Polysulfide speciation and reactivity in Chromate-contaminated soil

Maria Chrysochoou^{a*} and Chad P. Johnston^a

^a Department of Civil and Environmental Engineering, University of Connecticut, Storrs, CT 06269, USA

*Corresponding author: tel: +1 860 486 3594 fax: +1 860 486 2298, e-mail:

maria.chrysochoou@uconn.edu

Abstract

Calcium polysulfide (CPS) has been observed to maintain a reducing capacity for prolonged time periods when used to treat Cr(VI)-contaminated soils. This study utilized bulk and micro-X-ray Absorption Near Edge Structure (XANES) spectroscopy to investigate sulfur speciation in soil samples treated with CPS in batch and column studies and to determine the source of the reducing potential. Bulk XANES spectra indicated the presence of two dominant sulfur species: elemental sulfur, which is the product of the sulfide-chromate redox reaction, and thiosulfate ($\text{S}_2\text{O}_3^{2-}$). Micro-XANES analyses confirmed these findings and showed that elemental sulfur precipitated as large particles, while thiosulfate was diffuse within the soil grains and thus available to react with chromate that leached from slowly dissolving PbCrO_4 . Micro-X-ray Fluorescence (μXRF) analyses indicated a close association of Pb and thiosulfate, so that PbS_2O_3 is a likely sink for thiosulfate, accounting for up to 20% of the total S added. Sorption of thiosulfate on iron oxides below pH 8 is a second retention mechanism for thiosulfate in the solid. Given that thiosulfate cannot reduce chromate but can reduce solid-bound Fe(III) under neutral pH conditions, it is hypothesized that ferrous iron production is an additional mechanism to maintain reductive conditions in CPS-treated soils.

Keywords: hexavalent chromium, polysulfide, thiosulfate, XANES, remediation

1. Introduction

Chromium has been one of the top twenty contaminants on the Superfund Priority List of Hazardous Substances for the past 15 years. Treatment of toxic and hexavalent chromium (Cr(VI)) in soil and groundwater often relies on the reduction of mobile, anionic chromate (CrO_4^{2-}) to non-toxic and immobile cationic trivalent chromium (Cr(III)), either chemically or biologically [1]. Calcium polysulfide (CPS) is a reductant that has been used in the field at several Cr-contaminated sites [2 - 4] and to treat Chromite Ore Processing Residue (COPR) [5] and contaminated soil for prolonged time periods (>1 yr) [6 - 8]. Field studies reported successful reduction at initial aqueous chromate concentrations ranging from 60 $\mu\text{g/L}$ [9] to 200 mg/L [4]. COPR studies reported variable success with CPS reduction of solid-bound chromate. Specifically, Wazne et al. [7], Tinjum et al. [8], and Chrysochoou et al. [6] reported that chromate in COPR and soil appeared to be completely reduced using alkaline digestion and colorimetric analysis, contrary to the findings of complementary X-ray Absorption Spectroscopy and Diffraction analyses. However, the comparison of chemical and spectroscopic studies indicated that residual reductive capacity was presented both in CPS-treated COPR and contaminated soil for prolonged time periods (>1 yr) [6, 7]. This was not the case with COPR treatments based on sulfide, such as pyrite [10]. Thus, a difference in the reactivity and speciation of CPS compared to sulfide is required to explain the different behavior of these two reductants.

Recently, Chrysochoou and Ting [11] studied the kinetics of aqueous chromate reduction by CPS and the speciation of sulfur, with and without oxygen. Chromate reduction by CPS was observed to follow second-order kinetics and was significantly faster compared to sulfide that follows first-order kinetics. The influence of pH on oxidation kinetics was also observed to be different

for sulfide and CPS, with sulfide showing a constant acceleration with decreasing pH, while CPS showed a maximum at pH 7 under aerobic conditions. This behavior was attributed to the preferred oxidation of CPS to form thiosulfate in the presence of oxygen, while sulfide forms sulfite and sulfate. Thiosulfate is produced according to the reaction [12]:

In contrast, the oxidation of sulfide through the reduction of chromate produces elemental sulfur according to the reaction:

This study further explores the reductive capability and speciation of sulfur in a CPS-treated, chromate-contaminated soil, utilizing spectroscopic techniques in combination with a traditional column study.

