PRESSURE LEACHING OF DECOPPERIZED COPPER ELECTROREFINING ANODE SLIMES IN STRONG ACID SOLUTION

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Abstract: Anode slimes contain precious metals like silver, gold and platinum group metals (PGMs), base metals including copper, selenium, tellurium and nickel as well as other impurity elements. In order to recover valuable elements, it is important to be able to eliminate undesirable ones (e.g. Pb, Sb and Bi) at the initial stage. The aim of this study was to investigate the pressure leaching of pressure leached copper-free anode slimes in the laboratory-scale. Secondary autoclave leaching was performed in a strong acid medium with oxygen purging in order to dissolve residual copper, nickel and bismuth as well as other elements in a controlled way. Leaching tests showed that Cu, Ni, Bi, As, Te and Se were partially dissolved during the secondary autoclave leaching. The extraction of different metals showed the following variations: copper 65–100%, nickel 57–98%, bismuth 53–82%, arsenic 16–61%, tellurium ≤58% and selenium ≤57%. Furthermore, the effect of process conditions on the extraction of these elements was investigated using factor and regression analysis. The process variables investigated were: temperature (80–120 °C), partial pressure of oxygen (2–8 bar), sulfuric acid concentration (30–70 vol%) and solid concentration (200–400 g/dm^3). Based on the regression analysis, a valid model for the dissolution of arsenic during secondary leaching could be built.

Keywords: nickel, extraction, process parameters, bismuth, decopperization, autoclave leaching

Introduction

The processing of copper anode slimes is an additional economic driver for copper electrorefineries, due to the fact that slimes contain precious metals such as silver, gold and platinum group metals (PGMs) (e.g. Pt and Pd) as well as base metals like copper, nickel, selenium, tellurium and impurity elements such as lead, antimony and bismuth. Anode slimes have generally been processed by the combination of pyrometallurgical and hydrometallurgical methods. A typical process flowsheet

contains unit processes that extract the elements in the following order: Cu, Ni, Te, Se, Ag, Au, PGMs, however, the presence and concentrations of impurities can have a marked effect on both the number of process steps and their order (Hait et al., 2009). Nevertheless, it is important to remove the most undesirable elements like Pb, Sb, Bi, prior to the recovery of precious metals (Chen et al., 2008) and the removal of these impurities is normally achieved by Dore smelting followed by reduction and refining in a top blown rotary converter (TBRC) like, for example, a tilting rotating oxy-fuel (TROF) converter.

The control of antimony and bismuth impurities in copper electrorefining is also important as they have been reported to increase anode passivation and decrease the quality of cathodes (Kamath et al., 2003; Schlesinger et al., 2011). Bismuth dissolves as Bi^{3+} ions into the electrolyte (Kamath et al., 2003; Moats et al., 2012). Several studies have investigated the primary pressure leaching of anode slimes and characterized the copper anode slimes produced (Beauchemin and Chen, 2008; Chen et al., 2008; Chen and Dutrizac, 1993, 2004, 2005). Nevertheless, according to the literature, the secondary autoclave leaching of decopperized copper anode slimes focusing on base metal and impurity removal has not been significantly investigated previously.

In this paper, the secondary leaching step for decopperized anode slimes (i.e. the leach residue of pressure leaching) was studied. The main drawback in the use of TROF converter smelting is that bismuth cannot be recovered in a controlled manner, hence, the primary objective of this paper is to examine if pressure leaching in strong sulfuric acid would be a suitable process for systematic bismuth removal. Furthermore, the effects of temperature, partial pressure of oxygen, sulfuric acid concentration and solid concentration were also investigated.

Experimental

Experiments and equipment

Oxidative pressure acid leaching tests for decopperized anode slimes (raw material) were performed in a Buchi ecoclave 075. This laboratory scale titanium (Grade 2) autoclave had a total volume of 1.1 dm^3 and it was loaded with 0.8 dm^3 of solution as the recommended batch size for such autoclaves is 70-80% of the capacity (Goodwin, 1925). The autoclave was equipped with a Buchi cyclone 075 magnetic agitation unit, an oxygen inlet, a manometer, a temperature detector, a bursting disk and a sample system with a nitrogen inlet. Dried and homogenized raw material was used in all experiments. For each test 160, 240 or 320 g of anode slime was weighed and fed into the reactor chamber along with sulfuric acid. The solid concentrations were chosen according to Doucet and Stafiej (2007) who used the range from 27 to 35%. In order to achieve the optimal leaching conditions, an agitation speed of 400 rpm was used to ensure that the raw material was maintained in suspension (Hoffmann, 2000). Pressure

leaching was conducted for two hours thereafter the autoclave was cooled down to the room temperature and the leach residue were removed for filtration and washing.

