
<td>$(\text{m}^2)$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>$(\text{K})$</td>
</tr>
<tr>
<td>$T_{ref}$</td>
<td>Reference Temperature</td>
<td>$(\text{K})$</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Maximum rate of oxygen consumption by bacteria</td>
<td>$(\text{kmol} \cdot \text{bacteria}^{-1} \cdot \text{s}^{-1})$</td>
</tr>
<tr>
<td>$V_g$</td>
<td>Gas volume</td>
<td>$(\text{m}^3)$</td>
</tr>
<tr>
<td>$X$</td>
<td>Number of bacteria per volume of bed</td>
<td>$(\text{bacteria} \cdot \text{m}^{-3} \cdot \text{bed})$</td>
</tr>
<tr>
<td>$X_a$</td>
<td>Concentration of attached cells</td>
<td>$(\text{bacteria} \cdot \text{m}^{-3} \cdot \text{bed})$</td>
</tr>
<tr>
<td>$X_s$</td>
<td>Concentration of bacteria in solution</td>
<td>$(\text{bacteria} \cdot \text{m}^{-3} \cdot \text{bed})$</td>
</tr>
</tbody>
</table>
$X_{\text{sat}}$ Saturation concentration of bacteria attached to the surface of ore particles $(\text{bacteria} \cdot \text{m}^{-3}\text{bed})$

$X_{O_2, g}$ Ratio between oxygen and nitrogen in the gas. $(-)$

$X_{N_2}$ Volumetric fraction of nitrogen in the gas. $(-)$

$X_{H_2O, g}$ Volumetric fraction of water in the gas $(-)$
Greek letters

$\varepsilon_L$ Volumetric fraction of liquid
$\varepsilon_g$ Volumetric fraction of air
$\varepsilon_s$ Volumetric fraction of solid
$\mu$ Specific bacterial growth rate

$$  $\rho_{air}$ Incoming gas flow Density
$\rho_M$ Mineral Particle density
$\rho_p$ Initial particle Density
$\rho_B$ Bed Density
$\phi$ Particle shape factor
$\sigma$ Stoichiometric factor
$\mu_g$ Average gas viscosity
1. INTRODUCTION

Today the known copper reserves in Chile are estimated in 88 millions of tons, equivalent to the 25.8% of the whole of copper’s reserves around the world. The reserve is referred to the mineral available in the nature that can be processed with the actual technology and it is economically profitable. All the copper minerals cannot be treated today. In the mining area, the development and generation of new technologies have as the main objective that the minerals considered as resource at the present could be considered reserve in the future. The capacity to increase the mineral reserves through the research and knowledge is of great economic interest.

Leaching is an important process in mining industry. The Leach is a process that implies the dissolution of the specie(s) from the mineral host. In the recent years, bioleaching has been widely applied in industrial scale due to its low cost and environment friendliness.

The bioleaching arises in the late 1950s as an option to treat sulphide minerals that, hardly without the bacterial technology, can be treated by hydrometallurgy way. In the beginning the bioleaching was considered as an alternative to treat low-grade minerals, mixed minerals, or others that were hardly treatable by conventional hydrometallurgy methods. Now the question is: Why does not it treat the high-grade minerals also?

In general, microbial dissolution of metals involves direct adhesion/attack of the bacterial cell on the particle and/or allowing chemical oxidation, wich liberate the interest metal by ferric iron generated by microbially and/or through oxidation by air. The prolonged recycling of \( Fe^{2+}/Fe^{3+} \) couple by the bacteria is essential to keep an environment of high redox potential that is required for the efficient leaching. Ferric ion, which is a powerful oxidizing agent, allows the treatment of, for example, copper sulphide minerals.
Many of the phenomena that happen during the bioleaching are not totally understood and therefore, they need to continue being studied because these factors are fundamentals for the control and industrial application of this process.

The bioleach process can be carried on in heaps, dump, in-situ, or in reactors. It may be used to recover copper and other metals such as zinc, cobalt, and uranium. In the case of Uranium, the ferric ions oxidize the tretavalent uranium oxide, which is insoluble in acid, to hexavalent uranium oxide, which is then leached by the sulphuric acid. In the biooxidation of refractory gold ores, bacteria are used to oxidize, and therefore make soluble the iron sulphide matrix in which the gold particles are imbedded and thus make the gold available for cyanide leaching (Dresher, 2004).

Bioleaching in Heap and reactors have been modelled by several authors. For example, Casas et al. (1998) developed a two-dimensional model for heap or dump bioleaching of copper ore containing mainly chalcocite and pyrite. Crundwell (2001, 2005) modelled bacterial leaching in reactors, where a distribution was used to describe the particle size. The reaction in the particle was considered by using the shrinking core model. Lizama (2001) studied the copper bioleaching behaviour in an aerated heap, he measured oxygen concentration at different levels inside the heap. Sidborn et al. (2003), Sidborn and Moreno (2003) modelled heap leaching and studied the influence of several process variables on copper recovery with time. The impact of natural and forced aeration on the leaching process was studied in detail. Leahy et al. (2005) developed a model for heap bioleaching of chalcocite where the activity of the bacteria is temperature dependent.

2. **OBJECTIVES**

The aim of this thesis is the development of a model for heap bioleaching with forced aeration and a distribution of particle size. One- and two-dimensional models are developed. Simulations are carried out with the models and copper recovery, reaction advance, concentration of the species in the bed and temperature profiles are determinate as a function of time.

For heaps with a distribution of particle size, the possibility to find an appropriate average particle size, which was representative of the performance of the heap during the bioleaching, is studied.

And finally, to identify the zones where the aeration is not appropriate and to generate new aeration configurations.
3. THE BIOLEACH PROCESS

Leaching is a critical operation in Hydrometallurgy. The performance of the leaching sections of a processing plant usually has a significant impact on the performance of a plant LX-SX-EW (Crundwell, 2005). Mineral bioleaching research has been a great impact for the mining industry. In the recent years, bioleaching has been widely applied on an industrial scale because of the advantages of low cost and environment friendliness, without strict requirements of raw material composition, and is suitable for the treatment of complex and low-grade ores (Ehrlich, 2000). The Bioleaching of sulphide minerals has been applied in the extraction of copper (Brierley, 2001) and cobalt (Brochot et al, 2004), pre-treatment of refractory gold-bearing sulphides (Bouffard and Dixon, 2002). Investigations indicate that a number of mineral sulphides containing zinc, nickel, molybdenum, and manganese are some metals potentially recoverable through bacterial leaching (Shi, 2005).

**Figure 3.1:** Maximum solubility of the copper minerals in the sulphuric acid and cyanide of sodium solution (Zeballos et al., 2003)

Figure 3.1 shows that it is possible to treat by acid leaching the copper oxides like the cuprite, tenorite, chrysocolla and that some copper sulphur may be treated through of the dissolution by cyanid media, i.e., bornite, covellite, chalcocite, but in the other hand, is quite difficult to treat mineral like the chalcopyrite by hydrometallurgical processes.
Each year millions of tons of minerals are accumulated because of their low mineralogical grade or composition due to these minerals could not be treated at that time. The reason was that, recover the copper from them was not profitable economically with the technology available in that time. At the present there are other challenges: the mineral grades are lower than before and the composition makes very difficult the Hydrometallurgical treatment.

Bioleaching is used today in three different regimes dependent upon of raw material types to be processed (Dresher, 2004):

1) Dump Leaching: Waste rock, low grade ore or concentrator tailings (low grade, oxides and secondary sulphides) are leached where placed for disposal

2) Heap Leaching: Newly mined run-of-the-mine (ROM) material (intermediate grade, oxides and secondary sulphides) is disposed in a heap on an impervious natural surface or a pad and leached. ROM may be leached as mined or may be partially crushed and mixed with acid prior to depositing on heap; Primary Sulphides, e.g., chalcopyrite.

3) Agitated Leaching: Intermediate to high-grade, refractory minerals are deposited in a tank and leached using mechanical agitation, e.g., chalcopyrite concentrate.

There are several industrial operations that have Bioleaching (Dresher, 2004), they are shown in Table 1

Table 1: Industrial Operation with Acid Mine Drainage.

<table>
<thead>
<tr>
<th>Acid Mine Drainage</th>
<th>Company</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rio Tinto</td>
<td>Spain</td>
</tr>
<tr>
<td></td>
<td>El Teniente</td>
<td>Chile</td>
</tr>
</tbody>
</table>
**Table 2: Industrial Operation with Dump Leaching.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagdad</td>
<td>USA</td>
</tr>
<tr>
<td>Morenci</td>
<td>USA</td>
</tr>
<tr>
<td>Pinto Valley</td>
<td>USA</td>
</tr>
<tr>
<td>Sierita</td>
<td>USA</td>
</tr>
</tbody>
</table>

**Table 3: Industrial Operation with Heap Leaching.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerro Colorado</td>
<td>Chile</td>
</tr>
<tr>
<td>Cananea</td>
<td>Mexico</td>
</tr>
<tr>
<td>Chuquicamata SBL</td>
<td>Chile</td>
</tr>
<tr>
<td>Collahuasi</td>
<td>Chile</td>
</tr>
<tr>
<td>Escondida</td>
<td>Chile</td>
</tr>
<tr>
<td>Girilambone</td>
<td>Austria</td>
</tr>
<tr>
<td>Ivan Zar</td>
<td>Chile</td>
</tr>
<tr>
<td>Morenzi</td>
<td>USA</td>
</tr>
<tr>
<td>Punta del Cobre</td>
<td>Chile</td>
</tr>
<tr>
<td>Quebrada Blanca</td>
<td>Chile</td>
</tr>
<tr>
<td>Salvador QM</td>
<td>Chile</td>
</tr>
<tr>
<td>Zaldivar</td>
<td>Chile</td>
</tr>
</tbody>
</table>
Table 4: Industrial Operation with Bioleaching of Gold Concentrates.

<table>
<thead>
<tr>
<th>Company</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ashanti</td>
<td>Ghana</td>
</tr>
<tr>
<td>Fairview</td>
<td>Zambia</td>
</tr>
<tr>
<td>Harbour Lights</td>
<td>Australia</td>
</tr>
<tr>
<td>Mount Leyshon</td>
<td>Australia</td>
</tr>
<tr>
<td>Sao Bento</td>
<td>Brazil</td>
</tr>
<tr>
<td>Wiluna</td>
<td>Australia</td>
</tr>
<tr>
<td>Youanmi</td>
<td>Australia</td>
</tr>
</tbody>
</table>

Following early development work and application in the United States, Chile has become a major developer of bioleaching on an industrial scale. In 2001, there were 13 companies using bioleaching and 30 companies in all using LX-SX-EW technology. In 2001, Bioleaching constituted approximately 10% of Chilean copper production and heap and dump leaching, in general, constituted approximately 30% of the Chilean production. The First Chilean Plant to be put into operation was S.M. Pudahuel. The plant was initiated in 1982 using the Thin Layer Bacterial leach process (TLB), water saving process, and leaches copper oxides and secondary sulphide minerals (Dresher, 2004).
3.1. **Microbiology of Bioleaching**

The original bacteria used in bioleaching were native to the site where the leaching took place (Dresher, 2004). However, once bioleaching gained acceptance as a potentially viable method for the recovery of metals from low-grade ores, flotation tailings and waste materials, efforts were undertaken to optimise the bacteria for the operation intended. “Native” bacteria, sometimes termed mesophilic bacteria, are sensitive to elevated temperatures and to some of the metals being extracted. Thus, microorganisms were sought that can withstand higher temperatures, thermophilic (and even hyperthermophilic; i.e., 60°C or higher) microorganisms, and are tolerant to the metals being extracted. One of the first locations to be investigated for suitable thermophilic bacteria was the hot springs at Yellowstone National Park. Others have been a hot spring in Iceland, a coalmine in Western Australia, a volcano in Italy and a slagheap in Germany. Out of these collections have come starting cultures for a number of bacteria strains. For example, some bacteria in use today are: Acidianus brierleyi (Sulfolobus brierleyi), an aerobic, extremely acidophilic, thermophilic sulfur-metabolizing archaebacteria useful to 70°C, that was developed from a Yellowstone hot spring; Acidianus infernos, useful to 88°C, that was developed from mud from the crater of the Solfatara volcano in Italy; Sulfolobus metallicus, useful to 65°C, that was isolated from the lava field of the same volcano; Metallosphaera sedula, useful to 65°C, that was isolated from a thermal spring; Metallosphaera prunae, useful to 80°C, that was found in the smoldering slagheap of a uranium mine in Thüringen, Germany. In fact, natural thermophiles have been isolated from the high-temperature zones of dumps and stockpiles where normal, low-temperature bacteria have been used. To date, approximately 30 naturally occurring strains of microorganisms have been screened as being useful in bioleaching. While it is common to refer to the microorganisms used in bioleaching as being bacteria, strictly speaking, this is not the case since the thermophiles actually fall into another classification of microbiology, the archaea. This classification is shown at Table 5. Thus, for example, iron and sulfur oxidizing archaea are currently the microorganisms of choice in the bioleaching of chalcopyrite-containing ores and concentrates.
Table 5: Classification of the domains of life

<table>
<thead>
<tr>
<th>Three Domains of Life</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Archaea</strong></td>
<td>halophiles and thermophiles</td>
</tr>
<tr>
<td><strong>Bacteria</strong></td>
<td>cyanobacteria and heterotrophic bacteria</td>
</tr>
<tr>
<td><strong>Eukaryota</strong></td>
<td>animals, plants, chromists, fungi, alveolates, rhodophytes, flagellates, basal protest(s)</td>
</tr>
</tbody>
</table>

At present, the strains of microorganisms used in bioleaching have been cultured from natural strains using methods that are commonly used in other industries, for example, in cheese making, where mesophilic and thermophilic microorganisms are also used. These strains are identical to those found in nature. The only difference is that in some cases they have been selected for rapid growth on the ore or concentrate concerned and to the plant operating conditions. These strains have been characterized, mainly by DNA sequencing, and listed in the major biological species indices of the world. In the future, perhaps we can expect new, more efficient strains, introduced as a result of genetic manipulation.

Each microorganisms need some conditions for their correct growth and some conditions of temperature and pressure during the bioleaching. Some of these conditions are shown in Table 6.
Table 6: Description and recommended conditions by operation with bacteria (Ruiz, 2005).

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Bacteria grow up by oxidation of:</th>
<th>T °C</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Fe^{2+}$ $S^{2-}$ $S^0$ $S_O^2-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiobacillus ferrooxidans</td>
<td>✓ ✓ ✓ ✓</td>
<td>20 to 35</td>
<td>1.5 to 2.5</td>
</tr>
<tr>
<td>Thiobacillus thiooxidans</td>
<td>- ✓ ✓ ✓</td>
<td>20 to 35</td>
<td>1.5 to 2.5</td>
</tr>
<tr>
<td>Leptospirillum ferrooxidans</td>
<td>✓ ✓ - -</td>
<td>30</td>
<td>1.2 to 2.0</td>
</tr>
<tr>
<td>Sulfobacillus thermosulfidooxidans</td>
<td>✓ ✓ ✓ -</td>
<td>45 to 60</td>
<td>3.0</td>
</tr>
<tr>
<td>Sulfobacillus thermotolerants</td>
<td>✓ ✓ ✓ ✓</td>
<td>45 to 60</td>
<td>3.0</td>
</tr>
<tr>
<td>Leptospirillum thermoferooxidans</td>
<td>✓ ✓ ✓ ✓</td>
<td>45 to 60</td>
<td>3.0</td>
</tr>
<tr>
<td>Sulfolobus acidocaldarius</td>
<td>✓ ✓ ✓ ✓</td>
<td>60 to 80</td>
<td>3.0</td>
</tr>
<tr>
<td>Acidianus archae</td>
<td>✓ ✓ ✓ ✓</td>
<td>60 to 80</td>
<td>3.0</td>
</tr>
<tr>
<td>Metallosphaera archae</td>
<td>✓ ✓ ✓ ✓</td>
<td>60 to 80</td>
<td>3.0</td>
</tr>
<tr>
<td>Sulforococcus archae</td>
<td>✓ ✓ ✓ ✓</td>
<td>60 to 80</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Note: ✓ Indicate that the reactions can be in this conditions
- Indicate that the reactions are very unusual in these conditions.

Among these microorganism there is one in particular that concentrates the attention: The Thiobacillus Ferrooxidans. The dissolution of oxide minerals only needs an acid solution, obviously with particular conditions in each operation but, the sulphur mineral need a oxidating agent to liberate the metal and Thiobacillus Ferrooxidans has the ability of accelerating the conversion $Fe^{2+} / Fe^{3+}$. Its activity is essential to keep an environment of high redox potential that is required for the efficient leaching.

Therefore Thiobacillus ferrooxidans play an important role in the bioleaching (Muqing Qiu et al., 2006). Thiobacillus Ferrooxidans was first isolated in 1947 from an acid coal mine drainage (Feng and Li, 2002). This bacterium is an acidophilic-aerobic
microorganism and is able to catalyze the oxidation of metallic sulphides to sulphate through a multi-step mechanism

The bioleaching process could be divided, in presence of Thiobacillus ferrooxidans, in two stages:

i. A period of colonization of the ore by bacteria, when the bacteria first come in contact with the mineral surface, they begin to multiply, colonizing the available mineral surface (Lizama, 2003)

ii. A steady rate period where the leaching occurs.

In general, during the interaction bacteria/particle, three mechanism have been described,

1) The direct mechanism whereby bacteria attach to the mineral surface and solubilise the mineral species,
2) The indirect mechanism where the bacteria catalyze the regeneration of the ferric iron, and
3) The electrochemical route where the bacteria attach to the noblest mineral and galvanically protect the mineral from dissolution thus enhancing the oxidation of the less noble mineral(s) (Sampson et al., 2000).

However, the mechanisms for the oxidation of mineral sulphides are not completely understood (Deveci et al., 2004). The role of Thiobacillus ferrooxidans in bacterial leaching of mineral sulphides is controversial, in fact, exist experiments with control of redox potential that indicate no direct bacterial mechanism (Fowler and Crundwell, 1998; Fowler et al., 1999). According to these studies the role of the bacteria would be more easily discernible if the concentration of ferric and ferrous ions were maintained at set values throughout the experimental period. Under controlled conditions the experiments were conducted in the presence of Thiobacillus ferrooxidans and under sterile conditions. Analysis of the conversion of zinc sulphide in the absence of the bacteria and the analysis of the conversion of zinc sulphide in the presence of the bacteria produced the same results. This indicates that the only role of the bacteria under the conditions used is regeneration of ferric ions in solutions.
But, as well as, there are studies that indicate a single roll of regeneration of \( \text{Fe}^{3+} \), there are others that indicate that the bacteria serve the dual purpose of oxidizing ferrous ion and elementary sulphur, thus regenerating ferric and removing deposited sulphur.

### 3.2. Selection of the Leaching Method

The bioreaching was developed for the leaching of low-grade ore dumps, flotation tailings and other waste materials already in place (Dresher, 2004). As the technology has progressed it has moved to more processing-amenable methods, for example, heap leaching or leaching in a stirred tank. Each of these methods has a cost and therefore, as shown in Figure 3.2, the ore-grade and particle size are the controlling factors in a leaching process choice. Of course there are other factors to consider for selecting what method use, for example, the treatment of copper concentrates in situations where the capital costs of a smelter are not warranted and/or environmental considerations preclude smelting at that location.

![Figure 3.2: Leaching Process vs. Ore Grade and Comminution Size. (Dresher, 2004)](image-url)
3.3. The Reactions in the Bioleach Process

The main process in bioleaching of sulphide ores is the mobilization of metals constituent(s). This is accomplished through microbially promoted oxidation of the metal sulphide(s) (Earlich, 2000).

The dissolution of mineral particles by a lixiviant or reactant in solution results in the shrinkage of the particle. For the general reaction, such as:

\[ aA(s) + bB(aq) \rightarrow cC(s) + dD(aq) \]

There is the possibility that a solid reaction product forms on the surface of the unreacted material. For this reason, the standard model is referred to as the shrinking-core model, since it is the core of unreacted material surrounded by product that shrinks in size (Crundwell, 2005) as is shown in Figure 3.3.

