REMOVAL OF HEAVY METALS FROM GROUNDWATER AFFECTED BY ACID MINE DRAINAGE

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Abstract: Batch tests have been used to assess the level of the removal of metals (copper, nickel, cobalt, zinc, and chromium, in cationic and in anionic forms) from water at low pH values affected by acid mine drainage. The predominant processes which result in the removal with the use of zero-valent iron (Fe0) in Permeable Reactive Barrier Technology were evaluated. The most probable processes for each metal have been presented in drawings. There are: reductive precipitation leading to the metallic form, co-precipitation mainly with iron in the form of oxides and/or hydroxides and adsorption on the surface of iron corrosion products or on the surface of zero-valent iron.

Introduction

A large number of coal mines are located in the southern Poland and in the North-East and West of Spain. The dumping sites established there have a significant impact on the quality of ground and surface water. The leachates from these waste dumps may contain barium, boron, copper, cadmium, chromium, cobalt, lead, lithium, arsenic, zinc, nickel, molybdenum, manganese, selenium, and thallium. To protect ground and surface water from these contaminants the permeable reactive barrier (PRB) technology may be applied.

The coal mine waste material contains large amount of sulphide minerals. The predominant sulphides in coal mines are pyrite and marcasite (FeS_2), but other minerals may also be found, e.g. covellite (CuS), chalcopyrite ($CuFeS_2$), sphalerite ((Zn,Fe)S) and galena (PbS). When sulphide minerals are exposed to water and air, minerals are oxidized and create acidic, sulphate-rich drainage which is called the acid
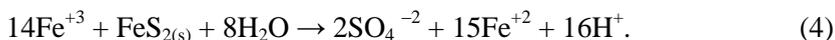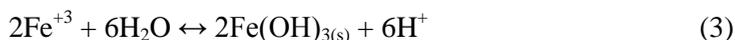
mine drainage (AMD) (Groudev et al., 2007). The reaction of pyrite with water and oxygen produces a solution of sulphuric acid and ferrous sulphate:

$$2FeS_{2\,(s)} + 7O_2 + 2H_2O \rightarrow 2Fe^{+2} + 4SO_4^{-2} + 4H^+. \tag{1}$$
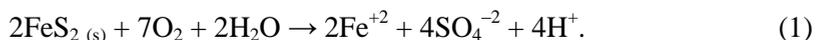
In non-altered natural systems, this reaction proceeds slowly in geologic time periods. When environment of this new solution is rich in O_2, Fe^{2+} is oxidized to Fe^{+3}:
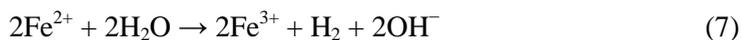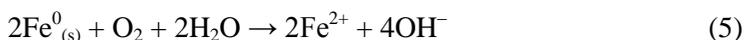
$$2Fe^{+2} + \tfrac{1}{2}\,O_2 + 2H^+ \rightarrow 2Fe^{+3} + H_2O. \tag{2}$$
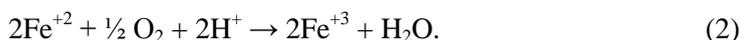
Fe^{+3} can react either with water (reaction 3) creating $Fe(OH)_3$ or with water and pyrite (reaction 4), thereby decreasing the pH in both equations and increasing ferrous iron in Eq. 4 (Jennings et al., 2008). These processes cause water to gain characteristic orange colour.

$$2Fe^{+3} + 6H_2O \leftrightarrow 2Fe(OH)_{3(s)} + 6H^+ \tag{3}$$

$$14Fe^{+3} + FeS_{2(s)} + 8H_2O \rightarrow 2SO_4^{-2} + 15Fe^{+2} + 16H^+. \tag{4}$$

Mobility of metals is increased at acidic pH created this way.

The paper aims to evaluate the level of copper, nickel, cobalt, zinc and chromium removal from solution (simulated groundwater affected by coal mine dumping sites) at neutral and low pH values. In order to achieve this objective zero-valent iron (Fe(0)) (ZVI) was employed as a reactive material in the PRB technology (Suponik, 2012). In this technology, the contaminants dissolved in groundwater are removed directly from aquifer by flowing through a permeable barrier filled with a reactive material. The application of zero-valent Iron to remove metals in cationic and anionic forms has been investigated (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). In the paper by Suponik (2013), it was concluded that rapid removal of metals in the ZVI occurs likely due to the reductive precipitation/coprecipitation and/or due to the adsorption onto the iron metal surface or/and onto the iron corrosion products. The type of mechanism depends on the type of metal removed, the other accompanying substances and physicochemical conditions in the ZVI bed.

The oxidation of zero valent iron to ferrous and ferric iron causes the increase in pH, the decrease in ORP, the consumption of dissolved oxygen and the generation of hydrogen (Puls et al., 1999). The chemical reactions proceeding in this material are the reactions of iron corrosion:

$$2Fe^0_{(s)} + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{5}$$

$$Fe^0_{(s)} + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{6}$$

$$2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^-. \tag{7}$$

(see also: reaction 2 and 3).

