

IN SITU Cr(VI) SOURCE REDUCTION WITH ZVI UNDER AN ACTIVE BUILDING

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ABSTRACT: Solid Waste Management Unit (SWMU) 25 is a former plating shop at the Charleston Naval Complex. During the RCRA Facility Investigation, hexavalent chromium concentrations in groundwater were identified at levels as high as 31,000 µg/L in the vicinity of the site. The source area was thoroughly characterized using vertical profile groundwater samples. This data was used to determine the extent of the target treatment area (TTA).

The remedial objective for the site was to reduce hexavalent chromium groundwater concentrations in the TTA to less than 100 µg/L. Zero Valent Iron (ZVI) was selected as the reductive medium that could best achieve the remedial objective. The patented FeroxSM process consists of the injection of highly reactive ZVI powder into contaminated subsurface zone. As part of the technology application, a fine iron powder is mixed with water to create a slurry which in turn is pressurized into a nitrogen gas stream. This process atomizes the slurry and allows the multiphase slurry to be injected within the subsurface. In low-permeability geologic materials, the gas is used as a precursor to the ZVI powder injection, inducing fractures within the formation prior to placement of the reactive ZVI powder. This injection method allows for the use of relatively low injection pressures which are required when emplacement of the ZVI material is necessary under and adjacent to buildings and subsurface utilities and where other delivery methods and surface intrusive processes are not feasible.

Approximately 37,000 pounds of ZVI were delivered into the TTA, which extended from approximately 5 to 30 feet below ground surface and encompassed 12,000 square feet. Most of the treatment area was located under an active industrial building. The reactive ZVI was injected in January 2002. Multiple groundwater sampling events have occurred after the injection operations, through May 2003.

Results 16 months following the injection show that the ZVI is still creating effective abiotic reducing conditions favorable for the reduction of hexavalent chromium. Although the 100-µg/L goal has not been achieved at all locations, it has been achieved in several significant areas. In areas where this goal has not been achieved, substantive hexavalent chromium reduction has been observed.

This paper presents the results of this corrective action and corresponding hexavalent chromium and water quality data reported over the subsequent 16 months of post-treatment monitoring. Operational challenges associated with implementation of the pneumatic-based injection method are also presented. For this project, these challenges related primarily to conducting field operations while the industrial facility was occupied, performing structural-based modeling to predict the building structure's response to the subsurface injections, and monitoring the structural response of the building during injection activities. The role of a potential passivating oxide film on the iron media is also

discussed with respect to the initial delay encountered in establishing reducing conditions at the site.

INTRODUCTION

Solid Waste Management Unit (SWMU) 25 is a former plating shop at the Charleston Naval Complex. During the RCRA Facility Investigation, hexavalent chromium (Cr VI) concentrations in groundwater were identified at levels as high as 31,000 $\mu\text{g/L}$ in the vicinity of the site. Based on site data and historical land use activities, it was determined that the source of groundwater contamination was a former plating shop. The waste acids from historical plating operations were conveyed through a utility trench that allowed them to leach into groundwater. Vertical groundwater profiling was performed to define the locations with the highest concentrations of Cr VI in the groundwater; this data was then used to define the extent of the target treatment area (TTA).

The geology at the SWMU-70 site consists of predominantly fine sands and sandy silts interbedded with sand to depths of 24 feet bgs. Thin plastic clay stringers have also been identified at depths greater than 15 feet bgs. An aquitard boundary is present at approximately 24 to 31 feet bgs consisting of dense dark olive silty clay.

The remedial objective for the site was to reduce hexavalent chromium groundwater concentrations in the TTA to less than 100 $\mu\text{g/L}$. Insitu chemical reduction using zero-valent iron (ZVI) was selected as the reductive medium that could best achieve the remedial objective.

The FeroxSM process, a patented in situ technology developed by ARS Technologies, consists of the use of a specialized iron product designated as H-200. The H-200 powder is directly reduced from iron ores and contains no toxic levels of elements more commonly found in waste iron stocks from which conventional iron filings originate. This purity also allows the H-200 material to be CODEX certified.

The H-200 particle possesses internal porosity's, which greatly enhance its surface area and, therefore, reactivity. Carbon molecules and other inclusions found within its structural matrix (not as a separate phase), are believed to further enhance its reactivity.

