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Technical Note

Zero-valent iron nanoparticles in treatment of acid mine water from *in situ* uranium leaching

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ABSTRACT

Acid mine water from *in situ* chemical leaching of uranium (Straz pod Ralskem, Czech Republic) was treated in laboratory scale experiments by zero-valent iron nanoparticles (nZVI). For the first time, nZVI were applied for the treatment of the real acid water system containing the miscellaneous mixture of pollutants, where the various removal mechanisms occur simultaneously. Toxicity of the treated saline acid water is caused by major contaminants represented by aluminum and sulphates in a high concentration, as well as by microcontaminants like As, Be, Cd, Cr, Cu, Ni, U, V, and Zn. Laboratory batch experiments proved a significant decrease in concentrations of all the monitored pollutants due to an increase in pH and a decrease in oxidation–reduction potential related to an application of nZVI. The assumed mechanisms of contaminants removal include precipitation of cations in a lower oxidation state, precipitation caused by a simple pH increase and co-precipitation with the formed iron oxyhydroxides. The possibility to control the reaction kinetics through the nature of the surface stabilizing shell (polymer vs. FeO nanolayer) is discussed as an important practical aspect.

1. Introduction

The reductive effect of zero-valent iron is commonly used for dehalogenation of chlorinated hydrocarbons, mainly of chlorinated ethenes (Wang and Zhang, 1997; Lowry and Johnson, 2004; Liu et al., 2005; Tsang et al., 2009). Zero-valent iron based (nano)materials could also be used to remove other classes of important organic pollutants like brominated diphenylethers, polychlorinated dibenzo-p-dioxins and other organochlorine pesticides (Kluyev et al., 2002; Shih and Tai, 2010; Yang et al., 2010). These properties were exploited in the construction of iron-filled permeable reactive barriers (Blowes et al., 2000; Rangsivek and Jekel, 2005; Wilkin et al., 2005; Ahn et al., 2006; Jia et al., 2007). The reductive properties of elemental iron and the sorption capabilities of the subsequently formed iron oxides can also be used for removing the heavy metals by turning them into less-soluble forms through changes in their oxidation state and/or by adsorption (Shokesand and Möller, 1999; Celebi et al., 2007; Lim and Zhu, 2008; Geng et al., 2009; Shih and Tai, 2010).

The advantages of zero-valent iron nanoparticles (nZVI) over macroscopic counterparts involve not only a higher reactivity induced by their larger specific surface area but also their mobility through the pores of an aquifer (Zhang, 2003; Nurmi et al., 2005; Kanel et al., 2007, 2008). To extinguish a high tendency for particle aggregation and rapid sedimentation, surface modification by organic or inorganic compound is routinely applied (e.g. Hydutsky et al., 2007; Johnson et al., 2009; Kim et al., 2009; Phenrat et al., 2009a); however, the surface modification decreases the nZVI reactivity (Phenrat et al., 2009c) and affects the ability of nZVI to remove toxic metals (Kanel et al., 2007). Nevertheless, nZVI mobility reaches to a few meters as a maximum, which prevents a metal facilitated transport to a distance endangering the living organisms out of the treated site (Sushil et al., 2007; Phenrat et al., 2009b). The addition of nZVI evokes alkaline reaction with water; hence, it can be applied for removal of toxic elements like heavy or transition metals from contaminated environment (Ponder et al., 2001; Li et al., 2006). These processes are related to various removal mechanisms like reductive mineral precipitation and co-precipitation, insoluble hydroxide formation, and adsorption (Li and Zhang, 2007). Reductive mineral precipitation is caused by a substantial decrease in oxidation–reduction potential (ORP) from oxidative to neutral or even anoxic conditions. Moreover, nZVI are oxidized and transformed to poorly crystalline iron oxyhydroxides which, together with other insoluble hydroxides, provide potential adsorption surface for cations. Such mechanisms have been extensively studied for the treatment of waters contaminated by, e.g., chromium, uranium, arsenic, zinc and nickel (Wilkin and

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McNeil, 2003; Li and Zhang, 2007; Coelho et al., 2008; Rao et al., 2009).

