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ARSENIC IMMOBILIZATION BY NANOSCALE ZERO-VALENT IRON

IMMOBILIZACJA ARSENU PRZEZ NANOŻELAZO NA ZEROWYM STOPNIU UTLENIEŃ

Abstract: Contaminated mine water from the Kank site (Czech Republic) containing arsenic at a concentration of approximately 85 mg/dm³ was tested in a reaction with elemental iron nanoparticles. In a reductive environment there was a reduction of As to the more soluble and toxic form of As(III) depending on the pH of the solution. Oxidation of elemental iron creates oxyhydroxides which incorporate As into their structure in the form of mixed complexes and thereby remove and bind dissolved As from the solution. The addition of 0.5 g/dm³ nZVI to the contaminated water leads to a significant decrease in ORP and concentrations of As to around the detection limit. The pH of the solution is not significantly affected by the addition of nZVI. The main competing anion for co-precipitation is represented by phosphates whose concentration after the addition of nZVI was reduced to 6.5% of the original value. The resulting precipitates were analyzed by XPS, XRF, XRD, SEM-EDX and Mössbauer spectroscopy. The presence of jarosite, Schwertmannite and also arsenic probably in the form of scorodite was confirmed.

Keywords: contaminated water, zero-valent iron, nZVI, arsenic

Introduction

Many pilot applications of iron nanoparticles have been performed throughout the world. The vast majority have focused on the removal of chlorinated hydrocarbons. One of the first pilot applications of this kind was carried out in 2001 at a site in Treton in the US, where the source of contamination was a release of a wide range of hydrocarbons (PCE, TCE, DCE, VC, chloroform, carbon tetrachloride) from a storage tank at an industrial plant [1].

The first pilot application of nanoparticles in the Czech Republic, and probably in the whole of Europe, took place in 2004 at the industrial site Spolchemie in Usti nad Labem, which was contaminated with chlorinated hydrocarbons, BTEX and mercury. The remediation again targeted the first of the aforementioned contaminants. Since then pilot applications have taken place at several sites in the Czech Republic, *eg* Kurivody, Rozmítal pod Tremsinem, Piest'any in Slovakia and full remediation applications in Spolchemie (Usti nad Labem), MARS (Svratka) and Písecna [2].

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In addition to the remediation of sites contaminated with chlorinated hydrocarbons, the use of nZVI is very effective for the treatment of inorganic contamination [3]. Examples include heavy metals [4] and anions. From the point of view of heavy metals hexavalent chromium and arsenic deserve special attention. The results of pilot testing of the use of nanoparticles for remediation of underground drinking water contaminated with arsenic in Canada were presented in 2010. Based on the results of column tests, the filter, filled with 50% sand and 50% iron nanoparticles, was integrated into the existing small biological water treatment system. This attained a 99.7% removal rate for arsenic with residual concentrations of less than 0.1 mg/dm^3 and a reduction in the concentrations of ammonia, iron and manganese. It can be assumed that the system is suitable for a small population of about 5,000 inhabitants [5].

Principle of interaction with arsenic

The behaviour of arsenic as a typical metalloid is somewhat different to most heavy metals. Its mobility in the environment and even in neutral pH stems from the fact that it occurs predominantly in an anionic form. Most toxic metals are precipitated under such conditions or are adsorbed on the surface of clay minerals or another solid phase in the form of cations [3]. In natural waters As occurs in two coexisting oxidation states. The transition between the two oxidation states of As^{3+} and As^{5+} can be made possible both chemically and biologically but the kinetics of the process is usually slow with equilibration being achieved in the order of weeks. This relates to the oxidation of As^{3+} and As^{5+} by dissolved oxygen and the reduction of As^{5+} to As^{3+} under anoxic conditions [2, 3]. Therefore, both the oxidation states of arsenic are usually present in groundwater simultaneously and their ratio varies according to the conditions, as shown in Figure 1. As^{5+} is more stable in neutral and alkaline waters under oxic conditions. In anoxic and anaerobic conditions it is reduced to As^{3+} which occurs at a normal pH of 5-9 as a neutral and strongly toxic arsenous acid H_3AsO_3 [2].

