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GOLD LEACHING BY USE OF AN *N*,*N*′-DISUBSTITUTED THIOUREA

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ABSTRACT

A novel reagent for gold leaching was synthesized and the leaching conditions investigated. The reagent, 1-phenyl-2-thio-3-(2-hydroxyethyl) urea, dissolved gold at relatively high yields (>95%) in the presence of an oxidant (Fe(III)) in a sulfuric acid solution at pH 0.9–1.2 at room temperature. The effects of certain leaching parameters, such as working pH, reagent-Au mol ratio, oxidant-Au mol ratio, contact time, and temperature are discussed.

Key Words: Gold leaching; Thioureation

INTRODUCTION

Gold is a noble metal that is interesting not only for its traditional value but also for its production methods. In nature, gold appears in metallic form or as a sulfide ore. The methods of gold recovery are selected based on both its granule size and its chemical environment.

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Amalgamation is the leaching process applied to gold granules smaller than 0.2 mm. Cyanidation is a leaching method frequently applied to metallic gold and its ores. However, the reaction rate of cyanidation is relatively low. In addition, the process is not selective enough for gold because of the extremely high complexation capability of the cyanide anion. Most of the cyanide used in gold metallurgy is consumed by the accompanying metals, such as Fe, Cu, Zn, and Hg. The cyanidation method residues highly contaminate soil and ground water. As a consequence, the complexed heavy metals strongly affect public health and influence all the elements of the environment. Cyanide application also causes air pollution. Because of these contamination problems, the cyanide recycling processes need to be under thorough control.

Thiourea, *N*,*N*′-ethylenethiourea, and thiosulfate have been suggested as alternative reagents to cyanide for gold leaching. The use of thiourea in noble metal leaching has been discussed for a long time (1–10). For example, several disadvantages have been reported for thiourea leaching. During gold oxidation, thiourea decomposes through formamidine disulfide to cyanamide and sulfur, which is sticky and prevents the attack of the reagent on gold. The use of SO_2 to reduce such irreversible decomposition of thiourea also inversely affects the gold dissolution. Thus, thioureation conditions are still the main objects of many studies.

Of the cyclic thioureas, *N*,*N*′-ethylenethiourea and *N*,*N*′-propylenethiourea have been examined (10) and researchers have claimed that ethylenethiourea had advantages of lower reagent consumptions. Although cyclic thiourea compounds, such as ethylenethiourea, are hardly oxidized and thus avoid the elemental sulfur formation under fixed conditions (11), those compounds are suspected carcinogens (12,13).

Leaching of gold in thiosulfate-based systems is promoted by ammonia and copper. However, the complex reaction pathway needs the thiosulfate production to be maintained with elemental sulfur at the plant site, where precautions should be taken for environmental safety (14–18).

Because of the problems associated with cyanide in gold leaching, other reagents and novel applications to gold leaching must be found. *N*-Methylthiourea is one of the reagents studied in our laboratories (19). In the present work we describe work on our investigation of the possible gold-leaching capacity of a novel substituted thiourea: 1-phenyl-2-thio-3-(2-hydroxyethyl) urea. The reagent is synthesized from ethanolamine and phenylisothiocyanate.

The oxidation of gold was performed by iron (III) salts under controlled conditions in the presence of the reagent.

EXPERIMENTAL

All the metal analyses were carried on a Shimadzu 670 model atomic absorption spectrophotometer. UV and infrared spectra were recorded on a Shimadzu UV 240 and on a Mattson 1000 FTIR spectrophotometer, respectively. ^{1}H NMR spectra and mass spectra were taken on a Bruker AC 200 L spectrometer and VG ZAB Spec GC-MS spectrometer, respectively.

Synthesis of 1-Phenyl-2-thio-3-(2-hydroxyethyl)urea

Phenylisothiocyanate (7.5 mL, 0.062 mol) was added dropwise into 3 mL ethanolamine (0.05 mol) in l00 mL toluene at 5–8°C. The crystals were filtered and crystallized twice from ethanol (125 mL). The yield was 8.7 g (88%), and the melting point was 137–138°C (decomp.). See Table 1 for spectrospectroscopy data of 1-Phenyl-2-thio-3-(2-hydroxyethyl)urea.

