AMMONIA PRESSURE LEACHING FOR LUBIN SHALE MIDDINGS

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Ammonia pressure leaching has been investigated as an alternative for hydrometallurgical processing of Lubin middlings – a shale-enriched flotation by-product. The effect of primary parameters: temperature, oxygen partial pressure, ammonia and ammonium sulfate concentration and stirring rate on leaching recovery of Cu, Ag, Zn, Ni, and Co were examined.

key words: hydrometallurgy, ammonia leaching, black shales

INTRODUCTION

Ammonia has been widely applied as an effective leaching agent in numerous hydrometallurgical processes for many years. Ammonia can be effectively used for leaching of base metals (Cu, Ni, Co, Zn) as well as for precious metals (Ag, Au) because of formation of soluble, very strong ammonia complexes. Moreover, ammonia has been considered as an attractive leaching agent due to its low toxicity, low costs and ease of regeneration by evaporation from alkaline solutions. An important advantage of ammonia environment in hydrometallurgy is its selectivity in terms of solubilization of desired metals and precipitation of undesirable iron in one unit operation (Meng and Han, 1996).

Ammonia leaching can be used in non-oxidative, oxidative and reductive leaching. It was first applied and developed for recovery of copper from its metallic and oxide raw materials. Copper forms well soluble and very stable complexes ([Cu(NH₃)₄]²⁺) and can be leached at ambient conditions due to the excellent solubility of ammonia in water.

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In industrial scale ammonia leaching with oxygen as oxidant was applied since 1954 for treatment of copper, nickel and cobalt sulfide ores and concentrates at Fort Saskatchewan by Sherritt Gordon (Forward, 1953). The Arbiter ammonia leaching process for sulfide flotation concentrates was developed in 1970’s in Anaconda (Kuhn et al., 1974). The process used ammonia leaching at 34.5 kPa with oxygen as oxidant. Copper in PLS was purified by means of solvent extraction and electrowon to marketable cathodes. The Arbiter ammonia process was also considered as an alternative for hydrometallurgical processing of Polish copper concentrates (KGHM Polish Copper).

Escondida (Chile) applied oxygenated ammonia solutions for partial leaching of copper from chalcocite concentrates at atmospheric pressure (Duyvetseyn and Sabacky, 1995). Solid residue after leaching, containing CuS, was subsequently floated to produce concentrate for smelter. It was successfully applied for several years to elevate the plant capacity at Escondida. The plant was closed after smelter expansion.

Decreasing copper recovery and concentrates grade observed at KGHM concentrators (particularly at Lubin) is a result of increasing concentration of shale fraction in Polish copper ores. Black shale is a lithological fraction exhibiting remarkably elevated concentration of base (Cu, Ni, Co, Zn) and precious metals (Ag, Au, PGE) with regard to dolomitic and sandstone fractions. Simultaneously, the growing presence of shale material is a primary reason for observed technical problems in flotation plans. Separation of black shale from the flotation circuit and application of hydrometallurgy for its processing was an idea presented by authors as a result of three years (2004–2007) laboratory investigations performed within the frame of BIOSHALE research project (d’Hugues et al., 2007, d’Hugues et al., 2008, Groudev et al., 2007, Chmielewski et al., 2007).

Selection of black shale feed and experimental determination of conditions for effective recovering of copper and other valuable metals (Fe, Ni, Co, Pb, Au, PGM…) from shale containing materials (ore, middlings, shale concentrates) was the general task at the starting point of the BIOSHALE project. The research program was initially focused on the geological shale samples collected for preliminary laboratory examinations (chemical and mineralogical analyses, non-oxidative, atmospheric and acid pressure leaching). After the extended period of experimental work, the shale middlings – tailings from the 1st cleaning flotation at Lubin Concentrator (ZWR Lubin) - were finally selected and accepted by a technical and engineering staff at KGHM as an only shale containing solid for hydrometallurgical laboratory tests and for future full scale alternative processing. Simultaneously, this material was unanimously recognized as the most troublesome solid in existing flotation circuit at Lubin Concentrator due to the high content of shale fraction (organic matter) and sulfide minerals fine dissemination. It is fully considered as a shale concentrate, which can be separated from the flotation circuit for hydrometallurgical treatment. Initial samples were collected of numerous shale ore fractions from various LGOM (Poland) deposits.
Chemical analyses exhibited varying metal content in the shale. For further laboratory studies the process alternatives were selected including chemical pretreatment with H₂SO₄ for flotation, non-oxidative leaching, atmospheric leaching and pressure leaching investigations as BIOSHALE project WP4 tasks. The laboratory tests undoubtedly confirmed that the assumptions made in the first stage of the work program were correct.

