ION EXCHANGE RESIN
USE FOR Au AND Ag SEPARATION FROM DILUTED SOLUTIONS OF THIOUREA

Ion exchange is one of convenient methods for precious metals recovery from diluted thiourea solutions. Desorption of gold and silver from resins can be made by displacement of complexes. The effect of various eluants on the precious and heavy metals elution efficiency were investigated.

Key words: *ion exchange resin, thiourea solution, gold, silver, adsorption, elution*

Smola s izmjenjivim ionima za separaciju Au i Ag iz razrijeđenih otopina tioureje. Izmjena iona je jedna od prikladnih metoda za izdvajanje skupih metala iz razrijeđenih otopina tioureje. Desorpcija zlata i srebra iz smola može se postići premještanjem kompleksa. Istraživao se utjecaj eluanata na učinkovitost eluacije skupih i teških metala.

Ključne riječi: *smola s izmjenjivim ionima, otopina tioureje, zlato, srebro, adsorpcija, eluacija*

INTRODUCTION

Thiourea leaching is one of the non-pollution methods for gold leaching. Strict regulations in water quality will be the reason for gradual replacement of toxic processing , such as cyanidation , by less toxic technology. The inability of cyanide to leach certain refractory ores efficiently is another reason for the change of leaching agent.

Literature on the recovery of gold from thiourea solutions is not very much spread. Various techniques to recover gold and silver from this solution have been investigated such as cementation with aluminium [1-5], lead and iron [5-8], adsorption on natural brown coal [9] and activated carbon [4, 7-9, 10-11], ion exchange [3, 4, 7, 12-20], solvent extraction [14], hydrogen reduction [4] and electrowinning [5, 21, 22].

Resins generally exhibit non-selective adsorption characteristics, resulting in high base metal loadings, which complicate the gold and silver desorption procedure and may poison the resins and contaminate the eluant.

The gold and silver method of loading from the poor thiourea solutions must be compatible with the elution procedure and be effective in recovering the gold. It should also be simple and, preferably, proven technology.

Different strong acid cation exchangers were investigated to adsorb precious metals from poor thiourea solu-

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tions in the previous work [20]. Therefore the objectives of this study were to investigate the elution of precious and matrix metals from loaded resin O-KS.

The strong binding of gold and silver complexes on ionex is the reason to choose multistep elution scheme with the aim to elute at the first step less strongly binded complexes of accompaning elements and so to increase the efficiency of precious metals desorption.
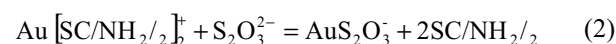
THE CHEMISTRY

Gold can be desorbed from ion-exchange resins either via a chemical reaction or by displacement. In methods using a chemical reaction , the gold complexes on resin are decomposed and opposite charged gold is formed and washed off the resin.

The exchange mechanism involved is:

$$\overline{X^+} + Au\left[SC/NH_2/_2\right]_2^+ = X^+ + \overline{Au\left[SC/NH_2/_2\right]_2^+} \qquad (1)$$
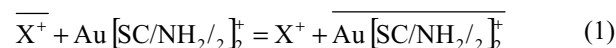
where X^+ is ionic form of the resin.

The elution of gold is a ligand - exchange process , when the thiourea ligand is replaced by thiosulphate. The complex anion $AuS_2O_3^-$ forms according to the scheme:

$$Au\left[SC/NH_2/_2\right]_2^+ + S_2O_3^{2-} = AuS_2O_3^- + 2SC/NH_2/_2 \qquad (2)$$

The reaction is forced towards the formation of more stable complex $AuS_2O_3^-$ with complex stability constant $\log\beta = 26$ against $\log\beta = 22$ for $Au[SC/NH_2/_2]_2^+$.

EXPERIMENTAL

Materials and methods

Experimental solution for sorption was prepared by leaching of gold bearing concentrate Hodruša, Slovakia. Composition of the leach liquors used in ion-exchange experiments are listed in Table 1..

Table 1.   **Chemical composition of leach liquors**
Tablica 1.   **Kemijski sastav baznih tekućina**

Solution	Au $[\mu gml^{-1}]$	Ag $[\mu gml^{-1}]$	Cu $[\mu gml^{-1}]$	Fe $[\mu gml^{-1}]$	Zn $[\mu gml^{-1}]$
A	7.8	6.1	83.2	5384	2130
B	8.5	4.8	74.7	3638	2240
C	7.7	6.1	85.0	5350	2184

The polystyrene strong - acid cation exchanger O - KS was examined in this investigation. Table 2. shows the characteristics of resin.

