Chapter 27

RESEARCH AND DEVELOPMENT ACTIVITIES FOR THE RECOVERY OF GOLD FROM NONCYANIDE SOLUTIONS

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ABSTRACT

Although most gold production from primary resources is achieved by cyanidation, many research activities have focused on alternative processes using noncyanide lixiviants. Such research has been prompted by environmental concerns and problems associated with the processing of refractory gold ores. Numerous research projects have been conducted to search for a noncyanide hydrometallurgical process for gold extraction. In this paper, a technical review of gold recovery from noncyanide solutions is presented, and new results are reported. Gold recovery techniques that are considered include activated carbon adsorption, cementation, solvent extraction, ion exchange, and reduction-precipitation.

INTRODUCTION

Although the gold price has dropped significantly since its high of about $800 in 1982, mine production of gold has continued to increase. Several large gold mines have been brought into production in recent years. The development of heap-leach technology for low-grade ore has extended the world resource base considerably. Also, new processes for the treatment of refractory gold ores have recently been developed.

The most common leaching process for gold dissolution involves cyanidation, a process that has been practiced for over a century. Industrially, the recovery of gold from dilute alkaline cyanide solutions is accomplished by the well-established procedures of carbon adsorption and zinc-dust cementation. Alternative processes have been studied extensively and include ion-exchange resin technology, solvent extraction and direct electrowinning. Research and development activities for the

recovery of gold from alkaline cyanide solutions have been reviewed and reported (Wan and Miller, 1990).

Although most gold production from primary resources is achieved by cyanidation, many research activities have focused on alternative processes involving noncyanide lixiviants. Noncyanide lixiviants for gold extraction have been considered because of environmental concerns associated with cyanidation. Also, in recent years, there has been considerable interest to develop lixiviants other than conventional cyanide in order to treat refractory gold ores. Generally, refractory gold ores require pretreatment prior to cyanidation for gold recovery. The resistance of refractory gold ores to conventional cyanide leaching can be related to the presence of carbonaceous materials (preg-robbing activity), gold association with sulfide minerals, and silica encapsulation. Thus, the processing of refractory ores is difficult and costly. Numerous research projects have been conducted to search for a noncyanide hydrometallurgical process for gold recovery from refractory ores.

Noncyanide lixiviants include the halide, thiourea, thiosulfate and thiocyanate systems. In this paper, a technical review of gold recovery from different lixiviants is presented and new research results are reported. Gold recovery techniques that are considered include carbon adsorption, cementation, solvent extraction, ion exchange and reduction-precipitation.

HALIDE SYSTEMS

Although most of the gold produced is the result of cyanide processing, there are a number of applications in which gold is produced from chloride solutions. Such applications are:
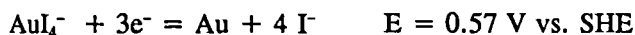
1. The refining of platinum group metals from matte-leach residues, where gold is extracted as a by-product.

2. The processing of anode slimes, where gold occurs as a minor constituent together with silver, selenium, and tellurium.

3. The recycle processing of scrap from the jewelery and electronic industries. In most of these cases, gold is extracted with a chloride electrolyte.

In addition, at Newmont Gold operations in Nevada, a chlorination process has proven to be a reliable and economic process for the treatment of carbonaceous refractory ore since operations first began in 1971. Most recently, a flash chlorination process was developed and this operation began in 1988 (Seymour et al., 1989). After chlorination, gold is recovered from the chloride solution by reduction of the gold chlorocomplex ion to metallic gold followed by redissolution via conventional cyanidation. Research has been carried out to search for a cost-effective method to recover gold directly from the chloride solutions and to avoid the neutralization and cyanidation steps. In recent years, considerable research has also been carried out for the bromide and iodide systems (Dadgar, 1989; Davis et al., 1993; Qi and Hiskey, 1993). Gold

recovery from these halide systems includes adsorption by activated carbon (Siegel and Soto, 1984; Avraamides *et al.*, 1985; McDougall and Fleming, 1987; Hughes and Linge, 1989; Sun and Yen, 1993), ion exchange (Hiskey and Jiang, 1990; Wan and Ball, 1990), cementation, solvent extraction (Salvado *et al.*, 1990), or direct reduction to gold precipitate by appropriate reducing reagents.

Gold Recovery by Activated Carbon Adsorption

Unlike the case of gold adsorption from alkaline cyanide solution by activated carbon (Sibrell and Miller, 1992), gold adsorption from halide solutions might be expected to involve electrochemical reduction, due to the relative instability of the gold halide complexes and the ability of activated carbon to act as a reductant. The standard reduction potentials for gold halide species are:

$$AuCl_4^- + 3e^- = Au + 4\ Cl^- \qquad E = 1.00\ V\ vs.\ SHE$$

$$AuBr_4^- + 3e^- = Au + 4\ Br^- \qquad E = 0.87\ V\ vs.\ SHE$$

$$AuI_4^- + 3e^- = Au + 4\ I^- \qquad E = 0.57\ V\ vs.\ SHE$$

whereas the reduction potential for activated carbon ranges from 0.1 to 0.4 V vs. SHE. Thus, it might be expected, based on thermodynamics, that activated carbon would reduce gold from halide solutions in the order: Cl > Br > I.

In chloride media, as in all halide solutions, Au(I) is relatively unstable, spontaneously and slowly disproportionating to metallic gold and Au(III). Since chloride is a strong complexing agent for Au(III), even at low concentrations of free chloride ions, the gold is present as $AuCl_4^-$.

