

OXIDATION AND PASSIVATION OF SULFIDE ORES IN GOLD AND MOLYBDENUM HYDROMETALLURGY

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Abstract

The ore raw materials of Au, Mo producing industry are predominantly sulphide. Technologies for their processing include the oxidation stage, for which chlorine, oxygen, ozone, nitric acid, Mn(IV), Fe(III), NaClO are used. The nature of the oxidant and ligand of metal ions determines the kinetics of dissolution of minerals. Gravimetric, redox-measurements with gold-bearing ore and concentrate of the Kokpatas field and dissolution electrokinetics using a rotating disk electrode, with chalcopryrite-mineral of Cu-Mo ores of Almalyk field are conducted. Dissolution of sulfide mineral under the redox potential or its equal anodic polarization is represented by steps: - dissolution of the outer layer of the mineral; - diffusion of Cu(II), Fe(III) ions out its volume, - enrichment of the interphase boundary with sulfur (passivation). Electrokinetics measurements with chalcopryrite revealed a similarity of the processes of its reagent and anodic dissolutions in an acid medium: both were accompanied by passivation of the surface. For chalcopryrite the diffusion coefficient of Fe (III), Cu (II) ions in its solid state was calculated.

Keywords: Sulphide ores, chalcopryrite mineral, electrokinetics

1. INTRODUCTION

Uzbekistan is one of the world's largest producers of gold, copper, molybdenum, supplying to the market also zinc, cadmium, rhenium, uranium. Crude ores of mining industry are predominantly of sulfide nature, such as copper-molybdenum raw materials of JSC "Almalyk MMC" and persistent gold-containing ores of JSC "Navoiy MMC". Their processing technologies include a step of ores' oxidation, either by means of firing Cu-concentrate in a reverberatory furnace, or roasting Mo-concentrate, bio-oxidation of gold ores. In hydrometallurgical technologies for these types of raw materials, the leaching kinetics depends on the nature of the metal ion and its ligand. Except for bio-oxidation, most sulfide ore's opening takes place in a chloride, bromide [1], iodide, fluoride [2], thiourea, thiosulfate [3] media provided with oxidizing agents: chlorine [4, 5], oxygen [6], nitric acid and oxygen [7-9], Mn(IV), Fe(III), hypochlorite [10, 11]. In a series of oxidants ozone is noted to oxidize chalcopryrite CuFeS₂ and pyrite FeS in solution: H₂SO₄ 30-50 g/l; ozone 100 mg/l with solid:liquid (S:L) ratio 1:(3÷75), temperature 45 °C, time (t) up to 3 h at Alaverdi plant of "Armenian Copper Programme Co", despite the high power consumption of its generation (14 kWh / kg O₃) [12].

Goal of the research: basing on oxidizers: hypochlorite and (ozone / oxygen + HNO₃) mixture, to consider the kinetics of refractory gold-containing ores opening. Their percolation leaching is cost-effective for ores Au-concentrates, but not for low-grade ores. The reason seems to be in the little-studied passivation phenomena of the metal sulfide's surface, which can only be overcome by an autoclave method. It was of interest to assess the chrono-redox and kinetics of ore's leaching by a behavior of the Au-concentrate from Kokpatas mineral deposit (Uzbekistan) and pure artificial chalcopryrite in the oxidizing system.

2. OXIDATION AND PASSIVATION OF SULFIDE ORES

2.1. Methodological bases

Samples of Au-containing ore and concentrate (Au 17 g/t) from Kokpatas deposit shredded to grinding class 0.074 mm, with pyrite and arsenopyrite in its composition (90-97% of total sulphide content), synthetic

chalcopyrite [13, 14], were the object of study. Oxidizing media redox-potential was controlled with potentiometer EV-74, Pt measuring electrode, saturated silver chloride electrode (s.c.e.) as a reference electrode in a 125 ml cell, where the ore samples were placed and a stopwatch was switched on. The mineral-aqua suspension was stirring for a time controlled on a magnetic stirrer (**Figure 1**).



