Treatment of copper-containing leaching residue by sulfation roasting followed by acid/water leaching

Nyamdelger Shirchinnamjil, Narangarav Tumen-Ulzii, Nemekhbayar Davaadorj, Khulan Byambasuren, Sarantsetseg Purevsuren, Ulziibadrakh Erdenebat, Enkhtuul Surenjav*

Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar 13330, Mongolia

*Author to whom correspondence should be addressed Enkhtuul Surenjav

Laboratory of Inorganic Chemistry Institute of Chemistry and Chemical Technology Mongolian Academy of Sciences Ulaanbaatar, Mongolia

E-mail: <u>enkhtuul@mas.ac.mn</u> ORCID: <u>https://orcid.org/0000-0002-2357-5339</u>

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, and proofreading process, which may lead to differences between this version and the official version of record.

Please cite this article as: Nyamdelger Sh., Narangarav T., Nemekhbayar D., Khulan B., Sarantsetseg P., Ulziibadrakh E., Surenjav E. Treatment of copper-containing leaching residue by sulfation roasting followed by acid/water leaching. *Mongolian Journal of Chemistry*, **24**(50), 2023, xx-xx <u>https://doi.org/10.5564/mjc.v24i50.1310</u>

Treatment of copper-containing leaching residue by sulfation roasting followed by acid/water leaching

- Nyamdelger Shirchinnamjil, <u>https://orcid.org/0000-0003-1242-7776</u>
 Narangarav Tumen-Ulzii, <u>https://orcid.org/0000-0003-0010-1402</u>
 Nemekhbayar Davaadorj, <u>https://orcid.org/0000-0001-5484-1807</u>
- Khulan Byambasuren, <u>https://orcid.org/0000-0002-5617-1605</u>
 Sarantsetseg Purevsuren, <u>https://orcid.org/0009-0005-8860-0928</u>
 Ulziibadrakh Erdenebat, <u>https://orcid.org/0000-0002-4397-9525</u>
- 9 Enkhtuul Surenjav*, https://orcid.org/0000-0002-2357-5339

Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar 13330, Mongolia

15 ABSTRACT

18

This research investigates the extraction of copper from copper-containing leaching residue, which includes 33.45% of copper, 14.14% of iron, 23.87% of sulfur and trace amounts of silver and other elements. Roasting the copper-containing residue under air and oxygen flow convert

- sulfides into sulfate, followed by water and acid leaching to extract copper. The process parameters, including leaching temperature, sulfuric acid concentration, leaching time, solid-to-
- 21 liquid ratio, and agitation speed, were optimized for both water and acid leaching methods. Results showed that the maximum copper dissolution efficiency was 93.12% with water leaching, and 97.16% with acid leaching. Chemical analysis revealed that the water and acid
- 24 leaching residue contained 48.13% and 31.64% of iron, respectively. This study provides valuable insights into the process optimization for copper extraction from copper-containing leaching residue, which can inform the development of more efficient and sustainable methods
- 27 for metal recovery.

Keywords: copper technogen concentrate, thermal analysis, air- and oxygen roasting, acid/water leaching

