Thermophilic mineral bioleaching performance: A compromise between maximizing mineral loading and maximizing microbial growth and activity

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Synopsis

Thermophilic bioleaching, conducted at temperatures in excess of 65°C, provides considerable benefit over mesophilic bioleaching, particularly through extending the extent of leaching of base metal minerals such as chalcopyrite. Thermophilic bioleaching is facilitated through a group of micro-organisms known as the Archae, well adapted to extreme environment. In order to maximize the space time utilization of the stirred tank reactor in the thermophilic bioleaching process, it is desirable to maximize the loading of the finely divided mineral phase present while not adversely affecting the microbial performance. In this paper, the effect of the loading of the solid particulate phase on the bioleaching performance of *Sulfolobus metallicus* was studied in a stirred tank reactor. Emphasis was placed on the effect of the concentration of the finely divided solid phase (35 – 75 μm). A model system comprised of 3% (w/v) pyrite in the presence of varying quantities of quartzite in the range 0 to 24% (w/v) was used to obtain the different solids concentrations.

The bioleaching experiments revealed similar bioleaching performance in the presence of 3 to 18% (w/v) total solids. Above 18% (w/v) total solids (15% quartzite loading), bioleaching was impaired progressively with increasing solids concentration. At the highest solids loading studied of 27% (w/v), bioleaching was still observed. In terms of mass transfer, oxygen transfer potential was not significantly influenced in the bioleaching process over the range of solids investigated.

Introduction

Microbial pre-treatment of refractory sulphidic ores in hydrometallurgy for the extraction of metals, such as copper and gold, has been practised over a considerable period, with active tank leaching processes used at commercial scale for some 15 years. The micro-organisms used in the commercial tank-based biohydrometallurgy processes, such as at the Fairview (South Africa), São Bento (Brazil) and Ashanti (Ghana) operations, are mainly mesophiles, although moderate thermophiles are currently used at the Youanmi Mine in Australia (Brierley, 1997). Study into the use of extreme thermophiles for mineral bioprocessing has been attracting increasing interest over recent years. Thermophiles grow at higher temperatures than the mesophiles, 65–85°C compared to 30–45°C. The oxidation reactions involved in the solubilization of mineral sulphides are exothermic, hence the ability of the thermophiles to grow at higher temperatures is advantageous in providing an improved driving force for heat removal. In addition, enhanced oxidation kinetics in terms of rate of reaction and extent of solubilization is a potential advantage of thermophilic bioleaching (Duarte *et al.*, 1993; Norris and Barr, 1988; Konishi *et al.*, 1995). The extent of leaching of base metals such as copper from refractory sulphidic minerals is greatly increased by the implementation of increased temperature.

Thermophilic bioleaching is facilitated by a group of micro-organisms known as the Archae which exist under a variety of extreme conditions. Archae such as *Sulfolobus* and *Metallosphaera* are known to lack a rigid peptidoglycan cell wall (König, 1988), the component from which bacteria derive their structural strength. In the Archae this is replaced by a protein layer. In addition, an increase in temperature causes the fluidity of tetra-ether based cellular membranes to increase (Kelly and Deming, 1988). Hence potential disadvantages of thermophilic bioleaching are that the thermophiles used for bio-oxidation appear to be sensitive to hydrodynamic conditions (Clark and Norris, 1996) and the presence of solids (Le Roux and Wakerley, 1988; Nemati and Harrison, 2000).

Maximum rates of mineral concentrate leaching have been shown to be maintained with a solids concentration of 6–8% w/v pyrite (Norris, 1997) and 9% w/v pyrite (Nemai and Harrison, 2000). Nemati and Harrison (2000) obtained mineral solubilization at 15% w/v pyrite in two distinct stages of solubilization: a growth-associated rate of 0.07 kg iron $m^{-3}h^{-1}$ and a non-growth-associated rate of 0.0017 kg iron $m^{-3}h^{-1}$. The bioleaching rate at 9% w/v

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pyrite was 0.09 kg iron $m^{-3}h^{-1}$. The preferred minimum mineral concentration for industrial application is 10% w/v mineral (Norris, 1997). Current mesophilic bioleaching processes are operated at 18–20% w/v concentrate (Oguz *et al.*, 1987). Knowledge of the effect of solids concentration on thermophilic bioleaching performance is therefore critical for optimization of thermophilic bioleaching for industrial application.

