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EFFECT OF TEMPERATURE AND IRON CONTENT ON IRON PRB DESIGN

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ABSTRACT: Granular iron column tests were conducted to confirm the change in granular iron reactivity at various groundwater temperatures and to compare 100% granular iron reactivity to measured reactivities in an iron/sand mixed zone. Half-lives for TCE were measured for iron contents (by weight) of 10%, 25%, 50% and 100% at temperatures of 25, 18, 14 and 9°C. It was observed that the TCE half-lives decreased with temperature exponentially and conformed to the theoretical Arrhenius equation. The temperature correction factors from a reference of 25°C for the 25%, 50% and 100% granular iron were: ×2 for 18°C, ×3 for 14°C and ×4 for 9°C. As expected, the TCE half-lives decreased proportionally to the weight percent in the 25% and 50% iron columns. The TCE half-lives in the 10% iron column were less affected by temperature and had values significantly lower than those predicted by direct scaling based on the iron content.

INTRODUCTION

Permeable reactive barriers (PRBs) constructed of granular iron have are effective passive remediation method for groundwater contaminated with a range of contaminants, mainly halogenated compounds (Gillham and O’Hannesin, 1994). A PRB is a constructed in-situ zone of reactive material placed across the path of contaminated groundwater. Major advantage of PRBs over other groundwater remediation approaches is the lack of above ground structures, no operating costs, low maintenance cost and the enhanced technical efficacy, particularly compared with pump-and-treat systems. There are currently more than 100 iron PRBs installed at volatile organic compound (VOC) contaminated sites (O’Hannesin, 2003).

Design of a granular iron PRB for VOC treatment often involves determination of site-specific degradation rates in a laboratory column test using site groundwater. Typically, laboratory tests are conducted at room temperature (25°C) and results are adjusted to reflect site groundwater temperature. Treatability testing is typically done with columns containing 100% granular iron. In some common construction methods, granular iron is typically mixed with sand due to construction width requirements. Therefore, an additional scaling factor is necessary to account for a decrease in reactivity in an iron/sand zone, compared to data obtained within a 100% iron column. This study was conducted to confirm the temperature and granular iron content scaling factors that are currently used for commercial application of iron PRBs.

MATERIALS AND METHODS

Laboratory studies were undertaken using four columns containing 10%, 25%, 50% and 100% by weight granular iron and a balance of sand. The granular iron (0.25 to 2 mm, -8 to +50 US Standard Mesh size) was obtained from a commercial source used in iron PRB applications. The sand was calcium carbonate-based with grain size gradation similar to that of granular iron. Hydraulic cnductivity values ranged from 5.8×10^{-2} to 9.2×10^{-2} cm sec^{-1} for all mixtures. The columns were constructed of Plexiglas™ with a length of 50 cm and an internal diameter of 3.8 cm. Seven sampling ports were positioned along the length at distances of 2.5, 5, 10, 15, 20, 30 and 40 cm from the inlet end in addition to the influent (0 ft; 0 cm) and effluent (50 cm). The columns received 10 mg/L of trichloroethene (TCE) dissolved in organic free distilled water containing 40 mg/L of $CaCO_3$. The flow in each column was maintained to obtain a residence time of 20 to 22 hrs.

Four temperatures (9, 14, 18 and 25°C) were selected to encompass a typical range of groundwater temperatures. At each temperature, each column was operated for 70 to 120 pore volumes, with a cumulative flow of about 400 pore volumes. The TCE concentration column profiles were collected periodically throughout the test. First-order TCE half-lives were obtained by fitting the profiles concentration vs. residence time, using a least square method. At steady state (>30 pore volumes), TCE profiles were used to determine half-life values. Due to inconsistencies with initial results obtained for both the 10% and 25% iron columns, additional columns were set up and tested again at the four temperatures. The data presented for the 10% and 25% columns are averages for the duplicate columns.

