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NON-OXIDATIVE LEACHING OF BLACK SHALE COPPER ORE FROM LUBIN MINE

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The beneficial effect of leaching of carbonate gangue of flotation middlings (tailings from 1st cleaning at Lubin Concentrator) with sulfuric acid prior to their final flotation, leaching or bioleaching has been presented. The leaching of flotation feed with sulfuric acid decomposes selectively the carbonate gangue and leads to liberation of sulfide minerals and enhanced flotation or leaching results. It was shown, that after decomposing of 50-70% of carbonates in flotation feed, both flotation recovery and concentrate grade increased considerably versus the results observed for unleached feed. Products of acidic leaching comprise gypsum, soluble magnesium sulfate and gaseous carbon dioxide. Carbon dioxide evolving during the reaction creates the non-oxidizing atmosphere in the pulp during leaching and therefore effectively prevents the digestion of metals from sulfide minerals. The beneficial effect of acidic leaching on flotation was evidently confirmed in pilot tests performed on several feed materials. The application of sulfuric acid leaching of flotation feed produced an enhancement of flotation results (metal recovery and concentrate grade) and provided a rational use of H₂SO₄, which becomes a troublesome and difficult-to-sale product of copper metallurgy. Non-oxidative leaching has to be unquestionably applied prior to the atmospheric, pressure or bio-leaching in acidic conditions.

Key words: copper ores, black shale, non-oxidative leaching

INTRODUCTION

Sedimentary nature of Polish copper deposits (LGOM - Legnica-Glogow Copper Basin, SW Poland) results in the presence of three ore fractions: dolomitic, sandstone, and shale. Most of sulphidic ores require exceptionally fine milling for efficient liberation of sulphide particles prior flotation. This is due to dissemination of fine metal sulfides in carbonate matter and in black shale-clay rocks that form the majority of the gangue. Dissemination of fine copper sulfides in carbonate matrix reduces considerably the susceptibility of the ore to effective liberation of metal-bearing

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minerals. A relative increase of fraction of shale-clays and carbonates in flotation feeds, which are known as mostly hard-to-treat in flotation circuits, is currently observed in Polish copper industry.

The genesis, lithology, geochemistry, mineralogical composition and observed properties of black shales in flotation circuits of Polish copper industry are unique with regard to carbonate and sand fractions (Konstantynowicz, 1990; Rydzewski, 1996). Black shale ores are mostly non-uniform material and the thickness of their layers in a deposit changes from 0.3 – 0.6 to even 1.7 m (Tomaszewski, 1985). The shale ore is composed of clay-dolomitic matter saturated with organic matter and with finely dispersed sulphide mineral particles. Black shale layers are the thinnest in the deposit but they represent on average 11 % of the ore in Rudna deposit, 17 % of Polkowice-Sieroszowice and 15 % of Lubin with growing tendency (Table 1). According to the latest data (Kubacz and Skorupska, 2007) the content of shale fraction in Lubin copper deposit has already reached 27 % and became the major problem in effective ore processing. The content of shale in Polish copper ores has almost doubled within last four years. Almost 64 % of all valuable metals and 60 % of their potential value are placed in shale fraction. It is interesting to mention that a high percentage of minor metals (above 75%) are concentrated in shale fraction.

Table 1. Distribution of the lithological ore layers and content of copper, silver, and organic carbon in feed of the KGHM copper concentrators in 2004 (Łuszczkiewicz 2004, Chmielewski, et al., 2007)

Content of ore fraction or component	Mine		
	Rudna	Polkowice - Sieroszowice	Lubin
Carbonate ore, %	33	75	25
Shale ore, %	11	17	15
Sand ore, %	56	8	60
Cu content, %	2.23	2.03	1.28
Ag content, g/Mg	53	40	67
TOC, %	1.49	1.66	1.62

The tendency of increase in the content of black shales in Polish copper ores is expected to be continued in forthcoming years. It is also known that with the shale content of 15 % for Lubin deposit, the share of copper and silver in the shale fraction was as high as 45 %. Near 80 % of organic carbon in the ore is concentrated in shale fraction. The content of organic carbon (TOC) in solids in flotation circuits is considered as a measure of shale concentration.

