UNDERSTANDING THE HEAP BIOOXIDATION OF SULFIDIC REFRACTORY GOLD ORES

by

SYLVIE C. BOUFFARD

B.Eng., Ecole Polytechnique de Montreal, 1996
M.A.Sc., The University of British Columbia, 1998

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Department of Metals and Materials Engineering

The University of British Columbia
Vancouver, Canada

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Abstract

An investigation has been conducted into the nature and rates of the physical, chemical, biological, and thermal processes involved in the heap biooxidation of pyrite from refractory gold ores. A heap-scale model of the *ideal* process was developed, aided by a systematic experimental approach, which accounts for the following phenomena.

**Grain-Scale Kinetics** – The thermal and chemical functionals driving the oxidation kinetics of the pyritic ore sample were modeled from batch, potentiostatic stirred-tank leaching tests using a pyrite concentrate prepared by flotation from the bulk ore.

**Particle-Scale Kinetics** – The influence of diverse pyrite occurrences within ore particles classified into six size fractions were quantified from isothermal, potentiostatic, upflow, packed bed experiments.

**Bacterial Kinetics and Dynamics** – Substrate (ferrous ions or elemental sulfur) oxidation and growth of iron- and sulfur-oxidizing cells were modeled over three specific temperature ranges with a dual, limiting-substrate Monod expression, coupled with temperature-dependent death rates. Reversible attachment of a predominantly attached population with few planktonic cells was modeled using a Langmuir isotherm. Biological parameters were either measured or estimated from small and large column leaching data, and were found to be in good agreement with published values.

**Solute Dynamics** – The backbone structure of the heap model was represented as stagnant pores of uniform or variable lengths, which are connected at one end to plug flow channels, and which are also in intimate contact with a uniformly distributed gas stream. Volumetric proportions of solid, liquid, and gas were measured in unsaturated columns under several conditions (binder addition,
agglomeration, particle size, column height, irrigation rate). Pore lengths were estimated from tracer residence time distribution curves.

**Heat Model** – A published heat model, comprised of heat conduction, generation, and advection by liquid, dry air, and vapor, coupled with climatically-dependent boundary conditions, was grafted onto the main model framework.

These elements were integrated into an unsteady-state system of non-linear partial differential equations, solved numerically with an explicit approach for chemical and biological reaction rates, and implicit finite difference approximations for concentrations.

Small and large column tests were performed with the same pyritic ore to estimate unknown biological parameters, to validate the model at the small scale, and to ascertain the influence of several operating factors on depth and lateral profiles of conversion (pyrite and elemental sulfur), concentrations, and temperature. Excellent fits of several types of leaching indicators reveal the rate-limiting step to shift from particle kinetics to oxygen gas-liquid mass transfer with increasing temperatures, particle kinetics, and head grade, as well as decreasing mass transfer coefficient. According to the model simulations, large pellets made up of rapidly-oxidizable pyrite leach zone-wise as a result of the rapid consumption of oxygen in meager concentrations within the pellet pores. Shorter heaps and large irrigation and aeration rates are suitable conditions for homogeneous leaching in heaps, and for avoiding temperature segregation and the establishment of overheated dead zones.
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Chapter 1

Introduction

1.1 Problem Definition

Rapid depletion of free-milling gold ores worldwide has forced the mining industry to turn to refractory gold deposits. Cyanide gold leaching of these “difficult to treat” ores gives unacceptably low gold recovery or is uneconomic for one or more of the following reasons [1]:

- Large quantities of reagents are consumed when gold occurs in the presence of minerals such as pyrrhotite and arsenopyrite.
- Carbonaceous materials present in gold ores may adsorb gold during leaching.
- Gold locked into oxidizable sulfide minerals cannot be adequately liberated, even by fine grinding.

Over the last several years, advances have been made toward the leaching of gold from many different types of refractory ores. In the treatment of ores containing deleterious carbonaceous components, the use of chlorine during leaching may
passivate the active surface of the carbonaceous matter, prevent gold adsorption, or, alternatively, destroy it entirely, as would roasting [1]. Thiosulfate and thiourea leaching [2], as well as resin–in–leach (e.g. the Penjom Process [3]), also hold much promise for the efficient recovery of gold from certain carbonaceous and copper–bearing ores. Recently, even direct bioleaching of gold appears to show promise for boosting recovery from tailings and ores [4].

However, sulfidic refractory gold ores are another matter entirely. In order to recover gold from these minerals, the sulfide lattice must first be broken down oxidatively [1]. A relatively large amount of sulfides (typically several weight percent) must be reacted with oxygen in order to render a very tiny quantity (typically a few grams per tonne) of gold amenable to cyanidation.

Extensive laboratory and pilot scale campaigns (e.g. BIOX® and MINBAC™ agitated bioreactors) have demonstrated the ability of iron– and sulfur–oxidizing microorganisms to catalyze the oxidation of sulfide minerals encapsulating finely disseminated gold particles [5,6]. Bioleaching is rapidly gaining acceptance alongside the more established pressure oxidation and roasting processes. Low capital investment, environmental friendliness, and minimal personnel and maintenance requirements are just a few of the advantages offered by bioleaching technologies. However, the aeration requirements and the ore value do not always justify the high capital and operating costs of stirred tanks. Hence, heap biooxidation may be a preferred technology for pretreating low-grade refractory gold ores.

A refractory gold ore heap is a shallow (3–15 m high, typically 6 m) pile stacked with pyritic and/or arsenopyritic ore, previously agglomerated or not, and operated under unsaturated flow conditions (Figure 1.1). The lixiviant solution carrying the reagents (ferric ions, sulfuric acid, microbes) enters at the top of the heap and percolates through the interstices of the ore particles. Reagents transfer from the bulk solution in the stagnant liquid held between agglomerates, and diffuse into the pores and fissures of the ore particles. There, they react with sulfide grains to

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generate ferrous ions, sulfuric acid, elemental sulfur, and heat, according to the following stoichiometric equations (Table 1.1).

Figure 1.1 Schematic diagram of a heap (Reproduced with permission from [7]).

Table 1.1 Chemical and biological reactions in heap leaching of pyritic and arsenopyritic refractory gold ores.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical</td>
<td>Pyrite: $\text{FeS}_2 + 2(6y+1) \text{Fe}^{3+} + (8y) \text{H}_2\text{O} \rightarrow 3(4y+1) \text{Fe}^{2+} + (2y) \text{SO}_4^{2-} + 2(1-y) \text{S}^0 + (16y) \text{H}^+ \text{ where } y \text{ is the sulfate yield}$</td>
</tr>
</tbody>
</table>

Arsenopyrite: $2 \text{FeAsS} + 2(6y+5) \text{Fe}^{3+} + 2(4y+3) \text{H}_2\text{O} \rightarrow 12(y+1) \text{Fe}^{2+} + (2y) \text{SO}_4^{2-} + 2(1-y) \text{S}^0 + 2 \text{H}_3\text{AsO}_3 + 2(8y+3) \text{H}^+$

Bio/Electrochemical       | $4 \text{Fe}^{2+} + 4 \text{H}^+ + \text{O}_2 \rightarrow 4 \text{Fe}^{3+} + 2 \text{H}_2\text{O}$                                                                 |

$\text{H}_3\text{AsO}_3 + 2 \text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + 2 \text{Fe}^{2+} + 2 \text{H}^+$

Biochemical               | $\text{S}^0 + \text{H}_2\text{O} + 3/2 \text{O}_2 \rightarrow \text{H}_2\text{SO}_4$                                                                 |

Chemical                  | Jarosite: $3 \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + \text{M}^+ + \text{H}_2\text{O} \rightarrow \text{MFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6 \text{H}^+$ where $\text{M}$ stands for $\text{K}^+$, $\text{Na}^+$, $\text{NH}_4^+$, $\text{Ag}^+$, $\text{V}_2\text{Pb}^{2+}$ and/or $\text{H}_3\text{O}^+$ |

Scorodite: $\text{Fe}^{3+} + \text{H}_3\text{AsO}_4 + 2 \text{H}_2\text{O} \rightarrow \text{FeAsO}_4.\text{H}_2\text{O} + 3 \text{H}^+$

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As microbes begin to attach and grow on ore surfaces via the assimilation of an inorganic carbon source (typically carbon dioxide), they catalyze the oxidation of ferrous to ferric ions using oxygen as an oxidant, thereby sustaining the high oxidation potentials required to break down the sulfide minerals. Whether microbes also catalyze the direct oxidation of sulfide minerals by molecular oxygen is still the subject of debate in the scientific community (e.g. [8]). Depending on the pH, excess ferric ions may form jarosite \((\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6)\) and scorodite \((\text{FeAsO}_4.2\text{H}_2\text{O})\) precipitates that deposit within the pores and interstices of the ore particles, possibly impeding diffusion and solution flow. The iron-rich lixiviant solution collected at the bottom of the heap may be neutralized before being recirculated back to the top of the heap. The major steps in the heap bioleaching process are thus the *advection* of lixiviant solution downward through the heap, the *advection* of air upward through the heap, the *diffusion* of reagents to the reaction sites, and the *chemical* and *biological reactions* at those sites.

When the desired degree of sulfide oxidation is achieved, the biooxidized ore is washed to eliminate the residual acidity and possible cyanicides. The heap is finally rinsed with a lime (or limestone) solution before the newly liberated gold is leached with a cyanide, thiosulfate, or thiourea solution. Alternatively, the heap is dismantled, and the ore is subsequently neutralized with lime or limestone, and either re-agglomerated and re-stacked for heap cyanidation, or else, milled and fed to a conventional tank cyanidation circuit.

Unlike secondary copper sulfide heap bioleaching, heap biooxidation of refractory gold ores is still a technology in its infancy. Over the past twelve years, Newmont Mining Corporation, under the technical direction of Dr. James A. Brierley, has led the way to the first commercial scale operation which began production in early 2000 at the Quarry mine in Carlin, NV. Although the progress of Newmont’s laboratory, pilot and full scale testing program has been well publicized, the research status of other companies following similar pursuits has rarely been disclosed. Those that have include the Zlata Mine in Bulgaria, Brohm Mining’s Gilt
This author has recently submitted a comprehensive literature review on the state of the art of heap biooxidation of refractory gold ores [9]. Forty papers describing small and large scale testwork, as well as modeling simulations, were analyzed to shed light on the nature of the physical, chemical and biological heap phenomena, and to explain tentatively why this technology has consistently suffered from lower than anticipated sulfide oxidation rates. Excerpts of this manuscript included in appendix A present the fine points of these research studies.

The review has demonstrated that most, if not all, column leaching experiments and heap pilot tests have determined primarily the improvement in gold recovery from ores with different physical, chemical, and mineralogical properties. For instance, biooxidation tests were performed by Burbank et al. [10] to improve the gold extractability from Carlin-type siliceous refractory sulfidic gold ores. These authors did not describe the mineralogy of the five ores tested, nor even comment on the differences in gold recovery observed from different samples.

Furthermore, even if there existed a common attribute between the studies carried out independently by different research organizations, the fact that key information (sulfide oxidation profiles with depth, oxygen concentration in the gas pore space, cell number profiles, temperature, etc.) was missing would still hinder the analysis of the data from these studies. For instance, both suspended (planktonic) and attached cells are rarely enumerated. However, the research work of Groudev and co-workers [11] has proven that the attached population far exceeds the planktonic population. Thus, modeling the microbiology of heap biooxidation processes with a prime focus on the suspended cell population may be misleading. It is imperative that the large capital and operating costs associated with conducting such studies be economically justified by careful planning, proper column design, and diligent monitoring in order to determine the extent of sulfide oxidation and cell activity.
Certainly, easily controllable operating parameters, including particle size [12,13], liquid flow rate [14,15], air flow rate [16], solution composition [15], agglomeration [15], and irrigation cycle time [12,15], have been tested in columns. As well, occasional pilot heap projects employing an agglomeration process similar to the patents of either Newmont Mining Company [17-21], GeoBiotics Inc. [22-24], or Echo Bay Mines [25] have been reported. These trials yielded mixed results, sometimes contrary to intuition [12], inconclusive evidence, and unvalidated biological model fits [26]. Furthermore, the selection of experimental conditions has also not been representative of typical heap leaching operations. That most column tests are conducted under uncontrolled conditions (changes in irrigation cycle time, solution composition, heating power during an experiment) further complicates the validation of deterministic models.

Despite the variability among the tests performed, a common theme has emerged. Pyrite and arsenopyrite heap biooxidation is very slow, requiring as long as 200 days to eliminate merely 35% of the sulfide matrix of low-grade ores grading typically less than 3% sulfide sulfur. Is this a fact that the industry must live with, or are there barriers that have yet to be overcome?

First, almost half of the studies reviewed were performed in non-aerated ore beds, for which models of oxygen diffusion in heaps [27] have been proposed by the research team of Dr. Robert Bartlett at the College of Mines and Earth Resources, University of Idaho, and later validated by this author using the oxidation data of Groudev and co-workers [11]. Furthermore, several heap biooxidation projects were performed by Newmont Gold Company and Newmont Mining Corporation in non-aerated heaps using the inoculation/agglomeration method described in Newmont's US patent 5,246,486, amended in 1998 to US patent 5,834,294, and generalized in 2002 to US patent 6,383,458 [28-30]. Briefly, the technology consists of forming particulates by mixing ore particles, fines, and clayey minerals with an inoculum comprising bacteria, and optionally, with an acid-resistant polymer. Newmont claimed that, in addition to agglomerating fines onto coarser particles, the single agglomeration/inoculation operation ensures a more uniform colonization of the ore surface by active microbes, shortens the lag phase, and
speeds up the oxidation. Over the course of a few years, heap operations were scaled up from 430 to 25,900 to 800,000 tonnes of ore. The biggest heap yielded only 35% of the sulfide minerals oxidized from siliceous ores after 180 to 240 days, and only 28% from the carbonaceous ores after 160 days [19].

Yet, it is undeniable that aerobic microbes require both oxygen and carbon dioxide for growth. The mere 0.03% carbon dioxide in air may still prove to be insufficient to sustain the rapid growth of autotrophic bacteria during the colonization stage. The issue of carbon dioxide supply has certainly not been addressed in the literature for pyritic ores. Whether carbon dioxide will in fact be the limiting substrate depends on the nature of the sulfide minerals and their topological particle leaching kinetics (not to be confused with grain kinetics), the interfacial gas/liquid mass transfer rate, the leaching environment (especially the temperature and potential), and the diffusion resistance through the pores of agglomerates and ore particles. It is worth noting, however, that the inorganic carbon demand might fluctuate as the dynamics of the system change.

What's more, very few experiments with aeration have ever been performed beyond the traditional laboratory scale columns, with the exception of Newmont's large-scale heap in 1996, and more recently, its $8-million bioleaching/biomilling facility handling 4.2 million tonnes annually [31]. The process is identical in all respects to Newmont's patented biooxidation technology, except that agglomerates spend only 100–150 days on the leach pad. The ore grading 1.8–2.0 wt% sulfide sulfur was crushed to less than 12.5 mm, agglomerated with mesophiles and moderate thermophiles, and placed onto three aerated pads, each 145 m wide, 308 m long, and 9 m high [20]. Zones located 1.5 m above the ground saw their temperature increase from 16 to 49°C one month after start-up. This persuaded the operators to reinoculate the pads with extreme thermophiles. Temperatures fluctuated between 32 and 60°C thereafter. On the other hand, the potential of the feed and leachate solutions remained constant at only about 470 mV vs Ag/AgCl. The project, which went into production in early 2000, had produced 66,000 oz of gold by year-end.

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Despite their simplicity of construction and operation, column tests suffer from high heat losses. The heat generated by the sulfide oxidation reactions is dissipated rapidly to the surroundings, and thus the bed temperature remains near ambient, unless, of course, external devices (heating tape, water jackets) are employed to supply heat and to control the bed temperature. Even if the supplies of oxygen and carbon dioxide were far in excess of the biological needs, mass transfer through the gas/liquid film may not be fast enough to maintain the highest possible growth rates. A review of the literature on trickle bed reactors [32] points to the need to evaluate solid/liquid and gas/liquid mass transfer coefficients in unsaturated beds operated under the conditions of liquid and gas flow rates typical of heaps. The mere 8 mg/L of oxygen dissolved in water at ambient temperature, and even lower concentrations at higher temperatures and in the presence of electrolytes, could prove to be critical, especially in heaps with high sulfide grades.

Very little insight about the influence of temperature on leaching kinetics was gained from those few column tests carried out with proper temperature control and aeration. The results from isothermal column tests carried out by Newmont researchers at 5, 10, and 20–24°C were predictable and of interest to sites located in colder climates or at higher altitudes [33]. An interesting testwork project was conducted in the mid-1990s by Cambior Inc. in collaboration with Little Bear Laboratories Inc. to determine the feasibility of heap biooxidizing intrusive and sedimentary refractory pyritic ore (2.6–8.9 wt% sulfide sulfur) originating from the Metates gold and silver deposit in northwestern Durango State, Mexico [34, 35]. The authors did not comment on the atypical potential profile, the formation of gypsum, the large variations among replicate tests, and ultimately the reasons why the 50 and 65°C columns leached more rapidly than the 25°C tests.

Temperature could indeed play a crucial role in heap biooxidation of pyritic ores. In light of the Arrhenius activation energy of pyrite oxidation (50–90 kJ/mole) published in the literature (references available in chapter 4), increasing the temperature from 25 to 45°C would roughly quadruple the oxidation rate. Microbes would then have to keep up by supplying ferric ions to sustain the higher chemical oxidation rates. Yet, the correct microorganisms, whether mesophiles (≈ 15–40°C),
moderate thermophiles (\(\approx 35-55^\circ\text{C}\)), and/or extreme thermophiles (\(\approx 55-80^\circ\text{C}\)) [36], must be present when most needed, thus the possible need to maintain a stock of inoculum on stand-by for future re-inoculation.

Despite the fact that the performance (i.e. sulfide oxidation rates) of large scale sulfidic refractory gold ore heaps has usually not met expectations, every possible resource has not yet been exhausted, or even explored. Obviously, heap biooxidation is a complex process, which requires the understanding of many interrelated phenomena, including bulk mass and heat transport, microbial growth, pore diffusion, oxidation kinetics, and hydrolysis reactions. To date, few investigators have attempted to model the process, with mixed results. Cathles and Schlitt [37] derived a model to predict the rate of copper dump leaching from porphyry copper mine waste. The model assumed the temperature-driven natural convection of oxygen to be rate limiting, and assumed diffusion controlled kinetics for chalcopyrite and pyrite oxidation. Solution chemistry, solution transport, and cell dynamics were completely ignored. Validation tests in large columns and a test dump were inconclusive. The models of Pantelis and Ritchie [38] and Casas et al. [39] are similar to the model of Cathles and Schlitt [37], the former employing a more realistic dump geometry, and the latter incorporating Monod kinetics for microbial growth. Neither has been validated with experimental data. None of these models is relevant when air is supplied to the base of heaps by low-pressure blowers, as has become common practice in the copper industry. Having overcome the oxygen diffusion and convection limitations, the flow and transport equations that define the rate at which solutes travel through the bed interstices, exchange across phase boundaries, and diffuse through water-filled pores should now constitute the backbone of any heap leaching model. The model of Liddell and Bautista [40] is strictly a solution speciation and precipitation model that ignores all transport, kinetic, and microbial considerations. Of the five, only the model of Harrington et al. [41] relates specifically to heap biooxidation of refractory gold ores. Using an intrinsic pyrite leaching rate expression from the literature and a measured sulfide grain size distribution, the authors found good agreement between the four experimental gold extraction data points and the model predictions. The gold extractability of the

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entire ore mass was predicted by the extent of oxidation of the individual sulfide grains undergoing leaching in a 1.2-m tall column intermittently aerated. This particle-scale shrinking-core leaching model ignores all heap-scale mass and heat transport, chemical, and biological phenomena. It considers the column as a “black box”.

Hence, for all intents and purposes, the hydrometallurgical community remains without a critical tool with which to interpret pilot-scale data, make intelligent design decisions about design and operating parameters, or diagnose existing heap biooxidation operations. The somewhat disappointing performance after a decade of laboratory, pilot, and full scale testing has hampered, in part, the successful commercialization of heaps for pretreating refractory gold ores. The lack of understanding and engineering expertise may even be preventing the wholesale adoption of a very promising technology.

1.2 Objectives

Careful testing and comprehensive customized process modeling is crucial in order to demystify the multiple chemical and biological phenomena occurring within, and ultimately to provide sound engineering principles for all heap leaching operations. What is needed from a model of this process, and what is lacking in those models discussed above, is the ability to:

- Forecast with relative accuracy the extent of oxidation during the course of the operation and throughout the heap;
- Design cost-effective heaps which perform to expectations;
- Troubleshoot effectively when problems arise;
- Perhaps most importantly, determine the effects of changing parameters (aeration rates, heap height, carbon dioxide enrichment, solution recycle, in situ inoculation, mineralogical treatment) on the rate-limiting steps, and
- Carry out realistic what-if scenarios using an inexpensive tool before heading out to the laboratory and plant.
For instance, if a heap which would normally be limited by the supply of oxygen is instead operated with an abundance of oxygen, then what step would become rate limiting? Would it be the supply of sulfuric acid to drive the ferrous oxidation reaction, perhaps, or the supply of carbon dioxide to sustain a viable heap biomass? At what point are all possibilities for increasing the oxidation rate exhausted?

The chief objective of this project is to develop a computerized code representing all of the important chemical, biological, and physical steps which might occur, in series or in parallel, from the microscale of the individual sulfide mineral grain to the macroscale of the entire heap and its surroundings. This work focuses exclusively on the less well understood sulfide oxidation aspect of the whole refractory gold ore heap leaching process. Such a model would benefit more than just our industrial sponsor, or even the gold mining industry in general. Similar problems are also encountered in the heap leaching of secondary copper sulfides. In fact, such a model would provide the foundation for understanding virtually any heap bioleaching process.

This fundamental, academic study employs a rigorous, unique, systematic method to model the heap biooxidation process. Our industrial sponsor has supplied a refractory gold ore hosting a major sulfide mineral (pyrite) whose leaching behavior is well understood. This is an ideal ore for validation purposes. Using this ore in each and every experimental phase of this project makes the modeling work all the more credible. Given the multiple tasks at hand, it was deemed essential to pay particular attention to certain model units, including the intrinsic oxidation kinetics of pyrite grains, the topological leaching kinetics of particles, and the solute hydrodynamics. Each of these themes is the subject of a comprehensive laboratory testwork program. Conception and testing of experimental apparatus and techniques to gather empirical information constitute the second objective of this project.

Validating the model predictions against the results from laboratory column tests performed under a variety of experimental conditions is an integral part of this work. It is true that the design, set-up, and operation of columns do not necessarily reflect industrial practice, especially with regards to the mode of
solution application, air distribution, ore agglomeration, and stacking. In other words, the model developed herein simulates the operation of an ideal heap. This project is the first attempt at deconvoluting systematically the results of validation column tests with respect to the principal rate processes involved, keeping the number of fitted parameters (for instance, cell growth rate) to a minimum.

A sensitivity analysis is performed using the finished mathematical model for the purpose of determining the hypothetical potential for improving the performance of heaps by manipulating various design and operating parameters. Any actual confirmatory pilot-scale leaching tests fall outside the scope of the present assignment, and could be undertaken in a subsequent project.

1.3 Outline

Chapter 2 (and publication [42]) first describes the design strategy and experimental methods employed in the set up, monitoring, and decommissioning of small and large isothermal column tests. The succinct analysis of the leaching performance of each column test, supported by numerous tables and graphs of experimental data presented in appendix B, identifies some ambiguities to be resolved by the development of the heap biooxidation model.

The solute hydrodynamic model presented in chapter 3 constitutes the backbone of the overall pyrite heap biooxidation model. Liquid advection, solute diffusion, and heap partitioning are just a few fundamental concepts integrated into the differential equations. Chapter 3, subject of publication [43], also reports on the column scale testwork performed to evaluate the unknown hydrodynamic model parameters. After a review of the current literature in section 3.1, a description of the experimental methods and a discussion of the principal findings follow. Lastly, sections 3.9 and 3.10 list symbols and references.

Chapter 4 develops a model of the leaching kinetics of non-uniform pyrite grains present in gangue particles of various sizes and shapes. The model output, i.e. number of moles of pyrite oxidized per kg of ore per unit time, is later integrated in
chapter 5 as a source term into the hydrodynamic model. In section 4.1, a review of the literature on the sterile oxidation kinetics of pyrite concentrate shows the limited applicability of the existing models. For this reason, two series of laboratory tests are performed to evaluate the kinetic model parameters characteristic of the pyritic ore tested. First, an electrochemical model (section 4.3) is proposed to fit the oxidation data points collected from sterile, stirred-tank leaching tests carried out with a pyrite flotation concentrate under different conditions of temperature and Fe(III)/Fe(II) ratio. Then, section 4.4 incorporates changes to the electrochemical model to address phenomena such as reagent diffusion through the pores of the gangue matrix, as well as variable shapes and sizes of pyrite occurrences. Sections 4.6 and 4.7 compile nomenclature and references, respectively.

Sections 5.2 to 5.6 of chapter 5 examine other essential model source terms, including chemical and biological reaction rates, cell adsorption, oxygen gas/liquid transfer, gas transport, and heat generation. Sections 5.7 and 5.8 outline the specific numerical methods employed to solve the complex non-linear system of partial differential equations. Section 5.9 summarizes the model features, suggests areas of future improvement, and recapitulates the model parameters yet undetermined. Pertinent references and a complete list of symbols are presented at the end of the chapter.

Chapter 6 first explores isothermal simulations at three different temperatures characteristic of the mesophilic, moderate thermophilic, and extreme thermophilic regimes to obtain values for the biological parameters that have yet to be determined by experimental means. The parameters are adjusted simultaneously for the model fits to match the experimental data of the column tests described in chapter 2. Isothermal model predictions are then compared to the leaching performance of other column tests for which one of the many experimental conditions (e.g. particle size, liquid flow rate, volumetric proportions, head grade) differed from the base case. Lastly, simulations are performed with the pellet subroutine to determine whether reagent diffusion through the pellet pores reduces the overall oxidation rate as compared to single-particle kinetics.
Several simulations are performed in chapter 7 to investigate scenarios under non-isothermal conditions in heaps of variable height with drip-point irrigation at high application rates. Under such conditions, air blowing rates may have more of an impact on heat transport than just providing sufficient oxygen to microorganisms. The influence of several other factors, including dripper spacing, preinoculation, mass transfer coefficient, and others, are examined to highlight the operator-controllable factors that dramatically shorten the biooxidation cycle while increasing the extent of sulfide oxidation.

Finally, chapter 8 surveys the principal findings from each chapter, with special emphasis on the logical train of thought that inspired the development of the model, and instigated research in specific, less well-understood areas. A discussion on how this research effort potentially impinges on the scientific community to promote worldwide collaboration, and on the mining industry to revisit heap leaching practice, follows.

1.4 References


Chapter 2

 Isothermal Column Tests

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2.1 Objectives

The primary objective of the column validation tests is to collect leach data that will inform the model development (chapter 3), and that will later be used to fit the parameters related to microbial growth, death, adsorption, and substrate limitation.

Ore preparation, agglomeration, and column operation procedures are presented in section 2.2. The sulfide and elemental sulfur oxidation profiles, together with the pH, potential, and precipitation history, are shown next to elucidate the effects of solution flow rate, ore agglomeration, ore particle size, aeration, carbon dioxide enrichment, inoculation, and temperature. The principal findings are finally highlighted in section 2.4.

2.2 Materials and Methods

2.2.1 Experimental Conditions

All factors at ambient temperature were studied in 8 columns of 24.1 cm internal diameter and about 3 m tall (Figure 2.1). Each column was comprised of two 1.25-m long sections, each equipped with a 12-mm thick perforated plate (6.4 mm holes evenly spaced) resting on top of a drainage plate 25 mm thick. Two columns were operated at ambient temperature under the standard conditions (Table 2.1, column A), while only one operating condition differed from its standard value in each of the remaining six columns.

Two banks of four identical columns of 10 cm internal diameter and 0.53 m tall were built and assembled, each within a 100-L water bath to evaluate the effects of increasing the temperature to 45°C and 65°C (Figure 2.2). All four columns were replicates of each other, and were dismantled at different time intervals. Aside from temperature, both banks were operated under identical conditions (Table 2.1, columns I and J).
Table 2.1   Experimental design and operating conditions.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>45</td>
<td>65</td>
</tr>
<tr>
<td>Ore size (mm)</td>
<td></td>
<td>&lt;12.5</td>
<td></td>
<td>&lt;3.3</td>
<td></td>
<td>&lt;12.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agglomeration</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agglomerating medium</td>
<td>M^1</td>
<td>S</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>-</td>
<td>M</td>
<td>M</td>
<td>20 g/L H_2SO_4</td>
<td>20 g/L H_2SO_4</td>
</tr>
<tr>
<td>Inoculation</td>
<td>M</td>
<td>-</td>
<td>M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid flow rate (L/(m^2*h))</td>
<td>5</td>
<td>2.5</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution composition</td>
<td>Variable</td>
<td>MH</td>
<td>MIJ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irrigation mode</td>
<td>Recirculation</td>
<td>Single-pass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air flow rate (L/min STP)</td>
<td>1.5</td>
<td>0</td>
<td>1.5</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO_2 in air (vol%)</td>
<td>2.5</td>
<td>-</td>
<td>0.03</td>
<td>2.5</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 The medium composition is described in the column of the same identification in Table 2.2.

Table 2.2   Characteristics of agglomerating and feed media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>M</th>
<th>S</th>
<th>MT</th>
<th>ET</th>
<th>MH</th>
<th>MIJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Mesophile inoculum</td>
<td>Sterile medium - column B</td>
<td>Moderate thermophile inoculum</td>
<td>Extreme thermophile inoculum</td>
<td>Regular feed - column H</td>
<td>Regular feed - columns I/J</td>
</tr>
<tr>
<td>[Fe_T] (g/L)</td>
<td>1.49-3.05</td>
<td>1.31</td>
<td>4.26</td>
<td>4.73</td>
<td>0.52</td>
<td>2.92</td>
</tr>
<tr>
<td>[SO_4^{2-}] (g/L)</td>
<td>9.5-13.3</td>
<td>8.3</td>
<td>18.8</td>
<td>21.9</td>
<td>3.5</td>
<td>9.4</td>
</tr>
<tr>
<td>pH</td>
<td>1.55</td>
<td>1.47</td>
<td>1.22</td>
<td>1.17</td>
<td>1.60</td>
<td>1.58</td>
</tr>
<tr>
<td>Potential (mV)*</td>
<td>&gt; 700</td>
<td>595</td>
<td>626</td>
<td>690</td>
<td>475-530</td>
<td>520-530</td>
</tr>
</tbody>
</table>

Note

- Overnight settling, followed by supernatant decanting
- 250 mg/L thymol, initial addition
- Overnight settling, followed by supernatant decanting
- Potential later found to be > 700 mV due to microbes
- Potential later found to be > 700 mV due to microbes
- 0.014 g/L MgSO_4.7H_2O
- 0.03 g/L (NH_4)_2SO_4
- 0.005 g/L KH_2PO_4

* Unless otherwise indicated, the reference electrode is Ag/AgCl at 22°C.

Chapter 2 - Isothermal Column Tests
2.2.2 Inoculum Preparation

Separate adaptation of each pure culture of *Leptospirillum ferrooxidans* (L. ferrooxidans) ATCC 29047, *Acidithiobacillus ferrooxidans* (A. ferrooxidans) ATCC 19859, and *Acidithiobacillus thiooxidans* (A. thiooxidans) ATCC 15494 to the recommended #2039 or #125 ATCC media lasted a few weeks. The incubator regulated the temperature to 30°C. After a few transfers, finely ground pyritic ore was added to each inoculum medium. Using the counting procedure described in section 2.2.5, cell numbers in the supernatant were routinely monitored.
After progressively adapting the three cultures to the same medium composition, the three inocula were poured into a single flask to scale up production of the mixed culture, or else to maintain a stock culture on stand-by at any time. Once the culture volume reached 500 L, agitation was stopped to allow the inoculum slurry to settle. The decanted supernatant became the agglomerating medium.

Microbial Insights Inc., Rockford, TN performed denaturing gradient gel electrophoresis (DGGE) analyses of the supernatant to identify the microorganisms present. This analysis was based on the polymerase chain reaction (PCR) amplification of the conserved region of the 16S rDNA gene extracted from a sample. The Ribosomal Database Project served as reference for sequencing the
excised bands. The inoculum originally contained *A. ferrooxidans*, *L. ferrooxidans*, and *A. thiooxidans*. However, the inoculum supernatant contained only one microorganism very closely related to the genus *Leptospirillum* (Figure 2.3, left).

![Inoculum, Agglomerate, Leachate bands](image)

**Figure 2.3** Bacterial diversity between inoculum (left), agglomerate (middle), and leachate (right), as identified by DGGE analysis. Letters associated with each band are described in section 2.3.2.1.

Inocula of moderate and extreme thermophiles were obtained from Little Bear Laboratories (Golden, CO) by adapting some of their stock cultures to the same pyritic ore over a period of two weeks. The cultures were shipped to UBC and immediately transferred *as per* the supplier’s instructions. The supplier did not identify the microbial species in both inocula, but mentioned that environmental isolates and ATCC cultures were cultivated in non-sterile media on metal sulfides. The two cultures were grown over the next two months before use. Just as with the mesophiles, two 125–mL shake flasks of each culture were kept on stand–by at 45°C (moderate thermophiles) and 68°C (extreme thermophiles).

### 2.2.3 Ore Preparation, Agglomeration, and Loading

Approximately 5,000 kg of pyritic refractory gold ore were jaw crushed to less than 19 mm, and split into two homogeneous 2,500–kg batches. Each batch was then
split into two 1,250-kg batches, each of which was divided into two homogeneous 625-kg batches. Each 625-kg batch was finally partitioned into three piles of 200 kg each. Each pile was stored in a 40-gal metal drum lined with a plastic bag and sealed until further use for the present column leaching experiments (chapter 2), tracer tests (chapter 3), as well as grain and particle kinetic tests (chapter 4).

Rotating the barrel of a 9-ft$^3$ cement mixer fitted with a plastic bin, which contained the as-is content of a drum and the agglomerating medium (Table 2.2), produced agglomerates for columns A to E, and H, after 20 min at 30 rpm. The as-crushed average ore size distribution before agglomeration (Figure 2.4, columns A–E + H) was fitted to the Gates–Gaudin–Schuhmann (GGS) function (Eq. 2–1) with parameters $q$ and $d^*$ of 0.39 (dimensionless) and 11.77 mm, respectively.

$$F\left(\frac{d}{d^*}\right) = \left(\frac{d}{d^*}\right)^q \quad (2-1)$$

Figure 2.4: Ore particle size distribution before agglomeration. Lines represent Gates–Gaudin–Schuhmann fits.
During agglomeration, three 1-kg ore samples collected randomly from each drum were assayed for the sulfur suite by gravimetry as BaSO₄, 31 elements by inductively coupled argon plasma (ICP 31) after multi-acid digestion, total gold by fire assay, whole rock assay, and the carbon suite (Table 2.3).

Table 2.3 Chemical characterization of the ore. Error = one standard deviation calculated from 27 replicate samples.

<table>
<thead>
<tr>
<th>Suite</th>
<th>Assay</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur group</td>
<td>Sulfide</td>
<td>2.54 ± 0.42%</td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>0.17 ± 0.06%</td>
</tr>
<tr>
<td>Elemental sulfur</td>
<td></td>
<td>&lt; 0.01%</td>
</tr>
<tr>
<td>Gold group</td>
<td>Total</td>
<td>1.08 ± 0.15 g/t</td>
</tr>
<tr>
<td>Carbon group</td>
<td>Total</td>
<td>0.19 ± 0.04%</td>
</tr>
<tr>
<td></td>
<td>Inorganic</td>
<td>0.04 ± 0.03%</td>
</tr>
<tr>
<td></td>
<td>Organic + graphite</td>
<td>0.15 ± 0.03%</td>
</tr>
<tr>
<td>Element</td>
<td>Iron</td>
<td>2.75 ± 0.24%</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>348 ± 55 ppm</td>
</tr>
<tr>
<td></td>
<td>Arsenic</td>
<td>0.23 ± 0.04%</td>
</tr>
<tr>
<td>Whole rock assay</td>
<td>Al₂O₃</td>
<td>8.70 ± 0.49%</td>
</tr>
<tr>
<td></td>
<td>BaO</td>
<td>0.29 ± 0.03%</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>0.26 ± 0.06%</td>
</tr>
<tr>
<td></td>
<td>K₂O</td>
<td>2.27 ± 0.15%</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>0.59 ± 0.09%</td>
</tr>
<tr>
<td></td>
<td>MnO</td>
<td>0.02 ± 0.01%</td>
</tr>
<tr>
<td></td>
<td>Na₂O</td>
<td>0.34 ± 0.03%</td>
</tr>
<tr>
<td></td>
<td>P₂O₅</td>
<td>0.21 ± 0.03%</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>77.37 ± 1.40%</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>0.35 ± 0.02%</td>
</tr>
<tr>
<td></td>
<td>Loss on ignition</td>
<td>4.15 ± 0.58%</td>
</tr>
</tbody>
</table>

Mineral phases were identified by X-ray powder diffractometry. A sample was mixed with ethanol and ground in a vibratory McCrone Micronising mill for 5 min to form a fine powder (< 10 μm). The X-ray powder diffraction data were collected at a scan step of 0.02°×2θ with a counting time of 2 s/step over a range of 7–100°×2θ with CuKα radiation on a standard Siemens D5000 Bragg–Brentano diffractometer equipped with a diffracted-beam graphite monochromator crystal. Phase-identification was performed with the Siemens Search-Match software and the
International Centre for Diffraction Data reference pattern library. The abundance of each phase was estimated by refining the X-ray powder diffraction data with the Rietveld program DBWS-9807 using the whole powder diffraction spectrum to characterize the composition and structure of a crystalline material [1]. Detection of quartz (SiO$_2$), muscovite (K$_2$O.3Al$_2$O$_3$.6SiO$_2$.2H$_2$O), and pyrite (FeS$_2$) confirmed the potassium, aluminum, silica, sulfide, and iron levels. Although some peaks matched marcasite (FeS$_2$), arsenopyrite (FeAsS), and kaolinite (Al$_2$O$_3$.2SiO$_2$.2H$_2$O), their levels were however within the range of detection (1–2 wt%).

Depending on the meteorological conditions and on the ore particle size, the moisture content varied between 4.2 and 8.5 kg solution/100 kg dry ore. Three 1-kg samples of moist agglomerates were taken before loading, and then dried and pulverized for head assays. Two 15-g samples of moist agglomerates were also taken, weighed precisely and preserved at 4°C with 10 mL of 0.2-μm filtered, iron-free mesophilic medium to determine the initial number of attached cells.

To study the influence of ore particle size prior to agglomeration, the content of one drum was fed through a rotary crusher to produce a homogeneous sample with particles smaller than 3.3 mm. The particle size distribution of a 25-kg ore sample was also well described by the GGS function ($q = 0.44, d^* = 3.08$ mm) (Figure 2.4, column G). Fairly spherical agglomerates 8 to 14 mm in size were produced and sampled as described above.

The content of one drum was riffled into two batches. The riffling process was repeated with each batch to yield finally eight 25-kg charges. The particle size distribution of one of the charges was also described by the GGS function ($q = 0.53, d^* = 12.09$ mm) (Figure 2.4, columns I and J). All agglomerates needed to load the eight I and J columns were produced together using only 50 kg (or 2 charges) added batchwise into a 3-L plastic container on bottle rolls (30 rpm, 10–20 min rotation). Four 1-kg samples of moist agglomerates were taken before loading, and then dried and pulverized for head assays.
Immediately after agglomeration, a thin layer of glass wool was set onto the perforated plate to prevent the loss of fines. Lowering a pouch filled with 5 kg of moist agglomerates (or dry ore particles for column F) avoided the breakup of the agglomerates upon discharge. After successive loadings, columns at ambient temperature contained about 150 kg of ore, while approximately 5 kg of ore filled the 45 and 65°C columns. Initial height, initial liquid holdup, and dry ore weight were measured. The top surface of the agglomerate bed was covered with a thin layer of glass wool and polyethylene balls to improve solution distribution.

A few weeks after start-up, the beds in columns A to E and H had slumped to about 84% (81.5–85.4%) of their initial height, while the bed of column G had slumped to 78%. On the other hand, column F loaded with non-agglomerated particles experienced a 1.1% slump only. The initial and final bulk density in columns A–I, with the exception of column F, averaged 1,352 and 1,626 kg/m$^3$, respectively.

Dry ore and stagnant liquid occupied about 66 and 17.9 vol%, respectively, of the total column volume after slumping. The bulk density of column F increased slightly from 1,769 to 1,789 kg/m$^3$. Columns loaded with non-agglomerated particles (column F) or with agglomerated fine particles (column G) retained even more solution (24 vol% → 14 wt%).

The solution and gas piping configuration differed slightly between the small and large columns. From the 4-L reservoir refilled every third day with fresh medium, the solution was pumped to the top of the small column where it dripped into the middle and trickled through the bed before draining through the bottom port into the leachate container. A calibrated rotameter controlled the flow of air blown through a port located directly underneath the perforated plate. To prevent air from bypassing the bed and escaping through the bottom liquid port, a small loop in the drainage tube retained some leachate, thus creating a hydrostatic head.

The configuration of the large columns was practically the same, except for (1) the volume of the feed reservoir (75 L), (2) the fast-flow pump redirecting the leachate from the bottom of the upper section to the top of the lower section, (3) the O-ring
seal between the cover plate and the upper flange of the lower section, and (4) the tube carrying the air from the lower to the upper sections.

Tubes were replaced and cleaned periodically to prevent build-up of fine particles and microbial waste products. Air and liquid channeling, as well as liquid ponding, occurred in columns F and G, and were temporarily alleviated by increasing the gas pressure or by drilling smaller vertical cores to redistribute the leaching solution.

### 2.2.4 Start-Up, Monitoring and Sampling

#### 2.2.4.1 Columns A and C to G

Solids-free mesophile inoculum was pumped at the preset rate (Table 2.1) during the first week. After this time, the leachate collected was mixed with 21 L of tap water and an added volume of solids-free inoculum to yield a total volume of 75 L. This solution was enriched with 0.5 g/L (NH$_4$)$_2$SO$_4$, 0.5 g/L MgSO$_4$.7H$_2$O, and 0.3 g/L KH$_2$PO$_4$. Its pH was adjusted to 1.7 with about 70 mL of reagent grade H$_2$SO$_4$. The feed solution was recirculated continuously until shutdown. If the pH in the reservoir happened to exceed 2.0 during the experiment, reagent grade H$_2$SO$_4$ was added to bring it closer to 1.7. Evaporative losses were periodically compensated by addition of tap water.

Liquid samples were collected routinely from the reservoir and from the drainage port of the upper and lower sections. The pH and potential were measured in-house with calibrated electrodes within a few hours of collection. The sulfate and metal concentration of a centrifuged portion of the sample were assayed by barium gravimetry and inductively coupled plasma (ICP), respectively, by International Plasma Laboratory Ltd. (Vancouver, BC). 4.5 mL of leachate was also preserved with 0.5 mL of 37 wt% formaldehyde to determine suspended cell numbers according to the procedure described in section 2.2.5. The mass and density of the leachate in the reservoir were measured using a mechanical scale and a 2-L graduated cylinder, respectively.
About 400 to 1,000 g of moist solids were collected from the surface of the ore bed of each section periodically. A 15-g sample was immediately transferred into a 50-mL plastic vial containing 10 mL of iron-free ATCC #2039 medium supplemented with 3.7 wt% formaldehyde. The tube was shaken to expose all solids and cells to the preservative, and stored at 4°C before use. The sample was analyzed by epifluorescence microscopy to determine the number of cells attached to solids. The weight of the leftover moist solids was measured to evaluate the moisture content after drying. Dried solids were pulverized with a ring-disk grinder, stored in paper bags, and later assayed for the sulfur suite by gravimetry and 31 elements by ICP scan after multi-acid digestion.

2.2.4.2 Column B

The leftover sterile solution previously used for agglomeration was pumped into column B during the first week. At the end of the seventh day, the same procedure was followed to make up the total volume to 75 L, except that the inoculum was replaced with the same H$_2$SO$_4$ solution. The pH was set to 1.7. The potential of the solution in the reservoir was adjusted to 650 mV with 3 mL of 30% w/v H$_2$O$_2$. No H$_2$O$_2$ was added during the first 48 days, after which time the potential in the reservoir was monitored daily and readjusted to ≥ 650 mV with H$_2$O$_2$ whenever necessary. H$_2$O$_2$ was added to oxidize ferrous ions in the absence of iron-oxidizing microorganisms. The potentials measured in the middle and at the bottom of the column were similar. Besides the initial dose of thymol dissolved in the leaching solution, no further addition took place. Liquid and solid samples were collected and assayed in the same fashion as described above.

2.2.4.3 Columns H, I and J

During the first week of operation, columns H, I, and J were irrigated with their regular feed solution (Table 2.1), kept at ambient temperature, to bring the pH down into the 1.5–2.0 range. For the next three days, the feed solution of columns I and J was temporarily substituted by 100 mL each of solid-free mesophile, moderate thermophile, and extreme thermophile inocula. A similar substitution with 28 L of mesophile inoculum occurred on day 10 for column H. The same series
of liquid assays were performed at least once a week. The temperature was measured periodically with a type K thermocouple at different levels within the small ore beds, and found to be 1 to 2 degrees lower than the bath’s temperature.

2.2.5 Cell Counting Procedure

Ms. Amy Chan and Dr. Curtis Suttle, UBC Department of Earth and Ocean Sciences, developed a method to enumerate the number of cells in solution and attached to solids. The procedure for liquid samples consisted of pipetting a precise volume from the well-mixed sample, and filtering it onto a 0.2-μm pore size, 25-mm diameter Anodisc filter (Whatman). Cells on the filter were stained with the nucleic acid specific fluorochrome SYBR Green 1 (Molecular Probes, OR). Each filter was incubated with 70 μL of dye (0.3 % SYBR Green I, made up in 0.02-μm filtered Milli-Q water) for 20 min, then mounted onto a glass slide with a small drop of 0.1% p-phenylenediamine (made up in phosphate buffer saline:glycerol) and stored in the dark at 4°C, or -20°C if not processed immediately. Using an epifluorescence microscope (Olympus AX70) with 1000× magnification, the number of cells per field of view was counted directly. Approximately 30 fields of view and a minimum of 200 cells were counted per slide. To test that the cells were homogeneously distributed, a minimum of three transects per slide, each consisting of at least 10 fields and 200 cells, were obtained across different portions of the slide. If the number of cells counted in each transect was within 20% of the average for the three transects, the distribution of cells was considered acceptable, and the slide was used to estimate the microbial abundance.

The procedure for solid samples consisted of detaching the cells from their solid substrate by adding first 10 mL of extraction buffer (iron-free ATCC 2039 medium containing 2% Tween 80), and topping it up with wash buffer (same medium, except with 1% Tween 80 concentration) to yield a ratio of 1 mL liquid per 1.5 g of ore. The slurry was vortexed vigorously for 5 s, followed by 30 min mixing at 225 rpm in a rotary orbit shaker. The slurry was centrifuged for 5 min at 800 g and 25°C in a swinging bucket rotor centrifuge. The supernatant was transferred into a sterile plastic tube (cell extract tube) and set aside. These steps were repeated.
once more to detach the remaining attached cells. Solids were vortexed with 10 mL of wash buffer for 5 s, followed by 15 min mixing at 225 rpm. The supernatant collected after centrifugation (25°C, 5 min, 800 g) was transferred in the cell extract tube. Solids were washed two more times. Combined cell extract and washes were vortexed. A 1-mL sample was pipetted and centrifuged for 2 min at 500 g to pellet the fines. Cells in the supernatant were enumerated using the same protocol described above. When necessary, a sample of the supernatant was diluted with the same medium to achieve an appropriate cell density for counting.

2.2.6 Shutdown Procedure

The leached residue of the tall columns was scooped out in 8 to 10 strata, whose thicknesses were measured. Agglomerates in small columns were dropped into a pre-weighed container after unscrewing the bolts holding the drainage plate to the bottom flange. The weight of each batch of wet agglomerates was noted immediately to calculate the moisture content. Visual inspection of the cores revealed fairly uniform ore wetting. One or two 15-g samples were collected after having mixed thoroughly the whole content of each batch to uniform consistency and color. All solids adhering to the column walls, tubes, and tools were washed into the containers, which were then placed in a 45°C oven until dry. After recording the dry weight, each batch of residue was cone crushed, riffled three times, and split to produce a 200-g sample. This sample was pulverized for 31 element and sulfur suite assays.

2.3 Results and Discussion

Appendix B presents the most relevant experimental data, organized, for each column, in the following order:

- Ore, iron, and sulfur mass balance;
- pH depth- and time-dependent profiles;
- Solution potential depth- and time-dependent profiles;
- Sulfate and iron depth- and time-dependent profiles;
Attached and suspended cell number depth- and time-dependent profiles;
- Attached cell number depth-profile at the time of shutdown;
- Sulfur speciation depth-profile at the time of shutdown, and
- Iron depth-profile at the time of shutdown.

Sections 2.3.1 to 2.3.9 briefly recap and scrutinize the principal findings of the column test, with references to figures presented in appendix B. Most figures were not included in the text in the interest of brevity.

2.3.1 Sulfide Oxidation Profiles

To determine the extent of oxidation in columns A to G, we first measured the sulfide grade from a small sample of partially-leached residue collected periodically. Grade inconsistencies were quickly attributed to poor sample representativeness. This problem was surmounted in column H by collecting fewer, larger samples of 20 kg. Setting up four replicates of columns I and J alleviated any sampling problems with these columns.

An estimate of oxidation (open symbols in Figures 2.5 to 2.9) was calculated using the amount of sulfate in the reservoir and in the stagnant liquid, fully cognizant of the non-negligible error incurred by ignoring sulfate precipitates and elemental sulfur. The ratio of the leftover to initial sulfide mass, both calculated using the sulfide grade and dry ore weight, provides a more accurate estimate. With the exception of a few columns, only one oxidation data point, shown as solid symbols in Figures 2.5 to 2.9, was determined at the end of each test. What appear to be error bars associated with the symbols are in fact the minimum and maximum oxidation values of the 8 to 10 residues recovered from any column. A long bar thus reflects non-uniform leaching profiles with depth. The minimum and maximum values were calculated from the ratio of the final to initial sulfide grades, a valid approach in this work because of the small differences between the initial and final solid masses (refer to mass balance tables in appendix B). Figures 2.5 to 2.9 are referred to and analyzed in greater depth in the following sections.
Figure 2.5  Sulfate- and sulfide-based oxidation profiles of columns A and H.

Figure 2.6  Sulfate- and sulfide-based oxidation profiles of columns C, F, and G.
Figure 2.7  Sulfate- and sulfide-based oxidation profiles of columns B, D, and E.

Figure 2.8  Sulfate- and sulfide-based oxidation profiles of column I.
2.3.2 Influence of Temperature

2.3.2.1 Columns A and H – 22°C

The pH dropped from 3.5 to 2.0 everywhere in the column after only 20 days and continued its descent to 1.5 for the next 130 days (Figures 2.10, B.1, B.2). It leveled off but dropped again to 1.3 by the end of the test. The first 50 days also saw a dramatic increase in potential from 400 to 700 mV, successively midway through the column, at the bottom, and finally in the reservoir (Figures 2.11, B.3, B.4). Thereafter, the potential remained practically constant, with frequent excursions of ± 100 mV observed in only one column. The uniform pH, potential, and attached and suspended cell number profiles (Figures 2.12, B.9), as well as the increasing iron and sulfate concentrations with depth (Figures B.5, B.6), are signs that oxidation occurred uniformly throughout both columns. Furthermore, in spite of the drip-point irrigation, no perceptible difference in the yellowish tint of the leached agglomerates was noted amongst the final eight residues and through the column cross-section.
Figure 2.10 Leachate pH at 22°C (diamond), 45°C (square), and 65°C (circle) in aerated, agglomerated ore beds.

Figure 2.11 Leachate potential at 22°C (diamond), 45°C (square), and 65°C (circle) in aerated, agglomerated ore beds.

Chapter 2 - Isothermal Column Tests
The ore surfaces were rapidly colonized by $2 \times 10^9$ cells/g dry ore (Figures 2.13, B.7, B.8). Interestingly, the attached cell numbers in all columns point toward this figure as being the maximum level, with only two exceptions in the case of column B. Scarcity of ferrous ions led to decreasing numbers of cells in solution. Attached cell populations exceeded planktonic populations by three orders of magnitude.

Although cell fluorescence was never proven scientifically to be an indicator of viability in this work, samples collected near the end of most column tests revealed attached cells to fluoresce brightly while those in suspension were dim with visible signs of cell disintegration and membrane distortion. Another feature distinguishing the two populations is the cell morphology. Ore agglomerates hosted thin, medium, and thick rods, straight or curved, as well as spherical cells. Only rod cells were observed in solution. The number of attached cells remained high regardless of the elevated soluble arsenic level ($\approx 3,000$ mg/L). However, under such high...
potentials and in the presence of dissolved iron, arsenic most likely occurred as arsenate, which is less toxic than arsenite.

Figure 2.13  Attached (filled symbols) and planktonic (open symbols) cell numbers at 22°C (diamond), 45°C (square), and 65°C (circle) in aerated, agglomerated ore beds.

Samples of leachate and moist agglomerates, both collected midway through column A after 10 months, were subjected to DGGE analysis. The DNA profile of the leachate revealed four bands, one of which (band B) failed to produce a distinguishable sequence (Figure 2.3, right). The other three organisms were closely related to the genus *Leptospirillum*, bands C and D being dominant. *Leptospirillum* species were also the only bacteria previously found in the pregnant solution from chalcopyrite ore column leaching tests previously inoculated with several species (*Acidiphilium cryptum, L. ferrooxidans, T. caldus, Sulfobacillus thermostosulphidooxidans*) [2].

In contrast, the DNA profile of the agglomerate sample revealed two prominent organisms (bands A and D), as well as two other faint bands (B and C) (Figure 2.3,
Sequence analysis of bands A and D showed a close affiliation to *A. ferrooxidans* and, surprisingly, to the moderately thermophilic *Sulfobacillus* sp., respectively. Band B was loosely related to *Leptospirillum* species, while band C failed to produce a distinguishable sequence. Occurrences of *A. ferrooxidans* and *L. ferrooxidans* in batch cultures [3] and columns [4] of pyritic ores, as well as at acid mine drainage sites (extensive body of work summarized in [5]), are very common. Previous identification of microbes colonizing copper [6] and pyritic [7] ore samples revealed that *A. ferrooxidans* is found exclusively in cooler environments and in solutions of relatively low acidity. The fact that such conditions prevailed everywhere in our column explains why both species flourished.

De Wulf-Durand *et al.* [2] have also reported this bacterial partitioning phenomenon in chalcopyrite column tests inoculated with *Acidiphilium cryptum, L. ferrooxidans, T. caldus, and Sulfobacillus thermosulfidooxidans*. The larger motility of *L. ferrooxidans*, some of which have a single, long flagellum [8], may explain this phenomenon. The lack of a flagellum on *Ferrobacilli* adsorbed onto copper ores [9] further supports this argument.

The inoculum originally contained *A. ferrooxidans*, *L. ferrooxidans*, and *A. thiooxidans*. However, the inoculum supernatant contained only one microorganism very closely related to the genus *Leptospirillum*. Given that *Leptospirillum* was supposedly the only microorganism present in the inoculum supernatant, questions arise as to the reintroduction of *A. ferrooxidans* in the column, and as to the origin of *Sulfobacillus*. These species most likely lived attached to the finely ground, non-sterile pyrite ore used as substrate for inoculum production. Fines may have been carried over into the supernatant during decantation. Moreover, the pyrite ore was non-sterile. Other sources of contamination include the shared use of equipment between this experiment and others in progress in the close vicinity, as well as large, uncovered, agitated inoculum tanks standing 10 m away. In fact, microorganisms soon contaminated column B containing an initial high level of thymol acting as a control, sterile test (discussed in section 2.2.4.2).
Research groups in the United States, Bulgaria, Germany, and Chile have observed a wide bacterial diversity and discovered new sequences from solid and solution samples collected in dumps, heaps, and waste piles. In contrast, our column of pyritic ore kept at ambient temperature hosted very few species with abilities to oxidize ferrous ions and/or elemental sulfur. *Leptospirillum* cells were omnipresent, whereas *A. ferrooxidans* and *Sulfobacillus* were exclusively adsorbed onto the ore.

