HISTORY OF THE RECOVERY OF COPPER DEPOSITS FROM ROMANIA

Camelia BĂDULESCU, Maria LAZĂR**, Eugen TRIASTĂ**

Abstract: *The paper includes a brief presentation of the copper deposits in Romania as well as their exploitation and processing technologies. Currently, in our country, only the copper deposit from Roșia Poieni is in operation, the other mining operations and processing plants being in conservation or in the process of conservation. The closure of mines in Romania is not an objective in it self, but is a natural consequence of the evolution of the Romanian economy after 1989, when investments in the nationale economy were reduced, which generated a significant decrease in the need for raw materials, including mineral resources and as a result, mining was out of order. Another reason for the initiation and development of mine closure programs was the unprofitability of mineral resources, (this economic situation being a consequence of the fact that copper and polymetalli ferous deposits in Romania are characterized by a very low content of useful elements: Cu, Pb, Zn, etc.), their economic inefficiency, due to causes related mainly to the technical conditions of access to the depositand its increasingly difficult operation, the moral and physical wear and tear of the machinery and equipment used.*

1. Introduction

The dynamic character of the copper ore reserves was mainly determined by three elements:

- discovery of new deposits;

- the improvement of existing technologies or the development of technologies on the basis of which some deposits considered at one time to be unusable can be considered reserves;

- imposing copper as a substitute for some metals, resulting in increased metal consumption / replacement of copper with other materials, resulting in decrease demand for metal.

In order to cover the demand for copper, imposed by the development and technical progress of the current society, it was necessary to exploit very large quantities of mining mass, due to the fact that they have low metal contents.

In the case of copper deposits, the average minimum exploitable content has continuously decreased from values of 4-5% recorded at the beginning of the twentie -th century, to contents that are currently at values of 0.30-0.40% Cu.

The current Strategy envisages, depending on the available financial resources, the continuation of the exploitation activity of the existing deposits and of the derived secondary resources, as well as there search activities – exploration and opening of new deposits, only in the conditions in which the economic efficiency can be ensured. In order to achieve the se objectives, EU directives and recommendations must be taken into account. Proposing mutually supportive priorities:

- developing an economy based on knowledge and innovation;

- sustainable growth - promoting a more efficient economy in terms of resource-use, ecological balance and maintaining competitiveness and promoting an economy with a high employment rate.

The rest of the mines, which have ceased operations and are approved for closure by government decisions, are included in the annual conservation, closure, greening and post-closure monitoring programs. These mines are in different stages: closed mines, mines with works in progress, mines in conservation for closure and mines unattacked.

2. Types of copper deposits

Based on geo chemical considerations, it can be stated that industrial copper deposit sfall into the following genetic types of deposits:

a. Liquefaction deposits - quite rare - which are characterized by the presence of chalcopyrite in exploitable quantities and contents of 1.0-1.5% Cu;

b. Deposits of contact metasomatism- have a relatively low importance, the Cu content rarely exceeding 2.0%. This category includes the deposits from: Sasca Montană, Ocna de Fier, Moldova Nouă

c. Hydrothermal deposits - are the most widespread and are the main source of copper.

The first place is occupied by the mesothermal class, in which the ore takes different forms.

In our country the mesothermal deposits are the largest and most important regarding the copper concentrations. According to their presentation, they are distinguished: filonium deposits, impregnation

* *Assoc.prof.eng. Ph.D, University of Petroșani*
***Prof.eng. Ph.D, University of Petroșani*

deposits (in sandstone) and disseminated (porphyric) deposits.

1. Vein deposit shave a limited spread, and the ore consists of chalcopyrite, calcosine, digenite, tetrahedrite, bornite, blende, galena, quartz and tourmaline. Chalcosine and covelina appear in the foundation area. The copper content is important (over 2%), and the ore reserves are sometimes special. Ex. Toroioaga, Nistru, Baia Sprie - partially, etc.

2. Impregnation deposits are located in lime stone and dolomite sand stones. The mineralized solutions of magma origin partially substituted the rocks encountered with copper sulphides - calcopirite, calcosine and borite.

3. Disseminated (porphyric) deposits are characterize by the shape of a network of various oriented branches and their localization in the porphyric facies of the granitic intrusions. The primary ore consists of pyrite, calcopirite, borite, molybdenite, with a content generally less than 0,4-0,6%. By chemical alterationthe ore has been enriched, reaching contents above 1-1.5% Cu. The extension of the mineralization occurs more in the horizontal plane, in depth being reduced, sometime sallowing for open pit operation. Ex: Deva, Roşia Poieni, Moldova Nouă.

