THE BIOLEACHING OF COPPER SULFIDE ORES IN SALINE MEDIA: SHAKE FLASK STUDIES

by

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Abstract

The feasibility of bioleaching two Chilean copper ores under saline conditions was evaluated by batch tests. Total copper content of the ores were 3.87% and 1.64%, respectively. Lower ore mineralogy was comprised of atacamite, chrysocolla, bornite, chalcopyrite, chalcocite, and minor pyrite, while Zaldívar's included brochantite, chrysocolla, chalcocite, and pyrite. Mixed bacterial cultures dominated by *Thiobacillus ferrooxidans* were used in all test work.

As the effect of chloride ion on copper extraction was of primary concern, shake flask tests at various chloride levels were conducted. Sterile (no bacteria) tests were run under conditions identical to corresponding bioleach tests to provide information on abiotic leaching. All bioleach tests demonstrated, by attaining high E_h levels, that adaptation occurred at all chloride levels tested. On initial exposure to concentrations above baseline culture tolerance, inhibition occurred, manifesting as lengthier lag times, the severity increasing with the difference in chloride concentration between culture tolerance level and the level in the test medium. With repeated exposure to media containing identical chloride levels, lag times decreased, demonstrating further evidence of bacterial adaptation to chloride ion.

Successful adaptation by bacteria was reflected by high copper extractions at all chloride levels for the bioleach tests, averaging 91.9% (Lower (Cl) test series) and 94.5% (Zaldívar (Cl) test series). As expected, the corresponding sterile tests did not achieve the same level of extraction, averaging 43.6% (Lower (Cl)) and 82.0% (Zaldívar (Cl)). Clearly, the Zaldívar ore was much more reactive to abiotic leaching than the Lower ore. While chloride-enhanced cupric-ion leaching was a factor for both sets of sterile tests, other factors may also have enhanced abiotic Zaldívar ore leaching. These factors are believed to include (a) conspicuous differences in mineralogical content and distribution, (b) apparently more acid-soluble copper mineralization, and (c) chloride-enhanced galvanic leaching.

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List of Symbols and Abbreviations

Symbols

[Cu(res)]	Copper assay (wt%) in final leach residue	-----
[Cu(media)]	Copper concentration of bacterial nutrient medium	*(mol-L^{-1})*
[Cu(filt)]	Copper concentration of filtrate	*(mol-L^{-1})*
[Cu(inoc-I)]	Copper concentration of inoculum In	*(mol-L^{-1})*
[Cu(inoc-O]	Copper concentration of inoculum Out	*(mol-L^{-1})*
Cu_i	Copper concentration of ith leachate sample	*(mol-L^{-1})*
[Cu(preg)]	Copper concentration of pregnant solution	*(mol-L^{-1})*
[Cu(wash)]	Copper concentration of wash solution	*(mol-L^{-1})*
F	Faraday's constant (96485)	*(C mol^{-1})*
R	Gas constant (8.3144)	*(J-$mol^{-1}K^{-1}$)*
M(res)	Mass of final leach residue	*(g)*
M(sample)	Mass of ore sample to undergo leaching	*(g)*
E_h	Reduction-oxidation potential with respect to SHE	*(V)*
Cu(filt)	Soluble copper in filtrate	*(g)*
Cu(inoc-I)	Soluble copper in inoculum In	*(g)*
Cu(inoc-O)	Soluble copper in inoculum Out	*(g)*
Cu(samples)	Soluble copper in *n* leachate samples	*(g)*
Cu(wash)	Soluble copper in wash solution	*(g)*
T	System temperature	*(K)*
M	Unit for molar concentration	*(mol-L^{-1})*
V(NaCl)	Volume of 211 g NaCl/L solution	*(L)*
V(filt)	Volume of filtrate	*(L)*

V(inoc-I)	Volume of inoculum In	*(L)*
V(inoc-O)	Volume of inoculum Out	*(L)*
V_i	Volume of leachate sample	*(L)*
V(Th)	Volume (theoretical) of leachate	*(L)*
V(wash)	Volume of wash solution	*(L)*

Abbreviations

AAS	Atomic Absorption Spectrophotometry
DNA	Deoxyribonucleic Acid
QGP-$BaSO_4$	Quantitative Gravimetric Precipitation as $BaSO_4$
SCE	Standard Calomel Electrode
SHE	Standard Hydrogen Electrode

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At this point, I would like to take the opportunity to thank many of the special people who have assisted me in this undertaking.

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Chapter 1 Introduction

Throughout their long history, copper ore leaching processes were believed to be based solely on inorganic chemical reactions. This concept has been long-lived despite the fact that microorganisms, particularly metal-sulfide oxidizing bacteria, have been intimately involved with ore-degradation processes possibly since life originated on the Earth. Man has only recently become aware of their critical role not only in industrial, man-made leach dumps and heaps, but also in any natural situations where sulfide mineralizations are exposed to air and water. It is these bacteria which either directly or indirectly catalyze the leaching of the metal-bearing sulfide minerals. Today, copper ore bioleaching is of great significance, both economically and environmentally.

For many copper producers, large and small, this "rediscovered" technology has been their economic salvation. While the inexorable and inevitable decline in ore grades has resulted in many innovative advances in mineral processing and pyrometallurgically-based smelting technology, many ore bodies, age-old and newly-discovered, are still considered uneconomical for exploitation and development. Copper ore bioleaching processes, characterized by comparatively lower capital and operating costs, have often proven to be best poised to utilize such ore deposits. If designed properly, such processes obtain the assistance of ubiquitous bacteria which greatly facilitate copper mineral dissolution reactions.

Yet, these very reactions, recognized as beneficial by copper producers, can paradoxically be harmful to the environment. This is because the desired product, highly acidic aqueous solutions containing heavy metals, is practically identical in content with the undesirable by-product of acid-mine drainage or acid-rock drainage. Consequently, great care must be undertaken in designing and engineering copper ore bioleaching processes, not only during the starting and operating phases, but also when administering the termination phase.

These processes, while relatively simple to operate, can be very complex in terms of the number and types of applicable reactions, which in turn, are affected by numerous factors. Consequently, it is standard practice to conduct lab-scale amenability tests to initiate any feasibility study. While the copper ore is tested extensively to evaluate the effects of various properties, the effect of water quality has been either taken for granted or not reported substantially in the literature. In particular, saline water supplies can greatly affect the viability of a copper ore bioleaching operation, a consequence of the well-known inhibitory or toxic effect of chloride ion on metal-sulfide oxidizing bacteria.

The objective of this thesis is to study the bioleaching of copper from various sulfide ores under saline conditions. This particular topic was selected to provide data on the industrial problem of copper ore bioleaching with saline process water, a subject of major importance to copper producers facing the possibility of using either groundwater or seawater in their operations.

This thesis has seven major sections. Chapter 2 provides the industrial background for the work to be undertaken. Chapter 3 summarizes the general literature concerning copper ore bioleaching, annotated with specific references to such leaching conducted with saline process water conditions. Chapter 4 describes the experimental procedures used in the current study. Chapter 5 discusses the experimental results. A results summary is given in Chapter 6, and recommendations for further work are given in Chapter 7.

Chapter 2 Background: Ivan and Zaldívar Heap Leaching Mine Sites

Chile, with one-fifth of the world's known copper reserves, is the world's leading copper-producing nation [1]. It is not surprising that this country's copper deposits have become popular exploration targets of many North American mining companies. Among the many noteworthy sites are El Teniente and Chuquicamata, the world's largest underground and open-pit copper mines, respectively. While the former is located southeast of the capital city of Santiago, the latter is located in a barren, mineral-rich region in northern Chile, the Atacama Desert.

Beginning near Tacna, Chile, the Atacama Desert extends southward 970 km and is bordered on the west by the Pacific Ocean and on the east by the Andes Mountains. Unlike typical deserts, it is not especially hot (e.g. the coastal port city of Antofagasta averages 20°C in January, 14°C in July), but with an average annual rainfall of less than 13 mm, it justifies its reputation as one of the world's driest places. Only one river, the Loa, traverses this region, running from the Andes Mountains westward to the Pacific Ocean. Possessing virtually no flora or fauna, this desert does have, in abundance, sand, gravel, salt beds, and most importantly, large deposits of economic minerals. Once famous for being the world's only source of natural sodium nitrate, it is now known for its very large deposits of copper minerals [2]. Two properties of commercial interest in this region are Minera Rayrock Ltda.'s Ivan Mine and Minera Zaldívar S.V.'s Zaldívar Mine (a 50/50 joint venture between Placer Dome Inc. and Outokumpu Copper Resources B.V).

2.1 Ivan Mine

The Ivan Mine (Figure 2.1), located at latitude 23° 20' 46" S and longitude 70° 16' 08" W, approximately 35-40 km northeast of the coastal port city of Antofagasta, is easily accessed by paved and unpaved roads. It is also in close proximity to existing railroad tracks, making a rail link highly feasible. Furthermore, electricity from the power grid serving the neighbouring Escondida copper mine is easily accessed as required [3].

At an elevation of 800 m above sea level, the site experiences little in the way of temperature extremes, with monthly averages ranging from 12°C (August) to 18 °C (January). Essentially waterless, the site experiences little rainfall, averaging less than 3 mm of precipitation annually [4].

Fresh water is supplied by pipeline into Antofagasta from the Andes Mountains. In an effort to find a more economical and closer water source, two groundwater aquifers, the Upper and Lower Desesperado basins, were discovered by Errol L. Montgomery & Associates, Inc. [5]. Located approximately 10 km west of the mine site (Figure 2.1), both aquifers are very saline (Table 2-1) with average chloride levels of 24 and 11 g/L for the Upper and Lower Desesperado, respectively.

According to a recent feasibility study [6], the Ivan Mine's proven and probable ore reserves are currently over 2 million tonnes with an average copper assay of 1.7% for oxides and 4.6% for sulfides.

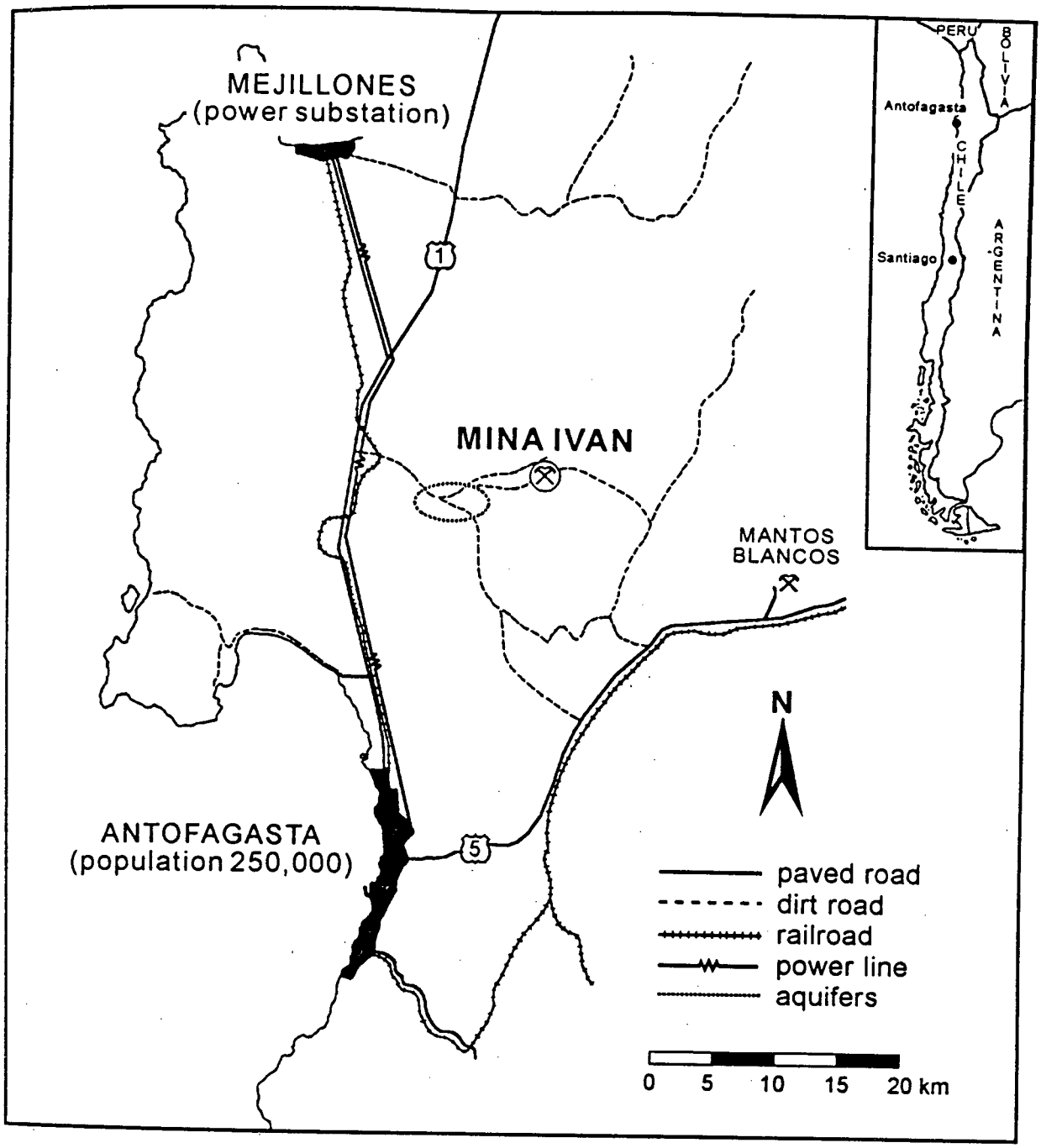


Figure 2.1 : Area map of the Ivan Mine site (after Hunt & Marquardt [7]).

Table 2-1: Average levels of selected constituents of the Upper and Lower Desesperado aquifers compared to seawater (after Errol L. Montgomery & Associates [5]).

Chemical Constituent	Concentrations in g/L		
	Upper Desesperado Aquifer	Lower Desesperado Aquifer	Seawater
calcium	3.72	2.50	0.41
magnesium	0.49	0.15	1.29
sodium	10.59	4.55	10.76
potassium	0.25	0.11	0.40
bicarbonate (as $CaCO_3$)	0.04	0.05	0.14
chloride	23.64	10.95	19.00
sulfate	1.68	1.32	2.70
nitrate (as NO_3)	0.17	0.06	<0.01
total dissolved solids	47.52	21.67	35.00

2.2 Zaldívar Mine

The Zaldívar Mine (Figure 2.2), centred at latitude 24°12'30" S and longitude 69°04' W, is located about 1400 km north of Santiago and 5 km north of the Escondida copper deposit. Like the Ivan Mine, it is linked by highway to the port city of Antofagasta, 196 km to the southeast. In addition, it is served by the Antofagasta-Salta narrow-gauge railway and by a nearby 2500 metre-long dirt airstrip maintained by Minera Escondida Limitada [8]. As with the Ivan Mine, electrical power can be easily obtained from the transmission grid serving the neighbouring Escondida copper mine [9].

Located on the western border of the Atacama desert, at an elevation of 3300 m above sea level, temperatures range from -7°C in the winter to 25°C in the summer. In keeping with the desert's reputation, precipitation is negligible, averaging less than 5 mm annually [8].

Like the Ivan Mine, it is probable that the Zaldívar Mine has no local source of fresh water and may have to depend on saline aquifers as well. A recent story in the print media [9] indicated that Placer Dome Inc. planned to build a freshwater pipeline to a source in the Andes mountains which is about 100 km from the mine site.

In stark contrast to the Ivan Mine's stated reserves, Zaldívar's copper ore reserves were last estimated at 1.1 billion tons grading 0.57% (0.2% cutoff), including the higher grade zone of 290 million tons grading at 1.16% Cu (0.7% cutoff) [9].

2.3 Current Operations

At both locations, the copper deposits occur as a cap of mixed oxides and supergene sulfides which overlays a deeper, lower-grade zone consisting of primary sulfide minerals. At Ivan, atacamite and chrysocolla are the main oxides, while bornite, chalcopyrite, and chalcocite are the main sulfides [6]. In contrast, Zaldívar's primary oxides are brochantite and chrysocolla, with chalcocite and pyrite being the main sulfide minerals [8].

To extract copper from these deposits, both copper producers intend to heap leach the ore (oxide, sulfide, or mixed), purify the pregnant solution by solvent extraction, and electrowin the resulting purified solution to recover high-quality cathode copper. Leaching of the oxides is easily achieved by chemical dissolution in sulfuric acid-based solutions. In contrast, leaching of the sulfides will utilize biologically-catalyzed leaching processes, often requiring longer periods of operation.

In choosing this method of operation, several advantages over the conventional pyrometallurgical methods are realized [10]. Namely, (1) economical treatment of low-grade ores, (2) smaller-scale, less capital-intensive operations, (3) lower operating temperature and energy requirements, (4) lower labour requirements, (5) minimal mineral processing requirements, (6) economic production of a relatively pure metal, and (7) elimination or reduction of potential environmental damage.

In any event, producing a relatively pure copper product is an attractive, and often more profitable option than attempting to produce a copper concentrate to sell to a smelter. Furthermore, by using this approach, the capital invested in the solvent extraction and electrowinning plants can be used for both the oxide and sulfide ores despite the fact that separate heap leach operations will have to be established.

It is well known that copper oxides leach more readily than their sulfide counterparts in sulfuric acid media [11]. At both sites, the presence of chloride ions due to the salinity of the nearest process water source may facilitate sulfide mineral dissolution by abiotic reactions. This is because chloride ion encourages the formation of soluble copper complexes and is a more aggressive lixiviant than sulfate ion. However, the bioleaching of copper sulfides under such conditions is not necessarily so straightforward because of physiological complications involving the catalytic microorganisms. Thus, as part of a desire for more data on this issue, Rayrock and Placer Dome have, by entirely different means, separately sponsored this metallurgical study to examine the effect of salinity on the bioleaching of their respective ores.

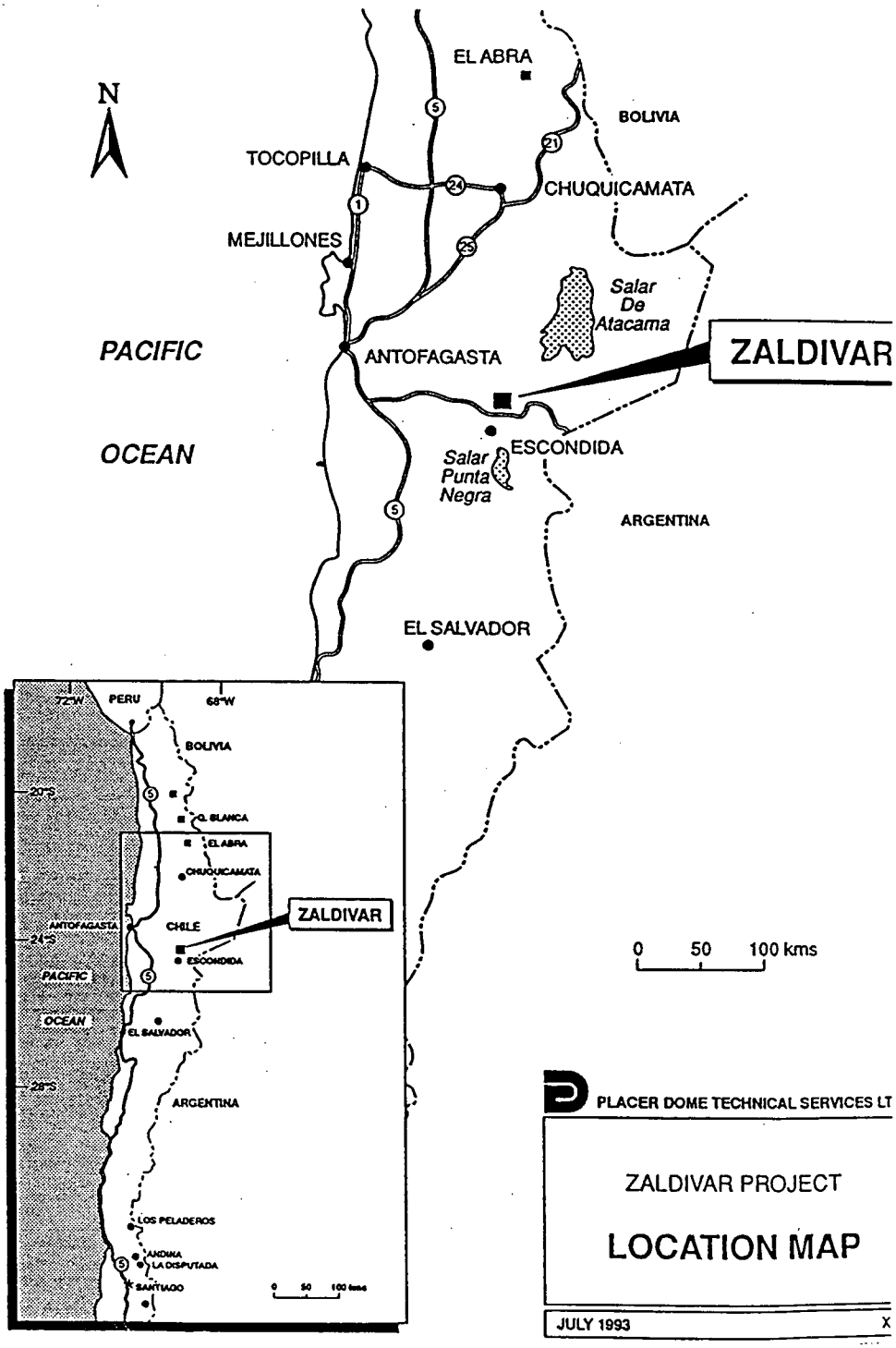


Figure 2.2 : Area map of the Zaldívar Mine site (after Placer Dome Inc. [8]).

Chapter 3 Literature Review: The Bioleaching of Copper Ores

Biohydrometallurgy is the subdiscipline of hydrometallurgy in which biological processes are utilized to achieve the process objective. It is an interdisciplinary subject which encompasses many fields including geology, economic geology, mineral processing, hydrometallurgy, chemistry, chemical engineering, and microbiology.

Biohydrometallurgy can be divided into the two broad categories of bioleaching and biosorption, the former being the more advanced with respect to industrial application. Bioleaching (also known as bacterial leaching, bacterially catalyzed leaching, biological leaching, microbial leaching, biochemical leaching, etc.) refers to the processes involving microbially catalyzed solubilization of metals from minerals in mining waste, whole ores, mineral concentrates, and metallurgical by-products. The following summarizes the literature concerning the general bioleaching of copper ores, annotated with references relevant to such leaching conducted under saline conditions.

3.1 Historical Perspective

Leaching of copper ores has its origins based in ancient times. Although early Roman, Phoenician, and Spanish miners had noted the presence of copper in mine drainage waters circa 1000 B.C. [11], the earliest known reference to a copper recovery process was written by the Chinese king Liu-An (177-122 B.C.). In his book, *Huainancius*, Liu-An clearly referred to the electrochemical process of copper cementation on iron [12]. About two centuries later, Pliny (23-79 A.D.) reported that *in-situ* copper ore leaching was being performed in the Spanish mines of Asturia, Gallacia, and Lusitania [13]. Around 166 A.D., Galen described the *in-situ* copper

ore leaching operation on the island of Cyprus, famous for its copper mines [14]. Besides the *in-situ* operation, sufficient archaeological evidence found later suggested that heap leaching had also been carried out at Cyprus [15].

In any case, apparently both the Chinese and the Europeans had been recovering cement copper from copper sulfate solutions generated by downward percolating surface waters which had dissolved metal oxides and sulfates of both the oxidation and the supergene mineralization zones of copper ore deposits and, by virtue of its ferric sulfate content, also leached secondary copper sulfides in the supergene zones.

During the Middle Ages, further development of this technique was not realized, probably due to the use of improved pyrometallurgical processes. However, the discovery, in late fifteenth-century Europe, that heaps of pulverized, partially-roasted sulfide ores could be leached by water to yield copper sulfate [16], revived interest in copper leaching processes. Even though copper leaching had been reported at Spain's Rio Tinto mine as early as 1670 [11], the first records of industrial-scale heap leaching of calcined ore would bear the year of 1752 [16]. Although the environmentally damaging practice of roasting at Rio Tinto did become prohibited in 1888, heap leaching of fractured run-of-mine ore continued until the 1970's [17, 18]. Currently, dump leaching is conducted at the site [11].

In spite of its success at Rio Tinto, the heap leach technique initially proved to be ineffective on the low-grade copper ores of the southwestern states of the U.S.A. Van Arsdale [19] attributed the success of the technique to "some obscure and mysterious quality either of the Rio Tinto ore or of the Spanish climate."

Several decades after its introduction in 1914, low-grade copper ore leaching did become established in this region of the U.S.A., the precursors of current world-class operations [11].

Today, *in-situ* and heap leaching operations are located primarily in Arizona and Nevada. In particular, the Blue Bird Mines of Ranchers Exploration and Development Corporation, Arizona, already famous for being the first copper recovery operation to use solvent extraction [16], is now considered by many researchers, including Murr [11], to be "one of the more important examples of heap leaching in the world." Large dump leaching operations are located in Nevada, Utah, Montana, Arizona, and New Mexico. The Bingham Canyon, Utah, leach dumps of Kennecott Copper Co. are probably the largest in the world, containing over two billion tons of rock [11]. Other dump, heap, and *in-situ* copper leaching operations exist in countries other than the U.S.A., including Africa, Canada, Japan, Australia, Bulgaria, Mexico, Zimbabwe, the former U.S.S.R., Portugal, the Rio Tinto mine in Spain [11], and Chile.

Van Arsdale's "mysterious quality" in the Rio Tinto heaps, namely metal-sulfide oxidizing bacteria, had been suspected, but not fully characterized, by soil researchers Rudolfs and Helbronner in 1922 [20]. Unfortunately, this first published evidence of microbial leaching of metal sulfides would be ignored until the isolation of the bacterial species, *Thiobacillus ferrooxidans*, from acidic coal mine drainage waters by Colmer and Hinkle, a quarter-century later [21]. Subsequent investigations between 1950 and 1951 by Colmer *et al.* [22] and Colmer and Temple [23] would characterize it as a chemolithoautotrophic microorganism. Soon after this discovery, the presence of this species was confirmed in the Bingham, Utah, copper leach dumps [24]. A decade later, this bacterial species was also found in the leach waters of the Rio Tinto mines [25], finally ending the mystery surrounding its copper recovery operations. Since then, a prodigious amount of experimental research into bioleaching has been conducted, resulting in a much greater understanding of the natural phenomena underpinning the process.

3.2 Mineralogy of Copper Ores: A Brief Synopsis

By definition, a mineral is a naturally occurring, crystalline substance with a definite chemical composition formed either by inorganic or organic processes. An ore is a natural deposit of aggregated minerals which can be profitably treated for recovery of a metal or metals of commercial value. Thus, copper ores contain not only the valuable ore minerals, but also, by association, usually worthless gangue minerals.

In the case of copper, primary sources of ore minerals include porphyry ores and veins. In porphyry ores, primary copper minerals are disseminated throughout the host rock which is commonly of igneous or volcanic origin. In veins, pre-existing fractures or fissures in the host rock are filled with minerals deposited from heated hydrothermal solutions.

In both types of copper deposits, alteration to secondary minerals usually occurs in the following manner. Near the surface, as a result of the activity of low-temperature, oxygenated waters, the primary or hypogene minerals often dissolve, producing a leached zone. Subsequently, some of the solubilized species are redeposited below and close to the groundwater table, producing zones of secondary or supergene mineral enrichment. As shown in Figures 3.1 and 3.2, copper minerals which exist at high E_h values (oxidizing conditions) are generally found above the water table, while those which exist at lower E_h values (reducing conditions) are generally found below the water table [27].

According to Scott [28], there are approximately 350 copper minerals, including minerals in which copper can substitute for other metals to some extent. The copper minerals of commercial interest include copper sulfides, sulfosalts, oxides, sulfates, hydroxy-sulfates, hydroxy-chlorides, carbonates, and silicates. A computer-assisted search with the MINFIND program [29] of all of

the known (up to circa. 1985) minerals revealed that 8 sulfide minerals consist of only copper and sulfur and that 8 sulfide minerals contain only copper, sulfur, and iron. These are listed in Table 3-1.

Of the 16 sulfide minerals listed, four are economically significant to the copper industry: chalcopyrite, chalcocite, bornite, and covellite. The remaining twelve are usually derived by alteration of these four primary minerals.

Chalcopyrite, a brass-yellow mineral, shares the nickname, "fool's gold", with pyrite (FeS_2), a mineral with which it is often associated. A widely occurring constituent of most sulfide ores, it is the primary copper mineral found in porphyry-copper deposits and in veined deposits, making it a very important source of copper [27].

Chalcocite, a lead-gray mineral, can occur as a primary mineral in veins associated with other sulfides. However, its primary occurrence is as a supergene mineral in enriched zones of sulfide deposits. It is one of the most important copper minerals, next to chalcopyrite [27].

Bornite is brownish-bronze when freshly fractured, but is also called "peacock ore" because of its variegated purple and blue-black tarnish. A widely occurring mineral, it is usually found in association with other sulfides, most likely as a primary mineral, less frequently as a secondary supergene mineral in vein deposits. It is a less important source of copper than chalcocite and chalcopyrite [27].

Covellite, an indigo-blue or darker mineral, occurs primarily as a supergene mineral in enriched zones of sulfide deposits. Derived from other copper minerals (e.g. chalcocite, chalcopyrite, bornite, enargite), it is not found in abundance and is often considered a minor copper ore mineral [27].

The sulfosalts are unoxidized sulfur minerals. Structurally, they differ from the sulfides in that the metalloids arsenic (As) and antimony (Sb) displace metals in the crystal lattice. The copper sulfosalts include tetrahedrite ($Cu_{12}Sb_4S_{13}$), tennantite ($Cu_{12}As_4S_{13}$), enargite (Cu_3AsS_4), and bournonite ($PbCuSbS_3$). All 4 sulfosalts are commonly found in hydrothermal vein deposits, often in association with chalcopyrite. Tetrahedrite and bournonite are the most commonly occurring sulfosalts, while tennantite and enargite are comparatively rarer in occurrence [27].

Although considered minor ore minerals, the copper oxides cuprite (Cu_2O) and tenorite (CuO) can be important sources of copper. Another minor ore is native copper, normally found as small occurrences in the oxidized zones of copper deposits. Other economically significant minerals include: chalcanthite ($CuSO_4 \cdot 5H_2O$), antlerite ($Cu_3SO_4(OH)_4$), brochantite ($Cu_4SO_4(OH)_6$), atacamite ($Cu_2Cl(OH)_3$), azurite ($Cu(OH)_2 \cdot 2CuCO_3$), malachite ($Cu(OH)_2 \cdot CuCO_3$), and chrysocolla ($Cu_4H_4Si_4O_{10}(OH)_8$) [27].

Table 3-1: Summary of Cu-S and Cu-S-Fe minerals found with MINFIND program.

Minerals with Cu and S only	
anilite	Cu_7S_4
chalcocite	Cu_2S
covellite	CuS
digenite	Cu_9S_5
djurleite	$Cu_{31}S_{16}$
geerite	Cu_8S_5
spionkopite	$Cu_{39}S_{28}$
yarrowite	Cu_9S_8

Minerals with Cu, S, and Fe only	
bornite	Cu_5FeS_4
chalcopyrite	$CuFeS_2$
cubanite	$CuFe_2S_3$
fukuchilite	Cu_3FeS_8
haycockite	$Cu_4Fe_5S_8$
idaite	Cu_3FeS_4
mooihoekite	$Cu_9Fe_9S_{16}$
mukundamite	$(Cu, Fe)_4S_4$

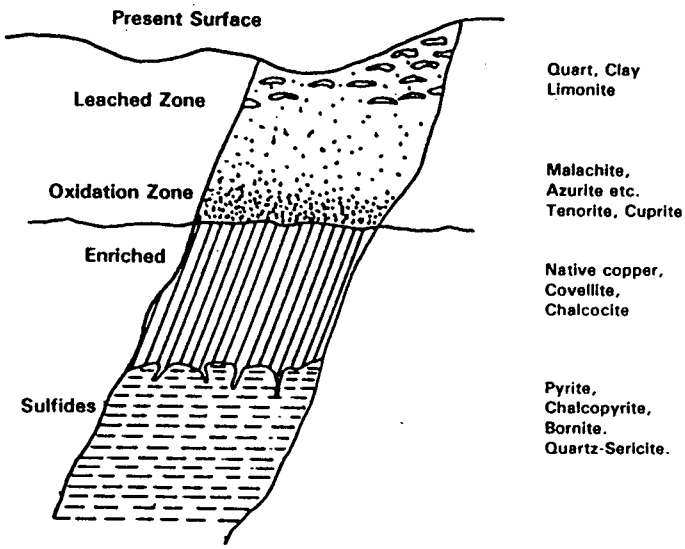


Figure 3.1 : Vertical section of upper portion of copper ore deposit illustrating zonation, water table, and typical copper minerals (after Bartlett [26]).

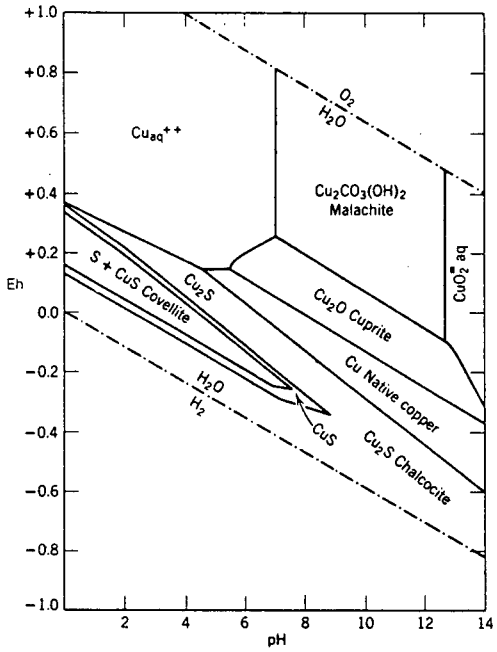


Figure 3.2 : Standard E_h-pH diagram of system Cu-H_2O-O_2-S-CO_2, 25°C and 1 atm. total pressure, presenting the stability of some copper minerals in supergene enrichment deposits (after Klein & Hurlbut [27]).

3.3 Copper Ore Leaching Methods

Hydrometallurgical recovery of copper from low-grade ores which cannot be economically treated by concentrating and smelting is facilitated by one of the following percolation methods: dump, heap, thin-layer, and *in-situ* leaching. The method chosen is dictated by economic concerns relating to the nature and occurrence of the mineral deposit under consideration. Compared to conventional smelting methods, the key advantage of these methods to producers is the low capital investment required to obtain a desired level of copper extraction. Occasionally, lower operating costs are experienced as well. Offsetting these advantages somewhat are t(e lower total copper recoveries as well as the longer operating lifetimes [30]. Yet, such operations can be profitable. Phelps-Dodge, a major copper producer, announced the ability to produce 1 pound (454 g) of copper for about $US 0.30 from their waste-ore leaching operations in 1986 [10]. This example confirms the general rule of thumb [31] which asserts that copper production from mining wastes and low-grade ores treated by bioleaching processes can be achieved at about one-third to one-half the cost of processing flotation concentrates by conventional smelting techniques. A brief description of each method will be outlined in this section.

Dump leaching involves the recovery of metal values from lean ores, usually the sub-marginal grade (< 0.4 wt% copper) mining waste from open-pit operations. In the past, this waste was often piled haphazardly near the mine site, without much planning for subsequent copper recovery. Nowadays, this uncrushed, fractured material is brought by truck or front-end loader to form truncated cones at suitable sites located in the mine's vicinity, making use of the local terrain. Typically, steep-sided valleys or hillsides that have prepared or pre-existing impervious walls or bottoms are used, to ensure adequate solution flow with minimal losses [30]. These dumps, consisting of approximately 4.5 m thick alternating layers of coarse lumps and fine-grained rock called "lifts", can be up to 200 m tall, 80 m wide at the top, 250 m wide at the bottom, and

can contain as much as 50,000-300,000 tons of ore [10]. Dumps such as those at Bingham Canyon, Utah are much larger. To maximize the surface area to volume ratio to improve aeration, "finger dumps", that is, dumps much greater in length than in width or height can be used. For example, at Anaconda's Butte, Montana copper mine, a "finger dump" 800 m long, 35 m high, and 200 m wide was raised [16].

Heap leaching is similar to dump leaching, but differs with respect to the grade of ore, the amount of preparation, the relative scale, and the final disposition of the leached ore. Run-of-mine ore, usually higher in grade than that used in dump leaching, after crushing, classifying, and even partial roasting, is carefully placed by stacking conveyor belts onto specially prepared bases to form small heaps [16]. These constructs or "lifts" are usually less than 4-5 m in height [16] and can be built atop one another to form multi-lift heaps, although there is a practical height restriction dictated by the need to avoid compaction and the associated lack of aeration. As with dump leaching, these heaps are usually located close to the mine site, making use of elevated, gently sloping regions. However, unlike dumps, heaps are periodically removed and replaced as required, depending on desired copper effluent levels. With regards to prepared bases or pads, options include cemented or chemically stabilized soil, clay lining, asphalt, and plastic sheet sandwiched between two sand layers [16].

A variation of heap leaching is "Thin-Layer" or TL leaching, a technology initially developed and patented in 1975 by Holmes and Narver Inc. [32]. Further development by Chile's Sociedad Minera Pudahuel (SMP), resulted in a patented improved version of the original process which has been successfully applied to oxide, sulfide, and mixed copper ores from the Lo Aguirre and La Cascada Chilean deposits [32]. In this process, the ore is crushed to 100% minus 1/4 inch, agglomerated by the addition of water and sulfuric acid or raffinate solution in a curing drum, and loaded onto prepared pads to form heaps typically 5 m in height [32]. Apparently, SMP

claims that the innovative part of the new patent is the acid curing-agglomerating step.

In-situ leaching, the least advanced of the methods, involves in-place leaching of minimally disturbed ore. Sites include underground mined out stopes, abandoned mines, caved mine workings, worked out areas, and entire permeable ore bodies prepared by explosives. Three types of this kind of leaching have been classified by Wadsworth [33]: (I) near surface above the water table, (II) near surface below the water table, and (III) deep deposits below the water table. Presumably, only Type I sites involving copper ore bodies have been successfully leached commercially by this technique. While there has been substantial work undertaken at various sites (the Dergtyarskii mine, former Soviet Union [34], the Miami Mine, Arizona [35], the Kimbley Pit, Nevada [36], and the Kosaka Mine, Japan [37]), it is clear that, by comparison with the publicized research on the other percolation methods, *in-situ* leaching is either not utilized commercially or reported in the literature to the same extent. Yet, there are notable sites in recent literature, including ENAMI's La Hermosa, Andacollo, Chile [38], Gunpowder Copper Ltd.'s Queensland, Australia [39], and Ranchers Exploration and Development Corporation's Old Reliable and Mammoth, Nevada, U.S.A. [11] operations. Evidently, this technology suffers from both the lack of operating data and the environmental problem of preventing groundwater contamination through solution losses.

Apart from the aforementioned differences, all four methods utilize essentially the same methodology (Figure 3.3). Ordinary mine water, prepared lixiviant, or acidified raffinate is applied to the top of the rock mass (heap, dump, or fractured ore body) by various means (sprinkling, flooding, or pumping in the case of *in-situ*) and allowed to percolate downward through the stationary material by gravity flow. Under the influence of the solution, atmospheric oxygen, and metal-sulfide oxidizing bacteria, copper oxides dissolve and copper sulfides oxidize, producing a copper sulfate pregnant solution. After recovery of this solution (again, in the case of

in-situ, by pumping), it is treated either by a cementation plant or by a solvent extraction-electrowinning (SX-EW) circuit to recover copper. In either case, the residual barren solution, after impurity removal and acid addition as necessary, is recycled back to the leaching site. It should be noted that Figure 3.3 is incorrect in indicating that spent electrolyte is also recycled back to the leaching site. Apart from solution bleeds to reduce impurity levels, this acid solution, which contains any residual copper after electrowinning, is normally recycled back to the solvent extraction plant, where it is used as a stripping solution.

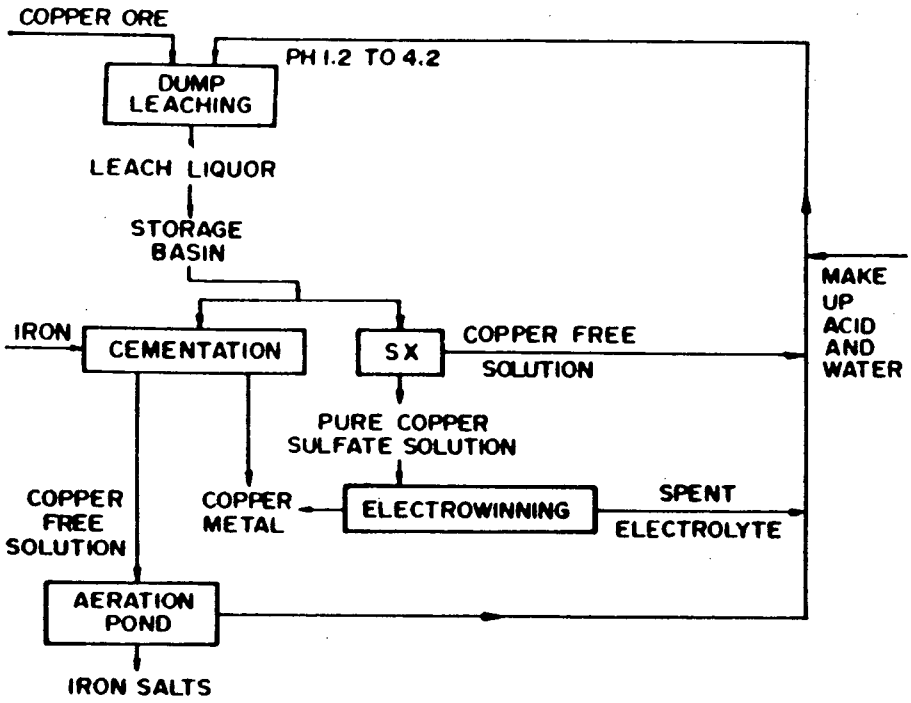


Figure 3.3 : Generalized flowsheet illustrating dump, heap, thin-layer, or *in-situ* leaching (after Gupta & Mukherjee [10]).

3.4 Microbiological Aspects of Bioleaching

Bacteria are single-celled prokaryotic organisms which are classified according to observable characteristics including morphology, physiology, nutrition, and genetics [40, 41]. In this section, general aspects of bacterial physiology and nutrition, descriptions of specific species of metal-sulfide oxidizing bacteria, interactions between these bacteria and other microorganisms, and the physiological effects of cations and anions on growth of such bacteria will be discussed.

3.4.1 General Bacterial Cell Physiology

To better understand how bacteria influence sulfide leaching, a brief introduction to the general features of a bacterial cell [40, 41] is necessary (Figure 3.4).

Unlike the cells of all higher organisms, the prokaryotic (from *pro*="early or primitive" and *karyo*="nucleus") or bacterial cell is characterized by the lack of a true nucleus. Furthermore, there are no membraned specialized organelles for specific cellular functions present.

The bacterial chromosome, a naked, deoxyribonucleic acid (DNA) molecule twisted into a closed loop, contains all of the genetic information needed to carry out metabolism, growth, and genetic replication.

Plasmids are small circular macromolecules of DNA which are present in some bacteria. Although not involved in cell replication, they contain supplemental genetic information which code for enzymes or proteins that directly affect the cell's ability to adapt to its environment.

Ribosomes are the small dark structures embedded in the cell cytoplasm. They act as underlying substrates when amino acids come together to form proteins.

The cell membrane is the semi-permeable boundary between the cell interior and the outside environment. Consisting of approximately 60% protein and 40% phospholipids, its essential function is to regulate the transport of chemicals into and out of the cell. Consequently, much enzymatic activity takes place at or adjacent to this membrane.

The cell wall, which encloses the cell membrane, provides the cell rigidity and protection from osmotic stress. Much of the structural strength of the cell wall comes from peptidoglycan, an organic polymer unique to prokaryotes. There are two major types of cell wall which can be determined visually by the retention (-positive) or non-retention (-negative) of the characteristic crystal-violet pigment of Gram's stain, even after washing with ethyl alcohol. The Gram-negative cell wall, Figure 3.5 (a), consists of a layer of phospholipids and lipoproteins outside of a thinner peptidoglycan layer. In contrast, the Gram-positive cell wall, Figure 3.5 (b), consists of an inner membrane covered by a relatively thick peptidoglycan layer. Furthermore, in Gram-negative cell walls, a space between the cell membrane and the peptidoglycan layer exists, called the periplasmic space. This feature, absent in Gram-positive organisms, reflects a fundamental difference in how substance-degrading enzymes are utilized between the two types of organisms.

Typically, prokayrotes have external coatings or glycocalx on their cell walls. Composed of either polysaccharides or proteins, this coating, depending on its nature, can be referred to either as a capsule (hard and dense) or as a slime layer (soft and pliable). In either case, the glycocalx, besides providing additional protection for the cell, is believed to expedite attachment of the cell to solid surfaces.

Some prokaryotes have flagella. These long filaments anchored in the cell's protoplasm can freely rotate, providing locomotion.

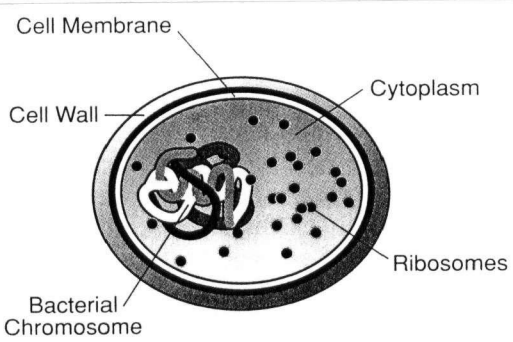


Figure 3.4 : Cross-section of a typical bacterial cell with major features marked (after Chapelle [41]).

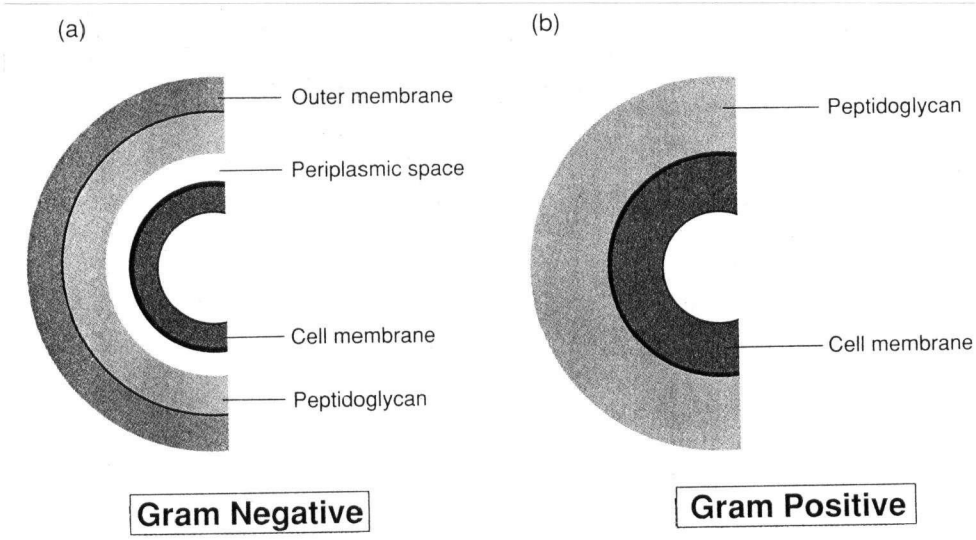


Figure 3.5 : Cross-section of (a) Gram-negative cell wall and (b) Gram-positive cell wall (after Chapelle [41]).

3.4.2 General Nutritional Requirements

According to Dunn [42], of all the elements that appear in the periodic table, at least 35-40 either have been demonstrated or have been claimed to be essential nutrients for microorganisms. However, only eight elements, six non-metals (C, O, H, N, P, S) and two metals (K, Mg), comprise an average of 98% of the dry weight of bacteria and fungi. These elements, which are usually required at levels in excess of 10^{-4} mol/L, are collectively termed macronutrients. The remaining elements are termed micronutrients and are usually found at levels less than 10^{-4} mol/L.

In general, most microorganisms are 80-90% water, with C, O, H, and N, the main cellular constituents, making up 90-95% of the dry weight [42]. Table 3-2 outlines all eight macronutrients while Table 3-3 lists the more notable micronutrients. In both tables, the relative proportions and the physiological functions of the listed nutrients in an average microbial cell's dry mass are described.

The most important of the macronutrients, carbon, is the major constituent of both cellular matter and energy accumulation processes. It is traditional to classify bacteria according to their source of this element. Heterotrophs, the group that includes most bacteria and algae, obtain their cellular carbon from existing organic matter. In contrast, autotrophs, the class which includes few bacteria and most fungi, obtain cellular carbon from carbon dioxide. Microorganisms which exhibit both autotrophy and heterotrophy are called myxotrophs. In this case, growth is typically autotrophic, but is stimulated by the presence of certain organic carbon substances.

Next in importance is oxygen. Besides its other physiological functions, oxygen (as O_2) is often the electron acceptor in bacterial respiration processes, including those used by metal-sulfide oxidizing bacteria. As such, they are aerobes, which require oxygen to function, while anaerobes

do not. This classification can be further subdivided with obligate aerobes (must have atmospheric oxygen to thrive) at one end of the scale and microaerobes (only need minute quantities of oxygen) at the other end.

Other than carbon, oxygen, and hydrogen, the remaining macronutrients and micronutrients are normally obtained from the substrate, which usually contains them as trace elements.

Table 3-2: Macronutrients used by most microorganisms (after Rossi [16] and Chapelle [41]).

Element	Wt.%	Physiological function
Carbon	50	cell matter, energy accumulation
Oxygen	20	energy exchange, cell water and matter, electron acceptor (as O_2)
Nitrogen	8-14	energy accumulation, ingredient for proteins, nucleic acids, coenyzmes
Hydrogen	8	energy exchange, cell water and matter
Phosphorus	1-3	energy accumulation (ADP/ATP), ingredient for nucleic acids, phospholipids, nucleotides, and coenzymes
Sulfur	0.5-1.0	energy accumulation, ingredient for proteins and coenzymes
Potassium	1	principal inorganic cation, cofactor for some enzymes, metabolism regulator
Magnesium	0.5	metabolism regulator, important cellular cation

However, in the laboratory, bacterial nutritional requirements are met, not only from the substrate under investigation, but also from specially formulated mixtures of industrial chemicals called culture media. While some are specially formulated for particular bacterial species, others

are more general and can be applied either to a single, pure species or to mixed cultures. Table 3-4 describes some of the culture media used with *T. ferrooxidans*. Silverman and Lundgren's [43] 9K medium (column 2) is the most popular medium of researchers, closely followed by Leathen's medium [44] (column 1).

Table 3-3: Micronutrients used by most microorganisms (after Rossi [16] and Chapelle [41]).

Element	Wt%	Physiological function
Calcium	0.5	same functions as magnesium
Sodium	2	important for halophilic organisms; not usually required by most bacteria
Chlorine	0.5	same as above
Iron	0.2	redox regulator, formation of cytochromes and other proteins
Cobalt	trace	probably redox regulator, component of vitamin B_{12}
Nickel	trace	probably redox regulator
Copper, Zinc, Molybdenum	trace	components of special enzymes

In spite of its popularity, the 9K medium does have criticisms. Many workers believe that the medium is too generous (i.e. rich in nutrients) and, if used, does not accurately reflect conditions in nature, where nutrients can be, and often are, scarce. Others are more concerned with the propensity of 9K to precipitate out iron and sulfate as jarosite during bioleaching tests. This tendency has been attributed to excessively high concentrations of K_2HPO_4 and $(NH_4)_2SO_4$ [47].

In an attempt to remedy the precipitation problem, Tuovinen and Kelly [45] and Norris and Kelly [46] proposed alternative culture media (columns 3 and 4, respectively), the former being regulated at pH 1.3 to further control jarosite precipitation. It is important to note that if this medium is employed, this pH level would exclude most, if not all, metal-solubilizing bacteria except those with very high acid tolerances like *T. thiooxidans* or those specifically adapted to high acidity.

Table 3-4: Some culture media used in lab-scale test work with *T. ferrooxidans* strains. All measures in grams unless otherwise stated.

Chemical Component	1 Leathen *et al.* [44]	2 Silverman and Lundren's (9K Medium) [43]	3 Tuovinen and Kelly [45]	4 Norris and Kelly [46]
$(NH_4)_2SO_4$	0.15	3.00	0.4	0.4
KCl	0.05	0.10	nav	nav
K_2HPO_4	0.05	0.50	0.4	0.4
$MgSO_4.7H_2O$	0.50	0.50	0.4	0.4
$Ca(NO_3)_2$	0.01	0.01	nav	nav
Distilled H_2O	1000	700	1000	2000
H_2SO_4	nav	1 mL of 10N soln	0.10N soln (to pH 1.3)	nav
$FeSO_4.7H_2O$	10 mL of 10% (w/v) solution	300 mL of 14.74% (w/v) solution	33.3	27.8

nav denotes no applicable value.

3.4.3 Specific Species of Bioleaching Bacteria of Interest

Not surprisingly, bacteria are intimately involved in the biogeochemical cycling of many elements [40, 41]. In particular, bacterial species which mediate the sulfur [48] and iron [40, 41] cycles by way of catalyzed inorganic reactions are of interest. Such chemolithoautotrophic bacterial species, especially *Thiobacillus ferrooxidans*, have been the focal point of research by many scientists studying bioleaching. Chemolithotrophs are literally "chemical rock eaters", bacteria which derive all metabolic energy from the oxidation of reduced inorganic chemicals such as minerals. Autotrophs are bacteria which derive all cellular carbon primarily from the fixation of atmospheric carbon dioxide by the energy-intensive Calvin reductive pentose phosphate cycle [40].

The following section describes the morphology, energy sources, and optimum living conditions of the three species of obligately chemolithoautotrophic, non-spore forming, slime-forming, Gram-negative, mesophilic, aerobic (requiring oxygen), and acidophilic (acid-loving) bacteria most commonly associated with bioleaching. It should be noted that, for the most part, exact biochemical mechanisms for the various metabolic functions will not be described here. Interested readers in such matters are advised to consult Rossi [16], or appropriate microbiology texts like those by Atlas [40] or by Chapelle [41].

3.4.3.1 *Thiobacillus ferrooxidans*

This bacterial species, first isolated in 1947 [21], is considered to be predominant in the oxidative leaching of a wide variety of sulfide minerals, including most copper sulfides of commercial interest (Table 3-5).

Table 3-5: List of sulfide minerals oxidized by *T. ferrooxidans* (after Karavaiko *et al.* [49]).

Sulfide Mineral	Chemical Formula
pyrite	FeS_2
marcasite	FeS_2
pentlandite	$(Fe, Ni)_8S_8$
pyrrhotite	$Fe_{(1-x)}S$
chalcopyrite	$CuFeS_2$
bornite	Cu_5FeS_4
covellite	CuS
chalcocite	Cu_2S
tetrahedrite	$Cu_{12}Sb_4S_{13}$
enargite	Cu_3AsS_4
arsenopyrite	FeAsS
realgar	AsS

Sulfide Mineral	Chemical Formula
violarite	Ni_2FeS_4
bravoite	$NiFeS_4$
millerite	NiS
polydimite	Ni_3S_4
antimonite	Sb_2S_3
cobaltine	CoAsS
molybdenite	MoS_2
sphalerite	ZnS
marmatite	(Zn, Fe)S
galena	PbS
geochronite	$Pb_5(SbAs_2)S_8$
orpiment	As_2S_3

Although its taxonomy implies a strictly rod-shaped morphology, Rossi [16] asserts that polymorphism is the case. Cells of *T. ferrooxidans* can vary from large rods with rounded ends, 1.6-1.7 microns long by 0.3-0.4 microns in diameter, to spheres, ovoids, and rods, 0.5-0.7 microns long by 0.3-0.4 microns in diameter. Typical of Gram-negative bacteria, its cells possess a multi-layered, inclusion-rich cell envelope, a non-compartmentalized interior containing genetic information, and a polar flagellum. Found naturally when sulfide minerals are exposed to air and water, these bacteria can occur singly, in pairs, or even in chains of 6-7 cells.

A much-studied species, this member of the genus *Thiobacillus* derives all metabolic energy from the oxidation of ferrous iron, reduced sulfur compounds (including metal-sulfide minerals), and perhaps, the oxidation of other metals [50, 51]. This energy is used for chemical transportation (nutrients in and waste out), physical movement, cell growth, and cell maintenance [52].

However, confusion exists in the scientific literature in that 2 other names for this species can still be found, indicating the difficulty in confirming its unique identity on nutritional bases. In 1947, Colmer and Hinkle [21], the co-discoverers of *T. ferrooxidans*, had demonstrative data detailing its ability to oxidize thiosulfate to sulfur and sulfuric acid, as well as its ability to oxidize ferrous sulfate in acid medium. In a 1959 paper, Leathen and Braley [53], doubting its ability to oxidize sulfur compounds, suggested another name, *Ferrobacillus ferrooxidans*. In 1960, Kinsel [54], apparently discovered a new bacterium in acid mine drainage, naming it *Ferrobacillus sulfooxidans*. Despite assertions by many investigators that all three species were one and the same, it would take until 1973 to prove and confirm the original name [55]. More recently, the wide variation in the reported leaching capabilities of *T. ferrooxidans* can partly be explained by the existence of (a) poorly identified strains of iron or sulfide mineral-oxidizing bacteria labelled as *T. ferrooxidans* and (b) correctly identified *T. ferrooxidans* strains which do exhibit reproducible variations in behaviour, such as optimum leaching temperature [56]. Harrison [57], in a review of 23 *T. ferrooxidans* strains of known ancestry, has apparently found a rational explanation: *T. ferrooxidans*' DNA is genomically more diverse for a single species because it includes material from 7 DNA homology groups. Furthermore, he stated that these groups are widespread and that "it is the microenvironment which selects for a given genotype, and the microenvironment suitable for each genotype is available worldwide", explaining *T. ferrooxidans*' remarkable ability to adapt to widely different habitats.

