



Mobilization of metals during treatment of contaminated soils by modified Fenton's reagent using different chelating agents

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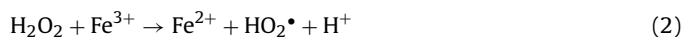
ABSTRACT

Changes in pH and redox conditions and the application of chelating agents when applying in situ chemical oxidation (ISCO) for remediation of contaminated sites can cause mobilization of metals to the groundwater above threshold limit values. The mechanisms causing the mobilization are not fully understood and have only been investigated in few studies. The present work investigated the mobilization of 9 metals from two very different contaminated soils in bench and pilot tests during treatment with modified Fenton's reagent (MFR) and found significant mobilization of Cu and Pb to the water in mg/l levels. Also Fe, As, Mn, Ni, Zn, Mg, and Ca mobilization was observed. These findings were confirmed in a pilot test where concentrations of Cu and Pb up to 52.2 and 33.7 mg/l were observed, respectively. Overall, the chelating agents tested (EDTA, citrate and pyrophosphate) did not seem to increase mobilization of metals compared to treatment with only hydrogen peroxide and iron. The results strongly indicate that the mobilization is caused by hydrogen peroxide and reactive species including oxidants and reductants formed with MFR. Based on these results, the use of chelating agents for ISCO will not cause an increase in metal mobilization.

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1. Introduction

Mobilization of metals to the groundwater when applying in situ chemical oxidation (ISCO) for remediation of contaminated sites has been observed [1,2] and transport of these metals may cause a release of metals to ecosystems, areas with water catchment, etc. at concentrations above threshold limit values. One of the most common ISCO technologies applies hydrogen peroxide activated by an iron catalyst. The Fe(II) mediated decomposition of hydrogen peroxide is known as modified Fenton's reagent (MFR) or catalyzed H₂O₂ propagation (CHP) and produces hydroxyl radicals according to reaction (1). These radicals react with more than 95% of contaminants of concern (COC) at near diffusion-controlled rates, i.e. $k > 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [3]. Depending on the catalyst used and the hydrogen peroxide concentration, MFR also generates the reactive oxygen species perhydroxyl radical (HO₂•), superoxide radical anion (O₂•⁻), hydroperoxide anion (HO₂⁻) and organic radicals [4] according to reactions (2)–(6).



The acidic properties of Fe(II) lowers pH to 3–4 in classical Fenton's system, when Fe(II) is added to deionized water. In soils and groundwater the influence on pH is more complicated since most of these systems possess a strong buffering capacity that will maintain pH in the neutral domain and result in iron precipitation as oxides and ineffective catalysis of hydrogen peroxide. As an alternative to lowering pH in the entire treatment area to 2–4 with e.g. sulfuric acid, several other methods have been used to catalyze the hydrogen peroxide. These include soluble iron [5–7], iron minerals [6,8–13], and chelated iron [14–18]. The main advantages of using chelated iron as catalysts are that the process can be conducted at neutral pH and that chelates may travel farther in the subsurface compared to soluble iron [4]. However, the dosage of oxidants has to be increased since the oxidation capacity of MFR will be lowered due to oxidation of the chelating agents. Studies have shown that the widespread used chelating agents for consumer products and industrial processes combined with poor biodegradability of

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Table 1
Characteristics of the used natural soils.

	Soil A	Soil B
Properties		
Organic matter	Low	Low
Sand	87%	92%
Clay and silt	13%	8%
Soil texture	Loamy sand	Sand
Contaminants	Fuel oil	Chlorinated solvents, hydrocarbons, pharmaceuticals, other
Buffer capacity	High	Low
Depth	3.5 m bgs	4–14 m bgs
Metals [$\mu\text{g/g}$]		
As	0.5	1.6
Co	2.3	<0.3
Cr	20.1	4.7
Cu	6.8	13.4
Fe	8060.0	189.0
Mn	213.0	2.4
Ni	4.2	36.9
Pb	4.6	20.6
Zn	19.7	3.0
Mg	1690.0	28.0
Ca	458.0	454.0

these chemicals have lead to accumulation of chelating agents in the environment and EDTA is now among the highest concentrated anthropogenic compounds in European surface waters [19]. An important issue is that chelating agents may enhance the mobility and transport of heavy metals once released into the environment and high concentrations are also able to remobilized metals out of sediments [20].