The paper shows a decrease in the concentration of metals in the aqueous solution for pH 3, 5 and 7. The matter in question is the type of predominant processes which cause the removal of these metals. The answer can be obtained by using advanced techniques such as X-Ray Photoelectron Spectroscopy, Energy-dispersive X-ray spectroscopy and X-ray diffraction. The authors of the paper, however, attempted to answer this question by analyzing the changes of physicochemical parameters and some chemicals in low and neutral pH.

Materials and method

The evaluation of the possibility of the removal of heavy metals from solution was performed in the form of batch tests in a MULTI BIO RS-24 BIOSAN programmable rotator equipped with 50 ml plastic tubes. For these tests the synthetic solutions with the initial pHs of ca. 3.0, 5.0, 7.0 were prepared – pHs of the solutions were adjusted by slow titration with ultra-pure sulphuric acid or with ultra-pure sodium hydroxide. The batch tests were carried out in five separate solutions: chromium, zinc, copper, nickel and cobalt. The synthetic solutions have simulated groundwater contaminated by coal mine waste dumps located in the Upper Silesia, Poland and in the North-East and West of Spain. Solutions containing metal (copper, chromium, zinc, nickel and cobalt) ions were prepared by adding the desired amounts of metal salts ($CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, $ZnSO_4 \cdot 7H_2O$, $CoCl_2$, $NiSO_4 \cdot 7H_2O$) into bottles and pouring distillated water; only one metal was dissolved in each sample.

In the batch tests, the solutions (copper, chromium, zinc, nickel and cobalt solution for every value of pH) were poured into five plastic tubes (50ml per each sample) and then 20, 30, 50, 75, 100 mg of ZVI was added to each sample. The tubes were then closed with corks. Each sample had to undergo two minutes of orbital rotation in a programmable rotator (with a speed range = 40 rpm) after which a 6 second reciprocal motion (with turning angle = 90°) with vibration motion followed. This sequence of shaking was repeatedly reiterated. The sequence continued for 1 hour (after this time constant value was achieved). After shaking the samples the solutions were passed through thick filters and assessed. The quantitative analysis of heavy metals (Cr^{6+}, Cu_{total}, Co_{total}, Ni_{total}, Zn_{total}) in solutions was carried out in the UV-Vis Spectrophotometer DR5000 HachLange. The concentrations of Ni, Co, Cu or Zn in the solutions were measured in a Spectrophotometer as a total value. Since there were no metals speciation (at the beginning) other than Ni^{2+}, Co^{2+}, Cu^{2+} or Zn^{2+} cations in the solutions the removal of the metals in the second oxidation state has been assessed in the paper.

Scrap iron (in the form of chips and swarfs (Fig. 1)) used in the batch tests was obtained from a machining plant. Table 1 presents grain-size distribution of scrap iron (Suponik, 2013). The material used in the batch tests has been cleaned before using – first with a thinner (painter's naphtha), dried in the moisture teller, and then, just

before the application, cleaned with distilled water. The density of this material amounted to 7.85 g/cm^3 (Suponik, 2013).

Table 1. Particle size distribution of zero-valent iron used in batch test (Suponik, 2013)

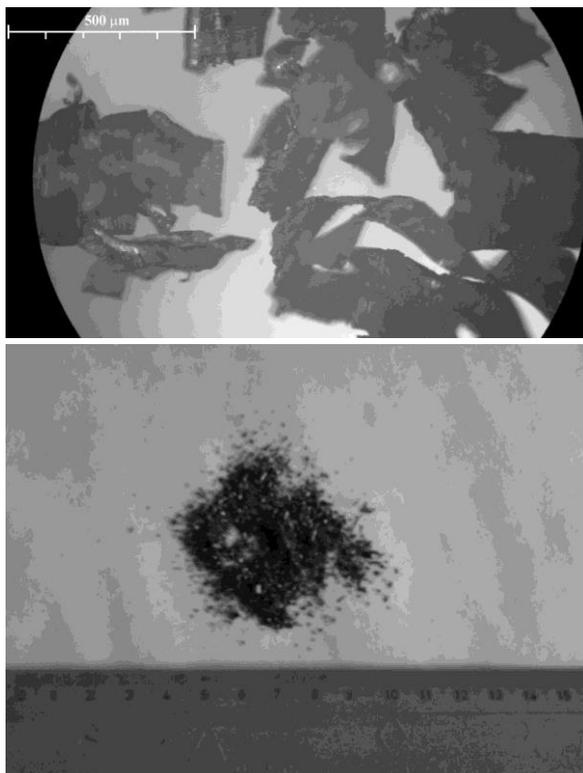| Particle size, mm	4.0–2.0	2.0–1.6	1.6–1.0	1.0–0.71	0.71–0.5	<0.5
Mass fraction, %	1.77	1.28	7.26	38.79	36.57	14.33

