LEACHING AND FLOTATION OF CONCENTRATE AND MIDDILGS IN FLOTATION CIRCuits OF CARBONATE - SHALE COPPER ORES
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ABSTRACT
An innovative hybrid technology for beneficiation of difficult-to-process sedimentary copper ores comprising acidic leaching stage of the feed combined with subsequent flotation has been presented. Acidic leaching, preceding the flotation process, plays a beneficial role of efficient chemical grinding for liberation of copper sulphide minerals finely disseminated in the copper-bearing carbonate-shale rocks. The process was applied on a fully industrial scale. Flotation results were analysed for both chemically modified and unmodified flotation feeds. After several months of industrial scale operation, it was found that both metals recovery and concentrate grade remarkably increased as a result of application of chemical modification of the flotation feed. Beneficial effects of chemical pre-treatment of flotation middlings on selectivity at a comparable concentrate yield in industrial flotation scale, revealed a considerable increase of the total copper recovery by 3.5 percent. Based on the industrial and laboratory investigations we consider a further development of the process and introduction of hydrometallurgy for better recovering of metals from low-grade copper concentrates.

Keywords: flotation hybrid technology, copper carbonate ores, feed acidic leaching

INTRODUCTION
Technological systems applied in mineral processing are becoming increasingly complex due to deteriorating process feed properties, complex mineralogical composition and declining content of valuable components. The observed global decrease of the quality of primary metal-bearing ores and a need for enhancement of metals production effectiveness result in growing complexity of technological circuits. Moreover, the observed declining of ores grade is frequently accompanied by growing difficulties in their upgradeability.

Application of chemical unit operations for modification of either flotation feeds or by-products in the flotation circuits provides a better utilization of low grade and hard-to-process ores. Iwasaki (1976) as well as Iwasaki and Prasad (1989) reviewed details of processing methods of hard-to-treat metals ores. They demonstrated that hybrid processes combining standard processing operations with chemical treatment of the feed, which usually utilize operations well known in chemical metallurgy, would be extensively applied in the upcoming years and by the end of the 21st century, they will dominate the processing technologies for metal-bearing ores. According to Cramer (2003), hydrometallurgical methods offer significantly reduced production costs with regard to standard methods based on flotation and pyrometallurgy (smelting). It is of particularly great significance during periods of economical fall, when metals prices are very low.

Lower processing costs play a significant role in utilization of primary ores with declining quality as well as in processing of secondary and waste materials, mainly from mining and metallurgy. Beneficiation of such materials

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for metals recovery requires elaboration of new more technologically advanced methods of processing in comparison to the currently used techniques. Accumulation of mineral wastes, which are either mining tailings or mineral processing wastes, are frequently considered as anthropogenic metals resources. Their categorization and utilization require similar regulations as for primary resources.

According to Iwasaki and Prasad (1989), introduction of chemical operations in physical processing of raw materials, and application of physical operations in chemical processes leads to notable simplification of technological flow-sheets and makes the resulting hybrid processes far less expensive. In the review of processing methods for hard-to-treat ores Tong and Jiayong (1991) presented basic criteria for selection of hybrid technologies for processing of continuously declining-in-quality ores and other raw materials, which contemporary civilization has to apply as metals resources.

Flotation technologies, combined with chemical treatment as a supporting operation for leaching of components, which are either hardly-upgradeable or unbearable for beneficiation, are most frequently described in the literature. Examples of application of chemical treatment of flotation feed or middlings within the flotation circuit of base metals are already known and have also been presented, and analyzed since the first half of the 20th century. In fact, such methods are used quite frequently. However, their details are either seldom disclosed in easy-to-access documents and papers or protected by patents. The details of such technologies are not available in handbooks and monographs on mineral processing or hydrometallurgy. Only Gaudin (1957), Glembockij et al (1961) and Mitrofanov et al (1984) presented a few examples of hybrid methods for processing of partially oxidized sulphide copper ores.

