Effects of intermittent irrigation on the extraction of copper from heap bioleaching systems

By

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DECLARATION

I, Eustice Vries, declare that I know the meaning of plagiarism and declare that all work in this document, save for that which is properly acknowledged, is my own. It is submitted of the Degree of Magister Scientae (MSc) at the University of Cape Town. This thesis has not been submitted for any degree or examination at any other university.

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ABSTRACT

The use of microorganisms for the regeneration of leach agents in the heap leaching of mineral sulfide ores is finding increasing application as a hydrometallurgical unit operation applicable to the treatment of the increasing low grade ores. These same microorganisms contribute to the formation of acid rock drainage (ARD) through the oxidation of base metal sulfides, particularly pyrite. In this research, the effect of intermittent irrigation on the extraction of copper and iron from a low grade chalcopyrite ore in the heap bioleaching system is investigated and compared with the effect under abiotic conditions. As a secondary investigation, the effect of the introduction of layers of fines, which may develop during the course of the operation of heaps, on copper extraction in heap bioleaching systems was also researched.

A chalcopyrite-containing low grade ore was chosen because the average ore grade of base metal-containing mineral reserves has decreased substantially. Further, chalcopyrite accounts for 70 % of the abundant low-grade copper sulfide ores globally. Over the past 30 years, limited research has been done on intermittent irrigation in the heap bioleaching system. In the previous work, it has been theorised that intermittent irrigation increases copper extraction in heap leaching systems. However, no adequate experimental data has been published to validate this claim. The claimed increase of copper extraction by applying intermittent irrigation would effectively decrease the reagent usage, in turn decreasing the operating cost of extracting copper in heap bioleaching systems.

The displacement of fines is a natural phenomenon in heap leaching; it has been reported to divide the heap into coarse (high permeable) zones and fine (low permeable) layers, both which negatively affect heap leaching. Conversely, in waste rock dumps a cover of fine material is often introduced to delay leaching and thereby ARD formation.

To fully understand the effects of intermittent irrigation on heap bioleaching systems, experiments were conducted at different intermittent irrigation frequencies and flow rates in test leaching columns set up to simulate heap bioleaching systems. To compare the effects of intermittent irrigation, different leaching types (abiotic and biotic agglomerated columns) and different packing types (biotic agglomerated and biotic layered columns) were tested. The biotic layered columns were used to simulate the fines layer development in heap leaching systems. These experiments were run for 114 days. The low grade chalcopyrite ore in the test leach columns was inoculated with a mixture of moderate and extreme thermophiles, maintained at a temperature of 65 °C and irrigated with a sulfuric acid solution at pH 1.15, which contained 0.5 g/L ferrous iron and nutrients. Redox potential, pH, Fe^{2+}, Fe^{3+}, total Fe and Cu concentrations were measured to monitor the performance of the heap bioleaching systems during the experiment. Furthermore, on completion of the experiment, analysis of the ore was conducted to account for precipitation, characterise ore properties and provide data to complete the mass balance.

The following conclusions were drawn from this research:

- Intermittent irrigation increased the copper leaching per unit volume of the irrigation solution in both abiotic and biotic heap leaching systems, indicating that reagent usage and operating costs could be decreased by using intermittent irrigation compared to continuous irrigation.
- Similar levels of copper extraction were observed in all the intermittently-irrigated heap bioleaching systems over the 114 day period, irrespective of the intermittent irrigation frequencies and resting (stagnant) periods. From this, it is hypothesised that the leaching reactions continue during the resting phase when irrigation has been stopped. This also confirmed that during the stagnant periods the reactants were sufficient to sustain an active microbial population which in turn facilitated the continued provision of Fe^{3+} and H^+ for the ongoing extraction of copper.
- Conversely, in the abiotic heap leaching system, the extent of copper extraction was a function of the volume of irrigant and thereby the amount of Fe^{3+} and H^+ supplied as reactants.
- Precipitation of iron in the ore bed increased in the biotic system over the abiotic system, owing to the presence of higher concentration of ferric iron. Further, precipitation increased in the intermittently irrigated bioleaching systems, owing to the build-up of higher concentrations of ferric iron during the resting stages.
- The layers of fines developed caused a decrease of copper extraction in heap bioleaching systems. However, the fine particles did not prevent the leaching reactions from taking place completely due to the fact that 75 % of the packed ore was coarse material. It is recommended that the effect of the relative ratio of coarse to fine material in these layers be investigated.

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NOMENCLATURE

Abbreviations

CeBER	- Centre for Bioprocess Engineering Research
PLS	- Pregnant leach solution
ARD	- Acid rock drainage

Terminology

Resting / stagnant period	- Time no feed was introduced to the columns
Low frequency intermittent irrigation	- 1 day feed on, 2 days feed off at 1 L/day
High frequency intermittent irrigation	- 2 days feed on, 1 day feed on at 1 L/day
High flow rate intermittent irrigation	- 2 days feed on, 1 day feed off at 1.5 L/day
Pregnant leach solution	- Mineral rich leach solution

Chemical Formulae

CO_2	- Carbon dioxide
Cu	- Copper
Cu_2S	- Chalcocite
$CuFeS_2$	- Chalcopyrite
Fe	- Iron
Fe^{3+}	- Ferric iron
Fe^{2+}	- Ferrous iron
FeS_2	- Pyrite
$FeSO_4.7H_2O$	- Ferrous sulfate heptahydrate
H_2O	- Water
H_2S	- Hydrogen sulfide
H_2SO_4	- Sulfuric acid
K_2SO_4	- Potassium sulfate
$(NH_4)_2SO_4$	- Ammonium sulfate
$NH_4H_2PO_4$	- Ammonium di-hydrogen orthophosphate
O_2	- Oxygen
S	- Elemental sulfur
Cu	- Copper
K	- Potassium

Al	- Aluminium
H^+	- Hydrogen ion
Phen	- Phenanthroline
Hydroxylamine	- NH_20H

NOMENCLATURE

Volume	L; mL
Time	min; day
Mass	g; mg
Particle size	mm
Flow rate (liquid)	L/day
Air Flow rate:	mL/min
Temperature	ºC
Redox Potential	mV
Concentration	g/L
Extraction	%
Intermittent frequency	Day
Hydrogen ion consumption	mol

CHAPTER 1

INTRODUCTION

1.1 Background

Microbial leaching of metal sulfides has developed rapidly in the course of the two decades. The recovery of metals by applying microorganisms to generate the leach agents is now an established biotechnological technique. The mobilization of metal cations from insoluble ores by biological oxidation and complexation processes is referred to as bioleaching (Rohwerder *et al*., 2003).

Typically, bioleaching is applied using one of two configurations: stirred tank bioleaching and heap bioleaching. Currently, much emphasis is being concentrated on the latter. In heap bioleaching, crushed ore is treated, thus avoiding the need for fine grinding and concentration steps usually needed for tank bioleaching. Two major downfalls of heap bioleaching are that it can take years to recover a mineral from the ore economically and the processes are normally not as controllable as in tank leaching.

It is a common fact that the average grades from copper mines are dropping. Furthermore, according to Wang (2005) chalcopyrite accounts for 70 % of the abundant copper sulfides in the world. It is expensive to extract low grade ore using conventional methods, which include ore concentration and direct ore smelting. Further milling, concentration and smelting puts a strain on the increasing costs of energy consumption and the emissions of greenhouse gases. Heap bioleaching is particularly applicable to low grade ores in which the mineral value does not justify milling and concentration.

In heap bioleaching, ore is crushed and stacked on an impermeable layer. The heap is then irrigated with a dilute sulfuric acid solution containing microorganisms and nutrients, while air is forced through the heap to supply both oxygen and carbon dioxide and for mineral oxidation. The microorganisms convert Fe^{2+} ions into Fe^{3+} ions. These, in turn, are powerful dissolution agents. Further the microorganisms oxidise reduced sulfur species to sulfate with the generation of hydrogen ions which assist in leaching. The leached copper solution drains out the bottom of the heap and can be sent for electro- winning or re-introduced in the heap for further concentration.

To understand heap bioleaching, an understanding of unsaturated packed bed reactors is important. This includes understanding the complexities of fluid flow, heat and mass transfer. The effectiveness of heap bioleaching is influenced by physical and chemical parameters, biological parameters factors, ore characteristics and heap geometry; these affect the yield of metal extraction (Pradhan *et al*., 2008). Phenomena such as leaching reactions, microbial attachment and growth, solute precipitation, gas/liquid mass transfer, heat generation, ore decrepitation and compaction influence are influenced by fluid flow and should be incorporated into the analysis of heap leaching (Bouffard & Dixon, 2001). The fluid flow achieved in the heap influences the physical, chemical and biological parameters, and is influenced by ore characteristics, geometry as well as nature of the irrigation and packing.

Muñoz *et al.* (1995) and Pradhan *et al.* (2008) describe a theory for postulated positive effects of intermittent irrigation. Stopping the feed to apply intermittent irrigation causes an inverse capillary effect which draws the liquid into the mass of ore where the mineral leaching takes place. Once the irrigation is re-started, the liquid moves out of the ore capillaries to the surface of the ore where new liquid washes off the mineral rich-liquid. This also ensures that unwanted salts in the ore are washed off continuously, thus enhancing intermittent irrigation. Another theory suggests that rest periods maximize the oxygen transfer to the microorganisms by decreasing the thickness of the liquid film around the mineral and enhances chemical oxidation by increasing the ferric ion concentrations (Brierley & Brierley, 1999). Also it had been claimed that coarse ore heap bioleaching systems are more efficient for intermittent irrigation (Muñoz *et al*., 1995; Pradhan *et al*., 2008).

The aim of this dissertation is to analyse and investigate the influence of fluid flow on the performance of the heap bioleaching of chalcopyrite, with emphasis on the irrigation frequency and the arrangement or packing of the ore. The two parameters were chosen because:

- Little experimental research has been published over the course of 40 years on the impact of intermittent irrigation.
- Introduction of intermittent irrigation will require the supply and pumping of less irrigant solution, provided the results show that the same amount of copper can be extracted over the same time interval with intermittent irrigation.
- Layers of fines and coarse material may develop in heaps over time as a natural process or in extreme conditions or mudslides. To investigate the effects of the introduction of zones of fines in the packing would give insight in the behaviour of

bioleaching in size segregated heaps. In order to simulate these heap structural influences, the following setups have been investigated:

- The ore was agglomerated to investigate uniform permeability, which is one of the most important requirements for effective heap leaching the ore
- In order to investigate heaps with low contact time, caused by high permeability zones, coarse material has been used.
- In order to investigate mud slides and the settling of fines to localised regions of the heap, the permeability of a heap is lowered and effective transfer of the reactants to the mineral are prevented, coarse material was layered between fines.

1.2 Thesis Structure

The thesis is divided into six chapters. Chapter 2 presents the literature review and Chapter 3 the materials and methodology. In Chapter 4 the data collected are presented and described for the leaching the different packings and irrigation types. In Chapter 5 the different types of intermittent irrigation across different types of packing and also each leach type are compared and discussed. Conclusions and recommendations are given in Chapter 6. This is followed by the reference list and appendices. The latter contain detailed analytical methods and data.

CHAPTER 2

LITERATURE REVIEW

2.1 Heap bioleaching

Heap bioleaching is a process used to extract copper and other metals from large amounts of crushed ore with low grade content with the aid of microorganisms. The base metals are leached from the heap of crushed mineral sulfide ore by the ferric iron and acid in solution. These leaching reagents are regenerated microbially. The feed solution is applied to the top of the heap. As the solution percolates downward, it becomes enriched by the copper (and/or other base metals) dissolved from the heaped ore, forming the pregnant leach solution (PLS). This is collected at the base of the heap by an impervious liner. From the liner, the PLS is redirected to a processing plant where the metals are extracted from the PLS via electrowinning. The liquid solution remaining after the electrowinning of copper is recycled as irrigation solution (Braslavsky, 2003).

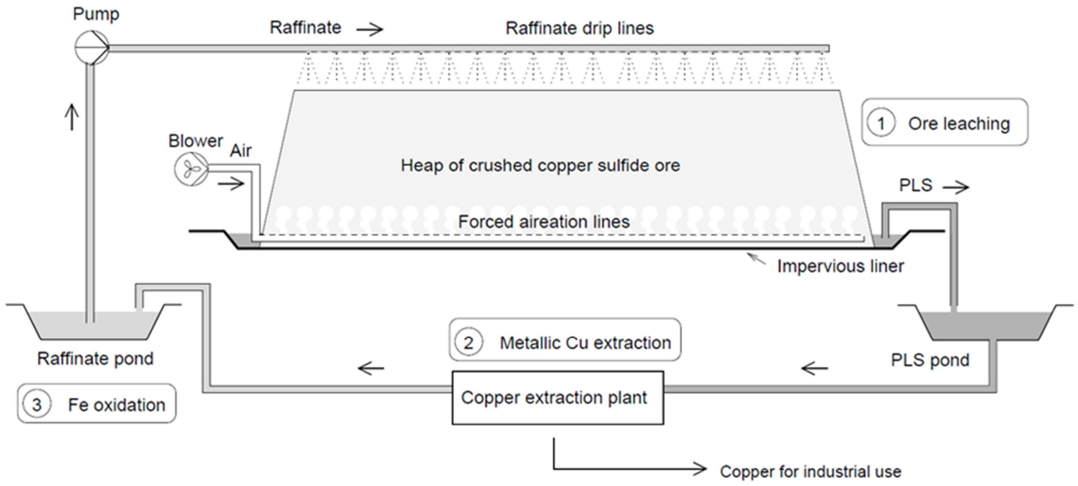

Figure 2-1: Typical heap bioleach flow diagram (Braslavsky, 2003)

Microbial leaching of an ore bed is a complex process that involves at least the following phenomena (Casas *et al*., 1998):

- Reactions of mineral species with sulfuric acid, Fe^{3+}, and dissolved oxygen;
- Hydrolysis and precipitation of complex compounds in solution, which mainly involves Fe^{3+} species and agglomerates;

- Transport, attachment, growth, and catalytic actions of microorganisms;
- Transport of aqueous species inside the ore particles;
- Transport of oxygen and water through the bed, with an air supply to the bed by natural convection and diffusion; and
- Heating and cooling of the bed, associated with exothermic and endothermic reactions and heat transfer to the environment.

These phenomena are best illustrated graphically by Petersen & Dixon (2006) in Figure 2-2.

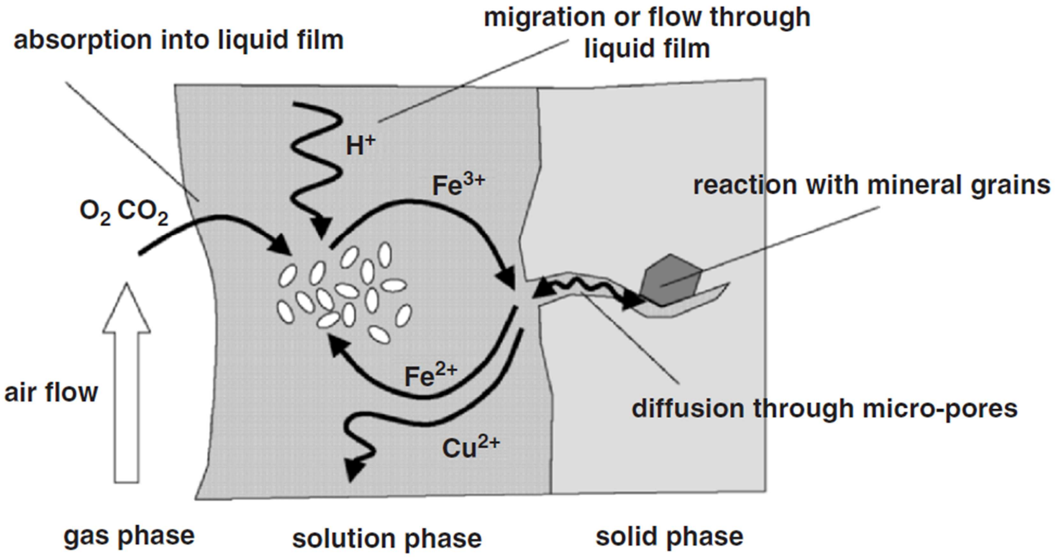

Figure 2-2: The mineral bio-oxidation reaction-transport network between gas, liquid and solid phases in heaps (Petersen & Dixon, 2006)

2.2 Packed bed reactors

While heaps are engineered structures it is recognised that they are heterogeneous in nature. The fluid dynamics have long been known to be highly variable, with heterogeneities within the heap controlling the distribution of fluid velocities and chemical reactions (Decker & Tyler, 1999).

There are two basic types of packed bed reactors: those in which the solid is the reactant and those in which solid is the catalyst. In chemical process industries, designers are normally concerned with a solid phase. In the biochemical processes the designer maybe concerned with either the solid as reactant or as catalyst (Sinnod, 2000). In the bioleaching experiences, the particles form the reactant, while also forming a physical support for catalytic microbes.

Packed bed reactors can be described as devices where gas and liquid streams merge. These streams are fed into each other by multiple-feed arrangements. These different phases are passed in the same encasing (system) which contains a packed bed of particles (Hessel *et al*., 2004). The liquid is distributed as uniformly as possible at the top of the column and flows downward, wetting the packing material. A gas is admitted at the bottom, and flows upward, contacting the liquid in a counter current fashion. An example of a packed bed is an absorber. Here, the gas contains some carrier species that is insoluble in the liquid (such as nitrogen) and soluble species such as carbon dioxide or oxygen. The soluble species is absorbed into the liquid, and the clean gas leaves the column at the top. The liquid rich in the soluble species may be taken out at the bottom or the transferred solutes maybe depleted during the transport through the column.

The following sequence of events takes place in a packed bed reactor (Denbigh & Turner, 1971):

- Mass-transfer of reagent from the fluid phase to the external surface of catalyst packing.
- Diffusion into the pores of the catalyst particles.
- Adsorption onto the catalyst surface.
- Reaction on the surface.
- Desorption of product from the catalyst surface.
- Diffusion out from the pores of the catalyst particles.
- Mass-transfer of product into the liquid phase.

In all cases, the structure of the bed strongly influences both heat and mass transfer processes within the bed. The flow pattern is extremely complex due to the presence of the packing which, together with diffusion and heat conduction, leads to the material and heat dispersion (Iordanidis, 2002).

2.3 Fluid flow in heaps

The heap can be considered as an unsaturated porous medium with three phases (liquid, gas and solid), which can have transient, spatially dependent fluid and heat flow. As a result, complex transient liquid flow models, accounting for liquid holdup and stagnant regions have been developed (Leahy *et al*., 2005).

When the smaller openings are flooded, the leaching solution finds its way through the larger channels. This free draining solution hereafter referred to as the flowing liquid, percolates as rivulets and films across the surfaces of the particles. The flowing liquid holdup corresponds roughly to the liquid collected during drainage, and depends on the packing characteristics, the fluid physical properties, the liquid flow rate and the gas flow rate (Bouffard & Dixon, 2001; Fagan *et a*l., 2012 ; Harrison, 2012; Ilankoon & Neethling, 2012). A substantial change in the holdup of flowing liquid is observed when the flow rate is large enough such that air-filled voids begin to pinch off and flooding occurs (Bouffard & Dixon, 2001).

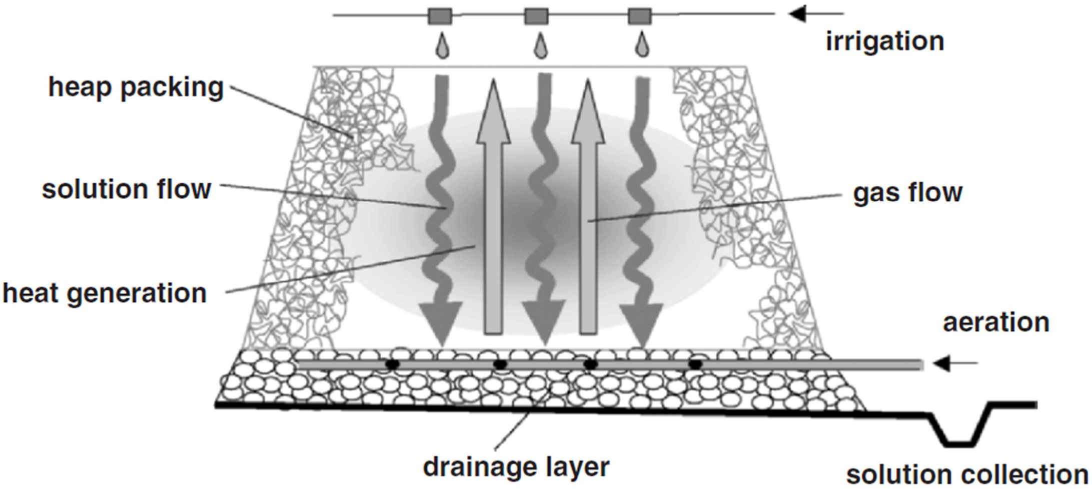

Figure 2-3: A Heap indicating the major heap transport effects (Petersen & Dixon, 2006)

As noted previously, phenomena such as leaching reactions, microbial attachment and growth, solute precipitation, gas/liquid mass transfer, heat generation and ore decrepitation and compaction are influenced by fluid flow and play a key role in heap performance (Bouffard & Dixon, 2001; Petersen *et al*., 2010; Chiume *et al*., 2012). In understanding the behaviour in heap bioleaching systems one has to understand the influence factors affecting heap bioleaching, discussed in the following sections.

2.3.1 Irrigation/Liquid flow rate

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 *et a*l., 2007).

Leahy *et al.* (2005) created a model which proves that copper is extracted faster at a higher liquid flow 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^{3+} concentration and hence faster copper extraction (Leahy *et al*., 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. Chuime *et al.* (2012) have described the influence of irrigation rate on microbial colonisation experimentally, with potential to extend this to interrogate Leahy's model.

2.3.2 Irrigation frequency (Intermittent irrigation)

To date, in application of heap leaching, continuous leaching is most typically applied for metal recovery. Several theoretical studies have proposed a benefit of intermittent irrigation, especially for leaching of coarse ore beds. Two such theoretical studies are those of Muñoz *et al.,* (1995) and Pradhan *et al.,* (2008). These suggested that intermittent irrigation would increase the metal dissolution per unit volume of irrigation solution added compared to continuous irrigation. In such cases, the attack solution is intermittently sprayed onto the surface of the heap and is allowed to percolate before a new solution is applied. This is postulated to set up an inverse capillary effect, which permits the leaching of coarse ores. 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 a new irrigation carries with it the dissolved metal ion and the process begins again with the introduction of a fresh liquid into the capillary. In this way, intermittent irrigation may be more effective for coarse ores 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. Thus, alternate irrigation and drying has been postulated to leach coarse particles and drain out soluble salts from their surfaces as well as increasing the diffusion of oxygen and carbon dioxide to the ore surface where active microorganisms are located. The frequency of irrigation is an important factor that has to be considered in these theoretical approaches. These two papers do not provide any scientific data to support the theories presented above.

Only three studies are reported in which the effect of intermittent irrigation has been investigated experimentally. Aslam & Aslam (1970) have demonstrated that intermittent irrigation implemented on a daily basis in the presence of microorganisms yield more copper than the intermittent irrigation done once in a week. Bruynesteyn (1983) suggested that in industry 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. These two studies do not explain the chemistry and physics behind the intermittent irrigation phenomena.

The latest study done by Saririchi *et al.* (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 intermittent irrigation was not a key parameter in leaching, but it was 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.

2.3.3 Irrigation ratio

The irrigation ratio is the ratio of the total volume of leach solution applied to the mass of the ore bed in m^3/ton to achieve a target recovery (Lizama *et al*., 2005). Apart from the mass of the heap the irrigation ratio can also be applied in terms of the height of a heap leaching system. The irrigation ratio controls the colonisation and steady-rate stages of bioleaching, as well as the acid and Fe balances. Lizama *et al.* (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. Li (2005) showed that a larger irrigation ratio enhances the advective transport of metal ions which contribute to a faster increase of concentration in the PLS. Li (2005) also showed that like the change of saturation, the change of copper mole fraction is more sensitive to the decrease of the irrigation ratio.

2.3.4 Temperature

The heat generated by exothermic reactions is transported with the flow of liquid. Hence, the temperature inside the bed increases with increasing depth. The highest temperature zone is located at the bottom where a large liquid flow path with an adequate oxygen supply is found (Moreno *et al.* 1998).

Heat generated by chemical reactions in a heap is transported via convection by the gaseous and liquid phases, and via conduction through the heap. Heaps assume temperature profiles depending on the irrigation and aeration rates, and these rates can be used to achieve a certain level of temperature control (Dixon, 2003).

Temperature is controlled by (Brierley & Briggs, 2002) :

- Heap depth – the higher the heap, the greater the heating.
- Irrigation – heat is removed from the heap by liquid flow
- Rest periods – warm the heap
- Excess air addition may also cool the heap through evaporation
- Evaporation of irrigation solutions may cool the heap
- Convection from heap sides and surface
- Radiation at night

Petersen (2010) found, through both experimental and theoretical evaluation, that gas–liquid mass transfer of oxygen does not vary greatly between different temperature heap leach scenarios and is not a significant function of temperature in the range between 22 - 68°C.

2.3.5 Aeration

As most of the metal leaching microorganisms are aerobic and chemolithotrophic in nature, aeration takes care of the supply of both oxygen and carbon dioxide to the leaching system. Carbon dioxide serves as a source of carbon needed for biomass generation. The interior of a heap, if not properly aerated, is prone to anoxic conditions. Aeration of bioleached heaps can accelerate bio-oxidation reactions by reducing the time of leach cycle. Copper leaching is directly related to oxygen consumption in the heap and increasing the rate of aeration, therefore, improved copper leaching (Lizama *et al*., 2005). Oxygen consumption, in turn, is related to microbial activity and the rate of forced aeration when the oxygen supplied to the heap is limited (Pradhan *et al*., 2008).

Gas liquid mass transport is important for the supply of oxygen to the heap. Gas transport in a heap is a function of heap permeability and saturation, heap temperature, oxygen depletion and water vapour production. When forced aeration is applied, the effect of gas diffusion on overall gas transport may be reduced (Dixon, 2003; Ogbonna, 2006). Many heap leaching systems are aerated by forced aeration. Bartlett & 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. Initiating a natural convection draft is uncertain and may not occur, leaving dead regions in a heap where insufficient oxygen is transferred to the ore. When natural convection does occur, a very long and uncertain time may be required to increase the temperature and accelerate air flow to a satisfactory velocity. Air flow will tend to channel through high permeability zones leaving low permeability regions stagnant (Bartlett & Prisbrey, 1996).

2.3.6 Heap height

Reducing the heap height not only affects the distribution of acid within a heap, but also affects heat generation, hence temperature distribution. A shorter heap effectively has less volume per unit cross sectional area, within which heat is generated, and therefore heat is removed more easily without raising temperatures as high as in a taller heap (Petersen & Dixon, 2007). Heap height is an important factor for the rise in temperature, which increases with the square of the heap height (Richie, 1997). Padilla *et al.* (2008) showed that an inverse relation exists between the height of a heap and its % extraction. This was further confirmed in the observation of Lizama *et al.* (2005) about the inverse relationship between recovery and heap height, discussed in section 2.3.3.

2.3.7 Particle Size

The rate of leaching is usually proportional to the total mineral surface in contact with the leach reagents and a further degree of complexity is added by the distribution of grains of different size and accessibility within the ore (Petersen & Dixon, 2006). This means that leaching rates normally increase with an increase in the surface area of a particle; the finer the particle, the more of the mineral is exposed to the reactants (Ogbonna *et al*., 2006). However the cost of grinding to achieve the finer particle size should be considered in designing the process to extract the mineral effectively. As discussed in Section 2.3.7, the size distribution in a heap influences the porosity and permeability of a heap, thereby influencing the leaching rates.

2.3.8 Permeability

Permeability of the heap is critical for good contacting of reactants for the recovery rates of a heap. If the heap material is too compact, the time of the leaching operation increases as the reagent liquid will only percolate through the heap slowly. If permeability in the heap is uneven, the leaching solution might cause channelling leaving parts of the heap untreated. The increase of fine particles would lead permeability to worsen rapidly and therefore, fine particles are often agglomerated to ensure a good permeability (BioMineWiki, 2008). With a higher permeability, the vertical velocity becomes larger, thus the fluid can flow downwards more quickly and at the same time the horizontal flow induced by capillary suction becomes less significant (Li, 2005).

Heap leaching systems can be divided into coarse channels, which are highly permeable zones and fine channels, which have low permeability (Kappes, 2002). It must be recognised that layers of fines and coarse material often develop in heaps over time as a natural process (segregation of sizes), whether the material is agglomerated or not (O'Kane Consultants Inc., 2000). This creation of fines may cause permeability issues restricting the effective fluid flow through the fine material and channelling of leachate in the coarse material. It is generally understood that heaps with higher permeability zones (coarse ore); have reduced the contacting time between the reactants and the ore. Uniform permeability is an important factor; agglomeration is used to eliminate excessive fines and prevent the blocking of flow channels, thus preventing the retention of the pregnant solution inside the heap and increasing the efficiency of the process (Miller *et al*., 2003).

Yang *et al.* (2008) has shown that the permeability of ore granular media during leaching evolves continuously. The total permeability deterioration during leaching is mainly due to the decrease of the seepage coefficient of the bottom zone. The ore particles subside under the actions of multiple factors, such as hydraulic power, gravity and chemical reactions. Some fine particles move downwards with leaching solution and deposit at the bottom zone. This decreases its porosity and effective diameter simultaneously and causes the seepage coefficient to decrease in the end (Yang *et al*., 2008).

Porosity of an ore particle allows the leaching solutions to penetrate the ore body (Pradhan *et al*., 2008). An important process at the particle level is the transport of reactants to, and reaction products from, reaction sites within the particle. This process is diffusion governed, and is limited by the size and porosity of the ore particle, the diffusion gradient, and the diffusivity of the species (Ogbonna *et al*., 2006).

2.4 Microbial cultures

The role of the microorganisms is to generate the leaching chemicals and to create the space in which the leaching reactions take place (Rawlings, 2005), thus the main function is the production of sulfuric acid for the solubilisation of metal sulfides, for the proton attack, and to keep the Fe in its oxidized Fe^{3+} state for an oxidative attack on the mineral.

Petersen & Dixon (2002) drew a comparison of the advantages of thermophilic over mesophilic bioleaching where they cited that chalcopyrite is the only sulfide mineral that does not respond well to mesophiles, primarily because of its tendency to “passivate” at the high solution potentials that are commonly associated with mesophile leaching. Thermophile bioleaching rates are generally significantly higher than those associated with mesophile bioleaching at comparable conditions (Petersen & Dixon, 2002). Norrris *et al.* (1986) also observed that thermophiles performed better than mesophiles in the leaching of chalcopyrite.

The main factor in determining which microorganisms are likely to dominate the commercial bioleaching processes is the Fe^{3+} to Fe^{2+} iron ratio or redox potential (Rawlings *et al*., 1999). Que *et al.* (2005), and Falco *et al.* (2003) showed that the bioleaching of chalcopyrite with mixed cultures were more efficient than the respective pure cultures alone

2.4.1 Thermophiles

Petersen & Dixon (2002) explained that *Sulfolobus*, *Acidianus* and *Metallosphaera* have been shown to leach chalcopyrite to high extractions at temperatures in the range 65 - 75°C (Petersen & Dixon, 2002). Gautier *et al.* (2007) observed that bioleaching of chalcopyrite in the presence of *Sulfolobus metallicus* is the result of the cooperative action of attached cells which catalyse copper dissolution through formation of thiosulfate, sulfite and bisulfite, and planktonic cells which further oxidize these intermediate compounds to bi-sulfate and sulfate.

Acidianus brierleyi is unique because it can both oxidize and reduce sulfur depending on the availability of oxygen (Segere *et al*., 1986) and has the ability to grow autotrophically on pyrite (FeS_2) whereas some *Sulfolobus spp* and other thermophilic archea used in bioleaching, cannot (Larsson *et al*., 1990). This is because of this ability to use carbon dioxide as a carbon source, all *A. brierley* requires to oxidize sulfur is a warm, acidic environment and a sulfur source.

The novel species of *Ferroplasma* is considered to be involved in the aerobic and anaerobic cycling of Fe within the heap bioleaching environment. According to Hawkes, *et al.* (2006) the role of the novel species of *Ferroplasma* within the heap is not fully understood.

Zhou, *et al.* (2007) showed that *Acidithiobacillus caldus* increases leaching efficiency compared to a Fe oxidizer alone by removing sulfur rich compounds that accumulate on the surface of sulfide minerals during bioleaching.

Auernik & Kelly (2010) cited that the key to bioleaching capacity in *Metallosphaera sedula* is the dissimilatory oxidation of Fe and sulfur, mediated by membrane-associated electron transport that is anchored by terminal oxidases, but also noted that research showed that precipitate formation is limiting to the Fe^{3+} availability.

2.4.2 Mesophiles

Acidithiobacillus ferrooxidans, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* play an important role in the bioleaching process. *A. thiooxidans* can only oxidize elemental sulfur, while *L. ferrooxidans* and *A. ferrooxidans* can oxidize Fe^{2+} (Watling *et al.* 2001). It should be noted that *A. ferrooxidans* oxidises Fe^{2+} and reduced sulfur components while *Leptospirillum ferriphilum* only oxidises Fe^{2+} (Escobar *et al.*, 2008). *A. ferrooxidans* is able to catalyse the oxidation of metallic sulfides to sulfate through a multistep mechanism in which oxygen is the terminal electron acceptor through the oxidation of Fe^{2+} to Fe^{3+} (Torma , 1977). Although *A. thiooxidans*is unable to oxidize Fe^{2+} ions into Fe^{3+} ions by itself, it is capable of oxidising elemental sulfur and reduced sulfur compounds from sulfide minerals and cooperating with some other Fe^{2+} oxidizing microorganisms (e.g., *A. ferrooxidans*, *L. ferrooxidans*) to contribute in the bio-oxidation of sulfide ores and concentrates (Leng *et al*., 2009). Experimental results indicated that *L. ferriphilum* is likely to perform optimally, at warm temperatures (25–42 °C) in heap bioleach operations before being taken over by thermophiles at higher temperatures (Ojumu *et al*., 2009). *Leptospirilli* have a slower growth rate compared to the *Acidithiobacilli and* they tolerate lower pH’s, higher redox potential of the medium and higher cultivation temperature (Rawlings *et al*., 1999).

2.5 Factors affecting microorganisms:

2.5.1 Temperature

In heap bioleaching applications, large temperature gradients are likely resulting in corresponding microbial activities at different parts of the heap (Halinen *et al*., 2009). Microorganisms are classified in terms of the temperature range in which they function optimally with optimum temperatures of 30 – 40 °C for mesophiles, around 50 °C for moderate thermophiles and above 65 °C for extreme thermophiles (Pradhan *et al*., 2008). According to Brierley & Briggs (2002) chemical reactions proceed more rapidly at higher temperatures, but according to Pradhan *et al.* (2008) below the optimum temperature certain microorganisms become inactive, while at temperatures above the optimum, they are rapidly destroyed. In simple terms the dominance of a microorganism can be altered by changing the reaction temperature of the system.

2.5.2 pH

Deveci *et al.* (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, while thermophiles have a greater tolerance (Deveci *et a*l., 2008). However Vilcáez *et al.* (2009) state that at pH values above 1.5, the large amounts of Fe^{3+} generated result in the formation of jarosite, which decreases the catalytic effect of thermophiles. On increasing the pH, hydroxide and sulfates become more dominant which may change the amount of substrates available to the microorganism and influence the enzymes that catalyse the chemical reactions. If the pH decreases a lot of stress is placed on the microorganisms. The higher the hydrogen ion concentration, the greater the difficulty some microorganisms have in rejecting the transport of the hydrogen ions across the cell membrane. It should also be remembered that low pH levels in combination with high temperatures increase the leaching rate of chalcopyrite (Vilcáez *et al*., 2008b).

2.5.3 Oxygen

Bioleaching microorganisms require oxygen, which accepts the electrons in the redox reactions catalysed by the microorganisms. (Brierley & Briggs, 2002). 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. As oxygen is required for oxidative metabolism, its depletion has rate limiting effect on bioleaching. If oxygen is sufficiently present at all the points of the heap, increase in aeration does not increase the leaching rate (Pradhan *et al*., 2008)

2.5.4 Carbon dioxide

Microorganisms require carbon for the synthesis of cellular components, which are obtained by the reduction of carbon dioxide in a complex metabolic pathway. Microorganisms expend energy in fixing this carbon. Carbon dioxide is generally available from the air added for oxidation (Brierley & Briggs, 2002).

2.5.5 Nutrients

Microorganisms have specific nutritional requirements synthesise biomass, which are normally nitrogen, phosphorus, potassium and magnesium. Magnesium and potassium are present in sufficient quantities from the degradation of rock in the acid leach, while nitrogen and phosphorous may be added for heap bioleaching. It should be noted that the addition of phosphorous is limiting due to its ability to precipitate with iron to form jarosite, which may influence the systems electrochemical response. It should be noted that in heap bioleaching nutrient addition is not essential as sufficient amounts for microorganisms may be available from the ore and ammonium nitrate blasting agents. (Brierley & Briggs, 2002)

2.5.6 Salinity and metal / metalloid concentrations

Microorganisms are relatively intolerant to the chloride ion, which disrupt the cell membrane and allow uncontrolled transport of NO^{3+} into the cell, which slow down the rate of Fe^{2+} oxidation. High concentrations of metals or metalloids can contribute to the increase total dissolved solids in which several potentially cations and anions are collectively at levels that can slow microbial Fe oxidation (Brierley & Briggs, 2002).

2.5.7 Redox potential

Importantly Fe^{2+}, Fe^{3+} and redox potential affects the oxidation kinetics and are interlink with each other. The ratio of Fe^{3+}:Fe^{2+} selects the microorganisms in a reactor (Rawlings *et al*., 1999), which can be described by two examples. When the redox potential is low and more Fe^{2+} is in solution, *A. ferrooxidans* dominates, because it has a faster growth rate and build up a larger number of cells in the system. If the redox potential increases due to higher

Fe^{3+}:Fe^{2+} ratio, *L. ferrooxidans* becomes dominant, because it has a higher affinity for Fe^{2+} (Brierley & Briggs, 2002).

It should also be taken into account that if high temperature leaching is used, the leaching rate increases with temperature, alleviating the effect of slow dissolution at a high redox, while a lower redox is better, but difficult to maintain with an active iron oxidising microbial community.

