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Polysulfide speciation and reactivity in chromate-contaminated soil

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HIGHLIGHTS

- Calcium polysulfide reduced Cr(VI) in soil except Cr(VI) bound in $PbCrO_4$ particles.
- 96.5% of injected sulfur remained in the soil column up to 50 pore volumes of flow.
- Sulfur was present as elemental sulfur and thiosulfate in the treated soil.
- Up to 20% of thiosulfate was retained as PbS_2O_3 in the treated soil.

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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 ($S_2O_3^{2-}$). Micro-XANES analyses confirmed these findings and showed that elemental sulfur precipitated as large particles, while thiosulfate was diffused 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.

1. Introduction

Chromium has been one of the top 20 contaminants on the Superfund Priority List of Hazardous Substances for the last 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 year) [6–8]. Field studies reported successful reduction at initial aqueous chromate concentrations ranging from 60 μg/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 year) [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

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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]:

$$S_x{}^{2-} + \tfrac{3}{2}O_2 \rightarrow S_2O_3{}^{2-} + (x-2)S^0 \quad (1)$$

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

$$2CrO_4{}^{2-} + 3CaS_5 + 10H^+ \leftrightarrow 2Cr(OH)_{3(s)} + 15S_{(s)} + 3Ca^{2+} + 2H_2O \quad (2)$$

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 ft) 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 (5000 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 concentrations point to anthropogenic contamination related to the facility activities. The two contaminants have been previously observed to be closely associated as $PbCrO_4$ [6]. The stoichiometry between the two elements indicates that 63.8 mmol/kg of Pb can be completely bound by the 96 mmol/kg Cr(VI) present in the sample. Other co-contaminants are Ni, which is present at higher than background concentrations (440 mg/kg). The soil is a glacial till with relatively high Fe content (32,000 mg/kg), which consists primarily of quartz and aluminosilicates such as feldspar and mica [6].

2.2. Column studies

Four columns were set up for this study, two control (denoted as CTRL-1 and CTRL-2) and two treated with approximately 0.5 pore volume (PV) (25 mL) of 29% CaS_5 solution (denoted as CPS-1 and CPS-2), which corresponded to 1× stoichiometric ratio for the chromate mass in the column. The column set up was identical to the column tests described in Chrysochoou et al. [13], and the description is also provided in the Supplementary Information. All columns were operated at 0.1 mL/min injected from the bottom of the column; this flow rate corresponds to the upper limit of groundwater flow observed at the site [13]. The entire system was closed to the atmosphere by purging both the influent and the effluent bottles with nitrogen. A leaching solution that simulated groundwater at the site was used for all columns as described in Chrysochoou et al. [13] and Table S2. The CPS solution was injected into the treated columns at PV 6 and all columns were monitored for a total of 50 PVs. The effluents from the columns were regularly analyzed for pH, redox potential, and Cr(VI) and total Cr concentrations. Selected measurements were taken for total S, Fe, Mn, Ni, and Pb concentrations. Upon termination, the columns were disassembled and characterized in three layers for total metals, total Cr(VI), pH, and redox potential. All analytical methods are presented in the Supplementary Information.

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. Thirty grams of soil was mixed with 3, 6, 12, and 24 mL of 29% CPS solution (1×, 2×, 4×, and 8× 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 2× 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 Supplementary 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 Laboratory. Micro-XRF elemental maps were acquired at 13.5 and 3.9 keV incident energies with a beam size of 10 μm × 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 using the chemical mapping analysis method described by Marcus [14] and employing $PbCrO_4$ and $Cr(OH)_3$ as XANES standards. Various spots of interest were selected for Cr K-edge μXANES and μXRD to probe Cr speciation. In addition, S XANES was performed on selected spots of a batch sample treated with 2× CPS for 2 months (details are discussed in [6]). Energy calibration for S was performed using $Na_2S_2O_3$.

3. Results and discussion

3.1. Column studies

Fig. 1 shows the pH, redox potential, chromate (as Cr(VI)), and total S in the column outflow. Under the conditions of the study, hexavalent chromium is either present as chromate ($CrO_4{}^{2-}$) or $HCrO_4{}^-$ below the pK_a of 6.5; for the remainder of the discussion, these species will be collectively referred to as Cr(VI). Fig. S1 shows the concentrations of total Cr, Pb, Fe, Ni, and Mn. The control columns maintained a pH of 5.5 and an Eh of 200 mV throughout the monitoring period. The Cr(VI) concentration ranged from 0.3 to 0.45 mg/L during the first 6 PVs, presumably due to initial flushing of exchangeable chromate; after PV 6 the Cr(VI) concentration remained constant at approximately 0.16 mg/L, indicating solubility control. Chrysochoou et al. [6] reported that $PbCrO_4$ was the primary sink for chromate in this soil, which was also confirmed by the bulk and micro-XANES analyses. Modeling of a Pb-Cr(VI) aqueous solution indicated that the solubility of Cr(VI) with