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OXIDATION AND DISSOLUTION OF METAL SULFIDES FROM FLOTATION WASTES IN CIRCULATING WATER – THE FATE OF SULFIDE SULFUR

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Dissolution of Zn, Pb, and sulfate ions in water from flotation lead-zinc ore tailings was investigated by passing water through columns filled with the waste. Conductivity, pH and concentration of selected ions in the effluent were measured and expressed as a function of exchange ratio of pore water (ER). Samples collected from the tailing after the experiments were investigated by X-ray photoelectron spectroscopy (XPS). Due to high concentration of carbonate minerals, which saturate the flowing water with hydrocarbonate ions, the concentration of both lead and zinc ions in the effluent is very low, below the standard for industrial waste water (except the very initial period). At the same time sulfide sulfur oxidizes partially to elemental sulfur, not to sulfates. For that reason the transfer of sulfates from the flotation wastes is rather limited.

Key word: flotation waste, sulfide oxidation, pyrite oxidation, sulfide minerals

INTRODUCTION

Modern industry uses significant amount of non-ferrous metals. Ores of non-ferrous metals, rich enough to be processed directly by pyrometallurgical methods, are practically exhausted and mainly low-grade ores are processed now. In the case of copper, processing of ores containing as low content of copper as 1% is still economically profitable. So, the production of non-ferrous metals is accompanied by the appearance of huge amounts of wastes. For example, the Polish copper industry, during 50 years of its activity, deposited 600 000 000 Mg (tones) of wastes on a depository place, occupying 2300ha of land (Łuszczkiewicz, 2000). The impact of the industrial wastes on the environment in Poland has been reviewed by Helios-Rybicka (1996). Non-ferrous metals appear in ores mainly as metal sulfides and the principal technology used for removal of valuable sulfide minerals from ores is froth flotation (Leja, 1982). Besides, the sulfides of the recovered metals ore may contain sulfide and

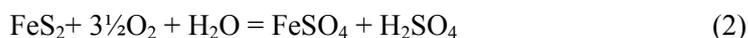
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non-sulfide minerals of other metals. These minerals are present in flotation tailings, creating a real danger for the environment, when the tailings are deposited in a field.

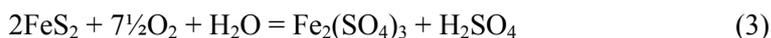
Special position in that respect occupies pyrite. Pyrite is the most abundant sulfide mineral (Craig and Vaughan, 1990) accompanying almost all sulfide and many non-sulfide minerals, including coal. At the same time pyrite has no application and in flotation process pyrite is directed to tailings. So, flotation tailings may contain as much as 60-70% of pyrite. Pyrite oxidizes relatively easily, and contrary to mono-sulfides, which oxidize to neutral sulfates according to the reaction:



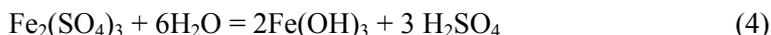
pyrite generates sulfuric acid during its oxidation



in the quantity of one mole of acid per one mole of pyrite. The amount of acid may be lower when pyrite iron oxidizes to trivalent state.



On the other hand, when pH of the surrounding aqueous phase increases above approximately 5.5, ferric sulfate hydrolyses according to the reaction:



creating additional amount of sulfuric acid. That sulfuric acid, together with dissolved trivalent iron are the main components of so-called acid mine drainage (AMD), i.e. waters flowing from worked-out mines, flotation waste deposits and sometimes from natural rocks containing pyrites (Doyle, 1990; Evangelou, 1995). Strongly acidic and oxidizing (due to the presence of trivalent iron) waters solubilize rocks containing otherwise insoluble minerals, causing contamination of the environment and sometimes leading to catastrophes of buildings (Moore and Luoma, 1990). At natural conditions (free access of CO_2) and circumneutral pH, most of sulfide minerals oxidize to insoluble carbonates (Salter and Jones, 1986; Banks et al., 1997). These carbonates create protective layers on the surface of sulfide grains and protect them from dissolution. When the rock contains minerals that have neutralizing properties (mainly carbonates of calcium and magnesium), waters outgoing from mines and depository places may be so pure that in many places they are used as the pot water for the surrounding localities (Banks et al., 1997). Therefore, lime and limestone are commonly used to decrease the concentration of iron and non-ferrous metal ions in water and wastes (Schwartz and Ploethner, 1999). The presence of carbonates not only decreases the rate of oxidation of sulfides and causes the precipitation of the metal ions as insoluble carbonates and trivalent iron as iron hydroxide, but also stabilizes pH at approximately 8 and decreases the activity of sulfide-oxidizing bacteria (Gleisner

and Herbert, 2002). On the other hand, the grains of limestone, when contacted with the acidic solutions containing dissolved iron, aluminium and non-ferrous metal ions may be covered by coatings composed mainly of complex Fe and Al sulfates and gypsum, sealing the surface of the grain from the contact with the solution and lowering their reactivity. The influence of carbonates on pyrite oxidation is complex. The presence of HCO_3^- ions increases the initial rate of pyrite oxidation, but this rate drops later on due to the formation of protective hydroxide coatings (Nicholson et al., 1988, 1990; Moses and Herman, 1991,). Sulfide minerals, including pyrite, may oxidize to elemental sulfur:



both in industrial leaching processes (Buban et al, 2000) as well as in wastes left in natural conditions (Byerley and Scharer, 1992). Naturally, from the point of view of the environment protection, that way of sulfide minerals oxidation is much more preferable. Unfortunately, ever-present bacteria usually oxidize sulfide sulfur to sulfates.