Acidic leaching of shale middlings appeared to be very effective from mineralogical and technical point of view. Favorable mineralogical composition of Lubin middlings (dominating content of copper in the form of chalcocite and bornite) and easy access to sulfuric acid, being, in fact, a waste material from copper smelters, makes this approach very attractive for future technological alterations (Chmielewski, 2007, Konopaca et al., 2007, Wódka et al., 2007).

One of the main reason, that black shale fraction became a serious problem in flotation of Polish copper ores is a very fine mineralization of metal-bearing sulfides and their dissemination in hydrophilic carbonate and organic matter. It is impossible to liberate these minerals only by means of mechanical grinding. Consequently, a great amount of metal values remain in flotation tailings and leads to hardly accepted metals loses. Very complex and expensive alteration in flotation and grinding circuits appeared to be ineffective in terms of declining flotation indexes. Both the recovery and concentrate grade have been decreasing remarkably, particularly at Lubin Concentrator.

An additional unfavorable effect has been lately observed during the flash smelting at Głogów II smelter. The growing content of shale fraction (Table 1) and, consequently, increase in organic carbon content - exceeding 9 % for Lubin and Polkowice - in the concentrate smelter feed, results in a notable diminishing efficiency of the process (Kubacz and Skorupska, 2007). Therefore, separation of shale fraction from the flotation circuits (e.g. Lubin middlings) and its individual, hydrometallurgical processing, postulated within the frame of BIOSHALE project, can be accepted as a key alternative for existing technologies. Such alteration can result in the following advantages:

- Integration of new technology with existing processes.
- Simplification of existing flotation circuits and enhancement of flotation efficiency.
- Increase of metals recovery in total (flotation concentrate + hydrometallurgy) – remarkable decrease of metals loses and environmental impact.
- Stabilization of organic carbon content in concentrates on the proper level, accepted for flash smelting process.
- Effective utilization of an excess of sulfuric acid – a byproduct or waste from smelting.

It seems rather to be obvious that due to observed apparent decline of copper ores quality and upgradeability, particularly from Lubin and Polkowice deposits (Table 1),
present beneficiation technologies are not able to guarantee the acceptable metals recovery and concentrate grade without significant technology alteration and urgent instruction of new alternative concepts. Ammonia leaching can be considered as an alternative process. This appeared to be urgent for Polish copper industry.

Table 1. Content of shale fraction in Polish copper ores mined from various LGOM deposits (Kubacz and Skorupska, 2007)

<table>
<thead>
<tr>
<th>Mine</th>
<th>Year</th>
<th>2002</th>
<th>2004</th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubin</td>
<td></td>
<td>18.8</td>
<td>15.0</td>
<td>27.0</td>
</tr>
<tr>
<td>Polkowice-Sieroszowice</td>
<td></td>
<td>11.3</td>
<td>13.3</td>
<td>11.2</td>
</tr>
<tr>
<td>Rudna</td>
<td></td>
<td>2.2</td>
<td>3.9</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The objectives of this paper was to evaluate the effect of key parameters (oxygen pressure, temperature, ammonia concentration, ammonium sulfate concentration, solid to liquid ratio and stirring rate) on the recovery of Cu, Ni, Co, Zn and Ag during ammonia pressure leaching of Lubin shale middlings - tailings from 1st cleaning at Lubin Concentrator.

Ammonia pressure leaching of Lubin shale middlings was selected as an alternative to acidic - atmospheric and pressure leaching. Ammonia leaching was expected to be applied without a need of carbonates acidic decomposition, as it was necessary for leaching in acidic media. Major advantage of ammonia solutions is confirmed leachability of most metals which are being recovered from shale enriched Lubin middlings (Cu, Co, Ni, Zn, Ag, Au…).

EXPERIMENTAL

LUBIN MIDDINGS CHARACTERIZATION

Shale middlings from Lubin Concentrator were collected and characterized in details in D.4.2. Deliverables within BIOSHALE European project, on the basis of 1st sampling campaign in 2006 and 2nd sampling campaign in 2007. Middlings from 2nd sampling campaign were used as a feed for ammonia leaching. It is well seen from Table 2, that chemical composition of material examined in 2007 was very similar to those used in previous investigations. Copper content was about 2.60 %, organic carbon was 6.30 % - lower than in 2006 campaign. The content of accompanying metals was observed to be almost identical, except of zinc. The comparison of chemical analyses of Lubin middlings samples from 2006 and 2007 evidently shows, that examined feed is fairly stable in terms of its chemical composition.
Table 2. Chemical characterization of Lubin shale middlings (1st and 2nd sampling campaigns – 2006 and 2007).

