Bioleaching and recovery of metals from final slag waste of the copper smelting industry

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ABSTRACT

Solid waste from the copper smelting industry may be harmful if disposed of in the environment, but it may be a valuable resource if metals can be recovered. The purpose of this study was to evaluate the acid bioleaching of metals from a sample of final smelter slag and the recovery of metals from the leach liquors. Bioleaching was tested in a continuously stirred tank reactor (CSTR) at 20-25 °C with 5% pulp density (particle size 75% <47 µm). The yields of metal solubilization after 29 days of contact were 41% Fe, 62% Cu, 35% Zn and 44% Ni. Metals were precipitated in a separate CSTR by titrating the leach liquors with sulfide-rich effluent from a sulfate-reducing fluidized-bed reactor (FBR) (25 ºC) to desired pH values. Over 98 % of the Cu precipitated at pH≥ 2.8 and over 99% of the Zn precipitated at pH≥ 3.9. The precipitation of Ni and Fe required higher pH values and was less efficient than Cu and Zn recovery. In addition, bulk precipitation of metals was also tested by feeding the leach liquor directly to another sulfate-reducing FBR. In order to reduce its toxicity and maintain stable sulfate reduction performance in the FBR, the leach liquor had to be diluted ten-fold and the pH adjusted from 0.6 to approximately 4.

KEYWORDS: bacteria, bioleaching, biotechnology, waste processing

INTRODUCTION

Solid waste streams from the copper industry contain high concentrations of metals that are harmful if released to the environment. These waste streams can be potentially valuable sources of metals (Bosecker 2001; Solisio et al. 2002). In Finland, final slag from the copper smelting industry is one of the most important metal-containing waste materials that are currently disposed of in land fills. Annual generation of final slag in Finland is about 352 900 tons. If the copper of the final slag could be recovered, it would supply 1.2 % of the annual Cu production in Finland.

The traditional method for solubilizing metals from solid waste materials is chemical leaching with strong acids. However, chemical leaching is economic only when recoverable metals are present at relatively high levels. Bioleaching with acidophilic, Fe- and S-oxidizing microorganisms has been proposed as an alternative treatment method for waste materials that have relatively low levels of valuable metals or are otherwise difficult to handle or treat (Brandl and Faramarzi, 2006; Vestola et al 2010). Once the metals are in the solution, additional unit processes are needed to recover the metals. Precipitation of metals as sulfides using biogenic H_2S offers several advantages over chemical hydroxide precipitation: lower effluent concentrations of metals, better thickening characteristics of the metal sludge and the possibility to recover valuable metals (Kaksonen and Puhakka 2007). The bioprocess is based on biological H_2S and alkalinity (HCO_3^-) production by sulfate-reducing bacteria (SRB) (reaction 1), metal sulfide precipitation with biogenic H_2S (reaction 2), and neutralization of the acidity of the water with alkalinity produced by the SRB in the oxidation of provided electron donors (reaction 3) (Kaksonen and Puhakka 2007).

$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$ where CH_2O = electron donor (1)

$H_2S + M^{2+} \rightarrow MS(s) + 2H^+$ where M^{2+} = metal such as Zn^{2+} (2)

66 $HCO_3^- + H^+ \rightarrow CO_2(g) + H_2O$ (3)

67

68 The aim of the present work was to evaluate the feasibility of the bioleaching of metals from final
69 slag waste and precipitating the metals from the leach liquors using biogenic sulfide.

70

71 **MATERIALS AND METHODS**

72 **Final slag**

73 The particle size of the final slag sample was < 0.2 mm, most particles being smaller than 0.06
74 mm. The slag contained 40.7% Fe, 1.7% Zn, 0.35% Cu, 0.08% Ni, 0.19% S and 0.09% C. The slag
75 consisted mostly of fayalite (Fe_2SiO_4), magnetite (Fe_3O_4), calcite ($CaCO_3$) and chromite
76 ($FeCr_2O_4$). Additionally the slag contained galena (PbS), Fe-arsenides (FeAs), quartz, barite
77 ($BaSO_4$), pentlandite ($(FeNi)_9S_8$) and Cu-Fe-Sn-Sb phases. Copper was present mostly as sulfides
78 and partly as arsenide and metallic copper. Iron and most of the zinc and nickel were oxides in
79 fayalite and magnetite. The material was freeze-dried before bioleaching.

80

81 **Bioleaching culture**

82 The culture used in the bioleaching experiment had been enriched from acidic waters of the
83 Talvivaara mine, Finland as previously described (Halinen et al. 2009). The culture was originally
84 enriched in media containing mineral salts and finely ground black schist ore, S^0 and ferrous
85 sulfate, pH 1.8. The enrichment culture contained bacteria related to *Acidithiobacillus ferrooxidans*
86 (99% similarity of the 16S rRNA gene), *Acidithiobacillus thiooxidans* (100%), *Acidithiobacillus*

caldus (96%), *Leptospirillum ferrooxidans* (98-99%) and *Sulfobacillus thermotolerans* (99%) (Dopson et al. 2007; Halinen et al. 2009). For the bioleaching experiments the culture was grown at 25 ºC in shake flasks in mineral salts medium (MSM) described by Dopson and Lindström (1999), with the exception that HBO_3 was replaced by H_3BO_3 and the initial pH was 1.8. The medium was supplemented with 1% S^0 (sterilized at 105 °C for 24 h) and 4.5 g l^{-1} Fe^{2+} as $FeSO_4 \cdot 7H_2O$ (filter sterilized).

Bioleaching of final slag

Bioleaching of the final slag was evaluated at 22±2 °C in a 125 l continuously stirred tank reactor (CSTR) with an 85 l working volume. The reactor was equipped with a mixer (0.78/0.45A 0.12 kW, 1380 U/min VEM VEB Elektromotorenverke, Thurm DDR/GDR) and aeration was supplied from the bottom at 1.5 l min^{-1}. The medium (MSM) was supplemented with 1% S^0 and 5% final slag, but no ferrous iron was added. The medium was adjusted to pH 1 with H_2SO_4 and a 10% inoculum was used. The pH was manually readjusted with H_2SO_4 to pH 1 daily for the first 8 days before the biological S^0 oxidation produced enough acid to lower the pH below 1. The leach solution was analyzed for redox potential, Fe^{2+}, sulfate and dissolved metals (Fe, Cu, Zn and Ni) once a week. Distilled water was added to compensate for the loss of water due to evaporation. After 39 days of contact, the solution was collected and stored at +4 ºC for metal precipitation experiments. The solids were washed twice with dilute H_2SO_4 (pH 2), rinsed twice with Milli-Q water, and dried at 25 °C for elemental analysis.

