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Dissolution of copper and nickel from nickel-rich anode slimes under oxidized pressure leaching

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Abstract

Anode slimes are valuable by-products in the electrolytic copper refinery process. This study aimed to investigate maximum extraction efficiency of Cu and Ni from slimes originating from the electrorefining of anodes containing high [Ni]. In addition, the extractions of Se, Te, As and Bi were determined. A factorial leaching series was conducted with $T = 140-160^{\circ}$ C, $[H_2SO_4] = 12-20\%$, $p_{O_2} = 2-8$ bars and solid/liquid ratio = 200-400 g/L. The highest Ni extraction of 99.7% was obtained with $[H_2SO_4] = 20\%$, $p_{O_2} = 8$ bar and $T = 160^{\circ}$ C while maintaining S/L ratio of 200 g/L. The extraction of copper was found to be within 97–99% in all the leaching experiments. Increasing acidity and decreasing S/L ratio increased the efficiency of Cu extraction. Mineralogical characterizations by SEM-EDX demonstrated the presence of Ag₂Se, BaSO₄, PbSO₄ and several oxide phases in the leach residue.

Keywords

Autoclave; copper electrorefining; extraction efficiency; modelling; secondary metal sources; valorization; sulphuric acid leaching; hydrometallurgy

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Introduction

The reserves of primary mineral resources are depleting fast (Oliveira et al. 2015). Therefore, every effort has to be made to process secondary metal containing sources such as slags, dusts and slimes formed in metal production processes. In copper production, anode slime is a by-product from electrorefining and a source of valuable metals (Dönmez et al. 1998; Liu et al. 2014). Since anode slime is formed from the insoluble impurities of the anode in the electrolysis process, the composition of the slime depends on the composition of the copper anodes (Schlesinger et al. 2011). Typically, copper anode slimes contain Cu, Ni, As, Ag, Sb, Au, Bi, S, Pb, Se, Fe and Te (Chen and Dutrizac 1993; Moats et al. 2016) and minor amounts of platinum group metals (Hait et al. 2009). Depending on the composition and morphology of the anode slimes, a number of pyro-metallurgical and hydrometallurgical processes or the combinations of these have been developed for the extraction of valuable metals (Hait et al. 2002; Hait et al. 2009; Kilic et al. 2013). Among the hydrometallurgical processes, pressure leaching is one of the common methods employed (Ying 1983; Swayn et al. 1993; Hughes 2000; Hait et al. 2009; Kilic et al. 2013). Pressure leaching parameters applied depends on the slime chemistry and the precious metals that are aimed to be extracted (Hait et al. 2009; Kilic et al. 2013).

Hydrochloric acid, nitric acid and sulphuric acid are the most frequently used leachants in the hydrometallurgical leaching of anodic slimes (Gill 1980; Holmes 1981; Everett 1994; Petrov et al. 1999; Amer 2002). Typically, all the metals are not extracted in one process step (Hait et al. 2009; Schlesinger et al. 2011). Commonly, Cu is the first metal to be extracted, often in sulphuric acid media (Dönmez et al. 1998; Hait et al. 2009; Kilic et al. 2013). It has been reported that it is favourable to use elevated temperature and pressure, as well as oxygen purging, for enhancing metal dissolution (Dönmez et al. 1998; Doucet and Stafiej 2007). Common process temperatures in anode slime leaching vary in the range of 125–150°C (Schlesinger et al. 2011), however leaching can also be conducted at higher temperatures (Chen and Dutrizac 1990a 1990b, 1990c; Dönmez et al. 1998; Doucet and Stafiej 2007; Shibayama et al. 2016). For example, O₂–H₂SO₄ leaching at 180°C have resulted in significant dissolution of Cu, Ni, Ag, Se, and Te (Vzorodov et al. 1982; Chen and Dutrizac 1990c; Järvinen 2000; Järvinen and Virtanen 2003; Chen and Dutrizac 2005).

