Pressure leaching of sulfide concentrate produced by Lubin Concentrator (KGHM "Polska Miedz" SA, Poland)

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Abstract: The rapidly declining quality of ores and concentrates produced by Lubin Concentrator (KGHM) makes the flotation concentrates exceptionally difficult-to-process by flash smelting. Currently, a hydrometallurgical process, using sulfuric acid with the presence of oxidants as a leaching medium, seems to be either a reasonable alternative or a complementary option to pyrometallurgy. The unique lithological, mineralogical and chemical properties of the concentrate were considered in a selection of the process route. Results of a pressure leaching of the copper sulfide concentrate from Lubin Concentrator (ZWR Lubin) with oxygenated aqueous H_2SO_4 solutions are presented. The effect of temperature from 120 to 200 °C, initial concentration of H_2SO_4 from 60 to 100 g/dm³, and oxygen partial pressure ranging from 0.5 to 2.0 MPa were investigated. The pressure leaching appeared to be an efficient process for recovering copper from the Lubin concentrate. At optimal leaching conditions (140 °C, 100 g/dm³ H_2SO_4, 1.0 MPa O2) 96% of Cu was extracted after 4 h.

1. Introduction

The quality of Polish copper ores and concentrates has been declining for years along with their growing complexity (Konstantynowicz-Zielińska, 1990; Rydzewski, 1996), which reflects unfavorable trends observed in the world copper metallurgy (The World Copper Factbook, 2015). These negative trends are perceived in particular at KGHM (Lubin Plant), where the most complex and hardest-to-treat ores are mined and beneficiated. Their properties, deteriorating for years, comprise a decreasing content of copper and silver in the feed (Kukuć and Bazan, 2013) and a growing amount of a shale fraction as well as increasing concentration of impurities (Pb, As, organic carbon) (Łuszczkiewicz and Chmielewski, 2006, 2008). This essentially affects the decreasing copper and silver content in flotation concentrates and considerably reduces recovery of these metals. These technological concerns became the main reason for growing interest in alternative recovery methods, using chemical and biological processes. Based on the extensive research on hydro- and biometallurgy developed over the years by different research groups (Gupta, 1990; Habashi, 1999, 2005, 2007; Peacey et al., 2003; Jansen and Taylor, 2000; Dreisinger, 2006; Marsden and Wilmot, 2007a-e; Ramachandran et al., 2007), application of hydrometallurgy at KGHM was also considered and investigated. Within the period of 2004 – 2007, several European research institutions, including Wroclaw University of Science and Technology (WUST) and KGHM Cuprum, carried out the BIOSHALE project, for which the objective was to develop innovative processes, including hydrometallurgy for exploitation of black shale ores. One of the deposits chosen for R&D studies was the Lubin copper deposit, because of the high shale fraction content.

The research involved atmospheric and pressure leaching of by-products and specially selected shale-enriched semi-products from the flotation circuits (Chmielewski, 2007; Wódka et al., 2007). At that time, hydrometallurgy at KGHM was considered mainly as a complementary process to existing

technologies. Presently, flotation products, difficult to beneficiate, require a very specific and individual approach because of particular obstacles in the traditional processing. These barriers are the high content of lead (5.42%), the elevated organic carbon concentration (9.44%), and the presence of arsenic (0.27%). Moreover, the Lubin copper deposit is characterized by the presence of carbonate gangue, very complex mineral and polymetallic composition, dissemination of metals in sulfide and carbonate matter. All these barriers disqualify Lubin concentrate as a direct feed to flash smelting. Hydrometallurgical processing is less demanding, however, it requires comprehensive investigations on laboratory and pilot scale combined with supplementing analyses and advanced mineralogical measurements. This follows from the fact that there is no universal technology which can be applied for every leaching feed. Considering the unique mineralogy of Lubin ores, none of the known hydrometallurgical technologies can be regarded as directly applicable for the KGHM concentrates. Electrochemical studies confirmed that unusual properties of concentrates and by-products from the KGHM technological circuits (dominating chalcocite and bornite mineralization, low content of chalcopyrite, presence of pyrite and organic carbon) are advantageous for hydrometallurgy. Likewise, it was found that the presence of intermineral galvanic effects increases notably a leaching rate (Chmielewski and Kaleta, 2011). The above features make the concentrate from Lubin Plant very useful as a feed to the leaching processes, as opposed to the world's dominant chalcopyrite concentrates, which are harder to leach.

Commonly known hydrometallurgical methods for copper production are mostly based on sulfate, sulfate/chloride, and chloride solutions. A selection of the leaching conditions is an important criterion and should be justified economically and environmentally. In the case of KGHM concentrates, the choice of leaching medium is based on easy access to sulfuric acid, which is being produced (~650000 Mg/y) in KGHM-owned smelters as a by-product during processing of copper sulfide concentrate by pyrometallurgy.

So far, atmospheric leaching was considered as the best way for processing of Lubin ores, due to relatively low costs and simple equipment. However, to reach high recoveries of Cu and accompanying metals (Co, Ni), it is necessary to add a considerable amount of ferric ions as an oxidizing agent and prolong leaching time to at least 7 h (Chmielewski et al., 2011).

