ADSORPTION OF GOLD FROM ACID THIOUREA AND CHLORIDE SOLUTIONS BY ION EXCHANGE RESINS

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ABSTRACT

The adsorption of gold from a thiourea-leach solution was studied in order to evaluate the possibility of using the thiourea leach process. Many commercial ion exchange resins were used for the extraction: UR-8 series resins as chelating and anionic resins and Amberlite as strong and weak acid resins.

The extraction of gold, as the cationic aurothiourou and anionic gold chloride complexes, from solution by acid cationic-exchange and base anionic resins was investigated. The effects of parameters such as pH, thiourea concentration, weight of resins, shaking time, and the presence of competing cations on the rate of extraction and the loading capacity for gold were studied.
thiosulfate complex, i.e. Au\((\text{CS(NH}_2)_2)^-\), are reported. Attempts were also made for understanding the involved mechanisms.

**Keywords:** Leaching; Gold extraction reagents; thiosulfate adsorption; Surface chemistry.

1. **INTRODUCTION**

The dominant chemical used in the gold industry has for many decades been cyanide in aqueous solution. This has been used for the initial leaching process to solubilize the gold and throughout the subsequent processes of purification to the elution of the gold from loaded activated carbon or ion exchange resins and its subsequent electrowinning. More recently, concerns about cyanide toxicity, its relatively slow kinetics, and its lack of selectivity in some refractory ores have prompted research into alternative lixiviants.

Among the reagents that have given promise as an alternative to cyanide in gold leaching are thiourea, thiocyanate or thionate which appear to be the more interesting. Thiocyanate has been investigated also as a possible alternative gold leaching agent [1]. This reagent is environmentally more acceptable than cyanide. The reaction occurs in an acidic medium; therefore, soluble oxidizing agents could be used. Besides, the complex formed between gold and thiocyanate \((\text{Au(SCN)}^+ = 1.3 \times 10^{-17} [2])\) is much more stable than the gold-chloride complex \((\text{AuCl}^- = 2.3 \times 10^{-11} [1])\) but less stable than the gold-cyanide complex \((\text{AuCN}^- = 7.8 \times 10^{-29} [2])\) or than the gold-thiourea one \((\text{Au(CS(NH}_2)_2)^- = 9.2 \times 10^{-25} [3])\). Leaching processes with thiourea were probably the first processes that have been developed to leach gold from its ores. It is known that the leaching reaction is very fast [3] but, as with cyanide, these processes are not selective since almost all metals form very stable chlorocomplexes.

With appropriate oxidants, some findings have shown [2-5] that thiourea can dissolve gold effectively in acidic solution and could thus be a potential substitution for cyanide leaching of solution. The overall reaction proceeds according to the following reactions [4, 5]:

\[
\text{Au} + 2\text{CS(NH}_2)_2^- \rightarrow \text{Au(CS(NH}_2)_2)^- + e^- \quad (1)
\]

\[
\text{Au} + \text{Fe}^{3+} - 2\text{CS(NH}_2)_2^- \rightarrow \text{Au(CS(NH}_2)_2)^- + \text{Fe}^{2+} \quad (2)
\]
from the above formulae, it can be noticed that the charged complex is positive in contrast with the negatively charged gold complexes formed in most other systems. It was also recognized that the ferric ion can speed up the reaction in acidic media of sulphuric acid. Thiourea method is advantageous superior in that gold and silver can be dissolved more rapidly than that in cyanidation method. The inferiority of thiourea method is the high cost and unestablished technology for recovering gold and silver from leachates for reusing thiourea.

The potential pollution problem of cyanide as well as its high complexing ability have encouraged the use of thiourea for precious metal leaching. A considerable amount of work has been carried out on leaching of gold with thiourea [3-9]. On the other hand, literature on the recovery of gold from thiourea solutions is much more sparse [10-13]. If gold dissolved by acidic thiourea solution is separated from leach solution by using adsorption process [10] or solvent extraction [13], the solution is recycled in a leaching step and hence thiourea leach process would become more attractive.

