Process for biological oxidation and control of dissolved iron in bioleach liquors

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A B S T R A C T

Iron has a central role in bioleaching and biooxidation processes. Fe^{2+} produced in the dissolution of sulfidic minerals is re-oxidized to Fe^{3+} mostly by biological action in acid bioleaching processes. To control the concentration of iron in solution, it is important to precipitate the excess as part of the process circuit. In this study, a bioprocess was developed based on a fluidized-bed reactor (FBR) for Fe^{2+} oxidation coupled with a gravity settler for precipitative removal of ferric iron. Biological iron oxidation and partial removal of iron by precipitation from a barren heap leaching solution was optimized in relation to the performance and retention time (τ_{FBR}) of the FBR. The biofilm in the FBR was dominated by Leptospirillum ferriphilum and "Ferromicrobium acidiphilum." The FBR was operated at pH 2.0 ± 0.2 and at 37 °C. The feed was a barren leach solution following metal recovery, with all iron in the ferrous form. 98–99% of the Fe^{2+} in the barren heap leaching solution was oxidized in the FBR at loading rates below 10 g Fe^{2+}/L h (τ_{FBR} of 1 h). The optimal performance with the oxidation rate of 8.2 g Fe^{2+}/L h was achieved at τ_{FBR} of 1 h. Below the τ_{FBR} of 1 h the oxygen mass transfer from air to liquid limited the iron oxidation rate. The precipitation of ferric iron ranged from 5% to 40%. The concurrent Fe^{2+} oxidation and partial precipitative iron removal was maximized at τ_{FBR} of 1.5 h, with Fe^{2+} oxidation rate of 5.1 g Fe^{2+}/L h and Fe^{3+} precipitation rate of 25 mg Fe^{3+}/L h, which corresponded to 37% iron removal. The precipitates had good settling properties as indicated by the sludge volume indices of 3–15 mL/g but this step needs additional characterization of the properties of the solids and optimization to maximize the precipitation and to manage sludge disposal.

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1. Introduction

Ferric iron is the key oxidant in biohydrometallurgical processes where sulfide minerals such as pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$), covellite (CuS) and sphalerite (ZnS) are oxidized. One of the main mechanisms of bacterial catalysis in the dissolution of sulfide minerals is based on the biological oxidation of ferrous iron with oxygen as the electron acceptor [1]. Fe^{3+} thus produced chemically oxidizes sulfide minerals and is reduced in this redox reaction to Fe^{2+}. Iron re-oxidation is essential in the bioleaching process because Fe^{3+} is an important electron shuttle and a chemical oxidant. Recirculation of Fe^{3+} and Fe^{2+} containing leach solutions back to the process is common practice but leads to the

accumulation of high concentrations of dissolved iron [2–4]. Fe^{2+} can be oxidized chemically in acid solutions, but microbial oxidation occurs 10^5–10^6 times faster compared to the chemical oxidation [5].

Various types of bioreactors, including fluidized-beds, packed-beds, trickle-beds, circulating-beds, agitated reactors and rotating biological contactors, have been tested for their potential for high-rate ferrous iron oxidation by acidophilic microorganisms. These reactor types and their performances are compared in Table 1. The tendency of iron-oxidizing microorganisms to grow on surfaces has been exploited in bioreactors with various cell immobilization matrices, thereby effectively ensuring high and stable biomass retention. The highest iron oxidation rates have been achieved in packed-bed and fluidized-bed bioreactors with granular activated carbon as the best support material [19,20].

In addition to abundant Fe-sulfides, common Cu-, Zn-, and Ni-sulfide minerals such as sphalerite, chalcopyrite ($CuFeS_2$), and pentlandite ($(Fe,Ni)_9S_8$) contain iron, and their acid leaching leads to the accumulation of iron in leach liquors. Accumulation of iron may result in adverse effects on the bioleaching due to iron precipitation on mineral surfaces, pipelines and orifices and toxicity of high iron concentrations to microorganisms. Biological iron oxidation has been studied in detail. There is, however, a very

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Table 1
Biological iron oxidation rates achieved in various bioreactor configurations.