The first replicate of column A was dismantled after 222 days and displayed uniform sulfate (0.53 wt%), elemental sulfur (0.20%), iron (1.67%) and sulfide (1.01%) depth-profiles (Figures B.11, B.13). A portion of the sulfate produced by the oxidation of 60% of the sulfide sulfur (Figure 2.5) precipitated as jarosite (= 3.4 wt% detected by XRD). Because of the initial 0.26 wt% CaO and 0.29 wt% BaO content (Table 2.3), sulfate may also have precipitated as CaSO$_4$ (gypsum) and BaSO$_4$, but these phases were not detected by XRD. Because of these observations and of the difficulty in calculating the CaSO$_4$ and BaSO$_4$ contents from just the final Ca and Ba grades of the residues, it was assumed that all sulfate present in the residues occurred as jarosite. The amount of jarosite precipitated, herein assumed to be potassium jarosite, was calculated as the product of the sulfate grade in the residue and the residue mass. This value was corrected for the amount of sulfate dissolved in the stagnant solution that was left to dry with the wet ore. Potassium jarosite may have amounted to 2.81 wt%. Assuming that jarosite occurs in the hydronium form has, however, little effect on the calculated amount (e.g. K$^+$ vs H$_3$O$^+$ → 2.81 vs 2.70 wt%).

The second replicate of column A was shut down 127 days later and rinsed with tap water for one month during which all soluble ions in the stagnant liquid were flushed out. The residue contained similar amounts of elemental sulfur, slightly less iron (1.42%) and sulfide (0.91%), but only half the sulfate (0.20%) and jarosite (1.48%) content (Figures B.10, B.12). Sixty-seven percent of the sulfide was oxidized (Figure 2.5). The unusually low sulfate and jarosite content, coupled with the error on the total sulfur mass balance, raised concerns as to the representativeness of the three original bulk ore samples collected. Indeed,
decreasing the original sulfide grade from 2.75 to 2.54 wt% would bring the oxidation down to 64%.

The mode of solution irrigation, whether in single pass or in recirculation, did not affect the pH, potential (> 700 mV) and attached cell number time- and depth-dependent profiles. These observations are also consistent with the findings of the Colorado Minerals Research Institute [10]. Sulfide oxidation at the top of both sections achieved 44 to 47% after 127 days (Figure 2.5). The reasons why no additional sulfide seems to have been oxidized in the next two months are unclear. After 188 days, the residues contained 0.05 wt% elemental sulfur, 1.24% sulfide, 1.64% iron, and possibly 1.54% jarosite (Figures B.60, B.61), regardless of the dilute concentrations of iron and sulfate in the feed solution (Figures B.58, B.59).

2.3.2.2 Column I – 45°C

Following a rapid drop in pH from 2.4 to 1.5 (Figures 2.10, B.62) during the first week, the potential increased from 380 mV to its final steady-state level of 700 mV within a few days after inoculation on day 6 (Figures 2.11, B.63). The inoculation day also marked a sharp transition of the sulfate-based oxidation profile. Five percent sulfide seems to have been oxidized before inoculation. This 5% gain is attributed, for the most part, to the dissolution of sulfate minerals amounting to 0.17 wt% sulfate sulfur at time zero (Table B.25). Calculations indicate that, at most, 2% of the sulfide sulfur could have been oxidized prior to inoculation. Oxidation slowed down appreciably past 70%, eventually reaching 81% after 220 days. Initial oxidation rates at 45°C are definitively larger than at 22°C.

While moderate thermophiles rapidly colonized the ore surfaces to reach the same maximum level as the mesophiles, the number of suspended cells dropped progressively to $10^6$ cells/mL (Figures 2.13, B.65). A sign of incessant oxidation was the larger sulfate concentration in the leachate than in the feed solution (Figure B.64). Yet, iron concentrations in the feed and in the leachate were eventually the same, if not lower in the leachate (Figure B.64). Iron precipitation definitely explains this phenomenon. The near perfect agreement between the oxidation values calculated from the sulfate in solution and from the sulfide in the residue.
would imply, at first sight, that jarosite is unlikely the prime iron precipitate. The XRD profile of the second leached residue showed, however, visible peaks matching jarosite, but no other iron precipitates fitted the remaining spectrum. A sulfur mass balance performed using the data available between the second and third dismantling times revealed that elemental sulfur oxidation explains the near perfect agreement between the sulfate and sulfide profiles. After 25 days, jarosite may have already accounted for 0.86 wt% of the ore, and may have increased to 1.40 wt% by the end of the test, as indicated by the sulfate grade in the residue (Table B.25).

2.3.2.3 Column J – 65°C

Columns controlled at 65°C also saw their pH values drop rapidly to a lower, constant level of 1.45 (Figures 2.10, B.67). The initial low potential of 350 mV increased almost linearly to ~700 mV over the course of 60 days (Figures 2.11, B.68). A potential transition from 600 to at most 730 mV vs SHE was also noted during the first 30 to 60 days in isothermal tests performed at 65°C by Little Bear Laboratories Inc. [11]. Attached extreme thermophiles took twice as long as moderate thermophiles to reach the same concentration (Figures 2.13, B.70). The above comments on precipitation at 45°C apply as well to the 65°C test. The jarosite content may have increased monotonically to 2.49 wt% after 220 days (Table B.28). This estimated level is greater than the jarosite content of 1.40 wt% at 45°C, but roughly equal to those measured in columns with recycled feed solution at ambient temperature. The 65°C experiment demonstrates that at least 85% of the sulfide sulfur is oxidizable. Oxidation at 65°C was just barely faster than at 45°C (Figure 2.9). Slower growth of iron-oxidizing extreme thermophiles and reduced oxygen saturation are the two most plausible explanations as to why the 65°C kinetics do not conform to the Arrhenius rate law.

2.3.3 Influence of Inoculation – Column B

It was anticipated that, in the absence of cells, the high initial potential of 650 mV would drop and remain low during the first phase of the test during which no \( \text{H}_2\text{O}_2 \) was added. Indeed it decreased to 440 mV after 20 days, but rose to 484 mV by
day 48 (Figure B.15). The 44-mV increase was at the time attributed to week-to-week fluctuations. In the following days H₂O₂ was added daily to control the potential to 650 mV. However, the potential climbed to 700 mV on its own never to drop again. Biological assays of the agglomerates and of the solution then revealed the number of cells to be comparable to those measured in inoculated columns (Figures 2.12, 2.13, B.17). Progressive colonization of ore was linked to the volatility of thymol, and thus its decreasing concentration in solution, and to the vigorously agitated 200-L inoculum tank standing 10 m away from the reservoir. Suffice it to say that oxidation was underway about 20 days after start-up, as shown by the distinct transition in the iron and sulfate concentration profiles around that time (Figure 2.7).

For the remaining 293 days, the potential and the attached cell numbers remained constant with time and uniform with depth. The pH decreased monotonically to 1.5 everywhere in the column (Figure B.14). These conditions led eventually to a uniform sulfide profile of 0.76 wt% (Figure B.19), or, in other words, 65.3% oxidation in 341 days (or, to be exact, 321 days after the ≈ 20-day lag period) (Figure 2.7). The iron (1.6 wt%), sulfate (0.6%), and elemental sulfur (0.11%) grades (Figures B.19, B.20) were also uniform with depth, except in the bottom half where slightly higher levels were measured. Potassium jarosite may have amounted to 2.31 wt%. This test was, for all intents and purposes, a replicate of column A.

2.3.4 Influence of Aeration – Column C

The only mode of air ingress to column C was through the open top of the column. Definite indicators, including:

- Potentials permanently less than 500 mV (Figures 2.14, B.22);
- Unusually large iron and sulfide levels in the residue (Figures B.26, B.27);
- Estimated 6.1 wt% jarosite precipitates found only in the upper 20% of the column, in contrast to an average 2.0 wt% everywhere else;
• Time-independent pH of 1.9 ± 0.1 (Figures 2.15, B.21), and
• Large depth/concentration gradient of planktonic and attached cells (Figures 2.12, B.24, B.25)

reveal that, in the absence of aeration, oxidation occurred in a narrow zone moving downward. Approximately 40% of the sulfide contained in the top 20% layer of the upper section was oxidized, leading to a minuscule overall 6.5% oxidation in 355 days (Figure 2.6). By the end of the test, solution ponding occurred most likely as a result of obstructed flow channels. Precipitates near the top of the column may have also impeded the diffusion of oxygen.

Figure 2.14 Leachate potential in performing (column A) and non-performing columns (columns C, F, and G).
The performance of column C is very poor in comparison to the aerated columns A and H. It does, however, compare fairly well to the results of Groudev and co-workers [4] from tests carried out in non-aerated columns. These researchers loaded 200 kg of ore grading only 0.8 wt% sulfide sulfur and crushed to less than 10 mm into columns of similar size. After one year, approximately 0.54 wt% (= 68% x 0.8 wt%) of the sulfide charge was oxidized, compared to 0.16 wt% (= 6.5% x 2.5 wt%) in the present experiment. Slightly larger oxidation rates were recorded in their experiments because of the external biological regeneration of ferric ions through intense reoxygenation of the solution before recirculation, thus leading to higher potentials in the feed solution.

2.3.5 Influence of Carbon Dioxide Depletion – Column D

As with columns A and E, the potential at both sampling points rose rapidly in column D to 700 mV (Figure B.29). It plateaued around 670 mV midway and fluctuated repeatedly between 500 and 700 mV at the bottom. The pH was
constant at 1.55 throughout the column for the first 60 days, but later dropped to 1.3 (Figure B.28). After 252 days, the eight residue fractions contained 0.21 wt% elemental sulfur, 0.52% sulfate, 1.56% iron, 1.72% jarosite, and 0.84% sulfide, except for the bottom one, which had an unusually large sulfide grade of 1.31% (Figures B.33, B.34). Sulfide oxidation reached 63% after 252 days (Figure 2.7). This figure must be interpreted with caution because of the large error (10.5%) on the sulfur mass balance. The inaccuracy of initial grade of the ore loaded in column D is the most plausible source of experimental error.

The suspended cell population dropped to $10^7$ cells/mL, while at least $10^9$ cells/g dry ore colonized all ore surfaces in 50 days (Figure B.31). The attached population outnumbered the planktonic population by three orders of magnitude. In determining whether the carbon dioxide supply was sufficient, any cells that may have crossed the flowing/stagnant interface were ignored to consider only those originally mixed with the ore particles during agglomeration. Cell concentration increased from $5 \times 10^6$ to $2 \times 10^9$ cells/g dry ore. Since column D contained roughly 135 kg of ore, this represented a net cell growth of $2.69 \times 10^{14}$. Assuming that microbes are cylindrical in shape, 0.5 μm in diameter, 1 μm in length, have a density of ≈1 g/mL, a dry weight of 30 wt%, and a carbon content of 50 wt% (dry weight basis) [12], calculations show that approximately 29 g of carbon dioxide were needed. Assuming further that carbon dioxide accounted for only 0.03 vol% of the 1.5 L/min (STP) (or 1.78 m$^3$/(m$^2$·h)) of air blown, the carbon dioxide supplied over the course of 50 days was 64 g, well in excess of the 29 g required. There was definitely no carbon dioxide shortage in this 1.6-m tall and 25-cm wide column. If column D had been 2 m taller, the demand would have matched exactly the carbon dioxide supplied from normal air.

The carbon dioxide calculation, the extent of oxidation, and the trends of the leach indicators suggest that column D was another replicate of column A.
2.3.6 Influence of Liquid Irrigation Rate – Column E

Neither the pH, the potential nor even the soluble iron and sulfate concentrations were affected by the lower flow rate of 2.5 L/(m²-h) in column E. As with columns A and D, the pH dropped to 1.5 everywhere in the column within about 150 days, and thereafter remained constant (Figure B.35). The number of suspended cells also decreased from $10^8$ to $10^7$ cells/mL at about the same time (Figure B.38). On the other hand, the attached population grew very rapidly to reach a steady-state level of $2 \times 10^9$ cells/g dry ore everywhere in the column in less than 25 days (Figure B.38). The potential in the middle and at the bottom increased from 400 to 700 mV in less than 7 and 20 days, respectively, and leveled off afterwards (Figure B.36). The sulfate (0.56 wt%), elemental sulfur (0.13%), iron (1.57%), and sulfide (0.96%) levels (Figures B.40, B.41) in the residue were also uniform with depth, taking into consideration the sampling and assay errors. Precipitation of sulfate and iron yielded ~ 2.33 wt% jarosite. About 58% of the sulfide was oxidized after 304 days (Figure 2.7). Decreasing the liquid flow rate thus had no effect on leaching kinetics.

2.3.7 Influence of Non-Agglomeration – Column F

To determine the true influence of non-agglomeration, it would have been preferable to load column F batchwise with dry, non-agglomerated ore particles and to spray the ore with inoculum in between. However, in less than a day the volume of inoculum needed to yield the same initial moisture content had already been delivered to the column. Given the very long timescale of leaching, ore preinoculation can absolutely be ruled out as a rate-limiting step at this scale.

Although less severe than in column G, air bypassing, and possibly channeling, could explain the jagged potential profile reaching sporadically 700 mV, but more often around 550 mV (Figures 2.14, B.43). The attached cell concentration (Figures 2.12, B.46), the potential (Figure B.43), and above all the iron and sulfide grade in the residue (Figures B.47, B.48), decreased with depth. Although the cell numbers everywhere in the column (Figures 2.12, B.46) were among the highest...
ever recorded, the sulfide extraction dropped from a high of 73% at the top to a low of 21% at the bottom, for an overall oxidation of 49% after 332 days (Figure 2.6). The large cell numbers detected everywhere may have in fact have been underestimated. An ore sample for cell count was collected after mixing the ore retrieved from each column core. If the cell numbers on the column periphery were in fact larger than in the centre, then combining the ore from the two zones would have in essence diluted their numbers. It is also worth noting that the elemental sulfur (average of 0.06 wt%) and sulfate grade (average of 0.71 wt%) in the residue ranked among the lowest and highest of all columns, respectively (Figure B.47). Potassium jarosite may have amounted to 3.33 wt%.

By the end of the test, the dense non-agglomerated ore bed was 2.0 m tall and contained 172 kg of dry ore and 20.5 kg of leaching solution. The ore and stagnant solution therefore occupied 73 and 24 vol% of the column volume, respectively, confining the air to the remaining 1% (vs 18% in agglomerated beds). This could certainly have affected the air distribution, explaining the vertical gradient of potential, sulfide and iron grades. The absence of a radial color gradient in the residues suggests otherwise. It is interesting to note that the extent of oxidation after more than 300 days in an agglomerated bed was comparable to the oxidation in the uppermost layer of a non-agglomerated bed.

2.3.8 Influence of Reduced Particle Size – Column G

All ore particles loaded in column G were smaller than 3.3 mm, in comparison to 12.7 mm in all other columns. The proportion (34 wt%) of material passing 0.3 mm in column G was roughly twice that of other columns (15%). Accumulation of these fines at the bottom of the lower section created such a large overpressure soon after start-up that air was escaping through the drainage tube. Increasing the air pressure and flow rate temporarily and partially dislodged the fines. Solution ponding and air channeling along the walls were signs that the lower bed had become totally impermeable only four months after start-up. The lower bed was dismantled into five sections of equal thickness to reveal yellow and gray zones on the periphery and in the core of the bottom fifth section, respectively. Ten times
more cells were attached at the periphery (Figures 2.12, B.53). Lack of oxygen in certain regions of the bed kept the potential low at around 500 mV, with occasional peaks of 600 to 700 mV (Figures 2.14, B.50). About 28% of the sulfide contained in the lower section was oxidized after 112 days, while 44% was leached from the top layer (Figure 2.6). The upper section experienced similar flow problems and was unloaded 79 days later. By that time, the solution pH and potential remained constant around 1.8 and 500 mV, respectively (Figures 2.15, B.49, B.50). The residue showed increasing sulfide grade with depth (Figure B.54), leading to local sulfide extractions ranging from 32 to 48%. Sulfate and iron precipitated to yield an estimated overall jarosite grade of 3.00 wt% (Figures B.54, B.55). The elemental sulfur content (0.2 wt%) of the residue (Figure B.54) was comparable to any other column.

The Colorado Minerals Research Institute had better success leaching 32 kg of ore (6.1 wt% sulfide sulfur) loaded in columns (20 cm in diameter, 76 cm tall) of roughly identical size to the present column setup [10]. The ore was also crushed to less than 3.3 mm and agglomerated in a drum with sulfuric acid and inoculum. The smaller weight to surface ratio could explain why 33% of the sulfide sulfur was oxidized in 160 days (or 2.0 wt% sulfide), compared to a maximum of 1.2 wt% in column G after the same period. Brierley and Luinstra [13] also observed that the extent of sulfide oxidation in columns 20 cm in diameter by 1.2 m tall packed with 45 kg of non-agglomerated ore (<6.4, <12.7, or <25.4 mm) was inversely proportional to the particle size.

2.3.9 Elemental Sulfur Oxidation

In the 22 and 45°C experiments, the sulfur grade increased and leveled off around 0.15 to 0.20 wt%, varying slightly with experimental conditions. Comparable grades of elemental sulfur were detected early in the 65°C column, but progressively dropped to 0.11 wt% and finally 0.03 wt% after 220 days.

These data were interpreted to highlight the influence of sulfur-oxidizing mesophiles, moderate thermophiles, and extreme thermophiles. To calculate the
total mass of elemental sulfur oxidized at any time with respect to the total theoretical mass of elemental sulfur formed in an abiotic environment, the following method was employed:

- Step 1: The elemental sulfur yield of the chemical pyrite oxidation was determined. As will be shown in chapter 4, each unit of sulfide sulfur generated approximately 0.4 unit of elemental sulfur, the balance sulfate.

- Step 2: Using the abiotic elemental sulfur yield (step 1), we calculated the total theoretical units of elemental sulfur produced if 100% of the ore sulfide sulfur content were oxidized.

- Step 3: Similarly, using the abiotic elemental sulfur yield (step 1), we calculated the theoretical units of elemental sulfur produced for the units of sulfide oxidized at any time.

- Step 4: The product of the measured elemental sulfur grade and the residue weight yielded the measured residual units of elemental sulfur. The difference between the measured units of elemental sulfur and the theoretical units of elemental sulfur produced (step 3) represented the units of elemental sulfur oxidized by sulfur-oxidizing cells.

- Step 5: Lastly, the ratio of the units of elemental sulfur oxidized (step 4) to the total theoretical units of elemental sulfur produced (step 2) corresponds to the oxidation percentage of Figure 2.16.

Care must be exercised in the interpretation of this plot, especially with regard to the rates estimated from the slopes. What is to say that the larger extent of sulfur oxidation at 65°C is not simply the result of more rapid sulfide oxidation kinetics? A look at the sulfur mass balance presented in appendix B will quickly show that elemental sulfur was always detected in non-negligible amounts in all residues. This evidence suggests that cells never faced a shortage of elemental sulfur. Thus, the rate of sulfur oxidation was not limited by the slower sulfide kinetics. With this in mind, a direct comparison of the slopes is now a valid approach to determine the influence of temperature. Figure 2.16 demonstrates that extreme thermophiles
oxidize elemental sulfur slightly more rapidly than moderate thermophiles, and more rapidly than mesophiles.

Figure 2.16  Extent of elemental sulfur oxidation at 22, 45, and 65°C, as calculated from the ratio of the amount of elemental sulfur oxidized to the total theoretical mass of elemental sulfur produced (= elemental sulfur produced when oxidation of 100% of the sulfide content generates 40% elemental sulfur). A value of 100% on the graph represents complete oxidation of all elemental sulfur that could theoretically be produced.

2.4  Conclusions

Table 2.4 compiles the principal measurements and observations of the isothermal column tests. The only true indicator of the extent of oxidation of iron-based sulfide minerals (pyrite, arsenopyrite) containing no other soluble marker (e.g. Zn, Cu) is the residue sulfide grade. Soluble iron and sulfate species were unreliable leach indicators as they precipitated to form jarosite. The latter was the sole precipitate detected by XRD under all temperature and solution conditions, even when the solution was not recirculated.
Table 2.4 Summary of observations of isothermal column tests.

<table>
<thead>
<tr>
<th>Column</th>
<th>Effect</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Base case*</td>
<td>• Presence of mesophiles and moderate thermophiles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Iron precipitation as jarosite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Uniform depth profiles of cell numbers, sulfide grade, and iron grade</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• 700 mV potential</td>
</tr>
<tr>
<td>B</td>
<td>No inoculation</td>
<td>• Cell contamination</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Uniform cell concentration with depth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Replicate of column A</td>
</tr>
<tr>
<td>C</td>
<td>No aeration</td>
<td>• Low potentials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Zone–wise downward leaching</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• More precipitation</td>
</tr>
<tr>
<td>D</td>
<td>Reduced CO₂ content</td>
<td>• Same oxidation rate as column A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• As high cell numbers as in column A</td>
</tr>
<tr>
<td>E</td>
<td>Reduced irrigation rate</td>
<td>• Same oxidation rate as column A</td>
</tr>
<tr>
<td>F</td>
<td>No agglomeration</td>
<td>• Low potentials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Plugging/channeling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Large cell numbers</td>
</tr>
<tr>
<td>G</td>
<td>Reduced particle size</td>
<td>• Low potentials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Plugging/channeling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Radial cell concentration gradient</td>
</tr>
<tr>
<td>H</td>
<td>Single–pass irrigation</td>
<td>• Replicate of column A</td>
</tr>
<tr>
<td></td>
<td>Shorter column</td>
<td>• Occurrence of precipitation</td>
</tr>
<tr>
<td>I</td>
<td>Temperature 45°C</td>
<td>• Faster leaching rate than column A</td>
</tr>
<tr>
<td></td>
<td>Shorter column</td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>Temperature 65°C</td>
<td>• Similar leachate rate as column I</td>
</tr>
<tr>
<td></td>
<td>Shorter column</td>
<td>• Lagging potential profile</td>
</tr>
</tbody>
</table>

* Conditions: preinoculation, inoculation, aerated, 3.0 vol% CO₂, 5 L/(m²·h) solution application rate, agglomerated, < 12.7 mm particle size, recirculation, 22°C, ≈ 1.6 m tall column

Oxidation occurred slowly beyond the first 100 days in all aerated columns operated at ambient temperature (except the very slow columns C and G), and eventually achieved 70% after one year. The remaining 30% most likely occurred as large pyrite grains in the coarser size fractions. Oxidation rates at 45 and 65°C were practically identical. Ten percent more sulfide sulfur (80% vs 70%) was oxidized.
from this same pyritic refractory gold ore in only 200 days at those higher temperatures. The inferior iron-oxidizing abilities of thermophiles and the slow transfer of oxygen from the gas to the stagnant solution may explain why the 45 and 65°C sulfide oxidation rates are virtually the same.

The pH rose above 2 during the first week or so because of acid neutralization by unidentified acid-consuming minerals, but soon dropped to a more-or-less steady state level of 1.4–1.5 at all temperatures tested. The potential rose quickly to 700 mV following inoculation in well aerated agglomerated ore beds containing a balanced proportion of fine and coarse particles, and operated at ambient temperature or 45°C. Only the test at 65°C showed an almost linear increase in solution potential during the first 60 days, followed by a plateau near 700 mV. Cell growth followed closely the rise in potential.

Neither irrigating at smaller flow rates, nor enriching the air with carbon dioxide, nor changing the composition of the feed solution had any notable influence on sulfide oxidation kinetics (Table 2.4). The column height did not affect the pH, potential, cell numbers, or oxidation kinetics in an aerated, agglomerated ore bed. Aeration indeed proved essential to successful biooxidation. A column 1.7 m or taller could face a CO₂ shortage during the exponential phase of cell growth if aerated with normal air at ambient temperature.

It could be argued that the difference in scale between small and large columns, and the possible liquid flow maldistribution resulting from the greater diameter, gives less credibility to a direct comparison of the oxidation performance at 22, 45, and 65°C. However, all reagents, including microbes, ferric ions, and ferrous ions, were already available at the reaction sites in the large columns, and thus did not need to be brought over by the flowing solution.

Inoculation during agglomeration is a nonessential step in columns because the initial 3 to 8 wt% moisture content of agglomerate contained very few cells in comparison to the steady-state population. In addition, inoculating the 5-kg columns with less than half of the inoculum volume to ore ratio applied in the 150-
kg columns resulted in comparable cell numbers after the same period of time. In contrast to cell attachment/detachment and growth, preinoculation and inoculum irrigation are of minor importance to cell colonization. Indeed, continuous irrigation with an inoculum during the 30–50 day colonization stage did not introduce enough cells to achieve the measured steady-state population.

In agreement with the findings of Groudev et al. [4], the results prove indisputably that the number of iron- and sulfur-oxidizing cells attached weakly and/or firmly onto ore particles far exceeds the number of planktonic cells. Thus, modeling the microbiology of the heap biooxidation process by considering solely the suspended microbial population is deceptive. Furthermore, this study has shown that some microbes were found exclusively attached to ore particles, while others survived on very low ferrous levels in both environments. It might prove beneficial to add finely ground ore to the inoculum tank. The inoculum slurry, and not just the clear supernatant, could be used as agglomerating medium, or perhaps sprayed onto the agglomerates as they discharge from the conveyor belt.

Non-agglomerated ore beds or those loaded with very small particles (< 3.3 mm) experienced severe air channeling and compaction. Unless the agglomerate structure is strengthened, decreasing the particle size must be very carefully weighted against proper solution and air distribution at the larger scale.

Elemental sulfur was always detected in amounts considerably smaller that would have been produced in an abiotic environment. Sulfur production from pyrite oxidation was always more rapid than its disappearance through microbial action. The sulfur-oxidizing capabilities of moderate and extreme thermophiles were superior to that of the mesophiles.

A rigorous model of the heap leaching process would provide definite answers to critical questions (e.g. lagging potential at 65°C, pH plateau vs temperature, sulfide kinetics at higher temperatures) raised in this experimental study. Some findings in this chapter will also guide the development of the heap model presented in the next chapter. For instance, the rapid initial acid consumption does not necessarily
warrant addressing the chemistry of acid-consuming and gangue minerals for this specific ore. The sulfide grade, cell number, and potential profiles, for example, will serve as baselines against which the model fits will be compared to determine the unknown biological parameters.

2.5 **Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C )</td>
<td>concentration (mole/L)</td>
</tr>
<tr>
<td>( d )</td>
<td>particle diameter (mm)</td>
</tr>
<tr>
<td>( d^* )</td>
<td>Gates–Gaudin–Schuhmann characteristic diameter (mm)</td>
</tr>
<tr>
<td>( q )</td>
<td>Gates–Gaudin–Schuhmann size distribution parameter (dimensionless)</td>
</tr>
</tbody>
</table>

2.6 **References**


Chapter 3

Solute Hydrodynamics

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3.1 Background

Flow and transport equations defining the rate at which solutes travel through the bed interstices, exchange across phase boundaries, and diffuse through water-filled pores, constitute the backbone of any heap leaching model. The hydrodynamics of single and multi-component solutes in porous media, as well as those of trickle bed reactors in the chemical engineering industry, are very well documented in the literature. Although heaps, packed towers, and trickle bed reactors can all be portrayed as packed bed reactors, the size of their packing material and their operating liquid and gas flow rates are radically different. Hence, this wealth of information is of limited use to the heap modeler.

The approaches taken by Dixon and Hendrix [1], as well as Sánchez-Chacón and Lapidus [2], to model heap hydrodynamics are scrutinized. One of the two critical facets considered was the distribution of the leaching solution throughout the heap and its impact on flow rates. A fraction of the leaching solution was assumed to be held up in the pores of the particles. In a dry ore bed, this solution would progressively push the air out of the smaller voids to form stagnant water pockets, thereby saturating the pores. Although Dixon and Hendrix [1] assumed that this liquid fraction existed only in the pores of the particles, Sánchez-Chacón and Lapidus [2] accounted also for the wetting of the external surface of the particles by a stagnant liquid film. Whether the water film is uniform or contiguous, or whether the stagnant pockets exist in the pores of the particles and/or at their interfaces, suffice it to say that the stagnant liquid fraction accounts typically for 17 to 32% of
bed void volume (or 7 to 13% of the total bed volume assuming a total bed porosity of 40%), as measured in copper dumps and columns loaded with rocks 5 to 152 mm in size [3]. The physical properties of the solution and the shape, size and wettability (i.e. contact angle) of the particles have been found to have a significant effect on the stagnant liquid holdup, as shown experimentally by Schlitt [4]. It is also worth noting that data measured in dumps are not directly transferable to heaps because the two processes differ widely in their geometries (rectangular vs conical), stacking techniques (1-15 m in height vs 60 m, agglomerates vs boulders, conveyor belt stacking vs truck dumping) and solution management procedures.

When the smaller openings are flooded, the leaching solution finds its way through the larger channels. This free draining solution, hereafter referred to as the flowing liquid, percolates as rivulets and films across the surfaces of the particles. The flowing liquid holdup corresponds roughly to the liquid collected during drainage, and depends primarily on the packing characteristics, and to a lesser extent on the fluid physical properties and on the liquid and gas flow rates. A substantial change of the flowing holdup is observed when the flow rate is large enough such that air-filled voids begin to pinch off and flooding occurs. Column tests reveal that the flowing liquid holdup increases from 0.017 to 0.025 m$^3$/m$^3$ bed over the range of liquid flow rates from 6 to 3,100 L/(m$^2$h) [4]. Flooding occurs at a flow rate of about 4,500 L/(m$^2$h), corresponding to a flowing liquid holdup of 19.6%.

The aforementioned pairs of authors [1,2] assumed that the flowing liquid moved vertically as a front through the bed (ideal plug flow behavior) at a constant velocity given by the product of the superficial velocity (e.g. 5-15 L/(m$^2$h) for sulfidic refractory gold and copper sulfide ores) and the degree of void saturation (assumed to be constant). From a theoretical standpoint, the velocity at any given location can be calculated more accurately using Darcy’s law, which takes into account the pressure gradient associated with the hydrostatic head (sum of gravitational and capillary forces) and the local permeability. Changes in permeability are attributed to decrepitation, weathering, compaction, segregation, precipitation and evaporation. The greater accuracy obtained by developing a
rigorous hydrodynamic model calling for local velocity calculations must be weighted against a simpler, yet less rigorous, model with shorter computation times. However, an assumption of constant velocity would be invalid for heaps operated with rest/rinse cycles [5].

As pointed out by Roman and Bhappu in their review of heap hydrology [6], a study of the hydrodynamics restricted to the notions of solution holdup and relative volumes would be incomplete without addressing the issue of solute transfer across boundaries and diffusion into stagnant pores. In similar fields of research, models have been derived on the basis of Fick’s law of diffusion, or using the concept of stirred tank reactors, or even with stochastic techniques such as random walk and Monte Carlo analyses. Both pairs of authors above [1,2] have exploited the first approach. Dixon and Hendrix assumed rapid mass transfer at the liquid/liquid interface and slow diffusion of the solute into the pores. The transfer rate was given by the diffusional flux at the interface. In addition to the hypotheses laid out in Dixon and Hendrix’s model, Sánchez-Chacón and Lapidus have also considered the existence of film mass transfer at the liquid/solid interface given by a first order linear term estimated from correlations pertaining to the hydrodynamics in trickle bed reactors. Although the agglomerates may be comparable in size to the packing material (Raschig rings, Berl saddles) of trickle beds, the liquid and gas flow rates in such reactors are nevertheless orders of magnitude larger than the conditions typical of heap leaching operations. Another common way of estimating transfer and diffusion rates is to perform tracer tests. Regrettably, there exists no published study relevant to heap leaching. Furthermore, those studies concerned with dump leaching are either purely qualitative [3], or else the interpretation (published in [7]) of the tracer curves (published in [4]) fails to address the issue of solute transport within the stagnant liquid. What is lacking from these previously-developed models is a set of reliable parameters that are representative of heap leaching operations.
3.2 Objectives

This chapter aims at combining the most important solute transport and transfer phenomena into a 1D mechanistic model of the heap leaching process under forced air advection, and to evaluate its parameters from actual experimental tracer curves. This study is divided into four parts. First, the bed porosity, the stagnant and flowing liquid holdup, and the initial slumping of an ore bed are determined under several sets of conditions. Second, a series of pulse and step tracer tests are conducted under different experimental conditions to obtain residence time distributions, from which model parameters are estimated using a least squares minimization scheme. Third, the goodness-of-fit of the three models proposed, coupled with their estimated parameters, is evaluated by comparing the numerical solution to the experimental residence time distribution. Finally, the experimental conditions selected in the second part of this work are arranged in sets of factorial experiments. A statistical analysis is carried out to determine the importance of agglomeration, binder addition, particle size, solution flow rate, and column height.

3.3 Transport Model Representation

On the basis of the seven diffusion models compiled and illustrated by Roman and Bhappu (Figure 5 of [6]), three two-phase models were developed to simulate the transport of aqueous species within a heap: mixed side-pore diffusion model (MSPD) (Figure 3.1), profile side-pore diffusion model with uniform pore length (PSPD) (Figure 3.2), and profile side-pore diffusion model with variable pore length (Figure 3.3). These models were originally used to simulate the transport of molybdate through a 30 cm long column packed with sediment collected from an uncontaminated aquifer [8]. A couple of years later these models were revisited to predict the effluent concentration response from spent heaps under both fresh and recycled water rinsing [9].
Chapter 3 - Solute Hydrodynamics

Figure 3.1 Representation of the MSPD model.

Figure 3.2 Representation of the PSPD model with uniform pore length.

Figure 3.3 Representation of the PSPD model with variable pore length.
The very large flat surface area of a heap, as compared to its narrow sloped sides, imposes a one-dimensional geometry with boundary conditions only at the top. The flowing liquid carrying the reagents and cells downward is assumed to move as a front at a constant velocity (plug-flow behavior assumption). Solute and cell transfers take place at the stagnant/flowing interface, and thus retard their transport to the bottom of the heap. The stagnant phase is viewed as an array of pores (or side branches) of uniform or variable lengths, oriented normal to the convection channels. No transfer takes place at the closed end of the pores. The diffusion driving force from the flowing liquid is assumed to be greater than the gradient between adjacent pores at all times. Hence, there is no “cross-talk” between individual diffusion (or stagnant) pathways.

As depicted in Figure 3.4 for the PSPD model with uniform pore length, ore particles bathe in the stagnant solution contained in a side branch. Ore particles occur as truffles (i.e. ore particles of low porosity coated by a very thin layer of fines) and spherical pellets (i.e. higher porosity agglomerates comprised of several particles of various sizes). Experimental evidence presented in chapter 4 supports the existence of these two types of agglomerates. Gas streams cross the stagnant solution everywhere throughout the pore.

Chemical and biological reactions outlined in Table 1.1 may occur within the stagnant liquid itself, at the surface of truffles, and throughout the porosities of pellets. Any chemical or biological truffle reaction terms, as well as any diffusive fluxes across the pellet interface, represent source terms within the bulk of the stagnant volume (MSPD model) or at each node of the side branch pore (PSPD model). Chapters 4 and 5 further describe the various forms of the source terms. In the interest of generality, the source terms in this chapter are represented by the symbol s.
Figure 3.4 Complete representation of sulfide heap biooxidation model comprised of five phases (flowing liquid, side branches of uniform length filled with stagnant liquid, truffles of various sizes, spherical pellets, air) and four reactions (chemical mineral sulfide oxidation, biological elemental sulfur oxidation, biological ferrous ions oxidation, oxygen transfer).

3.3.1 Mixed Side-Pore Diffusion Model

The concept of first-order mass transfer between the stagnant and flowing regions, which mathematically simplifies the concept of Fickian diffusion in the stagnant areas, has often been used to describe the physical non-equilibrium transport of solutes. According to the mixed side-pore diffusion (MSPD) model (Figure 3.1), the solution concentration is assumed uniform throughout the pore. The solute transfers at the flowing/stagnant interface only. The mass balance in the stagnant pores and its initial condition are given by:

\[
\begin{align*}
\varepsilon_s \frac{\partial C_{si}}{\partial t} &= k_a v (C_{fi} - C_{si}) + \varepsilon_s s_i \frac{\text{rate of input by reaction/fluxes}}{\text{rate of accumulation/fluxes}} \\
\text{I.C.: } C_{si}(0) &= C_{si0}
\end{align*}
\tag{3-1}
\]

where \( C_s \) and \( C_f \) are the concentration (mole/L) of species \( i \) (all species except oxygen) in the stagnant and flowing phase, respectively, \( a_v \) is the total exchange area per unit volume of heap (m\(^2\)/m\(^3\)), \( k_a v \) is the overall mass transfer coefficient at the interface (h\(^{-1}\)), \( \varepsilon_s \) is the stagnant liquid holdup (m\(^3\) solution/m\(^3\) heap), and \( s \) is...
the source term (mole/(m$^3$ stagnant-h)). The subscripts $s$, $f$, and $i$ refer to stagnant solution, flowing liquid, and solute species, respectively.

The mass balance in the flowing phase is given as follows, and, like Eq. 3–1, is valid for all species, except any species that dissolves into solution from the gas (e.g. oxygen or carbon dioxide):

$$\begin{align*}
\left\{ \begin{array}{l}
\text{Rate of} \\
\text{accumulation}
\end{array} \right\} &= \left\{ \begin{array}{l}
\text{Net rate of} \\
\text{input by advection}
\end{array} \right\} + \left\{ \begin{array}{l}
\text{Net rate of} \\
\text{input by transfer}
\end{array} \right\} \\
\frac{\partial C_{fi}}{\partial t} &= - \frac{\dot{m}_f}{\varepsilon_f \rho_f A} \frac{\partial C_{fi}}{\partial z} - \frac{ka}{\varepsilon_f} (C_{fi} - C_{si})
\end{align*}$$

(3–2)

I.C. 1: $C_{fi}(z,0) = C_{fi_0}$  
B.C. 2: $C_{fi}(0,t) = C_{fi_{feed}}$

where $\dot{m}_f$ is the flowing liquid mass flow rate (kg/s), $A$ is the heap cross-sectional area ($m^2$), $z$ is the depth (m), $\rho_f$ is the flowing liquid density (kg/m$^3$), and $\varepsilon_f$ is the volumetric proportion of the heap filled with flowing liquid ($m^3$ flowing solution$/m^3$ heap). Any homogeneous or heterogeneous reactions occurring within the flowing liquid are ignored.

Let us define the normalized height, $\zeta$, the time of advection, $t_a$, and the volumetric holdup ratio, $\Phi$:

$$\zeta = \frac{Z}{Z}, \quad t_a = \frac{\varepsilon_f Z}{\dot{m}_f} = \frac{\varepsilon_f Z}{A \rho_f}, \quad \Phi = \frac{\varepsilon_s}{\varepsilon_f}$$

(3–3)

where $Z$ is the total heap or column height (m), and $u$ is the liquid superficial velocity ($L/(m^2\cdot h)$).

Eqs. 3–1 and 3–2, and their respective conditions, are now rewritten thus:

$$\frac{\partial C_{si}}{\partial t} = \frac{1}{\Phi \varepsilon_f} ka (C_{fi} - C_{si}) + s_{si}$$

I.C.: $C_{si}(0) = C_{si_0}$

(3–4)
The MSPD model is entirely defined by three parameters ($t_a$, $\Phi$, and $k\alpha_v$).

### 3.3.2 Profile Side-Pore Diffusion Model with Uniform Pore Length

According to the PSPD model (Figure 3.2 and Figure 3.3), a diffusional transport mechanism controls the pore concentration profile. The transfer rate at the open end of the pores is then given by the diffusional flux, which depends on the concentration gradient in the stagnant phase at the interface. Fick's second law was derived with fluid volume fractions and molar concentrations, per unit heap volume (thus requiring the effective diffusivity, assumed constant over the domain). The mass balance along some reference diffusion pathway, coupled with its initial and boundary conditions, is given by:

\[
\frac{\partial C_{fi}}{\partial t} = -\frac{1}{t_a} \frac{\partial C_{fi}}{\partial \zeta} - \frac{k\alpha_v}{\varepsilon_f} (C_{fi} - C_{si})
\]

\[
\frac{\partial C_{si}}{\partial t} = D_{ei} \left( \frac{1}{\chi^n} \frac{\partial}{\partial x} \left( \chi^n \frac{\partial C_{si}}{\partial x} \right) \right) + \varepsilon_{si} s_{si} - \frac{e_s}{\varepsilon_s}
\]

I.C. $1$ : $C_{si}(x,0) = C_{si0}$  
B.C. $2$ : $C_{si}(X,t) = C_{fi}$  
B.C. $3$ : $\left. \frac{\partial C_{si}}{\partial x} \right|_{x=0} = 0$

where $x$ is the position ($\text{m}$) in the branch, $X$ is the uniform pore length ($\text{m}$), $C_{si}$ and $C_{fi}$ are the concentrations (mole/L) of species $i$ in the stagnant pore and in the flowing liquid, respectively, $n$ is a shape factor equal to 0 (linear diffusion), 1 (cylindrical), or 2 (spherical), $\varepsilon_s$ is the stagnant liquid holdup ($\text{m}^3$ solution/$\text{m}^3$ heap), and $D_e$ is the effective diffusivity whose units will be defined in the following equations. This equation has units of mole/volume heap–time.

Fick's first law may be written per unit heap volume thus:
\[ j = -D_{ei} \frac{\partial C_{ei}}{\partial \xi} \text{ mole area}_{\text{heap}} \cdot \text{time} \]

where \( D_{ei} \text{ [\text{volume}_{\text{stagnant}} / \text{length}_{\text{heap}}^2 / \text{time}] \)}

whereas the units of the simple diffusion coefficient are as follows:

\[
D \text{ [\text{length}^2 / \text{time}]}
\]

Hence, the effective diffusivity is related to the diffusion coefficient as follows:

\[
\frac{D_e}{D} = \frac{\varepsilon_s}{\tau_s^2} \frac{\text{volume}_{\text{stagnant}}}{\text{volume}_{\text{heap}}} \left( \frac{\text{length}_{\text{heap}}}{\text{length}_{\text{stagnant}}} \right)^2
\]

and Fick's second law may be rewritten as:

\[
\varepsilon_s \frac{\partial C_{si}}{\partial t} = \frac{\varepsilon_s D_l}{\tau_s^2 X^2} \left( \frac{1}{\varepsilon^n} \frac{\partial}{\partial \xi} \left( \varepsilon^n \frac{\partial C_{si}}{\partial \xi} \right) \right) + s_{si}
\]

Dividing through by the stagnant fluid volume fraction and defining a dimensionless pore length (\( \xi = x/X \)) gives the model diffusion equation per unit stagnant fluid volume:

\[
\frac{\partial C_{si}}{\partial t} = \left( \frac{D_l}{\tau_s^2 X^2} \right) \left( \frac{1}{\varepsilon^n} \frac{\partial}{\partial \xi} \left( \varepsilon^n \frac{\partial C_{si}}{\partial \xi} \right) \right) + s_{si}
\]

where the timescale for diffusion involves the diffusion coefficient, the tortuosity, and the square of pore length.

Taking the volume average by integrating over the domain volume:

\[
\int_0^1 \frac{\partial C_{si}}{\partial t} d\xi = \left( \frac{D_l}{\tau_s^2 X^2} \right) \int_0^1 \frac{1}{\varepsilon^n} \frac{\partial}{\partial \xi} \left( \varepsilon^n \frac{\partial C_{si}}{\partial \xi} \right) d\xi + \int_0^1 s_{si} d\xi
\]

and recognizing that:

\[
\int_0^1 \frac{\partial C_{si}}{\partial t} d\xi = \left( \frac{D_l}{\tau_s^2 X^2} \right) \left( \frac{1}{\varepsilon^n} \frac{\partial}{\partial \xi} \left( \varepsilon^n \frac{\partial C_{si}}{\partial \xi} \right) \right) + s_{si}
\]
\[ d\xi^{n+1} = (n+1)\xi^n d\xi \]  

\[ (n+1) \int_0^1 \frac{\partial C_{sl}}{\partial t} \xi^n d\xi = (n+1) \left[ \frac{D_i}{\tau_s^2 X^2} \right] \int_0^1 d \left( \xi^n \frac{\partial C_{sl}}{\partial \xi} \right) + (n+1) \int_0^1 s_{sl} \xi^n d\xi \]  

Recasting in terms of volume-averaged quantities gives, after slight rearrangement, per unit stagnant fluid volume:

\[ \langle \frac{\partial C_{sl}}{\partial t} - s_{si} \rangle = (n+1) \left[ \frac{D_i}{\tau_s^2 X^2} \right] \int_0^1 d \left( \xi^n \frac{\partial C_{sl}}{\partial \xi} \right) \frac{\text{mole}}{\text{volume}_{\text{stagnant}}} \cdot \text{time} \]  

By physical arguments, the integration of the right-hand side of Eq. 3-15 becomes the sink term for the advection equation, which is given per unit flowing fluid volume thus:

\[ \frac{\partial C_{fl}}{\partial t} = \frac{1}{t_a} \frac{\partial C_{fl}}{\partial \xi} - (n+1) \Phi \left[ \frac{D_i}{\tau_s^2 X^2} \right] \frac{\partial C_{sl}}{\partial \xi} \bigg|_{\xi=1} \]

I.C. 1: \( C_{fl}(\xi,0) = C_{f0} \)

B.C. 2: \( C_{f}(0,t) = C_{f,\text{feed}} \)

The PSPD model with uniform pore length is thus defined by three parameters (\( \varepsilon_s \), \( \varepsilon_r \), and \( \tau_s X \)) to be evaluated experimentally.

### 3.3.3 Profile Side-Pore Diffusion Model with Variable Pore Length

An additional level of complexity is introduced to the profile side-pore diffusion model by considering the pore length, \( \tau_s X \), to be variable. For pores of different lengths, a dimensionless pore length, \( \Xi \), that normalizes the pore length, \( \tau_s X \), with respect to a reference pore length, \( \tau_s X^* \), is defined. The selection of a pore length distribution function is somewhat arbitrary in the absence of data from experiments.
designed specifically to measure the actual distribution. The Gates–Gaudin–Schuhmann distribution function is used in this work for modeling the pore length. The normalized distribution has a single parameter, $m$, and is given by:

$$\frac{\Xi_{\text{max}}}{\Xi_{\text{min}}} \int f(\Xi) \, d\Xi = \int_0^1 m \Xi^{m-1} \, d\Xi = 1 \quad (3-17)$$

where $\Xi$ is the ratio of the pore length to the maximum pore length. The distribution reduces to a monosize length for values of $m$ smaller than 0.1 or larger than 10. Eq. 3–11 and 3–16 then becomes respectively:

$$\frac{\partial C_{si}}{\partial t} = \left( \frac{D_i}{\tau_s^2 X_{\text{max}}^2} \right) \left( \frac{1}{\Xi^2} \frac{\partial}{\partial \Xi} \left( \Xi^n \frac{\partial C_{si}}{\partial \Xi} \right) \right) + S_{si} \quad (3-18)$$

$$\frac{\partial C_{fi}}{\partial t} = -\frac{1}{t_a} \frac{\partial C_{fi}}{\partial \zeta} - (n+1) \Phi \left( \frac{D_i}{\tau_s^2 X_{\text{max}}^2} \right) \left| \frac{\partial C_{si}}{\partial \Xi} \bigg|_{\Xi=1} \right. \quad (3-19)$$

Combining Eq. 3–19 with Eq. 3–17 and integrating between $\Xi = 0$ and $\Xi = 1$ yield:

$$\frac{\partial C_{si}}{\partial t} = \int_0^1 m \Xi^{m-3} \left( \frac{\partial C_{si}}{\partial \Xi} \bigg|_{\Xi=1} \right) \, d\Xi \quad (3-20)$$

The PSPD model with variable pore length is thus characterized by four parameters ($e_{s_i}$, $e_{f_i}$, and $\tau_s X_{\text{max}}$, and $m$).

### 3.4 Experimental Methodology

#### 3.4.1 Ore Preparation

The particle size distribution (Figure 3.5) of the ore contained in a drum was best fitted by a Rosin–Rammler distribution:

$$F(\delta) = 1 - \exp(-\delta^q) \quad (3-21)$$
with parameters $q$ and $d^*$ equal to 1.64 (dimensionless) and 8.47 mm, respectively.

![Graph](image)

Figure 3.5  Ore particle size distribution fitted with the Rosin–Rammler function.

The content of a drum was loaded as-is (non-agglomerated) in columns. Two other fractions were agglomerated batchwise with 3 M H$_2$SO$_4$ with or without Nalco 9704 binder. A plastic bin was inserted into a cement mixer without baffles. Twenty-five kg of the bulk sample were placed into the bin with ~ 0.8 L of solution. When required, a known amount of binder was dissolved into the solution prior to its addition to the non-agglomerated ore to yield a final binder dosage of 0.5 kg/t ore. The cement mixer was tilted at 30° and rotated continuously for 30 min. The agglomerates had a final acid dosage of 9.4 kg H$_2$SO$_4$/t ore and a moisture content of 3.2 wt% before drying. They were spread evenly on a plastic sheet and left to dry for one week. The third and final fraction of the bulk sample was sieved through a 9.5 mm screen, and the undersize fraction was used as-is or agglomerated according to the procedure described above.
3.4.2 Experimental Apparatus

The experimental setup consisted of columns of 25.4 cm inside diameter and of variable height, whose arrangement was similar to that shown in Figure 2.1. A column was equipped with a shallow conical bottom plate for drainage, on top of which rested a perforated plate (6.4 mm holes evenly spaced) for gas distribution and ore support. Columns 50 and 180 cm tall were loaded with 45 and 137 kg of non-agglomerated or agglomerated ore, respectively. The initial height, $Z_0$, was recorded, and the bed slumped to a final height, $Z$, soon after solution application. Layers of 4 cm plastic balls were placed on top of the ore bed to improve solution dispersion. The solution was pumped from a 20 L pail using a peristaltic pump to the top of the column where it dripped onto an inverted 10 cm plastic funnel. A 30-cm long shaft passing through the funnel rotated at 30 rpm. The device was positioned at such a height above the bed that the liquid was evenly distributed without splashing on the wall of the column. A calibrated rotameter delivered 0.85 L/min (1.3 kg/(m$^2$h)) of nitrogen underneath the column perforated plate. The nitrogen flow rate was typical of heap leaching operations, and was not varied. All experiments were performed at ambient temperature and pressure.

3.4.3 Hydrology

The bed porosity (including the agglomerate porosity), $\varepsilon_h$, is defined as the ratio of the volume of solution pumped upward to fill the bed pore spaces to the volume of the empty column (product of surface area and height after slumping). The flowing liquid holdup, $\varepsilon_f$, corresponds to the volume of solution drained after interruption of the flow. An extremely small quantity of liquid was still draining after 24 h. Therefore, for practical reasons, the flowing liquid holdup was defined as the total volume of liquid collected after 24 h of drainage. The stagnant liquid holdup, $\varepsilon_s$, which includes the agglomerate porosity, was determined in two ways. The first method consisted of subtracting the 24-h drainage volume from the column saturation volume. According to the second method, the volume of stagnant water was given by the difference between the volume of solution pumped into a dry
column, and the volume of solution collected at the bottom after the onset of steady state flow (Figure 3.6).

![Graphical evaluation of total, stagnant, and recovered solution before and after steady state.](image)

Figure 3.6 Graphical evaluation of total, stagnant, and recovered solution before and after steady state.

The effects of the liquid flow rate, agglomeration, particle size, and height on the bed properties were studied in a series of tests described in Table 3.1. Experimental values of the flowing liquid holdup were used to evaluate the time of advection, $t_a$ (Eq. 3-3), thus decreasing the number of unknown parameters by one.

### 3.4.4 Tracer Studies

The remaining unknown hydrodynamic parameters ($\Phi$, $ka_v$, $\tau_sX$ or $\tau_sX_{\text{max}}$, and $m$) were deduced from a series of residence time distribution measurements carried out in a column with countercurrent flow of gas and liquid. Sodium nitrate (laboratory grade reagent salt dissolved in deionized water) was chosen as tracer. In a first approximation, this tracer served as a proxy for each of the species (ferric, ferrous, copper, zinc, sulfate ions, etc.) expected to be found in typical leaching solutions. Because the tracer is assumed non-reactive and to undergo neither sorption nor ion exchange, the source terms disappear from Eqs. 3-11, 3-15, and 3-18. The diffusion coefficient of this strong 1:1 electrolyte is given by:
\[
D_{NaNO_3} = 2 \left( \frac{1}{D_{Na^+}} + \frac{1}{D_{NO_3^-}} \right)^{-1} 
\]  

(3-22)

where the diffusion coefficients of sodium and nitrate ions in water at infinite dilution are \(1.33 \times 10^{-9}\) and \(1.90 \times 10^{-9}\) m\(^2\)/s, respectively, at 25°C [10]. The diffusion coefficient of sodium nitrate is thus estimated at \(1.56 \times 10^{-9}\) m\(^2\)/s.

Table 3.1: Experimental conditions and results of hydrology tests.

<table>
<thead>
<tr>
<th>Test</th>
<th>Ore*</th>
<th>Mass</th>
<th>Binder</th>
<th>(d_{\text{max}})</th>
<th>Slump</th>
<th>(u)</th>
<th>(e_{\text{h}}^{**})</th>
<th>(e_s)</th>
<th>(e_f)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(m(^3) voids/m(^3) bed)</td>
<td>(m(^3) liquid/m(^3) bed)</td>
<td>(m(^3) liquid/m(^3) bed)</td>
</tr>
<tr>
<td>a</td>
<td>NA</td>
<td>45</td>
<td>No</td>
<td>9.5</td>
<td>2.1</td>
<td>5.08</td>
<td>NM</td>
<td>0.23</td>
<td>0.032</td>
</tr>
<tr>
<td>b</td>
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<td>45</td>
<td>No</td>
<td>9.5</td>
<td>2.1</td>
<td>10.15</td>
<td>NM</td>
<td>0.23</td>
<td>0.032</td>
</tr>
<tr>
<td>c</td>
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<td>No</td>
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<td>6.5</td>
<td>5.05</td>
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<td>6.5</td>
<td>9.95</td>
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<td>Yes</td>
<td>9.5</td>
<td>6.5</td>
<td>---</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
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<td>No</td>
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<td>0.07-0.21</td>
<td>0.027-0.033</td>
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<td>No</td>
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<td>1.1-2.8</td>
<td>10.15</td>
<td>0.43</td>
<td>0.07-0.21</td>
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<td>0.10</td>
<td>0.024</td>
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<td>0.021</td>
</tr>
<tr>
<td>l</td>
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<td>1.1</td>
<td>---</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
</tbody>
</table>

* A: agglomerated, NA: non-agglomerated
** NM: not measured

Before the step or pulse injection of the tracer, the acidic solution generated on contact of the agglomerates with water was eluted. A 0.05 M NaNO\(_3\) solution was then pumped until the electrical conductivity measured by a conductivity flow-cell (Model 1481-65, Cole-Parmer) located downstream of the bottom drainage port was constant. The pulse injection then occurred by switching the inlet tubing from the 0.05 M solution pail into a 3.41 M NaNO\(_3\) solution flask. The injection was complete in less than 45 min, after which the inlet tube was wiped and re-immersed into the 0.05 M solution. The signal of the conductivity meter was amplified and recorded by a computer using a Keithley Metrabyte data acquisition card (model DAS-8) and Labtech Notebook data acquisition software. The
computer recording was synchronized with the introduction of each pulse or step. It was unnecessary to convert the conductivity readings into concentration values because of the linear relationship between the two over the range of concentrations tested. In total, fourteen tests, each characterized by a unique set of experimental conditions, were conducted to study the effects of the liquid flow rate, agglomeration, addition of binder, particle size, and column height (Table 3.2).

Table 3.2  Estimated parameters and goodness-of-fit of the PSPD model (spherical type of diffusion only) for all short and tall column experiments.

<table>
<thead>
<tr>
<th>Test</th>
<th>Tracer</th>
<th>Ore*</th>
<th>Binder</th>
<th>d</th>
<th>u</th>
<th>Z</th>
<th>nT</th>
<th>ε_f</th>
<th>ε_s</th>
<th>ε_es</th>
<th>τsX</th>
<th>R²</th>
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<td>0.23</td>
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<td>0.10</td>
<td>0.118</td>
<td>1.29</td>
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* A: agglomerated, NA: non-agglomerated

Chapter 3 – Solute Hydrodynamics
3.5 Numerical Simulations

3.5.1 Analysis of Experimental Data

The conductivity measurements for a step input were converted to dimensionless concentrations (\(= C/C_{\text{final}} \)) to yield the so-called \(F\) curve. For a pulse input, the conductivity measurements were first divided by the area under the concentration–time curve to generate the normalized \(C\) concentrations. The \(F\) values were then calculated by integrating the area under the \(C\)–time curve from zero to the time at which \(C\) is detected. The integration was performed using the simple trapezoidal method. In short, the \(C\) curve corresponds to the derivative of the \(F\) curve, and accordingly the \(F\) curve is the integral of the \(C\) curve.

3.5.2 Numerical Solution

The equations corresponding to the MSPD and PSPD models were transformed using the definition of the substantial rate derivative [11], expressed in dimensionless coordinates:

\[
\frac{D}{Dt} = \frac{1}{t_a} \frac{D}{D\zeta} = \frac{\partial}{\partial t} + \frac{1}{t_a} \frac{\partial}{\partial \zeta} \tag{3-23}
\]

A unit analysis reveals that the left- and right-hand side of Eq. 3-23 both have units of inverse time. This transformation facilitates the mathematical treatment of the model from the Lagrangian viewpoint, \textit{i.e.} via the tracking of fluid elements through the column. For this, a simple backward finite difference approximation is used [12]:

\[
\frac{DC}{D\zeta} = \frac{1}{\Delta \zeta} (C_{k,j} - C_{k-1,j}) \tag{3-24}
\]

where \(k\) is the column depth index and \(j\) is the time index. The integral on the right-hand side of Eq. 3-20 is solved with the Gauss–Legendre quadrature. The order of solution of the model equations is as follows. Step 1: all initial conditions are defined. Step 2: starting at time \(t = t_a\) and depth \(\zeta = 0\), the concentrations \(C_s\)
are determined using a fully implicit scheme in solving the second-order parabolic differential equation. Step 3: the pore entrance concentration gradient is calculated, and this and the pore entrance concentration are used to evaluate \( C_r \) at \( \zeta + \Delta \zeta \). Steps (2) and (3) are repeated for each depth increment until \( \zeta = 1 \). The procedure is then repeated for the new time, \( t + \Delta t \), using the new set of \( C_s \) concentrations. The algorithm’s code is written using the software Microsoft FORTRAN Visual Workbench version 1.0.