RESULTS AND DISCUSSION

Complete TCE degradation was achieved in all columns in the tested temperature range. Due to dechlorination of TCE, small amounts of cis 1,2-dichloroehtene (20 to 60 μg/L, <1% molar of initial TCE) were formed and degraded within the columns. No vinyl chloride was detected. The first-order degradation model provided good fits to the TCE concentration profiles, with r^2 values greater than 0.95. The obtained TCE half-lives are summarized in Table 1. As expected, TCE half-lives increased with both the decreasing temperature and decreasing iron content.

Table 1. Summary of measured TCE half-lives.

Temperature (°C)	**Column**			
	10%	**25%**	**50%**	**100%**
	TCE Half-life [a] (hrs)			
25	2.5 ± 0.3	1.6 ± 0.3	0.75 ± 0.3	0.45 ± 0.1
18	4.1 ± 0.8	3.5 ± 0.4	1.5 ± 0.4	0.87 ± 0.2
14	5.3 ± 0.5	4.2 ± 0.3	2.2 ± 0.3	1.4 ± 0.3
9	7.5 ± 0.7	4.9 ± 0.6	3.0 ± 0.3	2.0 ± 0.3

[a] Average ± standard deviation.

Figure 1 shows the temperature scaling factors for the measured TCE half-lives as a function of temperature, assuming a reference temperature of 25°C. The trends in scaling factors with temperature were similar for the 25%, 50% and 100% iron columns.

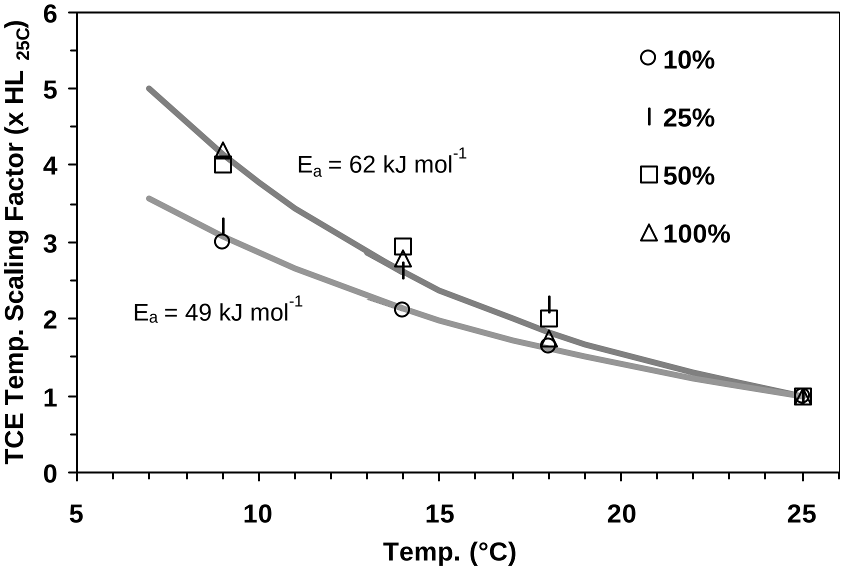

FIGURE 1. TCE half-life temperature scaling factors. The symbols indicate relative increase of TCE half-life in reference to the half-life value obtained at 25°C in each column. The lines represent the fits to the 100% data (activation energy, E_a = 62 kJ mol^{-1}) and to the 10% iron data (E_a=49 kJ mol^{-1}).

However, the TCE half-lives obtained for the 10% iron column appeared to be influenced by temperature to a lesser degree.