![Figure 3.3: Representation of the shrinking core phenomenon. (Chemical Reaction Engineering, Octave Levenspiel, Second Edition.)](image)

There are three modes of bacterial attack, one comes in contact with the mineral surface, then begin to multiply, colonizing the available mineral surface (Lizama, 2003), and (commonly accepted), the indirect and direct methods. In the indirect mode, \( \text{Fe}^{3+} \) was seen as the oxidant whereas in the direct mode it was \( \text{O}_2 \). In the
indirect mode, the aim of Thiobacillus ferrooxidans, which is the only organism capable of promoting leaching, is to regenerate ferric ions from ferrous ions in the bulk phase,

\[ 2\text{Fe}^{2+} + 0.5\text{O}_2 + 2\text{H}^+ \xrightarrow{\text{bacteria}} 2\text{Fe}^{3+} + \text{H}_2\text{O} \]

The ferrous ion resulted from the chemical oxidation of the metal sulphide in the ore by ferric ion,

\[ 2\text{Fe}^{3+} + \text{MS} \rightarrow 2\text{Fe}^{2+} + \text{M}^{2+} + \text{S}^0 \]

Where MS represents a metal sulphide, and M\(^{2+}\) the divalent metal ion formed in the oxidation of MS.

In addition to the oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) is also detected in bioleaching the oxidation of S\(^0\) to \(\text{H}_2\text{SO}_4\) as shows the equation below:

\[ \text{S}^0 + 1.5\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{bacteria}} \text{H}_2\text{SO}_4 \]

In the direct mode of bacterial attack of metal sulphide, the bacteria attacks a metal sulphide by attaching to its surface and oxidizing it enzymatically by conveying electrons to \(\text{O}_2\).

The bioleaching of sulphide minerals has been applied in the treatment of some metals. For example, the reactions involved in the biological oxidation of zinc sulphide are (Lizama, 2003):

\[ \text{ZnS} + 2\text{Fe}^{3+} \rightarrow \text{Zn}^{2+} + 2\text{Fe}^{2+} + \text{S}^0 \]
\[ 4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \xrightarrow{\text{bacteria}} 4\text{Fe}^{3+} + \text{H}_2\text{O} \]
\[ \text{S}^0 + 1.5\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{bacteria}} \text{H}_2\text{SO}_4 \]
For the treatment of uranium ores the reactions occurs between Thiobacillus ferrooxidans and other bacteria, such as Leptospirillum ferrooxidans, Thiobacillus thiooxidans, but the role played by these microorganisms in the uranium extraction process, either individually or jointly, is not well known (Muñoz et al., 1993):

\[
\begin{align*}
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} & \xrightarrow{\text{bacteria}} 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \\
4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 & \xrightarrow{\text{bacteria}} 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \\
\text{UO}_2 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4 & \longrightarrow 2\text{FeSO}_4 + \text{UO}_2(\text{SO}_4)_3^{4-} + 4\text{H}^+ \\
\end{align*}
\]

With respect to the sulphide copper mineral treatment some reactions for the chalcopyrite by Acidithiobacillus ferrooxidans (Mousavi et al., 2005) are:

\[
\begin{align*}
\text{CuFeS}_2 + \text{O}_2 + 4\text{H}^+ & \longrightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}^0 + 2\text{H}_2\text{O} \\
\text{CuFeS}_2 + 4\text{Fe}^{3+} & \xrightarrow{\text{bacteria}} \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0 \\
4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 & \xrightarrow{\text{bacteria}} 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \\
\end{align*}
\]

For the bioleaching of chalcocite by Acidithiobacillus ferrooxidans and Sulfobacillus the reactions are (Leahy et al., 2005):

\[
\begin{align*}
\text{Cu}_2\text{S} + 1.6\text{Fe}^{3+} & \longrightarrow 1.6\text{Fe}^{2+} + 0.8\text{Cu}^{2+} + \text{Cu}_{1.2}\text{S} \\
\text{Cu}_{1.2}\text{S} + 2.4\text{Fe}^{3+} & \longrightarrow 2.4\text{Fe}^{2+} + 1.2\text{Cu}^{2+} + \text{S}^0 \\
\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} & \longrightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \\
\end{align*}
\]

And the production of acid:

\[
\begin{align*}
\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+ & \xrightarrow{\text{bacteria}} \text{Fe}^{3+} + 0.25\text{H}_2\text{O} \\
\text{S}^0 + 1.5\text{O}_2 + \text{H}_2\text{O} & \xrightarrow{\text{bacteria}} \text{H}_2\text{SO}_4 \\
\end{align*}
\]
With respect to the bioleaching of marmatite concentrate (Shi and Fang, 2006) by Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans, the reactions are:

\[
\begin{align*}
[x\text{Zn},(1-x)\text{Fe}]S + O_2 + 4H^+ \overset{\text{bacteria}}{\longrightarrow} & x\text{Zn}^{2+} + (1-x)\text{Fe}^{2+} + S^0 + 2H_2O \\
4\text{Fe}^{2+} + O_2 + 4H^+ \overset{\text{bacteria}}{\longrightarrow} & 4\text{Fe}^{3+} + 2H_2O \\
2S^0 + 3O_2 + H_2O \overset{\text{bacteria}}{\longrightarrow} & 2\text{SO}_4^{2-} + 4H^+ \\
R + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6H_2O & \longrightarrow R\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 6H^+
\end{align*}
\]

In which \( R = H_3O^+, K^+ \) or \( NH_4^+ \)

The treatment of Sulphide-refractory ores gold by Acidithiobacillus ferrooxidans (Das and Sen, 2000) is necessary to dissolve the host minerals, exposing the gold for conventional cyanide treatment. The equations for dissolution of pyrite and arsenopyrite are:

\[
\begin{align*}
\text{FeAsS} + \text{Fe}^{3+} + 2H_2O + 3O_2 & \longrightarrow H_3\text{AsO}_4 + 2\text{Fe}^{2+} + H^+ + \text{SO}_4^{2-} \\
\text{FeS}_2 + 2\text{Fe}^{3+} & \longrightarrow 3\text{Fe}^{2+} + 2S^0 \\
\text{FeAsS} + 3.25O_2 + 1.5H_2O \overset{\text{bacteria}}{\longrightarrow} & \text{Fe}^{2+} + \text{SO}_4^{2-} + H_3\text{AsO}_4 \\
\text{FeS}_2 + 3.5O_2 + H_2O \overset{\text{bacteria}}{\longrightarrow} & \text{Fe}^{2+} + 2H^+ + 2\text{SO}_4^{2-} \\
\text{Fe}^{2+} + H^+ + 0.25O_2 \overset{\text{bacteria}}{\longrightarrow} & \text{Fe}^{3+} + 0.5H_2O
\end{align*}
\]
3.4. **Description of Methods of Processing**

3.4.1. **Bioleaching of copper ores in Heap**

The leaching is a hydrometallurgical process that can take place over a period from month to years. Leaching of copper from low-grade minerals and mine waste has become an important process in the mining industry. The large quantity of mining waste and the quantity of low-grade copper minerals generated make this a resource of great significance. The metal grades are often too low to support the high cost of ore grinding and agitation leaching. Copper mineral mainly include copper sulphides and oxides. The leaching agent used is sulphuric acid, which is continuously applied on top of the ore pile.

Bioleaching process is used for ores that contain stable sulphides mineral. The process is complex and involves a series of mechanism including biotically mediated oxidation of ferrous ions producing ferric ions in the presence of oxygen. Ferrous minerals are present as a product of pyrite oxidation. The ferric ions, in turn, oxidize the copper sulphides. At present, copper leaching is also applied to high-grade copper ores due to its competitive cost (Sidborn et al., 2003).

The heap bioleaching process involves the application of acid solutions and the presence of bacteria, occurring naturally or inoculated in solution (Leia et al 2005).

In the case of copper’s recovery plants, the mined copper ores are crushed with the intention to obtain an optimum particle size. In general, the crushed ore is mixed with sulphuric acid in an agglomerating device to consolidate the fines with the coarser ore particle and precondition the ore for bacterial development. Water or raffinate (effluent from the solvent extraction–electrowinning circuit) is added to optimise the moisture content for good agglomerate formation. If the ore is not too acid consuming, the acid requirement to precondition the ore can be met by agglomerating with raffinate. Raffinate usually contains a small population of bacteria, which inoculate the ore. The agglomerate and preconditioned copper ore is conveyed to the leach area where it is stacked 6 to 10 m high on a lined pad or on top of previously leached ore. Plastic
piping with ventilation holes is placed on the pad or lift to supply air to the bacteria during leaching. Aeration of the bioheaps is initiated soon after stacking the agglomerated ore. Low-pressure fans supply air to the ventilation system under the ore. The bioheap is irrigated with raffinate at an application rate that does not cause saturation. Pregnant leach solution (PLS) (effluent containing copper) is collected at the base of the bioheap is either (1) recycled to the top of the heap for irrigation (referred to as “intermediate leach solution” or “ILS”), or (2) direct to a SX/EW (solvent extraction/electrowining) circuit for copper recovery. The raffinate (barren solution from the SX/EW circuit) is returned to the bioheap for irrigation. Leach times vary among the operations, but are typically in the 200-day range for secondary copper ores. Copper recoveries also vary with 75% to 85% recoveries achieved at most operations. A typical Hydrometallurgy copper plant is shown in Figure 3.4.

Figure 3.4: LIX-SX-EW copper plant.
3.4.2. **Influence factors in Heap Bioleaching of copper**

**Aeration and oxygen concentration**

Thiobacillus Ferrooxidans needs oxygen for carry out the reactions of ferrous to ferric and the oxidation of sulphur to sulphate. In other words, the rate of reaction of $\text{Fe}^{2+} / \text{Fe}^{3+}$ and $S^0 / SO_4^{2-}$ is essential in order to improve the overall leaching kinetics.

\[
2\text{Fe}^{2+} + 0.5\text{O}_2 + 2\text{H}^+ \xrightarrow{\text{bacteria}} 2\text{Fe}^{3+} + \text{H}_2\text{O}
\]

\[
S^0 + 1.5\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{bacteria}} \text{H}_2\text{SO}_4
\]

The used of forced aeration increases the reaction rate in the pile and may significantly decrease the operation time, however the costs are increased. Then, bioheaps can be aerated for improving the process, but oxygen levels throughout the heap vary widely based on permeability, oxidation rates, sulphide-sulphur content, bacterial populations and other factors that are not well understood. Do the types of bacteria vary among areas of differing oxygen levels? Are there fewer bacteria in oxygen depleted areas? or does the same population exist, but just oxidize at a slower rate? Is it possible that bacteria capable of using alternative electron acceptors colonize portions of the bioheap that have limited oxygen? If so, are they important in bioheap leaching? (Brierley, 2000).

Diverse studies are referred when oxygen improves the operation of the Heap, because this element is fundamental for the aerobic reaction $\text{Fe}^{2+} / \text{Fe}^{3+}$, studies referred to it have been made, for example: Casas et al. (1996), Brierley (2000), Lizama (2001), Sidborn et al. (2003).

Lizama (2001) indicated that there is an empirical relationship among oxygen consumption, the height of the heap and the extraction of copper. This concept is shown in Figure 3.5.
Figure 3.5: Schematic representation of an aerated heap. Because of the very large surface area/height ratio, side effects are minimal and the leaching reactions are a function of heap height.

Sidborn and Moreno (2003) generated a two-dimensional model for bacterial leaching of copper minerals, which can handle aeration by natural and forced convection with and without aeration channels in the bottom of the Heap. The use of forced aeration increases the reaction rate in the pile and may significantly decrease the operation time, however the costs are increased.

Figure 3.6: Relative concentration of oxygen $\left(\frac{X_{O_{2g}}}{X_{O_{2g,\text{inlet}}}}\right)\cdot100$ at the edge of the heap, for natural convection (Sidborn and Moreno, 2003)
**Irrigation rate and irrigation solution composition**

C.L. Brierley (2001) indicated that the chemistry of the leach solution in bioheaps is the result of the quality of the water used to make up the leach solution, the mineralogy of the ore and the equilibrium condition established between the solution and the ore. In some geographical locations the local water quality may be poor with relatively high concentrations of $Cl^-$, $NO_3^-$, total dissolved solids ($TDS$) or all three. The $Cl^-$ content of the PLS and raffinate solutions from bioheap leaching is usually elevated when atacamite, a chloride-bearing copper mineral $\left[ Cu_4Cl_2(OH)_6 \right]$, is present along with the secondary copper sulphide minerals. Simply getting bacteria to grow in presence of high $Cl^-$, $NO_3^-$, $TDS$ concentrations can be challenging. When leaching starts, iron concentrations rapidly built in the solutions. The ultimate iron concentration in the solution is dependent on the ore-solution equilibrium, temperatures in the bioheap and aeration. Soluble iron concentrations in excess of 20-30 g/L are possible. If the ore contains arsenic minerals, solution arsenic concentrations increase rapidly. Most bioheaps are operated in “close cycle”. No bleed stream, other than solution retained in bioheaps that are taken off-line, is employed to remove heavy metals, high sulphate concentrations, high $TDS$, and potentially toxic constituents. Therefore, when equilibrium is exceeded, massive precipitations of iron and arsenic takes places in the bioheap. The nature of these precipitates that form under a variety of temperature conditions in the bioheaps is not well studied, nor is the effect of these precipitates on mineral’s oxidation.
Size distribution and agglomeration

The leaching performance depends on the interaction of the solid, that contains associated the metal with others species, the solution and a gas phase. If we considerer a bed constituted by big rocks, probably the aeration in this bed should be enough, because the space between each other allows good natural ventilation. In the beginning the reaction will occur in the surface, but little by little the diffusion process will be more and more important. In the other case, if we work with a small particle size, the permeability of the bed should be less than the other case, because in the same volume we can put more solid. The aeration may be not enough for the reactions, however if we put a forced aeration system the reaction should be fast, because the aeration improves and the specific area for the reaction is greater, in other words the place where occur the interaction solid-liquid–gas is greater than the other case.

The main objective of the agglomeration of ore is to form a uniform and highly permeable heap for leaching. The reality in a process plant is that the size distribution of the crushed ore is quite heterogeneous and it is very difficult to try to obtain a homogeneous particle size. Other good reason for using the agglomeration is that the interaction between the solid and the solution begins before to the solid arrives to the heap.

Figure 3.7: Description of Agglomeration process in Compañía Quebrada Blanca, Chile.
For example Figure 3.7 shows the agglomeration process of the Compañía Quebrada Blanca, Chile. After the primary, secondary and tertiary crushing process the material is deposited in a hopper of 150 Ton. The solid is transported by gravity using two strap that feed two agglomeration drums with 3 m. of diameter by 9 m. of length with an inclination of 7º, that operate at a speed of rotation of 6 rpm., where it is mixed with concentrated sulphuric acid and hot water from the cooling system of the generators of electrical energy. This process increases the material’s temperature and its humidity in a 10%, improving the porosity, oxygenation, permeability and the draining of the solution to facilitate the extraction of copper. The agglomerate mineral is distributed by tripper towards to two Heaps.

**Temperature**

Haddadin et al. (1995) indicated that the temperature is a cardinal parameter in a bacterial leaching process. Thiobacillus ferrooxidans is a mesophilic bacterium with an optimum temperature in the range of 25 to 37 C. However, the optimum temperature has not been precisely defined because it is subject to variation according to the different strains. The optimum temperature has been recognized to be pH dependent in that a decrease in pH lowers the optimum temperature for growth and iron oxidation.

Casas et al. (1998) indicated that the bacterial activity depends strongly of the temperature through the maximum specific respiration rate of the bacteria $V_m$. The expression for $V_m$ is a function of the temperature and it indicates that the Thiobacillus ferrooxidans has maximum activity around 37 ºC, as it is shown in Figure 3.8.
Maximum specific respiration rate of the bacteria

Figure 3.8: Maximum specific respiration rate of the bacteria $V_m$

**pH and Iron precipitates**

The iron precipitation has an important effect on the recovery of copper. For instance, jarosite precipitations occur because of the rapid oxidation of iron and the consequent increase of pH. The mechanism of ferric ion precipitations is as follows (in presence of Chalcopyrite) (Qui et al., 2006):

$$
\begin{align*}
4Fe^{2+} + O_2 + 4H^+ &\rightarrow_{\text{bacteria}} 4Fe^{3+} + 2H_2O \\
CuFeS_2 + 4Fe^{3+} &\rightarrow 5Fe^{2+} + Cu^{2+} + 2S^0 \\
2S^0 + 2H_2O + 3O_2 &\rightarrow_{\text{bacteria}} 2SO_4^{2-} + 4H^+ \\
3Fe^{3+} + 2SO_4^{2-} + 6H_2O &\rightarrow Fe_3(SO_4)_2(OH)_6 + 6H^+
\end{align*}
$$

From above reactions, the reaction products of ferric ion hydrolysis are readily observed. Jarosite $KFe_3(SO_4)_2(OH)_6$ is confirmed as the main phase in the ferric iron precipitations. The jarosite is coated on the surface of the ores and prevented the reactions of bioleaching.
3.5. **Bioreactors and other Bioprocesses**

3.5.1. **The Kasese Cobalt Company Ltd. (KCCL) plant reprocesses for recovery of cobalt**

The KCCL process has two objectives (Brochot et al. 2003). Firstly, it aims at extracting the valuable cobalt, trapped in sulphide minerals, from dredged mine tailings left behind by a closed mining activity. Secondly, by processing these tailings, the process significantly reduces the outgoing pollution caused by natural leaching of the tailings.

The KCCL process consists on:

- A bioleaching section comprising three stages of reactors (BIOCOs), in which the bacteria oxidise the pyrite and thus liberate metals (Co and Fe);
- A gravity section for the recovery of heavy particles (sulphides, containing heavy metals), which have not been oxidised during bioleaching. These heavy particles are recycled to the BIOCOs feed, with the aim of improving their oxidation rate;
- A neutralization section for the precipitation of iron;
- A belt filter from which the final solids residues is sent to the tailings pond;
- An iron removal section, to precipitate the final remaining iron. This section uses limenstone and air addition for the precipitation of oxides. The final liquor, which is recovered from the upper plant, is then sent to the bottom plant consisting of a solvent extraction and electrowinning circuit.

Figure 3.9 shows a flowsheet of the KCCL process where is possible to identify each stage.
Figure 3.9: The Kasese Cobalt Company Ltd. (KCCL) plant of cobalt recovery.

3.5.2. Gold Bioleaching process

Bioleaching is becoming increasingly used for the extraction of gold from refractory gold ore (Das and Sen, 2000). The sulphide-refractory gold ores contain gold in intimate association with sulphide minerals, typically pyrite and arsenopyrite. Gold is not liberated for recovery by conventional cyanide treatment even by very fine grinding. Thiobacillus ferrooxidans solubilize the host minerals, exposing the gold for conventional recovery. Three technologies are used commercially to treat sulphide-refractory ores and concentrates, namely roasting, pressure oxidation and bioleaching. Bioleaching is becoming more popular because it is economical, environmental friendly and easy to operate compared with other technologies.
3.5.3. **Bioreactors for Copper**

Historically, a large number of hydrometallurgical treatment processes have been developed to treat copper concentrates. These processes have all failed to achieve sustained commercial production due to one or more of the following list of difficulties:

1. Low copper recovery in the primary leach step.
2. Copper loss due to copper co-precipitation with iron hydrolysis products.
3. Difficult or incomplete precious metal recovery from leach residue.
4. Unconventional and difficult electrolysis step.
5. Difficult elemental sulphur recovery step from leach residue.
6. Excessive corrosion (especially chloride circuits).
8. Large energy requirements for mixing and oxygen dispersion.
9. Poor quality copper product that requires electrorefining.
Additional factors are often involved in preventing advancement of new technologies. These include:

1. New technology risk. Many of the new processes have unique chemistry, processing conditions or equipment. These processes have not had adequate commercial demonstration to mitigate risk.

2. Cost of licensing. The potential cost of licensing new technology while also assuming the risk of being first to commercially practice can mitigate against new technology selection.

