

Processing of Residual Gold (III) Solutions via Ion Exchange

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The processing of gold (III)-hydrochloric acid solutions by the anionic ion exchange Lewatit MP-64 resin has been investigated. The influence of several variables such as the temperature, the hydrochloric acid and metal concentrations in the aqueous solution and the variation of the amount of resin added has been studied. Moreover, a kinetic study performed in the uptake of gold (III) by Lewatit MP-64 shows that either the film-diffusion and the particle-diffusion models fit the adsorption process on the resin. Results obtained from batch experiments were applied to a continuous system using a vertical column. The loaded resin could be eluted by an acidic thiourea solution at 20°C. Various systems were investigated to precipitate gold from eluants, only the use of sodium borohydride allowed to accomplish the recovery of the metal from the pregnant solutions. Gold was recovered as fine particles, which were characterised by means of optical and scanning electron microscopy.

Key words – gold (III), Lewatit MP-64, hydrochloric acid

Introduction

Within the context of gold extraction, the dissolution step of gold-bearing materials is carried out using two main aqueous media: cyanide or chloride solutions, and if the first used the leaching of gold from raw materials, the latter is useful to recover this precious metal from secondary materials and residues, i.e. anode slimes and jewelry scrap. Both dissolution media required both a complexant (cyanide or chloride) and an oxidant (air or nitric acid/chlorine) to achieve acceptable leaching rates and yields.

In the particular case of chloride leaching and once gold is dissolved, the metal is presented in the solution as the gold (III)-chloro complex (AuCl_4^-) with square planar structure.

Very often, and prior to the ultimate gold recovery, a solution purification and/or concentration step is needed in order to produce a higher grade solution. Among the various separation/concentration steps, the use of liquid-liquid extraction, membrane technologies, carbon adsorption and ion exchange has been described [1-5]. In many cases, the adsorption of a solute in a solid support has the advantage over liquid-liquid extraction or even membrane technologies in that no mixing and settling requirements have to be fulfilled and organic phase loss through entrainment is eliminated, also the use of an intermediate step such as filtration is avoided.

Due to the anionic nature of the gold (III)-chloro complex, the use of anionic exchangers (and also chelating resins) on the adsorption of this precious metal had been reported in the literature [6-19]. In the present work, the adsorption and elution of gold (III) from hydrochloric acid solutions were investigated using the anionic exchange resin Lewatit MP-64. The influence of various parameters affecting the metals adsorption on the resin is studied and a kinetic study to explain the metal uptake is presented, whereas metal elution from the loaded resin is studied using acidic thiourea solutions. The final recovery from the eluates is accomplished by the use of an alkaline borohydride solution.

Experimental

The ion exchange resin Lewatit MP-64 (Fluka) was used to adsorb gold (III) from hydrochloric acid solutions. Lewatit MP-64 is a macroporous medium-basic anion exchange-crosslinked polystyrene matrix resin containing tertiary and quaternary ammonium groups (Cl^- form-free base). Prior to its use for gold adsorption, the resin was dry until constant weight. Aqueous Au(III) stock solution was prepared from solid HAuCl_4 (Fluka), whereas working solutions were prepared by dilution. Other chemicals used in the present investigation were of AR grade.

Batch adsorption (elution) experiments were carried out by mixing (750 min^{-1}) weighed amounts of dry resin with the aqueous metal (or acidic thiourea) solutions for the appropriate time. The remaining metal in the aqueous phase was determined by atomic absorption spectrometry and the

amount of metals loaded (or unloaded) on the resin phase was calculated by applying the mass balance. The fractional attainment of equilibrium (F) was determined as

$$F = \frac{[Au(III)]_{t}}{[Au(III)]_{e}} \quad (1)$$

where $[Au(III)]_{t}$ and $[Au(III)]_{e}$ are the metal concentrations in the resin at an elapsed time and at equilibrium, respectively. For the kinetic experiments the resin with grain size 0.9-0.5 mm were sieved (the average aqueous radius of particle being 0.35 mm), and the continuous kinetic experiments were performed using 0.06 g resin which were contacted with 200 ml solution containing known amounts of gold (III) in 0.03 M HCl, at the temperature of 20°C, under constant stirring (750 min⁻¹). Samples were taken periodically for atomic absorption spectrometry analysis of gold (III) concentration.