2.6 Mineralogy and leaching mechanisms

2.6.1 Mineralogy

Not all types of minerals are amenable to bioleaching. To be amenable to bioleaching with the microbial consortium used for this study, the mineral should contain Fe or a reduced form of sulfur. A mineral lacking these two compounds may be leached if it occurs with another mineral that contains that contains Fe and reduced sulfur, provided that the mineral is subjected to an attack by either Fe^{3+} and/or sulfuric acid (Rawlings, 2004). 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.

The dissolution of mineral sulfides in general can be defined as either acid-producing, which leads to a decrease in pH (pyrite dissolution) or acid-consuming, which leads to an increase in pH (chalcocite and chalcopyrite) dissolution (Plumb *et al*., 2008). Whether heap bioleaching of an ore is possible where chalcopyrite and pyrite are the major sulfide minerals, depends on the reactivity of the pyrite to reach sufficient temperatures for acceptable leaching kinetics (Van Staden *et al*., 2008)

It is difficult to understand the bioleaching process of complex ores, which contain several minerals (Jonglertjunya, 2003). To support this Watling, (2006) emphasised that little quantitative research on the correlation between ore mineralogy, reaction chemistry and leach residue mineralogy has been reported on the public domain.

2.6.2 Bioleaching mechanism of chalcopyrite ($CuFeS_2$)

Bioleaching can be divided into two indirect leaching mechanisms, which are thiosulfate and polysulfide mechanisms. One is based on the oxidative attack of Fe^{3+} on acid-insoluble metal sulfides involving thiosulfate as the main intermediate (Schippers *et al*., 1996). The other mechanism is started by proton and/or Fe^{3+} attack on acid-soluble metal sulfides with polysulfides and sulfur as intermediates (Schippers & Sand, 1999).

Tributsch, (1999) reviewed proposals and concluded that chalcopyrite bioleaching may have three different strategies which are indirect bioleaching, contact bioleaching and cooperative bioleaching. Research has found that bioleaching of chalcopyrite is a cooperative effort involving the simultaneous contact bioleaching of the pyritic phase of the mineral, which may swing towards thiosulfate and the indirect bioleaching of chalcopyrite, by way of polysulfide mechanism (Rodríguez *et al*., 2003).

Since chalcopyrite is considered an acid soluble it is safe to say that emphasis will be put on the bioleaching via the polysulfide mechanism.

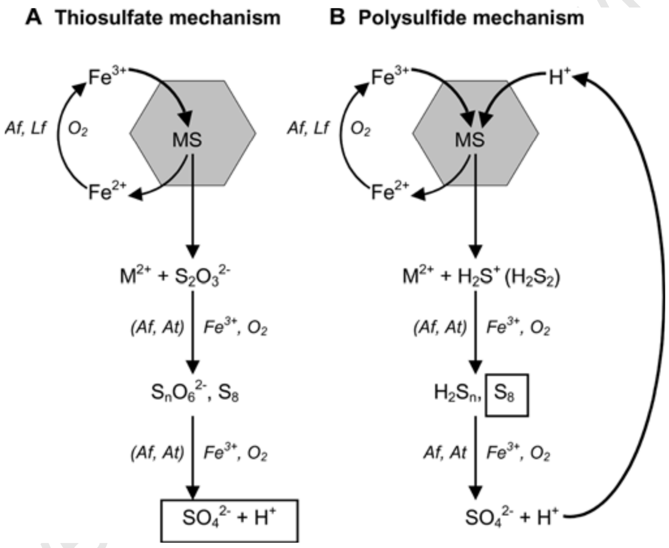

Figure 2-4: Schematic comparison of the thiosulfate (A) and polysulfide (B) mechanisms in (bio)leaching of metal sulfides (Schippers & Sand, 1999); (Schippers *et al*., 1996)

The ferric (Fe^{3+}) ion attacks the chalcopyrite at the surface, liberating the ferrous (Fe^{2+}), cupric (Cu^{2+}) and elemental sulfur (S^0) into solution:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \qquad (1)$$

These Fe^{2+} ions may also catalyse the oxidation by dissolved oxygen to release copper, which causes acid consumption.

$$CuFeS_2 + 4O_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O \qquad (2)$$

It has been confirmed that the Fe^{2+} ion released from chalcopyrite can be oxidized by the soluble oxygen to form sufficient amounts of Fe^{3+} can lead to copper extractions This copper extractions are said to comparable to that of thermophile leaching (Vilcáez *et al*., 2009).

Through microbial oxidation, the Fe^{2+} ions are rapidly oxidised in the presence of iron oxidizing microorganisms to the Fe^{3+} form, which is required to oxidise chalcopyrite.

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (3)$$

The acid dissolution (2) and Fe^{2+} oxidation reaction (3) processes are acid consuming, which normally leads to an increase of the pH in the bioleaching system.

Also through microbial oxidation elemental sulfur are oxidised by sulfur oxidising microorganisms to produce sulfuric acid, to counter balance the acid consumption reaction.

$$S^0 + \tfrac{3}{2}O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \qquad (4)$$

The thermophiles driving these two equations (3 & 4) are important, because it is responsible for converting the Fe^{2+} into the Fe^{3+}. This in turn creates the ferric sulfate ($Fe_2(SO_4)_3$), which is a powerful oxidizing agent that oxidizes the copper sulfide minerals, leading to the in situ leaching of copper by the sulfuric acid generated (Pradhan *et al*., 2008).

The net chalcopyrite reaction for leaching is:

$$CuFeS_2 + O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-} \qquad (5)$$

or

$$CuFeS_2 + O_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2H_2O + 2S^0 \qquad (6)$$

Jarosite formation:

$$Fe^{3+} + SO_4^{2-} + 6H_2\mathrm{O} + M^{2+} \rightarrow MFe_3(SO_4)_2(OH)_6 + 6H^+ \qquad (7)$$

Precipitations of iron sulfate are formed as jarosite are described as inherent to the utilization of thermophiles. This means that pH values above 1.5, the large amounts of Fe^{3+} generated results in the formation of jarosite (Eq. 7). Jarosite is normally an undesirable by-product, because its formation on the mineral surface passivates the leaching reactions. The catalytic effect of thermophiles can be boosted, if jarosite formation can be avoided. (Vilcáez & Inoue, 2009).

2.7 Problem statement

Though a lot of work has been done in the field of heap (bio) leaching, little work is reported to explain the influence and effects of intermittent irrigation in heap leaching systems. Only three papers have been published that include experimental research explaining intermittent irrigation: Aslam & Aslam, (1970), Bruynesteyn, (1983) and Saririchi *et al.* (2012). Unpublished research work by Du Plessis was done, but only cited in another paper by the researcher (Du Plessis *et al*., 2007).

The research done in these papers was not dedicated to explain the influence of intermittent irrigation, but was rather a small part of a bigger investigation. These papers also lack the necessary research results and controls to validate the influence of intermittent irrigation.

A recent study by Saririchi *et al.* (2012) lacks the appropriate controls and rigour for physical recovery results to validate the findings that intermittent irrigation has a positive effect on zinc heap leaching.

Theories have been postulated to describe the positive effects of intermittent irrigation, by Pradhan *et al.* (2008) and Muñoz *et al.* (1995), but no experimental research is available to support these theories.

An important natural phenomenon that normally occurs in heap leaching is displacement of fines in a heap. This fines displacement normally divides the heap into coarse zones and fine layers of low permeability, which both negatively influence heap leaching. Investigation the effects of intermittent irrigation in different packings might give another heap leaching control apart from biotic agglomerated leaching. Also this layered packing might also be modified to prevent the formation of acid rock drainage (ARD).

This lack in research since 1983 concerning the intermittent irrigation field prompted a curiosity to understand the influence of intermittent irrigation on the metal recoveries and microbial population behaviour in heap bioleaching. While this study is only a stepping stone in the development of the methodology of intermittent irrigation, the thesis addresses the impact of intermittent irrigation on the pH, redox, Fe^{2+}/Fe^{3+} oxidation, copper recovery, Fe precipitation and microbial behaviour by changing the following parameters of heap leaching systems:

- Abiotic or biotic columns
- Irrigation frequencies
- Irrigation rate
- Packing

2.8 Hypothesis and key questions

The lack of investigative work discussed in the previous section prompted an investigation into several questions raised with respect to intermittent irrigation. Three hypotheses have been formulated and the key questions derived from there are given below.

2.8.1 Hypothesis 1

On applying intermittent irrigation conditions to heap bioleaching systems, the copper extraction is unchanged relative to the continuous irrigation, resulting in increased copper recovered per unit volume of leach liquor.

- Does the copper concentration in the leachate vary on applying intermittent irrigation at the same flow rate and different resting times?
- Does the copper concentration in the leachate vary by applying intermittent irrigation at different flow rates and the same resting times?
- Does intermittent irrigation effect the time required to achieve the same extent of leaching?
- Are these affects influenced by different packing types?
- Does the copper concentration increase in the liquid permeate as the resting period increases?

2.8.2 Hypothesis 2

There is no impact on copper leached per volume of leach liquor when applying intermittent irrigation on abiotic leaching.

- Are the leaching reagents supplied in the feed, depleted completely regardless of the flow regime? (Note: the same key questions can be asked as in hypothesis 1)

2.8.3 Hypothesis 3

The nature of packing (agglomerated and layered ore) influences the efficiency of leaching by the formation of layers of fines between the regions of coarse material.

- Does the limitation of permeability or mass transfer (liquid and gas) decrease copper recovery?
- Is the absence of fines in the coarse layers in intermittent irrigation less beneficial, because the liquid hold up in the resting column is lower, potentially limiting the leaching reactions?

CHAPTER 3

MATERIALS AND METHODS

3.1 Ore

3.1.1 Characteristics

The low grade chalcopyrite ($CuFeS_2$) ore used in this study was sourced from a mine in the USA. A full mineralogical analysis, supplied by the mining company, is summarised in Table 3-1:

Table 3-1: Chemical characterization & mineral composition

Elements	Mining House analysis (%)	UCT Analysis (%)
Cu	0.700	0.587
Fe	3.000	2.629
S	2.300	1.070
K	2.400	Not analysed
Al	9.500	Not analysed
-	-	-

Minerals	Analysis (%)
Chalcopyrite	0.5 to 0.7
Pyrite	1.3 to 1.6
Other sulfides	< 0.1
Quartz	40 – 42 %
Clay minerals	15 – 42 %
Other	< 5 %

This difference between the analyses supplied by the mining house and conducted for this project may be attributed to the fact that 88 kg sub-sample of the ore was taken from the initial 40 ton sample received from the mining company, without representative sampling. The smaller sub-sample was representatively split for all further analysis and ore preparation for the experiments. An in-house analysis of the sub-sample used was performed on a representative sample of the 88 kg. It indicated that the copper, iron and sulfur differ from the mining company's analysis. The copper and iron was analysed following concentrated acid (HNO_3-HCl) digestion. These supernatants were analysed using an Atomic Adsorption Spectrophotometer (AAS). Sulfur content was done using a Leco sulfur analyser. The methodologies of this analysis can be seen in 3.8.

3.1.2 Preparation

A batch of 88 kg of ore was crushed and sieved into the following fractions: -20 mm, - 16 mm, -8 mm, -5.6 mm, - 2 mm, -1 mm, -250 µm. A generic size composition typical of that used for heap leaching (Dew *et al*., 2011; Govender *et al*., 2012) was generated to create representative ore samples for the leaching experiments. This was done by splitting the different sieved size fractions with a rotary splitter and combining them to provide 4 kg batches, consisting of the particle size distribution detailed in Table 3-2.

Table 3-2: Particle size distribution of the ore prepared by crushing to resemble a typical distribution of the agglomerated heap leach process

All sizes		*Coarse	
Size (mm)	**Fraction**	**Size (mm)**	**Fraction**
- 20 + 16	0.162	- 20 + 16	0.216
-16 + 8	0.293	-16 + 8	0.391
- 8 + 5.6	0.147	- 8 + 5.6	0.196
- 5.600 + 2	0.147	- 5.6 + 2	0.196
- 2 + 1	0.074	- 2 + 1	0.000
- 1 + 0.250	0.074	- 1 + 0.25	0.000
- 0.250	0.103	- 0.25	0.000

**Note: To generate the “coarse” ore sample, the material – 2mm was removed.*

3.1.3 Packing

Each column was charged with 4 kg of ore. As stated, this project investigated three different packing arrangements. In the “agglomerated ore”, the full size distribution was used and acid agglomerated prior to packing. For the “coarse ore the -2 mm fraction was removed. For the “layered packing”, the -2 mm fraction was removed from the bulk ore sample and these arranged in 2 x 2 layers (coarse ore – fines – coarse ore – fines). These are described in detail below.

3.1.4 Agglomerated columns

To agglomerate an ore batch of 4 kg, an acid water solution was prepared at a ratio of 50 mL water and 3.7 mL H_2SO_4 per kg of ore. This corresponds to 2 kg acid/ton ore and 5.5 % moisture, where 0.5 % comes with the ore. The acid was mixed thoroughly with the water required and added to the ore. This mixture was rotated in the bucket to agglomerate, to ensure a homogeneous clumpy sludge. The agglomerated ore was then immediately packed into the column. This agglomeration method was used in various experimental works at UCT as a standard method (Van Hille *et al*., 2010; Tupikina, 2011; Chiume *et al*., 2012).

3.1.5 Coarse ore columns

The -2 mm fines were not agglomerated with this ore and the fractions was adjusted accordingly as described in Table 3-2. The acid agglomeration method was done as described in section 3.1.4.

3.1.6 Layered columns

Ore was divided into two size ranges: coarse material (+ 2 mm size range) and fines (– 2 mm size range). These two size ranges were each split into two portions. These were packed into the column layer by layer in the following sequence: coarse, fine, coarse, fine. It should be noted that the layered columns was not treated with acid to agglomerate the different parts of ore.

3.2 Microorganisms cultures

Owing to chalcopyrite being the dominant copper sulfide mineral present in the low grade ore, the bioleaching experiments were run at 65 ^{O}C with a combination of a mixed thermophilic and mesophilic inoculum. The mixed thermophilic inoculum contained (>1%) *S. metallicus*, *Acidianus* sp, *Acidiplasma cupricumulans*, *Acidothiobacillus caldus*, *Metallosphaera hakonensis, L. ferriphilum*, *A. ferrooxidans*, *Acidi(thio)microbium ferrooxidans* and *A.* thiooxidans in the proportions illustrated. (See Figure 3-1, Figure 3-2, Figure 3-3). Each bioleaching column was inoculated at a concentration of 4 x 10^8 cells per 4 kg ore (See Figure 3-1, Figure 3-2 and Figure 3-3).

Table 3-3: Inoculum

Inoculum type	Temperature (ºC)	Microorganisms	Cell Counts per 4 kg of ore
Chalcopyrite stock culture 1	65	Extreme thermophiles	5 x 10^5
Chalcopyrite stock culture 2	65	Extreme thermophiles	6 x 10^7
Pyrite stock culture 3	50	Moderate thermophiles	2 x 10^7

Note: Stock culture 1 and 2 refer to two different stock cultures maintained under different operating conditions.

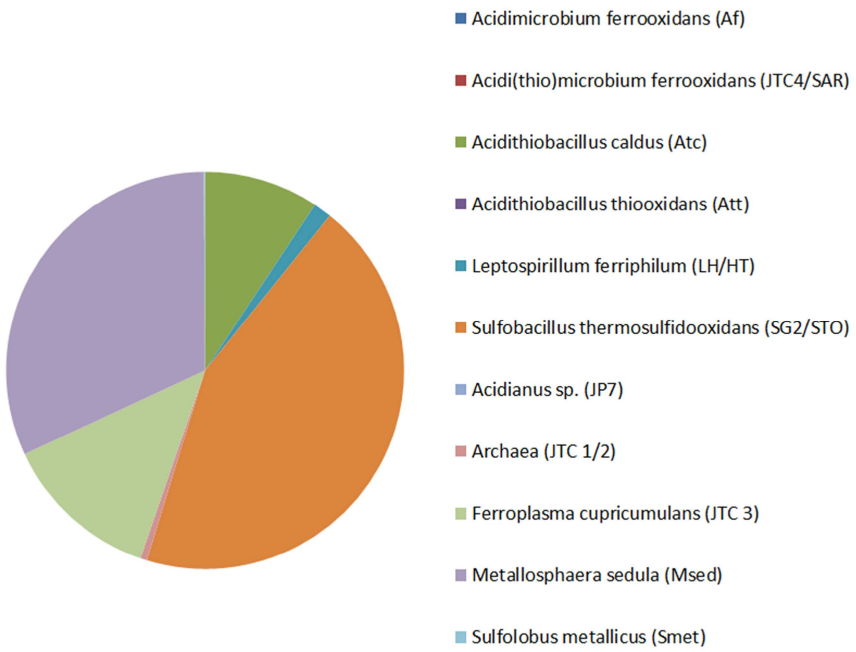

Figure 3-1: qPCR analysis and stock culture 1 - 65 °C, chalcopyrite, mixed

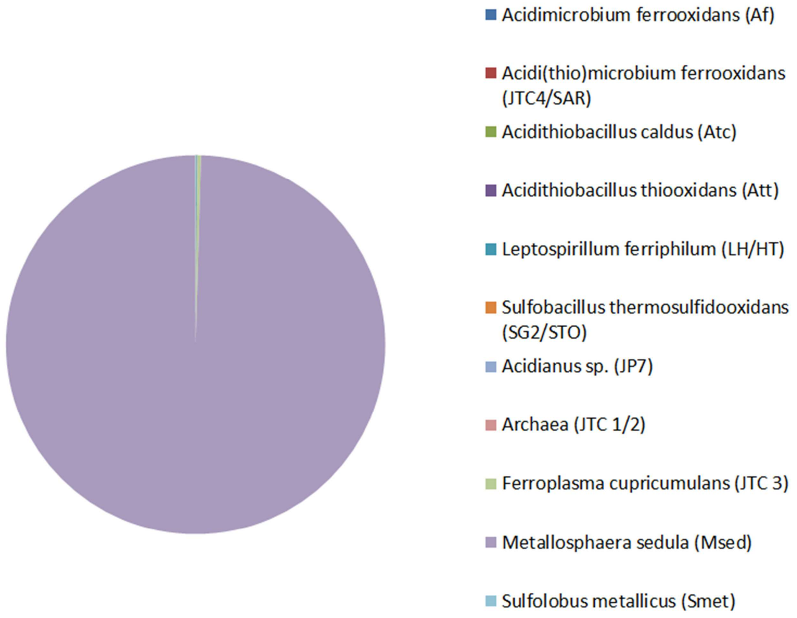

Figure 3-2: qPCR analysis and stock culture 2 - 65 °C, chalcopyrite, mixed

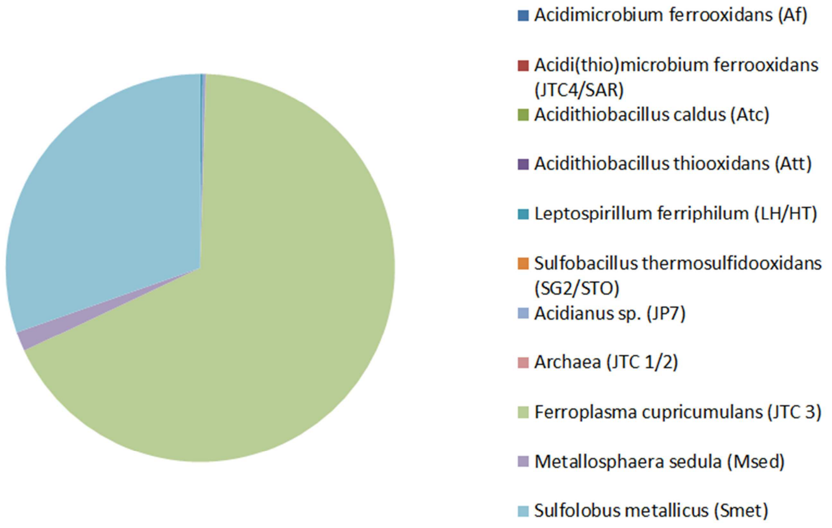

Figure 3-3: qPCR analysis and stock culture 3 - 50 °C, pyrite, mixed

3.3 Feed solution

A feed of basal salt medium with a low pH (1.15) was prepared, containing Fe^{2+} (0.5 g/L) and nutrients, equivalent to 50 g/L of NH_4^+, PO_4^{3+} and K^+. This feed was prepared by dissolving 49.78 g of $FeSO_4.7H_2O$, 183.3 mg of $(NH_4)_2SO_4$, 60.5 mg $NH_4H_2PO_4$ and 111.2 mg of K_2SO_4 in 20 L of distilled water. The pH was adjusted with concentrated H_2SO_4 to pH 1.15. To prevent microbial growth and contamination in the abiotic columns, sodium benzoate ($NaC_6H_5CO_2$) was added as a preservative at a concentration of 0.05 g sodium benzoate / L of feed.

3.4 Equipment setup

PVC columns were used to simulate heap bioleaching on the laboratory scale. These columns, illustrated in Figure 3-4 were 100 mm in diameter and 530 mm in height. The columns were charged with 4 kg ore, which was layered on a bed of marbles, supported by a sieve plate. A layer of marbles was placed on top of the ore to ensure uniform feed distribution (Bouffard & Dixon, 2001). Each column was heated with an electrical heating coil, wrapped around the column and insulated with aluminium tape. A control box supplies power to the heating coil and simultaneously controls the temperature at 65 °C by using two temperature sensors, one situated in the middle of the ore bed and one at the outside. Air was introduced into the bottom of the column. The air flow rate was controlled at 200 ml/min with a rotameter. This air was humidified by passing it through water to minimize evaporation. The PLS outlet was bent into a coil to create an air tight system. The feed solution was introduced into each column by a peristaltic pump, according to the specified irrigation protocol.

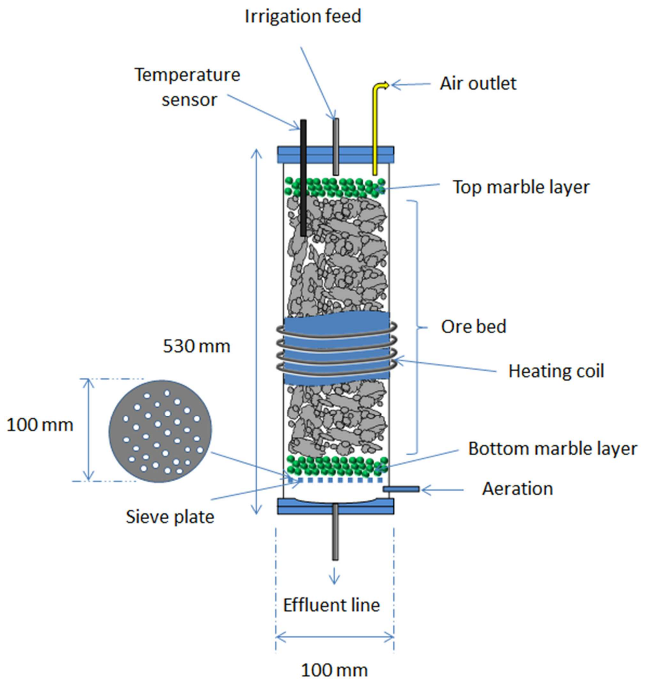

Figure 3-4: Schematic of heap leach column (adapted from van (Van Hille *et al*., 2010))

3.5 Experimental setup

Each column contained 4 kg of ore with a generic size distribution to create a representative ore body. These size ranges were -20 mm, -16 mm, -8 mm, -5.6 mm, -2 mm, -1 mm, -0.250 mm), except the coarse agglomerated where the fines (-2 mm) were removed. Three kinds of packing arrangements were used:

- Agglomerated packing: all size ranges
- Coarse packing (-20 +2 mm) where the fines were removed.
- Layered packing consisted of coarse ore (-20 +2 mm) layered between -2 mm fines.

Two different heap leaching experiments was done, which was bioleaching and abiotic leaching conditions using a range of irrigation methods. This allowed analysis of whether the irrigation pulses affected physiochemical conditions only or microbial conditions as well.

Two different types of irrigation methods were used, which was continuous and intermittent irrigation. These irrigation types were operated as follow:

- Continuous irrigation: (1 L/day)
- Intermittent irrigation 1: 2 days on I day off (1 L/day) – only experiment 2
- Intermittent irrigation 2: 1 day on 2 days off (1 L/day)
- Intermittent irrigation 3: 2 days on, 1 day off (1.5 L/day) – only experiment 2

Two different sets of experiments were conducted as shown in Sections 3.6 and 3.7. These experiments were operated at a constant temperature of 65 °C, pH 1.15 and aeration flow rate of 200 ml/min.

3.6 Experiment 1

In experiment 1 eight columns were operated for 107 days and setup to the configurations specified in Table 3.4. Here the columns were acid washed for 27 days. The intermittent irrigation was started immediately after the inoculation on day 27.

The data of experiment 1 is not discussed and could be seen as preliminary test work to eliminate the operational errors when experiment 2 was conducted. This data could not be compared to experiment 2 because:

- The pH meter was faulty thus a suspicion that the experiment was conducted above a pH of 1.15.
- The initial acid wash data for 30 days was not analysed for Fe and copper thus a full mass balance could not be conducted.
- The intermittent irrigation was started on the day the ore was inoculated, thus the microorganisms was not given enough time to attach to the ore.

Table 3-4: Layout experiment 1

Column	Irrigation Type	Intermittent type	Flow rate (L/day)	Volume 3 day cycle (L)	Packing	Leaching type
A	Continuous	n/a	1	3	Agglomerate All sizes (-20mm)	Acid
B	Intermittent	2 days on 1 day off	1	2	Agglomerate All sizes (-20mm)	Acid
C	Continuous	n/a	1	3	Agglomerate All sizes (-20mm)	Bio
D	Intermittent 1	2 days on 1 day off	1	2	Agglomerate All sizes (-20mm)	Bio
E	Continuous 1	n/a	1	3	Layered -20 + 2 mm layered between –2 mm fines	Bio
F	Intermittent 1	2 days on 1 day off	1	2	Layered -20 + 2 mm layered between –2 mm fines	Bio
E	Continuous 1	n/a	1	3	Agglomerate All sizes (-20 + 2 mm)	Bio
F	Intermittent 1	2 days off 1 day on	1	2	Agglomerate All sizes (-20 + 2 mm)	Bio

3.7 Experiment 2

In experiment 2, twelve columns were operated for 134 days and set up according to the configuration specified in Table 3-5. In this experiment, the acid wash was carried out for six days using the feed solution (including Fe and nutrients). The columns were inoculated on day six. The intermittent irrigation was started 14 days after inoculation to ensure that consistent microbial attachment took place across the columns.

Table 3-5: Layout experiment 2

Column	Irrigation Type	Intermittent type	Flow rate (L/day)	Volume 3 day cycle (L)	Packing	Leaching type
1	Continuous	n/a	1	3	Agglomerate All sizes (-20mm)	Acid
2	Continuous	n/a	1	3	Agglomerate All sizes (-20mm)	Bio
3	Continuous	n/a	1	3	Layered -20 + 2 mm layered between -2 mm fines	Bio
4	Intermittent 1	2 days on 1 day off	1	2	Agglomerate All sizes (-20mm)	Acid
5	Intermittent 1	2 days on 1 day off	1	2	Agglomerate All sizes (-20mm)	Bio
6	Intermittent 1	2 days on 1 day off	1	2	Layered -20 + 2 mm layered between -2 mm fines	Bio
7	Intermittent 2	1 day on 2 days off	1	1	Agglomerate All sizes (-20mm)	Acid
8	Intermittent 2	1 day on 2 days off	1	1	Agglomerate All sizes (-20mm)	Bio
9	Intermittent 2	1 day on 2 days off	1	1	Layered -20 + 2 mm layered between –-2 mm fines	Bio

Column	Irrigation Type	Intermittent type	Flow rate (L/day)	Volume 3 day cycle (L)	Packing	Leaching type
10	Intermittent 3	2 days on 1 day off	1.5	3	Agglomerate All sizes (-20mm)	Acid
11	Intermittent 3	2 days on 1 day off	1.5	3	Agglomerate All sizes (-20mm)	Bio
12	Intermittent 3	2 days on 1 day off	1.5	3	Layered -20 + 2 mm layered between -2 mm fines	Bio

3.8 Sampling and Analysis

Sampling was conducted every 3 days when the intermittent irrigation pumps were switched off. The following measurements were done on a continuous basis on the three day samples:

- PLS volume: This enabled quantification of the copper and Fe leached for mass balances and extraction efficiencies. It also provided verification of the constant feed rate.
- Feed rates were continuously monitored and logged to ensure constant feed rates.
- The pH was measured using a Metrohm 713 pH meter equipped with an AG 9101 Hersisau glass probe to ensure that the correct environment was maintained for efficient biooxidation (Section 3.8.1).
- Redox potential was measured with a Metrohm 704 meter equipped with a Pt.Ag/AgCl electrode. This provided an indication of microbial activity.
- Fe^{2+}, Fe^{3+} and total Fe analysis were determined via spectrophotometry using the phenanthroline method (Section 3.8.3) and also by Atomic Absorption assay (Section 3.8.5). It should be noted that the AAS for total Fe will only act as a check for the spectrophotometry total Fe analysis and will not be used in the discussions in Chapters 4 and 5.
- Cell counts were checked on a regular basis to determine the abundance of microorganisms in the PLS. Direct cell counting was done under a phase contrast microscope at 1000 fold magnification using a Thoma counting chamber (See section 3.8.7).

- Visual inspection on the colour of the PLS was regularly checked. This provided an indication of leaching activity and abiotic column contamination. The leachate from the bioleaching columns was typically orange/red because of the high ferric concentration, while that from the abiotic columns was clear.

The following measurements/tests were done on the leached ore:

- Samples of post leached collected ore were analysed for moisture content.
- The post leached ore was acid washed with a mixture of oxalic acid and phenanthroline to determine the amount of Fe and copper precipitated on the ore (See 3.8.4).
- Acid digestion was done to analyse the copper and total Fe on the pre and pre-leached ore (Section 3.8.6). This facilitates setting up the mass balances around the columns.
- Cell detachment was carried out as described in Section 3.8.7 to enable estimation of the abundance of attached microorganisms using microscopy and the microbial species present analysed using qPCR according to Tupikina *et al.* (2011).

3.8.1 pH

Sample pH measurements were taken by using a Metrohm 713 pH meter equipped with an AG 9101 Hersisau glass probe. The calibration of the pH was done every time a batch of samples was measured. This calibration was done with Metrohm 1 and 4 pH buffer solutions to ensure that the calibration was more than 95 %.

3.8.2 Redox potential

The redox potential was determined by using a Metrohm 704 meter equipped with a Pt.Ag/AgCl electrode. The electrode was tested on a daily basis by measuring a standard metro ohm redox solution of 48 mV at 25 ºC. The analytical error was found to be less than 1% against the standard.

The redox potential is related to the Fe^{3+}:Fe^{2+} ratio via the Nerst equation shown in Equation 8.

$$E = E_0 + \frac{RT}{zF}\ln\left(\frac{[Fe^{3+}]}{[Fe^{2+}]}\right) \tag{8}$$

Where: E = solution redox potential (V)

E_0 = standard potential of the reaction (V)

z = the number of electrons in the reaction

$[Fe^{2+}]$ = Ferrous concentration (M)

$[Fe^{3+}]$ = Ferric concentration (M)

3.8.3 Spectrophotometric Fe^{2+} and Fe^{tot} assays

The Fe^{2+} concentration in solution was measured spectrophotometrically using the colorimetric 1-10 phenanthroline method. This protocol was obtained from the CeBER database and was developed by Komadel and Stucki (1988).

A mixture of an ammonium acetate buffer solution and 1-10 phenanthroline indicator solution was added to a sample in a test tube and vortexed. The 1-10 phenanthroline indicator reacted with the Fe^{2+} ions present to form an orange colour complex ($(C_{12}H_8N_2)_3Fe^{2+}$) as per the following equation.

$$Fe^{2+} + 3\text{Phen} \rightarrow Fe(Phen)_3^{2+} \tag{9}$$

This orange colour indicates if any Fe^{2+} ions are present (the darker the orange colour the higher the Fe^{2+} concentration)

The absorbance was read at a wavelength of 510 nm with a spectrophotometer. The absorbance value is indicative of absorption by the complex and forms the basis of the quantitative determination of Fe^{2+}. The absorbance was converted to the Fe^{2+} concentration using a standard Fe^{2+} curve that was generated with standard solutions between 0 and 50 ppm. The standard curve and reagent preparation can be found in Appendix A.

After the Fe^{2+} reading was done, an excess of hydroxylamine was added to the same samples in the test tubes to convert all the Fe^{3+} present to the Fe^{2+} form accordingly to the following equation:

$$Fe^{3+} + 2NH_2\text{OH} \rightarrow Fe^{2+}N_2O + 4H^{+} + H_2O \tag{10}$$

After the Fe^{2+} conversion, the above spectrophotometric method was used; absorbance values were measured and compared to the Fe^{2+} standard curve.

Where the absorbance was found to be greater than 2, appropriate sample dilutions were made, because the correlation curve breaks if the absorbance is greater than 2 and the sensitivity of the assay is compromised. To ensure good reproducibility, samples were analysed in triplicate to an error of less than 2 %. The presence of copper in the sample can interfere with the phenanthroline Fe^{2+} assays above 150 mg/L; however the copper concentrations which was far below 10 g/L (Copper concentration) was low enough to ignore this effect (Govender *et al*., 2012).

3.8.4 Fe and copper precipitation determined by acid wash

The leached ore was acid washed to remove the precipitated Fe and copper to facilitate with the calculation of the mass balance and determine how much of the elements precipitated on the ore. This was done by adding 500 ml of a solubilisation mixture (hydroxylamine, 2 M oxalic acid in distilled water) as specified in Appendix A to 250 g of dry ore in an Erlenmeyer flask. The hydroxylamine was used to convert all the Fe ions to Fe^{2+} ions, while the oxalic acid only solubilises the precipitates without leaching the ore further. The flask was shaken in an incubator for 24 hours at $70^{O}C$ to solubilise the precipitated elements. The resultant solutions filtrated and analysed using spectrophotometric analysis (section 3.8.1) and AAS analysis (Section 3.8.1) and AAS analysis (Section 3.8.5). The remaining solid fraction was dried, weighed and processed through total acid digestion (Section 3.8.6) followed by AAS analysis by the Chemical Engineering Analytical laboratory. The detailed procedure is given in Appendix A.

3.8.5 Determination of Fe^{tot} and copper in solution by Atomic Absorbance analysis

The Fe^{tot} and copper concentrations in the PLS, the digestates and other solution samples were determined via Atomic absorption spectroscopy (Varian Spectra AA 10), in the Chemical Engineering Analytical Laboratory. This spectro-analytical procedure for the quantitative determination copper and Fe employs the absorption of optical radiation (light) by free atoms in the gaseous state. These analyses were mainly used to determine the amount of copper leached from the ore and also to validate the Fe analysis obtained spectrophotometrically.

3.8.6 Determination of Fe^{tot} and copper in ore by acid digestion

Acid digestion was done on the pre and post leached ore to transfer the analytes into solution so that they can be introduced into the determination step (AAS, see Section 3.8.5) of the copper and Fe concentrations in order to facilitate mass balances of copper and Fe. This was done in the Chemical Engineering Analytical Laboratory by heating the ore sample in a microwave pressure digestion system (CEM MARS Xpress MD 2147 microwave digestion system) with hydrochloric acid at 200 ^{O}C by applying microwave radiation.

3.8.7 Microbial concentration determination

Total cell counts were done on the PLS and detached samples using a Thoma Counting Chamber and the Olympus BX40 Microscope at x 1000 magnification using oil phase contrast optics. The detection limit of the direct counting method using this counting chamber is 3 X 10^5 cell/mL. Typically, the reproducibility indicated a 25% error. It is optimal to count between 30 and 300 cells per sample to reduce this error.

The cell concentration was determined by using the following equation:

$$Cell\ concentration\ \left[\frac{cells}{mL}\right] = \frac{cells\ counted}{\frac{Squares\ counted}{Total\ squares} \times volume\ of\ grid} \tag{11}$$

The cells were isolated from the post leach ore prior to the cell counting by using the detachment protocol developed in the Centre for Bioprocess Engineering Research at UCT (Govender *et al*., 2012). This protocol was developed to distinguish between interstitial, weakly attached and strongly attached cells. In this research it was only looked at interstitial and attached communities were considered.

The cell detachment took place in two stages. The first stage was to release the interstitial cells from the agglomerate by adding 250 g of post leached ore with 250 ml feed solution (in the absence of ferrous iron) in an Erlenmeyer flask and gently stirring. The solution was transferred to a JA centrifuge tube (the solids was not transferred) and centrifuged at 800 g. The clear supernatant solution with interstitial cells was weighed and labelled.

In the second stage to detach the ore-attached cells, ore from the interstitial detachment was mixed with a 250 ml of feed solution which contains 0.4 % Tween-20 and was vortexed. This solution was transferred to a JA-10 centrifuge tube, while the ore stayed behind in the Erlenmeyer flask. Again this solution was centrifuged at 800g and the clear supernatant was weighed and labelled. The second detachment was done 5 times and the solution phases pooled.

Microscopic cell counts were done on all the supernatant samples. These samples were also sent for DNA extraction and quantification using Nanodrop to quantify the organisms attached on the ore. This gave an indication of microbial abundance on heap bioleaching. It should be noted that all detachments were done with sterile equipment and solutions. A detailed protocol on detachment and solutions used are in Appendix A.

It should be noted that the PLS sample was used to monitor cell washout rates (which were negligible). The cell detachment was used to quantify the communities in heap bioleaching systems that were attached on the post leach ore.