The coexisting occurrence of organic contaminants and heavy metals in soil is a significant factor complicating remediation of contaminated sites, as the enhanced desorption of organic contaminants by the MFR reactions may lead to mobilization of heavy metals [1,2]. Also, chelating agents are used directly for extraction of heavy metals from contaminated soils [21–27] and to enhance phytoextraction of heavy metals from contaminated soils [28–30]. These fields of application indirectly suggest that using chelating agents for ISCO may increase metal mobilization.

Only few studies have investigated metal mobilization during treatment of contaminated soils with MFR. In these studies mobilization of Cd, Cu, Ni, Pb, Zn [1] and Pb [2] was investigated. Both studies used nitrilotriacetic acid (NTA) to keep Fe(III) in solution. The objective in this work is to investigate the mobilization of different metals from contaminated natural soils treated with MFR and to study the influence of pH, oxidation, and different chelating agents to obtain a better understanding of the mechanisms causing the mobilization of metals during MFR. Also, the results from bench scale experiments were compared to results obtained in a field scale pilot test. The present study focused on EDTA, a widely used non-biodegradable synthetic chelating agent. Attempts have been made to find more environmental compatible chelating agents to keep the iron catalyst in solution [17,31] and in the present study the performance of EDTA was compared to a biodegradable organic chelating agent (citrate) and an inorganic chelating agent (pyrophosphate) that is not degraded by MFR.

2. Materials and methods

2.1. Soil samples

Sandy soils from two different contaminated sites in Denmark were used for the experiments. The characteristics of the soils, referred to as soils A and B, are presented in Table 1 with average concentrations of different metals in the soils. The analysis by ICP-AES was based on triple determinations of 1 g of digested soil

sample and hence results deviated up to 30% for the different metals due to the heterogeneous nature of the soil samples.

2.2. Chemicals

Technical grades of hydrogen peroxide (33% H_2O_2) and sodium hydroxide (30% NaOH) were purchased from VWR international, LLC. Analytical grades of ferrous iron sulfate heptahydrate (>99% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), citric acid (>99% $\text{C}_6\text{H}_8\text{O}_7$), sodium pyrophosphate decahydrate (99% $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) and ethylenediaminetetraacetic acid, EDTA (99% $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$) were purchased from Merck and Sigma–Aldrich. Sulfuric acid (96% H_2SO_4) and nitric acid (65% HNO_3) were purchased from Bie & Berntsen.

2.3. Analytical methods

As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Mg, and Ca were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry, ICP-AES (Perkin Elmer Optima 3000DV) with detection limits of about 0.01 mg/l. All water samples were passed through a 0.45 μm filter and then immediately acidified with HNO_3 before analysis. Soil samples were digested in HNO_3 at 120 °C before analysis of the aqueous phase with ICP-AES. Solution pH was monitored using a Radiometer PHM210 pH meter.

2.4. Test setup

Each batch reactor consisted of a 100 ml Erlenmeyer flask with 50 ± 0.05 g of soil suspended in deionized water. 0.90 ml 0.10 M catalyst stock solution and 1.50 ml 33% hydrogen peroxide (1.13 g/cm^3) was added to the reactors to initiate the reactions, resulting in a total aqueous volume in each flask of 50.00 ml. Fe concentrations in all catalyst stock solutions were 0.10 M and in the chelated iron catalyst stock solutions the Fe(II):chelate molar ratio was 1:1. pH in all stock solutions were adjusted to 7.0 with NaOH or H_2SO_4 .

All tests were performed in duplicate in two identical reactors. Control reactors receiving only deionized water, deionized water with hydrogen peroxide, and deionized water with hydrogen peroxide and iron were performed in parallel. For soil B it was necessary to prepare a pH control reactor due to a low buffer capacity of the soil. This reactor received only soil and deionized water and pH was adjusted to 2.8 using 0.9 M H_2SO_4 . An overview of the reactors applied in the study is presented in Table 2. All samples were shortly stirred once a day. Reactions were carried out at 25 ± 1 °C in covered flasks and were allowed to proceed for 7 days. 10 ml aliquots were collected after 5 h and after 7 days. pH was monitored after 5, 24, 96, and 168 h. pH was not adjusted in the reactors and no buffer was used to maintain a constant pH. Varying pH may complicate interpretation of the results, but this was specifically chosen to simulate the conditions and results of a field scale application, where pH is not normally controlled through buffer addition. ICP-AES control analyses of all reagents showed that no metal impurities in these reagents could affect the results, hence the metal concentrations at time 0 could be assumed to be below detection limit of about 0.01 mg/l for the ICP-AES technique.

