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EFFECT OF LEACHING AID IN HEAP LEACHING OF COPPER ORES – COLUMN TEST STUDY

MSc (50/50) Research Report

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DECLARATION

I solemnly declare that the project report entitled “Effect of LixTRA leaching aid in heap leaching of copper ores – Column test study” submitted to the University of Witwatersrand in partial fulfilment for the degree of Master of Science in Engineering: Metallurgy and Materials Engineering, is my own work. This work was carried out under the supervision of Prof Kathryn Sole and Dr. Jack Bender. It has not been submitted before for any degree or examination to any other University.



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ABSTRACT

Solution percolation is critical in heap leaching applications. The use of leaching aids has been proven to improve the percolation of solution due to their effects on the surface tension. The introduction of leaching aids reduces the solution surface tension and ultimately improves the flow of solution through small pores or hard-to-flow areas.

This study focused on determining the effect of the BASF leaching aid, LixTRA 118, on the solution dynamics through narrow and wider particle size distributions within heaps, as well as evaluating its effect on the acid consumption and metal recovery.

The hydrodynamics of the solution were studied through drainage tests. The effect of the leaching aid was evaluated by comparing columns with and without a leaching aid. The same approach was used to evaluate its performance in terms of acid consumption and metal recovery.

The effect of the leaching aid was found to be more pronounced at wider particle size distribution ranges. This was found to be associated with the solution holdup inside the particle bed and the capillary actions. The latter was also responsible for the increase in metal recovery and acid consumption.

Further work is recommended to ascertain the effect observed with the consumption of leaching aid and the selectivity of copper over certain other metals.

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Chapter I.

INTRODUCTION

1.1 BACKGROUND

Heap leaching is a well-established hydrometallurgical technology that enables the economical extraction of valuable metals from low-grade ores. It consists of trickling a lixiviant through a pile of crushed ore to leach target minerals. Its profitability is well known to be limited by how well the leach solution is supplied or distributed through the heap (leaching of oxide ores) and by the oxygen mass transfer (oxidative sulfide leaching). These are intrinsically linked to the ore type, ore preparation, heap design, and ambient conditions. Therefore, a key aspect in successful operation of heap leaching is to recognize what parameters are limiting the rate of extraction and to find ways to control them (Petersen, 2019).

Two main causes limiting the rate of extraction in leaching operations have been identified. The first one is an excessive amount of fine and clayey materials. These create channeling and dormant or unleached areas within the heap, which ultimately result in poor metal extraction. The crushed ore agglomeration technique has been implemented to deal with this issue. It consists of agglomerating the stage-crushed ore prior to heap leaching it. An agglomeration step aims at conditioning the ore with the lixiviant to increase the metal extraction and to facilitate agglomeration by coalescing of fines onto large particles through liquid bridges (Dhawan et al., 2012). The use of lixiviant alone as a binder is usually not sufficient because it does not bind the material very strongly. Agglomeration aids or binders are often also added to form much stronger bonds and produce stable agglomerates that guarantee stability of the heap (Lewandowski & Kawatra, 2009). The solution pH and the binder operational pH are important parameters to consider in selecting the binder for heap leaching application. Cement, bentonite, some polymers, and other binders have been successfully employed in alkaline leaching conditions, such as in heap leaching of gold ores. However, for heap leaching of copper oxide ores and microbial leaching of sulfidic ores, most of the readily available binders are not capable to withstand the extreme acidic environment and the attack by microbial organisms (Bouffard, 2005). These environments weaken the bonds formed, causing agglomerates to break; thus, the heap reverts to solution channeling and pooling. There

is certainly more room for improvement with regards to the use of binders for agglomeration in heap leaching operations.

Other than the solution channeling and pooling due to fine and clayey materials being in excess, various other mechanisms have been found to limit the flow of solution and the transport of solutes during heap leaching. These mechanisms happen at different times and scales within the heap. Nonetheless, at different extents, they limit the overall metal extraction rate.

On a macroscopic scale, the leaching solution in a heap flows principally downward through larger pores, which exist between coarse ore particles. Evidently, here, gravity is the main driving force. In finer interstitial spaces and inside cracks, it is the capillary action that initially drives the flow of solution. After wetting, finer pores may become saturated with the solution. Owing to the concentration gradient, solutes could still diffuse in and out of the stagnant solution contained in the interstitial space between finer particles. However, the overall extraction rate would be controlled by the distance to the nearest flowing solution channel and the flowrate of solution through larger pores.

Capillary action occurs because of the solution surface tension, the cohesive forces between solution molecules, and the adhesion forces between the solid particles and the solution. The presence of surface tension forces liquids into shapes and motions that differ from what they would be in its absence (Trefethen, 1969). Scientifically, water, the solvent in heap leaching of copper ores, has a higher surface tension than most other liquids. This forces it to shrink to the minimum surface area possible when contacted with a particular surface. In a porous media, the surface tension will not allow water to move freely because the surface of the water is able to keep its shape, i.e., sand would hold more water than ethanol, even if the densities of ethanol and water are considered. This is possible because ethanol has a lower surface tension than water. The lower surface tension improves the wetting and the solution flow through the porous media.

Surface-active agents or surfactants have been employed in heap leaching to improve the metal extraction by improving the solution flow mechanisms. Surfactants reduce the lixiviant surface tension, which allows the solution to penetrate more fissures and flow through initially hard-to-flow areas. This results in higher metal recovery in the pregnant leach solution (PLS) due to the increased contact with the ore. Unfortunately, the heap

leaching industry has been sceptical in implementing the use of surfactants, possibly due to incompatibility of some of the leaching aids with downstream processes, such as solvent extraction (SX) or their effects on microorganisms in the case of bioleaching. There is a need to develop leaching aids that are more suitable to the metal extraction across the entire value chain.

BASF has developed a new leaching aid that has proven to increase metal recovery and was found to have no effect on downstream processes or microorganisms (Bender, 2017). Considerable testwork has been performed with various leaching aids. The aims have mainly been to measure their effects on extraction rates and determine whether or not they would affect SX and bioleaching. However, it is important to better understand the mechanisms of actions of these additives in order to maximize the metal recoveries and reduce the extraction period. This is the focus of this research.

1.2 RESEARCH PROBLEM

One of the biggest challenges associated with heap leaching is the poor solution percolation through voids and penetration into cracks. This results in extended leaching periods and poor metal recoveries (Ghorbani et al., 2016). Many scholars have studied ways to improve the performances of heap leaching operations, one of these being the use of surfactants or wetting agents as leaching aids.

The use of surfactants has unfortunately not been widely adopted by plant operations, possibly because no extensive studies have been done on the subject to guarantee that these surface-active agents would not have negative impacts on downstream processes. Understanding how and to what extent the leaching aid affects ores of different physical and chemical characteristics, as well as the impacts of the leaching aid on downstream processes, could facilitate their adoptions in plants operations. This would ultimately result in shortening of the leaching periods and reducing the cost of operations.

The proposed research seeks to evaluate the performance of the BASF leaching aid, LixTRA 118, at different ore particle sizes as well as its impact on acid consumption. To achieve this, column leach studies were carried out on copper oxide and mixed oxide and sulfide ores.

1.3 RESEARCH OBJECTIVES

The ultimate aim of this project is to better understand the mechanisms of actions of the BASF leaching aid in leaching of copper ores. More specifically, the objectives set out for this study are to:

- a. evaluate the drainage effect associated with different size fractions using LixTRA 118 as a leaching aid in heap leaching of a copper oxide ore;
- b. study the acid-consumption characteristics using LixTRA 118 to assist leaching of a mixed oxide and sulfide ore;
- c. ascertain the effect of dosage of the leaching aid on the recovery of copper and iron through the leaching period.

1.4 RESEARCH QUESTION

The central question in this study is how would the physical characteristics of copper ores affect the performance of the LixTRA 118 leaching aid?

The following are sub-questions:

- a. How significant is the effect of LixTRA 118 leaching aid on solution flow characteristics in a bed consisting of only finer particles compared with a bed that only contains coarser particles?
- b. How is the effect of the LixTRA 118 leaching aid on the solution flow in a bed containing a much wider particle size distribution compared with a bed that has a narrow particle size range?
- c. What is the effect of LixTRA 118 leaching aid on the acid consumption of a secondary copper sulfide ore?
- d. What is the effect of LixTRA 118 leaching aid on the metal recovery and contamination?
- e. How does the solution irrigation rate affect the consumption of the LixTRA 118 leaching aid?

1.5 THESIS OUTLINE

This thesis is divided into five chapters, organised in the following manner:

- a. The introduction is given in Chapter 1, in which the topic is introduced and its importance established. It also consists of the research problem and justification, the research objectives, the research question as well as the thesis outline.
- b. The literature review in Chapter 2 discusses principles of heap leaching operations and theories related to the flow of solution in a porous media. It also describes phenomena by which a surfactant can contribute to improving the flow of solution, which ultimately leads to improving the metal extraction. The LixTRA 118 leaching aid is introduced in this section.
- c. Chapter 3 presents the experimental procedure followed in this study.
- d. Chapter 4 presents the results and discusses the findings.
- e. The conclusion of the research and suggestions for future work are given in Chapter 5.

1.6 LIMITATIONS

This study is limited to the performance of the LixTRA 118 leaching aid on copper oxide and secondary sulfide ores.

Chapter II.

LITERATURE REVIEW

2.1 PRINCIPLES OF HEAP LEACHING

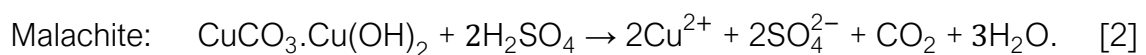
Heap leaching is the dominant hydrometallurgical extraction method for the treatment of free-milling gold, secondary uranium, acid-soluble copper and secondary-sulfide copper ores. The effectiveness of treating these ores is due to the low cost associated with heap leaching operations (Kappes et al., 2002).

In heap leaching, the ore is crushed and stacked on a pile from 6 to 10 m height. A leaching agent, which can either be the raffinate from SX or sometimes an intermediate leach solution, is sprinkled from the top of the heap at an irrigation rate of 5 to 20 L/m²/h (Natarajan, 2018). The solution is allowed to penetrate the heap and bring the metals into solution. In the case of bioleaching, aeration pipes are placed underneath the pile to provide air as the oxidant at a rate of 0.1 to 0.5 m³/m²/h. The air is assumed to rise through the unsaturated void spaces. The PLS is collected from an impermeable base at the bottom of the heap, which is sloped to direct the PLS to a collection pond. The complete cycle for heap leaching lasts from ten days to several months, depending on the ore type being processed (Schlesinger et al., 2011).

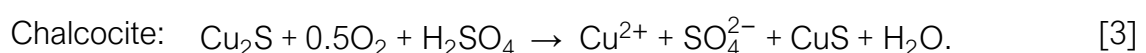
2.1.1 Copper Leaching

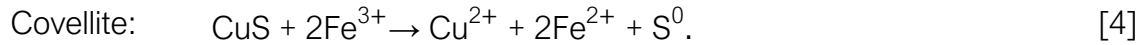
Copper leaching occurs according to the following main leaching reactions (Schlesinger et al., 2011):

Non-sulfidic copper minerals, such as malachite and tenorite, are leached directly by sulfuric acid according to:

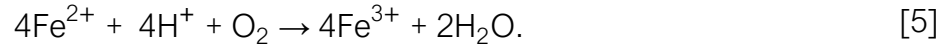


Leaching of secondary copper sulfide requires an oxidant, such as ferric iron or oxygen, to break the mineral lattice and release Cu²⁺ according to:





The ferric sulfate is regenerated by oxidation with atmospheric oxygen according to:



The leaching of refractory copper ores, such as chalcopyrite, requires high temperatures and pressures to economically leach them. The leaching of chalcopyrite is done at a temperature between 150 °C and 250 °C, according to the overall reaction:



2.1.2 Typical Copper Hydrometallurgical Recovery Route

A schematic of the heap leaching in a typical copper hydrometallurgical extraction route is presented in Figure 1.

