

Final Report

**Investigation of Alternate Ground Granulated Blast Furnace Slag
for the Saltstone Facility**

prepared by

Weiliang Gong, Hui Xu, and Ian L. Pegg

**Vitreous State Laboratory
The Catholic University of America
Washington, DC 20064**

for

**EnergySolutions, Federal EPC, Inc.
Columbia, MD 21046**

and

**Savannah River Remediation, LLC
Aiken, SC 29808**

July 24, 2015

Rev. 0, 8/26/15

Completeness of Testing:

This report describes the results of work and testing specified by the referenced SRR approved Test Plan(s). The work and any associated testing followed established quality assurance requirements and were conducted as authorized. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Results required by the Test Plan are reported. Also reported are any unusual or anomalous occurrences that are different from the starting hypotheses. The test results and this report have been reviewed and verified.

W. Gong: W. Gong Date: 8/26/15
VSL Project Manager

I.L. Pegg: I. Pegg Date: 8/26/15
VSL Program Director/Principal Investigator

G.A. Diener: G.A. Diener Date: 8/26/15
EnergySolutions Sub-Contract Manager

SRR Approval:

Steven Simner: S. Simner Date: 8/26/2015
Technical Representative
Savannah River Remediation, LLC

TABLE OF CONTENTS

SECTION 1 INTRODUCTION	4
1.1 Background	4
1.2 Objectives.....	4
SECTION 2 TEST MATRIX	6
SECTION 3 SAMPLE PREPARATION	8
3.1 Materials.....	8
3.2 Sample Preparation	8
SECTION 4 SAMPLE CHARACTERIZATION	10
4.1 Tests for Determining the Fresh Properties of Grouts	10
4.2 Tests for Determining the Properties of GGBFS	10
SECTION 5 RESULTS AND DISCUSSION	12
SECTION 6 CONCLUSIONS AND RECOMMENDATIONS	16
SECTION 7 QUALITY ASSURANCE.....	18
SECTION 8 REFERENCES.....	19

SECTION 1 INTRODUCTION

1.1 Background

The Saltstone facilities at the Savannah River Site (SRS) process and dispose of low-level radioactive salt solutions. The Saltstone Production Facility (SPF) immobilizes the salt solution waste by mixing it with a cementitious mixture to produce a free-flowing grout. Saltstone is comprised of a 45/45/10 wt% mixture of Thermally Beneficiated Class F Fly Ash (FA), Ground Granulated Blast Furnace Slag (GGBFS), and Type II Ordinary Portland Cement (OPC) mixed with salt solution at a water-to-premix (w/pm) ratio of approximately 0.6.

To date, the slag utilized as a component in saltstone, tank closure grout, and the Saltstone Disposal Units (SDU) concrete at SRS has been a Grade 100 GGBFS supplied by Holcim US Inc. (Birmingham, AL). Production of this material has ceased and alternative slag source(s) are currently being sought. Any alternate slag may have a different chemical composition in comparison to the currently utilized Holcim Grade 100 slag, and additionally, enquiries have indicated that Grade 120 slag is becoming more ubiquitously available than its Grade 100 counterpart. The slag grades are defined in ASTM C 989, *Standard Specification for Slag Cement for Use in Concrete and Mortars*, which essentially provides a comparison of the cured strength of 100% OPC with OPC-slag mixtures. Substituting with Grade 120 slag will result in a higher compressive strength slag-OPC composite than substituting with a Grade 100 material. The strength differential between the Grade 100 and 120 is provided by the smaller particle size and enhanced reactivity of the higher grade slag. Changes in source (chemistry) and grade (particle size and reactivity) have the potential to impact the fresh and/or cured properties of the cementitious materials produced at SRS, which could affect their processability or long-term performance.

This report describes the testing that has been conducted at the Vitreous State Laboratory (VSL) at The Catholic University of America to ensure that grout prepared with an alternate GGBFS exhibits equivalent performance characteristics to the current saltstone formulation. The work described in this report is responsive to the objectives outlined in the Savannah River Remediation (SRR) Statement of Work (SOW) G-SOW-Z-00022, Revision 0 [1] and the corresponding VSL Test Plan [2].

1.2 Objectives

The objectives of this work were to prepare saltstone grout compositions utilizing the existing GGBFS as well as up to four alternate GGBFS materials specified by SRR [1]. The grout mixes were prepared and subjected to the following property measurements:

- Viscosity.

- Yield stress.
- Time dependent assessment of gelation behavior during initial 24 hours of curing.
- Heat of hydration during initial 12 days of curing.

In addition, each GGBFS was analyzed for particle size distribution (PSD) and reduction capacity. Six grout samples for each composition are currently curing at room temperature and 100% relative humidity for potential additional future analysis to be defined by SRR at a later date.

SECTION 2 TEST MATRIX

For this work, SRR identified four alternate GGBFS materials that were included in the present testing program in addition to the GGBFS currently utilized in the SPF. The GGBFS materials tested are listed below:

- Holcim Grade 100 (currently utilized)
- Lehigh Grade 120
- Lafarge Grade 120
- Argos Grade 120
- Essroc Grade 100

Table 2.1 provides a summary of the test matrix for this work. All grout samples were prepared using a dry mix of 45 wt% Fly Ash, 45 wt% GGBFS, and 10 wt% Ordinary Portland Cement. The dry mix was combined at a w/pm ratio of 0.6 with the salt waste simulant specified in the SRR SOW and listed in Table 2.2 [1].

All of the samples from the test matrix were characterized with respect to the following properties using the methods described in Section 4:

- Viscosity.
- Yield stress.
- Time dependent assessment of gelation behavior during initial 24 hours of curing.
- Heat of hydration during initial 12 days of curing.

The gelation measurements were limited to 24 hours of curing since there is little benefit to determining gel that are longer than that; all of the present samples had gel time of less than 24 hours. Heat of hydration measurements were limited to 12 days due to schedule constraints and because the cumulative heat release curves have typically flattened out by that time. Thus, this duration is sufficient to provide direct comparisons between the tested materials.

Viscosity and yield stress are important rheological parameters that can affect pumping and transport of the saltstone grout to the SDUs. Gel time is another important processing parameter which can lead to process upsets if too short and excessive bleed water generation if too long. Heat of hydration during curing is important for modeling of thermal profiles in the SDUs.

In addition, each GGBFS material was analyzed for the following properties using the methods described in Section 4:

- Particle Size Distribution (PSD).
- Reduction capacity.

The particle size distribution affects surface area and reactivity and such data provide provide a simple means for comparison of alternative materials. The reduction capacity is an important parameter in the long-term performance of cured saltstone since reduction can improve the immobilization of some contaminants.

SECTION 3 SAMPLE PREPARATION

3.1 Materials

Waste Simulant. The composition of the salt waste simulant, ingredients, and their target weights to make one liter of salt waste simulant are listed in Table 2.2. Before a large batch of salt waste simulant was prepared, a half liter batch was prepared to determine the density using calibrated borosilicate glass flasks. Sodium hydroxide flake was slowly dissolved in deionized (DI) water and then the appropriate quantities of reagent grade chemicals were weighed and dissolved in the sodium hydroxide solution. The appropriate amount of DI water was then added into the flask to bring the volume to 0.5 liter. The density of the salt waste simulant was measured and determined to be 1.261 g/mL at ~22 °C.

To prepare a large batch of the salt waste simulant (e.g., 20 liters), the required quantity of sodium hydroxide flakes was dissolved in DI water in an ice bath while being stirred mechanically with an overhead laboratory stirrer. The appropriate quantities of the remaining chemicals were weighed and dissolved in the sodium hydroxide solution while stirring. Any water loss due to evaporation during dissolution of sodium hydroxide in DI water (which heats the solution) was compensated. The composition, ingredients, and their target weights to make 20 liters of salt waste simulant are listed in Table 2.3.

Dry Mix. Grout saltstone mixes were formulated using SEFA thermally beneficiated Class F fly ash, Holcim Type I/II Portland Cement, and the various types of GGBFS materials identified in Section 2. All of the grout samples were prepared with 10 wt% OPC, 45 wt% FA, and 45 wt% GGBFS at w/pm = 0.60. The SEFA fly ash and Lafarge GGBFS materials were samples obtained directly from the respective suppliers for previous work [5, 6]. Holcim Type I/II Portland Cement, GGBFS materials from Holcim, Lehigh, Essroc, and Argos were ordered by SRR and delivered to VSL directly from the respective suppliers. The mill reports, presented in the Appendix, provided certification of the grades of the GGBFS materials according to ASTM C 989.

3.2 Sample Preparation

The dry blend was prepared by mixing the prescribed amounts of solid components prior to the addition of the volume of the salt waste simulant required to achieve the desired w/pm ratio. The resulting mixture was mixed in a 7 quart planetary mixer at an intermediate speed for 10 minutes. The fresh grout samples, of about 4.6 kg batch size, were then subjected to testing for determination of the fresh properties, as described in Section 4. The compositions of the five grout mixes defined in the test matrix (Table 2.1) are shown in Table 3.1. Six saltstone grout samples for each GGBFS were cast into 2" x 4" cylindrical molds without lids. These were cured

in partially water filled, transparent plastic containers at room temperature and 100% relative humidity; the transparent plastic containers were sealed to prevent moisture loss. Constant free water was present on the sample surfaces, which indicated 100% RH. These samples, which are still curing under these conditions, were archived for possible cured property testing that may be performed at a later date as defined by SRR.

The fresh grout samples for isothermal calorimetry were prepared in a similar manner but in smaller batches. The dry components were premixed and then the salt waste simulant was added to the premixed solids and mixed at a high speed for 1 minute using a Viking hand held mixer; the batch size was about 176 grams. Approximately 7.5 grams of the fresh grout was used for each of the isothermal calorimetry experiments.

SECTION 4 SAMPLE CHARACTERIZATION

The saltstone grout samples were evaluated in terms of fresh properties (viscosity, yield stress, gel time, and heat of hydration over 12 days of curing). The GGBFS materials were evaluated for PSD and reduction capacity. Descriptions of the methods used for determining the various properties are provided below.

