Bioremediation and Sustainable Environmental Technologies—2017. Fourth International Symposium on Bioremediation and Sustainable Environmental Technologies (Miami, FL; May 2017). ©2017 Battelle Memorial Institute, Columbus, OH, www.battelle.org/biosymp. A. Barton and S. Rosansky (Chairs)

In Situ Chemical Reduction with ZVI and ZVI Sulfide

Michael D. Lee, Ph.D. (mlee@terrasystems.net) and Richard L. Raymond, Jr.
(Terra Systems, Inc. Claymont, DE USA)
Patrick Randall (Hepure, Flemington, NJ, USA)

ABSTRACT: A batch treatability study was carried out with a mixture of solvents (tetrachloroethene [PCE], carbon tetrachloride [CT], 1,2-dichloroethane [1,2-DCA], 1,1,1-trichloroethane [1,1,1-TCA], and bromoform [BF]); two zero valent iron (ZVI) products including Hepure's Ferox Flow (<37 to 149 microns) and Hepure Ferox Target (<44 microns); Terra Systems emulsified vegetable oil product – SRS; with and without added sulfide. Many of the treatments were bioaugmented with a dechlorinating enrichment. A column study was carried out for 45 days with the following treatments: 4% ZVI of a mixture of 40% Hepure PRB (297 to 2,380 microns) and 60% Hepure Flow (49 to 149 microns), 4% Hepure Target (<37 microns), and 4% Hepure PRB/Flow ZVI treated with calcium polysulfide. The influent for the columns was spiked with TCE and chloroform (CF).

There was an immediate reduction of PCE, 1,1,1-TCA, 1,2-DCA, CT, and BF in the first day for most of the ZVI-amended treatments compared to the control. Over the 70-day study, the treatments with ZVI and sulfide showed more complete removal of the chlorinated ethenes (up to 91.8%) than the ZVI treatments without sulfide (54.7 to 73.2%). 1,1,1-TCA was consumed completely in the ZVI and sulfide treatments and was reduced by 91.1 to >99.97% in the ZVI treatments without sulfide. 1,2-DCA was more resistant to degradation with a maximum of 52.3% removed in the SRS, Ferox Flow, and bioaugmentation treatment. Complete removal of the CT and BF were observed in all ZVI-amended treatments, but the reaction rates were generally faster for the ZVI treatments with sulfide. The PRB/Flow column amended with sulfide removed an average of 93.3% of the TCE and daughter products and 96.0% of the CF and daughter products compared to 79.2% of the TCE and daughter products and 78.6% of the CF and daughter products in the PRB/Flow column. More DCE, ethene, and ethane were generated with the PRB/Flow S column than the PRB/Flow column without sulfide. The Target column removed 95.8% of the TCE and daughter products and 77.2% of the CF and daughter products. When the retention times on the columns were less than about 2 days, the performance of the columns suffered.

The addition of sulfide increased the reactivity of the ZVI against PCE and 1,1,1-TCA. In the column study, the ZVI + sulfide promoted more complete removal of the TCE and CF than ZVI alone.

BACKGROUND

Zero valent iron (ZVI) has been extensively used to treat chlorinated solvents (Gilham et al., 1994). The combination of ZVI and sulfide can reduce the corrosion of iron with water and extend the reactivity of the ZVI (Han and Yan, 2016). Most of the applications of ZVI have been for chlorinated ethenes (PCE and TCE), chlorinated ethanes including 1,1,1-TCA and 1,1-dichloroethane or 1,1-DCA, and chlorinated methanes (CT and CF). 1,2-Dichloroethane or 1,2-DCA is generally resistant to attack by ZVI although the combination of ZVI with sulfide is more reactive against 1,2-DCA (Garcia et al., 2016). ZVI is known to react with bromoform or BF (Li et al., 2006). Sulfide can be added to ZVI with sodium sulfide, sodium dithionite, sodium thiosulfate, or other methods (Han and Yan, 2016). Above a S:Fe ratio of 0.025, the TCE transformation rates were similar.