Fig.1. Zero-valent iron (Fe(0)) used in batch test

Results and discussion

The concentration of metals measured in the tests decreased with the increase of the mass of ZVI applied in the tubes (Fig. 2). This phenomenon was observed for all assessed values of pH, however the lower was the value of pH in the metal ion solution the slower was the observed decrease of Ni(II), Co(II), Zn(II), Cr(VI) or Cu(II) concentration. In the case of Chromium and Copper that partially occurred due to the easy precipitation of copper and chromium(III) hydroxides at higher values of pH (i.e. for pH = 7). Moreover, in every test, at higher value of pH (i.e. for pH amounting to 5 and 7) the ferric hydroxides (e.g. FeOOH, Fe(OH)$_3$) may be created on

the surface of zero-valent iron, on which metals in cationic forms may be sorbed. These compounds (iron corrosion products) appear as a result of Fe^0 oxidation to Fe^{2+} and then to Fe^{3+}, mainly in the presence of dissolved oxygen in aqueous solutions.
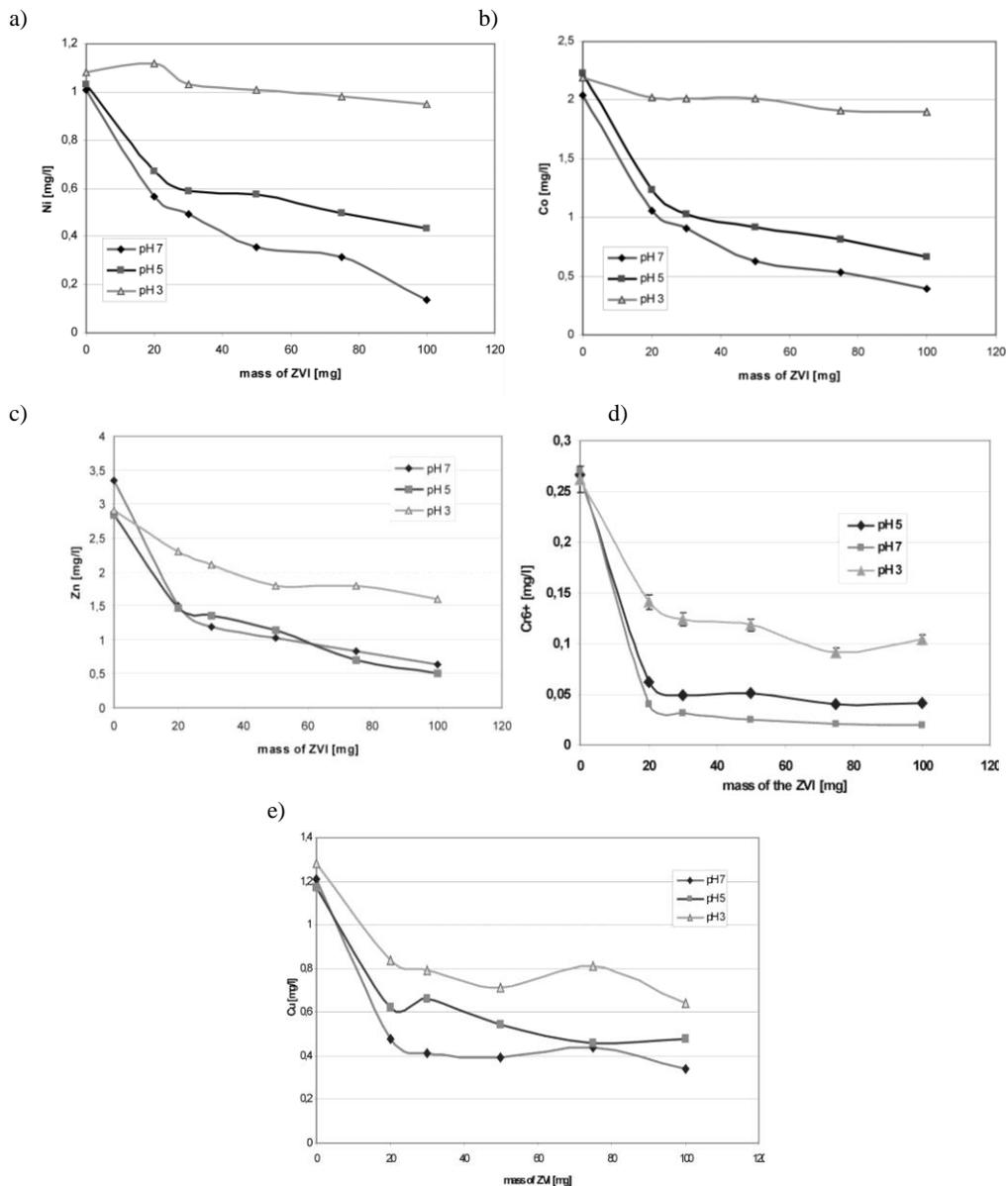
a)

b)

c)

d)

e)