<table>
<thead>
<tr>
<th>CONTENT</th>
<th>1st campaign</th>
<th>2nd campaign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu, %</td>
<td>2.72</td>
<td>2.60</td>
</tr>
<tr>
<td>Fe, %</td>
<td>1.76</td>
<td>1.89</td>
</tr>
<tr>
<td>Ni, g/Mg</td>
<td>374</td>
<td>328</td>
</tr>
<tr>
<td>Co, g/Mg</td>
<td>572</td>
<td>613</td>
</tr>
<tr>
<td>Pb, %</td>
<td>1.51</td>
<td>-</td>
</tr>
<tr>
<td>As, %</td>
<td>0.090</td>
<td>0.085</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CONTENT</th>
<th>1st campaign</th>
<th>2nd campaign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag, g/Mg</td>
<td>190</td>
<td>168</td>
</tr>
<tr>
<td>Zn, g/Mg</td>
<td>1200</td>
<td>740</td>
</tr>
<tr>
<td>S, %</td>
<td>2.95</td>
<td>2.62</td>
</tr>
<tr>
<td>Sso_4, %</td>
<td>1.45</td>
<td>2.47</td>
</tr>
<tr>
<td>C_total, %</td>
<td>14.30</td>
<td>10.4</td>
</tr>
<tr>
<td>C_org, %</td>
<td>8.96</td>
<td>6.30</td>
</tr>
</tbody>
</table>

Figure 1 exhibits the mineralogical composition of Lubin middlings and compares with composition of Lubin final concentrate currently produced as a feed for smelting. This analysis was made by BRGM laboratories and became a very important justification in discussion on considered technology alterations. The mineralogical composition of concentrate appeared to be very similar to the composition of the ore. Chalcopyrite (CuFeS_2) and bornite (Cu_5FeS_4), easiest to leach copper sulfides, are dominating in the material. The content of chalcopyrite (CuFeS_2), most refractory copper sulfide, is only about 20.6 %.

In contrary to concentrate, mineralogical composition of shale middlings appeared to be extremely favorable for hydrometallurgical treatment. Chalcocite was reported to be dominating (90.5 %) with some content of bornite (9 %). Chalcopyrite is a negligible component in this by-product. Such a mineralogical composition can be considered as an ideal for hydrometallurgical or biometallurgical treatment. The observed mineralogical composition of shale middlings exhibits evidently, that beneficial mineralogical segregation of minerals takes place during flotation process at Lubin Concentrator.
Metals value breakdown for 1 ton of Lubin shale middlings, presented in Table 3, indicates that the value of copper (217.3 US$) is even somewhat lower than the value of accompanying metals (Ag, Ni, Co, Zn, Pb) (250.9 US$), taking into account metals prices from 21 February 2008.

Table 3. Metals value in 1 ton of Lubin shale middlings (metal prices from 21 February 2008)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Content</th>
<th>Metal price, US$ (21 February 2008)</th>
<th>Value, US$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.7 %</td>
<td>8 050 US$/Mg</td>
<td>217.3</td>
</tr>
<tr>
<td>Ni</td>
<td>373 g/Mg</td>
<td>27 900 US$/Mg</td>
<td>10.4</td>
</tr>
<tr>
<td>Co</td>
<td>569 g/Mg</td>
<td>50 US$/lb</td>
<td>62.3</td>
</tr>
<tr>
<td>Pb</td>
<td>1.52 %</td>
<td>3 170 US$/Mg</td>
<td>48.2</td>
</tr>
<tr>
<td>Ag</td>
<td>180 g/Mg</td>
<td>17.5 US$/oz</td>
<td>127.2</td>
</tr>
<tr>
<td>Zn</td>
<td>1200 g/Mg</td>
<td>2 350 US$/Mg</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Value of Cu – 217.3 US$, Value of accompanying metals – 250.9 US$

It is very obvious that shale fraction has to be processed not only as a copper-bearing raw material but mainly as a polymetallic one. Separation of this fraction from flotation circuit and its processing for recovering of Cu and other metals is therefore fully justified.

