



Trace contaminant concentration affects mineral transformation and pollutant fate in hydroxide-weathered Hanford sediments

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ARTICLE INFO

Article history:

Received 18 April 2011

Received in revised form 18 August 2011

Accepted 16 September 2011

Available online 22 September 2011

Keywords:

Zeolite
Feldspathoids
Strätlingite
Cesium
Strontium

ABSTRACT

Prior work has shown that when siliceous sediments are infused with caustic radioactive waste, contaminant fate is tightly coupled to ensuing mineral weathering reactions. However, the effects of local aqueous geochemical conditions on these reactions are poorly studied. Thus, we varied contaminant concentration and $p\text{CO}_2$ during the weathering of previously uncontaminated Hanford sediments over 6 months and 1 year in a solution of caustic waste (pH 13, high ionic strength). Co-contaminants Sr, Cs and I were added at “low” (Cs/Sr: 10^{-5} m; I: 10^{-7} m) and “high” (Cs/Sr: 10^{-3} m; I: 10^{-5} m) concentrations, and headspace was held at atmospheric or undetectable (<10 ppmv) CO_2 partial pressure. Solid phase characterization revealed the formation of the zeolite chabazite in “high” samples, whereas feldspathoids, sodalite and cancrinite, were formed preferentially in “low” samples. Sr, Cs and I were sequestered in all reacted sediments. Native calcite dissolution in the CO_2 -free treatment drove the formation of strätlingite ($\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$) and diminished availability of Si and Al for feldspathoid formation. Results indicate that $p\text{CO}_2$ and contaminant concentrations strongly affect contaminant speciation in waste-weathered sediments, and are therefore likely to impact reaction product stability under any remediation scenario.

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1. Introduction

During the Cold War, the U.S. Department of Energy Hanford Site (WA) was the primary locale for plutonium extraction. For 40 years, large volumes of high-level radioactive waste (HLRW) were generated and stored in 177 buried single- and double-shell underground tanks [1,2]. Different chemical extraction and separation processes produced twenty-six chemically dissimilar waste streams that resulted in mixed tank wastes with elevated values of pH (8 to 14), ionic strength (2–16 M NaNO_3), temperature (60–110 °C), and dissolved aluminum [3–6]. Sixty-eight out of 149 single-shell tanks are suspected to have leaked, releasing millions of liters of HLRW waste to the vadose zone. According to Zachara et al. [7], vadose zone sediments are contaminated with various radionuclides, with ^{90}Sr , ^{137}Cs and ^{129}I among the most abundant (10^{-4} to 10^{-1} Ci L^{-1} for Sr, 5×10^{-2} to 8×10^{-1} Ci L^{-1} for Cs and 1 to 5×10^{-12} Ci L^{-1} for I [8]). Transport of contaminants from tank leaks to the Columbia River poses an important health risk to humans [9], emphasizing the need to characterize mechanisms of contaminant retardation in the vadose zone. To predict waste

plume migration and understand possible mechanisms of radionuclide sequestration at the Hanford Site, the impact of caustic waste leachate on surrounding sediments and transport processes must be elucidated.

Previous laboratory experiments on monomineralic systems showed that synthetic tank waste leachate (STWL) solutions dissolve primary tectosilicates [10–12], and clay minerals [13–15], resulting in silicon release. Silicon release into hyperalkaline, Al-rich STWL solution results in aqueous phase supersaturation with respect to highly reactive feldspathoid and zeolite minerals that precipitate from solution [10,11,14,16–20]. Reaction of multi-component Hanford sediments with STWL likewise revealed primary mineral dissolution and precipitation of feldspathoids NO_3 -cancrinite and NO_3 -sodalite [19–21], and zeolite A [19].

