LONGEVITY OF MICRO-SCALE ZVI AND ORGANIC CARBON IN PERMEABLE REACTIVE BARRIER APPLICATIONS

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Resume

A efetividade das aplicações de remediação *in situ* é geralmente baseada na duração dos produtos empregados para o tratamento da água subterrânea. Especificamente, nas aplicações de Barreiras Reativas Permeáveis (BRP), essa duração determinará a freqüência da reaplicação. BRPs compostas de Ferro Zero Valente granular (FZV), tradicionalmente instaladas em trincheiras, tem durabilidade comprovada por décadas no corpo d´água. Ultimamente, produtos injetáveis com FZV mais fino e/ou várias fontes de carbono aumentou porque a instalação via injeção direta costuma ser mais prática, apresenta melhor custo/benefício e é menos invasiva. EHC® é uma combinação integrada de carbono de cereais e FZV muito fino, especificamente formulado para fácil aplicação via injeção. O objetivo deste artigo é avaliar a duração do EHC® no lençol freático. Segundo cálculos teóricos, a durabilidade esperada do FZV presente no EHC® é da ordem de décadas e para a fonte de carbono é de seis anos nas condições normais do freático.

Abstract

Long term effectiveness of *in situ* remediation applications is often based on the longevity of the amendments employed for treatment of groundwater. In particular, in Permeable Reactive Barrier (PRB) applications, the longevity of the amendments employed will dictate the frequency of reapplication required. PRBs composed of granular Zero-Valent Iron (ZVI), traditionally installed via trenching, have proven to last for decades in the subsurface. In more recent years, injectable amendments with more fine-grained ZVI and/or various carbon sources has gained popularity as installation via direct push injection in many cases is more practical, cost-efficient and less invasive. EHC® is an integrated combination of plant-derived carbon and micro-scale ZVI specifically formulated for easy application via injection. The purpose of this paper is to assess the longevity of EHC in the subsurface. Based on theoretical calculations, the ZVI component in EHC would be expected to last for decades, whereas the carbon source would be expected to last for three to six years under normal groundwater conditions.

Key words

Longevity, ZVI, permeable reactive barrier, EHC

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1 - INTRODUCTION

EHC® is an integrated combination of controlled-release plant-derived carbon and micro-scale zero valent iron (ZVI) particles used for stimulating in situ chemical reduction of otherwise persistent organic compounds in groundwater. In evaluating the longevity of EHC, several consumption mechanisms of the reactive components need to be considered including ZVI oxidation and carbon fermentation due to consumption (reduction) of terminal electron acceptors (TEAs), anaerobic corrosion of ZVI; organic contaminant reduction; and trace metal reduction and precipitation.

These processes are not independent of one another and are also controlled by site conditions such as groundwater flow velocity, inorganic aqueous concentrations, VOC concentrations and temperature. Although it is somewhat difficult to separate the longevity of the iron from that of the carbon given that they are present together, theoretical calculations supported by results from long-term laboratory studies and mature field sites can be used to estimate the effective lifetime of EHC.

2 - THEORETICAL CALCULATIONS

2.1 - ZVI Consumption

The rate of ZVI oxidation is impacted by the concentrations of TEAs in inflowing groundwater. Complete reductive dechlorination of TCE and the corresponding ZVI oxidation can be expressed by Equation 1. Naturally occuring TEAs, including oxygen, nitrate and sulfate will also consume the ZVI (Equations 2 through 4).

$$C_2HCl_3 + 3Fe^0 + 3H_2O \rightarrow C_2H_4 + 3Fe^{2+} + 3Cl^- + 3OH^- \quad (1)$$

$$4Fe^0 + 3O_{2(aq)} + 12H^+ \rightarrow 4Fe^{3+} + 6H_2O \quad (2)$$

$$NO_3^- + 9\,H^+ + 4Fe^0 \rightarrow NH_3 + 3H_2O + 4Fe^{2+} \quad (3)$$

$$4Fe^0 + SO_4^{2-} + 9H^+ \rightarrow HS^- + 4Fe^{2+} + 4H_2O \quad (4)$$

Anaerobic ZVI corrosion on the other hand will occur independent of the presence of oxidized species in groundwater and is mainly dictated by the ZVI surface area. Tests conducted with different types of ZVI materials have indicated water corrosion rates on the order of 0.1 to 1 mmol/kg Fe/day, with a value of 0.8 mmol/kg Fe/day estimated for particulate ZVI used in EHC (Reardon, 2005).

To evaluate potential rates of ZVI consumption in an EHC PRB, theoretical calculations were performed for a hypothetical site, but similar calculations can be performed using site-specific data. Based on the assumptions presented in Table 1, the annual ZVI consumption rate would be about 4.1% of the ZVI available, resulting in an estimated ZVI lifetime of about 24 years at this hypothetical site.

Table 1. Theoretical calculations of ZVI longevity for a hypothetical case.

