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# Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Augmented Formulation Matrix Tests

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July 2015

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## EXECUTIVE SUMMARY

More than 56 million gallons of radioactive and hazardous waste are stored in 177 underground storage tanks at the U.S. Department of Energy's (DOE's) Hanford Site in Washington State. The HLW will be vitrified in the HLW facility for ultimate disposal at an offsite federal repository. A portion (~35%) of the LAW will be vitrified in the LAW vitrification facility for disposal onsite at the Integrated Disposal Facility (IDF). The pretreatment and HLW vitrification facilities will have the capacity to treat and immobilize all of the wastes destined for those facilities. However, a second facility will be needed for the expected volume of LAW requiring immobilization.

Cast Stone, a cementitious waste form, is being considered to provide the required additional LAW immobilization capacity. The Cast Stone waste form must be acceptable for disposal in the IDF. The Cast Stone waste form and immobilization process must be tested to demonstrate that the final Cast Stone waste form can comply with the waste acceptance criteria for the disposal facility and that the immobilization processes can be controlled to consistently provide an acceptable waste form product.

A testing program was developed in fiscal year (FY) 2012 describing in detail the work needed to develop and qualify Cast Stone as a waste form for the solidification of Hanford LAW. A statistically designed test matrix was used to evaluate the effects of key parameters on the properties of the Cast Stone as it is initially prepared and after curing. For the processing properties, the water-to-dry-blend mix ratio was the most significant parameter in affecting the range of values observed for each property. The single shell tank (SST) Blend simulant also showed differences in measured properties compared to the other three simulants tested. A review of the testing matrix and results indicated that an additional set of tests would be beneficial to improve the understanding of the impacts noted in the Screening Matrix tests.

A set of Cast Stone formulations were devised to augment the original screening test matrix and focus on the range of the test conditions. Fly ash and blast furnace slag were limited to either northwest or southeast and the salt solutions were narrowed to the Average and the SST Blend at the 7.8M Na concentration. To fill in the matrix, a mix ratio of 0.5 was added. In addition, two admixtures, Xypex Admix C-500 and Rheomac SF100 (silica fume), were added as an additional dry material binder in select compositions. As in the Screening Matrix, both fresh and cured properties were evaluated for the formulations.

In this study, properties that were influenced by the W/DM ratio in the Screening Matrix; flow diameter, plastic viscosity, density, and compressive strength, showed consistent behavior with respect to W/DM. The leach index for highly soluble components, sodium and nitrate, were not influenced by changes in formulation or the admixtures. The leach index for both iodine and Tc-99 show an influence from the addition of the admixture, Xypex Admix C-500. Additional testing should be performed to further evaluate the influence of Xypex Admix C-500 on the leach index over a range of admixture concentrations, Cast Stone formulations, and curing and storage conditions.

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## LIST OF ABBREVIATIONS

|       |                                            |
|-------|--------------------------------------------|
| BFS   | blast furnace slag                         |
| DOE   | U.S. Department of Energy                  |
| DPM   | disintegrations per minute                 |
| FA    | Fly ash                                    |
| FT    | fiscal year                                |
| HLW   | high-level waste                           |
| HTWOS | Hanford Tank Waste Operations Simulator    |
| IDF   | Integrated Disposal Facility               |
| LAW   | low-activity waste                         |
| OPC   | Ordinary portland cement                   |
| PA    | performance assessment                     |
| QAP   | Quality Assurance Program                  |
| SRNL  | Savannah River National Laboratory         |
| SST   | single shell tank                          |
| TCLP  | Toxicity Characteristic Leaching Procedure |
| WTP   | Waste Treatment and Immobilization Plant   |

## 1.0 Introduction

More than 56 million gallons of radioactive and hazardous waste are stored in 177 underground storage tanks at the U.S. Department of Energy's (DOE's) Hanford Site in Washington State. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed to treat and immobilize the waste as a glass waste form. The WTP includes a pretreatment facility to separate the wastes into high-level waste (HLW) containing most of the radioactivity and low-activity waste (LAW) containing most of the nonradioactive chemicals. The HLW will be vitrified in the HLW facility for ultimate disposal at an offsite federal repository. A portion (~35%) of the LAW will be vitrified in the LAW vitrification facility for disposal onsite at the Integrated Disposal Facility (IDF). The pretreatment and HLW vitrification facilities will have the capacity to treat and immobilize all of the wastes destined for those facilities. However, a second facility will be needed for the expected volume of LAW requiring immobilization.