The oxidation of sulfide minerals is a very important problem not only from the point of view of environment protection and it was the object of a countless number of studies. However, most of the published papers are devoted to the oxidation of pure minerals. The papers concerning the oxidation of sulfide minerals in complex mixtures, like flotation tailings, are rather scarce. The present paper is devoted to the oxidation of sulfide minerals in flotation wastes from the flotation plant at the ZGH Bolesław metallurgical complex. The ores processed there contain galena and sphalerite as the main valuable minerals and some oxidized lead and zinc minerals as well as significant amount of pyrite and marcasite. Oxidized lead and zinc minerals are much better soluble than respective sulfides and may dissolve to some extent even in the absence of oxidizing factors and the oxidation of pyrite may induce the solubilization of sulfides. On the other hand these ores contain high concentration of calcite and dolomite, which should depress the emission of lead and zinc ions from the wastes. Another problem is the possible emission of sulfates, which not always is depressed by carbonates of calcium and magnesium because the sulfates of both metals are relatively well soluble. So, the course of sulfides' oxidation and emission of potential contaminants from the mentioned tailings has been investigated experimentally with the special attention to the oxidation of sulfide sulfur.

EXPERIMENTAL

Flotation wastes were collected from flotation tailing pond where they had been left in a wet state and had the consistency of a dense suspension. The phase composition of the wastes was determined by X-ray diffraction, using the Siemens D 5005 (Bruker) instrument. Figure 1 presents the diffraction pattern of the wastes. It is

to be seen that the main minerals constituting the wastes were: dolomite, ca 40 mol%, calcite, ca 20 mol%, pyrite + marcasite, ca 30 mol%, and quartz, ca 10 mol%. Thorough diffraction analysis revealed also the presence of minor quantities (below 1%) of sphalerite, galena, cerusite and smithsonite. Particle size distribution of the wastes was measured by sieving through a set of laboratory sieves (Fritsch). As usually in flotation tailings, the particles size distribution was rather broad: 50 weight % of the grains had the diameter below 0.15 mm and 10 weight % below 0.05 mm. The sample (several tenths of kilograms) was homogenized and placed in tightly sealed plastic cans. Most of the experiments were performed with the wastes as received, however part of the sample was dried at 105°C to constant weight and used in the experiments in a dry state.

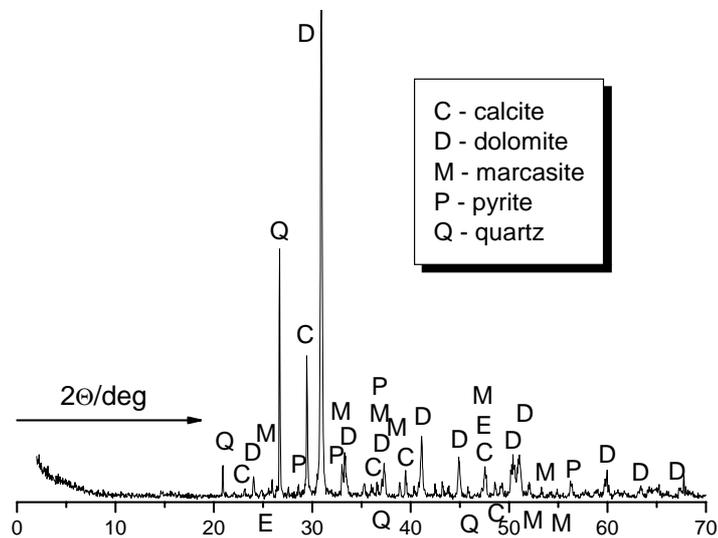


Fig. 1. X-ray diffraction pattern of investigated flotation tailings

Emission of metal ions and sulfates to the water flowing through the wastes was investigated by placing the wastes in a column made of organic glass depicted in Fig. 2 and passing distilled water from the top of the column to its bottom. Water being in equilibrium with air was used, but in one experiment water before the introduction to the column was bubbled with argon to remove oxygen. The internal diameter of the column was 5 cm. The height of the wastes in the column ranged from 9 to 42 cm, the weight (dry state) from ca 360 g to ca 1600 g, respectively. In the case of loading the wet wastes to the column, the bottom part of the column (between the outlet and the gilded mesh supporting the wastes) was first filled with water and then the wastes, in the form of dense suspension, were poured from the top to a predetermined high. Finally, the top of the column was filled with water and connected to the Mariotte

bottle supplying the inlet water and stabilizing the hydrostatic pressure. In the case of dried samples the column was filled with water to the height of a few centimeters above the gilded mesh supporting the wastes and the dry wastes were poured from the top to water portion by portion. After each portion of wastes water was added to keep all the time the level of water over the top of the wastes. Finally, the top of the column was filled with water and connected to the Mariotte bottle.

