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PRE-FLOTATION LEACHING OF POLISH CARBONATE COPPER ORE

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The copper ore deposit of LGOM (Legnica-Glogow Copper Basin) is located in the Foresudetic Monocline (SW Poland) and has a polymetallic character because of content of silver, lead, copper and accompanying metals such as cobalt, zinc, nickel, rhenium and gold. Over 110 metalliferous minerals were identified in the deposit. A sedimentary nature of the deposit results in necessity of fine grinding for effective liberation of sulfide particles prior to flotation. Fine dissemination of metalliferous minerals, particularly in the carbonate type ore, considerably reduces the susceptibility to effective liberation. A beneficial effect of non-oxidative leaching of carbonate gangue with sulfuric acid on copper ore flotation was presented in the paper. It was shown that the non-oxidative leaching of the flotation feed is a selective process leading to liberation of sulfide minerals disseminated in the gangue carbonate matrix. Acid leaching causes chemical decomposition of carbonate matter and releases fine grains of copper minerals. Kinetics of leaching of the investigated ore sample with various amounts of sulfuric acid were presented. It was shown that after decomposition of 70% of carbonates in the flotation feed, metal recovery and concentrate grade increased remarkable in comparison to the results observed for the unleached feed. The products of leaching contain solid hydrated calcium sulfate (gypsum), soluble magnesium sulfate and gaseous carbon dioxide. Carbon dioxide evolving during the reaction creates a non-oxidizing atmosphere in the pulp during leaching and therefore effectively prevents digestion of metals from sulfide minerals. The liberation of copper minerals due to leaching provides better separation of metallic ore components by flotation.

key words: leaching, flotation, carbonate copper

INTRODUCTION

The Polish copper ore deposit of the Foresudetic Monocline is rather difficult-to-process due to a specific mineralogical composition, presence of three different

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lithological layers and fine size of sulfide minerals. In the mined ores of the Legnica-Glogow Copper Basin, the copper-bearing sulfide minerals are present in three layers: dolomitic, sandstone and shale (Piestrzynski and Zalewska-Kuczmierczyk, 1996). Principal carriers of copper minerals are chalcocite (Cu_2S), bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), and covellite (CuS). Chalcocite is the major copper sulfide mineral that dominates in the deposit. Some ores require very fine grinding for efficient liberation of sulfide minerals prior to flotation because of fine sulfide grains which are disseminated in carbonate matrix mainly as complicated intergrowths.

The efficiency of the flotation process of copper-bearing minerals depends on the degree of liberation of sulfide minerals from gangue, which is most often accomplished during comminution. One of the concepts of treatment of copper ores, especially their carbonate fraction, suggests selective decomposition of gangue using sulfuric acid. Non-oxidative leaching of copper ore in an oxygen-free atmosphere seems to be a very efficient process for enhancement of the metal recovery.

NON-OXIDATIVE LEACHING

Selective leaching of the copper ore is based on chemical reactions between sulfuric acid and calcium as well as magnesium carbonate minerals (dolomite). Dolomite is a dominating gangue component of the Polish copper ores. This process, called either acid leaching or non-oxidative leaching, relies on treatment of the ore with less-than-stoichiometric amount of H_2SO_4 required for a total decomposition of carbonates. The amount of sulfuric acid applied in the leaching corresponds to the content of carbonates in the ore and must be controlled to maintain the final pH of the suspension on a proper level. Products of the decomposition of dolomite are solid hydrated calcium sulfate (gypsum $CaSO_4{\cdot}2H_2O$), soluble magnesium sulfate ($MgSO_4$), and gaseous carbon dioxide (CO_2). The following chemical reactions describe the non-oxidative leaching:

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2\uparrow + H_2O \tag{1}$$

$$3CaCO_3 + 3H_2SO_4 = 3CaSO_4 \cdot 2H_2O + 3CO_2\uparrow + H_2O \tag{2}$$

Carbon dioxide evolving during the reaction creates a non-oxidizing atmosphere in the slurry during leaching, and therefore effectively prevents the leaching of metals from the sulfide minerals (Chmielewski, 2007). Saturation of the slurry with CO_2 assures selective leaching of only carbonates. Liberation of sulfide minerals from the gangue minerals, when applying sulfuric acid, is rapid, mainly at the first stage of the process and it can be performed at ambient temperature in a standard reactor equipped with mechanical stirring.