2. Materials and Methods

2.1 Soil samples and characterization

Soil samples were obtained from a Cr-plating facility in Connecticut as described in Chrysochoou et al. [6]. Soil characteristics are shown in Table S1. Briefly, the soil is obtained from the surficial layer (top 5 feet) of an area adjacent to the facility that is highly contaminated with both Cr (11,900 mg/kg) and Pb (13,200 mg/kg). Approximately 40% of the Cr is present in the hexavalent form (5,000 mg/kg). The Cr source is the discharge of plating bath solutions from the facility into the soil, while the source of Pb is unknown. Prior to the initiation of this investigation the presence of Pb contamination in the soil was not suspected, but the very high

1
2
3
4 concentrations point to anthropogenic contamination related to the facility activities. The two
5
6
7 contaminants have been previously observed to be closely associated as PbCrO_4 [6]. The
8
9 stoichiometry between the two elements indicates that the 63.8 mmol/kg of Pb can be completely
10
11 bound by the 96 mmol/kg Cr(VI) present in the sample. Other co-contaminants are Ni, which is
12
13 present at higher than background concentrations (440 mg/kg). The soil is a glacial till with
14
15 relatively high Fe content (32,000 mg/kg), which consists primarily of quartz and
16
17 aluminosilicates such as feldspar and mica [6].
18
19
20
21

22 **2.2 Column studies**

23
24
25 Four columns were set up for this study, two control (denoted as CTRL-1 and CTRL-2) and two
26
27 treated with approximately 0.5 pore volume (PV) (25 mL) of 29% CaS_5 solution (denoted as
28
29 CPS-1 and CPS-2), which corresponded to 1X stoichiometric ratio for the chromate mass in the
30
31 column. The column set up was identical to the column tests described in Chrysochoou et al.
32
33 [13], and the description is also provided in the Supplementary Information. All columns were
34
35 operated at 0.1 mL/min injected from the bottom of the column; this flow rate corresponds to the
36
37 upper limit of groundwater flow observed at the site [13]. The entire system was closed to the
38
39 atmosphere by purging both the influent and the effluent bottles with nitrogen. A leaching
40
41 solution that simulated groundwater at the site was used for all columns as described in
42
43 Chrysochoou et al. [13] and Table S2. The CPS solution was injected into the treated columns at
44
45 PV 6 and all columns were monitored for a total of 50 PVs. The effluents from the columns were
46
47 regularly analyzed for pH, redox potential, and Cr(VI) and total Cr concentrations. Selected
48
49 measurements were taken for total S, Fe, Mn, Ni, and Pb concentrations. Upon termination, the
50
51 columns were disassembled and characterized in three layers for total metals, total Cr(VI), pH
52
53 and redox potential. All analytical methods are presented in the Supplemental Information.
54
55
56
57
58
59
60
61
62
63
64
65

2.3 Bulk XANES

A separate batch study was set up to conduct bulk XANES analyses using the same soil sampled for the column studies. 30 g of soil was mixed with 3, 6, 12 and 24 mL 29% CPS solution (1X, 2X, 4X and 8X stoichiometric ratios, respectively), and nitrogen-purged deionized water was added to achieve a total volume of 30 mL. The samples were mixed, purged with nitrogen, and sealed for 1 month prior to XANES analysis. The 2X stoichiometry was also tested at 0 days, 7 days, 2 months and 3 months of curing time. Control samples without CPS were prepared at 1 and 90 day time intervals. Triplicate samples were prepared for all dosages and curing times. XANES data were obtained at the Cr K-edge (5989 eV) and S K-edge (2472 eV) on beamline 4-3 at the Stanford Synchrotron Radiation Lightsource at the SLAC National Accelerator Laboratory; details are provided in Supplemental Information.

2.4 Micro-X-Ray Analyses

Two samples from the middle sections of the CTRL-1 and CPS-1 columns were prepared as 30 μm diamond-polished thin sections by Spectrum Petrographics (Vancouver, WA). Micro-XRF, μXRD and μXANES measurements were performed on beamline 10.3.2 at the Advanced Light Source, Lawrence Berkeley National Lab. Micro-XRF elemental maps were acquired at 13.5 keV and 3.9 keV incident energies with a beam size of 10 μm $\times$ 10 μm and a counting time of 120 ms/pixel. Fluorescence counts were collected for Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb in the 13.5 keV map and S in the 3.9 keV map with a seven-element Ge solid-state detector. Chromium mapping was performed at incident energies of 5980, 5993 and 6250 eV to obtain the background, Cr(VI) and total Cr signals, respectively. Energy calibration was performed using a Cr foil (5989 eV). The three maps were used to obtain maps for the Cr(VI) and Cr(III) signals