The primary sulphide minerals of copper have been difficult to leach for the purpose of direct copper extraction (Dresinger, 2006). In particular, chalcopyrite has been observed to undergo a type of “passivation” under a variety of oxidative leaching conditions. Over the last 10–15 years, a variety of biological and chemical leaching processes have emerged for overcoming the passivation of chalcopyrite. A number of these processes are now entering commercial production or are approaching this status. The BIOCOP™ process of BHP Billiton has now been commercialised at the Alliance Copper plant in Chile. The Total Pressure Oxidation technology has been implemented by Phelps Dodge at Bagdad, Arizona. The Mt. Gordon copper process and the Sepon copper process both use autoclave processes in the overall metallurgical circuit. In the Mt. Gordon circuit, the autoclave was used to leach copper while at Sepon the autoclave is used to produce acid and ferric sulphate to meet the requirements of an atmospheric leach. CESL and CVRD have completed a feasibility study to apply the CESL copper process in Brazil. PLATSOL™ technology for copper, nickel, cobalt and precious metal recovery is now under final feasibility study for application by PolyMet Mining at the NorthMet deposit in Minnesota, USA.

The number of available options for copper recovery from primary sulphides is multiplying. These processes are all successful in (1) dissolving copper from chalcopyrite concentrates, (2) purifying the leach solutions using modern separation processes and (3) recovering a high value, high purity copper metal product. The processes under development can be divided into predominantly sulphate and chloride processes. Within the sulphate grouping, processes can be sub-grouped as either
atmospheric or super-atmospheric in pressure and chemical or biological in the leaching process.

Copper hydrometallurgy has been extensively studied as an alternative route to chalcopryrite concentrate treatment. The challenge of process development for chalcopryrite leaching in sulphate media is generally to leach chalcopryrite quickly and completely with high yield of elemental sulphur. A high yield of elemental sulphur leads to reduced costs for oxygen or air for mineral leaching and reduced neutralization/acid disposal costs. To overcome the slow and incomplete leaching of chalcopryrite at lower temperature, the two problems of (1) passive films on the chalcopryrite surface and (2) the potential blocking and wetting of Chalcopryrite by liquid elemental sulphur must be addressed.

Different technologies for treatment of copper minerals are shown in Table 7 (Dresinger, 2006).
**Table 7**: Sulphate-based copper hydrometallurgy processes for ore or concentrate treatment. Status: P=pilot plant, D= demo plant, C=commercial facility

<table>
<thead>
<tr>
<th>Process</th>
<th>Status</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Regrind D80 (µm)</th>
<th>Special conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activox process</td>
<td>P</td>
<td>90-110</td>
<td>10-12</td>
<td>5-10</td>
<td>Fine grinding with high oxygen</td>
</tr>
<tr>
<td>Albion Process</td>
<td>P</td>
<td>85</td>
<td>1</td>
<td>5-10</td>
<td>Atmospheric ferric leaching of very finely ground concentrate</td>
</tr>
<tr>
<td>Anglo American-University of British Columbia process</td>
<td>P</td>
<td>150</td>
<td>10-12</td>
<td>10-15</td>
<td>Modest regrind combined with surfactants for Chalcopyrite leaching</td>
</tr>
<tr>
<td>Bactech/Mintek low temperature bioleach</td>
<td>P</td>
<td>35</td>
<td>1</td>
<td>5-10</td>
<td>Low T bioleach (35°C -50°C) requires very fine grind to overcome Chalcopyrite passivation.</td>
</tr>
<tr>
<td>BIOCOPTM process</td>
<td>C</td>
<td>65-85</td>
<td>1</td>
<td>37</td>
<td>High T bioleach (65°C -80°C) uses thermophilic bacteria</td>
</tr>
<tr>
<td>CESL copper process</td>
<td>D</td>
<td>140-150</td>
<td>10-12</td>
<td>37</td>
<td>Chloride catalyse leach of Chalcopyrite producing basic copper sulphate precipitate in the autoclave</td>
</tr>
<tr>
<td>Process</td>
<td>Status</td>
<td>Temperature (°C)</td>
<td>Pressure (atm)</td>
<td>Regrind D80 (µm)</td>
<td>Special conditions</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>-----------</td>
<td>-----------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Dynatec Process</td>
<td>P</td>
<td>150</td>
<td>10-12</td>
<td>37</td>
<td>Chalcopyrite is leached using low grade coal as an additive</td>
</tr>
<tr>
<td>Mt. Gordon process</td>
<td>C</td>
<td>90</td>
<td>8</td>
<td>100</td>
<td>Pressure oxidation of Chalcocite/Pyrite ore or bulk concentrate in an iron sulphate rich electrolyte</td>
</tr>
<tr>
<td>PLATSOL process</td>
<td>P</td>
<td>220-230</td>
<td>30-40</td>
<td>15</td>
<td>Total pressure oxidation in the presence of 10-20 g/L NaCl. Precious metals leached at the same time as base metals</td>
</tr>
<tr>
<td>Sepon Copper process</td>
<td>P and soon C</td>
<td>80-Copper 220-230-Pyrite</td>
<td>atm 30-40</td>
<td>100 50</td>
<td>Atmospheric ferric leach for copper from Chalcocite. Pressure oxidation of Pyrite concentrate to make acid and ferric sulphate for copper leach</td>
</tr>
<tr>
<td>Total pressure oxidation process</td>
<td>C</td>
<td>200-230</td>
<td>30-40</td>
<td>37</td>
<td>Extreme conditions of T and P designed to rapidly destroy Chalcopyrite and other sulphides.</td>
</tr>
</tbody>
</table>
3.5.4. Influence factors in Bioleaching In Reactors

Pulp densities andParticle size

The negative effects of high pulp densities and small particles size were early reported in bioleaching with mesophilic bacteria. The detrimental effect of high pulp densities is likely to be larger in operation with archaea because of their weaker cell wall that make susceptible to mechanical damage and metabolic stress caused by the intense agitation needed for maintaining an homogeneous suspension. On the other hand, decreasing particle size can reduce the leaching rate probably because of difficulties in the cell attachment when the diameters of the particles and cells become of similar magnitude. It is also likely that the rate of collision between particles increases as particle size diminishes. Valencia et al. (2003) studied the effect of the pulp density and particle size on the biooxidation rate of a pyritic gold concentrates by Sulfolobus metallicus. The results of this research are shown in the figure 3.12. In this case, the optimal conditions in this case are 7.8% pulp density and particle size of 35 µm.

![Response surface of the effect of particle size and pulp density on rate of iron solubilisation from pyrite by Sulfolobus metallicus in shake flask at 68 C Initial pH 2.0 and agitation of 220 rpm.](image)

Figure 3.11: Response surface of the effect of particle size and pulp density on rate of iron solubilisation from pyrite by Sulfolobus metallicus in shake flask at 68 C Initial pH 2.0 and agitation of 220 rpm.
**Temperature and Pressure**

For an efficient bacteria’s performance it is necessary to consider the appropriate condition of temperature and pressure for them, because under these conditions, the behaviour of the bacteria’s population will be the optima.

In one hand, it is well known that the temperature increases the kinetic of the reactions. At higher temperatures, the probability that two molecules will collide is higher. This higher collision rate results in a higher kinetic energy, which has an effect on the activation energy of the reaction. The activation energy is the amount of energy required to ensure that a reaction happens. Quantitatively the relationship between the rate a reaction proceeds and the temperature can be determined by the Arrhenius Equation:

\[
k_y = A \cdot e^{\left(\frac{-E_a}{RT}\right)}
\]

Regarding the amount of oxygen dissolved in the water, it is a function of the partial pressure of oxygen and the temperature. The mole fraction of oxygen in the water is given by the Henry’s Law:

\[
x = \frac{p}{H}
\]

Where \( x \) is the mole fraction of the solute in the liquid phase, \( p \) the partial pressure of the solute in the gas phase, expressed in atmosphere and \( H \) is the proportionality constant expressed in units of atmospheres of solute pressure in the gas phase per unit of concentration of the solute in the liquid phase.

Values for the Henry’s constant for different temperatures and pressures are shown in Table 8.
Table 8: Henry’s Constant for Oxygen, two different temperatures and pressures. (Perry’s Chemical Engineers Handbook, Seventh Edition.)

<table>
<thead>
<tr>
<th>Partial Pressure of $O_2$, mmHg</th>
<th>$10^{-4} \times H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$23^\circ C$</td>
</tr>
<tr>
<td>800</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>4.58</td>
</tr>
<tr>
<td>2000</td>
<td>4.59</td>
</tr>
<tr>
<td>3000</td>
<td>4.6</td>
</tr>
<tr>
<td>4000</td>
<td>4.68</td>
</tr>
<tr>
<td>5000</td>
<td>4.73</td>
</tr>
<tr>
<td>6000</td>
<td>4.8</td>
</tr>
<tr>
<td>7000</td>
<td>4.88</td>
</tr>
<tr>
<td>8150</td>
<td>4.98</td>
</tr>
<tr>
<td>8200</td>
<td></td>
</tr>
</tbody>
</table>

Then the Henry’s constant will be greater at a greater temperature, therefore the solubility of oxygen, in this case will be lower. If we want to increase the kinetic of the reactions inside the reactor the logical way is to increase the temperature, but in the biololeaching the reactions are aerobic, then the way for increasing the solubility of the oxygen in the process will be to increase the total pressure.
3.6. **Why is important to investigate and to use the bioleaching? Microbiological aspects**

Firstly, why is necessary investigating about microbiology and bioprocess? Apart from the obvious answer that bacteria is responsible for the oxidation of the sulphides minerals, a better understanding of the microbiology is paramount to future development of bioheap technology. We must comprehend the microbiology to advance the technology, expand the use of the process to a broader spectrum of base and precious metals ores, lower capital and operating cost and improve metal recoveries (Brierley, 2001). Table 9 shows some microbiological advancement and what influence they have in the bioleaching.

**Table 9: Advancements in ore bioheap applications based on microbiology**

<table>
<thead>
<tr>
<th>Microbiological advancement</th>
<th>Potential benefit to ore bioheap leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Employ bacteria that initiate oxidation at higher pH values and condition ore for conventional leaching bacteria.</td>
<td>Allow effective bioheap leaching of high-pH ores, expanding the types and numbers of ores deposits amenable to bioheap leaching.</td>
</tr>
<tr>
<td>Understand the adaptation or succession of leaching bacteria to the changing character of the leach solutions, high TDS situations, and possible synergistic toxic effects of multiple ions.</td>
<td>Allow use of poor quality water for make-up of the leach solutions and closed-circuit operation of the bioheaps, reducing capital and operating cost.</td>
</tr>
<tr>
<td>Understand succession of thermophiles in bioheaps, interpret their function and define their effects on minerals, precipitates and reagent consumption.</td>
<td>Extend bioheap leaching to more refractory ores (for example, chalcopyrite and enargite); potentially enhance metal recoveries and decrease leach times, reducing cost and improving overall process economics; refine development of bioheap leaching of mineral concentrates</td>
</tr>
<tr>
<td>Microbiological advancement</td>
<td>Potential benefit to ore bioheap leaching</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>Select for and employed $Cl^-$-tolerant, iron-oxidizing bacteria</td>
<td>Expand geographical regions for bioheap operations by using brackish waters and sea water for leaching</td>
</tr>
<tr>
<td>Describe heterotrophic and chemolithotrophic microflora in bioheaps as related to nutrients and function; ascertain role, if any, in heterothrophic degradation of entrained organics in raffinate</td>
<td>Define conditions that could be optimise bioheaps performance, reducing cost.</td>
</tr>
</tbody>
</table>
4. **MODELLING OF BIOLEACHING**

4.1. **Heaps modelling**

In general, a modelled system can be approached of different forms, from a kinetic point of view, interesting the velocity and possibilities of accelerating reactions and/or from a point of view of transport, interested in the phenomena of movements of each one of the species within the system, transports of mass and energy, considering physical aspects of this.

![Bioleaching Model](image)

**Figure 4.1**: Bioleaching Model of the ore bed. The main steps are both transport phenomena and chemical reactions.
Several studies exist on the behaviour of the Copper Heap leaching (Neuburg et al. 1991; Casas et al., 1996; Lizama, 2001; Zeballos et al., 2003; Wang et al., 2004; Sidborn et al. 2003; Sidborn and Moreno, 2003)

Bacterial leaching of an ore bed is a complex process that involves at least the following phenomena (Casas et al, 1996):

a) Reactions of mineral species with sulphuric acid, ferric ions and dissolved oxygen;

b) Hydrolysis and precipitation of complex compounds in dissolution, which mainly involves ferric-ions species;

c) Transport, attachment, growth, and catalytic actions of microorganism

d) Transport of aqueous species inside the ore particles;

e) Transport of oxygen and water through the bed, with an air supply to the bed by natural convection and diffusion; and

f) Heating and cooling of the bed, associated with exothermic reactions and endothermic reactions and heat transfer to the environment.

The mineral sulphide are oxidized and dissolved by ferric ions present in the leaching solution according to the following:

\[
MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S
\]

Where M represents the metal of interest, either copper or iron.

This reaction produces ferrous ions, which are continuously reoxidized to ferric ions under the catalytic action of the bacteria present either in the solution or attached to the ore, according to the following:

\[
2Fe^{2+} + 0.5O_2 + 2H^+ \xrightarrow{\text{bacteria}} 2Fe^{3+} + H_2O
\]

The reactions in the Heap are in many cases aerobic reactions, therefore is important to consider the oxygen transport mass (Crundwell, 2005):
Models of bioleaching in heaps and dumps have usually described the leaching rate assuming that the global kinetic is controlled by the rate of particles dissolution, which is commonly described in terms of the unreacted core model. However, in the bioleaching of sulphide ores by the irrigation of packed ore bed, there are situations in which the leaching rate is controlled by the aeration of the heap.

When the bacterial activity is the controlling factor, the rate of copper-sulphide dissolution is determined at the particle level by the rate of bacterial generation of ferric ions, but it is possible to consider that the ferrous ions in this case are present in excess, for this reason is better to express the oxidation rate in terms of oxygen. The rate of consumption of oxygen by bacteria can be described in terms of the Michaelis-Menten equation:

\[
\frac{d\alpha}{dt} = \frac{\sigma_1}{\rho_B G} X \frac{O_{2,L}}{V_m \left( K_m + O_{2,L} \right)}
\]

Where \( \alpha \) is the copper recovery, \( \sigma_1 \) is the stoichiometric factor and depend of the reactions, \( \rho_B \) is the bed density and \( G \) is the ore grade. With respect the same point, Sidborn et al. (2003) used the following expression:

\[
R_{O_2} = X \frac{O_{2,L}}{V_m \left( K_m + O_{2,L} \right)}
\]

Where \( R_{O_2} \) is the rate of consumption of oxygen by bacteria, \( X \) is the number of bacteria per volume of bed, \( V_m \) is the maximum specific respiration in the liquid solution and \( K_m \) is the Michaelis constant for the system.

Experimental determinations of bacteria numbers indicated that the iron-oxidizing activity of both attached and free bacteria is relevant to the leaching process. Therefore Neuburg et al. (1990) equations for the simultaneous growth of both
populations are to be considered in the model. The variation of the number of attached bacteria along a column could be expressed as:

\[
\frac{dX_a}{dz} = \mu X_a + K_{ads} X_S (X_{sat} - X_a) - K_{des} X_a
\]

And the variation of bacteria in the solution along the column as:

\[
\frac{dX_s}{dz} = \mu X_s - K_{ads} X_S (X_{sat} - X_a) - K_{des} X_s
\]

The total number of bacteria per unit volume of solution at any point in the column that are involved in the oxidative process could be then written as:

\[
X = X_s + \left(1 - \varepsilon_L\right) X_a
\]

Where, \(\varepsilon_L\) is the liquid fraction (volume of solution per unit volume of ore bed), \(\varepsilon_L\) represents the ore bed void fraction, \(X_a\) the concentration of attached cells, \(\mu\) the specific bacterial growth rate, \(X_s\) the concentration of bacteria in solution, whereas \(K_{ads}\) and \(K_{des}\) represents the absorption and desorption constants and \(X_{sat}\) the saturation concentration of bacteria attached to the surface of ore particles.

In order to determine under which conditions the process will be controlled by the number of bacteria present, Casas et al. (1996) indicated that population of \(10^{11} \frac{\text{bacteria}}{m^2}\) the dissolution of the mineral is controlled by the bacterial activity for a particles less that \(2\,cm\), also in this estimation was considered an effective diffusion coefficient for a ferric ions of \(5 \times 10^{-11} \frac{m^2}{s}\) and a Michaelis-Menten behaviour for bacterial activity were assumed. Therefore, we can expect that the model is valid for particles size of several centimetres. When the reaction has reached several centimetres into the particle, the process is controlled by diffusion and the model is not valid.
With respect the maximum specific respiration rate, $V_m$, Casas et al. (1996) consider the following expression:

$$V_m = \frac{6.8 \times 10^{-13} T e^{\frac{7000}{T}}}{1 + e^{\frac{236}{T} - \frac{74,000}{T}}}$$

Where $T$ is the temperature in Kelvin.

The Shrinking core model, (that include resistances due to the intrinsic dissolution kinetics of the mineral), is used to describe the diffusion resistance of the ferric through an inert porous layer of reacted material and the diffusion of ferric iron through the liquid film on the particle surface. Neuburg et al. (1990), Sidborn et al (2003), Sidborn and Moreno (2003), Wang et al. (2004) have considered the following model:

$$-\frac{dC_{Fe^{3+}}}{dt} = \frac{M_S}{\rho_M G \phi} 1 \left( \frac{\sigma}{D_e} \right) \left( \frac{r_c}{R_p} \right) (R_p - r_c) + \left( \frac{\sigma}{k_g} \right) \left( \frac{r_c}{R_p} \right)^2$$

Where $-\frac{dC_{Fe^{3+}}}{dt}$ is the rate of decrease of the unreacted core radius, $M_S$ is the molecular weight of the sulphide, $\rho_M$ is the mineral particle density, $\phi$ is the particle shape factor, $G$ is the grade of sulphide mineral, $k_s$ Global specific kinetics factor, $\sigma$ is the stoichiometric factor, $D_e$ is the effective diffusion coefficient, $R_p$ is the initial radius of sulphide particle, $k_g$ is the mass transfer coefficient in the liquid-solid film and $C_{Fe^{3+}}$ is the concentration of ferric ions in the leaching solutions.

Wang et al. (2003) studied the influence of silver ions in the leaching solutions. They suggested that the behaviour of silver ions in the bioleaching of chalcopyrite catalyzed by silver ions is the same as that of ferric ions in the bioleaching process of chalcopyrite without silver ions.
With respect to the particle, some authors indicate that it is not convenient to measure the radius of the mineral particle during the process of bioleaching. The change in particle radius can be expressed in function of the reacted fraction of the mineral particle (Neuburg et al., 1990, Wang et al., 2004):

\[
\alpha = 1 - \left( \frac{r_c}{R_p} \right)^3
\]

Where \( \alpha \) is the leaching rate. If the kinetic model for the silver ions is expressed in function of the leaching rate the equation is transformed to (Wang et al., 2003):

\[
\frac{d\alpha}{D_s \left(1-\alpha\right)^{\frac{1}{3}}} + \frac{\sigma R_p}{D_s \left(1-\alpha\right)^{\frac{1}{3}}} \frac{d\alpha}{\left(1-\alpha\right)^{\frac{1}{3}}} + \left(\frac{\sigma}{k_g} - \frac{\sigma}{D_s}\right) d\alpha = \frac{3M_{Ag}}{\phi GR_p \rho_M} C_{Ag} dt
\]

Bioheaps are aerated, but the oxygen levels throughout the heap vary widely based on permeability, oxidation rates sulphide - sulphur content, bacterial population and other factors that are not well understood (Brierley, 2001).