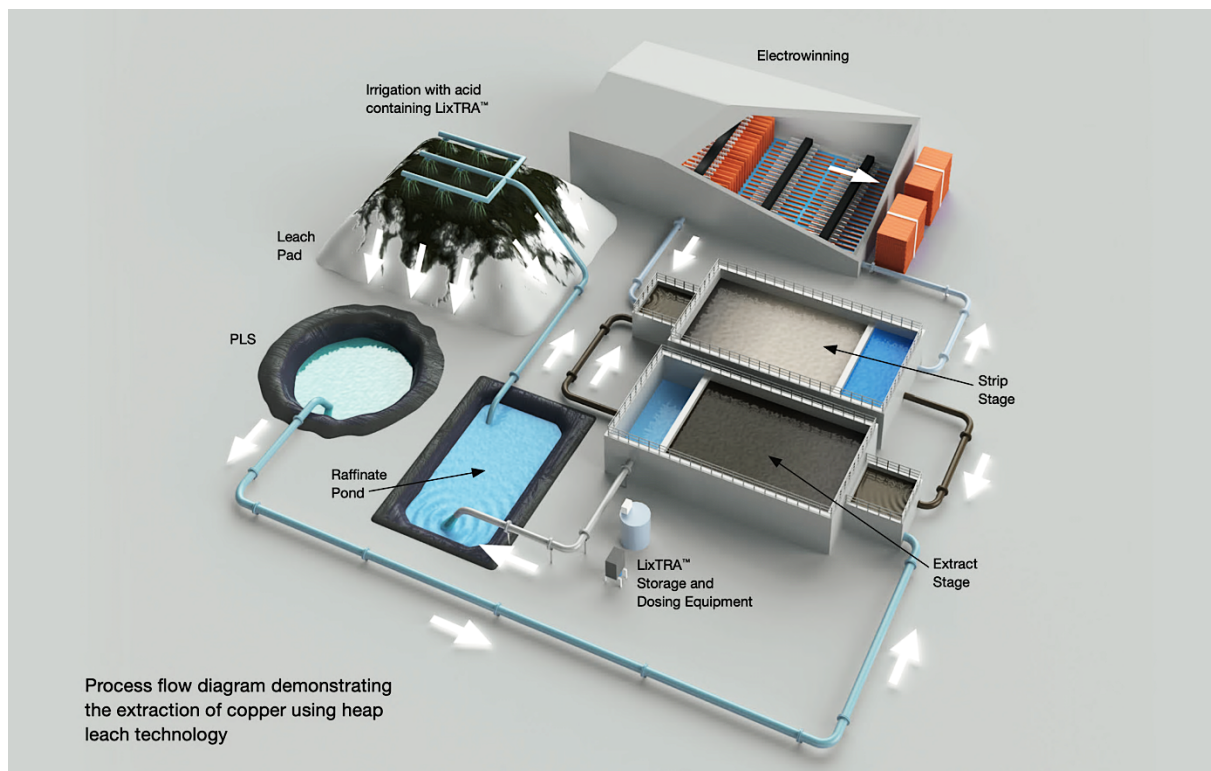


Figure 1: Typical process flow for treatment of low-grade copper ores (BASF, 2019).

After mining and crushing, the ore is piled onto a heap and sprinkled with leaching solution, which percolates through the heap and dissolves the metal into solution. This PLS exits the heap with a copper grade of 1 to 6 g/L and is fed into an extraction mixer along with an immiscible barren organic solution where the two solutions are intimately

mixed. The resulting emulsion is transferred to a settler, where the two solutions separate to give a metal-loaded organic solution (LO) on top and an aqueous solution depleted of the metal called raffinate at the bottom. The raffinate is recycled to the leaching stage, whilst the LO is transferred to the next mixer (strip mixer), where it is intimately mixed with a stripping solution. The resultant emulsion overflows into a settler, where it separates into a metal barren organic (BO) and a concentrated aqueous solution called pregnant strip solution (PSS). The copper grade in the PSS is about 40–50 g/L (Komulainen et al., 2009) and the acid, typically sulfuric, is 120–180 g/L (Evans, 2003). The BO is returned to the extraction stage, whilst the PSS is transferred to an electrowinning (EW) stage. In EW, metallic copper (99.99 %) is produced by electrodeposition onto stainless steel or sometimes copper cathodes. The solution depleted of the metal is recycled to the stripping stage.

2.2 HEAP LEACHING CHALLENGES

The major drawbacks of the heap leaching technology include the lower metal extraction, the long ramp-up times, and lengthy experimental programmes (Robertson et al., 2012). Additionally, a number of heap leaching operations have been found to exhibit a number of challenges, which include poor or lower-than-predicted recoveries, loss of solution flow or control within the heap, loss of heap stability under leach, failure of liner and/or solution recovery systems and overtopping of process water ponds. These effects may be the results of many compounding conditions (Lupo, 2012). Therefore, the duration of heap leaching operations can last from days to several months or years, as in the case of bioleaching. With time, the rate of leaching becomes slower, while the rate of gangue reagent consumption, the cost of pumping and other operating expenses (OPEX) remain more or less constant. Hence, ultimately, the rate of OPEX expenditure attributable to an old heap eventually becomes more than the revenue flow attributable to the metal extracted from it. Thus, the irrigation of leach solution is often discontinued after reaching recoveries of approximately 80 to 90 % or 70 to 80 % for copper oxides and sulfides operations, respectively (Petersen, 2016).

The irrigated leach solution percolates through the heap and arrives in the pores amongst particles by a combination of advection and capillary action. The acid diffuses through the solution to react with the minerals and dissolve them as metal complexes. These

diffuse into the solution, which gravitates to the bottom of the heap and to the ponds (Lapidus & Sánchez-Chacón, 1997). It has been found that the main factor limiting the kinetics of heap leach operations is seldom the reaction kinetics but rather the flow of the leach solution through the heap, into and out of the cracks and pores (Schlesinger et al., 2011). However, it is important to note that this is mostly true for acid leaching of copper oxides and bioleaching of secondary copper sulfides ores, which are widely practiced. In the case of bioleaching primary sulfides, the reaction kinetics can indeed be the rate-determining step.

Petersen (2016) and many other researchers have discussed a number of sub-processes that limit the overall leach process at different times and places within the heap. These processes are associated with the method by which solution flow is governed within the heap. They are controlled by both physical and chemical factors. Underestimating the complexity that drives the leaching kinetics is often the cause for heap leach underperformance (Petersen, 2016). Therefore, understanding the different processes or mechanisms occurring within the heap is essential for maximizing recovery and optimizing the leaching time.

Mechanisms occurring at various level within the heap are described in the following sections.

2.2.1 Heap-Scale Mechanisms

The solution flows primarily downward due to gravity and through spaces between particles. Areas with more fines exhibit small pores, which tend to be saturated, whilst those with larger particles remain unsaturated. With time, areas containing stagnant solution are developed and become challenging to the flow of solution, which, ultimately leads to low metal extraction. Crushed ore agglomeration has been practiced, aiming at counteracting the solution-channeling effect by ensuring heap homogeneity and better permeability. Figure 2 depicts what usually happens on a heap scale.

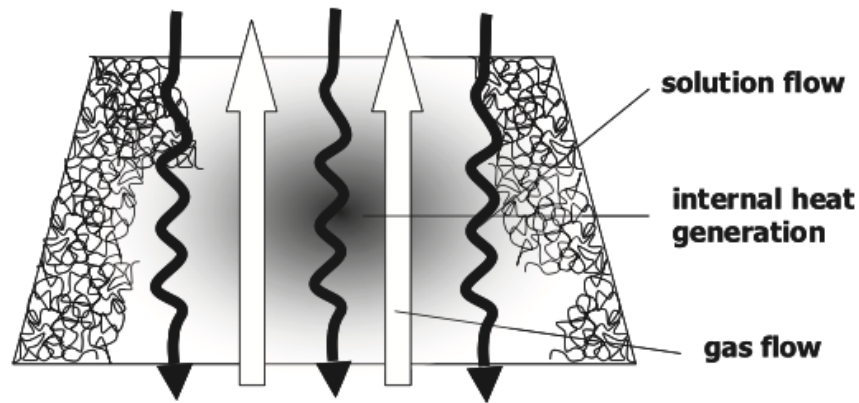


Figure 2: Schematic showing processes involved in heap bioleaching operations on a heap scale (Petersen, 2016).

2.2.2 Agglomerate-Scale Mechanisms

Agglomeration refers to a collection of particles held together by the bonds formed between particles and binding agents, added during agglomeration. The space between agglomerates and the pores within agglomerates can become saturated by stagnant solution. Diffusion of reagents (acid, CO_2 , O_2 and micro-organisms, etc.) and reaction products through the stagnant agglomerated zones could be a major rate-limiting factor. This is well illustrated in Figure 3.

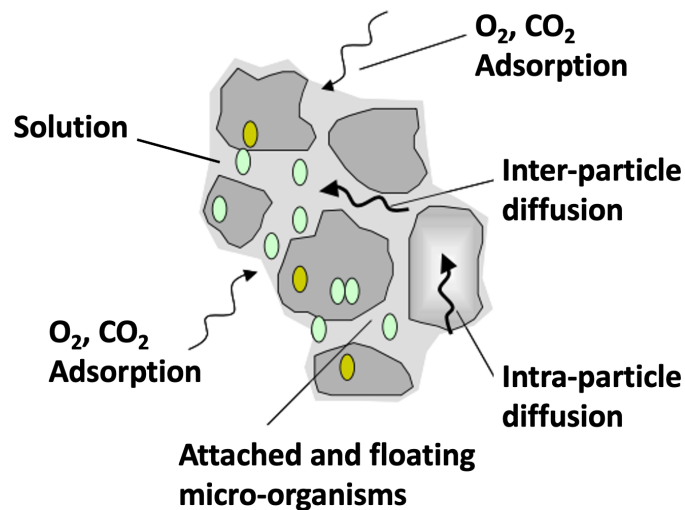


Figure 3: Schematic showing processes occurring on an agglomeration-scale level in heap bioleaching (Petersen, 2016).

2.2.3 Particle-Scale Mechanisms

Ore crushing for heap leaching applications is often limited to relatively coarser sizes in order to ensure heap stability. This limits the degree of liberation and causes the mineral species to remain embedded within the matrix of gangue minerals. During leaching, the

reagents need to diffuse through the pores and cracks within the particles to reach the valuable mineral species (Petersen, 2016). Ore porosity or permeability is necessary on a particle-scale level for migration of the solution, as shown in Figure 4.

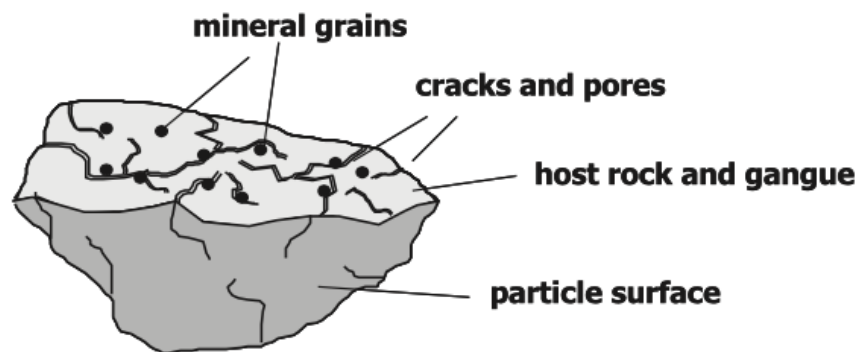


Figure 4: Schematic showing processes occurring at a particle-scale level in heap bioleaching (Petersen, 2016).