Figure 1 Ozone generator with redox-potential control system in ores samples oxidizing media



Figure 2 0.15 dm³ sealed vessels with Teflon inserts without pressure control



Figure 3 Laboratory autoclave with oxygen supply to the chamber and pressure up to 1.5 MPa

Solution's analyses on Cu, Fe were fulfilled on atomic absorptive spectrometer "Perkin-Elmer" RE 30300 [15], Au and Ag - on Aligent 7500 ICP MS; electrokinetic measurements - on a PI-50-1 potentiostat, with a rotating disk electrode (RDE) (\varnothing 5 mm), from synthetic chalcopyrite CuFeS_2 in Teflon, angular velocity (ω) 0-200 rpm [16-17]. Autoclaves at a temperature of 25-180 °C were applied for sulfid ore oxidizing of both types: 1) 0.15 dm³ sealed vessels with Teflon inserts without pressure control (**Figure 2**), 2) 0.5 dm³ - with forced oxygen supply to the chamber and pressure up to 1.5 MPa (**Figure 3**). Samples mass was always 12 g.; S:L ratio changed from 1: 5 to 1:75. Leaching solutions composition, %: No.1 - NaClO 17.0; H₂SO₄ 1.25 (120°C, 0.5-5 h); No.2 - HNO₃ 10, H₂SO₄ 1.25 (30-105 °C, 0.5-5 h), No.3 - H₂SO₄ 5.0; thiourea 5.0; bubbling O₂ (25 °C, 5 h); No.4 - H₂SO₄ 5.0; thiourea 5.0; oxidizer O₂, at a pressure range 0.1-1.5 MPa (110 °C, 5 h).

2.2. Experimental part

Extraction of gold and silver from Kokpatas ore concentrate containing, g/t: Au 14.6; Ag 14.8 is illustrated in **Table 1**.

Table 1 Recovery of Au and Ag from Kokpatas ore concentrate

Oxidation and leaching in solutions No. 1-4	Recovery, %	
	Au	Ag
Oxidation (No. 1)	0.34-0.13	64.2
Oxidation (No. 1), leaching (No. 3)	14.1	62.3
Oxidation (No. 2)	0.35-0.27	6.3-14.5
Oxidation (No. 2), leaching No. 3)	7.05	10.1-14.5
Autoclave oxidation (No. 4)	91.3±8.4	85.2±7.4

From **Table 1** it follows that the recovery of Ag from systems No. 1-3 is higher than that of Au, which is explained by its localization in the crystal lattice of sulphides in the form of Au⁰, Au⁺¹, Au⁺³, according to NGR (Messbauer) spectroscopy [18]. In addition, hypochlorite, other things being equal, is more effective than nitric acid. Contribution to the drop in Au recovery, in time, from 0.5 to 5 h, in solutions Nos. 1-3 is sulfides' passivation. Their depassivation in an autoclave is effective especially after the oxidation of sulfur by oxygen to the anion SO₄²⁻. However, this requires a temperature above 150-200 °C and an O₂ pressure over 2.0-2.5 MPa. In addition, the temperature rise above 119 °C (the melting point of sulfur) is impractical, since liquid sulfur blocks the surface of Au-concentrate particles, which reduces the Au recovery. It follows also from **Table 1**, that the recovery of Au from system No. 4 is higher than Ag, due to the destruction of sulfide crystal structures.

Gravimetric and redox measurements with Kokpatas ore in solution No. 2 - HNO₃ 5-55, H₂SO₄ 1.25; with bubbling with a mixture of O₃/O₂ (**Table 2**).

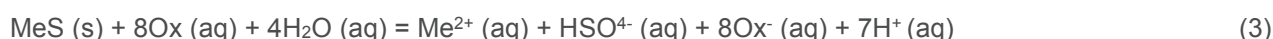
Table 2 Opening degree of ore (η, %), 20 min, 24 °C, S : L = 1:75