2.5. Pilot study

MFR was tested at the soil B site in pilot scale. A volume of about 110 m^3 of soil located 3–6 m bgs was treated with 20,500 l of stabilized 12.5% H_2O_2 and 10,250 l of chelated iron catalyst solution (ISOTECSM Cat 4260, patented catalyst from In-Situ Oxidative Technologies Inc.) in total over four injection events. Five injection points screened in two depths were used and the design radius

Table 2

Overview of test setup with concentrations in the aqueous phase for each reactor. All reactors include 50.0 g soil and 50.0 ml aqueous solution.

Reactor	H ₂ O ₂	Fe(II)	Fe(II)-EDTA	Fe(II)-citrate	Fe(II)-pyrophosphate
1	–	–	–	–	–
2	330 mM	–	–	–	–
3	330 mM	1.8 mM	–	–	–
4	–	–	1.8 mM	–	–
5	–	–	–	1.8 mM	–
6	–	–	–	–	1.8 mM
7	330 mM	–	1.8 mM	–	–
8	330 mM	–	–	1.8 mM	–
9	330 mM	–	–	–	1.8 mM
10 (pH)	–	–	–	–	–

of influence was 1.5 m. Metal concentrations were measured in filtered (0.45 μm filter) groundwater samples collected in the treated area and 2.5 m downgradient the nearest injection point before, during and after MFR injections.

3. Results and discussion

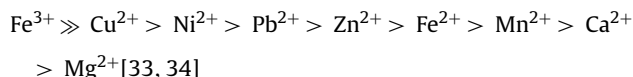
3.1. pH

The most important property affecting metal mobility in soils is pH [32]. The two soils used were very different regarding pH and buffering capacity. After 7 days of reaction, pH in soil A reactors was 7.2–7.7, whereas pH in soil B reactors was 2.1–6.7. pH measurements after 5, 24, 96 and 168 h in each reactor are presented in Fig. 1. The decrease in pH in soil B reactors was caused by reactions involving H₂O₂, probably because of partial oxidation of contaminants, e.g. to carboxylic acids, since the very low pH was only observed in reactors containing H₂O₂. It seems as if pH decreases during reaction and when all H₂O₂ had reacted or was decomposed, pH started to recover. Based on this, pH measurements in soil B reactors indicates that H₂O₂ was consumed fast (<24 h) in reactors 3, 7, and 8, whereas the reactions in 2 and 9 were slow (>96 h).

3.2. Metals—soil A

All metal concentrations in the aqueous phases of the reactors after 5 h and 7 days of reaction for soil A are presented in Fig. 2. Initially, the aqueous Fe concentrations in reactor 3–9 was 100 mg/l and from Fig. 2 it is seen that Fe was not maintained in solution in the reactors containing hydrogen peroxide. This indicates that the MFR is reacting with the chelated catalyst within hours. When the investigated metals are ordered according to their stability constants with EDTA, it is seen that Fe³⁺ forms the most stable

complex and it would be expected that Fe could still be found in solution.



However, no Fe was found after 5 h or 7 days in reactor 7. This strongly indicated that the EDTA was partly degraded by hydrogen peroxide and therefore not capable of keeping Fe in solution. Degradation of EDTA with MFR has been described in [4,17,35]. The stability constants are of limited value if the kinetics of the reactions is not considered. The Fe(II)-EDTA is rapidly oxidized to Fe(III)-EDTA even at pH 3 and generally coordination reactions with ligands containing multiple bonding groups, such as EDTA, are often kinetically hindered [36], e.g. the half life of Fe(III)-EDTA has been observed to be about 20 days due to slow exchange with Zn [37]. For this reason, it can be assumed that no significant exchange of Fe in the metal-ligand system occurs. However, other studies have shown a fast remobilization of adsorbed Pb and Ni with Fe(III)-EDTA which disagrees with the slow dissociation kinetics of Fe(III)-EDTA [38].

