

## Technology for increasing the precious metals content in copper concentrate obtained by flotation

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**Abstract:** In the established technologies, the use of classic depressants of pyrite, such as lime represents one of the main problems in the flotation of gold-bearing copper (Cu) ores. Lime addition leads to the depression of the noble metals - gold (Au) and silver (Ag) that end up in tailings. Thus, the operator incurs economic losses. The current paper presents research aimed at replacing in flotation of copper pyrite ore, bearing gold and silver, the classical depressor lime with catholyte, i. e. with solution obtained during the electrolysis of water (pure or aqueous solutions) using a diaphragm electrolyser. Data from the conducted research show an increase in the content of precious metals in the obtained copper concentrate - from 148.04 g/Mg Au and 112.8 g/Mg Ag achieved by classical process to 216.45 g/Mg Au and 174.03 g/Mg Ag obtained by the proposed treatment. At the same time the Cu recovery increased by 3 % and the grade of Cu concentrate was 27.5 % Cu (compared to 16.2 % in the classical process). It seems that the main parameter influencing the selection separation process is the catholyte pH value.

**Keywords:** gold-bearing copper concentrate, electrochemically aided flotation, catholyte

### 1. Introduction

Gold existence in commercially viable copper mineralization is a common event. Often it is uneconomic to mine the ore for its gold content, but that metal provides a considerable opportunity value for the mine operators of other ores (Sceresini, 2005). It is not feasible gold to be extracted by cyanidation when the copper mineralization contains bornite, enargite, tetrahedrite, chalcocite, azurite, malachite and other Cu hydroxides and/or sulfides (Medina and Anderson, 2020). Actually, in the case of Au-bearing copper-pyrite (Cu - Py) ores, the main target is producing of high grade copper concentrate, which means effective separation of copper and pyrite by Py depression and Cu flotation. In order to recover copper minerals (chalcopyrite, bornite, etc.), the pH of the flotation pulp has to be higher than 7 (Azizi et al., 2020) since in this way the pyrite depression is ensured. Addition of cyanide, sulphite, and increasing the pulp pH value are used to minimise pyrite flotation (Boulton et al., 2001; Mu et al., 2016a). However, these depression strategies show some disadvantages, for example environmental concerns. Pyrite depression by biopolymers is also achieved (Mu et al., 2016b), however the behaviour of gold present in the ores has not been studied in this case.

The pyrite depression under alkaline conditions is assigned to the competitive adsorption of hydroxyl (OH<sup>-</sup>) ions and the xanthate-based collector. There are critical pH values for sulfide minerals, below which xanthate ion can be adsorbed, while above that pH value xanthate adsorption is inhibited due to the competitive adsorption of OH<sup>-</sup>. It is found that the critical pH values for pyrite and chalcopyrite in the solution containing 25 mg/dm<sup>3</sup> potassium ethyl xanthate at room temperature are 10.5 and 11.8, correspondingly. Consequently, a selective flotation of chalcopyrite could be attained when the pulp pH value is adjusted to be between 10.5 and 11.8 (Park et al., 2020). In addition two other factors contribute to pyrite depression under alkaline conditions: (a) thermodynamic instability of the dixanthogen (adsorbed form of xanthate-based collector on pyrite surface) and (b) covering the pyrite surface with ferric hydroxide species (Fe(OH)<sub>3</sub>, FeO(OH)) that are hydrophilic (Mu et al., 2016a). It is

suggested that when lime is used to raise the pulp pH value,  $\text{CaSO}_4$  (that is relatively low soluble) is formed on the pyrite surface and this prevents collector adsorption (Bulatovic, 2007).

It is accepted that lime addition used to increase the pulp pH depresses the free gold flotation (Ahmad, 1951; Mbayo, 2020). The extraction of gold in the copper concentrate is hindered and Au is lost by passing to pyrite tailing. Glembotskii and Klassen (1981) stated that the pH value at which Au is depressed depends on the alkalizing reagent used. They have given values of pH 9.5, 10.8 and 11.8 when lime ( $\text{CaO}$ ), soda ( $\text{Na}_2\text{CO}_3$ ) and caustic soda ( $\text{NaOH}$ ) were used.