In the technology application, nitrogen gas is injected as a carrier fluid to emplace atomized ZVI slurry within the subsurface matrix. In low-permeability geologic materials, the gas first serves to induce pneumatic fractures within the subsurface prior to injection of the reactive powder. This pre-step allows for the atomized slurry to be injected using much lower pressures than conventional hydraulic injection and results in better distribution of the material within the subsurface. This lower pressure based process is particularly important when treating areas containing buildings and subsurface utilities. The minimal intrusive nature of the process was a key factor in its selection at the site since the application team wanted to minimize impacts to ongoing operations in the building above where most of the contaminated groundwater was located.

Based upon the physical characteristics of the geology soil which the injections are applied, the actual emplacement mechanism of the ZVI powder will vary. These mechanisms can be characterized into three categories; dispersion, fluidization, or fracture filling (Figure 1). In porous (coarse) materials such as gravel, the injection of iron powder will result in the dispersion around soil or rock particles, and will travel as far as the fluidization energy of the gas carrying the particle maintains enough velocity to keep it from settling. This critical velocity can be calculated using Stokes relationship. Under

this scenario, the injection of high volumes of gas and atomized slurry will result in local fluidization or movement and mixing of the ZVI particles within geologic material. In finer more cohesive soils such as silts and clays, the high volume/pressure injections result in the inducement of fracturing within the formation. Under this mechanism the emplacement of iron will be governed by the flow of gas within the fractures and the iron particles will settle into the created fracture network as their velocity decreases. Under field conditions where natural geologic heterogeneities are inherent to any formation, the actual emplacement will typically consist of all three types of emplacement mechanisms.

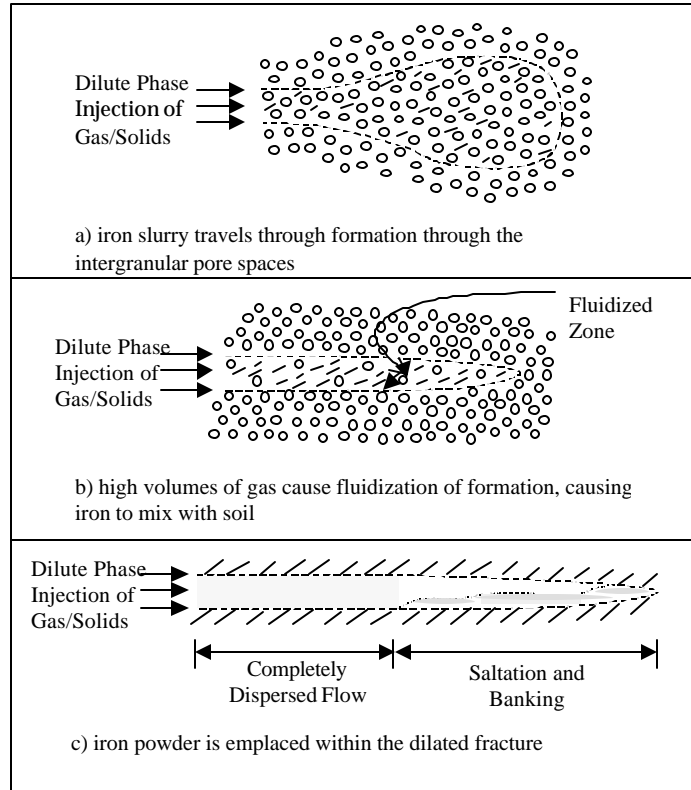


FIGURE 1. Mechanisms of iron powder emplacement during injection.

From U.S. Patent 6,012,517

The Chemistry of Cr(VI)

Reduction with ZVI. When naturally occurring in ground water, chromium occurs in two states, Cr(III) and Cr(VI). The valance state of chromium is strongly dependent on the pH and E_h of the groundwater. Trivalent chromium is present as $\text{Cr}(\text{OH})^{2+}$ in the pH range of 4 to 6.5 and is present as an insoluble hydroxide $\text{Cr}(\text{OH})_3$ when the pH is approximately 6.5 to 10.5.

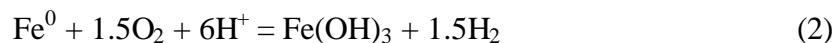
Cr(VI) species are more likely present in alkali and aerobic environments. In groundwater, Cr(VI) exists as oxyanions HCrO_4^- (dichromate) at pH less than 6 and CrO_4^{2-} (chromate) at pH greater than 6. Because Cr(VI) species are negatively charged, their sorption onto most soil particles (having negative charge) is poor and decreases at higher pH values. These chromate oxyanions are of greatest environmental concern due to their toxic and carcinogenic properties and their greater subsurface mobility when compared to a relatively less toxic and immobile Cr(III) species.