A selective chemical digestion of dolomite is shown schematically on Figure 1.

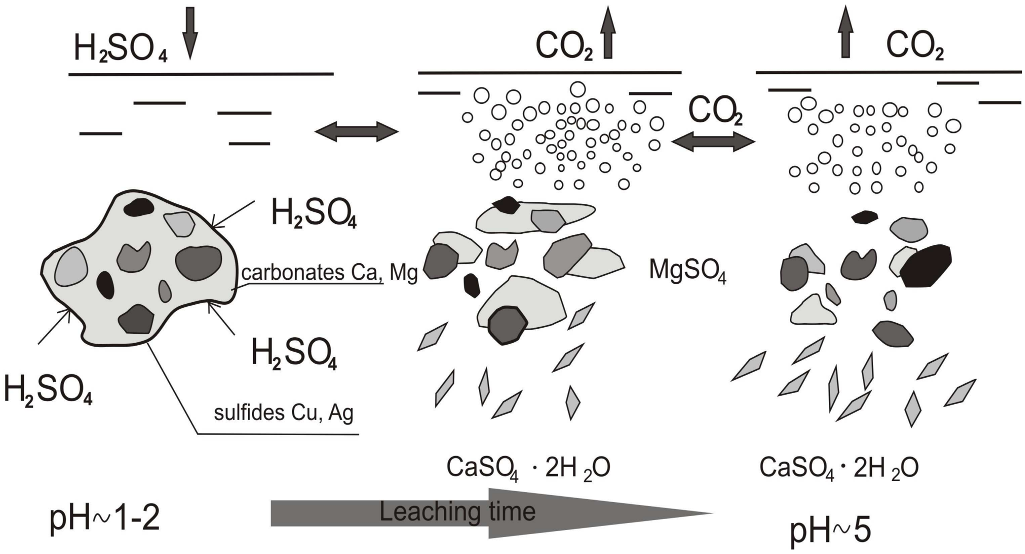

Fig. 1. A selective chemical decomposition of carbonate-sulfide intergrowths during non-oxidative leaching with sulphuric acid (Luszczkiewicz and Chmielewski, 2006)

Leaching of the flotation feed with H_2SO_4 reduces the size of particles due to liberation of the gangue minerals from the copper-bearing minerals. A low energy-consumption of the size reduction process is an important feature of this process in comparison to conventional methods of mechanical grinding. Traditional methods of grinding are not able to liberate fine minerals without overgrinding of already liberated copper sulfide minerals because overgrinding makes the flotation nonselective.

The amount of sulfuric acid required for leaching of dolomite is determined by the mass of sulfuric acid necessary for the total decomposition of carbonates present in 1 kg of the dry solid feed ($z_{H_2SO_4}^{\max}$). The content of carbonates in the investigated feed was determined analytically utilizing a laboratory procedure. I was calculated that 154 g H_2SO_4 / kg of dry solid feed is needed for their decomposition. A 70–80 % decomposition of carbonates by leaching was found to be satisfactory for subsequent flotation. The final pH of the slurry should be was maintained at about 5 (Chmielewski, 2007).

MATERIALS AND METHODS

The material used in laboratory investigations during the acid non-oxidative leaching was a copper ore from the Rudna Concentrator. The feed for all experiments contained about 90 % of particles below 75 µm in size. The material prepared in such a way was subjected to acidic leaching and subsequently to flotation. The flotation experiments were carried in the "Mekhanobr" mechanical laboratory flotation machine which was equipped with a 1 dm^3 cell. Standard flotation reagents were applied. The laboratory investigations were performed under constant conditions during flotation. The acid leaching with concentrated acid (95 % H_2SO_4) was performed in a glass reactor applying intensive mechanical stirring of the suspension. Total time of decomposing 70 % of carbonates in sulfide concentrate was 60 minutes. The scheme of laboratory experiments of unleached and leached materials is shown in Figure 2. The pH and redox potential were measured during flotation tests using a combination electrode. Under controlled conditions of the E potential it is possible to reach maximum recovery of copper at E about 0.2V (NEW) (Lekki, 1996). For the unleached material the pH varied from 7.1 to 7.6 and for leached material from 6.1 to 6.8.