Several researchers have investigated the fundamentals of gold loading by activated carbon from chloride solutions under various conditions. In the case of chloride, it has been found that metallic gold deposits superficially on the carbon surface and that the uptake of gold by activated carbon follows a mechanism whereby gold(III) is reduced to the metallic state. The reduction of gold at the carbon surface is analogous to an electrochemical cementation (contact reduction) reaction whereby a more noble metal ion is reduced to the metallic state by a more electropositive substrate. The schematic representation of this process is shown in Figure 1. Siegel and Soto (1984) observed spherical gold particles at the surface of activated carbon. McDougall *et al.* (1987) observed activated carbon particles coated with metallic gold after immersion in an $AuCl_4^-$ solution. Hiskey *et al.* (1990) found that metallic gold appeared as deposits both on the carbon surface and to a lesser extent in the pore space of the carbon particle. The metallic gold particles deposited predominantly at the carbon surface in the form of fine globules, and some pore reduction occurred due to the relative rate of solution ingress. The grain size of the globules ranged from 5 μm to 20 μm. Very fine spherules of micron-size gold were disseminated internally just below the carbon surface. Also, it was interesting to notice that the gold preferentially deposited at carbon edges and other surface irregularities as shown in Figure 2.

Gold loading onto activated carbon from bromide solution has also been studied (Dadgar, 1989; Mensah-Biney *et al.*, 1993; Pesic and Storhok, 1992). Mensah-Biney *et al.* (1993) suggested that gold loading on activated carbon was by mass transfer of AuBr$_4^-$ to the external surface and subsequent reduction to metallic gold. Their SEM examination clearly showed deposits of metallic gold on the carbon surface. The amount of elemental gold loaded was as high as 1200 mg Au/g of carbon. Contrary to these results, Pesic and Storhok (1992) reported that not much metallic gold was produced during gold adsorption from gold bromide solutions. In this regard, gold adsorption from bromide solutions was explained to be due to the adsorption of the AuBr$_4^-$ species. The nature of the proposed AuBr$_4^-$ adsorption reaction was not discussed. It appears that the presence and concentration of free Br$_2$ has a profound influence on the electrochemical discharge and formation of metallic gold at the activated carbon surface.

Figure 1. Schematic of the electrochemical reduction of gold at a carbon surface (Hiskey *et al.*, 1990).

Recently, the dissolution of gold in iodide-iodine solutions has been investigated to determine the fundamental solution chemistry and electrochemistry of the process (Davis *et al.*, 1993; Qi and Hiskey, 1993). Hiskey and co-workers (1990) examined the effect of iodide additions to a chloride solution in an attempt to overcome the superficial deposition of gold at the carbon surface. They found that increasing the iodide concentration in a gold chloride solution shifted the loading mechanism from electrochemical reduction to an adsorption-type mechanism. Their SEM examination revealed a decrease in the amount of metallic gold deposited with an increase in iodide concentration.

From a practical viewpoint, gold recovery from halide solutions using activated carbon has two major problems. First, reduction of gold by activated carbon makes conventional stripping difficult. Second, the finely precipitated metallic gold can be abraded from the activated carbon and lost in the tailings.
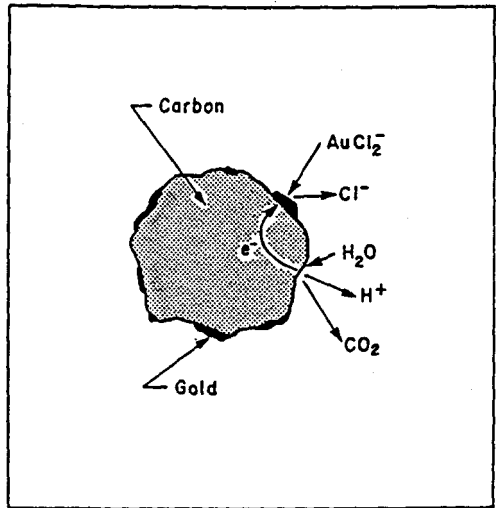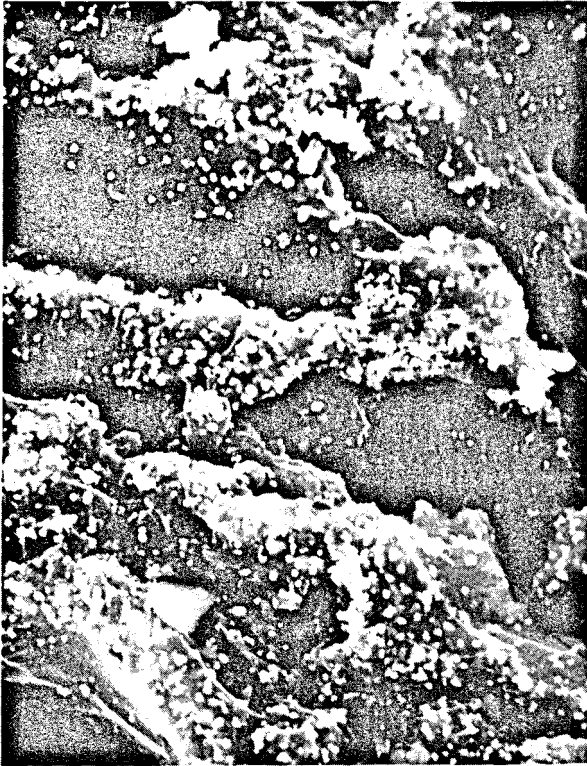
Figure 2. SEM micrograph of the carbon surface showing
deposited gold, 3000 × (Hiskey *et al.*, 1990).

Ion Exchange Technology

In the acid gold-chloride system, the existence of hypochlorite results in high oxidizing potentials. Of course, both strong-base and weak-base resins can load gold from such acidic chloride solutions; however, most of the commercial resins are not stable under such oxidizing conditions. The strong oxidizing agent, hypochlorite, attacks the polymeric linkages of the resin matrix and causes resin degradation.