4. Metamorphosed hydrothermal deposits are characterized by metallic concentrations of lensshape sand lenticular layers associated with epimetamorphic crystallineshale in which they are consistently intercalated, then shale texture and grainy blasto-porphyric structure. Metallic and gangue minerals have been deposited from hydrothermal solutions on crack sand pores of weakly consolidated rocks. Subsequently a regional metamorphism with knowneffect stook place, followedby a questandfallacy phase. Examples include the Gura Băii, Burloaia, Baia Borşa, Pojorâta, Leşul Ursului, Fundul Moldovei, Bălan and Altân Tepe.

3. Exploitation of copper

The Roşia Poieni depositis situated in the Poieni, Vârşi, Curmătura peak areas, the level of the approved reserves up tonowis 320 mil.tone. The exploitation of Roşia Poieni copper ore is done in the quarry. The exploitation of the quarry from Roşia Poieni, presupposes a classic technology, with descending steps, at a general slopeangle of 70°. Currently, the quarryis profiled in the form of an amphitheater, opening to the NW. A new work front wasopenedtothe SW. The final morphology of the quarry will retain a semicircular shape, opening to the NW.

The Altân Tepe mining operation, the only copper mine in Dobrogea, opened in 1915, eve during the First World War, for almost a century it was one of the most important mines in the country. In 1998 the mine was closed, although the Golden Hill (as translated from Turkish AltânTepe) still hides in its depths quite copper.

The Fagu Cetății Mine (Bălan) mined copper underground, closing in 1999.

4. Processing of copper deposits from Romania

Sulfur-containing copper ores recovered in our country have metal contents of over 0.3% Cu, which is found in the form of sulfuric minerals and in the form of oxide compounds (10-15%).

The deposits of copper ores that were exploited and processed in our country were grouped in:

-compact sulfide ore deposits;

-impregnation ore deposits: porphyry and stratiform.

Some of the copper ore processing technologies in Romania are selected for presentation.

4.1. Processing technology at Roşia Poieni processing plant

The Roşia Poieni deposit is situated in the Poieni, Vârşi, Curmătura peak areas, the level of the approved reserves up to no wis 320 mil.tone. The exploitation of Roşia Poieni copper ore is done in the quarry. Copper sulphide cantons in this phorphiric deposit contain 0.2-2% Cu and 0.008-1.1% Mo, they have large impregnations of copper minerals or their large concretes with molybdenite, pyrite in the gang, as well as intimate sulphides copper with molybdenite and pyrite.

At Roşia Poieni the ore contains pyrite, magnetite, calcopirite, marcasite, calcozine, coveline, molybdenite in quartz, sericite, clayey minerals.

The grinding of the ore is carried out in two stages: the first semiautogen in the closed mill, the spiral separator and the second in the closed ball mill with hydrocyclone up to the fineness of 60% - 0,074mm.

The technological flow of preparationis shown in figure 1. Flotation of ore iscarried out following the collective technology of Cu, S, Mo sulphides followed by the separation of the collective concentrate after a preliminary remake to the fineness of 90% -0,074 mm. Collective flotation is performed with amylxanthate + RC24 dithiophosphate collectors at pH = 7.5-8 (lime), AGF 250 sparkler, oil for molybdenum-containin gores separations. The separation of the collective concentrate is carried out at pH = 12 (lime) by dosingxanthate + dithiophosphate RC24 and spumant collectors.