The nickel content in copper anode slimes is averagely 2.5% (Moats et al. 2016), but for anodes containing more than average amount of nickel (Hait et al. 2009), the nickel content in slimes can be significantly higher (Chen and Dutrizac 1990a, 1990b, 1990c; Moats et al. 2007; Hait et al. 2009) even over 36% (Cooper 1971; Biswas et al. 1998). For example, in 2003 in Metallo Chimique Beerse (Belgium), the reported Ni content of the anode slime was 16% (Moats et al. 2007) and (Biswas et al. 1998) in slimes produced in Indian Copper Complex, Ghatsila was 36.7%. The leaching of nickel-rich anode slimes (Ni > 3%) has been investigated by Doucet and Stafiej (2007) in sulphuric acid media and at temperatures ranging between 120 and 160°C sparged with

oxygen at the beginning or at the end of the process. Based on their data, it is possible to obtain substantial Cu, Ni and Te extractions with 4–5 h retention time in leaching.

Several authors (Savin 1965; Decker and Peteghem 1976; Toyoda 1976; Subramanian et al. 1980; Yildirim and Bor 1985; Hoffmann 2000) have described the occurrence of reactions during leaching in H₂SO₄ medium in presence of oxygen. The process for treating anode slimes containing silver has been investigated (Subramanian et al. 1980), in which silver undergoes dissolution in dilute nitric acid and is finally recovered by electrowinning. The recovery of other metals, such as Se, Te, Ni and other precious metals along with silver, were also reported. Leaching of anode slimes obtained from Indian copper complex from Ghatsila (Hait et al. 2002) in H₂SO₄ media with MnO₂ and NaCl as additives resulted in 90% recovery of copper, 37% selenium and 66% tellurium respectively.

This study focusses on investigating the dissolution behaviour of copper and nickel from the nickel-rich anode slimes under oxidative pressure acid leaching. In addition, the target was to model Ni and Cu extraction along with other elements like Te, Se, Bi, As due to limited availability of literature. Some studies on the leaching efficiency of Cu and Te obtained by conventional microheating methods (Ma et al. 2015) has been supported by an accurate predicted model with R² values of 0.99 and 0.97 respectively. Also, a reliable statistical model at 95% confidence level based on Rechtscaffner experiment design for the optimization of antimony and arsenic removal (Wikedzi and Awe 2017) from de-copperized slime using alkaline sulphide has been reported. In one of the regression analysis described (Seisko et al. 2017), a valid model was obtained for arsenic extraction. Nevertheless, the models for Cu, Ni and Bi extraction did not show enough goodness of fit, goodness of prediction and reproducibility. Hence, the present study aimed at constructing mathematical models with high goodness of fit for Cu and Ni extraction by MODDE 8 software.

Experimental

Materials and methods

The investigated Ni-rich anode slime was obtained from Boliden Harjavalta, Finland. The chemical composition of the raw anode slime was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis, Table 1. The same technique was also conducted for the leach residue samples. The samples for solid analysis were pre-treated using microwave-assisted total dissolving in 100% aqua regia assisted by hydrofluoric acid (ETHOS Touch Control, Milestone Microwave Laboratory Systems, Italy) followed by solution analyses conducted by ICP-OES (Perkin Elmer Optima 7100 DV, USA) by Milomatic Oy. Furthermore, the raw anode slime was characterized by Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX) with a LEO 1450 VP (Carl Zeiss, Germany) and XMAX-50 mm2

detector using INCA Software (Oxford Instruments, UK). Tungsten filament was employed as a cathode and the applied acceleration voltage was 15 kV.

		5							
Ni (%)	Cu (%)	S (%)	Se (%)	Sb (%)	As (%)	Te (%)	Bi (%)	Ag (%)	Ba (%)
18.7	16.5	1.4	7.5	1.7	3.5	1.5	3.9	0.09	0.06

Table 1. Chemical analysis of the Ni-rich anode slime.

