Adsorption 2, 237–243 (1996)

Gold Recovery from Cyanide Solutions with a New Fibrous Polymer Adsorbent

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Received June 2, 1995; Revised February 2, 1996; Accepted February 12, 1996

Abstract. In a resin-in-pulp process for the recovery of gold cyanide from a very dilute solution it is desirable that the resin should exhibit the ability to load gold at the natural pH of the leach liquor and be stripped by an aqueous alkali. The present work describes the results of gold cyanide adsorption by new ion-exchange hollow fibers prepared by the amination of sulfochlorinated polyethylene. The fibers, chopped into suitably sized pieces, showed very fast adsorption and desorption of gold from mixed cyanide solutions.

Keywords: gold adsorption from dilute cyanide liquor, chelating hollow fibers, chemical modification of sulfochlorinated polyethylene

Introduction

Most of the total world production of gold—about 2000 tons per annum—is obtained by the carbon-in-pulp (CIP) process, which comprises the following steps: grinding of the ore to a fine powder in a water slurry (pulp), cyanide leaching of the gold from the pulp, adsorption of the gold cyanide onto activated carbon, and finally hot caustic elution and electrowinning to gold metal. The activated carbon may be regenerated by heat treatment, but some of it is lost due to fouling with organics and calcium. The considerable costs of regenerating the activated carbon at temperatures above 600°C are sufficient reason to consider ion exchange as an alternative process in gold recovery technology.

There are two major reasons ion-exchange resins have not found extensive application in gold recovery: strong base resins require expensive eluants such as thiourea, thiocyanide, zinc cyanide and/or polar organic solvents, while weak base resins are ineffective for loading gold at the normal leaching pH of 10–11. Therefore, a new sorbent for gold extraction would have to fulfil two main requirements: loading at the high pH of the gold cyanide liquor and easy and complete stripping with aqueous alkali. Recent reports of the synthesis of a series of resins exhibiting the required properties have opened up a new avenue of research. The resins, which are medium base resins prepared from polyamine, 1,3-diaminopropane, 2,4-diamino-2-methylpentane or chloromethylated styrene-divinylbenzene copolymer, have good selectivity for gold, high capacity at the leaching pH, and can be readily eluted with sodium hydroxide solution (Harris et al., 1992). However, they all suffer from the main drawback of granular ion-exchange resins, i.e., slow kinetic performance.

Our previous experience with gold cyanide extraction showed that sorbents having high accessibility to their active sites, e.g., silica modified by impregnation and subjected to γ-radiation polymerization, exhibit extremely good kinetics (Belfer and Streat, 1986). The effectiveness of ion-exchange materials for the sorption

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of gold can also be improved by using them in the form of ion-exchange fibers, which have improved diffusion properties. Recently, several publications have outlined the favorable performance of fibrous materials in hydrometallurgy and particularly in the gold industry (Soldatov, 1984; Tsumota et al., 1991; Belfer et al., 1992; Kotze and Cloete, 1992).

Our preliminary results with sulfochlorinated polyethylene (PESCl) fibers that were aminated with diaminopropane and then reacted with alkylbromide showed that the fibers have some strong base anion exchange functionality and are therefore able to extract gold cyanide from alkaline solutions (Belfer and Binman, 1991). The combination of good kinetic properties and good extraction ability at high pH of the solution in contact with the hollow fibers makes them potentially competitive with activated carbon. According to published data (Granovskyi et al., 1982; Telegina et al., 1982; Tsuchida et al., 1984), elution from activated carbon takes several hours, while our fibers could be stripped within a few minutes. An additional advantage that makes that our hollow fibers suitable for the common CIP technology is the fact that they may be cut up into squares of suitable size. This will obviate one of the main disadvantages of resins—their small particle size range, which calls for pulp-separating screens that are somewhat smaller than those currently used in CIP (Muir, 1982). Moreover, the elasticity of our fibers, in comparison with carbon or beads, makes them more mechanically stable in processes involving strong attraction forces.

