

P. B. Kowalczuk*, T. Chmielewski**

CHANGES OF ELECTRODE POTENTIAL IN THE NON- OXIDATIVE LEACHING

Received May 16, 2009; reviewed; accepted July 30, 2009

Simultaneous measurements of pH and redox potential using a platinum electrode as well as potential of copper sulphide electrodes during non-oxidative leaching of Lubin shale middlings with sulfuric acid have been applied to determine leaching kinetics and to evaluate its electrochemical parameters as well as to assess the changes taking place at the mineral/solution interface during leaching process. Significant decrease in both redox potential of the solution (from +350 mV to +50 mV, Ag₂AgCl) and potential of mineral electrodes were observed with increasing pH during carbonate decomposition with sulfuric acid. It is therefore concluded that the low value of red-ox potential is a parameter preventing oxidation of copper sulphide minerals present in leached material and prevents the transition of Cu and Fe to the solution. It was found that the non-oxidative leaching is a rapid and selective process, resulting in decomposition of calcium and magnesium carbonates and in saturation of the leaching slurry with carbon dioxide. It was recognized that with the increasing degree of carbonate decomposition from 50 to 100 % metals-bearing minerals liberation has remarkably improved, which beneficially facilitates and intensifies further upgrading or leaching processes.

key words: electrode potential, pH, leaching, sulphides

INTRODUCTION

Electrochemical monitoring of leaching process by means of redox potential using platinum and mineral electrodes prepared from copper sulfides is a

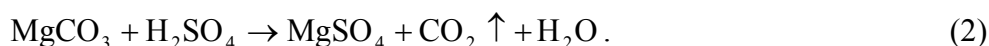
* Laboratory of Mineral Processing, Institute of Mining Engineering, Wrocław University of Technology, 50-370 Wrocław, Poland, e-mail: przemyslaw.kowalczuk@pwr.wroc.pl

** Division of Chemical Metallurgy, Faculty of Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland, e-mail: tomasz.chmielewski@pwr.wroc.pl

very important scientific and particle issue. This paper presents and discusses the use of pH and electrode potential measurements to monitor leaching kinetics of the Lubin shale middlings with H_2SO_4 .

PRINCIPLES OF NON-OXIDATIVE LEACHING

Acidic non-oxidative leaching of the copper shale fraction is based on the chemical reactions of sulfuric acid with calcium and magnesium carbonates. The carbonate minerals are the main component of the hydrophilic gangue which forms intergrowths and impregnations with copper sulfides or creates hydrophilic ultra-fine slimes on the surface of metal sulfides. The small size of the leached solid particles enhances the rate of leaching. The following chemical reactions describe non-oxidative leaching:



Hydrated calcium sulfate (gypsum) is solid reaction product. Water-soluble magnesium sulfate and gaseous carbon dioxide are two other products. Due to fine particle distribution of middlings, the leaching of carbonate gangue with H_2SO_4 appeared to be very rapid and can be easily performed at ambient temperatures in reactors with mechanical stirring of a standard construction (Chmielewski, 2007a, 2007b).

The amount of H_2SO_4 applied in non-oxidative leaching directly corresponds to the content of carbonates and must be precisely controlled to maintain the final pH of the pulp at a level enabling its direct transfer either to the flotation circuit without pH correction or to the leaching and/or bioleaching. Therefore, for the further flotation, the amount of sulfuric acid introduced to the leaching operation should be always kept below the analytically determined maximum amount of acid required for total decomposition of carbonates ($Z_{H_2SO_4}^{max}$). The maximum demand for acid ($Z_{H_2SO_4}^{max}$) is the mass of pure H_2SO_4 necessary for the total decomposition of carbonates in 1 kg of a dry solid feed. $Z_{H_2SO_4}^{max}$ should be determined analytically in laboratory tests.

H_2SO_4 is frequently introduced to the reactor containing shale slurry at a rate that assures total acid utilization in leaching. Usually, 70-80 % of determined $Z_{H_2SO_4}^{max}$ was applied in leaching, maintaining the final acidity of the slurry about at pH 5 or higher. This is the pH level that makes possible direct transfer of the slurry either to the flotation circuit without additional pH correction or to the leaching and/or bioleaching. If the residual solids are used for further atmospheric leaching, pressure leaching or bioleaching the amount of sulphuric acid exceeds the maximum demand to maintain pH at the required, acidic level.

