

Use of the ferrates (Fe^{IV-VI}) in combination with hydrogen peroxide for rapid and effective remediation of water – laboratory and pilot study

Petr Lacina and Scott Goold

ABSTRACT

In recent years, particles of iron in higher oxidation states (Fe^{IV-VI}), commonly called ferrates, have been presented theoretically as very effective oxidants. They can potentially be used for elimination of a wide range of organic and inorganic contaminants. However, so far the majority of applications have been carried out only as laboratory tests using model samples in many cases. The application of ferrates in remediation programs has so far proved to be more complicated with results failing to meet expectations. Therefore there is a necessity to consider the suitability of their use or consider their possible combination with other agents in order to reach required removal efficiencies in remediation. This study is focused on laboratory experiments using industrial groundwater leading to the proposal of a pilot field application realized as an ex-situ remediation. The combination of ferrates with hydrogen peroxide was used in this study in order to enhance the removal efficiency during pilot remediation of groundwater strongly contaminated by a wide range of organic contaminants. This combination has been shown to be very effective. During the 24-hour reaction time the majority of detected contaminants were removed by approximately 60–80%. Moreover, the unpleasant odor of the water was suppressed and suspended particles were removed by the flocculation effect of ferric sludge.

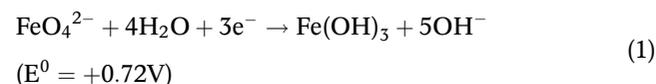
Key words | ferrates, groundwater, hydrogen peroxide, oxidation, radical oxidation, remediation

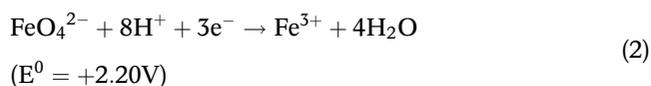
Petr Lacina (corresponding author)
 Scott Goold
 GEOTest, a.s.,
 Smahova 1244/112,
 627 00 Brno,
 Czech Republic
 E-mail: lacina@geotest.cz

INTRODUCTION

In recent years, particles of iron in higher oxidation states (Fe^{IV-VI}), commonly called ferrates (Sharma *et al.* 2005; Yates *et al.* 2014a), have been presented as a very effective remediation material in an effort to achieve greater utilization in remediation practice. The reasons are not only the relatively strong oxidizing properties capable of degrading a wide range of environmental contaminants, but also that they are environmentally friendly, which is a priority requirement for newly introduced remediation technologies and materials. During reactions ferrates are reduced to Fe^{III} and depending on the reaction conditions also to Fe^{II} (NanoIron co. 2015). In an aqueous environment various polyhydroxy complexes and hydroxides of iron are created, which are stable forms of iron commonly found in nature (Yates *et al.* 2014a) and therefore the environment is not burdened by other xenobiotics or potentially toxic products (Jiang & Lloyd 2002; Sharma 2002, 2011; Sharma

et al. 2005; Pucek *et al.* 2013). Strong oxidizing properties of ferrates are given by their high oxidation state. In the water environment they are unstable and they tend to rapidly reduce to stable forms of iron. During the reactions, ferrates act as a strong electron acceptor which removes electrons from their surroundings. This process leads to oxidation of their surroundings and simultaneously reduction of ferrates to stable forms of iron. Previous studies have shown that Fe^{VI} can be a stronger oxidant than ozone under certain conditions. Its redox potential (Eh) ranged from 0.72 V in basic medium (Equation (1)) to 2.20 V in acidic medium (Equation (2)) (Sharma *et al.* 2005, 2014; Tiwari *et al.* 2006; Pucek *et al.* 2013)





The oxidation efficiency of ferrates can be further supported by altering the pH or by the addition of oxidizing agents such as e.g., hydrogen peroxide. Ferrates are presented as an effective remediation material for a wide range of organic (Prucek *et al.* 2013; Sharma *et al.* 2014; Yates *et al.* 2014b) and inorganic (Filip *et al.* 2011; Sharma 2011; Machala *et al.* 2014) contaminants but also as an effective disinfectant agent (Jiang & Wang 2003; Sharma *et al.* 2005, 2014; Yates *et al.* 2014a). Moreover, the final products of their degradation in the water environment may serve as an effective adsorbent of oxidized contaminants as well as an effective coagulant and flocculant (Bartzatt *et al.* 1992; Jiang & Lloyd 2002; Lee *et al.* 2003, 2009; Filip *et al.* 2011; Yates *et al.* 2014a).

However, the real application of ferrates seems to be more complicated than expected. Ferrates exhibit strong oxidation abilities but only in the acidic environment where they have a very low stability. In strongly polluted water they are rapidly degraded without significant elimination of environmentally important organic contaminants. Their efficiency strongly depends on the conditions in the water environment and the results can vary. Many practically focused applications of ferrates thus can end in failure. Therefore there is a necessity to consider the suitability of their use or consider their possible combination with other agents (e.g., hydrogen peroxide) in order to reach required removal efficiency. Practical applications of ferrates would also be preceded by laboratory experiments on particular waters to be cleaned in order to verify the suitability of their use.

This study is focused on the practical pilot application of ferrates in combination with hydrogen peroxide in order to enhance the removal efficiency during the remediation of real groundwater. Laboratory experiments on real groundwater from two different localities were realized previously. One of these localities was selected for subsequent pilot verification of obtained results. On the basis of obtained results from laboratory experiments a field pilot application was proposed and realized as an ex-situ remediation in the area of an industrial factory in the Czech Republic.