INTRODUCTION

- The growing demand for copper has resulted in the depletion of copper ores with higher copper 33 content, leading to the treatment of complex polysulfides or copper ore with higher contents of 39 impurities such as Sb, Pb, Zn, As, Hg, Ni etc. Among these impurities, arsenic is particularly 39 challenging due to its toxicity. There are several significant polymetallic ore deposits in Mongolia
- 36 including Tsav, Boorchi, Tolbo, Kharmagtai and Asgat. In recent years, there has been interest in developing the Asgat deposit as well as other mineral deposits in the country, to meet the growing demand for metals and minerals worldwide. Asgat polymetallic deposit is estimated to
- 39 hold approximately 6402.6 thousand of tonnes of ore, boasting a valuable metal reserve including 2247.8 tonnes of silver, 7264.6 tonnes of copper, 31830.9 tonnes of antimony and 3319.8 tonnes of bismuth. Although Asgat is primarly known for its polymetallic ore composition,
- it can also be regarded as a potential source of copper due to the significant presence of tetrahedrite, which constitutes 72% of the Asgat concentrate [1-3].
 Processing of polymetallic concentrates is difficult task as it involves a variety of minerals such
- 45 as enargite (Cu₃AsS₄), tennantite (Cu₁₂As₄S₁₃) and tetrahedrite (Cu₁₂Sb₄S₁₃) associated with other sulfide minerals [4]. To separate the target metals from the polymetallic ore concentrate, scientists have focused on removing harmful impurities. Comprehensive study on thermal and
- 48 kinetic study of polymetallic copper concentrate was conducted by Mitovski *et. al* [5]. Tetrahedrite represents the main chemical source of copper (40-46%) and antimony (27-29%) along with other important elements including arsenic, bismuth, mercury, and silver. Two main
- 51 leaching methods for tetrahedrite have been identified- alkaline and acidic leaching [6]. Balaz et.al studied leaching of mercury and antimony from tetrahedrites of different characteristics using an alkaline solution [7] while the leaching of tetrahedrite using HCI in the presence of 54 ozone was studied by Ukasik et. al [8].
- The leaching residue can be further processed through an appropriate roasting process to convert the metals into extractable form by heating at high temperature [9-11]. Three types of
- 57 roasting methods are commonly used including oxidation roasting, chlorination roasting, and sulfation roasting [12]. However, oxidation roasting requires high temperatures and may lead to copper loss as copper ferrite. Chlorination roasting tends to generate toxic and corrosive
- oxychlorides [13]. On the other hand, sulfation roasting has been found to be quite suitable for subsequent processing. Nevertheless, during sulfation roasting, the reaction becomes complex when more than one sulfide is present in the sample.
- Roasting is a surface reaction that results in the formation of an oxide layer. This layer remains porous allowing oxygen to pass into the unreacted inner sulfide portion of the particle, while the resulting SO₂ gas is released [14]. The sulfuric gas then reacts with metal oxides and excess

- 66 oxygen to form sulfates, making the sulfation roasting process an environmentally friendly technology. To produce a mixed oxide- sulfate product sulfation roast is preferred, making it an ideal process for polysulfide compound. While there have been numerous investigations
- 69 conducted, our study provides a comprehensive analysis of copper extraction from copper technogen concentrate sourced from domestic ore deposits. This study aimed to assess the effectiveness of extracting copper from copper-containing

72 leaching residue of polysulfide concentrate. The process involved sulfation roasting followed by leaching with water and sulfuric acid. To determine the optimal conditions for sulfation roasting, the study examined the effects of roasting temperature and time under an air and oxygen

75 atmosphere. After roasting, the resulting product was leached using water and sulfuric acid to obtain a copper-bearing aqueous solution. Copper sulfate was the predominant compound in the solution.

78 EXPERIMENTAL

Materials: The raw material used in this study was the polysulfide concentrate obtained from the Asgat mining ore in Mongolia. The concentrate was initially subjected to alkaline-sulfide leaching

- 81 (using NaOH/Na₂S x 9H₂O) to obtain a technogen concentrate also named copper containing leaching residue, containing 33.45% copper, which was subsequently utilized for copper extraction.
- TG/DTA analysis: Thermal analysis of the copper technogen concentrate was carried out using Hitachi-TG/DTA 7300. The TGA/DTA analysis was performed under air atmosphere, in the temperature range of 30-1000 °C, at a heating rate of 20.0 °C /min.
- *Sulfation roasting:* Sulfation roasting experiments were conducted under air atmosphere using a temperature-controlled tube furnace equipped with a quartz tube. For comparison purposes, sulfation roasting experiments under oxygen were also carried out using a home-made tube
- 90 furnace. The oxygen flow is controlled via Brooks Sho-Rate flowmeter installed on the inlet. Sulfuric acid leaching: Acid leaching experiments were conducted to evaluate the effect of various parameters, including acid concentration, temperature, leaching time, solid-to-liquid ratio
- 93 and agitation speed. For each leaching experiment, 1.5-3 g of sample and 20 ml of acid with appropriate concentration were placed in a round bottom flask. The leaching time was varied from 30 to 120 mins, while the acid concentration used were 0.4M, 0.8M, 1.2M and 1.6M. The
- 96 leaching temperature ranged from 25 °C to 70 °C with solid-to-liquid ratio of 1:6.67 (15%), 1:8 (12.5%), 1:10 (10%), 1:13.33 (7.5%). Agitation speeds of 200, 300 and, 400 rpm were used with magnetic stirrer.

