INTRODUCTION

The world gold production has primarily come from a hydrometallurgical route utilizing cyanide lixiviant. Cyanidation has been practiced since a century ago. There were two alternatives in the recovery of gold from cyanide leach solution, i.e. zinc cementation and carbon adsorption. It appeared that the modified zinc cementation or the so-called Merrill-Crowe process had long been known as the standard method to recover gold from cyanide solution. However, there was a renewed interest in the application of carbon adsorption. And since 1980 the modified carbon adsorption process, known as carbon-in-pulp (CIP) or carbon-in-leach (CIL), has gain its popularity, replacing the Merrill-Crowe process.

Due to the disadvantages of cyanidation, such as slow leaching rate, interference by other metal ions, and particularly environmental problem (Chen, et al., 1980; Pyper and Hendrix, 1981), alternative lixiviants have intensively been investigated. Thiourea seems to be a potential substitute for cyanide, especially in the area(s) of highly concerned environment (Wen, 1982).

Thiourea leaching in acidic solution or acidothiourea-tion has been tried to be applied on Indonesia’s gold ores, particularly those of Jampang Experimental Mine, West Java (Wakamatsu et al., 1986; Ardiwilaga, 1989). The recoveries of gold from thiourea leach solutions using carbon adsorption (Ardiwilaga, 1991) and cementation (Ardiwilaga et al., 1994) have also been studied. The effects of various parameters were reported, and the combined process, either acidothiourea-carbon adsorption or acidothiourea-cementation, was in favour of leaching conditions of low concentrations of thiourea (10 g/l), sulfuric acid (4.9 g/l), ferric ion (1 g/l), and in the absence of sulfurdioxide. However, both carbon adsorption and cementation exhibited low gold recoveries, around 50%, provided that coconut-shell activated carbons of -32+60 mesh and lead (powder) cementant were used. In order to
get a minimum total gold recovery (combined process) of 90%, a gold recovery of at least 80% should be obtained in the carbon adsorption or cementation stage.

The chemistry of cementation using lead as a cementant/precipitant is indicated by the overall reaction shown below:

$$2 \text{Au} (\text{CS} (\text{NH}_2)_2)^{+} + \text{Pb} \rightleftharpoons 2 \text{Au} + \text{Pb} (\text{CS} (\text{NH}_2)_2)^{2+} \quad (1)$$

Meanwhile, the mechanism of the adsorption of gold thiourea complex, \( \text{Au} (\text{CS} (\text{NH}_2)_2)^{+} \), onto activated carbon has come into an agreement that gold thiourea complex is adsorbed without a chemical change (Schmidt, 1988; Fleming (in Swaminathan, et al., 1993).

This paper is concerned with an attempt to find a way in obtaining a high gold recovery performed by either carbon adsorption or cementation. Deaeration technique was selected to be applied for both carbon adsorption and cementation processes. The effects of dissolved oxygen on gold recovery are evaluated and the mechanisms are postulated.

**EXPERIMENTAL**

**Materials and Apparatus**

The feed solutions used for carbon adsorption and lead cementant experiments came from the acidothioureation of Cimanggu-type gold ore. The ore characteristics has been described in literature (Wakamatsu, et al., 1986; Ardiwilaga, 1991; Ardiwilaga, et al., 1994).

The reagents used in acidothioureation were all of analytical grade. Coconut-shell activated carbon of -32+%60 mesh and lead powder were employed in carbon adsorption and cementation experiments, respectively.

Batch leaching runs were carried out in a glass reactor provided with a glass cover having four-necked glass lid. The central neck was used for a stirring glass rod provided with a teflon blade and driven by a variable electric motor.

Carbon adsorption and lead cementation experiments were conducted in a vacuum-type Erlenmeyer flask. Agitation was facilitated using the mechanism described for leaching runs. To conduct experiments at elevated temperature, the unit was placed on a heater which was capable of providing a relatively constant temperature to the pulp. Deaeration was performed by using a vacuum pump.

**Procedure**

The acidothioureation pretreatment runs were conducted at ambient temperature, 20% solids, 24 hours of retention time, and 100 rpm of stirring rate. In each run, a measured amount of ground ore of minus 200 mesh was lixiviated using a leaching solution containing 10 g/l thiourea, 5 g/l sulfuric acid, and 1 g/l ferric ion.

