Assessment of the Cast Stone Low-Temperature Waste Form Technology Coupled with Technetium Removal - 14379

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ABSTRACT

The U.S. Department of Energy Office of Environmental Management (DOE-EM) is engaging the national laboratories to provide the scientific and technological rigor to support EM program and project planning, technology development and deployment, project execution, and assessment of program outcomes. As an early demonstration of this new responsibility, Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) were chartered to implement a science and technology program addressing low-temperature waste forms for immobilization of DOE aqueous waste streams, including technetium removal as an implementing technology. As a first step, the laboratories examined the technical risks and uncertainties associated with the Cast Stone waste immobilization and technetium removal projects at Hanford. Science and technology gaps were identified for work associated with 1) conducting performance assessments and risk assessments of waste form and disposal system performance, and 2) technetium chemistry in tank wastes and separation of technetium from waste processing streams. Technical approaches to address the science and technology gaps were identified and an initial sequencing priority was suggested. A subset of research was initiated in 2013 to begin addressing the most significant science and technology gaps. The purpose of this paper is to report progress made towards closing these gaps and provide notable highlights of results achieved to date.

INTRODUCTION

Low-temperature waste forms are being considered and used for solidification of large volumes of aqueous low-level wastes across the DOE complex. Frequently, these are cementitious waste forms, such as Saltstone being used at the Savannah River site for immobilizing low-activity wastes, and Cast Stone, which was recently selected at Hanford for solidification of secondary wastes from the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Cementitious materials are also being used to fill empty underground radioactive waste storage tanks as part of tank closure and are used in closure of contaminated facilities, such as the P and R Reactors at Savannah River, and reactors and reprocessing facilities at Idaho.

Another potential application for low temperature waste forms is as a supplemental immobilization technology for Hanford's Low-Activity Waste (LAW). The WTP LAW vitrification facility was not designed to process the entire volume of LAW retrieved at Hanford. Therefore, an additional supplemental LAW immobilization facility will be required. Up to two thirds of all Hanford retrieved LAW may need to be immobilized in the supplemental LAW facility. Four candidate technologies are under evaluation (i.e., a second LAW vitrification facility, bulk vitrification, fluidized bed steam reforming [FBSR], and Cast Stone). These technologies are under evaluation and completion of a Hanford Tank Waste Supplemental Treatment Technologies Report is a Tri-Party Agreement (TPA) Milestone (M-062-40ZZ) that is due in October 2014. Regardless of which supplemental technology is selected, the resultant LAW waste forms will be disposed of at the Hanford Integrated Disposal Facility (IDF).

The first three LAW immobilization options involve high-temperature processes, while Cast Stone represents a low-temperature process. The lower operating temperature for Cast Stone translates to the potential for lower construction and operating costs. Washington River Protection Solutions (WRPS) is conducting a research and development program to understand the performance of Cast Stone as a LAW waste form utilizing significant national laboratory involvement. The WRPS-led effort served as a basis to identify areas where national laboratory engagement would add benefit to DOE in advancing the use of Cast Stone to immobilize secondary waste streams at Hanford, aid their decision making process for supplemental LAW immobilization, and provide additional information for future performance assessments that will address cementitious waste forms.

Technetium-99 (^{99}Tc) is a long-lived radionuclide with an inventory estimate of about 30,000 curies in the Hanford tank wastes. Technetium is of particular importance because it has been shown, in performance assessments, to be a significant contributor to the potential long-term environmental impacts associated with disposal of secondary wastes and LAW in the IDF. The ^{99}Tc is found predominantly in the supernate fraction of the tank waste, the majority of which will be processed as LAW. In the LAW vitrification baseline process, the Tc is volatile at the processing temperatures of the LAW glass melter and the fraction of Tc that does volatize will be captured in the off-gas treatment system. To increase the amount of Tc retained in the LAW glass, the off-gas condensates with the captured Tc will be recycled to the LAW melter. Recycling the off gas condensates has the impact of increasing the number of LAW glass containers produced and extending the duration of the WTP mission.

