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Effects of hydrated lime on radionuclides stabilization of Hanford tank residual waste

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HIGHLIGHTS

- Hanford tank residual waste could be stabilized by grout.
- Addition of hydrated lime stabilized uranium from leaching through $CaUO_4$.
- XRD, SEM/EDS and thermodynamic model revealed uranium mineral transformation.

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ABSTRACT

Chemical stabilization of tank residual waste is part of a Hanford Site tank closure strategy to reduce overall risk levels to human health and the environment. In this study, a set of column leaching experiments using tank C-104 residual waste were conducted to evaluate the leachability of uranium (U) and technetium (Tc) where grout and hydrated lime were applied as chemical stabilizing agents. The experiments were designed to simulate future scenarios where meteoric water infiltrates through the vadose zones into the interior of the tank filled with layers of grout or hydrated lime, and then contacts the residual waste. Effluent concentrations of U and Tc were monitored and compared among three different packing columns (waste only, waste + grout, and waste + grout + hydrated lime). Geochemical modeling of the effluent compositions was conducted to determine saturation indices of uranium solid phases that could control the solubility of uranium. The results indicate that addition of hydrated lime strongly stabilized the uranium through transforming uranium to a highly insoluble calcium uranate ($CaUO_4$) or similar phase, whereas no significant stabilization effect of grout or hydrated lime was observed on Tc leachability. The result implies that hydrated lime could be a great candidate for stabilizing Hanford tank residual wastes where uranium is one of the main concerns.

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1. Introduction

During World War II and Cold War, nuclear reactors located at the U.S. DOE Hanford site produced plutonium for America's defense program. During the more than 40 years operation (1943–1987), millions of liters of hazardous chemical and nuclear liquid wastes, generated during plutonium extraction from uranium “fuel rods”, were stored in 177 underground storage tanks spread out into eighteen groups of tanks called tank farms (USDOE, 2016a). The tank farms are comprised of 149 early-built single shelled tanks (SST) and 28 later-built double-shelled tanks (DST). Leaking has occurred from about one third of the SST, thus posing a risk to the local environment including the Columbia River. In 1989, the U. S. Department of Energy (DOE), Environmental Protection Agency (EPA), and Washington State Department of Ecology entered into a legally binding accord, the Tri-Party Agreement (TPA), to clean up the Hanford Site, with retrieval of waste from the tanks as a priority. The goal of the tank waste retrieval program is to remove at least 99 percent of the waste to meet the criteria established by the Tri-Party Agreement (TPA) that governs Hanford cleanup. In the waste retrieval

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processes with water addition, the liquid supernatant is -pumped out of the tanks, whereas the removal of the residual waste at the tank bottom (such as slurries containing high concentrations of dissolved salts, solid precipitates, and salt cake) is technically challenging. Due to the challenges, a certain amount of residual waste will remain in the tank after tank retrieval operations are complete. The current final tank closure plan is expected to consist of adding cement or grout to stabilize the tank physical structure and further isolate the residual waste. Corresponding to the current retrieval goals of approximately 99 percent, residual waste volume remaining in the SSTs could be as much as 10.2 m^3 for the 100 series tanks and 0.85 m^3 for the smaller 200 series tanks, or even more if the limit of waste retrieval technologies is reached (USDOE, 2016b). Therefore, investigating the radionuclide leachability from these residual tank wastes is essential to develop long-term performance estimates for closed SSTs and to evaluate methods to improve that performance.

In the past 10 years, several studies has been conducted to characterize tank residual wastes and develop an understanding of the related radionuclide leaching models (Cantrell et al., 2006, 2011, 2013; Krupka et al., 2006). Krupka et al. (2006), for the first time, conducted detailed solid characterizations on C-203 and C-204 tank residual wastes, and reported that high soluble čejkaite [$Na_4(UO_2)(CO_3)_3$] is the dominant uranium crystalline phase together with poorly crystalline $Na_2U_2O_7$ or clarkeite [$Na(UO_2)O(OH)(H_2O)$] phases. Later as part of an ongoing project, phase characterization and leaching tests were also conducted on five retrieved tank residual wastes including tanks C-103, C-106, C-202, C-203, C-108, and one salt cake waste residual from tank S-112. Based on these solid characterizations and leaching test results, Cantrell et al. (2011) proposed a thermodynamic solubility model for uranium release from Hanford site tank residual wastes through uranium phase saturation indices calculations assuming the equilibrium was attained, and the evolution of related uranium phases as leaching progressed was estimated. Recently, instead of the normal static batch experiments, Cantrell et al. (2013) conducted a single-pass flow-through (SPFT) test to develop more realistic and representative models for release of U, Tc and Cr from Hanford site tank C-202, C-203, and C-103 residual waste, where three different leachant solutions (DI water, $CaCO_3$ saturated solution, and $Ca(OH)_2$ saturated solution) were used to simulate different leaching scenarios. Through further application of this thermodynamic solubility release model, Cantrell et al. (2014) tested three different chemical treatment methods by respectively using hydrated lime, ceramicrete, and ferrous iron/goethite to stabilize the tank residual waste and reduce contaminant release. Addition of hydrated lime was found to be an efficient and inexpensive way to stabilize uranium in the tank prior to tank closure (Cantrell et al., 2014).