4.1 Tests for Determining the Fresh Properties of Grouts

Rheological Properties. Rheological properties of the fresh grouts were determined using a Haake rheometer to measure the shear stress vs. shear rate behavior, which is typically interpreted using the Bingham model for fluid flow in freshly prepared pastes [3]. The model relates shear stress and shear rate in terms of the yield stress and the plastic viscosity at a fixed time after mixing of the saltstone components. The measurements were initiated approximately 10 min after the end of mixing of the saltstone components. The measurements were performed at room temperature. However, due to the rapid stiffening of fresh grouts, rheological measurements were performed immediately, without a delay for temperature equilibration.

Gel Time. Gel time is defined as the time at which grout slurries become non-pourable [3]. The following method has been used in previous studies [3-6]. Fresh grout is poured into a series of 100 mL plastic cups and left undisturbed. At certain time intervals, the grout is poured into an empty container. This is repeated until the fresh grout develops sufficient structure such that it does not flow as a result of its own mass. The time at which the grout does not flow from the cup is designated as the gel time [3]. Although simple, this method is somewhat subjective and requires a large number of samples in order to obtain a good time resolution.

Heat of Hydration. Heat of hydration, which includes the time dependence and the quantity of the heat generated during hydration of the pastes, was measured by isothermal calorimetry using a TAM Air Isothermal Calorimeter. The procedure was developed based on the methodology described by Harbour et al. [7]. All measurements were performed at 25°C. The heat flow produced by the samples was monitored during 12 days of curing.

4.2 Tests for Determining the Properties of GGBFS

Reduction Capacity. The reduction capacity of the GGBFS materials was determined using the method of Angus and Glasser [8], as adapted by SRNL [9]. In this method, the reduction capacity, reported in units of microequivalents per gram of solid, refers to the ability of the sample material to reduce a given mass of Ce(IV) per gram of the material. Briefly, about 0.5 grams (accurately measured) of each GGBFS material was added to 25 mL of 0.0608 M Ce(IV)

solution in a 200 mL Erlenmeyer flask and the mixture was stirred for one hour with a magnetic stirrer. Next, 0.1 mL of 0.025 M ferroin indicator ($\text{Fe}(\text{o-phenanthroline})_3^{2+}$) was added to the GGBFS-Ce(IV) solution, which was then mixed for about one minute. The GGBFS suspension was then titrated with 0.050 M ferrous ammonium sulfate solution using a calibrated 100 mL burette. The end point was determined by a color change from colorless to pink. The difference between the reduction of Ce(IV) without and with the GGBFS sample was then used to calculate the reduction capacity of the sample. Triplicate measurements were made on the Lehigh slag in order to estimate the reproducibility of the method; the results showed a relative standard deviation of less than $\pm 4\%$ for the reduction capacity measurements by this method.

Particle Size Distribution. The particle size distribution of each sample was determined using a particle size analyzer (Microtrac S3500), attached to an automated small-volume recirculator. This device employs light-scattering techniques using solid-state laser diodes as a light source and detection arrays in a logarithmic progression for light collection. Samples were suspended in water and subjected to ultrasonication for 30 seconds to ensure dispersion prior to measurement.

SECTION 5 RESULTS AND DISCUSSION

This section presents the results obtained for the materials characteristics of the five GGBFS materials and the fresh properties of the saltstone grout samples prepared according to the grout formulations defined in Tables 2.1 and 3.1. The respective data are provided in Tables 5.1 - 5.5. In addition, Figures 5.1 - 5.7 provide visual comparisons of rheological properties, normalized heat flow, and heat release of the five grout samples while Figures 5.10a and 5.10b provide visual comparisons of the particle size distributions of the five GGBFS materials.

Gel Times. Gel times determined by the pour method are summarized in Table 5.2. The gel times were between 40 and 55 minutes for all of the five grout samples.

Rheological Properties. The viscosities of the fresh grout samples are plotted against shear rate in Figure 5.1. Yield stress and plastic viscosity values that were determined by fitting the flow data of the down curve to the Bingham plastic rheological model are shown in Table 5.1. The Bingham model is given by:

$$\tau = \tau_0 + \eta_{pl} \cdot \dot{\gamma} \quad (4)$$

where τ = shear stress (Pa), τ_0 = yield stress (Pa), η_{pl} = plastic viscosity (Pa.s = 1000 centipoise), and $\dot{\gamma}$ = shear rate in s^{-1} . The linear correlation coefficients of the fits were better than 0.97 for all of the five grout samples.

As shown in Figure 5.1, the fresh grout samples prepared with Holcim, Lehigh, and Lafarge slag materials show very similar viscosities while the grout samples prepared with Argos and Essroc slag materials exhibit somewhat lower viscosities. The Bingham yield stress values shown in Table 5.1 follow a similar trend with the grout samples prepared with Holcim, Lehigh, and Lafarge slag materials having the highest values (between 7.06 and 7.67 Pa) and the grout samples prepared with Argos and Essroc slags showing lower values of 3.24 Pa and 5.52 Pa, respectively. Overall, these results indicate that all of the tested slag materials produced samples with similarly low viscosities and yield stress values. The observed differences in these properties from those of the baseline material are unlikely to be large enough to result in any significant differences in processability.

Heat of Hydration. Evolution of heat flow of isothermally curing grouts provides quantitative information regarding the hydration reactions that take place over a period of time. Heat flow was measured for all of five grout samples over a period of 12 days.

Figures 5.2 and 5.3 present the normalized heat flow as a function of curing time under isothermal conditions at 25 °C for the grout samples made with each of the five slag types. The grout sample made with Holcim slag differs from the other four materials in that it exhibits a double-peak heat flow pattern, which is most evident in Figure 5.3. The first peak occurs at 1.2 hours and the second, very wide peak occurs at 13.5 hours. All the other four grout samples show a single-peak heat flow pattern similar to what has been observed previously for saltstone grout samples with the 10-45-45 formulation; this difference is discussed in more detail below. The heat flow peaks for the grout samples with Argos and Essroc slags occur at about 2 hours and the peaks for the grout samples prepared with Lehigh and Lafarge slags occur at about 3 hours.

Figure 5.4 presents the accumulated heat release as a function of curing time for the grout samples prepared with five slag types. The grout sample with Holcim slag has the lowest heat release, followed by those Lehigh and Argos slags, which have slightly higher heat releases; the grout sample with Essroc slag has the highest heat release. The accumulated heat releases at 6, 24, 48, 168, and 288 hours for all the five grout samples are listed in Table 5.2. The 7-day heat releases for the five grout samples range from 56.33 J/g to 81.29 J/g. The grout sample with Holcim slag has the lowest 7-day heat release of 56.33 J/g, the grout sample with Lehigh slag has the second lowest 7-day heat release of 61.79 J/g, and the grout sample with Essroc slag has the highest 7-day heat release of 81.29 J/g. The 12-day heat releases for the five grout samples range from 60.63 J/g to 86.74 J/g. The grout sample with Holcim slag has the lowest 12-day heat release of 60.63 J/g, the grout sample with Lehigh slag has the second lowest 12-day heat release of 65.24 J/g, which is very close to the value for the grout sample with Holcim slag. The grout sample with Essroc slag has the highest 12-day heat release of 86.74 J/g. The highest heat release in the grout samples prepared with Essroc slag is rather unexpected since the slag is defined by the supplier as Grade 100. Since the only variable in the saltstone grout mixes was the slag type, the slag reactivity can be evaluated by comparing the 12-day heat release data of the grout samples prepared with different slag materials. The slag reactivity can thus be summarized in the following sequence:

Holcim (lowest) < Lehigh < Argos < Lafarge < Essroc (highest).

If the 12-day heat release data are normalized by the value of 60.63 J/g for the grout sample with Holcim slag, the relative reactivity of slag materials can be also expressed in the following order:

1.00 (Holcim), 1.08 (Lehigh), 1.14 (Argos), 1.31 (Lafarge), and 1.43 (Essroc).

It should be noted that the activity index of a slag sample determined by ASTM C 989 with slag partially replacing OPC is generally consistent with the relative reactivity for the slag on exposure to an alkaline salt waste simulant in this study. The only exception was for Essroc. However, although the Essroc slag was specified by the supplier as a Grade 100 slag, the activity index was reported to be as high as 124 and therefore the Essroc slag should be classified as a Grade 120 slag according to ASTM C 989.

The effect of the heat of hydration on the temperature rise in the SDUs depends on a number of factors. However, for a given pouring schedule, SDU geometry, and environmental conditions, the primary factors are the magnitude of the cumulative heat release and the heat capacity and thermal conductivity of the saltstone, all of which will change somewhat with time during curing. The heat capacity and thermal conductivity would not be expected to differ significantly amongst the saltstone materials produced from the five slags tested in the present work because of the general similarity of the compositional and physical properties of these materials and the resultant saltstone materials. Consequently, the cumulative heat release is expected to be the major factor in determining any variations in the temperature rise that would be expected. Since the time dependence of the cumulative heat release is very similar for saltstone produced from all of the tested GGBFS materials (Figure 5.4), to a first approximation, given the above assumptions, the temperature rise in the SDU would be expected to depend linearly on the 12-day heat release. Thus, for example, since the 12-day heat release for the Lehigh slag is about 8% higher than that for the baseline Holcim slag, the temperature rise for the former would be expected to be about 8% higher than that for the latter.

Effect of Holcim Slag Batches on Heat of Hydration. As noted above, the grout sample made with Holcim slag showed a distinct, two-peak heat flow pattern while the grout samples made with the other four slag types showed simple single-peak heat flow patterns (Figures 5.2 and 5.3). The two-peak heat flow pattern has not been observed previously for saltstone grout samples prepared with the 10-45-45 formulation and Holcim slag Grade 100. In order to clarify this inconsistency, additional isothermal calorimetry testing was conducted on the grout samples made with three different batches of Holcim slag Grade 100. The Batch 1 slag was the one used for the present study; the Batch 2 slag was used for the Cement Free Phase 3 study [10]; and the Batch 3 slag was used for the Cement Free Phase 2b study [6] (Table 5.3). Duplicate grout samples were prepared with each of these batches of the Holcim slag and the same simulated salt solution (1.594 M NaOH) and dry mix composition in order to investigate the reproducibility of the double-peak heat flow and any effects of different Holcim batches.