Carbon dioxide, evolving in reactions (1) and (2), creates a favorable oxygen-free atmosphere in the leached slurry and prevents the undesirable digestion of sulphides of valuable metals (Cu, Pb, Zn, Ni, Fe). This remarkably minimizes the metal losses to the solution and simplifies the entire non-oxidative leaching process. Therefore, saturation of slurry with CO₂ assures the selectivity of carbonate leaching. This was confirmed by the chemical analyses of the wastewater during numerous laboratory tests.

Selectivity of carbonate leaching from a flotation feed is, according to the proposed method, particularly beneficial for the process and guarantees chemical stability of metal sulfide minerals. Noticeably beneficial effects of the leaching with H₂SO₄ on subsequent flotation of copper ores were already observed during comprehensive laboratory investigations and several pilot plant tests with various flotation feeds from Lubin and Polkowice concentrators (Łuszczkiewicz and Chmielewski, 1999, 2006, 2008; Chmielewski et al., 2007, 2008).

The acidic non-oxidative leaching of the carbonate-containing flotation feed resulted in the apparent decomposition of solid particles by means of selective, chemical process which precisely and economically liberated sulfide minerals. Under oxygen-free conditions all metal sulfides remain chemically stable and susceptible for flotation. This selective “chemical grinding” is very efficient particularly for fine intergrowths, which can not be broken up with typical mechanical grinding. High selectivity and low energy consumption are, therefore, additional beneficial factors of this process (Łuszczkiewicz and Chmielewski, 1999, 2006).

The purpose of this paper was to evaluate the effect of non-oxidative leaching on both the redox potential in the slurry measured by means of Pt electrode and potential of copper sulphide electrodes made of minerals contained in the leached Lubin middlings. These potentials were compared with potentials recorded in the presence of oxygen and iron(III) ions.

EXPERIMENTAL AND MATERIAL

The feed material used in laboratory experiments on non-oxidative leaching was shale containing middlings – tailings from 1st cleaning flotation 1st circuit at Lubin Concentrator (ZWR Lubin). Chemical composition of the solid is given in Table 1. The high content of organic carbon in middlings (~ 9 %) and observed close correlation between metals concentration and organic carbon content make the Lubin middlings a shale concentrate.

Table 1. Chemical composition of Lubin middlings (tailings of 1st cleaning)

CONTENT					
Cu, %	Fe, %	Ni, g/t	Co, g/t	Pb, %	As, %
2.72	1.76	374	572	1.51	0.09
CONTENT					
Ag, g/t	Zn, g/t	S _c , %	S _{SO₄} , %	C _{total} , %	C _{org} , %
190	1 200	2.95	1.45	14.30	8.96

Very high content of carbonate matter in the middlings corresponds to utilization of 497 g H₂SO₄/kg of dry solid for total decomposition of carbonates. Any leaching or bioleaching unit operation taking place under acidic conditions requires previous non-oxidative leaching with acid in order to totally decompose of acid consuming components. Non oxidative leaching can also facilitate further upgrading by flotation or gravity methods as well as subsequent bioleaching or chemical leaching.

RESULTS AND DISCUSSION

Measurements of the potential, along with pH, during the sulfuric acid leaching under non-oxidative conditions were applied for identifying and evaluating possible changes taking place in the electrochemical parameters of the solid/solution interface during the process. It was expected that as a result of carbonate decomposition with sulfuric acid significant decrease of the potential of Pt and sulphide mineral electrodes in the leaching solution will be exhibited. The changes of electrode potential are mainly caused by the removal of oxygen from the solution and by the saturation with carbon dioxide. Non-oxidative leaching created in the course of the process can be monitored electrochemically.

Initially, the redox potential measurements with Pt electrode (versus Ag, AgCl reference electrode) were applied in order to assess changes in the magnitude of this potential as a result of saturation of leached suspension with carbon dioxide. The potential was recorded with time simultaneous with pH changes of leached solution (Fig. 1). Potential – time and pH – time relationships allow to determine the kinetic of reaction and to monitor the electrochemical conditions during the process of leaching.

