



A comparative evaluation of hexavalent chromium treatment in contaminated soil by calcium polysulfide and green-tea nanoscale zero-valent iron

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ABSTRACT

A column study for hexavalent chromium (Cr(VI)) removal from contaminated soil was performed using calcium polysulfide (CPS) and nanoscale zero-valent iron stabilized with green tea extract (GT-nZVI). Injection of CPS at 12 times the stoichiometric requirement ($12\times$) resulted in quantitative Cr(VI) removal for up to 195 days of equivalent groundwater flow. Solid-bound Cr(VI) was reduced up to $>99\%$ ($<2\text{ mg/kg}$). Treatment with CPS resulted in a short-term release of high sulfur concentrations. Injections of $12\times$ and $24\times$ stoichiometric GT-nZVI resulted in decrease in leachate pH from 6 to 2.5, which rebounded to 4.5 after the equivalent of 45 days and remained stable for the next equivalent 3 years. Metals concentrations in the effluent (Pb, Cr and Fe) increased following injection and quickly decreased, such that the mass flux was low with respect to the total amounts in the solid. Aqueous Cr(VI) was non-detect for the majority of the monitoring time, but concentrations eventually increased with respect to the control sample. Solid-bound Cr(VI) concentrations decreased by 30% and 66% in the $12\times$ and $24\times$ treatments, respectively. The low efficiency was attributed to increased sorption to iron surfaces at pH 2.5 and slow dissolution of PbCrO_4 , both of which were identified by micro-X-ray fluorescence and absorption analyses.

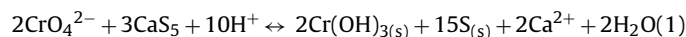
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1. Introduction

Chromium is one of the most frequent metal contaminants and is one of the top 20 contaminants on the Superfund priority list of hazardous substances for the past 15 years. Chromium is toxic and carcinogenic in its hexavalent form (Cr(VI)), while trivalent chromium (Cr(III)) is non-toxic and an essential micronutrient. Additionally, Cr(III) is insoluble at pH values greater than 5 [1], such that that the transformation of Cr(VI) to Cr(III) reduces both the toxicity and mobility of chromium in the environment. Thus, treatment of Cr(VI) in soil and groundwater often relies on the reduction of Cr(VI) to Cr(III), either with chemical reductants (reduced iron or sulfur forms) or by stimulating in situ biological reduction [2]. Among the various available reductants, calcium polysulfide (CPS) and nanoscale zero-valent iron (nZVI) are two promising reagents that have received relatively little attention in the peer-reviewed scientific literature thus far.

CPS has been used in the field at several Cr-contaminated sites [3–7] and to treat chromite ore processing residue (COPR) [8–12].

The reaction between CPS (denoted by its average chemical formula, CaS_5) and Cr(VI) is [8]:



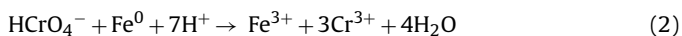
All reported field studies targeted the reduction of aqueous Cr(VI) in contaminated aquifers and reported successful reduction of dissolved Cr(VI) at a wide variety of initial concentrations (60 $\mu\text{g/L}$ at Hanford [6] up to 200 mg/L [3]). However, it is difficult to derive generalized conclusions on treatment efficiency from field data, given that the actual mass of chromium treated cannot be derived from the available information; typically, studies relied on the in situ oxidation reduction potential (ORP) to derive the radius of influence. Consequently, there is little documentation in the literature on CPS effectiveness as a function of soil conditions (pH, soil type, Cr speciation). COPR studies were more detailed and generally reported some success with CPS reduction of solid-bound Cr(VI), but the results are subject to interpretation depending on the type of test that was used to evaluate treatment success. Wazne et al. [10] reported that 62% of solid Cr(VI) was reduced with CPS addition at twice the stoichiometric ratio ($2\times$), while the EPA regulatory method (alkaline digestion with colorimetric analysis) yielded almost complete reduction. Similar results were reported by Tinjum et al. [12], who observed residual Cr(VI)-phases by X-ray diffraction in CPS-treated COPR, while alkaline digestion showed Cr(VI) concentrations $<10\text{ mg/kg}$. Similarly, Chrysochoou et al. [13] applied CPS in batch studies of highly contaminated soil from a

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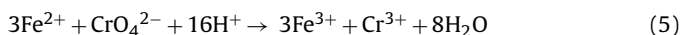
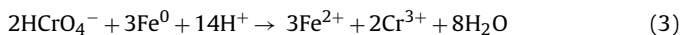
Cr plating facility in Putnam, CT and observed ongoing reduction of Cr(VI) during alkaline digestion. However, CPS was observed to maintain a highly reducing environment for a prolonged period of time even in the presence of oxygen, which rendered it a promising reductant for the treatment of deeper, less contaminated zones at the site.

Potential adverse effects of CPS have been reported to be the mobilization of Mn and As under reducing conditions, although natural attenuation of these elements down gradient of the reaction zone is thought to mitigate the associated risk [6,7]. Additionally, sulfate concentrations have been reported as high as 2500 mg/L [7], although the speciation and mobilization potential of various sulfur species have not been investigated in any field or laboratory study this far. Bewley and Clarke [9] found that sulfide and free sulfur were not present in the leachate of CPS-treated COPR. Chrysochoou and Ting [14] recently reported that the dominant product of calcium polysulfide oxidation in the presence of oxygen is thiosulfate ($S_2O_3^{2-}$), which has not been captured by field or lab measurements thus far.

In addition to calcium polysulfide, this study examines the use of nanoscale zero-valent Iron (nZVI) as an emerging reductant. The overall reaction for Cr(VI) reduction by ZVI is [15]:



The mechanisms of Cr(VI) reduction by ZVI and nZVI involve several different processes, including direct reduction by Fe⁰ and indirect reduction by Fe(II) [15,16] according to the reactions:



Depending on the pH conditions of the reactions, the products Fe^{3+} and Cr^{3+} may hydrolyze to produce different aqueous hydroxocomplexes and solid precipitates, leading to an overall negative, positive or zero balance for H^+ , causing pH changes [15,17]. Indirect reduction by the produced hydrogen in Eq. (4) is also possible [15]. Finally, adsorption and co-precipitation are additional immobilization mechanisms for Cr(VI) by ZVI [18].

ZVI technology has long been used to remediate Cr(VI) in groundwater in the form of permeable reactive barriers [19]. In recent years, attention has been paid to the use of ZVI nanoparticles that can be directly injected into the subsurface as a suspension [20]. Because the high reactivity of iron nanoparticles causes rapid agglomeration, several types of organic coatings, such as emulsions [21], polymers, and polyelectrolytes [22–24] have been developed to limit reactivity and enhance transport in the subsurface. Several studies have reported the effective use of both bare and stabilized nZVI particles to reduce Cr(VI) in water [21,25–29] and two studies have reported the application of nZVI stabilized with carboxymethyl cellulose (CMC) to treat Cr(VI)-contaminated soil as a promising treatment technology [26,27]. Despite the heightened interest in nZVI technology, its relative efficiency compared to traditional ZVI has recently been called into question [30,31]. Specifically, Noubactep and Caré [32] postulated that nZVI is not a strong reducing agent and that contaminant removal could also be attributed to sorption and co-precipitation.

