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ATMOSPHERIC LEACHING OF SHALE BY-PRODUCT
FROM LUBIN CONCENTRATOR

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The results of non-oxidative leaching with sulphuric acid followed by atmospheric leaching with oxygenated H₂SO₄ have been presented for shale containing middlings (tailings from 1st cleaning flotation) from Lubin Concentrator. It was found that all leaching or bioleaching processes performed in acidic media has to be preceded by non-oxidative decomposition of acid-consuming carbonate components to liberate finely disseminated metal-bearing minerals. Atmospheric leaching appeared to be very efficient process for recovering Cu, Ni and Co from Lubin middlings due to favorable mineralogical composition and fine diameters of leached particles. Maximum recovery of Cu, Ni and Co after 5 hours leaching was observed for experiments at 90 °C in the solutions containing 15 – 30 g/dm³ of Fe(III). Solid residue after atmospheric will be further processed by flotation or chloride leaching to recover Ag, Pb and precious metals.

Key words: shale ore, atmospheric leaching, copper

INTRODUCTION

Polish copper deposits (LGOM - Legnica-Glogow Copper Basin, SW Poland) exhibit unique, sedimentary nature (Rydzewski, 1996, Konstantynowicz, 1990). These results in the presence of three ore fractions: dolomitic, sandstone, and shale. From those three ore fractions shale fraction reveals two exceptional, opposite properties. It contains the highest concentrations of copper and accompanying metals (Ag, Ni, Co, Zn, Pb, V, Mo…) and simultaneously is the most troublesome in the flotation circuits (Tomaszewski, 1995). In the case of shale fraction observed is the dissemination of fine metal sulfides in the carbonate matter and in black shale-clay rocks that form the majority of the gangue. Such a fine dissemination of copper sulfides in carbonate-organic matrix considerably reduces the susceptibility of the ore to both effective liberation and flotation. A relative increase of quantity of shale-clay and carbonate

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fractions in flotation feeds, which are known as mostly hard-to-treat in flotation circuits, is currently observed. According to the latest data (Kubacz and Skorupska, 2007) the content of shale fraction in Lubin deposit has already exceeded 25 % and is expected to increase in coming years.

Complex and unique mineralogical structure as well as chemical composition of Polish copper ores mined from sedimentary deposits is the principal reasons for copper, silver and other metals losses to flotation tailings (Łuszczkiewicz 2000, 2004). The presence of shale creates additional technical, economical and ecological issues. The selective liberation of fine metals-bearing particles from the host matrix would be the only way to enhance metals recovery. However, it appears to be ineffective by physical methods in the existing milling circuits. Consequently, the hydrophilic gangue-sulphide intergrowths seriously reduce both flotation selectivity and the metal grade in the concentrate (Łuszczkiewicz, et al., 2006). Therefore, it can be concluded that the existing beneficiation technologies currently applied to Polish copper ores have already reached the limit of their technological efficiency (Chmielewski and Charewicz 2006, Łuszczkiewicz and Chmielewski 2006, Chmielewski, et al., 2007).

The application of modern hydro- or biometallurgy, well known and approved in the world for copper recovering, becomes an urgent necessity in Polish copper industry to reverse unfavorable trends in flotation results, particularly at Lubin Concentrator (Grotowski, 2007). The application of atmospheric leaching has to be considered as a complimentary process for processing of shale flotation by-product which is hardly to beneficiate using existing techniques. This approach, presented by author within the research program of BIOSHALE (Chmielewski and Charewicz, 2005, 2006a) primarily involves the separation of the most troublesome ore fraction (shale containing middlings) and introduction of hydrometallurgical methods for their alternative, effective processing.

EXPERIMENTAL AND MATERIAL

In the concept of separation and individual processing of shale-containing by-product from Lubin Concentrator two alternatives were initially considered (Fig. 1). First one was the shale flotation from run-of-mine ore by means of non-polar collectors, second was the flotation or separation of middlings – tailings from 1st cleaning in 1st flotation circuit. The comprehensive investigations of both alternatives resulted in elimination of the first approach and in an approval the Lubin middlings as a shale concentrate suitable for hydrometallurgical treatment.

The feed material applied for laboratory experiments on non-oxidative leaching followed by atmospheric leaching in oxygenated sulphuric acid 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. 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 atmospheric leaching taking place in acidic conditions required previous non-oxidative leaching with acid in order to decompose totally the acid consuming components, mainly calcium and magnesium carbonates (Łuszkiewicz and Chmielewski, 2006) Chmielewski, et al., 2007). The non-oxidative leaching was performed before each atmospheric leaching experiment.

