

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



<http://www.informaworld.com/smpp/title~content=t713708471>

<sup>a</sup> Mineral Sciences Laboratories Energy, Mines And Resources Canada, Ottawa, Ontario, Canada

**URL:** <http://dx.doi.org/10.1080/01496399108050525>

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **Recovery of Gold from Thiourea, Thiocyanate, or Thiosulfate Solutions by Reduction–Precipitation with a Stabilized Form of Sodium Borohydride**

**F. T. AWADALLA and G. M. RITCEY**

MINERAL SCIENCES LABORATORIES

ENERGY, MINES AND RESOURCES CANADA

555 BOOTH STREET, OTTAWA, ONTARIO K1A 0G1, CANADA

### **Abstract**

Sodium borohydride can be used as an efficient agent for reducing gold and silver in acidic solutions of thiourea, thiocyanate, thiosulfate, acid chloride, and acid nitrate. The Au(I) ion is reduced to metallic gold in the form of very fine crystals, as indicated by XRD and SEM analysis. The reduction reaction is carried out at ambient temperature for a very short period of time (30 s). The reduction of Au(I) in such solutions can be performed for a wide range of gold concentrations (2 mg/L–2 g/L). Different parameters controlling the rate of the reaction and the efficiency of borohydride were studied, namely: acidity, stoichiometry, thiourea concentration, the presence of foreign ions, and temperature. Gold reduction by sodium borohydride is more favorable in the presence of  $\text{Ag}^+$  and/or  $\text{Zn}^{2+}$  ions, while the presence of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  ions decreases the efficiency of borohydride. The reduction reaction is selective for gold and silver over base metals in a solution mixture since the reaction is carried out in acidic medium. High recovery is obtained (>99%) and the product is pure. Thiourea does not undergo any degradation reaction during the course of reduction, and it can be recycled. The process appears promising for the gold industry due to its simplicity, speed, and low capital investment requirements.

### **INTRODUCTION**

Different methods have been used to recover gold and silver from aqueous solutions. Among these methods is the Merrill-Crowe process in which zinc powder is used to cement gold from a cyanide solution (1). This process, which revolutionized the gold and silver industry, was widely used

until the 1960s and is still used in some operations. Aluminum powder has been found efficient for recovering gold from spent cyanide solution (2) and from an acidic solution of thiourea (3, 4). On the other hand, it has been shown that the use of lead powder as a cementing agent for gold and silver was totally inefficient in sulfuric acid solutions while zinc was found inappropriate in acidic thiourea liquors (5). Although the cementation process has the advantage of high gold and silver recovery, the quality of the product obtained is sometimes poor.

The first new approach to the recovery of Au and Ag cyanide complexes on activated carbon was patented by McQuiston in 1946 (6). Since that time, new developments have been introduced to this process and now carbon-in-pulp (CIP) is commercially used for gold recovery from cyanide solutions (7). In thiourea leaching of gold, adsorption of thiourea and other impurities onto the carbon and the difficulty of desorbing the gold and silver are obstacles to CIP processing which render its use unfavorable (8, 9). New gold extraction technologies using solvent extraction and ion exchange are currently being developed as possible alternatives to carbon for recovering gold from cyanide liquors and pulps (10). It has been reported that gold can be recovered from precious metals refining solutions by new extraction systems (11–15). Gold is recovered from the loaded organic phase by cementation and reduction with oxalic acid, sulfur dioxide, or hydrogen. Gold recovery with quaternary amines exhibits good selectivity, and the loaded organic phase can be readily stripped with acidic solutions of thiourea together with air sparging (16). Ion-exchange techniques have also been developed to recover gold from cyanide and thiourea liquors (17, 18). As compared with activated carbon, the ion-exchange resins offer the advantages of faster reaction rates, higher loading capacities, and cheaper elution and regeneration. On the other hand, the resins' cost is higher and their densities are low so that they tend to float out of leach pulps (19). A method has been patented to recover gold from thiourea solution in which the acidified solution is neutralized to pH 6.5 to precipitate gold with other impurities. This method is unselective. A further disadvantage is that acid must be added to lower the pH or the thiourea cannot be recycled because it decomposes (4).

Electrolysis has been used to recover gold from thiourea solution on a commercial basis. A two-stage electrolysis circuit with special cell designs has to be used in order to obtain high recoveries (20).

Hydrogen reduction under high pressure and temperature was also proposed to recover gold from thiourea solution; however, the kinetics is rather slow, and the use of a catalyst such as nickel or platinum is necessary to activate the reaction (21).

Sodium borohydride is used for many industrial applications which in-

clude pollution control and the recovery of heavy metals (22). Recovery of silver from photoprocessing and metal finishing industries and of gold from aqueous cyanide solution by using sodium borohydride (SBH) have both been patented (23, 24). However, the use of SBH in thiourea solution to recover gold and silver has not been as yet reported. Nontraditional leaching agents such as ammoniacal thiosulfate, acid chlorine, and acid thiourea have been investigated to dissolve gold and silver from ores (25, 26). Thiocyanate and acidified thiourea are being used as effective eluents for gold from loaded resins and solvents (18, 19, 27, 28).

A method to recover gold and silver from such solutions would be attractive to the gold industry. This study was initiated in order to investigate the various parameters controlling the rate and efficiency of gold and silver reduction by SBH. The recovery of gold from eluate or strip solutions from ion-exchange and solvent extraction, as examples to demonstrate the effectiveness of this method, are also investigated.

## EXPERIMENTAL

### Materials

1. Sodium borohydride is used as a stabilized aqueous solution containing 12% by weight  $\text{NaBH}_4$  and 40%  $\text{NaOH}$ . It is supplied by Morton Thiokol Inc. under the trade name VenMet solution. Typical properties of this solution are summarized in Table 1.
2. Standard gold solution, 1000 mg/L dissolved in 10%  $\text{HCl}$  or  $\text{HNO}_3$  acid, is supplied by SPEX Inc., SCP Science Division.
3. Analytical grade reagents used are: acids,  $\text{NaOH}$ ,  $\text{NaSCN}$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4$ ,  $\text{Ag}_2\text{SO}_4$ , and thiourea [ $\text{CS}_2(\text{NH}_2)_2$ ].

TABLE 1  
Typical Properties of VenMet Solution

Composition	
$\text{NaBH}_4$	$12.0 \pm 0.5\%$
$\text{NaOH}$	$40.0 \pm 2.0\%$
$\text{H}_2\text{O}$	Balance
Specific gravity:	1.4 (11.7 lb/gal)
Appearance	Off-white liquid
Viscosity	79 cPs at 23°C. Below 16°C becomes viscous. Below 13°C can crystallize
Solubility	Can be diluted with water
Stability	The decomposition of $\text{NaBH}_4$ is less than 0.1% per year in VenMet solution

## Equipment

The equipment used for measurements and analysis are: pH meter (Metrohm, model 632), Pt electrode vs SCE connected to pH-meter model 291 (Fisher), atomic absorption spectrophotometry (AAS), x-ray diffraction (XRD), copper target, and scanning electron microscope (SEM).