Scholars have proposed ways to improve ore porosity. These include granulation, classified heap construction (including agglomeration), use of a mechanical loose heap, as well as the addition of scale inhibitors and surfactants. All of these have proven to be effective (Ai et al., 2019).

Migration of the leach solution through small pores and rock fractures is achieved by capillary action. The latter is also the main driving force for wetting of the ore and ensuring the lateral distribution of the solution in heap leach operations (Yin et al., 2016). It depends on a number of factors including solution surface tension, adhesion forces between solid surface and liquid, as well as cohesion forces between molecules in the solution.

2.2.4 Mineral Grain-Scale Mechanisms

On an individual mineral grain within the ore particle, the chemical interaction taking place is similar to the pure mineral leaching. The kinetics are driven by the chemical conditions at the mineral surface in terms of reactant concentrations, the pH, the temperature, and the presence of other ions (Petersen, 2016). This is illustrated in Figure 5.

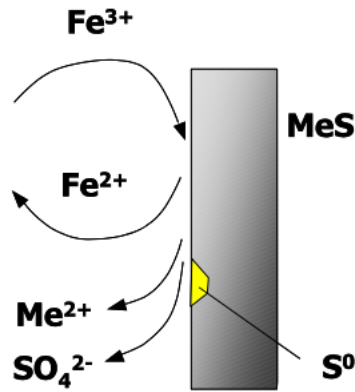


Figure 5: Schematic showing processes occurring on a mineral grain scale (Petersen, 2016).

The overall rate-limiting step in heap leaching is generally not the reaction on a grain-scale level but rather the flow of leach solution through the heap, into the pores and cracks, and, consequently the diffusion of the metal complex out of the cracks and down to the PLS pond (Miller, 2003).

Petersen (2016) argued that the reagent-limiting kinetics, such as the oxygen diffusion, the acid migration and rate of irrigation, are more prevalent at the beginning of the leaching process. During the leaching, however, the ore particles are surrounded by the solution, until the whole heap becomes wetted. The work from Van Genuchten & Wierenga (1979) and Petersen (2016) has suggested the presence of a layer of solution that remains stagnant around the particle. The leaching kinetics becomes also a function of the diffusion through the stagnant solution layer. The stagnant solution layer is enveloped by the bulk solution moving mainly by gravity (Figure 6). Therefore, the recovery of the metal from the cracks is controlled by the concentration gradient between the immobile solution inside the cracks and the bulk solution moving by gravity (Figure 7).

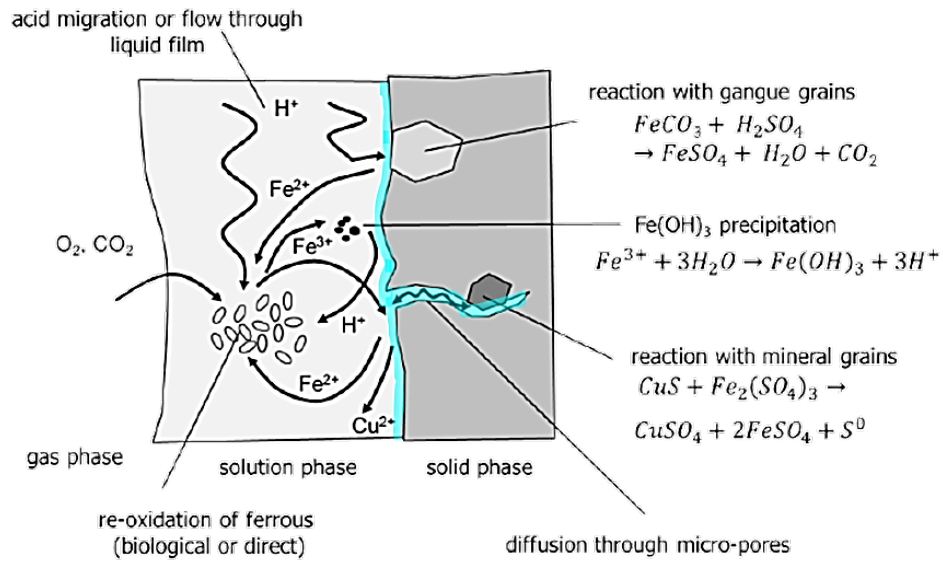


Figure 6: Schematic representation of the diffusion-reaction pathways at the particle scale in heaps, showing the stagnant solution layer around the particle (blue). Adapted from Petersen (2019).

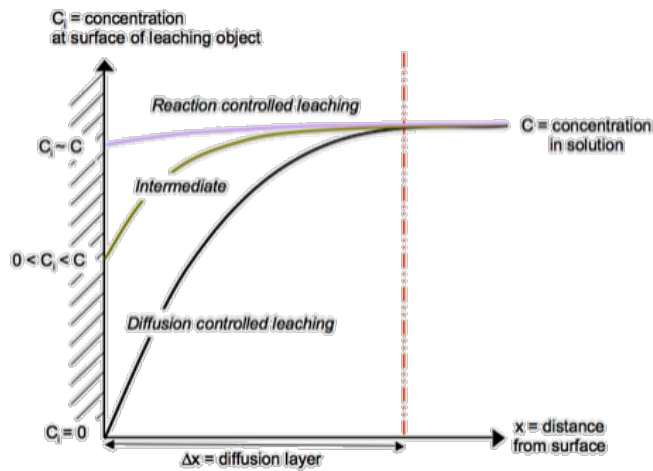


Figure 7: Leaching process at boundary between leaching object and solution (BioMineWiki, 2020).

2.2.5 Competitive Reactions In Copper Leaching

The recovery of metals from low-grade ores is often not optimal. This is due to the presence of gangue minerals and their interactions with the acid. The mineralogy of the gangue, its texture and relative particle size distribution, its reactivity with the acid under different conditions and the relationship to lithotypes and geological alteration in the orebody are fundamental aspects to understand in order to predict the ore behaviour during leaching (Chetty, 2018). Depending on these factors, the gangue will impact the operational cost, the acid consumption and, eventually, the copper recoveries.

Some of the issues associated with certain gangue minerals are:

- The reactivity of silicate gangue minerals and their effects on acid consumption is important to understand, as these minerals often form the bulk of the ore. Some silicate gangue minerals are largely soluble and can result in the formation of silica gel, which could cause blinding inside the heap. Some can be altered into new minerals like clay or form precipitates, which can hold acid.
- Ores with considerable amount of carbonate minerals are not treated via heap leaching due to the high acid consumption that would result.

2.3 AGGLOMERATION

A major problem in heap leaching operations is the presence of excessive fine materials produced during blasting and crushing. The fine materials cause channeling and pooling of leaching solution in some areas within the heap, resulting in certain areas of the heap not being contacted with the lixiviant (Figure 8). This, ultimately, leads to poor metal recoveries (Dhawan et al., 2012).

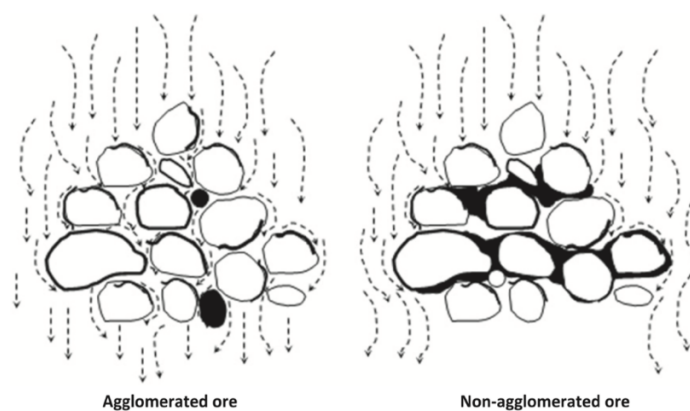


Figure 8: Comparison of solution percolation in agglomerated vs. non-agglomerated ores (Dhawan et al., 2012).

Considerable work has been done to limit the generation of fine materials. Two of the approaches are the implementation of high-pressure grinding rolls (HPGR) (Baum & Ausburn, 2011) and multi-stage crushing. The latter consists of crushing in series of two or three crushers. In addition to reducing the generation of fines, these techniques also reduce the energy consumption (Halder, 2018). Despite these efforts, significant amounts of fines are still generated during blasting due to the presence of soft or clayey materials (Dhawan et al., 2012).

Crushed ore agglomeration can be successfully considered and utilized as a pre-treatment step for heap leaching of ore containing significant amounts of fines and clay minerals (Dhawan et al., 2012). It consists of either agglomerating the fines onto coarse particles with water (or leach solution) or by binding the fines together prior to heap leaching. Very often, an agglomeration aid or binder is added to strengthen the adhesion forces between the water and the ore particles. This binder can be a liquid or solid that can form a bridge, or matrix, or that causes a chemical reaction (Bouffard, 2005). The strong bonds created by these binders will prevent degradation of the agglomerates as they come to contact with the leaching solution in the heap, thereby, ensuring heap stability (Lewandowski & Kawatra, 2009).

2.4 LEACHING AIDS

2.4.1 Mode Of Action

It is well known that leaching rates can be greatly improved after finely grinding the ore material (Mgaidi et al., 2003). This is because grinding increases the surface area that is necessary for the interaction between the leaching solution and the solid material – it increases the probability of contact occurring between the metal grain surfaces and the leaching phase (Deschenes et al., 2011). In heap leaching processes, as opposed to tank leaching, the ore particles are coarse and the flow of solution is governed simply by gravity and capillary actions. This results in long ramp-up times due to the high presence of hard-to-flow and often preferential flow areas within the heap (Robertson et al., 2012).

Leaching aids are basically surface-active agents (surfactant) that can modify the surface tension of the solution. In the context of heap leaching, a leaching aid reduces the lixiviant surface tension and changes its wetting behaviour. In doing this, it allows the solution to penetrate easily into fissures and micro-pores. It improves the permeability of the ore, allowing more contact with the mineral species and ultimately results in higher metal recoveries and extractions.

The action of surfactants was proven by a number of researchers to occur mainly according to the aspects discussed in the following sections (Ai et al., 2019).

2.4.1.1 Change of wettability

The main mode of lateral spread of leach solution throughout a heap is by capillary action. The latter occurs when the adhesion to the surface walls is stronger than the cohesive forces between the liquid molecules. Young (1805) and Dupre (1869) proposed a force balance approach to quantify the wetting behaviour at the contact angle between solid, liquid and gas phases (Nikolov & Wasan, 2014). The attempt to quantify the spreading phenomenon of the liquid onto a solid, led to Equation 7:

$$S = \sigma_{sg} - \sigma_{sl} - \sigma_{gl}, \quad [7]$$

where S is the spreading coefficient, σ_{sg} , σ_{sl} and σ_{gl} are the solid–gas, solid–liquid and gas–liquid interfacial tensions, respectively.

The larger the value of S , the stronger the ability of the liquid to spread (better wetting). Water, the main constituent of the leach solution, has a very high surface tension, which limits its ability to spread. From a practical point of view, the ability of solution to spread can be improved by the addition of a surfactant. Surfactants reduce the surface tension of the solution and thus improve the wettability. The solution can now flow faster, and easily penetrate small pores.

2.4.1.2 Improvement in solution flow

An unsaturated porous heap is often conceptualized as a bundle of capillary tubes (Yin et al., 2016). When a capillary tube is placed in a container that contains water, the water will rise in the tube to a certain height. This effect is due to the interfacial tension between the solid tube and the water (wetting agent) being higher than that between air (the non-wetting phase) and the solid tube. This is referred to as the capillary effect.

Capillary pressure is the pressure difference across the curved interface between two immiscible fluids in contact in a small capillary tube. The pressure difference is expressed in terms of wetting and non-wetting phase pressures (Fanchi, 2002), thus:

$$P_c = P_{nw} - P_w, \quad [8]$$

where P_c is the capillary pressure, P_{nw} and P_w , are, respectively, the pressures of the non-wetting and wetting phases.

