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## **RECOVERY OF PRECIOUS AND NON-FERROUS METALS FROM THE REBELLIOUS COMPLEX OF MINERAL RAW MATERIALS**

### **Abstract**

*The results of comprehensive researches aimed to develop the advanced technology of rebellious refractory minerals and ore processing are given in this paper. Some ways in solving the most challenging technological problems associated with complex ores enrichment and hydrometallurgical processing to recover precious and non-ferrous metals, biochemical leaching inclusive, as well as recommendations on processing of leaching solutions aimed at valuable components recovery are proposed. Effects of reagent X on dissolving the non-ferrous and precious metals as well as the associated elements from refractory ore, concentrates and metallurgical production wastes are shown.*

*Reagent X promotes metal leaching through a control of oxygen regime of leaching process. Reagent X, capable to form readily soluble metals hetero-complexes, plays a prominent part. Beneficial effects of reagent X on the mineral polarizing processes in alkali-cyanides media were found. Reagent X pre-treatment enhances metals recovery into solution by 20-30 % depending on the process time.*

*Process of Au, Cu, Zn etc., dissolving from rebellious gold-bearing raw materials was studied through the use of unique microorganisms strain; there are identified chemo-physical regularities of chemical leaching process, and the innovation technology of chemical leaching of gold-containing materials was developed.*

**Keywords:** *precious metals, non-ferrous metals, refractory ores, hydrometallurgy, sorption*

### **INTRODUCTION**

Complex mineralogical compositions of the ore are responsible for considerable engineering difficulties and lead to inadmissibly reduced recovery of principal metals in the enrichment processes. Many problems occur both in the ore processing and beneficiation of produced concentrates. Default of generalized criteria to evaluate the metamorphozation degree of the ore, default of assessment particular chemo-physical features through differences of homonymic minerals of the ore, effects of mentioned differences on associated interactions with minerals of enclosing rocks result in considerable metals losses in such

ore processing by the applied technologies for many years.

So, for example, referred to [1], over 100 tons of mineral raw materials are annually mined and processed per capita, out of which 95% go to waste. The annual volume of industrial waste overgrows one billion tons. So far, mentioned data prove an urgent necessity to diversify productions in mining and smelting industries provided that there are developed scientific concepts of resource-saving and environmentally sound technologies. Numerous engineering solutions are developed and implemented in the world industrial practice.

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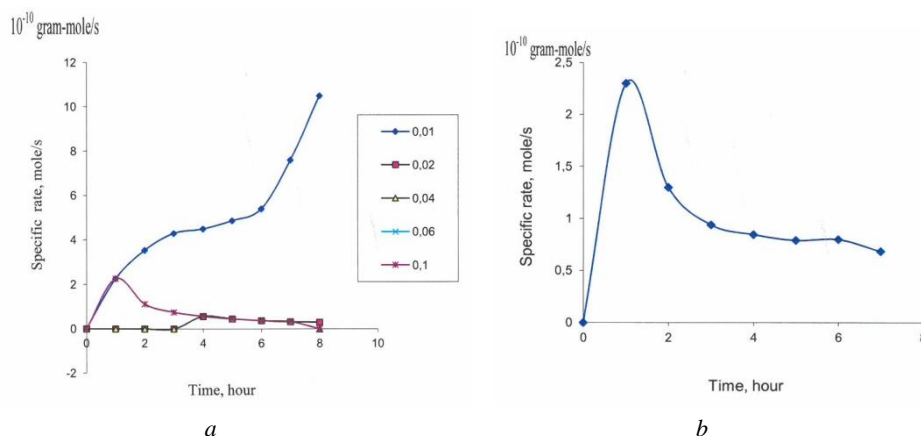
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## EXPERIMENTAL PART

In [2-6] it was shown that the amino acids may be used as the ore metal solvents combined with oxidants and salting-out agents in the sorption and heap leaching processes. At that individual reagents "X" among the amino acids capable to form readily soluble metals hetero-complexes are of crucial importance.