3.9 Ore moisture content

The moisture content of the ore was determined by splitting the ore sample retrieved representatively and using 50 % of the leached ore for moisture determination. An empty bucket had been weighed and the mass was recorded. The mass of the wet ore and empty bucket was weighed and recorded. The mass of the wet ore was calculated as follows:

$$\text{Mass of wet ore} = \text{mass of wet ore and bucket} - \text{mass of bucket} \tag{12}$$

The wet ore was dried in an oven for 24 hours and the mass of the dry ore and bucket was recorded. The weight of the dry ore was calculated with the following equation:

$$\text{Mass of dry ore} = \text{mass of dry ore and bucket} - \text{mass of bucket} \tag{13}$$

The % moisture was calculated with the following equation:

$$\%\ \text{moisture} = \frac{\text{mass of wet ore} - \text{mass of dry ore}}{mass\ of\ wet\ ore} \times 100 \tag{14}$$

3.10 Liquid hold up

The liquid hold-up was determined by feeding each column at a specific time, where the initial feed time was recorded. The feed was stopped when the first dropped was seen leaving the column and the time was recorded. Once all the liquid was drained from the column after the feed was stopped, the total drained liquid was measured with a measuring cylinder. The feed volume was determined by measuring (Equation 15) and weighing (Equation 16) the remaining 1 L initially used:

$$\text{Feed volume} = \text{volume of initial feed} - \text{volume of feed left} \tag{15}$$

$$\text{Feed mass} = \text{mass of initial feed} - \text{mass feed left} \tag{16}$$

3.11 Labelling system

The labelling of the columns in the legends of Figures follows the convention detailed in Table 3-6. There are different line colours for different flow types and these are labelled in the graphs in the following order:

- Continuous flow = black (♦)
- Intermittent irrigation 2 days on 1 day off = red (■)
- Intermittent irrigation 1 day on 2 days off = green (▲)
- Intermittent irrigation 2 days on 1 day off (1.5 L/day) = purple (●)

The packing are labelled as follow;

- Agglomerated = G
- Layered = L

The leach type:

- Abiotic = A
- Biotic = B

Table 3-6: Labelling of legends in graphs:

■ Column 4 I1.0(2:1)AG						
■	**Column 4**	**I**	**1.0**	**2:1**	**A**	**G**
Graph	Column number	Irrigation type (Intermittent/ continuous)	Daily flow rate (L)	Irrigation frequency: days off:days on	Leach Type Abiotic/ Biotic	Packing: Agglomerated/ Layered/ coarse

CHAPTER 4 : RESULTS AND DISCUSSION (I)

EFFECT OF INTERMITTENT IRRIGATION ON HEAP LEACHING SYSTEMS

This chapter describes the results obtained on studying intermittent irrigation of the different types of packings (agglomerated with fines present, coarse agglomerated with – 2 mm fines removed and layered) in abiotic and biotic systems. The leach performance was monitored through pH, Fe^{2+}, $Fe^{3+}$and total Fe concentrations and the copper concentration in the pregnant leach solutions (PLS) over a period of 3 months. Different types of intermittent irrigation are compared against continuous irrigation for each packing system with respect to leach performance. It should be noted that the AAS for total Fe will only act as a check for the spectrophotometry total Fe analysis and will not be used in the discussions in this chapter.

4.1 Abiotic heap leaching performance using agglomerated packing

This set of columns was packed with agglomerated ore and irrigated with a basal salt media at a feed pH of 1.15. The operating conditions (feed media, aeration, temperature, flow rates and intermittent frequencies) were similar to that of agglomerated biotic and layered biotic columns, with the exception of no inoculation. This was done to create a control to effectively compare the effects of intermittent irrigation on acid heap leaching systems to that of bio heap leaching systems (Sections 4.2 and 4.3).

4.1.1 pH of PLS

The initial high pH of the PLS in relation to the feed pH of 1.15 was a result of acid consuming reactions predominating, such as the dissolution of copper oxides and gangue minerals which are easily leached by sulfuric acid (Ahmadia *et al*., 2012). The drop in the net acid consumption during the first 60 days can be related to the decrease in the acid consumption reactions and the oxidation reactions which consume protons. After day 60, a constant pH of 1.2 to 1.3 was observed for the remainder of the experiment and may indicate the stabilisation of the leaching system and the depletion of the easy leachable mineral. The constant difference between feed and PLS pH in this later stage suggests a constant rate of dissolution of acid consuming minerals, typical of slow dissolution rates controlled by surface area. The easily leachable minerals can be described as ”the sulfide and oxide grains on the external surfaces of the ore particles that would be exposed to a higher concentration of reagents than those buried deep down within ore pellets would leach faster” (Bouffard & Dixon, 2001). This indicated that after the system reached steady state, the pH was governed by the amount of acid fed into the system and availability of the minerals exposed for leaching.

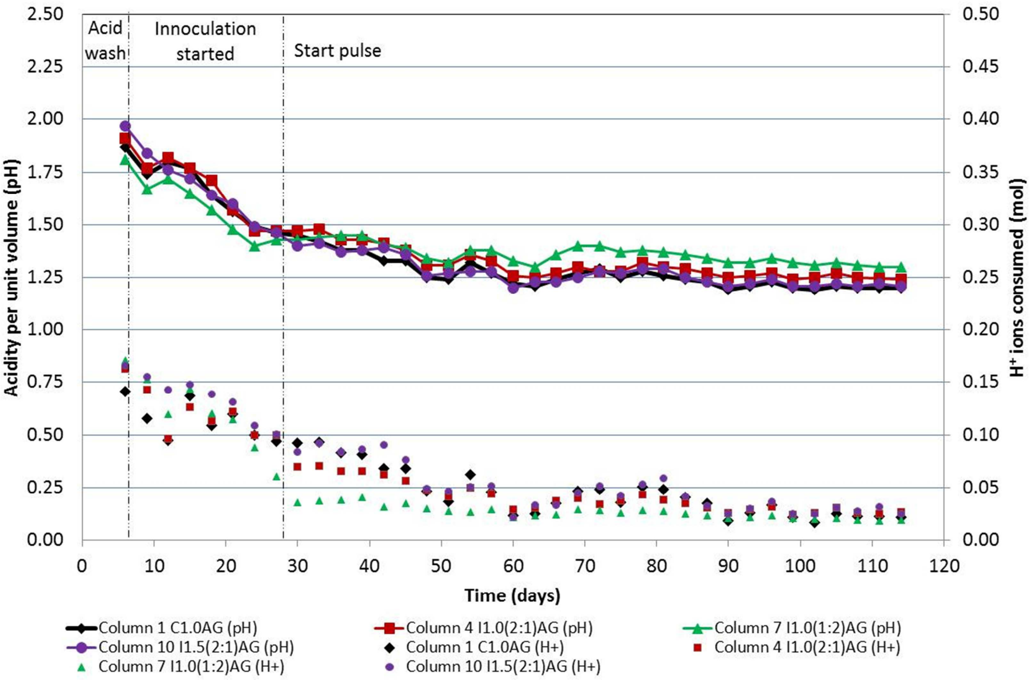

Figure 4-1: pH of PLS and net hydrogen ion consumption of ore agglomerated abiotic Columns 1, 4, 7 and 10

During the 1st 27 days abiotic columns 1, 4 and 10 operated similarly, but the inherent variation was noticeable for column 7, which had a low PLS pH. This suggested that after day 27 the pH of the PLS of Column 7 was higher than abiotic columns (1, 4 and 11).

In Figure 4-1 it seen that continuous Column 1 (1 L/day) had the same pH and acid consumption as intermittent Column 10 (2 days on, 1 day off; 1.5 L/day) in which a higher intermittent feed rate was applied such that the same overall volume was added to the system as in the continuous system. It was clear that the same amount of protons was consumed, hence the similar pH profiles. This was a clear indication that the mineral’s leach rate was not affected by applying intermittent irrigation at higher flow rates. The fact that the acid consumption (not acid consumption per unit volume) was the same for Columns 1, 4 (lower feed volume) and 10 indicated that the maximum acid consumption rate was achieved even when lower amounts of reagents were added. This indicated that the physical amount of acid (hydrogen ions) added to the system governs the pH of these columns and not the acid consuming reactions, due to the slow dissolution kinetics of chalcopyrite.

The daily pH for continuous Column 1 and intermittent Column 4 (2 days on; 1 day off) decreased at the same rate during the initial 63 day period. Intermittent irrigation (Column 4) displayed a higher acid consumption per unit volume than continuous irrigation (Column 1). The same amount of protons was consumed and thus a lower hydrogen ion concentration was left in the lower volume (Column 4) because less hydrogen ions were fed, hence the higher pH profile.

Applying the inherent variability as discussed above, to Column 7 it may be argued that decreasing the intermittent frequency from 1 day in Column 4 to 2 days in Column 7 increased the acid consumption per unit volume throughout the experiment. As expected decreasing the frequency of intermittent irrigation resulted in a higher acid consumption per unit volume for the lower leach volume added. However, the data indicated that the amount of reactants available to the system with the lower feed volume might be the rate limiting factor. This rate limiting factor cannot be confirmed because the bulk volumes (3 days) showed the same pH. It is hypothesised that the pH at the surface where the reactions happened may be much higher. As discussed above (Column 1 vs. 4), different amounts of hydrogen ions were introduced into the two systems, but the same amount of hydrogen ions was consumed and concentration of hydrogen ions left in Column 7 was lower than that of Column 4, thus the pH of Column 7 PLS was higher.

The daily pH of Column 4 (1 L/day) was higher than the pH of Column 10 (1.5 L/day), which had the same intermittent irrigation frequency (2 days on, 1 day off). As discussed above, the same amount of protons was consumed in both systems, but a higher amount of actual hydrogen ions was left in Column 10, hence the lower pH profile and subsequent lower acid consumption per unit volume. This indicated that intermittent irrigation at higher feed rates resulted in a lower acid consumption per unit volume, thus the amount of hydrogen ions added to this system was not rate limiting.

After day 60 when the easily leachable mineral was depleted, the rate of acid consumption was constant for all columns, irrespective of irrigation type or flow rate. This indicated that applying intermittent irrigation did not increase the acid consumption per unit volume, but had a similar actual acid consumption (total amount of hydrogen ions consumed). This could also be argued for all other columns (1, 4, 7 and 10) and it is apparent that acid consumption reactions continued to take place even in the resting periods when intermittent irrigation was applied. It can be concluded that when system steady state was achieved the irrigation type did not influence the acid consumption where the rate limiting step was the availability of the sulfide mineral on the surface of the ore i.e. when the reactants were in excess.

4.1.2 Redox potential

The redox potential of the feed solution containing 500 mg/L Fe^{2+} was 380 mV. The redox potential for all abiotic columns increased from 380 to 400 mV during the first 21 days of the experiment prior to intermittent flow and remained constant for the remainder of the experiment as shown in Figure 4-2. This low redox potential change is confined by the low Fe^{3+}/Fe^{2+} ratio, which was caused by the slow kinetics of chemical oxidation of Fe^{2+} to Fe^{3+} (Figure 4-3). This low redox potential is constant with the lack of microorganisms that constantly convert the Fe^{2+} to Fe^{3+} to provide their metabolic energy. Regular checks of the PLS under the microscope did not show any signs of microorganisms present, confirming that microbial Fe^{2+} oxidation is unlikely. The slight increase in redox potential may have been caused by microbial contamination, which was immediately treated with biocide to eliminate any microbial activity.

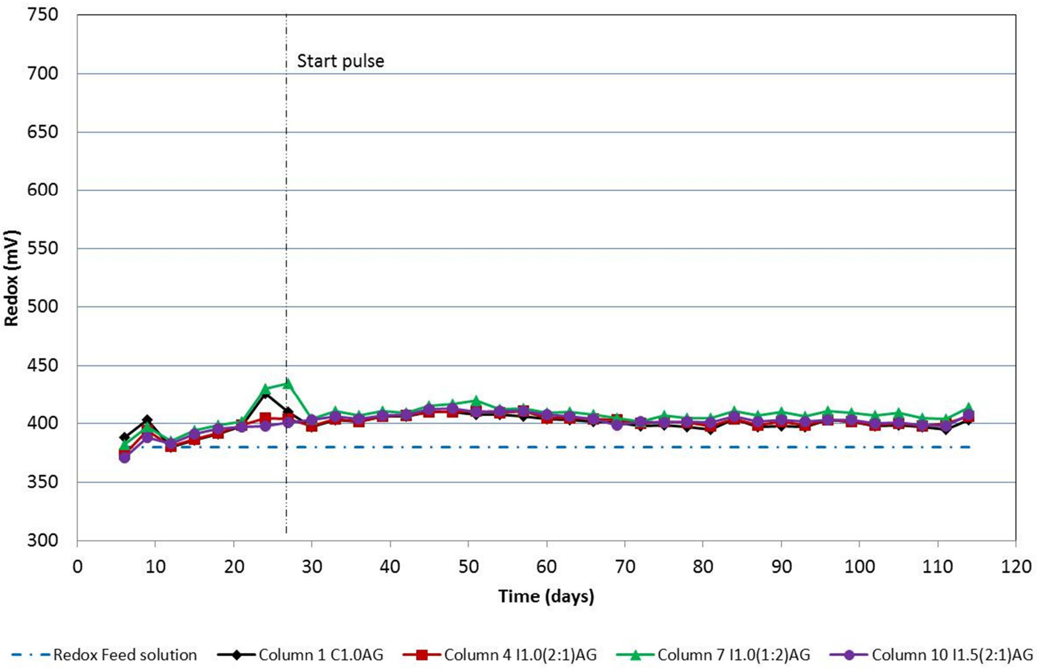

Figure 4-2: Redox of PLS for agglomerated abiotic Columns 1, 4, 7 and 10

4.1.3 Fe^{2+}, Fe^{3+} and total Fe concentration in PLS

A constant Fe^{3+} concentration of 100 mg/L (Figure 4-3) was observed in all abiotic columns after 30 days until the completion of the experiment. This low Fe^{3+} concentration is due the absence of microorganisms to regenerate the Fe^{3+}. The kinetics of chemical Fe^{3+} generation is normally slow even at 65 ºC. The very low pH also affects this. The low ferric concentration led to an incomplete mineral attack. The slow initial generation of Fe^{3+} corresponded to the lag in the redox system. The Fe^{3+} generated in this abiotic column was an indication of the chemical (abiotic) oxidation of Fe^{2+} and was confirmed by the increase in the redox potential of the PLS from 380 mV to 400 mV. According to Searby *et al*. (2006), abiotic oxidation to Fe^{3+} is significant at high temperatures but remains at a much reduced rate compared with the bioleach system. These similar Fe^{3+} concentrations indicated that the Fe^{3+} produced was proportional to the amount of reactants fed into the system. It can be concluded that the application of intermittent irrigation yielded approximately the same amount of Fe^{3+} per unit volume flow through the system. No jarosite formation was visually observed. The total Fe mass balance indicated that less than 2% of Fe added to the system precipitated on the ore.

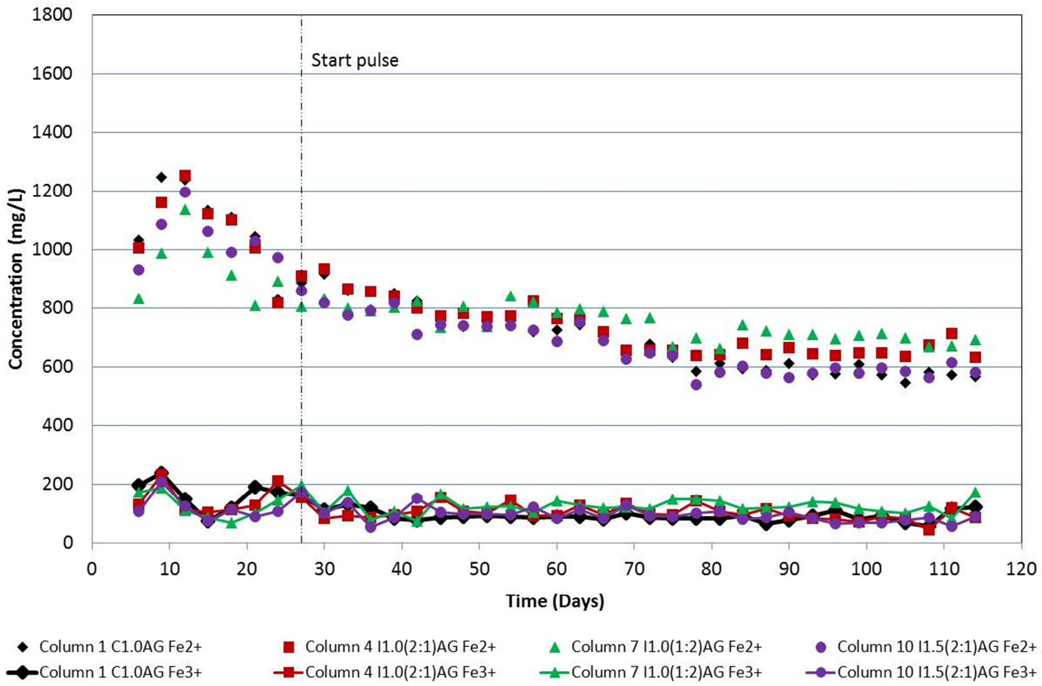

Figure 4-3: Fe^{2+} and Fe^{3+} concentration in PLS for agglomerated abiotic Columns 1, 4, 7 and 10

The total Fe concentration in solution is the sum of the Fe^{2+} and Fe^{3+} concentrations. The Fe^{2+} contributed dominantly to the total Fe concentration in this system. The discussion of the Fe^{2+} accumulated in the PLS can be related to the total Fe leached.

A peak of 1000 to 1200 mg/L Fe^{2+} concentrations (Figure 4-3) was found in all abiotic columns. This release of Fe in solution corresponds with the initial high acid consumption (Figure 4-1). The significant increase in Fe^{tot} concentration detected above the initial 500 mg/L Fe^{2+} in the feed solution (Figure 4-4), indicated that chemical leaching of the Fe containing minerals in the low grade ore took place over the duration of the leaching experiment. Between days 27 and day 69, a steady decrease occurred from 1000 to 650 mg/L in the Fe^{2+} concentrations and from 1200 – 1500 to 650 – 800 mg/L in total Fe concentration. This decrease was caused by the depletion of the easy leachable iron containing mineral with time, leading to slower leach rates. This was followed by a constant Fe^{2+} and total Fe concentration.

During the 1st 27 days, abiotic Columns 1, 4 and 10 produced similar Fe^{2+} concentration trends, but the inherent variation was noticeable for Column 7 that produced a lower Fe^{2+} concentration. Taking this variance into account it may be argued that Column 7 demonstrated a substantially higher Fe^{2+} concentration during intermittent irrigation than Columns 1, 4 and 10 throughout the experiment.

The fact that Columns 1, 4 and 10 produced a PLS with similar Fe^{2+} concentrations at the same Fe^{2+} leaching rate in the first 75 days, was an indication that the Fe^{2+} dissolution rate from the sulfide mineral was dependent on the amount of reactants introduced into the system. It can be safely concluded that Fe^{2+} dissolution in abiotic leaching columns during the “easy leachable mineral period” was influenced by intermittent irrigation or flow rates and the amount of leach reagents added to the system. It should be noted that the application of intermittent irrigation extracted the same amounts of Fe^{2+} per unit volume and was proportional to the amount of reactants (volumes) added to the system.

After the Fe^{2+} dissolution stabilised on day 75, the Fe^{2+} concentrations were higher for Columns 4 (1 L) and 7 (2 L) than in Columns 1 (3 L) and 10 (3 L), corresponding to different “three day feed volumes” and irrigation systems. The Fe extraction per unit volume was not proportional to the amount of reactants fed to the system across these columns. It can be concluded that intermittent irrigation increased Fe^{2+} dissolution in abiotic leaching columns per unit volume of feed during the steady state process of abiotic leaching, when provision of the reactants was the rate limiting step.

It should be noted that the precipitation has been regarded as negligible in the abiotic columns since an average of only 3 % of the available Fe was released during the oxalic acid wash method for Columns 1, 4 and 10, as shown in Table 4-1. However, in Column 7 the precipitation accounted for 7 % of the total iron available. Figure 4-3 show that the Fe^{3+} concentration for Column 7 was higher than that of Columns 1, 4 and 10. The low Fe precipitation found in abiotic systems was attributed to a large amount of the total Fe existing as Fe^{2+}, as seen in Figure 4-3, whereas precipitation or jarosite formation normally occurs owing to a high Fe^{3+} concentration.

Table 4-1: Total Fe Mass balance across the agglomerated abiotic leaching columns:

Column	**Fe in feed (g)**	**Fe in Pre leached ore (g)**	**Fe in post leached ore (g)**	**Fe in PLS (g)**	**Fe precipitated (g)**	**% Fe precipitated of total dissolved Fe in system**
1	50	105	69	85	2	2
4	39	105	73	69	2	3
7	27	105	81	48	3	7
10	54	105	69	88	2	2

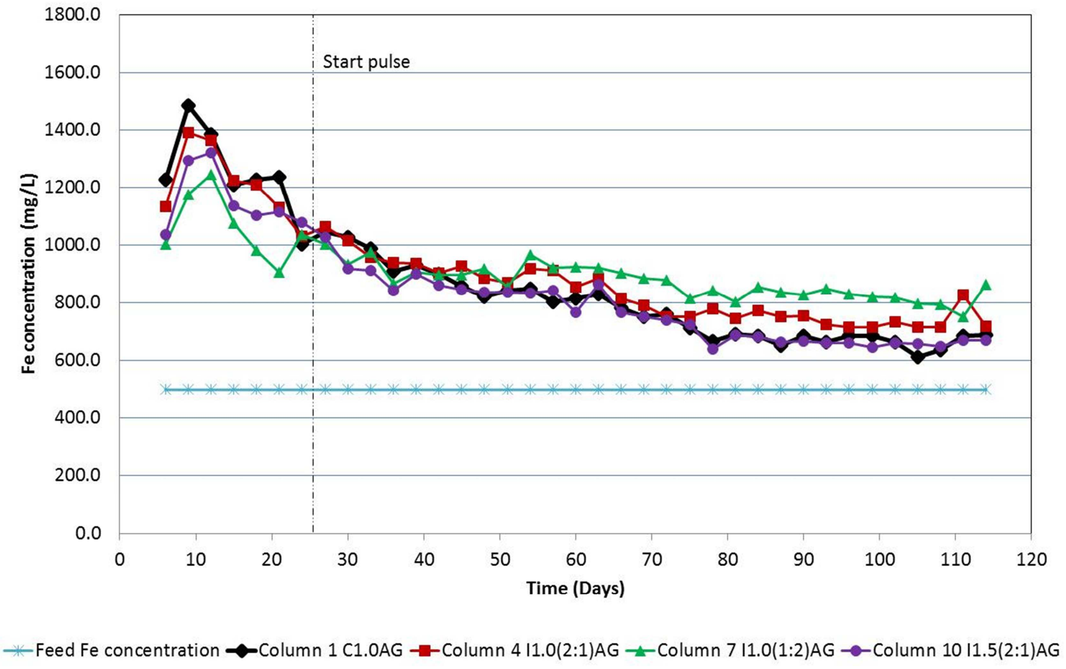

Figure 4-4: Total Fe concentration of PLS from agglomerated abiotic Columns 1, 4, 7 and 10

The performance of abiotic leaching is considered in terms of cumulative Fe extraction in Figure 4-5. The Fe recoveries for Columns 1, 4, 7 and 10 showed the extent of extraction at 35 %, 30 %, 22 % and 35 % respectively over 114 days.

The cumulative extraction of total Fe in the ore may also be considered on a basis of the volume of irrigant, as shown in Figure 4-6. The highest irrigation volume processed over 114 days was 105 L for Column 10, using intermittent irrigation at a high flow rate (1.5 L/day). Here a 34 % extraction was attained in 114 days, producing a similar Fe extraction of 34 % using a similar volume as continuous irrigated Column 1 (99 L). Intermittent Column 4 produced a Fe extraction of 30 % using reduced volume of 76 L higher than continuous Column 1 (99 L). Intermittent Column 7 produced a Fe extraction of 22 % using only 51 L.

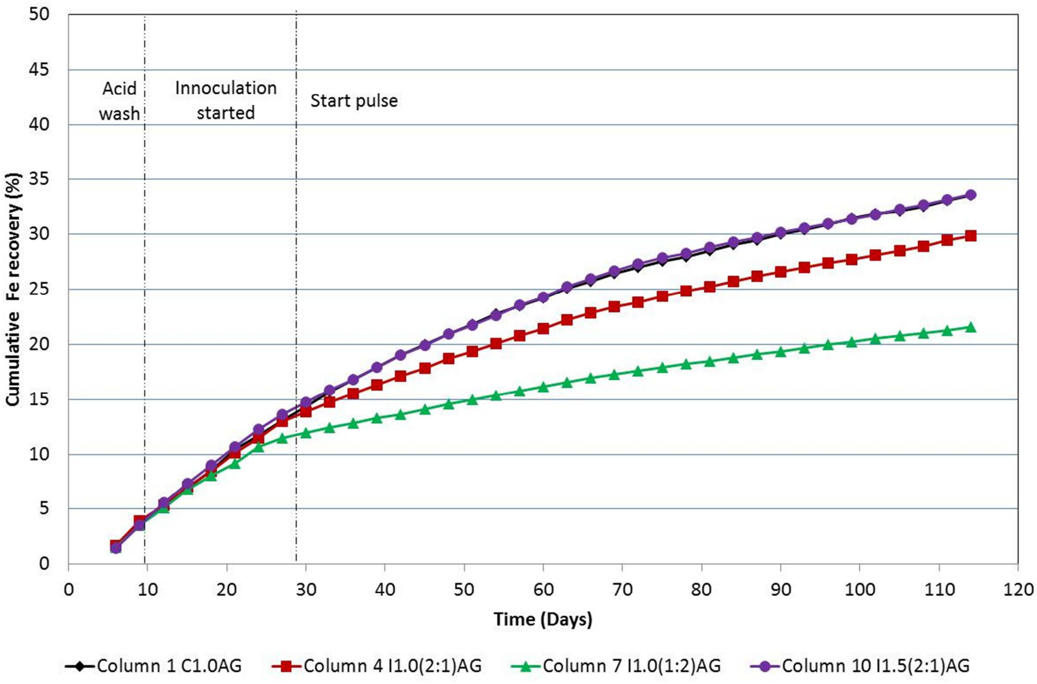

Figure 4-5: Cumulative total Fe extraction from ore (adjusted) of Abiotic Columns 1, 4, 7 and 10

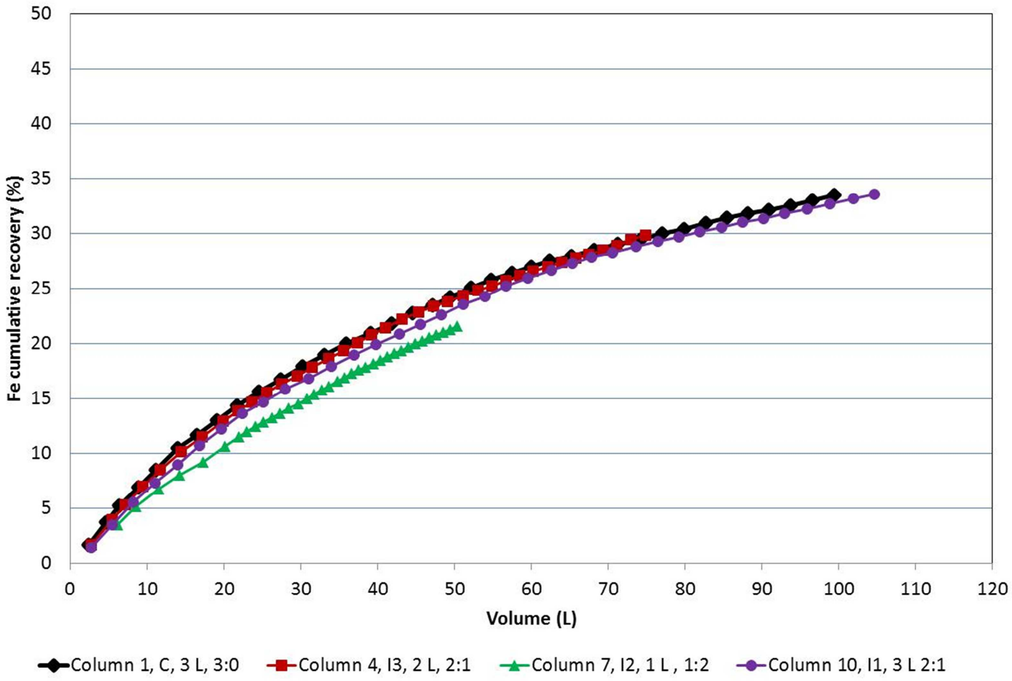

Figure 4-6: Cumulative Fe extraction (adjusted) vs. volume agglomerated abiotic Columns 1, 4, 7 and 10

4.1.4 Copper in PLS

Under uniform continuous leaching conditions imposed till day 27, the average copper concentration in the PLS was constant as shown in Figure 4-7. Thereafter, the PLS from Columns 4, 7 and 10 increased gradually to above 60 mg/L (average 75 mg/L) by day 63. Column 1 showed a lower increase to 50 mg/L, which indicated that the performance of Column 1 (per unit volume) was notably lower than the other abiotic leaching columns between days 27 and 63. After day 63, the release of copper decreased in all columns, plateauing from day 75 at the following concentrations: Column 1 at 30 mg/L, Column 4 at 45 mg/L, Column 7, 58 mg/L and Column 10 at 30 mg/L.

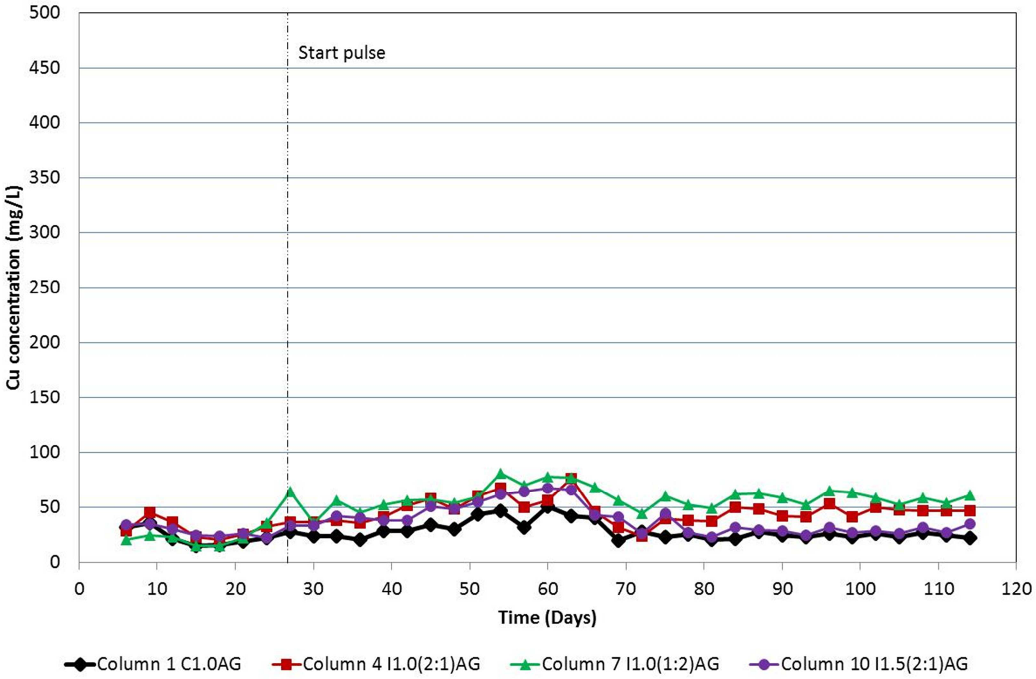

Figure 4-7: Copper concentration of PLS agglomerated abiotic Columns 1, 4, 7 and 10

Using the volume of PLS, the daily copper mass leached into the PLS was quantified in Figure 4-8. This shows a reversal in the trends because of the application of the different irrigation types and volumes: Column 1 (continuous, 1 L/day), Column 4 (2 days on, 1 day off; 1 L/day), Column 7 (1 day on, 2 days off; 1 L/day) and Column 10 (2 days on, 1 day off; 1.5 L/day). The copper recovered for Column 7 remained constant throughout the experiment at average of 0.07 g/day. Also Column 7 had the lowest leaching performance throughout the experiment compared to Columns 1, 4 and 10. Notably Column 10 showed an increase in the copper recovered, while Columns 1 and 4 showed similar leaching rates until day 63, which were lower than Column 10. After day 63 a general decrease occurred to below 0.08 g/day and Column 7 showed a lower leaching rate of 0.05 g/day.

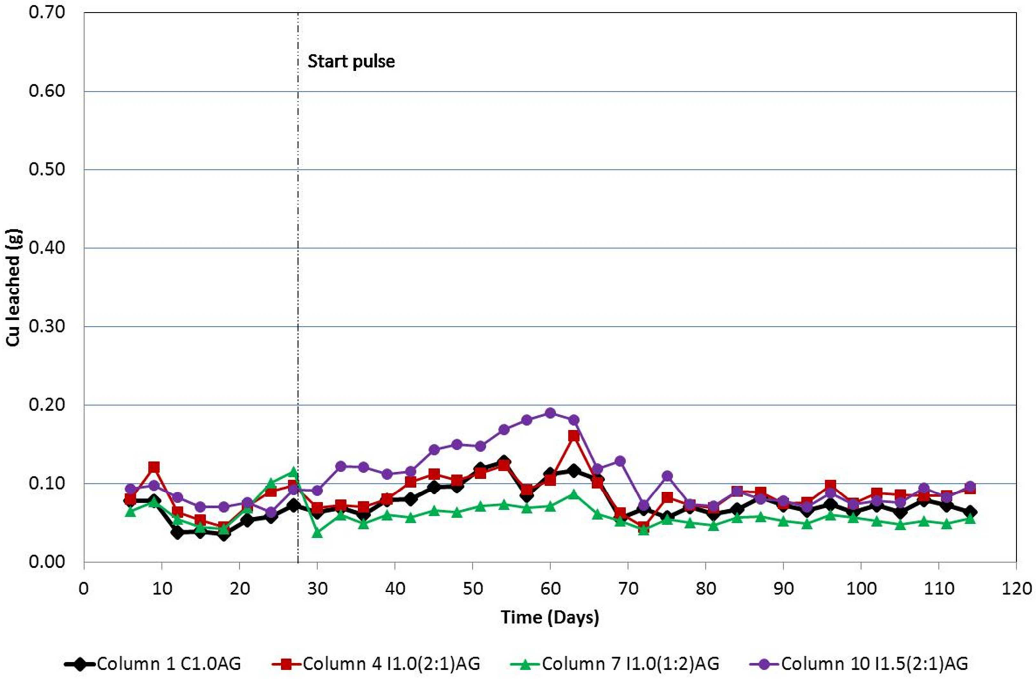

Figure 4-8: Copper extracted in PLS agglomerated abiotic Columns 1, 4, 7 and 10

The performance of abiotic leaching is considered in terms of cumulative copper extraction in Figure 4-9. The copper recoveries for Columns 1, 4, 7 and 10 showed extent of extraction at 12 %, 14 %, 10 % and 16 % respectively over 114 days.

The cumulative extraction of total copper in the ore may also be considered on a basis of the volume of irrigant, as shown in Figure 4-10. The highest irrigation volume processed over 114 days was 105 L for Column 10, using intermittent irrigation at a high flow rate (1.5 L/day). Here a 16 % extraction was attained in 114 days, exceeding the 12% extraction using a similar volume as continuous irrigated Column 1 (99 L). Intermittent Column 4 produced a copper extraction of 14 % using reduced volume of 76 L higher than continuous Column 1 (99 L). Intermittent Column 7 produced a copper extraction of 10 % using only 51 L.

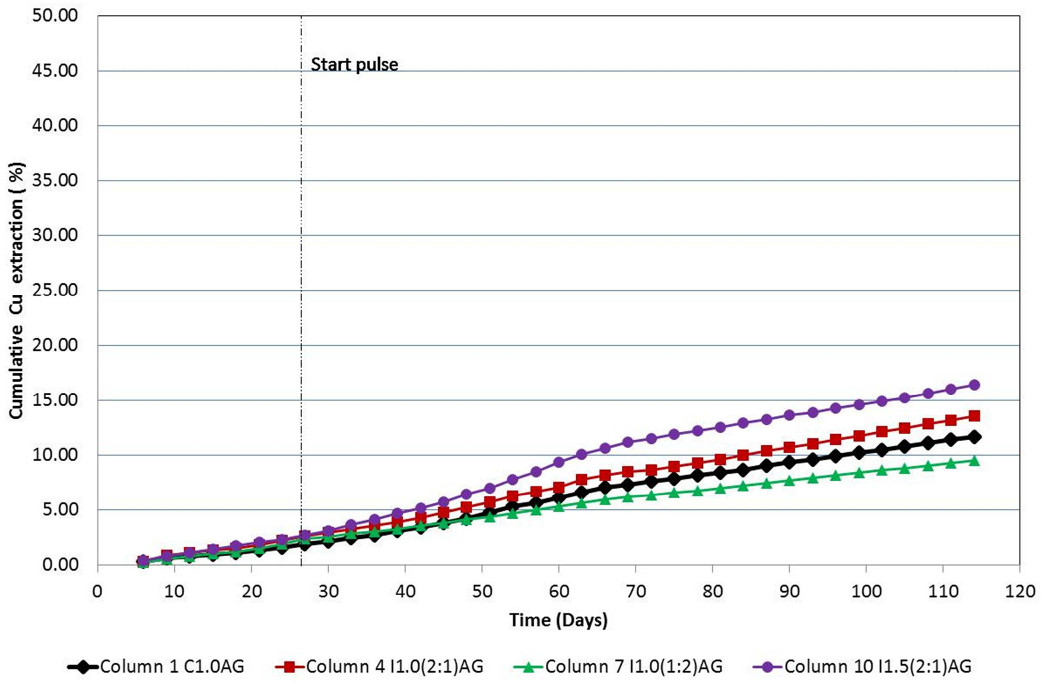

Figure 4-9: Cumulative copper extraction for agglomerated abiotic Columns 1, 4, 7 and 10

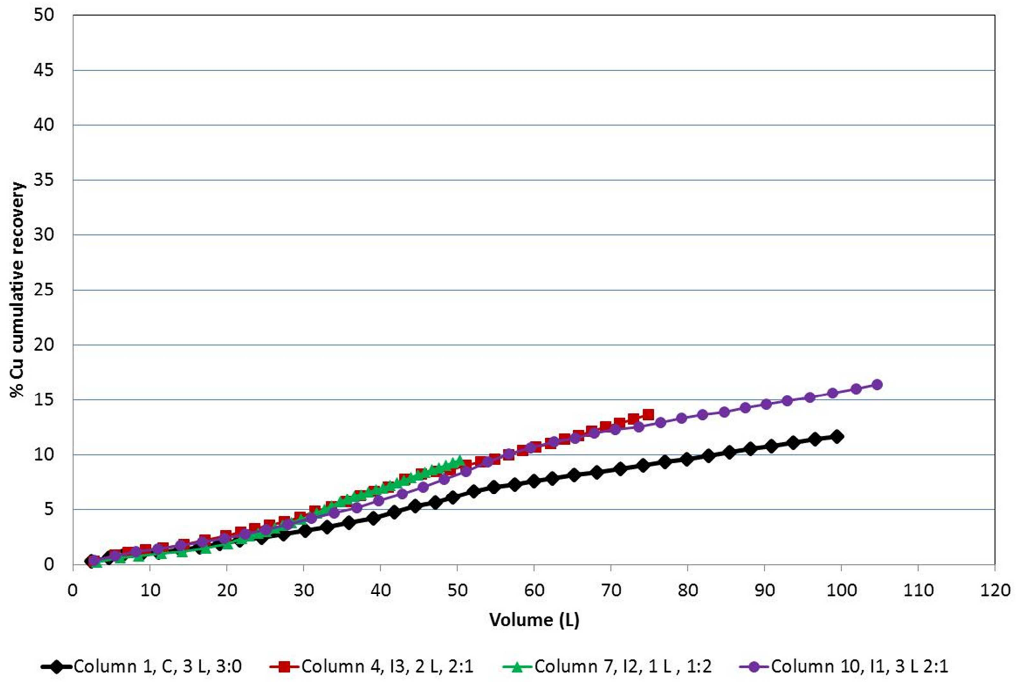

Figure 4-10: Cumulative copper extraction vs. volume agglomerated abiotic Columns 1, 4, 7 and 10

A general increase in daily copper extracted (Figure 4-8) during days 27 and 66 could be observed in the abiotic leaching Columns 1, 4, 7 and 10, which also indicated a general increase in the copper leaching rate. After day 63 a drop in daily copper extraction and subsequent constant copper extractions during the remainder of the experiment, indicated a constant copper leaching rate and was caused by the depletion of the easy leachable sulfide mineral. It should be noted that the dissolution kinetics of chalcopyrite normally decline with time in acidic sulfate media from the passivation of the mineral surface by elemental sulfur (Güler *et al*., 2012).