It is possible to use the redox action of elemental Fe to remove As from water. Because As^{3+} is five to twenty times more toxic than As^{5+} a decrease in redox potential due to the oxidation of Fe can theoretically lead to an increase in the toxic environment. In addition to the reduction in ORP corrosion also occurs, which leads to the formation of iron oxyhydroxides from which arsenic is usually very easily precipitated thus removed from water [6]. The effectiveness of the process is strongly dependent on the overall composition of the water. The most likely mechanism for the immobilization of arsenic is adsorption and co-precipitation with the oxides and hydroxides Fe^{2+} and Fe^{3+} .

In the first stage, water or dissolved oxygen causes corrosion of the metallic iron to produce the bivalent cation Fe^{2+} [3, 6]:

Subsequently, magnetite Fe_3O_4 , ferrous and ferric oxide are formed depending on the redox conditions and pH of the system according to the following equations:

Fig. 1. Eh-pH diagram for arsenic at a temperature of 25°C and arsenic activity of 10^{-3} mol/dm³

The final products of corrosion can be *eg* a mixture of amorphous iron oxyhydroxide and mineral phase - magnetite Fe_3O_4 , maghemite $\gamma\text{-Fe}_2\text{O}_3$ and lepidocrocite $\gamma\text{-FeOOH}$. Heterogeneous reactions of the corroding iron are complex and result in various adsorption surfaces for As^{3+} and As^{5+} . The products are the inner spherical surface complexes of As^{3+} and As^{5+} on oxyhydroxides Fe^{3+} [3, 6]:

The conditions for sorption of arsenic in an anoxic environment are not precisely described. Arsenic is adsorbed on the surface of iron in a non-specific form. In the presence of sulphate it probably forms sulphides of arsenic but the method of formation is not known [7]. Their preferential removal from the solution is stated when there is a presence of phosphates in water contaminated with arsenic. The first filtration through an activated mixture of metallic iron and sand in the column with an initial phosphorus concentration of 2 mg/dm³ and As^{3+} of 0.5 mg/dm³ completely removed the phosphorus but only 20% of the arsenic. The phosphorus also provides an inhibitive action in terms of corrosion. Silicates do not greatly affect the sorption behaviour of arsenic because the equilibrium sorption constants for hydrated iron oxides decrease in the order $\text{P} > \text{As}^{5+} > \text{As}^{3+} > \text{Si}$ [7].

Immobilization of arsenic can be significantly affected by the presence of chromium and humic acid in groundwater. In laboratory tests with modelled water there was

a decrease in the amount of removed As^{5+} of 27.9, 49.0 and 61.2% at concentrations of Cr(VI), 2, 5 and 10 mg/dm^3 , respectively. The presence of humic acid significantly inhibits the formation of iron oxyhydroxide probably due to the formation of soluble iron humate complexes. In the presence of hydrogen carbonates, the inhibitory effect of chromium on the removal of arsenic is suppressed.

Many studies deal with the possibilities of using elemental iron nanoparticles (nZVI) for the separation of arsenic from drinking water. A system was tested based on mixing the contaminated groundwater with iron nanoparticles iron fixed to a non-toxic biodegradable water-insoluble polymer (Ca-alginate). Removal of 85-100% of the initial concentration of 1-10 mg/dm^3 of As^{5+} was achieved within two hours, then the fixed nanoparticles were easily removed from the liquid stream [8].

The possibility of using iron nanoparticles was also tested for the specific conditions of mine water treatment from in-situ chemical leaching of uranium (Straz pod Ralskem). This water is strongly acidic and contains significant concentrations of aluminium, sulphate and a number of other contaminants, *eg* As, Be, Cd, Cr, Cu, Ni, U, V and Zn. Laboratory batch experiments showed a significant reduction in the concentration of the monitored pollutants due to the increase of pH and decrease of the redox potential of the system. The probable mechanisms are precipitation of cations in a lower oxidation state, precipitation due to the increase in pH, and co-precipitation with iron oxyhydroxides. From a practical point of view the possibility of controlling the reaction kinetics due to the stabilization of the polymer coating on the nanoparticles it is very important [4].

Several ongoing research projects deal with the fixation of iron nanoparticles on a suitable carrier (amphiphilic polysiloxane copolymer, SiO_2 or chitosan) to increase the reactive surface or prevent aggregation of the nanoparticles. The studies are currently in the phase of detailed characterization of the prepared materials and initial laboratory tests capturing arsenic or chromium [9-12].