Its oxidizing capacities with respect to iron and sulfur compounds have been well studied. *T. ferrooxidans* oxidizes ferrous sulfate according to equation 3-1 (Table 3-6), the rate of which has been demonstrated to be 10^5-10^6 times greater than the equivalent inorganic reaction at pH 2.5 [58]. Silver [59] has shown that strains of this species can oxidize S°, S^{2-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_2O_4^{2-}$, and SO_3^{2-}, with thiosulfate, tetrathionate, and sulfides being oxidized 5-8 times faster than the other compounds. Some of the oxidation reactions for selected iron and sulfur compounds and the associated free energies of reaction (per mole of O_2 or NO_3^-) are given in Table 3-6:

Table 3-6: List of oxidation reactions catalyzed by *T. ferrooxidans* and other bioleaching bacteria (after Rossi [16] and Karavaiko *et al.* [49]).

Oxidation Reaction of Interest	Free energy (kJ/mole O_2 or NO_3^-)	Equation Ref. No.
$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$	-46	(3-1)
$S^o + \frac{3}{2}O_2 + H_2O \rightarrow H_2SO_4$	-329	(3-2)
$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$	-442	(3-3)
$5S_2O_3^{2-} + 8NO_3^- + H_2O \rightarrow 10SO_4^{2-} + 4N_2 + 2H^+$	-467	(3-4)
$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$	-502	(3-5)

Given that (a) chemolithotrophy is the least efficient energy obtaining method for bacteria [40], (b) ferrous iron oxidation yields less energy per mole than elemental sulfur oxidation (Table 3-6), (c) ferrous iron oxidation can supply all energy requirements in the absence of sulfur

compounds [45], and (d) the previously-mentioned oxidation rates, it is not surprising that large amounts of substrate must be metabolized for bacterial growth to occur. This implication is confirmed by some fairly conservative bio-energetic calculations made by Rossi [16], who determined that while oxidation of 1 mole of ferrous iron should yield, in theory, 1.42 g of dry cells, only 0.5 g is usually produced. That is, each *T. ferrooxidans* cell, out of necessity, must oxidize 40-112 times its own mass in ferrous iron for biosynthesis. Keeping these ratios in mind, a leach liquor containing 10^{10} *T. ferrooxidans* cells per milliliter (0.106 g dry biomass), could promote the oxidation of 4.24-11.87 g of ferrous iron. According to Rossi [16], based on doubling times of 5 to 15 hours, this is equivalent to a rate of 0.14-2.37 g of ferrous iron or of 0.3-5.09 g of pyrite ore, on a per hour per milliliter of leach liquor basis, notwithstanding the energy derived from sulfur oxidation in the latter case.

T. ferrooxidans is viable at temperatures ranging from 28-40°C, with an optimum temperature range of 30-35°C [16, 49, 56]. Less acid-tolerant than *T. thiooxidans*, one of its satellite species, it will tolerate pH values ranging from about 1.4 up to 6, with optimum growth at pH 2.35 [16]. In spite of its preference for highly acidic environments, the interior of a *T. ferrooxidans* cell is maintained at a near-neutral pH, the precise mechanism having been postulated by Peters and Doyle [60].

3.4.3.2 *Thiobacillus thiooxidans*

This species, first isolated by Waksman and Joffe in 1922 [61], is morphologically and physiologically similar to the more studied *T. ferrooxidans*. In fact, these two species are often found together in the same leaching environments, sharing acidophily, growth on sulfur and reduced sulfur compounds, and essentially the same cell structure. Karavaiko [49] once described *T. thiooxidans*' cell morphology as a bacillus or a rod 0.5-0.8 microns wide by 1-2 microns long with a single-pole or a polar spirilla flagellum. Sometimes covered with slime, the continuous

cell walls contain various terminal fatty inclusions thought to be sites of sulfur oxidation [49]. When observed by light or electron microscope, this species will occur either as single cells or as a series of cells joined together to form chains.

Other than a slightly lower guanine and cytosine base pair content in its DNA, the major recognized difference between *T. ferrooxidans* and *T. thiooxidans* is the latter's apparent inability to oxidize ferrous ions. According to Norris [56], this species can only oxidize elemental sulfur and other reduced sulfur compounds. Norris also stated that *T. thiooxidans* cannot effectively leach sulfide minerals itself, its contribution to metal-sulfide leaching being restricted to oxidizing the elemental sulfur by-product produced by other bacteria. Norris' assertions are disputed by many, including Rossi [16] and Barrett *et al.* [62], who state that, like all members of the genus *Thiobacillus*, *T. thiooxidans* can oxidize S°, $S_2O_3^{2-}$, S^{2-}, the sulfide moiety, and reduced sulfur compounds including sulfide minerals.

T. thiooxidans is viable at temperatures ranging from 20-40°C, with an optimum temperature of 30°C [16, 56]. Characterized by its ability to grow in strong acid media between pH 0.6-4.5, with an optimum at pH 2.5, this species can accumulate up to 5-7% of self-produced sulfuric acid [49]. Ironically, since sulfuric acid is very hydrophilic, this species is sensitive to moisture content; below 11.4% on pure sulfur and 2.3% on soil, these bacteria perish.

3.4.3.3 *Leptospirillum ferrooxidans*

First isolated from Armenian copper sulfide deposits and described by Markosyan in 1972 [63], this species is often found in heterogeneous culture with either or both *T. ferrooxidans* or *T. thiooxidans*. In fact, it is often an acidophilic contaminant of so-called pure isolates of *T. ferrooxidans* strains [16]. Its cell morphology exhibits great variability, ranging from a helix with two to five spires to a curved rod or vibrio, 0.9-1.1 microns in length and from 0.2-0.4 microns

in diameter, with one polar flagellum, 18-22 nm in diameter [64]. Consequently, their cells are not only slightly thinner, but also are frequently more mobile than those of *T. ferrooxidans* [56]. Typical of members of the *Spirillaceae* family, vibrios are usually joined at their ends to form long spirals of varying lengths [16, 52]. Also, macroscopic aggregates of vibrios embedded in slime have been observed [56].

Unable to oxidize elemental sulfur, *L. ferrooxidans* readily oxidizes ferrous iron, albeit at slower rates than *T. ferrooxidans*. Norris [56] reported that the maximum growth rate of the most-studied strain on ferrous iron in shake flask culture is, at most, half that of a *T. ferrooxidans* strain. Its ability or inability to grow on metal sulfides is currently a source of contention. Markosyan [65] stated that metal-sulfide oxidation is accomplished indirectly via ferric ion produced by *L. ferrooxidans*' respiration processes and that pyrite and chalcopyrite oxidation comparable to that achievable by *T. ferrooxidans* only occurs in mixed cultures with *T. organoparus*. Yet, these statements are not supported by Norris and Kelly's [46, 66] findings, which demonstrated that *L. ferrooxidans* alone can oxidize pyrite and certain varieties of chalcopyrite. In addition, it was confirmed by these authors that mixed cultures of *L. ferrooxidans* and *T. thiooxidans* will actively grow and vigorously oxidize pyrite and chalcopyrite. Pending clarification of this metal-sulfide oxidizing ability, and its inability to oxidize elemental sulfur, *L. ferrooxidans*' role in mineral-sulfide leaching appears to be limited to oxidizing ferrous iron liberated by its own activities as well as those by other sulfide-oxidizing bacteria.

L. ferrooxidans is viable at temperatures ranging from 20-40°C, has an optimum temperature of 30°C, and grows at pH values ranging from 1.5 to 4.5 with an optimum pH of 3.0 [16].

3.4.4 Interactions Between Bioleaching Bacteria and Other Microorganisms

While the science of microbiology has, in general, developed from laboratory study of pure or monospecies cultures, it is also common knowledge that, in nature, microorganisms, with few exceptions, exist as complex, multi-species communities. So, it is not surprising that heterogeneous leaching environments such as leach heaps and dumps support a very diverse array of microorganisms living in balanced co-existence in natural microbial ecosystems. While the first systematic studies of microflora associated with *T. ferrooxidans* in mine drainage waters were undertaken in the 1960's [67, 68, 69], at least two decades would pass before significant studies of sub-surface leaching environments would be compiled by Groudev *et al.* [70] and Norris and Kelly [66]. From these reviews, it would appear that such ecosystems sustain not only mesophilic and thermophilic varieties of sulfur- and iron-oxidizing bacteria (*Thiobacillus*, *Leptospirillum*, *Metallogenium*, *Gallionella*, *Leptotrix*, *Sulfolobus*, *Sulfobacillus*, etc.), but also sulfur reducing bacteria, heterotrophic bacteria (*Thiobacillus*, *Desulfovibrio*, *Enterobacter*, *Pseudomonas*, *Caulobacter*, etc.), microscopic algae and protozoa (*Amoeba*, *Eutrepia*, etc.), and molds and yeasts (*Pullularia*, *Cladosporium*, *Spicaria*, *Penicillium*, *Rhodotorula*, etc.). Consequently, one must be cognizant of the possible types of interactions between microorganisms.

According to Richards [71], these microbial interactions can include any of the following: (a) competition, where nutrients are strongly contested between several species; (b) parasitism and predation, where one species can be either exploited or utilized as food by other species; (c) symbiosis or commensalism, where otherwise single species mutually benefit through co-existence; and (d) antagonism, where chemical aggression between species occurs.

In leaching environments, acidophilic, iron-oxidizing, and sulfide-oxidizing bacteria are considered to be the primary leaching agents, but they do not act in isolation. Competition for similar nutrients occurs between these primary species, while parasitic or predatory species (fungi,

algae, protozoa, molds, yeasts, some heterotrophic bacteria, bacteriophages, etc.) may consume or exploit them for food. Chemical aggression is likely limited to ensuring viable niches for survival. In this case, maintaining their preferred highly acidic environment is probably sufficient. The most interesting of the microbial relationships are symbiotic in nature. The remaining discussion will centre on examples of such relationships with relevance to sulfide leaching. It should be noted that only a brief sampling of the numerous possible interactions is possible since the exact details and consequences of all such interactions cannot be reviewed fully.

In many instances, mixed species may catalyze or enhance the leaching of ores which have proven to be less amenable to a pure species. For example, while *T. ferrooxidans* can thrive on pyrite, this ore does not support the growth of either *T. thiooxidans* or *L. ferrooxidans*. However, a mixed culture of *T. thiooxidans* and *L. ferrooxidans* metabolizes pyrite at rates greater than that achieved by a culture of *T. ferrooxidans* alone [66]. *T. ferrooxidans* in mixed culture with mixotrophs like *T. acidophilus* [56] and *T. organoparus* may have improved leaching capability. Likely, this is the result of removal of organic acids such as pyruvate which is excreted by *T. ferrooxidans* and can inhibit growth if accumulated. Lastly, some acidophilic heterotrophs have been shown to improve leaching by metal-sulfide oxidizing bacteria. Besides removing waste organics from the vicinity of *Thiobacillus* cultures, such heterotrophs may assist leaching in other ways. The oft-quoted studies by Tsuchiya *et al.* [72] and Trivedi and Tsuchiya [73] demonstrated that a mixture of *T. ferrooxidans* and the acid-tolerant, nitrogen-fixing *Beijerinkia lacticogenes* could be adapted to grow under acidic, high metal ion conditions and was much more efficient at leaching a copper-nickel concentrate than either pure culture alone. Based on these results, the authors postulated that either the *Beijerinkia* fixed nitrogen for the *Thiobacilli* in return for organic carbon or the *Beijerinkia* released surface-active polysaccharides to facilitate attachment by the *Thiobacilli* to the mineral surface.

3.4.5 Typical Bacterial Batch Growth Curve and Bacterial Adaptation

Bacteria reproduce by asexual binary fission. In this key stage of individual cell growth, a single mature cell, after replication of its genetic material, divides in half, producing two daughter cells, genetically identical to the parent (Figure 3.6). It should be noted that for the remainder of this section the term growth will refer to population growth as measured by the total number of bacteria present.

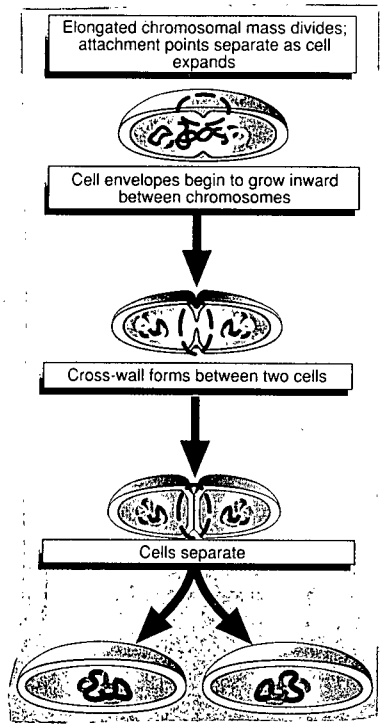


Figure 3.6 : Diagram illustrating typical bacteria reproduction via binary fission (after Chapelle [41]).

In batch growth at the laboratory level, a characteristic growth curve can be derived by plotting the number of observed bacteria versus time (Figure 3.7). 4 distinct regions or phases of growth can be identified. During the lag phase, freshly inoculated bacterial cells rarely divide at all, as they strive to adjust or adapt to their new environment. Once adaptation has been

accomplished, rapid division of the cells begins, indicating the beginning of the exponential or log phase. In this stage of development, cells grow rapidly, dividing as fast as possible. This phase does not last forever. Inevitably, a factor such as a shortage of key nutrients, an accumulation of toxic wastes, or a shortage of living space causes the bacteria to shift resources from reproduction to survival. In this stagnant or stationary phase, the death and growth rates equal, and the number of bacteria remains constant. Lastly, as nutrients are ultimately expended, the death stage occurs, with the population dwindling, individual cell membranes rupturing, and cell internals decomposing in the acid environment.

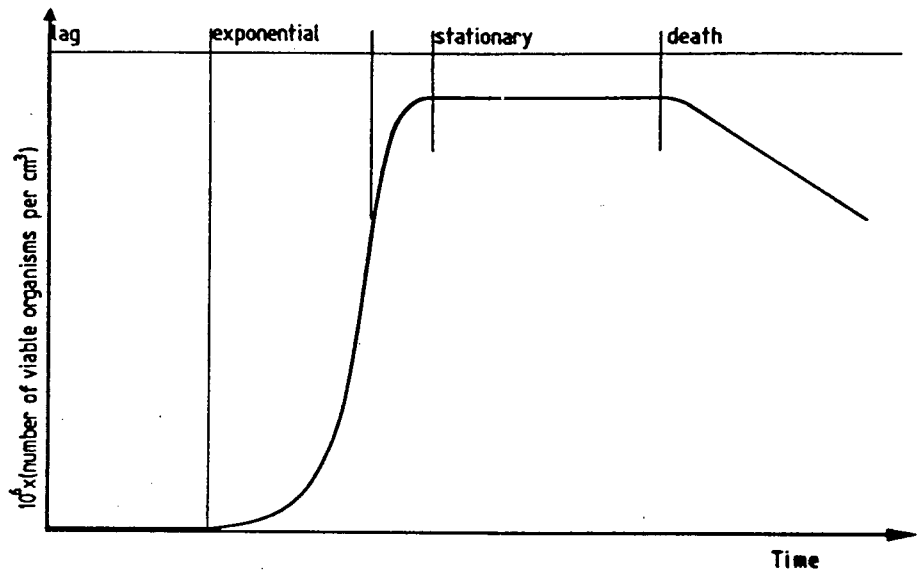


Figure 3.7 : Characteristic bacterial growth curve under laboratory (batch) conditions (after Rossi [16]).

The batch growth curve as shown applies equally to pure and mixed cultures. The only manner in which the curve can change is in the length or duration of the lag phase, reflecting the degree of adaptation. If mature bacteria are repeatedly inoculated into the same environment,

this lag phase eventually diminishes to a minimum (Figure 3.8). Eventually, the lag phase can become so short as to be virtually non-existent. Consequently, the adapted bacteria would mature and divide rapidly shortly after a transfer was completed. This result is the goal of most researchers concerned with bioleaching, batchwise or continuous--a culture in constant exponential phase growth. Such a culture would virtually consume its substrate quickly, as long as the environmental conditions do not change. More importantly from an industrial standpoint, such a culture under maximal growth rates would achieve maximum leaching rates if these optimal environmental conditions are maintained. While this condition is hardly practical for batch systems, it is likely to be a viable goal with continuous systems.

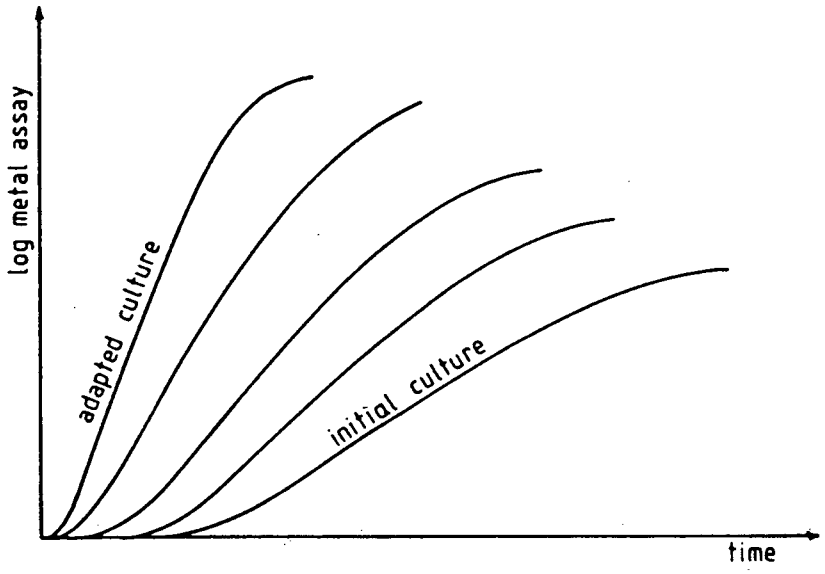


Figure 3.8 : Effect of repeated inoculation of initially non-acclimatized bacteria into the same environment (after Rossi [16]).

Given that adaptation is a key stage in bioleaching, it has been noted by Rossi [16] that two types can occur: physiological or genetic. In the former, all or nearly all cells in the population,

when subjected to a stimulus, change their observable properties or phenotype. This is a reversible process, since removal of the stimulus, in restoring the original environmental conditions, causes the cells to revert back to their original phenotype.

In contrast, genetic adaptation features the much rarer occurrence of mutation, a process in which bacterial cells with permanent changes in genetic character will suddenly occur, and become dominant in the population. Two forms of mutation can occur: selective or unselective. In the former, mutants have an immediate advantage in that, under the new environmental conditions, the remainder of the population is either severely inhibited or obliterated, making the takeover of the population a relatively simple matter. More often, the latter case occurs, in which the impairment of the original population over the mutant results in a slower growth rate of the former, eventually leading to its eventual suppression. The greater the difference in growth rate, the faster the original population will be replaced by the mutant strain.

Henceforth, it can be observed that the environment, in accordance with Darwin's oft-quoted dictum, "survival of the most fitted", and echoing Harrison [57], will select the most suitable bacterial strains, regardless if the necessary changes are physiological or genetic in origin.

3.4.6 Effect of Ions on Bioleaching Bacteria

Clearly, the growth of bioleaching bacteria is inexorably influenced by variations in the environment. Some of the known variables include temperature, water quality, presence of other microorganisms, water activity, presence (lack) of nutrients, aeration, substrate type, and the presence of inorganic or organic contaminants. In this section, the effect of water quality, specifically the presence of various inorganic ions, especially those pertaining to copper bioleaching

in saline water, will be discussed with respect to bacterial growth. While the majority of references are applicable to *T. ferrooxidans*, similar effects can be deemed to apply, by association, to mixed cultures, either enhanced or mitigated by symbiotic relationships.

Generally, it is well known that while the total lack of an essential trace element (or micronutrient) will prevent bacterial growth entirely, a deficiency will be reflected in batch culture as an increase in the lag phase and a decrease in specific growth rate and yield as compared to the optimum situation (Figure 3.9). On the other hand, an overabundance of these same elements has quite detrimental effects, since most of these elements are quite toxic at levels above basic requirements (usually less than 10^{-4} mol/L).

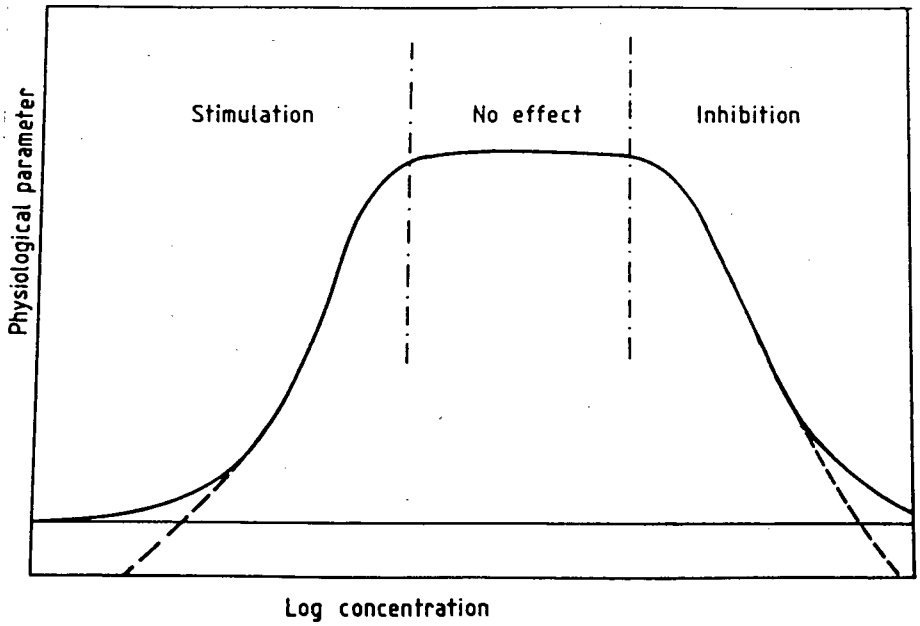


Figure 3.9 : Response in metabolic activity of a pure microbial culture exposed to extreme variations in concentration of a nutrient (after Edwards [74]).

In most of the following case studies involving *T. ferrooxidans*, the presence of various inorganic ions, above certain concentrations, will be demonstrated to inhibit, sometimes severely,

the oxidation of ferrous iron and/or the fixation of carbon dioxide. These physiological activities are considered key to overall growth of *T. ferrooxidans*. Any inhibition of these metabolic functions can be thought to implicitly result in significant disruption to the growth processes of such bacteria.

3.4.6.1 Effect of Cations

Distinctive of species of the genus *Thiobacillus*, and in particular, *T. ferrooxidans*, is the remarkable ability to tolerate heavy metal ion concentrations of the same order of magnitude encountered in hydrometallurgical processes [16, 52, 75, 76]. Tuovinen and Kelly [45] have quantified the inhibiting effect of various cations on both the ferrous ion oxidation and carbon dioxide fixation capabilities of one strain of *T. ferrooxidans*. Their results are summarized in Table 3-7.

This particular strain of *T. ferrooxidans* appears to have a very high initial tolerance for copper (about 65 g/L). In general, initial copper tolerances for strains grown on Fe^{2+} do vary widely, depending on the original habitat from which the strain was isolated; values reported from initial testing range from 1-60 g/L (strains in 2-10 g/L range-Tuovinen *et al.* [77]; strains up to 15 g/L-Karavaiko [49]; strains up to 60 g/L-Paknikar *et al.* [78]). It has been suggested by many investigators that this ability may be related either to specific plasmid-encoded resistance mechanisms of which ample evidence exists [41, 79] or to the very precise, highly selective, control and transport of heavy metals at the cell envelope exhibited by bacteria in general [80]. Chemical factors related to environment or growth conditions can also influence copper resistances [62]. These mechanisms include: (a) protonation of anionic sites on cell walls due to the low pH values of their media; (b) precipitation or conversion of toxic metal ions due to the presence of suitable complexing anions; (c) complexation into the polysaccharide-rich glycocalyx as a result of the presence of organic ligands secreted by cells; (d) the reduced bio-availability of toxic copper

species because of the presence of competing cationic species or substances; and (e) *T. ferrooxidans*' physiological requirement for the element in order to produce the copper-bearing enzyme rusticyanin [81], long thought to be key to its iron-oxidizing ability. Generally speaking, the more complex the medium, the more likely the toxic effects of copper ions are alleviated.

Regardless, not only do certain strains exhibiting high initial copper tolerance exist, but these and other strains also appear to have the capability to either adapt or mutate in order to tolerate higher copper levels, an ability that has been well documented [76, 77, 82]. Fairly recently, Norris *et al.* [83] reported the results of test work which demonstrated that a *T. ferrooxidans* strain which experienced moderate inhibition at 0.1 mol/L Cu could, after repeated culturing on chalcopyrite, be adapted to tolerate copper levels as high as 25 g/L. In addition, these same workers demonstrated that while a *L. ferrooxidans* strain was copper-sensitive in pure culture, the same strain in mixed culture with other bacteria on chalcopyrite could be adapted to withstand a 25 g/L copper level as well.

Lastly, both Dunn [42] and Hughes and Poole [80] made reference to the fact that the s-block elements sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca) are present, in cationic form, at relatively high concentrations in the physiological systems of most bacteria. They also noted that these cations are selectively distributed, with K^+ and Mg^{2+} concentrated inside the cell and Na^+ and Ca^{2+} outside it. Apparently, this particular distribution is fundamental to the biological functions of these cations on bacteria [84]. This last fact has implications for copper bioleaching in saline media--the possibility that most bacteria, including those most commonly encountered in copper bioleaching, may already be inherently resistant to the relatively high levels of the s-block elements, especially sodium and calcium, which are commonly found in saline water sources like underground reservoirs.

Table 3-7: Effect of various cations on biological activity of *T. ferrooxidans* suspensions (after Tuovinen and Kelly [45]).

Cation	Concentration (mol/L)	Percent inhibition of measured biological process	
		Fe^{2+} oxidation	$^{14}CO_2$ fixation
Co^{2+}	1.0	40	*na
	0.1	0	*na
Zn^{2+}	1.0	34	*na
	0.1	0	*na
Ni^{2+}	1.0	75	95
	0.1	0	0
Cu^{2+}	1.0	30	95
	0.5	14	73
UO_2^{2+}	0.05	14	78
	0.01	4	59

*na=not analyzed.

3.4.6.2 Effect of Anions

Certain anions inhibit *T. ferrooxidans*' iron oxidation capability to a larger degree than cations, as seen in Table 3-8, a partial compilation of data by Tuovinen and Kelly [45] based on the works of Andersen and Lundgren [85] and Razzell and Trussell [25]. According to Tuovinen *et al.* [77], the mechanisms for cation tolerance are much more efficient than the analogous mechanisms utilized for either metal anion or pure anion tolerance. Presumably, anions enter the cell interior more freely and consequently interfere with the internal metabolism of bacteria, especially enzymatic activity, to a much greater extent [86, 87].

Table 3-8: Effect of various anions on Fe^{2+} oxidation by *T. ferrooxidans* (after Tuovinen and Kelly [45]).

Chemical Compound	Concentration (mol/L)	Percent inhibition of Fe^{2+} oxidation	Reference
Sodium arsenite	0.025	0	[85]
Sodium arsenate	0.025	0	[85]
Sodium fluoride	0.0025	100	[85]
Sodium cyanide	0.00024	99	[85]
Sodium azide	0.00025	100	[85]
Sodium nitrate	0.07 0.094	40 100	[25] [25]
Sodium chloride	0.086 0.172	50 90	[25] [25]
Potassium chloride	0.257	90	[25]
Sodium sulfate	0.14	0	[25]

Razzell and Trussell [25], first determined, after extensive test work, that the presence of various inorganic salts, particularly chlorides and nitrates, inhibited iron oxidation by suspensions of bacteria later identified as *T. ferrooxidans*. Since subsequent test work with several different inorganic chlorides also inhibited iron oxidation, it was concluded that the phenomenon was caused by the anionic component, chloride ion. Concurrently, it was also determined that *T. ferrooxidans* was insensitive to sodium ion at the levels used in the tests.

Following up their work, Lazaroff [88] observed that chloride inhibition of iron oxidation of *T. ferrooxidans* decreased as sulfate ion concentration increased. His subsequent test work showed that inhibited growth was due to the demand of a relatively high proportion of sulfate

ions to chloride (or other) ions for iron oxidation. He opined that chloride inhibition could be equally viewed as a sulfate requirement (echoed later by Ingledew [89] and Fry *et al.* [90]), supporting the sulfate ion's role in binding Fe^{2+} to the cell envelope to facilitate iron oxidation. Also, he discovered that increased chloride tolerance does take place, after step-wise adaptation periods, eventually producing *T. ferrooxidans* strains capable of oxidizing ferrous iron in media containing an initially unfavourable anionic composition, possibly because of spontaneous formation of mutants able to function in such high-chloride, low-sulfate conditions.

More recently, Lawson [91] performed two sets of chloride-inhibited shake flask studies with a mixed culture dominated by *T. ferrooxidans* with varying amounts of *T. thiooxidans* and *L. ferrooxidans*. Under constant conditions of aeration, agitation, temperature (30°C), and nutrients (9K), she added varying amounts of chloride as sodium chloride to one set of tests, and as hydrochloric acid to the other. Inhibition of bacterial growth and bacterial growth rate was measured directly as the time required for positive ferrous iron oxidation. As seen in Table 3-9, NaCl addition definitely inhibited bacterial growth with a concentration of 0.6 % (w/v) halving the growth rate. When chloride ion was added as HCl, a definite sensitivity above the 50 ppm level was shown. Yet, Lawson also noted that growth did occur at higher levels, indicating that adaptation to higher chloride levels did develop.

A follow-up study by Lawson *et al.* [92] confirmed that while Na^+ is not toxic, Cl^- is toxic to a *T. ferrooxidans* strain cultured on a pyrite concentrate. Results indicated that chloride levels higher than 5 g/L had detrimental effects and that attempts to adapt the bacteria to chloride were not successful. Electron microscopy studies showed that the reason for chloride toxicity is cell membrane damage. It is likely that the associated damage to membrane transport systems allows chloride ion to more freely enter the cell interior, interfering with proton transport, denaturing proteins, affecting enzymatic processes, and ultimately, inhibiting bacterial metabolism.

These results imply that *T. ferrooxidans* strains adapted to high chloride levels can be developed, making their use in hydrochloric, ferric chloride, or other high concentration chloride-based leaching systems much more feasible. Today, the attribute that many bioleaching researchers worldwide would like to see improved in *T. ferrooxidans* is its chloride tolerance [16, 52, 93, 94, 95] above the 6 g/L level (equivalent to 0.172 mol/L or 1% (w/v) of NaCl); it is constantly the subject of genetic manipulation studies.

Table 3-9: Summary of chloride-inhibited shake flask tests with mixed culture dominated by *T. ferrooxidans* (30°C, 9K, no solid substrate) (after Lawson [91]).

Tests with NaCl addition	
g NaCl /100 mL	Days for positive growth
0	4
0.6	8
1.2	11
2.4	15
4.8	-

Tests with HCl addition	
ppm Cl^-	Days for positive growth
0[a]	3
10	3
50[b]	3
100	4
1000	5

[a] chloride removed from 9K, [b] chloride concentration in 9K.

3.4.6.3 Salinity

Many investigators, including Atlas [40] and Forage *et al.* [96], assert that there exists a group of bacteria and algae which survive or grow optimally in the low water activity environment created specifically by the presence of sodium chloride (NaCl) in solution. Microorganisms which are capable of surviving at NaCl levels as high as 4.5 mol/L but grow optimally at lower levels are termed halotolerant (e.g. *Staphylococus epidermis*, *S. aureus*, and salt-tolerant yeasts and

fungi). In contrast, halophilic organisms require NaCl for growth and grow optimally at concentrations approaching saturation levels. So, moderate halophiles, including many marine microorganisms, grow optimally under 0.2-0.5 mol/L saline solutions while extreme halophiles, which include the halobacteria and halococci, grow optimally in saline concentrations ranging from 2.5 mol/L to saturated solutions. Under this particular classification scheme, it should be noted that most metal-solubilizing bacteria of interest to biohydrometallurgists are considered to be freshwater bacteria. These are relatively salt intolerant, being able to only tolerate levels up to 1% (w/v) NaCl. High salt levels normally disrupt the membrane transport systems and denature the proteins of bacteria unsuited to such conditions [40].

Although the existence of halotolerant/halophilic metal-solubilizing or sulfur-oxidizing bacteria has long been postulated, there are few verified published reports. In 1928, Isachenko and Salimovskaya [97] isolated several halophilic strains which would be later grouped together by Zaslavsky [98, 99] as the species *Thiobacterium issatchenkoo*. Once thought to be a halotolerant/halophilic variant of *Thiobacillus thioparus* [49], there appeared to be little or no evidence of its ability to survive in salt solutions. In the late 1960's, strains of marine thiobacilli, some with distinctive characteristics in common with *T. thioparus* and demonstrating a growth requirement for seawater, were isolated from estuarine, neritic, and oceanic habitats [100, 101].

More recently, *Thiobacillus prosperus*, a marine bacterium isolated by Huber and Stetter [102], shows the most promise for bioleaching in saline environments. Its cells are Gram-negative rods, 3-4 μm long by 0.2-0.4 μm wide, with a 4 μm long polar flagellum. Growth was exhibited between 23-41°C, pH 1.0-4.5, and 0-3.5% NaCl (w/v). Like *T. ferrooxidans*, *T. prosperus* is an obligately chemolithoautotrophic aerobe, deriving its metabolic energy from inorganic sources like sulfide ores, other reduced sulfur compounds, and hydrogen sulfide. However, unlike *T. ferrooxidans*, it does not grow on elemental sulfur or ferrous iron.

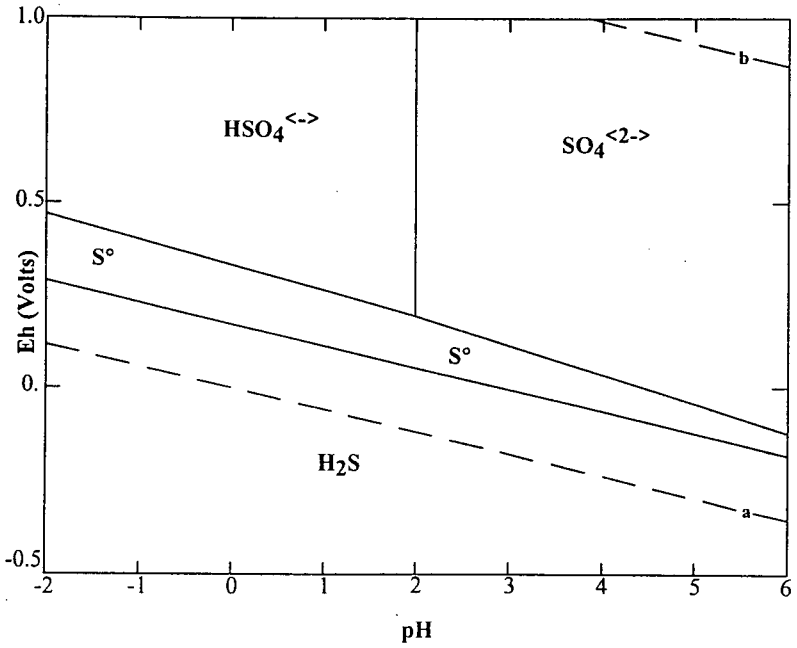
3.5 Thermodynamic Aspects of Copper Sulfide Leaching Systems

In this section, all of the E_h-pH diagrams presented were produced by the CSIRO Thermochemistry program [103]. Primary sources of free-energy data included *Standard Potentials in Aqueous Solution* [104] and the *INCRA IV Monograph on Copper* [105]. If these sources did not possess the required data, the Thermochemistry program's internal data was used instead, although this usage was kept to a minimum (See Appendix F for tables of (a) the species considered for stability and of (b) the researched free-energy data for specific species). CuO will appear to be the predominant species in the acidic high E_h domains of most diagrams involving Cu and S. In practice, hydroxides, sulfates, hydroxy-sulfates (e.g. jarosites), carbonates, and hydroxy-chlorides, anhydrous or hydrated, will exist in these regions. However, satisfactory free-energy data, external or internal to the program, for these compounds were lacking.

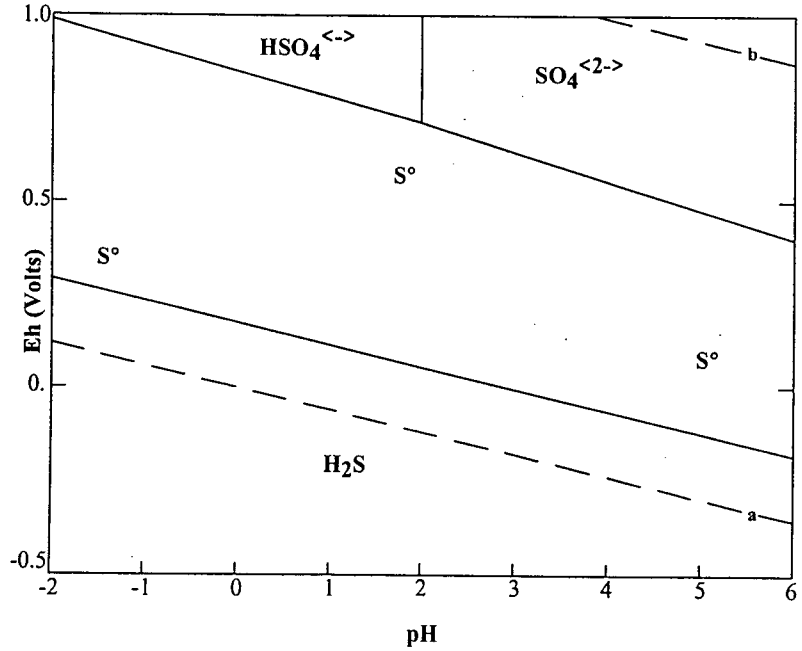
3.5.1 S-H_2O System

Figure 3.10 (a) shows the E_h-pH diagram for the sulfur-water system at 25°C under standard conditions. It is evident that elemental sulfur is thermodynamically stable in a relatively narrow zone of E_h under acidic conditions. However, this prediction is not reflected in industrial inorganic leaching practice with acidic ferric-ion based solutions. Peters [106] noted that sulfur is known to be far more stable with respect to oxidation, because it is unoxidized when undergoing abiotic leaching in acidic ferric ion solutions at the Fe^{3+}/Fe^{2+} redox potential of 0.771 V_{SHE}. Alternatively, since elemental sulfur is hydrophobic, aqueous lixiviants may not be as effective.

To account for its observed stability, Peters [106] artificially extended the sulfur stability area by destabilizing the sulfate/sulfur equilibrium line by 300 kJ/mol. Figure 3.10 (b) is the resulting diagram. It now accurately reflects hydrometallurgical observations under acidic ferric ion leaching conditions.



(a)



(b)

Figure 3.10 : E_h-pH diagrams for the S-H_2O system at 25°C, [S] solute species = 1 M, $P(H_2S(g))$=1 atm. under (a) standard conditions, and (b) when extended sulfur stability is realized by destabilizing the sulfate/sulfur equilibrium line by 300 kJ/mol.

3.5.2 Cu-S-H_2O System

Figure 3.11 (a) depicts the standard E_h-pH diagram at 25°C for Cu-S-H_2O. Covellite, CuS, is the only stable phase with a common region of stability with elemental sulfur. In contrast, chalcocite, Cu_2S, is not stable in the presence of sulfur, it converts to covellite via equation 3-6:

$$Cu_2S + S^\circ \rightarrow 2CuS \tag{3-6}$$

Clearly, covellite's stability zone is surrounded by that for chalcocite, suggesting that covellite can be both oxidized and reduced to yield chalcocite. According to Peters [106], under industrial leaching conditions, covellite does not oxidize to chalcocite, except in ore deposits (i.e. over geologic time). Meanwhile, chalcocite does leach to yield covellite and cupric ion by equation 3-7,

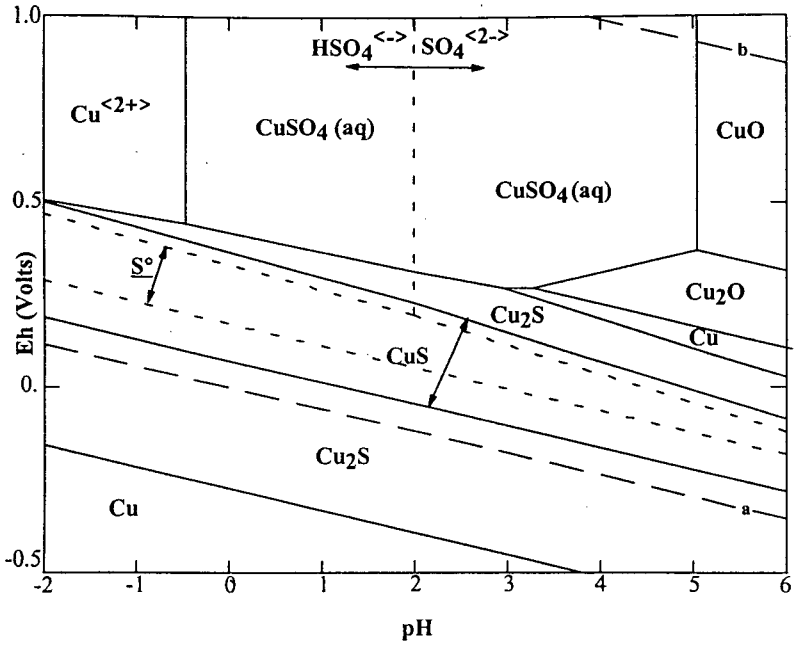
$$Cu_2S \rightarrow CuS + Cu^{2+} + 2e^- \tag{3-7}$$

and the by-product covellite leaches to yield cupric ion and elemental sulfur as follows:

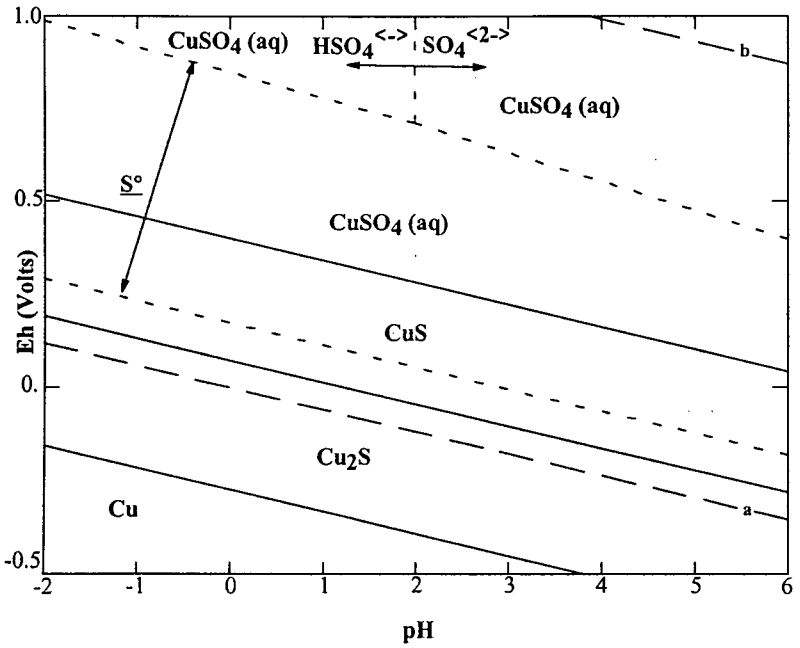
$$CuS \rightarrow Cu^{2+} + S^o + 2e^- \tag{3-8}$$

It is noteworthy that Figure 3.11 (a) does not exhibit a region of common stability for both cupric ion and sulfur, although both are known to be present when copper sulfides are leached, as illustrated by equations 3-7 and 3-8. Also, the soluble $CuSO_4$ (aq) species is present, occupying the region between -0.5 and 5 in pH and E_h values greater than 0.5 V_{SHE}.

Figure 3.11 (b) is the same diagram with extended sulfur stability. Both of the stability zones of covellite and $CuSO_4$ (aq) have expanded, at the expense of Cu_2S, Cu, CuO, Cu_2O, and Cu^{2+}. This diagram is now consistent with industrial leaching practice. That is, (a) covellite does not oxidize to chalcocite and (b) cupric ion and elemental sulfur do have a region of co-existence (keeping in mind that $CuSO_4$ (aq) dissociates readily to cupric and sulfate ions).



(a)



(b)

Figure 3.11 : E_h-pH diagrams for the Cu-S-H_2O system at 25°C, [S, Cu] solute species = 1 M, $P(H_2S(g))$=1 atm. under (a) standard conditions, and (b) when extended sulfur stability is realized by destabilizing the sulfate/sulfur equilibrium line by 300 kJ/mol.

3.5.3 Cu-S-Cl-H_2O System

Addition of the chloride ion ligand, Cl^-, to Figure 3.11 (a) results in Figure 3.12, the standard E_h-pH diagram at 25°C for Cu-S-Cl-H_2O. Cl^- addition stabilizes cuprous ion, resulting in the appearance of the CuCl phase, at the expense of cupric ion, $CuSO_4$ (aq), and Cu_2O. Cl^- also complexes cupric ion as the $CuCl^+$ complex is now present. Lastly, a basic copper chloride precipitate, $CuCl_2[CuO_2H_2]_3$, has appeared, replacing CuO (NB: According to the *INCRA IV Monograph on Copper* [105], the free energy data of atacamite correlates best with the afore-mentioned chemical formula).

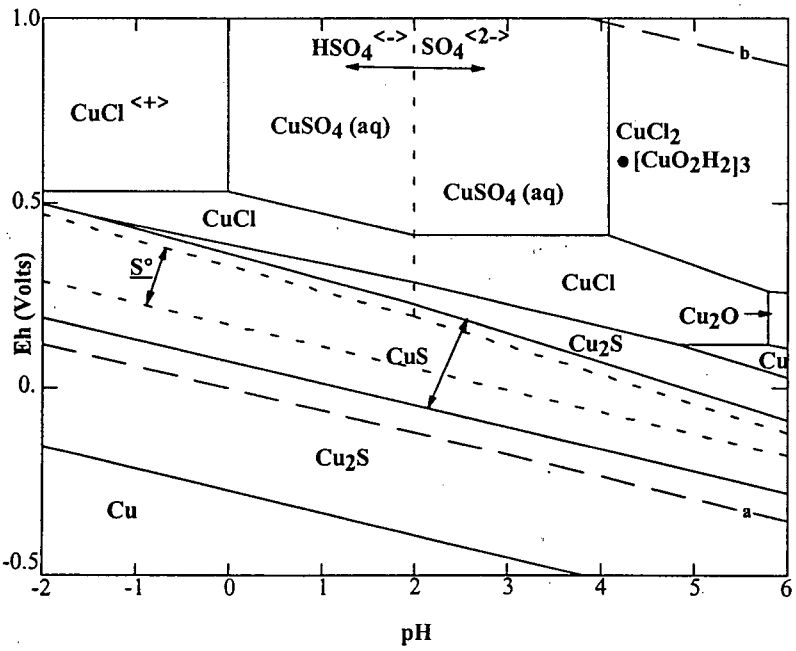


Figure 3.12 : E_h-pH diagram for the Cu-S-Cl-H_2O system at 25°C, [S, Cu, Cl] solute species = 1 M, $P(H_2S(g))$=1 atm. under standard conditions.

Figure 3.13 depicts the same diagram, with extended sulfur stability. Similarly to Figure 3.11 (b), the regions of stability for both covellite and $CuSO_4$ (aq) have greatly expanded at the expense of the CuCl, $CuCl^+$, and $CuCl_2[CuO_2H_2]_3$ phases. Thus, under industrial leaching conditions, like the other two chloride-containing phases, CuCl would be unstable.

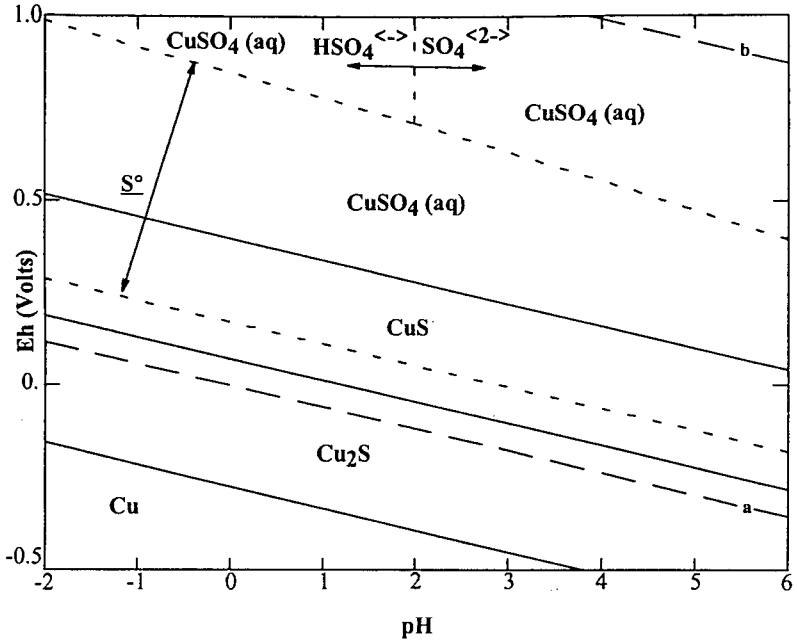


Figure 3.13 : E_h-pH diagram for the Cu-S-Cl-H_2O system at 25°C, [S, Cu, Cl] solute species = 1 M, P(H_2S(g))=1 atm. with extended sulfur stability realized by destabilizing the sulfate/sulfur equilibrium line by 300 kJ/mol.

3.5.4 E_h-pH Diagrams - Implications to Copper Ore Bioleaching

To begin this discussion, it is worth recalling that E_h-pH diagrams predict phase formation from a purely thermodynamic basis. Given enough time to achieve equilibrium, the described phases will form under strictly prescribed conditions. These diagrams neither contain any kinetic information nor do they predict the formation of intermediates since only the final phases are reported.

In the E_h-pH diagrams presented earlier, the first of each pair of figures describes the resulting phases under geologic time, while the second describes those under accelerated time to reflect hydrometallurgical leaching conditions. In both cases, only inorganic reactions capable of being modelled by thermodynamic principles are considered.

At this point, in order to help predict the same situations under bioleaching conditions, metal-sulfide oxidizing bacteria should be introduced. However, these microorganisms are alive, possess metabolism, require certain environmental conditions, and obviously, perform bio-chemical functions which are rate-dependent or kinetic in nature; hence, they cannot be modelled by thermodynamic principles. In spite of this difficulty, the operating regimes of such bacteria can be superimposed on an existing E_h-pH diagram as Lundgren and Dean [107] (Figure 3.14) and Wadsworth [108] (Figure 3.15) have done to help illustrate the situation. Generally, the regime for metal-sulfide oxidizing bacteria can be described as pH 0.5-3.0 and E_h 0.7-0.9 V_{SHE}.

Knowing that bioleaching involves elements of hydrometallurgical leaching conditions and those imposed by bacterial activity, it makes sense that the final outcome in term of product phases will be somewhere between the purely geologic and industrial situations. Also, some reasonable hypotheses can be postulated.

Leaching reactions will proceed at rates as fast or faster than those experienced under purely industrial leaching conditions, but not as slow in accordance with geologic time periods. Sulfide-oxidizing bacteria will facilitate such leaching, ensuring the predominance of sulfate and sulfate complexes. The addition of chloride ion, while resulting in the appearance in the $CuCl^+$, CuCl, and $CuCl_2[CuO_2H_2]_3$ phases under unit activity conditions, otherwise did not significantly affect the dominant copper phase in the region dominated by bacterial activity ($CuSO_4$ or Cu^{2+}). However, it should be noted that the Cu-Cl solid phases could, if precipitated from leaching solutions, play a significant role in the ultimate deportment of leached copper, provided that the right solution conditions are realized. Lastly, the highly oxidizing conditions enhanced by bacterial activity will ensure the predominance of highly-oxidized species.

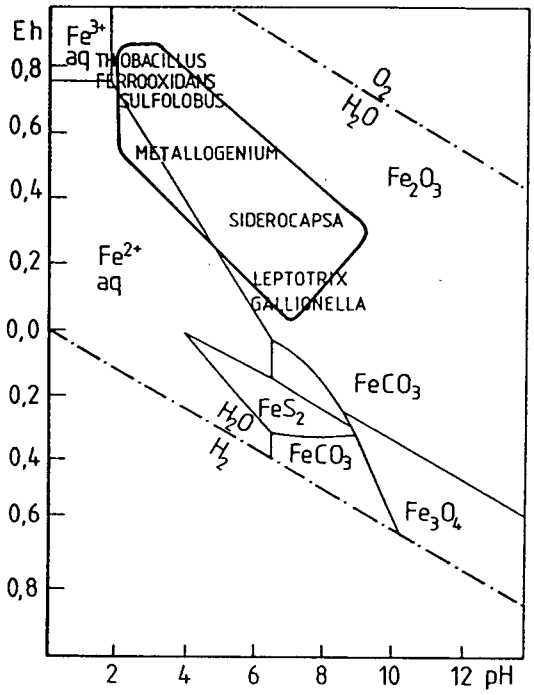


Figure 3.14 : E_h-pH diagram for the Fe-H_2O system showing the natural regimes of the main groups of iron bacteria (after Lundgren and Dean [106]).

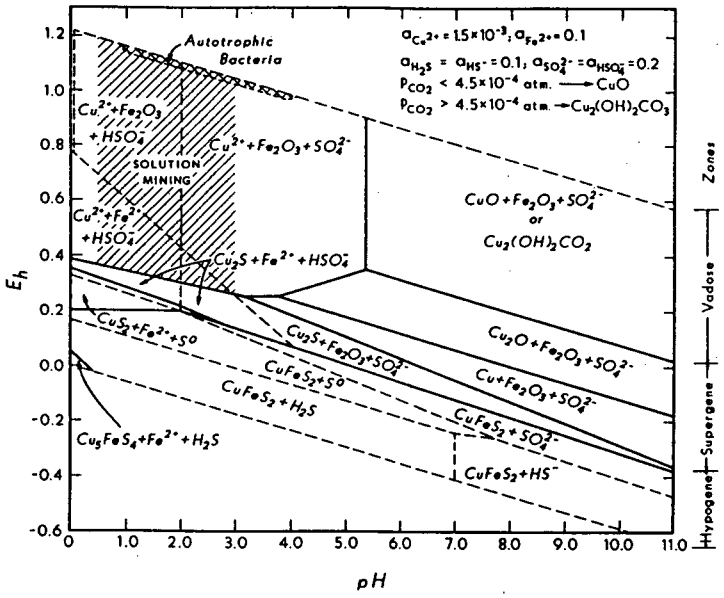


Figure 3.15 : E_h-pH diagram for the Cu-Fe-S-H_2O system illustrating zoning, solution mining region, and regime of bacterial activity (after Wadsworth and Miller [107]).

3.6 Copper Ore Leaching Reactions

In this section, only the overall reactions involving copper ore minerals will be provided, as intermediate products and reactions will have less emphasis. Reactions involving copper oxide minerals will be discussed briefly with respect to background theory, while those involving copper sulfide minerals will be discussed in more detail.

3.6.1 Copper Oxide Minerals

Historically, mixed oxide-sulfide ores have been leached with acidic ferric sulfate solutions [11]. It is common knowledge that sulfuric acid solutions readily leach the oxidized copper minerals (tenorite, cuprite, azurite, and malachite) as follows:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \tag{3-9}$$

$$Cu_2O + 0.5O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + 2H_2O \tag{3-10}$$

$$Cu(OH)_2 \cdot 2CuCO3 + 3H_2SO_4 \rightarrow 3CuSO_4 + 2CO_2 + 4H_2O \tag{3-11}$$

$$Cu(OH)_2 \cdot CuCO_3 + 2H_2SO_4 \rightarrow 2CuSO_4 + CO_2 + 3H_2O \tag{3-12}$$

Less significant in industrial practice are the reactions of these same minerals with ferric sulfate. These reactions, equations 3-13, 3-15, and 3-16, originally from Murr [11], have been modified to reflect the formation of hydronium jarosite, $H_3OFe_3(SO_4)_2(OH)_6$, which is commonly found in industrial practice. The reaction of cuprite with ferric sulfate, Equation 3-14, could not be resolved to produce hydronium jarosite without an iron-based sink for the electrons produced by the oxidation of cuprite; Fe^{2+} ion was logically and arbitrarily chosen to be the reduced product

of Fe^{3+} for the reaction to make sense.

$$5CuO + 3Fe_2(SO_4)_3 + 9H_2O \rightarrow$$

$$5CuSO_4 + 2H_3OFe_3(SO_4)_2(OH)_6 \quad (3\text{-}13)$$

$$Cu_2O + Fe_2(SO_4)_3 + 2H^+ \rightarrow 2Cu^{2+} + 2Fe^{2+} + 3SO_4^{2-} + H_2O \quad (3\text{-}14)$$

$$5Cu(OH)_2 \cdot 2CuCO_3 + 9Fe_2(SO_4)_3 + 22H_2O \rightarrow$$

$$15CuSO_4 + 6H_3OFe_3(SO_4)_2(OH)_6 + 10CO_2 \quad (3\text{-}15)$$

$$5Cu(OH)_2 \cdot CuCO_3 + 6Fe_2(SO_4)_3 + 13H_2O \rightarrow$$

$$10CuSO_4 + 4H_3OFe_3(SO_4)_2(OH)_6 + 5CO_2 \quad (3\text{-}16)$$

3.6.2 Copper Sulfide Minerals

In the bioleaching of copper sulfides, four leaching mechanisms of varying importance are thought to apply. While the first two, direct and ferric sulfate leaching, are assumed to jointly dominate in most situations, galvanic leaching being of minor importance, the last, ferric/cupric chloride leaching, can have significant effects on the efficiency of copper bioleaching operations, especially when process water is derived from saline sources.