Preparation of Pure Gold Powder

Pure gold (1 g at 99.9% purity) was dissolved in aqua regia (75 mL) in a water bath and evaporated until dryness in a hood. The residue was dissolved in distilled water and sodium metabisulfite solution was added dropwise during mixing. The fine gold precipitate was filtered through a sintered filter, washed with ethanol, and dried at 100–105°C.

Leaching Experiments

Acidic Solutions

Because in the preliminary experiments dissolution of gold was achieved below pH 2.5, sulfuric acid solutions with pH values between 0.0 and 2.1 were prepared at 0.3 pH unit intervals.

Oxidative Solutions

Acidic solutions adjusted to working pH values were used in the preparation of oxidative solutions containing $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 0.8 g/100 mL (0.0l66 mol/L) concentrations.

Experimental Procedure

During the experiments, a 4:1 reagent (L)-Au mol ratio was selected. This ratio is twofold of the stoichiometric ratio for gold complexation. A total of 0.0065

Table 1. Spectrometric Data of 1-Phenyl-2-thio-3-(2-hydroxyethyl)urea

Ultraviolet Spectral Data (Solvent: Water, pH 0.9)		Infrared Spectral Data (KBr Pellet)	
Wavelength nm	Molar Extinction Coefficient ε	Wavenumber cm^{-1}	Assignments
214	53000	3355	O–H
251	38000	3270	N–H
		3186	N–H
		3000	Arom. C-H
		1593	C=C
		1542	N–H
		1517	N–H
		1059	C=S

Mass Spectral Data (Electron Impact Method)		HNMR Spectral Data (Solvent: DMSO-*d*6)	
m/e	Abundance %	Chemical Shift δ, ppm	Proton Number; Group; Multiplicity
196	M$^+$, 55; molecular ion	3.55	4H; CH_2; t
178	M$^+$–H_2O, 69	4.73	1H; OH; s
162	43	7.08	1H; arom.; t
151	44	7.30	2H; arom.; t
131	39	7.45	2H; arom.; d
118	50	7.63	1H; NH; s
104	33	9.52	1H; NH; s
93	100		
86	14		
77	52		
65	30		

s: singlet; d: doublet; t: triplet

Solubility in water (pH 0.9) (g/100 mL): 0.200 (20°C); 0.463 (40°C).
Analysis: Calculated for $C_9H_{12}N_2OS$ C%: 55.10; H%: 6.12; N%: 14.28
Experimental C%: 55.20; H%: 6.43; N%: 14.23.

g (3.3×10^{-5} mol) Au and 0.0258 g (1.32×10^{-4} mol) ligand (L) were mixed with the oxidative solution at the working pH and volume to attain the Fe(III):Au mol ratio of 1:1, 2:1, or 4:1. The final volume of the suspension was completed to 10 mL with the acidic solution at the working pH.

The reaction mixture was heated in a liquid paraffin bath at selected temperatures for fixed time intervals. Temperature was controlled by a thermostated heater.

At the end of the heating period, the sample was filtered through a sintered filter. The filtrate was transferred into a volumetric flask (25 mL) and the flask was filled to the mark by the acidic working solution.

The leaching procedures under definite conditions were repeated several times ($n = 3$). Gold analyses in the filtrates were done ($n = 3$) by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The general reactions for dissolution of gold by an oxidant in the presence of a complexing agent are as follows:

$$L + H^+ \Leftrightarrow LH^+$$

$$Au + 2LH^+ + Fe^{3+} \rightarrow [\,AuL_2\,]^+ + Fe^{2+} + 2H^+$$

$$Au + 3LH^+ + Fe^{3+} \rightarrow [\,Au\,L_3]^+ + Fe^{2+} + 3H^+$$

According to the equations, metallic gold is oxidized by Fe(III) ions in the presence of reagent, and the cationic complexes $[AuL_2]^+$ and $[AuL_3]^+$ are transferred into the solution. The coordination number of Au^+ is 2. When L is thiourea, the $[AuL_2]^+$ complex is the most dominant species because its dissociation constant pK is 25 (20,21).

