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Recovery of ZnO and Cu from Brass Smelter Slag by Hydrometallurgy Process

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Abstract

Vietnam has many traditional copper casting craft villages from the North to the South, which resulting in large amounts of copper smelter slag containing Zn, Cu, Al, etc. In this study, zinc oxide and copper metal have been recovered from brass smelter slag (71.80 wt.% ZnO and 10.32 wt.% CuO) by a hydrometallurgical process. The brass smelter slag was leached in sulfuric acid with a concentration of 125-225 g/L H_2SO_4 at a leaching temperature of 30 - 70 °C for 30 - 120 min. The extraction percentage of Cu and Zn was obtained at 80.26% and 81.71%, respectively. The optimal leaching condition was determined as 175 g/L H_2SO_4 at 50 °C for 90 min. The leaching solution was purified by removing Fe, Mn and Al, etc. via oxidizing the ion Fe^{2+} to Fe^{3+} and having a pH of 5.5. The solution was continuously cemented by Zn metal at 60 °C for 60 min to obtain Cu metal with a high purity of 98.52 wt.% Cu. The solution purification with 85.43 g/L Zn was adjusted to a pH value of 8 - 8.5 to precipitate zinc hydroxide $Zn(OH)_2$. The precipitate was calcinated at 600 °C for 120 min to obtain ZnO (98.65 wt.%). The recovery of copper and zinc has become crucial due to the increasing prices of these metals and environmental factors involved.

Keywords: Recovery, slag, hydrometallurgy, zinc oxide, copper.

1. Introduction

Copper and its alloys are widely used in industry. They consist of brass, bronze, and copper metallic. Copper alloys are highly suited to recycling. Around 40% of the annual consumption of copper alloys is derived from recycled copper materials. Brasses are alloys made from copper and zinc. They exhibit good strength and ductility and are easily cold worked. Their properties are improved with increased zinc content up to 35% [1]. During the remelting and casting processes, the molten metals are oxidized and collected with flux to form brass smelter slag. It contains copper, zinc, and other metals in various quantities.

The most abundant metal present in the slag is zinc, but there is also a lot of copper present in the brass smelter slag, and copper has a high value, so it is possible to recover both zinc and copper at the same time.

From brass smelter slag [1,2], copper and zinc are separately recovered. Brass smelters make an important raw material for refining zinc and copper. Compared to copper smelters, they are also better for the environment, save energy, protect natural resources, contribute to the economy, and make less waste.

In Vietnam, there are many traditional copper casting craft villages that produce brass from North to South. One ton of brass produces 30 to 50 kg of slag [2]. The smelter slag of brass is a solid waste material such as zinc, copper, lead, chromium, etc. [2-4]. The traditional copper casting village produces a large amount of brass smelters in different regions, so the waste is often discharged directly to the spoil area or sold to waste treatment units to collect, which causes environmental harm, waste of resources and economic harm.

Dai Bai Village, in Bac Ninh province, is well-known for its over 1000-year-old copper casting tradition. There is a large amount of brass smelter slag. It is more than 400 tons per year [2].

Recently, recycling of metal from slag is continuously carried out in Vietnam and also in the world [2-11]. However, to effectively solve both economic and environmental problems, it is necessary to study the recycling of metal from slag. The processing technologies can be divided into two types: the first one is hydrometallurgy [3-11] and the other one is pyrometallurgy [11]. Ayfer K. *et al*. investigated recovering zinc and copper from brass ash and flue in a brass manufacturing plant in Turkey by combined pyro-hydrometallurgy [4]. Copper recovery from leach residue of brass ash by melting without flux and using various flux mixtures including CaO, NaCl, and

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$Na_2B_4O_7.10H_2O$. Zn is recovered by electrolysis of the solution after leaching brass ash and flue with H_2SO_4 and reducing Cu. Cu and Zn recovered with more than 99.5% purity. Zhimei X. *et al*. treated smelting slag of waste brass in a $ZnCl_2$-NH_4Cl solution system, the extraction percentages of zinc and copper were 88.37% and 90.85%, respectively [5]. Basir *et al.* developed a hydrometallurgical process for the recovery of copper, zinc, and lead from brass melting slag by applying sulfuric acid, hydrochloric acid, and ammonium hydroxide leaching processes in the presence of hydrogen peroxide as the oxidant [6]. Ahmed I.M *et al*. leached and recovered zinc and copper from brass slag by sulfuric acid and found that the zinc extraction was fast and increased with sulphuric acid concentration [9], where the percent recovery amounts to 95% and 99% for zinc and copper, respectively. Bahaa S. M. *et al*. investigated the recovery of copper from slag containing 11.4% copper [11]. The slag was leached in diluted sulfuric acid, and the copper was precipitated from the leaching solution by zinc powder, yielding a purity of 99.20%.