A general observation in the daily copper extractions during this 69 day period indicated that, as the copper was leached, the acid consumption and total Fe extraction (Figure 4-4) decreased with time. Although there was a general relationship during the 69 day period, no distinct relationships between the leaching of copper, Fe and acid consumption was seen in some columns during this period. This may be due to the leaching of Fe^{2+} and consumption of acid by sources other than chalcopyrite or the pH of the columns might be influenced by the passivation layer (Güler *et al*., 2012) . After the 69 day period as the column reached a steady leaching rate, all easy leachable minerals were depleted. It could be observed that there was a clear relationship between the pH profile, Fe extraction, copper extraction and reagents fed to the column per unit volume.

During the period from day 27 to 69 mentioned above, the daily copper extractions for continuous Column 1 (L/day) and intermittent Column 4 (1L/ day, 2 days on 1 day off) increased at similar copper extraction rates. It was clear that applying intermittent irrigation at the same flow rate (1 L/day) yielded the same amount of copper as continuous irrigation (Figure 4-8), thus leaching more copper per unit volume (Figure 4-7). This is in correlation with the similar amount of acid or hydrogen ions consumed (Figure 4-1) in Column 1 and 4 for the duration of the experiment irrespective of the amounts of reactants fed into the system. This similar copper extraction rate may be attributed to the fact that copper leaching continued during the resting period and the concentrated stagnant solution on the mineral surfaces was flushed out as soon as the irrigation was started (van Staden, 2007; Pradhan *et al*., 2008). It should be noted that Pradhan, *et al.* (2008) postulated this theoretically and van Staden *et al.* (2008) referred to this in unpublished work that was done previously. It may be concluded that applying low intermittent frequency irrigation at the same flow rate had the same extraction rate and that the lower addition of reactants did not have a rate limiting effect during the most active part of the heap leach, because leaching still took place during the stagnant period of the column.

From Figure 4-8, the increased daily copper extraction for column 10 was only noticeable between days 27 and 69. After day 69, the copper extraction was very similar for all the columns. The daily copper extractions for Columns 4 and 10 with an intermittent irrigation of 2 days on and 1 day off indicated that increasing the flow rate from 1 to 1.5 L/day caused an increase in the daily copper extraction and a higher leach rate in Column 10. Similarly it should be mentioned that continuous Column 1, which has the same daily copper extraction as Column 4, had a lower copper extraction than Column 10. This higher copper extraction was not in line with the amounts of acid consumed or the same extraction achieved for these 3 columns after day 69. Using the modelling approach Ogbonna *et al.* (2006) predicted that increasing the flow rate can lead to higher copper extrations in abiotic leaching particular, because of the higher supply of reactants in a shorter period of time. It should also be noted that Fe and hydrogen may get involved in the in the cyclic reactions and these may be different with more time in the stagnant phase. Also the high copper extraction may be attributed to the higher liquid velocity that may enhance the transfer of solutes from the interstitial liquid surrounding the ore (Chiume *et al*., 2012). These supported the observation that increasing the flow rate in intermittent irrigation can increase the leaching rate when the easy leachable mineral is available (most active part of the leaching process).

Comparing the total copper extractions (Figure 4-9) over 114 days, Column 10 showed the highest copper extraction. Notably Column 1 showed a total extraction lower than that of Column 4, but higher than that of Column 7. This indicated that applying intermittent irrigation at high flow rates increased the total copper % extraction in the abiotic system during the most active period (27 to 69 days) in the leaching experiment when the accessibility and slow dissolution rate of the available sulfide mineral was not a rate limiting factor. The lower copper extraction of Column 4 (vs. Column 10) indicated that applying intermittent irrigation at low flow rates and the same frequency may not provide enough reactants to increase copper extractions. The fact that the extractions of Columns 4 and 10 were both higher than that of Column 1 indicated that resting periods increased resultant extraction. As indicated earlier, during resting periods the leaching still takes place and a longer contacting time between the ore and the reactants occurs. Once the irrigation resumed, the concentrated solution in the interstitial regimes of the column is exchanged with fresh solution. Lower copper extractions of Column 4 suggested that the reactant supply was rate limiting in the abiotic Cu leaching. After day 69 the leaching rates of all columns was the same. This indicated that once the availability of the mineral is rate limiting, the leaching rates were influenced by the amounts of reactants added into the system. This also confirmed that the feed volume together with irrigation frequency played an important role in abiotic leaching.

Looking at the cumulative Cu extraction (Figure 4-10) on a volumetric basis across 114 days indicated that by increasing the feed volumes of intermittent irrigation (column 10) to such an extent that it equates the feed volumes of the continuous irrigation over the intermitted irrigation period, showed a higher copper extraction for Column 10 (16 %) than Column 1 (12 %). This indicated the benefits in an increase in extraction by applying intermittent irrigation at high flow rates when the reactant availability is rate limiting. Similarly the higher copper extraction in Column 10 compared with Column 4 (14 %) in 114 days, indicated that an increase in flow rate increased the copper extraction. By applying only 50 % of the leaching liquid across the 114 days, Column 7 (10 %), had a lower copper extraction than Columns 1 (12%), 4 (14 %) and 10 (16 %). This indicated that the amount of reactants was the rate limiting effect for Column 7, but its total extraction was higher per unit volume of reactants fed. This highlights the importance of reactions taking place during the stagnant phase.

The cumulative extraction of total copper on a basis of total volume of irrigant solution as shown in Figure 4-10 is compared using only 50 L of feed by taking Column 7 as the basis, due to the low total PLS volume. It showed that similar amounts of copper were extracted across the intermittent Columns 4 (9 % in 75 days), 7 (9 % in 114 days) and 10 (9 % in 57 days). However continuous Column 1 (6 % in 60 days) had the lowest copper extraction. This indicated that all intermittent irrigations gave better extractions per unit volume, correctly with equivalent delivery of reactants. This suggested the benefits of resting periods and no reactant limitation if the operation would be considered a volumetric feed basis. It took Column 10 only 57 days to achieve a 9 % extraction which indicates the benefit of higher flow rates and intermittent irrigation for an increased extraction rate of copper in abiotic systems. This was also confirmed that in 114 days Column 10 had the highest copper extraction by applying intermittent irrigation (vs. Column 1) and by increasing the flow rate (vs. Column 4).

4.2 Heap bioleaching performance using agglomerated packing

This set of columns was packed with agglomerated low grade ore and irrigated with a basal salt media containing nutrients at a feed pH of 1.15 in the same manner used for abiotic study reported in Section 4.1.1. However these columns were inoculated with mixed microbial culture (Section 3.2) on day 6. As previously, they were continuously irrigated until day 27 at which different irrigation regimes were introduced. Hence these biotic agglomerated columns were used to simulate the effects of heap bioleaching.

4.2.1 pH of PLS

In all the biotic agglomerated columns, the pH of the PLS decreased from an average of 2.0 to an average pH of 1.2 during the first 60 days of leaching (Figure 4-11). After this time, the pH remained constant for the remainder of the experiment. However, the pH of intermittent Column 8 (2 days on, 1 day off) showed a slight increase after day 33 to a pH of 1.45, where it remained consistently higher than the pH's of the other columns. The net hydrogen ion consumption had a similar decreasing trend until day 60 and remained constant until day 114. The drop in acid consumption in Columns 2, 5 and 11 (Figure 4-11) may be a result of the depletion of the easily leachable mineral or of the acid consuming gangue material. The stabilisation of acid consumption occurred after day 60, so it can be argued that steady a rate of acid consumption in bioleaching had been achieved. However the net hydrogen consumption of Column 8 dropped until day 30 and remained constant until day 114. This suggested that the low liquid flow rate constrained the acid consumption.

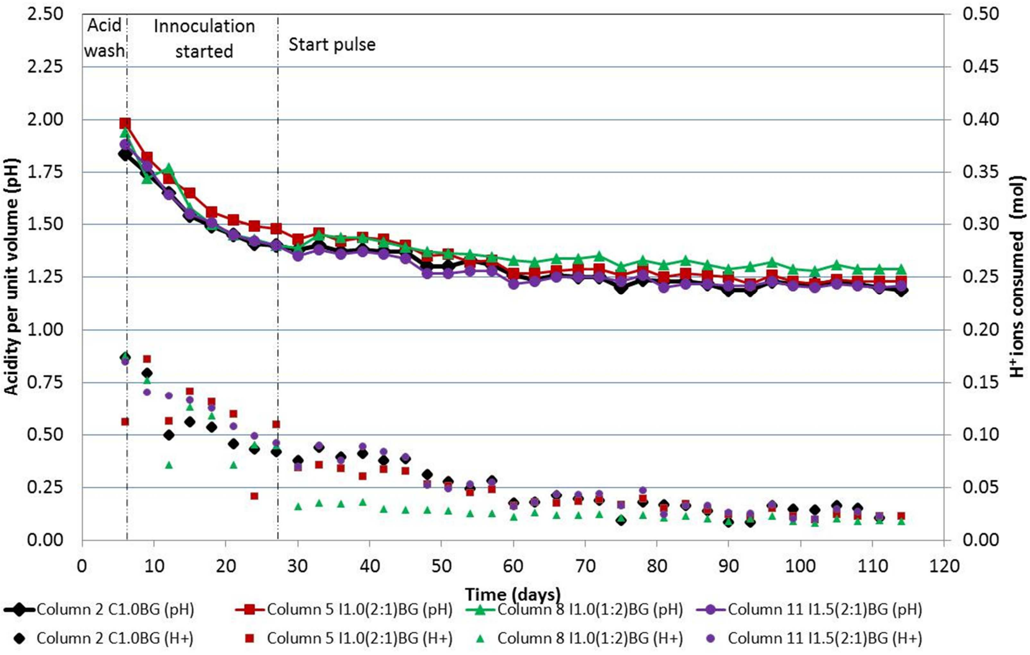

Figure 4-11: pH of PLS and net hydrogen ion consumption (actual not per unit volume) agglomerated bioleaching Columns 2, 5, 8 and 11

During the 1st 27 days biotic columns 2, 8 and 11 operated similarly, but the inherent variation was noticeable for column 5, which produced a higher pH. This suggested that after day 27 the pH of the PLS of Column 7 was lower than biotic columns 2, 8 and 11.

As the acid consumption dropped, similar amounts of acid were consumed by Columns 2, 5 and 11 from day 27 for the remainder of the experiment. The acid consumption for continuous Column 2 (1 L/day) and intermittent Column 11 (1.5 L/day) were the same per unit volume, because similar amounts of reactant (3L) were added over a 3-day period. It was clear that applying intermittent irrigation at higher feed rates did not affect the acid consumption. The higher acid consumption per unit volume and similar net hydrogen ion consumption of Column 5 indicated that adding lesser reactants did not influence the net hydrogen ion consumption of the system. This increase in pH was caused by the lesser remaining hydrogen ions in the PLS of Column 5.

Taking the inherent variability of the pH performance of column 5 into account, the pH of the PLS of Column 8 (1 day on, 2 days off) was higher than that of Column 5 (1 day on, 2 days off) throughout the experiment, but the total hydrogen ion consumption (calculated using the volume of PLS) was similar after day 60. This was an indication that during the active part of the leaching process the rate of feeding of reactants to the system in Column 8 was the rate limiting step in acid consumption. As the leaching process continued and the acid consuming minerals reduced, the requirement for acid was also reduced. This indicated that the acid consumption was proportional to the amount of reactants fed and the reactants were not in excess. It can be concluded that when the irrigation frequency became lower (Column 8), the amount of reagents decreased and became the rate limiting factor in acid consumption.

4.2.2 Redox potential PLS

An acid wash was done on all columns for the first 6 days of operation before inoculation with microorganisms (Section 3.2). The microorganisms act as bio-catalysts to oxidise Fe^{2+} to Fe^{3+} ions, which is essential for the dissolution of copper sulfides. In the first 18 days after inoculation the redox potential (Figure 4-12) for biotic Columns 2, 5, 8 and 11 under identical continuous irrigation increased from 380 mV to more than 600 mV. This redox increase was an indication of an active microbial community ensuring rapid oxidation of Fe^{2+} to Fe^{3+} and subsequent leaching conditions. The rate of microbial oxidation was greater than the Fe^{3+} leaching of the sulfide minerals present. The redox potentials of all the biotic Columns (2, 5, 8 and 11) decreased to 600 mV thereafter and was maintained around 600 mV. The inherent variation of the lower redox potential of Column 2 may have been caused by the slow detachment of the microorganisms. This inherent variation may be ignored because it was shown that the slow dissolution of the mineral was the rate limiting effect in the leaching reactions and had no impact on the copper extraction (4.2.2) or the Fe extraction (Section 4.2.3).

This high redox potential achieved in biotic columns was directly related to the decrease in Fe^{2+} and the increase in Fe^{3+} as seen in Figure 4-13, thus the increase in the Fe^{3+}:Fe^{2+} ratio, as related through the Nerst equation. The sustained redox potential of 550 – 660 mV was an indication of sustained microbial activity through the bioleaching process. Further it presents a Fe^{3+}:Fe^{2+} ratio, well adapted Cu dissolution from chalcopyrite. High redox potentials are normally associated with precipitation of Fe^{3+} (Watling, 2006), but also it should be remembered that leaching rates of chalcopyrite normally increase, with the increase in redox potential to an optimum value 670 mV. Above this optimum value pyrite leaching occurs selectively over chalcopyrite leaching (Hiroyoshi *et al*., 2000). However this optimum value was reported to be 630 mV by Güler *et al.* (2012). Thus a high redox potential is not conducive to chalcopyrite oxidation.

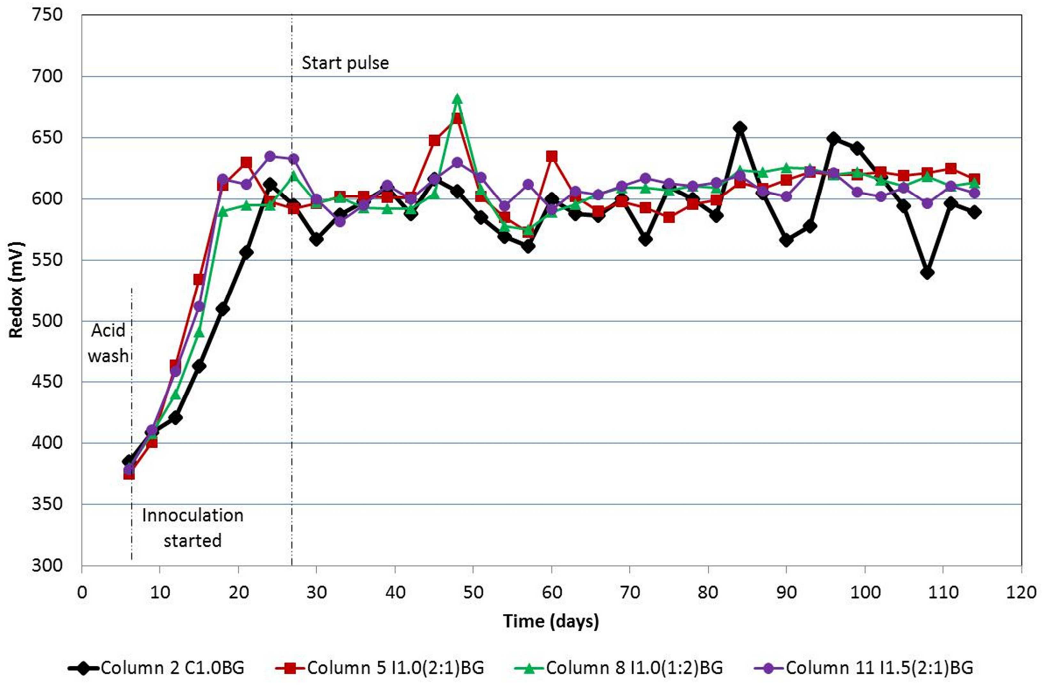

Figure 4-12: Redox of PLS agglomerated bioleaching Columns 2, 5, 8 and 11

4.2.3 Fe^{2+}, Fe^{3+} and total Fe concentration in PLS

There was an decrease in the Fe^{2+} concentration (Figure 4-13) in the first 18 days after inoculation (day 6) from 1000 mg/L to nearly 0 mg/L of Fe^{2+} ion concentration on day 18, where it remained constant for the remainder of the experiment. This drop in Fe^{2+} concentration for all columns was attributed to establishment of an activity iron –oxidising microbial community at the mineral surface (Leahy *et al*., 2004).

It is assumed that all Fe^{2+} ions that were fed into the system at 500 mg/L, and all the Fe^{2+} ions leached from the mineral, were oxidised to Fe^{3+}.This means that the iron exiting in the effluent exists mainly as Fe^{3+}. The discussion thus focuses on total Fe concentration by Fe^{3+} concentration to describe the effects of intermittent irrigation on leaching of sulfide minerals effectively.

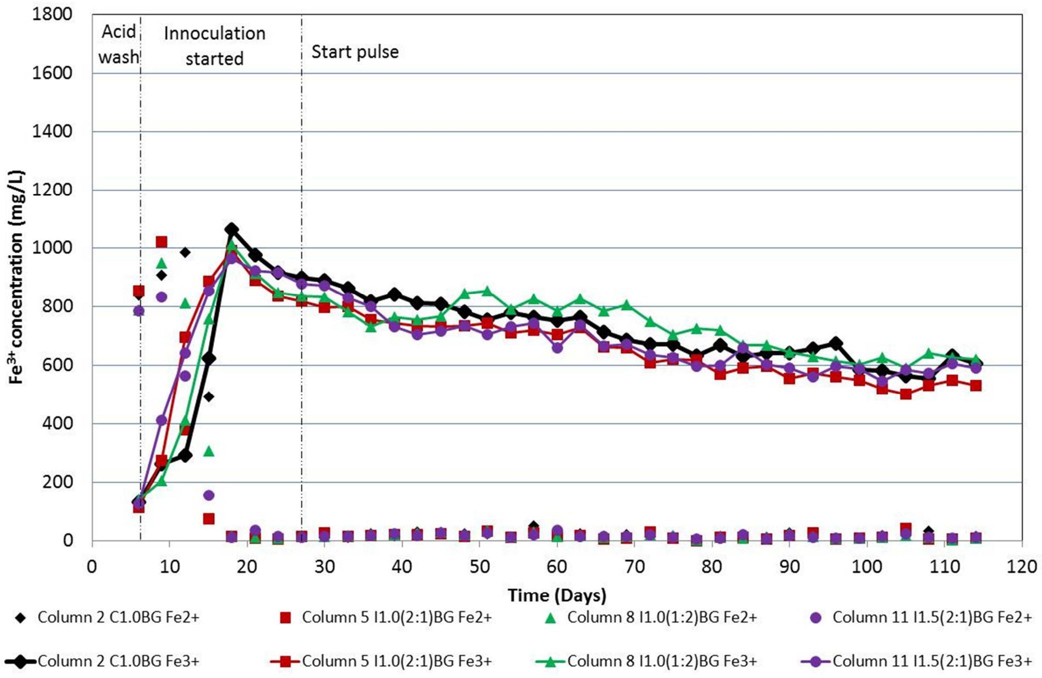

Figure 4-13 : Fe^{2+} and Fe^{3+} concentration in PLS agglomerated bioleaching Columns 2, 5, 8 and 11

Table 4-2: Total Fe Mass balance agglomerated bioleaching columns:

Column	Fe in feed (g)	Fe in Pre leached ore (g)	Fe in post leached ore (g)	Fe in PLS (g)	Fe precipitated (g)	% Fe precipitated of total dissolved Fe in system
2	53	105	70	78	11	12
5	40	105	75	56	14	21
8	26	105	76	40	15	27
11	59	105	70	81	12	13

The iron leached from the low grade ore partitioned between iron in solution and precipitated iron. This was quantified by calculating the last term for precipitation and validated using a mass balance, which was calculated with the daily Fe concentrations presented in Table 4-2. It was found that some 10 % more precipitation took place in the intermittent columns 5 and 8, operating at lower flow rates, than in Columns 2 and 11. In order to analyse the data effectively, the Fe precipitated in the column should be incorporated accordingly, to provide a measure for the total Fe leached. The following are reported:

- The unadjusted figure represents the actual Fe concentration in the PLS as it exited the column, thus the effective conditions in the free flowing liquid in the column influencing conditions experienced by the microbes and at the ore surface.
- The actual leaching of Fe from the ore (adjusted) was determined by including precipitate formed, using the adjusting factor presented in Table 4-2.
- It should be noted that the Fe ratio was assumed to be constant from day 1 up to day 114 as an approximation.

Table 4-3 compares the main differences between the Fe concentration in the PLS and actual Fe leached as determined by accounting for precipitation.

Table 4-3: General comparative table of total Fe concentrations after adjustments (day 27)

Comparison	Fe in PLS original	PLS + precipitated Fe
Column 2 vs. 5	Column 2 higher	Similar
Column 2 vs. 8	After day 39 Column 2 similar than 8	Column 8 higher after day 39
Column 2 vs. 11	Column 2 higher	Column 2 higher
Column 5 vs. 11	Column 5 similar than 11	Column 5 higher than 11

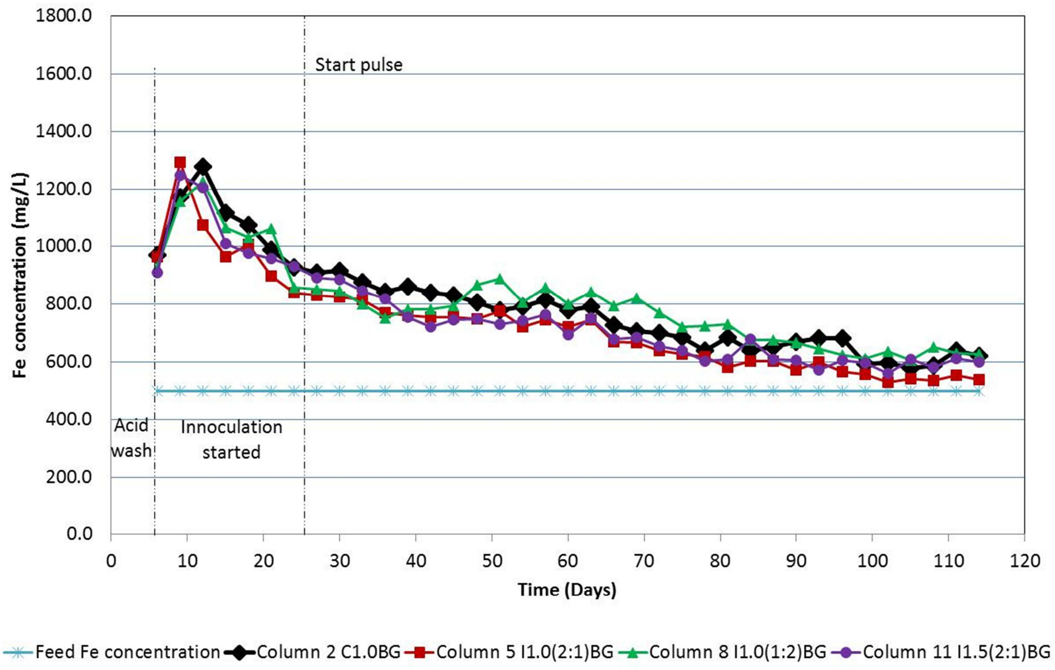

Figure 4-14: Total Fe concentration in PLS (not adjusted) of agglomerated bioleaching Columns 2, 5, 8 and 11

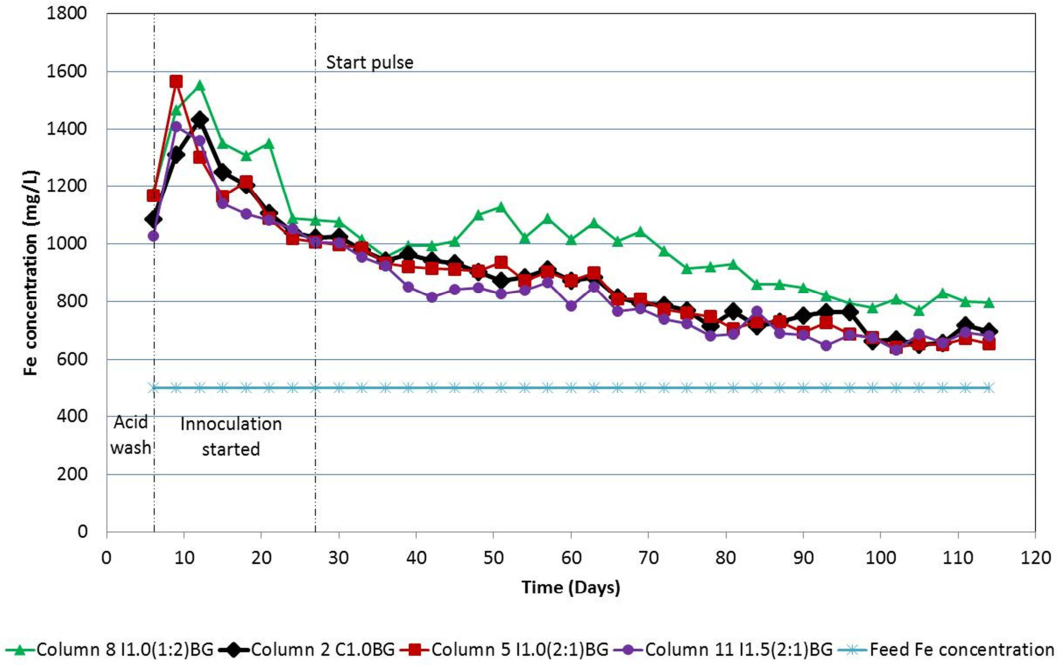

Figure 4-15: Amount of Fe leached (calculated by accounting for precipitation) from agglomerated bioleaching Columns 2, 5, 8 and 11

The total Fe exiting the column exceeded the feed Fe concentration of 500 mg/L, which shows that Fe leaching from the mineral took place for the duration of the experiment (Figure

4-14). A general decrease of the total Fe concentration from 1600 to 700 mg/L took place from day 27 to day 114. Column 8 had a higher Fe concentration than all the other columns over the most active leaching period. It should be noted that after day 75 all columns approached a constant Fe concentration, except intermittent Column 8. Column 8 showed an increase in Fe concentration after day 39 and continued to drop until day 96, whereafter the Fe concentration remained constant for the remainder of the experiment.

The Fe concentration data adjusted for precipitation in Figure 4-15 showed that Columns 2, 5 and 11 performed similarly, however Column 8 showed a higher leached Fe concentration. The performance of bioleaching is considered in terms of cumulative Fe extraction in Figure 4-16, based on the simplifying assumption of a consistent ratio of iron in solution to precipitated iron across the time course of the study. The Fe recoveries for Columns 2, 5, 8 and 11 showed the extent of extraction at 39 %, 31 %, 28 % and 38 % respectively over 114 days.

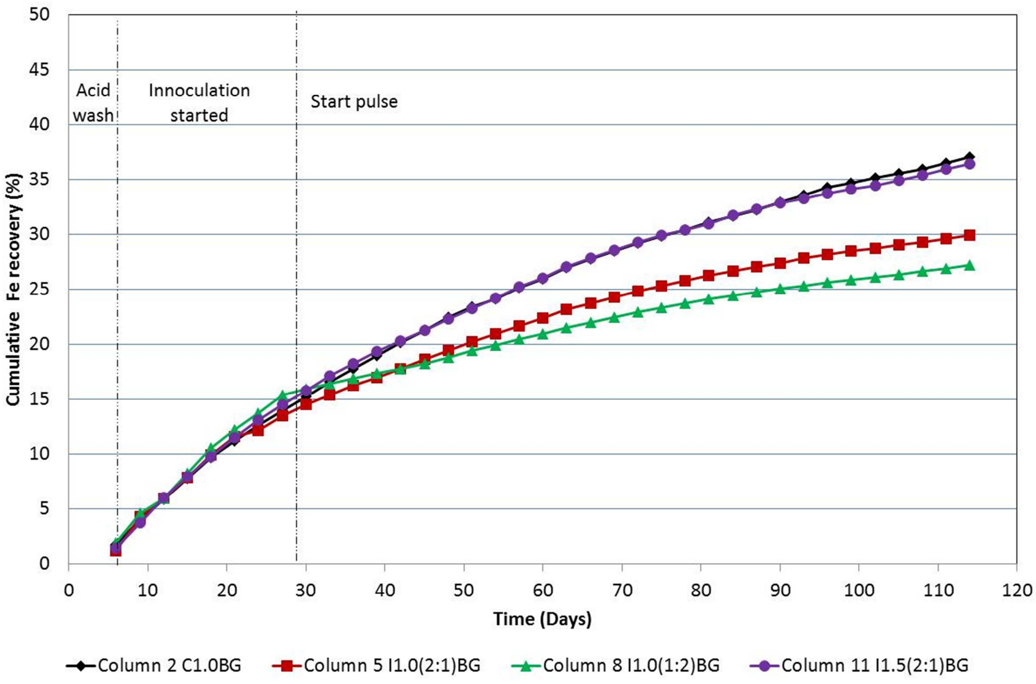

Figure 4-16: Cumulative total Fe extraction (adjusted) of bio agglomerated Columns 2, 5, 8 and 11

Cumulative extraction of total Fe (Figure 4-16) in the ore may also be considered on a basis of the volume of irrigation applied, as shown in Figure 4-17. The highest irrigation volume processed over 114 days was 109 L for intermittent Column 11 with a 36 % Fe extraction that was attained in 114 days. A similar Fe extraction of 37 % was attained for continuous

Column 2 at a flow rate of 100 L. Intermittent irrigated Columns 5 (77 L) and 8 (49 L) had total Fe extractions of 30 and 27 % respectively.

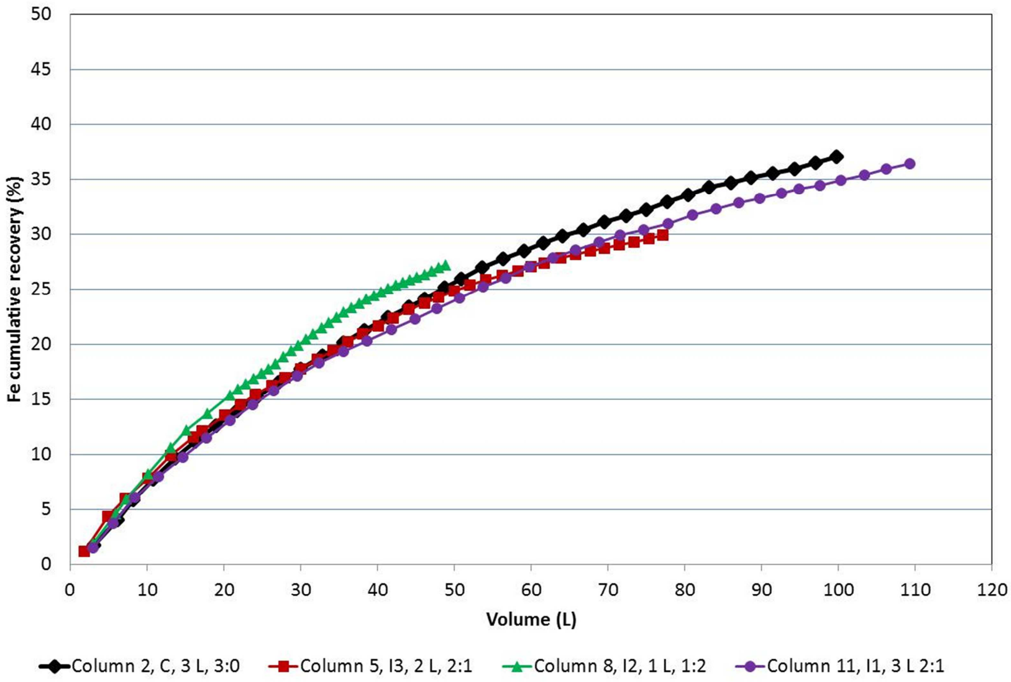

Figure 4-17: Cumulative Fe (adjusted) extraction vs. volume agglomerated abiotic Columns 2, 5, 8 and 11

The leaching of Fe under continuous and intermittent irrigation conditions is compared in the following sections using the continuously-irrigated base case for comparison.

Column 2 vs. 5, Fe removed in the PLS

Comparing the Fe concentration in the PLS from continuously irrigated Column 2 with intermittently irrigated Column 5 showed that a lower Fe concentration was removed from Column 5 than in Column 2 when intermittent irrigation was applied, as seen in Figure 4-14. Fe precipitation, as seen in Table 4-3 was 21 % for Columns 5 and 10 % for Column 2. This indicated that stagnant periods increased the chances of the precipitation of Fe, and caused the decrease in Fe concentration in the PLS. It may also be argued that the higher localised Fe concentration created by the on-going leaching during resting periods in Column 5, may have contributed to an increase in precipitation of Fe.

Column 2 vs. 5 (Adjusted), Fe leached

Following correction for precipitation (Figure 4-15, Figure 4-16), it is seen that on commencing intermittent irrigation after day 27, the extraction from continuous Column 2 and intermittent Column 5 (2 days on 1 day off, 1 L/day) were similar in terms of Fe extracted from the ore per unit volume PLS. This indicated that the Fe extraction was proportional to the amounts of reactant introduced into the system and that applying intermittent irrigation did not increase the Fe leached per unit volume.

Column 2 vs. 8 vs. 5 (Not adjusted), Fe removed in PLS

Column 8 (Figure 4-14) showed similar Fe concentrations to that of continuous Column 2 when applying intermittent irrigation. The higher Fe concentration of Column 8 as shown in Figure 4-15 showed that, by applying intermittent irrigation at long resting periods, a reduced amount of Fe was removed from the system as shown in Figure 4-15 and Figure 4-16. It may also be argued that by increasing the resting period in Column 8, the precipitation increased to 27 % (Table 4-3) as opposed to the 21 % precipitation found in Column 5 with a shorter resting period. As above, it may also be an indication that the higher concentration of Fe in Column 8, and its dominance as Fe^{3+} contributed to the increase in precipitation, hence the decrease in the Fe concentration of the PLS.

Column 2 vs. 8 (Adjusted), Fe leached

Decreasing the intermittent frequency from 2 days to 1 day feed for Column 8 resulted in a higher Fe extraction per unit volume after day 39 with respect to continuous Column 2 as seen in Figure 4-15. From comparison with the short resting time of Column 5 (1 day off) and its lower Fe extraction per unit volume, it may be argued that increasing the residence time of the stagnant solution may have increased the Fe extraction per unit volume (Figure 4-17). This may be due to the fact that leaching still occurred while the column was in its resting period (Van Staden *et al*., 2008) and the concentrated Fe was flushed out with the unwanted salts that build up during the long resting period (Pradhan *et al*., 2008). Also it was suggested that every time the feed was stopped, the oxygen uptake in the heap improved, thus the oxidative leaching of the chalcopyrite mineral increased (Van Staden *et al*., 2008).

Column 5 vs. 11 (not Adjusted), Fe removed in the PLS

Comparing Column 5 vs. 11 (until day 84) showed that Fe precipitation as seen in Figure 4-14 and Table 4-3 was higher for Column 5 (21 %) than Column 11 (10 %). This suggested that increasing the flow rate decreased the chances of Fe precipitation. Also the similar Fe concentration in the PLS for Column 5 as Column 11 (Figure 4-14) and subsequent higher Fe concentration of Column 5 as shown in Figure 4-15, showed that higher Fe concentrations in the column might have increased the chances of precipitation. It may also be argued that the higher flow rate might have reduced the precipitation of Fe in the column.

Column 5 vs. 11 (Adjusted), Fe leached

Following the increase of the flow rate for intermittent Column 11, a slightly higher amount of Fe was extracted for Column 11 than Column 5 over time as shown in Figure 4-16, while the extraction per unit volume was little changed (Figure 4-17). As argued previously the slow dissolution of the mineral and mean residence time of the reactants in the column was rate limiting factors in yielding more Fe per unit volume in Column 11.

Column 2 vs. 11 (Not adjusted), Fe in PLS

Comparing continuously irrigated Column 2 (1 L/day) and intermittently irrigated Column 11 (2 days on 1 day off, 1.5 L/day) in terms of the Fe concentration in the PLS (Figure 4-14), a lower PLS concentration was observed for Column 11 than for Column 2. This observation of dissimilar concentrations was also seen for the Fe extracted per unit volume (Figure 4-15) as the same fraction of Fe precipitated, as seen in Table 4-2 for both columns at 10 %. This similar precipitation indicated that the higher concentration of Fe in the continuous column did not increase the precipitation of Fe in continuous Column 2. It may be argued that the continuous removal of the leached Fe might have reduced the precipitation in the column.

Column 2 vs. 11 (Adjusted), Fe leached

Figure 4-15 showed that, in keeping the amount of reactants the same by increasing the flow rate in Columns 11 to 1.5 L/day while applying intermittent irrigation at 2 days on 1 day off, a slightly lower Fe per unit volume was extracted than in continuous Column 2 (1 L/day). The fact that Column 11 had the same amount of reactants as Column 2 showed that even if the Fe^{3+} in the system is high enough; a higher flow rate would not increase the rate of Fe dissolution. This was because the rate of dissolution of the sulphide mineral was much slower than the rate of reactants fed into the system. Also, the slightly lower Fe extraction per unit volume may have been caused by the decrease of the mean residence time of the reactants in Column 11, due to the higher flow rate and the low resting period of the stagnant solution (1 day) in the column.