Hence, this paper focuses attention on experimental data on gold adsorption on ion exchange resins. The adsorption characteristics of gold from an acidic thiourea solution were investigated in order to evaluate the possibility for the thiourea leach process. The solution was prepared by dissolving gold powder in an aqueous solution containing thiourea, ferric sulphate and sulphuric acid. Extraction of gold, as the cationic aurathiourea and anionic chloride complexes, from solution by acid cationic- and base anionic exchange resins was investigated. The effects of various parameters such as pH, thiourea concentration, weight of resins, agitation, and the presence of competing cations on the rate of extraction and the loading capacity for gold are reported. Gold chloride solution was also used as guide model to elucidate the mechanism of adsorption.

2-HISTORICAL BACKGROUND
With knowledge of the basic structure of the ion exchangers and control over the complete synthesis process, by 1955 it became possible to produce “tailor-made” exchangers to suit almost any problem dealing with ion exchange in aqueous solutions [14]. Then, introduction
of Resin In Pulp (RIP) two decades ago gave a boost to the gold industry. The use of resins to extract gold from cyanide solutions and pulps was first investigated in South Africa as early as 1961 [12], although the US Bureau of Mines conducted an even earlier investigation [13]. In the latter study, the use of weak-base resins to recover gold from cyanide solution was examined, but the process failed owing to the inability of weak-base resins to extract ions efficiently at the high pH values of cyanide leach liquors. The progress in the development of Resin In Pulp (RIP) for gold extraction has been achieved in the Soviet Union and Romania [17,18]. These progresses have therefore made one of the largest gold mines in the Soviet Union to use an anion-exchange resin to extract aurcyanide by the RIP process. This is believed to have been the world’s first application of RIP to the extraction of gold. In the process, non-selective absorption is followed by selective elution. Zinc, nickel, and cyanide are eluted first by dilute mineral acid. This then is followed by the elution of copper with an ammoniacal solution of ammonium nitrate and, finally, gold and silver are desorbed and eluted continuously, with acidified thiourea as the eluant. The unattractive features of the process are its complexity, and using of acid in the first stage of elution, which converts iron and cobalt on the resin to complex species that would be desorbed with difficulty.

Piksa [19] suggested to use thiourea as a possible complexing agent for gold and silver. A considerable amount of work has been carried out on leaching of gold with thiourea [3-9]. The stability and cataphatic nature of the metal-thiourea complex make the selective recovery of gold and silver by multiple methods possible. Some researchers [12,20] studied the use of activated carbon for the sorption of gold from acidic thiourea solutions. In a chloride media, gold is usually leached in an acidic environment. However, the complex AuCl₄⁻ is decomposed and the gold is reduced to its metallic form on the surface of activated carbon [20]. This explains why the use of activated carbon is less attractive in a chloride medium, because the presence of metallic gold makes it more difficult to process.

The solvent extraction of gold thiourea from solution has been accomplished using several reagents. Clerk, et al. (1977) [12] determined the optimum conditions for the recovery of gold from thiourea-hydrochloric acid solutions with trioctyl phosphine (TOP) as an extractant. Exchange fibers [21] synthesized from polyvinyl alcohol adsorbed gold from both sulphuric
and HCl-thiourea solutions. Ion exchange stripping processes of gold-thiourea system possess distinct possibilities for the processing of gold. However, data on the behaviour of gold thiourea with solid ion exchangers are very few.

3-EXPERIMENTAL

The ion exchange resins were obtained from Japan Organo Co., Ltd. at Tokyo. Details of the various resins tested are given in Table 1 and 2.

Table 1 Physical and Chemical Properties of Amberlite resins

<table>
<thead>
<tr>
<th>Resin matrix</th>
<th>Amberlite 200C</th>
<th>Amberlite IRC-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional groups</td>
<td>Sulfonic acid</td>
<td>Carboxylic acid</td>
</tr>
<tr>
<td>Physical form</td>
<td>Brown, spherical</td>
<td>White, spherical</td>
</tr>
<tr>
<td>Moisture retention</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>capacity, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Size</td>
<td>1.3 m^3/g</td>
<td>-</td>
</tr>
<tr>
<td>Apparent density, g/ml</td>
<td>1.263</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>Strong acid</td>
<td>Weak acid</td>
</tr>
<tr>
<td>Form</td>
<td>Na⁺</td>
<td>Na⁺</td>
</tr>
</tbody>
</table>

Table 2 Physical and Chemical Properties of Unicellex (UR-series)