The model parameters are estimated by the least square minimization technique. In this work, a multidimensional unconstrained nonlinear minimization routine was written to find the minimum value of the sum of squares of the residuals, \( SS_E \), by adjusting simultaneously two or three parameters (\( \varepsilon_s \) and \( kav \), \( \varepsilon_s \) and \( \tau_sX \), or \( \varepsilon_s \), \( \tau_sX_{\text{max}} \), and \( m \)). The coefficient of determination, \( R^2 \), is calculated to assess the adequacy of the fit (Eq. 3-25).

\[
R^2 = 1 - \frac{SS_E}{SS_F} \quad \text{where} \quad SS_E = \sum_{i=1}^{n_r} (F_i - \hat{F}_i)^2 \quad \text{and} \quad SS_F = \sum_{i=1}^{n_r} F_i^2 - \frac{1}{n_r} \left( \sum_{i=1}^{n_r} F_i \right)^2
\]  

(3-25)

### 3.6 Statistical Analysis

In this work, the effects of five factors (agglomeration, binder addition, particle size before agglomeration, solution flow rate, bed height) were investigated in 14 random tests (Table 3.2). Up to four replicates were tested for a given set of conditions. Not all replicates were perfectly genuine because of the time-consuming and labor-intensive nature of the loading/unloading and clean-up process between tests. The five factors were arranged in six pairs: agglomeration/size (pair 1), binder/size (pair 2), agglomeration/flow rate (pair 3), flow rate/size (pair 4), height/flow rate (pair 5) and binder/flow rate (pair 6). Each factor was tested at two levels, i.e. agglomerated or non-agglomerated, with or without binder, slow or fast flow rate, small or large particles, and short or tall bed. This factorial arrangement generated four sets of experimental conditions for each pair. The four means of the stagnant liquid holdup and of the pore length were then compared to one another.
3.7 Results and Discussion

Before commenting on the significance of the bed properties and model parameters, the shape of the $F$ and $C$ curves is discussed, and the model fits are compared to the experimental data.

3.7.1 Characteristics of Tracer Curves

The moderately asymmetric shape of the experimental step curves (Figure 3.7, Figure 3.8) and pulse curves (Figure 3.9, Figure 3.10), as well as the noticeably flat tail, suggest the presence of a significant stagnant fluid phase. The breakthrough was not instantaneous; the tracer concentration in the effluent increased progressively, hinting that the exchange between the stagnant and flowing phases, or likewise the diffusion throughout the stagnant pores, was slow. On a $C$- or $F$-curve plot, the advection time corresponds to the time at which the first non-zero concentration is detected. In light of the assumption of plug-flow behavior, the advection time corresponds to the minimum time the tracer in the flowing liquid would spend in the column before being detected in the effluent. This definition is strictly valid if (1) the transfer in the stagnant pores is slow, and (2) the flowing liquid phase moves down as a front at a constant velocity. By making use of the definition of $t_a$ and the data presented in Table 3.2, advection times of 1.4, 3, and 6 h were calculated for the three tests presented in Figure 3.7. The graphical values of 2, 5, and 10 h were roughly 1.6 times larger than the calculated ones. But most interesting of all is the relationship between the advection time and the two most important operating conditions, i.e. the flow rate and the column height. According to its definition, the advection time is directly proportional to the height and inversely proportional to the velocity. Increasing the final height, $Z$, from 0.58 to 1.64 m (a factor of 2.82) yielded an advection time roughly 2.5 times larger (Figure 3.7, Figure 3.8). Doubling the flow rate decreased the advection time by half.
Figure 3.7 Comparison of experimental and fitted $F$ concentration for short and tall columns (PSPD model with uniform pore length).

Figure 3.8 Comparison of experimental and fitted $F$ concentration for short and tall columns (PSPD model with variable pore length).
Figure 3.9 Comparison of experimental and fitted $C$ concentration for short and tall columns (PSPD model with uniform pore length).

Figure 3.10 Comparison of experimental and fitted $C$ concentration for short and tall columns (PSPD model with variable pore length).

Chapter 3 – Solute Hydrodynamics
3.7.2 MSPD vs PSPD Models

For the purpose of comparing the goodness-of-fit of the MSPD and PSPD models, the tracer effluent concentrations were fitted following a step input in 0.52 m (test 2, best case scenario) and 1.64 m (test 10, worst case scenario) tall columns under the conditions described in Table 3.2. The three coefficients of determination were evaluated for the specific case whereby: (1) the column is partitioned into 75 depth intervals, (2) each stagnant pore is separated into 20 regions (the MSPD model does not call for such a condition), and (3) the test duration is divided into 10 min intervals. Figure 3.11 reveals that the fits of the three models match perfectly the experimental $F$ concentrations, with minor deviations of the MSPD model fits observed near the breakthrough point ($< 10\%$ $F$ value) and near complete saturation of the pores ($> 90\%$ $F$ value). The deviations of the MSPD model fits were amplified in the 1.64 m column (Figure 3.12). Despite the shorter computational time, the MSPD model did not fit the experimental data as well as either of the two PSPD models (Table 3.3, Figure 3.11, Figure 3.12). In the context of actual heap leaching experiments whereby ions interact with solid minerals, the PSPD model may best describe changes in solute concentration in the stagnant pores as a result of transport/transfer phenomena coupled with chemical reactions.

Although the PSPD model with uniform pore length described remarkably well the data of all short column experiments (Table 3.2), the PSPD model with variable pore length fitted better the tracer curves of the tall columns (Figure 3.7 vs Figure 3.8, Figure 3.9 vs Figure 3.10, and Figure 3.11 vs Figure 3.12). A greater discrepancy was noted between the fitted and experimental points beyond 30 h (Figure 3.12) for the PSPD model with uniform pore length. By contrast, the three-parameter model yielded an excellent fit of all experimental $F$ data (Figure 3.12) no matter what type of diffusion (either spherical, cylindrical, or linear) (Table 3.3). More noteworthy is the much-improved fit of the $C$ concentration data with the addition of the pore length distribution parameter, $m$, to the model. The addition of a third parameter in the optimization routine minimized the error and yielded coefficients of determination of 0.999, suggesting a near-perfect fit.
Figure 3.11  Comparison of the MSPD and PSPD model fits for test 2 (best case scenario).

Figure 3.12  Comparison of the MSPD and PSPD model fits for test 10b (worst case scenario).

Chapter 3 – Solute Hydrodynamics
Table 3.3 MSPD and PSPD estimated parameters and goodness-of-fit for the three tall column experiments.

<table>
<thead>
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<th>Test 8</th>
<th>Test 10a</th>
<th>Test 10b</th>
</tr>
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<td>$u$ (L/(m$^2$.h))</td>
<td>$k_a$ (s$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>MSPD model</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>5.80x10^{-6}</td>
<td>1.15x10^{-5}</td>
</tr>
<tr>
<td></td>
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<td>0.0893</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_f$</td>
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<td>0.019</td>
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<tr>
<td></td>
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<td>10.08</td>
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<td>0.0902</td>
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<td>0.9982</td>
</tr>
<tr>
<td>PSPD model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uniform length</td>
<td>$\tau_sX$ (cm)</td>
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</tr>
<tr>
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<tr>
<td></td>
<td>$R^2$</td>
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<td></td>
<td>$\tau_sX = \frac{m}{m+1} \tau_sX_{max}$ (cm)</td>
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</tr>
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<td>Cylindrical</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Linear</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

In general, any fit can always be improved with a larger number of estimated parameters. Regardless of the experimental measurements of the stagnant liquid holdup, the $\varepsilon_s$ variable was always one of the two or three fitted parameters during the minimization search, and thus was never assigned any of the measured values. In some cases, the fitted $\varepsilon_s$ values were about twice as large as the measured ones (Table 3.2), suggesting, at first glance, lack of agreement between experimental and fitted data. However, even under similar experimental conditions, the measured $\varepsilon_s$ values differed in fact by as much as two-fold (Table 3.1). On that basis, the three-parameter PSPD model could well be simplified to a two-parameter...
PSPD model where $\tau_sX_{max}$ and $m$ would be the only two fitted parameters. Besides, $\varepsilon_s$ values can be easily measured in column tests.

### 3.7.3 Bed Void Fraction

The initial bed height decreased by ~5 cm just a few hours after the onset of irrigation, leading to a reduction of the height from 1.1 to 10.2% depending on the packing material (Table 3.1). Columns loaded with agglomerates experienced a slump 2 to 5 times larger than those packed with non-agglomerated material. This was expected since dry agglomerates are more spherical and more uniform in size than non-agglomerated ore. Both of these factors lead to a higher void fraction before wetting [13]. The bed after slumping had an average void fraction of 43% (Table 3.1), a value in good agreement with results previously reported in the literature for packed bed reactors [13].

### 3.7.4 Stagnant Liquid Holdup

When the liquid flow was at steady state, approximately 15% (range 7–23%) of the bed was filled with stagnant water (Table 1). The PSPD model predicted a stagnant liquid fraction of $12.6 \pm 4.4\%$ (95% confidence level) (Table 2). The experimental results, the estimated values, and the data available in the literature (7–13%) [3] were all in very good agreement. The analysis of the means reveals that, among all factors, the ore particle size before agglomeration had the most significant effect on the fraction of liquid held up because smaller agglomerates and/or particles have more surface area exposed to the stagnant liquid. As shown in Table 3.4 (pairs 1, 2, and 4), the finer the crush size, the larger the stagnant holdup.

### 3.7.5 Parameter $\Phi$

The experimental values (2.1–3.3%, average 2.8%) of the flowing liquid holdup determined after 24 h of drainage were in excellent agreement with data from the literature (1.7–2.5%) [4]. Using these values, the experimental ratio ($6.07 \pm 4.91$)
of the stagnant to flowing liquid holdup agreed very well with the fitted ratio, \( \Phi \), of 5.00 ± 1.80.

The effects of \( \Phi \) on the shape of the \( F \) curve are examined using the PSPD model with \( \Phi \) values of 1, 2, 5, 7, and 10, while maintaining every other parameter constant, including the flowing liquid holdup. Figure 3.13 clearly shows that the shape of the \( F \) curve progressively shifts from an elongated S-shape to a more rectangular wave (i.e. a step) with decreasing \( \Phi \) values. Interestingly, even when both phases are present in equal proportion (\( \Phi = 1 \)), the \( F \) curve looks very much like a step. Hence, the time required to saturate the pores with solute in a column containing a large proportion of stagnant liquid is greater than in a column with less stagnant liquid.

![Figure 3.13](image)

**Figure 3.13** Effect of \( \Phi \) at constant \( \tau_x \). Spherical type of diffusion (\( n = 2 \)).

### 3.7.6 Mass Transfer Coefficient

The estimated values of the parameter \( k_a \) for the 1.64 m tall column ranged from \( 5.8 \times 10^{-6} \) to \( 11.5 \times 10^{-6} \) s\(^{-1} \). In contrast, the same mass transfer coefficient (0.1–1.2
s\(^{-1}\)) in downflow and upflow trickle bed reactors was found to be about five orders of magnitude larger [14]. Two parameters are incorporated in \(ka_v\): the overall mass transfer coefficient, \(k\), and the interfacial area, \(a_v\). According to the correlation proposed for the mass transfer coefficient at the flowing/stagnant interface in saturated systems [15], and later modified for unsaturated systems [16], \(k\) is proportional to the velocity to the \(\frac{1}{3}\) power at low Re numbers. In the present experiments (Table 3.3), the ratio of \(k_{2u}/k_u\) is 1.90 compared to the theoretical value of 1.26. Because the original correlation [15] was proposed for saturated packed bed reactors with a total porosity ranging from 35 to 75\%, using it for predicting the mass transfer coefficient might be ill-advised given that, in these experiments, the flowing liquid holdup accounted for only 3\% of the total column. However, the experimental and theoretical ratios are comparable when the correlation is used as a tool in a sensitivity analysis of the velocity.

3.7.7 Pore Length

Results from 22 simulations indicate that the uniform pore length of the two-parameter PSPD model ranged from 0.60 to 2.55 cm, with an average of 1.32 ± 0.87 cm (95\% confidence interval) (Table 3.2). When pores are assumed to be of variable length, very few pores could be as long as 5 cm (Table 3.3). However, the pore length distribution function of the three-parameter PSPD model is defined by the maximum pore length \(\tau_sX_{\text{max}} = 5.2\) cm) and the size distribution parameter, \(m\). The average pore length of the distribution equals the ratio of \(m\) to \((m+1)\), multiplied by \(\tau_sX_{\text{max}}\). The average pore length of the three-parameter PSPD model was very similar to the uniform pore length of the two-parameter model (Table 3.3).

The limited number of tests carried out in the 1.64 m column indicate that the pore length increased by about 0.66 cm as compared to the shorter columns (Table 3.4). One possible explanation for the increasing pore length could be the coalescence of small flow channels into larger ones, thus leading to channeling [17]. However, the 0.66 cm increase was well within the 0.87 cm standard deviation of the mean of the
pore length. Thus, the trend was not statistically significant at a 95% confidence level. Furthermore, only three tests were performed in the taller column.

The PSPD model with its two parameters is thus applicable to a short column just as its predictions fit very nicely the tracer distribution of a taller column. Table 3.4 indicates also that the pores were shorter at higher velocities. Perhaps the effective distance between flow channels is smaller at higher flow rates, or else, the open-end of the stagnant pores is set in motion. Then again the average diminution is about 0.42 cm. One could argue on the basis of the standard deviation that this trend is also not statistically significant, and for good reason considering that the

<table>
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<th>Factor</th>
<th>Factor</th>
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<th>Trend</th>
<th>$\tau_sX$ (cm)</th>
<th>Trend</th>
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</tr>
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<td>Fast</td>
<td>0.143</td>
<td></td>
<td>1.26</td>
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</table>

* A: agglomerated, NA: non-agglomerated
** P.S.: particle size

Table 3.4  Comparison of the means of six two-factor sets.
two flow rates tested only differ by a factor of two. In addition, the column is far from saturation under these flow rate conditions.

But what would be the effect of varying the pore length on the shape of the tracer curve, keeping all other variables constant? Figure 3.14 shows five curves with values of $\tau_sX$ ranging from 0.5 to 5 cm for conditions typical of the tracer tests.

![Figure 3.14](image)

Figure 3.14  Effect of $\tau_sX$ at constant $\Phi$. Spherical type of diffusion ($n = 2$). Tortuous pore length, $\tau_sX$, has units of cm.

In contrast to the $\Phi$ curves shown in Figure 3.13, all curves depicted in Figure 3.14 cross each other in the neighborhood of $F \approx 0.6-0.7$. The shorter the pore length, the longer the time before the appearance of the solute at the bottom of the column. This suggests that, for smaller $\tau_sX$ values, the diffusion (or the interfacial transfer) is very fast such that all stagnant pores are totally saturated before breakthrough. Under these conditions, the stagnant and flowing phases make up a single phase, which in turn yields an $F$ curve characteristic of quasi-ideal plug-flow behavior. The curve stretches gradually to a more elongated $S$-shape with increasing pore length. This suggests that part of the solute in the flowing liquid
makes it through the entire column before the remaining solute has time to diffuse to the end of the pores.

In light of this discussion the definitions of the advection time and the diffusion time were re-examined. Calculations based on the flowing liquid holdup, the column height, and the flow rate, reveal the average advection time to be 2.7 h for all 22 tests performed. Similarly, the diffusion time was found to be about 31 h, which is approximately 12 times larger than the advection time. It is not surprising therefore that the tracer curves exhibit a long tail.

The remarkable fits obtained with the three models developed herein challenge a comment made by Roman and Bhappu [6] about the inadequacy of “diffusion models” to accurately predict the residence time distribution of a solute within the pores spaces of a heap. The three models may not be perfect analogs of the actual hydrodynamics of heaps, but as Levenspiel said, “in many cases we really do not need to know very much, simply how long the individual molecules stay in the vessel, or more precisely, the distribution of residence times” [18].

3.8 Conclusions

This investigation into the hydrodynamics of heap leaching reveals that the major transport and transfer phenomena are described remarkably well by the simple advection/mass transfer model (mixed side-pore diffusion model) or the slightly more complex advection/diffusion model (profile side-pore diffusion model). The void volume of a column packed with agglomerated or non-agglomerated ore was roughly 43%. Of that void space 28 to 47% was filled with water, the rest occupied by air. The liquid phase was partitioned into a flowing liquid phase and a stagnant liquid held in pores 0.6 to 2.5 cm in length. The ratio of stagnant to flowing liquid was approximately 5 to 6. A comparison of experimental and estimated values of the stagnant liquid holdup suggests that the original two-parameter profile side-pore diffusion model can be simplified to a one-parameter model wherein the sole unknown parameter would be the tortuous pore length, \( \tau X \). The long tail of the C
tracer curve indicated that the solute exchange at the interface of the two phases, or the transfer across the pores, is very slow.

Of the five factors tested (agglomeration, binder addition, particle size, liquid flow rate and bed height), the effects of the velocity and of the height were the most significant. Increasing the velocity and/or decreasing the column height somewhat shortened the stagnant pores. Their effect on the advection time was much more significant and totally predictable. The stagnant liquid holdup seemed to decrease very slightly regardless of whether the ore was agglomerated with binder or not.

Notwithstanding the excellent fit between the predicted and experimental curves, non-uniform solution application onto the ore bed in such large columns and onto heaps challenges the validity of the assumptions. Similarly, whether the model would still be applicable throughout the entire duration of the leach (possibly longer than one year) during which (1) the ore particles may disintegrate, (2) the fines may migrate toward the bottom of the heap, and (3) the precipitates may plug off some pores, remains to be seen. Remember that, according to the Rosin-Rammler particle size distribution, the original bulk sample contained roughly equal amounts of particles (1) passing 3.3 mm, (2) -6.35+3.3 mm, (3) -9.5+6.35 mm, and (4) -12.7+9.5 mm in size. How would the model parameters change if the experimenter purposely increased the fines content to expose more reacting surfaces to the leaching solution? Should the modeler also be concerned with interfacial phenomena, such as the adsorption/desorption of leaching reactants and products onto the agglomerates? These are all valid issues that could be addressed in future experimental work.

The three hydrodynamic models tested herein do not distinguish between diffusion through the stagnant solution held between agglomerates, followed by diffusion within the agglomerate pores. The two diffusion processes were simply assumed to occur in series within a single pore. In a similar way, the stagnant liquid holdup measured in agglomerated beds included any liquid saturating the pellet voids, wetting the truffle surfaces, and bridging between agglomerates. The predicted pore length and the stagnant liquid holdup may thus be slightly overestimated.
Decoupling the two diffusion processes and estimating the values of both parameters for only the side branches are challenging tasks. For instance, the pore length of 1 cm in a non-agglomerated bed increased by about 0.4 cm in the presence of both types (truffles and pellets) of agglomerates (Table 3.4, sixth column). This trend suggests indeed an overestimation of the pore length in agglomerated beds. If the estimated stagnant holdup value for agglomerated beds does in fact include the pellet porosity, then the true stagnant holdup value should be smaller. However, the stagnant holdup values in columns containing no pellets, i.e. non-agglomerated beds, are equal to or larger than those for agglomerated beds (fourth column). These contradictory findings highlight the critical influence of the ore particle size distribution, the ore wetting characteristics, the stacking method, and the type of agglomeration (e.g.: rolling drum vs conveyor belt) on the hydrological parameters.

Regardless of these considerations, the models developed herein provide a more than adequate fit of the tracer data. In the absence of meaningful experimental data pertaining to the hydrology and hydrodynamics of heaps, these models establish the foundations for a more advanced model of the heap leaching process. Because of its simplicity and its fewer parameters, the profile side-pore diffusion model with uniform pore length and spherical-type diffusion will constitute the backbone of the complete heap biooxidation model further developed in chapter 5.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_v$</td>
<td>total interfacial area per unit heap volume</td>
<td>$m^2/m^3$</td>
</tr>
<tr>
<td>$C$</td>
<td>concentration</td>
<td>mole/m$^3$</td>
</tr>
<tr>
<td>$d$</td>
<td>particle diameter</td>
<td>mm</td>
</tr>
<tr>
<td>$d^*$</td>
<td>reference particle diameter size</td>
<td>mm</td>
</tr>
<tr>
<td>$D$</td>
<td>solute diffusivity in stagnant pores</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$F$</td>
<td>experimental cumulative concentration</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$F_f$</td>
<td>fitted cumulative concentration</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$k$</td>
<td>overall flowing/stagnant liquid mass transfer coefficient</td>
<td>m/s</td>
</tr>
<tr>
<td>$m$</td>
<td>Gates–Gaudin–Schuhmann size distribution parameter</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$n$</td>
<td>geometry factor for diffusion</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>
\[ n_T \] total number of experimental data points
\[ q \] Rosin–Rammler particle size distribution parameter (dimensionless)
\[ R^2 \] coefficient of determination (dimensionless)
\[ SS_E \] sum of squares of the residual
\[ SS_F \] sum of squares of the observations \( F \)
\[ t \] time (h)
\[ t_a \] liquid advection time (h)
\[ u \] superficial bulk flow velocity \((L/(m^2 \text{ bed-h}))\)
\[ x \] position in the pore (cm)
\[ X \] pore length (cm)
\[ \bar{X} \] average pore length (cm)
\[ X^* \] Gates–Gaudin–Schuhmann characteristic pore length (cm)
\[ z \] depth (m)
\[ Z \] final heap height (m)

**3.9.1 Greek Letters**

\( \delta \) normalized dimensionless particle diameter
\( \varepsilon \) volume fraction
\( \zeta \) dimensionless depth position
\( \xi \) normalized dimensionless pore position
\( \tau \) dimensionless tortuosity factor
\( \Phi \) stagnant to flowing holdup ratio
\( \Xi \) dimensionless pore length

**3.9.2 Subscripts**

\( a \) advection
\( d \) diffusion
\( f \) flowing liquid
\( h \) heap
\( j \) time index
\( k \) depth index
\( max \) maximum
\( min \) minimum
\( s \) stagnant liquid
\( 0 \) initial

Chapter 3 – Solute Hydrodynamics
3.10 References


Chapter 4

Mineral Leaching Kinetics

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4.1 Background

Recalling the heap schematic in Figure 3.4 and the global source terms introduced in Eqs. 3–1, 3–11, and 3–18, this chapter defines the rate expressions for the chemical oxidation of pyrite from truffles and pellets in terms of three major components: temperature, chemistry, and grain topology. This rate expression constitutes one of four source terms. The biological oxidation rates of elemental sulfur and ferrous ions, as well as the oxygen transfer rate across the gas/liquid interface, constitute the other three source terms discussed explicitly in chapter 5.

The leaching kinetics of pyrite have generated a continual interest in the scientific community over the last forty years, above all because of the abundance of pyrite in all types of mineralogical deposits. More than ever, the rapid depletion worldwide of free-milling oxide gold reserves and the abundance of gold locked up within sulfidic refractory deposits fuel the need to better understand the leaching kinetics of pyrite in autoclaves, biological stirred-tank reactors, and heaps.

Several authors have proposed various mechanisms to elucidate the nature of the pyrite oxidation reaction and to explain the formation of unique intermediate products of reaction. The complex chemistry of aqueous sulfur species and the multi-step electron transfer reactions involved are two reasons for which the mechanisms have yet to be defined adequately. It is, however, well recognized that elemental sulfur and sulfate are the two most stable end-products formed by two concomitant pathways [1–7]. The heterogeneous, irreversible chemical oxidation of pyrite produces \( \varphi \) units of elemental sulfur and \( 4(2-\varphi) \) units of sulfuric acid, where \( \varphi \) is the molar yield of elemental sulfur per mole of pyrite, \( i.e.: \)

\[
\text{FeS}_2 + [1 + 3(2-\varphi)] \text{Fe}_2(\text{SO}_4)_3 + 4(2-\varphi) \text{H}_2\text{O} \rightarrow [3 + 6(2-\varphi)] \text{FeSO}_4 + 4(2-\varphi) \text{H}_2\text{SO}_4 + \varphi \text{S}_0 \quad (4-1)
\]
In the absence of elemental sulfur ($\varphi = 0$), the complete dissociation of pyrite to ferrous ions and sulfate involves the transfer of 14 electrons. On the other hand, only two electrons per mole of pyrite are exchanged in the production of 2 moles of elemental sulfur (i.e. $\varphi = 2$). Reported yields vary over a wide range, from 20 to 90%, under different conditions of potential, acidity, and temperature. Although the effects of acidity and temperature on the yield are less well understood, several independent studies [1-4,8,9] have clearly established a direct relationship between the sulfate yield and potential. Thus, the sulfur yield is taken as a model parameter to be determined experimentally for each ore tested under various temperature and solution conditions.

What is also needed in the development of an advanced heap leaching model is a mathematical expression representing the rate at which reactive pyrite grains of various sizes, present at particle surfaces or disseminated within particles and/or agglomerates, are oxidized when exposed to different reagent concentrations at various temperatures. This last sentence identifies three key fundamental aspects of the particle kinetics (topological, chemical, and thermal functions) described by a rate expression of the general form:

$$\frac{dX}{dt} = k(T) \cdot f(C) \cdot g(1-X)$$  \hspace{1cm} (4-2)

where $X$ is the pyrite conversion, $k(T)$ is the rate constant, expressed as a function of temperature, $f(C)$ is function of the solution composition represented symbolically as $C$ (e.g. ferric ion, ferrous ion, proton concentrations), and $g(1-X)$ represents changing particle topology, expressed as a function of the pyrite fraction unreacted. Further details on the significance of each parameter are presented in the next three sections.

4.1.1 Thermal Function

The rate constant $k(T)$ in Eq. 4–2 is usually expressed as an Arrhenius function of temperature:

\textit{Chapter 4 – Mineral Leaching Kinetics}
\[ k(T) = k_o \exp \left( - \frac{E_a}{R \left( \frac{1}{T} - \frac{1}{T_o} \right)} \right) \]  

where the subscript \( o \) indicates a reference condition, \( E_a \) is the activation energy (kJ/mole), and \( R \) is the universal gas constant (kJ/(mole-K)). An analysis of a comprehensive review published by Hiskey and Schlitt \[10\] on the oxygen pressure leaching of pyrite, as well as that of Boon \[11\] on the leaching kinetics of pyrite at ambient pressure in ferric sulfate or chloride media, revealed a large scatter (20–93 kJ/mole) among the few activation energy data for pyrite measured in chloride media.

4.1.2 Chemical Function

A review of the above two publications \[10,11\] highlighted the many different forms of \( f(C) \) (Eq. 4–2). Whatever the initial concentration of Fe(III) or the medium used, the rate was found to be a function of:

- Fe(III) concentration, with \[12\] or without \[13–15\] pH dependence;
- Fe(III) and Fe(II) concentration, with \[16\] or without \[16,17\] pH dependence;
- Fe(III) concentration and \([\text{Fe(III)}]/[\text{Fe(II)}]\) ratio \[6,7,18–24\], or
- \([\text{Fe(III)}]/[\text{Fe(II)}]\) ratio, with \[23\] or without \[24,25\] pH dependence.

A common aspect of these rate expressions is their dependence on the Fe(III) concentration to some power ranging from (-1.0) to (+1.0). The reaction order with respect to Fe(II) varies from (-0.4) to (-1.0). Three rate expressions give partial reaction orders with respect to the proton concentration from (-0.32) to (-0.50). Three electrochemical studies \[1,2,9\] have also shown that the oxidation rate, represented by the current density, depends on the hydrogen ion concentration to the power (-0.2) to (-0.5) over the pH range from 0.32 to 3.89 at 25–35°C.

To make sense of the observed kinetics and reaction orders, the following two electrochemical half-cell reactions are considered:

Chapter 4 – Mineral Leaching Kinetics


\[
\text{FeS}_2 + 4(2-\phi) \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + (2-\phi) \text{SO}_4^{2-} + \phi \text{S}^0 + 8(2-\phi) \text{H}^+ + (14-6\phi) \text{e}^- \quad (4-4)
\]

\[
\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+} \quad (4-5)
\]

which take place simultaneously on the pyrite surface at a potential \( E \), referred to as the mixed potential, at which the net production of electrons is zero. The mixed potential should not be mistaken for the solution potential, which is calculated from the Nernst equation. The pyrite leaching rate is given by Faraday’s law as:

\[
r = \frac{A_a i_a}{Z_a F} \quad (4-6)
\]

where \( A_a \) is the anodic reaction surface area, \( i_a \) is the anodic current density, \( Z_a \) is the number of moles of electrons involved in Eq. 4-4, and \( F \) is Faraday’s constant. Because the net current of the overall reaction is nil at the mixed potential, one can write:

\[
A_a i_a = -A_c i_c \quad (4-7)
\]

The rate-limiting electron transfer step in the anodic dissolution of pyrite sets the anodic current density. Mishra and Osseo-Asare [8], as well as Biegler and Swift [1], have suggested that pyrite undergoes a series of electron transfer reactions, starting with the adsorption of water:

\[
\text{FeS}_2 + \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)S}_2 + \text{H}^+ + \text{e}^- \quad (4-8)
\]

\[
\text{FeS}_2(\text{OH}) + 3 \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2\text{S}_2(\text{OH})_2 + 3 \text{H}^+ + 3 \text{e}^-
\]

\[
\text{Fe(OH)}_2\text{S}_2(\text{OH})_2 \leftrightarrow \text{Fe}^{2+} + \text{S}_2\text{O}_3^{2-} + 2 \text{H}^+ + \text{H}_2\text{O} + 2 \text{e}^-
\]

\[
\text{S}_2\text{O}_3^{2-} + 3(1-\phi) \text{H}_2\text{O} \leftrightarrow \phi \text{S}^0 + (2-\phi) \text{HSO}_3^- + (4-5\phi) \text{H}^+ + 4(1-\phi) \text{e}^-
\]

\[
\text{HSO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{HSO}_4^- + 2 \text{H}^+ + 2 \text{e}^-
\]

Assuming that the symmetry factors of the overall anodic (Eq. 4-4) and cathodic (Eq. 4-5) reactions are approximately 0.5, Mishra and Osseo-Asare [8] concluded that the first charge transfer step must be rate-limiting for the observed partial reaction order with respect to ferric ions to be \((+\frac{1}{2})\). On the other hand, Biegler and Swift [1] surmised that the second charge transfer was the slowest, despite the

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fact that the predicted Tafel slope differed from their experimental measurement. These authors even considered the third electron transfer to be limiting, leading to even larger slope differences.

Taking the first charge transfer step as rate-limiting, then the anodic current density of Eq. 4-4 is given by:

$$i_a = \frac{i_a}{i_a} = Z_a F k_a a_{FeS_2/H_2O} \exp\left(\frac{\beta_a FE}{RT}\right) - Z_a F k_a a_{FeS_2/OH^-} a_{H^+} \exp\left(\frac{-(1 - \beta_a)FE}{RT}\right)$$  (4-9)

Assuming that the mixed potential is much larger than the reversible potential, i.e. $|i_a| >> \left|\frac{i_a}{i_a}\right|$, and that the activities of pyrite and water are equal to 1, Eq. 4-9 simplifies to:

$$i_a = \frac{i_a}{i_a} = Z_a F k_a \exp\left(\frac{\beta_a FE}{RT}\right)$$  (4-10)

The cathodic current density of Eq. 4-5 is also given by:

$$i_c = Z_c F k_c a_2^s \exp\left(\frac{\beta_c FE}{RT}\right) - Z_c F k_c a_3^s \exp\left(\frac{-(1 - \beta_c)FE}{RT}\right)$$  (4-11)

where $a_2^s$ and $a_3^s$ refer to the activities of ferrous and ferric ions at the particle surface, respectively. Thus, at the mixed potential $E$:

$$A_c Z_c F k_c a_2^s \exp\left(\frac{\beta_c FE}{RT}\right) = A_c Z_c \left[-F k_c a_2^s \exp\left(\frac{\beta_c FE}{RT}\right) + F k_c a_3^s \exp\left(\frac{-(1 - \beta_c)FE}{RT}\right)\right]$$  (4-12)

Several studies have shown that the symmetry/transfer coefficients for pyrite, $\beta_a$, and iron, $\beta_c$, were 0.46 and 0.51, respectively (compiled in [9]). Assuming that $\beta_a = \beta_c = \beta = 0.5$, Eq. 4-12 can be simplified further to obtain an explicit expression for the mixed potential, thus:

$$E = \frac{RT}{F} \ln \left(\frac{A_c Z_c k_c a_3^s}{A_c Z_c k_c + A_c Z_c k_c a_2^s}\right)$$  (4-13)
Substituting Eq. 4–13 into Eq. 4–10, we find:

$$i_a = Z_a F k_a \left( \frac{A_c Z_c k_c a_3^s}{A_a Z_a k_a + A_c Z_c k_c a_2^s} \right)^{1/2}$$  \hspace{1cm} (4-14)

The relative importance of the two terms in the denominator of Eq. 4–14 gives rise to two cases.

Type I: \[ A_a Z_a k_a \gg A_c Z_c k_c a_2^s \] \[ \rightarrow \quad \frac{i_a}{F} = k_I \sqrt{a_3^s} \quad (4-15) \]

Type III: \[ A_a Z_a k_a \ll A_c Z_c k_c a_2^s \] \[ \rightarrow \quad \frac{i_a}{F} = k_{III} \sqrt[3]{a_3^s / a_2^s} \quad (4-16) \]

where \( k_I \) and \( k_{III} \) are temperature-dependent lumped rate constants defined in section 4.1.1, given by:

\[ k_I = \sqrt{\frac{A_c}{A_a} Z_a Z_c k_a k_c} \quad k_{III} = Z_a k_a \sqrt{k_c / k_c} \quad (4-17) \]

The form of Eq. 4–14 may thus correspond to the type I or III electrochemical leaching mechanisms first presented by Nicol [26]. The rate expression of type I, \( i.e. \) when the exchange current density of the two half cells (ferric reduction and mineral oxidation) are similar in magnitude, is only a function of the Fe\(^{3+}\) activity to the \((+\frac{1}{2})\) power. When the exchange current density of the oxidizing couple is several orders of magnitude greater than the dissolution reaction, the rate becomes a function of the ratio of the Fe\(^{3+}\) to Fe\(^{2+}\) activities to the \((+\frac{1}{2})\) power. Section 4.3 examines which of Eqs. 4–15 or 4–16 better suits the leaching data of the pyritic ore tested.

### 4.1.3 Topological Function

While the thermal and chemical functions are readily evaluated experimentally with fully liberated pyrite grains of small sizes, the topological function must be evaluated with the ore particles themselves containing liberated and occluded pyrite.
grains of diverse shapes or sizes. \( g(1-X) \) is the topological rate term which accounts for the change of reactive surface area with time.

4.1.3.1 Chemical-Controlled Models

One of the two classical approaches to modeling particle kinetics assumes the chemical reaction rate to be the slowest step. This applies to slow-oxidizing sulfide minerals, such as pyrite, occurring as individual grains or as grains disseminated throughout a porous gangue matrix. Elemental sulfur, if produced, must form a porous layer on the remaining sulfide core for the chemical reaction to be controlling.

If pyrite grains are assumed to be spherical and to shrink at a rate proportional to the progress of the leach, then we can write:

\[
g(l-X) = (1-X)^{\frac{2}{3}}
\]

This approach was employed to simulate the topological kinetics of coarse, spherical pyrite grains disseminated into a constant-size gangue particle [27,28]. Using the pyrite intrinsic leaching kinetic model previously derived by Zheng et al. [20] in conjunction with a measured sulfide grain size distribution, model predictions were found to be in good agreement with four experimental gold extraction data points [27,28]. The gold extractability of the entire ore mass was predicted by the extent of sulfide oxidation of individual grains undergoing leaching in a 1.2-m tall column, intermittently aerated. Bartlett [29] and Madsen and Wadsworth [30] have used a similar version of the chemical-controlled, shrinking-core model to describe the leaching of one or more copper sulfides. In this author’s opinion, the key to successful predictive modeling lies with the measurement of a representative grain size distribution and liberation, using, for instance, CSIRO's QEMSEM and QEMSCAN automated image analysis system.

4.1.3.2 Diffusion-Controlled Models

The very slow diffusion of dissolved oxygen [31] or ferric ions [27,28] through the very small pores of ore particles gives rise to a slowly moving sharp boundary
separating a reacted outer rim from an unreacted core. The oxidant concentration is nil beyond the reaction zone due to fast kinetics at the core boundary and/or the absence of open pores in the unreacted core. Whether it is the formation of a product layer and/or simply the few, tortuous pores in the particles that are retarding the diffusion of reagents, the topological rate term of the diffusion-controlled model takes the following form:

\[ g(1-X) = \frac{(1-X)^{\frac{1}{2}}}{2\left[1-(1-X)^{\frac{1}{2}}\right]} \]  

(4-19)

The original diffusion-controlled model developed by Braun et al. [31] was later extended to account for a number of factors, including particle size distribution [30,33], presence of several sulfide minerals [32–36], time-dependent shape and roughness factors [32–39], temperature, variation of grade within particles [31,37] and among particles of different sizes [32], etc. Ferric leaching of a variety of copper and iron sulfide minerals in heaps and dumps [30–39], as well as oxygen leaching of a submerged copper ore body [37,40] or pressure leaching of chalcopyrite [31,43], are just a few examples of case studies to which the diffusion-controlled model or one of its later versions has been applied.

Coupling kinetics with diffusion led Bartlett [29] and Dixon and Hendrix [42] to develop unsteady state mixed kinetic models for the leaching of mixed sulfides or any solid reagent from porous ore particles. Their models represent the relatively slow leaching of a mineral in a diffuse reaction zone located in between a fully oxidized outer rim and an unreacted core. At any time, the reaction zone is comprised of homogeneously distributed, non-porous grains at various stages of leaching. Concentration profiles of diffusing reactant and dissolved products cross each other within the reaction zone rather than converging to zero at the core/rim interface. Ore porosity, grain liberation, and grain and particle size and shape distribution, are key parameters to be determined \textit{a priori} for diffusion-controlled models to bear quantitative credibility, engineering utility and predictive capability.
4.1.3.3 Truffle Model

The chemical- and diffusion-controlled modeling approaches may fall short with the present pyritic ore sample. Indeed, even among particles of the same size, pyrite occurred as disseminated micron-size grains, as disks or plates sandwiched between gangue minerals, as veins, and filling open spaces. The latter three types of mineralization were noted for the most part in the coarsest fractions (> 3 mm). For example, 322 particles of (-12.7+9.5) mm in size were first separated into three groups (no visible grains, visible grains/patches, and disks/veins) and each assayed for sulfide. The bulk of the sulfide (63%) was found in the disks/veins-type particles with grades as high as 14 wt%, with only 27% of the sulfide in the first group (Table 4.1).

Table 4.1  Sulfide distribution between different types of grain mineralization.

<table>
<thead>
<tr>
<th>Size (mm)</th>
<th>No visible grain</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overall grade 1 (%)</td>
<td>Grade (%)</td>
<td>Prop. 2 (%)</td>
<td>Grade (%)</td>
<td>Prop. (%)</td>
<td>Grade (%)</td>
<td>Prop. (%)</td>
</tr>
<tr>
<td>-4+3.35</td>
<td>1.86</td>
<td>1.1</td>
<td>57.2</td>
<td>13.7</td>
<td>42.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-8+6.35 (Rep. 1)</td>
<td>1.63</td>
<td>0.8</td>
<td>42.0</td>
<td>3.0</td>
<td>12.4</td>
<td>14.1</td>
<td>45.6</td>
</tr>
<tr>
<td>-8+6.35 (Rep. 2)</td>
<td>1.99</td>
<td>0.8</td>
<td>34.4</td>
<td>5.7</td>
<td>32.9</td>
<td>13.0</td>
<td>32.7</td>
</tr>
<tr>
<td>-12.7+9.5</td>
<td>2.42</td>
<td>0.8</td>
<td>27.5</td>
<td>3.2</td>
<td>9.5</td>
<td>14.0</td>
<td>63.0</td>
</tr>
</tbody>
</table>

1  Sulfide grade in wt%
2  Weight proportion of sulfide in a given category

Heterogeneity of the sulfide grain distribution between particles also characterizes the (-8+6.35) mm fraction (Table 4.1). The non-negligible amount of sulfide not visible to the naked eye could still be exposed to the leaching solution via minuscule pores. What is more troublesome is the large variability in the head grade of the two (-8+6.35) mm fractions, which is explained, in part, by the presence of very high grade particles (in other words, nuggets).

The usual assumption of homogeneous distribution of monosize grains is invalid in this context. Furthermore, modeling the leaching of any of the observed types of liberated pyrite occurrences using, for instance, shrinking-plate or -cylinder
models, entails proper characterization of grain geometries using more sophisticated techniques than the naked eye.

Observed variations in pyrite grade, shape, and size distributions between ore particles of different sizes calls for a simpler strategy to model any diffusion and reaction phenomena taking place simultaneously within ore particles. A more generalized topological function proposed by Dixon and Hendrix [43] is written as:

\[ g(1-X) = (1-X)^\phi \] (4-20)

where \( \phi \) may vary over the course of the leach, taking values greater than or equal to 2/3. This is referred to in the present work as the *truffle model*. The choice of the term *truffle* is explained in the next section. The parameter \( \phi \) should, in principle, be evaluated for each particle size. A collection of particles will instead be modeled as a single-size class. The parameter \( \phi \) is not strictly speaking the weighted average of the individually-measured \( \phi \) parameters of fine, medium, and coarse particles in a particular assemblage, but rather fits the overall oxidation profile as obtained from leaching different size particles altogether in the same vessel.

4.1.3.4 Pellet Model

Experimental evidence suggests that agglomerates prepared by mixing crushed ore particles with any liquid may belong to either one of two types: *truffles* or *pellets*. Truffles, which were shown experimentally to account for 55 wt% of the agglomerates, are simply dusty, crushed ore particles with very little porosity (typically 1–4 vol%) (Figure 4.1).
Figure 4.1 Size distributions of unagglomerated ore particles, agglomerates, pellets, and truffles.
Pellets are relatively spherical, more porous aggregates comprised of several ore particles held together in close proximity by the agglomerating fluid. The complete saturation of the pellet pores excludes air. Measured truffle and pellet size distributions are shown in the bottom right and left graphs of Figure 4.1, respectively. All agglomerates smaller than 6 mm consisted exclusively of truffles.

In contrast to truffles that see the same reagent concentrations on their external surfaces, the ore particles in pellets bathe in a stagnant solution saturating the pellet pores. Reagents must therefore first diffuse through the pellet pores before accessing reactive pyrite grains on the external surfaces of the ore particles, and/or further diffusing into the minuscule pores of the same ore particles to reach embedded grains. The truffle model must therefore be altered to reflect these successive phenomena. A comprehensive pellet leaching model would consider both the oxidation kinetics of ore particles forming pellets, as discussed in section 4.1.3.3, and the physical arrangement of ore particles of different sizes within pellets of identical or variable sizes, as illustrated in Figure 4.2.

![Figure 4.2](image-url)

**Figure 4.2** Arrangements of ore particles into pellets showing decreasing levels of model sophistication.

However, considering the contentious reliability and reproducibility of the method employed to evaluate the proportion of truffles and pellets, it is extremely doubtful, if not impossible, to obtain statistically representative figures to represent any variations of particle size distribution between pellets of identical and different sizes. For this reason, pellets of any size will be assumed to contain the same
distribution of ore particles throughout their entire volume, i.e. fine, medium, and coarse particles are homogeneously distributed within the pellet volume. Just like the truffle model, the parameter $\phi$ will represent the average kinetics of the assemblage of fine, medium, and coarse particles forming pellets.

### 4.2 Overall Methodology

The mineral leaching rate expression (Eq. 4-21) requires the evaluation of five kinetic parameters (activation energy $E_a$, $f(C)$, elemental sulfur yield $\varphi$, rate constant $k_o$, and topological exponent $\phi$) for each ore type tested (four of them in Eq. 4-21).

$$\frac{dX}{dt} = k_o \exp \left(-\frac{E_a}{R \left(\frac{1}{T} - \frac{1}{T_0}\right)}\right) \sqrt{\frac{C_{Fe(III)}}{C_{Fe(II)}}} (1 - X)^\phi \tag{4-21}$$

The first three parameters are evaluated from a series of potentiostatic tests performed with a pyrite concentrate in sterile acid ferric sulfate media over the range of temperatures and solution potentials typical of heap conditions. The concentrate was prepared by floating a portion of the ore selected for the large-scale column tests described in chapter 2. Both the ore and the concentrate were found to contain the same sulfide minerals (pyrite, marcasite, arsenopyrite, and chalcopyrite) in the same relative proportions. The grain-scale kinetic experimental testwork is the subject of section 4.3, which outlines the experimental method, grain-scale kinetic model, and analysis of the results. A shrinking-sphere model was chosen to fit the leaching data in order to determine the three parameters needed ($E_a$, $f(C)$, $\varphi$).

An upflow, saturated packed bed reactor operated under a single set of temperature and potential conditions was then employed to determine the topological function of the particle kinetic rate expression. The results of this investigation are presented in section 4.4, together with the modeling strategy for an assemblage of ore particles of different sizes.
4.3 Grain-Scale Kinetic Tests

4.3.1 Materials and Methods

4.3.1.1 Concentrate Preparation

Forty kilograms of ore contained in another drum were ground to less than 100 μm. Each 4 kg batch of ground ore was floated for 10 min with 0.1 L of a 2 g/L sodium isopropyl xanthate solution and 5 mL of methyl isobutyl carbinol frother, followed by three successive cleaning stages. The concentrate produced was washed three times with 0.5 M H₂SO₄, followed by a final rinse with distilled water. The wet concentrate was sieved into several size fractions and air dried. Only particles smaller than 38 μm (400 mesh Tyler sieve) were used in the present experiments and kept in a sealed polyethylene container before use. A small sample of the concentrate, added to a NaCl solution containing Triton X-100 as a dispersant, was subjected to a particle size analysis carried out with the ELZONE® particle size counter. Figure 4.3 depicts the cumulative particle size distribution.

![Cumulative particle size distribution of concentrate.](image-url)
The concentrate contained 41.47 wt% Fe, 1.70% As, 0.47% Cu, 48.63% sulfide, 0.43% sulfate, 0.11% elemental sulfur, and the rest impurities, such as quartz. According to XRD/Rietveld quantification, pyrite, marcasite, arsenopyrite, and chalcopyrite accounted for 84.00, 11.24, 2.72, and 0.60 wt% (within < 2 wt% range of XRD detection) of the concentrate.

4.3.1.2 Apparatus

Experiments were performed in a 2.7 L glass vessel equipped with a water jacket, an overhead reflux condenser, one six-bladed 45° flat disc impeller mounted on a stirring shaft, a sparging tube, three baffles, and an overhead variable-speed stirrer (Figure 4.4). The vessel was sealed with a cover plate equipped with ports to hold probes, as well as a 5” long tube located adjacent to the stirring shaft and into which was inserted a thermocouple. With the exception of the vessel, all parts and fittings were made of stainless steel 316.

Figure 4.4 Experimental set-up (KMnO₄ and H₂SO₄ feed reservoirs not shown).
4.3.1.3 Reactor Preparation

At the beginning of each experiment, a known volume (typically 1 L) of 0.5 M H$_2$SO$_4$ was poured into the vessel. The solution was deaerated for 20 min by blowing nitrogen through the gas sparger while mixing the solution at 800 rpm. The effect of the agitation speed was not investigated as a rotation speed of 800 rpm ensured particle suspension (i.e. off-bottom). Known doses of ferric sulfate (analytical grade Fe$_2$(SO$_4$)$_3$.5H$_2$O) and ferrous sulfate (analytical grade FeSO$_4$.7H$_2$O) were then added. After complete dissolution, the solution potential was measured with a 9” long epoxy body platinum redox electrode (Ag/AgCl reference electrode). The working condition of the redox electrode was checked prior to each test with 5 standards of known Fe(III)/Fe(II) concentration ratio. The solution was heated to the desired temperature, later controlled to within 0.1°C of the desired setpoint by continuously circulating water from an external bath to the jacket. A 5-mL sample of the solution was taken before the addition of the concentrate to determine whether iron precipitation might have occurred during heating, which was never found to be the case. Avoiding precipitation by keeping the solution pH low ensured that iron would remain in solution and would serve as an easily measurable leaching indicator.

The nitrogen supply was shut off; otherwise, the concentrate would have floated to the surface and stuck to the walls of the vessel. Oxygen may have redissolved during the leach because the nitrogen supply was shut off and the sampling ports were opened occasionally. It could then be argued that oxygen and ferric ions would participate in the cathodic reactions. More than thirty years ago, Singer and Stumm [44] concluded, however, that direct pyrite oxidation by oxygen was not significant at pH less than 3.5. Moses et al. [45] supported this finding and reported that pyrite oxidation in a pH 2.0 medium containing ferric ions was at least two orders of magnitude faster than in an oxygen-saturated medium containing no ferric salts. Based on this compelling evidence, and considering the very low solubility of oxygen in a medium of high ionic strength at high temperature, one can ignore the role of dissolved oxygen in these tests.
4.3.1.4 Insights into Potentiostatic Tests

Potentiostatic experiments were designed to test the fit of the type III leaching model. Testing the applicability of the type I leaching model would have been extremely challenging from a computational and experimental standpoint, requiring perpetual changes to the potential setpoint, dictated by the on-line total iron concentration measurements. Suffice it to say that the type III leaching model has provided a very good fit of previously published experimental data.

The $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ activity ratio of Eq. 4–16 is related to the solution potential through the Nernst equation. Adding just enough of a powerful oxidant (e.g. potassium permanganate, potassium dichromate, hydrogen peroxide, ceric sulfate) to reoxidize Fe(II) back to Fe(III) to match the desired controlled potential should maintain the ratio of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ relatively constant during the course of leaching. Such potentiostatic tests have been performed as early as the mid-1980s with chalcopyrite [46] and pyrite [20], and more recently with chalcocite [47].

Potassium permanganate (Mn(VII)) has long been the preferred reagent in such tests because of (1) its high solubility in acidic sulfate media, (2) its large five electrons transferred per mole of Mn(VII) reduced to Mn(II), and (3) its relatively simple chemistry in the pH range of interest (pH 0–2). According to Figure 4.5, Mn(VII) is reduced to Mn(II) in the acidic region. Although not shown in Figure 4.5, a Mn(III) stability region opens up in the very acidic range ($\text{pH} < -2$) at potentials above 1.5 V vs SHE. Increasing the temperature by 50°C has very little influence on the $\text{Mn}^{2+}$ and MnO$_2$ stability regions. Solid, red-brown manganese dioxide (MnO$_2$) forms at potentials exceeding 1.0 V vs SHE.

The timer was turned on when a known amount of concentrate was added into the vessel. The potential immediately fell below the target setpoint. A PID controller activated a peristaltic pump, which delivered just enough of a 0.2 M KMnO$_4$ solution to reoxidize Fe(II) back to Fe(III) and maintain a constant solution potential. The potential was continuously monitored, and if necessary readjusted, throughout the run by the PID controller. The acidity of the leaching solution was also monitored by a KCl-filled pH electrode (saturated with AgCl, Ag/AgCl reference electrode) and
readjusted to the desired setpoint by addition of reagent grade H$_2$SO$_4$. The pH electrode was calibrated at the process temperature with pH buffers 1.0 and 4.0. The volume of H$_2$SO$_4$ and 0.2 M KMnO$_4$ added was also recorded to track any changes in the total volume of leaching solution.

Figure 4.5 Eh-pH diagrams for the Mn-S-H$_2$O system at 25°C (upper figure) and 75°C (lower figure). Activities of ions, complexes, and salts set equal to 1.
An attempt to perform a control test to verify that permanganate was not directly oxidizing the concentrate failed. The procedure consisted of mixing a known amount of pre-washed (24 h, 75°C, 0.5 M H₂SO₄) concentrate with 1 L of 0.5 M H₂SO₄ and 0.4 L of 0.2 M KMnO₄ at 75°C for 24 h. No ferric or ferrous sulfate salt was added prior to adding the concentrate. The pre-wash step aimed at dissolving any iron that would otherwise initiate the leach, consume KMnO₄, and oxidize the sulfides. Before adding permanganate, a constant drop of the slurry potential was noted, possibly indicating iron dissolution. In spite of these difficulties, Boloronduro [47] has demonstrated that chalcocite and covellite samples were not attacked by permanganate during a permanganate control test carried out under similar experimental conditions. It is therefore assumed that no direct interaction exists between pyrite and permanganate.

4.3.1.5 Analytical Methods

About 10 mL of slurry were sampled at regular intervals and centrifuged at 1000 rpm for 5 min. Five mL of supernatant were transferred into another plastic vial. The remaining solution and settled solids were resuspended and returned to the reactor. A 1-mL sample was diluted with 1.0 M HNO₃ in a range suitable for total iron assay by atomic absorption spectrophotometry (ATI Unicam 929 AA spectrophotometer).

At the end of the experiment, the slurry was filtered through a 2-μm filter paper, and the volume of filtrate measured. The residue was washed with 0.5 M H₂SO₄, followed by a final rinse with distilled water. The wash and rinse solutions were added together and their combined volume recorded. The leaching solution and the wash water were assayed for total iron. No soluble sulfur species were assayed.

The residue was left to dry at room temperature. The iron, copper, and arsenic content of the residue were determined by ICP following digestion. The sulfide, sulfate, and elemental sulfur content were assayed independently by two analytical companies using the same analytical methods.
4.3.2 Model Development

4.3.2.1 Grain-Scale Model

Pitting patterns (Figure 4.6) similar to the “cell footprints” reported by previous investigators were observed on the surfaces of the leached sulfide particles, even though all tests were carried out abiotically. Although neither the leaching solution nor the residue were tested for the presence of cells, the high acidity, the use of permanganate, and the sealed lid ports rule out microbial growth. The 30°C experiment was especially susceptible to contamination with mesophiles due to the 40 days of operation. However, the simple fact that the potential remained constant at about 625 mV vs Ag/AgCl, rather than increasing to > 700 mV (as is often observed in column leaching experiments under similar experimental conditions), further substantiates the absence of cells.

Figure 4.6 Chemically-leached pyrite/marcasite grains with corrosion pits.
Figure 4.7  Non-oxidized pyrite/marcasite concentrate grains of various sizes.

The overall extent of oxidation represented the sum of the individual extent of pyrite, marcasite, arsenopyrite, and chalcopyrite oxidation. The latter two sulfide minerals were present in such low amounts (< 3 wt%) that their contribution was ignored. Pyrite, marcasite, arsenopyrite, and chalcopyrite were thus represented by FeS\(_2\). The stoichiometry was assumed to be independent of temperature and solution chemistry, an assumption that was later proven true. The grains before leaching were polyhedral (Figure 4.7). Corners and edges would be the primary sites of attack, transforming the polyhedrons into spheres. No visible product layer of elemental sulfur was observed on the leached particles at any stage of leaching (Figure 4.6), giving reason to select a shrinking-sphere leaching model assuming chemical reaction control.

The anodic current of Eq. 4–6 was related to the conversion by the following equation:

\[
\frac{d n_q}{d t} = n_{0q} \frac{d X_q}{d t} = \frac{A_{aq} i}{Z_a F}
\]

(4–22)
where $X_q$ is the conversion of particles of initial diameter $d_{0q}$, $n_{0q}$ is the total number of moles of pyrite initially contained in particles of initial size $d_{0q}$ (Eq. 4–23), and the subscript $q$ represents a given class of grain size.

$$n_{0q} = \frac{M_0 w_q G}{M} \quad (4-23)$$

where $M_0$ is the total initial mass of concentrate loaded, $w_q$ is the mass fraction of particles of size $d_{0q}$, $G$ is the sulfide content, and $M$ is the molecular weight of pyrite (0.11985 kg/mole). $A_{aq}$ was related to the initial surface area $A_{0q}$ by:

$$A_{aq} = \kappa A_{0q} (1 - X_q)^{2/3} \quad \text{where} \quad A_{0q} = \frac{6M_0 w_q G}{\rho_p d_{0q}} \quad (4-24)$$

where $\rho_p$ is the experimentally measured particle density of 5.135 kg/m$^3$, and $\kappa$ is a proportionality constant less than 1, relating the anodic to total (anodic + cathodic) surface area.

A simplified equation for the conversion $X_q$ was obtained by combining Eqs. 4–22, 4–23 and 4–24 together with Eq. 4–16:

Type III: 

$$\int_0^t \frac{dX_q}{(1 - X_q)^{2/3}} = \frac{6Mk}{\rho_p d_{0q} Z_a} \int_0^t k_{III} \left( \frac{a_3}{a_2} \right)^3 dt$$ 

The conversion $X_q$ was obtained by integrating the left-hand side of Eq. 4–25.