There are several models about this topic, with natural aeration (Casas et al., 1996; Lizama, 2000; Sidborn et al., 2003) and forced aeration (Sidborn and Moreno, 2003, Lizama, 2001). In the case of natural aeration, the air is transported through the ore bed by diffusion and natural convection. The natural convection is generated by a decrease in the gas density, which was attributable to heating, humidification, and oxygen consumption (Casas et al., 1996; Sidborn et al, 2003).
For the forced aeration, the local velocity of air \( q_g \) can be expressed as:

\[
q_g = -\frac{\rho_g k_{rg} k}{\mu_f} \nabla P
\]

Where \( k \) and \( k_{rg} \) are the intrinsic and relative gas permeabilities of the bed, \( \rho_g \) is the gas density, \( \mu_f \) is the fluid viscosity and \( \nabla P \) denotes the fluid pressure gradient.

In general the oxygen mass balance is described by the advection-dispersion (AD) equation, in the case of the oxygen (Sidborn, 2003) this is:

\[
\epsilon_L \frac{\partial \rho \rho_{O_{2,g}}}{\partial t} = \rho_L D_{O} \nabla^2 \rho \rho_{O_{2,g}} - q_g \nabla \rho \rho_{O_{2,g}} - R_{O_{2}}
\]

Where \( \rho \rho_{O_{2,g}} \) is the concentration of oxygen, \( D_{O} \) is the dispersion coefficient in the gas phase and \( \epsilon_L \) the volume fraction of air.

In general the mass balance for chemical species \( i \) present in the system is represented by the AD equation (Neuburg et al., 1990; Sidborn et al., 2003, Sidborn and Moreno, 2003):

\[
\epsilon_L \frac{\partial \rho \rho_{i}}{\partial t} = \epsilon_L D_L \nabla^2 \rho \rho_{i} - q_L \nabla \rho \rho_{i} - \sum R_i
\]

Where \( \rho \rho_{i} \) is the concentration of species \( i \), \( D_L \) is the dispersion, \( q_L \) the liquid flow rate and \( R_i \) the reaction rate of species \( i \).

Neuburg et al. (1990) considered mass balance for oxygen in the gas phase and oxygen, ferrous ion, ferric ions, cupric ion and hydrogen ion in the liquid phase. Sidborn et al. (2003) and Sidborn and Moreno (2003) considered mass balance for Oxygen, ferric and ferrous ions and copper ions.
With respect to the energy balance in the Heap, Casas et al. (1996), Sidborn et al (2003) and Sidborn and Moreno (2003) considered that due to the exothermic reactions, the temperature of the bed is increased. In this case they considered that the energy transports through the ore bed by conduction and convection:

\[
C_{p,B} \rho \frac{\partial T}{\partial t} = k B \nabla^2 T - \rho_i q_i \nabla H_i - \rho_s q_s \nabla H_s - \sum \Delta H_R R_i
\]
4.2. **Reactors Modelling**

Leaching reactors are unique among tank operations. They generally involve three phases, one of which, the solid change in size.

The factors that need to be accounted for in a thorough design procedure are:

- Solids throughput
- Particle size distribution
- Retention time
- Reaction kinetics
- Slurry density
- Lixiviant throughput
- Circuit configuration

The dissolution of mineral particles by a lixiviant or reactant in solution results in a shrinkage of the particle. For a general reaction such as:

\[
(aA_{(s)} + bB_{(aq)}) \rightarrow cC_{(s)} + dD_{(aq)}
\]

There is the possibility that a solid reaction product forms on the surface of the unreacted material. For this reason the standard model is referred to as the shrinking core model. The shrinking core model is based purely on the geometry of the change in the surface area with the change of size.

In this case the research was focused in F. Crundwell’s works. Crundwell (2005) represent the shrinking core model for a spherical particle as:

\[
\frac{dr}{dt} = \cdot = \rho \left[ \frac{1}{k_f[B]^n} + \frac{1}{2D_B} \left( r - \frac{r^2}{R} \right) + \frac{1}{k_f} \left( \frac{r}{R} \right)^2 \right]
\]

\[
\cdot = \frac{-2\sigma}{\left( \frac{1}{k_f[B]^n} + \frac{1}{2D_B} \left( r - \frac{r^2}{R} \right) + \frac{1}{k_f} \left( \frac{r}{R} \right)^2 \right)}
\]
If the rate of shrinkage is controlled by the reaction at the surface, then:

\[
\frac{dr}{dt} = r = -\frac{2\sigma}{\rho}k_s[B]^n
\]

If and only if \( r \) is constant, the above expression can be integrated directly to yield the well-know form of the shrinking core model:

\[
1 - (1-\alpha)^\frac{1}{3} = \frac{rt}{R}
\]

Where \( \alpha \) is the conversion achieved after time \( t \), \( \dot{r} \) is the rate of dissolution at the surface in units of length per time, and \( R \) is the initial particle size. The conversion is related to the size by:

\[
\alpha = 1 - \left( \frac{r}{R} \right)^3
\]

The intrinsic rate of reaction, given by \( \dot{r} \), describe the mechanism of reaction at the surface. If the reaction is a simple reaction of order \( n \) and activation energy \( E_a \), then the rate of reaction is given by:

\[
r_s = kC^n e\left(\frac{-E_a}{RT}\right)
\]

Crundwell (2005) defined a dimensionless number called “leaching number” and he indicated that through this number is possible to understand the continuous leaching operations. The leaching number is defined as following:

\[
N_r = \frac{\dot{rt}}{r}
\]
Where $\bar{t}$ is the mean residence time, $\dot{r}$ is the rate of shrinkage of the particles (leaching kinetics) and $\bar{r}$ is the mean particle size. The leaching rate, $\dot{r}$, has units of meters per second.

Crundwell (2005) indicated that on order to achieve a particular conversion in continuous reactor, there are only three variables to manipulate: (i) the residence time, (ii) the particle size, and (iii) the intrinsic leaching rate (through the temperature). In other words, the importance of the leaching number is this: in order to increase the extent of leaching, if the rate must be increased, the initial particle size decreased or the leaching time lengthened.

The smaller a particle, the faster it dissolves due to the increase in a surface area that is available per unit mass. It is self-evident that a successful model of continuous leaching must be able to account for the effect of particle size on the performance of the reactor. In addition, particles with a range of sizes are fed to a tank reactor, and, due to the conditions of mixing, they may leave the reactor after having spent different times in the reactor. Since the reaction depend on the surface area, an effective model of the leaching must account for the change in both the particle size and the particle size distribution.

Models of the leaching of particulates in continuous reactors fall in two camps: the segregated-flow model and the population balance model (Crundwell, 2005). The underlying assumptions that distinguish these are subtle, and relate to the degree of micro-mixing in the reactor. At this moment the aim of this work is not to show in detail both theories, the point now is to show the leaching number as a possibilities for compare the different behaviours of the bioreactors.
**Table 10:** Comparison of the segregated-flow model and the population balance.

<table>
<thead>
<tr>
<th>Mixing assumption</th>
<th><strong>Well mixed reactor</strong></th>
<th><strong>Segregated-flow reactor</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation for homogeneous reactors</td>
<td>$QC_{in} = QC_{out} - rV$</td>
<td>$C_{out} = \int_{0}^{\infty} C_{batch}(C_{in},t) E(t) dt$</td>
</tr>
<tr>
<td>Equivalence condition for homogeneous reactors</td>
<td>Equivalent to each other only if the reaction is first order</td>
<td></td>
</tr>
<tr>
<td>Equation for heterogeneous reactors</td>
<td>$Qn_{in} = Qn_{out} - V \frac{dr n_{out}}{dr}$</td>
<td>$n(r) = \int_{0}^{r} n_{batch}(r) E(t) dt$</td>
</tr>
<tr>
<td>Equivalence condition for heterogeneous reactors</td>
<td>Equivalent to each other only if reaction is zero order</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.2:** A comparison of the population balance and the segregated-flow model for the leaching of a mineral by a lixiviant in stoichiometric proportion to mineral. The tank volumes to achieve 90% conversion differ between the two models by more than a factor of 2.5.
5. MODELLING AND SIMULATION

5.1. One dimensional transient model

A column of 10 meters height and 1 square meter at the base was considered. The solution of irrigation is added on the top of the heap, it was considered with a horizontal draining. The particle size was considered uniform and the ferrous ions are assumed in excess. The population of bacteria is considered constant during the process. The air in the bed is assumed saturated by water and it is a function of the temperature.

Figure 5.1: Description of the Bioleaching phenomena.

\[
\begin{align*}
4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ & \xrightarrow{\text{bacteria}} 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \\
\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{2+} & \rightarrow 15\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \\
\text{Cu}_2\text{S} + 10\text{Fe}^{2+} + 4\text{H}_2\text{O} & \rightarrow 10\text{Fe}^{3+} + 2\text{Cu}^{2+} + 3\text{SO}_4^{2-} + 8\text{H}^+
\end{align*}
\]
The mineral was considered a mixture of chalcocite, pyrite and rock host, which was considered no reactive.

The model considered the reactions as follows:

\[
\begin{align*}
Cu_2S + 10Fe^{3+} + 4H_2O &\rightarrow 10Fe^{2+} + 2Cu^{2+} + SO_4^{2-} + 8H^+ \\
4Fe^{2+} + O_2 + 4H^+ &\rightarrow 4Fe^{3+} + 2H_2O \\
FeS_2 + 8H_2O + 14Fe^{3+} &\rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+
\end{align*}
\]

5.1.1. Oxygen consumption

The rate of consumption depends of the bacteria activity, and it is calculated by the Michelis-Menten (Sidborn et al., 2003) expression as follows:

\[
R_{O_2} = XV_m \frac{O_{2,L}}{K_m + O_{2,L}} \left( \text{kmol oxygen} \cdot m^{-3} \text{bed} \cdot s^{-1} \right)
\]

Where \( X \left( \text{bacteria} \cdot m^{-3} \text{bed} \right) \) and \( M_{O_2} \) is the oxygen molecular weight. For \( V_m \) was used the experimental expression determined by Casas et al (1996).

\[
V_m = \frac{1}{M_{O_2}} \frac{6.8 \times 10^{-13} \Delta t_e}{1 + e^{\frac{236 - 7000}{14000}}} \left( \text{kmol Oxygen} \cdot \text{bacteria}^{-1} \cdot \text{s}^{-1} \right)
\]

The concentration of oxygen in the liquid, \( O_{2,L} \), can be calculated with the Henry’s law: “at a constant temperature the amount of gas a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of the gas in equilibrium with liquid”

\[
\frac{P_{O_2}}{He} = O_{2,L} \text{ (Henry’s law)}
\]
Where \( P_{O_2} \) is the oxygen pressure of the gas expressed in \((Pa)\), \( O_{2,L} \) was expressed in \((kmol \text{ oxygen} \cdot m^{-3} \text{ liquid})\) and \( He \) in \((m^2 \cdot kg \cdot kmol^{-1} \cdot s^{-2})\).

The gas is considered perfect gas:

\[
P_{N_2} V_g = n_{N_2} RT
\]

\[
C_{N_2} = \frac{n_{N_2}}{V_g} = \frac{P_{N_2}}{RT}
\]

Where \( P(Pa) \) is the pressure, \( T(K) \) is the temperature, \( R \left( kg \cdot m^2 \cdot s^{-2} \cdot kmol^{-1} \cdot K^{-1} \right) \) is the universal gas constant, \( M_{N_2} \left( kg \cdot kmol^{-1} \right) \) is the Molar weight of nitrogen.

In the case of the oxygen, we defined \( X_{O_{2,g}} \) as the ratio between the partial pressure of oxygen and the partial pressure of nitrogen:

\[
X_{O_{2,g}} = \frac{P_{O_2}}{P_{N_2}}
\]

Where \( X_{O_{2,g}} \) was expressed in \((kmol \text{ oxygen} \cdot kmol^{-1} \text{ nitrogen})\).

Then

\[
O_{2,g} = X_{O_{2,g}} C_{N_2} = \frac{n_{O_{2,g}}}{V_g} = \frac{P_{O_2}}{RT}
\]

In this case was necessary to determine the partial pressure for each element in the gas:

\[
P = P_{O_2} + P_{N_2} + P_{H_2O}
\]
The gas is saturated by water vapour, and for that reason is possible to considered the Antoine relations as following:

\[
\log P_{H_2O} = A - \frac{B}{(T-273.15) + C} \quad \text{(Antoine’s equation)}
\]

Then,

\[
P_{H_2O} = 10^\left( A - \frac{B}{(T-273.15) + C} \right) \cdot 133.3224
\]

Where \( A \), \( B \) and \( C \) are constant for the water vapour and \( T \) is the temperature in \( K \) and \( P_{H_2O} (Pa) \)

Combining the 3 equations it is:

\[
P_{N_2} = \frac{P - P_{H_2O}}{1 + X_{O_2,s}}
\]

And:

\[
P_{O_2} = \frac{P - P_{H_2O}}{1 + X_{O_2,s}} \cdot X_{O_2,s}
\]
5.1.2. **Mass balance of Oxygen**

![Oxygen Distribution and other species distribution around the particle.](image)

**Figure 5.2**: Oxygen Distribution and other species distribution around the particle.

In this case the oxygen concentration in the gas was considered with respect to the nitrogen concentration in the gas because this one is constant through the bed. Furthermore is necessary to considerer the equilibrium between the oxygen amount in the liquid and the gas.

\[
\varepsilon_L \left( \frac{C_{N_2} X_{O_{2g}} RT}{He} \right) + \varepsilon_g C_{N_2} \frac{\partial X_{O_{2g}}}{\partial t} = \varepsilon_g D_g C_{N_2} \nabla^2 X_{O_{2g}} + \varepsilon_L D_L \nabla^2 \left\{ \frac{C_{N_2} X_{O_{2g}} RT}{He} \right\} \\
+ F_{N_2} \nabla X_{O_{2g}} - q_L \nabla \left\{ \frac{C_{N_2} X_{O_{2g}} RT}{He} \right\} - R_O
\]

\[
\left( \varepsilon_g + \varepsilon_L \frac{RT}{He} \right) C_{N_2} \frac{\partial X_{O_{2g}}}{\partial t} = \left( \varepsilon_g D_g + \varepsilon_L D_L \frac{RT}{He} \right) C_{N_2} \nabla^2 X_{O_{2g}} + \left( F_{N_2} - q_L \frac{RT}{He} C_{N_2} \right) \nabla X_{O_{2g}} - R_O
\]
Where the second terms in the parenthesis correspond to the oxygen dissolved in the liquid:

\[
\frac{P_{O_2}}{He} \cdot \frac{O_{2,g}RT}{He} = \frac{X_{O_2,g}C_{N_2}RT}{He} = O_{2,L}
\]

Due to the small solubility of oxygen in water, the terms corresponding to the oxygen dissolved in the water phase may be neglected in most of cases.

Where \( F_{N_2} \left( m^3 \text{ nitrogen} \cdot m^{-2} \text{ bed} \cdot s^{-1} \right) \) is the incoming nitrogen flux and it was defined as:

\[
F_{N_2} = \frac{q_g \cdot \rho_{air} \cdot X_{N_2}}{M_{N_2}} \left( m^3 \text{ nitrogen} \cdot m^{-2} \text{ bed} \cdot s^{-1} \right)
\]

Where \( q_g \) is the incoming gas flux and it is expressed as \( \left( m^3 \text{ gas} \cdot m^{-2} \text{ bed} \cdot s^{-1} \right) \), \( \rho_{air} \) is the air density as \( \left( \text{kg air} \cdot m^{-3} \text{ gas} \right) \), \( X_{N_2} \) is the weight fraction of nitrogen in the air expressed as \( \left( m^3 \text{ nitrogen} \cdot m^{-3} \text{ gas} \right) \) and \( M_{N_2} \) in \( \left( \text{kg} \cdot \text{kmol}^{-1} \right) \) is the molecular weight.
5.1.3. **Mass Balance of Ferric Ions**

In general, the balance for species in solution was defined as:

\[
\frac{\varepsilon_L}{\partial t} \frac{\partial C_i}{\partial t} = \varepsilon_L D_L \nabla^2 C_i - q_L \nabla C_i - R_i
\]

The mass balance for the ferric ions in the liquid is then:

\[
\frac{\varepsilon_L}{\partial t} \frac{\partial C_{Fe^{3+}}}{\partial t} = \varepsilon_L D_L \nabla^2 C_{Fe^{3+}} - q_L \nabla C_{Fe^{3+}} - \sum R_{Fe^{3+}} \left( \text{kmol ferric ions} \cdot \text{m}^{-3} \text{bed} \cdot \text{s}^{-1} \right)
\]

Where \( \varepsilon_L \left( \text{m}^3 \text{liquid} \cdot \text{m}^{-3} \text{bed} \right) \) is the volumetric fraction of liquid, \( D_L \left( \text{m}^2 \cdot \text{s}^{-1} \right) \) is the dispersivity of the \( Fe^{3+} \) in the bed, \( q_L \left( \text{m}^3 \text{liquid} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right) \) is the flow density rate of liquid. \( \sum R_{Fe^{3+}} \) correspond to the expression to production and consumption of ferric ions. They were defined as:

\[
\begin{align*}
Cu_2S + 10Fe^{3+} + 4H_2O & \rightarrow 10Fe^{2+} + 2Cu^{2+} + SO_4^{2-} + 8H^+ \\
4Fe^{2+} + O_2 + 4H^+ & \rightarrow 4Fe^{3+} + 2H_2O \\
FeS_2 + 8H_2O + 14Fe^{3+} & \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+
\end{align*}
\]

The relation between the consumption rate of oxygen, \( R_{O_2} \), and the production rate of ferric ions, \( R_{Fe^{3+}} \), is:

\[
R_{Fe^{3+}} = 4R_{O_2}
\]

The consumption of ferric ions due to the dissolution of Chalcocite and Pyrite are:

\[
R_{Fe^{3+}} = 10R_{Ch} + 14R_{Py}
\]
$FPY$ and $mFPY$ were defined as the relation between the amount of pyrite and chalcocite in the mineral expressed in mass and moles respectively.

\[
FPY = \frac{\text{kg pyrite}}{\text{kg chalcocite}}, \quad mFPY = FPY \frac{M_{Ch}}{M_{Py}} \left( \text{kmol pyrite} \cdot \text{kmol}^{-1} \text{ chalcocite} \right)
\]

Then:

\[
R_{Fe^{3+}} = 10R_{Ch} + 14R_{Ch} \cdot mFPY
\]

\[
R_{Fe^{3+}} = (10 + 14mFPY)R_{Ch}
\]

Then the balance in the Heap is defined as:

\[
\varepsilon_L \frac{\partial C_{Fe^{3+}}}{\partial t} = \varepsilon_L D_L \nabla^2 C_{Fe^{3+}} - q_L \nabla C_{Fe^{3+}} + 4R_{O_2} - (10 + 14mFPY)R_{Ch}
\]
5.1.4. **Mass balance of copper**

For the copper in the liquid the balance is:

\[ \varepsilon_L \frac{\partial C_{Cu}}{\partial t} = \varepsilon_L D_L \nabla^2 C_{Cu} - q_L \nabla C_{Cu} + R_{Cu} \left( \text{kmol copper} \cdot m^{-3} \text{ bed} \cdot s^{-1} \right) \]

\( R_{Ch} \) represent the chalcocite leaching rate. The relation between the rate of consumption of chalcocite and the copper production is:

\[ R_{Cu} = 2R_{Ch} \]

For each chalcocite \( \text{kmol} \) consumed for unit of time and bed volume, 2 \( \text{kmol} \) of ions copper are produced. In other words the copper ions production is twice the consumption of chalcocite.