In pressure leaching, such issues are less pronounced. Pressure leaching exhibits numerous advantages, making this process very attractive due to the high leaching rates, the possibility of arsenic utilization or stabilization (as a low–solubility scorodite), and the total recovery of noble metals.

Currently, tests are being performed to apply pressure leaching for processing of final flotation concentrates of the specific properties and composition, making difficulties in their treatment by pyrometallurgy. The aim of this work was to evaluate the efficiency of pressure leaching for Lubin concentrates and to confirm the utility of this process for copper recovery.

2. Experimental

2.1 Material characterization

The KGHM deposits of copper ore localized in SW Poland are distinguished by the considerable diversity of chemical composition and high dissemination of metal-bearing minerals in the barren rock fraction. The commercial sulfide flotation concentrate produced by Lubin Concentrator (ZWR Lubin, KHGM "Polska Miedz" SA) is a polymetallic product of beneficiation, of which the quality has been decreasing for years. The content of metal-bearing minerals is approximately 27% of a concentrate mass. The remaining 73% of the concentrate is barren minerals, mostly calcite, dolomite, clay minerals, and quartz. The copper sulfides (chalcopyrite, bornite, chalcocite, and covellite) make up about 75% of the total metal-bearing minerals content (Fig. 1). Since 2009 the copper content has declined from 15.85 to 13.61% in 2015, and decreasing contents of silver and zinc have also been observed. Simultaneously, the concentration of other valuable metals present in the concentrate such as cobalt and nickel have remained at similar levels over this time (Tab. 1). The copper sulfide concentrate used in the experiments was obtained from the complete flotation process required to produce feed for the smelting process.

The concentrate was delivered in the form of an aqueous suspension where solid phase content was usually within the range of 49-52% by mass. The content of the carbonate fraction in solid phase varied

around 25%.

The distribution of particle size in concentrate production is mostly stable in time and shows that about 80% of particles are smaller than 80 μm in diameter (Fig. 2). The concentrate used as a feed for the pressure leaching experiments was not processed in any other preparation unit, for instance, additional grinding, preliminary decomposition of carbonate fraction, etc.

2.2. Leaching procedure

All pressure leaching experiments were performed in a 2 dm^3 titanium pressure reactor (autoclave) with 1 dm^3 working volume, manufactured by the PARR Instrument Company. The autoclave was equipped with Teflon elements such as removable liner, stirrer, and sampling tube. The leaching conditions: temperature, pressure, and stirring rate were maintained by electronic controllers.

The process parameters: temperature, oxygen pressure, the initial concentration of sulfuric acid and concentration of ferric ions were investigated within the ranges: 120 to 200 °C, 0.5 to 2.0 MPa, 60 to 100 g/dm^3 and 0 to 30 g/dm^3, respectively. Solid-to-liquid ratio (1/6) and stirring rate (400 rpm) were constant throughout the experiments. Before the leaching tests, the received concentrate was homogenized and analyzed for solid phase content and concentration of carbonate fraction (calcium and magnesium carbonates). The precise analysis of carbonates in the leaching feed was crucial for accurate preparation of acidified leaching solution and controlled carbonates decomposition. An additional amount of acid, used for decomposition of carbonates in the feed was included in the initial H_2SO_4 concentration. In each experiment, unprocessed water slurry containing 167 g of dry concentrate was introduced into 1.0 dm^3 of sulfuric acid solution. After decomposition of carbonate matter, performed outside the reaction chamber, a Teflon® liner with the reaction mixture was introduced into the autoclave.

Table 1. The content of copper and accompanying metals in final flotation concentrate produced by the Lubin Concentrator from 2009 to 2015

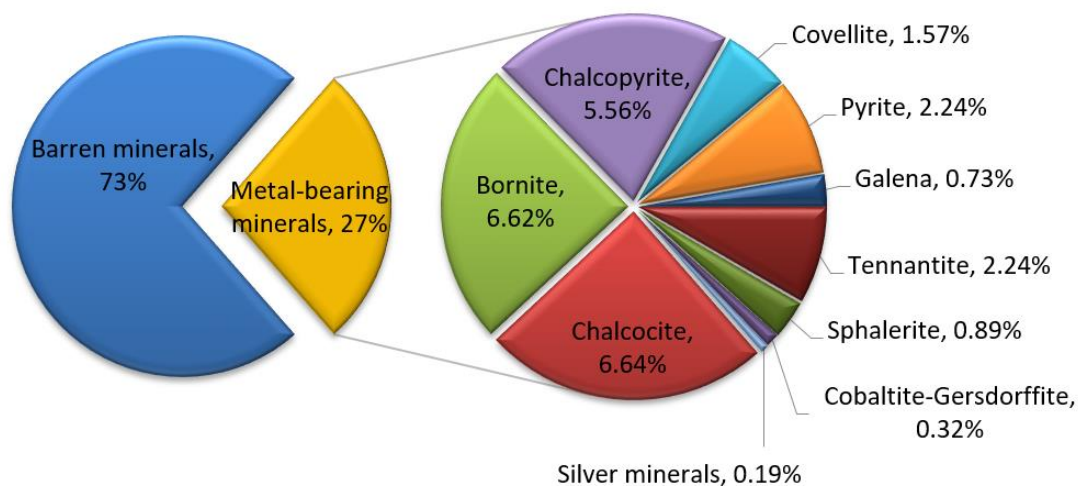| Year	Cu, %	Zn, %	Ni, g/Mg	Co, g/Mg	Ag, g/Mg	Pb, %	As, %	C_{org}, %
2009	15.85	0.947	415	1040	n/a	2.67	0.290	8.1
2010	15.26	0.928	488	1206	938	n/a	0.343	7.2
2011	14.56	0.570	483	1250	755	n/a	0.258	7.8
2013	14.01	0.680	519	1438	699	4.30	0.286	9.4
2015	13.61	1.090	497	1285	638	4.09	0.446	9.3

