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ZERO-VALENT IRON FOR REMOVAL OF INORGANIC CONTAMINANTS FROM LOW pH WATER

The coal mine waste dumps located in the southern provinces of Poland pollute groundwater with metals. As a result of batch experiments presented in the paper, it can be said that it is possible to remove chromium and copper from the groundwater (which is affected by acid mine drainage, thus characterized by low pH) with the use of zero-valent iron in permeable reactive barrier technology. The contaminants are removed from the aquifer by the flow of groundwater through a reactive barrier filled with a special reactive material. Rapid metal removal likely occurred due to the reduction and the precipitation/co-precipitation and/or due to the adsorption onto the iron metal surface or/and onto the iron corrosion products. In accordance with the research it has also been found that in more alkaline environment, the oxidation of Fe(0) proceeds slower. A rapid decrease of the redox potential as well as the increases of pH have also been observed in the batch tests when the dose of Fe(0) in solutions increased.

1. INTRODUCTION

The environment protection is one of the biggest issues in the southern provinces of Poland. The heavy industry located there has an effect on water, air, and soil quality. Disposal of wastes into the soil, CO₂ emissions and sequestration, burning waste dumps [1], industrial solid waste disposal and storage [2], etc. all these aspects appear in Upper Silesia. In every part of this region, it is easy to find a large number of industrial dumping sites, especially intended for hard coal mining. The leachates from these waste dumps may contain barium, boron, copper, cadmium, chromium, cobalt, lead, lithium, arsenic, zinc, nickel, molybdenum, manganese, selenium, thallium, sulphate and phosphates [3, 4], and thus, the quality of ground and surface water may be affected. Contaminants from waste dumps flow downward through the unsaturated zone,

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reach the groundwater and flow horizontally in the form of diluted solution which may pollute major groundwater basins (MGB) and surface water like rivers, lakes, etc. [2]. All those contaminants (mainly heavy metals) are particularly hazardous for human health, having the tendency to accumulate in living organisms and are highly toxic [5].

The Water Framework Directive (Directive 2000/60/EC of the European Parliament and of the Council) established in October 2000, commits European Union member states to achieve good qualitative and quantitative status of all water bodies by the year 2015. Therefore, the problems related to the waste dumps in Upper Silesia, and their impact on ground and surface water must be solved immediately.

In the presented paper, the possibility of removal of chromium and copper from synthetic water (simulating groundwater affected by coal mine waste dumps) has been assessed. Zero-valent iron (Fe(0), ZVI) used as a reactive material in PRB technology has been applied for this purpose. Within this technology, the contaminants are removed from the aquifer by the flow of groundwater through a permeable reactive barrier (PRB) filled with a reactive material. The application of ZVI for cationic and anionic metals removal has been investigated [6–11]. The principal suggested mechanisms are reduction and precipitation/co-precipitation, and adsorption.

The hypothesis formulated in the paper assumed that cationic and anionic metals may be removed from groundwater contaminated with coal mine waste dumps by means of ZVI used as a reactive material in the PRB. The questions arose what would happen with physicochemical parameters and with some chemicals at low pH due to acid mine drainage (AMD) which refers to the outflow of acidic water from, e.g. coal mine waste dumps [12]. The AMD effect is a result of sulphide minerals like pyrites exposure to atmospheric oxygen and water.

2. MATERIAL AND METHOD

The installation to carry out the batch tests was a programmable rotator equipped with 50 cm³ plastic tubes. 2 min orbital rotation was applied for each sample in a rotator (40 rpm) after which a 6 s reciprocal motion (with turning angle equal to 90°) with vibration motion followed. This sequence of shaking was repeatedly reiterated. The sequence continued for 1 h. For these tests, synthetic solutions with the initial pH of ca. 3.0, 5.0, 7.0 were prepared. The pHs of the solutions were adjusted by slow titration with ultrapure sulphuric acid or with ultrapure sodium hydroxide. For the batch tests, two separate chromium and copper ion solutions were used. They simulated groundwater contaminated with coal mine waste dumps located in the Upper Silesia. The initial concentrations of Cr(VI) and Cu(II) in the solutions amounted to ca. 0.8 mg/dm³ and 1.1 mg/dm³, respectively, exceeding the legally permitted ones [13]. Metal ion solutions were prepared by dissolving appropriate metal salts in distilled water.