Mining activities generally induce environmental problems related to a production of acid mine drainage caused by an extensive oxidation of metal sulphides, e.g., FeS_2 pyrite (Singer and Stumm, 1970; Lowson, 1982). The *in situ* chemical leaching of uranium from sandstones (cenomanian–turonian age) at Straz pod Ralskem (Czech Republic) comprises of an injection of sulfuric acid, with a portion of nitric acid as an oxidizing agent, into a sedimentary rock environment and the subsequent pumping of concentrated uranium-bearing solution. The resulting acid mine water and rock environment are characterized by a very low pH, typically below 2, a high ORP and by an elevated concentration of total dissolved solids (TDS) represented mainly by sulphates and a minority of nitrates, phosphates, ammonium, aluminum, iron, and other elements like V, Be, As, Cr, etc. (Benes et al., 1983). The contaminated water is located at a deep aquifer, but, in many cases, there exists natural hydrodynamic potential causing water upraising, whereby the contamination of drinking water sources can occur. Therefore, removal or immobilization of potentially-toxic species represents an important task. Recently, methods based on *in situ* application of biological materials (Senko et al., 2002; Bilgin et al., 2005; Costa et al., 2008) or chemical compounds (Matlock et al., 2002; Wilkin and McNeil, 2003; Li et al., 2006; Li and Zhang, 2007) were tested for the treatment of polluted waters extracted from contaminated aquifers, or at the borders of contaminated area, where the concentration of dissolved species is diluted.

The application of nZVI for the contaminants removal from acid mine water is based on the simultaneously induced changes in pH and ORP resulting in a transformation of the certain group of contaminants into a less-soluble form, followed by precipitation. The acid–base changes are caused by the interaction of nZVI with protons dissolved in water, where following oxidation reduction process takes place (Roh et al., 2000):

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{1}$$

The ongoing oxidation of Fe(II) to Fe(III) leads to the precipitation of iron oxides, hydroxides and oxyhydroxides at or close to the surfaces of nZVI particles (Roh et al., 2000; Phillips et al., 2003). The ORP changes are also related to a chemical reduction of selected contaminants induced by nZVI nanoparticles being oxidized simultaneously.

In this paper, we demonstrate the application of the commercial nZVI material for the treatment of real acid mine water containing a complex mixture of pollutants. Thus, for the first time, we examine an efficiency of nZVI for a treatment of the natural acid–water system originating from *in situ* chemical leaching of uranium, where various pollutants appear side by side and we discuss the possible mechanisms of their removal. The possibility to control the reaction kinetics is studied with the two nZVI materials differing in the character of the surface shell. As the key conclusion, an application of nZVI represents an extraordinarily efficient way for treatment of acid mine water as proved by a dramatic decrease in contents of all the monitored pollutants. This is due to the combined effects involving the changes in pH and ORP and sorption ability of particular secondary compounds. Compared to the organic polymer coating, the compact FeO shell allows to decelerate the reactions kinetics and, simultaneously, to achieve the comparable final changes in ORP and pH.

2. Material and methods

2.1. Materials and analytical techniques

In all experiments, we used the suspension of commercial nZVI material (NANOFER 25S) stabilized by organic polymer and supplied by Nano Iron company (Czech Republic). In this sample, nZVI particles are coated by polyacrylic acid (PAA), which stabilizes them against aggregation but does not create a compact surface layer on iron particles, keeping them well accessible to reactions. The weight ratio of PAA/nZVI corresponds to 1/10. The average size of the used nZVI particles is close to 60 nm from TEM observation (not shown), the Fe^0 content is about 70% and the active surface area is 20 $m^2\,g^{-1}$ as determined by Mössbauer spectroscopy and BET measurements, respectively. The original suspension with an iron concentration of 200 $g\,L^{-1}$ was homogenized by an intensive mixing for 10 min under Ar atmosphere. Subsequently, the particular amounts of nZVI were inserted into the reactive bottles containing mine water. The amount of nZVI in the working suspension was independently checked by weighing the dried reference sample. Bearing in mind the possibility to control the reaction kinetics, the core–shell Fe–FeO nanoparticles were prepared by thermally induced solid state route enabling to create a compact oxide layer on the nZVI surface (Filip et al., 2007). This material shows nearly the same content of Fe^0 (70%) and the comparable surface area (22 $m^2\,g^{-1}$).

