Statistical model of gold recovery from chloride media using Amberlite XAD-7

A. Filcenco - Olteanu[*], T. Dobre[**], R. Radulescu[*], E. Panturu[*], L. Grigoras[*] and R.I. Panturu[**]

[*]R&D National Institute for Metals and Radioactive Resources, 020917, Bucharest , Romania,
Phone: +40213690467, fax: +40213690466, e-mail: tonyfil2002@yahoo.com ; ioanpanturu@yahoo.com,

[**] Chemical Engineering Dept, University Politehnica of Bucharest, 011061, Bucharest, Romania,
Phone:+40214023927, tdobre@mt.pub.ro

Abstract: The paper presents a study on the statistical modeling of the results obtained in the selective recovery of gold from hydrochloric solutions using Amberlite XAD-7 ion-exchange resin. Experimental tests were conducted on real solutions obtained following selective leaching of gold from different metallurgical wastes, through wet chlorination. The influence of several variables such as: acidity of the working solution, the flow through the bed , temperature, eluent acidity, the flow rate and the acetone/hydrochloric acid ratio has been studied. As a result of the experimental tests performed, it was established that the optimum conditions for the adsorption step were: solution acidity 2.5M HCl, solution flow rate through the bed $1.11 \cdot 10^{-9}$ m^3/s (3Bev/h) and a room temperature. The loaded resin was eluted with an mixture of organic solvent (acetone) and hydrochloric acid. The process efficiency of the gold elution from the Amberlite XAD-7 resin is higher as the fictive flow rate of the eluent is lower and increases with the increase of the eluent acidity and with the increase of the acetone quantity in the eluent (with the increase of the volumetric ratio between acetone and hydrochloric acid). The gold recovery efficiency based on the Amberlite XAD-7 selective ion-exchange resin was over 99.8%.

Keywords: gold, chloride media, ion exchange resin, model

1. Introduction

Due to the fact that cyanide treatment applied in the industrial solubilisation of gold is extremely pollutant [1], research performed in recent years at international [2-4] and national [5,6] levels contributed to the development of eco-technologies which operate with high extraction outputs and use environment-friendly reactants.

Chlorine leaching has several advantages due to the higher dissolution rate of gold, low price of leaching reagents and non-polluting character The solubilisation of metallic gold through the in situ generation of chlorine as a result of the reaction between the sodium hypochlorite and the hydrochloric acid has been previously investigated [7,8]. In these conditions, the metal is present in the solution under the form of the gold (III)-chloro complex $(AuCl_4)^-$.

In many instances, before the final recovery of gold, a purifying and/or concentrating phase is necessary in order to obtain an advanced purity solution. Among the most frequently used methods, the liquid-liquid extraction, the membrane based techniques; the adsorption on coal and the ion-exchange have been extensively described by literature [9, 10]. In many cases, the adsorption of a solute in a solid support presents an advantage over the liquid-liquid extraction or even over membrane technologies in that no mixing and settling requirements need to be fulfilled. The organic phase loss through entrainment is thus eliminated and the use of an intermediate step such as filtration is avoided.

Ion-exchange resins are very scarcely used in the commercial extraction of gold from hydrometallurgical solutions, in spite of the advantaged offered by resins (higher loading rate, easier gold elution, etc.) as compared to active coal [11, 12]. However, the application of ion-exchange resins for gold separation from hydrochloric solutions is possible when the resin ensures a high selectivity for the $AuCl_4^-$ complex, enables the complex elution retained with simple environments which result in rich eluates and enable repeated use [13].Due to the anionic nature of the gold (III)-chloro complex, the use of the anion-exchangers (but also of the chelating resins) in the adsorption of this precious metal was extensively documented [14]. This paper investigates the gold (III) adsorption and elution from hydrochloric solutions by using Amberlite – XAD-7 ion exchange resin. The effect of different parameters was studied, both on the metal adsorption in the resin and on the gold elution from the loading resin. The final gold recovery from eluates (acetone and hydrochloric acid solution) was made by precipitation, using a hydroquinone solution.

2. Experimental

2.1. Materials and reactants

Experimental tests were performed on a solution obtained as a result of selective solubilisation of gold from different metallurgical wastes, through wet chlorination. For the preparation of the working solutions different

chemical reactants of analytical purity were used, such as the hydrochloric acid (HCl), acetone (C_3H_6O) and hydroquinone [H_4C_6 (OH)$_2$].

For the gold (III) retention from hydrochloric solutions the Amberlite XAD-7 ion-exchange resin was used (produced by Rohm & Haas). Amberlite XAD-7 is characterized by weak ester groups, with a medium pore size 80 Å, a specific surface 450 m^2/g , a pore volume 55% and resin particle size 20/50 mesh.