Then:

\[ \varepsilon_L \frac{\partial C_{Cu}}{\partial t} = \varepsilon_L D_L \nabla^2 C_{Cu} - q_L \nabla C_{Cu} + 2R_{Ch} \]

The chalcocite mineral dissolution rate is related to the rate of change of the unreacted core radius according to:

\[ \frac{\text{kg Cu}_2\text{S unreacted}}{m^3 \text{ bed}} = \frac{\text{volume of unreacted particle}}{\text{Total volume of the particle}} \cdot \frac{\text{Initial concentration of Cu}_2\text{S}}{\text{bed volume}} \]

Then:

\[ \frac{\text{kg Cu}_2\text{S unreacted}}{m^3 \text{ bed}} = \frac{4}{3} \pi r_c^3 \cdot G \cdot \rho_p \cdot \varepsilon_s \]
Then the chalcocite dissolution rate is:

\[ R_{Ch} = \frac{dr_c}{dt} = \frac{3}{R_p^3} \cdot c_{Ch} \cdot G \cdot \rho_p \cdot \frac{1}{M_{Ch}} \text{(kmol} \cdot \text{m}^{-3} \cdot \text{bed} \cdot \text{s}^{-1}) \]

Where \( G \) was defined as \( (\text{kg chalcocite} \cdot \text{kg}^{-1} \text{solid}) \), \( \rho_p \) is the initial particle density in \( (\text{kg} \cdot \text{m}^{-3} \text{solid}) \) and \( \epsilon_s \) is the volumetric fraction of solid and it is calculated assuming that the sum of the volume fractions of solid, gaseous and liquid phases equals unity:

\[ \epsilon_s + \epsilon_g = 1 \]

\( \frac{4}{3} \pi R_p^3 \) is the total volume of the particle, \( r_c \) and \( R_p \) denotes the shrinking core radius and the external particle radius respectively.

In the Heap there are only two kinds of reactive species, chalcocite and pyrite, according to the following reactions:

\[
\begin{align*}
\text{Cu}_2\text{S} + 10\text{Fe}^{3+} + 4\text{H}_2\text{O} & \rightarrow 10\text{Fe}^{2+} + 2\text{Cu}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ \\
\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} & \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+
\end{align*}
\]

In general if possible considered a total reaction as:

\[ aA + bB \stackrel{k_s}{\rightarrow} \text{Products} \]

Where is defined \( \sigma = \frac{a}{b} \). Therefore the reaction in the Heap is:

\[ \sigma \text{ Mineral} + \text{Fe}^{3+} \stackrel{k_s}{\rightarrow} \text{Products} \]
Where:

\[
\sigma = \frac{1 + m_{FPY}}{10 + 14m_{FPY}}
\]

The rate of change of the unreacted core radius, \( -\frac{dr_C}{dt} \), may be determined through the shrinking core model:

\[
-\frac{dr_C}{dt} = \frac{C_{Fe^{2+}}}{\sigma \rho_M} \frac{r_C^2}{r_C^2 + \left( R_p - r_C \right) r_C + 1} \left( \frac{R_p}{k_{film}} + \frac{R_p D_e}{k_{ash}} \right) \]

Where \( \rho_M \) is expressed as \( \left( \text{kmol mineral} \cdot m^{-3} \text{ solid} \right) \) and it was defined as following:

\[
\rho_M = \rho_p \cdot G \cdot (1 + m_{FPY}) \frac{1}{M_{Ch}}
\]

In other words, it represents the \text{kmol} reactive mineral per bed volume.
5.1.5. Variation of temperature inside the Heap: Energy Balance

The mineral contains a mixture of chalcocite, pyrite and rock host which was considered no reactive. The dissolution of both chalcocite and pyrite generate heat, this produce a variation in the energy inside the heap.

The model considered the reactions as follow:

\[
\begin{align*}
\text{Cu}_2\text{S} + 10\text{Fe}^{3+} + 4\text{H}_2\text{O} & \longrightarrow 10\text{Fe}^{2+} + 2\text{Cu}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+, \ \Delta H_{\text{Ch}} \\
\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} & \longrightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+, \ \Delta H_{\text{Py}}
\end{align*}
\]

The energy balance can be expressed as:

\[
\text{Accumulation} = \text{Conduction} + \text{Convection} + \text{Reaction}
\]

\[
\rho_b C_{p,b} \frac{\partial T}{\partial t} = k_B \nabla^2 T - \rho_L q_L \cdot \nabla H_L + F_{N_2} \cdot \nabla H_{N_2} - (\Delta H_R + \Delta H_S) \cdot R_{\text{ch}} \left( kJ \cdot m^{-2} \cdot \text{bed} \cdot s^{-1} \right)
\]

Where the heat of reaction was defined as:

\[
\Delta H_R = (\Delta H_{\text{Ch}} + F_{\text{PY}} \cdot \Delta H_{\text{Py}}) \cdot M_{\text{Ch}} \left( kJ \cdot \text{kmol}^{-1} \text{ chalcocite} \right)
\]

With \( \Delta H_{\text{Ch}} \left( kJ \cdot \text{kg}^{-1} \text{ chalcocite} \right) \) and \( \Delta H_{\text{Py}} \left( kJ \cdot \text{kg}^{-1} \text{ pyrite} \right) \).

The heat of solution of the reaction products was expressed as follow:

\[
\Delta H_S = \left( 2 \cdot M_{\text{CuSO}_4} \cdot \Delta H_{\text{CuSO}_4,\text{solution}} + m_{\text{PY}} \cdot M_{\text{FeSO}_4} \cdot \Delta H_{\text{FeSO}_4,\text{solution}} \right) \left( kJ \cdot \text{kmol}^{-1} \text{ chalcocite} \right)
\]

Where \( \Delta H_{\text{CuSO}_4} \) was defined in \( \left( kJ \cdot \text{kg}^{-1} \text{ CuSO}_4 \right) \) and \( \Delta H_{\text{FeSO}_4} \) in \( \left( kJ \cdot \text{kg}^{-1} \text{ FeSO}_4 \right) \).
The enthalpy variation in the liquid can be calculated as:

\[
H_L = C_{p,L} \left( T - T_{ref} \right) \left( \text{kJ} \cdot \text{kg}^{-1} \cdot \text{liquid} \right)
\]

Where \( C_{p,L} \) is the average specific heat of liquid and it was expressed in \( \left( \text{kJ} \cdot \text{kg}^{-1} \cdot \text{liquid} \cdot \text{K}^{-1} \right) \) and \( T_{ref} \) (K) is the reference temperature for the enthalpy calculations.

In the case of the enthalpy variation of the gas, the situation is different, because the chemical reactions produce an increase of the temperature that produce variations in the gas composition, in other words, the amount of water vapour in the gas has increased due to the evaporation.

The gas was considered as perfect gas, then:

\[
P_{N_2}V_g = n_{N_2}RT
\]

\[
C_{N_2} = \frac{n_{N_2}}{V_g} = \frac{P_{N_2}}{RT}
\]

\[
O_{2,g} = X_{O_{2,g}}C_{N_2} = \frac{n_{O_{2,g}}}{V_g} = \frac{P_{O_2}}{RT}
\]

We defined \( X_{H_2O_{wp}} \) as the ratio between of the partial pressure of the water vapour and the partial pressure of nitrogen:

\[
X_{H_2O_{wp}} = \frac{P_{H_2O}}{P_{N_2}}
\]
Then

\[ H_{2}O_{\text{vap}} = X_{H_{2}O} \cdot C_{N_{2}} = \frac{n_{H_{2}O_{\text{vap}}}}{V_{g}} = \frac{P_{H_{2}O}}{RT} \]

Where \( X_{H_{2}O_{\text{vap}}} \) was expressed in \((\text{kmol water vapour} \cdot \text{kmol}^{-1} \text{nitrogen})\)

The gas flow inside the heap is not constant, then the both oxygen and vapour water flows were defined as:

\[ F_{O_{2}} = X_{O_{2,g}} \cdot F_{N_{2}} \left( m^{3} \text{ oxygen} \cdot m^{-2} \text{ bed} \cdot s^{-1} \right) \]

\[ F_{H_{2}O} = X_{H_{2}O_{\text{vap}}} \cdot F_{N_{2}} \left( m^{3} \text{ water vapour} \cdot m^{-2} \text{ bed} \cdot s^{-1} \right) \]

Then the gas enthalpy was estimated according to:

\[ H_{g} = \Delta H_{\text{vap},H_{2}O} \cdot X_{H_{2}O_{\text{vap}}} \cdot M_{H_{2}O} + \left( C_{p,H_{2}O_{\text{vap}}} \cdot X_{H_{2}O_{\text{vap}}} \cdot M_{H_{2}O} + C_{p,g} \left( X_{O_{2,g}} \cdot M_{O_{2}} + M_{N_{2}} \right) \right) \left( T - T_{\text{ref}} \right) \]

Where \( H_{g} \) is expressed in \((kJ \cdot \text{kmol}^{-1} \text{nitrogen})\).
5.2. One dimensional transient model including distribution of particle size

In this section, the model is improved to consider the case of a bed formed by particles of different sizes. In general this distribution is not known a priori and experimental information is required. This information is normally presented as an distribution of particle size, \( f(R) \), or an accumulative distribution of particle size, \( F(R) \), where en both case the information is about the size of the particle and the faction below a certain particle size, as the Figure 5.3 shows.

![Accumulative particle size distribution](image)

**Figure 5.3:** Accumulative particle size distribution.

Then we can assumed that it is possible to represent a continuous function defining average radii, \( R_{pi} \) and some distribution, for example the weight fraction of particles, \( f_i \), with \( i=1,2,3...n \). Three different particles size were considered in the model, as Figure 5.4 shows, but to increase the number of size is straightforward. An equation is required for each size.
Figure 5.4: Distribution of particle size, considering three particle size.

For each case was necessary to calculate the variation of the particle size through the shrinking core model, then the copper mineral dissolution rate is:

\[
R_{Ch} = 3 \cdot \varepsilon_s \cdot G \cdot \rho_p \cdot \frac{1}{M_{Ch}} \cdot \sum_{i=1}^{3} \frac{dr_i}{dt} \cdot \frac{1}{R_{pl}} \cdot f_{3i} \left( \text{kmol chalcocite} \cdot \text{m}^3 \text{bed} \cdot \text{s} \right)
\]

\[
-\frac{dr_{Ci}}{dt}
\]

is the rate of change of the unreacted core radius, and it must be determined for the different sizes as:

\[
-\frac{dr_{Ci}}{dt} = \frac{C_{i\text{R}_m}}{\rho_m} \cdot \frac{\sigma}{r_{Ci}^2 + \left( R_{p_i} - r_{Ci} \right) r_{Ci} + \frac{1}{R_{p_i} D_{\text{ash}} k_{\text{film}}}} \left( \text{m} \cdot \text{s}^{-1} \right)
\]

In addition that, it is important to consider that the change of particle size can be measured with respect to the consumption rate of mineral in the particle, in other words, the shrinking core model can be expressed as a function of moles of chalcocite.
The amount of mineral in a particle can be expressed as follow:

\[ n_{\text{Ch}} = \frac{4}{3} \cdot \pi \cdot r_c^3 \cdot \rho_M \]

When it is known the moles of chalcocite that exist in a particle in each moment, it is possible to know the unreacted core radius in every moment too. The expression that gives the relation is:

\[ r_c = \sqrt[3]{\frac{3 \cdot n_{\text{Ch}}}{4 \cdot \pi \cdot \rho_M}} \]

Where the variation of chalcocite moles can be expressed as:

\[ \frac{d n_{\text{Ch}}}{dt} = S_{\text{ex}} \cdot \rho_M \cdot \frac{d r_c}{dt} \left( \text{kmol mineral} \cdot \text{s}^{-1} \right) \]

Where \( S_{\text{ex}} \left( m^2 \right) \) is the external surface particle and it was defined as:

\[ S_{\text{ex}} = 4 \cdot \pi \cdot R_p^2 \]

The chalcocite consumption was described as:

\[ R_{\text{Ch}} = -\frac{d r_c}{dt} \cdot r_c^2 \cdot \frac{3}{R_p^3} \cdot \varepsilon_s \cdot G \cdot \rho_p \cdot \frac{1}{M_{\text{Ch}}} \left( \text{kmol chalcocite} \cdot \text{m}^3 \cdot \text{bed} \cdot \text{s}^{-1} \right) \]

Then the expression can be redefined as:

\[ R_{\text{Ch}} = -\frac{d n_{\text{Ch}}}{dt} \cdot \frac{3 \cdot r_c^2 \cdot \varepsilon_s}{4 \cdot \pi \cdot (1 + mFPY) \cdot R_p^5} \]
Therefore the shrinking core model can be expressed also as follow:

\[-\frac{dn_{Ch}}{dt} = \frac{\sigma \cdot C_{Fe} \cdot S_{ex}}{1 + \frac{R_p \cdot \left(R_p - r_C\right)}{k_g \cdot r_C D_e_{ash}} + \frac{R_p^2}{r_C^2 \cdot k_r}}\]

For a system with three particle sizes, the expressions are:

\[-\frac{dn_{Ch_i}}{dt} = \frac{\sigma \cdot C_{Fe} \cdot S_{ex_i}}{1 + \frac{R_{p_i} \cdot \left(R_{p_i} - r_{C_i}\right)}{k_g \cdot r_{C_i} D_e_{ash}} + \frac{R_{p_i}^2}{r_{C_i}^2 \cdot k_{r_i}}}\]

Then

\[R_{Ch} = -\frac{3 \cdot \varepsilon_S}{4 \cdot \pi \cdot (1 + mFPY)} \sum_{i=1}^{3} \frac{dn_{Ch_i}}{dt} \cdot \frac{r_{C_i}^2 \cdot f_{3i}}{R_{p_i}^2} \]

It is very important to keep in mind the two forms for resolving and calculating the Shrinking core model, because when the operation times are long or the particle size are small, in the last part of the process the unreacted core radius, \(r_C\), diminish quickly, therefore \(\frac{dr_C}{dt}\) increase very fast, it can be produce instabilities in the resolution of the problem. In the other hand the variation of chalcocite moles, \(\frac{dn_{Ch}}{dt}\), in the last part of the bioleaching it is very slow.
5.2.1. **Initial and boundary conditions for the one-dimensional transient model**

**Top Boundary**

\[
\frac{\partial O_{2,g}}{\partial z} = 0 \text{ , } z = 10
\]

Only advective transport

\[
D_L \cdot \varepsilon_L \frac{\partial C_{Cu}}{\partial z} - q_L C_{Cu} = 0 \text{ , } z = 10
\]

No copper transportation through the boundary

\[
D_L \cdot \varepsilon_L \frac{\partial C_{Fe^{+}}}{\partial z} - q_L C_{Fe^{+}} = 0 \text{ , } z = 10
\]

No ferric ion transportation through the boundary

\[
T = T_{\text{irrigation}} \text{ , } z = 10
\]

The temperature on the top is the temperature of the irrigation liquid.

**Bottom Boundary**

\[
D_g \cdot \varepsilon_g C_{N_2} \frac{\partial O_{2,g}}{\partial z} - q_g O_{2,g} = q_{g,IN} O_{2,g,IN} \text{ , } z = 0
\]

Oxygen transportation through the boundary

Only advective transport

\[
\frac{\partial C_{Cu}}{\partial z} = 0 \text{ , } z = 0
\]

Only advective transport

\[
\frac{\partial C_{Fe^{+}}}{\partial z} = 0 \text{ , } z = 0
\]

Only advective transport

\[
\frac{\partial T}{\partial x} = 0 \text{ , } z = 0
\]

Only advective transport

If a solution from SX-EW is use as the irrigation solution, this contain concentrations both copper and ferric ions, then the boundary condition for copper and ferric ions in the top (\(z = 10\)) of the heap must be:

\[
D_L \cdot \varepsilon_L \frac{\partial C_{Cu}}{\partial z} - q_L C_{Cu} = q_L C_{Cu,IN}
\]

No copper transportation through the boundary

\[
D_L \cdot \varepsilon_L \frac{\partial C_{Fe^{+}}}{\partial z} - q_L C_{Fe^{+}} = q_L C_{Fe^{+},IN}
\]

No ferric ion transportation through the boundary
5.3. **Two-dimensional transient model.**

The two dimensional model considered a bed as shows the figure 7.3. In general the heap are extensive in size. If we considered a cross section of the heap it is repeated along the bed in many times.

![Figure 5.5: Description of the Heap](image)

The aeration system was considered equidistant with respect the center of the heap, for this reason the simulation considered only an internal section of the heap.

![Figure 5.6: Cross section description of the aeration channels in the heap](image)

The natural convection was considered negligible in the presence of the force aeration and the simulation was focused in an internal section of the Heap, no close to the edges.
The model was defined with respect to eight differential equations, oxygen balance:

\[
\frac{\partial X_{O_{2,g}}}{\partial t} = \left( \frac{\varepsilon_g D_g + \varepsilon_L D_L}{\varepsilon_L RT + \varepsilon_g He} \right) \nabla^2 X_{O_{2,g}} + \nabla \left\{ \left( F_{N_2} - q_L \frac{RT}{He} C_{N_2} \right) X_{O_{2,g}} \right\} - \frac{R_{O_2}}{e_g \cdot C_{N_2}}
\]

How it was commented before, the oxygen concentration in the liquid is neglected, then:

\[
\frac{\partial X_{O_{2,g}}}{\partial t} = D_g \nabla^2 X_{O_{2,g}} + \frac{\nabla \left\{ F_{N_2} \cdot X_{O_{2,g}} \right\}}{\varepsilon_g \cdot C_{N_2}} - \frac{R_{O_2}}{e_g \cdot C_{N_2}}
\]

The mass balance for copper and ferric ions in the liquid was considered as:

\[
\frac{\partial C_{Cu}}{\partial t} = \nabla \left( D_L \nabla C_{Cu} \right) - \frac{q_L}{\varepsilon_L} \nabla C_{Cu} + \frac{2}{\varepsilon_L} R_{Ch}
\]

\[
\frac{\partial C_{Fe^{3+}}}{\partial t} = \nabla \left( D_L \nabla C_{Fe^{3+}} \right) - \frac{q_L}{\varepsilon_L} \nabla C_{Fe^{3+}} + \frac{1}{\varepsilon_L} \left( 4R_{O_2} - (10 + 14mFPY) R_{Ch} \right)
\]

Energy balance in the heap,

\[
\rho_B C_{p,B} \frac{\partial T}{\partial t} = k_B \nabla^2 T - \rho_L \cdot q_L \cdot \nabla H_L + \nabla \left( F_{N_2} \cdot H_g \right) - (\Delta H_R + \Delta H_S) \cdot R_{Ch} \left[ \frac{kJ}{m^3 \text{bed} \cdot s} \right]
\]

And the Unreacted Core Model for the three different sizes:

\[
- \frac{dr_{Ci}}{dt} = \frac{\sigma \cdot C_{Fe^{3+}}}{\rho_M} \left( \frac{1}{r_{Ci}} + \frac{1}{R_{Pi} k_g} + \frac{1}{R_{Pi} D_e} + \frac{1}{k_s} \right)
\]
Where \( \nabla \) is equal to \( \left( \frac{\partial}{\partial x} + \frac{\partial}{\partial z} \right) \) for the two dimensional simulations.

The liquid flow, \( q_L \), was considered with a horizontal draining. The variation in the density gas was not considered, because the oxygen transport due to variations in the gas composition is small when the forced aeration is present. For the 2D model is necessary to consider both the vertical and horizontal components of the gas flow. According to Darcy’s law is possible to determinate the both vertical and horizontal gas flow component:

\[
u = -\frac{k}{\mu_g} \nabla P
\]

Where \( k \) is the permeability of the bed and \( \mu_g \) is the average gas viscosity. \( P \) is the pressure and \( u \) is the gas velocity, and it was defined as:

\[
u = \frac{q_g}{\varepsilon_g}
\]

where \( u \) was expressed in \( (m \cdot s^{-1}) \).
5.3.1. **Boundary conditions for the two dimensional transient model**

**Top Boundary**

$$\frac{\partial O_{2,g}}{\partial z} = 0, \ z = 10$$  
Only advective transport

$$D_L \cdot \varepsilon_L \frac{\partial C_{Cu}}{\partial z} - q_L C_{Cu} = 0, \ z = 10$$  
No copper transportation through the boundary

$$D_L \cdot \varepsilon_L \frac{\partial C_{Fe^{3+}}}{\partial z} - q_L C_{Fe^{3+}} = 0, \ z = 10$$  
No ferric ion transportation through the boundary

$$T = T_{irrigation}, \ z = 10$$  
The temperature on the top is the temperature of the irrigation liquid.

