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IRON ENHANCED ABIOTIC DEGRADATION OF CHLORINATED HYDROCARBONS

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INTRODUCTION

Since the 1970s, several researchers have investigated the ability of certain zero-valent metals or alloys to enhance the degradation of halogenated organic compounds in contaminated water. Iron, zinc, aluminum, brass, copper, and stainless steel have been studied at various times with varying degrees of success. Gillham and O'Hannesin have recently made a literature review and conducted tests on 14 halogenated aliphatic compounds using zero-valent iron as an enhancing agent (1). The results showed that rapid dehalogenation occurred on all of the compounds tested except dichloromethane. Based on these test results, EnviroMetal Technologies, Inc. proposed to remediate groundwater contaminated with chlorinated organic compounds using this technology.

The EPA Superfund Innovative Technology Evaluation (SITE) program has accepted this technology for demonstration. This demonstration project will include two processes, above ground reactor and in situ permeable wall. The demonstration on the above ground reactor is being conducted at a site in Wayne, New Jersey. The main contaminants at this site are tetrachloroethene (PCE) and trichloroethene (TCE). The in situ permeable wall process will be conducted at a site in upstate New York. This site is a shallow sand aquifer containing TCE, dichloroethenes, and 1,1,1-trichloroethane.

METHODOLOGY

Before the site demonstration, laboratory experiments were conducted on the contaminated groundwater to evaluate the efficiency of the process , under simulate site conditions. The procedures of this and the two demonstration processes are described below.

Column tests were undertaken in the laboratory to simulate the dynamic conditions of groundwater. The columns were constructed of plexiglass with a length of 50 cm and an internal diameter of 6.5 cm. Seven sampling ports were positioned at distances of 2.5, 5, 10, 15, 20, 30, 40 and 50 cm from the inlet end. The columns also allowed for collection of samples from the influent and effluent solutions. A total of three column experiments were set up, one control and two reactive columns. The control column was packed with 100% silica sand. One reactive column was packed with a mixture of 50% (by weight) granular iron and 50% (by weight) silica sand, while the other reactive column was packed with 100% granular iron. The mass of iron to volume of solution ratio for the 50% iron column was 3.4 g : 1 ml and for the 100% iron column was 8 g : 1 ml.

The above ground reactor was constructed of fiberglass with a height of 9 feet and an internal diameter of 8 feet. The reactor was packed from the bottom to the top with: 6" of pea gravel, 66" of granular iron, 24" of groundwater and 12" of air. The total weight of iron was 18003 kg with a porosity of about 0.4. The pore volume was calculated to be about 3400 L. Five sampling ports were positioned at distances of 21, 36, 48, 66 and 84 inches from the inlet end (top of the water level). The influent and effluent solutions were also collected. During the demonstration, groundwater was extracted from the site by passive recovery techniques, using tiles placed in the bottom of collection trenches (about 14 ft below the ground surface).

Groundwater flowed through the collection trenches to a sump, where it was pumped to the above ground reactor at a rate of 1.9 L per minute. This would let the water to have the residence time in the reacting medium of about 26 hours during which the TCE and PCE in the contaminated water would be completely dechlorinated according to the half lives of those two compounds obtained in the column test.

The in situ permeable reactive wall will be constructed by filling a trench with iron and inert materials. Groundwater will move naturally through the wall. The contaminants are expected to be dechlorinated after passing the reactive wall.

RESULTS

Column Tests

Tables 1-3 show the concentrations of PCE and TCE at different sampling positions with various pore volumes of the groundwater passing through the three columns. The results show that (1) for the control column containing only silica sand, the concentrations of PCE and TCE remained relatively constant over the entire length of the column, with the influent concentration very similar to the effluent concentration; (2) for the 50% iron/sand column, the observed decline in concentration with distance reflects that both PCE and TCE were degraded gradually along the column, at a distance between 15 and 20 cm from the influent, both compounds had degraded to below the detection limit (2.5 ug/L for PCE and 3.0 ug/L for TCE); (3) for the column with 100% granular iron, rapid declines in concentrations of PCE and TCE were observed, at a distance between 2 and 10 cm from the influent, both compounds had degraded to below the detection limit. The production of small amounts of 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cDCE), and vinyl chloride (VC) were observed in both reacting columns. However, 1,1-DCE disappeared rapidly in both columns, cDCE and VC were eventually dechlorinated in the 100% iron column. They were not completely removed in the 50% iron/sand column.