Type III: 

$$1 - X_q = \left[ 1 - k_{III}' \frac{d_{0q}}{a_3} \int_0^t \left( \frac{a_3}{a_2} \right)^3 dt \right]$$

where $k_{III}'$ is a rate constant whose temperature dependence is given by the Arrhenius relationship:

$$k_{III}' = \frac{2Mk \kappa k_{III}}{\rho_p Z_a} \quad (4-26)$$
where \( E_a \) is the activation energy. The overall conversion \( \bar{X} \) was calculated as the weighted sum of all \( X_q \):

\[
1 - \bar{X} = \sum_{q=1}^{Q} w_q \left[ 1 - \frac{k_{II}'}{d_{0q}} \int_{0}^{t} \frac{a_3^s}{a_2^s} dt \right]^3 = \sum_{q=1}^{Q} w_q \left[ 1 - \frac{k_{II}'}{d_{0q}} \int_{0}^{t} \sqrt{\omega} dt \right]^3
\]

where \( Q \) is the number of size classes arbitrarily chosen as 15 based on Figure 4.3, and \( \omega \) is the surface activity ratio. The surface and bulk activities were assumed equal. This assumption is revisited in section 4.3.6.

### 4.3.3 Thermodynamic Model

Free ferric and ferrous ions are among the numerous species formed following the multiple association of the seven elements (\{H\({}^+\}, \{O\({}^2^-\}, \{S\({}^6+\}, \{K\({}^+\}, \{Mn\({}^{2+}\}, \{Fe\({}^{3+}\}, \{e\({}^-\)\}) that define the Fe-S-Mn-K-H\(_2\)O system (Table 4.2). These elements were chosen on the basis of the six compounds (H\(_2\)O, H\(_2\)SO\(_4\), FeSO\(_4\).7H\(_2\)O, Fe\(_2\)(SO\(_4\)).5H\(_2\)O, FeS, KMnO\(_4\)) added, at any given time, to the reactor (Table 4.2). The activity of any species was calculated for every time step using an in-house ion-association speciation program, based on the fact that, at equilibrium, the total Gibbs free energy of the system has its minimum value [48].

When an expression for the total Gibbs free energy is written, the composition that minimizes the total Gibbs free energy of the system subject to material balance constraints must be found. The minimum value for the combined material balances and the total Gibbs free energy function then occurs when its partial derivative with respect to the number of each atom type present equals zero. For any single reaction \(k\) at equilibrium, the Gibbs free energy is given by the expression:

\[
\Delta G_k = \Delta G_k^o + RT \ln K_k = 0
\]
Table 4.2 List of elements, compounds, species, and precipitates present in the acidic iron sulfate potentiostatic experiments, and their thermodynamic parameters.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ΔG° (kJ/mole (25°C))</th>
<th>J°/(mole·K) (25°C)</th>
<th>{H⁺}</th>
<th>{O²⁻}</th>
<th>{S⁶⁺}</th>
<th>{K⁺}</th>
<th>{Mn²⁺}</th>
<th>{Fe³⁺}</th>
<th>{e⁻}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeSO₄₂⁻.H₂O</td>
<td>-157.3</td>
<td>-10.9</td>
<td>14</td>
<td>11</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂(SO₄)₃.5H₂O</td>
<td>-744.6</td>
<td>20.1</td>
<td>10</td>
<td>17</td>
<td>3</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeS₂</td>
<td>-756.0</td>
<td>131.8</td>
<td>2-φ</td>
<td></td>
<td>1</td>
<td></td>
<td>15-6φ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 M KMnO₄</td>
<td>555.1</td>
<td>281.6</td>
<td>1</td>
<td>1</td>
<td>-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When there is equilibrium between j species the expression becomes:

$$\Delta G_k = \sum_j v_{jk} (\Delta G_j^0 + RT \ln a_j) = 0$$  \hspace{1cm} (4-30)

where \(a\) is the activity of species \(j\) and \(v_{jk}\) is the stoichiometric factor for species \(j\) in reaction \(k\). By defining Lagrange’s unspecified multipliers such that for any species \(j\) composed of elements \(i\):

$$\Delta G_j^0 + RT \ln a_j + \sum_i \alpha_{ij} \lambda_i = 0$$  \hspace{1cm} (4-31)

where \(\alpha_{ij}\) is the number of elements \(i\) involved in species \(j\), then for all values of \(\lambda\):
To find a solution, the standard Gibbs free energy functions must be solved simultaneously for all species \( j \) (Eq. 4-31) and the set of mole balances for all elements \( i \):

\[
\sum_j v_{jk} \alpha_j \lambda_j = 0
\]  

(4-32)

For dissolved species:

\[
\ln a_j = \ln m_j + \ln \gamma_j
\]  

(4-34)

For precipitates:

\[
\ln a_j = 0
\]  

(4-35)

where \( m \) is the molality and \( \gamma \) is the activity coefficient. Davies’ rule has been invoked to calculate the activity coefficient:

\[
\ln \gamma_j = -A_v z_j^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \right)
\]  

(4-36)

where \( z \) is the ionic charge, and \( A_v \) is the Debye-Hückel temperature-dependent parameter \( (A_v = 1.17 \text{ at } 25^\circ \text{C}) \), and \( I \) is the ionic strength, defined thus:

\[
I = \frac{1}{2} \sum_j m_j z_j^2
\]  

(4-37)

The program makes use of the standard Gibbs free energy, \( \Delta G^0 \), entropy, \( S \), and heat capacity, \( C_p \), data of each solute and precipitate. Even though there might have already been \( \Delta G^0 \) values available in the literature for iron sulfato-complexes, in the interest of internal consistency, these \( \Delta G^0 \) values were instead calculated using a set of equilibrium constants, \( K \), at 25°C and zero ionic strength, together with well-known \( \Delta G^0 \) values for \( \text{H}^+, \text{SO}_4^{2-}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{K}^+ \) and \( \text{Mn}^{2+} \) [49,50] (Table 4.2). Only \( \text{H}_2\text{O} \) was included as a precipitate since the high, controlled acidity of the medium (0.5 M \( \text{H}_2\text{SO}_4 \)) precluded the formation of ferric hydroxide and potassium jarosite. Furthermore, assays of the residue confirmed that very little, if
any, iron and manganese precipitated as jarosite and manganese dioxide, respectively.

The temperature and the initial number of moles of $\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4$, $\text{FeSO}_4\cdot7\text{H}_2\text{O}$, and $\text{Fe}_2(\text{SO}_4)_3\cdot5\text{H}_2\text{O}$, prior to adding the concentrate and the permanganate, were first included into the program to calculate the proton activity (pH) and the solution potential of the medium at time zero. The solution potential was given by:

$$E_h = -2.303\frac{RT}{F}\log a_e = \frac{RT}{F} e^{-}$$

(4-38)

where $E_h$ represents the potential with respect to the standard hydrogen electrode. To compare this value to the measured potential expressed in Ag/AgCl, a value of 223 mV was added to the $E_h$ value. With knowledge of the sulfate yield and the amount of $\text{KMnO}_4$ added at any given time, the number of moles of $\text{FeS}_2$ and $\text{H}_2\text{SO}_4$ were guessed, by trial and error, to achieve the same initial pH and potential previously recorded. Values of $m_j$ and $a_j$ were calculated after each iteration.

### 4.3.4 Yield vs $\text{KMnO}_4$ Additions

Nine stirred-tank experiments were initiated by adding 20 g of concentrate into 1 L of 0.5 M $\text{H}_2\text{SO}_4$ preheated to the desired temperature. The solution contained 0.56 g/L total iron as $\text{FeSO}_4\cdot7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3\cdot5\text{H}_2\text{O}$ salts to yield the desired nominal $[\text{Fe(III)}]/[\text{Fe(II)}]$ ratio (Table 4.3). By the end of the test, the pulp density had dropped from 2 to 0.3% while the total iron concentration had increased from 0.56 to $\approx 3.2$ g/L. The experiments were not repeated.

The measured yield was calculated as the weight ratio of elemental sulfur produced to sulfide decomposed. Three independent assays (1 – iron in residue, 2 – sulfide in residue, 3 – soluble iron in leachate/wash water/samples collected) were performed to determine the mass of sulfide oxidized. Table 4.3 reveals inconsistencies among the data calculated with method 3 – soluble iron; more $\text{FeS}_2$ seems to have been leached than loaded into the vessel. The three conversion results for a given test were not randomly distributed; the conversion calculated
using method 3 was always larger than that obtained with method 1, which was itself larger than that determined with method 2. Even using the same analytical method for measuring the sulfide sulfur content, the two analytical companies produced sulfide grade data with discrepancies of up to 7.9% for the same sample (for instance, 14.1 vs 22.0 wt%). Therefore, the exact amount of sulfide remaining cannot be precisely known. At best, the average of the three, or four, conversion points can be used to calculate the measured yield.

<table>
<thead>
<tr>
<th>Test</th>
<th>T (°C)</th>
<th>[Fe(III)]/[Fe(II)]</th>
<th>Final oxidation (%)</th>
<th>Leachate Method 3</th>
<th>Avg.</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Residence</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Method 1</td>
<td>Sulfide-1 Method 2</td>
<td>Sulfide-2 Method 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>30</td>
<td>284</td>
<td>93.2</td>
<td>93.1</td>
<td>99.9</td>
<td>95.4</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>304</td>
<td>91.1</td>
<td>89.4</td>
<td>92.0</td>
<td>90.8</td>
</tr>
<tr>
<td>C</td>
<td>47</td>
<td>291</td>
<td>93.6</td>
<td>90.7</td>
<td>94.0</td>
<td>91.9</td>
</tr>
<tr>
<td>D</td>
<td>55</td>
<td>307</td>
<td>94.7</td>
<td>92.1</td>
<td>95.3</td>
<td>105.5</td>
</tr>
<tr>
<td>E</td>
<td>65</td>
<td>279</td>
<td>96.5</td>
<td>91.9</td>
<td></td>
<td>102.9</td>
</tr>
<tr>
<td>F</td>
<td>75</td>
<td>270</td>
<td>96.1</td>
<td>96.2</td>
<td>96.3</td>
<td>96.7</td>
</tr>
<tr>
<td>G</td>
<td>55</td>
<td>30</td>
<td>94.3</td>
<td>93.2</td>
<td></td>
<td>105.2</td>
</tr>
<tr>
<td>H</td>
<td>55</td>
<td>70</td>
<td>94.7</td>
<td>92.7</td>
<td>95.3</td>
<td>97.1</td>
</tr>
<tr>
<td>I</td>
<td>55</td>
<td>120</td>
<td>95.5</td>
<td>93.6</td>
<td></td>
<td>98.6</td>
</tr>
</tbody>
</table>

The measured yield seems relatively independent of temperature over the range from 30 to 75°C (Figure 4.8), corroborating the findings of Biegler and Swift [1]. This opposes the observations of King and Perlmutter [6] who showed that the yield increased from 20 to 60% over the same temperature range.

The [Fe(III)]/[Fe(II)] ratio values between 3 and 300 did not affect the measured yield (Figure 4.9). Yet, three independent studies [6,7,9] have demonstrated experimentally that the yield increased from 60 to 90% with an increase in solution potential from 457 to 758 mV vs Ag/AgCl (same experimental range as present experiments). The potential is related to the Fe$^{3+}$/Fe$^{2+}$ activity ratio through the Nernst equation.
Figure 4.8 Influence of temperature on measured sulfate yield.

Figure 4.9 Influence of [Fe(III)]/[Fe(II)] ratio on measured sulfate yield.
The permanganate requirements per unit of pyrite oxidized are directly influenced by the sulfate yield (Eq. 4-1). An electron charge balance was performed to determine whether the amount of permanganate added and the theoretical amount predicted were the same. After executing the first step of the approach laid out in section 4.3.3, the number of moles of KMnO₄ and H₂SO₄ were guessed until convergence, knowing the number of moles of FeS₂ reacted by the end of the test and assuming that the measured yield was exact. Figure 4.10 shows discrepancies of (+10) to (+25)% between the measured and predicted KMnO₄ additions.

![Figure 4.10 Discrepancy between measured and predicted KMnO₄ addition. The predicted addition was calculated using the measured yield as an input parameter of the thermodynamic program.](image)

According to the predictions, an additional 80 to 250 mL of 0.2 M KMnO₄ solution should have been added. Arguments supporting the exactness of the KMnO₄ additions are listed below:

- The balance employed to monitor the KMnO₄ additions is a reliable instrument.
- The possibility that the molarity of the KMnO₄ stock solution was larger than 0.2 M must also be rejected given that the mass of KMnO₄ added in the stock...
solution was carefully weighed. Furthermore, some permanganate ions in the stock solution might have in fact oxidized some unknown reductants present in the deionized water used to make up the stock, thereby lowering the actual concentration.

- Notwithstanding the fact that assays have confirmed the absence of manganese precipitates in the residue, and that Mn$^{3+}$ species exist only in solution of extremely high acidity ([H$^+$] > 100 M) (Figure 4.5), the possibility of MnO$_2$ and Mn$^{3+}$ being formed must also be rejected on the basis that fewer electrons are transferred during the reduction of Mn(VII) to Mn(IV) or Mn(III). Thus more permanganate would have had to be added to control the potential to the same desired setpoint.

- The only other oxidant present in this Fe–Mn–K–S–H$_2$O system was oxygen. Its role in the overall cathodic reactions was ignored in developing the electrochemical model (section 4.3.2.1) on the basis of conclusive evidence.

These arguments give credence to the fact that KMnO$_4$ is the ultimate oxidant in this system where Fe(II) and Fe(III) ions are perpetually replenished and consumed. Thus how would the yield change if in fact the volume of KMnO$_4$ added were exact? This question is answered by inputting into the same thermodynamic program the total number of moles of FeS$_2$ reacted and KMnO$_4$ added, and searching this time for the value of the yield. Not surprisingly, Figure 4.11 reveals that the predicted sulfate yields were consistently smaller than the experimental ones over the entire range of temperatures and potentials tested. Between 6.6 and 19.1% (average of 13.2%) separated the predicted and measured yields.
The predicted yields suggest that more soluble or insoluble sulfur species would have been produced at the expense of sulfate. In the analysis of the data, sulfate and elemental sulfur have been assumed thus far to be the only two sulfur products. Several investigators have postulated the mechanism of pyrite oxidation as involving the formation of sulfoxyl intermediates, most notably thiosulfate \([3, 51, 52]\). Thiosulfate is highly unstable in acid, and disproportionates rapidly into elemental sulfur and sulfite, which, in turn, is quickly oxidized by Fe(III) to sulfate, such that intermediate sulfoxyl anions \((\text{SO}_3^{2-}, \text{S}_2\text{O}_3^{2-}, \text{S}_n\text{O}_6^{2-})\) are not detected. Elemental sulfur and sulfate, and of course any unreacted sulfide, seem to be ultimately the only sulfoxyl species present in the system. That is why the residue was assayed only for elemental sulfur, sulfate, and sulfide. Given that the elemental sulfur assay is key to calculating the yield, the discrepancy between the predicted and measured yields casts doubt on the total amount of elemental sulfur. Two analytical laboratories have assayed the same sample, and found about the same amounts of elemental sulfur. Thus, the accuracy of the analytical assay is not in dispute. Could it be that part of the elemental sulfur generated may have been

Figure 4.11 Experimentally measured and predicted sulfate yield.
lost during sampling, shutdown, and filtration? Calculations based on the predicted yields suggest that about 20 to 40% of the elemental sulfur would have been lost, which amounts to 0.52 to 1.38 g unaccounted for experimentally.

Figure 4.12 shows that elemental sulfur appeared as particles of $\approx 2$ μm in diameter. They were distinct from the remaining coarse pyrite grains (> 10 μm). This observation supports the mechanism of formation and subsequent disproportionation of sulfoxyl intermediates during pyrite oxidation. In addition, the strong hydrophobic nature of these particles made them adhere to any surfaces located above the waterline within the vessel during leaching. It is thus very plausible that some of the elemental sulfur formed may have been lost during washing, or could even have passed through the 2-μm filter paper.

![Figure 4.12 Abundance of discrete elemental sulfur particles surrounding the few remaining coarse pyrite grains.](image)

The fact that so much elemental sulfur could have been unaccounted for experimentally, plus the fact that no sulfur species other than sulfate were assayed in the leachate, challenges once again the premise that the predicted yields are
exact. The arguments put forth to support this hypothesis now seem to lack credibility. To confirm this hypothesis, the data collected from the third of our three independent methods is used to determine the extent of sulfide oxidation. The oxidation can also be calculated as the ratio of the amount of iron present in solution at any given time, minus the iron added at time zero before the concentrate addition, over the total iron charged with the concentrate. The iron in solution is obtained by taking solids-free liquid samples from the vessel at different time intervals, assaying them for total soluble iron, and multiplying the iron concentration by the volume of solution within the vessel.

Figure 4.13 presents the conversion data as solid squares, obtained from soluble iron data. Each point on the other two curves was calculated using (1) the thermodynamic program, (2) the actual total volume of permanganate added after that time, and (3) the predicted or measured yield. It is worth noting that the yields calculated thus far, whether measured or predicted, are those of the final residue. Because no solid samples were collected during the leach, one cannot confidently say that the yield didn't change during the course of leaching. However, inspection of Figure 4.11 reveals that there exists little variation of the predicted yields despite significant changes of temperature and ferric to ferrous ratio among the tests performed. On that basis the predicted yields were used to calculate intermediate oxidation data points.

Figure 4.13 displays the tests for which the smallest and largest discrepancy between predicted and measured yields, respectively, was noted in Figure 4.11. There is perfect agreement between the iron-based conversion data and the predicted oxidation points during the steep-rise portion of both curves. Small deviations (< 5%) observed in the plateau are at least partially explained by the inaccuracy of the total solution volume as a result of evaporative losses (average volume loss of 2.7%). The solution volume is indeed essential to calculate the total mass of soluble iron. Nevertheless, the gap between the conversion data and the oxidation points calculated with the measured yields is clearly larger than with the predicted yields. These plots appear to confirm the exactness of the predicted yields (Figure 4.11) using the permanganate method.
Figure 4.13 Comparison of true and predicted oxidation profile of test F – smallest difference between predicted and measured yields (above) and test I – largest difference (below).
A fourth independent method could have been used to corroborate the iron-based oxidation profile. The technique consists of performing several replicates of the same leaching test, stopping each one after a predetermined time and assaying the whole residue for iron and sulfide. This labor-intensive and time-consuming method was not employed in this work primarily because of the limited amount of concentrate available.

In summary, according to the permanganate method and thermodynamic calculations, each unit of sulfide sulfur oxidized generated approximately 0.4 unit of elemental sulfur and 0.6 unit of sulfate. The sulfur yield, $\phi$, is thus evaluated at 0.8 mole sulfur/mole pyrite oxidized.

### 4.3.5 Electrochemical Model Fits

The general procedure for calculating the rate constant, $k_{III}^\prime$, consisted first of determining the activity of Fe$^{3+}$ and Fe$^{2+}$ for 10 time steps for each of the 9 tests. The integral of Eq. 4-28 was calculated using the trapezoid rule. The model parameter, $k_{III}^\prime$, was estimated for each test using the SOLVER function of MICROSOFT® EXCEL 2000 to find the minimum value of the sum of squares of the residuals ($X_{predicted} - X_{experimental}$).

#### 4.3.5.1 Effect of Fe$^{3+}$/Fe$^{2+}$ Activity Ratio

The first series of tests examined the effect of the initial Fe(III) to Fe(II) concentration ratio of 30, 70, 120, and 300 at 55°C. The actual Fe$^{3+}$/Fe$^{2+}$ activity ratios, $\omega$, were found to be 4.0, 9.1, 15.0, and 40.6, respectively. The effect of the activity ratio on pyrite conversion is shown in Figure 4.14. The type III leaching model fits very nicely most data points below 90% conversion. With the exception of only one of the four values, $k_{III}^\prime$ was found to be about 1.16 $\mu$m/d at 55°C.
Another way of proving that the rate is proportional to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ activity ratio to the ($+\frac{1}{2}$) power consists of plotting the experimental rates per unit surface area ($= Z_a r_0/A_{aq} = i_0/F$ from Eq. 4–6) against the ratios ($= a_3^s/a_2^s$ from Eq. 4–16) on a log-log graph. The data points should form a straight line with a slope equal to 0.5. Evaluating the experimental rates is, however, difficult without knowledge of the true particle surface area, and even more so with a distribution of particle sizes.

The model fits always reach 100% conversion, whereas the experimental data plateau around 95%. Indeed, SEM photographs confirmed the presence of residual coarse sulfide grains in the residue. Furthermore, several oxidation profiles predicted with permanganate data display a plateau above 90% conversion. Underestimation of the coarsest size fraction or formation of a passivating nanolayer of elemental sulfur or polysulfide [9] are two possible explanations as to why the oxidation seems to cease before the last sulfide grain has disappeared. Holmes and Crundwell [9] have shown, however, that a layer of polysulfide
detected by Raman and XPS analysis on leached pyrite particles did not impede the progress of the reaction.

4.3.5.2 Effect of Temperature

The second series of tests investigated the effect of temperature at 30, 40, 47, 55, 65, and 75°C at the same initial Fe(III) to Fe(II) concentration ratio of \( \approx 300 \). Although the nominal ratio may have been the same, the effect of temperature not only manifested itself in the rate, but also changed the actual \( \omega \) ratio \( (a_{Fe^{3+}}^s / a_{Fe^{2+}}^s) \).

This ratio remained more or less constant throughout each test, and took values of 27.6, 33.2, 34.0, 40.6, 43.2, and 60.8 at the respective temperatures listed above.

Figure 4.15 illustrates the effect of temperature on pyrite conversion. Once again, there is very good agreement between the model fits and experimental data.

![Figure 4.15](image)

The activation energy, \( E_a \), is the slope of the line joining the six \((1/T, \ln k_{III})\) points. Before plotting the data, the fitted \( k_{III} \) values must be corrected for the effect of
temperature on the activity ratio. Indeed, adding the same amounts of FeSO$_4$.7H$_2$O and Fe$_2$(SO$_4$)$_3$.5H$_2$O salts into a H$_2$SO$_4$ solution heated to different temperatures yields increasing $\omega$ ratios with increasing temperatures. This effect is currently lumped into the fitted $k_{III}'$ values. The true $k_{III}'$ values were calculated in Eq. 4-39 using the $\omega_T$ ratio at a reference temperature $T_0$ chosen arbitrarily among the 6 temperatures tested.

$$k_{III-lumped}' \sqrt{\omega_T} = k_{III-true}' \sqrt{\omega_{T_0}}$$  

(4-39)

The Arrhenius activation energy was found to be 76.4 kJ/mole after correction of the rate constants (Figure 4.16). Without correction, the calculations underestimated the activation energy at 69.4 kJ/mole. The overall dissolution of pyrite is thus chemically controlled.

![Arrhenius plot for determining the effect of temperature.](image)

Figure 4.16  Arrhenius plot for determining the effect of temperature.

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4.3.6 Assumption Validation

Pyrite oxidation with ferric ions as oxidant conforms to the type III, chemical-controlled shrinking-sphere model, as given by the following equation:

\[
\frac{dX}{dt} = \frac{4.8 \cdot 10^{-8} \text{[m/h]}}{d_0 \text{[m]}} \exp\left[-9193\left(\frac{1}{T} - \frac{1}{328.15}\right)\right] \sqrt{\frac{a_3}{a_2}} (1 - X)^{2/3}
\]  \hspace{1cm} (4-40)

where the rate is strongly dependent on the temperature and activity ratio. Before determining whether the surface and bulk activities are the same, an expedient simplification is introduced in Eq. 4-40 to reflect the fact that the heap leaching model does not yet include a thermodynamic subroutine dealing with speciation. The activities of Fe\(^{3+}\) and Fe\(^{2+}\) are replaced by the concentrations of Fe(III) and Fe(II), respectively.

The speciation program was employed to establish a relationship between the free ion activity ratio and the total ion concentration ratio at a constant temperature. Figure 4.17 demonstrates that the two ratios are related through a temperature-dependent proportionality constant. The square root of the proportionality constant could not be fitted to a van’t Hoff function (Eq. 4-41). It could otherwise have been easily integrated into Eq. 4-40 as part of the existent Arrhenius relationship.

\[
\sqrt{\frac{a_3}{a_2}} = \sqrt{\frac{1}{k} \frac{C_{Fe(III)}}{C_{Fe(II)}}} = \frac{1}{k_0} \exp\left(-\frac{E_o}{RT}\right) \sqrt{\frac{C_{Fe(III)}}{C_{Fe(II)}}}
\]  \hspace{1cm} (4-41)
Instead, the pre-exponential constant and the activation energy were refitted using the method described in section 4.3.5 and the concentration data obtained from the speciation software for each time step (Eq. 4-42):

$$ k_a \exp\left[-\frac{E_a}{RT}\right] \sqrt{\frac{a_3^s}{a_2^s}} = k_c \exp\left[-\frac{E_c}{RT}\right] \sqrt{\frac{C_{Fe(III)}^s}{C_{Fe(II)}^s}} $$

where the subscripts $a$ and $c$ refer to activity- and concentration-based, respectively. The rate expression based on the concentration ratio takes the form:

$$ \frac{dX}{dt} = \frac{3.9 \cdot 10^{-8} \, [m/h]}{d_0 [m]} \exp \left[ -9302 \left( \frac{1}{T} - \frac{1}{328.15} \right) \right] \sqrt{\frac{C_{Fe(III)}^s}{C_{Fe(II)}^s}} (1 - X)^{2/3} \quad (4-43) $$

As shown in Figure 4.18 and Figure 4.19, there is little or no perceptible difference between the fits of Eqs. 4–40 and 4–43.
Figure 4.18  Shrinking-sphere concentration-based model fits showing the influence of temperature on pyrite conversion at 800 rpm and \([\text{Fe(III)}/\text{Fe(II)}] = 300\).

Figure 4.19  Shrinking-sphere concentration-based model fits showing the influence of the \([\text{Fe(III)}/\text{Fe(II)}]\) ratio on pyrite conversion at 800 rpm and 55°C.
Let us now turn our attention to the matter of a potential mass transport limitation. In section 4.3.2.1, it was assumed that the activities (now concentrations) of the ferric and ferrous ions at the mineral surfaces were equal to the bulk concentrations. Surface concentrations are related to the bulk concentrations through a mass transfer equation describing the diffusion through the stagnant boundary liquid layer around a particle. Equating the chemical reaction and mass transfer rates, both expressed per unit surface area of particle, yields:

\[ k_{s/l, Fe(III)} \left( C^s_{Fe(III)} - C^b_{Fe(III)} \right) = \nu_{Fe(III)} \frac{n}{A} \frac{dX}{dt} \]  

(4-44)

\[ k_{s/l, Fe(II)} \left( C^s_{Fe(II)} - C^b_{Fe(II)} \right) = \nu_{Fe(II)} \frac{n}{A} \frac{dX}{dt} \]  

(4-45)

where \( k_{s/l} \) is the solid/liquid mass transfer coefficient (m/h) under the operating conditions of the stirred-tank reactor, \( n \) is the number of moles of pyrite in a particle, \( A \) is the surface area of the pyrite particle, and \( \nu \) is the stoichiometric coefficient (mole/mole FeS\(_2\)). Only the initial stage of the leach, when practically no pyrite has been oxidized, is considered. Eqs. 4-44 and 4-45 can be written in terms of the initial particle size, \( d_0 \), as follows:

\[ \nu_{Fe(III)} \frac{n_0}{A_0} \frac{dX}{dt} = \nu_{Fe(III)} \frac{\rho_p G 4\pi \left( \frac{d_0}{2} \right)^3}{6M} \frac{dX}{dt} = \nu_{Fe(III)} \frac{\rho_p G d_0}{6M} \frac{dX}{dt} \]  

(4-46)

\[ \nu_{Fe(II)} \frac{n_0}{A_0} \frac{dX}{dt} = \nu_{Fe(II)} \frac{\rho_p G d_0}{6M} \frac{dX}{dt} \]  

(4-47)

where \( G \) is the pyrite grade (kg FeS\(_2\)/kg ore), \( M \) is the molecular weight of pyrite (0.11985 kg/mole), and \( \rho_p \) is the particle density (5,135 kg/m\(^3\)). The particle size is eliminated from the above two expressions by replacing \( dX/dt \) with Eq. 4-43:

\[ k_{s/l, Fe(III)} \left( C^s_{Fe(III)} - C^b_{Fe(III)} \right) = \nu_{Fe(III)} \frac{3.9 \times 10^{-8} \rho_p G}{6M} \exp \left[ -9302 \left( \frac{1}{T} - \frac{1}{328.15} \right) \right] \sqrt{\frac{C^s_{Fe(III)}}{C^s_{Fe(II)}}} \]  

(4-48)
This system of two non-linear equations may be solved for \( C_{Fe(II)}^s \) and \( C_{Fe(III)}^s \). Assuming the two mass transfer coefficients to be equal, Eqs. 4-48 to 4-49 may be combined to yield the following equation:

\[
\frac{-v_{Fe(III)}}{v_{Fe(II)}} \left( C_{Fe(II)}^s - C_{Fe(II)}^b \right) = \frac{C_{Fe(III)}^b}{C_{Fe(II)}^s} - \frac{1}{\frac{1}{\rho_p G} \exp \left[ -9302 \left( \frac{1}{T} - \frac{1}{328.15} \right) \right]} \sqrt{\frac{C_{Fe(III)}^s}{C_{Fe(II)}^s}} \tag{4-50}
\]

where \( Da \) is Damköhler's second number expressing the ratio of the chemical reaction rate to the mass transfer rate, given by:

\[
Da = \frac{3.9 \cdot 10^{-8} [\text{m/h}] \exp \left[ -9302 \left( \frac{1}{T} - \frac{1}{328.15} \right) \right]}{k_{sl}[\text{m/h}]} \tag{4-51}
\]

The mass transfer coefficient can be estimated from the Ranz and Marshall correlation [53] for free-falling spheres:

\[
Sh = \frac{k_{sl} d_0}{D} = 2 + 0.6 \Re^{1/2} \Sc^{1/3} = 2 + 0.6 \left( \frac{\rho_d u}{\mu} \right)^{1/2} \left( \frac{\mu}{\rho D} \right)^{1/3} \tag{4-52}
\]

where \( Sh \) is the Sherwood number, \( Re \) is the Reynolds number, \( Sc \) is the Schmidt number, \( D \) is the diffusivity (\( \approx 1 \times 10^{-9} \text{ m}^2/\text{s} \)), \( \rho \) is the medium density (\( \approx 1,000 \text{ kg/m}^3 \)), \( \mu \) is the medium viscosity (\( \approx 1 \times 10^{-3} \text{ Pa·s} \)), and \( u \) is the slip velocity between the fluid and a particle. The latter is approximated as the terminal velocity of the particle given by Stokes law for \( Re < 1 \):

\[
u_t = \frac{d_0^2 g (\rho_p - \rho)}{18 \mu} \tag{4-53}
\]

To prove whether the potentials selected in the present experiments fall under mass-transfer limitations, the terminal velocity, the mass transfer coefficient, and
The Da number were calculated for a typical test carried out at 55°C in 1 L of solution containing 3 g/L total iron and 20 g of 15 μm-size concentrate grading 95 wt% FeS₂. The terminal velocity, the Sh number, the mass transfer coefficient, and the Da number were found to be: 5.07×10⁻⁴ m/s, 2.52, 1.7×10⁻⁴ m/s (= 0.61 m/h) and 6.4×10⁻⁸, respectively.

The surface Fe(III)/Fe(II) concentration ratio was plotted against the bulk concentration ratio for a range of Da values encompassing the calculated one (Da = 6.4×10⁻⁸). Figure 4.20 demonstrates that the diffusion of ferrous ions away from the mineral surface is clearly rate limiting above a threshold ratio that is proportional to the Da number. This implies that while the bulk and surface ferric ion concentrations are the same, the ferrous ion concentration is larger at the surface than in the bulk. This holds the surface ratio (or potential) to a lower level than in the bulk.

Figure 4.20 Influence of the Da number on the bulk and surface [Fe(III)]/[Fe(II)] ratios for a total iron concentration of 3 g/L and particles of FeS₂.

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According to Figure 4.20, deviations from the diagonal for ratios between 30 and 300 for Da values less than or equal to approximately $10^{-7}$ are small enough to justify making the assumption in the first place. This graph explains also why an attempt at testing a Fe(III)/Fe(II) concentration ratio of 816, which eventually failed in the later stages due to operational troubles, hinted, nonetheless, that the initial rate would be the same as a test carried out at Fe(III)/Fe(II) of 300. Boon and Heijnen [54] have also observed the leaching rate of pyrite to reach a maximum at potentials above 700 mV vs Ag/AgCl (30°C) at 600 rpm. They also concluded that Fe(II) mass transfer was rate limiting at higher potentials.

4.4  Particle–Scale Kinetic Tests

The main purpose of the previous grain-scale kinetic investigation was to determine the temperature and chemistry functions of the particle kinetic model, as well as the elemental sulfur yield. These parameters will now serve as the basis for modeling the topological kinetics of the same sulfide grains disseminated throughout a gangue matrix of quartz.

4.4.1  Modeling Strategy

Measuring the leaching kinetics of a representative sample of truffles or pellets is an ill-conceived experimental plan. The leaching kinetics of the assemblage tested would not necessarily fit another ore assemblage having a different size distribution, thus requiring further testwork. In this investigation, a more flexible approach is employed to evaluate the rate constant $k_0$ and the topological exponent $\phi$ of any assemblage, as presented graphically in Table 4.4.
First, the leaching kinetics of several particle size fractions are measured separately under conditions of constant temperature and solution potential to obtain a set of $(t,X)$ experimental data for each size fraction $q$ tested (step 1). Since the objective of the work is to model a distribution of ore particles of different sizes as single-size particles, the leaching profile of each size fraction is not modeled separately. Instead, each $X$ for a given size fraction $q$ is first multiplied by its weight fraction, $w_q = F(d_{\text{upper size range}}) - F(d_{\text{lower size range}})$, obtained from a cumulative size distribution plot. All weighted $X_q$ for the same $t$ are added together to construct a single, overall weighted conversion plot (step 2):
where $G$ is the sulfide head grade of the $q$ particle size fraction, $w$ is the weight fraction, $Q$ is the number of size fractions tested, and $X$ is the conversion from each of the actual experimental oxidation profiles. The last step consists of fitting the two, as yet unknown model parameters of Eq. 4–21 using the series of points $(t, \overline{X})$.

### 4.4.2 Experimental Methodology

#### 4.4.2.1 Procedures

The same pyritic refractory gold ore particles contained in another drum were sieved into six size classes ($-12.7+9.5$, $-8+6.35$, $-4+3.35$, $-2.36+2$, $-2+1$, $-0.425+0.3$ mm), washed with tap water, and dried. Each batch was successively riffled and split to collect about 200 g for head assay. With the exception of the smallest particles, a weighed amount (typically 1–2 kg) of each fraction was loaded into a 40-cm long column 7 cm in diameter, standing upright in a water bath kept at 60–65°C. The same solution contained in an insulated, stirred reservoir irrigated all columns. 1.3 g FeSO$_4$.7H$_2$O, 350 g Fe$_2$(SO$_4$)$_3$.5H$_2$O, and 192 g H$_2$SO$_4$ were initially dissolved in 80 L of deionized water to yield a pH of 1.65, a total iron concentration of 1 g/L, and a $[\text{Fe(III)}]/[\text{Fe(II)}]$ ratio of $\approx$ 300.

The feed solution was pumped rapidly from the reservoir through a heat exchanger tube immersed in the water bath. The solution was injected at the bottom of the bed. The overflowing solution was recirculated back to the reservoir, where a platinum combination redox electrode (Ag/AgCl reference, Sure-Flow junction-type model from Thermo Orion to prevent jarosite from clogging the junction) connected to a controller would detect drops in potential and automatically activate a pump to deliver 0.2 M KMnO$_4$. The KMnO$_4$ stock was eventually replaced by 30% w/v H$_2$O$_2$ because of the unexpected formation of manganese dioxide and subsequent
uncontrolled addition of KMnO₄. The pH was not controlled. Evaporative losses were compensated by periodic addition of deionized water. Leaky tubes and fittings, formation of manganese dioxide, and evaporative losses were reasons for discarding the leftover, spoiled feed solution and replenishing the reservoir with fresh solution intermittently. Nitrogen was blown in the reservoir to prevent microbial growth. Although neither the solution nor the ore were assayed for cell numbers, the fact that the potential kept dropping when the potential control mode was purposely deactivated, thus requiring the continuous addition of H₂O₂ during the three months of testing, seems to rule out contamination.

The pumps were turned on when the temperature in the reservoir reached 60°C. The pumping rate was adjusted to about 0.1 L/min such that the difference in potential between the inlet and outlet ports of the column would not exceed 40 mV. The columns and the reservoir soon reached the same temperature (≈ 55°C). The columns were taken apart at a predefined time (which varied with particle size) by first turning off the pump and draining the filling solution. Fine jarosite precipitates were easily washed off from the coarser particles with deionized water, which were then further washed and air dried. The intact and broken dried particles were weighed precisely, riffled, and split to collect one or two ≈ 75-g samples. The samples were pulverized and assayed for sulfide grade. The oxidation percentage was calculated from the head grade and the total residual sulfide amount, and corrected for the sulfide sulfur that would have leached, at least partially, if it had not been collected previously for assay. The remaining particles were weighed and reloaded into the column. This sampling/shutdown procedure was repeated about five times during the experiment to get a broad sulfide oxidation profile.

Anticipating that the potential drop across a bed of particles ranging in size between 0.3 and 0.425 mm would be much larger than 40 mV, a stirred tank configuration was preferred for this size fraction. Approximately 700 g of particles were added instantly in a 20-L stirred-tank vessel containing a preheated (55°C) ferric sulfate leaching solution (38.4 g H₂SO₄, 0.27 g FeSO₄·7H₂O, and 69.9 g Fe₂(SO₄)₃·5H₂O dissolved in 16 L deionized water). The vessel stood in a water bath kept at ≈ 60°C, and was equipped with one four-blade flat disc impeller mounted on a
stirring shaft, an overhead variable-speed stirrer, a N₂-sparger, and a redox electrode of the same model. The potential was held constant by addition of 0.2 M KMnO₄.

The overhead stirrer and the controller were turned off at preset times prior to the whole content of the reactor being filtered on a 2-μm filter paper. The filtrate was disposed of, while the wet solids (jarosite plus remaining particles) were successively dried, weighed, riffled, split, and sampled according to the method described above. The remaining solids were weighed and reloaded into the same vessel, which contained a new, preheated batch of solution. This sampling procedure was also repeated several times.

4.4.2.2 Assumption Verification

The Fe(III)/Fe(II) concentration ratio was thus set and controlled to 300 in the bulk solution. The electrochemical reaction of FeS₂ grains in stirred tanks was shown in section 4.3.6 to be the rate-limiting step at Fe(III)/Fe(II) concentration ratios less than 300. To determine whether this is also true in saturated fixed beds, the rates of mass transfer and chemical reaction are revisited. The right-hand side term of Eq. 4-44 represents the number of moles of Fe(III) consumed per unit time per surface area where ion transfer takes place. Reaction and transfer surfaces are the same for pyrite grains. That is why A in Eq. 4-44 was defined as the surface area of spherical grains of size \(d_0\). As for particles containing grains of pyrite, reaction still occurs on the grain surfaces, but Fe(III) and Fe(II) ion transfer can occur both on, and in the vicinity of, the sulfide grains. Eq. 4-46 must be corrected to reflect the fact that the surface area for transfer is larger than the reaction surfaces, according to:

\[
 k_{slFe(III)} \left( C_{Fe(III)}^s - C_{Fe(III)}^b \right) = v_{Fe(III)} \left( \frac{A_g}{A_p} \right) \left( \frac{n}{A_g} \frac{dX}{dt} \right) = v_{Fe(III)} \left( \frac{M_g}{M_p} \right) \left( \frac{n}{A_g} \frac{dX}{dt} \right)
\]

where the subscripts \(g\) and \(p\) refer to sulfide grain and particle, respectively. Although the peculiar grain shapes observed could affect the rate constant and exponent 2/3 in Eq. 4-43, the pyrite oxidation rate per grain surface area \(A_g\)

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(second bracketed term) is assumed unchanged. The transfer surface area is taken as the particle surface $A_p$. The ratio of the two surface areas is approximated as the pyrite to ore weight ratio, which was measured to be $\approx 4.1$ kg FeS$_2$/kg ore for all size fractions tested. Eq. 4–50 is then written as:

$$\frac{-v_{Fe(III)}}{v_{Fe(II)}} \left( C^s_{Fe(II)} - C^b_{Fe(II)} \right) = C^b_{Fe(III)} - C^s_{Fe(II)} \left[ \frac{1}{Da} \left( \frac{C^s_{Fe(II)} - C^b_{Fe(II)}}{M_g \rho \rho G} \right)^2 \right] \sqrt{\frac{M_g}{M_p}} \rho G \text{Eq. 4-56}$$

The Da number, or more precisely the solid/liquid mass transfer coefficient, is estimated from a correlation derived by Dwivedi and Upadhyay [55] for fixed beds at low Re numbers:

$$\varepsilon \frac{Sh}{Re \ Sc^{1/3}} = 0.4548 Re^{-0.4069} \frac{k_{sli} d_0}{D} = 0.4548 \left( \frac{\mu}{\rho D} \right)^{1/3} \left( \frac{d_o u_p}{\mu} \right)^{0.5931} \text{Eq. 4-57}$$

where $u$ is the solution superficial velocity evaluated at $4 \times 10^{-4}$ m/s, $d_0$ is the size of the packing material (taken for the purpose of the exercise from 0.001 to 0.01 m), $\varepsilon$ is the bed porosity ($\approx 0.4$), $D$ is the liquid diffusivity ($\approx 1 \times 10^{-9}$ m$^2$/s), $\rho$ is the medium density ($\approx 1,000$ kg/m$^3$), and $\mu$ is the medium viscosity ($\approx 1 \times 10^{-3}$ Pa-s). The mass transfer coefficients, $k_{sli}$, are found in the narrow range from $2.6 \times 10^{-6}$ to $6.6 \times 10^{-6}$ m/s, which are approximately 50 times less than the mass transfer coefficient estimated for 15 μm particles in stirred tanks. Taking the average of the $k_{sli}$ values, the Da number is estimated to be $3 \times 10^{-6}$ at 55°C. When this value and the corrected surface area term are inserted into Eq. 4–56, together with the calculated bulk Fe(III) and Fe(II) concentrations corresponding to the Fe$_T$ concentration ($\approx 1$ g/L) and bulk ratio ($\approx 300$) tested, the surface Fe(III) and Fe(II) concentrations are evaluated to be 0.989 and 0.0085 g/L, respectively, leading to a surface Fe(III)/Fe(II) concentration ratio of 117.

The chemical oxidation rate (Eq. 4–21) is 1.6 times smaller when changing the Fe(III)/Fe(II) concentration ratio from 300 to 117. This error becomes more
negligible when the oxidation kinetics of fines, whose surface potential is definitely equal to the bulk potential (similar analysis performed, but not shown, with 400 μm particles using Brauner’s equation [56] for estimating the mass transfer coefficient in stirred-tank reactors for Re > 1), is ultimately combined with the kinetics of the coarse particles. Based on this supporting evidence, and for lack of a more rigorous and complex analysis, the Fe(III)/Fe(II) concentration ratio will be assumed equal to 300 in determining the rate constant $k_0$ in Eq. 4–21.

4.4.2.3 Particle Size Distributions

Keeping in mind that the ultimate objective of this project is to compare the heap leaching model predictions to the column data, the three size distribution functions (Figure 2.4) of the ten column tests were used. Label ore 2 (Figure 4.21) refers to the size distribution of the crushed ore particles (also shown in Figure 4.1, top graph) loaded as–is in column F. Label ore 1 corresponds to the size distribution of particles forming truffles. Roughly 55 wt% of the ore content in columns A–E and H–J is characterized by ore 1. The remaining 45 wt% are pellets whose size distribution is labeled ore 4. The size distribution of ore particles forming the 12-mm pellets loaded in column G is shown in Figure 4.21 under the label ore 3.

The particles from only two distinct size classes combine to form the pellets of ore 4: fines smaller than 2 mm (the mortar) and coarse particles larger than 6 mm (the bricks). The bimodal distribution of particles forming pellets seems to suggest the existence of two main types of pellets, as shown in Figure 4.2 (middle). A pellet made up of a coarse particle coated by a layer of fines should, however, be considered as a truffle surrounded by pellets of only a few mm in size. According to these more realistic pellet/truffle representations and considering the size distribution of non-agglomerated ore particles (ore 2), one may assume that all ore particles smaller than roughly 3 mm (55 wt%) form pellets (ore 3), while the rest remain as truffles (ore 5). In contrast to the pellet size distribution shown in the bottom left graph of Figure 4.1, the pellets made up of only fines can be larger and smaller than 6 mm. Their size distribution is unknown in this work.
Because of the limited number (6) of size fractions tested, particles whose sizes fall outside any of the 6 size ranges tested were added into the nearest size fraction bin in the calculations of step 2.

4.4.3 Results and Discussion

The oxidation time is shown proportional to the particle size (Figure 4.22, Figure 4.23). Oxidation curves generated by the leaching of sulfide grains from small particles are rather smooth (Figure 4.22). The nugget effect clearly manifests itself as scattered data points with increasing particle size (Figure 4.22, Figure 4.23). This factor was somewhat alleviated by cutting down on the number of samples collected while increasing the sample mass by as much as ten times. Another important source of error is the rather large variation of the head grade between replicates of the same size fraction (Table 4.1). Sample representation is truly the single most important prerequisite of this experimental technique. The low initial sulfide grade and the imprecision of the assay make matters even worse.
The grain-scale oxidation rate, expressed as unit sulfide leached/initial unit sulfide present per time and now referred to as the global rate, was shown to decrease over time. According to the shrinking-sphere model, the oxidation rate, expressed as unit leached per surface area per time, is, however, constant under conditions of constant temperature and solution chemistry. It is the decreasing surface area of the particle that explains why the global rate diminishes over time. It is worth noting in Figure 4.22 and Figure 4.23 that the general trend of a shrinking-sphere model does not match the quasi-linear oxidation profiles of the larger size fractions. That the global oxidation rate appears to be constant during the first 120 days implies that the surface area of the sulfide occurrences remained practically unchanged. The presence of large veins and discs seem to support this hypothesis.

![Figure 4.22](image)

Figure 4.22 Oxidation profiles of three size fractions. Conditions: temperature = 55°C, [Fe(III)]/[Fe(II)] = 300, fast recirculation. Lines do not represent model fits, but indicate general trends.

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The non-visible sulfide component of the (-4+3.35) mm fraction, which initially accounted for 57% of the total sulfide (Table 4.1), was oxidized after 100 days. Very long leaching times of about 100 days are required to oxidize 80% of the sulfide contained within particles 2−4 mm in size. More than a year thus seems the minimum time to completely oxidize the sulfide content of the largest particles at 55°C.

The shrinking sphere model, coupled with a Rosin-Rammler grain size distribution, was fitted nicely to the (-0.425+0.3) mm fraction (not shown herein), but attempts failed with larger fractions. After integrating Eq. 4−21 to yield the conversion with time, the parameters $k_0$ and $\phi$ were chosen to minimize the squared error between the fit of Eq. 4−21 and the weighted experimental data points (step 3), while ensuring that the trend beyond day 120 (last sampling day) would eventually approach 100%. Because of the different sampling times, only five weighted experimental data points were calculated for each ore assemblage (Table 4.5).
values of the parameters are presented in Table 4.6, while the model fits are shown as lines in Figure 4.24.

Table 4.5 Set of five raw or treated fractional oxidation values for each of the six size fractions tested.

<table>
<thead>
<tr>
<th>Size (mm)</th>
<th>-0.425+0.3</th>
<th>-2+1</th>
<th>-2.36+2</th>
<th>-4+3.35</th>
<th>-8+6.35</th>
<th>-12.7+9.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 d</td>
<td>0.72</td>
<td>0.28</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>20 d</td>
<td>1.00*</td>
<td>0.55</td>
<td>0.20</td>
<td>0.14</td>
<td>0.09</td>
<td>0.07</td>
</tr>
<tr>
<td>53 d</td>
<td>1.00</td>
<td>0.77</td>
<td>0.43</td>
<td>0.39</td>
<td>0.23</td>
<td>0.17</td>
</tr>
<tr>
<td>84 d</td>
<td>1.00</td>
<td>0.91</td>
<td>0.82</td>
<td>0.73</td>
<td>0.39</td>
<td>0.32</td>
</tr>
<tr>
<td>110 d</td>
<td>1.00</td>
<td>0.91</td>
<td>0.82</td>
<td>0.66</td>
<td>0.47</td>
<td>0.28</td>
</tr>
</tbody>
</table>

* Italicized numbers were interpolated using linear regression of the entire series of raw data because of scatter and/or nonexistence of raw data. Numbers were extrapolated for the (-0.425+0.3) mm fraction.

Table 4.6 Fitted topological leaching parameters.

<table>
<thead>
<tr>
<th></th>
<th>Ore 1</th>
<th>Ore 2</th>
<th>Ore 3</th>
<th>Ore 4</th>
<th>Ore 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$ (d$^{-1}$)</td>
<td>0.0014</td>
<td>0.0049</td>
<td>0.0250</td>
<td>0.0173</td>
<td>0.00045</td>
</tr>
<tr>
<td>$\phi$ (-)</td>
<td>2.00</td>
<td>3.20</td>
<td>2.68</td>
<td>3.20</td>
<td>1.06</td>
</tr>
</tbody>
</table>

The model fits of ores 1 to 4 capture well the rapid conversion of fines in less than 10 days, and the slow rising segment of each curve representing the oxidation of medium to coarse sulfide grains (Figure 4.24). The fit is even more impressive in the absence of fines (ore 5). A random distribution of the data points on both sides of the line would yield a better fit. The fact that the overall oxidation profiles of five ore samples with widely different particle size distributions can be modeled with the same simple equation by varying only two parameters attests to the reliability and usefulness of the proposed method.
The rate constant $k_0$ increases dramatically with increasing amounts of fines. The fairly similar reaction orders ($2 < \phi < 3.2$) are found in a range where the assumption of a single average $\phi$ value for the entire reaction time is less compelling [43]. As shown in Figure 5 of reference 43, the wider the grain size distribution, the larger the deviations of the model fit calculated with a single average $\phi$ value with respect to the actual conversion vs time data. The time to approach complete oxidation also increases drastically with increasing $\phi$ values. For instance, according to the fitted parameters of ore 2, 240 days would be required to oxidize 85% of the sulfide content. Only 5% more would be oxidized in the next 215 days, while oxidizing 10% more would necessitate a minimum of 950 days, or 2.6 years. There is no available information in the literature on sulfidic refractory gold ores to substantiate these extrapolations. The model parameters could certainly be refined with a more complete set of weighted experimental data. Nevertheless, the model and its estimated parameters predict satisfactorily the time required to leach a significant proportion (75%) of the sulfide charge. By contrast,
as much as 50% of sulfide minerals in heap bioleaching operations are left non-
oxidized before cyanidation (chapter 1).

It is worth noting that the proton concentration effect discussed in section 4.1.2 is
lumped into the parameter \( k_0 \). Since the average pH of the leaching solution
pumped in the upflow saturated columns (this chapter) and in the test columns
(chapter 2) varies by 0.15 pH units over time, the proton concentration effect is
ignored in the topological rate law. Any diffusion effects in the minuscule existing
pores of the ore particles, possibly obstructed by the build-up of jarosite, are not
accounted for specifically. Nor are the less than probable diffusion resistances
between the second smallest, but fast reacting, particles (-2+1 mm) as a result of
flow maldistribution in the packed bed reactor. The effects of these phenomena are
instead lumped into the rate constant \( k_0 \) in Eq. 4-21 leaving, however, the
activation energy unchanged.

The fitted parameters were found to be very sensitive to any variation of the sulfide
head grade, which itself has a fairly large standard deviation. It is needless to
reemphasize that the mediocre quality of the data casts some doubt on the
suitability of the fitted parameters. However, what the model lacks in accuracy, it
gains in simplicity and tractability when embedded in the kinetic subroutine of the
heap leaching model.

4.5 Conclusions and Recommendations

4.5.1 Pyrite Oxidation Chemistry

This investigation into the ferric leaching chemistry of a pyrite/marcasite
concentrate in acidic sulfate medium reveals that sulfate and elemental sulfur were
the two oxidation products. The abundance of small, discrete elemental sulfur
particles in the residue suggests the formation and subsequent disproportionation
of sulfoxy intermediates such as thiosulfate. The measured yield, calculated as the
ratio of elemental sulfur detected in the residue to the amount of sulfide leached,
was found to be totally independent of temperature (30-75°C) and
[Fe(III)]/[Fe(II)] ratio (3–300). Each unit of sulfide oxidized apparently yielded 0.72 unit of sulfate, the rest elemental sulfur (measured yield).

Because of the intrinsic relationship between KMnO₄ additions and sulfate yield, thermodynamic calculations based on the actual amounts of H₂O, FeSO₄·7H₂O, Fe₂(SO₄)₃·5H₂O, H₂SO₄, FeS₂, and KMnO₄ present in the vessel at any time have shown that the predicted yield was consistently lower than the measured one by 6.6 to 19.1%, suggesting that more elemental sulfur had been formed than was measured. The predicted sulfate yield of 58.9% was also independent of temperature and potential.

Although the conversion data points calculated using the thermodynamic program in combination with the predicted yields were in excellent agreement with the true oxidation-time profile obtained from soluble iron data, the shortcomings of the thermodynamic predictions should not be ignored, including:

- Incomplete set of ΔG° values in every one of the four databases consulted;
- Lack of consistency in any one database;
- Large variability of ΔG° and log K values between databases, and
- Inaccuracy of the Davies’ model predictions in systems of modest ionic strength (ex.: for a 1:1 solute, the model breaks down for I > 0.5).

Potassium permanganate (KMnO₄) is a suitable oxidant for controlling the solution potential and a suitable indicator of the progress of the leach in a sulfate medium when the pH is maintained constant near 0.5. This last feature is especially important when oxidizing pyrite, which, upon dissolution, releases minute amounts of iron, sulfate, and elemental sulfur in a medium containing already large concentrations of those same species. The precipitation of iron and sulfate as jarosite makes matters even worse. The control problems experienced in the packed-bed columns indicate that permanganate may not fulfill both roles in less acidic solutions where jarosite and MnO₂ are expected to precipitate. The suggested method of multiple replicates should avoid the pitfalls of iron and manganese precipitation at lower acidity.

Chapter 4 – Mineral Leaching Kinetics
4.5.2 Grain-Scale Kinetic Model

The sterile ferric sulfate leaching of pyrite/marcasite was studied in the temperature range of 30 to 75°C, varying solely the Fe(III)/Fe(II) concentration ratio while maintaining the acidity constant at 0.5 M H$_2$SO$_4$. Pyrite oxidation with ferric ions as oxidant conforms to the type III, chemical-controlled shrinking-sphere model at Fe(III)/Fe(II) concentration ratios lower than 300 in the present stirred-tank experiments. The shrinking-sphere model nicely fitted all experimental points below 90% conversion in spite of the rather angular shape of the grains and discrete corrosion patterns on the grain surfaces.

A mathematical analysis of the three-step process (Fe(III) diffusion, electrochemical reaction, Fe(II) diffusion) reveals that, under certain conditions of high potential, the diffusion of ferrous ions towards the bulk solution is not rapid enough to maintain the potential at the surface as high as in the bulk. For instance, decreasing the temperature and/or increasing the particle size decreases the chemical oxidation rate, increases the Da number, and ultimately flattens the concentration gradient through the boundary layer.

Although the six $k_{III}'$ values shown in Figure 4.16 were nicely fitted by a single line, one could envisage passing a line through the first four points, and another through the last three. One or two additional tests should be performed at temperatures between 40 and 55°C to determine whether a change in mechanism takes place in the neighborhood of 47°C. Moreover, since one of the four fitted $k_{III}'$ of the Fe(III)/Fe(II) series was different from the other three, further tests should be carried out at lower ratios to confirm whether $k_{III}'$ is independent of the solution chemistry.

The validity of Eq. 4–40 (or Eq. 4–43) could be challenged in systems of lower acidity more typical of heap environments. Indeed, several authors have attributed a ($-\frac{1}{2}$) reaction order to the proton concentration. Changing the acidity will definitely change the activity ratio and may affect the rate constant. By decreasing the H$_2$SO$_4$ concentration from 0.5 to 0.05 M while keeping the same amounts of...
ferric and ferrous sulfate salts as loaded in test D and the same temperature (55°C), the Fe$^{3+}$/Fe$^{2+}$ activity ratio decreases from 40.5 to 27.2. The time to completion drops by 1.2-fold. A one order of magnitude change in acidity also leads to a proton activity of 0.04, compared to 0.35 in 0.5 M H$_2$SO$_4$ solution. If the proton activity were to be included in the rate expression and raised to a ($^{-\frac{1}{2}}$) power, the rate would be 3 times larger at lower acidity. Therefore, the change in the activity ratio apparently does not explain totally the faster kinetics noted by previous researchers. It remains to be proven experimentally whether this holds true with this particular pyrite. All things considered, an in-depth pH study may prove to be a futile exercise, if particle kinetics were later shown not to be the rate-limiting process at the heap scale. If need be, Eq. 4–40 (or Eq. 4–43) can be revised to account for the proton concentration.

