Physicochem. Probl. Miner. Process. 51(2), 2015, 731−743

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received January 16, 2015; reviewed; accepted March 24, 2015

SPECIES FORMED ON IRON SURFACE DURING REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS

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Abstract: The subject of the research covered in this paper is the removal of copper (Cu^{2+}) cations from water at low pH (initial values of pH 3 and 6) by means of zero-valent iron. The chemical states and atomic concentrations of solids formed on the surface of zero-valent iron, and the type of deposited polycrystalline substances have been analyzed with the use of XPS and XRD. The type of process causing the copper removal from water at low pH, corresponding to the effect of acid mine drainage, has been identified by analyzing the changes of physicochemical parameters and specified chemicals content in water.

Cu^{2+} was removed from water for the initial pH of 6 was much more effective than at lower pH. The formation of $Cu_xFe_{3-x}O_4$, where $x \le 1$, and to a lesser degree Cu_2O, Cu^0 and/or CuO and/or Cu_2S, were the basic processes of the removal of copper at almost neutral pH of water (pH about 6), while the formation of copper in metallic form and Cu_2O, as well as probably CuO, were the basic processes for lower pH (pH about 3). The adsorption of Cu^{2+} on the surface of shell covering square-shaped cold-rolled steel sheet cell was an additional process causing the removal of copper from water at almost neutral pH.

Keywords: *water, zero-valent iron, copper, x-ray photoelectron spectroscopy, diffraction*

Introduction

The waste material from mine waste disposal sites may contain large amounts of sulphide minerals. The leachate from these objects may be characterized by low concentration of dissolved oxygen (DO), low pH values (about 2 to 5), high total dissolved solids (TDS) and high concentration of metals in ionic form as well as sulphates. These leachates are called acid mine drainage (AMD). The leachate may contain different kinds of contaminants. Copper released from mine waste disposal sites as a result of AMD possesses a danger to ground and surface water. This element is an essential trace element for living organisms, but its intake at high levels can cause detrimental health effects (Rangsivek and Jekel, 2005). When addressing

http://dx.doi.org/10.5277/ppmp150230

groundwater contaminated by waste disposal sites the copper in cationic form should be ranked in priority based on their toxicity and persistent characteristics.

In order to protect groundwater in the vicinity of mine waste disposal sites, the permeable reactive barrier (PRB) technology may be applied. Zero-valent iron (ZVI, Fe^0) has been used as a reactive material in the presented tests.

The possibility of removing copper cations (Cu^{2+}) from water using ZVI has been considered for many years. Despite that, the type of products generated on the surface of this material in case of low pH values of water (and in specified chemical conditions) and the type of processes that cause the purification of the water may be interesting in the view of effective application of ZVI in PRBT. The main objectives of the paper, thus, are the identification of the products formed on the surface of ZVI as a result of the purification of water and the identification of the predominant processes which result in the removal of Cu^{2+}. The latter shall be performed by means of an analysis of the changes of physicochemical parameters and some chemicals in low pH water, and based on the products formed on the surface of ZVI and their properties.

Materials and method

Although the cells used in the batch tests were called ZVI, they were made of steel (in accordance with EN 10131:2006, this was "cold rolled uncoated and zinc or zinc-nickel electrolytically coated low carbon and high yield strength steel flat products for cold forming"). The cells were square-shaped, made of cold-rolled steel sheet (0.5 mm thickness), and their dimensions and masses amounted to 5x5 mm and 0.1 g, respectively. Just before their use, the cells were immersed in concentrated nitric acid for ca. 120 s and in demineralised water for about 120 s. Subsequently, they were immediately used in the batch tests. The tests were conducted in a programmable MULTI BIO RS-24 BIOSAN rotator equipped with plastic tubes filled with synthetic AMD solutions (to eliminate the headspace, a gaseous phase above the solutions, the volume of the solution was 58 cm^3) with the initial pH of 3.0 and 6.0 and with iron cells. Only one iron cell was applied in each plastic tube. The pH of the solutions was adjusted by a slow titration with a ultra-pure sulphuric acid solution (0.1 mol/dm^3) or with ultra-pure sodium hydroxide solution (0.1 mol/dm^3). Copper ion solutions were prepared by adding desired amounts of metal salt ($CuSO_4 \cdot 5H_2O$) into bottles and pouring distillated water. The concentration of copper in solutions at pH 3 and 6 amounted to 3.51 mg/dm^3 and 2.96 mg/dm^3, respectively. The intention of the authors was to exceed several times the allowable concentration of copper within the meaning of legal regulations available in the Journal of Laws (2014, item 1800).