Cast Stone, a cementitious waste form, is being considered to provide the required additional LAW immobilization capacity. The Cast Stone waste form must be acceptable for disposal in the IDF. The Cast Stone waste form and immobilization process must be tested to demonstrate that the final Cast Stone waste form can comply with the waste acceptance criteria for the disposal facility and that the immobilization processes can be controlled to consistently provide an acceptable waste form product. Further, the waste form must be tested to provide the technical basis for understanding the long-term performance of the waste form in the disposal environment. These waste form performance data are needed to support risk assessment and performance assessment (PA) analyses of the long-term environmental impact of the waste disposal in the IDF.

A testing program was developed in fiscal year (FY) 2012 describing in detail the work needed to develop and qualify Cast Stone as a waste form for the solidification of Hanford LAW.<sup>1</sup> The initial phase was to conduct screening tests to evaluate the impact of key parameters including ranges in waste composition, waste stream concentrations, sources of dry materials, and mix ratios of waste (free water basis) to dry blend. Four simulant waste compositions and two waste concentrations were selected for testing. Three simulant waste compositions were chosen from the output of the Hanford Tank Waste Operation Simulator and the fourth waste simulant was chosen to be comparable with prior testing.<sup>2</sup> A statistically designed test matrix was used to evaluate the effects of these key parameters on the properties of the Cast Stone as it is initially prepared and after curing.<sup>3</sup> Final waste form properties measured included compressive strength, porosity, cured density, Toxicity Characteristic Leaching Procedure (TCLP) leach test, and the EPA Method 1315<sup>4</sup> leach test. For the processing properties, the water-to-dry-blend mix ratio was the most significant parameter in affecting the range of values observed for each property. The single shell tank (SST) Blend simulant also showed differences in measured properties compared to the other three simulants tested.

Table 1-1 shows the formulations investigated in the Screening Matrix testing. Review of the testing matrix and results indicated that an additional set of tests would be beneficial to improve the understanding of the impacts noted in the Screening Matrix tests. To focus the range of the test conditions, the fly ash and blast furnace slag were limited to either northwest or southeast and the salt solutions were narrowed to the Average and the SST Blend at the 7.8M Na concentration. To fill in, or augment the matrix, a mid-range mix ratio of 0.5 was added. In addition, two admixtures, Xypex, Admix C-500, and Rheomac SF100, a silica fume material, were added as an additional dry material binder in select compositions as a five weight percent replacement for the dry blend. Table 1-2 contains the matrix of formulations investigated in this work. Shaded boxes indicate formulations will also be prepared with technetium for leach testing.

**Table 1-1. Formulations Evaluated in Screening Matrix Testing.**

| Waste Composition |                      | Fly Ash Source/Blast Furnace Slag Source (Northwest or Southeast) |            |            |            |            |            |            |            |
|-------------------|----------------------|-------------------------------------------------------------------|------------|------------|------------|------------|------------|------------|------------|
|                   |                      | NW/NW                                                             | NW/SE      | SE/NW      | SE/SE      | NW/NW      | NW/SE      | SE/NW      | SE/SE      |
| 5M                | Average              | •                                                                 | •          |            |            |            |            |            | ••         |
|                   | High SO <sub>4</sub> |                                                                   |            | •          |            | •          | •          |            |            |
|                   | High Al              | •                                                                 | •          |            |            | •          | •          |            | •          |
|                   | SST Blend            |                                                                   |            | •          |            | •          | •          |            |            |
| 7.8M              | Average              | •                                                                 | •          | •          |            | ••         | ••         |            |            |
|                   | High SO <sub>4</sub> | ••                                                                | ••         |            | •          |            |            | ••         |            |
|                   | High Al              |                                                                   |            | •          |            | •          | •          | •          |            |
|                   | SST Blend            | •                                                                 | •          |            | •          |            |            | •          |            |
| <b>Mix Ratio</b>  |                      | <b>0.4</b>                                                        | <b>0.4</b> | <b>0.4</b> | <b>0.4</b> | <b>0.6</b> | <b>0.6</b> | <b>0.6</b> | <b>0.6</b> |

