The Use of Ultrasound to Restore the Dehalogenation Activity of Iron in Permeable Reactive Barriers

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In situ permeable reactive barriers (PRBs) containing iron as the reactive agent have gained popularity in the past decade as a near-passive, in situ groundwater remediation technology for halogenated solvents. Although zero-valent iron has been shown to be effective for this purpose, a continuing problem is the loss of system reactivity over time. This loss is due, at least in part, to a build up of corrosion products on the iron or other precipitates within the PRB. The lifetime of the barrier could be significantly extended with a technology that could remove materials occluding the surface area of the reactive material. The purpose of this research was to investigate the field-scale application of ultrasonic energy to rejuvenate an in situ PRB with the goal of enhancing/restoring the rate of trichloroethylene (TCE) degradation. Extensive laboratory and field analyses were conducted to examine the impact of ultrasound on iron under various conditions. Results indicate that a sonication period as brief as 30 minutes has a significant positive impact on the first order rate constant for TCE degradation. Field data from the application of ultrasound to two permeable reactive barriers (one at NASA Kennedy Space Center, FL and the other in the western United States) will be presented.

Reduction in dechlorination rates and flow problems have been linked to deposition of material mainly carbonates in highly alkaline water, on the iron surface (Johnson and Tratnyek, 1995, Mackenzie et al., 1999). Bridging between iron particles can result in plugged pore spaces at the upstream face of a barrier and interfere with the hydraulics of a remediation system (Mackenzie, et al., 1997). In an aquifer with significant alkalinity, and especially under even moderately aerobic conditions, eventual blinding of the iron surface and reduced reactivity will occur at the upstream portion of the permeable barrier, where the greatest contaminant mass transfer takes place. A technology that can maintain or restore wall performance is needed and the use of ultrasound for this purpose may be applicable.

Ultrasonics refers to periodic stress waves that occur at frequencies in excess of 20 kHz. Effects produced by ultrasonic waves arise from cavitation, which occur in those regions of a liquid that are subjected to rapidly alternating pressures of high amplitude. These high pressures are relieved by the radiation of intense shock waves (Brown and Goodman, 1965). The periodic application of ultrasound as a cleaning process may provide an opportunity to enhance a zero-valent iron PRB through iron surface maintenance. Improved efficiency and increased activity due to surface changes created by sonication have also been noted in lithium (Lindley, 1990), zinc (Suslick and Doktycz, 1990), and copper catalysts (Lindley et al., 1987). Although ultrasound is normally used in liquid mediums, it has been found that ultrasonic energy can move

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through saturated porous media. Experiments have been reported that show ultrasonic energy can pass through water-saturated soil at energy levels adequate to clean an iron surface to a distance of 54 cm (Cannatta,1998).

Extensive batch studies were conducted to examine the impact of ultrasound on iron under various conditions. In addition, the effect of ultrasound on TCE degradation in the absence of iron was evaluated and no destruction of TCE occurred at the energy used in this work. Variables that were examined include the following: the type of iron (100-mesh or coarse iron filings), ultrasound treatment and length of use, and the condition of the iron (acid-washed, unwashed). Table 1 shows the first-order rate constants for the disappearance of TCE for both types of iron in acid-washed and unwashed conditions. Acid-washed iron was more effective in the removal of TCE for both types of iron and 100-mesh iron was superior to iron filings. This effect is primarily due to increased surface area and agrees with the findings of previous researchers that the reaction is surface-area dependent (Johnson et al., 1996). When acid-washed 100-mesh iron or iron filings were studied, it was found that the beneficial results of ultrasound were negligible (an improvement of only 2.0%). This result is not surprising considering the acid washing process removes surface debris and oxidation products thus exposing more reactive iron surface. The influence of ultrasound on iron that was unwashed was more dramatic. As shown in Table 1, the rate constant for unwashed, 100-mesh iron increased by 33.3 %. Unwashed iron filings showed a similar change with an improvement of 24.1%.

Table 1. Comparison of first order rate constants ($hr^{-1} \bullet g\ Fe^{-1}$($x\ 10^{-3}$)) and surface area ($m^2/g$) before and after US for iron under different conditions.

Iron	Condition	No US	US	No US	US	% change in surface area
		k_{obs}, 1st Order Rate Constants $hr^{-1} g\ Fe^{-1}$($x\ 10^{-3}$)		Surface Area (m^2/g)		
100 mesh	Unwashed	3.75	5.00	3.09	4.12	+33.3
	Acid-washed	6.42	6.54	4.28	5.40	+26.2
Iron Filings	Unwashed	2.70	3.36	0.77	2.07	+169
	Acid-washed	4.74	4.68	1.92	2.91	+51.6

In addition to laboratory studies, two field studies have been performed to date. A research PRB was installed at Cape Canaveral Air Force Station (CCAFS), Florida to test the effectiveness of ultrasound at field scale. The ultrasound units were also tested at a PRB in the western United States. Ultrasound was applied to the PRBs and reactive material samples were taken before and after sonication. These samples were brought back to the University of Central Florida for laboratory studies. Data show that the use of ultrasound in the field does increase the effectiveness of the iron for TCE degradation.

The PRB located at Launch Complex 34 (LC34), CCAFS, in east central Florida has been in place over three years. The PRB placed at this site was not intended to treat the site's entire plume, but was constructed to evaluate the installation technique and the use of ultrasound. Several observation and monitoring wells (10-cm diameter) were placed in front of, inside, and behind the PRB. Ultrasound was applied by use of a submergible 600-W, 40- kHz or 3,000-W, 25-kHz resonators that could be lowered into the wells and held at various depths for the intended treatment period. Core samples were taken (within 30 cm of the well) before and after treatment and the iron was removed from these samples under a nitrogen atmosphere. The iron was then used in bag laboratory experiments to determine the first-order rate constants for the disappearance of TCE. Iron taken from all depths showed an improvement after field application of ultrasound. Table 2 shows percentage improvement for TCE degradation rate constants after ultrasound application (as compared to samples taken pre-ultrasound) at various depths of treatment. Rate constants improved from 21 to 67 percent. These data show that exposure time and power used are both important aspects of treatment.

Table 2. Rate constants before and after ultrasound for field experiments (CCAFS**).**

Relative Depth	30 min at 40 kHz	90 min at 40 kHz	30 min at 25 kHz	90 min at 25 kHz
	Percentage Improvement of Half-Life Compared to Unsonicated Samples			
Shallow 7-12 ft.	24	41	58	67
Intermediate 13-18 ft.	22	28	41	66
Deep 18-26 ft.	21	33	45	59

The second PRB used for field tests had one 5-cm well at the entrance side of the PRB (already in place) that was used for the 40-kHz resonator and two 10-cm wells that were installed to test the 25-kHz resonator. The second field demonstration produced similar results with first-order rate constant improvements (compared to unsonicated iron) of 64-73% with the 25-kHz, 3000-W resonator and 40% with the 40-kHz resonator. Based on results of laboratory and field demonstrations, it was concluded that ultrasound application is a practical and successful maintenance tool for improving iron reactivity in PRBs.

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