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# Heap leaching technology – current state, innovations and future directions: A review

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#### Abstract

Heap leaching is a well-established extractive metallurgical technology enabling the economical processing of various kinds of low-grade ores, which could not otherwise be exploited. However, despite much progress since it was first applied in recent times, the process remains limited by low recoveries and long extraction times. It is becoming increasingly clear that the choice of heap leaching as a suitable technology to process a particular mineral resource, which is both environmentally sound and economically viable, very much depends on having a comprehensive understanding of the underlying fundamental mechanisms of the processes and how they interact with the particular mineralogy of the ore body under consideration. This paper provides an introduction to the theoretical background of various heap leach processes, offers a scientific and patent literature overview on technology developments in commercial heap leaching as a processing around the world, identifies factors that drive the selection of heap leaching as a processing

technology, describes challenges to exploiting these innovations, and concludes with a discussion on the future of heap leaching.

<B>Keywords: </B>Heap leaching, agglomeration, hydrometallurgy, mineralogy, copper, gold

# Introduction

Percolation leaching processes can be defined as the selective removal of metal values from a mineral by causing a suitable solvent or leaching agent to seep into and through a mass or pile of material containing the mineral. The principle of using percolation leaching to produce mineral concentrates from mining materials is not new, however. Already in the 16th century the extraction of copper using percolation leaching processes was known to be practiced in the Hartz Mountains area in Germany and at mines near the river Rio Tinto in Spain.

Depending on the characteristics of the deposit and the ore, commercial percolation leaching is generally grouped into the following (John, 2011):

- 1. In-situ Leach (ISL) (Underground);
- 2. Dump Leach (DL) (Run of Mine (uncrushed) ore);
- 3. Heap Leach (HL) (Crushed and/or agglomerated ore);
- 4. Vat Leach (VL) (crushed ore or concentrates); and
- 5. Agglomerated Fines Heap Leach (AFHL) (crushed ore or concentrates).

The types of percolation leaching with a summary of typical criteria are given in Table 1.

In this paper the focus is entirely on heap leaching and all associated technology. Heap leaching began to be used from the middle of the 20<sup>th</sup> century when the former Bureau of Mines of the United States developed heap leaching technology to recover precious metals from low-grade heaps of ore using cyanide solutions, adsorption onto activated carbon and recovery by electrowinning (Scheffel, 2002). Thus, gold and silver heap leaching began with the first Cortez heap leach in 1969 in Nevada as the "birthplace" of modern gold heap leaching (Kappes, 2002). At the same time, the first modern copper heap leach operation may have been the Bluebird copper oxide mine in 1968 (Bartlett, 1998), followed in the early 1970s by a few other small operations in the Western United States. Heap leaching of uranium, using either acid or alkaline solutions, has been practiced by uranium producers already since the late 1950s. Large-scale heap leaching can be said to have begun in 1980 when three major copper projects were commissioned in Chile, and, at almost the same time, a large number of gold projects were commissioned in the Western United States (Kappes, 2002; Bartlett, 1998).

Ever since, modified technologies have been developed continuously that allowed this technology to be applied to many different types of minerals, climates and operations of any size (Habashi, 2005a; Kappes, 2002; Scheffel, 2002; Prasad <I>et al</I>., 1991), and beyond copper oxide, uranium and gold, it today has a wide range of applications, including copper sulphide ores, gold-bearing pyritic ores, and non-metallic minerals such as saltpeter (Valencia <I>et al</I>., 2008) as well as soil remediation (Scheffel, 2010; Brierley, 2008; Padilla <I>et al</I>., 2008; Wu <I>et al</I>., 2007; Hanson and Samani, 1994). Heap leaching is typically used for

low-grade deposits, but it is also sometimes applied to small higher-grade deposits in remote or politically high-risk locations to minimize capital cost. Heap leaching from low-grade ores has become a major contributor to the total global production of copper, gold, silver, and uranium (Padilla <I>et al</I>., 2008). Heap leaching also has been considered for zinc (Lizama <I>et al</I>., 2012; Petersen and Dixon, 2007) and nickel (Carlsson and Büchel, 2005; Shakir <I>et al</I>., 1992) and more recently for platinum group metals (PGMs) bearing ores and electronic scrap (Mwase et al., 2014; Ilyas <I>et al.</I>, 2013). It has been demonstrated as a viable low-cost approach to treat ore from open-pit mining operations with low-grade and complex run of mine (ROM) ores, agglomerated flotation tailings and also for the treatment of coarse rejects from semi-autogenous grinding (SAG) circuits (Hiskey, 1983).

The currently expanding use of heap leaching is due to the fact that many developing countries have significant mineral reserves, and in those countries mining constitutes one of the main sources of income. Heap leaching is suitable here because of its technical simplicity and low capital cost. This is the case for countries such as Mexico, Peru and Zambia (Vladimir, 2015; van Staden, 2011). Heaps and dumps present a number of advantages and disadvantages compared to conventional processing of sulphide ores (i.e. concentration by crushing, grinding, and flotation, followed by smelting or agitation leaching of the concentrate) (Ghorbani <I>et al</I>., 2011a; Kyle, 2010; Brierley, 2008; Marsden, 2006; Miller, 2003a; Rawlings <I>et al</I>., 2003; Acevedo, 2002; Bartlett, 1998; McClelland, 1988; Dorey <I>et al</I>., 1988; Herkenhoff and Dean, 1987; Hiskey, 1986; McClelland <I>et al</I>., 1983; Potter, 1981; Chamberlin, 1980). These are summarised in Table 2.

While heap leaching enjoys considerable success, challenges remain, both technical and commercial, which hinder the technology from achieving its full potential. Superficially, heap leaching appears to be deceptively simple – this has led to a somewhat careless attitude in the early days of gold heap leaching in the 1970s and 80s, when many projects were launched by small companies with limited technical support and understanding of the process (Schnell, 2013; John, 2011; Scheffel, 2002; Brierley and Brierley, 2001), ultimately resulting in numerous failed projects.

The increase in typical commercial heap height and size has not come about purely as a result of economic efficiency, but is also a function of available surface area (John, 2011; Thiela and Smith, 2004; Brierley and Brierley, 2001). Heap leach facilities have over the years become relatively sophisticated and complex in design and operation, but still numerous metallurgical, geotechnical, and environmental challenges remain (Lupo, 2010).

Heap construction needs to be done such that proper solution percolation and recovery can occur, and therefore proper selection of particle size blend, agglomeration additives, heap stacking and surface preparation, solution drainage, and correct pipe work for irrigation and drainage is essential to ensure an operation's profitability (Chadwick, 2007; Ulrich <I>et al</I>., 2003; Schlitt, 1992). The piled material is invariably heterogeneous and practically no in-situ control can be exerted, except for intermittent pH adjustment of irrigated solution, addition of some nutrients for bioleaching or manipulation of irrigation rates (Pradhan <I>et al</I>., 2008). Compared with agitated tank reactors, heap reactors are more difficult to aerate efficiently and liquor channelling, as well as the undesirable formation of gradients of pH and nutrient levels (in

bioleaching operations), are difficult to manage (Pradhan et al., 2008; Rawlings, 2005), although the authors are not aware of any heap leach operations that are actually nutrient limited. Moreover, the rates of oxygen and carbon dioxide transfer that can be obtained are low, and extended periods of operation are required in order to achieve sufficient conversions in sulphide heaps (Petersen, 2010). Problems with heap percolation may also arise from ore mineralogy, more specifically presence of clay minerals (Harneit, <I>et al</I>., 2006; Schlitt, 2005; Baum, 1999), resulting in increased clogging of heaps over time due to swelling and gradual decrepitation.

Some types of heap leaching are commercially successful (U, Cu and Au) and some remain novel ideas or under-commercialised (Zn, Ni, Mn, Co and primary-sulphide copper). The reason the heap leaching of some commodities has not yet been commercially successful is less because of problems around mobilising them through heap leaching, but more due to the ability to achieve high recovery efficiencies of the metal from low-concentration solutions without destroying the lixiviant. Solvent extraction (SX) reagents, ion-exchange (IX) resins and activated carbon adsorption were the key enablers for successful Cu, U and Au/Ag heap leaching. On the other hand, similarly efficient reagents have not yet been identified for the recovery of Zn, Co, Mn and Ni without significant pH modification to the PLS through neutralisation of the sulphuric acid lixiviant (John, 2011; Galbraith <I>et al</I>, 2003).

Besides the technical feasibility of the heap leaching process in a particular context, other factors such as economic, environmental and the long-term operational plan of the mine that supplies the feed ore, as well as social concerns must be considered as part of a feasibility study. Lusinga (2011), based on work by Marsden (2008), developed a methodology and a spreadsheet model with a view to integrating techno-economic and environmental objectives simultaneously during decision making for process selection. The study, which focussed on the copper industry, showed that such considerations are far from straightforward and highly site specific. Quite frequently copper heap leaching is used in parallel with concentration of higher grade materials by flotation to still extract value from materials which are below the cut-off grade. Similarly, gold mines use agitated leaching for high-grade ores and heap leaching for marginal grade ores that otherwise would be considered waste rock. A common recovery plant is often employed for both operations, which is favourable for overall process economics.

Given experiences of the past and the long learning curve in successful heap operation, as well as the related developments and challenges that went with it, it is increasingly apparent that 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 towards the development of this understanding on many different fronts. This scientific and patent overview touches on various current heap leach technologies and detailed discussion of the underlying leaching chemistry and mechanisms in use with various minerals. This review paper further identifies some key factors driving heap processes, describes challenges in current state and concludes with a discussion about future directions of heap leaching technology.

# The Heap Leaching Process

At its simplest, crushed ore is piled on an impermeable pad, and leaching reagents are introduced by irrigation from the top. The leaching solution varies, depending on the type of ore to be processed, and may consist of a strong acid (typically, sulphuric acid for copper or nickel ores) or a dilute cyanide solution (for gold and silver bearing ores). The desired mineral is extracted and the solution becomes increasingly loaded as it percolates through the pile. Leaching may be facilitated by micro-organisms resident within the ore bed, especially in the presence of sulphide minerals. The PLS is collected by a drainage system at the base of the pile and channelled to the PLS pond. The PLS is then pumped to the processing facility where the value metal is recovered. The barren leach solution (BLS) is pumped to the barren solution pond from where, after solution make-up, it is reapplied to the surface of the heap (Watling, 2006). A typical heap leaching circuit is shown in Figure 1.

## Macro Scale Heap Operation

Typical heap heights are between 4 m and 10 m, though in cases where insulation is important, heaps may be as high as 18 m (Kappes; 2002). Heaps usually have a large surface area, in the order of 0.5 km<sup>2</sup>. The leach pad below the heap is a significant element of a heap leach design. The ideal location for the heap is a nearly flat (1% slope), featureless ground surface to ensure that all solution will flow across the surface towards collection ditches on the base or sides of the heap. Where the slope exceeds 3%, the front edge of the heap (30 to 50 meters) should be graded flat to provide a buttress to prevent heap failure by sliding. However, heaps can be placed in fairly steep-walled valleys (see table 4) with side slopes up to 20% due to the support by the rock (Kappes; 2002; Majdi <I>et al</I>., 2007). The maximum rock size of

the granular ore materials considered for percolation leaching ranges from large ROM cobble and boulder rock fragments to fine crushed sand and gravel particles. In heap leaching, the top sizes usually range from 10 to 40 mm. Generally, a P<SUB>80</SUB> of less than 6 mm is unacceptable because the bed permeability becomes poor (Brierley and Brierley, 2001), although the fines content, regardless of top size, is potentially more critical in this context. The heap is aerated from a network of pipes buried at the base of the heap into which air is pumped, with typical air flow rates being 0.02 to 0.08 m<sup>3</sup> t<sup>-1</sup> h<sup>-1</sup> (du Plessis <I>et al</I>. 2007). The leach solution is distributed across the top of the heap by either sprinklers or drip emitters and then flows downwards through the heap under gravity. Typical solution volumetric fluxes range between 4 and 20 L m<sup>-2</sup> h<sup>-1</sup> (Rossana and Brantes, 2010; Readett <I>et al</I>., 2006; Helle <I>et al</I>., 2005; Rawlings, 2005; Kappes, 2002). Metal extraction rates in secondary copper sulphides heap leaching typically show an initially fast leaching rate, reaching up to 50-60 percent extraction over the first few months (relating to conversion of chalcocite to covellite), followed by a slower constant rate period reaching up to 80-90 percent copper extraction over the following 12-24 months (Dixon and Petersen, 2003). For oxide copper minerals, whether alone or in mixed sulphide/oxide ores, more than 90 percent extractions can be achieved in as little as 30 days.

## Bulk solution (and gas) flow

Once the irrigation process has started, the solution percolates down through the entire heap until it reaches the impermeable geo-membrane layer at the base of the leach pad. As discussed above, the pad is usually built on a slight slope towards a series of solution drains - this causes the solution to flow towards these drains once it has reached the drainage layer(Thiela and Smith, 2004). Thorough percolation of lixiviants through the heap improves dissolution of metals. The percolation rate of the liquid should be slow enough to provide sufficiently long-lived contact of the lixiviant with the ore particles to affect dissolution, and also needs to be fast enough to supply reagent at the required reaction rate. Therefore, achieving a uniform permeability is required for optimal flow of leach fluids throughout the heap bed (Ilankoon and Neethling, 2012; Readett <I>et al</I>., 2006).

In descriptions of heap hydrodynamics, the solution in a bed may be simplified by dividing it into two phases, stagnant (immobile) and flowing liquid (Figure 2). Stagnant liquid is found in crevices between and in the pores of the ore particles in the ore bed, even if not under irrigation. This trapped solution would progressively push air out of the smaller voids to form stagnant acid pockets by saturating the pores (Bouffard and Dixon, 2001). Although Dixon and Hendrix (1993), in modelling heap processes, assumed that the trapped liquid is only in the pores of particles, Sánchez-Chacón and Lapidus (1997) also accounted for a stagnant liquid film over the particles surface. The dissolution reactions all occur in the stagnant liquid whence the various species diffuse to the flowing liquid (Sheikhzadeh <I>et al</I>. 2005). The stagnant solution hold-up in a bed can be affected by physical properties of the solution and the ore, including shape, agglomeration, size and wettability (contact angle) (Bouffard and Dixon 2001; Schlitt, 1992). Typically it accounts for 17 to 32% of the bed void volume or 7 to 13% of total bed volume (assuming a bed porosity of 40%) as measured in copper dumps and columns containing rocks ranging in size from 5 to 152 mm (Bouffard and Dixon, 2001). The flowing liquid phase moves down through the bed under gravity (Sheikhzadeh <I>et al</I>. 2005). This liquid starts to flow when small channels (such as pores) are flooded, after which it drains through the bed as rivulets and films across the ore particles' surfaces. The flowing liquid volume at steady state is primarily influenced by the packing characteristics of the bed as well as the physical properties of the fluid, the liquid flow rate and the gas flow rate (Bouffard and Dixon, 2001). If the liquid flow rate is high enough to cause air-filled voids to become pinched off, the voids will rapidly fill and 'flood'. Flooding can cause substantial increases in the flowing liquid volume and can also impact gas flow patterns, sometimes causing gas mass transfer limitations (Petersen, 2010; Petersen <I>et al</I>, 2010; Bouffard and Dixon, 2001; Bartlett, 1998). Air flow will tend to channel through high permeability zones (which might be less saturated with solution), leaving low permeability (often flooded) regions stagnant and oxygen starved (Lizama, 2001; Bartlett and Prisbrey, 1996).

## Solute diffusion between and within particles

Heap leaching involves physical and chemical transport of precious metals within the heap. The leaching reagents during their journey downwards with the flowing solution first have to diffuse into the ore particles and react with the metal bearing minerals in the ore, and then the resultant metallic complexes have to diffuse back into the solution (Sánchez-Chacón and Lapidus, 1997). The transport of the solute is influenced by the way the solute interacts with the solid-liquid matrices in the porous medium. The rate-limiting mass transfer between stagnant and mobile liquids leads to the physical non-equilibrium of solute. Further, instantaneous and rate-limited chemical interaction of the solute with the particles in the solid matrix also leads to a chemical

non-equilibrium of the solute (Bartlett, 1998). The process of dissolution and diffusion of metal into the leaching solution, and its subsequent collection in the drainage layer can be correlated with the theories of non-ideal flow and solute transport through porous media (Brusseau <I>et al</I>., 1990). The effect of 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 distribution between flowing channels and stagnant (flooded) zones (Dixon and Petersen, 2003).

## Solute-mineral reaction phenomena

The leaching reactions occur when the lixiviant comes into contact with the metal bearing minerals in the ore. The principal mechanisms by which minerals dissolve in typical heap leach operations are (Shayestehfar <I>et al</I>., 2008; Helle <I>et al</I>., 2005):

- pH controlled dissolution in acid (Cu oxides, acid soluble U);
- oxidative dissolution in acid (Cu sulphides, U) or base (U); and
- ligand based dissolution in alkali solution (Au and Ag in cyanide solution)

Detailed reaction chemistry of these and other systems under development (such as for example NH<SUB>3</SUB> leaching of copper oxides) is discussed in Section 3.2, and kinetic aspects in Section 3.3.

Copper oxide minerals dissolve rapidly in acidic sulphate leach solutions. In uranium leaching, acid leaching has the advantage of being more effective with difficult-to-leach ores with complex mineralogy due to the higher solubility of uranyl sulphate complexes. The amount of copper that

is ultimately extracted from a more common mixed (oxide and sulphide) ore heap largely depends on the percentage of the heap exposed to acid-oxidising conditions. In this regard, the principal obstacle to successful leaching is the persistence within the leaching system of low Ehhigh pH microenvironments. Such an environment may exist within an individual mineral grain, an ore fragment, or some large part of the heap cut off from the flowing solution or gas supply. In most copper deposits iron is present in a variety of oxide, hydroxide, sulphate, sulphide and silicate minerals that react readily with the leach solution. Depending on the relative abundance of these minerals, leaching may release a significant quantity of ferric or ferrous ions into the leach solution and cause Eh to go either up or down, as the case may be. Fe species are a key redox catalyst in the dissolution of sulphide minerals, or for the oxidation of U(III) and U(IV) species to the soluble U(VI) form. Sulphide minerals oxidize by means of three general mechanisms: (1) direct application of oxygen, (2) by ferric ions, and (3) the action of microbes, although the latter is effectively also oxidation by ferric ions which are regenerated by microbial action (Crundwell, 2003).

While the specific mechanisms operating at the surface of a dissolving sulphide grain are still debated, various studies have shown that ferric iron dissolves sulphides 100 to 1000 times faster than oxygen under heap leach conditions (ambient or slightly elevated temperatures). In heap leaching, the oxidation of iron by the direct action of oxygen is limited by the low solubility of oxygen in water and the difficulty in replenishing oxygen from the gas phase to the leach solution in the deeper parts of heaps. It is now generally accepted that mineral bioleaching is a combined chemical/microbial process in which ferric-iron and protons form the reactants in the leaching reaction. The key role of the microorganisms is to generate/regenerate these leaching

agents. Moreover, it is well established that microorganisms form an exopolysaccharide (EPS) layer when they attach to the mineral (Sand and Gehrke, 2006). Bioleaching reactions take place most rapidly and efficiently within this EPS layer and therefore the EPS serves as the reaction space (Sand and Gehrke, 2006; Tributsch, 2001).

The oxidation of gold is a prerequisite for its dissolution in alkaline cyanide solution. Although gold is inert to direct oxidation, in the presence of a suitable complexing agent such as cyanide gold is oxidized and dissolved to form the stable [Au(CN<SUB>2</SUB>)<sup>-</sup>] complex ion. Oxygen is reduced and hydrogen peroxide is formed as an intermediate product and becomes the oxidizing agent in two parallel steps (Marsden and House, 2006; de Andrade Lima and Hodouin, 2006). The chemistry of this reaction is discussed further in section 3.2.1

The dissolution of the sulphide minerals tends to be slow unless mediated by microorganisms. The reaction is, however, exothermic and will result in self-heating of the ore. Heat builds up in the heaps due to rapid sulphide-to-sulphur and sulphur-to-sulphate oxidation. The self-heating of sulphides is associated with oxidation reactions under moist conditions. If the heat generated is greater than the heat dissipated, the material temperature will rise. Sulphide self-heating can be beneficial as higher temperatures enhance reaction kinetics, but in extreme cases it can lead to auto-ignition if the heap contains combustible material, as is sometimes observed in heaps of pyritic coal spoils (Petersen and Dixon, 2003; Bhakta 2003; Rosenblum and Spira, 1995). Iron sulphides are the minerals most associated with this self-heating; pyrrhotite oxidation can be very rapid even in the absence of biotic mediation (Rao and Leja, 2004; Rosenblum and Spira, 1995).

Also pyrite oxidation is a strongly exothermic reaction and this lies in the fact that it always oxidises to at least 50% SO<SUB>4</SUB>, whereas most other sulphides only go to S<sup>0</sup>. Oxidation of pyrite according to the Eq. (1) results in a liberation of 265.5 kcal/mol FeS<SUB>2</SUB>.

 $\operatorname{FeS}_2 + 3O_2 \rightarrow \operatorname{FeSO}_4 + SO_2 \qquad \text{Eq. (1)}$ 

It has been noted that some sulphides in galvanic contact with pyrite can oxidize at a much faster rate due to separation of the anodic dissolution of the sulphide mineral and cathodic reduction reactions on the pyrite surface (Wang et al., 2009; Rao and Leja, 2004; Rosenblum and Spira, 1995). The rate of heating is directly related to the rate of oxidation by releasing heat of reaction of the reduction of oxygen in particular (Petersen and Dixon, 2003). Aqueous complexation and secondary mineral precipitation/dissolution can affect the heat generation.

# Solution treatment

#### Value recovery

#### SX-EW

Heap leaching became an attractive technology only with the arrival of robust and economical recovery techniques. For copper, it was solvent extraction and electrowinning (SX-EW) which provided the necessary motivation for copper heap leaching practice. The highly selective LIX® reagents (hydroxyoximes – chelating agents) allow Cu to be extracted from the relatively low-

tenor heap leach solutions over a wide pH range without any requirement to neutralize the generated acid during extraction. This in fact presented a 'magic bullet' for Cu heap leaching (John, 2011). Also, the practice of plating on stainless steel to yield A- and premium-grade cathodes, have contributed significantly to copper SX-EW becoming a widely accepted technology (Ulrich et al., 2003). The ease of operation and the production of top quality electrolytic metals close to the mine site (rather than production of an impure copper cement requiring further thermal refining), make the economics of the SX processes attractive. It is suitable and feasible in the range of small to medium scale operations, where on-site smelting would not be economically feasible. Refined copper produced by means of SX-EW accounts for over 20 pecent of the world production (John, 2011; Reddy et al., 2005; Grosse et al., 2003; Aylmore and Muir, 2001; Kedem and Bromberg, 1993). SX was also used in the HydroZinc<sup>TM</sup> process, a demonstration Zn heap leach process, but the Zn leach liquor first needed to be neutralised to remove Fe before SX, as no sufficiently selective extractant was available (Harlamovs, 2001; see section 5.5 c).

## Adsorption and IX processes

In the 1970's the adsorption process for the recovery of gold using activated carbon was commercialised (Srithammavut, 2008). The use of resin adsorbents for the recovery of gold from leach liquors is a relatively underdeveloped area of hydrometallurgy because of the abundance of cheap activated carbon adsorbents. Resin adsorbents are more expensive than carbon, and their application requires the installation of specialized apparatus (Grosse <I>et al</I>., 2003; Aylmore and Muir, 2001; Bolinski and Shirley, 1996).

Even though thiosulphate is considered to be one of the most promising alternatives to cyanide, it is difficult to recover the gold thiosulphate complex (Aylmore and Muir, 2001). The same processes that are used for cyanide leach liquors have also been applied to recover gold from ammoniacal thiosulphate leach liquors with varying degrees of success. Aurothisosulphate Au(S<SUB>2</SUB>O<SUB>3</SUB>)<SUB>2</SUB>C=SUB>3</SUB>)<SUB>2</SUB>C=SUB>3</SUB>)<CONDENTION (Aylmore and Muir, 2001). Carbon adsorption is not therefore as convenient for thiosulphate leaching as it is for cyanidation.