The groundwater contaminated by mine waste disposal sites is characterized by high concentration of sulphates and low values of pH. These two parameters have a great impact on the concentration of oxygen in water. The concentration of dissolved oxygen in groundwater (in unconfined aquifer) located next to coal mine waste disposal sites in the south of Poland amounted, based on own research, to about 6 mg/dm^3. In order to reduce the concentration of oxygen in the samples of water and to adjust their condition to the that of a contaminated aquifer, the solutions were heated to 35 ^{o}C before using them in the batch tests. This way, the initial concentration of DO amounted to about 6 mg/dm^3. The ambient air temperature in the laboratory was about 22 ^{o}C.

After filling, the plastic tubes they were closed with corks. Each sample had to undergo five minutes of orbital rotation in a programmable rotator with a speed range of 20 rpm. After that, a 6 second reciprocal motion (with a turning angle of 90^o) with vibration motion followed. This sequence of shaking was repeatedly reiterated. The sequence continued for 24 hours and after this time a constant values were achieved. After shaking the samples, the solutions were passed through thick filters and subjected to chemical analysis. The quantitative analysis of chemicals in solutions was carried out for Cu_{tot}, Fe^{2+}, Fe_{total} with the use of UV-Vis Spectrophotometer DR5000 HachLange. The concentration of copper in the solutions was measured as a total value (Cu_{to}). Since, at the beginning there were no copper species in the solutions other than Cu^{2+}, the removal of the copper in the second oxidation state has been assessed in the article. The concentration of dissolved Fe^{3+} was calculated as a difference between Fe_{total} and Fe^{2+}. The pH, oxidation-reduction potential (ORP), dissolved oxygen and conductivity were measured with the Knick PORTAMESS meters.

The measurements were carried out twice. The results, shown in Table 1, were calculated using the arithmetic mean.

In order to verify the identity of products created on the surface of iron cells and to assess the mechanisms of the water purification using ZVI, the following tests were conducted on iron cells before and after the batch tests:

- identification of elements and determination of atomic concentrations of solids located on the surface of the iron cells before and formed after the batch tests. These measurements were carried out with the use of X-ray Photoelectron Spectroscopy (XPS). Measurements were performed using a PHI 5700/660 Multipurpose Electron Spectrometer based on two separate test chambers joined by an UHV transfer system by Physical Electronics using monochromatized $Al_{K\alpha}$ radiation (hν = 1486.6 eV). The energy resolution of the spectrometer equipped with a hemispherical energy analyzer was about 0.3 eV. The anode was operated at 15 kV and 225 W. Survey and multiplex high-resolution spectra (HRES) were measured in ultrahigh vacuum. HRES were fitted using mixed Gaussian and Lorentzian functions and Shirley background with the application of MultiPak program. The range in survey mode was from –2 to 1400 eV. The measurement parameters for survey mode and HRES were respectively: pass energy 187.85 and 23.50; step 0.800 eV and 0.100 eV; time per step 20 ms and 100 ms. The size of the analyzed area (in HRES) was 1.0–1.5 × 2.0–2.5 mm,

- determination of polycrystalline substances located on the surface of iron cells before and after the batch tests. These measurements were carried out with the use of x-ray diffraction (XRD). X-ray Multipurpose Diffractometer EMPYREAN by PANalytical was used for the analysis of solid objects. The diffractometer was equipped with PreFIX (pre-aligned, fast interchangeable X-ray) modules making a change in the optical path effortless for the user. The PDF4+ database was used for identification of chemical compounds. Crystal lattice parameters were measured.