3.6.2.1 Direct - Bacterially Mediated Enzymatic Leaching

Direct leaching of metal sulfides by bacteria is an important issue to reviewers of bioleaching [11, 16, 52, 75]. By general consensus, there are strong indications that sulfur-oxidizing bacteria, particularly those of the genus *Thiobacillus*, aided possibly by the presence of either extracellular glycocalx-like organic materials or other surface-active agents, adsorb onto mineral surfaces in order to directly facilitate solubilization by way of a corrosion process. Natarajan [109] has observed that such bacterial corrosion seems to be concentrated on surface defects, crystallographic vectors, and surface heterogeneities of the substrate being studied. Supporting his observations are SEM photographs of bacteria directly attached to these particular sites on crystals of pyrite [11, 110] and chalcopyrite [110, 111]. Furthermore, it is well documented that bacterial oxidation of either the elemental sulfur or the metal-deficient polysulfide by-product of leaching is also facilitated by physical contact with bacteria. However, in spite of these and other advances in current knowledge, the precise modes of attachment, points of attachment, and the exact biochemical pathways employed by the bacteria remain sources of debate among researchers.

According to Murr [11], some of the overall reactions applicable to the direct bioleaching of copper and iron minerals (pyrite, chalcopyrite, chalcocite, and covellite) are as follows:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \tag{3-17}$$

$$CuFeS_2 + 7.5O_2 + H_2SO_4 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + H_2O \tag{3-18}$$

$$Cu_2S + 0.5O_2 + H_2SO_4 \rightarrow CuSO_4 + CuS + H_2O \tag{3-19}$$

$$CuS + 2O_2 \rightarrow CuSO_4 \tag{3-20}$$

3.6.2.2 Indirect - Bacterially Enhanced Electrochemical Leaching

There is substantial evidence in the literature that the leaching of sulfide minerals is, at the very least, partly electrochemical in nature [11, 112, 113, 114]. Supporting this premise is ample data that these minerals are semiconductors and that they exhibit a rest potential in solution. Summaries of data relevant to copper leaching are contained in Tables 3-10 and 3-11. Besides exhibiting the delocalized electron behaviour distinctive of conductors and semiconductors, many base metal sulfides exhibit nonstoichiometry, resulting in enhanced conductivity (i.e. lower resistivity) through the formation of electron holes or excess electrons. An excess of metal cations (or a deficiency of sulfur anions) conforms to an electron donor defect typical of n-type semiconductors while the converse situation (metal deficiency or sulfur excess) produces an electron acceptor defect characteristic of p-type semiconductors [116].

By combining this background knowledge with the known properties of bioleaching bacteria, two electrochemically-based, indirect, bacterially-enhanced leaching mechanisms can be described, namely ferric sulfate and galvanic leaching.

Superficially, both ferric sulfate leaching and galvanic leaching appear to depend solely on the potential differences which can exist between charged species of ionic and solid nature. In practice, the real situation is more complex as other physical, electrochemical, and biological factors exist which can affect both the thermodynamics and the kinetics of the overall reaction. According to Natarajan [109], these factors include relative surface areas of the electrodes (area effect), inter-electrode distance (distance effect), nature and duration of contact between species, electrode conductivity, various electrolyte properties (e.g. pH, conductivity, oxygen availability, presence of other redox species), and the presence or absence of microorganisms.

Table 3-10: Summary of electronic properties of selected sulfide minerals in copper bioleaching (after Koch [114] and Shuey [115]).

Mineral Name	Resistivity (ohm-m)	Conductor Type	Ionic Structure
bornite	10^{-3}-10^{-6}	p	$(Cu^{+})_5Fe^{3+}(S^{2-})_4$
chalcocite	$4x10^{-2}$-$8x10^{-5}$	p	$(Cu^{+})_2S^{2-}$
chalcopyrite	$2x10^{-4}$-$9x10^{-3}$	n	$Cu^{+}Fe^{3+}(S^{2-})_2$
covellite	$8x10^{-5}$-$7x10^{-7}$	metallic	$(Cu^{+})_2S_2^{2-}$
pyrite	$3x10^{-2}$-$1x10^{-3}$	n, p	$Fe^{2+}S_2^{2-}$

Table 3-11: Summary of rest potentials of selected sulfide minerals in copper bioleaching.

Mineral Name	Rest Potential (V vs. SHE)	Measuring Conditions		Reference
		Solution	Temperature	
pyrite	0.63	1.0 M H_2SO_4	25°C	[117, 118]
chalcopyrite	0.52	1.0 M H_2SO_4	20°C	[119]
chalcocite	0.44	1.0 M H_2SO_4	20°C	[120]
covellite	0.42	1.0 M $HClO_4$	25°C	[121]

3.6.2.2.1 Ferric Sulfate Leaching

In ferric sulfate leaching, iron-oxidizing bacteria, especially *T. ferrooxidans* and *L. ferrooxidans*, continuously regenerate the lixiviant, ferric sulfate, by oxidizing ferrous sulfate according to equation 3-1 (Table 3-6). If this solution is formed in the presence of a metal sulfide

mineral, a corrosion cell is formed. That is, a redox reaction between the cationic oxidant, Fe^{3+}, and a solid, semiconducting, metal sulfide electrode. Since the sulfide mineral, as seen in Table 3-11, would typically be at a rest potential lower than that of the solution, the resulting redox reaction would cause mineral oxidation to be coupled to reduction of the ferric sulfate oxidant.

The following equations, after Murr [11], describe the overall reactions for typical ferric sulfate leaching of the copper sulfide minerals of economic interest (chalcocite, covellite, bornite, and chalcopyrite) and of pyrite, which is almost always present in copper sulfide ores.

$$Cu_2S + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + CuS \quad (3\text{-}21)$$

$$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S^o \quad (3\text{-}22)$$

$$Cu_5FeS_4 + 2Fe_2(SO_4)_3 + 6O_2 \rightarrow 5CuSO_4 + 4FeSO_4 + S^o \quad (3\text{-}23)$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^o \quad (3\text{-}24)$$

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^o \quad (3\text{-}25)$$

In general, it is a common conception that the elemental sulfur produced by these reactions, if left unoxidized, would eventually encapsulate the ore particles, creating a diffusion barrier that would effectively halt all further ferric sulfate leaching. However, if the by-produced sulfur is porous, as is usually the case for low temperature leaching, such leaching may only be inhibited as diffusion is only slowed. Regardless, both *T. ferrooxidans* and *T. thiooxidans* oxidize elemental sulfur to sulfuric acid by equation 3-2 (Table 3-6), thus reducing or eliminating any such impediment to diffusion and leaching.

3.6.2.2.2 Galvanic Leaching

In galvanic leaching, two sulfide minerals in direct contact in a conducting solution form a galvanic cell. The mineral with the lower mixed potential will behave anodically, while the other mineral with the higher mixed potential will act as a cathode. Thus, the former will be oxidized and solubilized while the other is passivated.

A noteworthy example of such a system has been described [122] between pyrite and chalcopyrite, two minerals commonly found together in copper ore deposits (Figure 3.16).

On the cathodic pyrite surfaces, the reduction of oxygen occurs, forming water:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (3\text{-}26)$$

On the anodic chalcopyrite surfaces, the following dissolution reaction occurs:

$$CuFeS_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^o + 4e^- \qquad (3\text{-}27)$$

According to Berry *et al.* [122], the effectiveness of galvanic leaching of chalcopyrite-pyrite mixtures is enhanced by the activity of iron and sulfur-oxidizing bacteria. As with ferric sulfate leaching, these bacteria facilitate the oxidation of intermediate ferrous iron and elemental sulfur via equations 3-1 and 3-2 (Table 3-6), regardless of source, allowing the dissolution of chalcopyrite to proceed unimpeded.

While chalcopyrite-pyrite mixtures are most common in copper leaching operations, other similar contact systems can be envisioned not only between copper and iron minerals (e.g. covellite-pyrite, bornite-pyrite, chalcocite-pyrite, etc.), but also between copper minerals and other non-ferrous minerals (e.g. chalcocite/sphalerite, etc.) when complex ores are considered.

Taken literally at a superficial level, this type of leaching is apparently most significant with ores in which intergrown minerals are in intimate contact. Yet, stirred tank leaching of particles can also permit such intimate particle-particle contact to occur as well.

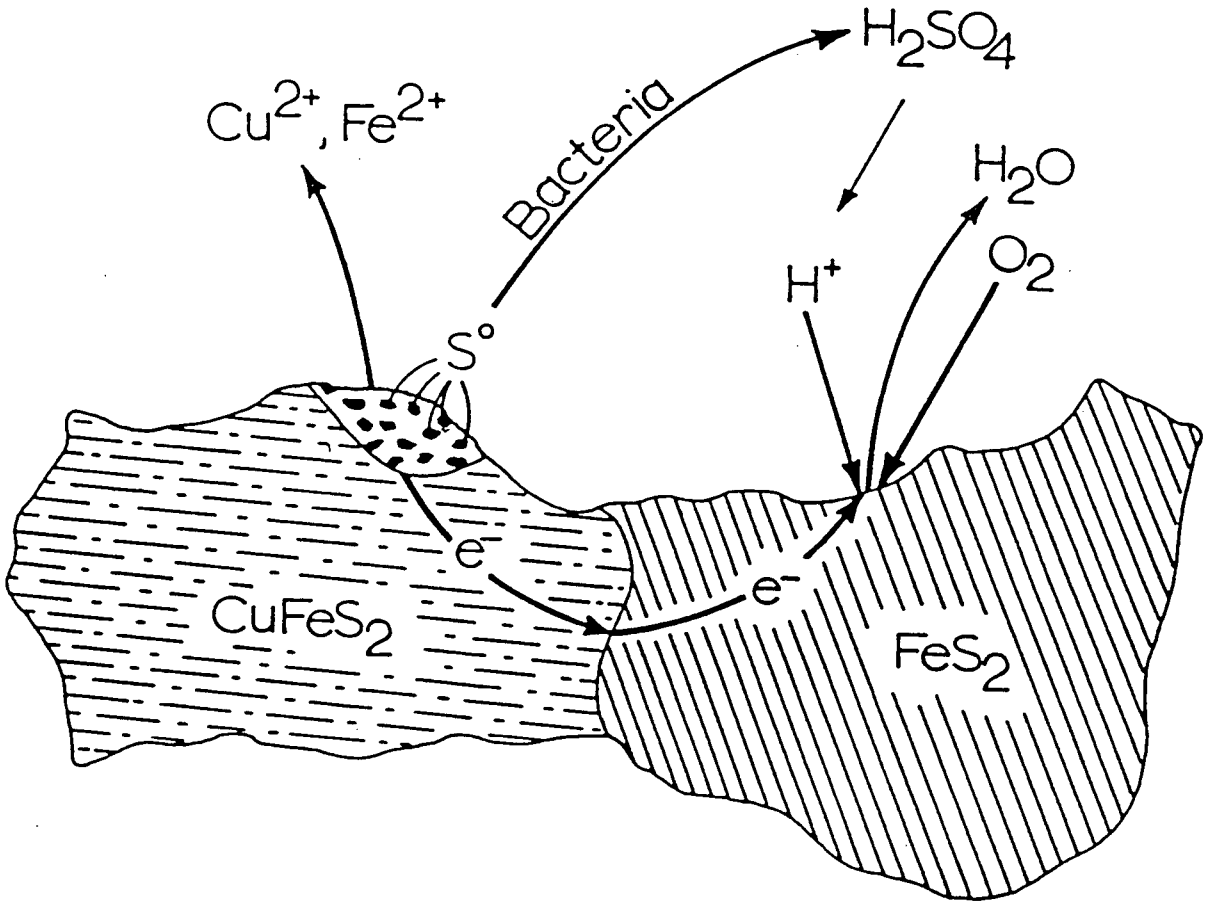


Figure 3.16 : Illustration of bacterially enhanced galvanic leaching mechanism between pyrite and chalcopyrite (after Murr [11]).

3.6.2.3 Indirect-Ferric/Cupric Chloride Leaching

As noted in recent reviews by Dutrizac [123], Hoffmann [124], and Ngoc *et al.* [125], the chemistry of chloride-based leaching processes for recovering copper from ores and concentrates has been studied for more than a century. The attractive features of this technology include (a) the high solubility of copper chlorides compared to sulfates, (b) the highly effective oxidizing capability of ferric and cupric chlorides, (c) the mineral solubilization-enhancing formation of water soluble chloride complexes such as $CuCl_3^-$, $CuCl_4^{2-}$, $CuCl_2^-$, $CuCl_3^{2-}$, and (d) the increased chloride and hydrogen ion (H^+) activities in HCl solutions made with alkali or alkaline earth chlorides [10]. It is noted that, while numerous leaching processes based on this technology have been developed, none are currently in commercial use, in spite of demonstrated success at the pilot plant scale.

The most promising of these processes are those based on ferric chloride, like the methods developed by the U.S. Bureau of Mines [126], MINTEK [127], Cymet (Cyprus Metallurgical Corporation) [128, 129], Elkem (Elkem Spigerverket A/S, Oslo, Norway) [130], U.B.C.-Cominco (University of British Columbia - Consolidated Mining and Smelting Company of Canada) [131], the joint partnership of Tecnicas Reunidas, Nerco Minerals, and Imperial Chemicals Industries known as Hydrometals JV [132, 133], and Great Central Mines [134]. Also, of note are the cupric chloride based processes, in particular, those developed by Duval Corporation [135, 136, 137] and Minemet Recherche [138].

With respect to ferric chloride leaching of a chalcopyrite-pyrite mixture, the reactions are postulated to be as follows:

$$CuFeS_2(s) + 3FeCl_3(aq) \rightarrow CuCl(s) + 4FeCl_2(aq) + 2S^o(s) \qquad (3\text{-}28)$$

$$CuFeS_2(s) + 4FeCl_3(aq) \rightarrow CuCl_2(aq) + 5FeCl_2(aq) + 2S^o(s) \quad (3\text{-}29)$$

$$FeS_2(s) + 2FeCl_3(aq) \rightarrow 3FeCl_2(aq) + 2S^o(s) \quad (3\text{-}30)$$

$$S^o(s) + 4H_2O(aq) + 6FeCl_3(aq) \rightarrow 6FeCl_2(aq) + 6HCl(aq) + H_2SO_4(aq) \quad (3\text{-}31)$$

The corresponding, postulated reactions for cupric chloride attack are given as follows:

$$CuFeS_2(s) + 3CuCl_2(aq) \rightarrow 4CuCl(s) + FeCl_2(aq) + 2S^o(s) \quad (3\text{-}32)$$

$$FeS_2(s) + 2CuCl_2(aq) \rightarrow FeCl_2(aq) + 2CuCl(s) + 2S^o(s) \quad (3\text{-}33)$$

$$S^o(s) + 4H_2O(aq) + 6CuCl_2(aq) \rightarrow 6CuCl(s) + 6HCl(aq) + H_2SO_4(aq) \quad (3\text{-}34)$$

During inorganic ferric chloride leaching of any sulfide ore or concentrate containing copper minerals, the $CuCl_2$ by-product generated will also participate in the leaching process [125]. Secondly, the elemental sulfur by-product is very stable, this premise supported by many fundamental studies reporting its dominant nature in the final product [123]. Thirdly, it should be noted that most of the above-mentioned processes operate at temperatures near the solution boiling point. This last fact arose from observations by other researchers that chalcopyrite leaching is highly temperature dependent [123].

It is noteworthy that Jones and Peters [139], in laboratory tests involving chalcopyrite, asserted that ferric chloride is a more effective lixiviant than ferric sulfate, particularly as particle size decreased, ferric ion concentration increased, or as temperature increased. Examination of

the surface of leached chalcopyrite particles revealed that ferric chloride leaching attacks the entire surface while ferric sulfate leaching tends to be limited to selected regions such as grain boundaries. This result supports the observation that fine grinding, if all grains have been fully liberated, is beneficial for the former but not the latter.

Such indirect chloride leaching of copper sulfides can have implications, no matter how small, for the bioleaching of copper (and iron) sulfides in saline media. First, ferric or cupric chloride leaching of such sulfides will undoubtedly occur in these situations, although the extent of such leaching may be limited by the optimum bioleaching temperature of 35°C. This is considerably lower than the operating temperatures of the aforementioned processes. Second, the presence of alkali or alkaline earth chlorides in saline groundwater can enhance sulfide dissolution through copper chlorocomplex formation, subject to the limited chloride tolerances of the resident bacteria. It is significant that many of the earlier-mentioned processes feature brine solutions made with chloride salts, making use of the associated advantages. However, it must be mentioned that no less an authority than O. H. Tuovinen, a recognized expert in the field of biohydrometallurgy, in a recent book [76], made a dissenting statement about the viability of copper bioleaching under saline conditions, stating that, "At present, therefore, there is no recognized microbiological basis for developing biohydrometallurgical applications for ferric-chloride leaching in chloride environments."

3.6.3 Gangue Mineral Reactions

As noted by many reviewers including Rossi [16], the presence in ore bodies of oxides of alkaline metals, carbonates, silicates, and aluminosilicates results in increased sulfuric acid consumption of leaching operations. Equation 3-36 is the generalized equation representative of acid (proton) solubilization of constituent rock minerals (such as aluminosilicates) usually considered to be gangue minerals.

$$(mineral)M^{+} + H^{+}R^{-} \rightarrow H^{+}(mineral) + MR \quad (3\text{-}36)$$

where R^- could be any of the following ions: NO_3^-, $R'COO^-$, HCO_3^-, or SO_4^{2-}.

The next two equations represent the general formation of soluble metal-organic complexes or chelates under acidic bioleaching conditions. In the following equations, the complexing or chelating ligands (denoted as L) produced by microorganisms promote metal removal from the gangue minerals in the host rock.

$$(mineral)M^{+} + H^{+}L^{-} \rightarrow H^{+}(mineral) + LM \quad (3\text{-}37a)$$

$$H^{+}L^{-} + LM \rightarrow [L_2M]^{-} + H^{+} \quad (3\text{-}37b)$$

3.6.4 Importance of Iron Precipitation and Jarosite Formation

One of the most important aspects in bioleaching is the deportment of the ferric sulfate that is catalytically generated by bacterial activity. Besides being reduced in mineral solubilization reactions, forming ferrous sulfate, significant amounts can hydrolyze to form different types of iron precipitates, as seen in the following equations, after Hackl *et al.* [140]:

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \quad (3\text{-}38)$$

$$Fe_2(SO_4)_3 + 2H_2O \rightarrow 2Fe(OH)SO_4 + H_2SO_4 \quad (3\text{-}39)$$

$$3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2H_3OFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad (3\text{-}40)$$

Unfortunately, the above overall reactions do not fully describe the actual process, particularly equation 3-38; there exists an entire series of 4, hydrolysis-driven, aqueous ferric hydroxide complexes [141, 142], including the forerunner to $Fe(OH)_3$, the precise nature and composition depending on the total dissolved iron content and, in particular, on the solution pH:

$$Fe^{3+}(aq) + nH_2O \leftrightarrow Fe(OH)_n^{(3-n)+}(aq) + nH^+ \tag{3-41}$$

Under normal dump leaching conditions [28], (pH 2 to 5, total iron concentration = 10^{-1} to 10^{-4} M), the n=3 precipitate prevails, since the n=4 complex is unstable and the other two complexes remain soluble. Thus, for n=3 and at pH > 4, limonite, $Fe(OH)_3 \cdot xH_2O$, precipitates extensively,

$$Fe(OH)_3^0(aq) + xH_2O \leftrightarrow Fe(OH)_3 \cdot xH_2O \tag{3-42a}$$

and subsequently ages to goethite, $\alpha FeO(OH)$:

$$Fe(OH)_3 \cdot xH_2O \rightarrow \alpha FeO(OH) + (x+1)H_2O \tag{3-42b}$$

Alternatively, the *T. ferrooxidans* generated ferric ion, in the presence of acidic ferrous sulfate solutions containing ammonium or alkali metal ions, can be converted into jarositic compounds by the following reaction sequence proposed by Trivedi [143]:

$$Fe^{3+} + 2SO_4^{2-} \rightarrow Fe(SO_4)_2^- \tag{3-43a}$$

$$Fe(OH)_3 + Fe(SO_4)_2^- + H_2O + \tfrac{2}{3}M^+$$

$$\rightarrow \tfrac{2}{3}MFe_3(SO_4)_2(OH)_6 + \tfrac{2}{3}SO_4 + H^+ \qquad \text{(3-43b)}$$

where M can denote H_3O^+, NH_4^+, Na^+, K^+, etc.

Regardless of the precise process, the primary variables affecting iron precipitation include temperature, solution composition (especially the presence of complexing ions and the total iron content), and pH. Generally, during copper bioleaching, significant amounts of ferric iron does precipitate, releasing sulfuric acid, lowering the pH, and ensuring that the remaining iron, ferrous and ferric, remains in solution. A specific drawback of such precipitation is the possibility that such by-products will coat mineral sulfide surfaces, reducing permeability and oxygen diffusion, eventually impeding or terminating any further leaching, biotic or abiotic, altogether.

3.7 Kinetic Studies of Chalcocite & Covellite Leaching

In this section, selected kinetic studies of chalcocite and covellite leaching have been reviewed to provide a suitable background for discussion of the experimental results in Chapter 5.

In 1930, Sullivan [150] reported his findings from bottle-roll tests of chalcocite in acidic ferric sulfate solutions conducted at temperatures below 50°C. Mineral dissolution was described to occur in two steps. The first, oxidation of Cu_2S (equation 3-44a), was rapid until about 50% copper dissolution, while the second, oxidation of CuS (equation 3-44b), took place at a relatively slower rate.

$$Cu_2S + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + CuS \quad (3\text{-}44a)$$

$$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + 2S^o \quad (3\text{-}44b)$$

His results indicated that the leaching rate did not depend on the ferric sulfate concentration, as long as adequate amounts of ferric ion were present. Under a constant ferric-ion concentration, the rate was unaffected by acid strength. Despite a substantial change in surface area per unit mass over the particle size range tested (-10 mesh to 200-mesh), essentially no difference in leaching rate was detected, provided that the mineral particles were exposed to solution attack. Lastly, the copper leaching rate was found to be greatly affected by temperature (e.g. 73% copper dissolution required 1, 5, and 15 days at 50°C, 35°C, and 23°C, respectively).

The bacterially-mediated, oxidative leaching of iron-free, pulverized chalcocite directly by cell suspensions of *Thiobacillus ferrooxidans* has been studied in detail [152, 153]. Results indicate that leaching occurred in two steps. The first, consisting of the oxidation of Cu_2S to CuS and Cu^{2+} (equation 3-45a), was reported to occur at a much faster rate [153] than the second, slower oxidation of CuS to Cu^{2+} and S° (equation 3-45b).

$$Cu_2S \rightarrow CuS + Cu^{2+} + 2e^- \quad (3\text{-}45a)$$

$$CuS \rightarrow Cu^{2+} + S^o + 2e^- \quad (3\text{-}45b)$$

A subsequent study by Beck [154] determined that bacterial activity increased the rate of equation 3-45a by about 40 times and confirmed that chalcocite oxidation (equation 3-45a) proceeded kinetically faster than covellite oxidation (equation 3-45b).

Acid ferric chloride leaching of chalcocite was studied by King *et al.* [155]. X-ray powder diffraction studies of partially leached mineral revealed a succession of products with compositions ranging between Cu_2S and CuS. From their observations, a two-stage leaching process can be postulated, with overall reactions as follows:

$$Cu_2S + 2FeCl_3 \rightarrow CuCl_2 + CuS + 2FeCl_2 \qquad (3\text{-}46a)$$

$$CuS + 2FeCl_3 \rightarrow CuCl_2 + 2FeCl_2 + S^o \qquad (3\text{-}46b)$$

The first stage, applicable to almost 50% copper dissolution, was completed in less than 4 minutes at temperatures between 40°C and 80°C. In contrast, second stage leaching was strongly affected by temperature since quicker kinetics were observed at higher temperatures. It was deduced that the first stage was controlled by copper-ion diffusion in the particles and that the second stage was chemically controlled by the oxidation of S^{2-} ions in CuS to form elemental sulfur.

The leaching rate was unaffected by acid (HCl) strength. Increasing the ferric ion concentration up to 0.25 M resulted in increased first-stage leaching, but additional increases proved to have no further effect. Addition of ferrous chloride to ferric chloride solutions yielded the exact same net increase in copper dissolution that resulted with an identical addition of ferric chloride. On the other hand, ferrous chloride (no ferric chloride present) solutions produced slow leaching. Like Sullivan's results, virtually no difference in leaching rates was observed over the particle size fractions tested (425-600 μm, 150-300 μm, and 75-106 μm).

After reviewing Marcantonio's [156] results with ferric sulfate leaching of suspended chalcocite particles at 95°C, Wadsworth [157] developed an electrochemical model. The leaching

process was hypothesized to proceed by a single cathodic reaction (equation 3-47a) and at least two sequential anodic reactions (equations 3-47b and c), keeping in mind that the model required a conducting solid (Cu_2S or CuS) present:

$$Fe^{3+}(aq) + e^{-}(Cu_2S, CuS) \rightarrow Fe^{2+}(aq) \qquad (3\text{-}47a)$$

$$Cu_2S \rightarrow CuS + + 2e^{-}(Cu_2S, CuS) + Cu^{2+}(aq) \qquad (3\text{-}47b)$$

$$CuS \rightarrow + S^{o} + 2e^{-}(CuS) + Cu^{2+}(aq) \qquad (3\text{-}47c)$$

Cheng and Lawson [159] studied the leaching of narrowly sized synthetic chalcocite in acidic oxygenated sulfate-chloride solutions. Tests at four distinct temperatures (65, 75, 85, 94°C) were conducted in a stirred and oxygen-sparged 2 L glass reactor containing the leach solution. Prior to test commencement, the leach solution was oxygenated for at least 2 hours at the selected temperature, after which 2 g of mineral sample was added.

Leaching was described to occur in two stages, the anodic reactions being those described earlier in section 3.5 [106] and in Wadsworth's model [157]:

$$Cu_2S \rightarrow CuS + Cu^{2+} + 2e^{-} \qquad (3\text{-}48a)$$

$$CuS \rightarrow Cu^{2+} + S^{o} + 2e^{-} \qquad (3\text{-}48b)$$

As with the acid oxygen pressure leaching of chalcocite [158], the cathodic reaction was the reduction of O_2, forming water.

$$0.5O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O \qquad (3\text{-}49a)$$

On combining the cathodic and anodic reactions, the following overall reactions for chalcocite and by-produced covellite leaching under these conditions are:

$$Cu_2S + 2H^+ + 0.5O_2 \rightarrow Cu^{2+} + CuS + H_2O \qquad (3\text{-}49b)$$

$$CuS + 2H^+ + 0.5O_2 \rightarrow Cu^{2+} + S^o + H_2O \qquad (3\text{-}49c)$$

Of particular interest to this author was that the leaching behaviour of chalcocite at 85°C under 0.5 M HCl, 0.5M HNO_3, and 0.25 M H_2SO_4 solutions proved to vary widely, despite the fact that the acidity was essentially identical for all three cases. The high leaching rate experienced under 0.5 M HCl was attributed to the presence of chloride ion, while the rate difference between the nitric and sulfuric acid was due to the difference in oxidizing power of the two acids. Analysis of the filtrates led to the conclusion that when chloride ions were present, either alone or associated with sulfate or nitrate, very rapid increases in dissolution rate were experienced, leading to essentially complete dissolution of the copper.

To conclude, Cheng and Lawson maintained that the role of chloride ion was to disrupt the passivating sulfur layer which forms on the particle surface, its complexing effect on copper being of secondary importance.

3.8 Lab-Scale Methods of Evaluating Ore Bioleaching Amenability

As seen in the previous sections, there exists a multitude of variables, known and unknown, which can affect the viability of an industrial bioleaching operation.

According to Tuovinen [76], such processes have been tested at the lab or bench scale with a multitude of samples exhibiting various sulfide mineralizations from many geographical regions. It is common knowledge that no two ores are identical. Even within the same ore body both the

distribution of minerals and the concentrations of metals can vary widely. It is these variations which compel evaluation of multiple samples because the resulting mixture of mineralogical and geochemical properties can dramatically influence the feasibility of bioleaching the ore material. Clearly, bioleaching profiles of mineral samples from each mineralization are unique due to variation in inclusions, mineralogical compositions, acid consumption properties, metal concentrations, and the types and quantities of intermediate or final by-products.

Empirical evaluation of the potential for bioleaching of a copper ore usually involves some combination of the following laboratory-scale techniques: shake flasks, columns, and continuous stirred-tank reactors. While each technique may prove valuable in exploring the effects of various variables (aeration, particle size, pulp density, temperature, nutrient requirements, etc.), they also exhibit intrinsic shortcomings which must be taken into account before industrial scale-up operations can be attempted [16, 76]. In this section, these experimental methods and their limitations are briefly described.

3.8.1 Shake Flask Technique

The shake flask technique allows the examination of many variables in a fairly rapid fashion. Typically, the equipment consists of bottom-baffled, 250 mL Pyrex Erlenmeyer flasks with air-permeable stoppers clamped onto a fixed platform in a temperature-controlled rotary shaker. Suspensions consisting of fixed amounts of media, bacteria, and ground ore/concentrate/mineral samples are shaken continuously in the flasks by the rotary motion, ensuring homogeneous mixing and constant surface agitation in order to enhance dissolution of atmospheric oxygen and other gases (e.g. CO_2) necessary for bacterial metabolism. To ensure survival of bacterial strains, banks of bacteria not used in actual testing are usually maintained in flasks under constant conditions for as long as necessary.

Each actual experiment is started by first allowing the media and solid sample to acclimatize for a fixed period of time (e.g. 24 hours), then adjusting the pH to a fixed value prior to adding the fixed amount of inoculum from a late-log phase bacterial bank. At regular intervals (e.g. daily), agitation is interrupted, evaporative losses are replaced, pH and Eh are measured, pH is adjusted as necessary to maintain test conditions, and aliquots of supernatant solutions are removed for metal analysis. This regimen continues until the test is terminated and the final solids and solutions are obtained. To ensure reliability, duplicate tests are often run in parallel. The biological contribution to metal dissolution is determined by running baseline sterile tests (no bacteria present).

Besides the advantage of more flexibility, shake flask testing is characterized by lower cost, less supervision time, and smaller test samples of ore. Considered useful for screening and preliminary testing for physiological and kinetic investigations, this method is severely limited by continuously changing conditions. Since steady state is not possible, it is difficult to accurately control variables to examine the effects of experimental factors due to amplification, minimization, or negation. Consequently, data from this method is often not considered to be suitable for modelling or scaleup.

3.8.2 Column Technique

This method is less flexible than shake flasks because of size and time constraints but does provide data which is more representative of industrial heap or dump leach situations. Usually, the main piece of equipment consists of a column, constructed from Perspex pipe, transparent plexiglass, or opaque polyvinyl chloride (PVC), supported vertically from a steel trestle or framework. A perforated plate, supported by steel brackets or rods, is located at the bottom end, sometimes with a layer of fiberglass on top. The charge of coarse material to be investigated rests on the plate, and can be added to fill the column almost to the top. Lixiviant, which is stored,

prepared, and collected in a vessel situated directly beneath the column, is circulated to the top of the column by means of a peristaltic pump with an adjustable flow rate. Even solution distribution can be ensured either by placing another layer of fiberglass on top directly beneath the lixiviant outlet or by using spray nozzles. Inspection ports can be located at various positions along the column height to facilitate the obtaining of rock samples, leach solution samples, and other data (e.g. E_h, pH, dissolved oxygen concentration, T).

Column test initiation and maintenance is essentially the same as that for a shake flask test, the only differences imposed by the scale and time involved. Acid acclimatization could take up to a week or more. The size of the inoculum, if desired, will be considerably larger. The volumes to be compensated for evaporation will also be larger. The metal values analyzed will probably be considerably magnified with respect to concentration. Sterile and duplicate tests can be run, subject to economic constraints. Columns can be run in series to simulate actual dump/heap depths and conditions to a very real extent. Lastly, a solvent extraction step to reduce the copper levels and to simulate actual return of raffinate could be added as well.

Column tests share the same basic advantages of shake flask testing, tempered by size and time constraints. Depending on the size of the material being tested, such tests are often of long duration, taking up to several months or years to complete. However, the data, as mentioned earlier, will probably be more realistic and useful in modelling and scaleup. A characteristic feature of such tests, analogous to commercial-scale dump/heap operations, is zoning in the ore material with distinct physical and chemical gradients; such zones may display differences in redox potential, types and quantities of iron precipitation, elemental sulfur formation, and sulfide oxidation extent.

3.8.3 Continuous Stirred-Tank Reactor (CSTR) Technique

Both of the previously mentioned methods have a severe drawback; the environmental changes incurred during operation make any generated kinetic data unsuitable for developing models to be eventually used in designing commercial bioleaching plants. In contrast, for tank leach applications, a continuous stirred-tank reactor which allows aeration, complete mixing of suspended solids and control of environmental parameters can provide very useful kinetic data more amenable for modelling and scaleup purposes.

Currently, there are no commercial-scale continuous biological leaching plants for copper sulfide ores or concentrates, such work being still at the laboratory stage. However, there has been considerably more success with pilot plants and commercial plants utilizing continuous stirred tank biooxidation technology to pretreat refractory gold ores and concentrates. Regardless, the main problem of this technology is cost-associated with running continuously for the desired period of time, usually several months.

3.8.4 Other Limitations of Lab-Scale Testing

Of course, lab-scale testing can only attempt to simulate or represent the real situation in an actual heap or dump. The scale of operations cannot be compared (e.g. millions of tonnes vs. tens of kilograms or grams). Other factors include aeration, permeability, heat generation and loss, solution channelling, ore fragment sizes, particle size distributions, rock weathering, clay formation and stratification, precipitate formation, and organic matter accumulation and stratification [144]. Most of these factors are difficult or virtually impossible to duplicate on a laboratory scale.

3.9 Specific Studies of Copper Ore Bioleaching in Saline Media

From earlier sections, it is clear that the presence of chloride ion unquestionably inhibits the growth of bioleaching bacteria. However, given both the current popularity of low-grade copper sulfide ore leaching and the unequivocal importance of process water quality on bacterial growth, it is surprising that relatively little industrial research on the effect of such a situation on copper extraction efficiency has been reported in the scientific literature.

3.9.1 Early Studies

Ehrlich and Fox [69], in a 1967 paper, suggested that bacterial extraction of copper from low-grade copper sulfide sources may indeed be influenced by environmental effects, be they physical, chemical, or biological. This notion was investigated for pyrite in a 1965 work by Corrick and Sutton [145], who studied the effect of varying specific nutritional factors on pyrite oxidation. They concluded from their manometric (oxygen-uptake) studies of percolator-style tests that the optimum concentrations of the following compounds for maximum pyrite oxidation were:

Table 3-12: Summary of optimum concentrations of chemical compounds to achieve maximum pyrite oxidation during percolator leaching with *T. ferrooxidans* (after Corrick and Sutton [145]).

Chemical compound	Optimum concentration
ammonium sulfate	34 ppm
dipotassium hydrogen phosphate	34 ppm
magnesium sulfate	34 ppm
potassium chloride	34 ppm
calcium nitrate	67 ppm

If these compounds were utilized in excess of these values, ammonium sulfate excluded, inhibition of pyrite oxidation was experienced. Nowadays, much higher levels of these nutrients are used in lab tests without inhibition. Obviously, inhibition of biological functions is affected greatly by the degree of prior adaptation to trace nutrient concentrations by the culture under study.

Earlier still in the same decade, Razzell and Trussell [146] released their results of stationary fermentation culture-based leaching of copper sulfides with a strain of *T. ferrooxidans* grown on 9K medium at pH 2.5. In the tests of interest, they investigated the effect of adding various inorganic compounds, in the presence and absence of bacteria (sterility ensured by the addition of 100 ppm of mercuric nitrate), on the leaching of chalcopyrite and chalcocite mineral samples. Each test, consisting of 50 mL of salt solution and 0.5 g of mineral sample, was run in a 300 mL screw-capped bottle, probably at ambient temperature. Monitoring consisted of tracking the soluble iron and copper levels in each test.

Specifically, in the tests with chalcopyrite, identical results were obtained with iron sulfate addition (ferric or ferrous). Without bacteria, ferrous ion was predominant and the soluble copper concentration increased as the amount of iron sulfate increased. In contrast, with bacteria present, ferric ion predominated, and the copper concentration appeared to decrease with increasing iron sulfate addition. In both cases, the amount of soluble iron decreased with increased iron sulfate addition, particularly at the longer leaching times (57-90 days).

More relevantly, the chalcocite tests investigated the effect of adding ferrous sulfate and sodium chloride. Without bacteria, the addition of these compounds, singly and in combination, tripled the soluble copper concentration realized by the control flasks at 6 days. While the presence of bacteria alone had similar results, the addition of either compound to a bacteria-laden test increased the soluble copper concentration six times. If added jointly with bacteria, the resulting

copper concentration was barely higher than that of the control. To account for this discrepancy, the authors postulated that this result possibly reflected the formation of a dark Cu-Fe precipitate, as was experienced with the corresponding chalcopyrite leaching tests. Presently, it has been noted that the copper loss could also have been as by-produced atacamite ($Cu_2Cl(OH)_3$ (see Figure 3.12 in section 3.5.3), a dark-hued secondary mineral usually derived from cuprite or malachite.

Having already shown that chalcopyrite leaching will occur at sodium chloride levels which apparently block bacterial iron oxidation [25], the authors maintained that this idea held for chalcocite leaching as well, confirming why the soluble iron remained in the ferrous form. Furthermore, the authors maintained that both ferrous sulfate and sodium chloride exert a non-specific salting effect, which increased the spontaneous leaching rate but did not apparently interfere with bacterial leaching.

3.9.2 Column studies

Murr *et al.* [147] performed acid-aqueous-chloride column leach tests with Phelps-Dodge porphyry copper mine waste as part of a proposed hydro-saline process. In 0.1 m diameter columns, 5-7 kg of crushed and sized waste were, for 6-8 week periods, subjected to KCl or NaCl concentrations ranging from 0.04 to 0.17 M, pH 2 (mediated via H_2SO_4 addition), and 28°C conditions. KCl and NaCl were used as naturally saline reservoirs frequently contain various concentrations of either salt. The results (Figure 3.17 and 3.18) indicated that both the amount and rate of copper recovery increased either with increasing chloride concentration or with decreasing particle size, in accordance with established theory. However, it was noted by the authors that (a) metal-solubilizing bacteria, particularly *T. ferrooxidans*, were not viable at concentrations in excess of 0.1 M of either salt and (b) any bacterially mediated reactions would not be very rapid. Neglecting the possibility of adaptation by the native bacteria, it was postulated that other abiotic reactions involving either ferric or cupric chloride were taking place.

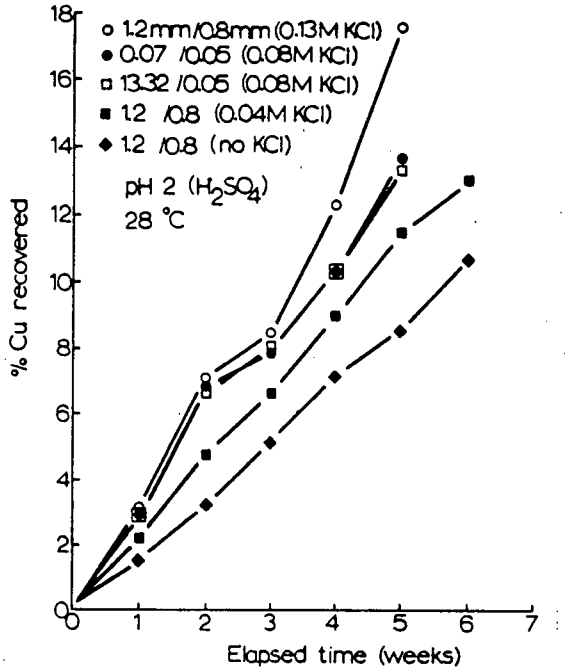


Figure 3.17 : KCl column leaching with Phelps-Dodge copper-bearing waste; the effect of particle size and KCl concentration (after Murr *et al.* [147]).

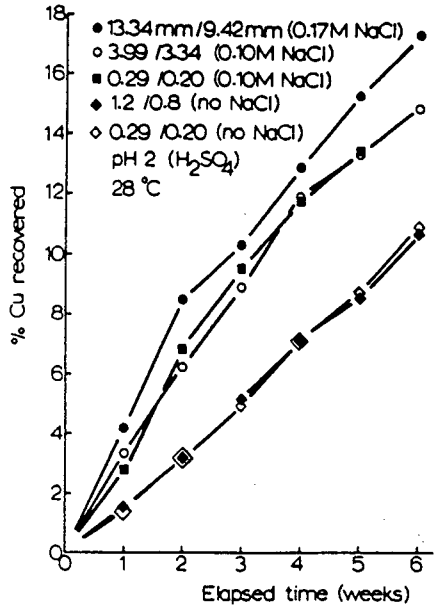


Figure 3.18 : NaCl column leaching with Phelps-Dodge copper-bearing waste; the effect of particle size and NaCl concentration (after Murr *et al.* [147]).

Surprisingly, in a similar study carried out 8 years earlier, Dutrizac and MacDonald [148] had surpassed Murr *et al.*'s [147] work by simulating dump leaching at different temperatures and at a NaCl level of 6 g/L (equivalent to 3.6 g/L Cl^-). The raw ore from Quebec's Golden Manitou Mine assayed 3.60% Cu and 4.30% S. The dominant sulfide was chalcopyrite associated with minor pyrite; the major gangue minerals were quartz, chlorite, dolomite, and siderite. In each test, a charge of 3 kg of crushed -1/4 inch ore, loaded to a 1 meter depth in a 2 inch ID glass tube, was subjected to various temperature/leach time regimes and a circulated leach solution containing 0.1 M Fe^{3+}, 0.1 M H_2SO_4, and 0 or 6 g/L NaCl. Their results are summarized in Table 3-13:

Table 3-13: Effect of NaCl on copper dissolution from Golden Manitou chalcopyrite ore (0.1 M Fe^{3+}, 0.1 M H_2SO_4) (after Dutrizac and MacDonald [148].

Temperature	NaCl Added	Leaching Time	Dissolved Copper
(°C)	(g/L)	(hrs)	(g)
60	0	1330	10.2
	6	1330	17.0
40	0	1080	7.71
	6	1080	4.67
25	0	793	0.87
	6	793	0.36
25*	0	1000	2.12
	6	1000	1.22

* ore from Opemiska Mines, Quebec (1.52% Cu).

Given that 1 g of dissolved copper roughly corresponds to 1 percent Cu recovery, it is apparent that, at 40°C, while the test with 6 g/L NaCl had little better than half the recovery of the salt-less test, this result is nevertheless (a) 10 times better than the same test at 25°C and (b)

8 times better than the no-salt test at 25°C. Clearly, this result, achieved near the optimal temperature range for mesophilic bacteria, is favourable for bioleaching under such conditions. However, the authors, like Murr *et al.* [147], made no comment at all about this possibility, emphasizing only the inorganic leaching aspects of this system. An alternate, perhaps more plausible, explanation of the less than optimal performance of this particular system is poor chloride tolerance by the indigenous bacteria.

Interestingly, Groudeva and Groudev [149] asserted that a mixed culture of chemolithotrophic bacteria used to column leach a pyritic lead-zinc-copper ore was able to survive the high chloride concentrations associated with second stage leaching with a $FeCl_3$-HCl-H_2SO_4 mixture aimed to solubilize the lead content. In particular, this culture, dominated by *T. ferrooxidans*, was claimed to be able to grow at chloride ion concentrations as high as 15 g/L.

3.9.3 Recent Pilot (site-specific) Studies

To date, the only industrial study of water-quality inhibited sulfide bioleaching was described in a paper written by Rusin *et al.* [150]. In it, an investigation into the poor performance of a copper sulfide dump leach-solvent extraction-electrowinning operation was described. After determining that the number of indigenous bacteria in the leach solution, raffinate, and the leached sulfide dump were significantly lower than that in an unleached dump, it was concluded that inhibitory factors in the leach solution and raffinate must be present. While the majority of the toxicity would be attributed to residual organic chemicals carried over from the solvent extraction step, the presence of chloride ion at a level of 5.832 g/L in the leach solution, was deemed to be near enough to the minimum inhibitory level of 10.240 g/L for the indigenous *T. ferrooxidans* strain, and thus, was deemed to be an important factor for consideration as well.

3.10 Summary

On reviewing the scientific literature, it is clear that there is ample physiologically-based evidence that the presence of chloride ion in the process water will adversely affect key metabolic functions of the metal-sulfide oxidizing bacteria involved in copper bioleaching, with the severity of the resulting inhibition dependent on the tolerance level. However, there is research data suggesting that the bacteria can tolerate chloride if sufficient pre-adaptation or mutation has taken place. Also, some researchers suggest that the alkali cations associated with groundwater salinity may already be tolerated by metal-sulfide oxidizing bacteria. From the industrial standpoint, there is indirect evidence, from earlier and more recent studies, that the presence of chloride ion affects the leaching of metal sulfides commonly encountered in bioleaching operations. Most of this recent data ignores the possible implications with respect to any indigeneous bacteria ubiquitously present. Consequently, it can be concluded that there exists a distinct lack of quantitative research data which substantially explores the metallurgical implications of such a situation. In particular, there is a lack of substantial evidence linking chloride-contaminated process water, bacterial activity, and poorly performing operations based on copper sulfide leaching.

It is the primary objective of this thesis to provide, via lab-scale experiments, more concrete, metallurgically-based evidence as to the feasibility of using chloride-contaminated process solutions in copper bioleaching of several different ore samples obtained from the Ivan and Zaldívar Mines. Subdivided further, the sub-objectives are (a) to determine the feasibility of such leaching qualitatively via E_h/pH observations of adaptation experiments at various chloride concentrations and (b) to determine quantitatively via copper-mass balances if it is possible to obtain reasonably high copper extractions from the same sets of experiments.

Chapter 4 Experimental

To achieve the study objectives, the shake flask method was used. As mentioned earlier, this lab-scale method permits fairly rapid evaluation of experimental variables on the bioleaching of copper ores. The following summarizes the background, equipment, experimental parameters, leaching procedures, analytical methods, and decisions made in this thesis.

4.1 Ore Samples Used In Shake Flask Tests

Three different chalcocitic ore samples were used in the testwork, two from Minera Rayrock and one from Minera Zaldívar. Table 4-1 summarizes the copper, iron, and sulfide sulfur contents as well as the primary sulfide minerals of each ore sample used in this thesis.

In the case of the Mina Ivan and the Lower ores, the copper and iron contents were determined by the author in-house at the hydrometallurgical laboratories at U.B.C. (Vancouver, B.C.). This was achieved by treating two representative samples with hot, oxidizing aqua-regia solution, boiling to reduce volume, completing the dissolution with warm bromine, and analyzing a dilute aliquot of the resulting solution for the metals of interest by atomic absorption spectrophotometry (AAS). In this case, copper and iron were analyzed with a Thermo Jarell Ash Smith-Hieftje 4000 Atomic Absorption Spectrophotometer and nitric acid-based standard solutions. Sulfide sulfur content for these two ores, as reported by Chem Met Consultants (Vancouver, B.C.), was determined by two different methods. For the Mina Ivan ore, it was determined as the difference between the total sulfur content in a representative sample as determined with a Leco machine and the sulfate sulfur content in another representative sample leached with a 10% Na_2CO_3 solution, the leachate subsequently treated to achieve quantitative, gravimetric precipitation of $BaSO_4$ (QGP-$BaSO_4$). For the Lower ore, this was determined by leaching a single representative sample with a 10% Na_2CO_3 solution, rejecting the leachate containing solubilized sulfates, totally

oxidizing the residual sulfur content in the leached solids with concentrated HNO_3 and a KBr/Br_2 solution, and QGP-$BaSO_4$. In both cases, other sulfur species present, considered minor, would be included in the reported sulfide sulfur content.

The assay on the Zaldívar ore was conducted at International Plasma Laboratory (IPL) located in Vancouver, B.C. Copper and iron content was determined by subjecting a representative sample to chemical digestion with an aqua-regia/$HClO_4$ mixture, boiling to dryness, reboiling in 5% HCl, and analyzing a dilute aliquot of the resulting solution by AAS. For total sulfur, a separate sample was first boiled in perchloroethylene, the resulting solution containing the elemental sulfur content being taken to dryness, and reoxidized in KBr/Br_2 solution, prior to QGP-$BaSO_4$. The residual solids from the perchloroethylene boiling step were boiled in 5-10% Na_2CO_3, selectively dissolving the sulfate content which was rejected. The post-Na_2CO_3-boil solids were treated with HNO_3 and Br_2, prior to QGP-$BaSO_4$, to determine the sulfide sulfur content.

Samples from the two Minera Rayrock ores were ground, in a ring mill located in U.B.C.'s Geology department, such that 80% (P_{80}) would pass a 200 mesh (75 μm) Tyler screen prior to utilization in test work. The Zaldívar ore sample from the Rhyolite Zone, courtesy of Placer Dome Inc., arrived at U.B.C. preground to -200 mesh (75 μm). See Appendix A for size analyses of the Mina Ivan and Lower ores.

Table 4-1 : Head assays of sulfide ore substrates used in shake flask test work.

Copper Ore Substrate	Wt% Cu	Wt% Fe	Wt% S^{2-}	Sulfide Mineralogy
Mina Ivan[a] (Minera Rayrock)	5.33	2.50	2.12	Cu_2S with minor $CuFeS_2$, Cu_5FeS_4, CuS, and FeS_2.
Zaldívar[b] (Minera Zaldívar)	1.64	2.63	1.14	primarily Cu_2S, FeS_2, and minor $CuFeS_2$.
Lower[a] (Minera Rayrock)	3.87	4.23	1.14	Cu_2S with minor $CuFeS_2$, Cu_5FeS_4, CuS, and FeS_2.

[a] Cu, Fe content determined by author, sulfide sulfur (S^{2-}) content by Chem Met Consultants.
[b] Cu, Fe, and S^{2-} content determined by International Plasma Laboratory.

4.2 Variables Investigated In This Study

Table 4-2 summarizes the pH parameters (starting values and upper operating limit), the variables investigated (chloride and iron levels), and the bacterial nutrient solutions used for all tests conducted in this study.

The pH Start Value and pH Upper Operating Limit for the Mina Ivan and both Lower series were arbitrarily set to primarily limit sulfuric acid consumption while maintaining a viable pH range for the bacteria. Since pH 2.35 was deemed to be the optimum pH for *T. ferrooxidans*, a pH less than 2.5 was thought to be a reasonable starting point for inoculating fresh media with active bacteria. At the other end of the scale, pH 2.86, was deemed a reasonable Upper Operating Limit. In contrast, the same two pH parameters were both set at pH 2.0 for the Zaldívar tests, again arbitrarily.

The values for the various ionic levels tested were arbitrarily set to provide as much quantitative data as possible in order to establish worthwhile trends.

Table 4-2 : Shake flask test parameters of interest for the test series.

Culture Series	Bacterial Nutrient Media	pH Start Value	Chloride Ion (Cl^-) Levels Tested (g/L)	pH Upper Operating Limit
Mina Ivan	9K	<2.5	0, 0.6, 1.8, 5, 8	2.86
Zaldívar (Cl)	9K	<2.0	0, 2.5, 5, 6, 7, 8, 9, 10	2.00
Lower (Cl)	9K-5Cu	<2.5	0, 0.6, 1.8, 2.5 3, 4.2, 5, 5.5	2.86

Culture Series	Bacterial Nutrient Media	pH Start Value	Ferrous Ion (Fe^{2+}) Levels Tested[b] (g/L)	pH Upper Operating Limit
Lower (Fe)	xK-5Cu[a]	<2.5	0, 0.5, 1, 2, 4, 6	2.86

[a] x denotes variable Fe^{2+} level in the medium.
[b] Note: [Cl^-] maintained at 2.5 g/L for this series.

4.3 Typical Shake Flask Procedures

Throughout the experimental phase, there were three shake flask applications: the bioleach test, the sterile leach test, and the stock culture. Their internal contents could include fixed amounts of ore samples, bacterial nutrient solutions, inorganic chemicals of interest, and bacteria. Bioleach tests involved all four factors. Sterile tests involved the use of the first three factors, but bacteria were replaced with a fixed amount of a bactericidal solution (2 g thymol/L methanol). These tests, identical in background chemical composition to their bioleach equivalents, were performed to provide a baseline of chemical leaching and to provide a means of measuring the bacterial

contribution to leaching. The stock cultures (i.e. flasks operated to maintain certain bacterial cultures for inoculating bioleach tests) were virtually identical to bioleach tests in composition and execution, but all procedures pertaining to obtaining sample data for metallurgical balance purposes were usually omitted.

Every shake flask application, be it a bioleach test, a sterile leach test, or a stock culture, was started and operated in similar fashion, differing as the specific application required. Also, all daily measurements of interest (i.e. flask weights, slurry E_h, slurry pH, sulfuric acid additions, and evaporative losses) and observations pertaining to each application were recorded, with the date and time, in activity log sheets for a permanent record.

4.3.1 Starting and Inoculating A Flask Application

Each shake flask including its stopper, was weighed to determine its dry, tare weight. Next, 8±0.05 g of ore sample was carefully weighed, by difference, into the flask.

Subsequently, 70 mL of bacterial nutrient solution and the required volume of 211 g/L NaCl stock solution were added to the flask. After mixing the resulting slurry, the initial pH was measured. If the pH was neither less than nor equal to the Start Value pH, the pH was lowered to this required level by the addition of 6 mol/L H_2SO_4 in 50 μL increments, with the final pH value and the total volume of added acid recorded in the log. This sterile (no bacteria) flask, with its foam stopper, was then weighed to determine the sterile weight, prior to clamping it in a temperature-controlled, rotary-action shaker.

Approximately 23-24 hours later, the flask was retrieved from the shaker and weighed to determine the weight of water lost overnight to evaporation. Subsequently, this difference would be made up from squirt bottles and eyedroppers containing deionized water.

While dipping the E_h probe sufficiently deep into the flask, the contents were swirled to ensure good mixing. Once a constant E_h value was attained, it was recorded into the log. Then, the probe was removed, rinsed off with deionized water, and wiped dry before proceeding with the next task.

Again, while the flask contents were swirled, the pH of the acidified slurry was measured and, if necessary, adjusted again with 6 mol/L H_2SO_4 as necessary to maintain the Start Value pH. For most tests, this action was necessary since it was probable that some acid-consuming reactions involving both gangue and ore minerals would have occurred in the first 24 hour period.

At this point, the flask was ready for inoculation with bacteria. In the case of a bioleach test or a stock culture, this consisted of transferring 5 mL of slurry from an already-monitored, mature, healthy late log-phase stock culture (indicated by two successively close E_h measurements after a sharp rise) into the now pH-standardized slurry in the flask. In the case of a sterile leach, 5 mL of the bactericidal solution was added instead. Also, in the case of a bioleach test, a 1 mL supernatant sample from the stock culture was taken prior to any transferring of slurry. This was necessary to determine the amount of soluble copper and iron which had been added to the new flask.

Once inoculated, the flask was weighed again before storing it in the shaker. This last weight, the system weight, was used during subsequent monitoring. In addition, the time of weighing was recorded. It was desirable that this time be reasonably close to the time that the sterile flask was weighed during the previous day, in order to maintain consistency in the procedure. Finally, the stock culture's volume of solution that was transferred to the new flask was replaced with deionized water before it too was returned to the shaker.

4.3.2 Monitoring and Sampling of Shake Flasks

Table 4-3 summarizes the monitoring and sampling frequencies of the tests described in this work:

Table 4-3 : Monitoring and sampling frequencies for all shake flask test series.

Ore Used	Variation /Series Type	Monitoring Frequency	Sampling Frequency
Mina Ivan	Iron/Chloride	Daily	Every 2 days
Lower	Iron	Daily	Every 2 days
Lower	Chloride	Daily	Every 2 days
Zaldívar	Chloride	Weekdays only	Every Mon., Wed., & Fri. per week of test

Monitoring for each test consisted of weighing each flask, making up for evaporative losses with deionized water, recording the time for this action, and measuring the E_h and pH. In the case of the sterile tests, sterility was maintained by periodic 1 mL additions of the bactericide prior to making up for the evaporative losses. For the Lower sterile tests (Fe and Cl), the interval between such additions was every 3-4 days, while the Zaldívar (Cl) sterile tests were refreshed every Monday and Friday of each week of operation after initiation. If the pH was greater than the Upper Operating Limit (Table 4-2), the pH was lowered by addition of 6 mol/L H_2SO_4.

Subsequently, any required sampling of the bioleach and sterile tests, the frequency described in Table 4-3, was conducted. After permitting the contents of each test flask undergoing sampling to settle for a minimum of 20 minutes, a single, 1 mL supernatant sample was taken for copper and iron analysis. Afterwards, the volume lost to sampling by each flask was replaced by identical volumes of deionized water.

4.3.3 Terminating Shake Flask Leaching Experiments

For the majority of the early scoping work conducted with Mina Ivan ore, a test was considered complete after obtaining a final supernatant pregnant solution sample. That is, no attempt was made to recover and analyze either the wash solution or the final residue. Consequently, no complete mass balance was possible. All extractions were based solely on the pregnant solution analysis and the assayed head.