The porosity of the wastes in the column was calculated from the known volume, weight, and specific density of dry wastes. For the wet wastes the porosity amounted to 0.31 – 0.35 and it was relatively constant during the experiment. Only two experiments were performed with the dried wastes, the porosity in both experiments was changing from approximately 0.52 at the beginning to approximately 0.46 at the end. The amount of water that has flown through the column was expressed as the exchange ratio (ER) of the pore water. Constant hydrostatic pressure was kept during the experiment and expressed as the hydraulic gradient (ratio of the difference between the level of outlet and inlet and the height of the column (see Fig. 2). Hydraulic gradient was different in different experiments and in particular experiment it was between 0.25 and 5. Samples of outlet solution were collected regularly, weighted, and then pH, conductivity, and concentration of selected ions were determined. Conductivity and pH were measured using a CX551 multifunction meter (Elmetron). In one experiment the concentration of oxygen in the outlet solution was measured with the use of CTN-9202S Clark-type electrode (ZTP Elsent). Concentration of selected ions in the outlet solution was measured with the NOVA 60 photometer (Merck). The concentration of following ions was controlled in the outlet solution: Ca^{2+} , Cd^{2+} , Cl^- , CrO_4^{2-} , Cu^{2+} , Fe^{2+} , Fe^{3+} , K^+ , Mg^{2+} , Mn^{2+} , Mo(VI) , Na^+ , Ni^{2+} , Pb^{2+} , SO_4^{2-} , Ti^{3+} , Zn^{2+} but only Ca^{2+} , Cl^- , Fe^{2+} , Fe^{3+} , Mg^{2+} , Na^+ , Pb^{2+} , SO_4^{2-} , and Zn^{2+} appeared in measurable quantity. The experiments were conducted in the thermostated room at $24.5 \pm 0.5^\circ\text{C}$.

In several cases, at the end of the experiment wastes were carefully removed from the column in a way not to mix them, and small samples from the top, middle and bottom of the column were collected. The samples were tightly closed in plastic containers and transferred to the XPS (X-ray photoelectron spectroscopy) laboratory at the University of Turku (Finland) where the XPS spectra of the samples were measured. Each wet sample was firmly pressed to the surface of a special conducting carbon foil and mounted in the forechamber of the spectrometer. During pumping-off

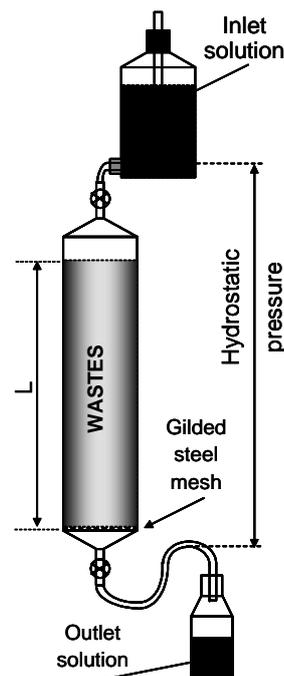


Fig. 2. Column used in the experiments

the forechamber the samples naturally dried. When the pressure in the forechamber dropped to the appropriate level the sample was introduced to the measuring chamber and the spectrum acquired. Photoelectron spectroscopic investigations were performed using the Perkin-Elmer ESCA 5400 spectrometer with monochromatized Al K_{α} X-ray source. More information on the measuring system and the spectra interpretation may be found in previous papers (Nowak et al., 2000 a,b). Investigated wastes were composed mainly of non-conducting substances. Measuring the XPS spectra of such substances presents a real problem due to so-called charging. That was eliminated by applying flood-gun. Such procedure introduces however some uncertainty in the recorded binding energy (BE) values. It was overcome by applying correction. Two lines were chosen as reference for correction: Si 2p of quartz (103.3 eV) and C 1s of so-called carbon contamination (285 eV). Both lines were sufficiently strong – quartz appeared in the wastes in the quantity of approximately 10 mol%, as stated by XRD analysis, and carbon contamination appear in any sample contacted with atmospheric air. The position of both lines is known with good precision (Moulder et al., 1992). Weighted (versus the distance from both reference lines) mean position between the lines chosen as reference lines was assumed as the position of the analyzed line. However, such correction was valid only for those emission lines that were placed either between the above mentioned lines or very close to one of them. Fortunately, the most important lines, namely S 2p (162 - 168 eV), Pb 4f (~142 eV), Mg $KL_{23}L_{23}$ (Auger, ~301 eV), Ca $2p_{3/2}$ (~347 eV) fulfilled those conditions. However, neither Fe $2p_{3/2}$ (~707 eV) nor Zn $2p_{3/2}$ (1022 eV) may have been properly corrected. So, only shape of the band and their intensity was analyzed in such a case.

RESULTS

The best way to estimate the total concentration of ionic species in a solution is to measure its conductivity (Evangelou, 1998). Naturally conductivity is a non-specific quantity and it cannot replace the chemical analysis of the solution but if the qualitative composition of the solution is constant, conductivity gives a quick measure of the concentration.