All laboratory experiments were performed with a sample of an acid mine water (labeled B, Table 1) collected in a leaching field "B", which represents typical mine water from the uranium mining area of Straz pod Ralskem (Czech Republic). In order to get water samples with various TDS mineralization in a range of 10^2–10^4 $mg\,L^{-1}$, the water sample was diluted 5-, 10-, 25- and 125-times by demineralized water (Watek, Demiwa 3). Hence, we were able to assess the fundamental efficiency of the contaminant immobilization method in various stages of the remediation process or, potentially, in different parts of the contaminated area. Accordingly, the diluted samples were labeled by the dilution factor in a subscript (e.g., B_{10} indicates the sample which was diluted 10 times). Both original water and diluted samples were filtered and their pH and ORP characteristics were measured prior to nZVI application, as well as after the batch experiments. The reproducibility of all experiments was tested on acid mine water collected in another location – a leaching field "A". The representative data are included in Supplementary material (Table A1).

The concentrations of the toxic cations and anions were determined in the accredited laboratory of AQUATEST, a.s., using an ICP-OES (Perkin Elmer, Optima 5300 DV) and an ionic chromatography (Dionex, ICS-90). The detection limits of ICP analyses ranged from 0.003 to 0.01 $mg\,L^{-1}$ depending on a metal. The detection limits for anions ranged from 1 to 5 $mg\,L^{-1}$ depending on the type of anion and degree of dilution. Uncertainty of detection is less than 10% (three duplicates) for pH ±0.2. The measurements of ORP were carried out using a laboratory multimeter (WTW, Multi 350i, electrodes WTW SenTix 41). The TDS parameter was simply

Table 1
Chemical composition and selected physico-chemical parameters of the studied acid mine water from the uranium mining area of Straz pod Ralskem (Czech Republic).

Sample B	$mg\,L^{-1}$	Sample B	$mg\,L^{-1}$
pH	1.83	Mg	22.4
κ ($mS\,m^{-1}$)	1280	Cr	5.18
F^-	13.8	Cd	0.157
SO_4^{2-}	12 600	Mn	6.1
NO_3^-	215	Cu	0.725
NH_4^+	175	Ni	8.1
PO_4^{3-}	133	Pb	0.026
Cl^-	23.4	SiO_2	25.1
NO_2^-	3.84	Na	10.9
U	19.32	V	5.64
As	2.48	Ca	142
Be	0.282	Zn	29.9
K	22.3	Fe	607
Al	1810		

calculated as a sum of analytically determined concentrations of cations and anions.

Content of Fe^0 and structural forms of iron oxides/oxyhydroxides were determined by ^{57}Fe Mössbauer spectroscopy in a constant acceleration mode with a ^{57}Co(Rh) source. Spectra were collected in a frozen sample (260 K) to prevent the sample oxidation during the measurement. A pure α-Fe foil was used as a calibration standard. Spectra were fitted by the Lorentz functions using the CONFIT2000 program (Žák, 2001).

2.2. Experimental set-up

Acid–base titration was performed with the 25-times diluted mine water sample (B_{25}) with the aim to evaluate the neutralization capacity. The volume of 125 mL of the sample was titrated stepwise by 0.1 M NaOH (Lach-Ner, Czech Republic) and the equilibrium pH values were recorded. The equilibration times for the determined points vary from about 10 to 100 min.

Kinetic experiments, tracking both pH and ORP (WTW, Multi 350i) changes in time, were carried out by an addition of nZVI suspension (set to a total amount of 0.2 g of Fe) into 200 mL of mine water samples (B_5 and B_{10}). The samples were instantly agitated on a horizontal shaker (220 rpm) and the values of pH and ORP were simultaneously recorded. Content of elemental iron after nZVI application (at the end of experiments) was measured by Mössbauer spectroscopy.

Batch equilibrium experiments were performed in order to determine changes in both solution chemistry and the physicochemical parameters. Five milliliter of nZVI suspension (set to a total amount of 1 g of Fe) was added into 1 L of mine water sample in a reagent bottle, which was capped and sealed by a Parafilm to avoid the contact with atmosphere. The samples were agitated on a revolving shaker (0.5 rpm; PluNoTech, Czech Republic) for 10 d and finally analyzed for concentration of selected contaminants.

