PRESSURE LEACHING OF SHALE ORE IN OXYGENATED SULPHURIC ACID

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The effect of initial temperature, sulphuric acid concentration and oxygen partial pressure on pressure leaching of shale fraction of copper ore is presented. Leaching was performed in the autoclave in the temperature range of 100 -180 °C using oxygen as an oxidizing agent. Tailings from 1st cleaning of Lubin Concentrator (ZWR Lubin) were used as a shale material exhibiting elevated contents of metals and organic carbon. Process was performed at sulphuric acid concentration from 20 to 50 g/dm³. The high efficiency of pressure leaching for copper, cobalt, nickel, iron and zinc from polimetallic shale middlings of the Lubin Concentrator was revealed.

Key words: pressure leaching, shale ore, copper

INTRODUCTION

Pressure hydrometallurgy has an extensive application, particularly in processing of zinc, nickel, and copper sulphides and in pretreatment of refractory gold ores, in which gold is finely dispersed in sulphidic lattice. Especially, the pressure hydrometallurgy is widely used in nickel recovering from laterite ores.

Currently, the tests are undertaken to apply hydrometallurgy for process of byproducts and wastes of copper refining (anode slimes) and for recovery of metals from ores and raw materials of the specific properties and composition, making difficulties in their treatment by pyrometallurgy (black shale ores, tailings).

Pressure hydrometallurgy exhibits numerous advantages creating intensive investigation of it at industrial scale. The main advantages of application of pressure leaching processes are:
- high rate of reaction
- elimination of SO₂, other gases and dust emission

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- high selectivity of pressure leaching
- possibility of arsenic utilization or stabilization (as a low – solubility scorodite)
- total recovery of noble metals
- no restriction of the scale production.

Pressure leaching can be applied in a large scale - to teragram (millions ton) per year of refractory gold ores or to produce several tons of nickel and cobalt from their sulphidic or laterite raw materials.

In the sulphidic copper ores originated from Polish deposits (LGOM - Legnica - Glogow Basin, SW Poland) the content black shale fraction has been increasing systematically, particularly in recent years (Kubacz and Skorupska, 2007). The black shale ores exhibit unique properties. They contain more copper, base metals and noble metals than sandstone or carbonate fraction. The elevated carbonate and organic coal content as well as the metals-bearing minerals dissemination occurring in the black shale ore make significant difficulties in the flotation and causes remarkable metals losses, which has to be limited (Grotowski, 2007).

During the comprehensive investigations on application of bio- and hydrometallurgy for alternative processing of black shale fraction the non-oxidative leaching, atmospheric leaching in oxygenated sulphuric acid, acidic leaching under oxygen pressure and bioleaching have been considered as optional processes for recovering of copper and base metals from shale by-product (middlings) of Lubin Concentrator (Chmielewski and Charewicz, 2006; 2006a). Tailings of 1st cleaning were selected as a shale concentrate for further alternative, hydrometallurgical treatment.

The pressure leaching in H₂SO₄ solution, at elevated temperatures and in the presence of pressurized oxygen. Sulphuric acid is produced at KGHM smelters as a by-product during the processing of copper sulphide concentrate by pyrometallurgy and is the most suitable, cheap and easy-accessible leaching agent.

The tailings of the first cleaning flotation (middlings) of the first circuit at Lubin Concentrator (ZWR Lubin) were selected for the laboratory investigations as a shale concentrate. This material can not be effectively upgraded by flotation and creates serious issues in copper ore flotation, predominantly at Lubin Concentrator. It appears, that the separation of the middlings from the flotation circuit and utilisation for leaching purposes is quite easy. Moreover, the middlings have an enormously advantageous composition with regard to pressure hydrometallurgy. Bornite and chalcocite, the most easy leachable copper sulphides, are dominating copper minerals. Moreover, the tailings contains up to 9 % or organic carbon and some 30 % of carbonates that must be decomposed by sulphuric acid prior to pressure leaching.

