

Understanding the Natural Mechanisms for Chromium Mobilization in Groundwater

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Hexavalent chromium, when introduced in the human body, increases the risk of cancer, and kidney/ liver failure. Historically, concern for hexavalent chromium contamination in groundwater has been confined to areas affected by anthropogenic sources of hexavalent chromium. These include leather tanneries, chromium plating factories, stainless steel producers, and chrome pigment manufacturers. Natural sources of Cr(VI) in groundwater were historically not considered a significant source of Cr(VI). This was because while Cr is found in abundance in certain soil and rock types, the vast majority of it is Cr(III) in ultramafic rocks and its soil derivatives. Manganese oxides are the primary oxidants of Cr(III) to Cr(VI) at environmentally relevant conditions. Both manganese oxides and Cr(III) minerals have limited solubility, rendering the dissolution and subsequent oxidation of Cr(III) to Cr(VI) unlikely. However in recent years elevated levels of Cr(VI) have been found in places far from those anthropogenic sources. In fact, Izbicki et al. (2015) found that 25% of wells sampled throughout the state of California exceeded the 10 ppm EPA maximum contaminant level (MCL) in drinking water for Cr(VI). In these areas, the concentration of Cr(VI) reaches as high as 70 ppm, which is 7 times the MCL. Not only do the northern and eastern parts of California have elevated Cr levels in the soil and bedrock, but there is an annual change in water table level of tens of feet due to irrigation.

Numerous studies have focused on the reduction of Cr(VI) to Cr(III), as it is relevant for the remediation of the anthropogenically sourced contamination. However, a stronger geochemical understanding is needed of the naturally-occurring oxidation of Cr(III) to Cr(VI). We hypothesize that the shifting redox conditions between the dramatically different annual water table levels are part of the cause. The objective of this work is to enhance our understanding of the factors that affect the reaction of Cr(III) minerals with birnessite (MnO_2). We intend to study the effect of hydrologic and geochemical constraints on the oxidation of Cr(VI) by MnO_2 . We conducted a series of diffusion-limited flow-through experiments with and without MnO_2 . Additionally, we supplied aqueous Mn(II) to determine the potential for Mn(II) oxidation and subsequent interaction with Cr(III) minerals.

We first synthesized birnessite and two types of Cr(III) minerals commonly found in the environment: $\text{Cr}(\text{OH})_3$ and $\text{Cr}_{0.25}\text{Fe}_{0.75}(\text{OH})_3$. These minerals were confirmed using XRD. These Cr(III) minerals were then coated onto fine quartz sand grains, rinsed, and allowed to dry. The concentration of the minerals on the sands was determined by extracting the minerals off of the sands using 6M hydrochloric acid, and then analyzing using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The $\text{Cr}(\text{OH})_3$ - and $\text{Cr}_{0.25}\text{Fe}_{0.75}(\text{OH})_3$ -coated sands were suspended in a cylindrical agar gel aggregate with birnessite in a Mn:Cr molar ratio of 1:10 and 1:2.5, respectively. This 3cm x 1.5cm cylinder was capped on both sides with rubber stoppers, and surrounded by 4.5mm glass beads in a flow-through reactor (Figure 1). The beads simulated advective flow regions in porous media. Synthetic groundwater media was pumped through the reactors at 0.6mL per hour. We ran twelve reactors total. Each Cr(III) mineral-coated sand was run in duplicate, and each sand was treated with Mn in one of three ways: (1) in four reactors, birnessite powder was mixed directly into the aggregate (+Bir), (2) in the next four, 0.17mM MnCl_2 was present in the groundwater media (+ Mn_{aq}), and (3) in the last four Mn was not present in either the aggregate or the groundwater media (No Mn). The reaction was allowed to proceed for 20 days, with the oxidized, aqueous Cr(VI) diffusing out of the aggregate and into the advective flow.

Samples were taken every 4 hours for the first 40 time-points, then reduced to every 24 hours for a total of 20 days. These samples were then diluted by a factor of 3 in 2% nitric acid and analyzed for several redox active metals, including total aqueous Cr, on an ICP-OES.

While results from the +Bir treatment were interesting, the present discussion focuses on data from the second and third treatments because the sands used in these reactors originate from the same batch. During the first five days of the experiment, we observed an initial spike in the aqueous Cr(VI) concentration in all the reactors (Figure 2). Reactors with Cr(OH)₃-coated sands exhibited a much higher average Cr(VI)_{aq} maxima (4.5μM and 3.5μM for +Mn_{aq} and NoMn treatments, respectively) than the reactors containing Cr_{0.25}Fe_{0.75}(OH)₃-coated sands (1.6μM and 2.1μM for +Mn_{aq} and NoMn treatments, respectively). We propose that the difference observed in initial Cr(VI) peak heights is a function of mineral solubility of Cr(OH)₃ versus Cr_{0.25}Fe_{0.75}(OH)₃ and total Cr available for oxidation. Cr(OH)₃ is more soluble than Cr_{0.25}Fe_{0.75}(OH)₃, allowing the mineral to dissolve and subsequently oxidize to a greater extent than the Cr_{0.25}Fe_{0.75}(OH)₃ minerals. Additionally, Cr_{0.25}Fe_{0.75}(OH)₃ dissolves incongruently, which gradually decreases the stoichiometric Cr:Fe ratio of the mineral and reduces the solubility. While the differences in Cr(VI) generation between the two Cr(III) minerals for each treatment was as predicted, the comparison between the two treatments (+Mn_{aq} and NoMn) for each Cr(III) mineral yielded surprising results. Of the reactors with Cr(OH)₃, the ones without Mn(II)_{aq} had a lower peak of Cr(VI) than the reactors with Mn(II) in the groundwater (Figure 2). We suggest that some sorbed Mn(II) may undergo abiotic, metal oxide surface-catalyzed oxidation and enhance Cr oxidation. On the other hand, of the reactors with Cr_{0.25}Fe_{0.75}(OH)₃, the opposite trend was observed: the No Mn reactors peaked higher than the +Mn_{aq} reactors (Figure 2). We hypothesize that for the +Mn_{aq} treatment, surface passivation caused by a precipitation of manganese carbonates likely reduces the surface reactivity of the Cr_{0.25}Fe_{0.75}(OH)₃-coated sands. Interestingly, Mn(II) does not appear to be contributing to Cr oxidation in the +Mn_{aq} treatment, unlike for the reactors containing Cr(OH)₃-coated sands.