1
2
3
4 using the chemical mapping analysis method described by Marcus [14] and employing PbCrO_4
5
6 and $\text{Cr}(\text{OH})_3$ as XANES standards. Various spots of interest were selected for Cr K-edge
7
8 μXANES and μXRD to probe Cr speciation. In addition, S XANES was performed on selected
9
10 spots of a batch sample treated with 2X CPS for 2 months (details are discussed in Chrysochoou
11
12 et al. [6]). Energy calibration for S was performed using $\text{Na}_2\text{S}_2\text{O}_3$.
13
14
15
16
17
18
19
20

21 **3. Results and Discussion**

22 **3.1 Column studies**

23
24
25
26
27 Figure 1 shows the pH, redox potential, chromate (as $\text{Cr}(\text{VI})$) and total S in the column outflow.
28
29 Under the conditions of the study, hexavalent chromium is either present as chromate (CrO_4^{2-}) or
30
31 HCrO_4^- below the pK_a of 6.5; for the remainder of the discussion, these species will be
32
33 collectively referred to as $\text{Cr}(\text{VI})$. Figure S1 shows the concentrations of total Cr, Pb, Fe, Ni and
34
35 Mn. The control columns maintained a pH of 5.5 and an Eh of 200 mV throughout the
36
37 monitoring period. The $\text{Cr}(\text{VI})$ concentration ranged from 0.3 to 0.45 mg/L during the first 6
38
39 PVs, presumably due to initial flushing of exchangeable chromate; after PV 6 the $\text{Cr}(\text{VI})$
40
41 concentration remained constant at approximately 0.16 mg/L, indicating solubility control.
42
43 Chrysochoou et al. [6] reported that PbCrO_4 was the primary sink for chromate in this soil, which
44
45 was also confirmed by the bulk and micro-XANES analyses. Modeling of a Pb-Cr(VI) aqueous
46
47 solution indicated that the solubility of $\text{Cr}(\text{VI})$ with respect to PbCrO_4 at pH 5.5 and Pb
48
49 concentration of 0.3-0.5 mg/L is 0.05-0.13 mg/L, which is quite close to the measured
50
51 concentration. In the treated column, the $\text{Cr}(\text{VI})$ concentration decreased to non-detectable
52
53 values (<0.025 mg/L) upon injection of CPS and remained below the detection limit for the
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4 remainder of the experiment (PV 50). The redox potential (Fig. 1b) initially decreased to -500
5
6 mV at PV 6, but increased to positive values by PV 10 and progressively returned to the control
7
8 value of 200 mV. Similarly, the pH was initially influenced by the injection of alkaline CPS
9
10 solution (pH 11.5), but progressively returned to near-neutral conditions by PV 50.
11
12
13

14
15 Sulfur leaching was very high immediately following injection, reaching 3,660 mg/L at PV 6. It
16
17 decreased to 70 mg/L by PV 12, 20 mg/L by PV 20 and reached background values by the end of
18
19 the experiment. The effluent was also monitored using a sulfide-specific probe, which indicated
20
21 that sulfide was present only during the initial PV following injection; by PV 10, it was below
22
23 the detection limit (0.003 mg/L). Although the exact speciation of sulfur in the effluent was not
24
25 determined, possibilities include thiosulfate ($\text{S}_2\text{O}_3^{2-}$), sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}).
26
27

28
29 Thiosulfate has been found to form preferentially as a result of CPS oxidation [11, 15]. Despite
30
31 the high concentration of sulfur in the outflow, the overall amount leached (~210 mg) was very
32
33 small compared to the amount added (5,800 mg), which corresponds to 96.5% of sulfur retained
34
35 in the soil.
36
37
38

39
40 The strongly reducing environment and elevated pH conditions created by CPS resulted in
41
42 mobilization of metals, including Cr(III), Pb and Ni (Fig. S1). The dissolved metal front was
43
44 quickly attenuated as the redox potential returned to positive values at PV 10. No substantial
45
46 mobilization of Fe or Mn was observed at any time point (Fig. S1).
47
48
49

50
51 The post-mortem analyses of the column soil yielded non-detectable values of Cr(VI) in the solid
52
53 using the conventional EPA methods 3060A and 7196. This method has been previously to be
54
55 unreliable in CPS-treated solids [6], thus bulk and micro-XANES analyses were employed
56
57
58
59
60
61
62
63
64
65

1
2
3
4 instead to assess the true extent of chromate reduction in the solid phase, as well as speciation of
5
6 sulfur.
7
8