The effect of initial temperature, sulphuric acid concentration and oxygen partial pressure on pressure leaching of shale fraction of copper ore has been investigated to evaluate the leaching ability of the shale fraction (middlings) separated as tailing of 1st cleaning from Lubin Concentrator. Pressure leaching examinations were performed in the 2 dm³ autoclave in the temperature range from 100 to 180 °C using oxygen as an
oxidizing agent. The pressure leaching was always preceded with non-oxidative acidic pretreatment of the feed in order to totally decompose the acid-consuming components, predominantly carbonates.

THEORETICAL ASPECTS

The decomposition of carbonates during the noon-oxidative treatment preceding pressure leaching follows the reactions:

$$\text{MgCO}_3 + \text{H}_2\text{SO}_4 = \text{MgSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \quad (1)$$

$$\text{CaCO}_3 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 \cdot \text{2H}_2\text{O} + \text{CO}_2 + \text{H}_2\text{O} \quad (2)$$

The carbonate acidic decomposition is a necessary selective process in which the evolving gaseous carbon dioxide leads to hindering of the metals leaching from their sulphide minerals. Magnesium sulphate formed during the carbonates decomposition is easy soluble, whereas calcium sulphate precipitates as a crystalline gypsum $\text{CaSO}_4 \cdot \text{2H}_2\text{O}$.

The leaching mechanism of the sulphide metals in the sulphuric acid solutions under oxygen pressure depends on temperature range, sulphuric acid concentration and oxygen pressure. At temperatures below 150 °C the major amount of sulphide sulphur is oxidized to elemental sulphur during the leaching according to the following reactions:

$$\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 + \text{O}_2 = 2\text{CuSO}_4 + \text{S}^0 + 2\text{H}_2\text{O} \quad (3)$$

$$\text{Cu}_5\text{FeS}_4 + 6\text{H}_2\text{SO}_4 + 3\text{O}_2 = 5\text{CuSO}_4 + \text{FeSO}_4 + 4\text{S}^0 + 6\text{H}_2\text{O} \quad (4)$$

$$\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 + \text{O}_2 = \text{CuSO}_4 + \text{FeSO}_4 + 2\text{S}^0 + 2\text{H}_2\text{O} \quad (5)$$

The chalcocite dissolution takes place by forming covellite as intermediate product whereas chalcopyrite may forms during bornite dissolution.

At the temperatures above 150 °C mechanism of leaching changes remarkably and sulphates are forming as products of sulphide oxidation:

$$2\text{Cu}_2\text{S} + 5\text{O}_2 + 2\text{H}_2\text{SO}_4 = 4\text{CuSO}_4 + 2\text{H}_2\text{O} \quad (6)$$

$$4\text{Cu}_3\text{FeS}_4 + 37\text{O}_2 + 6\text{H}_2\text{SO}_4 = 20\text{CuSO}_4 + 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O} \quad (7)$$

$$4\text{Cu}_3\text{FeS}_4 + 17\text{O}_2 + 4\text{H}_2\text{O} = 4\text{CuSO}_4 + 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4 \quad (8)$$
Ferric ions, present in the pressure leach solution, can precipitate as a goethite or jarosite depending on sulphuric acid concentration and temperature. Iron, existing in the ore is initially solubilised as Fe(II) ions and next oxidized by oxygen to Fe(III) ions:

\[
\text{Cu}_3\text{FeS}_4 + 9\text{O}_2 + 2\text{H}_2\text{SO}_4 = 5\text{CuSO}_4 + 2\text{FeSO}_4 + 2\text{H}_2\text{O} \quad (9)
\]

\[
4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 = 2\text{Fe}_2\left(\text{SO}_4\right)_3 + 2\text{H}_2\text{O} \quad (10)
\]

