Microwave Pretreatment for Thiourea Leaching for Gold Concentrate

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Received: 4 September 2017; Accepted: 27 September 2017; Published: 1 October 2017

Abstract: In this research, we studied the use of microwave pretreatment to enhance the efficiency of Au leaching from gold concentrate. The gold concentrate was pretreated using microwaves with different irradiation time. The sample temperature was increased up to 950 °C by the microwave irradiation. A scanning electron microscope-energy dispersive spectrometer showed the evolution of microcracks and the reduction of sulfur on the mineral surface. X-ray diffraction data also showed the mineral phase shift from pyrite to hematite or pyrrhotite. A leaching test was conducted for the microwave-treated and untreated gold concentrates using thiourea. Although the thiourea leaching recovered 80% of Au from the untreated concentrate, from the treated concentration, the Au could be recovered completely. Au leaching efficiency increased as the microwave irradiation time increased, as well as with a higher composition of thiourea.

Keywords: microwave; pyrite; thiourea leaching; gold

1. Introduction

For the efficient recovery of gold from ore, cyanidation has been widely used in extractive metallurgy for the past 100 years. Recently, considerable attention on non-cyanide lixiviants has been arisen in the metallurgical industry due to the increasing environmental concerns over cyanidation [1,2].

Thiourea, one of the alternative lixiviants, has been recognized as a potentially viable lixiviant. It can generate relatively strong gold complexes and promptly leach gold ores when catalyzed by ferric ions, and it is eco-friendly due to its low toxicity [3,4]. However, there are ores that are not amenable to treat by cyanide and thiourea, such as pyrites. Inside pyrite, for example, a considerable amount of Au exists as a refractory and invisible state. In order to recover Au from such a concentrate, it is important to decompose pyrites [5,6].

A roasting process using electric furnaces and high-pressure oxidation has been used to decompose pyrites in Au concentrates. However, the roasting process is uneconomical and involves environmental problems [7,8]. A microwave process has been reported as an alternative for the roasting process. It has many advantages, such as being selective to specific substances, using a non-contact method from the energy source, rapid and uniform energy transfer, and convenient operation in terms of generation source manipulation [9,10].
Previous studies have reported on the microwave treatment for various minerals. Uslu et al. [10] conducted research on the desulfurization of coals using microwaves. Huang and Rowson [11] treated pure pyrite and marcasite using microwaves in a mid-temperature (50 °C) nitric acid solution. Ma et al. [12] studied the microwave treatment for the removal of sulfur and arsenic in Au concentrate. Amankwah and Pickles [13] reported the use of microwaves as a pretreatment process for gold recovery from carbonaceous sulfide concentrate by cyanide leaching. However, few studies have explained the relationship between the microwave irradiation and the enhancing leaching efficiency of Au from the gold concentrate.

In this research, we investigated the effect of microwave pretreatment on the recovery of gold from the gold concentrate by thiourea leaching. Alteration of the mineral phase was analyzed by comparing scanning electron microscope-energy dispersive spectrometer and X-ray diffraction data before and after the microwave treatment. Leaching experiments were conducted for the gold concentrates with and without microwave treatment.

2. Materials and Methods

2.1. Gold Concentrates

The gold concentrate (38–45 µm) was obtained through the flotation process from an operating gold mine (Haenam, Korea). Mineral composition of the gold concentrate was analyzed using X-ray diffraction (X’Pert Pro MRD, PANalytical, Almelo, The Netherlands). To determine the chemical composition of the concentrate, the sample was digested with aqua regia. The solution chemistry was analyzed using atomic absorption spectrophotometers (AA-7000, Shimadzu, Kyoto, Japan). The sulfur contents on the concentrate was determined using a carbon-sulfur analyzer (CS-800, Eltra, Haan, Germany).

2.2. Pretreatment of Gold Concentrate Using Microwaves

Gold concentrate (50 g) was placed in a 1 L open vessel ceramic container. To measure the temperature of the sample, type K thermocouple was buried 5 mm beneath the surface of the concentrate sample [14–20]. The concentrates were microwave-irradiated with a variable power (maximum output 1000 W) and a 2.45 GHz kitchen type microwave oven was used for microwave heating for 10, 30, 50, and 70 min. The weight of the sample was measured after microwave treatment. X-ray diffraction (XRD) and scanning electron microscope-energy dispersive spectrometer (SEM-EDS; S4800, Hitachi, Tokyo, Japan) analyses were conducted to observe the change in the mineral phase. The chemical composition of the sample was analyzed through aqua regia digestion, and atomic absorption spectrophotometers (AAS).