9 10 **3.2 Bulk XANES**

11
12
13 Figure 2 shows the percentage of Cr(VI) in the solid determined by bulk XANES as a function of
14
15 time and CPS dosage. The majority of reduction at 2X stoichiometry occurred during the first 30
16
17 days of curing, with Cr(VI) decreasing from an average of 30% to 17% ($p < 0.001$); this
18
19 corresponds to absolute Cr(VI) concentrations of 4,000 mg/kg and 2,040 mg/kg for an average
20
21 total Cr concentration of 12,000 mg/kg (Table 1). These results are in good agreement with
22
23 μ XANES results reported by Chrysochoou et al. [6] for 60-day cured batch samples. No
24
25 statistically significant differences ($p_{1M-2M}=0.57$, $p_{2M-3M}=0.2$) were observed between subsequent
26
27 data points, so that Cr(VI) reduction substantially slowed down or altogether stopped at 30 days.
28
29 The redox potential remained, however, at -500 mV in all samples up to 90 days, given that they
30
31 were closed to the atmosphere, and the pH was constant at 11. When the stoichiometry of added
32
33 CPS was increased from 2X to 8X at 30 days curing time, the Cr(VI) percentage decreased to
34
35 11% ($p_{2X-8X}=0.007$), while the intermediate dosage of 4X did not yield a statistically significant
36
37 difference in the Cr(VI) percentage ($p_{2X-4X}=0.83$). Similarly, the redox potential was at -500 mV
38
39 and the pH at 11 for all samples tested.
40
41
42
43
44
45
46
47

48 The S XANES spectra of the cured samples and reference compounds are shown in Fig. 3, and
49
50 the primary peak positions of the different oxidation states are summarized in Table 1. The
51
52 reference compounds had similar features and peak positions to standard spectra reported
53
54 elsewhere [16, 17]. The spectrum of pure calcium polysulfide showed peaks at 2471.6 eV and
55
56 2473.4 eV, which correspond to the absorption energies of sulfide and elemental sulfur,
57
58
59
60
61
62
63
64
65

1
2
3
4 respectively. Similar results were reported by Vairavamurthy [17], who assigned the 2473.3 eV
5
6 peak to di- and polysulfidic sulfur. The oxidation states of the polysulfide ions are -2 at the end
7
8 and 0 in the middle of the chain [18], so that the peak positions and formal oxidation states are in
9
10 agreement. Two additional peaks were observed at 2479.8 and 2481.4 eV, which are similar to
11
12 secondary peak positions of thiosulfate (2480 and 2481.6 eV). It is plausible that some
13
14 thiosulfate is formed in the polysulfide solution upon exposure to the atmosphere. One difference
15
16 that could distinguish the two compounds is that the height ratio of the two peaks in the CPS
17
18 spectrum is 1.005, while the respective ratio in the $\text{Na}_2\text{S}_2\text{O}_3$ spectrum is 1.23; this is likely
19
20 because the zero oxidation state in the CPS chain contributes intensity to the 2480 eV, but not to
21
22 the 2481.6 peak.
23
24
25
26
27
28

29 The spectra of the cured samples all had quite similar features. Attempts to fit the experimental
30
31 spectra by linear combination of the standard compounds yielded poor results because of self-
32
33 absorption effects and because the physical state of the sulfur species in the samples was not
34
35 identical to the standard spectra, which is required for accurate quantitative analysis of S
36
37 XANES spectra [19]. Thus, we use qualitative observations to draw conclusions about S
38
39 transformation in the soil.
40
41
42
43
44

45 Peaks were observed for all samples at 2473.3, 2480.0 and 2481.4 eV, and a few spectra had a
46
47 shoulder at 2471.6 eV. This peak that indicates the presence of sulfide species (either as sulfide
48
49 or polysulfide) was identified in samples cured for 0 and 7 days at 2X CPS dosage and in
50
51 samples cured for 1 month at 4X and 8X stoichiometry. Thus, residual reductive capacity in the
52
53 form of sulfide was observed at short curing times or high dosages. In contrast, longer curing
54
55 times ($\geq 1\text{M}$) and lower dosages ($\leq 2\text{X}$) exhibited broadening of the 2473.3 eV peak, which is
56
57 characteristic of the elemental sulfur spectrum (Fig. 2b). The peaks at 2480.0 and 2481.4 eV may
58
59
60
61
62
63
64
65

be attributed to several species, including elemental S, polysulfide, thiosulfate and galena. Galena has a characteristic peak at 2477.9 eV that was not identified in any of the sample spectra and was thus excluded from further consideration. Polysulfides are only stable in solution at alkaline pH, since their pKa values are at 9.2 or higher [20]. The pH of the batch samples was maintained above 10 up to 1 month of curing and above 9 up to 3 months of curing at 2X stoichiometry, so that the presence of polysulfides is not implausible in any of the samples with peaks at 2471.6 eV. In the remaining samples, the spectrum appears to be a combination of elemental sulfur and thiosulfate. A broader peak at 2473.3 eV indicates a higher amount of elemental sulfur, while a more pronounced peak at 2481.4 eV indicates a higher concentration of thiosulfate. Using this criterion, it appears that the 1M-1X sample had a higher thiosulfate concentration, while 1M-2X had some thiosulfate but more elemental sulfur, and higher dosages had residual sulfide/polysulfide that dominated the spectra. The spectra obtained at 2X dosage up to 3 months of curing showed that thiosulfate was present up to 90 days, with the sulfur peak at 2480.0 being slightly more pronounced at 90 days, indicating that additional reactions occurred, albeit at a slow pace.