Similarly, most of the Lower ore tests were considered terminated after the final supernatant pregnant solution sample was obtained. However, the final residue (but, unfortunately no wash solution) was recovered for these tests. In these tests, partial mass balances were prepared with the following assumptions: (a) all soluble copper was in the pregnant solution (i.e. no copper was believed to have re-precipitated during the leach or the filtration step), and (b) a calculated pregnant solution volume was used instead of a measured one.

The Zaldívar (Cl) ore tests, a select few of the Lower (Cl) ore tests, and a set of six check tests on various ores underwent a more thorough treatment to obtain the key values for a metallurgical balance. In these cases, the flask contents were filtered, the filter cake was repulped with deionized water, and the resulting slurry was refiltered (i.e. a repulp wash). In the process, the following data were obtained: a filtrate volume, a filtrate sample analysis, a wash volume, a wash sample analysis, a residue weight, and a residue assay.

4.4 Equipment

All of the shake flask experiments were carried out in well-cleaned, bottom-baffled, 250 mL Erlenmeyer flasks capped with Jaece air-permeable foam stoppers. The specialized glass-blowing required to produce the baffles on the bottoms of the otherwise standard 250 mL

Erlenmeyer flasks was performed by Canadian Scientific Glassware Ltd., Richmond, B.C., Canada. The experiments were run continuously at 250 rpm and 35°C in a New Brunswick Scientific Model G-25 rotary shaker. The air was not enriched with carbon dioxide (CO_2) as atmospheric conditions were deemed sufficient.

For the duration of the shake flask test work, pH and E_h measurements were made with an Accumet 915 pH/E_h meter connected to the appropriate probes. The pH probe used was a non-refillable Canlab Model 5503-20 combination glass pH probe (Ag/AgCl reference) in tandem with an automatic temperature compensation probe. E_h measurements were conducted with an Orion Model 9678-00 combination redox probe filled with a reference solution containing 4M KCl saturated with Ag/AgCl. For the latter, an offset value applicable at 25°C of +199 mV was added to all readings to convert them to the SHE scale.

To ensure good readings, calibration checks and probe maintenance were employed. In the case of pH, a 2 buffer calibration (initially pH 4 and pH 1, later changed to pH 2 and pH 1) method was carried out daily and the efficiency (slope of the correlation between E_h and pH as automatically calculated by the Accumet 915) noted. In the event that calibration could not be achieved or if the efficiency of the pH probe was less than 90%, the probe was cleaned or replaced. To prevent buildup of an iron-precipitate layer on the glass portion of the pH probe, the following cleaning regimen was performed daily: (a) swirl in 0.1 mol/L HCl for 30 seconds, (b) rinse off with deionized water, (c) swirl in 0.1 mol/L NaOH for 30 seconds, (d) rinse off with deionized water and (e) repeat (a)-(d) twice more. In the event that this regimen was ineffective, swirling in 0.1 mol/L EDTA solution would be used in a final effort before the pH probe was replaced.

With regards to the E_h probe, periodic checks of its performance, as outlined in the manual, were carried out by checking that the difference in potential between 2 standard solutions (A: 0.1 mol/L potassium ferrocyanide and 0.05 mol/L potassium ferricyanide, B: 0.01 mol/L potassium

ferrocyanide, 0.05 mol/L potassium ferricyanide, and 0.36 mol/L potassium fluoride) was about 66 mV. Otherwise, maintenance was limited to changing the reference solution when the 2 standards check was unsatisfactory or when precipitates formed inside the probe. Occasionally, particularly when internal precipitate build-up was heavy, the entire redox probe was disassembled to facilitate cleaning.

All samples of leach solutions, serial transfers of bacterial inocula, additions of sulfuric acid, and additions of sodium chloride solution were performed with the aid of an Eppendorf micropipette. Periodically, the micropipette was cleaned and calibrated to ensure its performance.

4.5 Bacterial Nutrient Media

A.C.S. analytical grade chemical reagents were used to prepare the nutrient solutions used in the experiments. In general, the following version of Silverman and Lundgren's [43] 9K medium was used: 3.00 g/L $(NH_4)_2SO_4$, 0.50 g/L KH_2PO_4, 0.50 g/L $MgSO_4.7H_2O$, 0.10 g/L KCl, 45.25 g/L $FeSO_4.7H_2O$, pH $\leq$ 2 via small additions of 6 mol/L H_2SO_4 as needed.

To produce 1 L of 9K, the following solutions were first prepared in separate beakers. Solution A consisted of 3.00 g $(NH_4)_2SO_4$, 0.50 g KH_2PO_4, 0.50 g $MgSO_4.7H_2O$, 0.10 g KCl, and 0.01 g $Ca(NO_3)_2.4H_2O$ dissolved in approximately 500 mL of deionized water. For Solution B, 45.25 g $FeSO_4.7H_2O$ was dissolved in approximately 300 mL of deionized water with 3.2 mL of 6 mol/L H_2SO_4 (12 N H_2SO_4). After Solution B was added to Solution A in a large beaker, constant stirring provided by a magnetic stirrer and a magnetic stir bar, the mixture was made up to 1 L with deionized water. The pH of the final mixture, if greater than pH 2.00, was adjusted to at least this value by a small addition of 6 mol/L H_2SO_4 (12 N H_2SO_4) solution.

For the experiments with Lower ore, a 5 g/L Cu variation of the standard 9K media, denoted 9K-5Cu, was created by adding $CuSO_4.5H_2O$. Ferrous (Fe^{2+}) ion variation was attained by varying the amount of $FeSO_4.7H_2O$ in the 9K-5Cu medium; hence the notation xK-5Cu, x denoting the Fe^{2+} level in g/L. To achieve the required levels of chloride (Cl^-) ion, calculated volumes of 211 g/L NaCl stock solution were added to each flask as required.

After each withdrawal of nutrient solution for bioleach objectives, the storage containers of the various iron-containing media solutions were de-aerated by argon purging, prior to re-capping and re-sealing with Parafilm "M" laboratory film. These actions were done to minimize the occurrence of premature atmospheric oxidation of ferrous ion to ferric ion.

4.6 Bacterial Cultures - Origins and Generational "family" trees

At the start of the bioleaching program, three samples of mixed cultures dominated by bacterial species of the genus *Thiobacilli* were obtained as donations from Bacon, Donaldson and Associates Ltd. (Richmond, B.C., Canada) for adaptation to the Mina Ivan ore and chloride ion. Their designations and origins are summarized in the following table:

Table 4-4 : Summary of designators and origins of bacteria initially used.

Type/ Designator Used for Culture Series	Substrate on which the bacterial culture was originally grown	Chloride Adaptation Level
A	Gibraltar Mines Ltd. copper concentrate (28.5 wt% Cu)	None
B	Pyrite	5 g/L
C	Pyrite	None

Initial shake flask test work with these cultures demonstrated that the bioleaching of Mina Ivan ore was feasible in the presence or absence of ferrous iron and chloride ion [162]. Generational trees for the A, B, and C series cultures are in Appendix B, Figure B.1, B.2, and B.3. Unfortunately, the original B culture (see Appendix B, Figure B.2), after demonstrating viability on Mina Ivan ore and 8 g/L chloride, was irrecoverably lost, perhaps due to a batch culture-related delayed reaction to the stressor, chloride ion.

As a consequence, a replacement culture had to be obtained or cultured. A culture of C series bacteria was gradually adapted, by batch culture techniques, to both Mina Ivan ore and increasing levels of NaCl, in an attempt to generate a culture acclimatized to the Mina Ivan ore, 9K, and a 5 g/L Cl^- level (labelled B*). Despite its early promise, this culture also failed, after attaining the desired level of chloride adaptation (Appendix B, Figure B.4).

Another set of bacterial cultures acclimatized to pyrite ore and various NaCl levels (8000 ppm, 9000 ppm, and 10000 ppm) was received from Bacon, Donaldson and Associates Ltd. (Richmond, B.C., Canada). These cultures were maintained at the same NaCl levels on a pyrite ore and 9K medium. After 5 successful serial transfers, a sixth-generation 10,000 ppm NaCl-resistant bank on pyrite ore was used to inoculate a new B series bank (9K, Mina Ivan ore, and 5 g/L chloride). Succeeding banks with bacteria acclimatized to this new ore/media combination were used to inoculate the chloride-containing columns as referenced in Leong *et al.* [162] (Appendix B, Figure B.5).

To initiate the Lower ore studies, a culture from the new B series bacteria was sub-cultured to grow on Lower ore, 9K, and 2.5 g/L chloride. After adaptation to the new conditions was achieved, this bank culture, L-STD, was maintained continuously to inoculate the Lower (Fe) (Appendix B, Figure B.6) and later on, the Lower (Cl) (Appendix B, Figure B.7) series.

For the Zaldívar ore leaching experiments, a solution sample from Minera Zaldívar's Chilean operations was delivered to the hydrometallurgical laboratories at U.B.C. After arrival, the bacterial culture contained in this liquid sample was initially grown and maintained on Mina Ivan ore on 9K medium with no additional chloride. Subsequently, this culture was adapted to Zaldívar ore and 5 g/L chloride, prior to its use as an inoculum for the Zaldívar (Cl) study (Appendix B, Figure B.8).

4.7 Analysis of Samples

Many of the Mina Ivan and Lower ore leach series samples were analyzed by the author at the hydrometallurgical laboratories at U.B.C., the balance completed with the assistance of Mr. Harold Eng, a research engineer working at the same facilities. All aliquots of sample solutions (leach samples, filtrate samples, wash samples) were made up with dilute nitric acid prior to being analyzed for copper and iron content by AAS with the aforementioned Thermo Jarell Ash Smith-Hieftje 4000 Atomic Absorption Spectrophotometer. Like the starting ore material, each experimental leach residue was assayed in duplicate. In each case, two chemical digestions (protocol described earlier in section 4.1) of carefully weighed, non-identical amounts of the finely ground material, were carried out, prior to analysis of a dilute aliquot of the resulting solution by AAS for copper and iron content.

In contrast, the Zaldívar leach series solution samples (leachate samples, media solution samples, supernatant inoculum samples, filtrate samples, and wash samples) were analyzed by personnel at Placer Dome Inc.'s Research Centre Assay Laboratory (PDI-RC-AL) and at IPL. The first 88 solution samples were analyzed for iron and copper content by AAS at PDI-RC-AL. Interferences in the analysis were minimized by making up the dilute aliquots being analyzed for

copper in 7.5% H_2SO_4, and those being analyzed for iron in 5% HCl. The remaining 171 solutions samples were analyzed by AAS at IPL, the dilute aliquots being made up with aqua regia to match the background matrix of their standards.

The Zaldívar final leach residues were analyzed at IPL in two lots, 4 in the first, and 16 in the second. The methodology for determining copper, iron, total sulfur, elemental sulfur, and sulfide sulfur content for the residues was the same as that used to assay the Zaldívar ore, as described earlier in section 4.1. The first lot of four residues was analyzed, in full accord with this methodology, for copper, iron, total sulfur, elemental sulfur, and sulfide sulfur content. The second lot was assayed only for copper, iron, and sulfide sulfur content. In the second lot, the sulfide sulfur content of each residue was determined by QGP-$BaSO_4$, after the selective rejection of both the elemental sulfur and the sulfate sulfur content from a representative sample.

Selected samples from the final leach residues and the initial starting ores from the Lower test series (Fe and Cl) were scanned with a Siemens D5000 X-ray powder diffractometer located in U.B.C's Geology Department in an attempt to determine their mineralogical composition.

Chapter 5 Results and Discussion

5.1 Theory & Data Treatment Considerations

5.1.1 System E_h-Relevance to Bioleaching

The E_h, or the reduction-oxidation (redox) potential of a system with respect to the standard hydrogen electrode (SHE), is of great significance in bioleaching systems. This thermodynamic quantity, if measured properly, is important to our understanding of the chemistry of aqueous systems. If the pH is known as well, the relative stability of the various phases (solid, aqueous) subjected to an aqueous lixiviant, as described by a theoretical E_h-pH diagram, can be predicted, subject to constraints imposed by kinetic phenomena.

The absolute redox potential of a given half-cell (reduction or oxidation) reaction cannot be measured. Potential measurements can only be made with respect to another reference half-cell reaction of known potential. According to IUPAC convention, this standard reference electrode reaction,

$$2H^+ + 2e^- \rightarrow H_2 \qquad (5\text{-}1)$$

has been assigned an E_h value of 0.00 V_{SHE} under standard conditions at 25°C. However, the use of this reference electrode is usually impractical. For this reason, the reference electrode is usually either a saturated calomel electrode (SCE) or a silver/silver chloride electrode which, under standard conditions at 25°C, have measured potentials of 0.245 V_{SHE} and 0.200 V_{SHE} respectively.

Redox measurements are usually made with an electron-accepting platinum sensing electrode coupled to an electron-donating reference electrode. Natarajan and Iwasaki [160] remind workers that the reactive nature of platinum electrodes may result in measured potentials that

cannot be equated with theoretical values. Problems can arise from the measurement procedure, electrode maintenance and preparation, the presence of dissolved oxygen, electrode poisoning, and the presence of competing/interfering redox species, resulting in mixed potentials.

In heterogeneous situations like those found in bioleaching, mixed potentials are inevitable, given the variety of possible redox species which may be present. Yet, it is important to distinguish the relative importance of the redox couples present. As with many hydrometallurgical systems, the oxidation reaction of ferrous to ferric ion (written here in accordance with IUPAC convention as a reduction reaction),

$$Fe^{3+} + e^{-} \leftrightarrow Fe^{2+} \tag{5-2}$$

or the ferric/ferrous reaction couple is considered to predominate, especially in the high E_h regimes, when relative concentrations of possible redox species are considered. This couple's importance becomes even more evident when the Nernst Equation is applied to equation 5-2 as follows,

$$E_h = E^o - \frac{(2.303RT)}{(F)} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \tag{5-3}$$

where E°, the standard redox potential of the ferric/ferrous couple at 25°C, is 0.771 V_{SHE}.

Another redox couple of note is the one pertaining to cuprous to cupric ion oxidation (written here in accordance with IUPAC convention):

$$Cu^{2+} + e^{-} \leftrightarrow Cu^{+} \tag{5-4}$$

While it doesn't have the prominence of the ferric/ferrous couple in leaching, the cupric/cuprous couple can help explain leaching situations in the lower E_h regimes. The Nernst Equation, as applied to equation 5-4 is as follows:

$$E_h = E^o - \frac{(2.303RT)}{(F)} \log \frac{[Cu^+]}{[Cu^{2+}]} \qquad (5\text{-}5)$$

where E°, the standard redox potential of the cupric/cuprous couple, is 0.153 V_{SHE} at 25°C.

On reviewing equation 5-3 it is apparent that, if the total iron in a system is constant, any situation favouring a higher concentration of ferric ion compared to ferrous ion will result in an increase of the system E_h, greatly increasing its sulfide mineral oxidation capacities. For instance, the presence of iron-oxidizing bacteria, particularly *T. ferrooxidans*, can greatly enhance sulfide mineral leaching in this fashion.

While a definitive link between the number of iron-oxidizing bacteria present and the system E_h has yet to be established, it is well known that, during the exponential growth phase, when both the bacterial population and the ferrous iron oxidizing capacity increase rapidly, the system E_h increases rapidly as well. Furthermore, the system E_h typically plateaus during both the lag and stationary phases, occasionally decreasing during the death phase if sufficient amounts of reducing minerals remain unleached. Thus, for bioleaching systems, the bacterial batch growth curve (Figure 3.7, page 38) is considered to closely parallel the system E_h curve for the same time period. In other words, the system E_h is a qualitative indicator of bacterial activity.

5.1.2 Head Basis for Extraction Calculations

There are two bases which can be applied when calculating copper extraction: assayed head or calculated head. The former method is simply the percentage, by mass, of copper with respect to all of the elements contained in the starting material, as determined by assay. The latter is essentially identical to the first, but is determined by a more laborious process based on a copper mass balance. It is the percentage, by mass, of all copper contained in all samples and final products, less any soluble copper externally introduced into the leach test, compared to the mass of the ore sample undergoing testing.

While the first is more convenient, it does have one conspicuous drawback, its dependence on two figures, accurate copper assays of a representative sample of both the starting material and the final leach residue. It is this flaw that the second method addresses. Any errors in the assayed head are generally minimized by effectively, "calculating an assay" for each test, to reflect any geological anomalies or variations in the starting material.

Consequently, calculated heads are preferred for metallurgical calculations, despite the fact that its determination relies on multiple assays. Calculations dependent on a calculated head could be subject to the compound effect of various analytical or procedural errors. However, since calculated head determination involves a mass balance, any large errors are usually noticed, unless the errors are systematic in one direction (i.e. all too high or all too low).

So, concerns about compound errors in determining a calculated head are usually alleviated by the fact that a mass balance had been performed. Assayed head determinations can make no such claim; hence, they are both less reliable and less believable.

In this thesis, all graphical figures and calculations involving copper extraction were based on calculated head, according to convention, unless otherwise stated.

5.1.3 Copper Extraction Calculations

Given the aforementioned difficulties in obtaining much of the required data for proper metallurgical balance considerations, it was deemed necessary to explain in more detail, in this section, some of the terms and equations used to calculate copper extractions, prior to discussion of the results. The data portrayed in a large proportion of the tables and graphs to be discussed are largely dependent on these extraction calculations. Sample calculations involving the equations discussed in this section are given in Appendix C.

5.1.3.1 Volume Determinations

All intermediate extraction calculations depended on a theoretical volume of leach solution, *V(Th)*, which was the simple sum of all of the volumes of solutions used at the start of each test, neglecting volumes associated with sulfuric acid additions (which were very low), miscibility, solution density, and solubility concerns. In all cases, the following equation applied:

$$V(Th) = V(media) + V(NaCl) + V(inoc - I) \tag{5-6}$$

where *V(media)* was the volume of bacterial nutrient media, *V(NaCl)* was the volume of 211 g/L NaCl solution, and *V(inoc-I)* was the measured volume of bacteria-containing slurry used to inoculate each test.

With respect to final extraction calculations, many of the leach tests did not have any data on filtrate or wash volumes. In these tests, *V(Th)* was assumed to apply. In other words, all soluble copper at test termination was considered to be contained in the final pregnant solution, the copper concentration represented by the last supernatant leachate sample.

In tests where a more rigorous treatment was performed, actual measured volumes for filtrate and wash solutions { *V(filt)* and *V(wash)* } were used instead of *V(Th)*. Also, the associated analysis values { *[Cu(filt)]* and *[Cu(wash)]* } were utilized as well.

5.1.3.2 Calculated Head Determination

In general terms, the calculated head of a leach test is the difference between all copper values output during the test and all external soluble copper values input, divided by the mass of the ore sample, as shown in the following equation:

$$C.H. = \frac{\Sigma(Cu\ \ outputs) - \Sigma(soluble\ \ Cu\ \ inputs)}{Mass\ \ of\ \ ore\ \ sample\ \ to\ \ be\ \ leached} x\,100\% \tag{5-7}$$

The first summation term in equation 5-7 includes all copper values associated with *n* supernatant leachate samples, the filtrate solution, the wash solution, the final residue, and any inoculum-associated soluble copper serially transferred to succeeding tests (as was the case for the Lower (Fe) and the Lower (Cl) test series, but not the Zaldívar (Cl) test series). This term, in expanded equation form, is as follows:

$$\Sigma(Cu\ \ outputs) = Cu(samples) + Cu(inoc - O) + Cu(filt) + Cu(wash) + M(res)\,[Cu(res)] \tag{5-8}$$

where

$$Cu(samples) = \sum_{(i=1)}^{(i=n)} \{V_i Cu_i\} \tag{5-8a}$$

$$Cu(inoc - O) = V(inoc - O)\,[Cu(inoc - O)] \tag{5-8b}$$

$$Cu(wash) = V(wash)\,[Cu(wash)] \tag{5-8c}$$

$$Cu(filt) = (V(filt) - 10^{-3})\,[Cu(filt)] \tag{5-8d}$$

It should be noted that the factor 10^{-3} that is in the expression for *Cu(filt)* and other similar calculations is the volume of solution (1 mL=10^{-3} L) already included as part of the copper content associated with leachate samples.

If no wash or filtrate data was available, the *Cu(wash)* and *Cu(filt)* terms in equation 5-8 were omitted and replaced by the single term,

$$Cu(preg) = (V(Th) - 10^{-3})\,[Cu(preg)] \tag{5-8e}$$

resulting in the following revised equation:

$$\sum(Cu\ \ outputs) = Cu(samples) + Cu(inoc - O) + Cu(preg) + M(res)\,[Cu(res)] \tag{5-9}$$

The second summation term in equation 5-7 includes all soluble copper present in the nutrient medium and in the inoculum used to initiate the leach test. In equation form, it is as follows:

$$\sum(soluble\ \ Cu\ \ inputs) = V(media)\,[Cu(media)] + V(inoc - I)\,[Cu(inoc - I)] \tag{5-10}$$

5.1.3.3 Solution-Based Copper Extraction Equations

In this thesis, each data point in an extraction-time plot represents the copper extraction achieved at a given point in time when a supernatant leachate sample was taken. In other words, each data point is a calculation which attempts to account for all copper solubilized during the

leach test, up to and including the sample. Obviously, any soluble copper introduced into the test by means other than leaching of the ore sample must be deducted from the summation (such as copper in the nutrient medium and in the inoculum), just as is done when determining calculated head. Since it was not possible to accurately determine the actual leachate volume whenever each supernatant sample was taken, *V(Th)*, as determined by equation 5-6, was used for all such calculations. The generalized equation for the copper extraction calculated at the *j*th sample, *Ext(j)*, is applicable for the majority of the extraction data points associated with the leach tests discussed in this thesis:

$$Ext(j) = \frac{\left\{\sum_{i=1}^{i=j}(V_i Cu_i) + Cu(inoc - O) + Cu(leachate) - \sum(soluble\ \ Cu\ \ inputs)\right.}{M(sample)\ \times\ C.H.} \times 100\% \qquad (5\text{-}11)$$

with $$Cu(leachate) = (V(Th) - 10^{-3})Cu_j \qquad (5\text{-}11a)$$

being the copper in the leachate when the *j*th sample was taken, *C.H.* being the calculated head, all other terms as defined earlier. If a test was used to inoculate a subsequent test, the *Cu(inoc-O)* term applied for all calculations beginning from the first sample after inoculation.

With leach termination, two different situations can occur. In the first, in which there is a lack of wash and filtrate data, equation 5-11 still applies, as the copper level in the pregnant solution will be represented by Cu_j, the final leachate sample, in all cases. On the other hand, with rigorous treatment upon leach termination, actual filtrate and wash data was incorporated into equation 5-11, resulting in equation 5-12:

$$Ext. = \frac{Cu(samples) + Cu(inoc - O) + Cu(filt) + Cu(wash) - \sum(soluble\ \ Cu\ \ inputs)}{M(sample)\ \times\ C.H.} \times 100\%$$

5.1.3.4 Residue-Based Copper Extraction Equations

Another expression of copper extraction can be determined for each leach test with knowledge of the mass of the starting ore material, the mass of the final leach residue, the copper analysis of the final leach residue, and a head analysis (assayed or calculated). Such ultimate extraction calculations should be in good agreement with the final solution-based extraction calculation, reflecting the degree of control of the mass balance.

According to convention, ultimate copper extractions are determined with a calculated head as follows:

$$\%Ext. = \frac{\{M(sample)\ C.H. - M(res)\ Assay(res)\}}{(M(sample)\ C.H.)} \cdot 100\% \qquad (5\text{-}13)$$

with *M(sample)* as the mass of ore used in the leach test in grams, *C.H.* as the calculated head determined by equation 5-8 in wt% Cu, *M(res)* as the mass of the leach residue in grams, and *Assay(res)* as the copper content in the residue in wt% Cu.

The analogous expression involving the assayed head, *A.H.*, can also be utilized:

$$\%Ext. = \frac{\{M(sample)\ A.H. - M(res)\ Assay(res)\}}{(M(sample)\ A.H.)} \cdot 100\% \qquad (5\text{-}14)$$

5.1.4 Total Sulfuric Acid Consumption

As mentioned earlier, no two ores, even from within the same ore body, are identical in their properties. One property which is relatively easily determined during lab-scale bioleaching

is sulfuric acid consumption. Acid consumption is dependent on a number of factors including: (a) the amounts of acid-consuming gangue minerals, (b) the amounts of acid-consuming ore minerals, (c) the amounts of acid generated by hydrolysis reactions (iron and copper precipitates, other compounds), and (d) the amount of acid generated through bacterially catalyzed oxidation of elemental sulfur, reduced sulfur compounds, and sulfide minerals.

All acid consumptions were determined, on a kg H_2SO_4/tonne ore basis, with the following equation:

$$A.C. = \frac{V(acid)(6\ mol\ H_2SO_4/L)(98\ kg/1000\ mol\ H_2SO_4)}{M(sample)(tonne\ ore/1x10^{+6}\ g\ ore)} \qquad (5\text{-}15)$$

where *V(acid)* was the volume in L of 6 M H_2SO_4 used in the leach test, and *M(sample)* as defined earlier.

It should be noted that, for completeness, all of the sulfuric acid consumption figures presented in this section were based on reagent-grade sulfuric acid used throughout this study which had a purity of 98%.

5.2 Lower (Fe) Shake Flask Test Series

Inocula from a bank culture acclimatized to 9K, Lower ore, and 2.5 g/L chloride ion were used to inoculate Set 1 of this series (Appendix B, Figure B.6), in which only the amount of soluble ferrous iron was varied, all other conditions held constant. Subsequently, 5 mL of inoculum from Set 1 were used to initiate Set 2, and so on (Set 2 starts Set 3, etc.).

It should be made clear at this point, that due to experimental difficulties, all data pertaining to Set 2 of this series has been omitted and will not appear in any figures or be discussed.

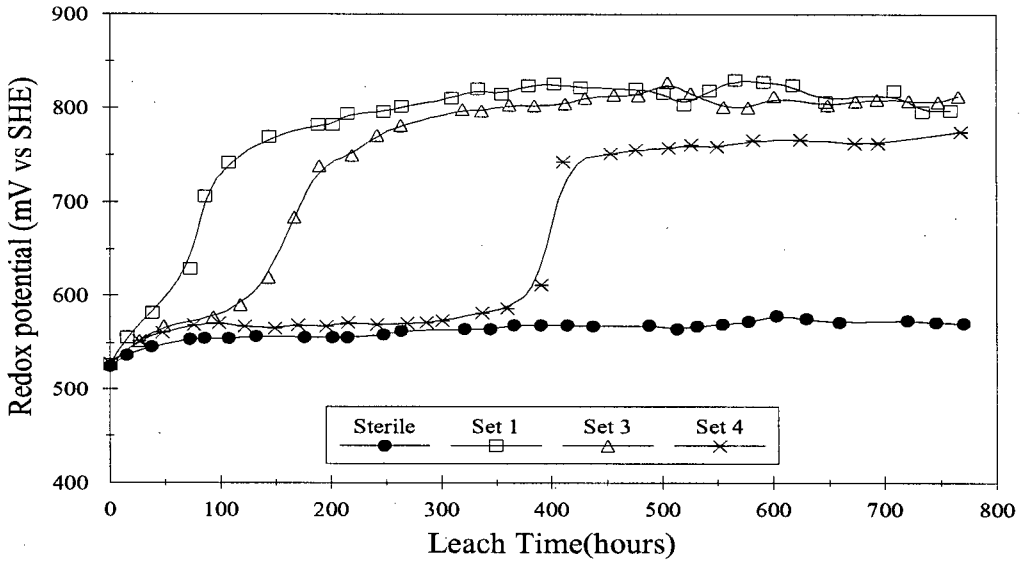
5.2.1 Effect of Ferrous Iron Level on Bacterial Acclimatization

Figure 5.1 (a-g) are E_h vs time plots of the Lower (Fe) series tests at a fixed ferrous iron (Fe^{2+}) level. These plots depict the effect of ferrous iron on culture adaptation, as qualitatively indicated by lag time, from generation to generation (i.e. set to set).

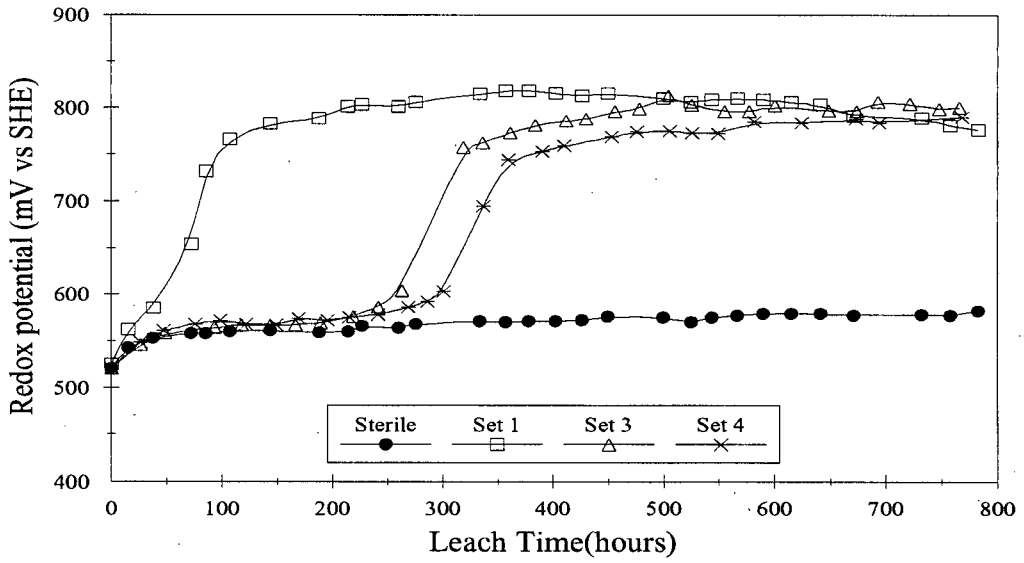
These figures apparently indicate that reverse acclimatization behaviour, or increasing lag time with consecutive transfers into identical media, did occur, in general. Only the 6 g/L Fe^{2+} plot, Figure 5.1 (f) clearly displayed the opposite trend. In other words, inhibition occurred, with succeeding generations having longer lag times than the initial culture. This result should have been expected, bearing in mind the difference in iron levels between that of the inoculating bacteria and of the media in the majority of the tests. However, at the time, a procedural error was thought to have seriously affected the viability of the bacteria for all of the experiments in this series.

This error, very late serial transferring of inocula from the initial generation of tests (Set 1) to the next (Set 2), could manifest itself in ways similar to an inhibition reaction, such as longer lag times. As such, the "expected" inhibition, compounded by the procedural error, probably severely weakened the cultures generated in Set 1. Consequently, very weak and very depleted inocula were probably transferred to Set 2, which exhibited such poor results (i.e. very long lag time) that all related data was considered to have little usefulness. Similar behaviour was observed in Sets 3 and 4 as well.

Figure 5.2 plots the E_h-time data from selected sterile tests from the Lower (Fe) series. Figure 5.3 plots the acclimatization (E_h-time) data from selected bioleach tests from Set 1 of this series.

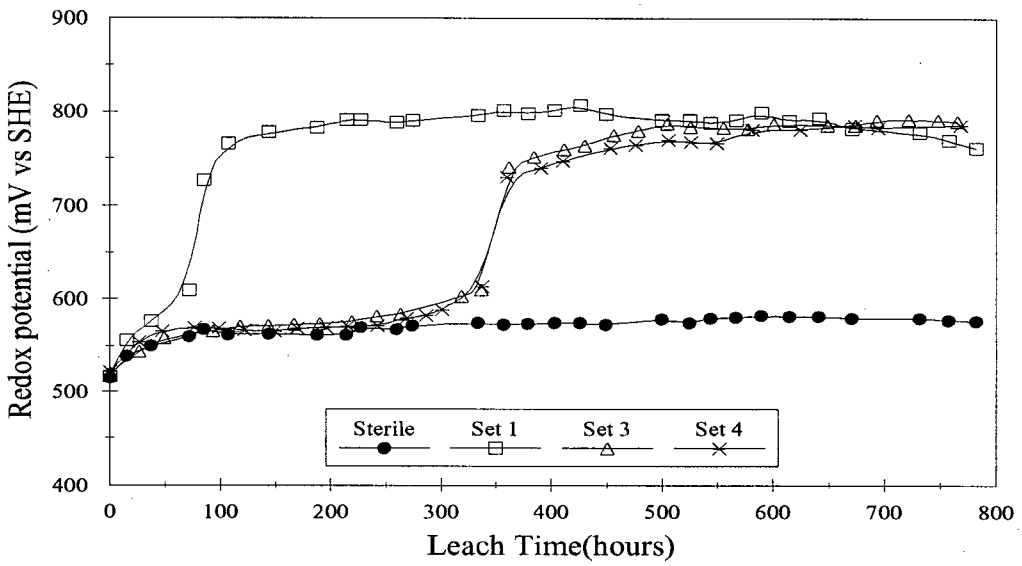


(a)

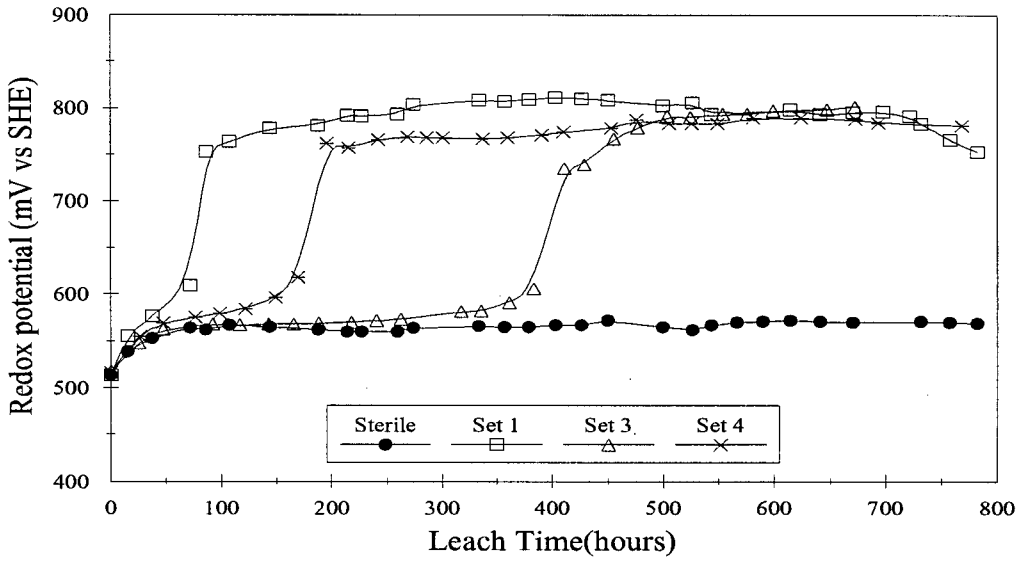


(b)

Figure 5.1 : Acclimatization plots - Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level): E_h versus time for bioleach tests, (a) 0 g/L Fe^{2+}; (b) 0.5 g/L Fe^{2+}.

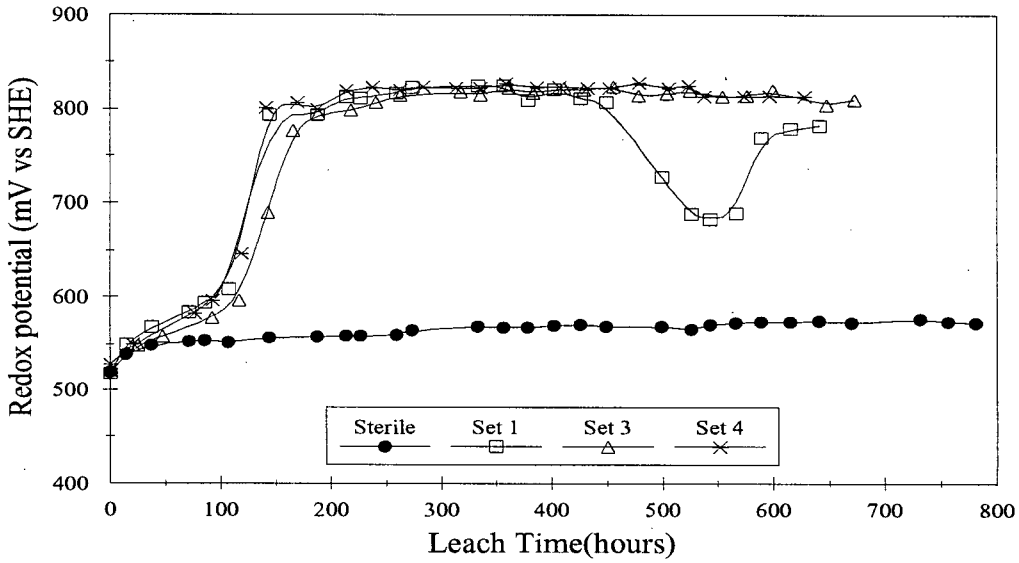


(c)

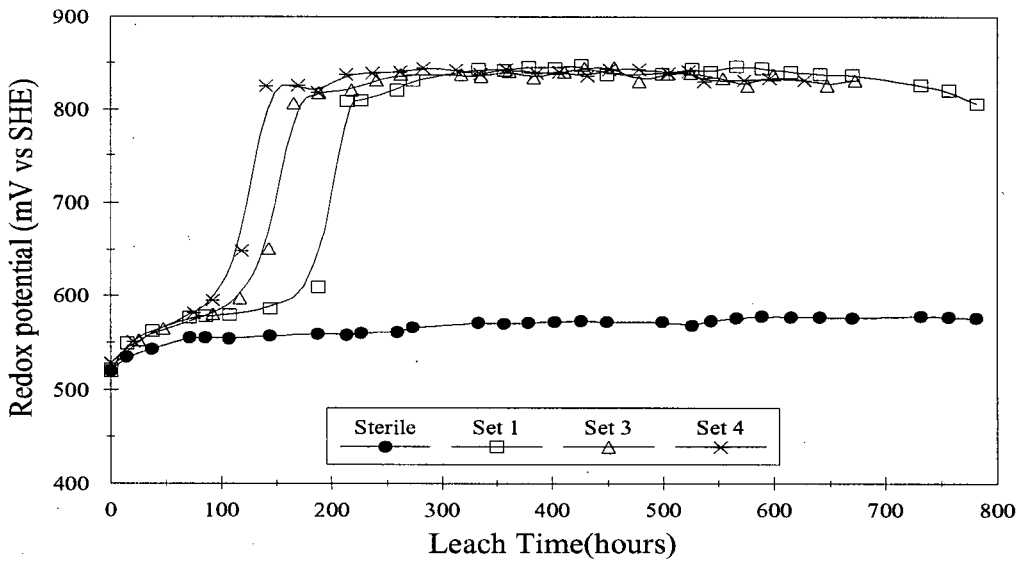


(d)

Figure 5.1 : Acclimatization plots - Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level): E_h versus time for bioleach tests, (c) 1 g/L Fe^{2+}; (d) 2 g/L Fe^{2+}.

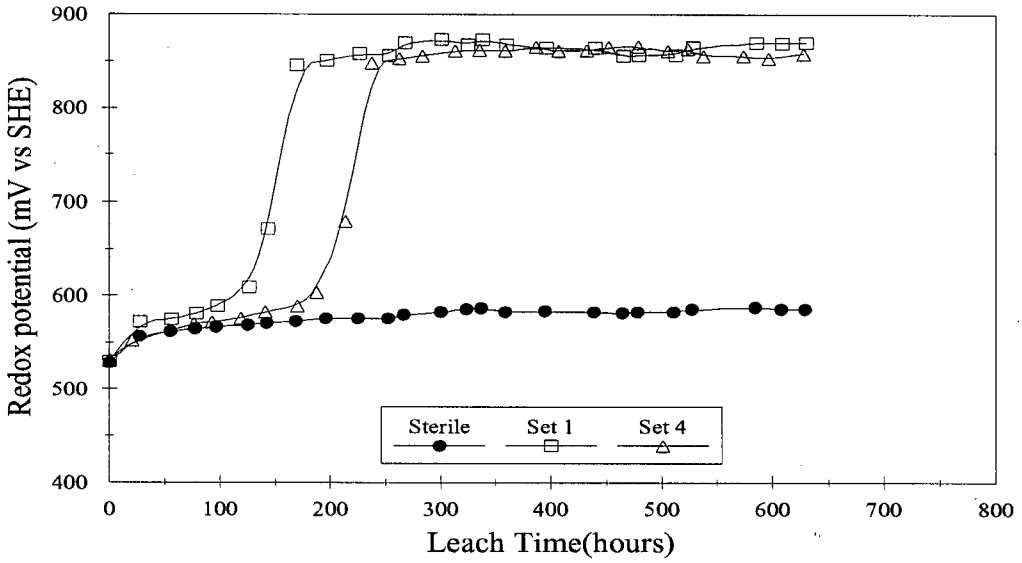


(e)



(f)

Figure 5.1 : Acclimatization plots - Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level): E_h versus time for bioleach tests, (e) 4 g/L Fe^{2+}; (f) 6 g/L Fe^{2+}.



(g)

Figure 5.1 : Acclimatization plots - Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level): E_h versus time for bioleach tests, (g) 9 g/L Fe^{2+}.

The sterile tests did behave as expected. As shown in the bottom-most curves in Figure 5.1 (a-g) and in Figure 5.2, the redox potentials of these tests did not vary greatly from the 500-600 mV range. Clearly, bacterial iron oxidation was inhibited, leaving the source of ferric iron, an important factor contributing to the system E_h, solely attributable to any chemical oxidation of ferrous iron that might have occurred. Also, Figure 5.2 demonstrates the effect of varying iron level on the final E_h, or iron-level effect. That is, the tests with higher ferrous iron level had higher E_h plateaus than those with lower ferrous iron levels. Evidently, the higher E_h levels are the consequence of more ferric iron inorganically generated in response to the higher initial ferrous iron levels. While this result suggests that copper extraction will probably be enhanced by the addition of ferrous iron, the lack of bacterial activity due to the action of the bactericide will undoubtedly ensure that the E_h remains relatively low, resulting in slow extraction rates.

In Figure 5.3, contrasting sharply with the sterile leach shown, all of the bioleach tests plateaued in the 800-900 mV range, with the higher plateau E_h values distributed generally in accordance with the iron-level effect. In terms of acclimatization, the bioleach tests behaved conversely to what was expected, as the sharp drop in ferrous iron level (as much as 9 g/L) was presumed to cause inhibition, since the inocula used to initiate this series were acclimatized to 9 g/L Fe^{2+}. The 0 g/L Fe^{2+} test had a shorter lag than either the 6 g/L or the 9 g/L tests, a somewhat unexpected result. If one recalls the method by which these tests were inoculated, this result could be explained as a consequence of inconsistent transferring. That is, some inocula were better than others, in terms of the number and health of the bacterial cells.

It is significant that in Figure 5.3 the 2 g/L test had a final E_h plateau below that of the 0 g/L test. This last result could indicate some systematic problem present, since all of the bioleach tests in this set, during the time interval between 550 hours and termination, experienced an E_h drop of at least 50 mV. Two possible explanations exist: (a) a problem with the E_h probe resulting in a systematic decline in readings or (b) a general population decline in all of the cultures, indicative of cultures entering the death phase of development. While the first explanation is possible, the lack of a probe check at the time notwithstanding, the second concurs well with the aforementioned procedural error.

Thus, one could conclude that sharp changes in initial ferrous iron level cause negative growth or inhibition in the bacterial cultures, depending on the initial level of adaptation. If the procedural error hadn't occurred, this conclusion is foregone. As it stands, the result is essentially inconclusive.

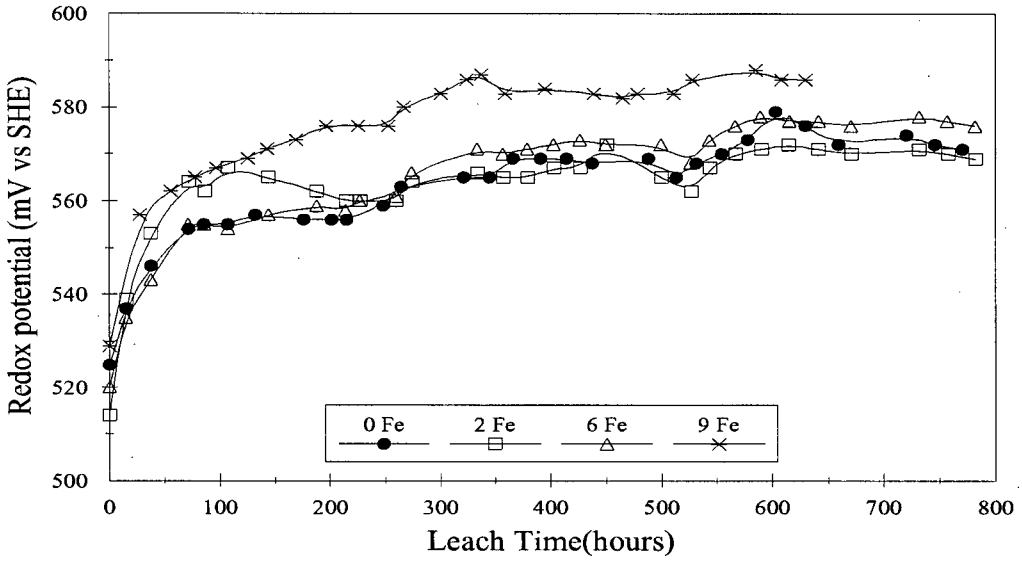


Figure 5.2: Redox potential (E_h) vs. time plots of selected sterile leaches of Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level).

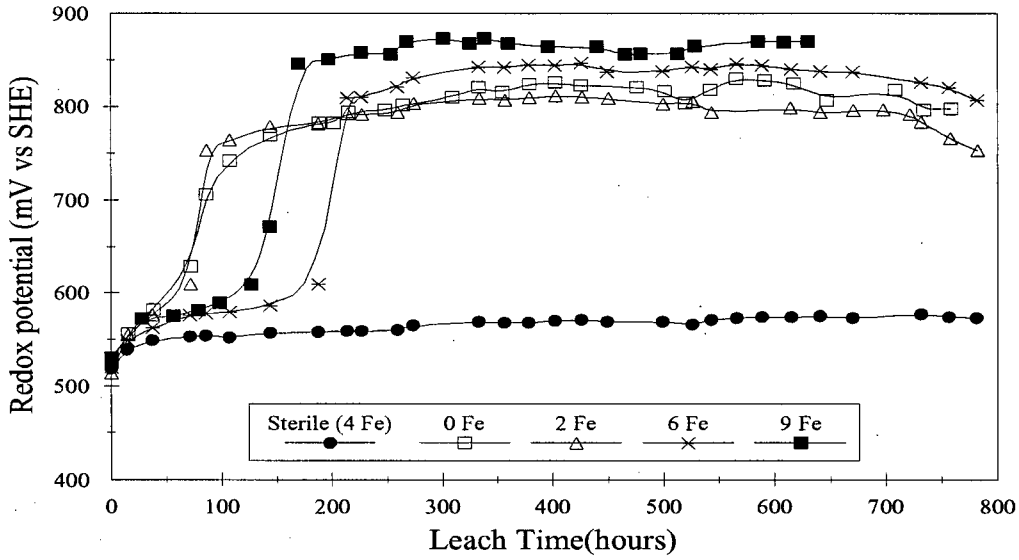


Figure 5.3 : Redox potential (E_h) vs time plots of selected bioleach tests and a sterile test (4 g/L Fe^{2+}) from Set 1, Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level).

5.2.2 Effect of Ferrous Iron Level and Bacteria on Copper Extraction

Due to procedural difficulties encountered early in this series, copper extraction as a function of time plots could only be generated for selected tests from Set 1 of the series.

Since rigorous treatment of final products was not executed for these tests, *V(Th)*, as calculated by equation 5-6 (page 104), applied for all copper extraction calculations, including the final, as calculated with equation 5-11 (page 107).

Figure 5.4 shows the copper-extraction plot data from all of the sterile tests. In general, yields are fairly constant in the 40-50% range, irrespective of initial iron content. These results, typical of first-stage chalcocite leaching with inorganic oxidizing agents, as seen in section 3.7, are consistent with the expected behaviour of such tests.

Figure 5.5 plots copper-extraction vs time for selected bioleach tests in Set 1 and a representative sterile test. Compared to the sterile test (bottom curve), all of the bioleach tests shown experienced very high copper yields on the order of 95%, regardless of iron content. So, initial ferrous iron level, within the range 0-1 g/L, does not appear to have had much of an effect on the copper extraction, while the effect of bacteria is clearly evident. Copper extraction data for the tests conducted between 2-6 g/L Fe^{2+} were not plotted since the respective curves oscillated wildly, indicating either analytical and procedural difficulties, and no meaningful trend could be discerned.

Table 5-1 summarizes the ultimate copper extraction results obtained at the end of the tests for this series. These calculations, conducted using equation 5-14 (page 108), depended on final leach residue analyses, the assayed head, and the masses of both the starting ore material and the final residue. In general accordance with the extraction-time plots, ultimate extractions were high

(averaging 94.2%) for the bioleach tests, while those for the sterile tests were low (averaging 48.7%). Regardless of initial ferrous iron concentration, the copper extractions, bioleach and sterile, hardly varied from these respective averages.

It can be concluded that while the presence of bacteria significantly enhanced copper extraction, as expected from the E_h-time plots, the effect of initial ferrous iron had a negligible impact.

Table 5-1: Summary of ultimate copper extraction obtained for Lower (Fe) series based on final residue analyses and the assayed head.

Fe^{2+} Level	Sterile Leaches	Set 1 Leaches	Set 3 Leaches	Set 4 Leaches	Leach Averages
(g/L)	% Cu Extracted	% Cu Extracted	% Cu Extracted	% Cu Extracted	% Cu Extracted
0.0	47.7	94.8	96.4	92.6	94.6
0.5	50.7	93.4	95.8	93.9	94.4
1.0	51.5	94.0	94.0	94.9	94.3
2.0	48.3	94.2	93.6	95.7	94.5
4.0	46.1	na	94.2	93.2	93.7
6.0	47.7	93.5	94.3	93.2	93.7
	48.7 (steriles)				94.2 (All leaches)

na=not available due to loss of test.

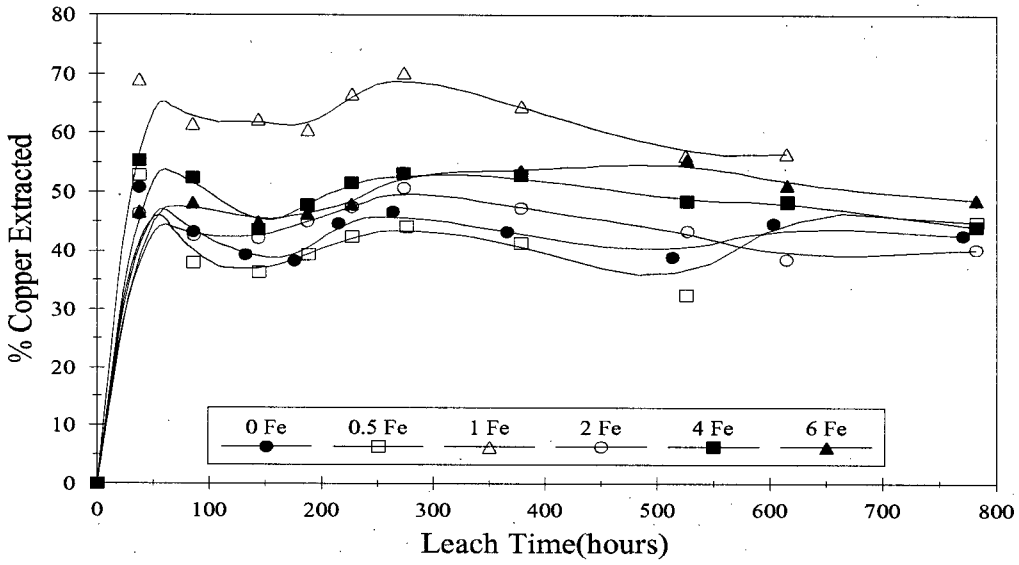


Figure 5.4 : Copper extraction vs. time plots for all sterile tests, Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level).

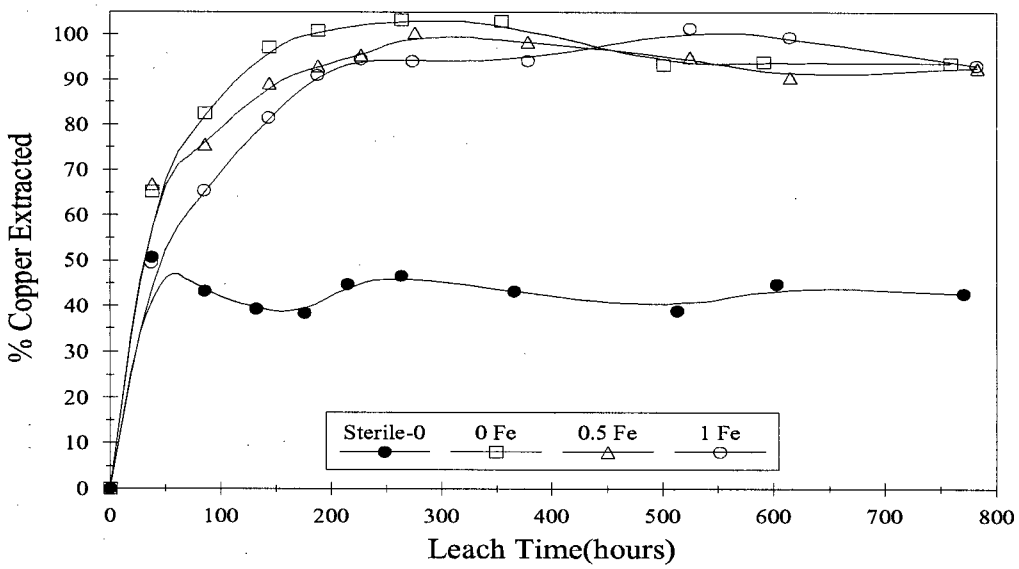


Figure 5.5 : Copper extraction vs. time plots for selected bioleach tests and a sterile test (0 g/L Fe^{2+}), set 1, Lower (Fe) series (Lower ore, 2.5 g/L Cl^-, variable Fe^{2+} level).

5.2.3 Effect of Bacteria and Ferrous Iron Level on Total Acid Consumption

Table 5-2 summarizes the total acid consumption results, as computed using equation 5-15 (page 109), for the sterile tests and the bioleach tests from Sets 1, 3, and 4 of this test series.

Two definite trends can be discerned. First, the sterile tests generally required more make-up sulfuric acid than their bacteria-laden counterparts, confirming that the bacteria generate some acid towards their own requirements. Second, the lower the level of initial Fe^{2+} ion present at the start of the test, the higher the amount of make-up acid required, regardless if bacteria were present or absent. That is, increased initial Fe^{2+} ion levels led to increased Fe^{3+} ion production (abiotically or biologically generated) and subsequently, increased acid (H^+) generation from hydrolysis of Fe^{3+} (see equations 3-38, 3-39, 3-40, and 3-43, section 3.6.4). The high final pH values indicating higher acid requirements, and the low final iron levels indicative of iron precipitation, shown for the sterile tests and the Set 1 bioleach tests listed in Table 5-2 support this hypothesis.

Table 5-2: Summary of sulfuric acid consumption for Lower (Fe) series.

	Sulfuric Acid Consumption of Leach tests (kg/t)								
$[Fe^{2+}]$ (g/L)	Sterile	End pH	End [Fe] (g/L)	Set 1	End pH	End [Fe] (g/L)	Set 3	Set 4	Average
0.0	40.16	2.86	0.10	32.94	2.74	0.05	29.31	32.98	31.74
0.5	32.98	2.58	0.29	29.31	2.76	0.03	25.71	25.62	26.88
1.0	25.59	2.85	0.33	25.55	2.85	0.02	21.96	18.34	21.95
2.0	18.34	2.86	0.37	14.68	2.86	0.04	14.68	10.99	13.45
4.0	8.09	2.69	0.08	na	na	na	3.66	7.32	5.49
6.0	3.68	2.53	1.35	3.67	2.36	0.11	3.67	7.34	4.89

na=data not available due to loss of test.

5.3 Lower (Cl) Shake Flask Test Series

5.3.1 Effect of Chloride Level on Bacterial Acclimatization

Figure 5.6 is a summary plot depicting E_h-time data for all of the sterile tests in the Lower (Cl) test series. Following this figure are detailed plots of E_h-time data for all of the tests in the entire series, leaches and associated steriles, segregated by chloride level, labelled as Figure 5.7 (a-h).

As observed in Figure 5.6 and the bottom curves in Figure 5.7 (a-h), the E_h in these sterile tests was limited to the 500-600 mV range and the increase in E_h with time was not large. Hence, bacterial activity was non-existent in these tests, ferrous iron was predominant, and leaching was limited.

A noteworthy, but minor trend in the E_h plateau values can be more easily discerned in Figure 5.6 (b) which provides a close-up of the 500-600 mV region. All of the sterile tests plateaued in the 570-590 mV range, with the E_h plateau value increasing with increasing chloride concentration.