## Procedure

A test solution, 100 mL, of 10 mg/L Au in thiourea solution (7 g/L) was used to study most of the parameters of concern. The solution was stirred gently by a magnetic bar. In thiocyanate and thiosulfate solutions, the same procedure was applied but the salt concentration was 10% by weight.

Kinetic studies were performed in 500 mL of test solution at the desired pH. Samples were withdrawn at particular time intervals and analyzed for the desired metals by AAS.

The effect of temperature was examined in a similar way. The glass reactor was placed in a thermostatted water bath to control the temperature, and the solution was stirred by a mechanical stirrer. The reaction time was 2 min unless otherwise stated.

The reduction efficiency was calculated by comparing the concentration of gold actually reduced (Au in solution – Au remaining) to the concentration of gold in the original solution.

## RESULTS AND DISCUSSION

When a calculated amount of VenMet (V) solution was added to 100 mL of thiourea solution (7 g/L) containing 100 mg/L Au at pH 1.5, a fine black precipitate formed immediately. The product was separated on a filter paper and determined by x-ray diffraction to be metallic gold (Fig. 1). Scanning electron microscope analysis also revealed that the particles were very fine. The diameter of each particle was less than 1  $\mu\text{m}$  (Fig. 2).

Systematic studies were conducted on synthetic solutions of gold in thiourea solution to determine the quantity of VenMet solution required to achieve complete reduction. The effects of other parameters such as pH, gold concentration, thiourea concentration, temperature, time, and the presence of foreign ions were also studied in order to optimize the process. Analysis of thiourea by titration with mercuric nitrate both before and after the reduction was also performed.

## Stoichiometry

According to the reducing power of SBH, eight electrons per molecule are available to reduce M(I) ion. Gold is present in the monovalent form

A00105 3/20/89 S= 0.050 T=10.000 AWADALLA - AU ON FILTER PAPER  
PDF ( 1) =4,784 AU

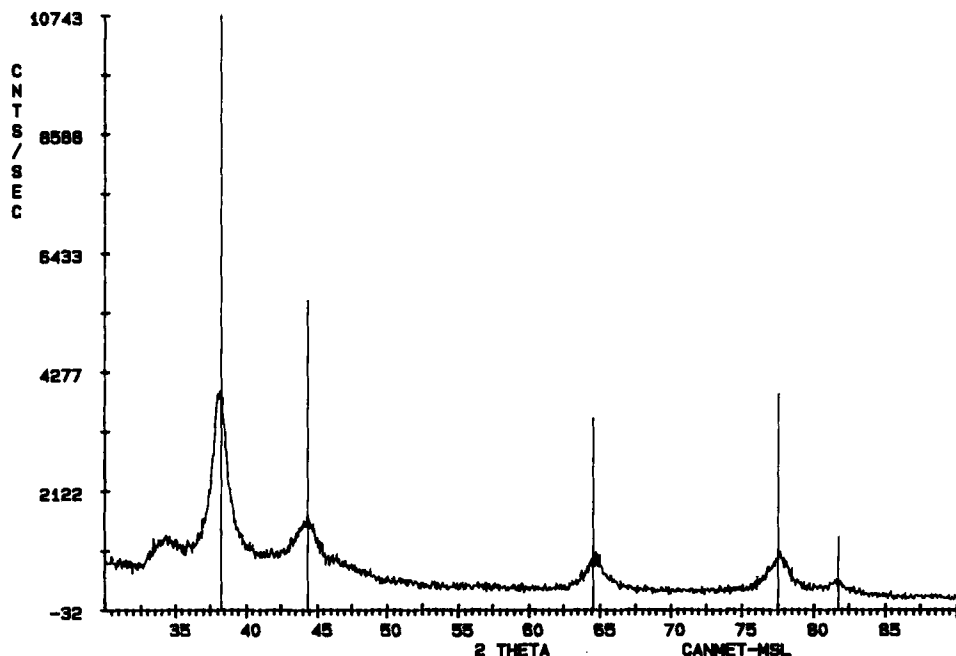
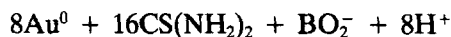


FIG. 1. X-ray diffraction pattern for the reduced product of Au(I) in acidic thiourea solution for sodium borohydride.

when complexed with acidic thiourea. The reduction reaction can be represented as follows:



According to this reaction, 1 mol SBH can reduce 8 mol of gold(I) ion. In practice, excess amounts of SBH are required to drive the reaction because of the requirement for a low pH. Figure 3 shows the effect of concentration in terms of the molar ratio of SBH/Au as a function of pH on the reduction efficiency of gold from thiourea solution. As seen in this figure, the excess requirements for SBH decreased as the pH increased, and the required SBH/Au(I) molar ratios were in the order of 100, 25, 10, and 3 at pH 1.5, 2.0, 2.5, and 3.0, respectively. However, at pH 2.5

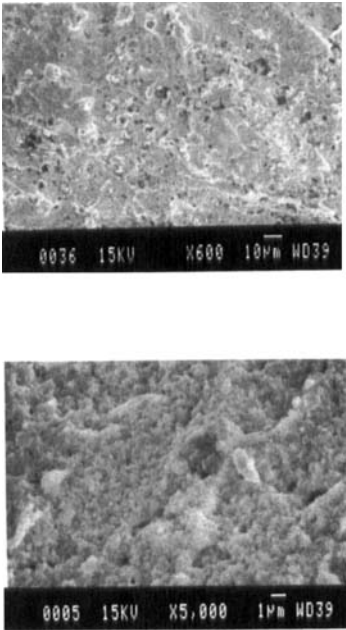


FIG. 2. Photomicrographs of metallic gold powder obtained by the reduction of Au(I)-thiourea complex with SBH.

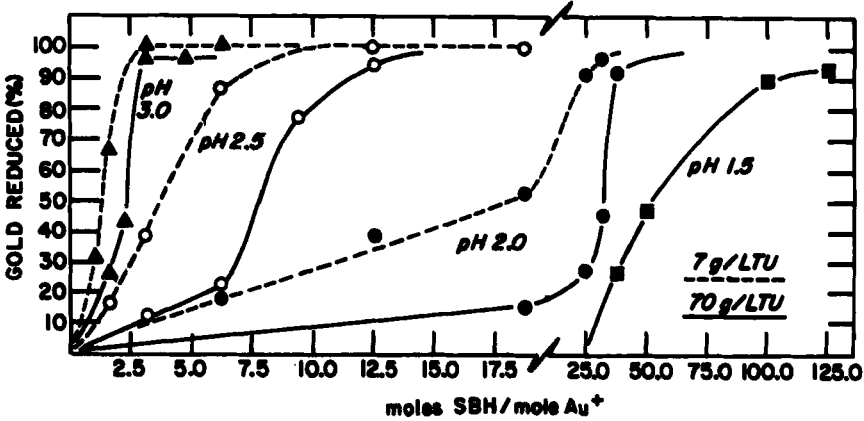


FIG. 3. The effect of pH and thiourea concentration on the reducing power of SBH at different amounts of SBH added. Au = 10 ppm, time = 2 min at room temperature.

