



ZVI and SRS[®]-Z Columns with Sulfidation for Treatment of VOCs and Hexavalent Chromium

June 16th, 2021

Sulfidation of zero valent iron (ZVI) has many benefits for remedial treatment as demonstrated in this column study: sulfidation:

- improves the extent of degradation of ZVI,
- increases the longevity, and
- reduces undesired hydrolysis reactions with water.

Column tests were conducted with SRS[®]-Z (custom blended 5 to 40% ZVI plus Terra Systems, Inc. (TSI) slow-release substrate emulsified vegetable oil with a fast release substrate, nutrients, and vitamin B₁₂) alone and in combination with two loadings of a sulfidation agent (SA). SRS[®]-Z is a very flexible formulation and can be prepared with 2, 4, 44, or <125 μm ZVI particles as needed, and is customizable for your site conditions.



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All column treatments received 10 g/kg of a 4 μm ZVI, the treatments with SRS[®] received 15 g/kg, and the treatments with SA received between 1 and 5 g/kg of the SA. Solutions of 1.3 to 3.1 mg/L TCE, 0.72 to 3.1 mg/L 1,1,1-trichloroethane (ITCA), and 2.9 to 4.8 mg/L Chloroform (CF) were prepared as the influent. A mixture of bioaugmentation cultures including *Dehalococcoides* and *Dehalobacter* were added on Day 15 to all treatments. On Day 17, 1.1 g/L of SA was added to the influent. Below are the removals through Day 29. The average retention time was 57 hours.

Table I: Column Studies of ZVI and SRS[®]-Z with Sulfidation

Day		Retention Time Hours	TCE % Reduction from Influent	% CE w/o Gases Reduction from Influent	% CE Final DP	CF % Reduction from Influent	% CM Reduction	ITCA % Reduction from Influent	% CA w/o Gases Reduction from Influent
8	10 g/kg ZVI	57.8	63.0	62.8	4.3	52.8	37.9	78.9	46.2
15		29.0	75.5	75.1	4.1	75.0	56.9	95.2	70.9
22		57.4	50.0	49.5	6.1	42.4	25.4	73.6	16.7
29		45.6	80.8	80.0		75.5	60.1	92.9	77.9
Avg ± SD		47.5	67.3±13.8	66.9±13.6	4.8±1.1	61.4±16.5	45.1±16.4	85.2±10.5	52.9±27.7
8	10 g/kg ZVI- 1 g/kg SA	78.4	83.0	82.4	22.7	30.6	29.8	82.1	79.3
15		29.4	94.2	93.6	25.0	64.6	62.8	95.8	93.9
22		56.6	94.6	93.5	14.6	54.5	51.6	96.1	89.2
29		51.6	97.7	96.9	32.3	81.4	77.8	98.2	94.2
Avg ± SD		54.0	92.4±6.4	91.6±6.3	23.7±7.3	57.8±21.2	55.5±20.2	93.1±7.4	89.2±7.0
8	SRS [®] -Z	78.4	78.7	78.7	0.0	25.0	25.0	55.3	51.5
15	15 g/kg SRS [®]	29.4	79.4	79.2	0.6	50.0	45.7	81.0	70.4
22	10 g/kg ZVI	56.6	69.4	69.0	2.2	39.4	31.8	78.2	44.8
29		51.6	70.0	69.1	10.5	65.5	56.9	86.7	67.2
Avg ± SD		54.0	74.4±5.4	74.0±5.7	3.4±4.9	45.0±17.1	40.0±14.3	75.3±13.8	58.5±12.3
8	SRS [®] -Z Low SA	43.6	93.0	86.9	21.4	95.8	88.3	99.5	82.0
15	15 g/kg SRS [®]	34.6	98.9	96.8	18.4	99.7	93.5	99.9	89.7
22	10 g/kg ZVI	71.0	99.4	95.7	27.0	99.8	90.9	99.8	71.2
29	1 g/kg SA	68.2	>99.98	98.1	21.9	>99.99	92.4	99.9	84.1
Avg ± SD		54.4	97.8±3.2	94.4±5.1	22.2±3.6	98.8±2.0	91.3±2.3	99.8±0.2	81.8±7.7
8	SRS [®] -Z High SA	53.8	88.7	84.2	22.5	91.4	85.3	98.7	86.8
15	15 g/kg SRS [®]	31.0	97.3	95.0	14.6	99.4	95.1	99.8	93.1
22	10 g/kg ZVI	87.6	98.8	93.8	23.1	99.3	93.9	99.8	78.3
29	5 g/kg SA	61.7	99.2	95.8	28.6	>99.99	94.9	99.8	84.5
Avg ± SD		58.5	96.0±4.9	92.2±5.4	22.2±5.8	97.5±4.1	92.3±4.7	99.5±0.5	85.7±6.1

The treatments with SA outperformed the ZVI or SRS[®]-Z without SA. More final chlorinated ethene degradation products (ethene, ethane, and acetylene) were generated with SA. Less dichloromethane and chloromethane were produced with the SA increasing the extent of the chlorinated methane removals. Less 1,1-dichloroethane, 1,1-dichloroethene, and chloroethane were produced with SA with increased chlorinated ethane (CA) reduction. SRS[®]-Z with low SA performed the best. The addition of the SA to the influent on Day 17 increased the removal efficiency on Day 29 over the previous sampling period at Day 22.

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TSI has conducted similar batch and column experiments with other forms of sulfidated ZVI. In another of our column studies,

- TCE was reduced by an average of 99.2% with a 130 μm ZVI sulfidated ZVI compared to 79.0% with a 130 μm ZVI non-sulfidated ZVI, clearly demonstrating enhanced dechlorination with the sulfidated ZVI.
- Our laboratory studies were not conducted for long enough to show increased longevity of the sulfidated ZVI but that has been reported by others in laboratory studies.
- Hexavalent chromium and total chromium were reduced from about 90 mg/L to 0.12 mg/L or less by the columns containing ZVI and Low SA, SRS[®]-Z, and SRS[®]-Z plus Low and High SA. The total chromium was reduced to below 0.02 mg/L indicating precipitation onto the ZVI. A column with 15 g/kg SRS[®] and 1.5 g/kg SA was not effective against either hexavalent chromium or total chromium.

These results are very encouraging for the combination of SRS[®], ZVI, and sulfidation to treat chlorinated solvents and chromium.

For more information or to develop treatability protocols for your site, please contact:

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