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Dissolution behavior of copper concentrate in acidic media using nitrate ions

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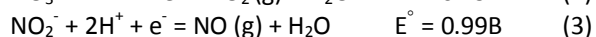
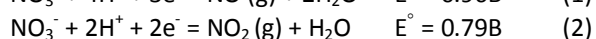
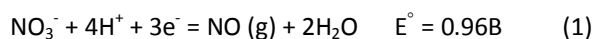
Abstract: This study was conducted to investigate the dissolution process of copper concentrate using sodium nitrate (NaNO_3) in a sulfuric acid (H_2SO_4) medium under various controlling parameters, including dissolution temperature, time, particle size, solid/liquid (S/L) ratio and concentration of NaNO_3 and H_2SO_4 . The thermodynamic probability of mineral dissolution (CuFeS_2 , Cu_2S , CuS , FeS_2) reaction in the concentrate was estimated by standard Gibbs energy. The activation energy (E_a) for the dissolution of copper concentrate was calculated as 15.96 kJ/mol. Batch experimental results show that about 89.9% of copper in the intact concentrate have been leached and it increased to 96.5% at the fraction with $<25.4\mu\text{m}$ particle size. Copper leaching rate has direct correlation with increase in time, temperature, solid/liquid (S/L) ratio and H_2SO_4 concentration. The XRD and XRF analyses of the solid residue after leaching revealed the presence of elemental sulfur.

Keywords: oxidation of chalcopyrite and chalcocite, leaching, sulfuric acid,

INTRODUCTION

Mongolia has rich copper and copper deposits. Chalcopyrite and chalcocite are important minerals of copper sulfide. The sulfide concentrate can be produced by a floatation of raw minerals containing copper sulfide, and then it is treated by pyrometallurgical process. However, the pyrometallurgical technology treating copper concentrate has some disadvantages which are incomplete treatment and producing large amounts of sulfur dioxide (SO_2) in the environment as an air pollutant. Many hydrometallurgical technology studies have been investigated by avoiding SO_2 production [1-3].

In order to leach chalcopyrite and chalcocite under atmospheric or high pressure leaching conditions in sulfate or chloride medium, ferric and copper ions, bacteria, oxygen and other oxidizers can be used as leaching agents [1]. The nitrate/nitrite with high oxidative potential is possible to utilize for leaching of sulfide minerals in sulfuric acid medium [4]:



There are two ways to oxidize metal sulfide by nitric acid as suggested by Habashi [5]. Firstly, NO_3^- ion is an oxidant which is reduced to NO or NO_2 during the reaction. Secondly, oxygen is also an oxidant arising

from decomposition of nitric acid. Oxidative dissolution of a sulfide concentrate using nitrate as the leaching agent in an acidic medium takes place with formation of elemental sulfur [6-8], and a minor part of sulfide sulfur oxidizes to the sulfate under certain conditions. Miroslav, *et al.* [6] determined the optimal leaching conditions of chalcopyrite concentrate by sulfuric acid (H_2SO_4) and sodium nitrate (NaNO_3) under different parameters. They found that the leaching reaction was followed by the mixed control kinetic model, and the activation energy was 83 kJ/mol. As their results, the highest leaching rate was 75.5% when the temperature was 90°C and duration at 240 min.

Rajko *et al.* [8] investigated the dependency of dissolution for copper (I) sulfide (Cu_2S) by H_2SO_4 solution with NaNO_3 on several controlling parameters. The degree of dissolved copper increased with increase in all the controlling parameters. Leaching reactions of Cu_2S are followed by the first order with respect to the concentration of NaNO_3 , and by the second order with respect to the concentration of H_2SO_4 , respectively.

