

L.YE. SARGSYAN, D.L. TOVMASYAN, M. KH. MOATASEM

PERFECTION OF POLYMETALLIC ORE FLOTATION CYCLE TO OBTAIN AN EFFECTIVE CONCENTRATE FOR RECOVERY OF METALS

A perfectible bulk flotation simplified technology was developed to produce initially a collective polymetallic concentrate for further treatment by a "sulphatization roasting → 2-step leaching → metal cementation" method to recover all valuable metals besides the noble metals, and after this, recover gold and silver from the base metal leaching residuum by cyanide leaching and following electrowinning. It has been showed that all gold bearing sulphides copper, zinc, lead and iron were successfully passed from polymetallic ore into collective concentrate which is a pleasurable perspective for complex and effective recovery of all valuable metals contained.

Keywords: flotation, sulphide, polymetallic concentrate, pyrite, chalcopyrite, sphalerite, galena, reagent regime.

Recently the mineralogical structure and interrelation of minerals in Shahumian gold-bearing copper–zinc–lead polymetallic ores have been studied using X-Ray and microscopic methods to estimate the recoverabilities of valuable metals, and it was shown that the gold (as well as silver) is intimately associated with the sulphides as fine unliberated grains. Majority of gold occurred in sulphide minerals grains, which must be decomposed in order to let gold to be recovered. And some minerals are so much intergrown with each other (especially, sphalerite with chalcopyrite and chalcopyrite with galena) that it is quite impossible to separate them in convenient industrial milling and flotation processes.

On the other hand, in the processes of selective mineral flotation there are many technological losses of valuable metals (Cu, Zn, Pb, Au, Ag, others), since it is very difficult to separate one sulphide mineral from others especially galena (PbS) from sphalerite (ZnS) or chalcopyrite (CuFeS₂).

Due to intergrowth of minerals, the Kapan Processing Plant a long time cannot produce separate copper, zinc and lead concentrates and at present it produces only individual Zn-concentrate and complex Cu-Pb-Au-concentrate (see technological scheme in Fig. 1) using: as an activator - copper sulphate CuSO₄·5H₂O (600 g/t consumption) and sodium sulphide Na₂S (50 g/t); lime CaO (8000 g/t) as pH modifier; a complex collector containing izobutyl xanthate – 55 % (50 g/t), amyl xanthate – 15 % (15 g/t) and aerophine 3418A – 30 % (24 g/t); dowfroth and nasfroth frothers (70 g/t); zinc sulphate ZnSO₄·7H₂O (2500 g/t) as a depressor for sphalerite.

According to Mill assays, both concentrates apart from main metals contain a significant amount of byproduct metals. For example, zinc concentrate (55...58 % Zn) contains about 1.5 % Cu, 1.1 % Pb, 2.0 % Fe, 8 g/t Au and 150...200 g/t Ag; in copper concentrate (22...26 % Cu) about 0.7 % Zn, 0.1 % Pb, 30.0 % Fe, 1.5...3.2 g/t Au, 50...100 g/t Ag; and in copper-gold concentrate (20...22 % Cu) about 6.0 % Zn, 6.0 % Pb, 25.0 % Fe, 80...120 g/t Au and 1500...2000 g/t Ag are available.

The amounts of copper, zinc, lead and other non-ferrous metals as well as iron in ores are so high that it is not profitable to use the direct cyanide leaching technology (without flotation) to recover initially gold and silver, because of ability of corresponding minerals also to dissolve in dilute alkaline cyanide solutions, and their reactions may

consume cyanide salt (NaCN) and oxygen, as well as produce a variety of solution species which can reduce the efficiency of gold leaching and subsequent recovery processes.