It was shown that cysteine at 0.01 g E/dm<sup>3</sup> concentrations had the utmost effect on gold recovery from flotation concen-

trates. Up to 22.57 % recovery rates were achieved that is about twice as compared to the benchmarks (13.7%). Specific rate of gold dissolving increased over time and it reached 10<sup>-9</sup> mole/s for eight hours. At higher amino acids concentrations this regularity was not observed (Fig. 1, a). Comparison of this value with the alternative variant without cysteine (Fig.1, b) revealed a substantial advantage to introduce 0.01 gE/dm<sup>3</sup> cysteine into pulp before leaching start-up.



**Figure 1** Specific rate of gold dissolving in the process of flotation concentrate chemical leaching in the presence of cysteine (a) and Control (b)

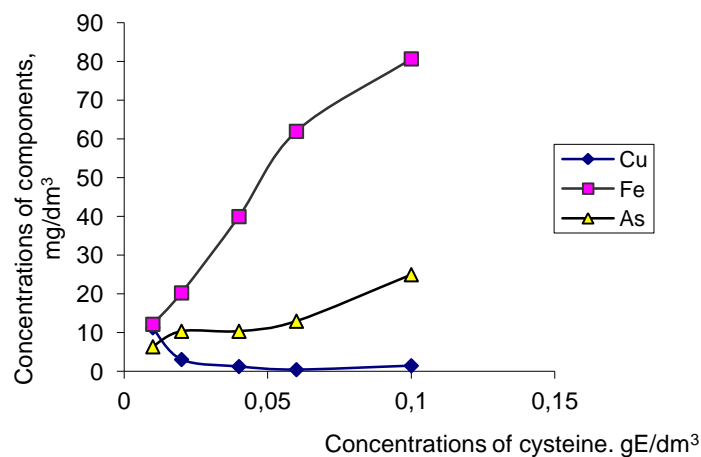
Similar effects of cysteine are observed in copper leaching process. Increasing cysteine concentration promotes recovery of such associated elements as iron and arsenic (Fig. 2).

It was shown that concentration of oxygen, which provides an oxidizing trend of processes, occurred in pulp, increases with cysteine introduction. In course of leaching process, the oxygen concentration in pulp substantially decreases at all studied cysteine concentrations, in particular, during first five hours of leaching. In further running of leaching process, the oxygen concentration again increases.

It was found that electric conductivity of pulp increases only at higher cysteine con-

centrations (0.06–0.1 gE/dm<sup>3</sup>). Leaching process itself is characterized by increased electric conductivity as compared to the initial values for 2 – 5 times at 0.01–0.04 gE/dm<sup>3</sup> and remains higher in all course of leaching process, where jump fluctuations of electric conductivity are observed at higher concentrations.

Detailed analysis of all parameters for the first five leaching hours revealed substantial decrease of oxygen concentration in the first process hour associated with rated-down gold dissolving and stabilized electric conductivity. Near to 6<sup>th</sup> hour, the pattern varied: rate of gold recovery into solution increased concurrently with a sharp increase of oxygen concentration.



**Figure 2** Dependences of copper, iron and cyanic recovery on cysteine concentrations at 20°C

Probably this five-hour inhibition of gold dissolving was due to intense yield of other elements into solution, in particular, the iron yield which concentration increased only in the first leaching hours.

With temperature increasing (from 20°C to 30°C), the rate of gold recovery at lower cysteine values increased pro rata to the increased process time duration. Quantity of dissolved oxygen decreased in course of eight-hour experiment and generally electric conductivity increased approximately by 2%.

Increasing of mill rotation speed from 200 rpm to 400 rpm resulted in the increased gold yield by twice or more at 0.01 gE/dm<sup>3</sup> of cysteine concentration showing dependence in a direct proportion. With increasing the amino acids concentration trend to increased gold recovery into solution remains, however at substantially lower level. Increasing of mill rotation speed at 0.02 gE/dm<sup>3</sup> cysteine in pulp resulted in substantially increased oxygen concentration in pulp. At that, pulp electric conductivity remains practically unvaried. We controlled cysteine concentrations in pulp during the whole leaching process. It was found that in the process of concentrate leaching amino

acid was not consumed rather it affected only the leaching process performance.