In the batch tests, the metal ion solutions were poured into five plastic tubes (50 cm^3 per each sample) and then 50, 100, 200, 300, 400 mg of ZVI were added to every sample (which corresponds to 1, 2, 4, 6, and 8 g/dm^3 of ZVI). After shaking the samples for 1 h, the solutions were passed through thick filters and then the following parameters were measured: pH (PORTAMESS 913 pH with an electrode SenTix 41), oxidation-reduction potential ((PORTAMESS 913 pH with an electrode POLYPLAST ORP), dissolved oxygen (DO, PORTAMESS 913 Oxy with oxygen probe SE 30), conductivity and temperature (PORTAMESS 913 Count).

Metal content in solutions was determined by the following methods:

Cr(VI). UV-Vis spectrophotometer DR5000 HachLange by the 1,5-diphenyl-carbohydrazide method (method 8023 of Hach Co.) at 540 nm.

Cu total. UV-Vis spectrophotometer DR5000 HachLange by the bicinchoninate method (method 8506 of Hach Co.) at 560 nm. The concentration of copper in the solutions was measured with a spectrophotometer as a total value (Cu total). Since, there were no copper speciation (at the beginning) in the solutions other than the Cu(II), the removal of copper in the second oxidation state has been assessed in the paper.

Fe(II). UV-Vis spectrophotometer DR5000 HachLange by the 1, 10-phenanthroline method (method 8146 of Hach Co.) at 510 nm;

Fe total. UV-Vis Spectrophotometer DR5000 HachLange by the FerroVer method (method 8008 of Hach Co.) at 510 nm. The concentration of dissolved Fe(III) was calculated as a difference between Fe total and Fe(II).

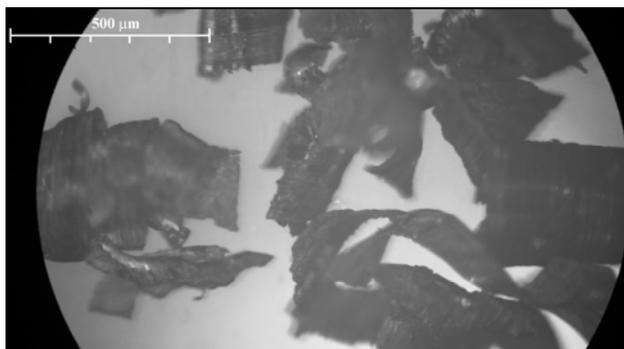


Fig. 1. Zero-valent iron Fe(0) used in the batch test [14]

Scrap iron (in the form chips and swarf, Fig. 1) used in the batch tests was taken from the machining plant. Table 1 presents its grain-size distribution [14]. The maximum size of the iron grains amounted to 4 mm. The material used in the size grading, in the measurements of the density and 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. For the correct measurement of the

iron density (according to Polish Standard [15]), benzene (analytically pure) was applied in the test and a pycnometer with a sample was heated in a water bath (distilled water did not penetrate into the whole porosity of the measured material). The density of ZVI used in the tests amounted to 7.85 g/cm^3 .

Table 1

Particle size distribution of zero-valent iron used in a batch test [14]

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

3. RESULTS AND DISCUSSION

Under reduction conditions in the plastic tubes filled with ZVI and with Cu(II) and Cr(VI) solutions, the concentration of these metals decreased dynamically (depending on the initial pH), with the increase of the amount of ZVI used in the tests (thus also the increase of dose of ZVI in solutions), from ca. 1.11 mg/dm^3 to 0.12 mg/dm^3 and from 0.81 mg/dm^3 to 0.04 mg/dm^3 for copper and chromium, respectively. The higher pH of metal ion solution, the faster decrease of Cu(II) and Cr(VI) concentration was observed (Fig. 2). Since formation of hydroxides on the surface of zero-valent iron is much faster at higher pH, the analyzed metals may be easier removed from solutions.