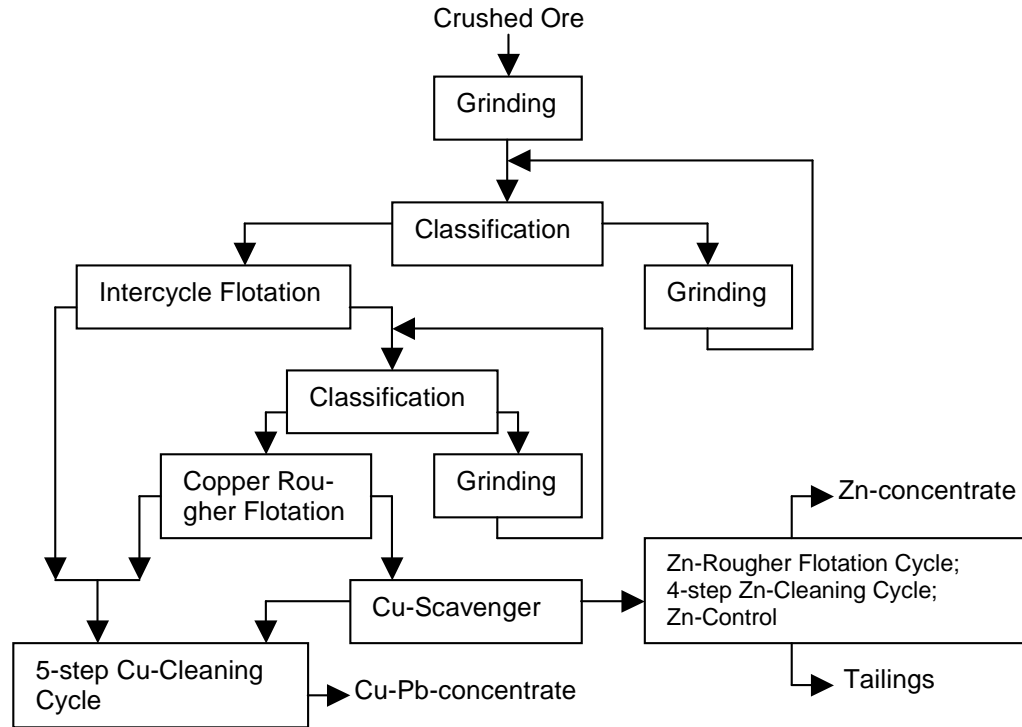


Fig. 1. Simplified Flow-Sheet of the Commercial Polymetallic Ore Flotation Cycle
(by the Technological Instruction of Kapan Processing Plant, 2009)

Taking into account above mentioned disadvantages of selective sulphide flotation method, a perfectible technology was developed (Fig. 2) to produce initially a collective polymetallic concentrate (containing all valuable minerals, including gold and silver) which will be treated then by a “sulphatization roasting → 2-step leaching → metal cementation” method to recover all valuable metals, apart from gold and silver, and after this, recover the noble metals from the base metal leaching residuum by cyanide leaching and following electrowinning.

According to this technology, flotation is used as a pre-concentration method to allow more expensive refractory ore treatment to be performed on a smaller fraction of the mineral. Under these conditions, the flotation circuit is operated to recover all the minerals containing gold, i.e. bulk flotation. Conditions do not necessarily have to be optimized for free gold recovery since this is readily recovered with other floatable minerals (i.e. sulphides).

In general, the mineral's behavior during froth flotation is controlled by its surface properties and these are a function of its chemistry, structure and the surface species formed by reactions during processing [1].

Gold is naturally floatable in industrial systems [2], which means that it can be recovered without collector addition [3,4]. This is due to the adsorption of hydrocarbons (and

other reactions) depending on gold metallic properties, particularly, its high electrical conductivity, which allows surface electrochemical reactions occurring catalytically and selectively.

Gold hydrophobicity is enhanced by the addition of flotation collectors such as xanthates, dithiophosphates (DTP) and mercaptobenzothiolates (MBT), as used in sulphide mineral flotation (usually 25...75 g/t collector concentration is used).