Sulfidogenic fluidized-bed reactors

The precipitation of metals from the bioleach liquors was studied at 25 ºC using two sulfidogenic fluidized-bed reactors (FBR A and FBR B) with a working volume of 0.55 l and with 0.32 l silicate mineral (Ø 0.5-1 mm, Filtralite, Norway) as the biomass carrier (Figure 1). The carrier material was previously used in sulfidogenic FBRs fed with lactate, ethanol and reed canary grass hydrolyzate as electron donors (Kaksonen et al. 2006; Lakaniemi et al. 2010). The mixed FBR culture contained SRB related to the genera *Desulfovibrio, Desulfotomaculum*, *Desulfobulbus*, *Desulfurispora*, *Desulforhabdus* and *Desulfobacca* (Kaksonen et al. 2004b,c, 2007). The carrier was fluidized by FBR recycle flow maintaining 20% bed expansion.

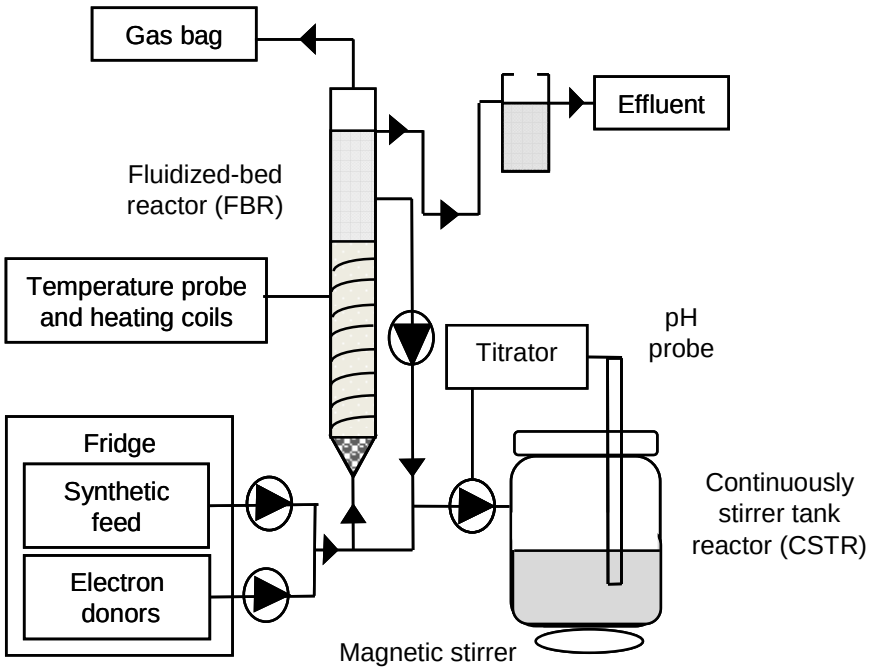


Figure 1. Schematic diagram of the sulfate-reducing FBR and CSTR.

The FBRs were initially operated in batch mode for 5 days and thereafter fed with a synthetic sulfate-containing solution, increasing the concentration stepwise (Table 1). Lactate and ethanol were fed as electron and carbon sources from separate reservoirs. The hydraulic retention time (HRT) in the empty bed volume was gradually decreased from 24 h to 20 h on days 87 and 76 in FBR A and FBR B, respectively, and in FBR A further to 16 h on day 123.

Precipitation of metals from bioleach liquor using biogenic sulfide

After 130 days of operation the effluent of FBR A was used for precipitating metals from the bioleach liquor in a CSTR (Figure 1). Known volumes of the bioleach liquor (pH 0.6) with metal concentrations of 9900 mg l^{-1} Fe, 117 mg l^{-1} Cu, 235 mg l^{-1} Zn, and 15 mg L^{-1} Ni were placed in the CSTR and titrated to desired pH values (1.7–6.5) with the sulfide-containing effluent from FBR A using a high-precision 780 pH meter (Metrohm AG) with a LL Syntrode PT1000 30 P.F pH electrode (Metrohm AG). Nine separate experiments were conducted to test the precipitation of metals at various final pH values. Due to the very low pH of the initial bioleach liquor and the limited operational volume of the CSTR, the alkalinity of the bioreactor effluent was not sufficient to increase the pH to values above pH 5. Therefore, for testing final pH values over 5, additional $CaCO_3$ supplementation was used. After reaching the final pH, the solution in the CSTR was sampled for analysis of dissolved metals.

Table 1. Composition of synthetic feeds (pH 4.0 adjusted with HCl) in FBR A and FBR B.

Synthetic feed	**Concentration (g l^{-1})**				
	A: 0-75 d **B: 0-75 d**	**A: 76-98 d** **B: 76-103 d**	**A: 99-109 d** **B: 104-119 d**	**A: 110-140 d**	**A: 141 – 192 d**
$Na_2SO_4 \cdot 10H_2O$	1.45	1.45	2.18	2.90	3.08
$MgSO_4 \cdot 7H_2O$	1.2	1.2	1.8	2.4	2.5
NH_4Cl	0.11	0.11	0.11	0.11	0.11
KH_2PO_4	0.056	0.056	0.056	0.056	0.056
$FeSO_4 \cdot 7H_2O$	0.3	0.3	0.45	0.6	0.3
Ascorbic acid	0.1	0.01	0.01	0.01	0.01
Na-thioglycollate	0.1	0.01	0.01	0.01	0.01
Electron donors					
Yeast extract	0.2	-	-	-	
Na-lactate	0.4	0.4	0.6	0.8	0.8
Ethanol	0.16	0.16	0.24	0.32	0.32

Bulk precipitation of metals within the bioreactor

From day 120 onwards FBR B was used for the precipitation of metals directly from bioleach liquor. The bioleach solution was diluted due to the high sulfate and metal concentration, supplemented with mineral nutrients and the pH was adjusted with NaOH from 0.6 to 3.5-4.3. The dilution of the bioleach solution was decreased stepwise to increase loading of the FBR B (Table 2). The performance of FBR B was monitored by measurements of the feed and effluent pH, acidity or alkalinity, sulfate, dissolved organic carbon (DOC) or lactate, ethanol and acetate and dissolved metals. The effluent was additionally analyzed for dissolved sulfide.