Even though EDTA, citrate, and pyrophosphate as well as their formed metal complexes are designed to solubilize metals and keep them in solution, they can also adsorb on e.g. iron minerals in the soil. This sorption is strongly dependent on pH and while metal ions in general show increasing adsorption with increasing pH, adsorption of metal complexes decreases with increasing pH. At lower concentrations compared to the concentrations used in this study, the chelates can significantly increase metal adsorption onto mineral surfaces [39]. The adsorption was not within the scope of this work and more details on the EDTA metal adsorption in the environment can be found in [36]. When only chelated Fe was used in reactors 4–6, EDTA was able to maintain Fe in solution for

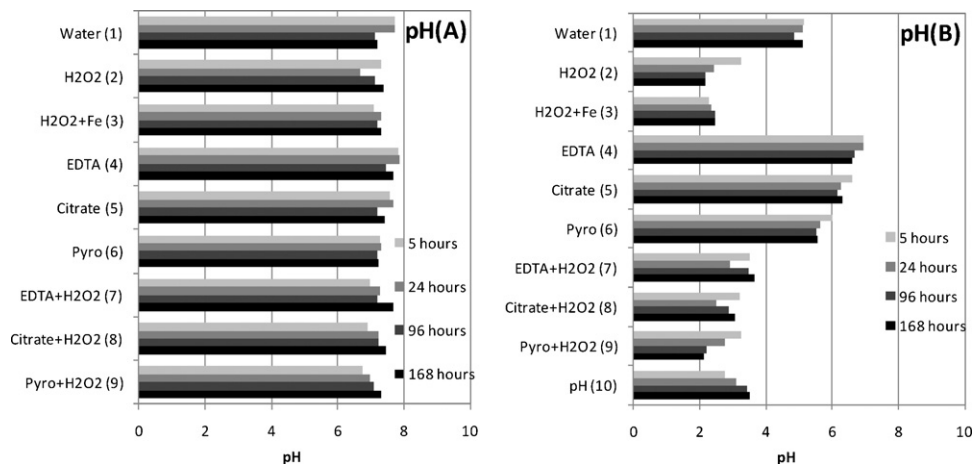


Fig. 1. Average pH in all soil A and soil B reactors after 5, 24, 96 and 168 h.

