Cast Stone Formulation for Nuclear Waste Immobilization at Higher Sodium Concentrations

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Abstract

Low activity radioactive waste at U.S. Department of Energy sites can be immobilized for permanent disposal using cementitious waste forms. This study evaluated waste forms produced with simulated wastes at concentrations up to twice that of currently operating processes. The simulated materials were evaluated for their fresh properties, which determine processability, and cured properties, which determine waste form performance. The results show potential for greatly reducing the volume of material. Fresh properties were sufficient to allow for processing via current practices. Cured properties such as compressive strength meet disposal requirements. Leachability indices provide an indication of expected long term performance.

Introduction

A low temperature waste form known as Cast Stone is being considered to provide supplemental Low Activity Waste (LAW) immobilization capacity for the U.S. Department of Energy Hanford site. The Cast Stone waste form and immobilization process must be tested to demonstrate compliance with the waste acceptance criteria for the disposal facility and to demonstrate that the immobilization processes can be controlled to consistently provide an acceptable waste form product. Further, Cast Stone must be tested to provide the technical basis for understanding the long-term performance of the waste form in the disposal environment. The Savannah River National Laboratory (SRNL) and the Pacific Northwest National Laboratory (PNNL) recently issued an assessment of the state of low temperature waste form development for Hanford and identified approaches for addressing technology needs.[1] This study enhances the existing Washington River Protection Solutions (WRPS) research and development program with the national laboratories to understand the performance of Cast Stone as a LAW waste form.[2,3]

The flow sheet projected for Cast Stone utilizes dry reagents (collectively referred to as premix) including ordinary portland cement, fly ash, and blast furnace slag (or slag cement). Fly ash is used in the premix due to its lower cost as compared to cement and slag. Fly ash also serves as a heat sink during curing of mass pours, reacting more slowly over time than cement or slag. Blast furnace slag is used in the premix to promote a reducing environment, which decreases the leachability of chromium and technetium in the waste form.[4]

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The LAW to be immobilized in Cast Stone is derived from the aqueous solutions and dissolved saltcake in the Hanford waste storage tanks.[6] The waste will be treated prior to processing by first removing strontium and transuranic elements using precipitation and filtration. Ion exchange columns will be used to remove cesium. The effluent from the ion exchange columns will then be concentrated in an evaporator. The concentrated LAW feed will be an alkaline solution of mainly sodium along with nitrate, hydroxide, nitrite, and carbonate, with small concentrations of several radioactive fission products. Minor components include aluminum and potassium, with anions including chloride, fluoride, phosphate, and sulfate. The LAW is expected to contain Resource Conservation and Recovery Act metals (e.g., As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) and underlying hazardous constituents (e.g., Sb, Be, Ni, and Tl), which are important with respect to land disposal restrictions.

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The LAW feed is to be mixed with the solid reagents and gravity-fed into containers for curing and disposal. To date, the testing performed with either simulated waste or actual waste had a sodium concentration of around 5 M.[5] The Savannah River Site (SRS) Saltstone Production Facility (SPF) originally operated between 3 and 7 M sodium. Recent proposed changes in the LAW salt processing flow sheets could further increase the sodium concentration for low temperature waste forms.[1] Increasing the sodium concentration in Cast Stone has the potential to significantly reduce the overall volume of the waste form, increase waste throughput rates, and reduce the time and expense needed to complete cleanup missions.

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. The anticipated volume of the Cast Stone waste form necessary to immobilize a given mass of salt can be calculated as a function of salt solution sodium molarity and the water to premix ratio (mass basis), as shown in Figure 1. As the plot illustrates, a significant reduction in the necessary volume of Cast Stone (and associated 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 ratio. Therefore, this study targeted the compositional region shaded in Figure 1.

Experimental Procedure

Based on the potential for Cast Stone volume reduction shown in Figure 1, a series of Cast Stone test mixes was selected for this high sodium concentration study. Three factors were chosen for the experimental matrix. The concentration of sodium in the simulated salt solution was varied between 7 and 10 M, which has the largest impact on reducing Cast Stone volume for a given amount of LAW (Figure 1). Water to premix ratio was varied from 0.6 (current SRS SPF baseline) up to 0.7. The blast furnace slag portion of the premix was varied from the Cast Stone baseline of 47 wt % to a reduced level of 25 wt %. Removal of technetium from the waste stream prior to immobilization is being considered in conjunction with supplemental LAW technologies to enhance the baseline Hanford Waste Treatment and Immobilization Plant (WTP) flowsheet;[1] therefore, a waste form with less reducing capacity (less slag) may be both acceptable and less expensive. Additional fly ash was used when the amount of slag in the premix was reduced, and the amount of cement was held constant.

The factors were used to develop a central composite experimental design, which is shown in Table 1. This design utilizes the three factors each at three values. It also includes six replicates of the centroid test mix, noted in the table, which allows for an analysis of the reproducibility of the fabrication and characterization methods used in the study.