METHODS

Materials and chemicals

Ferrates – powdery composite ENVIFER (LAC Ltd Co., Czech Republic) – contained iron in higher oxidation

states in the following forms: $\text{K}_2\text{Fe}^{\text{IV}}\text{O}_3$, $\text{K}_3\text{Fe}^{\text{V}}\text{O}_4$ and $\text{K}_2\text{Fe}^{\text{VI}}\text{O}_4$ (total content of Fe \approx 18.4 mass%). Analysis by Mössbauer spectroscopy showed the following proportion of oxidation states: $\text{Fe}^{\text{IV}} < 3$ mol%, $\text{Fe}^{\text{V}} \approx 57 \pm 3$ mol%, $\text{Fe}^{\text{VI}} < 3$ mol%. The composite additionally contained 19 ± 3 mass% of K_2O as a result of the production processes. In water, Fe^{V} is disproportionated to Fe^{VI} and Fe^{III} (Kokar-ovtseva *et al.* 1972; Kolar *et al.* 2015). The value of ratio $\text{Fe}^{\text{VI}}/\text{Fe}^{\text{V}}$ of this product after dissolution in water was 0.81. 1 g of ENVIFER dissolved in water thus created approx. 85 mg of Fe^{VI} . Other chemicals used were as follows: technical hydrogen peroxide 35% (EURO – Sarm Ltd, Czech Republic) and sulfuric acid (Chromservis Ltd, Czech Republic).

Laboratory tests

Laboratory tests were carried out as batch tests with real groundwater from two localities, one of which was chosen for the following pilot field application and the verification of the results obtained during these tests. During these experiments, changes in the concentration of priority pollutants were monitored. Water from the first locality (locality A) was strongly contaminated by chlorinated ethenes (CEs) – total value of CEs (Σ CEs) ranged from 60 to 70 mg/l. Water from the second locality (locality B) was collected from the area where the field verification of laboratory results was planned. Significant monitored contaminants in this case were benzene, toluene, ethylbenzene and xylenes (BTEX). The main goal of these tests was to verify and compare the efficiency of ferrates and the efficiency of ferrates in combination with hydrogen peroxide under various conditions to find the most suitable and efficient method of the pilot application for the ex-situ remediation.

During batch tests, closable reagent bottles of about 1 litre volume were used and filled with 1 litre of tested water. Two parallel sets each with six reagent bottles were prepared. The bottles were labeled as sp. 1–6. The first set (set A) was prepared with water from locality A, and the second set (set B) was prepared with water from locality B. Both sets included various combinations of possible applications. Each of the bottles represented one type of sample prepared in the following way:

- sp. 1 Ferrates (0.5 g/l) + pH adjustment ≈ 3 + H_2O_2 (5 ml/l),
- sp. 2 Ferrates (0.5 g/l) + H_2O_2 (5 ml/l),
- sp. 3 Ferrates (0.5 g/l) + pH adjustment ≈ 3 ,
- sp. 4 Only a dose of ferrates (0.5 g/l),

- sp. 5 Only a dose of H₂O₂ (5 ml/l),
 sp. 6 Blank.

The dose of the composite ENVIFER was 0.5 g/l, which corresponds to the doses commonly used during laboratory tests (Prucek *et al.* 2013). The composite was dosed as a fine powder. After weighing on an analytical balance, it was quantitatively transferred into a reagent bottle with tested groundwater. Then the bottles were enclosed and their content was mixed vigorously for 30 min with the use of magnetic stirrers. After this time, the following steps in the selected samples were done: pH adjustment by 50% H₂SO₄ (sp. 1 and 3) and then application of 5 ml hydrogen peroxide (sp. 1, 2 and 5). Closed bottles with prepared water samples were put on a shaker and shaken at regular intervals so that after every 6 hours they were shaken for 5 min. At regular intervals, the lids of the bottles were opened to release the accumulated gases (mainly sp. 1 and 2). Samples for analysis (each about 100 ml) were collected after 24, 48, 96, and 168 hours. Each collected sample was filtered through a filter paper to remove the sludge before further processing. The treatment of the samples with final analysis using headspace gas chromatography–mass spectrometry (GC–MS) was carried out by accredited laboratories. All samples were processed within 24 hours after collection.

Pilot field application

For pilot validation of results obtained from the laboratory tests, an area of an industrial company was chosen in the Czech Republic (locality B). Groundwater in this locality is a very complex matrix contaminated with a wide range of organic contaminants. The most important groups are aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes) and chlorinated aromatic hydrocarbons (chlorobenzene, o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene). During the initial monitoring of raw groundwater the values of qualitative parameters determined were as shown in Table 1. A list of detected contaminants and their concentration level before the test can be seen in Table 2.

Pilot verification of results by ex-situ method was carried out in July 2014 as a container test using a 1,000 litre intermediate bulk container (IBC) made of high density polyethylene (HDPE). The container was filled with 900 l groundwater pumped out from a borehole, which was located in the selected area. In the first step, 350 g of the ENVIFER (≈ 0.4 g/l ≈ 34 mg Fe^{VI}/l) was applied into the container and then the content was mixed vigorously for 15 min. After a visible reduction of all dosed ferrates, when the colour of the

Table 1 | Qualitative parameters of the raw groundwater

Parameter	Value	Unit
pH	6.29	
Conductivity	4,270	μS/cm(20 °C)
Acidic neutralizing capacity (ACN _{4.5})	17.50	mmol/l
Chemical oxygen demand (COD _{Cr})	1,090	mg/l
Biochemical oxygen demand (BOD ₅)	551	mg/l
Total hardness	8.05	mmol/l
NH ⁴⁺	37.8	mg/l
Total inorganic nitrogen	10.66	mg/l
Sulfates	855	mg/l
Chlorides	504	mg/l
Nitrates	<3.0	mg/l
Nitrites	<0.10	mg/l
Phosphates	2.92	mg/l
Mineralization	3,537	mg/l
Halogenated organic compounds (AOX)	6.42	mg/l

Table 2 | The list of contaminants detected in groundwater and their concentration level (c) before the start and at the end of the pilot test