Pyrometallurgical processing aims to reduce the slag by carbon and collect the zinc as a vapor. The zinc in the vapor can be oxidized to produce zinc oxide. However, pyrometallurgy requires high energy consumption, which requires high-grade raw materials on a large scale. Hydrometallurgical methods are now much more popular than others for getting zinc out of copper slag.

In this study, the recovery of zinc oxide and copper metal was investigated from brass smelter slag by using the hydrometallurgy process.

2. Experimental Procedure

2.1. Materials

Raw material was used by the Brass Smelter Slag from Quang Giang Copper Casting Company (Bacninh Province) as shown in Fig. 1. The X-ray diffraction (XRD-Bruker D8-Advance) analysis of the brass smelter slag concentrate (Fig. 2) indicates that the main compositions are ZnO and CuO, Al_2O_3, $ZnAl_2O_4$. The chemical composition of brass smelter slag was analyzed by X-ray Fluorescence (XRF-Viet Space 5008P) as shown in Table 1 and Fig. 3. Many elements were present in smaller amounts (Al, Mn, Si, etc.) with a concentrate containing 71.8% ZnO and 10.32% CuO, for example.

Fig. 1. Brass smelter slag used in this study.

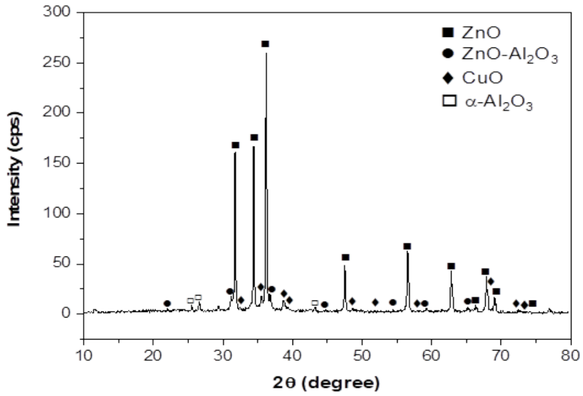

Fig. 2. X-Ray Diffraction pattern of Brass smelter slag.

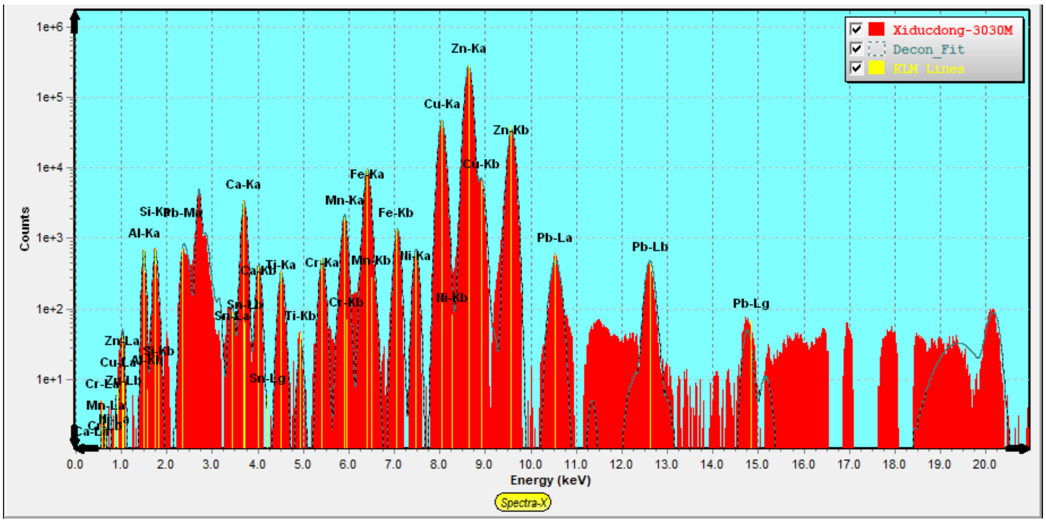

Fig. 3. X-ray Fluorescence spectrum of Brass smelter slag

Table 1. A mineralogical composition of the Brass smelter slag characterized by XRF.

