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. There are major components are SiO₂, Fe₂O₃ and Al₂O₃, but they also contain reactive sulphide minerals such as pyrite. The sulphides in the flotation concentrate is fully converted to an oxide form during oxidative roasting, hence the chemical composition of the roasted concentrate can be considered as a copper slag. We used high temperature smelting with additives to dissolve Au from the gold concentrate into a molten copper. 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 the 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, in 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 were 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, in 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 may 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, contained in minerals and native metals that have not been separated by froth flotation process.

In recent years, Investigators in the Korean had paid special attention to recycle the gold tailings and developed several technologies of recover 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 with fine and floatable, gold content is enriched to sulphide mineral as a flotation concentrate. The flotation concentrate is well known that iron sulphide minerals 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 is widely used on 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 very toxic. Also, the recovery of gold from leach solutions have been processed by various methods as the cementation, carbon adsorption, electrowinning and ion solven extraction [8].

Currently, the gold mining company in Jeonnam Province, Korea is producing abundant quantity of tailings have affected the landscape, which causes pollution in the area. South Korea has been already supporting to recycle the solid wastes on finding innovative methods of utilizing solid waste management. There is therefore a significant need to developing other reuses and commercially viable application for mine tailings in order to minimize the disposal costs and the impact on the environment.

Therefore, this study aims 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 as like metallurgical slag. The pure copper containing gold is considered like-blister 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 is completely recycled the regenerated concentrate slag for recovery iron and value added products as abrasive blasting, roofing granules, concrete and other materials [9-12]. The sulphides in the flotation concentrate is fully converted to an oxide form during oxidative roasting, hence the chemical composition of the roasted concentrate can be considered as a copper slag. We also recently examined recovery of pig iron containing copper from copper smelting slag by reduction smelting, and successfully performed and produced the pig iron [9-11].

The flotation concentrate from gold mining tailings in Jeonnam Province were used in this research. Our 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 from EGM company in Jeonnam Province were used in this study. Since the tailings were already milled down to 70 μm, they were easily excavated and processed. Its 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 SiO₂, Fe₂O₃ and Al₂O₃ 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, these were contained of 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, which Au content in the flotation concentrate were found to be 110 ppm. The result of the XRD analysis could be found that the main crystal phases in the flotation concentrate from gold tailings were quartz (SiO₂), hematite and pyrite (FeS₂) as shown in Fig. 2.
Table 1. Chemical composition of the flotation concentrate from gold tailings by XRF and ICP analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>ZnO</th>
<th>CaO</th>
<th>P₂O₅</th>
<th>Au, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>37.49</td>
<td>34.26</td>
<td>21.13</td>
<td>4.20</td>
<td>1.47</td>
<td>0.90</td>
<td>0.35</td>
<td>0.20</td>
<td>110</td>
</tr>
</tbody>
</table>

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 was 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 φ26 alumina crucible was placed inside it by using the φ45 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 is 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.

**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 occurs in association with pyrite is hardly extracted by cyanide leaching. Therefore, several technology 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:

\[
4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2
\]  \(\text{(1)}\)
FeS₂ = FeS + S  \quad (2)
3FeS + 5O₂ = Fe₃O₄ + 3SO₂  \quad (3)
4Fe₃O₄ + O₂ = 6Fe₂O₃  \quad (4)
S + O₂ = SO₂  \quad (5)
SO₂ + 1/2O₂ = SO₃  \quad (6)

In the roasting, toxic gases of SO₂ is produced and polluted environment seriously. 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 is chemical composition of the gold flotation concentrate after roasting as determined by the X-ray Fluorescence, has low content trioxide sulphur of 4.97 wt.%. As shown Table 3, it was found that the amount of main component such as Fe₂O₃ was increased.

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 Fig. 5, quartz, hematite phases and zinc ferrite (ZnFe₂O₄) are presented in the samples. It is indicated that pyrite (FeS₂) completely formed to oxide form. To summarize, the Sulphur was greatly removed from flotation concentrate from tailings and new oxide phase of zinc ferrite formed in the roasting.

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

<table>
<thead>
<tr>
<th>Element</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>ZnO</th>
<th>CaO</th>
<th>P₂O₅</th>
<th>CuO</th>
<th>PbO</th>
<th>TiO₂</th>
<th>Cr₂O₃</th>
</tr>
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<tbody>
<tr>
<td>Weight %</td>
<td>33.10</td>
<td>54.33</td>
<td>4.97</td>
<td>3.22</td>
<td>1.20</td>
<td>1.35</td>
<td>0.26</td>
<td>0.65</td>
<td>0.14</td>
<td>0.40</td>
<td>0.23</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**Figure 4.** EDS pattern and chemical composition of the 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 a reaction at high temperatures of 1400, 1500 and 1600°C, and changing the chemical composition of the gold concentrate with CaO additives in order to form as a metallurgical slag with low viscosity.