Experiments were performed as a full factorial test in order to determine the effect of leaching parameters on extraction of metals (see Table 1). The investigated parameters were: $T = 80$, 100 and 120 °C, $p_{oxygen} = 2$, 5 and 8 bars, solid concentrations of 200, 300 and 400 g/dm^3 and [H$_2$SO$_4$] = 30, 50 and 70 vol% of 95–98% H$_2$SO$_4$. The temperature range was selected according to Zhang and Yan (2013) who found that the highest copper extraction was achieved at leaching temperature of 99.85 °C. The oxygen partial pressure range was chosen according to Weichert et al. (2013) who used the oxygen partial pressure of 5 bars. High sulfuric acid concentrations were selected to improve the process performance with the leaching time of only 2 hours. Combinations of parameters for factorial test were determined by Modde 8.0 software. In addition, two center point experiments were performed in order to determine the reproducibility of the results.

Table 1. Secondary pressure leaching parameter investigated in the factorial leaching test series
(experiments 1-18) for metal extraction from decopperized anode slime

Exp No.	Temperature (°C)	Oxygen Partial Pressure (bar)	Solid Concentration (g/dm^3)	H$_2$SO$_4$ Concentration (vol%)
1	80	2	200	30
2	120	2	200	30
3	80	8	200	30
4	120	8	200	30
5	80	2	400	30
6	120	2	400	30
7	80	8	400	30
8	120	8	400	30
9	80	2	200	70
10	120	2	200	70
11	80	8	200	70
12	120	8	200	70
13	80	2	400	70
14	120	2	400	70
15	80	8	400	70
16	120	8	400	70
17	100	5	300	50
18	100	5	300	50

Methods

The extraction of the various elements was calculated by comparing the elemental concentration of leach residue to the initial elemental concentration in the raw material (decopperized slime) according to Eq. (1). As the mass of slime decreases during the leaching process due to the dissolution of soluble elements into the solution, the mass of the residue can be determined by comparing the concentration of insoluble elements left after leaching to the initial concentration of elements in the raw material. For example barium can be used as reference element since it does not dissolve during acid leaching treatment. The concentrations of dissolved barium in the leach solution varied from 0.07 to 9.21 mg/dm^3, while the average rate of barium dissolution was found to be 1.42 mg/dm^3. In the extraction equation it is assumed that the amount of elements not remaining in the leached slimes is dissolved into the leaching solution

$$E = 1 - \frac{m_{n-l} \cdot c_l \cdot 10^{-3}}{m_r \cdot c_r} \cdot 100\% \tag{1}$$

where m_{n-l} represents the fixed mass of leach residue (kg), c_l the mass fraction of an element in leached slime (mg/kg), m_r the initial mass of raw material (kg) and c_r the initial mass fraction of an element in the raw material (mg/kg).

Results and discussion

Elementary and extraction analyses

The decopperized anode slime raw material used in this study was collected at the Boliden Harjavalta copper refinery from the filter press which is located immediately after the autoclave process. The solid samples were analyzed both before and after secondary pressure leaching to determine the amount of elemental extraction and allow the characterization of the compounds in slimes. Prior to the analyses, slimes were dried at 60 °C for 24 hours. These dried slimes were subsequently ground in an agate grinding vessel and then leached with *aqua regia* at 90 °C (Labtium, Espoo). The resulting solutions were analyzed for the concentrations of Cu, Bi, Ni, As, Te and Se using the inductively coupled plasma mass spectrometry ICP-MS). Table 2 presents the analyzed metal concentrations in the raw material used.

Table 2. Composition of decopperized slime used as raw material in the leaching tests

Bi (%)	Se (%)	Te (%)	Ag (%)	As (%)	Ba (%)	Cu (%)	Ni (%)	Pb (%)	Sb (%)
11.6	10.5	2.0	21.4	2.6	9.7	1.8	0.1	9.7	4.5

Table 3 presents the respective metal extractions to the solution based on mass balance between raw material and residue. The elementary analyses of slimes showed

that Sb, Ag, Ba and Pb did not dissolve during autoclave leaching. In contrast Cu, Ni and Bi were shown to have undergone a substantial level of dissolution, whereas As, Te and Se dissolved only slightly. However, the extractions of Te and Se were not valid due to too wide variation of extraction values. Therefore, these results are not presented in Table 3.