The principal technetium species found in LAW is the pertechnetate form (TcO_4^- with an oxidation state of +7), which is highly soluble and readily mobile in subsurface environments (vadose zone and aquifer sediment pore water/groundwater). Because the majority of the ^{99}Tc will be immobilized as LAW, with a smaller fraction immobilized as a secondary waste Cast Stone waste form, it will remain on the Hanford site at the IDF; only a small fraction will be shipped away to a geologic repository with the immobilized high-level waste (IHLW). Past studies have shown that ^{99}Tc will be the primary dose contributor to the IDF Performance Assessment (PA), which focuses on groundwater protection. Due to its soluble nature and potential volatility during high-temperature vitrification processes, effective technetium management is important to the success of the overall Office of River Protection (ORP) Project mission.

DESCRIPTION

This section provides a high-level overview of the data gaps/issues in the area of 1) assessing the long-term performance of low-temperature waste forms and 2) technetium removal.

Assessing the Long-term Performance of Low Temperature Waste Forms

In its Engineering &Technology Roadmap, DOE-EM identified a technical risk and uncertainty associated with assessing the long-term performance of waste forms (DOE-EM 2008). Specifically,

> "Evaluating the performance of the integrated waste closure unit requires extrapolation of short-term performance data to extended periods of time. Current materials (i.e. glass, grout, etc.) are commonly used to immobilize high-level and low-level radioactive wastes. Storage for extended periods of time (100's or 1,000's of years) is difficult to predict and leads to uncertainties in the long-term performance of the closure unit. Additional data and integrated approaches are needed to provide the necessary understanding of the behavior of the closure unit over the long-term so that appropriate strategies can be selected and so that performance assessments will be based on improved predictive capabilities."

DOE-EM identified a strategic integration and crosscutting initiative to:

> "Develop programs and approaches (including accelerated test protocols) to improve understanding of long-term waste form performance. Integrate the information gained with improved understanding of contaminant transport to enhance long-term risk assessment and predictive modeling capabilities."

With this background, a number of recent relevant documents were reviewed to identify science and technology gaps associated with conducting PAs and risk assessments (RAs) of waste form and disposal system performance. Included were reviews by the National Academy of Sciences (NAS 2009, 2010, 2011), the U.S. Nuclear Regulatory Commission review of the Saltstone Performance Assessment (PA) (NRC 2012), previous Hanford PA and Risk Assessment work (Mann et al. 2003; McGrail et al. 2003; Pierce et al. 2004), reviews by the Cementitious Barriers Partnership (CBP 2009a, 2009b), and other technology risk reviews (Bredt et al. 2008).

The science and technology gaps identified were grouped into the following broad categories and summaries were developed:

- Hydraulic Properties
- Effective Diffusion Coefficients
- Solubility and Partition Coefficients (K_d)
- Cast Stone Formulation and Impact on Properties
- Impact of Curing Conditions and Scale on Cast Stone Properties
- Expected Fracturing in Cast Stone with Time
- Technetium Speciation and Impacts of Redox Changes
- Cast Stone Long-Term Weathering
- Multi-Component Interactions
- Cast Stone Contaminant Release Model–Conceptual and Numerical
- Uncertainty Analysis and Methodology for PAs
- Transformational Approaches for Waste Solidification.

Technetium Removal

This effort focused on developing additional information concerning Tc removal technologies that could support DOE in making decisions on a number of areas including support for "Glass by 2019", LAW recycle operations, and supplemental pretreatment.

The science and technology gaps associated with technetium removal were identified and grouped into the following broad categories:

- Removal of Tc from Off-Gas Streams
- Identification of Conditions for Non-Pertechnetate Species
- Development of Methods for Removing Non-Pertechnetate Species
- Development of an Alternative Tc Removal Elutable Resin
- Pretreatment of WTP LAW and the Temperature Effect on Resin Performance
- Alternative Waste Forms for Tc Eluate.

As part of this overall effort, technical approaches to address the science and technology gaps for both the long-term performance of low temperature waste forms and Tc removal were identified, and an initial sequencing priority was suggested. The following table summarizes the most significant science and technology needs and the associated approaches to address them.

