



Setting and stiffening of cementitious components in Cast Stone waste form for disposal of secondary wastes from the Hanford waste treatment and immobilization plant



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ABSTRACT

Cast Stone is a cementitious waste form, a viable option to immobilize secondary nuclear liquid wastes generated from the Hanford Waste Treatment and Immobilization Plant. However, no study has been performed to understand the flow and stiffening behavior, which is essential to ensure proper workability and is important to safety in a nuclear waste field-scale application. X-ray diffraction, rheology, and ultrasonic wave reflection methods were used to understand the specific phase formation and stiffening of Cast Stone. Our results showed a good correlation between rheological properties of the fresh mixture and phase formation in Cast Stone. Secondary gypsum formation was observed with low concentration simulants, and the formation of gypsum was suppressed in high concentration simulants. A threshold concentration for the drastic change in stiffening was found at 1.56 M Na concentration. It was found that the stiffening of Cast Stone was strongly dependent on the concentration of simulant.

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1. Introduction

Secondary nuclear wastes to be processed at the Hanford Waste Treatment and Immobilization Plant (WTP) include liquid effluents from processing of high-level wastes (HLW) and low-activity wastes (LAW) [1]. A portion of technetium ⁹⁹Tc (one of the critical radioactive components in the Hanford tank waste owing to its long half-life, 0.2 million years) and other constituents of concerns (COCs) can volatilize and escape from the LAW melter and will be incorporated into a secondary liquid waste. A viable option to process such secondary liquid wastes is a cementitious waste form called Cast Stone. Generally, Cast Stone consists of Type I or II Portland cement, Class F fly ash, Grade 100 or 120 blast furnace slag (BFS), as well as secondary liquid waste. Class F fly ash is intended to prevent fast heat generation during the early hydration that might be associated with the high ionic strength of secondary waste solution. Blast furnace slag (BFS) is used to serve as a cementitious and pozzolanic binder as well as a reductant for radioactive technetium to reduce Tc(VII) to less mobile Tc(IV). Studies by Lockrem et al. [2] and Cooke et al. [3] have demonstrated that the addition of BFS as a

reductant in the Cast Stone does not degrade the performance of the waste form.

While Cast Stone has already been identified as a good candidate waste form for further evaluation and optimization, most characterization of Cast Stone has been focused on the leachability of ⁹⁹Tc [4]. General information on strength development is available, but detailed characterization of the flow and stiffening behavior of Cast Stone is still required. The flow and stiffening behavior of Cast Stone is connected to its rheology, which can be described in practice as the workability. The workability can impact the amount of labor, flowability, and quality of compaction by affecting the amount of entrapped air voids. Characterization of rheological properties of Cast Stone is even more important than in other applications of cementitious materials such as construction concrete, because the Cast Stone will contain nuclear wastes requiring specific care in terms of handling and human exposure to radiation.

The hydration reaction is mainly associated with cement in Cast Stone and includes drastic changes in ionic strength, pH, surface charges, and growth of hydration product [5,6], which will greatly affect the rheological behavior of Cast Stone paste. Although the reaction is not as significant as in the case of pure cement, BFS (or in some cases fly ash) also presents a certain degree of hydration so that the hydration of cement and slag can affect the rheological behavior of Cast Stone. Since hydration has been known to dictate pore characteristics (e.g., pore structure and pore-size distribution) of the final reaction product [7], it will also influence the leachability of the radioactive species incorporated into the waste form. Therefore, the

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hydration, rheological properties, and leachability of the waste cannot be considered separately.

The present work focuses on early stiffening and setting of Cast Stone pastes, involving Cast Stone specimens with various waste loadings and different types of simulants, in addition to specimens with each component of Cast Stone (i.e., cement, fly ash, and slag). Setting and stiffening of Cast Stone specimens were monitored using both rheological and Ultrasonic Wave Reflection (UWR) measurements: the former focuses on the early part of the hydration period while the latter focuses on monitoring the overall trend in stiffening associated with hydration. X-ray diffraction (XRD) analysis was also used to assess the mineral phases responsible for stiffening of Cast Stone. The combination of rheological and UWR measurements, along with studies of hydrated phases via XRD, provides better insight to the make-up process of Cast Stone in the early stage.

2. Experimental procedures

2.1. Simulant

Secondary waste simulants used in preparing the samples are based on the baseline caustic scrubber solution from the low-activity waste (LAW) melter off-gas treatment system (simulants S1, S2, and S3) and a blended composition (S4) that includes a bleed stream from the LAW off-gas submerged bed scrubber (SBS) and wet electrostatic precipitator condensate. The target compositions of different simulants shown in Table 1 were adapted from an analysis of a G2 flow sheet model run (MRQ 09-0019 Scenario 5.0.22a) provided to Pacific Northwest National Laboratory (PNNL) by Washington River Protection Solutions (WRPS) [8]. This spreadsheet provides estimates of the caustic scrubber composition for 241 monthly times. These target compositions were charge-balanced for the 11 major components (OH^- , NO_3^- , Al, CO_3^{2-} , Cl^- , NO_2^- , PO_4^{3-} , SO_4^{2-} , Si, K, and F^-) using sodium and then normalized to a constant sodium concentration (moles per mole Na). Therefore, 0.52 M, for example, denotes a simulant with 0.52 mol sodium per liter.