3. Results and discussion

3.1. Acid–base titration of mine water

The studied mine water reveals a high neutralization capacity caused by a significant amount of TDS. The course of titration curve of 25-times diluted mine water sample (see Fig. 1) indicates a rapid pH increase from an initial value of 3.05 to a value above 4, requiring an addition of approximately 2.5 mL of NaOH. Evidently, due to a high Al concentration, the increase in pH value from about 4 to 5 requires a relatively high amount of NaOH (about 7 mL) because of $Al(OH)_3$ precipitation. An addition of another 4 mL of NaOH causes a significant increase in pH over 9 (see Fig. 1).

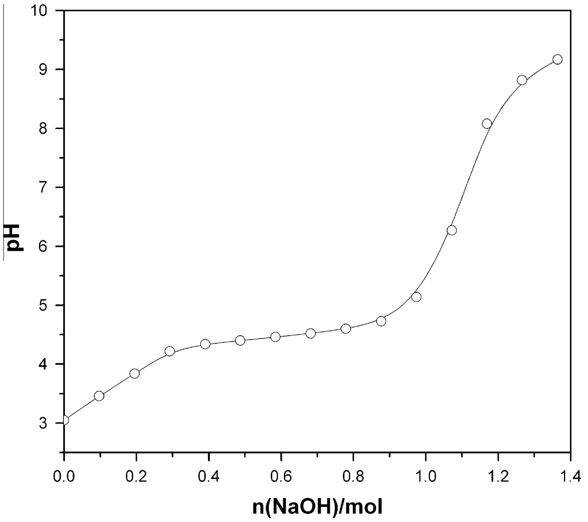

Fig. 1. Potentiometric titration curve of acid mine water sample B_{25}.

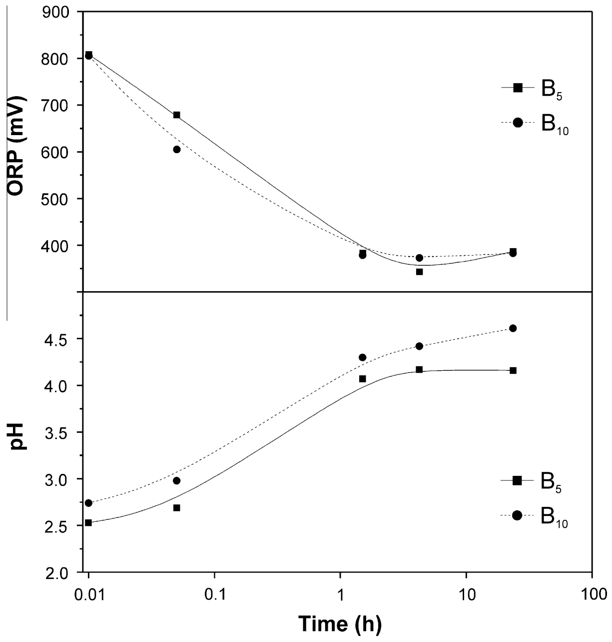

Fig. 2. The time dependences of ORP (top) and pH (bottom) in acid mine water samples induced by addition of nZVI (1 g L^{-1}).

3.2. Kinetic experiments

The acid–base titration of 25-times diluted mine water sample showed a relatively fast kinetics in the range of minutes or tens of minutes. Reaction with nZVI is significantly slower due to ongoing surface reactions. The kinetic experiments carried out for B_5 and B_{10} samples with addition of nZVI suspension containing 1 g L^{-1} of Fe(0) are shown in Fig. 2. Due to the alkaline reaction of nZVI, an increase in pH from the initial value up to a value of 4 was achieved in the interval of minutes (Fig. 2). Subsequently, the pH increase continues but, depending on TDS of the samples, this shift towards alkaline environment terminates gradually due to the decreasing reactivity of nZVI. Consequently, the formation of insoluble hydroxides caused alkalinity to be consumed and pH decreased to below 5. Analogously to the pH changes, the ORP decrease down to 200–300 mV is rapid and again depends on the initial TDS of the samples (see Fig. 2). However, such a decrease in ORP is followed by a slow increase to about 380 mV in the case of both samples. This secondary increase could be explained by a complete consumption of accessible nZVI and formation of secondary iron oxides as proved by Mössbauer spectroscopy. Fig. 3 shows the Mössbauer spectrum of the initial nZVI sample prior to a reaction with metallic pollutants (upper spectrum) and the spectrum of the sample after the reactions with pollutants contained in acid mine water (bottom spectrum). Indeed, all elemental iron (the sextet with a hyperfine magnetic field of 33 T in the upper spectrum) is fully oxidized as illustrated by a disappearance of this spectral component in the sample after reaction (bottom spectrum). On the other hand, new Fe(III) doublet with the hyperfine parameters (isomer shift $\delta = 0.39$ mm s^{-1} and quadrupole splitting $\Delta E_Q = 0.72$ mm s^{-1}) corresponding to $Fe(OH)_3$ appears in the reacted sample and the content of Fe_3O_4 (two sextets with the

