Development of a Performance and Processing Property Acceptance Region for Cementitious Low-Level Waste Forms at Savannah River Site – 13174

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ABSTRACT

The Saltstone Production and Disposal Facilities (SPF and SDF) at the Savannah River Site (SRS) have been treating decontaminated salt solution, a low-level aqueous waste stream (LLW) since facility commissioning in 1990. In 2012, the Saltstone Facilities implemented a new Performance Assessment (PA) that incorporates an alternate design for the disposal facility to ensure that the performance objectives of DOE Order 435.1 and the National Defense Authorization Act (NDAA) of Fiscal Year 2005 Section 3116 are met. The PA performs long term modeling of the waste form, disposal facility, and disposal site hydrogeology to determine the transport history of radionuclides disposed in the LLW. Saltstone has been successfully used to dispose of LLW in a grout waste form for 15 years.

Numerous waste form property assumptions directly impact the fate and transport modeling performed in the PA. The extent of process variability and consequence on performance properties are critical to meeting the assumptions of the PA. The SPF has ensured performance property acceptability by way of implementing control strategies that ensure the process operates within the analyzed limits of variability, but efforts continue to improve the understanding of facility performance in relation to the PA analysis. A similar understanding of the impact of variability on processing parameters is important from the standpoint of the operability of the production facility. The fresh grout slurry properties (particularly slurry rheology and the rate of hydration and structure formation) of the waste form directly impact the pressure and flow rates that can be reliably processed. It is thus equally important to quantify the impact of variability on processing parameters to ensure that the design basis assumptions for the production facility are maintained.

Savannah River Remediation (SRR) has been pursuing a process that will ultimately establish a property acceptance region (PAR) to incorporate elements important to both processability and long-term performance properties. This process involves characterization of both emplaced product samples from the disposal facility and laboratory-simulated samples to demonstrate the effectiveness of the lab simulation. With that basis confirmed, a comprehensive variability study using non-radioactive simulants will define the acceptable PAR, or "operating window" for Saltstone production and disposal. This same process will be used in the future to evaluate new waste streams for disposal or changes to the existing process flowsheet.

INTRODUCTION

Development of a cementitious waste form for disposal of decontaminated, aqueous salt solutions at the Savannah River Site dates back to the late 1970s. Several flowsheet iterations were evaluated in an effort to produce a monolithic solid with limited permeability and high retention capability for heavy metals before finally settling on a three-component blend of Portland cement (OPC), blast furnace slag (BFS), and pulverized fly-ash (PFA). The Saltstone Production Facility was constructed during the late 1980s and commissioned in 1990 in preparation for full-scale processing and disposal of salt waste from the SRS high-level waste (HLW) tank farms. Delays in salt processing greatly reduced the operational requirement for Saltstone and the facility operated intermittently through the early 2000s.

Interim salt processing was initiated in 2007 which provided a new feed source for waste processing at the Saltstone Production Facility. The facility was extensively modified to improve the maintainability of individual process components and reduce radioactive dose to the facility operations and maintenance personnel. Also a new disposal unit design was proposed and developed that offered numerous improvements over the original structures built early in the facility's operational life. It was recognized early in the planning stages for these changes that there would be potentially significant impacts to the processability of fresh grout slurries as well as the overall performance of the disposal facility. In order to quantify these impacts, SRR Engineering initiated a long-term variability study with the goal of comprehensively documenting the important input and output parameters for the Saltstone Production Facility. Similar studies have been previously performed for HLW glass waste forms [1] that will ultimately be transported off-site for disposal in a deep geologic federal waste repository. While the scope of these studies is not identical, they are analogous in the sense that both have an ultimate goal of quantifying the impact of compositional changes on both processing and performance properties and ensuring that an overlapping region exists for these two important property envelopes.

Variability in vitrified HLW glass wastes has been characterized to a degree that properties can now be predicted based on a chemical analysis of the feed prior to introduction to the melter. Both processing parameters (liquidus temperature, melt viscosity) and performance properties (alkali leach resistance, homogeneity and phase stability) are both included in the model, which ensures there is minimal risk of feed remediation once glass melting and pouring is initiated. A similar strategy for variability study development has been pursued for cementitious LLW grout. The long term goal is to develop a comprehensive database of experimental test data to define a compositional production region which then bounds a defined set of output criteria. While the ultimate product control strategies may vary from facility to facility in their specific details, the overall vision for both processes is the same. This paper describes the work initiated to date and a general status of the program, while identifying some of the additional work planned for future years to continue to expand the size of the existing dataset.