<table>
<thead>
<tr>
<th>Resin matrix</th>
<th>UR-30</th>
<th>UR-50</th>
<th>UR-3900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional groups</td>
<td>Iminodiacetic Acid groups (IDA)</td>
<td>Iminodiacetic Acid groups (IDA)</td>
<td>Amine</td>
</tr>
<tr>
<td>Physical form</td>
<td>Brown, spherical</td>
<td>Brown, spherical</td>
<td>Brown, spherical</td>
</tr>
<tr>
<td>Moisture retention capacity, %</td>
<td>45 - 50</td>
<td>55 - 60</td>
<td>53 - 68</td>
</tr>
<tr>
<td>Particle Size, mesh</td>
<td>20-60</td>
<td>20-50</td>
<td>20-60</td>
</tr>
<tr>
<td>Apparent density, g/ml</td>
<td>770-820</td>
<td>780-810</td>
<td>760-850</td>
</tr>
<tr>
<td>Type</td>
<td>Chelating</td>
<td>Chelating</td>
<td>Strong basic</td>
</tr>
<tr>
<td>Form</td>
<td>H⁺</td>
<td>H⁺</td>
<td>Cl</td>
</tr>
</tbody>
</table>
Fe₂(SO₄)₃·XH₂O, ZnSO₄·7H₂O, CuSO₄·5H₂O, and crystalline thiourea were all of chemical reagent grade. Various gold solutions were prepared for these series of experiments. Gold chloride solution is usually prepared by dissolving pure gold in aqua regia, followed by boiling to remove excess nitric acid. In this experiment tests, 1000 ppm standard solution of HAuCl₄ in 1.5 N HCl used for atomic adsorption, were utilized after dilution to 3 or 5 ppm. Gold thiourea solutions were prepared by dissolving pure elemental gold (99.99%) in acidodihioxen solution. A determined amount of crystalline thiourea (CS(NH₂)₂) has been dissolved in deionized water, then adding sulphuric acid and finally the prefixed amount of solid ferric sulphate.

The gold/sulphur exchange resin adsorption experiments were performed in a 50 cc Erlenmeyer flask using 40 cc of gold solution and prescribed weight of the ion exchange resin. The resulted mixture was then shaken using a thermostatic water bath shaker (at 150 rpm and at room temperature) at selected time. This speed was selected to prevent the attrition of the ion resins, but still ensuring a good solid/liquid contact.

After a prescribed time, the aliquots of the solution were collected, filtered and analyzed using Atomic Adsorption Spectroscopy (AAS) to determine the gold concentration remaining in solutions and occasionally base metals (Fe, Cu or Zn). It should be stressed that standard reference solutions used for the AAS contained metal ions with additives as in the test solution to avoid any influence on the determination of gold by AAS [22]. The depletion of gold content was determined and then the percentage of gold adsorbed by ion exchange resin was calculated.

4. RESULTS AND DISCUSSION

Adsorption from Acid Chloride Solution

A series of experiments was carried out to determine the required time for achieving equilibrium state. The results are shown in Figs. 1 and 2. Fig. 1 shows the effect of retention time on the adsorption of AuCl₄⁻ by Amberlite 200C using test solution containing 5 ppm AuCl₄⁻. It can be seen from this Figure that the adsorption rate is very slow. Since the resin loading does not approach a plateau (i.e., equilibrium state) even after 6 hrs, with adding 2.0 g
Fig. 1. Effect of shaking time on the adsorption of AuCl₄⁻ on Amberlite 200C at various resin weight.

Fig. 2. Effect of shaking time on adsorbability of AuCl₄⁻ by ion exchange resins.
resin only about 28% adsorption rate can be obtained after 70 minutes, however, by using UR 3900 resin (see Fig. 2), the rate was faster at the initial stage, since more than 46% of AuCl\(^+\) was adsorbed in less than 10 minutes. The resin reached in this case approached plateau after 20 minutes contact with the solution. Fig. 2 also indicates the inferiority of using Amberlite 200C to adsorb gold chloride complex in comparison with that of UR-3900 resin. The effect of resin weight on the adsorption rate of AuCl\(^+\) on both Amberlite 200C and UR-3900 at different initial AuCl\(^+\) concentration values is shown in Fig. 3. It shows the dependence of the rate of adsorption on resin type. The major conclusion which can be drawn from these results is that a complex-forming process with the resin could control the rate of gold adsorption in case of using strong acidic resin (Amberlite 200C). Fig. 3 also shows that by adding 1.6 g of UR-3900 resin could lead to adsorb about 55% of gold from solution with initial concentrations of 3 or 5 ppm AuCl\(^+\). The figure also points out to the over all superiority of AuCl\(^+\) adsorption ability by Amberlite 200C as by UR-3900. This can be explained on the basis of the mechanism of adsorption of anionic complex of AuCl\(^+\) on both resins. That is AuCl\(^+\) adsorption by strong acid cationic resin (Amberlite 200C) is controlled by physical adsorption of AuCl\(^+\) on resin. It is worth mentioning that Amberlite 200C has a macrotreticular structure that is a truly macroporous structure which facilitates the diffusion of AuCl\(^+\) ions inside the resin particles. Pure ion exchange mechanism in this case can not occur. But in case of using strong base anionic resin (UR-3900) the ion exchange mechanism may be represented as follows, where R represents the polymeric resin matrix:

\[
R-NR_2^+; Cl^- + AuCl^- \rightarrow R-NR_2^+; AuCl^+ - Cl^- \tag{3}
\]

**Adsorption from Acid Thiourea Solution**

A comparison study of the adsorption ability of Amberlite 200C and IRC-50 resin and UR series resin is summarized in Fig. 4. From this figure, it would be noted that nearly 100% Au(Tu)\(_2^+\) adsorption can be obtained by using 1.6 g of Amberlite 200C. This reveals the superiority of Au(Tu)\(_2^+\) adsorbability on strong acid cation (Amberlite 200C) in comparison with both weak acid resin (Amberlite IRC-50) and UR-series resins. The same figure suggests that strong acid resin of macrotreticular structure (Amberlite 200C) is the most effective resin to extract gold from acid thiourea solution. The ion exchange mechanism
Fig. 3 Effect of resin concentration on AuCl₄⁻ adsorption on UR and Amberlite resins.

Fig. 4 Effect of resin concentration on the adsorption of Au(Te)₂⁺ on UR and Amberlites resins.
between the mobile ion, Na\(^+\), in Amberlite 200C resin phase, and Au\(\text{[Tu]}_2\)\(^+\) ion in aqueous phase may be assumed as follow:

\[
\text{R-SO}_3\text{Na}^+ + \text{Au[Tu]}_2\text{[Tu]}^+ \rightleftharpoons \text{R-SO}_3\text{Au[Tu]}_2\text{[Tu]}^+ + \text{Na}^+
\]

The influence of thiourea concentration on adsorbability of resins was investigated by varying CS\((\text{NH}_2)_2\) in the range from 0.3 to 20 g dm\(^{-3}\). Fig. 5 shows this influence on the adsorbing ability of strong and weak acid resin, Amberlite 200C and IRC-50, respectively. The test conditions are given on the same figure. From this figure, it can be seen that thiourea concentration does not affect significantly the \(\text{Au[Tu]}_2\)\(^+\) adsorbability by the two resins. This finding is considered as an advantage to use SLP process, since the leaching process is dependent on concentrations of thiourea.

Several experiments have been conducted to study the effect of pH and base metal ions on \(\text{Au[Tu]}_2\)\(^+\) adsorption from the leach solution. Figs. 6 and 7 show these effects of pH on \(\text{Au[Tu]}_2\)\(^+\) adsorption by Amberlite 200C and IRC-50, respectively. Fig. 6 indicates the dependence of \(\text{Au[Tu]}_2\)\(^+\) adsorption on resin weight. The adsorption decreases with decreasing resin weight. As depicted in Fig. 6, approaching the plateau \(\text{Au[Tu]}_2\)\(^+\) adsorption value can be attained at pH 1.2. When the pH exceeded 2.4, red brown precipitates of Fe(OH)\(_3\) were observed (indicated on the graph by dotted line). This precipitation appears to have no adverse effect on \(\text{Au[Tu]}_2\)\(^+\) adsorption. However, Fig. 7 indicates that a plateau does not appear at the studied pH range by using Amberlite IRC-50. It seems from Figs. 6 and 7 the dependence of adsorption rate on pH (increases with increasing pH) is indicative of a process controlled by particle diffusion i.e., particle diffusion values increases under these conditions [23].

