



Water Rock Interaction [WRI 14]

Chromium geochemistry in a wetland environment

Patrick Longmire^{*a}, Michael Dale^b, and Kim Granzow^b

^aEnvironmental Geochemistry, LLC, 122 Placita de Oro, Santa Fe 87501, USA

^bNew Mexico Environment Department, 1183 Diamond Dr., Los Alamos 87544, USA

Abstract

Cooling tower water ranging between 7 to 18 mg/L of Cr(VI) was released to a stream channel entering a wetland at Los Alamos National Laboratory, New Mexico, USA from 1956 to 1972. The wetland contains between 5700 and 27,000 kg total Cr mainly as Cr(III), with a median mass of 11,000 kg total Cr, representing 21 to 49 % of the total Cr. Chemical analyses conducted on wetland sediments show that 97.3 to 99.9 % of the Cr is stable as Cr(III). Mass balance calculations confirm that there are sufficient concentrations of Fe(II) along with the organic-rich sediments to maintain Cr(III) stability within the wetland.

© 2013 The Authors. Published by Elsevier B.V.

Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013

Keywords: chromium, wetland, redox chemistry, solid organic matter

1. Introduction

The aqueous environmental geochemistry of Cr is of considerable interest to physical scientists and toxicologists for quantifying the fate and transport of this metal in surface and subsurface environments. Rai and Zachara [1] report that Cr might occur as nontoxic Cr(III) and toxic Cr(VI) in aqueous solutions, and provide detailed discussions on Cr adsorption and precipitation. Chromium(III) precipitates as $\text{Cr}(\text{OH})_3$ and $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ under reducing conditions [1], typically encountered within organic-rich sediments including wetlands and peat bogs. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was extensively used in Technical Area(TA-3) industrial cooling towers as anticorrosion and antifouling agent from 1956 to 1972 at Los Alamos National Laboratory (LANL), New Mexico, United States [2]. The total mass of Cr(VI) released from the TA-03 cooling towers primarily as CrO_4^{2-} ranges between 31,000 and 72,000 kg, with

* Corresponding author. Tel.: 001-505-983-7715

E-mail address: longmire@cybermesa.com.

concentrations ranging between 7 to 18 mg/L of Cr(VI). Discharge of sanitary and industrial treated effluents produced an extensive wetland within the canyon containing abundant cattails, grasses, shrubs, partially decomposed solid organic material (SOM), and deciduous trees. The sinuous-shaped Sandia wetland occupies approximately 11,900 square meters along the canyon floor [2]. This wetland contains between 5700 and 27,000 kg Cr(III), with a median mass of 11,000 kg total Cr, representing 21 to 49% of the total Cr released from TA-03 cooling tower discharges [2]. Los Alamos National Laboratory is considering limiting the volume of treated-industrial discharge water released from TA-03 to Sandia Canyon and as a consequence, portions of the Sandia wetland may become dewatered and dry out under reduced surface-water flow. This raises concerns about the potential oxidation of Cr(III) to Cr(VI) within the wetland during dewatering, drying, and decay of solid organic matter (SOM) as well as physical destabilization of wetland sediments.

2. Experimental

Batch leaching experiments were conducted on eight diverse Sandia wetland samples to quantify the potential release of Cr during dewatering and drying of the wetland material [2]. Two sediment samples collected from an organic depleted and oxidized area (sample 600108) upstream from the currently active wetland and from an organic-rich area containing relic cattails (sample 600115) of the wetland are discussed in this paper. These two diverse sediment samples bound redox conditions controlling variability of Cr speciation and Cr(III) oxidation within the wetland. Details of the design of the batch leaching experiments are provided by LANL [2]. Leaching experiments were conducted by reacting diverse wetland material with deionized water and sanitary wastewater systems (SWWS) effluent after various periods of drying. Drying times included 1, 2, 4, and 12 months prior to conducting the leaching experiments. Leachate samples were filtered through 0.22 micrometer membranes and analyzed for total dissolved Cr, dissolved Cr(VI), and other major ion and trace solutes using ICP-OES and ICP-MS [2].

