

# Potential applications of thiourea in the processing of gold\*

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## SYNOPSIS

The aqueous chemistry of gold(I) that has found practical application is mainly the chemistry of the anionic complexes involving ligands such as cyanide, sulphite, and the halides. The one potential exception is the cationic gold(I)-thiourea ion. While many laboratory studies have been made during the past decade, the application of thiourea in the processing of gold is only now reaching the development stage.

While thiourea is relatively inexpensive, recent interest has probably been spurred mainly by the novel technology that could arise out of the cationic properties of the gold-thiourea ion.

This review outlines the chemistry of gold and thiourea, and discusses the possible use of thiourea in the processing of gold with respect to dissolution, solvent extraction, ion exchange, electrowinning, electroplating, electroless deposition, electro-etching, and electropolishing.

## SAMEVATTING

Die waterchemie van goud(I) wat prakties toegepas word, is hoofsaaklik die chemie van die anioniese komplekse waarby ligande soos sianied, sulfiet en die haliede betrokke is. Die een moontlike uitsondering is die kationiese goud(I)-tio-ureumioon. Hoewel daar gedurende die afgelope dekade baie laboratoriumstudies uitgevoer is, bereik die gebruik van tio-ureum by die verwerking van goud nou eers die ontwikkelings stadium.

Hoewel tio-ureum betreklik goedkoop is, is die onlangse belangstelling waarskynlik hoofsaaklik toe te skryf aan die nuwe tegnologie wat uit die kationiese eienskappe van die goud-tio-ureumioon kan voortspuit.

Hierdie oorsig beskryf die chemie van goud en tio-ureum in hooftrekke en bespreek die moontlike gebruik van tio-ureum by die verwerking van goud met betrekking tot oplossing, oplosmiddelstraksie, ionuitruiling, elektro-winning, elektroplatering, elektrolose afsetting, elektroëtsing en elektropolering.

## Introduction

Hydrometallurgical processes for the extraction of gold and the gold-plating industry have to date been based largely upon the use of the soluble anionic ions of gold such as the cyanide, sulphite, and halide complexes of gold(I). Despite the obvious utility that a cationic species could have in the processing and uses of gold, it is only during the past decade that attempts have been made to take research results to a stage where gold-processing technology includes the use of cationic species of gold. At this stage, it appears that the gold(I)-thiourea ion<sup>1</sup>  $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$  will be the first to achieve industrial importance, particularly since the use of thiourea can not be ruled out on the basis of economic considerations.

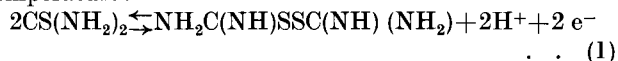
It is the purpose of this paper to review the fundamental chemistry of gold and thiourea, and to indicate the possible applications of thiourea in the future processing of gold.

## Redox Reactions

The oxidants used for the dissolution of gold in acidic solutions of thiourea also oxidize thiourea in successive stages to form a number of products<sup>2</sup>. An understanding of these redox processes is essential before the action of this liquor upon gold can be described.

The first product is formamidine disulphide, which is formed with relative ease in acidic solutions by the

action of oxidants such as hydrogen peroxide<sup>3</sup> at room temperature:



In view of this rapid reaction, formamidine disulphide must be assumed to be the active oxidant for the dissolution of gold in thiourea solutions<sup>4</sup>. Reaction (1) is followed by slower reactions that form products in which sulphur has a higher oxidation state, for example, sulphur or even sulphate ions; these products therefore gradually accumulate in the solution. These secondary redox reactions are only partial in acidic or neutral solutions unless vigorous oxidants such as acidic dichromate are used, when the oxidation products are urea and sulphate ion<sup>2</sup>. In alkaline solution (pH 8), this latter reaction is quantitative even with mild oxidants<sup>5, 6</sup>. The reactions of thiourea with gold(III) and iron(III) are of special interest. The redox reaction with gold(III) is rapid in acidic solutions, and the reduction to gold(I) is quantitative; this reaction has been recommended for the analytical determination of gold(III)<sup>7, 8</sup>. Only one ion of gold(I)-thiourea is known<sup>1</sup>, namely  $[\text{Au}(\text{CS}(\text{NH}_2)_2)_2]^+$ . The reaction between iron(III) and thiourea is slow<sup>9</sup> because of the formation of very stable metal-ligand co-ordination bonds. The complex  $[\text{Fe}(\text{III})\text{SO}_4(\text{CS}(\text{NH}_2)_2)]^+$  (stability constant  $\log \beta = 6,64 \pm 0,63$ ) was identified in a mixed sulphate-thiourea medium, and, upon completion of the reduction process, the complex  $[\text{Fe}(\text{II})(\text{CS}(\text{NH}_2)_2)]\text{SO}_4$  was identified.