Results for gold recovery from hypochlorite solution using some anion exchange resins are shown in Figure 3 (Wan and Ball, 1990). Resins used in this study were: Ionac SR-3, manufactured by Sybron Chemical Inc.; Dowex 21-K, by Dow Chemical; and PAZ-1-P, made in Israel.

The results presented in Figure 3 indicate that all these anion exchange resins behave as strong-base resins and that gold can be extracted over a wide pH range. However, except in the case of Dowex 21-K resin, no hypochlorite ion can be detected in the acidic solution after adsorption due to resin reaction with hypochlorite. All these resins were found to be physically degraded in such acidic hypochlorite

solutions.

The anion exchange resin was also reported to be degraded by complexed bromine. Mensah-Biney *et al.* (1993) studied the loading characteristics of the anion exchange resin, PAZ-4. They suggested that the mechanism for loading consisted of initial adsorption of the $AuBr_4^-$ species by a simple ion-exchange process followed by reduction to elemental gold by an electron exchange reduction reaction. Again, as in the case of the chloride system, the resin was observed to be oxidized and degraded in such solutions.

Reagents reported for the extraction of Au(III) from chloride media are molecules containing C-O bonds. Dibutyl "Carbitol" (DBC) is a long-chain ether used in the commercial refining of gold from platinum. Not only are ethers capable of extracting gold from acid chloride solutions, but it has been reported that long-chain carboxylic acids as well as alcohols, esters and ketones (*e.g.*, MIBK) will extract gold from acid chloride solutions (Fieberg and Edwards, 1978). Fritz and Millen (1973) demonstrated that XAD-7 and XAD-8 polyacrylic ester resins possess the ability to selectively load Au(III) from 1 M HCl solutions. They believed that the ion pair, $H_3O^+ \cdots AuCl_4^-$, was adsorbed on the resin through the formation of a weak bond with the ester oxygen of the polymer matrix.

Figure 3. Gold adsorption from chloride/hypochlorite solution by SR-3, Dowex-21K, and PAZ-1-P resins.

These neutral polyacrylic ester adsorbents also appear to be much less active with respect to hypochlorite oxidation (Wan and Ball, 1990). It was found that gold adsorption on the neutral polyacrylic ester adsorbents is a strong function of solution pH. Gold can be adsorbed in acidic solutions and be removed by stripping with an alkaline solution. Figure 4 illustrates the equilibrium isotherms for gold extraction from hypochlorite solution by XAD-8 at different pH values. Experimental data confirm that increased pH values lower the extent of gold loading on the resin. It is evident that gold can be loaded from acidic hypochlorite solution and stripped from the resin with alkaline solutions.
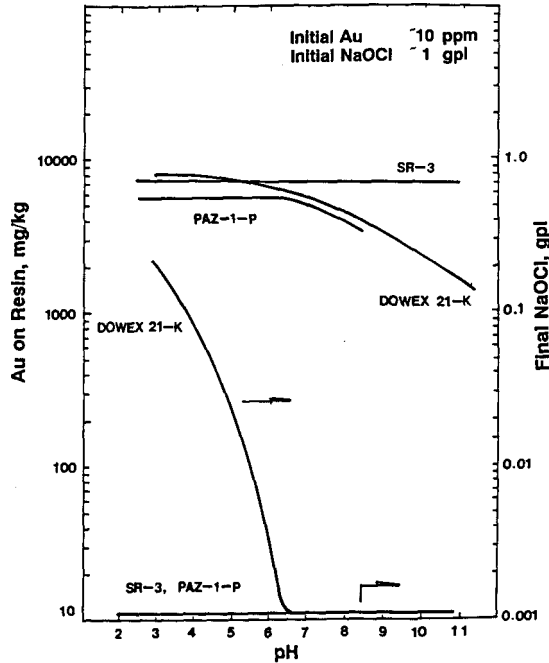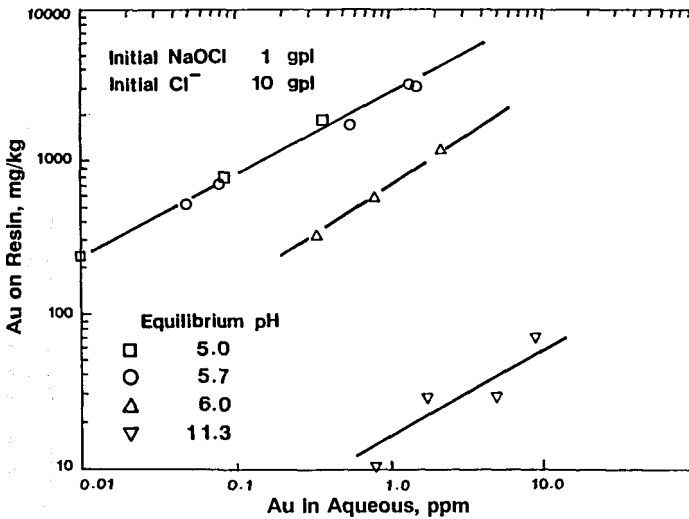
Figure 4. Effect of pH on gold adsorption for XAD-8.

Adsorption of ions by neutral polymeric adsorbents generally involves weak forces such as hydrogen bonding forces or dispersion forces since they lack stronger bond forming functional groups in their structure. Thus elution of gold is expected to be easier than elution from ion exchange resins. On the other hand, the loading capacity of neutral polymeric adsorbents might be expected to be significantly less than that of ion exchange resins because of the nature of the adsorption process. It is important to note that the polyacrylic ester resins are less reactive with hypochlorite when compared to other resins; thus, degradation by oxidizing agents is expected to be less severe.