Although the solubility of the reagent is very low in the solutions of acidic working pH values, gold oxidation and dissolution of the reagent progressed simultaneously. In the experiments in which high yields of gold leaching were obtained, all of the reagents had been dissolved.

The leaching experiments were performed with a ligand-Au mol ratio of 4:1, which is onefold in excess of the theoretical stoichiometric ratio. During the experiments, the gold particle size was kept in the range of $(+)150-(-)100$ mesh.

Other parameters that possibly influence the leaching yields were investigated. Thus, the dependencies of leaching yields were established regarding the parameters: 1) contact time, 2) pH, 3) oxidative reagent-Au mol ratio, and 4) temperature of the reaction medium.

Complexation of gold (I) by the ligand was followed by the comparison of UV spectra. Complexation caused the disturbance and blueshifts of the main peaks of ligand (202 and 241 nm peaks) along with an important decrease in intensity (Fig.1).

The data showed an interesting dissolution behavior of metallic gold in the presence of reagent. Results are outlined in Figs. 2–8. When the parameters are independently discussed, the optimum leaching conditions are apparent. Cooperative actions of the parameters are important.

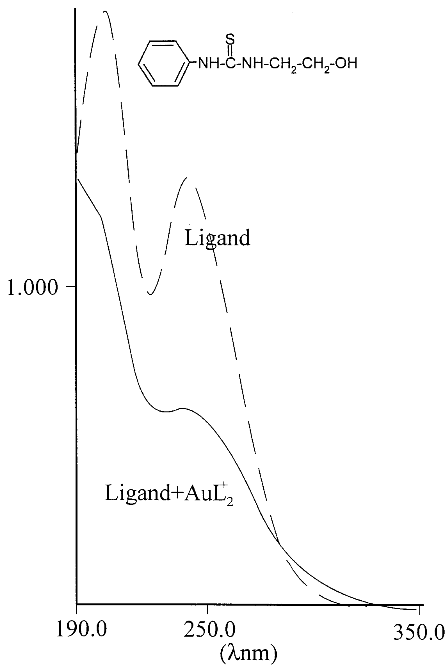

Figure 1. UV spectra of the ligand and the gold (I) complex in the leaching solution in a water solvent at pH 0.9.

Influences of Oxidant-Au Mol Ratio and Contact Time

The Fe(III)-Au mol ratio is an important parameter in the gold dissolution mechanism. During the preliminary experiments, we observed that 4:1 and higher oxidant-Au ratios have secured almost similar yields. Higher iron (III) concentrations did not cause any negative effect on leaching. This reagent behavior is contrary to that of thiourea, which allows relatively stable complexes with impure metals, such as iron, to aggravate the gold dissolution (22). As a consequence, in our experiments, the lower oxidant-Au ratios of 1:1, 2:1, and 4:1 could be applied.

For fixed pH conditions of the suspension, the effects of both contact times and oxidant ratios on the leaching yields are shown in Figs. 2–4. In general, for a specific contact time, increase in the Fe(III)-Au mol ratio caused higher leaching yields than those obtained by use of lower molar ratios.

Effects of pH and Contact Time

Figures 5–7 show that the rate and extent of gold dissolution strongly depend on pH. The pH ranges in which the highest leaching yields were obtained are dif-