A portion (80 ml) of clarified pregnant solution was introduced to the carbon adsorption/cementation reactor. The experiments were conducted at 100 rpm of agitation and 25 g/l carbon or lead cementant loading. The other parameters were tested at two levels, i.e., retention times of 1 hour and 4 hours, temperatures of ambient and 40°C, pH of natural (as received) and 2.5 (by addition of aqueous ammonia) and reactor atmosphere of natural (atmospheric) and deaerated.

**RESULTS AND DISCUSSION**

The previous works (Ardiwilaga, 1991, Ardiwilaga, et al., 1994) revealed that the highest gold recovery of around 50% was achieved for both carbon adsorption and cementation processes. However, the performance of lead cementation appeared to be fairly better. Therefore, in order to improve gold recovery of lead cementation, the technique employed by Merrill-Crowe process for cyanide system was applied in this study. Deaeration of pregnant (leach) solution resulted in the improvement of zinc cementation for the recovery of gold from cyanide complex solution. Thus, lead cementation in thiourea system will be discussed first.

**LEAD CEMENTATION**

Cementation reaction is electrochemical in nature. In the gold recovery from gold thiourea complex solution using lead powder, gold is precipitated or cemented while lead metal goes into solution. The half cell reactions involved in the cementation process can be presented as follows:

**Anodic**

$$\text{Pb} + 4\text{CS} (\text{NH}_2)_2 \rightleftharpoons \text{Pb} (\text{CS} (\text{NH}_2)_2)^{2+} + 2e^- \quad (2)$$

**Cathodic**

$$\text{Au} (\text{CS} (\text{NH}_2)_2)^{+} + e^- \rightleftharpoons \text{Au} + \text{CS} (\text{NH}_2)_2 \quad (3)$$

**Effect of deaeration**

The previous work (Ardiwilaga, et al., 1994) indicated that lead cementation at atmospheric pressure resulted in gold recovery of 42%, provided that the experiment was conducted at 25 g/l lead powder loading, 1 hour of retention time, and ambient temperature. Under the same cementation condition but using deaerated pregnant solution, the gold recovery drops to 29%, as shown in Table 1. Further
drop in gold recovery is observed, when the natural (as received) pH of the pregnant solution is adjusted to 2.5. According to the previous work (Ardiwilaga, 1993), this pH adjustment could improve the recovery of cemented gold. It can be seen from Table 1 that the gold recovery is only 12%. Thus, cementation in thiourea system is not improved under deaerated conditions, as it is the case in cyanide system. Lower gold recovery is even obtained in thiourea system.

**Mechanism**

Under atmospheric condition, the pregnant solution contains some dissolved oxygen. The concentration of dissolved oxygen in water in equilibrium with air at 25°C is 4.1 ppm (Weast, 1964). According to Pletcher and Sotiropolous (1995), using Pt, Ag, and Au microdiscs, oxygen is reduced leading to the production of hydroxide ions and the formation of a layer at a cathode surface with a higher pH than the bulk solution due to reaction:

\[ O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^- \quad (4) \]

or

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (5) \]

In the meantime Alberty and Calvo (1983, in Pletcher and Sotiropolous (1994)) confirmed experimentally that pH changes occur at the gold electrode surface. Such changes in pH may be described as follows, using the reactions suggested by Pletcher and Sotiropolous (1994):

**Reduction reactions:**

\[ Au + H_2O + 2e^- \rightarrow Au + 2OH^- \quad (6) \]

\[ Au + H_2O + e^- \rightarrow AuH + OH^- \quad (7) \]

**Oxidation reactions:**

\[ Au + H_2O \rightarrow AuO + 2H^+ + 2e^- \quad (8) \]

\[ Au + H \rightarrow Au + H^+ + e^- \quad (9) \]

Since the oxygen reduction in either reaction (4) or (5) is occurring in alkaline environment (Pletcher and Sotiropolous, 1995), the cathodic reaction of oxygen reduction is the case for cyanide system, in which the cementation is operated in alkaline environment. The hydroxide ions produced by oxygen reduction are sufficient to produce an alkaline environment close to the surface which determines the potential for H adsorption (Pletcher and Sotiropolous, 1994). The oxygen reduction (reaction (4) or (5)) and the hydrogen adsorption (reaction (6) and (7)) seems to retard the cementation process in cyanide system. Therefore, the zinc cementation practice to recover gold from cyanide complex solutions is performed under deaerated conditions.