2.3. Kinetic Au Leaching Experiments

Au leaching experiments were conducted for the microwave-treated and untreated concentrates using various lixiviants with different composition. Experimental conditions are presented in Table 1. Lixiviants were prepared in a 250 mL flask by mixing 100 mL of thiourea solvents (36.4–52.0 mM) with 0.6 g of additional solvent (sodium sulfate) and 3.5 g of oxidant (ferric sulfate). Prepared lixiviant has pH 1.3. Because sulfur in Au concentrates inhibits Au leaching, we used the additives, such as SO2, Na2SO3, or Na2S2O5, and oxidants, such as H2O2 or Fe2(SO4)3, to improve the rate of Au leaching [5,21–24].

The concentrates (10 g) were added to the lixiviant. The sample was agitated at 70 °C for 1 h using a mechanical stirrer with 120 rpm. Supernatants were withdrawn every 10 min. The dissolved gold in the solution was measured using AAS. The rate of Au leaching was determined by following equation [25]:

\[ E = E_l \left(1 - e^{-kt}\right) \] (1)
where \( E_1(\%) \) is the Au concentration in the leaching solution at time \( t \), \( E_t(\%) \) is the maximum concentration of Au, and \( k \) (min\(^{-1}\)) is the leaching rate constant.

### Table 1. Experimental conditions of microwave pretreatment and thiourea leaching.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Irradiation Time (min)</th>
<th>Thiourea (mM)</th>
<th>Sodium Sulfate</th>
<th>Ferric Sulfate (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>34.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>34.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>30</td>
<td>34.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>50</td>
<td>34.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>70</td>
<td>34.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>70</td>
<td>43.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>70</td>
<td>52.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3. Result and Discussion

#### 3.1. Effect of Microwave Irradiation on Gold Concentrate

The gold concentration was irradiated with microwaves for 10, 30, 50, and 70 min. As the irradiation time increased, sample temperature increased with non-linearity (Figure 1a). The sample temperature was rapidly increased for the first 10 min, and the rate became lower after that. In the early irradiation time, the temperature increased with the rate of 1.12 \(^{\circ}\)C:s\(^{-1}\). By the microwave treatment, mass of the gold concentrate was reduced significantly (Figure 1b).

![Figure 1. (a) Sample temperature, and (b) loss of the sample mass and the sulfur contents during the microwave irradiation.](image)

Table 2 presents the chemical composition of the gold concentrates treated with microwaves. By the microwave irradiation, the sulfur contents were reduced significantly from the concentrate. Particularly in the early irradiation time, as the temperature increase to 670 \(^{\circ}\)C, the samples showed significant reduction in the sample mass as well as the sulfur content (Figure 1b). Further microwave irradiation resulted in further mass loss and the depletion of sulfur in the concentrates, so that the microwaves for 30 min achieved approximately 94.43% reduction in sulfur content. From 10 to 70 min, the percent loss of the total mass and the sulfur content increased almost linearly as the temperature increased. The weight loss could be fitted with \( y = 0.0189x - 6.2811 \), and the sulfur loss with \( y = 0.2483x - 120.53 \). The ratio of the two slopes (0.0189/0.2483 = 0.076) was less than the sulfur content of the raw concentrate (0.20), which indicates that other substances such as water and solvent were also removed during the microwave heating. The intercept of trend lines shows that the removal of weight and sulfur started around 332 \(^{\circ}\)C and 485 \(^{\circ}\)C, respectively.
Table 2. Chemical composition of gold concentrates after the microwave treatment with different irradiation times.

<table>
<thead>
<tr>
<th>Irradiation Time (min)</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Co</th>
<th>S*</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>10.460</td>
<td>40.560</td>
<td>290</td>
<td>140</td>
<td>4550</td>
<td>2550</td>
<td>20.140</td>
<td>1026</td>
<td>133</td>
</tr>
<tr>
<td>10</td>
<td>10.412</td>
<td>40.588</td>
<td>296</td>
<td>152</td>
<td>4566</td>
<td>2249</td>
<td>11.454</td>
<td>1022</td>
<td>139</td>
</tr>
<tr>
<td>30</td>
<td>10.388</td>
<td>41.356</td>
<td>291</td>
<td>144</td>
<td>4597</td>
<td>2188</td>
<td>14.455</td>
<td>1012</td>
<td>150</td>
</tr>
<tr>
<td>50</td>
<td>10.401</td>
<td>41.599</td>
<td>284</td>
<td>143</td>
<td>4603</td>
<td>1384</td>
<td>13.22</td>
<td>996</td>
<td>152</td>
</tr>
<tr>
<td>70</td>
<td>10.122</td>
<td>42.560</td>
<td>277</td>
<td>138</td>
<td>4612</td>
<td>1355</td>
<td>11.20</td>
<td>999</td>
<td>159</td>
</tr>
</tbody>
</table>

* measured using a carbon sulfur analyzer.