This trend could be explained if the cupric/cuprous couple (equation 5-4, page 101) can be presumed to be the primary driving force. That is, cupric ion leaching of chalcocite (equation 5-16), followed by cuprous ion oxidation to cupric ion due to dissolved O_2 (equation 5-17) could be taking place, as follows:

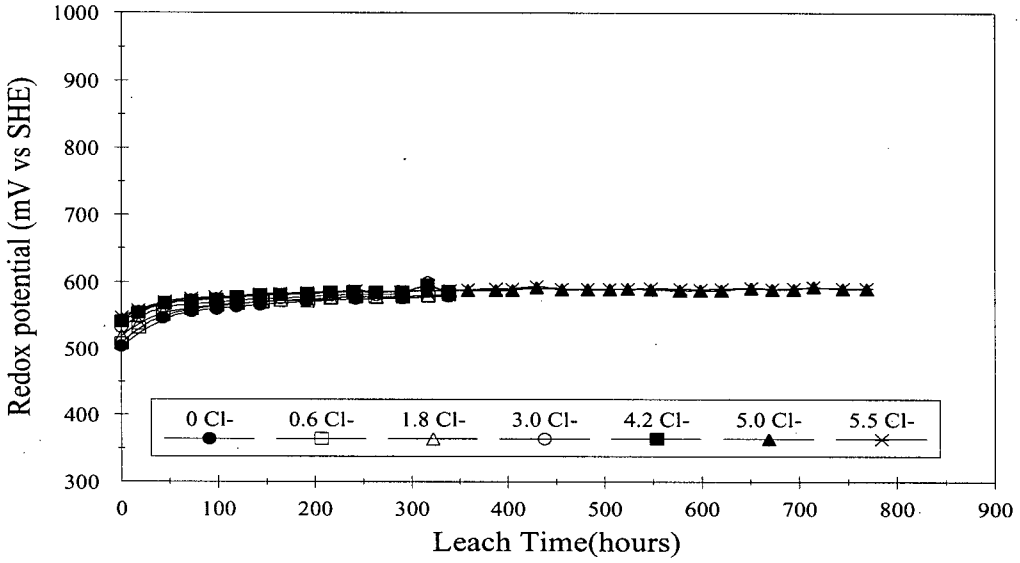
$$Cu_2S + Cu^{2+} \rightarrow CuS + 2Cu^{+} \qquad (5\text{-}16)$$

$$2Cu^{+} + \tfrac{1}{2}O_2 + 2H^{+} \rightarrow 2Cu^{2+} + H_2O \qquad (5\text{-}17)$$

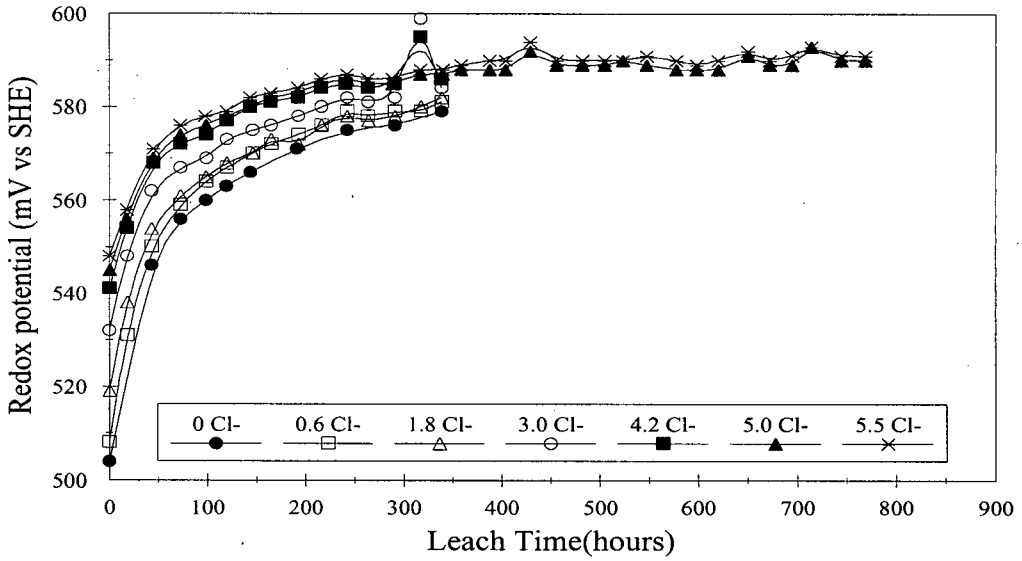
Furthermore, if one recalls that the E° for the cupric/cuprous redox couple at 25°C is 0.153 V_{SHE}, this explanation does make sense, on considering the E_h levels observed in these tests and the fact that no initial ferric ion was present. Also, the presence of at least 5 g/L Cu^{2+} in solution in the test medium of these sterile tests (recall the medium is 9K-5Cu) is probably more than sufficient to initiate reaction 5-16. It is also true that cuprous ion (Cu^{+}), in sulfate media, reacts with O_2 much faster than with any other species, instantaneously oxidizing to Cu^{2+} as fast as it is produced; in the leach tests this oxidation is facilitated by the constant aeration of the leach slurries during storage in the rotary shaker. Also, it is likely that this oxidation reaction is faster than the leaching reaction, ensuring an adequate supply of lixiviant. The presence of chloride ion provides an additional forward driving force for equation 5-16, according to Le Chatelier's Principle, because chloride complexation decreases the amount of by-produced cuprous ion. Thus, as the chloride level increases, cuprous ion activity decreases due to complexation, cupric ion activity increases due to fast oxidation of cuprous ion, and the cupric/cuprous activity ratio increases, resulting in the observed trend in E_h.

Figure 5.7 (a-h) are the acclimatization (E_h) plots for each set of bioleach tests (and the corresponding sterile) for a given chloride level. In each plot, contrasting sharply with the curve from the sterile test, all 5 curves pertaining to the bioleach tests plateaued at the same level in the 800-900 mV range, providing substantial evidence of both bacterial activity and ferric ion predominance.

Figure 5.7 (a-c) all exhibited decreasing lag time with each succeeding generation (indicated by the set number). This evidence of decreasing adaptation with adaptation time is in accordance with expected theory. That is, the bacteria adapted well to the gradual decrease in the chloride level from the base concentration of 2.5 g/L Cl^{-} and showed no dependence on chloride ion.

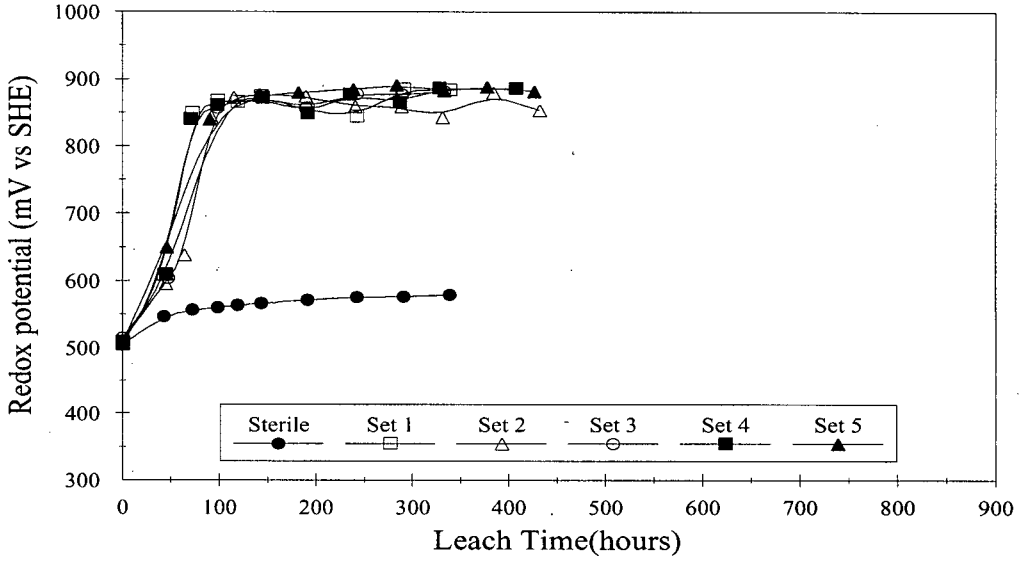


(a)

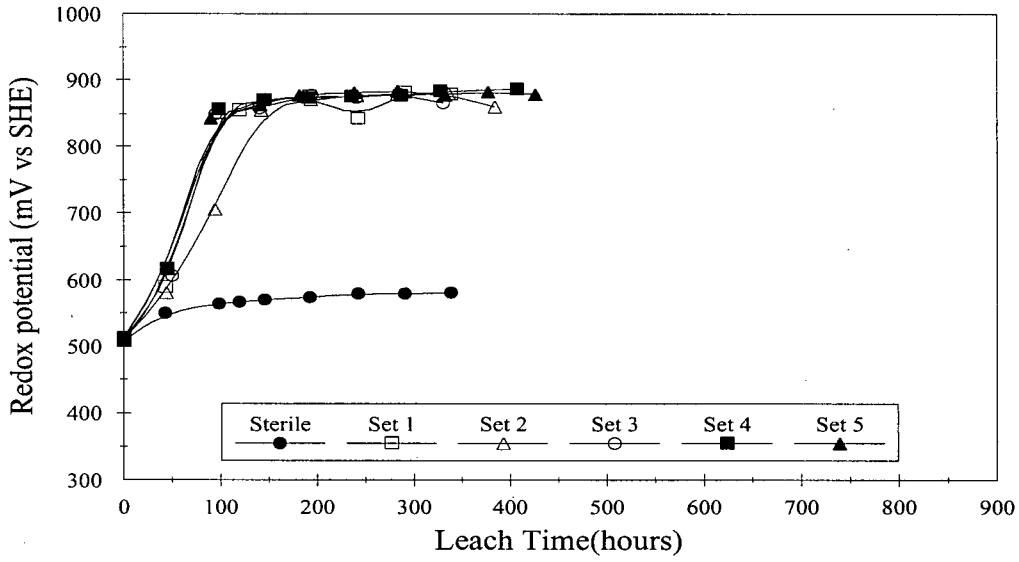


(b)

Figure 5.6 : Redox potential (E_h) vs time plots for all sterile tests, Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level, NB: 2.5 g/L Cl^- curve omitted), (a) original format; (b) close-up of 500-600 mV region.

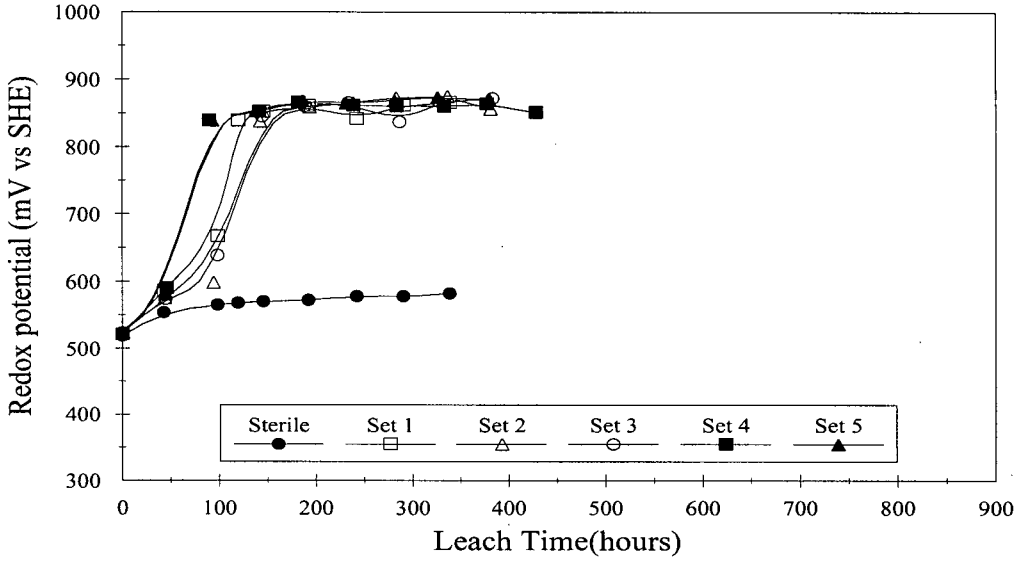


(a)

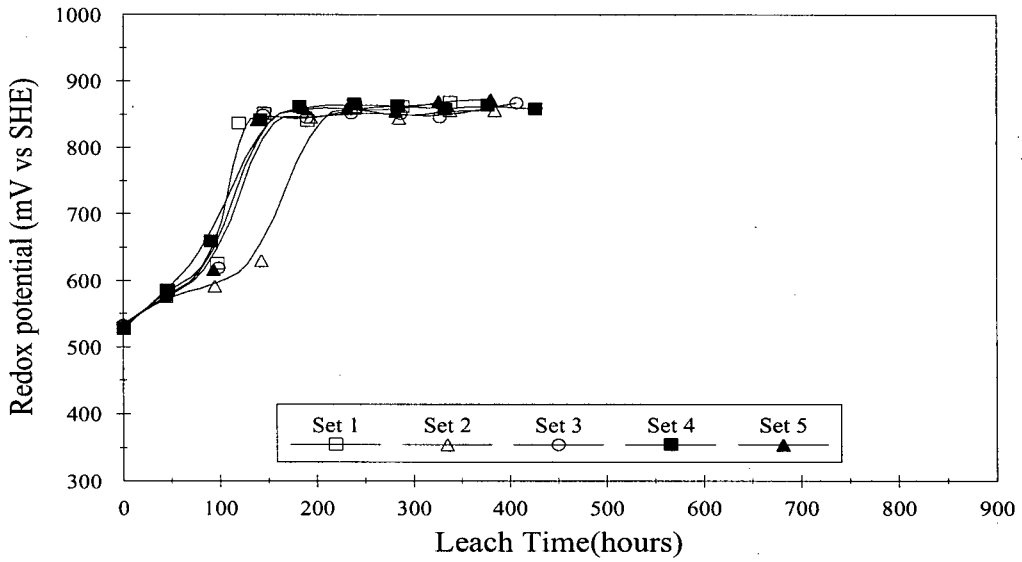


(b)

Figure 5.7 : Acclimatization plots - Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level): E_h versus time for bioleach tests, (a) 0 g/L Cl^-; (b) 0.6 g/L Cl^-.

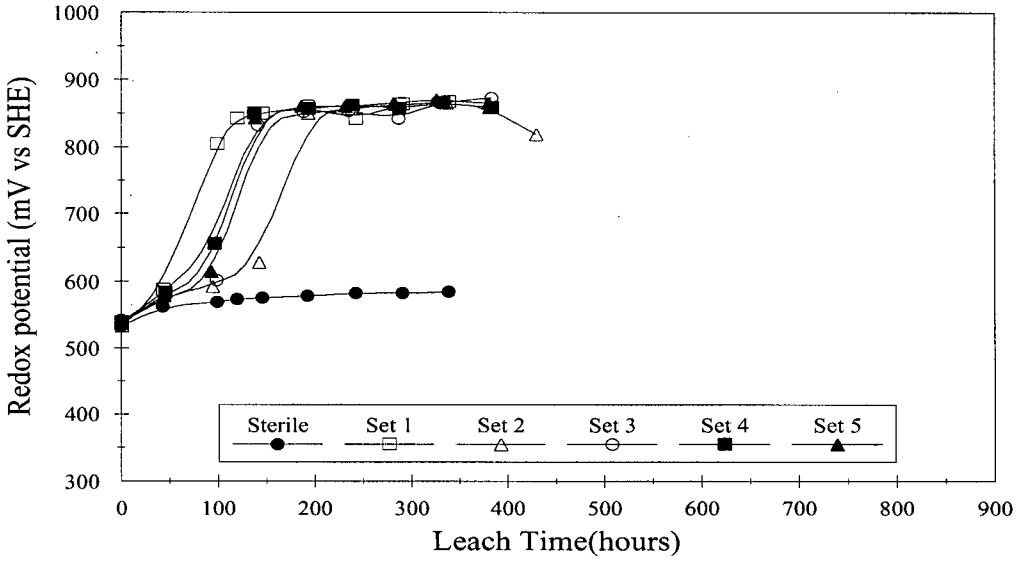


(c)

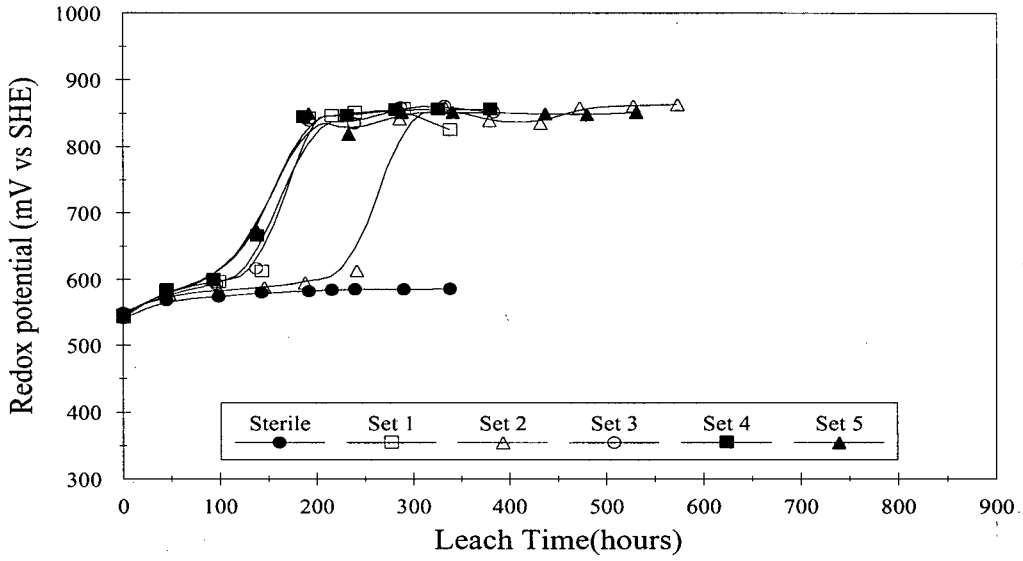


(d)

Figure 5.7 : Acclimatization plots - Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level): E_h versus time for bioleach tests, (c) 1.8 g/L Cl^-; (d) 2.5 g/L Cl^- (sterile test omitted).

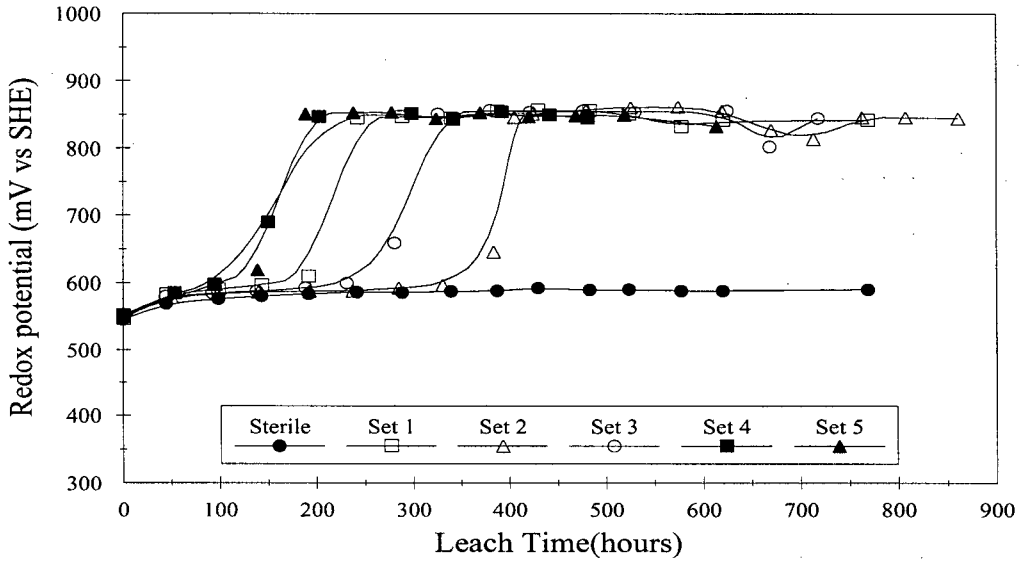


(e)

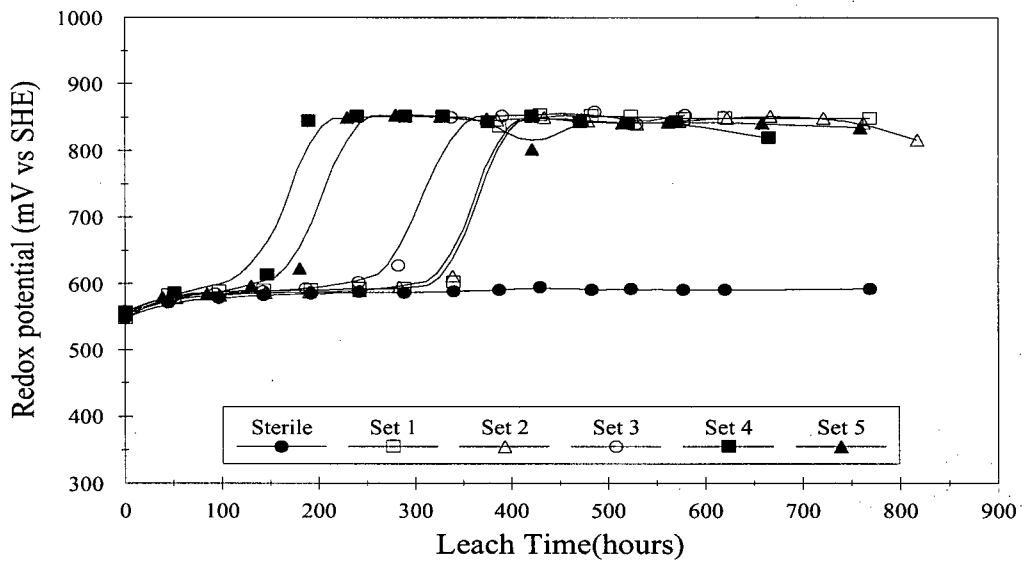


(f)

Figure 5.7 : Acclimatization plots - Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level): E_h versus time for bioleach tests, (e) 3.0 g/L Cl^-; (f) 4.2 g/L Cl^-.



(g)



(h)

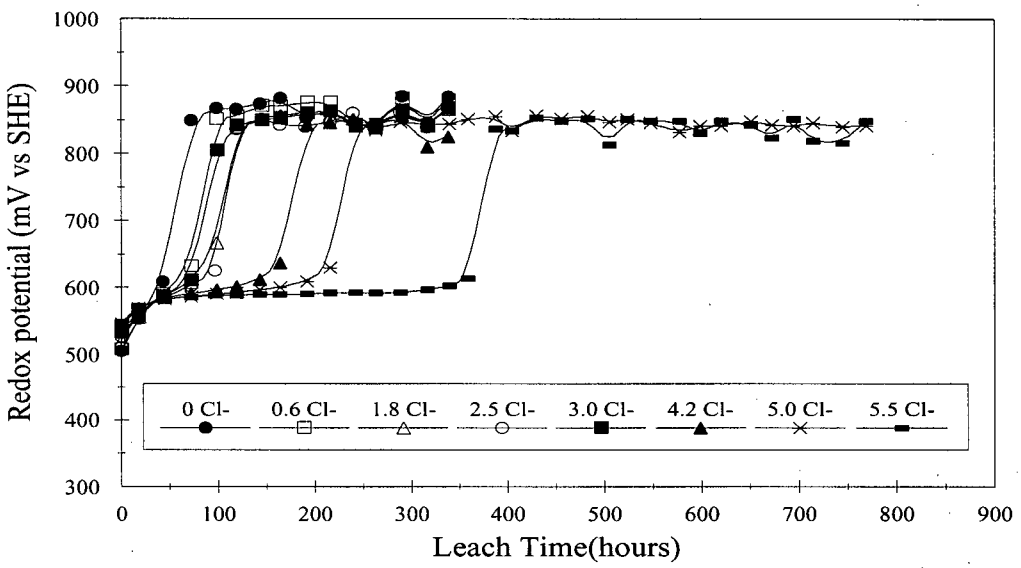
Figure 5.7 : Acclimatization plots - Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level): E_h versus time for bioleach tests, (g) 5.0 g/L Cl^-; (h) 5.5 g/L Cl^-.

The other tests, set at chloride levels greater than 2.5 g/L Cl^-, as seen in Figure 5.7 (e-h), all displayed increased lag at the second-generation level, followed by a progressive decrease in succeeding generations (or increasing set number). Clearly, inhibition behaviour induced by the higher chloride levels did occur, but it was generally observed to be attenuated with succeeding generations, agreeing well with Figure 3.8 (page 39), providing qualitative evidence of adaptation.

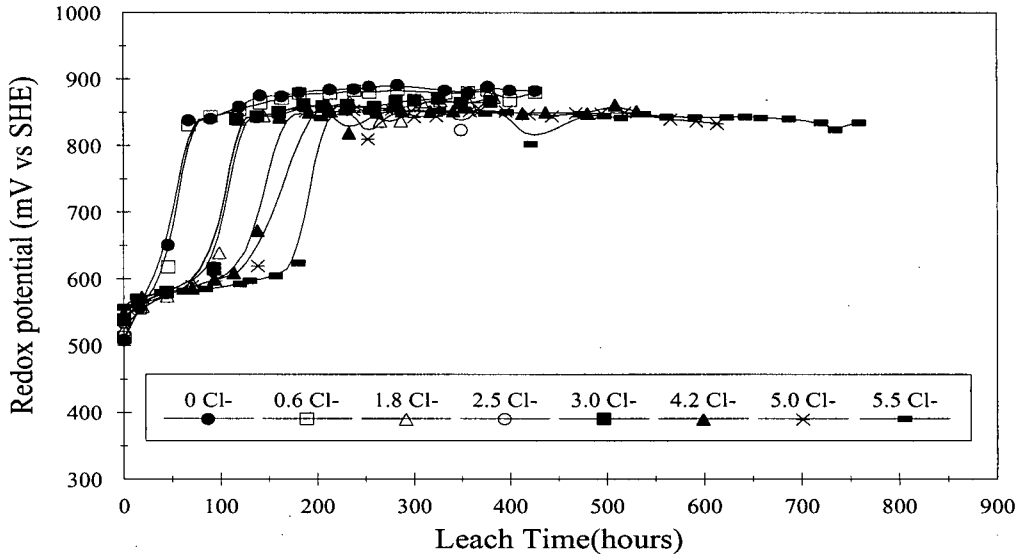
However, it is clear that identical behaviour also occurred with the tests set at 2.5 g/L Cl^-, illustrated in Figure 5.7 (d). It is unlikely that the base culture was not adapted to this level, given the number of repeated serial transfers undertaken prior to utilizing it to initiate this test series. More likely, a poor transfer occurred between sets 1 and 2, resulting in inhibited behaviour arising from a depleted culture of inoculating bacteria.

Also, the final E_h plateau values for all of the bioleach tests in a given set demonstrated a tendency to decrease with increasing chloride level, as shown in Figure 5.8 (a) and Figure 5.8 (b) for sets 1 and 5, respectively. It is likely that complexation of chloride ion with the bacterially-generated ferric ion resulted in a decrease in the ferric ion activity. This effect increased as chloride concentration increased, resulting in lower E_h plateau values for the affected bioleach tests.

Thus, it was shown that the adaptation level of the bacteria in the inoculum was clearly key to the acclimatization of the bacteria in a given bioleaching test. In this series, bioleach tests set at chloride levels below the baseline adaptation level (2.5 g/L Cl^-) easily adapted, while those with higher chloride values clearly exhibited inhibition before ultimately adapting, albeit requiring substantially more time to do so. Final E_h plateau values for the bioleach tests decreased with increasing chloride ion levels, a consequence of ferric ion complexation. As for the sterile tests, higher chloride levels induced very minor increases in final E_h, probably caused by chloride-enhanced cupric-ion leaching.



(a)



(b)

Figure 5.8 : Redox potential (E_h) vs time plots for all of the bioleach tests in a specified set of the Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (a) Set 1; (b) Set 5.

5.3.2 Effect of Bacteria and Chloride Level on Copper Extraction

Figure 5.9 is a plot depicting copper extraction vs time data for all of the sterile tests in the Lower (Cl) test series. Following it are similar copper extraction-time plots for all of the tests in the entire series, leaches and associated steriles, segregated by chloride level, labelled as Figure 5.10 (a-h).

Since rigorous treatment of final products was not executed for many of these tests, *V(Th)*, calculated by equation 5-6 (page 104), applied for most copper extraction calculations, as calculated with equation 5-11 (page 107). Otherwise, for the few tests completed rigorously, equation 5-12 (page 107) applied.

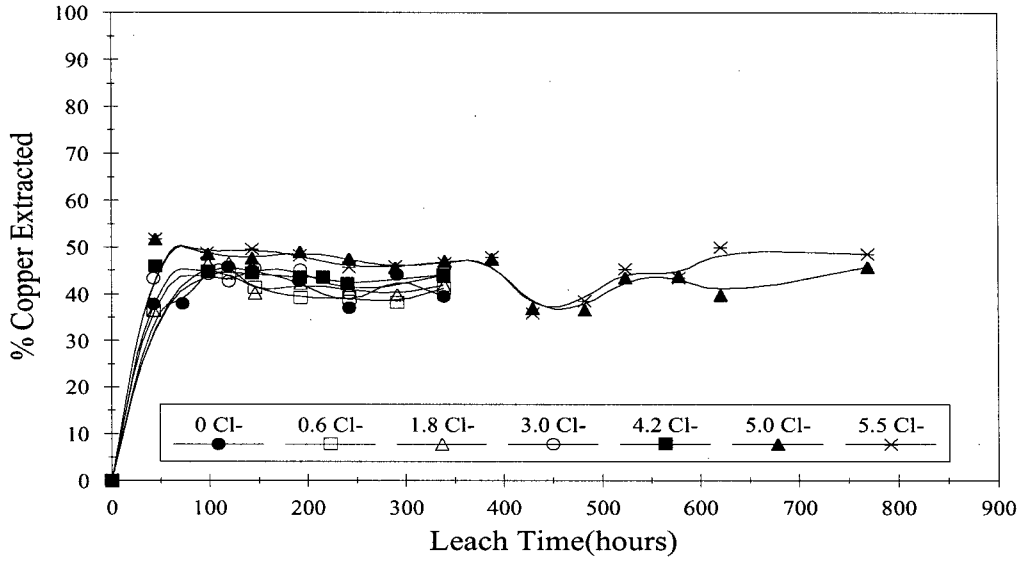
As observed in Figure 5.9 (a) and the bottom curves in Figure 5.10 (a-h), copper extraction for the sterile tests was limited to 40-50%. This result, typical of first-stage leaching of chalcocitic ores by inorganic lixiviants as seen in section 3.7, concurs well with the earlier predictions based on redox potential in section 5.3.1, and also agrees with the chloride-assisted cupric-ion leaching situation described in section 5.3.1 as well.

A closer examination of the curves in Figure 5.9 (a), facilitated by expanding the vertical scale as shown in Figure 5.9 (b), reveals an interesting trend. In spite of the obvious oscillations in the plot data, the final copper extractions exhibited gradual increases with increasing chloride concentration. That is, the highest extraction was found to be associated with the sterile test having the highest chloride concentration (5.5 g/L Cl^-). Incidentally, this same test also had the highest final redox potential (see Figure 5.6 (b)), as well. This result was not unexpected as it is logical to infer that the higher the redox potential, the greater the likelihood that the copper sulfide minerals will oxidize under the prevailing conditions. While this result lends support to the hypothesis that increasing the chloride concentration will lead to greater copper extraction from

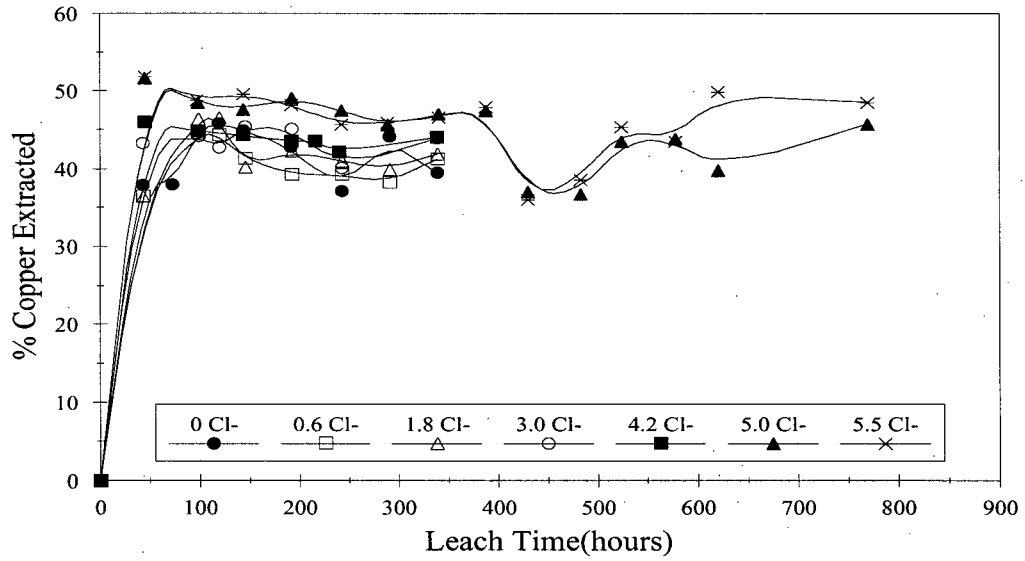
ferric/cupric chloride leaching reactions (section 3.6.2.3) as well as the fact that chloride ion is a more aggressive lixiviant than sulfate (section 3.7), as expected from the literature, there is no doubt that the lack of bacterially-catalyzed reactions will ultimately constrain the final yield to be low. Thus, sterile leaching improved slightly with increased chloride concentration.

Figure 5.10 (a-h) plot copper extraction-time data for all 5 consecutive bioleach tests and the corresponding sterile at a given chloride level. Without exception, each plot's bioleach curves exhibited sharp initial slopes indicative of rapid leaching that terminated in the 85-95% range, outperforming the sterile test by a wide margin. Clearly, the presence of bacteria enhanced the leaching of the ore at a fixed chloride level. It is also noteworthy to observe that the extraction curves' slopes flattened with set 2, before exhibiting a tendency to increase again with sets 4 and 5. While this trend is not universal, as certain curves definitely experienced fluctuation, it does indicate that increasing acclimatization may lead to increasing copper extraction.

Figure 5.11 (a-e) plots copper extraction-time data for all bioleach tests in a given set. While there is no difference in the actual curves and the extractions, these plots do demonstrate a significant trend, that the initial slopes of the bioleach tests tended to decrease as chloride concentrations increased. That is, the initial leaching rates appear to be affected by the chloride concentration. This trend is quite evident in Figure 5.11 (a-d), but is apparently not the case in the last plot, Figure 5.11 (e). In this plot, some of the tests in the middle of the chloride range (1.8, 2.5, and 3.0 g/L) unexpectedly experienced very low initial extractions, quite unlike their counterparts in sets 1 through 4. While the obvious reason for this result could be due to poor analyses of the samples for these tests, an alternative is a poor transfer of bacteria during test inoculation. As mentioned earlier, a transfer depleted in bacteria will exhibit inhibited behaviour due to a low number of healthy cells. Supporting this contention is the increased lag times for these same tests, as seen in the E_h plot for set 5, Figure 5.8 (b).

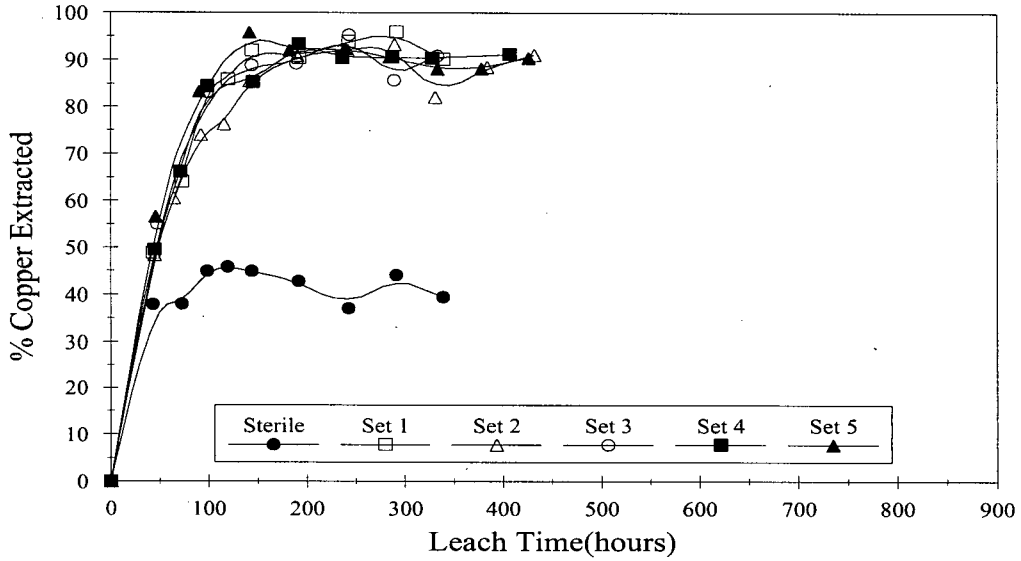


(a)

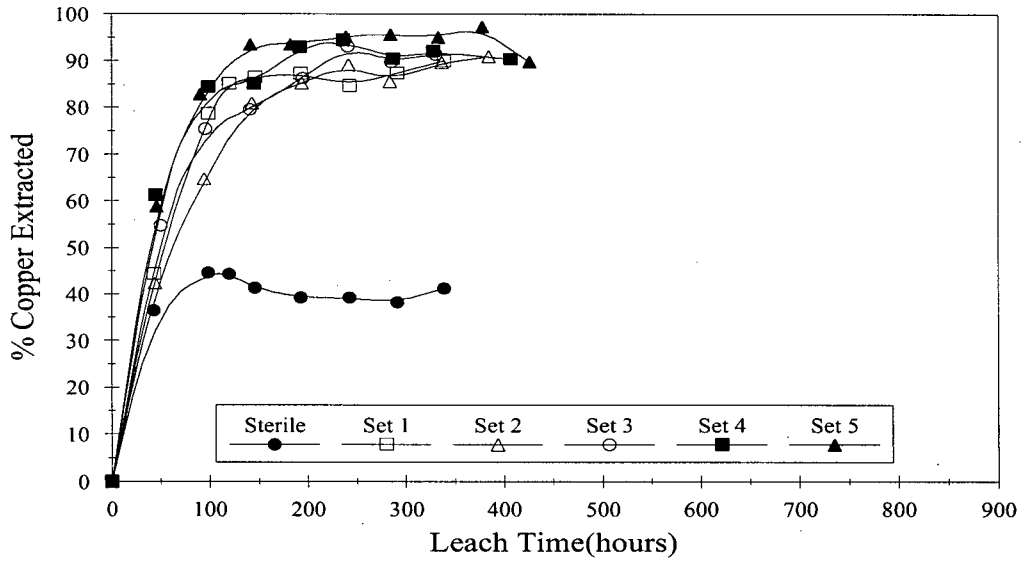


(b)

Figure 5.9 : Copper extraction vs. time plots for all sterile tests, Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (a) normal scale; (b) close-up, (expanded vertical scale).

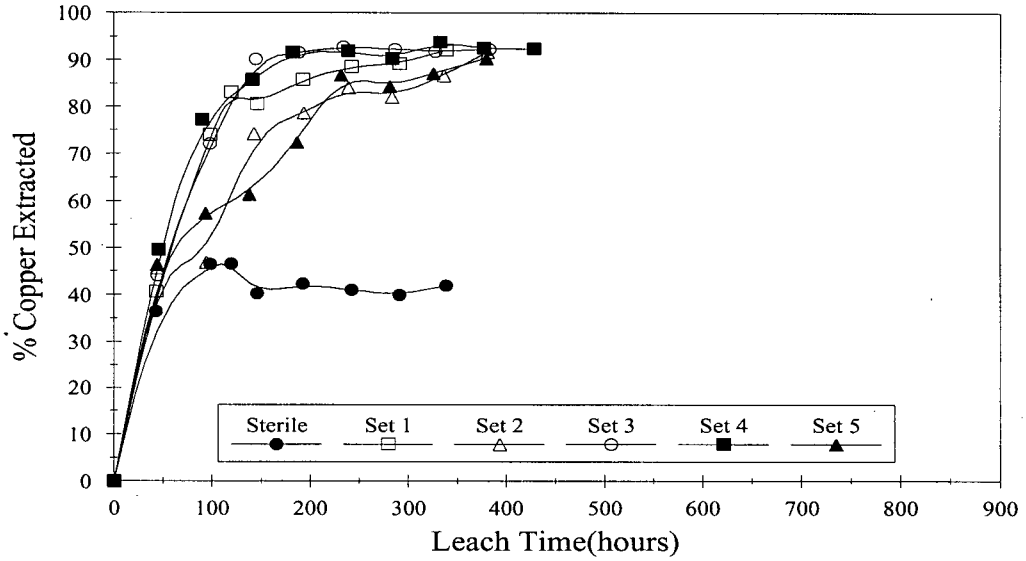


(a)

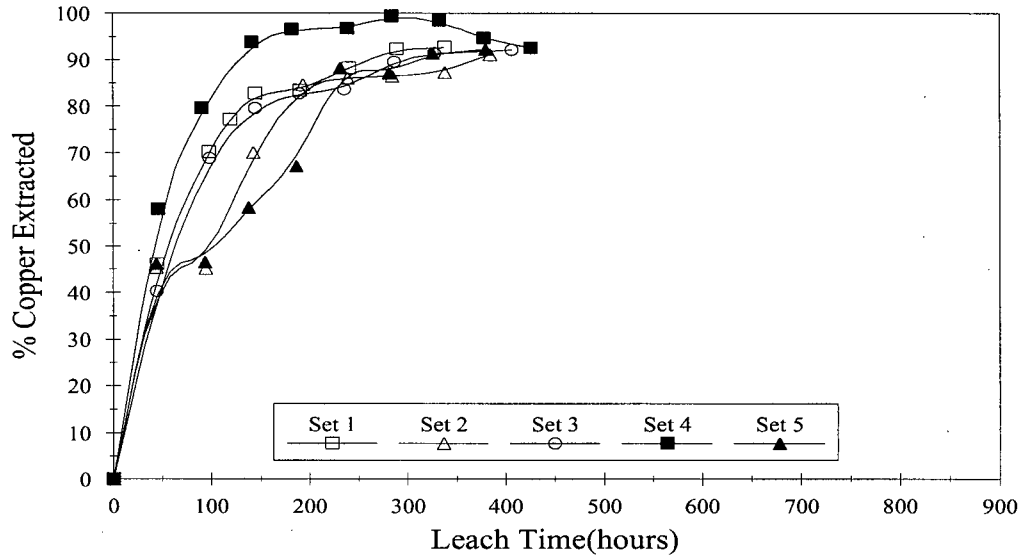


(b)

Figure 5.10 : Copper extraction vs. time plots for all tests at a given chloride level, Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (a) 0 g/L Cl^-; (b) 0.6 g/L Cl^-.

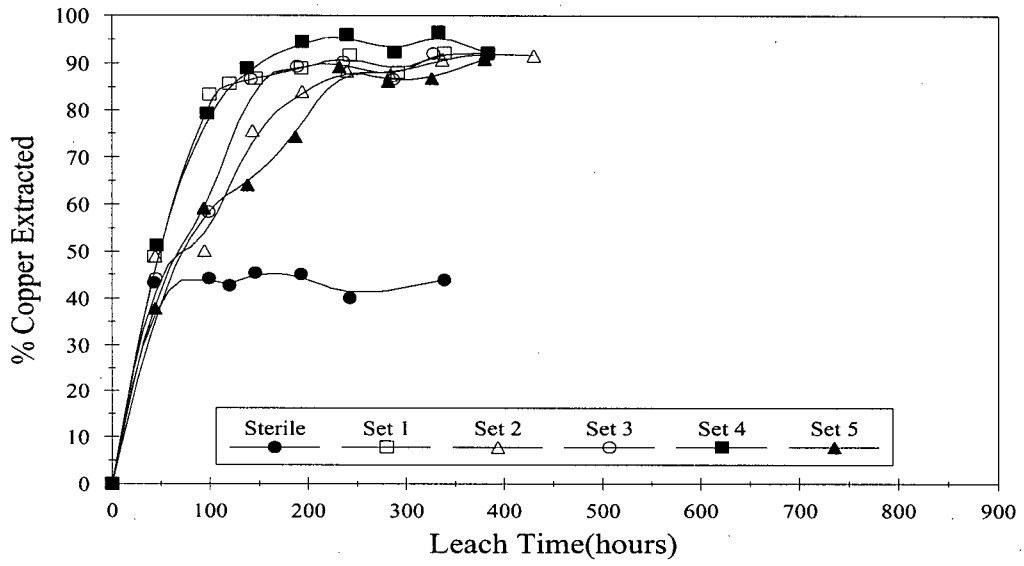


(c)

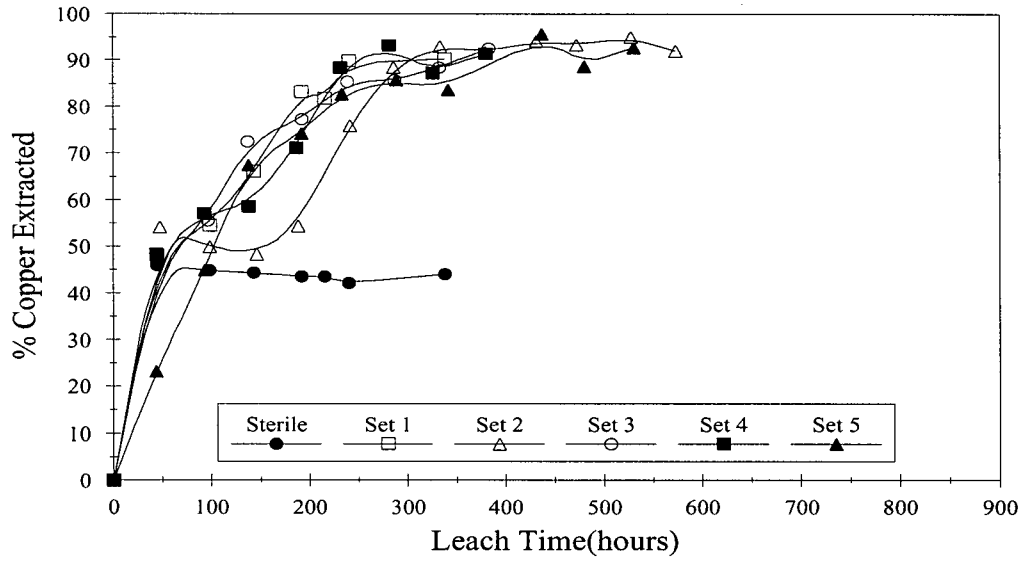


(d)

Figure 5.10 : Copper extraction vs. time plots for all tests at a given chloride level, Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (c) 1.8 g/L Cl^-; (d) 2.5 g/L Cl^- (sterile test omitted).

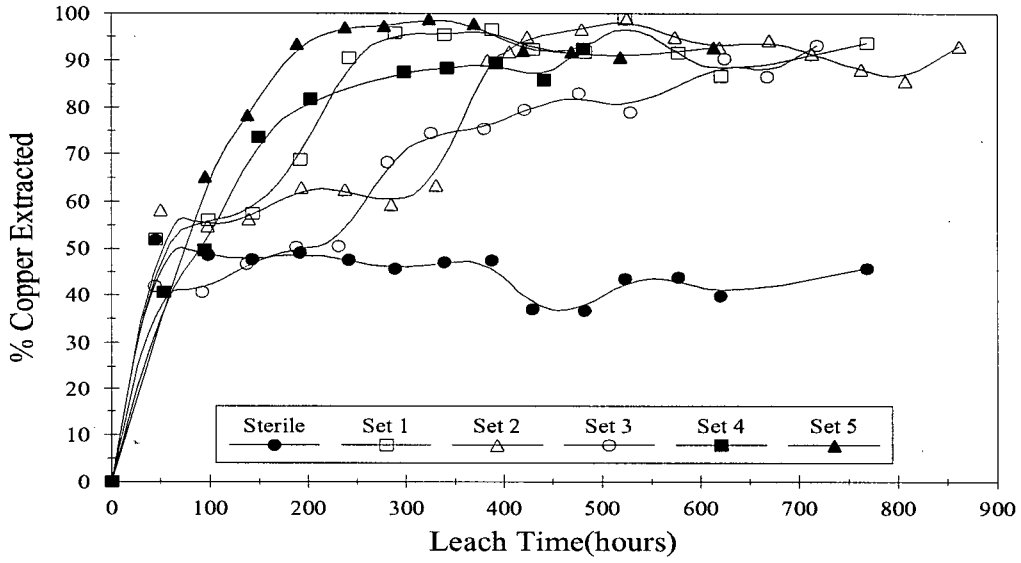


(e)

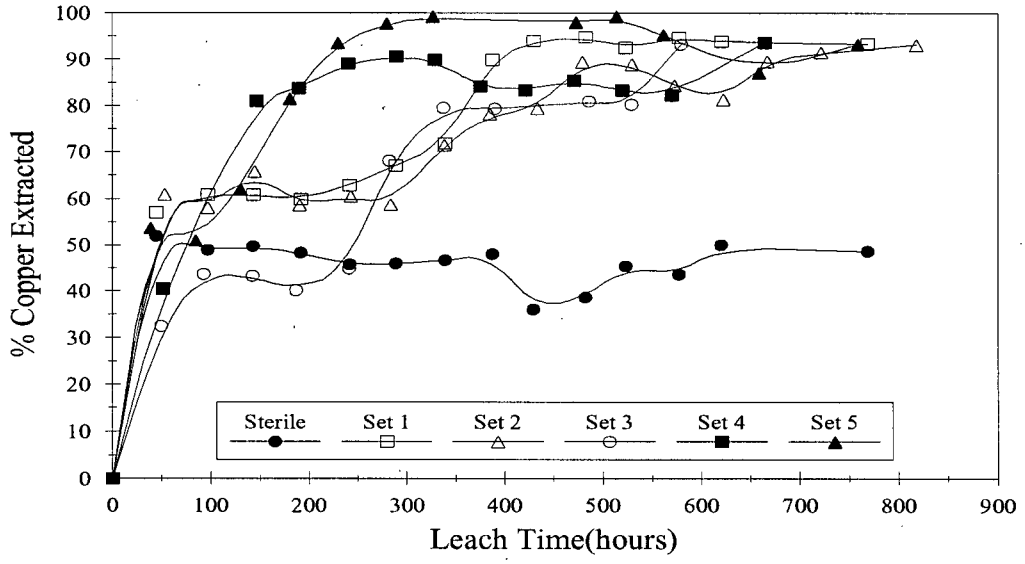


(f)

Figure 5.10 : Copper extraction vs. time plots for all tests at a given chloride level, Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (e) 3.0 g/L Cl^-; (f) 4.2 g/L Cl^-.

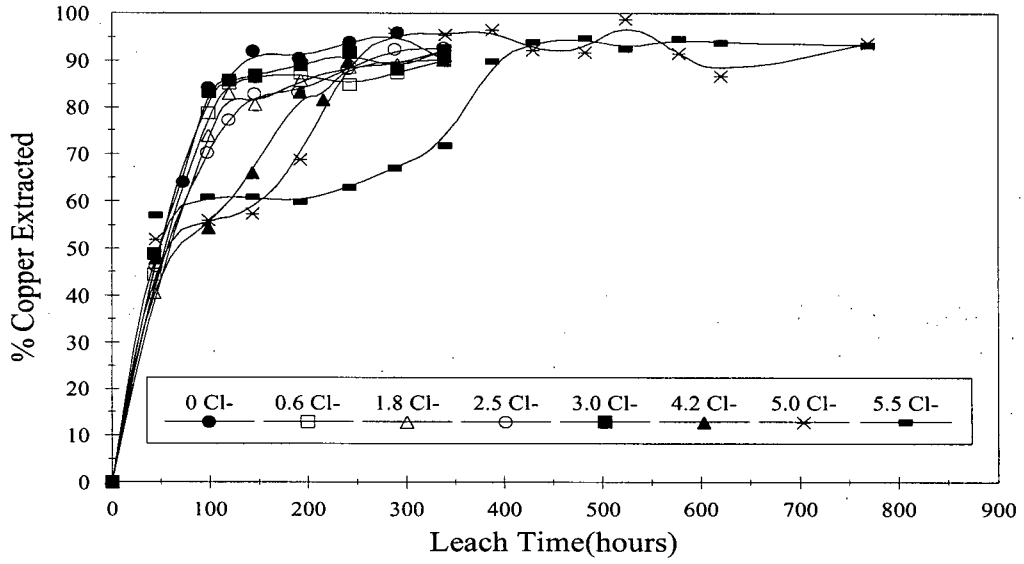


(g)

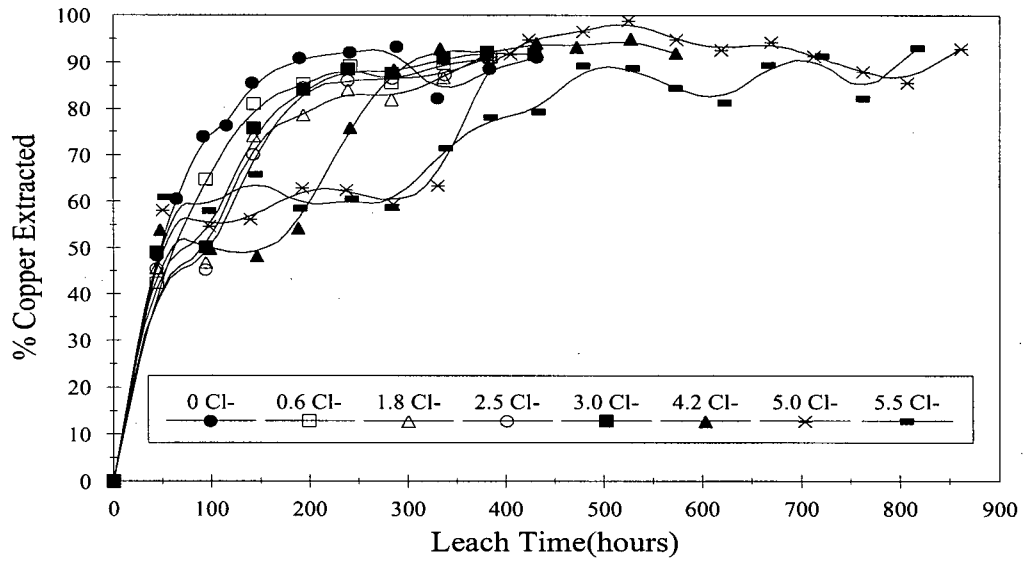


(h)

Figure 5.10 : Copper extraction vs. time plots for all tests at a given chloride level, Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (g) 5.0 g/L Cl^-; (h) 5.5 g/L Cl^-.

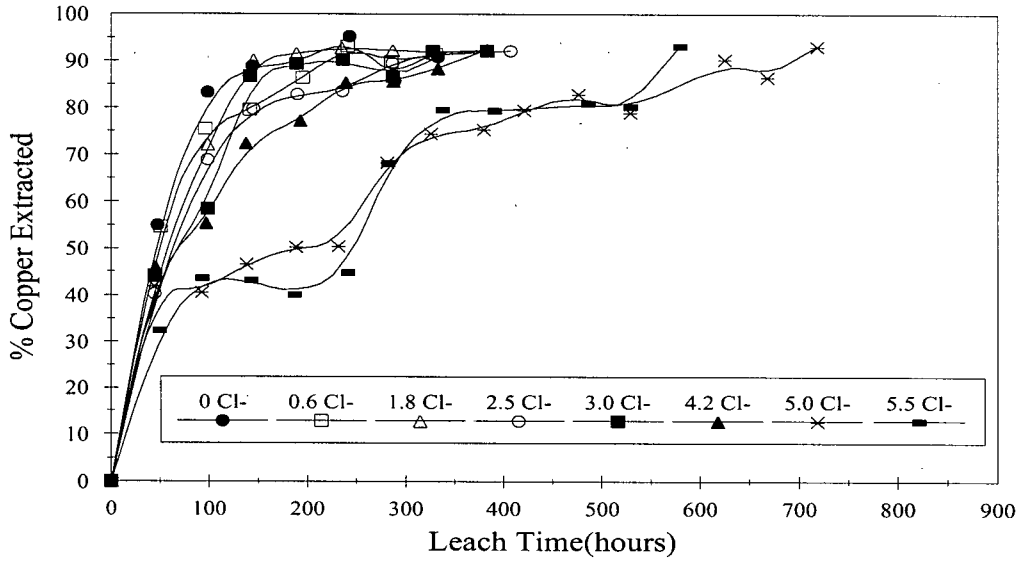


(a)

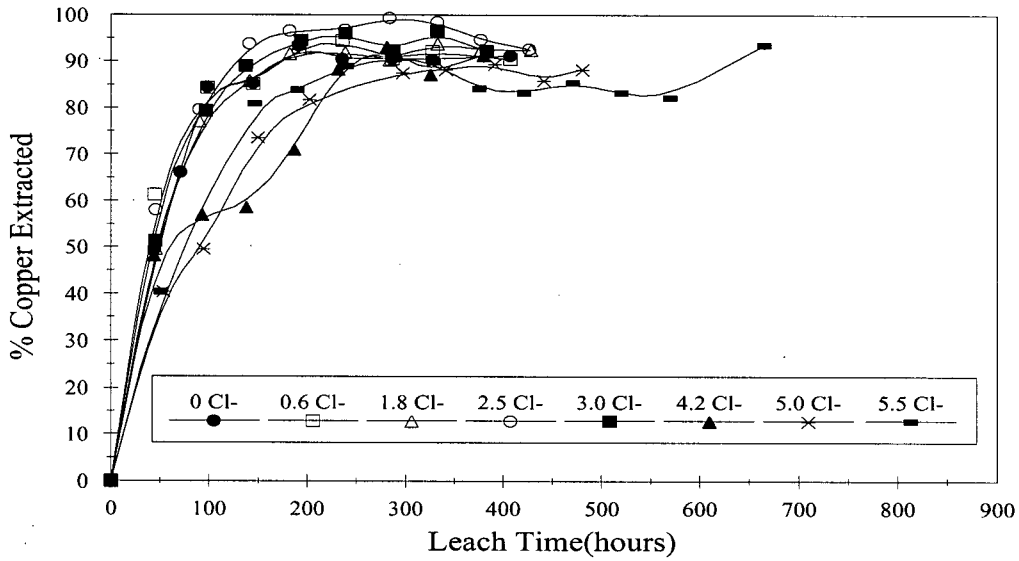


(b)

Figure 5.11 : Copper extraction vs. time plots for all bioleach tests in a specified set of the Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (a) Set 1; (b) Set 2.