Under laboratory conditions 99% arsenic adsorption was observed on the surface of iron in a period of several to tens of minutes [6]. By applying several concentrations of nanoparticles (0.5, 2.5, 5, 7.5 and 10 g/dm^3) to the solution at a concentration of As^{3+} 1 mg/dm^3 and pH 7 more than 80% of the total arsenic was removed after 7 minutes from all of the tested concentrations except 0.5 g/dm^3 and 99.9% after 60 minutes. Adsorption was best at a pH range of 4-10, whereby 88.6 to 99.9% of the arsenic was removed. At a pH less than 4 or greater than 10 there was a sharp decrease in adsorption, which may be caused by a suppressing of the dissociation of anions of arsenic and reduction in the adsorption on the heavily protonated surface of the hydrated iron oxides.

A similar effect of pH was observed for As^{3+} adsorbed on amorphous iron oxide, synthetic goethite and magnetite. The process is probably irreversible under normal conditions [13]. Some studies have reported up to 20% desorption for As^{5+} and 11% for As^{3+} for an input concentration of As^{3+} in contaminated water of 10 mg/dm^3 [6].

On freely corroding iron media, *eg* during the treatment of drinking water, there was no measurable reduction of dissolved As^{5+} to As^{3+} in water because under these conditions the redox potential is not sufficiently low. A reduction in the concentration of bound As^{5+} or As^{5+} dissolved in water in closed systems was observed after a few hours and in another study after 30-60 days [7, 14]. If the specific surface of nanoparticles of iron ranges between 25 to 30 m^2/g then it is increase by corrosion to approximately 37 m^2/g due to the action hydrated iron oxides.

In another study, arsenic was removed using laboratory prepared iron particles with a specific surface of $49 \text{ m}^2/\text{g}$ and size in the range of 20-40 nm. The effectiveness and adsorption kinetics were monitored in batch experiments. Arsenic was effectively eliminated at a pH of 7 and temperature of 20°C . The effectiveness of the removal of As^{3+} reached over 99% within 60 minutes. The measured equilibrium data correspond very well with the Langmuir and Freundlich sorption model, the regression coefficient was higher than 0.95 for both models. The adsorption capacity of the sorbent in a single layer reached 76.3 mg/g . Approximately 21% of the sorbed As^{3+} was desorbed by a solution of 0.1 mol/dm^3 of sodium hydroxide. The presence of the competing ions SiO_3^{2-} and H_2PO_4^- significantly reduced the amount of removed arsenic, the effect of other ions was minimal [15, 16].

Information on the maximum adsorption capacity of iron nanoparticles varies according to the test conditions. For example, a capacity of 4.4 mg/g of nanoparticles is given for a pilot test removing As^{3+} in column [17] or 3.5 mg/g of nanoparticles in batch laboratory experiments using the Freundlich adsorption isotherm calculation [18]. An order of magnitude higher capacity is given for the preceding oxidation of As^{3+} to As^{5+} by hypochlorite in water containing 1.9 mg/dm^3 of competitive phosphorus and 18 mg/dm^3 of silicon. The consumption of iron is increased by the presence of organic substances *ie* approximately 2 mg of Fe^{2+} to 1 mg dissolved organic carbon (DOC) [7].

This article focuses on research of the interaction of Fe nanoparticles with real contaminated water from the Kank site which contains As at concentrations of up to 85 mg/dm^3 . In addition to studying the changes in the composition of the water due to the action of various concentrations of nZVI, the solid precipitate containing As was analyzed in detail.

Experimental set-up

Laboratory tests of the effectiveness of iron nanoparticles in the immobilization of arsenic in a trivalent and pentavalent form were carried out in a batch arrangement for modelled and real contaminated water from the mining site of Kank near the town of Kutna Hora. Tasks included the optimization of nanoparticle dosage, examination of the effects of pH and an assessment of the effects of the co-precipitation of selected ions on the remedial process.