Beginning of leaching was controlled after the introduction of sulfuric acid to the solution. In the leaching process the pH was observed to increase, while decrease of the potential of Pt and mineral electrodes was recorded. Both of these parameters characterized the rapid process of carbonate decomposition under non-oxidative conditions.

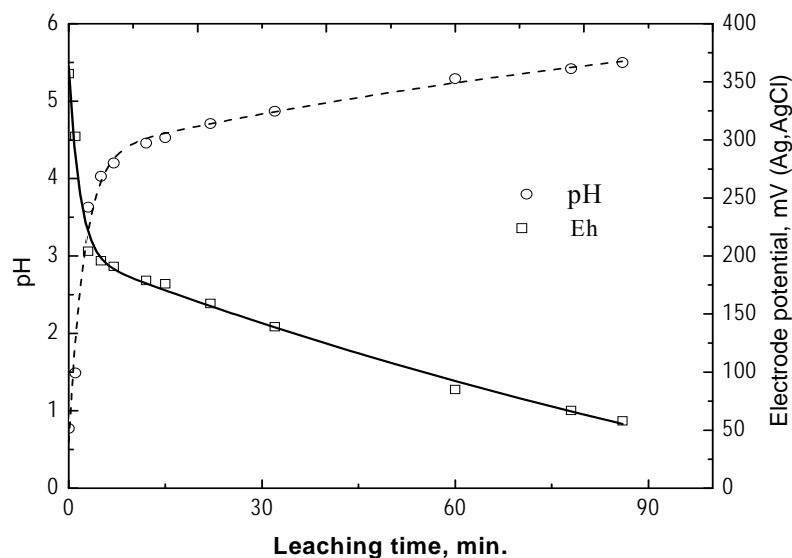


Fig. 1. pH and electrode potential vs. leaching time for non-oxidative leaching of Lubin middlings for 70 % of carbonate decomposition

Leaching process leads to significant changes in electrochemical properties in the solution. During the initial few minutes of leaching a sharp decrease in the potential of platinum electrode by about 150 mV took place with further decrease at the end of the experiment (Fig. 1). Over the whole testing period Pt electrode potential decreased markedly for different degrees of carbonate decomposition from +350 mV to +50 mV (Ag, AgCl).

Table 2. Chemical composition of Lubin shale middlings after non-oxidative leaching at different degree of carbonate decomposition (R_w) with H_2SO_4

Carbonates decomposition R_w , %	Cu, %	Fe, %	Ag, g/t	Ni, g/t	Co, g/t	Zn, g/t	C_{org} , %	As, %
0	2.60	1.890	168	328	613	740	6.30	0.085
30	2.50	1.760	165	325	605	690	6.52	0.080
50	2.52	1.789	162	315	603	660	6.52	0.086
70	2.30	1.648	157	326	588	660	6.54	0.073
90	2.52	1.717	168	327	606	720	6.49	0.088

After the consumption of all the available acid, subsequent changes in pH values resulted only from the saturation of the solution with carbon dioxide, and at this stage of tests, the process of non-oxidative leaching was considered to be complete. The observed low potential of red-ox electrode, prevented oxidation of sulphide minerals

present in leaching material and prevented the transfer of metal ions (mainly Cu and Fe) into the solution. This was also confirmed by chemical analysis of the material from non-oxidative leaching (Table 2).

The potential – pH curve in Fig. 2 shows the good correlation between the red-ox potential and pH of the solution during the 90 minutes of non-oxidative leaching. It may be found that with increasing pH, the potential for leaching decreases over the leaching time, which is the result of the saturation with carbon dioxide. A similar effect is obtained for all degrees of carbonate decomposition in the range of 30 – 90 %. The control of non-oxidative leaching can be therefore performed by monitoring two independent parameters – pH and redox potential.

