Reduction and Retention Processes Within Arid Subsurface Environments

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Introduction

Significant subsurface chromate contamination has occurred at the Hanford Site (Washington, USA), the location of plutonium production since World War II. Chromate used as a corrosion inhibitor was discharged to unlined surface cribs, resulting in contamination reaching the Columbia river [1]. Additionally, thousands of liters of hot (>100 C^o), caustic (pH>14) chromate, containing high-level nuclear waste (HLW) from the REDOX process has leaked 70 m deep into the vadose zone after multiple failures of single shell tanks in the S-SX tank farm [2].

Once introduced into the environment, chromium persists as either Cr(III) or Cr(VI). Hexavalent Cr exists primarily in groundwater systems as the oxoanion CrO_4^{2-} (chromate), which exhibits high water solubility over much of the environmental pH range, is a strong oxidant, and is a known mutagen, teratogen, and carcinogen [3,4]. Chromate only weakly interacts with soil/sediment solids at neutral pH and above, and commonly exhibits high subsurface mobility [5,6]. Trivalent chromium is relatively non-toxic, forms strong complexes with soil minerals, and forms sparingly soluble hydroxide precipitates at circumneutral pH [7].

Hexavalent chromium can be reduced by Fe(II) (aq) [8,9], sorbed Fe(II) [10-13], organic matter [14], Fe(II) bearing minerals and sulfide compounds [11,15], and through microbial reduction [16]. In anaerobic soils and sediments, Fe(II) is expected to be the dominant reductant between pH 5 to 9, with sulfide having an appreciable contribution at lower pH [17,18]. In aerobic, arid environments, with limited reduced organic matter, chromate reductants are essentially restricted to Fe(II) -bearing mineral phases.

In this work, we examine the reduction of chromate by sediment obtained from the Hanford Formation underneath the Interim Disposal Facility (IDF) in the 200 East Area of the Hanford Site with two objectives in mind: (i) to identify what conditions are required for chromate reduction, and (ii) to determine which minerals are a source of Fe(II) for chromate reduction.

Methods and Materials

Sediment Description

Sediment samples were obtained from borehole C3177, drilled during 2001 in the middle of the 200 East Area, at the northeast corner of the Interim Disposal Facility (IDF) of the Hanford Site. A detailed description of the core collection and geochemistry is available in Horton et al. [19] and Walker et al. [20]. All samples are mineralogically similar, the sand-size fraction being dominated by quartz, plagioclase feldspar, potassium feldspar and mica [19] and the clay-size fraction being dominated by smectite, chlorite, illite, and kaolinite. Hanford Formation sediments also contain trace amounts of magnetite, ilmenite, and biotite [21].

Column Design and Flow Conditions

The influence of various chemical pretreatments on chromate reduction under hydrodynamic conditions was investigated in experiments conducted using columns 10 cm in length having a 1 cm inner diameter. One column was packed with 15 g of H_2O-saturated IDF 4 that had been sonicated in Milli-Q water for 8 h. The other four columns were dry-packed with 15 g of IDF 4. After packing, three of these columns were treated by pumping 10 pore volumes of extractant (10 mM oxalate, 0.5 M HCl, or 0.5 M NaOH) through the column. After extraction, these five columns were equilibrated with 10 pore volumes of 0.2 mM $CaCl_2$ at pH 8. Flow of a feed solution, containing 0.2 mM K_2CrO_4 in 0.2 mM $CaCl_2$, adjusted to pH 8 with dilute NaOH, was then initiated.

The porosity of the packed material was approximately 50%. Flow velocities upward through all columns were maintained at ca. 1.7 pore volumes per day, equivalent to a pore water velocity of approximately 17 cm d^{-1}. The effluent from all columns was sampled periodically. All columns, except the 10 M NaOH and the 0.02 mM K_2CrO_4, were run at least until the concentration of Cr(VI) in the effluent was equal to the influent concentration (complete Cr(VI) breakthrough). At the conclusion of each set of experiments, the individual columns were flushed with one pore volume of distilled deionized water. The sediments were removed and stored at 10 ºC.

Solid-phase Micro Analysis

Synchrotron micro-X-ray fluorescence (μ–XRF) mapping and micro-X-ray absorption spectroscopy (μ–XAS) measurements were performed at GSE-CARS beamline 13-ID-C at the Advanced Photon Source (APS, Argonne, IL). The APS ring operates at 7 GeV with a current of 102 mA. Energy selection at the APS with a liquid N_2-cooled Si (111) monochromator. The incident X-ray beam was focused to a size of either 5 x 10 μm (APS) using two Si mirrors in a Kirkpatrick-Baez geometry. Sediments from the batch reactions were mounted on Kapton tape and attached to a x-y translation stage; the incident beam intensity (I_0) was measured with an in-line ionization chamber, and fluorescence yield was measured using a multielement Ge solid-state detector and normalized by I_0. X-ray absorption spectra were recorded on selected regions of the samples on the basis of elemental associations obtained from μ–XRF maps. The spectra represented are the average of 2 to 8 scans, depending on Cr concentrations.

XAS data were processed using WinXAS 3.1 [22] and the SixPACK [23] interface to IFEFFIT [24]. XANES data were background-subtracted and normalized to an unit edge step. The ratio of the Cr pre-edge peak to post-edge amplitude was used to determine the concentration of Cr(VI) [15].