For the study of the adsorption in continuous system, a mini-glass column (internal diameter 0.8 cm), provided with a porous frit, filled with 1 g of resin, were fed with the corresponding aqueous solution. Samples were regularly collected and analysed.

Precipitation tests were carried out by mixing (300 min⁻¹) in a glass reactor the gold (I)-thiourea solution with the alkaline sodium borohydride solution for the appropriate time and 20°C. The elementary gold powder was filtered, washed with 50 ml of acetone, 50 ml of distilled water, and was dry in a dessicator. The morphology and size of the powder obtained were studied by optical and scanning electron microscopy. Moreover, X-ray spectrometry analysis was done to check the composition of the powder.

Results and discussion

Gold adsorption

Batch experiments: 0.13 g resin were used to adsorb gold (III) from a solution (200 ml) of 20 mg/l Au(III) and 0.03 M HCl at different temperatures. Figure 1 indicates that the initial rate of metal uptake by the resin is dependent of the temperature, increasing with the increase of this variable, though the equilibrium is reached with every temperature at 120 min contact. The thermodynamic quantities ΔG° , ΔH° and ΔS° calculated by means of the usual relations are given in Table 1. The positive value of the enthalpy change indicate an endothermic reaction whereas the positive entropy change characterizes an increase disorder of the system when gold (III) is adsorbed onto the resin.

The influence of the presence of HCl in the aqueous solution was also studied using HCl concentrations ranging from 0.03 to 1 M. The results obtained from these experiments are shown in Fig. 2, and it can be seen that the increase of HCl in the aqueous phase increases the rate of metal absorption up to 0.5 M and then decreases, this can be attributable that at higher acidities, the equilibrium

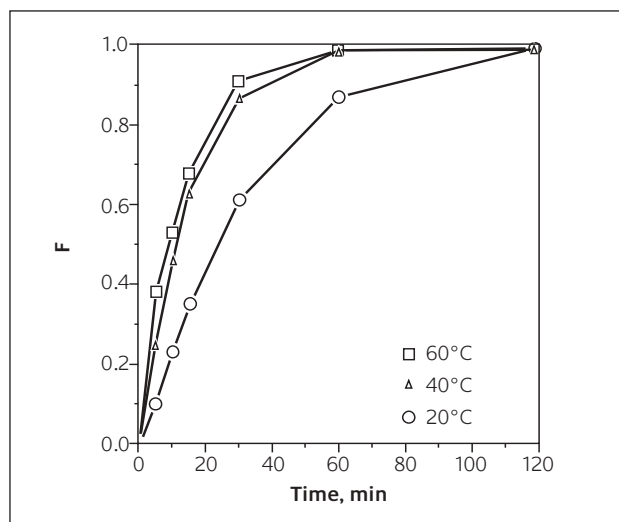
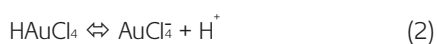


Figure 1

Influence of temperature on metal uptake by the resin

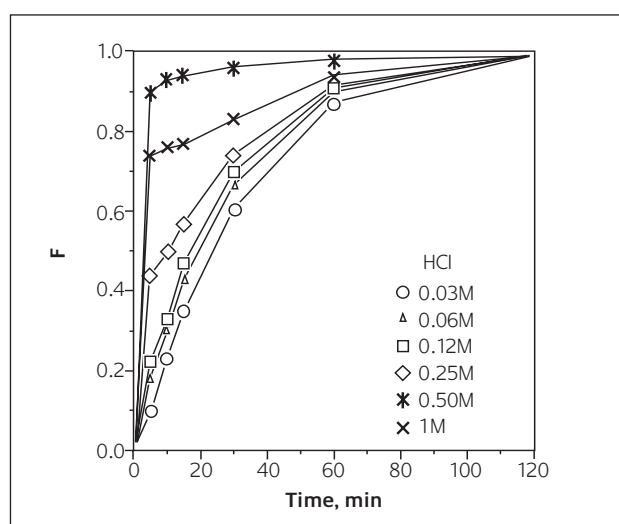


Figure 2

Influence of HCl concentration on metal adsorption by the resin. Initial solution (200 ml): 20 mg/l Au(III) and HCl. Temperature 20°C

