

GOLD RECOVERY FROM FLOTATION CONCENTRATE FROM GOLD MINE TAILINGS USING DISSOLVE SMELTING

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Abstract

Gold flotation concentrate may contain relatively high concentrations of valuable metals such as iron, copper, and zinc, and occasionally, even precious metals such as gold. The major components of the concentrate are SiO₂, Fe₂O₃, and Al₂O₃, but it also contains reactive sulphide minerals such as pyrite. The sulphides in the flotation concentrate are fully converted into an oxide form during oxidative roasting, therefore, the chemical composition of the roasted concentrate is considered to be a copper slag. High temperature smelting with additives to dissolve Au from the gold concentrate into a molten copper was used in the research. Gold greatly dissolved at 1600°C under a CaO/SiO₂ ratio of 1.25, suggesting the increase in the dissolution of gold into molten copper with decreasing viscosity of the molten slag-like concentrate at high temperatures.

Keywords: Gold; Flotation concentrate; Dissolve smelting; Viscosity

1. Introduction

Gold has been considered a precious metal since ancient times; it has been widely used for commercial exchanges and savings, for making jewelry and, more recently, in medicine, communication, electronics, and other fields. Gold also backs the currencies of many countries around the world. The Republic of Korea launched domestic gold production approximately 20 years ago [1]. According to the national mining statistics, about 240 kg of gold was produced from then to 2012, another 413 kg in 2013 and 284 kg in 2014. About 96% of the gold produced in the Republic of Korea was mined in Jeonnam Province, in the southwest of the country [2-4], and it is mainly recovered from gold ore by conventional cyanidation, during which the ore is crushed, finely ground, and cyanide-leached in a series of agitated tanks to solubilize the gold and carbon adsorbs. However, cyanide leaching can be too expensive, since it consumes high amounts of strong acids or cyanides, and is also highly toxic [5].

Gold mining produces great amounts of gold mine tailings: 100 tons are produced daily just in the Republic of Korea [6]. Gold mine tailings may contain relatively high concentrations of valuable metals such as iron, copper, and zinc, and occasionally, even precious metals such as gold and

silver, which are contained in minerals, and native metals that have not been separated by froth flotation process.

In recent years, researchers in Korea had paid special attention to the recycling of the gold tailings, and they developed several technologies for the recovery of gold from tailings using flotation and cyanidation, which combined process that including flotation. Flotation is appropriate for processing the gold-bearing sulphide raw material, which is fine and floatable, and gold content is enriched to sulphide mineral, which is used as a flotation concentrate. It is well known that iron sulphide minerals used as a flotation concentrate, such as arsenopyrite, pyrite, and pyrrhotite are host minerals for native gold, as well as 'invisible gold' [7]. The conventional cyanidation process and flotation process are widely used for gold recovery from gold ore and gold mine tailings. The cyanide leaching of the tailing may be too expensive because it requires high consumption of strong acid or cyanide, and it is very toxic. Also, the recovery of gold from leach solutions have been processed by various methods as the cementation, carbon adsorption, electrowinning, and ion solvent extraction [8].

Currently, the gold mining company in Jeonnam Province, Korea, is producing abundant quantity of tailings that have affected the landscape and caused

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pollution in the area. South Korea has been already supporting the recycling of the solid wastes, and trying to find innovative methods of utilizing solid waste management. Therefore, there is a significant need for developing other ways of reuse and commercially apply mine tailings in order to minimize the disposal costs and the impact on the environment.

Therefore, the aim of this study is to find some eco-friendly way to recover Au from gold mine tailings by dissolving into molten copper at high temperatures with changing the chemical composition of the molten concentrate, such as metallurgical slag. The pure copper containing gold is considered like-blisters copper, which is cast into anodes ready for electrolytic refining. Consequently, the gold can be separated from pure copper during electrolytic refining. It is thus possible that the regenerated concentrate slag can be completely recycled for iron recovery and value added products such as abrasive blasting, roofing granules, concrete, and other materials [9-12]. The sulphides in the flotation concentrate are fully converted to an oxide form during oxidative roasting, hence the chemical composition of the roasted concentrate can be considered as a copper slag. Recovery of pig iron containing copper from copper smelting slag by reduction smelting was also recently examined, and successfully performed, and produced the pig iron [9-11].

The flotation concentrate from gold mining tailings in Jeonnam Province was used in this research. The experiments included the desulphurization roasting and dissolution of Au in the concentrate into molten copper at high temperatures.