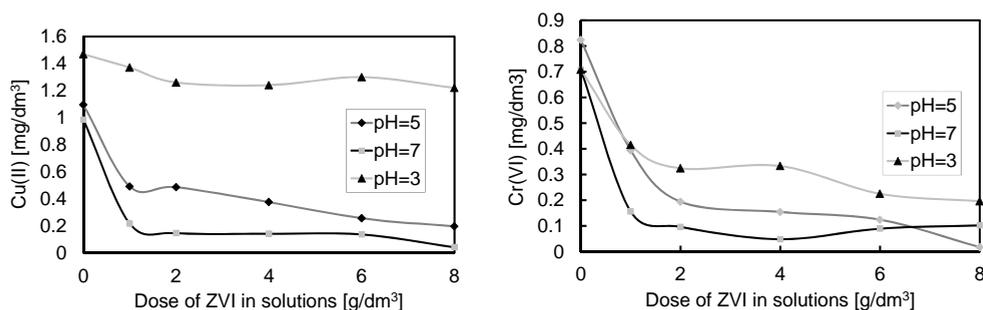


Fig. 2. Concentration of: a) Cu(II), b) Cr(VI) in solutions (initial pH: 3, 5, 7) for various doses of ZVI

The values of ORP for both solutions decreased gradually with the increase of the dose of ZVI in solutions and were dependent on the initial pH (Fig. 3). The lower values of pH in the tests, the higher initial values of ORP occurred in the solution and the faster were the decreases of this potential for larger dose of ZVI in solutions. This

occurred because generally higher values of pH cause lower oxygen-reduction potential for the same reaction.

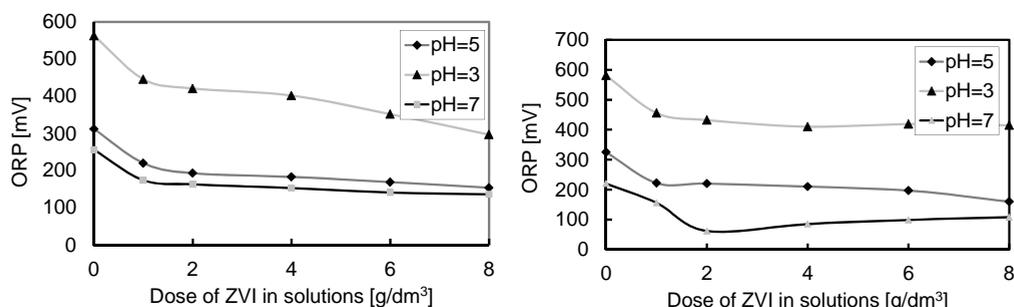
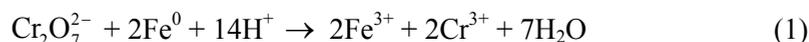


Fig. 3. Oxygen reduction potential (ORP) of: a) copper, b) chromium solutions (initial pH – 3, 5, 7) for various doses of ZVI

The overall reaction for the hexavalent chromium, which occurs in water as an oxyanion in the form of CrO_4^{2-} or as $\text{Cr}_2\text{O}_7^{2-}$, can be expressed as:

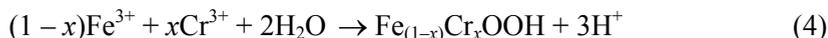


In further steps, chromium Cr(III) may be removed from solution in the following steps (Fig. 4).

- precipitation as chromium hydroxides (reaction (2)) and oxides (reaction (3)):



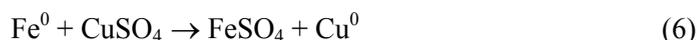
- co-precipitation with iron as a mixed chromium-iron oxyhydroxide [16]:



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



$\text{Cu}(\text{II})$ has a higher standard electrode potential than $\text{Fe}(0)$, thus, this hazardous cation is removed by iron from groundwater:



More information about the removal of copper from groundwater in the PRB may be found elsewhere [14].