TABLE 1. Summary of High Priority Research Needs

Research Need	**Approach**
Effective Diffusion Coefficients	Extend effective diffusivity measurements in support of the LAW supplemental immobilization testing program and expanded secondary waste immobilization tests
Solubility and K_d	Perform additional adsorption-desorption tests using Cast Stone leachates
Cast Stone Formulation and Impact on Properties	Expand existing LAW supplemental immobilization Cast Stone testing program to include waste chemistries relevant to the secondary waste stream
Impact of Curing Conditions and Scale on Cast Stone Properties	Curing impacts with focus on controlling porosity
Expected Fracturing in Cast Stone with Time	Literature reviews looking at effect of carbonation reactions and effects of sulfate attack and ettringite formation
Technetium Speciation and Impacts of Redox Changes	Technetium speciation characterization in Cast Stone Characterization of technetium oxidation front Leaching of non-pertechnetate technetium from Cast Stone
Cast Stone Long-Term Weathering	Porosity changes with weathering Literature review on natural analogs and ancient cements
Removal of Tc from Off-Gas Streams	Initial development of separation and removal parameters; Screening of Secondary Waste disposal options; Process selection; Technology insertion optimization
Identification of Tank Conditions that form Non-	Determine whether a Tc(IV) pathway to Tc(I) carbonyl compounds is viable in alkaline solutions;

Pertechnetate Species	Determine the rates of oxidation of n-Tc compounds to better predict potential changes in the fraction of soluble non-pertechnetate technetium that may occur upon waste transfers/processing
Development of an Alternative Technetium Removal Elutable Resin	Develop an alternative Tc removal resin to SuperLiq 639 to at least a Technology Readiness Level (TRL) of 4
Pretreatment of WTP LAW and the Temperature Effect on Resin Performance	Develop Tc isotherms, column ion exchange behavior, and resin stability at elevated temperatures up to 50°C
Alternative Waste Forms for Tc Eluate	Evaluation of alternative immobilization processes for Tc, such as co-precipitated with iron oxides or sorbed to Sn(II) apatite

Limited funding was made available in FY13 to begin addressing three challenges associated with low temperature waste form performance and three challenges focused on technetium removal. For low temperature waste forms, these included 1) determining effective diffusion coefficients for key contaminants, 2) formulation activities to increase waste loading, and 3) tests to understand the redox capacity of Cast Stone monoliths. Within the technetium removal focus area, activities included 1) methodologies to remove technetium from the off-gas streams, 2) identification of conditions that would enable the formation of non-pertechnetate species, and 3) alternative waste forms for technetium eluate. High-level results from a subset of these efforts are summarized in the following section.

DISCUSSION/CONCLUSIONS

Cast Stone Formulation at Higher Sodium Concentrations

Formulation of Cast Stone at high sodium concentrations is of interest since a significant reduction in the necessary volume of Cast Stone and subsequent disposal costs could be achieved if an acceptable waste form can be produced with a high sodium molarity salt solution combined with a high water to premix (or dry blend) ratio. The objectives of this study were to evaluate the factors involved with increasing the sodium concentration in Cast Stone, including production and performance properties and the retention and release of specific components of interest. Three factors were identified for the experimental matrix: the concentration of sodium in the simulated salt solution, the water to premix ratio, and the blast furnace slag portion of the premix. The salt solution simulants used in this study were formulated to represent the overall average Hanford tank waste composition (after retrieval). The cement, blast furnace slag, and fly ash were sourced from a supplier in the Hanford area in order to be representative.

The test mixes were prepared in the laboratory and fresh properties were measured. Fresh density increased with increasing sodium molarity and with decreasing water to premix ratio, as expected given the individual densities of these components. Rheology measurements showed that all of the test mixes produced very fluid slurries. The fresh density and rheology data are of potential value in designing a future Cast Stone production facility. Standing water and density gradient testing showed that settling is not of particular concern for the high sodium compositions studied. Heat of hydration measurements were made and may provide some insight into the reactions that occur within the test mixes, which may in turn be related to the properties and performance of the waste form. These measurements showed that increased sodium concentration in the salt solution reduced the time to peak heat flow, and reducing the amount of slag in the premix increased the time to peak heat flow. These observations may help to describe some of the cured properties of the samples, in particular the differences in compressive strength observed after 28 and 90 days of curing.

Samples were cured for at least 28 days at ambient temperature in the laboratory prior to measuring cured properties. The low activity waste form for disposal at the Hanford Site is required to have a compressive strength of at least 500 psi. After 28 days of curing, several of the test mixes had mean compressive strengths that were below the 500 psi requirement. Higher sodium concentrations and higher water to premix ratios led to reduced compressive strength. Higher fly ash concentrations decreased the compressive strength after 28 days of curing. This may be explained in that the cementitious phases matured more quickly in the mixes with higher concentrations of slag, as evidenced by the data after 90 days of curing, where only one composition had a mean compressive strength of less than 500 psi. Leach indices were determined for the test mixes for selected contaminants of interest (sodium, nitrate, nitrite, iodide and chromium). The leaching performance of the mixes evaluated in this study was not particularly sensitive to the factors used in the experimental design. This may be beneficial in demonstrating that the performance of the waste form is robust with respect to changes in the mix composition.