The salt solution simulants used in this study were derived from the Hanford Tank Waste Operation Simulator (HTWOS) to represent the overall average composition. The HTWOS overall average composition[2] is given in Table 2 using concentrations in terms of moles of species per mole of Na. This salt simulant composition was modified to produce 7.0, 8.5, and 10.0 M Na simulants. The phosphate and fluoride levels were reduced to minimize the amount of insoluble fluorophosphate formation.

Chromium and iodine concentrations in the salt solution simulants were adjusted to support leaching experiments. Targeted concentrations were selected such that measureable values were expected to result (i.e., measured values would be above analytical detection limits) while attempting to avoid unrealistically high concentrations that may falsely represent waste form performance. Chromium concentrations that corresponded to the HTWOS 95th percentile composition were selected (4.3×10^{-3} M/M Na). Iodine concentrations were selected based on an anticipated detection limit of 0.5 ppb in the leachate and to allow the reporting of a leachability index for iodine of at least 11 at this detection limit. Note however that these limitations resulted in a targeted iodine concentration in the simulated salt solutions that was approximately two orders of magnitude higher than the expected concentration.[2] Future testing at more realistic iodine concentrations may be beneficial.

The simulated salt solutions were prepared using the method described in Appendix A of Russell et al.[6] The presence of undissolved solids was observed in all of the simulants due to their high salt concentrations. It was assumed that the future Cast Stone production facility would have the ability to process this material.

Targeted and measured compositions of the salt solution simulants are given in Table 3. Compositions were measured using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Agilent 730ES, Agilent Technologies, Santa Clara, CA) analyses for cations and Ion Chromatography (IC) (Dionex ICS-5000, Thermo Fisher Scientific Inc., Sunnyvale, CA) analyses for anions. Analyses of the total solutions were performed using samples diluted with deionized water such that the solids were dissolved. Analyses of the supernatants were performed using decanted and filtered samples. A review of the data presented in Table 3 shows that the measured concentrations met their targeted values within reason for the purposes of this study.

The cement, blast furnace slag, and fly ash used in this study were sourced from a supplier in the Hanford area (Lafarge North America, Pasco, WA). The premix materials were batched at the appropriate ratios for each mix in the test matrix and stored in sealed plastic bags. The premix was blended by manually shaking the bags.

The test mixes were prepared by mixing the appropriate masses of simulated salt solution and premix in the laboratory. The salt solution was batched into a three liter plastic pitcher. The pitcher was set under a mixer (Caframo, Ltd., Georgian Bluffs, Ontario) with an impeller consisting of four elliptical blades. The impeller was placed as close as practical to the bottom and side of the pitcher without making contact in order to maximize shear. The mixer was started at a speed of 400 rpm, and the premix was gradually added from its bag to the salt solution over a period of 1-2 minutes. Agglomerates of the premix material were observed on the bottom of the pitcher after mixing NWS-01. Therefore, for the remaining mixes, the mixer speed was increased incrementally as the premix was added, up to a final speed of 850-950 rpm. This was successful in minimizing unincorporated solids. Mixing continued for a total of about 10 minutes for each composition. A paddle was used as a baffle to break the vortex at higher mixing speeds in order to minimize air entrainment.

Immediately after mixing, samples were poured for rheology, density, and heat of hydration measurements,[a] and a series of plastic molds was filled to support measurements of bleed water, compressive strength, and leachability indices. The samples for cured properties measurements were placed into zip top plastic bags containing a moist towel to maintain a humid curing environment. The samples were cured for at least 28 days at ambient temperature in the laboratory prior to cured properties analyses.

Rheological properties of the freshly prepared test mixes were measured with a Haake VT550 rotoviscometer (Thermo Fisher Scientific Inc., Waltham, MA). The VT550 was used to obtain a

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[a] The isothermal calorimeter used for heat of hydration measurements can support eight simultaneous samples. Therefore, only the first eight test mixes could be measured after fabrication of the large batches. Smaller batches of the targeted compositions were later fabricated for the remaining heat of hydration measurements using a vibratory mixer (Resodyn™ Acoustic Mixers, Inc., Butte, MT).

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flow curve (shear stress versus shear rate data) using a concentric geometry, cylindrical bob and cup (model MV2). The MV2 bob was selected given its range of measurement and design (e.g., the only shearing surface is the cylinder itself). Measurements were obtained at the temperature of the slurry (i.e., the temperature as measured at the end of the mixing activities). The functionality of the VT550 was checked using a National Institute of Standards and Technology (NIST)-traceable N35 Newtonian viscosity oil standard at 25 °C at the beginning of each day. The VT550 was considered functional if the resulting flow curve, analyzed as a Newtonian fluid, was within ±10% of the NIST viscosity value. The flow curve used for the measurements consisted of an up curve with a linear increase in shear rate from 0 to 300 s^{-1} linearly over 2 minutes, a hold period at a shear rate of 300 s^{-1} for 30 seconds, and a down curve with a linear decrease in shear rate from 300 to 0 s^{-1} over 2 minutes. This flow curve was developed to collect data over a short time period due to the potential for gelling of the test mixes. Potential issues associated with this method are over-estimation of the properties on the up curve and under-estimation of the properties on the down curve if the fluid is very thin, due to the MV2 inertia effects. However, these issues were not observed for these test mixes. The rheology data were analyzed using a Bingham Plastic rheological model, providing yield stress and plastic viscosity values. The Haake software converts the rotational rate of the rotating surface of the bob into a shear rate assuming the material being measured is a Newtonian fluid. This shear rate is used when modeling the flow curve as a Bingham Plastic fluid. Both the up and down curves were fitted to the Bingham Plastic rheological model.[7]