The Fe(III) compounds formed during leaching can also act as an oxidizing agent:

\[
\text{Cu}_3\text{S} + 2\text{Fe}_2\left(\text{SO}_4\right)_3 = 2\text{CuSO}_4 + \text{FeSO}_4 + \text{S}^0 \quad (11)
\]

\[
\text{Cu}_3\text{FeS}_4 + 6\text{Fe}_2\left(\text{SO}_4\right)_3 = 5\text{CuSO}_4 + 13\text{FeSO}_4 + 4\text{S}^0 \quad (12)
\]

If the ore contains pyrite it will undergo digestion with oxygen, forming sulphuric acid:

\[
2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \quad (13)
\]

Dissolution of nickel, cobalt and zinc sulphides in sulphuric acid solution at elevated temperature under oxygen pressure proceeds in the similar way.

**FEED MATERIAL CHARACTERISATION**

The feed material applied for laboratory experiments on non-oxidative leaching followed by pressure leaching in sulphuric acid and under oxygen pressure 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 1. The content of organic carbon was very high (about 9 %) and confirmed that the middlings can be actually recognized as a shale concentrate for individual processing.

The content of carbonates in the middlings corresponded to the utilization of 497 g H$_2$SO$_4$/kg of dry solid for total decomposition of carbonates. Therefore, the application of pressure leaching in acidic conditions strictly required previous non-oxidative leaching with acid in order to decompose totally the acid consuming components, mainly calcium and magnesium carbonates (Łuszczkiewicz, Chmielewski, 2006) Chmielewski et al., 2007). The non-oxidative leaching was therefore performed before each atmospheric leaching experiment.
Pressure leaching of shale ore in oxygenated sulphuric acid

Table 1. Chemical composition of Lubin middlings (tailings of 1st cleaning) applied for pressure leaching as a shale concentrate feed

<table>
<thead>
<tr>
<th>CONTENT</th>
<th>Cu, %</th>
<th>Fe, %</th>
<th>Ni, g/t</th>
<th>Co, g/t</th>
<th>Pb, %</th>
<th>As, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubin concentrate</td>
<td>2.72</td>
<td>1.76</td>
<td>374</td>
<td>572</td>
<td>1.51</td>
<td>0.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CONTENT</th>
<th>Ag, g/t</th>
<th>Zn.g/t</th>
<th>Sng, %</th>
<th>Ss04, %</th>
<th>Ctotal, %</th>
<th>Corg, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubin shale middlings</td>
<td>190</td>
<td>1200</td>
<td>2.95</td>
<td>1.45</td>
<td>14.30</td>
<td>8.96</td>
</tr>
</tbody>
</table>

Figure 1 presents mineralogical composition of the Lubin copper sulphide concentrate and the tailings of 1st cleaning (middlings), respectively. The differences in composition are clearly visible.

Lubin flotation copper concentrate, similarly to concentrates from Polkowice and Rudna, contains chalcocite and bornite as dominating copper sulphides. Some 30 % of copper is however in the form of chalcopyrite and covellite – most refractory minerals. Such a mineralogical composition of Lubin concentrate makes this material favorable for hydrometallurgical treatment.

During the flotation of copper ore in Lubin Concentrator observed is a specific segregation of some copper sulphides in the middlings shale fraction. The shale middlings exhibit chalcocite as the predominant (above 90 %) and the most leachable copper sulphide mineral. Bornite (some 9 %) is the second dominating and easy leached copper mineral in middlings. Chalcopyrite and covellite, the most refractory copper sulphides are represented in middlings as minor, trace components. Therefore,
the mineralogical composition of middlings seems to be almost ideal for application as a feed for oxidative leaching, including pressure leaching in oxygenated sulphuric acid.

The sample of Lubin middlings was collected for about 14 days to get the most representative material. It was stored in the form of slurry (58.4 % of solids) in sealed containers to avoid the effect of oxygen.