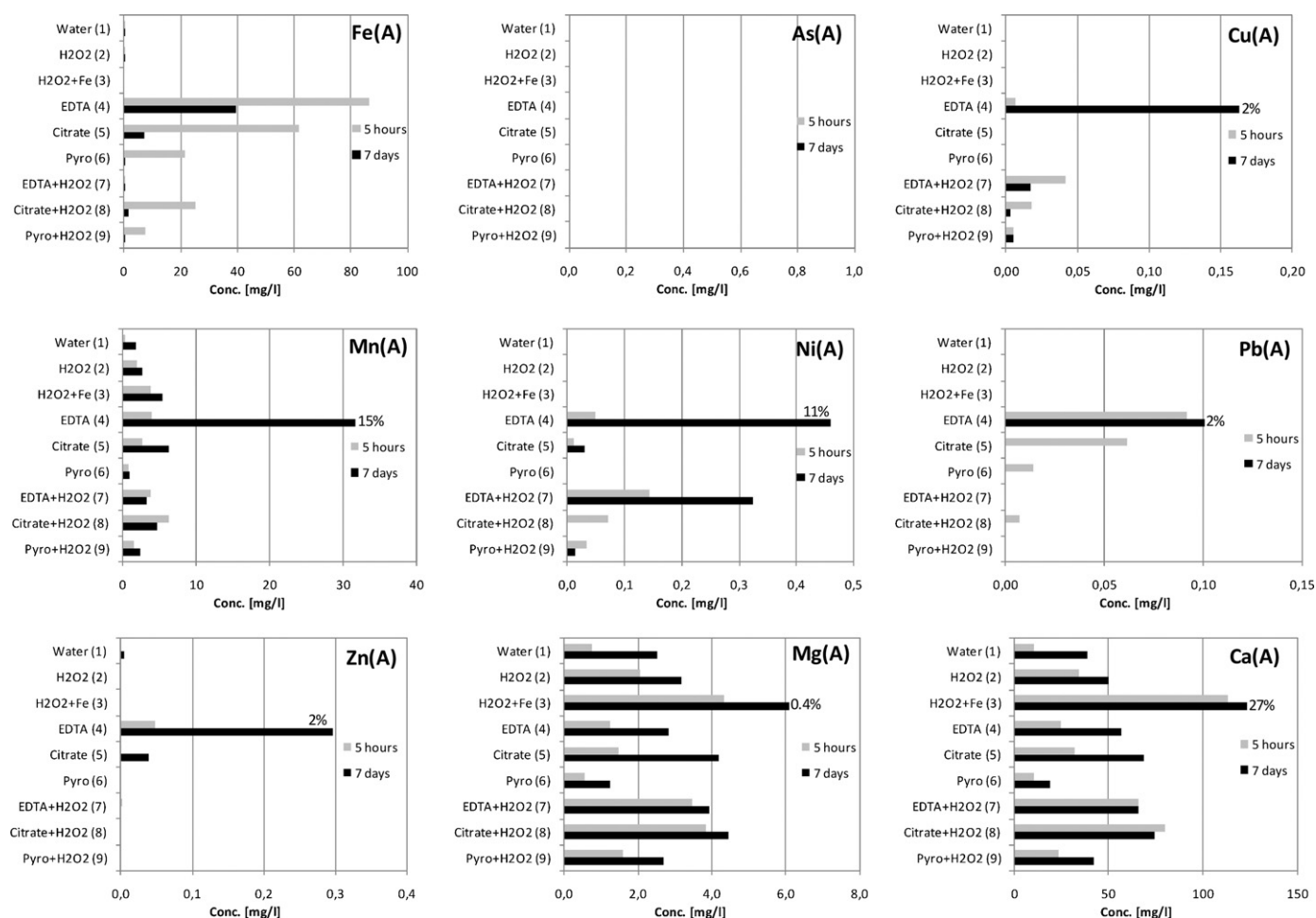


Fig. 2. Average metal concentrations in soil A reactors after 5 h and 7 days of reaction. Note the different scales. The highest degree of mobilization compared to a maximal theoretical mobilization (calculated as 100% mobilization of the metals analyzed in the soils, Table 1) is shown for each metal except Fe and As.

the longest time and pyrophosphate for the shortest time. This is ascribed the slow kinetics of metal exchange in Fe(II)-EDTA. No additional Fe was released in any of the reactors even though the Fe concentration in the soil was high. Mn was mobilized in all reactors with the most significant release occurring when EDTA-Fe(II) was used.

Overall, it is seen that the EDTA-Fe(II), reactor 4, is causing the most significant release of metals over time. This applies for Cu, Mn, Ni, Pb, and Zn, of which small concentrations were mobilized. EDTA-Fe(II)-H₂O₂ also caused some mobilization, but in lower concentrations. This difference further strengthens the assumption that EDTA is partly oxidized by H₂O₂ and thereby not able to keep the metals in solution.

Results for the reactors containing citrate were in many cases comparable to the EDTA reactors since these two organic chelating agents have similar properties and affinities to the investigated metals. The inorganic pyrophosphate caused the lowest mobilization of metals in all cases, but was not very effective for maintaining the iron in solution and therefore probably not effective as a catalyst for the MFR.

For all measured concentrations of metals in the reactors, except Ca, it is seen that the displaced amounts of metals are very low compared to the maximal concentrations obtainable if all metals were mobilized. Mg and Ca were found in all the reactors and the control reactor with only de-ionized water, generally with increasing concentrations with time.

3.3. Metals—soil B

Because of the very low buffer capacity of soil B, pH dropped significantly in all reactors containing H₂O₂ as shown in Fig. 1. Overall, a significant mobilization of several metals increasing with time occurred in all reactors and especially in the reactors containing H₂O₂. The mobilization was partly caused by the low pH, but as the control reactor 10 shows, decreasing the pH was not enough to mobilize the observed concentrations. The MFR reactions therefore seemed to increase the displacement of metals. Aqueous solubility and exchange of metals depends by order of magnitude on their oxidation state [32]. As presented in the introduction, the MFR reactions are able to promote the formation of several reactive oxygen species including strong reductants (superoxide). In [1] it was suggested that superoxide has the potential to rapidly reduce and mobilize transition metals (M):



For reduction of Cu(II) by superoxide, this is supported by a large second order rate constant of $6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [40]. The Cu data presented in Fig. 3 fits with this proposed mechanism since very high concentrations (5.42–9.81 mg/l) of copper was released in all reactors containing H₂O₂. No Cu was observed in the other treatment reactors and only 0.74 mg/l was measured in the pH control reactor, demonstrating that the mobilization is not caused by pH alone. Another suggestion for the increased mobilization in the