Complex mineralogical structure and chemical composition of Polish copper ores mined from sedimentary deposits are the principal reasons for rather high losses of copper, silver and other metals to flotation tailings. This additionally creates serious technical, economical and ecological issues. The selective liberation of these fine

particles would be the only way to enhance metal recovery. However, it appears to be either inefficient or very costly by physical methods in the existing milling circuits. Consequently, the hydrophilic gangue-sulphide intergrowths greatly reduce both flotation selectivity and the metal grade in the concentrate, particularly at Lubin Concentrator.

Table 2. The comparison of chemical composition of three lithological copper ore fractions: sandstone, shale, and dolomite in Polish copper deposits (KGHM, unpublished data)

Chemical component	Sandstone	Shale	Dolomite
SiO ₂ , %	69.82	30.63	19.03
Al ₂ O ₃ , %	4.22	10.01	6.18
CO ₂ , %	6.50	9.90	29.16
CaO, %	7.34	7.94	21.93
MgO, %	2.19	4.05	11.76
Na ₂ O, %	0.25	0.32	0.29
K ₂ O, %	1.11	2.18	1.34
C _{org} , %	0.40	8.04	0.72
S _S , %	0.82	2.64	0.71
S _S O ₃ , %	2.91	1.81	1.68
FeS ₃ , %	0.19	0.66	0.54
FeO, %	0.62	0.49	0.48
Fe ₂ O ₃ , %	0.53	1.01	0.74
MnO ₂ , %	0.16	0.15	0.29
Cu, %	2.67	10.48	2.10
Zn, %	0.04	0.078	0.03
Pb, %	0.05	0.41	0.14
Ag, g/Mg	29	186	58
Ni, g/Mg	46	278	60
Co, g/Mg	19	189	40
V, g/Mg	59	1204	120
Mo, g/Mg	40	255	30

Due to presently observed and forecasted unfavourable changes in mineralogical composition of the ore, the increase in grade of copper concentrates can be only accomplished by lowering the copper recovery. Therefore, it can be concluded that beneficiation technologies currently applied to Polish copper ores have already reached the limit of their technical efficiency. The only way to considerably reduce

observed losses of copper, silver, and other metals to the flotation tailing is a recognition and application of an entirely novel approach, involving major changes in the flotation circuits (Łuszczkiewicz, et al., 2006; Łuszczkiewicz and Chmielewski, 2006). This approach primarily involves the separation of the most troublesome shale fraction and application of hydrometallurgical and/or biometallurgical processes to its alternative, efficient processing. Such idea is the base of process alternatives suggested by BIOSHALE project partners (Chmielewski and Charewicz, 2006) and was recently seriously considered and discussed at ICNOP Conference (Grotowski, 2007).

Copper shale fraction exhibits substantially elevated concentrations of organic fraction, sulphidic sulphur, copper, silver and other metal values (Ni, Co, V, Mo, Pb, Zn) (Table 2). From the chemical analyses of numerous geological samples of shale ore we have found that the higher content of the organic matter implies the higher metal content in the shale (Chmielewski, et al., 2007). Separation of the organic shale rich fraction and its bio- or hydro-metallurgical processing seems to be the only reasonable way of effective recovering of all valuable metals from shale and reducing the observed metal losses.

Currently applied methods of ore mining and processing do not respect specific properties of the shale fraction, which is mined, comminuted and floated together with dolomitic and sand fractions. The presence of shale fraction in the flotation circuits creates serious technical troubles and leads to hardly acceptable metal losses to flotation tailings (Łuszczkiewicz, 2000). Copper recovery at Lubin Concentrator has been remarkably decreasing for several years reaching some 86-87 % with a concentrate grade less than 17 %. Similar unfavorable effect has also been observed for silver.

