

Impact of Cr(VI) as a Co-Contaminant on the Adsorption and Desorption of U(VI) in Hanford Sediments Under Mildly Alkaline Oxidic Conditions

MARIAH DOUGHMAN¹, YELENA KATSENOVICH²,
RAVI GUDAVALLI², KEVIN O'SHEA², HILARY
EMERSON¹, JAMES E SZECSDY¹, KENNETH C
CARROLL³, XIAOLIANG HE¹ AND NIKOLLA QAFOKU⁴

¹Pacific Northwest National Laboratory

²Florida International University

³New Mexico State University

⁴University of Washington

Presenting Author: mariah.doughman@pnnl.gov

Monitored natural attenuation is a common approach for remediation of contaminants in the subsurface. However, when contaminants are commingled, their transport may be challenging to predict due to competitive reactions. Hence, the objective here is to understand the fate of hexavalent uranium [U(VI)] in the presence of hexavalent chromium [Cr(VI)] in conditions similar to those at Hanford, a Department of Energy legacy nuclear site in Washington State.

Column and batch experiments, along with thermodynamic equilibrium speciation modeling, were conducted to investigate the impact of Cr(VI) on U(VI) attenuation mechanisms in carbonate-rich sediments. Experiments tested slightly alkaline conditions (pH~8) in the presence of major groundwater components with different U(VI):Cr(VI) molar ratios. An order of magnitude excess of adsorption sites is expected in Hanford sediments, even at the highest contaminant concentrations, based on previous estimates of adsorption site density (~3.8 $\mu\text{mol}/\text{m}^2$). Speciation modeling predicted relatively weakly adsorbing, aqueous calcium uranyl carbonates (neutral/negatively charged) and chromate.

For the lower molar ratios of U(VI):Cr(VI), no difference was observed between adsorption distribution coefficients, K_{ds} , calculated from the batch experiments. For the higher molar ratios of U(VI):Cr(VI), batch experiment U(VI) K_{ds} were 0.8 ± 0.2 L/kg in the absence of Cr(VI) and 1.4 ± 0.3 L/kg at a 1:10 U:Cr μM ratio. Results of the column experiments agreed well with those of the batch experiments. Larger U(VI) K_{ds} in the presence of Cr(VI) were observed in both batch and column experiments. This could be due to the increase in the ionic strength and/or a potential change in the U(VI) aqueous speciation which likely favored the formation of charged species that could adsorb strongly. However, this claim is still under investigation. Initial modeling simulations of batch and column experiments data confirmed that rate-limited and non-linear U(VI) adsorption to Hanford Site sediments have occurred. Understanding the transport mechanisms of U(VI) under the conditions observed in the subsurface is critical in the

development of effective passive remediation strategies for complex contaminated sites with U(VI) and other co-contaminants. Furthermore, once the natural attenuation of a contaminant is understood, a variety of remediation strategies including the possibility of monitored natural attenuation may be evaluated.