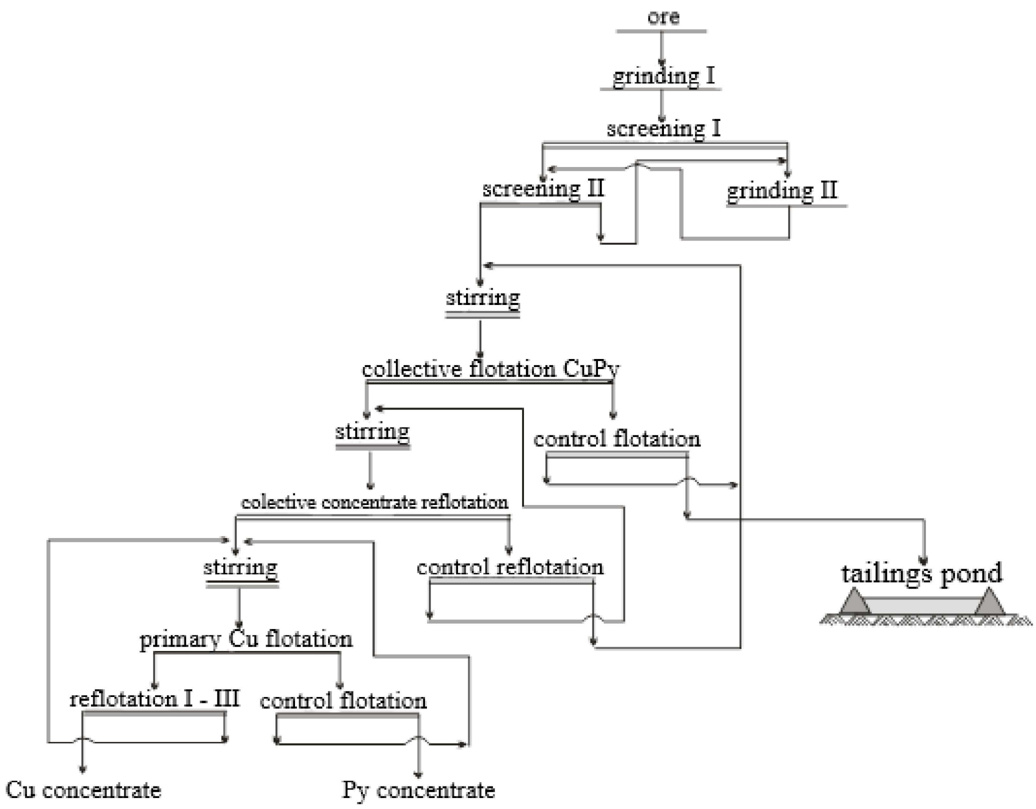

Fig. 1. *The technological flowsheet of the porphyric copper ore processing from Roşia Poieni*

In order to improvethe quality of the pyrite concentrate, it is envisaged tha tafter thickening by flotation with amylxanthateand sulfuric acid activator.

From an ore with 0.28% Cu, 1.53% S results in a copper concentrate with 16.5% Cu, 66% Cu extraction.

The sterile from the Roşia Poieni copper plant is spilled into the Valea Şesii.

The chemical analyzes carried out on sterile sample staken from the Sasa Valley tailing spondshowed that the copperis in the form of carbonate in the amount of 0.028-0.039%, in the form of sulphides in the weight of 0.184-0.265%.

The granulometric analysis carried out shows a weight of the grainsize -0,074mm of 45-47%.

The mineralogical characteristics of the sterile sample show that useful minerals and mainly calcopirite are present both in the form of free pellets with dimensions ranging from 3-5µm to 0.1-0.2 µmand overgrown with the gangue minerals. The volumetric weight varies between 1.55-1.80t / m3 at a depth of 10m.

Laboratory research to recover copper, the only element of economic interest, focused on flotation, testing four technological variants under different working conditions, there sultsachieved making it possible to advance the idea of possible recovery of this chemical element

4.2. Processing technology at Moldova Nouă processing plant

Processing technology and source of the material from the tailings ponds at Moldova Nouă plant.

The mineralogical composition of the Moldova Nouă mine (Caraş-Severin County) is: calcopirite, pyrite, magnetite, tetrahedrite and molybdenite as useful minerals and quartz, sericite as gangue minerals.

At the Moldova Noua processing plant, the ore is crashed into gyratory crushers and then grinded and screened simptotically to 60% -0,074 mm fineness in two steps: the first milling step is semi-autogenous in open circuit with spiral separators and the second the milling step takes place in two ball mills working in closed circuit with a spiral separator and hydrocyclones.

Flotation of the ore is collectively Cu-Py, followed by separation in distinct concentrates, the working medium being made at a pH of 7.5-8 with lime, using as collector reagents amyl xanthate and dithiophosphates, foam AGH -250, sodium silicate for depressing gangue minerals and oil for molybdenum collection (Figure 2). The porphyric cupriferous ore from Moldova Noua has a content of 0.62% Cu, 2.72% S, 0.0043% Mo, resulting in a copper concentrate of 14.5% Cu, 38.7% S, 0.651% Mo, to a 68.3% Cu extraction and a pyrite concentrate with 0.99% Cu, 47.6% S at an extraction of 65% S.

