

DE-FG02-07ER64405 Final Report
Chromium isotopes and indicators of hexavalent chromium reduction

The broad goal of this project was to advance development of a new technology for identifying and quantifying natural or artificial attenuation of hexavalent chromium contamination in groundwater systems. The new method uses stable isotope ratio measurements ($^{53}\text{Cr}/^{52}\text{Cr}$) made using multicollector ICP-mass spectrometry. The main objectives of this project were completed during the project period, including a one-year no-cost extension related to a delay in recruiting a highly qualified grad student.

In the Idaho National Laboratory (INL) component of the project, M.S. student Amanda Raddatz measured Cr stable isotope ratios of Cr(VI) in over 60 groundwater samples from the Snake River Plain aquifer. The data strongly suggest the existence of weak to moderate natural attenuation of Cr(VI) via reduction along flow paths just below the water table, and an absence of reduction along deeper flow paths. We estimate that less than half of the contaminant has been lost to Cr(VI) reduction over the past few decades, but it appears that natural reduction does occur despite the presence of dissolved oxygen in the aquifer. This is an important result, going against the conventional wisdom. These findings were presented in the highly regarded journal *Environmental Science and Technology*.

In the second part of the project, laboratory experiments have determined $^{53}\text{Cr}/^{52}\text{Cr}$ fractionation factors (i.e., site-specific calibration factors to relate extent of reduction to $^{53}\text{Cr}/^{52}\text{Cr}$ values) for various reactions relevant to the permeable reactive "ISRM" barrier in the Hanford 100-D area. A series of experiments with pure solid phases found in the barrier, and natural material retrieved from the barrier, yielded isotopic fractionation values (epsilons) ranging from -2.1 to -3.9 per mil. These results provide much-needed calibration of Cr isotope fractionation in reactive barriers and will enable interpretation of Cr isotope data being collected to improve understanding of processes within the barriers. These findings are reported in a paper recently accepted by *Environmental Science and Technology*.

The two lesser objectives of the project are also complete. Although the Los Alamos National Lab (LANL) component of the project was funded almost entirely by LANL, the present project allowed for better interpretation of the data. As in the INL study, it appears Cr(VI) has been partially removed from the water via Cr(VI) reduction in certain zones where water flows through basaltic rock. A journal article is being written by LANL collaborator Jeff Heikoop. Data were collected for the Hanford 100-K area calcium polysulfide (CPS) pilot treatment test. Breakthrough of Cr(VI) through the pilot scale redox barrier has been slow and the data set is not yet rich enough to allow important interpretations. We plan to informally continue this project as long as sampling continues.