3.3 Micro-X-Ray Analyses

Three μ XRF maps were acquired for the column samples, with a total area of 7.1 mm² in the untreated sample and 8.8 mm² in the treated sample. The tricolor Cr(VI)-Si-Fe maps are shown in Fig. S2, and the Cr(VI)-Pb-S maps for the column and batch samples are shown in Fig. 4.

Cr(VI) was primarily present as small grains in the interstitial spaces between larger quartz and feldspar grains and associated with Pb. The bulk measurements of the two compounds indicate that up to 66% of Cr(VI) may be bound as PbCrO₄. The correlation coefficient between the

counts of the two elements was 0.57, which provides an excellent agreement between the two measurements. Cr(VI) association with Fe was observed in a few grains in the untreated sample (Fig. S2). While the overall correlation coefficient between Fe and Cr(VI) counts was very low for the entire area ($R^2=0.08$), it was 0.94 when these grains were isolated. This indicates that some of the Cr(VI) was sorbed on Fe oxide coatings, a mechanism that is plausible at pH 5.5 of the untreated soil. The correlation coefficient for Pb and Cr(VI) counts increased from 0.57 in the untreated areas to 0.92 in the treated area, indicating that Cr(VI) that was not present as $PbCrO_4$ was preferentially reduced upon CPS addition. This is corroborated by the fact that areas with low Cr(VI) counts were preferentially eliminated in the treated sample. The bulk measurements indicate that approximately 1/3 of the initial Cr(VI) was not bound by Pb and more available for reduction. The batch XANES analyses further showed that this more available Cr(VI) fraction was reduced by 30 days curing, and that the remaining fraction that was almost exclusive present as $PbCrO_4$ was recalcitrant to treatment, despite the persistence of highly reducing environment (-500 mV).

The μ XRF maps (Fig. 4c and Fig. 4d) show that sulfur was present in two main forms: concentrated in bright green spots and diffuse within the matrix, where it was associated with other elements, particularly Pb and Cr. Given that Pb presented high correlation with Cr(VI) in the treated maps, we isolated the areas with high S-Cr and S-Pb correlations, the tricolor maps of which are shown in Fig. 5. Six points were selected in these areas (Fig. 5) and subjected to μ XANES analysis, the spectra of which are shown in Fig. 3d.

Points P0 and P1 were mostly green (Fig. 5a and Fig. 5b), which corresponds to S in the tricolor maps, and the respective μ XANES spectra closely matched elemental sulfur. Thus, it is

1
2
3
4 concluded that the bright green areas in Fig. 4d correspond to pure elemental sulfur, produced by
5
6 the reaction of (poly)sulfide and chromate, as predicted by redox reaction (1).
7
8
9

10 Figure 5a indicates that even when Pb was in close proximity, there was limited tendency for
11
12 sulfide to be scavenged and form galena (PbS), but remained as free Pb (more likely Pb
13
14 carbonate or oxide) after chromate was released from PbCrO_4 , which was observed to bind
15
16 practically all available Pb in the untreated sample (Fig. 4a and Fig. 4b). The area around P2 was
17
18 similar, and the μXANES spectrum was quite close to elemental sulfur, but it clearly included
19
20 another species, most likely thiosulfate. Points P3 and P4 show even more prominent features
21
22 similar to thiosulfate in the region around 2480 eV. The μXRF map indicates that the
23
24 corresponding points consist primarily of S (green) with some Pb (blue) as well.
25
26
27
28
29

30 The area with the most prominent association of Pb and S was the grain around P6 (Fig. 5f). The
31
32 μXANES spectrum indicated that S was present primarily as thiosulfate, which forms PbS_2O_3
33
34 with a solubility of 300 mg/L at 15 °C H_2O [21]. While the solubility of this compound is
35
36 relatively high, the high sulfur concentrations in the column effluents (Fig. 1d) and the high
37
38 ability of S to remain in the solid may be conducive to its stability, especially at short time
39
40 frames. Its continuous dissolution in water may in fact be favorable towards additional reduction
41
42 of slowly released chromate. Figure 5e supports this notion, given that the μXANES shows a
43
44 clear thiosulfate spectrum, while the μXRF map indicates the co-existence of all three elements,
45
46 with Cr(VI) contributing the majority of the observed counts (as indicated by the pink color). A
47
48 large grain with high Pb-S correlation was also observed in the column sample (Fig. 4e),
49
50 however no XANES spectrum is available for that area.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