On the contrary, the lead cementation in thiourea system is performed in acidic environment. The gold recovery is lowered when deaeration is applied. If hydroxide ions are added, by adjusting the pH from natural pH (=1.67) to pH 2.5, the gold recovery is also reduced. The oxidation reactions (8) and (9) are likely to be maintained by conducting the cementation process under atmospheric pressure and at natural pH. Recovery of gold from thiourea complex solution using lead requires some amounts of dissolved oxygen. Therefore, the deaerated condition is not recommended for the cementation of gold thiourea complexes.

**CARBON ADSORPTION**

**Effect of deaeration**

It can be seen from Table 1 that in the presence of dissolved oxygen, gold recovery from thiourea leach solution using carbon adsorption is 52%, provided that adsorption experiment was conducted at 25 g/l of carbon loading (carbons of -32+60 mesh), 1 hour of retention time, and ambient temperature (leaching conditions: 10 g/l thiourea, 5 g/l sulfuric acid, 1 g/l ferric ion, and 20% solids). This is in agreement with the previous work (Ardiwilaga, 1991). Table 1 also shows that a lower gold recovery (=42% Au) is observed when elevated temperature an elevated temperature (=40°C) and a longer retention time (=4 hours) are experimented. The gold recovery can be increased when the reactor is deaerated, keeping the other variables constant. Further increases in gold recovery are obtained by increasing the retention time (Table 1 indicates a gold recovery of 73% Au at 1 hour and 81% at 4 hours). Furthermore, when the natural pH of the leach solution is adjusted to about 2.5, the gold recovery drops to 30% Au under a deaerated condition (see Table 1).

The observed data indicate that gold recoveries from thiourea leach solutions using carbon adsorption are improved under deaerated conditions, while pH is maintained at the natural pH. This phenomenon is quite different as compared with the cyanide system. While Adams (1990) concluded that oxygen shows an insignificant effect on the adsorption of aurocyanide onto carbon under all practical conditions (high ionic strength), Woollacott and Guzman (1993) demonstrated that gold adsorption increases as the dissolved oxygen is increased under the same conditions.
Mechanism

Since gold thiourea and gold cyanide complexes are adsorbed onto activated carbon without a chemical change one would expect that the same behaviour would be performed by both complexes. The expectation is not in accordance with the experimental results, as described above. The observed phenomena are therefore explained by the differences in charges, i.e. gold thiourea complex is positively charged \((Au\,(CS\,(NH_{2})_{2})^{2+})\), while a negative charge is associated with gold cyanide complex \((Au\,(CN_{2}^{-})\).

According to electrochemical theory of carbon adsorption, as proposed by Frumkin (in Habashi, 1980), when oxygen is in contact with an aqueous suspension of charcoal, it is reduced to hydroxyl groups and \(H_{2}O_{2}\) is liberated:

\[
\text{O}_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \quad (10)
\]

Since the electrons are supplied by the charcoal, it will acquire a positive charge. To maintain electrical neutrality on the surface of the charcoal, anions are attracted to the charcoal, resulting in their adsorption. This mechanism explains the adsorption of the negatively charged gold cyanide complexes onto activated carbons, which is widely practiced in the presence of dissolved oxygen. The adsorption of positively charged thiourea complexes onto activated carbons requires another mechanism.

As described in the literature (Schmidt, 1988; Gallagher, et al., 1990; Ardiwilaga, 1991; Lu and Bai, 1992; Swaminathan, et al., 1993), and confirmed by the present study, the positively charged gold thiourea complexes are adsorbed onto activated carbons in the presence of dissolved oxygen. It seems reasonable, therefore, that the activated carbon, either of coconut-shell or apricot pit, possesses adsorption sites of negative surface charge. And, as mentioned above, the adsorption of gold thiourea complexes onto activated carbon is improved under deaerated conditions. It can be postulated that the absence of dissolved oxygen produces a large negative surface charge or the dissolved oxygen retards the adsorption of gold thiourea complex by activated carbon.

CONCLUSIONS

From the discussion mentioned above it can be concluded that:

1. The gold recovery from thiourea leach solution using cementation process decreases from 42% to 29% as deaeration is performed in the reactor. The cementation process is likely to be in favour of hydrogen desorption and oxygen adsorption at the surface of cemented gold, while natural pH is being performed.
2. The gold recovery from thiourea leach solution using carbon adsorption increases from 52% to 73% (in 1 hour) or 81% (in 4 hours) as the process is conducted on deaerated leach solution. The surface of activated carbons seems to have adsorption sites of negative and positive surface charges. Deaeration produces a large negative surface charge.

REFERENCES