The oxidative pressure acid leaching for nickel-rich anode slime (raw material) were performed in a laboratory-scale titanium autoclave (Ti Grade 2, Büchi Ecoclave 075), which had a total volume of 1.1 dm³ and a recommended batch size of 0.75 dm³ (Goodwin 1925). Further details on the autoclave leaching methodology have been reported in a previous work of Weichert et al. (2013) and Seisko et al. (2017). Dried and homogenized raw material was used in all the experiments. Eighteen representative samples for the leaching experiments were prepared by using a spinning riffler. For each test, weighed amounts of the anode slime sample based on the S/L ratio (200–400 g/L) were taken and fed into the autoclave reactor along with H₂SO₄. Agitation speed of 1000 rpm was employed. Pressure leaching experiments were conducted for two hours, followed by cooling of the autoclave to room temperature. During the experimental run, solution samples were taken at intervals of 0, 5, 10, 20, 30, 60 and 120 min. Finally, the leach residue was collected through filtration, washing and drying steps.

The experiments were performed based on a factorial series in order to determine the effect of leaching parameters (Table 2) on the extraction of metals. The investigated parameters were: T = 140, 150, 160 and 180° C, oxygen partial pressure (p_{O_2}) = 2, 5 and 8 bars, solid/liquid (S/L) ratio 200, 300 and 400 g/L, [H_2SO_4] = 12, 16 and 20%. Before starting the experiment, the partial pressure of water vapour was first noted and then the required amount of oxygen was added to maintain the p_{O_2} . The pressure in the autoclave was kept constant by adding oxygen during the leaching experiments. The acid used in the experiments was H₂SO₄ (analytical grade, Merck, 95–97%).

Experiment No.	H_2SO_4 (%)	<i>T</i> (°C)	S/L (g/L)	p_{O_2} (bar)
N1	20	140	200	2
N2	12	140	400	2
N3	12	140	200	2
N4	20	140	400	2
N5	12	180	200	2
N6	12	180	400	2

Table 2. Parameters investigated in the factorial leaching test series of Ni-rich anode slimes (experiments 1–18).

N7	12	140	400	8
N8	20	140	200	8
N9	16	160	300	5
N10	20	160	400	8
N11	16	150	300	5
N12	20	160	200	8
N13	20	140	400	8
N14	12	160	200	8
N15	12	160	400	2
N16	12	160	400	8
N17	12	150	200	5
N18	20	160	200	2

Modelling studies using MODDE 8 software

The results were analyzed utilizing MODDE 8 (MKS Data Analytics Solution) modelling tool. Particularly the extractions of copper and nickel were investigated to build regression models for predicting the extraction as a function of $[H_2SO_4]$, *T*, S/L ratio and p_{O_2} . Both extractions based on solid and solution analysis were used. When utilizing the solution analysis data, additionally, leaching time was used as a variable. Prior to modelling, the distributions of the raw data was investigated. If the data was normally distributed, the modelling efficiency and model validity were better than with skewed distribution of the data. The distributions were evaluated calculating the adjusted Fisher–Pearson Standardized Moment Coefficient (SMC) (Bartolucci et al. 2015) from the raw data. In a normally distributed data, the SMC value (absolute value) is less than 1, whereas with the value over 1 the data are moderately skewed, and with the value over 2 severely skewed. The models built were evaluated with the Summary of fit tool of MODDE 8 software, where the models were validated regarding correlation coefficients R^2 and Q^2 . While building the models, the outlier results were excluded. In addition, the deviations SDY (standard deviation of Y) and RSD (residual standard deviation) were detected. In the Summary of fit evaluation, Table 3, R^2 represents the goodness of fit and Q^2 the goodness of prediction (Eriksson et al. 2008).

Evaluation values	Limits for a good model
Q^2	> 0.5
R ² -Q ²	< 0.2–0.3

Results and Discussion

Characterisation studies by SEM-EDX

Prior to leaching, the characterization studies by SEMEDX was performed on the raw material to obtain the most abundant slime constituents as noticed in Figure 1. Nickel oxide with inclusions of Zn, Co, Fe, As-Sb-Bi-O with inclusions of Cu, copper/silver-selenides/telluride sulphate and barite were the most common phases observed in the SEM micrograph, Figure 1. These phases have also been observed by several authors (Beauchemin and Chen 2008; Chen and Dutrizac 1996; Chen and Dutrizac 2005). Barite is employed as a mould wash in the anode casting and it releases from the anode surface to the slime layer without undergoing reaction during electrolysis. However, it agglomerates slime particles together.



