

Characterization of ternary surface complexes of lead chloride on hematite in dependence of temperature and salinity – experimental versus modeled data

DEJENE LEGESSE DRIBA¹, SIMONA REGENSPURG¹, MARCO DE LUCIA² AND STEFAN PEIFFER²

¹GFZ German Research Centre for Geosciences, International Centre for Geothermal Research, Potsdam, Germany, dejene@gfz-potsdam.de,

regens@gfz-potsdam.de

²GFZ German Research Centre for Geosciences, Section 5.3, Hydrogeology, Potsdam, Germany

marco.delucia@gfz-potsdam.de

²Department of Hydrology, University of Bayreuth, Bayreuth, Germany S.Peiffer@uni-bayreuth.de

Adsorption of aqueous metal cations onto mineral surfaces can affect metal speciation and mobility in a range of geologic systems. In order to accurately model metal speciation and transport on iron-oxides, the effect of pH, temperature and ionic strength on its adsorption property and stability constants must be determined. The surface complex modeling approach CD-MUSIC (chargedistribution multi-site complexation) requires the definition of many parameters including equilibrium constants for protonation and deprotonation, metal sorption and back ground electrolyte sorption reactions etc. However, the lack of many of those parameter particularly for Pb adsorption onto hematite surface requires the implementation of experimentally determined data. In this study, Pb+2 adsorption experiments were performed in hematite bearing NaCl solutions as a function of pH value (3-9), ionic strength (0.5M and 5M) and temperature (25-150 °C). The required surface complex parameters (SCP) were derived through an iterative procedure of fitting the experimental data-set with simulation results by implementing the geochemical speciation code PhreeqC coupled with the non-linear optimization program UCODE_2005. Model results reveal that the simulation represents well the experimental conditions and reflects the dependency of Pb adsorption on different experimental parameters. In addition, it was found that lead-chloride ternary complex adsorption configuration provides a good fit to all Pb+2 adsorption data. Accordingly, the derived SCP data set will furnish for the development of a thermodynamically consistent surface complex database to estimate lead sorption in a geological environment of high temperatures and salinities.

The influence of flow field heterogeneity on the observed $\delta^{53}\text{Cr}$ fractionation factor during abiotic chromate reduction

J.L. DRUHAN^{1*}, K. MAHER¹, K.L. WEAVER¹ AND C.N. MCCLAIN¹

¹Department of Geological and Environmental Sciences, Stanford University, Stanford, CA, 94305

(*correspondence: jdruhan@stanford.edu)

Hydrogeochemical processes governing groundwater quantity and quality are often inferred from fluid samples that are the flux-weighted average of a heterogeneous system. The stable isotope ratios of these samples are commonly interpreted through simplified fractionation relationships that inherently assume a homogeneous chemical composition and fluid residence time. Here, we present application of an isotope-specific rate expression for chromate reduction in the CrunchFlow reactive transport code to simulate the steady state distribution of $\delta^{53}\text{Cr}$ across multiple realizations of a spatially correlated heterogeneous flow field (Figure). Our results demonstrate that a flux-weighted average value collected across the mean flow gradient yields a variable observed fractionation factor despite a fixed ratio of kinetic rate constants for the isotopologues of chromate. This variability is thus directly attributable to the physical heterogeneity of the porous media. We demonstrate that for a specified correlation function and characteristic length scale of the permeability structure, the observed fractionation factor is predictably linked to the fluid residence time distribution. These simulations serve as the basis for a series of flow-through column experiments using simplified heterogeneity to demonstrate variability in observed fractionation factors.

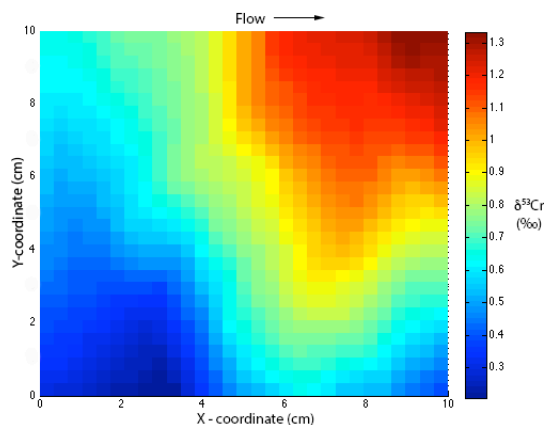


Figure: steady state $\delta^{53}\text{Cr}$ across a heterogeneous flow field