EFFECTS OF SOME FACTORS ON THE IRON REMOVAL FROM RICH-IN-IRON WASTE SOLUTIONS BY MEANS OF GOETHITE AND HEMATITE PRECIPITATION PROCESSES

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ABSTRACT: Biohydrometallurgical processing of raw materials enriched with non-ferrous metals is based on the direct and indirect mechanisms of the oxidative leaching of their sulfides, and accumulation of the released ions in the pregnant leach solution. Further, the leached non-ferrous metals are separated from each other and concentrated in rich electrolytes by means of the relevant solvent extraction processes, while the dissolved iron accumulates in raffinate which needs some additional processing steps for its removal from the solution. This study presents some results about the effects of the operating temperatures (25 – 90 °C), pH (2 – 4), and the applied seeding rate on the chemical oxidation of ferrous ions and removal of ferric iron as goethite and hematite from rich-in-iron waste solutions generated during the processing of final copper slags.

Keywords: goethite, hematite, iron, pregnant leach solutions

ВЛИЯНИЕ НА НЯКОИ ФАКТОРИ ВЪРХУ УТАЯВАНЕТО НА ЖЕЛЯЗО ОТ ОТПАДНИ ВОДИ ПОД ФОРМАТА НА ГЬОТИТ И ХЕМАТИТ

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РЕЗЮМЕ: Процесите на преработка на минерални суровини, богати на цветни метали чрез методите на биохидрометалургията се базират на прекия и непряк механизъм на окисление на сулфидите и натрупване на образуваните йони при този процес в продукционните разтвори. Разтворените цветни метали се разделят един от друг и концентрират в богати разтвори посредством съответните процеси на течностна екстракция, докато разтвореното желязо се акумулира в рафината, което налага допълнителни стъпки за неговото отстраняване от разтвора. Настоящето изследване представя някои резултати за влиянието на температурата (25 – 90 °C), pH (2 – 4), и концентрацията на внасяните зародиши върху химичното окисление на феро йоните и утаяването на желязото, като гьотит или хематит от отпадни разтвори, богати на желязо, образуващи се при преработката на крайни медни шлаки.

Ключови думи: гьотит, хематит, желязо, продукционни разтвори

Introduction

Iron plays a main role in the hydrometalurgy where the processing of non-ferrous metals from different types raw materials (low-grade ores, flotation concentrates, technogenic wastes) is carried out usually at acidic pH. At such conditions, ferric iron is stable in solution and because of its strong oxidative properties oxidizes and leaches a wide range of sulfides. Ferrous iron ions generated as a result of that process are regenerated back to ferric state due to the ability of iron oxidizing chemolithotrophic bacteria to gain energy for their growth on the account of that process. Thus, the higher concentration of the chemical oxidant is maintained during the raw material processing, which combined with very acidic pH, determines the higher concentration of non-ferrous metals in the generated pregnant leach solutions (PLS). The next step in the typical hydrometallurgical flowsheet is the solvent extraction process (SX). It is based on the consecutive separation of the base metals in PLS and their many-fold concentration into separate aqueous stream-rich electrolyte. From there, the dissolved non-ferrous metals deposit as zero valent state form under the relevant optimal current and voltage regime supplied to the electrowining cell (Davenport et al., 2002).

The classical way of iron removal from waste solution is the chemical oxidation of ferrous iron, neutralization of the water acidity and iron (hydro)oxides formation as a result of the ferric iron hydrolysis. The latter process is connected with the non-ferrous metals or toxic elements co-precipitation in a different extent and the formed iron minerals, as a result, are with a low quality to other industries, which impose their disposal and long-term storage. The main products of chemical neutralization, in dependence on temperature and pH, are jarozite, schwertmanite, goethite, or hematite. Because of the higher iron content and some properties (color, bulk density and higher settling velocity), goethite and hematite are preferred end products of the iron removal from iron rich waste solutions (Ismael and Carvalho, 2003)