2. Experimental

2.1 Materials

Samples of flotation concentrate from gold tailings provided by EGM company in Jeonnam Province was used in this study. Since the tailings were already milled down to 70 μm , they were easily excavated and processed. The mineralogical composition of the flotation concentrate was determined by X-ray fluorescence (XRF), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), and X-ray diffraction analysis, which were performed at the Department of Metallurgical Engineering at the Pukyong National University (Republic of Korea); the results are shown in Table 1 and Figs. 1 and 2. As shown in Table 1, the mass fractions of SiO_2 , Fe_2O_3 , and Al_2O_3 in the flotation concentrate from gold tailings were about 37%, 34%, and 4%, respectively. The results of SEM-EDS analysis on the particle of the flotation concentrate indicated that main

constituent elements of the flotation concentrate were found to be Fe, S, and Si, which were present with 41.06 wt.%, 7.11 wt.%, and 15.34 wt.%, respectively, as shown in Fig. 1. In addition, Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to evaluate the Au content in the samples, where Au content in the flotation concentrate was found to be 110 ppm. The result of the XRD analysis showed that the main crystal phases in the flotation concentrate from gold tailings were quartz (SiO_2), hematite, and pyrite (FeS_2) as shown in Fig. 2.

Table 1. Chemical composition of the flotation concentrate from gold tailings by XRF and ICP analysis

Element	SiO_2	Fe_2O_3	SO_3	Al_2O_3	K_2O	ZnO	CaO	P_2O_5	Au, ppm
Weight %	37.49	34.26	21.13	4.20	1.47	0.90	0.35	0.20	110

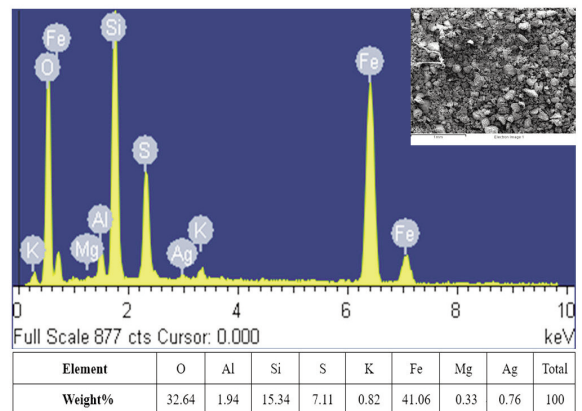


Figure 1. EDS pattern and chemical composition of the flotation concentrate from gold tailings

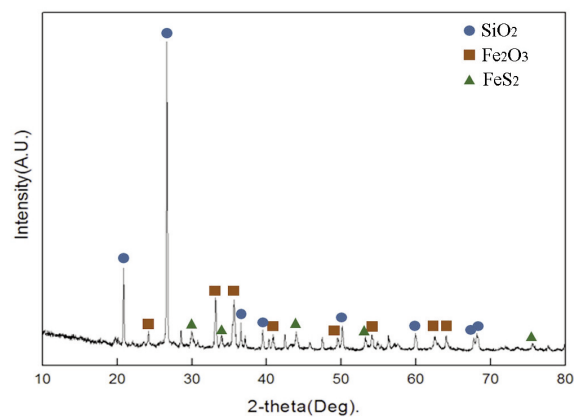


Figure 2. XRD pattern of flotation concentrate from gold tailings

2.2 Experimental Apparatus

The experiments on dissolution of gold in the flotation concentrate from tailings into molten copper were performed using a high-frequency induction

furnace consisting of a cooler, a controller, and a heater box. The controller regulated the heating temperature by adjusting the voltage. The installation space was small, and the additional equipment, including a dust collector, was miniaturized to reduce operational difficulties and costs. Fig. 3 shows the schematic diagram of a heater box, where the high-frequency induction is generated; it provides enclosed equipment and eliminates dust and flue gas from the furnace. Argon gas was charged into the heater box to maintain an inert atmosphere. An alumina crucible was chosen to prevent chemical reactions with the flotation concentrate during the experiments. Electricity was conducted and $\phi 26$ alumina crucible was placed inside it by using the $\phi 45$ graphite crucible by necessary thermo-generator. The crucibles were placed in the heater box, and the temperature was measured using a thermocouple.