Fig. 2. Particle size analyses of Lubin middlings raw and subjected to the non-oxidative acidic leaching at various degree of carbonate decomposition (within 30 – 90 %).
Particle size analyses for Lubin middlings (Figure 2) indicate that applied material was rather coarse from the point of view of hydrometallurgy. Parameter $d_{80}$ exceeded 100 µm even after non-oxidative leaching with $\text{H}_2\text{SO}_4$. Additional microscopic SEM (Figure 3) observations lead to the conclusion that most coarse particles are formed by shale material, which can not be decomposed during chemical treatment, even in the presence of oxygen (Figure 3D). Therefore, separation of particle fraction above 70–80 µm and their additional regrinding seem to be very desirable to facilitate further leaching. During ammonia leaching Lubin middlings were applied using neither chemical pretreatment nor mechanical grinding. This was in order to compare the ammonia leaching results with previous atmospheric and pressure leaching, where same feed was applied.

Fig. 3. SEM mineralogical analyses of Lubin shale middlings before leaching (A,B,C) and after atmospheric leaching in acidic conditions (D).
AMMONIA LEACHING PROCEDURE

All ammonia leaching experiments were performed in 1 liter Parr autoclave. Leaching solution was composed of ammonia, ammonium sulfate and oxygen under pressure as an oxidizing agent (NH$_3$ + NH$_4^+$ + O$_2$).

Ammonia solutions as a leaching medium for Lubin middlings can be considered as an excellent alternative for acidic oxidative solutions. The reason for that are very high stability constants of ammonia complexes for silver, gold, cobalt, copper, nickel and zinc (Table 4).

Aqueous ammonia + ammonia salt solutions as complexing medium is an effective and selective leaching agent for copper, silver, nickel, cobalt and zinc. Leaching of sulfide minerals takes usually place in the presence of oxygen under pressure within 1–20 atm. and at temperatures within 110 – 200 ºC. Solubilized metals are in the solution in the form of stable ammonia complexes, while sulfidic sulfur is oxidized to sulfate(VI) ion. No formation of elemental sulfur is observed during the process. This is an important advantage of the process.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemical formula</th>
<th>Stability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$</td>
<td>[Ag(NH$_3$)$_2$]$^+$</td>
<td>1.7⋅10$^7$</td>
</tr>
<tr>
<td>Au$^+$</td>
<td>[Au(NH$_3$)$_2$]$^+$</td>
<td>1⋅10$^7$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>[Co(NH$_3$)$_6$]$^{2+}$</td>
<td>5.0⋅10$^{33}$</td>
</tr>
<tr>
<td>Co$^{3+}$</td>
<td>[Co(NH$_3$)$_6$]$^{3+}$</td>
<td>5.0⋅10$^{13}$</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>[Cu(NH$_3$)$_4$]$^+$</td>
<td>3.8⋅10$^9$</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>[Cu(NH$_3$)$_4$]$^{2+}$</td>
<td>4.8⋅10$^{12}$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>[Ni(NH$_3$)$_6$]$^{2+}$</td>
<td>1.26⋅10$^9$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>[Zn(NH$_3$)$_4$]$^{2+}$</td>
<td>3.98⋅10$^7$</td>
</tr>
</tbody>
</table>

The following reaction takes place for copper, nickel and cobalt sulfides:

\[ 2\text{Cu}_2\text{S} + 12\text{NH}_3 + 4\text{NH}_4^+ + 5 \text{O}_2 = 4[\text{Cu(NH}_3)_4]^{2+} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (1) \]

\[ \text{CuS} + 4\text{NH}_3 + 2 \text{O}_2 = 2 [\text{Cu(NH}_3)_4]^{2+} + \text{SO}_4^{2-} \quad (2) \]

\[ \text{NiS} + 6\text{NH}_3 + 2 \text{O}_2 = [\text{Ni(NH}_3)_6]^{2+} + \text{SO}_4^{2-} \quad (3) \]

\[ 2\text{CoS} + 10\text{NH}_3 + 2\text{NH}_4^+ + 9/2 \text{O}_2 = 2[\text{Co(NH}_3)_6]^{3+} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (4) \]

Particularly substantial advantage of ammonia leaching for solids containing copper-iron and iron minerals (chalcopyrite, bornite, pyrite, pyrrhotite) is that iron present in the solid can not be dissolved in alkaline ammonia solution. Fe is oxidized to insoluble iron(III) oxide and precipitates from the solution. The following reaction can be observed for pyrrhotite:
Ammonia pressure leaching for Lubin shale middlings

$$4\text{FeS} + 6\text{NH}_3 + 4\text{H}_2\text{O} + 9\text{O}_2 = 2\text{Fe}_2\text{O}_3\downarrow + 2\text{HSO}_4^- + 2\text{SO}_4^{2-} + 6\text{NH}_4^+$$  (5)

Therefore, selective separation of copper and iron takes place in one leaching operation.