The presented above facts indicate, that technological advances based on a combination of chemical and physical methods are barely known among mineral processing specialists. In the latest period of development of hydrometallurgy, many new ideas have to be subjected to frequent and dynamic changes. However, a lack of sufficient knowledge on appropriate selection of proper materials for machinery construction as well as improper managing procedures and process control, create a barrier for the development of new ideas (Bergh et al, 2001). This is a result of insufficient understanding of basic aspects of modern hybrid processes based on chemistry, hydrometallurgy and physicochemical methods such as flotation.

Described and evaluated in this work hybrid process combines flotation with sulphuric acid leaching of the feed. This hybrid process is called FLF (Flotation-Leaching-Flotation) and has been already applied on industrial scale. In the literature, only few such hybrid processes have been discussed and they deal with a controlled removal of magnesium from sphalerite concentrates with sulphuric acid (Szolomicki 1995; Cichy et al, 2007; Gorman et al, 1976; Yigit and Saridede, 2010). A typical hybrid process, which combines ammonia leaching of chalcocite concentrates with subsequent flotation of preleached solids, was applied by Escondida (Chile) and was described by Duyvesteyn and Sabacky (1995). Liu et al (2011) investigated the process of flotation and leaching of low grade middlings in the circuit of beneficiation of carbonate copper ore in the Yunnan province of China.

The sedimentary Polish copper deposits of LGOM (Legnica - Glogow Copper Basin) located in SW Poland has a complex nature (Rydzewski 1996; Niec and Piestrzynski 1996). The ores consists of three lithological layers: easy-upgradeable and low grade (<1% Cu) sandstone, fairy-upgradeable carbonate (0.5 – 1.5% Cu), and poorly-upgradeable clay-dolomitic-bituminous black shale (>2% Cu). A mixture of these three totally different lithological types is the feed for processing in concentrators. Among the three ore fractions, the black shale reveals two exceptional and contradictory properties. It exhibits the highest concentrations of copper (>2%) and accompanying metals (Ag, Ni, Co, Zn, Pb, V, Mo…) but simultaneously is the most troublesome in terms of flotation upgradeability. Moreover, the metal sulphides present in the shale fraction are finally disseminated in the carbonate matter and in the black shale-clay material. Such a fine dissemination of copper sulphides in the carbonate-organic matrix considerably reduces the susceptibility of the ore to both effective sulphides liberation and froth flotation. This essentially affects the declining copper content in flotation concentrates and lowers recovery of metal. It is also the main reason of growing cost of copper production (Konieczny et al, 2009). Therefore, the standard methods of beneficiation appear to be insufficient and it became necessary to apply new FLF technology to enhance the minerals liberation by chemical leaching with H2SO4 and to elevate flotation results indices.

In our previous papers comprehensive investigations on application of a chemical pre-treatment of the flotation feed with sulphuric acid for a part of the poorly-upgradeable material (flotation middlings) have been described (Luszczkiewicz and Chmielewski 2006, 2008; Chmielewski and Luszczkiewicz 2002, 2010; Chmielewski et al, 2010). The final effect of these long term investigations was construction of an industrial scale FLF facility. A clay-
carbonate fraction of the ore was separated from the plant flotation circuit. This fraction is hard-to-upgrade in the existing standard process operations and overloads the process circuits due to very fine dissemination of the metal-bearing sulphides, difficulties in their liberation during standard milling, and high content of easily-floating organic matter. The separated troublesome fraction is then subjected to a controlled acidic pretreatment with sulphuric acid in stirred reactors prior the flotation. The result of the chemical pretreatment operation is about 70% decomposition of the carbonate matrix and effective chemical liberation of the metal sulphides. The pulp, after leaching, exhibits much better flotation properties and is subsequently returned to the flotation system in order to separate gypsum created during leaching and finally to the cleaning flotation stage. Cleaning flotation of the material after gypsum separation is the final stage of the FLF system.