4.2.4 Copper in PLS

In Figure 4-18, two distinct Cu concentration profiles for agglomerated biotic columns (2, 5, 8 and 11) could be observed after day 27 when intermittent irrigation was started. In the first period between days 27 and 66, Columns 2, 5, 8 and 11 produced a high Cu concentration. This was followed by a decrease in Cu concentration during the following period (to day 70-80) whereafter the Cu concentrations remained constant until day 114 (second period). The following maximum regions of the Cu concentration were achieved during the first period as stated above:

- Column 2 at 100 – 175 mg/L between days 33-60
- Column 2 at 160 – 200 mg/L between days 32-57
- Column 8 at 350 – 440 mg/L between days 33-51
- Column 11 peaked to 175 on day 32, then decreased to below 100 mg/L until day 63.

The daily Cu concentrations of Columns 2, 5 and 11 dropped to an average concentration of 50 mg/L around day 66, whereafter it remained approximately constant until day 114. However the daily concentrations for Column 8 decreased on day 78 to 120 mg/L, after which it fluctuated between 100 and 200 mg/L. It should be noted that Column 8 had the highest concentrations, followed by Columns 5, 2 and then 11 during this active period of the heap, when the highest leaching occurred.

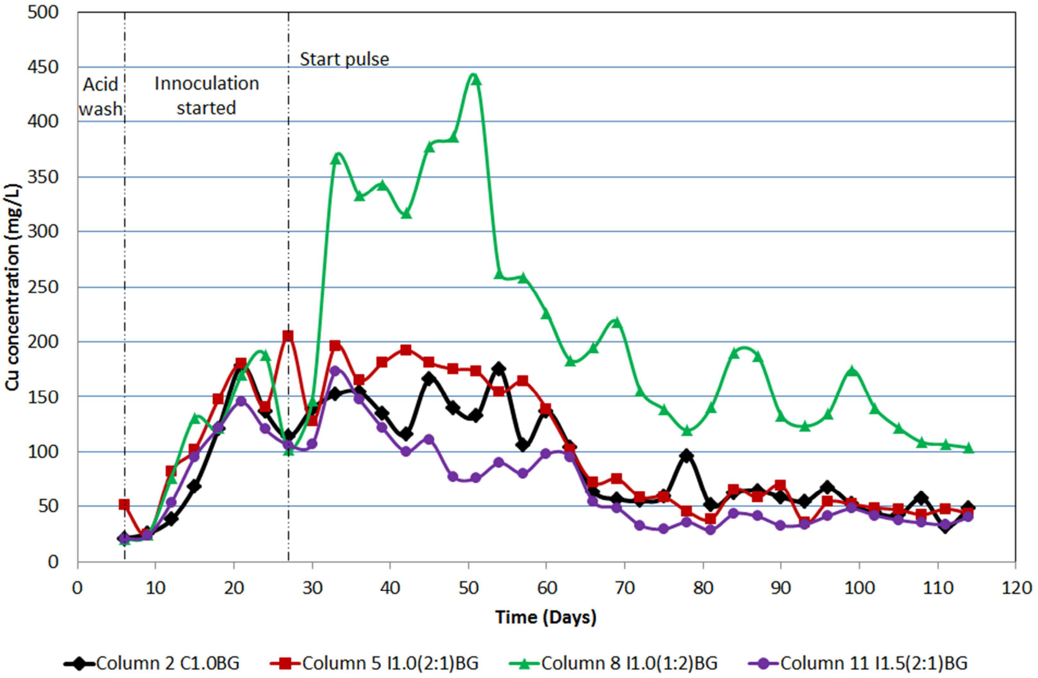

Figure 4-18 Copper concentration of PLS agglomerated bioleaching Columns 2, 5, 8 and 11

The daily mass of copper extracted (not per unit volume but per column) over the 114 day period is quantified in Figure 4-19. This differs from the daily concentrations because of the application of the different irrigation types and volumes: Column 2 (continuous, 1 L/day), Column 5 (2 days on, 1 day off; 1 L/day), Column 8 (1 day on, 2 days off; 1 L/day) and Column 11 (2 days on, 1 day off; 1.5 L/day). The daily copper concentrations (Figure 4-18) are used to discuss the copper extraction per unit volume due the fluctuation in the amount of copper extracted daily (Figure 4-19). These fluctuations may have been caused by channelling of the leach liquid, velocity fluctuations, unsaturated liquid flow, solution chemistry or passivation of mineral surfaces (Sheikhzadeh *et al*., 2005; Kinnunen *et al*., 2006) as well as by the different feed volumes used to quantify the concentrations of the different columns. The fluctuations in the daily copper extracted make it difficult to compare the behaviours of the columns between days 27 and 66 without considering cumulative extraction, however the following important factors were considered:

- The influence of the different flow regimes on the actual copper extracted per column and not the copper extracted per unit volume, shown in Figure 4-18, illustrated that the extent of extraction per column was similar despite the varying irrgation regimes.
- The different leaching stages in the heap were identified: rapid period (days 27 to 66) and slow leach period (day 66 to day 114). This can be explained by the depletion of a

readily available mineral phase, followed by the leaching of a more recalitrant or less available phase.

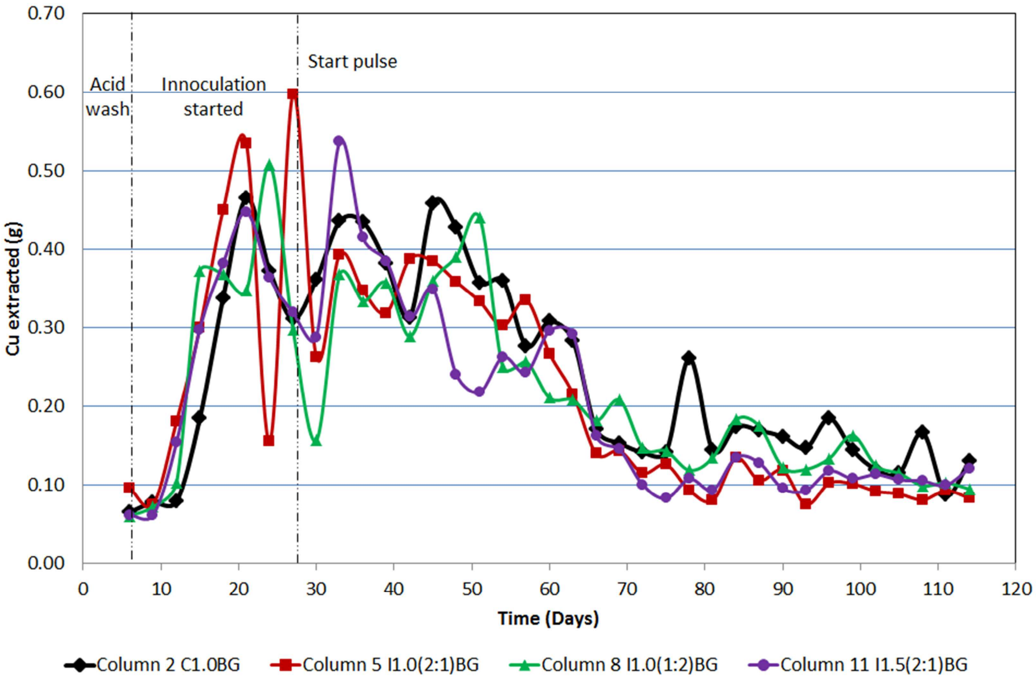

Figure 4-19: Copper extracted in PLS agglomerated bioleaching Columns 2, 5, 8 and 11

The cumulative copper extraction is shown in Figure 4-20. A linear increase in copper extraction occurred from day 27 till day 63 for Columns 2 and 11; and to day 50 for Column 8. Thereafter the rate decreased with Columns 2 and 8 maintaining a higher leach rate than Column 11. The copper extractions for Column 2, 5, 8 and 11 showed total copper extractions at 38 %, 34 %, 34 % and 33 % respectively over 114 days.

As stated in Section 4.1.4 cumulative extraction of total copper (Figure 4-20) in the ore may also be considered on a basis of the volume of irrigation applied, as shown in (Figure 4-21). The highest irrigation volume processed over 114 days was 100 L for continuous Column 2 with a 38 % extraction that was attained in 114 days. Intermittent irrigated Columns 5, 8 and 11 had similar total copper extractions of 33 – 34 % following of 77, 49 and 109 L use of irrigant respectively.

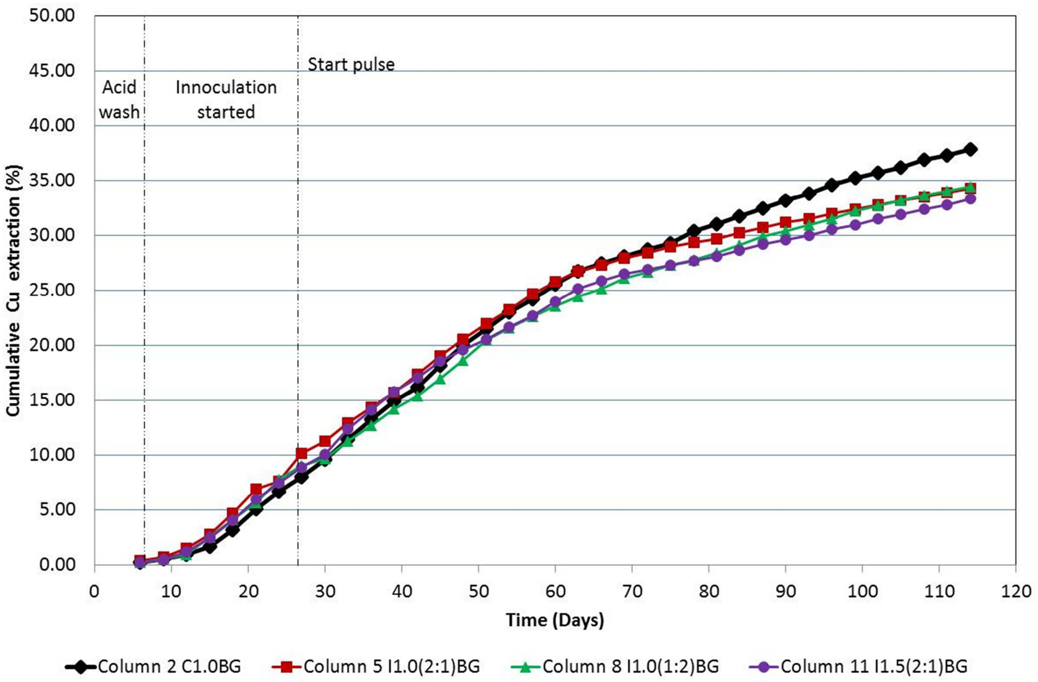

Figure 4-20: Cumulative copper extraction agglomerated abiotic Columns 2, 5, 8 and 11

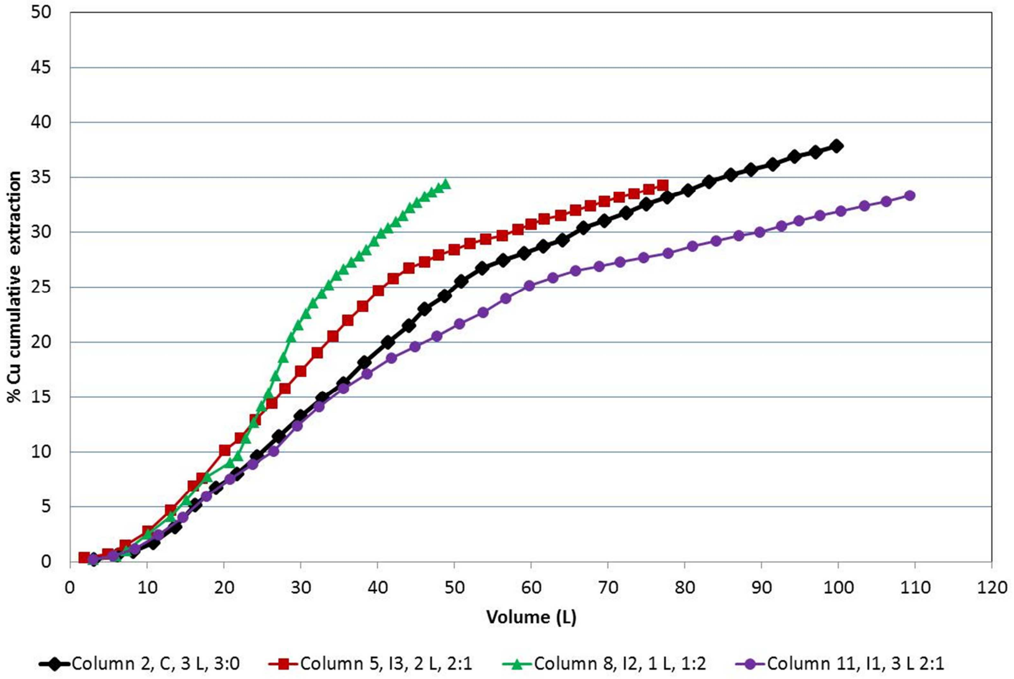

Figure 4-21: Cumulative copper extraction vs. volume agglomerated abiotic Columns 2, 5, 8 and 11

It should be remembered that the microorganisms in bioleaching do not leach the mineral directly, but facilitate the leaching process by generating the Fe^{3+} ion, which are a powerful oxidizing agent that is responsible for the dissolution of copper sulfide minerals and well as the hydrogen required for leach reactions (Pradhan *et al*., 2008).

There were two distinct periods in the heap bioleaching of chalcopyrite (Figure 4-18 and Figure 4-19) characterised by rapid (~ 0.4 g per column per 3 day cycle) and slow (~0.2 g per column per 3 day cycle) leaching. The most active part of the heap (days 27 to 66) corresponds to extraction of easy leachable minerals, hence the increase in copper extraction. The second period was from day 66 onwards, where the concentration dropped to a constant value indicating a constant lower rate of copper extraction. This may be attributed to the depletion of rapidly leachable minerals, lowering either more recalcitrant minerals or less accessible minerals. These dissolution curves were in line with literature, which suggest that the bioleaching process took place in three distinct phases: low dissolution (latency, up to day 10), maximum dissolution (exponential, between days 10 to 60) and the levelling off of the process (stationary, after day 60) (Rodriguez *et al*., 2001).

Between days 27 and 66, the average copper concentrations (Figure 4-18) of continuous Column 2 were lower than that of intermittent Column 5 (2 days on 1 day off). This indicated that applying intermittent irrigation may yield a higher copper extraction per unit volume. Similarly Figure 4-19 and Figure 4-20, which present the total copper extracted per column, indicated that Column 2 and 5 had similar average extractions of total copper per column, yielded 27 % of that available by day 69. This indicated that the same amount of copper was extracted at a reduction in PLS volume of $^1/_3$. It was clear that the rate limiting step was the rate of dissolution of copper from the mineral rather than the amount of reactants added to the two bioleaching systems. This indicated that applying low frequency intermittent irrigation at 2 days on and 1 day off did not negatively impact leaching efficiencies, as long as the reactants added were enough to drive the copper leaching reactions forward.

After day 66, when the readily available mineral was depleted, the daily copper concentrations in the PLS from Columns 2 and 5 were similar, i.e. the copper extraction was similar per unit volume, imply that the total copper extracted per 3 day cycle was higher for continuous Column 2. This indicated that when the availability of the mineral becomes the rate limiting factor, the copper extracted was influenced by the fluid flow. This may relate to transport effects, concentrate driving force, reagent availability or microbial viability and requires further investigation.

During days 27 and 66, decreasing the intermittent frequency to 1 day on, 2 days off for Column 8 caused a major increase in the copper concentration with respect to the continuous Column 2 and intermittent Column 5. The high copper extracted per unit volume suggested that in the resting period the copper concentration in the stagnant solution increased. This was confirmed by the amount copper extracted per column (actual copper recovered in a column not per unit volume) on a basis of the 3 day cycle (Figure 4-19) as well as the cumulative extraction (Figure 4-20) in the corresponding 66 day period which was 27 % and 25 % respectively for Columns 2 and 8. The cumulated u extraction showed a decrease in extraction rate of Column 8 following the leaching of easy accessible minerals (day 54). It also highlighted similar total copper extraction achieve across varying irrigation regimes. At 50 days, extractions were 22 %, 22 %, 21 % and 21 % across the 4 Columns (2, 5, 8 and 11), increases to 27 %, 27 %, 25 % and 26 % at 66 days and to 38 %, 34 %, 34 % and 33 % at 114 days.

During days 27 to 66, applying intermittent irrigation at a high volume (1.5 L/day) for intermittent Column 11 (2 days on 1 day off) indicated that the copper concentration was lower than that of continuous Column 2 and intermittent Column 5. This indicated that the copper extraction per unit volume decreased when intermittent irrigation at higher flow rates was applied. It has already been established that intermittent irrigation increased the copper recovered by unit volume. As the flow rate increases, the mass transfer between the solid particles and the solution also increases, but the mean residence time in the column decreases (Sadowski & Szubert, 2007). This may indicate that during this active period of leaching the slow dissolution rate decreased the copper extraction during the “on days” of high flow rate with intermittent irrigation and not the low mean residence time. It should be noted that the leaching reactions are the same throughout the 3 day period and was not only a dilution event of concentration.

After day 66 the daily copper concentration for intermittent irrigation at the high flow rate Column 11 remained lower than Column 2, thus the total daily copper extraction was lower than that of Column 2. This indicated that irrespective of the availability of the mineral to be leached, the low mean residence time in the column caused by the high flow rate may have caused a decrease in the extraction of copper. It should also be noted that if the dissolution of the sulfide mineral is slow and act as the rate limiting steps, higher reactant feed rates will not increase the leaching rates of the sulfide minerals.

As indicated above, cumulative copper extraction varied between 33 and 38 % over 114 days. In Figure 4-21, the cumulative copper extracted is presented per unit volume which indicated that similar extractions were achieved for Columns 5 (77 L), 8 (49 L) and 11 (109 L) at 34 %, 34 % and 33 % respectively. Continuous Column 2 (100 L) had a extraction of 38 %. It was clear that by using a $^1/_2$ of the liquid in Column 8, ¾ in Column 5 or 100 % in Column 11 only produced 4 % lesser copper extraction than continuous Column 1. This was an indication that the same reactions took place during the stagnant periods for intermittent Columns 5, 8 and 11 as continuous Column 2. Also this similar copper extraction between the intermittent columns was an indication that the length of the resting periods did not influence the rate of copper extraction. Also as stated before the fact that Column 11 produced a similar copper extraction was also an indication that higher flow rates will not increase the copper extraction if the rate limiting steps are the slow dissolution of chalcopyrite or the availability of the mineral in bioleaching systems. This is quite different from abiotic leaching (Figure 4-10), because, with bioleaching, the irrigation volume does not define the availability of the leach reagent, but the biological activity does. In emphasising the benefits of intermittent irrigation and lower feed volumes it took 93 days for continuous Column 2 achieve a similar extraction copper extraction of 34%, but at volume of 83 L of feed, which was still higher than the volume of Column 7 at 50 L. This indicates that the bio activity can be maintained at intermittent irrigation or lower volumes without a major flow load to produce enough reactants to leach the mineral efficiently.

If the extraction is compared by only using 50 L of feed by taking Column 8 as the basis due to the low feed volume, it showed that different amounts of copper was extracted for columns 2 (26 % in 60 days), 5 (28 % in 72 days), 8 (34 % in 114 days) and 11 (22 % in 54 days). The fact that similar amount of reactants of 50 L added, yielded higher copper extractions for intermittent Columns 5 and 8 than continuous Column 2, indicate the benefits of applying intermittent irrigation due to the higher copper extraction per unit volume. The higher copper extraction for Column 8 than Column 5 indicated the copper extraction per unit volume increases as the resting periods increase. The lower copper extraction of intermittent Column 11 than intermittent Column 5 and continuous Column 2, emphasise that higher feed rates (reactant additions) will not necessarily increase the copper extraction if the rate limiting effect is the slow dissolution of the mineral or the availability of the mineral.

4.3 Heap bioleaching performance using layered packing

As with the agglomerated abiotic and biotic columns described in Sections 4.1 and 4.2, all columns were irrigated with a basal salt media containing nutrients at a feed pH of 1.15. These columns (3, 6, 9 and 12) were inoculated with the same mixed culture of microorganisms (Section 3.2), used for agglomerated bioleaching on day 6 and were irrigated continuously until day 27 to allow consistent colonisation before intermittent irrigation was applied from day 27. As described in Section 3.1.6, this set of columns was packed in layers of fines (- 2 mm) and coarse (+ 2 mm) material in the following order from the top of the column: - 2mm, + 2 mm, - 2 mm + 2 mm. This was done to simulate the effects of the displacement of fines in a heap, normally caused by liquid flow through the heap or disruptions to the packing. It also may inform approaches for minimizing leaching reactions causing ARD (acid mine drainage) in waste rock dumps. It should be noted that interference occurred with the feed rate to Column 9 during the first 27 days which could only be rectified after a new pump was made available after the 27 days.

4.3.1 pH of PLS

The pH of the PLS decreased from an average of pH 2.2 for Columns 3, 6 and 9 to an average of pH 1.45 during the first 27 days and decreased further to a pH of 1.3 over the period until day 48. An average pH of 1.25 was found by day 114. The pH profile for intermittent Column 9 (1 day on, 2 days off) was slightly higher than the other columns owing to the lower feed rate; the decrease from the initial pH was from pH 2.25 to a pH of 1.54 until day 27. After day 27 the pH dropped to pH 1.37 by day 81 where after it remained constant until day 114.

The experimental variance is demonstrated by comparing Columns 3, 6 and 12 under common leaching conditions from day 1 to 27, showing adequate reproducibility. However, during the 1st 27 days, the pH performance of Column 9 was higher than that of Column 7, due to a lower feed volume applied to Column 9, but followed similar hydrogen consumption trends than Columns 3, 6 and 12 until day 114. This indicated that the feed rate during the 1st 27 days did not affect the hydrogen consumption. It may be argued that the behaviour for all bio layered columns was similar over this initial period, taking the above argument into account.

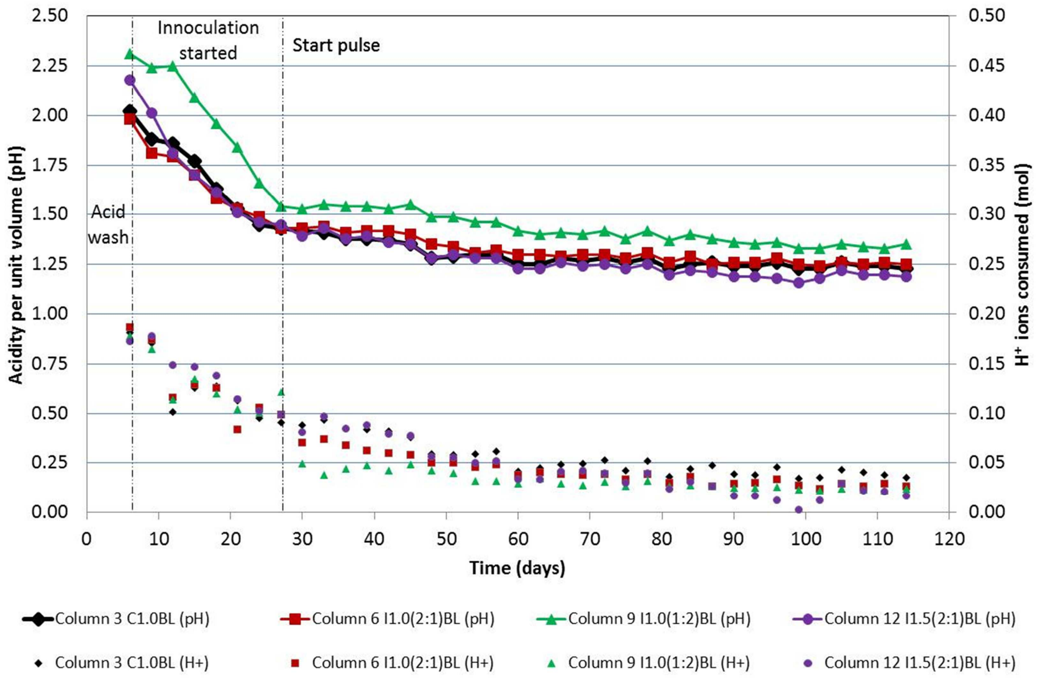

Figure 4-22: pH of PLS and net hydrogen ion consumption layered bioleaching Columns 3, 6, 9 and 12

The initial pH of the PLS of the layered columns before day 27, shown in Figure 4-22, was slightly higher than that of abiotic leaching (Figure 4-1) and agglomerated bioleaching (Figure 4-11). The individual layers in these columns were not acid agglomerated; hence the initial acid neutralisation had not occurred prior to packing in the layer columns. The pH showed a similar decreasing trend to the abiotic and agglomerated bioleaching columns after intermittent irrigation was applied on day 27, with the exception of Column 9 which had a higher pH performance during the 1st 27 days of operation owing to lower federate. Here the pH remained slightly higher during the first 57 days. As established for the bioleaching agglomerated columns (Section 4.2.1), the mineralogy of the ore governs the acid consumption. It cannot be established whether the acidity was dominated by the acid consuming and microbial acid generating reactions of the microbial conversion of Fe^{2+}. This is due to the fact that it is uncertain how the microbial activities affect these reactions and the only data is the net values, which are similar.

The pH is a measure of acidity per unit volume. The total number of hydrogen ions consumed depends on this and the feed volume. The daily PLS pH decreased for all columns until day 60, after which it remained constant until day 114. The decline in the first

60 days could be attributed to the depletion acid consuming gangue minerals, and associated reduction in the reactant requirements for hydrogen ion consumption also reduced.

The daily pH (Figure 4-22) for continuous Column 3 and intermittent Column 6 (2 days on; 1 day off) decreased at the same rate during this 54 day period, but the net hydrogen ions consumption was lower for Column 6. This indicated that for bio layered columns, when applying intermittent irrigation at high frequencies, the net hydrogen ion consumption was decreased. It might be that the increased generation of acid by the microorganism during the stagnant period neutralised the gangue minerals.

The daily pH for Column 12 (2 days on; 1 day off, 1.5 L/day) was similar to that of continuous Column 3 until day 54. It may be that the wettability of the ore in column 12, compared with column 6, increased for the coarse particles due to the high flow rate. After day 54 the net hydrogen ion consumption for column 12 dropped at a faster rate than that of column 3. This may be an indication that, after day 54, the drop in the net hydrogen ion consumption owed to the rate of dissolution of the gangue mineral being slower than the rate at which the reactants were supplied or that the acid generation rate increased. The similar pH of column 6 (2 days on; 1 day off, 1 L/day) and 12 (2 days on; 1 day off, 1.5 L/day) after day 54 indicated that higher flow rates at the same frequency did not increase the net hydrogen ion consumption where the slow acid consumption of the mineral was the rate limiting effect.

The daily pH for intermittent Column 9 (1 days on; 2 days off) was higher than that of continuous Column 3 throughout the experiment. It should be noted that the feed rate of Column 9 was 2 L in 3 days (as opposed to 3L in 3 days) from day 6 to day 27, due to constant pumping errors during this period. It was evident that before day 27 the same amount of hydrogen was consumed, thus the higher pH in the PLS (lower amount of hydrogen ions left). It may be concluded that this low feed rate during the initial 27 days had no effect on the amount of hydrogen consumed, because the reactants were in excess. After day 27, when decreasing the intermittent frequency, the higher pH persisted and a drop in the net hydrogen ion consumption occurred. It may be argued that the wettability of the coarse fraction and the low reactive surface, especially during the stagnant period might have contributed to the low net hydrogen consumption. It was clear that as the availability of the acid consuming minerals decreased and as the leaching process continued, the hydrogen ion consumption dropped.

4.3.2 Redox potential

An acid wash was done on all columns for the first 6 days of operation before inoculation with microorganisms (Section 3.2). The microorganisms act as bio-catalysts to oxidise Fe^{2+} to Fe^{3+} ions and reduced species to hydrogen and SO_4^{2+} where Fe^{3+} and hydrogen are essential for the dissolution of copper sulfides. Hence, where microbial activity is not rate limiting, the rise in redox potential occurs. After inoculation, the redox potential (Figure 4-23) for layered biotic Columns 3, 6 and 12 increased from 380 mV on day 6 to 650 - 700 mV on day 18 and dropped to redox potentials of 600 mV, where it remained in the range 580 to 630 until day 114. However, Column 9 only increased to 560 mV from day 6 to day 18, subsequently decreasing to 460 mV on day 24. Following introduction of intermittent irrigation the redox increased to 650 mV by day 33, where it remained constant for the remainder of the experiment. This low redox potential in Column 9 may be related to the low or initial flow rate or potentially a less effective drip inoculation owing to the unplanned reduction in feed rate in the early stages of this experiment (see above), causing attachment of the microorganisms to be slower (lag phase).

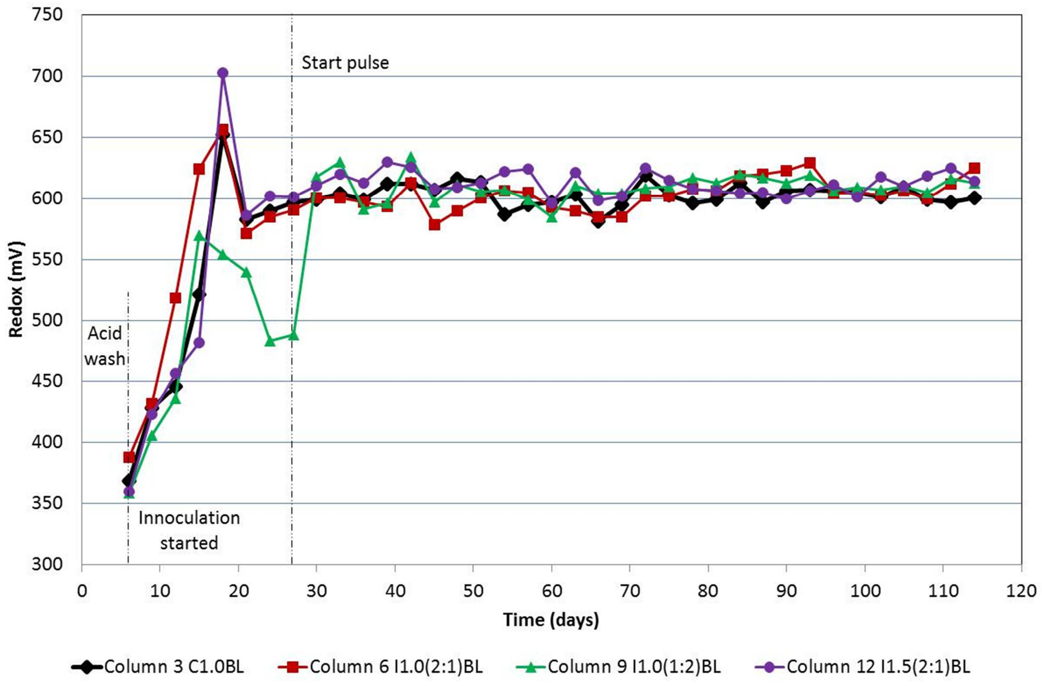

Figure 4-23: Redox of PLS layered bioleaching Columns 3, 6, 9 and 12

4.3.3 Fe^{2+}, Fe^{3+} and total Fe concentration in PLS

As in the biotic agglomerated columns (Section 4.2.2), there was a decrease in the Fe^{2+} concentration (Figure 4-24) in the first 18 days after inoculation (day 6) from 900 mg/L to 0 mg/L for all layered bioleaching columns (3, 6, 9 and 12). This drop in Fe^{2+} concentration for all columns could be attributed to the fact that during the attachment of microorganisms to the mineral surface, the microorganisms colonised the ore bed and established an activity such that the rate of bio conversion of Fe^{2+} to Fe^{3+} exceeded the mineral leach rate. In this case, optimal microbial activity was assumed when the Fe^{2+} concentration reached approximately 0 mg/L and the maximum redox potential was achieved. However Column 9 increased to 200 mg/L by day 27 , returning to 0 mg/L on day 30 and then remaining constant for the remainder of the experiment. This increase was coupled with a low redox potential during days 21 and 30. This could be assumed to be due to poor microbial performance during this period.

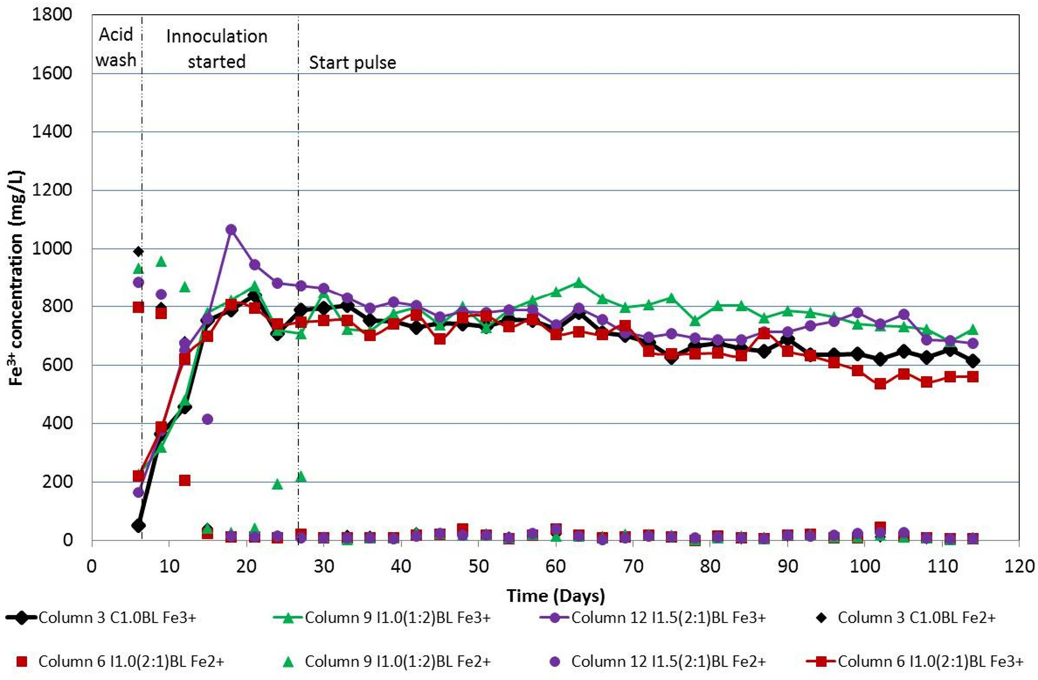

Figure 4-24: Fe^{2+} and Fe^{3+} concentration in PLS layered bioleaching Columns 3, 6, 9 and 12

All Fe^{2+} ions fed into the system at 500 mg/L and all the Fe^{2+} ions leached from the mineral were oxidised to Fe^{3+}. The total iron exiting in the effluent exists as Fe^{3+}. Hence the leaching of iron and its removal from the column is discussed in terms of total Fe (equivalent to Fe^{3+}).

Table 4-4: Total Fe Mass balance bioleaching layered columns:

Column	Fe in feed (g)	Fe in Pre leached ore (g)	Fe in post leached ore (g)	Fe in PLS (g)	Fe precipitated (g)	% of Fe precipitated from total volume leached
3	69	105	69	97	9	9
6	43	105	75	60	13	18
9	26	105	76	43	12	23
12	66	105	61	101	9	9

The precipitation of Fe in the column was quantified after 114 days on recovering the solid fraction, using an oxalic acid wash (Section 3.8.4). The iron recovered to each fraction (PLS, precipitation and unleached ore) is quantified in Table 4-4. In Section 4.2.1, it was found that 10 % more precipitation of Fe took place (Table 4-4) in the intermittent Columns 6 and 9 with lower flow rates than in continuous Column 3 or intermittent column 12 with equivalent flow rates. In order to analyse the data effectively, the Fe precipitated in the column was incorporated accordingly, to calculate the total Fe leached from the ore. This adjustment addressed the Fe leaching in the following manner:

- The unadjusted figure represents the actual Fe in the PLS as it left the column and the effective conditions at the ore surface.
- The leaching of Fe from the ore (including precipitate) was calculated using the adjusting factor presented in Table 4-4. This compensates for the precipitated Fe not reporting to the PLS. It should be noted that the assumption on the Fe ratio was assumed to be constant from day 1 up to day 114.

The comparative Table 4-5 shows the differences after the adjustment factor was applied.

Table 4-5: General comparative table of total Fe concentrations after adjustments (day 27)

Comparison	PLS original	PLS adjusted
Column 3 vs. 6	Similar up to day 51 after day 93 Column 6 lower	Similar until day 36, but Column 6 slightly higher after day 36 and similar after day 93.
Column 3 vs. 9	Similar up to day 51, after day 51 Column 9 higher.	Higher until day 114
Column 3 vs. 12	Column 12 higher. Similar between days 63 and 74.	No change
Column 6 vs. 12	Column 6 lower until day 114	Similar until day 90, after day 90 Column 6 lower
Column 6 vs. 9	Column 6 higher until day 114	Column 6 higher also higher than Column 9, but the difference in concentration is lesser.

It should be noted that the adjusted Fe concentration (Table 4.4 and Table 4.5) was used to discuss the leaching of the total Fe from the mineral as shown in Figure 4-26. The Fe concentration in the PLS was higher than the feed Fe of 500 mg/L, which shows that Fe leaching from the mineral took place for the duration of the experiment. Between days 18 and 27 a sharp decrease in all Fe concentrations took place. The high concentration for Column 9 was caused by pumping problems between day 6 and 27 and fewer volumes were fed into the system, hence the higher copper concentrations.

As from day 27 the Fe concentration in all columns remained constant between 800 and 1000 mg/L. After day 75 the Fe concentration decreased to below 800 mg/L for Columns 3, 6 and 12 where it remained constant. After day 75 the concentration for Column 12 was higher than those of Columns 3 and 6, but lower than Column 9. However the total Fe concentration in Column 9 had an increase after day 51 to 1100 mg/L until day 63 and decreased to 900 mg/L by the end of the experiment.