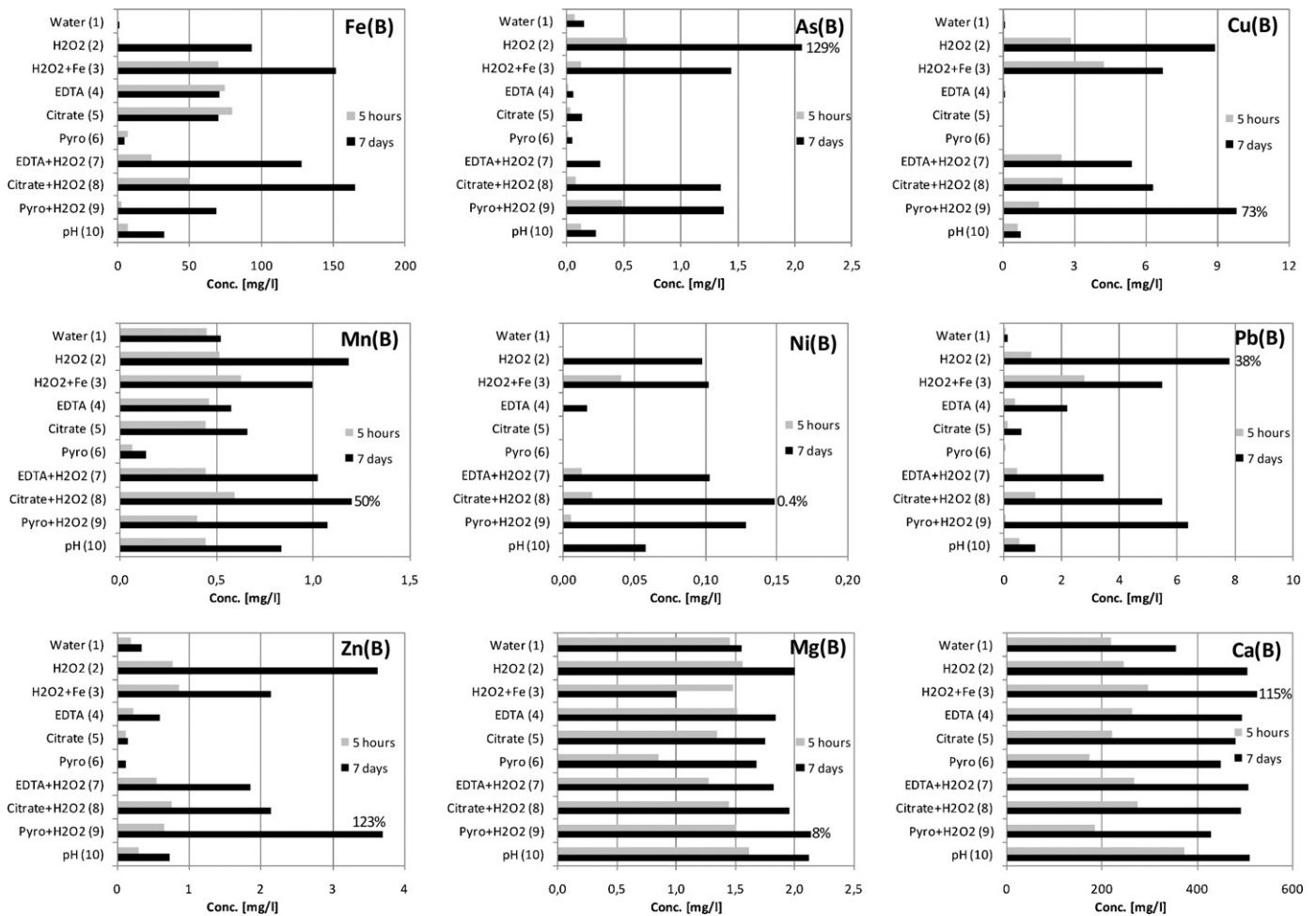


Fig. 3. Average metal concentrations in soil B reactors after 5h and 7 days of reaction. Note the different scales. The highest degree of mobilization compared to a maximal theoretical mobilization (calculated as 100% mobilization of the metals analyzed in the soils, Table 1) is showed for each metal except Fe.

presence of H_2O_2 is the fact that oxalic acid and other small acids are produced when aromatic rings are oxidized by hydroxyl radicals [41]. These acids can strongly chelate some metal cations. Aromatic structures are abundant in soil organic matter. Therefore, it is possible that these organic acids contribute, along with the acidity, to solubilization some of the metal cations.