Compounds	(wt.%)
ZnO	71.8
CuO	10.32
Fe_3O_4	3.17
MnO	2.38
CaO	1.94
Al_2O_3	7.34
SiO_2	2.28
Other	0.27

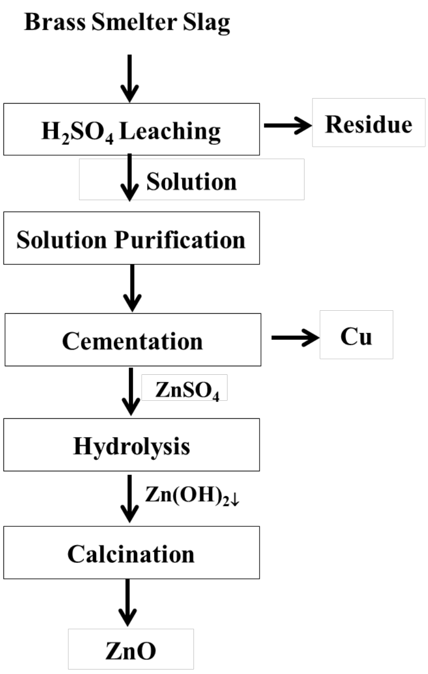

Fig. 4. Experimental procedure

2.2. Methods

The zinc and copper recycled from brass smelter slag by hydrometallurgy process as show in Fig. 4.

Leaching experiments to recover zinc and copper

Leaching of brass smelter slag was performed in order to dissolve zinc and copper into solution by the H_2SO_4 acid. In order to determine the optimum extraction conditions, leaching conditions such as H_2SO_4 acid concentration, temperature, and time have been investigated. The efficiency of Zn and Cu extraction was evaluated by these containing in residue. The residue was washed and dry, it continuously treatment by HNO_3 and HCl mixing to convert Zn and Cu to Zn^{2+} and Cu^{2+}. These ions were determined by EDTA complexometric titration in pH value matching.

Efficiency of extraction of metals was determined following the equation:

$$\eta = \frac{m_{Me\,slag} - m_{Me\,residue}}{m_{Me\,slag}} \times 100\% \qquad (1)$$

- η: Efficiency of extraction of metals (Zn, Cu, Fe) (%)
- $m_{\mathrm{Me\ slag}}$: Mass of metals in slag (Zn, Cu, Fe) (g)
- $m_{\mathrm{Me\ residue}}$: Mass of metals in residue (Zn, Cu, Fe) (g)

The leaching experiments were done in a glass reactor with a Teflon-covered mechanical stirrer, and the reactor was placed in a water bath controlled by a thermostat. The brass smelter slag was leached in an H_2SO_4 solution with a liquid to solid mass ratio of 1:5. The efficiency of the leaching process was investigated by effect of H_2SO_4 concentration (125 ÷ 225 g/L). temperature (40 ÷ 70 ºC) and time (30 ÷ 90 min).

Solution purification

The leaching solution was purified by removing iron impurity, Fe^{2+} was oxidized to Fe^{3+} by adding H_2O_2. Acid residues have been used for neutral leach iron by precipitating ferric hydroxide $Fe(OH)_3$.

Cementation

Cementation experiments were carried out by adding zinc powder into the solution in a 500-mL beaker, using a heater magnetic stirrer at temperature 60 ºC with 350 rpm stirring speed. After filtration, the concentrations of metals in cementation solution were determined by analytical chemical method.

The leaching solution removed impurities by control the pH value. The solution was continuously cemented by zinc metal to obtain copper metal.

Conversion of zinc to hydroxide by using ammonia

The $ZnSO_4$ solution was hydrolyzed by addding gradually NH_3 to modify the pH value to 8, the solution was kept at pH = 8 at room temperature for 30 min to form $Zn(OH)_2$ precipitation.