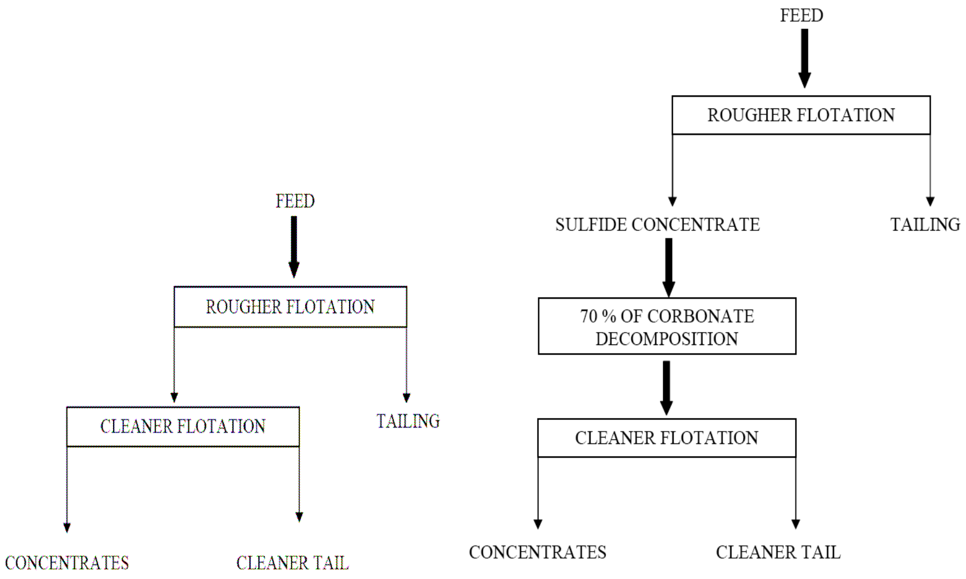

Fig. 2. Scheme of laboratory investigations

RESULTS

The kinetics of non-oxidative leaching of the feed was investigated by measuring the pH and redox potential as a function of reaction time. The redox potential and pH-time curves depended on the used amount of sulphuric acid. The leaching kinetics of the feed were investigated at various degrees, from 30 to 100 %, of carbonates decomposition. Figure 3 illustrates a relationships between the pH and leaching time of the investigated ore.

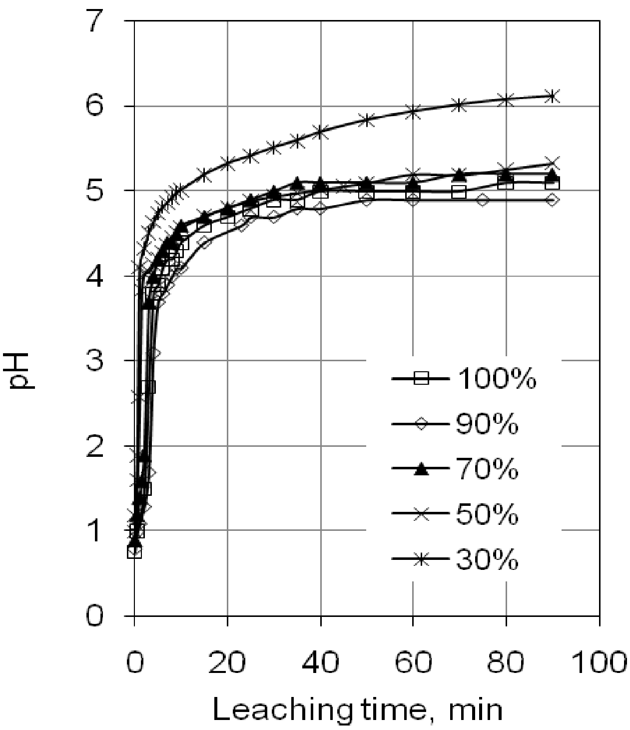

Fig. 3. pH-time relationship for non-oxidative leaching. Copper ore at various degrees of carbonate decomposition (from 30 to 100 %) was investigated