Fig. 2 presents SEM cross-section of middlings grains. The dissemination of minerals (white areas) and gangue (grey areas) are clearly visible.

Fig. 2. SEM pictures of untreated samples of Lubin middlings exhibiting fine dissemination of metals-bearing minerals in carbonate and shale matter

The separation of shale fraction in the form of middlings and subsequent treatment by means of hydrometallurgical method was proposed during extensive research in the frame of BIOSHALE project program. Hydrometallurgy (or biometallurgy) are expected to be satisfactory methods for recovering of copper, base metals and silver, which concentration is very high (Tab. 1) Concentration of copper is in ore is 2.72 % and concentration of silver is 190 g/t. Taking into account the market value of metals in Lubin middlings (Table 1), this material has to be recognized as a polymetallic.
EXPERIMENTS

The effect of the temperature, oxygen partial pressure and sulphuric acid concentration on the kinetics and efficiency of pressure leaching of Lubin middlings have been investigated. All experiments were carried out at temperatures between 100 and 180 °C and under oxygen pressure within the range of 0.25 – 1.0 MPa.

The experiments were performed in 2.0 dm$^3$ autoclave having the internal equipment made of teflon. The following experimental procedure was used: A teflon beaker containing 1.0 dm$^3$ of solution of the required concentration of sulphuric acid and the required amount of the middlings was introduced into the autoclave. The liquid to solid phase ratio (s/l) was kept 1:10 in all experiments. The stirring was switched on when the decomposition of carbonates with H$_2$SO$_4$ begun prior to the main leaching. After carbonates decomposition (ca. 60 min.) autoclave lid was installed, and the slurry was purged two times with nitrogen. The heating was switched on and as the temperature rose to 100 °C the nitrogen was removed from the autoclave.

After the temperature reached the require level the solution “zero sample” was drawn off for chemical analyses. Subsequently, the mixture of 50 % of oxygen and 50 % of nitrogen was introduced into the autoclave to establish the required oxygen partial pressure. During the experiments samples of the solution were taken periodically to determine metals concentration (Cu, Zn, Ni, Co, As). Metals concentration was analyzed at Quality Investigation Center (CBJ) in Lubin by ASA spectrometry.

Solid samples of middlings before and after each pressure leaching test were examined by mineralogical SEM microscopy to evaluate the composition of the solid and to assess the effectiveness of applied leaching parameters range.

RESULTS AND DISCUSSION

EFFECT OF TEMPERATURE ON PRESSURE LEACHING OF THE SHALE MIDDDLINGS

Pressure leaching of Lubin middlings was examined at elevated temperatures from 100 to 180 °C while concentrations of Cu, Fe, Ni, Co and As were analysed in the samples taken during the leaching. Experimental results are shown in Figs. 3 for Cu, Fe, and Co, respectively. The observed effect of temperature was quite complex and the following observations have been done:

- leaching of copper in oxygenated sulphuric acid at 100 °C required about 120 min. of activation time. This was most likely due to the formation of H$_2$S observed at the initial stage of the process. Remarkable acceleration of the process was subsequently detected after 120 min. of activation
- unexpectedly, at 120 °C no copper leaching was detected. This might be most likely explained as a hindering effect produced by the presence of elemental sulphur at its melting point
− at temperatures exceeding 140 °C the leaching appeared to be very rapid, although some decrease of Cu concentration was observed at 160 and 180 °C versus 140 °C. Co-precipitation of iron compounds or sorption on organic matter are the only explanation of observed effects

− the rate of leaching of Fe from Lubin middlings increases with temperature up to 120 °C, then iron concentration slightly drops as the result of precipitation of iron(III) oxide (Fe₂O₃) or goethite (FeOOH). The appearance of soluble iron in leaching solution results from leaching of Cu-Fe sulphides, mainly bornite – Cu₃FeS₄ and chalcopyrite – CuFeS₂.