3. Results

Most of the Sandia wetland leachates are characterized by circumneutral pH values ranging from 6.19 to 8.04 [2]. Leachates produced from sample 600115, however, have acidic pH values ranging from 3.70 to 5.04. The acidity associated with these samples results from deprotonation of reactive functional groups, consisting of aromatic and aliphatic carboxylic acids present in humic and fulvic acids [2]. Corrected Eh values range from +101 to +526 mV in the leachate samples and generally become more oxidizing as drying times prior the leaching increased [2].

Sample 600108 was collected from the channel bank upstream of the active Sandia wetland containing very small amounts of SOM [2]. Variable concentrations of total Cr and Cr(VI) were measured in the leachates under different drying periods shown in Fig. 1a (left side). Maximum Cr(VI) concentrations leached from sample 600108 occurred at the first month of drying with sustained release of lower concentrations of Cr(VI) occurring afterwards. Chromium(III) comprises approximately 15 to 83 percent of total dissolved Cr leached from sample 600108. Dissolved concentrations of Cr(VI) varied from 3.25 to 14.49 $\mu\text{g/L}$ and from 2.94 to 11.46 $\mu\text{g/L}$ in the deionized water and SWWS effluent, respectively (Fig. 1a). Similar concentrations of DOC were leached from sample 600108 using deionized water or SWWS effluent (Fig. 1a). Sources of DOC measured in leachates include residual organic compounds present in SWWS effluent and remnant SOM associated with Sandia wetland material. Soluble SOM has undergone partial oxidation resulting from dewatering and drying at this sample location within the wetland.

Sediment sample 600115 was collected from a dry bank near the eastern boundary of the Sandia wetland and results of the batch leaching experiments are shown in Fig. 1b (right side). The sample contains a very high abundance of SOM consisting of decayed or partly decomposed cattails [2].

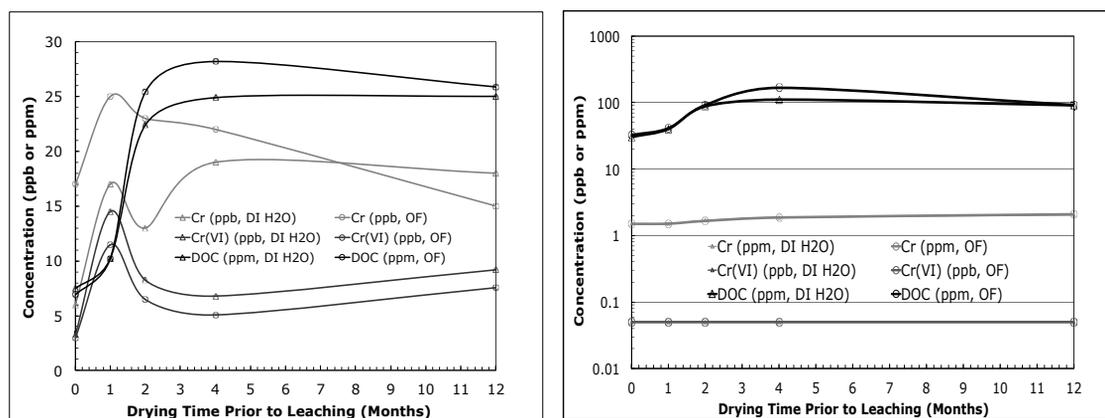


Fig. 1ab. Sample drying time (in months) prior to leaching versus dissolved concentrations of total chromium (Cr) (ppb), hexavalent chromium [Cr(VI)] (ppb), and dissolved organic carbon (DOC) (ppm) in samples 600108 (1a, left) and 600115 (1b, right). DI and OF mean deionized water and SWWS outfall, respectively.

Dissolved concentrations of Cr(VI) leached from sample 600115 were less than analytical detection (0.05 $\mu\text{g/L}$) using ICP-MS with Cr(III), possibly occurring as a Cr(III)-humate complex or colloid, comprising 100 percent of total Cr (Fig. 1b). Concentrations of total dissolved Cr in the deionized water and SWWS leachates associated with sample 600115 increased from 1.50 to 2.03 mg/L and from 1.50 to 2.09 mg/L, respectively (Fig. 1b). Concentrations of DOC increased from 30 to 111 mgC/L in the deionized water leachates, and from 32 to 167 mgC/L in the SWWS effluents. Mass balance calculations were performed to evaluate the stability of Cr(III) in the presence of Fe(II) and Mn(IV) within the Sandia wetland under present-day conditions [2]. Analytical results for 4 sediment samples collected from saturated portions (organic-rich) of the Sandia wetland are provided in Table 1.