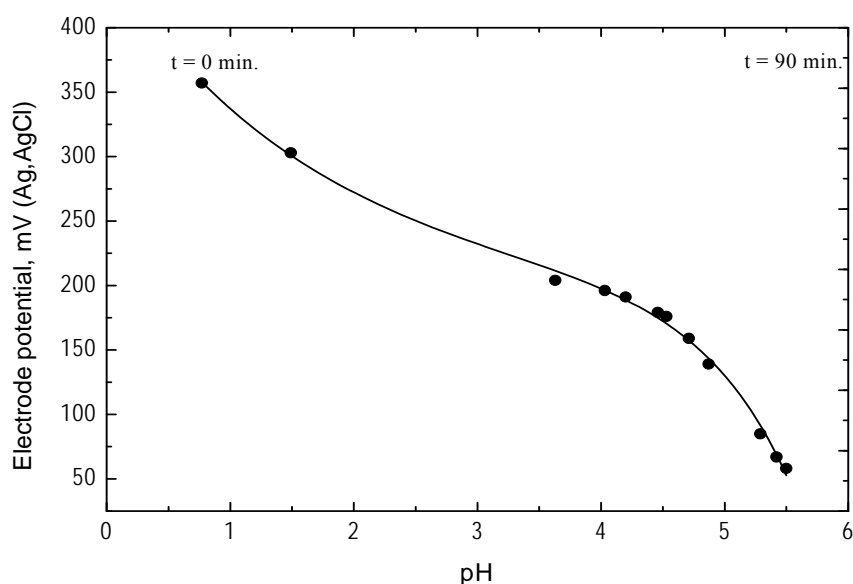
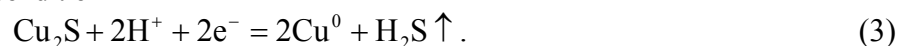


Fig. 2. Electrode potential vs. pH for non-oxidative leaching of Lubin shale middlings for 70 % of carbonate decomposition

It is possible that significant decrease of redox potential observed in non-oxidative leaching with sulfuric acid, may result in reductive decomposition of copper sulphide minerals, and in the evolution of hydrogen sulphide (H_2S). However, this unwanted reaction product was not detected, confirming the absence of the reaction (3) of cathodic reduction of chalcocite to metallic copper in the leaching process under non-oxidative condition



The presence of hydrogen sulfide in the leaching tests was not confirmed for any of the sulphide minerals contained in Lubin middlings leached with sulphuric acid.

From the E-pH diagram for the Cu-S- H_2O system (Fig.3) (Goodenough et al., 1988) it can be seen that the formation of hydrogen sulfide in a reduction reaction (3)

within the pH range of 0 - 2 is possible only below the potential of about -250 mV (SHE), while the anodic movement of copper to the solution in the form of Cu^{2+} is possible above +350 mV. In the course of our study of non-oxidative leaching of Lubin middlings neither the top nor the bottom of the potential range was reached. Therefore, no danger of chemical decomposition of copper sulphides can be expected in this selective process.