The Kank site near Kutna Hora is a former mining reserve and metallurgical plant, which was one of the largest producers of silver, copper, zinc and lead between the 13th and 16th century. In addition to the metals of interest the mined ore also contained arsenic, iron, cadmium and sulphur. Production was discontinued for economic reasons in 1991 and the mine was flooded. Pumped mine waters contain very high concentrations of trivalent arsenic, which are exceptional even on a global scale, and are typically between 65 and 85 mg/dm^3 based on the season and rate of precipitation. The pH value is approximately 3, the concentration of iron is more than $3,500 \text{ mg/dm}^3$, zinc 620 mg/dm^3 , sulphates $10,000 \text{ mg/dm}^3$, phosphate 0.7 mg/dm^3 , and aluminium 20 mg/dm^3 . The amount of copper, nickel and cadmium ranges in the tenths of mg/dm^3 . Total mineralization is $20,000\text{-}25,000 \text{ mg/dm}^3$. The concentrations of the individual components of the mine water vary in relation to the ongoing natural processes in the mining zone.

The materials used for the tests included iron nanoparticles from the company TODA and NANOFER 25S nanoparticles (NANOIRON, Czech R.), which are supplied as an aqueous dispersion stabilized with a biodegradable organic modifier. A solution was decanted from the iron nanoparticles and 20 g of the nanoparticles were weighed and quantitatively transferred into a container mixer. The resulting suspension was added to 100 cm³ of distilled water and agitated under a stream of argon for 10 minutes. Then the pH was adjusted to 7 by addition of hydrochloric acid. Concentrations of Fe⁰ were determined by dissolving the sample suspension of nZVI in concentrated hydrochloric acid and subsequently analysed using ICP (Optima 3000, Perkin-Elmer).

Contaminated water in an amount of 0.35 dm³ and a measured volume of the nZVI stock solution were transferred to Stohmann flasks, the air above the surface was displaced using argon (for at least 1 minute), and the flasks were immediately sealed and shaken on a laboratory shaker for 7 days. After the test, the samples were centrifuged for 10 minutes using a high frequency centrifuge at 9,000 rpm. Subsequently pH and ORP measurements were taken from the liquid, the colour was recorded and total and trivalent arsenic or sulphates and phosphates were analysed.

pH and ORP were measured using a combined pH electrode (Monokrystal TURNOV, Czech R.) on a HANNA (Czech R.) pH meter. Conductivity was determined according to ISO 7888:1985, sulphates were determined gravimetrically with barium chloride (according to TNV 757,476), phosphates by spectrophotometry with ammonium molybdate (ISO 6878), nitrates with liquid chromatography (EN ISO 10304-2) and fluoride after digestion and distillation (ISO 10359-2). Semiquantitative determination of elements (Al, Be, Ca, Cu, Cd, K, Mg, Si, Na, Ni, P, S, Mn, and Zn) was performed using ICP-OES, arsenic using the AAS method, and As³⁺ using the AAS hydride technique in a citrate buffer environment of pH 5.

Analysis of the solid phase (precipitates) of the Fe oxides was performed using X-ray photoelectron spectroscopy (XPS) with an aluminium and magnesium anode for identification of auger transitions. The spectra were calibrated at the C(1s) peak of C-C bonds. The sample was analyzed using X-ray powder diffraction (XRD) for the identification of all crystalline and amorphous phases, X-ray fluorescence spectroscopy (XRF) for the determination of the chemical composition of the sample and Mössbauer spectroscopy (MS) for the identification and quantitative determination of the representation of the iron-containing phase, including valent metal. Further measurements were carried out by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to determine the size of the morphological parameters of the particles in the sample.

Results and discussion

Groundwater from the contaminated area of Kaňk near Kutna Hora contains arsenic mainly in the form of As(III). Two samples were taken from the site, the first in the spring had an As(III) concentration of 84.1 mg/dm³, while the second in the autumn reached 73.9 mg/dm³. Despite preserving the water samples under an inert atmosphere there was a partial aeration and spontaneous oxidation reaction, which was confirmed by ORP. This led to the precipitation of arsenic on the corrosion products of the iron present in the water

and a significant reduction of concentrations in the solutions (approximately 6 mg/dm³ for the spring water and 24 mg/dm³ for the autumn water).

