



DISSOLVED IRON AND MANGANESE TRENDS IN EHC AMENDED AQUIFERS

EHC[®] is a controlled-release, integrated carbon and zero valent iron (ZVI) particulate material used for stimulating reductive dechlorination and enhanced bioremediation in a subsurface environment. Oxidation (corrosion) of ZVI particles contained in EHC is an integral part of the in situ chemical reduction (ISCR) processes using ZVI-based substrates such as EHC. The role of ZVI in ISCR can be summarized as follows:

- Acts as an electron donor, lowers redox state and consumes competing terminal electron acceptors: $\text{Fe}^{\circ} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$;
- Generates cathodic hydrogen gas for use as an energy source by microbial processes (Tratnyek et al., 2003): $\text{Fe}^{\circ} + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_{2(\text{aq})} + 2\text{OH}^{-}$;
- Provides direct treatment of chlorinated hydrocarbons (CAHs) via hydrogenolysis and halo-elimination (Arnold and Roberts, 2000): e.g. (TCE); $3\text{Fe}^{\circ} + \text{C}_2\text{HCl}_3 + 3\text{H}^{+} \rightarrow \text{C}_2\text{H}_4 + 3\text{Fe}^{2+} + 3\text{Cl}^{-}$.
- Dissolved ferrous iron (Fe^{2+}) forms precipitates within and downgradient of an EHC amended zone. The abiotic reduction of CAHs by reduced iron minerals is a major attenuation pathway (Wilson, 2003; Ferrey et al., 2004; Lee and Batchelor, 2002).

Dissolved Iron - Field Trends

In some applications, an increase in dissolved iron of 10 mg/L to more than 100 mg/L after EHC placement has been observed in wells located directly in amended zones. The dissolved iron levels varied depending on the EHC placement configuration, EHC application rate, and aquifer conditions. Experience from these sites suggests that the dissolved iron concentration will decrease gradually with time and along groundwater flow path. The initial generation of high levels of dissolved iron is in agreement with the observed ZVI corrosion trends, which show an initially high corrosion rate followed by the establishment of a steady long-term rate (Reardon, 2005). Decreasing iron concentration trends along the flow path from an EHC zone correspond with the expected reduction-oxidation and dissolution-precipitation geochemical processes that occur as treated groundwater flows downgradient.

Rarely are the dissolved iron concentrations found to be problematic. For example, Peale *et al.* (2008) performed a pilot-scale EHC evaluation at a site in Oregon and provided a detailed analysis of dissolved iron trends within and downgradient of an EHC treatment zone. Because the pilot was located about 70 ft upgradient of a river, dissolved iron fate was a part of the technology evaluation. The reported iron data showed that dissolved iron concentration decreased gradually with time and along groundwater flow path. Site groundwater was impacted by 100s mg/L of total CAHs and a relatively high dosage of 1% (soil mass basis) EHC in a 21 ft wide aquifer zone was used. The observed initial iron concentration increased within the EHC zone to about 1,000 mg/L. Iron concentration decreased to below background levels of 46 mg/L (an MGP legacy) within 9 months after installation. The trends in a downgradient monitoring well located 20 ft from the edge of the EHC zone showed an initial iron concentration of 300 mg/L and a subsequent decrease to below the

background value within 6 months. Notably, the long-term dissolved iron levels in the EHC pilot and directly downgradient were consistently below the background level within the 2 year observation period. An equilibrium geochemical modeling of the pilot geochemical data indicated that precipitation of mineral phases, including carbonates and sulfides, were likely controlling the long-term fate of dissolved iron in the vicinity of the installation. No river impacts due to dissolved iron were detected downgradient of the pilot.

Zero-valent iron only permeable reactive barriers (PRBs) can be of particular relevance to an EHC system, and similar downgradient dissolved iron data trends have been obtained. For example, at a site in Australia, a ZVI PRB was placed in an acidic aquifer with DOC levels of 100s mg/L (Stenning *et al.*, 2008). The ZVI treated water had a pH of around 6.5, along with dissolved Fe concentration of up to 50 mg/L (*i.e.*, similar to the chemistry of EHC-treated water). Dissolved iron in a downgradient well (5 ft from the PRB) was present at a concentration of <5 mg/L, although an increasing trend was observed with time suggesting a decreasing buffering capacity of this aquifer zone.

Dissolved Manganese - Field Trends

Increase in dissolved manganese concentrations have been observed at some EHC sites, where aquifer conditions were aerobic and sediments contained manganese (III, IV) oxides and oxyhydroxides. This is an expected effect of a reductive dissolution of oxidized Mn (III and IV) phases and the creation of a more soluble Mn(II) under ISCR conditions. In neutral pH conditions, $MnCO_3$ (rhodochrosite) tends to control solubility of Mn(II) (Appelo and Postma, 2007). Since, neutral pH is observed in EHC ISCR zone (*i.e.*, a buffering or pH balancing effect of iron corrosion and carbon fermentation), this precipitation process is likely responsible for the observed decreases in dissolved Mn with operating time and groundwater flow path in the downgradient aquifer.