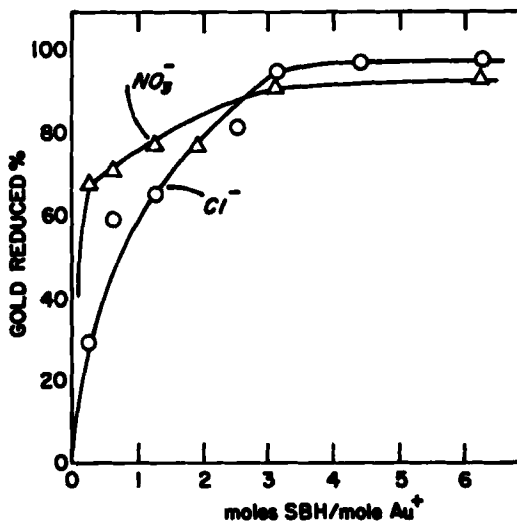


FIG. 4. The reduction of Au ion in chloride and nitrate solutions by SBH. Au = 10 ppm, pH = 2.5, time = 2 min at room temperature.

the molar ratios required in the case of Au-HCl and Au-HNO<sub>3</sub> complexes are about one-third those for the thiourea solution (SBH/Au = 3, as shown by Fig. 4). In thiosulfate and thiocyanate solutions, the molar ratio needed for complete precipitation is even less than unity since the pH of the reaction is nearly neutral (pH 6.0) (Figs. 5 and 6).

### Effect of Initial pH

One of the most important factors in the efficient use of VenMet solution is pH control. Borohydride reduction is normally carried out at pH 5–7. If the pH is below 5, borohydride undergoes hydrolysis, and consequently the consumption of borohydride may increase. Thiourea is stable in acidic medium, but thiourea undergoes degradation at higher pH. Therefore, SBH reduction was tried in an acidic solution of thiourea. Fortunately, it was found that the reduction was efficient. SBH was added in the form of VenMet solution so that the alkaline content of VenMet solution would be expected to increase the pH of the solution during the reaction. However, the pH was only raised slightly by the small volumes required. Figure 3 shows the effect of pH in the range 1.5–3.0 on the reduction efficiency of SBH at different molar ratios of SBH/Au. As shown by this figure, as the initial pH of gold-thiourea solution increased, more efficient gold reduction was obtained with lower quantities of VenMet solution needed.



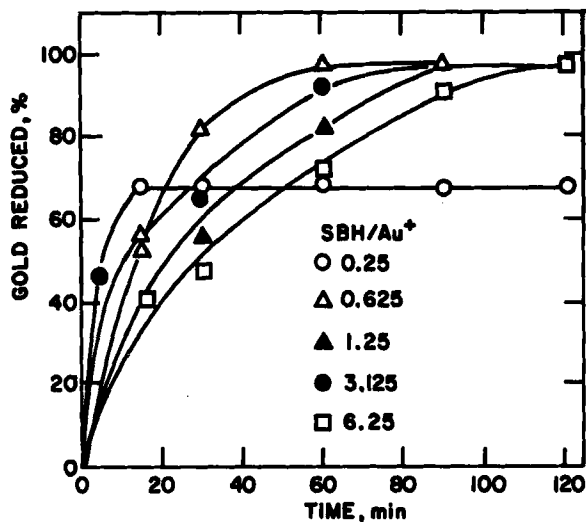


FIG. 5. Kinetics of reduction of Au(I) in 10 g/L thiosulfate solution.  $V = 500$  mL,  $Au = 10$  ppm,  $pH = 6.0$  at room temperature.

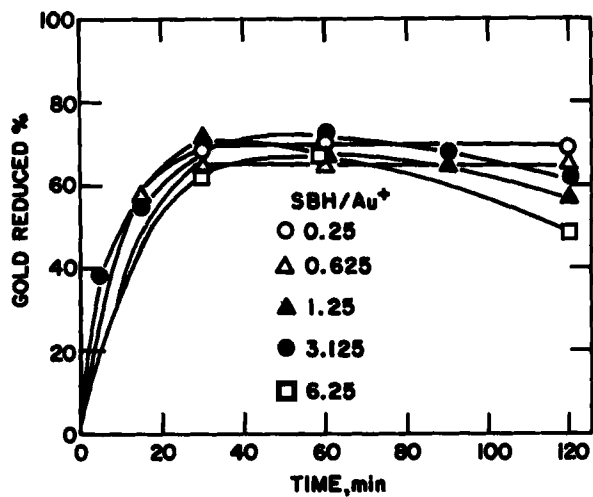


FIG. 6. Kinetics of reduction of Au(I) in 10 g/L thiocyanate solution.  $V = 500$  mL,  $Au = 10$  ppm,  $pH = 6.0$  at room temperature.

At a SBH/Au molar ratio equal to about six, no reduction occurred at pH 1.5, while at pH 2.0 the reduction was initiated. It was almost complete at pH 2.5 (Fig. 3).

On analyzing the thiourea before and after the reaction (initial pH 1.5–3.0), it was found that its concentration remained the same, indicating the stability of thiourea during the reduction. Thiourea could thus be readily recycled, adding some economical advantages for the process.

In pure solutions of gold containing HCl or  $\text{HNO}_3$ , complete reduction of gold was obtained at lower borohydride consumptions (Fig. 4).

In thiosulfate solution containing gold, the reduction was initiated at pH 4 since a yellowish-white precipitate was formed at lower pH. It was found that at an SBH/Au molar ratio equal to 0.625, complete reduction of gold was obtained at pH 6.0 (Fig. 5).

In thiocyanate solution containing 10 mg/L gold ion, the maximum reduction obtained was found not to exceed 70%, regardless of the quantity of SBH added (Fig. 6). It was noticed that after 5 min reaction time, maximum efficiency was obtained only if the initial pH was adjusted to 2.5. More or less than this value resulted in a decrease of gold reduction efficiency (Fig. 7). However, the efficiency improved if the reaction was

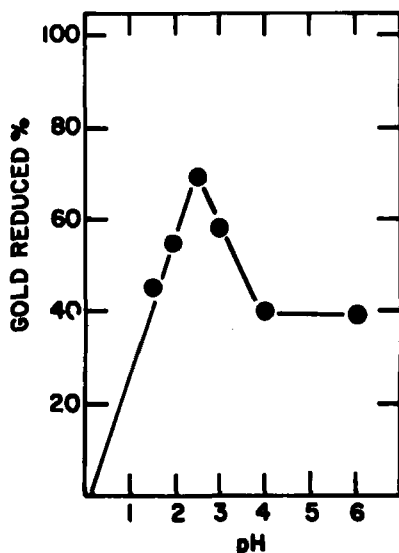


FIG. 7. The effect of initial pH on the reduction efficiency of SBH for Au(I) in 10 g/L thiocyanate solution.  $V = 100$  mL,  $\text{Au} = 10$  ppm, time = 5 min,  $\text{SBH/Au} = 3.125$  at room temperature.

conducted at pH 2.5 to 6.0 for a longer time. On the other hand, when 500 mg/L gold ion in 2.44 *M* thiocyanate solution containing 25% by volume dimethylformamide solution was reduced by adding 0.1 mL VenMet solution at pH 8 and for a period of 15 min, 93% gold reduction was obtained. This mixture of thiocyanate and dimethylformamide solution has been found efficient to enhance gold elution from anion-exchange resins (29).

