Mineral dissolution and secondary precipitation on quartz sand in simulated Hanford tank solutions affecting subsurface porosity

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ABSTRACT

Highly alkaline nuclear waste solutions have been released from underground nuclear waste storage tanks and pipelines into the vadose zone at the US Department of Energy's Hanford Site in Washington, causing mineral dissolution and re-precipitation upon contact with subsurface sediments. High pH caustic $NaNO_3$ solutions with and without dissolved Al were reacted with quartz sand through flow-through columns stepwise at 45, 51, and 89 °C to simulate possible reactions between leaked nuclear waste solution and primary subsurface mineral. Upon reaction, Si was released from the dissolution of quartz sand, and nitrate-cancrinite [$Na_8Si_6Al_6O_{24}(NO_3)_2$] precipitated on the quartz surface as a secondary mineral phase. Both steady-state dissolution and precipitation kinetics were quantified, and quartz dissolution apparent activation energy was determined. Mineral alteration through dissolution and precipitation processes results in pore volume and structure changes in the subsurface porous media. In this study, the column porosity increased up to 40.3% in the pure dissolution column when no dissolved Al was present in the leachate, whereas up to a 26.5% porosity decrease was found in columns where both dissolution and precipitation were observed because of the presence of Al in the input solution. The porosity change was also confirmed by calculation using the dissolution and precipitation rates and mineral volume changes.

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1. Introduction

Hundred million liter volumes of liquid radioactive wastes, generated from processing activated nuclear fuels for separation of plutonium (1943–1989), have been stored in massive underground tanks at the Hanford Site in Washington State. The waste chemical composition is generally characterized as hyperalkaline (pH of 9–14) and high-ionic strength (I = 2–14 M) solutions with high concentrations of dissolved Al (0.7–2 M). These wastes contained high concentrations of ^{137}Cs and ^{90}Sr and other radionuclides. The waste solutions in the tanks exhibited high temperatures (up to >100 °C) caused by self-boiling due to chemical reaction and radionuclide decay for several decades (Serne et al., 1998; Zachara et al., 2007). The temperature in the nearest sediment was estimated to be as high as 120 °C, and in the sediments 20 m below the tanks it could be still as high as 70 °C (Pruess et al., 2002) or 50 °C at 40 m below the tanks (Liu et al., 2003). Approximately 67 single-shell tanks or the ancillary pipelines of the total 177 waste tanks have released fluids to the subsurface. These releases, about 1.9–3.8

million liters of high-level nuclear waste fluids, have migrated into the underlying sediments (Zachara et al., 2007). The Pleistocene-age Hanford Formation (coarse-grained glacio-fluvial gravels and sands) and Pliocene-age Ringold Formation (fluvial-lacustrine gravel/sand/silt) are the primary geological units in the unconsolidated sediments of Hanford's vadose zone. The primary minerals in these sediments are silicate minerals, including quartz, feldspar, mica (biotite and muscovite), and smectite, as well as basaltic rock fragments (Zachara et al., 2007).

Contact of the released hyperalkaline tank fluid with the underlying sediments has caused geochemical changes, resulting in primary mineral dissolution and precipitation of secondary minerals (Bickmore et al., 2001; Chorover et al., 2003, 2008; Qafoku et al., 2003; Mashal et al., 2004; Zhao et al., 2004; Deng et al., 2006a,b; Rod et al., 2010; Chang et al., 2011). The caustic tank leachate dissolves silicate minerals and the released Si can react with Al, Na, and anions such as NO_3^-, CO_3^{2-}, or OH^- from tank wastes to form secondary mineral precipitates. Several laboratory studies have focused primarily on mineral transformations, and observed the specific pathways of mineral alteration under different geochemical conditions (such as temperature and OH^- concentration). Different types of secondary minerals may form depending on the specific nature of the Hanford waste solutions released and the degree of their interaction with the underlying sediments of the Hanford

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formation (the farther the waste fluids migrate away from the point of release the more pH neutralization, temperature reduction, and dilution occur). The secondary minerals that precipitate vary from amorphous aluminosilicates and zeolite to more crystalline sodalite and cancrinite. However, in general, crystalline feldspathoids such as sodalite and cancrinite [$Na_8Si_6Al_6O_{24}(NO_3)_2$] can be formed at temperatures above 40 °C and at high NaOH (>1 M) solutions (Bickmore et al., 2001; Mattigod et al., 2002; Qafoku et al., 2003; Mashal et al., 2004; Deng et al., 2006a). Compared to the primary minerals, these neo-formed secondary minerals demonstrate elevated sorption capacity resulting from increased surface adsorption and co-precipitation of radionuclides such as Sr and Cs (Chorover et al., 2003; Mon et al., 2005; Um et al., 2005; Choi et al., 2006; Rod et al., 2010; Chang et al., 2011).

In addition to elevated sorption capacity (adsorption + co-precipitation) due to the formation and precipitation of secondary minerals, mineral dissolution and precipitation reactions can alter pore structure and flow behavior through the matrix, thereby creating more complex interactions between reaction and transport processes in the subsurface environment (Um et al., 2005). Previous laboratory works have focused on identifying the most important variables that govern the dissolution–precipitation rates and mechanisms of the interaction between solution and solid, such as exploring quartz and clay mineral dissolution and precipitation under different pH and temperatures (Rimstidt and Barnes, 1980; Knauss and Wolery, 1988; Brady and Walther, 1989; Bauer and Berger, 1998). Although quartz dissolution and Hanford Site-specific characterization of neo-formed precipitates have been studied (Qafoku et al., 2003; Bickmore et al., 2006), very little work has explored the kinetics of mineral dissolution together with secondary precipitation under high Al-containing caustic waste tank solutions, as well as the impact of these reactions on permeability changes in the porous media.