n/a = not available

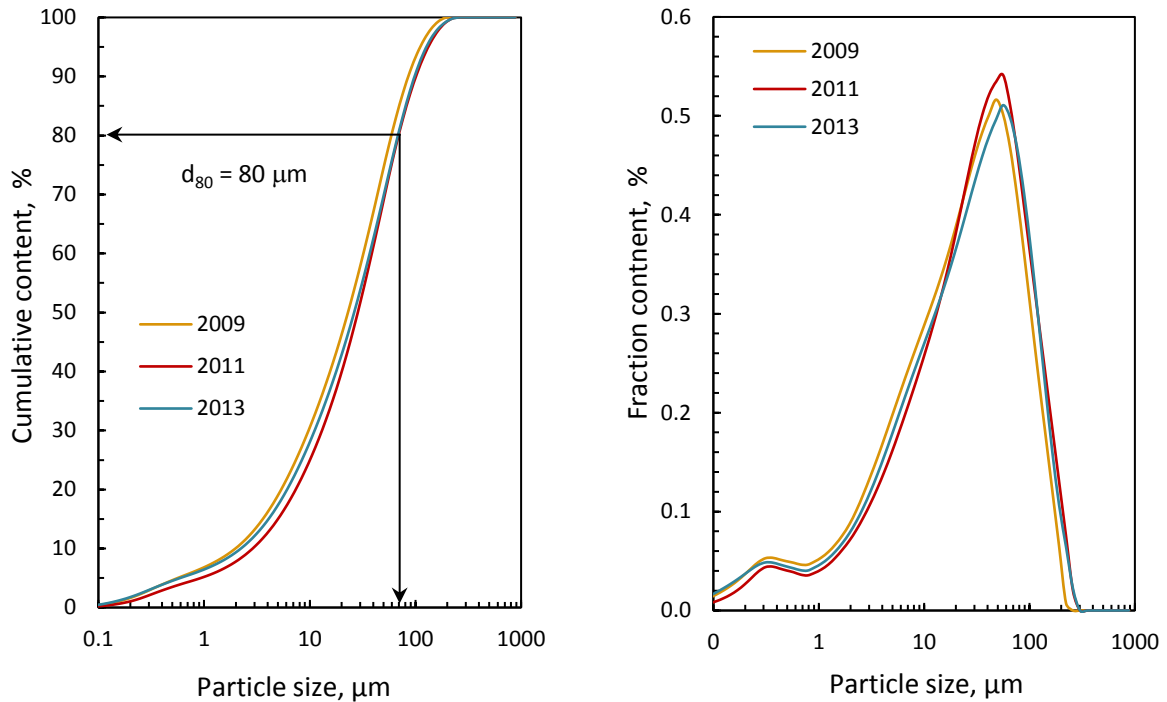Fig. 1. Lithological and mineralogical composition of examined Lubin flotation concentrate

Fig. 2. Particle size analyses of Lubin flotation concentrate in 2009, 2011 and 2013

A "time zero" sample was taken when the temperature in the reactor reached the desired level, just before the introduction of oxygen. The subsequent samples were taken systematically every 30 minutes for the next 4 hours. All samples collected during the experiments were filtrated and analyzed for metals (Cu, Fe, Zn, Co, Ni) concentration by atomic absorption spectrometry (AAS). Acid concentration was determined by pH-metric titration with masking of metal cations. Only the results of copper and iron leaching are presented and discussed here.

The final recovery of copper and iron was calculated based on the following equation:

$$R = \frac{100 * C}{C_{max} * m_{(s)}}$$ (1)

where: R – final Cu/Fe recovery in the solution, C – final concentration of Cu/Fe in the solution, C_{max} – maximal concentration of Cu/Fe in the solution calculated on the basis of concentrate content, $m_{(s)}$ – mass of the dry solid phase in the leached slurry sample.

3. Results and discussion

3.1 Effect of temperature

The investigated temperature of the process varied between 120 and 200 °C, whereas pressure and initial concentration of sulfuric acid were kept constant at 1.0 MPa and 100 g/dm³, respectively. The results showed that the total copper extraction changed between 88 and 97% at 200 and 140 °C, respectively. As can be seen from Fig. 3, the Cu extraction rate was increasing from 120 to 140 °C, and decreasing at temperatures above 160 °C. Moreover, the recovery-time relationships for all temperatures revealed a characteristic period of leaching initiation, during which the extraction of copper was low or undetectable. This initial leaching period indicates a solid conversion of copper sulfides (covellinisation), described during prior studies on the concentrates from Lubin Plant (Muszer et al., 2013). The authors demonstrated that due to this process chalcopyrite transforms directly to covellite (chalcopyrite → covellite), whereas bornite conversion occurs gradually. At first, bornite undergoes transformation to chalcocite which then transforms to covellite (chalcopyrite → chalcocite → covellite). The structure of covellite formed during these alterations confirms the mechanism.

