Measurements of the rest potential of copper sulfide electrodes and pyrite, present in copper ores and concentrates from Lubin Concentrator, have been carried out. Moreover, measurements of sulfide-sulfide contact potential and galvanic current were also performed using deoxygenated sulphuric acid solutions as well as the solutions saturated with oxygen and containing Fe(III) ions. Significant galvanic interactions were observed for sulfide couples exhibiting high potential difference, particularly when copper sulfides were short-circuited with pyrite. According to mineralogical data for Lubin polymineral copper concentrate, chalcocite and bornite are dominating with chalcopyrite and covellite as minor copper minerals. Expected is advantageous affect of pyrite in promoting the kinetics of copper leaching from Lubin concentrate as a result of observed galvanic interactions between pyrite and copper sulfides.

keywords: copper concentrate, sulfide electrode, galvanic interactions

1. INTRODUCTION

Polish copper deposits, known as LGOM (Lubin-Glogow Copper Basin, SW Poland) exhibit unique, sedimentary nature (Rydzewski, 1996; Konstantynowicz, 1990) and consist of three lithological ore fractions: dolomitic, sandstone, and shale. The shale fraction exhibits the highest concentrations of copper and accompanying metals (Ag, Ni, Co, Zn, Pb, V, Mo etc.) and simultaneously is the most troublesome material in the flotation circuits (Tomaszewski, 1995; Łuszczykiewicz, 2000; 2004).
Moreover, the shale fraction reveals the fine dissemination of metal-bearing sulfides in the carbonate matter and in the black shale-clay rocks that form the majority of the gangue. Such a fine dissemination of copper and other metals sulfides in the carbonateorganic matrix considerably reduces susceptibility of the ore to both effective liberation and subsequent upgrading by means of flotation. At present observed is an increase of quantity of shale-clay and carbonate fractions in flotation feeds, which are known as mostly hard-to-treat in flotation circuits. According to the latest data (Kubacz and Skorupska, 2007) the content of shale fraction in Lubin deposit may already reach as much as 25 % and is expected to increase in coming years.

A complex and very unique mineralogical and chemical composition of the Polish copper ores, mined from the LGOM sedimentary deposits, is the principal reason for copper, silver and other metals losses to flotation tailings (Łuszczkiewicz, 2000; 2004). The metals losses are found to be particularly high in Lubin Concentrator. Additionally, the presence and elevated content of shale create numerous technical, economical and ecological issues both in flotation and in flash smelting.

Selective liberation of fine metal-bearing mineral particles from the host matrix would be the only way to enhance metals recovery in flotation. However, it appears to be in-effective in the existing milling circuits. Consequently, the hydrophilic gangue-sulfide intergrowths seriously reduce both the flotation selectivity and metal grade in the concentrate (Łuszczkiewicz et al., 2006). Therefore, it can be concluded that the existing beneficiation technologies currently applied for processing of the Polish copper ores have already reached the limit of their technological efficiency and require substantial alterations (Chmielewski and Charewicz, 2006; Łuszczkiewicz and Chmielewski, 2006; Konopacka et al., 2007).

According to the KGHM technological data, the techniques of copper production, currently used at KGHM have to be considerably modified in order to enhance or at least to maintain their efficiency. It has also been generally acknowledged that the application of modern hydro- or biometallurgy becomes a potential alternative and necessity in the Polish copper industry to reverse unfavorable trends in flotation results, particularly at Lubin Concentrator (Grotowski, 2007). Flotation – smelting – refining processes, currently used at KGHM, became not enough efficient for acceptably high recovering of Cu and accompanying metals (Ag, Ni, Zn etc), due to the decline of ore grade and decrease of its quality. Moreover, cobalt and zinc are totally lost.

The application of atmospheric leaching, preceded by non-oxidative carbonates decomposition, is recently considered as an alternative or as a complimentary process for processing of shale flotation by-product which is hardly to beneficiate using existing techniques. This approach, presented by a group of authors from Wroclaw University of Technology within the research program of BIOSHALE project (Chmielewski and Charewicz, 2006; Chmielewski, 2007), primarily involves separation of the most
troublesome ore fraction (shale containing middlings) and introduction of hydrometallurgical methods for their alternative effective processing.