150 Table 2. Composition of diluted bioleaching liquor fed to the fluidized-bed reactor (FBR) B. The
151 water was supplemented with 0.22 g l^{-1} NH_4Cl, 0.056 g l^{-1} KH_2PO_4, 0.01 g l^{-1} ascorbic acid and
152 0.01 g l^{-1} Na-thioglycollate.

Parameter	**Composition**					
	120-139 d	**140-152 d**	**153-201 d**	**202-238 d**	**239-247 d**	**250-259 d**
Dilution factor of bioleaching liquor	50	40	20	13	10	5
Na-lactate (g l^{-1})	0.8	0.8	0.8	1.2	1.6	3.2
Ethanol (g l^{-1})	0.32	0.32	0.32	0.47	1.3	2.5
pH	3.5-4.0	3.8	4.0	3.7	4.3	4.1

153

154 **Analytical methods**

155 Solution pH was determined in unfiltered samples using a WTW315i - or WTW330i-pH meter and
156 a SenTix21 -, SenTix41- or SenTix81 -electrode. Redox potential was measured from unfiltered
157 samples using a Platin Combination Electrode Blueline 31 Rx (Schott Instruments GmbH, Mainz,
158 Germany). Total alkalinity was analyzed by titrating unfiltered samples with 100 mM HCl to
159 4.50±0.05 according to the standard SFS-EN ISO 9963-1 (Finnish Standards Association 1996).
160 Mineral acidity was analyzed by potentiometric titration with 100 mM NaOH to pH 4.5 and total
161 acidity by titration to pH 8.3 according to the standard SFS 3005 (Finnish Standards Association
162 1981).

163 For analyses of sulfate, ethanol, lactate, acetate, soluble metals and dissolved sulfide, solids were
164 removed from the samples by filtration (0.45 µm). Dissolved sulfide was analyzed colorimetrically

(Shimadzu UV-1601, Japan) (Cord-Ruwisch 1985) and sulfate by ion chromatography (Dionex DX-120, Sunnyvale, CA) according to standard SFS-EN ISO 10304-2 (Finnish Standards Association 1997).

Lactate, ethanol, and acetate were determined initially by liquid chromatography (Waters 510) using a Shodex Sugar SH1011 column (Showa Denko K.K.) and refractive index detector (WGE Dr. Bures GmbH & Co. KG). After 175 days of reactor operation ethanol and acetate were measured by gas chromatography (Hewlett Packard 5890II, Corvallis, OR) using an HP-Innowax column (Agilent, USA) and a flame ionization detector. The concentration of lactate was then calculated as the difference between DOC (Shimadzu TOC-5000 Total Organic Carbon Analyzer, Tokyo) and ethanol and acetate concentrations.

Ferrous iron (Fe^{2+}) was determined colorimetrically with the *o*-phenanthroline method 3500-Fe (APHA 1992). Soluble metal concentrations were measured with an atomic absorption spectrophotometer (AAS, Perkin Elmer 1100, Oak Brook, IL) according to standards SFS 3044 (Finnish Standards Association 1980a) and SFS 3047 (Finnish Standards Association 1980b). Additionally selected samples were analyzed by inductively coupled plasma emission spectrometry (Thermo Jarrel Ash Iris ICP-AES, USA) at Labtium Ltd.

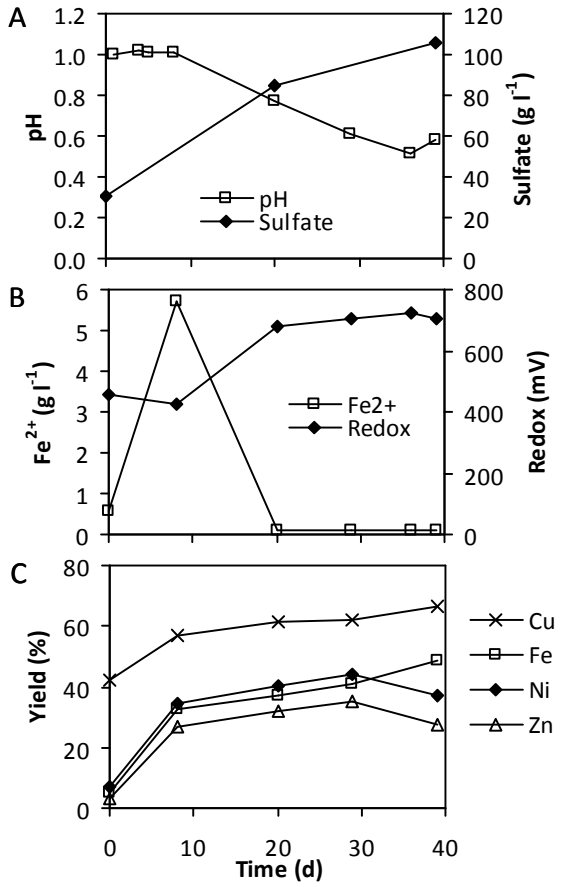
Total suspended solids (TSS) and volatile suspended solids (VSS) were analyzed from the FBR samples according to standard EN 872:2005 (Finnish Standards Association 2005). Volatile solids (VS) were determined from FBR carrier material according to standard SFS 3008 (Finnish Standards Association 1990). Elemental composition of the leaching residues was analyzed by inductively coupled plasma emission spectrometry by a commercial laboratory.

RESULTS AND DISCUSSION

Bioleaching

The pH of the bioleaching liquor was adjusted during the first 8 days with H_2SO_4 to 1.0. The cumulative acid consumption during this period was 0.51 kg H_2SO_4/kg of final slag. Thereafter, biological oxidation of the supplemented sulfur to H_2SO_4 decreased the solution pH from 1.0 to 0.6 within 39 days of operation (Figure 2A). Concomitantly the sulfate concentration increased to 106 g l^{-1} (Figure 2A). Fe^{2+} concentration increased initially to 5.7 g l^{-1} as Fe was solubilized from the slag, but after 20 days the concentration remained < 0.1 g l^{-1} Fe^{2+} due to biological Fe^{2+} oxidation as indicated by the increase in redox potential from approximately 450 mV to >700 mV (Figure 2B). The yields of metal solubilization after 29 days of contact were 41% Fe, 62% Cu, 35% Zn and 44% Ni (Figure 2C). By day 39, the yields of Fe and Cu solubilization increased to 58% and 65%, respectively, whereas the yields of Zn and Ni decreased, suggesting precipitation (Figure 2C).