VARIABILITY STUDY DEVELOPMENT

Demonstration of Feasibility and Parameter Definition

The first step in creation of a process variability study required the identification of some key properties and subsequent demonstration that, at nominal compositions, sufficient reproducibility could be achieved on grout replicates that a variability study could generate worthwhile data. Initial testing was performed in 2005 [2] that identified a small subset of properties of both the fresh slurry and cured grout for reproducibility testing. This effort concluded that the inherent measurement variation was sufficiently small that a larger scale study appeared viable. Having demonstrated the reasonableness of the strategy, the second step involved the identification of important output variables related to the overall processability and ultimate performance of the Saltstone waste form. The most important fresh grout slurry properties were identified to be: viscosity, gel time (the transition from liquid-solid suspension to a solid that is not freely-flowing), bleed water generation, and setting time. The primary properties of interest for the monolithic waste form are: porosity, heat of hydration (extent of reaction), hydraulic conductivity, density, and leachability. Much of this data is available for OPC pastes using potable water as the mixing medium. However, the high dissolved salt content in the waste processed at the Saltstone Production Facility has a significant impact on the reaction chemistry of the cementitious materials which necessitated the performance of this testing program. The presence of radionuclides in the waste further complicates the issue, given that for several properties there was a large amount of analytical method development required before actual sample testing could be performed.

Once the fresh and cured properties of interest were documented, the third step in setting up the study was defining the input variables so that their impact on properties could be documented. The early testing focused on water-to-cementitious material ratio, salt solution temperature, cementitious material composition, and anion concentration in the salt solution [3]. Subsequent testing has since identified the curing conditions as an important variable on the properties of the cured waste form [4,5].

Fresh Slurry Properties

There are several physical characteristics of the Saltstone slurry which must be controlled in order to ensure that the process operates reliably and within the design parameters for the major components of the production facility. The rheology of the mixture has a direct impact on the system pressure of the transfer line from the production facility to the disposal unit and will impact the efficiency and performance of the grout pumping system. Since the cementitious material is a mixture of spherical flyash particles and angular cement and slag particles, both the available mixing water and the relative composition of the dry materials are important input variables. Saltstone grouts are non-Newtonian fluids with measurable yield stress and thixotropic behavior, thus the shear history of the fluid also plays a role in the overall system performance. A matrix of 27 different grout mixtures was tested for rheology in 2011 to bound the expected variability of several of the above described input parameters [6][6]. Depending on the location of a given disposal cell, the total length of the grout transfer line can vary from 1000 to 2500 feet. Given the obvious impact on the different head requirements for the pumping system with such a significant difference in transfer line length, it is clearly important to understand the rheology of the fresh slurry.

The rate of structure formation in the grout also has important implications for facility processability. There are numerous single-point failures in the production facility that could cause temporary disruptions in the mixing and transfer of grout. A mechanical failure of the Saltstone mixer or the grout transfer pump will result in long sections of system piping containing a static and reactive product. The facility design includes a redundant pig launcher that cleans most of the piping by forcing a rubber ball down the length of the transfer facility from the point of production to the discharge in the disposal cell. Early slurry characterization efforts defined a duration called "gel time" which represented the time at which a fresh slurry would no longer flow out of a form under the influence of its own weight. This was a conservative method to bound the period which a grout slurry could remain static and still be fluidized. More recently, a force balance calculation has been performed to define the maximum yield stress that the launcher can overcome as a function of wetted pipe surface area and available launcher pressure [7][7]. Future studies will incorporate this methodology as it is more representative of the facility design and accounts for piping configuration changes as disposal cell location varies.

There are several other properties important to facility operations in the disposal cell itself, although these generally tend to relate directly to those discussed above. Slurry rheology and reactivity will impact the flowability of the grout once it is discharged and placed in the cell. Also the amount of bleed expressed during initial set will relate to the rate of reaction and the settling velocity of the particles before significant hydration structure has been created.

Cured Grout Properties

DOE O 435.1-1 and NDAA Section 3116 (10 CFR 61) require that LLW disposal at SDF must have a Performance Assessment which provides reasonable assurance that disposal will comply with specified performance objectives. The demonstration of long-term performance is achieved through mass-transport modeling that projects the fate of radionuclides and other chemicals disposed of in grout during the period of assessment [8]. The PA considers properties of the waste form, the disposal cell, and the disposal-site-specific hydrogeology in modeling the migration of radionuclides and chemicals during the assessment period. There are both chemical and physical property assumptions made for the cementitious waste form, and proposed changes to the current disposal flowsheet must be evaluated with a clear understanding of how those changes could impact these properties.