•• Indicates duplicate samples prepared

**Table 1-2. Formulations Developed to Augment the Initial Testing.**

| Waste Composition |           | Fly Ash Source/Blast Furnace Slag Source (Northwest or Southeast) |                 |                 |            |            |                 |                 |            |
|-------------------|-----------|-------------------------------------------------------------------|-----------------|-----------------|------------|------------|-----------------|-----------------|------------|
|                   |           | NW/NW                                                             | NW/NW/<br>C-500 | NW/NW/<br>SF100 | SE/SE      | NW/NW      | NW/NW/<br>C-500 | NW/NW/<br>SF100 | SE/SE      |
| 7.8M              | Average   | 51                                                                | 52              | 61              | 53         | 54         | 55              | 62              | 56         |
|                   | SST Blend | 57                                                                | 58              | 63              | 64         | 59         | 60              | 65              | 66         |
| <b>Mix Ratio</b>  |           | <b>0.5</b>                                                        | <b>0.5</b>      | <b>0.5</b>      | <b>0.5</b> | <b>0.6</b> | <b>0.6</b>      | <b>0.6</b>      | <b>0.6</b> |

Note: Shaded boxes indicate formulations that were also prepared with technetium for leach testing.

## 2.0 Experimental Procedure

The simulant preparation, dry blend materials, and grout slurry sample preparations are the same as those detailed in Reference 1.

### 2.1 Simulant Selection

For the augmented formulation matrix, two chemical simulants were selected from the set of four simulants used in the initial screening tests of Cast Stone formulations for LAW<sup>3</sup>. They included a saltcake simulant used in previous testing of LAW immobilization technologies and the overall average chemical simulant based on the Hanford Tank Waste Operations Simulator (HTWOS) flowsheet modeling of the LAW feed that is anticipated to be sent to a supplemental immobilization facility<sup>5</sup>. The chemical compositions of the salt waste simulants used in this study appear in Table 2-1. The target compositions are from Table 3-2 in Reference 1. The compositions have been adjusted from the mol/mol Na in the reference to represent the salt solutions used in this study to a mol/L basis. The hazardous chemicals, cadmium, chromium, lead, and nickel, were added at the same concentrations as described in Section 3.3.1 of Reference 1. Table 2-2 are the concentrations of the hazardous metals added to the 7.8M Na salt solution. Concentrations of components added specifically for the leach testing, chromium, technetium, and iodine, were also added to the salt simulant. The chromium value in Table 2-2 corresponds to the HTWOS 95th percentile chromium concentration. Technetium was added at the same concentrations as in Reference 1. Natural iodine was used in place of I-129. Table 2-3 shows the concentrations of technetium and iodine used in this study. The 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 detection limits) while attempting to avoid unrealistically high concentrations that may falsely represent waste form performance. In this study, iodine concentrations were selected for testing that would allow the reporting of a leach index for iodine of at least 11 at a detection limit of 0.5 ppb in the leachate.<sup>6</sup> To achieve this, NaI was spiked in in 100X the HTWOS maximum equivalent concentration of I-129 on a mass basis.

**Table 2-1. Composition of Salt Simulants for Augmented Matrix Samples (from Table 3-2, Reference 1)**

| Waste Constituent                                                                                                                                                                | SST Blend Saltcake | HTWOS Overall Average |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|-----------------------|
| Concentration (mol/L) <sup>(a)</sup>                                                                                                                                             |                    |                       |
| Na                                                                                                                                                                               | 7.8                | 7.8                   |
| K                                                                                                                                                                                | 0.0156             | 0.0546                |
| Al                                                                                                                                                                               | 0.1014             | 0.4758                |
| Cl                                                                                                                                                                               | 0.0702             | 0.0624                |
| F                                                                                                                                                                                | 0.0468             | 0.0468 <sup>(b)</sup> |
| SO <sub>4</sub>                                                                                                                                                                  | 0.1404             | 0.1326                |
| PO <sub>4</sub>                                                                                                                                                                  | 0.078              | 0.078 <sup>(b)</sup>  |
| NO <sub>2</sub>                                                                                                                                                                  | 0.663              | 0.8814                |
| NO <sub>3</sub>                                                                                                                                                                  | 3.9156             | 2.5272                |
| CO <sub>3</sub>                                                                                                                                                                  | 0.741              | 0.429                 |
| TOC Total                                                                                                                                                                        | 0.4446             | 0.117                 |
| Free OH                                                                                                                                                                          | 0.7566             | 2.4336                |
| (a) After charge balancing.<br>(b) Concentration of F and PO <sub>4</sub> <sup>3-</sup> reduced from HTWOS values because of solids formation observed in preliminary simulants. |                    |                       |