Table 1

Thermodynamics quantities of Au(III) adsorption on Lewatit MP-64 resin

ΔH°	32 kJ/mol
ΔS°	0.15 kJ/mol K
ΔG°	-11 kJ/mol

begins to shift to the left and the gold (III) in the aqueous phase is in the form of the non-adsorbable $HAuCl_4$ species, besides this, it is also probable that the increases in kinetics with HCl concentrations up to 0.5 M may be due to that the resin swells more and so access to the pores becomes easier; on the other hand, above 0.5 M HCl there is not appreciable increase in the swelling and kinetics falls due to increased competition from chloride. Typical metal uptakes at equilibrium are shown in Table 2.

Table 2*Metal uptake by the resin at various HCl concentrations*

HCl, M	[Au(III)], mg/g
0.03	30.5
0.06	30.6
0.12	29.7
0.25	28.9
0.50	28.3
1	26.2

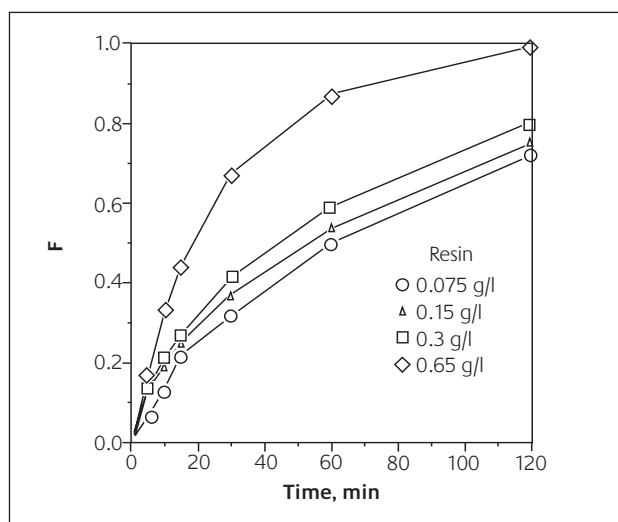
The influence of the initial gold concentration on metal loading was studied by adding 0.13 g resin to a 200 ml solution containing 160, 80, 40 and 20 mg/l Au(III) and 0.03 M HCl at 20°C, with results showing that the adsorption rate was fast at the initial stage: more than 85% of gold was adsorbed in 60 min with the resin loading approaching a plateau after 120 min contact with the solution. More than 95% of gold was adsorbed by the resin within 120 min of contact for all initial gold concentrations. The resin loading ranged 30.5 to 237.5 mg/g depending on the initial gold concentration.

The effect of resin concentration on metal loading was also studied. Concentrations of 0.075, 0.15, 0.3 and 0.65 g/l resin were used to contact a 200 ml solution containing 160 mg/l Au(III) and 0.03 M HCl at 20°C. Results obtained (Fig. 3) showed that there seems to be a dependence of the adsorption rate upon concentration, the resin of 0.65 g/l adsorbed near 85% of gold from the solution in near 60 min with a resin loading of 206.8 mg/g. On the other hand, the gold adsorption using a concentration of 0.075 g/l resin was 9.5% and 21.5% in 30 min and 120 min, respectively, with a resin loading of 202.7 and 458.7 mg/g. It seems obvious that a minimum resin concentration of 0.65 g/l is required to have a better adsorption kinetic.