The increase in the sample temperature by the microwave irradiation is due to high absorption of microwave energy by the sulfide minerals, such as pyrites, in the gold concentrate. McGill et al. [26] reported that the temperature of pyrites was increased to 1019 °C by exposure to microwaves for 6.75 min with 2.5 °C·s⁻¹ of temperature increasing rate. Huang and Rowson [11] reported that the temperature of pyrites (0–63 μm) was increased at a rate of 7.5 °C·s⁻¹ by microwave irradiation for a shorter time period (40 s) [26]. The temperature was not increased continuously by long-term microwave irradiation. The maximum temperature of the minerals (pyrite) did not change significantly in our experiments. In the case of the inorganic material, the dielectric loss rate and the absorption rate were determined even when the material was microwave-irradiated for a long time [27].

The rapid removal of sulfur for the first 10 min is because of the destruction of the mineral structure by microwave irradiation. We can see that almost all the of sulfur was already reduced from the concentrate at 30 min. The reduction in the sample weight due to an increase in microwave irradiation time was due to pyrites that absorbed microwave energy and were thermally decomposed so that S was volatilized to become SO₂, and subsequently be removed [11]. Haque [15] reported that pyrites emitted sulfur fumes as they generated pyrrhotite when irradiated by microwaves for 3–5 min at 2450 MHz and 30 W.

3.2. Mineralogical Change in Gold Concentrate by Microwave Irradiation

To study the mineralogical alteration of gold concentrates by microwave irradiation, XRD analysis was conducted for microwave-treated gold concentrates, and it compared with raw gold concentrate (Figure 2). The diffraction lines showed that the raw concentrate was mainly composed of pyrites and quartz (Figure 2a). However, the gold concentrates treated with microwaves for 10 min showed the diffraction lines of hematite and pyrrhotite as well as those of quartz and pyrite (Figure 2b). The pretreated sample also revealed a significant reduction in the intensity of diffraction lines of pyrite compared to concentrate samples without irradiation. This is because pyrite is a hyperactive mineral that absorbs microwaves well, while quartz is a mineral that is transparent to microwaves, so that only pyrite reacted with microwaves and thermally decomposed selectively. The occurrence of the diffraction lines of hematite and pyrrhotite in the pretreated sample after microwave irradiation suggests the mineral phase of pyrite was changed into that of hematite and pyrrhotite [9,13,28]. Mineralogical phase change of pyrite is possible at 750 °C [11,29–31].

![Figure 2](image-url) X-ray diffraction (XRD) patterns for the gold concentrates (a) before and (b) after microwave irradiation for 10 min (H: hematite; Py: pyrite; Ph: pyrrhotite; Q: quartz).
Figure 3 presents the SEM-EDS analysis for raw and microwave-treated samples. Idiomorphic cubic pyrites were observed (Figure 3a). EDS analysis on the surface of the pyrites showed that the ratio of Fe and S was about 1:2 (at %). Figure 3b showed that the microwave irradiation developed microcracks on pyrite surface, so that the phase of the pyrites was changed to a porous phase. The EDS analysis showed that sulfur atoms on the pyrite surface were replaced by oxygen completely. The reduction in S and occurrence of O after the microwave irradiation was due to the occurrence of thermal stress, thermal decomposition, and oxidation in the pyrites simultaneously due to microwave heating [15]. Since microwaves selectively react to specific sulfur minerals, thermal stress occurs at the boundary between gangue and sulfur minerals [32,33], and this thermal stress incurs microcracks at the boundary of minerals whose thermal expansion coefficient is different from each other, or inside the minerals [28]. Very high temperature obtained in the boundaries could also produce thermal fracturing [34,35]. The generated microcracks and faults are ultimately followed by thermal fracturing, and this thermal fracturing degrades the strength of the sulfur minerals, thereby facilitating the crushing and milling of ore minerals, resulting in increased Au liberation efficiency from Au concentrates [32,33].