Experimental data proved that in the presence of reagent "X" in leaching pulp lead to 50% saving of cyanic acid. Quantum-chemical computations of potential chemical reactions in pulp allow assuming high probability of hetero-complex (amino acid-Au-cyanide) formation. This complex, as well as Au(CN)<sub>2</sub><sup>-</sup>, is negatively charged that is critically important to analyze chemistry of leaching processes. The initial metal fixation with amino acid makes easier further cyanide-ion addition. In case of cysteine, there is possible presence of complex as (amino acid-Au-amino acid) due to cyanide deficiency.

Introduction of 0.01 gE/dm<sup>3</sup> cysteine into leaching solution provided 22.57% gold recovery rendering beneficial effects on gold dissolving rate. However, in the first five hours of leaching process some adverse events occurred, probably due to intensive recovery of such associated elements as iron, arsenic and antimony into solution. Concentrations of amino acid subjected to temporal fluctuations remained by the end of leaching process at their initial level, that is, cysteine was not consumed. Temperature factor and

agitation rate render beneficial effects equalizing initial 5-hours inhibition of gold leaching process. Increasing of oxygen concentration and electric conductivity in presence of cysteine evidences intensified oxidizing processes in pulp. Quantum-chemical computations confirm involvement of cysteine in leaching process, which probably, promotes formation of gold heterocomplex compounds.

By similar way, the leucine effects were studied on leaching process. In presence of leucine with increasing its concentrations from 0.01 gE/dm<sup>3</sup> to 0.06 gE/dm<sup>3</sup>, the gold recovery increased from 57.04 % to 71.42%, respectively. At that, the specific rate of metal recovery into solution increased (Fig. 3). Metal content in solution reached 8.9 mg/dm<sup>3</sup>. Equilibrium gold concentration reached the steady state in three leaching hours practically to the full extent. Reaction order defined through the Van't Hoff diagram method was equal to 0.34.

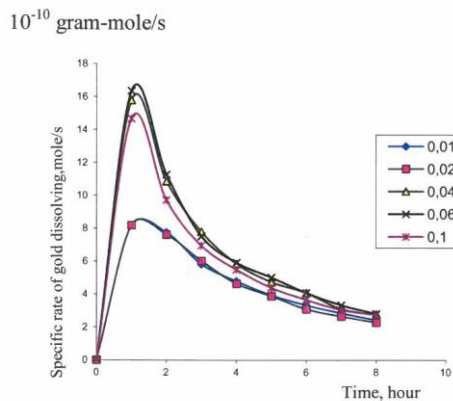
The addition of 0.01 - 0.02 gE/dm<sup>3</sup> leucine into leaching solution affects no oxygen regime of pulp. Further increasing leucine concentrations led to somewhat

decreased oxygen concentrations. In leaching process at 0.01 gE/dm<sup>3</sup> leucine the oxygen concentration sharply increased, especially, in the first leaching hours. At extended time of leaching process, the oxygen content in pulp jumped. At higher concentrations, oxygen content in pulp was stable.

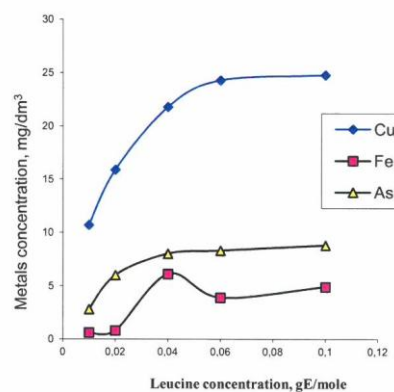
Electric conductivity was substantially increased only when 0.1 gE/dm<sup>3</sup> of amino acid were added. In leaching process, as a rule, it increased, with exception of alternative of 0.1 gE/dm<sup>3</sup> leucine.

Rate of copper recovery into solution rose with increasing amino acid concentrations up to 0.06 gE/dm<sup>3</sup>. Arsenic and iron recovery increasing up to 0.04 gE/dm<sup>3</sup> (Fig. 4) was observed with increased concentrations of leucine.

As it seen from experimental data, the best results by gold recovery into solution were achieved in presence of 0.04-0.06gE/dm<sup>3</sup> leucine. Data follow-up by oxygen regime, electric conductivity and variations of leucine quantity in pulp allowed revealing that oxygen concentrations during practically the whole leaching period remained at level of 6 mg/dm<sup>3</sup>.