Results

The applicability of ZVI in PRB in the treatment of AMD is well established. The research concerning the removal of metals using this material has been conducted for several years (Wilkin and McNeil, 2003; Rangsivek and Jekel, 2005; Li and Zhang, 2007; Fiore and Zanetti, 2009; Puls et al., 1998; Groudev et al., 2007, Klimkova et al., 2011). The literature, however, includes conflicting reports on the mechanism for individual metals. For instance according to Wilkin and McNeil (2003), when the value of pH is lower than 7, the process causing the removal of metals in the cationic form is adsorption onto either the iron surface or the iron corrosion products. In the research presented by Li and Zhang (2007), the predominant removal mechanism for metals with a much more positive and slightly more positive standard electrode potential than that of iron, is respectively the reductive precipitation and the sorption and/or reductive precipitation. The authors referred to above state that the sorption/surface complex formation is the removal mechanism for metal ions with a standard potential very close to or more negative than that of iron. At this point it should be made clear that the type of process obviously depends on the chemical and physicochemical composition of the solution. In general, sorption as a removal mechanism is not preferred because soluble copper (Cu^{2+}) remains in its more soluble oxidation state, and in the case of change in the physicochemical conditions it may be released back to the environment.

Karrabelli et al. (2008) claimed that up to the pH value of 6.5, copper exists in solution mainly in the form of Cu^{2+}. In the pH range between 7 and 9.5, cationic species like $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$, and $Cu_3(OH)_4^{2+}$ are dominant. Beyond these values, $Cu(OH)_2$ and the anionic species $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ become increasingly effective. In the presented study, due to their pH values, copper ions are expected to occur in a divalent form during the experiments.

In accordance with the results presented in Table 1, the iron cell had the ability to remove copper (Cu^{2+}) from synthetic water when the pH was low and almost neutral. The lower the pH values in copper solutions, the slower the observed decrease of Cu^{2+} concentrations. Moreover, more Fe^{2+} appeared in water with a lower initial pH value, than in high pH water. Thus, it has been concluded that the oxidation of ZVI proceeds faster at low pH, which has been confirmed by other researchers, e.g. Kowal and

Swiderska-Broz (1996). Similar variations and a faster decrease of ORP for lower values of pH in the tests have been observed in research presented by Suponik (2015).

Table 1. Physicochemical parameters and concentrations of chemicals in solution used in batch test for initial pH of 3 and 6

Stage of the batch test	pH	Cond., µS/cm	ORP mV	DO mg/dm^3	Cu^{2+} mg/dm^3	Fe^{2+} mg/dm^3	Fe^{3+} mg/dm^3
Parameters for initial pH = 3							
initial values	3.00	1068	441	5.9	3.51	BDL	0.08
values after 24 hrs of shaking	4.82	407	144	5.0	1.54	6.68	9.65
Parameters for initial pH = 6							
initial values	6.00	182	354	6.3	2.96	BDL	0.09
values after 24 hrs of shaking	6.39	228	148	5.5	0.67	0.22	4.26

BDL – below detection limit

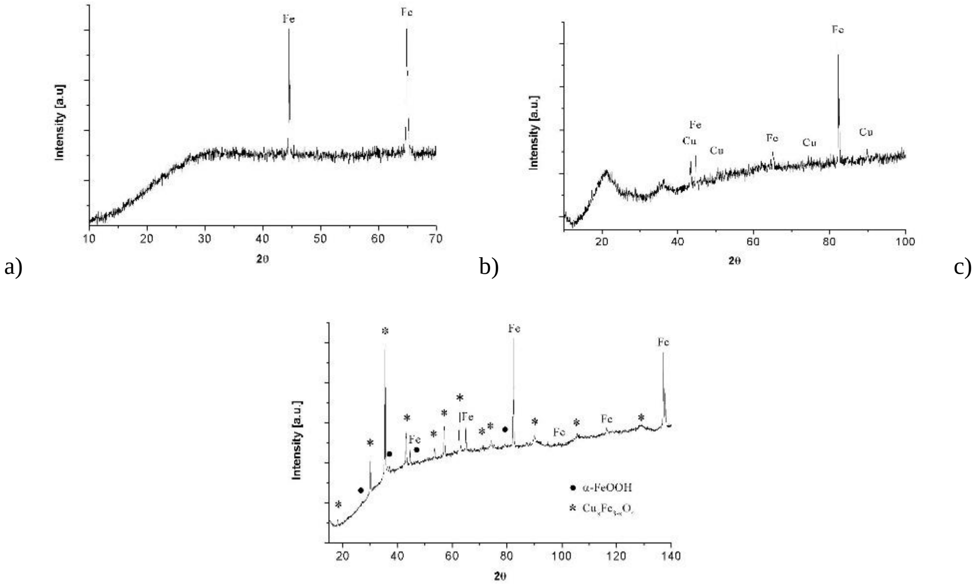

Fig. 1. XRD graph of iron cell: a) before the batch test; b) after the batch test for initial pH of the solution amounting to 3; c) after the batch test for initial pH of the solution amounting to 6. Fe – iron in metallic form; Cu – copper in metallic form