Contaminant	Concentration before test (μg/l)	Concentration after test (μg/l)
benzene	340 ± 85	170 ± 42
toluene	363,000 ± 90,700	103,000 ± 25,700
Σxylenes	480 ± 120	130 ± 32
1,2,4-trichlorobenzene	62 ± 15	18 ± 4
o-dichlorobenzene	19,000 ± 4,700	5,800 ± 1,400
m-dichlorobenzene	3,700 ± 920	970 ± 240
p-dichlorobenzene	4,900 ± 1,200	1,300 ± 320
Σchlorinated ethenes	520 ± 130	<2
ethylbenzene	140 ± 35	44 ± 11
chlorobenzene	2,900 ± 720	800 ± 200
naphtalene	3,600 ± 900	1,200 ± 300
phenol	3.0 ± 0.7	<2.0
Σcresols	50 ± 12	220 ± 55
Σdichlorophenols	9.0 ± 2.2	8.1 ± 2.0
Σchlorophenols	12.0 ± 3.0	<2.0
aniline	730 ± 180	320 ± 80
N-ethylaniline	4.6 ± 1.1	4.2 ± 1.0
2,4,6-trimethylaniline	130 ± 32	<2
nitrobenzene	2,100 ± 520	2,300 ± 520

water had changed from violet to orange, the first dose of hydrogen peroxide with a volume of 4.5 l (≈ 5 ml/l) was

applied. The content of the container was stirred with a submersible pump in regular intervals (30 min). 4 hours after the first dose of hydrogen peroxide was applied the second dose was applied, again an amount of 4.5 l (≈ 5 ml/l). The test was terminated after a further 19 hours. The entire reaction process including the application of ferrates and the two following applications of hydrogen peroxide thus lasted 24 hours. A concise time schedule for the pilot test with particular operations is shown in Table 3. Throughout the test significant physical-chemical parameters notably pH, Eh and concentration of dissolved oxygen were observed. For the measurement of selected parameters, a multiparameter probe Aquaread AP-2000 (Aquaread[®] Ltd, UK) was used.

Before starting the test a 20 litre canister of the same material as the IBC was filled with the groundwater. This canister represented a blank sample. In this canister no applications were done, only mechanical and measuring

tasks (i.e., mixing, sampling and measurements of selected physical-chemical parameters) with the same timetable as in the case of the IBC.

RESULTS AND DISCUSSION

Results of laboratory tests

Laboratory tests were carried out with groundwater from two localities, one of which was selected for the pilot test. During the laboratory tests, changes in the concentration of priority contaminants, depending on the reaction time and the type of the prepared sample, were monitored. In the case of the test with groundwater from locality A (set A), the change of total concentration of CEs (Σ CEs) was observed (Figure 1). In the case of the tests with groundwater from locality B (set B), the change in the total concentration of benzene, toluene, ethylbenzene and xylenes (Σ BTEX) was observed (Figure 2). Figures 3 and 4 show the overall removal efficiency of priority contaminants after 24 hours for each of the prepared samples.

Obtained results from both laboratory tests showed that ferrates alone or hydrogen peroxide alone did not cause a significant decrease in targeted contaminants in comparison with the blank sample (sp. 4, 5 and 6). In such heavily polluted groundwater, ferrates were degraded rapidly and

Table 3 | The time schedule of the pilot test with substantial operations

Time (hrs)	Operation
0	Filling the container (900 l)
0.5	Application of the ferrates (350 g)
1.25	Application of 1st dose of H ₂ O ₂ (4.5 l)
5	Application of 2nd dose of H ₂ O ₂ (4.5 l)
24	Termination of the test

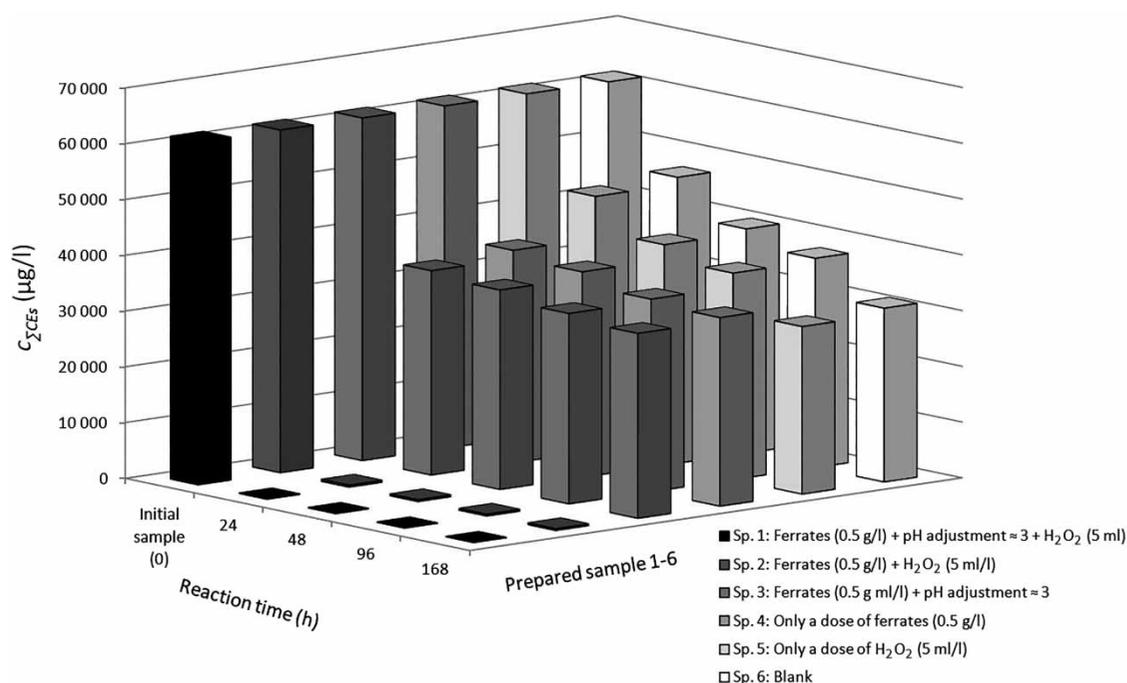


Figure 1 | The concentration change of Σ CEs during the laboratory tests (set A).