Table 2.   **The caracteristics of O - KS resin**
Tablica 2.   **Svojstva smole O - KS**

Category	strong-acid cation exchanger
Skelet	styrene co-polymer
Functional group	- SO$_3$H on a skeleton of styrene co-polymer
Size of granule in air-dry state [mm]	0.3 - 1.2
Full exchange capacity in air-dry state [mg-eq g^{-1}]	5

Batch adsorption tests were conducted using 250 ml fla-sks and an orbital shaker. The flasks were filled with 200 ml solution plus 10 ml of swelled resin. The mixture was shaken at 600 min^{-1} frequency for defined time and at 20-25 °C.

Batch elution of resins was conducted with same apparatures used in loading. Eluation was carried out with various eluants using 10 ml of swelled resins plus 100 ml or 50 ml solution at room temperature. In some occasion a second contact was provided.

Dynamic sorption and elution tests were performed in glass tube with diameter 10 mm containing 10 ml of swelled resin. Thiourea leaching solution passed through the column at rate of 100 ml/hour. The solution was continuously collected into 10, 15 or 25 cm^3 flasks and analyzed. The ion exchanger was washed with distilled water during changes of eluant.

Cation exchangers in H$^+$ form resp. NH$_4^+$ were used.

Reagent grade chemicals and distilled water were used in experimental tests. Metals ion analyses were performed by atomic adsorption spectroscopy (AAS). Thiourea analysis was performed by titration method.

RESULTS AND DISCUSSION

Adsorption was carried out with the actual acid thiourea solution coming from the leaching of the gold concentrate sample given in Table 1..

Good results have been obtained with the use of strong acid cation exchangers. They showed good adsorption efficiency for the gold and silver thiourea complexes but with low selectivity against matrix metals, particularly copper and iron [20].

The results of sorption of gold and silver and matrix metals on the strong acid kationic exchanger O-KS are presented in Tables 3. and 5.. As can be seen from the data presented, the sorption of precious metals is sufficiently high, more then 80 %, but not sufficiently selective.

Table 3.   **Efficiency of adsorption of metals from solution B**
Tablica 3.   **Učinkovitost adsorpcije metala iz otopine B**

From solution	Au [%]	Ag [%]	Cu [%]	Fe [%]
B	97.0	88.2	85.8	14.9
Conditions: static adsorptin + 10 ml swelled exchanger, 7 hours preparation of loaded resin for three step static elution with: HNO$_3$ + H$_2$O$_2$ - NH$_4$NO$_3$ - /NH$_4$/$_2$S$_2$O$_3$				

The aim of the present work was to find the possibility of the selective elution of precious and matrix metals by means of multistep scheme.

Amonium thiosulphate influence to the elution efficiency of Au, Ag

Static elution scheme included three steps : I. - 10% HNO$_3$ + 1% H$_2$O$_2$; II. - 1M NH$_4$NO$_3$; III. - 10% (NH$_4$)$_2$S$_2$O$_2$.

The adsorption conditions for preparing of the loaded resin is given in Table 3.. The results of the static elution experiment are given in the Figure 1.. It was established that precious metals can be eluated into amonium sulphate solution with higher efficiency (Au over 85% and Ag over 95%) against sodium thiosulphate. Iron and zink were removed in the first two steps of elution with good efficiency.

Table 4.   **The comparison of leaching and eluant solution**
Tablica 4.   **Usporedbe osnovne otopine i otopine eluanta**

Solution	Au $[\mu gml^{-1}]$	Ag $[\mu gml^{-1}]$	Cu $[\mu gml^{-1}]$	Fe $[\mu gml^{-1}]$	Zn $[\mu gml^{-1}]$
Leaching	8.45	4.83	74.73	36388	2240
Eluant 10% (NH$_4$)$_2$S$_2$O$_3$	21.1	12.1	171.9	124.3	72.7
	2.5 x ↑	2.5 x ↑	2.3 x ↑	291 x ↓	30.8 x ↓

In the Table 4. there are compared compositions of leach liquor against the eluant of amonium thiosulphate.

The rise of concentration of precious metals in the first bed of eluate was 2.5 times and a very significant lowering of iron and zink was observed 293 and 31 times respectively. Concentration of copper increased in final step solution 2.3 times and it was not really eluated into first two steps.
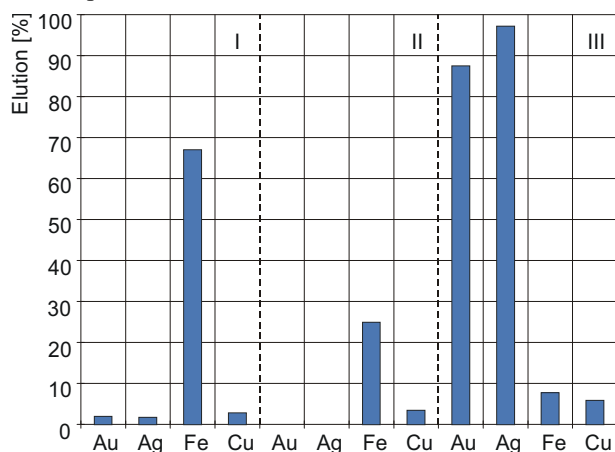