### Kinetics

When VenMet solution was added to gold(I)–thiourea complex, immediate precipitation resulted, indicating the fast kinetics of the reduction reaction. As shown by Fig. 8, the conversion reached its maximum after 30 s.

On the other hand, the reduction behavior of gold in thiosulfate solution was different. The reaction took about 1 h at pH 6.0 when a lower amount of SBH/Au (0.625) was added (Fig. 5), and completion was attained even more slowly as the SBH/Au ratio was increased.

Figure 6 represents the kinetics in thiocyanate solution. At all molar ratios of SBH added, maximum efficiency (70%) was achieved after 30 min. However, if the reaction was left for a longer time, redissolution of

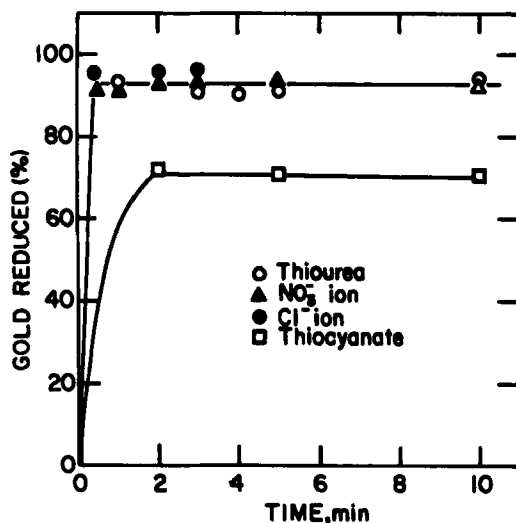


FIG. 8. Kinetics of reduction of Au(I) in 7 g/L thiourea, 10 g/L thiocyanate, HCl, and HNO<sub>3</sub> solutions on adding calculated amounts of SBH. V = 500 mL, Au = 10 ppm, pH = 2.5, SBH/Au = 9.3 for thiourea and 3.1 for thiocyanate, HCl, and HNO<sub>3</sub> at room temperature.

gold occurred. This happened because the VenMet solution increased the final pH to 10, increasing the leaching action of thiocyanate solution.

### Effect of Thiourea Concentration

Increasing the thiourea by a factor of 10 to 70 g/L would decrease the reduction efficiency of SBH to some extent as shown in Fig. 3; however, this effect becomes negligible at higher pH when compared with the SBH required to reach complete reduction. This result is in contrast with similar work done using hydrogen under pressure and temperature as reducing agents (21), where the reduction efficiency was greatly inhibited as the thiourea concentration was increased.

### Effect of Gold Concentration

Thiourea as an alternative leachant for gold ores has received much attention of late (30). Moreover, it is being used as a stripping agent for gold from loaded solvents and resins (16, 17, 19). Therefore, it was important to carry out the reduction from very dilute solutions (as in leach liquors) as well as from more concentrated liquors (such as strip solutions). It was found that SBH was effective in both cases (Table 2). The barren solution contained less than 0.2 mg Au/L.

### Effect of Foreign Ions

Foreign ions are always associated with gold and silver ions in thiourea leach liquors. Therefore, the study of the effects of impurities such as copper, iron, cobalt, nickel, and zinc during the reduction of gold and

TABLE 2  
Reduction of Gold Ion by SBH in Thiourea Solution Containing Different Concentrations of Gold<sup>a</sup>

Au <sup>+</sup> concentration (mg/L)	pH, final	Au in solution (mg/L)	Au recovery (%)
2	2.58	0.06	97.0
5	2.73	0.16	97.0
10	3.18	0.0	100.0
20	10.29	0.0	100.0
50	9.12 <sup>b</sup>	0.0	100.0
100	2.23 <sup>c</sup>	0.05	99.95

<sup>a</sup>Conditions: V = 100 mL, mol SBH/mol Au = 9.4, thiourea = 7 g/L, initial pH = 2.5, time = 2 min.

<sup>b</sup>Initial pH = 2.0; at pH > 2.0, gold starts to precipitate.

<sup>c</sup>Initial pH = 1.5; at pH > 1.5, precipitation of gold starts.

silver by SBH is of prime importance. These ions were added in the form of sulfates to Au–thiourea solution, and their behavior was studied by comparing their concentrations in the thiourea solution before and after reduction.

The presence of Ag ion was found to enhance the reduction efficiency of Au ion; when the concentration of Ag ion was increased, the reduction efficiency of gold increased accordingly (Fig. 9). For example, in the presence of 10 and 100 mg/L of Ag ion, it was found that the amount of SBH required was decreased by 33 and 83%, respectively. The precipitation of gold in such a solution was performed not only by the SBH reduction mechanism but also by the cementation of gold on silver metal produced by the action of SBH on silver ion. On the other hand, a very small excess of SBH (based on Ag + Au needs) was required to precipitate all the silver content. This renders the process more economic because silver can be recovered. The reduction in such cases could be performed in two steps to precipitate gold and silver metal separately in good yield and higher purity.

Like silver ion, zinc ion enhances the reduction efficiency of Au ion (Fig. 10). The effect in this case is stronger than with Ag ion; for example,

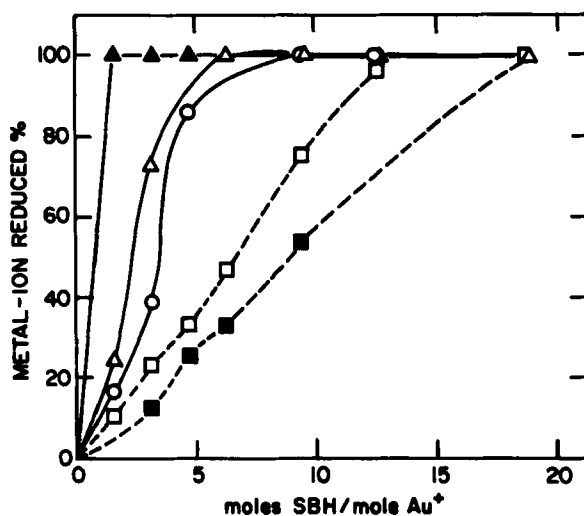


FIG. 9. Reduction of Au(I) in 7 g/L thiourea solution in the presence of Ag(I) with SBH. pH = 2.5, time = 2 min at room temperature. (○) Au (10 ppm Au + 0 ppm Ag); (△) Au (10 ppm Au + 10 ppm Ag); (▲) Au (10 ppm Au + 100 ppm Ag); (□) Ag (10 ppm Ag + 10 ppm Au); (■) Ag (100 ppm Ag + 10 ppm Au).