**Figure 3** Specific rates of gold dissolving in the process of biochemical leaching of flotation concentrate in the presence of leucine (0.01-0.1 gE/dm<sup>3</sup>)



**Figure 4** Dependence of copper, iron and arsenic recovery on leucine concentration 20°C

Electric conductivity progressively increased from 3 mCm/cm to 7 mCm/cm in

the first 4 hours, and then it remained at this level by the end of leaching process. Con

centration of leucine after jumped variations, remained at its initial level, this is, similarly to cysteine alternative, the amino acid was not consumed in leaching process.

The gold recovery/temperature dependences were studied at different leucine concentrations. It was found that at 0.01 gE/dm<sup>3</sup> leucine concentration, the rate of gold recovery into solution practically does not depend on temperature, only the rate of equilibrium concentration reaching was intensified. At higher leucine concentrations (0.02; 0.04 gE/dm<sup>3</sup>) with increasing temperatures (from 20°C to 30°C), the gold recovery into solution increased. The same behavior pattern was observed in copper leaching, while for iron and arsenic there was observed the contrary: increasing temperature led to decreased iron and arsenic recovery into solution. Optimal temperature of gold leaching was 30°C. At this temperature the 4-hours leaching provided 88.35 % gold recovery into solution where leucine content in solution reached 0.04 gE/dm<sup>3</sup> and at rate of mill rotation up to 300 rpm. Energy of activation of gold dissolving reaction at optimal leucine concentration (0.04 gE/dm<sup>3</sup>) reached 45.43 kJ/mole.

Intensified pulp agitation rendered beneficial effects on gold and copper recovery only at 0.01 gE/dm<sup>3</sup> leucine in pulp. Specific gold dissolving rate increased with increasing mill rotation rate up to 400 rpm providing 80.15 % gold recovery in 7 leaching hours. Inverse correlation was observed at increasing amino acid concentration. Iron and arsenic recovery increased with increasing of mill rotation rate.

With intensified pulp agitation the oxygen content in pulp increased during first 2-3 leaching hours. Pulp electric conductivity increased, then equalized and remained at higher level by the end of experiment.

Leucine used in concentrations ranging from 0.01 gE/dm<sup>3</sup> to 0.06 gE/dm<sup>3</sup> gave rise to gold recovery from 57.04% to 71.42%. In leaching process at 0.01 gE/dm<sup>3</sup> leucine, the oxygen content and solution electric conductivity increased, in particular, in first leaching hours. Gold and copper recovery into solution increased at 0.02 gE/dm<sup>3</sup> and 0.04 gE/dm<sup>3</sup> leucine concentrations with temperatures increasing, while, on the contrary, iron and arsenic recovery decreased. As with cysteine, leucine was not consumed in 8-hours leaching process.

Quantum-chemical computations proved that amino- and acid groups interact in the leucine. Effects of electron-accepting carboxy group and electron-donating oxygen atom of hydroxyl group on amine groups determine acidity degree and are characterized by proton affinity. Leucine showed the highest E<sub>H+c</sub> (considering sign) and, hence, the lowest hydration energy (Table 1). Exactly leucine showed the lowest energy of complexes formation in solutions.

In estimating energy of multicomponent systems formation, as with cysteine, there was preferred formation of gold complex, firstly, with leucine anion, then bonding second ligand – cyanide ion. Leucine anion as the first ligand in solution showed higher reaction capacity as compared to cysteine, while, on contrary, by its activity as the second ligand (E<sub>3 pcm</sub>), it was weaker (Table 1).