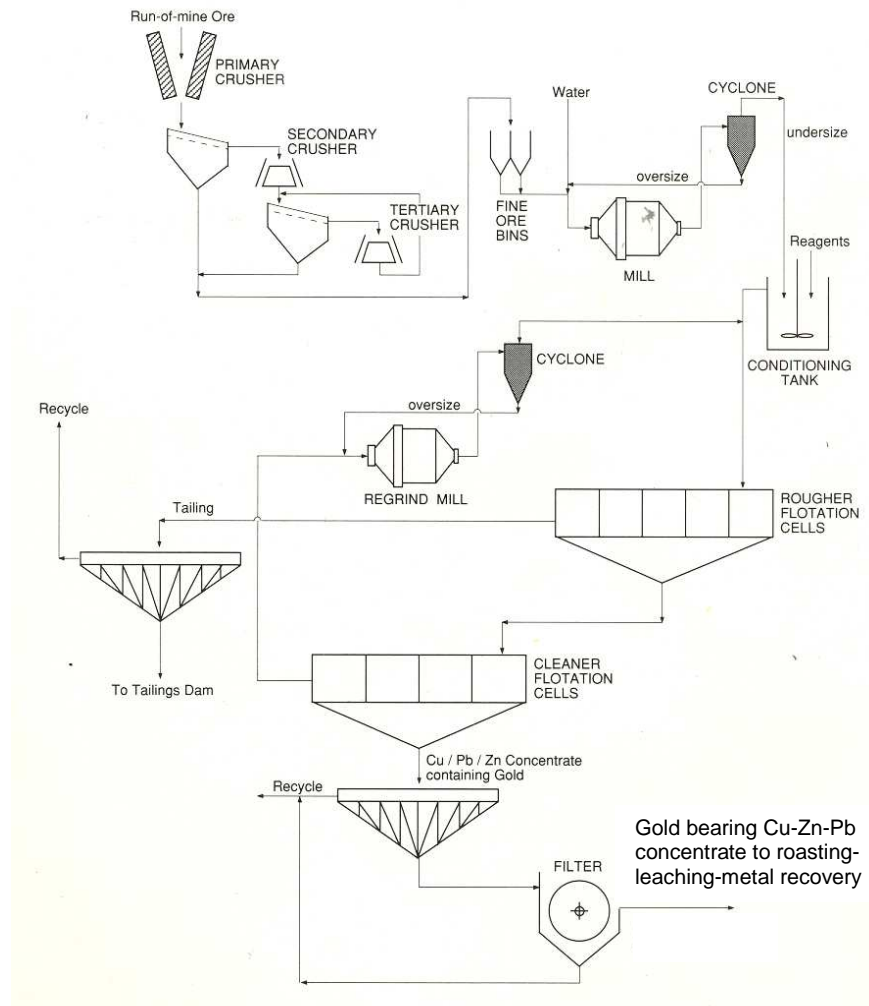
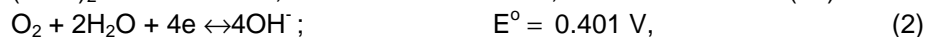
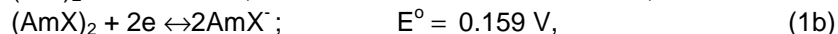
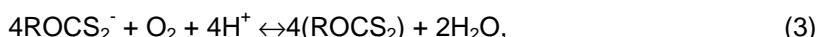


Fig. 2. Schematic Flow of the Flotation Process to Obtain Collective Gold-bearing Cu - Zn - Pb Collective Concentrate

The mechanism by which gold hydrophobicity is enhanced is similar to that of certain sulphides, e.g. pyrite [2]. Xanthate ions are oxidized on the gold surface to form the neutral dimer dixanthogen:



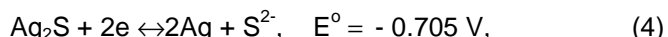
where Et and Am indicate ethyl (C2) and amyl (C5) alkyl groups. The non-polar liquid, dixanthogen forms oily surfaces rendering them hydrophobic. The oxidation of xanthate ions in bulk solution is very slow:



where R is a hydrocarbon chain (for sodium ethyl xanthate $\text{R}=\text{C}_2\text{H}_5\text{OCS}_2\text{Na}$). The equation (3) demonstrates that the conducting surface of gold or semi-conducting minerals (e.g. chalcopyrite, sphalerite and galena) is required for dixanthogen formation.

Oxide and silicate minerals are not electrical conductors and cannot sustain redox couples described by equations (1) and (2). Hence the collecting action of the reagent is very selective for gold and sulphides which means that reagent additions are typically low.