The new approach in the iron removal process from PLS is the iron oxides formation with almost constant mineralogy and a chemical content free from other non-ferrous metals or toxic elements. In that case, the iron oxides could be used as an iron source in the steel industry (Torfs and Vliegen, 1996.) or in preparation of suitable sorbents for treatment of waters polluted by toxic elements (Mohan and Pittman Jr., 2007). That approach imposes the requirement of a preliminary transfer of

dissolved iron from the bulk solution into a separate only-iron-containing water stream which is achieved by means of solvent extraction process. Different kind of compounds are used into the practice for that purpose – organic phosphorous-containing compounds (Hirato et al., 1992) (tributhyl phosphate (TBP), 2-ethylhexyl) phosphate (DEHPA) (Sato et al., 1985), a tertiary carboxylic acids (Versatic acid; Thorsen et al., 1984) or amino-phosphoric acid (phosphonomethylated alkylamine (EU2), Delmas etal., 1996). The transfer of dissolved iron in a separate water stream enables the application of suitable measures for its precipitation as iron oxides with higher iron content and a good filterable characteristic. In most cases, goethite and hematite are preferred end products. Goethite (α-FeOOH) is formed at pH 2-3, temperatures below 70 °C and at lower concentration of ferric iron (Agatzini et al., 1986). Hematite has been reported as an end product at a temperature greater than 100 °C and under pressure oxidation of greater than 5 bar (Dutrizac and Riveros, 1999). In that case, intermediate irons oxides are formed (as akagenite in chloride media), which are transformed later into hematite. When the reaction takes place at lower temperature (50-90 °C) and in the presence of hematite seeds, however, hematite is formed directly (Cohen et al., 2005).

The article presents results about the effect of pH, temperature, and seeding rate on the goethite and hematite precipitation processes from rich-in-iron waste solution generated during bacterial leaching of final copper slags.

Materials and methods

All batch experiments about the iron precipitation from rich-in-iron waste leach solutions were carried out in 1 L reactors supplied with a propeller. The iron precipitation as goethite formation was studied at temperatures 25 and 50°C, while at 90°C the hematite formation was studied. The relevant temperature during the tests were maintained by a water bath. The chemical neutralization of the acidic pH was carried out by means of addition of alkaline solution (5 M NaOH) at a regime of permanent agitation (250 rpm). In the case when goethite formation was studied, the solutions were aerated with mini compressor as the air splurged in the zone determined by the lower propeller level and the reactor`s bottom. pH and Eh values were measured periodically depending on the added bases to the solution.

The effect of seeding rate (0.2 – 5.0 g/L) on the iron precipitation was studied by addition of finely ground samples (below 25 microns) of goethite (or hematite) to the waste solutions in the beginning of the chemical neutralization. The concentration of total and ferric iron in the solutions was determined by means of spectrophotometric method in the presence of sulfosalicylic acid at acidic and alkaline pH, respectively.

Some important characteristics (settling velocity, total suspended solids (TSS) (Eaton et al., 2005a) and sludge volume index (SVI) (Eaton et al., 2005b)) of already formed iron oxides were measured in the graduated sedimentary cone with volume of 1 L at a constant temperature.

Table 1.
Data about the solutions used in this study

Parameter	Pregnant leach solution	Rich-in-iron waste solution
pH	0.48-0.67	1.82 – 1.95
Eh, mV	345 – 360	710 – 770
Fe^{3+}, mg/L	825 – 1050	8650 – 11440
Fe^{2+},mg/L	29370 – 32837	130 – 255
Fe total, mg/L	30195 – 33890	8780 – 11695
Cu, mg/L	225 – 281	< 0.6
Al, mg/L	222 – 250	18.5 – 24.2
Ca, mg/L	1074 – 1326	18– 45
Mg, mg/L	188 – 240	3.3 – 8.8