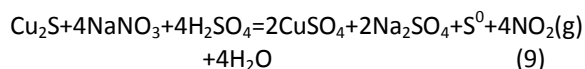
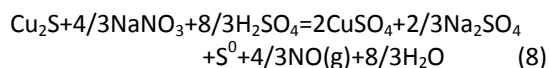
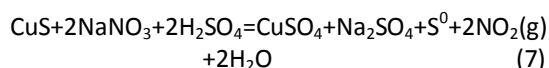
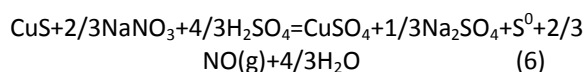
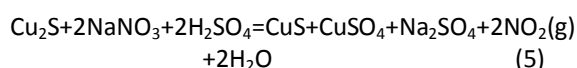
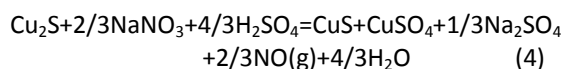
In this study, the sulfide minerals behavior in copper concentrate have been investigated by dissolution process using NaNO_3 in a H_2SO_4 medium associated with the effect of particle size, temperature, time, solid/liquid (S/L) ratio and concentration of NaNO_3 and H_2SO_4 . The thermodynamic analysis was

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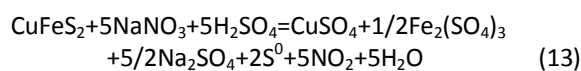
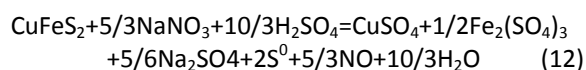
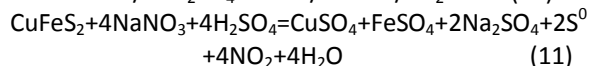
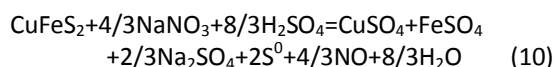
examined for chemical dissolution reaction, and their standard Gibbs energy was estimated as well.

Chemical Reaction and Thermodynamics: The chemical reactions in the Cu_2S - CuFeS_2 - FeS_2 - H_2SO_4 - NaNO_3 - H_2O system during oxidative dissolution process of sulfide minerals (chalcocite Cu_2S , chalcopyrite CuFeS_2 , pyrite FeS_2) in an acidic medium are presented on the basis of literature data, reaction production and XRF and XRD analyses of solid residues.

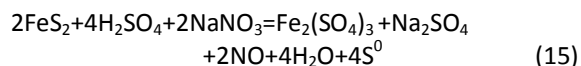
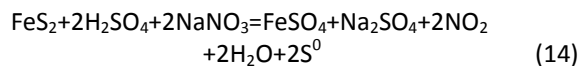
The main reactions for the chalcocite [8]:



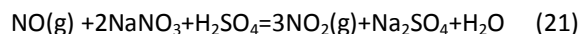
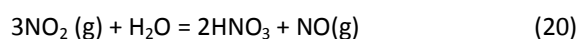
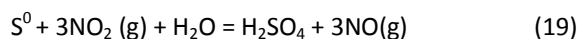
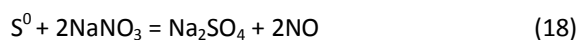
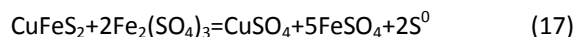
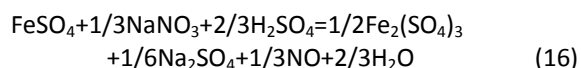
The main reactions for the chalcopyrite [6]:



The main reactions for the pyrite:



The other reactions in the system [6,8]:



Thermodynamic analysis contained calculation of standard Gibbs energy. To explain the possibility of reactions (4-21), the change of Gibbs free energy was estimated at temperature ranged in 25°C-95°C and obtained results are shown in Table 1 (Calculated data are based on the thermodynamic values (ΔG° , ΔS° , ΔH°) of chemical element and its compounds). As seen from the results, the Gibbs energy has always negative values which clearly indicated that they are all thermodynamically feasible at atmospheric

Table 1. The values of standard Gibbs energy of reactions in the Cu_2S + CuFeS_2 + FeS_2 + NaNO_3 + H_2SO_4 + H_2O system at temperature from 298K to 368K