Experimental tests were performed in a laboratory set up, schematically presented in Figure 1.
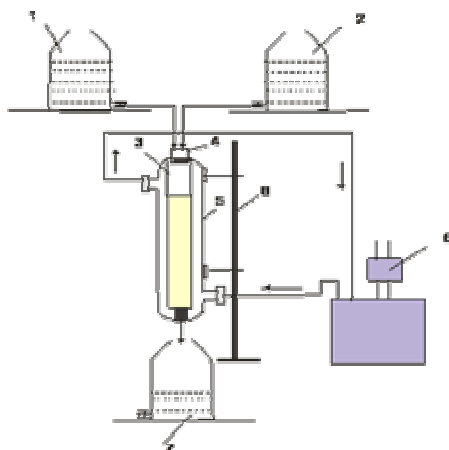

Figure 1. Experimental set up

1 – supply container for the chloro-auric solution, 2 – supply container for the washing solution and eluent, 3 – glass column with AMBELITE XAD-7 resin bed , 4 - rubber cork with feeding hoses going through , 5 – heating shell, 6 – thermostat-controlled water bath, 7 – effluent collecting container, 8 - support

The installation consisted in a glass column (3) 0.135 m long (Lc=0.135 m), with an inner diameter 0.010 m (Dc=0.010 m), loaded with Amberlite XAD-7 resin. In order to study the influence of temperature on the ion exchange dynamics, the ion-exchange column was provided with a heating shell (5). The installation was equipped with a lab thermostat (6) linked to a pump for re-circulating the heating agent. In its upper end, the column was equipped with a rubber cork (4) through which two hoses passed to connect the feeding containers (container 1 for the auriferous solution, container 2 for the washing and eluting solution) and the ion exchange column. The column feeding was gravitational. The obtained effluents were analyzed with an atomic mass adsorption spectrometer of the *VARIAN* spectrAA-880 type.

2.2. Working method

In the adsorption step, the acid auriferous solution which contained 0.6 g Au/l, 4.33 g Cu/l, 1.65 g Sn/l, 0.45 g Fe/l, 0.37 g Pb/l and had a free acidity of 2.5M HCl was passed through the ion exchange column at a pre-selected flow rate (for example, 3 BEV/h, in which 1 BEV is the volume of solution equal to the volume of resin in the ion exchange column).

In order to study the effect of different parameters on the metal adsorption in the Amberlite XAD-7 resin, the alternative to raise the breakthrough curves was chosen, according to a 2^3 factorial plan. The analyzed parameters and their variation ranges are presented in Table 1.

TABLE 1. Analyzed parameters and their variation domain

Analyzed parameters	Variation domain
acidity (A, M)	2 – 3
flow rate, (Gv, m^3/s)	$0.83 \cdot 10^{-9}$ - $1.39 \cdot 10^{-9}$
temperature (T, ºC)	20 – 30

The washing of the ion-exchange resin was made with a 3M HCl solution in order to completely replace the feeding solution and simultaneously remove the complex anions retained by the resin, besides gold.

The loaded and washed resin was eluted with a mixture of organic solvent (acetone) and hydrochloric acid. In order to study the effect of different parameters on the gold elution in the Amberlite XAD-7 resin, the alternative to raise the breakthrough curves was chosen, according to a 2^3 factorial plan. The analyzed parameters and their variation range are presented in Table 2.

TABLE 2. Analyzed parameters and their variation domain

Analyzed parameters	Variation domain
Eluent acidity (A, M)	2 – 3
Flow rate, (w$_f$, m/s)	$1.77 \cdot 10^{-5} \rightarrow 5.31 \cdot 10^{-5}$
acetone: hydrochloric acid ratio	2 - 3

The auriferous eluate thus obtained is a solution of tetrachloro-auric acid in a mixture of acetone and hydrochloric acid. The AAS analysis of elutes sample proved that the main accompanying elements (Fe, Pb, Cu) were lower than 5 ppm concentrations.

3. Results and Discussion

3.1. The adsorption phase

Figures 2 and 3 present the breakthrough curves obtained in the case of the adsorption of an auriferous solution of 0,6 g Au/l concentration, tested at two different acidities and two different temperatures respectively.