In this study, the effect of the solid particulate concentration was investigated on the bioleach performance of *Sulfolobus metallicus* using pyrite as a model mineral. In contrast to the study of Nemati and Harrison (2000), a constant pyrite concentration of 3% (w/v) with varying quartzite concentrations was used to obtain various solids concentrations. This eliminated possible toxic effects due to the sulphide mineral and the increased solubilization of iron and sulphate with increased solids concentrations.

Experimental methods and materials

Experimental apparatus and procedure

The bioleach experiments were conducted in fully baffled stirred tank reactors (STR) of 1 *l* capacity and working volume of 0.70 *l*. The reactor was jacketed and maintained at a temperature of between 68 and 70°C. A four-pitch blade stainless steel impeller of diameter 0.058 m set at a clearance of 0.01 m from the reactor base was used to provide agitation. Compressed air without any enrichment with oxygen or carbon dioxide, except in the experiments testing carbon dioxide limitation, was supplied at a rate of 2 *l* min^{-1}. The bioreactor was operated batch-wise at an agitation rate of 560 rpm at which complete suspension of the solids was obtained (observed visually). In each experiment, the reactor was charged with 550 ml medium, 150 ml inoculum, 21 g pyrite (3% w/v) and a varying quantity of quartz to make up the total solids concentration up to 27% (w/v) total solids (using increments of 3% w/v). The initial concentration of the micro-organisms was 2-4x10^8 cells ml^{-1}. A low agitation speed of approximately 285 rpm was initially applied, to provide mild hydrodynamic conditions for the adaption of the micro-organisms and a rapid increase in microbial population. When the biomass concentration increased by 2-3x10^8 cell ml^{-1} to 4-7x10^8 cell ml^{-1}, the agitation rate was increased to approximately 560 rpm. Samples were taken from the reactor on a regular basis and analysed for ferrous and ferric iron concentrations, microbial cell concentration, pH and redox potential. Continuous measurement of the pH and redox potential of the leachate were not possible as the harsh environment caused by the low pH, presence of solid particulates and high temperature, damaged the glass electrode.

Analytical procedure

A 15 ml sample was taken daily and the solid particulates were removed by decantation. The concentration of ferrous iron was determined by titration against 0.017 M potassium dichromate in the presence of *N*-phenyl anthranilic acid as an indicator (Vogel, 1989). To determine the concentration of total iron, ferric iron was reduced to ferrous iron using stannous chloride as reducing agent, followed by titration against potassium dichromate. The ferric iron concentration was estimated by subtracting the ferrous iron concentration from the total iron concentration. Since part of the iron precipitated during leaching the iron concentration of both the suspension and the supernatant were determined. The total concentration of released iron was measured after acid digestion. The precipitated iron was digested by heating 2 ml of sample containing 2 ml concentrated hydrochloric acid. The concentration of iron in solution was determined using the supernatant of a centrifuged sample. The concentration of cells free in suspension was measured by direct counting using a Petroff-Hauser-type cell counter (haemocytometer) of 0.02 mm depth and 1/400 mm^2 area. The pH and redox potential were measured at room temperature. The redox electrode was a combined platinum/reference redox cell.

Particulates

The pyrite was obtained from BHP-Billiton (Randburg, South Africa). The size fraction of concentrate used was 38–75 μm and the relative density of the pyrite was 5.0 kg m^{-3} (measured). The composition of the ore was 42.2% iron and 50.5% sulphur. Quartz was obtained from Consol (South Africa) and a size fraction of 38–75 μm was used. The quartzite acted as an inert solid material that allowed different solids loading to be tested without changing the pyrite concentration. Consequently the dissolved metal ion concentration and ionic strength that increase with leaching did not increase with increasing solids loading. Hence changes in leaching performance can be attributed to the solids loading only rather than to the combined effect of solids loading and dissolved solutes. The relative density of the silica was 2.6 kg m^{-3}.