IX and SX are used for concentration and recovery of uranium from pregnant leach liquors. IX circuits can be used independently, or as a first step to extract uranium, after which further concentration occurs in an SX circuit. IX is ideally suited to treat leach liquors with lower uranium concentrations and that is why uranium heap leaching is a feasible route. The use of ion-exchange recovery in the copper industry is not widespread. This is due to the fact that LIX reagents (hydroxyoximes- chelating agents) used in copper SX processes are more efficient, selective and economical to use.

#### Cementation

Historically, copper was recovered from leach solutions through cementation (precipitation from solution by the replacement of copper in solution by metallic iron). This has been a source of relatively inexpensive copper; however, the cement copper produced is relatively impure compared to electrowon copper and must be smelted and refined along with flotation concentrates. Typically, cemented copper contains between 65 and 85 percent copper, with

oxides of iron and other traces of silica and aluminium oxides. In addition, it consumes the acid, opposed to SX which preserves the acid in the process overall. The copper cementation process is being phased out (except as a subsidiary method of copper production) (Srithammavut, 2008; Grosse <I>et al</I>., 2003).

The Merrill-Crowe process, which is a form of cementation, is a recovery technique where gold can be recovered from pregnant leach liquor by adding a pulverized metal. The common precipitants are zinc and copper, although iron or aluminium is also sometimes used. Both Zn and Cu complex with CN and can't be recycled and therefore this route presents a disposal problem. The particles with cemented gold are removed from the solution using a plate and frame filter press. Just as Cu SX-EW replaced cementation of copper on iron, activated carbon adsorption replaced Merril Crowe precipitation of gold and silver on zinc dust.

#### Lixiviant regeneration

The acidic raffinate solution that leaves the SX stage is recycled back to the heap via the raffinate (barren) pond. In copper leaching, an acidic make-up stream is combined with the raffinate in order to get the feed solution to specification; this may contain microorganisms and nutrients (Pradhan et al., 2008; Rawlings, 2005), although the authors are not aware of operations that actively do so. Ore leaching is not a selective process, and the resulting PLS may often include different species besides the desired metal, especially of dissolving gangue species which are not recovered in the SX stage. Increased element concentrations result in increased density and viscosity of the process water and the formation of secondary insoluble reaction products that may migrate through the bed and block solution channels, coat mineral surfaces or cause

crud in the SX stage (Watling, 2006). Raffinate bleed may be taken from the main raffinate flow in order to control levels of dissolved salts (Mg and Al sulphates) via evaporation ponds. In the process described by Kunz (2001), the bleed stream is pre-neutralized and fed to a secondary solvent extraction stage, where the rest of the raffinate copper is removed before pumping the purified bleed to effluent treatment in an evaporation pond.

In copper recovery, the SX process generates a clean and highly concentrated advance electrolyte; however, it is inevitable for some contaminants, like Fe<sup>2+</sup>, Fe<sup>3+</sup> and Cl<sup>- </sup>ions, to be carried over into the EW tank house, causing current efficiency loss or poor deposit quality. To maintain an acceptable level of impurities, a determined volume of rich electrolyte is bled and replaced with process water. This purge or bleed stream is commonly sent to the raffinate pond, which is finally used for heap leaching. As the bleed stream has a significant copper content – usually above 35 grams per litre - the impact of its discharge to raffinate compromises overall recovery by an unwanted recirculating copper load (Guzman, 2008; Sánchez-Chacón and Lapidus, 1997). Badilla and Haussmann (2013) introduced the emew® technology for copper recovery from electrowinning bleed before sending it to the raffinate. Results of the column tests – with raffinate fed with both emew®-treated and untreated bleed – showed a difference of 8.9% of copper recovery in favour of the emew® treated stream.

## Heap location

The greatest tonnage of heap-leached copper comes from the dry parts of the world such as inland Australia, south western United States, north western Mexico, Chile and Peru in South

America, and Myanmar's dry central region. A common problem faced by most operators is supply of sufficient water to make up for the evaporation and process losses that occur in heap leaching. Essentially, all of the water either ends up evaporating or tied up in spent heaps. Water usage varies with the climatic conditions and the leach time required for economic extraction of the copper. The shorter the leach time the less solution irrigation is required and the lower the evaporative water loss per tonne of ore leached. Alternative irrigation systems such as drippers minimise losses by evaporation, but these also have some limits in terms of the leach rate that can be achieved (Rossana and Brantes, 2010; Miller, 2003b). Low temperature can be a problem in gold heap leaching. Many Nevada gold heap leach operations report a significant recovery decrease in winter, which is offset the following summer (Mellado <I>et al</I>, 2011). Talvivaara's heap bio-leaching operation, which could remain operation in ambient conditions as low as -20°C, is, on the other hand, an example of the beneficial authothermal oxidation of large quantities of pyrrhotite and pyrite in the ore (Saari and Riekkola-Vanhanen, 2011).

High ambient temperature at a heap location is not a direct problem and no heap operations have reported problems with operating at elevated temperatures. In very hot desert areas where drip irrigation is used, the heat of the day will significantly heat the solution. Radiation heating and cooling of the heap surface plays a role in area of high insolation, especially in high altitude deserts such as in Northern Chile (Dixon, 2000). In dry climates, evaporative losses are high, but heap leaching is less problematic in warm and humid climates. As the prevalence of rainfall increases, the water balance becomes much more important to overall heap performance and solution management, as is the case for heaps operated in tropical climates.

Several gold heaps are located in the high Andes of South America (Comco at Potosi, Bolivia; Yanacocha and Pierina, Peru; Refugio, Chile) at altitudes above 4000 meters. Although oxygen availability at these altitudes is only 60% of that at sea level, gold heap leaching proceeds at rates similar to that at sea level (oxygen is required for the process, but is not usually rate-limiting in a gold heap leach operation)(Mellado <I>et al</I>., 2011; Rossana and Brantes, 2010). Copper sulphide leaching, on the other hand, is likely to be severely hampered at high altitude (Petersen, 2010).

# Potential environmental impacts of heap leaching

Although one of the reasons for introducing heap leaching technology has been a perceived reduced environmental impact compared to other operations, especially pyrometallurgical processes, little effort has been made to assess and improve the environmental effects of this leaching system (Mellado <I>et al</I>., 2011). Environmental concerns associated with heap leach facilities revolve primarily around failure to contain process solutions within the heap leach circuit. Their potential release into the receiving surface and subsurface environment would impact on the health of people, livestock and ecosystems (van Zyl and Bronson, 1994). Heap leaching is arguably the mode of extractive metallurgy where companies should have the strongest economic imperative to impose the most stringent of environmental controls, particularly in the context of preventing solution losses from the process water circuit (Mellado <I>et al</I>., 2011; van Zyl and Bronson, 1994). The ultimate closure of the Talvivaara operation is attributable to a strongly net positive water balance, resulting in the accumulation of low-grade raffinate solution from an excess of melt-water percolating through the heap, the

storage of which ultimately resulted in spill-overs and leaks. Although this is an issue of solution management rather than heap leach technology, the large surface area of heaps does facilitate the ingress of significant quantities of excess precipitation in boreal and tropical climates, which needs to be accounted for.

The heap leach infrastructure is spread over a much larger area than other metallurgical plants, over which it is much harder to achieve effective access control. Allied to this, the process solution is often exposed to the environment in open solution trenches and process ponds rather than being contained in process vessels and pipes with limited access, thus posing a much greater threat to animals. There may also be potential risks to worker health and safety associated with the windblown dispersion of process solution droplets (and dust) from the leach pad, particularly from facilities using spray (as opposed to trickle) irrigation, even though these are likely to be limited in aerial extent. Beyond the immediate confines of the heap leach pad, there exist a potential for process solution release from the leach pad circuit to cause deterioration of water quality in the receiving environment, sometimes to the point of compromising its beneficial use (Rossana and Brantes, 2010; Norton and Crundwell; 2004). A reclamation plan is generally a standard requirement of permitting today. The long-term, post-operational stability of the heaps, pits, and waste dumps must be ensured.

Rock-dumps have often been likened to leaching heaps, and leachate generation from such dumps follows the same principles as heap leaching, but usually without the controls to contain such leachates. It could be argued that in the absence of low cost treatment options such as heap leaching, many low-grade ores would not be economically processed and stored in dumps instead, posing a long-term environmental risk through continuing leachate generation.

# Ores and Leach Chemistry in Heap Leaching

The chemistry involved in heap leaching is of a complex nature, primarily with regard to chemical environment, gangue mineralogy and particle effects in terms of size and fracturing. Hence, it is of some significance to study in some detail the chemistry involved in a particular heap leaching process (Gericke, 2011; Pownceby <I>et al</I>., 2007; Harneit, <I>et al</I>., 2006; Schlitt, 2005; Baum, 1999), rather than referring to it in a generic fashion.

## Ore types

Metal dissolution (by either chemical or by microbial methods) depends on the nature of the mineral ore, i.e. its precise chemical composition, ore type or its origin (Benvie, 2007; Pownceby <I>et al</I>., 2007; Schlitt, 2005; Baum, 1999). Each mineral has a unique level of potential solubility, with the dissolution kinetics being limited by a multitude of reaction products. For example, it has been observed that the oxidation of different metal sulphides proceeds via different intermediates (Watling, 2006; Rawlings <I>et al</I>. 2003; Olson <I>et al</I>. 2003).

The manner in which gold occurs, and its association with the gangue minerals, dictates whether or not the ore can be processed by cyanide heap leaching (Vaughan, 2004). In sulphidic refractory gold ores, fine gold particles may be highly disseminated and locked up in sulphide minerals such as pyrite and arsenopyrite, such that cyanide solution is unable to access the gold

chemically or physically. Iron sulphide minerals, which are common constituents of gold ores, are oxidized to some extent during the cyanide leach, thus resulting in the formation of acid. These acids are neutralized by the lime used in the cyanide leach sequence. Copper minerals may be dissolved by the cyanide leach solution and thus consume large quantities of NaCN and oxygen. Arsenic-bearing minerals may also interfere with cyanidation. Realgar (AsS) and orpiment (As<SUB>2</SUB>S<SUB>3</SUB>) react rapidly with the cyanide solution and inhibit the dissolution of gold. Arsenopyrite (FeAsS), however, generally oxidizes very slowly in an aerated cyanide solution and has very little adverse effect on the leaching of gold. Stibnite (Sb<SUB>2</SUB>S<SUB>3</SUB>) strongly inhibits cyanidation (Vaughan and Kyin, 2004). Carbonaceous ores are difficult to treat because fine-grained carbonaceous material in ores adsorbs gold from pregnant leach solution. A major problem of such ores is to determine how much gold recovery is lost because of preg-robbing and how much is lost because of refractory sulphides (Vaughan and Kyin, 2004). When both, sulphides and carbonaceous matter, are present then the ore is classified as a double refractory ore and it requires pre-treatment before leaching.

Copper ores exist in different forms of oxides, primary and secondary sulphides. The efficiency of leaching depends strongly upon the minerals that make up the ore. For example, whereas tenorite (CuO) and malachite (Cu<SUB>2</SUB>(CO<SUB>3</SUB>)(OH)<SUB>2</SUB>) might require only hours of leaching, even at low temperatures, other copper oxides, such as cuprite (Cu<SUB>2</SUB>O), require oxidation and more leach time, and in the case of chrysocolla (CuSiO<SUB>3</SUB>·2H<SUB>2</SUB>O), due to the hard silicate mineral structure, slower leaching behaviour prevails, requiring strong acid. Chalcocite

(Cu<SUB>2</SUB>S) and covellite (CuS) require months of heap leaching and chalcopyrite would require years of dump leaching.

Some oxide minerals, such as copper in iron compounds and "wad" (neotocite), a manganiferrous copper compound, can have dissolution rates approaching that of secondary minerals. Therefore, these minerals may not reach their ultimate economic extraction if the heap leach design considers only the fast-leaching copper oxide minerals (Baum, 1999).

The processing response of an ore is determined by the nature of its constituent minerals. Maximum recoveries are largely determined by the uranium minerals, while the gangue, by virtue of its higher concentration, typically accounts for the majority of reagent consumption. Uranium most commonly occurs as various oxide minerals that require oxidative leaching for solubilisation. U(IV)<sup> </sup>has a low solubility in both dilute acid and carbonate (alkali) solutions (Lottering <I>et al</I>., 2008). Leaching of uranium-bearing minerals is accomplished by oxidation of the insoluble U(IV) form to the acid soluble U(VI) form in an acid environment (as the complex, [UO<SUB>2</SUB>(SO<SUB>4</SUB>)<SUB>3</SUB>]<sup>4+</sup>). There are minerals described as refractory, such as brannerite, which requires more aggressive leach conditions and is unleachable under the prevailing conditions of a heap (Lottering <I>et al</I>., 2008). Uranium is typically recovered in acid circuits using sulphuric acid, or in alkaline circuits using a sodium carbonate bicarbonate mix. Acid leaching is the preferred method, but alkaline leaching is used when the ore contains a high amount of calcium carbonate (calcite) and magnesium carbonate (dolomite). The selection of acid or alkaline leach is based on a number of key process drivers which have been discussed in detail by Lottering  $\langle I \rangle$  et al $\langle I \rangle$ . (2008).

Ore type and mineralogy effects in the niche applications of heap leaching for commodities such as nickel, caliche mineral, zinc sulphide and PGMs are discussed in the section 5.5.

At the particle scale, leaching is governed by the way in which mineral grains are distributed within a single particle. 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. Sulphide minerals also exhibit a surface rest potential and can therefore corrode by galvanic action (Deschênes <I>et al</I>, 2001, 2000, 1999). The direct microbial interaction with exposed mineral surfaces (contact leaching mechanism) is important in heap bioleaching, as bacterial attachment is a function of available substrate surfaces (Chiume <I>et al</I>, 2012; Africa <I>et al</I>. 2010; Sand and Gehrke, 2006). The presence of metal sulphides (mostly pyrite/pyrrhotite) in the ore tends to promote bacterial activity in heaps. Pyrite typically occurs in all ores treated by heap leaching. Pyrite does not contribute valuable metal, can lead to precipitation of potentially interfering ferri-hydroxides and jarosite, and in aerated heaps scavenge available oxygen. However, its presence in ores also holds some advantages (van Staden, 2007a; Rawlings, 2004; Sand and Gehrke, 2006):

• Iron acts as an important intermediary electron carrier in sulphide oxidation reactions, and pyrite is a key source of such iron.

• The gangue reactions occurring during the heap leaching of whole ores invariably result in a net acid demand in the heap, and the oxidation of the pyrite content of the ore is probably the cheapest source of acid available. • In those cases that rely on elevated heap leach temperatures (namely the heap leaching of refractory sulphide ore and of uranium ore), the oxidation of pyrite provides a very cheap source of heat.

Therefore, in any of the possible heap leach applications it is possible that the addition to the ore of an external pyrite-rich material has to be considered to augment the natural pyrite content, either for the purpose of acid generation, and/or for the purpose of heat generation in the heaps (van Staden, 2007a).

## Reaction chemistry

#### For Au and PGMs

The cyanidation process has proven to be an effective and economical option for successful gold extraction over time. For gold, it works well at ambient conditions, and, depending on the grade of ore, cyanide leaching can be carried out in open vats or open dumps and heaps (Srithammavut, 2008; Grosse et al., 2003). Furthermore, from a variety of reagents investigated as alternatives (sodium bisulphide, thiosulphate, thiocyanate, thiourea, hypochlorite, bromide and iodide solutions) cyanide has proven to be the most effective and the most environmentally acceptable reagent – despite its perceived toxicity. This is due to the fact that cyanide undergoes natural degradation reactions which can render it non-toxic (decomposing to carbon dioxide and nitrogen compounds). These natural reactions have been utilised by the mining industry as the most common means of attenuating cyanide. However, the rate of natural degradation is largely dependent on environmental conditions and may not produce an effluent of desirable quality in

all cases<SUB> </SUB>(Barter, 2001). The chemistry of leaching gold and silver from their ores is essentially the same for both metals. A dilute alkaline solution of sodium cyanide dissolves these metals even at very low concentrations. However, copper, zinc, mercury and iron are the most common soluble impurities that can result in significant losses of cyanide if present in significant quantities in the gold bearing mineral.

A general reaction for gold dissolution is as Eq. (2):

 $4Au + 8 < I > CN </I >^{<I>-</I>} + < I > 0 </I >_{<I>2</I>} + 2 < I > H </I >_{<I>2</I>} 0 \rightarrow$  $4Au(CN)^{<I>-</I>}_{<I>2</I>} + 40H^{-} Eq. (2)$ 

The gold dissolution rate is dependent on the concentration of NaCN and the alkalinity of the solution, which is normally maintained at an alkaline pH of 9.5 to 11. Silver is usually not as reactive with cyanide as gold. This is because gold almost always occurs as the metal, whereas silver may be present in the ore in many different chemical forms some of which are not cyanide-soluble. The silver may be present mixed into the crystal structure as in galena, or be an essential part of the mineral itself as in pyargyrite. A few silver minerals are not sulphides such as silver chloride, known as cerargyrite (horn silver). Silver also occurs mixed with gold as tellurides. Native silver metal does occur in certain places, but unlike gold, it is fairly uncommon.

The level of cyanide in the heap ranges from 100 to 600 ppm NaCN. The free cyanide concentration in the PLS averages 110 ppm, enough to ensure sufficient free cyanide for leaching in the lower parts of the heap, but this is not tightly controlled. Cyanide consumption,

via complexation, volatilization, natural oxidation or oxidation by ore components typically ranges from 0.1 to 1.0 kg per tonne of ore. The chemistry involved in the dissolution of gold in the heap-leach cyanidation treatment is the same as that for the agitation-cyanidation process. In heap leaching, the oxygen essential for the dissolution of gold is introduced into the cyanide solution as it is being sprinkled upon the ore heap. Oxygen and carbon dioxide absorbed from the air may also cause chemical losses of cyanide according to the following reactions (Srithammavut, 2008; Grosse et al., 2003; MacPhail et al., 1998):

Eq. (3)

Eq. (4)

$$2NaCN + O_2 + 4H_2O \rightarrow Na_2CO_3 + (NH_4)_2CO_3$$

$$NaCN + CO_2 + 2H_2O \rightarrow HCN + NaHCO_3$$

The downstream SART process was developed into a technically feasible process by SGS Lakefield Research and Teck Corporation in 1997 (MacPhail <I>et al</I>., 1998), with full-scale commercial application at Newcrest's Telfer Mine in W. Australia (Barter, 2001). This technology has made CN heap leaching of cupriferous Au ores viable, because both the Cu and the CN can be recovered. The process involves releasing the cyanide associated with the copper cyanide complex, allowing it to be recycled back to the leach process as free cyanide, with recovery of the copper as a valuable, high-grade Cu<SUB>2</SUB>S by-product (Estay <I>et al</I>., 2012, 2010).

### For Oxides

Acid leaching is confined to acid-soluble, oxide-type ores that are not associated with acidconsuming rock types containing high concentrations of calcite (such as limestone and dolomite). Some ores require a form of concentration and/or pre-treatment, such as roasting or calcification before leaching, although this approach is not considered for heap leaching. Typical acidic hydrochloric (HCl), leaching agents include acid sulphuric acid (Fe<SUB>2 (H<SUB>2</SUB>SO<SUB>4</SUB>), and iron sulphate </SUB>(SO<SUB>4</SUB>)<SUB>3</SUB>). Citric acid (C<SUB>6</SUB>H<SUB>8</SUB>O<SUB>7</SUB>) has also been studied as an alternative lixiviant for zinc oxide dissolution. Sulphuric acid is the most common lixiviant used for on the extraction of oxidized copper ores.

The oxidised source of copper is well known for their amenability to sulphuric acid leaching. oxide-containing The important minerals azurite most copper are (Cu<SUB>3</SUB>(CO<SUB>3</SUB>)<SUB>2</SUB>(OH)<SUB>2</SUB>), malachite (Cu<SUB>2</SUB>(CO<SUB>3</SUB>)(OH)<SUB>2</SUB>), tenorite (CuO), cuprite (Cu<SUB>2</SUB>O), chrysocolla ((Cu,Al) < SUB > 2 < /SUB > H < SUB > 2 < /SUB > Si < SUB > 2 < /SUB > 0 < SUB > 5 < /SUB > (OH) < SUB > 0 < SUB > 1 < SUB > 0 < SUB >4</SUB>·n(H<SUB>2</SUB>O)) brochantite and (Cu<SUB>4</SUB>(SO<SUB>4</SUB>)(OH)<SUB>6</SUB>). Most of these dissolve easily in dilute sulphuric acid. The reactions are shown below:

$$Cu_3(CO_3)_2(OH)_2 + 3H_2SO_4 \rightarrow 3CuSO_4 + 2CO_2 + 4H_2O$$
Eq. (5)

$$< I > Cu_2(CO_3)_2(OH)_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + CO_2 + 3H_2O$$
Eq. (6)

$$\langle I \rangle CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \langle I \rangle$$
 Eq. (7)

$$< I > Cu_2 O + H_2 SO_4 \rightarrow Cu + Cu SO_4 + H_2 O$$
Eq. (8)

$$< I > CuSiO_3.2H_2O + H_2SO_4 \rightarrow CuSO_4 + SiO_2 + 3H_2O$$
Eq. (9)

$$< I > Cu_4(SO_4)(OH)_6 + 3H_2SO_4 \rightarrow 4CuSO_4 + 6H_2O$$
Eq. (10)

All the reactions above commonly show that copper is leached from the ore as copper sulphate. Besides copper, oxides of iron present in the ore are also leached. It is therefore necessary to exercise control over the amount and strength of the acid to be used for leaching to obtain maximum copper and minimum iron extraction. Use of too low an acid concentration is not desirable, as it can lead to precipitation of hydrous ferrie oxides that can adversely influence copper extraction and solution percolation. The preponderance of gangue carbonate minerals (such as calcite) in some copper oxide ore deposits tends to result in a tremendous increase in acid consumption, thus a more selective reagent is needed for such deposits. As a consequence, ammonia has attracted a lot of research interests because it does not react with carbonates and rejects iron, which ultimately reduces the cost (Larba<I> et al</I>. 2013; Mena and Olson, 1985; Paul and Ferron, 1983). More detail about ammonia heap leach is given in section 5.4e.

#### Oxidative leaching

The oxidative heap leaching of copper sulphide ores is becoming increasingly important as oxide ores are becoming depleted. While the leaching of some secondary copper minerals such as chalcocite has been demonstrated and practiced for many years, the same is not true of minerals such as covellite and the primary sulphides, such as chalcopyrite, which are considerably less reactive. The main approach to the heap leaching treatment of such ores has been bio-leaching. It is now generally accepted that mineral bioleaching is a combined chemical/microbial process in which ferric and protons form part of the reactants of the leaching reaction. The function of bacteria is mainly to enhance oxidative leaching by iron (III) ions by bio-catalysis of the re-oxidation of iron (II) by oxygen (van Staden, 2007b). The important reactions in bioleaching of sulphide minerals are represented in Eq. (11 to 13).

 $MeS + 2Fe^{3+} \rightarrow Me^{2+} + 2Fe^{2+} + S^{o}$  Eq. (11)

 $4Fe^{2+} + 0_2 + 4H^+ \rightarrow Fe^{3+} + 2H_20$  Eq. (12)

 $2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$  Eq. (13)

The ferrous iron produced in Eq. (11) is re-oxidized back to ferric iron as shown in Eq. (12) by iron-oxidizing microorganisms, so that the leaching reaction in Eq. (11) can continue in a cyclic manner. The sulphur species are oxidized to sulphuric acid by sulphur oxidizing microbes. The role of the microorganisms in the solubilisation of metal sulphides is not only to provide sulphuric acid for proton attack, but also to keep the iron in the oxidized ferric state for an oxidative attack on the mineral. From the latter, it can be seen that the microbial ferrous-iron oxidation to ferric-iron is a critical sub-process in the bioleaching of sulphide minerals.