Table 1. The concentrations of the selected ions in consecutive stages of one of the experiments with wastes loaded as wet to the column. Exchange ratio (ER), pH and conductivity (κ) of the effluent are also given. Weight of the wastes in the column was 1600 g (in the dry state), height 39 cm, and hydraulic gradient 5.0. All concentrations are given in mgdm^{-3} , conductivity in mScm^{-1}

Stage	ER	pH	κ	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Na^+	Cl^-	Pb^{2+}	Zn^{2+}
I	0.64	7.90	3.88	620	302	2980	41	74	1.6	3.1
II	3.12	8.02	2.41	660	36.5	1600	<10	<5	0.9	2.3
III	5.58	8.00	0.37	51	13.4	44	<10	<5	0.09	0.25

Figure 3 presents the changes of conductivity and pH of the outlet of the column as a function of exchange ratio (ER) of the pore water in two experiments performed at identical conditions. The repeatability of the results of the experiments was rather good, as may be seen. The course of the dependence of both κ and pH on ER in all experiments was similar to that presented in Fig. 3. The experiment may be divided into three stages (marked in Roman numerals in the figure). Typical concentrations of the most important ions present in the effluents from the column in consecutive stages of one of the experiments are presented in Table 1.

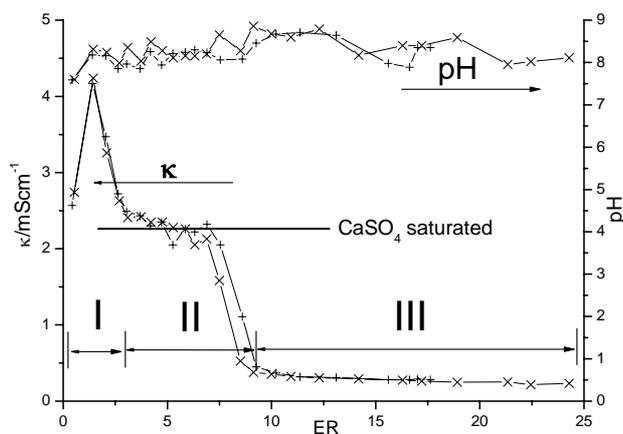


Fig. 3. The change of pH and conductivity of the outlet solution of the column in two experiments performed at identical conditions: height of the wastes 16 cm, weight of wastes (dry state) 660 g, hydraulic gradient 5.0

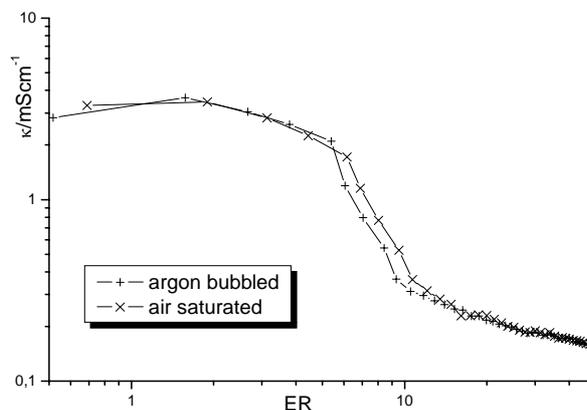
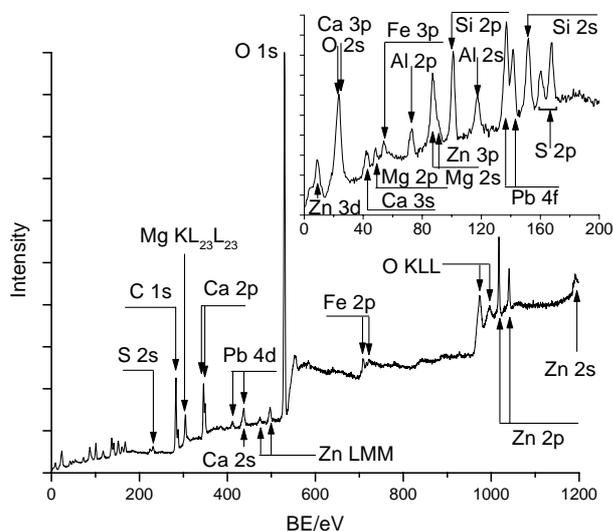


Fig. 4. Conductivity changes in two experiments: in one of them water in equilibrium with atmospheric air was used, in the other experiment water was bubbled with argon to remove oxygen before introduction to the column. All other parameters of the experiments were identical: hydrostatic gradient = 4.0, mass of the sample = 350 g, height of the waste layer 9.0 cm