Pressure leaching of cobalt was practically not observed at temperatures 100 and 120 °C with detected concentration of cobalt about 5 mg/dm³. Remarkable acceleration of leaching of Co was observed at temperatures above 140 °C and detected concentration of cobalt grown-up to 40 – 50 mg/dm³.

Quite complex kinetic curves for nickel (not presented here) indicated that at 120 °C the highest leaching recovery was observed with the final Ni concentration of about 180 mg/dm³. At temperatures exceeding 140 °C the leaching rate of nickel decreases, which are hard to explain at this stage of investigation and require detailed analysis of post-leaching residues from the leaching process, particularly the mineralogical forms of metals.

The concentration vs. leaching time relationships for leaching of arsenic was similar to those of cobalt. Pressure leaching of arsenic was nearly not observed at temperatures 100 and 120 °C when detected concentration of As was about 10 mg/dm³. Significant increase in leaching rate of As was observed at temperatures above 140 °C while concentration of arsenic grown-up to 70 – 90 mg/dm³.

From results of pressure leaching it is well seen, that very effective recovery of metals from Lubin middlings can be observed for experiments performed at temperatures exceeding 140 °C. At 140 °C observed were the highest Cu, Co and As recoveries. It was also detected that at temperatures exceeding 180 °C iron control became possible as a result of precipitation of FeOOH or Fe₂O₃. Arsenic, a harmful contaminant, will require a removal procedure prior to recovering of copper, nickel and cobalt. Precipitation of crystalline scorodite – Fe₃(AsO₄)·(OH)·2H₂O at temperatures above 180 °C could be taken into consideration.

The relationship presented in Fig. 3 are characterized by rapid copper, iron and cobalt leaching during the initial 60 minutes. Subsequently, a slower increase in copper, iron and cobalt concentration is observed. The first, very rapid step of leaching, lasting 30 to 60 minutes is, most likely due to initial fast leaching of easy leachable copper minerals - bornite and chalcocite, the once existing in the shale ore originated from Lubin. The second, slow step is probably due to leaching of chalcopyrite and covellite the most refractory copper minerals. The fact that concentration of ferrous ions in the solution before introduction of oxygen is 1.0 g/dm³ suggest that ferric partly occurred as a oxides in the shale ore. Maximum recovery of copper (97 %) and cobalt (80 %) was observed at 140° C and above 90 % for Fe at 160
\( ^\circ C \). However, in the investigated range of temperatures nickel did not leach well. Nickel leaching recovery rarely exceeded 10 % in most experiments. Neither lead nor silver was detected in the solution.

Fig. 3 Effect of temperature on the pressure leaching of copper, iron and cobalt from Lubin middlings. Oxygen partial pressure – 0.5 MP, concentration of H\(_2\)SO\(_4\) – 5 %, solid to liquid ratio, s/l – 1:10
The effect of sulphuric acid concentration on the metals leaching was investigated in the range of 20 to 50 g/dm³ at temperature of 140 °C and oxygen partial pressure 0.5 MPa. Fig. 4 presents concentration – leaching time relationships for copper and cobalt at different sulphuric acid concentrations. Copper doesn’t leach before introduction of oxygen and course of copper leaching resembles those observed during investigations of the effect of temperature.

Only for concentration of sulphuric acid 30 g/dm³ a highest leaching rate and highest concentration of copper in the solution was observed. There are two steps of pressure leaching. The ferric ion starts to leach sulphidic minerals before the oxygen introduction. There were also observed some differences in ferric concentration depending on sulphuric acid concentration. For 20 g/dm³ of H₂SO₄ the concentration of ferric ions in solutions was 680 mg/dm³ and for 50 g/dm³ of H₂SO₄ the concentration of ferric raised to 940 mg/dm³.