APPROACH

A batch treatability study was carried out with a mixture of solvents (PCE, CT, 1,2-DCA, 1,1,1-TCA, and BF) and two ZVI products including Hepure's Ferox Flow (<37 to 149 microns) and Hepure Ferox Target (<37 microns) with and without added sulfide. The target sulfide/iron ratio was 0.1 S/Fe. The treatments are shown in Table 1. The tapwater was amended with 15 mM HEPES buffer (pH 6.1), 500 mg/L sulfate, and spiked with a methanol solution of PCE, CT, 1,2-DCA, 1,1,1-TCA, and BF. All ZVI and ZVI-sulfide treatments were also bioaugmented on day 43. In addition, a column study was carried out with a mixture of 40% Hepure PRB (297 to 2,380 microns) and 60% Hepure Flow and 40% Hepure PRB and 60% Hepure Flow treated with calcium polysulfide. Sacrificial samples were collected for VOCs and dissolved hydrocarbon gases (methane, ethene, ethane, and acetylene) after 1, 7, 22, 43, and 70 days.

TABLE 1. Treatments.

Treatment	ZVI Particle Size	Spiked Water	ZVI	Sodium Sulfide Nonahydrate	SRS	Culture Added on Day
	μm	g	g	g	g	
Control		532				
Ferox Flow	<37-149	530	5.3			43
Ferox Flow Sulfide	<37-149	531	5.3	2.3		43
Ferox Target	<37	532	5.3			43
Ferox Target Sulfide	<37	531	5.3	2.3		43
SRS Flow	<37-149	523	5.3		8.8	43
SRS Flow Sulfide	<37-149	525	5.3	2.3	8.8	43

Column studies were performed using the following ZVIs: mixture of 40% Hepure PRB (297 to 2,380 microns) and 60% Flow (<37 to 149 microns), Hepure Target (<37 microns), and Hepure 40% PRB and 60% Flow treated with sulfide. The tests were designed to evaluate the effectiveness of the two ZVI and the combination of ZVI and sulfide to treat TCE and CF. The study used 4% by weight ZVI loadings in sand packed into 24-inch-long, 2-inch diameter PVC columns. The column with Hepure PRB/Flow Sulfide included treatment with calcium polysulfide at a S/Fe ratio of 0.11. The column flow rates generally ranged from 0.020 to 0.32 mL/min or retention times of 1.0 to 11 days. The study was run for six weeks with samples collected from the influent and effluents from the columns at four time points.

Batch Studies Results. There was an immediate reduction of PCE, 1,1,1-TCA, 1,2-DCA, CT, and BF in the first day for most of the ZVI-amended treatments compared to the control (Table 2). PCE decreased by a maximum of 23.3% in the Target + Sulfide treatment. The greatest reduction in 1,1,1-TCA concentrations was in the Ferox Flow treatment. 1,2-DCA reductions were limited with only 2.3 to 18.2% reductions. The Target ZVI was most reactive towards CT (76.1% reduction) and BF (83.8% reduction).

TABLE 2. Percent degradation relative to control for first day.

Treatment	Ferox Flow	Flow + Sulfide	Target	Target+ Sulfide	SRS-Z	SRS-Z Sulfide
PCE	16.7	8.3	8.3	23.3	-8.3	-8.3
1,1,1-TCA	36.8	21.1	31.6	26.3	10.5	10.5
1.2-DCA	11.4	13.6	2.3	18.2	11.4	11.4
CT	56.7	22.2	76.1	33.3	16.7	11.1
BF	53.6	26.8	83.8	21.4	44.6	44.6

Over the 70-day study as seen in Table 3, the treatments with ZVI and sulfide showed more complete removal of the PCE (80.8 to 97.9%) than the ZVI treatments without sulfide (72.5 to 76.7%). The ZVI and bioaugmentation cultures transformed the parent compounds to daughter products; for example, PCE is transformed to TCE, cis-1,2-dichloroethene (cis-DCE), vinyl chloride (VC), ethene, ethane, and acetylene. 1,1,1-TCA is reduced to 1,1-dichloroethane, 1,1-dichloroethene, chloroethane, and potentially VC, ethene, or ethane. 1,2-DCA could be reduced to VC or chloroethane. CT is reduced to chloroform (CF), methylene chloride, and chloromethane; methane is a potential product, but anaerobic biodegradation of carbon substrates can also generate methane. Finally, BF is reduced to dibromomethane, bromomethane, and potentially to methane. The overall removal of the chlorinated ethenes excluding final daughter product gases ranged from 54.7% for Flow to 91.8% for Target + Sulfide. 1,1,1-TCA was consumed completely in the ZVI and sulfide treatments and was reduced by 91.1 to >99.97% in the ZVI treatments without sulfide. Much of the 1,1,1-TCA was transformed to daughter products as only 12.0% (Control) to 60.6% (SRS + Flow) of chlorinated ethanes were removed. 1,2-DCA was more resistant to degradation with a maximum of 52.3% removed in the SRS + Flow treatment. Complete removal of the CT and BF were observed in all ZVI-amended treatments, but the reaction rates were generally faster for the ZVI treatments with sulfide. Most of the CT was degraded with the ZVI as the sum chloromethanes were reduced by 81.8% (Target) to 96.3% (SRS + Flow + Sulfide). Most of the BF was completely degraded with the ZVI as the sum brominated methanes were reduced by 97.5% (SRS and Flow) to 100% (SRS + Flow + Sulfide).

