Using Nickel as a Catalyst in Ammonium Thiosulfate Leaching for Gold Extraction

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The use of copper as a catalyst for gold leaching in ammonium thiosulfate solution might cause the high consumption of thiosulfate. Also, the high copper consumption is resulted in the zinc precipitation process for recovering the gold from the pregnant solution. In this investigation, nickel was used as a catalyst to minimize the reagent consumption. On a 100 mass%-75 μm of silicate type gold ore containing 16 g/t Au and 0.2 mass% of Fe and C, the nickel catalyzed ammonium thiosulfate solution could extract 95% of gold with the 1.2 kg/t-ore of ammonium thiosulfate consumption in 24 hours at the most favorable reagent combination of 0.0001 mol/dm³ NiSO₄, 0.05 mol/dm³ (NH₄)₂S₂O₃ and 0.5 mol/dm³ NH₄OH at pH9.5, while the standard cyanidation at 0.02 mol/dm³ (1.0 g/dm³) NaCN consumed around 1.5 kg/t-ore NaCN. In the concentration range of 0.0001~0.005 mol/dm³ Ni²⁺, the ammonium thiosulfate consumption was 1~5kg/t-ore, while the ammonium thiosulfate consumption of copper catalyzed lixiviant was greatly increased from 3 kg/t-ore to 21 kg/t-ore as the increase of Cu concentration range of 0~1.

Nickel consumption on the cementation process was less than 50%. For extracting gold from the copper bearing sulfide ore, a higher ammonia and thiosulfate concentrations were required with 0.0001 mol/dm³ of Ni²⁺. The ammonium thiosulfate consumption with nickel as a catalyst on the copper bearing sulfide ore was about 1~5 kg/t-ore less than that using copper as catalyst.

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1. Introduction

The solubility of gold in a diluted solution of potassium cyanide was demonstrated by Elsner in 1846, as shown in eq. (1):¹

\[ 4\text{Au} + 8\text{KCN} + 2\text{H}_2\text{O} \rightarrow 4\text{KAu(CN)}_2 + 4\text{KOH} \] (1)

In 1887, cyanidation was patented by MacArthur and the Forrester brothers, and further developed to the practical use for gold recovery. Since then, cyanidation has been used as a standard gold extraction process. The gold pregnant solution has been processed by cementation, CIP/CIL (carbon in pulp/carbon in leach) or ion exchange for gold recovery.²⁻⁴

However, cyanide has a high toxicity with the time weighted average exposure limit of 5 mg/m³.⁵ Some incidents have occurred with spilled cyanide and a resulting environmental pollution.⁶⁻⁷ Several countries such as the Czech Republic, Turkey and the USA in states such as Colorado, Wisconsin and Montana, have campaigned to ban cyanide applications.⁸⁻¹² Also, when processing refractory ore containing sulfide and carbonaceous minerals, it is difficult to extract gold by cyanidation without pre-treatment, such as roasting, pressure oxidation and bio-oxidation, etc.¹³⁻¹⁵

Due to above environmental, political and technical concerns, the development of non-cyanide process has been focused on an alternative in the study of gold extraction.

There are various non-cyanide lixiviants being proposed by many investigators for gold extraction: thiourea, bromide, iodine, thiocyanate and thiosulfate.¹⁶⁻²⁴ Among these lixiviants, thiosulfate has been suggested as the best cyanide substitute.²⁵⁻³²

Thiosulfate (S₂O₃²⁻) is the least toxic and cheapest chemical which can stabilize gold in aqueous solution. Up to 12 g thiosulfate can be taken daily by mouth with no ill effects.⁵ The current market price for ammonium thiosulfate is only US$0.30/kg.¹³ In addition to thiosulfate as a major reagent, both ammonia and cupric ion are required in the gold leaching process. Ammonia is required to stabilize the catalyst of cupric ion and modify the pH. The time weighted exposure average limit of ammonia is 35 mg/dm³.⁵

There has been extensive research on thiosulfate leaching for gold extraction since the 1970s.²⁹⁻³¹,³³⁻⁴¹ Ammonium thiosulfate leaching process is also applicable for the heap leaching process.²⁸,³¹ However, there are problems in commercializing the thiosulfate process in the gold milling industry, the problems are the most notably high reagent consumption and varying gold extraction results for the different ores under the same leaching conditions. Furthermore, the conventional gold recovery process of CIP (carbon in pulp) on cyanidation can not be applicable in non cyanide process.²⁸,⁴¹,⁴² The alternative gold recovery process by cementation using zinc, copper and aluminium powders as well as ion exchange has not been systematically studied, hence a favourable process is not still established.¹¹,¹³⁻¹⁵,¹⁷⁻¹⁹

In our previous studies on the copper catalyzed ammonium thiosulfate leaching system, the most favorable reagent combination to give high gold recovery with small thiosulfate consumption was extensively researched and evaluated by both thermodynamic and experimental approaches.⁵²,⁵³ The best experimental result showed that 94% of gold extraction and 3 kg/t-ore of ammonium thiosulfate consumption could be achieved using 0.3 mol/dm³ NH₄OH, 0.0001 mol/dm³ CuSO₄, 0.05 mol/dm³ (NH₄)₂S₂O₃ at pH 9.5 for a −200 mesh (−75 μm) silicate type ore containing 16 g/t Au. Using zinc powder, nearly 100% of gold could be recovered from the pregnant solution. However, thiosulfate gold leaching using copper as a catalyst had the following
problems:
(1) Since the stability of the cuprous thiosulfate complex is higher than that of the cuprous ammine complex thermodynamically, the cupric ammine complex is reduced to a cuprous thiosulfate complex, causing an oxidation of thiosulfate to tetrathionate through the intermediate product of a cuprous ammine complex as shown in eqs. (2) and (3).