Table 3. The extraction of Cu, Ni, Bi and As to the solution
during secondary autoclave leaching of raw material

Exp no.	Cu (%)	Ni (%)	Bi (%)	As (%)
1	100.0	97.1	61.3	22.4
2	90.7	89.7	76.6	44.3
3	86.4	93.8	74.3	18.4
4	87.6	92.7	82.2	53.5
5	95.9	97.5	75.1	18.9
6	82.8	94.0	78.5	32.6
7	97.4	94.9	70.3	16.1
8	85.7	88.0	77.9	18.1
9	92.4	96.1	69.0	53.7
10	65.2	91.4	71.4	54.0
11	83.5	96.6	71.7	39.4
12	73.5	95.0	70.9	60.7
13	81.8	57.2	68.3	42.4
14	95.2	87.7	70.4	44.1
15	100.0	82.0	68.4	45.6
16	84.2	95.1	65.9	31.8
17	83.7	90.8	53.2	34.2
18	98.7	92.7	70.4	32.6

The extraction results show that the level of metal extraction varied between 65.2-99.9% for copper, 57.2–97.5% (nickel), 53.2–82.2% (bismuth) and 16.1–60.7% (arsenic). Additionally, the extractions of tellurium and selenium were ≤58.1% and ≤57.1%, respectively. Cu analyses in experiments 1 and 15 (<1 mg/kg) differed significantly from the other measured concentrations, indicating analysis error. Additionally, regression analysis of Bi dissolution indicated that experiment 17 was a random error due to the significant discrepancy in distribution. When performing regression analyses and defining a model for the extraction of Cu or Bi, experiments 1 and 15 for Cu and 17 for Bi were removed.

Table 4 summarizes the effect of temperature, solid concentration, sulfuric acid concentration, the combination of temperature and solid concentration as well as the combination of temperature and sulfuric acid concentration on extraction of Cu, Ni, Bi and As. A positive effect indicates that by increasing the value of variable the metal

extraction increases, while the opposite stands for a negative effect. Only variables and variable combinations that have a statistically proven effect on dissolution of at least one metal are shown in Table 4.

Table 4. The effect of variables on elemental dissolution. Experiments 1 and 15 were excluded from Cu analysis, experiment 17 from Bi analysis, experiments 10, 12 and 14 from Te analysis and experiments 9, 10 and 17 from Se analysis

	T	[Solids]	[H$_2$SO$_4$]	Combinations of variables	
				T·[Solids]	T·[H$_2$SO$_4$]
Cu	-	-	Negative	-	-
Ni	-	Negative	-	-	-
Bi	Positive	-	Negative	-	Negative
As	Positive	Negative	Positive	Negative	Negative

T stands for temperature, [Solids] solids concentration and [H$_2$SO$_4$] sulfuric acid concentration

Temperature increase was shown to affect positively on bismuth and arsenic dissolution, solid concentration negatively on nickel and arsenic dissolution as well as sulfuric acid concentration negatively on copper, bismuth, tellurium and selenium dissolution, though positively on arsenic dissolution. All the affecting variable combinations had negative effects. The combination of temperature and solid concentration affected negatively arsenic dissolution, as well as, the combination of temperature and sulfuric acid concentration influenced negatively bismuth and arsenic dissolution. Additionally, sulfuric acid concentration increase indicated a negative effect on the extractions of Se and Te, though these results were not shown, due to the inaccuracy of the analyzed Te and Se values. According to the regression analysis, a valid model could be built on arsenic extraction (Eq. 2):

$$E_{As} = (-107.9) + 1.367T + 0.163[\text{Solids}] + 1.272[\text{H}_2\text{SO}_4]$$
$$-0.002T \cdot [\text{Solids}] - 0.008T \cdot [\text{H}_2\text{SO}_4] \tag{2}$$

Other models (for Cu, Ni and Bi) did not have high enough goodness of fit, goodness of prediction, validity or reproducibility.

SEM-EDS analyses

The compositions of slimes were analyzed by scanning electron microscope with energy dispersive spectrometry (SEM-EDS). Fig. 1 shows a SEM-EDS analysis of the pressure leached (decopperized) anode slime used as the raw material in the secondary pressure leaching tests. From the results it can be seen that the anode slime contained numerous phases including BaSO$_4$ (Spectra 1-3), bismuth-rich Sb-As-Bi oxide phases with molybdenum (Spectrum 4), Ag-Cl phases (Spectrum 5), Ag-Cl-Se oxide phases (Spectrum 6), PbSO$_4$ with barium (Spectrum 7) as well as silver selenides (Spectra 8

and 9). Additionally, the slimes were shown to contain Ag-Sb-Bi-As-Te-Se oxide and $BaSO_4$-$PbSO_4$ phases.