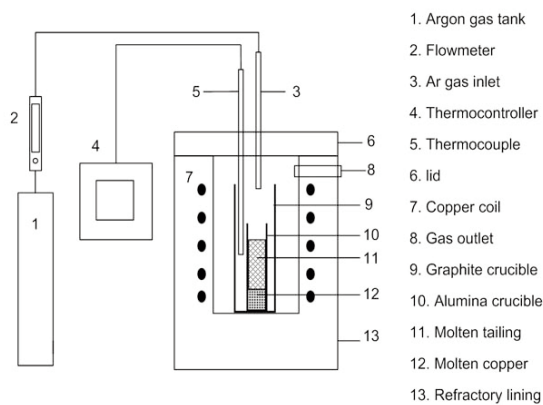


Figure 3. Schematic diagram of an experimental apparatus for Au recovery from flotation concentrate

2.3 Experimental Procedure

The two following experiments were conducted to investigate the possibility of recovering Au from flotation concentrate from the tailings.

Desulphurization roasting of the flotation concentrate: Roasting involves a thermal gas-solid reaction during which sulphides are oxidised to SO_2 gas at high temperature between 500°C and 700°C . As mentioned before, flotation concentrate from the tailings contain high amounts of sulphur. As a consequence, during the smelting process, molten (Fe, Cu) S matte are formed between the molten copper and the flotation concentrate, preventing the dissolution of Au from the latter into the former. Therefore, the samples were roasted at 700°C for 5–7 h in air atmosphere.

Table 2. Chemical composition of flotation concentrate from gold tailings after roasting by XRF

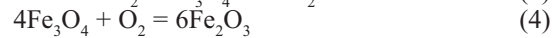
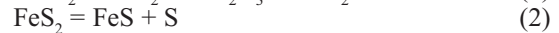
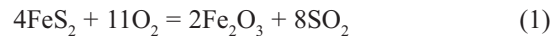
Element	SiO_2	Fe_2O_3	SO_3	Al_2O_3	K_2O	ZnO	CaO	P_2O_5	CuO	PbO	TiO_2	Cr_2O_3
Weight %	33.10	54.33	4.97	3.22	1.20	1.35	0.26	0.14	0.65	0.40	0.23	0.11

Dissolution of Au into molten copper at high temperatures: Au was recovered from flotation concentrate from the tailings by smelting at high temperatures, thus changing their chemical composition. The tailings samples were mixed with pure copper at a ratio of 5:10 (for a total quantity of 150 g), and the mixture was placed in the alumina crucible. Then, the smelting sequence was as follows: 120 min at 1250°C , 20 min at 1400°C and, finally, 30 min at 1400°C , 1500°C , and 1600°C . Additives were used in the smelting experiment to change the chemical composition of the gold flotation concentrate: CaO was added at a CaO/SiO_2 ratio of 1.0–1.25 at 1600°C .

3. Consideration and results

3.1 Desulphurization roasting of the gold flotation concentrate

The gold, which occurs in association with pyrite, is hardly extracted by cyanide leaching. Therefore, several technologies for the recovery of gold include flotation of a sulphide concentrate, and roasting at 500 to 700°C [13-16]. The roasting liberates the gold, making it more amenable to dissolution in the molten copper, and produces sulphur dioxide and trioxide. The roasting of sulphide is a complex reaction, and several components are formed during the process. The main chemical reactions are:



During the roasting, toxic gas SO_2 is produced, which causes serious pollution to the environment. This treatment still involves the production of sulphuric acid.

The roasting experiments on the removal of sulphur from the flotation concentrate were conducted at high temperature of 700°C for 5 to 7 h in air. Higher temperature of 700°C and sufficient time for 7 hours were required for the almost-complete removal of sulphur. The results of roasting are presented in Table 2 and Fig. 4. Table 2 shows the chemical composition of the gold flotation concentrate after roasting as determined by the X-ray Fluorescence, and it has low content trioxide sulphur of 4.97 wt.%. As shown in Table 3, it was found that the amount of main component such as Fe_2O_3 was increased.