\[
2[Cu(NH_3)_4]^{2+} + 2S_2O_3^{2-} \rightarrow 2[Cu(NH_3)_2]^+ + S_4O_6^{2-} + 4NH_3 \quad (2)
\]

\[
[Cu(NH_3)_4]^{2+} + 2S_2O_3^{2-} \rightarrow [Cu(S_2O_3)_2]^{3-} + 4NH_3 \quad (3)
\]

(2) Although either the increase of ammonia concentration or the decrease of thiosulfate concentration can make the cupric ion stable as a cupric ammine complex, the cupric ion is the important electron acceptor to oxidize gold. And, a substantial amount of cupric ion is required in the ammonium thiosulfate leaching of gold extraction. Also, gold extraction kinetics and thiosulfate consumption are nearly influenced by the level of copper concentration.\(^{52}\)

(3) In the study of gold cementation by zinc, copper and aluminium powders, zinc powder was found to be the best metal powder to recover gold at lower ammonia (0.3 mol/dm\(^3\)) and thiosulfate (0.05 mol/dm\(^3\)) concentrations.\(^{52}\) But almost all of the copper in the solution was co-precipitated along with the gold since the stability of the copper ions is lower than that of zinc ions thermodynamically.\(^{52,53}\) Thus, the addition of cupric ions is required for recycling the barren solution to the leaching circuit, increasing the total reagent consumption.

In order to reduce the reagent consumption in the thiosulfate leaching of gold, nickel ion was used instead of copper ions in the present investigation. Effects of oxygen, ammonia, copper and thiosulfate on both gold extraction and thiosulfate consumption were investigated using the same ore studied on the conventional copper catalyzed system.\(^{52}\) The gold in the pregnant solution was cemented by zinc powder. The optimal reagent composition found in this investigation was evaluated thermodynamically. Gold leaching tests for various sulfide minerals were also conducted and evaluated for their feasibility.

### 2. Thermodynamic Discussion on Gold Leaching and Recovery

Figure 1 shows the Eh-pH diagram of the Ni-NH\(_4\)OH-S\(_2\)O\(_3\)\(^{2-}\) system for the reagent combination of 0.5 mol/dm\(^3\) NH\(_4\)OH, 0.5 mol/dm\(^3\) S\(_2\)O\(_3\)\(^{2-}\) and 0.005 mol/dm\(^3\) Ni\(^{2+}\). The concentrations of reagent except Ni\(^{2+}\) are within the range applied on the previous experimental project of the copper catalyzed gold leaching.\(^{52}\) Free energies of formation used in this calculation are listed in Table 1.\(^{54-61}\) Nernst Equations applied for this Eh-pH diagram is shown in Table 2. The result of Fig. 1 suggests that the electrode potential in the couple of \([\text{Ni}_3\text{O}_4]/[\text{Ni}(\text{NH}_3)_6]^{2+}\) may work for gold oxidation in ammonium thiosulfate solution, while that in the couple of \([\text{Cu}(\text{NH}_3)_4]^{2+}/[\text{Cu}(\text{NH}_3)_2]^{2+}\) works as an oxidant for gold.\(^{53}\)

In the gold leaching by nickel as a catalyst, nickelous oxide

![Fig. 1 Eh-pH diagram for the Ni-NH\(_4\)OH-S\(_2\)O\(_3\)\(^{2-}\)-H\(_2\)O system at the condition of 0.5 mol/dm\(^3\) NH\(_4\)OH, 0.005 mol/dm\(^3\) Ni\(^{2+}\) and 0.5 mol/dm\(^3\) S\(_2\)O\(_3\)\(^{2-}\). Nernst Equations (N1)~(N11) are shown in Table 2.](image)

#### Table 1: Free energy of formation for various species\(^{54-61}\)

<table>
<thead>
<tr>
<th>species</th>
<th>(\Delta G) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>-237.18</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>-157.29</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>-26.57</td>
</tr>
<tr>
<td>S(_2)O(_3)(^{2-})</td>
<td>-522.50</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>-48.24</td>
</tr>
<tr>
<td>Au(^+)</td>
<td>163.20</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>434.18</td>
</tr>
<tr>
<td>Cu(^{3+})</td>
<td>50.00</td>
</tr>
<tr>
<td>Ni(OH)(_2)</td>
<td>-447.3</td>
</tr>
<tr>
<td>Au(OH)</td>
<td>134.86</td>
</tr>
<tr>
<td>Au(OH)(_3)</td>
<td>-289.15</td>
</tr>
</tbody>
</table>