In the research reported here, hydrated lime addition as a chemical stabilization approach is tested on the uninvestigated residual waste from Tank C-104 in which waste retrieval operations have been completed and higher uranium was reported in the residual waste (11.5 wt.%). The scope of this study is to investigate the effect of this added hydrated lime, in combination with grout, on radionuclide stability in the residual waste in Tank C-104, taking into account a potential scenario where meteoric water infiltrates through the vadose zone, into the tank interior that is filled with layers of grout or hydrated lime, and ultimately contacts the residual waste. Column leaching experiments were conducted to simulate field scenarios, and the uranium and technetium concentrations were monitored in the effluents as a function of leaching times. This study represents the first solid phase characterization and leaching test to be conducted on Hanford tank C-104 residual waste.

2. Materials and methods

2.1. Tank C-104 residual waste materials and chemical stabilization agents

Removal of the C-104 pumpable waste liquids was completed in 1989 as part of an overall single-shell tank interim stabilization effort. It is one of 16 tanks located in an area known as C Farm which was constructed during 1944–1945. Tank C-104 has been retrieved and the residual waste is estimated to be 6.9 m^3 which contains high concentrations of radionuclides.

Tank residual waste samples were collected by the DOE contractor, Washington River Protection Solution (WRPS). The chemical components of the residual waste were determined using a $KOH-KNO_3$ fusion method developed at PNNL (Deutsch et al., 2004) and an acid digestion procedure based on a modified version of U.S. Environmental Protection Agency (EPA) SW 846 Method 3050B (USEPA, 2000) (see Supplementary Data for details). The mean concentrations of major components and contaminants of concern in the residual waste are shown in Table S1 (Hulse, 2013). In terms of radionuclides, the major radionuclide of concern in Tank C-104 residual waste is U (11.5 wt. %), with Tc (1.6E-06 wt. % or 1.6 μg/g) and Th (0.3 wt. %) to a lesser extent. The collected tank residual waste sample was ground in an agate mortar and pestle to break up small aggregates and create a powder of uniform particle size (<2 mm) for further use in this study.

The grout formula used in this study is based on that used for bulk fill grout given in RPP-RPT-49701, Rev. 0 (Quigley, 2011). Briefly, the grout recipe (wt.%) was F fly ash (14.51%), Portland cement type I/II (4.82%), ACROS pure sand (68.79%, 10–100 mesh), and water (11.89%). The grout was made by mixing the dry ingredients thoroughly first, followed by mixing with water. The mixture was then poured into plastic tubes, and cured for 30 days under room temperature. After 30 days the grout was broken up and sieved to obtain materials of 50 μm - 2.0 mm size fraction. Analytical grade hydrated lime [$Ca(OH)_2$] was purchased from Sigma-Aldrich and used as received.

2.2. Solid phase characterization

2.2.1. X-ray diffraction (XRD)

Powder XRD was used to identify the crystalline phases present in the un-leached and leached residual waste samples. The highly radioactive and dispersible samples were prepared for XRD through encapsulating samples in resin and covered by Kapton® film. Details of sample preparation and XRD analysis are available in Supplementary Data.

2.2.2. Scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDS)

SEM/EDS analysis was conducted to characterize the morphologies and chemical compositions of solid phases present in the original unleached C-104 tank residual waste sample. The details of SEM/EDS analysis methods are presented in Supplementary Data. As the sample was not a polished thin section, reliable quantitative data cannot be extracted from the EDS analyses; however, qualitative analysis is still available to provide valuable information.

2.3. Column leaching experiments

Column leaching experiments were conducted to evaluate the leachability of contaminants of concern. This approach was used because it is expected to provide a more realistic simulation of a tank waste closure scenario in which meteoric water infiltrates through the vadose zone into the tank interior, then contacts and