Micro-organism

The thermophilic culture used in this research was *Sulfolobus metallicus (BC)* isolated from coal tips in Birch Coppice and provided by BHP-Billiton, South Africa. The culture was grown aerobically in a stirred tank reactor in a medium containing 0.4 kg m^{-3} $(NH_4)_2SO_4$, 0.5 kg m^{-3} $MgSO_4.7H_2O$, 0.2 kg m^{-3} KH_2PO_4 and 0.1 kg m^{-3} KCl. Of the 700 ml working volume of the stock culture, 200 ml was drawn daily and replaced with an equivalent volume of medium and 6.0 g pyrite. The stirrer speed was set at 350 rpm and the culture temperature was maintained at 68°C. The water lost due to evaporation was replaced with distilled water before drawing and feeding, to retain a constant liquid volume while preventing salts concentration through evaporation. This inoculum was used for all the bioleach experiments.

Results and discussion

The rate of leaching of iron from pyrite is shown as a function of time across the range of particulate concentrations from 3% to 27% in Figure 1. These particulate concentrations are comprised of 3% pyrite and the remainder quartz. Through analyses of these data, the bioleach rate can be derived under each set of operating conditions. A bioleach rate of 0.113 kg m^{-3} h^{-1} (R^2 = 1.00) was observed with an extent of leaching of 91% using 3% pyrite. Addition of quartz in the range of 6 to 15% (w/v) decreased the bioleach rate to an average of 0.095 kg m^{-3} h^{-1} (R^2 = 0.98)

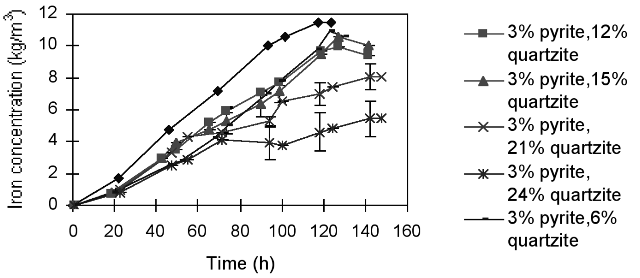

Figure 1—Effect of solids loading on the rate of iron leaching of pyrite in the presence of *Sulfolobus metallicus* on exposure to 3% pyrite and 0 to 24% inert quartzite

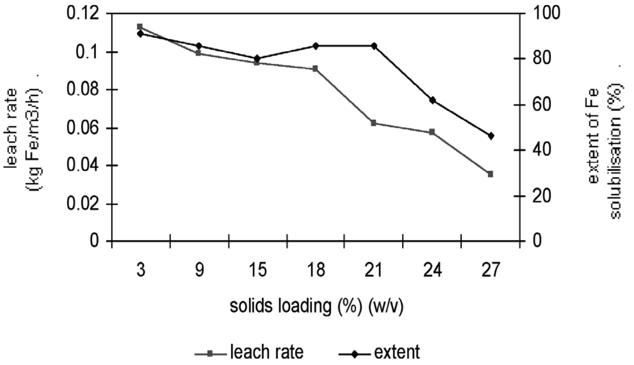

Figure 2—Bioleach rate and extent of iron solubilization as a function of total solids loading (comprised of 3% pyrite, the remainder quartz)

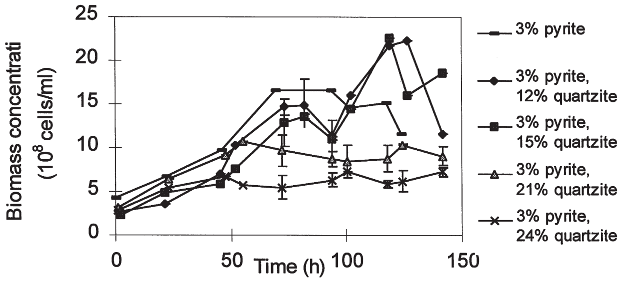

Figure 3—Effect of solids loading on the growth rate of *Sulfolobus metallicus* on exposure to 3% pyrite and 0 to 24% inert quartzite