Figure 1. **Efficiency of three step static elution: I. 10%HNO₃+1%-H₂O₂, II. 1M NH₄NO₃, III. 10% /NH₄/₂S₂O₃**
Slika 1. **Učinkovitost tri stupnja statičke eluacije: I. 10%HNO₃+-1%H₂O₂, II. 1M NH₄NO₃, III. 10% /NH₄/₂S₂O₃**

Four steps of dynamic elution scheme included the eluants: I. - 1M H_2SO_4; II. - 10% HNO_3 + 1% H_2O_2; III. - 1M NH_4NO_3; IV. - 10% $(NH_4)_2S_2O_3$.

The adsorption conditions for preparing of the loaded resin is given in Table 5..

Table 5. **Efficiency of adsorption of metals from solution A**
Tablica 5. **Učinkovitost adsorpcije metala iz otopine A**

From solution	Au [%]	Ag [%]	Cu [%]	Fe [%]	Zn [%]
A	90.3	81.5	20.7	52.4	21.1

Conditions: static adsorptin + 200 ml swelled exchanger, 7 hours The preparation of loaded resin for four step static elution with: H_2SO_4 - HNO_3 + H_2O_2 - NH_4NO_3 - /NH_4/₂S_2O_3

Into this dynamic elution scheme a futher step was included for elution of base metals by sulphuric acid (1M H_2SO_4) against static elution scheme. The results are presented in Figure 2..

Essential amount of iron and zink was removed in the first step by elution with sulphuric acid solution (summary 74% Fe and 85% Zn). The elution of Cu in the second step with nitric acid solution reached 72.6% Cu.

In the step of elution with 1M NH_4NO_3 solution there are no precious metals eluted and very low efficiency of ma-trix metals is reached. However, it is an important step from the point of conversion from H^+ to NH_4^+ form of exchanger before using amonium thiosulphate solution as a eluant.
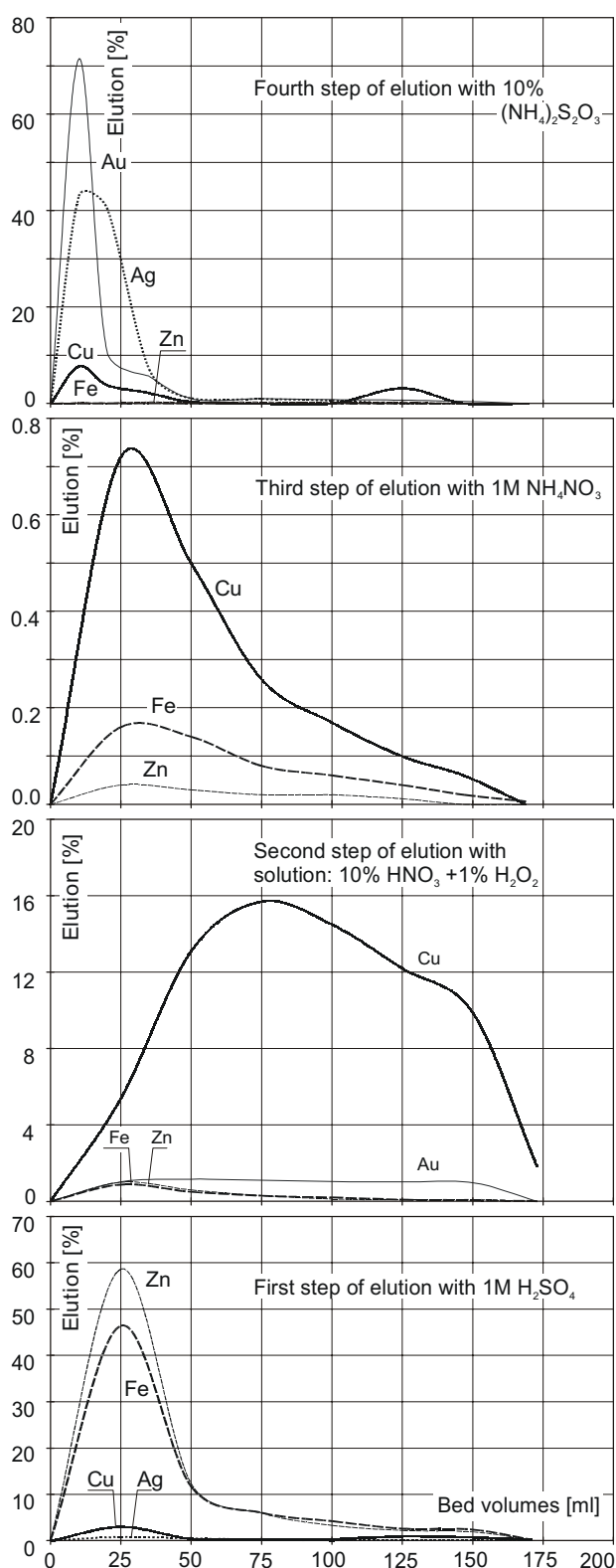