Equation number	$\Delta G^\circ 298$ [6, 8] (kJ/mol)	$\Delta G^\circ 343$ (kJ/mol)	$\Delta G^\circ 353$ (kJ/mol)	$\Delta G^\circ 363$ [6, 8] (kJ/mol)	$\Delta G^\circ 368$ (kJ/mol)
(4)	-146.32	-148.84	-149.38	-149.85	-150.18
(5)	-156.92	-168.26	-171.02	-174.96	-175.17
(6)	-125.84	-128.51	-129.51	-130.41	-130.28
(7)	-136.44	-148.5	-151.47	-155.52	-155.92
(8)	-272.15	-277.04	-278.35	-280.27	-280.09
(9)	-293.36	-316.98	-322.73	-330.48	-331.35
(10)	-331	-348.06	-349.59	-341.4	-351.89
(11)	-352.3	-350.06	-354.91	-391.6	-362.43
(12)	-396.1	-414.01	-415.85	-408.2	-418.61
(13)	-422.7	-464.08	-471.58	-471.2	-482.82
(14)	-	-200.46	-204.02	-	-209.34
(15)	-	-493.01	-496.32	-	-501.03
(16)	-65.1	-66.46	-66.78	-67.1	-67.27
(17)	-70.5	-83.93	-84.22	-73.2	-84.64
(18)	-362.6	-373.95	-376.96	-382.4	-381.48
(19)	-346.7	-344.7	-367.55	-344.7	-368.04
(20)	8.4	21.99	24.67	25.5	28.69
(21)	-15.9	-29.98	-33.37	-37.7	-38.46

pressure and temperatures of 25°C, 70°C, 80°C, 90°C and 95°C for reactions (4-21) except reaction (20).

The greater negative values of ΔG_T for reaction (9) than for reaction (8) indicate that its occurrence has higher thermodynamic possibility for chalcocite. Moreover, the higher negative ΔG_T value for reaction (13) than reaction (12) suggests that it occurs with higher thermodynamic probability for chalcopyrite. However, we suggest reaction (15) possibly stands to overall reactions in the

$\text{Cu}_2\text{S} + \text{CuFeS}_2 + \text{FeS}_2 + \text{NaNO}_3 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ system.

EXPERIMENTAL

Materials: The copper sulfide concentrate obtained from *Erdenet* mining plant was used. XRD analysis reveals that the sample contains 38% of chalcopyrite (CuFeS_2), which is primary mineral of copper sulfide, with small amounts of chalcocite (Cu_2S), covellite (CuS) and pyrite (FeS_2). Chemical compounds of concentrate were determined by XRF and wet chemical analysis. Results show that Cu, Fe and S were main elements with content of about 24.78%, 19.96% and 31.4%, whereas accompanying elements as Zn, Al and Mo were 0.605%, 0.529% and 0.156%, respectively. Particle size fractions (+74.00, -74.00+43.18, -43.18+38.10, -38.10+25.40 and -25.40 μm) were obtained by dry sieving. The mass percentage and copper content in each fraction are summarized in Table 2.

Experimental procedure: Two different samples, copper concentrate (Sample 1) and particle size classified sample (Sample 2), were used in batch

Table 2. Content of copper in concentrate for different particle size

Particle size (μm)	Mass, %	Cu, %
+74.00	5.9349	15.79
-74+43.18	18.81	17.15
-43.18 +38.10	8.234	16.47
-38.10+25.40	48.97	27.40
-25.40	14.99	26.80

experiments. Leaching experiment was carried out in a 0.5L of temperature resistant and 3-necked glass reactor equipped with stirrer, thermometer and cooler. The calculated volumes of H_2SO_4 and NaNO_3 solutions were added into the glass reactor and heated at the selected temperature. When the temperature was reached, the solid concentrate was added and that moment is taken for beginning of reaction. The stirring performed at 300 rpm, temperatures of 70°C, 80°C 90°C and 95°C, leaching times of 30 to 240 min, S/L ratio of 1:10-1:60, while the particle size fractions leached were +74.00 μm and -25.4 μm . The H_2SO_4 and NaNO_3 concentrations were in the range of 0.5M-2.5M and 0.2M-1.0M. The

content of copper and iron in S/L phases after leaching were determined by chemical analysis (iodometric and complexometric methods). The solid residues after leaching were determined by X-ray diffractometer (Enraf Nonius Delft) and X-ray fluorescence (Rigaku SQX) analyses.