Figure 1. Backscattered electron micrograph showing the surface morphology of slime particles in the pure anode slimes: (1) Barite, (2) Bi-rich Cu-As-Sb-Bi oxides, (3) (Zn, Co, Fe)-bearing Ni oxides, (4) (Cu, Ag) selenide, (5) complex oxide species (Cu-As-Ag-Se-Te-S-O)

The Cu-As-Ag-Se-Te-S-O oxidate phase compounds were also observed in the anode slimes. Since this phase consists of irregular shaped particles (Spectrum 5, Figure 1), it can be assumed to consist of various complex compounds, like Cu-arsenate, Cu-selenide, Cu-sulphate or metallic Ag particles embedded in the matrix (Chen and Dutrizac 1990c).

Extractions

The effect of various parameters such as T, $[H_2SO_4]$, p_{O_2} and S/L ratio on the extraction efficiency of metals was investigated. The extraction percentage of base metals Cu, Ni along with other elements are presented in Table 4.

Exp.	Extraction of elements (%)									
Runs	Ni	Cu	S	Se	Sb	As	Te	Ag	Ba	Bi
N1	47.9	99.2	47.3	34.5	20.0	64.8	68.5	70.8	33.0	40.0
N2	45.0	96.8	55.6	43.3	54.3	62.3	81.0	93.1	-	34.4
N3	35.5	98.9	55.1	46.4	7.2	57.5	77.1	30.7	20.0	8.5
N4	43.1	98.9	49.5	5.2	9.0	49.3	60.4	29.4	10.7	6.9
N5	99.7	99.6	59.2	84.8	40.1	70.4	89.6	60.5	-	42.2
N6	47.6	98.2	53.5	59.3	23.2	53.1	47.6	36.2	13.0	12.4
N7	13.5	98.5	70.3	71.4	6.8	52.4	82.3	-	-	4.5
N8	62.1	99.1	65.7	70.3	7.4	60.3	82.2	-	-	15.1
N9	93.6	99.5	75.4	87.0	-	47.9	80.5	15.5	-	29.0
N10	95.2	99.7	69.2	80.1	10.6	49.3	68.4	18.3	-	-
N11	66.6	99.0	68.0	75.6	8.4	52.3	77.7	22.6	-	8.6
N12	99.7	99.9	45.2	85.5	-	70.2	58.1	81.5	1.7	20.6
N13	48.3	98.9	57.5	53.3	-	44.3	68.2	71.1	18.9	28.4
N14	83.7	99.5	51.0	88.7	-	46.8	50.7	77.7	37.3	11.6
N15	38.3	97.4	56.0	46.1	3.1	46.5	49.1	68.7	-	28.4
N16	42.3	98.5	40.8	75.9	-	45.5	22.2	68.3	-	24.9
N17	74.3	99.5	40.1	85.3	-	55.6	53.6	76.9	-	27.5
N18	99.5	99.8	44.2	84.3	19.8	65.4	65.2	80.7	-	52.3

Table 4. Extraction of elements into the solution in leaching experiments N1-N18, based on the analysis of the leach residue.

Extraction of Copper

The extraction of copper was shown to be in the range of 97–99% in all the experiments (N1–N18, Table 4), the maximum extraction percentage being 99.9% in run N12. These extractions were defined in the investigated parameter range S/L = 200–400 g/L, $p_{O_2} = 2-8$ bars, $[H_2SO_4] = 12-16\%$ and T = 140-160 °C. To get a comprehensive picture of the extraction process, mathematical model on the extraction of copper was built, Equation (1). The evaluation of the Cu model is presented in Figure 2 and Table 5. Values presented in Table 5 indicates a valid model for copper, extraction values based on solid analysis of the leach residue.

Cu extraction (%) =
$$99.2804 + 0.0917 [H_2SO_4] - 0.0052$$
 S/L [1]

where $[H_2SO_4]$ is in mass-% and S/L in g/L.