![Diagram of processing steps](image)

**Fig. 1. PWR general concept of separate processing of shale ore from Lubin Concentrator by means of hydro- and bio-metallurgy**

**Table 1. Chemical composition of Lubin middlings (tailings of 1st cleaning) applied for atmospheric leaching**

<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>2.72</td>
<td>1.76</td>
<td>374</td>
<td>572</td>
<td>1.51</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Content</th>
<th>Ag, g/t</th>
<th>Zn, g/t</th>
<th>S, %</th>
<th>Sso4, %</th>
<th>C_total, %</th>
<th>C_org, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>1 200</td>
<td>2.95</td>
<td>1.45</td>
<td>14.30</td>
<td>8.96</td>
<td></td>
</tr>
</tbody>
</table>

Middlings from Lubin Concentrator (Table 1) exhibit elevated contents of copper, silver and other base metals, which are present in the solid as sulphides. Solubilisation of metals from their sulphidic minerals is only possible when oxidation agent is added to the leaching system. Gaseous oxygen and iron(III) ions were selected for this purpose, taking into account technical, economical and ecological aspects. Laboratory tests were performed at various temperatures (25, 60, 80, 90 °C), sulphuric
acid (20, 50, 120 g/dm$^3$) and iron(III) (0, 7, 15, 30 g/dm$^3$) concentration. Analysed were the concentration – leaching time relationships for Cu, Fe, Ni, Co, and As. Solid residue were examined for metals content and mineralogical SEM observation were conducted to asses the liberation of remaining metals (Ag, Pb, Au, PGM…) for further recovery.

Polish copper ores, in contrast to majority of world copper chalcopyrite - deposits, exhibit very favourable mineralogical composition with regard to hydrometallurgical and biometallurgical processing. Chalcocite (Cu$_2$S) and bornite (Cu$_5$Fe$_3$S$_8$) are the dominating minerals while chalcopyrite (CuFeS$_2$) and covellite (CuS) are the minor copper minerals. Detailed mineralogical analysis of Lubin middlings, performed by BRGM in the frame of BIOSHALE project (Auge et al., 2007) unexpectedly revealed, that practically only chalcocite/digenite and bornite are dominating copper minerals in Lubin middlings with traces of chalcopyrite and covellite – most refractory copper minerals. Consequently, we could expect quite high recovery of copper and other base metals from middlings even at mild conditions. The presence of finely dispersed grains of copper sulphide in shale-dolomitic middlings gangue is additional beneficial factor, particularly after their liberation by non-oxidative leaching.

Separation of organic fraction along with shale-containing middlings has an additional beneficial effect leading to the reduction of organic carbon in the feed, what is particularly significant for the flash smelter at Głogów II metallurgical plant. Presently observed elevated content of organic carbon in concentrates already exceeds about 9% and is the main reason for undesirable, significant decrease in smelter throughput (Kubacz, 2007).

RESULTS AND DISCUSSION

EFFECT OF CONCENTRATION OF H$_2$SO$_4$

According to Cu concentration – leaching time plots for atmospheric leaching of Lubin middlings in oxygenated sulphuric acid (Fig. 2) the process of copper solubilisation starts only when oxygen was introduced to the leaching system. It means that there is no oxidized copper in the solid subjected to leaching in sulphuric acid solution. Copper is present in the middlings exclusively in the sulphidic form and requires an oxidant to be solubilised. In contrary, iron digestion was observed to leach even in not oxygenated acidic solution. It was the evidence of presence of iron in the oxidized form. Additional increase in iron concentration following the oxygen introduction, can be explain by the solubilisation of Cu-Fe sulphides, mainly bornite – Cu$_5$Fe$_3$S$_8$, one of the dominating copper sulphides in the Lubin middlings.

Very fine copper mineralization in the Lubin middlings and exceptionally beneficial mineralogical composition of the leaching feed, resulted in superior leachability of middlings even at ambient conditions. About 40% of Cu was observed to leach out in experiments conducted at 21 °C. The concentration of Cu in the leaching pregnant solution was about 1.6 g/dm$^3$ after 6 hours of leaching at s/l = 1:5.
Atmospheric leaching of shale by-product from Lubin Concentrator

The effect of concentration of sulphuric acid was examined on atmospheric leaching of Lubin middlings at various temperatures (25-90 °C) at solid/liquid ratio from 1:5 to 1:4 and at the oxygen flow rate of 30 l/h. The concentration of copper vs. leaching time plots at 70 °C (Fig. 3.) indicates the favorable effect of acid concentration between 20 g/dm³ and 50 g/dm³. Further increase in H₂SO₄ concentration was rather less significant. Similarly, minor effect of concentration of sulphuric acid was observed for Ni, Co and As leaching. Therefore, the H₂SO₄ concentration was kept at the level of 50 g/dm³ for all leaching experiments.