Application of nZVI

The first test monitored the dependence of arsenic concentrations on the dose of nZVI (TODA) (Fig. 2, Table 1). The addition of nZVI in the target concentrations of 0.1 to 1.4 g/dm³ resulted in an increase in pH from approximately 2.5 to 4.5 based on the dose of iron and a reduction of ORP from 600 mV to about 350 mV.

Fig. 2. Dependence of pH, ORP and As on the concentration of nZVI

Table 1

Effectiveness of the immobilization of As

Sample		CE 26/0	CE 26/1	CE 26/2	CE 26/3	CE 26/4	CE 26/5	CE 26/6	CE 26/7
Con. Fe onset	[g/dm ³]	-	0.11	0.23	0.45	0.69	0.89	1.17	1.40
pH	[-]	2.6	2.5	2.5	2.8	4.2	4.3	4.4	4.6
ORP	[mV]	619	610	601	394	325	340	299	261
Con. As _{total}	[mg/dm ³]	5.18	3.96	2.17	0.19	0.03	0.02	0.02	0.01
Con. As(V)	[mg/dm ³]	5.15	3.94	2.26	0.18	0.01	0.01	0.01	0.01
Effectiveness of removal of As _{total}	[%]	-	23.6	58.1	96.3	99.4	99.6	99.6	99.8
Effectiveness of removal of As ⁵⁺	[%]	-	23.5	58.1	96.5	99.8	99.8	99.8	99.8
Con. SO ₄ ²⁻	[g/dm ³]	10.9	11.0	10.5	11.0	10.8	11.1	10.5	11.0
Con. NO ₃ ⁻	[mg/dm ³]	4.54	4.18	1.95	1.44	1.08	1.20	1.44	0.66
Con. PO ₄ ³⁻	[mg/dm ³]	5.66	4.57	2.50	0.42	0.37	0.38	0.37	0.37

The nZVI dose needed for immobilization of arsenic in real waters is heavily dependent on the concentration of iron capable of competitive sorption and co-precipitation with iron oxohydroxides. In the test waters the nZVI concentration needed to eliminate the As was approximately 0.5 g/dm^3 , which led to a residual concentration of arsenic around the detection limit, *ie* approximately 20 µg/dm^3 . Interestingly, at this concentration of nZVI the ORP decreased significantly (about 300 mV) but there was a negligible change in pH (an increase at higher concentrations of nZVI of about 3 g/dm^3). The main competing anions for co-precipitation are phosphates whose concentration after the addition of nZVI reduced to 6.5% of the original value, *ie* from 5.66 to 0.37 mg/dm^3 . Again, it is interesting that the effective dose of nZVI of 0.5 g/dm^3 causes a significant decrease in the concentration of phosphates. Similarly there was a significant loss in the amount of nitrate in the solution, up to 85%, during immobilization. The competitive ability of sulphates at concentrations of 10 g/dm^3 was not proven.

Influence of pH

In a further experiment, the influence of pH on the concentration of arsenic by artificially fixing the pH was monitored. In a series of ten flasks with 200 cm^3 of mine water the pH was adjusted from 1 to 10. The changes were again controlled and corrected and 7 days after the test the concentrations of As^{3+} , total arsenic and ORP were measured. Table 2 shows the test results with the mine water collected in autumn. Samples labelled /0 are of mine water without pH adjustment. The first result is a change in ORP depending on the pH (Fig. 3). By increasing the pH the ORP decreases more or less linearly, which corresponds approximately to the constant ratio between the different oxidation states of As. The difference between the spring and autumn water is relatively small and the dependence of ORP on pH is approximately the same.

Fig. 3. ORP dependency on fixed pH

At a pH of 1 and 2 there is a dissolution of bound As to the solution and the majority remains in the solution in the form of As(III). From around pH 3 a solid phase is formed composed primarily of metal oxides in which the arsenic was also bound. The residual concentration in the solution decreased and in the alkaline environment ranged in tenths of mg/dm^3 . The amount of As(III) in the solution decreases at first and increases again from pH 5 (except for pH 9, where the concentration of As is very small and the determination effort is extreme).

