
Large particle effects in chemical/biochemical heap leach processes - A review

Yousef Ghorbani, Jochen Petersen, Megan Becker, Aubrey Mainza, Jean-Paul Franzidis,

Department of Chemical Engineering, University of Cape Town, Private Bag X6,

Rondebosch 7701, South Africa

Email: yousef.ghorbani@uct.ac.za

Abstract

Heap leaching is gaining in popularity as a low cost technology for mineral extraction from low-grade ores. Unique to heap leaching is the relatively coarse upper particle size, typically 12-25 mm for crushed and agglomerated ores and larger for run-of-mine dump leaching operations. Leaching from such large particles is poorly understood and commonly assumed to follow shrinking core type behavior, although this is a gross simplification in most cases.

At the particle scale, leaching is governed by the way in which mineral grains are distributed within a single particle and how well they are accessible through pores and cracks to leaching reagents flowing through the heap bed. This review investigates the current state of knowledge with respect to the understanding of leach mechanisms and mineral distributions prevailing, in large particles in heaps and the tools to characterize these. This is including the study of Key parameters in heap leaching, Visualization techniques for ore characterisation. The connection between comminution and leaching behavior, Particle models within heap leach modeling.

The economics of heap leaching are strongly governed by the trade-off between slow rate of leaching from large particles and the cost of crushing finer. A sound understanding of the underlying mechanisms will greatly inform future technology choices in the area of heap leaching.

Keywords: Large particle, Heap leaching, Ore mineralogy, Particle models.

1. Introduction

High-grade ore resources in the world are in decline and therefore increased attention is given to lower grade and more complex ores. Complex sulphide ores are in many cases difficult to treat with conventional mineral processing methods, and the concentrates produced are often not clean enough, which renders these ores difficult to commercialise (Sandström, and Petersson, 1997).

With the typical ore grades that are mined dropping and the economic and environmental cost of energy increasing, less energy intensive metal extraction techniques are becoming more attractive. One of these methods is heap leaching, which has gone from a relatively obscure extraction technique used only for difficult ores or as a waste recovery process to a mainstream technology. For instance, currently heap leaching accounts approximately for 20 percent of the worldwide copper production (Linus, 2010, Padilla et al., 2008).

From its first implementation for the recovery of gold from low-grade ores by cyanidation in the early 1970s, heap leaching has developed into a key hydrometallurgical technology, in conjunction with solvent extraction and electrowinning, for the recovery of base metals, primarily copper from both oxides and secondary sulphides, but has been considered more recently also for nickel, zinc and uranium.

However, with each new development, it becomes increasingly apparent that the successful application of heap leaching technology will ultimately depend on our having an ever more complete understanding of the fundamental processes underlying it. Much work has been done toward the development of this understanding, on many different fronts. Heaps are finally coming to be viewed for what they have always been: complex but versatile unit operations, which can only be designed and operated, to their full potential with the aid of sophisticated modeling tools (Dixon, 2003).

This paper gives a comprehensive overview of the current understanding of leach mechanisms of, and mineral distributions prevailing within, large particles and modeling approaches taken. The economics of heap leaching are strongly governed by the trade-off between slow rate of leaching from large particles and the cost of crushing finer. A sound understanding of the underlying mechanisms will greatly inform future technology choices in the area of heap leaching.

2. Heap leaching

Heap leaching from low-grade ores has become a major contributor to the extraction of economically important metals, notably copper, gold, silver, and uranium (Padilla et al., 2008). Crushed or run-of-mine ore (ROM) is piled on an impermeable pad and leaching reagents are introduced by irrigation from the top. The desired mineral is extracted and the solution becomes increasingly loaded as it percolates through the pile. Leaching may be facilitated by microorganisms resident within the ore bed. The pregnant leach solution (PLS) is collected by a drainage system at the base of the pile and channeled to the PLS pond. The PLS is then pumped to the processing facility where the value metal is recovered. The “barren” leach solution is pumped to the barren solution pond from where, after solution make-up, it is reapplied to the surface of the heap

(Watling, 2006). Despite the current widespread use of heap leaching in industry, the process is still limited by low recoveries, long extraction times, and high operation costs, especially in terms of acid consumption. Hence, there is a need to optimize heap operations in terms of extraction operating costs. The knowledge that informs such optimization is derived from the investigation of the interactions between the physical, chemical and biological processes that drive a heap; such investigations can be carried out with the aid of mathematical models (Dreisinger, 2006, Acevedo, 2002, Mellado et al., 2009).

2.1. Heap leaching and conventional methods

Heaps and dumps present a number of advantages and disadvantages (Table 1) compared to conventional milling and flotation of sulphide ores (Acevedo, 2002, Brierley, 2008). In the immediate future, heap leaching is likely to be a major area of expansion, though new patented processes (Thiel and Smith, 2004, Nathsarma, et al., 2008). In the United States, approximately one-third of gold and nearly 30 percent of total new copper production come from heap leaching. Nearly all new copper and gold mines involve some ore processing by heap leaching (Acevedo, 2002, Brierley, 2008).

Table 1: Advantages/disadvantages of heap leaching.

Advantages	Disadvantages
Low capital and operating costs	Lower recoveries than mill/float or mill/leach
Absence of milling step, may require crushing and agglomeration	Long leach cycles and hold-up
Simplicity of atmospheric leach processes	Lengthy pilot test programme
Can be used to treat low-grade ores, wastes and small deposits	Large footprint
Absence of liquid-solid separation step allows countercurrent operation	Acid-mine drainage from spent heaps
Metal tenor may be built up by recycling solution over heaps	
Simplicity in equipment and operation	
Shorter start-up times	
Less intensive environmental regulatory concerns	
Acceptable yields	

Operated correctly, heap bioleaching offers economic recovery of resources that would be too marginal for other process routes, such as concentration followed by smelting or autoclaving (Petersen, and Dixon, 2007). This method is employed with abandoned and/or underground mines where the ore deposits cannot be mined by the conventional methods since they are either low grade or of small deposits or both. Heap bioleaching has become a reasonably well established technology for the extraction of low-grade secondary copper sulphides and the oxidation of refractory gold ores. At present, the technology is being developed also for the recovery of primary copper sulphides using thermophilic microbes (Nathsarma et al., 2008, Petersen, and Dixon, 2007).

2.2. Kinetic aspects in heap (bio)leaching

Although the concept of heap bioleaching appears to be very simple, the sub-processes taking place within the heap are rather complex and their interactions not yet fully understood. Dixon and Petersen (2003) distinguished between different processes ranging from the macro to the grain-scale, as is illustrated in Figure 1. At the macro scale, kinetic is governed primarily by transport of mass and energy into, through, and out of the heap structure. This involves the solution, heat and gas flows across the heap. Macro-scale processes are essentially the “flow” processes in the heap, i.e. solution flow, gas flow and heat flow.

At the aggregate scale, gas uptake into liquid phase, intra-and inter-particle diffusion within the stagnant zones, and bacterial growth and oxidation are all contributing to the leaching kinetics. Aggregate scale processes as ‘meso’-scale, occur at the level of a cluster of ore particles. The important processes at this level are oxygen uptake into solution, diffusion of dissolved chemical species through the inter-particle pores, and microbial processes.

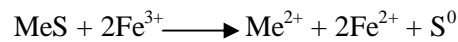
Oxygen is a key reactant in heap bioleaching, as the microbes can oxidize ferrous iron and sulfur only to the extent to which oxygen is available in the system. Oxygen uptake into solution is a temperature dependent mass transfer step. The mass transfer coefficient is subject to measurement, and has been highlighted as an important parameter in heap leach modeling (Bouffard, 2003, Petersen, 2010).

The dissolved chemical species (reactants and reaction products), must diffuse through stagnant solution occupying the bed voidage in order to be recovered in the leaching solution, or to take part in chemical reactions within the ore particles. The extent of the effect of this inter-particle pore diffusion on extraction rate and mineral leaching depends on the length of the diffusion pathway, which may be significant for systems with poor solution distribution (Dixon and Petersen, 2003).

At the particle scale, leaching is governed by the way in which mineral grains are distributed within a single particle - this is referred to as the topological effect. Mineral grains may be present as anything from free grains to encapsulated local spots inside a particle. Their distribution and accessibility within particles directly determine the leachability of the target mineral. Furthermore, in low-grade ores the mineralogy of the gangue matrix is also of some significance, as it can interfere with mineral leaching and biological phenomena. The assumption that the mineral grains are uniformly distributed in the ore particle, coupled with relatively fast mineral dissolution, lends itself to the shrinking core kinetics model (Park and Levenspiel, 1977). In reality, the minerals may occur as free grains or in grain clusters, and may be distributed on the particle surface or as inclusions in veinlets within the ore.

Another important process at the particle level is the transport of reactants to, and reaction products from, reaction sites within the particle. This process is diffusion governed, and is limited by the size and porosity of the ore particle, the diffusion gradient, and the diffusivity of the species.

Finally, at the grain scale, the chemical and electrochemical interactions at the grain surface determine the leaching kinetics (Harneit et al., 2006). The key mineral leaching reaction in bioleaching of a sulfide mineral is the oxidation of the metal sulfide (MeS) by ferric ions (Ogbonna, 2006):



The chemical reactions are primarily a function of temperature (characterized by the activation energy), and concentration of reactants. Although the principal mechanisms of such reactions are understood, the exact values of critical parameters for each specific case are subject to measurement (Dixon and Petersen, 2003).