In this study, we employed a type of nZVI that is coated by polyphenols present in green tea, and was developed by the U.S. Environmental Protection Agency (USEPA) in cooperation with a local Connecticut company (Verutek) [33]. The effectiveness of the two reductants (CPS and green tea nZVI or GT-nZVI) was evaluated using flow-through columns packed with contaminated soil obtained from a CT plating facility. Emphasis was given to evaluating secondary effects of treatment application to soil properties and leachability of secondary elements. Additionally, we explored

the influence of Cr(VI) speciation in the solid to treatment efficiency and removal mechanisms.

2. Materials and methods

2.1. Experimental setup

Soil columns were made of clear acrylic tubes with an inner diameter of 3.4 cm and a 17.5 cm length. Approximately 280 g were packed manually in five layers in each column, with a target dry density of 1.7 g/cm³, which was the lower end of field densities reported in Nikolaidis et al. [34]. The resulting pore volume was 55 mL. All columns were operated using a peristaltic pump at 0.1 mL/min injected from the bottom and the effluent was collected at the top using sealed bottles. The entire system was closed to the atmosphere by purging both the influent and the effluent bottles with ultra-high purity $N_{2(g)}$ (Airgas, Radnor, PA).

A calcium polysulfide solution (29%) was obtained from Best Sulfur Products (Fresno, CA). GT-nZVI was prepared according to the method of Hoag et al. [33]. Briefly, a 0.1 M ferric chloride solution was prepared with analytical grade $FeCl_3$ (Fisher Scientific, Pittsburgh, PA). Then 20 g/L green tea was brewed by bringing water mixed with loose-leaf green tea to 80 °C. The solutions were then mixed in a 2:1 ratio of $FeCl_3$ to green tea solution. This yielded a final solution with a concentration of 66 mM total iron concentration.

The following seven columns were setup:

- Two control (CTRL-1 and CTRL-2): untreated soil flushed with synthetic groundwater. CTRL-1 was terminated after 65 pore volumes (PV), and column CTRL-2 after 250 PV.
- Three columns treated with GT-nZVI (nZVI-1, nZVI-2 and nZVI-3): column nZVI-1 was treated with 110 mL of the 66 mM GT-nZVI suspension, which corresponds to 12 times the stoichiometric ratio required to convert all Cr(VI) in the column to Cr(III), assuming that all Fe was present as Fe(0). nZVI-1 was then flushed with synthetic groundwater and terminated after 65 PV. Column nZVI-2 was treated with 110 mL of GT-nZVI, then flushed with groundwater and treated with another 110 mL at 215 PV before it was terminated at 250 PV. Column nZVI-3 was treated with 220 mL of GT-nZVI (24×), flushed with synthetic groundwater and terminated after 66 PV. The stoichiometric ratio of 12× was chosen based on the results of Li et al. [24], which indicated a range of 5×–13× for successful immobilization of Cr(VI) using nZVI.
- Two columns treated with CPS (CPS-1 and CPS-2): both columns were treated with 12× CPS, which corresponded to 1.2 mL of 29% CPS solution further diluted in 100 mL DI water. Both columns were flushed with synthetic groundwater and terminated after 40 PV because Cr(VI) remained under the detection limit following the injection of CPS at the 6th pore volume.

2.2. Column characteristics and operation

A detailed description of the site, sampling techniques and soil characteristics are provided in Chrysochoou et al. [13]. Briefly, the facility is located in Northeastern Connecticut with glaciofluvial soils typical of New England Morphology. Soil sampling revealed high Cr(VI) concentrations (up to 10,000 mg/kg) in the upper 2 m of soil adjacent to the facility, while deeper layers down to the groundwater table at 8.5 m had average concentrations below 100 mg/kg. However, because of the high mobility of Cr(VI), groundwater concentrations remain high (up to 2 mg/L) and a pump-and-treat well has been in continuous operation at the site.

For the purposes of this study, soil obtained from the depth interval 1.5–8.5 m was mixed, homogenized and split into equal

Table 1
Chemistry of untreated soil.

pH	6.8
Cr(VI)	100 mg/kg
Cr(total)	325 mg/kg
Fe	25,300 mg/kg
Mn	490 mg/kg
K	24,840 mg/kg
Pb	160 mg/kg

portions using a sample splitter. This soil was located in the unsaturated zone immediately below the highly-contaminated surficial layer (top 5 ft) and had relatively low Cr(VI) concentrations (Table 1). The purpose of the study was to investigate whether the soil could be effectively treated by injecting reducing agents in order to prevent future migration of Cr(VI) to the saturated zone in the event that the upper, highly contaminated layers were excavated and disposed of.

The influent solution was simulated groundwater (Table 2), excluding sulfate. The synthesis was based on groundwater analysis for major cations in July 2008 and anion data from Johnson et al. [35]; the carbonate and bicarbonate concentrations were calculated for pH 6.5. The salts used to simulate the groundwater were of analytical grade (Fisher Scientific, Pittsburgh, PA), and their respective concentrations were as follows: 0.2 mM CaCl₂, 0.06 mM MgCl₂, 0.04 mM KCl, 0.44 mM NaCl and 0.2 mM NaNO₃; trace cations and anions were omitted for simplicity.

Column effluents were sampled periodically and analyzed for pH, Eh, and concentrations of dissolved oxygen (DO), Cr(VI), total Cr (Cr_{tot}) and total Fe (Fe_{tot}). Selected points were also analyzed for Pb in both treatment types, and sulfide (S²⁻) and total S (S_{tot}) in the CPS-treated effluent. Upon termination, the columns were taken apart and divided into five equal layers (three for the CPS-treated columns). The soil of each layer was then homogenized and analyzed for pH, Eh, Cr(VI) and total metals. All solid-phase analyses were performed in duplicate and the average values are shown in the tables and graphs.

2.3. Analytical methods

Aqueous pH measurements were conducted using an InLab Pro pH electrode (Mettler-Toledo, Columbus, OH). Soil pH analysis was conducted according to method ASTM D4980-89. Total Cr(VI) was extracted from soil samples according to method EPA 3060A. Total Cr(VI) concentrations for all digested soil and column effluent samples was conducted according to EPA 7196A. Total metals concentrations were analyzed using a 3000 Series Atomic Absorption Spectrometer (Thermo Scientific, Waltham, MA) according to methods EPA 7010 (graphite furnace) and EPA 7000B (flame). Spectrometer calibration and drift were monitored periodically using blank, spiked, and duplicate samples. Aqueous sulfide

Table 2
Groundwater composition that was simulated for the column studies.