Generally, the chloride solution contains a host of other metal ions depending on the minerals present in the leaching system. Selectivity considerations are of particular interest since the adsorption of other metal ions on the resin reduces the loading capacity for gold. Test results indicate that the polyacrylic ester adsorbents provide a high selectively for gold with respect to other base metal ions, as shown in Table 1.

Gold adsorption from chloride/hypochlorite solution by polyacrylic ester adsorbents has been found to be an interesting possibility. Gold loading can be performed in an acidic media, and elution of gold is possible with an alkaline strip solution. No additional regeneration procedure is required. Important features of the process are the stability of the adsorbent and its loading capacity. Cyclic experiments were performed to test the stability of the XAD-8 adsorbents in chloride/hypochlorite solutions. Gold was loaded at pH 4.2 and stripped at pH 10.5. After 16 days of

Table 1. Adsorption of Cu, Zn, and Ni on XAD-8
from Chloride/Hypochlorite Solution

Metal	Equilibrium pH	NaOCl gpl	Cl⁻ gpl	Metal in Solution, ppm Initial	Metal in Solution, ppm Final	Loaded %
Cu	5.5	0.95	11.2	4	4	0
	5.6	0.95	11.2	9	9	0
Zn	5.3	0.99	9.6	4	4	0
	4.4	0.99	9.8	10	10	0
Ni	5.4	0.99	9.6	4	4	0
	5.5	0.99	9.7	9	9	0

loading/stripping, no physical degradation was observed. The photomicrographs shown in Figure 5 indicate that no breakdown of the resin occurred after 16 days of cyclic testing.
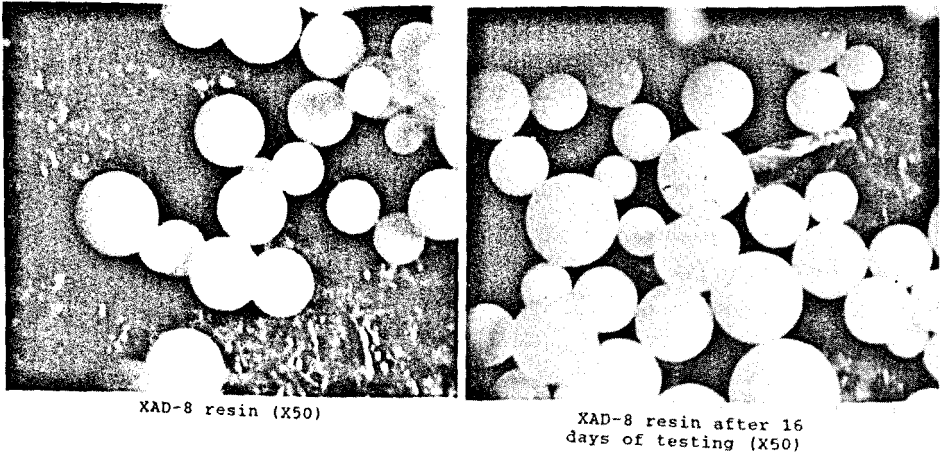

XAD-8 resin (X50)

XAD-8 resin after 16 days of testing (X50)

Figure 5. Photomicrographs of XAD-8 as-received
and after 16 days of cyclic testing.

Cementation

Zinc dust cementation is a well-known gold recovery process based on electrochemical reaction phenomena (Wan and Miller, 1990). Such cementation reactions are possible for gold recovery from acid halide solutions, although consumption of the active metal, such as zinc, is significant. Generally cementation reactions are found to be boundary-layer mass-transfer-controlled reactions in the absence of complicating factors (anodic closure, passivation, alloy formation, etc.), and the gold halide systems are no exception.

By way of example, gold cementation from acid chloride solutions is particularly interesting when contrasted to gold cementation from alkaline cyanide solutions. Depending on experimental conditions, both reactions can be found to be first-order processes limited by boundary-layer diffusion. However, in the cyanide system, anodic closure can lead to virtual cessation of the reaction, and this is revealed by the tenacious protective gold deposit shown by the SEM micrograph presented in Figure 6. In contrast, gold deposition at the zinc surface from an acid chloride solution is dendritic and rather fragile, as is evident from Figure 6. Under these circumstances, the reaction is sustained because of the availability of anodic sites. However, due to the fragile nature of the deposit, redissolution may occur when the gold dendrites are broken from the surface and are no longer in contact with the zinc anode.

In the chloride system, there is a strong tendency for alloy formation. Both XRD and SEM/EDAX analyses verify the presence of AuZn alloys in the surface deposit. In the case of cementation from alkaline cyanide solution, alloy formation is only
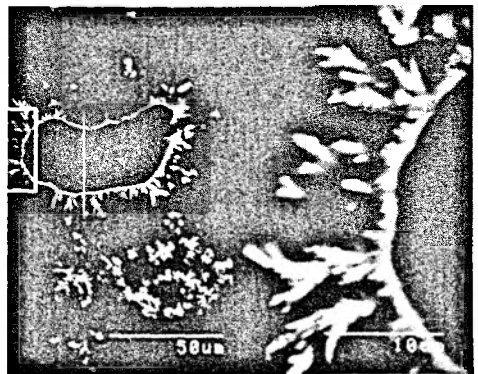
$Au(CN)_2^-/Zn$ System
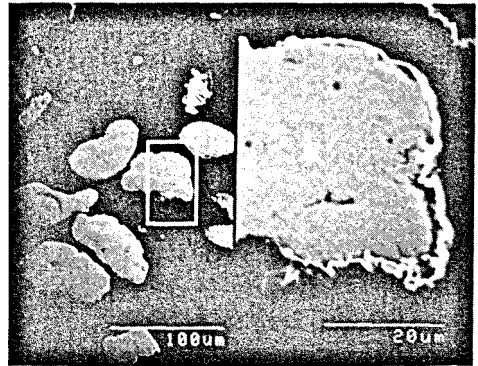
$AuCl_4^-/Zn$ System