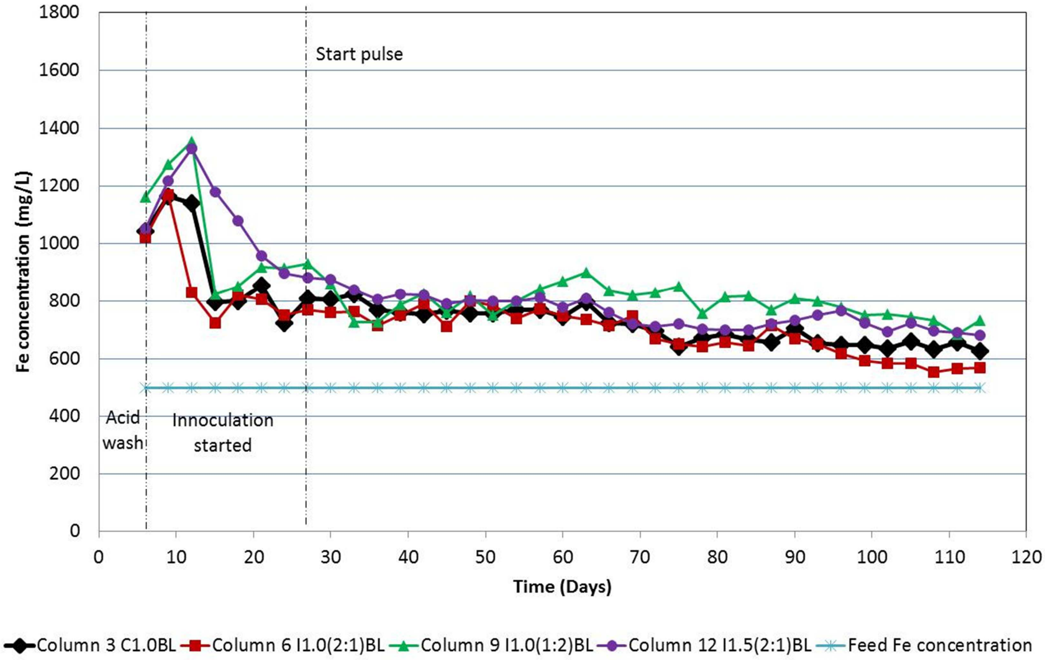

Figure 4-25: Total Fe concentration values (not adjusted) agglomerated bioleaching Columns 3, 6, 9 and 12

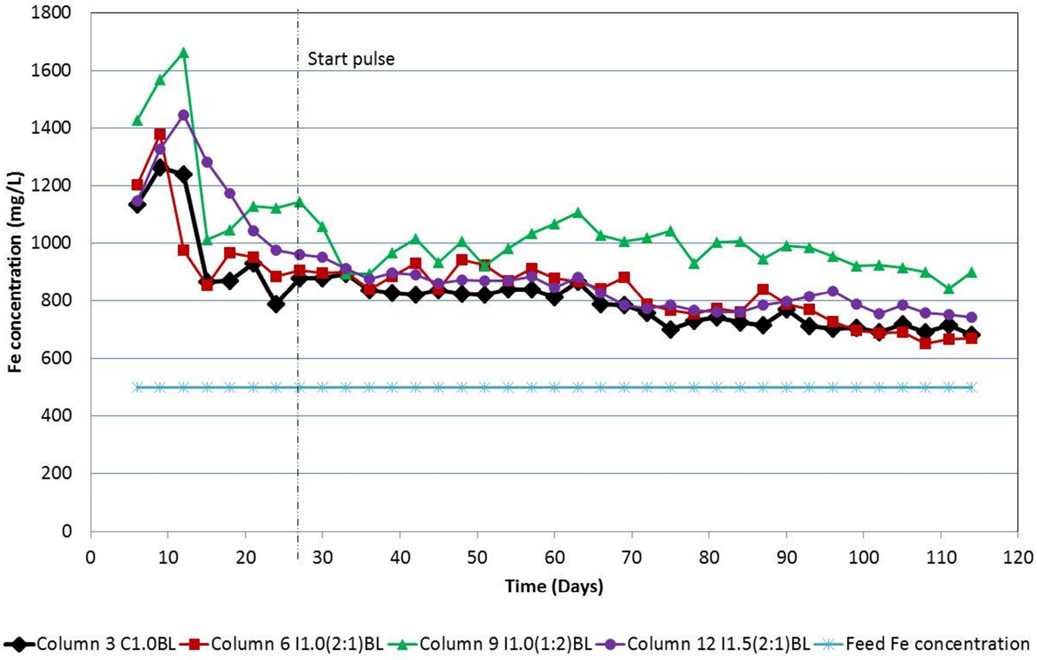

Figure 4-26: Fe leached (adjusted) from the layered bioleaching Columns 3, 6, 9 and 12

Precipitation in columns as a function of irrigation regime

As discussed in 4.2.3, the inherent variation of the 1st 27 days of Columns 3, 6, 9 and 12 of the Fe concentrations showed variation when the columns were operated at similar conditions as seen in Figure 4-25 and Figure 4-26. Hence only major trends in iron liberation are considered.

The Fe precipitation pattern for bio- agglomerated and bio-layered columns was similar. It was found that Columns 6 (18 %) and 9 (23 %) had higher precipitation than continuous Column 3 (9 %) and intermittent Column 12 (9 %) according to Table 4-4; and by comparing the differences in concentrations between the actual Fe leached (Figure 4-25) and Fe in PLS (Figure 4-26). Also the precipitation pattern was similar and increased according to the concentration of the Fe in the column as discussed in Section 4.1.3. It was clear that the resting periods had an effect on the precipitation of Fe. Column 9, with the highest Fe concentration, had the highest precipitation. This was followed by Column 6 with the lower concentration, which had a lower Fe precipitation. The fact that intermittent Column 12 (1.5 L/day) had a similar precipitation, but higher a concentration than Column 3 (1 L/day) was an indication that it might be that the higher flow rate could have increased the washout rate. The similar Fe concentrations per unit volume achieved for Columns 6 and 12, with the same stagnant periods (1 day) and higher Fe precipitation for Column 6 might be an indication that flow rates also played an important role in minimizing precipitation.

The inherent variation showed Columns 3 and 6 had a similar performance before day 21 according to the adjusted Fe concentration data shown Figure 4-26. However Columns 9 and 12 had higher Fe concentrations before day 21.

The cumulative Fe recoveries for Columns 3, 6, 9 and 12, shown in Figure 4-27, showed an extent of extraction at 40 %, 32 %, 27 % and 26 % respectively over 114 days. This cumulative extraction may also be considered on a basis of the volume of irrigation solution applied, as shown in Figure 4-28. The highest irrigation volumes processed over 114 days were 105 L for continuous Column 3 and intermittent Column 12 with a 32 % and 40 % extraction respectively. This was followed by Column 6 with 28 % extraction at 77 L and Column 9 at 45 L with a Fe extraction of 27 %.

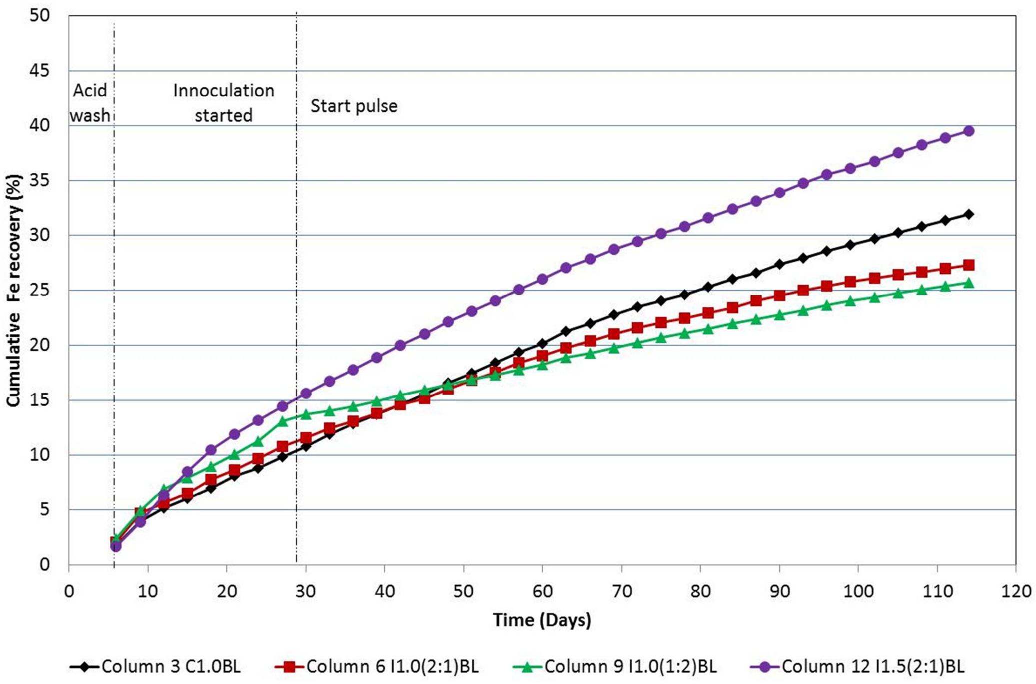

Figure 4-27: Cumulative total Fe extraction from ore (adjusted) of bio layered columns 3, 6, 9 and 12

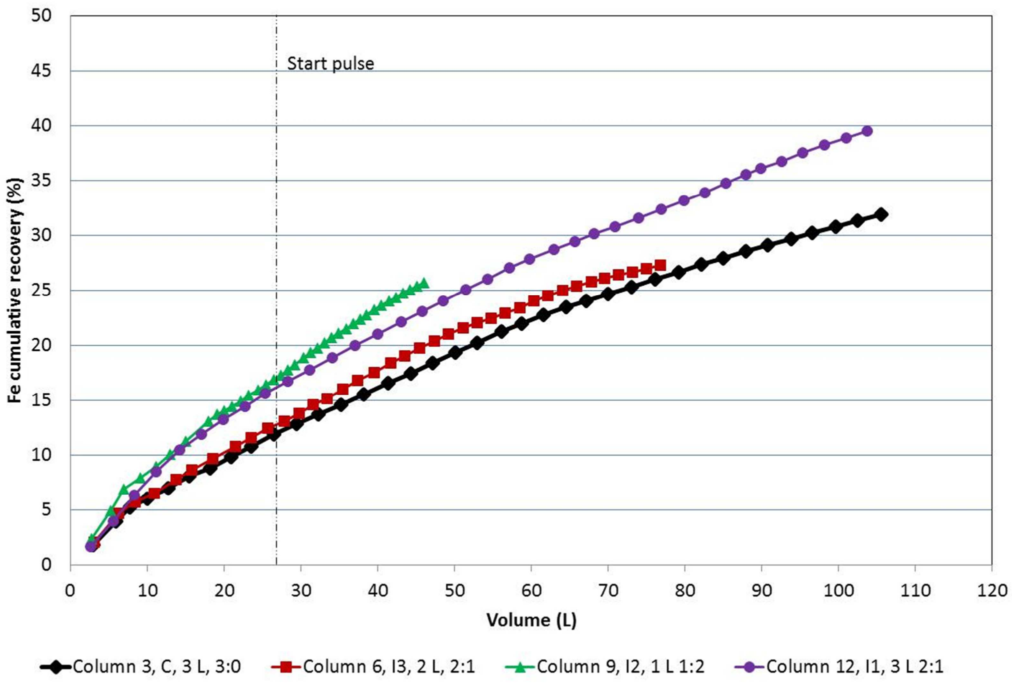

Figure 4-28: Cumulative Fe extraction (Adjusted) vs. volume agglomerated abiotic Columns 3, 6, 9 and 12

Column 3 vs. 6 (Adjusted), Fe leached

After day 27 the PLS of continuous Column 3 had a lower Fe concentration than that of intermittent Column 6 (2 days on, 1 day off, 1 L/day) as seen in Figure 4-26, however the difference on a cumulative basis was small (Figure 4-27). This was an indication that the amount of reactants added were not limiting the mineral sulphide leaching and that leaching taking place during the stagnant period resulted in excess leaching agents. The wettability of the coarse fraction and availability of the mineral may be refuted, because the lower amount of reactants added during the leaching of intermittent Column 9 had a higher Fe leached per unit volume. It might be that the resting period during intermittent irrigation was not sufficient, although an influence was detected, to increase the Fe extraction per unit volume substantially.

Column 3 vs. 9 (Adjusted), Fe leached

Taking the inherent variation into account it showed that Column 9 had a higher Fe concentration than Column 3 before day 27. However this variation is not high enough to make a substantial impact on Column 9's performance after day 49, due to the significantly higher Fe concentration. Decreasing the intermittent irrigation from 2 days to 1 day in the 3 day cycle for Column 9 (1 day on; 2 days off) resulted in a higher Fe extraction per unit volume than continuous Column 3 as seen in Figure 4-26 and Figure 4-28. It was clear that increasing the residence time of the stagnant solution increased the Fe leaching rate per unit volume, because Fe leaching occurred during the stagnant periods of no irrigation. It may also be argued that this increase in Fe extraction was favoured in coarse bioleaching because draining and drying of the capillaries is faster than ionic diffusion, which was in line with literature from Muñoz *et al*. (1995) and Pradhan *et al*. (2008). This may be assumed because 75 % of the coarse material was layered between fines.

Column 3 vs. 12 (Adjusted), Fe leached

Inherent variation showed that Column 12 had a higher Fe concentration than Column 3 before day 27. However, after day 27, the Fe leached from continuous Column 3 was similar than that of intermittent Column 12 (1 day on, 2 days off, 1.5 L/day), both in terms of concentration (Figure 4-26) and cumulative leach rate (Figure 4-27 and Figure 4-28). This suggested that the resting periods did not increase the Fe extraction in coarse particles as discussed above during days 27 and 114. The availability of the mineral might have been the rate limiting factor that prevented a higher leach rate.

Column 6 vs. 12 (Adjusted), Fe leached

Increasing the flow rate in Column 12 to 1.5 L/day and keeping the intermittent frequency the same at 2 days on and 1 day off, showed similar Fe extractions to intermittent Column 6 at 1 L/day (Figure 4-26). This was an indication that the amount of reactants was not the rate limiting step in extraction but the availability of the mineral.

The higher Fe extraction from all intermittently irrigated columns with respect to continuous Column 3 was evidence that intermittent irrigation increased Fe extraction per unit volume, especially in coarse material. The fact that intermittent Column 9 had a higher Fe extraction per unit volume was an indication that increased resting periods increase Fe extraction over the conditions studied.

4.3.4 Copper in PLS

Two distinct regions within the copper concentration profiles for layered bioleaching Columns 3, 6 and 9 (Figure 4-29) could be observed after day 27 when intermittent irrigation was started. In the 1st period the daily copper concentrations in the PLS of Columns 3, 6 and 12 increased between day 27 and 66. This was followed by a decrease in Cu concentrations, whereafter the Cu concentrations remained constant until day 114 (second period). The following maximum regions of the Cu concentration were achieved during the first period as stated above:

- Column 3 at 60- 75 mg/L after day 45 - 63.
- Column 6 at 120 – 200 mg/L between days 33 - 60
- Column 9 increases to 214 mg/L on day 30 remained high until day 114 between 160 – 250 mg/L.
- Column 12 at 50 – 70 mg/L between days 30 - 63.

The daily copper concentrations of Columns 3, 6 and 12 dropped to an average concentration of 50 mg/L on day 66, where it remained approximately constant until day 114. However the daily copper concentrations for Column 9 remained high after the drop from 250 mg/L to 171 mg/L and remained constant until day 114.

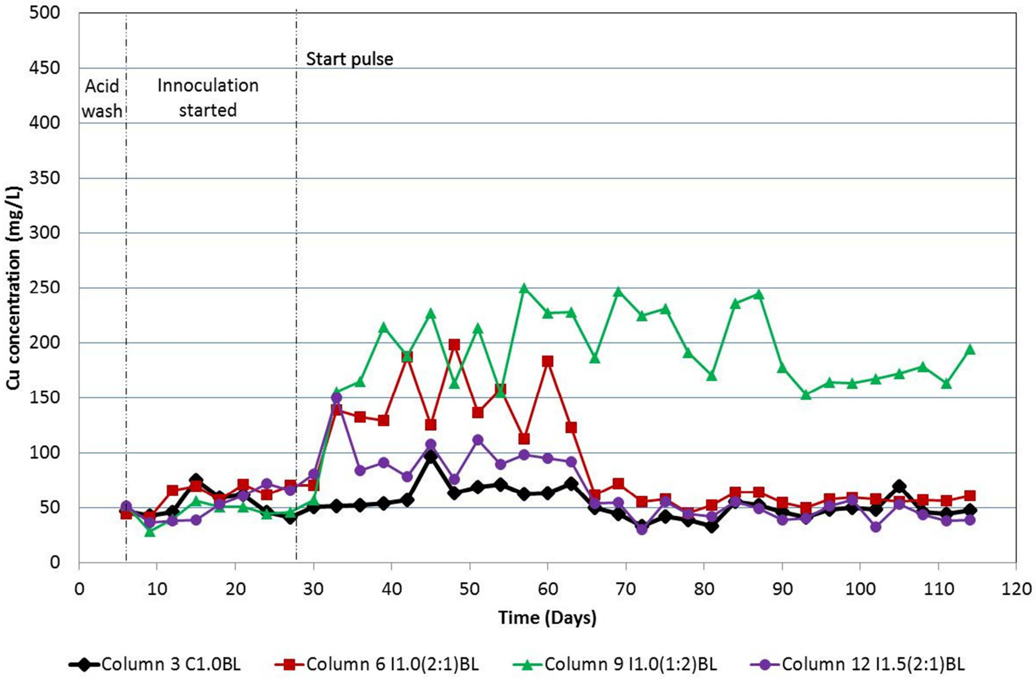

Figure 4-29: Copper concentration of PLS from the layered bioleaching Columns 3, 6, 9 and 12

The daily copper mass extracted (not per unit volume but per column) over the 114 day period is quantified in Figure 4-30. This differs from the daily concentrations because of the application of the different irrigation types and volumes: Column 3 (continuous, 1 L/day), Column 6 (2 days on, 1 day off; 1 L/day), Column 9 (1 day on, 2 days off; 1 L/day) and Column 12 (2 days on, 1 day off; 1.5 L/day). As an estimation it was clear that the daily total copper extraction from day 27 to day 72 (not day 66 as above) from high to low were Columns 6, 12, 3 and 9. After day 72 the daily copper extractions decreased for Columns 2 (0.1 g), 12 (0.13 g) and 3 (0.15 g) remained constant. However Column 9 remained high at 0.2 g, before dropping on day 96 to a daily copper average of 0.15 g.

The important factors that were considered in analysing Figure 4-23 were:

- The influence of the different flow regimes on the actual copper extracted per column and not the copper extracted per unit volume as shown in Figure 4-29.
- The different leaching stages in the heap: active period (days 27 to 66) and when the leachable mineral was depleted (day 66 to day 114).
- The performance of Column 9, which continued to have high Copper extractions throughout the experiment.

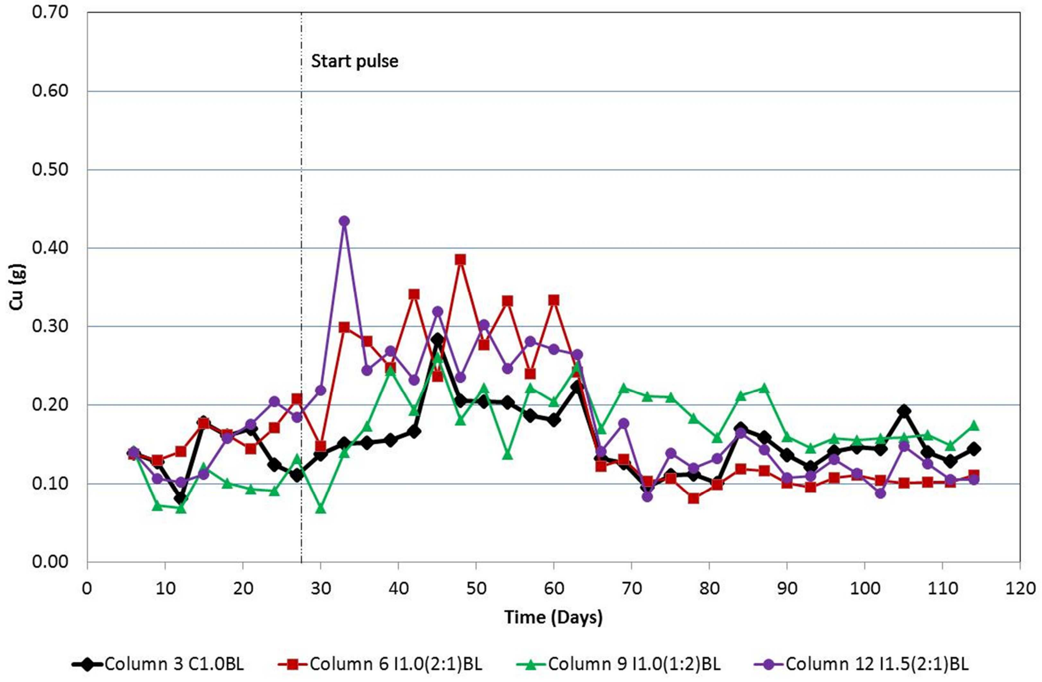

Figure 4-30: Copper extracted in PLS layered bioleaching Columns 3, 6, 9 and 12

The performance of layered bioleaching can also be explained by the cumulative copper extraction shown in Figure 4-31. A linear increase in copper extraction occurred from day 27 till day 66, but dropped from day 66. Notably the daily copper extractions for Columns 6 and 12 were similar. The daily cumulative copper extractions of Column 3 decreased after day 27 and were lower than Columns 6 and 12, but higher than Column 9. After day 66 the cumulative daily copper extractions for Column 3 were lower than Column 9. Noticeably the cumulative daily copper extractions for Column 9 remained linear for the remainder of the experiment. The total cumulative copper extractions for Columns 3, 6, 9 and 12 were 24 %, 28 %, 26 % and 28 % respectively over 114 days. The lower daily cumulative copper extraction observed for Column 3 after day 27 could be attributed to the low copper extraction before day 27, due to low feed rates/volumes. If the data before day 27 were not taken into account, the cumulative copper extraction would have been the same for Columns 3 and 9 until day 66 (not shown).

The cumulative extraction of total copper (Figure 4-31) may also be considered on a basis of the volume of irrigation applied, as shown in (Figure 4-32). The highest irrigation volumes processed over 114 days was 105 L for continuous Column 3 and intermittent Column 12 with a 24 % and 28 % extraction respectively. This was followed by Column 6 with 28 % extraction at 77 L and Column 9 at 45 L with a copper extraction of 24 %.

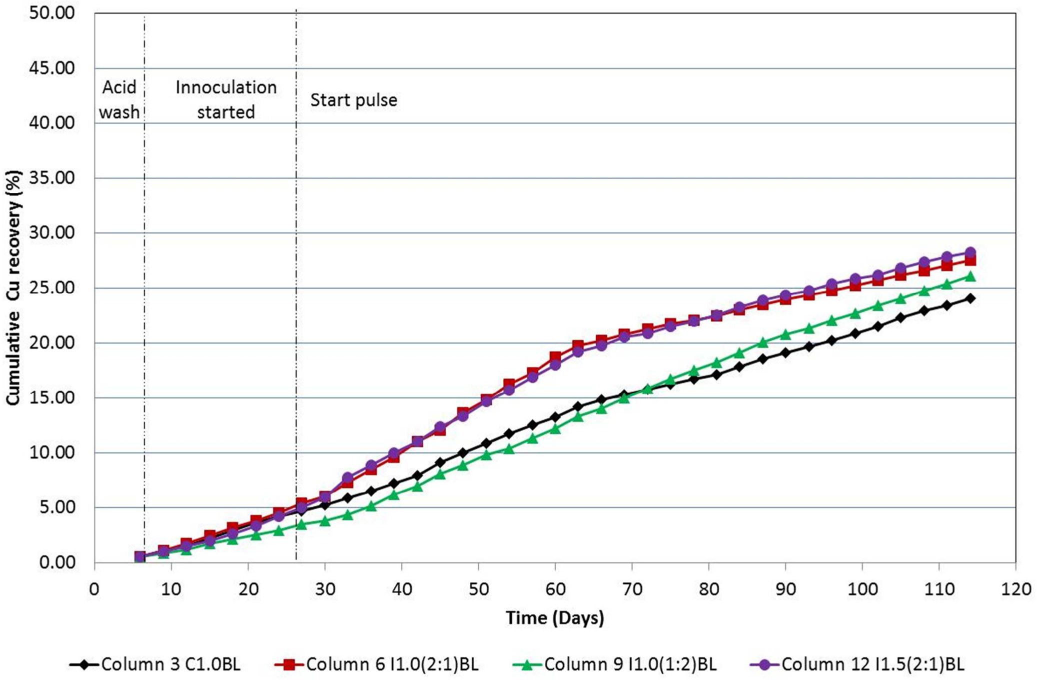

Figure 4-31: Cumulative copper extraction for layered bioleaching Columns 3, 6, 9 and 12

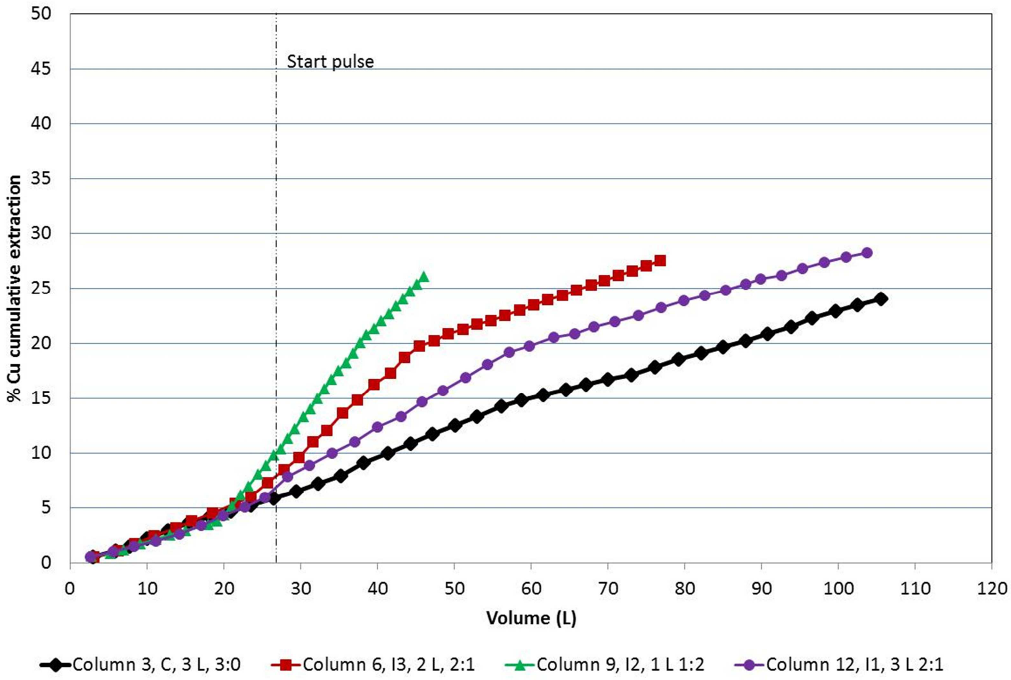

Figure 4-32: Cumulative copper extraction from layered bioleaching Columns 3, 6, 9 and 12

It should be remembered that the Fe^{2+} dissolution was in proportion with the reactants added as discussed in section 4.3.2 but the Fe^{2+} in the feed solution and subsequent Fe^{3+} conversion may have eliminated the rate limiting effects of the dissolution agent. This indicated that the copper leaching was independent of the Fe^{2+} leached from the mineral.

There were two distinct periods in the bioleaching of layered chalcopyrite (Figure 4-29 and Figure 4-30), which may be described as the most active part of the heap (days 27 to 66) where easy leachable minerals were leached, hence the rapid copper extraction. The second period was from day 66 onwards, characterised by a constant rate of copper extraction (see discussion in Section 4.2.4).

The daily copper concentrations (Figure 4-29) of continuous Column 3 between days 27 and 66 were lower than that of all the intermittent columns (6, 9 and 12). This indicated that applying intermittent irrigation irrespective of the frequency and flow rate yielded a higher copper extraction per unit volume. It may actually be argued that no change in the copper extracted per unit volume could be observed in continuous Column 3 for the duration of the experiment, but the actual copper extraction per column (Figure 4-30) showed that there was an increase in copper extraction between days 27 and 66. In order to continue this discussion it should be emphasised that 75 % of the coarse ore (+ 2 mm) was layered between 25 % of the fine particles (- 2mm). The influence of the coarse particles and fines could be observed in the low copper extractions (up to 28 %) as opposed to bio agglomerated columns, which had total extractions up to 40 %. Fines may cause permeability issues, restricting the effective fluid flow through the fine material and channelling the leachate in the coarse material, leaving some parts of the column untreated. More importantly the effective contact area of the ore particle is also reduced by the increase in particle size. Focus will be shifted to the effects of coarse material, because the increase in copper extraction in intermittent columns (6, 9 and 12) was in line with literature which suggested that intermittent irrigation favoured coarse particles in copper extraction *(Muñoz et al*., 1995; Pradhan *et al*., 2008). Also this alternate draining and drying of the capillaries is faster than ionic diffusion through a static capillary, and therefore increases leaching rate and eliminates salts on the mineral surface.

Ignoring the influence of packing as discussed above, increasing the flow rate to 1.5 L/day in intermittent irrigation showed that Column 6 yielded a higher copper extraction per unit volume than Column 12 between days 27 and 66. Similarly it should be mentioned that the total copper extraction for Columns 6 and 12 were similar. This may be argued, as in section (4.2.4), that increasing the flow rate will not increase the rate of the leaching reactions or yield more copper if the slow dissolution of the mineral is the rate limiting factor.

Decreasing the intermittent frequency showed that intermittent Column 9 (1 day on; 2 days off) had a higher copper extraction per unit volume than Column 6 (2 days on; 1 day off) between days 27 and 66. Similarly the actual copper extracted per column was higher for Column 6 than 9. Decreasing the intermittent frequency and increasing the resting period will increase the copper extraction per unit volume, which indicated that during the resting period leaching reactions were still taking place. However the actual copper extracted (which was higher for Column 6) indicated that the rate limiting effect was the reagent addition. During the two days stagnant period most of the available reactants may have been used up.

After day 66, Columns 3, 6 and 12 had similar concentrations. This indicated that the copper extraction was proportional to the amount of reactants added and intermittent irrigation had no effect on copper extraction when steady state was achieved. However increasing the resting period showed that Column 9 had a higher copper extraction per unit volume. This indicated that the increase in the resting period when the availability of the mineral is the rate limiting factor increases the residence time of the stagnant solution. This may in turn increase the effective transfer of ions between the mineral particle and stagnant solution, thus increasing the copper dissolution. Once the irrigation was started the concentrated liquid moved out the capillaries and was washed off in the PLS.

The cumulative copper extracted (Figure 4-31) indicated that intermittent Columns 6 and 12 had a total copper extraction of 28 % and had the same extraction rate throughout the experiment up to day 88. These similar extractions strengthened the fact that higher flow rates will not increase the copper extraction, if the rate limiting step is the slow dissolution of the mineral. However, after day 88 the extraction rate of Column 6 decreased faster than Column 12. This indicated that increasing the reactant volume will increase the copper extracted if the rate limiting step shifts towards the low availability of the mineral. The linear increase in copper extraction rate for Column 9, indicated that within time (30 days extrapolation, not shown) the cumulative copper extraction will be similar than that of Columns 6 and 12. This indicated that within time the low reactants will not be the rate limiting step in the copper extraction and the longer resting period will increase copper extractions.

The cumulative copper extracted per unit volume (Figure 4-32) in 114 days indicated that intermittent Columns 3 (105 L, 24 %), 6 (77 L, 28 %), 9 (46 L, 26 %) and 12 (104, 28 %) had different copper extractions over a 114 days. The application of ½ of the feed volume to Column 9 and ¾ of the feed volume to Column 6 confirms the fact that the copper extraction was not dependent on the feed volumes to the system. It may also be emphasised that the microbial activity, which was responsible for the generation Fe^{3+}, was not influenced by the resting periods. It may also be argued that the porosity of the coarse layers was not influence by the low volumes introduced into the system and that efficient wettability was achieved. The fact that Column 12 had a similar copper extraction than Columns 6 and 9 also gave an indication that, as long as the mineral is wet enough, the addition of more reactants did not increase the copper extraction. It may be concluded that the same reactions take place in the column irrespective whether the intermittent irrigation was applied or not.

The extraction has been compared on only using 46 L of feed by taking intermittent Column 9 as the basis due to the low feed volume., This showed that different amounts of copper were extracted for Columns 3 (12 % in 47 days), 6 (20 % in 63 days), 9 (26 % in 114 days) and 12 (15 % in 51 days). Similarly Columns 6 and 9 indicated that, as in agglomerated leaching (Section 4.3.4), the benefits of applying lower feed volumes with intermittent irrigation increase the copper leaching per unit volume. The higher flow rate of intermittent

Column 12 yielded a lower copper extraction than Columns 6 and 9. This was an indication that the lower mean residence time of the reactants (51 days) decreased the copper extraction rate. The low copper extraction for Column 3 suggested the importance of resting periods to maximise extraction per unit volume. It was clear that time was also an important factor to apply intermittent irrigation effectively (to minimize the amount of reacts to be used) to increase the copper extracted in bio layered columns.

4.4 Ore moisture content and liquid-hold up

The moisture content of the ore is shown to be at an average of 7 % by weight for all columns irrespective of the type of irrigation applied as shown in Table 4-6. The fact that the intermittent irrigation columns had similar moisture content to the continuous columns was an indication that the stagnant periods when the irrigation was stopped did not influence the moisture content in the column in an extreme manner. It can be safely concluded that evaporation was minimized throughout the leaching process by the addition of moisturised air. Also the high flow rates of Columns 10, 11 and 12 did not increase the average % moisture of the ore. It was already established in the previous discussions (Sections 4.1 and 4.2) that the moisture content in the ore was enough to maintain microbial activity and the necessary reagents to drive the leaching process during the stagnant periods.

On examining the individual layers of the coarse and fine particles, it was found that the % moisture of the finer partitions was higher than the moisture content of the agglomerated columns. Also the moisture content of the coarse layers was lower than that of the moisture content in the agglomerated columns. This was expected since the permeability of the fine partitions would decrease and the permeability for the coarse particles would increase. The fact that the average moisture content in the layered column was similar to those in the agglomerated columns was an indication that the fine layers did not increase the average moisture content of the column.

It is important to note that that the columns retain 7 % moisture content regardless of the irrigation regime. This suggests that there were no significant drying in the columns during the rest period, so the mineral surfaces remain wet.

Table 4-7 showed that the liquid holdup increased for layered Columns 3, 6, 9 and 12 which was ranged from 350 to 580 minutes. This was much higher than the liquid hold up in the agglomerated columns, which had liquid holdup between 90 and 129 minutes. This high liquid holdup in the layered columns was caused by the low permeability of the fine layers in these columns. In the layered columns the highest liquid holdup was observed for Column 12 at 580 minutes, which also had the highest flow rate at 1.5 L/min. Similarly in comparison the liquid holdup in high flow rate agglomerated Columns 10 and 11 was 93 and 105 minutes respectively. This was an indication that the fine layers restricted the fluid flow if high feed rates are applied, but not enough to increase the Cu and Fe substantially as shown in Figure 5-1and Figure 5-3.

Table 4-6: % moisture in columns:

Column	Mass wet ore	Mass dry ore	% moisture
1	2014	1860	8
2	2072	1926	7
3.1	167	140	16
3.2	746	712	5
3.3	226	191	15
3.4	773	739	4
3 average	1911	1782	7
4	1820	1712	6
5	2126	1984	7
6.1	205	170	17
6.2	673	648	4
6.3	242	207	14
6.4	750	723	4
6 average	1869	1749	6
7	1969	1859	6
8	2073	1957	6
9.1	219	187	15
9.2	735	707	4
9.3	186	160	14
9.4	818	788	4
9 average	1958	1842	6
10	1777	1666	6
11	1827	1707	7
12.1	168	150	11
12.2	742	707	5
12.3	193	150	23
12.4	740	698	6
12 average	1844	1705	8

** It should be noted that the layers in Columns 3, 6, 9 and 12 had been treated an analysed as individual samples.*

Table 4-7: Liquid hold up in columns

Column	Liquid residence time (min)	Measured drainage (ml)	Measured feed (ml)
1	129	37	58
2	144	40	94
3	353	-	223
4	134	28	66
5	90	39	86
6	437	63	298
7	90	41	88
8	105	54	59
9	465	50	320
10	93	41	78
11	105	45	90
12	583	70	370

4.5 Repeatability

The repeatability and inherent variations can be observed through analysing the first 27 days of operation during which all columns were operated under the same conditions. This means that the conditions across the four columns used for each leaching type were similar. All the columns were conducted at a temperature of 65 °C and irrigated at 1 L/day with a sulfuric acid solution with a pH 1.15 and contained 0.5 g/L ferrous iron.

It was clear from Sections 4.1, 4.2 and 4.3 that the pH's, redox potentials, Fe^{2+} concentrations, Fe^{3+} concentrations and total Fe concentrations had inherent variations, which are discussed in Sections 4.1, 4.2 and 4.3. However the inherent variations of the Cu were minimal or non-existent. This was an indication that the inherent variations of the pH, Fe and redox potential had a low impact on the extraction of Cu from chalcopyrite.

It should be mentioned that Column 9 had a lower cumulative Cu extraction before day 27. Applying this inherent variation does not indicate a difference in the performance of this column with relation to the other columns (3 and 6). This inherent variation was a result from low feed volumes due to pumping problems in the 1st 27 days, thus under performance of the column may be ruled out.

4.6 Cell detachments

Following the termination of each column experiment, the micro-organisms present on the ore were detached from the ore and quantified. These were divided into those micro-organisms associated with the ore, but not attached to it (interstitial cells) and those strongly or weakly attached (requiring vortexing with or without detergent to dislodge). The results, presented in Figure 4-33 and Figure 4-34, show that healthy microbial communities are established on the agglomerated ore, characterised by some 5-7 × 10^7 cells per kg ore. Conversely the microbial communities in the abiotic columns were below the detection limit. In the layered columns, a higher cell concentration was found in the layers of fine material than in the coarse layers. The cell concentration in the coarse layers was one to two orders of magnitude less that in agglomerated ore.