Cation	C (eq./L)	Anion	C (eq./L)
Al ³⁺	6.78 × 10 ⁻⁶	Cl ⁻	4.73 × 10 ⁻⁴
Ca ²⁺	4.01 × 10 ⁻⁴	F ⁻	2.42 × 10 ⁻⁵
Cd ²⁺	2.49 × 10 ⁻⁷	Br ⁻	5.13 × 10 ⁻⁶
Cr ³⁺	1.37 × 10 ⁻⁴	SO ₄ ²⁻	3.06 × 10 ⁻⁴
Mg ²⁺	1.20 × 10 ⁻⁴	NO ₃ ⁻	2.10 × 10 ⁻⁴
Mn ²⁺	1.09 × 10 ⁻⁶	HCO ₃ ^{-a}	3.55 × 10 ⁻⁴
Ni ²⁺	4.74 × 10 ⁻⁶	CO ₃ ^{2-a}	4.17 × 10 ⁻⁹
K ⁺	4.35 × 10 ⁻⁵	PO ₄ ³⁻	n.d.
N ⁺	6.61 × 10 ⁻⁴	NO ₂ ⁻	n.d.
Zn ²⁺	2.60 × 10 ⁻⁶		

n.d.=not detected

^a Carbonate and bicarbonate calculated at pH 6.5

concentrations were determined using an Accumet silver/sulfide ion selective electrode (Fisher Scientific, Pittsburgh, PA). Total sulfur in the CPS treated effluents was determined turbidimetrically as sulfate according to method EPA 3754 following oxidation all sulfur species to sulfate using 30% hydrogen peroxide under alkaline conditions [36]. Elemental analysis of soil samples via X-ray fluorescence was conducted according to method EPA 6200 using an Innov-X Alpha XRF spectrometer.

2.4. X-ray absorption spectroscopy

Micro-X-ray fluorescence (μXRF), and micro-absorption near edge structure (μXANES) analyses were performed on the untreated soil used in this study at beamline 10.3.2 at the Advanced Light Source [37], to investigate the Cr(VI) speciation in the solid. Because of the low concentration of Cr(VI), it was not possible to obtain the respective data for treated samples.

Approximately 5 g of dry soil was prepared as a diamond polished 30 μm thin section by Spectrum Petrographics (Vancouver WA). Micro-XRF elemental maps were acquired at 13.5 keV incident energy with a beam size of 10 × 10 μm² and a counting time of 120 ms/pixel. Fluorescence counts were collected for Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, K and Pb with a seven-element Ge solid-state detector. From elemental distribution maps, various spots of interest were selected for Cr K-edge μXANES to probe Cr redox state. Cr chemical mapping was performed at incident energies of 5960, 5993 and 6250 eV to obtain the background, Cr(VI) and Cr_{tot} signals, respectively. Energy calibration was performed using a Cr foil (5989.02 eV) [38]. The three maps were used to obtain maps for the Cr(VI) and Cr(III) signals using the chemical mapping analysis method described by Marcus [39].

All μXANES spectra were collected in fluorescence mode, pre-edge background subtracted and post-edge normalized using custom LabView software. All XANES scans were performed using Quick XAS (QXAS) [40] with 20 lines and 10 s per line to avoid beam-induced reduction on the standards and the samples. Cr(III) and NaCrO₄ standards were provided as a courtesy of P. Nico. Three XANES standards of pure CaCrO₄, PbCrO₄ and BaCrO₄ (analytical grade, Fisher Scientific) were previously obtained at the beamline [13]. Two additional standards were obtained for Cr(VI) sorbed on goethite and ferrihydrite. Adsorbed chromate standards were prepared in N₂-purged deionized water at pH 5 and ionic strength of 0.01 M NaCl. Suspensions of two-line ferrihydrite and goethite were prepared using the methods of Schwertmann and Cornell [41]. Initial chromate and sorbent concentrations were 5 mM chromate and 10 g/L goethite [42] and 2.5 mM chromate and 2.5 g/L ferrihydrite [43]. Samples were equilibrated for 24 h, pH adjusted periodically when needed, and centrifuged prior to analysis.

3. Results and discussion

3.1. CPS treatment

The injection of CPS at PV 6 resulted in a decrease of the Cr(VI) concentration from 0.5 mg/L to non-detectable values (<25 μg/L), which were sustained until the end of the monitoring time (40 PV) (Fig. 1a). The control columns had a maximum Cr(VI) concentration of 0.15 mg/L, which slightly exceeds the 0.11 mg/L surface water protection criterion of the Connecticut Department of Energy and Environmental Protection (CTDEEP). The control columns sustained a Cr(VI) concentration of 0.1 mg/L for 50 PV, which declined to 0.05 mg/L after 150 PV and eventually decreased to non-detectable (<25 μg/L) concentrations at 180 PV. The hydraulic conductivity in the saturated zone at the site ranges from 4.74 × 10⁻³ cm/s to 9.59 × 10⁻⁵ cm/s and the hydraulic gradient from 0.04 to 0.05

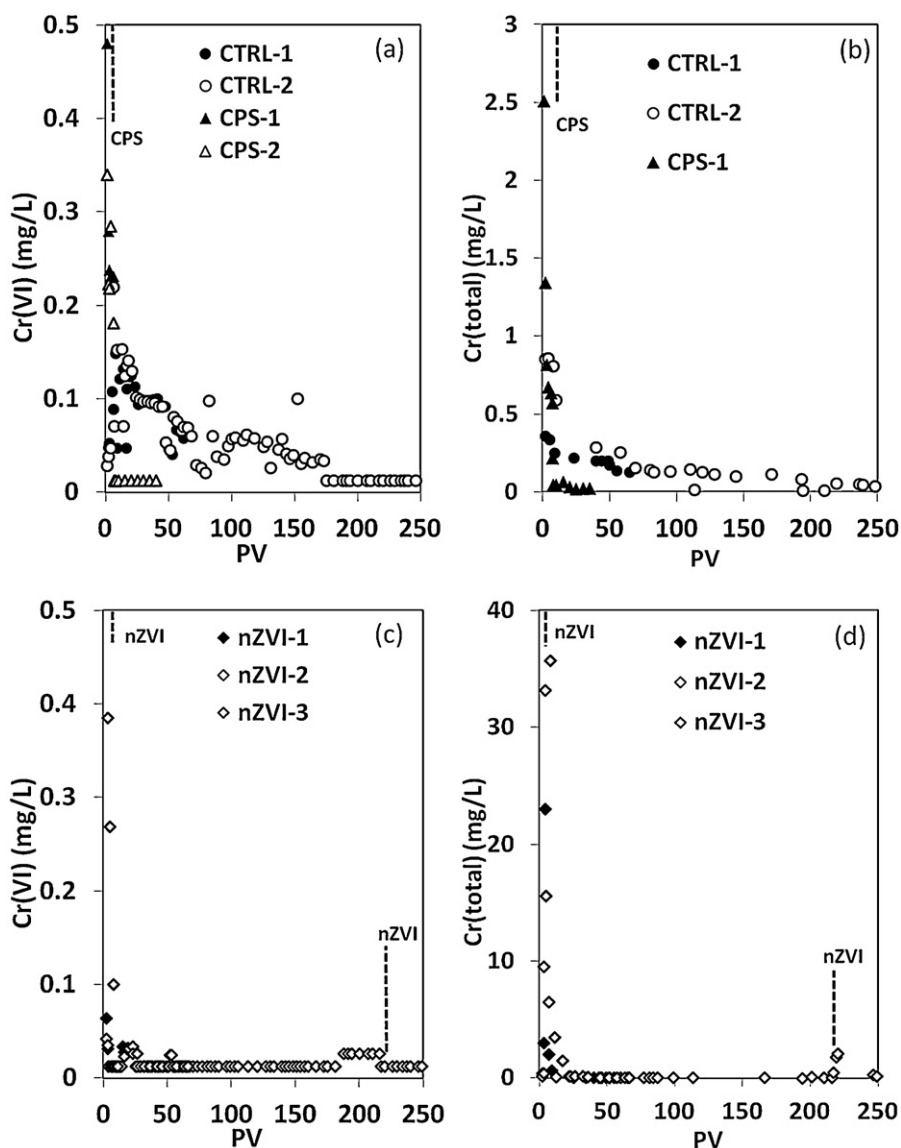


Fig. 1. Cr(VI) (a, c) and total Cr (b, d) in CPS and GT-nZVI treated columns.