The leaching process appeared to be very rapid. After 5–10 minutes the pH of the slurry was equal to 4. It can be assume that further increase of the pH was caused by CO_2 removal from the slurry.

It can be seen from Figure 4 that pH-time carbonate decomposition kinetics can be well related to the redox potential at the initial stage of the process. A significant decrease of the redox potential from about 360 mV to about 140 mV was observed after introduction of H_2SO_4 to the feed slurry. The leaching was completed when the acid was used up. At that point the suspension's pH was around 5. The constant values of the pH and redox potential were resulted from the saturation of the solution with CO_2. They permit to determine the direction of reaction and control of the non-oxidative leaching. The potential of the combination electrode, valid for Ag/AgCl reference system, during non-oxidative leaching at 100 % carbonate decoposition is shown in Figure 4.

Undoubtedly, the presence of carbon dioxide in the leaching suspension caused the red-ox potential to drop.

Flotation of the unleached material was performed to compare reference results for the outcome achieved by flotation after acid leaching. The results of flotation experiments are given in tables 1 and 2 and in Figure 5.

A relationship between separation parameters, recovery of copper in the concentrate and recovery of remaining (non-copper) components, also called ~~as~~ the Fuerstenau upgrading curve (Drzymala and Ahmed, 2005) is shown in Figure 5. Fuerstenau's curves can be plotted in one graph for different recoveries of various ores, which metal contents in the feed are at different levels.

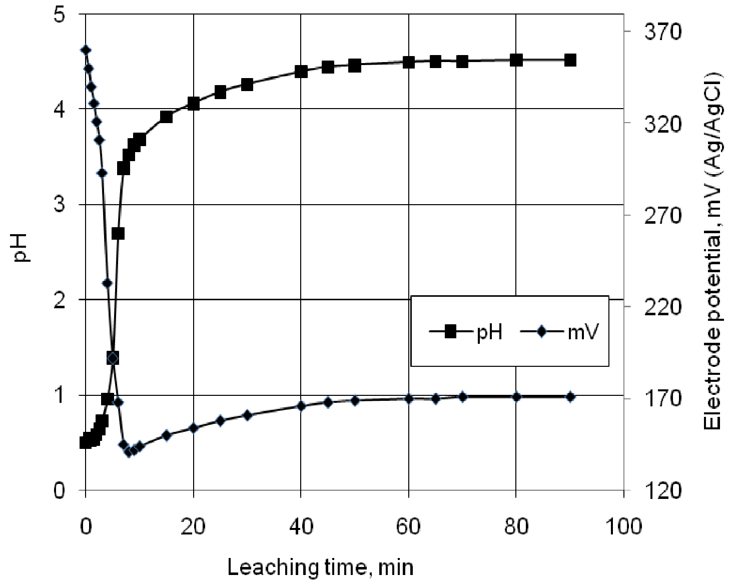

Fig. 4. Potential of combination electrode, valid for Ag/AgCl reference system, during non-oxidative leaching

Table 1. Results of reference flotation

Product	Yield, %	Copper content, %	Copper recovery, %
C-1	1.27	15.54	12.03
C-2	1.66	15.87	16.05
C-3	4.31	12.95	33.95
Cleaning tail	10.44	4.16	26.45
Tailing	82.32	0.23	11.53
Feed (calculated)	100.00	1.64	
Feed assay		1.47	

During comparing leached and unleached materials, it was noticed that both copper content in the concentrate and copper recovery of leached material were higher by 1.5% and 0.9% in the leach feed, respectively. All comparisons were performed for a constant recovery of 88% and a constant yield of 16%.