The $Zn(OH)_2$ precipitate was separated from a solution by filtration and wash, then calcinated at 600 ºC for 120 minutes to obtain ZnO.

The chemical composition and phase components of production were determined by X-ray Fluorescence (XRF- Viet Space 5008P) and X-ray diffraction (XRD), respectively. Microstructural were examined by optical microscopy (OM-Keyence VHX-700).

3. Results and Discussion

3.1. Leaching of Brass Smelter Slag

The brass smelter slag was leached in H_2SO_4 solution as following the reactions:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O \quad (1)$$

$$CuO + H_2SO_4 = CuSO_4 + H_2O \quad (2)$$

$$Al_2O_3 + H_2SO_4 = Al_2(SO_4)_3 + H_2O \quad (3)$$

$$H_2SO_4 + SiO_2 = H_2O + Si(SO_4)_2 \quad (4)$$

$$Fe_2O_3 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O \quad (5)$$

$$MnO + H_2SO_4 = MnSO_4 + H_2O \quad (6)$$

$$CaO + H_2SO_4 = H_2O + CaSO_4 \quad (7)$$

Effect H_2SO_4 concentration

The leaching parameter of brass smelter slag was selected at 50 ºC for 90 min with various sulphuric acid concentrations of 125, 150, 175, 200, and 225 g/L as shown in Table 2 and Fig. 5. Copper and zinc dissolution increased as the H_2SO_4 concentration increased from 125 to 175 g/L. The extraction percentage of Zn changed from 67.82% to 80.26% and the value of Cu from 45.76% to 81.71%. The extraction percentage of zinc was kept constant at a higher concentration, while the extraction percentage of copper was 90% at 225 g/L H_2SO_4. Ahmed *et al.* also studied the leaching of copper and zinc in brass slag. The extraction of copper and zinc increased with H_2SO_4 and then decreased with a further increase in time. The same result was obtained in the study of Ahmed I. M *et al.* [9].

This result can be explained that the Zn content in brass smelter slag consists of ZnO and another compound of $ZnO.Al_2O_3$ (Fig. 2). The $ZnO.Al_2O_3$ composition was negligible dissolved in H_2SO_4 meanwhile leaching efficiency of Cu increased at higher H_2SO_4 content. However, solution viscosity increased at higher acid concentration. reflecting difficult to filler sludge [10]. The H_2SO_4 concentration was used at 175 g/L for the next studies.

Table 2. Effect of H_2SO_4 concentration on extraction percentage

C_{H2SO4} (g/L))	η_{Zn} (%)	η_{Cu} (%)
125	67.82	45.76
150	69.13	58.83
175	80.26	81.71
200	80.91	82.12
225	81.80	88.20

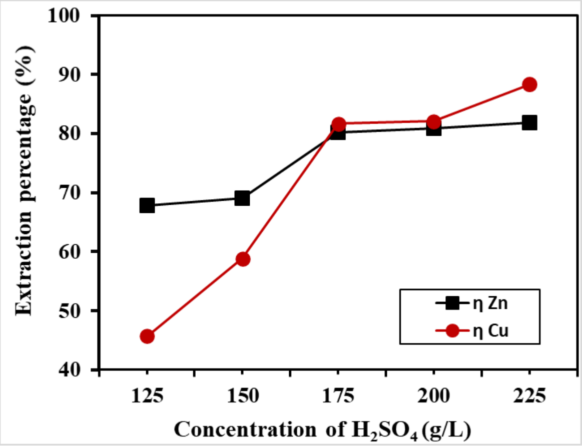

Fig. 5. Variation of the extraction percentage of zinc and copper from brass smelter slag with the H_2SO_4 concentration

Effect of leaching temperature

At the leaching condition of 175 g/LH_2SO_4 and 90 min, the temperature was predetermined as 25, 40, 50, 60 and 70 ºC. The results were shown in Table 3 and Fig. 6. The content of the extracted zinc and copper increased with the increasing temperature because diffusion of molecular was faster. The leaching was more efficient and increased in high temperatures [4].