## Oxidative Dissolution

The dissolution of gold in acidic solutions of thiourea was reported as long ago as 1941 by Plaksin and Kozhuchova<sup>10</sup>, and was observed again by Preisler and Berger<sup>3</sup> in 1947, but there was a considerable time lag

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before this discovery was investigated in depth<sup>4, 11-16</sup> and the practical feasibility demonstrated by the dissolution of gold from a crushed ore<sup>4, 13</sup>.

Oxidants that have been added to acidic solutions of thiourea to effect the dissolution of gold include formamidine disulphide<sup>3, 4, 10</sup>, hydrogen<sup>4, 12, 14, 15</sup> and sodium peroxide<sup>12</sup>, dissolved oxygen<sup>4</sup>, and iron(III)<sup>4, 12-14</sup>. Additions of formamidine disulphide and hydrogen peroxide produce identical results<sup>4</sup>, and the rate of gold dissolution is similar in hydrochloric and sulphuric acid media; nitric acid appears to retard the process<sup>13</sup>. The rate of dissolution of gold is rapid and increases with increasing concentrations of thiourea and of oxidant, being controlled partially by chemical and by transport phenomena. In accord with this observation, the activation energy of the dissolution reaction,  $E_a$ , is 28,1 kJ/mol over the temperature range<sup>4</sup> 3 to 35°C. The rate of dissolution decreases with the age of the liquor. The secondary redox-reaction products of the thiourea appear to cause a passivation of the surface of the gold. The rate of the passivation reaction appears to be rapid, and its effect has been observed as a grey-black film on the surfaces of gold exposed to the action of these solutions. However, the rate of dissolution of gold in a solution containing 0,1 M sulphuric acid, 0,1 M thiourea, and 0,01 M formamidine disulphide is as much as  $1,1 \times 10^{-8}$  M cm<sup>-2</sup> s<sup>-1</sup>, which is at least five times faster than is possible with conventional cyanide solutions. Thus it has proved feasible to decrease the time for the extraction of gold from a typical crushed ore from 24h to about 5h using this solution of thiourea, and to about 0,5h using an acidic solution containing 1,0 M thiourea and 0,1 M formamidine disulphide. Approximately 0,4 kg of thiourea (and 6 kg of sulphuric acid) are consumed for each ton of ore treated.

The initial rate of dissolution of gold in a freshly prepared acidic solution of thiourea containing iron(III) as the oxidant is rapid, and is controlled only by the rate of diffusion of the oxidant to the surface of the gold. Although the efficiency of this liquor decreases with its age, it appears that the oxidation of thiourea by iron(III) does not immediately yield the secondary redox-reaction products that retard the rate of gold dissolution when other oxidants are used. The most rapid rate of dissolution of gold in acidic solutions of thiourea is therefore obtained with iron(III) as oxidant. However, the reaction between iron(III) and thiourea leads to a prohibitively high consumption of reagent — 5 kg per ton of ore treated<sup>13</sup>. Iron(III) appears to be much more effective in sulphate than in chloride medium<sup>13</sup>.

The use of acidic solutions of thiourea for the oxidative dissolution of gold in an ore can thus be recommended only when an extremely high rate of extraction is required. The consumption of reagents renders this technique uneconomical when compared with conventional cyanidation techniques. However, acidic solutions of thiourea could well prove to be a less-toxic and less-corrosive alternative to the cyanide, aqua regia, or hydrogenbromide/bromine treatments currently used in the wet-chemical extraction of gold from gold-bearing materials and in the chemical etching of gold and gold alloys.

## Electroless Plating

A number of solutions containing gold and thiourea have been patented as electroless gold-plating solutions<sup>17, 18</sup>. However, there is some doubt as to whether the reduction of gold(I)-thiourea to gold metal by the action of a soluble reducing agent is utilized in any of these processes.