Another, recently discussed approach comprises the application of atmospheric or pressure leaching for processing of the Lubin copper sulfide concentrates. Lowering the concentrate grade may simultaneously result in a significant increase of metals recovery. Application of alternative hydrometallurgical processing of such a concentrate may lead to increasing production of copper, silver, lead, nickel, zinc and cobalt. The last two elements are totally lost in current technologies.

The copper flotation concentrates produced at Lubin Concentrator are of polymetallic and polymineral composition. They contain chalcocite (Cu₂S) and bornite (Cu₉FeS₄) as dominating copper sulfides, whereas chalcopyrite (CuFeS₂) and covellite (CuS) are minor minerals (KGHM, 2007; Łuszczkiewicz, 2009). Moreover, in recent years was also observed an increasing content of pyrite (FeS₂), which appeared to be a beneficial component in terms of mechanism alteration and enhancing the kinetic of copper leaching. Electrochemical nature of sulfides flotation (Chanturija and Vigdergauz, 2009) and leaching along with electrocatalytic properties of pyrite has already been described (Majima and Peters, 1968; Nowak et al., 1984; Holmes and Crundwell, 1995) and used for leaching of copper sulphidic concentrates in the Galvanox Process (Dixon and Mayne, 2007), where finely ground FeS₂ is added to the leaching slurry to intensify the process in a galvanic manner, by facilitating the charge transfer from the oxidant to dissolved sulfide. The presence of numerous sulphidic copper, iron, zinc and lead minerals in the feed to leaching can advantageously result in mutual electrochemical interactions caused by different potentials attained by sulfides in leaching conditions. These interactions have already been examined for conditions of non-oxidative leaching of the Lubin shale middlings (Kowalczyk and Chmielewski, 2010) and are expected to result in significant acceleration of copper leaching.

In this work results of laboratory investigations performed for electrodes prepared from natural copper sulfides and pyrite, which are dominating minerals in the Lubin copper flotation concentrate are presented. Sulphuric acid solutions, deoxygenated, oxygenated and containing Fe(III) ions, simulating the leaching conditions, were applied. Investigated were rest potentials, contact potentials and galvanic contact currents for selected mineral couples of highest potentials differences. The results were interpreted in terms of leaching kinetics of the Lubin concentrate in acidic oxygenated Fe(III) solutions.

2. AIM OF THE WORK

Examination of electrochemical phenomena existing during non-oxidative and oxidative leaching of the copper sulfide concentrate provides enormous amount of basic information important for both future leaching kinetics and leaching mechanism.
The following mineralogical and electrochemical aspects have been examined for sulfide minerals present in the Lubin flotation concentrate:

- mineralogical evaluation of the feed in terms of possible mutual impacts of various sulfides contained in the concentrate,
- evaluation of electrochemical control of non-oxidative and oxidative leaching using oxygen and Fe(III) ions,
- correlation of measured rest potentials of sulfides with their leachability in sulphuric acid solutions,
- selection of sulfide-sulfide systems exhibiting strongest galvanic interactions under leaching conditions,
- indication of possible electrode processes on sulfides during leaching,
- quantitative evaluation of galvanic interactions by means of measurements of contact potentials and contact currents for selected sulfide systems.

3. EXPERIMENTAL

3.1. ELECTRODES AND MEASUREMENTS

The sulfide electrodes applied in reported measurements have been prepared from handpicked samples of natural copper sulfides and pyrite from Polish LGOM copper deposits. A sample of individual mineral was initially cut and ground to the near rectangular shape of about 0.5 – 1 cm³. Electrical contact between the mineral specimen and copper wire was made using silver-impregnated conducting epoxy resin. Subsequently, the contacted sample was mounted in epoxy resin and after hardening the working face of the electrode was ground and polished using emery paper.

The solutions were prepared from analytical grade regents (sulfuric acid, iron(III) sulphate, gaseous oxygen and argon). Rest potential of sulfide electrodes was measured and recorded versus Ag, AgCl, KCl electrode (Eh = +0.197 V), which was connected to a thermostated measuring cell with a Luggin capillary. The solution was either deoxygenated with argon to simulate non-oxidative conditions, or saturated with oxygen in the presence of Fe(III) ions, to simulate oxidative leaching conditions. Galvanic currents were recorded under different conditions, after connecting two selected electrodes with electrical wire.