Impurities in gold (usually Ag and Cu) are more reactive than gold and can form hydrophilic surface phases. Molar volume increases associated with reactions of these impurities forming coatings on gold, e.g. Ag_2S formation:



which has a molar volume change of 183 %. Conversely, the hydrophobicity of native gold increases if silver is leached from the surface regions [5], since this reduces the hydrophilic portion of the metal surface.

Also, it is very well known that the flotation behavior of a sulphide mineral, when it is mixed with other sulphide minerals in an ore, can be substantially different from that predicted by single mineral. The reasons suggested for this behavior are attributed to galvanic interactions between sulphide minerals [6,7].

The flotation of copper sulphides, e.g. chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), chalcocite (Cu_2S) and covellite (CuS), is relatively straightforward with thiol collectors, and differs from gold-pyrite-arsenopyrite flotation because a Cu-xanthate compound is formed, which renders the copper minerals hydrophobic. In the case of chalcopyrite flotation dixanthogen is also present [2].

Chalcopyrite is floated with ethyl xanthate over a wide pH range (4...11) due to the stability of cuprous xanthate. It can only be depressed at $\text{pH} > 11\text{...}12$, unless cyanide or sulphide are added. Flotation is also possible with dithiophosphates and the whole range of xanthates (sodium aerofloat, methyl, ethyl, butyl and amyl xanthates [2]). Data on copper minerals, galena (PbS) and sphalerite (ZnS) flotation for base metal recovery are available in review [8]. The successful activation and flotation of sphalerite in complex Pb / Zn and Cu / Zn ores is shown in [9].

Since in our case gold is associated also with pyrite (FeS_2), mainly in a locked shape, this type of mineral association has to be flotation concentrated. Pyrite tends to oxidize in air which affects its surface properties and flotation behavior. In the presence of xanthate collectors in oxygenated solutions, the pyrite surface is rendered hydrophobic by the formation of dixanthogen, through the same electrochemical mechanism as that for gold.

Gold telluride minerals are not as natural hydrophobic as clean native gold, but are at least as floatable as most sulphide minerals [2]. But tellurides, and galena (PbS) as well, in polymetallic ore are everywhere associated with chalcopyrite and sphalerite grains, so they eyewitness that, they can be floated together with these minerals.

Therefore, it is well-grounded that in order to reach an effectively joint flotation of gold with copper, zinc and lead sulphide minerals and pyrite as well from polymetallic ore-pulp, the following changes are carried out in the commercial flotation reagent composition:

- *Zinc sulphate ($ZnSO_4 \cdot 7H_2O$) (16 %) was excluded* from the reagent complex since it is used in commercial (working) flotation technology as a depressant for sphalerite (ZnS), but sphalerite will not to be depressed in our case;
- *Lime (Cao) was excluded* from the reagent complex since it depresses gold and iron sulphides, as well as lead, marmatitic zinc and certain minerals if excess used that is not necessary [10], and in it's exchange a *soda (Na_2CO_3) ash as a pH-modifier was added* to reagent complex (250...1500 g/t) which assists flotation of precious metals and sulphides, by acting as gangue slime dispersant [10];
- In exchange of *isobutyl xanthate* (in Complex Collector) was proposed to apply *methyl xanthate* to which are simultaneously response chalcopyrite, sphalerite, galena and pyrite, as well as borite, covellite and chalcocite in the presence of activators [2].

Taking into account these changes the better reagent regime is recommended for gold bearing collective Cu – Zn - Pb concentrate flotation technology (see Fig. 2):

- To the 1-st milling cycle (into ball mill) - *Soda (Na_2CO_3) ash (300 g/t) + Sodium sulphide (Na_2S , 50 g/t) / pH = 7...8;*
- To the rougher flotation cycle (into conditioning tank) – *Complex collector* (20 g/t) + Copper sulphate ($CuSO_4 \cdot 5H_2O$, 600 g/t) + Pine-oil T-66 (30 g/t) / pH = 8...9, 10 minutes duration;*
- To the cleaner flotation cycle - *Complex collector* (10 g/t) + Copper sulphate ($CuSO_4 \cdot 5H_2O$, 450 g/t) + Pine-oil T-66 (15 g/t) / pH = 8...9; 15 minutes duration,*

where Complex collector* = Methyl xanthate (55 %) + Amyl xanthate (15 %) + Aerofine 3418A (35 %). In industrial applications, abovementioned concentrations might be corrected.