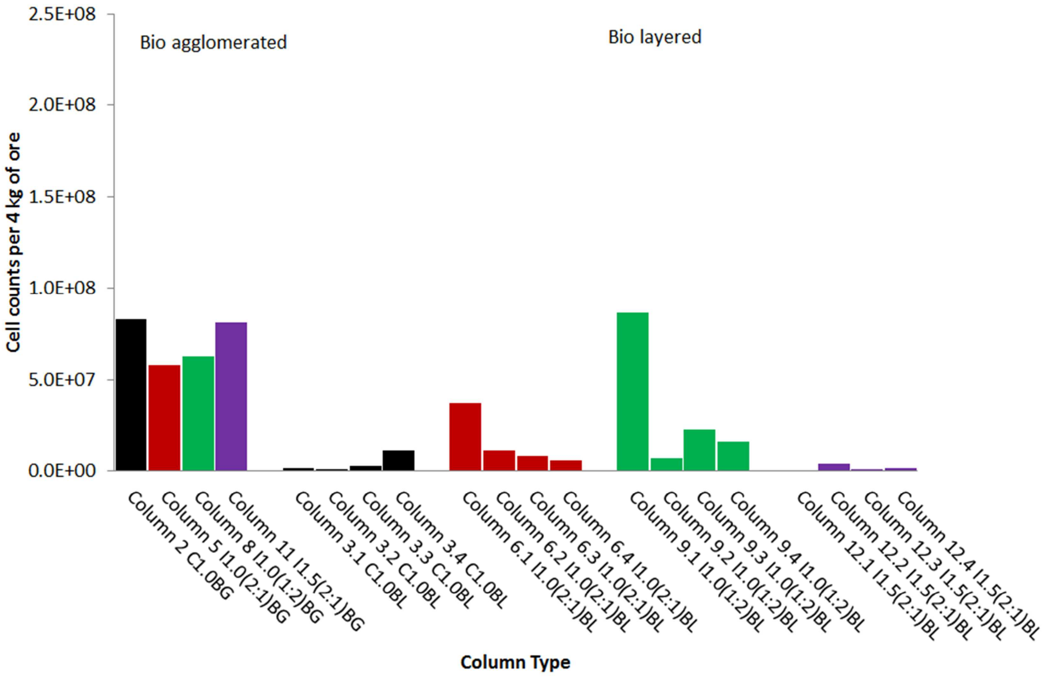

Figure 4-33: Microbial attachment for attached cells (strong plus weak) on post leached ore (fine layer: 3.1, 3.3, 6.1, 6.3, 9.1, 9.3, 12.1, 12.3 and coarse layer: 3.2, 3.4, 6.2, 6.4, 9.2, 9.4, 12.2, 12.4)

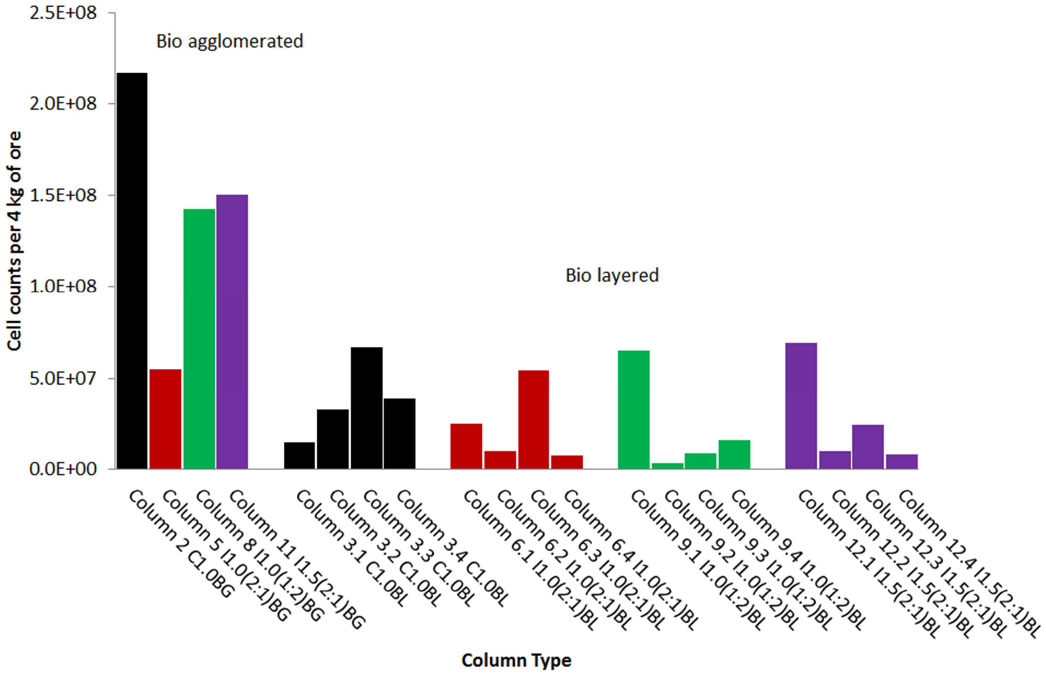

Figure 4-34: Microbial attachment for interstitial cells from drained ore bed on post leached ore (fine layer: 3.1, 3.3, 6.1, 6.3, 9.1, 9.3, 12.1, 12.3 and coarse layer: 3.2, 3.4, 6.2, 6.4, 9.2, 9.4, 12.2, 12.4)

CHAPTER 5 : RESULTS AND DISCUSSION (II):

EFFECT OF INTERMITTENT IRRIGATION ON FEED TYPE AND PACKING

In this chapter, the effects of intermittent irrigation on the different types of leaching (bio and abiotic) and different packings (agglomerated vs. layered) are compared, using the experimental data presented in Chapter 4. It should be noted that the cumulative total copper and Fe extractions are used in these comparisons. This is to discuss the overall influence of leaching types and packings on chalcopyrite leaching. The total copper and Fe extractions are compared at day 114 where liquid phase data is used because the columns were taken down over a period of 30 days. The total mass, provided in Table 5-2 and Table 5-3, is determined using the full time frame of the experiment. It should be noted that the AAS for total Fe will only act as a check for the spectrophotometry total Fe analysis and will not be used in the discussions in this chapter.

5.1 Biotic vs. abiotic leaching (leach type)

5.1.1 Copper extraction as a function of irrigation regime

The total copper extraction for the bio agglomerated Columns 2 (38 %), 5 (34 %), 8 (34%) and 11 (33 %) in each flow type (continuous irrigation or intermittent) was higher than its corresponding abiotic agglomerated Columns 1 (12 %), 4 (14 %), 7 (10 %) and 11 (16 %) for the same flow type, as shown in Figure 5-1. The low leaching that occurred in the abiotic columns was caused by the absence of microorganisms that oxidise Fe^{2+} ions to Fe^{3+} ions and generate acid, thereby regenerating these leach agents. Fe^{3+} is a powerful dissolution agent that oxidizes the base metal sulfide minerals to a soluble form (Pradhan *et al*., 2008). In abiotic leaching the low Fe^{3+}concentration prevented the dissolution reactions running to completion (Bolorundu, 1999), hence the low copper dissolution. Dissolution of chalcopyrite in an acid Fe^{3+} medium can be described by Equation 17, which suggested that adequate provision of the Fe^{3+} is crucial for chalcopyrite leaching (Lizama *et al*., 2003).

$$\mathrm{CuFeS_2 + 4Fe^{3+} + 3O_2 + 2H_2O \rightarrow Cu^{2+} + 5Fe^{2+} + S^0} \qquad (17)$$

It was clear that the amount of copper leached from the chalcopyrite was negatively affected by the low Fe^{3+} concentrations in the abiotic leaching system (Kametani & Aoki, 1985). As shown and discussed in Section 4.1.4, the copper extraction of abiotic leaching was dependent on the amount of reactants introduced to the system, while in biotic leaching (Section 4.2.4), extraction was independent of the rate of reactant supply, owing to the regeneration of the leach agents by the microorganisms present. In this case, it is postulated that the extraction was dependent on the availability of the mineral. The fact that similar total copper extractions were achieved across the different irrigation strategies in bio agglomerated leaching was an indication that intermittent irrigation had little effect over time on bioleaching. This was an indication that leaching took place during the stagnant periods and during the irrigation periods, the copper rich liquid was washed out. The postulated limitation of mineral availability in the bio agglomerated columns may be an explanation that intermittent irrigation did not increase the leaching rates. During the stagnant period, the moisture content was at an average of 7% as shown in Table 4-6. This was enough to sustain the microbial population and, in turn, the dissolution reagent to drive the copper leaching reactions forward in bioleaching. However in abiotic leaching the absence of microorganisms and the slow rate of chemical oxidation to regenerate the Fe^{3+} resulted in the depletion of oxidation reactants in this liquid layer. This explains the dependence observed of acidic/oxidative leaching on the rate of supply of the feed solution and thereby reactants. The copper extracted in abiotic leaching, although low $^{1}/_{3}$ of that through biotic leaching) demonstrated that a portion of the leaching under biotic conditions may result from chemical oxidation of the ferrous iron formed, as described by (Searby, 2006).

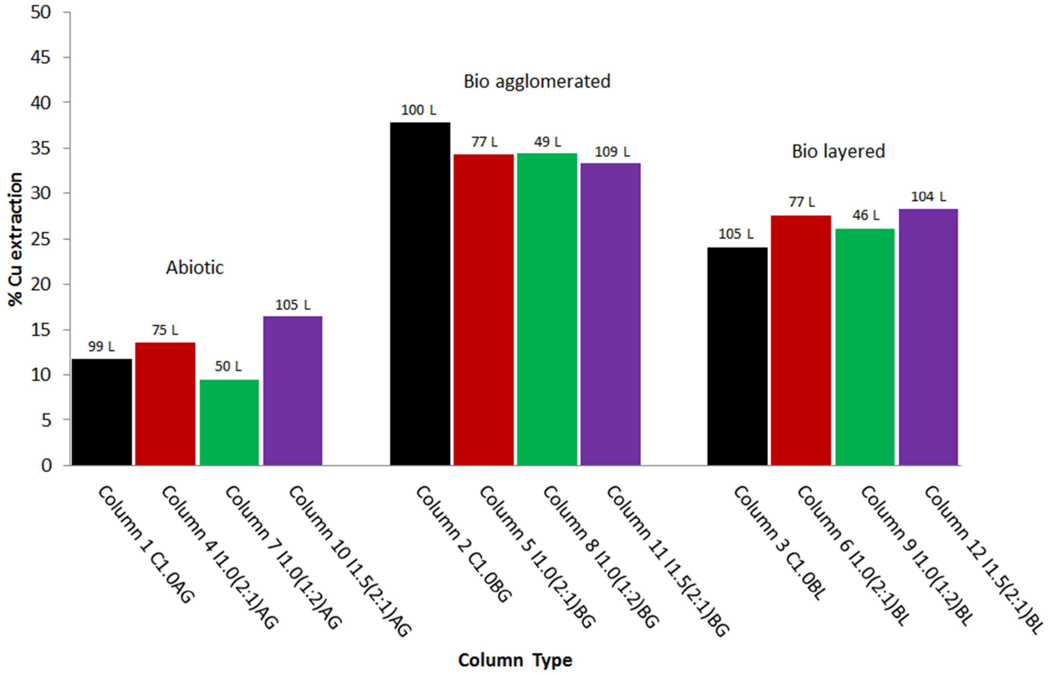

Figure 5-1: Total copper extraction at 114 days

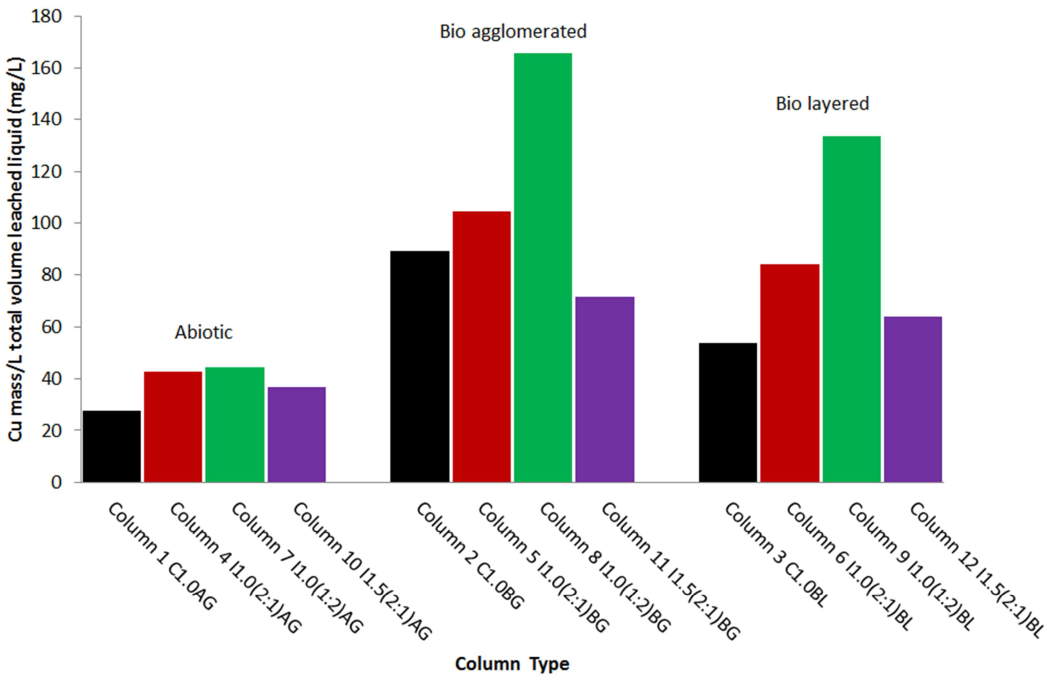

Figure 5-2: Total mass of copper extracted per unit volume of PLS over 114 days

Considering the total copper extracted per unit volume of PLS over 114 days, shown in Figure 5-2, it is clear that, in both abiotic and biotic systems, the copper extracted per unit volume increased for all intermittent columns. In biotic leaching, the highest copper extraction per unit volume of 166 mg/L was found for intermittent Column 8 (1 day on, 2 days off) while the copper extraction per unit volume for Column 5 (2 days on, 1 day off) was 100 mg/L and for Column 2 (3 days on) 89 mg/L. The abiotic intermittent Column 4 (1 day on, 2 days off) and Column 7 (2 days on, 1 day off) displayed a similar copper extraction per unit volume of 43 – 44 mg/L which was slightly higher than that of continuous irrigation in Column 1 of 28 mg/L. This illustrated that when the Fe^{3+} ion is the rate limiting reagent, the residence time of the stagnant solution does not affect the copper leaching per unit volume in intermittent columns to the same extent. However the significant increase in copper per unit volume in biotic columns indicated that if the leaching reagents are in excess and mineral availability controls the rate of leaching, an increase in residence time of the liquid does not increase the total copper leached per unit time, but does increase the copper leached per unit volume.

The lower copper leached per unit volume for both continuous Columns 1 and 2, relative to the intermittently irrigated columns under the same operating conditions, indicated that continuous flushing had little effect on copper leaching. This was confirmed by increasing the flow rate to 1.5 L/day in Columns 10 and 11 while using an intermittent irrigation regime of 2 days on followed by 1 day off. This indicated that an increase in reagent supply does not increase the rate of reaction if the availability of the mineral becomes the rate limiting effect as indicated by Ogbonna (2006).

5.1.2 Iron leaching as a function of irrigation regime

Figure 5-3 shows similar total Fe leaching patterns were achieved for abiotic Columns 1 (35 %), 4 (32 %), 7 (25 %) and 10 (35 %) as well as for the biotic Columns 2 (37 %), 5 (30 %), 8 (27 %) and 11 (35 %) over 114 days of operation. This similar behaviour between intermittent irrigated columns of a specific leaching type (abiotic and bio agglomerated columns) indicated that the Fe leached was dependent on the amount of reactants fed into the system and not the type of leaching.

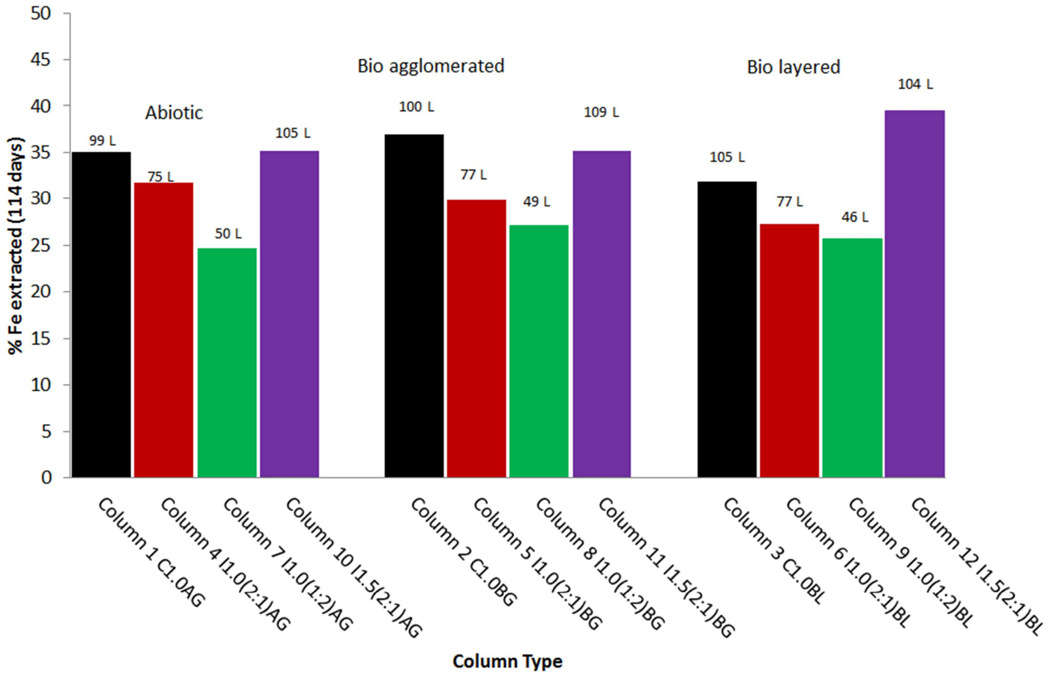

Figure 5-3: Total Fe extraction over 114 days (Including precipitation).

Table 5-1: Component mass balance of Fe leached from chalcopyrite ($CuFeS_2$)

Column	Actual Mass of Cu (g)	Theoretical Mass of Fe leached from $CuFeS_2$ (g)	Fe leached from other minerals (g)	Actual total Fe leached (g)	% Fe leached from other minerals relative to total Fe leached %
1	3	2	34	37	93
4	3	3	31	33	92
7	2	2	24	26	92
10	4	3	34	37	91
2	9	8	31	39	80
5	8	7	24	31	78
11	8	7	21	29	75
12	8	7	30	37	82
3	6	5	29	34	85
6	6	6	23	29	80
9	6	5	22	27	80
12	7	6	36	41	86

The component mass balance in Table 5-1, using the stoichiometry of chalcopyrite ($CuFeS_2$), indicated that in the abiotic columns 92 % of the Fe leached was from other sources than chalcopyrite. The particular mineral(s) from which this Fe was leached cannot be confirmed due to the limited amount of data available on the mineralogy, as shown in Table 3-1, and the absence of data of sulfate in solution. Owing to the low redox potential maintained in the abiotic columns, it may be refuted that the Fe leached was from pyrite due to the fact that pyrite leaching takes place selectively above 650 mV (Hiroyoshi *et al*., 2000; Güler *et al*., 2012).

The chalcopyrite leaching accounts for between 28 and 49 % of the amount of Fe leached in the biotic systems. However the total Fe leached (Figure 5.3) showed a small difference in Fe leaching between abiotic and bioleaching systems. Also Table 5-1 showed that only 80 % of the total Fe leached came from other sources in bioleaching, while biotic leaching showed 90 % Fe leached from other sources. This however does not follow convention that the Fe leached in abiotic columns is lesser than in biotic columns as shown with Table 5-1.

The following explanations might be plausible for the Fe leaching in biotic columns being lower than expected relative to the abiotic columns:

- The higher precipitation of Fe in the biotic columns, owing to both the higher overall iron concentration and higher redox potential, could have caused passivation effect around the gangue minerals. This means that the diffusion of the leaching reactants to the mineral occurred more slowly.
- Although chemical iron oxidation contributes to Fe^{2+} oxidation, it may simply be that the easy leachable mineral was already depleted in biotic leaching and more Fe leaching might happened in time since the leaching rate for abiotic leaching is much slower than that of intermittent irrigation.

5.2 Effect of Packing Type: Bio agglomerated vs. bio layered leaching

5.2.1 Copper extraction as a function of irrigation regime

The total copper recovery (Figure 5-1) for the bio agglomerated Columns 2 (38 %), 5 (34 %), 8 (34 %) and 11 (33 %) in each flow type (intermittent or continuous) was higher than for the corresponding bio layered Columns 3 (24 %), 6 (28 %), 9 (26 %) and 12 (28 %). This was in line with Miller *et al.* (2003) who demonstrated that uniform permeability is an important factor in effective leaching in a heap. This lower leaching rate that occurred in the bio layered columns was caused partly by the low contact time of reactants with the coarse ore fraction. Also, the layers of fines were characterised by high moisture content of 14 – 17% (Table 4-6) which caused low permeability and decreased the gas-liquid mass transfer rate to the leaching environment. The bioleaching rate is dependent on the oxygen transfer rate while microbial colonisation is dependent on the supply of carbon dioxide; hence limitation of gas-liquid mass transfer slows down the dissolution of the mineral sulfides including the chalcopyrite. It should be remembered that oxygen plays a key role in the regeneration of the Fe^{3+} ion to act as the oxidizing agent of the sulfide mineral (Córdoba *et al*., 2009). This layered phenomenon is normally caused by mud sliding and the movement of fines to the lower parts of the heap with time (O'Kane Consultants Inc., 2000). The rate of chalcopyrite leaching was strongly affected by the packing arrangement in heap bioleaching as well as by inconsistencies in packing inadvertently introduced into the heap.

Both the agglomerated and layered bioleaching systems were similarly affected by irrigation types, irrespective of the packing type. In bio agglomerated leaching all intermittent columns gave the same extraction in 114 days (33-34 %), with continuous irrigation yielding 38 % extraction. Also in the bio layered leaching all intermittent columns gave a similar extraction between 26 and 28 % in 114 days, but continuous irrigation gave a slightly lower extraction of 24 %. Analysis of the first 27 days of leaching during which the four columns for each packing type were leached under the same conditions suggested that an extraction difference of 4% was not significant at a high confidence interval. Hence, it may be argued that similar extractions were achieved for all columns and the intermittent irrigation did not increase the copper extracted over the 114 day time period. However, the copper leaching was influenced by the packing type. This is another indication that when the leach reagents were in excess owing to their microbial regeneration, the availability of the mineral becomes the rate limiting effect.

Considering the total copper extracted per unit volume over 114 days (Figure 5-2), similar patterns of copper extracted per unit volume were observed for the corresponding intermittent columns for the agglomerated and layered packing. For each packing, the copper extracted per unit volume was the highest for intermittent columns 8 and 9 (1 day on, 2 days off), followed by Columns 5 and 6 (2 days on, 1 day off); i.e. the copper extractions in these 4 intermittent columns were higher than in their counterpart continuous Columns 2 and 3. This was an indication that decreasing the irrigation frequency during intermittent irrigation while maintaining the same flow rate increased the copper leaching per unit volume, irrespective of packing type. It was also clear, that leaching continued during the stagnant period. The fact that both the high flow rate intermittent Columns 11 and 12 (1.5 L/day, 2 days on, 1 day off) had a lower copper per unit volume than the low flow rate intermittent Columns 5 and 6 (1 L/day, 2 days on, 1 day off) showed that increasing the flow rate did not increase the copper leaching rate where the availability of the mineral was the rate limiting effect. Agglomerated continuous Column 2 displayed a higher copper extraction per unit volume than its layered column counterpart, Column 3. This may be due to the coarse material in the layered packing providing a decreased contact time between the leach agents and the mineral. It may also be that the coarse material provided a lower active surface area, hence decreasing the availability of the mineral in this region of the column. Also the fines might have caused channelling of the leach liquid down the side of the column as well as decreased permeability with respect to both gas-liquid mass transfer and the liquid phase. When comparing the continuously irrigated column with the intermittent column receiving the same liquid volume, similar extractions per unit volume were observed. However with the agglomerated packing, the continuous irrigation yielded a higher extraction per unit volume (Column 2 vs. 11) whereas the opposite was found for intermittent irrigation (Column 3 vs. 12). This may be explained by the associated oxygen ingression.

5.2.2 Fe leaching and recovery

As discussed in Section 5.1.2 for the biotic and abiotic agglomerated columns, a similar leach pattern for Fe was achieved for bio agglomerated Columns 2 (37 %), 5 (30 %), 8 (27 %) and 11 (35 %) and bio layered Columns 3 (32 %), 6 (27 %), 9 (26 %) and 12 (39 %) for 114 days. This is shown in Figure 5-3. This similar pattern of leaching of Fe indicated that the amount of Fe leaching was influenced by the amount of reactants added to the system. Notably the total Fe leaching was higher for continuous irrigated Column 2 of bio agglomerated leaching than bio layered leaching. This may be due to a low contact time between the reactants and the mineral caused by the coarse particles, which in turn increased the permeability of this area of the packing. It may also be due to the coarser particles lowering the surface area of the mineral, thus lowering the availability of the mineral to be leached and eventually the rate of leaching. The leaching in the layered columns may also have been influenced by the fine layers with low permeability which had a moisture content of 15 % as shown in Table 4 6 . This low permeability might have caused short circuiting of the leach liquid, thus reducing the contact time between the ore and the reactants.

The total Fe leached was slightly higher in the high flow rate intermittent Column 12 (1.5 L/day) of bio layered leaching, than its counterpart in the bio agglomerated Column 11, which also had a flow rate of 1.5 L/day. This may be due to the fact that the high flow rate in these columns might have increased the mass transfer of reactants between the leachate and the mineral. The Fe precipitation (Table 5-3 5-3) in these two high flow rate columns was 10 % lower than the columns with intermittent irrigation, as shown in Table 4-2 and Table 4-4. It might be that the precipitation in the intermittently irrigated columns at the lower flow rate effectively decreased the diffusion of the reactants to the mineral as discussed in Section 5.1.2. This similar argument may be used to explain the higher Fe leaching in continuous Columns 2 and 3.

On the other hand the higher Fe leaching of Column 12 in comparison to Column 11 might have been influenced by higher flow rate that increase the wettability of the coarse fractions in the layered columns and the lower permeability due to the fine layers. This could be seen in the high liquid holdup of layered Column 12 of 580 min as opposed to the liquid holdup in column 11 of 105 minutes. Since the coarse fraction of agglomerated columns was separated from the fines, it may be safe to assume that the bulk of the leaching comes from the coarse ore owing to the saturated nature of the layers of fines. This was in line with the theory mentioned by Pradhan *et al.* (2008) and Muñoz, *et al.* (1995) that intermittent irrigation increased Fe leaching in coarse heap leaching, but may only be true for high flow rate intermittent irrigation systems, since all lower flow rate intermittent columns (1 L/day) showed a lower Fe leached than Column 12. The higher flow rate may be expected to increase the wetted surface area in the coarse layers (Fagan, personal communication).

5.3 Fe precipitation

Copper precipitated will not be discussed as the copper is a minor component in jarosite formation or Fe precipitation. The copper mass balance suggests that the copper precipitation is negligible (Table 5-2) and the precipitate was only analysed for Fe (Table 5-3 5-3).

Table 5-2: Copper Mass balance conducted across each column over full time period leached

Column No	Copper in ore - Pre-leach (g))	* Copper in ore - post leach (g)	Copper in effluent PLS (g)	Copper Precipitated (g)	* Copper Leached (%)
1	23	20	3	0	12
4	23	20	3	1	14
7	23	21	2	0	10
10	23	19	4	0	16
2	23	14	9	0	38
5	23	15	8	0	35
8	23	15	8	0	35
11	23	15	8	0	34
3	23	17	7	0	29
6	23	17	7	0	29
9	23	17	7	0	28
12	23	16	7	0	31

** Calculated value*

5.3.1 Abiotic vs. biotic agglomerated columns

A greyish colour was observed in the leached ore in the abiotic columns, which indicated that little Fe precipitation had occurred in abiotic leaching system. The Fe precipitated was quantified as: Columns 1 (2 g), 4 (2 g), 7 (3 (g) and 10 (2 g) as shown in Table 5-1 and

Figure 5-4. This was in contrast with the brown yellowish colour observed in the biotic columns that showed a much higher Fe precipitation. This was quantified using an oxalic acid extraction as Columns: 2 (11 g), 5 (14 g), 8 (15 g) and 11 (12 g). This low Fe precipitation in the abiotic columns may be due to the low Fe^{3+} concentration shown in Figure 4-3. High Fe^{3+}concentration is known to drive precipitation and jarosite formation especially above a pH of 1.5 (Vilcáez & Inoue, 2009). There was similar Fe precipitation in abiotic systems with the different irrigation types (continuous or intermittent), differing irrigation frequencies and flow rates, except for intermittent Column 7. The intermittent biotic columns showed a higher Fe precipitation than the continuous biotic columns. This suggested that the longer resting periods caused an increase in the Fe^{3+} concentration in the retained liquid, thereby increasing the chances of precipitation of Fe.

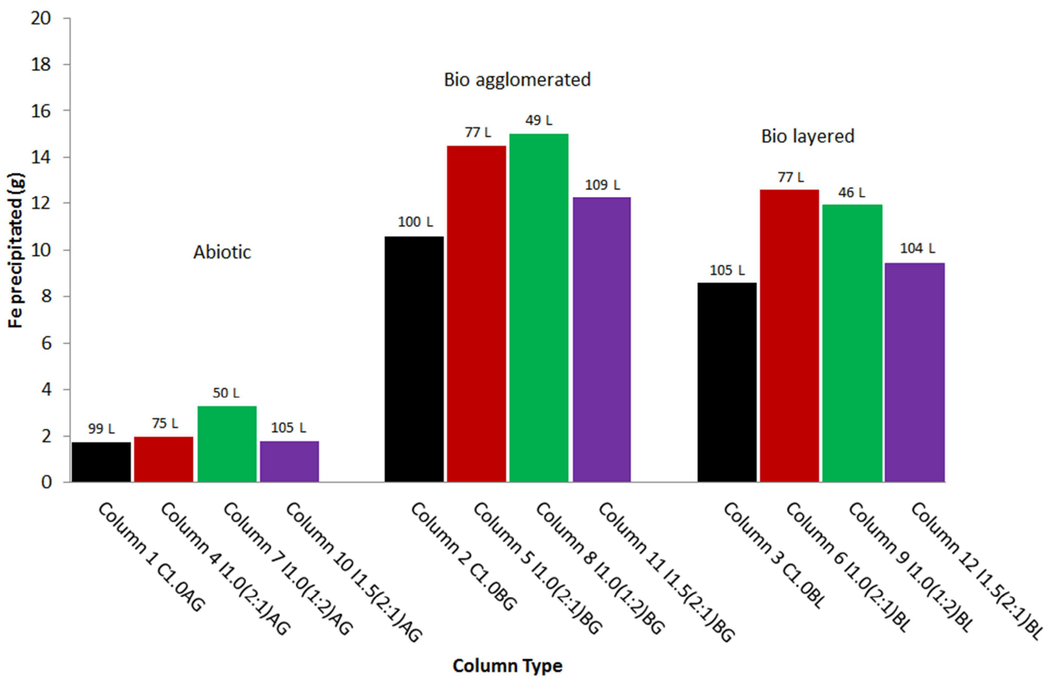

Figure 5-4: Fe precipitation determined on the ore on completion of the leaching experiment (114 – 134 days)

5.3.2 Bio agglomerated and bio layered columns

A brownish orange colour on the ore was only observed in bio agglomerated (Columns 2, 5, 8 and 11) and bio layered columns (Columns 3, 6, 9 and 12). This was an indication that precipitation occurred in the bioleaching columns due to the large amounts of Fe^{3+} generated by microorganisms. It must be noted that no work has been carried out to establish if the precipitate was jarosite; it was soluble in oxalic acid and in hydrochloric acid, consistent with jarosite. Comparing the bio agglomerated and bio layered columns showed that the continuous Columns 2 (11 g) and 3 (9 g) had a lower Fe precipitation than intermittently irrigated Columns 5 (14 g), 8 (15 g), 6 (13 g) and 9 (12 g). This indicated that continuous irrigation lowered the risk of Fe precipitation, because it prevented the build-up of high concentration regions or periods in the column and on the ore. This finding is consistent with the increased volumetric concentration of Fe^{3+} in the intermittently irrigated columns as well as the potential for a localised increase (in terms of time and space) in Fe^{3+} concentration. Columns 11 and 12, operated at the higher flow rate of 1.5 L/day, showed a lower Fe precipitation of 13 g and 9 g respectively, in both bio agglomerated and bio layered columns. This low precipitation in the continuous columns may be attributed to the continuous removal of leached Fe and thus reducing the time available to accumulate on the ore or increase the concentration of the stagnant liquid.

The high Fe precipitation that was observed in intermittent Columns 5 (14 g), 8 (15 g), 6 (13 g) and 9 (12 g) in both bio agglomerated and layered systems indicated that the increase in iron concentration in the stagnant solution increased precipitation on intermittent flow. As discussed in Sections 4.2.3 and 4.3.3, the high Fe precipitation might have been caused by the high Fe concentration of the PLS. The lower precipitation in Columns 11(12 g precipitation) and 12 (9 g precipitation), irrigated intermittently at an increased flow rate, showed that higher flow rates (1.5 L/day) increase the dilution rate of the concentrated Fe generated during the stagnant phase.

The fact that bio layered columns had a slightly lower Fe precipitation could be attributed to the fact that the coarse material lowered the active surface area of the mineral, thus decreasing the area to be precipitated.

Looking at the amount of Fe precipitated as a fraction of the total Fe leached (Figure 5-5) indicated that, in both packing systems, the shortest irrigation time used in Columns 8 and 9 (1 day on, 2 days off, 1L/day) gave a higher Fe precipitation per total Fe leached at 21% and 27 % than Columns 5 and 6 (2 days on, 1 day off, 1L/day) with a precipitation of 18 and 23 % respectively. This higher Fe precipitation per unit of total Fe leached was an indication that lower PLS volumes with higher Fe concentrations increased the likelihood of precipitation. Resting periods had a significant influence on the precipitation of Fe in the system due to the increase in Fe concentrations during the stagnant phase. Similarly the higher flow rate in Columns 11 and 12 (2 days on one day off; 1.5 L/day), compared to Columns 5 and 6 (2 days on, 1 day off; 1 L/day) increased the dilution of the concentrated

Fe generated during the stagnant phase. It also showed that the continuous removal of iron in Columns 2 and 3 effectively kept the Fe concentration low during the leaching period.

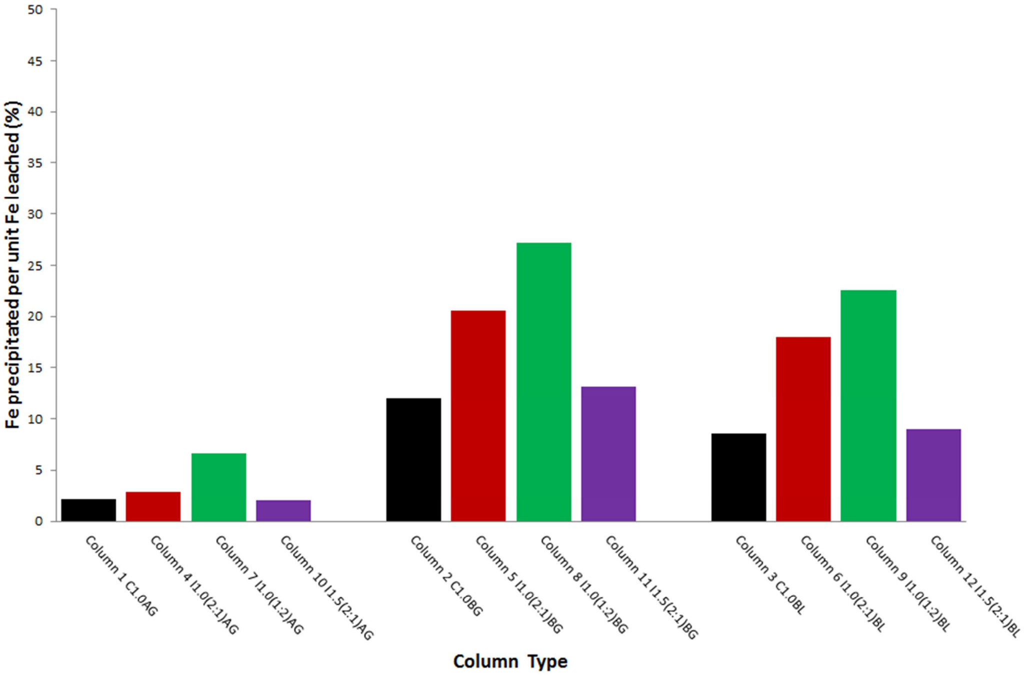

Figure 5-5: Fe precipitated per unit total Fe leached

Table 5-3: Fe mass balance conducted across each column over full time period leached *

Column No	Fe in ore- pre-leach (g)	Fe added in feed (g)	* Fe in ore - post- leach (g)	Fe in PLS (g)	Fe Precipitated (g)	* Fe Leached (%)
1	105	50	69	85	2	31
4	105	39	73	69	2	27
7	105	27	81	48	3	21
10	105	54	69	88	2	30
2	105	53	66	82	11	33
5	105	40	72	59	14	29
8	105	26	74	42	15	28
11	105	59	66	85	12	33
3	105	69	69	97	9	30
6	105	43	75	60	13	26
9	105	26	76	43	12	26
12	105	66	61	101	9	37

** Calculated value*

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

The effect of intermittent irrigation on the extraction of copper in heap leaching systems was investigated by applying three different regimes of intermittent irrigation and comparing these with the continuous irrigation at 1 L/day, corresponding to 5 L/m^2/h typically used at large scale. Two of these intermittent irrigation systems were applied to investigate the effect of the duration of the resting period during intermittent irrigation at a constant flow rate i.e. “1 day on, 2 days off” and “2 days on, 1 day off” at 1 L/day. Furthermore, to simulate high flow rate in intermittent systems whilst keeping the resting period fixed at 2 days on and 1 day off, the third intermittent irrigation rate was increased to 1.5 L/day. Further, the latter system used the same amount of irrigant as continuous irrigation. All irrigation variables mentioned above were applied in both the abiotic and the biotic leaching systems to investigate the effect of intermittent irrigation on each leaching type, where the abiotic agglomerated leaching system acted as a control against the biotic agglomerated leaching system. This facilitated the investigation of the effect where the irrigant is the supply of the leach agent and where supply of leach agent is independent of the irrigant supplied. Also, layered packing was introduced with these different irrigation variables to simulate the effect of the displacement of fines in heap leaching. It should be noted that only copper was used as an indicator of the extent of the leaching of the base metal sulfide ores since the bulk of the Fe was leached from the iron-containing gangue and would not be a true indicator of the extent of mineral sulfide leaching. The extent of leaching will be discussed by referring to the total copper extracted in each column over the time period and the total copper extracted per unit volume by referring to Figure 5-1and Figure 5-2.