[34], which translates to a groundwater velocity between 4 and 18 mm/d. Based on the used flow rate of 0.1 mL/min and a 55 mL PV, it follows that 180 PV corresponds to 879 days of groundwater flow. Given that the soil was obtained from the unsaturated zone, in actuality, it would take much longer for Cr(VI) to wash out from the soil in the field. This is in agreement with the sustained high Cr(VI) concentrations observed in the pump-and-treat well at the site (2 mg/L in 2009 after 14 years of operation).

Cr_{tot} concentrations (Fig. 1b) continuously decreased from 2.5 mg/L to 0.02 mg/L in the DPS-treated columns, and no spike was observed following the injection of CPS at PV 6. The control columns also showed a steady decline from 0.6 mg/L to 0.05 mg/L, which was sustained through the end of the experiment. The effluent pH (Fig. 2) slightly increased from 6.5 in the control columns to 8.5 in the CPS-treated columns immediately following CPS injection at PV 6. The CPS solution has an alkaline pH (11.5) and Cr(VI) reduction should also cause an overall pH increase, assuming that the resulting products are Cr(OH)₃(s) and elemental sulfur (Eq. (1)). The soil pH is favorable for precipitation of Cr(III), so that this assumption is valid. The soil and effluent pH were progressively buffered to pH 7 by PV 15. Potential buffering reactions include the precipitation

of CaCO_{3(s)} with free Ca²⁺ provided by CPS and the exchange of H⁺ with the abundant iron surfaces in the soil. Iron oxide surfaces are positively charged below their points of zero charge (typically at or above pH 9) and will release H⁺ when the pH is increased [44]. Thus, the pH increase was favorable in this case because the solubility of Cr(III) is minimized in the pH range 7–9 [1].

Secondary release of elements following CPS treatment was most pronounced for sulfur (Fig. 3a). Injection of CPS caused an increase in leached S_{tot} up to 543 mg/L in PV 7, which decreased to 117 mg/L by PV 8 and to 3 mg/L by PV 20. Although the exact speciation of S is unknown, the use of a sulfide probe indicated that it was not present as sulfide. Although field studies have indicated that sulfate leaching is significant upon CPS treatment [7,9] and that sulfide and free sulfur are not mobilized [9], recent CPS analysis indicated that it forms preferentially thiosulfate (S₂O₃²⁻) as oxidation species in the presence of oxygen [14]. Even though our column was purged with N₂, it is possible that thiosulfate formed with residual oxygen remaining in the column and in the influence groundwater immediately following the CPS injection. Therefore, sulfate and thiosulfate are thought to collectively account for the high, though short-lived, sulfur leaching in CPS-treated columns.

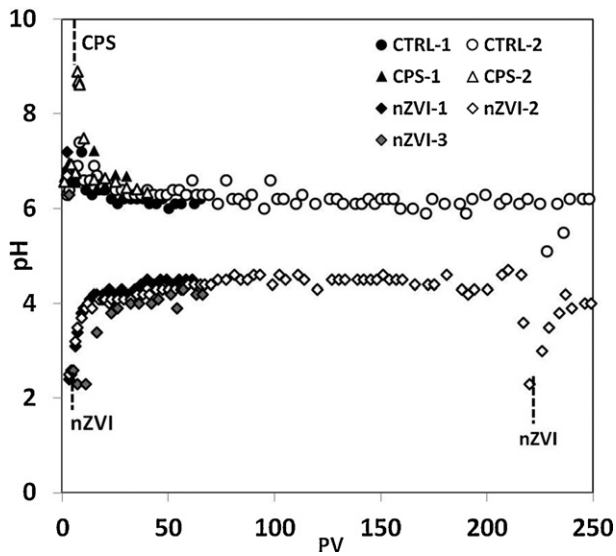


Fig. 2. pH in the column effluents.

The total mass of S added to the column was 278 mg and the approximate total mass in the effluent based on Fig. 3a was 50 mg. Thus, ~80% of the added S was retained in the treated columns within the time frame of the test.

The effluent Fe_{tot} concentration increased slightly to 2 mg/L immediately following injection and returned to background values (<0.5 mg/L) by PV 10. The Mn concentration in the outflow increased from 0.01 mg/L to 0.2 mg/L immediately following injection and remained at 0.1 mg/L by PV 40, when the columns were terminated. A study by the United States Department of Energy [6] showed an increase in groundwater Mn concentrations to 0.1–0.35 mg/L in one of four CPS injection wells at the Hanford Site. The secondary maximum contaminant level (MCL) for Mn is 0.05 mg/L because of its ability to impact drinking water taste and color [45]. Given the relatively small exceedance of this criterion and the enhanced natural attenuation of Mn upon entering oxic environments, Mn mobilization is likely not significant for the area of interest. Finally, Pb concentrations remained below the detection limit (10 μ g/L) over the duration of the experiment in both the control and CPS-treated columns.

Post-mortem analysis of treated soil following termination of the columns (Tables 3 and 4) showed that CPS injection reduced 99% of Cr(VI) in the soil ($p < 0.05$ using an unpaired Student's t -test). A caveat for this result is that residual CPS or thiosulfate may have reduced Cr(VI) during the alkaline digestion, a phenomenon that was previously observed in CPS batch tests [13]. XRF analysis of the soils (Fig. 4) confirmed that the Cr, Fe and Pb concentrations in all columns were statistically the same ($p < 0.1$ for all three elements). Soil pH ranged from 6.5 to 8.5, indicating some variability in the amount of buffering imparted by the soil and potentially the CPS;