**Table 1** Complexing energy at different sequence of ligands addition, kcal/mole

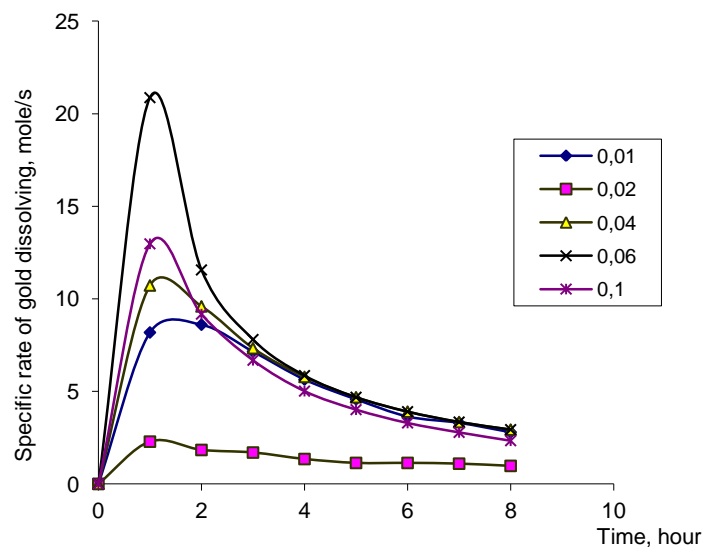
	E1, kcal/m	E1pcm, kcal/m	E2, kcal/m	E2pcm, kcal/m	E3, kcal/m	E3pcm, kcal/m
Leucine- + Au <sup>+</sup> + CN <sup>-</sup>	-296.183	-112.560	-121.894	-72.848	-66.259	-28.798
Notes: E1 – cyanide-ion and amino acid are concurrently combined with gold; E1=E(AminAuCN) – E(Au) - E(Amin-) - E(CN) E2 - at first, gold interacts with amino acid, then the second ligand adjoins: cyanide -ion E2=E(AminAuCN) - E(AuAmin) – E(CN <sup>-</sup> ) E3 - at first, gold interacts with cyanide-ion, then amino acid adjoins E3=E(AminAuCN) – E(AuCN) - E(Amin-)						

It was found that the serine at concentration  $0.01 \text{ mg/dm}^3$  provides up to 65.8 % gold recovery into solution in seven hours of chemical leaching. With increased serine content up to  $0.04 \text{ gE/dm}^3$ , the gold recovery increased up to 66.78%. Presence of  $0.06 \text{ gE/dm}^3$  amino acid in pulp stepped up the metal recovery.

Specific gold dissolving rate increased with increasing serine content in pulp from  $0.01 \text{ gE/dm}^3$  to  $0.06 \text{ gE/dm}^3$ . In leaching process it evenly decreased (Fig. 5). Reaction order defined through the Van't Hoff diagram method was equal to 1.04.

It should be noted a more efficient cyanide use in leaching process. Its residual concentration in pulp decreased with increasing serine content in solution.

Increasing leaching process temperature up to  $30\text{-}40^\circ\text{C}$  was the most efficient for serine concentration  $0.1 \text{ gE/dm}^3$ . At  $30^\circ\text{C}$  gold was recovered into solution by 14.9% and at  $40^\circ\text{C}$  by 42.6% and more as compared to leaching conditions at  $20^\circ\text{C}$ . In the whole, 8-hours leaching at addition of  $0.1 \text{ gE/dm}^3$  serine in pulp allowed to recover up to 98.7% gold in solution. By a similar way copper content in solution increased, while iron and arsenic concentrations decreased. Increasing serine content from  $0.01 \text{ gE/dm}^3$  to  $0.1 \text{ gE/dm}^3$  concurrently with increasing temperature resulted in sharp decreasing of antimony concentration (from  $65.7 \text{ mg/dm}^3$  at  $0.01 \text{ gE/dm}^3$  serine up to  $12.7\text{-}23.5 \text{ mg/dm}^3$  at  $0.06\text{-}0.1 \text{ gE/dm}^3$  amino acid).



**Figure 5** Changes in specific gold dissolving rates (at different initial quantity of serine,  $\text{gE/dm}^3$ ) in process of the Akbakay flotation concentrate leaching

With increased temperature up to  $30^\circ\text{C}$  oxygen content in leaching pulp decreased while electric conductivity increased (in particular, at  $0.01 \text{ gE/dm}^3$  and  $0.1 \text{ gE/dm}^3$ ). Energy of gold dissolving reaction activation reached  $21.72 \text{ kJ/mole}$ .

Oxygen regime at minimal serine concentration in pulp was improved with increased agitation rate, while this parameter got worse with increased serine concentration. Electric conductivity was not subjected to somewhat significant modifications.