No.	Solution, composition, %	Mass (g)		Redox potential (s.c.e.) (mV)	η, %, relative to the control
		initial	final		
2.1	5% H ₂ SO ₄ + 5% HNO ₃ + ore + O ₃ /O ₂	1.04	0.739	+ 840	87.75
2.2	5% H ₂ SO ₄ + 15% HNO ₃ + ore + O ₃ /O ₂	1.03	0.718	+ 930	90.96
2.3	5% H ₂ SO ₄ + 25% HNO ₃ + ore + O ₃ /O ₂	1.04	0.702	+ 960	98.54
2.4	5% H ₂ SO ₄ + 35% HNO ₃ + ore + O ₃ /O ₂	1.05	0.718	+ 985	96.79
2.5	5% H ₂ SO ₄ + 45% HNO ₃ + ore + O ₃ /O ₂	1.04	0.716	+ 1000	94.46
2.6	5% H ₂ SO ₄ + 55% HNO ₃ + ore + O ₃ /O ₂	1.03	0.724	+ 1030	89.21
5	Control (1 h in a conc. HNO ₃ + O ₃ /O ₂)	1.03	0.687	-	-

The degree of opening of ore samples (η) No. 2.1-2.6 in this medium, with a step-by-step transition from 5 to 55% HNO₃, first increases from 87.7% to 98.5%, at the maximum (in 25% HNO₃), then decreases to 89% (55% HNO₃). The form of the dependence η - [HNO₃] is an inverted parabola. The surface of sulphide ore, with the buildup of redox-potential, is passivated.

The reason for its passivation is the formation of a film of elemental sulfur on a surface in a system with redox potential: + 960 mV.

The analysis of φ-pH (Pourbaix diagrams) in the behavior of sulphides of the 2-valent metal suggests dissolution reactions in acids: non-oxidizing (1) and oxidizing (2, 3); (s) = solid, (aq) = aqua; (for example, for Fe (II)) (**Figure 4**) [19]:



It follows from the Pourbaix diagrams that reaction (1) often is not realizable. On the other hand, it happens that it is thermodynamically favorable, but the kinetics of oxidation (dissolution) is slowed due to passivation of the surface (**Table 1**). For chalcopyrite, for example, passivators are proposed as follows: elemental sulfur, polysulphides, jarosites and jarosite-like compounds.

The kinetics of dissolution of chalcopyrite by the RDE method, which ensures equal surface availability during diffusion of discharged particles, and the possibility of calculating the particle flux to the interaction zone, is

studied (**Figures 4-6**). This method is convenient in that it allows maintaining the anodic polarization of chalcopyrite at potentials φ equal to the values of redox potential shown in **Table 2**, without introducing an oxidizing reagent into the solution. The mixed potential of the electrode, in the absence of an oxidizer in the H₂SO₄ solution, is not in equilibrium. The anodic polarization of chalcopyrite was maintained in the range $\varphi = + (750 \div 950)$ mV.

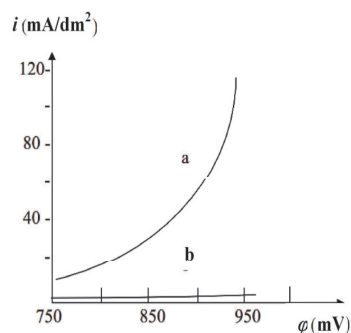


Figure 4 Dependence of i_a - φ , at 20 °C, in 5% H₂SO₄, the time of the onset of polarization is 5 sec (a) and 55 sec (b).

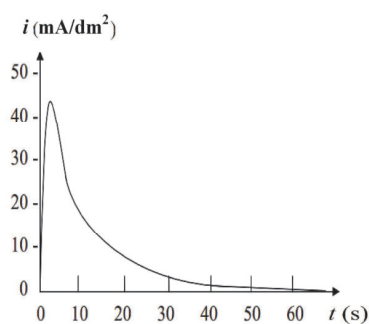


Figure 5 Dependence of i_a on the polarization time, $\varphi = +850$ mV, 20 °C, in a solution of 5% H₂SO₄.