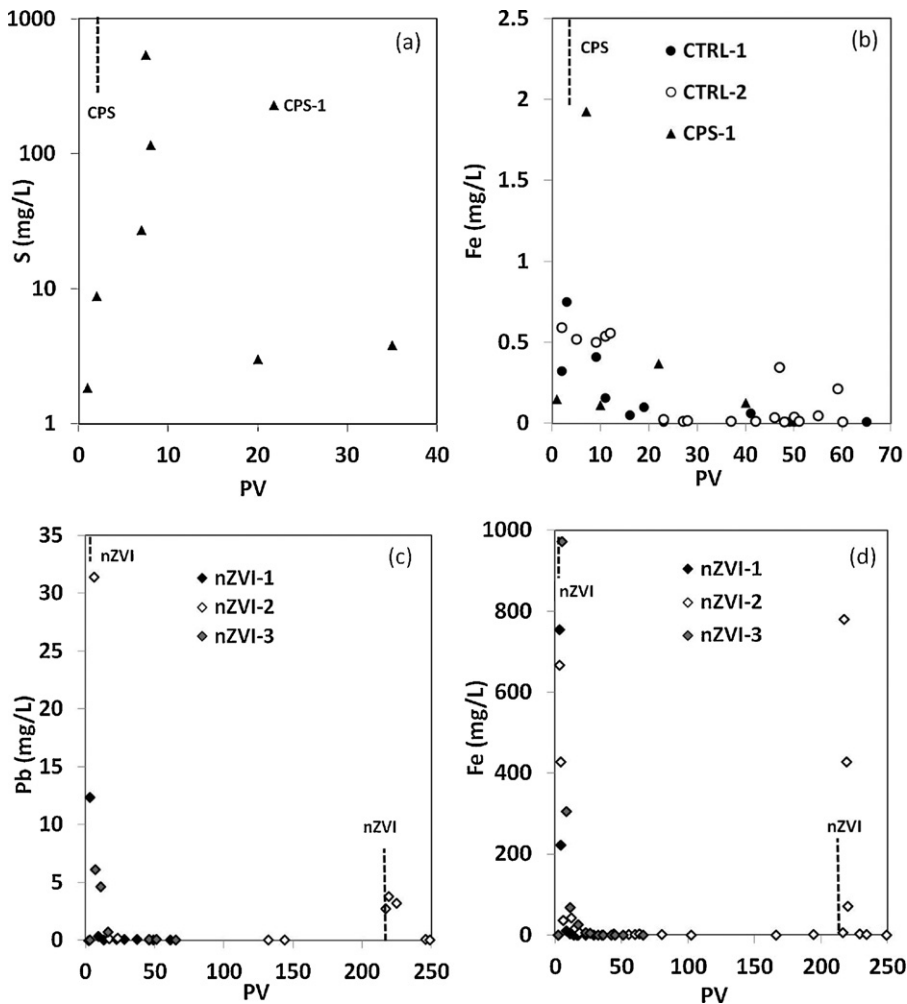


Fig. 3. S in CPS-treated column: (a) Fe in CPS-treated column, (b) Pb in nZVI treated column, (c) Fe in nZVI treated column effluents.

Table 3
Post-mortem Cr(VI) concentrations in the column soils (all data in mg/kg).

	CTRL-1	CTRL-2	CPS-1	CPS-2	nZVI-1	nZVI-2	nZVI-3
Bottom	68	28	1.0	1.6	58	16	28
Lower middle	136	41	–	–	73	43	41
Middle	103	52	1.0	1.4	96	38	52
Upper middle	139	27	–	–	57	32	27
Top	77	28	1.3	1.0	77	38	28

Table 4
Post-mortem pH in the column soils (all data in mg/kg).

	CTRL-1	CTRL-2	CPS-1	CPS-2	nZVI-1	nZVI-2	nZVI-3
Bottom	6.8	6.7	7.6	7.5	5.1	5.0	5.3
Lower middle	7.0	6.9	–	–	4.8	4.9	5.4
Middle	7.0	6.8	7.0	8.4	4.7	5.0	5.2
Upper middle	6.9	6.8	–	–	4.9	5.0	5.2
Top	6.8	6.7	6.4	7.4	4.9	5.0	5.2

however, most values were near-neutral. Thus, Cr(VI) treatment by CPS was deemed effective.

3.2. GT-nZVI treatment

Injection of GT-nZVI at PV 2 resulted in an immediate decrease in Cr(VI) concentration to <25 µg/L (Fig. 1c), and was sustained throughout the monitoring period with two exceptions: a slight rebound to 33 µg/L observed between PV 15–25 and then after PV 188. The addition of a second pulse of GT-nZVI resulted in a decrease of Cr(VI) concentration to <25 µg/L until the end of monitoring (250 PV). Cr_{tot} concentration increased to ~35 mg/L upon GT-nZVI injection and declined to 0.65 mg/L by PV 9 and 0.15 mg/L by PV 22. Effluent pH decreased from 6.5 to 2.5 following GT-nZVI injection and rebounded to pH 4 by PV 15 and to pH 4.5 by PV 50, after which it remained constant until the second injection event. The increase in pH from 2.5 to 4 coincided with the decrease in total Cr concentration from 35 mg/L to below pre-injection levels (0.1 mg/L).

The GT-nZVI suspension has a pH of ~1.5 that is stable regardless of exposure to oxygen and progressive corrosion. This is in contrast to the pH evolution in granular ZVI and other types of nZVI

solutions, which have an equilibrium pH of approximately 9 [46,47]. ZVI corrosion leads to the formation of Fe(OH)₂(s) and/or Fe₃O₄(s), both of which have an approximate equilibrium pH of 9 [46]. Accordingly, Cullen et al. [48] reported an increase in soil pH upon injection of nZVI mixed with polyacrylic acid. This assumes that all iron in the nZVI suspension is in the zero-valent form. However, the preparation method of GT-nZVI involves the use of Fe(III)-based salts. Hoag et al. [33] did not address the question of the fraction of iron that is reduced to ZVI through reaction with the green tea extract. A batch test conducted in the authors' lab with aqueous Cr(VI) showed that 63% of the total Fe in the GT-nZVI could account for the observed reduction of dissolved Cr(VI) [49]. Further studies are required to account for particle agglomeration and passivation, but it is reasonable to assume that the low and stable pH of the GT-nZVI suspension is due to the acidity imparted by residual dissolved Fe(III). Fe(III) hydrolyzes according to the equation



This assumes that Fe³⁺ precipitates and does not take into account the formation of other hydroxo-complexes such as Fe(OH)²⁺ and Fe(OH)₂⁺, which have pK_a values of 2.2 and 6.3. However, the dissolved Fe(III) concentration at pH > 3 is very low, so that these complexes may be ignored. Then 3 mol of H⁺ are produced per mol free Fe³⁺. The addition of 110 mL nZVI of 66 mM Fe corresponds to approximately 6 mmol of H⁺ assuming that 30% of the total iron remained as Fe(III) in solution. This corresponds to the addition of 21 mmol H⁺ per kg soil in the column.

In addition, the reduction of Cr(VI) by nZVI has been previously observed to result in soil acidification; Franco et al. [26] observed that soil pH decreased from 7 to 2.9 in Cr(VI)-contaminated soil treated with CMC-stabilized nZVI. In order to explain this phenomenon, it is necessary to consider the various processes that cause Cr(VI) reduction by ZVI, shown in Eqs. (3)–(5). Depending on the solution pH, the products and proton balance may be different [17]. In the pH range 4 and 6, Fe(OH)₂⁺ and CrOH₂⁺ are produced, leading to an overall neutral reaction, while at higher pH values the precipitation of Fe(III)-Cr(III) (hydr)oxides will lead to an overall proton surplus. Buerge and Hug [17] observed a reddish-brown precipitate that was attributed to amorphous Fe(III)-Cr(III) hydroxide at pH values as low as 4. Thus, the reduction of Cr(VI) at pH values greater than 4 (which was observed in the initial soil environment) will result in H⁺ production and thus a pH decrease. In the presence of oxygen, additional Fe(III) production and precipitation may enhance this effect.

In order to calculate the imparted acidity on the soil, it is necessary to know the exact mechanisms of Cr(VI) reduction and the overall stoichiometry of Fe required to reduce Cr(VI). Gould et al.