After the conversion, leaching of the copper minerals occurs. The comparison of leaching rates for the concentrates collected between 2009 and 2013, as presented in Fig 4, shows that the period of leaching

initiation shortened from 90 to 30 min at temperature of 180 °C - characteristic for covellinisation. For concentrates gathered after 2013, this process was only observed at temperatures of 200 °C or higher. It seems that covellinisation behavior is dependent on the mineralogy and chemical composition of a given concentrate (Table 1).
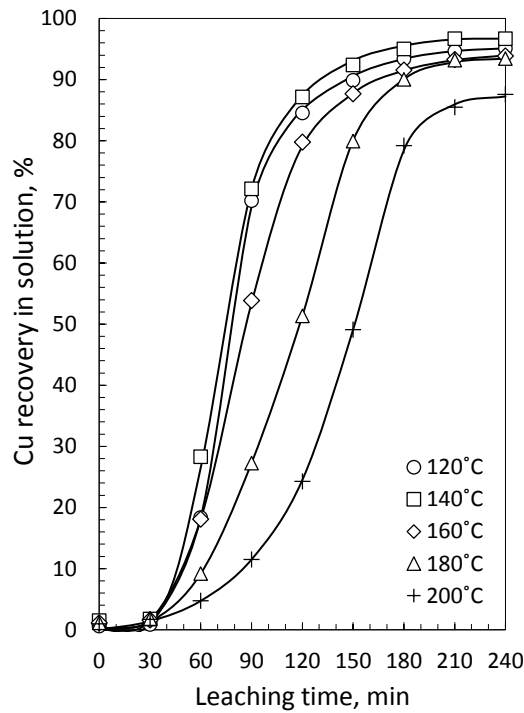

Fig. 3. Effect of temperature on the leaching recovery of copper. Oxygen partial pressure 1.0 MPa, 100 g/dm³ H₂SO₄, s/l = 1:6, stirring rate 400 rpm
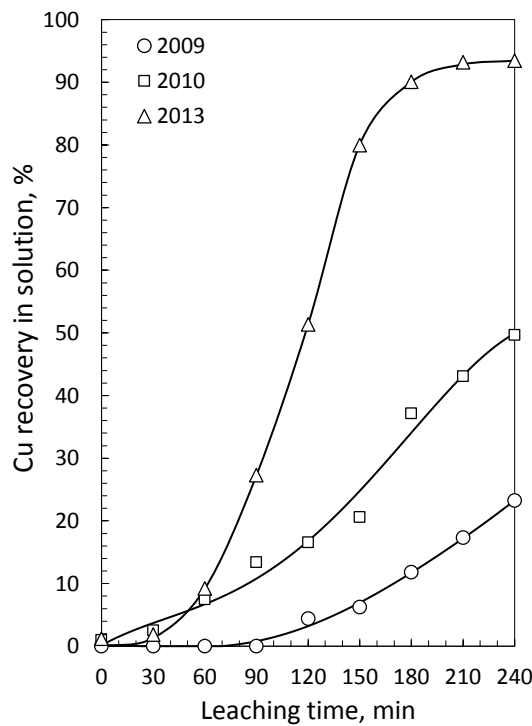

Fig. 4. Effect of temperature on the leaching recovery of copper for the concentrates produced in 2009-2013. Temperature 180 °C, oxygen partial pressure 1.0 MPa, 100 g/dm³ H₂SO₄, s/l = 1:6, stirring rate 400 rpm

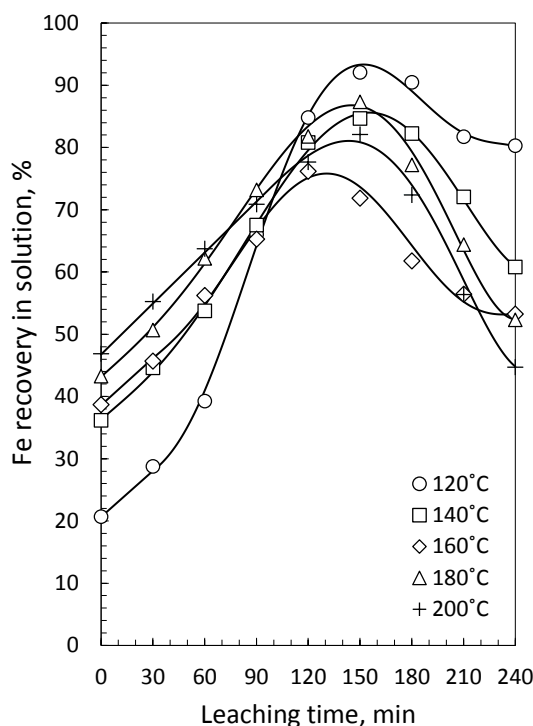Fig. 5. Effect of temperature on the leaching recovery of iron. Oxygen partial pressure 1.0 MPa, 100 g/dm³ H₂SO₄, s/l = 1:6, stirring rate 400 rpm