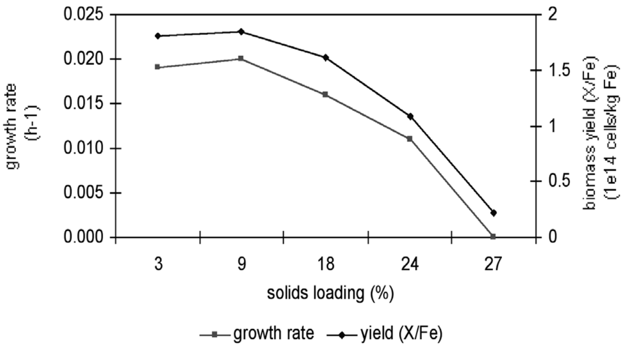

Figure 4—Microbial growth rate and biomass yield ($Y_{X/Fe}$) in terms of microbial cells produced per kg iron oxidized as a function of total solids loading (comprised of 3% pyrite, the remainder quartz)

and the extent of leaching to 86%. The addition of 21% quartz further reduced the bioleach rate to 0.057 kg m^{-3} h^{-1} (R^2 = 0.98) and the extent to 62%. The bioleach rate and extent of pyrite solubilization using 24% quartz was 0.035 kg m^{-3} h^{-1} (R^2 = 0.99) and 46%, respectively. These results are depicted in Figure 2. Thus, bioleaching performance is optimum at 3% pyrite and similar to that up to 18% total solids concentration. Thereafter, the bioleaching performance is progressively impaired with higher solids concentrations.

The microbial cell concentrations achieved in suspension are given as a function of time across the range of particulate concentrations studied in Figure 3. It has been shown previously (Nemati and Harrison 2000, Sissing 2002) that the planktonic microbial concentration is an appropriate measure of the biomass phase. The cell concentration profiles for the experiments in the presence of 0 to 15% quartz (total solids loading of 3 to 18%) exhibited similar growth rates ranging from 0.016 to 0.020 h^{-1} (R^2 = 0.95 – 1.00) for the first 50 h of the experiment. Thereafter the growth rate remained constant in the presence of 3% pyrite and increased in the presence of 3% pyrite with 6–15% quartz. In the presence of 21% quartz, a maximum growth rate of 0.011 h^{-1} was observed, followed by a stationary phase after 95 hours. The specific growth rate in the presence of 24% quartz exhibited no growth throughout the experiment.

The yields in terms of microbial cells produced per kg iron oxidized in the presence of 0 and 6% quartz are similar. The yield is lower in the presence of 15% quartz. A further decrease is observed with 21% quartz, and by a factor of 10 in the presence of 24% quartz. This is illustrated in Figure 4. The reduced yield suggests that the micro-organisms are becoming less efficient at utilizing the iron for growth.

During the exponential growth phase, higher specific activity (rate of iron released per microbial cell) is observed at lower solids loading, i.e. 0–15% quartz exhibited higher activity than 21% quartz (24% total loading), and 24% quartz (27% total loading) exhibited the lowest activity. This is shown in Figure 5. The similarity in activity across the solids loading range during the stationary phase suggests the efficiency of the micro-organisms in converting ferrous iron present to ferric iron at the various solids loading is similar in the absence of microbial growth. However, the microbial cell concentration decreases with solids loading. Hence the

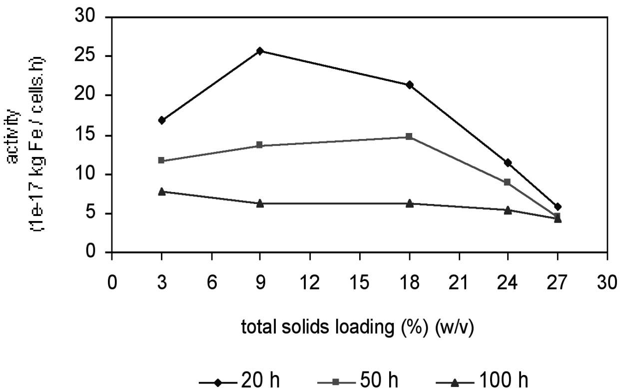

Figure 5—Microbial cell activity in terms of specific pyrite oxidation rate as a function of solids loading and duration of experiment

decrease in pyrite oxidation with solids loading in the stationary phase corresponds to a lower microbial cell concentration as opposed to lower micro-organism activity. In the exponential growth phase, both reduced specific activity and a decreased biomass concentration contribute to the decreased leaching performance.