Table 2
Mine water collected in autumn, concentration of arsenic in $[\text{mg/dm}^3]$ and ORP in $[\text{mV}]$

Parameter	CE 63/0	CE 63/1	CE 63/2	CE 63/3	CE 63/4	CE 63/5	CE 63/6	CE 63/7	CE 63/8	CE 63/9	CE 63/10
pH onset	3.0	1.1	2.1	3.0	4.0	5.0	6.1	7.0	8.0	9.1	10.0
pH end	2.8	1.1	2.1	3.0	4.1	5.0	6.0	7.0	8.0	9.1	10.1
ORP end	574	604	605	571	458	353	213	86	-264	-374	-400
Con. As_{total}	24.4	88.3	64.5	22.3	3.12	3.81	3.08	3.85	0.58	0.14	0.51
Con. As(III)	9.8	53.1	46.5	10.4	0.16	1.27	2.18	2.98	0.37	0.03	0.36
As(III) [%]	40	60	72	47	5	33	70	77	64	21	70

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Table 3
Elemental composition of precipitates in wt.% (sample labelled 63/0 is the precipitate of the relevant mine water without pH adjustment, the next numbers after the backslash indicate the adjusted pH values). The remainder to 100% are light elements (especially oxygen)

Element Exp.	Composition [wt%]								
	63/0	63/3	63/4	63/5	63/6	63/7	63/8	63/9	63/10
Si	0.36	0.27	0.26	0.37	1.00	0.98	0.64	0.48	0.41
P	0.20	0.16	0.08	0.06	0.03	0.01	6.41	5.95	5.47
S	7.41	7.67	6.59	6.51	7.68	6.92	0.05	0.08	0.08
Cl	0.30	0.11	0.06	0.06	0.07	0.07	0.02	0.02	0.03
K	0.05	0.05	0.03	0.02	0.04	0.03	0.39	0.55	0.93
Ca	0.61	0.34	0.47	0.55	0.89	0.53	0.09	0.37	1.11
Mn	0.01	0.02	0.02	0.03	0.09	0.07	47.4	49.0	47.7
Fe	39.3	40.1	43.6	44.8	43.6	45.9	8.00	5.90	5.70
Zn	0.07	0.12	0.28	0.52	1.37	5.43	1.67	1.13	1.05
As	16.2	15.4	13.3	10.3	6.90	3.46	0.64	0.48	0.41
Mg	-	0.21	-	-	0.32	0.22	0.15	0.24	0.98
Na	-	-	0.34	0.45	0.21	0.38	0.78	2.20	2.90
Al	-	-	0.44	1.39	1.40	0.83	0.22	0.11	0.10

The resulting precipitates were filtered, dried, and subjected to X-ray spectral and X-ray diffraction analysis. The precipitates were predominantly of an amorphous character

with the appearance of phases based on FeO , As_2O_5 , As_2O_3 , ZnO_2 and mixed oxides of iron and arsenic. The elemental composition of the precipitates is shown in Table 3. The variable composition of the precipitates is noticeable depending on the pH of the solution with the most relevant transition being between pH 7 and 8. The proportion of iron significantly decreased with increasing pH from approximately 40 to 6 wt.%, while the representation of manganese increased from hundredths to almost 50%. The amounts of phosphorus rose and sulphur fell around one order of magnitude with increasing pH, respectively. The amount of arsenic decreased from approximately 15% at pH 3 to up to 0.4% at pH 10, which is due to the increased amounts of precipitates formed.

The development of pH and ORP indicates that the concentration of arsenic in the solution is controlled by the product of the solubility of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). The gradual decrease in pH and increase in ORP occurs due to oxidation of divalent to trivalent iron, and its precipitation in the form of scorodite (Fig. 4). The overall reaction of iron and arsenic can be described as follows:

Figure 4 shows that the mine water from the Kank site (original and diluted water) is on the border between scorodite and corresponding forms of dissolved species of H_2AsO_4^- and H_3AsO_4 .