In the bacterial leaching of sulphide 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 <I>Acidithiobacillus ferrooxidans</I> and <I>Leptospirillum ferrooxidans</I>, maintain high Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios due to continued oxidation as part of their respiratory process. Various other oxidants have been explored as aids for copper sulphide

oxidation, such as H<SUB>2</SUB>O<SUB>2</SUB> (Li <I>et al</I>., 2010), sodium nitrate (Sokic <I>et al</I>., 2009), Cu<sup>2+</sup> (Nicol, 2010; Hiroyoshi <I>et al</I>., 2000), and Cr<sup>6+</sup> (Aydogan <I>et al</I>., 2006; Antonijevic and Bogdanovic, 2004) and direct supply of Fe<sup>3+</sup> (Kaplun <I>et al</I>., 2011; Li <I>et al</I>., 2010). Nitrogen species (nitrate and nitrite) are strong oxidizing agents and take on a "catalytic" oxidant role, as has been reported on the treatment of various sulphide ores (FeS<SUB>2</SUB>, PbS, ZnS, CuS, NiS) for a range of operating temperature, pressure and oxidant/acid amount. Minerals containing nitrogen species such as NO<SUB>3</SUB><sup>-</sup> can accelerate the kinetics and increase total metal extraction, mostly for copper, in heap process (Anderson, 2003). Arias (1998) introduced heap leaching of copper ore using sodium nitrate as an oxidizing chemical reactive in a sulphuric acid leaching solution. Ingesol Ltda is the assignees of this patent, but no commercial application has been reported in the literature.

## Special case CuFeS<SUB>2</SUB>

Approximately 70 percent of the world's copper reserves consist of low-grade chalcopyrite, where the grade is considered too low to concentrate and which cannot be economically processed in any way other than heap leaching (Córdoba <I>et al</I>., 2008). The success of heap leaching with oxides and secondary sulphides has opened up doors for many field trials for the processing of chalcopyrite for future commercial exploitation. Many copper producers have realized that some chalcopyrite is indeed being leached in dumps, and with this realization more substantive efforts have been made lately to understand how this occurs and how it can be enhanced. Currently there are no targeted chalcopyrite heap leaching operations at commercial

scale. It is well known that chalcopyrite resists leaching in sulphate media. Many investigators have concluded that a passivating layer forms on the surface of the mineral during leaching which hinders further copper dissolution (Hackl <I>et al</I>., 1995). A large number of sulphate based processes have been developed to overcome the slow rate of chalcopyrite leaching. A review of acidic sulphate, sulphate–chloride and sulphate–nitrate process options has been offered by Watling (2013). One key approach to the treatment of such ores has been bio-leaching, which in the case of chalcopyrite is only viable under conditions of elevated temperature. The function of the bacteria is mainly to enhance oxidative leaching by ferric by catalysis of the re-oxidation of ferrous by oxygen. Table 3 shows some of the methods that have been patented in this respect.

Heap bioleaching of chalcopyrite is still in its infancy (Zeng <I>et al</I>., 2011; Wu <I>et al</I>., 2007) with the preliminary results of some pilot tests in Chile (Dew <I>et al</I>., 2011), Iran (Gericke<I> et al</I>., 2009) and in Inner Mongolia, China (Asian Miner News, 2008) having been presented only recently. Chalcopyrite bioleaching requires elevated temperatures to be successful. The challenges are how to engineer bioleach dumps and heaps to achieve and sustain higher temperatures. It is also a challenge to maintain and control different microbial populations within these massive bioreactors to ensure effective leaching of pyrite, generation of heat and leaching of chalcopyrite. A final challenge is the distribution of the oxygen required for these reactions throughout the heaps. The bioleaching of chalcopyrite in situ and in dumps is a practical option only because the low and slow recoveries are offset by the low processing costs (Schnell, 1998).

An alternative approach to chalcopyrite leaching involves the use of chloride ions in an acidic sulphate system at ambient temperatures. The leaching of chalcopyrite in chloride media has been reviewed and advanced by Dutrizac (1992). Early processes were focused on the leaching of concentrates under aggressive conditions, for example the CLEAR process and the INTEC process (Lunt <I>et al</I>., 1997). Kinnunen and Puhakka (2004) reported that the presence of 0.25 g /L of Cl<sup>--</sup> enhanced copper yield of bioleaching at temperatures between 67 and 90°C but decreased copper yield at 50°C. Li <I>et al</I>. (2000) focused their electrochemical studies on the leaching of chalcopyrite in mixed sulphate-chloride media and found that the presence of chloride enhanced chalcopyrite oxidation.

Nicol and co-workers (Miki and Nicol, 2011; Nicol et al., 2010; Velásquez-Yévenes et al., 2010a, 2010b) conducted a wide-ranging study of the dissolution of chalcopyrite in chloride solutions containing cupric ions and dissolved oxygen. Initially, it was shown that the rate of chalcopyrite dissolution was enhanced when leaching was conducted at the range of 550-620 mV SHE at 35 °C in a solution containing: 0.2 M HCl, 0.008 M Cu<sup>2+</sup> (simulating raffinate) and 5-15 mg L<sup>-1</sup> dissolved O<SUB>2</SUB> (Velásquez-Yévenes et al., 2010a). Leaching at potential <540 mV caused reduced rates of chalcopyrite dissolution and covellite or chalcocite formed on some chalcopyrite surfaces.

Although initial test work on concentrates and milled ores showed that chalcopyrite could be successfully leached under appropriate conditions using dilute chloride solutions at ambient temperatures, column tests on ores containing primarily chalcopyrite have demonstrated that the rates of leaching at temperatures below about 25°C are generally too low for economic recovery
of copper by this method in dynamic heaps (Nicol <I>et al</I>., 2011). Operation at locations with higher temperatures or the development of methods to economically heat the solutions to above 25 <sup>o</sup>C may be a prerequisite for successful implementation of chloride leaching of ores containing primary copper sulphide minerals (Nicol <I>et al</I>., 2011; Basson <I>et al</I>., 2010). Further details of the chalcopyrite leaching in chloride have been discussed in the recent review by Watling (2014). Chloride heap leaching based on the research by Nicol and co-workers was patented by Muller (2006), describing a heap leaching method used to recover copper from a primary copper sulphide mineral wherein an acidic chloride/sulphate solution in the presence of oxygen causes dissolution of the copper sulphide, if the surface potential of the mineral is kept below 600 mV (vs. SHE).

Manabe (2008) patented a method of leaching copper sulphide ore using iodine. The objective of this invention was to provide a method of efficiently leaching copper from a copper sulphide ore containing chalcopyrite or enargite as a main constituent under a range of conditions for actual operation. This study indicated that the copper leaching rate from a copper sulphide ore containing chalcopyrite or enargite can be significantly improved using a sulphuric acid solution containing iodide ions and ferric (III) ions in an excessive amount relative to the iodide ions.

Although a significant number of potential routes for chalcopyrite dissolution have been identified and in some case implemented at commercial scale, the fundamental mechanisms and kinetics of the leaching of chalcopyrite remain poorly understood, however. In their recent review, Kawashima <I>et al</I>. (2013) concluded that whilst much has been observed at the

macro-scale regarding the chalcopyrite leach process it is clear that interpretation of these phenomena is hampered by lack of understanding at the molecular or atomic scale.

## **Reaction Kinetics**

The major factors affecting the dissolution rate of metals of interest at the mineral-solution interface are lixiviant concentration, temperature, pH, dissolved oxygen, presence of other metals and ions in solution. Leach kinetics (i.e. mineral grain dissolution rate) are controlled by a combination of these physico-chemical factors and mineral composition of the ore (oxide/sulphide) and the location of mineral grains within ore particles. Leach recovery rates generally increase under higher lixiviant concentrations, temperature and dissolved oxygen and higher pH (>9) for cyanide leach and lower pH (<2) for acid leach conditions.

### Reagent concentration

The leach rate has been found to increase with increasing concentration of sulphuric acid (Aydogan <I>et al</I>, 2006; Dreisinger and Abed, 2002). Low pH values can minimise hydrolysis and precipitation of Fe<sup>3+</sup>, and the effect becomes more obvious when the acid is very concentrated at 3-5 M (Antonijevic and Bogdanovic, 2004). Ferric ion concentration in the medium plays an important role in the bioleaching process of sulphide ores (Rodríguez et al., 2003). Vilcáez et al. (2009) reported that additional ferric ions only enhance the initial leaching rates but not the final leaching yields. Studies found in literature concluded that Fe<sup>3+</sup> concentration above 0.01M does not affect chalcopyrite bioleaching kinetics (Konishi et al., 2001; Hirato et al., 1987, Dutrizac, 1981). Fe addition can cause

precipitation and heap clogging problems, and also a high concentration of Fe in the PLS will affect the extraction process and needs to be removed before SX.

Gold dissolution, on the other hand, is usually fast and governed by diffusion of the dissolved species. It increases with increasing cyanide concentration at low levels. Maximum cyanide concentration is 0.075% KCN or 0.06% NaCN, equivalent to 600 ppm, and beyond this maximum excess cyanide has no effect (Srithammavut, 2008).

#### Temperature

Chemical reactions proceed more rapidly at higher temperatures. Although the rate of decomposition is sufficiently fast at 40 or 50°C for some minerals, in case of others (e.g. chalcopyrite) temperatures of 70 °C are required for the process to be rapid enough to be economically viable. An increase in temperature can also improve the yield of copper because the quantity of sulphur and other oxidation products that coat the mineral surface (passivation) is reduced (Rawlings, <I>et al</I>, 2003; Brierley and Briggs, 2002). In bioleaching, different types of organisms dominate mineral degradation processes as the temperature changes (see section 3.5). A comprehensive monitoring program at an industrial bioleaching heap at the Escondida mine in Chile since 2006 indicated that an increase in heap temperature causes variation in microbial community from predominantly mesophilic to thermo-tolerant and moderately thermophilic species (Acosta <I>et al</I>, 2014).

Many Nevada gold heap leach operations report a significant recovery decrease in winter, with a rapid increase the following summer. Laboratory column tests show that recovery rate drops

significantly when the temperature drops below 5 <sup>o</sup>C. Also, solution viscosity increases significantly as temperature drops. This affects both the heap and the process plant. Thus, cold heaps tie up more process solution (and more gold inventory) than warm heaps (Mellado <I>et al</I>, 2011; van Zyl and Bronson, 1994).

pН

Low pH levels in combination with high temperatures increase the leaching rate of chalcopyrite (Srithammavut, 2008). In bio-leaching, maintaining the pH in the preferred range between 1 and 2 is also important for ferric ion and acid regeneration by the microbial population. Thus, the capability to accurately predict leaching solution pH and acid consumption during copper ore leaching is important for the evaluation of leaching performance and cost. Deveci (2008) has shown that pH has a significant effect on the dissolution process, controlling the oxidative activity of microorganisms. The bioleaching performance of mesophiles tends to deteriorate with increasing acidity from pH 2.0 to 1.2. For thermophiles Vilcáez <I>et al</I>. (2009) showed that at pH values above 1.5, large amounts of Fe<sup>3+</sup> generated results in the formation of jarosite, which decreases the catalytic effect of thermophiles. Increased acid concentrations in industrial raffinate solutions of the heap bioleaching process at Minera Escondida Ltd. (MEL)-Antofagasta, Chile, produced changes in the distribution and activity of the microbial population present in the process (Zepeda <I>et al</I>., 2013).

In cyanide heaps cyanide consumption is high below a pH of 9.5. Above a pH of 11, metal recovery decreases. A degree of pH level adjustment is achieved through the addition of lime during agglomeration prior to heap stacking, but this does not amount to pH control. Increasing

pH level reduces gold dissolution rate because adsorption of OH<sup>-</sup> ion onto the gold surface decreases the surface available for cyanide leaching (Habashi, 2005b).

### pO<SUB>2</SUB>

Since oxygen is the key reagent in any oxidative heap leach process, none of the chemical reactions taking place in the heap can proceed at a rate faster than the rate of oxygen mass transfer from the gas phase to the liquid phase (Lizama, 2009). Oxygen is often a limiting reagent in heap bioleaching processes of sulphide minerals and therefore aeration helps to increase leaching rates. It also could be a way to control the temperature in the heap as the leaching reactions are mostly exothermic (Petersen and Dixon, 2002b; Dixon, 2000). Bioleaching microorganisms require oxygen, which accepts the electrons in the redox reactions catalysed by the microorganisms (Brierley and Briggs, 2002; Acevedo and Gentina, 1993). Copper leaching is directly related to oxygen consumption in the heap and oxygen consumption, in turn, is related to microbial activity and the rate of forced aeration (Lizama <I>et al</I>, 2005).

It has been proven that the rate of dissolution of gold in cyanide solution is directly proportional to the amount of dissolved oxygen present (Bouffard and West Sells, 2009; La Brooy <I>et al</I>. 1994). Gaseous oxygen is also required in cyanide heap leaching, but the demand is minimal and often fully satisfied by the initial gas holdup entrained upon ore stacking. Dissolved oxygen concentration has no significant effect on cyanide consumption, but faster leaching kinetics has been observed by using higher dissolved oxygen concentrations (Srithammavut,

2008). Any side reactions in which the cyanide solution is deprived of its oxygen content will cause a decrease in the rate of gold leaching (Habashi, 2005b).

The solubility of oxygen in aqueous solution has been well studied, and thermodynamic correlations are available in the literature (for example Tromans, 2000). The study by Petersen<I> </I>(2010) through both experimental and theoretical evaluation shows that gasliquid mass transfer of oxygen in heap leach scenarios is remarkably constant between different systems and is not a significant function of temperature in the range 22-68 °C. This may be surprising, given the rapidly declining solubility of oxygen with increased temperature in this range, but the study has shown that this is offset by an increased mass transfer coefficient. The results indicate that heap bio-leaching as a process is determined by the rate of gas-liquid mass transfer of oxygen into solution in all the cases studied, which cover different materials, temperatures and microbial consortia. While operating heaps at low temperatures may be limited even more by slow mineral leaching kinetics, thermophilic heap bio-leaching certainly cannot progress any faster than the rate of oxygen gas-liquid mass transfer allows, even though it may be the preferred route for chalcopyrite leaching (Basson <I>et al</I>., 2006). Operating heaps at high altitude and in highly saline solutions further limit the rate of oxygen mass transfer and hence the overall rate of metal recovery (Mellado <I>et al</I>., 2011; Rossana and Brantes, 2010; Petersen, 2010). If oxygen is sufficiently present at all the points of the heap, an increase in aeration rate does not increase the leaching rate (Pradhan <I> et al</I>, 2008). This is due to the fact that mass transfer into the liquid phase is driven primarily by oxygen partial pressure in the air, which wouldn't change at increased flow rates. The oxygen requirements for the heap reactions are relatively low if the reacted sulphide produces elemental sulphur. If the elemental

sulphur is oxidized to acid then the oxygen requirements increase significantly by a factor of four.

### Foreign ions and ionic strength

High concentrations of metals or metalloids can contribute to the slowing or inhibition of microbial Fe oxidation (Brierley and Briggs, 2002). Inhibitory concentrations of dissolved metals, such as arsenic, copper, mercury, nickel, uranium, etc., on microbial growth and ferrous oxidation have been reported by many authors (Cabrera <I>et al</I>., 2005; Wang <I>et al</I>., 2004; Nies, 1999; Garcia and Silva, 1991). A heap operation also requires control of the ionic strength of the leach solution to sustain bacterial activity. Microorganisms are relatively intolerant to the chloride ion, which disrupts the cell membrane and allows uncontrolled transport of NO<SUB>3</SUB><sup>+</sup> into the cell, which slows down the rate of Fe<sup>2+</sup> oxidation (Brierley and Briggs, 2002). In bioleaching the presence of chloride is detrimental to microbial growth, but the degree of inhibition varies between strains. It is also of interest that while the catalytic effect of Ag<sup>+</sup> in chalcopyrite bioleaching is well established (Wang <I>et al</I>., 2004; Ahonen and Tuovinen, 1990; Miller et al., 1979, 1981; Price and Warren, 1986) this ion is also highly inhibitory at concentration greater than 1µM (Garcia and Silva, 1991). In heap bioleaching the dissolution of gangue minerals from igneous ore materials can lead to the build-up of considerable concentrations of Mg and Al sulphates in the recycled leach solution. This may interfere with microbial ferrous iron oxidation, which drives the oxidation of the target minerals (Ojumu <I>et al</I>., 2007, 2008a). It has also been reported that aluminium concentrations exceeding 10g/L adversely affected the growth of an unspecified ferrous iron oxidizer (Blight and Ralph, 2004). The concentration of ions in solution has an effect on the ionic strength of the solution and hence on solution thermodynamics. High overall ionic strength will depress the activity of individual ions (Argun et al., 2007). By the same token the presence of high ionic strength also depresses the solubility of oxygen in solution (Tromans, 2000; Petersen, 2010).

In gold leaching, the presence of base metal ions such as Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup> and Zn<sup>2+ </sup>in the cyanide leach solution will retard the cyanidation of gold (Shiers <I>et al</I>., 2005; Kinnunen and Puhakka, 2004). Since the sulphide minerals are to some extent soluble in cyanide solutions, there will always be some sulphur species present in the leaching solution. It is generally believed that the presence of such species results in high consumption of cyanide and oxygen. Sulphide reacts with cyanide, resulting in the formation of thiocyanate. However, some results of kinetic studies suggest that sulphur species also directly affect the gold leaching reaction by forming a passive layer of Au<SUB>2</SUB>S on the gold surface (Jeffrey and Ritchie, 2001; Lorenzen and van Deventer, 1992). An exception is galena which shows increased gold dissolution under atmospheric condition (Jeffrey and Ritchie, 2001). Copper minerals can dissolve and form a copper variety cvanide CuCN. of complexes such as Cu(CN)<sup>2-</sup>, Cu(CN)<SUB>3</SUB><sup>2-</sup> and Cu(CN)<SUB>4</SUB><sup>3-</sup> depending on pH. Copper dissolution has a detrimental effect on gold dissolution since it consumes cyanide and oxygen. Addition of lead solution. for instance lead nitrate. Pb(NO<SUB>3</SUB>)<sup>2</sup>, can enhance gold leaching kinetics. It is observed that lead nitrate prevents the formation of a passivation film on gold surface and activates the surface of a passivated gold particle. Downstream processing can be challenging and costly with complex mixtures of soluble metals. Copper concentrations of around 100 ppm have been known to have a detrimental effect on the carbon adsorption of gold from cyanide leachate, and, as discussed earlier, the SART process has made CN heap leaching of cupriferous Au ores more viable (Marsden and House, 2006). Thiosulphate is a more effective lixiviant of high-copper ores than cyanide because ammoniacal thiosulphate leaching is less sensitive to contamination by unwanted cations.

## Gangue chemistry

Ore and gangue mineralogy is fundamental to the metallurgical behaviour, and therefore to the technical and economic amenability of an ore to exploitation. Minor changes in gangue mineralogy can have a significant impact on the requirements for acid curing and agglomeration prior to heap leaching, and on the acid consumption, metal extraction, and PLS chemistry during leaching.

## Reagent consumption by gangue minerals

Acid consumption is considered as the main controlling economic factor in the heap leaching of oxide ores (Rich, 2008). Acid consumption during copper leaching is a function of acid consuming minerals in the ore and their leaching properties as well as their association with the host rock (Plumb <I>et al</I>., 2007). In all ore leaching processes the gangue (undesired) minerals also consume lixiviants along with the metals of interest; copper, zinc, iron in gold ore leaching; iron, aluminium, magnesium, manganese, calcium and potassium in copper and nickel

ore leaching, to name a few. Certain gangue minerals like calcite (CaCO<SUB>3</SUB>) are very reactive to acid and will dissolve completely in contact with even very dilute sulphuric acid solutions. Ores that contain a significant proportion of such minerals will be clearly unsuitable for acidic heap leaching. However, more commonly silicate minerals constitute the most significant acid consuming component of the ore. The silicate minerals react incompletely with sulphuric acid, and with several of them the extent of acid-gangue reaction is a function of the acid strength. The moderate reactivity to acid of these gangue minerals limits their acid consumption sufficiently such that acid heap leaching of the ore can be economically viable with a relatively low valuable metal grade. It therefore leaves a degree of control over the acid consumption and permits an economic optimum to be sought between acid costs and leach kinetics, by varying the acid curing parameters and the acidity of the irrigation liquor in a matrix of metallurgical tests. It has been postulated that gangue acid leaching can over time help liberate valuable mineral (Free, 2010; Free and Jurovitzki, 2010; Baum, 1999, 1996; Horlick <I>et al</I>., 1981).

Temperature is another important parameter to consider in gangue reactions, which is becoming very relevant in efforts to do high temperature heap leaching. It should be ensured that the extraction benefit realised by the increased heap temperature is not offset by the concomitant increase in gangue acid consumption (Free and Jurovitzki, 2010; Horlick <I>et al</I>., 1981). The gangue minerals consume cyanide and oxygen in solution or they re-adsorb gold from solution. In uranium leach processes employing sulphuric acid as the lixiviant, only a relatively small quantity of acid is actually used in extracting uranium from the host ore. The remainder of the acid is consumed by the gangue constituent elements. Many new uranium projects that are

being considered in recent times have potential gangue acid consumption in excess of 95%. In contrast, alkaline leach processes do not experience the same high reagent consumption rates as acid processes. The solubility of many of the impurity elements in uranium ores (such as Fe, Mg, and Al) in the alkaline leach is quite low (Adams, 2005; Mular <I>et al</I>., 2005).

Ammonia leach processes, which operate in an alkali regime, allow selective extraction of base metal sulphides from an ore by forming stable metal-ammine complexes, whilst being inert to iron and acid consuming gangue. Hence ammoniacal leaching of base metals is potentially an attractive route as an alternative to acid bioleaching (Muzawazi and Petersen, 2015).

## Secondary precipitation

In addition to lixiviant consumption, re-precipitation of products of some of these gangue minerals have potentially negative effects on leach permeability by plugging up of the pores in the heaps. The extent of ferric iron hydrolysis is dependent on the pH; in general, ferric iron has an extremely low solubility at a pH of >2.5. High concentrations of Fe<sup>3+</sup> in solution, due to a lack of demand as oxidant, may precipitate as ferric hydroxide or as Fe(III)-hydroxysulphates such as jarosite (KFe<SUB>3</SUB>(SO<SUB>4</SUB>)<SUB>2</SUB>(OH)<SUB>6</SUB>) or schwertmannite

(Fe<SUB>16</SUB>O<SUB>28</SUB>(SO<SUB>4</SUB>)4H<SUB>16</SUB>). Jarosite precipitation is an important phenomenon that is observed in many bacterial bioleach systems. During bioleaching, monovalent cations (e.g., K<sup>+</sup> and Na<sup>+</sup>) released from the alteration of silicate phases (e.g. mica as a potassium aluminium silicate) present in the

ore may promote the precipitation of ferric iron mainly as K-jarosite, which is controlled by pH (Ahonen and Tuovinen, 1995). The limited extraction of metals has often been attributed to the formation of these secondary phases during bioleaching (Harmer <I>et al</I>., 2006; Ahonen and Tuovinen, 1995). Jarosite causes an obstruction to mineral-microbe contact by forming a mass transfer barrier to nutrients, oxygen, and carbon dioxide. Precipitation of iron hydroxide and jarosite phases in the leaching system may suppress the metal solubilisation by preventing contact between the leaching agent and the mineral. The solubility of iron species is defined by Downloaded by [University of Exeter] at 01:57 24 November 2015 their concentration in solution and pH. Thus, the optimization of these parameters may greatly improve metal recovery. Eneroth and Koch (2004) reported that ammonium jarosite was predominant at pH 1.6 in ferrous-iron oxidation by <I>At. Ferrooxidans,</I> and at pH 3.2 schwertmannite was observed. The study by Kupka <I>et al</I>. (2007) has shown that schwertmannite is dominant at low temperature oxidation of ferrous-iron by <I>At. Ferrooxidans</I>. Ferric-iron precipitate has been reported to hinder oxidation by forming a diffusion barrier (Nemati <I>et al</I>., 1998) and reducing free ferric-iron available for leaching.

# Bioleaching

In general, the types of micro-organisms found in heap leaching processes are similar to those found in stirred tank processes. The most important micro-organisms in bioleach processes that operate from ambient temperatures to about 40°C are considered to be a consortium of iron- and sulphur-oxidizing <I>Acidithiobacillus ferrooxidans</I>, the sulphuroxidizing <I>Acidithiobacillus thiooxidans</I> and <I>Acidithiobacillus caldus</I>, and the ironoxidizing <I>Leptospirillum ferrooxidans </I>and <I>Leptospirillum ferriphilum</I> (Rawlings and Johnson, 2007; Rawlings, 2005; Franzmann <I>et al</I>., 2005; Rawlings, 2004). At moderately thermophilic conditions<I> At. caldus</I>, <I>L. ferriphilum, Sulphobacillus</I>-like bacteria, and<I> Ferroplasma</I>-like archaea seem to dominate (Okibe et al.,<I></I>2003), while species of <I>Acidimicrobium</I> may also occur in<I> </I>systems operating at temperatures around 50°C (Rawlings,<I> </I>2005). Thermophilic consortia are typically dominated by<I> </I>archaea, with species of <I>Sulpholobus, Acidianus</I>, and<I> Metallosphaera</I> being most prominent (Rawlings and Johnson, 2007).