Fig 2. The concentration of: a) Ni(II); b) Co(II); c) Zn(II); d) Cr(VI); e) Cu(II); in three solutions (the initial pH = 3; 5; 7) for various masses of ZVI

In accordance with one of the author's previous work (Suponik, in press) the oxidation of Fe^0 to Fe^{2+} was evidenced by creation of reduction conditions in the water which was in contact with the reactive material as well as by the formation of ferrous iron in it. In this work, it has been presented that more ions of divalent iron appeared in water with lower initial pH value than in water which was characterized by higher value of pH. Thus, it was concluded that the oxidation of ZVI proceeds faster in low pH, which has also been found by other researchers, e.g. Kowal and Swiderska-Broz (1996). This occurs mostly due to the processes described by reactions 5 and 6. With high probability, as a result of reactions 2, 7 and others Fe(II) may be oxidized to Fe(III), which is then (under suitable conditions) precipitated in various forms. These precipitates cover ZVI with thin shell. In the said article (Suponik, in press) it has also been confirmed that more ferric iron is formed in solution with high pH values than in solutions with lower values of pH.

Iron oxides and oxyhydroxides are widespread in the nature and play an important role in many geological and biological processes. All together, there are many iron oxides and oxyhydroxides. They may be divided into (Cornell and Schwertmann, 2003):

- oxides: iron(II) oxide – FeO; iron(II,III) oxide – Fe_3O_4; iron(III) oxide – Fe_2O_3 among which are alpha phase (α-Fe_2O_3), beta phase (β-Fe_2O_3), gamma phase (γ-Fe_2O_3), epsilon phase (ε-Fe_2O_3),
- hydroxides: iron(II) hydroxide ($Fe(OH)_2$) and iron(III) hydroxide ($Fe(OH)_3$),
- oxide/hydroxides: goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), feroxyhyte (δ-FeOOH), ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$ approx.), high-pressure FeOOH and green rust ($Fe^{III}_x Fe^{II}_y (OH)_{3x+2y-z} (A^-)_z$; where A^- is Cl^- or $0.5SO_4^{2-}$).

In accordance with James Newton Butler (1998) the form of the precipitated phase for ferric oxyhydroxides depends strongly on the composition of the precipitating solution and the age of the precipitate. It also depends on the redox potential and the value of pH. Thus, it is difficult to foresee the type of iron compound formed on the surface of scrap iron used in the tests.

In the research presented in paper by Suponik (in press) it has also been shown that during the metals removal pH increased. Higher increases of pH were observed for its low initial value (i.e. pH = 3), as the oxidation of Fe(0) proceeded more rapidly in low pH. Similar results were obtained in the experiments presented in this paper. Figure 3 shows changes of pH (mean values of all tests) during application of different ZVI masses used in plastic tubes.

Most of heavy metals precipitated at basic conditions, but the optimum pH for precipitation of various heavy metals varies significantly. Table 2 presents the theoretical equilibrium concentrations of different metals hydroxides at pH 4.11, 5.81, 7.21 (the pH values correspond to 100 mg of ZVI used in the tests). They were calculated according to solubility product (K_{sp}) of metals hydroxides.

Although the redox potential is a very important parameter in regard to precipitation of metals hydroxides (that can not be neglected), the values presented in Table 2 show the compounds which are readily precipitated. $Fe(OH)_3$ and especially $FeOOH$ and Fe_3O_4 (not included in the Table 2) are sparingly soluble compounds, so in the presence of Fe^{3+} in water (under appropriate conditions) these compounds are easily precipitated.

Xu et al. (2010), Huang et al. (2005), Music and Ristic (1988), Lagashetty et al. (2010) and Djafer et al. (1989) studied the adsorption of heavy metals (Cr(VI), Cu(II), Zn(II), Pb(II) and others) on iron oxides and hydroxides (e.g. $FeOOH$, $Fe(OH)_3$, Fe_2O_3). They have shown that these metals are easily removed from water, hence it can be claimed that these compounds are a good medium for the removal of metal ions from groundwater. Djafer et al. (1989) also claimed that the adsorption of metallic cations increased with the increase in pH of water.

It can be hypothetically said that the co-precipitation of metals analyzed in this work with ferric ions (crating metal-iron hydroxides or oxides, e.g. $Fe_2Me_1O_4$ – where Me means metal ions) may also be one of the processes of metal removal from water in reactive barrier. The same applies to the adsorption of heavy metals directly on the surface of zero-valent iron (although this is less likely).
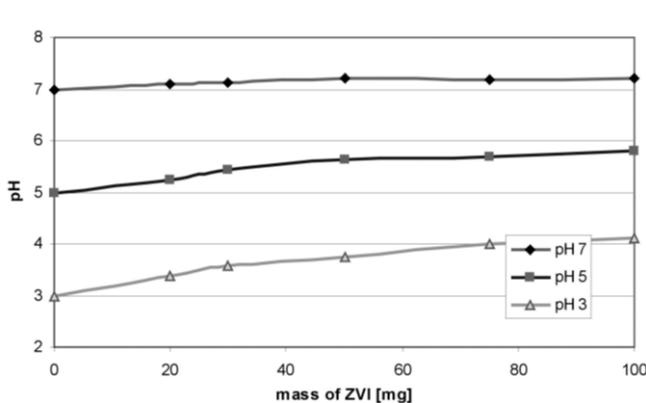