Figure 1 presents the diffraction patterns after X-rays interacted with crystalline substances on iron cells before and after the batch tests. Based on Fig. 1a it can be claimed that iron is found on the surface of iron cell assessed before the batch tests (as might be expected). The lattice parameters of pure iron are similar to the parameters of many alloys in which the main component is iron. According to the XRD graphs obtained after the batch tests (Fig. 1b and 1c) it can be concluded that copper and iron in metallic forms are present on the cell surfaces in case of the initial pH of the solution of 3 (Fig. 1b). In case of the initial pH of 6 (Fig. 1c) it can be concluded that α-FeOOH, magnetite in the form of $Cu_xFe_{3-x}O_4$ (where $x \leq 1$) and metallic iron are present. In both cases iron comes from the substrate (is located under the first atomic layers). The formation of magnetite was also investigated by Grosvenor et al. (2004) and Karrabelli et al. (2008). The latter noticed (on the basis of XRD analyses) a slow development of iron oxides, primarily in the forms of Fe_3O_4 and γ-Fe_2O_3.

A protective "passivating" magnetite layer on Fe^0 surface is formed due to low oxygen Fe^0 corrosion (Furukawa et al., 2002). It may mask the redox active sites and, as other corrosion products, reduce the barrier permeability by occupying available pore space. On the other hand, the formation of these products on large surfaces may be beneficial for the immobilization of metals in ionic forms by means of sorption (Rangsivek and Jekel, 2005).

Table 2. Atomic concentrations of elements (expressed as percentages) on the iron cells before and after the batch tests for initial pH of the solutions amounting to 3 and 6 – on the basis of XPS measurements

elements	Stage of the batch test				
	values before the batch tests, in atom %	values after 24 hrs of shaking for initial pH = 3, in atom %		values after 24 hrs of shaking for initial pH = 6, in atom %	
	XPS - survey mode	XPS - survey mode	XPS - HRES	XPS - survey mode	XPS - HRES
C	62.64	26.32	26.38	34.65	37.41
N	0.99			0.67	
O	29.30	55.71	52.55	46.54	43.54
Na	0.25				
P				2.61	3.47
S		1.12	0.97	0.79	0.96
Cl				0.22	
Ca				0.98	0.97
Fe	6.81	15.59	18.76	10.38	10.21
Cu		1.26	1.35	3.16	3.44

The atomic concentration of elements on the iron cells before and after the batch tests are presented in Table 2. Depending on the type of samples the measurements were performed several times. Since the results of the tests were similar the values for one chosen measurement were presented in Table 2. Each assessed sample contained carbon and oxygen. The presence of these elements and nitrogen has been explained by contamination of the samples (by atmospheric air and other factors) in their transport for the measurements. For that reason, these results have not been taken into consideration in further analysis (except for carbon and oxygen contained in carbonates and oxygen contained in metal oxides). Calcium (which the presence in the solution is explained by incorrect distillation) has probably formed (with sulphur and carbon) $CaSO_4$ and/or $CaCO_3$, where the calcium carbonate is more likely due to the fact that Ca was only present on the iron cell when the pH was higher (Table 2).

Due to the importance of the main problems raised in this article, the further part of the analysis in this paragraph takes into account only iron and copper. In this case, the atomic concentrations of iron and copper on iron cells for initial pH of solution equal to 3 and 6 amounted respectively to 93.69% and 74.83% for iron and 6.31% and 25.17% for copper. This means that copper was better removed from the solution at a higher initial value of pH, which was to be expected and was also presented in a paper by Suponik (2015).

The HRES spectrums for C1s, S2p, Ca2p, O1s, Fe2p and Cu2p are shown in Fig. 2. The binding energy of the XPS lines was normalized to the binding energy of C1s = 285eV. The lines were standardized to the same height.