The column contained approximately 3,300 mg of Pb (13,200 mg/kg in 250 g soil) or approximately 16 mmol, which could bind up to 32 mmol or 1,024 mg of S as PbS_2O_3 . This is approximately 20% of the total S that was retained in the soil column (5,600 mg). Thiosulfate does not form any other insoluble precipitates in soil environments, so that the only other known retention mechanism is sorption to iron oxides, which are positively charged at $\text{pH} < 8-9$ [22]. Even though no crystalline iron oxides were identified in the soil matrix by XRD, the high Fe concentration in the soil indicates that amorphous Fe oxyhydroxides are most likely present. Given that polysulfides create an alkaline environment, a sorption mechanism is likely not favored for anionic thiosulfate at short curing times; however, as the pH decreased below 8 after 20 PV in the column experiments, sorption may enhance thiosulfate retention in the soil.

3.4 Implications for treatment

The XANES and micro-XANES results clearly indicated that there are two main sulfur species that are present in CPS-treated soil long-term (days and months after treatment): elemental sulfur, which is the main oxidation product by reaction with chromate, and thiosulfate. Both were present under strongly reductive conditions (-500 mV) in the absence of oxygen. While thiosulfate is a reductant for Cr(VI), it requires strongly acidic conditions for effective reduction; above pH 2.5, the kinetic rate of reduction becomes almost zero [23]. IETEG [2] reported no Cr(VI) reduction by NaS_2O_3 at neutral pH conditions and 3 hrs of reaction time. Thus, it is considered unlikely that direct reduction of chromate by thiosulfate is a viable long-term reductive mechanism in CPS treated soil.

The production of naturally occurring Fe(II) in soils treated with CPS and sodium dithionite has been previously reported [24, 25]. The mobilization of iron in the column outflow in the initial

PVs after CPS injection (Fig. S1) is indicative of reduction of Fe bound in Fe(III)-oxides in the soils, however, the long-term fate of Fe in the column is unknown. The presence of thiosulfate can aid the persistence of Fe(II) that remains sorbed on iron oxides at the alkaline pH of the soil via two mechanisms: direct reduction of Fe(III), or scavenging of oxidants, including any dissolved oxygen. Su and Ludwig [26] observed retardation in the rate of Fe(II) oxidation in the presence of dithionite and attributed this phenomenon to oxygen scavenging by dithionite and sulfite, both of which are used in the petroleum industry to strip oxygen from water [27, 28]. Thiosulfate has been shown to react with Fe(III)-bearing phyllosilicates to produce Fe(II) and $S_4O_6^{2-}$, even though it is a less potent reductant compared to sulfide and dithionite [29]. In acidic conditions, thiosulfate decomposes to sulfite and elemental sulfur, while it is stable in neutral environments [30]. Thiosulfate will react with oxygen only in the presence of a mineral catalyst, such as pyrite (FeS_2) and sphalerite (ZnS) doped with transition metals [31, 32]. Given the apparent absence of sulfidic minerals, oxygen scavenging is likely not an important mechanism; persistence of Fe(II) viable mechanism to sustain long term reductive environment. If this conclusion holds, the presence of iron in the system can enhance CPS performance. Additional studies on the fate of iron in the system are required to investigate this hypothesis.

5. Conclusions

Treatment of Cr(VI)-contaminated soil with a stoichiometric dosage of CPS indicated that the majority of sulfur (96.5%) was retained within the soil column for 45 PV, which corresponded to approximately 3.5 months of groundwater flow at the site, with a velocity of 0.03 m/d. Sulfide and low redox potential were short lived in the column effluent, with the redox potential increasing from -460 mV to +130 mV after 3 PV of simulated groundwater flow. Chromium(VI) was not detected in the column effluent at any time point after CPS injection, even though it was

1
2
3
4 established from previous studies that it is mostly bound in the soil as PbCrO_4 and thus leaches
5
6 slowly from the solid matrix into solution.
7
8