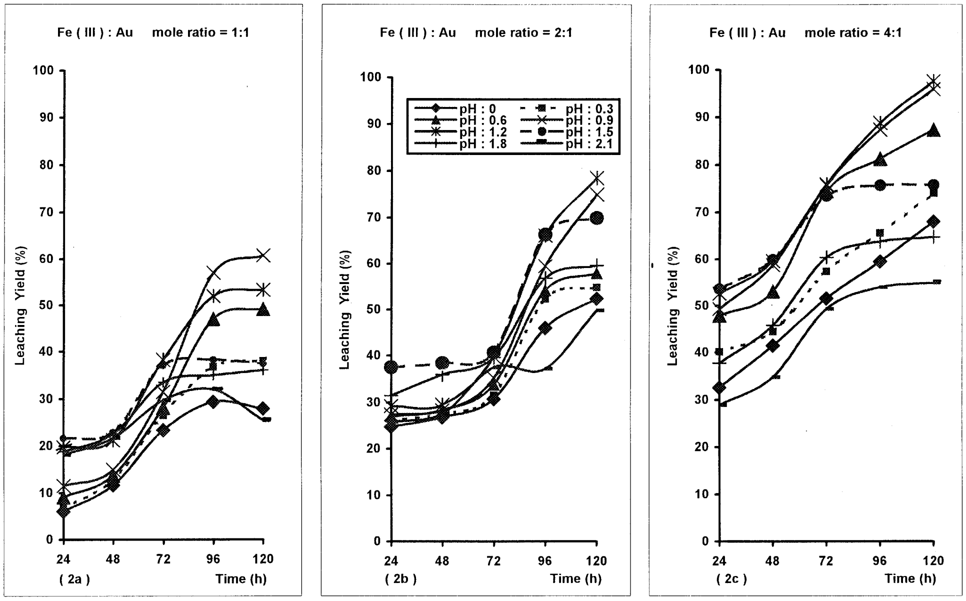

Figure 2. Dependence of leaching yields on the contact times at different oxidant-Au mol ratios at 20°C.

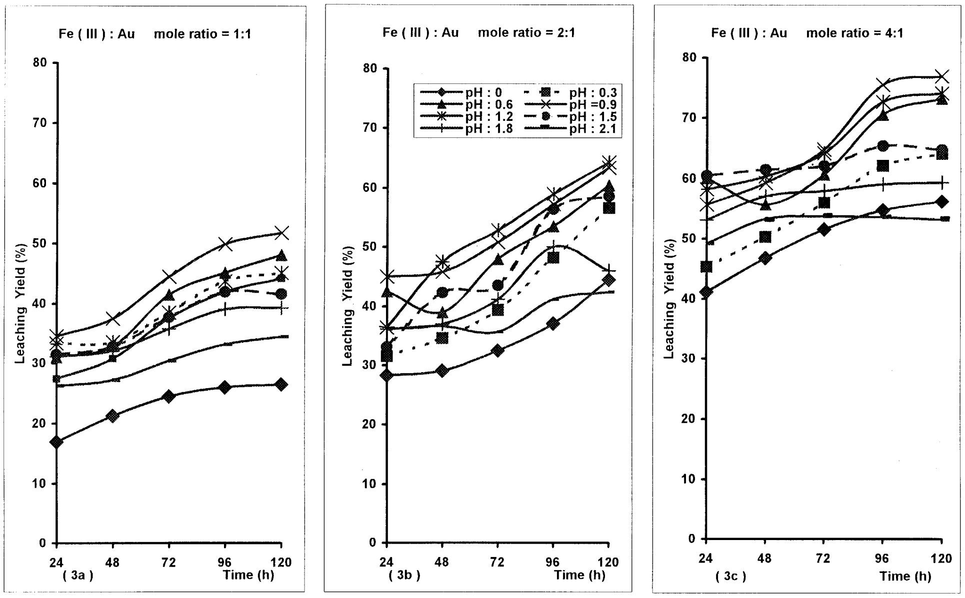

Figure 3. Dependence of leaching yields on the contact times at different oxidant-Au mol ratios at 40°C.