The first stage was always short ($ER \leq 3$) and characterized by a high concentration of dissolved substances, these substances being magnesium and calcium sulfates. The second stage was longer and the main ionic component of the effluent was calcium sulfate. The conductivity in this stage was equal to the conductivity of saturated solution of gypsum. Third stage lasted to the end of the experiment and the composition of the solution during that stage of the process was dominated by carbonate complexes of calcium. The most pronounced difference between different experiments appeared in stages I and II, depending on the state of the wastes before the start of the experiment (wet or dry). When the wastes were dried before the experiment, pH in stage I was much lower (~ 5.5 at the beginning) and quite a lot of Fe^{2+} appeared in the effluent. No iron in the effluent of the column was ever observed in the case of wastes loaded to the column in the wet state. In the case of wastes loaded to the column in the dry state, the duration of stage II was much longer than in the case of wastes loaded as wet. In the later case, when the layer of the wastes in the column was rather short, stages I and II were not so clearly resolved. Starting from the beginning of stage III the concentrations of ions were continuously diminishing and the conductivity of the effluent was diminishing too (see Fig. 4) in parallel to the concentration of calcium. The maximum value of ER for which the data in Fig. 4 are showed is 50, but the conductivity (and in parallel the concentration of Ca^{2+} , Pb^{2+} and Zn^{2+}) continued to decrease as long as the experiment was conducted (the same was observed for all experiments). The longest experiment lasted 146 days; the highest ER value attained was 145 (not in the same experiment). The conductivity in the third stage of the process was determined mainly by the dissolution of carbonate minerals present in the wastes, so it is not surprising that the conductivity did not depend on the presence of oxygen in the influent water (see Fig. 4). However, the concentrations of both lead and zinc, in two parallel experiments with oxygen free water in one of them (Fig. 4) was also the same within the limit of the analysis accuracy up to the $ER = 50$ (then the experiment with oxygen free water was stopped). Table I presents the concentrations at the very beginning of stage III of the experiment. In all experiments, after 10 – 30 exchanges of pore water the concentration of both SO_4^{2-} and Mg^{2+} dropped below the limit of detectability (5 mgdm^{-3} in the case of both ions). In one of the experiments the concentration of oxygen in the effluent of the column was measured. A short column (9 cm) and relatively high hydraulic gradient (3.0) were applied, but after 41 exchanges of pore water the concentration of oxygen in the effluent was still below the limit of detectability.

Figure 5 presents the survey XPS spectrum of the wastes after dismantling the column. Except the emission lines of Ca, Mg, O, C, Fe, Pb, Zn, S and Si, relatively strong Al line appeared in the spectrum. Aluminium occurs in the wastes probably as several different aluminosilicates, having different diffraction patterns. For that reason they have not appeared in the XRD analysis. Both Pb and Zn emission lines were stronger than may be expected basing on the composition of the wastes.

Fig. 5. Survey XPS spectrum of the wastes after 21 exchanges of pore water and dismantling off the column. Sample taken from the bottom part of the column. Hydraulic gradient during experiment 5, weight of the wastes in column 660 g (in dry state), height of the wastes in the column 16 cm



The obvious explanation is that most of lead and zinc appeared in the adsorbed state, on the surface of calcite, dolomite and iron hydroxides produced by oxidation of pyrite. The BE of the Pb 4f_{7/2} line was approximately 0.7 eV higher than that for lead carbonate. Contrary to lead and zinc, the emission line of iron (Fe 2p) was weaker than might be expected. At pH that was inside the column, the concentration of trivalent iron in the solution is extremely low (Dyer et al., 1998). So, the concentration of iron species in the solution was too low to cause the adsorption of iron at the surface of carbonates. On the other hand iron hydroxides and hydrated oxides are very good adsorbents and their surfaces was probably covered by adsorbed ions. XPS is a surface-sensitive method and even monolayer coverage may decrease significantly the emission of electrons from the background. Figure 6 presents the S 2p line of the XPS spectra of the samples collected from different parts of the column. For the sake of comparison the S 2p line of the XPS spectrum of a pyrite sample fractured and then exposed to atmosphere is presented in Fig. 7.

Despite some uncertainty, connected with the procedure of BE correction, the interpretation of the S 2p spectra of waste samples is straightforward. Both sulfide sulfur and oxidized sulfur may be easily discriminated in the spectrum. Most of the emission at the BE of sulfide sulfur may be unequivocally ascribed to pyrite (~162.6 eV), but a weak shoulder at the position close to either the sulfur in galena (161 eV) or sphalerite (161.5) (Laajalehto et al., 1994) may be visible too. Note further, that the spectrum for the sample collected from the top of the column differs strongly from those of both the samples collected from the middle and the bottom of the column as well as from the spectrum of wastes before loading to the column.

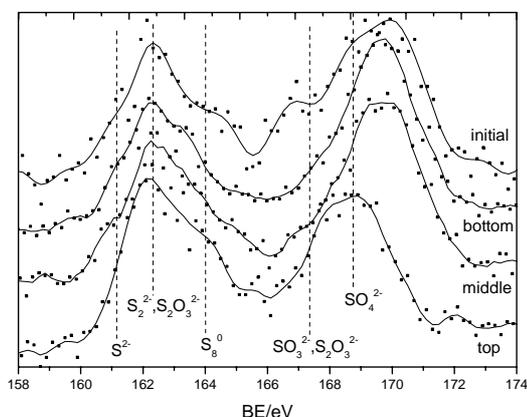


Fig. 6. S 2p region of the XPS spectra of the wastes after dismantling off the column. Samples taken from different parts of the column, as described in figure. Spectrum of the wastes before loading to the column (initial) is presented too. Parameters of the experiment like in Fig. 5. Thiosulfate appear twice at two different BEs, because thiosulfate ion has two different sulfur atoms that give the emission at different binding energies. Points – measured data. Continuous lines – data smoothed by the ORIGIN program