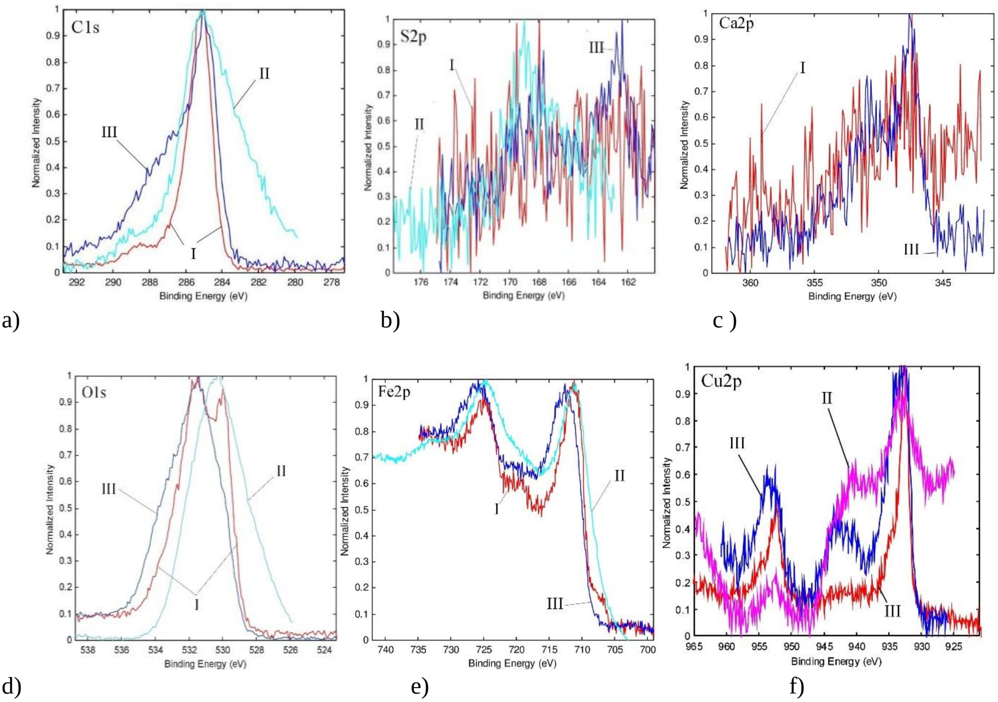

Fig. 2. High resolution a) C1s; b) S2p; c) Ca2p; d) Os1; e) Fe2p; f) Cu2p spectrum for iron cells before and after the batch test. Binding energy of the XPS lines normalized to the binding energy of C1s = 285 eV; lines standardized to the same height; I – cell before the test, II – cell after the test, initial pH = 3, III – cell after the test, initial pH = 6

Based on the C1s spectrum (Fig. 2a) obtained from the iron cell batch test with the initial pH of solution amounting to 6, it can be said that carbonate has probably formed on the surface of the cell (e.g. C1s 289.6 eV - $CaCO_3$). At the same time, the Ca2p spectrum shows that both $CaCO_3$ ($Ca2p_{3/2}$ 346.9 eV - $CaCO_3$) and $CaSO_4$ ($Ca2p_{3/2}$ 348.0 eV - $CaSO_4$) can be generated under these conditions (Fig. 2c). The S2p spectrum presented in Fig. 2b confirms the presence of sulphates on the cell but for the initial pH of the solution amounting to 3 it is $CaSO_4$ (S2p 169.0 eV and 169.3 eV), while for the initial pH of 6 it is rather $FeSO_4x7H_2O$ (S2p 168.0 eV). Furthermore, in case of the initial solution pH of 6, Cu_2S (S2p 162.4 eV - Cu_2S) and/or FeS_2 (S2p 162.9 eV - FeS_2) may also be formed but in very small quantities (Fig. 2b) because the photoelectric lines corresponded to the sulfides are very week. In addition, it is a lack of evidence for the presence of FeS_2 and Cu_2S in the crystalline form on X-ray diffractograms (Fig. 1). Main contribution to the C1s line comes from hydrocarbons deposited on the surface. It always happens when a sample is stored in air atmosphere. The binding energy of the C1s line coming from hydrocarbons is 285.0 eV. Deflection of the C1s spectrum to the right to the value about 283 eV for the initial pH = 3 is explained by the effect of loading. In the case of the iron cell immersed in a solution of pH = 3, the surface of the sample was heterogeneous. This caused various parts of the sample to be charged in various degrees. The correct neutralization of the entire surface was impossible, as evidenced by a shift towards lower binding energy of other lines (e.g. O1s, Fe2p in Fig.2), including the line C1s.