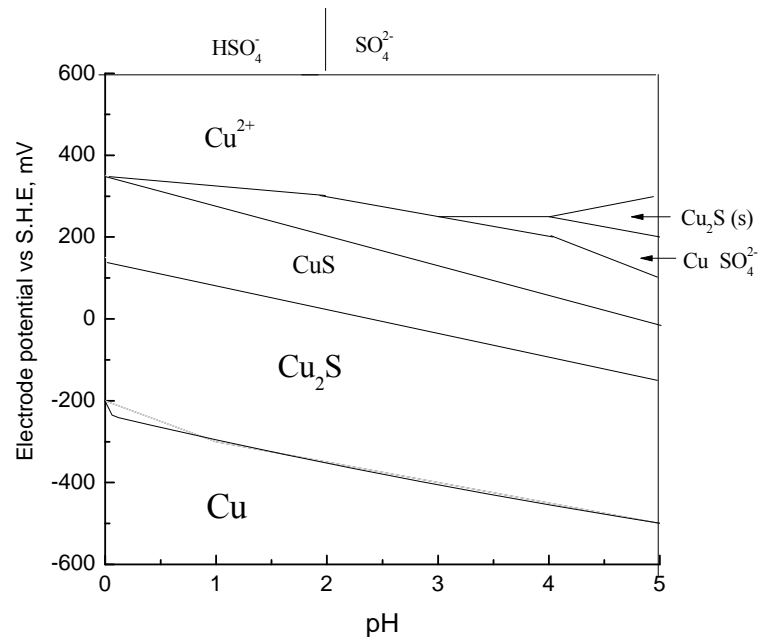


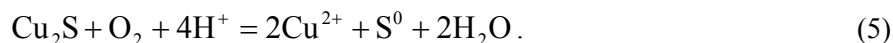
Fig. 3. E-pH diagram of Cu-S-H₂O system at 25 °C based on Goodenough et al., 1988

The behavior of sulphide minerals changes markedly in terms of their stability when oxidation agent (air, oxygen, iron(III) ions) is introduced to the solution. Copper ions are liberated into the solution as the process of anodic oxidation of sulphide minerals and cathodic reduction Fe(III) ions to Fe(II) takes place simultaneously, according to the following reaction:

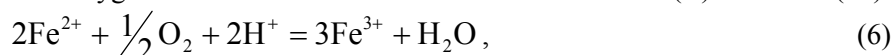


The effect of increase of Pt redox electrode potential and sulphide minerals electrodes is expected to be significant in the presence of oxidation agent. Consequently, metal ions concentration in the solution starts to increase as sulphides are subjected to leaching.

In our experiments, we have initially changed the conditions of leaching process, from non-oxidative to oxidative, by the introduction of gaseous oxygen into the leached slurry. Two types of reaction take place in the presence of oxygen. First is the leaching of copper sulphides according to reaction:



The presence of oxygen initiates also the reaction of oxidation of Fe(II) ions to Fe(III):



and increase of the rest potential of electrodes was recorded. Changes in potential of electrodes (Pt red-ox electrode and mineral: bornite, chalcopyrite) are shown in Figs 4, 5, and 6 during the leaching process performed initially as non-oxidative (about 130 minutes) and then as oxidative, in presence of O_2 and Fe(III) ions.

As it was already shown (Figs 1 and 2), the electrode potential during non-oxidative leaching decreases rapidly with increasing pH. When non-oxidative conditions at total decomposition of carbonates were achieved, gaseous oxygen was introduced to the solution and increase of electrode potential (red-ox and minerals) occurred (Figs 4, 5, and 6). The observed increase in potential of the mineral electrode is a measure of changes in the conditions of the digestion of the mineral in the aqueous environment. The introduction of oxygen to the solution raises the value of bornite and chalcopyrite electrodes potential slightly above +300 mV, which corresponds to the area of sulphides digestion, even at small solubility of oxygen under examined acidic conditions.

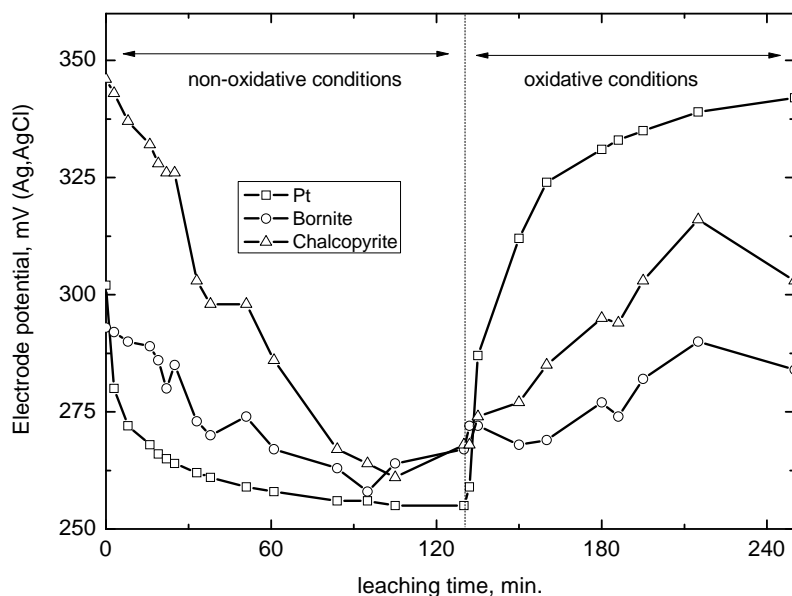


Fig. 4. Potential of electrodes vs. leaching time under non-oxidative and oxidative conditions (oxygen was introduced after 130 minutes) for total carbonate decomposition