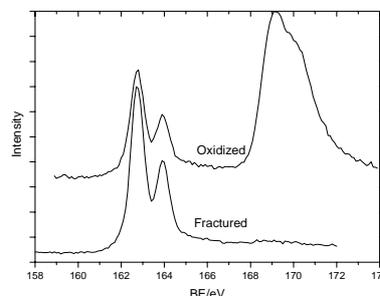


Fig. 7. Example of the S 2p line of the XPS spectrum of the freshly fractured and oxidized surface of pyrite. Coal pyrite from the coal mine Jastrzębie in Poland. After fracturing pyrite was oxidized 10 days in air

The obvious reason is that the concentration of dissolved ions (Fe^{2+} , HCO_3^- , and SO_4^{2-}) at the top of the column is the lowest and the concentration of oxygen the highest. So, the top of the column is best “cleaned off” the soluble and desorbable species and at the same time the conditions for pyrite oxidation are the best there. The position of the emission line that may be ascribed to sulfates in the case of that sample is similar to the case of oxidized pyrite (compare Fig. 6 and 7) and may be ascribed to sulfate on the surface of pyrite. However, the sulfate line in both the samples from the middle of the column and from the bottom of the column is shifted towards higher BE by approximately 1 eV. It may be postulated that down the column sulfate ions appear mainly in the adsorbed state, at the surface of the carbonate minerals and iron hydroxides. The lead line, which was ascribed to the lead ions on the surface of calcite, also showed the shift in the direction of higher BE. Note, that the proportion of sulfate sulfur is lowest at the top of the column and highest at the bottom. In the case of initial sample both sulfate at the surface of pyrite and adsorbed sulfate appear. It also seems that the intermediate-valence sulfur (sulfite? thiosulfate?) appear in the initial sample and, to the less extent at the top of the column. Interesting question is the possible presence of elemental sulfur. A shoulder at the position expected for elemental sulfur evidently appears in the spectrum of initial sample and to a lesser extent in the spectrum of the sample from the top of the column. Note that neither elemental sulfur nor intermediate-valence sulfur are visible in the spectrum of

oxidized pyrite (Fig. 7). In the spectrum (not showed) of the sample collected from the experiment where ER ratio was much higher (61), the emission at the BE characteristic for elemental sulfur was much higher (in comparison to other forms of sulfur).

DISCUSSION

The following picture of the process of oxidation of metal sulfides and generation of contaminants in the flotation wastes from the ZGH Bolesław may be presented, basing on the column tests and the XPS spectra. The main source of sulfates in the water flowing through the wastes is the dissolution of sulfates formed by oxidation of metal sulfides (mainly pyrite) during the storage of the wastes. After dissolution of the sulfates (stage I and II of the experiment) the concentration of sulfates transferred to the flowing (air-saturated) water was rather low, below the standards for industrial waste waters. The degree of oxidation of the wastes may be estimated from the total amount of sulfates liberated from the wastes during stages I and II of the experiment. In accordance with commonly accepted opinions the oxidation of sulfides is much faster when waste is kept in the dry state as compared to the wastes kept under the surface of water. In the case of the waste kept as dry, ferrous sulfate and sulfuric acid formed in reaction (2) rest at the surface of pyrite. When the wastes are poured into water, both H_2SO_4 and FeSO_4 dissolve and the pH of the solution drops. Sulfuric acid reacts with calcite and dolomite inside the column according to the reactions:



Well soluble ferrous sulfate appears in the effluent of the column. When the wastes are kept under the water, both sulfuric acid and ferrous sulfate dissolve immediately after their formation. Sulfuric acid react with calcite and dolomite according to reactions (6) and (7) and ferrous sulfate oxidize to ferric sulfate:



When pH of the pore water grows up the hydrolysis of ferric sulfate occurs (reaction 4). So, no ferrous sulfate is present in pore water. Magnesium sulfate is very well soluble and it leaves column in stage I of the process. The solubility of gypsum is limited - part of it precipitates already during the storage of the wastes and is removed during stages I and II of the experiment. So, wastes kept as wet contain sulfate ions in the form of gypsum both precipitated and dissolved in pore water, and in the form of dissolved magnesium sulfate. When the experiment starts, the incoming water first replaces water containing dissolved sulfates in pores, and then dissolves gypsum so the only sulfates that may be observed by XPS in the sample collected from the top of the column are those from the oxidation of sulfides by oxygen (reactions 1 and 2).

However, when water flows down the column the concentration of sulfates grows up and sulfate ions adsorb at the surface of carbonate mineral grains and iron hydroxides. As a result the ratio of sulfates grows up down the column.