\(\Delta G\) values for various species in the reaction system are shown in Table 1. The Eh-pH diagram is shown in Fig. 1.
Table 2: Nernst equations applied in Eh-pH diagram at 298 K on Metal-Ammonia-Thiosulfate-Water System (The presence of other polythionate species was not considered.)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Half cell reaction</th>
<th>Nernst equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Au + 2S\textsubscript{2}O\textsuperscript{3−} \rightarrow Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{3−} + e\textsuperscript{−}</td>
<td>$E = 0.15 + 0.059 \log[Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{3−}] - 0.118 \log[S\textsubscript{2}O\textsubscript{3}^2−]$</td>
</tr>
<tr>
<td>B2</td>
<td>Au + 2NH\textsubscript{3} \rightarrow Au(NH\textsubscript{3})\textsubscript{3} + e\textsuperscript{−}</td>
<td>$E = 0.12 + 0.059 \log[Au(NH\textsubscript{3})\textsubscript{3}] - 0.118 \log[\text{NH}_\text{3}]$</td>
</tr>
<tr>
<td>B3</td>
<td>Au(NH\textsubscript{3})\textsubscript{2} + 2NH\textsubscript{3} \rightarrow Au(NH\textsubscript{3})\textsubscript{4} + 2e\textsuperscript{−}</td>
<td>$E = 0.89 + 0.059 \log[[\text{NH}<em>\text{3}]\textsubscript{2}√+][[\text{NH}</em>\text{3}]\textsubscript{2}√] − 0.059 \log[\text{NH}_\text{3}]$</td>
</tr>
<tr>
<td>B4</td>
<td>Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{3−} + 4NH\textsubscript{3} \rightarrow Au(NH\textsubscript{3})\textsubscript{3} + 2S\textsubscript{2}O\textsubscript{3}^2− + 2e\textsuperscript{−}</td>
<td>$E = 0.81 + 0.059 \log[[\text{NH}<em>\text{3}]\textsubscript{2}√+][[\text{NH}</em>\text{3}]\textsubscript{2}√] + 0.059 \log[S\textsubscript{2}O\textsubscript{3}^2−] − 0.118 \log[\text{NH}_\text{3}]$</td>
</tr>
<tr>
<td>B5</td>
<td>Au(NH\textsubscript{3})\textsubscript{2} + 3H\textsubscript{2}O = AuO\textsubscript{2} + 2NH\textsubscript{3} + 6H\textsuperscript{+} + 2e\textsuperscript{−}</td>
<td>$E = 0.50 + 0.030 \log[[\text{AuO}<em>\text{2}^−]/[\text{NH}</em>\text{3}]] + 0.059 \log[\text{NH}_\text{3}] − 0.177 \text{pH}$</td>
</tr>
<tr>
<td>B6</td>
<td>Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{3−} + 3H\textsubscript{2}O = AuO\textsubscript{2} + 2S\textsubscript{2}O\textsubscript{3}^2− + 6H\textsuperscript{+} + 2e\textsuperscript{−}</td>
<td>$E = 0.38 + 0.030 \log[[\text{AuO}<em>\text{2}^−]/[\text{NH}</em>\text{3}]] + 0.059 \log[S\textsubscript{2}O\textsubscript{3}^2−] − 0.177 \text{pH}$</td>
</tr>
<tr>
<td>B7</td>
<td>Au(NH\textsubscript{3})\textsubscript{2} + 3H\textsubscript{2}O = Au(OH\textsubscript{3}) + 2NH\textsubscript{3} + 3H\textsuperscript{+} + 2e\textsuperscript{−}</td>
<td>$E = 2.29 + 0.059 \log[\text{NH}<em>\text{3}] − 0.089 \text{pH} − 0.030 \log[\text{Au(NH}</em>\text{3})\textsubscript{2}^+]$</td>
</tr>
<tr>
<td>B8</td>
<td>Au(S\textsubscript{2}O\textsubscript{3})\textsubscript{3−} + 3H\textsubscript{2}O = Au(OH\textsubscript{3}) + 2S\textsubscript{2}O\textsubscript{3}^2− + 3H\textsuperscript{+} + 2e\textsuperscript{−}</td>
<td>$E = 2.27 + 0.059 \log[S\textsubscript{2}O\textsubscript{3}^2−] − 0.089 \text{pH} − 0.030 \log[\text{Au(S}_\text{2}O\textsubscript{3})\textsubscript{3−}]$</td>
</tr>
<tr>
<td>B9</td>
<td>Au + H\textsubscript{2}O = Au(OH\textsubscript{3}) + 2H\textsuperscript{+} + e\textsuperscript{−}</td>
<td>$E = 3.03 − 0.059 \text{pH}$</td>
</tr>
</tbody>
</table>

Equations B2, B3, B4, B7, N3 and N8 are calculated with eq. F1.
(Ni₃O₄), formed from nickel ammine complex, act as an oxidant for gold. The oxidation reaction of nickel ammine complex is shown as the combination of anodic reaction (4) and cathodic reaction (5):

\[
3\text{Ni(NH}_3\text{)}_6^{2+} + 8\text{OH}^- \rightarrow 3\text{NiO}_4 + 18\text{NH}_3 + 4\text{H}_2\text{O} + 2e^- \tag{4}
\]

\[
1/2\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \tag{5}
\]

The nickelous oxide (Ni₃O₄) in eq. (4) is reduced back to a nickel ammine complex with the oxidation reaction of gold as shown in the combination of cathodic reaction (6) and anodic reaction (7):

\[
\text{Ni}_2\text{O}_4 + 18\text{NH}_3 + 4\text{H}_2\text{O} + 2e^- \rightarrow 3\text{Ni(NH}_3\text{)}_6^{2+} + 8\text{OH}^- \tag{6}
\]

\[
2\text{Au} + 4\text{NH}_3 \rightarrow [\text{Au(NH}_3\text{)}_2]^+ + 2\text{e}^- \tag{7}
\]