Clarification of the role of microorganisms and their interaction with different minerals in ore sample has been investigated lately using new techniques and devices. These studies have resulted in a number of novel technical and methodological patents on the application of microorganism in heap leaching (Kuwazawa, 2009; Kohr, 2004; de Kock and du Plessis, 2004; Crundwell, 2002; Hunter, 2001; Hunter and Williams, 1999; Hunter, 1999; King, 1998; Batty, 1997; Johansson <I>et al</I>., 1994; Brierley and Hill, 1991). Other aspects receiving attention include the mechanism of microbial attachment to mineral surfaces, the effect of process parameters such as irrigation rates on microbial colonization, the isolation and identification of salt-tolerant mineral-oxidizing acidophiles and the effect of the build-up of elements such as sulphates, aluminium and magnesium (as discussed in Section 3.3.5), which could inhibit microbial performance. Several strategies for the inoculation of heaps have been described, and the overall conclusion is that there would likely be a considerable time saving in inoculating new heaps with a microbial consortium (or consortia) at the appropriate points in time, rather than waiting for microorganisms to grow naturally (Gericke, 2011). The development of relatively

rapid, robust methods for the identification and quantification of microbial strains, both attached and planktonic, in bioreactor samples have greatly assisted in clarifying the role of microorganisms in mineral bioprocesses (e.g., Govender <I>et al</I>., 2013; Johannes <I>et al</I>., 2006; Sand and Gehrke, 2006; Johnson and Hallberg, 2005; Crundwell, 2003).

# Heap Technology

## Ore preparation

The metallurgy of the ore dictates the method by which the ore should be prepared prior to leaching. Ore preparation can range from none (for ROM ore) to crushing, crushing and agglomeration, or agglomeration only [for fine-grained ore or tailings). The major purposes of ore preparation for heap leaching are to produce an ore fine enough to allow sufficient liberation of valuable minerals and to have an ore permeable and stable enough to allow an adequate leaching rate throughout the heap. The amount of effort and expense incurred in ore preparation is directly related to the economics of the metal recovery.

## Comminution

Ore crushing is generally done in multiple steps; in primary crushing (i.e. jaw crushers) the particle size is reduced down to 10 to 15 cm, and in secondary/tertiary crushing it is reduced to the optimum size while also producing as many micro-cracks in the ore particle as possible for improved solution penetration. Generally, cone crushers are used for secondary crushing. If the ore is very porous, little or no crushing may be necessary because of the advanced degree of

natural liberation of the target metal. Such ROM ore material can be placed directly on the leach pad after minimal breakage following normal production related blasting or even simple shovelling with mining equipment. High surface exposure of the valuable mineral is desirable in metal extraction processes because the extraction rate is directly proportional to the exposed surface area. However the cost of grinding to achieve the finer particle size has to be considered in designing the process to extract the mineral effectively (Ogbonna <I>et al</I>., 2006). The economics of heap leaching were found to be strongly governed by the trade-off between the slow rate and limited extent of leaching from large particles and the cost of crushing finer (Schnell, 2013). It is known that leaching from large particles occurs only at the surface and in subsurface regions, which are accessible from the surface by cracks and pores (Ghorbani <I>et al</I>., 2013a; Liddell, 2005). The presence of micro-cracks plays a key role in the diffusion of reagents throughout particles during leaching and is significant for the further analysis of the effect of comminution method on downstream ore processing. Over the last decade the use of High Pressure Grinding Rolls (HPGR) has gained significant importance and popularity, since they offer some metallurgical benefits (Baum and Ausburn, 2011). Van der Meer (2011) found that micro-cracking, resulting from the high-pressure inter-particle comminution process was responsible for generating lixiviant pathways and therefore improving leach extraction recovery. McNab (2006) reported 10-11% increase in gold leaching due to the HPGR micro-fracturing effect. HPGR may also reduce the need for binder in agglomeration because the compression forms flakes of aggregated ore that are fairly stable when exposed to a trickling cyanide solution (Baum and Ausburn, 2011; Chamberlin, 1989). In 2009, the first commercial HPGR for a heap leach operation in gold (Goldfields-Tarkwa Mine, Ghana) has been commissioned. This installation is considered as the first full-scale industrial test in order to prove the general suitability of HPGRs for heap leaching. Positive results (the authors could not find any published results regarding the success of this industrial practice) from this operation could also influence the SX-EW heap leach operations in the copper industry (Burchardt <I>et al</I>, 2010).<I></I>While HPGR may lead to improved heap leaching for hard ores, operators may face problems with soft and sticky ores (Dhawan <I>et al</I>, 2013). Ghorbani <I>et al</I>. (2013b) reported that the residues from leach experiments with material prepared using the HPGR product contained more fine particles than those after leaching a cone crusher product. If excessive amounts of fines are generated during the leaching process, permeability is reduced as the leaching process progresses, which can have a negative effect on percolation, especially over long periods of heap leaching operation. It would also prevent a uniform flow of the solution through the heaps.

In addition to comminution by HPGR, since the late 1980s microwave heating of ores has been proposed as a means of, firstly, reducing the net comminution energy, and secondly, enhancing the liberation of value mineral phases (Kingman and Rowson, 1998). Selective heating of distributed mineral phases has the potential to induce controlled fracture within the rock (Haque, 1999). If the fracturing takes place along the grain boundaries of value mineral phases, these phases could be effectively liberated, allowing increased accessibility of lixiviant solutions into the ore particle (Jones <I>et al</I>, 2005; Kingman <I>et al</I>, 2004; Batterham, 2002). Usually, microwave energy is costly, mainly due to the low conversion efficiency from electrical energy (50% for 2450 MHz and 85% for 915 MHz, although this efficiency is still higher than that of conventional heating). Studies showed that the process of thermal treatment was

uneconomical when compared to the use of conventional grinding alone (Prasher, 1987), due to the large energy requirements associated with heating the bulk ore to the required temperatures. The cost of heat treatment and subsequent grinding could be as high as 6 times that of conventional grinding alone (Scheding <I>et al.,</I> 1981). The key limitation is that the mineral processing industries treat large tonnages of ore per day (several thousand to over 30,000 tonnes). Currently, the highest microwave power generator available is 75 kW at 915 MHz.

To treat such a large tonnage of ore or concentrate a number of generators would have to be operated in parallel, which may not offer a cost advantage over the conventional process. In fact the ratio of cost of heat input to additional metal value gained makes thermal treatment uneconomical. However, for high value product recovery or low tonnage treatment microwave energy can offer a cost advantage over the conventional process (Koleini et al., 2012). Since heap leaching is usually defined as a low-cost process for extraction of minerals from large volumes of low-grade ore materials, application of microwave technology remains questionable, mostly from an economical point of view.

## Agglomeration

Non-uniform percolation of solution throughout the heap caused by the presence of fines is a common problem, which occurs to some extent with all heap-leachable ores. The solution chooses the path of least resistance, commonly called channelling. If enough fine material has built up, there is a chance the solution may not be able to flow downwards at all; this is referred to as blinding. These particles clog the spaces between the larger ore particles and result in an uneven distribution of the leaching solution. This leads to poor interaction between the ore and

leach solution, producing inadequate metal recoveries, or the need to extend the leach time (Sheikhzadeh and Mehrabian, 2007; Readett <I>et al</I>., 2006; Lipiec and Bautista, 1998). The conventional solution to this problem is agglomeration. The effect of agglomeration is to immobilise the fines by causing them to adhere either to each other or to larger ore particles and greatly reduces the segregation during stacking and consequently percolation problems (Lewandowski <I>et al</I>., 2010; Lewandowski and Kawatra, 2009; Lu <I>et al</I>., 2007; Velarde, 2005; Bouffard, 2005). Investigations of agglomeration agents and methods have resulted in a number of patents such as agglomerating agents for clay containing ores (Polizzotti, 1989), a systematic method for heap leaching agglomeration considering optimum reagent concentration and curing time (Miller, 2010; Miller <I>et al</I>., 2009; Adam and Scott, 2009; Michael, 2006).

Additional additives (binders) are needed to prevent agglomerates from breaking up as leaching solution percolates through the heap. A whole suite of different materials have been proposed as binders (Lewandowski <I>et al</I>, 2006; Underwood, 1998; Polizzotti, 1994, 1989; Oliphant and Walker, 1989). It is desirable that a particular binder does not affect the leach chemistry during irrigation and the subsequent processes for metal recovery. This is in turn strongly linked to the leaching chemistry, with, for example, cementitious binders not suitable for acid heap leaching, but common in gold heap leaching. Garcia and Jorgensen (1997) recommended agglomeration of ore with binder if the ore contains more than 10-15% of fines (-74 $\mu$ m). Lime, molasses and wood fibres have been tried, but the agglomerates resulting from using these binders disintegrated completely within a couple of hours of immersion in water (Bouffard, 2008). Amaratunga (1995) used  $\beta$ -hemihydrate of gypsum as a binder with pyrrhotite tailings and

reported agglomerates of poor strength. Cement provides the best strength because of the formation of calcium silicates hydrates, during curing. However, cement-based agglomerates when allowed to dry immediately after agglomeration disintegrated partially or completely when less than 50kg/t of cement were added. Type II Portland cement and lime are two well-known binders used in gold and silver leaching, but these are strictly limited to use in alkaline leaching environments (Underwood, 1998). Very few binders have been tested for the copper industry, possibly because of the binder cost, large consumption and curing issues, and a limited selection Downloaded by [University of Exeter] at 01:57 24 November 2015 of acid tolerant and microbial resistant binders (Lewandowski <I>et al</I>., 2006; Bouffard, 2005). It is known that adding cement or lime to sulphide ores results in precipitation of gypsum and jarosite (Bouffard, 2005). A binder in copper heap leaching should withstand the very acidic environment and should not interfere with maintenance of a high bacterial population survival (Lewandowski <I>et al</I>., 2010). Polymeric combinations as copper heap leaching agglomeration aids have been patented by Kerr (1997) and Bonin and Gross (1988). The performance of polymers products varies, depending on the composition of the feed material that is being used and the product qualities desired (Pietsch, 2005).

# Heap design

Numerous innovations and patents have been recorded in the area of heap design and construction from different technical, economical, and environmental points of view (Schnell, 2013; Caceres, 2013; Caro and Ekenes, 2012; Lang, 2009; Hunter and Williams, 2005; Breitenbach, 2004; Ulrich <I>et al</I>., 2003; Miller, 2003a; Thiela and Smith, 2003; Crundwell and Norton, 2002; Kappes, 2002; Strachan and van Zyl, 1987; Lesty and Surjous, 1984). These are described and discussed in the following subsections.

Pad preparation, liners and drainage systems

Heap liner design has evolved into a well-developed science with due consideration given to the interaction between the various components such as the foundation, under-liner, geo-membrane, over-liner, as well as collection and air injection piping. The most preferred pad liner system in current heap leach practice is the composite liner with an overlying drain cover fill (Breitenbach<I> et al</I>., 2013; Lupo, 2010: Breitenbach and Smith, 2006). In general, liner systems for leach pads may consist of a single composite or double composite liner with a leakage collection layer (Figure 3). Single composite liner systems generally consist of a geo-membrane liner placed over a compacted bedding soil liner. This type of configuration is commonly used in areas that experience low hydraulic head (typically less than 1 m). A double composite liner system consists of two geo-membrane liners separated by a leak collection/drainage layer. A double composite liner system is normally only used where high hydraulic heads (several meters) may occur, such as in valley leach facilities.

Testing has indicated that both, high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) geo-membranes, are suitable for containment of acidic solutions and metal leaching products, for periods of over 50 years (Lupo, 2010; Breitenbach and Smith, 2007; Renken <I>et al.,</I> 2005). The geo-membrane lined heap leach pads for the 21st century have an estimated operating life times of 10 years or more, compared to the more typical periods of 3 to 5 years reported in the past for gold and silver heap leach operations. It is worthwhile to note

that spent heaps present a long-term footprint and even if liners are stable for active operation, there may still be long-term leakage if no proper closure procedure is in place. Application of the modern and multi-layered co-extruded geo-membranes, have been introduced through various patents (Maziers <I>et al</I>., 2004; Bray <I>et al</I>., 2004; Nicholas and Rhee, 1996; Gary, 1991). The heap leach pad cannot be 'fixed' or 'upgraded' after construction. What is initially designed and built must be lived with for the life of the mine.

If economically feasible, the drain material should be designed to act as a filter for the ore and should be resistant to chemical breakdown. If placing a complete drainage blanket is not feasible, the area around the collection pipes should be protected. Selected gravel materials and/or geotextiles have worked at several sites. Acid resistant materials should be used for all parts of the pipe network, including couplers, ties and fasteners. Manufactured couplers are the best, as it has been reported that pipes have become pulled apart beneath heaps where inappropriate couplings had been used (Lupo, 2010; Breitenbach and Smith, 2007; Renken <I>et al</I>, 2005; Maziers <I>et al</I>, 2004; Ulrich <I>et al</I>, 2003). Different researchers (Lupo, 2010; Thiel and Smith, 2004; van Zyl and Bronson, 1994) have classified leach pads into different categories (Table 4).

Inter-lift liners are becoming universal for oxide copper ores and will probably be adopted by the emerging nickel heap-leaching industry. These thin geo-membranes are used to separate lifts of fresh ore from underlying leached ore to reduce acid consumption, and have the additional benefit of allowing drainage of PLS before it enters leached ore with declining permeability. Both raincoats and inter-lift liners represent a new view of geo-membranes: neither needs to be

"near defect free" as we strive to achieve for containment liners, as both are flow restrictors rather than environmental barriers (Steemson <I>et al</I>., 2010; Breitenbach and Smith, 2007, 2006).

### Heap stacking methods

The choice of a particular stacking method will depend on: planned throughput (high tonnages normally use mobile stacking conveyor), heap type, heap height, particle size (coarse ROM ore will require trucks) and ore properties (permeability, etc.). Heap construction practice plays an important role in the overall performance of a heap leach. There are two principal options: truck dumping and conveyor stacking. The heaps are constructed by dumping from haul trucks, stacking with a front-end loader or mechanical stacking with or via telescopic/grasshopper conveyor belts with travelling bridges (radial stacker) in sequential lifts (Kappes, 2002; Bartlett, 1998). The major disadvantage of truck dumping is the compaction of the ore due to the weight of the trucks and their loads (Kappes, 2002). Several studies have indicated large trucks noticeably compact ore to a depth of two meters. Consequently the heap surfaces often need to be ripped before leaching is commenced in order to break up the compacted zone, thereby improving the permeability of the top of the heap (Kappes, 2002; Bartlett, 1998). Where rock is hard and contains very little clay, it is possible to maintain high permeability even when ore is crushed and dumped with trucks. Stacking by both truck dumping and conveyor stacking causes segregation of the ore - the fines remain near the top, and the coarse material rolls to the base of the lift, creating a highly permeable zone at the base. To control the degree of this segregation the ore may be partially agglomerated (wetted to cause the fines to stick to the coarse material) prior to loading onto the trucks.

Conveyor stacking, especially for agglomerated ore, is commonly used for handling of large quantity of crushed material for its ease/mobility, more homogeneous ore grain size distribution in the heaps and its favourable economics over truck loading of leach pads. Also, equipping conveyors with automated water sprays, applied during stacking, has a practical advantage over pre-wetting the ore material for leaching and providing dust control. Conveyer stacking allows for the gentle placement of ore which can help minimise compaction and segregation of the ore. In some cases where the heap height is significant, the base of the heap can become compacted due to the large drop from the conveyer to the ground. This problem can be overcome largely by leaving the stacker at the full height of the pile and then allowing the ore to slide down the existing heap (Kappes, 2002; Bartlett, 1998), although this may results in the same segregation as observed with truck dumping. Johnson (1983) patented a cellular heap leach process wherein a heap is constructed from a number of cellular heaps formed by loading ore onto an impermeable pad having a raised berm network to separate the pad surface into a multitude of reservoirs. A method for forming a number of ore piles with one repositionable conveyor was introduced by Bernard and Kelly (1998). In this manner, significant system down time conventionally experienced in moving a conventional shiftable conveyor is avoided. This method later improved for multiple lift stacking (Bernard, 2002). TNT's patented Superportable<sup>TM</sup> technology allows fully independent movement of each piece of mobile conveying equipment on the stacking pad. Super-portable<sup>TM</sup> conveyors,

with each mobile conveyor at a capacity of 2,600 t/h (and more recently 5,467 t/h) are used in support of stacking operations at Morenci copper heap leach operations (www.tntinc.com).

### Irrigation systems

It is well established that the solution dripping onto the surface is distributed throughout the depth and breadth of the heap by the combined effects of gravity and capillary action (Afewu and Dixon, 2008; Schlitt, 1992). The irrigation pipe network for each heap comprises main lines at ground level and heap supply header pipes along the top of the heap, which distribute solution over the surface of a stacked heap through a variety of spreading devices such as rotating impact sprinklers, wobbler sprinklers, Bagdad wigglers and pressure drip emitters. In general, irrigation methods can be divided into sprinklers and emitters. Characteristics of these two categories are given in Table 5.

Investigation of irrigation systems and devices has been the subject of many different studies and patents (Guzman, 2008; Burgmayer, 2002; Lane, 1999; Krieg, 1998; Allen, 1994; Brown 1988; Krauth, 1987; Bodine, 1986; Kohorn, 1980). The effective flow areas for most leaching emitters are small, and they often require the solution to be clarified to 150 or finer mesh to avoid clogging. Wobbler® technology minimizes clogging without requiring expensive filtration. Channelling and plugging problems associated with drip systems make it difficult to achieve even solution/ore contact, especially in the upper section of a leach pad. Regardless of whether the choice is sprinklers or drip irrigation, one of the often overlooked design features is the changing head along the length or width of a heap and the need to provide the necessary pressure regulation to ensure uniform solution distribution (Guzman, 2008; Burgmayer, 2002).

A method of injecting leach solutions applied directly into specific areas in Nevada heap leach operations was presented by Wan and Brierley (Wan and Brierley, 1997; Wan, 1997). The method, trademarked Hydro-Jex<sup>©</sup>, uses techniques similar to those developed for the oil and gas industry. The Hydro-Jex© application provides a direct means of delivering leaching reagents to the targeted areas and is thus an important tool for heap leach operations that can improve metal recovery, change solution chemistry and reduce rinsing time and closure expense (Rucker, 2015; Rucker <I>et al</I>., 2009a, b; Seal, 2005; Bhakta, 2003; Wan and Brierley, 1997; Wan, 1997). Hydro-Jex© re-leaching was undertaken at the Valley Leach Facility at AngloGold Ashanti's Cripple Creek and Victor Gold Mine (CC&V) (Seal <I>et al</I>., 2011), supported by geophysical monitoring.

### Aeration lines

As is discussed in sections 2.2 and 3.3.4, the rate limiting step in oxidative heap leaching is often gas-liquid mass transfer, and the interior of a heap, if not properly aerated, is prone to anoxic conditions. Initially heap/dump operations relied on natural advection, but this was found to be inadequate. Bartlett and Prisbey (1996) emphasise the importance of oxygen diffusion in heap bioleaching by analysing the effects of natural convection and gaseous diffusion in heap leaching systems. Some operations use low-pressure air blowers at the bottom of the heap (Watling, 2006), while others use on-off irrigation; all with the same purpose in mind, to create an oxidative environment. In many cases, air is actively blown into the heap through perforated piping connected to fans installed at the foot of the heap. As the heaps/dumps are usually very big, this has to be done in as economical a way as possible. The general approach has been to

blow low-pressure (typically 7-21 kPa<SUB>g</SUB>) air through corrugated HDPE pipes buried in the ore or within inert overliner material under the ore. The air holes are usually small (1-4 mm) and tend to become blocked very quickly. Blocking of air holes is caused by fine solids and precipitates/crystals, which are carried to the air pipes by the leach solutions percolating through the heap/dump (Bouffard and West-Sells, 2009; Bartlett and Prisbrey, 1996).

Production underperformance of Girilambone Copper Company (GCC) in Australia and Compañia Minera Quebrada Blanca (CMQB) in Chile was the breaking point to adopt forced aeration to leach secondary copper sulphides. These operations recognized the role of oxygen as a critical component for leaching chalcocite. In 1996, GCC began to use forced aeration, followed by CMQB later that year as well. The significantly improved recovery of copper from an aerated chalcocite test heap at Girilambone prompted the strategy of re-mining and aeration of under-performing heaps (Lancaster and Walsh, 1997). A review of the historic production records at CMQB by Scheffel (2006) reveals that the actual forced aeration and increment of the leach volume were done at the same time; as a consequence it is unclear whether the forced aeration alone improved production. However, forced aeration of heaps has shown no statistically significant improvement in leach kinetics for ore grades less than 1.5% copper as chalcocite. Scheffel (2006) suggested that forced aeration may be beneficial in operations where the gaseous porosity (as opposed to the liquid porosity) is marginal or when the copper grade is over 1.5% as chalcocite.

Paul and Johnson (1975) patented a thin layer leaching method as a first generation effort to improve aeration within bioleach heaps. In this method, the ore sample is spread on a permeable

substrate in a thin layer about one-half to one meter thick to ensure a short diffusion part of oxygen. Castillo and Smithson (2001) introduced an air distributor for use in heap or dump leaching systems with an air pipe having a series of holes for releasing air from the pipe and one or more protective membranes spaced outwardly of the air holes to shield the air holes. Menacho (2010) patented a heap leaching aeration system for a bed of ore that is laid upon a basal layer and that has a gas source located upstream for supplying gas and aeration pipes that distribute the gas downstream to the bed. Each aeration pipe has spaced-apart gas emitters that distribute gas to the bed and the aeration pipes extend through the bed towards the basal layer. Recently, different air distributor techniques and tools have been investigated in terms of their effect on air pressure and mechanical characteristic of piping systems (Harvey, 2007; Harvey <I>et al</I>., 2007; Castillo, 2001). Sierakowski and Waddell (1995) introduced the concept of fluorocarbon fluids as gas carriers to supply air into base metal heap leaching operations. In this method, leaching of precious and base metal values is achieved by contacting a metal-bearing ore or ore concentrate with a solution of an oxidizing gas dissolved in a perfluorinated hydrocarbon liquid and thus extracting the precious or base metal from the metal-bearing ore into a subsequent aqueous rinse.

In his theoretical study of heat distribution within heaps, Dixon (2000) has clearly shown that forced aeration can significantly enhance heat management in heaps (effectively through a redistribution of heat by the upwards transport of humid air). While this may not directly benefit the reaction rate through improved oxygen supply, it indirectly enhances leaching rates through better temperature distribution within the heap (Petersen and Dixon, 2007). A large column study by Petersen et al. (2010) has also indicated that in bioleaching operations the supply of CO<SUB>2</SUB> rather than oxygen is the critical factor in designing aeration systems.

#### Ore heap density

It is not uncommon for the ore volume to compact by 5% to 20%, resulting in a slump of the lift height during the first few weeks of the leaching cycle, depending on the geology of the ore and particle size distribution (PSD) being treated. Compaction of the ore results in changes in the bulk density of the material. In return, an increased density changes all the other hydraulic properties of the ore (porosity, saturated hydraulic conductivity, capillary pressure and solution retention capacity). Ore density is a "master" variable that has significant impact on the hydrodynamic response of an ore under leach(Guzman, 2011). The ore heap density varies from that of a loose dry fill material during lift placement to a uniformly wetted, loaded, and consolidated dense granular fill over time in multiple lift heap leaching operations. The ore material generally consolidates by about 7 to 10 percent for gold and silver heaps and by about 10 to 15 percent for copper and zinc heaps. Most of the heap densification occurs within the first 15 to 30 m of ore heap fill from the bottom, although it is depends on ore type, particles size and the amount of ore on top of the consolidated section. Heap bulk density controls the physical and hydraulic response of the ore and generally varies from 1.4 to 1.9 t m<sup>-3</sup>. Typical heap moist unit weight densities range from 1.8 to 2.1 t m<sup>-3</sup> with maximum unit weight densities occurring during leaching operations (Guzman, 2011; Bouffard and West-Sells, 2009; Breitenbach, 2004; Lizama, 2001; Lancaster and Walsh, 1997; Bartlett and Prisbrey, 1996). Therefore precise integrated hydrodynamic and stacking tests are indispensable to assess the changes in bulk density as a function of overburden, simulate percolation process and define maximum lift and heap height.