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The densities of the freshly prepared mixes were measured with weight per gallon sample cups (Paul N. Gardner Company, Inc., Pompano Beach, FL) using a simplified version of ASTM D 1475, *Standard Test Method For Density of Liquid Coatings, Inks, and Related Products*.[8] Prior to testing, the volume of the sample cup with the cap in place was verified with ASTM Type I water at room temperature following the calibration steps in the ASTM D 1475 method. To

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measure each sample, the container was filled with fresh slurry to form a meniscus. The container was capped and the excess material expressed from the overflow was wiped away. The container was wiped to remove any slurry from the outer surfaces and then placed on a balance to obtain the mass of the sample. The fresh density was then calculated from the mass of the sample divided by the known volume of the container.

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Observations of free liquids or standing water were made for each of the test mixes following the method described by Harbour, et al.[9] The volume percentage of standing water was determined by measuring the residual liquid remaining atop samples cast into 2.5 cm diameter by 10 cm cylindrical plastic molds. The measurements were made after about 24 hours from mixing and again after about 72 hours to check for reabsorption. The amount of the liquid was measured as a mass due to the minimal volumes. The density of the liquid was assumed to be the same as that of the simulated salt solution used to prepare the mix in order to convert to a volume basis.

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Heat of hydration data were collected for each test mix using a Thermometric TAM Air Isothermal Calorimeter (TA Instruments, New Castle, DE) at a constant temperature of 25 °C following ASTM C-1679.[10] Sample size was approximately 18 g. Each sample was run for about 300 hours to capture as much data as practical, since hydration continues almost indefinitely. The calorimeter allows for eight samples to be measured concurrently. The data collected were reviewed to determine the total heat generated normalized to the amount of dry blend materials in the sample, the time to peak heat flow, and the peak normalized heat flow.

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The uniaxial compressive strength of each text mix was measured in triplicate after 28 and 90 days of curing following ASTM C 39/39M.[11] Triplicate samples of each test mix were cast into 5 cm diameter by 10 cm cylindrical plastic molds. After the curing period, the molds were removed with an oscillating saw. The sample mass was measured with a laboratory balance and

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its dimensions (length and diameter) were measured with calipers. It was then placed into a hydraulic load frame (CM-3000-LXI, Test Mark Industries, East Palestine, OH) for uniaxial compression testing. Unbonded neoprene pad caps were used on both ends of the specimens to account for the uneven surfaces.[13] The loading rate was set to approximately 0.24 MPa/s (35 psi/s) per the ASTM procedure. The data logging threshold was set to 1780 N (400 lb) and the break threshold was set to 2220 N (500 lb). The maximum load at fracture was recorded.

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Densities of the cured samples were measured on pieces of samples tested for 28-day compressive strength. Portions of the failed compressive strength samples were collected from internal pieces of the primary sample to limit the extent of drying. Density was determined using a laboratory balance to measure sample mass and a helium pycnometer (Quantachrome Multipycnometer, Quantachrome Instruments, Boynton Beach, FL) to measure sample volume. The porosity was measured following a procedure described elsewhere.[14] The porosity measurements took place immediately after the compression testing to minimize potential bias imparted by drying.

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The potential settling of solids in the early stages of curing was of interest given the relatively high water to premix ratios in the test matrix. It was hypothesized that settling would lead to a density gradient in the material, which could be measured after curing. For this method, samples were cast into 2.5 cm diameter by 10 cm cylindrical plastic molds and cured for at least 28 days. Each mold containing the Cast Stone was then sectioned with a hacksaw into three pieces of approximately equal size representing the top, middle, and bottom of the sample. The density of each sample was determined as described earlier after removing it from the plastic mold. Measurements were made as quickly as possible to minimize bias due to drying. The volume of each section (top, middle, and bottom) was measured three times by helium pycnometry, with the

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average of these values used in calculating the density of the section. An analysis of variance was conducted for the density gradient measurements of each text mix.