From the presented figures one could notice that along with the increase of acidity in the solution, there also occurs a slight raise of the breakthrough time and implicitly of the saturation time, due to the increase of the resin effective capacity. A possible explanation would be that at a lower acid concentration the resin is incompletely protonated, whereas at higher acidity, the competition between the existing ions becomes significant.
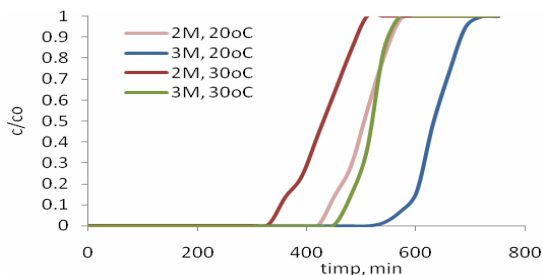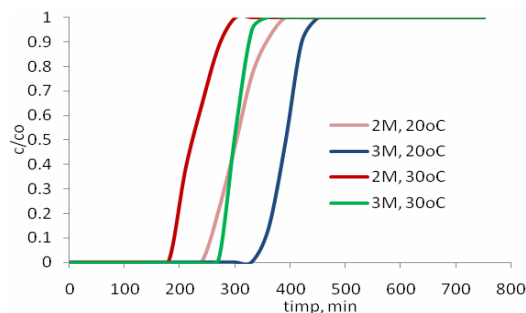
Figure 2. Evolution in time of the AuCl$_4^-$ ion concentration in the column effluent for a factorial 2^3 experiment
($c_0 = 0.6$ g/l , for solution acidities of 2M and 3M and temperatures of 20°C and 30°C respectively, Gv= $0.83 \cdot 10^{-9}$ m^3/s)

Figure 3. Evolution in time of the AuCl$_4^-$ ion concentration in the column effluent for a factorial 2^3 experiment
($c_0 = 0.6$ g/l , for solution acidities of 2M and 3M and temperatures of 20°C and 30°C respectively, Gv = $1.39 \cdot 10^{-9}$ m^3/s)

The resin's effective capacity diminishes with the increase of the feeding rate; a sensible modification of the beakthrough curves upon the change of the feeding rate was noticed. When a fixed bed operating system functions under far from equilibrium conditions, the reduction of flow will determine a significant sharpening of the curve; thus the solute loss due to adsorption kinetics will be minimum. When the ion exchange in the bed operates close to equilibrium (extended contact time), a drop in the flow rate will leave the breakthrough curve practically unaffected.

The loading kinetic of gold in the Amberlite XAD-7 ion-exchange resin is influenced by temperature. Thus, a temperature raise would determine a raise in the gold adsorption rate in the resin and hence a reduction of the operation time.

It was noticed that the resin has an effective capacity of 15 g Au/l resin if the gold concentration in the effluent is under 1 mg/l.

As a result of the experimental tests performed, it was established that the optimum conditions for the adsorption step were: solution acidity 2.5M HCl, solution flow rate through the bed 1.11 $\cdot 10^{-9}$ m^3/s (3Bev/h) and a room temperature. The adsorption efficiency was 99.8%.

By using the NCSS 2007 program, sub-program Design Expert, to process the experimental data for a 2^3 plan [8,15], the following correlation was obtained, describing the efficiency of the adsorption process:

$$E = 0.405 + 0.58 \cdot X_1 - 9.78 \cdot 10^{-3} \cdot X_2 - 1.28 \cdot 10^{-11} \cdot X_3 - 0.13 \cdot X_1^2 + 0.0033 \cdot X_1 \cdot X_2 - \quad (1)$$
$$- 2.32 \cdot 10^{-11} \cdot X_1 \cdot X_3 + 5.95 \cdot 10^5 \cdot X_2 \cdot X_3$$

This correlation clearly indicates the manner in which each factor and even each binary factor interaction influences the obtained response. If this relation is adapted to work out for other compositions, it can be used for technological sizing and assessment processes.

3.2. The elution step

The gold elution from the resin was made with a mixture of acetone and hydrochloric acid. The use of acetone for the elution of gold is based on the assumption that the gold (III) chloro complex [AuCl$_4$]$^-$ is retained due to the polarizing forces that exist between the anionic species and the charge bearing sites of the resin. Elution based on acetone determines a change of the dielectric constant of the environment which leads to the [AuCl$_4$]$^-$ desorption. The role of the hydrochloric acid consists in the resin re-protonation and thus in its simultaneous regeneration which enables it's re-use in a new adsorption cycle.

Previous research has demonstrated that the proportion in which the two components of the eluent are mixed up influences the efficiency of the process and implicitly the volume of eluent needed to recover the gold retained by the resin. The elution kinetic function of the acetone: hydrochloric acid ratio is presented in Figure 4.