More profound effect of potential raise was observed when Fe(III) ions were added to the leaching slurry (Fig. 5). Iron(III) is apparently the most efficient leaching agent in terms of reaction rate. Its presence evidently increases the potential of both Pt and chalcopyrite electrodes. Chalcopyrite exhibits the potential value slightly above + 400 mV, which is considerably higher when compared to that observed in the presence of oxygen. Similar effect was observed when bornite electrode was applied for electrochemical examinations (Fig. 6). The observed potential changes for Pt, chalcopyrite and bornite electrodes confirm that the iron(III) ions are significantly more effective leaching agent for copper sulphides than the oxygen. The presence of oxygen in leaching system together with Fe ions is necessary to regenerate Fe(II) to Fe(III) according to reaction (6).

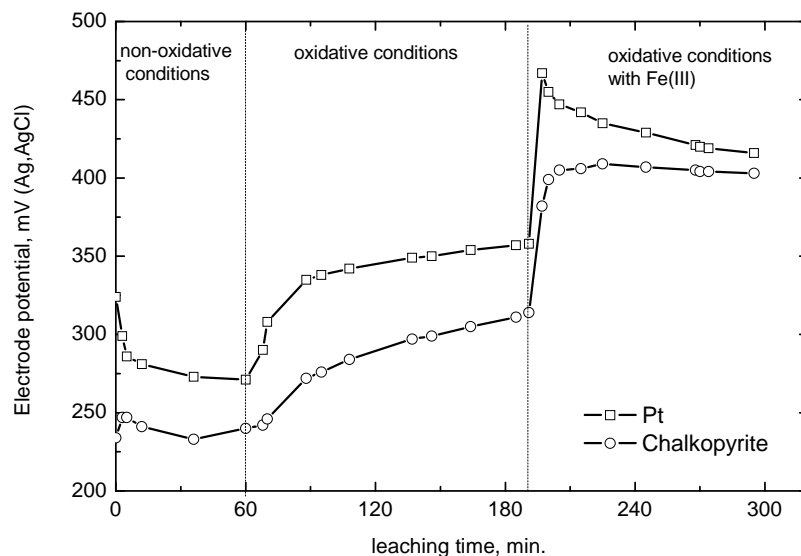


Fig. 5. Potential of Pt and chalcopyrite electrodes vs. leaching time in non-oxidative leaching and under oxidative conditions after introduction of oxygen (60 minutes) and in the presence of Fe(III) (20 g/dm^3). Total carbonate decomposition

Digestion of metal sulphide minerals in hydrometallurgical leaching processes follows the mechanism similar to corrosion and can be initially evaluated and compared using the E – pH diagrams. This electrochemical mechanism of leaching was previously studied for sulphides from Polish copper deposits (Chmielewski, 1982). Chalcocite and bornite were recognized as a easy-leached copper sulphides, whereas chalcopyrite – as the most refractory in terms of leaching rate. Therefore, sulphides exhibiting the highest rest potential in leaching media are more stable in terms of both thermodynamics and kinetics (FeS_2 , FeAsS , CuFeS_2). Sulphides with lower rest potentials are much more easily leached (PbS , Cu_2S) (Ahonen, 2006).