Taking into account that the examined concentrates contained iron-bearing minerals (mainly pyrite and chalcopyrite and bornite) the pregnant leach solution also contained iron. The experimental results (Fig. 5) show that leaching of iron was already observed when the reactor was heated up to the set temperature in a non-oxidative atmosphere. The concentration of iron at a "time zero" was found to increase with the increasing temperature of the process; iron recovery at 200 °C reached 46%. Upon introducing oxygen, the process of Fe extraction continued to increase for 120 to 150 min, depending on the temperature. In the course of leaching, ferrous ions were oxidized to ferric ions and partially precipitated after 120 minutes of leaching. As can be seen from Fig. 5, there is no direct correlation between the temperature of the process and maximum concentration of iron in the solution. However, the final iron content decreases with the increase of temperature. It can be attributed to the hydrolysis of Fe(III) and precipitation of solid iron(III) compounds, probably to a hydrated form of hematite.

When examining the effect of temperature on metals extraction, unusual pressure changes were observed. Specifically, at temperatures between 140 and 200 °C, when the leaching of copper reached the plateau (180 – 210 min of the process), the total pressure in the autoclave started to increase systematically, in some cases exceeding twice the initial value. The distinctive odor of pregnant leach solutions may indicate that the pressure rise was caused by oxidation of the organic fraction present in the concentrate. Based on the results presented above the temperature of 140 °C was chosen as optimal and used in further tests.

3.2 Effect of initial sulfuric acid concentration

Solutions produced during the leaching stage are usually directed to the further processing in order to separate and recover precious metals (Cu, Zn, Co, Ni). The acidity of pregnant leach solutions affects the efficiency of separation processes, e.g., solvent extraction or ion exchange. These processes can be problematic, especially in the case of copper extraction from highly acidic solutions. For this reason, in the next series of experiments, the initial concentration of sulfuric acid was reduced from 100 g/dm³ to 80 and 60 g/dm³ and the effect on leaching efficiency was investigated. The experimental leaching curves, for Cu and Fe, are presented in Figs. 6 and 7, respectively. It can be seen that the decrease of H₂SO₄ concentration was not beneficial for copper recovery. Pressure leaching of the Lubin material in 80 g/dm³ sulfuric acid resulted in 90% of Cu recovery and reached a plateau after

150 minutes; a further 90 min of leaching was unproductive. In the case of experiment with 60 g/dm^3 acid solution, after 4 h of leaching, copper extraction reached only 82%. The shape of leaching curve indicates that the process was still in progress, but that rate was slow, therefore, the expected Cu recovery after prolonged leaching would not change significantly.
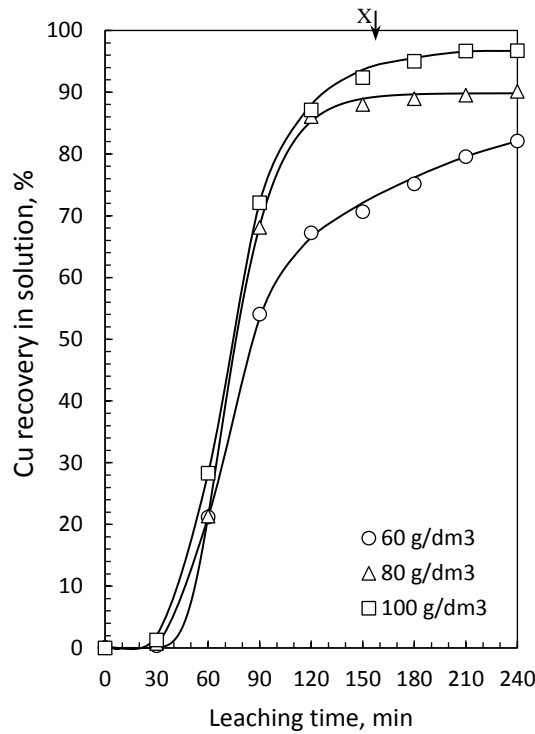

Fig. 6. Effect of initial acid concentration on the leaching recovery of copper. Temperature 140 °C, oxygen partial pressure 1.0 MPa, s/l = 1:6, stirring rate 400 rpm
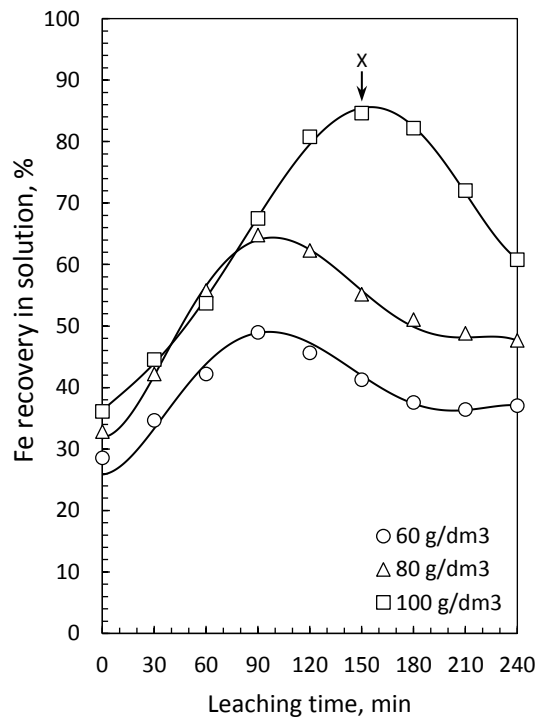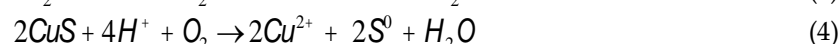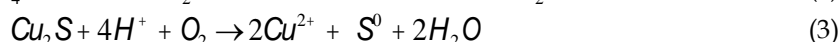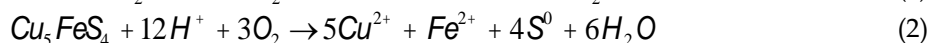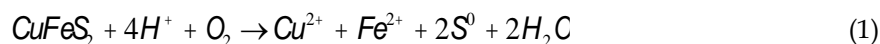