Water corrosion rate (mmol/kg/day)	**EHC zone width (m)**	**EHC rate (mass)**	**ZVI mass (kg)**	**Velocity (m/day)**	**Porosity**	**Flow rate per 1 sq m (L/yr)**
0.8	6	0.5%	**21.6**	0.1	0.25	**9125**
	Influent (mg/L)	***Mass flux (g/yr)***	***Mass flux (mol/yr)***	***ZVI used (mol/yr)***	***ZVI used (g/yr)***	***% ZVI used per year***
Water corrosion	**---**	**---**	**---**	**---**	353.2	1.64%
DO	5	45.6	1.43	1.90	106.5	0.49%
TCE	5	45.6	0.35	1.04	58.3	0.27%
NO3	5	45.6	0.74	2.94	164.8	0.76%
SO4	10	91.3	0.95	3.80	212.9	0.99%
					Total	**4.1%**
				ZVI Longevity (yrs)		**24**

2.2 – Carbon consumption

The carbon component of EHC is comprised of fine-grained plant derived fibrous organic carbon particles. Because of the predominance of cellulose and hemicellulose in the particles, these particles will degrade more slowly (last longer) than other more soluble forms of carbon such as lactates, oils, and other glucose based amendments.

Carbon consumption (decay) in the subsurface is often assumed to follow a first order model. A first order carbon decay constant (K) of 1.6 x 10^{-3} day^{-1} was obtained in cellulose columns used to promote denitrification exposed to a nitrate flux of about 70 to 75 mg/L nitrate-N at room temperature (Vogan 1993). This equates to a 50% loss of cellulose in about 300 days or 10 months. Lower rates of degradation (K of 5E-4 day^{-1}) were obtained in sawdust columns exposed to the same flux. Sawdust contains a relatively higher proportion of hemi-cellulose and lignin. In-situ sawdust based denitrifying systems have operated for 15 years at field temperatures (Robertson et al, 2008).

Given that the carbon demand in the above conditions is far greater than that usually occurring in organic contaminant plumes, these published carbon degradation rates indicate that the carbon component of EHC should also last for years in the subsurface.

3 - ESTIMATE OF EHC LONGEVITY FROM FIELD PROJECTS

Field studies show that concentrations of dissolved organic carbon (DOC) commonly peak between 3 to 12 months after EHC injection and then decrease after approximately 2 years. A similar pattern has been observed for iron, measured both within and downgradient from an EHC injection zone, with more elevated concentrations observed during the first year (Figure 1).

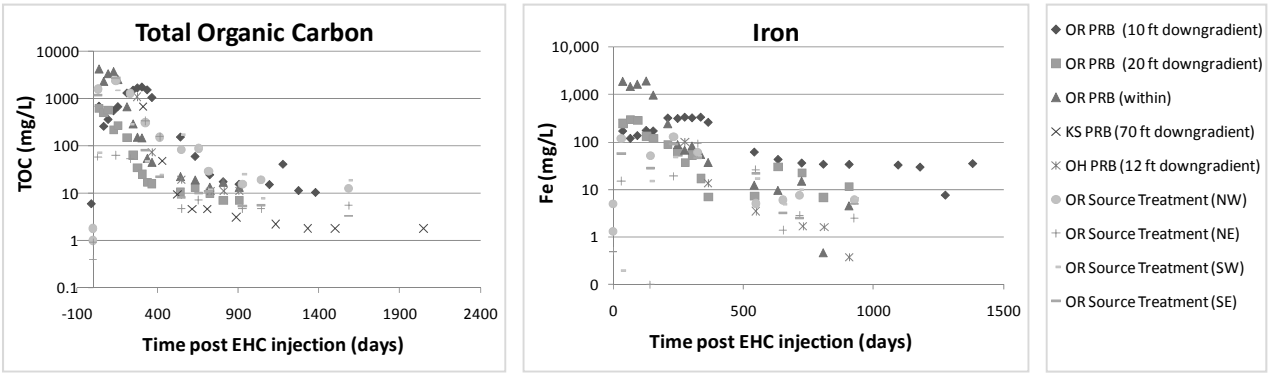

Figure 1. Total organic carbon and iron measured in groundwater within and downgradient of EHC injection zones.

Despite the observed decline in DOC and iron in groundwater after the first year, field data suggest that reducing conditions may be maintained and biological degradation promoted for several years after EHC application. The first full-scale EHC PRB, installed in April 2005, is still promoting around 95% reduction of carbon tetrachloride (CT) in inflowing groundwater six years after installation. After an initial acclimatization period of approximately 5 months, a half life of between 1 and 3 days has been maintained for CT within the reactive zone (Figure 2), despite declining levels of dissolved organic carbon in groundwater.

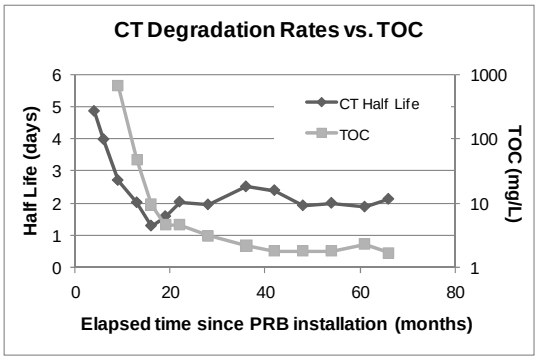

Figure 2. CT half lives within PRB vs. TOC.

4 - SUMMARY

There are many factors that can influence the actual longevity observed at a given site. Factors such as temperature, groundwater flow velocity, electron acceptor demand, mass loading applied, installation method, and inorganic chemistry are just a few of the factors that could affect the actual longevity. However, it appears that longevity of 5 years for EHC may be achievable in most subsurface environments.

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