The results of this study demonstrate the potential to achieve significantly higher waste loadings in Cast Stone and other low temperature, cementitious waste forms (please see Fox et al. 2013 for full details of the study). Additional work is needed to elucidate the hydration mechanisms occurring in Cast Stone formulated with highly concentrated salt solutions since these reactions are responsible for determining the performance of the cured waste form. The thermal analyses completed in this study provide some preliminary insight, although the limited range of the factors in the test matrix hindered the identification of individual component effects. Future work should involve broader factor ranges to identify the roles played by each of the components in the mix via thermal analyses, analytical microscopy, and characterization of phase formation.

Cast Stone Monolith Extended Leach Testing

In this task, Cast Stone contaminant release data are being measured for longer time periods than the typical 63 to 91-d time periods generally recommended for cementitious waste forms by organizations involved in test standards development (e.g., American Society for Testing and Materials [ASTM], American Nuclear Society [ANS], and the Environmental Protection Agency [EPA]). A key goal of this activity is to measure the leach properties of Cast Stone for longer time periods in order to bolster future IDF performance assessment and risk assessment evaluations. Specifically, the objectives of the Cast Stone monolith extended leach testing focus on four activities:

1. Extend the leaching times for selected ongoing EPA-1315 tests on Cast Stone monoliths made with LAW simulants beyond the conventional 63-day time period in an effort to evaluate long-term leaching properties of Cast Stone to support future performance assessment activities.
2. Start new EPA-1315 leach tests on archived Cast Stone monoliths made with

four LAW simulants using two leachants (deionized water and simulated Hanford IDF Site vadose zone pore water).

3. Evaluate the impacts of varying the iodide loading (starting iodide concentrations in one LAW simulant: 7.8 M Na Average simulant) by manufacturing additional Cast Stone monoliths and repeating the EPA-1315 leach tests using deionized water and the IDF Site vadose zone pore water as leachants.
4. Evaluate the impacts of using a non-pertechnetate form of Tc that is present in Hanford SST and DST tanks. In this activity, the LAW 7.8 M Na Average simulant was spiked with a Tc-gluconate species, then solidified into Cast Stone monoliths, and subsequently leached using the EPA-1315 leach protocol with deionized water and IDF site vadose zone pore water as the leachants. The leach results for Cast Stone monoliths using the LAW simulant, but with the Tc-gluconate spike, are being compared to Cast Stone monoliths made with the same LAW simulant spiked with pertechnetate, which are being leached in both deionized and IDF site vadose zone pore water.

One concern with the iodide-bearing Cast Stone leach testing performed to date is that, in order to have measurable concentrations of iodide in the leachates, the iodide concentration in the Cast Stone specimens were spiked up to two orders of magnitude higher than the projected average concentration in the LAW waste. The previous iodide leach results for Cast Stone and other cementitious waste forms may be biased high because of the unrealistically high iodide waste loading (see for example Atkinson and Nickerson 1988, Clark 1977, and Lockrem et al. 2005). Leach tests with a combination of ^{125}I iodide radiotracer and low concentrations of stable iodide representing the projected concentrations of ^{129}I in the actual waste are being performed and should help resolve this issue. The starting iodide concentrations were chosen to range between the average calculated ^{129}I mass concentration in LAW waste (based on the Hanford Tank Waste Operations Simulator [HTWOS] analyses) up to twice the maximum ^{129}I mass concentration in LAW waste.

A second concern is that all the previous Cast Stone leach tests were performed using deionized water as the leachant. Deionized water is generally considered an aggressive leachant that does not purport to represent the fluids that will interact with buried wastes within the IDF facility. Thus, to more realistically evaluate Cast Stone leach properties, an IDF relevant leachate, simulated Hanford formation vadose zone sediment pore water, is being used in many of the leach tests.

To date, the various leach tests have been sampled and leachates analyzed for key contaminants (NO_3, NO_2, Na, Cr, Tc and I) for the standard 63-d time period and longer (between 91-d and 257-d) time periods. In the presentation, some of the key results will be discussed.

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