Figure 2. Copper extraction during pressure acid leaching of Ni-rich anode slimes, predicted with the Cu model.

Table 5. R², Q², standard deviation of the response and standard deviation

Cu model	R^2	Q^2	SDY	RSD	Ν
Cu extraction (%)	0.6981	0.5412	0.6749	0.3983	16

The model for copper extraction (Equation 1) was built exclusively using variables [H_2SO_4] and S/L ratio, since T and p_{O_2} showed to be insignificant terms within the investigated parameter range. The equation suggests that increasing acidity had a positive effect on the copper extraction, whereas increasing S/L ratio decreased copper extraction. The probability values of T and p_{O_2} terms were too high (>0.05) as the errors in these were large.

Building a valid copper model was challenging, since copper had fast dissolution kinetics in all experiments (for instance in experiments, N3 and N6, 88% and 80% dissolution occurred within 10 min), and there was not wide variation in the extractions. Therefore, a valid PLS (Pregnant Leach Solution) model could not be built. Nevertheless, the copper extraction model, based on solids analysis, was shown to be valid (Table 5, Figure 2) and the skewness i.e. the histogram (Figure 3(a)) of the response data still moderate [SMC value = (-)1.399] (Bartolucci et al. 2015). The measured vs. Predicted as well as the residual vs. Predicted plots of the Cu extraction are presented in Figure 3(b) and (c). The model had slightly low correlation values, which could not be improved with transformation of the response (to logarithmic or other). Therefore, the predictions demonstrated in Figure 2 with the copper extraction model can be regarded as approximate.



Figure 3. A) Histogram, B) measured vs. predicted plot and C) residual vs. predicted plot for copper extraction.

Extraction of nickel

The extraction of nickel varied between 13.5 and 99.7% reaching the maximum in runs N5 $([H_2SO_4] = 12\%, T = 180^{\circ}C, S/L = 200 g/L, p_{O_2} = 2 bars)$ and N12 $([H_2SO_4] = 20\%, T = 160^{\circ}C, S/L = 200 g/L, p_{O_2} = 8 bars)$ The extraction decreased to 35.5% in experimental run N3, conducted at lower *T* (140°C) while maintaining other parameters similar to run N5. Similar increase in extraction efficiency from 53.9 to 90% of nickel has been reported (Yang et al. 2015) with increase in *T* from 140°C to 170°C during pressure leaching of copper anode slimes. Hence, it was clearly evident from Table 4 that *T* was an essential parameter which caused an increasing effect especially on the dissolution of nickel, as supported by the literature (Bäckström 2010). A similar behaviour was observed in the copper extraction process where the yield slightly decreased from 99.6 to 98.9% in the experimental runs N5 and N3, respectively. Moreover, increase in *[H₂SO₄]* from 12 to 20% for constant values of *T* (140°C), S/L ratio (200 g/L) and $p_{O_2} = 2$ bars resulted in increase in the extraction of nickel (Table 4) from 35.5 to 47.9% in runs N3 and N1, respectively. One remarkable observation was that the Ni extraction showed a similar increasing trend from

13.5 to 48.3% (N7 vs N13) and 42.3 to 95.2% (N16 vs N10) even for the higher S/L ratio (400 g/L) and higher p_{O_2} (8 bars) with increase in [H_2SO_4] from 12 to 20%. Ni extraction percentage was lowest in experimental run N1 (47.9%), when [H_2SO_4] was raised to 20% for S/L ratio of 200 g/L, $T = 140^{\circ}$ C and $p_{O_2} = 2$ bars.

Noticeably, increase in p_{O_2} from 2 to 8 bar at identical [H₂SO₄] of 20%, S/L ratio of 200 g/L and T of 140°C increased the Ni extraction from 47.9 to 62.1% in experimental runs (N1 vs N8) respectively (Table 4). However, only a slight rise in the Ni extraction from 99.5 to 99.7% with increase in p_{O_2} from 2 to 8 bars was noticed at 160°C for similar values of S/L ratio and [H₂SO₄] as above in runs N18 and N12. Hence, in general higher p_{O_2} increased the efficiency of nickel extraction in the above investigated experimental runs. Higher p_{O_2} during the leaching process might have initiated maximum interaction between the solid slime, oxygen and H₂SO₄ thereby resulting in faster dissolution of nickel. One of the key observation was that increase in p_{O_2} from 2 to 8 bars for larger S/L ratios (400 g/L) did not increase the Ni extraction by a significant fraction irrespective of the changes in [H₂SO₄] and increased T.

