



## Research paper

## Development of a carbonate crust on alkaline nuclear waste sludge at the Hanford site



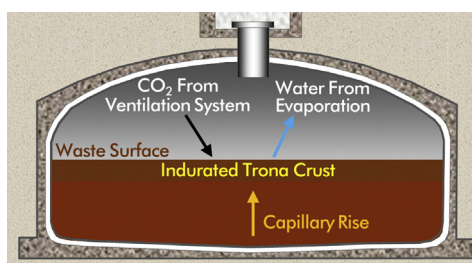
Jason S. Page\*, Jacob G. Reynolds, Tom M. Ely, Gary A. Cooke

Washington River Protection Solutions LLC, Richland, WA, 99352, USA

## HIGHLIGHTS

- A hard crust which inhibited nuclear waste remediation efforts was examined.
- Formation of carbonates from CO<sub>2</sub> absorption was shown to have caused the crust.
- The lowered pH converted gibbsite and clarkite to dawsonite and cejkaite.
- A model is presented to aid other remediation efforts of alkaline legacy wastes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Hard crusts on aging plutonium production waste have hindered the remediation of the Hanford Site in southeastern Washington, USA. In this study, samples were analyzed to determine the cause of a hard crust that developed on the highly radioactive sludge during 20 years of inactivity in one of the underground tanks (tank 241-C-105). Samples recently taken from the crust were compared with those acquired before the crust appeared. X-ray diffraction and scanning electron microscopy (SEM) indicated that aluminum and uranium phases at the surface had converted from (hydr)oxides (gibbsite and clarkite) into carbonates (dawsonite and cejkaite) and identified trona as the cementing phase, a bicarbonate that formed at the expense of thermonatrite. Since trona is more stable at lower pH values than thermonatrite, the pH of the surface decreased over time, suggesting that CO<sub>2</sub> from the atmosphere lowered the pH. Thus, a likely cause of crust formation was the absorption of CO<sub>2</sub> from the air, leading to a reduction of the pH and carbonation of the waste surface. The results presented here help establish a model for how nuclear process waste can age and can be used to aid future remediation and retrieval activities.

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*Abbreviations:* EDS, energy dispersive spectroscopy; PLM, polarized light microscopy; PUREX, Plutonium Uranium Extraction Plant; SEM, scanning electron microscopy; SPC, solid phase characterization; TGA, thermogravimetric analysis; XRD, X ray diffraction.

\* Corresponding author.

E-mail address: [jason.s.page@rl.gov](mailto:jason.s.page@rl.gov) (J.S. Page).

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## 1. Introduction

Between 1945 and 1989, the Hanford Site, near Richland, WA, produced two-thirds of the total plutonium for the United States nuclear arsenal [1]. As a result, the Hanford Site currently maintains about 56 million gallons of nuclear waste in the form of supernatant liquid, crystallized saltcake, and settled fine particulate sludge, which is stored in underground concrete tanks with steel liners. In total, this is the largest inventory of nuclear waste at any location in the world [1]. Initially, this waste was stored in single-shell

tanks with solitary steel liners, but the tanks were prone to failures causing release of the material to the environment. In order to limit the leaks, most of the free liquid was retrieved (transferred) by year 2002 into newer, more robust, 1 million gallon capacity, double-shell tanks. Sludge, saltcake solids, and a limited amount of interstitial liquid remained in the single-shell tanks [1]. Currently, the Hanford Site is retrieving the remaining solids from the single-shell tanks into the double-shell tanks, awaiting the completion of a waste immobilization facility.

At the time of this writing, the Site is currently finishing the retrieval of the first single-shell tank farm (C Farm), which has 16 tanks, into the double-shell tanks that will eventually feed the waste immobilization facility. Due to unanticipated waste properties, such as hard crust formation, cemented layers, and large particulate [2], the retrievals in C Farm have taken more than 17 years. In addition, limitations in retrieval technologies have left some waste behind in the tanks, generally in the form of a solid waste heel [2,3] which represents a possible environmental risk after the tanks are closed [4–8].

In standard jet sluicing, the technique traditionally used for moving nuclear waste slurries between tanks [2,9,10], a jet of liquid (usually supernatant waste from the receiving tank) is impinged on the waste to mobilize the slurry into a pump suction inlet [10]. This technique was unsuccessful in breaking up and pumping the unanticipated hard crusts. This forced the development of high-pressure mobile arms that could be deployed closer to the waste surface [9], but tank obstructions prevented that technology from reaching all of the waste. In addition, sluicing techniques were not desired for tanks that were suspected to leak because they introduced liquids that could migrate out of the tank and into the environment [11]. To overcome this limitation, a vacuum technology was developed that had minimal success at removing the hard surface crusts, but it did successfully remove the soft material underneath [11].