Table 5 exhibits the range of parameters applied during the ammonia leaching investigations of Lubin middlings presented in this paper.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Ammonia Conc., M</th>
<th>Oxygen partial pressure, atm</th>
<th>(NH$_4$)$_2$SO$_4$ conc., g/dm$^3$</th>
<th>s/dm$^3$</th>
<th>Stirring rate, rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>120–180</td>
<td>1.5–3.0</td>
<td>5.0–12.5</td>
<td>50–100</td>
<td>1:10</td>
<td>200–500</td>
</tr>
</tbody>
</table>

Aqueous ammonia + ammonia salt solution is an effective and selective complexing leaching agent for copper, silver, nickel, cobalt and zinc. Leaching of metal sulfide minerals contained in the Lubin shale middlings (Table 2) takes place in the stirred reactor under oxygen pressure at vigorous stirring rate in order to saturate the solution with oxygen. Effect of ammonia concentration was initially examined for copper leaching from the middlings (Figure 4). It is well seen that within the investigated ammonia concentration range leaching of copper is very efficient and can be, in terms of metals recovery, compared with acidic pressure leaching. Copper recovery was about 90 % after 90 minutes of leaching. Further increase in copper recovery was not observed as a result of copper minerals encapsulation in the shale fraction.

RESULTS AND DISCUSSION

Leaching recovery of nickel and zinc was found to be lower than it was observed for copper. About 60–70 % of nickel and slightly above 70 % of zinc was leached out. Dissemination of Ni and Zn in shale organic and carbonate matter can explain the observed results and hindering the leaching process.

Stirring rate appeared to be a key parameter for ammonia leaching of copper from Lubin middlings (Figure 6). We found that highest reaction rate for applied reactor can be observed when stirring rate was kept within the range of 400–500 rpm. Similarly to Figure 4, maximum leaching recovery was about 90 %.

Silver was observed to leach in ammonia solution (Figure 7) and the highest leaching rate was observed for stirring rate 400 and 500 rpm. Apparently lower leaching rate was observed when stirring rate was in the range of 200 – 3000 rpm. Silver leaching recovery was in the range of 50 – 60 %. Dissemination of silver in coarse particles of shale was the main reason for such a recovery, which can be improved by additional grinding of middlings coarse fraction. Zinc leaching was observed to be most
effective when stirring was 500 rpm. Maximum leaching recovery was in the range of 70 – 80 %.

Fig. 4. Effect of ammonia concentration on Cu leaching from Lubin middlings temp. 140°C, s/dm³ = 1:10, pO₂ = 7.5 atm, (NH₄)₂SO₄ concentration - 50 g/dm³, stirring rate - 400 rpm.

Fig. 5. Effect of ammonia concentration on Ni and Zn leaching from Lubin middlings temp. 140°C, s/dm³ = 1:10, pO₂ = 7.5 atm, (NH₄)₂SO₄ concentration - 50 g/dm³, stirring rate - 400 rpm.
Fig. 6. Effect of stirring rate (in rpm) on Cu leaching rate
temp. = 140°C, s/dm³ = 1:10, pO₂ = 7.5 atm, (NH₄)₂SO₄ = 50 g/dm³, NH₃ = 2 M

Fig. 7. Effect of stirring rate (in rpm) on Ag and Zn leaching from Lubin middlings
temp. = 140 °C, s/dm³ = 1:10, pO₂ = 7.5 atm, (NH₄)₂SO₄ = 50 g/dm³, NH₃ = 2 M.
Fig. 8. Effect of stirring rate (in rpm) on Ni and Co leaching from Lubin middlings temp. = 140°C, s/dm$^3$ = 1:10, pO$_2$ = 7.5 atm, (NH$_4$)$_2$SO$_4$ = 50 g/dm$^3$, NH$_3$ = 2 M.