Kinetic studies showed a time dependency of primary phase dissolution, neophase formation, and contaminant sorption. Qafoku et al. [21] suggested that NO_3 -sodalite forms early, transforming to NO_3 -cancrinite by dissolution–reprecipitation. Both neophases are capable of co-precipitating significant amounts of cationic Cs and Sr into framework and cage sites [10,11,14,16,17], whereas uptake of iodide by such cation exchangers is likely limited. When STWL solutions are spiked with Si in the presence of cations (Cs, K, Sr, Ca, Mg, Al, Na), both sodalite and cancrinite precipitate and a ~1:1 Si:Al molar ratio zeolite forms at either high Cs concentration (500 mM)

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[22] or short reaction time [23]. Furthermore, the presence of K^+ and divalent cations (Mg, Ca, Sr) slows the precipitation of cancrinite and sodalite in STWL solutions [22].

Prior studies of contaminant uptake by Hanford sediment, showed that Cs^+ sorbs selectively on frayed-edges and inter-lamellae of native micaceous minerals (illite, biotite, muscovite, and vermiculite) [5,6,24,25]. Conversely, a large fraction of Sr^{2+} sorbed to labile ion exchange sites (Mg^{2+} exchangeable) early in the sediment-STWL reaction sequence becomes increasingly recalcitrant to Mg^{2+} exchange over months to years of reaction time, and EXAFS data indicate Sr incorporation into zeolite and feldspathoid neophases [11]. Uncontaminated Hanford sediments were previously reacted for 6 months with STWL containing low concentration of Cs and Sr (10^{-5} M) and I (10^{-7} M), and contaminant release was investigated in column experiments designed to model the removal of the caustic source wherein a synthetic background pore water was infiltrated through STWL-reacted sediments [25]. Transport simulation showed that Cs release depends on ion exchange even at long desorption times, whereas Sr release was consistent with dissolution from feldspathoid at steady-state. Additionally, contaminant desorption from sediments reacted in CO_2 -free environments was higher than desorption from sediments reacted at atmospheric pCO_2 [25]. Iodide behavior is controlled by ion exchange on protonated mineral surface hydroxyl groups [26,27], leading to high mobility and limited retention in the sediments, particularly at high pH. No desorption study has been carried out on iodide in STWL-reacted in Hanford sediments.

In monomineralic systems, initial Cs and Sr concentrations strongly affect the rate of tetrahedral Al (Al^{IV}) solid phase formation, with more rapid precipitation at lower Cs/Sr concentration. Our prior studies [13,14,16] indicated that despite high (2 M) background Na^+ concentration in STWL, the rate of incongruent weathering of specimen clay minerals exhibited negative dependence on trace contaminant concentration (10^{-5} to 10^{-3} M). Also, at high contaminant concentration, Cs and Sr partitions into less crystalline solids that dissolve readily upon a shift to fresh water leaching [13,14,16], whereas at lower concentrations, they are bound into more dissolution-recalcitrant species [17]. In so far as they affect mineral transformation rates, Sr and Cs concentrations may therefore control the rate of their own sequestration into recalcitrant solid-phase weathering products. In specimen mineral systems, (i) the concentrations of contaminants [14] and (ii) the presence of free cations [22] combine with reactant mineralogy [11,13,16] to control the couplings between mineral weathering and contaminant fate. We postulate similar processes affect contaminant uptake in complex Hanford sediments.

Although present at trace concentration relative to background Na^+ , the prevalence of Sr^{2+} and Cs^+ nonetheless affects mineral transformation rates measured in specimen clay systems. The extent to which the same effect occurs in complex natural sediments thus remains unclear [11] and warrants high-resolution geochemical research. In the current study, we tested this effect using detailed synchrotron-based X-ray diffraction and spectroscopy to characterize Hanford sediment weathering induced by STWL reaction. Two contaminant concentrations and two different pCO_2 levels (presence and absence of atmospheric CO_2) were used to span the ranges of those parameters expected in the field. Variations in pCO_2 should affect the stability of carbonate species. Since prior work indicates that contaminant release is controlled by mineral dissolution [25], a precise characterization and quantification of reaction products is needed to predict the fate of STWL-weathering products upon re-introduction of native pore-water solutions. This study aims to facilitate predictive modeling of contaminant fate at Hanford by providing an improved understanding of waste-sediment reactions.