Table 3. Value of metals in 1 tone of Lubin middlings (metals prices of 30 April 2007)

Metal	Content	Price, US\$	Value, US\$
Cu	2,7 %	7 820 US\$/t	211.1
Ni	373 g/t	50 100 US\$/t	18.7
Co	569 g/t	30 US\$/lb	37.4
Pb	1,52 %	2 000 US\$/t	30.4
Ag	180 g/t	13 US\$/oz	81.0
Zn	1200 g/t	4 300 US\$/t	4.4

Due to both elevated content of copper (several times higher than in the ore) and presence of significant amounts of valuable metals (Ag, Pb, Ni, Co, Zn, V, Mo...) shale fraction is considered to be the most significant and valuable fraction among

three lithological layers of Polish copper ores. This fraction, as a hardly upgradable, is concentrating during the flotation in the middlings - tailings of 1st cleaning at Lubin Concentrator. The comparison of market values of copper and accompanying metals contained in this shale enriched fraction indicates nearly equal magnitudes (Table 3). The value of copper is about US\$ 211 whereas value of other metals (Ag, Ni, Co, Zn, Pb) is US\$172, considering the metal prices at the end of April 2007. Therefore, shale middlings from Lubin Concentrator is a polymetallic material which requires modern and specific methods of treatment for successful recovering of metals.

Chemical analyses of samples of copper ore collected from various mining areas of KGHM indicate good correlation between the total organic carbon (TOC) content and the content of metals: Cu, Ag, Ni, Co (Figs 1-4) (Chmielewski, et al., 2007).

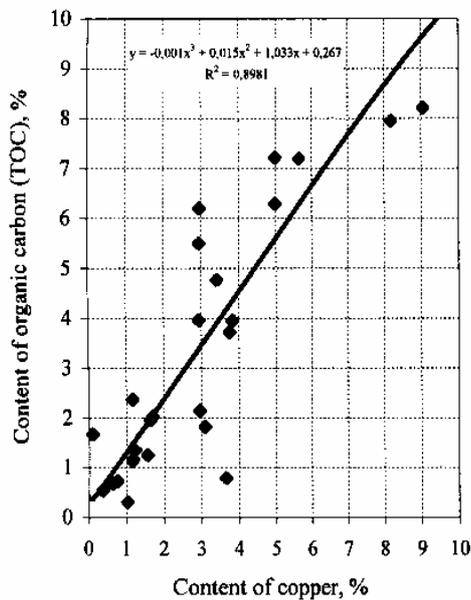


Fig. 1. Organic carbon vs. Cu content in ore samples from KGHM deposit.

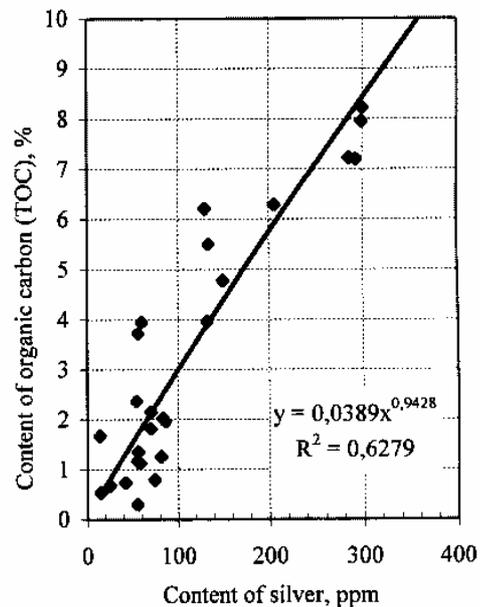


Fig. 2. Organic carbon vs. Ag content in shale ore samples from KGHM deposits

While grinding a low liberation of metal-bearing minerals finely disseminated in shale gangue is observed. Moreover, the flotation of liberated particles became difficult due to slimes of hydrophilic shale components. These two phenomena create significant troubles in effective flotation of shale.