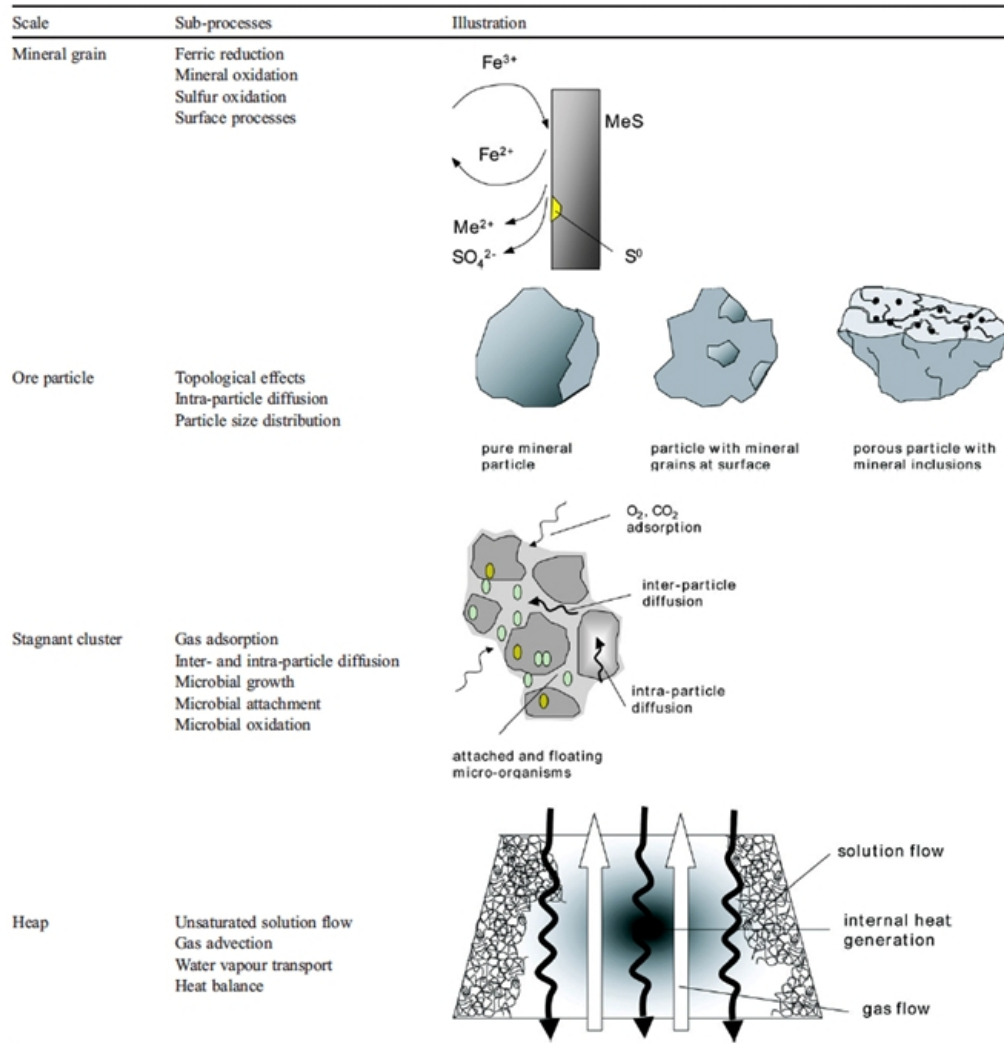


Figure 1: Schematic representation of sub-processes in heap bioleaching (Source: Dixon and Petersen, 2003).

3. Leaching rate during the heap processes

Metal extraction rates in heap leaching typically show an initially fast leaching rate, reaching up to 50-60 percent copper extraction over the first few months, followed by a slower constant rate period reaching up to 80-90 percent copper extraction over the following 12-24 months (Figure 2). This is believed to represent the change in leaching from the readily accessible grains on the particle surface to the more inaccessible grains within particles

(Watling, 2006). Typical recovery in base metal heap leaching is about 60-70 percent (Dreisinger, 2006, Thiel and Smith, 2004, Brierley, 2001) over a 1-2 year period, after which operation is usually discontinued due to the slow rates. Rapid leaching occurs in all size classes only initially, leading to near complete conversion in the smallest size, but only partial conversion in the larger sizes. After this initially rapid phase leaching slows down dramatically, and there is no significant difference in the rate of leaching of either mineral. This was explained by the fact that after depletion of easy-to-leach surface minerals ferric iron does indeed have to migrate deeper into particles via a pore network and the reduced ferrous form return to the surface to be re-oxidised. Hence, it is likely that the grains near the surface will be depleted much more rapidly, and a slower-leaching mineral at the surface might dissolve preferentially over a fast-leaching mineral deep inside a particle (Ogbonna, Petersen, and Laurie, 2006).

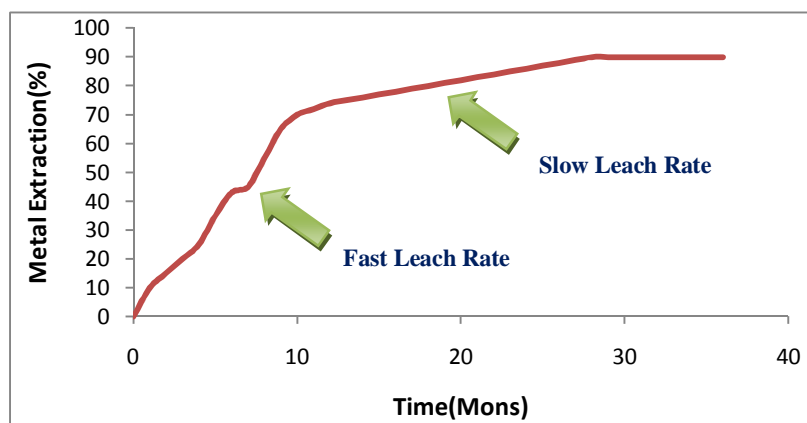


Figure 2: Metal extraction rate in heap leach process (Source: Ghorbani et al., 2009).

In the bacterial leaching of sulfide minerals, ferric iron is the key oxidizing agent and soluble iron species are the main determinants of redox potential. Active iron oxidizing bacteria, such as *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, maintain high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios due to continued oxidation as part of their respiratory process. Precipitation of iron hydroxide and jarosite phases in the leaching system may suppress the metal solubilization by preventing the contact between the leaching agent and the mineral. The solubility of iron species is defined by their concentration in solution and pH.

The bacterial leaching process requires acidic conditions, the acidity often being simultaneously produced by the oxidation of pyrite and hydrolysis of ferric ion. The acid may be neutralized in various acid-consuming reactions such as the leaching of carbonates and some silicate minerals. As in all biochemical and chemical processes, the rates of leaching reactions are also temperature dependent. Therefore, evaluation of the temperature effects on the bacterial leaching is considered to be particularly important (Ahonen, and Tuovinen, 1995, YIN et al., 2008)

The solid/liquid contact area, which in low-porosity rocks is mainly a function of particle size of the material, is a major factor in determining the kinetics of the leaching reactions. Typical to leaching processes is their

selectivity with respect to certain minerals or groups of minerals. Leach solution is also able to penetrate into micro-fissures and micro-pores of the rock mass, thus reducing the need for energy consuming crushing and grinding operations. The optimization of a leaching process thus requires quantitative information on the effect of grain size, as well as on the propagation of the leaching effect inside the mineral grains.

Permeability is critical for the recovery rates from a heap (as well as from dump and in-situ operations). If the heap material is too compact, the leaching operation time increases as the reagent liquid will only slowly percolate through the heap. If permeability in the heap is uneven, the leaching solution might cause channeling, leaving parts of the heap untreated. Therefore, fine particles are often agglomerated to ensure a better overall permeability.

3.1. Particle size distribution in the heap

The term 'particle' has a number of meanings when considering the heap leach process. For the ore supplied to the heap, it is the particle size distribution of the crushed ore. This is a wide range generally from 50 mm to sub-micron. Most heap leach operations now recognise the need to agglomerate the ore to improve the percolation rate and minimise channeling in the heap. The agglomerated ore has a different size distribution with a slight increase in the top size but a very large decrease in the small size. Ores present in heaps have a relatively coarse top particle size, typically 12-25 mm for crushed and agglomerated ores and larger for run-of-mine dump leaching operations (Figure 3). Leaching from such large particles is commonly assumed to follow shrinking core type behavior, although this is a gross simplification in most cases. There are virtually no literature sources, which offer any evidence for the validity of this assumption in the given context. Recent experimental evidence suggests that in fact leaching from large particles occurs only at the surface and in subsurface regions, which are accessible from the surface by cracks and pores (Liddell, 2005, Malmström et al., 2008, Sracek et al., 2006). This indirectly also relates leaching behavior to the method by which the ore has been crushed prior to leaching.

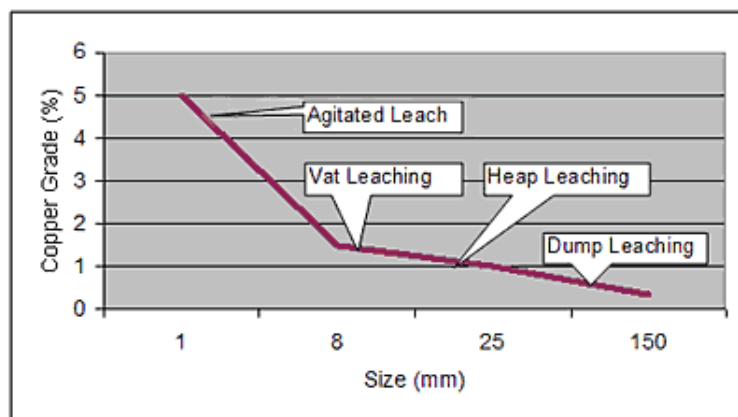


Figure 3: Particle size distribution in heap leaching process (Source: William, 2010).

3.2. Mechanism of the leaching from large particles

It is worth emphasizing that, when coupled sequential phenomena are involved, the slowest step will control the overall rate of the process if it is significantly slower than the other processes. As can be seen from the shrinking core model the change in particle size has an inverse squared effect on the effective leach rate. Any small increase in effective particle size can have a significant effect on the overall diffusion leach rate. One of the challenges in understanding heap leaching is to determine the actual effective particle size (of the meta-particle) being leached (Graeme, 2003). Due to larger ore particles, sizes encountered in heap leaching, chemical diffusion within the solution filled rock pores always affect extraction rates. However, mixed leaching kinetics occur when slow reacting mineral grains (e.g., chalcocite) or very large mineral grains are present within the ore. In these cases the mineral dissolution rate must be considered along with diffusion (Bartlett, 1992).

Leaching of minerals from whole ore particles, where the key reagent has to migrate from the particle surface, will result in a rim-leaching effect in larger particles, where all mineral near the surface is depleted first before the leach front can migrate further into the particle, and even the rate of chalcocite leaching, which is intrinsically rapid, is controlled by the rate at which ferric iron diffuses into the particle. Furthermore, pyrite and covellite 'scavenge' ferric iron migrating in from the surface before it can reach unreacted chalcocite deeper in the particle, as shown in Figure 4.

As Figure 4 and 5 indicate, leaching in the larger particles proceeds in layers from the surface in, with chalcocite leaching first, followed by covellite and pyrite in parallel, whereas further leaching of any component deeper inside the particle is inhibited for lack of ferric iron, thus creating a rim- or surface layer leaching effect. In the smallest size class, this effect does not occur since the rate of ferric diffusion is not limiting over the much shorter diffusion distance. If there exists competition between different mineral phases, then this is likely to be skewed in favour of the slower-leaching mineral once the fast-leaching mineral has been depleted from the surface, rather than leaching more of the fast-leaching mineral deeper inside the particle. The effect is exaggerated with increasing particle size.

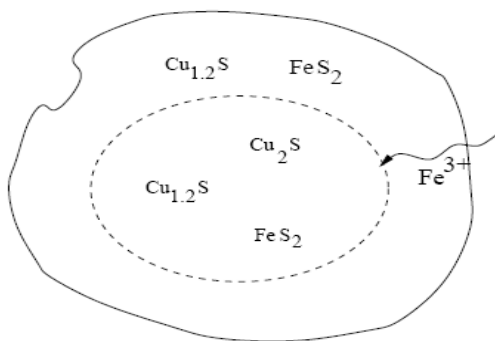


Figure 4: Schematic representation of ferric diffusion through rim leach.