The overall reaction from (4) to (7) is expressed as the following reaction (8):

\[
\text{Catalyzed by [Ni(NH}_3\text{)]}_6^{2+} \downarrow \rightarrow 4\text{Au} + 8\text{NH}_3 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4[\text{Au(NH}_3\text{)}_2]^+ + 4\text{OH}^- \tag{8}
\]

Since the aurous ammine complex is not stable, the aurous ammine complex in eq. (8) is immediately converted to a stable aurous thiosulfate complex according to reaction (9), as discussed in the previous study on copper catalyzed system.²²

\[
[\text{Au(NH}_3\text{)}_2]^+ + 2\text{S}_2\text{O}_3^{2-} \rightarrow [\text{Au(S}_2\text{O}_3\text{)}_2]^3- + 2\text{NH}_3 \tag{9}
\]

The sum of reactions (8) and (9) gives reaction (10), which is the overall gold oxidation reaction in a nickel catalyzed system.

\[
4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4[\text{Au(S}_2\text{O}_3\text{)}_2]^3- + 4\text{OH}^- \tag{10}
\]

Figure 2 shows the Eh-pH diagram of the Au-NH₄OH-S₂O₃²⁻ system for the reagent combination of 0.5 mol/dm³ NH₄OH, 0.5 mol/dm³ S₂O₃²⁻ and 5 × 10⁻⁵ mol/dm³ Au. Compared to Fig. 1, the electrode potentials of aurous ammine complex at pH9.5 is located in higher regions than those of nickel ammine complex. Thus, it is considered that the stable formula of Au⁺ is [Au(S₂O₃)₂]³⁻ rather than [Au(NH₃)₂]⁺ in the nickel catalyzed ammonium thiosulfate solution. As well, the higher stability of nickel ion against aurous ion suggests minimizing the loss of the catalyst of nickel ion in the gold cementation by zinc. It means that the reagent cost is reduced to recycle the barren solution to the gold leaching stage, while the copper catalyzed system coprecipitated the entire catalyst of cupric ion along with gold. The chemistry of gold cementation by zinc powder is expressed as eq. (11).

\[
2\text{Zn} + [\text{Ni(NH}_3\text{)}_6]^{2+} + 2\text{S}_2\text{O}_3^{2-} + 2\text{H}_2\text{O} \rightarrow [\text{Zn(S}_2\text{O}_3\text{)}_2]^3- + [\text{Zn(NH}_3\text{)}_4]^{2+} \tag{11}
\]

Also, some nickel precipitation by zinc powder could occur as shown in eq. (12):

\[
2\text{Zn} + [\text{Ni(NH}_3\text{)}_6]^{2+} + 2\text{S}_2\text{O}_3^{2-} + 2\text{H}_2\text{O} \rightarrow [\text{Zn(NH}_3\text{)}_4]^{2+} + [\text{Zn(S}_2\text{O}_3\text{)}_2]^2- \tag{12}
\]

\[+2\text{NH}_3 + 2\text{OH}^- + \text{H}_2 \uparrow + \text{Zn} \downarrow \]

Figure 3 summarizes the schematic electrochemical mechanism of ammonium thiosulfate leaching of gold, which corresponds to eqs. (4) to (10).

3. Experimental

3.1 Gold leaching

3.1.1 Ore sample

Gold ore sample was supplied from Hishikari Mine, Kagoshima Japan by Sumitomo Metal Mining, Co., Ltd. The total amount of ore sample was 150 kg, and the ore size was inch 15~20 cm (0~8 inch). Those ore was crushed to −1.70 mm (−10 mesh) by jaw crusher (Denver H5902CB), a gyratory crusher (Allis-Chalmers) and a crushing roll.
(Sturtevant Laboratory Roll). The crushed ore was divided into 2 kg each using a rotation vibratory feeder. Finally, the 2 kg crushed ores were passed through a riffle 3 times, and then 0.3 kg samples were packed into paper bags for leaching samples.

Table 3 shows the results of chemical analysis of the ore. The ore matrix was silicate. The gold grade was 16.26 g/t by the fire assay method. From a 0.5 g of pulverized sample, was dried in an oven, and assayed for gold by the fire assay method.65,66) From a 0.5 g of pulverized sample adsorption spectrophotometer. The gold leached residue was filtered by a filter press. The filtered cake of two opposite quadrants, was used for leaching. The 150 g ground sample was put into a 2 dm³ bottle, and the calculated amounts of ammonia, ammonium thiosulfate and copper sulphate or nickel sulfate were fed into a bottle, and then a water was added to make a 33 solids% of slurry. The bottle was rolled on a bottle roller for 24 hours at an ambient temperature. Rotation speed of the bottle was about 60 rpm measured by a VMR digital taco meter.

After the leaching test, the gold pregnant solution was filtered using a vacuum pump with a buchner funnel and collected for gold assay. The filtered cake (residue) was washed with a 100 cm³ of water 4 times to wash out all gold pregnant solution trapped in the residue. The total volumes of pregnant and washed solutions were measured by a cylinder. The gold concentrations were measured by an atomic absorption spectrophotometer. The gold leached residue was dried in an oven, and assayed for gold by the fire assay method.65) The percentage of gold extraction was calculated from the total amount of gold in the leached residue and the pregnant solution as following:

Gold Extraction [%] = \[ \frac{[(Au)_{preg.sol.} + (Au)_{washed.sol.}]}{[(Au)_{preg.sol.} + (Au)_{washed.sol.} + (Au)_{residue}]} \times 100 \] (12)

where

- [(Au)_{preg.sol.}]: total amount of gold in pregnant solution [mg]
- [(Au)_{washed.sol.}]: total amount of gold in washed solution [mg]
- [(Au)_{residue}]: total amount of gold in leached residue [mg]

3.1.3 Thiosulfate analysis

The consumption of thiosulfate ion in a gold pregnant solution was assayed by the iodimetric titration method after the leaching.67) Procedure of the iodimetric titration was as follows:

(1) A 10 cm³ of thiosulfate solution was taken into a 50 cm³ beaker, pH of the solution is measured. If the pH is higher than 8, the solution pH was neutralized to be around pH 7~7.5 by 10 vol% H₂SO₄ solution (The total added volume of 10 vol% H₂SO₄ solution should be noted). This neutralized thiosulfate solution was transferred into a 25 cm³ burette for the iodimetric titration.