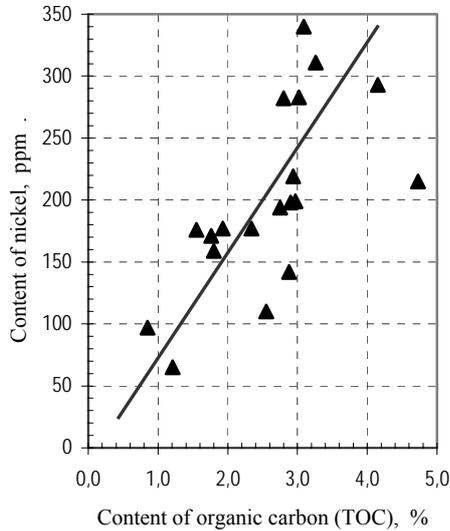


Fig. 3. Ni vs. organic carbon content in shale ore samples from KGHM deposits

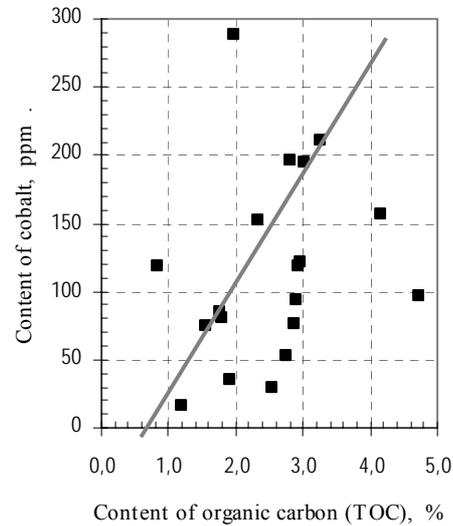


Fig. 4. Co vs. organic carbon content in shale ore samples from KGHM deposits

GENERAL CONCEPT OF SHALE PROCESSING AT LUBIN CONCENTRATOR

The concept of separation and further hydrometallurgical and/or biometallurgical processing of middlings (shale fraction) from existing flotation circuit at Lubin Concentrator (tailings from 1st cleaning) was elaborated during the investigations performed within the BIOSHALE project founded by European Commission (European project contract NMP2-CT-2004 505710). The process was initially suggested and is currently investigated at Wrocław University of Technology (PWR) (Chmielewski, et al., 2007). Its idea was presented in Fig. 5 (Chmielewski and Charewicz, 2005, 2006). The idea accepts an introduction of novel processes with the necessity retaining the existing flotation circuits, which are the only source of final concentrates for metallurgical plants.

The Lubin middlings, exhibiting remarkably elevated concentration of shale fraction, will be initially directly applied or alternatively upgraded by non-polar flotation, leached in non-oxidative conditions with H_2SO_4 for decomposition of carbonates, and finally processed by atmospheric leaching, pressure leaching or bioleaching. The leaching pregnant solutions will be subsequently purified and metals will be separated using standard methods – mainly SX/EW. Alternatively, the pregnant solutions can also be processed in existing technological circuits at KGHM. The Ag, Pb, Au and PGM containing solid leaching residue will be additionally processed by flotation or leaching procedures for recovering of metals (Fig. 6).

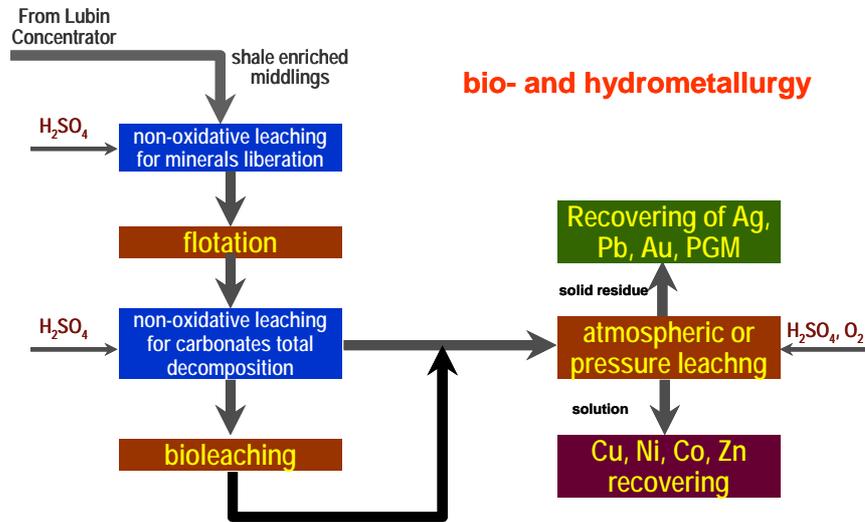


Fig. 6. General concept of bio- & hydrometallurgical processing of shale middlings from Lubin Concentrator and the role of non-oxidative leaching