TABLE 1
CONTROL COLUMN (100% SILICA SAND)

		Distance Along Column (cm)								
		Influent								Effluent
		0	2.5	5	10	15	20	30	40	50
	Pore Volume	Organic Concentration (ug/L)								
PCE	1.03	12394	12272	11863	2914	9997	10718	8896	2858	7709
	2.15	11031	9978	9798	8709	8050	9932	10947	11504	10061
	5.00	8305	8867	9640	9241	9213	9349	9012	10196	8841
TCE	1.03	508	465	490	319	444	404	400	242	234
	2.15	432	442	334	317	384	415	423	437	387
	5.00	298	273	305	291	293	304	287	330	273

Flow Velocity = 44 cm/day (1.44 ft/day)
Porocity = 0.39

TABLE 2
REACTIVE COLUMN I (50/50 Iron/Silica Sand)

		Distance Along Column (cm)								
		Influent								Effluent
		0	2.5	5	10	15	20	30	40	50
	Pore Volume	Organic Concentration (ug/L)								
PCE	1.25	11882	73	0.7	0	0	0	0	0	0
	6.73	9327	5317	2790	0	0	0	0	0	0
	11.28	9438	7037	3781	0	0	0	0	0	0
	15.73	9434	6646	3712	47	0	0	0	0	0
	21.67	8934	4188	2480	249	0	0	0	0	0
	24.95	4593	3073	1851	285	0	0	0	0	0
	31.00	4360	1630	2000	388	0	0	0	0	0
	33.86	5062	3114	1681	302	0	0	0	0	0
	38.81	4846	2842	1805	486	1	0	0	0	0
	40.92	4316	2406	1314	379	3	0	0	0	0
TCE	1.25	462	133	0	0	0	0	0	0	0
	6.73	312	704	748	0	0	0	0	0	0
	11.28	379	589	636	90	0	0	0	0	0
	15.73	390	564	656	127	0	0	0	0	0
	21.67	361	495	397	143	0	0	0	0	0
	24.95	1160	730	500	132	0	0	0	0	0
	31.00	1042	374	516	157	4	0	0	0	0
	33.86	986	621	365	108	4	0	0	0	1.5
	38.81	1136	534	324	141	12	0	0	0	0
	40.92	938	400	213	105	12	0	0	0	0

Flow Velocity = 55 cm/day (1.8 ft/day)
Porocity = 0.34

The test results show that the degradations of both PCE and TCE follow first order kinetics. Therefore the half lives of these two compounds in the two reactive columns were calculated according to the equation:

$$t_{1/2} = 0.693/k \qquad (1)$$

where $t_{1/2}$ is the half life (the time at which the initial concentration, C_0, declines by one-half), k is the first order rate constant which is calculated according to the following equation:

$$\ln (C/C_0) = -kt \qquad (2)$$

where C is the concentration in solution at time t. From the experimental results, the half lives of PCE and TCE in the reaction columns are calculated to be as follow:

(1) For 50% iron/sand column - PCE:0.67 hrs, TCE:1.10 hrs
(2) For 100% iron column - PCE:0.42 hrs, TCE:0.52 hrs

Demonstration Using Above Ground Reactor

The sampling was started after about 3 pore volumes of water had passed through the reactor. The water samples were collected about once per week. So far, four sets of samples have been collected and analyzed. The results are shown in Table 4. In the first three sets of samples, all PCE and TCE were completely dechlorinated after passing through 12" of iron. No chlorinated hydrocarbons were observed (detection limit for all the probable products was 1.0 ug/L). In the fourth set of samples, the concentration of PCE was very high (13000 ug/L), so it did not completely disappear until the solution passed through about 24" of the reactive iron. The quantities of TCE increased first and then disappeared after the solution had passed through 24" of iron.