It is related to the interfacial tension, the pore size and the contact angle by (Yin et al., 2016):

$$P_c = \frac{2\sigma_{gL}\cos(\theta)}{r}, \quad [9]$$

where σ_{gL} is the interfacial tension between the liquid and the gaseous phase, θ is the contact angle between a liquid drop and the solid surface, r is the radius of the pore or tube.

Capillary action can also be expressed in terms of the pressure head, which is the height to which the wetting fluid rises in the capillary tube. The equation is stated as:

$$h = \frac{2\sigma_{gL}\cos(\theta)}{\rho g r}. \quad [7]$$

In this equation, h is the capillary head, ρ is the density, while g is the gravity.

From the equation, it can be deduced that, as the pores in the porous media become smaller, the effects of interfacial forces become even more important. This results in further increase in capillary head.

In heap leaching, small pores are almost always present. Therefore, capillary action often causes upward vertical movement of solution due to the pressure gradient between the solid surface and the wetting fluid (Mikhailov et al., 2018). As leaching progresses, these capillaries can become saturated with solution. Gravity alone will not be enough to pull the solution down through the pores. This effect should, to some extent, reduce the flowrate of the PLS being collected at the bottom because gravity is the main driving force.

The upward rising of solution can be counteracted by increasing the pore sizes or reducing the surface tension of the solution. The reduction of the surface tension of water will encourage the flow of solution through capillaries as the interaction with the solid surface is reduced.

2.4.1.3 Decrease in viscosity of lixiviant

Darcy's law of water flow in unsaturated porous medium shows the dependency of the hydraulic conductivity on both the fluid and the medium properties (Zheng & Bennett, 2002). This relationship is expressed thus:

$$K = Cd^2 \frac{\rho_d}{\eta}. \quad [8]$$

In this equation, K is the permeability, C is a constant that depends on the heap structure and porosity, d is the ore particle size, ρ_d is the unit mass of the solution and η the solution viscosity.

This equation can be used to describe the retention and distribution or the penetrability of the lixiviant and solutes in a heap. It is true that once the heap has been constructed, the parameters C and d would hardly change (Ai et al., 2019). This leaves the permeability of the ore to depend mainly on the solution characteristics. Therefore, a reduction in viscosity, which is achievable by addition of a surfactant, can improve the flow of the lixiviant through the heap voidage.

2.4.1.4 Adsorption

Surfactant can adsorb onto the ore surface and into fissures between particles. This promotes extension of fissures (wedge action), which is beneficial for solution penetration and ultimately metal recovery.

2.4.2 **Process Compatibility**

In the process of winning metal from low-grade ores by hydrometallurgical routes, the PLS produced from heap leaching is transferred to the SX stage where it is purified, and the metal upgraded to levels that are amenable to EW (Figure 1). It is critical that any additives introduced at any stage also be compatible with the downstream processes (Vest et al., 2009).

The performance of the SX process is strongly affected by the presence of any foreign species that interfere with the interfacial characteristics. This is because it is an interfacial process (Sole & Tinkler, 2016). Thus, with leaching aids being generally surfactants, an excess of these in the leach solution could cause the formation of a stable dispersion, leading to an increase in settling rate and phase separation time. The increase in contact

time between the PLS and the SX organic can lead to increased entrainment losses, poor transfer kinetics, hydrolytic degradation of the extractant, and/or nitration of the extractant if conditions are suitable. It is therefore critical to control the concentration of surfactants to levels that are compatible with SX operations.

Mining industries have not widely adopted the use of leaching aids. This is possibly because of the effects that some surfactants may have on downstream processes. Whilst several leaching aids exist and work differently, it is necessary to assess their compatibility as well as that of any other additive on downstream processes. In the case of secondary sulfide minerals, it is also important in the case of bio-heap leaching processes that the leaching aid does not interfere with the biological respiration necessary to convert the mixed sulfide copper to copper sulfate in solution (Bender, 2017).

Bender (2017) evaluated the effect that the new BASF leaching aid, LixTRA 118, had on SX operations. He found no significant effect on the phase disengagement when using the leaching aid in the appropriate dosage, which is approximately 25 mg/L. At doses up to four times the operating dosage, the aqueous-continuous phase disengagement times (PDT) were within the error of the experimental method. At extremely high concentrations, ten times dosage, there was still no significant effect on the aqueous-continuous phase disengagement. The organic-continuous PDT was not affected at any concentration of leaching aid tested, at up to fifty times the operating dosage. In normal operations, a dose of fifty times or even ten times the optimum dose would be practically impossible considering the volumes of lixiviant in the system. It should be relatively easy to keep from substantially overdosing the lixiviant.

Bender (2017) also tested the compatibility of LixTRA 118 with sulfur- and iron-oxidizing and heterotrophic bacteria. The testwork was conducted by Universal Bio Mining (USA), which is a research group working on biological heap leaching. The test results showed that there was no negative effect on certain bacteria whilst, on others, there was an initial loss of population followed by a recovery and scavenging of organic from the death of organisms.

2.4.3 LixTRA 118 Leaching Aid

LixTRA™ 118 leaching aid is a non-ionic polymer. It is meant to be added in small quantities to the irrigation system of copper heap and dump leach processes.

The properties of LixTRA can be found in the following Table 1.

Table 1: Properties of LixTRA 118.

Physical form	Clear liquid
Colour (Gardner)	< 3
pH of a 5 % aqueous solution	6.0 to 7.5
Viscosity at 25 °C	Approx. 300 cP
Specific gravity	1.1 g/cm ³

Chapter III.

METHODOLOGY

This chapter presents the experimental techniques that were used in order to obtain the necessary data to conduct the study. The study consisted of two parts. The first aimed at quantifying the effect of the LixTRA 118 leaching aid on solution drainage through various particle size distributions, whilst the second was focused on determining the LixTRA 118 effect on the acid consumption. The term 'leaching aid' in this section refers to LixTRA™ 118.

3.1 EFFECT OF LixTRA ON SOLUTION PERCOLATION THROUGH NARROW AND WIDER PARTICLE SIZE DISTRIBUTIONS

A copper oxide ore from Radomiro Tomic copper mine (Chile) was used to conduct the study. The ore had an average copper grade of 0.46 % and about 0.3 % of total iron. The ore was sieved and classified into four size fractions; namely, particles smaller than 1 mm, particles smaller than 4 mm but larger than 2 mm, particles between 6 and 7 mm, and particles between 12 and 13 mm particles. These fractions were loaded separately into four columns. The in-between fractions were removed to obtain considerably different fractions, which would result in considerably different solution flow characteristics. An additional column was loaded with the mixture of the selected fractions, at 25 % by mass each. The latter was chosen instead of the original size distribution to eliminate any potential effects from the fractions not considered in the earlier selection.

Clear polyvinyl chloride (PVC) pipes of dimensions 152.4 mm diameter x 1000 mm height were used as columns in this study. A total of roughly 90 kg of the ore was sieved so that enough of the targeted size fractions were obtained after sieving.

Diluted sulfuric acid at 10 g/L was used to leach the ore. This concentration was obtained from previously conducted bottle roll tests. The leaching aid was added to the acid solution prior to leaching. The two components were mixed using an overhead stirrer for two hours to achieve homogeneity. The mixture was then pumped from a 1 L bottle into the column using high-precision peristaltic pumps. The PLS flowing from the column was redirected into the bottle and recycled via the same pumps, until the leach cycle was complete. The solution flowrate was set at 10 L/m²/h in all the columns. It was verified after every second day using a stopwatch, a 250 mL cylinder and a scale.

Figure 9 shows a schematic of the setup used to conduct the study. Figure 10 shows a photograph of the setup.

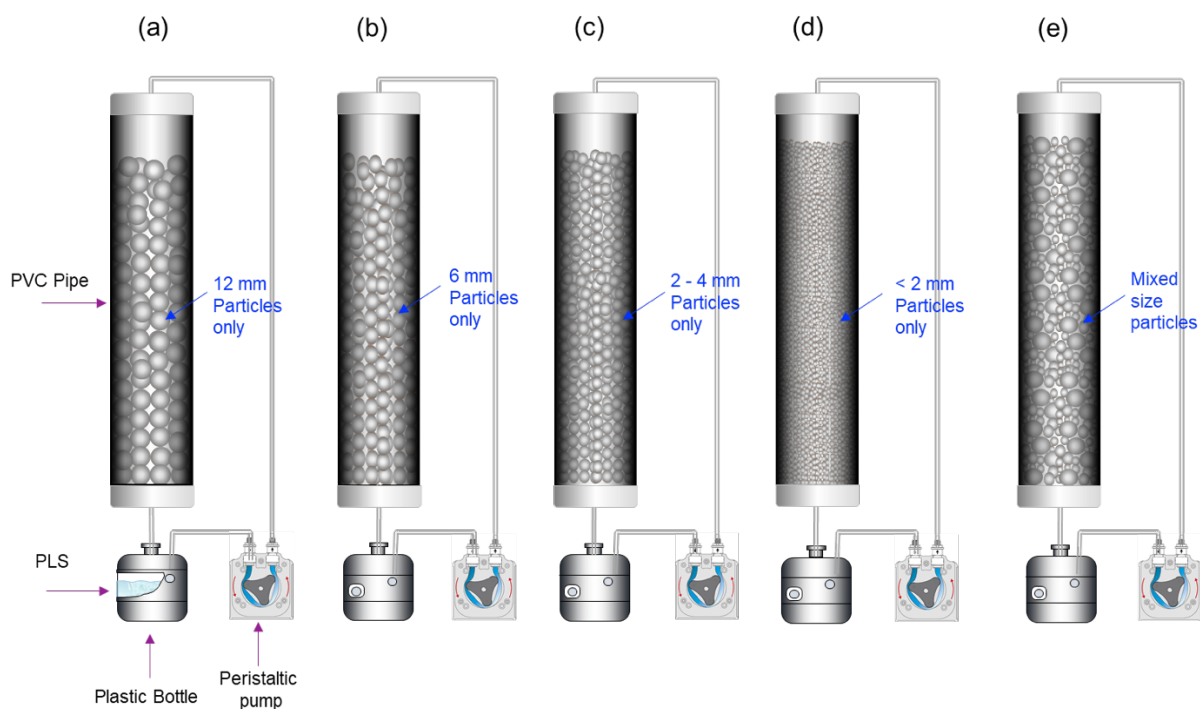


Figure 9: Experimental columns containing different particles sizes as setup for this work. (a) Column containing 12 mm particles only, (b) column containing 6 mm particles only, (c) column containing 2–4 mm particles, (d) column containing below 2 mm particles only, (e) column containing mixed particle sizes.



Figure 10: Column setup to investigate effect of leaching aid on solution drainage. BASF Laboratory, Tucson, USA.

The leach cycle lasted for five days in order to give sufficient residence time to the surfactant to penetrate the ore. At the beginning of each cycle, fresh leach solution was introduced. The concentration of the surfactant and the lixiviant flowrate were the same in all five columns and maintained throughout the leach cycle. A total of four cycles were carried out with the leaching aid concentrations of 25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L. The concentrations were varied in this order to ensure that the early cycles always had lower surfactant concentration in the system and the later ones had the highest.

At the end of each cycle, drainage tests were conducted. These tests consisted of stopping the irrigation of lixiviant into the columns and measuring the drainage of the liquor held-up in the columns. The test lasted for 1040 minutes (17 hours) to ensure that the columns drained out completely.

Five additional columns loaded with the same fractions of materials were set up adjacent to the previous columns. Those columns contained no leaching aid. They served as controls, in order to quantify the effect of the leaching aid.

3.2 EFFECT OF LEACHING AID ON DRAINAGE THROUGH VARIOUS PARTICLE SIZE DISTRIBUTIONS

An experiment was then carried out to ascertain the effect of the leaching aid on the drainage through different mixtures of particle sizes. Three particles size ranges, comprising a narrow, an intermediate, and a wider range, were carefully prepared by first classifying the initial material into specific sizes ranges and recombining the appropriate sizes into specific particle size distributions. Figure 11 shows the particle size distributions in question.