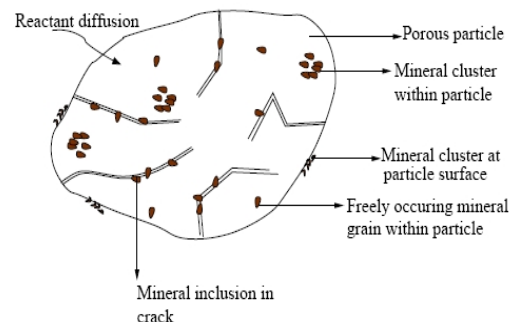


Figure 4: Cross section of an ore particle.

The abundance of the target minerals near the surface is in fact quite critical in determining the overall rate of leaching and the likely economic extraction from an ore of a given particle size distribution. For lower

porosities, the rate of release of minerals from within the ore particles would be even slower and may in fact restrict feasible mineral leaching from the particle surface (or a shallow surface layer).

Leaching in the larger particles proceeds from the surface inwards, whereas further leaching of any component deeper inside the particle is dependent on ferric iron migrating towards it, thus creating a rim-or surface layer leaching effect. In the smallest size class this effect does not occur since the rate of ferric diffusion is not limiting over the much shorter diffusion distance (Figure 5) (Graeme, 2003).

3.2.1 Chemical Weathering

Oxidation of sulphides in a rock by chemical and biochemical leaching is a natural phenomenon; similar to the process that occurs in heap leaching. Investigating of mechanism of weathering could provide useful understanding of heap kinetics, especially for leaching from large particles. The intrinsic properties of the sulphides (chemical composition, crystal structure, defect density and distribution, etc.) largely control their rate of oxidation, but also varies with the ambient physio-chemical settings (Strömberg and Banwart, 1999, Gerke et al., 1998, Evans and Banwart, 2006, López et al., 2007) For example, marcasite and framboidal pyrite will oxidize quickly while crystalline pyrite will oxidize slowly (Malmström et al., 2008).

Of particular importance is the presence of a fluid phase (e.g., oxygenated water) that facilitates the oxidation process by providing for a variety of reactions to occur at the fluid-mineral interface as well as serving to remove oxidation products from the interface that may otherwise impede further reactions. The nature and extent of reactions occurring at the sulphide-solution interface are very much dependent on the composition of the solution, which in turn is influenced by the enclosing mineral assemblage (except at very high flow rates). Therefore, rock-forming minerals that occur together with a sulphide or an assemblage of sulphides also indirectly affect the rate of oxidation of the latter. To elucidate the oxidation of sulphide minerals in a rock, both the chemical and physical aspects of mineral-solution interaction have to be considered (Malmström et al., 2008, Evans and Banwart, 2006, López et al., 2007).

a. Chemical aspects

Since all sulphide minerals were formed in the presence of an oxygen-depleted fluid under conditions far removed from the oxygen-rich atmosphere of the earth surface (Lefebvre et al., 2001), they are unstable when exposed to an oxygenated environment. In the presence of a contacting fluid phase, the relative stability of sulphide minerals can generally be assessed with the aid of pH-Eh diagrams, provided the persistence of metastable mineral phases, either primary or formed during oxidation, is taken into consideration (Malmström et al., 2008, Evans and Banwart, 2006). Since, under acidic conditions, most metals tend to remain in solution as dissolved ions, and a variety of processes (including microbial mediation and electrochemical reactions) readily occur to accelerate the oxidation of various sulphides, the ability of the associated non-sulphide minerals to control the solution pH is perhaps the most important factor influencing the rate of oxidation of sulphides in a

rock. In-situ neutralization of the acid generated during sulphide oxidation by reactions with the associated non-sulphide minerals usually lead to the formation of secondary mineral coatings on the reacting sulphides. Depending on the nature and thickness of the coatings thus formed, oxidation of the relevant sulphide(s) occurs at a reduced rate or is totally arrested.

Mineral-solution interaction involving rock-forming minerals, especially non-silicates, in a sulphide containing rock also affect the oxidation rate of the associated sulphides by modifying the composition and ionic strength of the solution concerned. For example, upon investigating the mechanism of pyrite oxidation in aqueous mixtures, pyrite oxidation rates increased linearly with substrate concentrations of CaCO_3 and NaHCO_3 , whereas solutions of Cl^- and SO_4^{2-} inhibited pyrite oxidation. Thus, dissolution of halite and gypsum in a sedimentary rock containing pyrite would impede the oxidation of pyrite while the dissolution of carbonate would enhance the process. While other iron sulphides are likely to behave similarly as pyrite, the influence of different salt types and ionic strength on the rate of oxidation of other metallic sulphides is not clear (Malmström et al., 2008, López et al., 2007, Lefebvre et al., 2001).

b. Physical aspects

The extent that a mineral assemblage can affect the chemistry of an associated liquid phase (solution) is largely determined by the duration of contact between the reacting minerals and the solution. The longer the contact time, the more closely the solution chemistry will be governed by the relevant mineral-solution equilibrium (Malmström et al., 2008, Evans and Banwart, 2006).

4. Key parameters in heap leaching

During the leaching process, physical, chemical and biologic reactions take place in the ore bed under irrigation, and natural subsidence, dissolution, deposition and solute transfer occur as a result. Hence the pore structure of the bed continues to evolve and has temporal and spatial variability (Kirjavainen and Heiskanen, 2007). Bacterial and chemical leaching are influenced by environmental, biological and physico-chemical factors, which affect the yield of metal extraction (Table 2) (Sandström, and Petersson, 1997, Ahonen, and Tuovinen, 1995, Pradhan et al., 2008, Souza et al., 2007, Dwivedy, 1995, Malik et al., 2004, Prosser, and Box, 1983). Correct chemical and physical conditions must exist for the percolation leaching system to function: a suitable ore particle size, access of oxygen and humidity to the mineral surfaces, reduced acid consumption, the presence of sulphides susceptible to bacterial oxidation, and minimal precipitated basic ferric salts, which might block the percolation channels (Olubambi et al., 2007, Deveci, 2004). Acid consumption by gangue minerals is a very important parameter for heap leaching performance, because the major rate-limiting step is the lateral diffusion of acid and a faster rate of acid gangue dissolution effectively lengthens the distance over which the acid must diffuse, and makes it more difficult for acid to penetrate to the back of the pores (Helle et al., 2005).

sulphuric acid is usually a major processing cost. Maintenance of the pH in the preferred range between one and two for microbial iron and sulphur oxidation is also important for ferric ion and acid regeneration by the microbial population (Helle et al., 2005).

In addition, the geometry of the heap may also affect the bioleaching process and rate of recovery. For these leaching systems to function, the leach environment must be kept in such conditions that the bacteria requirements are adequately met (Helle et al., 2005, Suzuki, 2001, Kirjavainen, and Heiskanen, 2007).

In addition, the geometry of heap may also affect the heap leaching process and rate of recovery. For these leaching systems to function, the medium must be kept under such conditions that the bacterial requirements are adequately met. When the environment can maintain these optimal conditions, an adequate yield of copper can be obtained (Drouet and Navrotsky, 2003).

Table 2. Factors and parameters influencing bacterial mineral oxidation and metal mobilization (source: Pradhan et al., 2008, Kirjavainen, and Heiskanen, 2007).

Physical and chemical parameters	Biological parameters	Properties of the minerals to be leached	Processing
<ul style="list-style-type: none"> • Temperature • pH • Redox potential • Water potential • Oxygen content and availability • Carbon dioxide content • Mass transfer • Nutrient availability • Iron(III) concentration • Light • Pressure • Surface tension • Presence of inhibitors and etc 	<ul style="list-style-type: none"> • Microbial diversity • Population density • Microbial activities • Spatial distribution of microorganisms • Metal tolerance • Spatial • Distribution of microorganisms, attachment to ore particles, • Adaptation abilities of microorganisms, and • inoculums 	<ul style="list-style-type: none"> • Mineral type • Acid consumption, • Mineral composition • Mineral dissemination • Grain size • Surface area • Porosity • Hydrophobicity • Galvanic interactions • Formation of secondary 	<ul style="list-style-type: none"> • Leaching mode (in situ, heap, dump, or tank leaching) • Pulp density • Stirring rate (in case of tank leaching operations) • Heap geometry (in case of heap leaching)

4.1. Properties of heap leach ores

Copper sulphide ores exhibit close similarities and complexities in their mineralogical associations and properties, which often pose challenges during their hydrometallurgical processing (Olubambi et al., 2008). These complexities therefore necessitate a detailed mineralogical characterization of such ores in determining an optimal processing route for its constituent minerals and metals. The impact of mineralogy on leaching and bioleaching should not be ignored. Extensive mineralogical analysis of ore types around a deposit is required before developing a flow sheet (Olubambi et al., 2007, Helle et al., 2005, Olubambi et al., 2008a,b, Shayestehfar et al., 2008, Dai and Jeffrey, 2006, Senanayake, 2005, Baláz, 1994). The factors that are influenced by the mineralogy of an ore are (Dai and Jeffrey, 2006, Baláz et al., 1994, Senanayake, 2007):

- (1) The degree of comminution required for effective liberation of the desired mineral;
- (2) Applicability of physical beneficiation techniques for upgrading the ore;

- (3) The nature and quantity of lixiviant to be used;
- (4) Leach liquor characteristics;
- (5) Residue mineralogy.

Mineral phase characterisation, an important objective for mineralogists and process metallurgists, requires the recognition of specific minerals as well as complete quantitative phase analysis of assemblages. In mineral processing applications in particular, an adequate appreciation of the mineralogy and its effects on treatment processes is required to make effective decisions on technology development for a given resource. The mineralogy of ores is a key factor in predicting their expected behavior during subsequent processing (Pownceby et al., 2007).

4.1.1. Crystallography direction

It is well recognised that the surfaces of crystals are not atomically smooth, even under ideal equilibrium conditions. They contain numerous microtopographical features. Some of the more important of these are presented schematically in Figure 6, which shows crystalline terraces (atomically flat regions), steps and kink sites. Arrows indicate the relative number of orthogonal directions in which atoms (ions) may move from the different surface sites in order to become solvated. The height of the steps may vary from atomic to polyatomic size and mineral surfaces cleaved under carefully controlled conditions exhibit numerous steps varying in height from < 5 nm to > 100 nm. Consequently, milled minerals should exhibit a variety of micro-topographical patterns, composed of steps of different heights separated by terraces of varying size and shape that are generated during fracture and abrasion of the mineral particles (Tromans et al., 2002, Tromans and Meech, 1999).