**Table 2-2. Hazardous Metals in the 7.8M Na Salt Simulant**

| Waste Constituent | Concentration (mol/L) |
|-------------------|-----------------------|
| Cd                | 2.49E-04              |
| Cr                | 3.35E-02              |
| Pb                | 4.00E-04              |
| Ni                | 5.16E-03              |

**Table 2-3. Technetium and Iodine Concentrations in 7.8M Na Salt Simulant**

| Waste Constituent | Concentration (Ci/L) | Concentration (mol/L) | Concentration (mg/L) |
|-------------------|----------------------|-----------------------|----------------------|
| Tc-99             | 3.22E-04             | 1.96E-04              | 19                   |
| I                 | --                   | 1.94E-04              | 25                   |

## 2.2 Dry Blend Materials

The basic Cast Stone dry blend is composed of 47 wt% blast furnace slag (BFS), 45 wt% Class F fly ash (FA), and 8 wt% ordinary portland cement (OPC; Type I/II). This blend ratio was used for all the mixes prepared. One of the BFS and the high-Ca fly ash (FA) materials were from a supplier available in the Pacific Northwest. The second BFS and the low-Ca FA are the same materials used in the Saltstone processing facility at the Savannah River Site in South Carolina. The OPC was obtained from a supplier in the Pacific Northwest, however, performance of cement is not specific to region as it is with pozzolanic materials. The characterization of these materials is detailed in Section 4.0 of Reference 1.

### 2.3 Sample Preparation

The Cast Stone specimens were prepared by mixing aliquots of the simulant batches and the dry blend mixes and then either measuring the fresh properties of the slurry or casting the slurry into molds to cure. Table 2-4 is the formulations used in this study. For brevity, the fixed components, salt solution sodium molarity—7.8M Na, and the source of cement—NW, were omitted from the table. The mixing process is described in Section 5.0 of Reference 1.

**Table 2-4. Augmented Matrix Formulations**

| Mix # | Simulant  | Fly Ash Class F | Blast Furnace Slag | Admixture     | Dry Blend Mix       | W/DM |
|-------|-----------|-----------------|--------------------|---------------|---------------------|------|
| 51    | Average   | NW              | NW                 | None          | 8:45:47:0:0         | 0.5  |
| 52    | Average   | NW              | NW                 | Admix C-500   | 7.6:42.75:44.65:5:0 | 0.5  |
| 53    | Average   | SE              | SE                 | None          | 8:45:47:0:0         | 0.5  |
| 54    | Average   | NW              | NW                 | None          | 8:45:47:0:0         | 0.6  |
| 55    | Average   | NW              | NW                 | Admix C-500   | 7.6:42.75:44.65:5:0 | 0.6  |
| 56    | Average   | SE              | SE                 | None          | 8:45:47:0:0         | 0.6  |
| 57    | SST Blend | NW              | NW                 | None          | 8:45:47:0:0         | 0.5  |
| 58    | SST Blend | NW              | NW                 | Admix C-500   | 7.6:42.75:44.65:5:0 | 0.5  |
| 59    | SST Blend | NW              | NW                 | None          | 8:45:47:0:0         | 0.6  |
| 60    | SST Blend | NW              | NW                 | Admix C-500   | 7.6:42.75:44.65:5:0 | 0.6  |
| 61    | Average   | NW              | NW                 | Rheomac SF100 | 7.6:42.75:44.65:0:5 | 0.5  |
| 62    | Average   | NW              | NW                 | Rheomac SF100 | 7.6:42.75:44.65:0:5 | 0.6  |
| 63    | SST Blend | NW              | NW                 | Rheomac SF100 | 7.6:42.75:44.65:0:5 | 0.5  |
| 64    | SST Blend | SE              | SE                 | None          | 8:45:47:0:0         | 0.5  |
| 65    | SST Blend | NW              | NW                 | Rheomac SF100 | 7.6:42.75:44.65:0:5 | 0.6  |
| 66    | SST Blend | SE              | SE                 | None          | 8:45:47:0:0         | 0.6  |

#### 2.3.1 Tc-99 Additions

To prepare the sample containing Tc-99, an addition of a 0.5mCi/ml solution of NH<sub>4</sub>TcO<sub>4</sub> was added to the proper quantity of salt solution simulant to make duplicate samples for leach testing. The Tc-99 containing salt solution was then mixed with the dry blend materials as above. Table 2-5 shows the Tc-99 additions.