Several studies have shown that degradation kinetics of VOCs in the presence of granular iron conform to the Arrhenius equation (e.g.: Johnson et al., 1996; Su and Puls, 1999). For two measured reaction rates (k_{T1} and k_{T2}) at temperatures T_1 and T_2 (in °K), the Arrhenius equation can be represented as:

$$\ln\left(\frac{k_{T2}}{k_{T1}}\right) = \frac{E_a}{R} \times \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (1)$$

where:

k = first-order reaction rate,
E_a = activation energy (J/mol),
R = ideal gas constant (8.314 J/K mol)
T = absolute temperature (°K)

The Arrhenius equation was used to fit the laboratory data and to develop a general relationship between the relative TCE half-life and temperature. The Arrhenius equation fit to the 25%, 50% and 100% iron column data resulted in an activation energy (E_a) value of 62 kJ mol^{-1} (Figure 1). For the 10% iron column, a fitted E_a value of 49 kJ mol^{-1} was obtained. The reported values of E_a vary from 15 kJ mol^{-1} to 55 kJ mol^{-1}, depending on the type of VOC and the iron source (Tratnyek et al., 2003). For example, an average value of 35 kJ mol^{-1} was reported for TCE reacting with both reagent- and construction-grade iron (Su and Puls, 1999).

Figure 2 shows the iron % scaling factors for the measured TCE half-lives as a function of iron content, assuming a reference iron content of 100%. The typical design

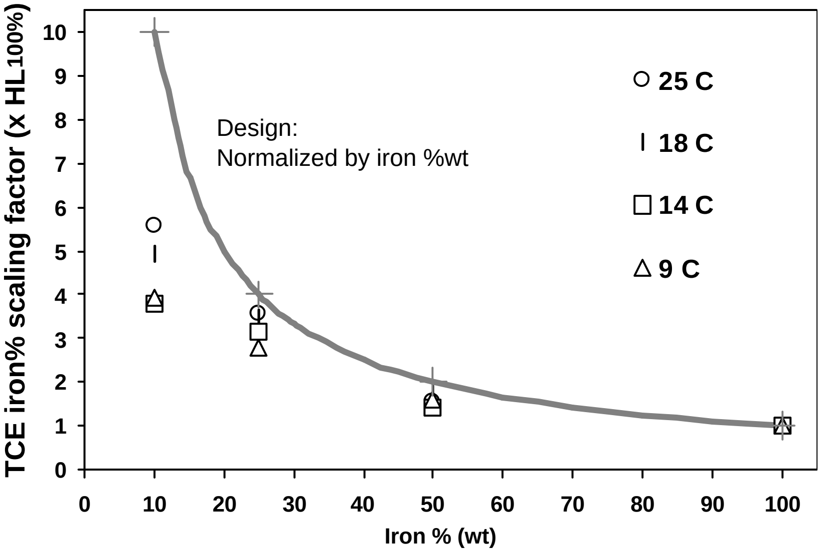

FIGURE 2. TCE half-life iron content scaling factors. The symbols indicate relative increase of TCE half-life in reference to the half-life value obtained for the 100% iron column.

approach to scaling half-lives from 100% iron is the direct use of iron % as the scaling factor. The design line using this method is shown in Figure 2. The predicted TCE half-lives for 25% and 50% iron were slightly lower than those measured in the laboratory columns. However, the predicted line overestimated the TCE half-lives in the 10% iron column, with the measured value increasing from 100% iron by a factor of 4 to 6, compared to the predicted factor of 10 (Figure 2).

The TCE half-lives in the 10% iron column did not follow the general trends observed in the 25%, 50% and 100% columns. The reason for this discrepancy is currently under investigation. Although this phenomenon is interesting, it may have limited practical implications on the design, because a minimum 25% by weight of iron in iron/sand mixes is typically used in commercial applications. This minimum iron content requirement is used to assure an adequate contact time of VOCs with iron grain surfaces, as contaminated groundwater flows through the iron/sand zone.

CONCLUSIONS

The TCE half-life decrease with temperature in 100% iron and in iron/sand mixes was exponential and it conformed to the Arrhenius equation. The temperature correction factors from a reference of 25°C for 25%, 50% and 100% iron were: ×2 for 18°C, ×3 for 14°C and ×4 for 9°C. Temperature influence was less pronounced in the 10% iron/sand column. The TCE half-lives decreased proportionally to the weight percent iron for all columns. Linear scaling of 100% iron half-lives according to iron content appears a conservative, but realistic, design approach for use in granular iron PRB applications.

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