Figure 2. **Efficiency of four step dynamic elution: I. 1M H₂SO₄, II. 10% HNO₃+1%H₂O₂, III. 1M NH₄NO₃, IV. 10% /NH₄/₂S₂O₃**
Slika 2. **Učinkovitost četri stupnja dinamičke eluacije: I. 1M H₂S-O₄, II. 10% HNO₃ +1%H₂O₂, III. 1M NH₄NO₃, IV. 10-% /NH₄/₂S₂O₃**

In the last step of dynamic four steps elution 91% Au and 95% Ag efficiency was reached in 10% $(NH_4)_2S_2O_3$ solution.

Maximum concentrations in individual bed volumes of eluant achieved are given in the Table 6.. To compare with leach liquor, 12.7 times (1273%) increasing of Au and 6.2 times (543%) of Ag was reached. Concentrations of base metals were decreased 945 times (to 0.1%) for Fe and 109 times (to 0.9%) for Zn.

Table 6.   **The comparison of leach liquor and the highest volume of eluant**
Tablica 6.   **Usporedbe osnovne tekućine i najvećeg volumena otopine eluanta**

Solution	Au [μgml^{-1}]	Ag [μgml^{-1}]	Cu [μgml^{-1}]	Fe [μgml^{-1}]	Zn [μgml^{-1}]
Leaching	7.79	7.00	83.2	5384	2130
Eluant 10% $(NH_4)_2S_2O_3$	99.2	38.0	68.5	1.7	14.6
	12.7 x ↑	5.4 x ↑	1.2 x ↓	3167 x ↓	146 x ↓

The breakthrough curves of Au, Ag, Fe, Cu, Zn, and Sb on the cation exchanger O - KS as a second sorption contact of resin after four steps dynamic elution are presented in Figure 3.. It is evident that the sorption efficiency of precious metals was not much affected by the presence of other metals.
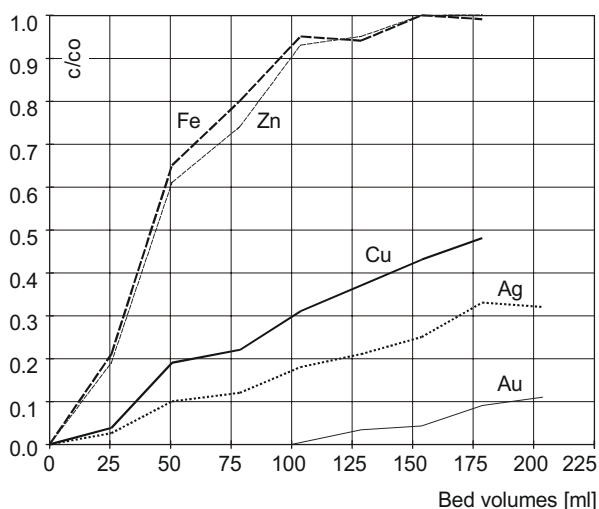

Figure 3.   **Second dynamic adsorption on the resin O - KS from the solution C after four step elution**
Slika 3.   **Druga dinamička adsorpcija na smolu O - KS iz otopine C nakon četvrtog stupnja eluacije**

CONCLUSIONS

Strong acid cationic ion exchange resin O - KS showed good efficiency of loading the gold and silver thiourea complexes from the solutions containing iron, copper, zink, antimony. [20].

Elution of Au, Ag and Cu, Fe, Zn from strong cation exchanger O - KS was carried out by various eluants. The following conclusions can be drawn from this study:

- ammonium thiosulfate solution has shown the best perfomance to elute gold and silver;

- four steps elution scheme alows to obtain selectively Fe and Zn into sulphuric acid solution with 74% respectively 85% efficiency and 73% Cu into nitric acid solution;

- the increase of concentration of Au and Ag in eluant was achieved 13 times and 6 times respectively. On the other hand, the lowering Fe and Zn was 3130 times and 150 times respectively against the leach liquor;

- second sorption contact of resin gave acceptable levels of sorption efficiency of precious metals.

As the elution method has also to be economically viable, the reagent consumptions should be monitored.

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