The rate law governing the adsorption of gold (III) by Lewatit MP-64 had been determined using the experimental conditions described in the Experimental section. Three possible adsorption mechanisms had been evaluated if the adsorption of gold (III) into the resin must be considered as a liquid-solid phase reaction which includes the diffusion of gold (III) species from the aqueous solution to the resin

Table 3*Regression coefficients and kinetic parameters for the models tested*

Equation	[Au(III)], mg/l	r ²	k, min ⁻¹
ln(1-F) = -kt	125	0.992	0.017
	250	0.992	0.013
ln(1-F ²) = -kt	125	0.996	0.013
	250	0.994	0.007
3-3(1-F) ^{2/3} -2F = kt	125	0.989	0.004
	250	0.986	0.003

**Figure 3***Effect of resin concentration on loading kinetics*

surface, the diffusion of ions within the resin and the moving boundary process. The rate equations for these cases are

i) film-diffusion controlled process [20]

$$\ln(1 - F) = -kt \quad (3)$$

ii) particle-diffusion controlled process [21]

$$\ln(1 - F^2) = -kt \quad (4)$$

iii) moving boundary process [22]

$$3 - 3(1 - F)^{2/3} - 2F = kt \quad (5)$$

in all the above equations, k is the corresponding rate constant. The test of the mathematical models used to explain the adsorption of gold (III) onto the resin (Table 3) shows that the metal uptake can be well explained by either film and particle-diffusion controlled processes. It should be noted here that often loading rate is firstly determined by particle-diffusion and as the solute concentration in the aqueous phase drops it changes to film-diffusion.

The mechanism of gold (III) adsorption by the resin can be represented by the general reaction where R represents the unreactive part of the resin, in the above equation and for

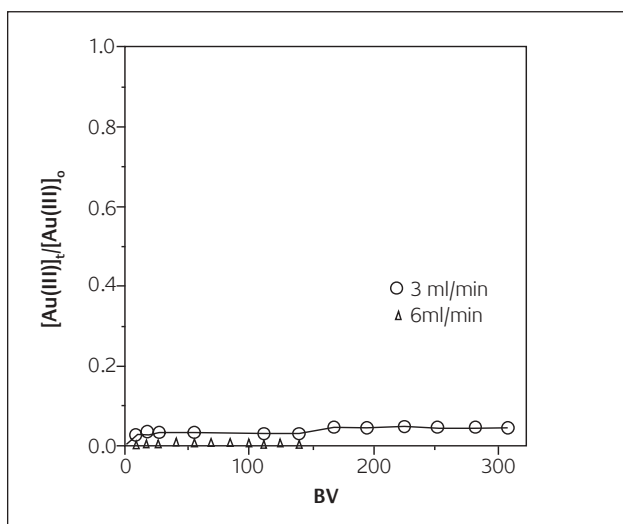


Figure 4
Influence of the flow rate on gold (III) adsorption breakthrough curves. Initial solution: 80 mg/l Au(III) and 0.03 M HCl. Temperature 20°C. Column 1 g resin

simplicity, the reaction had been represented considering only the quaternary ammonium groups of the resin.



Continuous experiments: Results obtained from batch experiments were used to investigate the continuous adsorption of gold (III) by the resin Lewatit MP-64 packed in a column.

Figure 4 shows the influence of the flow rate on the breakthrough curves. A decrease in the flow rate causes an increase of the breakthrough capacity, such an increase can be ascribed to a higher residence time which affects mostly the gold adsorption due to the previously observed adsorption kinetics of the metal. The breakthrough capacities were estimated higher than 36 mg/g (after near 150 BV) and 79 mg/g (after near 320 BV) for flow rates of 3 ml/min and 6 ml/min, respectively.