9
10 Bulk and micro-XANES analyses confirmed that Cr(VI) that was not present as PbCrO_4 was
11
12 completely reduced, while PbCrO_4 was recalcitrant to treatment, despite the persistence of a
13
14 reducing environment as indicated by the redox potential. The soil maintained a reducing
15
16 capacity even after sulfide was no longer detected in solution. Both bulk and micro-XANES
17
18 analyses indicated that sulfur speciation in both the batch and column solids was a combination
19
20 of elemental sulfur and thiosulfate. The micro-XRF analyses indicated that elemental sulfur
21
22 precipitated as larger discrete particles, while thiosulfate was observed to be diffuse within the
23
24 soil grains, associated in some cases with Pb. It is concluded that PbS_2O_3 may have bound up to
25
26 20% of sulfur within the soil column. Sorption of thiosulfate to abundant iron oxides present is
27
28 also a likely retention mechanism in the soil below pH 8. Given that thiosulfate cannot reduce
29
30 chromate but can reduce Fe(III) even when bound in minerals under neutral pH conditions, it is
31
32 hypothesized that long term reduction of Cr(VI) in CPS treated soil may be enhanced by the
33
34 presence of Fe oxides.
35
36
37
38
39
40
41
42
43
44

45 **Acknowledgments.**

46
47

48
49 This work was supported by National Chromium Inc. Sirine Fakra and Matthew A. Marcus of
50
51 LBNL assisted with μXAS data acquisition and analysis. ALS-LBNL operations are supported
52
53 by the Director, Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy
54
55 under contract number DE-AC02-05CH11231. Portions of this research were carried out at the
56
57 Stanford Synchrotron Radiation Lightsource, a directorate of SLAC National Accelerator
58
59
60
61
62
63
64
65

Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy
Office of Science by Stanford University.

References

1. USEPA (United States Environmental Protection Agency), 2000. In situ treatment of soil and groundwater contaminated with chromium: Technical Resource Guide, EPA 625/R-00/004.
2. IETEG (Independent Environmental Technical Evaluation Group), 2005. Chromium (VI) Handbook. Boca Raton: CRC Press.
3. S.W. Petersen, K.A. Hedquist, Treatability test report for calcium polysulfide in the 100-K area, (2006) DOE/RL-2006-17.
4. P. Storch, A. Messer, D. Palmer, R. Pyrih, Pilot test for in situ geochemical fixation of chromium (VI) using calcium polysulfide, Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Battelle Press, Monterey, CA, 2002.
5. R.J.F. Bewley, S. Clarke, Field application of calcium polysulphide for ex situ treatment of soils contaminated with chromite ore processing residue, Land. Contam. Reclam. 18 (2010) 1-12.
6. M. Chrysochoou, D.R. Ferreira, C.P. Johnston, Calcium polysulfide treatment of Chromate contaminated soil, J. Haz. Mat. 179 (2010) 650-657.
7. M. Wazne, S.C. Jagupilla, D.H. Moon, S.C. Jagupilla, C. Christodoulatos, M.G. Kim, Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR), J. Haz. Mat. 143 (2007) 620-628.
8. J.M. Tinjum, C.H. Benson, T.B. Edil, Treatment of CrVI in COPR using ferrous sulfate–sulfuric acid or cationic polysulfides, J. Geotech. Geoenviron. 134 (2008) 1791-1803.

9. USDOE (United States Department of Energy), 2004. Hanford site. Evaluation of Amendments for mending the ISRM barrier. Technical Assistance Project #33, Final Technical Solutions Report.
10. M. Wazne, P. Papazoglou, M. Papastavrou, X. Meng, D. Dermatas, C. Christodoulatos, Remediation of Chromite Ore Processing Residue by Chemical Reductants, Conference Proceedings In situ and one site Bioremediation Symposium, Battelle, Columbus, Ohio, 2005.
11. M. Chrysochoou, A. Ting, A kinetic study of Chromate reduction by calcium polysulfide, *Sci. Tot. Environ.* 409 (2011) 4072-4077.
12. M. Chrysochoou, C. Johnston, G. Dahal, A comparative evaluation of Chromate treatment in contaminated soil by calcium polysulfide and nanoscale zero valent iron, *J. Haz. Mat.* 201-202 (2012) 33-42.
13. M. Avrahami, R.M. Golding, The oxidation of the sulphide ion at very low concentrations in aqueous solutions, *J. Chem. Soc. A* 0 (1968); 647-651.
14. M.A. Marcus, X-ray photon-in/photon-out methods for chemical imaging, *Trends Anal. Chem.* 29 (2010) 508–517.
15. W. Kleinjan, A. Keizer, A. Janssen, Kinetics of the chemical oxidation of polysulfide anions in aqueous solution, *Water Res.* 39 (2005) 4093-4100.
16. F. Jalilehvand, Sulfur: Not a “silent” element any more, *Chem. Soc. Rev.* 35 (2006) 1256-1268.
17. A. Vairavamurthy, Using X-ray absorption to probe sulfur oxidation states in complex molecules, *Spectrochim. Acta Part A* 54 (1998) 2009–2017.
18. A.J. Kamysny, A. Goifman, J. Gun, D. Rizkov, L. Ovadia, Equilibrium distribution of polysulfide ions in aqueous solutions at 25 °C: A new approach for the study of polysulfides’ equilibria, *Environ. Sci. Technol.* 38 (2004) 6633-6644.
19. G. Almkvist, K. Boye, I. Persson, K-edge XANES analysis of sulfur compounds: An investigation of the relative intensities using internal calibration, *J. Synchrotron. Radiat.* 17 (2010) 683-688.
20. G. Maronny, Constantes de dissociation de l'hydrogene sulfure, *Electrochimica Acta* 1 (1959) 58–69.