The final concentrations of the metals, the corresponding yields, and the residual levels of metals in the solids are summarized in Table 3. The yields obtained with CSTR leaching for Fe, Cu, Zn and Ni were lower than those reported by Vestola et al. (2010) for the same final slag sample (64% Fe, 100% Cu, 100% Zn and 100% Ni). Vestola et al. (2010) leached the slag in inoculated shake flasks which were supplemented with S^0 at pH 1.5 and incubated at 25 °C for 42 days.



206

207 Figure 2. Solution pH and sulfate (A), Fe^{2+} and redox (B), and metal yields (C) during the CSTR

208 leaching of final slag.

209

210 Table 3. Initial metal concentration and decrease in metal content of final slag after CSRT leaching
211 for 39 days.

Metal	**Initial concentration in slag (mg kg^{-1})**	**Final concentration in solution (mg l^{-1})**	**Solubilized (%) based on solution analysis**	**Decrease (%) in final slag metal content during bioleaching based on solids analysis**
Al	4600	40	17	26
As	337	13	77	79
Cd	17.3	0.8	92	69
Co	508	16	63	66
Cr	301	1.0	7	16
Cu	3530	120	68	66
Fe	407000	11800	58	55
Mn	424	11	53	91
Mo	825	1.7	4	20
Ni	845	18	43	46
Pb	754	4.0	11	12
Ti	1220	7.5	12	16
V	51.7	0.3	10	49
Zn	17400	565	65	64

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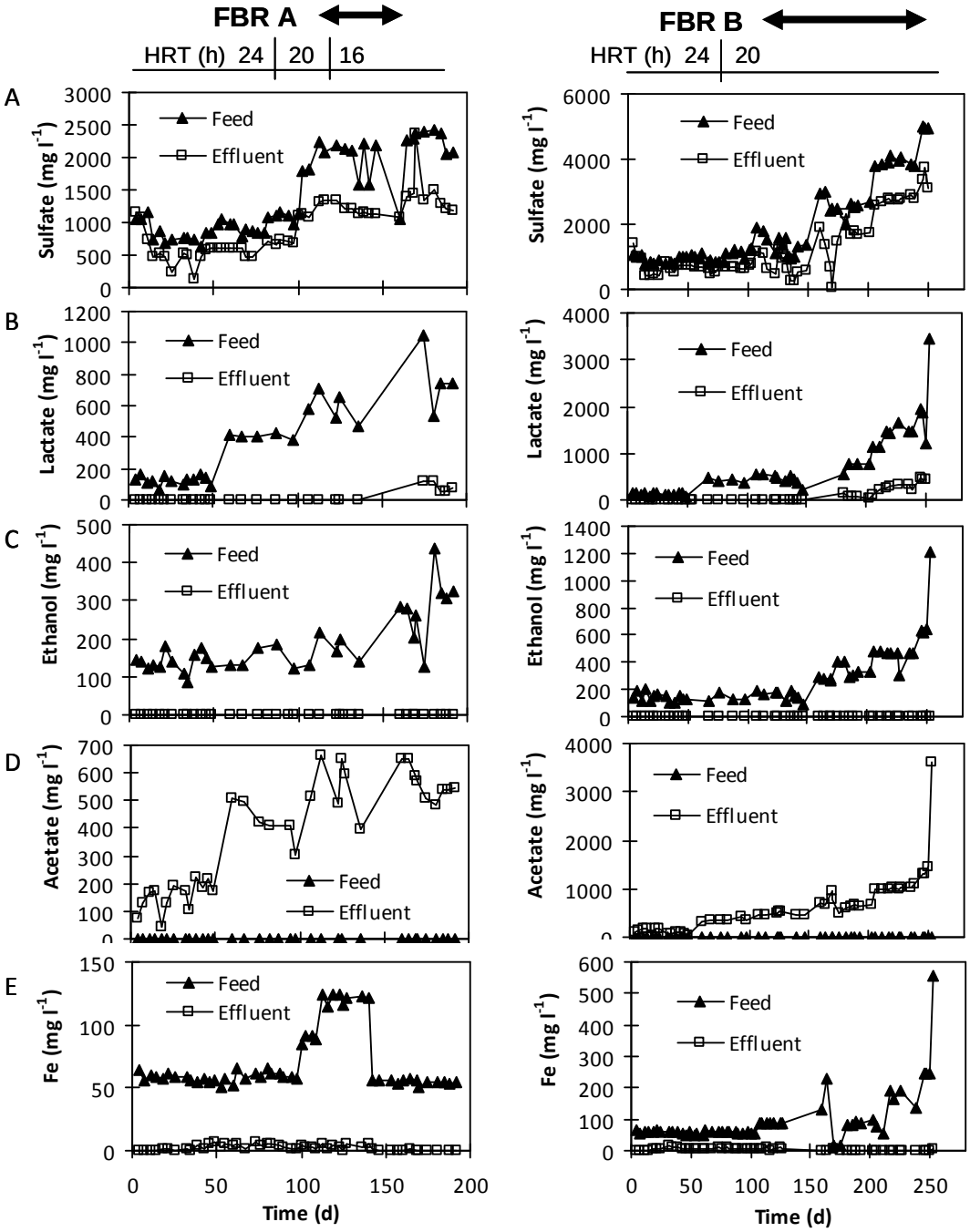
Performance of sulfidogenic FBRs

The precipitation of metals from the bioleach liquors was tested using sulfidogenic FBR A and FBR B for selective and bulk precipitation, respectively. Figures 3-7 show the performance of the FBRs before and during the precipitation experiments.

Sulfate reduction rates increased in both FBR A and FBR B as the influent sulfate concentrations increased (Figure 3A). During the selective precipitation of metals using effluent from FBR A, the average sulfate reduction rate was 1210 ± 360 mg l^{-1} d^{-1} (Figure 4A) with 39 ± 8% sulfate reduction (Figure 5A). The average total dissolved sulfide concentration in FBR A in the precipitation experiments was 324 ± 72 mg l^{-1} and the H_2S concentration 34 ± 35 mg l^{-1} (Figure 6A). In FBR B the highest average sulfate reduction rates (1550 ± 390 mg l^{-1} d^{-1}) with stable performance were obtained with ten-fold diluted bioleach solution (Figure 4A), and the corresponding percent sulfate reduction was 28 ± 4% (Figure 5A). The average total dissolved sulfide concentration in FBR B with ten-fold diluted bioleach solution was 175 ± 92 mg l^{-1} and the H_2S concentration 68 ± 29 mg l^{-1}. The highest average total dissolved sulfide concentration (271 ± 139 mg l^{-1}) was observed with 13-fold diluted bioleach solution and the corresponding H_2S concentration was 101 ± 53 mg l^{-1} (Figure 6A). With the five-fold diluted bioleach solution as the FBR B influent, biological sulfate reduction ceased, resulting in a decrease of the effluent dissolved sulfide concentration (Figure 6A). The sulfate reduction rates and efficiencies in the present study with the FBRs at 25°C are lower than those previously reported for lactate- and ethanol-fed sulfidogenic FBRs operated at 35°C (Kaksonen et al. 2003a; 2003b; 2004a; 2006). However, the rates were higher than reported by Sahinkaya et al. (2007) for ethanol-fed sulfidogenic FBRs operated at 8°C and at 65°C.