Redox reactions with ZVI powder involves Fe^0 oxidation and subsequent chromate ion reduction:

In a reducing environment, the iron will react following equation (1);



When oxygen is present, the iron will react following equation (2);



With the presence of chromate, the net reaction will be;



Standard electrode potentials at 25°C are -440 mV for the reaction $\text{Fe}^0 + 2\text{e}^- = \text{Fe}^{2+}$ and -0.771 mV for the reaction $\text{Fe}^{2+} + \text{e}^- = \text{Fe}^{3+}$. The ZVI iron provides a source of ferrous iron without having to introduce a ferrous salt, such as ferrous sulfate or ferrous chloride. Sulfate or chloride can tend to bring metals into solution. The reaction of ferrous iron alone has sufficient electrochemical reduction potential to reduce Cr(VI) to the insoluble Cr(III). However, the ZVI provides the additional 440 mV for reduction of Cr(VI), without introducing other anions into the subsurface system.

Reactions (1) and (2) increase pH of the system and generate insoluble Cr(III) hydroxide or solid solution $(\text{Cr}_x \text{Fe}_{1-x})(\text{OH})_3$ (as shown in the net reaction in Reaction (3)) as a result of the chromate reduction. In most cases, the hydroxide that is created is buffered by the soil in the system.

Once reduced, Cr(III) is significantly more stable than Cr(VI) as it forms complexes with ferrous iron and has the tendency to precipitate out of solution. The reversal of the chromium oxidative state from trivalent to hexavalent can only occur under some natural geochemical conditions (Palmer and Puls, 1994). These conditions are not expected to be encountered to a significant degree at SWMU 25.

Bench-Scale Treatability Studies. Bench-scale treatability studies were performed to determine the optimum dosing of ZVI to facilitate Cr VI reduction. Site groundwater and soil samples were used in the treatability tests. Groundwater samples subjected to ZVI dosings were analyzed for total chromium and Cr(VI) at 0, 5, 10 and 30 days from the start of the test, respectively. For each designated day, groundwater from a control vial and two reactor vials with different iron to contaminant mass ratios (1000:1 and 4000:1) were analyzed. The amount of trivalent chromium was determined as the difference between the total chromium and Cr(VI). Sediment from the reactor vials was analyzed for total chromium and Cr(VI) at days 0 and 30. In addition, geochemical parameters including pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO) were analyzed throughout the testing. These parameters were analyzed to determine the response of the system to the reduction of Cr(VI) by ZVI.

Table 1 presents the results of the treatability testing with groundwater. Total and Cr VI in groundwater decreased to near zero values after 30 days. This drop in total chromium is attributed to the reduction of Cr(VI) (naturally soluble) to trivalent chromium (naturally insoluble). As the reduction of Cr(VI) progresses, there is a corresponding drop in total chromium in groundwater. Conversely, as Cr(VI) reduces to trivalent state and precipitates from solution, an increase in trivalent chromium over time is seen in the sediments. The decrease in total chromium in the control vials is likely attributed to natural biological processes.

Chromium analysis was performed on sediments from the reactor vials on days 0 and 30 for the 1000:1 dosage. Table 2 and present the results from these analyses and indicates total reduction of Cr(VI) after 30 days, while total chromium remains relatively stable.

Geochemical parameters including pH, ORP, DO, and turbidity were measured from all reactor vials throughout the treatability study. The geochemistry data confirmed

TABLE 1. Chromium analysis results from treatability testing.

Days	Chromium Concentrations in Reactor Vials (mg/L)											
	Control				1000:1				4000:1			
	0	5	10	30	0	5	10	30	0	5	10	30
Total Chromium	77	36	41	20.7	77	12.1	7.9	ND	77	7.6	10.4	0.3
Hexavalent Chromium	34.6	17.3	17.3	19.2	34.6	ND	2.9	ND	34.6	1.1	6.4	ND
Trivalent Chromium*	42.4	18.7	23.7	1.5	42.4	12.1	5	0.3	42.4	6.5	4	0.3

*Calculated as the difference between Total and Hexavalent chromium.

TABLE 2. Chromium results in sediments during treatability testing.

Parameters	Concentration (mg/kg)	
	Day 0	Day 30
Total Chromium	190	182
Hexavalent Chromium	57.3	0
Trivalent Chromium	132.7	182

the proper chemistry existed in the samples to result in Cr(VI) reduction observed in the laboratory tests. Specifically: pH levels increased and ORP and DO levels decreased significantly.