**Bottom Boundary**

$$\frac{\partial O_{2,g}}{\partial z} = 0, \ z = 0$$  
Only advective transport

$$\frac{\partial C_{Cu}}{\partial z} = 0, \ z = 0$$  
Only advective transport

$$\frac{\partial C_{Fe^{3+}}}{\partial z} = 0, \ z = 0$$  
Only advective transport

$$\frac{\partial T}{\partial x} = 0, \ z = 0$$  
Only advective transport

**Side boundary (symmetric)**

$$\frac{\partial O_{2,g}}{\partial z} = 0, \ x = 0, \ x = 20$$  
Close Boundary

$$\frac{\partial C_{Cu}}{\partial z} = 0, \ x = 0, \ x = 20$$  
Close Boundary

$$\frac{\partial C_{Fe^{3+}}}{\partial z} = 0, \ x = 0, \ x = 20$$  
Close Boundary

$$\frac{\partial T}{\partial x} = 0, \ x = 0, \ x = 20$$  
Close Boundary
**Aeration Channel**

\[
D_g \cdot \varepsilon_g C_{N_2} \frac{\partial O_{2,g}}{\partial z} - q_g O_{2,g} = q_{g,IN} O_{2,g,IN}, \quad z = 0 \land 9.9 \leq x \leq 10.1
\]

Oxygen transportation through the boundary

Only advective transport

\[
\frac{\partial C_{Cu}}{\partial z} = 0, \quad z = 0 \land 9.9 \leq x \leq 10.1
\]

Only advective transport

\[
\frac{\partial C_{Fe^{3+}}}{\partial z} = 0, \quad z = 0 \land 9.9 \leq x \leq 10.1
\]

Only advective transport

\[
\frac{\partial T}{\partial x} = 0, \quad z = 0 \land 9.9 \leq x \leq 10.1
\]

Like the 1D model, if the irrigation solution contains concentration of copper an ferric ions, the boundary condition (\( z = 10 \)) for both elements will be:

\[
D_L \cdot \varepsilon_L \frac{\partial C_{Cu}}{\partial z} - q_L C_{Cu} = q_L C_{Cu,IN}
\]

No copper transportation through the boundary

\[
D_L \cdot \varepsilon_L \frac{\partial C_{Fe^{3+}}}{\partial z} - q_L C_{Fe^{3+}} = q_L C_{Fe^{3+},IN}
\]

No ferric ion transportation through the boundary
6. RESULTS AND DISCUSSIONS

6.1. One Dimensional transient model

For the one-dimensional transient case, the model considered the mass balances for the Cu(II), Fe(III), oxygen and the energy balance in the heap. In addition to these balances, one differential equations was used for describing the variation of the particle size with respect to time. The heap performance was studied with three different particle sizes. Ferrous ions were assumed in abundance in the heap. The bed porosity was considered to be constant for the different particle size even for the case with three particles sizes. The system was solved using the program FEMLAB® (Comsol).

The modelled heap was 10 m in height with irrigation on the top and aeration through the bottom. The dissolution of the mineral (pyrite and chalcocite) we carried out by ferric ions. Ferric ions were generated by oxidation of ferrous ions in presence of both bacteria and oxygen. The mass balance for de acid was not considered in the model. It was assumed a low pH, maintained in a appropriate value for the process. The bacteria concentration was considered constant and the bacteria activity is temperature dependent.

Initially, the mineral, the liquid, and the gas in the heap were assumed to have the same temperature. The incoming gas was considered to be dry, but at the bottom of the heap becomes water saturated due to the contact with the liquid.

The parameters values were taken from the literature. In these simulations, the main interest is to show the impact of the different parameters on the leach process, therefore, the exact value of the parameters is not important.

In a first set of simulations, the one-dimensional transient model was simulated during a period of 18 months using only a particle size. Figure 6.1 to Figure 6.3 show the copper concentration in the liquid along the heap for times of 1, 3, 6 and 12 months for particle radius of 0.06, 0.03, and 0.015 m respectively. The copper concentration
at the heap was greater for the smallest size due to mineral particles with small size have a greater external interaction surface, i.e., the area for diffusion of the ferric ions is increased.

In general, the cooper concentration along the heap height decreased with time. This is due to with time the diffusion resistance is increased and the amount of ferric ions transport to the surface of the unreacted core decreased. Some anomalies are in found the concentration profiles for the time of 1 month because the temperature in the heap had not reached its maximum value.

These results are valid for the conditions used in these simulations. For example for other aeration rate the concentration profiles could be quite different. The following conditions were used in these calculations: aeration rate $7 \cdot 10^{-5} \text{ m}^3\text{ gas} \cdot \text{m}^{-2}\text{ bed} \cdot \text{s}^{-1}$, irrigation rate $1.38 \cdot 10^{-6} \text{ m}^3\text{ liquid} \cdot \text{m}^{-2}\text{ bed} \cdot \text{s}^{-1}$, initial temperature of the heap, temperature of the incoming gas flow, and temperature of the irrigation solution was 15 °C.

Figure 6.1: Copper Concentration, Radius Size: 0.06 [m]
Figure 6.2: Copper Concentration, Radius Size: 0.03 [m]

Figure 6.3: Copper Concentration, Radius Size: 0.015 [m]
Figure 6.4 shows the variation of the copper concentration in the outlet with time. As expected from the copper concentration profiles, the outlet concentration was greater for the small size. However, the use of small particles in bioleaching increases the costs for reducing the size of the minerals.

At the beginning, the outlet copper concentration increased with time when the temperature within of the heap was increasing. Later, the concentration diminished during the bioleach process. At short times, the reaction occurs close to the particle surface, but afterwards the diffusion resistance for the ferric ions is more and more important, since the ferric ions need to penetrate a longer distance inside the particle to dissolve the mineral at the unreacted core.

![Copper Outlet Concentration](image)

**Figure 6.4:** Copper Outlet Concentration for three different size and 18 months.
At long times, when a part important of the copper has been recovered the outlet concentration decreases rapidly. This may be observed for the smallest size at time around 12 months.

The recovery of copper is shown in Figure 6.5 as accumulative curves. For the largest size only about 42% of the copper has been recovered in 18 months, while for the smallest size the recovery reached values around 75%. These results do not imply that from economic point of view is better to work with small particle size, because there are economic and operational reasons that make difficult the work with too small sizes. A small size increases the pressure drop through the heap and increases the costs for size reduction.

![Recovery of Copper](image)

**Figure 6.5:** Recovery of copper for three different sizes and 18 months of operation.
Regarding the temperature in the heap during the leaching, it increased during a period of about two-three months and then started to decrease. This occurs when the mineral dissolution rate diminished, as shown in Figure 6.4, because of the diffusion resistance for the ferric ions becomes more important. The decrease of the dissolution reaction rate implies that the heat generation is less and therefore, the temperature inside the heap starts to decrease.

The temperature profiles in the heap are shown in Figure 6.6, Figure 6.7 and Figure 6.8 at different leaching times for particle size of 0.06, 0.03 and 0.015 m, respectively. The temperature increased in almost 15°C for the smallest size at locations close to the bottom. For the medium size the temperature was increased about 12°C and for the biggest size 9°C. The temperature at the top was maintained in the three cases at 15°C, which corresponds to the temperature of the solution irrigate on the top. Afterwards, the temperature decreased. In the course of the reaction the temperature began to increase in the bottom of the heap because is the place where the mineral reaction is more intensive. The gas then evaporates a large amount of water in the lower zone of the heap, which condensates in the cold zones located at the upper part of the heap.

**Figure 6.6**: Temperature inside the Heap, Particle Size: 0.06 [m]
Figure 6.7: Temperature inside the Heap, Particle Size: 0.03 [m]

Figure 6.8: Temperature inside the Heap, Particle Size: 0.015 [m]
Although the temperature increase is a consequence of the dissolution of the pyrite and chalcocite, an important factor to consider is how the gas can transport energy through the bed. A significant part of the heat transport in the gas phase occurs by a process of evaporation-condensation of water. The gas evaporates water at the inlet at the bottom of the heap where the temperature is highest and condensates water vapour in the part with lower temperature.

In the oxygen concentration case, between the bottom and top of the heap, the oxygen in the gas diminished for the smaller size around 38% and for the greater it was almost 28%. The concentration of oxygen at the outlet (the top of the heap in this case) was quite high due to the high aeration rate used in these simulations. An adequate aeration implies that the concentration at the outlet would be sufficient low to avoid energy misuse and sufficient high to avoid small oxidation rates of the ferrous ions at the upper part of the heap.

Figure 6.9: Oxygen concentration in the gas, size: 0.06 [m]
Figure 6.10: Oxygen concentration in the gas, size: 0.03 [m]

Figure 6.11: Oxygen concentration in the gas, size: 0.015 [m]
Figure 6.12 to Figure 6.14 show the oxygen concentration in the liquid. The oxygen consumption was higher for the smaller sizes due to the kinetic reaction are faster when the specific area is increased and also due to the temperature is higher for this case. The oxygen consumption rate was greater at locations close to the bottom, because the temperature is larger there. Therefore the lowest oxygen concentration in the liquid occurred for the smallest size, because the temperature is the largest.

For the aeration rate used in these simulations, the oxidation rate of the ferrous ions to ferric is almost independent of the oxygen concentration. It is necessary keep in mind that the oxidation rate was considered as a Michaelis-Menten function. The Michaelis-Menten function indicates that for an oxygen concentration equal to $K_m$ the reaction occur at half of the maximum oxidation rate. In this particular case, the oxygen concentration in the liquid is much greater than $K_m$, in at least nine or six times, at the bottom and at the top, respectively. Therefore, the oxygen concentration is not an significant factor, since the process is occurring in the constant part of the Michaelis-Menten function. This also implies that the temperature plays an important roll in the process because the maximum specific respiration rate depends strongly of the temperature inside the heap.

![Oxygen Concentration](image)

**Figure 6.12**: Oxygen concentration in the Liquid. Particle Size: 0.06 [m]
Figure 6.13: Oxygen concentration in the Liquid. Particle Size: 0.03 [m]

Figure 6.14: Oxygen concentration in the Liquid. Particle Size: 0.015 [m]
As was stated before the oxidation rate was considered as a Michaelis-Menten function. The incoming gas flux considered in the simulations, \( q_g = 7 \cdot 10^{-5} \left( \frac{m^3 \text{gas} \cdot m^2 \text{bed} \cdot s^{-1}}{} \right) \), allows to obtain an oxygen concentration greater than \( K_m \) in several times. This situation indicates that we are working in the constant zone of the Michaelis-Menten curve. From this point of view perhaps it is possible to work with smaller fluxes, how Figure 6.15 shows. In other words, it is possible to indicate that to try to improve the system with greater aeration it is not the way, because the recovery of copper could be not enough for compensate the additional aeration system cost.

![Recovery of Copper](image)

**Figure 6.15:** Effect of the air flux variation on the recovery of Copper. \( q_g = 7 \cdot 10^{-5} \left( \frac{m^3 \text{gas} \cdot m^2 \text{bed} \cdot s^{-1}}{} \right) \), the half and the third part of itself
6.2. **One Dimensional Model transient including a Distribution of particle size.**

The One dimensional model where the heap is formed by mineral particles of different size is discussed. In general, the particle size distribution is described by a continuous function as shown in Figure 5.3. However, in order to introduce this distribution in the model, it has to be transformed into a discrete distribution, which may be presented as the histogram shown in Figure 6.16

![Distribution of Particle Size](image)

**Figure 6.16:** Discrete distributions of particle size and Accumulative discrete distribution of particle size, for the One dimensional transient model.

The copper outlet concentration with time for heap formed of particles 0.06, 0.03, and 0.015 m in radius and the outlet concentration for a heap with a particle size distribution are shown in Figure 6.17 for 18 months of operation. For a heap formed by particles of the three sizes, the performance is quite similar to a heap formed of particles of 0.03 m in radius. At the beginning the outlet concentration for the distribution is slightly over that for 0.03 m. After a time, about eight-nine months the outlet concentration falls down in direction to the bigger size.
Figure 6.17: Copper Outlet concentration for three different size and Copper outlet concentrations for a system with distribution size.

The behaviour shown in Figure 6.17 can be explained because at the beginning the reaction occurs on the surface of the particle. The smaller particles are then important in the overall reaction because they contribute with the 52% of the specific area for the reaction. For this reason, the curve for the copper outlet concentration at the beginning is between the small and medium sizes. Later, when the reaction has advanced it is controlled by diffusion, i.e., the biggest particle size become important. Therefore, the curve for the copper outlet concentration falls down and is found between the larger and medium size.
Figure 6.18 shows a comparison among the recoveries for the distribution of particle size and for each size. The behaviour between the distribution of particle size and the size $0.03\,[m]$ is quite similar.

Two average radii were calculated. The first one is the “weight average radius” where the weight fraction for each radius is used as weighting factor. For the particle size distribution used in these simulations the “weight average radius” was $r_{c,w} = 0.0345\,[m]$. The second one is the “surface average radius” where the specific surface fraction for each size is used as weighting factor. The “surface average radius” was, in this case, was $r_{c,s} = 0.0261\,[m]$. The objective of these calculations is determine if the leaching performance for a heap with a particle size distribution could be characterized by a heap with particles of only one size, some average size.
How was indicated above, at the beginning, the curve for the particle size distribution is close to that using the "surface average radius". The difference between them increases with time. The outlet concentration is then between the concentrations for both average radius. For times longer than one year \((3.15\cdot10^7\text{seg})\), the outlet copper concentration for the particle size distribution is below the concentration for the "weight average radius". This is due to a fraction significant of the copper in the small particles has been depleted.
Figure 6.20 shows the recovery profile for the distribution of particle size and both “average radius”. Before one year, the behaviour of the distribution of particle size curve and the “surface average radius” curve are quite similar. After one year of operation, the recovery of the distribution of particle size began to fell down, because the diffusion process in the greater particles is more important, then the copper concentration in the liquid began to diminish.

Figure 6.20: Recovery curves for a Heap with: “weight average radius”, “surface average radius” and Distribution of particle size.
6.3. Two-dimensional transient model with a Distribution of Particle Size

In the case of two-dimensional model, two different flow rates were considered for the incoming gas, with the intention to study the oxygen distribution and its influences during the process. Therefore two different flux rates were considered, they were taken from literature, the first one, \( q_1 = 2.4 \times 10^{-6} \left( m^3 \text{gas} \cdot m^{-2} \text{bed} \cdot s^{-1} \right) \) (Sidborn, 2000) and the second one \( q_2 = 7 \times 10^{-5} \left( m^3 \text{gas} \cdot m^{-2} \text{bed} \cdot s^{-1} \right) \) (Lizama, 2001). The simulation was performed until a time of 12 months.

The geometry considered was a central section of the heap. The edges of the heap were not considered. The selected geometry was 20(m) in wide and 10(m) in height. The aeration channel was considered in the middle of the section at the bottom of the heap and its size was 0.2(m). The natural convection due to the changes in the density of the gas was considered negligible, because forced aeration was used. The temperature for the irrigation solution and gas were considered 15(°C). The initial temperature of the heap was considered 15(°C) as well.

The heap was conformed by a distribution of particle size, in other words, it is conformed by three different particles sizes, 0.06(m), 0.03(m) and 0.015(m) with a weight distribution of 30%, 40% and 30%, respectively.

Figure 6.21 and Figure 6.22 show the normalized fraction oxygen in the heap as a surface plot and lines with constant pressure (isobars) for the two fluxes and 12 month of operation. For an intensive aeration the oxygen concentration at the top was 70% of the oxygen concentration in the inlet. This situation indicates that the oxygen concentration was great enough for allowing a good reaction kinetic. In the other case, with a smaller incoming gas flux, there are places in the heap where the oxygen concentration is almost zero. Therefore, can be expect a greater recovery of copper for a system where there is good aeration, but it does not mean that a greater gas flow is better for the process, for two basic reason: the system could be working in the
constant zone of the Michaelis-Menten kinetic curve, and the cost of the forced aeration system.

Figure 6.21: Surface of normalized fraction oxygen \( \left( X_{O_2g}/X_{O_2g, Inlet} \right) \cdot 100 \), pressure profiles and gas velocity. \( q_2 = 7 \cdot 10^{-5} \left( \text{m}^3 \text{gas} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right) \) for 12 months.

Figure 6.22: Surface of normalized fraction oxygen \( \left( X_{O_2g}/X_{O_2g, Inlet} \right) \cdot 100 \), pressure profiles and gas velocity. \( q_1 = 2.4 \cdot 10^{-6} \left( \text{m}^3 \text{gas} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right) \) for 12 months.
Figure 6.23 shows the copper concentration in liquid and temperature profiles for both fluxes. The copper concentration in the liquid for $q_2 = 7 \cdot 10^{-5} \left( \text{m}^3 \text{gas} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right)$ is almost the same for an equal level at the height heap. This situation occurs because there is a good aeration for any level in the heap, therefore we can expect that the rate of reacted particle is almost the same for a same level in the heap.

Figure 6.23: Cooper Concentration surface and temperature profile for $q_2 = 7 \cdot 10^{-5} \left( \text{m}^3 \text{gas} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right)$ and $q_1 = 2.4 \cdot 10^{-6} \left( \text{m}^3 \text{gas} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right)$ for 12 months.
It is possible to indicate that with low aeration several places where the reaction is too low. In Figure 6.23 it is possible to see the copper concentration in the liquid is higher close to the bottom and around to the centre of the heap. This situation can be explained because the liquid have come through the heap down, warming and becoming rich in copper, in the zone where the availability of oxygen is greater. The temperature is higher close to the aeration channel and the activity of bacteria is better with temperatures close to the \(310\, (K)\). The temperature in the case with good aeration arrived until \(297\, (K)\) and for the bad aeration around \(291\, (K)\).

As was discussed in the one-dimensional transient model, a larger gas flux is not always equivalent to great recovery and good heap performance. In the case of the oxygen concentration in the heap with the aeration flux \(q_2 = 7 \cdot 10^{-5}\, (m^3\, gas \cdot m^{-2} \cdot bed \cdot s^{-1})\) the oxygen in the gas diminished around a 30% between the Inlet and the top of the heap due to the oxidation reaction \(Fe^{2+}/Fe^{3+}\). If we considered a third of this flux, \(q_3 = 2.33 \cdot 10^{-5}\, (m^3\, gas \cdot m^{-2} \cdot bed \cdot s^{-1})\), the concentration in the liquid should be large enough for keeping the lowest oxygen concentration in the liquid around \(3\, ppm\), three times more than \(K_m\). Although it is certain that the recovery will be less, as was shown in Figure 6.15, but the cost of the aeration will be less too. This point is important when the difference between the production cost and sale cost of the metal in the market is narrow.

Therefore, flux \(q_3 = 2.33 \cdot 10^{-5}\, (m^3\, gas \cdot m^{-2} \cdot bed \cdot s^{-1})\) was considered for the next simulations. The normalized fraction of oxygen and the copper concentration are shown in Figure 6.24 and Figure 6.25. Of course the oxygen concentration in the gas will be less, but the copper concentration in the liquid is quite similar for 12 months.
Figure 6.24: Surface of normalized fraction oxygen \( \frac{X_{O_2}}{X_{O_2,\text{inlet}}} \cdot 100 \), pressure profiles and gas velocity. \( q_3 = 2.33 \cdot 10^{-5} \left( \text{m}^3 \text{gas} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right) \) for 12 months.

Figure 6.25: Cooper Concentration surface and temperature profile for \( q_3 = 2.33 \cdot 10^{-5} \left( \text{m}^3 \text{gas} \cdot \text{m}^{-2} \text{bed} \cdot \text{s}^{-1} \right) \) for 12 months.
The normalized oxygen concentration and temperature at four equidistant points between the aeration channel and the top of the heap were considered for a period of 12 months. Figure 6.26 shows the normalized oxygen concentration at 2, 4, 6 and 8 (m). The curves for the different levels have the same shape, but the availability of oxygen close to the aeration channel is greater. In accordance with that the gas goes through of the heap up, it diminishes its oxygen concentration due to the aerobic reactions.

Figure 6.26: Normalized fraction oxygen \( \left( \frac{X_{O_2g}}{X_{O_2g,\text{inlet}}} \right) \times 100 \) for four different heights in the heap for 12 months.