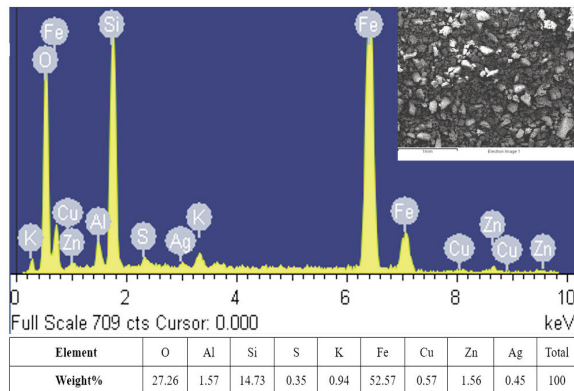


Figure 4. EDS pattern and chemical composition of the flotation concentrate from gold tailings after roasting

Fig. 4 shows EDS results of the chemical composition of the flotation concentrate after roasting. The main constituent elements were measured as flotation concentrate's components of Fe, Si, and Al. As shown in Fig. 4, the S content in the sample was decreased from 7.11 to 0.35 wt.% according to the increasing time at 700°C. Then, chemical components of flotation concentrate after roasting were obtained by XRD analysis. As shown in Fig. 5, quartz, hematite phases and zinc ferrite ($ZnFe_2O_4$) are presented in the samples. It indicates that pyrite (FeS_2) completely changed into oxide form. To summarize, the sulphur was greatly removed from flotation concentrate from tailings and new oxide phase of zinc ferrite was formed during the roasting.

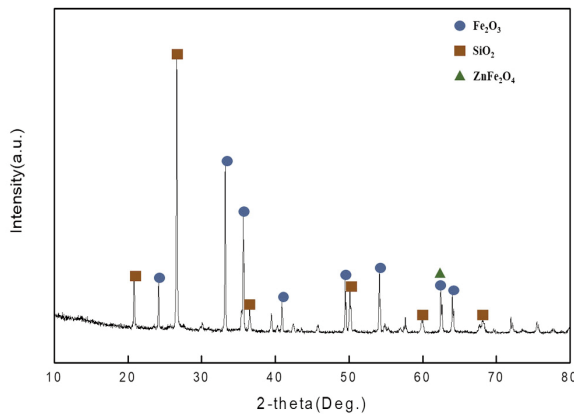


Figure 5. XRD pattern of flotation concentrate from gold tailings after roasting

3.2 Dissolution of Au in molten copper at high temperatures

In the dissolution experiment, the recovery of Au from the flotation concentrate from tailings was examined by dissolve smelting based on the no

reaction at high temperatures of 1400°C, 1500°C, and 1600°C, and changing the chemical composition of the gold concentrate with CaO additives in order to form a metallurgical slag with low viscosity.

Electric induction furnace is a type of melting furnace that uses electric current to melt the metal. The basic mechanism of induction heating is represented by alternating current that is produced in a coil by applying alternating voltage. The alternating current produces magnetic field around the coil, which has eddy currents with a same frequency, and opposite direction than coil currents. The induced eddy currents in the workplace generate heat in a thin surface layer, called skin depth, by ohmic or Joule effect [17]. The eddy currents can also be used to stir the hot metal, which is useful in ensuring that molten gold concentrate, such as metallurgical slag is in full contact with the molten copper on the surface. The circulation of the molten copper with opposite circulation of the molten gold concentrate might have a good effect on dissolving Au from molten concentrate into molten copper. In this case, the viscosity of the concentrate slag is required to be more low value to flow and related to the surface friction within the fluids. A schematic of the eddy currents induced in the induction furnace is shown in Fig. 6.

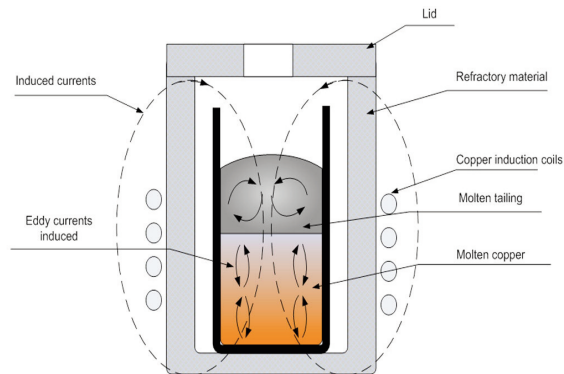
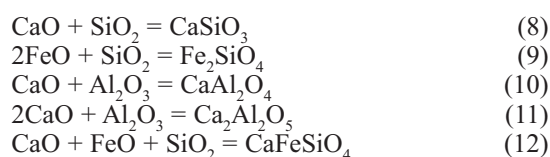