RESULTS AND DISCUSSION

Effect of particle size: The influence of particle size on the copper leaching rate was examined for five different size fractions (+74.00, -74.00+43.18, -43.18+38.10, -38.10+25.4 and -25.4 μm) at 90°C using solutions containing 1.5M H_2SO_4 and 0.6M NaNO_3 and S/L ratio of 1:60 at 240 min. Results are shown in Table 3, from where it can be seen that the copper dissolution increases with decreasing of particle size. Copper dissolution reached 60.8% and 90.3% for +74.00 μm and -25.4 μm particle sizes, respectively. This implies that the copper dissolution rate is highly dependent on the particle size. When the same leaching conditions were applied to concentrate, copper extraction was reached to 74.4%.

Fraction with particle sizes of -38.10-25.4 and -25.4 μm were unified, and then <25.4 μm of new

Table 3. Particle size and dissolution copper

Particle size (μm)	Dissolved Cu, %
+74.00	60.85
-74.00+43.18	52.23
-43.18+38.10	63.50
-38.10+25.40	82.77
-25.40	90.30
Concentrate	74.45

fraction was yielded by sieving. Thereafter, to investigate the other leaching parameters, a fraction <25.4 μm particle size (Sample 2) was chosen to compare with concentrate (Sample 1).

Effect of leaching time: The effect of leaching time on the copper dissolution, under following conditions: stirring speed 300 rpm, 1.5M H_2SO_4 and 0.6M NaNO_3 ,

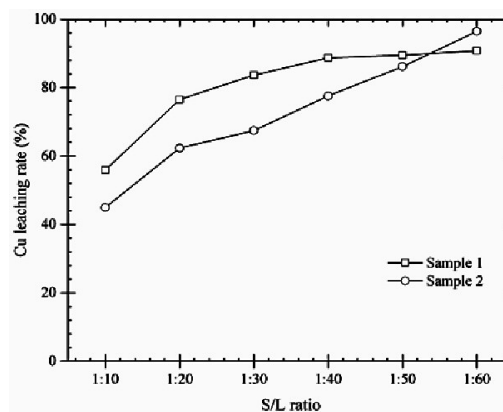


Fig. 1. Effect of leaching time on copper dissolution

S/L ratio of 1:60 at 90°C in various time ranged in 30-240 min from both samples is presented in Figure 1.

Increasing the leaching time resulted in increased copper dissolution which indicates linear relationship between dissolution rate and time. After 30 min of leaching, 55.8% of copper was dissolved from both samples. A copper dissolution reached to 95.5% and 86.9% for Sample 2 and Sample 1 when the time was increased to 240 min. Thereafter, 240 min was chosen for further experiments studying effect of other parameters.

Effect of S/L ratio: The effect of S/L ratio on the copper dissolution was investigated at stirring speed 300 rpm, 1.5M H₂SO₄ and 0.6M NaNO₃, 240 min at 90°C in variation of S/L ratio from 1:10 to 1:60. Experimental results are presented in Figure 2, where it can be seen that the copper extraction on both samples is highly influenced by the S/L ratio. It was achieved to 45.0% for Sample 2 and 55.9% for Sample 1 at the S/L ratio of 1:10.

While the S/L ratio was increasing to 1:60, about

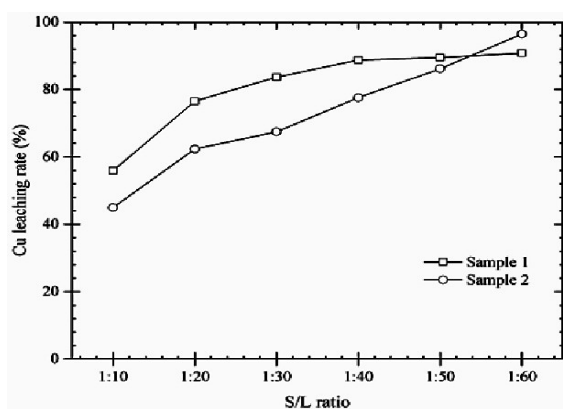


Fig. 2. Effect of S/L ratio on copper dissolution

96.5% and 90.8% of copper was dissolved from both samples, respectively. Clearly an intensive diffusion could be observed if the content of solid phase is decreasing with increasing in liquid phase content. To investigate the other leaching parameters, S/L ratio of 1:60 was chosen.