There has been no previous determination of the cementing agent or mechanism of induration of alkaline nuclear waste reported in the literature. Thus, the purpose of this study is to determine what is cementing the waste together, forming a hard crust in this tank, so that it can be either treated or prevented in the future at the Hanford Site or other sites with alkaline waste. While the mechanism of cementation of alkaline waste has not been determined previously, cemented soil surfaces are relatively common in nature and these cemented soil surfaces were hypothesized to be potential natural analogues to alkaline nuclear waste. Cemented laterite crusts are common in tropical soils. These crusts form where soils that are high in iron and aluminum hydroxides dry out [12]. Given the high concentrations of gibbsite and iron (hydr)oxides in Hanford Site waste, lateritization was seen as a potential analogue to crust formation in the waste. An alternative hypothesis was that salts cemented the crusts because salts have been found to cement soil surfaces when highly saline soil solution evaporates [13], and Hanford Site waste has extremely high electrolyte concentrations. By determining the cementing phase here, the applicability of these geological analogues are evaluated.

Given that these hard waste crusts were unanticipated and caused years of delay to the waste retrieval at C Farm, a better knowledge of how the crusts form would benefit future retrievals and provide a general understanding of how high alkaline materials can age and change in other tanks. This paper determines the composition of the hard crust in tank 241-C-105 and compares it to analysis results from material sampled before the hard crust existed in the tank. These results are used to create a mechanism of crust formation. Anticipating when a carbonate crust may form provides insights on how the waste can be better managed to avoid the development of surface crusts in the future.

## 2. Experimental

### 2.1. Sample collection

The Hanford Site operations personnel sampled waste from tank 241-C-105 in 1995 using a push mode coring method which forced a coring tube down into the sludge, retaining the material inside the core tube as described in an American Society for Testing Materials procedure [14]. The core samples were transferred to the on-site analytical laboratory for analysis, and the remaining sample material was archived in sample jars. In 2014, the archived sample from the upper core segment was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermo-gravimetric analysis (TGA) as described below.

In 2015, retrieval of tank 241-C-105 was initiated, but the presence of the hard crust on the surface of the waste impaired the transfer. As part of the work to retrieve the contents of the tank, the white crust material was sampled in 2015 using a clam-shell sampler. This material was transferred to the on-site analytical laboratory for SEM, XRD, and TGA analysis.

### 2.2. Scanning electron microscopy analysis

Specimens for the SEM analysis of the 1995 archived sample were prepared using a wet smear technique. To accomplish this, a 20- $\mu\text{m}$  pore size polycarbonate filter was placed on a vacuum filtration apparatus. A plastic disposable pipette was used to stir the sample in the vial which transferred a small portion of the sample onto the pipette tip. The loaded pipette was rubbed across the filter, smearing a portion of the wet sample across the surface. The vacuum was immediately turned on, removing a majority of the interstitial liquid from the solids. The filter was allowed to dry, and sections were cut and adhered to carbon planchets on aluminum SEM stubs using a carbon glue. The SEM stubs were then coated with carbon via a vapor deposition technique.

Specimens for the SEM analysis of the 2015 waste samples were prepared by lightly crushing the solids in a petri dish. The dispersed fragments were then lifted on SEM stubs using double-sided, adhesive carbon tabs. The samples were not carbon coated. In addition, cross-section specimens of larger, uncrushed particles from the 2015 samples were made to better determine the binding phases. To accomplish this, selected particles were placed in separate small plastic vials and a mixed epoxy (EpoxiCure 2; Buehler) was added. The filled vials were then placed in a vacuum desiccator for  $\sim 10$  min, removed, and placed in a fume hood overnight to fully cure. The solid epoxy plugs were then removed from the vials.

The epoxy-embedded particles were wafered using a low-speed saw (TechCut 4, Allied High Tech Products, Inc.) with a diamond-impregnated wafering blade and a propane-1,2-diol/water-based cutting fluid provided by the saw manufacturer. This was done by positioning each epoxy plug in a sample holder so that the blade would cut near the middle of the embedded particles, exposing a cross-sectional surface. A second cut created wafers  $\sim 0.5$  cm thick. These wafers were polished to a fine finish using consecutive sand papers ranging in grit size from 240 to 1500 (70–14  $\mu\text{m}$  abrasives). The sandpapers were dampened with reagent grade water to assist the polishing process and limit the spread of radioactive material in the fume hood. The wafers were also cleaned using a damp Kimwipe in between abrasion steps and when the polishing was completed. The polished wafers were mounted onto SEM stubs using conductive carbon adhesive tabs. The cross-sectioned specimens were not carbon coated.

An ASPEX Explorer SEM with an OmegaMax energy dispersive spectrometer (EDS) was used for this analysis. The instrument was operated with an accelerating voltage of 25 keV, and the samples were mounted at a working distance of 10–15 mm. A sample

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