Bench-Scale Treatability Conclusions. Treatability lab testing of Cr(VI) reduction with ZVI powder indicated that both a 1000:1 and 4000:1 iron to contaminant mass ratio were sufficient to reduce Cr(VI) to non-detectable levels in both groundwater and soil after 30 days. Based on these results, an iron dosage of greater than 1000:1 was determined to be adequate for field applications to reduce the concentrations of Cr(VI) at SWMU-70. A design dosage of 2500:1 was selected for implementation, to provide a “scale-up” factor of safety and increase the likelihood of achieving target treatment levels.

Full-Scale Treatment. Based on the results of the Bench-Scale study, a full-scale application of FeroxSM injections was performed within 16 boreholes (Figure 2) between January 8 and 28, 2002. Each injection event consisted of a 5- to 15-second injection duration and targeted a discrete 2-ft vertical interval within the borehole. The intervals were sealed using pneumatic packers that were inflated above the target injection zone. Starting at the deepest interval, injections were performed working upwards in the borehole. As the downhole injection equipment was

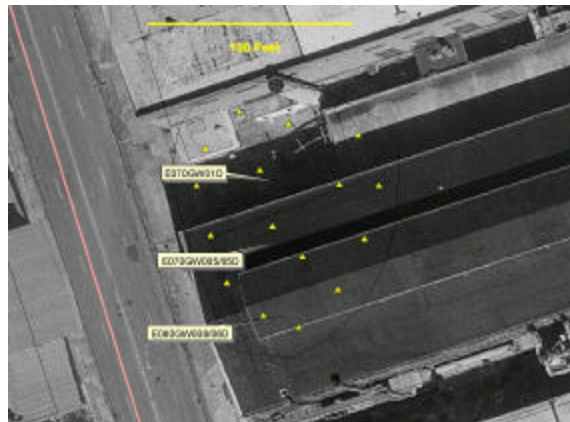


FIGURE 2. Plan view of 16 injection locations (boring locations in yellow).

raised, the sandy formation in the borehole collapsed under the down-hole equipment, forming a boundary layer below the injection nozzle and negating the need for a lower straddled packer.

The locations of the injection borings are presented in Figure 2. A total of 16,725 kg (approximately 37,000 pounds) of ZVI was injected into the subsurface. The amount of ZVI delivered to discrete boring intervals is presented in Figure 3. Following the injections, groundwater samples were collected from monitoring wells. Also, vertical profile samples (three different depths) of groundwater were collected from eight different locations.

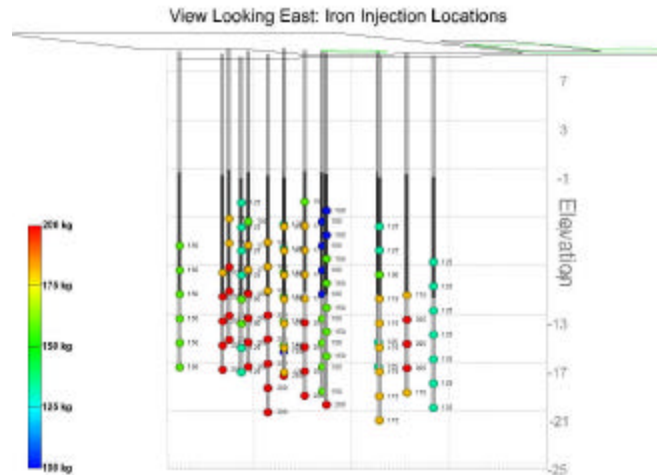


FIGURE 3. Profile view of mass of ZVI injected at specific intervals.

RESULTS

Monitoring well data is presented in Table 3. The first column represents pre-iron-injection data – the remaining data reflects post-injection results. Monitor wells E070GW005, -05D, -006, and -06D were not installed until after the iron injections were performed and several rounds of post-injection samples were analyzed. Overall, significant Cr(VI) reduction was observed at the site, based on data collected from the most recent sampling event. The most significant contaminant reductions were reported at E070GW001 (84%), -01D (74%), -005 (> 99%), -05D (> 99%), and -006 (94%).