This paper describes our results of extraction of gold cyanide from alkaline solution by means of hollow fibers.

Experimental

Fibers

PESCl hollow fibers were aminated and quaternized as follows. The PESCl obtained from the laboratory of Dr. E. Korngold (Korngold and Vofsi, 1991) were subjected to extraction with mixture of dichloroethane (DClE) and hexane in a Soxhlet apparatus to remove traces of the soluble by-products of sulfochlorination. Single fibers (0.5–1 m in length) that had been allowed to swell in DClE for 2–3 h at 45°C were then placed in a solution of amine in solvent at room temperature (25°C) overnight (24 h). Special care was taken to remove the water from both the diamine and the solvent (water analysis was performed with a Karl-Fisher titrator). The fibers were then washed several times with 0.1 N HCl, 0.1 N NaOH and water. Swelling was determined either by weighing the fiber first in the dry form and then in the wet form or by measuring the length of the fiber, first dry and then wet. The aminated hollow fibers in the deprotonated form were then quaternized with a solution of dimethylformamide (DMF) saturated with methyl bromide at 0°C. Thereafter the fibers were separated, washed and analyzed. Their capacity varied, depending on the time of reaction.

Capacity Determination

Total Ion-Exchange Capacity. Before measurement of the capacity, the fibers were quickly equilibrated alternately several times in 1.0 N HCl and 1.0 N NaOH. The dry samples were weighed (0.2 g), and each was placed in a 100-cm^3 volumetric flask, to which 50 cm^3 of 0.1 N HCl was added. After shaking the suspension for 24 h 5 cm^3 of the solution was back titrated with 0.05 N NaOH. The Cl^- concentration in the HCl was also analyzed (Cl^- capacity). The capacities of the ion-exchange fibers were calculated from the results of the titration as H^+ capacity (Q_{H^+}) or Cl^- (Q_{Cl^-}) capacity.

Capacity of Partly Quaternized Fibers. The dry samples in deprotonated form were weighed (0.2 g) and placed in 100 cm^3 volumetric flasks, to which 50 cm^3 of 10% NaCl were added. After shaking the suspension for 24 h, the solution in contact with the fibers was titrated with 0.05 N HCl with phenolphthalein as the indicator. The value of the strong anion exchange capacity of the fibers was calculated from the amount of added acid. Titration of the same solution was then continued with methyl orange as the indicator. The amount of weak anion exchange groups was calculated from the total amount of added acid.

Potentiometric Titration

The fibers (~1.0 g) in the deprotonated form were placed in a 250-cm^3 volumetric flask, to which was added 100 cm^3 of 0.1 N NaCl under an argon blanket. The suspension was shaken for 24 h, 1–2 cm^3 of 0.05 N HCl were added portion-wise, and shaking was continued for a further 24 h. After each portion the acid was added to the solution, the pH of the solution in contact with the of fibers was measured, and a potentiometric titration curve was plotted.

Metal Extraction

The pieces of cut fibers, 2 to 3 cm or 0.5–1 cm in length, were placed in a volumetric flask containing an aqueous cyanide solution (200 ppm CN^-) of gold ions (up to 1.5 ppm) or gold ions in mixture with another ions (pH 11). The suspension was then placed in a shaker, and 5-cm^3 samples of the solutions were taken every 5–10 min. Finally, the fibers were filtered off and eluted with 5 M NaCNS or 0.1% NaCN in a 1% NaOH solution. The concentrations of the metal ions in the aqueous solutions were determined by ICP-atomic spectroscopy (model OPTIMA 3000, Perkin Elmer).