Effect of sodium nitrate (NaNO₃) concentration: The influence of NaNO₃ concentration on the copper and iron leaching degree was studied in the solutions containing various initial NaNO₃ concentrations (ranged in 0.2M to 1.0M) at 90°C, and S/L ratio of 1:60 in solution containing 1.5M H₂SO₄.

The effect of changing the initial concentration of NaNO₃ is shown in Figure 3. The copper leaching degree was 72.6% at 0.2M concentration of NaNO₃ for Sample 2. It then increased to 85.7% when the concentration was also increased to 0.95M.

For the case of Sample 1, the dissolution degree was reached to 63.6% at 0.2M concentration of NaNO₃. Same trend as observed in the Sample 2, which presented that in high concentration of NaNO₃ was occurred higher dissolution. It is confirmed by an

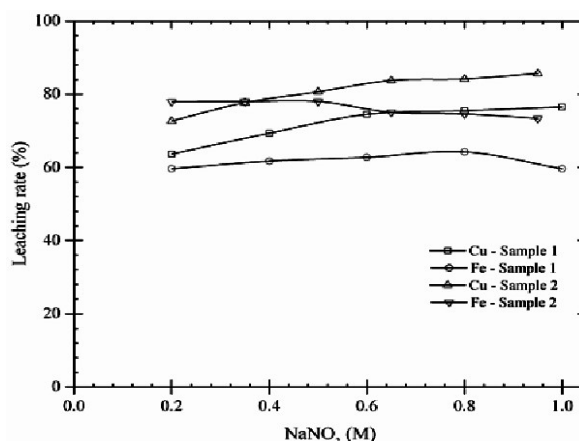


Fig. 3. Effect of NaNO₃ concentration on copper and iron dissolution

increased dissolution degree of 76.5% when the concentration was increased to 1.0M.

The iron dissolution rate was almost constant at the beginning of leaching and then slightly reduced until the end of time while the concentration of NaNO₃ was increasing.

Effect of sulfuric acid (H₂SO₄) concentration: The influence of H₂SO₄ concentration on the copper and iron leaching rate was investigated by the variance of the initial solution acidity (H₂SO₄ concentration range from 0.5 to 2.5M) at 90°C and S/L ratio of 1:60 in

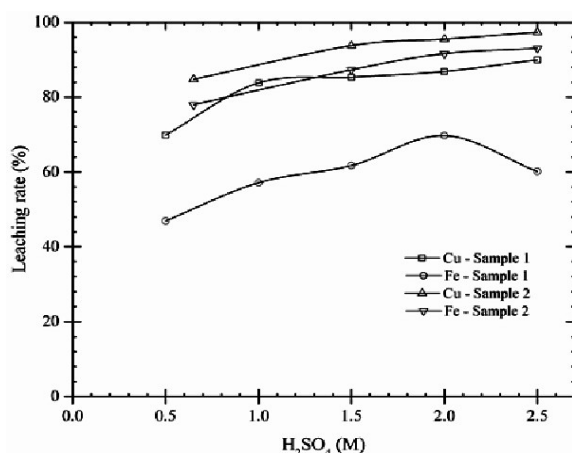


Fig. 4. Effect of H₂SO₄ concentration on copper and iron dissolution

solutions containing 1.0M NaNO₃. Experimental results are presented in Figure 4.

Results showed that the copper dissolution degree was strongly depended on the solution acidity. When low concentrations (0.65M, 0.5M) of H₂SO₄ were used, the leaching rate was relatively high (84.8% and 69.8%) for both samples. Furthermore, it showed the highest degree of 89.9% (Sample 1) and 96.4% (Sample 2) leaching at the highest concentration of H₂SO₄ (2.5M) at 240 min. According to Vracar, et al. [8], the formation of elementary sulfur in acid solution is favoured over H₂S and the oxidizing potential of NO₃⁻ ions increases with respect to

solution acidity (Eq. 1-3), which greatly contributes to the leaching of copper.