**EFFECT OF TEMPERATURE**

The effect of temperature was examined on atmospheric leaching of Lubin middlings with solutions containing 50 g/dm³ H₂SO₄ at s/l ratio of 1:4. Leaching tests were conducted at 25, 60, 80, and 90 °C. Results for Cu, As, Co and Ni are given in Figs. 4 – 7.

Temperature appeared to be the essential parameter for atmospheric leaching of middlings. Copper concentration after 5 hours of leaching (s/l = 1:4) increased from about 2.8 g/dm³ to 9.0 g/dm³ when temperature grew from 25 to 90 °C (Fig. 4).

The temperature was also evidently the most advantageous parameter for leaching of arsenic, cobalt and nickel (Figs. 5, 6 and 7).
Fig. 4. The effect of temperature on the atmospheric leaching of copper from Lubin middlings. ($s/l = 1:4$, oxygen – 30 dm$^3$/h, $H_2SO_4$ – 50 g/dm$^3$)

Fig. 5. The effect of temperature on the atmospheric leaching of arsenic from Lubin middlings. ($s/l = 1:4$, oxygen – 30 dm$^3$/h, $H_2SO_4$ – 50 g/dm$^3$)

Fig. 6. The effect of temperature on the atmospheric leaching of cobalt from Lubin middlings. ($s/l = 1:4$, oxygen – 30 dm$^3$/h, $H_2SO_4$ – 50 g/dm$^3$)

Fig. 7. The effect of temperature on the atmospheric leaching of nickel from Lubin middlings. ($s/l = 1:4$, oxygen – 30 dm$^3$/h, $H_2SO_4$ – 50 g/dm$^3$)
The addition of Fe(III) to solutions of atmospheric leaching of Lubin middling resulted in significant increase of copper, nickel, cobalt and arsenic leaching rate. The presence of Fe(III) created apparently higher copper leaching rate, particularly in its first period (Fig. 8). More pronounced effect of iron(III) was observed in Ni, Co, and As leaching (Figs. 9, 10, 11). Final concentrations of Co and Ni in solutions from atmospheric leaching with Fe(III) were about 5 times higher than those observed after leaching with oxygenated H₂SO₄ without Fe(III). Concentrations of Ni and Co after 5 hours of atmospheric leaching of Lubin middlings were 27 and 100 mg/dm³, respectively. Unfortunately, the addition of Fe(III) resulted in remarkably high arsenic leaching. The presence of As in leaching liquors has to be considered in forthcoming solutions purification steps.

Comparing the atmospheric leaching results presented in Figs. 9 – 11 on the basis of middlings analysis we may see a high leaching recovery of Cu, Co and As, while the recovery of nickel was the lowest among the considered metals. The leaching results in oxygenated sulphuric acid without Fe(III) for Ni, Co and As were correlated as a function of copper concentration in the leaching solution (Fig. 12). It is well seen that process of leaching exhibits acceleration as copper is being leached out from the middlings. This acceleration is most pronounced for arsenic while the least for nickel.
The presented correlations can be an evidence that Ni, Co and As are partially disseminated in copper sulphides (which dissolve at first) and partially form their own phases.

Fig. 10. The effect of Fe(III) on the atmospheric leaching of cobalt from Lubin middlings. (90 °C, s/l = 1:4, oxygen – 30 dm³/h, H₂SO₄ – 50 g/dm³)

Fig. 11. The effect of Fe(III) on the atmospheric leaching of nickel from Lubin middlings. (90 °C, s/l = 1:4, oxygen – 30 dm³/h, H₂SO₄ – 50 g/dm³)

Fig. 12. Correlation between concentration of Cu and other metals during atmospheric leaching of Lubin middlings at 70 °C, H₂SO₄ - 50 g/dm³
Mineralogical SEM analysis of middlings before and after atmospheric leaching (Fig. 13) indicated very fine dissemination of metals-bearing sulphides in carbonate and shale matter (Fig. 13 A, B, C). This is the major reason for observed elevated, growing and hardly accepted losses of metals in flotation tailings, particularly at Lubin.
Concentrator. Liberation of metals-bearing sulphide particles from complex carbonate- or shale-based intergrowths presented in Fig.13 A, B, C cannot be accomplished by mechanical milling in existing technological circuits. Consequently, only small part of metals from such a material can be recovered to the flotation concentrate. The application of novel approach, using bio- or hydrometallurgy is the only chance to solve the technical issues and to reduce the metals loses.