The same test was made for the temperature, considering the same equidistant points and the same period of time. The liquid has come warming itself up through the heap. The temperature increase close to the bottom is greater than the other points in the heap, as shown in Figure 6.27. This situation occurs because in the last portion of the heap the oxygenation is better and temperature is greater.
Figure 6.27: Temperature ($K$) for four different heights in the heap for 12 months.

Figure 6.28 and Figure 6.30 show the fraction of particle reacted for the larger and smaller size, respectively, with $q_g = 2.33 \cdot 10^{-5} \left( m^3 \text{gas} \cdot m^{-2} \text{bed} \cdot s^{-1} \right)$. The reacted particle percentages were, for the size $r_1 = 0.06[m]$ between 3% to 35%, for $r_2 = 0.03[m]$ were between 6% to 65% and for the smaller particle, $r_3 = 0.015[m]$, were between 10% to 96%. The higher fractions of reacted particles are in the middle section of the heap, because in the centre of the heap the aeration is better than, for example, at the sides of the heap. Then for a greater gas flux than $q_g = 2.33 \cdot 10^{-5} \left( m^3 \text{gas} / m^2 \text{bed} \cdot s \right)$ is possible to hope in the heap iso-horizontal lines for the fraction of reacted particle in a function of the height heap, in other words, for some level in the heap it is possible identify a characteristic fraction of particle reacted. This situation occurs because the aeration allows almost the same dissolution rate of the particles at the same height level of the heap, as Figure 6.28 to Figure 6.31 are shown.
Figure 6.28: Surface of normalized fraction oxygen \( \left( \frac{X_{O_2,g}}{X_{O_2,g,\text{inlet}}} \right) \cdot 100 \) and fraction of particle reacted for size \( r_i = 0.06[m] \). \( q_g = 2.33 \cdot 10^{-5} \left( \frac{m^3\text{ gas}}{m^2\text{ bed} \cdot s} \right) \) for 12 months.

Figure 6.29: Surface of normalized fraction oxygen \( \left( \frac{X_{O_2,g}}{X_{O_2,g,\text{inlet}}} \right) \cdot 100 \) and fraction of particle reacted for size \( r_i = 0.06[m] \). \( q_g = 7 \cdot 10^{-5} \left( \frac{m^3\text{ gas}}{m^2\text{ bed} \cdot s} \right) \) for 12 months.
Figure 6.30: Surface of normalized fraction oxygen \( \left( \frac{X_{O_2,g}}{X_{O_2,g,\text{inlet}}} \right) \cdot 100 \) and fraction of particle reacted for size \( r_3 = 0.015[m] \). \( q_g = 2.33 \cdot 10^{-5} \left( m^3 \text{gas/m}^2\text{bed} \cdot s \right) \) for 12 months.

Figure 6.31: Surface of normalized fraction oxygen \( \left( \frac{X_{O_2,g}}{X_{O_2,g,\text{inlet}}} \right) \cdot 100 \) and fraction of particle reacted for size \( r_3 = 0.015[m] \). \( q_g = 7 \cdot 10^{-5} \left( m^3 \text{gas/m}^2\text{bed} \cdot s \right) \) for 12 months.
The simulation, in the first part, has been made for a section of 20\(m\) and with only one channel of aeration in the middle of the heap. The aeration in the heap depends on how is the distribution of the gas flow, then for a lower aeration rate or inappropriate distance between the aeration channels, the requirements of oxygen will not be satisfied. This situation occurs because for a low aeration rate several zones in the heap will have bad or null aeration, and then an important part of the heap will not react, for example the zones between the aeration channels. Then one way for improving this situation is to consider a short aeration distance, because the oxygen distribution at the bottom of the heap will be more homogeneous, therefore the heap performance will be improved, however the installation cost are increased.

Figure 6.32 and Figure 6.33 show a section of the heap of 20\(m\) and two configurations. The first one with aeration channels each 10\(m\) and for the second case with aeration channels each 5\(m\). In the both case the flux rate was
\[ q_3 = 2.33 \cdot 10^{-5} \left( m^3 \text{gas} \cdot m^{-2} \text{bed} \cdot s^{-1} \right) \]

**Figure 6.32:** Surface of normalized fraction oxygen \(X_{O2g}/X_{O2g,Inlet}\) \cdot 100, pressure profiles and gas velocity with channels distance of 10\(m\) for 12 months.
Figure 6.33: Surface of normalized fraction oxygen \( \left( X_{O_2g}/X_{O_2g,\text{Inlet}} \right) \cdot 100 \), pressure profiles and gas velocity with channels distance of 5(m) for 12 months.

Figure 6.34 shows the oxygen concentration between aeration channels at the bottom of the heap. It is possible to see that we have a heap with a long distance, for example 20(m), the oxygen concentration fell down after two months around to 80%, it means that the concentration in the liquid is about 2 ppm. In the other case if we have aeration channels every 10(m) the oxygen concentration in the gas after two months will be between the 40% and 45% of oxygen, then the oxygen concentration in the liquid is 4.5 ppm. now, if we put the channels even more close, 5(m) the oxygen concentration in the gas is between 60% and 70%, for the same period. In this case, the concentration in the liquid is about 6 ppm.
Figure 6.34: Normalized oxygen concentration between the aeration channels for 12 months.

In the 1-D model the distribution of oxygen in the heap was not considered. The 2-D model included this variable. A comparison between a section with only one aeration channel with a great flux and other when we considered to increase the number of channels with a lower flux have been done. Diminishing the distance between the aeration channels allows to obtain a more homogenous oxygen distribution, in other words, the same reaction rate in any level of the heap. Figure 6.35 and Figure 6.36 show the reacted particles for a section of the heap with aeration channels each 5 m. Finally, the appropriate configuration should considerer several mineralogical, operational and economic variables.

It is necessary to indicate that another way for simulating is to take only one aeration channel and, in fact, half of one is enough, but it was considered appropriate to simulate all the section, because of this form is better to compare the three configurations, we keep the same geometry and it is better from a visual point of view.
Figure 6.35: Surface of normalized fraction oxygen \( \left( \frac{X_{O_2 g}}{X_{O_2 g, inlet}} \right) \times 100 \) and fraction of particle reacted for size \( r_j = 0.06[m] \). \( q_g = 2.33 \times 10^{-5} \left( \text{m}^3 \text{gas/m}^2 \text{bed} \cdot \text{s} \right) \) for 12 months.

Figure 6.36: Surface of normalized fraction oxygen \( \left( \frac{X_{O_2 g}}{X_{O_2 g, inlet}} \right) \times 100 \) and fraction of particle reacted for size \( r_j = 0.015[m] \). \( q_g = 2.33 \times 10^{-5} \left( \text{m}^3 \text{gas/m}^2 \text{bed} \cdot \text{s} \right) \) for 12 months.
7. **CONCLUSION**

A model for bioleaching of sulphide minerals of copper in heaps/dumps was developed, which comprises two separated versions: a 1-D transient model and 2-D transient model. The model considers forced aeration and a heap formed by particles of three sizes, where the reaction in the particles is described by the shrinking core model. The 1-D model considers a constant flow of air through the heap and includes equations for the transport of oxygen, dissolved metal (e.g. copper), and ferric ions, and heat transport. One equation for each particle size is also required, which describes the variation of the unreacted core radius with time. For the 2-D model a equation to determine the air flow distribution in the heap has to be included.

The parameters values used in the simulations were taken directly from the literature since the main objective of these simulations was to show the impact of the different parameters on the leach process. Therefore, the exact value of the parameters is not important. The differential equations in the model were solved by using the software Multiphysics® (Comsol).

The versions of the model (1-D and 2-D version) were developed for different applications. The 1-D transient model is a useful tool for describing the impact of the different parameters on the performance of the bioleach process. The main purpose of the 2-D transient model is to show the distribution of the aeration within the heap; to determine the zones with deficient or too much aeration. Moreover the 2-D model may show the distribution of temperature, concentration, and the unreacted core radius in the heap to identify the zones where the reaction is not appropriate and to generate new aeration configurations for optimising the heap performance.

The impact of the forced aeration, temperature and the bacterial activity are shortly highlighted below. Forced aeration has a strong influence on the performance of the heap. Although it is established that forced aeration improve the recovery of copper, the Michaelis-Menten kinetic may limit the impact of the aeration on the generation of ferric ions; larger gas fluxes do not always mean a proportional increase of the copper...
recovery. Similar recoveries of copper may be obtained for increasing gas flux if the concentration de oxygen in the solution is larger than about 5 ppm.

The bacterial activity is a function of the temperature. For the relationship used in this case, the greater bacterial activity is found for temperatures close to $37\, \text{°C}$ and it decreases rapidly if the temperature is higher or lower than that temperature. Therefore, the temperature affects strongly the oxidation rate of the ferrous ions. The temperature of the irrigation solution is raised when it go down through the heap, and since that availability of oxygen is better close to the aeration channels, it is expected that the oxidation reaction was much intensive there. Therefore oxygenation levels and temperature are two fundamental parameters in the process.

A heap or dump is formed by particles of different sizes, which react in different ways during the leach process. As was indicated above, the distribution of particle size was represented by three sizes with a given distribution function. The possibility of finding some average particle size, such that simulations using this average radius had a performance similar to that of the heap with the particle size distribution was addressed. Two average radii were tested. The first one is the “weight average radius” where the weight fraction for each size is used as weighting factor. The second one is the “surface average radius” where the specific surface fraction for each size is used as weighting factor. The simulations show that the performance of the heap can not be determined using an “average radius”, since a heap with a distribution of particle size has a different behaviour. In this thesis, it was considered that the heap was formed by three particle sizes, however, if it is needed the inclusion of one or more additional particle sizes is straightforward.

The distribution of the aeration channels was studied for different distances between channels. For the 10 m-high heaps, three distances were tested: 20, 10, and 5 m. The zones with deficient aeration are, In general, found between the aeration channels. Low oxygen concentration is also found in the upper part of the heap due to oxidation reaction. When the aeration channels are quite separate, the oxygen concentration between them is low, because the air flow is poor in these zones. One of the objectives of the aeration system is to obtain the same reaction rate at a same height. As shown
in the simulations, this may be obtained by increasing the gas flow or by designing an appropriate channel distribution. At the end, the aeration system is an economical decision, which has to consider several factors, such as particle size, type of mineral, number and type of bacteria, heap dimension, and equipment cost.

Several assumptions were made in the conceptual model, which are discussed below. The considered heap is a porous media, and the dispersion was considered just from a conceptual point of view. Probably if we add the expression and/or considerations necessary for estimating the transport of the species through the porous media, the results could be different. Therefore in the future it is necessary to consider experimental data for obtaining a validation of the model and to decide if this assumption is appropriate or not. In the oxygen distribution case, both temperature and composition change and they generate difference in the velocity distribution in the heap during the process. Probably this is an important thing to include in the next research.

The ferrous iron present in the bed was assumed to be in excess in the heap. This is a valid assumption when (1) the mineral contains considerable amount of pyrite, (2) the PLS is recycled to the top of the heap for irrigation, referred to as “intermediate leach solution” or “ILS”, or (3) when the raffinate (barren solution from the SX/EW circuit) is returned to the bioheap for irrigation direct to a SX/EW (solvent extraction/electrowining) circuit. But, if the heap is irrigated with fresh solution, the availability of ferric ions may be poor at the upper part of the heap. Moreover, ferric ions are added on the top of the heap when the leaching solution is recirculated. These aspects are not considered in the model, but if adequate data is available, its inclusion in the model is not difficult.

Some relationship which were used to evaluate the reaction kinetics for ferrous ion oxidation to ferric are somewhat uncertain and they would be evaluated carefully in the future. In the model, the bacterial population was assumed constant during the process. It is known that the concentration of bacteria is a complex function of the conditions prevailing in the heap; temperature, oxygen concentration, tracer elements,
etc. This was not included in the model because the available relationships are too uncertain and would be studied in more detail.

The model does not include the acid balance. One part of the acid come with the irrigation acid solution and the other part is generated from the oxidation of the pyrite. The amount of acid in the system was then considered to be sufficient for obtaining a sufficient low pH as required for the process.
8. REFERENCES

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9. **APPENDIX**.

9.1. **Appendix A: Dimensional Analysis.**

**Chemical equations:**

1. \( \text{Cu}_2\text{S} + 10\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow 10\text{Fe}^{2+} + 2\text{Cu}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ \)
2. \( 4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \)
3. \( \text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \)

**Oxygen consumption**

4. \( R_{O_2} = XV_m \frac{O_{2,t}}{K_m + O_{2,t}} \)

\[
\left[ \frac{\text{kmol Oxygen}}{m^3 \text{ bed} \cdot s} \right] = \left[ \frac{\text{bacteria}}{m^3 \text{ bed}} \right] \cdot \left[ \frac{\text{kmol Oxygen}}{\text{bacteria} \cdot s} \right]
\]

\[
\left[ \frac{\text{kg Oxygen}}{m^3 \text{ gas}} \right] + \left[ \frac{\text{kmol Oxygen}}{m^3 \text{ gas}} \right] + \left[ \frac{\text{kmol Oxygen}}{\text{kg Oxygen}} \right]
\]

5. \( V_m = \frac{1}{M_{O_2}} \frac{6.8 \times 10^{-13} T e^{7000/T}}{1 + e^{236-24,000/T}} \left[ \frac{\text{kmol Oxygen}}{\text{bacteria} \cdot s} \right] \)
Partial pressures.

Note: $1 \text{Pa} = \frac{\text{kg}}{\text{m} \cdot \text{s}^2}$

$1 \text{atm} = 101325 \text{ Pa}$

$1 \text{atm} = 760 \text{ torr}$

6. $P_{N_2} V_g = n_{N_2} RT$

\[
\left[ \frac{\text{kg}}{\text{m} \cdot \text{s}^2} \right] \left[ \text{m}^3 \right] = \left[ \text{kmol} \right] \left[ \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \cdot \text{kmol} \cdot \text{K}} \right] \left[ \text{K} \right]
\]

7. $C_{N_2} = \frac{n_{N_2}}{V_g} = \frac{P_{N_2}}{RT}$

\[
\frac{\text{kmol} \, N_2}{\text{m}^3 \, \text{gas}} = \left[ \frac{\text{kg}}{\text{m} \cdot \text{s}^2} \right] \left[ \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \cdot \text{kmol} \cdot \text{K}} \right] \left[ \text{K} \right]
\]

8. $O_{2,g} = X_{O_{2,g}} C_{N_2} = \frac{n_{O_{2,g}}}{V_g} = \frac{P_{O_2}}{RT}$

\[
\left[ \frac{\text{kmol Oxygen}}{\text{m}^3 \, \text{gas}} \right] = \left[ \frac{\text{kmol} \, O_2}{\text{kmol} \, N_2} \right] \left[ \frac{\text{kmol} \, N_2}{\text{m}^3 \, \text{gas}} \right] = \left[ \frac{\text{kmol} \, O_2}{\text{m}^3 \, \text{gas}} \right] = \left[ \frac{\text{kg}}{\text{s} \cdot \text{m}} \right] \left[ \frac{\text{kg} \, m^2}{\text{s}^2 \cdot \text{kmol} \cdot \text{K}} \right] \left[ \text{K} \right]
\]

9. $\log P_{H_2O} = A - \frac{B}{(T - 273.15)} + C$ (Antoine’s equation)

Note: in the Antoine’s equation the pressure is expressed in $P_{H_2O} [\text{torr}]$, then it is necessary to transform to $[\text{Pa}]$
\[ P_{H_2O} = 10^{\frac{B}{(T-273.15)+C}} \cdot 133.3224 \left( Pa = \frac{kg}{m \cdot s^2} \right) \]

10. \( P = P_{O_2} + P_{N_2} + P_{H_2O} [Pa] \)

11. \( P_{N_2} = \frac{P - P_{H_2O}}{1 + X_{O_{2,s}}} [Pa] \)

12. \( P_{O_2} = \frac{P - P_{H_2O} \cdot X_{O_{2,s}}}{1 + X_{O_{2,s}}} [Pa] \)

13. \( He \left[ \frac{kg \cdot m^2}{s^2 \cdot kmol} \right] = \frac{P_{O_2} \left[ \frac{kg}{m \cdot s^2} \right]}{O_{2,L} \left[ \frac{kmol}{m^3} \right]} \)

**Mass Balance of Oxygen**

\[ \left( \frac{\varepsilon \cdot \frac{RT}{He} + \varepsilon_g}{C_{N_2}} \right) \frac{\partial X_{O_{2,s}}}{\partial t} = \left( \varepsilon_g \cdot D_g + \varepsilon_L \cdot D_L \cdot \frac{RT}{He} \right) C_{N_2} \nabla^2 X_{O_{2,s}} \]

\[ + \left( F_{N_2} - q_L \cdot \frac{RT}{He} \cdot C_{N_2} \right) \nabla X_{O_{2,s}} - R_{O_2} \frac{[kmol Oxygen]}{m^3 \cdot bed \cdot s} \]

\[ \frac{m^3}{s^2 \cdot kmol \cdot K} \cdot \frac{kg \cdot m^2}{m^2 \cdot kg \cdot m^3 \cdot gas} \cdot \frac{kmol N_2}{kmol Oxygen} = \frac{m^3}{s^2 \cdot kmol \cdot m^2 \cdot N_2 \cdot m^3 \cdot s} \frac{kmol Oxygen}{kmol N_2 \cdot s} \]

\[ + \left( \frac{kmol N_2}{m^2 \cdot bed \cdot s} + \frac{m^3 \cdot \text{liquid}}{m^2 \cdot bed \cdot s} \cdot \frac{kmol N_2}{m^3 \cdot gas} \right) \frac{kmol Oxygen}{kmol N_2 \cdot m} = \frac{kmol Oxygen}{m^3 \cdot bed \cdot s} \]

Or:
\[
\frac{\partial X_{O_2,s}}{\partial t} = \left( \varepsilon_g D_g + \varepsilon_L D_L \right) \left( \frac{RT}{R \text{He}} \right) \nabla^2 X_{O_2,s} + \left( \frac{F_{N_2} - q_L}{R \text{He}} \right) \left( \frac{RT}{C_{N_2}} \right) \nabla X_{O_2,s} - \frac{R_{O_2}}{\left( \frac{RT}{R \text{He} + \varepsilon_g} \right) C_{N_2}} \left[ \text{kmol Oxygen} \right] \left[ \text{kmol N}_2 \cdot \text{s} \right]
\]

\[
\left[ \frac{\text{kmol Oxygen}}{\text{kmol N}_2 \cdot \text{s}} \right] = \frac{m^2}{s} \left[ \frac{\text{kmol Oxygen}}{\text{kmol N}_2 \cdot m^2} \right] + \frac{\text{kmol N}_2}{\text{m}^3 \text{bed} \cdot \text{s}} \left[ \frac{\text{kmol Oxygen}}{\text{kmol N}_2} \right] - \frac{\text{kmol Oxygen}}{\text{m}^3 \text{gas} \cdot \text{m}^3 \text{bed}}
\]

15. \[ F_{N_2} = \frac{q_g \cdot \rho_{air} \cdot X_{N_2}}{M_{N_2}} \left[ \frac{\text{kmol N}_2}{\text{m}^3 \text{bed} \cdot \text{s}} \right] \]

\[
\left[ \frac{\text{kmol N}_2}{\text{m}^3 \text{bed} \cdot \text{s}} \right] = \left[ \frac{\text{m}^3 \text{gas}}{\text{m}^3 \text{bed} \cdot \text{s}} \right] \left[ \frac{\text{kg air}}{\text{m}^3 \text{gas}} \right] \left[ \frac{\text{kg N}_2}{\text{kg air}} \right] \left[ \frac{\text{kg N}_2}{\text{kmol N}_2} \right]
\]