An increase in S/L ratio from 200 to 400 g/L for $[H_2SO_4] = 12\%$, $T (180^{\circ}C)$ and p_{O_2} (2 bars) demonstrated a notable decrease in the nickel extraction from 99.7 to 47.6% (N5 vs. N6). However, the nickel extraction decreased by a smaller margin from 83.7 to 42.3% (N14 Vs N16) for similar increase in S/L ratio (200 to 400 g/L), p_{O_2} being 8 bars, $T = 160^{\circ}C$ and $[H_2SO_4] = 12\%$ as noticed in Table 4. These results clearly suggested that lower S/L ratio resulted in a higher nickel extraction efficiency irrespective of the changes in other parameters. Results also established that when all the parameters were high i.e. S/L ratio (400 g/L), $T (160^{\circ}C)$, $[H_2SO_4]$ (20%) and $p_{O_2} = 8$ bars, the extraction percentage of Ni seemed to be the best as the value decreased by only 4.5% from 99.7 to 95.2% noticed in experimental runs N12 and N10.

Models for predicting nickel extraction were built similarly as for copper extraction. However, the models built by using the leaching residue analysis data were not valid according to the correlation coefficients and other evaluation values. Thus, the Ni models were built for nickel extraction (Table 6, Equations 2–4) by using the solution analysis data both as a function of time, utilizing all the analyzed solution samples, Ni Models 1 (Equation 2) and 2 (Equation 3), and predicting only the final extraction using exclusively the data of the final PLS, Ni Model 3 (Equation 4). Ni Model 2 was built transforming the time to power 0.5 and including the combined effect terms $[H_2SO_4] \cdot S/L$, $[H_2SO_4] \cdot t^{0.5}$ and $T \cdot S/L$. The transformation lowered the standard deviations and improved the correlation coefficients.

Table 6. R^2 , Q^2 , standard deviation of the response and standard deviation of the residue values of the Ni models.

Ni model	R^2	Q^2	SDY	RSD	Ν
¹ Ni (%)	0.6731	0.6382	25.417	14.844	121
² Ni (%)	0.7640	0.7214	25.107	12.628	120
3 Ni t = 120 min (%)	0.8589	0.7095	25.649	10.870	15

¹Ni (%) = -201.781 + 1.52165 [H₂SO₄] + 1.45964 T - 0.0930554 S/L + 1.28257 p_{O_2} + 0.201309 t [2] ²Ni (%) = -317.908 - 2.80582 [H₂SO₄] + 2.62617 T + 0.3372 S/L + 1.07996 p_{O_2} - 2.63189 t^{0.5} +

$$1(\%) = -317.908 - 2.80582 [H_2SO_4] + 2.62617 T + 0.3372 S/L + 1.07996 p_{O_2} - 2.63189 t^{0.5} + 0.009528 [H_2SO_4] \cdot S/L + 0.337393 [H_2SO_4] \cdot t^{0.5} - 0.00375955 T \cdot S/L$$
[3]

$$19528 \left[H_2 SO_4\right] \cdot S/L + 0.33/393 \left[H_2 SO_4\right] \cdot t^{0.5} - 0.003/5955 I \cdot S/L$$
[3]

Where [H_2SO_4] is in mass %, T in °C, S/L in g/L, p_{O_2} in bar and t in minutes.