**Table 2-5. Tc-99 Additions to Salt Solutions**

| Mix # | Mass Salt Solution (g) | Salt Solution density (g/ml) | Salt Solution Volume (ml) | Mass Dry Blend (g) | 0.5mCi/ml NH <sub>4</sub> TcO <sub>4</sub> to add (mCi) | 0.5mCi/ml NH <sub>4</sub> TcO <sub>4</sub> to add (dpm) | 0.5mCi/ml NH <sub>4</sub> TcO <sub>4</sub> to add (ml) | Tc-99/sample (dpm/kg) |
|-------|------------------------|------------------------------|---------------------------|--------------------|---------------------------------------------------------|---------------------------------------------------------|--------------------------------------------------------|-----------------------|
| 51TC  | 336.65                 | 1.35                         | 250.10                    | 414.1              | 0.08                                                    | 1.79E+08                                                | 0.16                                                   | 2.38E+05              |
| 52TC  | 336.65                 | 1.35                         | 250.10                    | 414.1              | 0.08                                                    | 1.79E+08                                                | 0.16                                                   | 2.38E+05              |
| 53TC  | 333.30                 | 1.35                         | 247.61                    | 410.0              | 0.08                                                    | 1.77E+08                                                | 0.16                                                   | 2.38E+05              |
| 54TC  | 359.08                 | 1.35                         | 266.76                    | 368.1              | 0.09                                                    | 1.91E+08                                                | 0.17                                                   | 2.62E+05              |
| 55TC  | 359.08                 | 1.35                         | 266.76                    | 349.7              | 0.09                                                    | 1.91E+08                                                | 0.17                                                   | 2.62E+05              |
| 56TC  | 355.90                 | 1.35                         | 264.40                    | 364.9              | 0.09                                                    | 1.89E+08                                                | 0.17                                                   | 2.62E+05              |
| 57TC  | 344.05                 | 1.36                         | 253.40                    | 405.0              | 0.08                                                    | 1.81E+08                                                | 0.16                                                   | 2.42E+05              |
| 58TC  | 344.05                 | 1.36                         | 253.40                    | 405.5              | 0.08                                                    | 1.81E+08                                                | 0.16                                                   | 2.42E+05              |
| 59TC  | 366.43                 | 1.36                         | 269.89                    | 359.5              | 0.09                                                    | 1.93E+08                                                | 0.17                                                   | 2.66E+05              |
| 60TC  | 366.43                 | 1.36                         | 269.89                    | 359.5              | 0.09                                                    | 1.93E+08                                                | 0.17                                                   | 2.66E+05              |

## 2.4 Quality Assurance

The SRNL work scope was performed in accordance with a Quality Assurance Program (QAP) that meets the Quality Assurance criteria specified in DOE Order 414.1D, Quality Assurance; 10 CFR 830, “Nuclear Safety Management,” Subpart A, “Quality Assurance Requirements,” paragraph 830.122; and also meets the requirements of ASME NQA-1-2004, Quality Assurance Requirements for Nuclear Facility Applications, including NQA-1a-2005 and NQA-1b-2007 Addenda, or later version. The SRNL work scope was performed in accordance with Savannah River Site Manual 1Q, QAP 2-3 (Control of Research and Development Activities). Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

## 3.0 Results

Immediately after mixing, samples were poured for rheology, density, and heat of hydration measurements, 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. Measurements of the fresh and cured properties of the test mixes are described in Section 6.0 of Reference 1.