- 1
2
3
4 21. HSDB (Hazardous Substances Databank) URL: <http://toxnet.nlm.nih.gov/cgi-bin/sis/search> [Accessed
5
6 15 September 2013]
7
8
9 22. G. Sposito, The chemistry of soils. 1 ed., Oxford University Press, New York, 1989.
10
11 23. I. Baldea, G. Niac, The Reaction between Chromate and Thiosulfate. 11. The Kinetics of Tetrathionate,
12
13 Formation. Inorg. Chem. 9 (1970) 110-114.
14
15
16 24. M. Ridley, Summary report on the subsurface chromium reduction treatment test at riverbank army
17
18 ammunitions plant, Lawrence Livermore National Laboratory, (2007) UCRL-TR-231326.
19
20
21 25. L. Zhong, N. Qafoku, J. Szecsody, J.E. Dresel, Z. Zhang, Foam Delivery of Calcium Polysulfide to the
22
23 Vadose Zone for Chromium(VI) Immobilization: A Laboratory Evaluation, Vadose Zone J. 8 (2009) 976-
24
25 985.
26
27
28 26. C. Su, R.D. Ludwig, Treatment of Hexavalent Chromium in Chromite Ore Processing Solid Waste Using a
29
30 Mixed Reductant Solution of Ferrous Sulfate and Sodium Dithionite, Environ. Sci. Technol. 39 (2005)
31
32 6208-6216.
33
34
35 27. E. S. Jr. Snavely, Chemical removal of oxygen from natural waters, J. Petrol. Technol. 23 (1971) 443-
36
37 446.
38
39
40 28. B. L. Knight, Reservoir stability of polymer solutions, J. Petrol. Technol. 25 (1973) 618-626.
41
42
43 29. J.W. Stucki, G.W. Bailey, H. Gan, Oxidation-reduction mechanisms in iron-bearing phyllosilicates, Appl.
44
45 Clay Sci. 10 (1996) 417-430.
46
47
48 30. D. Lyons, G. Nickless, The lower oxy-acids of sulfur, in: G. Nickless (Ed.), Inorganic Sulphur Chemistry,
49
50 Elsevier, Amsterdam, 1968, pp. 509-532.
51
52 31. Y. Xu, M. Schoonen, R. Strongin, Thiosulfate oxidation: Catalysis of synthetic sphalerite doped with
53
54 transition metals, Geochim. Cosmochim. Acta 60 (1996) 4701-4710.
55
56 32. Y. Xu, M. Schoonen, The stability of thiosulfate in the presence of pyrite in low-temperature aqueous
57
58 solutions, Geochim. Cosmochim. Acta 59 (1995) 4605-4622.
59
60
61
62
63
64
65

33. ESRF (European Synchrotron Radiation Facility) ID21 Sulfur XANES datatase. URL:

<http://www.esrf.eu/UsersAndScience/Experiments/Imaging/ID21/php> [Accessed 15 September 2013]

Table 1. Peak positions in S K edge spectra of pure S compounds

Compound	Oxidation State	Main peak (eV)	Additional peaks (eV)
FeS ₂	-2	2471.5	
PbS ^a	-2	2472.7	2482.0
CPS	-2, 0	2471.6, 2473.4	2479.8, 2481.4
S ₈	0	2473.2	
Na ₂ S ₂ O ₃	-2, +6	2472.6	2480.0, 2481.6
Na ₂ SO ₃	+4	2479.0	2481.0, 2482.6
Na ₂ SO ₄	+6	2483.4	

^aSpectrum obtained from ESRF ID21 Sulfur XANES datatase (ESRF, 2013)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5