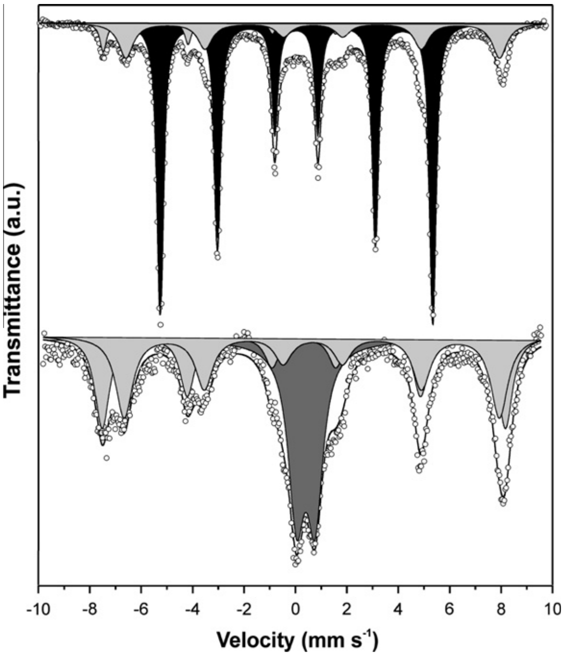

Fig. 3. Mössbauer spectra of nZVI prior (upper spectrum) and after reaction (sample B_5; bottom spectrum) with acid mine water. Black – elemental iron; light gray – magnetite Fe_3O_4, dark gray – $Fe(OH)_3$.

hyperfine magnetic fields of 48.7 and 45.3 T, Schneeweiss et al., 2006) dramatically increased.

3.3. Batch experiments

The batch experiments, performed on non-diluted and up to 25-times diluted mine water samples, aimed to simulate the situation in the various parts of the contaminated area.

3.3.1. pH and ORP changes

An addition of nZVI suspension containing 1 g of Fe(0) results in an increase in pH to the values between 3.7 and 7.1 depending on the dilution of the initial solutions (Fig. 4). Providing that the same amount of nZVI is used, the more the sample is diluted and hence the higher the initial pH is, the more pronounced is the effect of the pH change. This is further supported by a blank sample of demineralized water which displays pH close to a value of 10 due to a low buffering capacity (see Fig. 4).

Simultaneously, the addition of nZVI revealed a significant effect on the ORP values, which strongly depends on the mine water dilution. The effect of nZVI addition is most pronounced in the case of the least diluted sample B_5, where the ORP value decreased to around 0 mV compared to 477 mV for the non-diluted sample. An additional dilution does not have such a significant effect on ORP and its value changes only slightly.

3.3.2. Efficiency and mechanisms of the contaminant removal

ORP and pH changes induced by the nZVI addition are reflected in the changes of chemical composition of mine water samples. Sulphates, the most concentrated species in the studied mine water samples, are not significantly reduced (2–5%), contrary to the published data for a macroscopic iron (Wilkin and McNeil, 2003). Similarly, concentrations of non-reducible ammonium remain almost unchanged. On the other hand, aluminum is the macro-component displaying the highest change in the concentration. In the case of the undiluted sample B_0, the changes are negligible, but already for the sample B_5, dissolved aluminum decreased to 7.5% of its initial content and, for the more diluted sample B_{10}, the concentration dropped down even to 2% of the original value. Furthermore, the pH value increases above 4 due to the probable precipitation of aluminum (oxo)-hydroxide. Based on the geochemical modeling, aluminum potassium sulphate (alunite) can be also formed in a small quantity. This is in good accordance with the results published for nZVI as well as for macroscopic iron in general (Wilkin and McNeil, 2003).