Figure 6. Schematic diagram of an induction furnace showing circulation between molten copper and gold concentrate

During the smelting process, the residual sulphur in the concentrate can be oxidized with the atmospheric oxygen, thus copper is also oxidized at the border between molten copper and concentrate slag, where it forms a copper oxide that may be successively lost to the molten slag, according to the following oxidation reaction:



The chemical reactions between the major oxides in the gold concentrate, such as FeO , SiO_2 , CaO , Al_2O_3 , and Fe_2O_3 , form the following molecular compounds:



The experiments were conducted at temperatures up to 1600°C, and the thermodynamic analysis of these chemical reactions was performed using HSC Chemistry 5 software, which confirmed that CaO•SiO₂ and 2FeO•SiO₂ were the main molecular compounds, and that SiO₂ and the oxides are constituents of the molten concentrate as the metallurgical slag for the dissolve smelting. Table 3 shows changes of Gibbs free-energy in the chemical reactions between the major oxides in the flotation concentrate.

Viscosity is the most important physiochemical property of metallurgical slag, as it plays an important role in chemical reactions and mass transfer during smelting process. It greatly depends on the temperature and internal structure of the slag, which viscosity of any slag composition decreases with the increase in temperature. Therefore, experiment was examined at high temperature. At first, when the temperature of experiment was based on no reaction at high temperature smelting was performed at 1300°C, an area of intergranular agglomeration was observed, with no general smelting shape. At higher temperatures of 1400°C, 1500°C, and 1600°C, the gold concentrate was entirely smelted, and a slag shape was observed. Therefore, these were the temperatures selected for the next phase of the experiment, during which the gold in the molten concentrate dissolved well in the molten copper, reaching content of 30 ppm, at 1600°C. Thus, the recovery rate of Au also reached 54.5% when the experiment temperature was 1600°C. This result indicates that the dissolution of gold in molten copper

increases as the viscosity of the molten concentrate decreases at high temperatures. Fig. 7 shows effects of Au content in the copper and recovery rate for dissolve smelting.

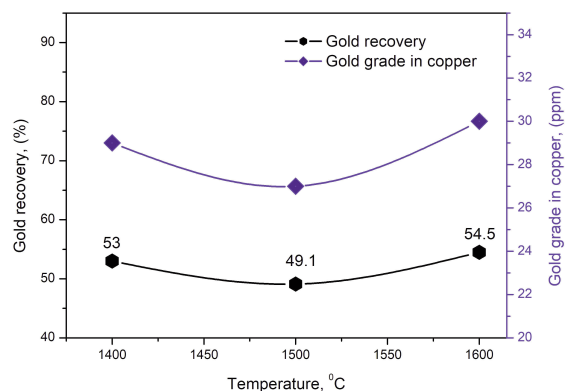


Figure 7. The effect of Au recovery on various temperatures

Since the amount of CaO in the gold mine tailings was quite low (the measured mass fraction was 0.35 wt.%), a reaction between SiO₂, FeO, and Fe₂O₃ occurred. The structure of the molten concentrate was considered according to the binary system FeO–SiO₂ and the ternary system FeO–Fe₂O₃–SiO₂, and it was found to be a 2FeO•SiO₂ + SiO₂ system, with a high melting point and viscosity [17]. In the case of CaO/SiO₂ ratio from 1.0 to 1.5, the structure of the concentrate slag was represented by the phase diagram of the ternary system CaO–Fe₂O₃–SiO₂ presenting the structure of a eutectic compound such as CaO•SiO₂ + 2CaO•Fe₂O₃ [18]. In the ternary system CaO–Fe₂O₃–SiO₂, the physical properties derived from the state diagram were confirmed by predicting the content of CaO, SiO₂, and Fe₂O₃ as the ternary system; the melting point associated with this composition was confirmed to be about 1300°C. The influence of the rising temperature of the slag

Table 3. Gibbs free-energy changes in the chemical reactions between the major oxides in flotation concentrate

