

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

**Sorption and Desorption of Cr(VI) in Hanford
Sediments as an Indication of Natural
Attenuation Capacity**

DOE-FIU SCIENCE & TECHNOLOGY
WORKFORCE DEVELOPMENT PROGRAM

Date submitted:

December 16, 2022

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Submitted to:

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement # DE-EM0005213



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EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2022, a DOE Fellow intern, Mariah Doughman, spent 8 weeks on a summer internship at the Pacific Northwest National Laboratory (PNNL) under the supervision and guidance of Nik Qafoku, chief scientist and laboratory fellow, Jim Szecsody, hydrogeologist, and Hilary Emerson, earth scientist. The intern's project was initiated on June 27, 2022, and continued through August 19, 2022 with the objective of measuring adsorption and desorption of Cr(VI) in batch and column experiments to determine if the concentration of Cr(VI) remaining in the subsurface is behaving as predicted and if mobility is reduced by natural processes.

Cr(VI) is relatively mobile as an anionic species under the oxidative, slightly alkaline conditions characteristic of the Hanford Site. Once active remediation is complete, there is still a need to understand contaminant fate and mobility in the subsurface to quantify release and generate data to support the potential for passive remediations like monitored natural attenuation (MNA) that may be considered. The objective of this study was to measure adsorption and desorption of Cr(VI) in batch and column experiments to determine if the concentration of Cr(VI) remaining in the subsurface is behaving as predicted and if mobility is reduced by natural processes. Solid-water distribution coefficients, K_d , measured in batch isotherm experiments (Cr concentration of 0.05-0.53 mg/L) ranged from 0.63-1.66 L/Kg. These values were significantly larger than the K_d of 0.04 L/Kg determined from a Cr(VI) (0.2 mg/L) column experiment. From this experiment, a retardation factor of 1.25 was also determined. This illustrates the importance of comparing multiple experimental techniques to determine contaminant fate and mobility at laboratory scale. Overall, these results indicate that Cr(VI) remains mobile under natural site conditions. The mobility of Cr(VI) under natural conditions is an important consideration assessing the feasibility for passive remediation strategies (e.g., MNA) after active remediation is complete.

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1. INTRODUCTION

Hexavalent chromium [Cr(VI)] was used as a corrosion inhibitor during weapons production and is now a contaminant of concern at the Hanford Site due to its discharge to the subsurface through spills during handling, pipeline leaks, and disposal to cribs. Cr has the potential to enter the groundwater via downward migration through the vadose zone and contaminate the Columbia River, a major water resource in the Pacific Northwest. Cr is regulated as a contaminant due to its toxic effects as a mutagen, teratogen, and carcinogen.¹ To remediate this contaminant, active remediation (e.g. source removal, soil flushing, pump-and-treat) may be used; and, once complete, there may be a need to understand contaminant fate in the subsurface to quantify long-term mobility and to assess the potential for a passive remediation technique like monitored natural attenuation (MNA) to be considered. A fundamental understanding of Cr in the subsurface is necessary for successful remediation of the site. Parameters that need to be considered include pH, redox conditions, total concentration of chromium, the effect of mineral surface functional groups, the presence of competing anions, and the dynamic properties of the mineral in contact with the aqueous solution.² Under oxic conditions present at the Hanford Site, Cr is in hexavalent form as calcium chromate (CaCrO_4) or as the oxyanion (CrO_4^{2-}).

From previous studies, Cr adsorption in the vadose zone will most likely occur through an outer sphere complex on iron and aluminum oxides^{3,4,5,6,7} and kaolinite^{8,9} due to their high zero points of charge and large surface areas. Cr will compete for sorption sites with major groundwater anions including carbonate (CO_3^{2-}) and sulfate (SO_4^{2-}) and will experience electrostatic repulsion at the mineral surfaces under site conditions (pH above the pH of zero-point charge).^{7,10} This means that it is possible that Cr will have minimal adsorption and will be relatively mobile in the subsurface. However, questions still remain regarding the behavior of Cr under site-specific conditions with co-contaminants that may compete for adsorption sites. Therefore, the objective of this study was to add to the understanding of Cr fate and mobility through natural Hanford sediment under slightly alkaline conditions with additional contaminants like NO_3 and U. This was accomplished by conducting batch and column experiments and measuring the solid-water distribution coefficient for each experiment.

2. RESEARCH DESCRIPTION

Cr batch adsorption experiments were conducted with potassium chromate (K_2CrO_4 , High Purity Standards) and Hanford formation sediment (≤ 2 mm grain diameter). One 2L batch of artificial groundwater (AGW) used in the experiment was created using the formulation shown in Table 1. AGW was placed in 50 mL polypropylene centrifuge tubes and spiked with Cr to reach variable concentrations (0.05, 0.10, 0.25, 0.40, 0.53 mg/L). Solution pH was measured using a Thermo Scientific Orion Versa Star pH meter with a Thermo electrode calibrated using standard pH buffers 4.01, 7.00, 10.00 (Fisher). After minor adjustments with NaOH (0.1 M), the final pH for each concentration was 7.95 ± 0.04 .

