Contract No:

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Disclaimer:

Low Temperature Waste Form Process Intensification

This study successfully demonstrated process intensification of low temperature waste form production. Modifications were made to the dry blend composition to enable a 50% increase in waste concentration, thus allowing for a significant reduction in disposal volume and associated costs. Properties measurements showed that the advanced waste form can be produced using existing equipment and processes. Performance of the waste form was equivalent or better than the current baseline, with approximately double the amount of waste incorporation. The results demonstrate the feasibility of significantly accelerating low level waste immobilization missions across the DOE complex and at environmental remediation sites worldwide.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

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Signature **Date**

LDRD-2014-00100
LDRD Report

Low Temperature Waste Form Process Intensification

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Thrust Area: CI-1, Process Intensification and Smart Manufacturing

Project Type: Supplemental

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Low temperature waste forms are utilized for the immobilization of low activity waste and other hazardous materials. These waste forms benefit from the use of inexpensive raw materials (and materials that would otherwise be considered wastes themselves) and require a minimal amount of energy for processing. However, the volume of low temperature waste forms can be large relative to the volume of waste immobilized. The process of immobilizing waste in a low temperature waste form would be significantly intensified by increasing the concentration of waste in the material. Improved understanding of waste incorporation in low temperature waste forms will allow for volume reductions of 50% or more, which will greatly reduce the disposal footprint and cost.

FY2015 Objectives

- Develop an improved understanding of the retention of contaminants in low temperature, cementitious waste forms such that a step-change reduction in waste form volume can be achieved
- Identify potential processing issues when waste concentration is increased
- Measure waste form performance when formulated at high waste concentrations
- Identify changes to dry blend composition that improve waste form performance

Introduction

The objective of this study was to develop an improved understanding of the retention of contaminants in low temperature, cementitious waste forms such that a step-change reduction in waste form volume can be achieved. Figure 1 demonstrates this potential reduction in waste form volume. The area within the solid red outline represents the region of recent operation of the Saltstone Production Facility at the Savannah River Site (SRS). The area within the dotted and shaded red outline represents compositions tested by SRNL in a preliminary study for Hanford Cast Stone development, where it was shown that a waste form could be produced with a concentrated feed

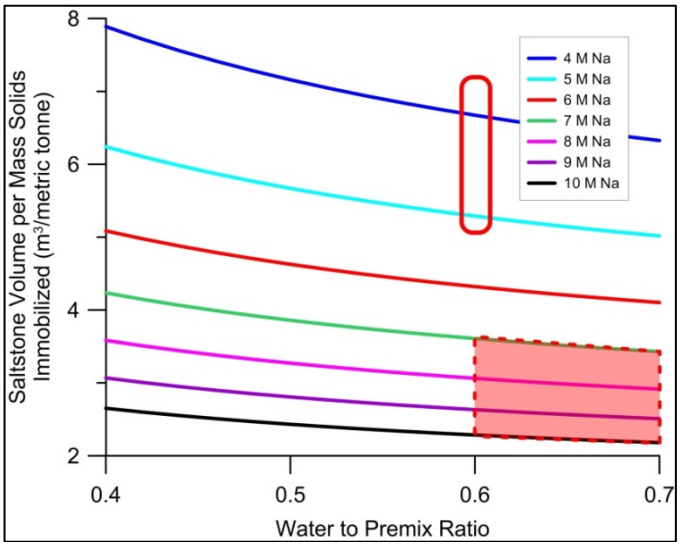

Figure 1. Calculated waste form volume as a function of sodium molarity and water to premix ratio

material and retain acceptable properties.[1] As shown in Figure 1, concentrating a low activity waste (LAW) salt solution feed from 5 M sodium to 8 M sodium would reduce the volume of the waste form by approximately 50%, and would reduce mission life cycle costs by a similar percentage.

The study reported here continued to investigate the properties and performance of low temperature forms fabricated with high sodium concentration simulated LAW solutions, along with the addition of new dry blend (or premix) components. It was hypothesized that variation in the amounts of blast furnace slag and fly ash in the dry blend composition, as well as the addition of geopolymer materials, could offer improved retention of contaminants of concern, while continuing to meet other material processing and performance requirements.

Approach

A series of low temperature waste form test mixes was developed in two stages for this study. The first stage was a set of three mixes designed to test hydraulic conductivity of waste forms produced with higher sodium concentration LAW feeds. The second stage was a larger set of mixes designed to test the impact of changes to the dry blend composition when combined with higher sodium concentration LAW feeds, in terms of both fresh and cured properties.