Table 2.
Data about iron hydrolysis carried out at ambient temperature when the alkaline solution was added gradually during the test

t, min	Parameter			
	Base consumption, ml NaOH/ L	pH	Eh	Fe_{total}, mg/ L
10	6	3.02	625	2320
20	22	3.18	620	990
30	32	3.23	615	970
40	40	3.60	579	690
50	47.6	4.43	440	10.4

Table 3.
Data about iron hydrolysis carried out at ambient temperature when the alkaline solution was added almost at once at the test`s start

t, min	Parameter			
	Base consumption, ml NaOH/ L	pH	Eh	Fe_{total}, mg/ L
10	38.7	3.35	585	2015
20	40.5	3.28	542	720
30	42.3	3.47	503	255
40	44.7	3.55	480	64.2
50	47.6	4.45	415	6.2

Results and discussion

The pregnant leach solution (PLS) generated during the bacterial leaching of final copper slag in a continuously operated bioreactor was used in the study. For that reason, the solution characterized with very high concentration of dissolved iron which ranged between 27 – 34 g/L, as the relative content of ferric iron was around 3 % from the above-mentioned value (Table 1). Copper was the base metal leached easily from the processed raw materials and it separated and concentrated from the PLS into copper-rich solution by means of solvent extraction process with ACORGA LS 4202. The optimal pH for that process was around 2.0 and the copper extraction from PLS was low when the process was realized in the presence of iron. So, the very high iron concentration in PLS imposed the need for a stage of preliminary oxidation of ferrous iron followed by extraction and separation of the generated ferric iron ions into a separate rich-in-iron waste solution. The chemical oxidation of ferrous iron by stabilized hydrogen

peroxide solution (30 %) was applied in that case and the oxidized iron was extracted from the PLS by means of 15 % solution of DEHPA. The formed rich-in-iron waste stream was with acidic pH (in the range of 1.8 – 2.0), as a result, it had deep red color because more than of 97.5 % of the iron in solution was in the ferric state. The copper concentration transferred by this process was negligible (Table 1).

Table 4.
Effect of the temperature during the chemical neutralization of rich-in-iron waste solution on some important characteristics of the produced slimes

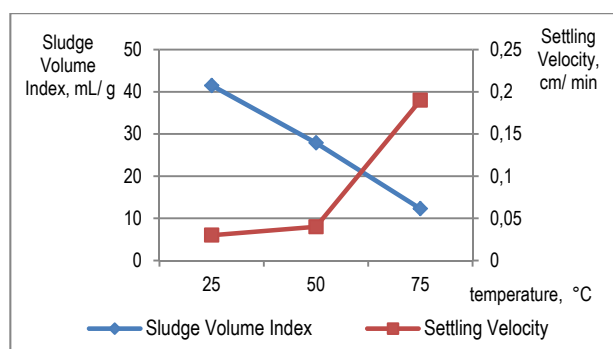| Parameter	Temperature		
	25°C	50°C	90°C
Residual iron concentration, mg/	10.4	3.6	4.4
Total suspended solids (TSS), g/L	21.8	21.5	15.7
Sludge volume index (SVI), mL/ g	41.5	27.9	12.3
Settling velocity, cm/ min	0.03	0.04	0.19

Fig. 1. Effect of the temperature on the iron removal from rich-in-iron waste solution

pH and Eh values were invaluable during the characterization of the ferric iron precipitation. The ferric iron hydrolysis simultaneously decreased the oxidant concentration and generated hydrolytic acidity into the solution. For that reason, Eh values gradually decreased while the pH values remained almost constant despite the added bases (Tables 2-5).

Two different approaches were applied to the process of iron hydrolysis. The first was connected with the gradual addition of alkaline solution as the main aim was to maintain pH in the range of 3.00- 3.20 (Table 2). As an alternative, the already known amount of bases was added at the test beginning and during the next 60 minutes the changes of water chemistry were only monitored (Table 3). However, the results showed that regardless of the way of alkaline solution addition, the iron hydrolysis was carried out with higher rate and more than of 80 % of the iron precipitated during the first ten minutes in both cases. However, the residual lower iron concentration was measured when the needed amount of alkaline solution was added almost all in the beginning of the test in comparison to the variant when it was added serially. For that reason, the needed amount of bases was added at once at the start of all

other experiments. In both cases, the formed iron precipitates had yellowish color which is a typical feature of goethite. The freshly formed goethite particles suspended in water for a long time which determined the highest value of sludge volume index (SVI) (more than 40 mg/ L) and their very low settling velocity (Table 6, Fig. 1).