Table 1: AGW Formulation

Constituent	formula weight (g/mol)	Concentration (mmol/L)	Concentration (g/L)
NaHCO ₃	84.0	1.59	0.13
KHCO ₃	100	0.12	0.01
MgSO ₄ •7H ₂ O	246	0.37	0.09
MgCl ₂ •6H ₂ O	203	0.25	0.05
CaCl ₂ •2H ₂ O	147	1.07	0.16
Add 0.150 mL per liter of 1M HCl for pH 7.8			

Tabletop dried sediment (0.7500 ± 0.0004 g per tube) was placed in 15 mL polypropylene centrifuge tubes in triplicate. Spiked AGW (0.750 ± 0.001 mL) was added to the sediment containing centrifuge tubes. A control without sediment was also prepared to measure the amount of Cr adsorbed on the tube and the cap or lost during pH measurement. Centrifuge tubes were placed on an end-over-end tube revolver at 8 rpm, as shown in Figure 1.



Figure 1: Sediment samples in an end-over-end tube revolver at 8 RPM.

For adsorption equilibrium experiments, samples were sacrificed and only measured once (to ensure a constant solid:solution ratio) at the following times to establish time to equilibrium: 1 hour, 3 hours, 8 hours, 1 day, 2 days, 3 days, 4 days, 5 days, 7 days, and 14 days after the addition of the spiked AGW to the sediment. Prior these sampling times, the samples were centrifuged at 4,500 RPM for 30 minutes (Sorvall ST Thermo Scientific Centrifuge). The supernatant was then removed from the sediment and placed in a new vial for storage. Samples were stored in a refrigerator until chemical analyses.

Samples collected during the batch adsorption experiment were diluted with 2% nitric acid (HNO_3) prior to analyses on a ThermoFisher Scientific iCAP RQ inductively coupled plasma-mass spectrometer (ICP-MS). This instrument was calibrated with Cr standards (0.0001-0.075 mg/L) that were prepared from 1,000 mg/L commercial K_2CrO_4 stock solution (High Purity Standards). Cr samples were diluted $10\times$ with 2% HNO_3 respectively.

A pseudo one-dimensional column adsorption and desorption experiment was conducted using K_2CrO_4 (0.2 mg/L), Hanford formation sediment (fine sand with 20% by weight addition of vermiculite), AGW, and bromide (Br^- , 80 mg/L) as a tracer. Sediment was packed into a stainless-steel column (133.33 mL) and physical parameters were determined and shown in Table 2.

Table 2: Physical Parameters of the Packed Column

Sediment mass	257 g
Bulk Density	1.93 g/mL
Porosity (fraction)	0.28

Total Pore Volume	37.43 mL
Darcy Flux	24 ft/day

Using a Hitachi L-6000 pump, Cr spiked AGW with a Br⁻ tracer was injected into the bottom of a vertically oriented column at a flow rate of 1 mL/min for 4.6 pore volumes (PV) and then non-spiked AGW was injected for the desorption limb at a flow rate of 1 mL/min for 4.3 PV. Two stop flow events at 4.6 PV (104 hours) and 5.5 PV (26 hours) were conducted. Samples (48) were collected using an ISCO FOXY 200 Fraction Collector. This setup is shown in Figure 2.



Figure 2: Packed sediment column setup with Hitachi pump and FOXY fraction collector.

The effluent fluid samples were analyzed for Cr using the colorimetric EPA method 7196A.¹¹ Samples (2 mL) were reacted with 2% HNO₃ (20 μL) and diphenylcarbazide (50 μL) for 8 minutes to produce a red-violet color and were analyzed on a HACH DR/4000U Spectrophotometer at 540 nm as shown in Figure 3. The retardation of Cr was determined using Equation 1. Where ρ_b is bulk density and θ is porosity.