Leaching indices were determined following the EPA 1315 procedure[15] using 5 cm diameter by 10 cm cylindrical samples of each of the test mixes after curing for approximately 28 days. The testing was performed in duplicate. The leachates were analyzed via ICP-OES for cations, IC for anions, and Gas Chromatography – Mass Spectroscopy (GC-MS) (HP 6890, Agilent Technologies, Santa Clara, CA) for iodine. Initial concentrations of the contaminants in the waste form were determined via the chemical composition measurements of the cured samples, reported elsewhere.[16] The targeted iodine concentrations were used as the initial concentrations of iodine since the preparation for chemical analysis of the cured samples resulted in a significant loss of iodine. Leachability indices were determined for several of the components of the waste form, in particular nitrate, nitrite, iodine, chromium, and sodium. The average of the two duplicate leachability indices for each contaminant is reported. In cases where the concentration of the contaminant in the leachate was below the method detection limit, that detection limit was used in calculating the leachability index, with the leachability index reported as being greater than the calculated value. When duplicate analyses both produced a greater than value, the mean of the two values was reported as a greater than (>) value.

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Results

An increase in temperature of the slurry may indicate early hydration reactions, and can potentially be linked to other properties of the waste form. The temperature of the salt solution for each test mix was measured with an immersed Type K thermocouple prior to adding the premix. The temperature was measured again while mixing after all of the premix had been added to the salt solution. A third temperature measurement was taken at the end of the 10 minute mixing cycle. Temperature increases for each of the text mixes were generally small: on the order of 2 °C.

Flow behavior of the fresh Cast Stone slurry is an important parameter in designing a production facility, and will dictate the way the material is transported and fills a container or tank.

Results of the rheology measurements are given in Table 4. In general, all of the slurries were very flowable, which should aid in the design of production and disposal facilities. Density of the fresh Cast Stone slurry is also a property of importance in designing a production facility. The measured fresh density values for each test mix ranged from 1.75 to 1.84 g/ml, which is comparable to material produced at the current SRS SPF.

The presence of standing water is a preliminary indication that settling may have occurred in the mix and is also of interest for disposal facility design. Settling is of potential concern at the higher water to premix ratios investigated in this study due to the lower yield strength of the mixes. The standing water is reported as the percentage volume of fluid measured relative to the volume of hardened Cast Stone. Only three of the test mixes exhibited measureable standing water after 24 hours, and in each case the volume of liquid was small (< 0.6 vol %). Mix NWS-09 was the only composition with standing water remaining after 72 hours from mixing (0.4 vol %). Mix NWS-09 was also one of the most fluid slurries, with the lowest measured plastic viscosity and the second lowest yield strength (Table 4). It may be hypothesized that the combination of relatively low salt solution concentration (7.0 M Na), high water to premix ratio (0.70), and low slag content (25 wt % of the premix) of mix NWS-09 led to the observation of free liquid remaining after 72 hours. The relatively low volume of standing water would have to

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be further evaluated to determine whether it would be of concern to the design of a Cast Stone disposal facility.

Heat of hydration data are shown in Table 5. In general, the time to peak heat flow is shorter for the mixes fabricated with the 10.0 M sodium salt solution. Other conclusions related to the peak normalized heat flow and the normalized heat are difficult to draw based on the amount of variation in the data.

Compressive strength is commonly used as an indication of the overall quality (mix design and preparation) of the sample. The LAW waste form for disposal at the Hanford Site is required to have a compressive strength of at least 3.45 MPa (500 psi).[12] Most of the samples broke in the side fracture manner – identified as Type 5 in ASTM C39/39M – which is noted to be common with the use of unbonded caps. A compressive strength value was calculated for each specimen, and the mean of the triplicate values for each of the test mixes for each of the curing periods is reported in Table 6. After 28 days of curing, several of the test mixes had mean compressive strengths that were below the 3.45 MPa requirement. Those test mixes with higher mean compressive strengths after 28 days of curing tended to be those made with the 7.0 M Na salt solution. All of the test mixes exhibited higher mean compressive strengths after 90 days of curing. NWS-03 was the only test mix with a mean compressive strength below 3.45 MPa after 90 days of curing.

Density and porosity of the cured Cast Stone can be used as inputs to predictions of the performance of the waste form. Density was determined for three samples from each test mix,

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and the mean density data are reported in Table 7. The porosity was also measured on pieces of samples tested for compressive strength, and the data are reported in Table 7.

As mentioned earlier, settling of the solid particles is of potential concern at the higher water to premix ratios investigated in this study due to the lower viscosity of the slurries. Measurements of the density of cured Cast Stone samples as a function of height in the mold used for curing were used to determine whether settling had occurred. If settling occurred, the bottom section would be expected to have a higher density than the top section. The mean density values for the top, middle, and bottom sections of each test mix are tabulated in Table 8. Those mixes that are highlighted in Table 8 had differences in the means of the measured densities among the top, middle, and bottom sections that were statistically significant at the 95% confidence level. NWS-03 is the only mix that had a density at the bottom of the sample that was higher than that of the top of the sample with statistical significance. While some of the other mixes exhibited differences that were statistically significant, the magnitude of those differences is quite small, such that it would not be appropriate to draw further conclusions. Mix NWS-03 had a combination of high sodium molarity (10.0 M), high water to premix ratio (0.70), and low slag content (25 wt % of premix), and exhibited the lowest measured yield stress

The determination of leachability indices is a potential method of providing empirical data for use in modeling contaminant release from the waste form to the environment. Select leachability indices for the test mixes are reported in Table 9. The chromium concentrations in the leachates were below the method detection limit for many of the leaching intervals, resulting in leachability indices being reported as greater than values. The leachability indices for iodine, sodium, nitrite, and nitrate were generally similar. Any relationship between the values reported in Table 9 and the compositions of the test mixes is not readily obvious.