Table 5.
Data about iron hydrolysis carried out at 50 °C from rich-in-iron waste solution

t, min	Parameter			
	Base consumption, ml NaOH/ L	pH	Eh	Fe$_{total}$, mg/ L
10	37.0	3.00	695	1825
20	41.4	3.26	605	546
30	43.4	3.48	586	72.0
40	46.8	4.00	575	14.3
50	47.3	4.04	386	3.6

Table 6.
Data about iron hydrolysis carried out at 90°C from rich-in-iron waste solution

t, min	Parameter			
	Base consumption, ml NaOH/ L	pH	Eh	Fe$_{total}$, mg/ L
10	24.7	3.00	645	1510
20	28.3	3.28	590	475
30	30.0	3.52	568	58
40	31.3	3.96	532	9.5
50	31.5	4.06	367	2.2

Table 7.
Effect of the seeding rate with goethite on the iron hydrolysis at 50° and some important characteristics of the produced slimes

Parameter	Goethite seeding rate, g/ L				
	0	0.2	0.5	1.0	5.0
Residual iron concentration, mg/ L	3.6	2.9	3.3	4.2	4.5
Total suspended solids (TSS), g/L	21.5	21.6	22.1	22.6	25.5
Sludge volume index (SVI), mL/ g	27.9	23.7	23.7	19.3	27.8
Settling velocity, cm/ min	0.04	0.10	0.10	0.14	0.14

Slightly different approach for the iron removal from acidic solutions was applied in Kaksonen et al., (2014a, 2014b). It was based on the bacterial oxidation of ferrous iron and the acidity consumption by the mesophilic chemolithrophic consortia, consisting of *Acidithiobacillus ferrooxidans* and *Leptospirilum ferrooxidans*, growing at room temperature in a two-stage continuous stirred bioreactors. The produced ferric iron hydrolyzed instantly as jarosite. An equilibrium between the processes of bacterial oxidation and chemical precipitation existed which determined almost constant pH (2.05- 2.06) in bioreactors. At such conditions, the ferrous oxidation rate was in the range of 1.0 – 1.1 g.L/ h as both rates (ferrous iron oxidation and ferric iron precipitation) increased with increase of the solution`s pH. In the same trend, the particles size

diameter increased also and they were in the range of 14 microns, which determined sludge volume index (SVI) about 12 mL/g.
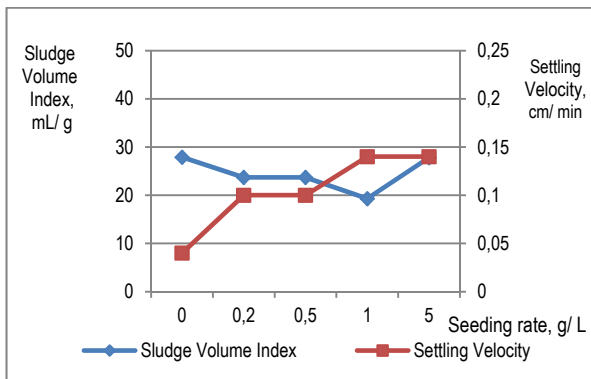

Fig. 2. Effect of the seeding rate with goethite on the iron removal from rich-in-iron waste solution at 50°C

Table 8.

