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CYANIDE LEACHING OF POLYMETALLIC ORE TREATMENT RESIDUUM AND THE RECOVERY OF NOBLE METALS FROM LEACH LIQUOR

The particularities of cyanide leaching of a gold-bearing residuum remaining after removing copper, zinc and lead from Cu/Zn/Pb/Fe sulphatized roast-calcine by its hydrometallurgical treatment, and electrowinning of gold and silver from obtained leach liquor are investigated. The optimum technological regimes of these processes are established.

Keywords: residuum, cyanide leaching, sodium cyanide, potential, anodic and cathodic reactions, electrowinning, current density, current efficiency.

The tested gold-bearing residuum (oxide concentrate with 74.2 m*g/kg* Au and 1034.2 m*g/kg* Ag) of about – 0,071 *mm* particle size, had the following main mineral composition (%): 47.9 Fe_2O_3, 20.7 SiO_2, 10.9 Al_2O_3, 5.5 $Fe(OH)_3$, (CaO + MgO) and the rest. It was obtained from Cu/Zn/Pb/Fe sulphatized roast-calcine after removing from it copper and zinc (by acid leaching) and lead (by the method of sodium chloride leaching) [1]. Due to these processes gold and silver grains become in a free condition without any ties with chalcopyrite, sphalerite and galena [2, 3].

To recover gold and silver from this residuum, the cyanide leaching with the followed electrowinning can be used as a preferable method [4]. Cyanide (NaCN, KCN or $Ca(CN)_2$) is more acceptable complexant among a limited number of ligands which form complexes of sufficient stability in aqueous solutions. It is universally used in gold extraction processes because of its relatively low cost and great effectiveness for gold dissolution. On the other hand, despite some concerns over the toxicity of cyanide, it can be applied with a little risk to health and environment. The oxidant most commonly used in cyanide leaching is oxygen, supplied from air, which contributes to the attractiveness of the process. In relevance to electrowinning, it is usually used for treatment of high-grade gold solutions, however there is some potential for its application to dilute leach solutions, i. e. without solution concentration by carbon adsorption and elution.

The analysis of gold and silver in liquid phases after each test was carried out by using an Atomic Adsorption Spectroscopy (AAS) method (on AA240FS analyzer). Leach residues at the end of each stage were also analyzed for gold and silver to establish mass balance and determine both precision metals recovery rates. For this aim an Emission Spectral analysis is used on a DFC-13 spectrograph (Russia) at the “Spectroscopic” laboratory of Institute of Geological Sciences NAN RA.

Ionic concentration of free CN^- in cyanide solutions was determined by titration with silver nitrate using rhodamine as an indicator.

Cyanide leaching experiments (with leach samples of 125 *g*) were carried out in Central Laboratory of Kapan Processing Plant which is the unique producer of Cu/Zn/Pb/Fe - sulphide concentrates with very high content of gold and silver. Leaching tests (24 h) with

constantly missing slurry (S:L=1:8) were performed in a glass reactor of 1 liter capacity equipped with a pitched blade turbine impeller rotating at 600 rotary/min (Fig. 1). Sodium cyanide salt (NaCN) concentration was maintained at 0.4; 0.5 or 0.6 *g/l* over the leaching period and the consumption of cyanide was recorded. The solution temperature was controlled by a mercury thermometer.

Metal recovery tests were carried out in a model packet-bed electrowinning cell with two perforated stainless steel plate anodes and a steel wool cathode basket of 16 *mm* thick (Fig. 2). The cell operated with solution and current having parallel flow directions. The useful contact area of the cathode is approximately 10 cm^2. The pregnant solution is continuously circulated from a storage tank through the electrowinning cell and back into the storage tank. The flow rate was controlled by a tap placing on the exit tube of the cell, and the electrolyte temperature was controlled by a mercury contact thermometer.

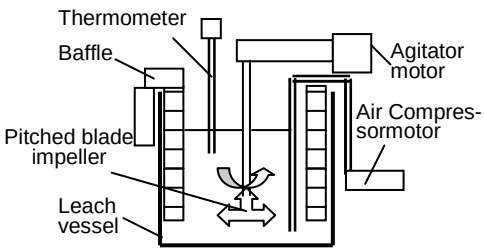

Fig. 1. An experimental set-up for cyanide leaching of the oxide residuum

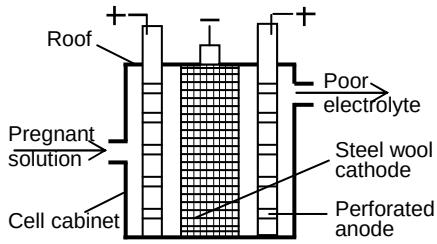

Fig. 2. A model packet-bed electrowinning cell (schematic)

Fig. 3 shows the effect of cyanide concentration on gold dissolution from the tested residuum over the leach time. It is seen that increasing the concentration of cyanide salt promotes the gold dissolution. The highest gold dissolution was obtained with 0.6 *g/l* sodium cyanide salt concentration. It is relevant to note that in these conditions over an initial leaching period of 6.5 *hours* approximately 97 *%* of gold was dissolved and while over the following 17.5 *hours* the extraction of gold is negligible.