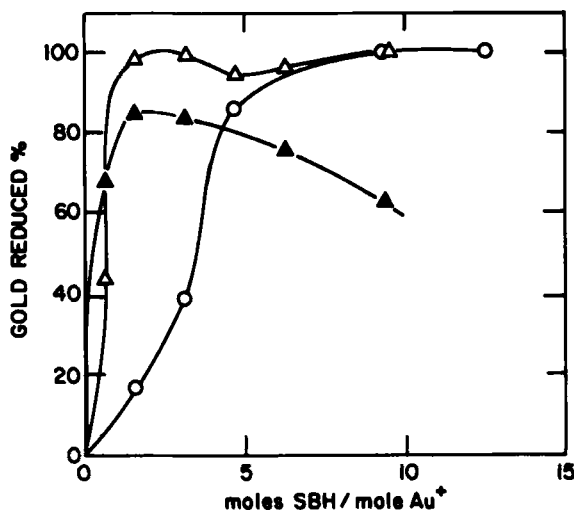


FIG. 10. Reduction of Au(I) in 7 g/L thiourea in the presence of Zn(II) with SBH. pH = 2.5, time = 2 min at room temperature. (○) 10 ppm Au + 0 ppm Zn, (△) 10 ppm Au + 10 ppm Zn, (▲) 10 ppm Au + 100 ppm Zn.

the presence of 10 mg/L Zn ion in thiourea solution containing 10 mg/L Au decreases SBH consumption by 83% (as is the case when adding 100 mg/L Ag to 10 mg/L Au). The addition of zinc ion was found effective even at lower solution pH's (Fig. 11). The gold precipitate in this case was found free from zinc since SBH has proved incapable of reducing zinc ion (31). It is postulated that this phenomenon may be explained by the amphoteric nature of Zn ion in such acidic solutions. Zinc ion acting as a pseudobase decreases the pH drop during reduction. Consequently, less reagent is consumed in order to achieve the complete removal of gold ion. The final pH of the treated solution increases slightly as in the case of an Au-thiourea solution containing no zinc ion. The redox potential values are decreased by the same amount with and without Zn (Table 3).

Other metal ions such as iron(II), cobalt, nickel, and copper have a negative effect on gold reduction by SBH (Figs. 12–15). The order in terms of decreasing reduction efficiency of SBH for gold in the pH range 1.5–2.5 was found to be: Fe(II) > Co(II) = Ni(II) > Cu(II). The gold product obtained was almost pure since these metal ions only undergo significant reduction at SBH concentrations higher than those required to reduce most of the Au(I) (30). However, the effect of these ions is decreased when the pH of solution is increased to 3.0 (Figs. 13B and 14B).

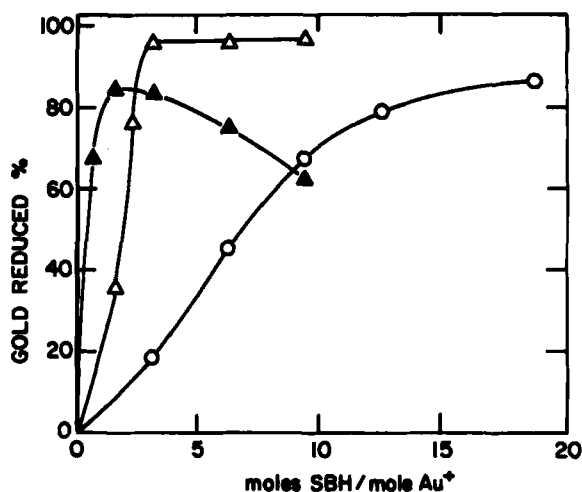


FIG. 11. Reduction of Au(I) in 7 g/L thiourea solution in the presence of Zn(II) at different pH values with SBH. Au = 10 ppm, Zn = 100 ppm, time = 2 min at room temperature. pH: (○) 1.5, (△) 2.0, (▲) 2.5.

### Effect of Mixture

The reduction of gold ion in thiourea solution in the presence of Ag, Cu, and Fe(II) ions was initiated by adding calculated amounts of SBH to the solution mixture after adjusting the pH to 1.5. Table 4 summarizes the results. Nearly all of the gold together with about 65% of the silver were reduced on adding the optimum amount of SBH. Accordingly, the product obtained was less pure (Table 4A). If the reduction was performed in two stages, higher grade gold and silver products precipitate separately with good yield (Table 4B).

TABLE 3  
Redox Potentials (referred to SCE) and pH's of Treated Au-Thiourea Solution in Comparison with Solution Containing Zinc Impurity<sup>a</sup>

Mol SBH/ mol Au	10 mg/L Au solution		10 mg/L Au + 10 mg/L Zn		10 mg/L Au + 100 mg/L Zn	
	pH final	E (mV)	pH final	E (mV)	pH final	E (mV)
1.56	2.55	84	2.58	146	2.56	128
3.13	2.63	133	2.63	146	2.63	182
6.25	2.70	194	2.80	205	2.87	205
9.38	2.86	217	3.31	215	3.27	205

<sup>a</sup>Conditions: V = 100 mL, Au = 10 mg/L, initial pH = 2.5, TU = 7 g/L, time = 2 min.

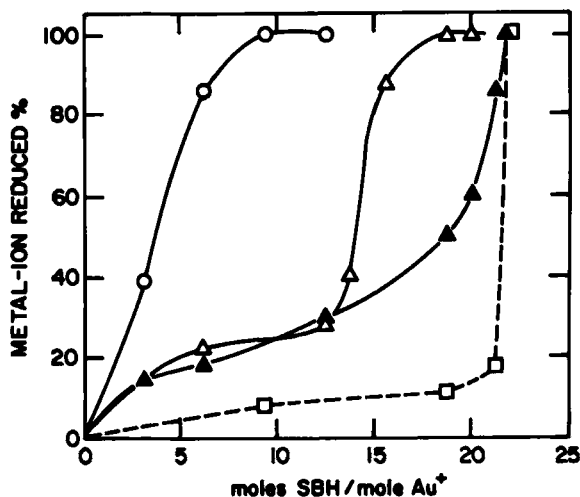


FIG. 12. Reduction of Au(I) in 7 g/L thiourea in the presence of Fe(II) with SBH. pH = 2.5, time = 2 min at room temperature. (O) Au (10 ppm Au + 0 ppm Fe); ( $\Delta$ ) Au (10 ppm Au + 1 ppm Fe); ( $\blacktriangle$ ) Au (10 ppm Au + 10 ppm Fe); ( $\square$ ) Fe (10 ppm Fe + 10 ppm Au).