The pH profiles across the range of solids loading are similar. The profiles for redox potential are similar for solids loading of 3% pyrite in the presence of 0 to 15% quartz. A decrease in the maximum redox potential is observed in the presence of 21% quartz and a further decrease with 24% quartz, owing to the reduced conversion of ferrous to ferric iron.

The effect of solids loading on bioleaching kinetics may be due to the effect of the gas–liquid mass transfer, restricting the supply of oxygen and carbon dioxide to the micro-organisms. An attempt to verify this theory was made by determining the mass transfer coefficient and saturation concentration for oxygen transfer using a dynamic method at various solids loading. The mass transfer coefficients measured at the various solids loading are similar across the range from 0 to 24% (w/v) quartz in the presence of 3% pyrite. If oxygen is a limiting factor, oxygen demand will be greater than the oxygen transfer potential (OTP). As the pyrite concentration remained constant, oxygen demand in terms of pyrite solubilisation remained constant. OTP, which is dependent on k_La, saturated and critical dissolved oxygen concentrations, only varied with k_La as the dissolved oxygen concentrations would remain unchanged due to the similar conditions of the experiments. As k_La did not vary with solids loading, OTP would not vary. Since both oxygen demand and OTP are similar over the range of solids loading, oxygen limitation is not a factor affecting bioleaching over the range investigated.

Conclusions

The bioleaching performance in the slurry bioreactor was not affected by solids loading in the range 6 to 18% (w/v), comprised of 3% pyrite and 3 to 15% quartz in a finely divided form prepared by screening to provide a 38–75 μm size fraction. A bioleach rate of 0.095 kg m^{-3} h^{-1} was maintained. Bioleaching performance was increasingly impaired by the further increase in solids loading to 27% (w/v) comprised of 3% pyrite and 24% quartz. The bioleaching performance followed the same trend as microbial cell growth. Similar growth rates for *Sulfolobus metallicus* of 0.016 to 0.020 h^{-1} were found in the presence of 3 to 18% (w/v) total solids loading (3% pyrite and the remainder comprised of quartz). The growth rate decreased by 39% in the presence of 24% total solids loading, and no growth rate was observed in the presence of 27% total solids loading. The yield in terms of microbial cells produced per kg iron oxidized remained constant at 1.6-1.9x10^{14} cells kg Fe^{-1} at solids loading of 3 to 18% (w/v) total solids loading (comprised of 3% pyrite and the remainder quartz). The biomass yield decreased with increased solids loading above 18% total solids loading. The decrease in pyrite oxidation with increasing solids loading is due to a decrease in microbial cell concentration in the stationary phase. In the exponential growth phase, the decreased pyrite oxidation resulted from both a decreased microbial concentration and a decreased specific activity.

The findings of this study using a model system in which the pyrite loading was maintained constant at 3% (w/v) and the solids loading varied through the addition of inert quartz can be usefully compared to the study of Nemati and Harrison (2000). In their study, the loading of the particulate phase was varied through varying the pyrite concentration. Leaching performance was impaired at 12 to 15% loading, compared to 21 to 24% loading in this system. In Nemati and Harrison's system, the system failed at 18% solids loading at which rapid microbial cell death was observed on suspension of the particulate phase. In the pyrite-quartz system, system failure occurred at 27% loading. This comparison suggests that while the physical presence of the particulate phase compromises leaching performance at high solids loading (of some 20% (w/v) or more), physicochemical stresses may compound the microbial response, impairing leaching at lower solids concentrations. The interaction between hydrodynamic and physicochemical stress in mediating a biological response as well as the mechanism through which leaching performance is impaired and can be restored form the subject of our ongoing research.

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