Table 3. Effect of leaching temperature on extraction percentage

Temperature (°C)	η_{Zn} (%)	η_{Cu} (%)
30	65.21	58.83
40	73.04	71.91
50	80.26	81.71
60	80.26	83.52
70	81.56	91.79

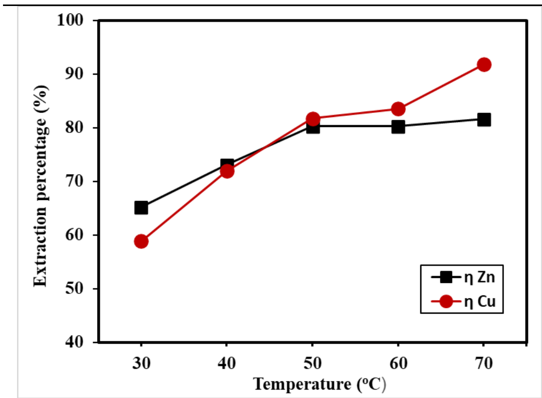

Fig. 6. Extraction percentage of zinc and copper from brass smelter slag under variable leaching temperature

The leaching efficiency of Cu and Zn were observed as 81.71% and 80.26% respectively at 50 ºC. The leaching efficiency of Cu increased up to 91.79% while that of Zn was negligible at higher leaching temperature. Higher temperature increases exothermic of Zn leaching reaction. The zinc was lost due to possible polymerization and hydrolysis at a leaching temperature of about 70 ºC [9]. Therefore, the leaching temperature of 50 ºC was chosen in this study.

Effect of leaching time

Experiments were done with H_2SO_4 with a concentration of 175 g/L at 50 ºC and different leaching times, such as 30, 60, 90, and 120 minutes, to see how leaching time affected the amount of zinc and copper that was extracted.

As shown in Table 4 and Fig. 7, the extraction percentage of zinc and copper increased with the leaching time. The extraction percentage of zinc increased from 74.34% to 80.26% while that of copper increased from 65.37% to 81.71%. However, the extraction percentage of zinc and copper have slightly increased with the time. At long leaching time, high amount of iron and silica which were difficulty extracted dissolved [10]. The time was chosen 90 min for leaching process.

Table 4. Effect of leaching time on extraction percentage

Time (min)	η_{Zn} (%)	η_{Cu} (%)
30	74.34	65.37
60	76.95	78.44
90	80.26	81.71
120	81.56	83.02

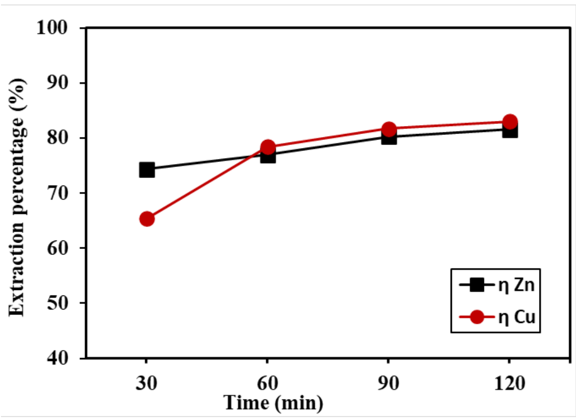

Fig. 7. Extraction percentage of zinc and copper from brass slag under variable leaching time

Table 5. Leaching solution concentration (g/L)

Concentration (g/L)		
Zn	Cu	Fe
71.8	10.23	3.17

Based on the result of leaching effect on extraction percentage of zinc and copper from Brass slag, the optimum leaching parameter was determined as the H_2SO_4 concentration of 175 g/L, temperature of 50 ºC and 90 min. In this leaching condition, the extraction of zinc and copper are 80.26% and 81.71%, respectively. Concentrations of some metals in the leached solution was shown in Table 5.