A number of authors have found similar compound structures from autoclave leached slimes including Beauchemin et al. (2008) and Chen and Dutrizac (2005) who reported that such slimes consist primarily of $BaSO_4$, Sb-As-Bi-O phase, $PbSO_4$ and Ag_2Se. In addition, although Sb-As-O phase was one of the main component of these autoclave leached slimes (Beauchemin et al., 2008; Chen and Dutrizac, 2005), it was found to contain also fine grained Ag-Se-rich particles with minor amounts of Cl, Au and S (Chen and Dutrizac, 2005). Both Beauchemin et al. (2008) and Chen et al. (2008) concluded that the presence of the Sb-Bi-As-O phase resulted from precipitation of the dissolved Sb, As and Bi during autoclave leaching process.
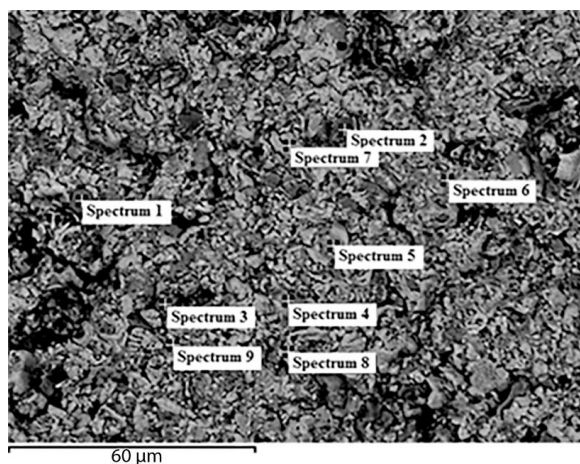
Fig. 1. SEM-EDS analyses of pressure leached decopperized anode slime
used as raw material in leaching tests

Secondary leached slimes that were treated at either the minimum or maximum parameter level were further analyzed in order to determine if there was any variation in the slime mineralogy. Fig. 2 displays the SEM-EDS image of secondary leached raw material, which is leached with the minimum parameter values (Experiment 1 in Table 1: temperature 80 °C, oxygen partial pressure 2 bar, solid concentration 200 g/dm^3 and 30 vol% of sulfuric acid). In contrast, Fig. 3 presents the SEM-EDS image of raw material, which is leached with the maximum parameter values (Experiment 16 in Table 1: temperature 120 °C, oxygen partial pressure 8 bar, solid concentration 400 g/dm^3 and 70 vol% of sulfuric acid).

According to Fig. 2, larger $BaSO_4$ inclusions (Spectra 1-3) were surrounded by other phases containing the Bi-Sb-As-Se-Te-Ag oxide phase (Spectrum 4), Pb-Sb-As-Cl-Te-Ag oxide phase (Spectrum 5), $BaSO_4$-$PbSO_4$ (Spectrum 6), silver selenides (Spectra 7 and 8) and Se-Ag-Pb oxide phases (Spectrum 9). Furthermore, the leach

residues contained a number of large gold grains, $BaSO_4$-$PbSO_4$, Bi-Sb-As-Te and Bi-Sb-Ag-Se-Te oxide phases.

In contrast, it can be seen in Fig. 3, that the leached residues contained many phases like the Bi-Sb-As-Se-Te oxide phase (Spectra 1 and 2), $BaSO_4$ (Spectrum 3), silver selenide oxide phases (Spectra 4 and 8), silver selenides (Spectra 5 and 6), gold-silver selenides (Spectrum 7) and Se-Ag-Au-Te oxide phases (Spectrum 9). Furthermore, these slimes were also found to contain bismuth-rich Bi-Sb-Ag-Se-Te-Cl oxide and Pb-Sb-As-Se-Te-Ag, which might be formed during oxidation of the original phases as well as $BaSO_4$-$PbSO_4$ phases, of which $BaSO_4$ originated from anode mould and insoluble $PbSO_4$ was formed in the electrolyte.