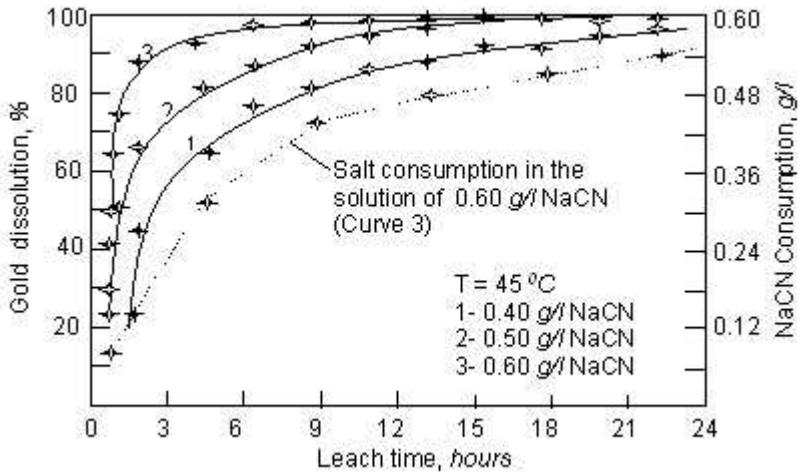

Fig. 3. The effect of cyanide concentration on gold dissolution (curves 1-3) and cyanide consumption over the leach time

High gold recoveries suggested the presence of very negligible quantities of encapsulated gold particles which did not come into contact with cyanide solution. This fact is due to previously sulphatizing roasting of raw material (polymetallic concentrate) which completely converses the sulphide minerals into porous water-soluble sulphates (thus exposes the locked-up gold in these minerals). Therefore after base metals recovery from corresponding roast calcine, gold and silver in process residue are actually present predominantly in free conditions.

It should be noticed that the cyanide salt (NaCN) consumption and the leach time are spend mainly to dissolve gold and silver because the base metal contents are very small. Consequently the cyanide concentration depends on its quantities in oxide residuum. On the other hand, spare cyanide quantities are not quite disturbed, since the leach liquor can be recycled after gold and silver are recovered from it by electrowinning. Practically 0.55…0.58 *g/l* of NaCN is enough to leach 74.2 *mg/kg* Au and 1034.2 *mg/kg* Ag from the tested oxide concentrate for about 22 *hours*.

The analytical results of liquid and solid products obtained from cyanide leaching of the tested residuum in comparison with primary concentrations of gold and silver as well as other components are represented in Table.

Table

AAS analysis of the liquid product and mineralogical analysis of solid residual obtained from cyanide leaching of oxide residuum in comparison with its primary composition

Primary oxide residuum	Main mineralogical composition, *%:* Fe_2O_3 – 47.9, SiO_2 –20.7, Al_2O_3 – 10.9, (CaO+MgO) – 15.0, $Fe(OH)_3$ – 5.5, $CuFeS_2$ – 0.03, ZnS – 0.02, PbS – 0.05, $PbSO_4$ – 0.01, Au – 74.2 *mg/kg*, Ag – 1034.2 *mg/kg*
Liquid product (cyanide leaching solution)	Main ionic concentration, *mg/l* (in 1,0 *liter* filtered cyanide leach solution): Cu^{2+} - 11.2, Zn^{2+} - 12.0, Pb^{2+} - 12.1, Fe^{2+} - 10.1, Fe^{3+} - not, Cd^{2+} - not, Bi^{2+}- not, Sb^{2+} - not, As^{2+} - not, Au^{+} - 9.1, Ag^{+} - 124.9, CN^{-} - 25.0
Solid residual (tailings)	Main mineralogical composition (after Au and Ag recovered), *%:* Fe_2O_3 – 47.7, SiO_2 –20.55, Al_2O_3 - 10.73, (CaO+MgO) – 15.02, $Fe(OH)_3$ – 5.6, $CuFeS_2$ – 0.01, ZnS – 0.01, PbS – 0.02, $PbSO_4$ – not, Au – 0.17 *mg/kg*, Ag – 4.3 *mg/kg*