Fig. 3. The mean value of pH for solutions (copper, chromium, zinc, nickel and cobalt)
tested for various masses of ZVI and for various initial values of pH (pH = 3; 5; 7)

As the pH of the water passing through zero-valent iron substantially increases, the precipitation of metal hydroxides may play an important role in the immobilization of metals. This fact has also been noticed by Li and Zhang (2007). In accordance with Table 2 the following hydroxides are characterized by a low solubility at pH >7.21: $Cu(OH)_2$, $Cr(OH)_3$ – while in lower pH values, copper hydroxide readily dissolves in water.

Table 2. Theoretical equilibrium concentrations of different metals hydroxides and oxides
at 4.11, 5.81, 7.21 pH (these values correspond to 100 mg of ZVI used in the tests)
which were calculated based on the solubility product constant K_{sp}

Metal hydroxide	K_{sp}	pH	$[Me^{n+}]$, mol/dm^3	$C[Me^{n+}]$, mg/dm^3
Fe(OH)$_2$	$4.8 \cdot 10^{-16}$	pH = 4.11	28922.86	$2.60 \cdot 10^9$
		pH = 5.81	11.5144	1034798.949
		pH = 7.21	0,0182	1640.05
Fe(OH)$_3$	$3.8 \cdot 10^{-38}$	pH = 4.11	$1.78 \cdot 10^{-08}$	$1.90 \cdot 10^{-03}$
		pH = 5.81	$1.41 \cdot 10^{-13}$	$1.51 \cdot 10^{-08}$
		pH = 7.21	$8.90 \cdot 10^{-18}$	$9.51 \cdot 10^{-13}$
Cu(OH)$_2$	$5.6 \cdot 10^{-20}$	pH = 4.11	3.373	329151.8072
		pH = 5.81	0.00134	130.7438
		pH = 7.21	$2.13 \cdot 10^{-6}$	0.2078241
Ni(OH)$_2$	$1.6 \cdot 10^{-14}$	pH = 4.11	963855.422	$8.94 \cdot 10^{10}$
		pH = 5.81	383.69	35572182.25
		pH = 7.21	0.6084	56401.52091
Co(OH)$_3$	$2.5 \cdot 10^{-43}$	pH = 4.11	$1.17 \cdot 10^{-13}$	$1.72 \cdot 10^{-08}$
		pH = 5.81	$9.29 \cdot 10^{-19}$	$1.37 \cdot 10^{-13}$
		pH = 7.21	$5.84 \cdot 10^{-23}$	$8.60 \cdot 10^{-18}$
Co(OH)$_2$	$1.6 \cdot 10^{-18}$	pH = 4.11	96.3855	8959036.145
		pH = 5.81	0.0383693	3566.427
		pH = 7.21	$6.08 \cdot 10^{-5}$	5.65136
Zn(OH)$_2$	$1.3 \cdot 10^{-17}$	pH = 4.11	783.133	77851204.82
		pH = 5.81	0.31175	30991.1271
		pH = 7.21	$4.90 \cdot 10^{-4}$	49.138
Cr(OH)$_3$	$5.4 \cdot 10^{-31}$	pH = 4.11	0.253	26022.54
		pH = 5.81	$2.01 \cdot 10^{-06}$	$206.83 \cdot 10^{-3}$
		pH = 7.21	$1.27 \cdot 10^{-10}$	$1.30 \cdot 10^{-05}$

In accordance with standard electrode potential, the metals in cationic and anionic forms, such as Ni^{2+}, Cu^{2+}, Co^{2+} and $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, may also be removed from groundwater as a result of reductive precipitation/coprecipitation, as all these ions are characterized by a higher standard electrode potential than iron (Fe^0). Finally, these metals may be precipitated out in a reactive material as Ni^0, Cu^0, Co^0 and $Cr_xFe_{(1-x)}OOH$ (see reaction 11) (Puls et al., 1998), $Cr(OH)_3$ and Cr_2O_3 (ITRC, 2011).

Figures 4–8 show the conceptual models for Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} and Cr^{6+} removal from water with the use of ZVI.