Temperature, °C	CuO	3CaO•P ₂ O ₅	CaO•SiO ₂	2FeO•SiO ₂	2CaO•Al ₂ O ₃	CaO•FeO•SiO ₂	CaO•Al ₂ O ₃
700	-137.00	-694.706	-90.856	-23.303	-13.015	-14.92	-14.12
800	-120.24	-688.638	-90.898	-21.952	-13.191	5.857	-12.315
900	-103.64	-682.602	-90.802	-20.442	-13.423	28-maj	-9.979
1000	-87.187	-676.714	-90.732	-18.954	-13.717	52.722	-7.142
1100	-70.552	-671.069	-90.702	-17.522	-14.076	78.403	-3.827
1200	-52.382	-666.395	-90.715	-16.17	-14.503	105.449	-0.058
1300	-39.145	-662.62	-90.774	-14.925	-15.001	133.777	4.147
1400	-27.876	-659.046	-90.882	-13.134	-15.569	163.654	8.769
1500	-16.812	-655.652	-91.04	-9.233	-16.211	195.814	13.793
1600	-5.939	-652.416	-91.249	-5.483	-16.925	229.081	19.204



viscosity was confirmed by varying the experimental temperature.

The next factor of the experiment was changing the structure of the concentrate slag to decrease the viscosity and improve the dissolution of gold in the molten copper. The slag viscosity depends also on its basicity and the CaO/SiO_2 ratio. In the experiment, CaO/SiO_2 ratios of 1.0, 1.25, and 1.5 were used at a temperature of 1600°C .

The results of smelting combined with additives were as follows. The gold in the concentrate slag was dissolved into the molten copper, reaching the highest amount of 82 ppm by decreasing the viscosity at a CaO/SiO_2 ratio of 1.25, but by increasing this ratio to 1.5, the dissolved content was decreased down to 70 ppm, while the gold recovery rate was highest 74.5%. The results of Au recovery in each CaO/SiO_2 ratio is shown in Fig. 8.

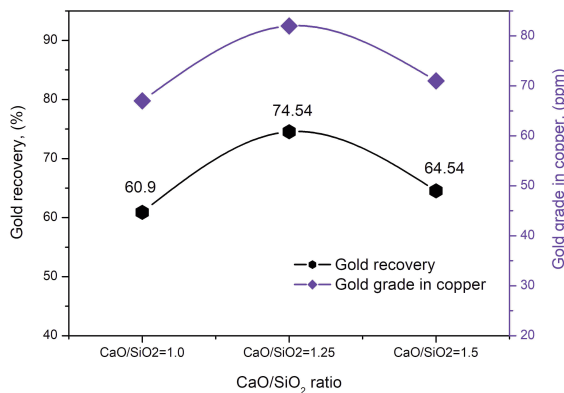


Figure 8. The effect of Au recovery on various CaO/SiO_2 ratios

In the experiment without additives, the grades of gold dissolved in the copper were of 29, 27, and 30 ppm at 1400, 1500, and 1600°C , while the gold recovery rates were 53, 49.1, and 54.5%, respectively (Fig. 9(a)). With the CaO addition at CaO/SiO_2 ratio of 1.0, the gold grade in the copper was 67 ppm and recovery rate reached 60.8% as shown in Fig. 9(b). When the CaO addition increased to CaO/SiO_2 ratio of 1.25, the gold grade and recovery rate reached highest values of 82 ppm and 74.54%, respectively. It was observed that the amount of gold dissolved into the molten copper (30 ppm) was about three times lower than that obtained at the same temperature, which demonstrates that the addition of CaO can significantly improve the viscosity behavior of the concentrate slag. Fig. 9 shows comparison of effect of Au recovery depending on the various temperatures and CaO addition.

As shown in Figs. 10 (a) and (b), the appearance of concentrate slag samples are different according to the presence of CaO additives, in which appearance of concentrate slag without additives is glass-like slag,

but concentrate slag with CaO addition at CaO/SiO_2 ratio of 1.25 is metallurgical slag.