The project team wanted to evaluate Cr(VI) reduction in the location with the highest pre-injection concentrations. This location was generally a slice that ran in the direction of the subsurface utility trench where the source leached from. To construct the section of this axis for both pre-and post-treatment data, the pre-and post-treatment groundwater data were loaded into the software package Environmental Visualization System (EVS) to allow kriging and visualization of the data. Following this, a section from the same axis in both krigged data sets was extracted for visualization purposes. The results of this evaluation (i.e., pre- and post-treatment data) are presented in Figures 4 and 5. This figure, along with the data presented in Table 3, indicates that post-treatment Cr(VI) results have decreased significantly, as compared to pre-treatment results.

The increase of hydrogen concentrations in groundwater is a reliable indicator that the ZVI is active in an area near a monitoring point. A pH increase (see reaction 3) is expected with the emplacement of ZVI, with the liberation of hydroxide ion. The E_h values alone (a calculated value based on oxygen reduction potential [ORP]) were not determined to be sufficiently reliable as a treatment indicator due to the variability in field measurements. However, E_h is a useful, and inexpensive, field parameter that is useful in the overall assessment geochemical conditions. Methane results also indicate a highly reducing condition in the groundwater.

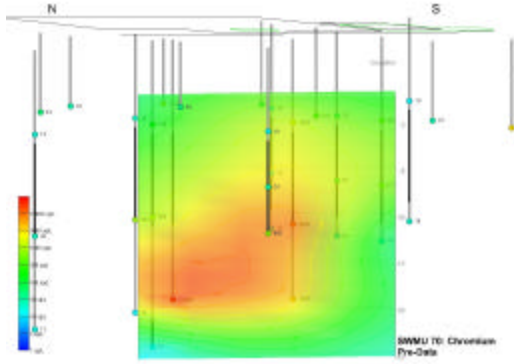


FIGURE 4. Pre-treatment cross section of Cr VI plume through most contaminated slice.

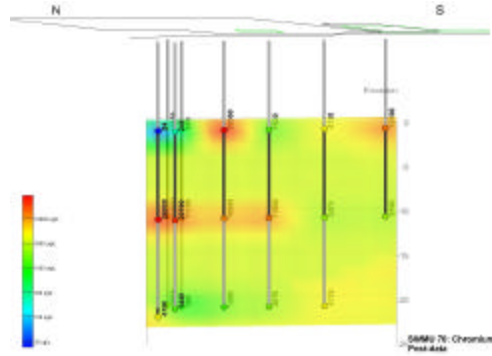


FIGURE 5. Post-treatment cross section of Cr VI plume through most contaminated slice.

Monitor well E070GW01D contained the highest pre-treatment Cr VI concentrations. Review of the data in Table 3 shows that hydrogen levels did not increase as quickly as expected. One explanation of the delayed onset of increased hydrogen concentrations is that hydrogen concentrations actually did increase shortly after the injections, but had reduced at the time of the first monitoring event, due to the formation of an oxide or passivation layer on the surface of the iron particle. Melitas et al., (EST, 2001) presented that higher corrosion potentials and lower corrosion currents are observed with increasing chromate concentrations. However, over time, a steady-state is achieved with the surface passivation. Steady state performance may be attributed to continuous new generation of diffusion pathways and reaction sites arising from crack formation in the oxide layer. This is consistent with the previous reports that only thin passive films may remain nonporous, since internal stresses lead to crack formation as the oxide film grows (Reardon, 1995; Balko and Tratnyek, 1998). This reaction is indicative of an oxidant/passivator like chromate.

Ground surface heave measurements were taken during each injection using surveying transits in conjunction with heave rods. In most cases, heave ranging from 0.125 to 0.75 inch was recorded, confirming fracture propagation or soil void space dilation. Surface heave measurements cannot distinguish these two mechanisms. Within the building, heave was consistently less than 0.5 inch.

During all injections, a structural support column located closest to the injection point was monitored for movement using a graduated tape and a survey transit. The movement criteria, as calculated using computer modeling for the gas injection structural analysis, was determined to be 0.5 inch. This maximum movement was not compromised during the entire field demonstration.

In addition to structural movement, crack gauges were installed at random locations prior to the beginning of any field work on the outside of the building along pre-existing cracks. These gauges were monitored throughout the field application for crack propagation or dilation. No movement was observed.

At this time, it is unknown how much longer the iron will continue to react and generate ferrous iron for the Cr VI reduction. Even when the iron is exhausted, a side-benefit of the iron injections could result in further reduction of Cr VI through biotic

TABLE 3. Results at monitoring wells over time.