Figures 5.5 and 5.6 present the normalized heat flow data obtained from those tests. The plots clearly show that the grout samples prepared with three different batches of Holcim slag all show the two-peak heat flow pattern that was observed previously in this study. The grout samples with the two newer batches of slag (Batch 1 and Batch 2) show very close heat flow behavior in terms of peak time and maximum heat flow. The grout samples prepared with the older batch of slag (Batch 3) have a slightly higher maximum heat flow than the grout samples with the newer batches of slag. It is also worth noting that the 12-day heat release for Batch 3 is very close to that observed for the Lehigh slag. Figure 5.7 presents the normalized heat release data for the grout samples prepared with these three batches of Holcim slag. Again, the grout samples with the newer batches of slag show almost identical heat release values at all curing times and the grout samples prepared with the older batch of slag show a slightly higher normalized heat release. Very good reproducibility of the heat of hydration measurements was observed for all of the duplicated grout samples, as shown in Figures 5.6 and 5.7 and in Table 5.4. For example, the three sets of normalized heat flow data with the Batch 1 slag exhibit a relative standard deviation of about 1% or less at all of the curing times (Table 5.4).

As evident from Table 5.3, in the previous tests, the three batches of Holcim slag were used for preparing 10-45-45 grout samples with salt waste simulants with different NaOH concentrations. The effect of NaOH concentration on heat of hydration is shown in Figures 5.8 and 5.9. The grout sample made with the Batch 1 slag and the 1.57 M NaOH simulant (this study) has two distinct flow peaks. The early peak of around 1.5 hours is believed to be associated with alkali activation of OPC while the peak at 10 to 13 hours is associated with alkali activation of GGBFS. The other two grout samples were made with salt waste simulants that have higher NaOH concentrations and exhibit only one heat flow peak. Apparently, the two separate heat flow peaks tend to shift and merge as the NaOH concentration in the simulated salt solution is increased. At higher NaOH concentration, geopolymerization of GGBFS in highly alkaline salt waste simulants is usually accelerated and thus the heat flow peak for GGBFS occurs earlier. Evidently, the higher NaOH causes the heat flow peak for GGBFS to shift to earlier times where it merges with the heat flow peak for OPC at around 1.5 hours, producing a single heat flow peak with a long tail extending to more than 12 hours (Figure 5.8). The effect of NaOH concentration is also evident in the normalized heat release of the grout samples. The grout samples prepared with the high NaOH simulant show a much higher heat release than the ones with lower NaOH simulants (Figure 5.9).

Particle Size Distribution. The particle size distribution of a slag material is one of the key parameters that determine the rate and degree of hydration of the saltstone grout sample. In general, the smaller the particles, the more reactive is the slag. Table 5.5 lists particle size characteristics determined in the present work for all the five slag materials along with the data from the respective mill reports. Figures 5.10a and 5.10b provide visual comparisons of the particle size distributions for the five slag materials. The mean particle sizes range from 13.8 μm to 20.5 μm for the five slag materials. Among them, the Lafarge slag has the smallest particle size (13.8 μm) and the Argos slag has the largest particle size (20.5 μm). The Holcim and Essroc slag materials have the smallest particle sizes determined in the present work and have the largest Blaine fineness values (about 640 m^2/kg). However, the measured mean particle size for Essroc slag (17.6 μm) is smaller than that for Argos (20.5 μm) but the Essroc slag has a smaller Blaine fineness (439 m^2/kg) than the Argos slag (511 m^2/kg). These differences likely reflect the fact that the fineness values are dependent on the entire particle size distribution and not just the mean particle size.

Reduction Capacity of Slag Materials. Reduction capacity testing was performed in triplicate for the Lehigh slag and in duplicate for most of the others. The results are shown in Table 5.5. The reduction capacities of the slag materials range from 537 $\mu\text{eq/g}$ to 831 $\mu\text{eq/g}$. There was little correlation between the measured reduction capacity values and the sulfide contents given in the respective mill reports. While sulfide is believed to contribute to the majority of the reduction capacity of a slag sample, the availability of sulfide species to reduce Ce(IV) to Ce(III) also depends on the dissolution rates of slag in the acidic Ce(IV) solution.

SECTION 6 CONCLUSIONS AND RECOMMENDATIONS

To date, the slag utilized as a component in saltstone, tank closure grout, and the SDU concrete at SRS has been a Grade 100 GGBFS supplied by Holcim US Inc. from their plant located in Birmingham, AL. Production of this material has ceased and alternative slag source(s) are currently being sought. Changes in slag source (chemistry) and grade (particle size and reactivity) have the potential to impact the fresh and/or cured properties of the cementitious materials produced at SRS, which in turn may affect their processability or long-term performance. Testing was performed on the present Holcim GGBFS slag and four potential alternative GGBFS materials selected by SRR. The testing included the GGBFS materials themselves as well as the fresh properties of saltstone samples made from those materials. The objective of this work was to collect data to ensure that grout prepared with an alternate GGBFS exhibits equivalent performance characteristics to the current saltstone formulation.

The results from this work show that the five GGBFS materials tested produced grouts with broadly similar properties:

- Yield stress ~ 7 Pa, except for Argos (5.52 Pa) and Essroc (3.24 Pa)
- Viscosity ~51 – 72 cP
- Gel time ~50 – 55 min, except for Argos (45 min) and Essroc (40 min)
- Holcim showed the lowest 12-day heat release (61 J/g), followed by Lehigh (65 J/g); Essroc was highest (87 J/g).

The reduction capacities and particle size distributions of the five GGBFS materials are also quite similar:

- Reduction capacity 722 – 831 $\mu\text{eq/g}$, except for Argos (537 $\mu\text{eq/g}$)
- Mean particle size ~ 14 – 18 μm , except for Argos (21 μm).

Based on these results, the four new GGBFS materials that were tested appear to be reasonable candidates to consider as potential replacements for the present Holcim Grade 100 GGBFS. However, amongst these, the Argos and Essroc GGBFS materials tended to exhibit properties that were more disparate from those of the Holcim Grade 100 GGBFS material. In particular, the Argos material exhibited the lowest reduction capacity, which is an important parameter in the long-term performance of the cured saltstone, especially with respect to technetium immobilization. Similarly, the Essroc material exhibited the highest heat release, which is a potentially important factor for curing in the vaults and the extent of flammable vapor generation. Consequently, both the Lehigh and the Lafarge GGBFS materials would be better choices in these respects. Amongst these two materials, the Lehigh GGBFS has a higher reduction capacity and a significantly lower heat release. In fact, the Lehigh material exhibits the

highest reduction capacity of all of the materials tested (about 12% higher than Holcim) and the lowest heat release of all of the alternative materials tested (about 8% higher than Holcim).

The effect of the heat of hydration on the temperature rise in the SDUs depends on a number of factors. However, for a given pouring schedule, SDU geometry, and environmental conditions, the primary factors are the magnitude of the cumulative heat release and the heat capacity and thermal conductivity of the saltstone, all of which will change somewhat with time during curing. The heat capacity and thermal conductivity would not be expected to differ significantly amongst the saltstone materials produced from the five slags tested in the present work because of the general similarity of the compositional and physical properties of these materials and the resultant saltstone materials. Consequently, the cumulative heat release is expected to be the major factor in determining any variations in the temperature rise that would be expected. Since the time dependence of the cumulative heat release is very similar for saltstone produced from all of the tested GGBFS materials (Figure 5.4), to a first approximation, given the above assumptions, the temperature rise in the SDU would be expected to depend linearly on the 12-day heat release. Thus, for example, since the 12-day heat release for the Lehigh slag is about 8% higher than that for the baseline Holcim slag, the temperature rise for the former would be expected to be about 8% higher than that for the latter.

Overall, therefore, Lehigh Grade 120 GGBFS appears to be a reasonable replacement for the current Holcim Grade 100 GGBFS and is the recommended selection based on the results from the present work. Lafarge Grade 120 GGBFS is the second best choice amongst the materials tested and is recommended as a back-up option based on the results from the present work. The Argos and Essroc materials remain potential candidates but SRR would need to determine the impacts and acceptability of the more disparate saltstone properties produced by these materials, such as lower reduction capacities and higher heats of hydration, prior to use.

SECTION 7 QUALITY ASSURANCE

Testing was performed according to the existing quality assurance program that is in place at the VSL. That QA program is compliant with applicable criteria of 10 CFR 830.120, Nuclear Safety Management; Office of Civilian Waste Management DOE/RW-0333P, Quality Assurance Requirements and Description (QARD) Revision 20; the American Society of Mechanical Engineers (ASME) NQA-1, 2000; and DOE Order 414.1 C, Quality Assurance. The VSL quality assurance program is supplemented by a Quality Assurance Project Plan for SRR work conducted at VSL; test and procedure requirements by which the testing activities were planned and controlled are defined in that plan. The program is supported by VSL standard operating procedures that were used for this work.

This work did not include any HLW waste form affecting activities and therefore the requirements of DOE/RW-0333P were not applicable.

SECTION 8 REFERENCES

- [1] “General Technical and Quality Requirements For EnergySolutions/Vitreous State Laboratory for Investigating Alternate GGBFS Sources for Saltstone,” Statement of Work, G-SOW-Z-00022, Rev. 0, Savannah River Remediation, LLC, Aiken, SC, April 20, 2015.
- [2] “Investigation of Alternate Ground Granulated Blast Furnace Slag for the Saltstone Facility,” W. Gong and I.L. Pegg, Test Plan, VSL-15T3740-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 5/14/2015.
- [3] “Operational and Compositional Factors that Affect the Performance Properties of ARP/MCU Saltstone Grout,” M.M. Reigel, T.B. Edwards, and B.R. Pickenheim, SRNL-STI-2011-00665, Savannah River National Laboratory, Aiken, SC, February 2012.
- [4] “Development of Cement-Free Saltstone Formulations - Phase 1,” A.E. Papathanassiou, W. Gong, and I.L. Pegg, VSL-12R2420-1 Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 2/28/2013.
- [5] “Development of Cement-Free Saltstone Formulations - Phase 2,” A.E. Papathanassiou, W. Gong, H. Xu, Howard Abramowitz, and I.L. Pegg, VSL-14R2890-1 Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 2/17/2014.
- [6] “Development of Cement-Free Saltstone Formulations - Phase 2b,” W. Gong, H. Xu, H. Gan, K. Gilbo, and I.L. Pegg, VSL-14R2890-1 Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 10/31/2014.
- [7] “Heat of Hydration of Saltstone Mixes – Measurement by Isothermal Calorimetry,” J.R. Harbour, V.J. Williams, and T.B. Edwards, SRNL-STI-2007-00263, Savannah River National Laboratory, Aiken, SC, May 2007.
- [8] “The Chemical Environment in Cement Matrices,” M.J. Angus and F.P. Glasser, *Mar. Res. Soc. Symp. Proc.* 50: 547-556 (1985).
- [9] “Reduction Capacity of Saltstone and Saltstone Components,” K.A. Roberts and D.I. Kaplan, SRNL-STI-2009-00637, Rev. 0, Savannah River National Laboratory, Aiken, SC, November, 30, 2009.
- [10] “Development of Cement-Free Saltstone Formulations - Phase 3,” W. Gong, K. Gilbo, and I.L. Pegg, Test Plan, VSL-14T3350-1, Rev. 0, Vitreous State Laboratory, The Catholic University of America, Washington, DC, 9/30/2014.