The overall reaction for the hexavalent chromium, which occurs in water as an oxyanion in the form of CrO_4^{2-} or as $Cr_2O_7^{2-}$ can be presented as (Suponik, in press, Suponik, 2013):

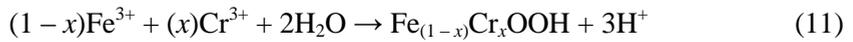$$Cr_2O_7^{2-} + 2Fe^0 + 14H^+ \rightarrow 2Fe^{3+} + 2Cr^{3+} + 7H_2O. \tag{8}$$
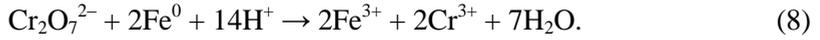
In further steps, chromium Cr(III) may be removed from solution by (Fig. 4):
- precipitation as chromium hydroxides and oxides, such as $Cr(OH)_3$ (reaction 9) and Cr_2O_3 (reaction 10),

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \tag{9}$$

$$2Cr^{3+} + 3H_2O \rightarrow Cr_2O_3 + 6H^+ \tag{10}$$

- co-precipitation with iron as mixed chromium-iron oxyhydroxide (Puls et al., 1998),

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH + 3H^+ \tag{11}$$

- adsorption on the surface of iron corrosion products e.g. FeOOH,

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \tag{12}$$

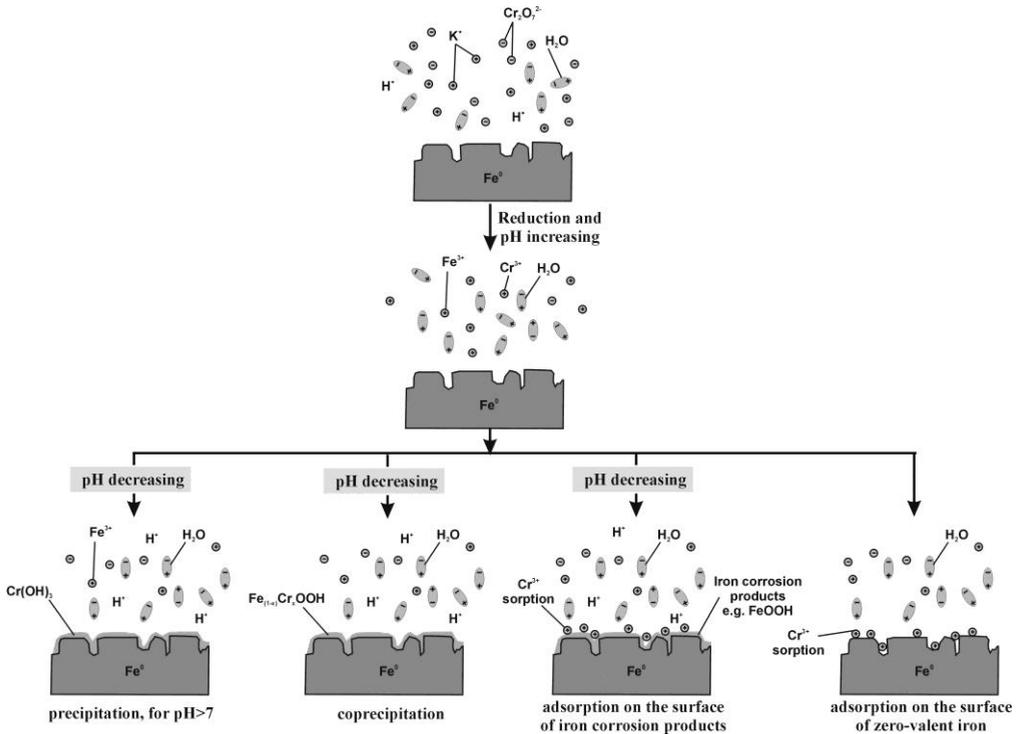- adsorption on the surface of zero-valent iron.