In the O1s spectrum for the cell before the batch test (Fig. 2d), two peaks are noticeable. The binding energy that corresponds to the peaks amounts to 530.4 eV and 531.4 eV, indicating that respectively iron oxides (e.g. Fe_2O_3 - O1s 529.9 eV) and hydroxides (O1s from min 530.9 to max 532.0 eV – hydroxides) – mainly iron hydroxides (because iron is the main element presented on the surface of cell, see Table 2), are probably generated on the surface of the iron cell. Although in case of the second peak (i.e. for 531.4 eV) carbonates (O1s from min 530.5 to max 531.5 eV – carbonates) and sulphates (O1s from min 531.5 to max 532.5 eV – sulphates) might also be formed, Figs. 2a and 2b do not indicate the presence of these compounds. These compounds, and also other than iron metal oxides (O1s from min 528.1 to max 531.1 eV – metal oxides), as well as hydroxides (O1s from min 530.9 to max 532.0 eV - hydroxides) may be formed on the iron cell in case of the initial pH amounting to 6, while for the initial pH = 3, less sulphates, carbonates and hydroxides are likely to form, in comparison with metal oxides causing a shift in the peak to the right.

The spectrums of Fe2p (Fig. 2e) obtained from cells before and after the test for initial pH of solution amounting to 3, indicate the presence of Fe_2O_3 (Fe2p 710.9 eV - Fe_2O_3) and/or Fe_3O_4 (Fe2p 710.8 eV – Fe_3O_4) and iron in the metallic form (Fe2p 707.0 eV). The spectrum for initial pH = 6, on the other hand, indicates the presence of $FeSO_4$ (Fe2p 712.1 eV – $FeSO_4$) and/or α-FeOOH (Fe2p 711.8 eV – α-FeOOH) as well as Fe_3O_4 and Fe_2O_3. Iron hydroxides can form a passivation layer of increasing thickness on the surface of ZVI, with the progress of corrosion. This reduces its reactivity.

The binding energy (Cu2p) that corresponds to the compounds formed on the surface of iron cells for both initial pHs are 932.5 eV and 934.0 eV, which means that the following copper compounds may be formed:

- for binding energy 932.5 eV: copper in metallic form (Cu2p 932.6 eV – Cu_{metal}), Cu_2S (Cu2p 932.5 eV), Cu_2O (Cu2p 932.5 eV – although this is unlikely because Cu_2O is formed in oxygen-containing environment), $CuFeO_2$ (Cu2p 932.6 eV) – generally Cu in metallic form and in first oxidation state,
- for binding energy 934.0 eV: $CuFe_2O_4$ (Cu2p 933.8 eV), CuO (Cu2p 933.7 eV – although this is unlikely because CuO is formed in an oxygen-containing environment) – generally Cu in second oxidation state.

The peaks, that correspond to the binding energy of 940.5 eV, result from the fact that the surface of the cells was heterogeneous.

Discussion

Based on the present research, it may be stated that iron oxides and iron in metallic form have been found on the surface of iron cell before the batch tests.

In the case of a cell applied in the solution, pH of which was 3, Cu^0 has formed, causing the removal of copper from the solution. Furthermore, Cu_2O, CuO and Fe_2O_3 were probably formed on the surface of the iron cell as well, but to a lesser degree, as these compounds are formed in an oxygen-containing environment. In the substrate of created layers, Fe^o has also been identified.

Pure magnetite and magnetite, in which copper replaces iron creating $Cu_xFe_{3-x}O_4$ that is mainly $CuFe_2O_4$ and $Cu_{0.5}Fe_{2.5}O_4$, have formed on the surface of the iron cell for initial pH of the solution amounting to 6. The lattice parameters of pure magnetite are similar to the parameters of this mineral, in which iron was substituted by copper. Copper can replace iron in every structure. The XRD diffraction pattern of Fe_3O_4 is very similar to the $CuFe_2O_4$ and $Cu_{0.5}Fe_{2.5}O_4$ ones. Magnetite is present in regular structures as well as in orthorhombic, tetragonal, rhombohedral and monoclinic structures and the XRD diffraction pattern for these are similar. Due to very similar ionic radii of copper and iron, the differences in the diffraction pattern can be only observed in the intensities.

