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Silicon control of strontium and cesium partitioning in hydroxide-weathered sediments

Jon Chorover [a,*], Sunkyung Choi [b], Paula Rotenberg [c], R. Jeff Serne [d], Nelson Rivera [b], Caleb Strepka [e], Aaron Thompson [a], Karl T. Mueller [e], Peggy A. O'Day [b]

[a] *Department of Soil, Water and Environmental Science, University of Arizona, Tucson, AZ, USA*
[b] *School of Natural Sciences, University of California, Merced, CA, USA*
[c] *Tetra Tech Rizzo, One Grant Street, Framingham, MA, USA*
[d] *Applied Geology and Geochemistry, Pacific Northwest National Laboratory, Richland, WA, USA*
[e] *Department of Chemistry, Pennsylvania State University, University Park, PA, USA*

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Abstract

Cation partitioning and speciation in an aqueous soil suspension may depend on the coupling of reaction time, sorbate amount and mineral weathering reactions. These factors were varied in sediment suspension experiments to identify geochemical processes that affect migration of Sr^{2+} and Cs^{+} introduced to the subsurface by caustic high level radioactive waste (HLRW). Three glacio-fluvial and lacustrine sediments from the Hanford Site (WA, USA) were subjected to hyperalkaline ($pH > 13$), Na–Al–NO_3–OH solution conditions within a gradient field of (i) sorptive concentration (10^{-5}–10^{-3} m) and (ii) reaction time (0–365 d). Strontium uptake (q_{Sr}) exceeded that of cesium at nearly all reaction times. Sorbent affinity for both Cs^{+} and Sr^{2+} increased with clay plus silt content at early times, but a prolonged slow uptake process was observed over the course of sediment weathering that erased the texture effect for Sr^{2+}; all sediments showed similar mass normalized uptake after several months of reaction time. Strontium became progressively recalcitrant to desorption after 92 d, with accumulation and aging of neoformed aluminosilicates. Formation of Cs^{+} and Sr^{2+}-containing cancrinite and sodalite was observed after 183 d by SEM and synchrotron μ-XRF and μ-XRD. EXAFS data for $q_{Sr} \approx 40$ mmol kg^{-1} showed incorporation of Sr^{2+} into both feldspathoid and $SrCO_3$(s) coordination environments after one year. Adsorption was predominant at early times and low sorbate amount, whereas precipitation, controlled largely by sediment Si release, became increasingly important at longer times and higher sorbate amount. Kinetics of contaminant desorption at pH 8 from one year-weathered sediments showed significant dependence on background cation (Ca^{2+} versus K^{+}) composition. Results of this study indicate that co-precipitation and ion exchange in neoformed aluminosilicates may be an important mechanism controlling Sr^{2+} and Cs^{+} mobility in siliceous sediments impacted by hyperalkaline HLRW.

1. INTRODUCTION

Sorption of metal ions at the soil particle-aqueous solution interface is characterized by a continuum from surface complexation to precipitation. Whereas adsorption tends to predominate at short times and low sorbate concentrations, longer contact times and higher concentrations may favor the formation of surface precipitates (Chorover and Brusseau, 2008). When such precipitates form as a result of interactions between exogenous metals and soluble products of sediment weathering (e.g., Al, Fe or Si), incongruent dissolution of native minerals may control the mechanism of metal uptake to the solid phase (Scheidegger et al., 1996; Chorover et al., 2003; Voegelin et al., 2005). In addition, increased sorbate-sorbent contact time may produce sorbate species that exhibit slower release kinetics because

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[*] Corresponding author. Fax: +1 520 621 1647.
E-mail address: Chorover@cals.arizona.edu (J. Chorover).

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of recrystallization or ripening processes (Ainsworth et al., 1994; Scheckel et al., 2000). Hence, prolonged contact of metal or radionuclide contaminants with actively weathering sorbents can result in a time evolution contaminant speciation and mobility.

The release of caustic high level radioactive waste (HLRW) into soils and sediments represents a scenario where mineral weathering reactions may impact the trajectory of contaminant sorption processes. Mineral transformation thus can influence strongly the environmental geochemistry of radionuclides (Ildefonse et al., 1990; Riley and Zachara, 1992; Brady and Kozak, 1995). Approximately 100 million gallons of HLRW were generated in the US during the Cold War as a result of the reprocessing of irradiated uranium fuel and plutonium extraction for nuclear weapons production. This HLRW has been stored in massive underground tanks at U.S. Department of Energy (DOE) facilities including the Hanford Site in Washington, the Idaho National Engineering Laboratory and the Savannah River Site in South Carolina, where it also has been introduced by accidental release into the subsurface environment. Similar sites comprising underground storage of HLRW exist worldwide and many have documented accidental release of radionuclide-containing fluids. At the Hanford Site, 67 of 177 underground tanks are suspected to have leaked over 3800 m^3 of HLRW into the vadose and saturated zones (DOE, 1995; Ahearne, 1997). Most of the tank-waste leachate is characterized by high ionic strength ($Na–NO_3$, $–NO_2$), high pH and $Al(OH)_4^-$ concentration, and concentrations of radionuclides (^{99}Tc, ^{137}Cs, ^{90}Sr, ^{129}I, ^{238}U) that vary with location. The bulk of the radioactivity released was ^{137}Cs and ^{90}Sr, amounting to more 1 million curies, with mass concentrations up to milligrams per kilogram of solution (Behrens et al., 1998; Serne et al., 2002b). These radionuclides are dissolved in hyperalkaline solutions that react with underlying sediments to create an extreme subsurface geochemical environment that is also one of the most contaminated in the world (NRC, 2006; Zachara et al., 2007). Adsorption of cationic contaminants is expected to be mediated by high surface area constituents in the sediments, particularly phyllosilicate minerals (clays and mica) (Sposito et al., 1999).