### 3.1 Flow Consistency (Modified ASTM D6103)

The Flow diameters in this study ranged from 187 mm (Mix 57) to 319 mm (Mix 55) and were bounded by the flow diameters in the initial Screening Matrix. Table 3-1 is the flow diameters measured in this study. The addition of the Xypex Admix C-500 increased the average flow diameter over mixes with the same dry blend source and water to dry materials ratio. Addition of the Rheomac SF100 did not noticeably affect the flow diameter. Plots of these results along with the values from the initial Screening Matrix appear in Figure 3-1. It can be seen from the plot that the flow diameter of the mixes prepared with a 0.5 W/DM ranged between mixes prepared with the 0.4 and 0.6 W/DM ratios.

**Table 3-1. Average Flow Diameter of Mixes in this Study**

| <b>Mix Number</b> | <b>Water-to-Dry Blend Ratio</b> | <b>Admixture Added</b> | <b>Average Flow Diameter (mm)</b> |
|-------------------|---------------------------------|------------------------|-----------------------------------|
| 51                | 0.5                             | None                   | 205.1                             |
| 52                | 0.5                             | Xypex Admix C-500      | 230.2                             |
| 53                | 0.5                             | None                   | 209.5                             |
| 54                | 0.6                             | None                   | 246.6                             |
| 55                | 0.6                             | Xypex Admix C-500      | 319.0                             |
| 56                | 0.6                             | None                   | 248.0                             |
| 57                | 0.5                             | None                   | 187.0                             |
| 58                | 0.5                             | Xypex Admix C-500      | 216.5                             |
| 59                | 0.6                             | None                   | 217.7                             |
| 60                | 0.6                             | Xypex Admix C-500      | 238.3                             |
| 61                | 0.5                             | Rheomac SF100          | 210.8                             |
| 62                | 0.6                             | Rheomac SF100          | 245.0                             |
| 63                | 0.5                             | Rheomac SF100          | 208.1                             |
| 64                | 0.5                             | None                   | 197.6                             |
| 65                | 0.6                             | Rheomac SF100          | 230.1                             |
| 66                | 0.6                             | None                   | 226.0                             |