(2) The thiosulfate solution prepared in procedure 1 was filtered against 5 cm³ of I₂ solution, containing a 2~3 cm³ of 0.5 g/dm³ starch solution as indicator, in a 50 cm³ beaker for iodimetric titration. The end point is reached, when the colour of I₂ solution changed from deep brown to colour less. The total volume of thiosulfate solution required for titration was applied to evaluate the thiosulfate concentration.

To analyze a 0.2~0.5 mol/dm³ thiosulfate solution, a 0.05 mol/dm³ iodine solution was used. In the range of 0.01~0.2 mol/dm³ thiosulfate solution, a 0.02 mol/dm³ iodine solution was used. The iodine solution was prepared by dissolving 0.05 mol/dm³ I₂ with 40 g of KI in 1 dm³ flask. The starch solution was made by dissolving a 1.0 g of soluble starch in a 500 cm³ water by heating. The accuracy of the iodimetric titration was confirmed using standard ammonium thiosulfate solutions.

From the data obtained from the iodimetric titration presented above, thiosulfate concentration was evaluated to the following equation:

\[ M_I = \frac{2 \times M_t \times L_1}{L_2 \times \frac{V_1}{V_2}} \] (14)

Where, \( M_I \) is thiosulfate concentration [mol/dm³]; \( M_t \) is iodine concentration [mol/dm³]; \( L_1 \) is initial iodine volume (In this procedure, 5 cm³ at constant); \( L_2 \) is thiosulfate solution volume to titrate iodine solution [cm³]; \( V_1 \) is initial thiosulfate solution volume (In this procedure, 10 cm³ at constant); \( V_2 \) is thiosulfate solution volume [cm³] after pH adjustment.

Based on the thiosulfate concentration obtained from eq. (14), the total ammonium thiosulfate consumption during leaching was evaluated to the following:

Ammonium Thiosulfate Consumption [kg/t-ore] = \[ \frac{148 \times V_{lixviant} \times [S_2O_3^{2-}]_{consumed}}{W_{sample}} \] (15)

where, 148 is the molecular weight of ammonium thiosulfate at 1 mol /g/mol; \( V_{lixviant} \) is total volume of ammonium thiosulfate lixiviant utilized in leaching [dm³]; \([S_2O_3^{2-}]_{consumed}\) is total amount of thiosulfate consumed [mol/dm³]; \( W_{sample} \) is ore sample weight utilized for leaching [kg].
3.2 Gold cementation from ammonium thiosulfate solution

Zinc powders (supplied from Alfa Aesar) were used for gold cementation. The average diameter of the powder was 45 μm and purity was more than 98%. A known amount of the metal powder was added to a 50 cm$^3$ pregnant solution of the leaching experiments described in the section 3.1, and the suspension was gently agitated by a magnetic stirrer for 30 minutes at an ambient temperature under atmosphere.

After the gold cementation, the pulp was filtered immediately with a micro filter. The filtrate was assayed for gold, nickel, thiosulfate and ammonia. Gold, nickel and thiosulfate concentrations were evaluated in the same manner described in section 3.1. The ammonia concentration was measured by Nessler’s method (JIS 0102). Nessler’s method is a semi-quantitative method, and the standard deviation is around ±0.5 mol/dm$^3$ NH$_4^+$/NH$_3$.

To investigate the feasibility of recycling the ammonium thiosulfate solution, the concentrations of ammonia, nickel and thiosulfate before and after the gold cementation process were evaluated.

4. Results and Discussion

4.1 Preliminary gold leaching test

Figure 4 shows the gold extraction result from a silicate type ore by using the reagent combination of 0.005 mol/dm$^3$ NiSO$_4$, 0.5 mol/dm$^3$ (NH$_4$)$_2$S$_2$O$_3$ and 0.5 mol/dm$^3$ NH$_4$OH at pH 9.5. The gold extraction at 24 hours was 95% and the ammonium thiosulfate consumption was about 5 kg/t-ore, while 21 kg/t-ore of ammonium thiosulfate was consumed when 0.001 mol/dm$^3$ CuSO$_4$ was used as a catalyst. The ammonium thiosulfate consumption with copper catalyst was about 4 times higher than that with a nickel catalyst. It was obvious that the nickel ion significantly decreased the thiosulfate consumption.

4.2 Effect of ammonia, nickel and thiosulfate on gold extraction and ammonium thiosulfate consumption

The effects of ammonia, nickel and thiosulfate concentrations on gold extraction and thiosulfate consumption were investigated at the standard reagents composition of 0.5 mol/dm$^3$ NH$_4$OH, 0.005 mol/dm$^3$ NiSO$_4$ and 0.5 mol/dm$^3$ (NH$_4$)$_2$S$_2$O$_3$. The reagent concentrations was varied in the range of 0.1~0.5 mol/dm$^3$ NH$_4$OH, 0.0001~0.0005 mol/dm$^3$ NiSO$_4$ and 0.01~0.5 mol/dm$^3$ (NH$_4$)$_2$S$_2$O$_3$.