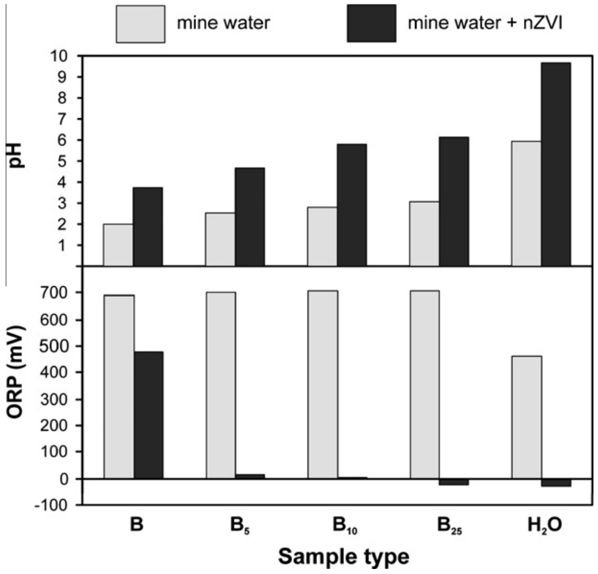

Fig. 4. The changes of pH and ORP in variously diluted acid mine water samples after addition of nZVI. The sample labeled as H_2O is distilled water used as a blank.

In principle, the toxicity of the studied acid mine water is considerably given also by the presence of various micro-components, i.e., by compounds being present at low concentrations but exhibiting a high toxicity. In general, the undiluted sample B_0 is affected by nZVI addition only slightly, B_5 and B_{10} show significant trends in

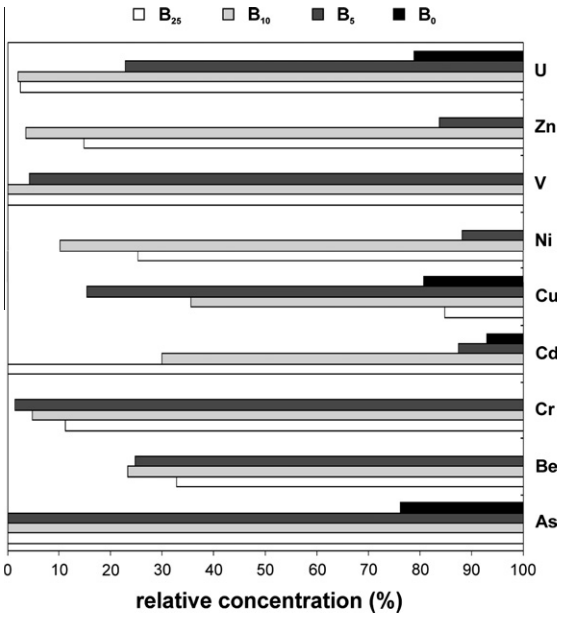

Fig. 5. Relative concentration changes of the monitored pollutants in sample B as obtained after addition of nZVI (1 g L^{-1}).

percentage of removed metals and the most diluted sample B$_{25}$ exposes lower relative removal (see Fig. 5), but it is due to lower initial concentrations and values close to the detection limits. We can subdivide these components into three groups according to the supposed mechanisms of their response to nZVI addition (Li and Zhang, 2007):

(A) Compounds (metals) that are reducible by nZVI into a less soluble and less toxic forms (i.e., Cr, Cu, U, V). For example, in the mine water with a low pH and high ORP, chromium occurs in the Cr(VI) form as chromates. By reaction with nZVI, chromates are reduced to Cr(III) and precipitate (Cao and Zhang, 2006; Li and Zhang, 2007; Xu and Zao, 2007).

Following this reduction route, chromium concentration decreases down to 1.5%, 4.8% and 11% of the initial values for the samples B$_{5}$, B$_{10}$ and B$_{25}$, respectively (see Fig. 5). Uranium(VI) in a form of uranyl (UO_2^{2+}) is reduced to a less soluble uranium(IV) ion (UO^{2+}), resulting in a decrease in concentrations down to 23%, 2.1% and 2.5% for the samples B$_{5}$, B$_{10}$ and B$_{25}$, respectively.