EXPERIMENTAL AND MATERIAL

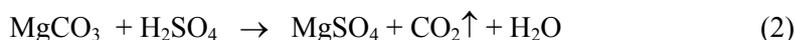
The feed material used in laboratory experiments on non-oxidative leaching was shale containing by-product (middlings) – tailings from 1st cleaning flotation 1st technological circuit at Lubin Concentrator (ZWR Lubin). Chemical composition of the solid was given in Table 4. The content of organic carbon was very high (about 9 %) and confirmed that the middlings can be actually recognized as a shale concentrate. The content of carbonates in the middlings was very high and corresponded to utilization of 497 g H_2SO_4 /kg of dry solid for total decomposition of carbonates. Therefore, the application of any leaching or bioleaching unit operation taking place in acidic conditions requires previous non-oxidative leaching with acid in order to totally decompose of acid consuming components.

Table 4. Chemical composition of Lubin middlings (tailings of 1st cleaning)

CONTENT					
(I) Cu, %	Fe, %	Ni, g/t	Co, g/t	(b) Pb, %	As, %
2,72	1,76	374	572	1.51	0.09
CONTENT					
Ag, g/t	Zn, g/t	S _c , %	SsO ₄ , %	C _{total} , %	C _{org} , %
190	1 200	2.95	1.45	14.30	8.96

PRINCIPLES OF NON-OXIDATIVE LEACHING

Acidic non-oxidative leaching of the shale copper fraction is based on the chemical reactions between sulfuric acid and calcium or magnesium carbonates. These carbonates are the main component of the hydrophilic solid which forms intergrowths and impregnations with copper sulfides or creates hydrophilic ultra-fine slimes on the surface of metal sulfides. Small diameter of the leached solid particles is beneficial for a high rate of heterogenic leaching. The following chemical reactions describe the leaching:



Hydrated calcium sulfate (gypsum) is as a solid reaction product, whereas water-soluble magnesium sulfate and gaseous carbon dioxide are two other products. Due to fine particle distribution of middlings the leaching of carbonate gangue with H_2SO_4 is very rapid and can be performed at ambient temperatures in reactors with mechanical stirring of a simple construction.

The amount of H_2SO_4 applied in the non-oxidative leaching directly corresponds to the content of carbonates and must be precisely controlled to maintain the final pH of the pulp at a level enabling its direct transfer either to the flotation circuit without pH correction or to the leaching and/or bioleaching. Therefore, for the further flotation, the amount of sulfuric acid introduced to the leaching operation should be always kept below the analytically determined maximum amount of acid required for total decomposition of carbonates.

The key parameter determining the amount of H_2SO_4 required for leaching of carbonates is the maximum demand for acid, ($z_{\text{H}_2\text{SO}_4}^{\text{max}}$), which is the mass of pure H_2SO_4 necessary for the total decomposition of carbonates in 1 kg of a dry solid feed. The $z_{\text{H}_2\text{SO}_4}^{\text{max}}$ parameter should be determined analytically from laboratory tests. H_2SO_4 is introduced to the reactor containing shale slurry at a rate that assures its total utilization. Usually, 70-80 % of determined $z_{\text{H}_2\text{SO}_4}^{\text{max}}$ was applied in leaching, maintaining the final pH of the slurry about 5 or higher. This is the pH level enabling direct transfer of the slurry either to the flotation circuit without pH correction or to the leaching and/or bioleaching. If the solid is used for further atmospheric leaching, pressure leaching or bioleaching the amount of sulphuric acid adequately exceeds the maximum demand to maintain pH at the required, acidic level.

Carbon dioxide, evolving in reactions (1) and (2), creates the favorable oxygen-free atmosphere in the leached slurry and prevents the undesirable digestion of sulphides of valuable metals (Cu, Pb, Zn, Ni, Fe). This minimizes the metal losses to the solution and remarkably simplifies the entire process. Therefore, saturation of a slurry with

CO₂ assures the selectivity of carbonate leaching. This was confirmed by the chemical analyses of the wastewater during numerous laboratory tests.

A selective chemical decomposition of non-floatable carbonate-sulfide intergrowths is schematically shown in Figure 7. The diagram indicates that the change of composition of solid takes place while the reaction proceeds. Selectivity of carbonate leaching from flotation feed is according to the proposed method particularly beneficial and secures a high chemical stability of metal sulfide minerals. Noticeably beneficial effects of the preleaching with H₂SO₄ on flotation of copper ores were observed during comprehensive laboratory investigations and several pilot plant tests with various flotation feeds from Lubin and Polkowice concentrators.