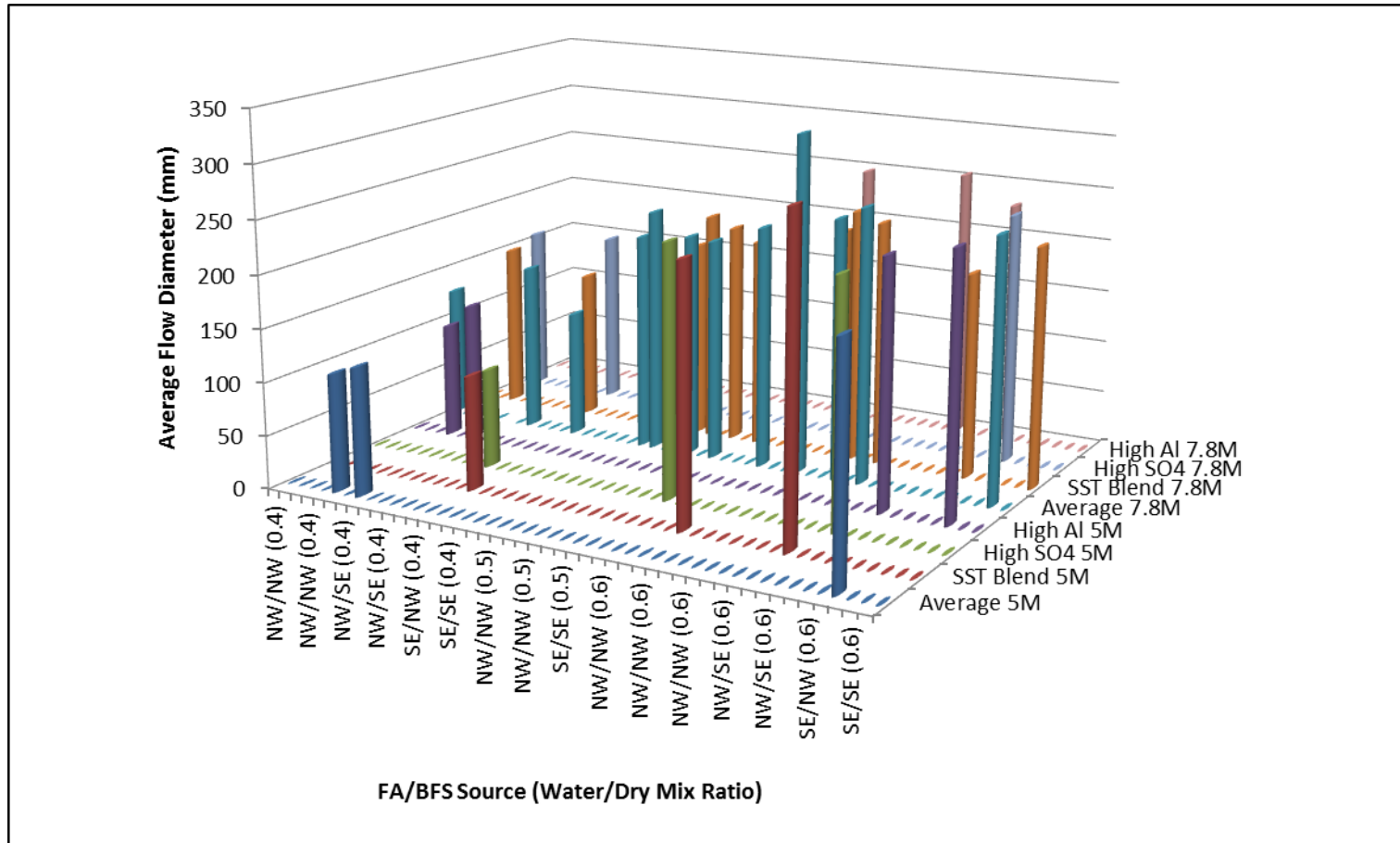


Figure 3-1. Average flow diameter of the results of this study plotted with the results of the Screening Matrix testing from Reference 1.



### 3.2 Gel Time

Measured gel times ranged from 5 minutes—Mix 61, to 105 minutes—Mix 55, Table 3-2. The gel times of mixes prepared with dry blend materials from the Pacific Northwest were shorter than gel times from formulations prepared with southeastern fly ash and BFS. Additions of Xypex Admix C-500 lengthened the gel time, whereas additions of the Rheomac SF100 did not affect the gel time. The gel times measured for the formulations in this study are plotted along with the gel times of the Screening Matrix formulations from Reference 1 in Figure 3-2.

**Table 3-2. Measured Gel Times for Augmented Matrix Formulations**

| Mix Number | Water-to-Dry Blend Ratio | Admixture Added   | Gel Time (min) |
|------------|--------------------------|-------------------|----------------|
| 51         | 0.5                      | None              | 7              |
| 52         | 0.5                      | Xypex Admix C-500 | > 30           |
| 53         | 0.5                      | None              | 60             |
| 54         | 0.6                      | None              | 30             |
| 55         | 0.6                      | Xypex Admix C-500 | 105            |
| 56         | 0.6                      | None              | 60             |
| 57         | 0.5                      | None              | 45             |
| 58         | 0.5                      | Xypex Admix C-500 | 20             |
| 59         | 0.6                      | None              | 97             |
| 60         | 0.6                      | Xypex Admix C-500 | > 80           |
| 61         | 0.5                      | Rheomac SF100     | 5              |
| 62         | 0.6                      | Rheomac SF100     | 30             |
| 63         | 0.5                      | Rheomac SF100     | 85             |
| 64         | 0.5                      | None              | 15             |
| 65         | 0.6                      | Rheomac SF100     | > 51           |
| 66         | 0.6                      | None              | 23             |