Table 2.1. Test Matrix.

Sample ID	Wt%							w/pm Ratio
	Cement – Holcim OPC Type II	Fly Ash – SEFA Class F	GGBFS*					
			Holcim Grade 100	Lehigh Grade 120	LaFarge Grade 120	Argos Grade 120	ESSROC Grade 100	
BFS-1	10	45	45	0	0	0	0	0.6
BFS-2	10	45	0	45	0	0	0	0.6
BFS-3	10	45	0	0	45	0	0	0.6
BFS-4	10	45	0	0	0	45	0	0.6
BFS-5	10	45	0	0	0	0	45	0.6

Note: All grout samples utilized the waste simulant composition in Table 2.2

Table 2.2. Chemical Compositions, Reagents Used, and Target Masses to Make One Liter of Salt Waste Simulant.

Analyte	Target Molar Concentration	Reagent	Molecular Weight	Assay	Target Mass (g)
Al	0.054	Aluminum Nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.13	0.992	20.421
CO_3^{2-}	0.176	Sodium Carbonate, Na_2CO_3	105.99	0.998	18.691
PO_4^{3-}	0.012	Sodium Phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	380.12	1.000	4.561
SO_4^{2-}	0.059	Sodium Sulfate, Na_2SO_4	142.04	0.999	8.393
NO_3^-	3.159	Sodium Nitrate, NaNO_3	84.99	0.997	269.306
NO_2^-	0.368	Sodium Nitrite, NaNO_2	69.00	0.997	25.467
NaOH	1.594	Sodium Hydroxide, NaOH	40.01	0.992	64.290
H_2O	N/A	D.I. Water	18.02	1.000	849.870

Table 2.3. Chemical Compositions, Reagents Used, and Target Masses to Make Twenty Liters of Salt Waste Simulant.

Analyte	Target Molar Concentration	Reagent	Molecular Weight	Assay	Target Mass (g)
Al	0.054	Aluminum Nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.13	0.992	408.412
CO_3^{2-}	0.176	Sodium Carbonate, Na_2CO_3	105.99	0.998	373.827
PO_4^{3-}	0.012	Sodium Phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	380.12	1.000	91.230
SO_4^{2-}	0.059	Sodium Sulfate, Na_2SO_4	142.04	0.999	167.862
NO_3^-	3.159	Sodium Nitrate, NaNO_3	84.99	0.997	5386.124
NO_2^-	0.368	Sodium Nitrite, NaNO_2	69.00	0.997	509.333
NaOH	1.594	Sodium Hydroxide, NaOH	40.01	0.992	1285.805
H_2O	N/A	D.I. Water	18.02	1.000	16997.407

Table 3.1. Recipes for Saltstone Grout Mixes with Different Slag Types (wt%).

Test#	Variation	OPC	FA	GGBFS	Waste Simulant	Sum
BFS-1	Holcim Slag Grade 100	5.33	23.97	23.97	46.74	100.00
BFS-2	Lehigh Slag Grade 120	5.33	23.97	23.97	46.74	100.00
BFS-3	Lafarge Slag Grade 120	5.33	23.97	23.97	46.74	100.00
BFS-4	Argos Slag Grade 120	5.33	23.97	23.97	46.74	100.00
BFS-5	Essroc Slag Grade 100	5.33	23.97	23.97	46.74	100.00

Table 5.1. Properties of Fresh Grout Samples Prepared with Different Slag Types.

Grout ID	GGBFS Type	Rheology		Gel Time by Pour Method
		Yield Stress (Pa)	Plastic Viscosity (cP)	
HOL-BFS-GT	Holcim Slag Grade 100	7.14	67.75	50 min
LEH-BFS-GT	Lehigh Slag Grade 120	7.67	57.65	55 min
LAF-BFS-GT	Lafarge Slag Grade 120	7.06	71.69	50 min
ARG-BFS-GT	Argos Slag Grade 120	5.52	55.61	45 min
ESS-BFS-GT	Essroc Slag Grade 100	3.24	50.72	40 min

Table 5.2. Heat of Hydration of Grout Samples Prepared with Different Slag Types.

GGBFS Type	Normalized Heat Release, J/g					Heat Flow Data	
	6 hrs	24 hrs	48 hrs	7 days	12 days	Peak Time, hrs	Max Heat Flow, mW/g
Holcim Slag Grade 100	9.60	29.66	41.42	56.33	60.63	First: 1.16 Second: 13.48	First: 0.66 Second: 0.38
Lehigh Slag Grade 120	25.31	42.33	50.17	61.79	65.24	3.06	1.43
Lafarge Slag Grade 120	22.47	44.89	55.92	73.67	79.71	3.03	1.21
Argos Slag Grade 120	27.17	45.06	53.25	65.38	68.94	1.89	1.64
Essroc Slag Grade 100	22.59	46.49	60.59	81.29	86.74	2.15	1.52

Table 5.3. Information on Grout Samples Prepared with Different Batches of Holcim Slag.

Slag Batch	CUA#	Grout ID	Alkalinity of Salt Waste Simulant	Project	Reference
Batch 1	#124544	HOL-BFS-IC	1.60 M NaOH	This study	This study
Batch 2	#124084	Ref-ST-IC	2.06 M NaOH	Cement Free Phase 3	[10]
Batch 3	#123513	CF2.00M1	2.50 M NaOH	Cement Free Phase 2b	[6]

Table 5.4. Heat of Hydration of Grout Samples Prepared with Different Batches of Holcim Slag.

Slag Batch	Grout ID	Normalized Heat Release, J/g					First Peak		Second Peak	
		6 h	24 h	48 h	168 h (7 d)	288 h (12 d)	Peak Time, hours	Max Heat Flow, mW/g	Peak Time, hours	Max Heat Flow, mW/g
Batch 1	HOL-BFS-IC	9.60	29.66	41.42	56.33	60.63	1.16	0.66	13.48	0.38
	HOL1-BFS-IC1	9.73	30.07	41.01	55.49	60.12	1.17	0.64	11.19	0.40
	HOL1-BFS-IC2	9.58	29.78	40.80	55.21	59.67	1.23	0.64	11.83	0.40
	Mean	9.64	29.84	41.08	55.68	60.14	-	-	-	-
	Stand. Dev.	0.08	0.21	0.32	0.58	0.48	-	-	-	-
Batch 2	HOL2-BFS-IC1	9.41	28.98	39.76	54.71	58.97	1.49	0.50	9.96	0.41
	HOL2-BFS-IC2	9.11	28.64	39.78	55.30	59.99	1.49	0.51	10.80	0.40
Batch 3	HOL3-BFS-IC1	11.25	34.81	45.89	61.78	66.70	1.81	0.56	8.54	0.54
	HOL3-BFS-IC2	11.10	34.12	45.24	60.88	65.58	1.68	0.59	10.16	0.53

Table 5.5. Characteristics of GGBFS Materials for Preparing Saltstone Grout Samples.

GGBFS Type	Mill Report Data			VSL Determined Slag Characteristics		
	Activity Index	Sulfide	Blaine fineness (m ² /kg)	Vol. % Particles Passing 22 μm	Mean Particle Size, μm	Reduction Capacity, μeq/g
Holcim Slag Grade 100	116	1.0%	643	78.72	16.05	722
Lehigh Slag Grade 120	124	0.9%	539	73.39	18.47	812
Lafarge Slag Grade 120	129	0.8%	642	85.88	13.76	740
Argos Slag Grade 120	125	0.9%	511	67.94	20.54	537
Essroc Slag Grade 100	124	0.8%	439	75.50	17.62	831