Figure 6. Gold deposits at the zinc surface from cyanide solution and from acid chloride solution.

detected when the reaction is limited with respect to the free cyanide concentration. At high concentrations of free cyanide, when sufficient cyanide is present to complex the zinc released to solution, only pure gold is detected at the zinc surface.
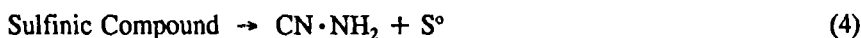
ACIDIC THIOUREA SYSTEM

Gold is leached in acidic solutions of thiourea, according to the following anodic reaction,

$$Au + 2CS(NH_2)_2 = Au(CS(NH_2)_2)_2^+ + e^- \tag{1}$$
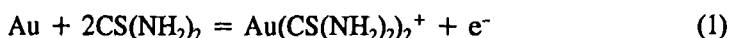
which requires an oxidant, and it has generally been acknowledged that the use of ferric ion in sulfuric acid solutions is the most effective.

However, it is important to note that thiourea is unstable and can be oxidized in a number of other reaction steps:

$$2CS(NH_2)_2 = (CSNH_2NH)_2 + 2H^+ + 2e^- \tag{2}$$

$$(CSNH_2NH)_2 \rightarrow CS(NH_2)_2 + \text{Sulfinic Compound} \tag{3}$$

$$\text{Sulfinic Compound} \rightarrow CN \cdot NH_2 + S^\circ \tag{4}$$

Reaction (2) is a reversible reaction between thiourea and formamidine disulfide. Formamidine disulfide decomposes to yield thiourea and a sulfinic compound which further decomposes to cyanamide and elemental sulfur. Controlling the redox potential is very important in order to prevent the chemical degradation of thiourea, which certainly would impact gold recovery from acidic thiourea solution.

The oxidation reaction products of thiourea using different oxidants, *e.g.,* hydrogen peroxide and ferric ion, were identified by HPLC and UV/visible spectroscopy (Bukka *et al.,* 1992). Results indicate that the reaction products in each case were different. In the case of ferric ion oxidation of thiourea, the reaction points to the formation of formamidine disulfide. The product from hydrogen peroxide oxidation remains unknown. Results also indicate that the oxidation reaction of thiourea by ferric ion does not go to completion and appears to achieve an equilibrium position when 50% of the thiourea is converted to formamidine disulfide. Further, at relatively longer reaction times, oxidation of formamidine disulfide forms sulfur, among other oxidation products.

Thiourea leaching has been studied by several researchers as a potential substitute for cyanidation. The fast dissolution rate compared to cyanidation is one advantage of thiourea leaching. Some refractory gold ores are specially treated using thiourea. In certain geographic locations thiourea leaching has been considered because of environmental concerns associated with cyanidation. Thiourea has been used for years in the treatment of thyroid diseases and currently is considered to be noncarcinogenic to humans. Acidic thiourea solutions for certain applications could offer a nontoxic

option for processing gold and silver.

Potential applications for thiourea in the processing of gold have been reviewed and the chemistry of the thiourea-gold system has been discussed in the literature (Groenewald, 1977; Hiskey, 1981). Also, thiourea leaching of gold from different ores has been reported (Nomvalo, 1986; McInnes *et al.*, 1989). Recently, Tremblay *et al.* (1993) studied percolation leaching with a thiourea solution for processing a low-grade gold sulfide deposit. They concluded that to limit the thiourea decomposition and to optimize gold extraction, it was necessary to maintain the leaching potential between 0.42 to 0.45 V (SHE).

Pressure oxidation followed by acidic thiourea leaching was found to give high gold extractions for refractory sulfide ores (Yen and Wyslouzil, 1986), especially carbonaceous sulfide ores (Ball and Wan, 1990). Biooxidation treatment followed by acidic thiourea leaching was also effective for gold extraction from a preg-robbing carbonaceous-sulfide ore (Brierley and Wan, 1990).

A number of investigations on gold recovery from thiourea solution have been reported in recent years and several options for gold recovery reported. These include activated carbon adsorption (Hisshion, 1984; Deschenes, 1986; Fleming, 1987; Schmidt, 1988), cation exchange adsorption (Simpson *et al.*, 1984; Nakahiro *et al.*, 1992), cementation (Teutli *et al.*, 1990), hydrogen reduction (Deschenes *et al.*, 1989), electrowinning (Ghali and Dupuis, 1989), and reduction-precipitation with sodium borohydride (Awadalla and Ritcey, 1990). Most of the tests have been conducted in the laboratory, and no work has been published to show the effect of leach solution recycle. Only one small-scale industrial application of thiourea leaching with carbon adsorption was reported at New England Antimony Mines, New South Wales (Hisshion and Waller, 1984). Gold antimony concentrate was leached with thiourea and the pregnant solution treated with activated carbon to recover gold. The loaded carbon was sold as a gold-carbon concentrate with a gold concentration of about 6 to 8 kg/t. No further information was reported.

Activated Carbon Adsorption

Gold recovery from acidic thiourea solutions by activated carbon adsorption is reported to be very high. One of the major drawbacks of the process is the high loss of thiourea (about 30%) in the leach solution due to adsorption by activated carbon. Although thiourea-loaded carbon can be washed out by hot water, this wash must be performed in the absence of oxygen (Schulze, 1984). Fleming (1987) found that the gold-thiourea is loaded onto carbon without undergoing chemical change, *i.e.*, as the $Au(CS(NH_2)_2)_2^+$ species, and the loading mechanism is similar to that observed in the cyanide system, adsorption occurring as an ion pair. However, excess thiourea in solution plus an oxidant such as ferric ion has a deleterious effect on the adsorption of the gold-thiourea complex, and the capacity is reduced by up to 90% due to oxidation of excess thiourea producing elemental sulfur. It appears that thiourea

undergoes oxidation to formamidine disulfide, which is strongly adsorbed onto carbon and subsequently further oxidizes to elemental sulfur. The elemental sulfur physically deposits in the carbon macropores, thereby impeding the diffusion and adsorption of the gold thiourea complex.