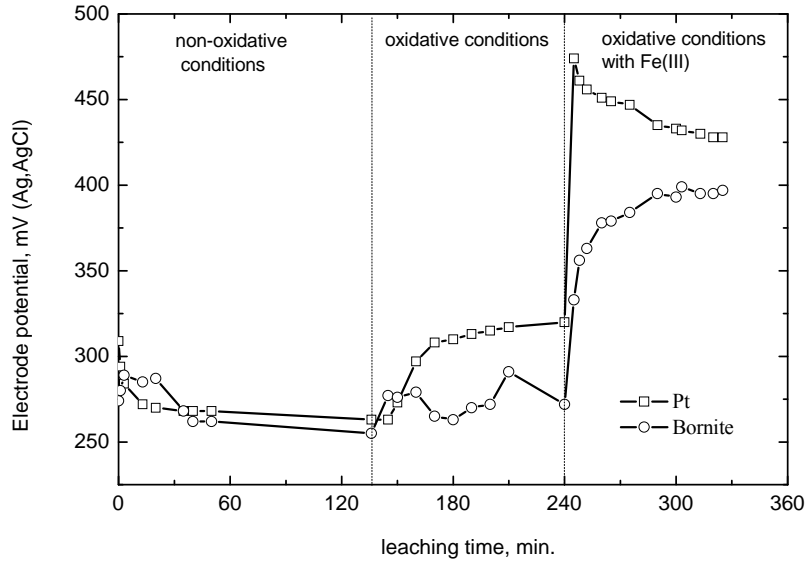


Fig. 6. Potential of Pt and bornite electrodes vs. leaching time in non-oxidative leaching and under oxidative conditions after introduction of oxygen (~ 130 minutes) and in the presence of Fe(III) (Initial concentration of Fe(III) – 20 g/dm³). Total carbonate decomposition

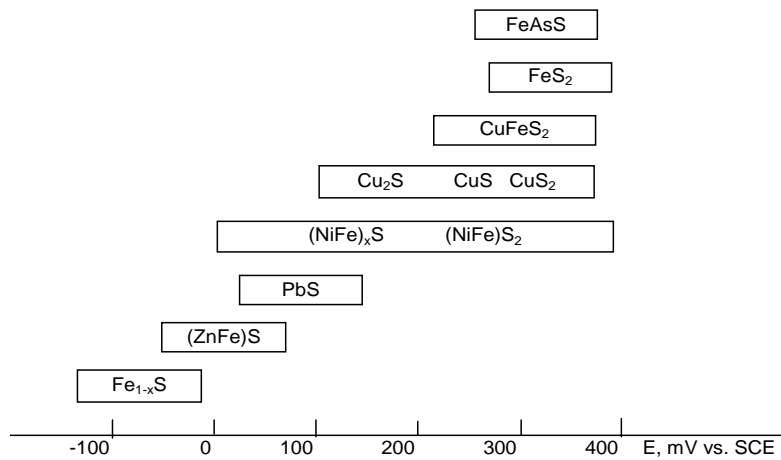
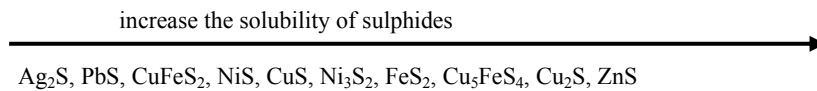


Fig. 7. The rest potentials of electrodes made of different sulphide minerals (Ahonen, 2006)

The ability of sulphides to dissolution under acidic conditions can also be characterized on the basis of a series of solubility discussed by Łętowski (1975):



Therefore, from our leaching experiments and simultaneous measurements of electrode potentials it can be seen that the magnitude of sulphide rest potential is the measure of leaching susceptibility in acidic environment. Redox potential and potential of sulphide electrode can be also utilized as a way of monitoring of leaching conditions. This was confirmed by electrochemical tests presented in this paper (Figs 4 and 6).

CONCLUSIONS

Measurements of the redox potential by means of Pt electrode and the rest potential of natural copper sulphide electrodes is a good method of evaluation of copper leaching conditions, both non-oxidative and oxidative. The observed magnitudes of potential changes in non-oxidative acidic leaching, along with thermodynamic evaluation with E- pH diagrams indicate, that the leaching process is very selective and copper sulphides remain stable in terms of metals digestion. Introduction of oxygen leads to essential increase of electrodes potential to the region where metals dissolution starts. Most remarkable increase of electrodes potential can be observed when iron(III) ions are the leaching agent.