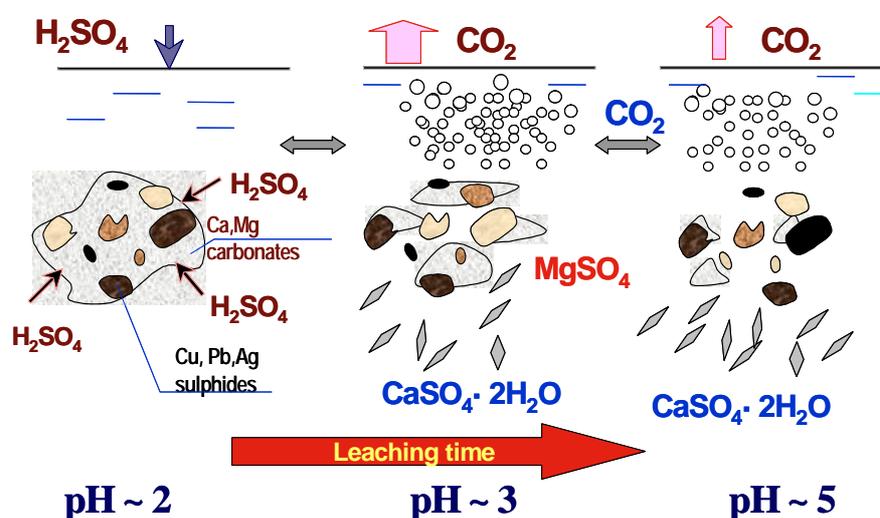


Fig. 7. A selective chemical decomposition of carbonate-sulfide intergrowths during the non-oxidative leaching of a shale feed with sulphuric acid

Another advantage of the non-oxidative leaching is the benefit of the heat effect ($\Delta H_r < 0$). According to the calculations, by means of the HSC Chemistry ver. 2 (Outokumpu), 0.262 kWh/kg CaCO₃ and 0.150 kWh/kg MgCO₃ is created during leaching with H₂SO₄. As a consequence, an increase of pulp temperature to about 30 °C was observed during leaching. This higher pulp temperature increased the reaction rate and favourably improved the rejection of CO₂ after leaching. This heat effect can be particularly beneficial for plants operating under cold climatic conditions.

The acidic non-oxidative leaching of the carbonate-containing flotation feed resulted in the apparent decomposition of solid particles by means of chemical, selective process which precisely and economically liberated sulfide minerals. Under oxygen-free conditions all metal sulfides remain chemically stable and susceptible for

flotation. This selective “chemical grinding” is very efficient particularly for fine intergrowths, which can not be disintegrated with typical mechanical milling. High selectivity and low energy consumption are, therefore, additional beneficial factors of this process. We also believe that an application of leaching on industrial scale would remarkably simplify milling circuits or even eliminate some milling operations, leading to the further reduction of processing costs.

KINETICS OF NON-OXIDATIVE LEACHING

Kinetics of non-oxidative leaching of shale middlings from Lubin Concentrator was investigated at various degree of carbonate decomposition – from 20 to 100 %. The analytically determined content of acid-consuming minerals (carbonates) corresponded to maximum sulphuric acid consumption, $z_{H_2SO_4}^{max} = 497$ g/kg.