Fig. 4. Stability diagram for arsenic in mine water from the Kank site. Activity of the main components is: $\text{Fe}^{2+} = 1.0 \cdot 10^{-2}$, $\text{SO}_4^{2-} = 2.0 \cdot 10^{-2}$, $\text{H}_2\text{AsO}_4^- = 2.0 \cdot 10^{-4}$. The squares represent undiluted mine water. The circles represent mine water diluted 1:1. The triangles represent mine water diluted 1:3

Study of the solid products of arsenic immobilization

Mine water from the site is subject to oxidation reactions on contact with the atmosphere which results in partial spontaneous immobilization of arsenic. It co-precipitates with its corrosion products of iron present in the water and reduces the concentration of iron in the solution. The equilibrium value after precipitation was pH 3.4, the total content of As was 77.4 mg/dm^3 , As(III) was 63.2 mg/dm^3 and total content of Fe was 3.240 mg/dm^3 . The surface composition of the resulting solid phase, as determined by XPS with an Al and Mg anode, is shown in Figure 5 and Table 4.

Table 4

Elemental composition of soil samples [atomic %]

Element (orbital)	O(1s)	C(1s)	Fe(2p)	As(3d)	S(2p)
Concentration	54	26	8	8	3

Fig. 5. Overview of spectra with the identification of elements

Measurement of the individual spectra of major peaks showed that the position of peak O(1s) at 531.8 eV corresponds to metal oxides, in this case possibly oxides of iron and arsenic. The O(1s) peak showed only one component and it is not possible to distinguish whether the oxygen is bound to the iron or arsenic. Peak Fe(2p) at 712.2 eV corresponds to iron in the form of a natural oxide. The component has a greater half-width (3.3 eV) so it is probably a mixture of iron oxides Fe_2O_3 and Fe_3O_4 . According to available literature, the peak of arsenic As(3d) at 45.6 eV corresponds to arsenic bound to oxygen, *ie* As_2O_5 . The compound Na_2HAsO_4 or ions derived from this compound are also mentioned in scientific studies dealing with the analysis of sediments or rocks from mines containing arsenic. The

presence of sodium on the surface of the sample could not be demonstrated by the measurement, and hydrogen was not observable using the XPS technique. If arsenic is present in the form of such a compound, it cannot be distinguished from purely oxide forms using this method. Available sources agree that a component with a binding energy of 45.6 eV corresponds to pentavalent arsenic. If the arsenic is in a sulphide form, As(3d) would have to be at a value between 43.0 and 44.0 eV in the high resolution spectrum. This was not observed. Considering the half-width of the As(3d) peak (1.9 eV) arsenic is not likely to occur in any other distinguishable type of bond.

Three components are observable in the decomposition of the C(1s) peak. In addition to the C-C bonds used for calibration the other two components are probably carbon and oxygen bonds. Due to the low intensity of the signal of the C(1s) peak it is necessary to consider this decomposition as being approximate. No component corresponds to the carbides of iron or arsenic in the decomposition of the C(1s) peak. For the carbide of arsenic no information was found in the literature on the energy in the C(1s) peak, but for all other metal carbides, the C(1s) peak contains a component with a lower binding energy of between 282 to 284 eV and such a component in the C(1s) peak was not observed.

The precipitates in the sample were identified by X-ray powder diffraction (XRD) as being crystalline phase jarosite ($\text{K}(\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6)$), natrojarosite ($\text{Na}(\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6)$) and Schwertmannite ($\text{Fe}^{3+}_{16}(\text{OH}.\text{SO}_4)_{12-13}\text{O}_{16} \cdot 10-12\text{H}_2\text{O}$). The results are consistent with the X-ray fluorescence spectroscopy (Table 5). Incorporation of arsenic cannot be confirmed by this method.

The result of the Mössbauer spectroscopy measurement (Fig. 6) is in accordance with the X-ray powder diffraction, whereby the jarosite (40 atom.%) and Schwertmannite (60 atom.%) phases were identified.

Table 5

Chemical composition of the precipitates (XRF method)

Parameter	Concentration [%]	Parameter	Concentration [ppm]
Fe ₂ O ₃	57.040	Cu	33
SO ₃	11.940	Zn	875
As ₂ O ₃	6.648	Ga	34
K ₂ O	1.300	Rb	43
MgO	0.598	Sr	166
Na ₂ O	0.584	Y	2
CaO	0.180	Zr	6
ZnO	0.145	La	114
SiO ₂	0.105	Pb	51
Cl	0.037		
P ₂ O ₅	0.028		
SrO	0.028		
MnO	0.026		

The precipitate sample for measurement by scanning electron microscopy was mounted on double-sided adhesive carbon tape and measured without plating. The accompanying EDX spectra on Figure 7 only show the presence of the previously detected elements. A different distribution of the arsenic on the surface of the sample and in the internal structures was not demonstrated.