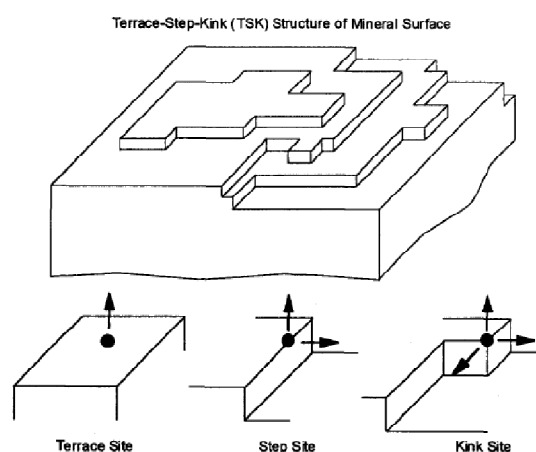


Figure 6 Schematic diagram showing a Terrace-Step-Kink structure of mineral surfaces and the general location of terrace, step and kink sites for dissolution (source: Tromans, and Meech, 2002).

Tromans, and Meech, (2002), have discussed surface-controlled mechanisms of mineral dissolution. They recognised the presence of more reactive and less reactive surface sites and the enhanced reactivity of edge

(step) sites. Attention is confined to differences between terrace and step sites only, because these are far more numerous than kink sites and are likely to be more important in determining overall mineral dissolution rates.

4.1.2. Mechanical imperfections

The initial bacterial activity on the surfaces of the sulphide minerals occurred mostly along former cracks, fractures, lineation, grain boundaries, and zone contacts, contacts between different generations or compositions, etc. Mechanical imperfections are deviations in the sulphide crystal structures. Such defects usually contain high amounts of strain energy. This energy is released when the strain in the crystal is released, and can thus be of use to the bacteria during the oxidizing process. The rate of oxidation will therefore be higher at sites of defects, containing strain energy (Dai and Jeffrey, 2006, Chandraprabha et al., 2003, Ubaldini et al., 1997).

4.1.3. Composition

A comparison of the rates of leaching of the various compositional zones within the mineral crystals suggests that the composition of the sulphides plays a fundamental role in the mode of bacterial oxidation. Figures 7 and 8 show the relatively As-rich zones in the S-rich arsenopyrite and pyrite crystals have preferentially oxidized by the bacteria, at a rate faster than the As-poor zones. These As-rich zones contain the major proportion of submicroscopic gold present in the sulphides. Therefore, this preferential oxidation of high gold-bearing areas accounts for the enhanced gold liberation during the early periods of bacterial oxidation.

This preferential oxidation of the As-rich areas can be interpreted to indicate that the bacteria have a preference for the element As and/or Au. This can be explained considering that the incorporation of Au and As atoms within the As-rich zones in the S-rich arsenopyrite will create strain in the crystals, due to the difference in sizes between Au and As atoms and the atoms they replace in the sulphide structures. Therefore, due to the high amount of strain energy available in the As-rich areas, initial bacterial oxidation will proceed at these sites at a rate faster than in the relatively unstrained As-poor areas in arsenopyrite and pyrite is therefore the result of the presence of defects, created by additional As and Au atoms present in the sulphide crystal lattice (Chandraprabha et al., 2003, Ubaldini et al., 1997, Aghamirian and Yen, 2005).

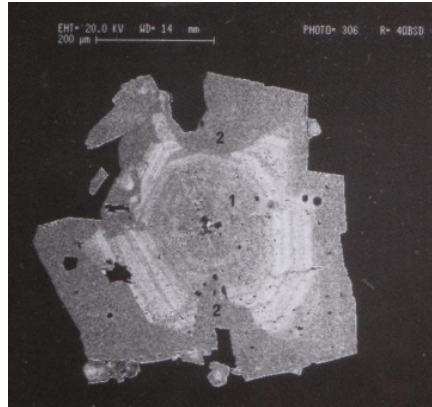
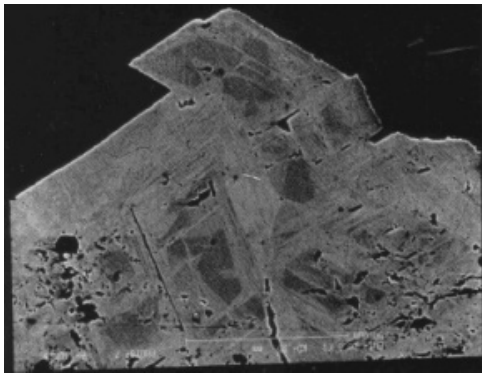
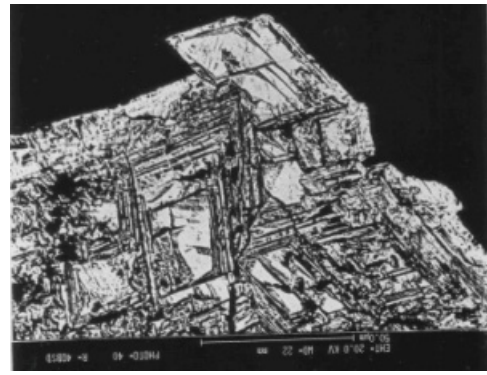


Figure 7: an Angnes pyrite crystal, showing two generations of pyrite: the first generation(1) constitutes concentric zones with rhythmic variations in As content; the second As-poor generation(2), crystallized after a period of resorption(electron backscatter images)(source: Chandrababha et al., 2003).



a



b

Figure8: A zoned arsenopyrite crystal with S-rich area(dark grey) and As-rich areas(light grey) before oxidation(a) and after being bacterially oxidized for 6 hours(b). The As-rich area has been oxidized, while the S-rich regions were not attacked at all (electron backscatter images) (source: Chandrababha et al., 2003).

4.1.4. Particle Size and shape

Particle size and shape are the factors, which determine the surface area of the particles. With a few exceptions, the reactions involved in mineral treatment are heterogeneous (i.e. the reaction takes place at the boundary between phases) and, hence, the rate is expected to be proportional to the interfacial area. The most significant point to be made about these two factors is that there are a number of instances where the rate is not dependent on the particles size (Deveci, 2004, Mazuelos et al., 2001, Strömberg, and Banwart, 1999). Leaching kinetics is affected by the particle size of the material that is leached and generally, a smaller particle size gives faster leaching kinetics since finer particles have a larger surface area.

It shows that particle size distribution alone does not provide relevant mineralogical information for understanding bioleaching behavior.

Attention should not be solely given to particle sizes, but more to the mineralogical and elemental distribution within the sizes and the interaction of the minerals/phases within the ore. The mineralogical and elemental distribution within the various particle sizes not only affects the mineral–microbe interaction and the galvanic

interaction, but also the precipitate formation on the surfaces, which in turn plays a role in the metal dissolution process. Therefore, to obtain optimum results during base metals recovery from complex sulphide ore, processing must start from a completely detailed mineralogical study (Olubambi et al., 2007).

4.1.5. Grain distribution and free surface

The mineral grains can be classified, according to their accessibility to leach solutions, into five classes (Figure 9) (Rossi, 1990):

- a) Grains exposed to the leach solutions at the surface of particles (e.g. grains numbered 1, 2 and 4);
- b) Grains exposed to the leach solutions via pores or cracks (e.g. grains numbered 9, 10 and 11);
- c) Grains which become exposed to the leach solutions only after other grains have reacted (e.g. grains numbered 14);
- d) Grains from which pores or fissures that do not debouch at the particle surface depart (e.g. grains numbered 18 and 19);
- e) Grains located inside the particles and not connected to a pore (e.g. grains numbered 21 and 24).

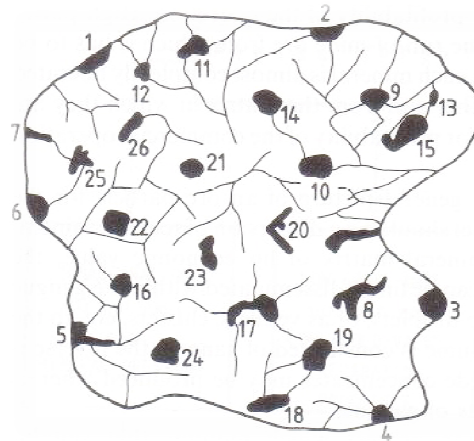


Figure 9: Grain distribution in single particle of ore.

Type (d) and (e) do not contribute to the rate, at least in the early stages of leaching, but can become involved in the leaching process if, as a result of the prolonged contact with leach solutions, new cracks and fissures are generated in the gangue, thus making them accessible to leach solutions. For the particles of the type shown in Fig. four rate regimes can be identified according to their size:

The particle size is comparable with the size of the mineral grains; this is the case of high-grade run of – mine ores or of concentrates. In this case, the reaction rate is close to that for the fully liberated grains and the inert matrix plays a minor role. Leaching is surface- chemical- reaction controlled. This regime is manifested by a shrinking of the particle as the reaction proceeds.

The particle size is larger than that of the mineral grains, although the latter are all accessible to the leach solutions from the start of the reaction. Most of the surface of the mineral grains is surrounded by impervious inert gangue and leach solution can only access thereto through the pores and/ or cracks. Leaching is therefore

still surface-chemical- reaction controlled, but the gangue reduces the rate by blocking access of the leach solutions to most of the surface. Thus, diffusion control comes into play. Particle size does not affect reaction rate.

The ratio between particle radius and embedded mineral grain radius is even larger than in the two preceding cases. The characteristic feature of this situation is that not all the grains are accessible at the start of leaching, although the overall rate is still controlled by the surface chemical reaction. Accessibility to the inner grains is hindered by the outer mineral grains and the inert gangue. The rate exhibits a further reduction, this regime is observed in the largest particles sizes: the kinetics is diffusion-controlled or mixed (diffusion and surface chemical reaction controlled). The effect of the gangue is to increase the diffusion path length- thereby reducing the overall rate still further (Rossi, 1990).

4.1.6. Porosity

The rate of reaction of a particle with a reagent in a fluid phase in which it is immersed is usually controlled either by molecular diffusion through a boundary layer extending into the fluid or by the reaction at the surface. If the particles contains cracks ore holes, which are open to the fluid, reagent diffusion into the interior of the particle, and reacts there. Under steady state conditions, the rates of diffusion and reaction are the same, and this state is maintained by a concentration gradient of the reagent within the holes. If the chemical reaction is slow, the concentration gradient is shallow and that in the bulk fluid. Under these circumstances, the reaction proceeds on the walls of holes at virtually the same rate as on the external surfaces. In other words, the area over which reaction takes place is not the external area but the total area, including that of all open pores (Cariagaa et al., 2005). As it is not unusual for the internal area to be far greater than the external area, the porosity becomes a dominant factor. Frequently, the first experimental evidence found for this is that the rate of reaction is independent of particle size. Also, as with polycrystalline material, the particle may disintegrate as reaction proceeds, but this is unlikely to lead to a significant increase in the rate because the total area does not increase. It must be emphasized that the pores which are of paramount important to the reactivity of a mineral usually have at least one dimension $< 0.1 \mu\text{m}$. they cannot be observed with a microscope, although in a few synthetic materials they have been observed with an electron microscope. Their extent is normally determined by sorption of gases, such as nitrogen or water vapor, and mercury penetration (Bachu and Cuthiell, 1990, Thomas et al., 2008).