Part of sulfide sulfur evidently oxidizes to elemental sulfur, as may be inferred from the XPS spectra. The formation of elemental sulfur may be supported by following reasoning. If all oxygen, present in the influent water (saturated with air) had oxidized sulfide sulfur to sulfates according to reactions (1) and/or (2) the concentration of sulfates in the effluent would have been 13.7 mgdm^{-3} , as may be easily calculated. However in all performed experiments the concentration of sulfates dropped down below 5 mgdm^{-3} soon after the end of stage II of the experiment and no oxygen was found in a control experiment after 41 exchanges of pore water. That is in apparent contradiction with the relatively high amount of sulfates observed by XPS, especially because both Mg and Zn sulfates are very well soluble in water, the solubility of CaSO_4 is relatively (comparing to carbonate) high and even lead sulfate is orders-of-magnitude better soluble than lead carbonate. The best explanation is that the sulfate observed by XPS appears mainly as adsorbed on the surface of carbonates. Note, that even very small amount of a substance dispersed homogeneously on the surface may contribute very strongly to the XPS spectrum. Formation of elemental sulfur is a very important aspect of the process. If the oxidation of sulfides present in wastes proceeded completely to elemental sulfur there would be no formation of sulfuric acid and the emission of contaminants to the environment would be much lower. In the literature concerning the oxidation of pyrite by dissolved oxygen at circumneutral pH no formation of elemental sulfur was reported (Nicholson et al., 1988, 1990; Moses and Herman, 1991) and other sulfides (galena and sphalerite) were present in the investigated wastes in minor quantity as compared to pyrite + marcasite, so they could not be the source of elemental sulfur observed by XPS. The formation of elemental sulfur on the surface of sulfide minerals is now extensively studied in our laboratory.

Similar situation, like in the case of sulfate ions, occurs in the case of zinc and lead ions. The concentrations of both metals in the effluent during stage III of the experiment were low and below the standard for industrial waste water, obviously kept at such low level by low solubility of cerussite and smithsonite (or hydrocerussite and hydrozincite). High and constant concentration of HCO_3^- ions is due to the presence of high amount of calcite and dolomite that saturate the solution. Note, that higher concentration of zinc and lead ions in stage I and II of the experiment may be ascribed to very high concentration of Ca^{2+} and Mg^{2+} ions that cause lowering the concentration of carbonate ions according to the solubility product of calcite and dolomite. Rather high ratios of lead and zinc dissolution as indicated by the XPS spectra is obviously due to the sorption of the ions of both metals at the surface of carbonate minerals and iron hydroxides. That sorption is well documented in the literature (Zachara et al., 1991; Rimstidt et al., 1998; Godelitsas et al., 2003; Rouff et al., 2004).

CONCLUSIONS

The dissolution of zinc, lead, and sulfate ions in water from the flotation wastes containing relatively high concentration of pyrite and marcasite (~30 mol%) and minor quantities of sulfide and oxidized minerals of zinc as well as lead is strongly suppressed due to beneficial influence of carbonate minerals present in the wastes (calcite and dolomite). Concentration of zinc and lead is kept low due to the saturation of the flowing water by the carbonate ions from the dissolution of calcite and dolomite. Calcite and dolomite are much better soluble than carbonates of zinc and lead and, according to the solubility product, the concentration of zinc and lead species in the presence of calcite and dolomite is much lower than in the saturated solution of pure zinc and lead carbonates. At the same time the sulfide sulfur of metal sulfides present in the wastes is oxidized partly to elemental state, which diminished the amount of sulfate ions generated during the contact with air-saturated water. Altogether, it makes the investigated wastes relatively safe to dispose, providing that they are placed below the surface of water.

REFERENCES

- BANKS D., YOUNGER P.L., ARNESON R.-T., IVERSON E.R. AND BANKS S.B., 1997, *Mine-water chemistry: the good, the bad and the ugly*, Environmental Geology, **32**, 157 - 174.
- BUBAN K.R., COLLINS M.J., MASTERS I.M. AND TRYTTEN L.C., 2000, *Comparison of direct pressure leaching with atmospheric leaching of zinc concentrates*, in: Lead-zinc 2000, Proceedings of the Lead-Zinc Symposium, Pittsburgh, USA, (J.E. Dutrizac, J.A. Gonzalez, D.M. Henke, S.E. James and A.H-J. Siegmund, editors), The Minerals, Metals and Materials Society, Warrendale, 727 - 738.
- BYERLEY J.J. AND SCHARER J.M., 1992, *Natural release of copper and zinc into the aquatic environment*, Hydrometallurgy, **30**, 107 - 126.
- CRAIG J.R. AND VAUGHAN D.J., 1990, *Compositional and textural variations of the major iron and base-metal sulfide minerals*, in: Sulfide deposits – their origin and processing (P.M.J. Gray, G.J. Bowyer, J.F. Castle, D.J. Vaughan and N.A. Warner - editors), The Institution of Mining and Metallurgy, London, 1 - 16.
- F.M. DOYLE, 1990, *Acid mine drainage from sulfide ore deposits*, w: Sulfide deposits – their origin and processing (wydawcy - P.M.J. Gray, G.J. Bowyer, J.F. Castle, D.J. Vaughan i N.A. Warner), The Institution of Mining and Metallurgy, Londyn, 301 - 310.
- DYER J.A., SCRIVNER N.C. AND DENTEL S.K., 1998, *A practical guide for determining the solubility of metal hydroxides and oxides in water*, Environmental Progress, **17**, 1 - 8.
- EVANGELOU V.P., 1995, *Pyrite Oxidation and Its Control*, CRC Press, Boca Raton, USA.
- EVANGELOU V.P., 1998, *Environmental Soil and Water Chemistry. Principles and Application*, J. Wiley&Sons, Nowy Jork
- GLEISNER M. AND HERBERT R.B. JR., 2002, *Sulfide mineral oxidation in freshly processed tailings batch experiments*, Journal of Geochemical Exploration, **76**, 139 - 153.
- HELIOS-RYBICKA E., 1996, *Impact of mining and metallurgical industries on the environment in Poland*, Applied Geochemistry, **11**, 3 - 11.
- GODELITSAS A., ASTILLEROS J.M., HALLAM K., HARISSOPOULOS S., PUTNIS A., 2003, *Interaction of calcium carbonates with lead in aqueous solutions*, Environ.Sci.Techl., **37**, 3351-3360.
- LAAJALEHTO K., KARTIO I. AND NOWAK P., 1994, *XPS Study of Clean Metal Sulfide Surfaces*, Applied Surface Science, **81**, 11-15.
- LEJA J., 1982, *Surface Chemistry of Froth Flotation*, Plenum Press, Nowy Jork.