Results and Discussion

Gold Uptake by Aminated Fibers

The PESCl fibers were aminated with four different amines. The conditions of amination and the capacity of obtained fibers are summarized in Table 1. These results are representative of numerous experimental runs, in which parameters such as amine concentration, type of solvent, temperature and reaction time were varied. The details of the preparation of aminated PESCl is an issue of special interest and will be reported separately. The samples taken for this comparative study were chosen in terms of their high total capacity and good mechanical properties. A general view of the fibers is presented in Fig. 1.

Table 1. Properties of aminated fibers prepared at 25°C.

Amine	Solvent	Conc. in solvent (%)	Reaction time (h)	Capacity Q_{H^+} (meq/g)	Capacity Q_{Cl^-} (meq/g)
DAP[a]	—	100	24	1.10	1.14
DETA[b]	Toluene	50	24	1.80	1.70
TETA[c]	DMF	20	24	1.25	0.70
TETA[d]	Toluene	50	24	1.07	0.75

[a]DAP—diaminopropane, [b]DETA—diethylenetriamine, [c]TETA—triethylenetetramine, [d]DEPA—tetraethylenepentamine.

The kinetics of gold cyanide uptake by these four types of fiber are presented in Fig. 2, in which gold concentration in the solution (at pH 11) that was in contact with the fibers was plotted as a function of time. The experiment was planned to last for 1 h because our previous results showed very fast kinetics (Belfer et al.,

Figure 1. Aminated hollow fibers cut into pieces. Scale is given in inches.

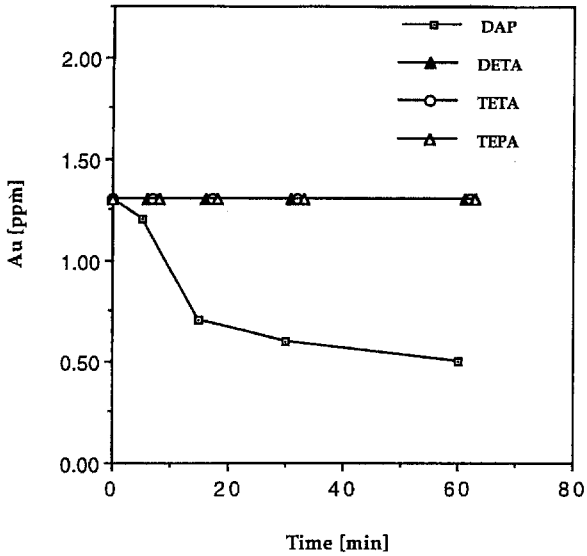

Figure 2. Decrease of gold concentration in solution as a function of time for different fibers. DAP = diaminopropane, DETA = diethylenetriamine, TETA = triethylenextetramine TEPA = triethylene pentamine.

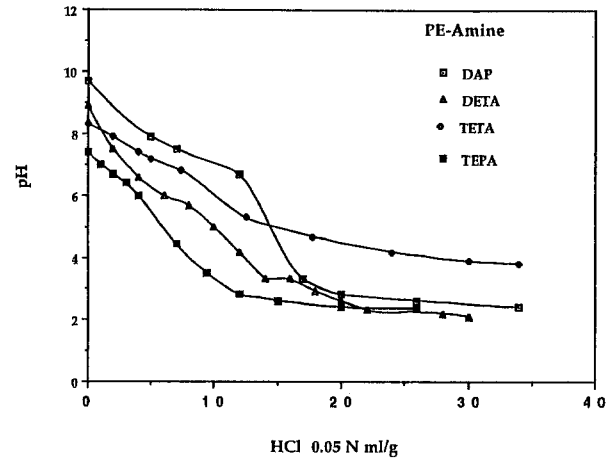

Figure 3. Potentiometric titration of aminated polyethylene fibers. See legend to Fig. 2 for an explanation of the abbreviations.

1992). From the Fig. 2 it can be seen that only the fiber aminated with diaminopropane showed gold extraction at this pH.