Fig. 7. Effect of initial acid concentration on the leaching recovery of iron. Temperature 140 °C, oxygen partial pressure 1.0 MPa, s/l = 1:6, stirring rate 400 rpm

The iron leaching efficiency was also dependent on sulfuric acid concentration and decreased with dilution of the acid solution (Fig. 7). The final Fe extraction reached 37% when using 60 g/dm³ H2SO4 and was 24% lower than with 100 g/dm³ H_2SO_4. Similar to the effect of temperature, the iron leaching curves show characteristic maxima, indicating the beginning of iron(III) compounds precipitation. For 60 and 80 g/dm³ H_2SO_4 solutions, these maxima were detected 90 min after introducing oxygen into the autoclave, and their values were significantly lower compared to the 100 g/dm³ solution. Probably, this effect is related to acid consumption in the course of the leaching process. Sulfuric acid is used up in the solubilization of minerals and oxidation of extracted ferrous ions. The leaching reactions of the predominant copper minerals present in the Lubin concentrate (Eqs. 2-5) show that the leaching process requires a high concentration of hydrogen ions. Equations (2) and (3) are net equations only and consist of covellinisation reactions followed by leaching of the covellinisation products as represented by equations (4) and (5).

$$CuFeS_2 + 4H^+ + O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2C \tag{1}$$

$$Cu_5FeS_4 + 12H^+ + 3O_2 \rightarrow 5Cu^{2+} + Fe^{2+} + 4S^0 + 6H_2O \tag{2}$$

$$Cu_2S + 4H^+ + O_2 \rightarrow 2Cu^{2+} + S^0 + 2H_2O \tag{3}$$

$$2CuS + 4H^+ + O_2 \rightarrow 2Cu^{2+} + 2S^0 + H_2O \tag{4}$$

Based on these reactions, and the composition of the concentrate investigated (Fig. 1), the theoretical value of acid needed for sulfide minerals dissolution was calculated to be about 25 g/dm³. These calculations assumed that the influence of Fe(II) oxidation and Fe(III) hydrolysis were mutually compensating in relation to hydrogen ions concentration.

Results presented in Fig. 8 show that in the case of 100 g/dm³ H_2SO_4 solution, total acid consumption (the difference between initial and final values) reached this theoretical value (27 g/dm³), while for the remaining solutions was lower: 23 g for 80 g/dm³ solution and only 7 g for 60 g/dm³ solution.

All the obtained curves show characteristic area of acid concentration stabilization, after 120-150 min of leaching. The detailed analysis of experimental data (Figs. 6-8) indicates that leaching of Cu, Fe and H_2SO_4 consumption are strictly related to each other. It can be seen that the beginning of plateau of Cu recovery, Fe precipitation and acid consumption stabilization take place at the same time - point "X", marked in the figures for 100 g/dm³ solution. Therefore, the acid consumption rate is an important factor which can be a measure of the progress and efficiency of leaching. Moreover, after about 120 min of the process, the curves for 60 and 80 g/dm³ solutions are converging toward similar values (approx. 55 g/dm³); simultaneously leaching slows down resulting in lower Cu recovery. This effect indicates that the examined pressure leaching process requires heavily acidic environment.
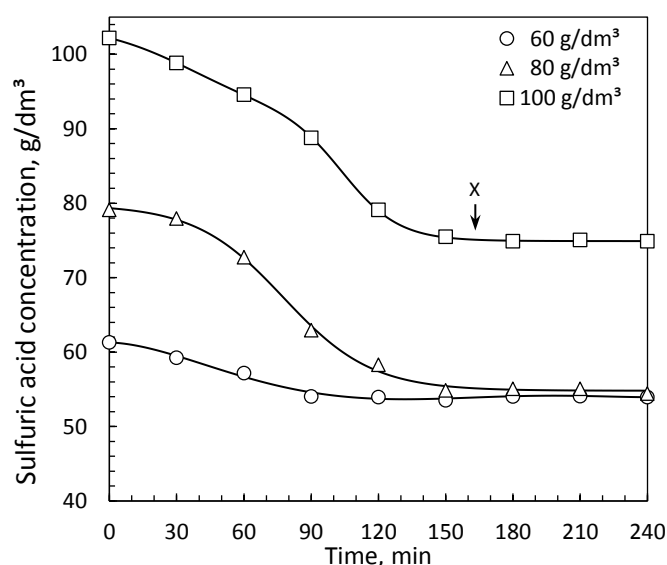

Fig. 8. The changes of sulfuric acid concentration during the leaching process. Temperature 140 °C, oxygen partial pressure 1.0 MPa, s/l = 1:6, stirring rate 400 rpm

Considering the above, the amount of acid needed for effective copper recovery must include acid required for minerals dissolution and the appropriate surplus ensuring the correct environment for the process.