Results

Influence of Chemical Pre-Treatment

Several chemical extractions along with sonication were used to target different types of weathering rinds to investigate the inhibition of Cr(VI) reduction. Sonication was used to simulate physical abrasion, 0.5 M NaOH to promote dissolution of silicate phases, 10 mM oxalate to provide a complexant to dissolve Fe(III) and other metal (hydr)oxide phases of limited stability, and 0.5 M HCl to induce acidic dissolution of metal oxide and carbonate phases.

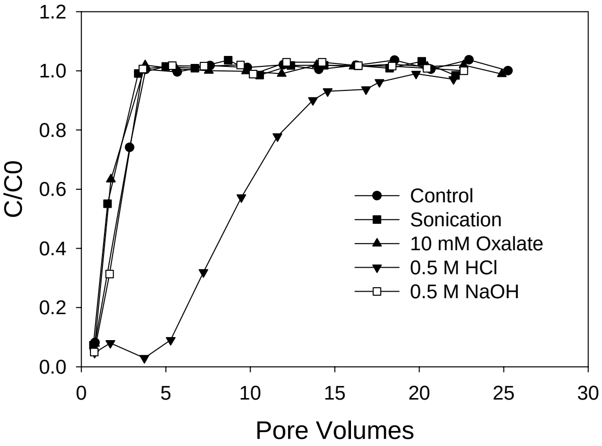

Fig. 1. Effect of sediment pre-treatment on Cr(VI) breakthrough. Influent contained 0.2 mM K_2CrO_4, while the sediment was treated as indicated in the key.

Relative to the control (no treatment), retardation of Cr(VI) breakthrough occurred only after treatment with 0.5 M HCl (Fig. 1); in this treatment, the solid-phase Cr was exclusively in the trivalent state (Fig. 2 & 3). As a consequence of Cr retention, 8.3 x 10^{-4} moles Cr / kg sediment remained in the solid phase in the 0.5 M HCl -treated column, In the other columns, only 1 x 10^{-5} moles Cr kg^{-1} sediment were deposited. Reduced chromium was also observed along the edges of mica grains (Fig. 3), many of which were hand-picked grains.

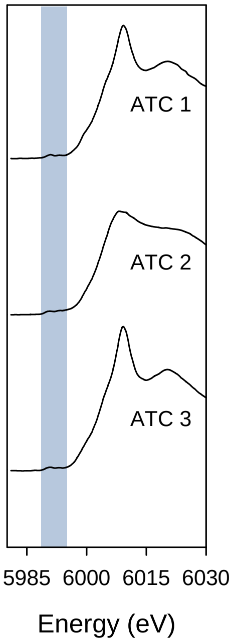

Fig 2. Micro-XANES spectra from 3 points of high Cr concentration in the acid treated columns (ATC). Grey box indicates region of diagnostic Cr(VI) pre-edge feature.

Discussion and Results

Chromate reduction by Hanford formation sediments is governed by surface modification of ferrous iron-bearing minerals. In oxic environments, such as the Hanford subsurface, chromium reduction is generally inhibited by ferric-(hyrdr)oxide weathering rinds. Indeed Zachara et al. [25] observed ferric (hydr)oxide rinds on biotite grains obtained from the Hanford formation. The presence of such a layer diminishes the rate of chromate reduction, due to the required transfer of electrons, or Fe(II), from the underlying unoxidized mineral to the aqueous interface, as illustrated for synthetic magnetite [26].

Chromate reduction occurred only after acid extraction and was not observed after oxalate, base, or sonication treatments (Fig. 1). The chemical treatment experiments, where chromate reduction only occurred after acid extraction and was not observed after oxalate, base or sonication treatments (Fig. 1), support the importance of surface modification for chromate reduction. Once the mineral surface has been modified by acid extraction, Cr(VI) reduction proceeds rapidly (Fig. 1).

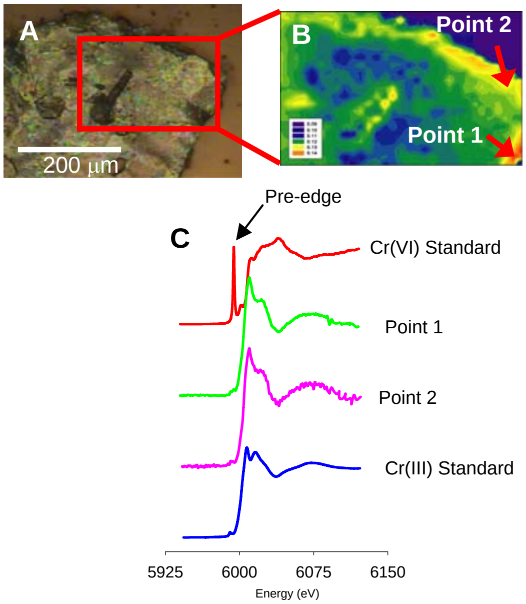

Fig. 3. A) photo-micrograph of handpicked mica grain. B) X–ray fluorescence map of Cr distrubtion (high Cr = red). C) Micro-XANES spectra from points 1 and 2 in B.

Attenuation of chromium beneath leaking HLW tanks at the Hanford Site is governed by the reactivity of ferrous iron-bearing mineral phases, which is controlled by mineral solubility and surface reactivity. Without pretreatment surface coatings on these sediments prevent chromate reduction. In general, the mobility of chromate in aerobic environments with low organic carbon will be determined by the presence of ferrous iron bearing mineral phases and their reactivity.

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