4.5.3 Particle–Scale Kinetic Model

The particle model expression retains the same deterministic temperature and solution chemistry features of the grain model. The particle model assumes complete liberation of pyrite grains, as well as negligible diffusion resistances through the particle pores. It captures well the principal leaching trends of fine and coarse sulfide grains embedded into particles. The exponent $\phi$ takes on values between 1 and 3.2, well above the 2/3 exponent of shrinking spheres. The rate constant $k_0$ is also smaller than that of fully-liberated pyrite grains.

The model should ideally have been validated by performing a series of saturated column tests at different temperatures and Fe(III)/Fe(II) concentration ratios. Lack of sample representativeness is, however, a serious drawback of the proposed experimental methodology for ores containing no soluble leaching indicator (e.g. Cu, Zn). Attempts at modeling particle kinetics of ores from different deposits containing one or more sulfide minerals necessitate prior laboratory testwork.
4.6 Nomenclature

*\( a \)  ion activity (–)

*\( A \)  grain surface area (m\(^2\))

*\( C \)  concentration (mole/L)

*\( C_p \)  heat capacity at constant pressure (J/(mole·K))

*\( d \)  particle diameter (m)

*\( D \)  liquid diffusivity (m\(^2\)/s)

*\( \text{Da} \)  Damköhler's second number (chemical reaction rate/diffusion rate)

*\( E \)  mixed potential (V)

*\( E_a \)  activation energy (J/mole)

*\( E_h \)  solution potential vs SHE (V)

*\( F \)  Faraday's constant (96,485 C/mole electron)

*\( \Delta G^0 \)  standard Gibbs free energy change (J/mole) (unit activities)

*\( G \)  pyrite grade (kg pyrite/kg ore)

*\( i \)  current density (A/m\(^2\))

*\( I \)  ionic strength (–)

*\( k_{sl} \)  solid/liquid mass transfer coefficient (m/h)

*\( k \)  lumped rate constant (arbitrary units)

*\( k' \)  lumped rate constant (arbitrary units)

*\( K \)  equilibrium reaction constant

*\( M \)  molecular weight (kg/mole)

*\( M \)  mass of pyrite or gangue minerals (kg)

*\( M_0 \)  initial mass of concentrate (kg)

*\( m \)  molality (mole/kg water)

*\( n \)  number of mole of pyrite in a pyrite particle (mole)

*\( P \)  pulp density (kg ore/L solution)

*\( Q \)  total number of size fractions

*\( r \)  rate (mole pyrite/h)

*\( R \)  universal gas constant (8.314 J/(mole·K))

*\( \text{Re} \)  Reynolds number (= \( d_0 \mu \rho / \mu \))

*\( S \)  entropy (J/(mole·K))

*\( \text{Sc} \)  Schmidt number (= \( \mu / (\rho D) \))

*\( \text{Sh} \)  Sherwood number (= \( k_{sl} d_0 / D \))

*\( t \)  time (h or d)

*\( T \)  temperature (K)
\( u \) \hspace{1em} \text{particle or superficial velocity (m/s)}
\( w \) \hspace{1em} \text{weight fraction of particles in a given size class}
\( X \) \hspace{1em} \text{experimental conversion (-)}
\( \bar{X} \) \hspace{1em} \text{artificial weighted conversion (-)}
\( z \) \hspace{1em} \text{valency of ionic species (-)}
\( Z \) \hspace{1em} \text{number of moles of electrons per mole of reaction}

### 4.6.1 Greek Letters

\( A_\varphi \) \hspace{1em} \text{Debye-Hückel parameter \( \approx \ln(10)(2.719 \times 10^{-6}T^2 - 7.477 \times 10^{-4}T + 0.4896) \) with \( T \) [K]}
\( \alpha_{ij} \) \hspace{1em} \text{number of atoms of species \( j \)}
\( \varepsilon \) \hspace{1em} \text{packed bed void fraction (m}^3\text{ pores/m}^3\text{ column)}
\( \gamma \) \hspace{1em} \text{ion activity coefficient}
\( \kappa \) \hspace{1em} \text{ratio of the anode to total surface area (-)}
\( \lambda \) \hspace{1em} \text{Lagrange's unspecified multiplier (-)}
\( \mu \) \hspace{1em} \text{viscosity (Pa} \cdot \text{s)}
\( \nu \) \hspace{1em} \text{stoichiometric coefficient}
\( \phi \) \hspace{1em} \text{topological rate exponent (-)}
\( \rho \) \hspace{1em} \text{density (kg/m}^3\text{)}
\( \omega \) \hspace{1em} \text{ratio \( a_{Fe^{3+}} / a_{Fe^{2+}} \)}
\( \varphi \) \hspace{1em} \text{elemental sulfur yield (mole sulfur produced/mole FeS}_2\text{ oxidized)}

### 4.6.2 Subscripts

\( a \) \hspace{1em} \text{anode (unless otherwise indicated)}
\( c \) \hspace{1em} \text{cathode}
\( g \) \hspace{1em} \text{sulfide grain}
\( i \) \hspace{1em} \text{element}
\( j \) \hspace{1em} \text{species}
\( k \) \hspace{1em} \text{equilibrium reaction}
\( o \) \hspace{1em} \text{reference}
\( p \) \hspace{1em} \text{gangue particle}
\( q \) \hspace{1em} \text{size class}
\( t \) \hspace{1em} \text{terminal or truffle}
\( 2 \) \hspace{1em} \text{ferrous ions}
\( 3 \) \hspace{1em} \text{ferric ions}
\( I \) \hspace{1em} \text{type I leaching mechanism}
III type III leaching mechanism
0 initial

4.6.3 Superscripts

b bulk
s surface

4.7 References


Smith, E.E. and Shumate, K.S., 1970. The sulfide to sulfate reaction mechanism: A study of the sulfide to sulfate reaction mechanism as it relates to the formation of acid mine waters, Water Pollution Control Research Series, Ohio State University Research Foundation.


Boon, M., Brasser, H.J., Hansford, G.S. and Heijnen, J.J., 1999. Comparison of the oxidation kinetics of different pyrites in the presence of
**Thiobacillus ferrooxidans** or **Leptospirillum ferrooxidans.** Hydrometallurgy, 53: 57–72.


5.1 Introduction

Chapter 3 described the basic heap hydrodynamic structure for transport and diffusion of solutes through stagnant and flowing solutions. In this chapter, the ferric oxidation rate expression for pyrite grains in truffles or pellets (chapter 4) becomes one of four possible source terms in the stagnant phase mass balance. While pyrite oxidation consumes ferric ions (5-1), microbes may simultaneously replenish the ferric ions by oxidizing ferrous ions in the presence of dissolved oxygen and sulfuric acid (5-2).

\[
\text{FeS}_2 + [1+3(2-\varphi)] \text{Fe}_2(\text{SO}_4)_3 + 4(2-\varphi) \text{H}_2\text{O} \rightarrow [3 + 6(2-\varphi)] \text{FeSO}_4 + 4(2-\varphi) \text{H}_2\text{SO}_4 + \varphi \text{S}^0 \quad (5-1)
\]

\[
2 \text{FeSO}_4 + \frac{1}{2} \text{O}_2(\text{d}) + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \quad (5-2)
\]

Pesic et al. [1] have shown that the time required to achieve 50% oxidation of 0.001 M Fe(II) in sterile and biotic media at ambient temperature at pH 1.45 differed by as much as six orders of magnitude (0.5 h vs 3780 d, respectively). For this reason, the rate of ferrous ion oxidation is assumed to occur by a biological mechanism only.

Microbes may also catalyze the oxidation of elemental sulfur (5-3) produced by pyrite oxidation.

\[
\text{S}^0 + \frac{3}{2} \text{O}_2(\text{d}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad (5-3)
\]

According to Figure 3.4, dissolved oxygen needed to sustain the biological reactions (5-2) and (5-3) is provided at any position within the side branches by mass transfer (5-4) from the air blown at the base of the heap.

\[
\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{d}) \quad (5-4)
\]
Although the oxygen concentration is assumed uniform within each stagnant node, this ultimate oxidant must further diffuse into the pellet pores to oxidize ferrous ions and elemental sulfur.

In the absence of a reliable set of temperature-dependent equilibrium constants for the many different forms of jarosite, the present work ignores the precipitation of jarosite (reaction 5-5) for the following reasons:

\[
3 \text{Fe}_2(\text{SO}_4)_3 + 14 \text{H}_2\text{O} = 2 \text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6 + 5 \text{H}_2\text{SO}_4 \tag{5-5}
\]

- The acid produced by the precipitation of jarosite may only be vital to sustain the oxidation of pyrite in the absence of sulfur-oxidizing cells, at low feed acid concentration, and/or at very high elemental sulfur yield. It is definitely not vital to sustain the oxidation of elemental sulfur.

- More importantly, less than 5 wt% of the total iron fed and leached in all column experiments was precipitated.

Because the ore tested contained very low amounts of arsenopyrite, thus the single-mineral rate expression (chapter 4), the present model disregards any reactions involving arsenic species (Table 1.1). The set of transportable components thus comprises: \([\text{Fe}_2(\text{SO}_4)_3, \text{FeSO}_4, \text{H}_2\text{SO}_4, \text{O}_2(d), \text{O}_2(g)]\). The stoichiometric matrix is:

\[
\nu_{ij} = \begin{pmatrix}
1 & \ldots & j \\
\vdots & & \ddots \\
i & & & 1
\end{pmatrix}
\]

\[
\begin{bmatrix}
\text{Fe(III)} & \text{Fe(II)} & \text{H}_2\text{SO}_4 & \text{O}_2(d) & \text{O}_2(g) \\
-1+3(2-\varphi) & 0 & 1 & 0 & 0 \\
3+6(2-\varphi) & 0 & -2 & 0 & 0 \\
4(2-\varphi) & 1 & -1 & 0 & 0 \\
0 & -\frac{3}{2} & -\frac{1}{2} & 1 & 0 \\
0 & 0 & 0 & -1 & 0
\end{bmatrix}
\tag{5-6}
\]

where the subscripts \(i\) (1 .. 5) and \(j\) (1 .. 4) refer to species and reaction number, respectively.

This chapter first explores in section 5.2 the constituents of the rate expressions of reactions 5-2 to 5-4 from a conceptual and fundamental point of view, rather than

Chapter 5 - Model Add-Ons
from an experimental angle, such as in chapter 4 for the pyrite oxidation rate. Sections 5.3 to 5.6 integrate the chemical, biological, physical, and thermal source terms into the model hydrodynamic backbone. Next, the numerical methods and the order of solution employed to solve the complex system of equations are presented in section 5.8. Lastly, the model features and parameters are summarized, and recommendations are formulated for certain subroutines.

5.2 Mathematics of Microbial Kinetics

5.2.1 Net Cell Growth

Several modeling and experimental studies of iron- and sulfur-oxidizing cell growth were reviewed throughout this project. These and an analysis of microbial mathematics [2] indicate that the cell growth rate, $dY_{\text{tot}}/dt$ (cells/(L-h)), is proportional to the cell concentration, $Y_{\text{tot}}$ (cells/L), and to the specific growth rate, $\mu$ (h$^{-1}$):

$$\frac{dY_{\text{tot}}}{dt} = \mu_{k} Y_{\text{tot}}$$

(5-7)

where the subscript $k$ refers to mesophile ($k = 1$), moderate thermophile ($k = 2$), or extreme thermophile ($k = 3$) cells. Unless otherwise indicated, the subscript $k$ is dropped in the upcoming equations in the interest of clarity and simplicity.

This equation describes exponential (or logarithmic) growth under constant environmental conditions. Several factors, including temperature, pH, ionic strength, substrate concentration, and concentration of inhibiting substances, influence the specific growth rate. The Monod rectangular hyperbola, the most widely used expression for substrate concentration, is written as:

$$\mu = \mu_{\text{max}} (T, pH, \ldots) \left( \frac{C_{Fe(II)}}{K_{Fe(II)} + C_{Fe(II)}} \right) \left( \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \right)$$

(5-8)
for iron-oxidizing cells consuming both oxygen and ferrous ions, where $K$ is the saturation constant (mole/L), and $\mu_{\text{max}}$ (h$^{-1}$) is the maximum growth rate under specific environmental conditions. Based on the findings of the above studies, this author expanded the ferrous ion Monod term of Eq. 5–8 to include threshold ferrous ion concentration, competitive inhibition of cells and ferric ion, and substrate inhibition, leading to the following expression:

$$
\mu = \mu_{\text{max}} \left[ \frac{C_{\text{Fe(II)}} - C_{t,\text{Fe(II)}}}{C_{\text{Fe(II)}} - C_{t,\text{Fe(II)}} + \left( \frac{(C_{\text{Fe(II)}} - C_{t,\text{Fe(II)}})^2}{K_{I_{\text{Fe(II)}}}} \right) + K_{\text{Fe(II)}} \left( 1 + \frac{C_{\text{Fe(III)}}}{K_{I_{\text{Fe(III)}}}} + \frac{\gamma_{\text{tot}}}{K_{I_{\text{Fe(III)}}}} \right)} \right] \left[ \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \right]
$$

(5-9)

where $K_I$ is an inhibition constant (mole/L) and $C_t$ is the threshold Fe(II) concentration (mole/L).

Published values of the specific growth rate constant, $\mu$, for *A. ferrooxidans* and *L. ferrooxidans* range from 0.06 to 1.78 h$^{-1}$ (compiled in refs. 3–5). Tsaplina *et al.* [6] reported growth rate values of 0.03–0.15 h$^{-1}$ for the moderately thermophilic *Sulfobacillus thermosulfidooxidans* VKM 1269 grown on both pyrite and thiosulfate under myxotrophic conditions in batch and continuous cultures. Melamud and Pivovarova [7] reported that the same strain grows at least ten times more rapidly in 9K medium ($\mu = 0.49–0.84$ h$^{-1}$). Nemati and co-workers measured growth rates of *Acidianus brierleyi* ($\mu = 0.043$ h$^{-1}$) on ferrous ions [8] and *Sulfolobus metallicus* ($\mu = 0.018–0.025$ h$^{-1}$) on pyrite [9] at 68°C in shake flasks. For sulfur, published values of $\mu$ for *A. ferrooxidans* [10] and *A. thiooxidans* [11,12] range from 0.04 to 0.11 h$^{-1}$ at 30°C.

The lack of generality, unreliability, inconsistencies, and scatter in the reported parameters of Eq. 5–9 are attributed to strain differences, stage of culture growth, culture adaptation, medium composition, reactor type, inhibitory effects, incomplete sampling protocols, and inadequate data interpretation and analysis. These data constitute, nonetheless, first guess values in the estimation of the biological parameters in chapter 6.
The form of Eq. 5-9 is also far too intricate for the present heap biooxidation model, which, instead, simplifies the above two Monod terms to the following general expression:

$$\Pi = \left( \prod_i \frac{C_i}{K_i + C_i} \right) \left( \prod_j \frac{KI_j}{KI_j + C_j} \right)$$  \hspace{1cm} (5-10)

where $\Pi$ is the product of all Monod terms defining the growth rate with decreasing substrate concentration (left bracketed term), multiplied by the product of all inhibition terms describing the increasing inhibitor concentrations (right bracketed term). The $i$ terms represent Monod concentration terms for ferrous ion or elemental sulfur, as well as oxygen. The $j$ terms represent inhibition concentration terms for salts such as magnesium, aluminium, or chloride. The $K$ and $KI$ parameters are the saturation and inhibition constant (either mole Fe(II)/L or mole S/kg ore), respectively. The concentration $C_i$ for all species, except elemental sulfur, have units of mole/L, while that of elemental sulfur is expressed in mole S/kg ore. Eq. 5-10 ignores any change in the size/shape of elemental sulfur, and treats it like any other soluble component. This approach is reasonable in light of the fact that elemental sulfur was precipitated out of solution as 2 $\mu$m particles, as supported by photographs of the leached residue (Figure 4.6).

For the specific case of one substrate and one inhibitor, Eq. 5-10 yields two sets of combinations at low and high concentrations of substrate and inhibitor (Table 5.1). At low substrate concentrations, $\Pi$ becomes a first-order function of the substrate concentration. The rate is independent (i.e. zero order) of the substrate concentration at high levels. $\Pi$ thus tends toward 1 in the absence of inhibition effects. On the contrary, $\Pi$ approaches zero with increasing inhibitor concentrations.
Table 5.1 Influence of limiting or excess substrate and inhibitor concentration on the growth rate

<table>
<thead>
<tr>
<th>Case</th>
<th>Expression</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_i \gg K_i$</td>
<td>$\Pi = \left( \frac{C_i}{C_i} \right) \left( \frac{KI_j}{KI_j + C_j} \right) = \frac{KI_j}{KI_j + C_j}$</td>
<td>Zero-order with respect to $C_i$</td>
</tr>
<tr>
<td>$C_i \ll K_i$</td>
<td>$\Pi = \left( \frac{C_i}{K_i + C_i} \right) \left( \frac{KI_j}{KI_j + C_j} \right) \to 0$</td>
<td>First-order with respect to $C_i$</td>
</tr>
<tr>
<td>$C_j \gg KI_j$</td>
<td>$\Pi = \left( \frac{C_j}{K_j + C_j} \right) \left( \frac{KI_j}{KI_j} \right) = \frac{C_j}{K_j + C_j}$</td>
<td>Tends toward 0</td>
</tr>
<tr>
<td>$C_j \ll KI_j$</td>
<td>$\Pi = \left( \frac{C_j}{K_I + C_j} \right) \left( \frac{KI_j}{KI_j + C_j} \right) \to \frac{C_j}{K_I + C_j}$</td>
<td>Zero-order with respect to $C_j$</td>
</tr>
</tbody>
</table>

The present biological model further excludes any salt inhibition effects, but considers a cell inhibition term. This reduces Eq. 5–10 to:

$$\Pi = \left( \frac{C_{Fe(II)}}{K_{Fe(II)} + C_{Fe(II)}} \right) \left( \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \right) \left( \frac{KI_y}{KI_y + Y^{tot}} \right)$$

(5–12)

Values of $K_{Fe(III)}$ vary over almost four orders of magnitude, between 0.00002 to 0.123 mole Fe(II)/L for mesophilic growth on ferrous ions (compiled in refs. 3–5). Five studies on *A. ferrooxidans* growth reported $K_{O2}$ values between $1.8 \times 10^{-6}$ and $51 \times 10^{-6}$ mole $O_2$/L (compiled in ref. 4).

Eq. 5–12 also rejects carbon dioxide as the third, possibly limiting substrate. The discussion in section 2.3.5 pointed to the need to supply carbon dioxide primarily during the initial stages of biooxidation in the presence of small cell populations. The fact that cell numbers in the present column tests remain constant thereafter does not necessarily imply that the microbes present were immortal. Cells were more likely in dynamic growth/death equilibrium. The scientific community believes that, besides carbon dioxide in air, cells can utilize carbon released during the
degeneration of dead cells. Even if this hypothesis were proven unfounded, the carbon demand of a grown population (i.e. later stages of biooxidation) must be significantly smaller than during their exponential growth stage.

Eq. 5-7 focuses exclusively on the exponential growth stage. It fails to address the stationary and death phases, which are of vital importance to inoculated ore beds with constant cell numbers. For this reason, the degradation of cellular (i.e. endogenous) components has been modeled as:

\[
\frac{dY_{\text{tot}}}{dt} = Y_{\text{tot}} (\mu - k_e)
\]  

(5-13)

where \( k_e \) is the endogenous decay rate constant (h\(^{-1}\)) [2]. However, according to the simple form of Eq. 5-13, decay occurs even in the presence of large substrate concentrations, when, in fact, the endogenous metabolism characterizes a starvation survival behavior. This author has thus altered Eq. 5-13 to rectify this incongruity, as follows:

\[
\frac{dY_{\text{tot}}}{dt} = Y_{\text{tot}} k_g (\Pi (1 + k_e) - k_e)
\]  

(5-14)

where \( k_g \) (h\(^{-1}\), previously referred to as \( \mu_{\text{max}} \) in Eq. 5-9) depends on temperature and other factors, and \( k_e \) is the dimensionless endogenous decay constant relative to the growth rate constant \( k_g \) (i.e. takes values equal to or larger than 0). The endogenous decay term becomes significant for small \( \Pi \) values, as demonstrated in Eq. 5-15:

High concentrations:  \( \Pi \to 1 \)  
\[
\frac{dY_{\text{tot}}}{dt} = Y_{\text{tot}} k_g
\]  

(5-15)

Low concentrations:  \( \Pi \to 0 \)  
\[
\frac{dY_{\text{tot}}}{dt} = Y_{\text{tot}} k_g (\Pi + (\Pi - 1) k_e)
\]

Eq. 5-14 still lacks a term for cell death, due, for instance, to protein denaturation, in environments where the temperature exceeds the upper temperature of cell viability, as well as explicit growth and death temperature functions. The following
expression was therefore derived to represent the net increase of the total cell population:

\[
\frac{dY^\text{tot}}{dt} = \gamma^\text{tot}k_g \left[ f_g(T)(1+k_e)-k_e \right]-f_d(T)
\]

in terms of the true growth rate (first term in bracket), minus the endogenous decay rate (second term), and minus the death rate (third term). Rather than using normalized growth, \( f_g(T) \), and death, \( f_d(T) \), temperature functions as proposed in Eq. 5–16, microbiologists commonly employ the Ratkowski expression (Eq. 5–17) to directly relate the growth rate to the temperature [13]:

\[
\sqrt{k_g} = b_1(T-T_{\text{min}})[1-\exp(b_2(T-T_{\text{max}}))]
\]  \hspace{1cm} (5–17)

Evaluating the \( b_1 \) and \( b_2 \) parameters requires experimental data for the true growth rate. Because of the dubious accuracy of some published parameters (confidential information), this author opted instead to empirically fit the asymmetrical, bell-shaped curves of the growth rate, \( k_g \), vs temperature, \( T \), published by Norris [14] for mesophiles, moderate thermophiles, and extreme thermophiles. First, three critical temperatures were extracted from each curve: \( T_{\text{min}} \) (°C) – minimum temperature of viability, \( T_{\text{max}} \) (°C) – maximum temperature of viability, and \( T_{\text{opt}} \) (°C) – temperature yielding the maximum growth rate. Second, the growth rate values on each curve were normalized with respect to the maximum growth rate. Lastly, the shape of the normalized curve was empirically fitted to the following expression:

\[
f_g(T) = \frac{B}{\exp(\theta)+\exp(-A\theta)} \quad \text{where} \quad B = \frac{1}{A^2} + \frac{A}{1+A^2}
\]  \hspace{1cm} (5–18)

\[
\theta = \ln(B \cosh \pi) \left\{ -1 + \left( \frac{T-T_{\text{min}}}{T_{\text{max}}-T_{\text{min}}} \right) \left( 1 + \frac{1}{A} \right) \right\}
\]  \hspace{1cm} (5–19)

which involves only one fitted parameter (the skew factor \( A \)) previously evaluated from Eq. 5–20 by least squares minimization.
Eq. 5-18 describes an asymmetrical, bell-shaped curve whose maximum \( f_g \) value of 1 occurs at the optimum growth temperature, \( T_{opt} \) (Figure 5.1). Thus, \( k_g \) is a constant corresponding to the growth rate constant measured at \( T_{opt} \). The \( f_g \) value at \( T_{min} \) and \( T_{max} \) is equal to the reciprocal of \( \cosh(\pi) = 0.086 \). In the interest of simplicity, the growth temperature function was also chosen to adjust the decay rate to temperature.

\[
T_{min} + (T_{max} - T_{min}) \left[ \frac{A}{(1 + A)^2} \ln \left( \frac{A}{(1 + A)^2} \ln(B \cosh \pi) \right) + \frac{1}{1 + A} \right] = T_{opt}
\]  

(5-20)

Figure 5.1 Temperature-dependent growth (solid) and death (dashed) functions for mesophiles (diamond), moderate thermophiles (square), and extreme thermophiles (circle). The shape of the curve is based on the data extracted from reference 14.
The measured death rates of *A. ferrooxidans* exposed to temperatures 2 to 4°C above $T_{\text{max}}$ [15] inspired the selection of an exponential function to describe the normalized death temperature function, $f_d(T)$:

$$f_d(T) = B \exp \left[ 2 \left( -1 - \frac{1}{A} + \frac{T - T_{\text{min}}}{T_{\text{max}} - T_{\text{min}}} \left( 1 + \frac{1}{A} \right) \right) \right]$$  \hspace{1cm} (5-21)

This function takes values larger than 0.01 for temperatures only a few degrees less than $T_{\text{max}}$, and obviously all those above $T_{\text{max}}$. The shapes of $f_g(T)$ and $f_d(T)$, and the values of $T_{\text{min}}$, $T_{\text{max}}$, and $T_{\text{opt}}$, are shown in Figure 5.1 for each type of cells.

In summary, Eq. 5-16 must be formulated for each type of iron- and sulfur-oxidizing cells, with a given set of biological parameters for each of the three types of microorganisms (mesophiles, moderate thermophiles, extreme thermophiles).

### 5.2.2 Biological Oxidation of Ferrous Ions and Elemental Sulfur

The most common expression employed in the literature describes the cell growth rate as a linear function of the biological substrate consumption rate, according to:

$$r_j = \frac{\text{d}C_{\text{Fe}}}{\text{d}t} \text{ or } \frac{\text{d}C_{\text{S}_2}}{\text{d}t} = -\sum_k y_k^{\text{tot}} \frac{k_g f_g(T)}{y_g}$$ \hspace{1cm} (5-22)

where $y_g$ is the specific cell yield (cells/mole substrate), interpreted as the number of cells required to oxidize one mole of substrate (not the number of cells produced per mole of substrate oxidized). The cell yield must be evaluated for each cell type. The summation term represents the contribution of mesophiles, moderate thermophiles, and extreme thermophiles to the oxidation of a common substrate. The endogenous decay and cell death rates do not appear in Eq. 5-22 as they both relate to cell numbers, not to the substrate concentration.

Microorganisms may divert substrates away from synthesis and growth processes, thus providing energy to maintain existing structures and functions such as motility [2]. The maintenance term is typically modeled as a constant, $k_m$ (mole substrate/(cell-h)):
However, this popular approach leads to an erroneous situation as the substrate disappears. As \( \Pi \to 0 \), the substrate consumption rate, \( r_j \) (mole/(m\(^3\).h)), is still finite \((-\gamma_k^{\text{tot}} f_g(T) k_m)\), which implies substrate consumption even in the absence of substrate. Bringing \( \Pi \) outside the bracketed term solves this contradiction.

\[
r_{j=2 \text{ or } 3} = \frac{dC_{Fe^{(II)}}}{dt} \ \text{or} \ \frac{dC_{S^0}}{dt} = -\sum_k \gamma_k^{\text{tot}} f_g(T) \left( \frac{k_g \Pi}{Y_g} + k_m \right)
\]  

(5-23)

Because of the limited availability and scatter of the few maintenance coefficient data, the present work assumes no maintenance requirements, thus setting \( k_m \) to zero.

### 5.3 Component Mass Balances

#### 5.3.1 Pellet Pore

Like Eq. 3-11, the mass balance for all soluble species, including oxygen, in the fully saturated pellet is thus given by:

\[
\frac{\partial C_{pl}}{\partial t} = \left\{ \text{Rate of accumulation} \right\} + \left\{ \text{Net rate of input by diffusion} \right\} + \left\{ \text{Net rate of production} \right\}
\]

\[
\frac{\partial C_{pl}}{\partial t} = \left\{ \frac{D_i}{\varepsilon_p^2 R^2} \left( \frac{\partial^2 C_{pl}}{\partial \zeta^2} + \frac{2 \partial C_{pl}}{\partial \zeta} \right) \right\} + s_{pi} \left[ \text{mole/m}^3 \text{ pore h} \right]
\]

(5-25)

\[
s_{pi} = \frac{(1 - \varepsilon_p \rho_o)}{\varepsilon_p} \left[ v_1 G_{FeS_2} k_p(T) f(C)(1 - X_p) \phi_p + v_{i3} r_{p3} \right] + v_{i2} r_{p2}
\]

I.C. 1: \( C_{pi}(\zeta, 0) = C_{pl_0} \)  
B.C. 2: \( C_{pi}(1, t) = C_{si} \)  
B.C. 3: \( \frac{\partial C_{pl}}{\partial \zeta} \bigg|_{\zeta=0} = 0 \)
where:

- $\zeta$ is the normalized position in a pellet of uniform radius $R$ (m), shape (in this case, spherical, thus $n = 2$), density, and porosity $\varepsilon_p$ ($\text{m}^3$ pellet pore/$\text{m}^3$ pellet)
- $C_{pi}$ is the concentration (mole/L) of species $i$ in the pores of the pellet
- $\tau_p$ is the pellet pore tortuosity (m/m)
- $s_p$ is the source term (mole/(m$^3$ pore-h))
- $r_{pj}$ are the reaction rates of elemental sulfur (reaction 5–3, mole/(kg ore-h)) and ferrous ions (reaction 5–2, mole/(m$^3$ pore-h)) determined in section 5.2.2
- $v_j$ is the stoichiometric factor of species $i$ in reaction $j$
- $G_{FeS_2-p}$ is the pellet pyrite grade (mole/kg)
- $X_p$ is the pyrite conversion in pellet
- $\rho_o$ is the ore density (not bulk density) (kg/m$^3$)

The first bracketed term in the second equation of Eq. 5-25 represents the pyrite leaching rate for pellets determined in chapter 4. The units of mole/(kg ore-h) of both bracketed terms are converted to mole/(m$^3$ pellet pore-h) by multiplying the product of the ore density and the ratio of ore to pore volume. The liquid diffusivity $D$ (m$^2$/s) is given by the Wilke and Chang empirical correlation [16a]:

$$D_{i-H_2O}(T_1) \frac{\mu(T_1)}{T_1} = D_{i-H_2O}(T_2) \frac{\mu(T_2)}{T_2}$$

where $\mu$ is the viscosity of water (Pa·s) and $T$ is the temperature in Kelvins. This correlation is valid for species $i$ diffusing in dilute solution in water. The diffusivities of iron, sulfuric acid, and oxygen were found to be $0.98 \times 10^{-9}$, $1.06 \times 10^{-9}$, and $2.1 \times 10^{-9}$ m$^2$/s, respectively, at 25°C [17].
5.3.2 Stagnant Side Branch

After a slight rearrangement of the stagnant pore mass balance of Eq. 3-11, the component flux at the pellet/stagnant pore interface and the truffle reaction term were incorporated to yield the following expression:

\[
\frac{\partial C_{si}}{\partial t} = \left\{ \text{Rate of accumulation} \right\} = \left\{ \text{Diffusion rate} \right\} + \left\{ \text{Truffle reaction rate} \right\} + \left\{ \text{Pellet diffusive flux} \right\}
\]

\[
\frac{\partial C_{si}}{\partial t} = \left( \frac{D_i}{\tau_s X^2} \right) \left( \frac{\partial^2 C_{si}}{\partial \xi^2} + \frac{n}{\xi} \frac{\partial C_{si}}{\partial \xi} \right) + \left( s_{si-energy} + s_{si-flux} \right) = \frac{\text{mole}}{\text{m}^3 \text{pore} \cdot \text{h}}
\]

\[
s_{si-flux} = \frac{\rho_0 \gamma_f \xi_0}{\varepsilon_g} \left[ \psi_1 G_{FeS_2-t} k_t (C) (1 - \lambda_s) v_{i1} s_{3} + v_{i2} s_{2} \right]
\]

I.C. 1: \( C_{si}(\xi, 0) = C_{si0} \)

B.C. 2: \( C_{si}(1, t) = C_{fi} \)

B.C. 3: \( \frac{\partial C_{si}}{\partial \xi} \bigg|_{\xi=1} = 0 \)

where

- \( \xi \) is the normalized side branch pore position in a pore of length \( X \) (m)
- \( n \) is the shape factor
- \( \epsilon_s \) is the stagnant liquid holdup (m\(^3\) stagnant/m\(^3\) heap)
- \( C_{si} \) is the concentration (mole/L) of species \( i \) in the stagnant pore
- \( \tau_s \) is the side branch tortuosity (m/m)
- \( s_s \) is the source term (mole/(m\(^3\) stagnant volume-h))
- \( r_{sj} \) are the reaction rates of elemental sulfur (reaction 5-3, mole/(kg ore-h)) and ferrous ions (reaction 5-2, mole/(m\(^3\) stagnant volume-h)) determined in section 5.2.2
- \( v_{ji} \) is the stoichiometric factor of species \( i \) in reaction \( j \)
• $G_{FeS_2-t}$ is the truffle pyrite grade (mole/kg)
• $X_t$ is the pyrite conversion of truffles
• $\gamma_t$ is the truffle proportion (kg truffle/kg ore)

Eq. 5–27 does not apply to species dissolved into solution by gas/liquid transfer. Section 5.5 deals with the component balance for one such species: oxygen.

Because the pellet diffusive flux term (second bracketed term of the third equation in Eq. 5–27) has units of mole/(m$^3$ pellet pore-h), this term was multiplied by the factor of Eq. 5–28 having units of m$^3$ pore/m$^3$ stagnant volume to convert its units to mole/(m$^3$ stagnant pore-h).

$$
\left(1 - \gamma_t\right) \frac{\varepsilon_p}{\varepsilon} \frac{\varepsilon_o}{\varepsilon} \left(\frac{\rho_o}{\rho_o}\right) = \frac{m^3 \text{ pore}}{m^3 \text{ stagnant}}
$$

$$
\left[\begin{array}{c}
\text{(kg ore as pellet)} \\
\text{(kg ore total)}
\end{array}\right] \frac{\left(\begin{array}{c}
\text{m}^3 \text{ ore as pellet} \\
\text{m}^3 \text{ pellet}
\end{array}\right)}{\left(\begin{array}{c}
\text{m}^3 \text{ ore total} \\
\text{m}^3 \text{ heap}
\end{array}\right)} \left(\begin{array}{c}
\text{m}^3 \text{ stagnant} \\
\text{m}^3 \text{ heap}
\end{array}\right) = \left(\begin{array}{c}
\text{kg ore total} \\
\text{kg ore as pellet}
\end{array}\right)
\left(\begin{array}{c}
\text{m}^3 \text{ ore total} \\
\text{m}^3 \text{ ore as pellet}
\end{array}\right)
$$

5.3.3 Flowing Liquid

The component balance of the flowing liquid (Eq. 3-16) remains unchanged.

$$
\frac{\partial C_{fi}}{\partial t} = - \frac{1}{t_a} \frac{\partial C_{fi}}{\partial \zeta} - (n + 1) \frac{\varepsilon_s}{\varepsilon_f} \left(\frac{D_{fi}}{\tau_s^2 X^2}\right) \frac{\partial C_{si}}{\partial \zeta} \bigg|_{\zeta=1}
$$

I.C. 1: $C_{fi}(\zeta,0) = C_{fi0}$

B.C. 2: $C_{fi}(0,t) = C_{fi,feed}$

• $\zeta$ is the normalized heap depth
• $\varepsilon_f$ is the flowing liquid holdup (m$^3$ flowing/m$^3$ heap)
• $C_n$ is the concentration (mole/L) of species $i$ in the flowing liquid
• $t_a$ is the liquid advection time (h) (Eq. 3–3)

### 5.4 Cell Mass Balance

Although the component matrix (Eq. 5–6) does not include mesophiles, moderate thermophiles, and extreme thermophiles, Eqs. 5–25, 5–27, and 5–29 can also apply to any types of cells after taking into account phenomena such as cell adsorption and motility of the suspended cell population.

A relationship between attached and suspended cell populations is needed. A recent review of microbial leaching models highlighted the multiple approaches to model adsorption phenomena [18]. The Langmuir [9] and Freundlich [10] adsorption isotherms were shown to adequately fit the equilibrium surface and suspended cell concentration in slurries of low pulp density. In this work, the two populations are related by a quasi–Langmuir/quasi–linear adsorption isotherm:

$$
\frac{Y_{att}(t)}{Y_{max}(t)} = \left( \frac{K_{ads} Y_{susp}(t-1)}{1 + K_{ads} Y_{susp}(t-1)} \right) = m Y_{susp}(t)
$$

where $Y_{att}$ is the concentration of attached cells expressed as cells/kg ore, $Y_{susp}$ is the planktonic cell population (cells/L), and $K_{ads}$ is the adsorption constant (L/cells). The subscript $t$ refers to the actual time index and $(t-1)$ to the previous time index.

This expression is easily integrated into Eqs. 5–25 and 5–27. For instance, the mass balance on a unit volume in the pellet pore is now written as:

$$
4\pi r^2 \Delta r \frac{\partial}{\partial t} \left( Y_{susp} \frac{\rho_o (1 - \varepsilon_p)}{\varepsilon_p} Y_{att} \right) =
4\pi (r + \Delta r)^2 \left( \frac{D_k}{\tau_p^2} \frac{\partial Y_{susp}}{\partial r} \right)_{r+\Delta r} - 4\pi r^2 \left( \frac{D_k}{\tau_p^2} \frac{\partial Y_{susp}}{\partial r} \right)_{r} + (4\pi r^2 \Delta r) s_{pk} \left( Y_{att}, Y_{susp} \right)
$$

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where the cell diffusivity, $D_k$, due to motility was experimentally shown to be $0.4 \times 10^{-9}$ to $5.6 \times 10^{-9}$ m$^2$/s [19].

After replacing $Y_{pk}^{att}$ by $\omega Y_{pk}^{susp}$, dividing Eq. 5-31 by $(4\pi \Delta r)$ and taking the limit as $\Delta r \to 0$, we find:

$$
(1 + \kappa_p) r^2 \frac{\partial Y_{pk}^{susp}}{\partial t} = \frac{D_k}{\tau_p^2} \left[ \frac{\partial^2 Y_{pk}^{susp}}{\partial \xi^2} + \frac{2}{\zeta} \frac{\partial Y_{pk}^{susp}}{\partial \zeta} \right] + r^2 s_{pk} \left[ (1 + \kappa_p) Y_{pk}^{susp} \right]
$$

(5-32)

where

$$
\kappa_p = \frac{\rho_o (1 - \varepsilon_p)}{\varepsilon_p}
$$

(5-33)

Taking the derivative of the first term on the right-hand side, dividing by $r^2$, and normalizing the radial position, the final expression of the cell balance in the pellet pore is given as:

$$
(1 + \kappa_p) \frac{\partial Y_{pk}^{susp}}{\partial t} = \left\{ \frac{D_k}{\tau_p^2 R^2} \left[ \frac{\partial^2 Y_{pk}^{susp}}{\partial \xi^2} + \frac{2}{\zeta} \frac{\partial Y_{pk}^{susp}}{\partial \zeta} \right] + s_{pk} \left[ (1 + \kappa_p) Y_{pk}^{susp} \right] \right\}
$$

(5-34)

In a similar way, Eqs. 5-27 and 5-29 now become respectively:

$$
(1 + \kappa_s) \frac{\partial Y_{sk}^{susp}}{\partial t} = \left\{ \frac{D_k}{\tau_s^2 X^2} \left[ \frac{\partial^2 Y_{sk}^{susp}}{\partial \xi^2} + \frac{n}{\zeta} \frac{\partial Y_{sk}^{susp}}{\partial \zeta} \right] + s_{sk} \left[ (1 + \kappa_s) Y_{sk}^{susp} \right] \right\}
$$

(5-35)

Stagnant phase:

$$
\left. \begin{array}{l}
(1 - Y_f) \frac{\partial \varepsilon_f}{\partial \xi} \frac{\partial Y_{susp}^{susp}}{\partial \xi} + \frac{3 D_k}{\tau_p^2} \frac{\partial Y_{pk}^{susp}}{\partial \zeta} \right|_{\xi = 1}
\end{array} \right)
$$

(5-36)

Flowing liquid:

$$
\frac{\partial Y_{sk}^{susp}}{\partial t} = \frac{1}{t_a} \frac{\partial Y_{sk}^{susp}}{\partial \xi} - (n + 1) \frac{\varepsilon_f}{\varepsilon_f} \left\{ \frac{D_k}{\tau_s^2 X^2} \frac{\partial Y_{sk}^{susp}}{\partial \zeta} \right\}_{\xi = 1}
$$

Note that $Y_{fk}^{att}$ does not exist and that $\kappa_s$ is given by:

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\[ \kappa_s = \frac{\rho_o \varepsilon_o \gamma^t}{\varepsilon_s} \]  

(5-37)

### 5.5 Oxygen Mass Balance

Assuming that the gas phase is in intimate contact with the stagnant solution, oxygen necessary for the oxidation of ferrous ions and elemental sulfur can bypass the *flowing liquid/diffusion pore* route by transferring directly from the gas to the stagnant phase (Figure 3.4). Therefore, each unit volume in the stagnant pore becomes a separate batch reactor from the oxygen point of view.

Eq. 5-29 thus becomes irrelevant. Just like any other soluble species, oxygen does need to diffuse into the saturated pores of the pellets to get to the reaction sites, and thus Eq. 5-25 is left unchanged. Only Eq. 5-27 must be rewritten for oxygen in each unit volume of stagnant liquid:

\[
\frac{\partial \dot{C}_{sO_2}}{\partial t} = r_{O_2(d)} + r_{sO_2} + \left[ (1 - \gamma_t) \frac{\varepsilon_p}{1 - \varepsilon_p} \frac{\varepsilon_o}{\varepsilon_s} \right] \left[ \frac{3 D_{O_2}}{R^2 \tau_p} \frac{\partial C_{pO_2}}{\partial \xi} \right]_{\xi=1}
\]  

(5-38)

\[ r_{O_2(d)} = k_L a \left( C_{O_2}^* (T, C_{sl}) - \dot{C}_{sO_2} \right) \]  

(5-39)

where \( k_L \) is the overall gas/liquid mass transfer coefficient (m/h), \( a \) is the interfacial area per unit volume of stagnant solution (m\(^2\) area/m\(^3\) stagnant solution), and \( C^* \) (mole/L) is the temperature– and salinity–dependent oxygen saturation. The *salting out* effect will be ignored in this work because of the low to moderate iron and sulfate leachate concentrations in the validation column tests.

To this author’s knowledge, there exists no correlation to estimate the gas–liquid mass transfer coefficient under conditions of extremely low superficial liquid velocity in porous media. For lack of a better tool, \( k_L a \) was estimated to be 0.3 h\(^{-1}\) by
setting the liquid flow rate to be 5 L/(m$^2$.h) in Turek and Lange’s correlation for low-velocity trickle bed reactors [20]. It is worth noting, however, that flow rates typical of heap leaching processes are three orders of magnitude smaller than the minimum flow rate condition tested in their study. The mass transfer coefficient was also calculated to be $\approx 3$ h$^{-1}$ using correlations for columns packed with Raschig rings or Berl saddles compiled in Perry’s Chemical Engineers’ Handbook [21]. The method presented in chapter 3 of reference 16b to estimate the mass transfer coefficient from a gas into a falling liquid film was employed as well. The thickness of the film (≈ 1 mm) and the specific surface area (≈ 1000 m$^2$/m$^3$) were calculated using the experimental values of $\varepsilon_s$ and $\varepsilon_0$. The $k_La$ value was found to be in the order of 10 h$^{-1}$. At last the mass transfer coefficient was estimated to be $\approx 6.5$ h$^{-1}$ from actual leaching data collected from tests carried out in the same column setup as described in chapter 2, and loaded with ores containing sulfide minerals of another nature (proprietary information).

The solubility of oxygen in pure water takes the following thermodynamically-based equation [22]:

$$C_{O_2}^* = p_{O_2} \exp\left(\frac{68623 - 1430.4 T - 0.046 T^2 + 203.35 T \ln(T)}{RT}\right) \tag{5-40}$$

where $p_{O_2}$ is the oxygen partial pressure (atm) dependent on the water vapor partial pressure, $p_v$, with temperature, and $R$ is the gas constant ($8.314$ J/(mole-K)).

Depending on the heap height and local heap temperatures, the partial pressure of oxygen may decrease significantly from local atmospheric levels as the air moves upward through the heap, due to the depletion of oxygen and the increase in absolute humidity with increasing heap temperatures. The oxygen gas balance is derived based on the following assumptions:

- The overall flow of dry air is not diminished by the consumption of oxygen (the “Boussinesq approximation”).
- The axial diffusion of oxygen is negligible compared to advection.
Pseudo steady state is assumed.

The steady-state oxygen gas balance within a heap is written thus:

$$\frac{d}{dz} \left( \frac{G_g C_{O_2}}{\rho_g} \right) = \varepsilon_s r_{O_2(d)}$$

(5-41)

where the subscript $g$ refers to the total gas (dry air ($= N_2+O_2+CO_2$+others) + vapor). Noting the Boussinesq approximation, then the gas mass flux is written:

$$G_g = G_a (1 + \psi)$$

(5-42)

where $\psi$ is the water vapor saturation (i.e. equilibrium mass ratio of water vapor to dry air, Eq. 5-43).

$$\psi = \psi(T) = \frac{0.6242 p_v(T)}{p - p_v(T)}$$

(5-43)

By the ideal gas law, the gas mass density and molar oxygen gas concentration are defined respectively thus:

$$\rho_g = \frac{p M_g}{RT} \quad C_{O_2} = \frac{p_{O_2}}{RT}$$

(5-44)

where, again by the Boussinesq approximation, the gas molecular weight is defined thus:

$$\frac{(1+\psi)}{M_g} = \frac{1}{M_a} + \frac{\psi}{28.87} + \frac{\psi}{18.02}$$

(5-45)

Applying these results to the oxygen gas balance gives:
Carrying out product-rule differentiation gives, after slight rearrangement:

\[
\frac{G_a}{\rho} \frac{d}{dz} \left[ \left( \frac{1}{M_a} + \frac{\psi}{M_v} \right) p_{O_2} \right] = \varepsilon_s r_{O_2}^{(d)} 
\]

where the prime denotes differentiation with respect to temperature. Hence, the oxygen gas balance is a quasi-linear, inhomogeneous, first-order, ordinary differential equation.

\[
d\frac{p_{O_2}}{dz} = \frac{p\varepsilon_s r_{O_2}^{(d)} - \left( \frac{\psi \frac{\partial T}{\partial z}}{M_v} \right) p_{O_2}}{1 + \frac{\psi}{M_v}}
\]

5.6 Heat Conservation

Heat transport is especially important in sulfide heap leaching, in which one or more highly exothermic sulfide oxidation reactions take place, because of the sensitivity of cells to elevated temperatures and the strong temperature dependence of the oxidation reactions. Understanding the thermal behavior of heaps requires knowledge of the ambient environmental conditions and of the heat generating potential of the ore. The heat conservation model developed by Dixon [23] constitutes the whole foundation of this section.

An enthalpy balance is derived based on the following assumptions:

- The heap is comprised of three phases: a continuous stagnant phase consisting of all solids and stagnant solution, a liquid phase flowing downward, and a gaseous phase flowing upward.
- All three phases are in thermal equilibrium at any depth within the heap.
- The gaseous phase is saturated in water vapor at all points within the heap.
- All physical and thermal properties of the heap remain constant and uniform throughout the leach cycle.
The general enthalpy balance is summarized as follows:

\[
\frac{\partial T}{\partial t} = \frac{1}{\tau_c} \frac{\partial^2 T}{\partial \xi^2} - \left[ \frac{f_c(T)}{\tau_c} - \frac{f_v(T)}{\tau_a} \right] \frac{\partial T}{\partial \xi} + S \tag{5-48}
\]

with

\[
\xi = \frac{z}{Z} \quad \bar{S} = \frac{S}{\rho C_p} \quad \tau_c = \frac{\rho C_p \bar{k}^2}{k} \quad \tau_f = \frac{\rho C_p Z}{\Gamma_f C_{pf}} \quad \tau_a = \frac{\rho C_p Z}{\Gamma_a C_{pa}}
\]

where \( \bar{k} \) is the average heap thermal conductivity (W/(m·K)), \( \tau_c, \tau_f, \) and \( \tau_a \) are the timescales of conduction, liquid-phase advection, and gas-phase advection, respectively, \( \Gamma_f \) and \( \Gamma_a \) are the mass fluxes of water and dry air (kg/(m²·h)), respectively, \( C_{pf} \) and \( C_{pa} \) are their respective heat capacities (J/(mole·K)), and \( S \) is the volumetric rate of heat generation given by the following expression:

Stagnant phase:

\[
S_s = \frac{1}{3600} \left( \sum_{j=1,3} \rho_o \gamma_{j} \varepsilon_{j} \sum_{j=1,3} \Delta H_{r_{j} \cdot r_{j}} + \varepsilon_{s} \Delta H_{r_{s} \cdot r_{s2}} \right) [\mathcal{W}] \quad \text{m}^3 \text{heap}^{-1}
\tag{5-49}
\]

Pellet pores:

\[
S_p = \frac{1}{3600} \left( 1 - \gamma_{p} \right) \varepsilon_{o} \left( \sum_{j=1,3} \rho_o \Delta H_{r_{j} \cdot r_{j}} + \frac{\varepsilon_p}{1 - \varepsilon_p} \Delta H_{r_{2} \cdot r_{22}} \right) [\mathcal{W}] \quad \text{m}^3 \text{heap}^{-1}
\tag{5-50}
\]

where \( \Delta H_{r} \) is approximated as (-8,800\( \phi \) + 16,000), 204,941, and 623,560 J/mole of reaction \((5-1), (5-2), \) and \( (5-3), \) respectively, over the temperature range of interest.

The functional \( f_c(T) \) in Eq. 5-48 incorporates boundary effects such as liquid phase evaporation at the heap surface, while the functional \( f_v(T) \) combines effects of latent and sensible heat carried in the water vapor in the gas phase. The influence of solar radiation and day-night cycles are incorporated through the following initial and boundary conditions:

\[
\text{B.C.1: } - \frac{1}{\tau_c} \frac{\partial T}{\partial \xi} \bigg|_{\xi=0} = \sum q + \frac{1}{\tau_f} \left[ T - T_{f} \right]_{\xi=0}
\tag{5-51}
\]
This enthalpy balance is a second-order, non-linear partial differential equation with mixed non-linear boundary conditions. The reader is referred to the nomenclature section for a detailed description of the parameters introduced in Eq. 5–50, as well as to Dixon’s publication for additional information on the heat model [23].

### 5.7 Solving the Source Terms

A pseudo steady state (PSS) approximation is invoked for those components simultaneously produced and consumed to prevent severe numerical restrictions. Although four of the five components meet this condition, it is more reasonable to use the PSS approximation for iron in the stagnant and agglomerate phases because the pyrite system tends to operate at very high potentials, i.e. very low Fe(II) levels. The very low solubility of oxygen in water justifies the use of the approximation, but only in the stagnant phase where it is both consumed and produced. The approximation is an unnecessary condition for $S^0$ and $H_2S_0$ because both are always detected in non-negligible amounts at any time and any depth in both small and large columns.

#### 5.7.1 Pellet Pore

Recalling Eq. 5–25 and invoking the PSS approximation for $C_{pFe(II)}$ in the pellet pores gives:

$$s_{pFe(II)} = 3[1 + 2(2 - \varphi)] \frac{\rho_o (1 - \varepsilon_p)}{\varepsilon_p} r_{p1} - 2 r_{p2} = 0 \quad (5–52)$$

Newton’s method may be used to solve for the steady state value of $C_{pFe(II)}$ by iterating on the following equation:
\[ C_{p\text{Fe(II)}}^{\text{new}} = C_{p\text{Fe(II)}}^{\text{old}} - s_{p\text{Fe(II)}} \left( \frac{ds_{p\text{Fe(II)}}}{dC_{p\text{Fe(II)}}} \right)^{-1} \]  

(5-53)

until the ferrous rate is zero. In this way, the ferrous concentration will never drop below zero numerically. The derivative of the ferrous rate with respect to \( C_{p\text{Fe(II)}} \) is thus:

\[ \frac{\partial s_{p\text{Fe(II)}}}{\partial C_{p\text{Fe(II)}}} = 3[1 + 2(2 - \varphi)] \frac{\rho_o (1 - \varepsilon_p)}{\varepsilon_p} \frac{\partial r_{p1}}{\partial C_{p\text{Fe(II)}}} - 2 \frac{\partial r_{p2}}{\partial C_{p\text{Fe(II)}}} = 0 \]  

(5-54)

Recognizing that the ferric concentration is simply the difference between the total and ferrous iron concentrations, the derivative of each reaction rate with respect to \( C_{p\text{Fe(II)}} \) is given as follows:

\[ \frac{\partial r_{p1}}{\partial C_{p\text{Fe(II)}}} = -\frac{1}{2} G_{\text{FeS}_2} k_{1-p} \exp\left( -\frac{E_{\text{at}}}{R} \left( 1 - \frac{1}{328.15} \right) \right) \frac{C_{p\text{Fe(III)}}}{C_{p\text{Fe(II)}}^{3}} \frac{C_{p\text{Fe(II)}}}{(1 - X_p)^{t_p}} \]  

(5-55)

\[ \frac{\partial r_{p2}}{\partial C_{p\text{Fe(II)}}} = \sum_{k=1}^{3} g_{\text{FeFe,k}} f \frac{K_{\text{FeFe,k}}}{(K_{\text{FeFe,k}} + C_{p\text{Fe(II)}})^2} \frac{C_{p\text{Fe(II)}}}{(K_{\text{O2,k}} + C_{p\text{O2}})} \]  

(5-56)

### 5.7.2 Stagnant Side Branch

Invoking the PSS approximation for \( C_{s\text{Fe(II)}} \) and \( C_{s\text{O2}} \) in the stagnant pores gives:

\[ s_{s\text{Fe(II)}} = 3[1 + 2(2 - \varphi)] \frac{\rho_o (1 - \varepsilon_p)}{\varepsilon_p} \]  

(5-57)

\[ s_{s\text{O2}} = \frac{k_{1-p}}{\varepsilon_s} (C_{\text{O2}}^{*} - C_{s\text{O2}}) - \frac{3 \rho_o (1 - \varepsilon_p)}{\varepsilon_p} r_{s1} - \frac{1}{2} r_{s2} + \]  

\[ \left[ (1 - \gamma_t) \frac{\varepsilon_p}{(1 - \varepsilon_p)} \varepsilon_o \right] ^{\frac{3 D_{\text{O2}}}{R^2 \tau_p^2 \varepsilon}} \frac{\partial C_{p\text{O2}}}{\partial \zeta} \right]_{\varepsilon=1} \]  

(5-58)
which are solved simultaneously by a multidimensional Newton’s method to satisfy
the following two equations:

\[
s_{sFe(II)} = \frac{\partial s_{sFe(II)}}{\partial C_{sFe(II)}} \left(C_{sFe(II)}^{new} - C_{sFe(II)}^{old}\right) + \frac{\partial s_{sFe(II)}}{\partial C_{sO2}} \left(C_{sO2}^{new} - C_{sO2}^{old}\right) = 0
\]

(5-59)

\[
s_{sO2} = \frac{\partial s_{sO2}}{\partial C_{sFe(II)}} \left(C_{sFe(II)}^{new} - C_{sFe(II)}^{old}\right) + \frac{\partial s_{sO2}}{\partial C_{sO2}} \left(C_{sO2}^{new} - C_{sO2}^{old}\right) = 0
\]

(5-60)

Here, because of the fact that there are only two equations, the oxygen concentration difference term in Eq. 5-60 can be isolated and substituted into Eq. 5-59 to yield a single ferrous-dependent expression similar to Eq. 5-52 to be solved easily by Newton’s method. The same procedure is repeated with the ferrous concentration difference term in Eq. 5-59 to yield a single oxygen-dependent expression. The number of partial derivatives (Eqs. 5-61 to 5-64) increases to 4.

\[
\frac{\partial s_{sFe(II)}}{\partial C_{sO2}} = 3\left[1 + 2(2 - \varphi)\right] \frac{\rho_o(1-\varepsilon_p)}{\varepsilon_p} \frac{\partial r_{s1}}{\partial C_{sO2}} - 2 \frac{\partial r_{s2}}{\partial C_{sFe(II)}} = 0
\]

(5-61)

\[
\frac{\partial s_{sO2}}{\partial C_{sFe(II)}} = -2 \frac{\partial r_{s2}}{\partial C_{sO2}}
\]

(5-62)

\[
\frac{\partial s_{sO2}}{\partial C_{sFe(II)}} = -\frac{1}{2} \frac{\partial r_{s2}}{\partial C_{sFe(II)}}
\]

(5-63)

\[
\frac{\partial s_{sO2}}{\partial C_{sO2}} = -K_L a - \frac{3 \rho_o \varepsilon_o \gamma_t}{2 \varepsilon_s} \frac{\partial r_{s3}}{\partial C_{sO2}} - \frac{1}{2} \frac{\partial r_{s2}}{\partial C_{sO2}}
\]

(5-64)

Two of the four partial derivatives on the right-hand side of Eqs. 5-61 to 5-64 are similar to Eqs. 5-55 and 5-56. The other two are written thus:
dr_2 \over ds_2 \frac{\partial s_2}{\partial C_{SO_2}} = - \sum_{k=1}^{3} \gamma_{Fe,sk}^{tot} k_{Fe,k} f_{g,Fe,k}(T) \left( \frac{K_{O_2,k}}{K_{O_2,k} + C_{SO_2}} \right)^2 \left( \frac{C_{Fe(II)}}{K_{Fe,k} + C_{Fe(II)}} \right) (5-65)

\frac{\partial s_3}{\partial C_{SO_2}} = - \sum_{k=1}^{3} \gamma_{S,sk}^{tot} k_{S,k} f_{g,S,k}(T) \left( \frac{G_S}{K_{S,k} + G_S} \right) \left( \frac{K_{O_2,k}}{K_{O_2,k} + C_{SO_2}} \right)^2 (5-66)

5.8 Order of Solution

The algorithm's code is written using the MICROSOFT FORTRAN VISUAL WORKBENCH version 1.0 software. All physical parameters within the heap remain uniform and constant throughout the leach cycle. The order of solution of the model equations is as follows:

1. All initial conditions are defined. The volume of the heap occupied by the stagnant solution is assumed to be initially fully saturated. This assumption is reasonable considering that short and tall columns were fully wet after a few hours and in less than 5 days, respectively.