3.2 Removal of Impurity in Leached Solution

In the leaching process, other impurities were also dissolved in H_2SO_4 solution. Depending on the composition of raw materials and leaching conditions, the impurities dissolve in solution with different contents. Zinc solution consists of some impurities such as copper, lead, iron, manganese, alkaline metal, etc., which exist in sulfate salts. To obtain a high purity of zinc oxide, the solution must remove impurities before the hydrolysis process. The solution can be purified by the following methods:

pH modification

Metal hydroxide soluble in water as flowing reaction

$$Me^{n+} + nOH^- = Me(OH)_n \quad (8)$$

At much lower pH values compared to the relative solubilities of metal hydroxides as a function of pH, the metal hydroxides can be present at much higher concentrations at lower pH values [12]. In other words, metal hydroxides are more soluble under acidic conditions. This makes sense when we consider Le Chatelier's law: at low pH values, hydroxide ions (one of the products of the dissolution reaction) are very scarce in solution. So, the dissolution equilibrium should want to shift to the right towards the products of hydroxide and the dissolved metal ion. A second observation at a given pH, trivalent metal ions (aluminum and ferric iron) are less soluble than divalent metal ions.

The Zn^{2+} content in 1M solution is 65 g/L, zinc precipitated to form hydroxide at pH value of 5.9. When pH was adjusted within the range of 5.2 and 5.4, the iron and other impurities (Al, Ca, etc..) would be also reduced depending on these concentrations. However, almost of Zn did not precipitate under that pH level

The iron in leaching solution exists as Fe^{2+}, the value of pH for Fe^{2+} ion hydrolyzed at 6.7, the Zn^{2+} is also hydrolyzed with Fe^{2+} at that pH value. To avoid the loss of zinc in removal of iron impurity process, the iron has to oxidize to change from Fe^{2+} to Fe^{3+} and then ferric ions can be hydrolyzed and precipitated as ferric hydroxide at the pH of 1.6. The leaching solution can oxidize Fe^{2+} ions to Fe^{3+} ions by strong oxidizing agents such as H_2O_2, MnO_2, $KMnO_4$.

The goal of this process is to remove Fe and other impurities like Mn, Al, etc… in solution.

$$2Fe^{2+} + H_2O_2 + 2H^+ = 2Fe^{3+} + 2H_2O \quad (9)$$

$$Fe^{3+} + 3OH^- = Fe(OH)_3\downarrow \quad (10)$$

When pH value of the leaching solution was 1, the H_2O_2 was added for oxidation of Fe^{2+} to Fe^{3+} ion as reaction (9). After that, pH value of the solution was modified for occurrence of reaction (10).

Table 6 identified that the solution has a small amount of Fe at pH value from 4 to 4.5. At pH value of 5, most of Fe was removed on solution. However, the high pH value indicated that the concentration of Zn and Cu decreased following Fe precipitation. The pH value was chosen as 5.0 for removing Fe.

Table 6. Solution concentration after pH modification

Metal (g/L)	pH value			
	4.0	4.5	5	5.5
Zn	68.02	66.52	65.00	54.72
Cu	10.92	10.85	10.69	8.42
Fe	0.48	0.24	trace	trace

3.3 Recovery of Copper Metal

Depending on the Cu concentration in solution, the recovery of Cu can be processed differently by methods such as electrolysis, cementation, or ion extraction [2, 9, 11]. In this study, the cementation process was used to obtain Cu metal from purified solution by using Zn metal at 60 °C for 60 minutes. Purity of the Cu precipitate (Fig. 8) was 98.52 wt.% by analytical chemical method.

3.4 Recovery of ZnO

To recover the zinc, the purified solution was adjusted at pH 8 by addition of NH_3. When the pH of the solution was 8, the zinc was recovered as a precipitate of zinc hydroxide, $Zn(OH)_2$ according to the reaction:

$$Zn^{2+} + 2OH^- = Zn(OH)_2 \quad (11)$$

On other hand, zinc can be recycled with different compounds such as $ZnCO_3$ or $ZnSO_4$ [8, 9].

The $Zn(OH)_2$ precipitate was calcinated at 600 °C for 120 min to obtain ZnO powder as shown in Fig. 9. The phase compositions of final sample were confirmed by XRD analysis (Fig. 10). According to XRD patterns, the final product was confirmed in the form of zinc oxides.