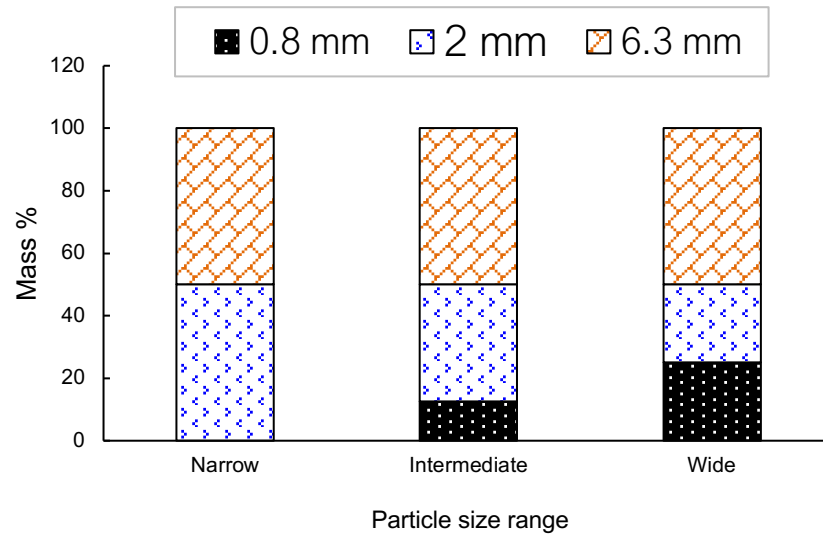


Figure 11: Particle size distributions used to conduct study of effect of LixTRA on different particle size ranges.

The constituted particle size mixtures were homogenized by dry mixing before loading them into separates columns of 40 cm height and 10 cm diameter. The top size in the mixtures was 6.3 mm as opposed to 12.5 mm in the previous section, to account for the columns sizes. Nevertheless, in both cases, the sizes of the columns were sufficiently large to prevent preferential flow of the solution down the sides of the columns (the wall effect).

One litre of 35 g/L sulfuric acid concentration was used to leach the ore for five days, to allow the solution to recirculate at least once. The concentration of leaching aid was 75 mg/L.

Figure 12 shows a photograph of the setup used to investigate the effect of the leaching aid on the solution drainage through various particles size ranges.



Figure 12: Column setup to test effect of LixTRA on flow through different particle size distributions. BASF Laboratory, Tucson, USA.

3.3 BOTTLE ROLL TESTS

The starting acid concentration used in column leaching tests was established from previously conducted bottle roll tests on the same materials. The bottle roll tests were performed with the primary objective to determine the acid consumption, although, typically, the total leachable copper and leaching of other metals like iron, would often be determined. The procedure used was the BASF standard test, summarized into the following steps:

- Crushing down the ore to 80% below 75 μm .
- Prepare and add 400 mL of 250 g/L sulfuric acid into 1 L Nalgene bottle.
- Roll the bottle on the laboratory roller running at 80 rpm and allow leaching to take place for 24 h.
- When complete, collect a sample of the aqueous PLS from the bottle and filter it through a Whatman 4 filter paper.
- Titrate the filtered PLS sample and a sample of the starting 250 g/L acid to determine the acid concentration of each sample. In this case, an automated acid-base potentiometric titrator was used. It measures the concentration of the

acid/base by neutralizing it with a standard solution of base/acid of known concentration.

- The acid concentration of the ore was determined by subtracting the acid in the PLS from the acid in the starting solution. The difference in these acid concentrations was the amount of acid that was consumed by the ore.

3.4 EFFECT OF LixTRA 118 ON ACID CONSUMPTION

A Chilean mixed copper oxide and sulfide ore was used to confirm the observations made in previous tests that suggested that LixTRA 118 may have properties that reduce or prevent excessive acid consumption during heap and dump leaching of copper ores.

Two groups of three columns running at 6, 15, and 20 L/m²/h flowrates were set up. One group contained the leaching aid, with the initial concentration at 100 mg/L to ensure that there was sufficient surfactant to react with the ore sample, whilst the second had no leaching aid to serve as control. All six columns had the same ore. The particle size distribution was prepared to ensure that the sizes were consistent between the columns with and without the leaching aid. This was achieved by precisely classifying the ore sample using a sieve shaker and then recombining particles between 12 and 13 mm, particles between 6 and 7 mm, particles between 4 and 2 mm, and particles smaller than 2 mm at percentages of 25 % each. Thereafter, these particles were combined and dry mixed before being transferred to the columns.

Figure 13 shows a photograph of the setup used to conduct the study.



Figure 13: Column setup to test effect of leaching aid on acid consumption. BASF Laboratory, Tucson, USA.

Sulfuric acid was used as lixiviant at an initial concentration of 23 g/L. High-precision peristaltic pumps were used to pump the leach solution from the plastic containers to the columns. This was to ensure that the flowrates were maintained throughout the leach cycle. The solution flowrates were measured on a weekly basis, and appropriate corrections were done when necessary. The solution flowing down the columns were re-directed to the plastic containers and mixed with the leach solution.

A sample of PLS was collected on a daily basis, to measure the pH, the free acid content, the copper concentration, the solution surface tension, and the leaching aid concentration. These were measured using a pH meter, an automated potentiometric titrator, an atomic adsorption spectrophotometer (AAS), a tensiometer, and a liquid chromatography mass spectrometer (LCMS), respectively.

Chapter IV.

RESULTS AND DISCUSSION

The purpose of this study was to better understand the mechanisms of action of the LixTRA 118 leaching aid in leaching of copper ores.

This section presents the results obtained from the column study conducted and attempts to discuss the major findings on the dynamics of the solution in heap leaching of copper ores. This is done to help understand specifically:

- a. the drainage effect associated with different particle size fractions using the LixTRA 118 leaching aid;
- b. the acid consumption characteristics using LixTRA 118 to assist the leaching of a mixed oxide and sulfide ore;
- c. the leaching aid consumption at various solution irrigation rates.

Suggestions on aspects to further investigate to understand certain observations made during the study are also presented in this section.

4.1 EFFECT OF LixTRA ON SOLUTION DRAINAGE THROUGH NARROW AND WIDER PARTICLE SIZE DISTRIBUTIONS

4.1.1 Effect of Particle Size on Solution Drainage Rate

The effect of increasing particle size on the rate of solution percolation or drainage through a mono-size particle bed in the absence of the leaching aid is shown in Figure 14. Three particles size ranges were used to conduct the study. The drainage tests were conducted on the last day for a duration of 1040 minutes. The results showed that the solution drained faster through the smaller particles than through the larger ones.

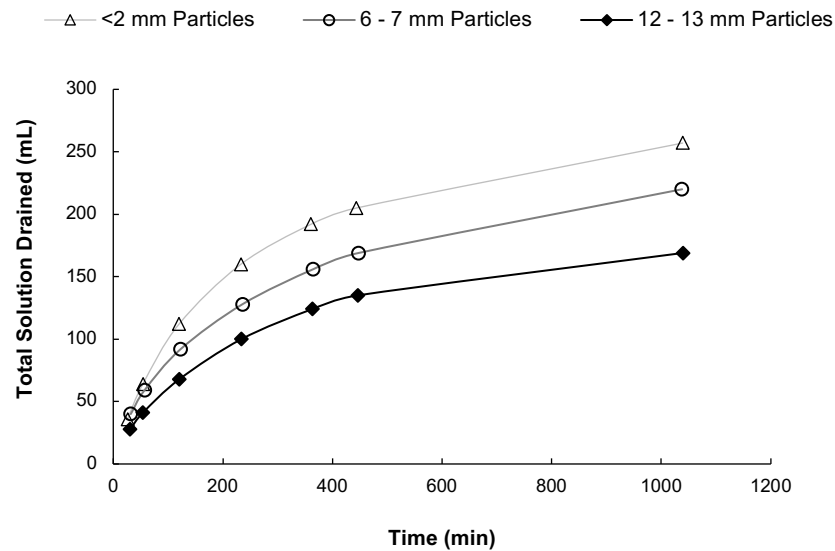


Figure 14: Effect of particle size on drained volume over time.

This can be explained by the difference in voidage between the bed of larger and that of smaller particles. The latter must have retained a larger solution inventory during the 5 days leaching than the coarser particles. This could have been due to the relatively smaller voidage and perhaps the saturation of smaller pores, which could have been caused by the high interaction between the ore particle surface and the solution. Thus, the level of saturation before conducting the drainage tests was lower in the bed of coarser particles.

Another reason for the faster drainage in the finer mono-sized materials could be, to an extent, because more capillary action was present in the smaller than in the coarser materials. This would be in line with the observation made by Yin et al. (2016) that smaller particles exhibit higher capillary rise velocity and heights than larger particles, which are important parameters in driving forces of the solution percolation through the heap.

4.1.2 Effect of LixTRA on Solution Drainage Through Different Particle Sizes

The concentration of the leaching aid in the solution was varied from 25 mg/L to 50 mg/L and 100 mg/L. The solution drainage characteristics at the leaching aid concentration of 25 mg/L are shown in Figure 15. The results showed little effect on the drainage through smaller particles; however, with larger particles, the drainage rate was considerably reduced.

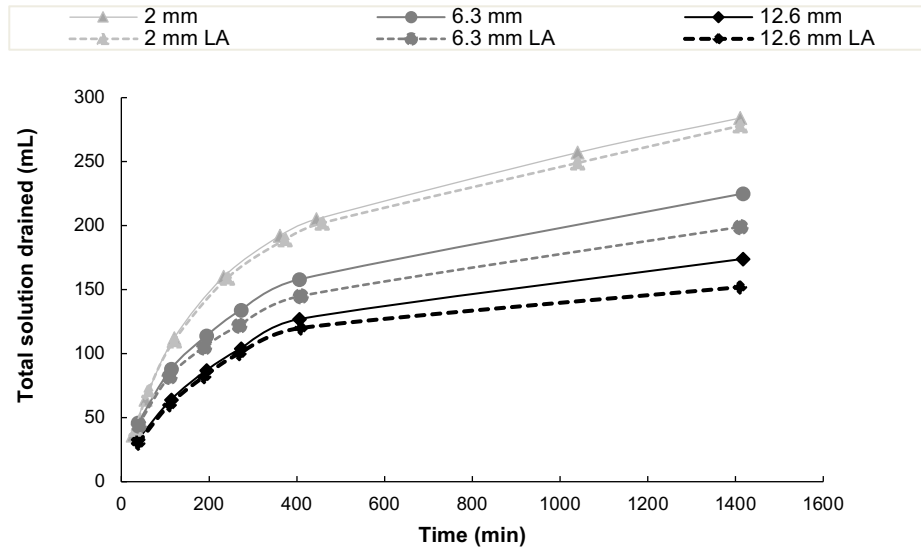


Figure 15: Effect of adding 25 mg/L of LixTRA (LA) on solution drainage through various size fractions.

The addition of the leaching aid should increase the flow of solution through the bed of particles. This is because the high interaction between the solid surface and the solution, which causes retardation to the flow, would have been reduced. However, when considering the drainage test results of the finer ore beds with and without the leaching aid added, the difference was insignificant, although the finer beds were supposedly the ones with much higher capillary action. One logical explanation of the insignificant effect would be that capillary action was negligible; meaning that the predominant driving force was gravity. This could justify the fact that the amounts of solution drained at the beginning of the drainage tests are comparable, particularly for the first 300 minutes. This aligns with the observation that beds consisting of particles of the same sizes exhibited less capillary action than those with much wider particle size distribution range.