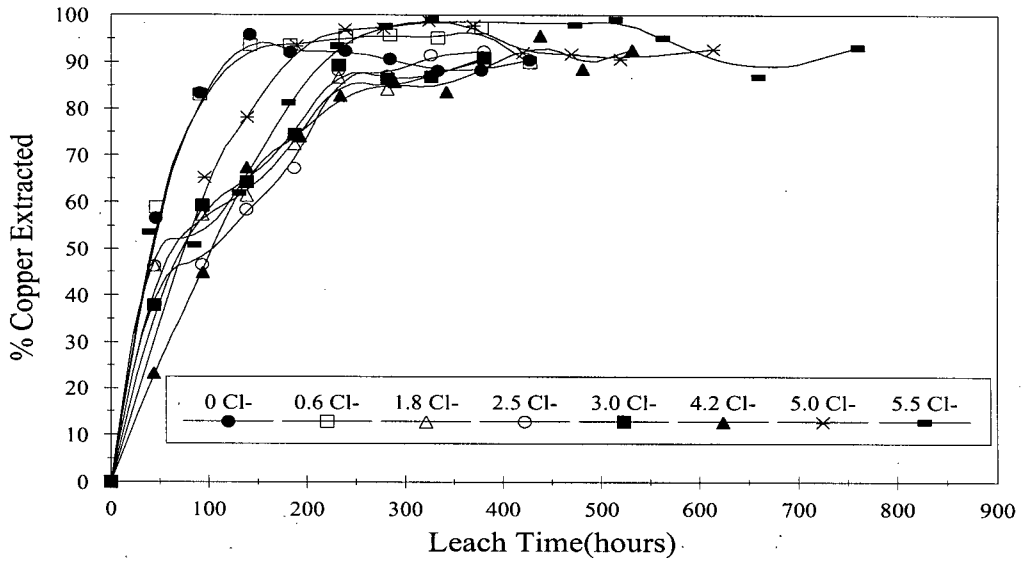


(c)



(d)

Figure 5.11 : Copper extraction vs. time plots for all bioleach tests in a specified set of the Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (c) Set 3; (d) Set 4.



(e)

Figure 5.11 : Copper extraction vs. time plots for all bioleach tests in a specified set of the Lower (Cl) series (Lower ore, 9 g/L Fe^{2+}, variable Cl^- level), (e) Set 5.

Figure 5.11 (a-c) also demonstrates the two-step chalcocite leach (described in section 3.7) at the higher chloride levels (4.2, 5.0, 5.5 g/L). Chalcocite to covellite oxidation is quite fast (up to 50% copper extracted), needing approximately 50 hours. In contrast, covellite to $CuSO_4$ oxidation can be quite slow (50-100% copper extraction), clearly demonstrating the need for an active bacterial population and significantly more leaching time.

Tables 5-3 and 5-4 summarize the copper extraction calculations based on the final leach residue and the assayed head (equation 5-14, page 108) and the calculated head (equation 5-13, page 108), respectively. Regardless of basis, some trends can be perceived. Firstly, at a fixed chloride level, the bioleach tests definitively outperformed the corresponding sterile test by a wide margin. Also, all of the bioleach tests conducted at a fixed chloride level had very little variation in their extractions. Next, as observed in Figure 5.9 (b), a minor improvement in copper extraction for the sterile tests was achieved as the chloride concentration increased. Lastly, in each set, there

was a slight increase in copper extraction for the bioleach tests as the chloride concentration increased. Unlike the corresponding trend in the sterile tests, which demonstrated an approximate 10% increase over the chloride range, this perceived trend in the bioleach tests is less apparent (3% over the same range), but it does apparently exist.

The aforementioned trends were often ambiguous in Table 5-3, but were more conspicuous in Table 5-4. Also, it is interesting to observe that a conspicuous, sometimes very large, difference exists between the initial ore grade and the calculated head assays from the various tests in this series; obviously, calculated heads are better suited for these types of calculations. Clearly, difficulty with control of the copper mass balance, in assaying, or in obtaining representative test samples, has occurred in this series. This issue is discussed in greater detail in section 5.6.

Table 5-3: Summary of copper extraction for Lower (Cl) series based on final residue analyses and the assayed head (3.87 wt% Cu).

Cl^- Level	Ultimate Copper Extractions (%) for Lower Cl Series Leaches (Based on Initial Assay Head Basis and Final Solids Assay)					
(g/L)	Sterile	Set 1	Set 2	Set 3	Set 4	Set 5
0.0	46.1	91.3	91.7	91.8	91.8	91.5
0.6	45.6	91.1	91.3	91.5	91.7	91.2
1.8	46.9	92.3	91.9	92.9	93.0	91.7
2.5	na	93.0	91.7	92.8	93.6	93.3
3.0	47.9	92.9	92.6	93.1	93.1	92.0
4.2	47.9	90.9	93.3	93.6	92.5	92.6
5.0	54.3	94.5	94.6	93.9	92.8	93.5
5.5	55.8	94.8	94.6	93.4	93.6	94.2

na means no data available due to loss of test.

In conclusion, the extraction results (curves and solids-based calculations) for this test series agreed well with the predictions from the E_h-time plots in section 5.3.1. The bioleach tests exhibited substantially higher ultimate extractions (averaging 92.7% by assayed head, 91.9% by calculated head) than the sterile tests (averaging 49.2% by assayed head, 43.6 by calculated head), clearly demonstrating the positive effect of bacteria. At a fixed chloride level, the bioleach test copper extractions were not observed to improve significantly with increasing generations, indicating that whatever gains that were achieved in terms of adaptation (decreased lag time) were not realized in increased extraction. The sterile tests' extractions increased slightly with higher chloride concentrations. In any given generation (set) of bioleach tests, copper extraction was observed to increase marginally with increasing chloride concentration. Initial bacterially-assisted copper leaching rates, as observed in the slopes of copper-extraction vs. time plots in a given set, apparently decreased with increasing chloride concentration.

Table 5-4: Summary of copper extraction for Lower (Cl) series based on final residue analyses and the calculated head [figure in parentheses]. Assayed head was 3.87 wt% Cu.

Cl^- Level	Ultimate Copper Extractions (%) for Lower (Cl) Series Leaches (Based on Calculated Head Basis and Final Solids Assay)					
(g/L)	Sterile	Set 1	Set 2	Set 3	Set 4	Set 5
0.0	39.4 (3.45)	90.2 (3.41)	91.0 (3.61)	90.8 (3.50)	91.1 (3.58)	90.4 (3.48)
0.6	41.2 (3.58)	90.0 (3.46)	91.0 (3.73)	91.4 (3.81)	90.4 (3.35)	90.0 (3.34)
1.8	42.0 (3.54)	92.1 (3.73)	91.8 (3.80)	92.3 (3.54)	92.4 (3.56)	90.3 (3.36)
2.5	na	92.6 (3.69)	91.2 (3.64)	92.3 (3.58)	92.5 (3.32)	92.4 (3.36)
3.0	44.1 (3.60)	92.1 (3.49)	91.6 (3.49)	92.2 (3.47)	92.3 (3.41)	91.0 (3.37)
4.2	44.0 (3.60)	90.1 (3.59)	91.9 (3.24)	92.4 (3.31)	91.4 (3.33)	92.7 (3.93)
5.0	45.6 (3.26)	93.6 (3.33)	93.1 (2.97)	93.1 (3.46)	92.5 (3.75)	92.9 (3.48)
5.5	48.6 (3.32)	93.4 (3.02)	93.1 (3.08)	93.2 (3.76)	93.5 (3.82)	93.2 (3.27)

na indicates no data due to loss of test.

5.3.3 Effect of Bacteria and Chloride Level on Total Acid Consumption

Table 5-5 summarizes the total acid consumption (computed with equation 5-15, page 109) of the sterile tests and the bioleach tests from Sets 1 to 5 of this series.

The sterile tests in this series required essentially the same amount of initial make-up sulfuric acid addition as their bioleach equivalents (3.66 vs 3.76 kg per tonne of ore), if the sole outlier can be discounted. Furthermore, this particular level of acid consumption was essentially unaffected by the chloride level throughout the test series, the average amount remaining practically unchanged. Thus, at the 9 g/L Fe^{2+} level, for this ore, it can be concluded that acid consumption was unaffected by either chloride concentration or bacterial activity.

Table 5-5: Summary of sulfuric acid consumption for Lower (Cl) series.

[Cl^-]	Sulfuric Acid Consumption of Leach Tests (kg/t)						
(g/L)	Sterile	Set 1	Set 2	Set 3	Set 4	Set 5	Average
0.0	3.66	3.67	7.34	3.66	3.68	3.67	4.40
0.6	3.66	3.66	3.66	3.67	3.69	3.66	3.67
1.8	3.66	3.66	3.65	3.67	3.67	3.68	3.67
2.5	na	3.66	3.66	3.69	3.67	3.67	3.67
3.0	3.67	3.67	3.66	3.67	3.66	3.66	3.66
4.2	3.67	3.66	3.66	3.67	3.68	3.65	3.66
5.0	3.67	3.65	3.67	3.68	3.68	3.68	3.67
5.5	3.66	3.66	3.66	3.66	3.67	3.64	3.66
Avg.	3.66						3.76

na indicates data unavailable due to test omission.

5.4 Zaldívar (Cl) Shake Flask Test Series

As seen in Figure B.8 in Appendix B, the initial inoculum used to initiate the Zaldívar (Cl) test series was from a bacterial culture acclimatized to 9K, 5 g/L Cl^-, and Zaldívar ore. This first set of serial transfers was used to initiate 4 tests (0, 2.5, 5, and 6 g/L Cl^-) and one bank (6 g/L Cl^-). Subsequently, the 6 g/L Cl^- bank, 6-7 days after the log phase had occurred (i.e. rapid rise in E_h), was used to inoculate the next two tests and another bank. The next two transfers at the 7 and 8 g/L Cl^- levels were performed in the same fashion. Finally, the series ended with the 9 g/L Cl^- bank initiating the final two tests.

5.4.1 Effect of Chloride Level on Bacterial Acclimatization

Figure 5.12 plots the redox potential, E_h, over time for all of the sterile tests in the Zaldívar (Cl) test series. E_h was limited to the 550-625 mV range. Therefore, bacterial activity was non-existent in these tests and ferrous iron predominated over ferric, presumably.

One minor trend in the E_h plateau values can be discerned. Although all of the sterile tests finished in the 600-625 mV range, those with the higher chloride levels (7, 8, 9, 10 g/L) tended to finish with the highest E_h values. Again, this is likely through chloride-assisted leaching of chalcocite, as observed for the sterile tests of the Lower (Cl) series. However, it should be noted that only a small amount of cupric ion is present in these tests initially, from the inoculum, unlike the Lower (Cl) series, but this amount may be sufficient to initiate the reaction sequence described in section 5.3.1. The higher E_h plateau may also be due to higher iron levels or some other reaction sequence present.

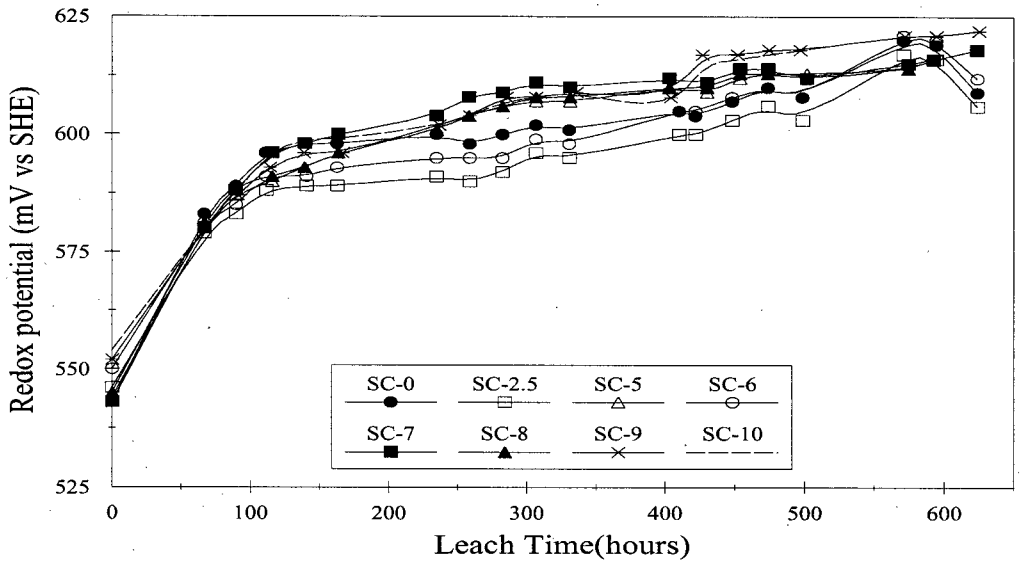


Figure 5.12 : Redox potential (E_h) vs. time plots for all sterile tests, Zaldívar (Cl) series (Zaldívar ore, 9 g/L Fe^{2+}, variable Cl^- level).

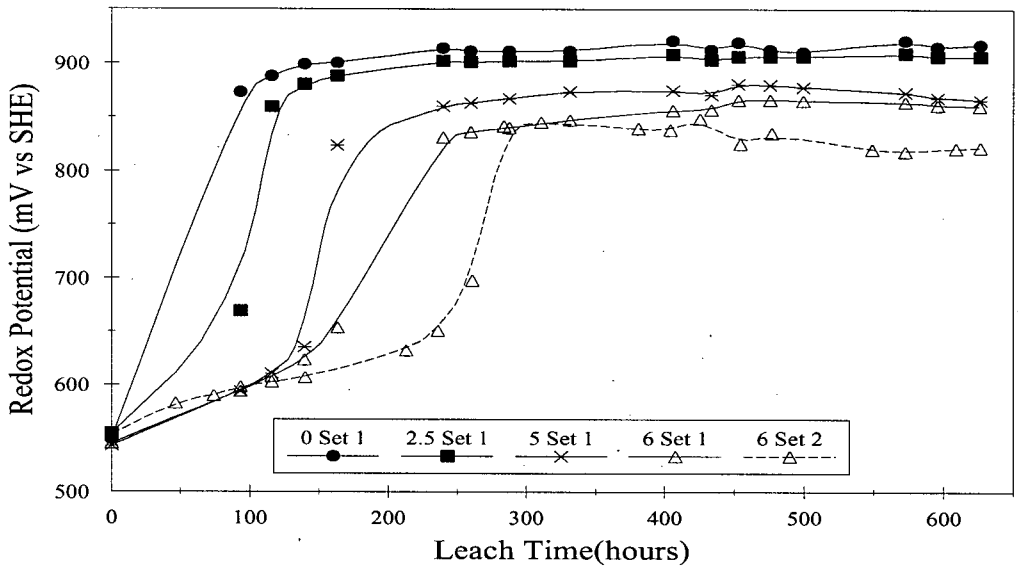
Figure 5.13 (a-d) plots E_h vs. time for all of the bioleach tests in the Zaldívar (Cl) series. Keeping in mind that the inoculum had been acclimatized to 5 g/L Cl^-, an obvious trend can be discerned. Clearly, the tests carried out at less than this base chloride level had significantly shorter lag times, while those at higher levels had longer lag times. As seen in Figure 5.13 (a), the bioleach test at 0 g/L Cl^- had a shorter lag than the test at 2.5 g/L Cl^-, again demonstrating that the bacteria can quickly adapt back to lower chloride levels and that there is no dependence on chloride ion. In contrast, a modest increase of 1 g/L Cl^- over the base level unquestionably inhibited growth, as both 6 g/L Cl^- bioleach tests required almost two-thirds more time to acclimatize. Also, the second test at 6 g/L Cl^- required even more time than the first, an unexpected result.

Inhibition, measured by lag time, continued to increase as chloride level increased in step-wise fashion from 6 to 9 g/L, as illustrated by Figure 5.13 (b) and (c). Only the 10 g/L Cl^- bioleach test exhibited a decrease in lag time compared to that of a test set 1 g/L Cl^- lower, possibly

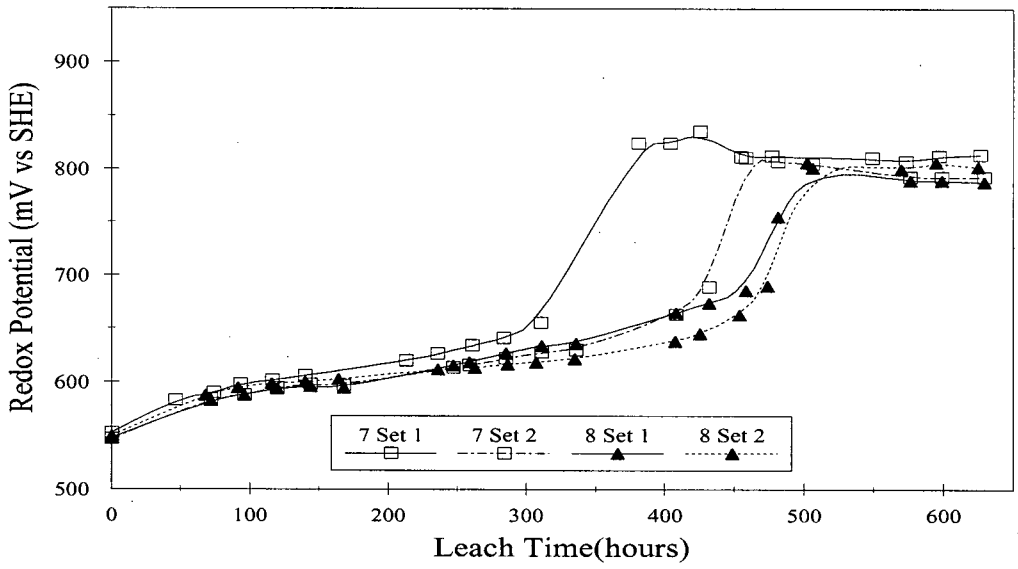
indicating better adaptation. Also, virtually all of the second generation (Set 2) bioleach tests generally required more adaptation time compared to their first generation (Set 1) counterparts, the 9 g/L test being the sole exception to this trend.

As seen in Figure 5.7 (a-h) in section 5.3.1, Figure 5.13 (a-c) illustrates that the final E_h level achieved by each bioleach test decreased as the chloride level increased, the full "spectrum" being illustrated in Figure 5.13 (d). This result plainly demonstrates the complexing power of chloride ion, the variable of interest in this series. As the chloride level increased, more ferric ion was complexed, reducing its activity in the system, decreasing the ferric/ferrous activity ratio, and ultimately lowering the plateau E_h.

Thus, adding chloride in excess of the initial adaptation level clearly inhibited the bio-leaching bacteria in this test series, as indicated by the increased lag in both the first and second generations of bioleach tests. Given the opportunity, it is likely that additional generations may have led to reduced lag times, as experienced with the Lower (Cl) series. With the sterile tests, higher chloride levels induced only minor increases in the plateau E_h, consistent with the trend observed with the Lower (Cl) sterile tests.

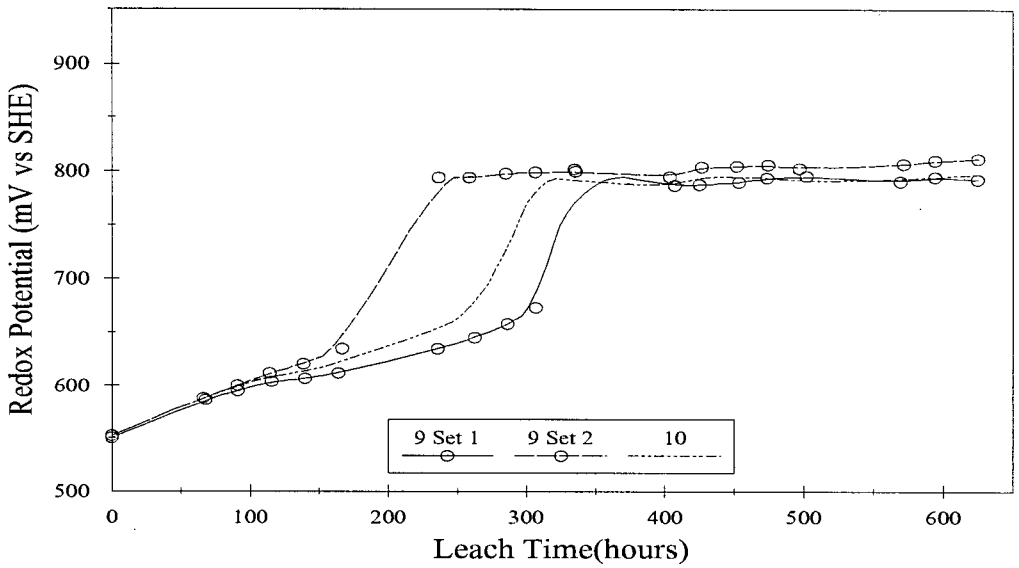


(a)

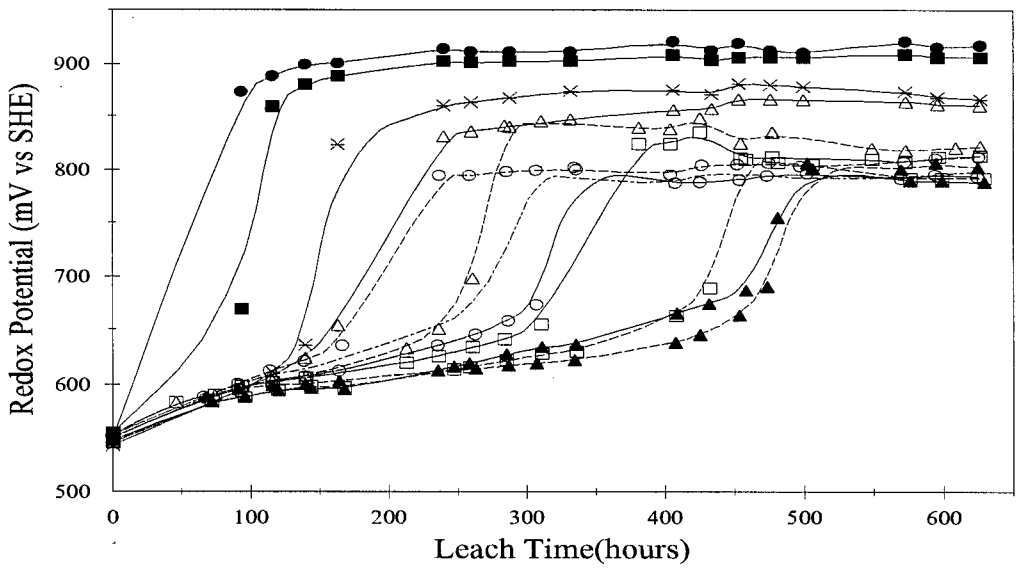


(b)

Figure 5.13 : Redox potential (E_h) vs. time plots for Zaldívar (Cl) series (Zaldívar ore, 9 g/L Fe^{2+}, variable Cl^- level), bioleach tests (# indicates chloride level in g/L, Set # indicates generation), (a) 0 Set 1, 2.5 Set 1, 5 Set 1, 6 Set 1, and 6 Set 2; (b) 7 Set 1, 7 Set 2, 8 Set 1, and 8 Set 2.



(c)



(d)

Figure 5.13 : Redox potential (E_h) vs. time plots for Zaldívar (Cl) series (Zaldívar ore, 9 g/L Fe^{2+}, variable Cl^- level), bioleach tests (# indicates chloride level in g/L, Set # indicates generation), (c) 9 Set 1, 9 Set 2, and 10; (d) all of the bioleach tests in this series (NB: same legend as previous three figures).

5.4.2 Effect of Bacteria and Chloride Level on Copper Extraction

Figure 5.14 plots copper extraction (computed with equation 5-12, page 107) data for all of the sterile tests. Surprisingly, yields were extremely high, in the 70-90% range, with the highest results for the 2.5, 6, 9, and 10 g/L Cl^- tests. These results are inconsistent with ordinary first-stage leaching of a chalcocitic ore, such leaching usually being limited to 50% extraction (section 3.7). Also, they suggest that chloride-ion based leaching reactions, operating at the low redox potentials displayed in Figure 5.12, were contributing to overall copper recovery. While it is unmistakeable that the highest extractions were associated with the two highest chloride levels, other extractions of similar values are spread over the chloride range, obscuring any meaningful trend. Regardless, these results demonstrate that the Zaldívar ore is much more reactive than the Lower ore under similar solution conditions. The reasons for this difference in reactivity between the two ores under sterile conditions will be thoroughly examined in section 5.5.

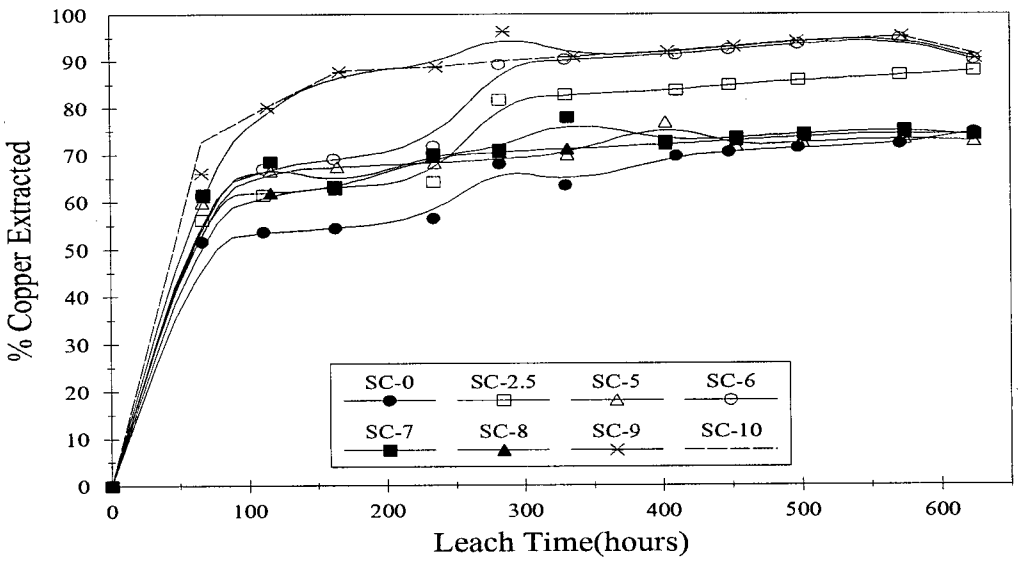


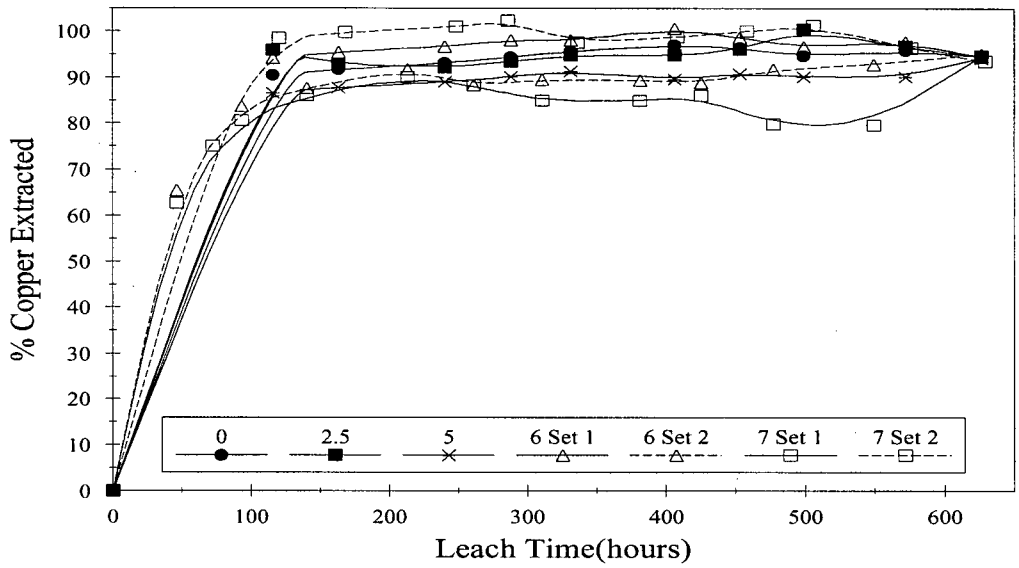
Figure 5.14 : Copper extraction vs. time plots for all sterile tests, Zaldívar (Cl) series (Zaldívar ore, 9 g/L Fe^{2+}, variable Cl^- level). (Legend: SC means sterile control, # is chloride concentration in g/L).

Figure 5.15 (a-e) are plots of copper-extraction (computed with equation 5-12, page 107) vs time data for all of the bioleach tests ranging over the chloride range tested in this series.

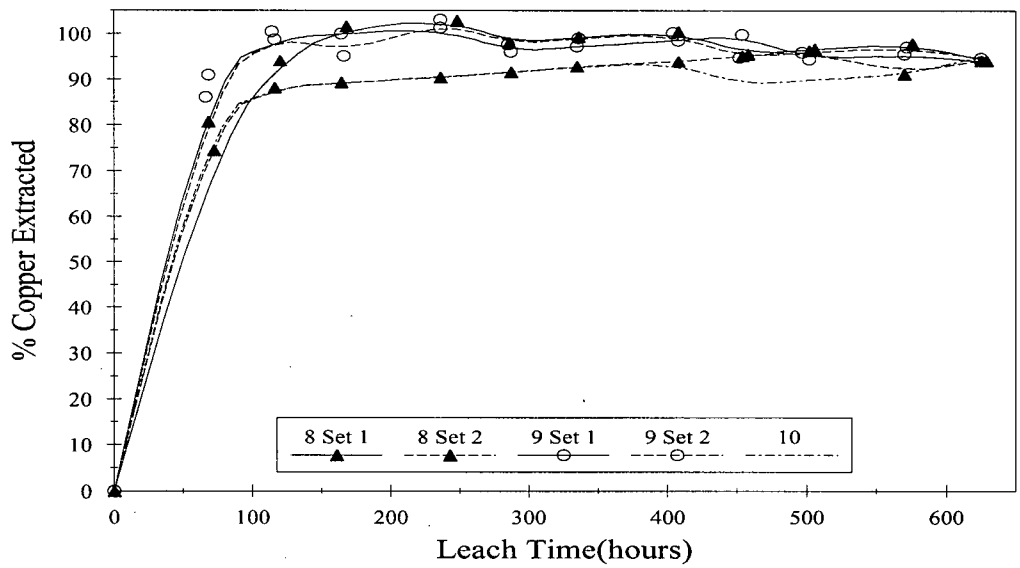
As can be seen in Figure 5.15 (a), (b), and less clearly in (e), there is a generally upward trend in copper extraction with increasing chloride level. This trend is not consistent as oscillation did occur in the curves pertaining to the 7 g/L (Figure 5.15 (a)), and the 9 g/L Cl^- tests (Figure 5.15 (b)). On reviewing the solution data, it is apparent that this oscillation may be related to abrupt surges and plunges in the sample copper concentration on the order of 0.1 g/L.

It is noteworthy that, except at the 7 g/L Cl^- level, there was no improvement in copper extraction for the second generation (set) tests, reflecting the increased lag times noted in section 5.4.1. It is a strong possibility that the different inoculation procedure, in depleting the inoculum to the second-generation bioleach tests of well-adapted bacteria, significantly affected the overall copper extraction of these tests.

Figure 5.15 (c) and (d) illustrate not only that the biological contribution to overall leaching is minimal, but also that the inorganic contribution is more strongly affected by the increasing chloride concentration. Quite clearly, the copper extraction of the 9 g/L Cl^- sterile test outperformed its 2.5 g/L Cl^- counterpart and definitively provides a very large proportion of the overall leaching in the corresponding bioleach test.

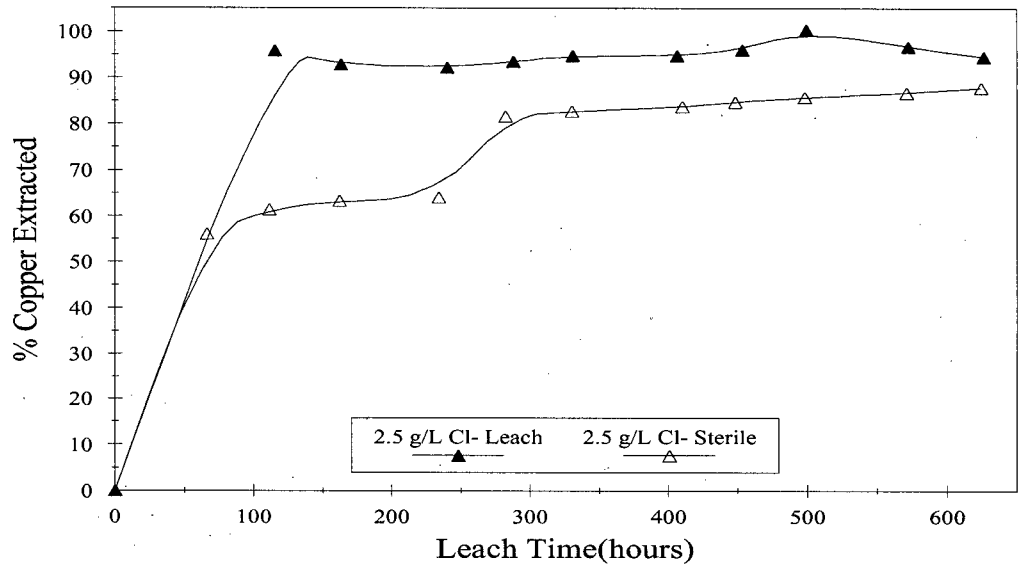


(a)

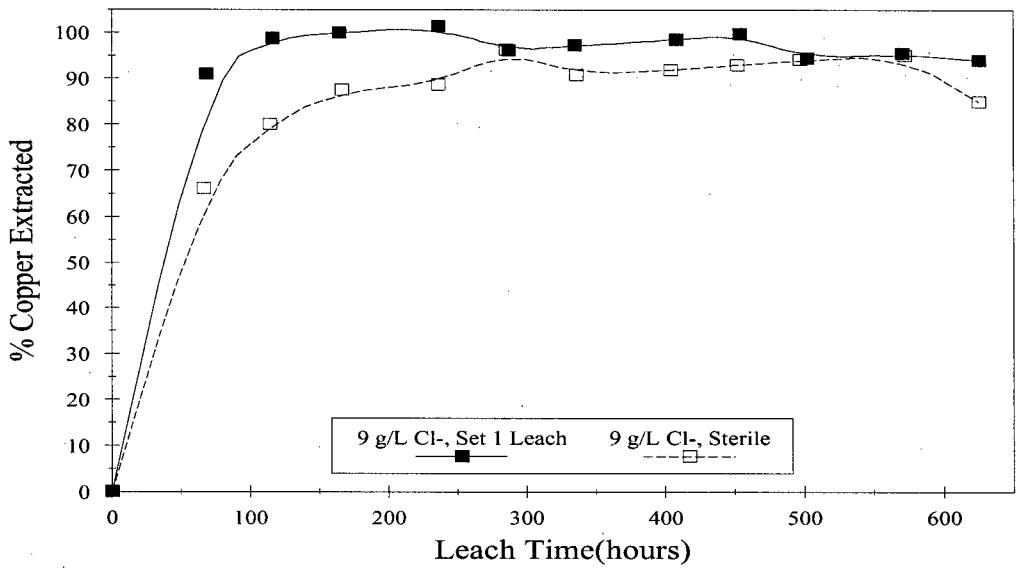


(b)

Figure 5.15 : Copper extraction vs. time plots, bioleach tests, Zaldívar (Cl) series (Zaldívar ore, 9 g/L Fe^{2+}, variable Cl^- level). (Legend: # indicates chloride level in g/L, Set # indicates generation), (a) 0 Set 1, 2.5 Set 1, 5 Set 1, 6 Set 1 & 2, 7 Set 1 & 2; (b) 8 Set 1 & 2, 9 Set 1 & 2, 10.

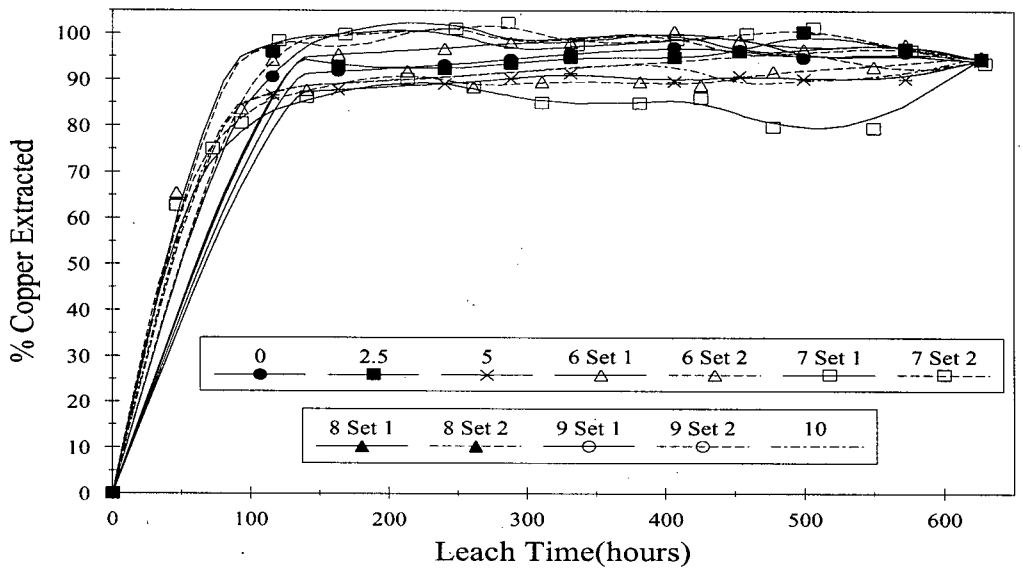


(c)



(d)

Figure 5.15 : Copper extraction vs. time plots, bioleach tests, Zaldívar (Cl) series (Zaldívar ore, 9 g/L Fe^{2+}, variable Cl^- level). (Legend: # indicates chloride level in g/L, Set # indicates generation), (c) 2.5 Set 1 & 2.5 sterile test; (d) 9 Set 1 & 9 sterile test.



(e)

Figure 5.15 : Copper extraction vs. time plots, bioleach tests, Zaldívar (Cl) series (Zaldívar ore, 9 g/L Fe^{2+}, variable Cl^- level). (Legend: # indicates chloride level in g/L, Set # indicates generation), (e) all of the bioleach tests in the series together.

Table 5-6 summarizes the calculated copper extractions based on the final leach residue analyses and the assay head (equation 5-14, page 108) while Table 5-7 summarizes similar calculations determined with the calculated head (equation 5-13, page 108). Regardless of basis or the type of test, these extraction figures agreed well with the extraction plots in Figure 5.14 and Figure 5.15. Also, there appears to be a general correlation between extractions and increasing chloride level. This trend is strong for the sterile tests, but is weak for the bioleach tests.

It is very interesting to observe that the calculated head assays in Table 5-7 bracket the initial head assay value by ± 0.1 wt% Cu, indicating both good control of the copper mass balance and a representative head assay.

Table 5-6: Summary of copper extraction for Zaldívar (Cl) series based on final residue analyses and assayed head (1.64 wt% Cu).

Cl^- Level	Ultimate Copper Extraction (assay head basis) for the Leach tests in the Zaldívar (Cl) series			
(g/L)	Sterile	Set 1	Set 2	Average
0.0	73.3	95.0	na	95.0
2.5	87.4	94.9	na	94.9
5.0	73.0	94.2	na	94.2
6.0	90.5	95.0	95.0	95.0
7.0	74.6	94.3	93.7	94.0
8.0	74.4	94.4	94.5	94.5
9.0	91.4	94.4	95.1	94.8
10.0	92.0	95.1	na	95.1
	82.1 (steriles)			94.7 (leaches)

na=data unavailable; only a single test was carried out at this chloride level.

Table 5-7: Summary of copper extraction for Zaldívar (Cl) series based on final residue analyses and calculated head.

	Sterile Leaches		Set 1 Leaches		Set 2 Leaches	
[Cl^-] (g/L)	Calc. Head	% Cu Extracted	Calc. Head	% Cu Extracted	Calc. Head	% Cu Extracted
0.0	1.73%	74.7	1.52%	94.6	na	na
2.5	1.70%	87.8	1.54%	94.6	na	na
5.0	1.63%	72.8	1.65%	94.3	na	na
6.0	1.61%	90.3	1.51%	94.5	1.69%	95.1
7.0	1.61%	74.1	1.74%	94.6	1.62%	93.6
8.0	1.63%	74.2	1.61%	94.3	1.59%	94.3
9.0	1.52%	90.7	1.53%	94.0	1.50%	94.7
10.0	1.53%	91.4	1.62%	95.0	na	na

na=data unavailable; only a single test was carried out at this chloride level.

To conclude, the bioleach test results indicate that copper extraction, regardless of calculation method, is essentially unaffected by the background chloride ion level in this series. However, this is not the case for the sterile tests, which exhibit a strong correlation between copper extraction and increasing chloride level. The high extraction results of the sterile tests indicate that the lack of a bacterial presence (and associated higher E_h level) was not as significant for this ore's leaching behaviour, as it was for the Lower ore. Moreover, these results suggest that a larger fraction of the copper mineralization in this ore is either more acid soluble or more amenable to inorganic-based leaching than is typical for a chalcocitic ore. This will be examined in greater detail in section 5.5.

5.4.3 Effect of Bacteria and Chloride Level on Total Acid Consumption

Table 5-8 summarizes the total acid consumption, computed using equation 5-15 (page 109), of all leaches, sterile and bacteria-laden, in this test series.

Although the number of tests was relatively small, some definite trends can be discerned. On average, the sterile tests generally required more make-up sulfuric acid than their bacteria-laden counterparts. As seen in earlier sections, this result confirms the idea that the bacteria must generate some acid towards maintaining their environment.

Next, the amount of makeup-acid for the sterile tests appears to be independent of chloride level, averaging 15.7 kg sulfuric acid per tonne of ore. The higher requirements of the 6 and 7 g/L Cl^- level tests could be explained by the presence of more acid-demanding constituents in a given sample as a result of poor sampling technique.

This trend does not appear to be the case for the bioleach tests, since a significant deviation occurs at chloride levels higher than 5 g/L. It is significant to note that the starting culture for this test series was acclimatized to this identical chloride level before this series began. While the differences in the acid volume could be explained as acid measuring errors (a consideration when one uses a micropipette to measure 50 μL increments of 6 mol/L sulfuric acid) or ore sampling errors (more acid-demanding minerals in the ore sample than average), the possibility of decreased ferric ion activity due to the presence of relatively high levels of chloride ion does exist. That is, taking into account the chloride ion's greater affinity for ferric ion compared to the sulfate ion, it is conceivable that less ferric ion could be incorporated into jarosite, resulting in a greater acid demand. As hypothesized, this may not be likely, when one considers the amount

of chloride present in a given test against a large background of sulfate ion. Lastly, thought should be given to the likelihood that, at these chloride levels, the bacterial requirements for hydrogen and sulfate ion could not be met, resulting in higher acid requirements.

Thus, one could conclude that (a) sterile tests required more acid than bioleach tests independent of chloride level and (b) that bioleach tests carried out at chloride levels higher than 5 g/L required more acid, possibly due to increased bacterial requirements.

Table 5-8: Summary of sulfuric acid consumption for Zaldívar (Cl) series.

Cl^- Level	Sulfuric Acid Consumption of Leach Tests (kg/t)			
(g/L)	Sterile	Set 1	Set 2	Average
0.0	14.77	11.01	na	11.01
2.5	14.69	11.02	na	11.02
5.0	14.71	10.97	na	10.97
6.0	18.46	11.06	14.69	12.88
7.0	18.37	14.73	16.94	15.84
8.0	15.43	14.75	10.99	12.88
9.0	14.66	14.68	15.29	14.99
10.0	14.62	15.39	na	15.39
	15.71 (steriles)			13.46 (leaches)

na=data unavailable; only a single test was carried out at this chloride level.

5.4.4 Effect of Bacteria and Chloride Level on Sulfide Sulfur Oxidation

Table 5-9 summarizes the percent sulfide sulfur (S^{2-}) oxidized during each test in the series. Sulfide oxidation was calculated by assaying the sulfide sulfur content of both the initial ore and the final residue of each test.

On reviewing the data for the sterile tests, sulfide sulfur oxidation appeared to generally increase with increasing chloride concentration. In contrast, the bioleach tests in both sets did not exhibit any clear trend with chloride level, as sulfide sulfur oxidations oscillated throughout the range of chloride values tested.

It is also clear that, at any given chloride level, except 2.5 g/L, the presence of bacteria generally had a definite, positive effect on sulfide sulfur oxidation, as expected. The variability in this effect may well reflect either on the effectiveness of the bactericide or on the effect of an abiotic reaction catalyzed by the higher chloride concentrations. In the case of the 2.5 g/L Cl^- sterile and bioleach tests, a disproportionate amount of acid soluble minerals in the test sample may have distorted the results, as has been already noted in the copper extraction results in section 5.4.2.

Lastly, only the first four bioleach residues from set 1 (namely 0 Set 1, 2.5 Set 1, 5 Set 1, 6 Set 1) were assayed for elemental sulfur. As indicated in Table 5-9, these contained only 0.02-0.03%. It is likely that the other bioleach test residues would contain similar amounts of elemental sulfur. Hence, this incomplete sulfide sulfur oxidation can be directly attributed to unreacted pyrite, since it would be the last mineral to be oxidized because of its nobility.

Table 5-9: Summary of sulfide sulfur oxidation for Zaldívar (Cl) series.

Cl^- Level	% S^{2-} Oxidized in Zaldívar (Cl) Leach Residues		
(g/L)	Sterile	Set 1	Set 2
0.0	35.1	71.2[a]	na
2.5	81.0	76.9[a]	na
5.0	31.2	69.9[a]	na
6.0	56.3	69.0[a]	78.3
7.0	34.8	64.9	50.3
8.0	35.2	58.7	69.1
9.0	52.9	63.7	76.0
10.0	57.4	75.6	na

[a] these residues assayed 0.02-0.03% elemental sulfur.
na=data unavailable; only a single test was carried out at this chloride level.

5.5 Compare & Contrast: the Lower (Cl) and Zaldívar (Cl) sterile tests

If the extractions from the sterile tests from the two chloride series (Lower and Zaldívar ores) are compared, some explanations for the higher results for the Zaldívar tests can be offered. As a corollary, the bacterial contribution in the bioleaching tests can also be more meaningfully evaluated at the same time.

To begin, acid-soluble copper mineralization in both ores must have played a significant role in sterile leaching, as this copper content would have rapidly solubilized on exposure to acid media. Only indirect information on acid-soluble copper content is available for both ores. An assay performed by Chem Met Consultants on a sample of Mina Ivan ore (same ore body as Lower

ore, same size range) suggested as much as 14% as a rough figure for the Lower ore, while an assay in a recent master's thesis [163] (same source in ore body, larger size range) reported 32% for the Zaldívar ore; these rough figures suggests that, compared to the Lower ore, up to twice as much acid-soluble copper is present in the Zaldívar ore. In the Lower ore, atacamite and chrysocolla are the likely participants in such leaching, while brochantite and chrysocolla are the counterparts in the Zaldívar ore. Of course, the copper-bearing sulfide common to both ores, chalcocite, is also susceptible to acid solubilization to a lesser degree. It is significant that the Zaldívar tests, on average, required more sulfuric-acid makeup than their Lower ore counterparts (steriles: 15.71 vs 3.66 kg/t, leaches: 13.46 vs 3.76 kg/t). While this large difference could be partially attributed to the lower pH parameters (pH Start Value, Upper Operating pH Limit, Table 4-2) for the Zaldívar (Cl) test series, it is not inconceivable that a substantial fraction was consumed solubilizing acid-soluble copper, if it wasn't consumed by gangue mineral reactions (section 3.6.3).

Chloride-assisted cupric-ion leaching of chalcocite is another factor in the sterile leaching of both ores. Firstly, the Lower ore's chalcocite content, as suggested by the earlier-mentioned Mina Ivan assay, could be as much as 31% of the total copper content. In the Zaldívar ore, chalcocite was reported to make up 30-60% of the total sulfide content and 85-90% of the total copper content [163]. While there was not as much initial cupric ion in the Zaldívar ore, the small amount present in the inoculum was probably sufficient to initiate the reaction sequence described in section 3.7 to exploit the large chalcocite content. In addition, the higher Cl^- levels probably enhanced this reaction sequence by complexation and by the larger solubilization driving force appreciated with the associated higher E_h values (Figure 5.12), resulting in increased extractions at the higher chloride concentrations (Figure 5.14, 5.15 c & d). In contrast, the Lower sterile tests, also undergoing cupric-ion leaching, were subjected to smaller driving forces (lower chloride

level and lower E_h levels, Figure 5.6 (b)) and did not experience large extractions (Figure 5.9 (b)), despite a larger initial cupric ion concentration. This was probably due to its comparatively lower chalcocite content.

Lastly, galvanic leaching (described in section 3.6.2.2.2) may have had a part in the high copper extractions experienced by the Zaldívar sterile tests as well. This is probably largely due to the Zaldívar ore's high initial pyrite content (possibly 40-70% of the total sulfide content, if chalcocite and pyrite are the primary sulfides as reported for the Zaldívar ore [8]). In the Lower ore, only minor amounts of pyrite are reported present (<5%); this particular leaching mechanism is probably not as predominant for this ore. As seen in Table 5-9, there are large amounts of unreacted sulfide in most of the final residues of the Zaldívar sterile tests, increasing with chloride concentration. This observation strongly suggests chloride-enhanced galvanic leaching was occurring. That is, intimate contact between pyrite and chalcocite particles suspended in solution probably did occur, resulting in anodic dissolution of chalcocite, aided by copper complexation with chloride ion.

5.6 Sources of Error for Calculations-Analysis and Discussion

Table 5-10 summarizes the loss, by percentage and equivalent copper mass, from the overall copper mass balance for all of the leach tests, categorized by type (sterile, bioleach). Also, certain extraction-time curves exhibited significant oscillations as the direct result of fluctuations in analyzed copper concentrations of supernatant leachate samples. In addition, while calculated heads from the Zaldívar ore tests tended to bracket the assayed head very closely (± 0.1%), those from the Lower ore tests ranged widely from the assayed head. Clearly, there are some obvious trends, some of which can be explained in terms of procedural errors, systematic errors, and

random errors, as well as differences in operating procedures. These errors must be considered carefully, in order to accurately evaluate the relevance or validity of all calculations related to copper extraction.

Table 5-10: Summary of copper losses from mass balances for all test series. (Equivalent copper masses based on 8 g sample and assayed head of ores used, Lower: 3.87 wt% Cu, Zaldívar: 1.64 wt% Cu)

Leach Series, test type	% Losses (min, max) (assayed head basis)	Equivalent Mass of Copper Lost (8 g basis/assayed head)
Lower (Fe), sterile	1.5-6.0	0.005-0.019
Lower (Fe), bioleach	4.5-7.5	0.014-0.023
Lower (Cl), sterile	3.2-7.2	0.010-0.022
Lower (Cl), bioleach	0.5-10.2	0.002-0.032
Zaldívar (Cl), sterile	0.5-7.2	0.0007-0.009
Zaldívar (Cl), bioleach	0.9-8.0	0.001-0.010

Generally, sterile tests suffered less losses than their bioleach counterparts. This can be attributed to the fact that no inocula (in or out) were required for such tests, compared to the bioleaching tests. Ambiguity about the copper content transferred still existed. This was because 5 mL of slurry was actually transferred to a bioleach test, while the associated sample drawn for analysis consisted of 1 mL of supernatant leachate. Consequently, only the amount of soluble copper transferred was known, while the amount of metal (copper or iron) entrained and native to the leach residue transferred was not. Furthermore, the amount of solid leach residue transferred in an inoculum was unknown, as pulp densities of inoculating cultures or tests were never measured. Estimated to contain as much as 5% of the solids from the inoculating culture, this amount of solids could be very significant to copper balances in all bioleach tests performed. While this is a problem for the Zaldívar tests, it is doubly so for both Lower series, as there is a

lack of knowledge about this transferred copper for both the inoculating and the inoculated test. Incidentally, this procedural flaw is the reason why the final iron content of virtually every shake flask test, regardless of type, was always in excess of the starting iron content; the iron contained in the entrained jarosite was never evaluated. In retrospect, the best way to evaluate an inoculum's metal content is to actually draw and assay a slurry sample whenever a serial transfer is executed.

If compared on an ore basis, it was obvious that the Zaldívar ore tests, regardless of type, experienced less losses than the Lower ore tests (Fe and Cl). Primarily, this was because rigorous end-stage treatment was performed on all Zaldívar ore tests to obtain measurements on all final leach products at termination. This was not the case for the majority of the Lower (Cl and Fe) tests, as poor handling of final leach products resulted in ambiguities with regards to the final leach solution data. Consequently, final leachate copper for all of these tests had to be estimated from an assumed final volume ($V(Th)$) and the analysis of a supernatant sample of the leachate. This approach underestimated (a) the real filtrate volume due to solution densities greater than 1 g/cc and (b) the real copper value because of copper entrained with the solids. Short of redoing the bulk of the test work, it was decided that this estimating approach was the best means of providing meaningful, but not entirely reliable quantitative data for the thesis.

Another reason for the better execution of the Zaldívar ore tests was the fact that the operating procedures were different. Not only was the inoculation methodology for the bioleach tests different (compare Figure B.8 to Figure B.7 in Appendix B), but the monitoring and sampling regimens were less stringent than was the case for the Lower ore tests (Table 4-3). The inoculation method used in the Zaldívar (Cl) series, while not necessarily successful at facilitating culture adaptation, was nonetheless successful in eliminating half of the associated mass-balancing problems with the method used for both Lower series. The less stringent regimens, combined with a less ambitious testing program, enabled the research to be carried out at a reasonable pace,

and, unknowingly, reduced any probe-related losses.

Indeed, throughout the entire testing program, no attempt was made to reduce or eliminate the losses of solution or leached solids during monitoring of E_h or pH. Unfortunately, due to the monotonous nature of the monitoring, no thought was taken to consider the implications of neglecting to wash such seemingly minor accumulations on the respective probes back into the shake flasks. These often daily losses, combined together, may prove to be very significant and account for a major proportion of the discrepancies in the mass balance. An attempt was made to judiciously adjust the extraction data to reflect the losses; however, it soon became apparent that this endeavour was not only ill-advised, but also a waste of time. So, of the three series, the Zaldívar (Cl) tests were the least affected by this situation, while both Lower series were very severely affected. Not surprisingly, the extraction results, as well as the calculated heads, ostensibly reflect this fact.

In an attempt to evaluate the magnitude of such probe-related losses, a separate set of bioleach and sterile tests utilizing 8±0.05 g samples of the Mina Ivan and Lower ores was performed. The specific starting conditions of the tests summarized in Table 5-11 were chosen to also evaluate other topics deemed relevant to clarifying the magnitude of perceived errors in the original test work.

To facilitate comparison, these tests were subjected to an absolute "no losses tolerated" regime from start to finish. All inputs and outputs were carefully measured and analyzed. After monitoring, probes were washed back into shake flasks and any excess water evaporated carefully. No inoculations from one test into another test were permitted with this series of tests, thus eliminating that possible source of error. At termination, rigorous end-stage treatment was applied

to obtain all final test data of relevance. In spite of poor leaching by some of the bioleach tests, thereby necessitating re-inoculation, all tests in the set were successfully terminated after 5 weeks (Summaries in Appendix D).

Not surprisingly, the error in the mass balances did improve, averaging 4.2% for all six tests, thus proving the effect of controlling daily losses and final leach data. Also, the calculated heads for all 6 tests were reasonably close to the assayed heads, especially when compared to those calculated for both Lower series. Furthermore, the projected extraction figures behaved reasonably well, with wild oscillations not obviously present, as was the case for several tests conducted in the earlier 3 test series.

Table 5-11: Summary of starting conditions for check tests. Concentrations of inorganic species are nominal values in g/L.

Test Label	Test Type	Media Name	Fe^{2+} Level	Cl^- Level	Cu^{2+} Level
5MI(8)	Leach	9K	9.0	5.0	0.0
SC[5MI(8)]	Sterile	9K	9.0	5.0	0.0
5MI(8) Set 2	Leach	9K	9.0	5.0	0.0
L9S(8) RLT5	Leach	9K-5Cu	9.0	5.5	5.0
L-STD RLT0	Leach	9K	9.0	2.5	0.0
L-STD RLT5	Leach	9K-5Cu	9.0	2.5	5.0

While the reinoculation of some of the check tests may have affected the final error, it is also possible that the 5 g/L copper background level, a fixture in the Lower ore test series (Fe and Cl), may have had some bearing, as well. That is, the copper content associated with this initial copper level, which must be deducted in the mass balance and related calculations, was overshadowing the copper actually leached from the ore. Supporting this contention is the fact that

the single Lower bioleach test initiated with no copper background level, LSTD-RLT0, had the best error (1.06%) in the set, while its 5 g/L copper counterpart, L-STD RLT5, had an error 1.5 times greater (2.9%).