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Discussion

JMP Version 9.0.0[17] was used to conduct the statistical analyses of the data collected in this study, following the design of experiments outlined earlier. The Stepwise routine within JMP's Fit Model Platform was utilized to investigate for significant effects among the terms in a candidate response surface model consisting of linear terms, quadratic terms, and terms representing possible pair-wise interactions in the three factors under study: sodium molarity, premix composition, and water to premix ratio. The discussion that follows is limited to the linear terms of the model fits in order to relate the results most directly to the compositions of the test mixes.

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Mix NWS-16 also had a relatively low mean compressive strength. Note however that the standard deviation of the triplicate measurements of this mix was 4.16 MPa, which is greater than the mean value. Also note that mix NWS-16 was one of the centroid replicates, the others of which had much higher compressive strength values after 90 days of curing. It is possible that some of the NWS-16 triplicate specimens contained flaws that led to an unusually low mean measurement.¶

The analysis of the yield stress data showed that increasing the water to premix ratio decreased the yield stress. Increasing the concentration of slag in the premix increased the yield stress. The model showed that increasing sodium molarity increased yield stress, although this was a weaker effect. The analysis of the plastic viscosity data showed that increasing water to premix ratio decreased the plastic viscosity. Increasing sodium molarity increased the plastic viscosity. Increasing the concentration of slag in the premix increased the plastic viscosity, although this was a weaker effect. In general, all of the slurries were very fluid.

Fresh density increased with increasing sodium molarity, which is expected since higher sodium concentrations increase the density of the salt solution. Fresh density decreased with increasing water to premix ratio, which is expected since the density of the premix materials is higher than that of the salt solution. There is a spread in the fresh density values for the six replicates in the study, which had some impact on the ability of the model to fit the study data.

Similar to the results for the fresh density data, higher sodium molarity and lower water to premix ratios lead to higher cured density values. Increasing the water to premix ratio and increasing sodium molarity were shown to increase porosity. The increased water to premix ratio likely leads to a higher volume of pore fluid, resulting in the higher porosity measurements. The reasoning behind the sodium molarity effect on porosity is not clear from these experiments. The porosity of the waste form can potentially impact its hydraulic properties and other performance criteria.

Heat of hydration measurements 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. The least squares regression analysis for the time to peak heat flow data showed that increased sodium concentration in the salt solution reduced the time to peak heat flow. Reducing the amount of slag in the premix increased the time to peak heat flow. Higher water to premix ratios also increased the time to peak heat flow, although this was a weaker relationship. These observations may help to describe some of the cured properties of the samples, such as compressive strength as described below. The least squares regression model fit for the peak normalized heat flow data was poor due to scatter in the data, thus conclusions regarding the normalized heat flow data cannot be drawn. The least squares regression model fit for the normalized heat data was not particularly good (R-squared value of 0.79), although the results indicate a weak relation to the composition of the premix. Higher slag concentrations appeared to increase the normalized heat. This may indicate that more energy is released due to hydration reactions involving slag as opposed to those involving fly ash.

After 28 days of curing, the least squares regression analysis showed that higher sodium concentrations and higher water to premix ratios led to reduced compressive strength. This may be due to the larger amounts of porosity in these mixes, as described earlier. 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 for the time to peak heat generation, also described above. After 90 days of curing, the least squares regression analysis showed that higher sodium concentrations and higher water to premix ratios again led to reduced compressive strength. Interestingly, the premix composition did not have a significant effect on compressive strength after 90 days of curing. It is possible that further curing over this extended time period nullified any influence of the premix composition.

Mixes NWS-03 and NWS-16 stood out as having relatively low compressive strengths. Mix NWS-03 had a combination of high sodium molarity (10.0 M), high water to premix ratio (0.70), and low slag content (25 wt % of premix). NWS-03 was the only mix to exhibit a statistically significant density gradient, which, along with its low measured yield stress, indicates that settling likely occurred early in the curing process. It is hypothesized that these factors led to the relatively low compressive strength of this mix. The standard deviation of the triplicate measurements of Mix NWS-16 was 4.16 MPa, which is greater than the mean value. Also note that mix NWS-16 was one of the centroid replicates, the others of which had much higher compressive strength values after 90 days of curing. It is possible that some of the NWS-16 triplicate specimens contained flaws that led to an unusually low mean measurement.