### Effect of Temperature

Temperature in the 25–80°C range was examined for the reduction of gold in thiourea solution. As seen in Fig. 16, slight increases in the reduction efficiency are obtained with increasing temperature. The reaction accordingly can be performed at ambient temperature with high efficiency. This is in contrast to the work using hydrogen reduction under pressure in which high temperature was required to achieve effective reduction (21).

### Reduction of Gold from Acidic Thiourea Strip Solution

Recent studies showed that gold could be extracted from cyanide leach liquors by either solvent extraction or ion-exchange techniques (16, 19). The gold and other impurities can be stripped from the loaded organic phase and resin by acidified solutions of thiourea. Reduction reactions were performed in the strip solution using SBH. Encouraging results were obtained, as shown in Table 5. The method involves pH adjustment to the limits of solution stability with respect to precipitation, adding small amounts of VenMet solution to conduct the reaction, and filtration to separate the precipitate. As observed from the table, the reaction is very efficient; 90% of Au was precipitated from strip solution of loaded solvent when a particular amount of SBH was added (1.25 mol SBH/mol Au).



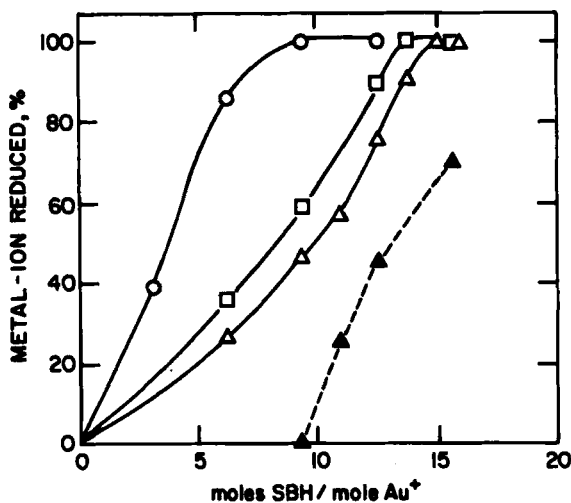


FIG. 13A. Reduction of Au(I) in 7 g/L thiourea solution in the presence of Co(II) with SBH. pH = 2.5, time = 2 min at room temperature. (○) Au (10 ppm Au + 0 ppm Co); (Δ) Au (10 ppm Au + 10 ppm Co); (□) Au (10 ppm Au + 1 ppm Co); (▲) Co (10 ppm Co + 10 ppm Au).

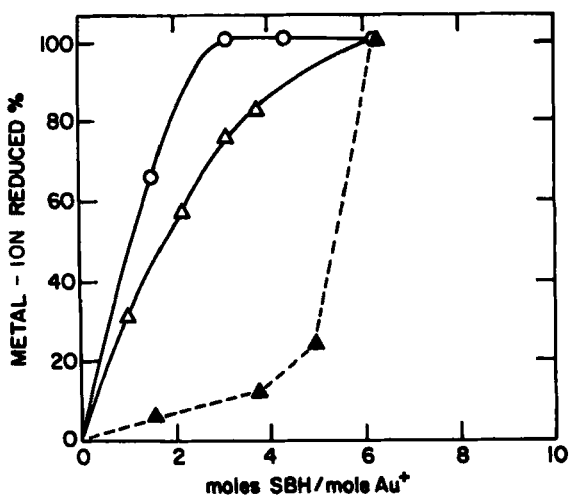


FIG. 13B. Reduction of Au(I) in 7 g/L thiourea solution in the presence of Co(II) with SBH. pH = 3.0, time = 2 min at room temperature. (○) Au (10 ppm Au + 0 ppm Co); (Δ) Au (10 ppm Au + 10 ppm Co); (▲) Co (10 ppm Co + 10 ppm Au).

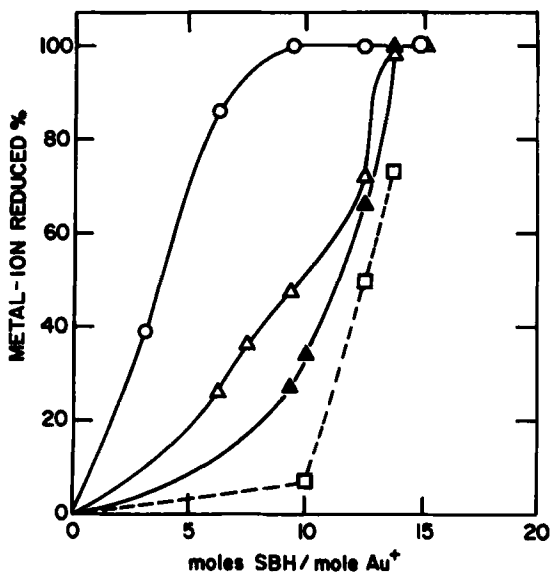


FIG. 14A. Reduction of Au(I) in 7 g/L thiourea solution in the presence of Ni(II) with SBH. pH = 2.5, time = 2 min at room temperature. (○) Au (10 ppm Au + 0 ppm Ni); (△) Au (10 ppm Au + 1 ppm Ni); (▲) Au (10 ppm Au + 10 ppm Ni); (□) Ni (10 ppm Ni + 10 ppm Au).

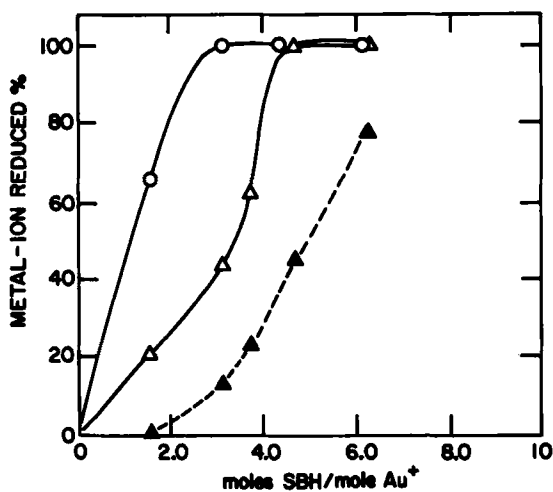


FIG. 14B. Reduction of Au(I) in 7 g/L thiourea solution in the presence of Ni(II) with SBH. pH = 3.0, time = 2 min at room temperature. (○) Au (10 ppm Au + 0 ppm Ni); (△) Au (10 ppm Au + 10 ppm Ni); (▲) Ni (10 ppm Ni + 10 ppm Au).