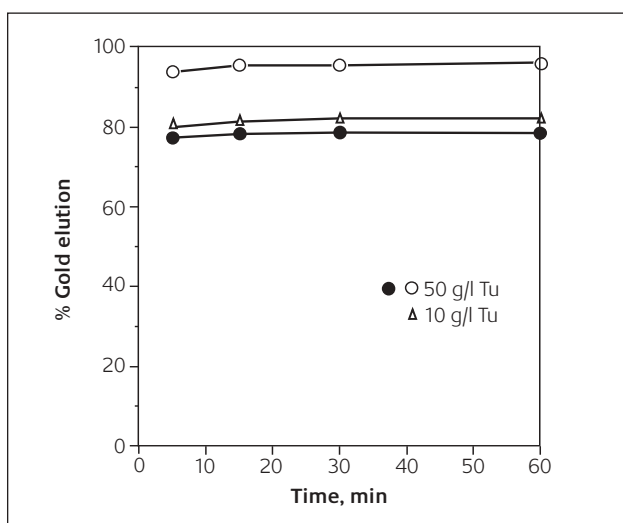


Figure 5
Metal elution using acidic (0.01 M HCl) thiourea solutions. Temperature 20°C. 1: solution/resin ratio 154. 2: solution/resin ratio 305

Gold elution

Anionic exchangers have high loading capacities but are also difficult to be eluted. An effective method to elute gold (III) should be by the use of a strong complexant for the metal and thus releasing gold from the resin. In the present investigation, acidic thiourea solutions were investigated as eluant for gold due to the relatively high stability constant that gold presented with this ligand ($Au(CS(NH_2)_2)_2^+$, $\beta_2 = 2 \times 10^{32}$ [1]).

A resin loading of 90 mg/g was used in these elution tests. The effect of the thiourea concentration on metal adsorption was first study and results were shown in Fig. 5. It can be seen that the increase of thiourea concentration increases the percentage of metal desorption, but does not apparently affect the kinetics of metal desorption. On the other hand, the variation of the volume of the elution solution used to release the metal from the resin has also a negligible effect

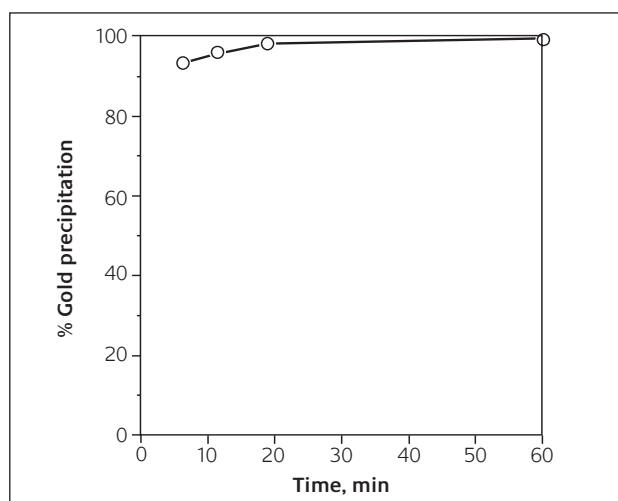


Figure 6
Gold precipitation from gold-thiourea solution using alkaline sodium borohydride. Aqueous phase: 50 mmol/l $NaBH_4$ and 0.06 M NaOH. Temperature 20°C

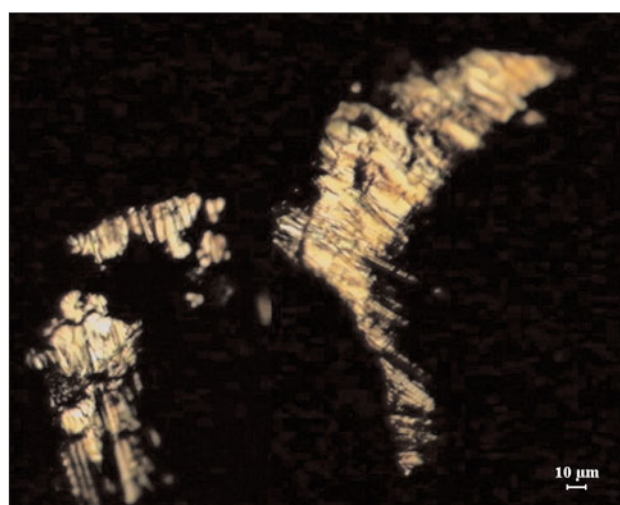


Figure 7
Optical image of gold particles obtained by reductive precipitation with alkaline $NaBH_4$ solution