It was observed that when using an eluent with an acetone: HCl ratio less than 1, the elution is complete but involves the use of a larger volume of solution. For an acetone: HCl ratio = 1.5, the elution is made in 2.5 BEV solution (a solution volume equivalent to the resin volume in the column) thus recovering 99.5% of the gold retained in the resin, while for an acetone: HCl ratio = 2.5, the gold elution is made in proportion of 99.5% in a 1.5 BEV solution.
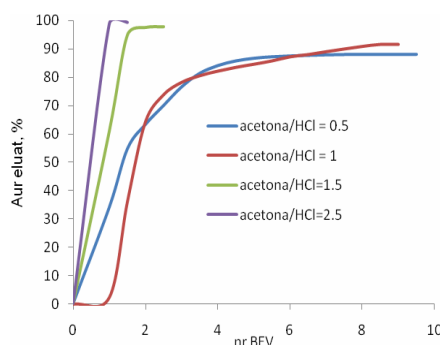

Figure 4. The elution kinetic function of the acetone: HCl ratio

The effect of the eluent acidity (given by the concentration of hydrochloric acid used in the eluent mixture) over the process efficiency is given in Figure 5. One can notice that the elution isotherms are similar, which

indicates that one can also use a 1 M hydrochloric acid solution for the eluent mixture to obtain an efficiency over 99%.
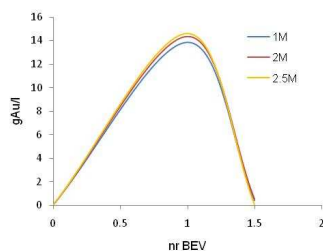

Figure 5. Gold elution curves function of the hydrochloric acid concentration

The gold elution kinetic function of the eluent flow rate is presented in Figure 6. The eluent flow rate through the resin bed influences both the elution process efficiency and the quality of the final product. In order to obtain as concentrated as possible solutions of tetrachloro-auric acid, the flow rate of the eluent through the bed must be as low as possible (1Bev/h).
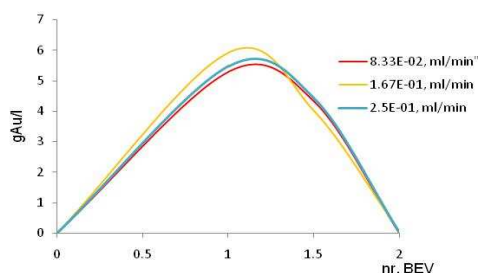

Figure 6. Gold elution curves function of the elute flow rate

In this case as well, by using the NCSS 2007 program, sub-program Design Expert, in processing the experimental data for a 2^3 plan, the following correlation was obtained, describing the efficiency of the adsorption process:

$$E = 62.70 + 27.48 \cdot X_1 - 1.18 \cdot 10^5 \cdot X_2 + 2.20 \cdot X_3 - 5.07 \cdot X_1^2 + 2.64 \cdot 10^4 \cdot X_1 \cdot X_2 \quad (2)$$
$$-0.935 \cdot X_1 \cdot X_3 + 2.64 \cdot 10^4 \cdot X_2 \cdot X_3$$

This correlation clearly indicates the manner in which each factor and even each binary factor interaction influences the obtained response. The process efficiency of the gold elution from the Amberlite XAD-7 resin is higher as the supposed flow rate of the eluent is lower and increases with the increase of the eluent acidity and with the increase of the acetone quantity in the eluent (with the increase of the volumetric ratio between acetone and hydrochloric acid).

Following the elution step, a tetrachloro-auric acid ($HAuCl_4$) solution results, in an 2.5 M acetone – hydrochloric acid environment. The atomic absorption analysis performed on the obtained eluate indicates that the accompanying elements Fe, Ag, Cu, Pb, Zn are in concentrations smaller than 5 ppm.

The gold recovery from the tetrachloro-auric acid solutions with efficiency higher than 99% was made by reductive precipitation, using a 5% hydroquinone solution.

4. Conclusions

The Amberlite XAD-7 type **non-ionic** resin may be successfully used in the separation, purification and concentration of gold from complex composition ionic solutions, with 99.8% efficiency.

The gold adsorption on Amberlite XAD-7 from acid solutions is influenced by the solution acidity, the flow rate of the solution through the resin bed and the temperature.

The $[AuCl_4]^-$ elution from the loaded resin may be performed with an efficiency higher than 99% with the aid of an acetone: HCl mixture. Gold is recovered from the eluate by reductive precipitation, using a 5% hydroquinone solution. In order to obtain metallic gold of min. 99.96% purity, the auriferous powder is subsequently melted at $1060^{\circ}C$.

By adapting the statistic models obtained from the processing of experimental data in a way to respond to other compositions, one can use these data for technological sizing and assessment processes.

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