		04/05/01	02/12/02	05/01/02	05/09/02	07/11/02	11/19/02	05/22/03
E070GW001	pH	6.12	5.99	5.6	5.8	5.77	6.3	5.83
	DO (mg/L)	5.4	1.13	1.14	0.84	0.67	5.77	6.03
	ORP (mV)	192	162	201	176	172	193	188
	Eh (mV)	392	362	401	376	372	393	388
	Total Cr (ppb)	2580	1650	NS	1680	2000	289	343
	Cr6+ (ppb)	2070	770	NS	1450	1420	358	333
	Hdrogen (nM)	1.2	NS	0.52	NS	3.9	140	12
	Methane (ug/L)	3.2	NS	0.03	NS	2.1	0.46	NS
E070GW01D	pH	6.07	7.25	6.46	6.4	8.84	6.45	5.85
	DO (mg/L)	0.4	0	0	0	0	0.3	1.58
	ORP (mV)	216	123	143	144	-129	68	151
	Eh (mV)	416	323	343	344	71	268	351
	Total Cr (ppb)	30600	12200	NS	14100	12500	11500	12500
	Cr6+ (ppb)	31000	1350	NS	14800	9200	15300	8180
	Hdrogen (nM)	14	NS	29000	NS	43000	31000	32000
	Methane (ug/L)	630	NS	32	NS	52	110	NS
E070GW005	pH	NS	NS	NS	NS	6.07	5.94	5.06
	DO (mg/L)	NS	NS	NS	NS	0	1.38	1.43
	ORP (mV)	NS	NS	NS	NS	-26	112	93
	Eh (mV)	NS	NS	NS	NS	174	312	293
	Total Cr (ppb)	NS	NS	NS	NS	2930	183	284
	Cr6+ (ppb)	NS	NS	NS	NS	4300	6	7.89
	Hdrogen (nM)	NS	NS	NS	NS	73000	490	3.9
	Methane (ug/L)	NS	NS	NS	NS	5.7	10	NS
E070GW05D	pH	NS	NS	NS	NS	7.34	6.55	5.63
	DO (mg/L)	NS	NS	NS	NS	0	0.19	1.29
	ORP (mV)	NS	NS	NS	NS	-90	36	-12
	Eh (mV)	NS	NS	NS	NS	110	236	NS
	Total Cr (ppb)	NS	NS	NS	NS	1950	987	2820
	Cr6+ (ppb)	NS	NS	NS	NS	1350	140	5.84
	Hdrogen (nM)	NS	NS	NS	NS	39000	28000	67
	Methane (ug/L)	NS	NS	NS	NS	59	460	NS
E070GW006	pH	NS	NS	NS	NS	6.03	5.92	5.17
	DO (mg/L)	NS	NS	NS	NS	0	0.3	1.29
	ORP (mV)	NS	NS	NS	NS	32	115	80
	Eh (mV)	NS	NS	NS	NS	232	315	280
	Total Cr (ppb)	NS	NS	NS	NS	6850	1390	953
	Cr6+ (ppb)	NS	NS	NS	NS	4030	2500	239
	Hdrogen (nM)	NS	NS	NS	NS	33000	740	250
	Methane (ug/L)	NS	NS	NS	NS	37	330	NS
E070GW06D	pH	NS	NS	NS	NS	9.17	6.47	5.89
	DO (mg/L)	NS	NS	NS	NS	0	0.26	1.27
	ORP (mV)	NS	NS	NS	NS	-222	26	-76
	Eh (mV)	NS	NS	NS	NS	-22	226	124
	Total Cr (ppb)	NS	NS	NS	NS	504	3.2	3000
	Cr6+ (ppb)	NS	NS	NS	NS	16	21	458
	Hdrogen (nM)	NS	NS	NS	NS	64000	460	1700
	Methane (ug/L)	NS	NS	NS	NS	840	1800	NS

processes created by the reducing conditions created by the iron. The site will continue to be monitored to evaluate the progress of Cr VI reduction.

REFERENCES

Balko and Tratnyek. *Phys. Chem. B* 1998, *102*, 1459 (as cited in Melitas et al.)
 Melitas, N., Chuffe-Moscoco, O., and Farrell, J. Kinetics of Soluble Chromium Removal from Contaminated Water by Zerovalent Iron Media: Corrosion Inhibition and Passive Oxide Effects. 2001.*Environ. Sci. Technol.*, *35*, 3948-3953.
 Palmer, C.D., Puls, R.W. Natural Attenuation of Hexavalent Chromium in Groundwater and Soils. 1994. EPA/540/5-94/505.
 Reardon, E.J. *Environ. Sci. Technol.* 1995, *29*, 2936 (as cited in Melitas et al.).