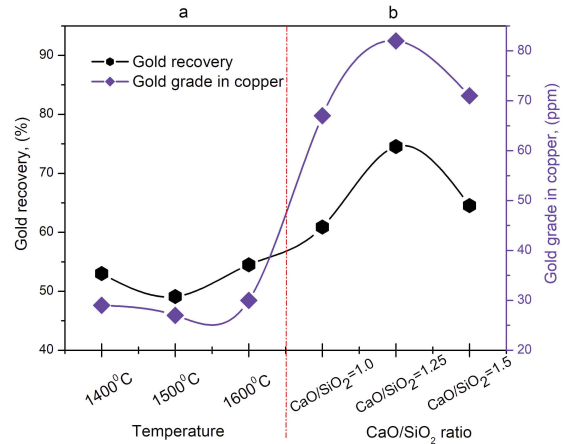


Figure 9. Comparison of effect of Au recovery on temperature and CaO addition

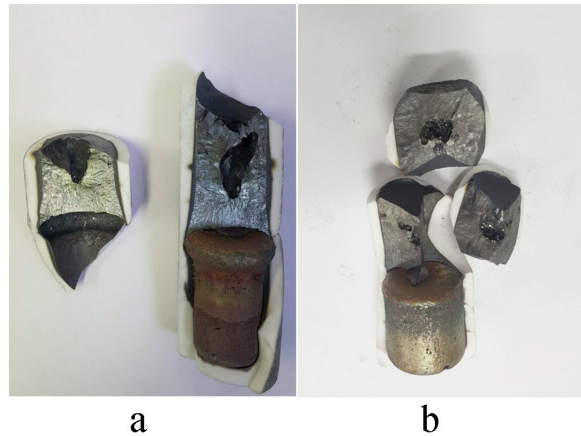


Figure 10. Samples of gold concentrate slag and pure copper obtained (a) without and (b) with CaO additives at 1600°C

4. Conclusion

In this work, the flotation concentrate from gold mine tailings Jeonnam Province was sampled, characterized and used for the recovery of Au using dissolve smelting. The chemical data obtained with different analytical methods such as XRF, XRD, SEM-EDS, and ICP-AES, confirmed by the mineralogical results, showed the presence of some uncommon elements in the flotation concentrate, i.e., gold content of 110 ppm, which makes the EGM gold mine tailings a secondary source of these materials.

The changes in the Au content in the flotation concentrate were examined in relation to the temperature and the CaO addition while dissolving Au from the flotation concentrate into the molten copper by smelting. The following main results were observed:

1) Sulphur was greatly removed from flotation concentrate from the tailings and new oxide phase of zinc ferrite formed at 700°C for 7 hours in the roasting,

2) The main components of the flotation concentrate from EGM gold mine tailings after roasting were SiO₂, Fe₂O₃, and Al₂O₃, with mass fractions of about 33 wt.%, 54 wt.% and 3 wt.%, respectively, which is quite consistent with the eutectic compound 2FeO•SiO₂ + SiO₂, and it is heavy smelting molten concentrate in the form of metallurgical slag. The experimental results suggested that a primary factor decreasing the viscosity of concentrate slag was the high temperature, and the optimal smelting temperature was at 1600°C,

3) The optimal CaO/SiO₂ ratio in the metallurgical slag that affects the formation of a fusible slag and decreases its viscosity was examined. The recovery of gold reached 74.45% under a CaO/SiO₂ ratio of 1.25 at 1600°C, which indicates a good decrease in the concentrate slag viscosity,

Finally, it appears that recovery of gold from flotation concentrate from gold mine tailings can be achieved through dissolve smelting at high temperature. However, whether the combination of temperature and structure of the formed concentrate slag are main factors enhancing the gold dissolution into molten copper is still needed to be clarified in future experiments. The results presented in this work might be further used as a start point for optimization of the recovery based on dissolve smelting.

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DOBIJANJE ZLATA IZ FLOTACIJSKOG KONCENTRATA DOBIJENOG IZ JALOVINE PUTEM TOPLJENJA I RASTVARANJA

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Apstrakt

Flotacijski koncentrat zlata može sadržati visoke koncentracije vrednih metala kao što su gvožđe, bakar i cink, a povremeno i plemenite metale kao što je zlato. Glavne komponente koncentrata su SiO₂, Fe₂O₃ i Al₂O₃, ali on sadrži i reaktivne sulfidne minerale kao što je pirit. Sulfidi u flotacijskom koncentratu u potpunosti prelaze u oksidni oblik tokom oksidativnog prženja, pa se stoga hemijski sastav prženog koncentrata smatra bakarnom šljakom. Tokom istraživanja je primenjeno topljenje na visokim temperaturama sa dodacima za rastvaranje Au iz koncentrata zlata u rastopljenom bakru. Zlato se većim delom rastvorilo na 1600°C, kada je odnos CaO/SiO₂ iznosio 1,25, što sugerise da se povećava rastvaranje zlata u rastopljenom bakru uz smanjenje viskoznosti rastopljenog koncentrata pri visokim temperaturama.

Ključne reči: Zlato; Flotacijski koncentrat; Rastvaranje topljenjem; Viskoznost.