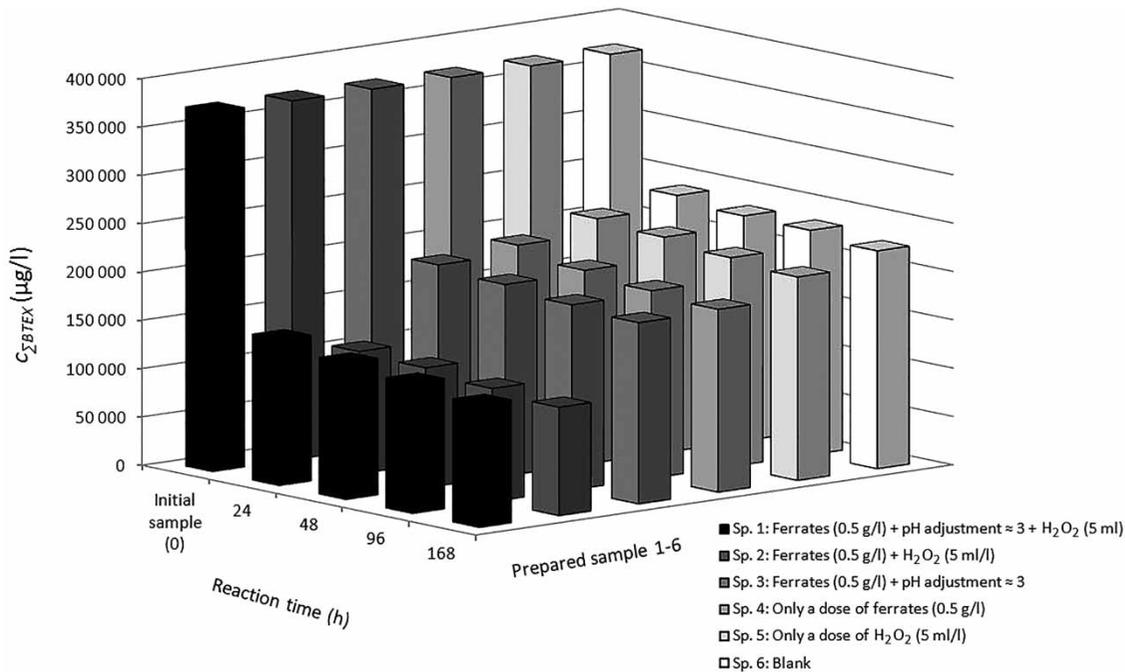


Figure 2 | The concentration change of Σ BTEX during the laboratory tests (set B).

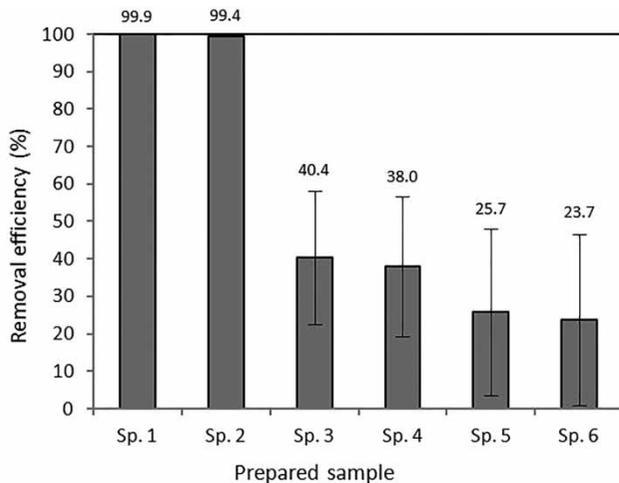


Figure 3 | Removal efficiency of Σ CEs after 24-hour reaction time (set A).

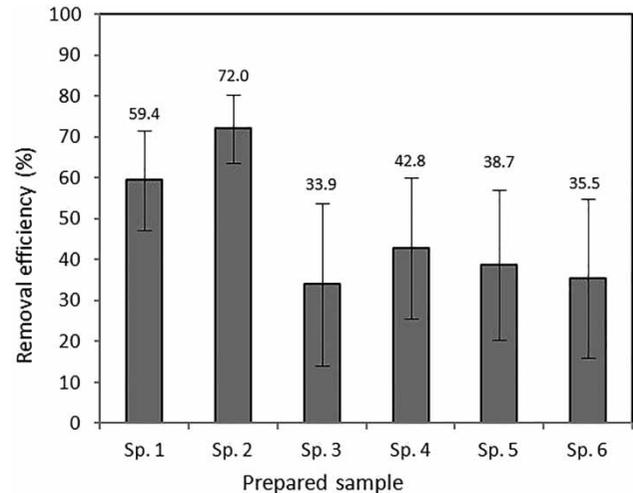


Figure 4 | Removal efficiency of Σ BTEX after 24-hour reaction time (set B).

their oxidative effects were probably consumed for the oxidation of easily oxidizable ballast substances contained in the water. Conversely, in the case of samples with hydrogen peroxide alone, slow and long decomposition of the peroxide without significant influence on selected contaminants has been observed. Adjustment of pH to lower values caused a slight increase in the removal efficiency in ferrate samples, but not significantly (sp. 3).

However, a significant increase in the removal efficiency has occurred in cases of combination for both

these materials (sp. 1 and 2), when the rapid decrease in concentration of selected contaminants was observed. In case of water from locality A (set A), almost 100% removal efficiency for monitored contaminants (CEs) was observed, irrespective of whether the pH was previously adjusted or not. In the case of water from locality B (set B), the removal efficiency for targeted contaminants (BTEX) ranged from 60 to 75% depending on the particular contaminant. The highest efficiency was observed for combination of ferrates with hydrogen peroxide without previous pH adjustment.