# Heap operation

## Application of leach solution

### Irrigation rate

Selection of the optimum application rate requires knowledge of the range of permeability and moisture retention ability that exists within the heap. The zone of lowest permeability (often the surface layer) determines the maximum effective application rate. Application rates in excess of this will result in ponding, short-circuiting and channelling of solution, leaving areas of the heap not penetrated by the solution and hence unleached. High application rates tend to promote flow through the coarser-textured segregated material. This can lead to flooding, depriving those areas of the bed of air. In bioleach operation this will cause the bacteria to become deprived of oxygen and carbon dioxide, resulting in a decrease in microbial activity and hence metal recovery (Watling, 2006; Bartlett, 1998). Furthermore, high solution application rates will primarily dilute the PLS that leaves the heap, while not enhancing or even limiting recovery. Alternate flow rates which are actually being used in industrial applications were justified by a sensitivity analysis by Mellado <I>et al. </I>(2011). They proposed an exponential decreasing flow rate path that can be used as an alternative with the corresponding economical benefits.

Variations in the leach solution application rate can sometimes be advantageous. An example of this is with gold leaching, where decreasing the solution feed rate can offset the decrease in metal leaching that tends to happen over time. Furthermore, changes in solution feed rates may be called for due to the evolution of the heap permeability. If the solution flow rate is too low, leaching times may become too long which in turn could make a heap economically unfeasible (Watling, 2006).

The appropriate irrigation rate in heap leach operations depends on the mineral type. The irrigation rate for leaching secondary copper sulphides is limited essentially by the permeability of the heap. Since the dissolution of secondary sulphides is predominantly oxidative, flow is necessary to ensure the presence of oxidants such as oxygen in the gaseous phase and ferric in the aqueous phase. The irrigation ratio controls the colonisation and steady-rate stages of bioleaching, as well as the acid and Fe balances. The heap modelling study by Dixon and Petersen (2003) showed that chalcocite leaching is governed by acid reagent supply. Lizama <I>et al</I>. (2005) showed that if two columns of different heights are irrigated at the same rate, the shorter column receives a greater amount of reagent per mass of reacting ore in a given time period and faster reagent feed, which will result in a faster leach.

# 4.1.1.1 <B>Intermittent or pulsed irrigation</B>

Continuous irrigation is most typically applied in heap leaching. At the same time it is widely thought that intermittent irrigation favours metal dissolution. Several studies have suggested intermittent irrigation would be beneficial, especially for leaching of coarse ore beds (Muñoz <I>et al</I>., 1995; Pradhan et al., 2008). According to these, intermittent irrigation would increase the metal dissolution per unit volume of irrigation solution added when compared to continuous irrigation. In such cases, the leach solution is intermittently sprayed onto the surface of the heap and is allowed to percolate before fresh solution is applied. During irrigation, the

capillary forces draw the liquid into the mass of the ore. When irrigation ceases, the liquid drains out from the capillary and remains on the surface, and renewed irrigation carries with it the dissolved metal ion, and the process begins again with the introduction of fresh liquid into the capillary. In this way, intermittent irrigation may be more effective than continuous irrigation, since the alternate draining and drying of the capillaries is considerably faster than the simple ionic diffusion through a static capillary full of fluid.

It has been claimed that coarse ore heap bioleaching systems are more efficient during intermittent irrigation (Pradhan <I>et al</I>., 2008; Muñoz <I>et al</I>., 1995). Aslam and Aslam (1970) have demonstrated that intermittent irrigation implemented on a daily basis in the presence of microorganisms yields more copper than intermittent irrigation done once in a week. Bruynesteyn (1983) suggested that the irrigation frequency (cycle) in intermittent irrigation is determined by the rate of evaporation and the concentration of the metal in the exiting liquid phase. The most recent study done by Saririchi <I>et al</I>. (2012) considered the effects of intermittent irrigation on heap leaching systems. They claimed that more than 70 % of zinc was extracted in 80 days under intermittent irrigation, compared with conventional bioleaching which showed 50 % over a similar period. They also suggested that while intermittent irrigation was not a key parameter in leaching, it was still required to sustain and improve microbial activity in the column. This research, however, does not give explicit recovery results to support their claim and lacks the necessary validation data.

Intermediate leach solution

high acid concentration, is fed to those heaps that have been leached to greater than 50% copper recovery. The solution exiting these heaps, called "intermediate leach solution" or ILS, becomes the feed to fresher heaps from which less than 50% of the copper has been recovered, which then produce PLS suitable for SX recovery. ILS ponds effectively allow two-stage counter-current leaching and permit recovery of low-grade leach solution from towards the end of the leach cycle in the primary heap, where the acid consumption per kg copper leached (the 'leach ratio') tends Downloaded by [University of Exeter] at 01:57 24 November 2015 to increase. Through that the ILS advances and is built up into high-grade PLS in the secondary heap. Pond levels and solution grades are controlled, depending on existing conditions, by directing each individual heap effluent stream to either the PLS, ILS or raffinate drains. In staged-leaching facilities, the ILS collection pond is placed closest to the heap compared to the PLS pond. This prevents solids washed off the heaps from reporting directly to the PLS pond (Pradhan <I>et al</I>., 2008; Lizama <I>et al</I>., 2005). Wetting agents

Wetting agents are chemicals that act to reduce the surface tension of the liquids. A reduction in surface tension can result in increased flow and a more thorough wetting of the heap when wetting agents are added to the leaching solution of heap leach operations. In this way, wetting agents have the potential to produce the following benefits.

In a two-stage leach operation, the barren solution from the SX plant ("raffinate") which has a

1. Increased recovery as a result of solution flow into regions of the heap that would otherwise be 'dry zones' or unleached regions.

2. Increased solution-metal contact as a result of improved penetration into voids and cracks in the ore particles, resulting in increased metal dissolution and recovery.

3. Reduced leaching time, which in turn reduces leaching agent and pumping costs.

4. Reduced need for agglomeration or special treatment of certain ores.

Wetting agents also have the potential disadvantage of reducing metal recovery. This can occur if wetting agents form a hydrophobic layer at the solution/air or solution/solid interface and retard diffusion of the reactants to the metal surface or products away from the surface.

A number of studies have been completed on the use of wetting agents to improve heap leaching efficiency, with mixed results. Browner and Strickland (1992) found that although a given surfactant increased the rate of solution percolation, metal dissolution was reduced. Arnold and Pennstrom (1988) found that the effect of wetting agents to be dependent on ore type. Even small increases in recovery result in a very favourable return on investment because the cost of the wetting agent addition is relatively low. Frank <I>et al</I>. (1991) have patented acid leaching of copper ore in heaps with a fluoroaliphatic surfactant. Dissolving a small amount, for example 10 to 100 ppm, of the surfactant in the aqueous sulphuric acid leaching solution improves the amount of copper values leached and recovered. The surfactant is not extracted into organic medium in the SX circuit, and does not cause a stable emulsion to be formed during extraction.

Efficient heap bioleaching requires the presence of an effective and appropriate indigenous bacterial population. Bacterial inoculation with the leach liquor cannot be effective, since many organisms are naturally adherent to the ore particle surfaces and do not penetrate to the interior depths. The StickiBugs<sup>™</sup> approach (Gericke <I>et al., </I>2005) as an inoculation strategy with a surfactant additive has been introduced by Mintek. The StickiBugs<sup>™</sup> process is capable of generating a sufficiently large population of desirable bacteria and to facilitate attachment to inner depths of heaps. Bacterial activity can thus be enhanced following effective inoculation. The StickiBugs<sup>™</sup> process prevents the desirable bacterial population from remaining at the top of the heap and facilitate their penetration into the heap. The process relies on the fact that bacteria lose their adhesion tendency if deprived of an essential nutrient.

#### Curing and leach/rest cycles

Curing is a pre-treatment in which concentrated sulphuric acid is added to a crushed ore either on a belt conveyor or in an agglomerating drum to start reactions with acid soluble copper and gangue minerals. If done in rotating drums, this agglomerates the fine material with larger particles ensuring acidification and wetting of the ore prior to stacking (Watling, 2006). The first patent on curing was related to the cleaning of molybdenum ores from copper sulphides by adding sulphuric acid at its boiling point (Morgan, 1933). Another publication was related to the curing of uranium minerals (Smith and Garrett, 1972) using 10% acid solution at 95 <sup>o</sup>C. The thin layer leaching method (see section 5.4a) includes acid curing prior to leaching (Paul and Johnson, 1975). The patent mentions several beneficial effects of curing, including generation of metal salt crystals that enhance bed permeability, crack generation which enhances diffusion of solutes within the ore particles and accelerates leaching. It also supports dehydration and carbon dioxide evolution from carbonate gangue. Farlas <I>et al.</I> (1995) have shown that copper oxides such as malachite and chrysocolla react with concentrated sulphuric acid to form copper sulphate crystals. After the curing period, subsequent leaching with raffinate easily dissolves the copper sulphate. A process for ferric curing of copper sulphides was patented by Fountain (1997) in that a heap is leached with PLS from an associated dump leaching operation. The use of dump PLS ensures high ferric concentrations. According to Fountain (1997), ferric curing can be conducted using more than 10 g/L of ferric.

Leach/rest cycles can also improve the economics of leaching, especially in the case of older heaps. During the periods of no irrigation, stagnant solution remains in a fraction of the void spaces and the dissolution of valuable metal species will continue in this liquid. When irrigation is recommenced, the liberated metal ions that have built up in the stagnant solution are washed out of the heap. In this way a limited flow of high-grade pregnant liquor can be economically maintained. This cyclical approach can dramatically reduce the operating costs for irrigation (pumping) and metal recovery from the PLS, as its grade will be higher (Guzman, 2011; Burgmayer, 2002; Lane, 1999). In principle, however, rinse/rest cycles are the same as intermittent irrigation, except the cycle time is longer.

#### Heat transport

Heat generated by exothermic chemical reactions in a heap is transported via convection by the gaseous and liquid phases, and via conduction through the heap solid mass. The accumulation of heat in the heap is determined by the balance of the heat of reaction during leaching, heat transport downward with the flow of warm water and heat transport upwards through the flow of water vapour with the rising air as well as boundary conditions such as insolation at the heap surface (Petersen and Dixon, 2007; Dixon, 2000).

In heaps in which the aeration rate is small, the temperature inside the bed increases with increasing depth. The highest temperature zone is located near the bottom (Moreno <I>et al</I>. 1999). Several investigators have done heat balances around dump and copper sulphide heap leaching operations (Mellado <I>et al</I>., 2011; Leahy <I>et al</I>., 2007; Dixon 2003; Petersen and Dixon, 2002a; Brierley and Briggs, 2002; Betty, 2000; Dixon, 2000; Marsden <I>et al</I>., 1995). Heat transport is especially important in copper sulphide heap leaching, in which one or more highly exothermic sulphide oxidation reactions take place, for several reasons. First, the bacteria, which catalyse the oxidation reactions, are sensitive to temperature. Secondly, many oxidation reactions central to copper recovery from secondary ores are strongly temperature-dependent. For example, arguably the oxidation of so-called blue remaining covellite, or blaubleibender, which is the intermediate product of chalcocite oxidation, has a high activation energy and its rate of dissolution is therefore strongly temperature dependent (Dixon, 2000).

A number of methods have been described in respect of generating heat in a heap:

• Acid conditioning of ore using hot water to add heat to the heap and promote more rapid oxidation (Schnell, 1997);

• Increasing the heat-generating capacity of the heap with, for example, additional sulphides (Kohr et al., 2002);

• Heat transfer to heap irrigation solution via a flexible, heat-absorbing distribution mat with parallel spaced emitter tubes (solar heating) (Lane, 2000);
- Heat transfer to heap leach solution from another process (Batty and Norton, 2003; Schnell, 1997).
- Aeration with humidity and temperature control to maintain a heap environment suitable for thermophiles (Winby and Miller, 2000);
- Managed aeration and irrigation to maximise heat conservation in the heap (Norton and Crundwell, 2004); and
- Addition of carbon (carbonate, carbon dioxide, organic carbon) to the heap to enhance microbial growth and activity at temperatures above 60 °C (du Plessis and de Kock, 2005).

The two main operational controls, that facilitate the management of heat retention in a heap, are air flow and irrigation rates. Irrigation rates have direct or indirect beneficial effects on microbial activity and thus heat generation. Reduced irrigation rates cause increased gradient effects and may result in the accumulation of soluble salts and the development of high osmotic potentials, both of which could have a detrimental impact on microbial activity (du Plessis <I>et al</I>., 2007).

Dixon (2000) presented a fundamental model of heat flows within a heap reactor, indicating the ratio of irrigation to aeration is a critical parameter in the distribution of heat. In later studies (Petersen and Dixon, 2007; Dixon and Petersen, 2003) this heat model was integrated with a heap reactor model and clearly identified critical operating ranges in which heat retention in heaps would be maximised. Leahy <I>et al</I>. (2005) confirmed in a separate modelling study that copper will be extracted faster at a higher liquid flow rate at a fixed aeration rate. This is a

result of the fact that a faster liquid flow rate causes more cooling and allows microorganisms to survive in greater numbers, leading to higher Fe<sup>3+</sup> concentration and hence faster copper extraction (Leahy <I>et al</I>., 2005). This finding is, of course, dependent on whether excessive heat is generated in a heap or whether heat retention is the key for maintaining desired high temperature conditions for chalcopyrite leaching, as indicated by the column tests by Petersen and Dixon (2002b). HotHeap<sup>™</sup> is a biological heap leach operating philosophy coupled with an instrumentation and control system that maximizes heat conservation and thus bioleaching kinetics. The HotHeap<sup>™</sup> control system was patented by Crundwell and Norton (2002) and goes back to original model by Dixon (2000).

#### Heap Height

Generally, the higher the height of a heap, the lower is the permeability in the lower zones and therefore the maximum operating irrigation rate. However, there can be substantial process or operational benefits in operating at a higher heap height, such as reduced operating costs in multi-stacking. Reducing the heap height not only affects the distribution of acid within a heap, but also affects heat generation and hence temperature distribution. A shorter heap effectively has less volume per unit area footprint, within which heat is generated, and therefore heat is removed more easily without raising temperatures as high as in a taller heap (Petersen and Dixon, 2007). Padilla <I>et al</I>. (2008) showed that an inverse relation exists between the height of a heap and its rate of extraction. This was further confirmed by the observations of Lizama <I>et al</I>. (2005).

Padilla <I>et al</I>. (2008) suggested that the heap height and the leaching time had the greatest effects when determining the most optimal circuits. They suggested that the optimum, from an economic perspective, does not necessarily represent maximum recovery, and that the copper concentration of the outflow solution from the heap is not a good indicator of maximum extraction. Heap height does not remain constant after leaching is started due to collapse or slumping of the bed. This slumping causes a decrease in the bed voidage and permeability (increase in bulk density) which can affect the gas and liquid flows (Wu <I>et al</I>., 2009; Lizama <I>et al</I>., 2005).

#### Solution management

Management of leach solutions is an important part of a heap leach operation, both to maximize metal recovery and to prevent the loss of reagent bearing solution to the environment. The selection of a particular solution management system for a heap leach facility will change according to design criteria established from metallurgical testing and the ore production and processing cycle. Depending on the types of and grades of ore materials to be treated using heap leaching, either single or multi-stage leaching will be required to maximize value metal recovery from the heap. The design of solution pond capacities is predicated on: the tonnage of ore to be processed per month or annum, the leach cycle time, solution application rate, the area under leach, the exposed lined area of pad not stacked with ore, total ore tonnage to be stacked on the leach pad and final height of stacked ore. Ponds are sized to have sufficient capacity to allow operators flexibility to optimize processing of the pregnant solution and safely to manage the

liquids in cases of power outages and major rainstorm events (Guzman, 2008; Schlitt, 2006; Sánchez-Chacón and Lapidus, 1997).

Storm water ponds should be kept empty and not used as make-up water storage facilities. Common design practice is to have the following ponds, located downslope of the heap: PLS pond, BLS pond, Pregnant Pond Bottom (Double Geomembrane), ILS, Overflow/Stormwater Pond (standby for emergencies), Detoxification pond (standby for emergencies). Considering that the pregnant solution is the most valuable asset of the mine operation and for environmental protection purposes, current design practice for ponds is to install double layer of composite liner system fitted with leak detection pipes and pumps (Ilankoon and Neethling, 2012; Domic, 2007; Readett <I>et al</I>., 2006). The aeration requirements may also adversely affect both the water and heat balances in the heap, assuming that the air exiting a heap or dump is saturated air at the operating temperature of the heap. Therefore, blowing an excessive amount of air will evaporate a substantial amount of water. This will increase make-up water requirements. In addition, Schlitt (2006) has postulated that evaporation will remove a significant amount of heat which could lead to significant cooling in the heap, thus retarding the leaching rate. On the other hand, Dixon's (2000) work has shown that air cooling may in fact be necessary to avoid over-heating the heap, especially bio-heaps. Aeration rates high enough to result in over-cooling of the heap are unlikely to be applied in operational practice due to limited permeability of heaps to air flow.

Overall evaporative losses include the sprinkler losses, convective loss from air flowing through the heap, and losses due to heating/evaporation from ponds and from other areas not sprinkled. These have been determined at several Nevada operations to be up to 20% of total solution

pumped in summer months and 10% annually, with direct sprinkler losses accounting for about 60% of that (Schlitt, 2006). Use of drip irrigation can reduce but not eliminate evaporative loss. In tropical climates, noticeable losses occur even during the rainy season. The pipes and emitters are typically covered with a thin layer of ore, which allows for operation in very cold climates (prevents freezing) as well as very hot climates (minimises evaporation). Where rainfall is high and evaporation rate is low, some operations (such as at Yanacocha, Peru, altitude 3500 meters) cover the side slopes with plastic to minimize rain collection. Others (Rio Chiquito, Costa Rica-Mallon Minerals Corp) have tried to cover the entire heap during the rainy season, but this has not worked very well because of the mechanical difficulties of moving the cover (Domic, 2007; Schlitt, 2006). In West Africa and Central America it is acceptable practice to treat and discharge excess solution during the rainy season. The worst water balance situation occurs in cool, damp climates such as high altitude operations. In such climates, rainfall and snowfall may be significant and evaporation is minimal. In areas of high seasonal rainfall, PLS can be significantly diluted and excess solutions must be retained in storage ponds to be used during periods of high evaporation. Spray irrigation may have to be used to enhance evaporation of excess solution, but this can be counter- productive, or incompatible with heap permeability as discussed in the section 4.2.3. Site drainage of storm run-off is a critical component of any pad design.

Plastic balls or other floating devices, such as Hexa-Cover® cover (Hexa-Cover, 2014), that cover the entire surface of process ponds, are quite effective tools to minimize evaporation mostly in the dry areas such as the North of Chile. These, together with netting or the use of air

cannons also help to minimize direct access of migratory birds to the ponds (Gunson et al., 2012).

Wick drains, commonly known as Prefabricated Vertical Drains or PVDs, are prefabricated strips of flexible polypropylene, have recently been applied for improvement of drainage from heaps which contain clay minerals. This technology has been used in some of the Freeport-McMoRan operations including El Abra (Chile) and Safford (USA) (Todd, 2014; Alexander <I>et al</I>., 2013). The technique is very promising but further development is required to refine the conceptual integration of wick drains into the process of heap design.

A further aspect that needs to be kept in mind is that, when the heap leaching cycle has been completed, the remaining moisture within it – typically 5 to 8% – is abandoned or disposed of along with the ore. As this solution may still contain significant concentrations of dissolved value metal, this presents a considerable operational loss (Guzman, 2008; Sánchez-Chacón and Lapidus, 1997). Another concern regarding solution management is the temperature of process solutions as they collect in the ponds. Low solution temperatures can retard the extraction rate leading to inefficient recovery during SX. This is often overlooked in column testing, which is typically done under warmer ambient conditions at the laboratory (Domic, 2007; Schlitt, 2006; Readett <I>et al</I>., 2006).

Heap covers and heat shields

Raincoats are becoming much more common in the industry as mine sites employing heap leaching move increasingly into wetter climates. Many new operations are already located in or planned for the tropics, including northern Peru, equatorial Brazil, Central America, Philippines and West Africa. High rainfall dilutes operating solutions and surplus water can trigger the need for significant water treatment costs (Thiela and Smith, 2004). Raincoats serve the dual purpose of reducing water entry into the process circuit and related issues of dilution of reagents and surplus water balance, and protection of the surface of the heap from erosion and damage to the agglomerates (Breitenbach and Smith, 2007).

In a commercial heap, which typically has an effective perimeter length of several kilometres, the heat loss through the side walls is negligible compared to the heat generated within the bulk of the heap. In a high temperature heap leach, where the average ore temperature is greater than 50<sup>o</sup>C, the principal heat losses occur in two areas: a) at the base of the heap where warm solution drains out of the ore and relatively dry cool air enters the ore; and b) at the top of the heap where irrigation solution is distributed on the ore surface at a relatively low temperature, hot saturated air leaves the ore surface and heat loss from the surface to the surroundings occur. The latter, for example requires that in n cold climates the heaps must be protected against freezing (Saari and Riekkola-Vanhanen, 2011).

Several options have been considered for conserving this lost heat, and thereby increasing the internal temperature of the heap, including (Mellado <I>et al</I>., 2011; Dixon, 2000; Schnell, 1997):

- Decreasing the solution irrigation rate;
- Increasing the aeration rate;

• Installing an evaporation shield to the heap surface; this reduces the effective surface heat transfer coefficient and resulting heat losses and increases the average heap temperature. Recent industrial practice has seen heaps being covered with plastic sheeting;

- Heating the irrigation solution; and
- Heating the air, with and without humidification, in the aeration system

Energy issues play a key role in the economical aspect of the heap design process, and most heap operations are in remote areas. Using solar heat as an energy source for the heap leaching of minerals has been investigated and patented with different researchers and companies (Hernandez <I>et al</I>., 2011; Eksteen <I>et al</I>, 2012; Renato and Flavia, 2006; Lane, 2001).

# Heap leach test work

The testing of ores for heap leach amenability is relatively complex and needs proper planning of the programme and outcomes. The amount of testing necessary to determine and optimize heap leach amenability and conditions for any feed material is determined by the ore type, grade, size of deposit, and the overall financial commitment a particular company is willing to make. It is very easy to either "under-test" or "over-test" a particular deposit or feed material. Heap leaching has inherent risks that can be largely eliminated if the operating practice is informed by initial and on-going laboratory testing. The performance of the process is usually not known for several weeks or months after the ore is stacked, and at this point, it is not economical to reprocess the ore. Mistakes made in the initial plant design or operating practice, for instance by not crushing finely enough, or by not agglomerating or stacking properly, can result in cash flow problems that might persist for up to a year after the problem is solved. During production, laboratory tests, including column leach tests, should be continued on a regular basis, since the initial ore samples are seldom representative of the entire ore body as it is stacked on the heap over time. Table 6 shows heap leach test work with typical progress in phases and aims (de Andrade Lima 2006; Varas and Videla, 2003; Kappes 2002; Baum, 1999; Carter, 1999; Garcia and Jorgenson, 1997).

A soluble metal test is necessary to assay and establish the achievable recovery. Test methods depend on the valuable metal to leach. Bottle-roll or shake-flask tests are normally performed first, to obtain an initial indication of maximum achievable extraction and acid consumption. However, the latter are normally overestimated in rolling bottles; hence the acid consumption results must be treated as only semi-quantitative. Also, the continuous tumbling of ore particles in the bottle results in attrition, leading to higher extraction from increased particle surface.