The first patent<sup>17</sup> is a good example of immersion plating rather than of true electroless plating, since the solution, which consists typically of Au(I)-thiourea, KCl, HCl, and K-acetate (at pH 4) contains no reducing agent. It was found that a pore-free deposit of gold could be plated upon a copper surface, the copper itself probably acting as reducing agent.

In the second patent, a solution consisting of KAu(CN)<sub>2</sub>, thiourea, NH<sub>4</sub> citrate, and CoCl<sub>2</sub> is used; the Co(II) ion probably functions as a reducing agent, although the patent specifies its function to be that of catalyst for the deposition of gold. The pH value of this solution is not specified but, from the composition of the solution, is unlikely to be sufficiently low to ensure the conversion of Au(CN)<sub>2</sub><sup>-</sup> to Au(thiourea)<sub>2</sub><sup>-</sup>. The electroless plating of gold thus probably occurs direct from the cyanide of gold.

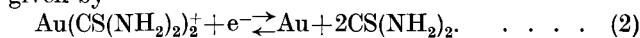
The more likely role of thiourea in electroless gold-plating solutions appears to be that of levelling agent. An example of this can be found in a patented electroless plating solution<sup>19</sup> at pH 3,5 containing KAu(CN)<sub>2</sub>, Na<sub>2</sub> EDTA, citric acid, NH<sub>4</sub> citrate, and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>SO<sub>4</sub>, as well as thiourea in amounts of less than 1 g/l.

## Electrochemistry

The electrochemistry of thiourea has been investigated on platinum<sup>3, 20-23</sup> and graphite<sup>24</sup>, which function as inert surfaces, and on lead<sup>24</sup>, which becomes passive in solutions of thiourea. Over the entire potential range 0,9 to 2,1 V, thiourea is oxidized on platinum to formamidine disulphide, which is partially decomposed to cyanamide and sulphur at the higher potentials in this range<sup>23</sup>. The current efficiency up to a potential of 1,4 V is 100 per cent and, at more positive potentials, decreases because of the simultaneous liberation of oxygen at the anode. The anodic formation of formamidine disulphide on platinum is reversible<sup>3, 19, 23</sup>, and the standard reduction potential<sup>3</sup>  $E_0$  is 0,420 V, a value that was found<sup>3</sup> to be independent of pH over the range 0 to 4,3. The rate of oxidation is, however, strongly dependent upon pH<sup>21</sup>. The electrochemical anodic transfer coefficient<sup>20, 21</sup>  $\beta$  is approximately equal to 0,8, and the exchange current<sup>21</sup>  $i_0$  is  $(2,1 \text{ to } 14,7) \times 10^{-6}$  A cm<sup>-2</sup>.

## Electrochemical Dissolution

The anodic dissolution of gold is rapid up to anodic overpotentials of 0,3 V (Fig. 1)<sup>25</sup> and nearly reaches the maximum diffusion-controlled rate, the reaction being given by<sup>1</sup>



The exchange current density is greater than  $10^{-6}$  A cm<sup>-2</sup>, and the dissolution proceeds with a current efficiency of 100 per cent. At anodic overpotentials of 0,4 V and higher, thiourea is oxidized to formamidine disulphide and other sulphur-containing compounds, and the

dissolution of gold becomes partly inhibited, while the current efficiency of gold dissolution decreases markedly. The passivation of the gold surface at the higher anodic potentials results in a hysteresis loop in the curve of current versus potential, and, as the concentration of the inhibiting reagents in the system builds up, the current values at the peak in this curve are further depressed. This also affects the value of the standard reduction potential ( $E_o$ ) of reaction (2); on a fresh gold surface,  $E_o$  is 0,352 V (at 30°C) but, on a passivated surface, this value increases<sup>25</sup> to as much as 0,41 V. This variation in the value of  $E_o$  arises even if the gold electrode is not subjected to anodic potentials but also when the solution contains increasing amounts of contaminants; under such conditions, values of  $E_o$  ranging from 0,336 to 0,395 V were obtained<sup>1</sup>.