Fig. 4. Conceptual model for chromium(VI) removal from water with the use of ZVI

Cu(II), Ni(II), Co(II) also have a higher standard electrode potential than Fe(0), thus, iron may displace these hazardous cations from groundwater. Although the reduction and precipitation of Cu (to metallic form) is more probable, some Cu(II) may be adsorbed on the surface of iron corrosion products (see reaction 12) or on the surface of zero-valent iron (less likely). Moreover, low solubility of copper hydroxide at pH>7 indicates that this compound may also precipitate in this condition. In the case of metals analyzed, it should be also noted that co-precipitation in the form of metal-iron hydroxides or oxides (e.g. Fe_2CuO_4) may result in the removal of metal ions:
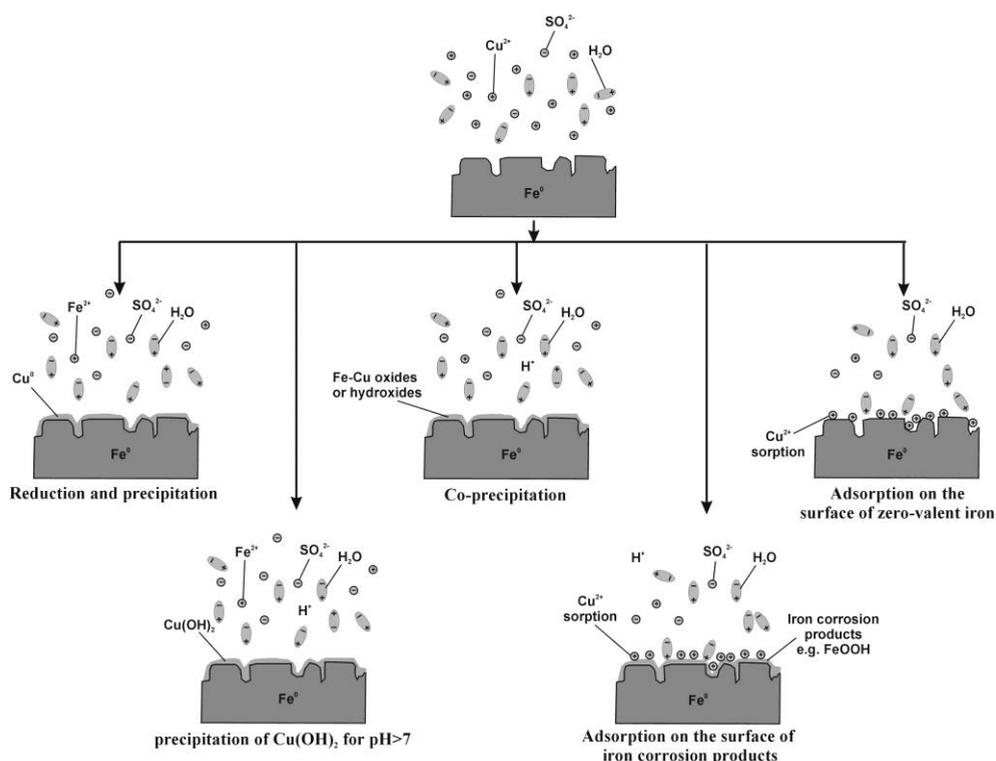
$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2. \tag{13}$$

Fig. 5. Conceptual model for copper(II) removal from water with the use of ZVI

According to the study by Li and Zhang (2007), 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. The predominant removal mechanism, for metals with a considerably 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. Thus it can be said with a high probability that the main processes for nickel(II), cobalt(II) and zinc(II) removal are the adsorption on the

surface of iron corrosion products and the adsorption directly on the surface of zero-valent iron (less likely). It should not be forgotten in this place about the possibility of co-precipitation with iron, forming oxides and/or hydroxides (e.g. $Fe_{(1-x)}Ni_x(OH)_2$, $Fe_{(1-x)}Co_x(OH)_2$, $Fe_{2.5}Zn_{0.5}O_4$). In the case of cobalt and zinc, the process of reductive precipitation into metallic form is also possible, but a small difference between the standard electrode potential of Fe^0 and Co^0 and Ni^0 reduces this probability (Figs 6, 7).
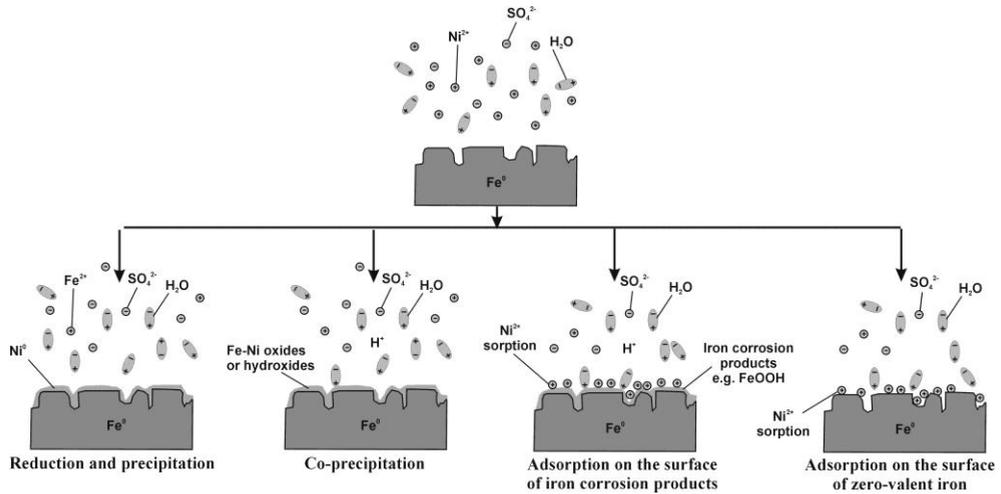
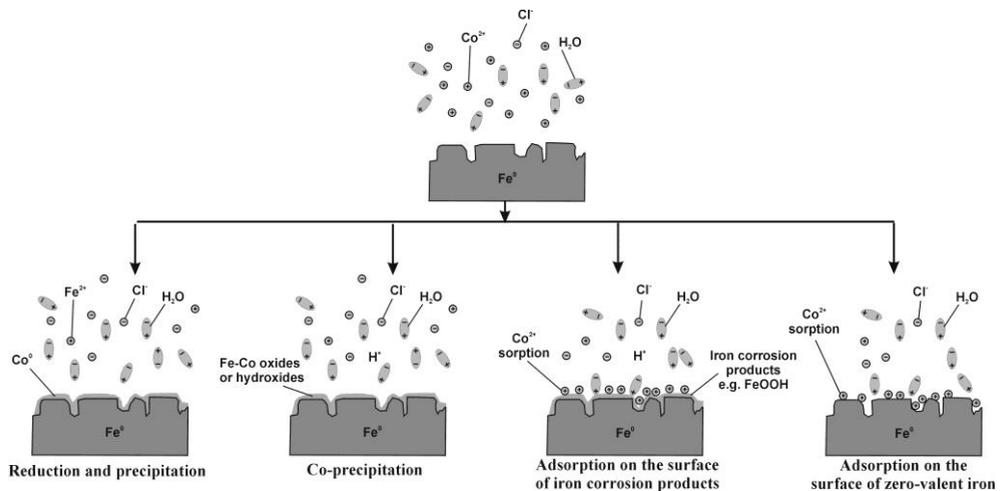Fig. 6. Conceptual model for nickel (II) removal from water with the use of ZVI