The purpose of a column leach test is to collect information (recovery vs. time) on the ore being evaluated against which scale-up to industrial scale can be validated, allowing a projection of the commercial heap leach performance under different operating scenarios. The columns provide more accurate extraction and acid consumption data under trickle bed conditions, as well as an initial indication of potential percolation problems (Bouffard and West-Sells, 2009). Test columns used in the literature vary widely in height, from as little as 50 cm up to 6 m and in diameter from 10 cm to 2 m. Petersen and Dixon (2003) compared the leaching in columns of different height and found that short columns would leach faster due to the fact that there were

no reagent supply limitations. Similar results were obtained by Lizama <I>et al</I>. (2005). Recoveries at the column test stage are often much higher and faster than would be found in full scale practice. This is largely because of the following reasons (Varas and Videla, 2003; Kappes 2002; Baum, 1999; Garcia and Jorgenson, 1997; Potter, 1981):

- The ore is packed more uniformly in columns than it would be in a heap;
- Wall effects: larger porosity near the column wall facilitates solution and air channelling.

In order to eliminate any wall effects in the leach column, and consequently preferential solution and gas flow channels, ore samples should be sized correctly, based on the size of column diameter. Since the kinetics and pregnant leach solution composition vary with lift height in commercial size heaps, a more realistic indication of leach kinetics and impurity build-up is obtained in taller columns, at a lift height equivalent of an actual heap (typically 6 metres). A problem with column test work is that internal heat generation is too low relative to heat losses through the column walls to achieve any significant self-heating. During column tests actual heap temperatures need to be estimated and controlled through external heating. A new simulation apparatus patented by BHP Billiton SA Limited (van Buuren, 2003) consists of a sixmetre tall simulation column (trademarked as SimCol<sup>TM</sup>) with temperature controlled insulation (i.e. heat losses are eliminated by heating the outside of the column to within a degree lower than measured on the inside) to circumvent this problem. Further detail of this column design is discussed in section 6.1. Cribs are big concrete boxes, generally with one side closed by pieces of wood that allow loading of material without compaction, and unloading by sections to analyse residues (recoveries vs. heap heights). Generally these are used in copper mines to emulate a rectangular section of an industrial heap, to reduce the risk of scale-up. A pilot heap is a large scale heap test and commonly contains between 5,000 to 50,000 tonnes of ore (depending full scale operation size and ore type) and is tested in closed cycle at the optimum conditions indicated by column and cribs testing, at preferred height and stacking method (de Andrade Lima 2006; Varas and Videla, 2003; Kappes 2002).

1. <B>Applications</B>

5.1 <B>'Classic' Au-CN</B>

Heap leaching has been employed for gold ores since the late 1960s and is gaining increased interest throughout the world, especially for exploiting low-grade ores, mine waste materials, or deposits too small to justify the construction of a conventional milling and recovery facility. Heap bioleaching has been commercially applied in the pre-treatment of gold bearing ores where the gold is occluded in sulphide minerals (Brierley 2008; Watling, 2006). Although the conventional processing plants still produce relatively more gold, the successful application of heap leaching to the extraction of gold from low-grade deposits has been one of the main factors contributing to higher output, especially in the United States. Heap leaching accounts for the majority of operations in the western U.S. As a result of this interest, new developments and major advancements in heap leaching technology continue to come forth, with heap leaching accounting for about 25% of primary mine produced gold and 10% of primary silver (Marsden

and House, 2006; Kappes, 2002; La Brooy <I>et al</I>. 1994). Table 7 shows historical and present commercial gold heap leaching plants.

## 'Classic' Cu-Acid and Cu sulphides (bio) leach

Heap leaching of oxide copper ores with copper cathode recovery by SX-EW is now well established as a low-cost method of copper recovery. This technology has been commercially applied also in the leaching of secondary copper ores that contain copper sulphides such as chalcocite (Cu<SUB>2</SUB>S) and covellite (CuS) (Brierley, 2008; Readett <I>et al</I>, 2006; Watling, 2006). Not surprisingly, the heap leaching of chalcopyrite, both the most abundant and the most refractory copper sulphide, is a key industry target and currently there are significant development efforts underway to try to extend heap leaching to low-grade chalcopyrite ores. In many cases the mineralogy of ore body changes from oxides to mixed, secondary and primary with mine depth. This indicates that a mining process plan which includes heap operation must be flexible enough to allow joint treatment of ores with diverse mineralogy, including oxide and sulphide species.

Table 8 shows the historical commercial copper heap and dump leaching operations.

For oxide ores, Cu recoveries are typically in the range 75-95% within 30-100 days. On-off heaps (see section 4.2.1) are now also used in the leaching of oxide ores as well as sulphide ores rather than the original permanent heaps. A secondary sulphide heap leach requires air injection into the heap to promote bacterial oxidation, and leaching rates are much slower and less predictable with leach times, typically in the range of 250 to 600 days to achieve 80-90% Cu

extraction. Currently about 20% of the world copper production is produced from heap leaching of oxide copper and, more recently, chalcocite ores (Augustin <I>et al</I>., 2012; Pradhan <I>et al</I>., 2008; van Zyl and Bronson, 1994) (Table 9 for heap and Table 10 for dump leaching). Most of these operations are in Chile, USA and Australia.

# 'Classic' Uranium

While heap leaching was introduced in the uranium industry in the 1950s, when Portugal began to use the technology for extraction of uranium from low-grade uranium ore (Scheffel, 2002), its use waned as environmental concerns and low commodity prices made extraction of low-grade material unattractive, as there were large amounts of high-grade uranium ores suitable for conventional processing at that time. As the high-grade uranium ores have been consumed, many countries have turned to heap leaching for extraction of uranium from low-grade ores (Alta, 2011; Taylor, 2007; Carlsson and Büchel, 2005; Scheffel, 2002; Shakir et al., 1992).

Future uranium heap leach projects will benefit from the extensive heap leaching experience gained in copper and gold heap leaching, including strong acid cure, heap construction techniques and operating strategies. At present, commercial operations use acid leaching, although it is reported that alkaline heap leaching has been tested in China, and could be worth investigating for high acid consuming ores (Alta, 2011; Taylor, 2007, 2009). Bacterial heap leaching is also being investigated for more complex, low-grade uranium ores (Gericke et al., 2008).

Current projects focusing on acid-based heap leaching include those at Ranger in Australia, Rössing in Namibia and Somaïr in Niger, while the first commercial use of alkaline leaching was operational only temporarily at Areva's Trekkopje mine in Namibia in 2012 before the plant was put on 'care and maintenance'. Carbonate leaching of uranium ores offers the possibility of using binders, such as cement, when agglomeration of fines is needed (Taylor, 2007). With uranium ores, the additional key benefit of agglomeration or wetting the ores as soon as possible is reduction in the dust emissions from conventional dry crushing circuits, which will provide a cleaner and safer operating environment. Agglomeration is an integral part of new and future heap leaching uranium operations (Alta, 2011).

# **Emerging processes**

#### **BTL** Process

An important breakthrough in bioleaching technology has been the process developed by Sociedad Minera Pudahuel (SMP) in Chile, named the bacterial thin layer leaching Process (BTL). This process has been applied at their plants of Lo Aguirre and La Cascada. The tin layer (TL) process patented by SMP (Domic, 1984; Rauld <I>et al.,</I> 1986) appears based on the patented process by Paul and Johnson (1975). Originally thin layer leaching was developed to process copper oxides, but it was subsequently modified to accommodate an increased contribution from sulphide minerals in the ore (Montealegre <I>et al.,</I> 1995). The key features are (i) curing, in which concentrated acid is added to the crushed ore and reacts with acid soluble and gangue minerals, and (ii) consolidation of fines with larger particles in a rotating

drum, which ensures even acidification and wetting of the ore prior to stacking. In those cases where organic-free raffinate is used for curing/acidification, bacteria may also be distributed through the ore before it is stacked in carefully designed heaps so as to create a bed that exhibits good permeability for both solutions and gases. Typically, a short-duration acid leach (18 days) recovers 80% of copper from oxides, and between 30 and 40% of copper from bornite and chalcocite. The transition to a heap bioleach is accomplished by constructing heaps of the acid-leached, crushed ore (100% less than 6 mm particle size) stacked to 5–6 m high. Solution pH is controlled to ~1.8 to optimize bacterial activity. Leach effluents typically contains 2–3 g/L total soluble iron, 20–30 g/L sulphate and ~10 <sup>6</sup> bacterial cells/mL. Temperatures inside the heap are in the range 12–27 °C. Leach duration is markedly longer than that required for the oxides, and typically ranges from 150 to 210 days for 75–80% recovery of copper from bornite and chalcocite.

## GEOCOAT<sup>™</sup> and GEOLEACH<sup>™</sup> Process

GeoBiotics, LLC have developed and patented several technologies for biooxidation or bioleaching of sulphide ores and concentrates in an engineered heap environment. The two principal technologies are the GEOCOAT<sup>™</sup> and GEOLEACH<sup>™</sup> processes (Harvey et al. 1998; Harvey and Bath, 2003). Both technologies incorporate the patented HotHeap<sup>™</sup> control philosophy to ensure optimum biological performance. In the GEOCOAT<sup>™</sup> process, sulphide flotation or gravity concentrate slurry is coated onto crushed and sized support rock, which may be barren or may contain sulphide or oxide mineral values. The coated material is stacked on a lined pad for biooxidation. The process is applicable to the biooxidation of refractory sulphide

gold concentrates and to the bioleaching of copper, nickel, cobalt, zinc, and polymetallic base metal concentrates. Mesophilic or thermophilic biological systems are used to catalyse the sulphide oxidation reactions (Petersen, 2010; Petersen <I>et al., </I>2010). A commercial GEOCOAT<sup>™</sup> plant was built at the Agnes gold mine In South Africa in 2003. In Australia, GBS Gold has entered into a License Agreement with GeoBiotics for the use of the GEOCOAT<sup>TM</sup> refractory ore treatment process at its Union Reefs operations centre in Northern Territory to treat refractory gold concentrate (Harvey and Bath, 2003). For the leaching of whole ores GeoBiotics has developed the GEOLEACH<sup>™</sup> bio-heap leaching process for sulphide ores which, for, as they claim, modest capital expenditure, will enable existing acid leaching of sulphide ores, significantly increasing copper recovery and reducing leach time on the pad. The GEOLEACH™ technology is designed to maximize heat conservation through careful control of aeration and irrigation rates. Construction and commissioning of a GEOLEACH™ demonstration plant started in 2009 at the Quebrada Blanca copper mine in Chile. The driving force behind the GEOLEACH<sup>™</sup> process is that most sulphide whole ore leaching systems have enough energy present in the sulphides to allow the heap to obtain very high temperatures, but poor heat management prevents significant temperature rise. Both the processes are simple, robust, and ideally suited to operation in remote locations (Soleimani <I>et al</I>., 2011; Pradhan <I>et al</I>., 2008; Harvey and Bath, 2003; Johansson <I>et al</I>., 1999).

# BIOPRO<sup>™</sup> technology

The patented BIOPRO<sup>™</sup> process involves heap inoculation during acid conditioning and agglomeration, (Brierley, 1997) and has been implemented for the biooxidation of refractory

gold ores prior to gold extraction. Newmont has used the capabilities of mineral oxidizing microorganisms to develop a process for the pre-treatment of lower grade (0.09-2.0 g/t of gold) sulphidic refractory gold ores at Carlin. The bio-oxidation process results in the oxidation of sulphidic minerals with increased exposure of gold for subsequent gold recovery. Development of Newmont's patented bio-heap technology (BIOPRO<sup>TM</sup>) to treat low-grade refractory gold ores began in 1989 and involved many laboratory column tests, pilot plant tests and large-scale demonstration plant tests in the late 1990s. The biooxidation heap pre-treatment process involves crushing ore followed by applying a solution containing the microorganisms to the ore, as the ore is stacked on plastic lined pads (Dunne <I>et al., </I>2009; Brierley <I>et al</I>, 1995; Simmons, 1994).

# Thiosulphate leaching- an alternative to cyanidation in gold processing

Thiosulphate has been considered as an alternative lixiviant for gold due to the growing environmental and public concerns over the use of cyanide. Acceptable gold leaching rates using thiosulphate are achieved in the presence of ammonia with cupric ion acting as the oxidant (Abbruzzese <I>et al</I>., 1995; Cao <I>et al</I>., 1992; Gong et al., 1993; Langhans <I>et al</I>., 1992; Tozawa <I>et al</I>., 1981). Interest in the use of non-cyanide methods for dissolution of gold is due to increasing concerns regarding the toxicity of cyanide and the inability of cyanide solution to effectively leach carbonaceous or complex ores. Newmont developed this technology for the recovery of gold from low-grade carbonaceous sulphidic refractory ores that contained preg-robbing material (Wan <I>et al., </I>1993). A combined bio-oxidation-thiosulphate heap process for high-sulphide ores and a direct thiosulphate leach

process for the low-sulphide ores, followed by RIP gold extraction, have been developed by SGS to the point where it is a technically and economically viable alternative to cyanidation for some gold bearing ore bodies (www.sgs.com/mining). A method for thiosulphate leaching of precious metal values from precious metal ores has also been introduced as a patent by Clayton (1993), which was later modified by Hackl (2002). Thiosulphate leaching can be considered as a nontoxic alternative to conventional cyanidation (Wan and Brierley, 1997; Wan, 1997). Although not as aggressive a leaching agent as cyanide, thiosulphate offers several technological advantages, including its lower toxicity and greater efficiency extracting gold associated with preg-robbing ores. Leaching by thiosulphate suffers from less interference by cations such as lead, zinc, and copper. In some cases, the gold dissolution rates can even be faster than for conventional cyanide treatment. The main disadvantage of thiosulphate, however, is reagent consumption and the lack of a suitable gold recovery method. Thiosulphate in the presence of oxygen in solution can leach gold. However, without the presence of ammonia, passivation of gold occurs through the breakdown of thiosulphate to form a sulphur coating on the gold particles. Copper (II) is also required to significantly increase the rate of gold dissolution. Despite the multitude of papers in this area, industrial applications where thiosulphate is used instead of cyanide are apparently limited to a silver ore plant in Mexico (Wan, 1997). Once a retrofitted thiosulphate leach circuit goes into full-scale production in 2014, Barrick Gold's Goldstrike mine will be the largest scale use of the alternative lixiviant in the world (CIM, 2014). Research has shown that some ores are well suited to thiosulphate leaching, while others show hardly any extraction. The solution chemistry and the mineralogical factors affect the

effectiveness of ammoniacal thiosulphate systems. The chemistry of the ammoniacal

thiosulphate system is very complicated due to the simultaneous presence of complexing ligands such as ammonia and thiosulphate, the cupric-cuprous (Cu (II)-Cu (I)) redox couple, and the possibility of oxidative decomposition reactions of thiosulphate involving the formation of additional sulphur compounds such as tetrathionate (Kerley, 1983). The presence of sulphides can affect the above series of reactions. Since modern gold and silver leaching has been moving to very complex ores, the successful application of thiosulphate leaching depends not only on the dissolution behaviour of gold and silver, but also critically on the behaviour of the associated minerals (Feng and Van Deventer, 2002; Wan and Brierley, 1997; Wan <I>et al</I>, 1993).

#### AmmLeach

Alexander Mining have developed a new ammonia heap leaching process for copper oxide deposits at their Leon copper project in Salta Province, northwest Argentina. There is significant potential for its use on other base and precious metals. Initial laboratory test work results for zinc are highly promising, with the potential for a breakthrough in the development of a new low-cost SX-EW processing route. In addition, it has the potential for a major breakthrough in the processing of previously untreatable zinc oxide deposits, with the development of the first heap leach zinc mines (Wana and LeVier, 2003). Alexander Mining has secured a patent for its ore processing method of ammoniacal leaching in the Democratic Republic of Congo (DRC) to process copper and cobalt oxides (Balashov, 2012). The process uses ammonia-based chemistry to selectively extract metals from ores. The difference from acid leaching is that the leaching is conducted in moderately alkaline solution with ammonia present as a complexant. The use of alkaline conditions allows the use of AmmLeach on high-carbonate ores where acid consumption

would be prohibitive. The process has an extremely high selectivity for the target metal over iron and manganese, which are insoluble under AmmLeach conditions. Calcium solubility is also significantly suppressed by the presence of carbonate and extremely low sulphate levels in the leaching solutions. These features ensure that there are no potential problems due to jarosite or gypsum precipitation reducing permeability in the heap or scaling problems in the SX plant. Additionally, silica is also insoluble in the process, removing problems associated with formation of unfilterable precipitates common within an acid leach process during pH adjustment and the handling of high viscosity solutions. Ammonia, unlike acid, does not react with aluminosilicates and ferrosilicates, whose products can cause drainage and permeability problems in heaps (Welham, 2007; Wana and LeVier, 2003). In theory, all the ammonia can be recovered; however, Dutrizac (1981) found losses of 5% to 20% when he investigated the ammoniacal percolation of chalcopyrite in a column. Ammonia losses appear to be the most significant technical barrier to commercial adoption of the process. The solubility of NH<SUB>3</SUB> in water will increase with decreasing pH and is reduced at higher pH, and it has a low vapour pressure at ambient conditions. In heap leaching, it might be difficult to see how the need for good gas circulation for oxygen transport is compatible with the requirement to minimise ammonia evaporation (Muzawazi and Petersen, 2015). Decommissioning of the heap is extremely simple as no neutralisation is necessary and the potential for acid mine drainage is virtually eliminated. Alexander Mining believes the following metals are particular targets for the AmmLeach process (Welham, 2007; Wana and LeVier, 2003):

• Copper and silver in stratabound carbonate and weathered oxide deposits;

- Zinc in mixed oxide deposits;
- Nickel and cobalt in lateritic deposits;
- Gold, silver and copper in leached porphyries; and
- Polymetallic base metal deposits, especially uranium.

#### Cuprochlor<sup>®</sup> Process

Antofagasta Minerals plc and Lakefield Research Ltd have developed and patented a chlorideenhanced heap leach process called "Cuproclor" that uses NaCl or CaCl<SUB>2</SUB> additions to generate the lixiviant. The Cuprochlor® Process can be used on a variety of ore types including oxides, mixed oxide and sulphide ores, as well as sulphide ores containing chalcocite, covellite and bornite. The Cuprochlor® process was implemented in Minera Michilla (MIC) in 2001 and is operating to date, to leach copper sulphide minerals (Aroca <I>et al</I>., 2012). The most distinctive feature of the Cuprochlor® Process is the addition of calcium chloride salt (CaCl<SUB>2</SUB>) in the agglomeration step, which improves the properties of the stack and provides a chloride medium for the leaching. The process consists of the fine crushing of copper ores followed by agglomeration using calcium chloride and sulphuric acid. The calcium chloride is dissolved in water and mixed with the ore where it reacts with the sulphuric acid to form gypsum and chloride ions. The chloride ions stabilise copper ions within the heap, and catalyse the formation of ferric ions which in turn liberate copper from copper sulphides. The pregnant solution then undergoes SX-EW. According to Antofagasta Minerals, the process offers a number of advantages over bacterial leaching, including higher recoveries and lower leaching times. In column tests, Cuprochlor® recovered almost 65% of the copper after 50 days compared with bacterial recoveries in the region of 37% over the same time period. At Michilla, using some 12 kg/t of calcium chloride, the mine achieved copper recoveries of 90% within 120 days (Aroca <I>et al</I>., 2012). As is discussed in section 3.2.4, BHP Billiton has made significant progress in the area of chloride heap leaching, with promising results and process development, but most of these studies have not been published due to company confidentiality policies.

#### BioSigma Technology

In 2002, Codelco Chile and JX Nippon Mining and Metals Co. created BioSigma to foster strategic collaborations with universities, research institutes, engineering companies to develop bioleaching technologies in the mining industry. Bioleaching technologies developed by BioSigma SA use microorganisms adapted to live on the extreme conditions presented on heaps and dumps used on copper mining. Since 2005, promising results at the laboratory scale lead to their validation as processes with stacks of 2,500 tonnes of sulphide minerals at Chuquicarnata, Codelco Norte and in 2012 in a 50,000 t heap of primary low-grade sulphide ore in the Andean Division. The application of BioSigma Technology improved the copper extraction rate by 30 to 50 percent (BioSigma, 2014; COCHILCO, 2014). Based on the favourable results of the above industrial test, Codelco recently decided to introduce BioSigma technology in the Radomiro Tomic mine. In the initial phase the technology will be applied to 3.6 million tons of low-grade primary copper sulphide ores. Now that the mine is becoming exhausted of oxide ores to which conventional hydro-metallurgical process can be applied, the decision to apply the new

technology will extend the operating life of the mine. However, besides these claims and the demonstration trials it remains unclear what the specific achievements over and above conventional heap bioleaching have been to date using BioSigma technology.

Others

#### Commercial Nickel heap operations

Approximately 65% of global nickel production comes from non-laterite or sulphide nickel ores; however, 75% of the known nickel "in the ground" is contained in laterites, and production from laterites is expected to exceed non-laterites in the coming decade. Heap leaching of nickel laterites (Readett and Fox, 2010; Taylor, 2009) has become more attractive lately for the same reasons it did in gold, silver, and copper and appears to be moving into commercial practice. The main concerns with nickel laterites are the high acid consumption, potential breakdown of the aggregated mineral structures and that nickel is highly integrated into the laterite ore, which requires that the mineral structure to be decomposed completely to extract the nickel. In addition, as with gold and copper ores, too much clay will cause the solution to channel through the ore and not thoroughly soak the heap (Saari and Riekkola-Vanhanen, 2011; Taylor, 2009). Inter-lift liners are required, both to reduce acid consumption and to manage the low permeability. Most nickel laterite deposits are in high rainfall climates, including Panama, Myanmar, Ghana, Costa Rica, Peru, Brazil and the Philippines, and therefore require extensive use of raincoats. Leached ore is very weak structurally and wet, requiring considerable investment in stabilization and closure. Due to site climatic conditions and nature of the wastes, strict closure requirements will generally apply (Saari and Riekkola-Vanhanen, 2011; Readett <I>et al</I>., 2006). Recently, application of heap leaching for extraction of base metals, mostly nickel from laterites, has been investigated by different researchers and as result of that, several novel processes have been patented (Table 11).

A review of the relevant literature indicates that one of the first serious studies on the column leaching of nickel laterite ores for possible heap leaching application were conducted on Greek laterite ores; first from the Litharakia deposit (Agatzini-Leonardou <I>et al</I>., 2009), and subsequently the Triada (Karidakis <I>et al</I>., 2005) and Kastoria deposits. The heap leaching invention of Agatzini-Leonardou <I>et al</I>., (2009) described the recirculation of leaching solution, through one or more heaps, both with and without acid addition between each cycle. Heap leaching for nickel has followed a variety of different development routes, with separate technologies being used in the treatment of sulphide and laterite ores. One of the early leaders in laterite processing, European Nickel, put its Caldag project in Turkey on 'care and maintenance' following permitting delays and is instead focusing on Acoje in the Philippines. The company acquired Acoje following its merger with Rusina Mining, which had already begun a leaching trial on the mixed limonite-saprolite ore at the end of 2009. European Nickel is now proceeding with a full feasibility study on Acoje. Meanwhile, work at Caldag, where it began its pilot- scale testwork in 2005, has proved that acid leaching can produce a high-grade mixed nickel-cobalt hydroxide concentrate, at lower capex and operating costs compared to conventional recovery technologies (Readett <I>et al</I>., 2006). Other heap leaching processes for nickel are Vale's Piauí Project in Brazil and Metallica Minerals' Nornico project in Australia, for which the authors could not find any published reports. Talvivaara has been the only place in the world utilizing heap bioleaching in nickel extraction on an industrial scale. Construction of the process was begun in spring 2007 and first metal sulphides were produced at the plant in October 2008. The development of the heap bioleaching process was begun in a 17 000 tonnes on-site pilot heap operated during 2005-2008 and has continued as a full-scale industrial heap (Saari and Riekkola-Vanhanen, 2011) until late 2014 when the company went bankrupt following an environmental spill (see section 2.7). It should be noted that the leaching process generates heat primarily while the fast-leaching pyrrhotite reacts, but that does not necessarily last until all nickel and copper have been leached.