- Water leaching: In the water leaching experiment 0.27-0.84 g sample and 20 ml of water were placed in a conical flask and subjected to different temperature ranging from 25 °C to 70 °C, with agitation speeds ranging from 200 to 500 rpm at 100 rpm intervals. The leaching time varied between 30, 60 and 120 mins, with solid/liquid ratios of 1:25, 1:50 and 1:75.
- After completion of the leaching process, the slurry was filtered and the leaching residue was washed continuously with distilled water and dried in an oven. The leachates and leach residue
- were analyzed using ICP-OES, XRD, SEM and chemical analysis to determine the constituents.

RESULTS AND DISCUSSION

Asgat polymetallic ore concentrate is composed of several metals, including 0.91% silver, 18.2% copper, 19.4% antimony, 2.03% arsenic, and 1.6% bismuth, as well as other elements. In order to remove toxic contaminants such as antimony, arsenic, and bismuth, the concentrate was subjected to alkaline-sulfide leaching. The activation energy for antimony leaching from the

- 111 tetrahedrite by alkaline-sulfide leaching was calculated as 81.43 kJ/mol which indicates the leaching is controlled by surface chemical reaction [15]. These findings are consistent with those of other researchers [16].
- The elemental composition of Asgat concentrate and leaching residue are compared in Table 1 [15]. The alkaline-sulfide leaching residue contains 33.45% of copper, 14.14% of iron, 23.87% of sulfur, 0.73% of silver and other trace elements such as silicon, aluminium and sodium.
- 117 According to the XRD analysis, the leaching residue contains chalcopyrite (CuFeS₂), covellite (CuS), chalcocite (Cu₂S), pyrite (FeS) and argentite (Ag₂S) as well as non-ore sulfide minerals as shown in Fig. 1 and Table 2.

1	2	n
4	- 2	υ

Table 1. The elemental composition of concentrate and the leaching residue

Sample	Elements, %								
Gample	Ag	Sb	As	Cu	Fe	Zn	Pb	Bi	S
Concentrate	0.91	19.40	2.03	18.20	10.6	0.51	0.09	1.67	13.60
Leaching residue	0.73	0.14	0.22	33.45	14.14			0.93	23.87



Fig. 1. XRD analysis of copper-containing leaching residue

126 Table 2. Phase identification by XRD analysis of copper-containing leaching residue

Formula	Contents, %
CuFeS ₂	43.24
Cu ₂ S	6.03
CuS	3.51
Ag ₂ S	6.95
NaAlSi ₃ O ₈	38.47
	Formula $CuFeS_2$ Cu_2S CuS Ag_2S NaAlSi ₃ O ₈

TG/DTA analysis: TGA/DTA thermogravimetric analysis was conducted to study the sample's
 initial oxidation temperature, and mass change during the 30-1000 °C temperature range. The comparison of TGA/DTA results with XRD phase identification of the sample will help to understand the complex reaction mechanism during the sulfation roasting. TGA/DTA analysis
 was done for copper-containing leaching residue at a heating rate of 20.0 °C/min in the

- temperature range of 30-1000 °C under air atmosphere. As seen from the thermogravimetric curve cf. Fig 2 when the sample is heated from room
- temperature till 315 °C there is slow weight loss of 2.9% was observed due to the evaporation of moisture and organics as well as hydrates decomposition. Eventually, the weight increase was observed and become 100.02% at 343.29 °C indicating the sulfides are oxidized and sulfates
- produced. Roasting the sample further from 343 to 600 °C results in weight gain of a maximum of 128.99% at 600.79 °C indicating the sulfation roasting fully occurred at this temperature range based on the theoretical calculation. The weight increase up to 600 °C is attributed to the
- 141 production of copper sulfate. However, the iron sulfate production will also affect weight increase. After 600 °C the weight loss occurs till 943.52 °C resulting the sulfur oxide which is associated with the decomposition of sulfates. To summarize, when copper-containing leaching
- residue is subjected to thermal analysis, weight gain of 28.7% occurs at a temperature range of 350-600 °C, whereas the total weight loss is 14% during the entire roasting at 25-1000 °C.