Solid residue after the atmospheric leaching performed for various experiment parameters (Fig. 13 C, D, E) exhibited the presence of residual amounts of most refractory copper minerals (covellite and chalcopyrite) requiring either more reactive leaching parameters (temperature) or longer leaching time for higher copper recovery. In the solid residue after the atmospheric leaching we could not observe the presence of the sulphide-carbonate intergrowths, which were chemically decomposed during the non-oxidative preleaching. Dominating are the fine disseminated minerals in organic matter, which was only partially decomposed at the atmospheric leaching parameters. The organic shale particles contain both fine particles of copper residual minerals and minerals not leached in sulphate solution (galena, silver minerals).

CONCLUSIONS

Shale-containing by-product from flotation circuits at Lubin Concentrator (which exhibited remarkably elevated content of organic carbon) can be efficiently processed hydrometallurgically, using non-oxidative leaching with sulphuric acid followed by atmospheric leaching in oxygenated H_2SO_4 and in the presence of iron(III). High carbonate content, a specific and unique feature of Polish copper ores, and fine dissemination of metal-bearing minerals (predominantly sulphides) in carbonate and shale matter unquestionably require a chemical pretreatment of the shale solid prior the atmospheric 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) and Lubin shale concentrates is quite rapid, selective, and relatively simply-controlled process. Selective liberation of metal sulphides in non-oxidative leaching remarkably improves their flotatability while total decomposition of carbonates makes further atmospheric or pressure leaching more efficient.

Atmospheric leaching in oxidized sulphuric acid can be applied to recover Cu, Ni, Co and As from Lubin middlings and from shale concentrates. Leaching results were very satisfactory predominantly due to advantageous mineralogical compositions of Lubin copper minerals, with chalcocite and bornite as principal components. The most advantageous parameters for atmospheric leaching are: concentration of H_2SO_4 – 50 g/dm³, solid/liquid ratio, s/l = 1:4, temperature – 90 °C, concentration of Fe(III) – 30 g/dm³, and percolating oxygen as an oxidizing agent. Atmospheric leaching of Lubin middlings leads to about 9 g/dm³ Cu in leaching solution after about 5 hours of one-stage leaching. Concentrations of Ni, Co, and As are 27 mg/dm³, 100 mg/dm³,
and 140 mg/dm³, respectively. Lead, silver, and precious metals remain unleached in the leaching solid residue and will be recovered by means of flotation or leaching in downstream operations. Large part of organic matter was not subjected to decomposition after the atmospheric leaching and still contained the fine particles of metals-bearing minerals.

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REFERENCES


Przedstawiono wyniki badań nad ługowaniem nieutleniającym za pomocą kwasu siarkowego i ługowaniem atmosferycznym w natlenionym roztworze H₂SO₄ i w obecności jonów Fe(III) półproduktem flotacji (odpad I czyszczenia ZWR Lubin). Badany półprodukt stanowił materiał o wysokiej koncentracji frakcji łupkowej i został uznany za koncentrat tej frakcji. Wykazano, że procesy ługowania utleniającego lub bioługowania prowadzone w warunkach kwaśnych muszą być bezwzględnie poprzedzone procesem niucléacji rozkładu składników węglanowych w celu uwolnienia bardzo drobno rozproszonych mineralów metalonośnych. Ługowanie atmosferyczne okazało się procesem bardzo efektywnym w odniesieniu do badanego półproduktau łupkowego. Proces zapewnia skuteczne odzyskanie do roztworu Cu, Ni, Co dzięki korzystnemu składowi mineralogicznemu frakcji łupkowej. Maksymalny stopień wylugowania metalu, po 5 godzinnym procesie, obserwowano w doświadczeniach prowadzonych w temperaturze 90°C i obecności jonów Fe(III) o stężeniu w zakresie 15-30 g/dm³. Pozostałość stała po ługowaniu atmosferycznym będzie poddana procesowi flotacji lub ługowaniu chlorkowemu dla odzyskania srebra, ołowiu i innych metali szlachetnych.