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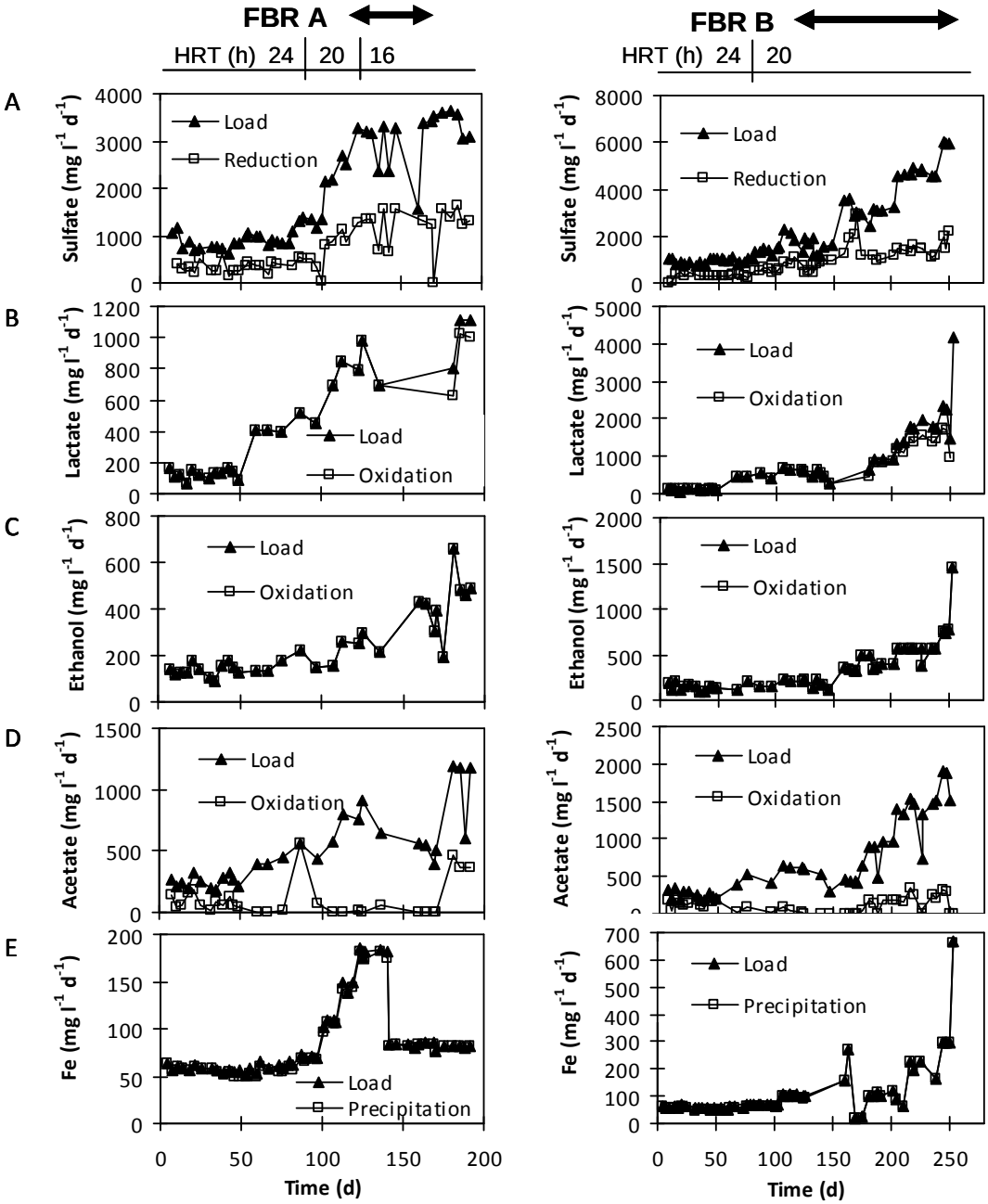
239 Figure 3. Feed and effluent sulfate (A), lactate (B), ethanol (C), acetate (D) and dissolved Fe (E)
240 concentration in FBR A (figures on the left) and FBR B (figures on the right). The bold arrows
241 show the time of selective metal precipitation with FBR A effluent and the bulk precipitation of
242 metals in FBR B.

Lactate oxidation was nearly 100% in both FBR A and FBR B, and the effluent lactate concentration remained below the detection limit during the first 150 days of the time course (Figures 3B, 4B and 5B). However, in the latter part of the time course, when lactate oxidation was estimated from the DOC, ethanol, and acetate measurements, the extent of lactate oxidation was calculated to be 87 ± 8% and 81 ± 8% in FBR A and FBR B, respectively (Figure 5B). The efficiency of ethanol oxidation was 100% in both FBRs throughout the study (Figures 3C, 4C and 5C). The influent lactate and ethanol were partially oxidized incompletely to acetate, and the effluent acetate concentrations increased (Figure 3D) with lactate and ethanol loads (Figures 4B and C). The average effluent acetate concentration and acetate oxidation efficiency in FBR A during the selective precipitation of metals were 573 ± 90 mg l^{-1} and 34 ± 5%, respectively (Figures 4D and 5D). The corresponding values in FBR B during the highest loading (ten-fold diluted leach solution) were 1240 ± 130 mg L^{-1} and 15 ± 6%, respectively (Figures 4D and 5D). The acetate oxidation efficiencies were lower than those reported by Kaksonen et al. (2004a) for an ethanol-fed sulfidogenic FBR operated at 35°C. Sahinkaya et al. (2007) also observed that the acetate oxidation efficiency was relatively low (18 ± 9%) in an ethanol-fed sulfidogenic FBR operated at 8°C. Acetate oxidation is important for alkalinity production in sulfidogenic bioreactors. Sulfidogenic lactate oxidation produces some alkalinity even if the oxidation is incomplete and acetate accumulates, whereas with ethanol the complete oxidation is required to produce alkalinity.