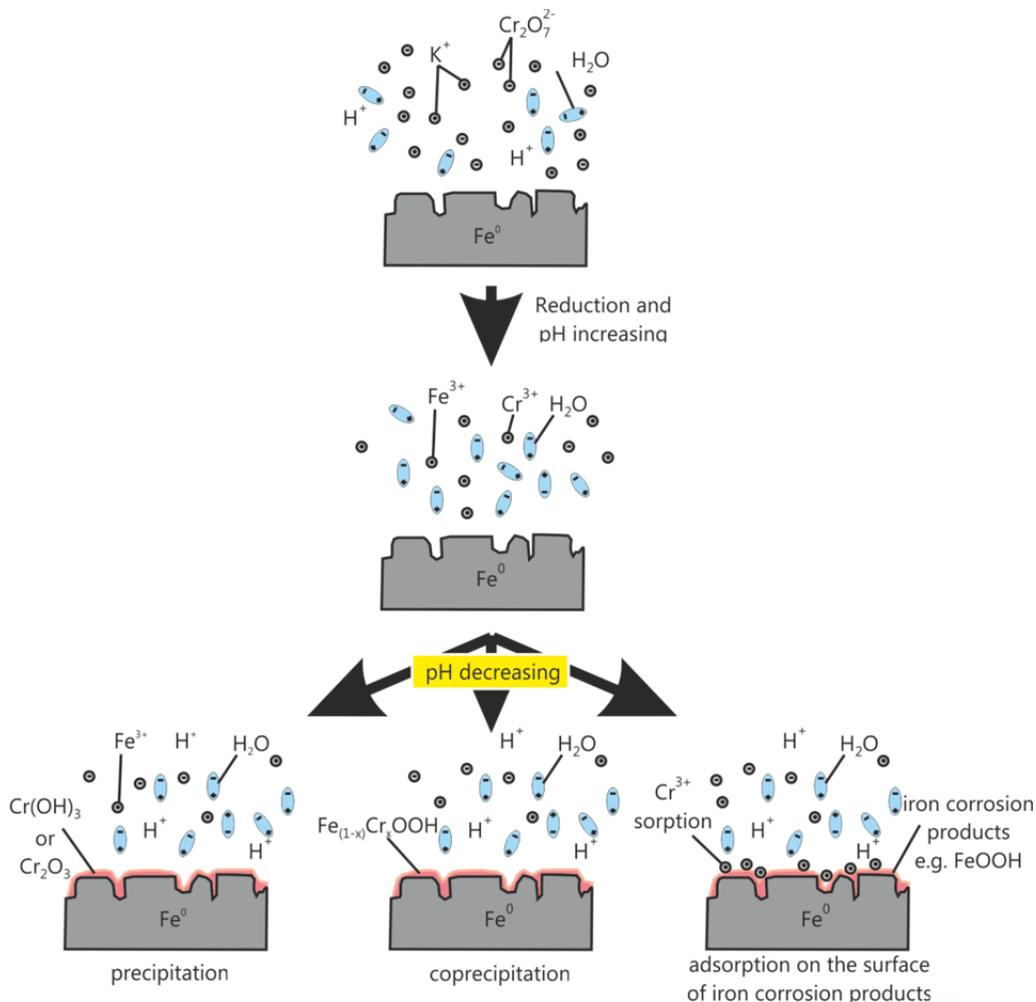


Fig. 4. Conceptual model for chromium(VI) removal from water with the use of ZVI

Although reduction and precipitation of Cu is more probable, some Cu(II) may be adsorbed on the surface of iron corrosion products or on the surface of zero-valent iron (less likely) (Fig. 5).

The oxidation of $\text{Fe}(0)$ proceeds faster at low pH [17], which was evidenced by the fact that more ions of iron ($\text{Fe}(\text{II})$) were found in water at lower initial pH upon increasing dose of ZVI in solutions (Fig. 6). This occurred mostly due to processes described by reactions (7) and (8).