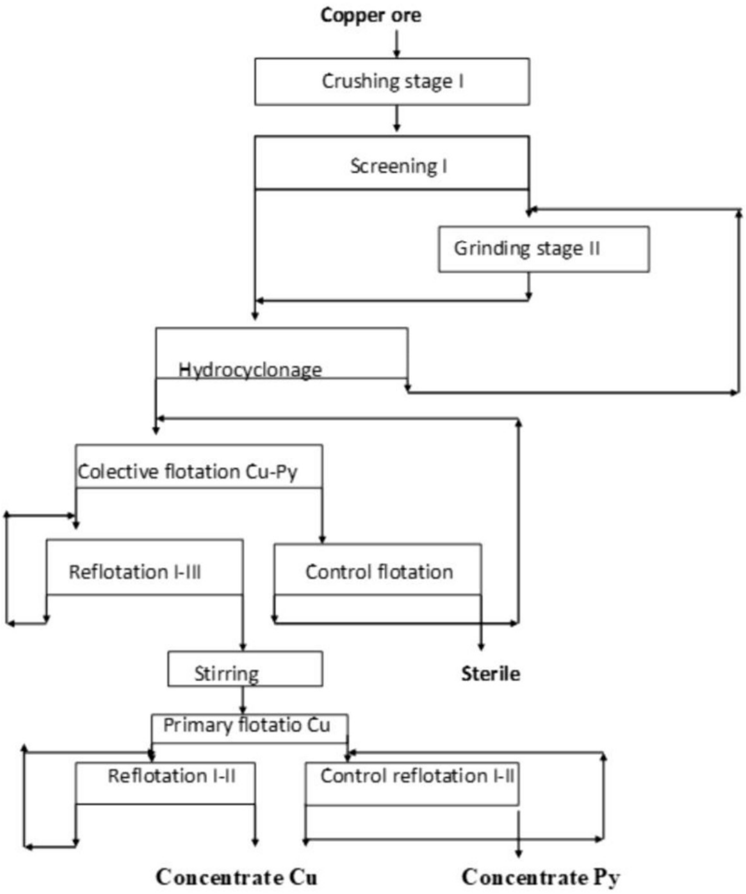

Fig. 2. *The technological flowsheet of the porphyric copper ore processing from Moldova Nouă*

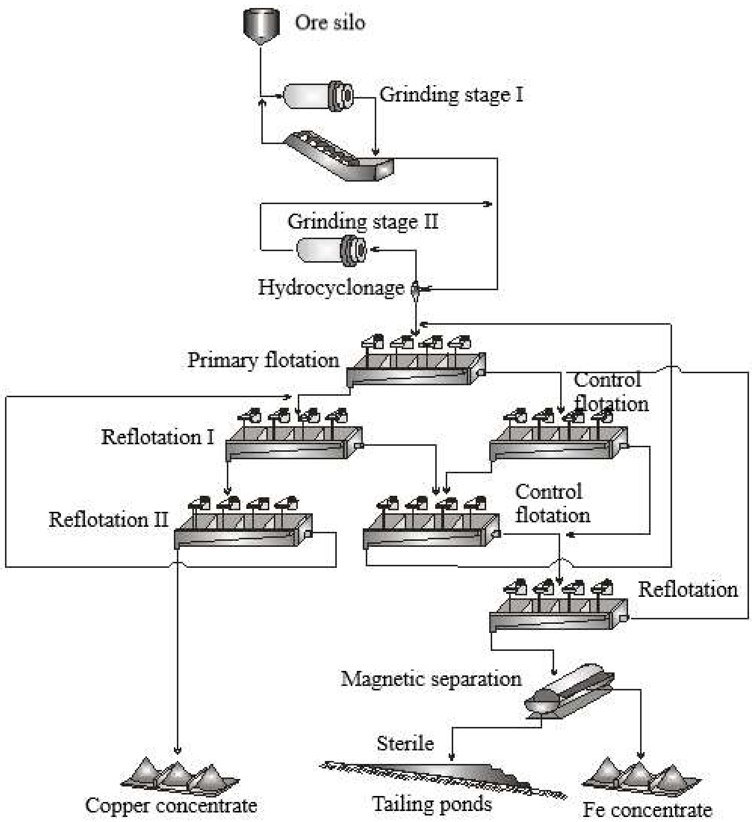

Fig. 3. *The technological flow of impregnating copper ore from E.M. Deva*

4.3. Processing technology at Deva processing plant

Processing technology and source of the material from the tailings ponds at DEVA plant.