The other multifunctional diamines attached to the PESCl fibers did not take up the gold cyanide under these conditions. The ability of the ion exchanger prepared from a medium base diamine to extract gold cyanide at a high pH is in full agreement with previously published data (Harris et al., 1992). In order to elucidate the ability of polyethylene-diaminopropane fibers to extract gold at high pH, potentiometric titrations were performed for all the fibers (Fig. 3). The initial pH value of 9.8 and the relatively rapid change of pH in the vicinity of the equivalence point at pH 13 characterized the base functional groups ($-NH_2$) in the polyethylene-diaminopropane fibers. The other three potentiometric curves are characteristic of polyfunctional exchangers with weaker base properties. The gradual change of pH at the neutralization point is typical of multifunctional amines in which weak base groups (—NH—) are present together with primary amino groups, e.g., diethylenetriamine, triethylenetetramine and triethylenepentamine.

It is likely that the polyethelene-DAP fibers have functional groups with stronger base properties. In other words, polyethylene-diaminopropane behaves as a anion exchanger bearing amino groups that are active at pH values higher than 7. There are some possible explanations for this behavior. Firstly, polyethylene-DAP fibers show no differences in their Cl^- and H^+ capacities. This means that no (or at least a very small amount) of strong acid groups are present in the polymer matrix. (Note: strong acid groups may form an internal salt with the amino groups, and their presence is therefore undesirable). Secondly, our aminated fibers, which represent a family of polysulfamido-amine polyelectrolytes, contain sulfamide groups $-SO_2NH-$ that may act as weak cation exchangers at high pH values (March, 1985). It appears that the presence of sulfamide groups is essential for both gold extraction and elution. When ion pair formation like $Na^+[Au(CN)_2]^-$ occurs at high pH, the ion pair might be extracted by a weak acid group (sulfamide) and or a weak base group (primary amine), due to the close proximity of these two types of groups in aminated PESCl hollow fibers (Scheme 1, in which all possible reactions between the fiber and the gold complex in solution are presented). A mechanism has been suggested by Tye and Green (1994) to explain the gold uptake by a phenol-formaldehyde-based weak-base resin.

Scheme 1

$$\text{PE-SO}_2\text{NH(CH}_2)_3\text{NH}_2\text{H} \cdot \text{X} + \text{Na[Au(CN)}_2]_{(aq)} \rightarrow$$

anion exchange

$$\text{PE-SO}_2\text{NH(CH}_2)_3\text{NH}_2\text{H} \cdot \text{OH}$$

anion exchange

$$\text{PE-SO}_2\text{NH(CH}_2)_3\text{NH}_2\text{H} \cdot \text{Au(CN)}_2 + \text{NaX}_{(aq)}$$

ion pair exchange

$$\text{PE-SO}_2\text{NH(CH}_2)_3\text{NH}_2 \cdot \text{Na[Au(CN)}_2] + \text{HX}_{(aq)}$$

$$\text{PE-SO}_2\text{(Na)(CH}_2)_3\text{NH}_2\text{H} \cdot \text{[Au(CN}_2)] + \text{HX}_{(aq)}$$

Table 2. Quaternization of polyethylene-diaminopropane hollow fibers.

Time (h)	Capacity (meq/g)			Quaternization (%)
	Strong	Weak	Total	
0	0	1.44	1.44	0
16	0.14	1.30	1.44	10
24	0.23	1.21	1.44	15
48	0.58	0.86	1.44	40

Gold Uptake by Alkylated Amino-Fibers

The next series of experiments was aimed at enhancing the basicity of the amine functionality by means of alkylation. Table 2 summarizes the results of the alkylation of diaminopropane-containing fibers with methyl bromide in DMF at different times. The percentage of strong base amine groups increased with time.

The effect of the amount of strong base groups (10%, 15% or 40%) on the absorption gold cyanide from alkaline solution was then evaluated. A remarkable difference in uptake kinetics was clearly evident within as little as the first 4 min. The samples with 40% of the strong-base groups adsorbed more than 50% of gold, the 10%-sample adsorbed less than 20% of the gold, and the unmodified fibers were able to extract only 5% of gold. The mechanism of gold cyanide uptake by polyethylene diaminopropane is given in Scheme 2.