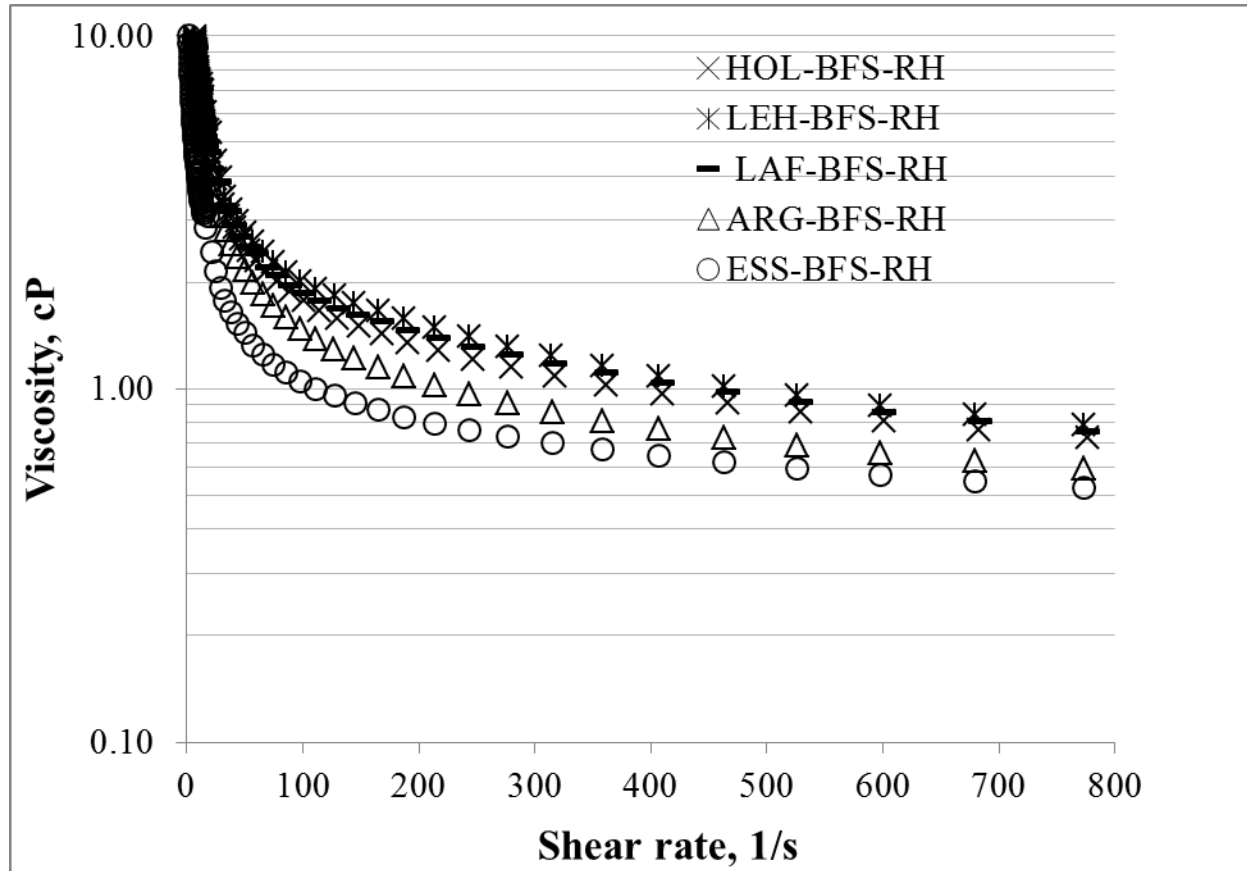


Figure 5.1. Viscosity as a function of shear rate for five saltstone grout samples.

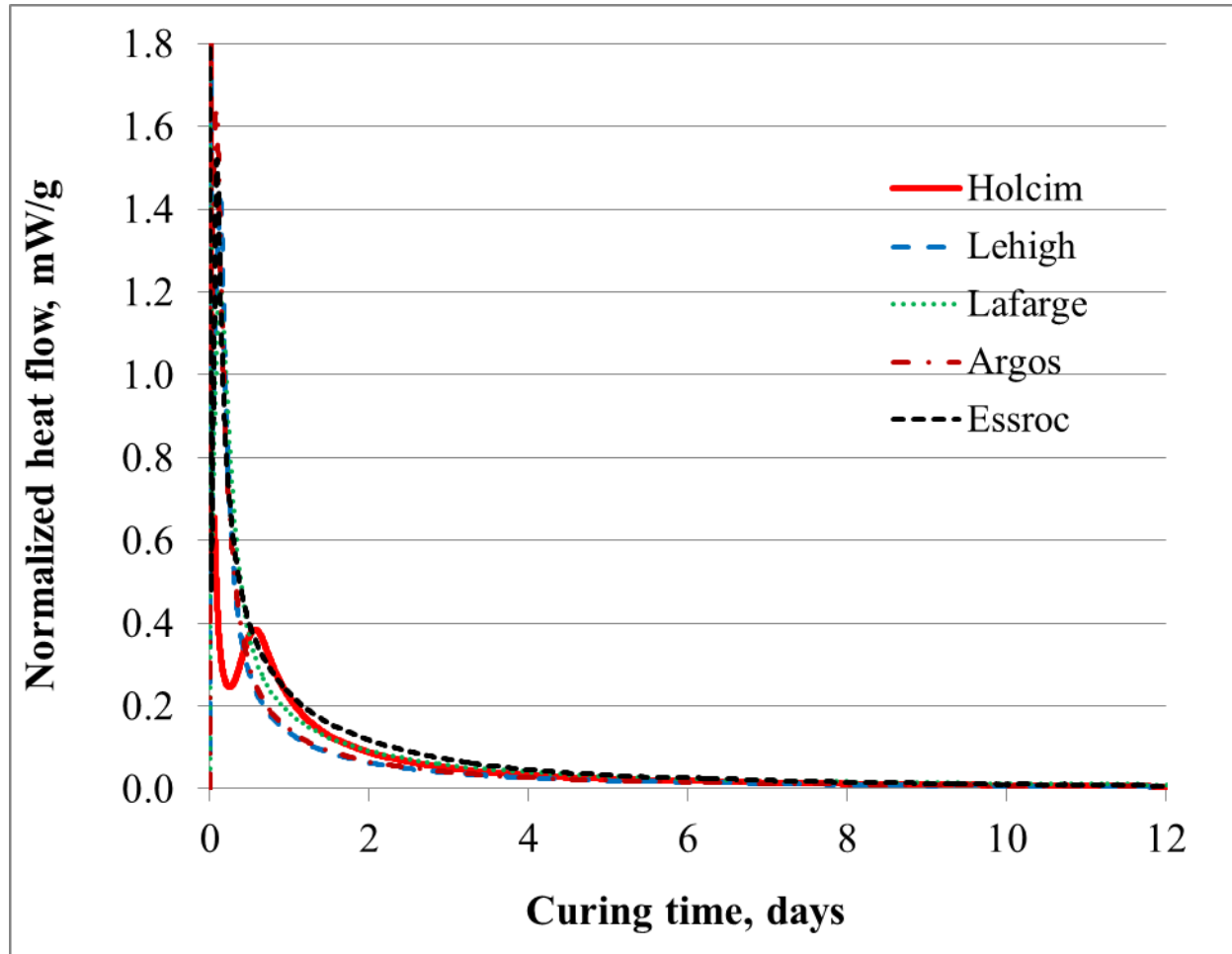


Figure 5.2. Effect of GGBFS type on normalized heat flow from saltstone grout samples.

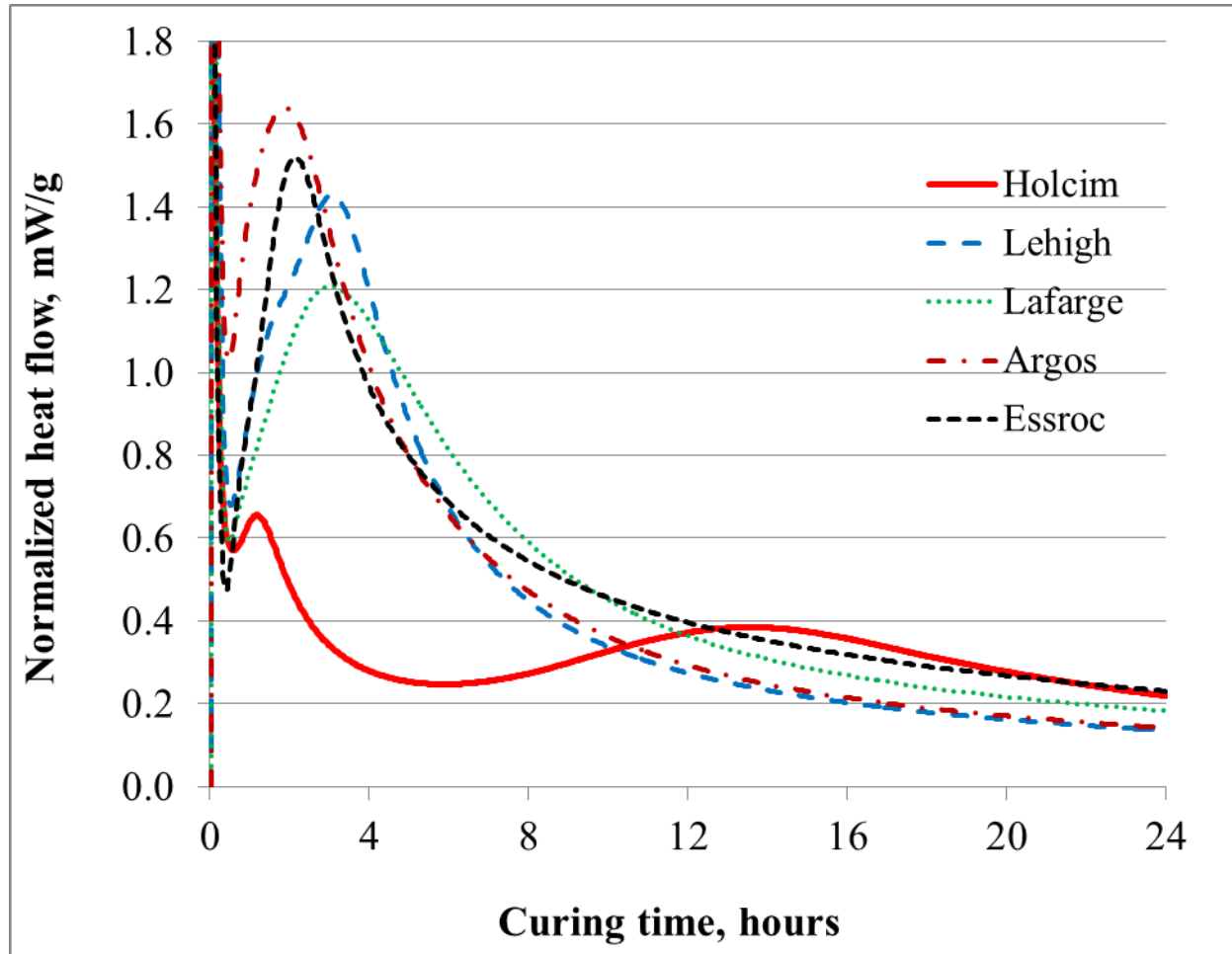


Figure 5.3. Effect of GGBFS type on normalized heat flow from saltstone grout samples during the first 24 hours.