$$R = 1 + \frac{\rho_b}{\theta} K_d \quad \text{Equation 1}$$

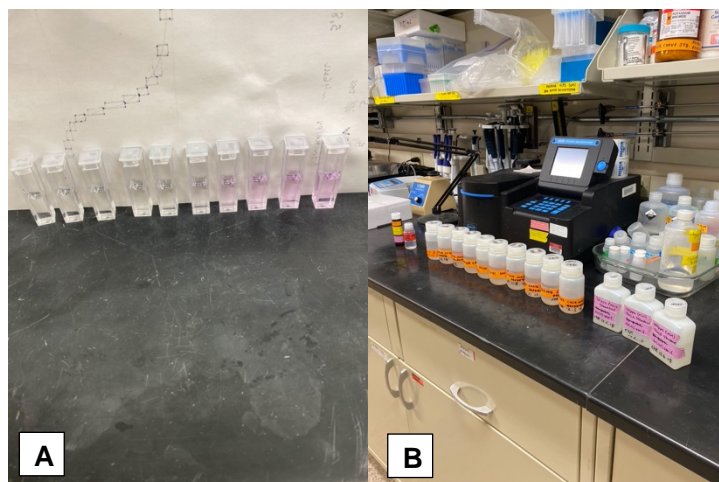


Figure 3: A) samples reacted with 2% HNO₃ (20 μ L) and diphenylcarbazide (50 μ L) after 8 minutes. B) HATCH spectrophotometer, Cr standards, 2% HNO₃, and diphenylcarbazide.

Samples (1 mL) were analyzed for Br⁻ using an Accumet ion selective electrode (shown in Figure 4) and sodium nitrate (5 M, 20 μ L).



Figure 4: Ion selective probe and meter for Br⁻ analysis.

3. RESULTS AND ANALYSIS

Adsorption at higher initial concentrations of Cr(VI) decreased, indicating exhaustion of available adsorption sites on the sediment. This is shown in Figure 5. The lack of adsorption may be due to the negative charge on the surface of the iron and aluminum oxides able to adsorb CrO_4^{2-} causing Cr(VI) to experience repulsion. It is also probable that CO_3^{2-} and SO_4^{2-} present in the AGW competed for adsorption sites on the sediment further causing a decrease in adsorption.

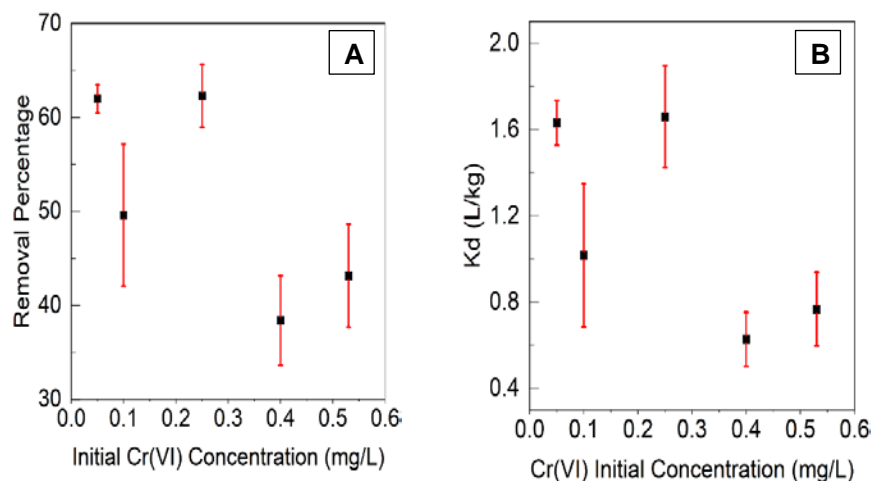


Figure 5: A) Percent of initial Cr(VI) concentration removed during batch experiments, B) K_d versus initial Cr(VI) concentration (mg/L) for initial concentration range of 0.05-0.53 mg/L.

As shown in Figure 6 from the column experiment, the adsorption ($K_d=0.036$ L/kg) and retardation ($R=1.25$) of Cr is minimum, and the curve is similar to Br^- . The difference in K_d between the batch and column experiments is due to an increase in access to clay adsorption sites in batch experiments from an increase in mixing and abrasion potentially breaking up particles and exposing additional sites and a longer residence time. There was also a much longer residence time that Cr(VI) experienced with sediment (14 days) in batch experiments compared to the column experiment (2 hours) allowing for increased adsorption. Batch experiments allowed for the investigation of possible adsorption capacity of the sediment for chromium whereas the column experiment was executed to better mimic field-relevant sediment/water ratios and residence time. The difference in results indicates the importance of analyzing adsorption using multiple techniques. Results from both sets of experiments confirm that Cr is relatively mobile under site relevant concentrations and conditions. Iron and aluminum oxides^{3,4,5,6,7} and kaolinite^{8,9} were likely responsible for the adsorption occurring in Hanford formation sediment. This is due to their high specific areas, as high as several hundreds of m^2g^{-1} , and the oxides' point of zero charge being located in the neutral or slightly basic pH range (i.e., positively charged near neutral pH, attracting negatively charged Cr ions).^{10,12,13,14}