![Figure 3. Scanning electron microscope-energy dispersive spectrometer (SEM-EDS) results for pyrite on microwave irradiation time with (a) 0 min, (b) 10 min.](image)

### 3.3. Gold Leaching

#### 3.3.1. Effect of Microwave Irradiation on Au Leaching Efficiency

Thiourea leaching experiments for gold recovery were conducted for gold concentrates microwave-treated for different irradiation times (Figure 4a). The results showed that the microwave treatment enhanced the rate of Au leaching. Without microwave treatment (Experiment A), the Au leaching rate was about 78.1% after 60 min of the leaching experiment, whereas the Au leaching rate was about 95.5% after 50 min (Experiment D). In particular, the Au leaching rate reached 100% after an irradiation time of 70 min (Experiment E). Microwave treatment resulted in differential thermal expansion within the ore as a result of the varying loss factors of the constituents in the gold concentrate. In addition, these treatments may create high temperature internal gas phases, which lead to structural distortion and breakdown of the ore [36]. Since thiourea used as the Au solvent in this study can dissolve Au faster and had lower toxicity than cyanide, it has been used as an alternative solvent to cyanide [37,38].
The maximum leaching percent of Au according to an increase in concentration of thiourea mixed percent at all samples irradiated by microwaves for 70 min was more than 100%. The leaching rate change from pyrite to hematite or pyrrhotite. The Au leaching experiment was conducted using a mixed solvent, and the highest rate was 0.0901 min

3.3.2. Effect of Thiourea Concentration on Au Leaching Efficiency

Lixiviants with different concentrations of thiourea were used for gold leaching from the samples that were microwave-treated for 70 min. The result showed that as the concentration of thiourea increased, the Au leaching rate increased (Figure 4b). Based on the experimental results, the leaching parameters of the leaching experiment conditions estimated using Equation (1) are presented in Table 3. The maximum leaching percent of Au according to an increase in concentration of thiourea mixed solvent without microwave irradiation was verified as 81.4158%. However, the maximum leaching percent at all samples irradiated by microwaves for 70 min was more than 100%. The leaching rate constant, which was a rate parameter, was increased from 0.0561 to 0.0783 min\(^{-1}\) as the microwave irradiation time increased from 0 min to 70 min. In particular, the temperature of the sample suddenly increased at the Experiment E condition, whose temperature was 850°C or higher. Elution efficiency of the gold depending on the amount of thiourea showed no significant change. However, the elution rate of gold increased with the amount of solvent added. For this reason, the enhancement of gold leachability was probably due to the increase in surface area as a result of pyrite oxidation and the formation of a porous hematite structure.

Table 3. The summary of leaching parameter for Au leaching test using Equation (1).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(E_L) (%)</th>
<th>(k) (min(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>81.42</td>
<td>0.0561</td>
<td>0.9804</td>
</tr>
<tr>
<td>B</td>
<td>84.06</td>
<td>0.0601</td>
<td>0.9780</td>
</tr>
<tr>
<td>C</td>
<td>88.45</td>
<td>0.0612</td>
<td>0.9757</td>
</tr>
<tr>
<td>D</td>
<td>96.02</td>
<td>0.0624</td>
<td>0.9768</td>
</tr>
<tr>
<td>E</td>
<td>100.00</td>
<td>0.0783</td>
<td>0.9830</td>
</tr>
<tr>
<td>F</td>
<td>100.00</td>
<td>0.0837</td>
<td>0.9805</td>
</tr>
<tr>
<td>G</td>
<td>100.00</td>
<td>0.0901</td>
<td>0.9773</td>
</tr>
</tbody>
</table>

The leaching rate constant increased according to the increase in the concentration of the thiourea mixed solvent, and the highest rate was 0.0901 min\(^{-1}\) at the Experiment G condition.

4. Conclusions

In this study, we investigated the effect of microwave pretreatment on the recovery of gold from gold concentrate by thiourea leaching. As the microwave irradiation time increased, the sample temperature increased and the total mass of the samples was reduced; in particular, the sulfur was significantly removed from the concentrates. The microwave treatment resulted in a mineral phase change from pyrite to hematite or pyrrhotite. The Au leaching experiment was conducted using a
thiourea mixed solvent. The gold leaching from the concentrate could be significantly enhanced by the microwave pretreatment due to the microcracks that developed on the pyrite surface. The results of this study confirmed that the microwave irradiation could be used as an effective pretreatment process to enhance gold recovery in advance of the hydrometallurgy process.

**Acknowledgments:** This subject is supported by Korea Ministry of Environment (MOE) as “Advanced Technology Program for Environmental Industry” (Technologies for the Risk Assessment and Management 2016000140010).

**Author Contributions:** Nag-Choul Choi carried out the transport experiments, participated in the reference research, and drafted the manuscript. Bong-Ju Kim participated in the design of the study, and supervised the research work. Kanghee Cho carried out the model analysis. Soonjae Lee revised and edited the manuscript. Cheon-Young Park conceived of the study, participated in its design and coordination, and helped to draft the manuscript. All authors read and approved the manuscript.

**Conflicts of Interest:** The authors declare that they have no competing interests.

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