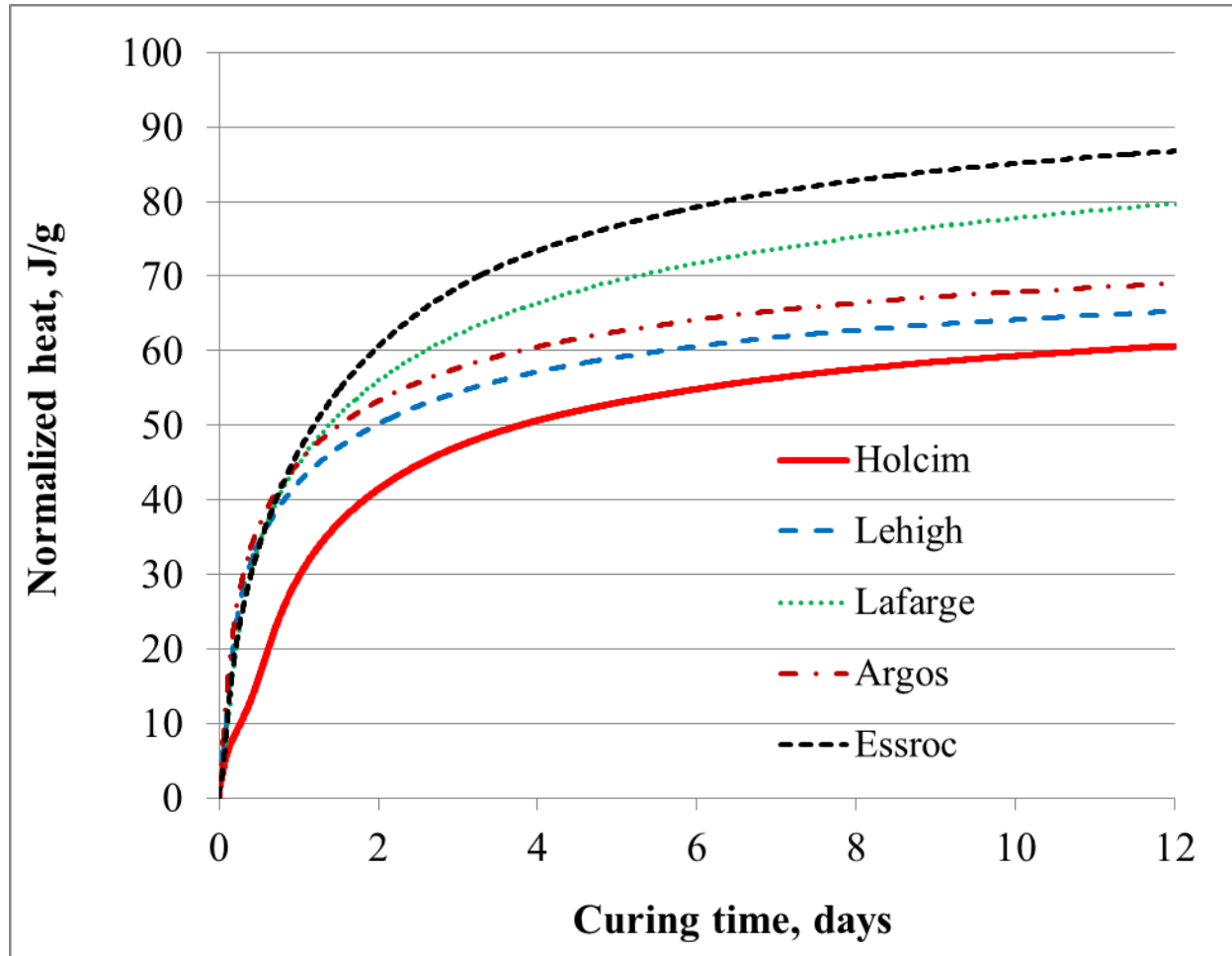


Figure 5.4. Effect of GGBFS type on normalized heat release from saltstone grout samples.

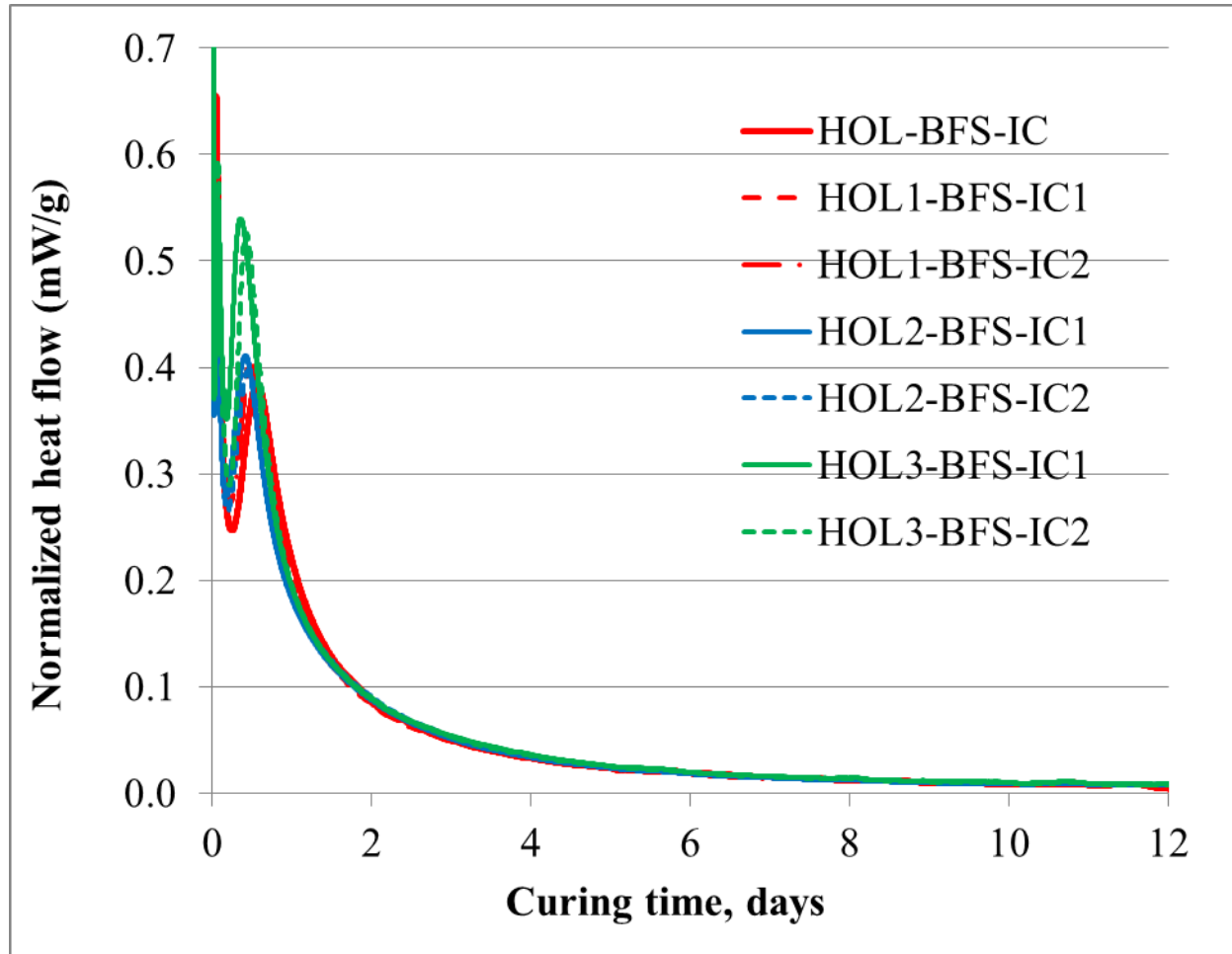


Figure 5.5. Effect of different Holcim slag batches on normalized heat flow from saltstone grout samples.

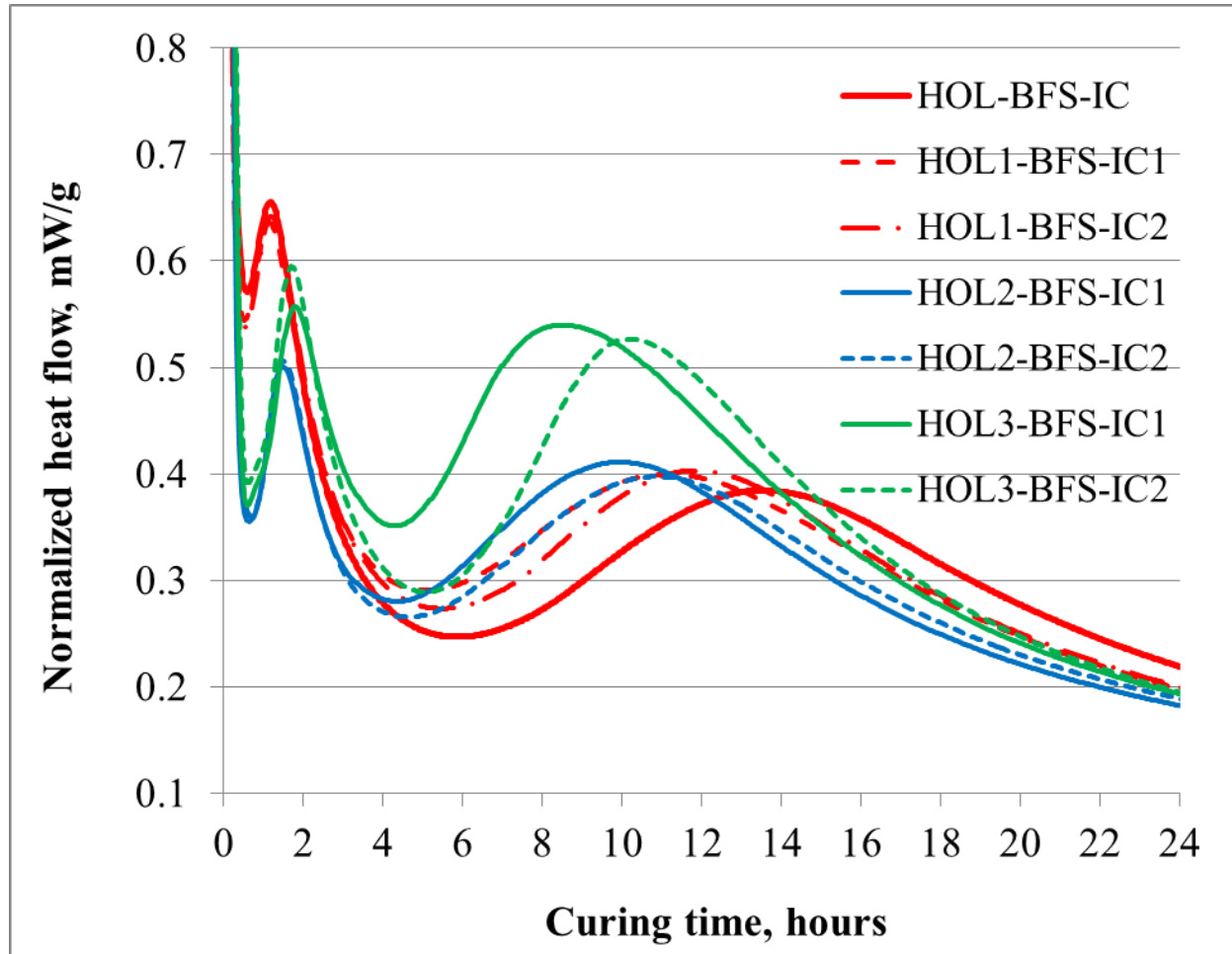


Figure 5.6. Effect of different Holcim slag batches on normalized heat flow from saltstone grout samples during the first 24 hours.