Table 2. Flotation results of feed after acid leaching

Product	Yield, %	Copper content, %	Copper recovery, %
C-1	1.41	31.04	25.85
C-2	1.89	22.84	25.44
C-3	2.72	12.90	20.71
Cleaning tail	10.13	2.78	16.62
Tailing	83.85	0.23	11.38
Feed calculate	100.00	1.69	
Feed assay		1.47	

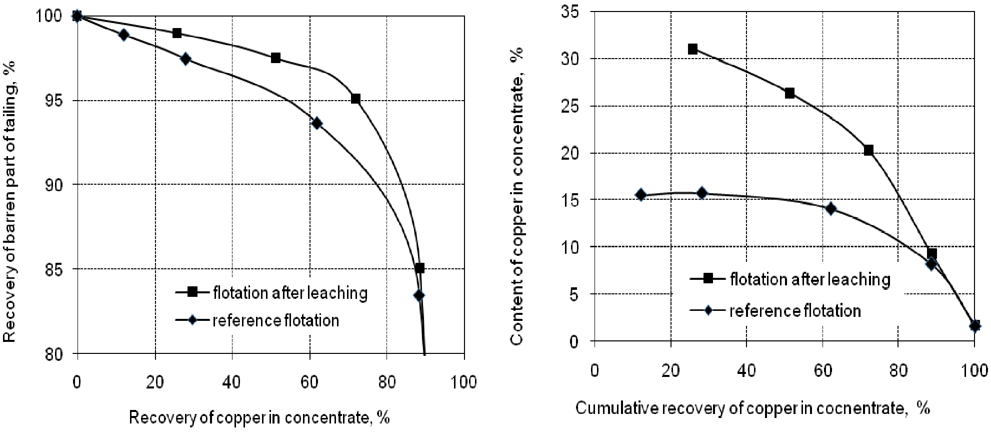

Fig. 5. A section of upgrading curves of copper ore flotation for unleached and leached feeds. Based on date from Table 1 and 2

CONCLUSSION

A beneficial influence of acid leaching on the enrichment of Polish copper ore in comparison with the unleached material was noticed. A 70% decomposition of carbonate of the flotation feed leads to an enhanced recovery and content of copper in the concentrate. The leaching of the flotation feed with H_2SO_4 can be used as an effective operation for selective liberation of sulfide minerals. Carbon dioxide evolving during the reaction of sulfuric acid with carbonate gangue creates beneficially non-oxidative conditions, preventing the digestion of metals from sulfide minerals.

The pH and redox potential permit to determine the direction of reaction and control the non-oxidative leaching.

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Przedstawiono wpływ kwaśnego ługowania krajowej rudy węglanowej za pomocą kwasu siarkowego. Głównym celem procesu jest uwolnienie minerałów miedzionośnych, które są rozproszone i zamknięte w skale węglanowej w postaci drobnych wpryśnięć i zrostów. Dolomit w złożach Legnicko-Głogowskiego Okręgu Miedziowego stanowi główny składnik skały płonnej. Kwaśne ługowanie zapewnia rozkład minerałów węglanowych i gwarantuje skuteczne uwalnianie ziarn kruszcowych. W wyniku rozkładu skały węglanowej powstaje krystaliczny gips ($CaSO_4 \cdot 2H_2O$), rozpuszczalny siarczan magnezu ($MgSO_4$) oraz ditlenek węgla (CO_2). Wydzielający się podczas ługowania CO_2 tworzy w zawiesinie warunki nieutleniające i zabezpiecza mieszaninę przed dostępem tlenu, utleniaczem minerałów siarczkowych. Dzięki selektywnemu rozkładowi minerałów węglanowych następuje podwyższenie wskaźników flotacji w porównaniu z nadawą nieługowaną. Zaleta tego procesu jest również wykorzystanie stężonego kwasu siarkowego do chemicznej obróbki. Pozwala to na zagospodarowanie dużych ilości tego kwasu, co jest istotne w okresie malejącego popytu na ten produkt.

słowa kluczowe: ługowanie, flotacja, ruda węglanowa