Fig. 6. Mössbauer spectrum (red line) of the sediment sample (measured at room temperature). The green line is the Schwertmannite spectrum and the blue line is the jarosite

Fig. 7. SEM microscope and EDX spectrum recording

Conclusions

The work focussed on the immobilization of arsenic mine waters from the Kaňk site in the Czech Republic. This water has a very high content of dissolved arsenic, which based on the conditions can be up to 85 mg/dm^3 . Tests were performed with the addition of varying amounts of nZVI of from 0 to 1.4 g/dm^3 . The results showed that the effective concentration of nZVI is approximately 0.5 g/dm^3 , which leads to residual concentrations of arsenic at the level of the detection limit. Interestingly, at this concentration ORP decreased significantly (about 300 mV) but there was only a negligible change in pH. Phosphates are the main competing anion for co-precipitation whose concentration reduced to 6.5% of the original value after the addition of nZVI. Again, it is interesting that the effective dose of nZVI of 0.5 g/dm^3 causes a significant decrease in the concentration of phosphates. Similarly, during immobilization there was a significant decrease in the amount of nitrates in the solution, *ie* up to 85%.

The issue of the effect of pH on the concentration of various forms of arsenic in the solution was addressed in a separate part of the laboratory tests. Arsenic in the pentavalent form is stable in a wide range of pH values in contact with the atmosphere, with trivalent arsenic undergoing gradually oxidation to the pentavalent form. In the presence of sufficient oxygen the equilibrium is the same as in the case of the dissolved pentavalent form. In the absence of oxygen for oxidation both forms remain in the solution. Oxidation of As^{3+} to As^{5+} is slow, which may be caused by the slow interaction of arsenic with oxygen or by slow the diffusion of oxygen into the water. The fastest oxidation was observed at a neutral pH.

Attention was also paid to the study of solid products of the immobilization of arsenic in mine water from the Kaňk site. Special analysis using X-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy, scanning electron microscopy (SEM) and X-ray spectral (XRF) and X-ray diffraction (XRD) focused on the surface of the precipitates and identification of the oxidation state of arsenic. The results of each method are identical or complementary. Measurement of a sample of sediment confirmed the presence of jarosite, Schwertmannite as well as arsenic. The incorporation of arsenic into the structure of jarosite and Schwertmannite was not clearly demonstrated despite the observed shifts in the values of quadrupole splitting from the tabulated values during the Mössbauer analysis.

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IMMOBILIZACJA ARSENU PRZEZ NANOŻELAZO NA ZEROWYM STOPNIU UTLENIEŃ

Abstrakt: W Kańk (Czeska Republika) znajduje się zanieczyszczona woda z kopalni, zawierająca arsen o przybliżonym stężeniu 85 mg/dm³. Została ona poddana reakcji z nanocząteczkami żelaza na zerowym stopniu utlenienia (nZVI). W zależności od pH roztworu w środowisku redukcyjnym przebiegała reakcja redukcji As do bardziej rozpuszczalnej i toksycznej formy As(III). Poprzez utlenienie elementarnego żelaza powstają tlenowodorotlenki, łączące się z As w postaci kompleksów mieszanych, tym samym usuwając As z zanieczyszczonego roztworu. Dodatek 0,5 g/dm³ nZVI do zanieczyszczonej wody prowadzi do znaczącego spadku wartości ORP i obniżenia stężenia As do granic wykrywalności. Dodatek nZVI nie ma znaczącego wpływu na wartość pH roztworu. Głównym anionem konkurującym w współstrąceniu As jest anion fosforanowy, którego stężenie po dodaniu nZVI zmniejszyło się do 6,5% w porównaniu do wartości wyjściowej. Powstały osad został poddany analizie metodami: XPS XRF, XRD, SEM-EDX i spektroskopią Mössbauerowską. Została potwierdzona obecność jarosytu, schwertmannitu oraz arsenu prawdopodobnie w postaci skorodytu.

Słowa kluczowe: zanieczyszczona woda, nanożelazo na zerowym stopniu utlenienia, nZVI, arsen