It is seen from the illustrated diffractogram (Fig. 3) and qualitative estimate, that gold bearing copper, zinc, lead and iron sulphide minerals were successfully passed from polymetallic ore into collective concentrate which is a pleasurable and suitable perspective for complex and simultaneously effective recovery of all valuable metals contained intergrown gold and silver.

By the data of silicate-chemical and mineralogical analysis an experimental sample of collective concentrate (14.5% Cu, 8.25% Zn, 9.32% Pb, 23.41% Fe, 0.21% Cd, 32.36% S; 17,5 g/t Au; 241.8 g/t Ag) assayed at the Chemical laboratory of Kapan Processing Plant using above recommended technological principle and corresponding reagent regime has the following main mineral composition (%): 12.31 ZnS, 22.92 FeS₂; 42.64 CuFeS₂; 10.96 PbS; 0.26 CdS; 4.84 SiO₂; 2.56 Al₂O₃; and (CaO + MgO) the rest. This is a quite satisfied result for high flotation grade to be guaranteed.

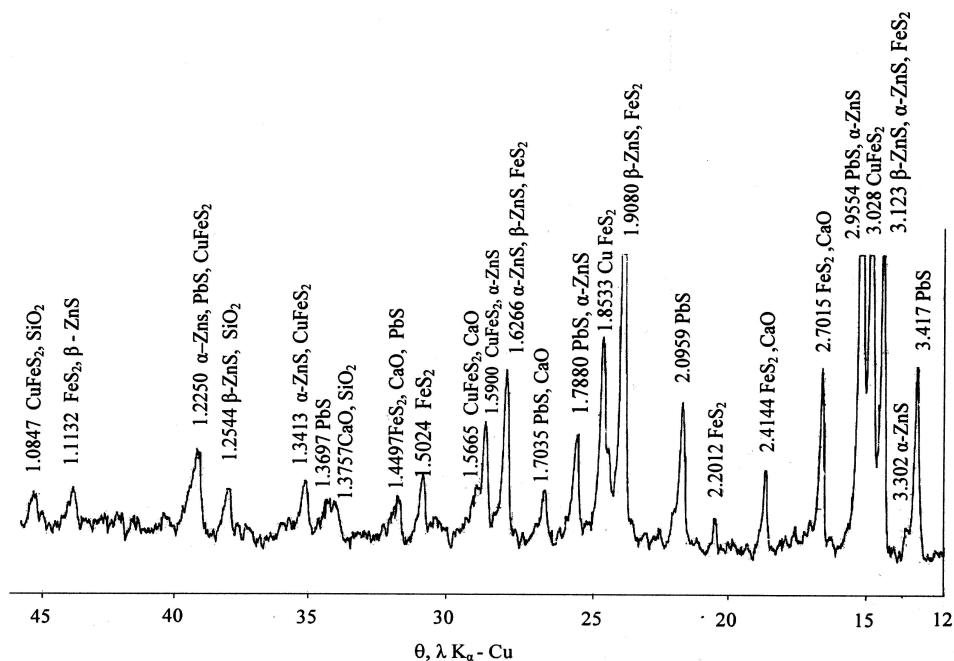


Fig. 3. Diffractogram of the gold-bearing collective polymetallic concentrate

REFERENCES

1. **Mustafa S., Hamid A., Naeem A., Murtaza S.** Upgradation of Chalcopyrite Ore by Flotation // Jour. Chem. Soc. Pak.- 2005.- V. 27, No 2.- P. 115-123.
2. **Marsden J., House I.** The Chemistry of Gold Extraction. Ellis Horwood Limited.- Chichester (England), 1992.- 597 p.
3. **King R.P.** Principles of Flotation. S. Afr. Inst. Min. Metall.- Johannesburg.- 1982.- 268 p.
4. Bath M.D., Duncan A.J., Rudolph E.R. Some factors effecting gold recovery by gravity concentration // J. S. Afr. Inst. Min. Metall.- 1973.- V. 73 (11).- P. 363.
5. Wenqian W., Poling G.W. Methods for recovering fine placer gold // Can. Inst. Min. Metall. Bull. - 1983.- V. 76 (860).- P. 47.
6. **Nakazawa H., Iwasaki I.** Effect of pyrite-pyrrhotite contact on their floatabilities // Miner. Metall. Process.- 1985.- N 2.- P. 206-211.
7. **Ekmekci Z., Demirel H.** Effects of galvanic interaction on collectorless flotation behavior of chalcopyrite and pyrite // Int. J. Miner. Process.- 1997.-N 52.- P. 31-48.
8. **Forsberg E.** Sulphide Mineral Flotation – Developments in Mineral Processing.- Vol. 9.-Elsevier.- Amsterdam, 1988.-270 p.