If the chemical reaction is fast, the concentration gradient is steep, and reagent is consumed before it penetrates into the particle. Under these circumstances, the internal surfaces play no part and particle size is the important factor, as with non-porous particles.

Another situation arises with fast reaction particles of $< 10 \mu\text{m}$ diameter. With normal agitation, the thickness of the diffusion boundary layer is greater than the radius of the particles. The rate of diffusion across this layer is determined by its thickness, which almost independent of particle size. Thus, the overall rate of reaction also

becomes less dependent on particles size, but it is still sensitive to agitation (Cariagaa et al., 2005, Muñoz et al., 1997)

4.1.7. Geotechnical characteristics of the ore

The understanding of the heap leach kinetics can be advanced by the analysis of the geotechnical characteristics of the leached ore (Graeme, 2003).

These characteristics can indicate potential problems and can be used to determine the semi-quantitative changes in field kinetics as compared with column kinetics.

The application of this approach allows a more rigorously based determination of 'scale up factors' than has been the case the date.

Significant geotechnical parameters such as bulk density/ stress characteristic, limit moisture Capacity and particle density are used to determine the effect of changes on the diffusion controlled leach rate. By consideration of the geotechnical reaction of the ore, mass the leach rate changes are related to changes in these variables.

4.2. The connection between comminution and leaching behaviour

While minerals response to breakage is influenced by their mineralogical properties, comminution in turn affects mineral and elemental distribution within particle size ranges. Mineralogical differences within varying particle sizes therefore affect their responses and behaviour in different conventional and bioleaching media. Owing to the differences in the mineralogical compositions at different particle sizes, there exist some variations in microbial–mineral interaction. This might result from the differences in the electrochemical galvanic interactions, as galvanic interactions depend on the mineralogical association between the phases present (Cruz, et al., 2005, Mehta and Murr, 1983, Liu et al., 2008, Urbano, A.M. Meléndez et al., 2007, Berry et al., 1978).

4.2.1. Concept of exposure and liberation

Since most minerals have some unknown grain size distribution, texture, exposure, and spatial distribution within the ore particles, they must be initially "unlocked" or "liberated" before separation can be undertaken. The procedure is to crush the ore so that the valuable mineral grains are exposed and can be extracted during the heap leaching process (Miller et al., 2003). The concept of exposure and liberation of a particular mineral in an ore feed may be graphically expressed as shown in Figure 10. In a typical mineral dressing process, the ore feed must be reduced by fracture into particles with sizes smaller than the valuable mineral grains. These liberated mineral grains can then be separated from each other and concentrated based on their distinct physical and chemical properties. Considering hydrometallurgical extraction of metallic values, the mineral grains need not necessarily be liberated as free grains; since partial exposure of mineral grains may provide sufficient surface front for chemical attack by leaching solution (Hsieh et al., 1995).

As mentioned above, crack distribution plays a key role in partial exposure of mineral grains. This relates leaching behavior to the method by which the ore has been crushed prior to leaching. The first processing step of a mineral processing plant is usually the crushing of the raw material. Rocks with large diameters excavated in the mining operation and are then reduced in size by crushers suitable for subsequent process steps. The design of a crushing plant is based on the material to be crushed. Several types of crushers using different physical effects of comminution (e.g. compression, impact) can be chosen. Especially crushers in the first and second stage (jaw, gyratory and roll crushers) use the effect of comminution by compression of single particles within the processing zone of the machine (Unlanda and Szczelina, 2004).

High-pressure grinding rolls (HPGR) technology has been available for over 20 years. In this time, it has become a standard comminution device for cement clinker grinding. The HPGR is between 20 and 50 percent more efficient than conventional crushers and mills (Daniel, 2007). The comminution principle (compression as a breakage mechanism) involved is different from that in conventional crushers or tumbling mills (impact as breakage mechanism). As a result, the product from a HPGR is different, and may be expected to have a different behaviour in downstream processes (Aydoğan et al., 2006). The HPGR breaks particles predominantly in an autogenous way, unlike other comminution devices. The grinding force is transferred from one particle to the next, with a small proportion of the particles coming into direct contact with the rolls (Michael John Daniel, 2007). Figures 11a, b) show the fracturing that occurs because of the application of high pressure. Cracks often occur at the grain boundaries resulting in liberation of the minerals, and giving leach solutions better access to the particles. Figure 12) compares the extraction from the leaching of a semi-refractory gold ore from South Africa crushed by HPGR and a cone (impact) crusher. This confirms that the leachability of the ores was better after high pressure grinding, particularly for coarser size fractions. Perceived fracture mechanisms taking place in HPGR inter-particle comminution.

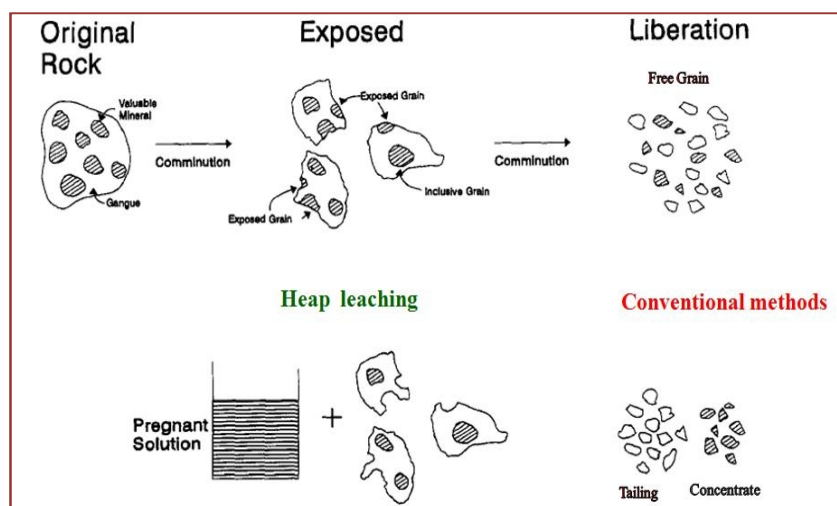


Figure 10: The concept of exposure and liberation of mineral by hydrometallurgy and that by physical separation process (Source: Hsieh et al., 1995).

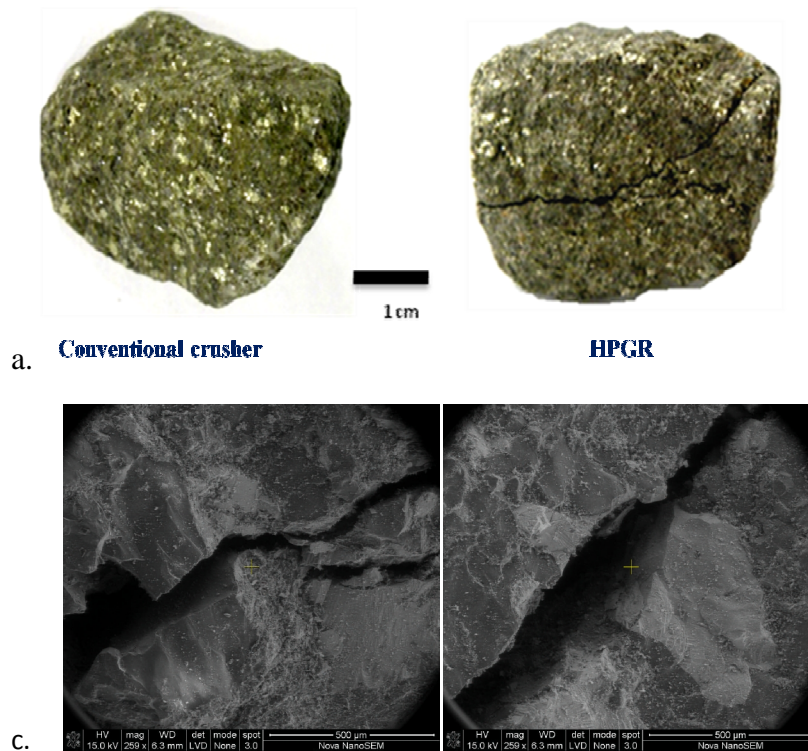


Figure 11: HPGR product properties, a. Crushed Particle, b. inter-granular cracks of two zinc ore particles (Source:Yousef et al., 2010).

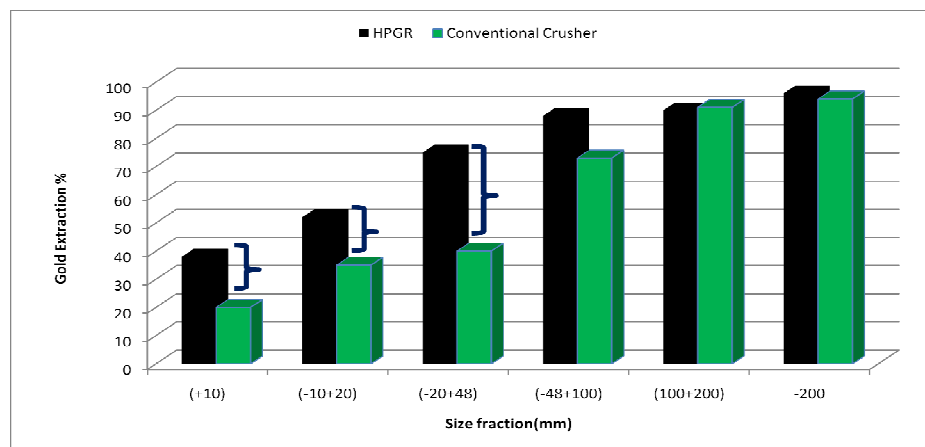


Figure 12: Leachability of gold ore from South Africa (Source: Daniel, 2007).