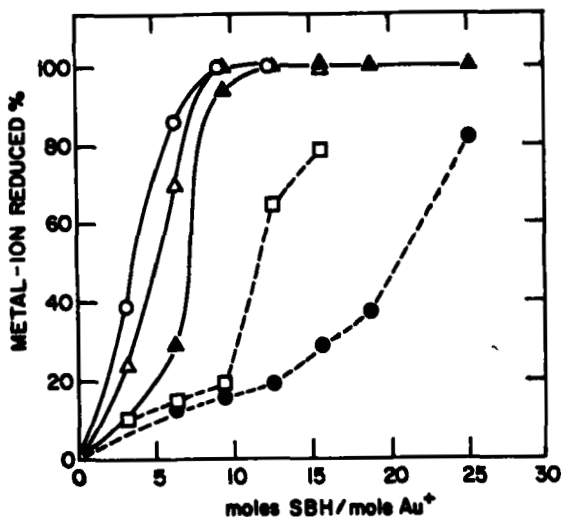


FIG. 15. Reduction of Au(I) in 7 g/L thiourea solution in the presence of Cu(II) by SBH. pH = 2.5, time = 2 min at room temperature. (O) Au (10 ppm Au + 0 ppm Cu); ( $\Delta$ ) Au (10 ppm Au + 10 ppm Cu); ( $\square$ ) Au (10 ppm Au + 100 ppm Cu); ( $\bullet$ ) Cu (10 ppm Cu + 10 ppm Au); ( $\blacktriangle$ ) Cu (100 ppm Cu + 10 ppm Au).

The purity of the product obtained was better than 98%. The recovery could be increased if excess SBH was added.

An eluate solution of loaded resin was treated in a similar way. Gold removal was essentially complete ( $\approx 99\%$ ). The barren solution obtained had about 2 mg Au/L, and the product analysis is shown in Table 6.

### Economics

As demonstrated by the previous two examples, the recovery of gold from strip solution using SBH is very efficient, fast, and simple, and equipment needs are also relatively simple and low cost. As an example, the price of SBH required to remove gold from a solvent extraction strip solution as previously discussed was calculated. It was found that 3 lb VenMet solution, worth \$10 U.S. was enough to precipitate 1 lb gold of high purity (1 lb VenMet solution = \$2.3–3.3 U.S.).

### CONCLUSIONS

1. Gold ion can be reduced effectively to metallic gold from acidic solutions of thiourea, thiosulfate, thiocyanate, HCl, and HNO<sub>3</sub> by the addition of SBH as VenMet solution.

TABLE 4A  
Reduction of Mixture with SBH in One Stage<sup>a</sup>

Metal ion	Concentration of barren solution (mg/L)	Recovery (%)	Purity of product (%)
Au	0.63	98.74	57.0
Ag	17.09	65.82	38.0
Cu	21.5	14.00	4.0
Fe	24.22	3.12	1.0

<sup>a</sup>Composition of solution, mg/L = Au = 50, Ag = 50, Cu = 25, and Fe = 25; TU = 7 g/L, V = 100 cm<sup>3</sup>, time = 5 min, T = 25°C, pH initial = 1.66, SBH/Au = 12.5.

TABLE 4B  
Reduction of Mixture with SBH in Two Stages

Metal ion	Concentration of metal ion in barren solution (mg/L)		Recovery (%)		Purity (%)	
	1st stage	2nd stage	1st stage	2nd stage	1st stage	2nd stage
Au	5.348	1.24	89.30	76.85	83.2	10.9
Ag	45.2	13.88	9.60	69.30	8.9	82.8
Cu	21.19	21.48	7.60	0.0	7.1	0.0
Fe	24.58	22.19	0.84	9.7	0.8	6.3

<sup>a</sup>Initial pH = 1.5 and 2.68 for 1st and 2nd stage, respectively. 1st stage SBH/Au = 9.375. 2nd stage SBH/Au = 3.125.

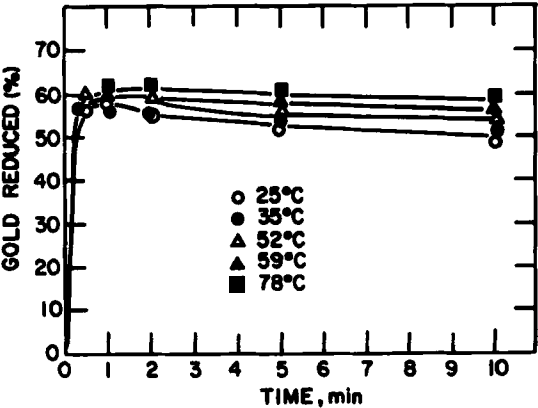


FIG. 16. The effect of temperature on the reduction of Au(I) in 7 g/L thiourea solution by SBH at different time intervals. V = 500 mL, Au = 10 ppm, pH = 2.5, SBH/Au = 3.125.

TABLE 5  
Reduction of Gold from 0.5 M Thiourea Strip Solution by SBH<sup>a</sup>

	Au	Zn	Cu	Ni	Fe
Composition of strip solution (mg/L)	1940	960	72.2	247.6	33.2
Composition solution after adding SBH (mg/L)	203	960	68.9	247.0	3.2
Recovery (%)	89.5	0.0	4.5	0.0	90.5
Purity of the product (%)	98.12	0.0	0.19	0.0	1.69

<sup>a</sup>V = 25 mL, initial pH = 0.2, then adjusted with NaOH to pH = 0.8, time = 5 min at room temperature, VenMet = 0.1 mL (SBH/Au = 1.25).

2. The reduction reaction is very fast; it takes about 30 s to attain the maximum.
3. The reaction is efficient at ambient temperature; increasing the temperature up to 80°C only increases the reduction efficiency slightly.
4. The SBH reduction can be applied to leach solutions containing low gold concentrations (2 mg/L) as well as to strip solutions containing some grams per liter of gold.
5. In thiourea–Au solution, zinc and silver ions enhance the reduction efficiency of SBH. Copper, iron, cobalt, and nickel ions have an adverse effect.
6. In the presence of mixtures of foreign ions with Au–thiourea acidic solution, gold can be recovered selectively by carefully controlling the amount of reagent added.

TABLE 6  
Reduction of Gold from 0.5 M Thiourea Eluate Solution by SBH<sup>a</sup>

	Au	Zn	Cu	Ni	Fe
Composition of eluate (mg/L)	128	345.3	4.18	4.29	3.36
Composition after SBH (mg/L)	1.82	269.3	5.54	5.05	4.30
Recovery (%)	98.6	22.0	0.0	0.0	0.0
Purity (%)	62.4	37.6	0.0	0.0	0.0

<sup>a</sup>Initial pH = 0.24, then adjusted to pH = 2.5 by NaOH, V = 25 mL, time = 5 min at room temperature, SBH/Au = 3.75.

7. Silver can be recovered separately from a mixture of Au and Ag ions if the reaction is performed in two stages.
8. Thiourea is stable during the course of reduction. It does not undergo any degradation reaction.
9. The process is simple and fast, and it needs simple and inexpensive equipment in comparison with other methods used to recover gold.