REFERENCES

- AHONEN, L., 2006, *Biohydrometallurgy – electrochemical and thermochemical aspects*, In: *Perspectives for applying bioleaching technology to process shale-bearing copper ores*, BIOPROCOP'06, Lubin 2006, KGHM Cuprum, Wrocław 2006.
- CHMIELEWSKI, T., 1982. *Intensification of leaching of copper sulphide concentrates In the light of electrochemical investigations*. PhD thesis, Wrocław University of Technology, 1982 (in Polish).
- CHMIELEWSKI T., 2007a, *Non-oxidative leaching of black shale copper ore from Lubin Mine*, Physicochemical Problems of Mineral Processing, 41, 323-348.
- CHMIELEWSKI T., 2007b, *Atmospheric leaching of shale by-product from Lubin concentrator*, Physicochemical Problems of Mineral Processing, 41, 337-348.
- CHMIELEWSKI T., ŁUSZCZKIEWICZ A., KONOPACKA Ż., 2007, *Separation and concept of processing of black shale copper ore from Lubin mine*, Proc. VIII International Conference on Non-ferrous Ore Processing, Wojcieszycze (Poland), May 21-23, KGHM Cuprum, Wrocław 2007, 171-184 (in Polish).
- CHMIELEWSKI T., ŁUSZCZKIEWICZ A. AND KONOPACKA Ż., 2008, *Acidic pretreatment of hard-to-tread copper ore flotation middlings to facilitate flotation efficiency*, Proc. XXIV International Mineral Processing Congress, Beijing – China, Sept. 24-28 2008, vol.1, (Wan Dianzuo et al., Eds.), Science Press Beijing 2008, 1189-1200.
- GOODENOUGH, M.R., KELSALL, G.H., LIANG, Z., 1988. *Electrochemical decomposition of covellite (CuS) particles in a bipolar packed bed electrode*. Electrochemistry in mineral and metal processing II.
- LETOWSKI, F., 1975, *Principles of Hydrometallurgy* (Handbook), PWN Warszawa, (in Polish).

- LUSZCZKIEWICZ A., CHMIELEWSKI T., 1999, *Acid treatment of copper sulfide concentrate in the flotation circuit*. Proceedings V International Conference of Nonferrous Ore Processing, Szklarska Poręba, 25-27.10.1999, Publ. CBPM Cuprum, IMN, 59-66.
- LUSZCZKIEWICZ A., CHMIELEWSKI T., 2006, *Technology of chemical modification of by-products in copper sulphidic ore flotation systems.*, Rudy i Metale Nieżelazne, R-51, Nr.1, pp. 2-10 (in Polish).
- LUSZCZKIEWICZ A., CHMIELEWSKI T., 2008, *Acid treatment of copper sulfide middlings and rougher concentrates in the flotation circuit of carbonate ores*, Int.J.Min.Process 88 (2008) 45-52.

Kowalczyk P., Chmielewski T., *Zmiany potencjału elektrod podczas ługowania nieutleniającego*, Physicochemical Problems of Mineral Processing, 44 (2010), 115-126 (w j. ang)
<http://www.minproc.pwr.wroc.pl/journal>

Pomiary pH i potencjału redox (za pomocą elektrody platynowej) podczas nieutleniającego ługowania kwasem siarkowym pozwalają równocześnie określić kinetykę oraz zmiany parametrów elektrochemicznych zachodzących w roztworze podczas prowadzonego procesu. W czasie rozkładu węglanów za pomocą kwasu siarkowego zaobserwowano w roztworze ługującym znaczny spadek potencjału redox roztworu (od +350 mV do +50 mV, względem elektrody Ag,AgCl) przy jednoczesnym wzroście pH. Tak niskie wartości potencjału red-ox uniemożliwiają utlenianie siarczokowych minerałów miedzi obecnych w ługowanym materiale i przechodzenie metali do roztworu. Stwierdzono, że ługowanie nieutleniające jest procesem szybkim i selektywnym, powodując wyłącznie rozkład węglanów wapnia i magnezu. Uznano, że w miarę zwiększenia stopnia rozkładu węglanów wzrasta udział uwolnionych ziaren minerałów użytecznych, co ułatwia i intensyfikuje dalsze procesy wzbogacania lub ługowania.

słowa kluczowe: potencjał elektrody, pH, ługowanie, siarczki