Although the differences in drainage rates were negligible, the columns containing leaching aids consistently drained less solution than those without leaching aid. This effect could be justified by the difference in pore saturation levels at the beginning of the drainage tests. The leaching aid could have allowed more solution to drain out during the leaching period, resulting in less solution inventory in the columns prior to the start of the drainage tests. This could also be why the gaps between the corresponding lines increased over the drainage period (Figure 15), which would result in differences in final (total) cumulated solution volumes at the end of the tests.

Contrary to the observation made in Figure 15, tests done by Bender (2017) on various copper ores showed an increase in drainage rates upon addition of the leaching aid. Additionally, the final cumulated volumes of solution drained were almost identical in columns with and without leaching aid. If this is true, it could be that the dose of 25 mg/L of LixTRA 118 added in our first test was simply not sufficient for this material. The next section attempts to explain the results obtained after increasing the leaching aid dose from 25 mg/L to 50 mg/L and 100 mg/L in columns with mono-sized particles and with the mixture of particles.

The effect of LixTRA 118 leaching aid on solution drainage was more pronounced in the column loaded with the mixture of particles than in the columns with mono-size particles (Figure 16). At a leaching aid concentration of 25 mg/L, the column with the mixed sized particles brought about 18 % increase in extent of drainage; however, the same dosage of leaching aid in the columns with 2 mm and 6.3 mm particles reduced the solution drainage rate by about 5 % and 10 %, respectively. Another observation is that the increase in leaching aid increased the rate of drainage, although this was not the case in the column with the coarsest particles.

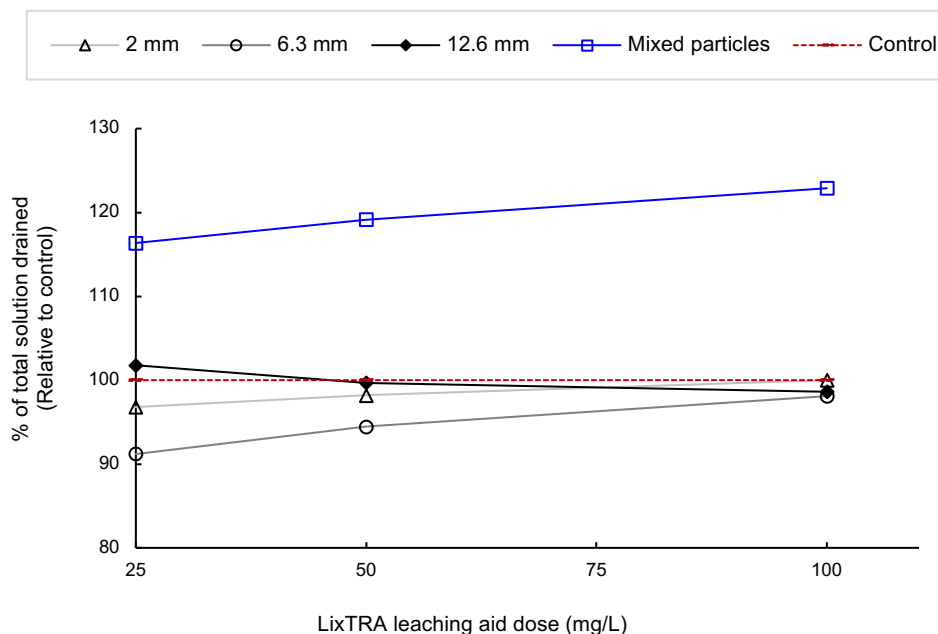


Figure 16: Value of total solution drained as a percentage of control volume.

The greater effect observed on the wider particle size distribution compared with the more uniformly sized particles aligns with the finding from Bouffard and West-Sells (2009), who established that metal recovery could be correlated to the volume of leach solution

contained within the heap. The material with a much wider PSD would retain more solution. Therefore, additional contact time will be available for the metal to interact with the acid that will dissolve it. In the same way, if ore beds of similar characteristics are considered, the volume of solution retained should be the same, provided that the irrigation rate is the same, because gravity and capillary action within the beds would be the same. Whilst the flow within a uniformly sized particle bed is dominated by the vertical gravitational force at macropore level, the flow characteristics become more complex as the particle size distribution widens. Both vertical and lateral flows are present, and there is more capillary action due to the number of fine pores. Therefore, the addition of leaching aid will encourage free flowing of solution through previously hard-to-flow areas, which will result in an overall increase in percolation rate.

4.1.3 Effect of Leaching Aid on Drainage Through Various Particle Size Distributions

The performances of the leaching aid on the solution drainage through a narrow, an intermediate, and a wider particle size range are presented in Figures 17a, 17b and 17c, respectively. The results show evidence of an increase in flow rate as the particle size range widened. They also show that the drainage of the columns containing the leaching aid (LA) was consistently faster than that of the controls. These observations are in line with the discussion made in Section 4.1.2.

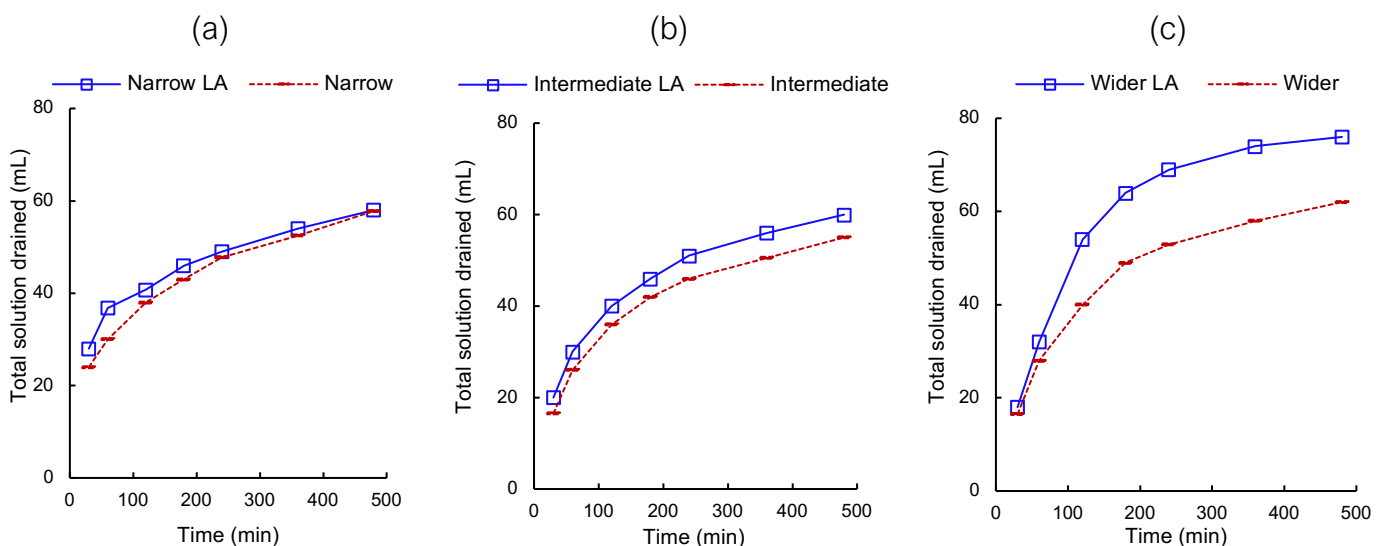


Figure 17: Effect of LixTRA 118 (LA) leaching aid concentration on solution drainage through (a) narrow PSD, (b) intermediate PSD, and (c) a wider PSD.

4.2 EFFECT OF LixTRA 118 ON ACID CONSUMPTION

It is known that, beside poor percolation rate, a high content of acid-consuming gangue can make an ore unsuitable for heap leaching. Gangue acid consumption can be reduced by using higher irrigation rates at lower lixiviant acid strength (Robertson & Van Staden, 2009), although this would usually require a tradeoff between the metal extraction and the acid consumption. Irrigation rates as high as 15 L/m²/h are used at times. The effect of LixTRA 118 on the acid consumption, the metal recovery, and the contamination (leaching of unwanted metal) was therefore evaluated at different solution flowrates.

4.2.1 Effect of Irrigation Rate on Acid Consumption

Figure 18 shows the effect of increasing the irrigation rate on the acid consumption. It is evident that the increase in the irrigation rate caused an increase in acid consumption, particularly as the rate was increased from 6 to 15 L/m²/h. This is certainly because of the higher solution hold-up and consequently the residence time in the ore bed.

The further increase of the irrigation rate to 20 L/m²/h did not, however, increase the acid consumption. It is understood that, at this point, due to the materials and solution characteristics, the acid consumption was no longer governed by the acid supply.

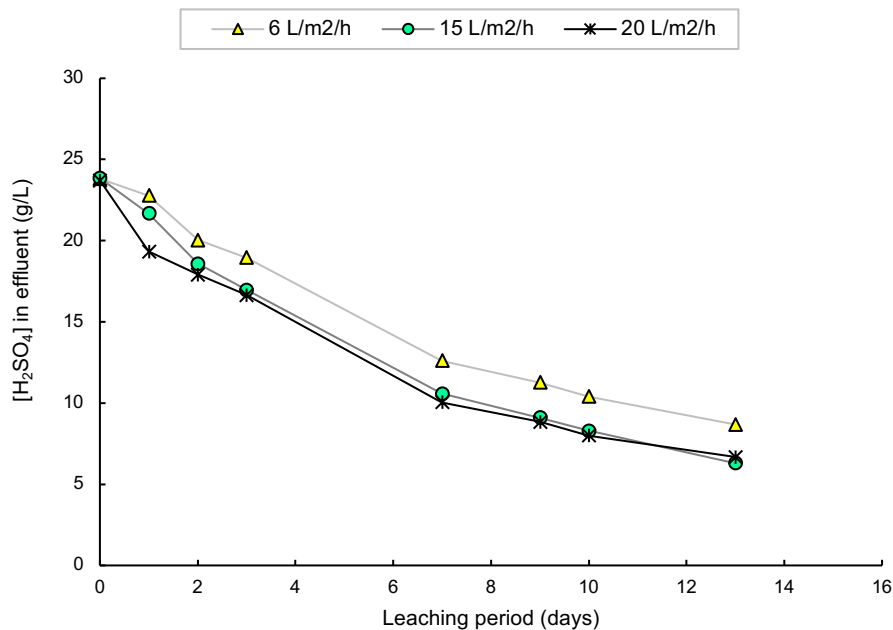


Figure 18: Effect of solution flowrate on acid concentration. Ore: A mixed oxide and sulfide copper ore from Chile; Leaching agent: 35 g/L sulfuric acid; Initial leaching aid: 70 mg/L.

4.2.2 Effect of LixTRA on Acid Consumption

Experiments were carried out to evaluate the effect of the addition of leaching aid on the acid consumption. The results are shown in Figure 19 and expressed as a percentage of the acid concentration in the corresponding column without a leaching aid. The results show that the addition of leaching aid increased the consumption of acid – the acid concentrations in the PLS from the columns containing LixTRA 118 were lower than those without.

The increase in flowrate from 6 L/m²/h to 15 L/m²/h increased the consumption of acid by an additional 5% to 10 %, respectively.