2. Starting at time \( t = t_g \) and heap depth \( \zeta = 0 \), the rates of reaction in the pores of the pellets are calculated at each of the \((NR+1)\) nodes using the PSS approximation for iron, and the \( C_p \) concentrations for all other components.

3. The rates of heat generation are calculated at each pellet node. The total heat generated over each pore volume is then evaluated by the trapezoidal method.

\[
\int_{a}^{b} f(x) dx \approx \frac{b - a}{2N} \left[ f(x_0) + 2 f(x_1) + 2 f(x_2) + 2 f(x_3) + \ldots + 2 f(x_{N-1}) + f(x_N) \right] (5-67)
\]

where all \( x_i \) values are equally spaced.

4. The new \( C_p \) concentrations at all \( NR \) nodes are solved numerically by fully implicit finite difference approximations of the form:

\[
\frac{\partial^2 u}{\partial x^2} + \frac{n \partial u}{\partial x} + \kappa f(u) = \frac{\partial u}{\partial t} (5-68)
\]
\[ \frac{\partial^2 u}{\partial x^2} + \frac{n \partial u}{\partial x} \big|_{x=0} = \frac{1}{n \Delta x^2} \left[ \left( i + \frac{n}{2} \right) u_{i+1}^{j+1} - (2 i) u_{i}^{j+1} + \left( i - \frac{n}{2} \right) u_{i-1}^{j+1} \right], 0 < i < N \]

\[ = \frac{2(n+1)}{x^2 \Delta x^2} \left[ u_{i+1}^{j+1} - u_{i}^{j+1} \right], i = 0 \]

\[ = \frac{1}{x^2 \Delta x^2} \left[ \left( i + \frac{n}{2} \right) u_{i+1}^{j+1} - (2 i) u_{i}^{j+1} + \left( i - \frac{n}{2} \right) u_{i-1}^{j+1} \right], i = N \] (5-69)

\[ \kappa f(u) = \kappa f \left( u_i^j \right) \] (5-70)

\[ \frac{\partial u}{\partial t} = \frac{u_{i+1}^{j+1} - u_{i}^{j}}{\Delta t} \] (5-71)

where \( i \) is the pore index (\( i = 0 \) at the end of the pore) and \( j \) is the time index. Since all the variables in the \( j \)th time level are known, and those of the \((j+1)\)th time level are unknown, except at the pore entrance, a system of \( N \) equations with \( N \) unknowns is generated, each with one variable in each of the \((i-1)\)th, \(i\)th, and \((i+1)\)th pore levels. The \( N \) algebraic equations form the following tri-diagonal coefficient matrix.

\[
\begin{bmatrix}
\psi_{i=0} & (2(n+1)\mu) & \psi_{i=0} & (1+\frac{n}{2})\mu & \psi_{i=0} & \psi_{i=0} \\
(1-\frac{n}{2})\mu & (1+\frac{n}{2})\mu & \psi_{i=0} & \psi_{i=0} & \psi_{i=0} & \psi_{i=0} \\
(2-\frac{n}{2})\mu & (2+\frac{n}{2})\mu & \psi_{i=0} & \psi_{i=0} & \psi_{i=0} & \psi_{i=0} \\
\vdots & \vdots & \ddots & \ddots & \ddots & \ddots \\
(N-1-\frac{n}{2})\mu & \psi_{i=0} & \psi_{i=0} & (N-1+\frac{n}{2})\mu & \psi_{i=0} & \psi_{i=0} \\
(N-\frac{n}{2})\mu & \psi_{i=0} & \psi_{i=0} & \psi_{i=0} & \psi_{i=0} & \psi_{i=0}
\end{bmatrix}
\] (5-72)

where \( \mu = \frac{\Delta t}{x^2 \Delta x^2} \)

\[ \psi_{i=0} = -2(n+1)\mu \quad \psi_{i=0} = -2\mu - 1 \] (5-73)
The solution vector is given by:

\[
\begin{bmatrix}
-u_0^j - \kappa \phi(u_0^j) \\
-u_1^j - \kappa \phi(u_0^j) \\
-u_2^j - \kappa \phi(u_0^j) \\
\vdots \\
-u_{NX-1}^j - \kappa \phi(u_{NX-1}^j) \\
-u_{NX}^j - \kappa \phi(u_{NX}^j) - \frac{\mu}{N} \delta_{j}^{\text{ent.}} (N+n/2)
\end{bmatrix}
\]  

(5-74)

The vector of unknowns is solved by Gaussian elimination.

5. The pellet entrance concentration at node \((NR+1)\) is set equal to the \(C_s\) concentration at the side branch node. The pellet entrance concentration gradient is calculated.

6. The truffle rates of reaction in the stagnant pores are calculated at all \((NX+1)\) side branch nodes using the PSS approximations for iron and oxygen, and using the \(C_s\) concentrations for all other components.

7. The truffle rates of heat generation are calculated at each side branch node, and that, together with the integrated pellet rate of heat generation, are integrated over each stagnant pore volume by compound quadrature.

8. The new \(C_s\) concentrations are determined at all \((NX+1)\) nodes using a fully implicit scheme in solving the second-order parabolic differential equation, taking into account the pellet diffusive fluxes.

9. Eq. 5-29 is transformed into an ordinary differential equation through the definition of the substantial rate derivative [24], expressed in dimensionless coordinates:

\[
\frac{D}{Dt} = \frac{1}{t_a} \frac{D}{D\zeta} \frac{\partial}{\partial t} + \frac{1}{t_a} \frac{\partial}{\partial \zeta}
\] 

(5-75)

A unit analysis reveals that the left- and right-hand side of Eq. 5-75 both have units of inverse time. This transformation facilitates the mathematical treatment of the model from the Lagrangian viewpoint, \(i.e.\) via the tracking
of fluid elements through the column. For this, a simple backward finite difference approximation [25] is used on the left–hand side of Eq. 5–76. The $C_f$ concentration at $(z+\Delta z)$ is set equal to the new $C_s$ concentration at node $(NX+1)$, as shown in the following schematic and in Eq. 5–76.

\[
\frac{1}{t_a} \left( \frac{C_f(IZ) - C_f(IZ-1)}{\Delta \zeta} \right) = \frac{1}{t_a} \left( \frac{C_s(NX+1) - C_f(IZ-1)}{\Delta \zeta} \right)
\]

\[
(n+1) \left\{ \frac{D}{\tau_s^2 X} \right\} \frac{1}{\varepsilon_f} \left( \frac{C_s(NX+2) - C_s(NX)}{2\Delta x} \right)
\]

(5–76)

10. Steps 2 to 9 are repeated for each depth increment until $z = Z$ (or $\zeta = 1$).

11. The fractional oxidation of pellets and truffles, as well as the overall fractional oxidation integrated over each stagnant volume and over the entire depth of the bed, are evaluated by compound quadrature.

12. After expanding the node grid and calculating the average surface heat flux based on a 24-h moving time average, the new $T(z)$ temperatures are determined using a fully implicit scheme, including central differences for the heat conductive and advective terms and a forward difference for the accumulation term, in solving the second–order, non–linear partial differential equation (Eq. 5–48).

13. The oxygen partial pressures are calculated by explicit finite differences.

14. The procedure is then repeated for the new time, $t+\Delta t$, using the new set of $C_p$ and $C_s$ concentrations, $O_2$ partial pressures, and temperatures $T(z)$.
5.9 Conclusions

5.9.1 Model Features

A pyrite heap biooxidation model has been developed and coded in FORTRAN. A 1D, height-based advection model with \( n \)-shape side branch diffusion serves as the model backbone. The heap parameters, including the stagnant liquid, flowing liquid, and ore volumetric proportions, are assumed constant in time and depth. The numerical code allows variations of the feed concentrations. A particle kinetic model is included as source term in each node of the side branches to represent the chemical pyrite oxidation rate of truffles. The non-agglomerated particle size distribution is indirectly taken into consideration in defining two topological parameters characteristic of the whole distribution. The solute transfer rate at the interface between the stagnant liquid and the spherical pellets of uniform size, as well as the biological oxidation rate of ferrous ions and elemental sulfur by mesophilic, moderately thermophilic and extremely thermophilic, planktonic and attached, iron- and sulfur-oxidizing microorganisms, are also grafted as source terms in each node. The net biological growth rate is modeled as death and growth processes, including Monod terms for each of the two limiting substrates (ferrous ions and oxygen). Cell viability is restricted to three temperature ranges. The Langmuir adsorption isotherm relates the reversible adsorption of attached and planktonic cell populations. Invoking the pseudo-steady state approximation for the two limiting substrates (ferrous ions and oxygen) overcomes numerical instabilities associated with negative concentrations. If required, the heat subroutine can be invoked to simulate non-isothermal behavior. A vertical gradient of oxygen partial pressure is calculated based on the gas/stagnant liquid mass transfer rate in each node of the side branches, as well as the effects of humidification.

The input parameters can be classified into three types:

- Taken directly from standard textbooks (e.g. diffusivity, saturation concentration, humidity);
- User-specified (e.g. number of nodes, heap height, air blowing rate, geographic location), and
- Estimated from previous testwork or refined through simulations (e.g. mineral rate constants, biological growth rate constants);

The model parameters that belong to the latter category are summarized in Table 5.2, along with internal and external references that the reader may consult to learn about the experimental and numerical methods employed to evaluate the parameters.

5.9.2 Recommendations

The numerical code in its current form required occasional additions of switches and if-then statements in the mineral and biological rate subroutines in order to avoid numerical instabilities. For instance, all chemical and biological rates were set to zero, and no further chemical oxidation of pyrite was assumed to occur (i.e. no increase in conversion), when the total number of all three types of cells was less than \(1 \times 10^7\) cells/L. Without this conditional statement, the PSS approximation calculations could not be resolved satisfactorily. Introducing a chemical ferrous oxidation rate term should avoid, in principle, the numerical instabilities associated with this situation. However, the numerical method employed to solve the PSS approximation is robust and handles very small oxygen concentrations.

Absence of sulfur-oxidizing cells, replacement of the feed solution by tap water, and presence of net acid-consuming sulfide minerals could lead to more serious deficit of sulfuric acid in certain parts of the heap than that observed in columns in the initial stages of leaching. There is therefore a need to integrate acid concentrations into the PSS approximation, particularly if the precipitation reaction (5–5) were also to be considered.
Summary of kinetic and hydrodynamic model parameters to be evaluated from experimental testwork in chapters 4 and 5 or from tuning exercises in chapter 6.

### Mineral Leaching Kinetic Parameters
- Rate constant $k_0$
- Activation energy $E_a$
- Chemistry functional $f(C)$
- Topological exponent $\phi$
- Abiotic elemental sulfur yield $\varphi$

### Heap Hydrodynamic Parameters
- Ore volumetric proportion $\varepsilon_0$
- Stagnant liquid holdup $\varepsilon_s$
- Flowing liquid holdup $\varepsilon_f$
- Weight proportion of truffles $\gamma_t$
- Mass transfer coefficient $k_L\alpha$
- Shape factor $n$
- Pore length $\tau_sX$

### Biological Kinetic Parameters
- Growth rate constant $k_g (\times 6)$
- Decay rate multiplier $k_e (\times 6)$
- Cell inhibition factor $KI_Y (\times 6)$
- Substrate growth Monod factor $K (\times 6)$
- Cell yield $Y (\times 6)$
- Adsorption constant $K_{ads} (\times 6)$
- Oxygen growth Monod factor $K_{O_2} \rightarrow [3-5]$
- Maximum adsorption $Y_{max} \rightarrow$ Chapter 2
- Minimum viable temperature $T_{min} (\times 6)$
- Maximum viable temperature $T_{max} (\times 6)$
- Optimum temperature $T_{opt} (\times 6)$
Although the flow and kinetics subroutines of the current model already fill in the

gaps of many published heap leaching models, future modeling efforts should be
directed at the following issues, including:

- **Gas/liquid hydrodynamics in non-ideal heaps:**
  - Rigorous 2D-3D advection model based on actual liquid distribution piping
    system
  - Ore mass-based model because of initial and progressive slumping
  - Initial wetting phase
  - Rest/rinse cycles
  - Formal numerical treatment of solution recycling and/or intermediate
    conditioning
  - Time- and depth-dependent flow and heap parameters

- **Mineral kinetics:**
  - Distribution of pellet sizes
  - Global approach to handle any solid mineral (e.g. S°)
  - Close vicinity of slowly- and rapidly-oxidizable sulfide minerals (e.g. grain
    occlusion, galvanic interactions)

- **Gas transport:**
  - Rigorous 2D-3D advection model based on actual air distribution piping
    system
  - *Salting out* effect on O₂ saturation
  - Evaluation of gas/liquid mass transfer coefficient

- **Biological models:**
  - Dual substrate consumption
  - Ferrous ion and sulfur biological oxidation kinetics in stationary phase,
    and not exclusively limited to exponential growth phase
  - Oxidation kinetics in exponential phase for moderate and extreme
    thermophiles
  - Rigorous modeling of adsorption/desorption in packed bed reactors
  - Influence of solution chemistry on cell activity
  - Modeling of direct microbial oxidation processes, if any
### 5.10 Nomenclature

- **a**: interfacial area per unit stagnant volume (m²/m³ stagnant solution)
- **A**: heap cross-section (m²) or temperature skew parameter of biological model
- **b**: Ratkowskii temperature parameter
- **B**: temperature parameter of biological model
- **C**: concentration (mole/L)
- **C***: saturation concentration (mole/L)
- **Cₚ**: heat capacity (J/(kg·K))
- **d**: declination (°)
- **D**: liquid diffusivity (m²/s)
- **Eₐ**: activation energy (J/mole)
- **f**: temperature dependence of the rate constant (-)
- **F₁₂**: heap-to-sky view factor (-)
- **G**: grade (mole/kg ore)
- **h**: heat transfer coefficient (W/(m²·K))
- **k**: rate constant (units specific to each expression) or thermal conductivity (W/(m·K))
- **K**: saturation constant (units specific to each expression)
- **KI**: inhibition constant (units specific to each expression)
- **kₑ**: overall gas-liquid mass transfer coefficient (m/h)
- **l**: latitude (°)
- **Le**: Lewis number (= ρₑCₚₑDₑ/kₑ)
- **ṁ**: mass flow rate (kg/s)
- **M**: molecular weight (kg/mole)
- **n**: shape factor (= 0, 1, or 2)
- **NR**: number of pore agglomerate nodes (-)
- **NZ**: number of vertical nodes (-)
- **NX**: number of side-branch nodes (-)
- **P**: partial pressure (atm)
- **q**: heat flux by conduction (W/m²)
- **R**: pellet radius (m), or gas rate constant (= 8.314 J/(mole·K))
- **r**: position in pellet (m)
- **rᵢ**: reaction rate of reaction j (mole/(m³·h) or mole/(kg·h))
- **sᵢ**: reaction rate of component i (mole/(m³·h))
- **S**: rate of heat generation per unit heap volume (W/m³)
- **T**: temperature (°C or °K)
\[ t \quad \text{time (h)} \]
\[ t_a \quad \text{flowing liquid advection time (h)} \]
\[ t_{\text{att}} \quad \text{atmospheric attenuation factor} \ (-) \]
\[ x \quad \text{position in the side-branch pore (m)} \]
\[ X \quad \text{conversion (-) or length of side-branch pore (m)} \]
\[ Y \quad \text{cell concentration (cells/kg ore or cells/L)} \]
\[ y \quad \text{cell yield (cells/mole Fe)} \]
\[ z \quad \text{depth (m)} \]
\[ Z \quad \text{heap height (m) or number of moles of electrons per mole of reaction} \]
\[ \Delta H_r \quad \text{heat of reaction (J/mole reaction)} \]

5.10.1 Greek Letters

\[ \alpha \quad \text{heap surface solar absorptivity (-)} \]
\[ \beta \quad \text{ratio of vapor to dry air heat capacities} \ (C_{pv}/C_{pa}) \]
\[ \gamma \quad \text{proportion of particles as truffles or pellets (kg/kg)} \]
\[ \Gamma \quad \text{mass flux (kg/(m}^2\text{-h)}) \]
\[ \varepsilon \quad \text{volume fraction (m}^3\text{/m}^3\text{) or heap surface grey-body emissivity (-)} \]
\[ \zeta \quad \text{normalized heap depth (-)} \]
\[ \eta \quad \text{effectiveness factor (-)} \]
\[ \kappa \quad \text{partitioning coefficient (attached cells/suspended cells)} \]
\[ \lambda \quad \text{latent heat of vaporization (J/kg water)} \]
\[ \Lambda \quad \lambda/C_{pa} \]
\[ \mu \quad \text{viscosity (Pa-s)} \]
\[ \nu_j \quad \text{stoichiometric coefficient of component i in reaction j (mole/mole reaction)} \]
\[ \xi \quad \text{normalized position in side branch (-)} \]
\[ \rho \quad \text{density (kg/m}^3\text{)} \]
\[ \tau \quad \text{tortuosity (m/m) or timescale of advection or conduction} \]
\[ \phi \quad \text{topological exponent (-)} \]
\[ \psi \quad \text{water vapor saturation (= equilibrium mass ratio of water vapor to dry air)} \]
\[ \varsigma \quad \text{linear adsorption coefficient (cells/kg ore / cells/L solution)} \]
\[ \omega \quad \text{relative humidity (-)} \]
\[ \Omega \quad \text{ratio of dry air to liquid mass fluxes} \ (\Gamma_a/\Gamma_l) \]
\[ \varsigma \quad \text{normalized position in pellet (-)} \]
\[ \varphi \quad \text{elemental sulfur yield (mole S}^0\text{/mole FeS}_2\text{)} \]
5.10.2 Subscripts

a  dry air
ads  adsorption
att  attenuation
c  conduction
d  death
e  endogenous
f  flowing liquid
g  growth
i  species/component
j  reaction
k  cell species (mesophile, moderate thermophile, or extreme thermophile)
m  maintenance
max  maximum
min  minimum
o  ore or reference state
opt  optimum
p  pellet
r  reaction
s  stagnant solution
sky  sky
$S^o$  elemental sulfur
t  truffle or threshold
v  vapor
0  initial
∞  ambient

5.10.3 Superscripts

att  attached cells
sus  suspended cells
tot  suspended and attached cells

5.11 References


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Chapter 5 - Model Add-Ons


# Chapter 6

## Isothermal Model Simulations

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</tbody>
</table>
6.1 Introduction

The kinetic and hydrodynamic parameters of the pyrite heap biooxidation model (chapter 5) were measured experimentally in chapters 3 and 4. In this chapter, the yet unknown biological parameters are first determined in section 6.2.1 by fitting the model predictions to the experimental results of the basic 22°C, 45°C, and 65°C column tests previously described in chapter 2. The model and its three sets of biological parameters are then employed to test the model predictive capabilities against the performance of other column tests whose irrigation flow rate and packing characteristics differed from the base cases. Finally, section 6.3 discusses the numerical difficulties encountered after integrating the pellet subroutine into the main framework, and the resolution found. Simulations are then performed to evaluate the influence of the proportion of truffles, pellet size, and kinetics. A detailed list of nomenclature is available in section 5.10.

6.2 Truffle Simulations

6.2.1 Tuning Exercises

The parameters listed in Table 6.1 to Table 6.6 are common to the three basic cases examined in the next three sections. The estimated parameters in italic fonts include an independent set of five biological parameters for each type of cells (mesophile, moderate thermophile, or extreme thermophile), plus the gas/liquid mass transfer coefficient common to all three case studies. Assuming that only one of the three types of cells was active at any of the three temperatures tested, the five biological parameters of each iron- and sulfur-oxidizing cells belonging to one cell type were adjusted simultaneously to best fit altogether 1) the sulfide/sulfate oxidation profile, 2) the Fe(III)/Fe(II) concentration ratio trend, 3) the cell number profile, 4) the total iron concentration in the bulk, 5) the potential profile, and 6) the elemental sulfur grade.
Table 6.1  Heap design parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>22°C</th>
<th>45°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z (m)</td>
<td>Active heap height</td>
<td>1.68</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>( \varepsilon_0 ) (m³ ore/m³ heap)</td>
<td>Volumetric proportion of ore</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>( \rho_0 ) (kg/m³)</td>
<td>Ore density</td>
<td>2,454</td>
<td>2,454</td>
<td>2,454</td>
</tr>
<tr>
<td>( \rho_0 \varepsilon_0 ) (kg/m³)</td>
<td>Ore packed density*</td>
<td>1,626</td>
<td>1,626</td>
<td>1,626</td>
</tr>
<tr>
<td>( T_0 ) (°C)</td>
<td>Initial/set heap temperature</td>
<td>22</td>
<td>45</td>
<td>65</td>
</tr>
<tr>
<td>( \varepsilon_s ) (m³ stagnant/m³ heap)</td>
<td>Stagnant bed moisture**</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>( \varepsilon_f ) (kg/kg ore)</td>
<td>Stagnant bed moisture</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>( \varepsilon_f ) (m³ flowing/m³ heap)</td>
<td>Flowing heap moisture</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>( \varepsilon_f ) (kg/kg ore)</td>
<td>Flowing heap moisture</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* Measured after slumping and assumed constant during leach.
** Demonstrated in section 2.2.6 the wetness of all core residues, thus assumed uniform in depth and constant in time.

Table 6.2  Heap operational parameters. Only the relevant parameters are listed. Italicized parameters were evaluated by tuning exercises.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>22°C</th>
<th>45°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P ) (atm)</td>
<td>Atmospheric pressure</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>( n )</td>
<td>Shape factor</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( \tau X ) (m)</td>
<td>Side-branch length</td>
<td>0.0125</td>
<td>0.0125</td>
<td>0.0125</td>
</tr>
<tr>
<td>( \Gamma_f = \dot{m}_f / A ) (kg/(m²·h))</td>
<td>Solution application rate</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>( k_L a ) (h⁻¹)</td>
<td>G/L transfer coefficient</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>( T_r ) (°C)</td>
<td>Reference temperature</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>( E_a ) (kJ/mole)</td>
<td>Transfer activation energy</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 6.3  User-defined numerical parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>22°C</th>
<th>45°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta t ) (h)</td>
<td>Simulation time step</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>( N_t )</td>
<td>Time increments</td>
<td>1480</td>
<td>904</td>
<td>904</td>
</tr>
<tr>
<td>( N_Z )</td>
<td>Active heap nodes</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>( N_X )</td>
<td>Side branch nodes</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

Chapter 6 – Isothermal Model Simulations
Table 6.4  Mineral leach kinetic parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>22°C</th>
<th>45°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{FeS2} ) (mole/kg)</td>
<td>Pyrite mineral grade</td>
<td>0.37</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>( G_{FeS2} ) (kg/kg)</td>
<td>Pyrite mineral grade</td>
<td>0.045</td>
<td>0.045</td>
<td>0.045</td>
</tr>
<tr>
<td>( C_s^o_{\text{-initial}} ) (mole/kg)</td>
<td>Initial elemental sulfur grade</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( C_s^o_{\text{-initial}} ) (kg/kg)</td>
<td>Initial elemental sulfur grade</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( X_{FeS2-initial} ) (-)</td>
<td>Initial pyrite conversion</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( X_{FeS2-initial} ) (-)</td>
<td>Initial elemental sulfur conversion</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( T_0 ) (°C)</td>
<td>Rate reference temperature</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>( k_o ) (h(^{-1}))</td>
<td>Pyrite rate constant at ( T_0 ) (ore 2)</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>( E_a ) (kJ/mole)</td>
<td>Pyrite activation energy</td>
<td>76.4</td>
<td>76.4</td>
<td>76.4</td>
</tr>
<tr>
<td>( \phi ) (-)</td>
<td>Pyrite topological exponent</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>( \varphi ) (mole ( S^o )/mole ( FeS_2 ))</td>
<td>Elemental sulfur yield</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 6.5  Initial and feed solution solute and cell concentrations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>22°C</th>
<th>45°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Fe]_{\text{initial}}) (mole/L)</td>
<td>Initial Fe concentration</td>
<td>0.018</td>
<td>0.053</td>
<td>0.053</td>
</tr>
<tr>
<td>([H_2SO_4]_{\text{initial}}) (mole/L)</td>
<td>Initial acid concentration</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>([Fe-cell]_{\text{initial}}) (cells/L)</td>
<td>Initial Fe-oxidizing cell numbers</td>
<td>(10^9)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>([S^o-cell]_{\text{initial}}) (cells/L)</td>
<td>Initial ( S^o )-oxidizing cell numbers</td>
<td>(10^9)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>([Fe]_{\text{feed}}) (mole/L)</td>
<td>Feed Fe concentration</td>
<td>Variable</td>
<td>0.053</td>
<td>0.053</td>
</tr>
<tr>
<td>([H_2SO_4]_{\text{feed}}) (mole/L)</td>
<td>Feed acid concentration</td>
<td>Variable</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>([Fe-cell]_{\text{feed}}) (cells/L)</td>
<td>Feed Fe-oxidizing cell numbers</td>
<td>(= 10^{10})</td>
<td>Step change (10^{11}→0)</td>
<td>Step change (10^{11}→0)</td>
</tr>
<tr>
<td>([S^o-cell]_{\text{feed}}) (cells/L)</td>
<td>Feed ( S^o )-oxidizing cell numbers</td>
<td>(= 10^{10})</td>
<td>Step change (10^{11}→0)</td>
<td>Step change (10^{11}→0)</td>
</tr>
</tbody>
</table>

Chapter 6 – Isothermal Model Simulations
Table 6.6 Biological parameters. Italicized parameters were evaluated by tuning exercises.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Fe- Meso</th>
<th>Fe- Mode</th>
<th>Fe- Extr</th>
<th>S°- Meso</th>
<th>S°- Mode</th>
<th>S°- Extr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_g$ (h)</td>
<td>Growth rate constant</td>
<td>0.11</td>
<td>0.09</td>
<td>0.11</td>
<td>0.007</td>
<td>0.009</td>
<td>0.035</td>
</tr>
<tr>
<td>$k_e/k_g$ (%)</td>
<td>Decay rate multiplier</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$K$ ($10^{-3}$ mole/L)</td>
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<td>0.05</td>
<td>0.05</td>
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<tr>
<td>$K I_Y$ ($10^{12}$ cells/L)</td>
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<td>—</td>
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<td>$y$ ($10^{12}$ cells/mole)</td>
<td>Yield</td>
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<tr>
<td>$K_{ads}$ ($10^{-12}$ L/cell)</td>
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</tr>
<tr>
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<td>Skew factor</td>
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<td>0.367</td>
<td>0.553</td>
<td>0.089</td>
<td>0.367</td>
<td>0.553</td>
</tr>
</tbody>
</table>

* Meso: mesophiles, mode: moderate thermophiles, extr: extreme thermophiles

The three cases examine the leaching of pyrite in a bed loaded with truffles. Evaporative losses (experimental average -1.8 wt% and -4.4 wt% of total solution applied at 45 and 65°C, respectively) were judged small enough to assume the liquid flow rate to be constant at 5 L/(m²·h). The principal differences between the three isothermal case scenarios include:


Chapter 6 – Isothermal Model Simulations
• Column height: mesophilic – 1.68 m, moderate and extreme thermophilic – 0.4 m;

• Inoculation period and cell concentration: mesophilic – before and after agglomeration, moderate and extreme thermophilic – only the first 3 h after start-up;

• Iron and sulfuric acid concentrations in the feed solution: mesophilic – increasing levels, moderate and extreme thermophilic – constant levels.

The concentrations for the mesophilic case were calculated using high-order polynomial equations fitted to the experimental concentration data measured in the column reservoir. Total iron and cell number concentrations were straightforwardly obtained from time/concentration profiles shown in appendix B. The H$_2$SO$_4$ concentrations were calculated using the following set of equations:

$$\begin{align*}
[\text{Fe}_\tau] &= [\text{Fe}^{\text{SO}_4}_2^-] + [\text{FeH}^{\text{SO}_4}_4^{2+}] + [\text{Fe}^{\text{SO}_4}_4^+] \\
[\text{SO}_4] &= [\text{HSO}_4^-] + [\text{SO}_4^{2-}] + [\text{FeH}^{\text{SO}_4}_4^{2+}] + [\text{Fe}^{\text{SO}_4}_4^+] + 2[\text{Fe}^{\text{SO}_4}_2^-] \\
2[\text{H}_2\text{SO}_4] &= [\text{HSO}_4^-] + [\text{H}^+] + [\text{FeH}^{\text{SO}_4}_4^{2+}] \tag{6-1}
\end{align*}$$

where $[\text{H}_2\text{SO}_4]$ is the sought concentration, $[\text{SO}_4]$ and $[\text{Fe}_\tau]$ are the total sulfate and iron concentrations, respectively, obtained from time/concentration plots in appendix B, and $[\text{H}^+]$ is calculated from the measured pH. The thermodynamic program (chapter 4) predicted that the species listed in Eq. 6–1 would be predominant under the pH and potential conditions of column A. Their relative proportions are given by:

$$\begin{align*}
[\text{Fe}^{\text{SO}_4}_2^-] &\approx 0.16 [\text{Fe}_\tau] \\
[\text{FeH}^{\text{SO}_4}_4^{2+}] &\approx 0.13 [\text{Fe}_\tau] \\
[\text{SO}_4] &\approx 0.71 [\text{Fe}_\tau] \\
[\text{HSO}_4^-] &\approx [\text{SO}_4^{2-}] \tag{6-2}
\end{align*}$$

The calculated $[\text{H}_2\text{SO}_4]$ concentrations were then fitted to a high-order polynomial.

The graphs are organized either as a function of time (mesophilic case – Figure 6.1, moderate thermophilic case – Figure 6.2, extreme thermophilic case – Figure 6.3) or column depth (mesophilic case – Figure 6.4, moderate thermophilic case – Figure
6.5, extreme thermophilic case – Figure 6.6). The time plots show experimental data, where available, and the model fit. The depth plots contain a series of model lines corresponding to different, equally-spaced times. All depth profiles, with the exception of the sulfide conversion, correspond to the pore entrance (node \( NX+1 \)) location. The sulfide conversion represents the integrated oxidation over the side branch. The orientation of the arrow tip captures the progression of the lines in quantity and in space. For instance, the following arrows indicate:

- Indicator increases (upward tip)/decreases (downward tip) everywhere throughout the heap at the same time.
- Indicator increases (upward tip) at the top at first, and later at the bottom.
- Indicator decreases (downward tip) at the bottom at first, and later at the top.
- A combination of during the first stage, followed by in the next stage.

In brief, the following arrow (\( \uparrow \downarrow \)) indicates first the vertical downward movement of a decreasing wave, followed by an increasing front moving toward the bottom of the column.

6.2.1.1 Time Profiles

The same kinetic parameters, the same \( k_L a \) value, and the six sets of ten biological parameters yield excellent fits of the time profile of oxidation at 22°C (Figure 6.1, top left) and 45°C (Figure 6.2, top left), and a reasonable fit at 65°C (Figure 6.3, top left). Besides the very small number of experimental data points (4) available for comparison, a number of reasons explain the overestimation of the experimental data, especially at 65°C. First, the precision of the sulfide assay could easily shift the experimental data points by ± 10%. Secondly, the predictions of the topological model may be inaccurate beyond 75% oxidation because the kinetic tests (chapter 4) were terminated at \( \approx 80\% \) oxidation before the conversion had reached 100%. Furthermore, the fact that the experimental oxidation values on the last sampling day are practically identical at 45 and 65°C, in spite of the 20°C difference in temperature between the two tests, suggests that roughly 85 wt% of
the sulfide sulfur content of this ore is oxidizable. The topological particle model, whose final predicted oxidation value is close to 100% (without ever reaching it, unless the exponent, \( \phi \), is less than 1), does not address the concept of maximum extractable sulfide grade.

The time profile of the leachate iron concentrations is also well modeled at any temperature, whether in recirculation (Figure 6.1, middle left) or in single-pass (Figure 6.2 and Figure 6.3, middle left). Polynomial expressions were used to fit the iron and sulfuric acid feed data at 22°C for the model boundary condition. At 45 and 65°C, the model captures the very rapid rise associated with the oxidation of rapidly-oxidizable pyritic fines. The concentration reaches a maximum, and later decreases as the iron produced by pyritic fines exits the column, leaving behind the slow-leaching coarse pyrite grains. The iron concentration eventually approaches the initial feed concentration of 3 g/L when nearly 80% of the pyrite content is oxidized.

The coupled pyrite/ferrous ion oxidation reactions form a net acid-consuming system when the elemental sulfur yield equals 0.8 mole S⁰/mole FeS₂ and when little sulfur is oxidized. These conditions occur over the first 25 days during which the fitted acid concentration drops from 3 to 2.3–2.6 g/L along the column (Figure 6.2 and Figure 6.3, bottom left), resulting in a rise in pH from 1.5 to 1.6 (Figure 6.2 and Figure 6.3, bottom right). The pH was estimated as the logarithm of the sulfuric acid concentration. The short inoculation period at 45°C and 65°C, coupled with the absence of elemental sulfur in the ore treated, explains the longer time required for the growth of the sulfur-oxidizing population (Figure 6.5, bottom right). Beyond day 25, the system becomes acid-producing as sulfur-oxidizing cells initiate the oxidation of elemental sulfur (Figure 6.2, top right). The leachate sulfuric acid concentration increases to 5–5.5 g/L by day 65 (Figure 6.2 and Figure 6.3, bottom left). It then drops to the level of the feed concentration (3 g/L) when both pyrite and elemental sulfur are almost depleted.
Figure 6.1  Evolution of conversion (top left), sulfur grade (top right), iron concentration (middle left), potential (middle right), sulfuric acid (bottom left), and pH (bottom right) over time at 22°C. Comparison of experimental and fitted data.
Figure 6.2  Evolution of conversion (top left), sulfur grade (top right), iron concentration (middle left), potential (middle right), sulfuric acid (bottom left), and pH (bottom right) over time at 45°C. Comparison of experimental and fitted data.
Figure 6.3  Evolution of conversion (top left), sulfur grade (top right), iron concentration (middle left), potential (middle right), sulfuric acid (bottom left), and pH (bottom right) over time at 65°C. Comparison of experimental and fitted data.
As shown in Figure 6.1 (bottom right), calculating the pH as the logarithmic of the sulfuric acid concentration grossly overestimates the proton concentration in a ferric sulfate media where protons bind to form iron sulfate complexes. Better agreement between the measured and calculated pH values exists for the 45 and 65°C columns (Figure 6.2 and Figure 6.3, bottom right, respectively), whose feed iron and sulfuric acid concentrations were maintained constant at much lower levels than at 22°C.

The model calculates the potential using the following experimental relationship:

\[
\text{Potential [mV]} = 24.15 \ln \left( \frac{C_{Fe(III)}}{C_{Fe(II)}} \right) + 473.43 @ 22^\circ C
\]  

The fitted potential values are underestimated during the first 100 days at 22°C (Figure 6.1, middle right) and 45°C (Figure 6.2, middle right). The model better fits the potential data at 65°C (Figure 6.3, middle right). Could the discrepancies between the fitted and measured potentials be explained by the fact that the potential electrode was immersed in the leachate solution collected over the course of 3 to 4 days, rather than in the leachate collected directly from the drainage port at any instant? It is hypothesized that cells contained within the leachate solution may have oxidized ferrous ions over the course of only a few days, thus leading to higher potentials in the container. By extension, a similar phenomenon should have also been observed at 65°C. However, based on the presence of moderate thermophilic cells in the residues of the 22°C columns (Figure 2.3), it is believed that moderate thermophiles were most likely slightly active at the temperature (22°C) of the leachate receptable. Furthermore, a minuscule amount of ferrous ions must be oxidized for the potential to rise from 600 to 700 mV.

Although the differences between the measured and fitted potential values are smaller in the last stages of the leach, the model suggests that the leachate potential keeps increasing, when in fact, the measured potentials level off (Figure 6.1, Figure 6.2, and Figure 6.3, middle right). This is a mathematical artifact of the topological model and PSS approximation. According to this model, the square root
of the $\text{[Fe(III)]/[Fe(II)]}$ ratio, and thus potential, must increase to compensate for the diminishing $(1-X)^4$ term with increasing conversion. Indeed, the present value of the exponent, $\phi$, indicates that the latter term will become increasingly small, but will never reach zero.

The elemental sulfur grade is another important indicator. Despite several attempts at adjusting the biological parameters of sulfur-oxidizing cells, the model yields a very approximate time profile of the sulfur grade for each of the three temperatures tested, especially in the later stages of the leach (Figure 6.1, Figure 6.2, and Figure 6.3, top right). The left segment of the model fit represents the accumulation of elemental sulfur in the absence of a large number of sulfur-oxidizing cells everywhere throughout the bed (Figure 6.4, Figure 6.5, and Figure 6.6, bottom right). When the sulfur grade reaches a maximum, the sulfur-oxidizing cells are beginning to oxidize any accumulated and newly produced sulfur, which results in rapidly diminishing sulfur grades. The grade levels off, and occasionally later increases, in the last stages of the leach because of declining cell numbers at the top of the column (particularly evident in the 65°C test, Figure 6.3, top right). The sterility of the feed solution results in cell desorption, migration to lower depths, and wash off. The lack of experimental data at the two highest temperatures tested, the large variability of sulfur grade data between tests of similar duration at 22°C, and the non-uniformity of sulfur grade data with depth at 22°C, complicates further the assessment of the adequacy of the biological model developed. Furthermore, the present model may have in fact erroneously introduced two classes of microorganisms (iron- and sulfur-oxidizing cells), when in fact previous studies have demonstrated the ability of certain microorganisms (e.g. A. ferrooxidans) to consume more than one substrate for growth.

6.2.1.2 Sulfide Oxidation Depth and Lateral Profiles

The relatively flat depth profiles of conversion at 22°C indicate that sulfide oxidation proceeds fairly uniformly throughout the column. The uniformity of the model fits matches the experimental depth profiles of sulfide (Figure B.10, Figure B.11) and iron (Figure B.12, Figure B.13) grades in the 22°C residues. The column height
thus has no influence on supplying the necessary reagents to the reaction sites in the side branches beyond the cell colonization phase. Reasons include:

- The initial cell inoculation of truffles, as no cell colonization wave is observed in Figure 6.4, bottom left.
- The availability of all reagents, including cells, at reaction sites at all times.
- The lack of dependence of the chemical rate expression on total iron and/or proton concentration.

The depth profiles of conversion at 45 and 65°C (Figure 6.5 and Figure 6.6, top left) are characterized by several trends. First, discontinuities observed in the first vertical node of the depth profiles result from the numerical method employed, which sets the cell concentration in the first lateral node equal to that in the flowing solution. In this case, since the feed solution applied beyond the inoculation phase no longer brings in any cells, the cell concentration decreases drastically.

Second, the combined effects of no preinoculation, temporary inoculation, and short stagnant pores lead to an iron-oxidizing cell colonization wave (Figure 6.5 and Figure 6.6, bottom left). Cell breakthrough occurs between 10 and 20 days after inoculation. This results in a greater extent of oxidation at the top of the 45 and 65°C columns, and an initial lag in the time profile of conversion (Figure 6.3, top left). Iron generated within the pores is transferred to the flowing solution at the stagnant/flowing interface, explaining why the iron concentration in the flowing solution (Figure 6.5 and Figure 6.6, middle left) increases with depth in the early stages of the leach.
Figure 6.4 Predicted evolution of conversion (top left), oxygen concentration (top right), iron concentration (middle left), potential (middle right), iron-oxidizing cells (bottom left), and sulfur-oxidizing cells (bottom right) with depth at 22°C.
Figure 6.5  Predicted evolution of conversion (top left), oxygen concentration (top right), iron concentration (middle left), potential (middle right), iron-oxidizing cells (bottom left), and sulfur-oxidizing cells (bottom right) with depth at 45°C.
Predicted evolution of conversion (top left), oxygen concentration (top right), iron concentration (middle left), potential (middle right), iron-oxidizing cells (bottom left), and sulfur-oxidizing cells (bottom right) with depth at 65°C.

Chapter 6 – Isothermal Model Simulations
Third, the fact that moderate and extreme thermophilic sulfur-oxidizing cells were also introduced for only 3 h, coupled with the time required to build up a sufficient amount of elemental sulfur before initiating the growth of sulfur-oxidizing cells between days 25 to 50, explains why these cells are only detected in the leachate 40 to 60 days after start-up. The sulfur-oxidizing cell colonization wave, clearly seen in Figure 6.5 and Figure 6.6 (bottom right), has a more pronounced influence at 65°C on the depth profiles of sulfide oxidation between 40 and 60% and potentials around 550 to 600 mV (Figure 6.6, top left and middle right, respectively). Growth of sulfur-oxidizing cells in the upper layers of the bed diverts oxygen away from iron-oxidizing cells. This, in turn, lowers the potential and holds back pyrite oxidation. At the same time, the absence of sulfur-oxidizing cells in the bottom layers yields oxygen concentrations approximately 0.5 mg/L larger (Figure 6.6, top right) and greater pyrite oxidation rates. That is why slightly larger extents of oxidation are simultaneously observed at the top and bottom of the bed.

The sulfide oxidation profiles are uniform in the later stages of the leach. Unfortunately, this trend cannot be confirmed experimentally due to the unavailability of more than one core of residues collected from each of the short 45 and 65°C columns.

The profiles of any other leaching indicator also become uniform with depth at any of the three temperatures tested when the two cell populations have colonized the entire column. At any time during the leach, the conversion and sulfur grade profiles, as well as the potential, oxygen concentrations, and cell numbers, are also uniform in the lateral stagnant branches (plots not shown).

6.2.1.3 Biological Dynamics

A closer look at the values of the fitted biological parameters of iron-oxidizing cells (Table 6.6) reveals the growth rate constant, $k_g$ (0.09 - 0.11 h$^{-1}$), to be the same for all types of cells. It is in very good agreement with published values for mesophiles (0.06 - 1.78 h$^{-1}$) [1-3] and moderate thermophiles (0.03 - 0.84 h$^{-1}$) [4,5], but 2 to 5 times larger than values for extreme thermophiles (0.018 - 0.043 h$^{-1}$) [6,7]. The fitted Fe(II) Monod constant, $K_{Fe}$ (0.0001 mole/L), also lies in the range of
published values (0.00002–0.123 mole/L) [1–3]. The value of the cell inhibition term, \( K(Y) \) (100×10^{12} \text{ cells/L}), is so large that this term becomes irrelevant in the biological expression.

The cell yield, \( y \) (20×10^{12} \text{ cell/mole Fe(II)}), agrees well with reported values for any type of cells. For instance, published values of the yield for mesophiles range from 0.19 to 1.33 g dry weight/mole Fe(II), else 0.012 mole C/mole Fe(II). These values can be expressed as the number of cells generated per mole of Fe(II) by assuming that cells are cylindrical in shape, 0.5 \( \mu \text{m} \) in diameter, 1 \( \mu \text{m} \) in length, have a density of \( \approx 1,000 \text{ kg/m}^3 \), a dry weight of 30 wt\% and a carbon content of 50 wt\% [8]. Calculations reveal these yields to range from 3×10^{12} to 22×10^{12} cells/mole Fe(II). The fitted yield of extreme thermophiles compares very well to published values for *Acidianus brierleyi* (\( y = 12 \times 10^{12} \text{ cells/mole Fe(II)} \)) [6] and *Sulfolobus metallicus* (\( y = 3.7–81 \times 10^{12} \text{ cells/mole Fe(II)} \)) [7].

The model suggests that iron–oxidizing cells reproduce rapidly to reach a maximum level of mid-10^{12} cells/L in solution (Figure 6.4 – Figure 6.6, bottom left). To compare these figures to the experimental data presented in chapter 2 and appendix B, one must recall that this value represents the number of planktonic cells in equilibrium with the ore. For the 22°C case, we calculate, using Eq. 5–30 and its parameters (\( K_{ads} = 17 \times 10^{-12} \text{ L/cells}, Y_{max} = 1.5 \times 10^{12} \text{ cells/kg}, \) Table 6.8), the maximum number of planktonic and attached sulfur–oxidizing cells to be 10^{11} and 9.4×10^{11} cells/kg, respectively. The fitted number of planktonic and attached iron–oxidizing cells reach a maximum at 8×10^{12} cells/L and 1.5×10^{12} cells/kg, respectively. Therefore, the sum of the planktonic iron– and sulfur–oxidizing cells was calculated to be 8×10^{12} cells/L, in comparison to a measured value (5×10^{10} cells/L) two orders of magnitude smaller. However, the sum of the two attached population numbers (2.4×10^{12} cells/kg) agrees very well with the measured numbers (1×10^{12}–5×10^{12} cells/kg).

The adsorption model also indicates that, despite a significant, progressive, and regular drop (as large as 100 times) of the number of planktonic cells due desorption and transfer, the number of attached cells remains constant. Unless the
planktonic cell concentration drops below $10^{10}$ cells/L, the attached cell concentration lies in the plateau segment of the Langmuir isotherm, and is thus independent of the planktonic cell numbers.

The fitted number of planktonic cells in the leachate greatly overestimates the experimental figures averaging $10^{10}$–$10^{11}$ cells/L. With the exception of the too rapid growth of moderate and extreme thermophilic cells in the initial stages of the leach, the model correctly predicts the average number of attached cells. It also reflects the time independency of this leaching indicator. In this author’s opinion, however, the present cell numbers are the least reliable of all leaching indicators because the experimental cell counting procedure failed to distinguish between living and dead microorganisms, as well as iron- and sulfur-oxidizing cells.

According to the fitted parameters of sulfur-oxidizing cells, extreme thermophiles grow more rapidly than moderate thermophiles and mesophiles ($k_g = 0.035$ h$^{-1}$ vs $0.007–0.009$ h$^{-1}$), but none surpasses the growth rate of iron-oxidizing cells (Table 6.6). The number of planktonic sulfur-oxidizing cells does not exceed $10^{11}$ cells/L (equivalent to $1.1 \times 10^{12}$ attached cells/kg), and always lies in the linear segment of the Langmuir isotherm. Decreasing the adsorption constant from $67 \times 10^{-12}$ L/cell to $17 \times 10^{-12}$ L/cell accelerates the colonization of the 45 and 65°C beds to yield more uniform depth profiles of sulfur grade, but also later promotes increased desorption when replacing the inoculum by a sterile feed solution.

Some features of the biological model (e.g. differentiation of cell death due to endogenous processes or temperature shock) are novel. However, the values of these parameters cannot be determined from such complex, dynamic column experiments where the conditions of the cell habitat are maintained relatively constant (e.g. isothermal tests). Furthermore, simulations (not shown) with different $k_g$ values have demonstrated the illogicality of multiplying the death function, $f_d(T)$, by this parameter (Eq. 5-16) to evaluate the death rate. That is to say, for instance, that a mesophilic strain having a larger growth rate constant dies more rapidly than a mesophilic strain with a smaller growth constant when the temperature exceeds their maximum viable temperature. That, and the large
number of possibly unnecessary biological parameters, point to the need to revisit
the biological subroutine developed.

6.2.1.4 Oxygen Concentration Depth Profiles

The 22°C depth profiles reveal the oxygen concentrations to be at least larger than
5 mg/L (equivalent to an oxygen inhibition of at most 25%) (Figure 6.4, top right). The curves follow very closely the progression of sulfur-oxidizing cells, i.e. lower oxygen concentrations at the top of the column where iron- and sulfur-oxidizing cells are active, and higher oxygen concentrations at the bottom where only pyrite oxidation takes place. Oxygen concentrations increase immediately after the passage of the cell colonization wave and the oxidation of rapidly-oxidizable pyritic fines. The relatively high oxygen concentrations confirm the absence of a significant gas/liquid mass transfer resistance. The leaching of this relatively low grade pyrite ore in an isothermal column at 22°C thus appears to be controlled by particle kinetics.

The principal trends of the 22°C depth profiles are amplified in the 45 and 65°C oxygen concentration fits. Modeled oxygen concentrations drop to 1.6 mg/L (Figure 6.5, top right) and 0.4 mg/L (Figure 6.6, top right) during the first few weeks of the 45 and 65°C leach, respectively. Under these conditions, the biological rate is thus even lower at 38 and 20%, respectively, of the maximum rate under complete oxygen saturation.

The 45 and 65°C oxygen concentration profiles show discontinuities around 0.025 m (Figure 6.5 and Figure 6.6, top right). After verifying that the output log file did not contain any error statements incurred during the PSS calculations, one must conclude that the discontinuities are authentic. The dips are most likely related to the larger sulfur grades and the smaller numbers of sulfur-oxidizing cells near the very top of the column, and to a minor extent to slightly reduced oxygen partial pressures at the top.

Oxygen gas/liquid mass transfer thus seems to be the rate-limiting process in the earlier stages of the leach in the presence of abundant pyritic fines. The
phenomenon is more severe with increasing temperatures. The rate-limiting step slowly shifts from oxygen transfer to particle kinetics as pyritic fines and elemental sulfur are oxidized from the top downward. Oxygen concentrations eventually reach saturation. These conclusions are only as good as the estimate of the mass transfer coefficient, $k_{L}a$ (25 h$^{-1}$).

### 6.2.2 Validation Exercises

The predictive capabilities of the model are evaluated against the performance of three of the ten 22°C column tests described in chapter 2. The basic scenario consists of leaching pyrite in a 1.68 m bed of truffles inoculated with mesophiles before and after loading. The mesophilic parameters (Table 6.6) are left unchanged.

The principal trends depicted in Figure 6.7 demonstrate that decreasing the liquid flow rate from 5 to 2.5 L/(m$^2$.h) has no influence on the leaching kinetics of column E, and thus the time/oxidation profile (Figure 6.7, left). The model predictions of the leachate iron concentrations and potentials are in very good agreement with the experimental data (Figure 6.7, right).

![Figure 6.7](image)

Figure 6.7 Effect of reduced solution application rate on sulfide conversion (left), as well as on the leachate iron concentration and potential (right). Comparison of fitted and experimental data of column E.
The second case represents column F, which, of all columns, was the only one containing only truffles. As a result of the tighter packing, the ore and stagnant volumetric proportions increased from 0.64 to 0.73 m$^3$/m$^3$ and from 0.19 to 0.24 m$^3$/m$^3$, respectively. If the flowing solution holdup is left unaffected at 3%, the air was then confined to less than 1% of the column volume (vs 18% in other columns). These relative proportions were calculated using the final height of the column (2.0 m), the moisture content (13.6 kg water/100 kg dry ore) of the residues, and the total dry mass of the residues (172 kg).

According to the model predictions, neither the oxygen saturation (plot not shown), the potential (Figure 6.8, right), nor the oxidation rate (Figure 6.8, left) is reduced drastically by decreasing the gas holdup. The model also indicates that the non-preinoculation of the ore loaded in column F delays the instigation of uniform oxidation profiles by only 20 days, as compared to other preinoculated columns operated at 22°C (e.g. column E in Figure 6.7, left). There are significant differences between the predicted and measured potentials (Figure 6.8, right). Only the conversion in the uppermost layer of the bed matches the predicted conversion. However, the model cannot reproduce the depth/conversion gradient...
shown in Figure 6.8 (left) by the upper and lower extent of oxidations. Confining the air to $\frac{1}{4}$ of its normal volume most likely excluded oxygen from certain zones in the bed. The model in its current form does not address phenomena such as bed compaction and reduced gas permeability.

The last simulation examines a change in the maximum particle size from 12.7 to 3.3 mm before agglomeration (column G). Column G also experienced an increase in the stagnant liquid holdup (20.2 vol%) and ore packing (72.9 vol%, final bulk density = 1,788 kg/m$^3$), leaving a mere 6.9% to the gas and flowing phase. The topological kinetic parameters of ore 3 (chapter 4) were selected. The truffle model predicts that approximately 70% of pyrite in truffles is oxidized in 110 days, compared to a maximum of 45% measured experimentally (Figure 6.9, left).

![Figure 6.9](image)

Figure 6.9 Effect of reduced particle kinetics on sulfide conversion (left), as well as on the leachate iron concentration and potential (right). Comparison of fitted and experimental data of column G.

The difference between predicted and measured conversions increases with time. The model poorly predicts the leachate iron concentration and potentials (Figure 6.9, right). Approximately 200 mV separates measured and predicted potentials. Does the model lack predictive capability, or is a possible severe oxygen gradient impeding the oxidation, as hypothesized for the leach behavior of column F? The
ore bed of column G most likely collapsed because of the absence of coarse particles providing structural support. Ore compaction may then have confined the air to the sides of the column, forcing it to diffuse from the outer edges toward the center. The yellowish tint observed only in the middle portion of the core residue of column G supports this hypothesis (Figure 2.12).

6.3 Pellet Simulations

This section explores the leaching behavior of an ore sample comprised of truffles and pellets at different temperatures. The structure of the heap model was simplified because of numerical errors encountered under specific conditions. The subroutines of the heap model indeed calculated negative oxygen concentrations within the pores of the pellets when choosing a time step of 2 h. In other words, the rate source term multiplied by the time step was larger than the oxygen concentration available for reaction. The oxygen concentration at certain pore nodes in the pellet oscillated between negative and positive values. The extent of oxidation was thus overestimated, leading to larger cumulative errors.

Two options were considered to solve this numerical problem. Reducing the time step from 6 h to 1 s was a successful approach, though not practical from a computational time perspective. The second approach consisted of recognizing that the change in oxygen concentration at a given node over a period of 1 h was so small that the non-linear oxygen source term in the biological rate expression could be linearized using the concentrations at the old and new time steps, as given by:

$$\frac{C_{o_2}^{\text{new}}}{K_{o_2} + C_{o_2}} = \frac{C_{o_2}^{\text{old}}}{K_{o_2} + C_{o_2}}$$

The matrices (Eqs. 5-72 and 5-74) representing the Crank–Nicholson oxygen diffusion equations with source terms were rearranged. The newly-linearized source terms were taken out of the vector solution and included directly in the matrix of constants. A reasonable time step of 2 h could still be chosen while avoiding oscillating oxygen concentrations.
Simulations were performed to study the influence of temperature, topological kinetics, relative proportion of truffles and pellets, and pellet size. To shorten the computation time, the heap model was stripped of the vertical and side branch subroutines because the depth and branch profiles were shown to be uniform after cell colonization. Pellets and truffles were thus assumed indestructible, and the stagnant solution was thought to be contained in a well-mixed batch reactor. The computation time was of the order of a few minutes when \( NR = 30 \) and \( \Delta t = 2 \) h.

The pellet porosity was never measured in the present work, but an estimate was obtained from measurements of the liquid and ore volumetric proportions in a column. One of the findings in chapter 4 was the average proportion of the solid, liquid, and gas phases in a heap. A 100 m\(^3\) heap section was shown to contain approximately 60 m\(^3\) of ore and 13 m\(^3\) of stagnant solution. If 45 wt\% of the 60 m\(^3\) of ore loaded formed pellets having a typical porosity of 40 vol\% (Figure 4.1), the column would already contain 22 m\(^3\) of liquid in the pellet pores. That figure excludes the moisture on the external surfaces of the pellets and truffles. This estimate is by far in excess of the average experimental measurement of 13 vol\%. The stagnant liquid holdup measured in chapter 4 must therefore be partitioned between the pellet pores and the true side branch pores. Therefore, the pellet porosity was set to be 15 vol\% to avoid overshooting the stagnant volume of 13 vol\%.

6.3.1 Influence of Temperature

The topological kinetic parameters of ores 1 and 4 (chapter 4) were chosen for truffle and pellet kinetics, respectively (Table 6.7). Simulations were performed at 22, 45, and 65°C using the set of parameters of iron-oxidizing mesophiles (Table 6.6) for all types of iron-oxidizing cells. Sulfur-oxidizing cells were disregarded (i.e. no inoculation and zero growth rate). All other relevant heap design parameters and conditions are presented in Table 6.2, Table 6.7, and Table 6.8.