TABLE 3. Percent removal over 70-day treatability study relative to control day 1.

Treatment	Control	Flow	Flow + Sulfide	Target	Target+ Sulfide	SRS Flow	SRS+ Flow + Sulfide
PCE	0.0	72.5	95.5	76.7	97.9	73.3	80.8
Sum Chlorinated Ethenes w/o Gases	0.0	54.7	87.1	73.2	91.8	73.3	80.2
1,1,1-TCA	21.1	>99.97	>99.97	99.8	>99.97	91.1	>99.7
Sum Chlorinated Ethanes wo Gases	12.0	32.5	28.2	31.0	34.2	60.6	51.5
1.2-DCA	9.1	20.5	9.1	18.2	15.9	52.3	38.6
CT	27.8	>99.97	>99.97	>99.97	>99.97	>99.7	>99.7
Sum Chlorinated Methanes wo Gases	25.9	82.8	93.4	81.8	94.9	92.9	96.3
BF	8.9	>99.99	>99.99	>99.98	>99.99	>99.9	>99.9
Sum Brominated Methanes wo Gases	8.3	99.4	99.4	99.9	99.8	97.5	100.0

Table 4 shows the first order exponential half-lives calculated for each treatment. For PCE, the shortest half-lives of 12 to 16 days were observed in the Target + Sulfide and Flow + Sulfide treatments. Half-lives of less than 10 days were observed for 1,1,1-TCA with Flow, Flow + Sulfide, Target, and Target + Sulfide. Only with the SRS + Flow and SRS + Flow + Sulfide were moderate half-lives of less than 100 days achieved for 1,2-DCA. CT was rapidly degraded with a half-life of less than one day for Flow and between 1 and 10 days for Flow + Sulfide, Target, Target + Sulfide, and SFS + Flow + Sulfide. BF was rapidly degraded with a half-life of less than one day for Flow and between 1 and 10 days for Flow + Sulfide, Target, Target + Sulfide, and SFS + Flow + Sulfide treatments. The bioaugmentation culture added at Day 43 appeared to increase daughter product formation only in Flow, Flow + Sulfide, Target + Sulfide, SRS + Flow + Sulfide treatments for chlorinated ethenes and for the SRS + Flow and SRS + Flow + Sulfide treatments for chloromethanes. The BF or CF concentrations may have been inhibitory to further dehalogenation. Acetylene, a potential product from ZVI or ferrous sulfide was detected only in the Flow + Sulfide, Target, and Target + Sulfide treatments. The treatments amended with SRS, Flow, and SRS, Flow, and Sulfide showed similar to slightly longer half-lives for PCE, 1,1,1-TCA, CT, and BF, but were considerably faster for 1,2-DCA.

TABLE 4. Half-Lives for treatability study.

Compound	Control	Flow	Flow + Sulfide	Target	Target + Sulfide	SRS + Flow	SRS + Flow + Sulfide
PCE	517	39	16	33	12	37	22
1,1,1-TCA	236	6.6	8.6	8.0	4.9	22	10
1,2-DCA	446	282	753	717	866	75	86
CT	172	0.9	6.3	1.6	2.2	11	8.7
BF	795	0.8	5.5	1.6	1.1	22	4.7

Column Studies Results. TCE concentrations in the influent ranged from 410 to 760 μg/L with an average of 560 μg/L (Table 6). No daughter products such as cis-DCE or VC were detected in the influent. Ethene, ethane, and acetylene were not monitored in the influent.