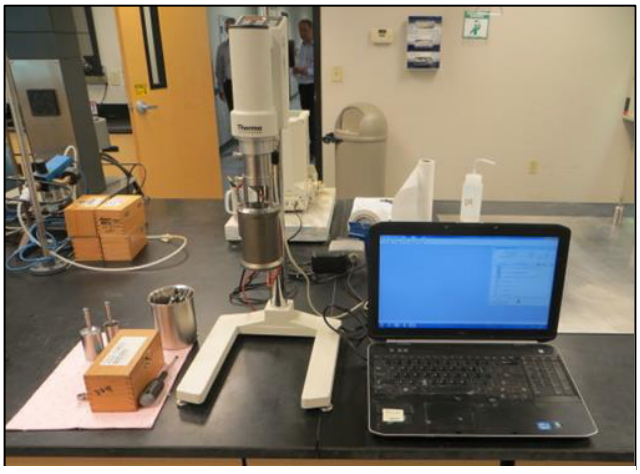

Figure 2. Rheometer for measurement of viscosity of fresh slurries

After preparation in the laboratory, the fresh properties of the mixes were measured. Fresh properties, including density, flowability, gel time, plastic viscosity (Figure 2), and yield stress determine the processability of the slurry. The intent was to develop formulations that can be processed using existing equipment and facilities, thus minimizing the need for any capital expenditures to process the waste form at higher waste concentrations. The experimental mixes were then cured for at least 28 days in preparation for cured properties measurements. Cured properties, including compressive strength and hydraulic conductivity (Figure 3), are indicative of the performance of the waste form in the disposal environment.

Results/Discussion

The results of selected fresh properties measurements identified no issues with processing slurries formulated with concentrated salt solutions and the additional dry blend components. Fresh densities were close to the calculated values for each mix, indicating no issues with preparation. Rheology measurements showed increases in plastic viscosity for all the test mixes relative to current SRS saltstone, but the slurries remained sufficiently flowable. Flow testing confirmed the results of rheology testing. The mix prepared with all metakaolin as the dry blend was the exception, and was too viscous for the rheology measurement. Gel times were generally longer than that of current SRS saltstone. This means that the mixes had a longer working time, but the potential impact on disposal method needs to be determined. The mix prepared with all metakaolin was again the exception, with a relatively short gel time of 31 minutes. The rheology, flow, and gel time data indicated that the all metakaolin mix reacted most quickly.

The cured properties measured included compressive strength and hydraulic conductivity for select samples. All of the text mixes had had sufficient compressive strength (>500 psi) after more than 28 days of curing, with the exception of the all fly ash and all metakaolin mixes. These two mixes remained plastic after the curing period. The addition of metakaolin improved compressive strength, but only when used in combination with cement and slag or fly ash.

Figure 3. Permeameter for measuring hydraulic performance of high salt concentration waste forms

Hydraulic conductivity was measured for only two of the text mixes due to time constraints. The two mixes performed well, with the results indicating that increasing the concentration of salts in the LAW simulant did not impact the hydraulic performance of the waste form. The impact of zeolite additions to the dry blend could not be determined from these tests due to the low measured values of hydraulic conductivity.

FY2015 Accomplishments

- Demonstrated successful immobilization of wastes concentrated to 10 M sodium (double that of current process)
- Fresh properties, which dictate the ability to produce this waste form in an economical facility, have been measured and demonstrate the ability to process with existing equipment
- Cured properties, including compressive strength and hydraulic conductivity, demonstrate acceptable performance of the waste form when waste concentration is doubled
- Modifications to the dry blend composition, particularly the addition of metakaolin, enable significant increases in waste concentration without detracting from performance of the waste form

Future Directions

- Additional testing should include hydraulic conductivity measurements for mixes prepared with 10 M Na salt solutions.
- A method for hydraulic conductivity measurements with a lower detection limit should be developed.
- More data are needed regarding mixes with metakaolin additions. The mechanisms by which metakaolin improves the waste form properties and performance are not yet understood.
- Leachability data are needed for mixes formulated with high sodium concentration feeds, for both simulants and radioactive salt solutions. These data could then be used to determine acceptability of the waste forms and to predict long term performance of the waste forms in the disposal environment.

FY 2015 Publications/Presentations

- Fox, K. M., A. D. Cozzi, K. A. Roberts, and T. B. Edwards, "Cast Stone Formulation for Nuclear Waste Immobilization at Higher Sodium Concentrations," *International Journal of Applied Ceramic Technology* (in press).
- Fox, K. M., A. D. Cozzi, E. K. Hansen, and K. A. Hill, "Low Temperature Waste Form Process Intensification: FY2015 Progress Report," *U.S. Department of Energy Report SRNL-STI-2015-00448, Revision 0,* Savannah River National Laboratory, Aiken, SC (2015).

References

1. Fox, K. M., K. A. Roberts, and T. B. Edwards, "Cast Stone Formulation at Higher Sodium Concentrations," *U.S. Department of Energy Report SRNL-STI-2013-00499, Revision 2,* Savannah River National Laboratory, Aiken, SC (2013).

Acronyms

LAW Low Activity Waste
SRNL Savannah River National Laboratory
SRS Savannah River Site