The aim of the paper is presentation and evaluation of a unique FLF chemical modification process applied on an industrial scale within the existing flotation circuit to assess the selectivity of the applied beneficiation process to carbonate fraction from the Polish copper ore. A special procedure, called here flotation analysis, was used for a quantitative evaluation of flotation efficiency. An additional evaluation of the flotation system based on chemical modification facility (FLF) was performed by comparing final flotation results of the system with results of a parallel standard flotation system without feed chemical pre-treatment.

EXPERIMENTAL

Materials and methods

Results of investigations presented in this paper comprise two data series from industrial scale tests. First, we present the data collected during a sampling campaign of the 1st technological circuit at the Polkowice concentrator. Next, the data regarding statistically processed flotation results in the 1st flotation line at the Polkowice concentrator performed with chemical modification of the middlings in the FLF system (refer Figure 1) are shown and compared with flotation results of the 2nd flotation line (refer Figure 2). The 2nd line utilizes the same material in the feed as the 1st line and operates in the same parallel system as 1st line, but works without the chemical treatment. The final concentrate grade in both 1st and 2nd line was very similar (about 25%).

![Figure 1. The flowsheet of the 1st flotation line with chemical treatment of middlings (by-product from I cleaning) with sampling points indicated](image-url)
The materials examined according to the flotation analysis procedure were products samples taken from the commercial scale flotation circuit with the FLF chemical modification system (refer Figure 1). The samples were subjected to laboratory scale flotation tests and process mass balances were calculated. On the basis of the industrial scale and laboratory data, it was possible to draw upgrading curves for the examined feeds.

Figure 2. The flowsheet of the 2nd flotation line (standard process without chemical treatment of middlings)

Two sampling campaigns were carried out for the flotation analysis. In the first campaign, at the beginning of the FLF process, the carbonates decomposition degree ($R_w$) was 26%. In the second campaign, $R_w$ was kept at the level of 86%. The carbonates decomposition degree $R_w$ was always below 100%. It means that the amount of sulphuric acid introduced to the FLF plant has to be strictly controlled at the level not exceeding the total decomposition of the carbonate matter.

The flotation analysis procedure of the product samples from the technological FLF node consisted of laboratory flotation of the examined samples collected from the flotation circuit (sampling points indicated in Figure 1). The flotation experiments were carried out in a 1-liter Mekhanobr type self-aeration laboratory flotation machine according to the scheme shown in Figure 3 (Sobierajski et al, 2006). Collected flotation results of fractional flotation for all samples were then arranged according to the increasing metal content in the products (refer Figure 3). From these data, it was possible to draw floatability curves for the industrial process.

Figure 3. The scheme of laboratory flotation experiments for samples taken from the industrial process in sampling points indicated in Figure 1
The following materials were subjected to flotation analysis (refer Figure 1):

- Feed M1 for leaching with sulphuric acid when $R_w = 26\%$
- Feed M1 for leaching with sulphuric acid when $R_w = 86\%$
- Concentrates C1 and C2 from de-gypsing flotation
- Concentrate C3 from scavenger de-gypsing flotation
- Tails T11 from scavenger de-gypsing flotation

**RESULTS AND DISCUSSION**

Results of the flotation analysis experiments for samples taken at the sampling points indicated in Figure 1 are presented both in the form of the Halbich grade-recovery and Fuerstenau recovery-recovery upgrading curves. The Fuerstenau curves, plotted according to the procedure described by Drzymala and Ahmed (2005), represent a relationship between recovery of valuable component in concentrate (Cu) and recovery of a second component (barren part of the ore) in the tailing. This upgrading curve allows comparing enrichment of different components of various ores having different feed composition in one graph. The plots in Figures 4 and 5 represent the floatability curves for four products samples from the industrial FLF node.

The floatability curves for a sample of the feed subjected to leaching process (sampling point M1, Figure 1) are shown in Figures 4 and 5. The curve for $R_w = 86\%$ indicates that the feed after leaching with $H_2SO_4$ exhibits evidently better floatability in comparison with the untreated feed, which was used for the acidic pre-treatment with $R_w = 26\%$. This is a result of circulation of the flotation products, predominantly the C2 and C3 products, which were returned to the upstream operations, that is to rougher-scavenger and 1st cleaning operations.