During the thermal treatment the following reactions are predicted. For example:

147
$$2CuFeS_{2} + 7.5O_{2} = 2Cu_{2}S + 2FeS + 2SO_{2} \Delta G_{823,15K} = 190 \text{ kJ/mol}$$
(1)
3FeS + 5O_{2} = Fe₃O₄ + 3SO_{2} \Delta G_{823,15K} = -1443.78 \text{ kJ/mol} (2)
2FeS + 3.5O_{2} = Fe₂O_{3} + 2SO_{2} \Delta G_{823,15K} = -1049.76 \text{ kJ/mol} (3)
150
$$Cu_{2}S + SO_{2} + 3O_{2} \rightarrow 2CuSO_{4} \Delta G_{823,15K} = -533.06 \text{ kJ/mol}$$
(4)
2CuS + SO_{2} + 3O_{2} $\rightarrow 2CuSO_{4} \Delta G_{823,15K} = -658.21 \text{ kJ/mol}$ (5)
Ag₂S + 2O₂ = Ag₂SO₄ $\Delta G_{823,15K} = -392.71 \text{ kJ/mol}$ (6)
153
$$FeS_{2} + 3O_{2} = FeSO_{4} + SO_{2} \Delta G_{823,15K} = -809.08 \text{ kJ/mol}$$
(7)



Fig. 2. Thermogravimetric analysis of copper-containing leaching residue

- 156 ΔG^{o_T} values for proposed reactions are calculated at 823.15K and it was found that all values except for Eq.1 are negative. This indicates that the reactions are thermodynamically feasible at the calculated temperature.
- 159 Roasting under air: The purpose of the roasting stage was to convert copper sulfide into easily soluble copper sulfate. In comparison to conventional roasting processes, we have an advantage in using lower roasting temperature and eliminating the need for added sulfuric acid
- [9] or sodium sulfite as sulfation agent [12]. To achieve this, the copper-containing leaching residue was underwent roasting in a Nabertherm tube furnace under an air atmosphere at varying temperatures, ranging from 400 to 600 °C as determined by TG/DTA analysis. Roasting
- times varied from 15 minutes to 3 hours.
 In this study, we examined the weight increase during sulfation roasting under varying times and temperatures. The results showed that the highest weight increase of 32.21% is occurred at 550
- ¹⁶⁸ °C for one hour of roasting time under air atmosphere as shown in Fig. 3. Additionally, the color difference of the roasted products can indicate whether sulfation roasting is complete. Lighter

colors were observed at lower temperatures or shorter roasting times, whereas completed

- roasting resulted in darker colors due to copper sulfation.
 The chemical composition of the roasted product is confirmed through an XRD study (refer Fig. 4) revealing that 67.8% of the product was comprised of copper sulfate, while 27.2% composed
- 174 goethite and 4.8% albite. This finding indicates that almost 95% of copper was successfully converted to copper sulfate during the roasting process. The oxidation of chalcopyrite, covellite and chalcocite during roasting was responsible for this conversion [17]. Furthermore, iron
- 177 compounds were also present in the roasted product in addition to copper sulfate. *Roasting under oxygen:* The copper-containing residue was subjected to roasting under varying conditions of temperature, time, and oxygen flow rate. The results of the study, depicted in Fig.
- 180 3, showed that the maximum weight gain for air roasting was 32.21% at one hour of roasting time, while oxygen roasting produced a maximum weight gain of 29.85%. However, when the roasting time was increased to three hours, the maximum weight gain for oxygen roasting was
- found to be 33.15%. X-ray diffraction (XRD) data indicated that with roasting times less than three hours at temperature less than 400 °C for oxygen roasting, FeS₂ and CuS still existed, suggesting that the sulfation roasting was not complete. At three hours of roasting time, copper
- 186 sulfates dominated, along with other minerals such as magnetite (Fe₃O₄), goethite FeO(OH), and iron sulfates Fe₂(SO₄)₃. Therefore, the optimum conditions for oxygen roasting were determined to be a roasting temperature of 400 °C, a roasting time of 3 hours, and an oxygen
- 189 flow rate of 20 ml/min (refer Table 3). XRD analysis of the roasted sample revealed a composition of 64.8% copper sulfate, 3.6% goethite, 4.5% hematite, 3.5% magnetite, and 18.7% albite with approximately 12% iron compounds present in the roasted product.