The impurities like copper, zinc and iron are inevitable in the solubilization of ores owing to the reactivities of thiourea with such minerals as chalcopyrite, pyrrhotite and pyrite which are often associated with gold ores. Figs. 8 and 9 show the effect of Fe\(^{3+}\) ion concentration on \(\text{Au[Tu]}_2\)\(^+\) adsorption by Amberlite 200C and IRC-50, respectively (precipitates of Fe(OH)\(_3\) were indicated on the graphs by dotted line). In Fig. 8 the experiments were conducted at
Fig. 5: Effect of thiourea concentration on the adsorption of Au(Ta)²⁺ by Amberlite.

Fig. 6: Effect of pH on the adsorption of Au(Ta)²⁺ by a strong acid resin (Amberlite 200C).
Fig. 7 Effect of pH on extraction of anion by a weak-acid resin (Amberlite IRC-50)

Fig. 8 Effect of initial ferric ion concentration on the adsorption of Au(Te)²⁺ by a strong-acid resin (Amberlite 200C)
Fig. 9 Effect of initial concentration of ferric ion on the adsorption of Au(Te)₂⁺ on Amberlite IRC-50

Fig. 10 Effect of initial ion concentration (Cu²⁺, Zn²⁺) on the adsorption of Au(Te)₂⁺ on Amberlite 200C
constant pH around 2.0. It can be seen that a slight decrease in Au(Tu)₂⁺ adsorption as Fe⁺ increased above 1.5 g dm⁻³. In the case of increasing Fe⁺ concentration to 4.5 g dm⁻³, an adsorption ratio of about 80% can be obtained. Almost the same trend of results can be noticed in Fig. 9, in case of using Amberlite IRC-50 (precipitates of Fe (OH)₃ were indicated on the graph by dotted line). These results demonstrate that Fe⁺, used as an oxidizing agent, does not markedly affect Au(Tu)₂⁺ adsorption by Amberlite 200C or IRC-50 resin. This is obviously an additional advantage of extraction of gold from acid thiourea solution by ion exchange resin.

Since copper is usually leached out simultaneously as an undesirable side reaction, the effect of the presence of Cu²⁺ ion is an important criterion of the feasibility of RJP in thiourea method. Fig. 10 shows the effect of Cu²⁺ and Zn²⁺ ion concentration on Au(Tu)₂⁺ adsorption by Amberlite 200C. It is easy to note that slight decreased in Au(Tu)₂⁺ adsorption on Amberlite 200C as Zn²⁺ increased. However, noticeable decreasing in Au(Tu)₂⁺ adsorption as Cu²⁺ increased on Amberlite 200C can be seen in this figure. When Cu²⁺ concentration exceeds 200 mg dm⁻³, white precipitate of copper thiourea complex (Cu(Tu)₃)⁻ [24] was observed (indicated on the graph by dotted line). The influence of copper is on two fronts: copper complexes the available thiourea used to leach gold and it also oxidizes a part of thiourea to formamidine disulfide [24, 25]. Inspection Figs. 8 and 10, it can be noticed that the order of decreasing adsorption on resins, as a result of metal ions addition parallels the order of decreasing hydrated ion size (Fe > Zn > Cu) [26] i.e. an ion of smaller hydrated size takes up less space inside the resin while satisfying the required of electrical neutrality.

The ionic strength of the aurothiourea solution was varied from 0.02 to 0.5 mg dm⁻³ by the addition of sodium chloride, and the effect on the extent of the loading rate was examined. The results (Fig. 11) show that ionic strength has little effect on the rate of adsorption. This is due to the increased competition between Au(Tu)₂⁺ and Na⁺ cations for active sites on the resins.

5. CONCLUSIONS

The extraction of gold from chloroauric and acid thiourea solutions was investigated by using different types of ion exchange resins. It was found that UR-3000 is the most suitable for extraction of the gold from chloride solution whereas Amberlite 200C is the most suitable for
the extraction from acid thiourea solution. It is therefore suggested to use strong acid resin for effectively separating of even small amounts of gold from larger amount of iron.

Figure 11: Effect of ionic strength on adsorption of Au(Te)_2^+ on Amberlite 200C

Amberlite 200C, the strong acidic resin of macrotetrical type, showed the highest adsorbability of gold complex due to its macroporous structure. The extraction process is independent on thiourea concentration, whereas it is decreased slightly by the presence of ferric ion. This is considered as superiority of using ion exchange, that their performance is not poisoned by the iniviant reagents. It is recommended to eliminate the Cu^{2+} ion prior to extraction of gold complex due to its high competition.
REFERENCES