Scheme 2

$$\vdash SO_2NH(CH_2)_3NH_2H \cdot X + Na[Au(CN)_2]_{(aq)} \rightarrow \vdash SO_2NH(CH_2)_3N(CH_3)_3X$$

$$\vdash SO_2NH(CH_2)_3NH_2Na[Au(CN)_2]$$
$$\vdash SO_2NH(CH_2)_3N(CH_3)_3\ Au(CN)_2$$

where $\vdash$ represents polyethylene.

Extraction of Gold from a Mixed Cation Solution

The ability our quaternized fibers to facilitate fast metal extraction from a solution containing gold or both gold and copper cyanides at pH ~ 11 was tested (Figs. 4 and 5). The higher the degree of quaternization, the faster the metal extraction. Fibers with 40% quaternization completely extracted the gold within 5 min, while 10 min was needed for fibers with 10%

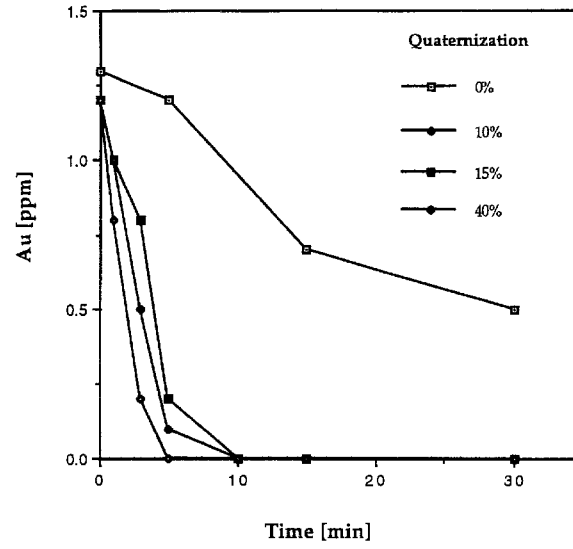

Figure 4. Decrease of gold concentration as a function of time for polyethylene-diaminopropane fibers with different degrees of quaternization.

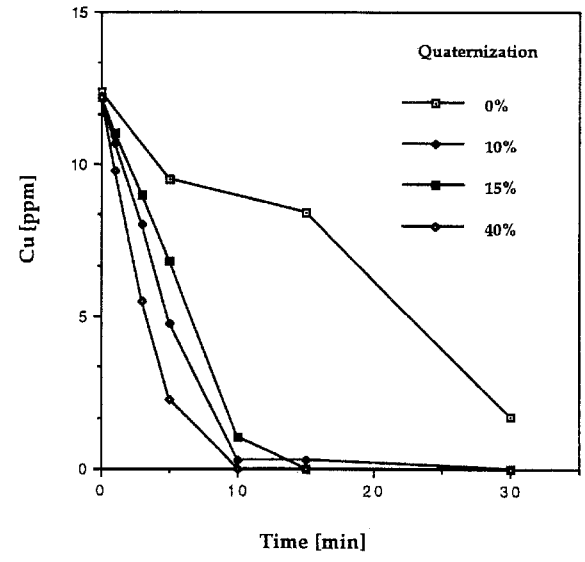

Figure 5. Decrease of Cu concentration as function of time for polyethylene-diaminopropane fibers with different degrees of quaternization.

quaternization. These results are in agreement with the results for gold extraction from solutions containing gold alone. The partially quaternized polyethylene-diaminopropane fibers were also able to extract copper ions from aqueous cyanide solutions at high pH. The difference between the two cyanide anions was that the gold cyanide extraction was much faster.