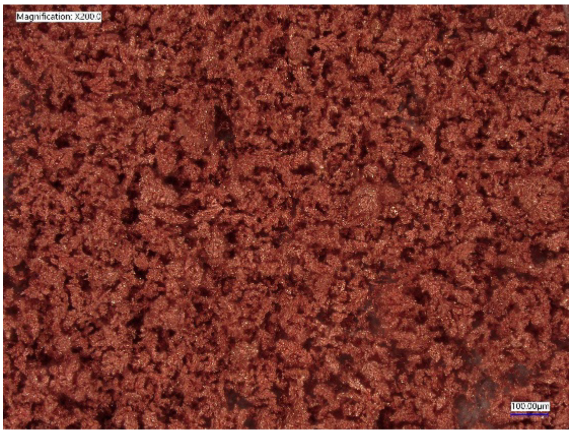

Fig. 8. Optical microscopy image of copper metal recycled from solution

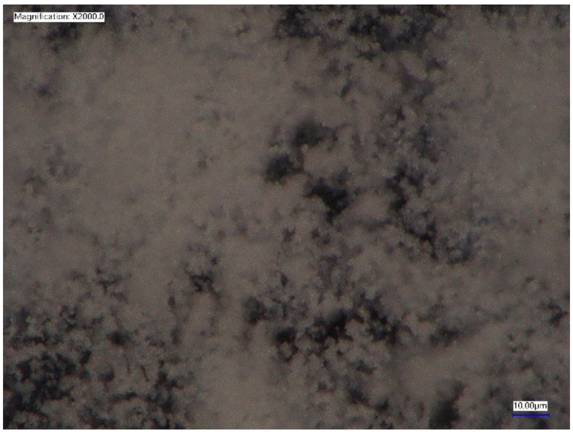

Fig. 9. Optical microscopy image of ZnO powder after calcination at 600 °C

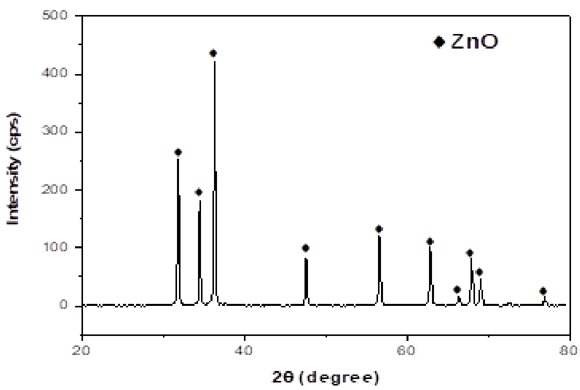

Fig. 10. XRD patterns of ZnO powder

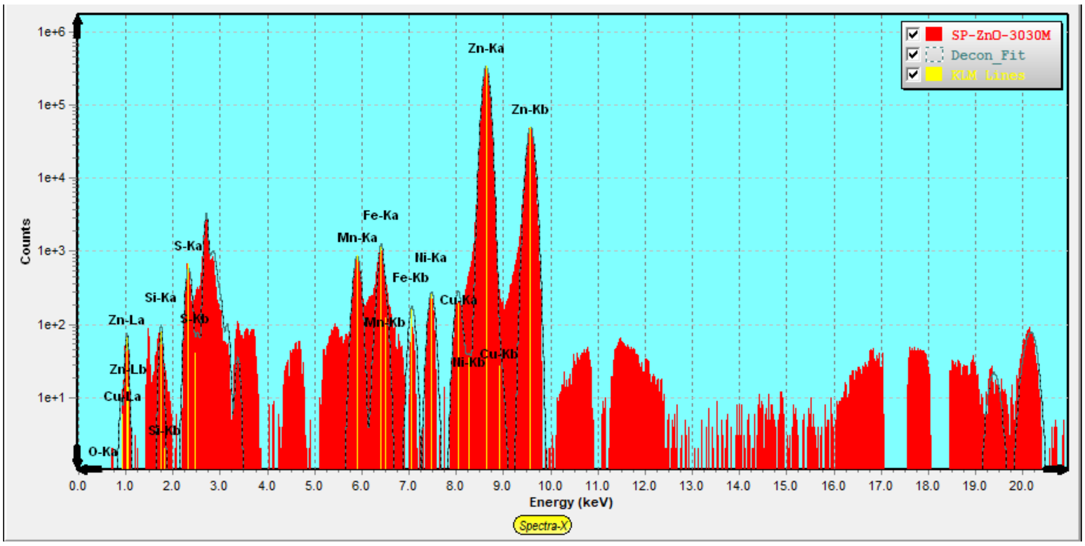

Fig. 11. X-ray Fluorescence spectrum of ZnO powder

Table 7. Composition of ZnO powder characterized by XRF

Composition	ZnO	SO_3	MnO	CuO	Other
(wt. %)	98.65	0.50	0.25	0.06	0.54

The composition of ZnO powder was analyzed by XRF as shown in Table 7 and Fig. 11. The XRF result of ZnO powder was shown in the names and quantitative of elements of different elements which were mostly Zn, O.