TABLE 3
REACTIVE COLUMN II (100% Grandular Iron)

Distance Along Column (cm)

	Pore Volume	Influent 0	2.5	5	10	15	20	30	40	Effluent 50
		Organic Concentration (ug/L)								
PCE	1.01	11963	0	0	0	0	0	0	0	0
	4.47	8227	1	0	0	0	0	0	0	0
	8.73	9602	462	0	0	0	0	0	0	0
	13.88	9847	1532	0	0	0	0	0	0	0
	19.25	7610	1136	6	0	0	0	0	0	0
	21.79	4535	923	14	0	0	0	0	0	0
	27.19	4476	1109	59	0	0	0	0	0	0
	29.62	5190	865	57	0	0	0	0	0	0
	33.02	4241	682	67	0	0	0	0	0	0
	34.85	4407	926	96	0	0	0	0	0	0
TCE	1.01	452	0	0	0	0	0	0	0	0
	4.47	282	6	0	0	0	0	0	0	0
	8.73	336	391.7	0	0	0	0	0	0	0
	13.88	384	541	10	0	0	0	0	0	0
	19.25	321	349	29	0	0	0	0	0	0
	21.79	1222	356	26	0	0	0	0	0	0
	27.19	1069	380	54	0	0	0	0	0	0
	29.62	1005	298	36	0	0	0	0	0	0
	33.02	1020	169	35	0	0	0	0	0	0
	34.85	998	262	46	0	0	0	0	0	0

Flow Velocity = 47 cm/day (1.54 ft/day)
Porocity = 0.40

TABLE 4
ABOVE GROUND REACTOR

		From the Influent (inch)						
	0	0	21#	36	48	66	84	96*
	Pore Volume	Concentration (ug/L)						
PCE	2.4	6200	6100	0	0	0	0	0
	8.8	9800	Nd**	Nd	Nd	Nd	Nd	0
	14.4	9700	Nd	Nd	Nd	Nd	Nd	0
	25.6	13000	8700	4200	0	0	0	0
TCE	2.4	110	0	0	0	0	0	0
	8.8	69	Nd	Nd	Nd	Nd	Nd	0
	14.4	130	Nd	Nd	Nd	Nd	Nd	0
	25.6	110	93	330	0	0	0	0

\# The reaction with iron started at 24" from influent port
* This is the effluent solution
** Not determined

The production of cDCE was observed between 0 and 12" below the iron surface. It was 92, 18 and 0 ug/L respectively at 12", 24" and 42" below the iron surface respectively. Small quantity of vinyl chloride (4.9 ug/L) was observed at 24" which disappeared at 42". At this sampling point, 1.5 ug/L of methylene chloride was observed which degraded to below 1.0 ug/L below the iron surface. The reaction process appeared to follow sequential dechlorination from PCE to TCE to cDCE and then to vinyl chloride and methylene chloride. However, all the chlorinated compounds were completely dechlorinated at the end if there was enough reactive iron.

CONCLUSIONS

The results from the column tests show that the 100% iron column can dechlorinate PCE and TCE much faster than the 50% iron/sand column. Also, the former column can completely dechlorinate the by-products but not the later column. Therefore the 100% iron column was used in the pilot scale experiment. The results obtained thus far showed that PCE, TCE and their chlorinated products can be completely dechlorinated in the above ground reactor.

The potential limiting factors of this technology such as: the possible formation of precipitates that might clog the treatment reactor's pore space and/or coat the iron surface and thus limiting water flow or reducing the reactivity of iron; the consumption of iron by its reaction with the chlorinated compounds to produce soluble iron compounds; and the increasing pH over time and thus impeding the reaction rate, are being studied. The approximate capital as well as the short and long term operating and maintenance costs are being evaluated.

The above ground reactor may replace the air stripper and activated carbon as methods of remediating halogenated organic compounds. The in situ permeable wall may permit passive treatment for a long period of time and thus eliminating the disposal or treatment of the pumped groundwater.

Acknowledgments

The author wishes to acknowledge S. Krishnamurthy of the United States Environmental Protection Agency (EPA) for his helpful discussion and critical review. He also wishes to thank Kim Lisa Kreiton of PRC Environmental Management, Inc (PRC) for her efforts in collecting and calculating the data in the above ground reactor demonstration and William Matulewicz of Rhode Engineering for his providing of the column test results. This research work was funded by EPA under Contract No. 68-CO-0047 to PRC.

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