During these reactions (only for sp. 1 and sp. 2) also slight effervescence in water samples was observed. This effervescence was observed until the presence of hydrogen peroxide in the sample was detected (using starch-iodide papers). In the case of sp. 1 and 2, the presence of hydrogen peroxide was detected for a maximum of 12–24 hours, unlike sp. 5, where the hydrogen peroxide was detected for more than 96 hours after its application. In the presence of ferric sludge, which was created by reduction of ferrates, disappearance of hydrogen peroxide from an aqueous medium was much more rapid. Thus a rapid and sharp decrease in concentration of monitored contaminants was observed only in systems containing radical particles, especially hydroxyl radicals (OH) (Hyeongsu *et al.* 2011; Hara 2012; Hrabak 2012). Considering these facts, it can be concluded that there likely proceeded radical oxidations in the case of sp. 1 and 2, when the ferric sludge, which

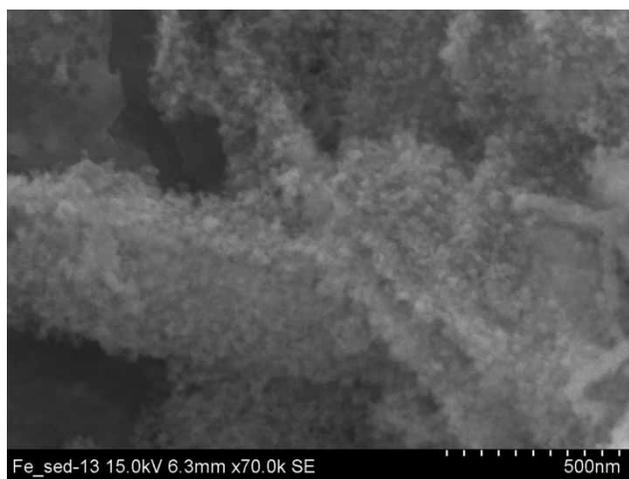


Figure 5 | Photograph of the ferric sludge created by the reduction of ferrates in water environment; taken with scanning electron microscope.

is characterized by its nanostructure (Figure 5), had catalyzed the radical decomposition of hydrogen peroxide to produce OH radicals. Moreover, it was found that this reaction runs repeatedly after each next addition of hydrogen peroxide to ferric sludge in the water, even without pH adjustment.

Results of pilot application

The purpose of the pilot field application was to verify the results of laboratory tests in practice. The container test took 24 hours and was carried out directly on the selected locality. All important operations done during the test are listed in Table 3. Their design and implementation was based on the procedures obtained during the laboratory tests. Before starting the test the groundwater was turbid, strong smelling and had a gray color. After the application of the ferrates, color of the water rapidly changed to slight orange (during a few minutes) as a consequence of presence of Fe^{3+} from reduction of ferrates. This reduction was associated with the formation of a flaky ferric sludge, which exhibited good sedimentation properties. After the application of hydrogen peroxide, a gentle effervescence in the whole volume of the container was observed. This reaction was accompanied by a slight increase in temperature of 2–3 °C (Figure 6). The rate of effervescence had a downward trend. At the end of the test it was not already observed at all and the presence of oxidizing agent (hydrogen peroxide) was also not detected (starch-iodide papers were used for detection). After the test concluded, the water was free of turbidity, slightly yellow and the sludge was deposited on the bottom of the container. Also the smell intensity was lower. The purification of water was caused by the creation of a flaky sludge, which was able to adsorb suspended particles causing the turbidity.

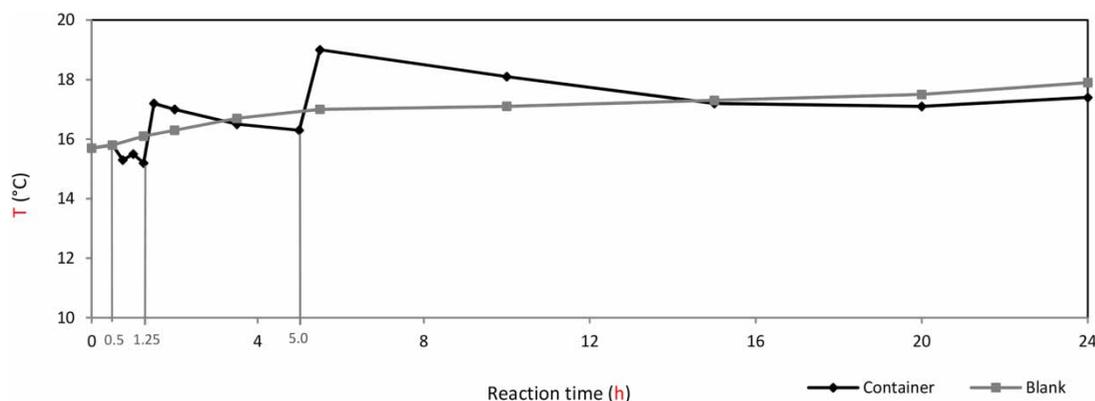


Figure 6 | The temperature of water in the reaction container and of the blank sample during the pilot test; the time axis includes times of the applications (corresponding to Table 3).