Dissolution and secondary precipitation is one of the major geochemical processes controlling radionuclide transport in the vadose zone at Hanford Site below the so-called "tank farms." The specific objective of this study was to monitor synchronous quartz dissolution and the secondary precipitation at elevated temperatures using simulated tank waste solution, and to quantify the porosity changes caused by mineral alteration based on the quartz sand dissolution rate and precipitation rate of nitrate-cancrinite. The mineral-solution reaction was carried out using flow-through columns and the dissolution–precipitation rates were determined based on quasi-steady-state breakthrough curves of the released Si and Al concentrations.

2. Materials and methods

2.1. Quartz sand

Quartz sand (fractionated to 200–300 μm in diameter; Sigma–Aldrich®) was used for the column packing. In order to purify the packed materials, before use, the quartz sand was soaked in a 2% nitric acid solution for 2 days, followed by rinsing with deionized water and oven-drying at 105 °C for 24 h. We used pure quartz sand instead of natural Hanford sediments to isolate the effects of newly formed mineral precipitates on pore structure changes.

2.2. Simulated tank waste leachate

A simulated tank waste leachate (STWL) was prepared as a tank waste surrogate that has leaked into the vadose zone at the Hanford Site tank farms. Reagent-grade chemicals were used to prepare a STWL consisting of 1 M $NaNO_3$, 1.04 M NaOH, 0.01 M $Al(NO_3)_3$, and 10^{-5} M $Sr(NO_3)_2$. A solution with the same composition, but without Al was also prepared (called STWL−Al). The measured pH of the synthesized STWL solution was 13.3 at room temperature. The chemical composition of the STWL represents the lower range of concentrations of chemical compositions found in Hanford tank waste.

2.3. Solid characterizations

The morphology of the reacted quartz sand was observed using a scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy (EDS) coupled with an Oxford 80-mm silicon-drift-detector (SDD), and a powder X-ray diffractometer (XRD) were used to identify chemical compositions and minerals. The XRD was a Philips X'Pert XRD, coupled with MDI Jade9; it was operated at 40 kV and 50 mA with a step size of 0.3° 2θ. Instead of using the reacted quartz sand from the test columns, the same quartz sand reacted in batch vials (5 g quartz + 50 mL Al-containing STWL (STWL+Al) at 89 °C for 50 days with twice supernatant solution refreshment) and unpacked materials from a similar flow through column [internal-diameter (ID) 0.46 cm × 10 cm length; the same packed pure quartz with STWL+Al solution flow through at 89 °C for 80 days] were used for the above solid characterization. The reacted samples above were washed three times using 95% ethanol, followed by rinsing with deionized distilled water to remove any remaining STWL salt ions on the precipitate. Between each washing step, centrifugation at 25,000 G for 45 min was used, which enabled all particles larger than 0.07 μm diameter to settle out of the washing solutions. The white-colored floating nitrate-cancrinite particles in the washing solution of the last step were separated from the quartz grain, dried, and used for XRD, SEM, and EDS analyses. In addition, after 28 days of reaction and removing the floating nitrate-cancrinite particle-containing supernatant, SEM images of the batch reacted quartz grain surface were also collected.

2.4. Column experiments

Two PolyEtherEtherKetone (PEEK) columns (S1 and S3), each with a 2.1-mm ID and 10-cm length, were packed with acid-washed pure quartz sand. One more PEEK column with a wider ID of 4.6 mm and shorter length of 5 cm (S5) was packed using the same quartz material. The initial porosity calculated was 0.37, 0.33, and 0.42 for packed columns S1, S3, and S5, respectively. A 5-μm frit was used at both ends of each column to hold the packed materials in place. The STWL with Al (STWL+Al) or without Al (STWL−Al) was introduced into different columns under saturated conditions and at stepwise changed temperatures. A solution of STWL−Al or STWL+Al was flowed through the S1 and S3 columns, respectively. Different pore structure changes were expected in these two columns because Al element is necessary for the formation of secondary aluminosilicate mineral precipitates (sodalite or cancrinite). The solution in the S1 column (STWL−Al) can only result in the dissolution reaction of the quartz surface, while that in the S3 column (STWL+Al) can form secondary mineral precipitates dominated by feldspathoids. The S5 column was also treated with STWL+Al, to duplicate the experimental conditions used for the S3 column in the larger column dimension. Similar dissolution and precipitation reactions were expected to occur in columns S3 and S5.

Three separated KLOEHN V6 syringe pumps were used to produce a steady flow of STWL solution to each column. The pumps offered a constant flow instead of constant pressure. As long as the pore space inside columns was not totally clogged, the syringe pumps maintain constant flow rates. The flow rate for all columns was initially set to a constant value of 0.07 mL/h, resulting in 13.1, 14.9, and 4.8 PV (pore volume)/day for columns S1, S3, and S5, respectively. This flow rate (0.07 mL/h), i.e., 0.24–1.3 m/day in