Reactors without birnessite or Mn(II) in the groundwater media should, in theory, have eluted no aqueous Cr(VI) as we had introduced no known oxidant into the system. Dissolved oxygen is not a major oxidant of Cr(III) at pH < 8.5. The No Mn reactors, however, produced aqueous Cr(VI) concentrations comparable to or more than those in +Mn_{aq} reactors. We ran batch experiments to determine what in our experimental setup might be causing the Cr(III) minerals to oxidize. We examined the importance of factors contributing to aggregate preparation, including solution temperature, pH, and light, on Cr oxidation. We found that light was a significant catalyst of Cr oxidation both during aggregate preparation and under experimental conditions. We hypothesize that interactions between light and the agarose may generate oxygen radicals or other chemical species that may enhance Cr oxidation in our experiment. In the future, we will prepare and run reactors in the dark to better represent Cr(VI) generation levels viable in structured subsurface soils and sediments. Additionally, we will examine the role of birnessite in Cr(VI) generation from Cr(III) minerals. Understanding these mechanisms will allow for research to be conducted into how human use and manipulation of aquifers could mobilize toxins, like Cr(VI), in freshwater resources.

Figures:

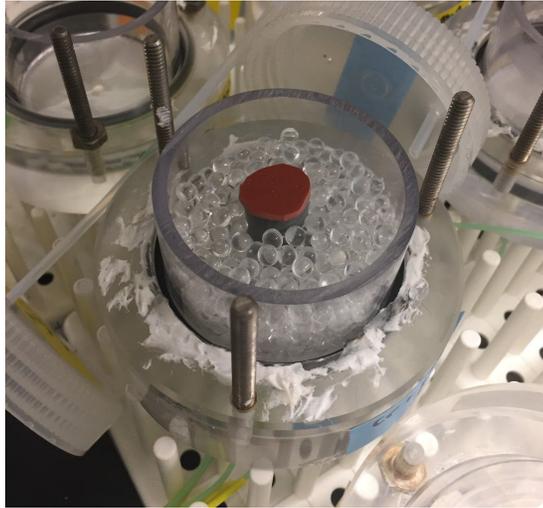


Figure 1: Diffusion-limited, flow-through reactors. The glass beads surround the Cr(III) mineral aggregate, which is capped by a rubber stopper to prevent advective flow through the aggregate.

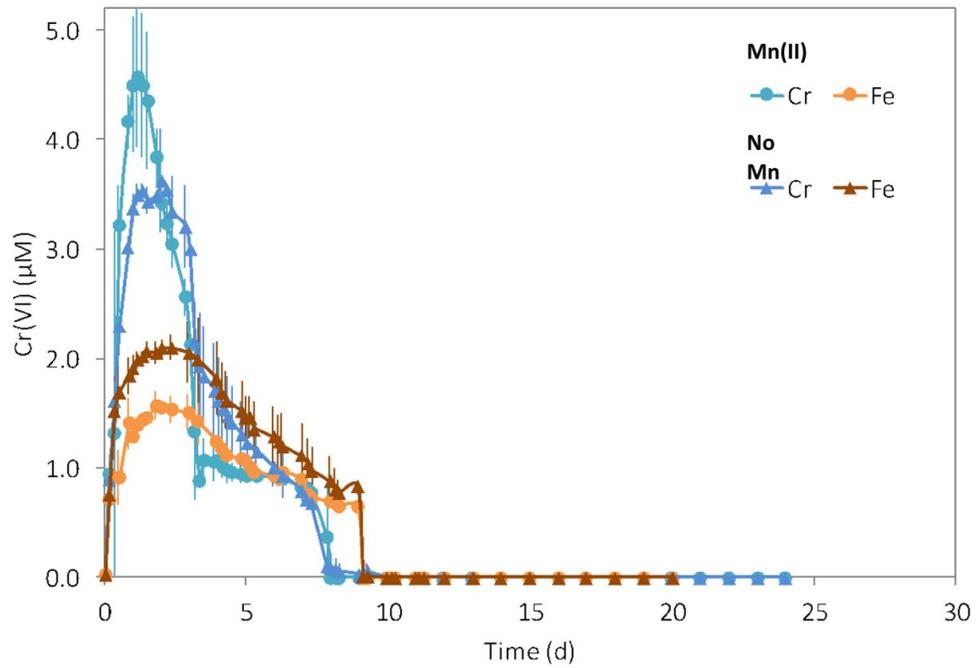


Figure 2: Aqueous Cr(VI) concentrations (μM) in groundwater effluent over time (days).

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