Reactor type	Support matrix	pH	Temperature (°C)	Aeration using	Maximum iron oxidation rate (g Fe^{2+}/L h)	Nature of precipitates (if any), other comments concerning precipitation	Reference
Fluidized-bed	Activated carbon	2.1 ± 0.2	37 ± 1	Air	8.2	Jarosites[a]	This study
Fluidized-bed	Activated carbon and jarosites	1.4 ± 0.1	37 ± 1	0.5% CO_2/ 99.5% O_2	26.4	Jarosites	[4]
Fluidized-bed	Activated carbon and jarosites	1.4 ± 0.1	37 ± 1	Air	6.9	Jarosites	[4]
Fluidized-bed	Activated carbon	1.35–1.5	23	Air	0.9	Jarosite, amount of precipitation was negligible, no problems of clogging	[6]
Flooded packed-bed	Siliceous stone	1.25	31	Air	11.25	Not mentioned	[7]
Inverse fluidized-bed	Activated carbon felt	1.05	40	Air	0.9	Not mentioned	[8]
Packed-bed	Expanded polystyrene	2.3	25	Air	0.72	Not mentioned	[9]
Packed-bed	Nickel alloy fiber	1.8	30	Air	20	N.d., extensive precipitation had a detrimental effect on iron oxidation rate and oxygen mass transfer rate to the medium	[10]
Packed-bed	Glass beads	1.35–1.5	23	Air	8.1	Jarosite, amount of precipitation was negligible, no problems of clogging	[6]
Packed-bed	Resin beads	1.35–1.5	23	Air	29.3	Jarosite, amount of precipitation was negligible, no problems of clogging	[6]
Packed-bed	Activated carbon	1.35–1.5	23	Air	52	Jarosite, amount of precipitation was negligible, no problems of clogging	[6]
Packed-bed	Poly(vinyl alcohol) gryogel	1.7	31	Air	3.1	N.d., above 95% of the initial iron was found to be in solution	[11]
Packed-bed	Polyurethane foam	1.7	30	Air	34.3	Not mentioned	[12]
Packed-bed	Quartz sand	2	20	Not mentioned	0.33	Not mentioned	[13]
Rotating biological contactor	Polyvinyl chloride	1.5–2.6	10–40	–	0.80	N.d., solid films of ferric iron developed on disk surfaces, maximum iron precipitation was around 9 g/day	[14]
Rotating biological contactor	Polyvinyl chloride	2.0–2.5	18	–	1.4	Not mentioned	[15]
Circulating-bed	Polyurethane foam	2.3	28	Air	1.56	N.d., 64% of initial total iron precipitated and mainly accumulated inside the support particles	[16]
Trickle-bed	Polyurethane foam	2.3	28–30	Air	4.4	Jarosites[b], extensive precipitation had a detrimental effect on iron oxidation rate	[17]
Airlift	Basalt, ferric iron precipitates	0–1.8	30	Air	8.1	N.d., initially used basalt was slowly removed and the ferric iron precipitates formed served as a biofilm carrier, these precipitates had highly suitable characteristics as a carrier material	[18]

N.d., not determined.
 [a] Precipitates characterized by X-ray diffraction analysis (unpublished results).
 [b] Solid phase analysis not performed.

limited amount of published information on simultaneous iron biooxidation and precipitation/removal processes and they are rarely reported in sufficient detail. Integration of these processes is essential for treatment of leach liquors since the concentration of dissolved iron must be controlled for successful leaching. A key process is the oxidation of ferrous iron in leach liquor for subsequent precipitation of Fe(III). In the present study, acidophilic bacteria were employed to oxidize ferrous iron in a bioprocess that involved a fluidized-bed reactor (FBR) coupled with a gravity settler. The specific objective of the study was to characterize the performance of bacterial oxidation of ferrous iron in an FBR which was integrated with partial precipitation of ferric iron in a gravity settler. The feed solution for the bioprocess was a barren heap leaching solution which had been treated for the recovery of valuable metals. Potential application of this process is for re-oxidation of dissolved iron in leach solution circuits followed by partial precipitative removal of ferric iron.

2. Materials and methods

2.1. Reactor setup

An FBR based system (Fig. 1) with granular activated carbon (Calgon Carbon Filtrasorb 200) as biomass carrier was used for the experiments at 37 °C. Sufficient liquid volume was maintained above the fluidized-bed to prevent the discharge of activated carbon particles from the FBR. The total working volume and the

fluidized-bed volume of the FBR were 500 and 340 mL, respectively. The bed expansion or fluidization ratio was adjusted to 30% with sufficient upward velocity of the fluid. Before the current experiments, the FBR was fed for 80 days at 37 °C with simulated multimetal ore bioheap leaching solution from which Cu, Zn, Ni and Co had been removed [21]. In the current experiments the FBR was fed with a barren heap leaching solution obtained from a multimetal heap bioleaching pilot plant at Talvivaara, Finland, retrieved after the recovery of target metals. This solution was supplemented with a mineral salts medium containing (g/L) $(NH_4)_2HPO_4$ (0.35),
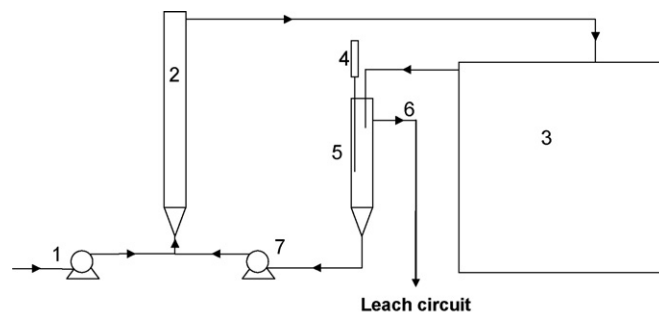
Fig. 1. Schematic diagram of the fluidized-bed reactor (FBR) system used for iron oxidation. (1) feed pump, (2) FBR, (3) settling tank, (4) aeration pump, (5) aeration unit, (6) final system effluent, (7) recycle pump. Not drawn to the scale. The settling tank had no special configuration to prevent discharge of the precipitates with the effluent.