In the process of running this last set of tests, data was also accumulated to evaluate the possibility either of copper entrainment or of the formation of a sparingly soluble copper chloride complex, both of which would incorporate in the final solids. This is a suitable course of action to undertake when considering losses on the order of 0.01-0.03 g of copper from each mass balance. Indeed, there are precedents for this hypothesis. Razzell and Trussell [146], during their study of bacterial leaching of chalcocite in the presence of sodium chloride and ferrous sulfate, in attempting to explain the final low copper level on test termination, noted that the formation of a Cu-Fe precipitate may have been involved. Other possibilities for copper-bearing precipitates include atacamite and CuCl, as seen in Figure 3.12 in section 3.5.3. Dutrizac [161] has noted that cupric iron, Cu^{2+}, can become incorporated into any of the alkali jarosites ($MFe_3(SO_4)_2(OH)_6$ where M = K^+, Na^+, NH_4^+, H_3O^+, 1/2 Pb^{2+}, Ag^+, etc.) by substituting for ferric ion, Fe^{3+}, in the lattice structure. While this incorporation is usually minor, it increases with increasing base metal or alkali sulfate concentration and pH, but decreases with increasing iron concentration. Although this incorporation is probably sensitive to temperature, it is plausible that copper could be lost in the jarosite that is known to form abundantly during shake flask bioleach tests.

Powder X-ray diffractometry of selected leach residues from the Lower (Fe and Cl) test series generated spectra which indicated the presence of potassium hydronium jarosite, $(K, H_3O)Fe_3(SO_4)_2(OH)_6$. This result is in accordance with both general knowledge and personal observations of the yellow colour of the bioleach test slurry after log-phase growth had occurred. So, entrainment in the jarositic portion of leach residues was still a distinct possibility.

Copper co-precipitation in the jarositic portion of the leach residue was tested by dissolving 1 g samples of leach residue (1 sample each from Lower series) in 100 mL of 0.9948 M HCl, decanting off the solution, and analyzing for copper. Duplicate tests on secondary samples replaced the decantation step with a filtering step, with subsequent analysis of the filtrate for copper. The test of the Cl series residue (9K-5Cu, 2.5 g/L Cl^-) indicated that it contained 0.0036-0.0037 g of copper, while the Fe series residue (0K-5Cu, 2.5 g/L Cl^-) tested was found to contain 0.009 g of copper, apparently confirming the hypothesis.

To attempt to quantitatively evaluate both possibilities from the carefully-controlled check tests outlined in Table 5-11, the mass of copper normally entrained in the filter cake was first calculated by multiplying the equivalent volume of entrained water in the cake by the measured specific gravity of the filtrate solution. Then, this value was compared to the amount of wash copper. In all of the check tests, the calculated cake-entrained copper was less than the wash copper, possibly indicating that a sparingly soluble copper chloride complex had formed during the washing or filtering of the final solids.

This result clearly contradicts thermodynamic predictions. While E_h-pH diagrams drawn up to reflect prevailing copper and chloride levels (Appendix F, Figure F.1 (a-f)) indicated that the formation of CuCl was unlikely to occur in the higher E_h regions encountered during actual leaching, there is no denying the fact that CuCl did exhibit a region of stability in the region around 0.5 V_{SHE} and pH 2-5 in Figure 3.12 (unit activity conditions). During the filtration step of the termination phase, it is conceivable that these particular conditions can be generated, making it possible for CuCl precipitation. Also, it should not be forgotten that many of the iron-bearing complexes, including the basic copper sulfates and jarosites, were not included in the E_h-pH diagrams discussed in section 3.5; these could have been the caches of any copper lost through co-precipitation.

Regardless, by failing to properly treat the final products, it is likely that the leached copper associated with the solids, entrained or not, was lost. The amount of copper lost by the Lower ore bioleach check tests with a 5 g/L Cu background (Appendix D), appears to be on the order of 0.03 g. This agrees well with the maximum loss actually experienced by the Lower (Cl) bioleach tests, apparently closing the balance.

To close this discussion, some random errors should be considered.

With regards to the Lower (Cl and Fe) series, the average error, based on two assays, of the final solids copper content was consistently in the 2-5% range. This error is apparently satisfactory, although certified assayers could probably do better, as was the case for the Zaldívar series. Incidentally, these are the best indicators of the degree of copper extracted for these series if the solids losses incurred during execution of the tests could be deemed minimal or negligible.

AA errors, including those incurred by dilution and flame fluctuation, were estimated to be 5%, based on regular checks with standard solutions. Considered a major factor in the metallurgical balance, a 5% variation in any of the sample copper figures was calculated to cause a change of 7% in the calculated extraction figures for any Lower series test. It should also be noted that background matching was not considered when making up the AA standards. That is, nitric acid-based standards were used to generate the calibrations used to calculate the iron and copper values from the bioleach leachate samples which had chloride backgrounds but were diluted for analysis with nitric acid. Concern about this problem mandated a check of the predicted Cu and Fe concentrations of standards prepared with 2% HCl against a calibration curve based on 2% nitric acid-based standards. Comparison of the two sets of standards (5 ppm Cu/5 ppm Fe and 10 ppm Cu/10 ppm Fe) for absorbances and predicted concentrations indicated a very slight increase in predicted Cu, while there was a very large increase in predicted Fe. Thus, it appears proven, to reasonable satisfaction, that the background matrix did not affect the predicted

copper concentrations in any significant fashion. However, true background matching when running AA analyses, at least with respect to the trace elements in the leachate (i.e. 0K), could have been attempted to at least minimize such background-related errors.

Incidentally, operation of the Thermo Jarell Ash Smith-Hieftje 4000 Atomic Absorption Spectrophotometer working with two lamps in double-beam mode was not as untroubled as the company's sales representatives claimed. There was a substantial amount of manual intervention required to ensure alignment (wavelength/mirror) of the source beams. Results were extremely sensitive to the input flowrate of sample analyte, which, while easily adjustable, was itself highly influenced by gas (air/acetylene) line pressures, the cleanliness of the very narrow (mm tolerance) input capillary tube, and the degree of cleanliness of the burner head. Often, this author, in attempting to reproduce the lean flame operating conditions deemed to produce optimum results, spent countless hours adjusting the instrument just to get reasonable results.

Lastly, the accuracy of the micropipette was not checked regularly to ensure reliability. At unknown times, the micropipette would perform less than optimally due to clogging of the internal mechanism. Consequently, the error on a 1 mL sample, typically the volume of a single supernatant leachate solution sample, could have been as high as 30%, an error which would have been propagated in the copper extraction calculations.

Thus, after all factors have been thoroughly considered, the primary source of error in extraction calculations was the failure to perform proper end-stage treatment on the leach tests, especially those pertaining to the Lower ore series (Fe and Cl). Related to poor end-stage treatment is the very high probability that copper did become lost in the solids (jarosite or copper complex), as indicated by the positive results of tests chosen to evaluate this possibility. Consequently, it is clear that all calculations for these tests consistently underestimated the amount of copper present in the final pregnant solution, resulting in low calculated heads and low final extractions.

Solution and solids losses incurred during monitoring were demonstrated to be significant, but not as deleterious as poor-end stage treatment; recall that the Zaldívar ore tests suffered only from probe losses, but did not demonstrate, in calculated heads, the clear difficulty in mass balance control evidenced in the Lower ore tests. Random errors did not appear to be very significant, although fluctuations in AA analyses did occur, resulting in large oscillations in the copper extraction curves of some leach tests.

Chapter 6 Conclusions

The Lower (Fe) series bioleach tests clearly experienced reverse acclimatization (i.e. inhibition), as evidenced by increasing lag time with increasing time, partly by design (i.e. large difference between the adapted Fe^{2+} level of bacteria in the inoculum and the Fe^{2+} level in the medium) and partly because of a procedural error (i.e. late serial transfer). Bioleach tests plateaued at high E_h values, while sterile tests plateaued at distinctly lower E_h values. Both bioleach and sterile tests exhibited an iron-level effect (higher E_h plateau values with increasing initial Fe^{2+} level).

Errors in solution-based copper extractions for this series were primarily attributable to improper treatment of final products, making solids-based copper extractions more reliable. These latter extractions were high for bioleach tests (averaging 94.2%), relatively lower for sterile tests (averaging 48.7%), and did not vary with initial iron level. As expected, sterile tests required more make-up sulfuric acid than their bioleach test counterparts. Regardless if bacteria were present or not, the amount of make-up acid increased as initial iron level (Fe^{2+}) decreased, proving the significance of the acid released through hydrolysis reactions.

The Lower (Cl) series leach tests exhibited easy and difficult adaptation, as indicated by E_h-time plots, the severity depending on the difference in chloride level between the base culture tolerance (2.5 g/L Cl^-) and the test medium. As expected, bioleach tests and sterile tests demonstrated clear differences in solution potentials. The sterile tests exhibited the trend of increasing E_h with increasing chloride level over a narrow E_h range, while the converse was true for the bioleach tests. The first can be interpreted as chloride-enhanced cupric-ion leaching phenomena, while the latter could be explained as a consequence of ferric-ion complexation by chloride ion. For tests set at chloride levels above the base level, lag times decreased with increasing time (increasing set or generation number), providing clear evidence of adaptation.

As with the Lower (Fe) series, solids-based extraction calculations were more reliable than those based on solution analysis. Bioleach tests exhibited substantially higher ultimate (solids-based) extractions (averaging 92.7% by assayed head, 91.9% by calculated head) than the sterile tests (averaging 49.2% by assayed head, 43.6% by calculated head), clearly demonstrating the positive effect of the presence of bacteria. A weak relationship between chloride level and copper extraction was observed with the sterile tests, while there was no relationship between chloride level and copper extraction for the bioleach tests. Sulfuric acid consumption was found to be unaffected neither by the presence of bacteria nor by the concentration of chloride ion.

In spite of a smaller number of tests, chloride inhibition was also observed in the Zaldívar (Cl) bioleach tests. Clearly, adding chloride ion in excess of the base level resulted in inhibition of the bacteria in bioleach tests, although adaptation, indicated by attainment of high E_h levels, still occurred. In this series, lag times continued to increase between the first and second generations; however, it is probable that these would have decreased with more generations. As with the Lower (Cl) work, sterile tests exhibited a direct relationship between E_h and chloride level, while bioleach tests exhibited an inverse relationship.

Extractions for the Zaldívar (Cl) tests, solution-based or solids-based, were more reliable primarily because of rigorous end-stage treatment, and tended to agree well. Surprisingly, the sterile tests exhibited very high extractions (averaging 82.1% by assayed head, 82.0% by calculated head) compared to the bioleach tests (averaging 94.7% by assayed head, 94.5% by calculated head). Clearly, factors other than cupric chloride leaching, as experienced with the Lower (Cl) test series, were making this ore much more reactive, compared to the Lower ore, when bacteria were not present. These include (a) conspicuous differences in mineralogical content (e.g. chalcocite, pyrite), (b) apparently more acid-soluble copper mineralization, and (c) chloride-enhanced galvanic leaching (e.g. pyrite-chalcocite couple). Reinforcing this concept is

the observation that a strong correlation between chloride level and copper extraction for the sterile tests does exist. A similar, but very weak relationship was observed to apply for the bioleach tests. Sulfuric acid consumption for the sterile tests was higher than that for their bioleach counterparts, independent of chloride level. In contrast, bioleach tests conducted at chloride levels greater than 5 g/L required more makeup acid with increasing chloride level.

Chapter 7 Recommendations For Further Work

7.1 Specific Concerns

1. That the accepted, proper procedure to obtain metallurgical data be clearly established at the beginning of any research project. Due to haste and poor example, confusion existed in this author's mind as to the proper mass-balancing procedures employed when bacterial culturing to increase chloride tolerance and when metallurgical testing to quantitatively measure the effect of chloride ion on copper extraction from bioleaching experiments.

2. That a standard bacterial counting method be used in all test work involving bacteria. Other researchers in biohydrometallurgy routinely report the concentration of bacteria in the inoculum as well at other times during leaching tests; they're treated just like any other inorganic lixiviant or chemical substance. During the course of the empirical work, undesirable situations did occur which could have been prevented through proper monitoring of bacterial concentrations.

3. That the content of key sulfur-based species be determined in both the starting ore and the final residue in sulfide ore bioleaching studies. The deportment of sulfur species, particularly sulfide sulfur and elemental sulfur, can greatly assist in the analysis of the extraction results of ore bioleaching studies.

4. That bioleach testing be conducted with proper means of controlling/monitoring of the levels of inorganic ions in solution. For example, $[Cl^-]$ was inferred by calculation, but never measured quantitatively. Similarly, $[Fe^{2+}]$ was not determined at the start of each test; this level was calculated from the analyses of the various components added into each flask.

5. That sampling the pH-standardized slurry in a leach flask be conducted prior to inoculation with bacteria---in order to obtain a quantitative measure of the acid-solubilized copper under sterile conditions, providing a better means of determining the bacterial contribution to overall leaching.

6. That complete assaying (i.e. acid digestion) of a slurried sample from an inoculating culture be done instead of a simple analysis of the soluble metals in a supernatant sample. In doing so, a more complete job of mass-balancing can be achieved; in particular, the metals contained in the solids associated with the inoculum can be quantified, instead of being ignored.

6. That tests with industrial strength chemicals be carried out, in parallel, with the bioleaching program, in order to evaluate the relative efficiency of bacteria. In this thesis, this option was strongly considered, but never executed, due to time constraints.

7. That testing of the bactericide (2 g thymol/ L methanol) be conducted, in order to fully evaluate its efficiency as a bacterial inhibitor. A recent critical review of bacterial inhibitors [164] cited the work done by Leong *et al.* [162] as a specific example of thymol-inhibited bioleaching. The critics noted that the choice of inhibitor was "based more on tradition than necessarily on firm scientific evidence." Their research indicated that washing thymol-treated ore resulted in a resumption of normal abiotic and biotic leaching curves, suggesting that reversible sorption of the chemical to sulfide mineral surfaces was occurring. That is, thymol significantly affects the physical and chemical characteristics of ore samples; it apparently adsorbs at mineral surfaces, affecting dissolution rates. Furthermore, the critics drew attention to the fact that its use in representative sterile controls results in great exaggeration of bacterial contributions in ore leaching evaluation programs. This author was not aware of this potential difficulty during the empirical program, but is now greatly concerned about this question pertaining to thymol use.

7.2 General Concerns & Comments

1. That similar testing programs with other anions be conducted as there appears to be a deficiency in this area of research.

2. That similar testing programs be conducted with samples of on-site water sources and ore samples (and other environmental conditions with minimal simulation) from specific industrial sites as required. The study just completed was largely artificial in that the nutrient medium (e.g. 9K) was exceeding rich. In reality, the specific nutrients required by bacteria are often scarce. Furthermore, in industrial practice, companies will rarely add any amount of expensive chemical compounds to a low-cost, long retention time operation like a dump or heap leach. (In contrast, the same objection does not apply to agitated tank leaching as low retention times are desired.) Also, the combination of ions in the ore and the on-site water will often be complex; the current work was comparatively simple in this respect, but was less applicable to the actual situation at the mine site.

3. That results from such testing programs conducted at the laboratory scale be retested at the pilot scale at the mine site before proceeding with the actual industrial operation (heap leach, dump leach, agitated leach, etc.). It should be apparent that a positive result in the laboratory does not necessarily translate to similar results in the field, because of different physical and environmental considerations. For example, a bacterial strain successfully developed in the laboratory to operate under high chloride levels may not necessarily be any better than an indigenous strain already present at the mine site; indeed, indigenous strains are probably more robust than their laboratory counterparts.

4. That a testing program be conducted with a strain of *T. prosperus* [102], since its properties show much promise for copper ore bioleaching in saline environments.

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APPENDIX A: Sieve Analysis: Procedure and Summary of testing of the Lower and Mina Ivan ore samples used in this study

Synopsis:

To begin, when performing a sieve analysis of -100 mesh material, a standard procedure or method is followed. It consists of wet-screening a known amount of material through a fine mesh screen, drying the remaining portion prior to dry-screening with a standard sieve series. There is a reason for this procedure. It is to eliminate or minimize the potential problem of the smaller particles agglomerating together during the dry screen, in order to ensure an accurate analysis.

Methodology:

(1) Weigh, by difference, a fixed amount of the sample to be analyzed, into a tared beaker.

(2) Wet screen the contents with a 400-mesh screen, a bucket, a shower head water applicator attached to a water source, and a vibrator (or other source of oscillating motion, to facilitate the screening).

(3) After washing the resulting residue into tared, clean beakers (or other containers), dry in a low-temperature oven to drive off the accompanying water.

(4) After the residue has dried, determine its weight, and subtract this figure from the original amount of material; this is the amount of material which passed through the 400-mesh screen.

(5) Dry-screen the dry residue from (3) with a standard sieve series (or whatever series of sieves you choose to use) and an appropriate shaking machine (e.g. ROTAP) for a standard period of time (e.g. 15 minutes).

(6) From each sieve, carefully brush out the contents into a tared beaker, and record the weight for each portion, correlated with each sieve.

(7) You now have a distribution. If everything was done correctly, all of the weights of the various portions add up to the original fixed weight, with minimal skewing of the distribution by agglomeration.

Summaries of actual analyses

	Lower Rayrock Ore	Mina Ivan Ore
Sample:		
Date:	Nov. 23, 1992.	Nov. 23, 1992.
Total Sample Wt:	50.11 ± 0.02 g	50.03 ± 0.02g

Screen Opening (mesh)	Weight (g)
65	0.04
100	0.57
150	3.67
200	4.84
325	6.64
400	1.19
under size	33.16
Weight of portion (-200 mesh):	40.99
Percent of portion (-200 mesh):	81.8%

Screen Opening (mesh)	Weight (g)
65	3.80
100	2.55
150	4.22
200	3.80
325	6.68
400	1.23
under size	27.75
	35.66
	71.3%

APPENDIX B: "Family" trees or generational maps of bacteria cultures referenced in the thesis

The following figures are tree diagrams representing the serial transfers/generational mappings of the bacterial cultures discussed or referenced in the thesis. Values in brackets show the amount of ground ore, in grams, used in a bank or a leach. With regard to the leaches or the initial scoping shake flask tests as referenced in Leong *et al.* [162], the unbracketed number next to the series designator (the letter A, B, B*, or C) refers to the type of nutrient solution used, namely 9K or 0K (iron-free 9K). For the banks, the unbracketed value is the number of transfers accomplished to that point in time.

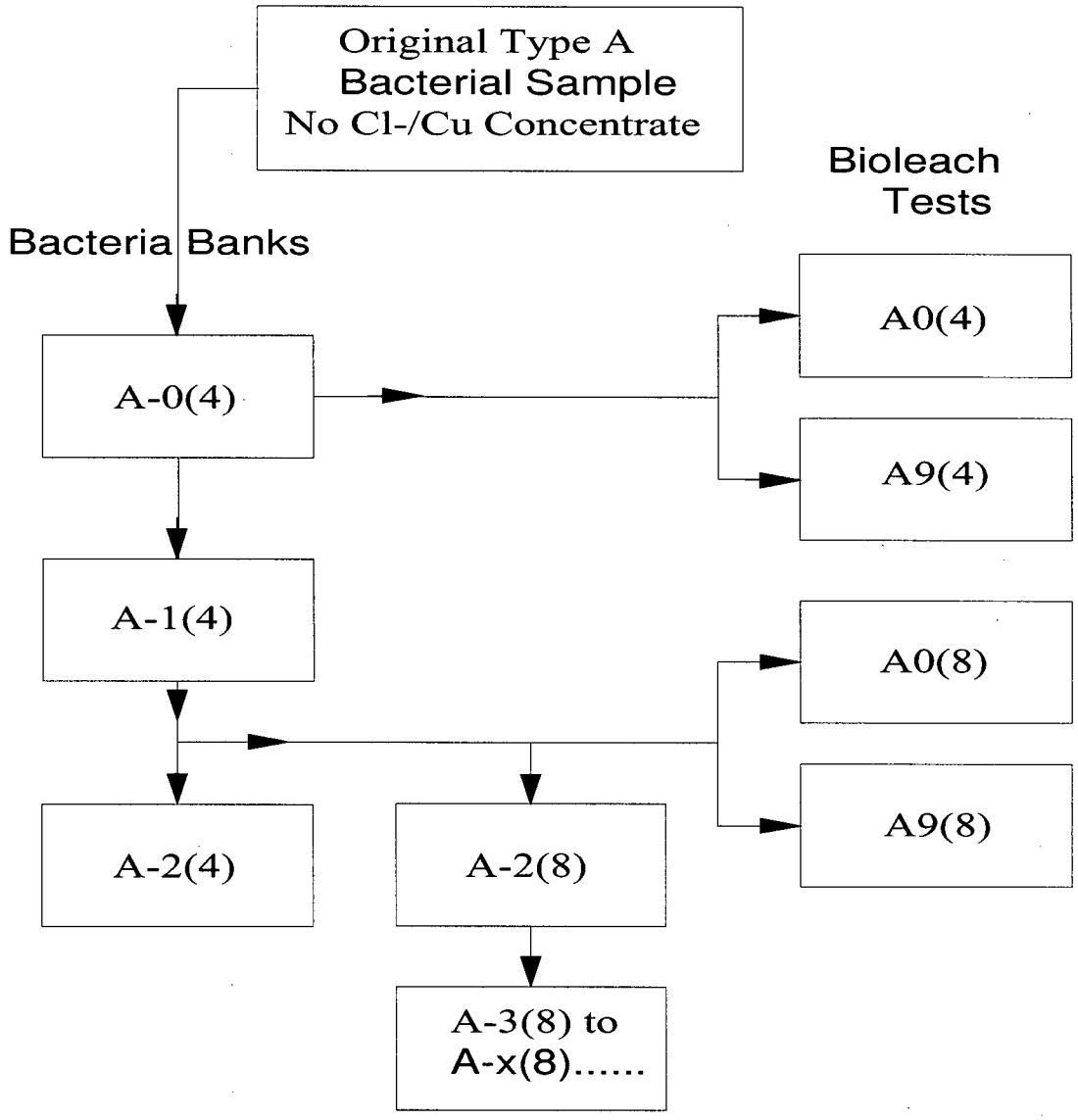


Figure B.1: Tree diagram representing the Series A bacterial culture initially from Bacon, Donaldson, & Associates Ltd., Richmond, B.C., Canada. Originally grown on a copper concentrate grading 28.5% Cu and no chloride in solution, this culture was maintained on Mina Ivan ore and 9K media.

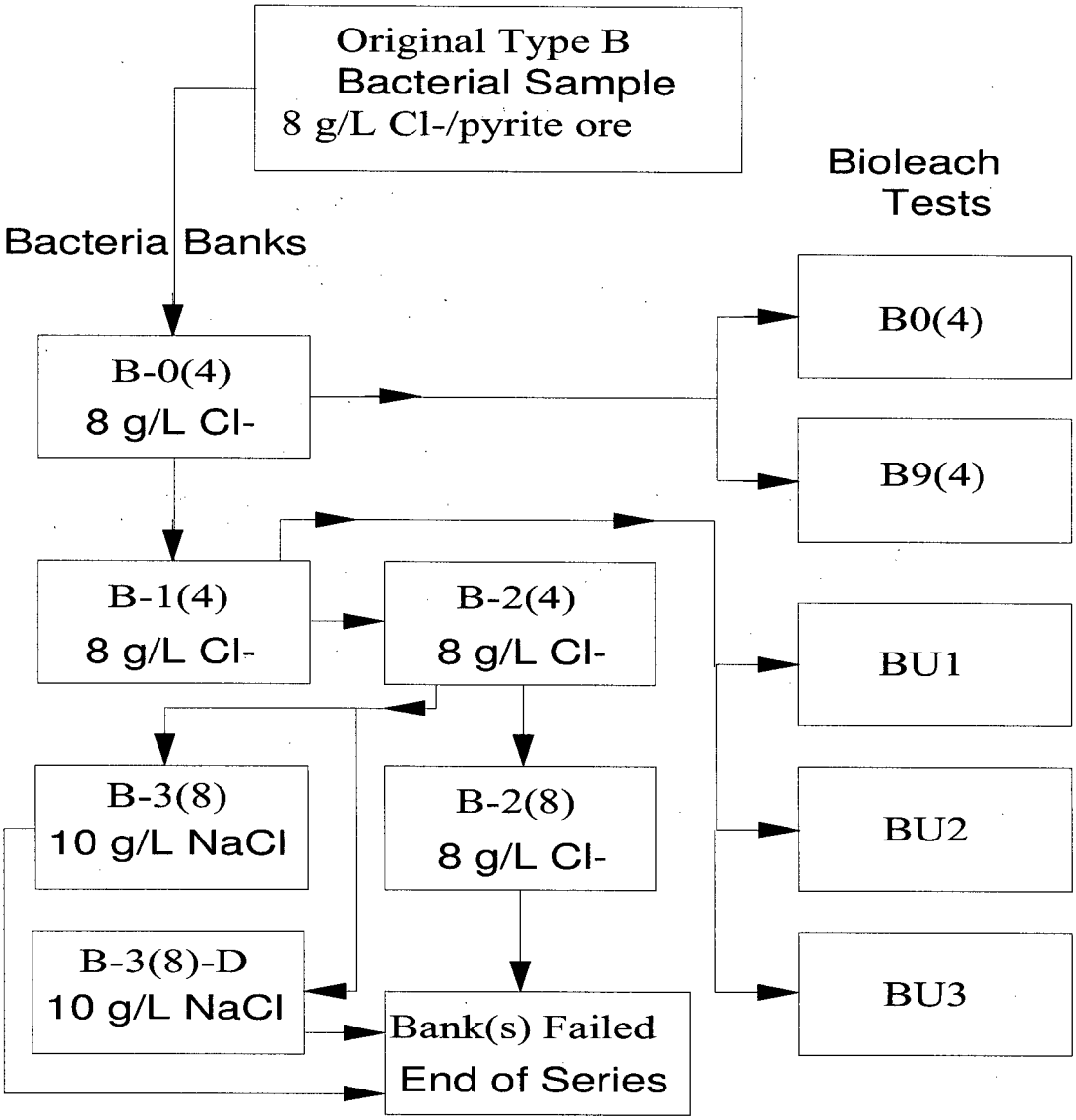


Figure B.2: Tree diagram representing the Series B bacterial culture initially from Bacon, Donaldson, & Associates Ltd., Richmond, B.C., Canada. Originally grown on a pyrite ore in a solution containing 8,000 ppm NaCl, this culture was subsequently maintained on Mina Ivan ore and 8,000-10,000 ppm of NaCl. Unfortunately, it perished, and was replaced by a new B culture (Figure B.5).

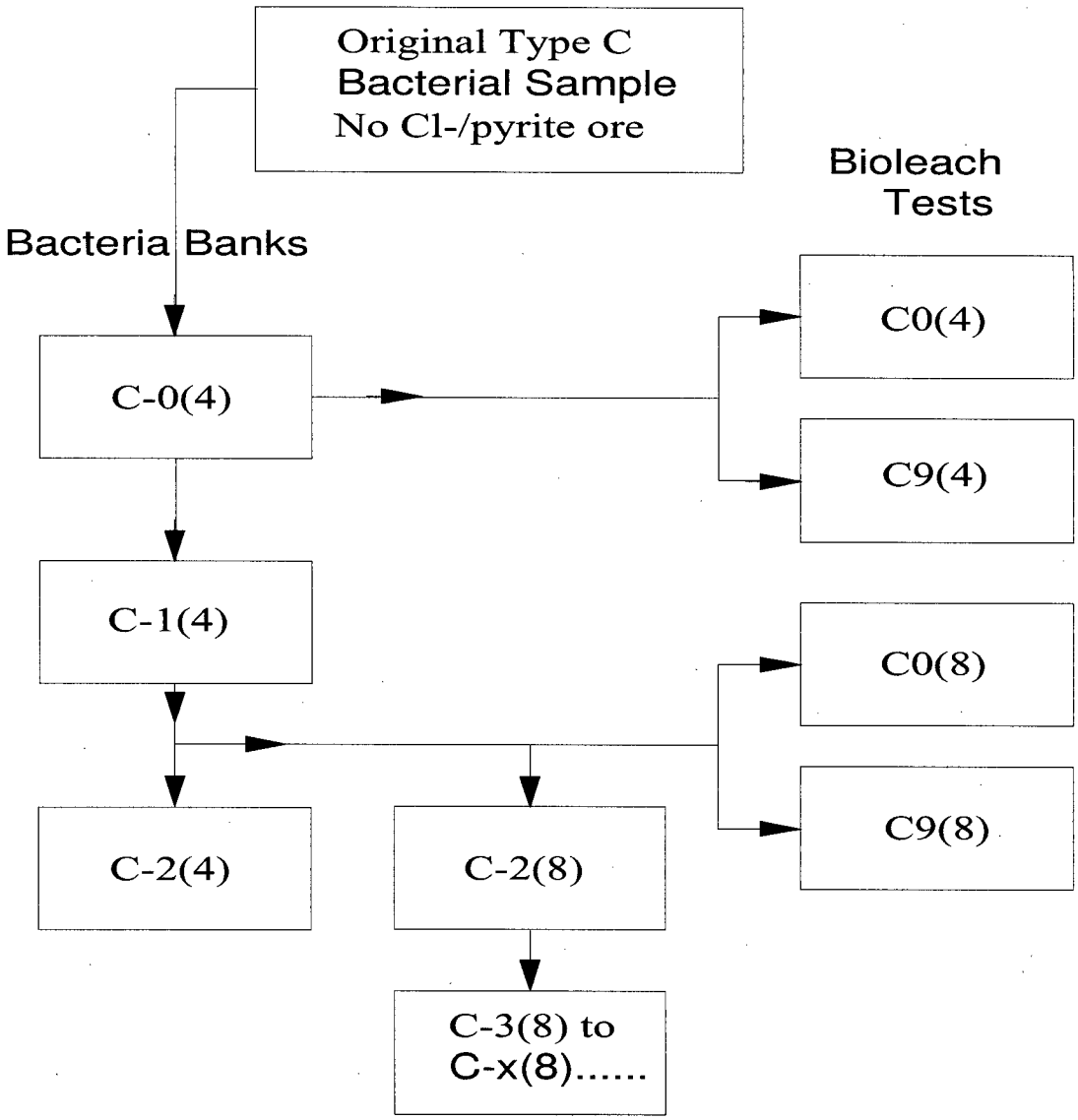


Figure B.3: Tree diagram representing the Series C bacterial culture initially from Bacon, Donaldson & Associates Ltd., Richmond, B.C., Canada. Originally grown on pyrite in media containing no chloride in solution, this culture was maintained on Mina Ivan ore and 9K media.

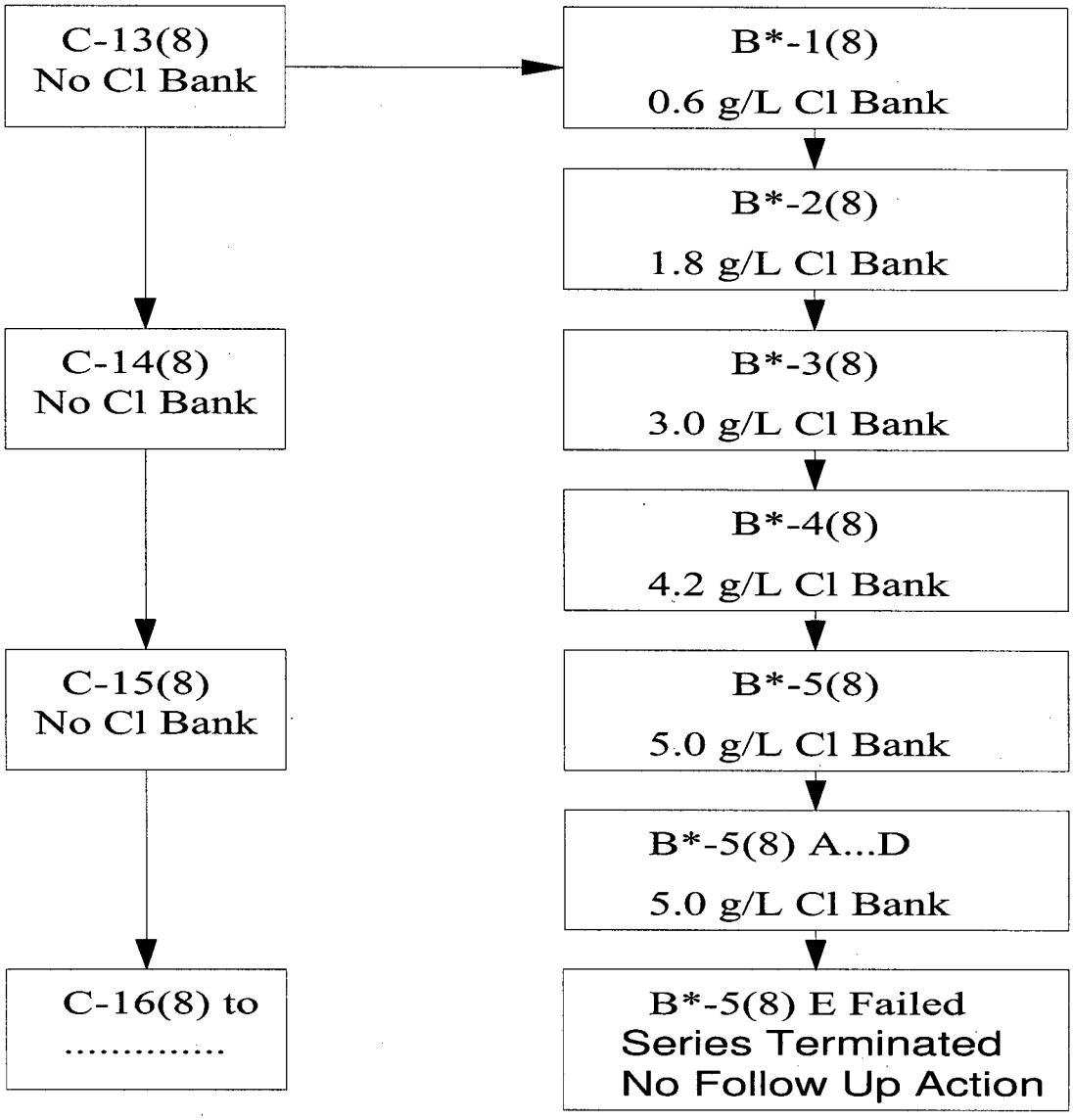


Figure B.4: Tree diagram representing the B* series bacterial culture. Subcultured from a C series bank, this series was an attempt by the author to develop a mixed culture on Mina Ivan ore with a high chloride tolerance by gradual adaptation. Like the original B series culture, this culture, after demonstrating 5 g/L Cl^- tolerance, could not be maintained and ultimately perished.

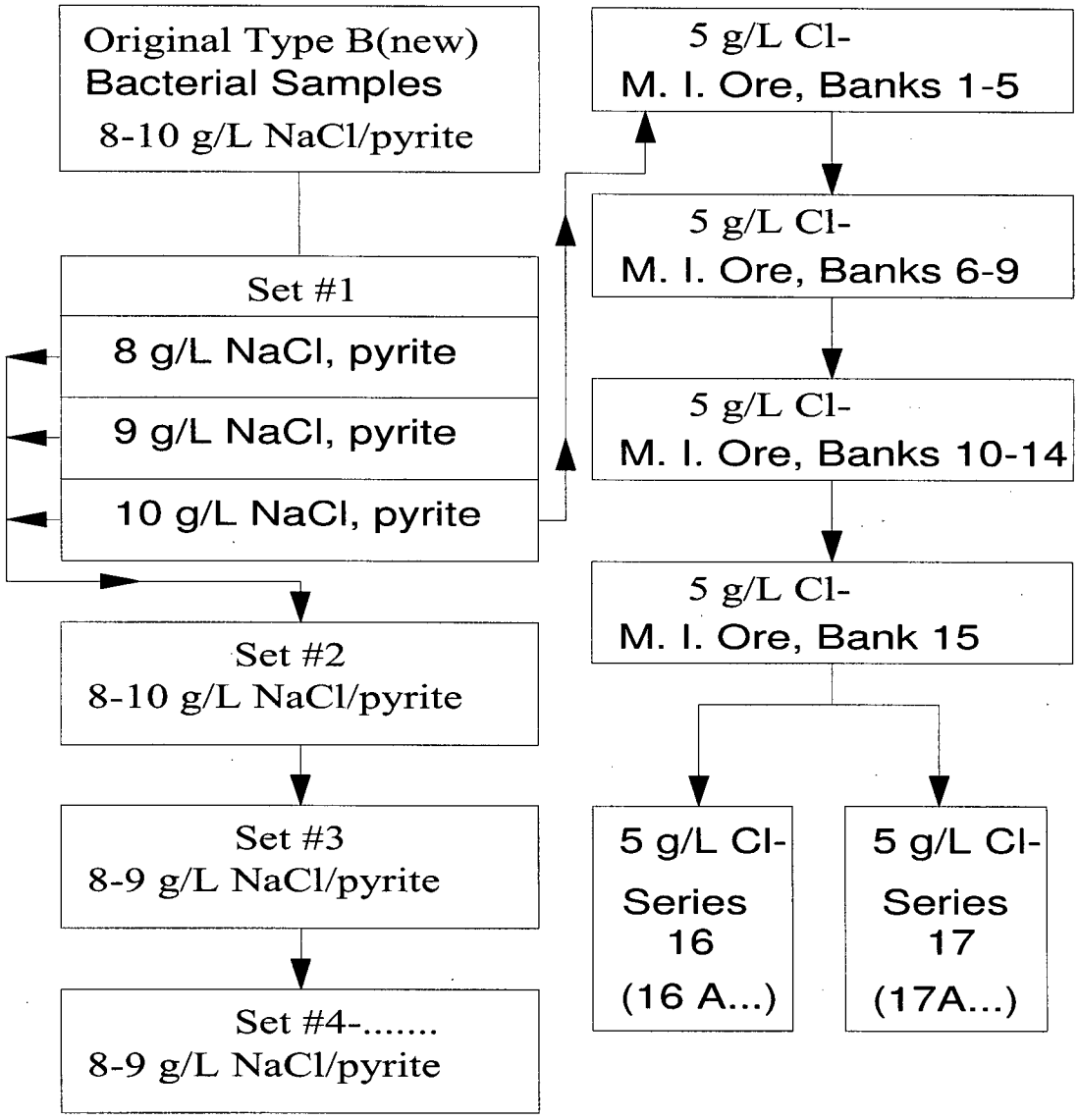


Figure B.5: Tree diagram representing the new Series B bacterial culture derived from a second set of cultures donated from Bacon, Donaldson, & Associates Ltd., Richmond, B.C., Canada. Originally grown on a pyrite ore in solutions containing 8,000-10,000 ppm NaCl, this culture was subsequently maintained on Haile pyrite ore, 8,000-10,000 ppm of NaCl, and 9K media. As shown, a serial transfer from the 10,000 ppm NaCl bank in Set #1 was used to initiate a single bank acclimatized to 5 g/L Cl^- and Mina Ivan ore, the primary antecedent for both Lower ore bacterial leaching series.

Figure B.6: Tree diagram representing the Lower (Fe) series of bioleaching tests. Tests were conducted with Lower ore and xK-5Cu medium (variable Fe^{2+} level), at a 2.5 g/L Cl^- level. Nomenclature: number after "L" indicates Fe^{2+} level in g/L, number after "Set" indicates generation number.

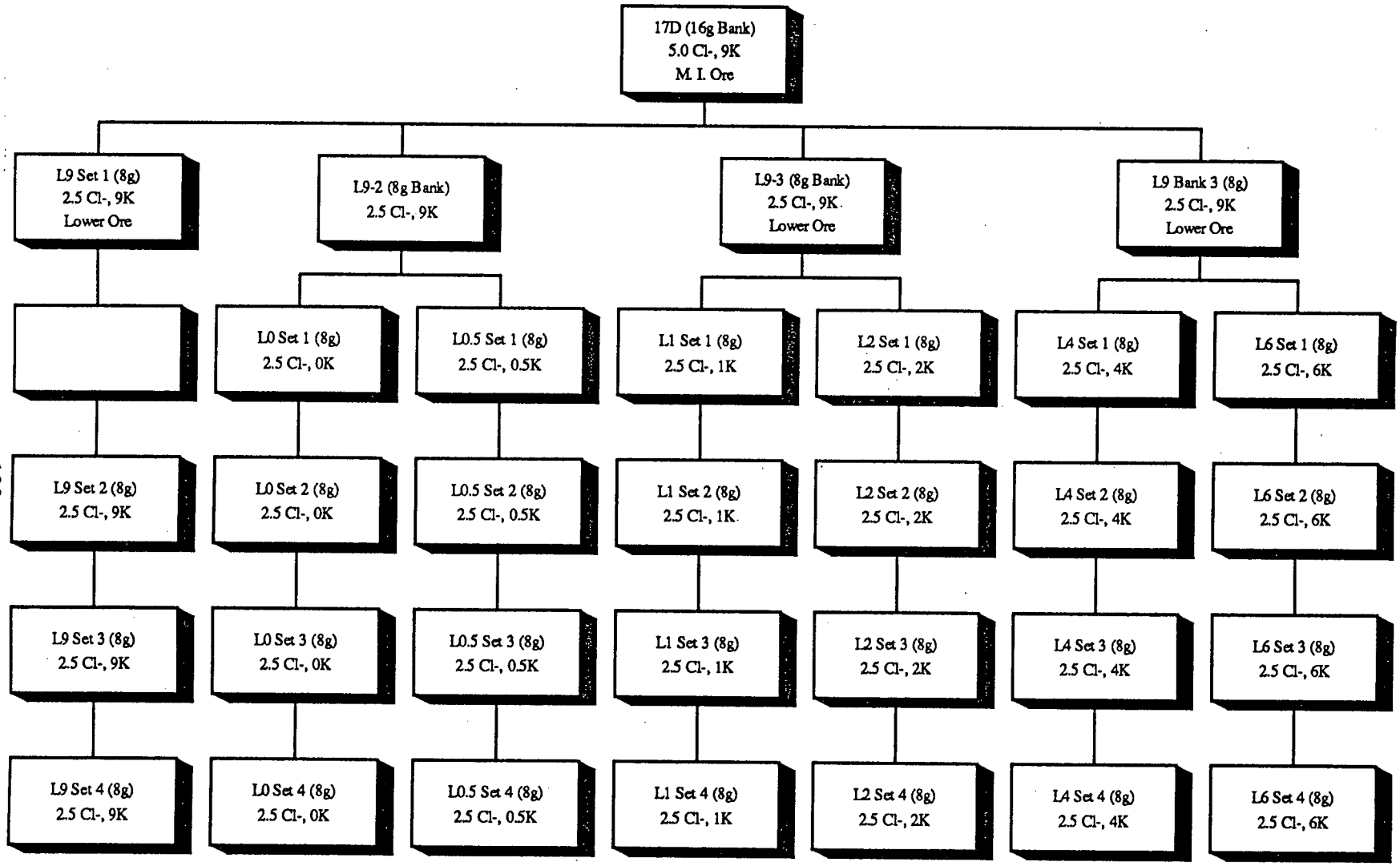

17D (16g Bank)
5.0 Cl-, 9K
M. I. Ore
L9 Set 1 (8g)
2.5 Cl-, 9K
Lower Ore
L9-2 (8g Bank)
2.5 Cl-, 9K
L9-3 (8g Bank)
2.5 Cl-, 9K
Lower Ore
L9 Bank 3 (8g)
2.5 Cl-, 9K
Lower Ore
L0 Set 1 (8g)
2.5 Cl-, 0K
L0.5 Set 1 (8g)
2.5 Cl-, 0.5K
L1 Set 1 (8g)
2.5 Cl-, 1K
L2 Set 1 (8g)
2.5 Cl-, 2K
L4 Set 1 (8g)
2.5 Cl-, 4K
L6 Set 1 (8g)
2.5 Cl-, 6K
L9 Set 2 (8g)
2.5 Cl-, 9K
L0 Set 2 (8g)
2.5 Cl-, 0K
L0.5 Set 2 (8g)
2.5 Cl-, 0.5K
L1 Set 2 (8g)
2.5 Cl-, 1K
L2 Set 2 (8g)
2.5 Cl-, 2K
L4 Set 2 (8g)
2.5 Cl-, 4K
L6 Set 2 (8g)
2.5 Cl-, 6K
L9 Set 3 (8g)
2.5 Cl-, 9K
L0 Set 3 (8g)
2.5 Cl-, 0K
L0.5 Set 3 (8g)
2.5 Cl-, 0.5K
L1 Set 3 (8g)
2.5 Cl-, 1K
L2 Set 3 (8g)
2.5 Cl-, 2K
L4 Set 3 (8g)
2.5 Cl-, 4K
L6 Set 3 (8g)
2.5 Cl-, 6K
L9 Set 4 (8g)
2.5 Cl-, 9K
L0 Set 4 (8g)
2.5 Cl-, 0K
L0.5 Set 4 (8g)
2.5 Cl-, 0.5K
L1 Set 4 (8g)
2.5 Cl-, 1K
L2 Set 4 (8g)
2.5 Cl-, 2K
L4 Set 4 (8g)
2.5 Cl-, 4K
L6 Set 4 (8g)
2.5 Cl-, 6K

Figure B.7: Tree diagram representing the Lower (Cl) series of bioleaching tests. Tests were conducted with Lower ore and 9K-5Cu medium, at various chloride levels. Nomenclature: initial figure indicates Cl^- level in g/L, number after "Set" indicates generation number.

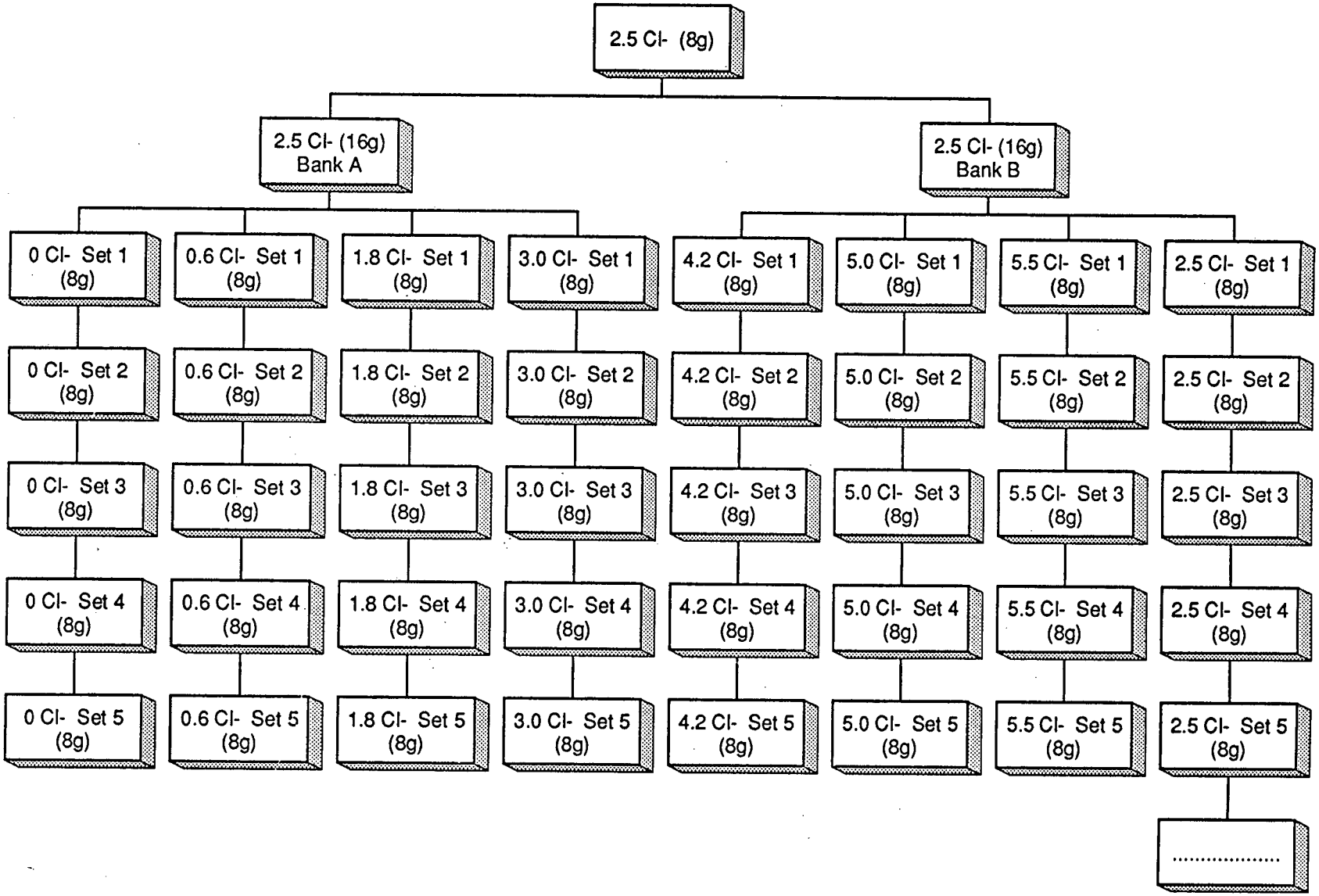
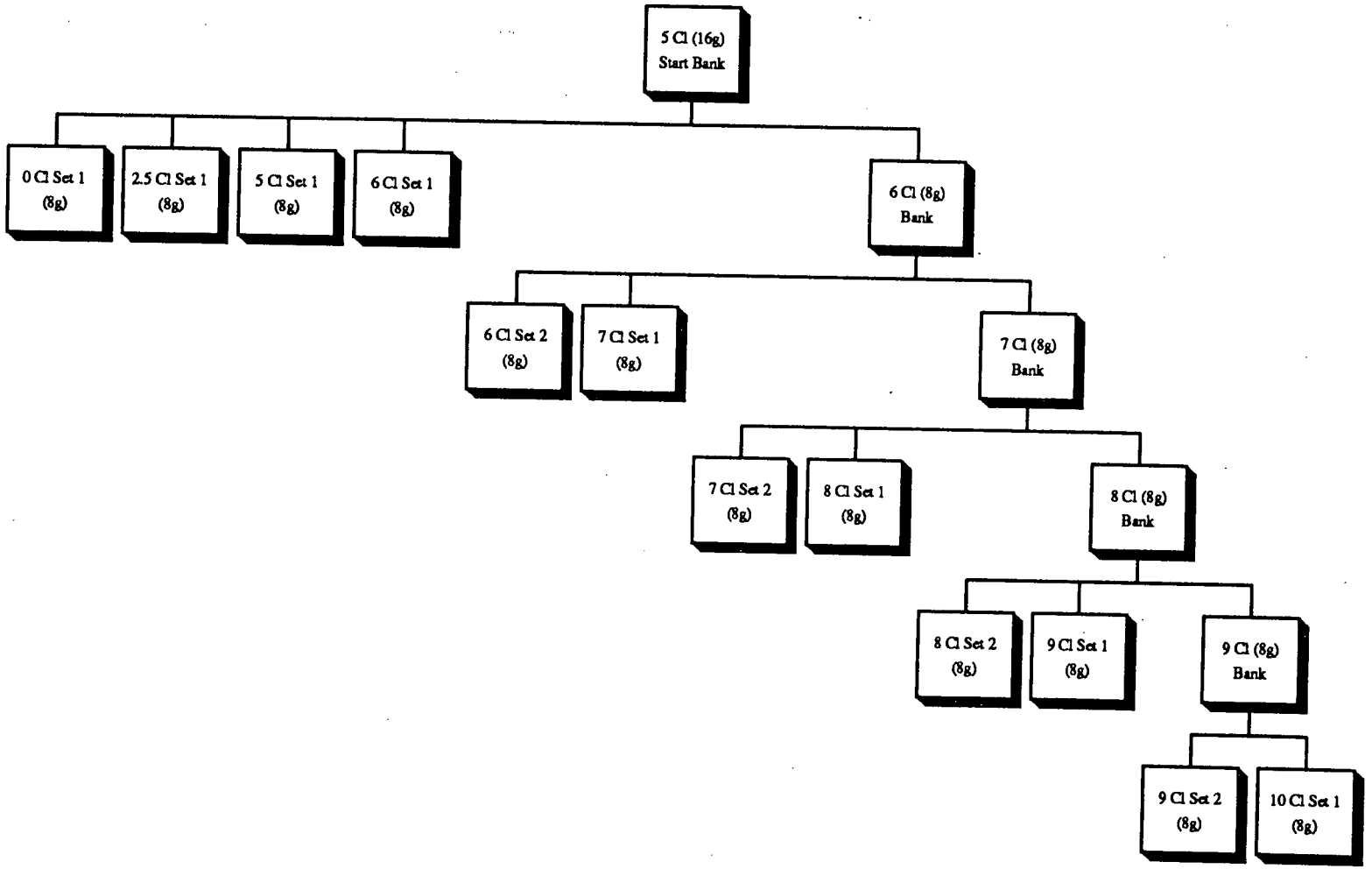

2.5 Cl- (8g)
2.5 Cl- (16g) Bank A
2.5 Cl- (16g) Bank B
0 Cl- Set 1 (8g)
0.6 Cl- Set 1 (8g)
1.8 Cl- Set 1 (8g)
3.0 Cl- Set 1 (8g)
4.2 Cl- Set 1 (8g)
5.0 Cl- Set 1 (8g)
5.5 Cl- Set 1 (8g)
2.5 Cl- Set 1 (8g)
0 Cl- Set 2 (8g)
0.6 Cl- Set 2 (8g)
1.8 Cl- Set 2 (8g)
3.0 Cl- Set 2 (8g)
4.2 Cl- Set 2 (8g)
5.0 Cl- Set 2 (8g)
5.5 Cl- Set 2 (8g)
2.5 Cl- Set 2 (8g)
0 Cl- Set 3 (8g)
0.6 Cl- Set 3 (8g)
1.8 Cl- Set 3 (8g)
3.0 Cl- Set 3 (8g)
4.2 Cl- Set 3 (8g)
5.0 Cl- Set 3 (8g)
5.5 Cl- Set 3 (8g)
2.5 Cl- Set 3 (8g)
0 Cl- Set 4 (8g)
0.6 Cl- Set 4 (8g)
1.8 Cl- Set 4 (8g)
3.0 Cl- Set 4 (8g)
4.2 Cl- Set 4 (8g)
5.0 Cl- Set 4 (8g)
5.5 Cl- Set 4 (8g)
2.5 Cl- Set 4 (8g)
0 Cl- Set 5 (8g)
0.6 Cl- Set 5 (8g)
1.8 Cl- Set 5 (8g)
3.0 Cl- Set 5 (8g)
4.2 Cl- Set 5 (8g)
5.0 Cl- Set 5 (8g)
5.5 Cl- Set 5 (8g)
2.5 Cl- Set 5 (8g)
.....

Figure B.8: Tree diagram representing the Zaldívar (Cl) series of bioleaching tests. Tests were conducted with Zaldívar ore and 9K medium, at various chloride levels. Nomenclature: initial figure indicates Cl^- level in g/L, number after "Set" indicates generation number.


5 Cl (16g)
Start Bank
0 Cl Set 1
(8g)
2.5 Cl Set 1
(8g)
5 Cl Set 1
(8g)
6 Cl Set 1
(8g)
6 Cl (8g)
Bank
6 Cl Set 2
(8g)
7 Cl Set 1
(8g)
7 Cl (8g)
Bank
7 Cl Set 2
(8g)
8 Cl Set 1
(8g)
8 Cl (8g)
Bank
8 Cl Set 2
(8g)
9 Cl Set 1
(8g)
9 Cl (8g)
Bank
9 Cl Set 2
(8g)
10 Cl Set 1
(8g)

APPENDIX C: Sample Raw Data, Extraction Results, and Calculations

A.(I) Sample Raw Data and Extraction Results for Leach Test with Rigorous Treatment of Final Products:

Expt. Name: L8.2S(8) Set 4

Expt. Type: Bioleach

Ore: Lower

Cl^- Level: 5.0 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Copper Content (g)
Ore	8.00	3.87	0.310
Solutions	Volume (mL)	g/L Cu	Copper Content (g)
Inoculum-I	5	7.18	0.036
Media	70	5.01	0.351
6M H_2SO_4 Acid	0.05	0	0
211 g/L NaCl	3.05	0	0

OUTPUTS:

Solids	Weight (g)	Wt% Cu	Copper Content (g)	% Copper Extracted (calculated head basis)
Leach Residue	8.69451	0.26	0.022	
Solutions	Volume (mL)	g/L Cu	Copper Content (g)	
Sample#				
1	1	6.51	0.0065	40.5%
2	1	6.77	0.0068	49.5%
3	1	7.61	0.0076	73.6%
4-inoc*	1	7.83	0.0078	81.8%
5	1	7.45	0.0075	87.6%
6	1	7.38	0.0074	88.3%
7	1	7.33	0.0073	89.4%
8	1	7.10	0.0071	85.9%
9-filtrate sample		7.10	0.0071	na
Inocolum-O	5	7.83	0.0392	na
Measured Balance of Filtrate	74	7.10	0.5254	na
Wash	490	0.070	0.04274	na
Final Extraction				92.5%

* indicates serial transfer of inoculum performed at this point.

A.(II) Identification of Values for Equation Variables From Raw Data:

SUMMARY OF TEST INPUTS:

Ore: 8.00 g of ore, 3.87% assay head

Inoculum-I: 5 mL @ 7.18 g/L Cu; Media: 70 mL @ 5.01 g/L Cu

Sulfuric Acid: 0.05 mL of 6M H_2SO_4; 3.05 mL of 211 g/L NaCl

Identified Input Variables:

M(sample) =	8.00 g
V(inoc-I) =	5×10^{-3} L
[Cu(inoc-I)]=	7.18 g/L Cu
V(media) =	0.070 L
[Cu(media)]=	5.01 g/L Cu
V(NaCl) =	3.05×10^{-3} L

SUMMARY OF TEST OUTPUTS:

Leach Residue: 8.6941 g assaying at 0.26% Cu

Samples: 9 1-mL samples in sequential order with the following copper concentrations in g/L [(6.51, 6.77, 7.61, 7.83*, 7.45, 7.38, 7.33, 7.10, 7.10), last is filtrate sample, * indicates inoculum-O sample value.]