Three contaminants were selected for the least squares regression analysis of the leaching data: nitrate, iodine, and sodium. The results for the nitrate leachability indices showed that there is a potential relationship between nitrate and premix composition, in that a higher concentration of fly ash led to a lower LI for nitrate, although there was scatter among the replicates. This may be related to faster maturation of the cementitious phases in the samples containing more slag. The models were poor fits for both the iodine and sodium leaching data, indicating that the results for these contaminants were fairly consistent, regardless of the mix composition. These results show that the leaching performance of the mixes evaluated in this study was not particularly sensitive to the factors used in this 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. Iodine was above the detection limit for all of the leachates. This indicates that lower, more representative iodine concentrations could be used for future testing.

Conclusions

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 ratio. The fresh density of the simulated Cast Stone prepared in this study 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.

Only one of the twenty test mixes exhibited standing water after 72 hours, and the amount of liquid was small. Settling of the mixes was further investigated via density gradient measurements of the cured samples. These measurements identified only one test mix where some settling appeared to have occurred, which corresponded to the lowest measured yield stress of the fresh slurries. Calorimetry indicated that more energy is released due to hydration reactions involving slag than fly ash. These measurements also showed that increased sodium concentration in the salt solution reduced the time to peak heat flow, and increasing the amount of fly ash 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. Higher fly ash concentrations appeared to decrease the normalized heat. 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 test matrices with broader factor ranges geared toward the identification of the roles played by each of the components in the mix via thermal analyses, analytical microscopy, and characterization of phase formation.

Cured density measurements were similar to the results for fresh density in that higher sodium molarity and lower water to premix ratios led to higher cured density values. Porosity measurements of the cured samples showed that increasing the water to premix ratio and increasing sodium molarity increased porosity. The increased water to premix ratio likely leads to a higher volume of pore water, resulting in the higher porosity measurements. The reasoning behind the sodium molarity effect on porosity is not clear from these experiments. The porosity of the waste form can potentially impact its hydraulic properties and other performance criteria.

After 28 days of curing, several of the test mixes had mean compressive strengths that were below the 3.45 MPa requirement for the disposal environment. Those test mixes with higher mean compressive strengths after 28 days of curing tended to be those made with the 7.0 M Na salt solution. Higher sodium concentrations and higher water to premix ratios led to reduced compressive strength. This may be due to the larger amounts of porosity in these mixes. Lower fly ash concentrations increased 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 for the time to peak heat generation. All of the test mixes exhibited higher mean compressive strengths after 90 days of curing, with only one composition having a mean compressive strength of less than 3.45 MPa. Mix NWS-03 had a combination of high sodium molarity (10.0 M), high water to premix ratio (0.70), and low slag content (25 wt % of premix), and also had the highest measured porosity and a gradient in cured density. It is hypothesized that these factors led to the relatively low compressive strength of this mix.

The measured leachability indices for the various contaminants were fairly consistent among the twenty mixes, indicating that the leaching performance of the mixes evaluated in this study was not particularly sensitive to the factors used in the experimental design. This is beneficial in demonstrating that the performance of the waste form is robust with respect to changes in the mix composition. A potential relationship between nitrate and premix composition was identified, in that a higher concentration of slag led to a higher LI for nitrate, although there was a lot of scatter among the replicates. This may be related to faster maturation of the cementitious phases in the samples containing more slag. The mechanisms of contaminant retention in Cast Stone waste forms are under further study. For example, it is hypothesized that iodine is not incorporated into the structure of the waste form but rather its migration is slowed by tortuous transport pathways. Microstructural analysis of the cementitious phases that form as a function of salt solution and premix chemistry will provide further insight into these mechanisms. A better understanding of disposal environment conditions is needed to determine acceptable levels of contaminant retention. Future studies will also investigate the hydraulic properties of Cast Stone waste forms formulated at higher sodium concentrations. Leaching of technetium is of interest for future work should technetium removal efforts be differed.

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Figure Captions

Figure 1. Calculated Cast Stone volume as a function of sodium molarity and water to premix ratio. Solid outline approximates region of current processing at the SRS SPF. Shaded area approximates high sodium concentration region of interest for this study.

Table 1. Test Mixes for High Sodium Cast Stone Study.

Identifier	Sodium Molarity (M)	Water to Premix Ratio	Dry Blend (wt %) Cement:Fly Ash:Slag	Targeted Waste Solids Loading (%)
NWS-01*	8.5	0.65	8:56:36	21
NWS-02	7.0	0.65	8:56:36	17
NWS-03	10.0	0.70	8:67:25	26
NWS-04	10.0	0.60	8:45:47	24
NWS-05*	8.5	0.65	8:56:36	21
NWS-06	7.0	0.70	8:45:47	18
NWS-07	10.0	0.60	8:67:25	24
NWS-08*	8.5	0.65	8:56:36	21
NWS-09	7.0	0.70	8:67:25	18
NWS-10	8.5	0.60	8:56:36	20
NWS-11	8.5	0.70	8:56:36	22
NWS-12*	8.5	0.65	8:56:36	21
NWS-13	10.0	0.65	8:56:36	25
NWS-14	8.5	0.65	8:45:47	21
NWS-15	10.0	0.70	8:45:47	26
NWS-16*	8.5	0.65	8:56:36	21
NWS-17	8.5	0.65	8:67:25	21
NWS-18	7.0	0.60	8:45:47	17
NWS-19	7.0	0.60	8:67:25	17
NWS-20*	8.5	0.65	8:56:36	21