The extraction of gold ions by 20% quaternized polyethylene-diaminopropane fibers (cut into ~0.5 cm

Table 3. Metals extraction by 20% quaternized polyethylene diaminopropane fibers to extract heavy metals.

Time (min)	Concentration in starting solution (ppm)					
	pH	Au	Cu	Zn	Co	Ni
0	11.2	1.4	11.4	3.4	3.5	3.0
5	11.0	0	0	0	0	0
Ion capacity (mg/g)		0.07	0.57	0.17	0.17	0.15

pieces) was also tested in presence of other heavy metal ions at high pH. It was found that the extraction of gold was not retarded by the presence of the whole range of heavy metals that are usually found in the gold cyanide slurry (Table 3).

Elution

The elution of gold ions by partially quaternized polyethylene diaminopropane fibers was tested with two different eluents, 5 N NaSCN or 0.1% NaCN in 1% NaOH aqueous solution. The elution with 5N NaSCN was carried out on 20% quaternized fibers after extraction of gold was made in the presence of copper ions. The concentration of CN^- was 200 ppm; the volume of feed solution was 30 ml; the volume of eluent was 15 ml. The results of extraction and elution are presented in Table 4. The table shows the changes of metals concentration in the solution with the time. We can see that extraction of gold was accomplished within 5 min (zero concentration), while 30 min was required for copper extraction. The better diffusion performance of gold cyanide was also revealed in the elution step. Mass balance calculation results, that the gold was completely eluted within 15 min, while only 57% of copper was eluted within this time.

Table 4. Extraction and elution* of Au and Cu by 20% quaternized polyethylene-diaminopropane fibers.

Extraction			Elution		
Time (min)	Au (ppm)	Cu (ppm)	Time (min)	Au (ppm)	Cu (ppm)
0	1.5	12.2	10	4.0	13.6
5	0	8.1	15	4.0	14.0
10	0	4.6			
15	0	1.7			
30	0	0			

*With 5 N NaSCN.

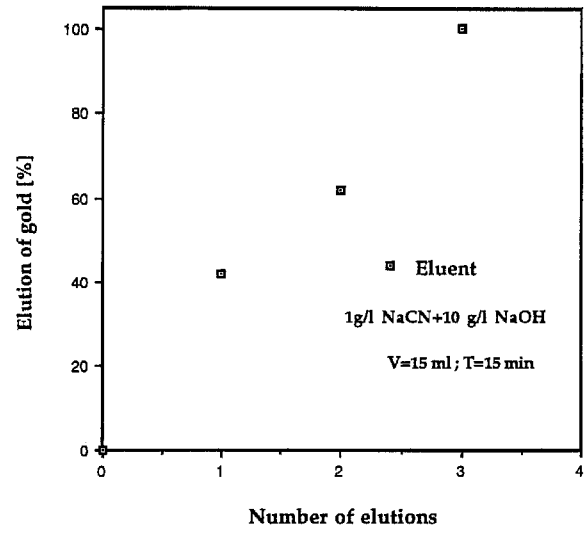

Figure 6. Degree of elution as function of number of elution stages.

Since a mixture of NaOH and NaCN appeared to be the most suitable eluent for industrial applications (Muir, 1982; Gren and Potgieter, 1984), its efficacy as an eluent was also studied. In this series of experiments, a higher weight of fibers (10 g) was taken for loading of gold (1.2 ppm) at pH 11 from 200 cm^3 of cyanide solution. Elution was performed with a mixture of 1 g/lNaCN + 10 g/l NaOH. From Fig. 6 it is evident that complete elution of gold ions can be achieved with this eluent in a three-step elution procedure. A contact time of 10 min was sufficient for each step.

Conclusions

A remarkable sorption and desorption performance of our chelating hollow fibers for a very dilute gold cyanide solution was observed, extraction and elution being achieved within 10–15 min. The physical configuration and mechanical stability of the fibers make them most attractive for the resin-in-pulp gold extraction technology.

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