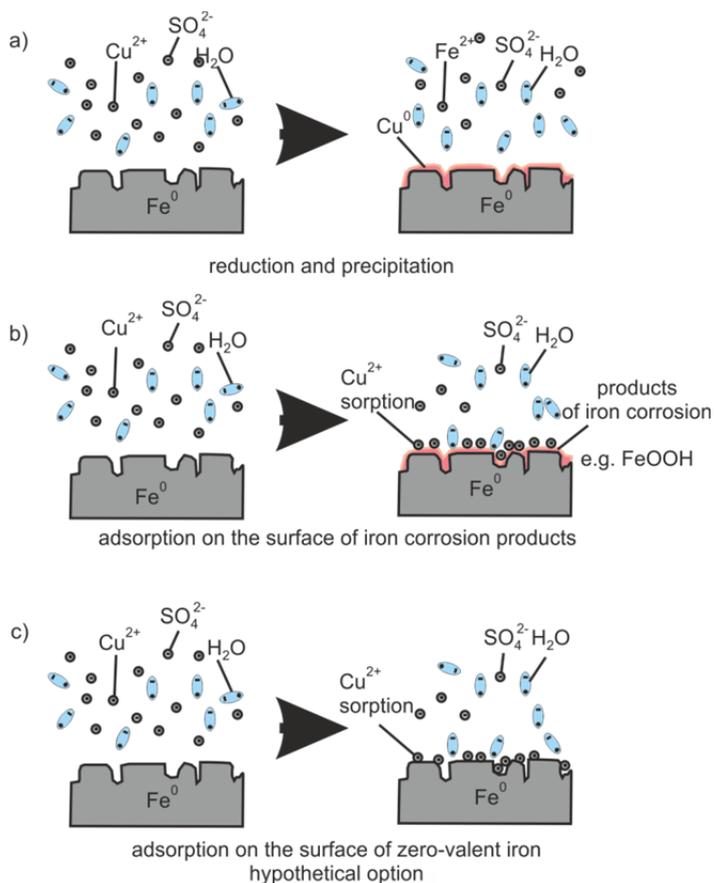


Fig. 5. Conceptual model of copper(II) removal from water with the use of ZVI

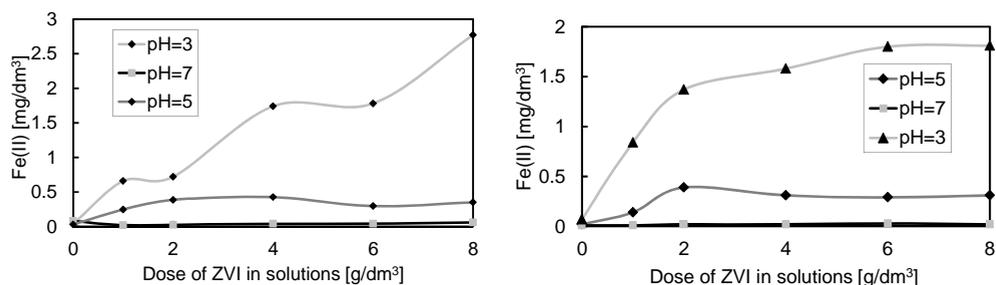


Fig. 6. Concentration of Fe(II) in: a) copper solutions, b) chromium solutions for various doses of ZVI

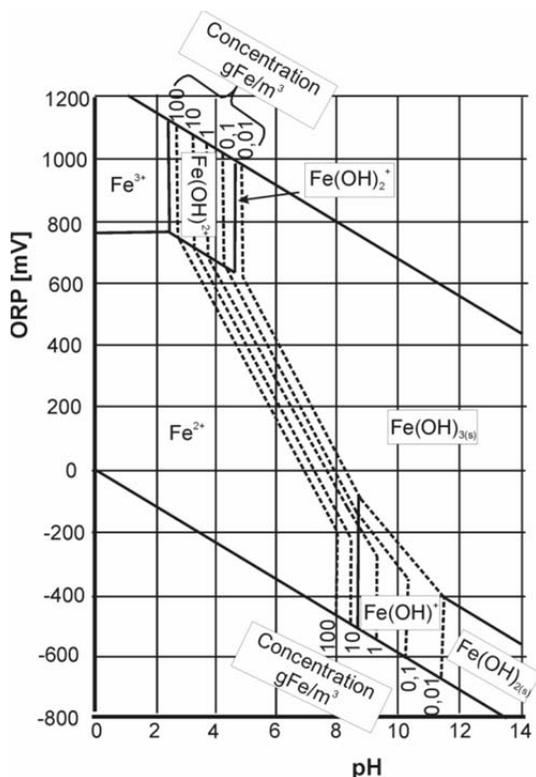


Fig. 7. Effect of pH and ORP on iron speciation (iron concentration: 0.01–100 g Fe/m³) [18]

As a result of hydrolysis, under conditions of high pH and in low ORP (see Fig. 7), Fe(II) generates Fe(OH)₂. In the presence of dissolved oxygen in water, however, and especially in alkaline environment, Fe(II) is oxidized to Fe(III), which then may produce Fe(OH)₃ or Fe₂O₃, FeOOH in a solid form



These precipitates cover ZVI with thin shells and, as a result, the oxidation of Fe(0) may proceed slower (transport of Fe(II) to solution is slower, as well as the transport of oxygen and protons – the acceptors of electrons – to ZVI). Thus, in more alkaline environment and in the presence of dissolved oxygen the oxidation of Fe(0) proceeds slower.