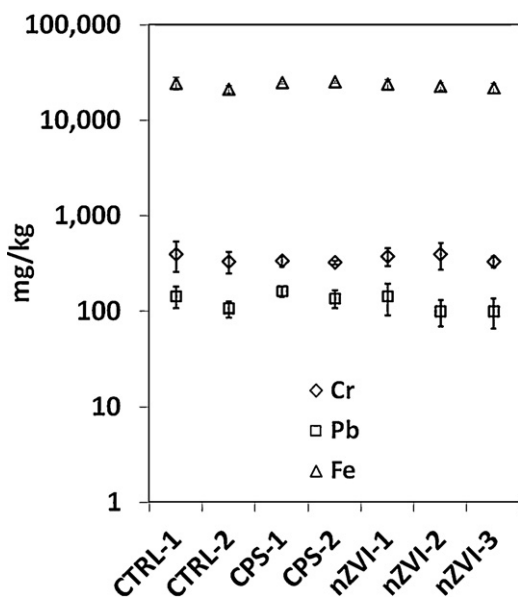


Fig. 4. Average total Cr, Pb and Fe soil concentrations in the columns upon termination of the tests.

[16] found that both direct and indirect mechanisms contribute to reduction of aqueous Cr(VI) by ZVI and that approximately 1.3 mol of iron was necessary to reduce 1 mol of Cr regardless of pH. However, the authors concluded that there was no constant balance between reactions (3) and (5). Subsequent studies detailed by Gheju [15] did not shed further light into the quantitative contribution of different processes to Cr(VI) removal by nZVI. To simplify calculations, we assumed that only Eqs. (3) and (5) were relevant for Cr reduction in the solid phase, that 1.3 mol of Fe were required to reduce 1 mol of Cr(VI) and that this leads to the production of $3 \times 2.3 = 6.9$ mol of H^+ if Cr^{3+} and Fe^{3+} precipitated as simple hydroxides. In the GT-nZVI columns the initial Cr(VI) concentration was 100 mg/kg and the average final concentration was between 24 and 72 mg/kg in the three columns (Table 3). This corresponds to an overall H^+ production between 6.7 and 10 mmol per kg soil. Thus, Cr(VI) reduction is an important contributor to soil acidification, even though hydrolysis of Fe(III) was the major source of H^+ .

The main buffering reactions for the imparted acidity are H^+ consumption by the iron surfaces in the soil and dissolution of $CaCO_{3(s)}$, which was observed in small amounts with X-ray diffraction in the untreated soil. Organic matter content was very low in the soil ([TOC] = 200 mg/kg) and thus likely not a significant contributor to buffering reactions. Following injection of GT-nZVI, the influent pH was 5.5, which simulates the groundwater pH at the site. After 200 PV of continuous synthetic ground water injection, the effluent pH remained at 4.5, indicating that the buffering capacity of the soil was inadequate to counter the acidity imparted by the nZVI injection (27–31 mmol H^+ per kg soil). Given that the influent pH was 5.5, soil reactions continuously consumed OH^- (or released H^+), which may be due to the slow release and reduction of Cr(VI), reduction of nitrate that was injected in low amounts (0.2 mM) in the synthetic groundwater, slow production and hydrolysis of Fe(III). Cation exchange processes between the synthetic groundwater and the positively charged iron surfaces are also likely an important source of H^+ into solution.

As a result of the acidic pH, Fe and Pb release from the soil also occurred at high concentrations (Fig. 3c and d). The injection of GT-nZVI (66 mM or 3696 mg/L Fe) resulted in Fe_{tot} effluent concentrations that reached 1000 mg/L immediately following injection. Again, as the effluent pH increased from 2.5 to 4, effluent $[Fe_{tot}]$ decreased to 3 mg/L in column nZVI-2 and 0.1 mg/L in column nZVI-1 (which were duplicate columns). The overall mass of Fe injected into each column was 406 mg and the cumulative mass leached was 70 mg in column T1 at 35 PV and 115 mg in column T2 at 215 PV before the 2nd injection. Thus, approximately 25% of the total Fe input was leached in column T2 after the equivalent of 1 year of groundwater flow. Given that the effluent was filtered through a 0.45 μm filter before it was collected, this amount of Fe does not include colloidal transport of agglomerated iron particles of larger size. A reddish-brown precipitate was observed on the collected filters upon disassembly of the columns, indicating that colloidal transport of Fe was likely to occur. The pH decrease also caused an increase in the Pb concentrations from non-detectable values (<10 $\mu g/L$) to a maximum of 31 mg/L upon injection. Similar to the total Cr_{tot} and Fe_{tot} trends, Pb also quickly decreased to 0.1 mg/L by PV 10 in the columns nZVI-1 and nZVI-2 and by PV 46 in column nZVI-3.

The differences in the residual soil Cr(VI) content (Table 3) between the CTRL-1 column, and the nZVI-1 and nZVI-3 columns that were terminated simultaneously were all statistically significant ($p = 0.09$ for nZVI-1, and $p = 0.006$ for nZVI-3 using the unpaired Student's *t*-test). Cr(VI) in nZVI-1 was reduced by 30% in nZVI-1 and 44% in nZVI-3. The differences between columns CTRL-2 and nZVI-2 were also statistically significant at the 90% confidence level ($p = 0.1$), indicating the additional injection of nZVI resulted in a 30% reduction in soil-bound Cr(VI) compared to the control. Soil pH

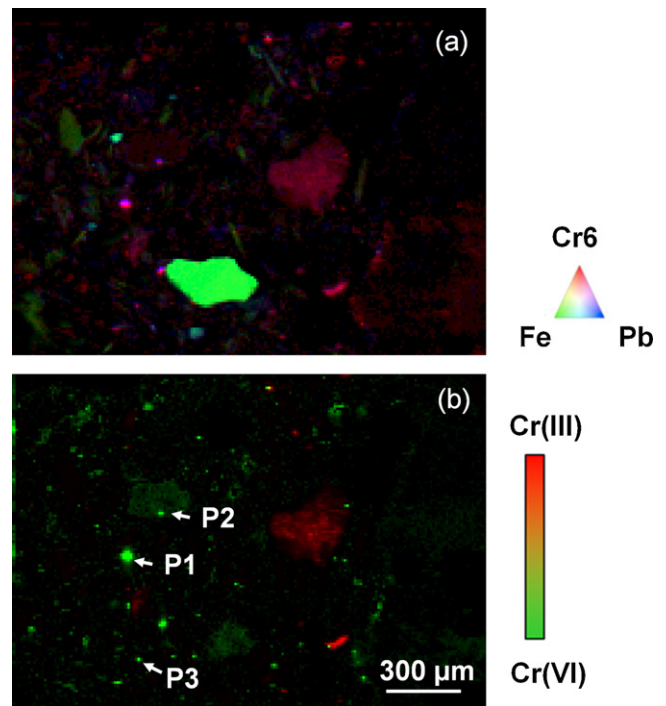


Fig. 5. (a) Tricolor μ XRF maps of untreated sample showing Cr(VI) association with Fe and Pb; (b) bicolor μ XRF map of trivalent and hexavalent chromium – intensities are not to scale.