Chanturiya (2008) proposed an extraction in the froth of the pyrite with increased content of gold. Slightly acidic medium ( $\text{pH} = 5.4$ ) and low concentration of xanthate ( $6 \times 10^{-3} \text{ g/dm}^3$ ) have to be used. Agorhom and co-authors (2015) proposed rougher flotation of the tailings from Cu-Py flotation to produce rougher Py concentrate that was used further to recover gold. This concentrate was reground and subjected to Au flotation where pyrite was depressed by using aeration and diethylenetriamine (DETA). The obtained Au concentrate was mixed with Cu rougher concentrate to improve Cu and Au grades of the produced Cu concentrate bearing Au. Thus, Au recovery was maximized, without detrimental effects on copper flotation.

However, it would be practical to find a way for direct Cu-Py flotation separation where Cu concentrate contains the major part of Au that present in the raw material. Such an approach is described in this paper. The basis of the proposed solution is the use of catholyte, obtained by water electrolysis, as alkalizing reagent in the ore milling and flotation, and imposing of an electrochemical impact (direct current) during the pulp conditioning and rougher flotation.

## 2. Materials and methods

### 2.1. Material

Copper-pyrite ore with a copper content of 1.49%, gold - 3.98 g/Mg, and silver - 44.5 g/Mg is used. The main Cu bearing minerals (as determined by Bruker D8 Advance powder diffractometer with Cu K radiation and a LynxEye detector) were chalcopyrite (containing approximately 36 % of all Cu), tennantite, enargite, tetrahedrite, luzonite and bornite. The ore is milled at 60% solids, in a ball mill where the liquid phase was catholyte, until 80% of the material was  $-0.08 \text{ mm}$  in size.

### 2.2. Method

The diaphragm electrolyser, used to obtain catholyte and anolyte, is a rectangular vessel with dimensions of  $40 \times 30 \times 25 \text{ cm}$ , made of chemically resistant plastic. Its anode and cathode compartments are separated by a conventional diaphragm used in diaphragm electrolyzers for chlorine-alkali electrolysis. The anode is made of titanium, the cathode is made of stainless steel (Panayotov and Panayotova, 2017). The electrolyser worked with tap water, with a small amount of a salt added to increase conductivity, at a current density of  $30 \text{ mA/cm}^2$  (preliminary determined as optimal) to obtain catholyte with (a)  $\text{pH} = 10$  and (b)  $\text{pH}$  approximately to 11.

The ground material (450 g) was placed in a laboratory flotation cell "Denver" (with a volume of  $2 \text{ dm}^3$ ) at solid to liquid ratio = 1 : 3. The liquid medium was the catholyte. The pulp was subjected for 10 min to an electrochemical influence (direct current in the range of 5 - 25  $\text{mA/cm}^2$ ) by introducing 2 electrodes straight in the pulp. Then reagents were added and the pulp was conditioned for 2 min while continuing the direct current application on the pulp. The reagents used were respectively: collector - mixture of isoamyl xanthogenate (widely used in sulfide ores flotation, as well as in the flotation of Au (Liu et al., 2022)) and Aerophine 3418A (found as an effective reagent in Au and Ag recovery (Agacayak, et al., 2021)) in a ratio of 7 : 1 at a consumption of 60 g/Mg, frother - pine oil at a consumption of 60 g/Mg. A certain amount of hydrated lime was added to the second produced catholyte in order to reach  $\text{pH} 11$  (about 1/10 of the classically used in the case when the pulp  $\text{pH} 11$  was achieved only by lime addition). Further, rougher flotation was carried out for 5 min (determined as optimal in preliminary experiments), while the current imposing ( $10 \text{ mA/cm}^2$ ) continued. Electrodes used to impose an electrochemical impact during the conditioning and flotation were made of high silicon cast iron with the same area of anode and cathode. They were installed on both sides of the classic flotation cell in order to avoid a negative impact on the hydrodynamics of the flotation process.