### Electroetching and Electropolishing

Electroetching of gold is often used to obtain a dull matt finish on gold and gold alloys for decorative purposes. Electropolishing is the selective electrolytic dissolution of the metal, which produces smooth and brilliant surfaces. Both these techniques rely upon the anodic dissolution of the metal, and can conveniently be described in terms of the typical curve of anodic current versus potential shown in Fig. 1. Gold and gold alloys (9 to 22 ct) can be etched in acidic solutions of thiourea at applied potentials up to the peak in the curve of current versus potential<sup>26</sup>; in general, this peak tends to shift to higher overpotentials as the caratage of the alloy decreases. At the higher potentials, where partial passivation of the gold surface sets in, both the smoothing and the brightening of the gold surface necessary for effective electropolishing can be achieved. Gold and gold alloys of a fineness of at least 8 ct can be electropolished in solutions<sup>27</sup> containing typically 0,3 to

0,7 M thiourea in 0,03 to 0,6 M  $H_2SO_4$ , and improved behaviour for the lower caratage alloys can be obtained by the addition of small amounts of metallic salts such as  $CuSO_4$ ,  $AgNO_3$ , and  $NiSO_4$  to these polishing solutions<sup>28</sup>.

### Electrodeposition

The reduction of gold(I)-thiourea occurs<sup>24, 29-33</sup> according to reaction (2) and is diffusion controlled at cathodic overpotentials between -0,15 and -0,35 V, after which slight inhibition occurs<sup>29</sup>. At the peak of the curve for cathodic current versus potential (Fig. 1), the activation energy<sup>24</sup> for the deposition of gold  $E_a$  is 25 to 29 kJ/mol, and, at the trough,  $E_a$  is 71 to 84 kJ/mol. The diffusion coefficient ( $D$ ) of  $Au[CS(NH_2)_2]_2^+$  at 30°C has been measured<sup>25</sup> as  $1,1 \times 10^{-5}$  cm<sup>2</sup>/s, and at 50°C  $D$  is<sup>30</sup>  $1,17 \times 10^{-5}$  cm<sup>2</sup>/s. The deposition of gold occurs with a current efficiency of 100 per cent, but, when the cathodic overpotential is increased to between -0,5 and -0,6 V, gold precipitation and hydrogen evolution occur simultaneously and the current efficiency drops markedly<sup>24, 31</sup>. Thiourea itself does not contribute to the cathodic reaction on platinum, gold, or titanium, but formamidine disulphide can be continuously reduced on a freshly deposited gold surface<sup>25</sup>. In the absence of gold(I)-thiourea in the solution, the reduction of formamidine disulphide causes rapid passivation of the gold surface; under these circumstances, the gold plate appears somewhat darkened in colour.

It has been shown that the cathodic deposition of gold from acidic solutions of thiourea can be used for the recovery of gold from such solutions<sup>33</sup> or for the production of gold plate; a finely crystalline semilustrous deposit of gold up to 1 mm thick could be plated before further electrolysis resulted in a noticeable deterioration in the deposit<sup>30</sup>. An advantage of this plating system may

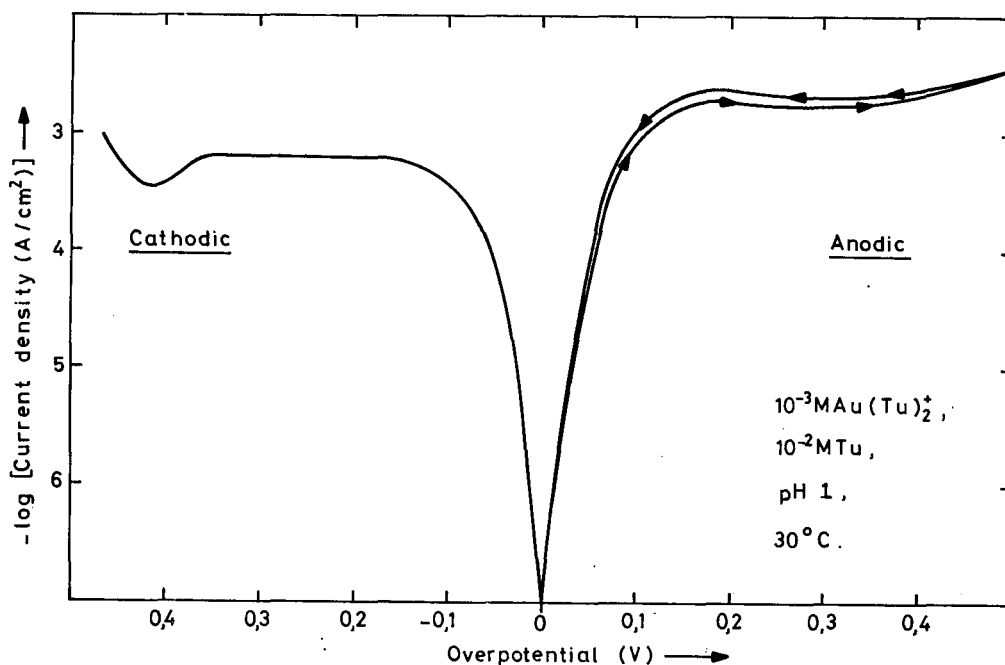


Fig. 1—Curves of anodic and cathodic current versus potential for the system gold-gold (I)-thiourea