From the results of this experimental series it is seen that gold and silver containing in this oxide product are quite leachable in dilute sodium cyanide solutions. This applies more accurately of course to its direct interactions with free cyanide-ions (CN^-) by the following reaction equations [4], proceeding in parallel:

$$2Au + 4CN^- + O_2 + 2H_2O = 2Au(CN)_2^- + H_2O_2 + 2OH^-, \quad (1)$$

$$2Au + 4CN^- + H_2O_2 = 2Au(CN)_2^- + H_2O_2 + 2OH^- \quad (2)$$

and

$$2Ag + 4CN^- + O_2 + 2H_2O = 2Ag(CN)_2^- + H_2O_2 + 2OH^-, \quad (3)$$

$$2Ag + 4CN^- + H_2O_2 = 2Ag(CN)_2^- + H_2O_2 + 2OH^-, \quad (4)$$

the result of cyanide-complexes in leach liquor is in complete conformity with well known E_h-pH equilibrium diagram for the system Au-H_2O-CN.

Cyanide concentration is relatively easy to control by the addition of concentrated cyanide solution, or a solid cyanide salt. The control of the oxidant concentration (i.e. dissolved oxygen) is not so easy because of the low solubility of oxygen in water under atmospheric conditions. Consequently the maximum rate of gold dissolution for processes that use air to provide oxygen in solution is determined by the conditions of temperature and pressure under which the process operates.

At sea level and at 25 $^{\circ}C$ the saturated concentration of dissolved oxygen in solution is 8.2 *mg/l* [5]. This value decreases with increasing altitude and increasing temperature. The corresponding cyanide concentration that gives maximum dissolution rate of gold at this oxygen concentration is approximately 0.005 %. Of course, for industry cases pure oxygen, oxygen enriched air, hydrogen peroxide or another oxygen source can be used in place of air to supply oxygen to the solution.

The full absence of Si, Ca and Mg in leach liquor means that its oxides are absolutely non-soluble in NaCN solution, and they completely remain in solid phase.

As to solution temperature, it is well known that the gold dissolution rate increases with temperature, as a result of increased activities and diffusion rates of reacting species, up to maximum at approximately 85 $^{\circ}C$. Above this temperature the decrease in oxygen

solubility outweighs the benefits of increased ionic activity and diffusion rates. Therefore, taking into account the experimental results [6] and experience of Ararat Gold Recovery Company during last years, optimum leaching temperature for this case was established as 45 $^{\circ}C$.

The influence of gold and silver concentration, solution flow rate and temperature on the recovery efficiency of these metals, as well as the current efficiency of electrowinning process is examined. The tests were performed with summary gold and silver content of: 26.8; 53.6; 80.4; 107.2 or 134.0 *mg/l*, and at flow rate of: 10; 20; 30; 40 or 50 $ml/min.cm^2$. The solution temperature was chosen: 30, 60 or 90 $^{\circ}C$. The cell current was 2.4 - 2.5 *A*. In all cases essential solution pH was kept at the level of 12.5…13.0 which was not changed during the electrolysis.

The metal recovery coefficient K_{rec} for the 1st passage of the solution through the electrowinning cell, and the current efficiency E_{curr} for each experiment were determined by the equations:

$$K_{rec} = (1 - M_{rem} / M_{in}).100\ \%. \quad (5)$$

The current efficiency for each experiment was determined by the equation

$$E_{curr} = (M_{in} - M_{rem})/M_t\ .100\ \%, \quad (6)$$

where M_{rem} is the summary quantity of gold and silver in the reservoir at the end of the 1_{st} passage, M_{in} is the initially gold and silver content, $M_t = m(0.2Au + 0.8Ag)$ is the summary molecular mass of Au and Ag for the case of Au : Ag = 1 : 4 in the solution which can be reduced on the cathode under the current I (*A*) in a time t (*s*); m is the amount of these molecules excused by the Faraday law: m = it / nF (n = 1 is the quantities of the electrons taking part in reaction, F = 96500); A_{Au} = 196.96 and A_{Ag} = 107.86 are the atomic masses of gold and silver, correspondingly.

The experimental results are presented in Figs 4, 5 and 6. These images show that the changes of gold and silver summary concentration in limits from 26.8 to 134 *mg/l* in solution has linear increasing influence on the metal recovery coefficient at its 1st passage through the cell (Fig. 4). The solution with (Au + Ag) concentrations lower than 10 *mg/l* is treated with very small efficiency, which is connected with decreasing of equilibrium potentials of $Au(CN)_2^- \rightarrow Au$ and $Ag(CN)_2^- \rightarrow Ag$ couples at low concentrations of cyanide complexes [7].