In the linear nickel extraction models (Ni models 1–3, Equations 2–4), the response was kept unchanged. In addition, logarithmic and power 0.25 response transformations were investigated to straighten the histogram distribution, which was moderately skewed having the SMC value (Bartolucci et al. 2015) of 1.216. The histogram is presented in Figure 4 and the measured vs. Predicted and residual vs. Predicted plots are shown in Figure 5. The transformations straightened the distributions. However, the predictions with the transformed models were significantly too high in optimal conditions within the studied variable ranges (highest amount of H₂SO₄, highest *T*, highest p_{O_2} and lowest S/L ratio). In the Ni models 1–3 (Equations 2–4) that error was minor. However, the Ni models 1 and 2 had a slight systematic error, which was detected when comparing the measured values to the predicted values. Of these models, that systematic error was lower in the Ni model 2 than in model1, and it did not exist in model 3.

Nonetheless, all these linear models were valid and could predict the measured Ni extractions reliably. The Ni models 1–3 (Equations 2–4) were valid according to their high correlation coefficients. Moreover, the standard deviations were slightly high. Ni model 1 (Equation 2) had the lowest correlation coefficients, but also the lowest difference between the coefficients, while Ni model 3 had the highest correlation coefficient values and difference between the coefficients. However, for Ni model 3, less data has been used and it did not show the effect of O2 since it was excluded as an insignificant term. Ni model 2 had the second highest correlation coefficient values and lower deviation values than model 1. Based on that, the combined effects of [H_2SO_4], T with S/L ratio and time may also affect the Ni extraction. Thus, model 2 can be regarded as the most accurate, but the predictions with it are still approximate. The statistical evaluation suggests that the nickel extractions can be predicted slightly more accurately with Ni model 2 and 3 (Equations 3 and 4) compared to the prediction of copper extraction with the Cu model presented earlier

(Equation 1). The predictions for Ni extraction during pressure acid leaching with Model 2 are presented in Figure 6.



Figure 4. Histogram for nickel extraction, from the solution analysis data of solution samples taken at intervals of 0, 5, 10, 20, 30, 60 and 120 minutes.



Figure 5. A)–D) measured vs. predicted plots and residual vs. predicted plots of Model 1 (A and B), Model 2 (C and D) Model 3 (E and F) for nickel extraction.



Figure 6. Nickel extraction predicted with Model 2. A) $[H_2SO_4] = 16\%$, T = 160 °C and S/L = 300 g/L, B) S/L = 300 g/L, $p_{O_2} = 5$ bar and t = 60 minutes and C) $[H_2SO_4] = 16\%$, $p_{O_2} = 5$ bar and t = 60 minutes.

Extraction of the other metals

The leaching efficiency of other metals like Te, Se, As and Bi obtained from the leaching residue analyses from various experimental runs by ICP-OES are shown in Table 4 and illustrated in Figure 7. Increase in *T* from 140 to 180°C for lower S/L ratio = 200 g/L, $p_{O_2} = 2$ bars, $[H_2SO_4] = 12\%$ in experimental runs N3 and N5 resulted in an increase in the leaching efficiencies of Se from (46.4–84.8%), As (57.5–70.4%), Te (77.1–89.6%), Ag (30.7–60.5%), and Bi (8.5–42.2%), respectively. A similar *T* increase from 140 to 160°C for S/L ratio = 400 g/L, $[H_2SO_4] = 12\%$ and $p_{O_2} = 8$ bars in the runs N7 and N16, however, resulted in a drop in the Te extraction percentage from 82.3 to 22.2% and S extraction from 70.3 to 40.8%. Moreover, a slight

increase in the Se content from 71.4 to 75.9% and a significant increase in the leaching efficiency of Ag was observed. Formation of more silver-rich copper/silver selenide/telluride compounds have been reported (Chen and Dutrizac 2005) to retard the dissolution of tellurium. Previous studies (Jennings et al. 1968) also suggested that tellurium dissolution decreased at temperatures above 135–160°C due to re-precipitation. However, substantial extractions of tellurium have been obtained also at 145°C (Doucet and Stafiej 2007). Tellurium usually present in copper tellurides can dissolve based on equation (Equation 5) (Bäckström 2010).

$$Cu_2Te + 2 H_2SO_4 + 5/2 O_2 + H_2O = 2 CuSO_4 + H_6TeO_6$$
[5]