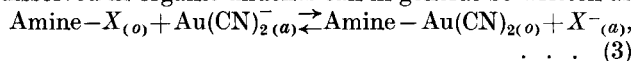
be derived from the fact that the cathodic evolution of hydrogen is markedly increased in the presence of thiourea (at least on silver surfaces)<sup>34</sup>, so that the problem of polymer formation<sup>35</sup> in the gold electroplate is not as likely to arise as when acidic cyanide solutions are used. In view of the anodic oxidation of thiourea, it will be necessary to separate the anode and cathode compartments of the electrolytic cell to avoid incorporation of sulphur in the gold plate<sup>25</sup>, as well as to prevent a measure of spontaneous dissolution of the gold by the oxidants formed during the reactions on the anode<sup>25, 30</sup>.

### Recovery of Gold

#### Gold(I)-Cyanide

Aside from isolated instances in the gold-plating and gold scrap-recovery industries, the extraction of gold from solution in industry is exclusively concerned with the extraction of gold(I)-cyanide from cyanide media. Although the recovery of this gold has long been accomplished by precipitation on metallic zinc, certain difficulties that have persisted in this technique have encouraged investigations in other directions. The failure of much of the research and development effort into the recovery of gold by solvent extraction and ion exchange to attain industrial acceptance can largely be attributed to the difficulty in obtaining the required selectivity of extraction and ease of recovery of the gold after extraction. Much of the research in this field during the 1960s, and even during the past few years, has been based upon the fact that gold can easily be stripped from amine extractants into acidic solutions of thiourea, thus providing a new way of overcoming traditional problems in this field.

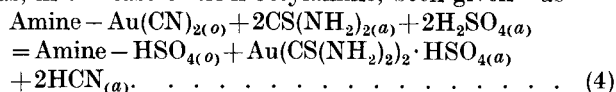
The role of thiourea in the stripping process should be viewed in conjunction with the extraction of gold(I)-cyanides by amine groups. Although there is not always agreement on the mechanism, the extraction of gold(I)-cyanide by means of long-chain amines dissolved in organic diluents can in general be written as



where the subscripts refer to the aqueous (*a*) and organic (*o*) phases, and  $X^-$  is some counter ion. Similar equations would naturally hold for amine-based ion-exchange resins. Infrared studies on a strongly basic anion-exchange resin that was saturated with gold(I)-cyanide have indicated the presence of gold on the resin as the  $\text{Au}(\text{CN})_2^-$  species<sup>36-38</sup>, which has been taken to confirm an electrostatic attachment to the resin. A similar conclusion was made after an infrared investigation of a solution of trialkyl ( $C_7-C_9$ ) benzyl ammonium ion in kerosene containing 40 per cent decylalcohol<sup>39</sup>; some authors<sup>40</sup>, however, have assumed that the difficulty encountered when gold is stripped by means of electrolytes from tertiary amines is indicative of homopolar bonding between the gold and the amine groups.

The difficulty in stripping the gold from these organic solutions is generally inversely related to the efficiency of extraction of gold(I)-cyanide by these amine extractants. The efficiency of extraction increases along

the series secondary<sup>41</sup> to tertiary<sup>40, 42-46</sup> to quaternary ammonium compounds<sup>47-50</sup>; the extraction efficiency also increases with an increase in the polarity of the organic diluent<sup>50, 51</sup>. Thus, with the quaternary group<sup>47, 48, 50</sup>, and even with some tertiary amines<sup>40, 43-46</sup>, it has been found possible to strip the gold(I) effectively only into acidic solutions containing thiourea. The reaction in which the gold is taken into aqueous solution as the  $\text{Au}[\text{CS}(\text{NH}_2)_2]_2^+$  complex ion has, in the case of tri-*n*-octylamine, been given<sup>46</sup> as