The recovery coefficient increases with increasing the solution temperature. This is explained first by increasing diffusion coefficient of the cyanide complexes, and second increasing the electrolyte conductivity. Besides the oxygen solubility decreases due to which decreases the amount of oxygen molecules striving to the cathode. The excessive temperatures are also not lucky with the environment requirements. The optimum solution temperature chooses is 90 $^{\circ}C$.

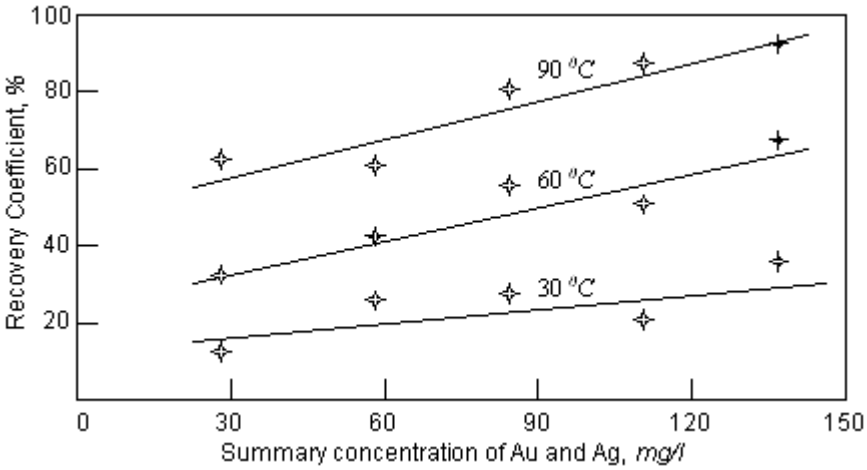

Fig. 4. Influence of gold and silver summary concentration on the recovery coefficient of metals from the solution at the 1st passage through the model electrowinning cell in different temperatures

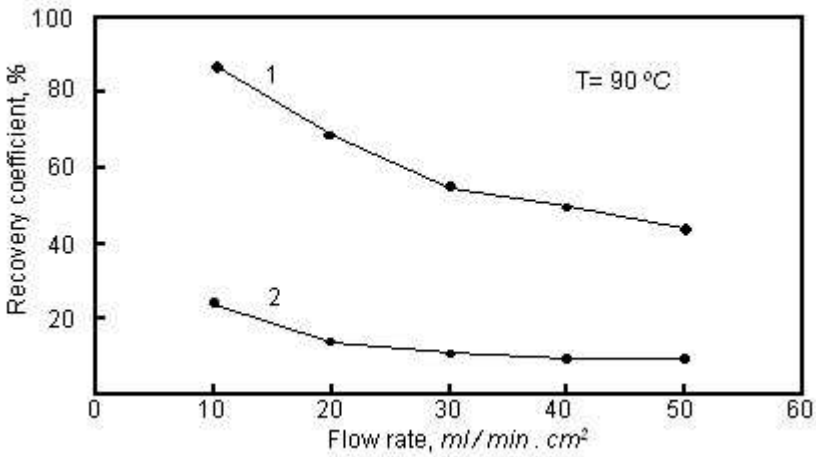

Fig. 5. Influence of solution flow rate on the metal recovery coefficient at the 1st passage through the model electrowinning cell with summary Au and Ag concentrations: 1 – 26.8 *mg/l*; 2 – 134 *mg/l*

From the graphics on Fig. 5 it is seen that increasing the flow rate of the solution through the cell leads to decreasing the metal recovery coefficient especially with high concentration of gold and silver.

However, from the point of view of electrolysis capability this does not mean that the process will be carried out at low flow rates. Therefore, as optimum solution flow rate it should be 30 *ml/min.cm*^{2} at which metal recovery coefficient curves begin to be linear, and which is well agreed with the data of international practice. This may be recommended for the industry electrowinning cells.

In order to establish the optimum cell current (or current density), the experimental dependencies of current efficiency – cell current and metal recovery coefficient – cell current (Fig. 6) were joined. As it is seen, the current efficiency (E_{curr}) of the cell decreases with increase of cathode current (up to 2 *%* at 5 *A*), while the metal recovery coefficient (K_{recov}) increases to a maximum. The optimum operating current is, therefore, the value at which both of dependencies are in the same position. It equals approximately to 4 *A* which corresponds to the current density of 40 *A/m*^{2}. At such current approximately 16.5 *%* of current efficiency which is higher than average industry indicator (5 *%* is typical for many gold recovery plants [8]).