The iron leaching rate was 46.9% for Sample 1 and 77.9% for Sample 2 in 0.5M concentration of H₂SO₄. When the solution acidity was increased to 2.5M, the dissolution rate was reached to 93.0% (Sample 2) and 60.0% (Sample 1), respectively.

Effect of temperature: Figure 5 shows the influence of reaction temperature on the copper dissolution at four different temperatures (70°C, 80°C, 90°C and 95°C) in dissolution time ranged in 15-240 min, 1.0M NaNO₃, 2.5M H₂SO₄ and S/L ratio=1:60. About 33.3% of copper was dissolved at 15 min after starting of the experiment at 70°C while it was 43.4% at 90°C (Sample 1). By the end of leaching time at 240 min, it was increased to 69.5% and 86.8% at 70°C and 90°C (Sample 1). By the end of leaching time at 240 min, it was increased to 69.5% and 86.8% at 70°C and 90°C, respectively. Regarding Sample 2, copper dissolution was 50.5% at 15 min, thereafter it increased to 95.9% by the end of dissolution time at 95°C.

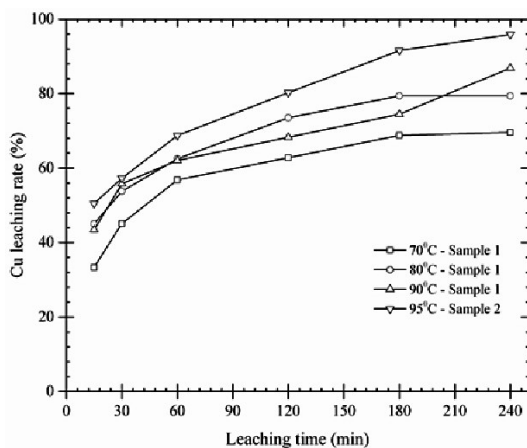


Fig. 5. Effect of temperature on copper dissolution

Copper dissolution from concentrate between 60 min and 180 min at 90°C was relatively lower than that of at 80°C, which might be caused by the formation of elemental sulfur during the dissolution that precipitated at the particle surfaces of minerals.

Activation energy for the leaching process of copper sulfide concentrate was estimated by using

$$k = Ae^{-E_a/(RT)} \quad (22)$$

the Arrhenius equation:

By taking logarithms, Eq. (22) converts to:

$$\ln K = \left(-\frac{E_a}{RT}\right) + \ln A \quad (23)$$

Where: $\ln K$ vs $1/T$ should be a straight line with slope of $-E_a/R$ and intercept $\ln A$. Thus, the value of E_a can be evaluated. The plot of $\ln K$ vs $1/T$ is shown in Figure 6. The calculated activation energy was 15.96 kJ/mol at temperature ranged from 70°C to 90°C.

Characterization of the solid residuals: Characterization of the solid residual after leaching

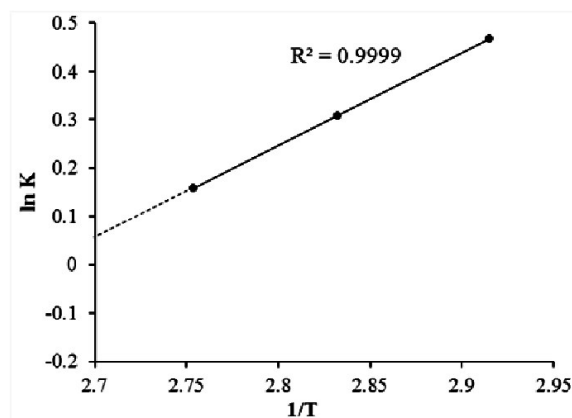


Fig. 6. Arrhenius plot for concentrate leaching

process was determined by XRD and XRF analyses. The solid residuals obtained at 90°C (Sample 1) and 95°C (Sample 2) under the following conditions: stirring speed 300 rpm, 2.5M H₂SO₄, 1.0M or 0.95M NaNO₃, S/L ratio of 1:60 and leaching time 240 min were selected. Results obtained by X-ray diffraction patterns of the Sample 1 and Sample 2 are shown in Figure 7 and Figure 8.