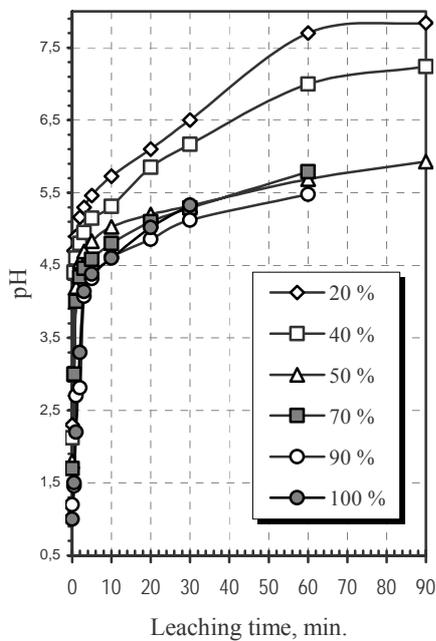


Fig. 8. pH vs. leaching time for non-oxidative leaching of Lubin middlings

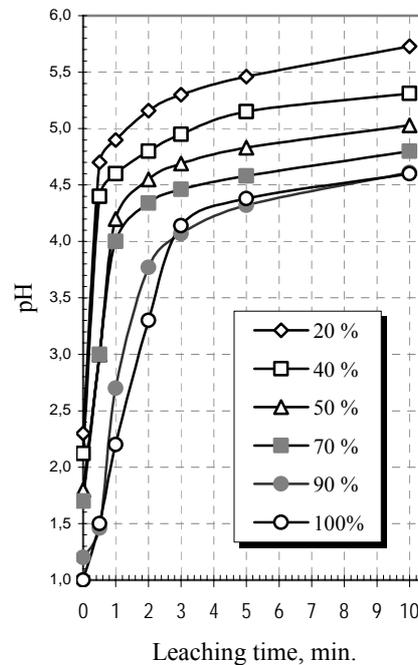


Fig. 9. pH vs. leaching time for initial stage of non-oxidative leaching of Lubin middlings

The process control of non-oxidative leaching is based on pH measurement of leached shale suspension after introduction of desired amount of sulphuric acid. On the basis of kinetic results for Lubin middlings (Figs 8 and 9) it was found that leaching is very rapid and after about 5 minutes almost entire amount of acid is already used up. The observed further pH changes (up to about 40-60 minutes) results from saturation of the slurry with CO_2 .

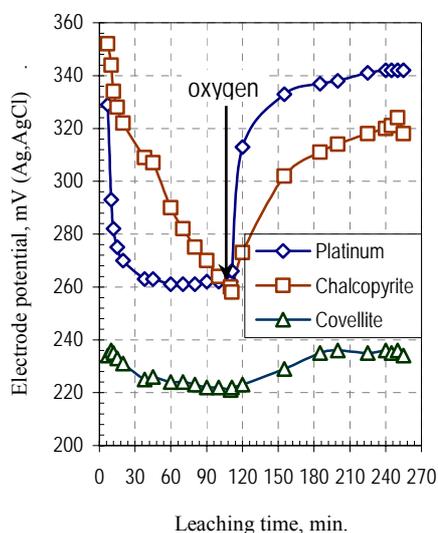


Fig. 10. Potential of platinum, chalcopyrite and covellite electrodes during non-oxidative leaching of Lubin shale by-product and after introduction of oxygen

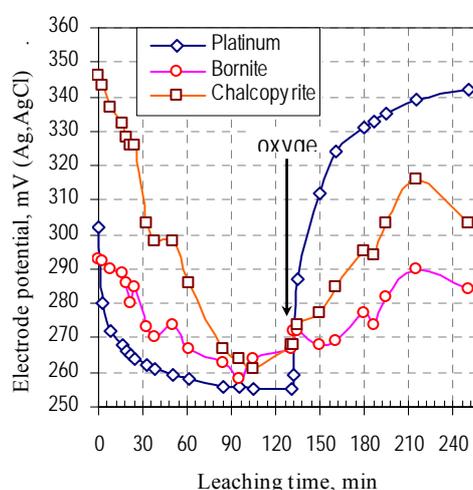


Fig. 11. Potential of platinum, chalcopyrite and bornite electrodes during non-oxidative leaching of Lubin shale by-product and after introduction of oxygen

The presence of carbon dioxide in the middlings leaching system allows for maintaining the low red-ox potential and preventing the digestion of metals. According to Figs 11 and 12 potential of platinum, chalcopyrite, covellite and bornite electrodes decreases to the region, where electrochemical liberation of metal ions to the solution can not be achieved. This was additionally confirmed by chemical analysis of solutions after various R_w - leaching grade of carbonates (Table 5). Introduction of gaseous oxygen under atmospheric pressure leads to remarkable increase in potential of all electrodes and to liberation of metals to the solution.