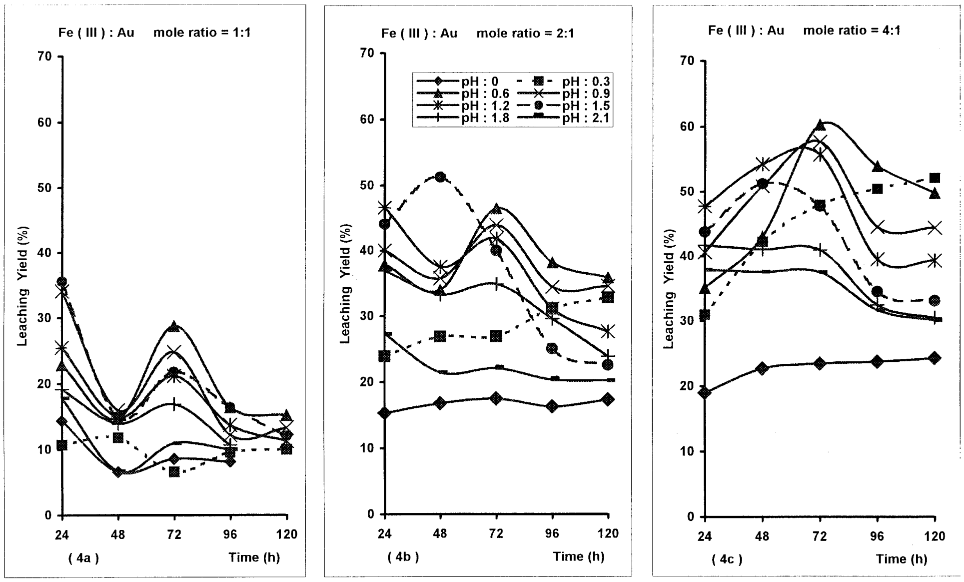

Figure 4. Dependence of leaching yields on the contact times at different oxidant-Au mol ratios at 60°C.

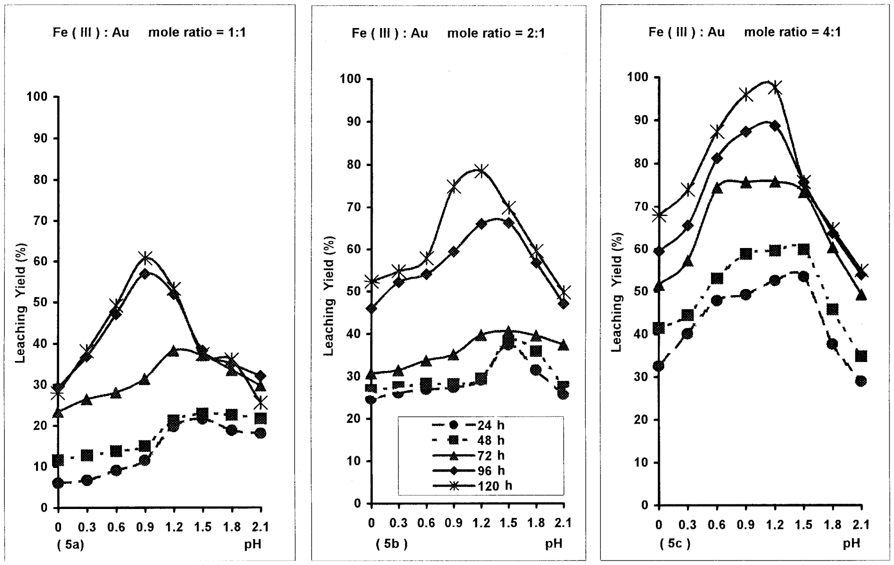

Figure 5. Dependence of leaching yields on pH values of leaching solutions for different contact times at 20°C.

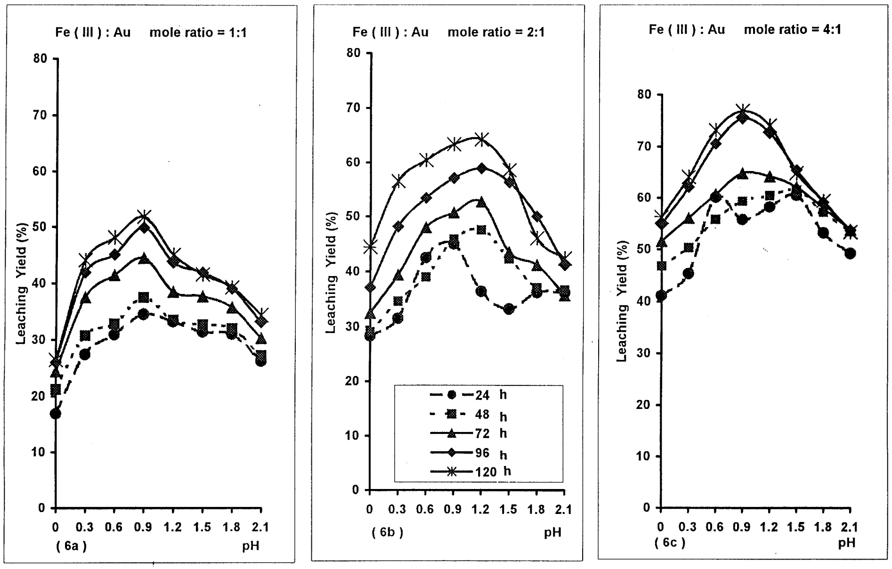

Figure 6. Dependence of leaching yields on pH values of leaching solutions for different contact times at 40°C.