4.3. Visualization techniques for ore characterisation

In recent years, automated mineralogy has become established as an essential enabling technology for the reliable acquisition of statistically sound comprehensive mineralogical and metallurgical data. This has had a revolutionary effect on the industrial use of such data in the study of geology, mining and mineral processing. Previously, using manual methods, it was not feasible to attempt this work because the large data sets required could not be assembled on a realistic timescale. There was a reliance on individual expert mineralogists and this

was not scalable. The speed, reliability, details and repeatability of the modern automated measurements have now made this type of analysis routine (Gottlieb, 2008). Usually such studies are conducted in order to evaluate and improve process efficiency. This quantitative data is usually derived from mineralogical classified images of the ores or plant products in question. The ability of image-based techniques to quantify liberation and association parameters of ore minerals makes them highly preferable to assay-type approaches. A large range of techniques is available for the acquisition of image data, and the ability of each of these systems to discriminate between mineral species varies widely. The ability for mineralogical discrimination is largely dependent on the cost and complexity of the system, the time available for analysis, and the spatial resolution of the output, 2-D and 3-D images. Simple image analysis of Red-Green-Blue (RGB) colour images, and even more complex systems such as hyperspectral imaging spectrometry, can acquire images rapidly but often have limited mineral identification ability. On the other hand, substantially more complex and slower systems based on elemental analysis using X-ray detection, electron microprobe analysis (EMPA), and energy dispersive spectrometer equipped scanning electron microscopes (EDS-SEM), can achieve extremely accurate discrimination between mineral species. The EDS-SEM systems, such as the QEMSCAN and the Mineral liberation analysis (MLA), have made huge advances in speed and accuracy in the last 20 years, and have become the dominant mineralogical imaging system used in the mining industry today (Pownceby et al., 2007, Benvie, 2007). The demand for accurate composition and phase distribution analyses in complex ore assemblages is increasing rapidly as mineral processing studies become more sophisticated. Significant grain boundary fracture will enhance the exposure/liberation of minerals during comminution. However, there is no convincing experimental evidence to describe the extent to which this actually occurs in practice or to indicate what processes can be employed to enhance intergranular fracture (Benvie, 2007). However, an improved understanding of the leaching from large particle systems can be achieved with the use of an advanced diagnostic and nondestructive technique, namely high resolution 3-D X-ray Computed Tomography (Miller et al., 2003, Yang et al., 2008, Solymar, and Fabricius, 1999, Lin and Miller, 2005, Garcia, Lin and Miller, 2009). To illustrate the potential of X-ray Tomography for exposure/liberation analysis in a heap leach context, an example is given in Figure 13 (Miller et al., 2003).

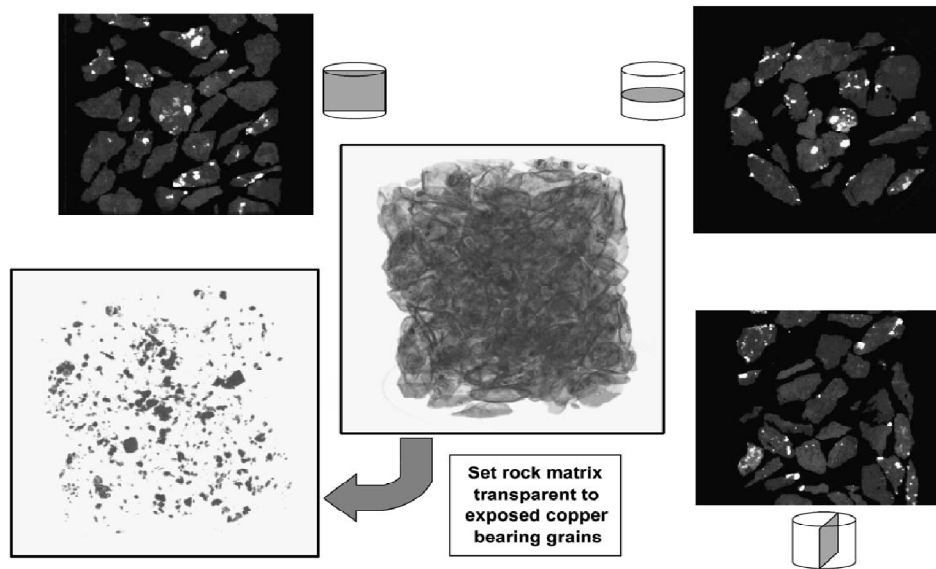


Figure 14: 3D semi-transparent image of a packed bed of copper ore particles (1.68 -1.19 mm). Dark gray represents the copper-bearing mineral grains and light gray represent the host rock. Three sectioned 2D images along the cutting planes of x-, y-, and z-axes are included to reveal textual details (Source: Miller et al., 2003).

5. Particle models within heap leach modeling

Considerable interest in hydrometallurgical metal extraction processes has led in recent years to the development of a number of mathematical models for these processes, including both heap leaching and acid rock drainage (Malmström et al., 2008, Sracek et al., 2006a,b, Strömberg and Banwart, 1999, Evans and Banwart, 2006, Lefebvre, Hockley, Smolensky and Gélinas, 2001, Lefebvre et al., 2001, Bouffard and Dixon, 2001). A critical assessment of the significant, public-domain, heap leach models has been undertaken by Dixon (2003). Although a number of experimental studies have been carried out which have allowed better understanding of the phenomenon and its operation, few studies have been carried out with the objective of optimizing the process, either experimentally or through the use of models (Petersen, and Dixon, 2007, Bartlett, 1992b, Mason et al., 1997, Leahy et al., 2007).

In general, heap leaching is simulated in columns charged with ore that are irrigated from the top and aerated from the bottom and then scale-up modeling is conducted based on these tests. Several column tests and some small pilot heap tests are required prior to design and construction of full-scale heaps. However, even comprehensive column test programs do not guarantee accurate prediction of full-scale heap behavior if not done with a comprehensive model (Lizama et al., 2005).

Most of the early heap bioleaching models dealt with leaching at the particle scale (Bartlett, 1992, Davis and Ritchie, 1986, Davis et al., 1986, Davis and Ritchie, 1987, White and Caenepeel, 1979, Braun et al., 1974, Roman and Olsen, 1974). More recent bioleaching models emphasize the effects of bulk scale phenomena, such as liquid flow, gas flow, and temperature distribution, on heap performance (Dixon and Petersen, 2003, Ogbonna et al., 2006, Leahy et al., 2007, Dixon, 2000, Leahy et al., 2005, Moreno et al., 1999, Pantelis et al., 2002,

Sidborn et al., 2003, Petersen and Dixon, 2002). Although both particle scale and bulk scale effects are important in heap bioleaching, little has been done to systematically integrate particle scale models into bulk scale models. Most existing bulk scale models account for the effect of particle topology using simplified models such as the shrinking core model, applied to an average particle size. Implicit in this is an assumption regarding the relative significance of particle scale phenomena, and which process (diffusion or reaction kinetics) is limiting at the particle scale. A conventional shrinking core approach would work only for gangue particles that are homogeneously porous and have mineral grains well distributed throughout (Liddell, 2005, Velardo, et al., 2002, Vegliò et al., 2001). The shrinking core model has been shown to be a poor predictor of leach kinetics based on the crushed ore size distribution. However, the model itself is a very useful tool to analyse commercial heap data (Graeme, 2003). Shrinking core models have proved to be extremely useful in describing the leaching behavior of many ores and flotation concentrates. although they tend to be used as empirical tools rather than in any predictive way: data is obtained from batch leaching which is fitted them according to the different shrinking-core equations, and then the one that gives the best fit is chosen as best representative of the system, There are no reliable criteria to predict a priori the rate-controlling regime in which a given system will operate. Clearly, obtaining these criteria will require a greater understanding of the controlling processes on a microscopic level (Liddell, 2005, Velardo et al., 2002, Vegliò et al., 2001).

Part of this difficulty in understanding leaching reactions lies in their heterogeneous nature and the variability from one ore or concentrate to another. However, another part stems from the fact that the conventional shrinking-core equations have been narrowly focused on the dissolved reactant and the particles being leached (Liddell, 2005). Models usually assume spherical geometry of the particles, although ore or concentrate particles are never spherically symmetric. Deviation from the spherical shape leads to an increase in the surface-to-volume ratio (Rossi, 1990). Furthermore, particle scale effects in heap bioleaching are influenced by other factors, including the particle size distribution, the ore mineralogy, surface properties, pore size distribution and microbial interactions.

Hence, the overall rate at which a mineral is dissolved from an ore particle is quite often the manifestation of a complex network of individual phenomena, each proceeding at its own intrinsic rate. For finely ground particles such as those encountered in tank leaching processes, leaching rates are typically controlled by the intrinsic kinetics of mineral breakdown. In a heap or dump leaching, however, mineral grains are usually embedded within larger ore particles or solution-filled agglomerates, and thus accessible only by diffusion through a network of pellet pores, if at all. In general, the intrinsic kinetics of leaching is usually be represented by an equation for the rate of mineral conversion of the general form:

$$\frac{dX}{dt} = k(T, d_0) f(C) w(1 - X)$$

where $k(T, d_0)$ is a rate constant which is a function of temperature (usually Arrhenius's law) and initial mineral grain size (or surface area), $f(C)$ is a function of the solution composition represented symbolically as C (e.g.

ferric ion, ferrous ion, proton concentrations) and $w(1-X)$ is a function of the fraction of mineral unreacted, which represents the changing topology of the mineral surface over the course of leaching. While the thermal and chemical functions are readily evaluated experimentally with small, fully liberated, mineral grains, the topological function must be evaluated with the ore particle themselves containing liberated and occluded grains of divers shape and sizes. Here the usual assumption of homogeneous distribution of monosize grains is invalid and the chemical and diffusion-controlled modeling approaches may fall short with these types of ore samples.

A generalized topological function initially proposed by (Dixon and Hendrix, 1993) is written as:

$$w(1-X) = (1-X)^{\phi}$$

Where the exponent ϕ may vary over the course of the leach, taking values greater than or equal to 2/3 (the shrinking sphere model) and may be as high as three when the distribution of effective grain size is particularly wide (Dixon and Hendrix, 1993). The parameter ϕ can in principle, be evaluated for each particle size and a collection of particle sizes can instead be modeled as a single-size class with a weighted average, although this approach remains entirely empirical (Bouffard and Dixon, 2001).

6. Summary and outlook

In order to effectively understand and formulate models for (bio) leaching from large particles, fundamental study of the rate controlling factor(s) is important. Comprehensive understanding would be achieved by the systematic investigation of leaching behavior at the surface and the interior of large particles in the context of chemical leaching and bioleaching of ores. In more specific terms, it is need to investigate leaching behavior of ore with the following objectives:

- To determine the effect of topology (surface properties) on the kinetics of (bio) leaching processes;
- To investigate intra-particle diffusion phenomena and their relationship with the pore and crack network, particle size distribution and mineralogy;
- To formulate appropriate modeling approaches to large particle leaching, this would allow optimization of heap leach operations in the trade-off between rates of extraction and degree and mode of comminution.

In order to understand more clearly the reagent diffusion through the large particles and to provide true and reliable physical parameters to formulate the relevant modeling approaches to large particle leaching, it is necessary to study the 3-D property of diffusion first. However, the use of traditional experimental methods cannot realize this as they are usually destructive and required physical serial sectioning, which is a reliance on individual expert mineralogists and this is not easily scalable. An improved understanding of the leaching from large particle systems can be achieved with high resolution 3-D X-ray Computed Tomography (CT) as it is non-destructive and processes could be followed directly during the treatment. Although some researchers have been done in this regard, but since this technique is new in mineral processing, further methodological work should

focus on adaptation and improving of this technique in the field of mineral processing, to see how X-ray Computed Tomography (CT) can help to comprehensive characterization of ore samples mostly coarse particles and also understanding of underlying processes.