3.2. CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF THE LUBIN CONCENTRATE

The copper flotation concentrate was taken from a commercial flotation circuit of the Lubin Concentrator (ZWR Lubin) in the form of water slurry. Mineralogical composition of the Lubin concentrate, compared with Polkowice and Rudna concentrates is shown in Table 1. Table 2 indicates the chemical composition of the Lubin concentrate.
Table 1. Mineralogical composition of the copper flotation concentrates at the KGHM concentrators (mean values for 2007-2008, Łuszczkiewicz, 2009)

<table>
<thead>
<tr>
<th>Concentrator</th>
<th>Bornite</th>
<th>Chalcocite, digenite</th>
<th>Chalcopyrite</th>
<th>Pyrite, marcasite</th>
<th>Covellite</th>
<th>Sphalerite</th>
<th>Tennantite</th>
<th>Galena</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubin</td>
<td>33.1</td>
<td>14.5</td>
<td>26.1</td>
<td>17.4</td>
<td>3.5</td>
<td>1.8</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Polkowice</td>
<td>13.6</td>
<td>55.5</td>
<td>12.0</td>
<td>10.9</td>
<td>3.7</td>
<td>1.2</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Rudna</td>
<td>24.8</td>
<td>40.4</td>
<td>7.2</td>
<td>15.0</td>
<td>5.8</td>
<td>3.1</td>
<td>1.5</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The Polish flotation copper concentrates from all three concentrators: Lubin, Rudna and Polkowice exhibit the dominating content of chalcocite and bornite, the easiest-to-leach copper sulfides. This is a unique and exceptionally beneficial attribute of the Polish copper concentrates with regard to their potential application for hydrometallurgical treatment. The content of chalcopyrite – most refractory copper mineral, is rather insignificant, except of the Lubin deposit, where chalcopyrite content is about a half of that of chalcocite and bornite.

Table 2. Chemical composition of the Lubin flotation concentrate (sample taken on 01. Sept., 2007)

<table>
<thead>
<tr>
<th>Component</th>
<th>Content in concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>15.64%</td>
</tr>
<tr>
<td>Ag</td>
<td>840 ppm</td>
</tr>
<tr>
<td>Zn</td>
<td>4600 ppm</td>
</tr>
<tr>
<td>Co</td>
<td>1216 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>216 ppm</td>
</tr>
<tr>
<td>Pb</td>
<td>2.15%</td>
</tr>
<tr>
<td>Corg</td>
<td>10.18%</td>
</tr>
<tr>
<td>S</td>
<td>10.8%</td>
</tr>
</tbody>
</table>

In contrary to the Polkowice and Rudna concentrate, Lubin concentrate is rather poor in terms of copper content (KGHM, 2007) and its quality is hardly accepted for flash smelting. Moreover, both concentrate grade and metal recovery have been remarkably decreasing in recent period. According to the latest data, copper content in the Lubin concentrate decreased to less than 15% (KGHM, 2009) whereas copper recovery at the Lubin concentrator has recently fallen to only 85.9% (KGHM, 2009). However, the Lubin concentrate is the richest in silver (850 ppm) and exhibits
evidently elevated content of Zn, Co, Ni and Pb (Table 2). Recovery of these metals is currently reported either as very low while cobalt and zinc are not recovered at all.

4. RESULTS AND DISCUSSION

4.1. REST POTENTIALS OF SULFIDE ELECTRODES

In order to compare different conducting and electrochemical properties of investigated sulfides, their resistivity, type of semiconductivity and rest potentials, reported in literature (Hiskey and Wadsworth, 1981; Mehta and Murr, 1983) and measured in this work in deoxygenated with argon sulphuric acid solutions with concentration of 50 g/dm³ the data are presented in Tables 3 and 4. A very good
correlation can be observed for rest potential measured in this work and found from the literature data (Hiskey and Wadsworth, 1981; Paramguru, 2002).

Earlier literature data discussed the effect of electrochemical properties of sulfides and their mutual galvanic interactions on flotation efficiency and selectivity (Kocabag and Smith, 1985; Majima, 1968; Biegler et al., 1977; Peters and Majima, 1968).