Also, in our recent study, it was found that the elemental sulfur precipitation at the carbon surface strongly affects gold recovery from thiourea solution. Activated carbon catalyzes the oxidation/degradation of thiourea resulting in the formation of elemental sulfur, which deposits in the carbon macropores and significantly reduces the carbon's effectiveness. The loading capacity drops significantly after several days of cyclic testing.

Elution of the gold-thiourea complex from the loaded carbon is found to occur quite readily. About 90% of the gold can be eluted from the carbon with inorganic stripping solutions or solutions with organic solvents. Sodium cyanide and sodium sulfide are effective eluates, and the rate of elution with cyanide is enhanced significantly by the addition of polar organic solutes or solvents. Yen *et al.* (1992) studied the use of organic solvents in thiourea solution to strip the gold thiourea complex from loaded carbon and found the effectiveness of the organic solvents to follow the order:

> Butanol > Acetonitrile > Diethyl Ether > Ethanol > Acetone

All elution methods generally recover precious metals, and a further scrubbing step is necessary if adsorbed impurities have to be removed in order to regenerate the capacity of the activated carbon. No studies have been published which consider the effect of activated carbon recycle on the efficiency of gold recovery.

Cation Exchange Resins

Cation exchange resins such as AG–50W–X8 or Amberite 200 have been tested by several investigators (Simpson *et al.*, 1984; Nakahiro *et al.*, 1992) for gold recovery from thiourea solutions. Although these results suggest that cation exchange resins would be effective, results from recent testing show that effective gold recovery from acidic thiourea using cation exchange resins is not possible. The acid leach allowed for the dissolution of a variety of metals and these metal cations loaded onto the cation exchange resin, thereby substantially reducing the gold-loading capacity. In addition, and most importantly, elemental sulfur coated the resin and significantly reduced resin capacity. Unless selective cation exchange resins are developed, it is unlikely that gold recovery from acidic thiourea solutions will be a viable process alternative.

Cementation

In the case of gold recovery from thiourea solutions, it seems that adsorption processes will not be too successful due to decomposition of thiourea and elemental sulfur formation. Another option for gold recovery from thiourea solution is cementation. Cementation of gold and silver from cyanide solutions is commonly practiced with the Merrill-Crowe Process. Powered zinc is added to the clarified, deaerated, pregnant cyanide solution. The zinc is removed from the solution using a plate-and-frame filter press. Both cyanide leach solutions and carbon strip solutions are commercially treated using zinc cementation. In acidic thiourea solutions, cementation with zinc is not possible. Zinc generates hydrogen gas in acidic solutions, which causes excessive zinc consumption.

Cementation of gold from thiourea solutions using iron has been pilot plant tested in China (Hu, 1989), where iron plates were used to cement gold from thiourea leach systems; however, no further information was reported. Cementation of silver from thiourea solution using aluminum has been studied (Teutli et al., 1990), and the authors concluded that the cementation rate was controlled by the dissolution of the passivating aluminum oxide layer. An induction time which occurred before initiation of cementation reaction was also attributed to the presence of the oxide layer. The addition of an undisclosed activator was found to eliminate passivation of the aluminum, and the silver cementation rate was improved.

From recent test results, aluminum cementation for gold recovery from thiourea solution was found to be technically viable, but deaeration is required to minimize aluminum consumption and prevent formation of the passivating aluminum oxide layer, thus maximizing the cementation rate. The length of the induction period is influenced by many factors and is driven by the thickness of the passivating aluminum oxide layer. The presence of oxidants and other impurities in the actual leach solutions prevents dissolution or removal of the oxide layer. Removal of the oxide layer by acid cleaning prior to addition of the thiourea solution substantially reduces the induction time.

After the induction period, the rate of gold cementation by aluminum was found to be relatively fast and nearly complete (>95%); recovery of the gold can be achieved in 10 to 45 minutes depending on the temperature. As might be expected, the cementation reaction, after the induction period, can be described using first-order reaction kinetics. The first-order rate is mainly dependent on the temperature, and the first-order rate constant was found to increase from 2.19 hr^{-1} at 23°C to 10.72 hr^{-1} at 40°C. The rate of cementation appears to be independent of the thiourea concentration within the range tested.

By way of example, Figure 7 shows the first-order reaction plots for tests performed with different degrees of deaeration. These tests were performed at pH 1.5-2.0 with 2 gpl thiourea at room temperature. One test was performed open to the air (dissolved O_2: 8.73 mg/ℓ), while the other tests were performed after bubbling
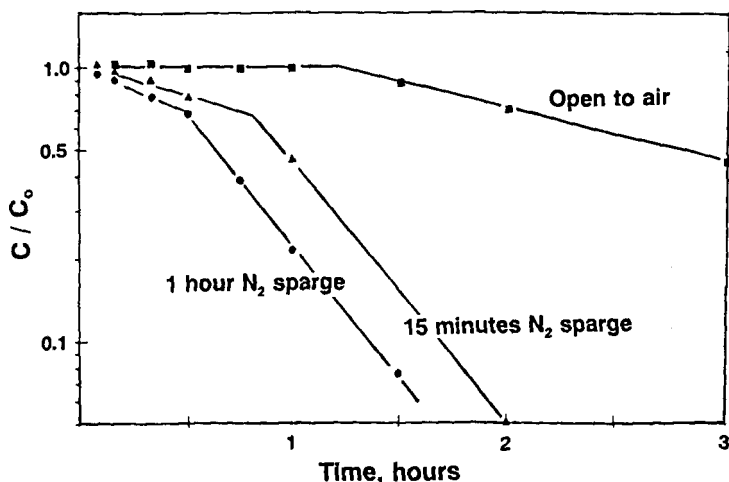
Figure 7. First-order reaction plots for gold cementation from thiourea
           solution by aluminum powder at different oxygen concentrations.