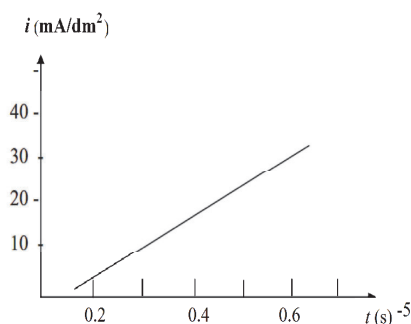


Figure 6 Dependence of i_a on the root of the square angular velocity of rotation of the RDE, $\varphi = +850$ mV

2.3. Result and its discussion

In **Figure 4** the dependence of the anode current density i_a of the anode oxidation of chalcopyrite on the potential φ , in its indicated range, at 20 °C, in 5% H₂SO₄, is offered. It can be seen that if the time from the moment the polarizing voltage is applied to the electrode is small (5 sec), then i_a increases, reaching a value of 120 mA/dm² (curve a). And if this time reaches 55 seconds, then i_a is small: not exceeding 3 mA/dm² (b).

The shape of the $i_a(t)$ curves can be of two types [14-16]: 1st, $i_a = \text{const}$: the rate is limited by the stage of electron transfer: the second - the decrease of i_a in the potentiostatic regime in time, which means diffusion control. For chalcopyrite, the current decay (**Figure 5**) at $\varphi = +850$ mV, characteristic for oxidative leaching (compare with the range from +840 to +930 mV at **Table 2**), indicates a diffusion control of the velocity. But the value of i_a was not affected by the rate of agitation of the solution, which rejects diffusion in the aqueous phase as the limiting stage of the oxidation reaction. For a process with diffusion control on a flat surface, the function $i_a(t)$ is described by the equation (4) [16]:

$$i_a(t) = \frac{n F D^{0.5} C_b}{\pi^{0.5} t^{0.5}} \quad (4)$$

in which $i_a(t)$ is the current density in time; n is the number of electrons transferred in the course of particle diffusion; D is the coefficient of their diffusion at the limiting velocity; C_b is the volume concentration of diffusing particles; F is the Faraday constant; t is time.

In **Figure 6** the dissolution current density of chalcopyrite as a function of $t^{-0.5}$: at a constant potential, looks like linear, which means diffusion control (in a solid body) of the reaction. The diffusion coefficients of metal ions in the solid phase: from the depth to the interface, through the sulfur crystal sublattice are calculated from the tangent of the slope of the graph. The diffusion coefficient (D_{Me}) of metal particles lies in the range: 10⁻¹⁵-10⁻¹⁴ cm²/s.

It is a combination of the diffusion coefficients for Cu²⁺ and Fe²⁺ (5):

$$D_{Me} = \left(D_{Cu}^{0.5} + D_{Fe}^{0.5} \right)^2 \quad (5)$$

where: D_{Me} is the diffusion coefficient of metal particles from chalcopyrite to a solution determined by (1); D_{Cu} and D_{Fe} are the diffusion coefficients of Cu and Fe in $CuFeS_2$.

It is assumed that the metal is "washed out" from the outer layers of the mineral. The diffusion control of the process speed is confirmed by the constancy of the function $i_a(t)$ in time (for $t > 30$ sec) with a chrono-potential of $\varphi = +850$ mV (**Figure 2**), which indicates a decrease in the diffusion coefficient of Cu and Fe due to the compaction of external layers of the mineral or with the formation of the phase of sulfur. At smaller excavations of polarization ($t < 30$ s), $i_a(t)$ rises with increasing φ . **Figure 1** (b) shows the dependence of $i_a(t)$ at an exposure of 55 sec in the range of potentials $\varphi = +(750 \div 950)$ mV. It can be seen that $i_a(t)$ depends little on φ , which is connected with the diffusion control of the reaction of oxidative dissolution in the solid phase and the high concentration of metal in it.

3. CONCLUSION

The process of dissolution of sulphide minerals is presented in the following sequence: - dissolution of the outer layer of the mineral - shortly high densities of the anodic dissolution current; - diffusion of Cu, Fe ions from the volume of the mineral, with their surface depletion; - enrichment of the mineral interface with sulfur, leading to a drop in the diffusion coefficients of metals; - formation of a diffuse layer deep into the surface of the mineral with its enrichment with sulfur (passivation). The observed "parabolic" leaching of the Kokpatas ore confirms this phenomenon. Electrokinetics measurements using chalcopyrite RDE were used to study the similarity of chemical leaching processes (in oxidizing medium) and anodic passivation in an acid medium.

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