As shows XRD analysis, the elemental sulfur is formed during the leaching process for both samples. The

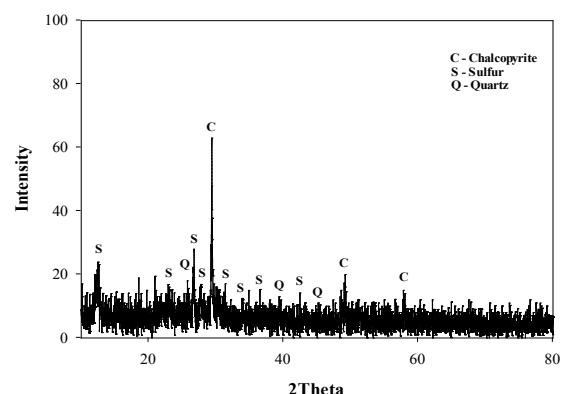


Fig. 7. X-ray diffractograms of leaching residue (Sample 1)

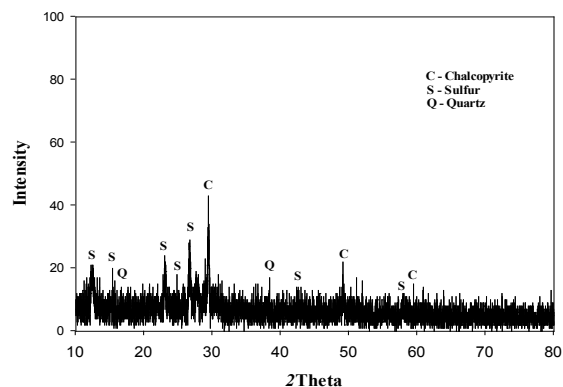


Fig. 8. X-ray diffractograms of leaching residue (Sample 2)

amount of sulfur in residual is higher than that of the chalcopyrite. However, it was not observed in the chalcocite (Cu_2S) and pyrite (FeS_2), indicating that those minerals have dissolved by the oxidation of nitrate ions in acidic solution. The chemical

Table 4. Chemical composition of leaching residual for Sample 1 and Sample 2

Sample	Mass (g)	Content (%)					
		Cu	Fe	S	Si	Zn	Pb
1	1.0044	5.6	7.8	50.26	4.86	0.02	0.019
2	0.9348	2.9	3.5	34.01	3.45	0.04	0.022

composition of the leaching residuals is presented in Table 4.

As seen the Table 4, the increment of the sulfur content is resulted by oxidized sulfide sulfur to elemental sulfur during the leaching process.

CONCLUSIONS

Comparisons in oxidative dissolution characteristic of the fraction with $<25.4\mu\text{m}$ particle size against copper concentrate in acidic sodium nitrate solution was studied during this research. The copper concentrate containing 24.78% of Cu, 19.96% of Fe, 31.4% of S, 0.605% of Zn and 0.156% of Mo was used. X-ray analysis reveals that the concentrate contains the chalcopyrite (CuFeS_2) with small amounts of chalcocite (Cu_2S), covellite (CuS) and pyrite (FeS_2).

It was determined that the leaching rate increased with increase in concentrations of sulfuric acid and sodium nitrate, leaching temperature and S/L ratio, and with decrease in particle size. About 89.9% of copper was dissolved from the concentrate under determined optimal conditions ($T=90^\circ\text{C}$, $t=240$ min, S/L ratio=1:60, concentration of H_2SO_4 : 2.5M, concentration of NaNO_3 : 1.0M) whereas it was 96.5%

in the fraction with $<25.4\mu\text{m}$ particle size with same conditions except for temperature (95°C) and NaNO_3 concentration (0.95M). Reactions appeared in $\text{Cu}_2\text{S}+\text{CuFeS}_2+\text{FeS}_2+\text{NaNO}_3+\text{H}_2\text{SO}_4+\text{H}_2\text{O}$ system are thermodynamically feasible based on calculation of Gibbs energy. The activation energy was calculated to be 15.96kJ/mol. XRD and XRF analysis of the leaching residues confirms that the elemental sulfur is formed during the leaching process.

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