Fig. 3. Weight gain vs. the roasting temperature under the air and oxygen roasting (roasting time is 60 mins)



Fig. 4. XRD analysis for effect of roasting time at optimum temperature (at 400 °C, O₂ roasted for 180 min (a) 120 min (b) 60 min (c); and at 550 °C air roasted for 180 min (d) 120 min (e) 60 min (f))

Sample	Temp./ °C	Gas	Time/min	Roasted product	
				Major phase	Minor phase
1	400	Air	60	CuSO ₄	FeO(OH), Fe ₂ O ₃
2	450	Air	60	CuSO ₄	Fe ₂ O ₃
3	500	Air	60	CuSO ₄	CuSO4x5H2O, FeO(OH)
4	550	Air	60	CuSO₄	CuSO4x5H2O, FeO(OH)
5	600	Air	60	CuSO ₄	FeO(OH), Fe ₂ O ₃
6	650	Air	60	CuSO ₄	FeO(OH), Fe ₂ O ₃
7	300	O ₂	60	CuSO ₄	CuFeS ₂ , FeS ₂
8	350	O ₂	60	CuSO ₄	CuFeS ₂ , FeS ₂
9	300	O ₂	180	CuSO ₄	FeO(OH), FeS ₂
10	350	O ₂	180	CuSO ₄	FeO(OH), FeS ₂ , CuS
11	400	O ₂	180	CuSO ₄	FeO(OH), Fe ₃ O ₄ , Fe ₂ (SO ₄) ₃

Table 3. Phase identification by XRD analysis during the sulfation roasting

- Composition of our sample, which includes metal sulfides such as chalcopyrite (CuFeS₂), covellite (CuS), chalcocite (Cu₂S), pyrite (FeS) and argentite (Ag₂S), makes the reaction during the roasting process highly complex. The chemical and mineralogical composition of the concentrate, as well as the temperature, are crucial factors in determining the product composition during sulfation roasting. However, other process parameters such as particle size, mixing, reaction time and roasting technique can also significantly impact the final product [18].
- The sulfation roasting process is complete at 550 °C during the air roasting, but, when oxygen roasting is used, a lower temperature of 400 °C is required for the sulfation process.

Leaching test with water: The copper technogen concentrate was roasted under optimum conditions and subsequently leached using water at various temperature to obtain a copperbearing aqueous solution. The water leaching experiments were conducted by varying the leaching time, temperature, agitating speed and solid-to-liquid ratio.

The dissolution efficiency (%), which is a measure of how much of the total copper is dissolved, was calculated using the equation given below:

 $Dissolution \ efficiency \ (\%) = \frac{Amount \ of \ dissolved \ metals}{Amount \ of \ metals \ in \ the \ sample} * 100$

- The copper dissolution efficiency was found to be at its highest with a rate of 91.68% at 60 minutes for the air roasted sample and 86.42% at 30 minutes for the oxygen roasted sample (refer to Fig. 5). With increase of leaching time, copper dissolution decreased for the oxygen
- 216 roasted sample. Iron dissolution was generally lower, with about 12% in present in the leaching solution and the majority remaining in the leaching residue.



Fig. 5. Copper and iron dissolution efficiency as a function of leaching time (S/L ratio 1:50, 500 rpm, 25 °C)

219



Fig. 6. Copper and iron dissolution efficiency as a function of agitation speed (air: 60 min, S/L ratio 1:50, 25 °C; oxygen: 30 min, S/L ratio 1:50, 25 °C)

The agitation speed is an another important parameter in leaching experiments, and its effect on copper and iron dissolution was studied within the range of 200-500 rpm. For the air roasted sample, the copper dissolution rate decreased slowly until 400 rpm but, increased to 91.68% at 500 rpm. The copper dissolution rate for the oxygen roasted sample increased gradually with

- the increase of agitation speed and reached a maximum value of 93.12% at 400 rpm. Iron dissolution was generally low for the air roasted sample, whereas for the oxygen roasted sample, high iron dissolution was observed, especially at 300 rpm (refer to Fig. 6). This can be attributed
- 231 to the increased molecular motion of iron sulfate as agitation speed increased, leading to a corresponding increase in iron dissolution.