3.3 Effect of oxygen partial pressure

A series of experiments with the oxygen pressure ranging from 0.5 to 2.0 MPa were performed at an initial sulfuric acid concentration of 100 g/dm³. The experimental results are presented in Figs. 9 and 10. It can be seen from Fig. 9 that the oxygen partial pressure affects both the leaching time and the copper extraction. The comparison of leaching curves shows that the effective leaching time, i.e. the time to reach plateau, can be significantly reduced when higher pressure is used. For example, the respective leaching times at 1.0 and 2.0 MPa are 200 and 120 min.

The increase of oxygen pressure, in the examined range, improves copper extraction, however this effect is most evident at lower pressure values (0.5 and 1.0 MPa). The maximum Cu recovery reached 98 %, when the material was leached at 2.0 MPa.

Analyzing the Fe recovery-leaching time relationships presented in Fig. 10, two observations were made. First, each leaching curve shows a characteristic shape, i.e., initial increase to the maximum value and then decrease. Second, the maximal iron concentration and final Fe recovery are inversely proportional to the oxygen pressure used in the experiment. It was described earlier (section 3.1.) that the shape of leaching curves can be related to the initial oxidation of Fe(II) and subsequent precipitation of iron compounds. It is therefore suggested that, at higher pressures (1.5-2.0 MPa), precipitation occurs more synchronously with iron leaching and results in declining of maximal concentration of Fe in the solution. Moreover, it seems that this is not the only explanation of this observation. The analysis of the combined Cu/Fe recovery curves shows that leaching of iron is correlated with Cu leaching (from the example in Fig. 11).
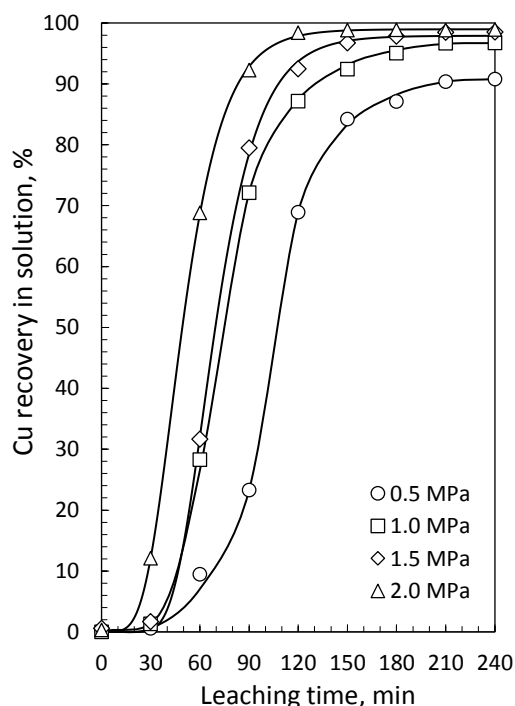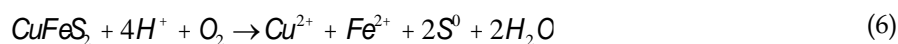

Fig. 9. Effect of oxygen partial pressure on the leaching recovery of copper. Temperature 140 °C, 100 g/dm³ H$_2$SO$_4$, s/l = 1:6, stirring rate 400 rpm

Ferrous ions released from the minerals are initially oxidized to ferric ions which may act as an oxidizing agent in Cu extraction. Exemplary equations are presented below:
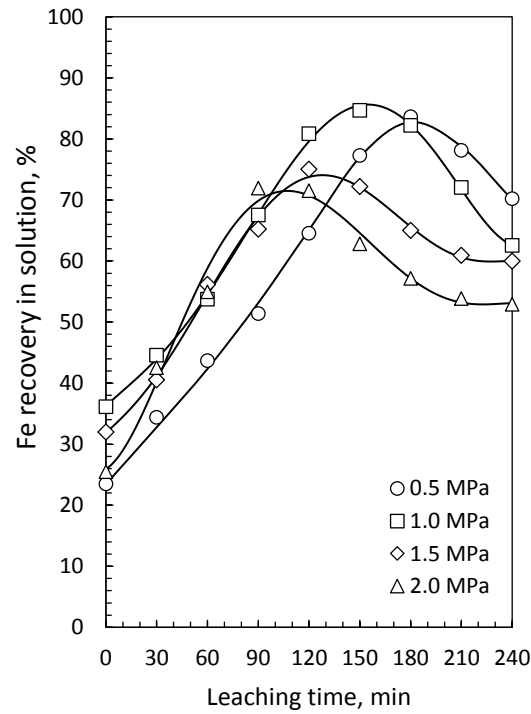
$$CuFeS_2 + 4H^+ + O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O \tag{6}$$