Nonetheless, increase in $[H_2SO_4]$ from 12 to 20% with increased S/L ratio = 400 g/L (N7, N13), $p_{O_2} = 8$ bars resulted in a decrease in the percentage of Se from (71.4–53.3%), Te (82.3–68.2%), As (52.4–44.3%) and S (70.3–57.5%) respectively. On the other hand, increase in p_{O_2} from 2 to 8 bars in experimental runs N1 to N8 had a significant effect on the leaching efficiency of other metals. The dissolution of S also increased from Figure 7. Leaching efficiencies of (a) Te (b) Se (c) As and (d) Bi obtained from the leach residues in different experimental runs. 47.3–65.7%, Se increased from 34.5 to 70.3% and the Te dissolution increased from 68.5 to 82.2% in experimental runs (NI, N8) for S/L ratio of 200 g/L, $[H_2SO_4] = 20\%$ and T at 140°C as presented in Table 4. However, increase in S/L ratio from 200 to 400 g/L for similar values of S/L = 200 g/L, $[H_2SO_4] = 20\%$ and T = 140°C, $p_{O_2} = 2$ bars in experimental runs (N1,N4) resulted in the decrease in the leaching efficiency of Se from (34.5–4.2%), As (64–49.3%), Te (68.5–60.4%), Bi (40.0–6.9%) and Ag (70.8–29.4%) respectively. Nevertheless, an increase in S from 45.2–69.2% and Te from 58.1–68.4% was observed in the runs N12 and N10 when the T was 160°C, $p_{O_2} = 8$ bars for the similar increase in S/L ratio from 200 to 400 g/L.



Figure 7. Leaching efficiencies of (a) Te (b) Se (c) As and (d) Bi obtained from the leach residues in different experimental runs.

Conclusions

The extraction percentage of copper from the anode slime leach residue varied in the range of 97–99%, the maximum being 99.9% (T = 160°C, S/L ratio = 200 g/L, $[H_2SO_4]$ = 20% and p_{O_2} = 8 bars). The parameters having the biggest effect on Cu extraction according to the Cu model built were $[H_2SO_4]$ and S/L ratio. The model indicated that increase of acidity enhanced Cu extraction, whereas increase in S/L ratio had an opposite effect. Higher $T(160-180^{\circ}\text{C})$ and $[H_2SO_4]$ (20%) and low S/L ratio (200 g/L) were in general shown to increase Ni extraction. The maximum Ni extraction of 99.7% was achieved in two leaching experiments (T = 80°C, S/L ratio = 200 g/L, $[H_2SO_4]$ =12%, p_{O_2} = 2 bars and T = 160°C, S/L ratio = 200 g/L, $[H_2SO_4]$ =20%, p_{O_2} = 8 bars). Three models (Ni Models 1, 2 and 3) were built to predict Ni extraction during oxidative pressure leaching of Ni-rich anode slimes. Models 1 and 2 took into account the Ni extraction as a function of leaching time, whereas Model 3 predicted only the final Ni yield into the solution. The Ni extraction model (Ni model 2) including the combined effect terms was shown to predict the Ni extraction from the investigated Ni-rich anode slimes most accurately. According to the models, increasing T, time, p_{O_2} and $[H_2SO_4]$ increased the Ni extraction efficiency, nonetheless, increase in S/L ratio from 200 to 400 g/L decreased the Ni extraction yield. Additionally, the leaching behaviours of impurities and minor metals were investigated. Increase in $[H_2SO_4]$ from 12 to 20% (S/L ratio = 400 g/L, T = 160°C, p_{O_2} = 8 bars) was shown to increase the dissolution of impurities such as S, Se, As and Te. The maximum extractions for these elements were 75.4% (S), 88.7% (Se), 70.4% (As) and 89.6% (Te). Nevertheless, increase in T from 140 to 160°C (S/L ratio = 400 g/L, $[H_2SO_4] = 12\%$, $p_{O_2} = 8$ bars) resulted in decrease in the leaching efficiency of Te from 82.3 to 22.2% and S from 70.3 to 40.8% with a slight increase in the Se extraction from 71.4 to 75.9%, and a significant increase in the leaching efficiency of Ag.

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