Figure 5 shows the effect of ammonia on gold extraction and ammonium thiosulfate consumption with 0.005 mol/dm$^3$ NiSO$_4$ and 0.5 mol/dm$^3$ (NH$_4$)$_2$S$_2$O$_3$. The gold extraction decreased from 95% to 60% as the ammonia concentration decreased from 0.5 to 0.1 mol/dm$^3$, while the ammonium thiosulfate consumption increased from 5 to 9 kg/t-ore. This result concludes that the increase of the nickel thiosulfate stability at the lower ammonia concentrations reduced the catalytic effectiveness for gold oxidation. Thus, the best concentration for gold extraction is 0.5 mol/dm$^3$ NH$_4$OH.

Figure 6 shows the effect of nickel concentration on gold extraction and ammonium thiosulfate consumption with 0.5 mol/dm$^3$ NH$_4$OH and 0.5 mol/dm$^3$ (NH$_4$)$_2$S$_2$O$_3$. The nickel concentration was varied in the range of 0.000~0.005 mol/dm$^3$. The result shows that both gold extraction and ammonium thiosulfate consumption were respectively constant at 95% and 5 kg/t-ore in the range of 0.0001~0.0005 mol/dm$^3$. At the nickel concentration of 0.001 mol/dm$^3$, the gold dissolution was not observed. The evidence suggests that nickel may act as a catalyst for gold extraction with small thiosulfate consumption. Also, the result, in which the gold oxidation was not initiated without the presence of a catalyst, confirms the reports from other researchers. The main cause of thiosulfate consumption in the nickel catalyzed system could be attributed to the natural degradation of thiosulfate in the gold leaching process. The minimum nickel concentration can be selected.
Au extraction, Au extraction, (NH₄)₂S₂O₃ on a 100 mass%-75 μm ground ore. Pulp density: 33 mass%, Ambient temperature, Atmospheric condition, Retention Time: 24 hours, Rotation speed: 60 rpm, pH 9.5. Δ: Au extraction, (NH₄)₂S₂O₃ consumption.

Fig. 6 Effect of nickel concentration on gold extraction and ammonium thiosulfate consumption with 0.5 mol/dm³ NH₄OH and 0.5 mol/dm³ (NH₄)₂S₂O₃ on a 100 mass%-75 μm ground ore. Pulp density: 33 mass%, Ambient temperature, Atmospheric condition, Retention Time: 24 hours, Rotation speed: 60 rpm, pH 9.5. Δ: Au extraction, (NH₄)₂S₂O₃ consumption.

Fig. 7 Effect of thiosulfate concentration on gold extraction and ammonium thiosulfate consumption with 0.005 mol/dm³ NH₄OH and 0.5 mol/dm³ (NH₄)₂S₂O₃ on a 100 mass%-75 μm ground ore. Pulp density: 33 mass%, Ambient temperature, Atmospheric condition, Retention Time: 24 hours, Rotation speed: 60 rpm, pH 9.5. Δ: Au extraction, (NH₄)₂S₂O₃ consumption.

Fig. 8 Gold extraction kinetics of the nickel catalyzed ammonium thiosulfate leaching at the condition of 0.5 mol/dm³ NH₄OH, 0.0001 mol/dm³ NiSO₄ and 0.05 mol/dm³ (NH₄)₂S₂O₃ at pH 9.5. Pulp density: 33 mass%, Ambient temperature, Atmospheric condition, Rotation speed: 60 rpm.

as 0.0001 mol/dm³.

Figure 7 shows the effect of thiosulfate concentration on gold extraction and reagent consumption in the range of 0.01−0.5 mol/dm³ (NH₄)₂S₂O₃. Nickel and ammonia concentrations were maintained at 0.005 mol/dm³ NiSO₄ and 0.5 mol/dm³ NH₄OH. The results show that the maximum gold extraction of 95% with the lowest ammonium thiosulfate consumption of 2 kg/t-ore was obtained at 0.05 mol/dm³ (NH₄)₂S₂O₃. The increase of thiosulfate concentration from 0.05 to 0.1 mol/dm³ increased the ammonium thiosulfate consumption from 2 to 5 kg/t-ore. In the range of 0.1−0.5 mol/dm³ (NH₄)₂S₂O₃, the ammonium thiosulfate consumption remained at 5 kg/t-ore. The 0.05 mol/dm³ (NH₄)₂S₂O₃ is the minimum concentration for achieving higher Au extraction under this reagent composition.