During the test substantial physical-chemical parameters such as pH, Eh and dissolved oxygen were monitored (Figure 7). In the case of pH, an expected growth of values after the application of ferrates was observed. The growth was caused by the presence of K_2O in the applied composite, which created potassium hydroxide in water medium. However, the water exhibited a

strong buffering capacity, and therefore the increase of pH was not as significant as expected. Due to this the pH remained in a range that is optimal for the formation of flakes of ferric iron sludge, which acted as an effective flocculant. A slight decrease in pH value occurred after the first dose of hydrogen peroxide, because of its weak acidic effects in an aqueous medium. After the partial decomposition of

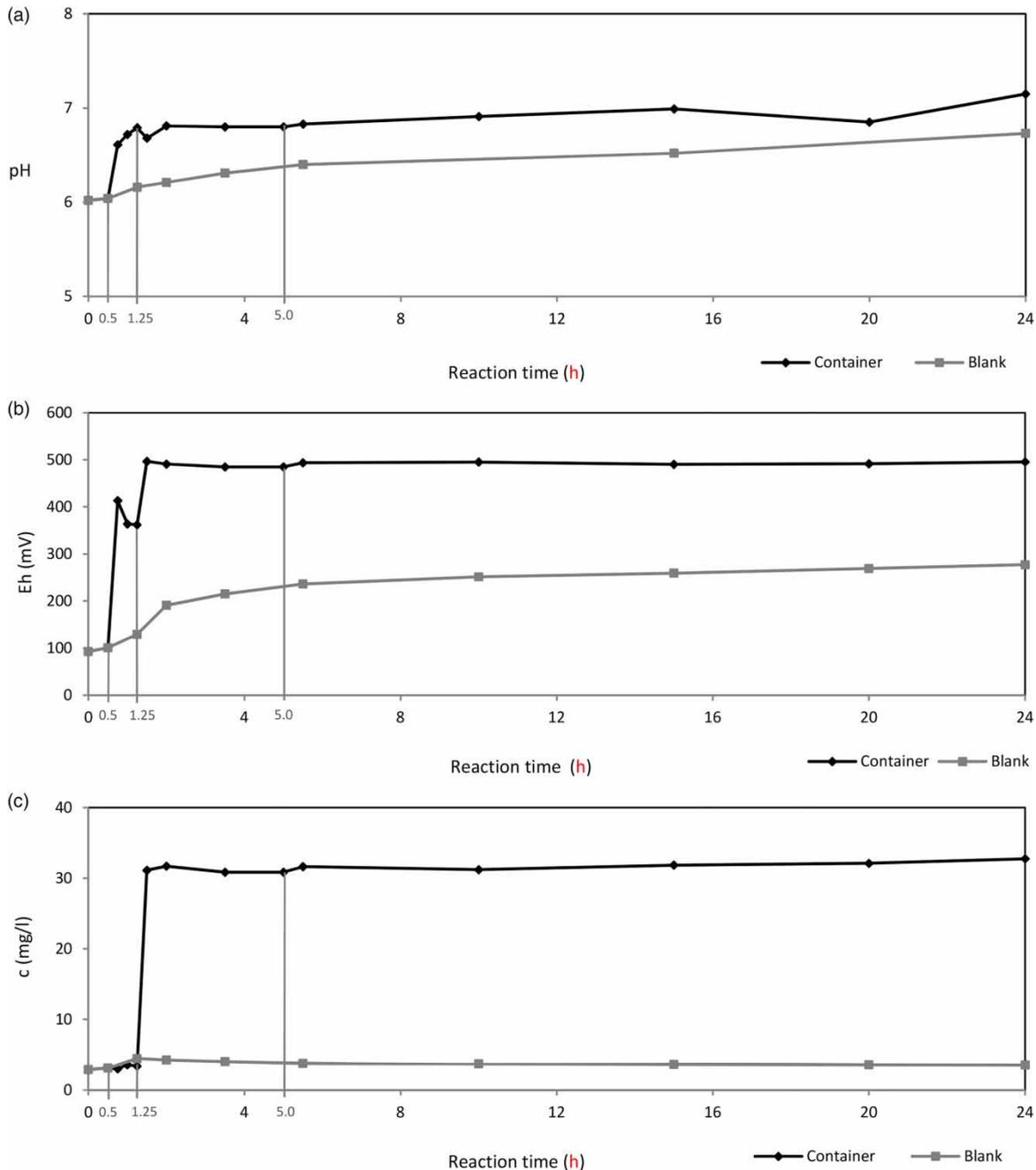


Figure 7 | Physical-chemical parameters monitored in the reaction container and in the blank sample during the pilot test: pH (a), Eh (b), concentration of dissolved oxygen (c); the time axis includes times of the applications (corresponding to Table 3).

the hydrogen peroxide, the value returned back to a higher level. After the second dose of hydrogen peroxide, a decrease in pH values was not observed, probably due to degradation products, which contributed to buffering capacity of the water. Eh increased significantly immediately after the application of ferrates and then a further increase occurred after the first dose of hydrogen peroxide. A significant increase in Eh together with dissolved oxygen show the formation of strong oxidizing conditions. The growth of dissolved oxygen concentration in the sample after the application of hydrogen peroxide was caused by decomposition of hydrogen peroxide.

For a comparison, the graphs in Figure 7 show the physical-chemical parameters of the blank sample, where measurements were carried out in parallel with the measurement in the IBC.

Samples for the analysis were taken immediately before start of the test and then after its termination. Their treatment and analysis were performed by accredited laboratories. Results are listed in Table 2. In order to evaluate the pilot test, changes between initial and final concentrations of detected contaminants were observed. On the basis of these results the removal efficiency of the pilot test was determined. Figure 8 shows overall removal efficiency of monitored contaminants at the end of the test, i.e., after 24 hours. For comparison, removal efficiency in the blank sample is also listed where changes in the concentrations were probably a result of mixing, volatilization, handling with sample, etc. The results have shown significant decrease in the concentration of almost all monitored contaminants during the container test in comparison with a blank sample. Removal efficiency of the majority of the

monitored contaminants ranged from 60 to 80%. Substances such as phenol, chlorophenol, N-ethylaniline and chlorinated ethenes were eliminated completely (removal efficiency $\approx 100\%$). The increase was observed only in concentration of cresols and nitrobenzene at the end of the test. This is a consequence of radical oxidation (in presence of OH radicals) of some aromatic substances when aromatic alcohols (cresols, phenols) can be created. Therefore high initial concentration of toluene was also the cause of very high concentrations of cresol at the end of the test. The slight increase in concentration of nitrobenzene is a consequence of the oxidation of aniline. Zero levels of the removal efficiency in Figure 8 mean no changes in the concentrations of monitored contaminants were observed during the pilot test (blank – xylenes, cresols, N-ethylaniline, nitrobenzene) or only a slight increase in concentration of these contaminants was observed (blank – dichlorophenols and chlorophenols).