TCE concentrations in the effluent from the PRB/Flow column were below detection limits (<10 μg/L) on Day 3, but increased to between 65 and 400 μg/L from Days 10 and 45. The retention time during this period of poorer performance ranged from 0.7 to 2.0 days which may have been limiting. Cis-DCE, ethene, and ethane were detected in the effluent from the PRB/Flow column, but not VC or acetylene. The dissolved gases ranged from 17.2 to 24.0% of the influent TCE concentrations. The percent removal of the total chlorinated ethenes (without gases) fell from 100% on Day 3 to between 47.0 and 88.8% from Days 10 to 45 with an average of 79.2%,

TCE concentrations in the effluent from the Target column were low (1-9 μg/L) on Day 3 to 10, but increased to between 46 and 49 μg/L from Days 27 and 32, and was 7 μg/L on Day 45. The retention time during this period of poorer performance from Days 27 to 32 ranged from 1.1 to 2.7 days, which may have been limiting. The retention time on Day 45 was 2.8 days which gave almost complete treatment (97.7%) of the influent TCE. Cis-DCE, ethene, and ethane were detected in the effluents from the Target column, but not VC or acetylene. The dissolved gases ranged from 14.5 to 22.8% of the influent TCE concentrations in the Target column. The percent removal of the total chlorinated ethenes (without gases) ranged from 96.8% on Day 3 to between 92.1 and 99.6% from Days 10 to 45 with an average of 95.8%.

TCE concentrations in the effluent from the PRB/Flow S column were relatively low (3-11 μg/L) on Day 3 to 10, but decreased to between non-detect (<0.5 μg/L) to 0.5 μg/L from

Days 27 to 45. The retention time during the early period of poorer performance ranged from 0.7 to 2.3 days which may have been limiting at the low retention times. The retention time on Days 27 and 45 were 1.6 to 2.3 days which gave almost complete treatment of the TCE. Cis-DCE was detected from Days 3 to 45. Ethene, ethane, and acetylene were detected in the effluent from the PRB/Flow S column, but not VC. The dissolved gases ranged from 8.2 to 42.5% of the influent TCE concentrations. The percent removal of the total chlorinated ethenes (without gases) ranged from 88.1% on Day 3 to 94.8 to 95.7% from Days 10 to 45 with an average of 93.3%.

Chloroform (CF) was detected in the influent at concentrations between 26 and 18 μg/L. No other chlorinated methanes (methylene chloride – DCM or chloromethane - CM) were detected in the Influent. Methane was not analyzed in the influent. Methane could be produced by reductive dechlorination of the chloroform or by biological processes utilizing hydrogen liberated from corrosion of water by ZVI. Methane was found in the effluents of the PRB/Flow column, but not the Target, or PRB/Flow + Sulfide columns. For the PRB/Flow column, complete removal of the CF was observed on Day 3, but CF and DCM were detected at Days 10, 32, and 45 with 50.0 to 88.0% of the chlorinated methanes removed. The Target column showed partial transformation of CF to DCM and CM with between 66.0% and 100% of the chlorinated methanes in the influent reduced. For the PRB/Flow S column, complete removal of the CF was observed except on Day 10. Chloromethanes was also detected on Days 10 and 45. Overall in the PRB/Flow + Sulfide column, 90.8 to 100.0% of the chlorinated methanes were removed. The Hepure PRB/Flow + Sulfide column performed the best on average in removing the chlorinated methanes followed by PRB/Flow, and Target.

Table 6 presents the average percent removal of the chlorinated ethenes and chlorinated methanes for the three ZVI columns. The Target performed the best followed by PRB/Flow Sulfide, and PRB/Flow.

The PRB/Flow + Sulfide column resulted in more complete removal of the TCE and Chloroform than the PRB/Flow column without the sulfide pretreatment. However, more DCE, ethene, and ethane were generated with the PRB/Flow S. Overall treatment of the chlorinated ethenes and chlorinated methanes without gases were higher with the PRB/Flow Sulfide column than the PRB/Flow column.

When the retention time on the column was less than about 2 days, the performance of the ZVI columns suffered particularly for the PRB/Flow. The retention times had a variable effect on the Target ZVI TCE effluent concentrations.

TABLE 5. Column studies results.