Table 3. Conducting properties and rest potentials of selected copper sulfides and pyrite (Hiskey and Wadsworth, 1981)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Resistivity, $\Omega$m</th>
<th>Semiconductivity type</th>
<th>Rest potential, mV (SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>$0.1 - 3 \times 10^{-2}$</td>
<td>n, p</td>
<td>630</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>$0.2 - 9 \times 10^{-3}$</td>
<td>n</td>
<td>530</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>$10^{-2} - 10^{-5}$</td>
<td>p</td>
<td>440</td>
</tr>
<tr>
<td>Covellite</td>
<td>$10^{-4} - 10^{-6}$</td>
<td>p</td>
<td>420</td>
</tr>
<tr>
<td>Copper</td>
<td>$1.7 \times 10^{-8}$</td>
<td>metallic conductor</td>
<td>340</td>
</tr>
</tbody>
</table>

According to the data shown in Tables 3 and 4, chalcocite can be recognized as electrochemically the most active mineral among all copper sulfides, exhibiting the lowest rest potential (+151 mV vs. Ag,AgCl). Bornite with the rest potential of +195 mV, is only slightly less active than chalcocite. In contrary, covellite, exhibiting potential of +290 mV, and chalcopyrite, exhibiting the highest rest potential (+330 mV) among copper sulfides, are the least active or most refractory in terms of leachability. Pyrite was found to reveal the highest rest potential among all examined sulfides. Its potential was found to be + 434 mV (Ag, AgCl).

Table 4. Results of measurements of rest potentials of sulfide electrodes (at 25ºC) and literature data (Mehta and Murr, 1983)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Measured rest potential mV, (Ag, AgCl)</th>
<th>Rest potential (literature) mV, (Ag, AgCl) (Mehta and Murr, 1983)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcocite</td>
<td>+ 151</td>
<td>+ 183</td>
</tr>
<tr>
<td>Bornite</td>
<td>+ 195</td>
<td>+ 223</td>
</tr>
<tr>
<td>Covellite</td>
<td>+ 290</td>
<td>+ 253</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>+ 330</td>
<td>+ 363</td>
</tr>
<tr>
<td>Pyrite</td>
<td>+ 434</td>
<td>+ 464</td>
</tr>
</tbody>
</table>

From measured rest potential of copper sulfides and pyrite (Table 4) we can anticipate galvanic interactions between minerals, because those of evidently higher potential (pyrite, chalcopyrite) will play the role of a cathode (reduction of oxygen or
iron(III) ions) whereas minerals of lowest potential (chalocite, bornite) will be dissolved anodically with a considerably elevated rate.

From the measurements of the rest potential the following galvanic couples were set up for further measurements of contact potentials and galvanic current:

- chalcopyrite – chalcocite
- chalcopyrite – chalcocite
- chalcopyrite – chalcocite
- pyrite – chalcocite
- pyrite – bornite
- pyrite – covellite.

4.2. REST POTENTIALS OF SULFIDES DURING LEACHING

Rest potentials of a platinum electrode and selected sulfide electrodes as well as sulfide – pyrite couples were recorded in H₂SO₄ solution (50 g/dm³) at temperatures 25, 50, 70, and 90°C. Figures 2 and 3 exhibit experimental data collected at 70°C. Non-oxidative conditions were simulated by deoxygenation of the solution with argon. Gaseous oxygen and iron(III) ions of concentration of 1 g/dm³ were used to create oxidative conditions. It is well seen from potential – time plots that an apparent decrease in sulfide electrode potential reflects non-oxidative conditions. Within the period of 20 minutes the rest potential of chalcocite and bornite electrodes decreases about 100 mV. Such a potential observed under non-oxidative conditions is too low for dissolution of copper from its sulfidic form.

When gaseous oxygen was introduced to the solution, an increase of the rest potential was recorded (Figs 2 and 3). This indicates a very slow minerals digestion. When iron(III) ions were present, the increase of potential was very evident, even at very low Fe(III) concentration, applied for presented measurements. This is a clear evidence that Fe(III) ion is a considerably much better leaching agent than oxygen, due to their faster reduction on sulfides surfaces in comparison to oxygen.

After copper sulfide electrodes were coupled with the pyrite electrode, the observed increase of the rest potential in the presence of oxygen and iron(III) ions was found to be more evident (Figs 4 and 5) due to expected electrochemical interactions (Table 4). This is the result of formation of galvanic couples between more noble pyrite, which was a cathode, and covellite or chalcopyrite, which were anodes in the galvanic pyrite - covellite and pyrite - chalcopyrite couples.