Electric induction furnace is type of melting furnace that uses electric current to melt the metal. The basic mechanism of induction heating that alternating current is produced in a coil by applying alternating voltage. The alternating current produces magnetic field around of the coil, which has an eddy currents with a same frequencies and opposite in direction with a 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 as the metallurgical slag are fully contacted to the molten copper by surface. The circulation of the molten copper with opposite circulation of the molten gold concentrate might be effected a useful 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 on the 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](image-url)
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:

\[ 2\text{Cu} + \text{O}_2 = 2\text{CuO} \]  

(7)

The chemical reactions between the major oxides in the gold concentrate, such as FeO, SiO\(_2\), CaO, Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\), form the following molecular compounds:

\[ \text{CaO} + \text{SiO}_2 = \text{CaSiO}_3 \]  

(8)

\[ 2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4 \]  

(9)

\[ \text{CaO} + \text{Al}_2\text{O}_3 = \text{CaAl}_2\text{O}_4 \]  

(10)

\[ 2\text{CaO} + \text{Al}_2\text{O}_3 = \text{Ca}_2\text{Al}_2\text{O}_5 \]  

(11)

\[ \text{CaO} + \text{FeO} + \text{SiO}_2 = \text{CaFeSiO}_4 \]  

(12)

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·SiO\(_2\) and 2FeO·SiO\(_2\) were the main molecular compounds, and that SiO\(_2\) and the oxides are constituted the molten concentrate as the metallurgical slag for the dissolve smelting. Table 3 is changes of Gibbs free-energy in the chemical reactions between the major oxides in the flotation concentrate.

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

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>CuO</th>
<th>3CaO·P(_2)O(_5)</th>
<th>CaO·SiO(_2)</th>
<th>2FeO·SiO(_2)</th>
<th>2CaO·Al(_2)O(_3)</th>
<th>CaO·FeO·SiO(_2)</th>
<th>CaO·Al(_2)O(_3)</th>
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<tr>
<td>900</td>
<td>-103.64</td>
<td>-682.602</td>
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<td>-13.423</td>
<td>28.5</td>
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<td>1100</td>
<td>-70.552</td>
<td>-671.069</td>
<td>-90.702</td>
<td>-17.522</td>
<td>-14.076</td>
<td>78.403</td>
<td>-3.827</td>
</tr>
<tr>
<td>1200</td>
<td>-52.382</td>
<td>-666.395</td>
<td>-90.715</td>
<td>-16.17</td>
<td>-14.503</td>
<td>105.449</td>
<td>-0.058</td>
</tr>
<tr>
<td>1600</td>
<td>-5.939</td>
<td>-652.416</td>
<td>-91.249</td>
<td>-5.483</td>
<td>-16.925</td>
<td>229.081</td>
<td>19.204</td>
</tr>
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</table>

Viscosity is a most important physiochemical property of metallurgical slag, as it plays an important role at 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 based on no reaction at high temperature smelting was 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 were 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...
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 is 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 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/SiO₂ ratio. In the experiment, CaO/SiO₂ 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/SiO₂ ratio of 1.25, but by increasing this ratio to 1.5, its dissolved content was decreased down to 70 ppm, while that gold recovery rate was highest 74.5%. The results of Au recovery in each CaO/SiO₂ ratio 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 that gold recovery rates were 53, 49.1 and 54.5%, respectively (in Fig. 9(a) column). 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) column. When the CaO addition increased to CaO/SiO$_2$ ratio of 1.25, the gold grade and recovery rate were 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 behaviour of the concentrate slag. Fig. 9 shows comparison of effect of Au recovery depending on the various temperatures and CaO addition.

As shown Figs. 10 (a) and (b), the appearance of concentrate slag samples are different according to the without and with 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 like 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. Conclusions

In this work, the flotation concentrate from gold mine tailings Jeonnam Province were sampled, characterized and used for recover of Au up studies using dissolve smelting. The chemical data obtained with different analytical methods such as XRF, XRD, SEM–EDS and ICP–AES, and 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 SiO$_2$, Fe$_2$O$_3$ and Al$_2$O$_3$, with mass fractions of about 33 wt.%, 54 wt.% and 3 wt.%, respectively, which is quite consistent with the eutectic compound 2FeO·SiO$_2$ + SiO$_2$, and it is heavy smelting molten concentrate as a 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/SiO$_2$ ratio in the metallurgical slag affects the formation of a fusible slag and decreases its viscosity. The recovery of gold reached 74.45% under a CaO/SiO$_2$ 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 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.
Acknowledgments

Departments of Metallurgical Engineering of Pukyong National University, Republic of Korea, where several of the experiments presented in this study were performed, are gratefully acknowledged.

REFERENCES

Table captions

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

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

Figure captions

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

<Figure 2> XRD pattern of flotation concentrate from gold tailings

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

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

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

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

<Figure 7> Effect of Au recovery on various temperatures

<Figure 8> Effect of Au recovery on various CaO/\text{SiO}_2\text{ ratios}

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