Based on the obtained results, the combination of ferrates with hydrogen peroxide seems to be a very effective way for quick removal of a wide range of organic contaminants not only from groundwater, but also from wastewater and other types of water purified by ex-situ method. Although ferrates used independently in model samples theoretically exhibit strong oxidative effects, in highly polluted real waters they are rapidly degraded to a stable form of iron (ferric sludge) without significant effects on the important and often chemically stable contaminants. The efficiency of the reaction is, however, possible to increase with the addition of hydrogen peroxide to the created ferric sludge in the water. The dual oxidation efficiency thus can be combined – efficiency of ferrates alone and then efficiency of radical oxidation, which is

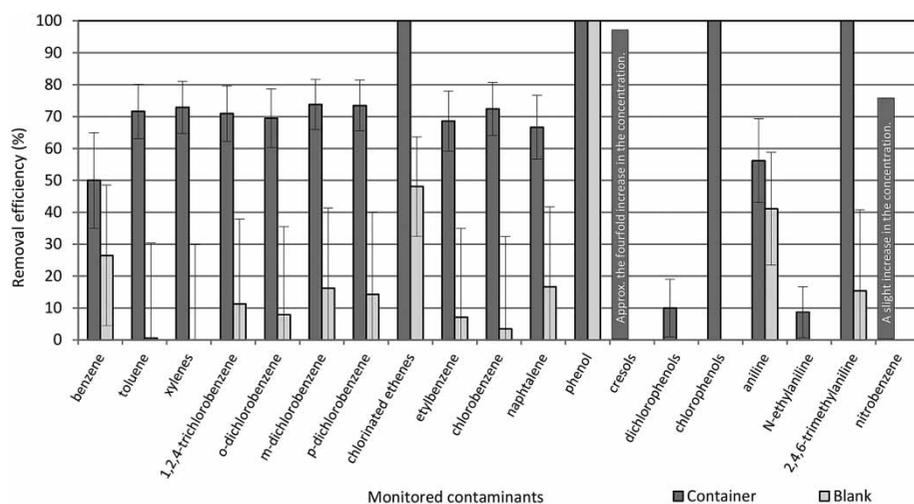


Figure 8 | Total removal efficiency of monitored contaminants at the end of the pilot test, compared to the blank.

initiated subsequently after the addition of hydrogen peroxide to water containing the created ferric sludge. In this case, the created sludge likely acts as a catalyst for radical degradation of hydrogen peroxide even without pH adjustment. Removal efficiency thus may be comparable to the Fenton oxidation. However, in the case of ferrates, the water is not salted and no other substances are applied to an aqueous environment (as sulfates, acids, etc.) because ferrates are a 'clean' iron, only in the higher oxidation state. From the viewpoint of environmental protection, the combination of ferrates with hydrogen peroxide seems to be very interesting – ferrates are reduced to $\text{Fe}^{3+}/\text{Fe}^{2+}$ as the form of various polyhydroxy complexes and hydroxides, which are nontoxic and commonly occurring in nature, and hydrogen peroxide is degraded to O_2 and H_2O .

From the presented results it is also clear that the presence of ferric sludge in decontaminated water is a prerequisite for successful remediation. Therefore, the combination will be suitable notably for ex-situ remediation of groundwater. Under such conditions, the remediation may be rapid and effective. In the case of in-situ remediation, this combination is not as effective, because in rock environments the migration of ferrates and flushing of their sludge by groundwater may occur. In addition, the reaction proceeds very rapidly (within 24 hours). So in a heavily contaminated rock environment no effect would likely be observed or the effect will be only short term as a consequence of the incessant supply of contamination from the surroundings (Lacina *et al.* 2014).

CONCLUSIONS

The use of ferrates during the remediation of heavily contaminated groundwater and wastewater does not provide the results previously expected. Therefore it is necessary to start thinking about other options for their use (such as further purification, coagulation, flocculation, disinfection, etc.) or use them in combination with other agents, which will assist in achieving the expected effectiveness in remediation practice. One of the possibilities is their combination with hydrogen peroxide where nanostructured sludge from the reduction of ferrates acts as an effective catalyst for radical decomposition of peroxide. The goal of this study was to test the effectiveness of combining ferrate with hydrogen peroxide in laboratory conditions and then to propose pilot tests on the basis of the obtained results. This combination showed a relatively high efficiency during remediation of even heavily contaminated water and simultaneously the

environment was not loaded by degradation products. Ferrates were finally reduced to natural forms of iron (hydroxides and polyhydroxy complexes) and the final products of the hydrogen peroxide degradation were oxygen and water. Therefore no more possible contaminants were discharged into the aqueous environment and also there was no problem with further increases of the salinity of the water. The reaction proceeded relatively rapidly even without pH adjustment or other interventions into the reaction conditions. In addition, the sludge formed by reduction of ferrates acted as an effective flocculant. However, the presence of this sludge in purified water is the necessary condition for successful remediation. Therefore the reaction is not suitable for in-situ remediation, but conversely it can be effectively utilized during an ex-situ remediation where fast and efficient elimination reactions are required.

ACKNOWLEDGMENT

This study was supported by the Technology Agency of the Czech Republic 'Competence Centres' (project TE01020218).