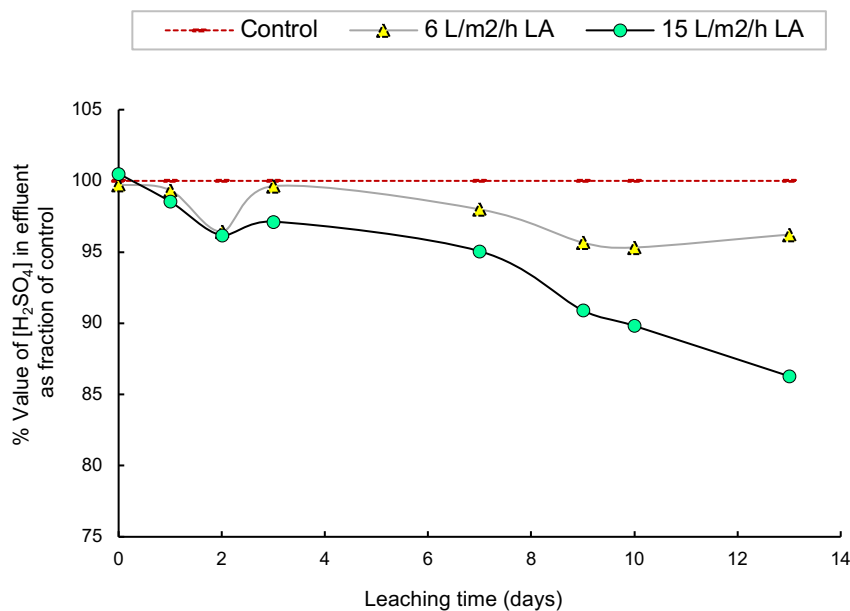


Figure 19: Effect of LixTRA 118 (100 mg/L initial concentration) on acid consumption at 6 L/m²/h and 15 L/m²/h.

The significant reduction of acid in the PLS from the columns containing the leaching aid could be justified by the same fact that more solution is held up in the bed with the addition of the leaching aid. Therefore, the resulting increase in residence time cause an increase in acid consumption.

It is also possible that the addition of the leaching aid improved wetting and facilitated the kinetics of acid diffusion at macro- and micropore level and therefore, increased the leaching of additional copper as well as other metals.

4.2.3 Effect of Solution Irrigation Rate and LixTRA 118 on Copper and Iron Recoveries

The resulting effects of LixTRA 118 and the irrigation rates on the copper recoveries are presented in Figures 20 and 21.

Figure 20 shows the recovery of copper from columns with and without LixTRA 118, running at an irrigation rate of 6 L/m²/h. Despite the fact that the data may well be within the experimental error, the leaching-aided column consistently produced more copper than the control. The final copper concentration in the column with LixTRA 118 was about 4.5 % higher than the column without the leaching aid.

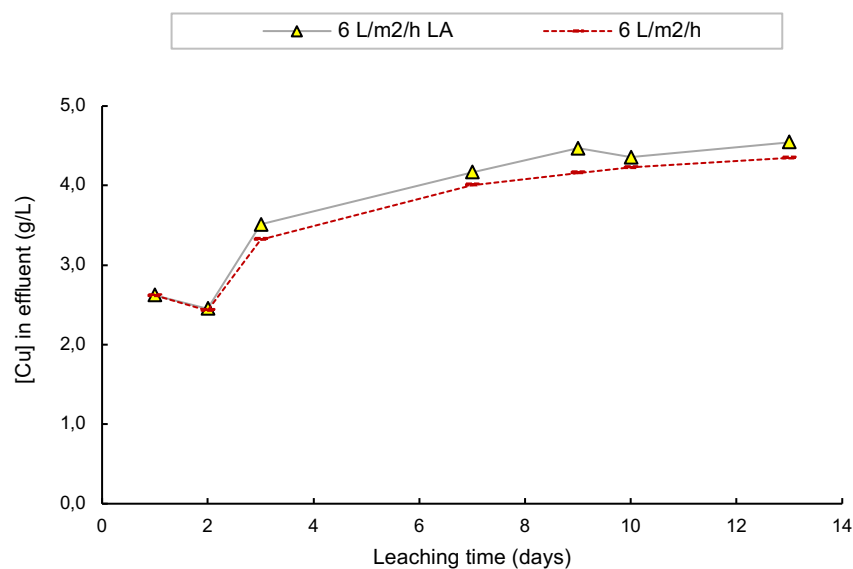


Figure 20: Effect of 100 mg/L initial LixTRA 118 (LA) concentration on copper recovery at irrigation rate of 6 L/m²/h.

Figure 21 shows the results of increasing the flowrate to 15 L/m²/h. As opposed to the observation made at low irrigation rate, the copper concentration in the effluent from the leach-aided column was lower than the control, although, once more, the data could still be within the experimental error. It may well be that this resulted from the increased acid consumption, which is discussed in section 4.2.2. Hence, less acid was available to leach additional copper into solution.

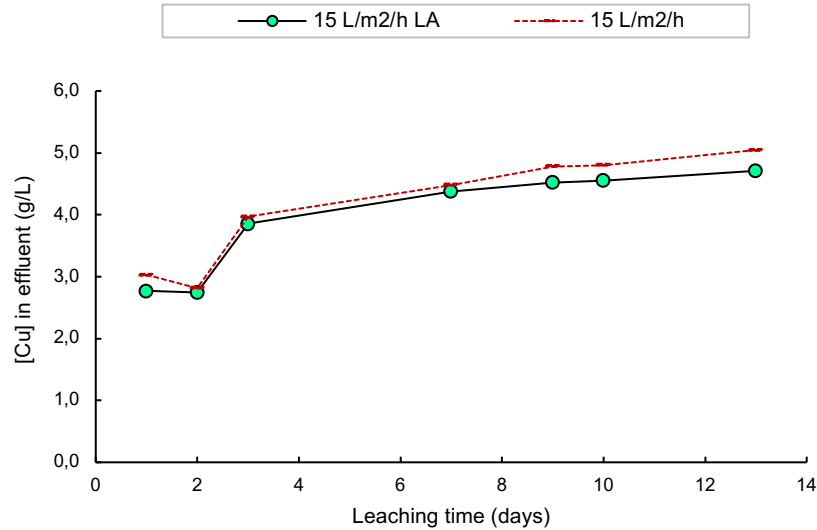


Figure 21: Effect of 100 mg/L initial LixTRA 118 (LA) concentration on copper recovery at irrigation rate of 15 L/m²/h.

The discontinuity at the second datapoint observed on Figures 20 and 21 resulted from a solution addition. This was necessary to have sufficient volume of acid to leach the ore sample.

It is well known that the leaching aid, being a surfactant, improves the wetting of the ore by reducing the cohesive forces between water molecules. As a result, leaching of both the metal and the gangue in solution should increase.

Figure 22 shows the effect of LixTRA 118 on the iron recovery at slower irrigation rate. The results showed no significant difference between the columns with and without LixTRA 118. This implies that the leaching aid had practically no effect on the iron recovery.

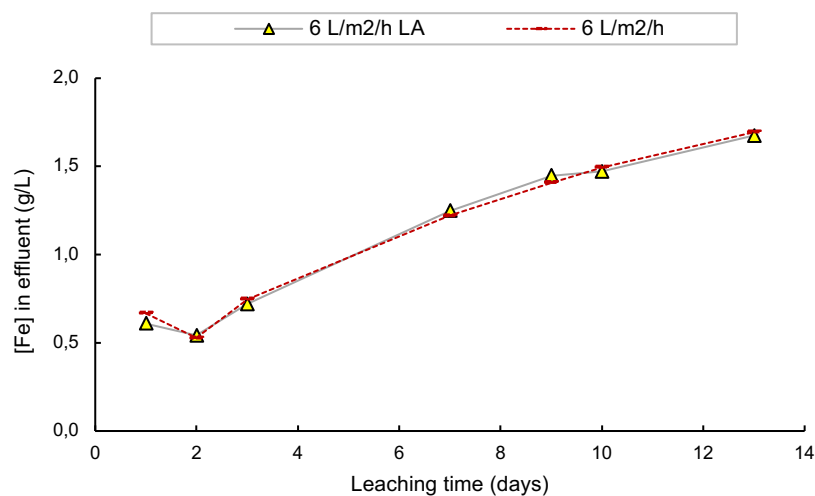


Figure 22: Effect of 100 mg/L initial LixTRA 118 (LA) concentration on iron contamination at 6 L/m²/h irrigation rate.

Figure 23 shows the results of iron recovery at 15 L/m²/h irrigation rate. It can be seen that both columns, with and without LixTRA 118, ran similarly for the first seven days. Later, the concentration of iron from the column without LixTRA 118 started to increase and culminated in 5 % more iron leached than the column with LixTRA 118 after 13 days of leaching.

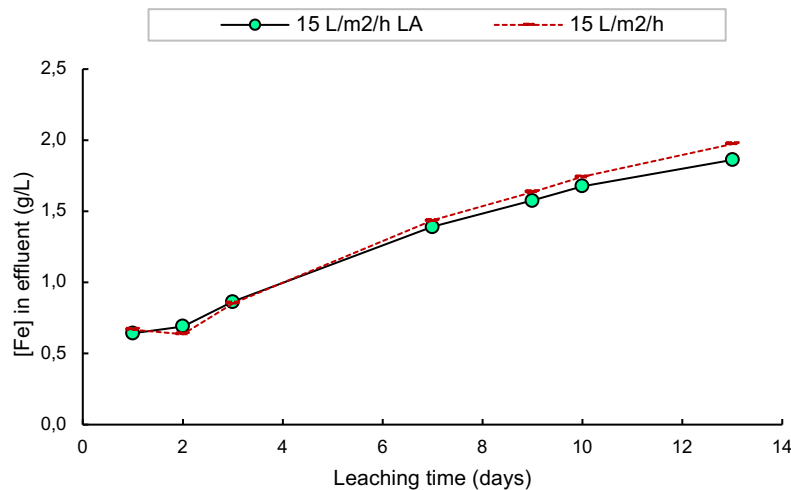


Figure 23: Effect of 100 mg/L initial LixTRA 118 (LA) concentration on iron contamination at 15 L/m²/h irrigation rate.

According to the theory of capillary action and diffusion mechanisms, the leaching aid should not only increase the recovery of the targeted metal, but also the dissolution of unwanted metals. Therefore, the acid consumption was expected to increase with the addition of LixTRA 118 due to wetting of the acid-consuming minerals. The results presented in Figure 22 and Figure 23 are contrary to what was anticipated. The amount of iron dissolved was similar in both columns with and without LixTRA 118, which suggested that this leaching aid might have some degree of selectivity for copper over iron. Further work is required to better understand the effect on other metals, such as iron and cobalt that are usually associated with the processing of copper ores.

4.2.4 Effect of Solution Flowrate and Leaching Time on Consumption of LixTRA 118

The effect of leaching on the downstream processes is very important. Whilst a study by Bender (2017) has shown that the effect of LixTRA 118 on SX and bioleaching was practically nil, it was important to demonstrate whether the concentration of this leaching aid would remain unchanged over the leaching period in a closed circuit.

Figure 24 shows the consumption of LixTRA 118 for 13 days of leaching. The results are presented as percentage values of the initial concentration of the leaching aid. It shows that the leaching aid was consumed faster at higher irrigation rates.

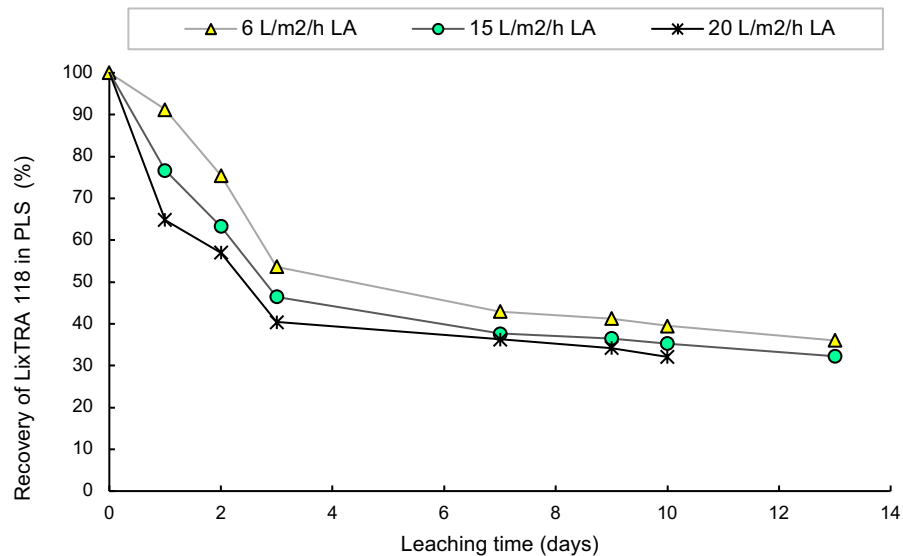


Figure 24: Effect of flowrate and leaching time on consumption of LixTRA 118.