**Mass balance of copper.**

16. \[ \varepsilon_L \frac{\partial C_{Cu}}{\partial t} = \varepsilon_L D_L \nabla^2 C_{Cu} - q_L \nabla C_{Cu} + 2R_{Ch} \]

\[
\left[ \frac{\text{m}^3 \text{liquid}}{\text{m}^3 \text{bed}} \right] \left[ \frac{\text{kmol Cu}}{\text{m}^3 \text{liquid} \cdot \text{s}} \right] = \left[ \frac{\text{m}^3 \text{liquid}}{\text{m}^3 \text{bed}} \right] \left[ \frac{\text{m}^2}{\text{s}} \right] \left[ \frac{\text{kmol Cu}}{\text{m}^3 \text{liquid} \cdot \text{m}^2} \right] - \left[ \frac{\text{m}^3 \text{liquid}}{\text{s} \cdot \text{m}^2 \text{bed}} \right] \left[ \frac{\text{kmol Cu}}{\text{m}^3 \text{liquid} \cdot \text{m}} \right] - \left[ \frac{\text{kmol Cu}}{\text{m}^3 \text{bed} \cdot \text{s}} \right]
\]

17. \[ \frac{\text{kg Cu}_2S \text{ unreacted}}{\text{m}^3 \text{bed}} = \frac{4}{3} \pi r_c^3 \cdot G \cdot \rho_p \cdot \varepsilon_s \]

\[
\frac{\text{kg Cu}_2S \text{ unreacted}}{\text{m}^3 \text{bed}} = \left[ \frac{\text{kg Cu}_2S}{\text{kg solid}} \right] \left[ \frac{\text{kg solid}}{\text{m}^3 \text{solid}} \right] \left[ \frac{\text{m}^3 \text{solid}}{\text{m}^3 \text{bed}} \right]
\]
18. \[ R_{Ch} = \frac{dr_c}{dt} \cdot r_c^2 \cdot \frac{3}{R_p^3} \cdot G \cdot \rho_p \cdot \varepsilon_s \cdot \frac{1}{M_{Ch}} \]

\[
\left[ \frac{\text{kmol Cu}_2S}{m^3\text{bed} \cdot s} \right] = \left[ \frac{m}{s} \right] \left[ m^2 \right] \left[ \frac{1}{m^3} \right] \left[ \frac{\text{kg Cu}_2S}{\text{kg solid}} \right] \left[ \frac{\text{kg solid}}{m^3 \text{ solid}} \right] \left[ \frac{m^3 \text{ solid}}{m^3 \text{ bed}} \right] \left[ \frac{\text{kmol Cu}_2S}{\text{kg Cu}_2S} \right]
\]

19. \[ -\frac{dr_c}{dt} = \frac{\sigma C_{Fe^{3+}}}{\rho_M} \cdot \frac{r_c^2}{R_p^2 k_g} + \frac{(R_p - r_c) r_c}{R_p D_{e, \text{ash}}} + \frac{1}{k_x} \]

\[
\left[ \frac{\text{kmol Fe}}{m^3\text{liquid}} \right] = \left[ \frac{m}{s} \right] = \left[ \frac{k\text{mol mineral}}{m^2 \text{ solid}} \right] = \left[ \frac{\text{kmol Fe}}{m^3 \text{ liquid}} \right]
\]

\[
\left[ \frac{m}{s} \right] = \left[ \frac{m^2}{m^2} \right] + \left[ \frac{m \cdot m}{m \cdot s} \right] + \left[ \frac{1}{m^2} \right] = \left[ \frac{k\text{mol mineral}}{m^2 \text{ solid}} \right] \cdot \frac{m}{s}
\]

20. \[ \rho_M = \rho_p \cdot G \cdot \left(1 + mFPY \right) \cdot \frac{1}{M_{Ch}} \]

\[
\left[ \frac{\text{kmol mineral}}{m^3 \text{ solid}} \right] = \left[ \frac{\text{kg solid}}{m^3 \text{ solid}} \right] \left[ \frac{\text{kg Cu}_2S}{\text{kg solid}} \right] \left[ 1 + \frac{\text{kmol Py}}{\text{kmol Cu}_2S} \right] \left[ \frac{\text{kmol Cu}_2S}{\text{kg Cu}_2S} \right] = \left[ \frac{\text{kmol Cu}_2S + \text{kmol Py}}{m^3 \text{ solid}} \right]
\]
Mass balance of Ferric ions.

21. \( \varepsilon_L \frac{\partial C_{Fe^{3+}}}{\partial t} = \varepsilon_L D_L \nabla^2 C_{Fe^{3+}} - q_L \nabla C_{Fe^{3+}} + 4R_O - (10 + 14mFPY)R_{Ch} \left[ \text{kmol Fe}^{3+} \right] \left[ \text{m}^3 \text{bed} \cdot \text{s} \right] \)

\[
\begin{bmatrix}
\text{m}^3 \text{liquid} \\
\text{m}^3 \text{bed}
\end{bmatrix}
\begin{bmatrix}
\text{kmol Fe}^{3+} \\
\text{m}^3 \text{liquid} \cdot \text{s}
\end{bmatrix}
= \begin{bmatrix}
\text{m}^3 \text{liquid} \\
\text{m}^3 \text{bed}
\end{bmatrix}
\begin{bmatrix}
\text{m}^2 \\
\text{kmol Fe}^{3+} \\
\text{m}^3 \text{liquid} \cdot \text{m}^2
\end{bmatrix}
- \begin{bmatrix}
\text{m}^3 \text{liquid} \\
\text{m}^3 \text{bed}
\end{bmatrix}
\begin{bmatrix}
\text{kmol Fe}^{3+} \\
\text{m}^3 \text{liquid} \cdot \text{m}
\end{bmatrix}
- \begin{bmatrix}
\text{m}^3 \text{liquid} \\
\text{m}^3 \text{bed}
\end{bmatrix}
\begin{bmatrix}
\text{kmol Fe}^{3+}
\end{bmatrix}
\]

Energy Balance

22. \( \Delta H_R = \left( \Delta H_{Ch} + FPY \cdot \Delta H_{Py} \right) \cdot M_{Ch} \)

\[
\begin{bmatrix}
\text{kJ} \\
\text{kmol Cu}_2S
\end{bmatrix}
= \begin{bmatrix}
\text{kJ} \\
\text{kg Cu}_2S
\end{bmatrix}
+ \begin{bmatrix}
\text{kJ} \\
\text{kg Cu}_2S
\end{bmatrix}
+ \begin{bmatrix}
\text{kJ} \\
\text{kg Fe}_2S
\end{bmatrix}
\cdot \begin{bmatrix}
\text{kg Cu}_2S \\
\text{kmol Cu}_2S
\end{bmatrix}
\]

23. \( \Delta H_S = \left( 2 \cdot M_{CuSO_4} \cdot \Delta H_{CuSO_4, solution} + mFPY \cdot M_{FeSO_4} \cdot \Delta H_{FeSO_4, solution} \right) \)

Note: \(- R_{Ch} = 2 \cdot R_{CuSO_4, solution} \) and \(- R_{Py} = R_{FeSO_4, solution} \)

\[
\begin{bmatrix}
\text{kJ} \\
\text{kmol Cu}_2S
\end{bmatrix}
= \begin{bmatrix}
2 \cdot \text{kg CuSO}_4 \\
\text{kmol CuSO}_4
\end{bmatrix}
+ \begin{bmatrix}
\text{kJ} \\
\text{kg Fe}_2S
\end{bmatrix}
\cdot \begin{bmatrix}
1 \cdot \text{kg FeSO}_4 \\
\text{kmol FeSO}_4
\end{bmatrix}
\]

\[
\begin{bmatrix}
\text{kJ} \\
\text{kmol Cu}_2S
\end{bmatrix}
= \begin{bmatrix}
\text{kJ} \\
\text{kmol Cu}_2S
\end{bmatrix}
+ \begin{bmatrix}
\text{kJ} \\
\text{kmol Fe}_2S
\end{bmatrix}
\cdot \begin{bmatrix}
\text{kJ} \\
\text{kmol Fe}_2S
\end{bmatrix}
\]

24. \( H_L = C_{p,L} \left( T - T_{ref} \right) \)

\[
\begin{bmatrix}
\text{kJ} \\
\text{kg liquid}
\end{bmatrix}
= \begin{bmatrix}
\text{kJ} \\
\text{kg liquid} \cdot K
\end{bmatrix} \cdot K
\]
25. \[ P_{N_2} V_g = n_{N_2} RT \]

\[
\left[ \frac{kg}{m \cdot s^2} \right] \left[ m^3 \right] = \left[ kmol \right] \left[ \frac{kg \cdot m^2}{s^2 \cdot kmol \cdot K} \right] [K]
\]

26. \[ C_{N_2} = \frac{n_{N_2}}{V_g} = \frac{P_{N_2}}{RT} \]

\[
\frac{kmol N_2}{m^3 \text{ gas}} = \frac{\left[ \frac{kg}{m \cdot s^2} \right]}{\left[ \frac{kg \cdot m^2}{s^2 \cdot kmol \cdot K} \right]} [K]
\]

27. \[ O_{2,g} = X_{O_2,g} C_{N_2} = \frac{n_{O_2,s}}{V_g} = \frac{P_{O_2}}{RT} \]

\[
\left[ \frac{kmol \text{ Oxygen}}{m^3 \text{ gas}} \right] = \left[ \frac{kmol O_2}{kmol N_2} \right] \left[ \frac{kmol N_2}{m^3 \text{ gas}} \right] = \left[ \frac{kmol O_2}{m^3 \text{ gas}} \right] = \frac{\left[ \frac{kg}{s^2 \cdot m} \right]}{\left[ \frac{kg \cdot m^2}{s^2 \cdot kmol \cdot K} \right]} [K]
\]

28. \[ H_2O_{\text{sap}} = X_{H_2O, \text{sap}} C_{N_2} = \frac{n_{H_2O_{\text{sap}}}}{V_g} = \frac{P_{H_2O_{\text{sap}}}}{RT} \quad \text{and} \quad \frac{P_{H_2O_{\text{sap}}}}{P_{N_2}} = X_{H_2O_{\text{sap}}} \]

\[
\left[ \frac{kmol H_2O}{m^3 \text{ gas}} \right] = \left[ \frac{kmol H_2O}{kmol N_2} \right] \left[ \frac{kmol N_2}{m^3 \text{ gas}} \right] = \left[ \frac{kmol H_2O}{m^3 \text{ gas}} \right] = \frac{\left[ \frac{kg}{s^2 \cdot m} \right]}{\left[ \frac{kg \cdot m^2}{s^2 \cdot kmol \cdot K} \right]} [K]
\]

29. \[ F_{O_2} = O_{2,g} \cdot F_{N_2} \left[ \frac{kmol O_2}{m^2 \text{ bed} \cdot s} \right] \]

\[
\left[ \frac{kmol O_2}{m^2 \text{ bed} \cdot s} \right] = \left[ \frac{kmol O_2}{kmol N_2} \right] \cdot \left[ \frac{kmol N_2}{m^2 \text{ bed} \cdot s} \right]
\]
30. \[ F_{H_2O} = H_2O_{\text{vap}} \cdot F_{N_2} \]

\[
\begin{bmatrix}
\text{kmol } H_2O \\
m^2 \text{bed} \cdot s
\end{bmatrix} = \begin{bmatrix}
\text{kmol } H_2O \\
\text{kmol } N_2
\end{bmatrix} \cdot \begin{bmatrix}
\text{kmol } N_2 \\
m^2 \text{bed} \cdot s
\end{bmatrix}
\]

31. \[ H_g = \Delta H_{\text{vap, } H_2O} \cdot X_{H_2O_{\text{vap}}} \cdot M_{H_2O} + \left( C_{p,H_2O_{\text{vap}}} \cdot X_{H_2O_{\text{vap}}} \cdot M_{H_2O} + C_{p,g} \left( X_{O_2} \cdot M_{O_2} + M_{N_2} \right) \right) (T - T_{\text{ref}}) \]

\[
\begin{bmatrix}
kJ \\
\text{kmol } N_2
\end{bmatrix} = \begin{bmatrix}
kJ \\
kg \text{ } H_2O
\end{bmatrix} \cdot \begin{bmatrix}
\text{kmol } H_2O \\
\text{kg } \text{H}_2O
\end{bmatrix} + \begin{bmatrix}
kJ \\
\text{kg gas} \cdot K
\end{bmatrix} \cdot \begin{bmatrix}
\text{kmol } O_2 \\
\text{kg } O_2
\end{bmatrix} + \begin{bmatrix}
kJ \\
\text{kg } N_2
\end{bmatrix}
\]

32. \[ \rho_s C_{p,B} \frac{\partial T}{\partial t} = k_B \nabla^2 T - \rho_l \cdot q_l \cdot \nabla H_l + F_{N_2} \cdot \nabla H_g - (\Delta H_R + \Delta H_S) \cdot R_{ch} \begin{bmatrix}
kJ \\
m^2 \text{bed} \cdot s
\end{bmatrix} \]

\[
\begin{bmatrix}
\text{kg bed} \\
m^3 \text{bed}
\end{bmatrix} \cdot \begin{bmatrix}
kJ \\
\text{kg bed} \cdot s \cdot K
\end{bmatrix} = \begin{bmatrix}
kJ \\
m^2 \text{bed} \cdot s \cdot K
\end{bmatrix} + \begin{bmatrix}
kJ \\
\text{kg liquid} \cdot m \text{liquid}
\end{bmatrix} + \begin{bmatrix}
kJ \\
\text{kg liquid} \cdot m
\end{bmatrix}
\]

\[
\begin{bmatrix}
\text{kmol } Cu_2S \\
m^2 \text{bed} \cdot s
\end{bmatrix} = \begin{bmatrix}
\text{kmol } Cu_2S \\
m^3 \text{ solid}
\end{bmatrix}
\]

**Unreacted core model with respect to the mol dissolution rate.**

33. \[ n_{ch} = \frac{4}{3} \pi r_c^3 \rho_m \]

\[
\begin{bmatrix}
\text{kmol } Cu_2S \\
m^3 \text{ solid}
\end{bmatrix} = \begin{bmatrix}
\text{kmol } Cu_2S \\
m^3 \text{ solid}
\end{bmatrix}
\]
34. \[ r_c = \sqrt[3]{\frac{3 \cdot n_{ch}}{4 \pi \rho_M}} \]

\[ [m] = \sqrt[3]{\frac{[\text{kmol Cu}_2S]}{[\text{kmol Cu}_2S]}} \quad \frac{[m^3 \text{ solid}]}{[m^3 \text{ solid}]} \]

35. \[ \frac{dn_{ch}}{dt} = S \cdot \rho_M \cdot \frac{dr_c}{dt} \]

\[ \frac{[\text{kmol Cu}_2S]}{s} = \left[ \frac{m^2}{[m^2]} \right] \cdot \left[ \frac{\text{kmol Cu}_2S}{m^3 \text{ solid}} \right] \cdot \left[ \frac{m}{s} \right] \]

36. \[ R_{ch} = -\frac{dn_{ch}}{dt} \cdot \frac{1}{S \cdot \rho_M} \cdot r_c^2 \cdot \frac{3}{R_p^5} \cdot \varepsilon_s \cdot G \cdot \rho_p \cdot \frac{1}{M_{ch}} \left[ \frac{\text{kmol Cu}_2S}{m^3 \text{ bed} \cdot s} \right] \]

\[ R_{ch} = -\frac{dn_{ch}}{dt} \cdot \frac{3 \cdot r_c^2 \cdot \varepsilon_s}{4 \cdot \pi \cdot (1 + mFPY) \cdot R_p^5} \]

\[ \left[ \frac{\text{kmol Cu}_2S}{m^3 \text{ bed} \cdot s} \right] = \left[ \frac{\text{kmol Cu}_2S}{s} \right] \cdot \left[ \frac{1}{m^3 \text{ solid}} \right] \cdot \left[ \frac{m^3 \text{ solid}}{m^3 \text{ bed}} \right] \]
## 9.2. Appendix B: Model parameters for transient models.

Table 11: Model parameters for transient models.

### Latin letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Reference</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Perry’s Chemical Engineers Handbook</td>
<td>8.07131</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$B$</td>
<td>Perry’s Chemical Engineers Handbook</td>
<td>1730.630</td>
<td>Dimensionless</td>
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<td>$C$</td>
<td>Perry’s Chemical Engineers Handbook</td>
<td>233.426</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$C_{p,B}$</td>
<td>Sidborn, 2000</td>
<td>1.5 $,(kJ/kg\ text{\ bed}\cdot K)$</td>
<td></td>
</tr>
<tr>
<td>$C_{p,L}$</td>
<td>Sidborn, 2000</td>
<td>4.0 $,(kJ/kg\ liquid\cdot K)$</td>
<td></td>
</tr>
<tr>
<td>$C_{p,g}$</td>
<td>Sidborn, 2000</td>
<td>1.0 $,(kJ/kg\ gas\cdot K)$</td>
<td></td>
</tr>
<tr>
<td>$C_{p,vap}$</td>
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<td>1.864 $,(kJ/kg\ vapor\ water\cdot K)$</td>
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</tr>
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<td>$D_e$</td>
<td>Leahy et al., 2005</td>
<td>$9.5\cdot10^{-11}$ $,(m^2/s)$</td>
<td></td>
</tr>
<tr>
<td>$D_L$</td>
<td>Sidborn, 2000</td>
<td>$1.157\cdot10^{-6}$ $,(m^2/s)$</td>
<td></td>
</tr>
<tr>
<td>$FPY$</td>
<td>Sidborn and Moreno, 2005</td>
<td>2 $, (kg\ Pyrite/kg\ Chalcocite)$</td>
<td></td>
</tr>
<tr>
<td>$f_{31}$</td>
<td>Estimated</td>
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</tr>
<tr>
<td>$f_{32}$</td>
<td>Estimated</td>
<td>0.6</td>
<td>Dimensionless</td>
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<tr>
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<td>Estimated</td>
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<tr>
<td>$G$</td>
<td>Estimated</td>
<td>0.0063 $, (kg\ Cu_2S/kg\ solid)$</td>
<td></td>
</tr>
<tr>
<td>$H$</td>
<td>Estimated</td>
<td>10 $, (m)$</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_{Ch}$</td>
<td>Sidborn, 2000</td>
<td>-5917.0 $, (kJ/kg\ Cu_2S)$</td>
<td></td>
</tr>
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<td>$\Delta H_{Py}$</td>
<td>Sidborn, 2000</td>
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<td></td>
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<td>Parameter</td>
<td>Source</td>
<td>Value</td>
<td>Unit</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------------</td>
<td>-------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>$\Delta H_{\text{CuSO}_4\text{,solution}}$</td>
<td>Sidborn, 2000</td>
<td>417.0</td>
<td>(kJ/kg CuSO₄)</td>
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**Greek letters**

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Appendix D: One-dimensional transient model charts.

Figure 9.1: Ferric Ions Concentration, Size: 0.06 [m]

Figure 9.2: Ferric Ions Concentration, Size: 0.03 [m]
Figure 9.3: Ferric Ions Concentration, Size: 0.015 [m]

Figure 9.4: Unreacted Core Radius, Size: 0.06 [m]
Figure 9.5: Unreacted Core Radius, Size: 0.03 [m]

Figure 9.6: Unreacted Core Radius, Size: 0.015 [m]
1-D and 2-D Transient models for bioleaching of sulphide minerals of copper in heaps/dumps were developed for a bed with forced aeration and a heap formed by three particles sizes. Equations for the transport of oxygen, mass balance for copper and ferric ions, and heat transport were considered. The reaction in the particles was described by the shrinking core model.

The main purpose of this research is to show the impact of the different parameters on the leach process, to identify the zones where the aeration is not appropriate and to
generate new aeration configurations. The objective of the aeration system is to obtain the same reaction rate at a same height. This may be obtained by increasing the gas flow or by designing an appropriate channel distribution. At the end the aeration system is an economical decision, which has to consider several factors, such as particle size, type of mineral, number and type of bacteria, heap dimension, and equipment cost.

In addition that the possibility to find some “average radius” that represents a heap with a distribution of particle size also was studied. Two average radii were tested. Three different sizes with a given distribution function were considered. The first one is the “weight average radius” where the weight fraction for each size is used as weighting factor. The second one is the “surface average radius” where the specific surface fraction for each size is used as weighting factor. The simulations show that it is not possible find such average radius. This means that the performance of the heap can not be determined using an “average radius”, therefore a distribution of particle sizes has to be used.