Table 1. Chromium reduction capacity of Sandia Canyon wetland (saturated), Los Alamos, New Mexico, USA.

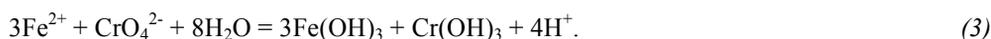
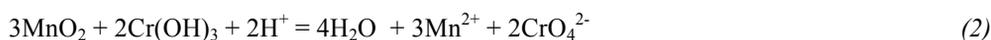
Parameter	Sample 07-236a	Sample 07-236b	Sample 07-92a	Sample 07-92b
Total Cr (mg/kg)	114.0	36.5	3580	18.5
Cr(VI) (mg/kg)	0.07	0.07	2.01	0.28
Cr(III) (mg/kg)	113.93	36.43	3587	18.22
Total Fe (mg/kg)	6380	6560	5970	970
Fe(II) (mg/kg)	6360	6540	2660	230
Mn(IV) (mg/kg)	170	94.8	294	18.9
moles Fe(II)/g soil $[\geq 3]$	84,600	87,000	1230	765
moles Cr(VI)/g soil				
moles Fe(II)/g soil $[\geq 1]$	36.9	67.9	8.9	12.0
moles Mn(IV)/g soil				

Concentrations of Cr(VI) and total Cr, mainly stable as Cr(III), range from 0.07 to 2.01 mg/kg and from 18.5 to 3580 mg/kg, respectively (Table 1). A reaction describing the reduction of Cr(VI) to Cr(III), in the

presence of SOM containing hydroquinone ($C_6H_6O_2$) that provides the reduction capacity for SOM discussed by McBride [3], is:



Sample 600108 contains much smaller amounts of SOM [2] and DOC resulting in a lower reduction capacity for Cr(VI) (Fig. 1a). Reduction of Cr(VI) to Cr(III), however, is easily accomplished with abundant SOM present within the Sandia Canyon wetland including sample 600115 (Fig. 1b). Results of X-ray absorption near edge spectroscopy (XANES) analyses show the association of Cr(III) with a form of hydrous ferric oxide (HFO), suggesting that Cr(III) precipitated as $Fe_xCr_{1-x}(OH)_3$ in sample 600115 [2]. Based on results of saturation index (SI) calculations using the computer program PHREEQC [4], SWWS leachates associated with sample 600115 are undersaturated with respect to amorphous $Cr(OH)_3$ (SI = -3.10) and Cr potentially is controlled by coprecipitation of $Fe_xCr_{1-x}(OH)_3$. Chromium reactivity in the presence of Mn(IV) and Fe(II) is shown in Eqs. (2) and (3):



According to Eq. (2) and Eq. (3), Cr(III) stability is favored when the mole ratio of Fe(II) to Mn(II) is greater than unity and three moles of Fe^{2+} are required to reduce one mole of CrO_4^{2-} . Mole ratios of Fe(II) to Cr(VI) range from 765 to 87,000 confirming robust stability of Cr(III) in the four sediment samples provided in Table 1. Stability of Cr(III) is further demonstrated with mole ratios of Fe(II) to Mn(IV) exceeding unity, ranging from 8.9 to 67.9.

4. Conclusions

Variable concentrations of dissolved Cr(VI) less than 20 $\mu\text{g/L}$ were leached from Sandia wetland samples during batch experiments conducted after drying the samples for one year or less. Higher concentrations of Cr(III) were leached from the organic-rich wetland samples compared to Cr(VI). Maintaining an active wetland by providing continual treated effluent will further attenuate Cr through (bio)chemical reduction and should minimize long-term potential releases of this metal to Sandia Canyon.

References

- [1] Rai D, Zachara JM. Geochemical behavior of chromium species: Electric Power Research Institute, interim report EA-4544, Palo Alto, CA, 1986.
- [2] Los Alamos National Laboratory. Investigation report for Sandia Canyon: LA-UR-09-6450; 2009.
- [3] McBride MB. *Environmental Chemistry of Soil*: Oxford Press, New York; 1994.
- [4] PHREEQC, Parkhurst DL, Appelo, CAJ. User's guide to PHREEQC (version 2)- a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: United States Geological Survey, Water-Resources Investigation Report 99-4259; 1999.