Chapter 6 - Isothermal Model Simulations
Table 6.7 Mineral leach kinetic parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Pellet</th>
<th>Truffle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{FeS_2}$ (mole/kg)</td>
<td>Pyrite mineral grade</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>$G_{FeS_2}$(kg/kg)</td>
<td>Pyrite mineral grade</td>
<td>0.045</td>
<td>0.045</td>
</tr>
<tr>
<td>$C_{S^2- initial}$ (mole/kg)</td>
<td>Initial elemental sulfur grade</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_{S^2- initial}$ (kg/kg)</td>
<td>Initial elemental sulfur grade</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$X_{pyrite-initial}$ (-)</td>
<td>Initial pyrite conversion</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$X_{sulfur-initial}$ (-)</td>
<td>Initial elemental sulfur conversion</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$T_0$ (°C)</td>
<td>Rate reference temperature</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>$k_0$ (h$^{-1}$)</td>
<td>Pyrite rate constant at $T_0$</td>
<td>0.00072</td>
<td>0.000058</td>
</tr>
<tr>
<td>$E_a$ (kJ/mole)</td>
<td>Pyrite activation energy</td>
<td>76.4</td>
<td>76.4</td>
</tr>
<tr>
<td>$\phi$ (-)</td>
<td>Pyrite topological exponent</td>
<td>3.2</td>
<td>2.0</td>
</tr>
<tr>
<td>$\varphi$ (mole S°/mole FeS$_2$)</td>
<td>Elemental sulfur yield</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 6.8 Design parameters conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_0$ (kg/m$^3$)</td>
<td>Ore density</td>
<td>2,500</td>
</tr>
<tr>
<td>$T_0$ (°C)</td>
<td>Initial/set heap temperature</td>
<td>22, 45, or 65</td>
</tr>
<tr>
<td>$\varepsilon_p$ (m$^3$ pore/m$^3$ pellet)</td>
<td>Volumetric proportion of pores in pellets</td>
<td>0.15</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>Pellet pore tortuosity (-)</td>
<td>1.0</td>
</tr>
<tr>
<td>$R$ (mm)</td>
<td>Pellet radius</td>
<td>4.5</td>
</tr>
<tr>
<td>$\eta$ (kg/kg)</td>
<td>Proportion of truffles</td>
<td>0.55</td>
</tr>
<tr>
<td>$\Delta t$ (h)</td>
<td>Simulation time step</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Total simulation time (d)</td>
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</tr>
<tr>
<td>$Nt$</td>
<td>Time increments</td>
<td>1200</td>
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<tr>
<td>$NQ$</td>
<td>Pellet pore nodes</td>
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<tr>
<td>$[Fe_T]_{initial}$ (mole/L)</td>
<td>Initial total Fe concentration</td>
<td>0.053</td>
</tr>
<tr>
<td>$[H_2SO_4]_{initial}$ (mole/L)</td>
<td>Initial acid concentration</td>
<td>0.03</td>
</tr>
<tr>
<td>$[Fe-cell]_{initial}$ (cells/L)</td>
<td>Initial Fe–oxidizing cell numbers</td>
<td>$10^8$</td>
</tr>
<tr>
<td>$[S^0-cell]_{initial}$ (cells/L)</td>
<td>Initial S°–oxidizing cell numbers</td>
<td>0</td>
</tr>
<tr>
<td>$[Fe-cell]_{feed}$ (cells/L)</td>
<td>Feed Fe–oxidizing cell numbers</td>
<td>$10^8$</td>
</tr>
<tr>
<td>$[S^0-cell]_{feed}$ (cells/L)</td>
<td>Feed S°–oxidizing cell numbers</td>
<td>0</td>
</tr>
</tbody>
</table>
Simulation results are shown in Figure 6.10 to Figure 6.13. Because of the greater proportion of fines in pellets (ore 4, Figure 4.21), pellets would be expected to leach faster than truffles under the same conditions of temperature and potential. Obviously, the solution conditions in the bulk and in the pellet pores must be different for the truffle conversion to be equal at 22°C (Figure 6.10, left) or superior to the pellet conversion at 45 (Figure 6.10, middle) and 65°C (Figure 6.10, right). The enhancement of the pellet conversion with increasing temperatures is also not as large as that of the truffle oxidation profile.

Figure 6.11 and Figure 6.13 reveal the pore oxidation and Fe(III)/Fe(II) concentration ratio to drop significantly toward the center of the pellet, leaving it completely non-oxidized. The reaction zone is confined to the outer rim. The very slow progression of the reaction zone toward the pellet core suggests diffusion-controlled, zone-wise kinetics.

Irregular oxidation and ratio profiles are the direct outcome of the limited supply of oxygen by diffusion through the pellet pores (Figure 6.12). It should be pointed out that, as opposed to the rapid consumption of oxygen along the pore length, comparable levels of iron-oxidizing cells (and sulfur-oxidizing cells) are observed everywhere in the pores (plots not shown) due to rapid inward diffusion of cells generated in the outer rim and their slow death. Disregarding the effects of temperature on oxygen solubility, we note oxygen to be more abundant throughout the pellet at 22°C. At higher temperatures, the oxygen concentration plummets in the outer 20% of the pellet radius. When expressed in terms of the pellet volume, we realize that 50% of the total pyrite charge is contained within this short distance. That is why the oxygen concentration barely increases in the pellet outer rim over the course of 40 days. In comparison to the oxygen profiles at 45°C, oxygen penetrates more deeply into the pores at 65°C after the same period of time. Faster mineral kinetics at higher temperatures in the presence of the same oxygen concentrations explains why the oxygen demand in the outer rim falls rapidly with increasing conversion.
Figure 6.10  Time/conversion profiles of truffles, pellets (9 mm) and whole ore ($V_t = 0.55$) at 22°C (left), 45°C (middle), and 65°C (right) in the absence of sulfur-oxidizing cells and using the same set of biological parameters.
Figure 6.11
Oxidation profile within the pore of a 9 mm pellet at 22°C (left), 45°C (middle), and 65°C (right), plotted every 5 d in the absence of sulfur-oxidizing cells and using the same set of biological parameters.
Figure 6.12  Oxygen concentration profile within the pore of a 9 mm pellet at 22°C (left), 45°C (middle), and 65°C (right), plotted every 5 d in the absence of sulfur-oxidizing cells and using the same set of biological parameters.
Figure 6.13 Profile of the [Fe(III)]/[Fe(II)] ratio within the pore of a 9 mm pellet at 22°C (left), 45°C (middle), and 65°C (right), plotted every 5 d in the absence of sulfur-oxidizing cells and using the same set of biological parameters.
The reaction zone moves toward the core of the pellet before the pyrite contained in the outer 20% layer of the pellet is completely oxidized. In fact, it appears as if the reaction zone will make its way over a fair distance before the remaining 5% sulfide sulfur is oxidized at 65°C (Figure 6.12, right). At the surface of the pellet, the very rapid oxidation tapers off as fines are depleted, leaving behind the remaining coarser particles that originally contain 35% of the sulfide sulfur (Figure 4.21, ore 4). The Fe(III)/Fe(II) concentration ratio rises by three orders of magnitude with the depletion of fines (Figure 6.13, middle and right). The topological kinetic parameters determined in chapter 4 explain entirely why the oxidation increases very slightly beyond 85% conversion. Chemical reaction becomes the rate-limiting process in the outer rim from that point on, but the diffusion resistance still prevails in the pellet core where fines have yet to be oxidized.

By analogy to the definition of the Damköhler number (chapter 4), one must conclude that the reaction rate of pyrite within the pellet pores exceeds the oxygen diffusion rate in the presence of rapidly-oxidizable pyrite. The relative magnitude of diffusion and reaction resistances are also conveniently expressed in terms of the effectiveness factor. The effectiveness factor, $\eta$, is defined as the total rate of sulfide oxidation throughout the entire pellet taken as a fraction of the total rate which would result from no diffusion limitation into the pellet, i.e. if the oxygen concentration throughout the pores were the same as the pellet surface concentration. In particular, for first-order reactions, $\eta$ is equal to the ratio of the average pore concentration relative to the surface concentration. In order to estimate roughly the effectiveness factor for each of the three simulations, it is assumed that the biological ferrous oxidation rate is first order with respect to the oxygen concentration. Calculations indicate that, at the beginning of the leach, $\eta$ decreases from 0.26 to 0.12 to 0.07 with increasing temperature, indicating that pore resistance becomes more important for the reasons discussed above. By day 40, the effectiveness factor at 45 and 65°C has increased to 0.16 and 0.22, respectively, because pyritic fines have been oxidized.
6.3.2 Influence of Kinetics and Proportion of Truffles

For comparison purposes at 45°C, pellets and truffles are assumed to have the same distribution of particles (i.e. same topological kinetics) and to be initially inoculated with iron- and sulfur-oxidizing cells \( (Y_{\text{susp}} = 10^8 \text{ cells/L}) \). Unless otherwise indicated, the values of the parameters are those in Table 6.2, and Table 6.6 (only moderate thermophiles) to Table 6.8. The effects of ore kinetics \( (\text{ore } 2 \text{ vs } \text{ore } 4) \) and proportion of truffles \( (Y_t = 0.05 \text{ vs } 0.95) \) on the overall conversion are shown in Figure 6.14. Predicted pellet pore profiles of Fe(III)/Fe(II) concentration ratio and sulfur grade are depicted in the top and bottom plots of Figure 6.15, respectively.

The oxidation profile of the whole ore is the weighted average of the leaching profiles of truffles and pellets (Figure 6.14). The overall oxidation profile for any other \( Y_t \) values lies anywhere between the two extreme curves. Increasing the proportion of pellets decreases the overall oxidation rate. However, for the same particle kinetics, the difference between the overall conversions at constant \( Y_t \) becomes smaller with time. Truffles appear to leach slightly more rapidly at higher \( Y_t \) values because of the smaller pellet oxygen demand.

Mathematically, the sole reason why the truffle and pellet oxidation profiles differ at a constant temperature is the Fe(III)/Fe(II) concentration ratio. Since the performance of the truffles is superior to that of the pellets, the time-average potential must be larger in the bulk than in the pellet pores. Figure 6.15 (top) indeed shows the bulk Fe(III)/Fe(II) concentration ratio in the neighborhood of \( 10^4 \) over the course of 100 days, whereas the pore ratio plummets by more than 6 orders of magnitude within 10% of the pellet radius in less than 5 days.

Increasing the topological rate constant leads to faster overall kinetics at large \( Y_t \) values, but yields almost identical overall oxidation profiles for samples made up almost exclusively of pellets (Figure 6.14, bottom). In short, if ore particles from the primary or secondary crushers were agglomerated to form only pellets, both the coarser (primary crusher) and finer ore samples would leach at similar rates.
Figure 6.14 Conversion/time profiles of truffle, pellet and whole ore as a function of kinetics (left: slow kinetics (ore 2), right: fast kinetics (ore 4)) and proportion of truffles (top: $\gamma_t = 0.95$, bottom: $\gamma_t = 0.05$). $R = 4.5$ mm, $T = 45^\circ$C.
Figure 6.15  Evolution of [Fe(III)]/[Fe(II)] ratio (top) and sulfur grade (bottom) profiles within a 9 mm pellet at 45°C, plotted every 5 d. Left: $\gamma_t = 0.05$, slow kinetics (ore 2). Right: $\gamma_t = 0.05$, fast kinetics (ore 4).
The fast mineral kinetics pull down the oxygen concentration within the reaction zone, beyond which the oxygen concentration is nil, and the potential is kept extremely low. Even the slow mineral kinetics are too fast to achieve oxygen saturation within the pores. That is why the two overall oxidation profiles for $\gamma = 0.05$ are nearly identical. As oxidation progresses, the steep oxygen concentration profile becomes flatter and moves inward. Oxygen concentrations are ultimately driving the pyrite and sulfur oxidation kinetics, as reflected by the quasi-vertical $[\text{Fe(III)}]/[\text{Fe(II)}]$ ratio (plots not shown, but similar to Figure 6.13).

It is worth noting that the sulfur grade profile has a parabolic shape (Figure 6.15, bottom), whose width and displacement speed are influenced by the biological parameters of sulfur-oxidizing cells and the mineral kinetics. The left-hand side of the parabola represents the outer rim of the pellet where the elemental sulfur produced has already been oxidized and where pyrite occurs in minute traces. The elemental sulfur grade is at its highest level in the middle zone where pyrite is about to be depleted. Only traces of elemental sulfur are detected in the pellet core because only a minor fraction of the pyrite has been oxidized in the presence of little oxygen. The large oxygen demand for sulfur oxidation in the middle zone retards the penetration of oxygen into the core. This is an example of two minerals with similar kinetics competing for the same reagent.

### 6.3.3 Influence of Pellet Size

Although agglomeration is desirable for proper solution and air distribution throughout the column, the binding of fines to form pellets may retard the overall column oxidation rate. The analysis of the pellet model predictions has so far been limited to the less realistic type of pellet structure (refer to Figure 4.2). How would the overall oxidation profiles change if only the $< 3$ mm fraction would agglomerate to form pellets of various sizes. Let us examine the pellet, truffle, and whole ore oxidation profiles if ore particles smaller than 3 mm formed spherical pellets of either 1, 2, 3, 6, 9, and 12 mm in diameter. For this purpose, the topological rate parameters of ore 3 are assumed to characterize the $< 3$ mm ore fraction, while
those of ore 5 best describe the leaching kinetics of the remaining coarse particles occurring as truffles. Pellets and truffles are assumed to be initially inoculated with \( Y_{\text{susp}} = 10^8 \) cells/L and to leach at a constant temperature of 45°C. The proportion of truffles is chosen as 45 wt% to reflect the actual proportion of particles larger than 3 mm (Figure 4.21, ore 2).

Figure 6.16 (top right) reveals the truffle oxidation profiles to be completely independent of pellet size. Increasing the pellet size has detrimental effects on the pellet and overall leaching rates. The oxidation rate of larger pellets is entirely controlled by oxygen diffusion. Even though the X- and Y-axis of Figure 6.16 (top left) correspond to the pellet size and extent of oxidation, respectively, each line in Figure 6.16 (top left) is similar to the plot of the effectiveness factor vs Thiele modulus shown in Figure 18.5 of Levenspiel [9]. This is true despite the fact that the biological ferrous oxidation rate with respect to oxygen is not strictly first order.

For the specific set of parameters tested, the transition from chemical to diffusion control occurs for pellets 3 mm in size. Pellets smaller than 3 mm behave essentially as truffles leaching uniformly throughout their entire volume, as shown by laterally uniform elemental sulfur grade profiles in Figure 6.17 (top left). The concept of pellet is superfluous when the ore particles forming pellets are of the same size or larger than the pellet itself. These ore particles behave as individual truffles surrounded by a liquid film in direct contact with air. The two types of stagnant holdups then become one, and the bed is essentially comprised of only truffles.

The very fast kinetics of fines pushes the Fe(III)/Fe(II) concentration ratios to the \(10^4-10^5\) range only at the pore entrance where oxygen is more abundant. The ratios plummet toward the non-leached pellet core as oxygen is completely utilized in the outer leached rim. This is seen indirectly in the elemental sulfur profiles (Figure 6.17). The inner edge of the reaction zone where sulfur begins to build up is exactly 1.2 mm in the 3, 6, and 12 mm pellets after 100 days.
Figure 6.16 Influence of pellet size on pellet (top left), truffle (top right) and whole ore (bottom) sulfide oxidation time profiles. $T = 45^\circ C$, $\gamma_t = 0.45$. 

Chapter 6 – Isothermal Model Simulations
Figure 6.17 Influence of pellet size (top left: $R = 0.5$ mm, top right: $R = 1.5$ mm, bottom left: $R = 3$ mm, bottom right: $R = 6$ mm) on sulfur production/depletion. Plotted every 5 d.
Increasing the proportion of fines in the as-crushed ore distribution should appreciably reduce the leaching time of the whole sample provided that either (1) the whole ore sample is not agglomerated, (2) fines form small pellets, or (3) fines are coated onto coarser particles as they discharge onto the heaps.

The overall oxidation profile of the pellet/truffle stirred-tank model (Figure 6.16, bottom) should not be compared directly to the 45°C oxidation profile of the truffle heap model (Figure 6.2, top left) primarily because of the different volumetric proportions, and the assumption of preinoculation of pellets/truffles in the former case. The two-zone oxidation profile of the heap model is, however, much like the oxidation profile of small pellets. Hence, the ore loaded in the 22, 45, and 65°C columns seems to be comprised of truffles and very small pellets that leach almost as rapidly as if they were non-agglomerated. That explains the very good fits of the three temperature-dependent oxidation profiles (Figure 6.1 to Figure 6.3, top left) despite the assumption of 100% truffles. In fact, if the pellet subroutine were integrated into the heap model, and the set of biological parameters were employed, the model would predict lower extents of oxidation than those measured or fitted by the truffle model. What’s more, the truffle model predictions were even slightly underestimated during the first 50 days.

6.4 Conclusions and Recommendations

6.4.1 Tuning Exercises

The ore sample provided was ideal for this academic modeling exercise because the presence of only one major sulfide mineral reduced the topological kinetics to a simple form, thereby eliminating the need to characterize assemblages of sulfide grains of various compositions. All mineral kinetic parameters having been determined from in-house tests, thirty biological parameters (5 for each type of cells) were adjusted successively to yield reasonable to excellent fits of the time profiles of sulfide and elemental oxidation, leachate total iron concentrations, and potentials at the three temperatures tested. The apparent oxidation plateau
observed at ambient temperature (Figure 2.5–Figure 2.7) could be entirely explained by the particle kinetics, without invoking, for instance, pore obstruction/precipitate formation phenomena limiting the accessibility of reagents to reactive sites.

Evolution of cell concentrations only in the leachate and sulfur grades reproduce inadequately the experimental trends. Model fits reveal uniform vertical and lateral sulfide and oxidation profiles at any of the three temperatures tested after cell colonization. Particle kinetics seems to be the rate-limiting process at 22°C. Oxygen transfer, followed by particle kinetics, appears to control the oxidation process at 45 and 65°C.

The slow-leaching segment of the conversion profile is characterized by high potentials, maximum cell numbers, and large oxygen concentrations. Under these conditions, the low ferrous concentrations set the biological rate to a fraction of its maximum value. Hence, the chemical oxidation rate is controlling the overall process. Microbial kinetics would potentially be the rate-limiting step during the oxidation of pyritic fines were it not for the slow rates of oxygen transfer. The fact that oxidation rates at 45 and 65°C were practically identical would imply that the leach cycle could not be shortened by increasing the proportion of fines through additional crushing. This outcome, however, only applies to isothermal columns.

The two-phase conversion profile (fine → coarse) also suggests that fines most likely occurred as small pellets with negligible pore diffusion resistance. That is probably why the truffle model satisfactorily fitted the three conversion profiles, and why the measured extents of oxidation in agglomerated beds and in the top layer of the non-agglomerated ore bed of column F were comparable.

That most biological parameters for iron-oxidizing cells were found to be in good agreement with published data measured in batch or continuous stirred-tank experiments supports the selection of Monod kinetics. Areas of contention include, however:

- Sensitivity of saturation constant, $K_{Fe}$, with increasing total iron concentrations;
• Treating elemental sulfur as a soluble reactant as opposed to a particulate of a few microns in size;

• Influence of solution chemistry (pH, salinity, trace elements, etc.) on oxidation and growth rate constants;

• Unreliability of the normalized death temperature function, \( f_d(T) \), inside and outside the range of viability;

• General form of the biological growth, endogenous decay, death, and oxidation modeling terms. For instance, the cell growth rate constant, \( k_g \), should multiply the left term in brackets in Eq. 5-16. A cell death rate constant, \( k_d \), should be defined to multiply the normalized death temperature function (right term in brackets in Eq. 5-16).

6.4.2 Validation Simulations

Using the complete set of measured and fitted parameters, the truffle model predicted nicely the extent of oxidation and total iron concentration in the column operated at the lower flow rate. Flow maldistribution in columns F and G is an important topic that the model does not yet tackle. Only the top layer of the pathological, non-agglomerated ore bed could be explained satisfactorily with the truffle model. Operational troubles experienced in non-agglomerated columns only 2 m high or containing large pellets of finely crushed material caution heap designers against such practices at the heap scale.

The large oxygen diffusion resistance from the gas to the liquid is very similar to the potential gradient in the Nernst layer of the pyrite grains (recall chapter 4). In the former case, the diffusion of oxygen from the gas/liquid interface to the mineral surfaces is slow, whereas, in the latter case, the resistance is attributed to the diffusion of ferrous ions away from the surfaces. Interesting questions arise, including:

• “Would it be economically and technically feasible to enrich air with oxygen in order to increase the oxygen partial pressure, and therefore, the overall oxidation rate?”
• “Would high grade ores be more rapidly oxidized in stirred tanks than in heaps on the basis of the practicality and economics of blowing air into stirred tanks?”

• “Would the overall kinetics be significantly improved at higher temperatures under gas/liquid mass transfer limitations by the injection of a surrogate oxidant in the feed solution?”

The design and commissioning of biological stirred tank reactors over the last decade should provide engineers with solid answers to the first two questions. The last one describes, in essence, the upflow saturated packed bed reactor (chapter 4) into which \( \text{H}_2\text{O}_2 \) was added to control the potential to the desired setpoint. An exact answer to the last question requires prior knowledge of the mineral kinetics and of the mass transfer coefficient in unsaturated beds. An experimental study could thus be undertaken to measure both gas/liquid and liquid/solid mass transfer coefficients under conditions typical of heap leaching processes.

6.4.3 Pellet Simulations

Testing the pellet subroutine showed oxygen pore diffusion to become the most severe resistance with increasing pellet size (typically larger than 3 mm) and/or faster mineral kinetics (higher temperature, larger proportion of fines leading to larger topological rate constant). These findings apply to the mineral tested (pyrite). Further simulations should be carried out to determine the increase of the effectiveness factor in the presence of sulfide minerals (e.g. sphalerite) with reduced ferric ion/oxygen demand.

Although no pellet/truffle heap simulations were performed in this work because of long computation times, the pellet model is well suited to an all-encompassing analysis, such as the one employed by Dixon and Hendrix [10], whereby all above factors are grouped in one or more dimensionless parameters. Else, the pellet/truffle heap model could be used in a slightly modified form, recognizing that oxygen pore diffusion is the controlling resistance generating a shrinking-core leaching pattern. Several authors have demonstrated that, under diffusion control,
the conversion of a solid reactant uniformly disseminated throughout a porous particle is predicted by Eq. 6-5.

\[ 1 - X_p = \left( \frac{1}{2} + \cos\left( \frac{\phi + 4\pi}{3} \right) \right)^3 \quad \text{where} \quad \phi = \cos^{-1}\left[ 1 - 2 \left( 1 - \frac{1}{2} \right) \right] \]

where \( \tau_d = \frac{\rho_o G_{FeS_p-pellet} R^2}{6b DC_{O2,s}} \)

where \( b \) is the stoichiometric molar ratio of pyrite to oxygen. Since the pellet simulations have shown that elemental sulfur in the outer rim of the pellet is almost fully oxidized before pyrite oxidation takes place in the core, the reaction stoichiometry in the pellet must be that of pyrite to sulfate (i.e., \( b = 4/15 \)). The time derivative of Eq. 6-5 (i.e. \( dX_p/dt \)) is related to the interfacial gradient through the following equalities.

\[ \frac{4}{3} \pi R^3 \rho_o G_{FeS_p-pellet} \frac{dX_p}{dt} = \frac{dN_{FeS_p-pellet}}{dt} = b \frac{dN_{O2_s}}{dt} = 4\pi R^2 b \left( \frac{D_{O2_s}}{\tau^2} \right) \frac{dC_{O2_s}}{dr} \]  

(6-6)

After deriving similar relationships for total iron and sulfuric acid, the gradients of these three chemical species can be incorporated into the component balances for the stagnant phase.

Since the pellet core is, for all intents and purposes, starved of oxygen, and pyrite and elemental sulfur oxidation occur in a narrow reaction zone, excessive agglomeration must be avoided. It seems preferable to dust fines onto coarser particles as they discharge from the conveyor belt onto the pad, as in GeoBiotics' patented GEOCOAT® technology. However, one must wonder whether the relatively short distances in the pellet core become totally negligible if certain critical reagents (e.g. sulfuric acid in copper and zinc sulfide heaps) must be carried over from the main flow channels to the pellet surface over significantly greater distances.
The present pyrite heap model is the first serious attempt at integrating the most basic physical, chemical, mineralogical, and biological phenomena of heap bioleaching into a single model. Particle kinetics and oxygen transfer were shown to be far more important in the pyrite system than microbial kinetics. This research project just begins to unravel the implications of the model simulations on industrial heap leaching practices, besides establishing guidelines for future research.

6.5 References


Chapter 7

Non-Isothermal Model Simulations

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7.1 Introduction

Numerous what-if scenarios could be simulated under isothermal conditions, but all would fail to address the critical issue of heat generation and transport through the heap and to the surrounding environment. The coupled heap/heat model is employed in this chapter to perform a sensitivity study on the effects of heap height, side branch pore length, air to liquid flow rates, gas/liquid mass transfer coefficient, preinoculation, and others, in order to identify the most critical operating factors and their optimum values. The thirteen factors studied and their low, base, and high case values are presented in Table 7.1, for a total of 21 simulations examining, among others, the depth- and time-dependent profiles of temperature and conversion during 200 days.

<table>
<thead>
<tr>
<th>Parameter</th>
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</thead>
<tbody>
<tr>
<td>Airflow rate, $\Gamma_a = \dot{m}_a/A$ (kg/(m$^2$h), dry basis)</td>
<td>0.5</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Liquid flow rate, $\Gamma_f = \dot{m}_f/A$ (kg/(m$^2$h))</td>
<td>2.5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Heap height, Z (m)</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Pore length, $\tau_x$ (cm)</td>
<td>15</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Ore kinetics</td>
<td>Ore 5</td>
<td>Ore 2</td>
<td>Ore 3</td>
</tr>
<tr>
<td>Preinoculation (cells/L)</td>
<td>$10^{-8}$</td>
<td>$10^8$</td>
<td>—</td>
</tr>
<tr>
<td>Inoculation (cells/L, each cell type)</td>
<td>$10^{10}$</td>
<td>$10^{10}$</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>Mass transfer coefficient, $k_{L,a}$ (h$^{-1}$)</td>
<td>2.5</td>
<td>25</td>
<td>250</td>
</tr>
<tr>
<td>Pyrite grade, $G_{FeS_2}$ (wt%)</td>
<td>—</td>
<td>4.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Initial heap temperature, $T_0$ (°C)</td>
<td>—</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Adsorption constant, $K_{ads}$ (L/cells)*</td>
<td>6.7/1.7</td>
<td>67/17</td>
<td>—</td>
</tr>
<tr>
<td>Growth rate of sulfur-oxidizing cells (h$^{-1}$)</td>
<td>—</td>
<td>Table 6.6</td>
<td>0.11</td>
</tr>
<tr>
<td>Extreme thermophiles (cells/L)</td>
<td>0</td>
<td>$10^8$</td>
<td>—</td>
</tr>
</tbody>
</table>

* The first and second adsorption constants refer to the iron- and sulfur-oxidizing adsorption constants, respectively.
The base case pore length was increased from 1.25 to 25 cm to reflect typical dripper emitter spacing in industrial practice. Because of possible acid limitation in longer pores, the initial and feed sulfuric acid concentration was set to 10 g/L. The complete set of physical, chemical, and biological parameters employed in chapter 6 serve as input parameters. To this list is added a set of parameters required by the heat module, including the geographic position of the heap, the climatic conditions, and the thermal and physical properties of the heap body, the solution, and the air (Table 7.2). In his publication, Dixon [1] gave details about the value and significance of these parameters. A detailed list of the nomenclature employed in this chapter is available in section 5.10.

7.2 Base Case Scenario

In contrast to the uniform vertical and lateral oxidation profiles observed under isothermal conditions at 22, 45, and 65°C, the very rapid rise in local (Figure 7.1, bottom left) and average (Figure 7.4, middle left) temperatures into the extreme thermophilic regime in a 10-m heap over the course of only 30 days creates discontinuities in the depth/oxidation profile (Figure 7.2, bottom left) beyond that time. Prior to day 30, the heap leaches fairly uniformly. The temperature at the top of the heap rapidly and permanently reaches 80°C to never drop later. The surface temperature of 65°C is unusually (possibly unrealistically) elevated (Figure 7.1, bottom left). The Chilton-Colburn analogy used to determine the surface mass transfer coefficient may possibly underestimate the evaporative losses, thus leading to an overestimation of surface temperatures.

Cell inactivity beyond 80°C, and absence of a chemical ferrous oxidation route in the numerical code, explain why internal temperatures level off at 80°C, as shown by the temperature plateau in Figure 7.1, bottom left. As well, pyrite oxidation, and thus heat generation, temporarily ceases in very hot regions, as illustrated by the superposed lines in Figure 7.2, bottom left. This result suggests that hot zones are not necessarily reliable indicators of chemical and biological activity.
Table 7.2 Parameters common to all simulations. Reference 1 provides further details about the measurement or estimation of these parameters. All other parameters taken from Table 6.1 to Table 6.6, unless otherwise specified.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average heap density</td>
<td>( \bar{\rho} ) = Calculated</td>
</tr>
<tr>
<td>Average heap heat capacity</td>
<td>( \bar{C}_p ) = Calculated</td>
</tr>
<tr>
<td>Average heap thermal conductivity</td>
<td>( \bar{k} ) = 1 W/(m·K)</td>
</tr>
<tr>
<td>Solution heat capacity</td>
<td>( C_{pr} ) = 4,184 J/(kg·K)</td>
</tr>
<tr>
<td>Solution temperature</td>
<td>( T_r ) = 20°C</td>
</tr>
<tr>
<td>Dry air heat capacity</td>
<td>( \bar{C}_{pa} ) = 1,000 J/(kg·K)</td>
</tr>
<tr>
<td>Air temperature</td>
<td>( T_a ) = 20°C</td>
</tr>
<tr>
<td>Air relative humidity</td>
<td>( \omega_a ) = 30%</td>
</tr>
<tr>
<td>Latent heat of vaporization</td>
<td>( \lambda ) = 2,360,000 J/kg</td>
</tr>
<tr>
<td>Water vapor heat capacity</td>
<td>( C_{pv} ) = 1,840 J/(kg·K)</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>( p ) = 1.0 atm</td>
</tr>
<tr>
<td>Ambient atmospheric relative humidity</td>
<td>( \omega_a ) = 30%</td>
</tr>
<tr>
<td>Surface heat transfer coefficient</td>
<td>( h ) = 5 W/(m²·K)</td>
</tr>
<tr>
<td>Water-vapor-in-air Lewis number</td>
<td>( \text{Le}_{v-a} ) = 1.25</td>
</tr>
<tr>
<td>Heap surface solar absorptivity</td>
<td>( \alpha ) = 0.7</td>
</tr>
<tr>
<td>Heap surface grey-body emissivity</td>
<td>( \varepsilon ) = 0.9</td>
</tr>
<tr>
<td>Heap-to-sky view factor</td>
<td>( F_{1,2} ) = 0.75</td>
</tr>
<tr>
<td>Atmospheric attenuation factor</td>
<td>( t_{att} ) = 0.9</td>
</tr>
<tr>
<td>Solar declination</td>
<td>( d ) = 0°</td>
</tr>
<tr>
<td>Latitude</td>
<td>( l ) = 40°</td>
</tr>
<tr>
<td>Minimum ambient temperature</td>
<td>( T_{\text{min}} ) = 0°C</td>
</tr>
<tr>
<td>Maximum ambient temperature</td>
<td>( T_{\text{max}} ) = 20°C</td>
</tr>
<tr>
<td>Minimum (night) sky temperature</td>
<td>( T_{\text{min}}^{\text{sky}} ) = -60°C</td>
</tr>
<tr>
<td>Maximum (noon) sky temperature</td>
<td>( T_{\text{max}}^{\text{sky}} ) = 40°C</td>
</tr>
<tr>
<td>Time step</td>
<td>( \Delta t ) = 5 h</td>
</tr>
</tbody>
</table>

Chapter 7 – Non-Isothermal Model Simulations
Because of the acid-consuming nature of the coupled pyrite/ferrous oxidation reactions, and the absence of elemental sulfur at the beginning of the leach, the leachate acid concentration drops from an initial level of 10 g/L to 4 g/L (Figure 7.2, top right). The negligible acid concentrations at the back end of the 25 cm long pore preclude further pyrite oxidation (plot not shown). The acid produced by the elemental sulfur oxidation at the bottom of the heap is carried downward, as shown by the increasing acid concentrations with depth (Figure 7.2, top right). It does not become available to the middle regions of the heap where the pyrite grade and the acid demand are the largest.
Figure 7.2 Evolution of iron concentration (top left), acid concentration (top right), sulfide conversion (bottom left), and sulfur grade (bottom right) in a 10 m heap (top = 0 m) under the base conditions.

The top, middle, and bottom plots in Figure 7.3 illustrate the rapid succession of mesophiles to moderate thermophiles, and finally to extreme thermophiles, respectively. When local temperatures exceed the upper cell viability temperature, mesophile and moderate thermophile cell numbers plummet at a rate proportional to their numbers and their growth rate. It is because of the lower value of their growth rates that sulfur-oxidizing cells persist longer than iron-oxidizing cells in parts of the heap where temperatures exceed their maximum viable temperature.
Figure 7.3  Evolution of iron-oxidizing (left) and sulfur-oxidizing (right) mesophile (top), moderate thermophile (middle), and extreme thermophile (bottom) numbers with depth and time in a 10 m heap (top = 0 m) under the base conditions.
Figure 7.4  Evolution of iron/acid concentration (top left), iron-oxidizing cell numbers (top right), temperature (middle left), potential (middle right), sulfide conversion (bottom left), and sulfur grade (bottom right) in a 10 m heap (top = 0 m) under the base conditions.
Only the first 30 days of the time profiles of iron-oxidizing cell numbers in the leachate (Figure 7.4, top right) truly reflect the type of cells active throughout the heap. During this time, iron-oxidizing mesophiles reach their maximum number. Moderate thermophile growth picks up very rapidly when the temperature reaches 42°C. These cells are quickly outnumbered by the proliferation of extreme thermophiles at the top and in the middle of the heap. The number of moderate thermophiles in the leachate remains nonetheless high because temperatures in the bottom 1 m are ideal for their growth (Figure 7.4, top right).

The convoluted oxygen profile (Figure 7.1, top right) displays two important features. The oxygen concentration plummets from an initial level of 9 mg/L to 0.5-1 mg/L for most of the duration of the leach. These features also characterized the profile of oxygen partial pressure (Figure 7.1, bottom left). The larger availability of oxygen at the bottom of the heap yields higher potentials (Figure 7.1, bottom right) and higher concentrations of iron-oxidizing extreme thermophiles. These reasons explain why the pyrite and elemental sulfur contained in the bottom of the heap are oxidized first. Oxidation of elemental sulfur begins at around day 100 (Figure 7.4, bottom right), as shown by the transition in the time profile of pyrite conversion (Figure 7.4, bottom left). Oxygen concentrations progressively increase back up to 6 mg/L with the depletion of both substrates. The oxidation wave then moves upwards into the heap.

### 7.3 Influence of Heap Height

The slower rise in the average temperature and the more moderate local temperatures far lower than in the 10 m heap (Figure 7.6, top left) lead to uniform oxidation profiles within a 5 m heap (Figure 7.6, bottom left), achieving conversions similar to those predicted in the bottom half of a 10-m heap. The cooler temperatures also control the degree of humidification, thus maintaining higher oxygen partial pressures than in a 15 m heap (Figure 7.6, middle). As the heap gets taller, the sulfide and elemental sulfur reaction zone is pushed toward the bottom of the heap (Figure 7.6, bottom right). Although the overall oxidation of the
shortest heap is 17% superior to that of the 10 m heap after 200 days, which is itself 17% larger than that of the 15 m heap after the same period, the tallest heap still contains the largest proportion of partially-oxidized material, surpassing the intermediate and shortest heaps by 1.1 and 1.8 times, respectively (Figure 7.5). The three simulations also indicate that at least 20% of the sulfide content is oxidized everywhere in the heap during the first 50 days (Figure 7.6, bottom). That, coupled with the fact that very high sulfide conversions are not necessarily essential to complete gold liberation from the sulfide matrix, point to the heap height as a determining factor in maximizing land usage and productivity.

Figure 7.5 Influence of the heap height, Z, on the overall time/oxidation profile.
Figure 7.6  Evolution of temperature (top), oxygen partial pressure (middle), and sulfide conversion (bottom) in short (left) and tall (right) heaps.

Chapter 7 - Non-Isothermal Model Simulations
7.4 Influence of Irrigation Flow Rate

Decreasing the liquid flow rate to 2.5 kg/(m²·h) leads to an additional 10% sulfide oxidation after 200 d in comparison to heaps irrigated at 5 or 10 kg/(m²·h) (Figure 7.7). It also reverses the temperature profile (Figure 7.8, left vs right).

![Figure 7.7](image)

Figure 7.7 Influence of the irrigation flow rate, $\dot{m}_f/A$, on the overall time/oxidation profile.

A heap irrigated at lower flow rates benefits from more uniform heating, particularly in the upper part of the heap (first few lines in Figure 7.8, top left), resulting in more uniform oxidation (Figure 7.8, bottom left). In the later stages of the leach, more rapid cooling everywhere throughout the heap, and particularly at the top of the heap (Figure 7.8, top left), results in an average heap temperature 5°C lower than if irrigated at 5 or 10 kg/(m²·h). Reducing the flow rate from 5 to 2.5 kg/(m²·h) doubles the predicted iron and acid concentrations in the leachate. However, the acid supplied at 2.5 kg/(m²·h) does not meet the initial acid demand.
2.5 kg/(m²·h) liquid flow

Progression with each line: 8.8 days

10.0 kg/(m²·h) liquid flow

Progression with each line: 8.8 days

Figure 7.8 Evolution of temperature (top) and sulfide conversion (bottom) at small (left) and large (right) irrigation rates in a 10 m heap (top = 0 m).

Doubling the irrigation flow rate to 10 kg/(m²·h) displaces the "hot-80°C" zone downward (Figure 7.8, top right), confining it to the lower half of the heap where temperatures do not exceed 80°C. With increasing flow rates, the solution carries more heat away from the top of the heap, leaving the first 2 m drastically underheated at temperatures close to that of the solution applied (Figure 7.8, top right). These wide temperature variations result in a maximum average temperature of 40°C. The upper and bottom 1/3 regions of the heap leach at relatively the same rate, and more rapidly than the middle zone (Figure 7.8, bottom right). The mesophilic population flourishes in the cooler environment at the top of the heap.
the heap, while extreme thermophiles colonize the bottom region. In summary, the model simulation reveal the minor influence of the application rate on the overall extent of oxidation, yet its severe effect on reversing the temperature profile. The operating costs of pumping and solution handling would endorse lower flow rates.

7.5 Influence of Air Blowing Rate

Like the heap height, the air blowing rate has a dramatic influence on the overall extent of sulfide oxidation (Figure 7.9), as well as on the average temperature (plot not shown), over a period of 200 days.

![Figure 7.9 Influence of the air blowing rate, \( \dot{m}_a/A \), on the overall time/oxidation profile.](image)

Reducing the air flow rate from 1.5 to 0.3 kg/(m\(^2\)-h) pushes the "hot" reaction zone toward the bottom of the heap (Figure 7.10, bottom left). In fact, only the bottom 4 m of the heap undergoes oxidation (Figure 7.10, bottom left) at temperatures not exceeding 70°C (Figure 7.10, top left). Nearly 100% of the oxygen is consumed in
the active region, thus yielding extremely low oxygen partial pressures of 0.01 atm in the top 4 m (Figure 7.10, middle left). As a result, very little pyrite is oxidized at the top of the heap during the first 200 d. What little heat is generated is rapidly carried downward, keeping temperatures as low as 20°C at the top of the heap (Figure 7.10, top left). In short, only the bottom of the heap undergoes oxidation due to the insufficient supply of oxygen in the gas stream.

Increasing the air flow rate to 4 kg/(m^2·h) reverses the temperature profile as the gas phase carries more heat upward in the form of latent heat of vaporization. Peak temperatures of 75°C are only noted in the first 4 m near the surface (Figure 7.10, top right), producing cooler temperatures everywhere else throughout the heap. The average temperature does not exceed 60°C. These conditions are very favorable to the concurrent growth of moderate and extreme thermophiles at the bottom and top of the heap, respectively. Increasing the aeration rate (relative to the solution irrigation rate) cools the heap, widens the reaction zone to the entire 10 m (Figure 7.10, bottom right), and increases the overall extent of oxidation to ~80% (vs 50% at 1.5 kg/(m^2·h)) after 100 days. The transition at around 80% conversion after 100 days results from the disappearance of the rapidly-oxidizable pyrite, leaving the coarser pyrite behind, and the absence of mesophiles and moderate thermophiles where needed. In brief, higher blowing rates generate more uniform oxidation with depth, faster overall leaching kinetics, and relatively cooler temperatures.

7.6 Influence of Gas/Liquid Mass Transfer Coefficient

The influence of the gas/liquid mass transfer coefficient on the overall extent of oxidation is shown in Figure 7.11 for arbitrary \( k_La \) values of 2.5, 25, and 250 h^{-1} under the base case conditions. Temperature and oxidation profiles at the two highest mass transfer coefficient values are practically identical. The reaction zone moves upward as peaking temperatures of 75°C at the bottom of the heap progressively decrease when the sulfide reserves are essentially depleted.
Figure 7.10  Evolution of temperature (top), oxygen partial pressure (middle), and sulfide conversion (bottom) at small (left) and large (right) aeration rates in a 10 m heap (top = 0 m).

Chapter 7 - Non-Isothermal Model Simulations
Figure 7.11 Influence of the gas/liquid mass transfer coefficient, $k_L a$, on the overall time/oxidation profile.

The oxygen mass transfer limitation experienced under both conditions is linked to decreasing oxygen partial pressures with increasing height, and not to the mass transfer coefficient per se. Decreased oxygen partial pressures are the result of the coupled effect of oxygen consumption by ferrous and sulfur biological oxidation reactions and air humidification (increase of the vapor pressure $\rightarrow$ decrease of the oxygen partial pressure).

Oxidation proceeds very uniformly throughout the heap at the lower mass transfer coefficient. In this case, the oxygen partial pressures remain high at 0.18–0.19 atm, except that the dissolved oxygen concentrations plummet to 0.1 mg/L everywhere, yielding uniform, almost constant potentials of 500 to 600 mV. The oxidation rate is very low, keeping the average temperature almost constant at 36°C. Only the bottom of the heap experiences higher temperatures less than 47°C.
The maximum rate at which oxygen can be transferred into the stagnant solution sets an upper limit on the biological kinetics. The maximum gas/liquid transfer is a constant given by:

\[ r_{sO_2} = k_L a \left( C^*_O (T, C_{si}) - C_{sO_2} \right) = k_L a C^*_O (T, C_{si}) \]  

(7-1)

Eq. 7-1 explains the linearity of the oxidation profile and the minute concentrations of oxygen within stagnant pores. Increasing the air flow rate is certainly not the technical solution sought to improve gas transfer in this situation. Only methods that can increase either \( k_L a \), \( C^* \), or both, will be beneficial. Since the oxygen saturation concentration is directly proportional to its partial pressure through Henry's law, increasing the oxygen partial pressure seems an ideal solution. However, oxygen production and handling costs must be weighed against increased revenues associated with faster, and possibly higher extractions. If no special measures are taken to enhance mass transfer, it is imperative that gas/liquid transfer coefficients be measured in unsaturated beds at low liquid and gas flow rates to better forecast production and leach cycles.

### 7.7 Influence of Sulfide Head Grade and Particle Kinetics

Tripling the pyrite head grade from 4.5 to 13.5 wt% markedly reduces the overall oxidation kinetics (Figure 7.12, square vs circle symbols). The model suggests that only 30% of the sulfide content is oxidized after 200 days in comparison to 75% for the lower head grade. Not surprisingly, the amount of sulfide oxidized, as calculated from the product of the head grade and the extent of oxidation, is fairly comparable in both cases. Besides the lower conversion, differences between the low and high head grade simulations include the prolonged periods of time during which the average temperature remains constant at 75°C and oxygen concentrations linger around 1 mg/L. Furthermore, there are no signs of cooling even after 200 days, and the reaction front travels upward even more slowly than in the lower grade heap.
To investigate the effects of particle kinetics on the heap overall oxidation kinetics, the topological kinetics of ore 5, ore 2, and ore 3 evaluated in chapter 4 were selected to represent the slow, medium, and fast kinetics cases. Three 200-d simulations were performed by changing solely the topological exponent and the rate constant (Figure 7.12). The simulations suggest that particle kinetics slightly change the overall oxidation profile because the oxygen partial pressures and concentrations are as low in all cases. All heaps appear to leach from the bottom upward. Complete conversion is reached in the bottom part of the heap in the presence of fast-leaching particles, as compared to 92% oxidation with medium kinetics (Figure 7.1, bottom left). Lower oxidation and lower heat generation rates in the presence of slow-leaching particles hamper the rise of the average internal temperature, thus keeping the heap cooler during the first 75 days.
7.8 Influence of Other Factors

Extending the side branch pore length to 35 cm, or shortening it to 15 cm, does not influence the extent of oxidation (Figure 7.13, left). The sulfuric acid net concentration gradient across the heap increases from 5 to 7.2 to 8 g/L with decreasing pore length from 35 to 25 to 15 cm. Longer pores are more acid-starved than shorter ones.

![Figure 7.13 Influence of the stagnant pore length, $t_{sX}$, (left) and the initial heap temperature (right) on the overall time/oxidation profile.](image)

Even though the heap may be several degrees hotter by the time solution application begins than at the time of stacking, the higher initial heap temperature does not accelerate the overall oxidation kinetics (Figure 7.13, right). However, when the heap is already 30°C warmer than its surrounding environment, the time required to reach an average heap temperature of 75°C is reduced by 25 days (plot not shown).
7.9 Biological Dynamics

7.9.1 Influence of Preinoculation

According to the model simulations shown in Figure 7.14, agglomerate preinoculation is an effective method for increasing local and overall extents of sulfide oxidation. While the preinoculated heap leaches uniformly at first and then upwards for the remainder of the leach cycle (Figure 7.1, bottom left), only the top of the non-preinoculated heap where iron-oxidizing cells are more abundant (Figure 7.15, bottom left) leaches in the initial stages, followed by more uniform leaching patterns (Figure 7.15, top left).

![Figure 7.14 Influence of ore preinoculation and degree of adsorption on the overall time/oxidation profile. The high adsorption ratio refers to 67 L/Fe-cells and 17 L/S-cells, while the low adsorption ratio corresponds to 6.7 L/Fe-cells and 1.7 L/S-cells.](image-url)
Figure 7.15  Evolution of sulfide conversion (top left), oxygen partial pressure (top right), temperature (middle left), sulfur grade (middle right), extreme thermophile iron-oxidizing numbers (bottom left), and extreme thermophile sulfur-oxidizing numbers (bottom right) in a 10 m, non-preinoculated heap (top = 0 m).
Because a narrower region of the non-preinoculated heap is actively oxidized, there is less heat generated, which engenders longer heating times requiring an additional 90 days for the average heap temperature to reach 73°C. Because temperatures rise less rapidly everywhere throughout the heap (Figure 7.15, middle left), and because the depth temperature profile is vertically inverted in comparison to that of the preinoculated heap (Figure 7.1, middle left), oxygen partial pressures remain larger after the same leach time (Figure 7.15, top right).

Breakthrough of iron-oxidizing mesophile cells occurs 50 days later when the feed solution is the only mode of inoculation. Figure 7.15 (bottom left) illustrates three stages in the colonization of the heap by iron-oxidizing extreme thermophiles. During the initial stages of the leach, when temperatures at the top of the heap are less than 50°C, colonization occurs very slowly through only one mode: attachment of cells introduced with the flowing liquid within deeper layers (very closely spaced lines in the bottom left corner of Figure 7.15 (bottom left).

When temperatures reach the minimum temperature of viability of iron-oxidizing extreme thermophiles, the colonization wave moves more rapidly toward the bottom of the heap due primarily to cell growth at the top of the heap, and, to a lesser extent, to the adsorption/desorption processes. The widely-spaced inverted U-shaped lines illustrate this phenomenon (Figure 7.15, bottom left). Lastly, after reaching a maximum level, the number of extreme thermophiles decreases from the top downward. As the extent of sulfide oxidation at the top of the heap approaches 80% (Figure 7.15, top right), the sulfide oxidation rate decreases rapidly. The net cell growth rate becomes negative.

The elemental sulfur produced in the non-preinoculated heap simply keeps building up (Figure 7.15, middle right) as the colonization wave of sulfur-oxidizing extreme thermophiles (Figure 7.15, bottom right) is lagging behind the heating front (Figure 7.15, middle left). The oxygen demand associated with sulfur oxidation explains why oxygen partial pressures remain at one-third saturation after 200 days (Figure 7.15, top right). In contrast, by this time, the oxygen partial pressures in a
preinoculated heap are at or approach saturation from the bottom up (Figure 7.1, top left).

Decreasing the adsorption constant by one order of magnitude (i.e. fewer attached cells with respect to the number of planktonic cells) promotes more rapid cell progression toward the bottom of the heap. Non-negligible levels of cells in the leachate are detected 35 days earlier than the 75 days for the non-preinoculated heap with large adsorption. The more rapid colonization results in increased rates of heating (75 vs 130 days to reach 73°C) and oxidation (40% vs 17% after 100 days). However, this latter effect is progressively attenuated beyond day 100, to such a degree that the extents of oxidation in both heaps are practically the same after 200 days. The partitioning of oxygen between iron–oxidizing cells and the now active sulfur–oxidizing cells explains, in part, the smaller differences with longer leaching times.

7.9.2 Faster Growth/Weaker Adsorption of Sulfur–Oxidizing Cells

Because of the acid depletion observed at the bottom of the heap at low solution application rates or at high aeration rates, increasing the sulfur–oxidizing cell growth rate $k_g$ from 0.003 to 0.11 h$^{-1}$ and reducing their adsorption constant $K_{ads}$ from 17 to 0.7 L/cells (Table 7.1) would be expected to increase the acid production. Figure 7.16 demonstrates that the sulfur–oxidizing extreme thermophilic population colonizes the bottom of the heap very rapidly (32 d) when reducing the adsorption constant. After 32 days, the population everywhere throughout the heap is two orders of magnitude larger (Figure 7.16, left vs right). Because of rapid colonization, the population grows even larger to $10^{11}$ cells/L when the temperature reaches their optimum range (55–80°C), in comparison to a maximum of $10^{10}$ cells/L in the presence of a more dominantly-attached population.
The larger cell abundance at the bottom of the heap results in a greater oxidation of elemental sulfur, thus producing more acid. A comparison of the solid and dashed lines in Figure 7.17 (left) confirms the lower overall elemental sulfur grade in the presence of more cells. Consequently, the overall, maximum vertical acid gradient decreases from 6 to 3.5 g/L (Figure 7.17, right). However, the oxidation of both sulfide and elemental sulfur still advance from the bottom to the top of the heap despite the larger sulfur-oxidizing population. Thus, the acid produced at node $i$ ($i$ increasing with depth) becomes available to node $i+1$. Node $i-1$ requires more acid than node $i+1$ to produce ferric ions for pyrite oxidation. Therefore, the simulation with faster growth/weak adsorption reveals a nearly identical time profile of sulfide oxidation (plot not shown).
7.9.3 Absence of Extreme Thermophiles

The microbiological community believes that *Archaea*, a class of extreme thermophilic microbes, do not occur naturally in heap bioleaching environments. Simulations were thus performed in the absence and presence of iron- and sulfur-oxidizing extreme thermophiles. Their presence would double the overall extent of oxidation from 35 to 75% after 200 d (Figure 7.18). Extreme thermophiles whose number in solution reach $10^{13}$ cells/L (plots not shown) would entirely control the oxidation in the bottom 70% region of the heap where temperatures exceed 60°C (Figure 7.19, top right) and where oxygen pressures and potentials (Figure 7.19, middle right) are higher.

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**Figure 7.17** Coupled influence of faster growth rate and weaker adsorptivity on the overall sulfur grade (left) and the leachate sulfuric acid concentration (right).
Figure 7.18 Influence of the presence of iron- and sulfur-oxidizing extreme thermophiles on the overall time/oxidation profile.

A simulation without extreme thermophiles reveals mesophiles to colonize the upper 20% of the heap, while moderate thermophiles survive within the upper 7 m and the lower 2 m (plots not shown). Internal temperatures never exceed 60°C and remain constant near 55°C – the assumed maximum viable temperature for moderate thermophiles (Figure 7.19, top left). The slightly too hot temperatures (above 55°C) between the 6th and 10th m (Figure 7.19, top left) kill the moderate thermophiles. Because the potentials (Figure 7.19, middle left) plummet between the 4th and 10th m in the absence of cells, sulfide oxidation reaches only 10% after 200 d (Figure 7.19, bottom left). Oxidation occurs at the top with mesophiles and at the bottom with moderate thermophiles (Figure 7.19, bottom left). These active zones move progressively toward the middle of the heap. In contrast, the heap inoculated with extreme thermophiles leaches uniformly during the first 24 d, and from the bottom up afterwards (Figure 7.19, bottom right).
Absence of extreme thermophiles

Progression with each line: 8.8 days

Presence of extreme thermophiles

Progression with each line: 8.8 days

Figure 7.19 Evolution of temperature (top), potential (middle), and sulfide conversion (bottom) in a 10 m heap in the absence (left) and presence (right) of extreme thermophiles.
7.10 Conclusions

The model predicts that as much as 46 and 75\% of the 2.35 wt\% sulfide content of this as-crushed pyrite ore could be oxidized in 100 and 200 days, respectively, in a 10 m heap irrigated at 5 L/(m$^2$·h) and aerated at 1.5 kg/(m$^2$·h). This oxidation rate of 0.018 wt%/d (= 2.35×75%/100) surpasses the maximum and average overall sulfide oxidation rate of 0.009 and 0.005 wt%/d reported for non-aerated pilot- and demonstration-scale heaps of similar heights [2–4]. Newmont’s aerated commercial heap achieves conversions of 35\% of its 1.45 wt\% sulfide sulfur content in 150 days, or 0.0033 wt%/d. The differences between the measured and predicted data can be attributed to a number of reasons, including:

- Slower mineral kinetics of Newmont’s sulfidic refractory gold ore.
- Uneven air distribution throughout the heap and air pipes submerged below the waterline are problems that have been known to occur at other sites.
- The clayey nature of the ore could decrease permeability.
- The absence of extreme thermophilic microorganisms in the feed solution.
- The large heat generation rates in pyrite systems (> 100 W/m$^3$) could dry out the stagnant solution at the top of the heap during the dry cycle of Newmont’s intermittent irrigation practice [5]. This could exacerbate precipitation and create local hot spots that, in turn, could inhibit or kill the microflora.

These few preliminary non-isothermal simulations have demonstrated how changing a single parameter can reverse the entire process, confining active oxidation zone(s) to certain parts of the heap. According to the model predictions, the severe oxygen transfer limitation, which was observed in the 65°C isothermal columns, is an issue in the relatively cooler parts of the heap. Cessation of all biological and chemical activity above 80°C is a bold assumption, which can be revisited by introducing a chemical ferrous oxidation rate term and by better characterizing the biodynamics of extreme thermophiles.
The fact that roughly 6.5% of the sulfide sulfur content has been oxidized by the time temperatures reach 40°C in a 10 m heap with $\frac{m_a}{m_f} = 0.8$, thereby slowing down the mineral kinetics through the $(1-X)^0$ term, also yields larger oxygen concentrations in comparison to the 45°C isothermal columns. Complex interactions emerge in non-isothermal columns between particle kinetics, head grade, oxygen transfer, acid concentrations, cell temperature sensitivity, and biological kinetics.

The heap height (whether small for uniform leaching profiles, or large to maximize the ore-to-pad surface ratio), high aeration rate, and preinoculation were stressed as critical controllable factors to achieve high sulfide conversions. A large aeration to irrigation rate ratio could avoid overheating. The irrigation flow rate and initial temperature have very little influence on the overall sulfide kinetics. Air humidification severely reduces the oxygen partial pressure with increasing height. This effect offsets the benefits of faster mineral kinetics and/or higher gas/liquid mass transfer coefficient to increase pyrite oxidation rates.

The key fundamental concepts outlined in sections 5.9.2 and 6.4 must be addressed to overcome the shortcomings of the current model. For instance, the predictions of the base case simulation indicate that the oxidation of 75% of the pyrite content over the course of 200 days consumes 30% of the oxygen supplied, i.e. reduces the dry air mass flow rate by only 7%. Because nearly all the oxygen supplied is depleted at the lower aeration rate of 0.3 kg/(m²·h), the error on the dry air mass flow rate increases to 21%. The Boussinesq assumption should be challenged under these specific conditions. The acid depletion observed in the middle and at the end of stagnant pores, and the resulting negative acid concentrations at these nodes, could be overcome with a pseudo-steady state approximation.