For comparison a "classical" flotation was carried out, i. e. grinding with tap water, addition of

hydrated lime to achieve the pulp pH of 11, current not imposed, collector, frother and flotation time - as above.

In both cases (classical and electrochemically aided flotation) the rougher copper concentrate (mixed with the concentrate from scavenger flotation) was subjected to two cleaning flotation stages - first one of 2 minutes and the second one of 0.5 minutes. An electric current was not imposed in the cleaning flotation. The reagents used were as in the rougher flotation however at dosage of 1/3 of the applied in the rougher.

Each value presented here is an average of results from 2 parallel experiments.

Copper and gold were assayed by AAS after suitable digestion (dissolution in aqua regia - 3 volumes of HCl mixed with 1 volume of HNO<sub>3</sub>) of the corresponding dried samples (Ramesh et al., 2001).

### 3. Results and discussion

It is found that grinding the ore in a catholyte medium required twice less time, compared to grinding in tap water, to reach the required size of particles entering flotation. This means a significant reduction in the amount of energy for grinding. Probably the use of catholyte (containing OH<sup>-</sup> ions in elevated concentrations) in the grinding process facilitates the destruction of mineral intergrowths and mineral liberation by making easier the fracturing of particles along grain boundaries which is more beneficial for the minerals liberation. It is known that OH<sup>-</sup> ions containing solutions (i.e. NaOH) is frequently used as a grinding additive (Chipakwe et al., 2020).

Results obtained on the effect of applied current density in the stage of electrochemical treatment before flotation, in the case when catholyte with pH 11 was used, are shown in Figure 1. As it can be seen, 20 mA/cm<sup>2</sup> can be considered as an optimum for Au recovery in Cu concentrate.

The grades (averaged figures from 2 parallel experiments) of concentrate obtained by using catholyte with pH 11, at 20 mA/cm<sup>2</sup> applied in preconditioning and conditioning stage were 27.5 % Cu, 216.45 g/Mg Au and 174.03 g/Mg Ag. Under the same conditions, when catholyte with pH 10 was used, the recovery of Cu, Au and Ag was 89.8%, 93.5 % and 80.05 % correspondingly, with the grade 18.4 % Cu, 182.1 g/Mg Au, 128.3 g/Mg Ag respectively. At the same time the classical flotation (at pulp pH 11) resulted in concentrate with recovery of Cu, Au and Ag of 88.30 %, 90.20 % and 75.95 % correspondingly and content of valuable metals - 16.2 % Cu, 148.04 g/Mg Au, and 112. 8 g/Mg Ag.

The loss of valuable metals in tailings was higher in the case of classical flotation. The recovery of Cu in tailings was 2.45 % and that of Au was 4.90 % in the case of classical flotation while for the electrochemically aided flotation (catholyte pH=11) the figures were correspondingly 1.25 % and 0.98 %.

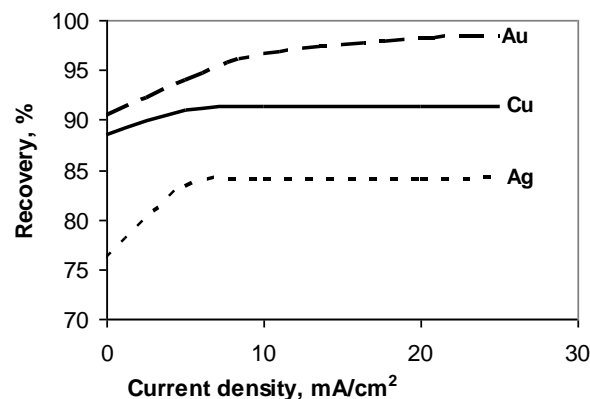


Fig. 1. Effect of applied current density in preconditioning and conditioning stage on the valuable metals recovery in the final concentrate

In addition, arsenic (As) recovery in tailings was increased from 22.9 % in the classical flotation to 31.40 % in the electrochemically aided flotation, which corresponds to less amount of As in the concentrate. The main generalized reactions proceeding on the cathode during water electrolysis are the following:





The major reaction most probably taking place on insoluble anode is



Actually, alkaline water solution obtained in the cathode compartment (catholyte) used in milling and flotation stage is the main reagent that ensures the needed pH value for Py depression without depressing Au. In addition,  $\text{O}_2$  formed on anode most probably facilitates further Py depression.