A similar response is expected for a group of metals whose standard electrode potential is above the Fe^0/Fe^{2+} pair potential value (Li and Zhang, 2007). In contrast to the previously mentioned compounds, Cu^{2+} is reduced by nZVI to zerovalent Cu^0 (Rangsivek and Jekel, 2005). This reaction probably takes place on the surface of nZVI particles (Li and Zhang, 2007) and the Cu concentration decreases down to 15% (B$_{5}$) and 35% (B$_{10}$) of the initial value. The relative decrease for B$_{25}$ is not so expressive, but the final Cu concentration (0.040 mg L^{-1}) is very similar to the value for B$_{10}$ (0.042 mg L^{-1}). A higher relative decrease in Cu concentration for the more concentrated samples would be related to a higher initial concentration. In this group, there could be also included other compounds that are reducible into zerovalent state by nZVI but, due to small differences in the standard electrode potentials, simultaneous sorption and precipitation processes of their cationic forms are more important in their removal mechanisms (Li and Zhang, 2007). For instance, this is the case of Ni.

(B) Compounds that are not chemically reducible by nZVI, but their concentrations are decreased due to the pH increase and subsequent precipitation, sorption and/or incorporation in the structure of the formed iron oxyhydroxides (i.e. Al, Be, Cd, Zn, Ni). In addition to Al (discussed above), Be is similarly sensitive to the change in pH according to the Reaction (1). At a higher pH, Be precipitates and, therefore, the concentration of Be decreased to about 30% for all three diluted samples.

An alternative possibility of microcomponent removal lies in their sorption on the surface and/or their incorporation in the structures of newly formed Fe-oxides and oxyhydroxides. Divalent cations like Cd^{2+} and Zn^{2+} insensitive to reduction by nZVI, are adsorbed or surface-complexed on iron oxyhydroxides (Li and Zhang, 2007). In our treated system, their concentrations decreased to 30% (Cd) and 3% (Zn) of the initial concentrations in the case of the sample B$_{10}$. For the most diluted sample, Cd is under the detection limit and Zn concentration is similar to that for B$_{10}$. The changes in the concentration of above mentioned Ni are smaller for more concentrated solutions, where the final concentrations are 88% (B$_{5}$), 10% (B$_{10}$) and 25% (B$_{25}$) of their initial values and again, the final concentrations for B$_{10}$ and B$_{25}$ are similar.

(C) Compounds with increasing solubility upon being reduced by nZVI and undergoing co-precipitation with the iron oxyhydroxides. This is the case of arsenic, which is less soluble in the As(V) form than in As(III) (Mok et al., 1988). On the contrary, arsenate(III) anions tend to be adsorbed and coprecipitated with hydrous ferrous/ferric oxides (Seidel et al., 2005; Jia et al., 2006; Mondala et al., 2006; Kanel et al., 2007), formed during oxidation of nZVI in water. Following this mechanism, concentrations of As decreased below the detection limits of ICP-OES (0.01 mg L^{-1}) after application of nZVI for all diluted samples.

Generally, the removal efficiency for various contaminants increases with increasing dilution factor, which is an important aspect from the viewpoint of large scale applications. A degree of dilution affects mainly the TDS parameter and initial pH of the solution. With increasing dilution (decreasing TDS), final values of pH and ORP are considerably changed and thus, the final chemical compositions of differently diluted solutions are different.

Finally, let emphasize the high reproducibility of the nZVI treatment as proved with the different sample of mining water (from the different location), which shows very similar results (Fig. A1 – Spplementary material).

3.4. Controlling the reaction kinetics through the surface stabilizing shell

In addition to a high efficiency of the contaminants removal, the reaction kinetics represents another important practical criterion for the *in situ* applicability of the nZVI, especially in the case of acid groundwater. In order to prevent a clogging of injection wells during the *in situ* process, the reactions of nZVI with contaminants should be rather slow. Simple monitoring of changes in pH and ORP, performed in this study, indicates relatively fast reactions after adding the commercial nZVI material composed of Fe(0) nanoparticles coated by the organic layer of polyacrylic acid. From this viewpoint, the Fe(0) nanoparticles coated by the compact FeO shell, developed in the laboratories of the research team (Filip et al., 2007), provide an effective solution of this task. The compact