#### Caliche mineral heap leaching

The caliche mineral is composed of sodium nitrate (saltpetre), sodium chloride, sodium sulphate, potassium chloride, and minor salts. At present, iodate is the most important component from economical point of view. Insoluble species such as quartz and other silicates are also present (Valencia et al., 2008; Pokorny and Maturana, 1997; Ericksen, 1983). In some cases, the soluble fraction of the caliche can reach up to 40% (Gálvez et al., 2012). Historically, the processing of caliche was done in mobile installations, with stirred and heated tanks, which was applicable to high-grade caliche ores with up to 50% of nitrate minerals (Lauterbach, 2004). When the amount of soluble minerals decreased in the caliche, new techniques were developed. The Shanks technology, introduced in 1878 used double wall tanks heated with vapour. In 1920, the Guggenheim process was introduced, which is characterized by the grinding of the caliche and lower temperatures (Valencia et al., 2008; Wisniak and Garcés, 2001). Nowadays, the gradual diminishing of caliche's grades and an increase of processing costs have resulted in the

implementation of heap leaching, which was productively introduced for this mineral at the beginning of the 1990s, almost 20 years later than to the metallic minerals (Valencia et al., 2008; Fleming, 1992). The leaching of saltpetre differs significantly from the leaching of copper and precious metals minerals. With saltpetre, there are several soluble species while in the case of copper and gold minerals there are few. In the case of copper and gold minerals, dissolution occurs through a chemical reaction; in the case of caliche, dissolution is driven by high solubility of the salts, and the final solutions are concentrated further for crystallisation (Valencia et al., 2008; Cariaga et al., 2005; Wana and LeVier, 2003).

In industrial operations, caliche heaps reach heights of up to 10 m and are irrigated with a nominal rate of 2 L/h/m<sup>2</sup>. The process is divided into 3 steps: impregnation, where the material is wetted; leaching, where the soluble species are dissolved and collected as enriched solution; and washing, where the remaining soluble species are removed using a leaching agent with low ion concentration. Each heap is built through the accumulation of 600,000 to 900,000 t of caliche mineral. In the leaching step, fresh water or partially enriched solution are used as leaching agents. The percolated solution is pumped to the iodate extraction plant, which by a reduction step recovers iodine. The resulting solution is then forwarded to evaporation ponds in which the nitrate is crystallized mainly as sodium nitrate. In a next step, sodium nitrate reacts with potassium chloride, obtained from salt deposits, to produce potassium nitrate as final product, which is used as a fertilizer. More details about the process have been reviewed by Pokorny and Maturana (1997).

Heap bioleaching of a zinc sulphide

A heap bioleaching process for the extraction of zinc has been introduced by Harlamovs (2001). Teck Cominco Metals Ltd. developed the HydroZinc<sup>™</sup> process, which combines heap bioleaching of a zinc sulphide ore followed by neutralisation, solvent extraction and Zn electrowinning. The heap bioleaching step was tested at laboratory scale using columns from 1 to 6 m in height and in a demonstration plant in two test heaps of 20×20×6 m using relatively high-grade ore samples from the Red Dog mine in Alaska containing 15.2% zinc. The longest running demonstration heap yielded 82% Zn extraction after 740 days on stream, with all heap tests showing similar rates of extraction. An economic evaluation of the overall process at full scale indicated favourable rates of return given the process parameters studied at the demonstration plant (Lizama <I>et al</I>, 2003). A modelling study of the zinc sulphide heap bioleach as employed in the Hydro-Zinc<sup>™</sup> process was done by Petersen and Dixon (2007). Calibrated against laboratory column data and validated against the pilot data, the model could predict heap performance reasonably well, allowing optimisation of operating conditions so to significantly increase leach rates. However, the process was not developed beyond the pilot stage.

# A novel sequential heap leach process of PGMs

A novel sequential heap leach process, consisting of a first stage bioleach followed by a cyanide leach step is a potential alternative route to process platinum group metal (PGM) containing Platreef ore directly, circumventing the energy intensive steps of milling, floating, smelting and pressure leaching (Mwase <I>et al.,</I> 2014). Testing this process was performed on crushed whole ore, after initial experiments conducted on low-grade Platreef flotation concentrate achieved promising results (Mwase <I>et al.,</I> 2012). Two samples of drill core Platreef ore

with size distributions of -25 mm + 1 mm and -6 mm + 1 mm were first bioleached in cylindrical columns, to simulate heap leaching, at 65 °C and then leached with cyanide solution at 50 °C in cylindrical columns. Overall the best results were achieved from the tests on the -6 mm + 1 mm size fraction sample. After 304 days 93% Cu, 75% Ni and 53% Co were extracted in the bioleach experiment, and after 60 days 57.8% Pt, 99.7% Pd and 90.3% Au in the follow-up cyanide leach experiment. Analysis using a mineral liberation analyser suggested that Pt and Pd were leached mostly from the tellurides, while the Pt arsenides appeared resistant to cyanide leaching. The extractions of base metals and PGMs achieved in this study, albeit comparatively low, potentially still represent an economically viable route, considering that a coarse ore heap leach would offer substantial savings in capital and operating costs by eliminating the milling, flotation and smelting steps of the conventional process.

It has been shown that PGM cyanidation occurs in the same manner as that of gold. Pt(II) and Pd(II) complexes form stable with cyanide, for example [Pt(CN)<SUB>4</SUB>]<sup>2-</sup> and [Pd(CN)<SUB>4</SUB>]<sup>2-</sup>. As in the case of gold, the reactions for PGMs can take place at ambient conditions, but generally show poor extraction levels (Mwase <I>et al</I>., 2012; Barter, 2001; Schouwstra and Kinloch, 2000; MacPhail <I>et al</I>., 1998; Torres and Costa, 1997; McInnes <I>et al</I>., 1994). High cyanide concentrations (>1 g/L) are usually required as compared to those used in gold leaching (around 0.25 g/L; Chamberlain and Pojar, 1984). In gold leaching such high cyanide concentrations are used when leaching less cyanide-soluble gold tellurides and arsenides, and when there is above 0.5% copper in the ore (Marsden and House, 2006; Adams, 2003).

# Heap leaching of electronic scrap

Hydrometallurgical processing routes for the recovery of value metals from electronic scrap with economic and ecological value generation (Cui and Zhang, 2008), mostly through bioleaching (Ilyas <I>et al.,</I> 2013), have shown interesting results and heap leach type processes would be a potential future direction for the recovery of metals from such materials. Due to the relatively low volumes of such waste materials, which are relatively high-grade, and the need to produce a benign residue, more intense leaching processes, such as tank leaching are probably a more efficient route to follow. However, a systematic study of heap leaching of electronic scrap and possible use of the plastics and other materials associated with the metals in electronic waste remains outstanding.

# Heap Modelling and Control

In order to fully realize the potential of heap leaching, a holistic model is required that accounts for as many of the complex micro- and macro-scale processes and their interactions as possible. One of the key difficulties in modelling heaps has been the lack of descriptive information in terms of heap behaviour during full-scale operation. Heap leaching is a fundamentally dynamic process and requires a plant-wide dynamic model to effectively simulate process behaviour. Many mathematical models and computer codes are available today to describe transport phenomena throughout heaps or dumps, but there are relatively few applications used in the design process and project engineering and operational optimization of existing plants. Over the past 40 years considerable progress has been made to develop predictive models of a generic

nature to facilitate heap design and control (Bennett<I> et al</I>., 2012; Leahy <I> et al</I>., 2007; Ogbonna <I>et al</I>., 2006; Dixon and Petersen, 2003; Sidborn <I>et al</I>., 2003; Pantelis <I>et al</I>., 2002; Dixon, 2000). Most of the early heap leaching models dealt with leaching at the particle scale (Sánchez-Chacón and Lapidus, 1997; Bartlett, 1992; Pantelis and Ritchie, 1991; Davis and Ritchie, 1987; Prosser and Box, 1986; Shafer <I>et al</I>., 1979; Braun <I>et al</I>., 1974; Roman and Olsen, 1974). More recent heap leaching models emphasize the effects of bulk scale phenomena, such as liquid flow, gas flow, and temperature distribution, on heap performance (Ilankoon and Neethling, 2013; Mellado <I>et al</I>., 2012; Leahy <I>et al</I>., 2007; Ogbonna <I>et al</I>., 2006; Liu <I>et al</I>., 2004; Lizama, 2004; Sidborn <I>et al</I>., 2003; Dixon and Petersen, 2003; Petersen and Dixon, 2002a,b; Pantelis <I>et al</I>., 2002; Bouffard and Dixon, 2001; Dixon, 2000; Moreno <I>et al</I>., 1999). Although both particle-scale and bulk-scale effects are important in heap bioleaching, little has been done to integrate systematically 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 ore particles of a particular size class that are homogeneously porous and have mineral grains well distributed throughout (Liddell, 2005; Velardo <I>et al</I>., 2002; Vegliò <I>et al</I>., 2001). Furthermore, 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 (Ghorbani et al 2013a, 2013c; van Buuren, 2003).

New control and modelling tools and techniques in heap leaching have provided the possibility of having the means to monitor some key parameters such as temperature, irrigation, aeration, solution pattern; microbial populations and mineralogy in heap operations at different scales. These could ensure compliance of a leaching operation as it was designed, take control of management through reporting and early warning of deviations; provide a database of the operation history for later analysis and simulation; contribute to the safety of the operation by minimizing the presence of the operators. Given the complexity of the heap process, such control interventions in general have to rely on the support of a sufficiently rigorous process model.

# Temperature control

For certain thermophilic micro-organisms, especially in the context of chalcopyrite bioleaching, high temperatures are essential. Since heap leach performance depends on parameters that cannot all be mathematically modelled or predicted with confidence, it is vital to verify experimentally whether high temperatures can indeed be achieved on a given ore type, and to optimise the conditions required for achieving and maintaining elevated temperature, prior to finalising the design of a heap leach plant. As is mentioned in section 4.3.3, the HotHeap<sup>™</sup> technology, which is based on the heat model developed by Dixon (2000), automatically balances the two bulk transport processes (water and gas) to maximize the accumulation of heat within the heap and thus has the potential to achieve effective control in the context of heap bioleaching.

A device has been patented by Petersen and Dann (2010) for measuring fluid flow within a heap using a heat stimulus. It consists of a processor and a number of sensor units buried in the heap, each unit having a heat source with at least one heat sensor located at a certain distance above and below the heater. The rate at which a heat pulse travels to the sensors allows deductions of the principal rate of fluid flow in the vicinity of the sensor.

Monitoring probes have been developed at Mintek for measuring multiple process variables including heat at various depths and locations in the heap. The HeapStar® heap leach administrative and guidance system was developed at Mintek (to assist operators in keeping track of the frequent interventions required particularly on a multiple cells heap with each at a different stage of operation; Gericke.<I>et al</I>., 2011).

One of the prerequisites for heat accumulation is the 'active' thermal insulation provided inside a massive heap by the exothermically reacting ore. To reproduce those conditions would require large scale and very costly piloting, unless a specially devised smaller scale experiment could be set up to simulate it, which is what the Mintek SmartColumn<sup>™</sup> and/or BHP Billiton SimCol<sup>™</sup> concept (van Staden, 2008) for simulating the environment at the centre of a heap is meant to do. It facilitates direct experimental observation of the development of the temperature profile, starting from ambient to the maximum that will be achieved during the operation of a heap under a selected set of operating parameters. This column patented by BHP Billiton SA Ltd. (van Buuren, 2003) and was used to conduct experiments on two ore samples of about 7 tonnes each at Mintek (Dew <I>et al</I>, 2011). The Simulation Column (SimCol<sup>™</sup>) is a novel pilot scale (six metres or ten metres in length and one metre in diameter) leach column where heat generation results from mineral sulphide oxidation only and not from applied external heating, which allows the simulation of the temperature profile of a column of ore in a commercial heap (Petersen <I>et al</I>, 2011). BHP Billiton-Base Metals has developed a mechanistic process

model to define design criteria for a commercial heap using input data derived from the results of SimCol<sup>TM</sup> tests. The temperature of the ore in the Simulation Column is measured throughout its length at points close to the column side walls and towards the centre of the ore column, using high accuracy RTD (Resistance Temperature Detector) probes. The application of the Simulation Column was demonstrated, showing that self-generation of heat from bioleaching of pyrite contained in the ore may be managed to sustain high operating temperatures, and with average temperatures of 70<sup>o</sup>C being achieved (van Buuren, 2003).

6.1 <B>Rinse-rest irrigation for heap wetting</B>

Rinse-rest cycles alter the flow rate of solution, and the level of saturation in the flowing channels and possibly elsewhere. As is discussed in section 4.3.1.2, the term 'Rest Periods' refers to the practice of periodically interrupting the supply of irrigation liquor for any length of time, before resuming irrigation. It is fairly widely accepted as a potentially useful operational variable in heap leaching, but possibly not equally widely applied as a standard practice and not fully exploited for its potential benefits, and the effects of rest periods on the fluid flow dynamics and transport phenomena in a heap have certainly not been fully described. The most obvious process parameters that can be manipulated by the use of rest periods are, namely (Guzman, 2011; Watling , 2006; van Staden, 2007a; Burgmayer, 2002):

• Control of the soluble metal content in the heap drainage solution. It has been found that, when the soluble metal concentration in the drainage from a heap reaches an uneconomically low level, leaching in the heap will continue for some time during a rest period, and after resuming

irrigation the heap will once again yield an economic soluble metal tenor for some time. In this manner the useful economic life of a heap can be extended.

• Improved aeration: oxygen uptake measurements during heap bioleaching laboratory experiments have shown that the uptake of oxygen rises during rest periods, signifying increased bacterial activity. This phenomenon is probably related to the creation of voids during the drainage of liquor from the heap during the rest periods, and is obviously very relevant to all heap leaching applications that rely on bacterial action (van Staden and Vercuil, 2005).

• To manage precipitation reactions: since the liquor content in a heap diminishes during a rest period, while the leaching reactions do not cease to proceed, conditions of super-saturation can develop, thereby encouraging precipitation reactions in the heap. This mechanism could therefore be employed to exert a certain extent of control over the rate of precipitation in the heap, so to ensure gradual precipitation as opposed to having a catastrophic precipitation event after an extended period of dissolved salt build-up, which is likely to block solution pathways.

Once the mineralogical, chemical and leaching characteristics of an ore are known, a preliminary rinse-rest period approach can be formulated, but its efficacy needs to be verified by closely monitored experimental trials. Irrigation needs to have maximum flows during the initial mass transfer limited phase and minimum flows to rinse the copper out during the chemical rate limited phase. In the leaching of oxide ores, the mass transfer and contact between the reactants (leach reagent and ore minerals) govern practically the entire process, whereas the leaching of sulphide ores also requires effective supply of oxygen (Watling <I>et al</I>, 2009).

The leach pad is a large area that traditionally requires the presence of operators for the control and monitoring of irrigation. The intelligent monitoring and automatic control of leaching through <I>in situ</I> measurement of key hydrometallurgical parameters in near real time have been developed, tested and successfully implemented both at the pilot and industrial scales (Schlumberger, 2015; Biohydro, 2014). These methods revolve around temperature, induction and distributed resistivity, volumetric moisture, and saturation and enhance understanding of heap leaching efficiency and completeness to increase production and prevent catastrophic losses and slope failures.

#### Aeration control

High air flow rates generally affect microbial activity and hence heat generation favourably (du Plessis <I>et al</I>. 2007). The modelling work by Dixon (2000) has shown that the most effective means of achieving a high degree of heat conservation within a sulphide heap in a high altitude desert climate is to blow air into the heap above a certain critical rate while maintaining a relatively low rate of solution irrigation. Any other means of conserving heat (such as heat shields, section 4.3.6) are only effective when this key criterion is met, and in most cases, the additional effect is minimal and probably would not justify the expense. Another important consideration is that the air flow rate needs to be high enough to prevent oxygen and carbon dioxide limitation at the top of the heap, as these gases are consumed as the air passes upwards. Work by Ojumu et al. (2008b) has shown that, given typical carbon uptake rates by bioleaching micro-organisms, CO<SUB>2</SUB> is in fact the much more limiting reagent than oxygen. Petersen <I>et al.

on a porphyry copper ore in a 6m column ran out of CO<SUB>2</SUB> in the lower parts, retarding microbial activity in the upper parts. Only enrichment with CO<SUB>2</SUB> could overcome that problem. Although CO<SUB>2</SUB> generation from the acid dissolution of carbonates in the ore was evident, this continued only for a short period of time, where after the column became net CO<SUB>2</SUB> consuming.

Poor permeability of ore beds can make aeration difficult and hence more expensive. Higher permeability tend to be found at the base of heaps due to the ore segregation that occurs during construction, so good air penetration, both vertically and laterally, results from aeration at the bottom of the heaps. Bartlett (1998) suggests that the higher the heap, the larger the allowable distances between the aeration points should be, presumably as mixing will occur during the longer path, but it is worth to note that even with mixing in the upper parts, there may still be poorly aerated zones in the lower reaches of the heap with such wider spacing. Heap aeration can also be passive, in which case air is drawn into the heap with the flowing liquid (Rawlings <I>et al</I>. 2003), although forced aeration tends to be more common as it allows for more operational control. The Ohio Research Institute for Transportation and the Environment (ORITE) at Ohio University, USA, conducted a unique full-scale field load test to simulate the aeration pipe installations at a copper process operated in Chile (Sargand et al. 2013). Load tests on two types of 249 mm diameter corrugated thermoplastic pipe products that are being used at the bottom of heap piles were conducted under in situ conditions with ore material packed around the pipes. The results indicated significant vertical deflection, affecting the performance of the aeration pipes.
### Solution pattern simulation

Despite the commercial achievements of heap leaching, there still is limited comprehension of the flow pattern within the heap. The liquid in heaps is affected by gravitational forces, surface tension and atmospheric pressure (Bartlett, 1998). Chemical engineering models that have been developed for trickle beds are often not suitable for heap leaching systems as they describe uniform particle size systems operated at comparatively higher flow rates (Bartlett, 1998). A variation of a classic Turner-structure approach to modelling packed bed chemical reactors was adopted by Bouffard and Dixon (2001) and later incorporated into the HeapSim simulation tool (Dixon and Petersen, 2003, 2004, 2007a, 2007b). This represents solute transport through the bed to be by advection through discrete channels and by diffusion transport through stagnant zones surrounding them. Although simplistic, this approach has been quite successful in the modelling of column leach data.

A more suitable description of heap hydrology is the unsaturated zone hydrology theory, a theory that was originally developed for soils (Wu <I>et al</I>., 2009; Bouffard and West-Sells 2009; de Andrade Lima 2006; Bouffard and Dixon, 2001). It predicts the solution flow paths based on hydraulic conductivity of an ore which in turn is highly dependent on the pore size distribution and therefore on the aggregate or ore particle size distribution and placement, the solution application rates and methods and the degree of saturation (de Andrade Lima, 2006). To formulate these factors into models renders them extremely complex, however, especially considering the high degree of inhomogeneity typical of heap packing.

Most of the studies done on heap hydrology have adopted a macroscopic approach via analysis of heap feed and effluent and have focused primarily on the issue of preferential flow and on the development of models to predict heap hydrodynamics. A key shortfall of this approach is the lack of direct observation and hence validation of model assumptions. X-ray computed tomography (CT) has been applied to evaluate the evolution of the pore structure along the length of a column (Yang <I>et al</I>, 2008; Lin and Miller, 2005). X-ray CT however provides limited signal contrast between the air and liquid phases in the presence of comparatively high-density solids. In the context of bioleaching, X-ray radiation could also sterilise the column.

Bouffard and West-Sells (2009) make note of a further method to study heap hydrology: electrical resistivity tomography (ERT). ERT was used to measure the moisture hold-up in test cells that had been embedded in a heap. ERT has been used by geotechnical consultants at Minera Escondida in Northern Chile, Cripple Creek heap in Colorado and at Phelps Dodge's Tyron property in New Mexico (Bouffard and West-Sells, 2009). A possible disadvantage of ERT is that it requires there to be electrical contact between the electrode and solution, so isolated pockets of solution may not be detected. ERT resolution is also much coarser than that of other tomographic techniques such as X-ray CT and magnetic resonance imaging (MRI) (Stevenson <I>et al</I>. 2010). The application of MRI to heap leaching has the potential to provide additional measurement capability by acquiring 3-D images of the liquid in an ore-packed column non-invasively as a leach progresses. It can readily differentiate between air and water, as signal is only detected from the water (Fagan et al., 2012). This technique is, however, limited to the small confines of a test column that can be fitted into a suitable MRI unit.

Dixon and Afewu (2011) present data from solution flow measurement through the ore bed in a large scale column using embedded tensiometers. Based on the simulation results using the comprehensive HeapSim-2D heap bioleaching model, it became clear that the hydrology of heaps under drip emitters can only be understood by modelling water flow and solute transport at the level of the individual drip emitter. It is also clear that hydrodynamic dispersion is key to the distribution of solutes away from the advection channels along the drip emitter axis, although Dixon and Afewu (2011) did indicate that this dispersion is significant only at high irrigation rates or very narrow dripper spacing, which are far from industrial practice.

Some success has also been achieved with imaging solution flow by positron emission tomography (PET) scanning (Petersen, 2015). Early results indicate that solution flow within a relatively small column is extremely inhomogeneous and resembles more closely the channel and stagnant zone model proposed by Bouffard and Dixon (2001) rather than homogeneous solution flow fields implied by other transport models.

Tracer tests can provide valuable insight into the residence time distribution (RTD) of heaps. This information is often used in conjunction with flow models to extract time-dependant hydrodynamic parameters such as axial dispersion, plug flow velocity and the rate of exchange of solutes between the stagnant and flowing liquid phases (Bouffard and West-Sells, 2009; de Andrade Lima, 2006). Tracer studies have been performed by Decker and Tyler (1999), Wu <I>et al</I>. (2007), Bartlett (1998) and Bouffard and West-Sells (2009) using NaCl or NaBr. Most of these studies were performed in columns, although Bouffard and West-Sells (2009) did column, crib and heap tests. The two most extensive tracer studies were performed by Bouffard

and Dixon (2001) and de Andrade Lima (2006). Bouffard and Dixon (2001) used a NaNO<SUB>3</SUB> tracer, whose concentration was measured by electrical conductivity, to evaluate hydrodynamic parameters and the effect that flow rate, agglomeration, binder addition, bed height and particle size distribution had on them. de Andrade Lima (2006) performed similar experiments, but used HCl as a tracer and measured pH to determine the effluent concentrations.

## Monitoring of microbial populations

In the area of microbiology, the monitoring of microbial populations in heaps using a combination of molecular and culture-based techniques is now possible and can provide an assessment of how microbial populations change in response to temperature and other heap conditions, which is especially important when treating chalcopyrite. The development of new culture-independent molecular techniques, such as polymerase chain reaction (PCR), denaturing gradient gel electrophoresis (DGGE) and fluorescent in situ hybridization (FISH), to detect and quantify populations, is a significant advancement and is a valuable tool in accurately describing biodiversity and following changes over time of microbial consortia present in bioleaching systems (Remonsellez et al., 2007; Coram-Uliana et al., 2006; Watling, 2006; Demergasso et al., 2005). These techniques do not, however, give an account of the viability of the organisms. Recently a method for the rapid assessment of active biomass in leach liquors based on the measurement of ATP concentration in test solutions was described (Okibe and Johnson, 2011), which could be a simple way of quantifying microbial activity.

There have, however, been relatively few studies on the microbiology of heap leach systems and most of these have analysed the liquid phases i.e. pregnant leach solutions and raffinate (Gericke,

2011; Johnson, 2008; Demergasso et al., 2005; Johnson and Hallberg, 2005; Crundwell, 2003). Since the micro-organisms are not only present in the liquid fraction, but also attached to the ores surfaces, it is important to include the attached population when assessing the microbial composition within the heap (Soto<I> et al</I>., 2013; Chiume <I> et al</I>., 2012; Africa <I> et al</I>., 2010). Molecular techniques, such as quantitative PCR, which will allow the identification and quantification of microbes in heap bioleach processes, have been developed at Mintek (van Staden <I> et al</I>. 2009). It is envisaged that the ability to correlate microbial types and numbers to changes in the chemical and physical environment in the heap with time would assist in solving process issues such as how a heap should be inoculated, which microbial cultures to add and when to inoculate. It could potentially be a step towards optimizing rates, achieving faster start-up and better metal extractions.