- LUSZCZKIEWICZ A., 2000, *Koncepcja wykorzystania odpadów flotacyjnych z przeróbki rud miedzi w regionie Legnicko-Głogowskim*, Inżynieria Mineralna, **1**, 25 – 35.
- MOORE J.N. AND LUOMA S.N., 1990, *Hazardous wastes from large-scale metal extraction*, Environmental Science and Technology, **24**, 1278 - 1285.
- MOSES C.O. AND HERMAN J.S., 1991, *Pyrite oxidation at circumneutral pH*, Geochimica et Cosmochimica Acta, **55**, 471 – 482.
- MOULDER J.F., STICKLE W.F., SOBOL P.E. AND BOMBEN K.D., 1992, *Handbook of X-ray photoelectron spectroscopy*, Perkin Elmer, Eden Prairie, USA.
- NICHOLSON R.V., GILLHAM R.W. AND REARDON E.J., 1988, 1990, *Pyrite oxidation in carbonate-buffered solutions: 1. Experimental kinetics. 2. Rate control by oxide coatings*, Geochimica et Cosmochimica Acta, **52**, 1077-1085, **54**, 395-402.
- NOWAK P. AND LAAJALEHTO K., 2000a, *Oxidation of Galena Surface – an XPS Study of the Formation of Sulfoxy Species*, Applied Surface Science, **157**, 101-111
- NOWAK P., LAAJALEHTO K. AND KARTIO I., 2000b, *A Flotation Related X-Ray Photoelectron Study of the Oxidation of Galena Surface*, Colloids and Surfaces A, **161**, 147-160
- RIMSTIDT J.D., BALOG A. AND WEBB J., 1998, *Distribution of trace elements between carbonate minerals and aqueous solutions*, Geochimica et Cosmochimica Acta, **62**, 1851-1863.
- ROUFF A.A., ELZINGA E.J., REEDER R.J. AND FISHER N.S., 2004, *X-ray absorption spectroscopic evidence for the formation of Pb(II) inner-sphere adsorption complexes and precipitates at the calcite - water interface*, Environ. Sci. Technol., **38**, 1700 - 17007.
- SALTER J.D. AND JONES M.P., 1986, *Galena alteration in bicarbonate environment*, Trans. Inst. Min. Metal., **95**, C95 - C106.
- SCHWARTZ M.O., PLOETHNER D., 1999, *Removal of heavy metals from mine water by carbonate precipitation in the Grootfontein-Omatako canal, Namibia*, Environmental Geology, **39**, 1117 - 1126.
- SIMÓN M., MARTIN F., GARCIA I., BOUZA P., DORRONSORO C. AND AGUILAR J., 2005, *Interaction of limestone grains and acid solutions from the oxidation of pyrite tailings*, Environmental Pollution, **135**, 65 – 72.
- ZACHARA J.M., COWAN C.E. AND RESCH C.T., 1991, *Sorption of divalent metals on calcite*, Geochimica et Cosmochimica Acta, **55**, 1549 – 1562.

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Nowak P., Socha R.P., *Utlenianie minerałów siarczkowych w odpadach flotacyjnych – przemiany siarki siarczkowej*, Physicochemical Problems of Mineral Processing, 40, (2006) 134-148, (w jęz. ang.).

Badano rozpuszczalność jonów Zn i Pb oraz siarczanowych z odpadów flotacyjnych rud cynkowo-olowiowych przepuszczając wodę przez kolumny wypełnione odpadami. Odcieki z kolumn badano oznaczając ich pH, przewodnictwo oraz stężenia wybranych jonów jako funkcję krotności wymiany wody porowej (ER) w odpadach. Z odpadów po doświadczeniu pobrano próbki, które badano metodą spektroskopii fotoelektronów generowanych promieniowaniem X (spektroskopia XPS). Stwierdzono, że dzięki dużej zawartości minerałów węglanowych, które nasycają przepływającą wodę jonami wodorowęglanowymi stężenia jonów cynku i ołowiu, poza początkowym okresem, są znacznie poniżej normy dla ścieków przemysłowych. Równocześnie siarczkowa siarka w znacznej części utlenia się do siarki pierwiastkowej a nie do siarczanów, co powoduje, że emisja siarczanów z odpadów jest stosunkowo niewielka.