Four simulants were selected for the experiments. Simulant S1 is the median composition from the analysis. The Resource Conservation and Recovery Act (RCRA) metals, technetium, and iodine amounts

were based on their maximum concentrations (moles per mole Na) over the 241 dates. Simulant S2 represents a low nitrate plus chloride concentration, and simulant S3 represents a high nitrate plus chloride concentration for that cluster. Simulant S4 was developed as a representative of the caustic scrubber solution blended with a bleed stream from the SBS condensate tank, which will receive liquids from the low-activity waste melter SBS and the wet electrostatic precipitator. For this simulant, it was assumed that 10% of the SBS recycle stream is purged to prevent a buildup of species such as chlorides or sulfates.

2.2. Components and mixing

The cement used in this study was a commercial Portland cement (Lafarge North America Corp.) satisfying both Type I and Type II requirements in ASTM (American Standards and Test Methods) C-150 [9]. ASTM class F fly ash [10] and grade 100 blast furnace slag [11] were also used. The properties of cementitious binders are presented in Table 2. Cast Stone pastes with simulant solution volume to weight of the cementitious materials (CM) ratios (S/CM) were prepared by mixing 347.04 g cementitious materials (27.76 g cement, 156.17 g fly ash, and 163.11 g BFS) with 135 ml simulant solution, making it a S/CM ratio of 0.389.

Cast Stone pastes were mixed by hand and using a single speed commercial blender for total mixing time of about 3–5 min. Liquid (simulant or water) was added to the dry ingredients in the blender container. The paste was hand-mixed for 2–4 min depending on the consistency of the mixture that affected the incorporation of all solid particles from the wall and bottom of the mixing container. After hand-mixing was completed, a blade cover was tightly closed on the container, and the container was attached to the blender base that applies the mixing shear forces. The mixing was done in the blender for 1 min and used for the experiments.

2.3. X-ray diffraction

The as-received Type I/II Portland cement, class F fly ash, and grade 100 BFS were analyzed with X-ray diffraction (XRD) to investigate the phase compositions in the raw cementitious materials. Hydrated Cast Stone specimens were also analyzed for identifying the phases responsible for the stiffening of Cast Stone paste. Hydrated Cast Stone specimens were collected at 5 min, 30 min, and 2 h after mixing. Collected specimens were placed in a 20-mL glass vial in order to stop hydration, as follows [12]. Approximately one-third of the vial was filled with paste and methanol was added. Then the vial was shaken to dilute the water. The Cast Stone slurry was allowed to settle, the top liquid layer (a mixture of pore solution and methanol) was removed using a pipette, and fresh methanol was added. The

Table 1
Composition of WTP secondary waste simulants.

Element (mol/l)	S1 Caustic scrubber median	S2 Statistical – cluster 1 3/16/2038	S3 Statistical – cluster 2 05/28/2024	S4 Caustic scrubber/10% of SBS blend
Na	1	1	1	1
Al(OH) ₃	9.39E–02	1.14E–01	9.22E–02	4.24E–02
Si	1.88E–03	2.04E–03	7.74E–04	1.39E–02
K	5.82E–04	6.51E–04	2.18E–03	2.87E–02
NH ₄ ⁺ (total)	–	–	–	4.41E–01
OH [–]	3.98E–01	3.98E–01	3.98E–01	1.02E–08
NO ₃ [–]	3.28E–01	1.90E–01	3.97E–01	1.13E+00
CO ₃ ^{2–}	2.28E–02	4.66E–02	3.94E–02	1.04E–02
Cl [–]	2.25E–02	2.17E–02	2.91E–02	1.04E–02
NO ₂ [–]	1.20E–02	1.05E–02	3.83E–02	4.31E–02
PO ₄ ^{3–}	6.87E–03	4.85E–03	6.03E–03	5.10E–03
SO ₄ ^{2–}	4.41E–03	5.81E–03	5.14E–03	4.36E–02
F [–]	5.57E–04	3.75E–04	4.42E–04	1.02E–08
Cr	2.03E–04	2.03E–04	2.03E–04	1.09E–03
Ag	6.27E–06	6.27E–06	6.27E–06	2.35E–05
As	3.48E–05	3.48E–05	3.48E–05	1.61E–05
Cd	1.57E–06	1.57E–06	1.57E–06	2.16E–05
Hg	1.13E–05	1.13E–05	1.13E–05	5.30E–06
Pb	8.99E–06	8.99E–06	8.99E–06	8.28E–06
Tc	1.81E–05	1.81E–05	1.81E–05	5.59E–04
Re	1.81E–05	1.81E–05	1.81E–05	5.59E–04
I	4.62E–06	4.62E–06	4.62E–06	6.29E–05
TOC (as oxalate)	9.39E–02	1.14E–01	9.22E–02	4.24E–02

Table 2
Properties of materials used in the experiments.

Chemical analysis (wt %)	Cement	Fly ash	Slag
SiO ₂	20.2	49.0	32.4
Al ₂ O ₃	4.8	16.1	12.2
Fe ₂ O ₃	3.4	6.2	0.9
CaO	64.0	14.1	43.4
Na ₂ O ^{eq}	0.5	4.24	0.88
MgO	0.8	4.6	4.9
CaCO ₃	3.2	–	–
SO ₃	2.7	0.8	4.9
C ₃ S	62.22	–	–
C ₂ S	10.98	–	–
C ₃ A	6.96	–	–
C ₄ AF	9.00	–	–
Specific gravity (kg/m ³)	3.15	2.58	2.89
Specific surface area (m ² /g)	1.05	–	0.515
Average particle size (μm)	19	41	17
Color	Gray	Light brown	White

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