nitrogen for 15 minutes (dissolved O_2: 0.79 mg/ℓ) and 60 minutes (dissolved O_2:
0.55 mg/ℓ) before adding the aluminum powder (minus 325 mesh). As compared to
gold recovery from cyanide solutions by zinc cementation (Merrill-Crowe), deaeration
has a similar effect on the aluminum cementation of gold from thiourea solutions.
Under the experimental conditions employed in the presence of air, the cementation
reaction was significantly inhibited, with only 60% gold recovery in 3 hours. As
shown in Figure 7, with some deaeration (O_2 < 1 mg/ℓ) complete gold recovery was
achieved within 2 hours.

Oxygen concentration also has a significant effect on the length of the induction
period. Most likely, oxygen reduction is competing with the cathodic cementation
reaction. The presence of oxygen passivates the gold cementation reaction due to the
formation of an oxide layer on the surface of the aluminum. Also, electrochemical
reduction of formamidine disulfide was found to contribute to the length of the
induction period for gold cementation. Formamidine disulfide is the first oxidation
product of thiourea and is usually present in thiourea solutions to some extent.

THIOSULFATE SYSTEM

Thiosulfate has been proposed as an alternative lixiviant for gold and silver
extraction and has been investigated by many researchers for the recovery of precious
metals. Work has been conducted on the recovery of Au and Ag from residues of the
ammoniacal leaching of copper sulfide concentrates (Berezowsky et al., 1978, 1979);
dissolution of pure gold (Tozawa et al., 1981); recovery of precious metals from

manganese ores (Perez and Galaviz, 1987; Zipperian, 1988); and gold leaching from carbonaceous ores (Hemmati *et al.*, 1989), copper-containing ore (Jiang *et al.*, 1992) and low-grade oxide ores (Langhans *et al.*, 1992).

The chemistry of thiosulfate leach has been reported to be very complex. Thiosulfate forms complex ions with a variety of metals. Decomposition of thiosulfate and various side reactions occur in the leach system depending on experimental conditions. The presence of oxygen or other suitable oxidants has been reported to assist the thiosulfate leaching reaction, although it is necessary that experimental conditions be controlled to minimize degradation of the thiosulfate.

The overall stoichiometry for the dissolution of gold in aqueous thiosulfate solutions in the presence of oxygen is

$$2\ Au\ +\ 1/2\ O_2\ +\ 4\ S_2O_3^{2-}\ +\ H_2O\ =\ 2\ Au(S_2O_3)_2^{3-}\ +\ 2OH^- \tag{5}$$
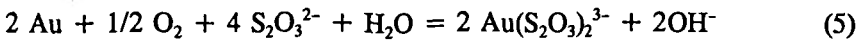
Cupric ion has been found to have a strong catalytic effect on the rate of oxidation. The catalytic influence of the cupric ion on the rate of reaction has been extensively studied by Flett *et al.* (1983). The presence of ammonia helps to stabilize the cupric state as the cupric tetrammine complex ion. The role of cupric tetrammine as a catalytic oxidant during gold dissolution is shown in equation (6):

$$Au\ +\ 5\ S_2O_3^{2-}\ +\ Cu(NH_3)_4^{2+}\ =\ Au(S_2O_3)_2^{3-}\ +\ 4\ NH_3\ +\ Cu(S_2O_3)_3^{5-} \tag{6}$$

Equation (6) depicts the Cu^{2+}/Cu^+ equilibrium that exists in ammoniacal thiosulfate solutions.

Under oxidizing conditions, oxidation degradation of thiosulfate to tetrathionate occurs and the oxidation reaction is promoted by cupric ion:

$$2\ (NH_4)_2S_2O_3\ +\ 1/2\ O_2\ +\ H_2O\ =\ (NH_4)_2S_4O_6\ +\ 2\ NH_4OH \tag{7}$$
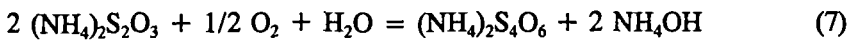
Thus, the amount of cupric addition or the concentration of cupric is very important in this leaching system.

It was found that addition of sulfite to the solution reduces the tetrathionate to thiosulfate and minimizes the formation of tetrathionate:

$$(NH_4)_2SO_3 + 2NH_4OH + (NH_4)_2S_4O_6\ =\ 2(NH_4)_2S_2O_3 + (NH_4)_2SO_4 + H_2O \tag{8}$$
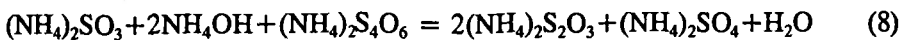
Equation (9) also depicts the equilibrium reaction between thiosulfate and sulfite/sulfide.

$$3SO_3^{2-}\ +\ 2S^{2-}\ +\ 3H_2O\ =\ 2S_2O_3^{2-}\ +\ 6OH^-\ +\ S \tag{9}$$
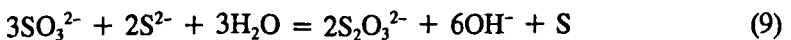
Two patents were assigned to Kerley (1981, 1983) for the addition of sulfite ions to control the stability of thiosulfate solutions during the leaching reaction. Sulfite ions react with any sulfide ions in solution, thereby preventing the precipitation of metal sulfides.