At the Deva processing plant was used copper impregnation ore which had the following mineralogical composition: bornit, covelin, calcopirite, pyrite in quartz, calcite, feldspar.

The technological flow of preparation is shown in figure 3. The ore subject to flotation is broken, crushedandscreened in two steps. The technology appliedis direct differential flotation that consists in pyrite and magnetite depressing with lime and flotation of a copper concentrate using an xanthate collector and a Flotarom foaming agent or AGF. From the flotation tailusing magnetic separation, the magnetite concentrate is obtained.

Copper concentrate contain 24% Cu and an extraction of 80% from an ore with0.26% Cu and 1.2% S. The content of copper in the tailings is 0.154% Cu.

4.4. Processing technology at Bălan processing plant

At the Bălan plant (Harghita county - Romania) were processed compact and impregnated ore containing pyrite, calcopirite, tretrahedrite, malachite in quartz, sericite, feldspar, carbonate.
The technological flow of preparationis shown in figure no.4.

The mined ore, classified at 60% - 0.074 mm, is subjected to collective flotation to obtain a collective Cu + Py concentrate which under goes to separation, resulting in individual copper and pyrite concentrates. Amillicxanthate, dithiophosphate RC-24 and AGF-250 dithiophosate or DM-80, while in the lime separation circuit for pyrite depression, amylxanthate and spumant collector.

This results in a copper concentrate with 15.3% Cu, 88.7% Cu extraction from ore with 0.54% Cu and 3.41% S.

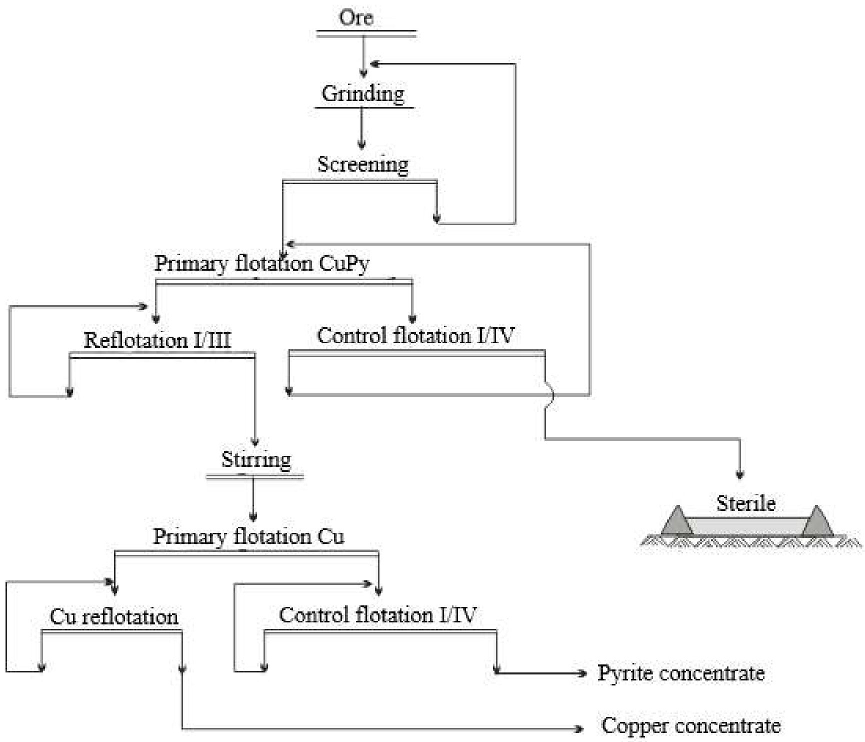

Fig. 4. *The technological flow of compact copper ore processing from Bălan*

4.5. Technology for processing polymetallic ores of lead, copper, zinc and sulfur

Sulfurous ore shave a complex mineralogical composition, but as minerals with industrial value are considered chalcopyrite, galena, sphalerite, pyrite, precious metals and dispersed elements. Silica, carbonates and clay minerals can be mentioned as gangue minerals.

In Romania, the preparation of complex lead, copper, zinc and sulfur ores is applied to the preparation facilities in Rodna, Herja, Şuior, Gura Băii, Baia Sprie and Săsar.

The technological flow for the preparation of the polymetallic complex ore from Şuior is presented in figure 5.