	Day	Retention Times Days	TCE (µg/L)	Cis-DCE (µg/L)	VC (µg/L)	Ethene (µg/L)	Ethane (µg/L)	Acetyl-ene (µg/L)	% µM Gases	Total CE w/o gases µM	% CE w/o Gases Reduction from Influent	CF (µg/L)	DCM (µg/L)	CM (µg/L)	Total CM µM	% CM Reduction
Influent	3		410	<0.5	<0.5					3.12		26	<2	<0.5	0.218	0.0
	10		580	<0.5	<0.5					4.41		25	<2	<0.5	0.209	0.0
	27		760	<0.5	<0.5					5.78		22	<2	<0.5	0.184	0.0
	45		490	<0.5	<0.5					3.73		18	<2	<0.5	0.151	0.0
PRB/Flow	3	3.6	<10	<10	<10	14	7.5	<1	24.0	0.00	100.0	<10	<40	<10	0.000	100.0
	10	0.7	65	<3	<3	11	11	<1	17.2	0.49	88.8	3	<10	<3	0.025	88.0
	32	1.0	400	2	<0.5	17	13	<1	18.0	3.06	47.0	11	<2	<0.5	0.092	50.0
	45	2.0	88	4	<0.5	18	6.1	<1	22.7	0.71	80.9	<0.5	3	<0.5	0.035	76.6
Target	3	3.2	9	3	<3	12	6.3	<1	20.5	0.10	96.8	<3	<10	<3	0.000	100.0
	10	5.7	1	1	<0.5	12	6.3	<1	14.5	0.018	99.6	<0.5	3	1	0.055	73.7
	27	1.1	49	8	<0.5	18	9.5	<1	16.6	0.455	92.1	0.9	3	1	0.063	66.0
	32	2.7	46	6	<0.5	22	16	<1	22.8	0.412	92.9	1	4	<0.5	0.055	69.9
	45	2.8	7	3	<0.5	15	9	<1	22.4	0.084	97.7	<0.5	3	<0.5	0.035	76.6
PRB/Flow Sulfide	3	6.6	11	28	<10	3.4	1.5	2.2	8.2	0.373	88.1	<10	<40	<10	0.000	100.0
	10	3.4	3	20	<0.5	14	4.7	<1	14.9	0.229	94.8	0.5	<2	0.5	0.014	93.3
	27	2.1	<0.5	24	<0.5	27	7	<1	20.7	0.248	95.7	<0.5	<2	<0.5	0.000	100.0
	45	1.6	0.5	18	<0.5	32	12	1.1	42.5	0.195	94.8	<0.5	<2	0.7	0.014	90.8

TABLE 6. Average percent removal of chlorinated ethenes and chlorinated methanes.

Percent Removal	Hepure PRB/Flow	Hepure Target	PRB/Flow Sulfide
Chlorinated Ethenes	79.2	95.8	93.3
Chlorinated Methanes	78.6	77.2	96.0

LESSONS LEARNED

The addition of sulfide increased the reactivity of the ZVI against PCE and 1,1,1-TCA and increased the rate of reaction against CT and BF. Treatment of the ZVI with sodium sulfide was effective in these studies. In the column study, the PRB/Flow ZVI + sulfide promoted more complete removal of the TCE and CF than PRB/Flow ZVI alone. The smaller Target ZVI generally gave higher removal efficiencies for the chlorinated ethenes than the PRB/Flow + Sulfide, but the PRB/Flow + Sulfide gave more complete removal of the chlorinated methanes. The addition of sulfide also seemed to alter the daughter products with more cis-DCE, ethene, and acetylene than the column with only the PRB/Flow ZVI.

REFERENCES

Garcia, A. N., H. K. Boparai, and D. M. O'Carroll. 2016. Enhanced Dechlorination of 1,2-Dichloroethane by Coupled Nano Iron-Dithionite Treatment. *Environmental Science and Technology* 50:5243−5251

Gillham, R. W. and Ohannesin, S. F. 1994. Enhanced Degradation of Halogenated Alphatics by Zero-Valent Iron. *Groundwater* 32(6):958−967.

Han, Y. and W. Yan. 2016. Reductive Dechlorination of Trichloroethene by Zero-valent Iron Nanoparticles: Reactivity Enhancement through Sulfidation Treatment. *Environmental Science and Technology* 50:12992-13001.

Li, X., Elliot, W.L., and Zhang, W. 2006. Zero-Valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering: Materials and Engineering Aspects *Critical Reviews in Solid State and Material Science* 31:111-122.