$$2Fe^{2+} + 2H^+ + O_2 \rightarrow 2Fe^{3+} + H_2O \qquad\qquad (7)$$

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \qquad\qquad (8)$$

Fig. 10. Effect of oxygen partial pressure on the leaching recovery of iron. Temperature 140 °C, 100 g/dm³ H₂SO₄, s/l = 1:6, stirring rate 400 rpm
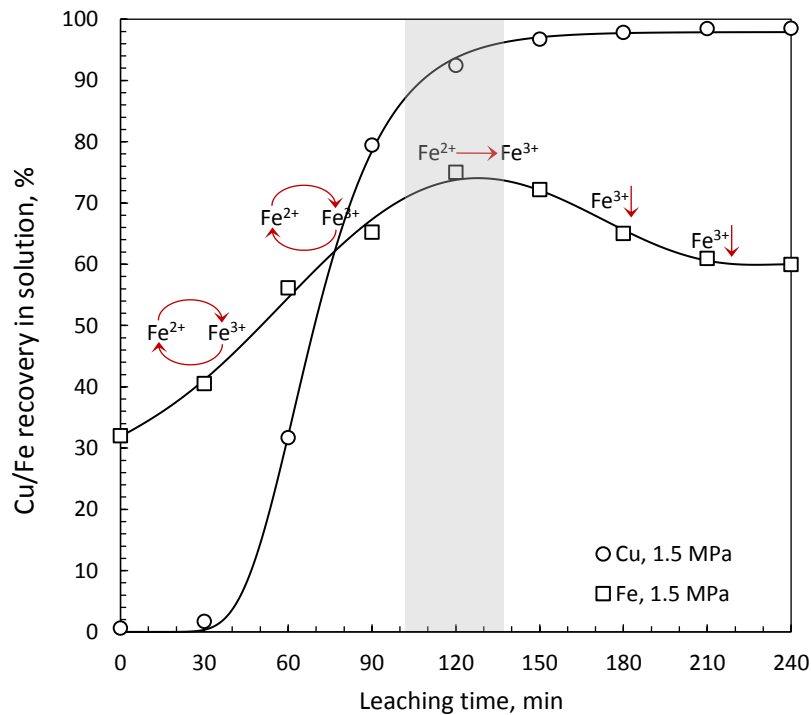

Fig. 11. Iron transformation cycle during the leaching process

During Cu leaching, ferric ions are reduced again to Fe²⁺ ions. This cycle of iron transformation Fe(II)-Fe(III)-Fe(II) lasts until the copper extraction is completed. At the time when Cu extraction approaches plateau (the grey area in Fig. 11), the leaching rate decreases, and hence the "iron cycle"

significantly slows down. It practically means that Fe(II) oxidation reactions (eq. 7) dominate reduction reactions (eq. 8); in consequence, the total concentration of Fe reaches maximum and subsequently decreases due to Fe compounds precipitation.

Similarly, to the temperature effect investigation, a significant rise of the total pressure in the autoclave occurred at the oxygen partial pressure in the range from 1.0 to 2.0 MPa. The leaching experiment at the oxygen pressure of 2.0 MPa resulted in the highest pressure increase of nearly 2.5 MPa. The pregnant leaching solution produced in this process had unusual dark brown color and characteristic odor suggesting the presence of organic compounds (C_{org} content – Table 1).

4. Conclusions

The performed studies demonstrated that pressure leaching of Lubin sulfide concentrate in an oxygenated sulfuric acid was effective in terms of extraction rate and copper recovery. All three of the examined parameters were crucial to the process efficiency. The maximum leaching rate and copper recovery (~97%) were observed at a temperature of 140 °C, whereas in the temperature range from 160 to 200 °C the leaching rate was decreased, and this can be explained in terms of covellinisation of the copper-iron sulfides.

Examination of the pressure leaching at oxygen partial pressures ranging from 0.5 to 2.0 MPa and at constant temperature of 140 °C exhibited that the extraction rate and copper recovery increased with increasing pressure. At the highest oxygen pressure examined (2.0 MPa) the recovery of Cu was near-quantitative.

The application of sulfuric acid solutions of initial concentration lower than 100 g/dm³ was not beneficial when the leaching process was performed at 140 °C and at oxygen partial pressure of 1.0 MPa. Analysis of the experimental data showed that pressure leaching requires a highly acidic environment to extract copper with high efficiency. The concentration of acid influences both the maximal and final iron concentrations in the leach solution. In the case where sulfuric acid concentration is sufficient – 100 g/dm³ – iron behavior indicates that it acts as an oxidant in the leaching process.

A satisfactory copper recovery can be reached at the following optimal values of examined parameters: 140 °C, 100 g/dm³ H_2SO_4 and 1.0 MPa. Increasing the oxygen partial pressure can shorten the leaching time, but results in abnormal total pressure changes during the process. These changes were probably due to decomposition of organic matter present in the black shale fraction.

Concluding, the pressure leaching is effective method of copper recovery from difficult to beneficiate sulfide concentrate, that is a polymineral and polymetallic material characterized by significant amount of impurities and unfavorable composition (low metal content) for smelting purposes.

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