### 6.2 <B>Process mineralogy </B>

Mineralogical characteristics are amongst the most important factors determining leachability, leach time, reagent consumption, insoluble losses, scale formation and equipment performance (Benvie, 2007; Pownceby <I>et al</I>., 2007; Baum, 1999). Despite the apparent operational simplicity, the coarse to very coarse nature of heap leach feeds produces a complex association of mineral species and mineral-pore spatial arrangements (texture) which impact on leaching outcomes. A thorough understanding of the mineralogical composition of the ore (in terms of both valuable minerals as well as gangue minerals), as well as the leach reaction kinetics and acid consumption under a range of operating conditions, is required to determine the optimal reagent strength specifications (especially in terms of acid). Insufficient attention to mineralogy

can lead to inadequate understanding of the reasons for variable ore performance and to much higher risks in plant design and commercial heap performance. This is discussed in more detail in sections 3.1 and 3.4. The differences in feed composition require different ore preparation procedures and especially ore blending for heap stacking. 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 (Gottlieb, 2008; Mular, <I>et al</I>., 2005). This quantitative data is derived from images of the mineralogically classified ores or plant products in question. 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 (Benvie, 2007; Pownceby <I>et al</I>., 2007). Recent developments in X-ray CT as an advanced diagnostic and non-destructive technique have indicated the potential for the technology to become a tool for the acquisition of 3-D mineralogical and structural data in the large ore particles used in heap leaching operations (Cnudde and Boone, 2013; Golab <I>et al</I>., 2013; Dhawan, <I>et al</I>, 2012; Ghorbani <I>et al.,</I> 2011b, 2013c; Miller <I>et al</I>., 2003).

# Conclusion and Outlook

Heap leaching has become a well-established technology choice for the treatment of low-grade ores over the past 50 years, enabling the economic exploitation of marginal deposits, often in remote locations in many parts of the world. Heap leaching has permitted many developing countries a first entry into the commodities market, paving the road for more sophisticated technology to follow. However, the focus has firmly remained on acid leaching of copper oxides,

uranium ores and cyanide leaching of gold ores. The oxidative leaching of secondary copper sulphides and refractory gold ores are the only other applications that have emerged at a significant scale since the late 80s, promoted by the realisation that leaching of these minerals is generally supported by natural bacterial oxidation.

In terms of heap technology, oxidative leaching requires aeration of heaps through aeration pipes placed underneath the heap before it is stacked, or through managed rinse-rest cycling. Furthermore, due to the different time-scale at which they leach (over years rather than months), maintaining high heap permeability has become a critical focus of heap design and management. Heap compaction during stacking and operation can significantly inhibit homogeneous solution flow through the bed, compounded further by rock decrepitation upon long-term exposure to acid and secondary precipitation of leached metals in the interstitial pores. Therefore, preparing a carefully blended feed to stack heaps and operating its irrigation so to avoid flooding and channelling is critical. However, the relationship between particle size distribution, ore mineralogy, nature of packing, heap height and heap permeability remains poorly understood and hence difficult to manage effectively. The long leach times of oxidative processes are founded on the slow rate of oxygen uptake from air, and slow diffusion of solutes within the pores of larger rock particles and through stagnant zones within the packing. Both these aspects are compounded by the distribution of liquid and gas in the bed and thus directly linked to heap permeability. It is therefore postulated that the inability to maintain effective percolation through heaps over the longer term is the single biggest obstacle to broader uptake of this technology in the mining industry.

Many interventions have been proposed and implemented to improve the performance of heaps, and some of them address the core issue of heap permeability. These include ore agglomeration, certain stacking methods, low impact irrigation, pulse irrigation schemes, building shallow heaps etc., all which have contributed to an overall incremental improvement in extraction from heaps over the past 20 years. But there has not been a true breakthrough intervention that allows oxidative heap leaching to operate at the same time scale as laboratory columns indicate is possible in the absence of permeability constraints. It is particularly in this area where future development work in heap leach technology must focus, be it through further improvements in the blending and agglomeration of ore, stacking methods and heights, use of filler material to maintain macro porosity, irrigation schemes or combinations of these. Mineralogical characteristics of the particular ore under consideration will need to be taken into account more systematically. Also, dedicated instrumentation to monitor gas and solution flow within heaps is still very limited and there is much scope for new technology to be developed.

Once the obstacle of long leach times and slow extraction rates can be overcome, heap leaching offers significant potential for further innovation. Many new ideas for heap leach processes, whether based on different commodities (Zn, Ni, PGMs), or novel chemistry (use of thiosulphate for gold, ammonia for base metals, chloride or thermophile micro-organisms for chalcopyrite) appear feasible at the laboratory scale, but are likely to be hampered by the same dilemma of heap permeability at the industrial scale.

Significant also for sulphide heap leaching is the auto-thermal nature of heaps, resulting in a selfheating effect from the exothermic consumption of oxygen. Much work has been done in understanding, modelling and controlling this effect for efficient operation at elevated temperatures, at which reaction rates are generally at their fastest, and at which thermophilic micro-organisms can thrive, which have shown a unique ability to assist in the dissolution of chalcopyrite. Effective heat control hinges, however, on good distribution of both gas and solution through the heap, and therefore again is linked to maintaining good heap permeability.

Environmental concerns around heap leaching require critical discussion. On the one hand, heap leaching does represent a significant energy saving (and reduction of the associated carbon footprint) relative to conventional minerals processing by obviating the need for milling, but, on the other hand, the relatively uncontrolled flows of large solution inventories containing corrosive and toxic chemicals through sprinklers, heaps, drainage systems and ponds offers many opportunities for leakage and contamination if not carefully managed. Spent heaps present as much of an environmental legacy as tailings dams. Although there have been some studies evaluating the environmental footprint of various Cu processing routes, there is still no clear indication as to the relative merits or demerits of heap leaching, and further study is indicated. Incidentally, heap leach technology could also play a role in the low cost recovery of metals from secondary resources to reduce the need for primary mining, as has already been shown in the context of certain e-wastes.

In conclusion then, it is likely heap leaching will remain the technology of choice for treating low-grade copper and gold ores in remote locations, but for it to become attractive for higher grades and different commodities, some significant improvements in achieving and maintaining good heap permeability for rapid and nearly complete extraction are still required. Care needs to be taken not to treat heap leaching as some sort of 'primitive' technology. For its optimal operation, fairly comprehensive knowledge of the ore and the mechanisms of heap leaching is required to understand and evaluate the impact of any particular intervention to improve performance. The failure to appreciate the complexity of heaps has resulted in many failed operations, historically and still at present. The long-term success of heap leaching as a technology choice requires a concerted high-level cross-disciplinary engineering approach from research and development to design to construction to operation to closure, as should be expected for the management of any modern technology.

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Table 1: The percolation leaching types and typical criteria (adapted from John, 2011): n.a. denotes not applicable.

| B>Particle size  |                |        |                      | <b>Irrigation<br/>rates</b> | <b>Lift</b>             | <b>Leach</b>     |  |
|------------------|----------------|--------|----------------------|-----------------------------|-------------------------|------------------|--|
| 2> (D < CLID> 20 | <b>Crushed</b> |        | <b>Agglomeration</b> | <b>(Lm<sup>-</sup></b>      | height                  | time             |  |
| .D>(F<50D>00 50D |                |        |                      | 2                           | <b>(m)</b>              | <b>(Vears)</b>   |  |
| nm)              |                |        |                      | h <sup>-</sup>              | < <b>D</b> >(III) <b D> |                  |  |
| )15              |                |        |                      | 1)                          |                         |                  |  |
| lber 2(          |                |        |                      |                             |                         |                  |  |
| 4000 mm          | Can be In      | n-situ | na                   | Wide and                    | na                      | Cu: >5 and U: 1- |  |
| 57<br>242        | Blasted        |        |                      | varied                      | 11.a.                   | 3                |  |
| ] at 01          |                |        |                      |                             |                         |                  |  |
| ₽<br>₩00-30 mm   | No             |        | No                   | 2-15                        | 8-75 m                  | Cu: >10 and Au:  |  |
| iversity of      |                |        | 6                    |                             |                         | 2-6              |  |
| ed by [Uni       |                | X      | 0                    |                             |                         | Cu: 1-4, Ni: 1-5 |  |
| କୁ<br>ୱୁପ-5 mm   | Yes            | Q      | Mostly               | 2-15                        | 2-10 m                  | U: 1-3, Au: 0.1- |  |
| Ā                | -0             |        |                      |                             |                         | 2                |  |
| 0-0.5 mm         | Yes            |        | Maybe                | 10-50                       | 1-5 m                   | 4-30 days        |  |
| -0.25 mm         | Yes and        | /or    | Yes                  | 2-15                        | 1-5 m                   | As per heap      |  |



Table 2: Advantages/disadvantages of heap leaching.

| <b>Advantages</b>  | <b>Disadvantages</b>  |
|--|---|
| <ul> <li>Low capital and operating costs</li> <li>Quick installation</li> <li>Low energy requirements in terms of comminution: only primary and secondary crushing required, but no milling</li> </ul> | <ul> <li>Recovery is generally lower than<br/>in agitated leaching</li> <li>Slow leach kinetics</li> <li>Large solution hold-up within ore<br/>bed</li> </ul>                     |
| <ul> <li>Can be used to treat low-grade ores, wastes and small deposits</li> <li>Simplicity in terms of equipment and</li> </ul>   | <ul> <li>Large footprint; needs suitable terrain</li> <li>Lack of options to control the</li> </ul>   |
| <ul> <li>operation</li> <li>No solid/liquid separation needed after the process</li> <li>No separate tailing disposal</li> <li>Metal tenor may be built up by recycling</li> </ul>                     | process<br>• Potential for accidental<br>environmental release of pregnant leach<br>solution (PLS)<br>• Lengthy large scale column test<br>work program required for design data; |
| <ul><li>less water requirement compared to</li></ul>   | may require large drill-core ore sample   |

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• Potential integration with other treatment options, e.g. integration with a pressure oxidation (POX) circuit to produce the sulphuric acid needed for leaching • Ramp-up time is generally lengthy

• Long-term closure issues due to the large footprint and potential acid rock drainage from spent heaps, especially if sulphides present

• More water lost by evaporation compared with other leaching methods

| Methods   | Inventor (s)                    |
|---|---------------------------------|
| High Temperature Leaching Process                                   | Dew <i>et al</i> ., 2007        |
| Method of leaching copper sulphide ores containing chalcopyrite     | Ohtsuka, 2006                   |
| A method for the bacterially assisted heap leaching of chalcopyrite | Hunter, 2001                    |
| Recovery of copper from chalcopyrite                                | Shaw, 2001                      |
| A process for the leaching of copper from chalcopyrite using ferric | Pinches <i>et al</i> .,<br>2001 |
| An improved method for heap leaching of chalcopyrite                | Miller and Winby, 1999          |

Table 3: The list of the patents for bacterially assisted heap leaching of chalcopyrite in the presence and absence of catalysts.

<B>Table 4</B><B>:</B> Typical classification of heap pads with characteristics and schematices (Schnell, 2013; Lupo, 2010; Thiel and Smith, 2004; van Zyl and Bronson, 1994).

| Leach pad<br>types | Characteristics                                       | Schematic (www.amec.com)                      |
|--------------------|---|---|
|                    |   |   |
|                    | • Needs large area for pad construction and expansion |   |
|                    | • Relatively flat topography                          |   |
|                    | preferred, but can be constructed in rougher          |   |
|                    | terrain   | <b>N</b>                                      |
|                    | • External solution and storm water                   |   |
|                    | ponds   | Ore heap under leach while continually loaded |
| Standard           | • Large flood/storm event capacity                    | Containment<br>berms<br>Grade to drain        |
|                    | due to larger active areas                            | Single-liner system - Ore storage             |
|                    | • Can tolerate variable ore                           |   |
|                    | production and leach cycle time                       |   |
| (                  | Relatively simple liner system                        |   |
|                    | (single-composite)                                    |   |
|                    | • Low initial capital cost                            |   |
|                    | • Consider incremental pad                            |   |

|             | expansion  |
|-------------|--|
|             |  |
|             |  |
|             | • Uses topography (valley,                       |
| Valley fill | drainages, basins) to form heap pad              |
|             | • Foundation slopes can often get                |
|             | very steep (40 to 50 percent)                    |
|             | • Generally more expensive than                  |
|             | other leach pads (more upfront earthworks)       |
|             | Requires hard, durable ore                       |
|             | • Can tolerate variable ore                      |
|             | production and leach cycle time                  |
|             | • Internal solution storage (no                  |
|             | external ponds). Internal pond double lined with |
|             | leak detection/ collection system.               |
|             | Requires pumping system for                      |
|             | internal pond(s)                                 |
|             |  |


| <br>• Need to build at least three pads or |  |
|--|--|
| cells to have continuous operation         |  |
|  |  |

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| <b>Irrigation<br/>systems</b> | <b>Characteristics</b>   | <b>Schematic (www.ore-<br/>max.com)</b> |
|-------------------------------|--|---|
| systems                       | <ul> <li>Gentle solution application</li> <li>Less evaporation losses (2 to 3 times<br/>less than sprays)</li> <li>Easy to install and can be installed<br/>in uneven surface</li> <li>Dripper tubes can be buried to<br/>provide a measure of insulation from low<br/>temperature surface conditions. Solution<br/>distribution not as even as sprays (improved by<br/>decreasing spacing)</li> <li>Less environment/ health issue due<br/>to reduced entrainment in air</li> </ul> |   |
|                               |  |   |

<B>Table 5</B><B>:</B> Characteristics of sprinklers or drip irrigation systems (Guzman, 2008; Burgmayer, 2002; Wan and Brierley, 1997; Wan, 1997).



| Heap leach test<br>work                      | Typical progress in phases  | Aim (s)  |  |
|--|---|--|--|
| Metallurgical test<br>work                   | <ul> <li>✓ Soluble metal</li> <li>✓ Shake flask test (bacterial leaching)</li> <li>✓ Bottle test</li> <li>✓ Columns</li> <li>✓ Cribs (concrete boxes)</li> <li>✓ Pilot (demo heap)</li> </ul> | To establish metallurgical parameters:<br>particle size, recoveries, leach agent<br>type and consumption, heap height,<br>irrigation rate, leach cycle, leaching<br>stages, impurities build-up, curing<br>requirement (acid dosage directly to the<br>ore previous irrigation). Additionally<br>for bio heap leaching: air flow rates,<br>bacterial compatibility, nutrient<br>requirements |  |
| Hydraulic and<br>geo-mechanical<br>test work | <ul> <li>Load percolation and load</li> <li>permeability</li> <li>Triaxial and direct shear</li> <li>test</li> </ul>  | Confirm irrigation rates, heap height,<br>heap stability, 'ripios' stability (on/off)  |  |

<B>Table 6</B><B>:</B> Heap leach test work, typical progress in phases and aims

Table 7: Historical and present gold heap leaching plants (Data presented here either are obtained from official organizations of the countries where gold heap leaching plants are located, or from official profiles of the companies which are/were operating the process. The list is not exhaustive, however, as many small-scale operations are notoriously difficult to track).

| <b>Plant</b>                  | <b>Location</b> | <b>Start-up or commissioned</b> | <b>Ounces of gold<br/>per year</b> |
|-------------------------------|-----------------|---------------------------------|------------------------------------|
| Cortez heap leach             | USA             | 1969-present                    | 1,500,000                          |
| Ortiz Gold Mine               | USA             | 1980-1986                       | 30,000                             |
| Chimney Creek Gold<br>Project | USA             | 1986-1990                       | 35,000                             |
| Sao Bento                     | Brazil          | 1990-present                    | 8,000                              |
| Fosterville                   | Australia       | 1991-present                    | 580,643                            |
| Harbour Lights                | Australia       | 1992-1994                       | 40.000-100.00                      |
| McDonald Gold heap            | USA             | 1993-1995                       | 285,000                            |

| leaching                      |           |              |               |
|-------------------------------|-----------|--------------|---------------|
| McDonald Gold<br>ROM leaching | USA       | 1993-1995    | 40,000        |
| Wiluna                        | Australia | 1993-present | 120,000       |
| Youanmi                       | Australia | 1994-1998    | 50,000-60,000 |
| Ashanti                       | Ghana     | 1994-present | 410,000       |
| Sansu                         | Ghana     | 1994-present | 420,000       |
| Newmont-Carlin                | USA       | 1995-present | 1,680,000     |
| Andacollo Oro                 | Chile     | 1995-present | 46,170        |
| La Coipa                      | Chile     | 1999-present | 178,287       |
| Tamboraque                    | Peru      | 1999-present | 27,000        |

| Agnes               | South Africa | 2003-2006    | 25,000          |
|---------------------|--------------|--------------|-----------------|
| Córrego do Sitio    | Brazil       | 2004-present | 245,000         |
| Los Filos           | Mexico       | 2005-Present | 300,000         |
| Refugio( Maricunga) | Chile        | 2005-Present | 236,368         |
| Sodzal              | Kazakhstan   | 2006-present | 89,000          |
| Walter Creek        | USA          | 2006-present | 333,383         |
| Kişladağ            | Turkey       | 2006-present | 300,000-335,000 |
| Bogoso/Prestea      | Ghana        | 2007-present | 176,000         |
| Kokpatas            | Uzbekistan   | 2007-present | 440,000         |
| Gedabek plant       | Azerbaijan   | 2009-Present | 54,000-60,000   |

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Table 8: Historical commercial copper heap and dump leaching operations now closed (Data presented here either are obtained from official organizations of the countries where copper heap leaching plants are located or from official profiles of the companies which were operating the process. The list is not exhaustive, however, as many small-scale operations are difficult to track).

| <b>Plant</b>             |  | <b>Location</b> | <b>Cathode copper<br/>production (t.a<sup>-<br/>1</sup>)</b> | <b>Years in operation</b> |
|--------------------------|--|-----------------|--|---------------------------|
|                          | Bluebird Mine                          | USA             | 6000   | 1968-1980                 |
| <b>Heap<br/>leaching</b> | Lo Aguirre                             | Chile           | 15,000   | 1980-1996                 |
|                          | Mount Gordon<br>(formerly<br>Gunpower) | Australia       | 33,000   | 1991-2008                 |
|                          | Mt. Leyshon                            | Australia       | 750  | 1992-1997                 |
|                          | Girilambone                            | Australia       | 14,000   | 1993-2003                 |
|                          | Ivan-Zar                               | Chile           | 10,000   | 1994-2012                 |
|                          |  |                 |  |                           |

|                          | Morenci biological<br>heap leaching | USA   | 108,000        | 1998-2001 |
|--------------------------|-------------------------------------|-------|----------------|-----------|
|                          | Equatorial<br>Tonopah               | USA   | 25,000         | 2000-2001 |
|                          | Safford Project                     | USA   | 93,000-109,000 | 2004-2007 |
|                          | El Abra                             | Chile | 147,000        | 2004-2009 |
|                          | Jinchuan                            | China | 10,000         | 2006-2009 |
|                          | Zijinshan                           | China | 10,000         | 2006-2009 |
| <b>Dump<br/>leaching</b> | El Abra Run-of-<br>Mine leaching    | Chile | 45,000         | 2000-2002 |
|                          |                                     |       |                |           |

Table 9: Present commercial copper (oxide and sulphide) heap leaching plants (Data presented here either are obtained from official organizations of the countries where copper heap leaching plants are located, or from official profiles of the companies which are operating the process. The list is not exhaustive, however, as many small-scale operations are difficult to track).

| <b>Plant</b>    | <b>Location</b> | <b>Cathode copper<br/>production (t.a<sup>-<br/>1</sup>)</b> | <b>Years in operation</b> |
|-----------------|-----------------|--|---------------------------|
| Lince           | Chile           | 37,700   | 1991-Present              |
| Girilambone     | Australia       | 14,100   | 1993-Present              |
| Cerro Colorado  | Chile           | 83,400   | 1993-Present              |
| Punta del Cobre | Chile           | 7,000-8,000  | 1994-Present              |
| Quebrada Blanca | Chile           | 63,000   | 1994-Present              |
| Biocobre        | Chile           | 12,000   | 1994-Present              |
| Cananea         | Mexico          | 54,750   | 1995-Present              |

| Phoenix deposit                   | Cyprus    | 8,000   | 1996-Present |
|-----------------------------------|-----------|---------|--------------|
| Andacollo Sulphuros<br>(Hipogeno) | Chile     | 4,000   | 1996-Present |
| Mt Cuthbert                       | Australia | 15,000  | 1996-Present |
| Andacollo-Cobre                   | Chile     | 21,000  | 1996-Present |
| Dos Amigos                        | Chile     | 10,000  | 1996-Present |
| Skouriotissa                      | Cyprus    | 8,000   | 1996-Present |
| Mantoverde (MVN)                  | Chile     | 57,000  | 1996-Present |
| Cerro Verde                       | Peru      | 54,200  | 1997-Present |
| Radomiro Tomic                    | Chile     | 300,000 | 1998-Present |

| Monywa                             | Myanmar   | 40,000  | 1998-Present |
|------------------------------------|-----------|---------|--------------|
| Nifty Copper                       | Australia | 16,000  | 1998-Present |
| Morenci engineered heap<br>Project | USA       | 365,000 | 1998-Present |
| Escondida Oxides                   | Chile     | 150,000 | 1998-Present |
| Zaldivar                           | Chile     | 132,088 | 1998-Present |
| Cobriza                            | Peru      | 3,000   | 1999-Present |
| Three valleys                      | Chile     | 14,000  | 1999-Present |
| Cerro negro (Planta)               | Chile     | 3,400   | 1999-Present |
| Media Luna                         | Chile     | 2,400   | 1999-Present |

| El Abra                      | Chile     | 153,314 | 2000- Present |
|------------------------------|-----------|---------|---------------|
| Delta                        | Chile     | 400     | 2005-Present  |
| Lisbon Valley                | USA       | 27,000  | 2006-Present  |
| Whim Creek and Mons<br>Cupri | Australia | 17,000  | 2006-Present  |
| Jinchuan copper              | China     | 10,000  | 2006-Present  |
| Spence                       | Chile     | 180,300 | 2007-Present  |
| El Soldado-Oxide             | Chile     | 2,000   | 2007-Present  |
| Gabriela Mistral             | Chile     | 30,000  | 2008-Present  |
| Caserones copper deposit     | Chile     | 30,000  | 2013-Present  |

Table 10: Present commercial copper dump leaching plants (Data presented here either are obtained from official organizations of the countries where copper dump leaching plants are located, or from official profiles of the companies which are/were operating the process. The list is not exhaustive, however, as many small-scale operations are difficult to track).

| <b>Plant</b>     | <b>Location</b> | <b>Cathode copper<br/>production (t.a<sup>-<br/>1</sup>)</b> | <b>Years in operation</b> |
|------------------|-----------------|--|---------------------------|
| Bagdad           | USA             | 88,000   | 1968-Present              |
| Los Bronces      | Chile           | 40,741   | 1980-Present              |
| Toquepala        | Peru            | 44,000   | 1980-Present              |
| Quebrada Blanca  | Chile           | 22,900   | 1994-Present              |
| Pinto Valley     | USA             | 10,000   | 1998-Present              |
| Zaldivar         | Chile           | 18,000   | 1998-Present              |
| Mantos Blancos - | Chile           | 46,200   | 1999-Present              |

| Oxide            |       |        |              |
|------------------|-------|--------|--------------|
| Mantoverde (MVN) | Chile | 6,000  | 1999-Present |
| Chuquicamata     | Chile | 26,000 | 2011-Present |
|                  |       |        |              |

<B>Methods</B> <B>Inventor (s)</B> Saprolite neutralisation of heap leach process Liu, 2008 Moroney, 2007 Limonite and saprolite heap leach process Hydrometallurgical method for the extraction of nickel and cobalt from Rodríguez and Wedderburn, laterite ores 2005 Process for extraction of nickel, cobalt, and other base metals from Pereira, 2005 laterite ores by using heap leaching and product containing nickel, cobalt, and other metals from laterite ores An improved process for heap leaching of nickeliferous oxidic ores Liu, 2005 Production of ferro-nickel or nickel matte by a combined Duarte <I>et al</I>., 2004 hydrometallurgical and pyrometallurgical process Process for recovery of nickel and cobalt by heap leaching of low-Liu and Mille, 2003 grade nickel or cobalt containing material

Table 11: The list of the patents for application of heap leaching processes in extraction of nickel from laterites.

| Heap leaching base metals from laterite ores               | Anthony and Purkiss, 2002    |
|--|------------------------------|
| Heap leaching of nickel containing ore with sulphuric acid | Davis <i>et al</i> ., 2000   |
| The recovery of nickel using heap leaching                 | Tunley, <i>et al</i> ., 1994 |
| Received Man   |                              |



Figure 1: Typical heap bioleach flow diagram for copper.

Figure 2: Schematic view of a heap section space occupied by ore particles, mobile and stagnant air, as well as mobile and stagnant liquid solution phase. Note the cut-out of a single particle indicating a micro-pore network continues inside the particles.



Figure 3: Typical single and double composite liner.