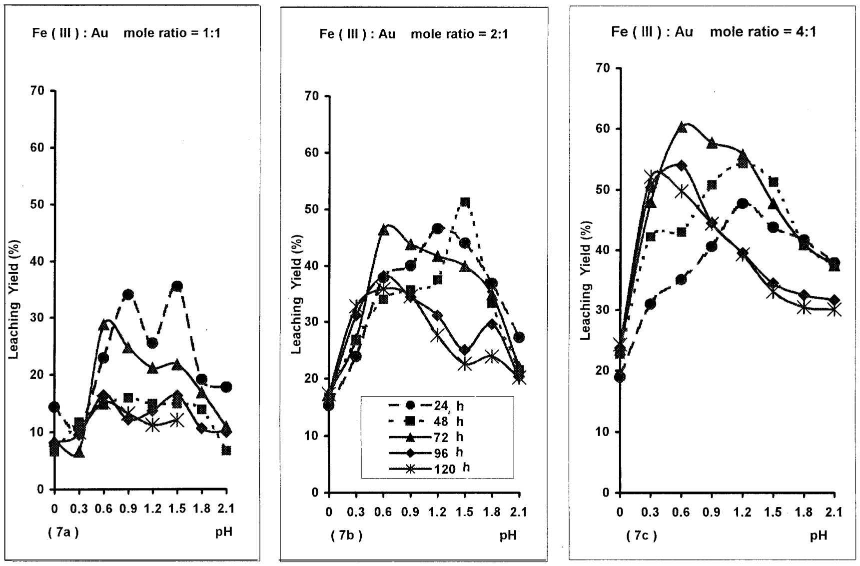

Figure 7. Dependence of leaching yields on pH values of leaching solutions for different contact times at 60°C.

ferent for different oxidant ratios. The optimum pH range for leaching yields higher than 90% was 0.9–1.2 for 120 hours of contact time with a 4:1 oxidant ratio.

For a fixed oxidant ratio at room temperature (20°C), the pH for maximum yield was shifted to 0.9–1.2 from 1.5 by increased contact time (Figs. 2a–c).Thus, if one prefers to start the leaching process at relatively low acidic conditions, the initial pH of 1.5 and should be lowered to pH 0.9 or 1.2 after 48 hours of contact time to obtain high leaching yields at room temperature (Figs. 5a–c).

At all the temperatures investigated 20°, 40°, and 60°C above pH 1.2, especially with longer contact times, increases in the oxidant ratios were associated with decreased leaching yields. In addition, for the oxidant ratios below 4:l, increasing the temperature to 60°C also created variable pH dependencies of leaching (Figs. 7a, 7b). For the 4:1 oxidant ratio, at 60°C, particularly after 72 hours of contact and above pH 0.6, the leaching yield dropped significantly (Figs. 4b, 4c, and 8c).

Effects of Reaction Temperature

Some important results appear from the data obtained at higher temperatures. The results indicate that 60°C is a critical temperature at which some com-