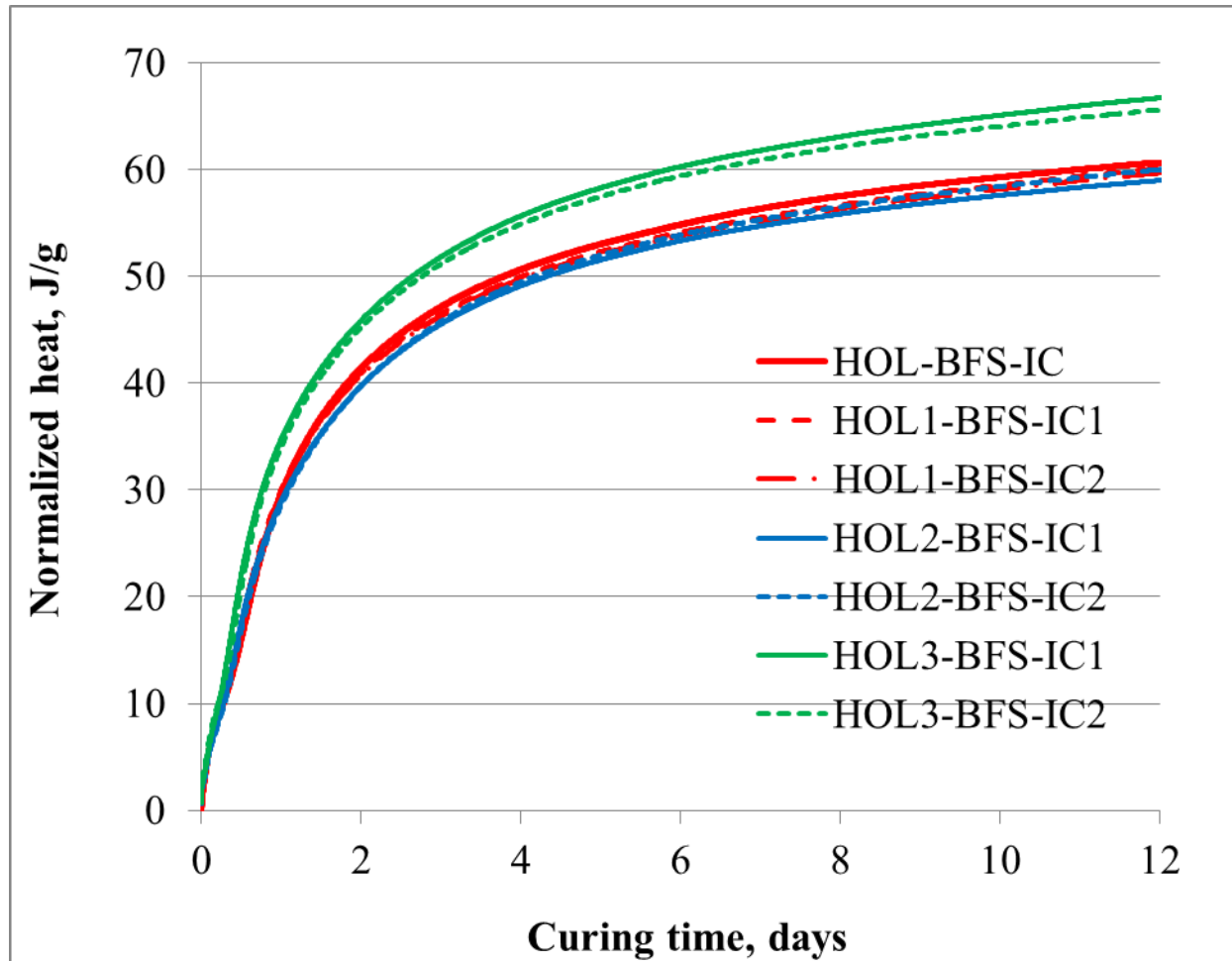


Figure 5.7. Effect of different Holcim slag batches on normalized heat release from saltstone grout samples.

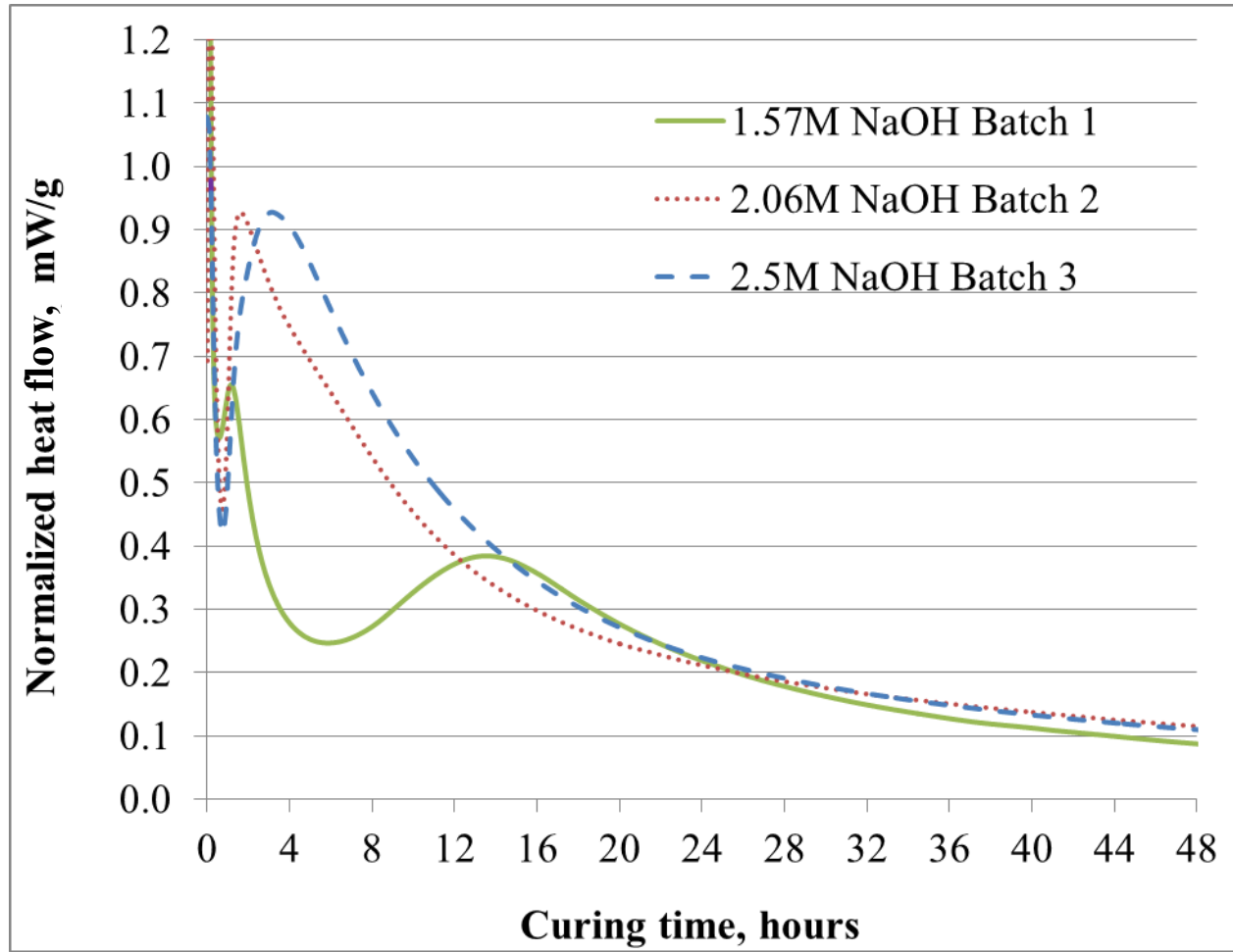


Figure 5.8. Effect of NaOH concentration in simulated salt solutions on normalized heat flow from saltstone samples.