Generally, sulphuric acid concentration was found to have an effect on middlings ferric leaching. For concentration of sulphuric acid below 20 g/dm³ the precipitation of ferric compounds have occurred after 60 minutes of leaching. There were also two
leaching steps for 30, 40, and 50 g/dm$^3$ concentrations of sulphuric acid, similarly to copper leaching. The highest concentration of ferric ions in solution has been reached for sulphuric acid exceeding 30 g/dm$^3$. Kinetic curves observed for Cu and Co leaching at acid concentrations above 30 g/dm$^3$ were almost identical.

There was no cobalt leaching detected before introduction of oxygen. The course of cobalt leaching resembles the copper leaching, i.e. there were observed two steps. The first step, in which the rate of cobalt dissolution was found high and the second one with evidently slow cobalt dissolution rate.

![Graph](image)

**Fig. 5.** Effect of sulphuric acid concentration on metals recovery by pressure leaching from Lubin middlings

Generally, a little effect of sulphuric acid concentration on cobalt and copper leaching have been found from H$_2$SO$_4$ concentrations above 3 % (Fig.6). A 97 % of leaching recovery of copper and 80 % of leaching recovery of cobalt recovery was reached regardless to sulphuric acid concentration. The highest iron recovery occurred for 30 g/dm$^3$ of H$_2$SO$_4$. Presented results suggest that high recovery of copper with simultaneous partial precipitation of ferric compounds is possible. However, it was evident, that at the lowest H$_2$SO$_4$ concentration (2 %) the precipitation of Fe(III) from the solution was observed, most likely as FeOOH and Fe$_2$O$_3$ and the concentration of Fe in solution decreased to about 1.3 g/dm$^3$. This precipitation of Fe was not detected at higher acid concentration (3-5 %). Iron control in the leaching solution at elevated temperature can be useful as a method of purification from the excesses of Fe prior the recovering of metals. His effect will be further investigated in details.
THE EFFECT OF OXYGEN PARTIAL PRESSURE ON CU, FE AND CO LEACHING

The effect of oxygen partial pressure was investigated in the range from 2.5 to 10 MPa. The leaching temperature (140 °C), sulphuric acid concentration (50 g/dm³) and liquid/solid ratio ratio (10 : 1) were kept constant. Figure 6 presents concentration – leaching time relationships for copper and cobalt. Two steps of leaching courses were found, similarly to the other experiments. Effect of oxygen partial pressure on leaching recovery of Cu, Fe, Ni, Co and As were collected in Fig. 7. Lead and silver were not solubilised during pressure leaching.

On the basis of results presented in Fig. 7 it can be seen that pressure leaching is a very efficient process. Oxygen partial pressure has a noticeable effect on copper, cobalt, arsenic and ferric solubilization. The highest recovery of metals was detected at oxygen partial pressure of 7.5 MPa. Solubilisation of nickel was highly reduced most likely due to the dissemination of Ni in pyritic phase, according to mineralogical examinations (Auge et al., 2007).

Table 2 summarises the pressure leaching experiments for Cu, Co, Ni, As and Zn on the basis of solid residue analysis. According to the presented data, only nickel leaching recovery was observed to be as low as 30-40 %. Copper, cobalt and zink can be easily leached out from the examined Lubin middlings. Pressure leaching can be therefore considered as an efficient alternative for processing of Lubin middlings.
Fig. 7. Effect of oxygen partial pressure on metals recovery from Lubin middlings. Temperature 140 °C, H₂SO₄ 50 g/l, s/l 1:10 (1 atm = 0.101 MPa)

Table 2. Recovery of metals during pressure leaching of Lubin middlings in oxygenated sulphuric acid

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature, °C</th>
<th>Oxygen partial pressure, atm</th>
<th>H₂SO₄ concentration, %</th>
<th>Leaching recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>PL/1/10</td>
<td>100</td>
<td>5</td>
<td>5</td>
<td>68.8</td>
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<td>PL/2/10</td>
<td>120</td>
<td>5</td>
<td>5</td>
<td>38.1</td>
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<td>PL/7/09</td>
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<td>140</td>
<td>5</td>
<td>5</td>
<td>98.3</td>
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CHARACTERIZATION OF PRESSURE LEACHING RESIDUE BY SEM MINERALOGICAL EXAMINATIONS