The copper and iron dissolution rates were also studied as a function of solid-to-liquid ratio, as

- shown in Fig. 7. For both air and oxygen roasted sample, the optimum solid-to-liquid phase ratio was found to be 1:50 with copper dissolution rates of 91.68% and 93.12%, respectively. We assume that water-insoluble compounds were also present in the roasted sample. At the 1:50
- 237 phase ratio, the iron dissolution rate was low, at 16.49% indicating that most of the iron compound was left in the leaching residue.

249



Fig. 7. Copper and iron dissolution efficiency as a function of solid-to-liquid phase ratio (air: 60 min, 500 rpm, 25 °C; oxygen: 30 min, 400 rpm, 25 °C)

During the water leaching experiment, the solution temperature was varied from 25 to 70 degree celsius. There was no significant change observed both air and oxygen roasted samples, therefore all other experiments were conducted at room temperature. (refer to Fig. 8). The effect of temperature on iron dissolution was minimal, as most of iron was left in the water leaching residue.



Fig. 8. Copper and iron dissolution efficiency as a function of temperature (air: 60 min, S/L ratio 1:50, 500 rpm; oxygen: 30 min, S/L ratio 1:50, 400 rpm)

Leaching test with sulfuric acid: To compare the effectiveness of acid versus water leaching, the roasted samples underwent acid leaching experiments with acid concentration, solid-to-liquid ratio, and agitating speed varied. As depicted in Fig. 9, copper dissolution was better with the oxygen roasted sample compared to the air roasted sample. Both air- and oxygen- roasted samples achieved optimal copper dissolution rates with a sulfuric acid concentration of 1.6M. Copper dissolution decreased with lower acid concentrations. The leaching time of 30 minutes was determined to be sufficient for achieving a dissolution efficiency of 98.43% in the oxygen roasted sample. However, the air roasted sample required an extended leaching time of 60 minutes to attain a slightly lower dissolution efficiency of 96.01%.



Fig. 9. The effect of leaching time and acid concentration on copper dissolution (air: 25 °C, S/L ratio 1:10, 300 rpm; oxygen: 25 °C, S/L ratio 1:10, 300 rpm)

Fig. 10 shows that the solid-to-liquid ratio had no significant effect on copper dissolution both for air- and oxygen- roasted samples. At an solid-to-liquid ratio of 1:8, the copper dissolution was approximately 90.37% for the air roasted sample and 98.43% for the oxygen roasted sample.
However, the dissolution of iron is highest with lower solid-to-liquid ratio, particularly for the

oxygen roasted sample.

- Fig. 11 illustrates the impact of agitation speed on copper dissolution. In the case of the air roasted sample, 200 rpm was determined to be the optimal agitation speed as it resulted in 97.16% copper dissolution. However, the iron dissolution rate was found to be relatively high. For the oxygen roasted sample, the highest copper dissolution rate (99.59%) was achieved at
- 300 rpm, with a lower amount of iron dissolved in the leachate.
 Leaching processes of copper compounds in the water and sulfuric acid proceeds via diffusion and activation energy were calculated as 6.05 and 8.70 kJ/mol.



276

279

Fig. 10. The effect of solid-to-liquid ratio on copper dissolution (air: 1.6M H₂SO₄, 25 °C, 60 min, 300 rpm; oxygen: 1.6M H₂SO₄, 25 °C, 30 min, 300 rpm)



Fig. 11. The effect of agitation speed on copper dissolution (air: 1.6M H₂SO₄, 25 °C, S/L ratio 1:8, 60 min; oxygen: 1.6M H₂SO₄, 25 °C, S/L ratio 1:13.3, 30 min)

282

Fig. 12 compares the water leaching residue and acid leaching residue obtained. The air- and oxygen- roasted samples (black and pink curves) primarily consist of chalcocyanite and goethite, 285 while the water- and acid-leached samples contain albite, anorthite, hematite, and goethite. The hard residue left after water leaching contains 33.4% albite (Na[AlSi₃O₈]), 7.1% anorthite 288 (CaAl₂Si₂O₈), 13.7% goethite (FeO(OH)) 14.5% maghemite (γ -Fe₂O₃), and 31.0% hematite (α -Fe₂O₃) with total iron accounting for 48.13% according to chemical analysis. The SEM-EDX analysis of the leaching residue confirms the presence of a high amount of iron 44.77% along with 44.94% oxygen, 0.82% silicon at measured point (refer Fig.13a). 291

This residue could be utilized as an iron resource and further processed to recover iron, thereby ensuring complete utilization of the raw material without generating any waste.