The concentration of Fe(III) in solutions is mainly caused by the increased concentration of dissolved oxygen (Fig. 8, reaction (9)). During the removal of chromium as a result of reaction (1), Fe(III) is also produced. Due to high concentration of dis-

solved oxygen in solutions (Fig. 9), the concentrations of Fe(III) in almost all examples were at least 2 times higher than the concentrations of Fe(II) (Fig. 10).

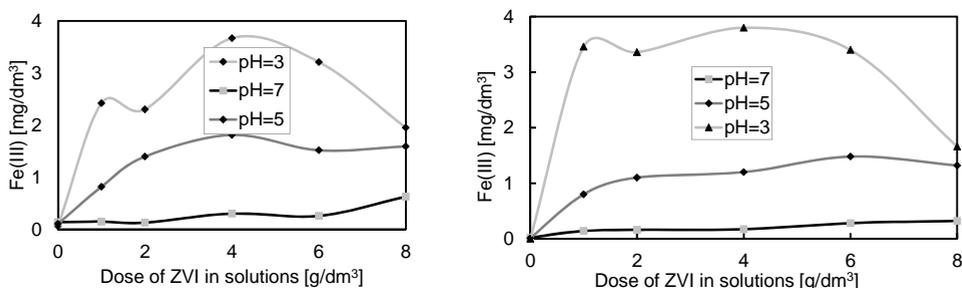


Fig. 8. Concentration of Fe(III) in: a) copper solutions, b) chromium solutions for various doses of ZVI. Initial pH: 3, 5, 7

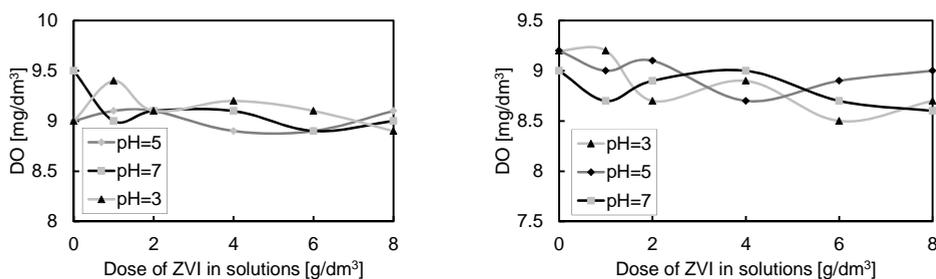


Fig. 9. Concentration of dissolved oxygen (DO) in: a) copper solutions, b) chromium solutions for various doses of ZVI. Initial pH: 3, 5, 7

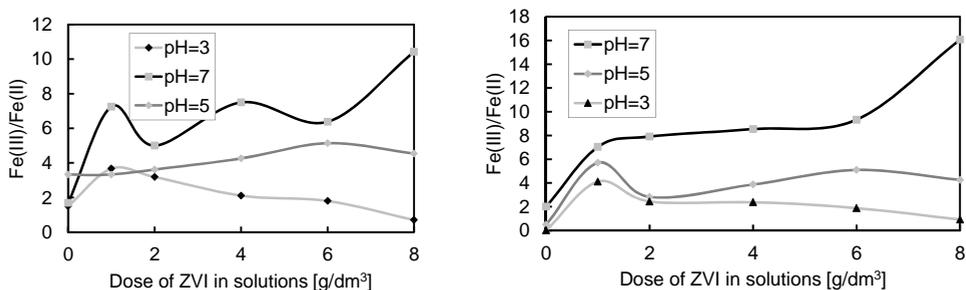


Fig. 10. Fe(III)/Fe(II) ratio for: a) copper solutions, b) chromium solutions for various doses of ZVI. Initial pH: 3, 5, 7

On the whole, the higher value of pH in solutions, the higher the value of the Fe(III)/Fe(II) ratio is (Fig. 10) because oxidation of Fe(II) to Fe(III) proceeds slower in acid environment, and thus, iron compounds, which are characterized by low solubility product (are sparingly soluble in water, e.g. $\text{Fe}(\text{OH})_3$, Fe_2O_3), are formed slower.