Anolyte, left over from the operation of the diaphragm electrolyzer applied to produce the catholyte, was added to the alkaline wastewater from the flotation process to achieve a final pH in the range of 7.2-7.4. This water meets the environmental requirements for discharge in natural water bodies (Regulation No. 6, 2000). In addition, its hardness is lower in comparison to wastewater from the classical treatment and this is a prerequisite for reduced efforts for its recycling with aim to be re-used in the flotation cycle.

Based on the experimental findings, a technology flow sheet is proposed - Figure 2.

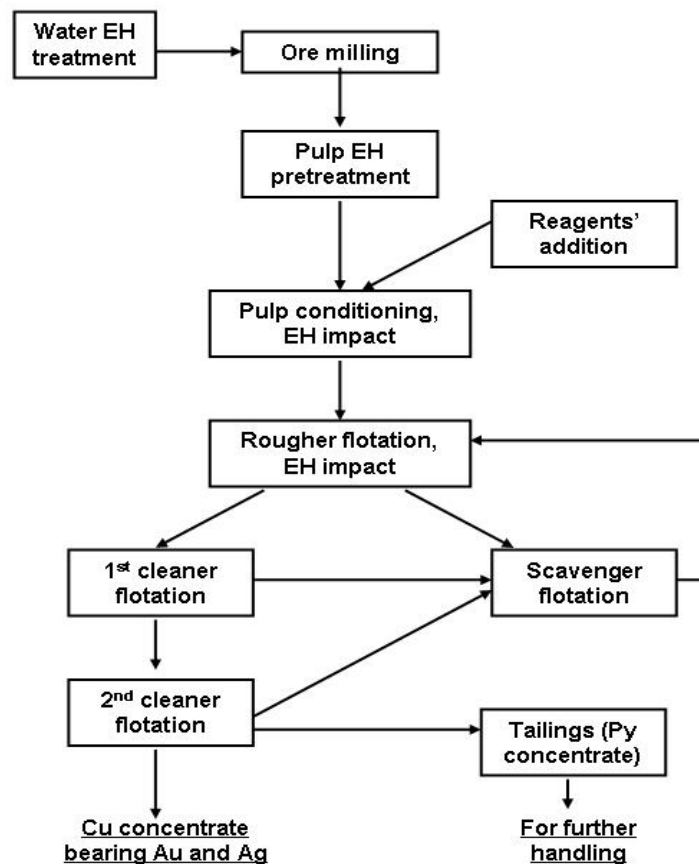


Fig. 2. Flow sheet of the proposed technology for flotation of Au-bearing Cu-Py ore (EH = electrochemical impact)

#### 4. Conclusions

Replacing the water used in the milling and flotation of gold-bearing copper-pyrite ore with catholyte obtained from electrolysis of water (aqueous solution) leads to an increase in the recovery of the precious metals in copper concentrate, while also improving the performance of the copper flotation.

The proposed technological solution creates an opportunity for establishing an environmentally friendly technology, as well as for a significant economic effect.

#### References

AGACAYAK, T., YILMAZ, N. B., 2021. *The effect of Aerophine 3418A collector dosage on Niğde (Ulukışla-Madenköy) complex Pb-Zn sulphide ore flotation.* Acad. Platf. J. Eng. Sci. 9-2, 309-313.