Gold Recovery from Thiosulfate Solution

So far, most research has been reported on thiosulfate leaching. Research on precious metal recovery from the thiosulfate solution is limited. Perez and Galaviz (1987) reported using a cementation process to precipitate gold and silver from the $Au/Cu/S_2O_3^{2-}$ solution by copper cementation. In the study of Berezowsky *et al.* (1979), precious metals were recovered from the thiosulfate leach solution using zinc dust cementation. They claimed that a major portion of the zinc was consumed by cupric ion in the thiosulfate solution; therefore, the zinc consumption was high, and the cement product contained appreciable amounts of copper and zinc. They suggested that a suitable reductant or sulfur dioxide should be used to reduce the cupric to cuprous prior to the zinc dust cementation. The characterization of the cementation reaction from the thiosulfate solution was not described.

Gallagher *et al.* (1987, 1990) studied activated carbon adsorption of gold complex ions with different ligands including thiosulfate, thiocyanate, chloride and thiourea. The adsorption of the gold complex was characterized by the change in solution concentration as a function of time. Gold concentration-versus-time profiles for the gold complexes $Au(S_2O_3)_2^{3-}$, $Au(SCN)_2^-$, $AuCl_4^-$, and $Au(SC(NH_2)_2)_2^+$ are shown in Figure 8. It is interesting to note that, among these gold complexes, only the $Au(S_2O_3)_2^{3-}$ species is different with respect to the adsorption by carbon. Results indicate that activated carbon has a very low affinity for $Au(S_2O_2)_2^{3-}$. The reasons for the very low loading of gold onto the carbon from the thiosulfate system have not been fully elucidated at this point, but various possibilities exist, including the relatively high negative charge of the complex, steric limitations due to molecular structure or specific interactions of the ligand group with carbon active sites. Lulham and Lindsay (1991) reported that the gold complex anion can be adsorbed from a thiosulfate solution by an adsorbent such as carbon or a resin after adding a small amount of cyanide to the system.

For anion exchange resin adsorption, it is also expected that gold cannot be recovered effectively from thiosulfate solutions by anion exchange resins, because thiosulfate
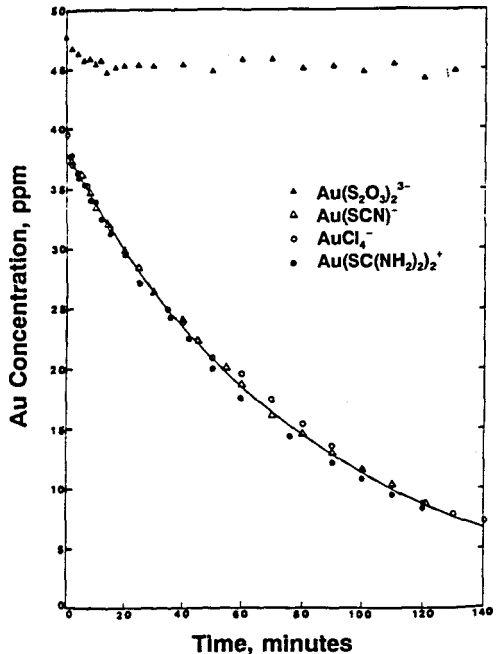

Figure 8. The adsorption of gold complex ions by activated carbon (Gallagher, 1987).

solutions are an effective eluant for stripping gold from loaded resins. Gold and silver can be adsorbed on anion resins only at very dilute thiosulfate concentrations. As reported by the Eastman Kodak Company (Degenkolb and Scobey, 1977; Mina, 1980), anion exchange resins, IRA–400 and IRA–68, are used for silver recovery only from thiosulfate photographic wash solutions. They reported that the resin capacity for silver adsorption was highly dependent on the thiosulfate concentration. Increasing the thiosulfate level from 1 ppm to 10 ppm resulted in a fourfold decrease in capacity in the case of silver adsorption. This information indicates that the thiosulfate concentrations in the gold-leaching system would be too high for gold adsorption on any of the commercial anion exchange resins.

SUMMARY

Research activities on gold recovery from halide solutions include activated carbon adsorption, resin ion exchange, and cementation. Unlike the case of gold adsorption from alkaline cyanide solution, gold adsorption by activated carbon from acidic chloride and bromide solutions involves electrochemical reduction, due to the relative instability of the gold halide complexes and the ability of activated carbon to act as a reductant. In the case of using ion-exchange technology to recover gold from halide solutions, both strong-base and weak-base resins can load gold from halide solutions. However, most of the commercial resins are not stable under high oxidizing potentials. Only neutral polyacrylic ester adsorbents, such as XRD–7 and XRD–8, appear to resist hypochlorite oxidation.

For gold recovery from thiourea solution, several options have been studied and reported. Adsorption processes both by activated carbon and cation exchange resin were found not to be successful in the thiourea system. Elemental sulfur from the degradation of thiourea deposits in the carbon macropores and significantly reduces the gold-loading capacity. Similarly, elemental sulfur deposition was found on the surface of cation-exchange resins and prevented gold adsorption from thiourea solutions. In addition, the acid thiourea leach allows for the dissolution of a variety of metals, and these cations load onto the resin, substantially reducing the resin gold-loading capacity. Other options for gold recovery from thiourea solution include direct reduction and cementation. Cementation using aluminum powder was found to be technically viable, but deaeration is required to minimize aluminum consumption and prevent formation of a passivating aluminum oxide layer.

In the gold-thiosulfate system, it was found that activated carbon has a very low affinity for the gold-thiosulfate complex anion. Only when the solution is treated with a small amount of cyanide can the gold complex ions be adsorbed on carbon from thiosulfate solutions. Gold cementation from thiosulfate solution with zinc dust is reported to be possible, but zinc consumption is high.

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