### Acknowledgments

The authors are grateful to the Natural Science and Engineering Research Council of Canada for providing necessary financial support. The authors also wish to acknowledge the contribution of Dr. R. Molnar for his encouragement, reviewing the manuscript, and providing valuable suggestions and comments.

### REFERENCES

1. N. P. Finkelstein, "The Chemistry of the Extraction of Gold from Its Ores," in *Gold Metallurgy in South Africa* (R. J. Adamson, ed.), Chamber of Mines of South Africa, Johannesburg, 284–351, (1972).
2. B. Calmanovici and L. Gal-Or, "Chemical Refining of Gold Following Recovery from Cyanide Solutions—II," *Met. Finish.*, 82(7), 19–22 (1984).
3. A. Van Lierde, P. Ollivier, and M. Lesoille, "Developpement du Nouveau Procédé de Traitement pour le Minerai de Salsigne," *Ind. Min. Tech.*, 1a, 399–410 (1982).
4. T. Odaka, S. Goto, I. Asakura, et al., "Method of Recovering Gold and Silver from Aqueous Solutions Containing Thiourea, Gold and Silver," Japanese Patent 60-103138 (1985).
5. G. Deschênes, "Investigation on the Potential Technique to Recover Gold from Thiourea Solution," in *Proceedings, International Symposium on Gold Metallurgy*, Winnipeg, 359–378, (August 1987).
6. F. W. McQuiston Jr. and T. G. Chapman, U.S. Patent 2,545,239 (March 13, 1951).
7. Anon., "Homestake Uses Carbon-in-Pulp to Recover Gold from Slimes," *World Min.*, 27(12), 44–49 (1974).
8. G. Deschênes and E. Ghali, "Leaching of Gold from Chalcopyrite Concentrate by Thiourea," 20, 79–202 (1988).
9. R. Schulze, "Hydrometallurgical Winning of Precious Metals Using Thiourea," German Patent DE 3,401,961 (August 1984).
10. D. M. Muir, *Prospects for the Recovery of Gold from Cyanide Liquors and Pulps by Solvent Extraction and by Ion Exchange*, CANMET Internal Report, MSL 88-78 (IR), (1988).
11. J. E. Barnes and J. D. Edwards, "Solvent Extraction at INCO's Acton Precious Metal Refinery," *Chem. Ind.*, 5, 151–155 (1974).
12. L. R. P. Reavell and P. Charlesworth, "The Application of Solvent Extraction to Platinum Group Metals Refining," in *Proceedings, International Solvent Extraction Conference '80*, Liege, Belgium, (1980).
13. R. F. Edwards, "Selective Solvent Extractants for the Refining of Platinum Metals," in *ISEC '77, CIM Special Volume*, Vol. 21, pp. 24–31 (1979).
14. G. B. Harris and R. W. Stanley, *Hydrometallurgical Treatment of Silver Refinery Anode*

- Slimes*. Presented at the 10th International [PM] Conference, Lake Tahoe, Nevada (June 1986).
15. G. P. Demopoulos, G. Pouskoupleli, and G. M. Ritcey, *A Novel Solvent Extraction System for the Refining of Precious Metals*. Presented at the International Solvent Extraction Conference '86. West Germany (1986).
  16. P. A. Riveros, "Studies on the Solvent Extraction of Gold from Cyanide Media," *J. Hydrometall.*, **24**, 135-156 (1990).
  17. G. R. Palmer, W. L. Staker, and R. G. Sandberg, "Recovery of Precious Metals from Cyanide Solutions Using Ion-Exchange Resins," in *Process Mineralogy VIII, Applications of Mineralogy to Mineral Beneficiation Technology, Metallurgy and Mineral Exploration and Evaluation, with Emphasis on Precious Metal Ores*, Phoenix, Arizona, 25-28 (1988).
  18. E. Becker, M. Knothe, and J. Lobel, "Gold Recovery from Non-Metallic Secondary Raw Materials by Leaching with Thiourea and Adsorption on Ion-Exchange," *Hydrometallurgy*, **11**, 265-275 (1983).
  19. P. A. Riveros, *Advances in Ion-Exchange and Solvent Extraction for Gold Recovery*, CANMET/MSL Division Report MSL 88-108 (OP&J), (1988).
  20. Anon., "Gold from Russia's Murantau Deposit," *Coal, Gold Base Miner. South. Afr.*, **26**, 75 (1978).
  21. G. Deschènes, G. M. Ritcey, and E. Ghali, "Reduction of Gold and Silver by Hydrogen from Thiourea Solutions," in *Proceedings, 2nd International Symposium on Precious Metals and Gold '89*, Las Vegas, Nevada (February 1989).
  22. E. A. Sullivan, *Industrial Removal and Recovery of Metals with Sodium Borohydride*. Presented at the Third International Meeting on Boron Chemistry, Germany (1976).
  23. L. B. Friar and K. M. Smith, "Recovery of Silver from Photographic Porcessor Effluents," U.S. Patent 4,279,644 (1981).
  24. D. J. George and R. M. Skomoroski, "Aluminum Containing Precipitating Agent for Precious Metals and Method for Its Use," U.S. Patent 719,805 (September 1976).
  25. D. Zipperian, S. Raghavan, and J. P. Wilson, "Gold and Silver Extraction by Ammoniacal Thiosulfate Leaching from a Rhyolite Ore," *Hydrometallurgy*, **19**(3), 361-375 (January 1988).
  26. J. Avraamides, "Prospects for Alternative Leaching Systems for Gold: A Review," in *Carbon-in-Pulp Technology for the Extraction of Gold*, Murdoch, Australia, 369-391 (July 1982).
  27. H. H. Law, "Recovery of Gold in Gold Plating Processes," U.S. Patent 4,372,830 (March 18, 1982).
  28. C. A. Fleming, "Novel Process for Recovery of Gold Cyanide from Strong-Base Resins," in *Extraction Metallurgy*, Vol. 85, London, U.K., 757-787 (September 1985).
  29. H. H. Law, "A Recovery of Gold from Ion Exchange Resins with Dimethylformamide/Water Mixture," in *Proceeding of the Sixth International Precious Metals Institute Conference*, Newport Beach, California, 503-507 (June 1982).
  30. C. Y. Chang and F. Lawson, "Leaching of Gold and Silver from Pyrite and Its Calcine with Aqueous Cyanide and Thiourea," *Aust. IMM Bull. Proc.*, **292**(4), 79-84 (1987).
  31. F. T. Awadalla, Z. Yin, and B. Pesic, *Reduction of Cobalt, Copper and Iron from Aqueous Solutions with Sodium Borohydride*. Presented at the Topical Symposium on Innovations in Materials Processing Using Aqueous. Colloid and Surface Chemistry at the AIME Annual Meeting, Las Vegas, Nevada (March 1989).

Received by editor April 30, 1990