*Replicates

Table 2. HTWOS Overall Average Salt Solution Simulant.[2]

Waste Constituent	Concentration (moles / mole Na)
Al	0.061
K	0.007
Na	1.000
Cl^-	0.008
CO_3^{2-}	0.056
F^-	0.006
NO_2^-	0.113
NO_3^-	0.324
PO_4^{3-}	0.010
SO_4^{2-}	0.017
TOC Total	0.015
Free OH^-	0.312
Cr	4.31E-03
Ni	6.47E-04
Pb	5.12E-05
Cd	3.20E-05
I	1.58E-04

Table 3. Targeted and Measured Salt Solution Simulant Compositions (mg/L).

Total		**Al**	**Cr**	**K**	**P**	**S**	**Si**
7.0 M Na	Targeted	11600	1565	1795	2125	3860	0
	Measured	11450	1025	2180	2015	2965	1
8.5 M Na	Targeted	14080	1900	2180	2580	4687	0
	Measured	12950	1210	2485	2195	3530	2
10.0 M Na	Targeted	16570	2236	2565	3035	5514	0
	Measured	15350	1290	2885	2565	3850	<1
Total		**F^-**	**Cl^-**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**	**PO_4^{3-}**
7.0 M Na	Targeted	840	2095	36380	140800	11565	6515
	Measured	<100	2050	37250	139000	11150	734
8.5 M Na	Targeted	1021	2543	44180	170970	14040	7910
	Measured	<100	2490	45050	168000	13550	1094
10.0 M Na	Targeted	1201	2992	51980	201140	16520	9310
	Measured	<100	3060	54700	199500	14850	2170
Supernatant		**Al**	**Cr**	**K**	**P**	**S**	**Si**
7.0 M Na	Targeted	11600	1565	1795	2125	3860	0
	Measured	11450	1380	2855	597	4365	4
8.5 M Na	Targeted	14080	1900	2180	2580	4687	0
	Measured	13600	1725	3480	644	4665	5
10.0 M Na	Targeted	16570	2236	2565	3035	5514	0
	Measured	16150	2060	4265	579	3400	6
Supernatant		**F^-**	**Cl^-**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**	**PO_4^{3-}**
7.0 M Na	Targeted	840	2095	36380	140800	11565	6515
	Measured	<100	2100	38050	142500	11450	738
8.5 M Na	Targeted	1021	2543	44180	170970	14040	7910
	Measured	<100	2565	46400	174500	12400	762
10.0 M Na	Targeted	1201	2992	51980	201140	16520	9310
	Measured	<100	3090	55950	203500	8960	559

Table 4. Rheological Properties of the Fresh Test Mixes.

Identifier	Yield Stress (Pa)	Plastic Viscosity (cP)
NWS-01*	2.34	83.4
NWS-02	2.91	51.8
NWS-03	1.68	73.1
NWS-04	4.05	117.1
NWS-05*	2.31	72.1
NWS-06	2.77	49.5
NWS-07	2.48	97.2
NWS-08*	2.50	62.7
NWS-09	1.86	41.0
NWS-10	4.00	85.3
NWS-11	1.96	57.5
NWS-12*	2.54	67.4
NWS-13	2.42	93.5
NWS-14	3.27	72.9
NWS-15	2.50	90.2
NWS-16*	2.57	65.7
NWS-17	2.07	59.5
NWS-18	4.87	71.8
NWS-19	3.03	54.8
NWS-20*	2.41	65.5

*Replicates

Table 5. Heat of Hydration Data for the Test Mixes.

Identifier	Normalized Heat (J/g)	Time to Peak Heat Flow (hr)	Peak Normalized Heat Flow (mW/g)
NWS-01*	293	66.6	2.4
NWS-02	338	68.6	1.5
NWS-03	310	50.1	2.1
NWS-04	315	38.9	3.8
NWS-05*	304	66.2	2.6
NWS-06	362	60.2	1.6
NWS-07	295	46.0	2.3
NWS-08*	305	65.2	2.7
NWS-09	289	84.6	1.0
NWS-10	284	69.2	1.7
NWS-11	285	73.3	1.4
NWS-12*	284	73.0	1.6
NWS-13	282	45.9	2.1
NWS-14	299	59.3	1.9
NWS-15	290	44.3	2.2
NWS-16*	284	72.9	1.6
NWS-17	267	77.5	1.4
NWS-18	335	58.1	1.4
NWS-19	294	75.8	1.4
NWS-20*	283	69.1	2.0

*Replicates

Table 6. 28 and 90-Day Compressive Strength Data.