The ore contains sphalerite, galena, pyrite, chalcopyrite, marcasite, silver sulpho salts, tetrahedrite in quartzgangue, limonite, calcite

The ore extracted from the mine is transported to the preparation plant with th ehelp of dumpers. The milling finenes sachieved in the first stageis 60% -0,074 µm. For the first stage of flotation milling, sodium cyanide is used as a depressant and sodium carbonate like environment regulator, and ethylxanthate mixed with amylxanthate ratio 1 / 1 isused as collector. Depression of zinc-bearing minerals is achieved by the use of zinc carbonate resulting from the reactionbetween zinc sulphate and sodium carbonate. In addition, sodium sulfite is added as a depressant.

It is worth mentioning that the flotation scheme that was applied with in this plantis of the collective-collective type selective in the sense that the copper and lead minerals are floated in a collective chalcopyrite - galena concentrate, and the zinc and sulfur minerals are floated in a blending-pyrite collective concentrate. At the end of the first flotation stage, the slurry is recirculated to the milling section, where it is hydrocyclonee dusing a 350 mm diameter hydrocyclone. This hydrocyclone is also feed by these condmillexhaust, and the thickening of the hydrocyclone is reintroduced intothe ball mill. The overflow of the hydrocyclone with a milling fineness of 75% - 0.074 μm constitutes the supply of these condstage of collective flotation galena - chalcopyrite. The chalcopyrite-galene collective concentrate obtained from the primary flotation circuit i subjected to theen richment flotation to which is added depressant in theform of zinc carbonate and sodium thiosulphate.

The selective chalcopyrite-galene flotation is performed after the desorption of the collecting reagents from the surfaces using sodium sulphide and the activated carbon. The galena is depressed with potassium chromate and caustic starch, and chalcopyrite is floated too btain the copper concentrate. The unflotated product from selective flotation thicken sand constitutes the lead concentrate.

After the collective flotation of the galena and the chalcopyrite, copper sulphateisadded as an activator for the flotation of the sphalerite and pyrite and in the presence of the same mixture of collectors the collective concentrate of the blend – pyrite is floated.

The sphalerite-pyrite collective concentrate is subjected to selective flotation in which pyrite is depressed with lime at pH = 11 and the blended is flushed to obtain the zinc concentrate. The chamber product (unflotated) resulting from the collective sphalerite – pyrite flotation is discharged as sterile, and the room product from the sphalerite - pyrite selective flotation constitutes the pyrite concentrate.