Solid residue after pressure leaching was examined by SEM (Fig. 8). It can be seen that unleached metal-bearing minerals (mostly covellite, chalcopyrite, pyrite and galena) are disseminated in shale organic matter (Figs. 8 B, C and D), which was practically not decomposed neither during non-oxidative nor pressure leaching. To liberate these particles for further metals recovering require is either further intensification of pressure leaching or additional milling to reduce particle size of unleached solid grains.

Some unleached minerals (CuS, CuFeS₂) remain in the solid as quite coarse, spongy structure requiring either longer leaching time or more intensive leaching parameters (Fig. 9 A).

Fig. 8. SEM pictures of pressure leached samples of Lubin middlings exhibiting fine dissemination of metals-bearing minerals in shale matter
CONCLUSIONS

Shale-containing by-products (middlings) - tailings of 1st cleaning from flotation circuits at Lubin Concentrator, which exhibited remarkably elevated content of organic carbon, can be efficiently processed hydrometallurgically by non-oxidative leaching followed by pressure leaching. High carbonate content, a specific and unique feature of Polish copper ores, and fine dissemination of metal-bearing minerals (predominantly sulphides) unquestionably require a chemical pretreatment of the shale feed with H₂SO₄ prior the atmospheric and pressure leaching in oxygenated solutions of sulphuric acid.

Non-oxidative leaching of Lubin middlings (Cu – 2.7 %, Pb – 1.52 %, Ni – 374 ppm, Co – 572 ppm, Ag – 170 ppm) is a very rapid, selective, and relatively simply-controlled process. Selective liberation of metal sulphides improves their flotatability while total decomposition of carbonates makes further pressure leaching more efficient.

Pressure leaching of Lubin middlings revealed, that the process is remarkably fast and efficient for recovering of Cu, Fe, Co and As with much lower recovery of Ni. To accomplish maximum recovery of metal, pressure leaching has to be conducted at temperatures above 140 °C and under oxygen pressure exceeding 5 atm. From pressure leaching experiments performed at temperatures 120 – 180 °C, under oxygen pressure 2.5 – 10 atm H₂SO₄ concentrations 2 – 5 %, and at solid/liquid ratio 1:10 it results that about 96 – 97 % of Cu, 96 % of Fe 96 % of As, and 82 % of Co can be recovered after about 2 hours of leaching. Much lower leachability of nickel (30-40 %) can be explain in terms of its dissemination in pyrite. It was also observed that at temperatures exceeding 160 °C precipitation of Fe as goethite or hematite commences, which can be applied as an iron control process for solution purification.

Pressure leaching with oxidized H₂SO₄ solutions was not efficient to leach of Ag, Pb, and precious metals. The solid residue after leaching must be either upgraded by flotation or subjected to leaching in chloride solutions to recover remaining metals.

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Przedstawiono badania wpływu temperatury, stężenia kwasu siarkowego i ciśnienia parcjalnego tlenu na ciśnieniowe ługowanie frakcji łupekowej rudy miedzi. Ługowanie prowadzono w autoklawie, pod ciśnieniem tlenu i w temperaturach od 100 do 180 °C. Nadawę do ługowania ciśnieniowego stanowił odpad I czyszczenia i ciągu technologicznego ZWR Lubin, który jest materiałem łupekowym o podwyższonej koncentracji metali i węgla organicznego. Proces ługowania prowadzono w roztworach kwasu siarkowego o stężeniu od 20 do 50 g/dm³. W badaniach wykazano wysoką skuteczność procesu dla ługowania miedzi, kobaltu, niklu, żelaza i cynku z półproduktem łupekowego ZWR Lubin.