Identifier	28-Day Compressive Strength (MPa)	90-Day Compressive Strength (MPa)
NWS-01*	3.38	7.58
NWS-02	9.31	18.55
NWS-03	1.17	3.17
NWS-04	4.83	8.27
NWS-05*	3.38	8.27
NWS-06	9.86	15.93
NWS-07	1.86	5.52
NWS-08*	3.86	8.83
NWS-09	4.69	15.17
NWS-10	5.72	10.62
NWS-11	2.21	7.17
NWS-12*	3.79	8.41
NWS-13	2.07	5.58
NWS-14	5.52	9.31
NWS-15	2.62	4.76
NWS-16*	3.31	3.72
NWS-17	2.76	7.93
NWS-18	15.17	23.86
NWS-19	7.38	22.20
NWS-20*	3.59	8.48

*Replicates

Table 7. Density and Porosity Data.

Identifier	Density (g/cm^3)	Porosity (%)
NWS-01*	1.78	64.3
NWS-02	1.77	61.3
NWS-03	1.80	68.3
NWS-04	1.83	63.7
NWS-05*	1.77	63.1
NWS-06	1.75	62.1
NWS-07	1.81	63.8
NWS-08*	1.78	63.9
NWS-09	1.73	62.9
NWS-10	1.82	61.8
NWS-11	1.77	65.3
NWS-12*	1.79	63.2
NWS-13	1.81	66.0
NWS-14	1.81	63.6
NWS-15	1.79	66.9
NWS-16*	1.78	63.3
NWS-17	1.77	62.2
NWS-18	1.80	58.0
NWS-19	1.78	58.3
NWS-20*	1.79	62.4

*Replicates

Table 8. Density Gradient Data for the Test Mixes.

Identifier	Location	Density (g/ml)	Identifier	Location	Density (g/ml)
NWS-01*	Top	1.72	NWS-11	Top	1.80
	Middle	1.75		Middle	1.78
	Bottom	1.62		Bottom	1.80
NWS-02	Top	1.33	NWS-12*	Top	1.82
	Middle	1.31		Middle	1.81
	Bottom	1.33		Bottom	1.82
NWS-03	Top	1.41	NWS-13	Top	1.84
	Middle	1.74		Middle	1.90
	Bottom	1.82		Bottom	1.82
NWS-04	Top	1.76	NWS-14	Top	1.83
	Middle	1.80		Middle	1.84
	Bottom	1.77		Bottom	1.84
NWS-05*	Top	1.77	NWS-15	Top	1.82
	Middle	1.72		Middle	1.83
	Bottom	1.73		Bottom	1.83
NWS-06	Top	1.72	NWS-16*	Top	1.80
	Middle	1.72		Middle	1.79
	Bottom	1.72		Bottom	1.79
NWS-07	Top	1.74	NWS-17	Top	1.78
	Middle	1.78		Middle	1.78
	Bottom	1.76		Bottom	1.80
NWS-08*	Top	1.79	NWS-18	Top	1.82
	Middle	1.75		Middle	1.82
	Bottom	1.69		Bottom	1.82
NWS-09	Top	1.75	NWS-19	Top	1.81
	Middle	1.77		Middle	1.81
	Bottom	1.75		Bottom	1.81
NWS-10	Top	1.84	NWS-20*	Top	1.81
	Middle	1.85		Middle	1.79
	Bottom	1.85		Bottom	1.81

*Replicates

Table 9. Select Leachability Indices (LI) for the Test Mixes.

Identifier	LI (Cr)	LI (I)	LI (Na)	LI (NO_2^-)	LI (NO_3^-)
NWS-01*	>11.2	7.7	8.0	7.9	7.8
NWS-02	>11.1	7.6	7.9	7.9	7.6
NWS-03	>10.7	8.0	7.8	7.8	7.6
NWS-04	>11.2	7.9	8.1	8.2	8.0
NWS-05*	>11.2	7.7	8.0	7.9	7.8
NWS-06	>11.2	7.7	7.9	7.8	7.8
NWS-07	>11.1	7.3	7.8	7.4	7.4
NWS-08*	>11.2	7.7	7.9	7.9	7.8
NWS-09	>11.3	7.3	7.8	7.5	7.5
NWS-10	>11.4	7.9	8.1	8.1	7.9
NWS-11	>11.2	7.6	8.0	7.9	7.7
NWS-12*	>11.2	7.8	8.1	8.1	7.9
NWS-13	>11.4	7.5	8.0	7.7	7.7
NWS-14	>11.2	7.9	8.1	8.2	8.1
NWS-15	>11.4	7.9	8.1	8.2	8.0
NWS-16*	>11.2	7.8	8.1	8.0	8.1
NWS-17	>11.0	7.4	7.6	7.6	7.6
NWS-18	>11.1	7.9	8.0	8.1	7.9
NWS-19	>11.2	7.4	8.0	7.6	7.5
NWS-20*	>11.2	7.8	8.0	8.0	7.9

*Replicates