This stripping treatment has no irreversible effect upon the organic extractant, which can be reloaded with gold(I)-cyanide without intermediate treatment<sup>45, 50</sup>; an enhancement in the concentration of the gold of at least three orders of magnitude is possible via this cycle<sup>50</sup>. However, despite the numerous references to the use of acidic thiourea solutions for the stripping of gold(I)-cyanide, the stoichiometry and mechanism of the process shown in equation (4) have not been established. Studies into this process are rather complex in that the distribution of the gold depends upon the exact composition of the organic phase, and upon the type of acid in the aqueous phase; there is also an experimental need for the use of sealed systems to prevent loss of the hydrogen cyanide from the aqueous phase while equilibrium is being established<sup>50</sup>. Furthermore, this equilibrium will also be affected by the amount of cyanide ion originally bonded to the amine in the organic phase, since this cyanide is stripped quantitatively into even slightly acidic solutions containing thiourea<sup>52</sup>.

The order of stripping of the metal-cyanide complexes from quaternary ammonium extractants is generally opposite to the order of extraction<sup>48</sup>. Thus, it is usually possible to strip copper, iron, and zinc complexes into solutions containing sufficient free cyanide, while gold and silver are not stripped at all. The gold and silver can then be selectively stripped into acidic solutions of thiourea.

Acidic solutions of thiourea have been used to improve the selectivity of the extraction of gold(I)-cyanide from ion-exchange resins loaded with the metal-cyanide usually found in cyanide leach liquors; studies were made on strongly basic ion-exchange resins (type AV-17<sup>53</sup> and Russian type AM<sup>54</sup>) and from a resin containing mixed (50 per cent of each) strongly and weakly basic groups (Russian type AP-2)<sup>55, 56</sup>; these resins are all prepared on a base of divinylbenzene and styrene copolymers containing quaternary or tertiary ammonium salts, or a mixture of these two<sup>36</sup>. The recommended stripping sequence for the Anionite AP-2 resin is removal of the zinc and nickel cyanides, together with free cyanide, by treatment with 5 per cent  $\text{H}_2\text{SO}_4$ , followed by treatment with 5 per cent thiourea in 2.5 per cent  $\text{H}_2\text{SO}_4$  to strip the gold, silver, and part of the copper; the noble metals are removed from the aqueous phase by electrodeposition or 'electroelution'; iron and the remaining copper are removed by a solution containing ammonium hydroxide, ammonium nitrate, and sodium hydroxide. With the strongly basic resin AV-17, a total

elution of the precious metals could be obtained only by use of a solution of hydrochloric acid and thiourea<sup>57</sup>; a complete process was proposed for the hydrometallurgical recovery of gold from cyanide solutions by means of ion exchange. It was found that treatment of the strongly basic resin AM with acidic thiourea sharply reduced the porosity of this resin, but that alkaline eluants such as sodium cyanide or hydroxide restored the original porous structure<sup>58</sup>; in addition, this treatment removed impurities such as the cyanides of iron and copper that tended to build up on the resin and to impair its capacity for gold adsorption<sup>59</sup>. Infrared investigation of the AM ion-exchange resin has indicated that the difficulty associated with the removal of iron, and also of zinc, is due chiefly to the accumulation of  $\text{Fe}(\text{CN})_6^{3-}$  on the resin and to the formation of bridged structures of the type  $\text{Au-CN-Zn}$ <sup>38</sup>. Pilot-plant studies have been reported involving the use of ion-exchange resins for the recovery of gold from cyanide solutions<sup>60-62</sup>; stripping of the gold by acidic thiourea forms an integral part of these processes.

The rate of adsorption of gold(I)-cyanide onto synthetic fabrics containing suitable N-containing active groups (2-methyl-5 vinylpyridine or polyethylene-polyamines) has been found to occur about twenty to thirty times as rapidly as on conventional strongly basic resins; although the capacity for gold adsorption was reduced, these fabrics had the advantage of being rather selective for gold. The gold was readily stripped from these fabrics into hydrochloric acid solutions containing thiourea<sup>63</sup>.