One of the primary physical barriers that Saltstone provides to limit chemical releases is the relative impermeability of the cementitious structure. The crystalline hydration products of the dry materials create a monolithic solid that maintains a relatively high degree of porosity with a tortuous path for groundwater flow. By segregating the salt solution in small interstitial pores within the grout structure with minimal interconnectivity, Saltstone maintains a low degree of hydraulic conductivity which limits the ingress of groundwater and thus the overall mass transfer of contaminants (both chemical and radiological) to the environment.

While limiting the total flow of groundwater through the waste form improves performance, it is also important that the Saltstone waste form provide high leach resistance against the groundwater ingress that does occur. During development of the Saltstone flowsheet, slag cements were shown to significantly improve the overall leachability of the grout by creating a chemically reducing environment within the monolith. The presence of iron/calcium sulfides in the slag served to ensure that the valence states of many trace heavy metals in the salt solution were kept in relatively immobile forms [9]. Thus maintaining a chemically reducing environment within the waste structure is an important feature to the overall performance of the disposal as it controls the mass transfer of chemical and radiological contaminants into the environment.

CURRENT STATUS OF VARIABILITY STUDY

The scope of such a research effort is understandably expected to stretch out over several years. While the experience gained in developing similar studies for glass waste forms is instructive, the long time frame needed to cure and react test samples compared to the relatively short time needed to cool and analyze glass samples significantly extends the duration of sample characterization. Additionally, in several instances significant analytical development has been required to create test methods for radiological samples. The added component of radiological contamination makes the effort needed for data collection significantly more challenging that similar studies on OPC pastes used for commercial purposes would require.

As of the time of writing, the Saltstone variability study has achieved most of the initial objectives identified as prerequisites when the program was conceived. Plant design reviews and operational experience has defined the most important processability parameters as well as a range of acceptable value. Performance Assessment modeling has identified the long-term properties of interest for the cured waste form and the values needed to ensure that the disposal facility will meet long term performance objectives. Analytical method development has been performed to ensure that test protocols are available to validate these properties against applicable basis requirements. Finally, development testing has identified the primary input variables that play a significant role in determining these properties.

PATH FORWARD FOR SALTSTONE VARIABILITY STUDY

With the foundations of the variability studies essentially complete, the focus for future efforts centers on data generation to expand the analyzed compositional region of potential salt solutions and cementitious material compositions. There are two significant scenarios that make this a focus of continued research.

The first driver that makes a broader understanding of compositional variability important is developing the capacity for predictive modeling of future waste streams. The Saltstone waste form is used to treat and dispose of decontaminated salt solutions from the HLW tank farms, effluent from the SRS evaporator systems that do not go to the site outfall, and low-level liquid discharges from the H-Canyon Separations facilities. Evaluation of some streams has typically required highly specific point-verification of resulting waste form properties, which has a slow turnaround time and comes late in the process when performing process impact reviews. A comprehensive model that could be used as a screening tool would significantly improve the ability of the facility to forecast the viability of future waste streams and could limit the amount of testing required when actual verification samples are produced.

The second major focus involves flowsheet optimization as a method of driving Saltstone efficiency. Much of the previous work has been performed with the objective of demonstrating that low level waste grouts can be produced that are processable and with cured properties that support facility disposal performance objectives. However, the potential exists to expand the set of currently tested grouts and realize life-cycle economies as well. Initial variability testing has shown that the cement used in the Saltstone premix does not appear to play a significant role in many of the properties of interest. Thus if a cement-free formulation can be developed that supports facility acceptance criteria, the batching and transfer of dry materials can be greatly simplified (with attendant reductions in maintenance and operational costs) while removing a source of variability from the production process. Similarly, the ratio of cementitious materials to free water directly impacts the volume of waste that can be disposed in a given volume of a disposal unit. Future variability testing that determines the performance boundaries for dissolved salt content relative to a given mass of dry material will allow for minimization of the overall volume of Saltstone disposed at SRS. This has significant impact to not only the startup costs of vault construction but also the life cycle costs for monitoring and maintenance of the disposal units once they have been filled.

CONCLUSION

The Saltstone variability study is a research effort that will likely stretch out for several years, although spending in the out-years is expected to retract significantly. This is consistent with the experience of similar efforts for high level waste glasses. The work performed to date has identified the input and output variables of interest as well as developed analytical techniques to ensure sufficient capability for data collection. The focus for future testing will center on compositional changes that have the potential to simplify the Saltstone process and optimize the balance between long-term performance and salt content in the waste form. The ultimate goal is a comprehensive database of waste form compositions and corresponding property measurements that can be used to predict fresh and cured property responses based on a forecasted change in input variables. This type of database provides a much more responsive and pro-active method of flowsheet optimization than single-point characterizations that require frequent repetition and validation.

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