Fig. 7. Conceptual model for cobalt(II) removal from water with the use of ZVI
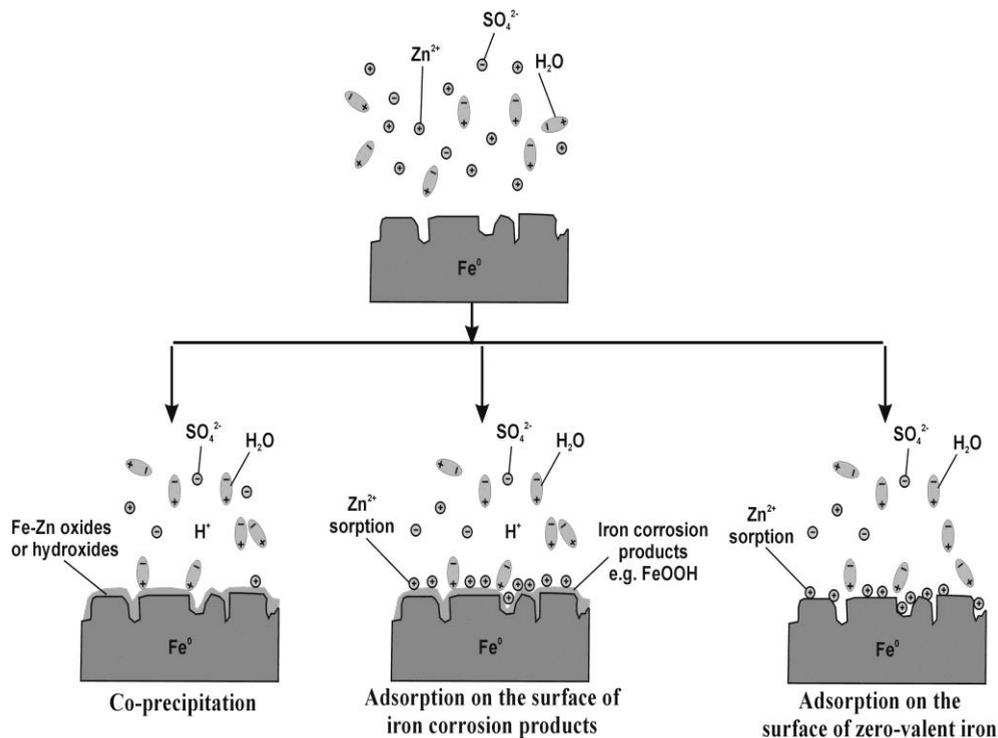
Fig. 8. Conceptual model for zinc(II) removal from water with the use of ZVI

Conclusions

All metals analyzed in the article have been removed from water when ZVI was used as a reactive material of PRB. pH had a large impact on the degree of removal, and on the processes which influence the removal of the individual metals. In general, the lower the pH, the slower is the removal of metals.

The processes that can result in the removal of copper, nickel, cobalt, zinc and chromium from water with the use of zero-valent iron are:

- reductive precipitation leading to the metallic form – relates mainly to copper, but also to a lesser extent nickel and cobalt;
- co-precipitation with iron in the form of oxides and/or hydroxides, e.g. for successive metal: $Fe_{(1-x)}Cr_xOOH$, $Fe_2Cu_1O_4$, $Fe_{(1-x)}Ni_x(OH)_2$, $Fe_{(1-x)}Co_x(OH)_2$, $Fe_{2.5}Zn_{0.5}O_4$;
- precipitation as a result of increase in pH – relates mainly to copper $Cu(OH)_2$ and chromium $Cr(OH)_3$, only for pH higher than 7;
- adsorption on the surface of iron corrosion products or on the surface of zero-valent iron – for all of the analyzed metals, although sorption directly on the surface of zero-valent iron is highly unlikely.

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