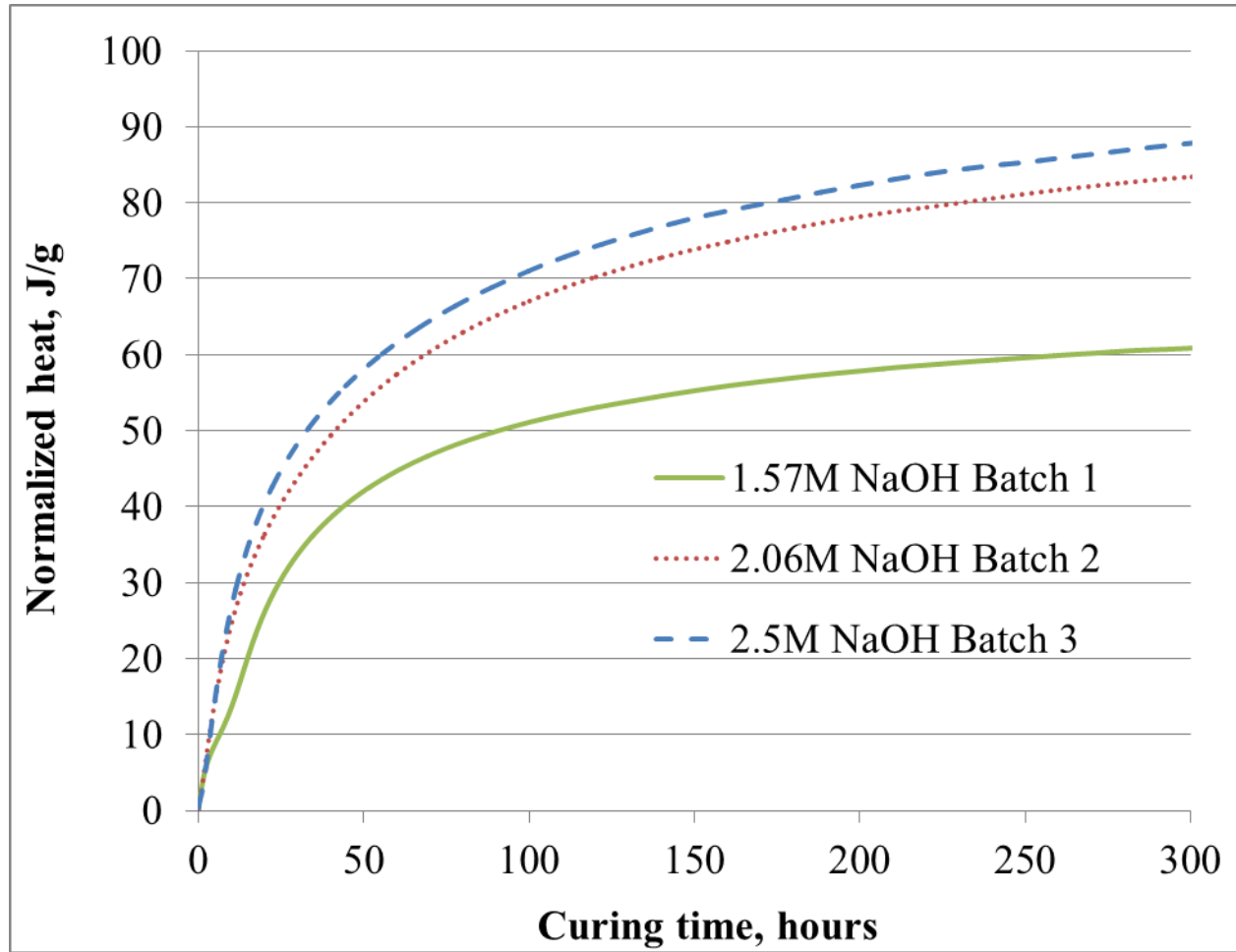


Figure 5.9. Effect of NaOH concentration in simulated salt solutions on normalized heat release from saltstone samples.

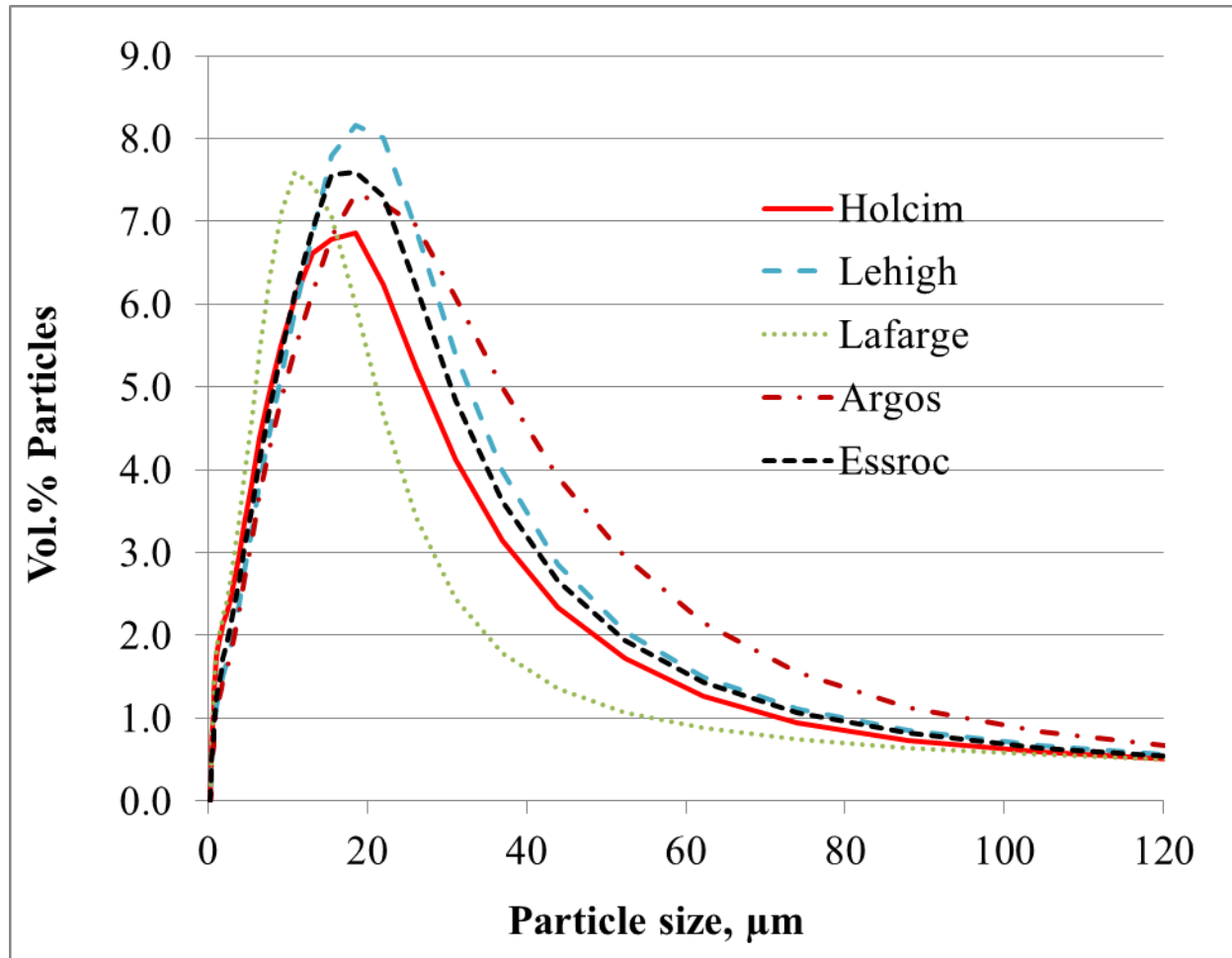


Figure 5.10a. Particle size distributions of various GGBFS materials in terms of volumetric statistics.

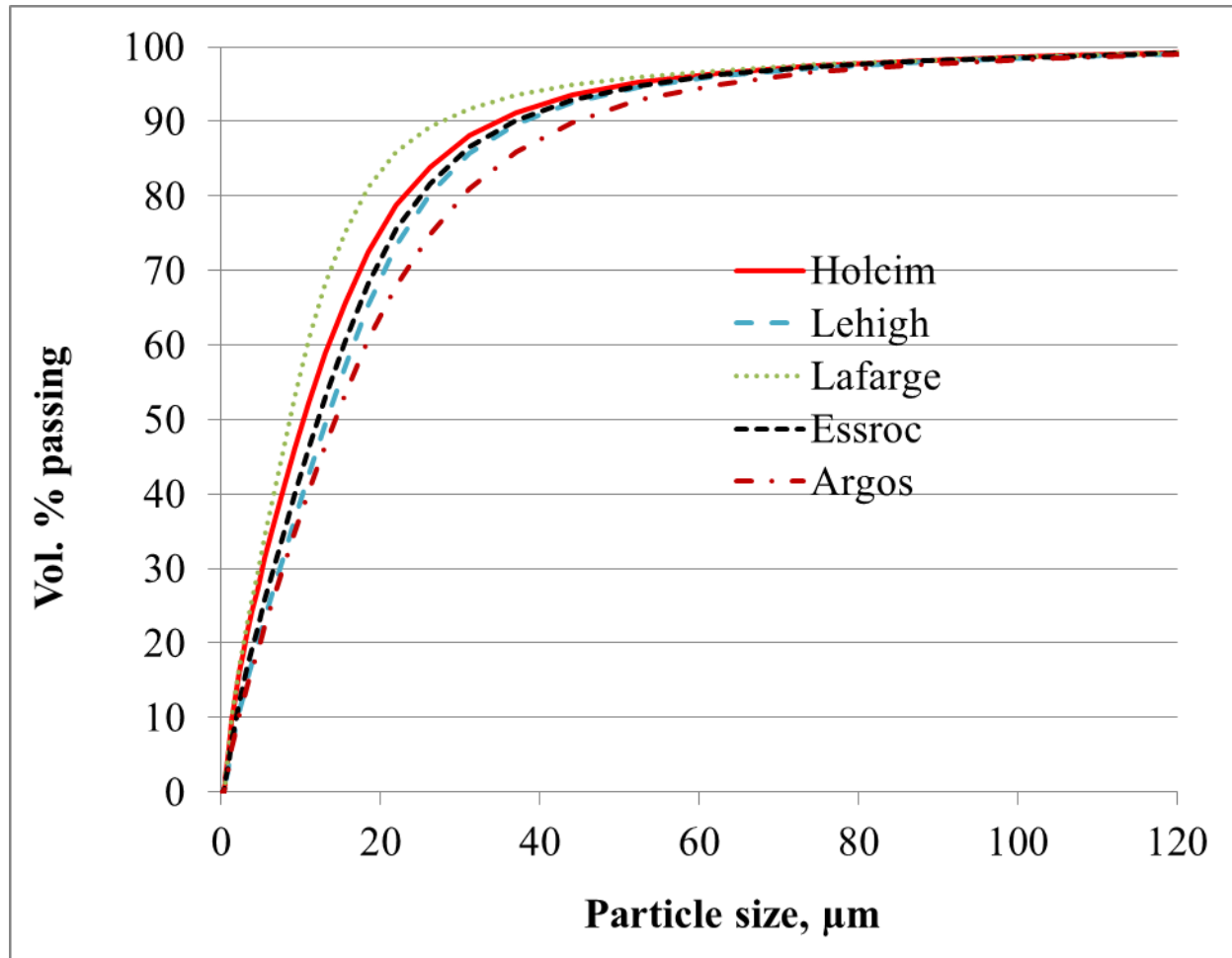


Figure 5.10b. Particle size distributions of various GGBFS materials in terms of volume percent passing.