The use of solvent-extraction techniques in hydrometallurgy is usually limited by losses of the organic phase due to a variety of reasons and, consequently, losses of extracted metal. In addition, these systems cannot be used for the direct treatment of pulps on account of intense emulsion formation and adsorption of the extractant onto the solid particles of the pulp. Many of these difficulties appear to have been overcome by immobilization of the liquid ion exchange on a porous support such as clay<sup>64</sup> and plastics such as polyethylene<sup>39, 65-67</sup> and polyurethane<sup>68</sup>. Gold was extracted from cyanide pulps by countercurrent adsorption using carrier granules of porous polyethylene containing a 10 per cent solution of trialkylbenzylammonium chloride in a mixture of kerosene and decyl alcohol<sup>39, 65, 66</sup> or in benzene and decyl alcohol<sup>67</sup>; stripping of the adsorbed metal cyanides from this organic medium was achieved by treatment with potassium cyanide for the removal of copper, iron, and some impurities, treatment with sulphuric acid for the removal of zinc and some of the nickel, extraction of the noble metals by acidic thiourea followed by electroelution of the noble metals, and, finally, removal of the last traces of impurities on the resin and regeneration of the extractant by treatment with sodium hydroxide<sup>69</sup>.

### Gold(I)-Thiourea

Various techniques have been investigated for the recovery of gold in acidic solutions of thiourea. In pilot-plant studies in which acidic thiourea was used to strip gold from ion-exchange resins or liquids, the gold

has been recovered by cementation on lead powder<sup>44, 53, 57, 60</sup> or by electrodeposition<sup>53, 57</sup>; 'electroelution' by simultaneous electrolysis of the acidic solution of thiourea in contact with the ion-exchange resin has been found to accelerate removal of the gold from the resin<sup>56</sup>. Activated charcoal has been used for the sorption of gold from acidic solutions of thiourea, and gold loadings of up to 17 per cent by mass of the charcoal are possible<sup>70</sup>; the carbon has to be ashed before the gold can be recovered. Tributylphosphate has been used for the solvent extraction of gold(I)-thiourea from hydrochloric acid solutions<sup>71</sup>, and the results have been applied<sup>72</sup> to an industrial solution containing gold, silver, copper, iron, zinc, and nickel. Tributylphosphate loaded on open-cell polyurethane foams has been used for the recovery of gold from sulphuric acid leach liquors containing thiourea<sup>73</sup>; the rate of gold sorption onto these foams was found to be equivalent to that on activated charcoal, but the loading capacity of the foam was about fifty times smaller than was possible with activated charcoal. These tributylphosphate-loaded foams have also been used for the chemical enrichment and separation of gold(I)-thiourea during reversed-phase chromatography<sup>74</sup>.

Strongly acidic cation-exchange resins are as effective as charcoal in extracting gold(I)-thiourea acidic solutions<sup>75</sup>, and have the advantage that the gold can be stripped effectively into alkaline cyanide solutions as the gold(I)-cyanide ion. Weakly acidic resins do not appear to be able to extract a great deal of gold from acidic solutions of thiourea. It has been reported that ion-exchange polyvinyl alcohol fibres effectively extract gold from acidic solutions of thiourea<sup>76</sup>.

### Conclusions

In the hydrometallurgy of gold, the most exciting applications appear to lie in the field of ion exchange where the cationic nature of the gold(I)-thiourea complex has made the selective recovery of gold a distinct possibility; developments in this field are mostly due to the Russians, and it will be interesting to see whether these possibilities will be recognized elsewhere in the future.

The rapid rate of dissolution of gold in thiourea should also find application in the analytical chemistry of gold, in the surface finishing of gold in the jewellery industry, and in the preparation of specimens for metallographical investigation. In the light of these developments, it appears safe to predict that thiourea could soon rank second in importance to cyanide in the processing of gold.

In time, these developments will generate an interest in the fundamental chemistry of this system. Thus, for example, there are at present no reliable data regarding the formation of the gold(I)-thiourea system, since all estimates in this regard have to be based upon electrochemical measurements on gold surfaces that are deleteriously affected in acidic solutions of thiourea. The kinetics and mechanism of the redox reaction between gold(III) and thiourea also deserve more thorough investigation, as does the conversion of gold(I)-cyanide to gold(I)-thiourea in acid solution, as well as the stripping processes involving these ions on

ion exchangers. The nature of the gold(I)-thiourea complex adsorbed on an ion-exchange resin has also not been described.

As concerns thiourea itself, no thermodynamic data relating to aqueous solution can be found. In this regard, there is certainly a need relating to its chemistry not only with gold but also with many other metals that form complexes with it.

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