After introduction of oxygen under atmospheric pressure only a slight increase of potential was observed for platinum, chalocite (about 20 mV) and bornite (about 50 mV) electrodes. An increase of the potential of sulfide electrode above the rest potential observed under non-oxidative conditions results in anodic dissolution of the mineral. For covellite, chalcopyrite and pyrite the increase of the rest potential in the presence of oxygen was rather insignificant.

The most noticeable raise of the rest potential of all examined sulfides and platinum was caused by iron(III) ions. Even if the Fe(III) concentration was as low as
1 g/dm³, the effect of this oxidant was very strong. This clearly explains why the presence of iron(III) in the oxidative leaching systems for copper sulfides is therefore strongly recommended.

The increase of the rest potential of sulfide minerals was observed to be very stable when oxygen was present in the solution as an oxidation agent for regeneration of Fe(II) to Fe(III). The presence of iron(III) ions and dissolved oxygen as regeneration agent is also recently considered for leaching of sulfide concentrates and by-products from flotation circuits at KGHM. For Fe(III) – O₂ system. For this system is observed the highest leaching recovery of copper from sulfidic ores and concentrates under atmospheric conditions (Chmielewski, 2009). The selection of a proper feed for hydrometallurgical processing, accepted by technical and economical factors, will be analysed and extensively investigated from year 2010 to 2013 within the HYDRO comprehensive research project financed by National Center of Research and Development, performed currently at the Faculty of Chemistry, Wroclaw University of Technology.

The highest increase of the potential of sulfide electrodes was detected after introduction of iron(III) to the solution (Figs 2 and 3). The elevation of the potential was observed to be very stable, since simultaneous regeneration of Fe(II) to Fe(III) takes place in the presence of oxygen. This undoubtedly explains the reason of application of Fe(III) + oxygen system as the most effective for leaching of copper sulfides. When the copper minerals were coupled with pyrite, known as most noble sulfide, the observed contact potential was evidently higher than for single electrodes (Figs 4 and 5).
The most significant effect of galvanic couples on the kinetics of anodic dissolution of copper sulfides can be reported from galvanic current measurements for copper sulfide electrodes short-circuited with pyrite electrode (Figs 6–9). The recorded galvanic current reflected the possible leaching rate of copper sulfides. It is clearly visible from the current – time plots that the contact current for pyrite-bornite couple was about 10-fold higher than that for the chalcopyrite-bornite couple.
5. CONCLUSIONS

Shrinking of copper resources along with declining of copper ores quality and simultaneous increase of demand for the metal in the Word leads to the commencement of exploitation of those copper resources, which in the past were not enough attractive and not mined. As a result of changing circumstances, novel hydrometallurgical techniques have been recently introduced for recovering of copper and accompanying metals from those resources, which remained as not applicable for flotation/smelting due to the complex character of ores and of a small scale of mining. The role of hydrometallurgy has been evidently growing in recent years and the need of application of hydrometallurgy in technological circuits at KGHM has also recently appeared.

It can be concluded that polymetallic and polymineral character of the Lubin concentrate, particularly the dominating bornite-chalcocite copper mineralization is advantageous in terms of excellent leachability. Moreover, elevated content of pyrite and chalcopyrite as well as the presence of numerous intermineral contacts, can substantially facilitate atmospheric leaching of the concentrate in sulphuric acid solutions containing oxygen and Fe(III) ions as leaching agents. This was confirmed in this work by mineralogical analyses, measurements of rest potentials of single mineral electrodes and potential changes of coupled copper minerals and pyrite. The measurements of contact currents between copper sulfides short - circuitied with pyrite
clearly indicates that relatively high content of pyrite in the Lubin concentrates may be beneficial if the concentrates were used as a feed for oxidative leaching with oxygenated acidic solutions of Fe(III).

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miedzi, natomiast zawartość chalkopyrytu i covellinu jest wyraźnie niższa. Można stąd oczekiwać korzystnego dla ługowania wpływu oddziaływania pirytu na ługowanie przejawiający się wzrostem szybkości ługowania miedzi w wyniku oddziaływań galwanicznych w układach piryt – siarczki miedzi.

*słowa kluczowe: koncentrat miedzi, elektrody siarczkoowe, oddziaływania galwaniczne*