The first hypothesis set up for this study addressed the impact of intermittent irrigation on bioleaching systems. The hypothesis was formulated as follows:

“On applying intermittent irrigation conditions to heap bioleaching systems, the copper recovery is unchanged relative to the continuous irrigation, resulting in increased copper recovered per unit volume of leach liquor”.

The extent of copper leaching was used as an indicator of whether the leaching of the sulfidic mineral was changed by intermittent irrigation in comparison to continuous leaching. It was found after the full duration of the experiment (i.e. 114 days) that the extent of copper extraction was similar across all the intermittent irrigation systems, irrespective of flow rate or resting period, for the bioleaching systems. The similar copper extraction during the different resting periods confirmed that during the stagnant periods the reactants available were sufficient to sustain an active microbial population as seen in Figure 4-12, which was confirmed by the high redox potential of 600 mV in the PLS (Figure 4-12), indicating a high Fe^{3+}:Fe^{2+} ratio in the PLS (Figure 4-13). The sustenance of an active microbial population as seen in Figure 4-33 is important because microorganisms are required to regenerate the dissolution agents (Fe^{3+} and the acid) so as to drive the leaching reactions and continuously maintain copper liberation. To assess whether fluid flow affected the extent of leaching of the chalcopyrite, different flow rates were tested. The copper extraction showed that an increase in the flow rate during the intermittent irrigation regime did not result in a change in the extent of the copper extraction under biotic conditions. This indicated that copper extraction using an intermittent irrigation was independent of the flow rate across the range tested as long as the reagent was not the rate limiting factor. The amount of copper extraction per unit volume of PLS increased with an increase in the resting period at a constant flow rate due to the lower feed volumes added during the active feed periods of intermittent irrigation. It was shown that only $^1/_3$ of the feed volume was required to yield copper extractions similar to continuous irrigation (where only the period of intermittent irrigation was considered i.e. disregarding the first 27 days of continuous leaching which was applied to all the columns before intermittent irrigation was initiated). In conclusion, the data generated through the experimental study supported the first hypothesis. However it should be noted that increasing the flow rate of intermittent irrigation do not increase the Cu per unit volume where the slow dissolution rate of the ore is the rate limiting effect.

The second hypothesis formulated addressed the effect of intermittent irrigation on abiotic leaching, as follows:

"There is no impact on copper leached per volume of leach liquor when applying intermittent irrigation on abiotic leaching".

The impact of intermittent irrigation on abiotic leaching was compared with its impact on copper leaching of biotic agglomerated columns discussed in the previous paragraph. Contrary to the bioleaching columns, it was found that for abiotic leaching using intermittent flow regimes had a minimal impact on the amount of copper extracted per unit volume of PLS. The Cu extraction per unit volume was similar in all abiotic leaching experiments irrespective of the type of irrigation applied. The extent of the copper extraction over the 114 days decreased as the length of the stagnant periods increased. This was a result of the depletion of reactants as the length of the resting periods increased because little regeneration of the leach reagents occurred during the resting periods. The inability of conditions in the abiotic columns to regenerate the dissolution reagent (Fe^{3+}) as shown in Figure 4-3 caused a rate limiting effect in copper extraction in intermittent irrigation. The increase in the intermittent irrigation flow rate and associated increase in reactant addition increased the copper extraction under abiotic conditions. The lower copper extraction per unit volume in the continuous column than the intermittent columns indicated that resting periods increased the copper extraction per unit volume of PLS in abiotic leaching. Largely the second hypothesis has been supported, owing to the supply of leaching reactants being limiting. The small increase in copper extracted during intermittent irrigation over continuous irrigation may be attributed to insufficient contact time for complete reaction under continuous irrigation or to the small contribution off chemical oxidation to the regeneration of leach agents.

The third hypothesis posed for this research addresses the packing of the ore:

"The nature of packing (agglomerated and layered ore) influences the efficiency of leaching by the formation of layers of fines between the regions of coarse material".

The impact of the displacement of fine material, as a natural phenomenon over time, on copper heap leaching was investigated in layered columns set up to simulate the coarse (highly permeable) zones and layers of fines (of low permeability) in a heap leaching system. It was found that the copper extraction from layered heap bioleaching was lower than that of agglomerated (non-layered) bioleaching columns in which both the fines and coarse particles were included in the agglomerates. This indicated that the development of fines in a heap leaching operation negatively affects the Cu extraction. These lower Cu extractions might have been caused by the reduction of the contact of the reactants with the active surface area of the coarse particles which accounted for 75 % of the packing mass (as shown in Table 3-2) of the ore in the column, which in turn decreased the availability of the mineral. The fact that similar levels of copper extraction were achieved between the irrigation regimes in the layered columns indicated that the leaching reagent was not a rate limiting effect in Cu extraction under biotic conditions. It may be argued that the fine layers affected the mass transfer of oxygen in the column by decreasing permeability which was confirmed by the high moisture content of 15 – 27 % in fine layers opposed to a low moisture content of 4 % in the coarse division shown in Table 4-6. Oxygen is required for both abiotic and biotic mineral oxidation reactions. Also the fine layers might have caused short circuiting of the flow to the wall of the column thus reducing the contact of the liquid with the coarse material. The similar Cu extraction over time indicated that an increase in the stagnant period produced an increase in the Cu leached per unit volume in heap bioleaching systems irrespective of the packings.

The higher copper extraction of bio-agglomerated columns indicated that bio agglomeration produced the ideal environment for effective copper extraction by eliminating rate limiting factors of the effective leaching area, wettability and low permeability. The development of pockets of low permeability which develop over time can influenced the efficiency of copper extraction, by leaving parts of the heap untreated. This research also shows the applicability in the prevention of ARD in layering fines in between waste ore and tailings by the lower extraction copper and iron, which is an indication of lower sulfide formation.

6.2 Recommendations

Based on the findings reported in this study it is recommended that the following should be investigated in further research.

- Longer resting periods in intermittent irrigation should be investigated to establish the most efficient cost-effective irrigation scheme to increase the Cu extracted per unit volume.
- In-depth research should be done on the effect of intermittent irrigation on the microbial population, its location and surface chemistry of the ore. This may be done in an experimental setup that allows in-bed sampling on a regular basis to determine the microbial behaviour, conditions in the stagnant liquid phase and ore surface conditions during the stagnant periods.
- An abiotic control should also be introduced in the layered packing to compare the effects of intermittent irrigation on the heap bioleaching system where fines accumulate. Further, covers are used to restrict the formation of ARD and it has been proposed that this could be improved by the inclusion of layers of fines within the waste rock dump. The abiotic test work would assist in confirming the value of this approach.

- Prevention of ARD formation under intermittent conditions could be studied through altering the permeability of the fines, layer thickness and number of fine layers.

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APPENDIX A : DETAILED METHODS

Acid wash method

- Prepare a 0.2 Molar hydroxylamine (Distilled water and) and oxalic acid solubilisation solution according to relevant stoichiometry as shown below.

1.1 Reagents and preparations

Hydroxylamine

Molecular weight = 69.49

$$Molarity = \frac{Molar\ Mass}{Volume}$$

$$Molarity = \frac{\frac{n}{moles}}{Volume}$$

$$0.2 = \frac{\frac{n}{69.49}}{2}$$

$$mass = 27.796$$

Oxalic Acid

Molecular weight = 126.09

$$Molarity = \frac{Molar\ Mass}{Volume}$$

$$Molarity = \frac{\frac{n}{moles}}{Volume}$$

$$0.2 = \frac{\frac{n}{126.07}}{2}$$

$$mass = 50.4$$

Add the calculated masses to 2 litres of distilled water to make up 0.2 M precipitation/solubilisation solution.

1.2 Wash Method

- Add 250g of dry ore to 500 ml solubilisation solution in an Erlenmeyer flask and shake in an incubator for 24 hours at 70 ºC.
- Filter shaken mixture after 24 hours.
- Measure filtrate and weigh the wet retentate. Ensure that dry filter paper is being weigh.
- Dry retentate and weigh. Pulverize retentate and send sample for acid digestion and subsequent Cu, Fe and S analysis.
- Measure total Fe on photo spectrometer. Add extra hydroxylamine to sample for Fe measurement.
- Filtrate can also be analysed by AA to determine Cu and Fe concentrations.
- Initial test on ore sample can be done to determine the amount of time to spend in a shaker. This is done by measuring the Fe total content of the solubilisation solution during the shaking procedure every two hours until a constant Fe is observed.

Fe analysis (Spectrophotometry)

2.1 Reagents and preparations

- Prepare 1-10 phenanthroline ($C_{12}H_8N_2.H_2O$) indicator solution
- Dissolve 2.127.08 mg of phenanthroline in 100 ml of distilled water.
- Dilute to 1000 ml inn a volumetric, covered with foil and for 24 hours. Cover volumetric flask with foil.
- Transfer solution to a storage bottle, which are covered with foil.
- Prepare ammonium acetate ($NH_4C_2H_3O_2$) buffer solution.
- Dissolve 250 g of ammonium in 150 ml of distilled water.
- Add 700 ml of concentrated glacial acetic acid.
- Stir and transfer to storage bottle.
- Prepare 1.8 acidified MilliQ water by adding sulfuric acid (H_2SO_4)
- Prepare a black solution in a test tube to calibrate the spectrophotometer. This blank contains:
- Set the spectrophotometer to 510 nm and zero.

2.2 Dissolved Fe^{2+} measurement

- Measure dissolved Fe^{2+} by adding and centrifuging the following solutions in a test tube:
    - 2 ml acetate buffer
    - 2 ml phenanthroline
    - 980 µl of MiliQ water.
    - 20 µl of sample.
- Transfer mixed solution to a 2 ml cuvette.
- Insert in calibrated spectrophotometer and record the wavelength.

2.3 Dissolved total Fe measurement

- Transfer solution back into the tube and add one scoop of hydroxylamine and vortex for two minutes.
- Allow to stand for 5 minutes, transfer solution back into cuvette and read the absorbance from the spectrophotometer.
- Transfer mixed solution to a 2 ml cuvette.
- Insert in calibrated spectrophotometer and record the wavelength.

2.4 Dissolved Fe^{3+}

- Subtract the wavelengths of the Total Fe from Fe^{2+} to give the Fe^{3+}.

2.5 Fe concentrations

- Prepare a standard curve, which is shown in Figure: A-1 (absorbance vs. concentration) by diluting ferrous Fe stock to 10, 20, 30, 40 and 50 $mg.l^{-1}$. Get the slope of the graph and identify in y = mx + c and use in calculation.
- Determine the various Fe concentrations from:

$$concentration = \frac{absorbance}{m} \times dilution$$

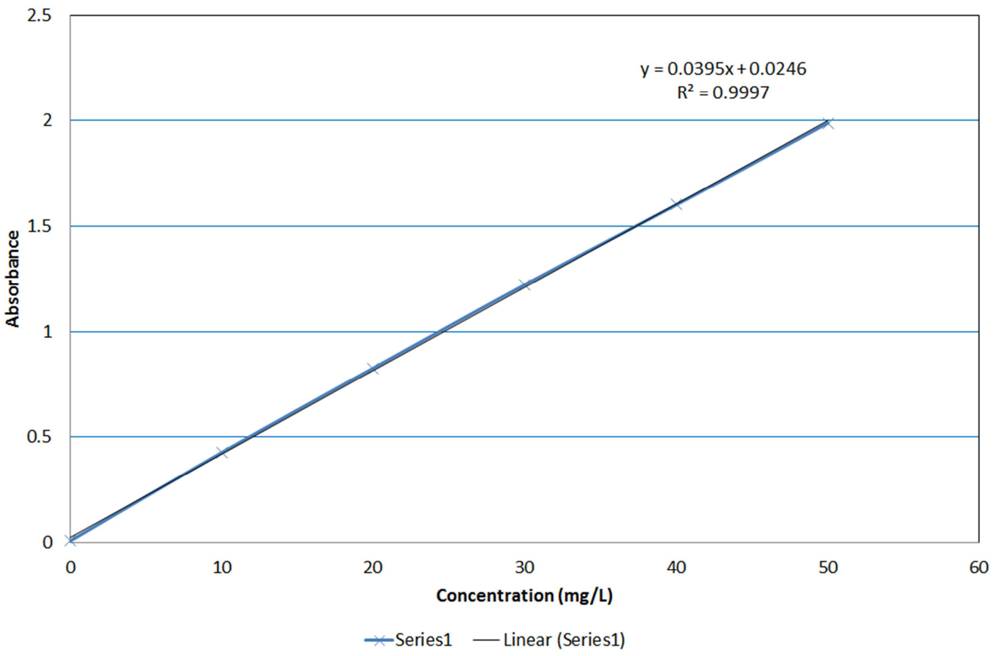

Figure A-1: Standard curved used to obtain the Fe^{2+} and total Fe concentration

Cell detachment

3.1 Preparation

- Make up two batches of 1.15 feed solutions without sulfur sulfate.
- Mix Tween 20 to one batch of the above mentioned feed solution to form a wash media of 0.4 % v/v.
- Sterilize all equipment (e.g. sealable bottles, Erlenmeyer flasks, JA-10 sample bottles and measuring cylinders), wash media and tween media before detachment process.

3.2 Interstitial cells

- Weigh 250 g of post leached ore.
- Weigh 250 ml wash media, record the mass and into an Erlenmeyer flask with post leached ore.
- Gently mix the mixture, while not detaching the strongly or weakly detach cells. 10 turns to the left and 10 turns to right would be enough.
- Transfer slightly settled suspension to a JA-10 tube. Try not to not transfer solids from the solution. Note that six detachments can be done at a time. Otherwise balance the

centrifuge tubes accordingly. Record the mass of any was media added to balance the centrifuge tubes if necessary.

- Centrifuge for 4 min at 800 g. Centrifuging time may be increased to clear solution if needed.
- Carefully remove the supernatant solution and record the total volume recovered.

3.3 Attached cells (weakly and strongly)

- Weigh 250 ml of tween solution and add to the remaining ore left in the Erlenmeyer flask.
- Shake it in an incubator at 65 ºC and 160 rmp for 24 hours
- Vortex solution for 2 minutes and transfers a slightly settled suspension to a JA-10 tube. Try not to not transfer solids from the solution. Note that six detachments can be done at a time. Otherwise balance the centrifuge tubes accordingly. Record the mass of any was media added to balance the centrifuge tubes if necessary.
- Centrifuge for 4 min at 800 g. Vortexing time may be increased to clear solution if needed.
- Carefully remove the supernatant solution and record the total volume recovered.
- Add 250 ml of tween solution and the remaining ore and centrifuge it for 2 minutes. Repeat the above transfer and centrifuging steps. Remember to record the supernatant solution volume and add it to the previous detached solution.

3.4 DNA extraction preparation

- Filter the supernatant solutions using a micro filtering system (45 µm). Wash the retentate off with 1.5 ml 0 K nutrient medium into a 10 ml Eppendorf tube. Ensure that all the cells are washed off in the 0 K nutrient medium. Vortex solution transfer solution to 1.5 ml Tube Eppendorf tube.
- Count cells and send for speciation and DNA Extraction.
- Centrifuge solution at ultra-high speed.
- Remove and discard supernatant
- Store cell mass in tissue lysis buffer.
- Send for DNA extraction
- Note: Centrifuging for an extra 10 minutes may clear any cloudy supernatant solution.

APPENDIX B : CALCULATIONS

Moisture content calculation

$$\%\, moisture = \frac{Wet\ ore\ mass - Dry\ ore\ mass}{Wet\ mass} \times 100$$

Copper recovery calculations

$$mass\ of\ copper\ extrated = Copper\ concentration \times Effluent\ volume$$

$$\%\, copper\ extraction = \frac{Mass\ of\ copper\ extracted}{Total\ mass\ copper\ in\ ore} \times 100$$

Net hydrogen calculations

$$pH\ =\ \log[H^+]$$

$$\therefore [H^+] = 10^{-pH}$$

$$moles\ of\ hydrogen = molar\ hydrogen\ concentration \times volume\ in\ PLS$$

$$net\ hydrogen\ consumption = moles\ of\ hydrogen\ in - moles\ of\ hydrogen\ out$$

Fe calculations

$$Fe^{2+}\ concentrantion = \frac{absorbance \times dilution}{m}$$

Where m is the slope of the of the absorbance vs concentration graph : y = mx + c

Similar calculation for total Fe concentration

$$Fe^{3+} = Fe^{tot} - Fe^{3+}$$

$$mass\ of\ Fe\ in\ PLS = Fe^{tot} \times PLS\ volume$$

$$total\ Fe\ leached = mass\ of\ precipitation + mass\ of\ Fe\ in\ PLS$$

Precipitation

$$\%\ preciptation = \frac{mass\ precipitation}{mass\ total\ Fe\ extracted}$$

Liquid hold up

$$Feed\ volume = volume\ of\ initial\ feed - volume\ of\ feed\ left$$

$$Feed\ mass = mass\ of\ initial\ feed - mass\ feed\ left$$

APPENDIX C : RAW DATA (THREE DAY INTERVALS)

Volume (ml)

Days	Column number											
	1	2	3	4	5	6	7	8	9	10	11	12
3	1440	2900	2660	2500	1000	3020	2980	2710	2100	2660	2860	1600
6	2460	3100	2960	2780	1860	3100	3100	2960	2700	2760	2940	2690
9	2200	3020	2960	2650	3100	3150	3100	2950	2530	2750	2600	2910
12	1720	2060	1780	1730	2190	2140	2310	1340	1748	2680	2870	2700
15	2540	2690	2350	2340	2930	2540	2970	2840	2150	2860	3120	2890
18	2270	2800	2690	2200	3050	2840	2750	3020	2000	2900	3150	2990
21	2760	2610	2740	2780	2960	2020	3040	2040	1840	2880	3080	2880
24	2600	2730	2700	2710	1100	2760	2830	2700	2050	2820	3020	2830
27	2600	2730	2700	2710	2910	2930	1800	2920	2900	2780	3000	2800
30	2600	2600	2700	1900	2060	2100	1070	1070	1200	2700	2700	2700
33	2840	2860	2920	1880	2000	2150	1080	1000	900	2890	3100	2890
36	2840	2810	2910	1940	2100	2120	1080	1000	1050	2980	2800	2900
39	2800	2830	2890	1940	1760	1920	1160	1040	1140	2970	3160	2940
42	2820	2700	2920	1960	2010	1820	1010	910	1030	3010	3120	2940
45	2820	2750	2920	1940	2120	1880	1150	950	1150	2800	3150	2960
48	3210	3050	3220	2180	2040	1940	1180	1010	1110	3100	3100	3100
51	2750	2700	2970	1890	1920	2020	1200	1000	1040	2700	2870	2700
54	2700	2050	2850	1820	1960	2100	910	950	890	2750	2920	2750
57	2650	2600	2970	1840	2040	2120	990	990	890	2820	3020	2860
60	2210	2250	2850	1840	1920	1820	910	930	900	2810	3020	2840
63	2770	2740	3090	2110	2110	1970	1120	1130	1100	2760	3060	2860
66	2610	2680	2650	2190	1940	1980	900	930	910	2760	3000	2600
69	2720	2700	2870	1940	1900	1820	930	950	900	3100	2990	3200
72	2450	2570	2900	1840	1960	1870	920	940	940	2790	3040	2710
75	2460	2410	2660	2060	2140	1840	910	1030	910	2500	2790	2510
78	2760	2720	2850	1880	2040	1800	960	990	960	2720	3000	2710
81	3020	2820	3050	1840	2080	1880	960	960	930	3020	3220	3120
84	3040	2780	3040	1800	2040	1860	920	960	900	2840	3120	2970
87	2920	2610	3020	1820	1800	1820	930	930	910	2710	3120	2910
90	2880	2750	2950	1760	1700	1840	900	920	900	2760	2910	2750
93	2850	2700	2900	1820	2120	1920	930	970	950	2800	2750	2700
96	2780	2750	2890	1840	1890	1840	920	990	960	2760	2830	2560
99	2750	2770	2920	1800	1940	1870	900	930	950	2690	2250	2000
102	2710	2710	3000	1740	1880	1800	900	890	940	2730	2700	2690
105	2710	2740	2750	1820	1880	1820	910	940	920	2930	2820	2750
108	2910	2900	3040	1790	1890	1800	890	910	910	2990	2980	2870
111	2870	2740	2890	1800	1940	1820	900	960	910	3020	2940	2770
114	2780	2710	3000	1990	1900	1820	910	910	900	2760	3010	2710

pH

Days	**Column number**											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
3	2.00	1.93	2.48	2.01	2.09	2.41	2.02	1.97	2.54	2.11	2.09	2.52
6	1.87	1.84	2.02	1.91	1.98	1.98	1.81	1.94	2.31	1.97	1.88	2.18
9	1.74	1.74	1.88	1.77	1.82	1.81	1.67	1.72	2.24	1.84	1.78	2.01
12	1.80	1.65	1.86	1.82	1.72	1.79	1.72	1.77	2.25	1.76	1.64	1.81
15	1.77	1.54	1.77	1.77	1.65	1.70	1.65	1.58	2.09	1.72	1.55	1.70
18	1.64	1.49	1.63	1.71	1.56	1.58	1.57	1.50	1.96	1.64	1.51	1.61
21	1.56	1.45	1.53	1.57	1.52	1.53	1.48	1.45	1.84	1.60	1.45	1.51
24	1.49	1.41	1.45	1.47	1.49	1.49	1.40	1.43	1.66	1.49	1.42	1.46
27	1.46	1.40	1.43	1.47	1.48	1.43	1.43	1.40	1.54	1.46	1.40	1.45
30	1.45	1.38	1.42	1.47	1.43	1.43	1.43	1.39	1.53	1.40	1.35	1.39
33	1.42	1.40	1.41	1.48	1.46	1.44	1.44	1.45	1.55	1.41	1.38	1.43
36	1.38	1.37	1.38	1.43	1.42	1.41	1.45	1.44	1.54	1.37	1.36	1.38
39	1.38	1.38	1.38	1.43	1.44	1.42	1.45	1.44	1.54	1.38	1.37	1.39
42	1.33	1.37	1.37	1.41	1.43	1.42	1.41	1.42	1.53	1.39	1.36	1.36
45	1.33	1.37	1.35	1.38	1.40	1.40	1.39	1.39	1.55	1.36	1.34	1.35
48	1.25	1.30	1.28	1.31	1.35	1.35	1.34	1.37	1.49	1.26	1.27	1.28
51	1.24	1.30	1.29	1.31	1.36	1.34	1.32	1.37	1.49	1.27	1.27	1.30
54	1.32	1.33	1.30	1.36	1.32	1.31	1.38	1.36	1.46	1.28	1.28	1.28
57	1.27	1.31	1.30	1.33	1.33	1.32	1.38	1.35	1.46	1.28	1.28	1.28
60	1.22	1.26	1.25	1.26	1.27	1.30	1.33	1.33	1.42	1.20	1.22	1.23
63	1.21	1.24	1.25	1.25	1.27	1.30	1.30	1.32	1.40	1.23	1.23	1.23
66	1.24	1.26	1.28	1.27	1.28	1.29	1.36	1.34	1.41	1.23	1.25	1.26
69	1.27	1.25	1.27	1.30	1.29	1.30	1.40	1.34	1.40	1.25	1.25	1.24
72	1.29	1.25	1.28	1.28	1.29	1.30	1.40	1.35	1.42	1.28	1.25	1.25
75	1.25	1.20	1.26	1.28	1.26	1.28	1.37	1.30	1.38	1.27	1.23	1.23
78	1.28	1.24	1.28	1.32	1.29	1.31	1.38	1.33	1.42	1.29	1.26	1.25
81	1.26	1.23	1.23	1.30	1.25	1.26	1.37	1.31	1.37	1.29	1.20	1.20
84	1.24	1.23	1.25	1.29	1.27	1.29	1.36	1.33	1.40	1.25	1.22	1.22
87	1.23	1.22	1.26	1.27	1.26	1.25	1.34	1.31	1.38	1.23	1.22	1.21
90	1.19	1.19	1.24	1.25	1.25	1.26	1.32	1.29	1.36	1.21	1.21	1.19
93	1.21	1.19	1.24	1.26	1.22	1.26	1.32	1.30	1.35	1.22	1.21	1.19
96	1.23	1.23	1.26	1.27	1.26	1.28	1.34	1.32	1.36	1.24	1.23	1.18
99	1.20	1.22	1.23	1.24	1.23	1.25	1.32	1.29	1.33	1.21	1.21	1.16
102	1.19	1.22	1.23	1.25	1.22	1.24	1.31	1.28	1.33	1.21	1.20	1.18
105	1.21	1.23	1.26	1.27	1.24	1.26	1.32	1.31	1.35	1.22	1.22	1.22
108	1.20	1.22	1.24	1.25	1.23	1.25	1.31	1.29	1.34	1.21	1.21	1.20
111	1.20	1.20	1.24	1.25	1.23	1.26	1.30	1.29	1.33	1.22	1.20	1.20
114	1.20	1.19	1.23	1.24	1.23	1.25	1.30	1.29	1.35	1.21	1.21	1.19

Redox (mV)

Days	Column number											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
3	367	367	347	365	367	349	365	365	345	360	362	345
6	388	385	369	374	375	388	382	380	359	371	379	360
9	403	409	428	394	401	432	397	408	406	388	411	423
12	380	421	446	381	464	518	385	440	436	383	459	457
15	386	463	521	387	534	624	394	491	570	391	512	482
18	391	510	652	392	611	656	399	590	554	396	616	703
21	398	556	583	399	630	571	402	595	540	397	612	586
24	426	612	590	405	598	585	430	595	483	398	635	602
27	410	595	597	404	592	591	435	619	488	401	633	601
30	397	567	599	398	596	601	404	597	618	403	600	611
33	403	587	604	404	602	601	411	601	630	406	581	620
36	402	598	599	402	602	597	407	593	592	404	595	613
39	406	609	612	406	601	593	411	592	596	407	611	630
42	406	588	612	407	601	613	409	592	634	408	600	626
45	410	616	607	410	648	579	415	604	597	412	617	608
48	410	606	616	410	666	590	417	682	611	413	630	609
51	408	585	614	411	602	601	420	608	605	410	618	613
54	408	569	587	409	585	606	412	578	607	411	594	622
57	406	561	595	411	573	605	413	575	599	411	612	624
60	404	600	597	405	635	593	409	589	585	408	592	596
63	403	588	604	405	602	590	410	595	611	406	606	621
66	402	586	581	404	590	585	408	604	604	404	604	599
69	401	600	595	403	598	585	405	609	604	399	610	602
72	398	567	619	400	592	602	402	609	608	402	617	625
75	399	610	603	402	585	602	407	607	610	401	613	615
78	397	600	596	401	595	608	405	611	617	402	611	608
81	395	586	599	398	599	606	405	609	613	401	614	606
84	404	658	613	404	614	618	411	624	620	406	619	604
87	397	605	597	399	608	620	407	622	617	402	606	605
90	398	566	606	402	615	623	410	626	613	403	602	600
93	397	578	607	399	622	629	406	625	619	402	623	606
96	403	650	606	403	620	604	411	620	606	403	621	611
99	402	641	605	402	620	605	409	622	609	403	605	601
102	398	618	601	399	622	603	407	615	607	400	602	618
105	399	594	609	400	619	606	409	611	610	401	609	610
108	397	540	599	398	621	600	405	618	605	399	596	618
111	395	596	597	400	625	612	404	611	617	398	611	625
114	403	589	601	406	616	625	414	614	613	408	605	614

Copper concentration (mg/L)

Days	Column number											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
3	305	251	120	116	383	124	304	126	103	248	303	144
6	32	21	47	29	51	44	21	20	53	34	21	52
9	36	25	43	46	24	41	25	24	29	35	23	37
12	22	38	46	37	82	66	23	76	40	31	53	38
15	15	68	76	23	102	70	15	131	57	24	95	39
18	16	120	60	20	147	57	16	122	51	24	121	53
21	19	178	62	26	180	72	23	170	51	26	145	61
24	22	136	46	33	141	62	36	188	44	22	120	72
27	28	114	41	36	205	71	64	102	46	33	106	66
30	24	139	51	36	127	71	36	146	57	34	106	81
33	24	152	52	38	197	139	56	367	156	42	173	151
36	21	154	52	36	165	133	45	333	165	41	148	85
39	28	135	54	41	181	129	52	343	214	38	122	91
42	28	116	57	52	193	187	57	317	188	38	100	79
45	34	167	97	58	181	126	57	378	228	51	111	108
48	30	140	64	48	175	199	54	386	163	49	77	76
51	44	132	69	60	173	137	59	440	214	55	76	112
54	47	175	71	68	154	158	81	263	155	62	90	90
57	32	106	63	50	164	113	70	259	250	64	80	98
60	51	137	63	57	139	183	78	226	227	68	98	95
63	42	103	72	76	102	123	77	184	228	66	95	93
66	40	63	50	46	72	62	69	195	187	43	54	54
69	20	57	44	32	75	72	57	218	247	42	48	55
72	28	55	33	24	58	56	44	156	225	26	33	31
75	23	59	42	40	59	58	60	139	231	44	29	56
78	25	96	39	38	45	45	52	120	192	27	36	44
81	20	51	33	38	38	53	49	140	171	24	29	42
84	22	62	56	50	66	64	62	191	236	32	43	56
87	28	65	53	49	58	64	63	187	244	30	41	49
90	25	59	46	42	69	55	59	133	178	28	33	39
93	23	54	42	42	35	50	53	123	153	25	34	41
96	26	67	49	53	54	58	65	135	164	32	41	51
99	23	52	50	41	52	60	63	175	164	27	48	57
102	27	44	48	50	49	58	59	139	168	29	42	33
105	23	42	70	47	47	56	53	122	173	26	38	54
108	27	57	46	47	43	57	59	109	179	32	35	44
111	25	32	45	47	48	57	54	107	164	27	34	38
114	23	48	48	47	44	61	61	104	194	35	40	39

Fe^{2+} concentration (mg/L)

Days	**Column**											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
3	1643	1731	783	1240	2194	870	1865	1263	695	1707	1785	717
6	1031	840	990	1005	854	799	832	790	932	931	785	887
9	1248	910	798	1160	1021	778	988	951	957	1087	834	842
12	1239	987	682	1252	379	207	1138	814	870	1196	563	677
15	1135	493	42	1123	75	23	992	306	42	1063	155	417
18	1109	12	12	1100	15	10	913	17	27	992	11	14
21	1045	11	14	1006	7	12	807	10	43	1028	34	11
24	830	9	15	818	5	8	893	8	193	972	12	14
27	887	12	17	910	15	21	806	15	221	858	12	9
30	916	26	10	935	27	7	831	15	11	817	14	9
33	858	10	17	865	13	10	800	16	2	776	14	8
36	795	22	16	857	17	10	792	20	9	791	16	10
39	849	16	8	843	19	10	801	18	10	816	22	6
42	824	27	25	800	21	18	824	27	26	710	15	15
45	773	22	22	773	22	21	734	27	23	742	27	23
48	735	22	16	781	14	38	804	21	18	739	16	17
51	753	23	22	769	32	17	735	35	19	738	27	18
54	759	12	12	774	11	7	843	13	9	739	11	10
57	719	50	16	823	26	17	819	30	19	724	20	22
60	726	25	20	763	18	40	784	15	15	686	34	40
63	741	24	15	759	15	19	796	17	14	753	15	14
66	703	14	13	719	6	10	787	9	9	688	12	3
69	651	19	18	657	9	12	765	14	21	627	13	9
72	676	28	19	655	27	19	766	19	21	647	20	15
75	631	14	15	656	8	12	667	16	19	637	11	12
78	586	5	5	638	0	0	697	1	4	541	6	10
81	611	15	8	641	11	14	663	12	10	581	7	11
84	595	7	7	681	10	10	742	8	14	603	19	10
87	588	10	8	640	4	5	720	9	7	579	5	5
90	610	27	16	665	17	18	708	23	21	564	16	19
93	573	24	17	643	27	19	709	14	19	578	11	15
96	576	5	10	637	6	8	696	8	12	595	9	16
99	607	9	10	646	6	9	708	8	11	577	9	24
102	571	15	12	646	11	46	712	11	18	595	13	28
105	546	17	11	634	41	13	697	16	13	584	24	27
108	582	30	7	673	4	10	669	12	8	563	9	10
111	572	5	4	713	5	5	672	3	4	613	7	5
114	566	15	8	632	8	7	691	8	10	583	11	7

Fe^{3+} concentration (mg/L)

Days	**Column number**											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
3	814	614	111	148	721	140	920	302	107	485	561	60
6	196	130	51	130	112	222	173	139	227	106	125	164
9	237	261	364	232	273	390	188	204	319	207	412	376
12	147	292	457	112	695	622	108	411	483	126	641	651
15	75	623	754	103	889	701	86	758	782	75	854	760
18	118	1063	788	111	991	809	68	1014	823	113	967	1063
21	190	978	841	126	892	794	101	914	874	89	924	945
24	174	918	708	212	836	741	144	849	720	106	919	881
27	159	899	791	154	817	748	197	837	709	171	879	873
30	111	890	796	81	797	753	103	832	850	102	872	865
33	131	865	805	92	802	754	177	784	724	136	831	831
36	117	820	754	84	755	704	76	732	717	53	802	795
39	81	843	751	94	743	740	106	765	776	84	731	817
42	77	814	728	105	735	773	73	755	800	153	705	804
45	86	810	746	154	732	692	165	767	737	103	718	766
48	88	784	741	106	735	762	114	846	800	98	734	784
51	92	757	733	102	743	768	122	854	731	99	705	781
54	89	779	757	144	711	731	124	793	789	94	731	789
57	85	765	753	90	719	756	104	827	822	120	745	789
60	89	754	725	92	704	706	142	784	853	82	659	738
63	89	766	781	127	729	716	126	827	885	111	738	795
66	80	714	711	96	663	705	118	786	827	81	666	755
69	100	688	702	134	659	735	120	808	798	127	672	711
72	86	673	678	99	611	649	115	749	808	92	635	695
75	81	672	628	96	620	639	149	704	830	89	628	708
78	81	634	666	141	618	641	147	725	753	101	597	693
81	81	670	675	106	572	642	142	720	805	108	601	688
84	92	631	659	94	592	635	114	669	804	81	659	689
87	65	642	648	114	598	708	118	668	761	86	605	715
90	77	643	690	92	555	650	121	644	786	105	590	715
93	90	657	636	84	573	632	141	631	781	84	562	735
96	110	675	637	79	562	610	136	616	765	65	597	749
99	79	584	638	70	550	584	114	604	740	69	587	780
102	92	581	622	88	519	538	108	626	735	67	547	742
105	67	563	649	82	500	573	99	590	732	76	584	775
108	55	557	627	44	532	544	125	641	723	86	572	686
111	114	634	653	117	551	561	81	627	681	57	605	686
114	122	605	617	86	531	563	173	620	723	88	590	675

Fe total concentration (mg/L)

Days	Column											
	1	2	3	4	5	6	7	8	9	10	11	12
3	2456	2345	894	1388	2914	1011	2785	1565	803	2192	2346	777
6	1227	970	1041	1135	966	1021	1005	929	1160	1037	910	1050
9	1485	1171	1161	1392	1293	1168	1176	1155	1276	1294	1246	1218
12	1385	1279	1139	1365	1074	829	1246	1224	1352	1321	1204	1328
15	1210	1117	796	1226	963	724	1078	1064	824	1138	1009	1177
18	1227	1074	800	1211	1006	819	981	1030	850	1105	978	1077
21	1236	989	855	1132	899	806	908	1063	917	1117	958	956
24	1003	927	723	1030	841	749	1037	857	913	1079	931	895
27	1047	911	807	1064	832	769	1003	852	929	1029	892	882
30	1027	916	806	1016	823	760	934	847	861	919	887	874
33	989	875	822	957	815	764	978	800	727	912	845	839
36	911	842	769	941	771	713	868	752	727	844	818	804
39	931	860	759	936	762	750	907	783	786	900	754	823
42	901	841	754	905	756	790	897	782	826	863	720	819
45	858	832	767	927	754	713	899	795	760	845	744	789
48	824	806	757	887	749	800	919	867	818	837	750	801
51	845	780	755	871	775	785	857	888	749	837	732	798
54	849	791	770	918	722	738	966	805	798	833	742	800
57	804	815	770	913	745	773	923	857	841	845	765	812
60	815	779	745	856	722	746	926	799	868	768	693	778
63	830	790	796	886	744	734	922	844	899	864	753	809
66	783	727	724	815	669	716	905	795	836	769	678	759
69	751	707	720	791	668	747	885	822	819	754	685	720
72	762	702	697	754	638	668	881	769	829	739	655	710
75	713	686	643	752	628	651	816	720	849	727	639	720
78	667	638	671	779	618	641	843	726	757	642	603	703
81	692	684	683	747	582	655	805	732	816	688	608	699
84	687	638	665	775	602	645	856	677	818	683	678	698
87	653	652	657	754	602	713	838	677	768	665	609	721
90	687	670	706	757	573	668	829	668	807	669	606	733
93	664	681	654	726	600	652	849	646	800	661	574	750
96	686	681	647	716	568	617	832	624	777	661	606	766
99	686	593	649	717	557	593	822	612	751	646	596	724
102	663	597	635	735	530	584	820	637	752	662	560	693
105	613	580	660	716	541	585	797	606	746	660	608	722
108	638	587	634	716	536	554	795	653	732	649	581	697
111	686	639	657	830	555	565	754	630	685	670	613	690
114	688	620	625	718	539	570	863	628	733	671	601	682

Microbial detachment data

Column	Interstitial (Cells/ 4 kg ore)	Attached (weak + strong) (Cells/ 4 kg ore)
2	2.172E+08	8.281E+07
5	5.469E+07	5.781E+07
8	1.422E+08	6.250E+07
11	1.500E+08	8.125E+07
3.1	1.456E+07	1.406E+06
3.2	3.250E+07	9.375E+05
3.3	6.689E+07	2.656E+06
3.4	3.844E+07	1.109E+07
6.1	2.467E+07	3.701E+07
6.2	9.688E+06	1.109E+07
6.3	5.407E+07	8.319E+06
6.4	7.656E+06	5.625E+06
9.1	6.474E+07	8.632E+07
9.2	3.281E+06	7.188E+06
9.3	8.706E+06	2.220E+07
9.4	1.563E+07	1.563E+07
12.1	6.944E+07	6.250E+05
12.2	9.844E+06	3.906E+06
12.3	2.456E+07	9.375E+05
12.4	7.813E+06	1.719E+06