Effect of the seeding rate with hematite on the iron hydrolysis at 90° C and some important characteristics of the produced slimes

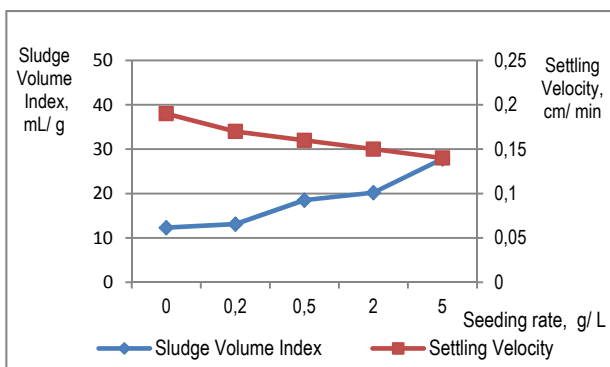| Parameter	Goethite seeding rate, g/ L			
	0	0.2	0.5	2.0
Residual iron concentration, mg/ L	4.4	5.2	6.4	3.0
Total suspended solids (TSS), g/L	15.7	15.9	16.2	17.7
Sludge volume index (SVI), mL/ g	12.3	13.1	18.5	20.2
Settling velocity, cm/ min	0.19	0.17	0.16	0.15

Fig. 3. Effect of the seeding rate with hematite on the iron removal from rich-in-iron waste solution at 90°C

Sasaki and Konno (2000) demonstrated that the particles size distribution of freshly formed iron mineral particles is affected by the rates of their crystallization and agglomeration. Both rates are affected by the local temperature during the process and the concentration of finely minerals particles, which could act as seeds to initiate and to accelerate later the agglomeration rate.

The results about the temperature effect on the rate of agglomeration showed that the higher the temperature was during the test, the higher the rate of iron precipitation was.

(Tables 5, 6). The formed iron oxides had dark brown color in that case, had higher bulk density which determined the lower value of SVI (with 33 % and 70.4 % for iron oxides formed at 50 °C and 90 °C, respectively) in comparison to the values measured at ambient temperature. However, the settling velocity of the particles formed at 50 °C was nearly the same as the velocity measured at 25 °C. The results from seeding experiments showed that the factor could improve considerably SVI and the settling velocity of the particles when the accurate dosage is applied. For example, the accurate dosage for the iron precipitation as goethite at 50 °C from solution with iron concentration 11500 mg/ L was 1g/ L. (Table 7). As a result, SVI decreased by 31 % and the settling velocity increased 3.5 time in comparison to the non-seeded variant at the same temperature (Figure 2). The sludge was bulkier when a higher seeding dosage was applied.

Interesting results about ferric iron precipitation as phosphate and hematite from chloride leach solution presented Masambi et al. (2016). In that case, the iron removal process was realized with PLS enriched with copper and nickel. Results showed that the iron removal as hematite reached 99.6 % at temperature 80 °C when pH of solution was 1.0 and the seeding rate was in the range of 10-15 g/ L. Copper and nickel co-precipitation were in range of 3.5 and 1.7 %, respectively.

The experiments about the iron removal at 90 °C from the waste solution with lower iron concentration generated slime consisted of iron oxides with brown-reddish color. The slime itself characterized by the optimal values of sludge volume index (SVI) and settling velocity (SV) (Table 8, Figure 3), was determined during this study. However, all seeding experiments with hematite carried out at 90 °C showed that seeding, irrespective of the applied rate, had a negative effect on the above-mentioned parameters of the produced iron-rich slimes.

Conclusions

1. The experiments about the chemical neutralization of acidic rich-in-iron showed very high iron removal (above 99.5 %) at all tested temperatures.
2. However, the iron precipitates formed only at 50 and 90 °C were characterized with acceptable for the practice values of Sludge Volume Index (SVI) and Settling Velocity (SV).
3. The seeding rate with 1 g/ L goethite at 50 °C had a highly positive effect on the iron removal from waste solution with iron concentration of 11500 mg/ L. The seeding experiments with hematite had a negative effect on the Sludge Volume Index (SVI) and Settling Velocity (SV) of the iron oxides formed from solution with iron concentration of 8650 mg/ L at 90 °C.

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