The morphology of the leaching residue after the water and acid leaching both for air (a,b) and oxygen (c,d) roasted samples were shown in Fig. 13. SEM-EDS analysis confirmed the intensity of energy peaks corresponding to Fe, O₂ and Si with about 44% of Fe content.

297



Fig. 12. XRD analysis of leaching residue compared with the roasted sample. a) acid leaching residue (O₂ roasted), b) water leaching residue (O₂ roasted), c) oxygen roasted sample, d) acid leaching residue (air roasted), e) water leaching residue (air roasted), and f) air roasted sample



300



306

Fig. 13. SEM micrographs of leaching residue; a) water leaching residue of air roasted sample b) acid leaching residue of air roasted sample; c) water leaching residue of oxygen roasted samples, d) acid leaching residue of oxygen roasted samples

309 *Copper bearing aqueous solution:* The resulting leach liquor after the water/acid leaching will be further utilized to produce a high-purity electrolyte with a high concentration of Cu through solvent extraction. This electrolyte will then be used to electroplate a pure cathode copper. Our

- 312 study suggests a shorter flowsheet of extracting the copper from the polysulfide concentrate, which includes a leaching process to remove the impurities such as arsenic, sulfation roasting, water/acid leaching and subsequent solvent extraction.
- 315

CONCLUSIONS

We systematically optimized the leaching processes for extracting copper from air and oxygen roasted samples using both water and sulfuric acid leaching methods. The parameters for water leaching included a temperature of 25 °C, agitation speed of 500 rpm, solid-to-liquid ratio of 1:50 and a leaching time of 60 minutes. For acid leaching, we used a temperature of 25 °C, agitation

321 speed of 200 rpm with a solid-to-liquid ratio of 1:8, and a leaching time of 30 minutes, with 1.6M H₂SO₄.

Our results indicated that acid leaching yielded a higher copper dissolution efficiency compared to water leaching, with values of 97.16% and 91.68%, respectively, for air roasted sample. Similarly, for the oxygen roasted sample, acid leaching achieved a copper dissolution efficiency of 95.53%, while water leaching resulted in 93.12%. Notably, both methods exhibited a certain

327 degree of iron dissolution efficiency, with approximately 15% and 30% present in the leachate for the air roasted and oxygen roasted samples, respectively.

XRD analysis confirmed the presence of hematite, goethite, magnetite and albite in the hard residue. After water and acid leaching, the hard residue contained 48.13% and 31.64%, total iron, respectively. This indicates that water leaching was more effective in separating the iron compound, resulting in a higher concentration of iron in the hard residue. In conclusion, our

- 333 study highlights the optimized leaching processes for copper extraction from roasted samples. Acid leaching exhibited superior copper dissolution efficiency, while water leaching demonstrated better separation of iron compounds. These findings contribute to the
- 336 understanding of efficient extraction methods and the potential for maximizing copper recovery while minimizing the presence of unwanted elements like iron.

339 ACKNOWLEDGMENTS

This research was supported by a fundamental research project from the Ministry of Education and Science of Mongolia funded by the Mongolian Foundation for Science and Technology under contract No. ShuSs. 2020/21.