9. **Ekmekci Z., Aslan A., Hassoy H.** Effects of EDTA on selective flotation of sulphide minerals // Physicochemical Problems of Mineral Processing.- 2004.-38.-P. 79-94.
10. Mining Chemicals Handbook American Cyanamid Co.- 1982.- 178 p.

SEUA. The material is received 07.02.2009.

Լ.Ե. ՍԱՐԳՍՅԱՆ, Դ.Լ. ԹՈՎՄԱՍՅԱՆ, Մ.Խ. ՄՈԱՏԱՍԵՄ

ԲԱԶՄԱՄԵՏԱՂԱՅԻՆ ՖԼՈՏԱՅՄԱՆ ՑԻԿԼԻ ԿԱՏԱՐԵԼԱԳՈՐԾՈՒՄԸ՝ ՄԵՏԱՂՆԵՐԻ ԿՈՐԶՄԱՆ ՀԱՄԱՐ ԱՐԶՈՒՆԱՎԵՏ ԽՏԱՆՅՈՒԹԻ ՍՏԱՑՄԱՍԲ

Մշակված է կատարելագործված ծավալային ֆլոտացման պարզեցված տեխնոլոգիա՝ նախապես միասնական բազմամետաղային խտանյութի ստացումով, որն այնուհետ պետք է վերամշակվի «սուլֆատացնող բովում → երկփուլ տարրալուծում → մետաղների նստեցում» մեթոդով, ազնիվ մետաղներից բացի, բոլոր մյուս արժեքավոր մետաղների կորզման և դրա սորախցուկի հետագա ցիանիդային տարրալուծման ու էլեկտրակորզման ճանապարհով ոսկու և արծաթի ստացման համար: Ցույց է տրված, որ ոսկետար պղնձի, ցինկի, կապարի և երկաթի բոլոր սուլֆիդները բազմամետաղային հանքաքարից հաջողությամբ անցնում են դեպի միասնական խտանյութ, ինչն արդյունավետ նախադրյալ է նրանում առկա բոլոր արժեքավոր մետաղների համալիր կորզման համար:

Առանցքային բառեր. ֆլոտացում, սուլֆիդ, բազմամետաղային խտանյութ, պիրիտ, խալկոպիրիտ, սֆալերիտ, գալենիտ, ազդանյութային ռեժիմ:

Л.Е. САРГСЯН, Д.Л. ТОВМАСЯН, М.Х. МОАТАСЕМ

СОВЕРШЕНСТВОВАНИЕ ПОЛИМЕТАЛЛИЧЕСКОГО ФЛОТАЦИОННОГО ЦИКЛА С ПОЛУЧЕНИЕМ ЭФФЕКТИВНОГО КОНЦЕНТРАТА ДЛЯ ИЗВЛЕЧЕНИЯ МЕТАЛЛОВ

Разработана усовершенствованная технология упрощенной объемной флотации с предварительным получением полиметаллического концентрата, который впоследствии должен обрабатываться методом “сульфатизирующий обжиг → двустадийное выщелачивание → цементация металлов” для извлечения всех ценных металлов, кроме благородных, с последующим цианированием кека выщелачивания и электроизвлечением золота и серебра. Показано, что все золотоносные сульфиды меди, цинка, свинца и железа из полиметаллической руды успешно переходят в коллективный концентрат, что является хорошей предпосылкой для комплексного и эффективного извлечения содержащих в нем всех ценных металлов.

Ключевые слова: флотация, сульфид, полиметаллический концентрат, пирит, халькопирит, сфалерит, галенит, реагентный режим.