If these compounds precipitated out completely on the surface of ZVI, they could protect ZVI against the oxidation – which occurred (to some extent) at higher pH. Hence the oxidation of ZVI at lower pH is faster. In such environment, the solubility of metals, and – as a result – the values of conductivity were higher (Fig. 11).

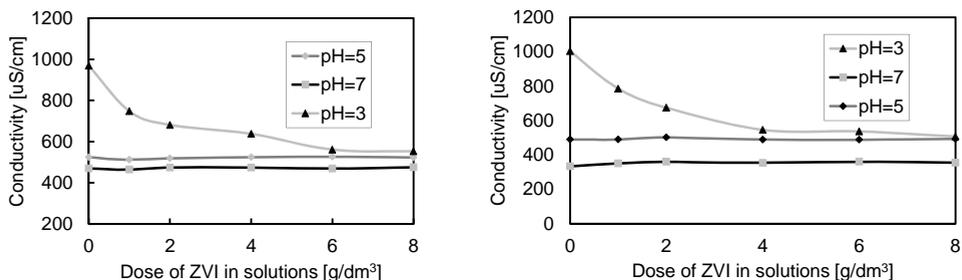


Fig. 11. Conductivity of: a) copper solutions, b) chromium solutions for various doses of ZVI. Initial pH: 3, 5, 7

The conductivity of solutions characterised by pH amounting to ca. 3 decreased with the increase of the dose of ZVI in solutions (Fig. 11), due to the value of pH increase in these tests (Fig. 12) and the presence of dissolved oxygen in the solutions (Fig. 9), which has probably led to the precipitate formation. For the rest of the solutions (for which pH amounted to ca. 5 and 7) the conductivity varied slightly (Fig. 11).

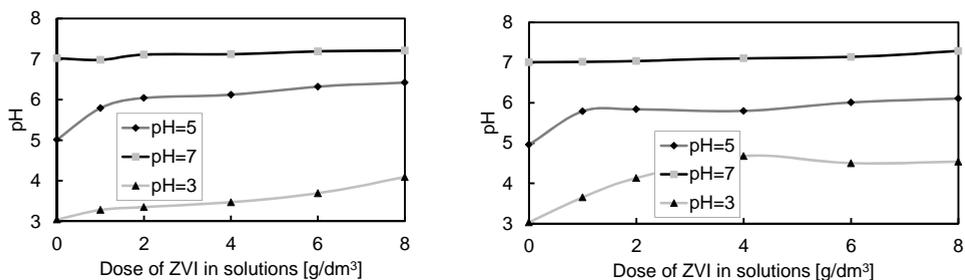


Fig. 12. pH of: a) copper solutions, b) chromium solutions for various doses of ZVI. Initial pH: 3, 5, 7

During removal of Cu(II) and Cr(VI), pH increased (Fig. 12). Relatively lower growth of pH was observed for Cu(II) solutions, due to the fact that only reactions (7)–(9) proceeded in the batch tests, while in the case of chromium solution reaction (1) had a higher impact on the change of pH.

In general, faster increase of pH was observed for its low initial value, as the oxidation of Fe(0) proceeded more rapidly at low pH, which has been mentioned above. The main acceptors of electrons in highly acid environment are protons (reaction (8)), while in solutions at pH > 4, oxygen dissolved in water is the main acceptor of elec-

trons (reaction (7)) [19]. Hence, for the initial value of pH = 3, reaction (8) proceeds first, and consequently, after achieving pH > 4, reaction (7) starts to dominate reaction (8) in the process of oxidation of Fe(0). Since at least two reactions ((7) and (8)) proceed in the solution at pH = 3 (the initial value), the increase of pH is higher than this of the solutions with higher initial pH.