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265 Figure 4. Sulfate load and precipitation (A), lactate load and oxidation (B), ethanol load and
266 oxidation (C), theoretical acetate load from oxidized lactate and ethanol, and oxidation (D), and Fe
267 load and precipitation (E) in FBR A (figures on the left) and FBR B (figures on the right). The
268 bold arrows show the time of selective metal precipitation with FBR A effluent and the bulk
269 precipitation of metals in FBR B.

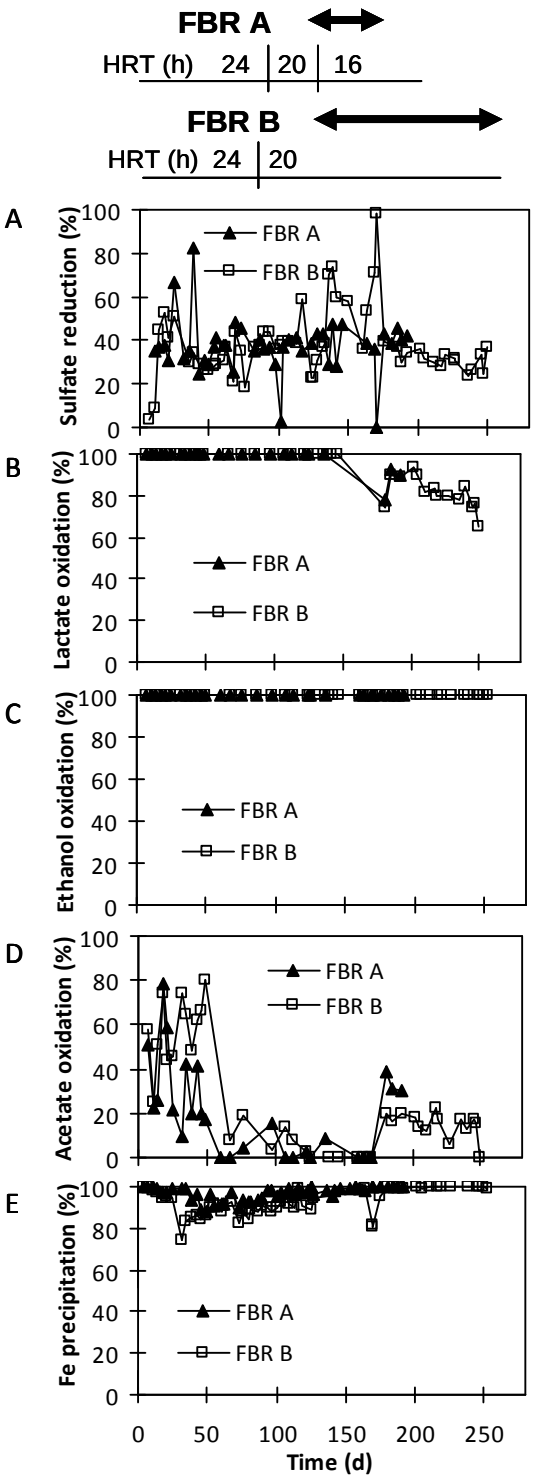


Figure 5. Percent sulfate reduction (A), lactate oxidation (B), ethanol oxidation (C), acetate oxidation (D) and Fe precipitation (E) in fluidized-bed reactors (FBR) A and FBR B. The bold arrows show the time of selective metal precipitation with FBR A effluent and the bulk precipitation of metals in FBR B.

In this study, alkalinity production in the FBRs during sulfidogenic electron donor oxidation increased with loading rates. The alkalinity thus produced increased the pH of the acidic (pH 3.5-4.3) influent to near neutral values in both FBRs. In FBR A the average effluent pH throughout the study was 7.5 ± 0.5 and alkalinity 8.5 ± 3.6 mM (Figures 6B and C). In FBR B average effluent pH was 7.1 ± 0.4 and alkalinity 12 ± 8 mM (Figures 6B and C).