Analysing Figure 24 and Table 1 together shows that the recovery of the leaching aid in the PLS was a function of the number of times that the solution recirculated. For example, the leaching aid recovery at 20 L/m²/h was about 40 % after three days (Figure 24). At this flowrate, the solution would have recirculated twelve times (Table 1). This number of cycles was reached after eight days using 6 L/m²/h (Table 1), and for which the recovery of the leaching aid was also approximately 40 %.

Table 2: Effect of flowrate on leach solution recirculation cycles.

Leaching time (days)	Number of times that the leach solution recirculated based on the flowrate set on the peristaltic pump		
	6 L/m²/h	15 L/m²/h	20 L/m²/h
0	0	0	0
1	1	3	4
2	2	6	8
3	4	9	12
5	8	20	27
7	11	26	35
8	12	29	39
11	15	38	51
13	18	44	58

Figure 24 shows that the concentration of leaching aid in the mobile solution decreased with the leaching time and was asymptotic to approximately 30 % of the initial leaching aid content. In conjunction with Table 1, it also shows that the asymptotic point was a function of the irrigation rate. The fact that the consumption of the leaching aid was not linear may suggest that either the reagent continuously decomposed as the bed is became saturated with the leaching solution or perhaps, there is a concentration level of the leaching aid beyond which further addition may be unnecessary. This, however, may be specific to certain characteristics of the heap. Further testwork would be required to ascertain this effect and understand the implications in more depth.

Chapter V.

CONCLUSION

Percolation rate is one of the most important parameters that determine the suitability of an ore to heap leaching. The presence of excessive fines particles or clayey minerals usually limits the rate of solution percolation and, ultimately, the metal recovery. Crushed ore agglomeration has been identified to improve metal extraction by improving ore homogeneity and permeability, whilst leaching aids, surfactants, which act at macro- and microscopic levels, act by improving the flow of solution within the heap.

The use of leaching aids in heap leaching applications has not been widely implemented. This is possibly due to the potential effect that these surfactants could have in downstream processes, such as SX and bioheap leaching, which both rely on surface properties of the fluids and solids. As a result, no extensive work has been done in this regard.

The focus of this study was firstly to investigate the effects of the addition of leaching aid on the dynamics of the leach solution in heaps of wider and narrow particles sizes. Secondly, the effects of the leaching aid on the acid consumption and metal recovery were determined.

The effect of leaching aid on the hydrodynamics was evaluated through drainage tests, comparing columns with and without leaching aid. Eight columns were loaded with mono-size particles of different sizes to form different narrow size ranges, whilst two others were loaded with the same ore particles but with wider particle size ranges.

The results showed that both particle size and the particle size range inside the heap affected the percolation rate. The solution percolated faster through small uniform particle sizes than through larger uniform ones. The results aligned with findings of other researchers who suggested that this was due to volume held within the bed, which was higher in the fine particle bed.

The results also showed that the effect of the leaching aid was more pronounced in the wider particle size range than in the narrower. This was found to be linked to the solution flow that improved with the reduction in solution surface tension as the leaching aid was introduced.

The second part of the study focused on the effect of the leaching aid on the acid consumption, metal recovery, and leaching aid consumption. The tests were conducted with columns loaded with the same material characteristics. The performance was evaluated by comparing columns loaded with the leaching aid and those without.

The results showed that the leaching aid increased the copper recoveries as well as the acid consumptions. This was in line with the fact that the introduction of leaching aid reduced the surface tension of the solution, which improved the wetting of the ore and facilitated solution flow in previously hard-to-flow areas. Owing to the improved wetting, additional copper was leached.

In light of the above, it was expected that more iron would be dissolved upon introducing the leaching aid. However, it was not the case. There was no significant difference between the column with and without LixTRA 118 in terms of iron content in the PLS. This suggested that LixTRA 118 could have some level of selectivity for certain metals over others; In this case, that of copper over iron. Further work is required to ascertain this effect and the implications thereof.

The final observation was that as leaching progresses, the concentration of the leaching aid in the PLS decreased somewhat asymptotically towards some value that could be dependent on how fast the solution is irrigated on the heap and the surface characteristics of the ore and solution.

Chapter VI.

REFERENCES

- Ai, C. M., Sun, P. P., Wu, A. X., Chen, X., & Liu, C. (2019). Accelerating leaching of copper ore with surfactant and the analysis of reaction kinetics. *International Journal of Minerals, Metallurgy and Materials*, 26(3), 274-282.
- BASF. (2019). *Novel LixTRA leaching technology for copper heap and dump leach processes*. Retrieved December 15, 2019, from Energy & Resources BASF: https://energy-resources.basf.com/global/en/mining_solutions/leaching_aids.html
- Baum, W., & Ausburn, K. (2011). HPGR comminution for optimization of copper leaching. *Minerals and Metallurgical Processing*, 28(2), 77-81.
- Bender, J. (2017). An effective new leaching aid successfully tested with oxides and mixed sulfide copper ores. *Nickel-Cobalt-Copper Conference*. 8, pp. 247-260. Melbourne: ALTA Metallurgical Services.
- BioMineWiki. (2020). *Leaching theory and kinetics*. Retrieved April 21, 2020, from Biominewiki: http://wiki.biomine.skelleftea.se/wiki/index.php/Leach_kinetics
- Bouffard, S. C. (2005). Review of agglomeration practise and fundamentals in heap leaching. *Mineral Processing & Extractive Metallurgy*, 26(3-4), 233-294.
- Bouffard, S. C., & West-Sells, P. G. (2009). Hydrodynamic behavior of heap leach piles: Influence of testing scale and material properties. *Hydrometallurgy*, 98(1-2), 136-142.
- Chetty, D. (2018). Acid-gangue Interactions in heap leach operations: A review of the role of mineralogy for predicting ore behaviour. *Minerals*, 8(2), 47-58.
- Deschenes, G., Fleming, C., Zhou, J., Hodouin, D., Amankwah, R., Ghali, E., & Choi, Y. (2011). Highlights of the five decades of gold ore processing in Canada. *50th World Gold Conference*. 50, pp. 20-45. Montreal: Canadian Institute of Mining, Metallurgy and Petroleum.
- Dhawan, N., Safarzadeh, M. S., Miller, J. D., Moats, M. S., & Rajamini, R. K. (2012). Crushed ore agglomeration and its control for heap leaching operations. *Minerals Engineering*, 41, 53-70.

- Evans, J. W. (2003). Metal Production: Electrometallurgy. In *Encyclopedia of Materials: Science and Technology* (2 ed., pp. 1-12). Amsterdam: Elsevier.
- Fanchi, J. R. (2002). Measures of rock-fluid interactions. In J. R. Fanchi, *Shared Earth Modeling* (pp. 108-132). Oxford: Gulf Professional Publishing.
- Ghorbani, Y., Franzidis, J.-P., & Petersen, J. (2016). Heap leaching technology - current state, innovations and future directions: a review. *Mineral Processing and Extractive Metallurgy Review*, 37(2), 73-119.
- Halder, S. K. (2018). *Mineral Exploration: Principles and Applications* (Vol. 2). Elsevier.
- Kappes, D. W., Mular, A. L., Halbe, D. N., & Barratt, D. J. (2002). Precious metal heap leach design and practice. *Mineral Processing Plant Design, Practice and Control* (pp. 1606-1630). Colorado: Society for Mining, Metallurgy, and Exploration.
- Komulainen, T., Doyle, F., Jämsä-Jounela, S.-L., & Rantala, A. (2009). Control of an industrial copper solvent extraction process. *Journal of Process Control*, 19(1), 2-15.
- Lapidus, G. T., & Sánchez-Chacón, A. E. (1997). Model for heap leaching of gold ores by cyanidation. *Hydrometallurgy*, 44(1-2), 1-20.
- Lewandowski, K. A., & Kawatra, K. S. (2009). Polyacrylamide as an agglomeration additive for copper heap leaching. *International Journal of Mineral Processing*, 91(3-4), 88-93.
- Lupo, J. F. (2012). Sustainable issues related to heap leaching operations. *Journal of the Southern African Institute of Mining and Metallurgy*, 112(12), 1021-1030.
- Mgaidi, A., Oulahna, D., Doods, J. A., & El Maaoui, M. (2003). Change in the surface area and dissolution rate during acid leaching of phosphate particles. *Industrial & Engineering Chemistry Research*, 42(10), 2067-2073.
- Mikhailov, G. A., Vashlaev, I. I., Kharitonova, Y. M., & Sviridova, L. M. (2018). Upward capillary leaching. *Hydrometallurgy*, 175, 273-277.
- Miller, G. (2003). Ore geotechnical effects on copper heap leach kinetics. *Hydrometallurgy 2003* (pp. 329-342). Vancouver: The Minerals, Metals & Materials Society.

- Natarajan, K. A. (2018). Chapter 5 - Methods in Biohydrometallurgy and Developments: Dump, Heap, In Situ, and Stirred Tank Bioleaching. In K. A. Natarajan, *Biotechnology of Metals* (pp. 81-106). Amsterdam: Elsevier.
- Nikolov, A., & Wasan, D. (2014). Current opinion in superspreading mechanisms. *Advances in Colloid and Interface Science*, 222, 517-529.
- Petersen, J. (2016). Heap leaching as a key technology for recovery of values from low-grade ores – A brief overview. *Hydrometallurgy*, 165, 206-212.
- Petersen, J. (2019). Heap leaching of copper ores – State of the science. *Annual conference of metallurgists hosting copper 2019*. 58. Montreal: Canadian Institute of Mining, Metallurgy, and Petroleum.
- Robertson, S. W., & Van Staden, P. J. (2009). The progression of metallurgical testwork during heap leach design. *Hydrometallurgy Conference 2009*. 52, pp. 31-42. Johannesburg: Southern African Institute of Mining and Metallurgy.
- Robertson, S. W., van Staden, P. J., & Seyedbagheri, A. (2012). Advance in high-temperature heap leaching of refractory copper sulphide ores. *Journal of the Southern African Institute of Mining and Metallurgy*, 112(12), 145-150.
- Schlesinger, M. E., King, M. J., Sole, K. C., & Davenport, W. G. (2011). *Extractive Metallurgy of Copper*. (5, Ed.) Oxford: Elsevier.
- Sole, K. C., & Tinkler, O. S. (2016). Copper solvent extraction: status, operating practices, and challenges in the African Copperbelt. *ournal of the Southern Institute of Mining and Metallurgy*, 116, 553-560.
- Trefethen, L. (1969). Film Notes For Surface Tension In Fluid Mechanics. In *Illustrated Experiments in Fluid Mechanics*. Boston: National Committee For Fluid Mechanics Films.
- Van Genuchten, M. T., & Wierenga, P. J. (1976). Mass transfer studies in sorbing porous media I. Analytical solutions. *Soil Science Society of America Journal*, 40(4), 473-480.
- Vest, M., Lutzerath, A., Friedrich, B., & Seelmann-Eggebert, H.-P. (2009). Improvement in copper heap leaching by use of wetting agents. *Global Growth of Nonferrous Metals Production*. 2, pp. 11-23. Innsbruck: European Metallurgical Conference.

- Yin, S. H., Wang, L. M., Chen, X., & Wu, A. X. (2016). Effect of ore size and heap porosity on capillary process inside leaching heap. *Transactions of Nonferrous Metals Society of China*, 26, 835-841.
- Zheng, C., & Bennett, G. D. (2002). *Applied Contaminant Transport Modelling*. New York: J. Wiley and Sons.