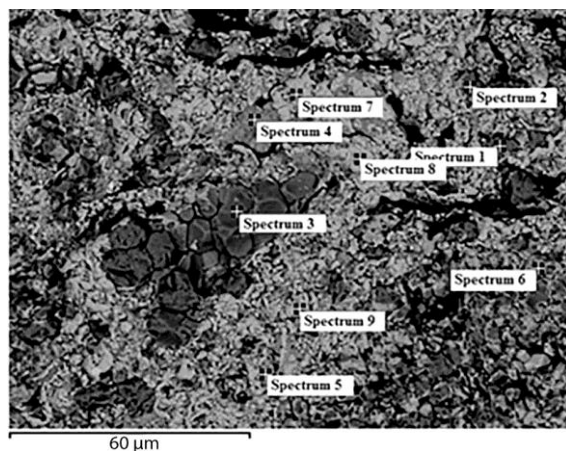Fig. 2. SEM-EDS analysis for leached residue after Exp. 1
(T = 80 °C, p_{oxygen} = 2 bars, solid concentration of 200 g/dm^3 and [H_2SO_4] = 30 vol%)
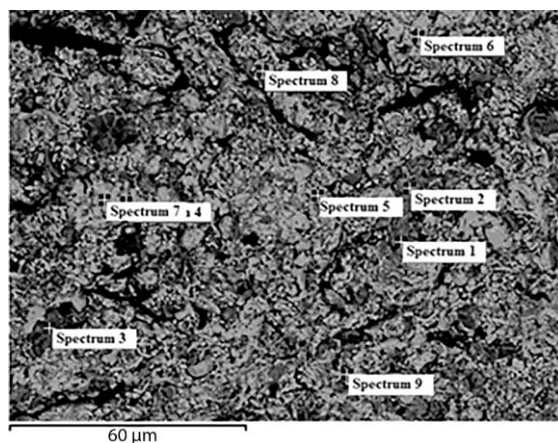
Fig. 3. SEM-EDS analysis for leached residue after Exp. 16
(T = 120 °C, p_{oxygen} = 8 bars, solid concentration of 400 g/dm^3 and [H_2SO_4] = 70 vol%)

Overall it was determined that both these slimes contain similar compounds that included $BaSO_4$, $BaSO_4$-$PbSO_4$, Bi-Sb-As-Se-Te oxide, silver selenides and multi-element oxide phases consisting of Pb, Sb, Bi, As, Se, Te, Ag and Cl. In addition, gold was also present in both slimes as gold grains, gold-silver selenides or Se-Ag-Au-Te oxide phase. Thus, it is clear from the results shown in Fig. 2 and 3 that no major differences could be observed between leach residues after secondary leaching under the minimum or maximum leaching conditions investigated.

Conclusions

In this study it was shown that the pressure leaching of decopperized anode slimes in strong sulfuric acid solution can be used to achieve significant extractions of copper, nickel and bismuth. Furthermore, this work demonstrates that arsenic, tellurium and selenium can also be dissolved, however, the amounts extracted were not as substantial as the leaching of Cu, Ni and Bi and were subject of higher variation. Elemental analyses were performed by ICP and the results showed the amount of Cu extracted to the solution varied from 65.2 to 99.9%, Ni from 57.2 to 97.5%, Bi from 53.2 to 82.2%, As from 16.1 to 60.7%, Te up to 58.1% and Se up to 57.1%. The leaching parameters resulting in the highest extraction were individual for each element, thus, the optimum values of variables must be chosen case by case according to an element of interest.

According to factorial test analyses, increase in temperature was shown to affect positively bismuth and arsenic dissolution, solid concentration influenced negatively nickel and arsenic dissolution, while sulfuric acid concentration negatively affected copper, bismuth, tellurium and selenium dissolution, but positively arsenic dissolution. Furthermore, all combinations of the affecting variables had a negative effect on extraction of the metals. The combination of temperature and solid concentration affected negatively arsenic dissolution as well as the combination of temperature and sulfuric acid concentration influenced negatively bismuth and arsenic dissolution. For the extraction of arsenic a valid model could be build according to regression analysis.

According to SEM-EDS analyses, autoclave anode slimes contained $BaSO_4$, $PbSO_4$, silver selenides, Sb-As-Bi oxide, Ag-Cl-Se oxide as well as Ag-Sb-Bi-As-Te-Se oxide phases. After a secondary autoclave leaching, anode slimes contained $BaSO_4$, $BaSO_4$-$PbSO_4$, Bi-Sb-As-Se-Te oxide and silver selenides. Additionally, secondary autoclave leached slimes contained a number of multi-element oxide phases that consisted of Pb, Sb, Bi, As, Se, Te, Ag and Cl. Furthermore, gold was present in slimes as gold grains, gold-silver selenides or Se-Ag-Au-Te oxide phase. From the SEM-EDS analyses, it was concluded that more complex anode slime structure was formed during the secondary autoclave leaching process, as it was clearly demonstrated by the presence of the complex oxide phases in the leach residue.

Acknowledgments

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