The higher concentration of dissolved oxygen (DO) in water, the faster oxidation of Fe(0) proceeds. According to Suponik [14], in the ZVI bed the DO is removed gradually as a result of reactions (7) and (9). In the presented paper, however, the concentration of DO is practically constant in every test, ranging from 9.5 mg/dm³ to 8.5 mg/dm³ due to the presence of oxygen in the air above the solutions in plastic tubes dissolving in water during the shaking process. Such situation does not occur in ZVI bed [14]. In order to eliminate this problem, the air in the tubes should be replaced with inert gas (e.g. argon).

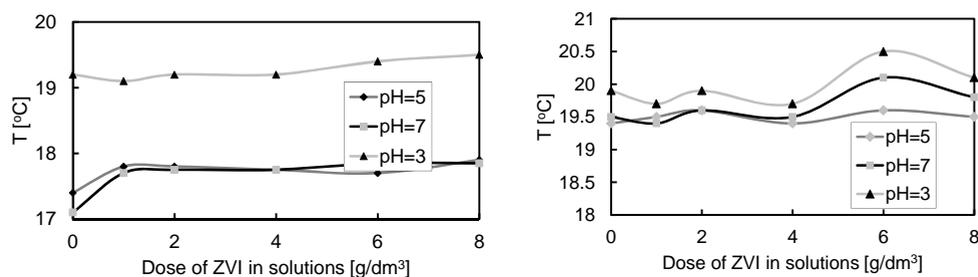


Fig. 13. Temperature of: a) copper solutions, b) chromium solutions for various doses of ZVI. Initial pH: 3, 5, 7

Table 2

Values of changes of thermodynamic functions at 298 K for some reactions proceeded (probably) in zero-valent iron

Reaction	ΔH_{298}° [kJ]	ΔS_{298}° J/K	ΔG_{298}° [kJ]
$\text{Cr}_2\text{O}_7^{2-} + 2\text{Fe}^0 + 14\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	-1179,666	-832,38	-931,616
$2\text{Fe}^0 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^-$	-523,884	-668,21	-324,758
$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$	-410,876	-631,51	-176,662
$\text{Fe}^0 + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu}^0$	-152,26	-5,55	-149,94

In the presented experiments, the temperature increase of the solution (with the increase of the dose of ZVI in solutions) was almost negligible (Fig. 13), although in the column test presented by Suponik [14], it was more noticeable. In a general case, the increase of temperature in solution may be explained by the negative value of standard

enthalpy of the reactions presented in Table 2, which might cause (among others) removal of Cu(II) and Cr(VI) from the solutions and the increase of iron concentration (Fe(II), Fe(III)). Adsorption of metals is also characterized by negative enthalpy values and for the physisorption and chemisorption, the enthalpy value varies from -4 to -80 kJ/mol and from -80 to -410 kJ/mol, respectively [20].

The temperature of air in the laboratory was changing during the tests, hence some variation of temperature was observed (Fig. 13).

4. CONCLUSIONS

The outflow of acidic water from coal mine waste dumps may pollute groundwater and surface water with metals in cationic and anionic forms. Scrap iron used in the PRB technology has an ability to remove Cu(II) and Cr(VI) ions from groundwater in acidic or neutral solutions. This occurred mainly due to the reduction conditions which were developed in the solutions; when the dose of ZVI in solutions increased in the tests the oxidizing-reducing potential (ORP) for copper and chromium solutions decreased gradually for all values of pH analysed in the paper. The lower values of pH in the tests, the faster the decreases of ORP for larger doses of ZVI in solutions were. The main mechanisms which caused the removal of Cu(II) and Cr(VI) ions from solutions are probably reduction and precipitation/co-precipitation, and adsorption.

It was also confirmed that in more alkaline environment, the oxidation of Fe(0) proceeds slower as in the presence of dissolved oxygen more Fe(III) is generated and solid Fe(OH)₃, Fe₂O₃, FeOOH may be produced. The precipitates cover ZVI with thin shells leading to slower oxidation of Fe(0) (the transport of Fe(II) to solution is slower, just as well as the transport of oxygen and protons – the acceptors of electrons – to the ZVI).

During the process of metals removal, pH is increasing. Due to oxidation of Fe(0) proceeding quicker at low pH, the higher increases of pH were noticed for its low initial value.

The reactions of Cu(II) and Cr(VI) ions removal and the reactions of oxygen reduction are spontaneous, proceeding with a negative enthalpy change.

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