- AGORHOM, E. A., SKINNER, W., ZANIN M., 2015. *Post-regrind selective depression of pyrite in pyritic copper-gold flotation using aeration and diethylenetriamine*. *Miner. Eng.* 72, 36-46.
- AHMAD, H. S., 1951. *Flotation of low-grade gold ores, Thesis presented to the Swiss Federal Institute of Technology of Zurich for the degree of doctoral of technical science*. Dissertatlonsdruckerei Leemann AG, Zurich, Switzerland, 75-76.
- AZIZI, A., MASDARIAN, M., HASSANZADEH, A., BAHRI, Z., NIEDOBA, T., SUROWIAK, A., 2020. *Parametric optimization in rougher flotation performance of a sulfidized mixed copper ore*. *Minerals* 10, 660.
- BOULTON, A., FORNASIERO, D., RALSTON, J., 2001. *A comparison of methods to selectively depress iron sulphide flotation*. Proceedings of the 4th UBC McGill International Symposium of Fundamentals of Mineral Processing - Interactions in Minerals Processing. Canadian Institute of Mining, Metallurgy and Petroleum Montreal, 141-152.
- BULATOVIC, S. M., 2007. *Handbook of flotation reagents: chemistry, theory and practice: 1 - Flotation of sulphides ores*. Elsevier, Amsterdam, Netherlands, 55-56.
- CHANTURIYA, E. L., 2008. *Scientific bases of gold - bearing pyrite recovery from pyrite - bearing waste products of copper-zinc sulfide ores*. <https://www.researchgate.net/publication/260506577>.
- CHIPAKWE, V., SEMSARI, P., KARLKVIST, T., ROSENKRANZ, J., CHELGANI, S. C., 2020. *A critical review on the mechanisms of chemical additives used in grinding and their effects on the downstream processes*. *J. Mater. Res. Technol.*, 9, 8148-8162.
- GLEMBOTSKII, V. A., KLASSEN, V. I., 1981. *Flotation methods for beneficiation*. Nedra, Moscow, Russia, 270-271 (in Russian).
- LIU, W., MILLER, J. D., SUN, W., HU, Y., 2022. *Analysis of the selective flotation of elemental gold from pyrite using diisobutyl monothiophosphate*. *Minerals*, 12, 1310.
- MBAYO, J. K., 2020. *Improving the gold leaching process of refractory ores and tailings using the jet leach reactor*. A dissertation submitted to the faculty of Engineering and the Built Environment, University of Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science in Engineering, Johannesburg, South Africa, 10-11.
- MEDINA, D., ANDERSON, C. G., 2020. *A review of the cyanidation treatment of copper-gold ores and concentrates*. *Metals*, 10, 897.
- MU, Y., PENG, Y., LAUTEN, R. A., 2016a. *The depression of pyrite in selective flotation by different reagent systems - A literature review*. *Miner. Eng.* 96-97, 143-156.
- MU, Y., PENG, Y., LAUTEN, R. A., 2016b. *The depression of copper-activated pyrite in flotation by biopolymers with different compositions*. *Miner. Eng.* 96-97, 113-122.
- PANAYOTOV, V., PANAYOTOVA, M., 2017. *Method for flotation extraction of precious metals in copper concentrate*. Bulgarian Patent No 66563 B1 - 2017.
- PARK, I., HONG, S., JEON, S., ITO, M., HIROYOSHI N., 2020. *A review of recent advances in depression techniques for flotation separation of Cu-Mo sulfides in porphyry copper deposits*. *Metals*, 10, 1269.
- RAMESH, S. L., SUNDER-RAJU, P. V., ANJALIAH, K. V., MATHUR, R., RAO, T. G., DASARAM, B., CHARAN, S. N., SUBBA-RAO, D. V., SARMA, D. S., RAM-MOHAN, M., BALARAM, V., 2001. *Determination of gold in rocks, ores, and other geological materials by atomic absorption techniques*. *Atom. Spectrosc.* 22, 250-257.
- Regulation No. 6 of 9.11.2000 on emission norms for the permissible content of harmful and dangerous substances in waste water discharged into water bodies. State Newspaper No. 97 of 28.11.2000, Sofia (in Bulgarian).
- SCERESINI, B., 2005. *Gold-copper ores. Developments in Mineral Processing Chapter 32. Advances in Gold Ore Processing*. Mike D. Adams, B.A. Wills Eds. 15, 789-824.