Inoculum-O Volume: 5 mL; Total filtrate volume: 75 mL

Wash Volume: 490 mL @ 0.070 g/L Cu

Identified Output Variables:

$M(res)$ = 8.6941 g

$[Cu(res)]$ = 0.26 wt% Cu

V_1-V_9 = 1×10^{-3} L

Cu_1 = 6.51 g/L Cu

Cu_2 = 6.77 g/L Cu

Cu_3 = 7.61 g/L Cu

$[Cu(inoc\text{-}O)] = Cu_4$ = 7.83 g/L Cu

Cu_5 = 7.45 g/L Cu

Cu_6 = 7.38 g/L Cu

Cu_7 = 7.33 g/L Cu

Cu_8 = 7.10 g/L Cu

$[Cu(filt)] = Cu_9$ = 7.10 g/L Cu

$[Cu(inoc\text{-}O)]$ = 5×10^{-3} L

$V(filt)$ = 75×10^{-3} L

$V(wash)$ = 0.490 L

$[Cu(wash)]$ = 0.070 g/L Cu

A.(III) SAMPLE CALCULATIONS:

Equation (5-6)

$$V(Th) = V(media) + V(NaCl) + V(inoc - I)$$

$V(Th)$=70.00 + 3.05 + 5.00 = 78.05 mL = 78.05 x 10^{-3} L

Equation (5-7)

$$C.H. = \frac{\sum(Cu\ \ outputs) - \sum(soluble\ \ Cu\ \ inputs)}{Mass\ \ of\ \ ore\ \ sample\ \ to\ \ be\ \ leached} x100\%$$

First Summation Term in Equation (5-7) is Equation (5-8)

$$\sum(Cu\ \ outputs) = Cu(samples) + Cu(inoc - O) +$$

$$Cu(filt) + Cu(wash) + M(res)[Cu(res)]$$

$Cu(samples)= \quad V_1Cu_1+V_2Cu_2+V_3Cu_3+V_4Cu_4+V_5Cu_5+V_6Cu_6+V_7Cu_7+V_8Cu_8+V_9Cu_9$

Since $V_1=V_2=V_3=V_4=V_5=V_6=V_7=V_8=V_9$=1x$10^{-3}$ L,

$Cu(samples)=$ 1x10^{-3} L(6.51+6.77+7.61+7.83+7.45+7.38+7.33+7.10+7.10 g/L Cu)

= 0.06508 g Cu

$Cu(inoc-O)= V(inoc-O)\ [Cu(inoc-O)]$ = (5x10^{-3} L)(7.83 g/L Cu) = 0.03915 g Cu

$Cu(filt) = (Vfilt-10^{-3})\ [Cu(filt)]$ = (75x10^{-3}-10^{-3})(7.10 g/L Cu) = 0.5254 g Cu

$Cu(wash) = V(wash)\ [Cu(wash)]$ = (0.490 L)(0.070 g/L Cu) = 0.03430 g Cu

M(res) [Cu(res)] = 8.6941 g (0.26%/100) g Cu

Second Summation Term in Equation (5-7) is Equation (5-10)

$$\sum(soluble\ \ Cu\ \ inputs) = V(media)[Cu(media)] + V(inoc-I)[Cu(inoc-I)]$$

= $(70\text{x}10^{-3}$ L)(5.01 g/L Cu) + $(5\text{x}10^{-3}$ L)(7.18 g/L Cu) = 0.38660 g Cu

So, *C.H.*= [{(0.06508 g Cu) + (0.03915 g Cu) + (0.5254 g Cu) + (0.03430 g Cu) + (8.6941 g)(0.26%/100)} - {0.38660 g Cu}] / (8.00 g) X 100% = 3.75%

Various Extraction Calculations

Equation (5-11)

$$Ext(j) = \frac{\left\{\sum_{i=1}^{i=j}(V_i Cu_i) + Cu(inoc-O) + Cu(leachate)\right\} - \sum(soluble\ \ Cu\ \ inputs)}{M(sample)\ \times\ C.H.} \times 100\%$$

Ext(1)=?

1st Term =V_1Cu_1=$(1\text{x}10^{-3}$ L)(6.51 g/L Cu)= 0.00651 g Cu

Cu(inoc-O) does not apply

Cu(leachate)= $(V(Th)\text{-}10^{-3})\ Cu_j$

= $(V(Th)\text{-}10^{-3})\ Cu_1$

= $((78.05\text{-}1)\text{x}10^{-3}$ L)(6.51 g/L Cu)

= 0.50160 g Cu

second summation term calculated earlier=0.38660 g Cu

So *Ext(1)*= { (0.00651 g Cu) + (0.50160 g Cu) - (0.38660 g Cu)} / (8.00 g X 3.75%/100) X 100%

= 40.5%

Ext(5)=?

1st Term = $V_1Cu_1+V_2Cu_2+V_3Cu_3+V_4Cu_4+V_5Cu_5$

$(1x10^{-3}$ L)(6.51+6.77+7.61+7.83+7.45 g/L Cu)

0.03617 g Cu

Cu(inoc-O) applies, calculated earlier = 0.03915 g Cu

Cu(leachate)= $(V(Th)-10^{-3})\ Cu_j$

= $(V(Th)-10^{-3})\ Cu_5$

= $((78.05-1)x10^{-3}$ L)(7.45 g/L Cu)

= 0.57402 g Cu

second summation term calculated earlier=0.38660 g Cu

Ext(5)= { (0.03617 g Cu) + (0.03915 g Cu) + (0.57402 g Cu) - (0.38660 g Cu) } / (8.00 g X 3.75%/100) X 100% = 87.6%

Ext(9)=?

Since this is for final extraction, equation (5-12) applies:

$$Ext. = \frac{Cu(samples) + Cu(inoc-O) + Cu(filt) + Cu(wash) - \sum(soluble\ \ Cu\ \ inputs)}{M(sample)\ \times\ C.H.} \times 100\%$$

1st Term = $V_1Cu_1+V_2Cu_2+V_3Cu_3+V_4Cu_4+V_5Cu_5+V_6Cu_6+V_7Cu_7+V_8Cu_8+V_9Cu_9$

= $(1x10^{-3}$ L)(6.51+6.77+7.61+7.83+7.45+7.38+7.33+7.10+7.10 g/L Cu)

= 0.06508 g Cu

Cu(inoc-O) applies, calculated earlier = 0.03915 g Cu

Cu(leachate)= *Cu(filt)* calculated earlier = 0.52540 g Cu

Cu(wash)= applies in this test, calculated earlier = 0.0343 g Cu

second summation term calculated earlier=0.38660 g Cu

Ext(9)= { (0.06508 g Cu) + (0.03915 g Cu) + (0.52540 g Cu) + (0.0343 g Cu) - (0.38660 g Cu) } / (8.00 g X 3.75%/100) X 100% = 92.4% (Final)

Acid Consumption?

Equation (5-15)

Acid Consumption= $0.05x10^{-3}$ L(6 mol H_2SO_4/L)(98 kg/1000 mol H_2SO_4)/(8.00 g ore)(tonne ore/$1x10^{+6}$ g ore) = 3.68 kg H_2SO_4/tonne ore

B.(I) Sample Raw Data and Extraction Results for Leach Test terminated without Rigorous Treatment of Final Products:

Expt. Name: L5S(8) Set 1

Expt. Type: Bioleach

Ore: Lower

Cl^- Level: 3.0 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Copper Content (g)
Ore	8.02	3.87	0.310
Solutions	Volume (mL)	g/L Cu	Copper Content (g)
Inoculum-I	5	8.46	0.042
Media	70	5.25	0.368
6M H_2SO_4 Acid	0.05	0	0
211 g/L NaCl	1.82	0	0

OUTPUTS:

Solids	Weight (g)	Wt% Cu	Copper Content (g)	% Copper Extracted (calculated head basis)
Leach Residue	8.8029	0.25	0.022	
Solutions	Volume (mL)	g/L Cu	Copper Content (g)	
Sample#				
1	1	7.11	0.00711	48.7%
2	1	8.28	0.00828	83.3%
3	1	8.26	0.00826	85.7%
4-inoc*	1	8.19	0.00819	86.8%
5	1	7.63	0.00763	89.0%
6	1	7.63	0.00763	91.7%
7	1	7.40	0.00740	88.1%
8-filtrate sample	1	7.45	0.00745	92.1%
Inocolum-O	5	8.19	0.0410	na
Theoretical Balance of Filtrate	75.82	7.45	0.5649	na
Wash	na	na	na	na
Final Extraction				92.1%

* indicates serial transfer of inoculum performed at this point.

B.(II) Identification of Values for Equation Variables From Raw Data:

SUMMARY OF TEST INPUTS:

Ore: 8.02 g of ore, 3.87% assay head

Inoculum-I: 5 mL @ 8.46 g/L Cu; Media: 70 mL @ 5.25 g/L Cu

Sulfuric Acid: 0.05 mL of 6M H_2SO_4; 1.82 mL of 211 g/L NaCl

Identified Input Variables:

M(sample) =	8.02 g
V(inoc-I) =	$5x10^{-3}$ L
[Cu(inoc-I)]=	8.46 g/L Cu
V(media) =	0.070 L
[Cu(media)]=	5.25 g/L Cu
V(NaCl) =	$1.82x10^{-3}$ L

SUMMARY OF TEST OUTPUTS:

Leach Residue: 8.8029 g assaying at 0.25% Cu

Samples: 8 1-mL samples in sequential order with the following copper concentrations in g/L [(7.11, 8.28, 8.26, 8.19*, 7.63, 7.63, 7.40, 7.45), last is filtrate sample, * indicates inoculum-O sample value.]

Inoculum-O Volume: 5 mL; Total pregnant solution volume: *V(Th)* = 76.82 mL

Wash Volume: none (all copper in pregnant solution)

Identified Output Variables:

$M(res)$ =	8.8029 g
$[Cu(res)]$ =	0.25 wt% Cu
V_1-V_9 =	$1x10^{-3}$ L
Cu_1 =	7.11 g/L Cu
Cu_2 =	8.28 g/L Cu
Cu_3 =	8.26 g/L Cu
$[Cu(inoc\text{-}O)] = Cu_4$ =	8.19 g/L Cu
Cu_5 =	7.63 g/L Cu
Cu_6 =	7.63 g/L Cu
Cu_7 =	7.40 g/L Cu
$[Cu(preg)] = Cu_8$ =	7.45 g/L Cu
$[Cu(inoc\text{-}O)]$ =	8.19 g/L Cu
$V(inoc\text{-}O)$ =	$5x10^{-3}$ L
$V(filt) = V(Th)$ =	76.82 x 10^{-3} L
$V(wash)$ =	na
$[Cu(wash)]$ =	na

B.(III) SAMPLE CALCULATIONS:

Equation (5-6)

$$V(Th) = V(media) + V(NaCl) + V(inoc - I)$$

$V(Th)$=70.00 + 1.82 + 5.00 = 76.82 mL = 76.82 x 10^{-3} L

Equation (5-7)

$$C.H. = \frac{\sum(Cu\ \ outputs) - \sum(soluble\ \ Cu\ \ inputs)}{Mass\ \ of\ \ ore\ \ sample\ \ to\ \ be\ \ leached} x100\%$$

First Summation Term in Equation (5-7) is Equation (5-9)

$$\sum(Cu\ \ outputs) = Cu(samples) + Cu(inoc - O) + Cu(preg) + M(res)[Cu(res)]$$

$Cu(samples)= V_1Cu_1+V_2Cu_2+V_3Cu_3+V_4Cu_4+V_5Cu_5+V_6Cu_6+V_7Cu_7+V_8Cu_8$

Since $V_1=V_2=V_3=V_4=V_5=V_6=V_7=V_8$=1x$10^{-3}$ L,

$Cu(samples)=$ 1x10^{-3} L(7.11+8.28+8.26+8.19+7.63+7.63+7.40+7.45 g/L Cu)

= 0.06195 g Cu

$Cu(inoc-O)= V(inoc-O)\ [Cu(inoc-O)]$ = (5x10^{-3} L)(8.19 g/L Cu) = 0.04095 g Cu

$Cu(preg) = (V(Th)-10^{-3})\ [Cu(preg)]$ =

= (76.82x10^{-3}-10^{-3})(7.45 g/L Cu) = 0.5649 g Cu

Cu(wash) = V(wash) [Cu(wash)] = 0 g Cu

M(res) [Cu(res)] = 8.8029 g (0.25%/100) g Cu

Second Summation Term in Equation (5-7) is Equation (5-10)

$$\sum(soluble\ \ Cu\ \ inputs) = V(media)[Cu(media)] + V(inoc-I)[Cu(inoc-I)]$$

= $(70\text{x}10^{-3}$ L)(5.25 g/L Cu) + $(5\text{x}10^{-3}$ L)(8.46 g/L Cu) = 0.40980 g Cu

So, *C.H.*= [{(0.06195 g Cu) + (0.04095 g Cu) + (0.5649 g Cu) + (8.8029 g)(0.25%/100)} - {0.40980 g Cu}] / (8.00 g) X 100% = 3.50%

Various Extraction Calculations

Equation (5-11)

$$Ext(j) = \frac{\left\{\sum_{i=1}^{i=j}(V_i Cu_i) + Cu(inoc-O) + Cu(leachate) - \sum(soluble\ \ Cu\ \ inputs)\right.}{M(sample) \times C.H.} \times 100\%$$

Ext(1)=?

1st Term =V_1Cu_1=$(1\text{x}10^{-3}$ L)(7.11 g/L Cu)= 0.00711 g Cu

Cu(inoc-O) does not apply

Cu(leachate)= *(V(Th)-10^{-3}) Cu^l*

= *(V(Th)-10^{-3}) Cu^l*

= $((76.82\text{-}1)\text{x}10^{-3}$ L)(7.11 g/L Cu)

= 0.53908 g Cu

second summation term calculated earlier=0.40980 g Cu

So *Ext(1)*= { (0.00711 g Cu) + (0.53908 g Cu) - (0.40980 g Cu)} / (8.00 g X 3.50%/100) X 100%

= 48.7%

Ext(5)=?

1st Term = $V_1Cu_1+V_2Cu_2+V_3Cu_3+V_4Cu_4+V_5Cu_5$

$(1x10^{-3}$ L)(7.11+8.28+8.26+8.19+7.63 g/L Cu)

0.03947 g Cu

Cu(inoc-O) applies, calculated earlier = 0.04095 g Cu

Cu(leachate)= $(V(Th)-10^{-3})\ Cu^{'}$

= $(V(Th)-10^{-3})\ Cu_5$

= $((76.82-1)x10^{-3}$ L)(7.63 g/L Cu)

= 0.57851 g Cu

second summation term calculated earlier=0.40980 g Cu

Ext(5)= { (0.03947 g Cu) + (0.04095 g Cu) + (0.57851 g Cu) - (0.40980 g Cu) } / (8.00 g X 3.50%/100) X 100% = 89.0%

Ext(8)=?

Since this is for final extraction, equation (5-12) applies:

$$Ext. = \frac{Cu(samples) + Cu(inoc-O) + Cu(filt) + Cu(wash) - \sum(soluble\ \ Cu\ \ inputs)}{M(sample) \times C.H.} \times 100\%$$

with *Cu(filt)* and *Cu(wash)* terms replaced by Cu(preg).

1st Term = $V_1Cu_1+V_2Cu_2+V_3Cu_3+V_4Cu_4+V_5Cu_5+V_6Cu_6+V_7Cu_7+V_8Cu_8$

= $(1x10^{-3}$ L)(7.11+8.28+8.26+8.19+7.63+7.63+7.40+7.45 g/L Cu)

= 0.06195 g Cu

Cu(inoc-O) applies, calculated earlier = 0.04095 g Cu

Cu(leachate)= *Cu(preg)* calculated earlier = 0.5649 g Cu

Cu(wash)= does not apply in this test, 0 g Cu

second summation term calculated earlier=0.40980 g Cu

Ext(9)= { (0.06195 g Cu) + (0.04095 g Cu) + (0.5649 g Cu) - (0.40980 g Cu) } / (8.00 g X 3.50%/100) X 100% = 92.1% (Final)

Acid Consumption?

Equation (5-15)

Acid Consumption= $0.05x10^{-3}$ L(6 mol H_2SO_4/L)(98 kg/1000 mol H_2SO_4)/(8.00 g ore)(tonne ore/$1x10^{+6}$ g ore) = 3.68 kg H_2SO_4/tonne ore

APPENDIX D: Check Test Summaries

The following are the summaries from the series of check tests conducted during early 1994.

Expt. Name: 5MI(8)

Expt. Type: Bioleach Check Test

Ore: Original Mina Ivan

Cl^- Level: 5.0 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Ore	8.00	5.33	2.50	0.426	0.200
Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Inoculum-I	5	4.13	0.75	0.021	0.004
Media	70	0.00	9.12	0.000	0.638
6M H_2SO_4 Acid	0.05	nav	nav	nav	nav
211 g/L NaCl	2.846	nav	nav	nav	nav
Theoretical System Volume, *V(Th)*	77.846		TOTAL INPUT (g):	0.447	0.842

nav=no applicable value

OUTPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Leach Residue	9.3838	1.694	7.518	0.159	0.705

Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Sample 1	1	1.72	6.35	0.00172	0.00635
Sample 2	1	1.92	5.67	0.00192	0.00567
Sample 3	1	2.06	5.14	0.00206	0.00514
Sample 4	1	2.14	4.73	0.00214	0.00473
Sample 5	1	2.26	4.48	0.00226	0.00448
Sample 6	1	2.18	4.46	0.00218	0.00446
Sample 7	1	2.27	4.00	0.00227	0.00400
Sample 8	1	2.33	3.66	0.00233	0.00366
Sample 9	1	2.46	3.27	0.00246	0.00327
Sample 10	1	2.46	2.91	0.00246	0.00291
Sample 11	1	2.38	2.79	0.00238	0.00279
Sample 12	1	2.45	2.64	0.00245	0.00264
Sample 13	1	2.46	2.47	0.00246	0.00247
Sample 14	1	2.55	2.34	0.00255	0.00234
Sample 15	1	2.56	2.17	0.00256	0.00217
Sample 16	1	2.58	2.09	0.00258	0.00209
Sample 17	1	2.58	2.11	0.00258	0.00211
Filtrate Sample	1	2.39	1.75	0.00239	0.00175
Inoculum	nav	nav	nav	nav	nav
Measured Balance Of Filtrate	86	2.39	1.75	0.2055	0.15050
Wash	666	1.67e-2	1.25e-2	0.0111	0.00829
			TOTAL OUTPUT (g):	0.417	0.927
			INPUT-OUTPUT (g):	0.030	-0.085
			%Lost of INPUT:	6.63	-10.11

Acid Addition Summary

Total Volume of 6M H_2SO_4 Added = 0.05 mL

Sulfuric Acid Consumption = 3.68 kg H_2SO_4/tonne ore

Copper Extraction Summary * based on assay head, ** based on calculated head

Sample	Total Leach Time (hrs)	Total Cu from Ore (g)	% Copper Extraction* (Soln. Anal)	Soln. E_h (mV SHE)		Recalc. % Copper Extraction** (Soln. Anal)
	0	0	0	508	% Copper	0
1	45.75	0.113	26.56%	561	Extraction*	28.54%
2	93.08	0.131	30.61%	568	(Solids Anal.)	32.90%
3	143.60	0.143	33.62%	571	62.72%	36.13%
4	188.77	0.152	35.56%	573	Calculated Head	38.22%
5	237.33	0.163	38.26%	575	4.96%	41.11%
6	285.83	0.159	37.33%	576	S.G.(filtrate)	40.11%
7	338.35	0.168	39.48%	578	1.0152 g/cc	42.43%
8	382.47	0.175	41.11%	578	Cake entrained Cu	44.18%
9	429.97	0.188	44.03%	578	0.0069 g	47.32%
10	482.70	0.190	44.60%	578	Wash Cu	47.94%
11	527.25	0.186	43.72%	580	0.0111 g	46.99%
12	575.15	0.194	45.56%	578	Cu ppt formed!	48.96%
13	621.60	0.197	46.31%	579		49.77%
14	672.08	0.207	48.53%	579		52.16%
15	718.47	0.210	49.31%	579		53.00%
16	766.10	0.214	50.28%	579		54.04%
17	817.45	0.217	50.88%	581		54.69%
Final	911.98	0.238	55.76%	585		59.93%

Expt. Name: SC[5MI(8)]

Expt. Type: Sterile Leach Check Test

Ore: Original Mina Ivan

Cl^- Level: 5.0 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Ore	8.02	5.33	2.50	0.427	0.201
Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Inoculum-I	5	0.00	0.00	0.000	0.000
Media	70	0.00	9.12	0.000	0.638
6M H_2SO_4 Acid	0.05	nav	nav	nav	nav
211 g/L NaCl	2.846	nav	nav	nav	nav
Theoretical System Volume, *V(Th)*	77.846		TOTAL INPUT (g):	0.427	0.839

nav=no applicable value

OUTPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Leach Residue	9.0098	2.154	7.356	0.194	0.663

Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Sample 1	1	1.40	6.37	0.00140	0.00637
Sample 2	1	1.57	5.73	0.00157	0.00573
Sample 3	1	1.69	5.32	0.00169	0.00532
Sample 4	1	1.68	4.71	0.00168	0.00471
Sample 5	1	1.84	4.62	0.00184	0.00462
Sample 6	1	1.80	4.54	0.00180	0.00454
Sample 7	1	1.88	4.23	0.00188	0.00423
Sample 8	1	1.93	3.91	0.00193	0.00391
Sample 9	1	2.01	3.49	0.00201	0.00349
Sample 10	1	2.00	3.12	0.00200	0.00312
Sample 11	1	1.99	3.05	0.00199	0.00305
Sample 12	1	2.07	2.87	0.00207	0.00287
Sample 13	1	2.07	2.67	0.00207	0.00267
Sample 14	1	2.13	2.57	0.00213	0.00257
Sample 15	1	2.13	2.41	0.00213	0.00241
Sample 16	1	2.14	2.32	0.00214	0.00232
Sample 17	1	2.13	2.32	0.00213	0.00232
Filtrate Sample	1	1.96	1.59	0.00196	0.00159
Inoculum	nav	nav	nav	nav	nav
Measured Balance Of Filtrate	83	1.96	1.59	0.1627	0.13197
Wash	696	1.11e-2	9.48e-3	0.0077	0.00660
			TOTAL OUTPUT (g):	0.399	0.867
			INPUT-OUTPUT (g):	0.029	-0.028
			%Lost of INPUT:	6.67	-3.37

Acid Addition Summary

Total Volume of 6M H_2SO_4 Added = 0.05 mL

Sulfuric Acid Consumption = 3.67 kg H_2SO_4/tonne ore

Copper Extraction Summary * based on assay head, ** based on calculated head

Sample	Total Leach Time (hrs)	Total Cu from Ore (g)	% Copper Extraction* (Soln. Anal)	Soln. E_h (mV SHE)		Recalc. % Copper Extraction** (Soln. Anal)
	0	0	0	509	% Copper	0
1	45.75	0.109	25.50%	554	Extraction*	27.32%
2	93.12	0.124	28.92%	567	(Solids Anal.)	30.99%
3	143.63	0.135	31.47%	571	54.60%	33.72%
4	188.80	0.135	31.68%	571	Calculated Head	33.95%
5	237.37	0.150	34.99%	578	4.97%	37.49%
6	285.87	0.148	34.69%	580	S.G.(filtrate)	37.17%
7	338.38	0.156	36.57%	578	1.0128 g/cc	39.19%
8	382.50	0.162	37.92%	580	Cake entrained Cu	40.63%
9	430.00	0.170	39.83%	579	0.0054 g	42.68%
10	482.73	0.171	40.12%	582	Wash Cu	42.99%
11	527.28	0.173	40.40%	584	0.0077 g	43.29%
12	575.18	0.181	42.33%	582	Cu ppt formed!	45.35%
13	621.63	0.183	42.81%	582		45.87%
14	672.12	0.190	44.39%	579		47.56%
15	718.60	0.192	44.89%	582		48.10%
16	766.13	0.195	45.57%	582		48.83%
17	817.48	0.196	45.88%	583		49.17%
Final	912.02	0.205	47.92%	582		51.35%

Expt. Name: 5MI(8) Set 2

Expt. Type: Bioleach Check Test

Ore: Original Mina Ivan

Cl^- Level: 5.0 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Ore	8.02	5.33	2.50	0.427	0.201
Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Inoculum-I	5	4.09	1.24	0.020	0.006
Media	70	0.00	9.14	0.000	0.640
6M H_2SO_4 Acid	0.10	nav	nav	nav	nav
211 g/L NaCl	2.846	nav	nav	nav	nav
Theoretical System Volume, *V(Th)*	77.846		TOTAL INPUT (g):	0.448	0.847

nav=no applicable value

OUTPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Leach Residue	9.7756	0.731	8.803	0.071	0.861

Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Sample 1	1	1.96	8.04	0.00196	0.00804
Sample 2	1	3.13	6.18	0.00313	0.00618
Sample 3	1	3.94	1.92	0.00394	0.00192
Sample 4	1	3.89	1.45	0.00389	0.00145
Sample 5	1	3.97	1.27	0.00397	0.00127
Sample 6	1	4.05	1.30	0.00405	0.00130
Sample 7	1	4.30	0.91	0.00430	0.00091
Filtrate Sample	1	2.90	0.52	0.00290	0.00052
Inoculum	nav	nav	nav	nav	nav
Measured Balance Of Filtrate	106	2.90	0.52	0.3074	0.05554
Wash	895	2.17e-2	1.18e-2	0.0194	0.00106
			TOTAL OUTPUT (g):	0.426	0.939
			INPUT-OUTPUT (g):	0.022	-0.092
			%Lost of INPUT:	4.80	-10.90

Acid Addition Summary

Total Volume of 6M H_2SO_4 Added = 0.10 mL

Sulfuric Acid Consumption = 7.34 kg H_2SO_4/tonne ore

Copper Extraction Summary * based on assay head, ** based on calculated head

Sample	Total Leach Time (hrs)	Total Cu from Ore (g)	% Copper Extraction* (Soln. Anal)	Soln. E_h (mV SHE)		Recalc. % Copper Extraction** (Soln. Anal)
	0	0	0	512	% Copper	0
1	44.23	0.132	30.91%	570	Extraction*	32.55%
2	90.68	0.225	52.68%	601	(Solids Anal.)	55.47%
3	141.17	0.291	68.16%	813	83.28%	71.77%
4	187.78	0.291	68.17%	822	Calculated Head	71.78%
5	235.18	0.302	70.54%	827	5.06%	74.27%
6	286.53	0.312	72.92%	829	S.G.(filtrate)	76.79%
7	381.07	0.335	78.42%	838	1.0136 g/cc	82.58%
Final	455.87	0.334	78.25%	822	Cake entrained Cu	82.39%
					0.0097 g	
					Wash Cu	
					0.0194 g	
					Cu ppt formed!	

Expt. Name: L-STD RLT0

Expt. Type: Bioleach Check Test

Ore: Lower

Cl^- Level: 2.5 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Ore	8.01	3.87	4.23	0.310	0.339
Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Inoculum-I	5	8.11	0.59	0.041	0.003
2nd Inoculum-I'	5	7.55	0.47	0.038	0.002
Media	70	0.00	9.12	0.000	0.638
6M H_2SO_4 Acid	0.05	nav	nav	nav	nav
211 g/L NaCl	1.394	nav	nav	nav	nav
Theoretical System Volume, *V(Th)*	76.394		TOTAL INPUT (g):	0.388	0.983

nav=no applicable value

OUTPUTS: (' 2nd inoculum volume/Cu content included in calcs from sample 10 on)

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Leach Residue	10.1947	0.238	10.389	0.024	1.059

Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Sample 1	1	2.17	5.98	0.00217	0.00598
Sample 2	1	2.17	5.28	0.00217	0.00528
Sample 3	1	2.35	4.99	0.00235	0.00499
Sample 4	1	2.35	4.56	0.00235	0.00456
Sample 5	1	2.39	4.43	0.00239	0.00443
Sample 6	1	2.20	4.36	0.00220	0.00436
Sample 7	1	2.28	4.15	0.00228	0.00415
Sample 8	1	2.35	3.76	0.00235	0.00376
Sample 9	1	2.34	3.25	0.00234	0.00325
Sample 10	1	2.77	2.87	0.00277	0.00287
Sample 11	1	3.04	2.71	0.00304	0.00271
Sample 12	1	3.43	1.01	0.00343	0.00101
Sample 13	1	3.53	0.81	0.00353	0.00081
Sample 14	1	3.69	0.66	0.00369	0.00066
Sample 15	1	3.76	0.61	0.00376	0.00061
Sample 16	1	3.73	0.54	0.00373	0.00054
Sample 17	1	3.60	0.46	0.00360	0.00046
Sample 18	1	3.87	0.35	0.00387	0.00035
Filtrate Sample	1	3.05	0.25	0.00305	0.00025
Measured Balance Of Filtrate	95	3.05	0.25	0.2898	0.02347
Wash	724	2.08e-2	2.45e-2	0.0150	0.00018
			TOTAL OUTPUT (g):	0.384	1.134
			INPUT-OUTPUT (g):	0.004	-0.151
			%Lost of INPUT:	1.06	-15.40

Acid Addition Summary

Total Volume of 6M H_2SO_4 Added = 0.05 mL Sulfuric Acid Consumption = 3.67 kg H_2SO_4/tonne ore

Copper Extraction Summary * based on assay head, ** based on calculated head

Sample	Total Leach Time (hrs)	Total Cu from Ore (g)	% Copper Extraction* (Soln. Anal)	Soln. E_h (mV SHE)		Recalc. % Copper Extraction** (Soln. Anal)
	0	0	0	504	% Copper	0
1	45.83	0.125	40.40%	556	Extraction*	40.94%
2	93.17	0.127	41.10%	567	(Solids Anal.)	41.65%
3	143.68	0.143	46.23%	574	92.16%	46.86%
4	188.83	0.146	46.99%	577	Calculated Head	47.62%
5	237.42	0.151	48.78%	579	3.82%	49.44%
6	285.92	0.139	44.82%	582	S.G.(filtrate)	45.43%
7	338.43	0.147	47.51%	581	1.0128 g/cc	48.15%
8	382.55	0.155	49.97%	581	Cake entrained Cu	50.64%
9	430.05	0.156	50.48%	583	0.0106 g	51.16%
10	482.78	0.168	54.12%	588	Wash Cu	54.85%
11	527.33	0.193	62.10%	619	0.0150 g	62.94%
12	575.23	0.227	73.32%	861	Cu ppt formed!	74.31%
13	621.68	0.239	77.06%	863		78.09%
14	718.55	0.255	82.40%	863		83.51%
15	766.18	0.265	85.42%	868		86.58%
16	766.10	0.266	85.85%	868		87.01%
17	817.53	0.259	83.64%	872		84.77%
18	912.07	0.285	91.89%	859		93.13
Final	986.90	0.282	90.83%	585		92.05%

Expt. Name: L-STD RLT5

Expt. Type: Bioleach Check Test

Ore: Lower

Cl^- Level: 2.5 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Ore	8.02	3.87	4.23	0.310	0.339
Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Inoculum-I	5	8.11	0.59	0.041	0.003
2nd Inoculum-I[!]	5	7.55	0.47	0.038	0.002
Media	70	4.85	8.76	0.340	0.613
6M H_2SO_4 Acid	0.05	nav	nav	nav	nav
211 g/L NaCl	1.394	nav	nav	nav	nav
Theoretical System Volume, *V(Th)*	76.394		TOTAL INPUT (g):	0.728	0.958

nav=no applicable value

OUTPUTS: ([!] 2nd inoculum volume/Cu content included in calcs from sample 10 on)

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Leach Residue	10.2099	0.293	10.180	0.030	1.039

Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Sample 1	1	6.48	6.93	0.00648	0.00693
Sample 2	1	6.38	6.20	0.00638	0.00620
Sample 3	1	6.43	5.70	0.00643	0.00570
Sample 4	1	6.38	5.23	0.00638	0.00523
Sample 5	1	6.28	4.83	0.00628	0.00483
Sample 6	1	6.30	4.48	0.00630	0.00448
Sample 7	1	6.30	4.20	0.00630	0.00420
Sample 8	1	6.25	3.93	0.00625	0.00393
Sample 9	1	6.20	3.68	0.00620	0.00368
Sample 10	1	6.13	3.20	0.00613	0.00320
Sample 11	1	6.08	3.00	0.00608	0.00300
Sample 12	1	6.45	2.73	0.00645	0.00273
Sample 13	1	6.83	0.88	0.00683	0.00088
Sample 14	1	6.90	0.68	0.00690	0.00068
Sample 15	1	7.10	0.60	0.00710	0.00060
Sample 16	1	7.10	0.55	0.00710	0.00055
Sample 17	1	7.15	0.41	0.00715	0.00041
Sample 18	1	7.23	0.30	0.00723	0.00030
Filtrate Sample	1	5.48	0.20	0.00548	0.00020
Measured Balance Of Filtrate	96	5.48	0.20	0.5261	0.01901
Wash	636	4.39e-2	3.33e-4	0.0279	0.00021
			TOTAL OUTPUT (g):	0.707	1.116
			INPUT-OUTPUT (g):	0.021	-0.159
			%Lost of INPUT:	2.87	-16.56

Acid Addition Summary

Total Volume of 6M H_2SO_4 Added = 0.05 mL Sulfuric Acid Consumption = 3.67 kg H_2SO_4/tonne ore

Copper Extraction Summary * based on assay head, ** based on calculated head

Sample	Total Leach Time (hrs)	Total Cu from Ore (g)	% Copper Extraction* (Soln. Anal)	Soln. E_h (mV SHE)		Recalc. % Copper Extraction** (Soln. Anal)
	0	0	0	532	% Copper	0
1	45.83	0.115	36.92%	567	Extraction*	39.59%
2	93.17	0.113	36.55%	575	(Solids Anal.)	39.19%
3	143.68	0.124	39.83%	581	90.38%	42.71%
4	188.83	0.126	40.67%	586	Calculated Head	43.61%
5	237.42	0.125	40.27%	587	3.61%	43.17%
6	285.92	0.133	42.90%	590	S.G.(filtrate)	46.00%
7	338.43	0.139	44.93%	590	1.0194 g/cc	48.17%
8	382.55	0.142	45.73%	591	Cake entrained Cu	49.03%
9	430.05	0.144	46.51%	591	0.0171 g	49.87%
10	482.78	0.138	44.37%	595	Wash Cu	47.57%
11	527.33	0.140	45.03%	597	0.0279 g	48.28%
12	575.23	0.176	56.82%	620	Cu ppt formed!	60.92%
13	621.68	0.213	68.74%	826		73.70%
14	672.17	0.226	72.90%	844		78.16%
15	718.55	0.249	80.37%	849		86.17%
16	766.18	0.257	82.66%	851		88.62%
17	817.50	0.268	86.26%	851		92.48%
18	912.07	0.281	90.53%	863		97.06%
Final	986.90	0.260	83.65%	848		89.68%

Expt. Name: L9S(8) RLT5

Expt. Type: Bioleach Check Test

Ore: Lower

Cl^- Level: 5.5 g/L

Fe^{2+} Level: 9.0 g/L

INPUTS:

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Ore	8.12	3.87	4.23	0.314	0.343
Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Inoculum-I	5	7.84	0.41	0.039	0.002
2nd Inoculum-I[!]	5	6.29	0.13	0.031	0.001
Media	70	4.85	8.76	0.340	0.613
6M H_2SO_4 Acid	0.05	nav	nav	nav	nav
211 g/L NaCl	3.119	nav	nav	nav	nav
Theoretical System Volume, *V(Th)*	78.119		TOTAL INPUT (g):	0.724	0.959

nav=no applicable value

OUTPUTS: ([!] 2nd inoculum volume/Cu content included in calcs from sample 10 on)

Solids	Weight (g)	Wt% Cu	Wt% Fe	Wt(Cu) (g)	Wt(Fe) (g)
Leach Residue	10.1041	1.138	8.877	0.115	0.897

Solutions	Vol. (mL)	g/L Cu	g/L Fe		
Sample 1	1	6.60	6.60	0.00660	0.00660
Sample 2	1	6.53	6.00	0.00653	0.00600
Sample 3	1	6.53	5.43	0.00653	0.00543
Sample 4	1	6.58	5.03	0.00658	0.00503
Sample 5	1	6.63	4.63	0.00663	0.00463
Sample 6	1	6.58	4.25	0.00658	0.00425
Sample 7	1	6.60	3.95	0.00660	0.00395
Sample 8	1	6.50	3.65	0.00650	0.00365
Sample 9	1	6.53	3.55	0.00653	0.00355
Sample 10	1	6.50	3.00	0.00650	0.00300
Sample 11	1	6.45	2.75	0.00645	0.00275
Sample 12	1	6.40	2.63	0.00640	0.00263
Sample 13	1	6.33	2.43	0.00633	0.00243
Sample 14	1	6.30	2.25	0.00630	0.00225
Sample 15	1	6.28	2.23	0.00628	0.00223
Sample 16	1	5.98	2.10	0.00598	0.00210
Sample 17	1	5.88	2.05	0.00588	0.00205
Filtrate Sample	1	4.98	1.65	0.00498	0.00165
Measured Balance Of Filtrate	89	4.98	1.65	0.4428	0.14685
Wash	655	4.3e-2	1.4e-4	0.0279	0.00896
			TOTAL OUTPUT (g):	0.700	1.117
			INPUT-OUTPUT (g):	0.025	-0.158
			%Lost of INPUT:	3.39	-16.42

Acid Addition Summary

Total Volume of 6M H_2SO_4 Added = 0.05 mL Sulfuric Acid Consumption = 3.62 kg H_2SO_4/tonne ore

Copper Extraction Summary * based on assay head, ** based on calculated head

Sample	Total Leach Time (hrs)	Total Cu from Ore (g)	% Copper Extraction* (Soln. Anal)	Soln. E_h (mV SHE)		Recalc. % Copper Extraction** (Soln. Anal)
	0	0	0	553	% Copper	0
1	45.73	0.137	43.56%	577	Extraction*	47.25%
2	92.93	0.138	43.80%	583	(Solids Anal.)	47.51%
3	143.58	0.144	45.87%	587	63.40%	49.76%
4	188.70	0.155	49.19%	589	Calculated Head	53.36%
5	237.32	0.165	52.53%	591	3.57%	56.98%
6	285.82	0.168	53.39%	592	S.G.(filtrate)	57.92%
7	338.33	0.176	56.11%	592	1.0226 g/cc	60.86%
8	382.45	0.175	55.72%	592	Cake entrained Cu	60.44%
9	429.95	0.184	58.41%	592	0.0149 g	63.36%
10	482.68	0.189	60.20%	593	Wash Cu	65.30%
11	527.23	0.192	60.95%	594	0.0279 g	66.11%
12	575.13	0.194	61.68%	592	Cu ppt formed!	66.90%
13	621.58	0.194	61.73%	591		66.96%
14	672.07	0.198	63.08%	589		68.43%
15	718.45	0.202	64.42%	590		69.88%
16	766.08	0.184	58.49%	593		63.44%
17	817.40	0.181	57.74%	593		62.64%
Final	864.95	0.175	55.59%	593		60.30%

APPENDIX E: Glossary

abiotic: not biotic, not involving or produced by organisms

biotic: pertaining to living organisms

cytoplasm: cell protoplasm external to the nuclear membrane

cytosine: pyrimidine base ($C_4H_5N_3O$) that codes genetic information in the polynucleotide chain of DNA or RNA

flagella: plural form of flagellum (any of various elongated filiform appendages that project singly or in groups from a cell and is the primary locomotive organ of many microorganisms)

genotype: all or part of the genetic constitution of a an individual (species) or group (family)

glycocalx: external coating of prokaryotes or bacteria. Composed of polysaccharides or proteins, this coating, depending on its nature can be referred to as a capsule (hard and dense) or as a slime layer (soft and pliable). Besides providing addition protection for the cell, believed to expedite cell attachment to solid surfaces.

Gram's Stain: method/staining medium for differential staining of bacteria by which some species remain colored and some are decolourized by treatment with a watery solution of iodine and the iodide of potassium after staining with gentian violet.

guanine: purine base ($C_5H_5N_5O$) that codes for genetic information in the polynucleotide chain of DNA or RNA

homology: likeness in structure between parts of different organisms due to evolutionary differentiation from the same or a corresponding part of a remote ancestor

lipoproteins: a conjugated protein that is a complex of protein and lipid

micron: (aka micrometer) unit of length equal to one millionth of a meter

peptidoglycan: polymer that is composed of polysaccharide and peptide chains and is found especially in bacterial walls (also called mucopeptide or murein)

phenotype: visible properties of an organism produced by the interaction of the genotype and the environment

phospholipids: any of various lipids in which phosphoric acid as well as a fatty acid are esterified to glycerol and which are found in all living cells in the bilayers of plasma membranes

polymorphism: quality or state of being able to assume different forms

polysaccharides: a carbohydrate that can be decomposed by hydrolysis to form two or more molecules of monosaccharides

protoplasm: organized colloidal complex of organic and inorganic substances (as proteins and water) that constitutes the living nucleus, cytoplasm, plastids, and mitochondria of the cell and is regarded as the only form of matter in which the vital phenomena are manifested

sterile: free from organisms, especially microorganisms

taxonomy: orderly classification of plants and animals according to their presumed natural relationships

APPENDIX F: Free Energy Data, E_h-pH Diagrams (Cu-S-Cl-H_2O) set at simulated activities close to conditions encountered in actual test work

Figure F.1 (a-f) are E_h-pH diagrams of the Cu-S-Cl-H_2O system with nominal concentrations used to represent various Cu^{2+}/Cl^- regimes as experienced in the actual bioleaching testing program. Cuprous ion activity was arbitrarily set at 5% of the nominal cupric ion activity. The limiting activity of Cu-Cl complexes was arbitrarily set to be one order of magnitude less the minimum of any of the copper (Cu^+ or Cu^{2+}) or the chloride ion activities (i.e. 0.1 x @MIN{[Cu^{2+}], [Cu^+], [Cl^-]}. Clearly, these are very simplified representations of the actual systems involved; they are used only to discuss the general stability of Cu-Cl precipitates and complexes.

With regards to all of the E_h-pH diagrams generated by the Thermochemistry program, the chemical species used as possible stable phases or ligands are listed in Table F-1 and the chemical species for which free energy data was externally researched are listed in Table F-2.

Table F-1: Chemical species used as possible stable phases or ligands in E_h-pH diagrams in the thesis.

Chemical Formula of Species as used in Thermochemistry Program	E_h-pH Diagrams in thesis, section 3.5 or Appendix F		
	S-H_2O / S(ext)-H_2O	Cu-S-H_2O / Cu-S(ext)-H_2O	Cu-S-Cl-H_2O / Cu-S(ext)-Cl-H_2O
H2 S (g)	[P]	[L]	[L]
H S O4 <-> (aq)	[P]	[L]	[L]
S O4 <2-> (aq)	[P]	[L]	[L]
H S <-> (aq)	[P]	[L]	[L]
S <2-> (aq)	[P]	[L]	[L]
S	[P]	[L]	[L]

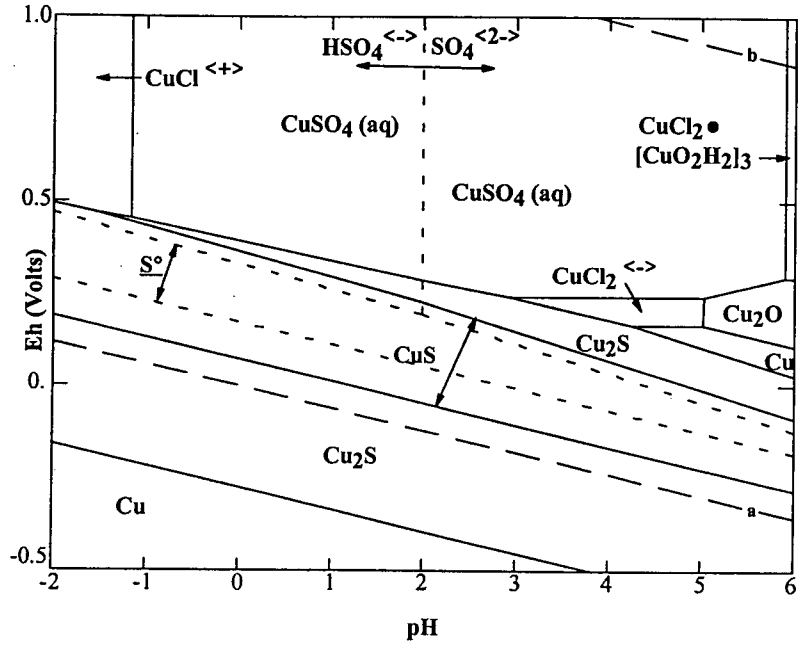
Table F-1, continued.

Formula of Species in Thermochemistry Program	S-H_2O / S(ext)-H_2O	Cu-S-H_2O / Cu-S(ext)-H_2O	Cu-S-Cl-H_2O / Cu-S(ext)-Cl-H_2O
Cu	NA	[P]	[P]
Cu <+> (aq)	NA	[P]	[P]
Cu <2+> (aq)	NA	[P]	[P]
Cu2 O	NA	[P]	[P]
CuO	NA	[P]	[P]
H Cu O2 <-> (aq)	NA	[P]	[P]
Cu O2 <2-> (aq)	NA	[P]	[P]
Cu2 S	NA	[P]	[P]
Cu S	NA	[P]	[P]
Cu S O4 (aq)	NA	[P]	[P]
Cl2 (aq)	NA	NA	[L]
Cl <-> (aq)	NA	NA	[L]
Cu Cl	NA	NA	[P]
Cu Cl <+> (aq)	NA	NA	[P]
Cu Cl2 <-> (aq)	NA	NA	[P]
Cu Cl3 <2-> (aq)	NA	NA	[P]
Cu Cl3 <-> (aq)	NA	NA	[P]
Cu Cl4 <2-> (aq)	NA	NA	[P]
Cu Cl2	NA	NA	[P]
Cu Cl2 (aq)	NA	NA	[P]
Cu Cl2[Cu O2H2]3	NA	NA	[P]

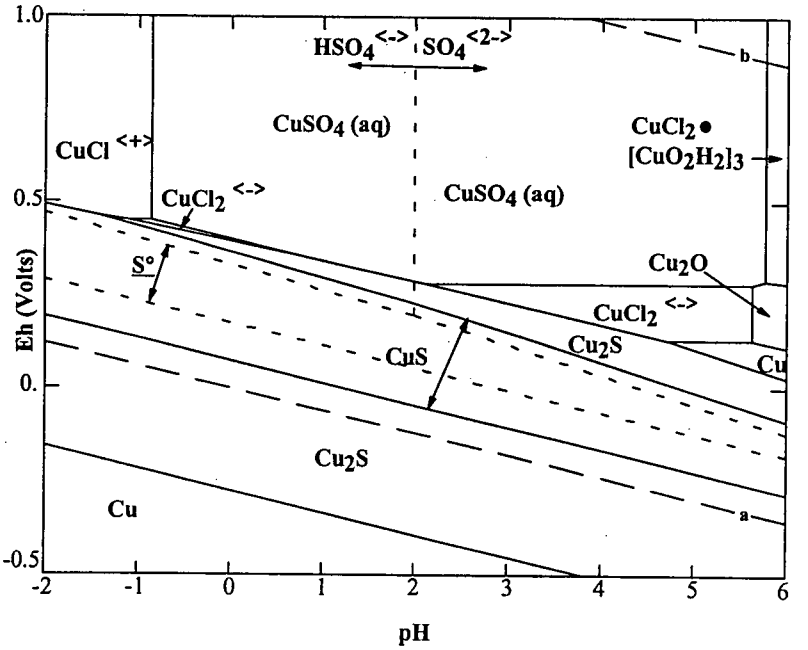
NA-not applicable; [P]-possible stable phase; [L]-ligand.

Table F-2: Researched free energy of formation data for specific chemical species used in E_h-pH diagrams in the thesis.

Formula as used in Thermochemistry Prog.	Chemical Name	Free Energy of Formation (J/mol)
H S O4 <-> (aq)	bisulfate ion, aqueous	-756010.
S O4 <2-> (aq)	sulfate ion, aqueous	-744630.
H S <-> (aq)	bisulfide ion, aqueous	+12050.
S <2-> (aq)	sulfide ion, aqueous	+86310.
Cu <+> (aq)	cuprous ion, aqueous	+50663.
Cu <2+> (aq)	cupric ion, aqueous	+65736.
H Cu O2 <-> (aq)	bicuprate ion, aqueous	-258757.
Cu O2 <2-> (aq)	cuprate ion, aqueous	-183809.
Cu S O4 (aq)	cupric sulfate, aqueous	-692915.
Cl2 (aq)	chlorine, aqueous	+6909.
Cl <-> (aq)	chloride ion, aqueous	-131355.
Cu Cl	cuprous chloride, solid	-119800.
Cu Cl2 <-> (aq)	cuprous dichloride complex, aqueous	-240500.
Cu Cl3 <2-> (aq)	cuprous trichloride complex, aqueous	-376000.
Cu Cl <+> (aq)	cupric chloride complex, aqueous	-68245.
Cu Cl2	cupric dichloride, solid	-173900.
Cu Cl2 (aq)	cupric dichloride, aqueous	-198045.
Cu Cl3 <-> (aq)	cupric trichloride complex, aqueous	-315700.
Cu Cl4 <2-> (aq)	cupric tetrachloride complex, aqueous	-433773.
Cu Cl2[Cu O2H2]3	basic cupric chloride precipitate	-1339003.

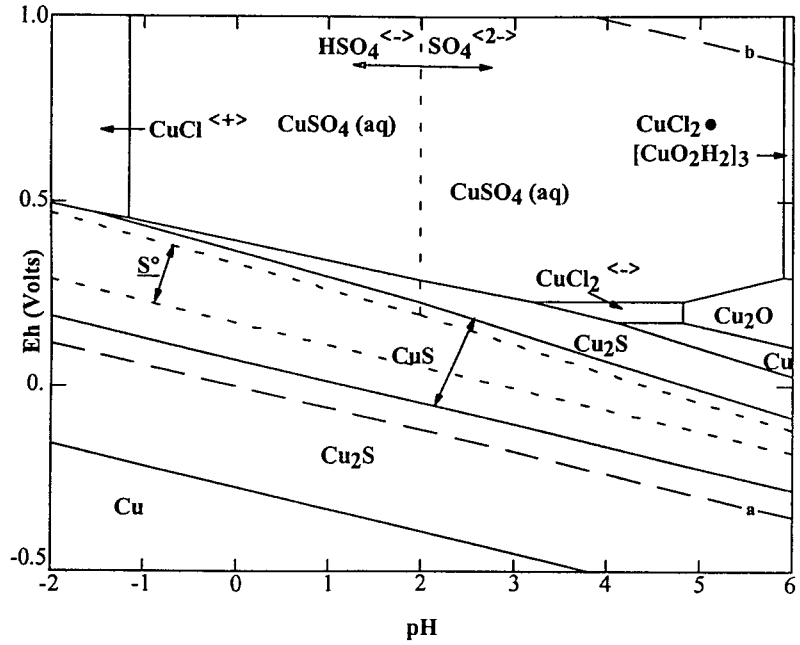


(a)

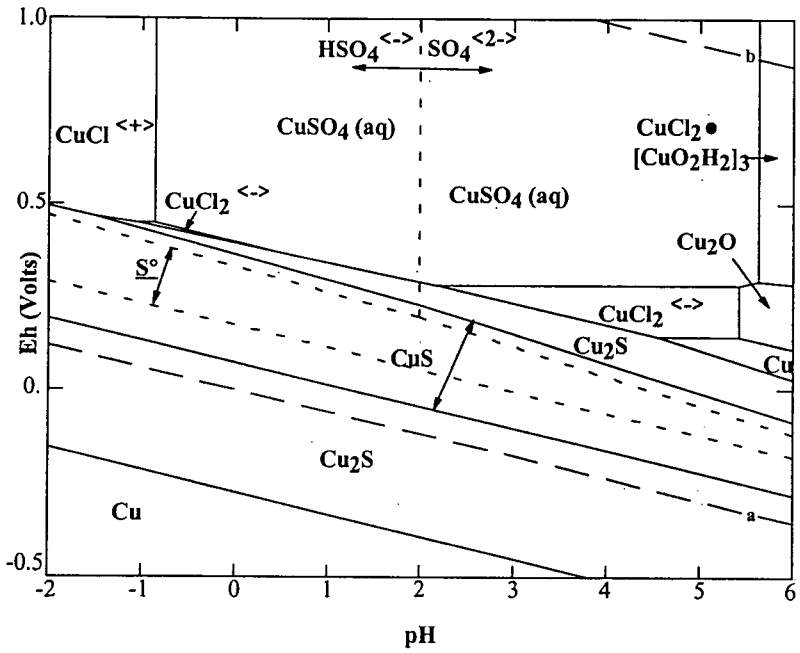


(b)

Figure F-1: E_h-pH diagrams for the Cu-S-Cl-H_2O system at 25°C, solids at unit activity, aqueous species without $Cu^{2+}/Cu^{+}/Cl^{-}$ at unit activity, $P(H_2S(g))$=1 atm., Cu^{2+}, Cu^{+}, and Cl^{-} concentrations defined as follows: (a) 5 g/L Cu^{2+}, 0.25 g/L Cu^{+}, 2.5 g/L Cl^{-}; (b) 5 g/L Cu^{2+}, 0.25 g/L Cu^{+}, 5.0 g/L Cl^{-}.

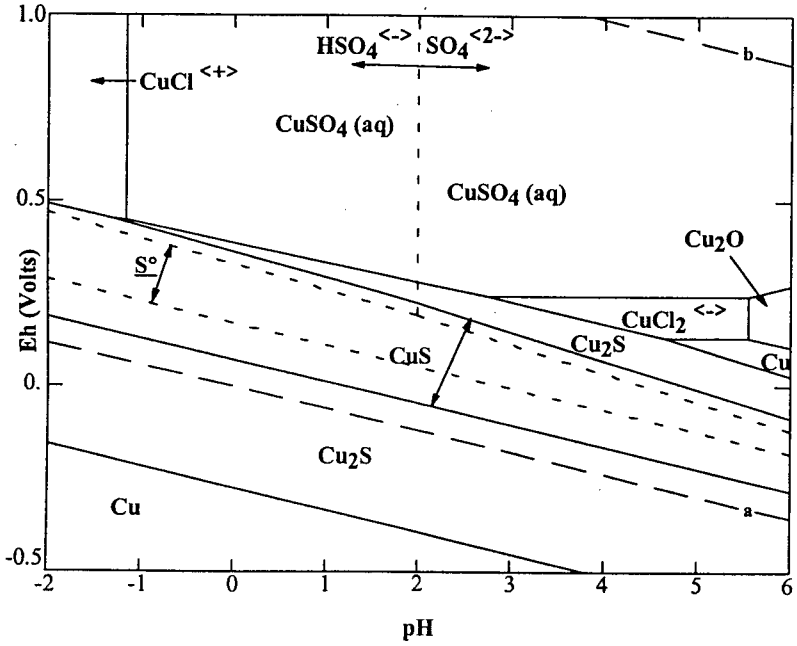


(c)

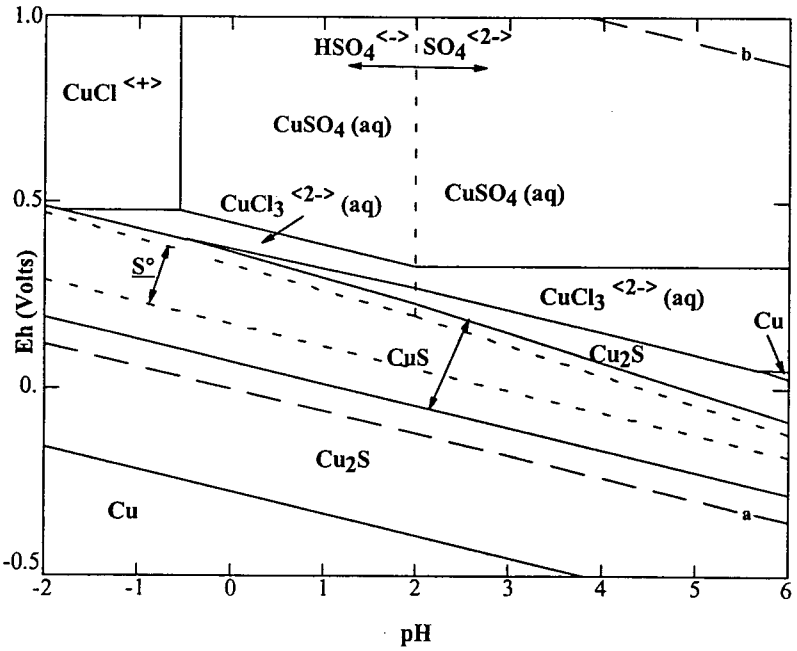


(d)

Figure F-1: E_h-pH diagrams for the Cu-S-Cl-H_2O system at 25°C, solids at unit activity, aqueous species without $Cu^{2+}/Cu^{+}/Cl^{-}$ at unit activity, $P(H_2S(g))$=1 atm., Cu^{2+}, Cu^{+}, and Cl^{-} concentrations defined as follows: (c) 8 g/L Cu^{2+}, 0.40 g/L Cu^{+}, 2.5 g/L Cl^{-}; (d) 8 g/L Cu^{2+}, 0.40 g/L Cu^{+}, 5.0 g/L Cl^{-}.



(e)



(f)

Figure F-1: E_h-pH diagrams for the Cu-S-Cl-H_2O system at 25°C, solids at unit activity, aqueous species without $Cu^{2+}/Cu^{+}/Cl^{-}$ at unit activity, $P(H_2S(g))$=1 atm., Cu^{2+}, Cu^{+}, and Cl^{-} concentrations defined as follows: (e) 1.5 g/L Cu^{2+}, 0.075 g/L Cu^{+}, 2.5 g/L Cl^{-}; (f) 1.5 g/L Cu^{2+}, 0.075 g/L Cu^{+}, 10.0 g/L Cl^{-}.