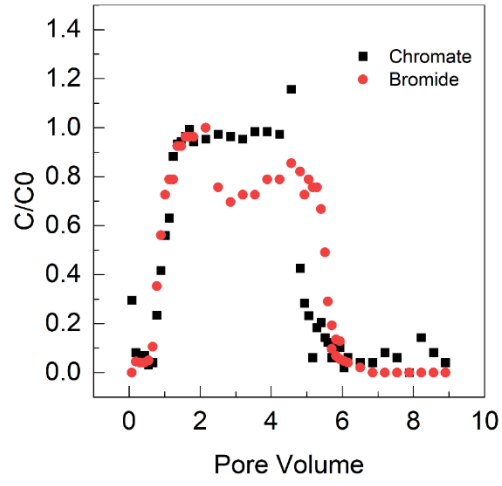


Figure 6: Cr and Br break through curves.

4. CONCLUSION

Cr(VI) adsorption to Hanford formation sediment is minimal in AGW at slightly alkaline pH (7.95 ± 0.04). K_{ds} measured in batch isotherm experiments at variable Cr concentrations (0.05-0.53 mg/L) ranged from 0.63-1.66 L/Kg. The K_d determined from the retardation factor (1.25) from the Cr(VI) (0.2 mg/L) column experiment was significantly smaller at 0.04 L/Kg. This is possibly due to electrostatic repulsion that Cr(VI) experiences from iron and aluminum oxides and kaolinite all of which have a point of zero charge at a pH lower than the pH of the AGW. Common anions present in the AGW including SO_4^{2-} and CO_3^{2-} may have outcompeted Cr for available adsorption sites on the sediment also causing minimal adsorption. The difference in results from the set of experiments illustrate the importance of comparing experimental techniques to determine contaminant fate and mobility at laboratory scale. Overall, these results indicate that Cr(VI) remains mobile under natural site conditions. The mobility of Cr(VI) under natural conditions is an important parameter to incorporate when considering possible passive remediation strategies (MNA) after active remediation is complete.

5. REFERENCES

- (1) Dresel, P.; Qafoku, N.; McKinley, J.; Fruchter, J.; Ainsworth, C.; Liu, C.; Ilton, E.; Phillips, J. Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site. **2008**, No. July, 1–144.
- (2) Geckeis, H.; Lützenkirchen, J.; Polly, R.; Rabung, T.; Schmidt, M. Mineral-Water Interface Reactions of Actinides. *Chem. Rev.* **2013**, *113* (2), 1016–1062. <https://doi.org/10.1021/cr300370h>.
- (3) MacNaughton, M. *The Adsorption of Chromium (VI) at the Oxide/Water Interface*; 1975.
- (4) Davis, J.; O Leckie, J. Surface Ionization and Complexation at the Oxide/Water Interface. 3. Adsorption of Anions. *J. Colloid Interface Sci.* **1980**, *74* (1), 32–43.
- (5) Benjamin, M. M.; Bloom, N. S. Effects of Strong Binding of Anionic Adsorbates on Adsorption of Trace Metals on Amorphous Iron Oxyhydroxide. In *Adsorption From Aqueous Solutions*; Tewari, P. H., Ed.; Springer: Boston, MA, 1981; pp 41–60.
- (6) Honeyman, B. D. Cation and Anion Adsorption at the Oxide/Solution Interface in Systems Containing Binary Mixtures of Adsorbents: An Investigation of the Concept of Adsorptive Additivity, Stanford University, 1984.
- (7) Zachara, J. M.; Girvin, D. C.; Schmidt, R. L.; Resch, C. T. Chromate Adsorption on Amorphous Iron Oxyhydroxide in the Presence of Major Groundwater Ions. *Environ. Sci. Technol.* **1987**, *21* (6), 589–594. <https://doi.org/10.1021/es00160a010>.
- (8) Griffin, R. A.; Au, A. K.; Frost, R. R. Effect of PH on Adsorption of Chromium from Landfill-Leachate by Clay Minerals. *J. Environ. Sci. Heal. Part A Environ. Sci. Eng.* **1977**, *12* (8).
- (9) Zachara, J. M.; Cowan, C. E.; Schmidt, R. L.; Ainsworth, C. C. Chromate Adsorption by Kaolinite. *Clay Clay Miner.* **1988**, *36* (4), 317–326.
- (10) Zachara, J. M. Adsorption of Chromate by Subsurface Soil Horizons. *Soil Sci. Soc. Am. J.* **1989**, *53* (2), 418–428.
- (11) US-EPA. *Method 7196A, Chromium, Hexavalent (Colorimetric)*; 1992.
- (12) Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1984.
- (13) Sposito, G. *The Chemistry of Soils*; Oxford University Press: New York, 1989.
- (14) Cornell, R.; Schwertmann, U. *The Iron Oxides*; VCH Publ, Weinheim, 1996.