Quantum-chemical study of potential serine/gold complexing in process of flotation concentrate leaching proved that the serine shows lower  $E_{H^+}$  (considering sign) as compared to leucine and, hence, higher hydration energy. This evidences higher reaction capacity of amino acid. Complexing energy of serine in solution was higher as compared to the leucine.

Probably, in the complexing process, as with other amino acids, gold cation is coordinated concurrently by two atoms: O and N. In case of leucine and serine molecules with optimal complex configuration the binding is coordinated towards to the carbonyl. Nevertheless, in compact serine molecule carbonyl oxygen and electron-donating oxygen atom of second hydroxyl group are also involved in Au binding that substantially promotes complex strengthening. Estimative analysis of multi-component systems formation energy/ligand bonding order dependences proved that the serine and leucine by their activity as first ligand in solution are closely equal, at that, serine anion in solution is the weakest second ligand.

## RESULTS AND DISCUSSION

It was found that the leucine substantially enhances gold recovery into solution in process of flotation concentrate biochemical leaching. Direct correlation of gold recovery with increased amino acid concentration supplied up to  $0.6 \text{ gE/dm}^3$ . As judged by leaching process itself, as well as conforming to data of quantum-chemical computations, leucine generates bound with gold, coordinated towards to carbonyl that substantially enhance binding energy and makes easy formation the heterocomplex compounds of amino acid-gold-cyanide type. As result, flotation concentrate leaching in presence of leucine is not associated with complicating effects observed where leaching process runs in presence of cysteine.

It was found that serine promotes gold and copper recovery, improves oxygen re-

gime and pulp electric conductivity. Increased leaching temperature up to  $40^\circ\text{C}$  concurrently with increased serine concentration up to  $0.1 \text{ gE/dm}^3$  provides 98.7% gold recovery. As with cysteine and leucine, the serine in leaching process is not consumed.

Estimation of different amino acids effects on metals dissolving features in process of flotation concentrate leaching allowed stating that the leucine and serine turned out to be very effective for gold and copper, especially in complex with temperature and agitation. Cysteine within studied range of factors variations promoted iron and arsenic yield. In terms of quantum-chemical study, serine is more active in liquid phase regarding to gold cation and gold cyanide as compared to leucine, at that it forms stronger complexes of amino acid-gold-cyanide type as compared to studied amino acids.

Experimental data give grounds to conclude that the amino acids formed in chemical leaching process act as catalysts for chemical reactions of gold dissolving. So, chemical leaching process efficiency may be monitored through changes in amino acid concentrations in leaching solutions and varied amino acids ratios depending on mineral compositions of process raw materials. In this case integrated processing technologies render beneficial effects.

## CONCLUSION

Research data on kinetics of anodic oxidation process of chalcopyrite and sphalerite sulfide minerals obtained by the potentiometric method allowed identifying beneficial effects of reagents "X" in the processes of minerals polarizing in alkali-cyanides media. Reagent "X"-assisted minerals pretreatment result in intensified dissolving processes through increase the polarizing current density in the process of anodic minerals oxidation in solutions of pH-9. Within potentials range of 0.3-2.0 V metals recovery increases by 20-30% depending on treatment time duration.

It was found that the serine, leucine and phenylalanine at temperature  $t = 30^{\circ}\text{C} - 40^{\circ}\text{C}$  and agitation intensity up to 300-400 rpm render ultimate effects on gold and non-ferrous metals recovery into solution providing over 90 % gold recovery in 6-8 hours or more of treatment process. At that, oxygen solubility in leaching solutions increases. Values of redox potentials defined for amino acid solutions confirmed functions of serine and leucine in generation of overvoltage at the electrodes providing favorable conditions to recover gold and non-ferrous metals into solutions.

Quantum-chemical computations confirmed the amino acids functions in metals complexing in solution. Stability and consistency of complexes with amino acids and cyanide ion for atoms, having d-open shells, increase in series  $\text{Fe} > \text{Zn} > \text{Cu} > \text{Au}$ .

Chemo-physical regularities of Au, Cu, and Zn dissolving from rebellious gold-containing raw materials in presence of reagents are identified, kinetic performances of mentioned process are specified and theoretical backgrounds of metals dissolving from

rebellious ores are built up, innovative technology of chemical leaching is developed.

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