From the above results, the optimum reagent combination can be proposed as 0.0001 mol/dm³ NiSO₄, 0.05 mol/dm³ (NH₄)₂S₂O₃ and 0.5 mol/dm³ NH₄OH at pH 9.5. Figure 8 shows the result of gold extraction with this reagent composition, which resulted in 95% recovery in 24 hours. The ammonium thiosulfate consumption was 1.2 kg/t-ore, while the reagent consumption of copper catalyzed lixiviant was 3−5 kg/t-ore under 0.0001 mol/dm³ CuSO₄, 0.05 mol/dm³ (NH₄)₂S₂O₃ and 0.5 mol/dm³ NH₄OH at pH 9.5 and the sodium cyanide consumption was about 1.8 kg/t-ore with the 0.02 mol/dm³ (1.0 g/dm³) NaCN at pH 10.5. This experimental result demonstrates the advantage of nickel catalyzed ammonium thiosulfate leaching.52,53)

For further confirmation, ammonia and thiosulfate concentrations were varied with 0.0001 mol/dm³ NiSO₄. Figure 9 shows that the decrease in the ammonia concentration from 0.5 to 0.1 mol/dm³ causes a decrease in the gold extraction from 95 to 75% and an increase in the ammonium thiosulfate consumption from 1.2 to 3.5 kg/t-ore. The result supports that 0.5 mol/dm³ NH₄OH is an optimum concentration with the combination of 0.0001 mol/dm³ NiSO₄ and 0.05 mol/dm³ (NH₄)₂S₂O₃.

Figure 10 shows that the decrease of thiosulfate concentration from 0.05 mol/dm³ to 0.01 mol/dm³ decreased the gold extraction from 95% to 30%. The result also supports that 0.05 mol/dm³ (NH₄)₂S₂O₃ is an optimum combination with the combination of 0.0001 mol/dm³ NiSO₄ and 0.5 mol/dm³ NH₄OH. Thus, the results of Figs. 9 and 10 confirmed that an optimum reagent combination is 0.0001 mol/dm³ NiSO₄, 0.05 mol/dm³ (NH₄)₂S₂O₃ and 0.5 mol/dm³ NH₄OH, which resulted in the 95% of gold extraction with 1.2 kg/t-ore of (NH₄)₂S₂O₃ consumption, experimentally. This optimum reagent combination was used to construct the Eh-pH diagram as shown in Fig. 11. At the
pH of 9.5, which was the gold leaching condition in Fig. 8, the stable region of the nickel ammine complex was wider than that of Fig. 1. This is due to the decrease of nickel and thiosulfate concentrations from 0.005 to 0.0001 mol/dm$^3$ and from 0.5 to 0.05 mol/dm$^3$, respectively. The equilibrium electrode potential for gold to form an aurous ammine complex was higher than that of nickel as compared to in Figs. 2 and 11. The result supports that metallic gold was oxidized to thiosulfate complex ($[\text{Au(S}_2\text{O}_3)_2]^{2-}$), while the nickel ammine complex was stable enough to act as a catalyst in eqs. (4)$\sim$(10).

4.3 Gold cementation and solution recycling

Figure 12 shows the result of gold recovery from a nickel catalyzed thiosulfate pregnant solution, which was obtained under an optimum leach condition of 0.0001 mol/dm$^3$ Ni$^{2+}$, 0.05 mol/dm$^3$ S$_2$O$_3^{2-}$, 0.5 mol/dm$^3$ NH$_4$OH and $5 \times 10^{-3}$ mol/dm$^3$ Au$^+$.

Figure 12 shows the result of gold recovery from a nickel catalyzed thiosulfate pregnant solution, which was obtained under an optimum leach condition of 0.0001 mol/dm$^3$ Ni$^{2+}$, 0.05 mol/dm$^3$ S$_2$O$_3^{2-}$, 0.5 mol/dm$^3$ NH$_4$OH and $5 \times 10^{-3}$ mol/dm$^3$ Au$^+$.

The stability of nickel in the ammonium thiosulfate solution during zinc precipitation suggests that the nickel catalyzed ammonium thiosulfate leaching has an advantage against the copper catalyzed ammonium thiosulfate leaching process for minimizing the
cost of reagent loss.

The feasibility of recycling the nickel catalyzed thiosulfate barren solution to the leaching stage followed by zinc precipitation was also evaluated. When the barren solution was recycled to the leaching stage, the solution composition was readjusted based on the analytical results of nickel and thiosulfate consumption. After four stages of recycling test, around 95% of gold was successively extracted with only 1–3 kg/t-ore of ammonium thiosulfate consumption. About 30–50% of nickel ion was replenished in each stage. Ammonia concentration was kept at the same value during the gold cementation process. This confirms that recycling the barren solution followed by zinc precipitation would not affect the gold extraction and the thiosulfate consumption.

In terms of the cementation using copper or aluminum powders, it was confirmed that a dissolved copper ion caused the thiosulfate consumption, and that aluminum was insoluble at low ammonia (0.3 mol/dm$^3$) and thiosulfate (0.05 mol/dm$^3$). The stability of copper and aluminum in an ammonium thiosulfate solution has been discussed in our previous study.(52,53) Thus, those processes were not feasible.

### 4.4 Extraction of gold ore containing sulfide minerals

In this section, the optimum reagent combination of nickel catalyzed ammonium thiosulfate leaching was investigated on four gold ores containing iron and copper sulfide minerals. The 24 hour standard cyanidation process at 1.0 g/dm$^3$ (0.02 mol/dm$^3$) NaCN was also conducted to compare with the thiosulfate leaching. Table 4 shows the assay result of four gold ore samples A, B, C and D. Three of the ores (A, B and C) contained 1.5–2.5 mass% S, 0.01–0.30 mass% Cu and 4–6 mass% Fe. Ore D contained 50 g/t Au, 30 mass% S, 28 mass% Fe and 0.1 mass% Cu. In the thiosulfate leaching test, the thiosulfate concentration was varied in the range of 0.05–0.4 mol/dm$^3$. The ammonia concentration was varied in the range of 0.5–4 mol/dm$^3$. The nickel concentration was maintained at 0.0001 mol/dm$^3$.