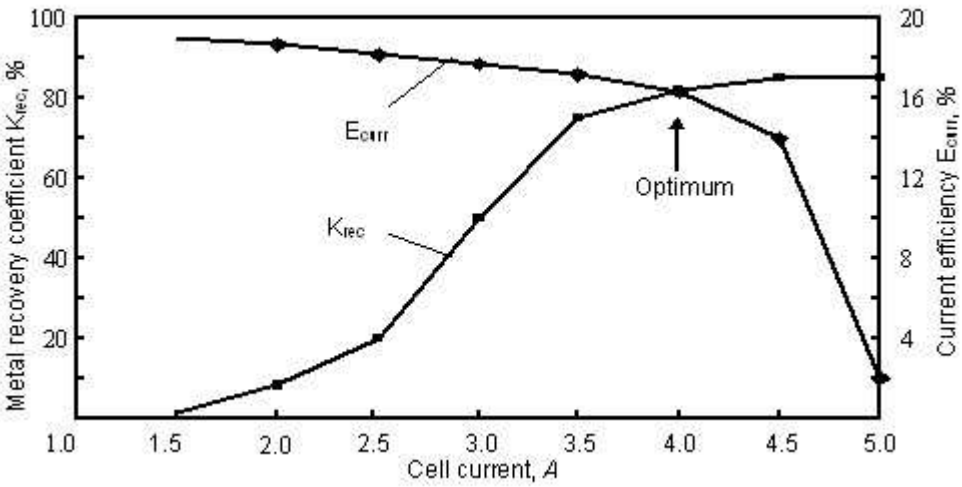

Fig. 6. The effect of increasing cell current on the current efficiency and metal recovery coefficient of the tested model electrowinning cell

So, by the time of experiments the optimum regimes can be chosen for the:

- oxide residuum cyanide leaching – solution temperature 45 ^0C, sodium cyanide salt consumption 0.55…0.58 *g/t*, leach time 22…24 *hours*, air innings;
- electrowinning - electrolyte temperature 90 ^0C, flow rate 30 *ml/min.cm*^{2}, current density 40 *A/m*^{2}.

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SEUA. The material is received on 17.02.2010.

ՄՈԱՏԱՍԵՄ Մ.Խ.

ԲԱԶՄԱՄԵՏԱՂԱՅԻՆ ՀԱՆՔԱՆՅՈՒԹԻ ՎԵՐԱՄՇԱԿՄԱՆ ՍՈՐԱԽՅՈՒԿԻ ՑԻԱՆԻԴԱՅԻՆ ՏԱՐՐԱԼՈՒԾՈՒՄԸ ԵՎ ԱԶՆԻՎ ՄԵՏԱՂՆԵՐԻ ԿՈՐԶՈՒՄԸ ԼՈՒԾՈՒՅԹԻՑ

Հետազոտվել են Cu/Zn/Pb/Fe սուլֆատացված բովվածքի հիդրոմետալուրգիական վերամշակմամբ պղնձի, ցինկի ու կապարի հեռացումից հետո մնացած ոսկետար սորախցուկի ցիանիդային տարրալուծման և ստացված լուծույթից ոսկու և արծաթի էլեկտրակորզման օրինաչափությունները: Հաստատագրվել են այդ գործընթացների լավարկային տեխնոլոգիական ռեժիմները:

Առանցքային բառեր. սորախցուկ, ցիանիդային տարրալուծում, նատրիումի ցիանիդ, պոտենցիալ, անոդային և կաթոդային ռեակցիաներ, էլեկտրակորզում, հոսանքի խտություն, հոսանքի արդյունավետություն:

MOATACEM M.X.

ЦИАНИДНОЕ ВЫЩЕЛАЧИВАНИЕ КЕКА ПЕРЕРАБОТКИ ПОЛИМЕТАЛЛИЧЕСКОЙ РУДЫ И ИЗВЛЕЧЕНИЕ БЛАГОРОДНЫХ МЕТАЛЛОВ ИЗ РАСТВОРА

Исследованы закономерности цианидного выщелачивания золотоносного кека, оставшегося после удаления меди, цинка и свинца, из сульфатизированного Cu/Zn/Pb/Fe огарка при его гидрометаллургической переработке и электроизвлечении из полученного раствора золота и серебра. Установлены оптимальные технологические режимы этих процессов.

Ключевые слова: кек, цианидное выщелачивание, цианид натрия, потенциал, анодные и катодные реакции, электроизвлечение, плотность тока, эффективность по току.