Table. 5. Concentration of metal ions in the solution from non-oxidative leaching of the Lubin middlings with H_2SO_4

Sample symbol	Carbonates decomposition, R_w , %	Leaching time, min.	Concentration of metal ion in solution, mg/dm^3				
			Cu	Fe	Ni	Co	As
NL-3/1	20	90	0.179	0.005	0.066	0.065	0.007
NL-3/2	40	90	0.216	0.025	0.099	0.097	0.006
NL-3/3	50	90	0.136	0.048	0.275	0.259	0.118
NL-3/4	70	60	0.194	0.020	0.191	0.248	0.023
NL-3/5	90	60	0.171	0.028	0.295	0.358	0.208
NL-3/6	100	60	0.114	0.027	0.271	0.325	0.205
NL-3/7*	100*	-	78.2	92.1	0.737	0.906	1.98

*) Analyzed after 24 hours from the termination of leaching (open to the atmosphere).

CONCLUSIONS

In order to reduce the growing losses of metals observed in the flotation circuits of Lubin Concentrator, the significant alteration has to be introduced into the existing flotation system.

The shale by-product (middlings), the most troublesome material in the flotation, has to be separated from the flotation circuits at Lubin Concentrator and alternatively processed by means of non-oxidative, atmospheric and/or pressure leaching. High content of acid-consuming minerals (calcium and magnesium carbonates) and dissemination of fine metal-bearing sulphides in dolomitic and shale host unquestionably require an application of non-oxidative leaching with sulphuric acid prior to the atmospheric or pressure leaching if acidic conditions are to be preferably applied. Total decomposition of carbonates is recommended to avoid hardly controlled acid consumption during the oxidative leaching.

Non-oxidative leaching of shale rich middlings appeared to be a very rapid (30 – 60 minutes) and selective process, exhibiting the remarkable pH changes as a process controlling parameter. Rapid liberation of carbon dioxide during the reaction of sulphuric acid with carbonate gangue creates beneficially non-oxidative conditions, preventing the leaching of copper, nickel, cobalt and zinc from their sulphides.

Partial and selective liberation of metal sulfides leads to enhanced liberation of metal-bearing minerals, what remarkably improves their floatability, while total decomposition of carbonates makes further atmospheric and pressure leaching more efficient. This has confirmed in additional, detailed investigations.

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Omówiono korzystny wpływ nieutleniającego ługowania węglanów za pomocą kwasu siarkowego z półproduktu flotacji (odpad I czyszczenie I ciągu technologicznego ZWR Lubin). Ługownie nieutleniające stosowano jako operację poprzedzającą flotację, ługowanie atmosferyczne, ługowanie ciśnieniowe lub bioługowanie. Proces kwaśnego ługowania nadawy do flotacji prowadzi do selektywnego rozkładu węglanów wapnia i magnezu i zapewnia uwolnienie siarczków metali z ich hydrofilnych wzrostów z węglanami. Efektem tego jest wyraźne podwyższenie wskaźników flotacji w porównaniu z nadawą nieługowaną oraz umożliwienie skutecznego, utleniającego ługowania metali w roztworach kwasu siarkowego. Wykazano, że po chemicznym rozkładzie 50 – 70 % węglanów zawartych w nadawie do flotacji następuje wyraźny wzrost uzysku oraz jakości koncentratu w porównaniu z flotacją materiału nieługowanego.

Produktami ługowania nieutleniającego są gips ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), rozpuszczalny w wodzie siarczan magnezu (MgSO_4) oraz gazowy ditlenek węgla (CO_2), który wytwarza korzystnie nieutleniającą atmosferę w ługowanej zawieszynie. Zapewnia to chemiczną stabilność siarczków metali, które nie ulegają roztwarzaniu w warunkach procesu. Korzystny wpływ procesu ługowania nieutleniającego na flotację został wcześniej potwierdzony dla innych flotowanych półproduktów i koncentratów miedzi. Zastosowanie kwasu siarkowego do ługowania nadawy do flotacji prowadzi nie tylko do podwyższenia wskaźników wzbogacania, ale również umożliwia racjonalne wykorzystanie kwasu, który staje się kłopotliwym i trudno zbywalnym odpadem procesu metalurgicznego. Ługowanie nieutleniające jest operacją, która musi być stosowana przed ługowaniem atmosferycznym, ługowaniem ciśnieniowym lub bioługowaniem w warunkach kwaśnych.