(Table 4) was approximately 5 in all treated columns, which agrees with the previous observation that the soil buffering capacity was insufficient to counter the acidity imparted by GT-nZVI.

The XRF results of the soil following treatment (Fig. 4) showed that there were no statistically significant differences between metals in the solid (Cr, Pb and Fe) remaining in the solid, with the exception of columns nZVI-3 and CTRL-1 ($p < 0.1$ for all three elements). This indicates that leaching of total Cr_{tot} and Pb in columns nZVI-1 and nZVI-2 was not significant compared to the control columns from a mass flux perspective. Although high concentrations of all three elements were observed in the outflow, they lasted only for a few pore volumes (~5–10 PV or 250 mL water), which corresponded to a small amount of mass with respect to the total concentration. This conclusion also applies to column nZVI-3, for which the leached mass of metals was not higher with respect to the other treated columns. The statistically significant, albeit small, differences in the post-mortem metal concentrations are rather attributed to the variability of the initial soil used the column.

3.3. Cr(VI) speciation

Fig. 5a shows the μ XRF maps of the untreated soil sample and the association of Cr(VI) with Fe and Pb. As was observed in the surficial soil by Chrysochoou et al. [13], Cr(VI) was not associated with larger soil grains, but rather with the small particles in the interstitial pores. Only one grain of approximately 300 μm diameter had Cr, which was Cr(III) co-precipitated with Fe (bright green particle in Fig. 5a). One bright Pb spot was associated with Cr(VI) and signaled the likely presence of $PbCrO_4$.

The Cr speciation map (Fig. 5b) showed that Cr was present predominantly as Cr(III). The distribution of the two oxidation states is not representative of the actual intensities; the Cr(VI) intensity was amplified in order to light up the areas with low Cr(VI) concentrations. The difficulty in identifying low concentrations of Cr(VI) in the chemical map extended to the difficulty of obtaining quality μ XANES spectra for Cr(VI) points. Only three points could be

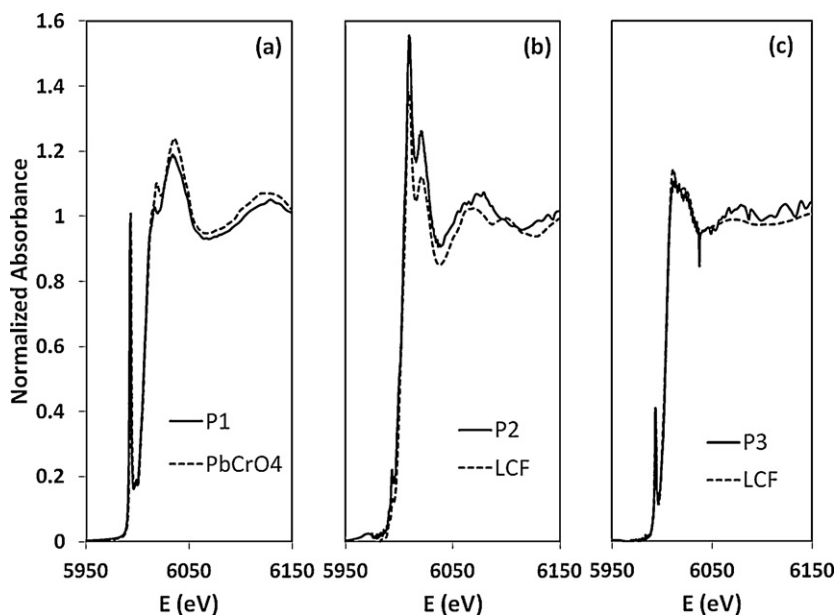


Fig. 6. XANES spectra of selected points compared to pure PbCrO_4 (a) and linear combination fitting (LCF) results (b) and (c). FH = ferrihydrite.

analyzed where the Cr(VI) pre-edge peak at 5993 eV was identifiable, labeled as P1, P2 and P3 in Fig. 5b. Fig. 6 shows the μ XANES spectra of the three points. Pure PbCrO_4 was a close match to P1, as expected from its association with Pb on the μ XRF map. Linear combination fitting (LCF) showed that P2 was predominantly Cr(III) present as $\text{Cr}(\text{OH})_3$ and Cr-spinel; the small pre-edge peak at 5993 eV was attributed to the presence of PbCrO_4 . P3 had a more pronounced pre-edge peak, and LCF yielded 38% of Cr(VI) sorbed on ferrihydrite combined with 58% $\text{Cr}(\text{OH})_3$ and 2% Cr metal. Thus, both PbCrO_4 and sorbed Cr(VI) were observed as possible species in the intermediate unsaturated soil at the site. Based on the total concentrations of Cr(VI) and Pb (Table 1), approximately 40% of the total Cr(VI) could be present as PbCrO_4 , while the rest would be available for sorption on the abundant Fe(III) (hydr)oxide surfaces in the soil. The speciation of Cr(VI) in the untreated soil affects its behavior and the prevailing mechanisms observed in each treatment.

4. Comparison of CPS and GT-nZVI treatments

There are two criteria by which to evaluate the performance of an in situ chemical stabilization treatment: (a) success in stabilizing the contaminant of interest and, (b) quality of the treated groundwater. These will be discussed separately for the two treatments.

In terms of contaminant stabilization, there are two aspects of interest: effectiveness for reducing soil-bound Cr(VI) and concentrations of leached Cr in the treated groundwater. Because of the difficulty in assessing the dependability of alkaline digestion to preserve oxidation state during the extraction of Cr(VI) in CPS-treated soil, we cannot answer the first question unambiguously. CPS injected in diluted form at a stoichiometric ratio of $12\times$ appeared to have reduced 99% of soil-bound Cr(VI). GT-nZVI reduced 66% of soil-bound Cr(VI) when injected in pure form at a stoichiometric ratio of $24\times$ in a single injection event, but only 30% at $12\times$ dosage. Even if the EPA method is not reliable in reducing conditions, these results clearly show that CPS maintained reducing conditions in the treated soil for longer time compared to nZVI (i.e., there was excess reductant left to react during the test). The differences in treatment efficiency between the two methods is related to the pH regime and speciation of Cr(VI) in the solid.

Based on the μ XRF and μ XAS analyses, Cr(VI) was present in the solid in two forms: PbCrO_4 (up to 40% based on total Pb) and sorbed on ferrihydrite and potentially on other iron oxyhydroxides present in the soil. Ferrihydrite has a point of zerocharge around 8 [50] so that its charge would be positive at $\text{pH} < 8$, attracting chromate and negative at $\text{pH} > 8$, repelling chromate. The same applies to most iron oxy(hydroxides), i.e. they are positively charged at neutral and acidic pH and negatively charged at alkaline pH. We can anticipate that for the CPS treatment, which temporarily increased the pH from 6 to 9, all sorbed Cr(VI) would desorb and be readily available for reduction by CPS. Chrysochoou and Ting [14] showed that sorbed Cr(VI) on goethite was reduced faster compared to aqueous Cr(VI) by CPS and this has also been showed for sulfide and ferrous reduction of Cr(VI) sorbed on Fe-bearing minerals [17,51]. However, it is less likely that PbCrO_4 would readily dissolve to release Cr(VI) into solution under these pH conditions. Mass action and conversion of PbCrO_4 to galena (PbS) could be a mechanism of Cr(VI) release, in addition to slow dissolution of Cr(VI) to maintain thermodynamic equilibrium with the solution. The persistence of reducing conditions in the form of thiosulfate is favorable to address leaching of residual solid-bound Cr(VI) in the form of PbCrO_4 . In any case, Cr(VI) concentrations remained non-detect in solution throughout the monitoring time of the CPS columns, which corresponds to 195 days of in situ groundwater flow.