The floatability curves for the material previously leached at $R_w = 26\%$ and $86\%$ clearly describe an increasing effectiveness of flotation of the pre-treated feed and it can be quantitatively compared with upgradeability of the standard untreated material. According to Figure 4, for the standard 1st cleaning concentrate quality having 10% Cu, the observed copper recovery was 30%. The Cu recovery increased remarkably to 50% when the feed for the process was pre-leached at $R_w = 86\%$. The flotation analysis of whole leached material (C2, C3, T1) at the concentrate quality of 1st cleaning indicates the copper recovery of 70% for $R_w = 26\%$ and above 90% for $R_w = 86\%$, respectively. Curves in Figure 5A show a pronounced improvement of floatability of the leached material in comparison with the unleached feed. In the Fuerstenau diagram, the upper and right axes represent theoretical limits of ideal upgradeability. A higher convexity of a curve towards the upper right corner of the diagram indicates better upgradeability of the investigated material and higher selectivity of flotation. This is a result of a better liberation of the sulphide minerals from the carbonate matrix accomplished by the chemical treatment. The acidic leaching appears to be much precise in liberation of the sulphide minerals in relation to the mechanical milling. It was described in our previous papers (Luszczkiewicz and Chmielewski 2006, 2008; Chmielewski and Luszczkiewicz 2002, 2010; Chmielewski et al, 2008).

Figure 6 presents a comparison of flotation efficiency of two independent parallel technological flotation lines at the Polkowice concentrator processing similar feeds and very similar concentrate grade (about 25% Cu). The 1st line was equipped with the FLF system for middlings from 1st cleaning with carbonate decomposition grade within the range of 40 – 86%. The 2nd line represents a standard process, as it was shown in Figure 2. The data used for the construction the relationships shown in Figure 6 represent final flotation results (copper recovery and weight percent that is concentrate yield) for 3 work shifts daily during 30 days of process operation.

The regression lines in Figure 6 evidently indicate that the Cu recovery increases remarkably in the flotation system equipped with the FLF facility for the chemically treated middlings.

It can be calculated from data shown in Figure 6. that at constant copper content in the concentrate equal to 25.3% Cu the copper recovery increases by about 3.5% for 1st flotation line representing the FLF process in regards to the 2nd line without chemical treatment.
Figure 4. Grade-recovery curves based on the flotation analysis method for industrial products samples selected from FLF node (refer Figure. 1)

Figure 5. Furestenau recovery-recovery curves based on the flotation analysis method for industrial products samples selected from FLF node (refer Figure. 1)
Figure 6. A comparison of final flotation results of two parallel technological lines: 1st – with chemical treatment of the feed, 2nd – standard process without treatment (3 work shifts daily during 30 days of process operation). The Cu content for all data point

CONCLUSIONS

Application of a new leaching hybrid FLF process, involving sulphuric acid treatment of flotation middlings combined with a subsequent flotation in the commercial system of beneficiation of Polish sedimentary copper ores resulted in a significant increase of the process selectivity. This was shown by means of an originally designed methodology, referred in the paper to as the flotation analysis, which is a special procedure of evaluation of sampled material in laboratory experiments. To characterize the process quantitatively, the floatability curves were generated using the experimental data in order to evaluate the efficiency of the process for both, with and without, chemical pre-treatments. A beneficial effect of the chemical pre-treatment of the flotation middlings on flotation selectivity was shown by means of floatability curves for the unleached and leached feeds. This beneficial effect was previously explained by the authors in earlier papers as intensive liberation of the sulphide minerals by selective chemical decomposition of the carbonate matter. It was found that the application of the FLF process on the industrial scale resulted in an increase of copper recovery by 3.5% at approximately constant copper content in the concentrate equal to about 25%.

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