For As, Ni, Pb, and Zn trends very comparable to the Cu mobilization were observed. It has also been suggested elsewhere that the release of Pb and other metals during treatment with MFR can be ascribed to superoxide [2].

Contrary to results from soil A, Fe was maintained in solution for the soil B tests and additional Fe was even mobilized from the soil matrix in five of the reactors, probably due to low pH. Mg and Ca were found in all the reactors and the control reactor with only de-ionized water, generally with increasing concentrations over time.

3.4. Field pilot test at soil B site

The high degree of mobilization of metal from soil B made it interesting to compare the bench scale results with results from a field test. A pilot test as described in Section 2.4 was conducted during 2010 at the soil B site. Results from monitoring of metals in the pilot study treatment area and 2.5 m downgradient are presented in Table 3. The results showed the same trends as the bench scale tests with a significant decrease in pH to about 2.5 after injection of H_2O_2 and catalyst as well as a significant mobilization of metals in the treatment area, but also 2.5 m downgradient the

Table 3

Results in mg/l from pilot study at the soil B site. A total of four MFR injection events were performed after 7, 63, 111, and 153 days. "n.a." not analyzed.

	Time (days)					
	0	29	79	135	175	247
Center of treatment area						
pH	5.78	2.66	2.65	2.41	2.26	2.64
Pb	2.20	39.00	52.20	9.47	8.60	2.40
Cu	1.40	16.00	33.70	28.20	12.00	1.60
Ni	0.01	0.35	0.25	0.14	0.14	0.02
Fe	16.00	63.00	60.00	130.00	64.60	26.00
Mn	0.66	1.80	1.70	3.90	1.38	0.40
2.5 m downgradient the nearest injection well						
pH	5.04	2.54	2.61	2.43	2.86	3.44
Pb	0.03	14.00	n.a.	9.50	5.31	n.a.
Cu	0.01	21.00	n.a.	28.10	11.80	n.a.
Ni	0.01	0.21	n.a.	0.14	0.19	n.a.
Fe	12.00	71.00	n.a.	160.00	62.80	n.a.
Mn	0.70	2.60	n.a.	4.40	1.37	n.a.

nearest injection well. Average groundwater velocity was estimated to be 0.17 m/day. Released metals were found in very high concentrations, especially Pb and Cu reaching concentrations of 52.2 and 33.7 mg/l, respectively 22 days after the first injection event. After 135 and 175 days the concentrations were almost identical in the treatment area and downgradient, suggesting that metals were transported out of the treatment area, since no H_2O_2 to cause further mobilization was observed in this downgradient

monitoring well. From these results it was evident that MFR under field conditions can cause significant mobilization and transport of metals. In a monitoring well placed 25 m downgradient, with an estimated groundwater transport time from the treatment area to the monitoring wells of about 150 days, a groundwater sample was collected after 175 days. Metal concentrations and pH in this sample were comparable to baseline conditions before MFR treatment. From the monitoring setup it was not possible to determine how far the metals were transported, except that it was more than 2.5 m and less than 25 m.

4. Conclusions

Mobilization of 9 metals from two very different contaminated soils treated with MFR was investigated in bench scale and mobilization from one of the soils was tested in pilot scale. Overall, the results showed that the used chelating agents (EDTA, citrate and pyrophosphate) did not seem to increase mobilization of As, Cu, Mn, Ni, Pb, and Zn compared to traditionally treatment with only Fe and hydrogen peroxide. This is likely because of a very slow exchange of metals in the Fe–ligand systems combined with the degradation of the chelating agents. The results strongly indicate that it is the hydrogen peroxide and the reactive species (oxidants and very likely reductants such as superoxide) created through initiating and propagating reactions that are responsible for the mobilization of the metals. This is further supported since most significant mobilization in all cases was observed in reactors where to hydrogen peroxide was added. The results also suggest that the chelating agents are partly or completely degraded during the MFR reactions. Pilot scale results from the soil B site confirmed the results obtained in the laboratory and showed a significant mobilization of especially Pb and Cu with concentrations in the treatment area up to 52.2 and 33.7 mg/l. Concentrations also increased significantly 2.5 m downgradient the injection points with concentrations of Pb and Cu up to 14.0 and 28.1 mg/l. 25 m downgradient, metals concentrations above baseline levels could not be observed suggesting that the mobilized metals precipitates or adsorbs to soil particles outside of the treatment area.

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