Observation from using this technique can be coupled with the results from the other modern automated mineralogy measurements, more traditional column leach experiments, and solution chemistry considerations in order to identify the progression of heap leaching. With such insight, it would be possible to describe leaching from within large particles with a more accurate model, and then use this tool in the economic optimization of heap leaching operations.

7. References

- Acevedo, F., Present and future of bioleaching in developing countries. *Electronic Journal of Biotechnology*, 2002, 52-56.
- Adelson, D. D., Pablo, S. P. and Versiane, A. L., Bioleaching and chemical leaching as an integrated process in the zinc industry. *Minerals engineering*, 2007, 20 (6), 591-601.
- Aghamirian, M.M. and Yen, W.T., Mechanisms of galvanic interactions between gold and sulfide minerals in cyanide solution. *Minerals engineering*, 2005, 18 (4), 393-412.
- Ahonen, L., Tuovinen, O. H., Bacterial leaching of complex sulfide ore samples in bench-scale column reactors. *Hydrometallurgy*, 1995, 37 (1), 22-36.
- Aydoğan, N. A., Ergün, L. and Benzer, H., High pressure grinding rolls (HPGR) applications in the cement industry . *Minerals Engineering*, 2006, 19(2), 130-142.
- Bachu, S. and Cuthiell, D., Effects of core-scale heterogeneity on steady state and transient fluid flow in porous media: numerical analysis. *International journal of rock mechanics and mining sciences geomechanics abstracts*, 1990, 27 (6), 341-352.
- Baláz, P., Kušnierová, M., Varencova, V.I. and Mišura, B., Mineral properties and bacterial leaching of intensively ground sphalerite and sphalerite- pyrite mixture. *International journal of mineral processing*, 1994, 40 (3-4), 273-291.
- Bartlett, R. W., Simulation of ore heap leaching using deterministic models. *Hydrometallurgy*, 1992, 29 (1-3), 231-243.
- Benzie, B., Mineralogical imaging of kimberlites using SEM-based techniques. *Minerals Engineering*, 2007, 20(5), 435-441.
- Berry, V.K., Murr, L.E. and Hiskey, J.B., Galvanic interaction between chalcopyrite and pyrite during bacterial leaching of low-grade waste. *Hydrometallurgy*, 1978, 3(4), 309-319.
- Bouffard, S. C. and Dixon, D. G., Investigative study into the hydrodynamics of heap leaching processes. *Metallurgical and Materials Transactions B.*, 2001, 32(5), 763-776.
- Bouffard, S.C., Understanding the Heap Biooxidation of Sulfidic Refractory Gold Ores. PhD dissertation University of British Columbia, 2003.
- Braun, R. L., Lewis, A. E. and Wadsworth, M. E., In-place leaching of primary sulfide ores: Laboratory leaching data and kinetics model. *Metallurgical and Materials Transactions B.*, 1974, 5(8), 1717-1726.
- Brierley, C. L., Bacterial succession in bioheap leaching. *Hydrometallurgy*, 2001, 59 (2-3), 249-258.
- Brierley, C.L., How will biomining be applied in future? *Transactions of Nonferrous Metals Society of China*, 2008, 18 (6), 1302-1316.
- Cariagaa, E., Conchac, F. and Sepúlveda, M., Flow through porous media with applications to heap leaching of copper ores. *Chemical engineering journal*, 2005, 111 (2-3), 151-164.
- Chandraprabha, M., Modak, J., Natarajan, K., Raichur A., Modeling and analysis of biooxidation of gold bearing pyrite-arsenopyrite concentrates by *Thiobacillus ferrooxidans*. *Biotechnol Prog*, 2003, 19(4), 54-65.
- Cruz, R., Luna-Sánchez, R.M., Lapidus, G.T., González, I. and Monroy, M., An experimental strategy to determine galvanic interactions affecting the reactivity of sulfide mineral concentrates. *Hydrometallurgy*, 2005, 78 (3-4), 198-210.
- Dai, X. and Jeffrey, M.I., The effect of sulfide minerals on the leaching of gold in aerated cyanide solutions. *Hydrometallurgy*. 2006, 82 (3-4), 118-231.
- Davis, G. B. and Ritchie, A. I. M., A model of oxidation in pyritic mine wastes: part 1 equations and approximate solution. *Applied mathematical modeling*, 1986, 10 (5), 314-322.
- Davis, G. B. and Ritchie, A. I. M., A model of oxidation in pyritic mine wastes: part 1 equations and approximate

- solution. *Applied mathematical modeling*, 1987, 11 (6), 417-422.
- Davis, G. B., Doherty, G. and Ritchie, A. I. M., A model of oxidation in pyritic mine wastes: part 2: comparison of numerical and approximate solutions *Applied mathematical modelling*, 1986, 10 (5), 323-332.
- Deschamps, T., Benzaazoua, M., Bussière, B., Aubertin, M. and Belem, T., Microstructural and geochemical evolution of paste tailings in surface disposal conditions. *Minerals engineering*, 2008, 21 (4), 341-364.
- Deveci, H., Effect of particle size and shape of solids on the viability of acidophilic bacteria during mixing in stirred tank reactors. *Hydrometallurgy*, 2004, 71 (3-4), 385-395.
- Dixon, D. G. and Petersen, J., *Hydrometallurgy of Copper*. Montreal, Canada, 2003.
- Dixon, D. G., Analysis of heat conservation during copper sulphide heap leaching. *Hydrometallurgy*, 2000, 58 (1), 27-33.
- Dixon, D. G., Heap biooxidation of refractory gold ore: Current state of the art. *Fifth International Conference in Honor of Professor Ian Ritchie, TMS (The Minerals, Metals & Materials Society)*, 2003, 289 - 314.
- Dixon, D. G., Hendrix, J. L., Theoretical basis for variable order assumption in the kinetics of leaching of discrete grains. *American Institute of Chemical Engineers (AIChE)*, 1993, 39(5), 904 - 907.
- Dixon, D.G. and Hendrix, J.L., A general model for leaching of one or more solid reactants from porous ore particles. *Metallurgical Transactions B*, 24, 1993, (1), 157-169.
- Dreisinger, D., Copper leaching from primary sulfides: Options for biological and chemical extraction of copper. *Hydrometallurgy*, 2006, 83 (1-4), 10-21.
- Drouet, C. and Navrotsky, A., Synthesis, characterization, and thermochemistry of K-Na-H₃O jarosites. *Geochimica et cosmochimica acta*, 2003, 67 (11), 66-74.
- Dwivedy, K.K., Bioleaching- our experience. *Hydrometallurgy*, 1995, 38 (1), 99- 111.
- Evans, K.A. and Banwart, S.A., Rate controls on the chemical weathering of natural polyminerale material. I. Dissolution behaviour of polyminerale assemblages determined using batch and unsaturated column experiments *Applied geochemistry*, 2006, 21 (2), 352-363.
- Garcia, D., Lin, C.L. and Miller, J.D., Quantitative analysis of grain boundary fracture in the breakage of single multiphase particles using X-ray microtomography procedures. *Minerals engineering*, 2009, 22 (3), 236-243.
- Gerke, H. H., Molson, J. W. and Frind, E. O., Modeling the effect of chemical heterogeneity on acidification and solute leaching in overburden mine spoils . *Journal of hydrology*, 1998, 209 (1-4), 166-176.
- Ghorbani, Y., Petersen, J., Morar, S. H., Becker, M., Mainza, A. and Franzidis, J.P., Estimation method of spatial distribution of surface and bulk porosity in large single ore particles by X-ray computed tomography. *Minerals Processing*, Cape Town South Africa. 2010.
- Ghorbani, Y., Petersen, J., Becker, M., Mainza, A. and Franzidis, J.P., Large particle effects in chemical/biochemical heap leach processes. *Minerals Processing*, Cape Town South Africa. 2009.
- Gottlieb, P., The Revolutionary Impact of Automated Mineralogy on Mining and Mineral processing. *The XXIV International Mineral Processing Congress*, 2008, 165-174.
- Graeme, M., Ore geotechnical effects on copper heap leach kinetics. *TMS (The Minerals, Metals and Materials Society)*, 2003, 329-342.
- Harneit, K., Göksel, A., Kock, D., Klock, J.-H., Gehrke, T. and Sand, W., Adhesion to metal sulfide surfaces by cells of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. *Hydrometallurgy*, 2006, 83(1-4), 245-254.
- Helle, S., Kelm, U., Barrientos, A., Rivas, P. and Reghezza, A., Improvement of mineralogical and chemical characterization to predict the acid leaching of geometallurgical units from Mina Sur, Chuquicamata, Chile. *Minerals engineering*, 2005, 18 (13-14), 1334-1353.