Copper, in this case, could have also created other forms, mainly Cu^0, Cu_2S, Cu_2O and CuO, while (as for pH = 3) there is no clear evidence which one was the main compound and if they are formed they have non-crystalline forms. The iron compounds such as $FeSO_4$ and/or Fe_2O_3, but mainly α-FeOOH, were also generated in these conditions. Since the distilled water was probably prepared incorrectly, $CaCO_3$ has also been created on the surface of the cell.

Upon visual inspection, the surface of iron cells used in the tests was covered tightly with black film for initial pH of 6 and with black-brown film for pH 3.

Oxidation of copper usually takes place from Cu_2O to CuO, which is characterized by black color – just as magnetite, hematite (which is may also be deep red) and goethite (which may also be brown). Cu_2O is red in color. This fact indicates either a lack or a small amount of this compound on the surface of the iron cells used in the tests. Rangsivek and Jekel (2005) and Uzum et al. (2009) claim that in the case of deoxygenated acidic conditions in water and for nano-scale ZVI in the presence of kaolinite clay, Cu^0 and Cu_2O have been formed on the surface of iron. Karabelli et al. (2008) have confirmed these results for pure nano ZVI in their studies and claimed that Cu^{2+} ions were removed primarily via a redox mechanism that resulted in the formation of Cu_2O and Cu^0. Both of these compounds were also detected in the XPS presented in the article (for pH = 3 and 6; see Fig. 2f). Yet only Cu^0 was confirmed by the XRD, but only for pH = 3 (see Fig. 1b). In general, it can be concluded that small amount of Cu_2O (red) and Cu^0 (orange-red color) were dominated by the black compounds. However, larger amount of Cu_2O and Cu^0 was formed for the cell submerged in a solution of pH = 3 (cell was black-brown), and smaller for pH=6 (cell was black).

Li and Zhang (2007) report that ions with standard electrode potential larger than that of Fe^{2+} are bound to nano ZVI as a result of redox reaction. The value of standard electrode potential for Cu^{2+} is higher than that of Fe^{2+} and the following reaction proceeds:

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0. \quad (1)$$

Considering the conclusions presented by Karabelli et al. (2008), Rangsivek and Jekel (2005) and Uzum et al. (2009), and the fact that the binding energy (in XPS) reported for metallic copper is very similar to Cu^+ in Cu_2O (Fig. 2f), it can be claimed that this compound appears also as a result of purification of water contaminated by copper ions, but more for initial pH of solutions 3 rather than 6. According to Karabelli et al. (2008), the redox reaction then might be written as follows:

$$Fe^0 + 2Cu^{2+} + H_2O \rightarrow Fe^{2+} + Cu_2O + 2H^+. \quad (2)$$

As provided by Furukawa et al. (2002), Roh et al. (2000), Rangsivek and Jekel (2005) and Uzum et al. (2009), the secondary minerals typically formed on the surface of ZVI as a result of purification of groundwater contaminated by metals in ionic forms are Fe_3O_4, $CaCO_3$, α-Fe_2O_3, α-FeOOH. These compounds were confirmed in the research presented in the article. Other compounds, not identified in the research, are: γ-FeOOH, $Fe(OH)_2$, $Fe_2O_3 \cdot 0.5H_2O$, $FeCO_3$, FeS_2, Fe_3S_4, mackinawite ($(FeNi)_{1+x}S$, where x is from 0 to 0.11), and green rust ($[Fe_{1-x}^{2+}\ Fe_x^{3+}(OH)_2]^{x+}\ [x/n\ A^{n-} \cdot mH_2O]^{x-}$, where x is the Fe^{3+}/Fe_{tot} ratio), which is usually created under neutral pH conditions. Although, according to Wilkin and McNeil (2003), green rust is a primary corrosion product formed on ZVI in sulphate rich solutions, it has not been observed by visual inspection on the surface of the iron cell and there has been no evidence of it in the presented results. This is probably due to the "pure" conditions of purification. As provided by Cornell and Schwertmann (1996), green rust is stable only at low grades of oxide reduction and its oxidation usually leads to the formation of Fe_2O_3 or γ-FeOOH. Roh et al. (2000) also reported that green rust is an intermediate stage and is finally transformed into α-FeOOH, γ-FeOOH, Fe_3O_4, and Fe_2O_3.