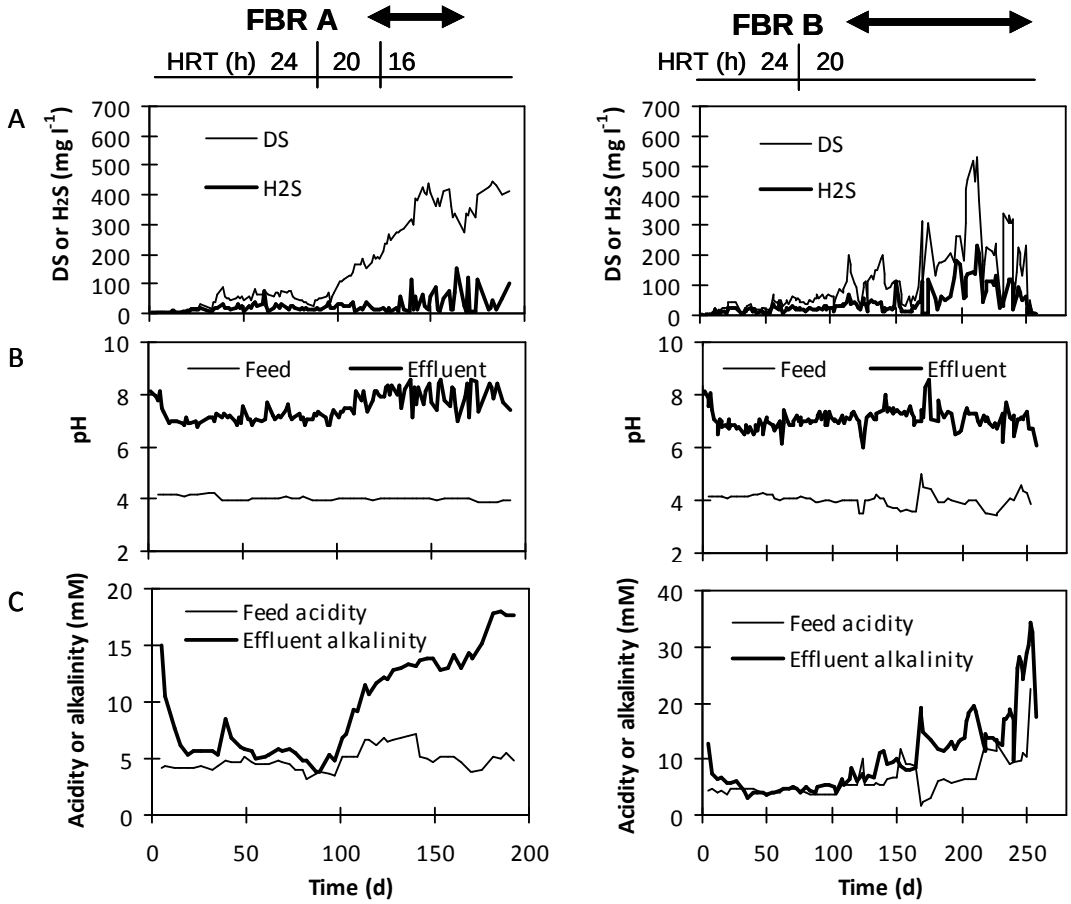
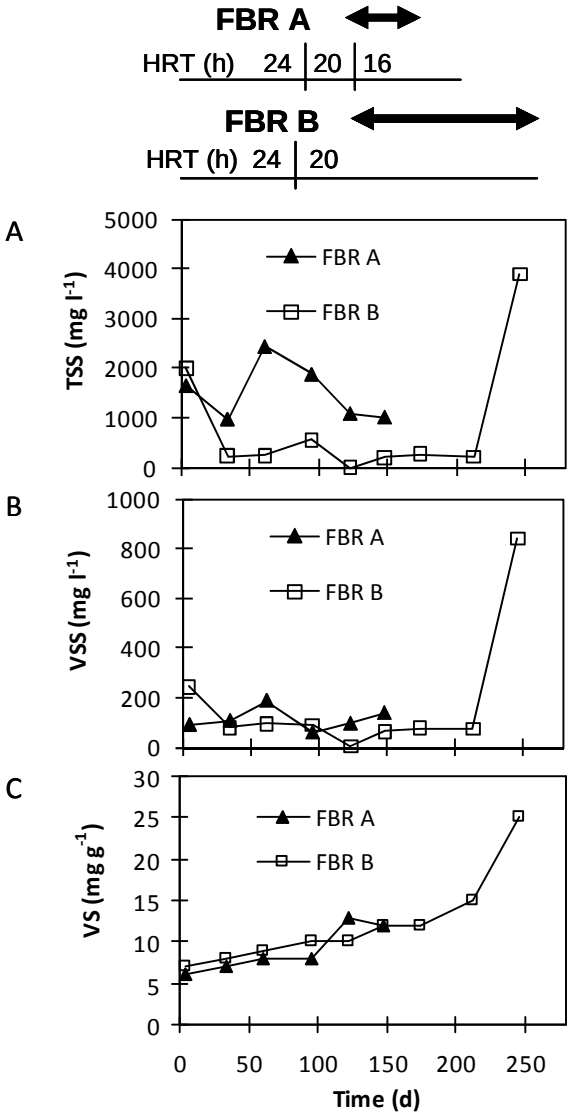


Figure 6. Total dissolved sulfide (DS) and H_2S in effluent (A), feed and effluent pH (B) and feed acidity and effluent alkalinity (C) in FBR A (figures on the left) and FBR B (figures on the right). The bold arrow shows the time of selective metal precipitation with FBR A effluent and thin arrow the bulk precipitation of metals in FBR B.

286 Accumulation of metal sulfide precipitates and biomass in the FBR was monitored by analysis of
287 TSS and VSS. The TSS and VSS concentration varied over time in both FBRs. The highest
288 concentrations (approximately 3900 mg TSS l^{-1} and 840 mg VSS l^{-1}) were observed in the FBR B
289 with the five-fold diluted bioleach solution as the influent (Figures 7A and B). The VS
290 concentration of carrier materials increased over time in both FBRs, indicating biomass growth. In
291 FBR A the increase was from 6 to 12 mg VS g^{-1} and in FBR B from 7 to 25 mg VS g^{-1} (Figure
292 7C). The average VS concentrations were in a similar range to those observed by Kaksonen et al.
293 (2003b) in lactate-fed sulfidogenic FBR operated at 35°C and by Sahinkaya et al. (2007) in
294 ethanol-fed FBR operated at 65 °C, but higher than those of ethanol- or formate-fed FBRs operated
295 at 8 °C (Sahinkaya et al. 2007) and 9°C (Auvinen et al. 2009), respectively.
296
297 The average influent and effluent Fe concentrations in FBR A throughout the study were 70 ± 24
298 mg l^{-1} and 2.2 ± 2.0 mg l^{-1}, respectively, corresponding to 84 ± 39 mg l^{-1} d^{-1} precipitation rate and
299 97 ± 3% precipitation efficiency (Figures 3E, 4E and 5E). In FBR B with the synthetic feed, before
300 starting the experiments with bioleach solution, the average influent and effluent iron
301 concentrations were 60 ± 12 mg l^{-1} and 5.9 ± 3.2 mg l^{-1}, respectively. The corresponding Fe
302 precipitation rate 64 ± 18 mg L^{-1} d^{-1} and precipitation efficiency 90 ± 5% (Figures 3E, 4E and 5E).



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304 Figure 7. Total suspended solids (TSS) (A), volatile suspended solids (VSS) (B) and volatile solids
305 (VS) (C) in the fluidized bed reactors (FBR) A and B. The bold arrows show the time of selective
306 metal precipitation with FBR A effluent and the bulk precipitation of metals in FBR B.

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Recovery of metals from bioleach liquor

The recovery of metals from the bioleach liquor obtained from final slag was studied in a CSTR by titrating the bioleach solution with sulfide containing alkaline effluent from FBR A to the desired pH values. Table 4 is a summary of the precipitation of Cu, Zn, Ni and Fe, volume ratio of the FBR effluent to the bioleach liquor, and additional $CaCO_3$ needed to adjust the pH.