4. Conclusion

This study was successfully investigated for the purpose of recovering the final of ZnO (98.65 wt.%) and Cu (98.52 wt.%) from brass smelter slag (71.8 wt.% ZnO and 10.32 wt.% CuO) by the hydrometallurgy process. The extraction percentage of zinc and copper were found to be 80.26% and 81.71% when brass smelter slag was leached in H_2SO_4 solution with 175 g/L at 50 °C for 90 min. The leaching solution was purified to recover copper metal by cementation, and zinc oxide was obtained with high purity. Thus, not only does the brass smelting slag recover high-grade ZnO and Cu, but it also helps to protect the environment by eliminating contaminants and conserving resources, time, and energy.

Acknowledgements

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References

[1] M. L. Free. - Hydrometallurgy Fundamentals and Applications. Springer. 1995. pp. 65-80.

[2] Nguyen H. Q.. Đo H. N.. Kieu Q. P., Recycling of copper from brass slag by hydrometallurgy, Conference on Environmental Protection in Mining Industry and Using of Coal. Minerals and Petroleum.1/2/ 2020.

[3] Chadalavada T. Divya A. N. Dumpa V., Performance of copper slage as replacement of fine aggregate with differect grades. J. Crit. Rev. Vol 7, pp. 731-735, 2020. http://dx.doi.org/10.31838/jcr.07.09.141.

[4] Ayfer K. and Muhlis N. S., Treatment of industrial brass wastes for the recovery of copper and zinc. Sep. Sci. Technol. Vol. 50, pp. 286-291, 2015. https://doi.org/10.1080/01496395.2014.952304.

[5] Zhimei X., Xiaosa Z., Xinglong H. Shenghai Y., Yongming C., Longgang Y., Hydrometallurgical stepwise recovery of copper and zinc from smelter slag of waste brass in ammonium chloride solution. Hydrometallurgy Vol. 197, pp. 105475, 2020. https://doi.org/10.1016/j.hydromet.2020.105475.

[6] Basir S.M. A., Mahmoud A. R., Hydrometallurgical recovery of metal values from brass smelter slag. Hydrometallurgy Vol. 53, pp. 31-44, 1999. https://doi.org/10.1016/S0304-386X(99)00030-4.

[7] A. Kilicarslan. M. N. Saridede. S. Stopic. B. Friedrich, Recovery of copper and zinc from brass wastes via ionic liquid leach. Proceedings of EMC. Vol 3. Germany pp. 1167 - 1171, 2013.

[8] Rashid K. N., Lyazzat A. M., Copper smelter slag leaching by using H_2SO_4 in the presence of dichromate. J. Chem. Technol. Metall. Vol. 54, pp. 657-662, 2019.

[9] Ahmed I.M.. Nayl A.A.. Daoud J.A., Leaching and recovery of zinc and copper from brass slag by sulfuric acid. J. Saudi Chem. Soc. Vol. 20, pp. S280-S285, 2016. https://doi.org/10.1016/j.jscs.2012.11.003

[10] Júlia M. M.. Alexandre S. G.. Achilles J. B.D.. Marcelo B.M., Hydrometallurgical separation of zinc

and copper from waste brass ashes using solvent extraction with D2EHPA. J. Mater. Res. Technol. Vol. 9**,** pp. 2319-2330, 2020. https://doi.org/10.1016/j.jmrt.2019.12.063.

[11] Bahaa S. M. and Asaad H. L, Recovery of copper from copper slag by hydrometallurgy method, from iraqi factories waste, Journal of University of Babylon for Pure and Applied Sciences, Vol. 26, No.7, pp. 179-199, 2018.

[12] J. Monhemius, Precipitation diagrams for metal hydroxides, sulphides, arsenates and phosphates, Transactions Institution of Mining & Metallurgy, 86, pp. C202-C206, 1977.