

FATE AND TRANSPORT OF Cr(VI) IN HANFORD SEDIMENTS TREATED WITH Al-RICH, HYPERALKALINE AND HYPERSALINE SOLUTIONS. N.P. Qafoku^{1,2}, C.C. Ainsworth¹, and J.E. Szecsody¹.¹Pacific Northwest National Laboratory, MSIN:K3-61, 902 Battelle Boulevard, P.O. Box 999, Richland, WA 99352.²Associated Western Universities, 723 The Parkway, Richland, WA 99352. Email: nik.qafoku@pnl.gov.

Introduction: Although chromate is highly mobile in the subsurface, recent observations of Cr transport from alkaline tanks suggest some retardation, but the mechanism is unknown. The leachates from the single shell tanks at Hanford site that have leaked in the underlying vadose zone were very alkaline, and contained large concentrations of NaNO₃, Al(OH)₄ and substantial quantities of hexavalent chromium, Cr(VI). Reaction of the tank fluids with the soil matrix causes dissolution of Fe(II)-bearing soil minerals, like biotite and chlorite, that may release Fe(II) into the soil solution. The inorganic reductant Fe(II) may promote the reduction of Cr(VI), and less soluble, less mobile Cr(III) species may be formed. In addition, the soil solution may become over-saturated with respect to different secondary solid phases that may precipitate under alkaline and relatively high temperature conditions. Because Cr(III) tends to occur in octahedral coordination with oxygen, it may therefore co-precipitate with Fe(III). The objective of this investigation was to study the mechanism that control the fate of Cr(VI) in the Hanford sediments treated with Al-rich, hyperalkaline and hypersaline solutions similar to the tank leachates.

Materials and Methods: Batch and column studies were conducted to simulate individual and coupled reactions of Cr(VI) transport through sediments. Metal-free systems were used to conduct 1-D column studies. The first column was initially leached with a 10 mg L⁻¹ Cr(VI) (Na₂CrO₄*4H₂O) solution to estimate Cr(VI) sorption in untreated sediments. When the full Cr(VI) breakthrough curve was completed the leaching solution was switched to the 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃*9H₂O, and 10 mg L⁻¹ Cr(VI) solution. When chemical steady-state was established, the flow interruption method was used to see if the chemical equilibrium was reached in the column. The second column was leached with the 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃*9H₂O, and 10 mg L⁻¹ Cr(VI) solution from the beginning. Different Al (0, 0.055 and 0.165 M) and NaOH (1 and 4 M) concentrations were used in other columns to estimate the effects of Al and NaOH on Cr(IV) fate and transport. The Cr(VI) input concentration was varied (10, 100 and 500 mg L⁻¹), and different residence times were applied as well. The columns were kept inside a water-bath at 50 °C. Batch experiments were conducted under similar conditions. All operations were performed under CO₂ and O₂ free conditions. At the end of experiments Al, Si, K, Mg, Ca, Ba, Mn and Fe contents

were determined in supernatants and solid sediments using ICP and EDXRF, respectively.

Results and Discussion: Experiments demonstrated that Cr(VI) transport through sediments: a) is nearly not retarded with neutral solutions, b) undergoes retardation with alkaline solutions as a result of Fe(II) production by mineral dissolution. The results from the first column showed that the concentration of Cr(VI) reached the level of the input solution in 1-2 pore volumes. However, when the leaching solution was switched to the 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃*9H₂O, and 10 mg L⁻¹ Cr(VI) solution, the Cr(VI) concentration decreased steadily and reached the steady-state concentration after approximately 25 pore volumes, which was approximately 35% less than the Cr(VI) concentration in the input leaching solution (10 mg L⁻¹). The mobility of Cr(VI) was retarded the same in the second column which was leached from the beginning with a 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃*9H₂O, and 10 mg L⁻¹ Cr(VI) solution. The Fe concentration in the leachate increased to a maximum of 3 mg L⁻¹ after 5 pore volumes, and decreased towards the steady-state concentration of ~1.3 mg L⁻¹ afterwards. The flow interruption clearly indicated rate-limited reactions; the Cr concentration decreased upon the stop flow. However, The Fe concentration nearly doubled in the first portion of leachate. The distribution of Cr in the sediments packed in the first column showed elevated Cr levels near the column outlet. The EDXRF analysis confirmed that the total amount of Cr varied from 45 in the untreated sediment, to 50 and 68 µg g⁻¹ in the 1-3 cm layer near the column inlet and outlet, respectively. The QXRD results showed a significant decrease in the biotite content (approximately 4%) and an increase in the hematite content in the sediments.

Since the amount of Cr(VI) and Cr(III) adsorbed on the surfaces of existing and newly formed secondary phases is likely to be small (pH≅14), it is possible however that the Fe(II) released upon mineral dissolution would have reduced Cr(VI) to Cr(III), which would have precipitated or co-precipitated under alkaline and relatively high temperature conditions (50 °C). Spectroscopic analyses that are to be performed will provide useful insights as to what mechanism affects Cr(VI) fate and transport. In this presentation, the results from other column and batch experiments with different Al, NaOH and Cr solutions, as well as the effect of the residence time on the fate and transport of Cr(VI) in the Hanford sediments will be also discussed.