In general, more chemical compounds were formed on the surface of the iron cell for higher initial pH of the solution. These conditions result in a much larger specific surface area. According to the research of Suponik (2015b) which was conducted using the same shaking methodology as shown in the presented article, the specific surface (obtained by Multi-point BET method) of cells increased from the value of 0.0312 m^2/g (for a cell which has not been used in the batch test) to 0.1206 m^2/g for initial pH of solution amounting to 3 and to 0.3354 m^2/g for initial pH = 6.

The affinity of Cu^{2+} sorption is generally determined by pH at the point of zero charge (pH_{PZC}). This parameter describes the condition (pH value) in which the electrical charge on the surface of ZVI is zero. If the ZVI surface is positively charged with respect to the PZC (under an acidic condition or pH below pH_{PZC} protons are sorbed on the functional group which results in the surface of cell having a net positive charge), the Cu^{2+} is not adsorbed on the ZVI surface. If the ZVI surface would be negatively charged with respect to the PZC (at above pH_{PZC} the oxygen atom stays deprotonized and the surface tends to have a net negative charge), the Cu^{2+} sorption would be directly adsorbed on the ZVI surface. The point of zero charge for most iron oxides is typically in the range of pH about 6 to 8 (for instance for Fe_3O_4 from 3.8 to 8.2; for α-FeOOH from 6.7 to 9.2) (Kosmulski, 2011), while for CuO and Cu_2S it is 6.9, 7.6 (Gonzalez and Laskowski, 1974) and <2 (He at al. 2009), respectively. In accordance with the research presented by Suponik (2015b), the pH_{PZC} of iron cells submerged in solutions, for the initial pH of 3 and 6 with the same shaking method used as in the present article, was about 6.2 in both cases. Thus, in the first case (initial pH = 3), the sorption of Cu^{2+} on the surface of cells is not possible, while it may occur in the second case – in the experiment in which the initial pH of the solution was 6 and the final pH was 6.39. The shell coating the cell following the test is characterized by roughly equal amounts of negative and positive charges, as the pH of the solution (6.39) is close to the pzc of the compounds formed on the surface of ZVI. Since both charges exist on the shell coating cell at this pH, the sorption of Cu^{2+}, as well as the negatively charged ions which are present in the solution, can occur at the cell surface.

As it has been said, except for the formation of Cu^0 and Cu_2O (emerging mainly for initial pH of the solution amounting to 3), the $Cu_xFe_{3-x}O_4$ is the main compound generated as a result of water purification from copper in ionic form, for initial pH of the solution amounting to 6. Ferrous and ferric ions created as a result of reactions 3, 4, 5, 6 (based on Puls et al., 1998) form $Cu^{2+}_{(x)}Fe^{2+}_{(1-x)}Fe^{3+}_2O_4$ in accordance with equation 7:

$$2Fe^0_{(s)} + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (3)$$

$$Fe^{0}_{(s)} + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^{-} \tag{4}$$

$$2Fe^{+2} + ½\,O_2 + 2H^{+} \rightarrow 2Fe^{+3} + H_2O \tag{5}$$

$$2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^{-} \tag{6}$$

$$(1 - x)Fe^{2+} + 2Fe^{3+} + xCu^{2+} + 2H_2O \rightarrow Cu^{2+}{}_{(x)}Fe^{2+}{}_{(1\text{-}x)}Fe^{3+}{}_{2}O_4 + 4H^{+} \tag{7}$$

where $x \leq 1$.

Conclusions

Copper released from mine waste disposal sites as a result of acid mine drainage poses a danger to ground and surface water. To protect the water, ZVI might be used. Under these conditions and at reduced oxygen content in water, copper in the second oxidation step was removed at the initial pH of 6 much more effectively than at lower pHs. The formation of magnetite (in which copper replaces iron), and to a lesser degree Cu_2O, Cu^0 and/or CuO and/or Cu_2S, were the basic processes in the removal of copper for almost neutral pH of the aqueous solution (pH about 6), while the formation of copper in metallic form and Cu_2O, as well as probably CuO, were the basic processes for lower pHs (pH about 3).

Since more chemical compounds, that is α-FeOOH, $CaCO_3$, Fe_2O_3 and $FeSO_4$ were formed on the surface of ZVI for almost neutral pH of aqueous solution (larger specific surface than for lower initial pH of solution was created) and the pH at the point of zero charge for shells coating ZVI was about 6.2 (the final pH for almost neutral pH of solution amounted to 6.39) the adsorption of Cu^{2+} on the surface of shells were additional process causing copper removal from water in these conditions.

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