REFERENCES

342

- Javkhlan O., Munkhtsengel B. (2021) Silver Deposits. In: Gerel O., Pirajno F., Batkhishig B., Dostal J. (eds) Mineral Resources of Mongolia. *Modern Approaches in Solid Earth Sciences*, 19, Springer, Singapore. <u>https://doi.org/10.1007/978-981-15-5943-3_9</u>
- Ochirbat P. (1999) Strategy and ecology of noble minerals complex development. UB, 347 -374
- Nyamdelger S., Burmaa G., Narangarav T-U. Ariunaa G. (2013) Dissolution behaviour of freibergite-tetrahedrite concentrate in acidic dichromate solution. *Mong. J. Chem.*, **14**(40), 36-40. <u>https://doi.org/10.5564/mjc.v14i0.196</u>
- Schlesinger M.E., King M.J., Davenport W.G. (2011) Extractive metallurgy of copper. Elsevier, UK. ISBN 978-0-08-096789-9
- Mitovski A., Strbac N., Mihajlovic I., Sokic M., Stojanovic J. (2014) Thermodynamic and kinetic analysis of the polymetallic copper concentrate oxidation process. *J. Therm. Anal. Calorim.*, **118**, 1277-1285. <u>https://doi.org/10.1007/s10973-014-3838-8</u>
- Aghazadeh S., Abdollahi H., Gharabaghi M., Mirmohammadi M. (2021) Selective leaching of antimony from tetrahedrite rich concentrate using alkaline sulfide solution with experimental design: Optimization and kinetic studies. *J. Taivan Inst. Chem. Eng.*, **119**, 298-312. https://doi.org/10.1016/j.jtice.2021.01.021
- Balaz P., Sekula F., Jakabsky S., Kamme, I.R. (1995) Application of attrition grinding in alkaline leaching of tetrahedrite. *Miner. Eng.*, 8(11), 1299-1308 <u>https://doi.org/10.1016/0892-6875(95)00097-A</u>
- Ukasik M., Havlik T. (2005) Effect of selected parameters on tetrahedrite leaching by ozone. *Hydrometallurgy*, **77**, 139-45. <u>https://doi.org/10.1016/j.hydromet.2004.10.017</u>

- Dimitrijevic M. D., Urosevic D.M., Jankovic Z.D., Milic S. M. (2016) Recovery of copper from smelting slag by sulphation roasting and water leaching. *Physicoche. Probl. Miner. Process*, 52(1), 409-421. <u>https://doi.org/10.5277/ppmp160134</u>
- Lucheva B., Iliev P., Kolev D. (2017) Hydro-pyrometallurgical treatment of copper convertor flue dust. J. Chem. Tech. Metall., 52(2), 320-325
- Gorai B., Jana R.K., Kha, Z.H. (2002) Electrorefining electrolyte from copper plant dust. *Mater. Trans.*, 43(3), 532–536. <u>https://doi.org/10.2320/matertrans.43.532</u>
- Zhao Y., Hou Y., Cui Y., Liang H., Li L. (2015) Recovery of copper from copper sulfide concentrate by sulfation roasting. *Inter. J. Nonferrous Met.*, 4, 9-13. <u>https://doi.org/10.4236/ijnm.2015.42002</u>
- Priya J., Randhawa N.S., Hait J., Bordoloi N., Patel J.N. (2020) High-purity copper recycled from smelter dust by sulfation roasting, water leaching and electrorefining. *Environ. Chem. Lett.*, **18**, 2133-2139. <u>https://doi.org/10.1007/s10311-020-01047-0</u>
- Shamsuddin M. (2021) Roasting of Sulfide Minerals. In: Physical Chemistry of Metallurgical Processes. Second Edition. *The Minerals, Metals & Materials Series, Springer, Cham.* <u>https://doi.org/10.1007/978-3-030-58069-8_2</u>
- Ariunaa G., Burmaa G., Nyamdelger S., Altansukh B., Nazgul M., Narangarav T-U. (2021) Some results of studies on leaching of toxic elements in Asgat polymetallic concentrate. *Bulletin of the Institute of Chemistry and Chemical Technology*, *4*(9), 17-25 <u>https://doi.org/10.5564/bicct.v4i9.1814</u>
- Samuel A.A., Samuelsson C., Sandström A. (2010) Dissolution kinetics of tetrahedrite mineral in alkaline sulphidemedia. *Hydrometallurgy*, **103**, 167-172 <u>https://doi.org/10.1016/j.hydromet.2010.03.014</u>
- Prasad S., Pandey B.D. (1999) Thermoanalytical Studies on Copper-Iron Sulphides. J. Therm. Anal. Calorim., 58, 625-637. <u>https://doi.org/10.1023/A:1010108729034</u>
- Nyamdelger Sh., Narangarav T-U., Nemekhbayar D., Sarantsetseg P., Surenjav E. *et al.*, (2022) Copper extraction from the sulphation roasted copper technogen concentrate. Bulletin of the Institute of Chemistry and Chemical Technology, **10**, 1-9. <u>https://doi.org/10.5564/bicct.v10i10.1483</u>