- Hsieh, C. S., Wen, S. B. and Kuan, C. C., An exposure model for valuable components in comminuted particles. *International Journal of Mineral Processing*, 1995, 43(3-4), 145-153.
- Kirjavainen, V. and Heiskanen, K., Some factors that affect beneficiation of sulphide nickel-copper ores. *Minerals engineering*, 2007, 20 (7), 629-641.
- Leahy, M. J., Davidson, M. R., Schwarz, M. P., A two-dimensional CFD model for heap bioleaching of chalcocite. *ANZIAM J*, 2005, 46(E), 439-457.
- Leahy, M.J., Davidson, M.R. and Schwarz, M.P., A model for heap bioleaching of chalcocite with heat balance: Mesophiles and moderate thermophiles. *Hydrometallurgy*, 2007, 85 (1), 24-39.
- Lefebvre, R., Hockley, D., Smolensky, J. and Gélinas, P., Multiphase transfer processes in waste rock piles producing acid mine drainage: 1: Conceptual model and system characterization. *Journal of contaminant hydrology*, 2001, 52(1-4), 137-151.
- Lefebvre, R., Hockley, D., Smolensky, J. and Lamontagne, A., Multiphase transfer processes in waste rock piles producing acid mine drainage: 2. Applications of numerical simulation. *Journal of contaminant hydrology*, 2001, 52(1-4), 165-178.
- Liddell, K. C., Shrinking core models in hydrometallurgy: What students are not being told about the pseudo-steady approximation. *Hydrometallurgy*, 2005, 79 (1-2), 62-72.
- Lin, C.L. and Miller, J.D., 3D characterization and analysis of particle shape using X-ray microtomography (XMT). *Powder technology*, 2005, 154 (1):61-73.
- Linus, S, *Copper Hydrometallurgy Processing Technologies*. 2010, Available:<http://www.thebeijingaxis.com>.
- Liu, Q., Li, H. and Zhou, L., Galvanic interactions between metal sulfide minerals in a flowing system: Implications for mines environmental restoration. *Applied geochemistry*, 2008, 23 (8), 2316-2339.
- Lizama, H.M., Harlamovs, J.R., McKay, D.J. and Dai, Z., Heap leaching kinetics are proportional to the irrigation rate divided by heap height. *Minerals engineering*, 2005, 18 (6), 623-638.
- Malik, A., Dastidar, M. G. and Roychoudhury, P. K., Factors limiting bacterial iron oxidation in biodesulphurization system. *International journal of mineral processing*, 2004, 73 (1), 34-42.
- Malmström, M. E., Berglund, S. and Jarsjö, J., Combined effects of spatially variable flow and mineralogy on the attenuation of acid mine drainage in groundwater. *Applied geochemistry*, 2008, 23 (6), 1419-1422.
- Mason, C. F. V., Turney, W. R. J. R., Thomson, B. M., Carbonate leaching of uranium from contaminated soils. *Environmental science and technology*, 1997, 31(10), 2707-2711.
- Mazuelos, A., Palencia, I., Romero, R., Rodríguez, G. and Carranza, F., Ferric iron production in packed bed bioreactors: influence of pH, temperature, particle size, bacterial support material and type of air distributor. *Minerals engineering*, 2001, 14 (5), 507-512.
- Mehta, A.P. and Murr, L.E., Fundamental studies of the contribution of galvanic interaction to acid-bacterial leaching of mixed metal sulfides. *Hydrometallurgy*, 1983, 9 (3), 235-342.
- Mellado, M. E., Cisternas, L. A. and Gálvez, E. D., An analytical model approach to heap leaching. *Hydrometallurgy*, 2009, 95 (1-2), 33-42.
- Michael J. D., *Energy efficient mineral liberation using HPGR technology*. 2007
- Miller, J. D., Lin, C. L., Garcia, C. and Arias, H., Ultimate recovery in heap leaching operations as established from mineral exposure analysis by X-ray microtomography. *International journal of mineral processing*, 2003, 72 (1-4), 331-342.
- Moreno, L., Martinez, J. and Casas, J., Modelling of bioleaching copper sulphide ores in heaps or dumps. *Process Metallurgy*, 1999, (9), 443-453.
- Muñoz, J. F., Rengifo, P. and Vauclin, M., Acid leaching of copper in a saturated porous material: Parameter

- identification and experimental validation of a two-dimensional transport model, *Journal of contaminant hydrology*, 1997, 27 (1-2), 11-23.
- Ogbonna, N., *Mathematical Modeling of Agglomerate Scale Phenomena in Heap Bioleaching*. Master Department of Chemical Engineering, University of Cape Town, South Africa, 2006.
- Ogbonna, N., Petersen, J. and Laurie, H., An agglomerate scale model for the heap bioleaching of chalcocite. *The Journal of The South African Institute of Mining and Metallurgy*, 2006, 106, 433-442.
- Olubambi, P.A., Ndlovu, S., Potgieter, J.H. and Borode, J.O., Effects of ore mineralogy on the microbial leaching of low grade complex sulphide ores. *Hydrometallurgy*, 2007, 86 (1-2), 96-112.
- Olubambi, P.A., Ndlovu, S., Potgieter, J.H. and Borode, J.O., Mineralogical characterization of Ishiagu (Nigeria) complex sulphide ore *International journal of mineral processing*, 2008, 87 (3-4), 83-97.
- Olubambi, P.A., Ndlovu, S., Potgieter, J.H. and Borode, J.O., Role of ore mineralogy in optimizing conditions for bioleaching low-grade complex sulphide ores. *Transactions of Nonferrous Metals Society of China*, 2008, 18 (5), 1234-1242.
- Padilla, G. A., Cisternas, L. A. and Cueto, J. Y., On the optimization of heap leaching. *Minerals engineering*, 2008, 21 (9), 673- 683.
- Pantelis, G., Ritchie, A. I. M. and Stepanyants, Y. A., A conceptual model for the description of oxidation and transport processes in sulphidic waste rock dumps. *Applied mathematical modeling*, 2002, 26 (7), 751-769.
- Park, J. Y. and Levenspiel, O., The crackling core model for the multistep reaction of solid particles. *Chemical engineering science*, 1977, 32 (2), 233-243.
- Pérez-López, R., Miguel Nieto, J. and Ruiz de Almodóvar, G., Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste: Column experiments. *Chemosphere*, 2007, 67 (8), 1637-1645.
- Petersen, J. and Dixon, D.G 2002. Systematic modelling of heap leaching processes for optimisation and design. *Proceedings of the EPD Congress and Fundamentals of Advanced Materials for Energy Conversion*. TMS, 757-771.
- Petersen, J. and Dixon, D.G., Modeling zinc heap bioleaching. *Hydrometallurgy*, 2007, 85 (2-4), 127-136.
- Petersen, J., Modeling of bioleach processes: Connection between science and engineering. *Hydrometallurgy*, 2010.
- Pownceby, M.I., MacRae, C.M. and Wilson, N.C., Mineral characterisation by EPMA mapping . *Minerals Engineering*, 2007, 20(5), 444- 461.
- Pradhan, K.C., Nathsarma, K., Srinivasa, R., Sukla, L.B. and Mishra, B.K., Heap bioleaching of chalcopyrite: A review. *Minerals engineering*, 2008, 21 (5), 355-362.
- Pradhan, N., Nathsarma, K.C., Srinivasa, R.K., Sukla, L.B. and Mishra, B.K., Heap bioleaching of chalcopyrite: A review. *Minerals engineering*, 2008, 21 (5), 355-371.
- Prosser, A.P., and Box, J.C. Simulation of the mineralogical and chemical aspects of heap and dump leaching as an aid to ore-proc. *Australasian Institute of Mining and Metallurgy*: 1983.
- Roman, R.J. and Olsen, C., Theoretical scale-up of heap leaching. *Solution Mining Symposium, AIME*. 1974, 211–229.
- Rossi, G., 1990. *Biohydrometallurgy*. McGraw-Hill, New York.
- Sandström, Å. and Petersson, S., Bioleaching of a complex sulphide ore with moderate thermophilic and extreme thermophilic microorganisms. *Hydrometallurgy*, 1997, 46 (1-2), 181-188.
- Senanayake, G., Review of rate constants for thiosulphate leaching of gold from ores, concentrates and flat surfaces: Effect of host minerals and pH. *Minerals engineering*, 2007, 20 (1), 5-14.
- Senanayake, G., Role of copper(II), carbonate and sulphite in gold leaching and thiosulphate degradation by oxygenated

- alkaline non-ammoniacal solutions. *Minerals engineering*, 2005, 18 (4), 409-421.
- Shafer, J.L., White, M.L. and Caenepeel, C.L., Application of the Shrinking Core Model for Copper Oxide Leaching. In *AIME Transactions AIME*, 1979.
- Shayestehfar, M.R., Karimi Nasab S. and Mohammadalizadeh, H., Mineralogy, petrology, and chemistry studies to evaluate oxide copper ores for heap leaching in Sarcheshmeh copper mine, Kerman, Iran. *Journal of hazardous materials*, 2008, 154, (1-3), 602-621.
- Sidborn, M., Casas, J. Martínez, J. and Moreno, L., Two-dimensional dynamic model of a copper sulphide ore bed. *Hydrometallurgy*, 2003, 71 (1-2), 67-81.
- Solymar, M. and Fabricius, I. L., Image analysis and estimation of porosity and permeability of Arnager Greensand, Upper Cretaceous, Denmark. *Physics and chemistry of the earth*, 1999, 24 (7), 587-599.
- Sracek, O., Gélinas, P., Lefebvre, R. and Nicholson, R. V., Comparison of methods for the estimation of pyrite oxidation rate in a waste rock pile at Mine Doyon site, Quebec, Canada. *Journal of geochemical exploration*, 2006, 91 (1-3), 99-112.
- Strömberg, B. and Banwart, S., Experimental study of acidity-consuming processes in mining waste rock: some influences of mineralogy and particle size. *Applied geochemistry*, 1999, 14 (1), 1-13.
- Strömberg, B. and Banwart, S., Weathering kinetics of waste rock from the Aitik copper mine, Sweden: scale dependent rate factors and pH controls in large column experiments. *Journal of contaminant hydrology*. 1999, 39 (1-2), 59-68.
- Suzuki, I., Microbial leaching of metals from sulfide minerals. *Biotechnology advances*, 2001, 19 (2), 119-129.
- Thiel, R. and Smith, M. E., State of the practice review of heap leach pad design issues. *Geotextiles and geomembranes*, 2004, 22 (6), 555-571.
- Tromans, D. and Meech, J. A., Enhanced dissolution of minerals: Conjoint effects of particle size and microtopography. *Minerals engineering*, 2002, 15 (4), 263-277.
- Tromans, D. and Meech, J. A., Enhanced dissolution of minerals: Microtopography and mechanical activation. *Minerals engineering*, 1999, 12 (6), 609-616.
- Ubaladini, S., Veglió, F., Toro, L. and Abbruzzese, C., Biooxidation of arsenopyrite to improve gold cyanidation: study of some parameters and comparison with grinding. *International journal of mineral processing*, 1997, 52 (1), 65-71.
- Unlanda, G. and Szczelina, P., Coarse crushing of brittle rocks by compression. *International Journal of Mineral Processing*, 2004, 74, 209-223.
- Urbano, G., Meléndez, A.M., Reyes, V.E., Veloz, M.A. and González, I., Galvanic interactions between galena-sphalerite and their reactivity *International journal of mineral processing*, 2007, 82 (3), 148-159.
- Vegliò, F., Trifoni, M., Pagnanelli, F. and Toro, L., Shrinking core model with variable activation energy: a kinetic model of manganiferous ore leaching with sulphuric acid and lactose. *Hydrometallurgy*, 2001, 60 (2), 167-179.
- Velardo, A., Giona, M., Adrover, A., Pagnanelli, F. and Toro, L., Two-layer shrinking-core model: parameter estimation for the reaction order in leaching processes. *Chemical engineering journal*, 2002, 90 (3), 231-240.
- Watling, H.R., The bioleaching of sulphide minerals with emphasis on copper sulphides - A review. *Hydrometallurgy*, 2006, 84 (1-2), 81-102.
- William, H.D. 2010. Producing Copper Nature's Way: Bioleaching. Available: <http://www.copper.org>.
- Yang, B.H., Wu, A.-X., Jiang, H.C. and Chen, X.S., Evolvment of permeability of ore granular media during heap leaching based on image analysis. *Transactions of Nonferrous Metals Society of China*, 2008, 18 (2), 426-433.
- YIN, S., WU, A. and QIU, G., Bioleaching of low-grade copper sulphides. *Transactions of Nonferrous Metals Society of China*, 2008, 18 (3), 707-721.