From the perspective of ionic potential and geochemical reactivity, Cs^+ and Sr^{2+} are analogues of K^+ and Ca^{2+}, respectively. Like K^+, Cs^+ has low hydration energy. This facilitates its inner-sphere coordination at charged siloxane sites on layer silicate surfaces and results in a particularly high affinity for frayed edge sites of micaceous minerals (Cornell, 1993; Kim et al., 1996; Sutton and Sposito, 2001; Bostick et al., 2002; Steefel et al., 2003). Similar in ionic potential to Ca^{2+}, the Sr^{2+} cation has higher hydration energy than Cs^+ and it typically forms outer-sphere surface complexes at negatively charged sites on clay minerals and oxides (Jeong et al., 1996; Sahai et al., 2000). Strontium mobility is also influenced by co-precipitation in $CaCO_3(s)$ or discrete $SrCO_3(s)$ precipitates (Parkman et al., 1998; Sahai et al., 2000; McKinley et al., 2007).

The extreme weathering environment associated with HLRW introduces additional factors that may affect Cs^+ and Sr^{2+} mobility. Several experimental studies have shown that reaction of Al-bearing caustic waste simulants with silicate minerals results in Si dissolution and subsequent co-precipitation with waste-derived Al to form feldspathoid solids, including cancrinite and sodalite, with near unit Si/Al molar ratio (Bickmore et al., 2001; Chorover et al., 2003; Qafoku et al., 2003b; Choi et al., 2005b; Mashal et al., 2005a). Feldspathoid formation is also observed when aqueous Si is present as a reactant in caustic aluminate solutions (Zheng et al., 1997; Deng et al., 2006). A principal finding of the prior research on weathering of Hanford sediments under HLRW conditions is that the identity and character of reaction products are dependent on the chemical composition of waste solution simulants and also on the time scale of reaction (Qafoku et al., 2003a,b; Mashal et al., 2004; Ainsworth et al., 2005; Mashal et al., 2005a). These weathering processes likely alter the geochemical mobility of Cs^+ and Sr^{2+}, since both ions can be incorporated into exchange sites in zeolites or feldspathoids (Perona et al., 1995; Mon et al., 2005). Silicates depleted during hyperalkaline reaction with Hanford sediments include the layer silicates biotite, smectite and kaolinite (Qafoku et al., 2003b; Ainsworth et al., 2005; Mashal et al., 2005a), which are also potential sorbents for Cs^+ and Sr^{2+}. Whereas new sorbent phases are known to form at the expense of native minerals, the net effect of mineral transformation on contaminant fate is unknown.

We hypothesized that under these conditions, the fate of Cs^+ and Sr^{2+} includes adsorption to mineral surfaces in the native sediments as well as incorporation into neoformed precipitates. We postulated that sorptive fate depends on (i) the identity of the contaminant (Cs^+ versus Sr^{2+}), since this influences its reactivity toward native and neoformed solids, and (ii) progress along the weathering reaction path. The objectives of the study, therefore, were (i) to examine the uptake and lability of Cs^+ and Sr^{2+} in STWL-impacted Hanford sediments as a function of reaction time and mineral transformation, (ii) to assess the microscale distribution and speciation of these contaminants in the reacted media (including dissolved, colloidal and sediment bound forms) and (iii) to measure the kinetics of contaminant desorption from weathered sediments in circumneutral background pore water simulants. We employed a multifaceted approach that combined measurements of reaction rate and extent with micro- and molecular-scale investigations of mineral transformation and contaminant speciation. The complement of methods helped to elucidate a transition from adsorption to co-precipitation of the cationic contaminants that occurs as the sediments traverse a two-dimensional field of sorbate amount and reaction time.

2. MATERIALS AND METHODS

2.1. Sample collection

Sediments similar in character to those beneath the leaking underground tanks at the DOE Hanford Site were collected from uncontaminated areas within the Hanford Formation (glacio-fluvial sediments) and Upper Ringold Formation (fluvial–lacustrine deposits). Hanford Coarse (HC) sediments, consisting of medium- to coarse-grained