Fig. 9. Effect of temperature on Cu ammonia leaching from Lubin middlings s/dm$^3$ = 1:10, pO$_2$ = 7.5 atm, (NH$_4$)$_2$SO$_4$ = 50 g/dm$^3$, NH$_3$ = 2 M, stirring rate - 400 rpm.
From previous mineralogical investigations we found that nickel was disseminated mainly in iron oxide phases (goethite). This was the reason of low leaching recovery observed both during acidic and ammonia leaching.

Temperature is a key parameter for ammonia leaching of copper from Lubin middlings. Leaching examinations carried out within the temperature range of 120–180 °C evidently shown, that ammonia leaching temperature for copper can not exceed 180 °C. Decrease in ammonia and oxygen dissolution seems to be the limiting factor at these leaching conditions. Observed results of copper leaching were, however, very satisfactory.

In contrast to copper, leaching of zinc was very effective and exhibited the highest level at 180 °C and recovery of zinc to the solution was about 95 %. Cobalt exhibited the highest recovery at temperatures below 160 °C. We suspect that reason for that was instability of ammonia complexes of Co at higher temperatures and precipitation of its hydroxyl compounds.

In all ammonia leaching experiments recovery of arsenic did not exceed 3 % and iron was completely insoluble at the experimental conditions.

Examination of the effect of oxygen pressure (Figure 11) shown that the highest leaching rate and highest leaching recovery were observed for the experiments performed at 12.5 atm of oxygen. Surprisingly, almost 100 % of Cu was leached out. It was evidently higher with regard to previous experiments carried out at 5 atm of oxygen pressure.

![Fig. 10. Effect of temperature on Co, and Zn leaching](image-url)

$s/dm^3 = 1:10$, $pO_2 = 7.5$ atm, $(NH_4)_2SO_4 = 50$ g/dm$^3$, $NH_3 = 2$ M, stirring rate - 400 rpm.
Fig. 11. Effect of oxygen pressure and ammonia sulfate concentration (in grams per liter) on ammonia Cu leaching from Lubin middlings.

Fig. 12. Eh-pH diagram for Cu–H₂O–NH₃–SO₄²⁻ system at 25 °C.
Another parameter examined during leaching test was concentration of ammonium sulfate – (NH₄)₂SO₄ (Figure 11). Recorded cooper concentration – leaching time plots indicated, that optimum concentration of ammonium salt was 50 g/dm³. The concentration of ammonium ions together with ammonia form a buffer solution and control the solution pH at the level where stability of copper tetraamina complexes is the highest (Figure 12). This corresponds to the range of 8–11. If the pH of ammonia – ammonium solution is either to low or exceeds the optimum level of pH, stability of copper complexes decreases.

CONCLUSIONS

Ammonia pressure leaching of Lubin shale middlings experiments appeared to be an efficient alternative for acidic atmospheric or pressure leaching. The following conclusions can be formulated after the detailed investigations of main process parameters:

- Ammonia pressure leaching in oxygenated NH₃ + (NH₄)₂SO₄ solution is an effective process for Lubin middlings, allowing the recovery of Cu, Ag, Ni, Co and Zn. Fe and As remain in the solid.
- Temperature, ammonia concentration, ammonium sulfate concentration, oxygen pressure and stirring rate are the key leaching parameters. The optimum range of parameters for recovery of metals are: ammonia concentration: above 1.5 M, ammonium sulfate concentration: 50 g/dm³, oxygen pressure: 12.5 atm., temperature: 120 – 160 °C, stirring rate: 400 – 500 rpm for the applied reactor,
- Above 95 % of Cu, 30 % Co, 70 % Ni, 95 % Zn and 60 % Ag can be recovered during 90–120 minutes leaching. Leaching rate and leaching recovery can be remarkably enhanced if coarse particles of shale will be separated for additional size reduction below 70 – 80 µm.
- Fe and As remain in the solid residue during ammonia pressure leaching.

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Badano proces ciśnieniowego ługowania amoniakalnego półproduktu flotacji z ZWR Lubin, wzbogaconego we frakcję łupkową. Ługowanie amoniakalne analizowano jako alternatywny sposób hydrometalurgicznego przetwarzania tego półprodukdu. Badano wpływ najważniejszych parametrów: temperatury, ciśnienia parciwalnego tlenu, stężenia amoniatu i siarkanu amonowego oraz szybkości mieszania na szybkość ługowania Cu, Ag, Zn, Ni i Co.

słowka kluczowe: hydrometallurgia, ługowanie amoniakalne, czarne łupki