Table 4. Percent metal precipitation, the ratio of fluidized-bed reactor (FBR) A effluent to bioleaching liquor, and additional use of $CaCO_3$ solution in precipitating metals from the final slag bioleach liquor (initial pH 0.6) in a CSTR using sulfide containing fluidized-bed reactor effluent.

pH	Precipitated (%)				FBR A effluent/bioleaching liquor (vol/vol)	vol-% of added 0.1 M $CaCO_3$ (% of final volume)
	Cu	Zn	Ni	Fe		
1.7	23	0	0	3	9	-
1.9	28	0	0	0	13	-
2.8	98	0	0	0	26	-
3.2	97	0	0	0	37	-
3.9	100	99	0	0	40	-
4.7	100	100	0	0	58	-
5.2	96	100	0	0	44	4
6.1	94	100	43	14	61	3
6.5	100	100	63	28	92	6

Over 98% of the Cu precipitated at pH≥ 2.8 and over 99% of the Zn precipitated at pH≥ 3.9 (Table 4). The precipitation of Ni and Fe required higher pH values and was less efficient. Only 43% and 63% of the Ni precipitated at pH 6.1 and 6.5, respectively. For Fe, the corresponding values were 14% and 28%, respectively (Table 4). Because acetate oxidation and alkalinity production in FBR A were incomplete (Figures 3D, 4D, 5D and 6C), relatively large volumes of FBR effluent were needed to increase the pH of the very acidic (pH 0.6) bioleach solution (Table 4). One way to decrease the required effluent/bioleach liquor ratio would be to leach the metals from the final slag at a higher pH as less alkalinity would be needed to increase the pH of the liquor. However, this may involve less optimal conditions for the bacteria and reduce the solubility of metals. Enrichment of acetate oxidizers in the FBR could enhance the acetate oxidation efficiency and alkalinity production in the sulfidogenic FBR. The pH ranges required for the precipitation of Cu and Zn were similar to those observed in previous studies, but Ni and Fe precipitation required higher pH values (Tabak et al. 2003; Bijmans et al. 2009). Tabak et al. (2003) tested the precipitative recovery of metals with a four-stage process using biogenic sulfide and mine water. In their study 99.8-100% of Cu (223 mg l^{-1}) precipitated at pH 2.2-2.8, when the pH was adjusted with KOH. The precipitation of Zn (630 mg l^{-1}) was 99-100% at a pH of 4.5, and that of Fe (514 mg l^{-1}) 98-100 % at pH 5.7-6.6 (Tabak et al. 2003). In the study by Bijmans et al. (2009), Ni was efficiently precipitated at pH 5.0.

Bulk precipitation of metals in FBR B

From day 120 onwards FBR B was used for studying the precipitation of metals from pre-diluted (pH 3.5-4.3) bioleach liquor within the bioreactor. Table 5 is a summary of the precipitation efficiency of Cu, Zn, Ni and Fe in FBR B with the various dilution factors used. Precipitation of Cu was 100 ± 1% and that of Zn and Fe 99 ± 1% during the highest loading (ten-fold diluted bioleach solution).

345 Table 5. Dilution of final slag bioleach solution fed to fluidized-bed reactor (FBR) B, feed and
346 effluent pH, feed metal concentrations and percent metal precipitation within FBR B during stable
347 reactor operation.

Dilution of bioleach liquor	Feed pH	Effluent pH	Feed (mg l^{-1})				Precipitated (%)			
			Cu	Zn	Ni	Fe	Cu	Zn	Ni	Fe
50x	4.1±0.1	7.4±0.1	2.3±0.1	11±0.1	0.38±0.03	86±6	100±1	98±1	96±5	96±2
40x	3.7±0.1	7.4±0.1	3.2±0.1	14±0.2	0.47±0.01	112±5	97±3	97±1	94±3	96±2
20x	4.0±0.5	7.3±0.5	6.1±0.6	20.5±4.1	0.98±0.18	96±67	99±1	99±1	98±4	99±2
13x	3.7±0.3	7.1±0.3	9.1±0.9	27.5±3.8	1.35±0.13	77±23	99±1	99±1	100±1	100±1
10x	4.3±0.3	7.0±0.3	12±1	35±1	2.4±0.1	245±1	100±1	99±1	96±1	99±1

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349 The Ni precipitation efficiency was 96 ± 1% (Table 5). The highest precipitation rates were 294 ±
350 2 mg Fe l^{-1} d^{-1}, 42 ± 2 mg Zn l^{-1} d^{-1}, 14 ± 2 mg Cu l^{-1} d^{-1}, and 2.9 ± 0.2 mg Ni l^{-1} d^{-1}. The effluent
351 pH stayed at ≥ 7 with dilution factors of 10-50 of the bioleach solution (pH 3.7-4.3) (Table 5).
352 However, when five-fold diluted bioleach solution (pH pre-adjusted to 4.1) was used, the effluent
353 pH decreased below 7 due to diminished sulfate reduction and alkalinity production. Consequently
354 stable metal precipitation could no longer be maintained with the lowest dilution tested (data not
355 shown). The use of the bioleach solution as FBR influent without diluting and pre-adjusting the pH
356 from 0.6 to approximately 4 was not possible as it completely inhibited the biological sulfate
357 reduction. The Zn precipitation rate observed in the present study for FBR B was higher but the Fe
358 precipitation rate lower than the rates reported by Lakaniemi et al. (2010) (16 ± 2 mg Zn l^{-1} d^{-1} and
359 840 mg Fe l^{-1} d^{-1}) in a FBR fed with reed canary grass hydrolyzate at 35°C. Higher Zn and Fe
360 precipitation rates (600 mg Zn l^{-1} d^{-1} and 300 mg Fe l^{-1} d^{-1}) were also reported by Kaksonen et al.

(2004a) in and ethanol-fed FBR at 35°C. The Fe precipitation rates reported by Sahinkaya et al. (2007) for ethanol-fed FBRs at 8°C and 65°C were lower (60 mg Fe l^{-1} d^{-1} and 90 mg Fe l^{-1} d^{-1}, respectively) as compared to the results of the present study.

CONCLUSIONS

The study was undertaken to evaluate the feasibility of acid bioleaching of metals from a sample of final smelter slag and the potential for recovering metals from the leach solutions by sulfide precipitation. Metal solubilization yields after 29 days of leaching in a continuously stirred tank reactor (20-25 °C) with 5% pulp density were 41% Fe, 62% Cu, 35% Zn and 44% Ni. Cu and Zn could be subsequently precipitated from the bioleach solution using an effluent from a sulfidogenic fluidized-bed bioreactor (25 ºC). Over 98 % of the Cu precipitated at pH≥ 2.8 and over 99% of the Zn precipitated at pH≥ 3.9. The precipitation of Ni and Fe required higher pH values and was less efficient. Due to the limited acetate oxidation and alkalinity production in the FBR, the volume of the FBR effluent needed to adjust the pH of the bioleach solution was relatively large. The effluent/bioleach liquor ratio could be decreased by leaching the metals at a higher pH and increasing the alkalinity production in the FBR by enriching for acetate oxidizers. Bulk precipitation of metals from the bioleach solution in the sulfidogenic FBR required dilution of the leach solution at least ten-fold and pre-adjustment of the pH from 0.6 to approximately 4.

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