In the case of GT-nZVI treatment, the speciation of Cr(VI) had the opposite effect. The acidic conditions induced by GT-nZVI injection favored the dissolution of PbCrO_4 , which is evidenced by the increased Pb leaching, but also favored increased sorption of Cr(VI) on iron oxyhydroxides which become increasingly positively charged with decreasing pH. The increase of Cr(VI) in the column outflow as the pH rebounded from 2 to 4.5 is evidence that sorbed Cr(VI) was partially released back into solution. Thus, a fraction of the Cr(VI) concentration decrease in the outflow may be attributed to increased sorption rather than reduction. This is in agreement with Noubactep and Caré [32], who pointed out that sorption and co-precipitation may be equally important removal mechanisms for nZVI and that it is not as potent a reductant as it is thought to be. Additionally, GT-nZVI is evidently oxidized much more quickly than CPS. Even though 75% of the injected Fe was retained within the column and the stoichiometry of the added Fe was very high ($12\times$ – $24\times$), a large fraction of the solid-bound Cr(VI) remained

unaffected. This raises the question of how effective the polyphenol coating was to protect nZVI particles from oxidizing. The post-mortem analysis of the soil (Tables 3 and 4) showed that Cr(VI) reduction in the soil was relatively uniform in the treated columns, with slightly higher efficiency in the bottom of the columns where GT-nZVI was injected. Additionally, the pH decreased uniformly within the column, indicating that the distribution of the injected solution was uniform. Thus, it is concluded that green tea was successful in facilitating nZVI nanoparticle transport within the columns. In terms of reducing aqueous Cr(VI) concentrations, nZVI was successful in reducing Cr(VI) in the outflow below the detection limit, as previously reported [20].

Comparing GT-nZVI with other studies, Franco et al. [26] reported better performance of soil treated with 4× and 8× nZVI stabilized with CMC, with Cr(VI) being reduced from 660 mg/kg to 15 mg/kg after treatment. They also reported that Cr(VI) was 30% labile and 60% exchangeable prior to treatment using the extraction test by James et al. [52], while Cr(VI) in the treated soil was 98% insoluble. The authors state that the insoluble fraction includes Cr(VI) that is chemically precipitated and sorbed, but cannot exchange with phosphate. Since we cannot directly compare the speciation of Cr(VI) in the two soils, it is difficult to compare the ability of the two nZVI forms to reduce Cr(VI). We postulate that PbCrO₄ in our soil was overall less available for reduction compared to the soil treated by Franco et al. [26]. Xu and Zhao [27] also employed CMC-stabilized nZVI to treated soil artificially contaminated with 83 mg/kg Cr(VI) and reported that leachable Cr(VI) was eliminated from the soil in batch and column studies with 10× CMC-nZVI addition, while leachable Cr(III) remained at relatively high levels because of the ability of CMC to solubilize Cr(III). Residual Cr(VI) in the treated soil was analyzed indirectly with leaching tests to assess the mobility of residual Cr, and they observed a 90% reduction in leachability with the Toxicity Characteristic Leaching Procedure (TCLP) and 76% reduction with the California Waste Extraction Test (WET), which utilizes a citrate solution at pH 5. Because the speciation of Cr is not resolved during the test and because of the tendency of leaching tests to induce additional reactions in the soil, the results of Xu and Zhao [27] are not directly comparable to ours. In addition, the use of an artificially contaminated soil may have allowed for an much greater availability of Cr(VI) for reduction with respect to the soils used in this study, which likely have substantial aging effects (e.g., slow diffusion into and out of micropores) resulting from decades-old contamination.

In terms of treated groundwater quality, both treatments presented some concerns. CPS treatment showed enhanced S leaching immediately following injection despite being diluted (1.2 mL CPS per 100 mL water), which would exceed groundwater protection criteria if converted to sulfate. However, these high concentrations were short-lived, so that long-term groundwater quality would not be compromised. Additionally, the pH of the column effluent quickly rebounded to background values and no significant leaching of Fe or other metals was observed. Slightly elevated Mn concentrations (0.1 mg/L) would likely quickly attenuate upon entering an oxic zone.

The injection of GT-nZVI had more adverse effects on water quality. The pH decreased to 2.5 upon injection, causing substantial mobilization of metals, including Fe, Cr(III) and Pb. Acidification of Cr(VI)-contaminated soil and water treated with other forms of nZVI have been previously reported [26]. Even though pH rebounded to 4.5 and metals leaching quickly decreased, the pH did not return to the control value of 6 within the equivalent of 3 years of groundwater flow.

Taking all these factors into account, it appears that CPS is a more promising treatment for Cr(VI) in the soils in this study and has overall more favorable properties for in situ injection, especially for acidic soils.

5. Conclusions

A comparative column study was conducted for the treatment of Cr(VI)-contaminated soil at a Cr plating facility using two agents: calcium polysulfide and nanoscale Zero-valent Iron stabilized with a polyphenol rich green tea extract. CPS injected at 12× stoichiometry resulted in non-detectable aqueous Cr(VI) throughout the monitoring time, which corresponded to 195 days of in situ groundwater flow. Solid-bound Cr(VI) in the CPS treated soil appeared to be >99% reduced (<2 mg/kg residual) using alkaline digestion and colorimetric analysis, although this method has been known to enhance Cr(VI) reduction in the presence of residual reductants in the solid. Regardless, it is expected that the mildly alkaline conditions induced by CPS (pH 7–9) would mobilize Cr(VI) sorbed on ferrihydrite, one of two Cr(VI) soil species identified by micro-XANES analyses. The remaining 40% was present as insoluble PbCrO₄, which would contribute only a very slow release of Cr(VI) from the soil matrix. The long residence time of CPS in the form of thiosulfates is favorable for slow-release species. CPS caused a short-term release of high concentrations of sulfur, which could pose an issue for groundwater quality, but quickly returned to background values.

The GT-nZVI was less successful in treating Cr(VI), both in the solid and in the aqueous phase. The injection of 12× and 24× GT-nZVI caused a decrease in leachate pH from 6 to 2.5, which rebounded to 4.5 after the equivalent of 45 days of monitoring and remained stable for the next equivalent 3 years of in situ groundwater flow. Metals release (Pb, Cr and Fe) was significant upon injection, but was reduced when the pH increased to 4.5. Cr(VI) concentrations were non-detect for the majority of the monitoring time, but eventually increased with respect to the control. This is attributed to two mechanisms: progressive release of strongly sorbed Cr(VI) following an increase in pH, and the dissolution of PbCrO₄. Concentrations of soil-bound Cr(VI) decreased by 30% and 66% in the 12× and 24× treatments, respectively.

Given the treatment performance and the potential impacts on groundwater quality, it is concluded from this study that CPS has more favorable properties as injectable reductant for Cr(VI) treatment in soils compared to GT-nZVI.

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