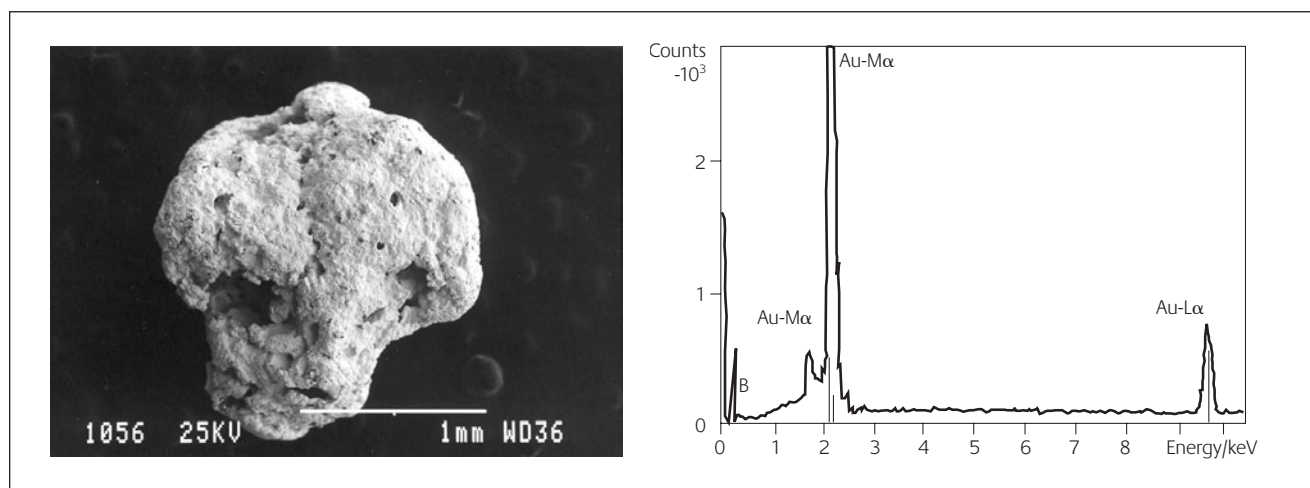
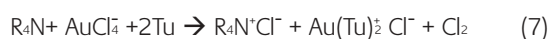


Figure 8

Secondary electron image of a gold powder particle (left). X-ray dispersive energy spectrum of the particle (right)

on the metal elution kinetic, though decreases the percentage of metal eluted (Fig. 5).

In the desorption stage, gold (III) is reduced to gold (I) and then complexed with thiourea (see above), which is released to the bulk solution. The elution reaction may be represented as



where Tu represents the thiourea ligand, in the resin phase here again only the quaternary ammonium groups are considered by simplicity. The above equation shows that the reaction would proceed to the right as the concentration of thiourea is increased; this fact have been demonstrated by the experimental results obtained from this investigation.

Gold precipitation

Several possible precipitation reagents have been tested (ascorbic acid, hydrazine sulphate) and it was found that only an alkaline sodium borohydride solution could effectively precipitate gold from the gold-thiourea solution. As can be observed from Fig. 6 optimum results were achieved by using $NaBH_4$ in alkaline solution, less than 5 min were required for 90% metal precipitation with almost quantitatively metal recovery after 20 min. Gold precipitates as a very fine powder and show different sizes. Some of them exhibit the aspect of this of Fig. 7; other, of coarser size with near spherical shape seem to be constituted by agglomeration of the former. This morphology is shown in Fig. 8. The X-ray spectrum of these particles only shows the different lines of gold as well as a very small peak in the low energy range that corresponds to the B-K α line (Fig. 8), though this can be attributable to an unsatisfactory washing step of the precipitate.

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