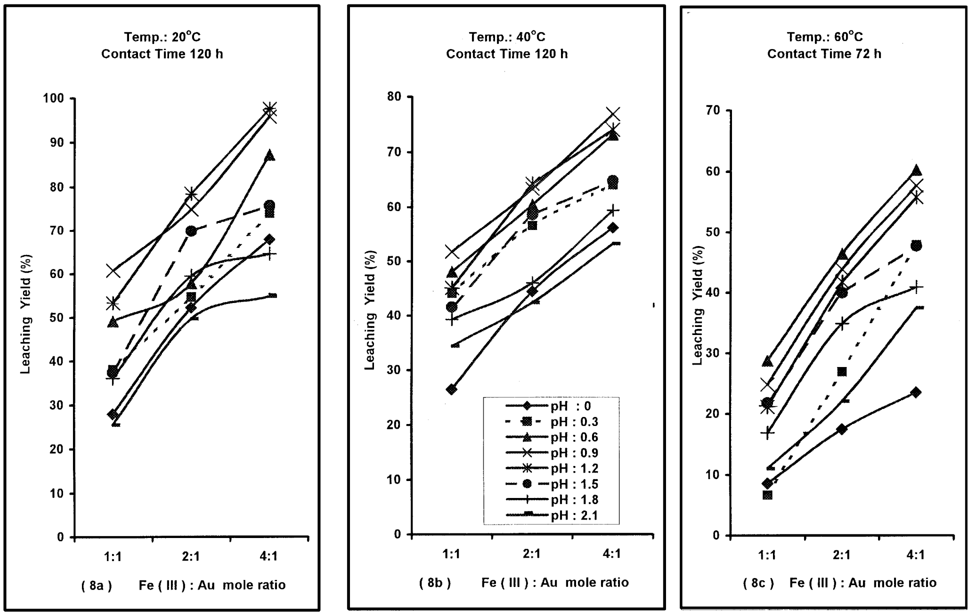

Figure 8. Dependence of leaching yields on the oxidant-Au mol ratios and on the reaction temperatures under optimum leaching conditions.

peting reactions effectively occur. Thus, we cannot presume that the rise in temperature should cause significant increases in leaching yields. On the contrary, contradictions are observed in the case of longer contact times. With a 4:1 oxidant ratio at pH 0.9, the highest yield at 40°C (76.9%) was obtained in 120 hours, which is lower than the optimum yield at room temperature (97.6%) (Figs. 2c, 3c, 8a, and 8b). In addition, the best yield at 60°C was only 60.3% and was obtained with 72-hour contact at pH 0.6 (Figs. 4c, 7c, and 8c).

After determining the effect of reaction temperature, we conducted several experiments. Infrared and mass spectral data of the reaction products showed that the reagent in the blank solution, Au^o, did not significantly decompose even at 60°C, which indicated that Fe(III) is not solely responsible for the lower yields. In the presence of gold, previously formed gold (I) complex becomes disproportionate such that metallic gold is produced. After observing this behavior, we heated the gold (I) complex solution obtained at room temperature. The decomposition extent of the complex at a definite pH depends on both temperature and reaction time.

As mentioned above, the rise in the temperature of the reaction does not help leaching. From the observed data, one sees that during the room-temperature leaching, increase in contact time resulted in higher yields, but at higher temperatures initial yield increases diminished after a definite contact time was reached. Relatively higher yields were obtained at pH values of 1.2 or 1.5 (Figs 7b and 7c). At those pH values, the longer the contact time, the lower the yield became. Longer contact times could be applied only at more acidic pH values (0.3–0.9). Similar results but with weak amplitudes were obtained in room-temperature leachings (Figs. 5b and 5c). Effects of temperature together with high oxidant ratios caused lower yields (Figs. 8a–c).

Thus, we concluded that, based on the leaching figures, one should first decide under which conditions the leaching could be performed.

CONCLUSION

The experimental results obtained in this study revealed that open-chain substituted thiourea derivatives may act as very effective leaching agents. If their chemical structure is appropriately chosen, they may not be self-oxidized as is thiourea. As a consequence, any additional precautions (such as SO_2 introduction) need not be taken. The proposed reagent did not cover the gold particles and was not oxidized to insoluble products when higher temperatures and/or longer contact times were applied. Thus, the leaching effect was not disturbed by secondary reactions and by physical inhibitions.

Optimum leaching conditions of gold were established as 120 hours at room temperature at a pH range maintained between 0.9 and 1.2 in sulfuric acid solution. A Fe(III)-Au mol ratio and the reagent-Au mol ratio higher than 4:1 and 2:1, respectively, were used. Thus the optimum yield of more than 95% can be obtained. Under the above mentioned conditions, the pseudo first-order leaching rate at room temperature was calculated as approximately 3×10^{-7} sec^{-1}. Metallic gold has been recovered from the dissolved gold complex after the addition of metabisulfide or its adsorption on activated carbon.

Further research, guided by the results obtained in this study, is still being applied to gold ores. The results will be announced when they are available.

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