Peale *et al.* (2008) showed that the dissolved manganese levels in the EHC pilot increased to about 5 mg/L and then gradually decreased over a 1 year period to below 0.2 mg/L. The temporal trend for manganese followed that of dissolved iron. Similarly, dissolved manganese of about 2 mg/L was generated downgradient of the ZVI PRB described above (Stenning *et al.*, 2008). Subsequently, the levels of manganese were buffered quickly within the downgradient aquifer zone.

Laboratory Data on Trace Element Leaching from EHC Amended Soil

In-house studies evaluated the amount of dissolved iron, manganese and various inorganic compounds that emanated from EHC and ZVI when applied to a sandy loam soil. A total of ten EHC columns were set up with the sandy loam soil. Five columns were set up with higher EHC application rates (average 25%) to simulate PRB-type remedial applications. The other five EHC columns were set up with lower EHC application rates (average 10%) to simulate direct injection or soil fracturing type remedial applications. The ZVI column was loaded with 100% ZVI to simulate a PRB-type remedial application.

Site groundwater was pumped into the columns via a peristaltic pump at a flow rate of 150 mL/day. After approximately 90 days, the effluents were analyzed for 33 inorganic analytes. The data show that only iron and manganese were potentially above their respective groundwater standards (Table 1).

TABLE 1 – Inorganic compounds emanating from ZVI and EHC treated soil – laboratory tests

Metal ¹	DRINKING WATER STANDARD ² [secondary standard] ³	SOIL CONCENTRATION	SAND CONTROL COLUMN (n= 2)	ZVI CONTROL COLUMN (100%) (n= 1)	EHC PRB COLUMNS (25%) (n= 5)	EHC FRAC COLUMNS (10%) (n= 5)
units	mg/l	mg/kg	Effluent (mg/L)			
Aluminum	[0.05 to 0.2]	5,960	0.05	<0.04	0.09	0.06
Antimony	0.006	<10	0.20	<0.2	0.46	0.22
Arsenic	0.01	8.00	0.02	<0.04	0.05	< 0.04
Barium	2.0	62.00	0.08	0.03	0.81	0.11
Beryllium	0.004	0.40	< 0.001	<0.001	< 0.001	< 0.001
Bismuth	n.a.	<2.3	< 0.023	<0.023	0.03	0.03
Boron	n.a.	0.90	0.21	0.12	0.46	0.40
Cadmium	0.005	<0.3	0.00	< 0.003	< 0.003	< 0.003
Calcium	n.a.	5220.00	87.70	41.10	506.32	88.73
Chromium	0.1	8.20	< 0.005	< 0.005	< 0.005	< 0.005
Cobalt	n.a.	5.00	< 0.005	< 0.005	0.01	< 0.005
Copper	[1.0]	5.20	0.01	< 0.004	< 0.004	0.02
Iron	[0.3]	5860.00	0.01	0.06	14.43	1.70
Lead	0.015	11.40	< 0.025	< 0.025	< 0.025	< 0.025
Lithium	n.a.	10.00	< 0.02	< 0.02	0.03	0.02
Magnesium	n.a.	5470.00	60.40	20.00	239.04	65.65
Manganese	[0.05]	67.80	< 0.002	0.08	2.42	0.25
Molybdenum	n.a.	<0.6	0.01	0.27	< 0.006	< 0.006
Nickel	n.a.	9.00	0.46	0.14	0.07	0.36
Phosphorus	n.a.	180.00	< 0.04	0.14	0.14	1.69
Potassium	n.a.	972.00	4.00	2.00	4.60	2.92
Selenium	0.05	3.70	< 0.03	< 0.033	< 0.033	< 0.033
Silicon	n.a.	859.00	13.50	7.50	20.94	12.72
Silver	[0.1]	<0.7	0.01	< 0.007	0.01	0.01
Sodium	n.a.	168.00	88.20	69.70	85.38	70.40
Strontium	n.a.	23.00	0.66	0.25	3.90	0.60
Sulfur	n.a.	60.00	43.90	46.80	4.00	26.90
Thallium	0.002	8.00	< 0.05	< 0.05	< 0.05	< 0.05
Tin	n.a.	<1.8	< 0.02	< 0.018	0.01	< 0.018
Titanium	n.a.	13.90	< 0.003	< 0.003	< 0.001	< 0.003
Tungsten	n.a.	<3	< 0.03	< 0.03	< 0.03	< 0.03
Vanadium	n.a.	9.00	0.00	< 0.003	0.01	< 0.003
Zinc	[5]	35.10	0.00	< 0.003	0.01	0.02

1 value of 1/2 the detection was used for non-detect. Antimony was present in Site water used in the study.

2 Reference <http://www.epa.gov/safewater/mcl.html#sec>

3 Secondary Drinking Water Standards are guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply. However, individual States may choose to adopt them as enforceable standards.

Summary

Although dissolved iron and manganese will be created within the EHC zone, these concentrations will decrease within a short distance from the EHC zone and with operating time. It is hard to predict what iron and manganese levels are to be expected at a certain distance with increasing operating time at a specific application. It is rare for the dissolved iron or manganese concentrations to be problematic post EHC or ZVI application. However, for EHC applications in sensitive areas (e.g., in a proximity of a surface water body) it may be prudent to conduct a field-scale pilot evaluation to assess these potential impacts.

References

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