Table 5 shows that the optimum reagent combinations for the ores were 0.1–0.3 mol/dm$^3$ (NH$_4$)$_2$S$_2$O$_3$ and 3–4 mol/dm$^3$ NH$_2$OH with 0.0001 mol/dm$^3$ NiSO$_4$. Overall, a higher ammonia concentration was required for the ores containing copper bearing sulfide minerals as compared to the silicate ore because the dissolved copper content from the sulfide mineral caused the thiosulfate consumption and retarded the gold extraction at the lower ammonia concentration. The blue color leach solution was the obvious evidence of copper dissolution. The gold extractions in thiosulfate leaching were larger than the results of cyanidation at 1.0 g/dm$^3$ (0.02 mol/dm$^3$) NaCN, but the reagent consumptions in thiosulfate leaching were obviously higher than that for cyanidation. For the copper bearing ore of sample A and the massive sulfide ore of sample D, 20 and 24 kg/t-ore of ammonium thiosulfate consumption occurred respectively, while 3–4 kg/t-ore NaCN was consumed with cyanidation. When copper was used as a catalyst, thiosulfate consumption was 25 kg/t-ore and 30 kg/t-ore respectively for samples A and D. For samples B and C, the thiosulfate consumption was 8 and 9 kg/t-ore respectively with nickel as a catalyst, while 13 and 10 kg/t-ore (NH$_4$)$_2$S$_2$O$_3$ was consumed respectively with copper as a catalyst. The gold extraction by thiosulfate with either copper or nickel as catalyst was relatively the same. However, the gold extraction by cyanidation was 8–21% lower than that by thiosulfate leaching.

### 5. Conclusion

Nickel catalyzed ammonium thiosulfate leaching test was carried out to investigate the optimum reagent combination on the variable types of ore at 100 mass%-200 mesh (75 μm). The optimum reagent combination was found as 0.0001 mol/dm$^3$ NiSO$_4$, 0.5 mol/dm$^3$ NH$_2$OH and 0.05 mol/dm$^3$ (NH$_4$)$_2$S$_2$O$_3$ for silicate type ore studied. Gold extraction was 95% with a 1.2 kg/t-ore of ammonium thiosulfate consumption. At an optimum reagent composition, zinc powder was the best media for gold cementation at nearly 100% of gold recovery. About 30–50% of nickel was co-precipitated along with gold by the cementation of zinc power. In the barren solution recycling test followed by cementation, the 4 stages of the solution recycling with nickel addition could give 95% gold extraction with 1–3 kg/t-ore of ammonium thiosulfate consumption successively. For the thiosulfate leaching of gold ores contained sulfide minerals,

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**Table 4** Assay results of gold ores contained iron and copper sulfide minerals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au (g/l)</th>
<th>Cu (mass%)</th>
<th>Fe (mass%)</th>
<th>S (mass%)</th>
<th>C (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25</td>
<td>0.3</td>
<td>5.2</td>
<td>2.5</td>
<td>0.8</td>
</tr>
<tr>
<td>B</td>
<td>7</td>
<td>0.01</td>
<td>6.4</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>0.1</td>
<td>4.3</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>D</td>
<td>50</td>
<td>0.1</td>
<td>28.2</td>
<td>30</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Table 5** Comparison of the gold extraction and the reagent consumption between the ammonium thiosulfate leaching and the standard cyanidation at 1.0 g/dm$^3$ (0.02 mol/dm$^3$) NaCN for 24 hours gold leaching test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optimum reagent combination</th>
<th>Au recovery (%)</th>
<th>Reagent consumption (kg/t-ore)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(NH$_4$)$_2$S$_2$O$_3$ (mol/dm$^3$)</td>
<td>NH$_2$OH (mol/dm$^3$)</td>
<td>NiSO$_4$/CuSO$_4$ (mol/dm$^3$)</td>
</tr>
<tr>
<td>A</td>
<td>0.2</td>
<td>3</td>
<td>0.0001</td>
</tr>
<tr>
<td>B</td>
<td>0.2</td>
<td>3</td>
<td>0.0001</td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>3</td>
<td>0.0001</td>
</tr>
<tr>
<td>D</td>
<td>0.3</td>
<td>4</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
the requirement of higher ammonia concentration and the result of higher thiosulfate consumption were unavoidable. The ammonium thiosulfate consumption in nickel catalyzed lixiviant was 1~5 kg/t-ore less than that in copper catalyzed lixiviant. The gold extraction was higher than that of the standard cyanidation at 1.0 g/dm$^3$ (0.02 mol/dm$^3$) NaCN. But the thiosulfate consumption on sulfide bearing gold ore was 3~7 times higher than the cyanide consumption.

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Mr. Toru Onozuka and Mr. Taro Aichi, Dowa Mining Co., Ltd., Japan are sincerely indebted for their management to Sumitomo Metal Mining Co., Ltd., Japan are sincerely indebted for their management to the requirement of higher ammonia concentration and the result of higher thiosulfate consumption were unavoidable. The ammonium thiosulfate consumption in nickel catalyzed lixiviant was 1~5 kg/t-ore less than that in copper catalyzed lixiviant. The gold extraction was higher than that of the standard cyanidation at 1.0 g/dm$^3$ (0.02 mol/dm$^3$) NaCN. But the thiosulfate consumption on sulfide bearing gold ore was 3~7 times higher than the cyanide consumption.

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