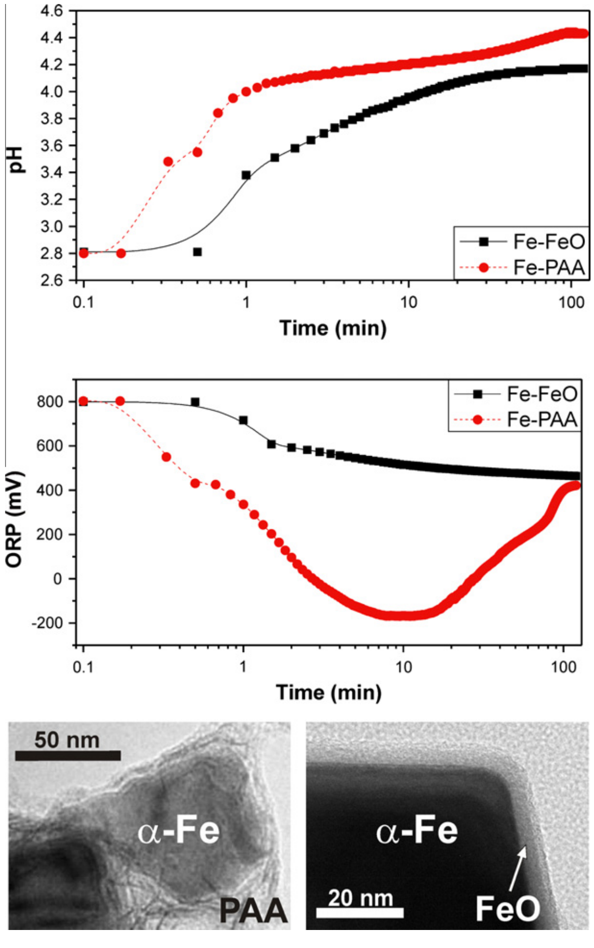

Fig. 6. The comparison of time dependences of ORP and pH in acid mine water sample (B$_{25}$) induced by addition of two kinds of nZVI stabilized by organic shell (polyacrylic acid, labeled Fe-PAA) and by inorganic shell (FeO, labeled Fe–FeO).

FeO shell surrounding nZVI particles effectively decelerates the reaction kinetics and changes in pH and ORP (see Fig. 6), as well as the precipitates formation. The finally achieved values of pH and ORP are nearly comparable, although the time courses, mainly in the case of ORP, are considerably different depending on the character of the shell (organic vs. inorganic). The reflection of different kinetics in efficiency of heavy metals removal will be further studied by the research team as well as deliverability of Fe/FeO particles. Due to acidic properties of the studied mine water, the compact FeO shell, acting as an inorganic and paramagnetic protection, can be rather advantageous. Paramagnetic shell could prevent the magnetic interactions among nZVI particles, which otherwise play an important role in the aggregation process (Phenrat et al., 2009a; Rosicka and Sembera, 2010). Moreover, the common polymeric shell is usually quickly dissolved in an acidic environment and there is a risk of the clogging of the injection wells due to the rapid precipitation of the secondary phases. From this point of view, the slower dissolution of the FeO shell (see Fig. 6) would be beneficial. Moreover, clay minerals, which usually complicate the transport properties of nZVI (Katsenovich and Miralles-Wilhelm, 2009), are almost fully dissolved in strongly acidic conditions (Altheide et al., 2010).

4. Conclusions

For the first time, nZVI nanoparticles were applied for the treatment of the real acid mine water sample originating from a mining area highly contaminated due to *in situ* chemical leaching of uranium ore. An application of nZVI leads to a considerable decrease in the contents of all the monitored contaminants (i.e., Al, U, V, Cr, Cu, Ni, Cd, Zn and As) as a common effect of the changed acid-basic and redox properties in the system. We studied an effect of sample dilution on the contaminant removal efficiency at one selected concentration of nZVI. The applied concentration of $1\ \mathrm{g\,L^{-1}}$ of nZVI was found to be sufficient for all diluted samples, but not for the undiluted one. In spite of assumed different mechanisms of the contaminant removal, the general positive decontamination effect is very promising for the consequent pilot and full scale applications, which are in progress. The study showed that the reaction kinetics can be dramatically affected by the character of the surface stabilizing shell. This would be beneficial mainly from the viewpoint of the large scale *in situ* applications. For these purposes, we plan to perform testing of deliverability of Fe/FeO core–shell particles as well as studying an effect of nZVI concentration.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.11.075.

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