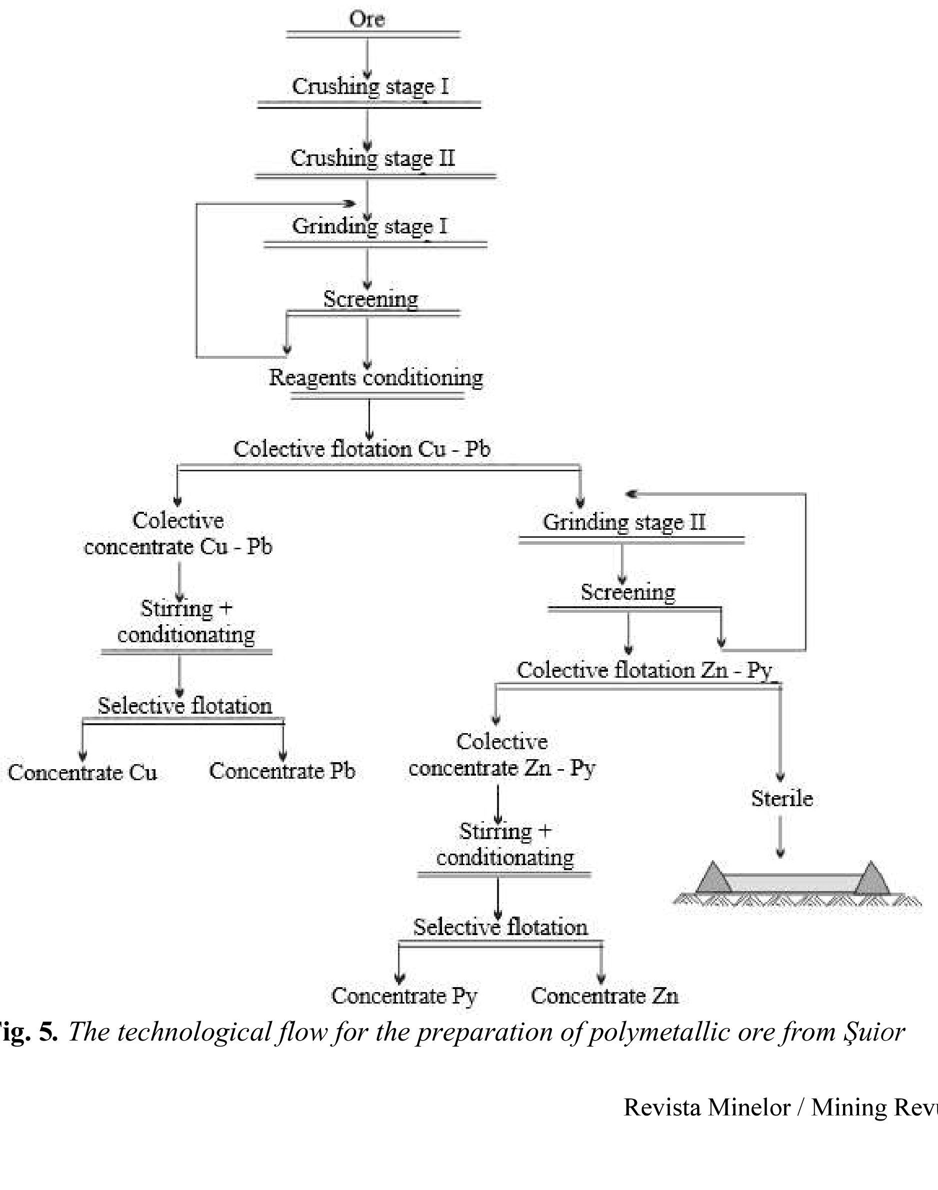

Fig. 5. *The technological flow for the preparation of polymetallic ore from Şuior*

4.6.The Altân Tepe tailings ponds belonging to processing plant

Location, year of commencement and end of pondactivity, material volume and safety class.

- The Altân Tepe - Iaz I settling pond was put into operation in 1971, storing sterile 0.57 mil. m^3, the dam height being 3m. The importance class of this dam is III.

- Altân Tepe - Iaz II settling pond was put into operation in 1992, storing sterile 0.1 mil. m^3, the dam height being 3m. The importance class of this dam is IV.

Processing technology and source of the material from the tailings ponds at ALTÂN TEPE plant. The copper deposit at Altân Tepe was exploited underground, being considered the one with the richcopper deposit in Romania with a metal content of approximately 3% Cu.

It is a deposit containing pyrite and magnetite which is associated with chalcopyrite, bornite, covelline. In the impregnations, predominates pyrite, which appears in the form of isolated crystals, small nests or even smalllenses that is accompanied by magnetite and chalcopyrite. Following the preparation, concentrates with 14-16% Cu and 38-40% S were obtained.

5. Conclusions

In order to obtain high metallurgical extractions, it is necessary to obtain copper concentrates with as high a metal content as possible, in order to achieve this goal it is necessary to process the ores.

For compact sulfuric copper ores, the concentration method is by flotation, in an alkaline medium (fig. 4), obtaining a concentrate with a copper content of 15.3%, and a metal extraction in concentrate of 88.7%.

Impregnating copper ores from porphyry or stratiform deposits, the method of concentration is by flotation in a weakly alkaline medium, with xanthates, (fig.1 and fig.3), obtaining a copper concentrate with a metal content of 24% and an 80% metal extraction.

When capitalizing on complex ores (fig. 5), the aim is to obtain distinct concentrates of Cu, Pb, Zn, Py, applying the double collective-selective flotation scheme.

Copper deposits in our country are characterizedby a low metal content (even below 0.25% Cu), therefore, although there are appreciable resources of copper ore of about 443 million tons, there are no technological facilities for processing copper ore, they were closed and then demolished due to the low recovery efficiency of copper from the ore.

Also, the profitability of viable mines requires a large investment contribution for reopening and refurbishment.

There are open pit operations whose opening and preparation works are suitable for the application of modern exploitation technologies, there is also the possibility of achieving technological concentrations such as: a preparation plant – several sources; - the association, in general, of copper minerals with other secondary elements (gold-silver, criticalminerals, etc.) (Roșia Poieni mining)

Market studies show a potential for rising prices for copper ores as well as positive social consequences on communities to a possible resumption of mining and processing of copper minerals in our country.

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