The *ideal* heap model must be validated beyond traditional isothermal laboratory columns using zone-wise temperature-controlled columns stacked with the same ore, and subsequently, by building pilot- and demonstration-scale heaps operated under non-transient conditions. Existing and future model subroutines must be validated beyond traditional isothermal laboratory columns using zone-wise temperature-controlled columns stacked with the same ore, and subsequently, by building pilot- and demonstration-scale heaps operated under non-transient conditions. Existing and future model subroutines must be validated beyond traditional isothermal laboratory columns using zone-wise temperature-controlled columns stacked with the same ore, and subsequently, by building pilot- and demonstration-scale heaps operated under non-transient conditions. Existing and future model subroutines must be
standardized and fully tested in order to minimize, if not completely eliminate, case-by-case “code microsurgery”. After equipping the FORTRAN numerical code with a user-friendly interface, the code could be integrated into commercial hydrometallurgical softwares. Engineers could use this sophisticated mathematical tool to perform a more exhaustive sensitivity study on the basis of industrial considerations (whether it be cycle duration, gold liberation, or extent of sulfide oxidation).

7.11 References


Chapter 8

Conclusions and Recommendations

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Understanding the nature, rate, and interrelationships between the multiple physical, chemical, biological, and thermal phenomena occurring in the sulfide biooxidation process for the treatment of refractory gold ores in ideal heaps was the subject of this research project. I have endeavored to demonstrate that the heap leaching process can be described quantitatively with a mathematical model, aided by a systematic experimental approach. In addition to Dixon’s heat model, the heap model is also comprised of the following subroutines derived without any recourse to purely empirical considerations.

8.1 Particle-Scale Kinetics

I have attempted to quantify the thermal, chemical, and topological functionals driving the oxidation kinetics of diverse pyrite grain occurrences within the ore
particles and ore assemblages through the development of a particle leaching model. Determining all three model features could have been performed with the pyritic ore particles themselves at the expense of very long oxidation times, lack of sample representativeness, sampling inaccuracy, equipment and space unavailability, and intense labor. Instead, a pyrite concentrate, which was prepared by flotation from the 5-tonne bulk ore sample, was leached rapidly in a stirred tank reactor to evaluate the effects of temperature (30–75°C) and solution chemistry ([Fe(III)]/[Fe(II)] = 30–300). Six ore samples of varying size fractions were then leached in upflow, saturated packed bed columns under only one set of conditions (temperature = 55°C, [Fe(III)]/[Fe(II)] = 300) to determine the influence of pyrite grain size, morphology, and occlusion. Very few researchers and modelers in the field of heap leaching have addressed this latter subject with the attention it deserves.

The sulfate yield (58 wt%) was shown to be independent of the medium composition and temperature using a thermodynamic speciation program which had permanganate addition as one of many inputs. The sulfate yield was later proven indispensable in determining the extent of elemental sulfur oxidation in columns inoculated with sulfur-oxidizing cells.

The grain leaching model expression was derived from a Butler-Volmer analysis of the anodic and cathodic reactions, assuming that (1) pyrite grains leached as shrinking spheres, and (2) that the surface and bulk Fe(III) and Fe(II) concentrations were the same. A rigorous analysis of diffusion and reaction rates near the pyrite surfaces confirmed the validity of the second hypothesis, and most importantly, stressed the importance of mastering process fundamentals before designing an experimental program.

The oxidation rate per unit surface area of the pyrite grain was shown to obey Arrhenius’ law (activation energy = 76 kJ/mole), and to be proportional to the square root of the Fe$^{3+}$/Fe$^{2+}$ activity ratio (or, alternatively, the Fe(III)/Fe(II) concentration ratio). The grain model in its two forms (either with activity of free ions, or else, concentration of total ions) fitted very nicely all experimental points.
below 90-95% conversion. The Fe(II) mass transfer limitation leaves the model chemical functional unsubstantiated at very high potentials, which are typical of pyrite heap systems.

Only the type III leaching model could be tested with computational ease because of the nature of the sulfide mineral tested and the potentiostatic method employed. Proving or rejecting the type I leaching model would involve measuring the initial leaching rates of pyrite grains of known surface area in media containing different Fe(III) concentrations for a given Fe(II) concentration.

After integrating the thermal and chemical functionals into the particle model, the latter was found to bear a close resemblance to the shrinking-sphere grain model. The calculated overall oxidation profiles of five real ore samples with widely different particle size distributions were nicely fitted by simply adjusting two size-dependent model parameters.

The versatility of the experimental method employed makes it possible to model the particle kinetics of any particle size distribution and any ore assemblage (truffle vs pellet). Future research in this area should be geared toward understanding the leaching and passivation behaviors of one or more sulfide mineral(s) in contact with one another. In my opinion, formulating a theoretical multi-mineral particle model on the basis of grain size and shape measurements will not be adequate to appreciate the complexities of electrochemical reactions. A reliable particle model can only be derived through careful experimentation under more than one set of test conditions.

8.2 Microbial Kinetics

Ferrous ions generated at the pyrite surfaces in an abiotic system have to diffuse back into the bulk to be reoxidized to ferric ions by KMnO₄ or H₂O₂. A comparison of the particle model predictions and column bioleaching results has proven that microorganisms are at least responsible for the oxidation of ferrous ions directly at
the mineral surfaces, thereby maintaining higher potentials than possibly achievable in abiotic stirred-tank reactors.

Planktonic and attached mesophiles, moderate thermophiles, and extreme thermophiles were assumed capable of multiplication, endogenous decay, death, and ferrous ion or elemental sulfur oxidation, each over a specific range of temperature, beyond which severe death rates were imposed.

Growth and oxidation rates were successfully modeled using Monod functions of only ferrous ion or elemental sulfur, and oxygen concentrations. Estimated biological parameters were found in good agreement with published values in the literature. Ignoring the effects of carbon dioxide concentration on growth was a reasonable assumption when blowing enriched air. Besides, the fact that none of the three cell populations exceeded $5 \times 10^{12}$ cells/kg dry ore in this pyrite system (and in other sulfide systems tested by the UBC Biohydrometallurgy Group) suggests that 0.03 vol% carbon dioxide in air may only be insufficient during the colonization phase. The steady-state attached population was modeled by the plateau of the Langmuir isotherm.

The presence of *Acidithiobacillus ferrooxidans* and/or *Sulfobacillus sp.*, which can utilize both reduced iron and elemental sulfur as growth substrates, explains why the elemental sulfur produced by the ferric leaching of pyrite at ambient temperature was further oxidized to sulfate. According to model simulations using non-optimized biological parameters, the elemental sulfur grade increases to a maximum level, at which point the rate of consumption exceeds the rate of production (grade decreases). Experimental data from 22 and 45°C columns revealed, however, the grade to remain practically constant.

8.3 Gas and Liquid Dynamics

A large, unsaturated column with even solution distribution was modeled as a uniformly-packed and non-compacted ore bed comprised of roughly 60 vol% of non-porous truffles and porous pellets, bathing in roughly 12 vol% stagnant
solution. The results from a statistical analysis regarding an increase in stagnant liquid holdup to roughly 17 vol% with decreasing particle size and/or in non-agglomerated beds were confirmed in subsequent large-scale leaching column tests.

Microbes and reagents, such as ferric ions, ferrous ions, and sulfuric acid, are carried by the flowing liquid (≈ 3 vol%) before crossing the stagnant/flowing interface. There, they diffuse into the stagnant solution, which was represented as spherical, cylindrical, or linear side branch pores of uniform or variable length (0.6–2.5 cm). The estimated pore length was only marginally affected by changing the crush size, agglomeration technique, or operating conditions. Reagents are either consumed biologically and/or chemically by truffles anywhere within the stagnant pores, or else transferred into the millimeters long pores of spherical pellets where they diffuse to internal reaction sites.

Concepts pertaining to the rate and distance of solute movement were integrated into three mathematical models (mixed side-pore and profile side-pore diffusion) in dimensionless form. Model parameters (stagnant liquid holdup, pore length) were determined from experimental tracer residence time distributions using a least square minimization approach. All twenty-three tracer residence time distributions were very satisfactorily fitted ($R^2 > 0.99$) by the profile side-pore diffusion model with uniform pore length. The effects of five factors (agglomeration, addition of binder, particle size, solution flow rate and bed height) were examined. Data from experimental tracer curves proved that the advection time is directly proportional to the column height, and inversely proportional to the flow rate.

The hydrodynamic model is suitable for modeling diffusion into side branch pores in a bed of truffles. When coupling the hydrodynamic model with pellet diffusion, values of the stagnant liquid holdup surrounding pellets/truffles and side branch pore length must be less than the estimates from tracer and hydrology tests. Using the truffle model to simulate oxidation in long-term leaching column tests with small particles and/or in non-agglomerated beds, which both experienced compaction and air channeling, yielded overestimated predictions of conversion.

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The gas phase, which occupies approximately 25 vol% of the total column volume in non-compacted beds, was assumed to be in direct contact with the stagnant solution. Oxygen transfers into the stagnant solution in order to meet the requirements of iron- and sulfur-oxidizing cells. The gas/liquid mass transfer rate was modeled to be proportional to both the mass transfer coefficient \((25 \text{ h}^{-1})\) and the difference between the oxygen saturation and bulk concentrations. Reduction of oxygen partial pressures with increasing heap height was the result of air humidification and biological consumption.

8.4 Principal Findings

A series of small and large isothermal column tests were conducted to assess the validity of the model and to challenge its predictions. One can use the model to predict the effects of changing one or more operating factors (heap height, aeration rate, irrigation rate, mode of inoculation, head grade, gas/liquid mass transfer coefficient, pellet size, mineral kinetics, climatic conditions, degree of pellitization, dripper spacing, etc.) on conversion, concentration, and temperature profiles in the absence of jarosite precipitation.

Fundamental and practical insights about diffusion and reaction rates within pellets are gained through the application of the pellet model to this real pyritic ore specimen. It was shown that a zone-wise, oxygen diffusion-controlled reaction regime prevails in pellets larger than 3 mm and comprised of rapidly-oxidizable pyrite. Pyrite and elemental sulfur grade profiles follow an asymmetrical, bell-shaped curve. However, the fast rising segment of the sulfide oxidation profiles of the 45 and 65°C columns, which tapers off beyond 60% conversion, seems to indicate that the agglomeration process produced mostly truffles.

Of the three key phenomena in series (oxygen transfer → biological ferrous oxidation → chemical pyrite oxidation) in an isothermal pyrite system of truffles, oxygen transfer, coupled with low dissolved oxygen concentrations, dictates the maximum achievable rate of the overall process based on the estimate of the gas/liquid mass transfer coefficient. Rapidly-oxidizable pyritic fines cause the
dissolved oxygen concentrations to plummet, particularly at higher temperatures as a result of faster mineral kinetics and lower oxygen partial pressure and solubility levels. Even though cells may still be in very small numbers in the early stages of the leach, biological kinetics are nonetheless faster than gas transfer. Increasing the sulfide head grade, accelerating the particle kinetics by crushing the sulfide grains, and/or decreasing the mass transfer coefficient all prolong the gas transfer-controlled regime.

With the disappearance of fines and the remaining coarser/occluded pyrite grains to be oxidized from the largest size fractions, the Fe(III)/Fe(II) concentration ratio progressively increases to reach a more or less constant level prescribed by the biological ferrous oxidation saturation constant. Under these conditions, the rate control shifts toward particle kinetics.

Homogeneous vertical and lateral sulfide oxidation profiles are typical only of isothermal columns as none of the reagents (sulfuric acid, ferric ions, oxygen) have to be transported from the bulk flow to the stagnant solution. The model predictions indicate that about one month would be required for cell numbers in non-preinoculated columns of 2 m to reach their maximum concentration, compared to less than 15 days if inoculated during agglomeration.

Depending on, among other things, the heap height, and irrigation and aeration rates, a pyritic heap may undergo zone-wise kinetics as the bottom of the heap tends to be cooler than the top. In fact, at low irrigation and aeration rates, the upper half of the heap may be too hot (80°C) for cells to be vigorously active. Slow oxygen transfer impedes oxidation in the cooler, active zones in a low-grade, pyritic ore heap, a situation even more critical when leaching a higher-grade ore.

Although it was originally proposed to test a variety of sulfidic refractory gold ore samples with varying mineralogies, ore availability, personnel, and time constraints forced us to limit the focus of this research to a single sample of pyritic refractory gold ore. Several reasons made this pyrite system ideal for tuning and validation tests, including:

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• The predominance of one sulfide mineral whose leaching kinetics are fairly well understood;

• The "cleanliness" of the ore sample and possible absence of cell growth inhibitors;

• The relative unimportance of iron precipitation.

However, an experimental study aimed at measuring the gas/liquid mass transfer coefficient in unsaturated packed beds operated at low irrigation and blowing rates is called for before the model is used in a more comprehensive sensitivity study. Although increasing the number of drip lines would theoretically reduce the pore length and minimize the acid concentration gradient across the pores, future studies should revisit the form of the sulfur-oxidizing biological model to better predict the elemental sulfur grade and pH.

8.5 Future Perspectives

The long-term acid-producing nature of the pyrite system raises concerns about decommissioning strategies. Model simulations have shown that the majority of the acid produced originated from the subsequent biological oxidation of elemental sulfur. Ultimately, to reduce operating costs associated with lime consumption for acid neutralization, physical, chemical, or biological strategies could be designed to selectively prevent sulfur oxidation, while sustaining ferrous oxidation. If such measures ineffectively controlled the acid production, forming waste rock piles with the biooxidized, gold-leached residue and neutralizing the acid mine drainage would be more economical than leaving the refractory gold ore on the biooxidation pad until complete pyrite oxidation. The following reasons support this argument.

• First, sulfide oxidation is only the first of two processes in the ultimate extraction of gold from refractory gold ores. In contrast, chalcocite heap leaching operations recover the desired product, copper, in the pregnant solution. Thus, the biooxidation step lengthens the overall gold leach process. To make matters worse, the biooxidation time is far longer than, for instance, the cyanide gold leaching step.
Second, gold extractability is not necessarily correlated to sulfide oxidation. Therefore, leaving ore under sulfide leach for extended periods of time decreases revenues once the refractory gold becomes extractable.

Third, according to model simulations, complete oxidation of the coarsest pyrite grains requires more than 300 d.

Lastly, even if the particles were crushed to smaller sizes to accelerate the sulfide oxidation kinetics and to shorten the biooxidation time, bed compaction, air channeling, and scarcity of oxygen in pellet pores would counteract the positive effects of finer crush size.

Very few of the many studies on pyrite bioleaching have been referred to in this thesis because of the narrow scope of their research work and the anecdotal nature of the data published. It became obvious in developing and testing the biological model that concepts and data required to express the biological processes of growth, consumption, death, and maintenance in mathematical terms have been inappropriately defined and/or are lacking in these studies, which, for the most part, have focused on stirred tank applications. Although biological kinetics were never found to be rate-limiting in this particular pyrite system, the specifics of each heap leaching operation (mineral, indigenous microorganisms, geographic location, etc.) support further research into biological dynamics. Any future, serious attempt at modeling sulfide biooxidation in heaps calls for a dialogue between chemists, engineers, microbiologists, and mathematicians. The parties must recognize the complexities of biological processes (e.g. rapid transition from exponential to stationary phase in packed bed reactors) based on the existing literature, propose a general approach to model the most important phenomena, such as the one employed in this work, and then devise creative experiments to measure the necessary parameters. These experiments may have to be repeated for each heap leaching application, just like any other experiment performed as part of a standard laboratory, pilot, or demonstration testing program.
Appendix A

Literature Survey
When Bacteria Are Gasping for Air!

University of Idaho, ID

The research team led by Dr. Robert Bartlett at the College of Mines and Earth Resources, University of Idaho, is well known for its models of oxygen diffusion in heap leaching. In the absence of natural or forced air ventilation, oxygen diffusion from the upper, horizontal surface of the heap through the air–filled interparticle void spaces is likely the rate-limiting process\(^1\). Bartlett and Prisbrey have also considered a mixed kinetic/diffusion model whereby the oxidation of disseminated coarse sulfide grains occurs in series with oxygen diffusion\(^2\). Depending on the rates of oxidation and diffusion, on the coarseness of the agglomerates and on the accessibility and size of the sulfide grains, a more-or-less narrow reaction front separates a fully oxidized upper layer from a non-oxidized lower bed; the heap leaches zone-wise. According to the model simulations, the penetration zone reaches about 2 to 4 m after 3 years in a heap comprised of an air void space of 10–30 vol\% and a pyrite grade of 0.5–2.0 wt\%. The depth is reduced by 30 to 50\% when the net gas bulk flow resulting from the simultaneous oxygen consumption and water evaporation is considered\(^3\). In light of these simulations, the authors have determined the optimum duration to maximize profitability on the basis of the gold price, capital amortization charge and interest rate\(^4\).

University of Nevada, Reno

While Bartlett and co-workers were modeling the diffusion process, Milayhov and Hendrix (Mackay School of Mines, University of Nevada, Reno) were testing the effects of solution recirculation and particle size in small, non-aerated columns of 8.9 cm in diameter and 90

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cm in height. The authors monitored the solution pH, potential, iron concentration, copper concentration, and bacterial numbers over a 32-day period. Recycling the solution affected marginally the gold recovery and the concentration profiles. Decreasing the particle size from 19.3 to 1.7 mm led to drastically different pH, potential and iron profiles. The relationship between particle size, potential and iron concentration was contrary to intuition. The authors did not explain why the column loaded with the smallest particles registered the lowest solution potentials (400 mV, reference electrode not specified), yet the largest iron concentrations. It does stand to reason that the greater the surface area exposed to the leaching solution, the larger the extent of oxidation. Pyrite oxidation is, however, more rapid at high solution potentials.

**U.S. Bureau of Mines**

Leaching 241 kg of an arsenic-bearing refractory gold ore (6.2 wt% As, 2.5 wt% sulfide sulfur) in a 6 m tall non-aerated column proved to be more challenging than anticipated, possibly because of the use of plain tap water as the leaching medium. Only 23% of the iron was oxidized after 300 days and no additional gold was recovered. Despite prior inoculation and agglomeration of the ore, as well as several changes to the irrigation cycle, the pH of the leaching solution remained neutral and the potential never exceeded 700 mV vs SHE. The core of the agglomerates remained dry while their surfaces were coated with precipitates.

**GENMIN Process Research, South Africa**

In addition to developing the commercial BIOX process, GENMIN has explored bacterial heap leaching for pretreating low-grade refractory sulfidic gold ores. Non-aerated columns of 31.5 cm in diameter by 2 m were filled with 250 kg of ore grading 4.2 g/t gold and irrigated continuously at a rate of 10 L/(m²h) for 180 days. Iron leaching stopped after 60 days, reaching a final extraction of 32%. No other parameter, not even the sulfide grade of the residue, was measured. Investigators have developed a pseudo-steady state mixed kinetics model, similar to the model of Braun et al., coupled with Monod kinetics for biological oxidation of ferrous ions. The near-perfect fit between the model predictions and the experimental results may in fact be fortuitous in light of the fact that the bacterial growth rate was clearly underestimated. This assumption leads to very

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small ferrous to ferric turnover rates, thus requiring very little oxygen to sustain the reaction. In fact, an oxygen diffusion limitation may account for the low iron extraction.

**Zlata Mine, Bulgaria**

During the last decade the Research and Training Centre of Mineral Biotechnology at the University of Mining and Geology in Sofia, Bulgaria has instigated a project to determine the technical and economic feasibility of bacterial pretreatment of gold-bearing ores. Groudev’s research team have designed and constructed a pilot-scale heap at the Zlata Mine in Western Bulgaria. First, the ore deposit was sampled to determine its amenability to bioleaching. Two hundred kg of ore (3.2 g Au/t, 0.8 wt% sulfide sulfur, 1.4 wt% iron) were crushed to less than 10 mm and loaded directly in a column of 24 cm in diameter and 1.8 m tall. The leaching solution, which contained a mixed culture of mesophile bacteria, nutrients and sulfuric acid, was recirculated at a rate of 37 L/(m² h), far in excess of the typical industrial practice of 5-15 L/(m² h). The authors recognized that, in the absence of natural or forced air convection, diffusion was the principal mode of gas transport. For this reason, they set up an external BACFOX reactor with intense aeration to regenerate ferric ions biologically and to reoxygenate the leaching solution before recirculation. As a result, the cell concentrations in solution (10⁶ cells/mL) and attached to the ore particles in the upper portion of the bed (10¹² cells/kg) were about one order of magnitude larger than any other cell concentration ever reported in the literature about column and heap leaching of sulfidic ores. This is one of the very rare instances where both suspended (planktonic) and attached bacteria have been enumerated.

Groudev and co-workers discovered that Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans prevailed over Acidithiobacillus thiooxidans, Acidithiobacillus acidophilus and other bacteria of the genus Acidiphilum. This diversity raises an interesting question as to whether some bacteria are found predominantly attached rather than suspended. If true, it might prove beneficial to add finely ground ore to the inoculum tank. The inoculum slurry could be used as agglomerating medium, or perhaps sprayed onto the agglomerates as they discharge from the conveyor belt.

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The average sulfide oxidation rate remained low at 5.7%/month, for a final oxidation of 68% after one year. Assuming that (1) particles were uniformly packed into the column, (2) gold particles were finely disseminated throughout the ore matrix, and (3) the column leached as a front (which the cell density appears to corroborate) as surmised by Bartlett and co-authors in their models of oxygen diffusion, then about 1.2 m of the column would have been leached after one year. Bartlett’s model predicts that, for this particular ore grading 1.5% pyrite, 11 months would be required to oxidize all sulfide minerals contained within a 1.2–m thick zone. Model and experimental results are thus in good agreement.

Gold extraction was the single most important parameter that would justify the next phase of the project. For this purpose, a unique gold leaching solution was concocted with 1 g/L protein hydrolysate, 15 g/L thiosulfate, 0.5 g/L copper and 0.5 g/L sulfate. The protein hydrolysate contained a myriad of gold-complexing amino acids. About 80% of the gold was leached from the biooxidized ore within 12 days under optimum conditions, while only about 15% was leached from the original ore. These encouraging results led to the construction of a pilot-scale heap stacked with 1,200 tonnes of the same ore material\(^\text{10}\). The shallow 2 m heap was inoculated with a mixed culture of iron- and sulfur-oxidizing bacteria. Forty–seven percent of the sulfide sulfur was oxidized after 6 months, while 68% of the gold was extracted, compared to 80% in column tests.

**Newmont Gold Company, CO**

More than a decade of dedicated effort on the part of Newmont Gold Company and Newmont Mining Corporation was invested in the development of the first commercial heap biooxidation process for low-grade refractory gold ores. The work began in the late 1980s with preliminary biooxidation tests to improve the gold extractability of Carlin–type siliceous sulfidic refractory gold ores\(^\text{11}\). A couple of years later Brierley and his colleagues proposed a biooxidation process for recovery of gold from heaps of low-grade sulfidic and carbonaceous gold ore materials, which culminated in 1993 in US patent 5,246,486, amended in 1998 to US patent 5,834,294\(^\text{12}\). The company also filed for a patent for an identical process to recover any metal value from sulfide ores.

In a nutshell, the technology consists of forming agglomerates by mixing ore particules, fines and clayey minerals with a bacterial inoculum, and optionally, with an acid-resistant polymer. Agglomerates are stacked in a heap and later moisten by continuously recirculating the leaching solution until the gold is liberated from the sulfide matrix. Gold

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is finally recovered with cyanide, thiourea, or thiosulfate solution. Newmont claimed that, in addition to agglomerating fines onto coarser particles, the single agglomeration/inoculation operation ensures a more uniform colonization of the ore surface by active bacteria, shortens the lag phase and speeds up the oxidation.

Operations were scaled up from 430 to 25,900 tonnes heaps stacked with inoculated agglomerates whose original particle size was typically less than 19 mm\textsuperscript{13,14}. The sulfide sulfur and gold content ranged from 0.4–2.0 wt% and 1.62–11 g Au/t, respectively. The leaching solution was pumped continuously at a rate of 10–12 L/(m\textsuperscript{2} h) and recirculated without prior intermediate iron control treatment. No air was blown at the base of the heaps. Potentials as high as 770 mV vs Ag/AgCl were measured in the leaching solution. Tests lasted anywhere between 65 and 190 days, after which time the samples collected were assayed for sulfide and gold. The extent of oxidation, which ranged between 35 to 70%, could not be correlated with the test duration. Approximately 50–60% of the gold was recovered from this initially almost completely refractory gold ore with either thiosulfate or cyanide solution.

The initial concentration of bacteria attached to the agglomerates was found to be about $6 \times 10^8$ cells/kg, and later increased by two orders of magnitude. Simple calculations clearly point out that irrigating the heap continuously with an inoculum, as may have occurred in this situation given that the leaching solution was recirculated continuously, could never have introduced enough bacteria to achieve the $10^{10}$ cells/kg levels measured only 65 to 190 days later. Therefore, introducing bacteria by whatever means, may that be inoculation during agglomeration or by irrigation, is only the first, minor step in bacterial colonization. On the other hand, bacterial attachment, followed successively by onset of oxidation, bacterial detachment and finally transport to lower depths, are key phenomena.

These test trials culminated in the construction of a demonstration facility in September 1994\textsuperscript{15}. The 457-m x 152-m heap built at Newmont Gold Company’s Quarry mine in Carlin, NV was designed to process 800,000 tonnes per annum of low-grade refractory gold-bearing ore. Forty percent of the ore was siliceous sulfidic refractory gold ore grading 1.71 g Au/t and 1.5 wt% sulfide sulfur; the rest was carbonaceous sulfidic refractory gold ore grading 3.42 g Au/t and 3.5% sulfide sulfur. The goal was to oxidize 50% of the sulfide sulfur before the end of the first year.

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An inoculum solution containing iron- and sulfur-oxidizing bacteria was produced in six 200,000 L tanks. Agglomeration of crushed ore particles (< 19 mm in size) and fines took place on a conveyor belt by spraying the inoculum to yield a moisture content of 4 to 12%. Agglomerates were then stacked separately to a height of 8.5–10.7 m onto five biooxidation pads, each utilizing a different liner base, conveyor transfer and stacking systems. No aeration system was in place.

Testwork began in January 1995. The leaching solution, which had an initial pH of 1.2–1.9, was recirculated continuously to the top of the heaps. Surprisingly the pH increased to 2.2–2.7 during the 160 to 240 days of operation. Thermocouples recorded average internal temperatures of 49 to 52°C, with hotspots from 60 to 75°C. No significant trend in the number of mesophile microorganisms was noted between the five depths at which agglomerate samples were collected\(^\text{16}\). Levels of bacteria in samples collected at the same depth varied by as much as five orders of magnitude. The number of moderate thermophile bacteria remained extremely low (< $1 \times 10^6$ bacteria/kg ore), if not undetectable. Potentials increased from 430 to 570–685 mV vs Ag/AgCl. Nevertheless, the heap did not perform as well as anticipated, with 35% of the sulfide minerals oxidized from siliceous ores after 180 to 240 days, and 28% from the carbonaceous ores after 160 days.

The pads were washed and dismantled. The biooxidized ore was neutralized with lime, re-agglomerated and stacked for its final leach with cyanide or thiosulfate. By mid 1996, the plant had produced 16,000 oz of gold, 40% of which was recovered by cyanidation of siliceous ores at a cost of US$4.00/t\(^{17}\). The remaining 60% was leached from carbonaceous ores with ammonium thiosulfate at a cost of US$5.00/t. Gold recoveries of 60 to 70% allowed Newmont Gold Company to boost reserves by 37 million grams of gold.

**Following the Installation of Air Blowers**

University of Idaho, ID

Harrington and co-workers ascribed the slowness of the biooxidation process to the intrinsic kinetics of coarse pyrite grains (100 μm) disseminated into a gangue matrix\(^\text{18}\).

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Using the pyrite leaching model derived a couple of years before by Zheng et al.\textsuperscript{19} in conjunction with a measured sulfide grain size distribution, the authors found good agreement between the four experimental gold extraction data points and the model predictions. The gold extractability of the entire ore mass was indeed predicted by the extent of oxidation of the individual sulfide grains undergoing leaching in a 1.2-m tall column intermittently aerated.

There may have been only four experimental points, but at least all four were truly representative. These authors quickly recognized the inherent flaw in using concentration–time profiles of soluble species (e.g. total iron, sulfate) to monitor the extent of oxidation of iron–containing sulfide minerals (pyrite, arsenopyrite) containing no other soluble leach indicator (e.g. Zn, Cu). Some of the problems include the mass of iron and sulfate unaccounted for in the stagnant solution held up in the column, as well as the precipitation of jarosite. Thus measuring the iron and sulfate concentration clearly underestimates the overall extent of oxidation. It is not surprising then that several concentration–time profiles reported therein leveled off in the later stages of the leach. Analyzing the sulfide grade of one or more solid samples collected at different locations within a heap or column is another alternative, but it is difficult to ensure that the samples collected will be representative of each agglomerate in the neighborhood of the sampling port. These authors opted instead to run several replicates of the same column under the exact same conditions. One of the columns was taken down at a predetermined time, and the biooxidized ore was dried, coned, quartered and finally assayed for elements and the sulfur suite.

In light of the different grain distributions of the two ores tested, Harrington and co-workers went on to develop two particle–scale shrinking–core leaching models (parabolic leaching and mixed kinetics), whereby diffusion of ferric ions in the leached outer rim through the pores of particles was at least one of the rate–limiting steps\textsuperscript{20}. Effective diffusivity, rock porosity and particle size were essential pieces of information. In their opinion, such models would better predict the oxidation of fine sulfide grains.

**Tenneco Minerals Company**

In the late 1980s, Tenneco Minerals Company considered heap biooxidizing a refractory pyritic carbonaceous gold ore grading 64 g Au/t and containing 2.9 wt% sulfide sulfur. Following six biooxidation tests in small reactors, two columns, each containing 8.5 kg of ore particles smaller than 12.7 mm, were set up to study the effect of the liquid flow rate


at 0.46 and 14.6 L/(m²·h)²¹. As expected, the iron concentration in the leaching solution pumped at the faster rate was approximately 4 to 5 times smaller, whereas the average iron extraction rate (11.7%/month) was about 1.5 times larger. What is most interesting was the linear iron extraction profile at extremely small flow rates, compared to the exponential rise, followed by a plateau, at larger flows. Both columns were aerated, hence this factor alone could not explain the larger iron extraction at higher flow. The total dissolved iron concentration and its possible effects on cell inhibition and precipitate formation may have played a role. Yet, both tests were deemed successful as a result of an additional gold recovery from 39 to only 46% after cyanidation.

Rhodes Mining NL, Australia

In 1993, Rhodes Mining NL of Perth, Australia acquired 100% ownership of the Lahoca gold deposit situated on the slopes of the Matra Mountains in northern Hungary. The reserves were estimated at 1.54 million oz of gold. The company opted for heap leaching the pyritic refractory deposit containing 2–2.5 g Au/t and 6.1 wt% sulfide sulfur. It mandated the Colorado Minerals Research Institute (CMRI) to evaluate the effects of ultrafine ore crushing, agglomeration, heap design, forced aeration and irrigation. The CMRI conducted the most comprehensive testwork to date with time-profiles of iron concentration, sulfide oxidation, pH, solution potential and dissolved oxygen²². The scale of the tests was relatively small with only 32 kg of agglomerated ore loaded in columns of 20 cm in diameter by 76 cm in height. Analogous to the procedure of the U.S. Bureau of Mines, the ore was crushed to less than 3.3 mm in size and agglomerated in a drum with sulfuric acid and inoculum. Immediately after agglomeration there were about 4·10⁹ bacteria per kg of ores, a cell concentration predictable in light of the concentration of bacteria in the inoculum (typically ~10⁸ cells/mL) and of the average moisture content of the agglomerates (3–10 wt%). No cell count was performed afterwards.

The highlight of this investigation was the influence of the irrigation mode on sulfide oxidation and gold recovery. Whether a fresh or recirculated leaching solution was pumped, the final sulfide oxidation (28–29% after 160 days) was the same. It affected obviously the total dissolved iron concentration, although not necessarily the iron leaching rate. The CMRI also examined the effect of a 30-day on/off cycle with fresh leaching solution. In this case again only 33% of the sulfide sulfur was oxidized after 160 days despite the relatively large air blowing rate (2.78 m³/(m²·h) STP). Although 33% oxidation in 160 days seems modest, let us not forget that the initial sulfide grade of the head sample was approximately three times larger than average.

Solid residues were collected, washed with an alkaline solution and submitted to a 5-day bottle-roll cyanidation test. Approximately 54 to 59% of the gold was recovered from the biooxidized residues, compared to 27% from the non-biooxidized ore. Gold recovery was directly proportional to the sulfide oxidation. Based on the column leaching results and on a preliminary economic analysis, Rhodes Mining NL was planning in 1997 to construct a pilot-scale heap with intermittent irrigation and forced ventilation at the Lahoca site.

Brohm Mining’s Gilt Edge Mine, SD

Faced with declining oxide reserves and 41 million tonnes of sulfide reserves containing an estimated 1.8 million oz of gold, Brohm Mining’s Gilt Edge Mine in Deadwood, South Dakota constructed a 7-m pilot heap comprised of two geotextile layers, 1-mm HDPE liner, 30 cm of crushed river rock, a network of 100 mm perforated PVC pipe, and 4,300 tonnes of inoculated agglomerates\textsuperscript{23}. The pipe was laid on top of the rock to facilitate air flow. The ore (4.91 wt% sulfide sulfur, 1.58 g Au/t) was crushed to less than 9 mm and fed, together with acidic well water and 50–100 g/t of Nalco 7534 polymeric binder, into an agglomeration drum to yield a final moisture content of 7.9%. The agglomerates were sprayed with an inoculum and immediately stacked on the pad. The heap was irrigated with an inoculated, acidic (pH 1.5–2.0), nutrient–rich solution at a rate of 2.4 to 9.6 L/(m\textsuperscript{2} h). Half of the leaching solution collected was neutralized with lime or limestone to pH 5.5–6.0, and then mixed with the second half and, if necessary, with fresh water. Due to the inefficiency of the neutralization treatment and severe winter conditions, changes were made to the mode of recirculation. At the termination of the test 11 months later, merely 21% of the sulfide sulfur had been oxidized, which resulted in an additional extraction of only 16% for a final gold recovery of 72%. The mine released a preliminary economic analysis in 1996 of the capital and operating costs for a heap biooxidizing 2.3 million tonnes of ore per annum. We are unaware of later pilot or commercial developments.

Newmont Gold Company, CO

While the non-aerated demonstration-scale heap was in progress, Brierley and Luinstra were evaluating the benefits of aeration. All tests were carried out in columns of 20.3 cm in diameter by 1.2 m in height, and packed with 45 kg of non-agglomerated but inoculated ore particles\textsuperscript{24}. The ore averaged 1.23 wt% sulfide sulfur and 25.9 g Au/t. The recirculated solution and air flowrates were adjusted to 12 and 920 L/(m\textsuperscript{2} h), respectively. The authors examined the effects of maximum particle size (6.4, 12.7 and 25.4 mm). Iron was leached at the same rate of 0.17 g/(L-day) for the first 60 days, after which time


it tapered off. As expected, the total iron concentration and the final sulfide oxidation both increased with decreasing particle size. The columns were rinsed and dismantled 98 days after start-up. The pH of the leached moist ore was increased and the ore subsequently agglomerated before the final cyanide leach. Surprisingly, more gold was extracted from the largest particles (62% gold extraction from 25.4 mm particles vs 54% for 12.7 mm vs 50% for 6.4 mm vs 18% from non-biooxidized ore). We can only speculate that the gold mineralization preferentially located along crystallographic orientation, pits and cracks might have played a key role, explaining the lack of correlation between the sulfide oxidation and the gold recovery. Another explanation could be the build-up of jarosite on the surfaces of the ore particles, which is prone to occur even in moderately dilute iron and sulfate solutions, and its effect on cyanide leaching.

A comparison of the performance of the smallest, non-aerated heaps (450–25,900 tonnes) vs the small aerated columns indicates, surprisingly, somewhat better sulfide oxidation rates in the absence of aeration (3.9–32%/month in heaps vs 11–16%/month in columns, given similar initial sulfide grade). The largest non-aerated heap (800,000 tonnes) recorded, however, the smallest oxidation rate of 5.1%/month. These observations suggest that, even though the smaller heaps were operated under natural convection, the supply of oxygen to the bacteria from the top and the sides might have been large enough to produce the required ferrous ions to meet the minuscule demand for pyrite oxidation.

Be that as it may, Newmont built a large-scale aerated heap in 1996, followed, in 1999, by the construction of an $8-million bioleaching/biomilling facility handling 4.2 million tonnes annually. The process is identical in all respects to Newmont's patented biooxidation technology, except that agglomerates spend only 100–150 days on the leach pad before being neutralized, ground and leached for gold. The company claims that this process requires less capital and yields higher recoveries.

The ore grading 1.8–2.0 wt% sulfide sulfur was crushed to less than 12.5 mm, agglomerated with mesophile and moderate thermophile bacteria, and placed onto three aerated pads, each 145 m wide, 308 m long and 9 m high. Zones located 1.5 m above the ground saw their temperature increase from 16 to 49°C one month after start-up. This persuaded the operators to reinoculate the pads with extreme thermophilic bacteria. Temperatures fluctuated between 32 and 60°C thereafter. On the other hand, the potential of the feed and leachate solutions remained constant at only about 470 mV vs Ag/AgCl. The project, which went into production in early 2000, had produced 66,000 oz of gold by year-end. The company anticipates generating US$40 million in free cash flow between 2000 and 2003 at a gold price of US$250.

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Echo Bay Mines

Like so many other gold producers, Echo Bay Mines has encountered deposits of refractory ores yielding lower recoveries. The company developed and patented in collaboration with Biomin Technologies S.A. (now Gold Fields Limited) the "Integrated Tank/Heap Biooxidation Process"\textsuperscript{27}, a process very similar to the one patented by Placer Dome Inc.\textsuperscript{28} and alleging rapid bacterial attachment, adaptation and multiplication. First a concentrate is produced by flotation or gravity concentration and then split into two separate fractions. The first is biooxidized in a BIOX\textsuperscript{®} reactor to build up a highly active inoculum. The second fraction bypasses the bioreactor and is mixed with the inoculum produced and the biooxidized concentrate. The slurry is dewatered and fed by auger to a rotary drum where it is agglomerated with a polymeric binder. It was later found that the addition of gravel during agglomeration reduced the breakdown of agglomerates. Agglomerates are then stacked onto a pad to a maximum height of 1.2 m. Wobblers distribute the leaching solution (unspecified composition) while air is blown through perforated PVC pipe buried underneath. The biooxidized agglomerates are slurried with lime at 40 to 60°C and leached in cyanide solution to extract the gold.

Agglomerate breakdown was rightfully thought to be the cause for the poor performance of the first ten 210-day trials (oxidation rate < 7.2%/month). Addition of gravel to the concentrate during agglomeration doubled the oxidation rate, but left the gold extraction unaffected (20%). These trials culminated in November 1998 in a final pilot plant test using a pyrite concentrate that had previously been leached with cyanide. Astoundingly, the oxidation rate was constant throughout the 90 days at 19.2%/month, a six-fold improvement from the first runs. Based on these promising results and on the economic prospects, the mine was going ahead with the installation of a 750 stpd plant\textsuperscript{29}.

Geobiotics Inc., CA

In its attempt to improve the performance of heaps, Geobiotics Inc. first proposed to separate fines/clayey minerals from coarse ore fragments, and to treat each fraction separately (roasting or tank leaching of fines, heap leaching of coarse particles), or simultaneously in heaps\textsuperscript{30}. The company is now well known for its GEOCOAT\textsuperscript{®} technology, which consists of spraying a slurried concentrate onto a support rock (waste or low-grade sulfide material 6 to 20 mm in size) as it discharges onto an aerated heap. Depending on the ore and support rock type, as well as the coating-to-support ratio, the 0.5-1.0 mm

thick gold/pyrite concentrate layer is typically biooxidized to from 47 to 97% in less than 90 days\textsuperscript{31}.

Following a two–year testing program, Geobiotics Inc. and Ashanti Goldfields Company Ltd. conducted a demonstration test heap in 1998 at Obuasi Operations in Ghana, West Africa. One hundred and twenty fives tonnes of sulfidic/carbonaceous concentrate were sprayed onto support rocks 6– 25 mm in size, and placed onto a 17.7–m by 19.8–m pad to a height of 3.8 m\textsuperscript{32,33}. The heap was inoculated with mesophiles after destroying the carbonates by acidification. Solid samples collected over the 88–day trial at different locations and depths within the heap have revealed a monotonic increase in gold recovery over time from 51 to 91% and no significant difference in gold recovery with depth. Ninety–one percent of the sulfide was oxidized in 88 days, giving rise to high internal temperatures, which would likely have exceeded 46°C if they had not been controlled by manipulating the solution application and aeration rates.

The experimental program laid out by Geobiotics Inc. for the Tres Amigos Mines, owned by Minera Finisterre S.A. de C.V., focused primarily on gold extractability\textsuperscript{34}. A successful series of small and large column experiments motivated a demonstration test in May 1997. Twenty-four tonnes of slurried concentrate, sprayed onto 250 tonnes of support rock (9.5–19 mm) were stacked onto a 10.2–m by 14.5–m pad to a height of 2.9 m. Temperatures measured at several depths within the heap were very sensitive to changes in irrigation cycles and aeration flow rates. The highest temperatures (45°C) were recorded about 1 m below the surface. Despite the temperature profile, the residue assays revealed that the heap leached uniformly with depth. After 30 days, 24.2% of the sulfide had been oxidized, which increased to 42.3% after 60 days. This additional 30-day biooxidation time had little effect on the overall gold extractability, which had already reached 93%. The benefits of reduced cyanide consumption with increasing biooxidation time would have to be weighed against the cost of cyanide consumption and destruction.

\textbf{Cambior Inc.}

Curiously enough, despite the crucial role that temperature plays in accelerating the leaching of pyrite in biological stirred-tank reactors and autoclaves, very little data from only two high-temperature column studies has been published. The results from


isothermal column tests carried out by Newmont researchers at 5, 10, and 20–24°C were predictable and of limited interest, unless, of course, the company were to build pads in colder climates or at higher altitudes. An interesting testwork project was conducted in the mid 1990s by Cambior Inc. in collaboration with Little Bear Laboratories Inc. to determine the feasibility of heap biooxidizing intrusive and sedimentary refractory pyritic ore (2.6–8.9 wt% sulfide sulfur) originating from the Metates gold and silver deposit in northwestern Durango State, Mexico. Part of the comprehensive program consisted of leaching ore particles of a certain size (either smaller than 6.3 or 19 mm) at constant temperature (either ambient, 50°C or 65°C) with recirculated or partially-bled solutions. Five to six kg of ore were agglomerated with an inoculum comprised of either mesophiles, moderate thermophiles, extreme thermophiles, or all three populations, and loaded into glass columns 10 cm in diameter and 61 cm in height.

The authors reported that sulfide oxidation rates were significantly larger in the high-temperature tests compared to tests carried out at ambient temperature. Unfortunately, the testwork program did not appear to include two columns run under identical conditions, except for their different temperature of 50 and 65°C. Therefore, no conclusion can be drawn about the effect of increasing the temperature from the moderate to the extreme thermophilic range. By the end of the testwork, the extent of oxidation, as determined from the sulfide grade in the residue, varied between 13 and 37%, with large variations observed even among replicate tests. Another report mentioned that up to 50% oxidation was achieved after 210 to 230 days, leading to improved recovery of gold (60–75%) and silver (40–70%).

However, the redox potential transition occurred about 30 to 60 days after start-up, during which time the potential increased slightly from 600 to at most 730 mV vs SHE. The abundance of bacteria during the initial period, as well as the already large extent of oxidation (about 13-24%) by day 60, suggests that the low redox potentials measured initially are intimately linked to the very rapid consumption of ferric ions, and conversely to the production of ferrous ions, in the chemical oxidation of pyrite. Rather than the heat being applied uniformly over the entire surface of the column, some columns had heating tapes wrapped around the middle 1/3 only. Operation and performance were, for the most part, comparable, except for the fact that an unusual precipitate (gypsum) was abundant in the heated region one day after start-up. Cooling temporarily restored solution flow, yet the columns eventually had to be dismantled. No reason was put forward to elucidate the provenance of the calcium on the basis of the ore mineralogy and/or solution composition.


Appendix A – Literature Survey
Based on the successful comprehensive testwork program, Cambior Inc. compared the capital and operating costs of eight biooxidation processes, and concluded that heap biooxidation, followed by heap cyanidation and precious metal recovery by the Merrill-Crowe process, was the most attractive of all. Although the capital expenses associated with the heap biooxidation module accounted for as much as 56% of the total capital expenditure (US$94.7 million), its operating costs (17.6% or US$0.63/tonne) pale in comparison to cyanidation processing costs (64.9% or US$2.32/tonne).
### B.1 Column A

#### Table B.1 Solid mass balance – column A.

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#### Table B.2 Iron mass balance – column A.

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<td>Samples (g)</td>
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#### Table B.3 Sulfur mass balance – column A (duplicate 1).

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### Table B.4  Sulfur mass balance – column A (duplicate 2).

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<td>Difference (%)</td>
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![Figure B.1](image)

**Figure B.1** pH profile – column A (duplicate 1).
Figure B.2  pH profile – column A (duplicate 2).

Figure B.3  Solution potential profile – column A (duplicate 1).

Appendix B - Isothermal Column Leaching Results
Figure B.4  Solution potential profile – column A (duplicate 2).

Figure B.5  Ion concentration profile – column A (duplicate 1).
Figure B.6  Ion concentration profile – column A (duplicate 2).

Figure B.7  Cell number profile – column A (duplicate 1).

Appendix B – Isothermal Column Leaching Results
Figure B.8 Cell number profile – column A (duplicate 2).

Figure B.9 Attached cell number/depth profile – column A.
Figure B.10  Sulfur speciation depth profile – column A (duplicate 1 – 349 d).

Figure B.11  Sulfur speciation depth profile – column A (duplicate 2 – 222 d).

Appendix B – Isothermal Column Leaching Results
Figure B.12 Iron and arsenic depth profile – column A (duplicate 1 – 349 d).

Figure B.13 Iron and arsenic depth profile – column A (duplicate 2 – 222 d).

Appendix B – Isothermal Column Leaching Results
### B.2 Column B

**Table B.5** Solid mass balance – column B.

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<td>Difference (%)</td>
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**Table B.6** Iron mass balance – column B.

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<td>Solution (g)</td>
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**Table B.7** Sulfur mass balance – column B.

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*Appendix B – Isothermal Column Leaching Results*
Appendix B – Isothermal Column Leaching Results

Figure B.14  pH profile – column B.

Figure B.15  Solution potential profile – column B.
Figure B.16 Ion concentration profile – column B.

Figure B.17 Cell number profile – column B.

Appendix B – Isothermal Column Leaching Results
Figure B.18  Attached cell number/depth profile – column B.

Figure B.19  Sulfur speciation depth profile – column B.

Appendix B – Isothermal Column Leaching Results
Figure B.20  Iron and arsenic depth profile – column B.
Table B.8  
Solid mass balance - column C.

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Table B.9  
Iron mass balance - column C.

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Table B.10  
Sulfur mass balance - column C.

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<td>Difference (g sulfur)</td>
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<td>63.5</td>
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Appendix B - Isothermal Column Leaching Results

315
Appendix B - Isothermal Column Leaching Results

Figure B.21  pH profile – column C.

Figure B.22  Solution potential profile – column C.
Figure B.23 Ion concentration profile – column C.

Figure B.24 Cell number profile – column C.

Appendix B – Isothermal Column Leaching Results
Figure B.25  Attached cell depth profile – column C.

Figure B.26  Sulfur speciation depth-profile – column C.

Appendix B – Isothermal Column Leaching Results
Figure B.27  Iron and arsenic depth-profile – column C.
## B.4 Column D

### Table B.11 Solid mass balance – column D.

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<td>139.5</td>
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<td>Sample (kg)</td>
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<td>Total (kg)</td>
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<td>138.6</td>
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<tr>
<td>Difference (kg)</td>
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### Table B.12 Iron mass balance – column D.

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<td>Samples (g)</td>
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### Table B.13 Sulfur mass balance – column D.

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<td>Ore (g sulfur)</td>
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<td>Solution (g sulfur)</td>
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<td>Total (g sulfur)</td>
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<tr>
<td>Difference (g sulfur)</td>
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<tr>
<td>Difference (%)</td>
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Appendix B – Isothermal Column Leaching Results
Figure B.28  pH profile – column D.

Figure B.29  Solution potential profile – column D.
Figure B.30 Ion concentration profile – column D.

Figure B.31 Cell number profile – column D.

Appendix B – Isothermal Column Leaching Results
Figure B.32 Attached cell number/depth profile – column D.

Figure B.33 Sulfur speciation depth profile – column D.
Figure B.34  Iron and arsenic depth profile – column D.
B.5 Column E

Table B.14 Solid mass balance - column E.

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Table B.15 Iron mass balance - column E.

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Table B.16 Sulfur mass balance - column E.

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<td>Ore (g sulfur)</td>
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<tr>
<td>Solution (g sulfur)</td>
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<td>Samples (g sulfur)</td>
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<tr>
<td>Total (g sulfur)</td>
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Appendix B – Isothermal Column Leaching Results
Figure B.35  pH profile – column E.

Figure B.36  Solution potential profile – column E.
Figure B.37 Ion concentration profile – column E.

Figure B.38 Cell number profile – column E.

Appendix B - Isothermal Column Leaching Results
Figure B.39  Attached cell number/depth profile – column E.

Figure B.40  Sulfur speciation depth profile – column E.

Appendix B - Isothermal Column Leaching Results
Figure B.41  Iron and arsenic depth profile – column E.
Table B.17  Solid mass balance – column F.

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<td>Sample (kg)</td>
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<td>4.8</td>
</tr>
<tr>
<td>Total (kg)</td>
<td>179.9</td>
<td>176.3</td>
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Table B.18  Iron mass balance – column F.

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<td>Solution (g)</td>
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<td>Difference (g)</td>
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Table B.19  Sulfur mass balance – column F.

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<td>Sulfide</td>
<td>Sulfate</td>
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<td>Ore (g sulfur)</td>
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<td>Solution (g sulfur)</td>
<td>416.0</td>
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<td>Samples (g sulfur)</td>
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<td>0.0</td>
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**Figure B.42** pH profile – column F.

**Figure B.43** Solution potential profile – column F.

*Appendix B – Isothermal Column Leaching Results*
Figure B.44  Ion concentration profile - column F.

Figure B.45  Cell number profile - column F.

Appendix B - Isothermal Column Leaching Results
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

1E+07 1E+08 1E+09 1E+10

Cell number (cells/g dry ore)

Figure B.46 Attached cell number/depth profile – column F.

Figure B.47 Sulfur speciation depth profile – column F.

Appendix B – Isothermal Column Leaching Results
Figure B.48  Iron and arsenic depth profile – column F.

Appendix B – Isothermal Column Leaching Results
B.7 Column G

Table B.17 Solid mass balance - column G.

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<td>Sample (kg)</td>
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</tr>
<tr>
<td>Total (kg)</td>
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Table B.18 Iron mass balance - column G.

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<td>Solution (g)</td>
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<td>3946.7</td>
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Table B.19 Sulfur mass balance - column G.

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<tbody>
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<td>Solution (g sulfur)</td>
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<td>Samples (g sulfur)</td>
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<td>Total (g sulfur)</td>
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<td>Difference (g sulfur)</td>
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<td>-121.8</td>
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<td>Difference (%)</td>
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Appendix B - Isothermal Column Leaching Results
Figure B.49  pH profile – column G.

Figure B.50  Solution potential profile – column G.

Appendix B – Isothermal Column Leaching Results
Figure B.51  Ion concentration profile – column G.

Figure B.52  Cell number profile – column G.

Appendix B – Isothermal Column Leaching Results
Figure B.53  Attached cell number/depth profile – column G.

Figure B.54  Sulfur speciation depth profile – column G.
Figure B.55 Iron and arsenic depth profile – column G.
## B.8 Column H

**Table B.20** Solid mass balance – column H.

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<tr>
<td>Total (kg)</td>
<td>121.8</td>
<td>116.5</td>
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<tr>
<td>Difference (kg)</td>
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<td>-5.3</td>
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**Table B.21** Iron mass balance – column H.

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<td>Solution (g)</td>
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<tr>
<td>Total (g)</td>
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<td>Difference (g)</td>
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**Table B.22** Sulfur mass balance – column H.

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<td>Solution (g sulfur)</td>
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<td>Samples (g sulfur)</td>
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<tr>
<td>Total (g sulfur)</td>
<td>4367.7</td>
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<td>Difference (g sulfur)</td>
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*Appendix B – Isothermal Column Leaching Results*
Figure B.56  pH profile - column H.

Figure B.57  Solution potential profile - column H.

Appendix B - Isothermal Column Leaching Results
Figure B.58  Ion concentration profile – column H.

Figure B.59  Cell number profile – column H.
Figure B.60  Sulfur speciation depth profile – column H.

Figure B.61  Iron and arsenic depth profile – column H.

Appendix B - Isothermal Column Leaching Results
### B.9 Column I

#### Table B.23 Solid mass balance – column I.

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<td>In (kg)</td>
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<td>4.1</td>
<td>4.2</td>
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<td>Out (kg)</td>
<td>4.1</td>
<td>4.0</td>
<td>3.9</td>
<td>4.1</td>
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<tr>
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<td>-0.2</td>
<td>-0.2</td>
<td>-0.1</td>
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<tr>
<td>Difference (%)</td>
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#### Table B.24 Iron mass balance – column I.

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<tr>
<td>In (g)</td>
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<td>Out (g)</td>
<td>182.3</td>
<td>623.6</td>
<td>331.8</td>
<td>244.9</td>
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<tr>
<td>Difference (g)</td>
<td>7.0</td>
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#### Table B.25 Sulfur mass balance – column I.

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<td>66.4</td>
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<td>588.4</td>
<td>680.6</td>
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<tr>
<td>Ore (g) Sulfate</td>
<td>7.6</td>
<td>6.1</td>
<td>7.6</td>
<td>7.1</td>
</tr>
<tr>
<td>Elemental</td>
<td>0.6</td>
<td>3.3</td>
<td>0.6</td>
<td>7.1</td>
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<tr>
<td>Sulfide</td>
<td>97.1</td>
<td>78.4</td>
<td>97.4</td>
<td>17.8</td>
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<td>Total (g sulfur)</td>
<td>171.7</td>
<td>179.9</td>
<td>694.0</td>
<td>712.7</td>
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<tr>
<td>Difference (g sulfur)</td>
<td>8.2</td>
<td>18.7</td>
<td>12.0</td>
<td>7.1</td>
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<td>Difference (%)</td>
<td>4.8</td>
<td>2.7</td>
<td>3.5</td>
<td>2.9</td>
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Figure B.62 pH profile - column I.

Figure B.63 Solution potential profile - column I.
Figure B.64  Ion concentration profile – column I.

Figure B.65  Cell number profile – column I.
Figure B.66 Iron extraction profile – column I.
### Appendix B - Isothermal Column Leaching Results

#### B.10 Column J

Table B.26  Solid mass balance – column J.

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<tbody>
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<td>4.5</td>
<td>4.4</td>
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<tr>
<td>Out (kg)</td>
<td>4.4</td>
<td>4.3</td>
<td>4.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Difference (kg)</td>
<td>-0.1</td>
<td>-0.2</td>
<td>-0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>Difference (%)</td>
<td>-2.2</td>
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Table B.27  Iron mass balance – column J.

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</thead>
<tbody>
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<td>515.6</td>
<td>233.6</td>
</tr>
<tr>
<td></td>
<td>Out</td>
<td>125.5</td>
<td>550.9</td>
<td>296.1</td>
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<tr>
<td>Ore (g)</td>
<td>In</td>
<td>125.2</td>
<td>124.6</td>
<td>124.7</td>
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<td></td>
<td>Out</td>
<td>74.7</td>
<td>56.5</td>
<td>55.4</td>
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<tr>
<td>Total (g)</td>
<td>In</td>
<td>207.9</td>
<td>640.2</td>
<td>358.3</td>
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<td>Out</td>
<td>200.1</td>
<td>607.4</td>
<td>351.5</td>
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<tr>
<td>Difference (g)</td>
<td>-7.7</td>
<td>-32.7</td>
<td>-6.8</td>
<td>-3.3</td>
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<tr>
<td>Difference (%)</td>
<td>-3.7</td>
<td>-5.1</td>
<td>-1.9</td>
<td>-1.4</td>
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</table>

Table B.28  Sulfur mass balance – column J.

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<th>3</th>
<th>4</th>
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</thead>
<tbody>
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<td>Solution (g)</td>
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<td>In</td>
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<td>131.2</td>
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<td></td>
<td>Sulfate</td>
<td>Out</td>
<td>8.3</td>
<td>7.9</td>
</tr>
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<td>Ore (g)</td>
<td>Elemental</td>
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<td>0.6</td>
<td>0.6</td>
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<tr>
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<td>Sulfide</td>
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<td>57.7</td>
<td>105.1</td>
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<td>Total (g sulfur)</td>
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<td>204.0</td>
<td>667.2</td>
<td>688.9</td>
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<td>2.0</td>
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</table>
Figure B.67  pH profile – column J.

Figure B.68  Solution potential profile – column J.

Appendix B – Isothermal Column Leaching Results
Figure B.69  Ion concentration profile – column J.

Figure B.70  Cell number profile – column J.

Appendix B – Isothermal Column Leaching Results
Figure B.71  Iron extraction profile – column J.