2. Material and methods

2.1. Sample collection

Sediments similar in character to those beneath the leaking tanks at the DOE Hanford Site were collected from the 218-E-12B Burial Ground excavation site [28], an uncontaminated area within the Hanford Formation. Sediments were air dried, sieved to obtain the <2 mm fraction, and used without further modification. This material is referred to as Hanford sediment (HS) in the following text.

2.2. Reaction procedure

We modified and upscaled the experimental conditions used by Chorover and co-workers [11,13,16,17] to simulate the contamination of pristine HS with Sr, Cs and I present in hyperalkaline solutions (see S-1 of the supplementary material for details). Briefly, 400 g of air-dry sediment were reacted with 20 kg of STWL. CsCl, $SrCl_2 \cdot 6H_2O$ and NaI were added to the STWL stock solution as “co-contaminants” to give treatments with two initial aqueous-phase concentrations termed “HIGH” (10^{-3} M Cs^+ and Sr^{2+} and 10^{-5} M I⁻) and “LOW” (10^{-5} M Cs^+ and Sr^{2+} and 10^{-7} M I⁻).

Sediments were reacted with STWL in carboys for 6 or 12 mo (182 or 365 d) in a 2×2 experimental matrix of four different aqueous geochemical conditions: STWL with LOW and HIGH contaminant concentrations reacted in atmospheric pCO_2 ($+CO_2$) and CO_2 -free ($-CO_2$) environments. This yielded eight sets of reaction products.

2.3. Solid phase characterization

Total element concentrations were measured by ICP-MS following Li-metaborate fusion [29] and INAA for iodine. For particle size analysis, water-suspended samples, sonicated for 10 s were analyzed with a Beckman Coulter LS 13 320 Laser Diffraction Particle Size Analyzer (Fullerton, CA). Cation exchange capacities (CEC) were determined by exchanging cations with cobalt-hexaminechloride (Cohex- $[Co(NH_3)_6]Cl_3$) [30]. In this case, 2 g of sediment were mixed with 25 mL of 12 mmol L⁻¹ Cohex and shaken for 2 h (corresponding to maximum exchange). CEC values were calculated from the loss of Co from solution (ICP-MS, PerkinElmer Elan DRC). External specific surface areas were determined using dinitrogen BET (Beckman Coulter SA-3100).

Diffuse reflectance Fourier transform infrared (DRIFT) spectra of the sediment samples were obtained on a Nicolet Magna 560 FTIR spectrometer (Thermo Sci., Waltham, MA) by averaging 400 scans per sample across the frequency range of 4000–400 cm⁻¹ (optical resolution of 4 cm⁻¹). Sample preparation consisted of grinding 9 mg of freeze-dried sediment with 441 mg of ground analytical spectroscopy-grade KBr crystals. X-ray diffractograms, acquired on the bulk and isolated fine fraction (FF) of all samples (see S-2 of the supplementary material), were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam line 11-3 operating at ~12735 eV in transmission mode, using a 345 mm radius Mar detector with 100 μ m pixels. Approximately 0.05 g of sample was packed between two layers of Scotch Magic tape to obtain a homogeneous thin layer sample. After calibration of the detector using finely ground LaB_6 crystals, five scans were combined per sample. Data were reduced using the Advanced Diffraction Machine software [31] with a mask covering the beamstop. Patterns were added, reduced, corrected from residual quartz saturation and systematic displacement and converted to those associated with $Cu-K\alpha$ radiation wavelength. Quantitative phase analysis was performed using the Rietveld module included in the X'Pert HighScore Plus software, details of the procedure for analysis are given in Section S-3

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