REFERENCES

- Bartzatt, R., Cano, M., Johnson, L. & Nagel, D. 1992 Removal of toxic metals and nonmetals from contaminated water. *J. Toxicol. Environ. Health* **35** (4), 205–210.
- Filip, J., Yngard, R. A., Siskova, K., Marusak, Z., Ettler, V., Sajdl, P., Sharma, V. K. & Zboril, R. 2011 Mechanisms and efficiency of the simultaneous removal of metals and cyanides by using ferrate (VI): crucial roles of nanocrystalline iron(III) oxyhydroxides and metal carbonates. *Chem. Eur. J.* **17**, 10097–10105.
- Hara, J. 2012 Chemical degradation of chlorinated organic pollutants for in situ remediation and evaluation of natural attenuation. In: *Organic Pollutants Ten Years After the Stockholm Convention – Environmental and Analytical Update* (T. Puzyn & A. Mostrag-Szlichtyng, eds). InTech, Rijeka, Croatia, pp. 345–365.
- Hrabak, P. 2012 A critical study of remedial utilization of modified Fenton reagent. PhD thesis, Technical University of Liberec, Liberec.
- Hyeongsu, C., Sungjun, B. & Woojin, L. 2011 Degradation of trichloroethylene by Fenton reaction in pyrite suspension. *J. Hazard. Mater.* **185**, 1355–1361.
- Jiang, J. Q. & Lloyd, B. 2002 Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Res.* **36**, 1397–1408.
- Jiang, J. Q. & Wang, S. 2003 Inactivation of *Escherichia coli* with ferrate and sodium hypochlorite: a study on the disinfection performance and constant. In: *Proceedings of the 3rd International Conference on Oxidation Technologies for*

- Water and Wastewater Treatment* (A. Vogelpohl, ed.). CUTEC-Series Publication No. 57, Papierflieger Verlag, Clausthal-Zellerfeld, Germany, pp. 403–411.
- Kokarovtseva, I. G., Belyaev, I. N. & Semenyakova, L. V. 1972 Oxygen compounds of iron (VI, V, IV). *Russ. Chem. Rev.* **41** (11), 929–937.
- Kolar, M., Kolarik, J., Jancula, D., Slunsky, J., Medrik, I., Filip, J., Marsalaek, B. & Zboril, R. 2015 Feráty: vlastnosti a přehled možných environmentálních aplikací (Ferrates: properties and the overview of possible environmental applications). In: *Sanační technologie XVIII – conference proceedings* (J. Bukhard & K. Petrakova-Kanska, eds). 1st edn, Ekomonitor, Chrudim, Czech Republic, pp. 152–154.
- Lacina, P., Dvorak, V., Vodickova, E. & Polenkova, A. 2014 Comparison of the efficiency of reduction and oxidation reactions using iron particles during in-situ remediation of groundwater contaminated by chlorinated ethylenes. *Podzemna Voda* **20** (2), 166–175.
- Lee, Y., Um, I. H. & Yoon, J. 2003 Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation. *Environ. Sci. Technol.* **37** (24), 5750–5756.
- Lee, Y., Zimmermann, S. G., Kieu, A. T. & Gunten, U. 2009 Ferrate (Fe(VI)) application for municipal wastewater treatment: a novel process for simultaneous micropollutant oxidation and phosphate removal. *Environ. Sci. Technol.* **43** (10), 3831–3838.
- Machala, L., Filip, J., Pucek, R., Tucek, J., Frydrych, J., Sharma, V. K. & Zboril, R. 2014 Potassium ferrite (KFeO₂): synthesis, decomposition, and application for removal metals. *Sci. Adv. Mater.* **6**, 1–9.
- NanoIron co. 2015 <http://www.nanoiron.cz/cs/envifer> (accessed 1 April 2015).
- Pucek, R., Tucek, J., Kolarik, J., Filip, J., Marusak, Z., Sharma, V. K. & Zboril, R. 2013 Ferrate(VI)-induced arsenite and arsenate removal by in situ structural incorporation into magnetic iron(III) oxide nanoparticles. *Environ. Sci. Technol.* **47**, 3283–3292.
- Sharma, V. K. 2002 Potassium ferrate(VI): an environmentally friendly oxidant. *Adv. Environ. Res.* **6**, 143–156.
- Sharma, V. K. 2011 Oxidation of inorganic contaminants by ferrates (VI, V, and IV)-kinetics and mechanisms: a review. *J. Environ. Manage.* **92**, 1051–1073.
- Sharma, V. K., Kazama, F., Jiangyong, H. & Ray, A. K. 2005 Ferrates (iron(VI) and iron(V)): environmentally friendly oxidants and disinfectants. *J. Water Health.* **3** (1), 45–58.
- Sharma, V. K., Homonnay, Z., Siskova, K. & Zboril, R. 2014 Mössbauer investigation of the reaction of ferrate(VI) with sulfamethoxazole and aniline in alkaline medium. *Hyperfine Interact.* **224**, 7–13.
- Tiwari, D., Kim, H.-U., Lee, S.-M., Yang, J.-K. & Kim, H. 2006 Ferrate(VI) for waste water treatment: oxidation of cyanide in aqueous medium. *Environ. Eng. Res.* **11** (6), 318–324.
- Yates, J. B., Zboril, R. & Sharma, V. K. 2014a Engineering aspects of ferrate in water and wastewater treatment – a review. *J. Environ. Sci. Health A* **49**, 1603–1614.
- Yates, J. B., Darlington, R., Zboril, R. & Sharma, V. K. 2014b High-valent iron-based oxidants to treat perfluorooctanesulfonate and perfluorooctanoic acid in water. *Environ. Chem. Lett.* **12** (3), 413–417.

First received 23 April 2015; accepted in revised form 23 July 2015. Available online 5 August 2015