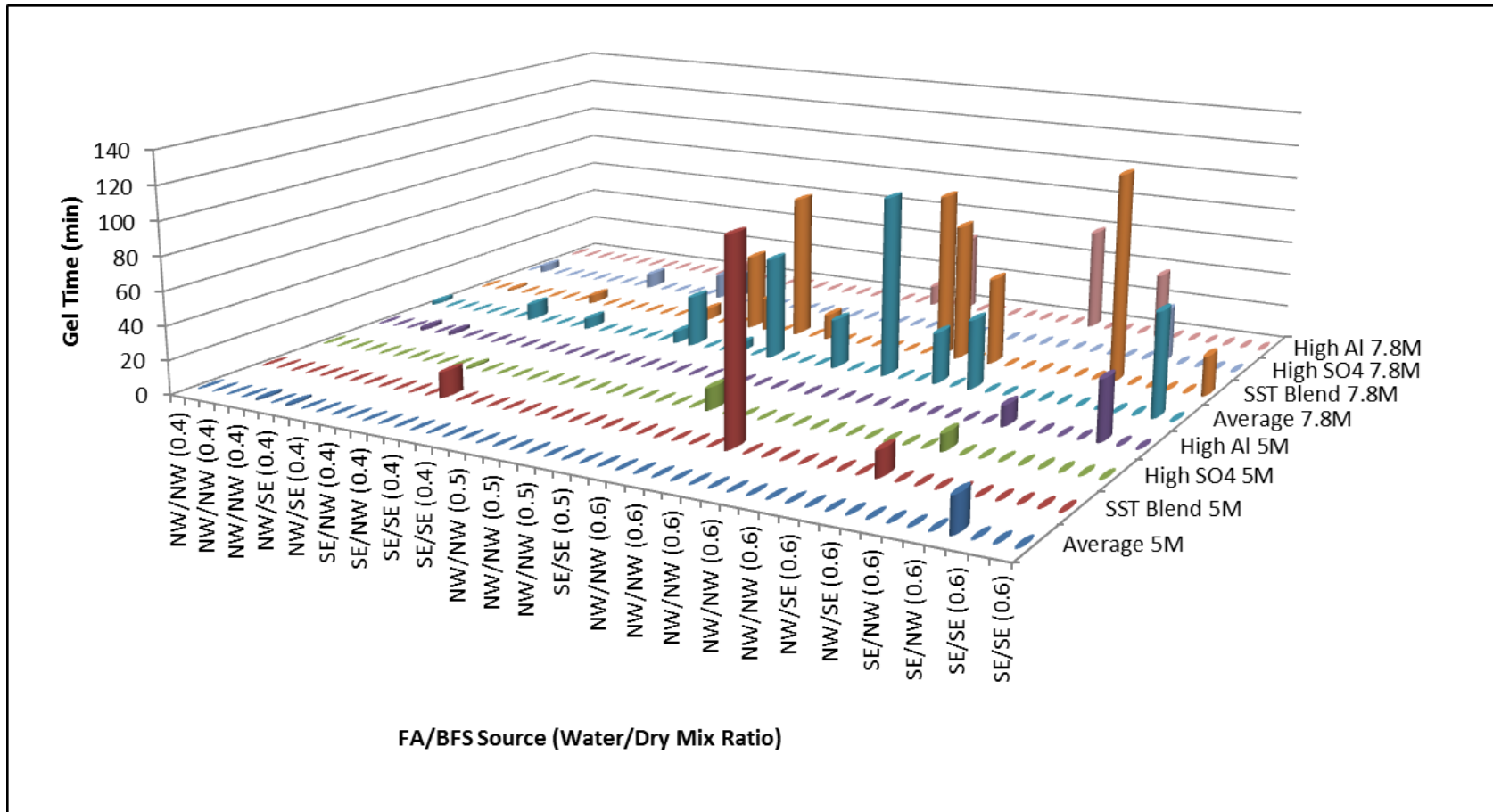


Figure 3-2. Average flow diameter of the results of this study plotted with the results of the Screening Matrix testing from Reference 1.

### 3.3 Slurry Rheology

Rheological measurements of freshly prepared mixes were measured following the method described in Section 6.4 of Reference 1. In this testing, only the plastic viscosity and yield strength were measured. For each mix, a flow curve (shear stress versus shear rate data) was generated using a concentric geometry bob and cup in a different viscometer (model Haake RS6000, ThermoFisher, Waltham, MA) than that used in the Screening Matrix work. The data were analyzed using the Bingham Plastic rheological model used in Reference 1, providing yield stress and plastic viscosity values. Table 3-3 shows the calculated plastic viscosity and Bingham Plastic yield strength calculated from the flow curves. In this testing, it was observed that formulations with the SST Blend salt solution had greater plastic viscosities and Bingham Plastic yield strengths than formulations made with the HTWOS Average salt solution. It was also noted that formulations made with a 0.5 W/DM had greater plastic viscosities and Bingham Plastic yield strengths than those made with a 0.6 W/DM. This is consistent with the observations in the Screening Matrix testing. Neither of the admixtures, Xypex Admix C-500 or Rheomac SF100, had measureable effect on either the plastic viscosity or the Bingham Plastic yield strength. Figure 3-3 and Figure 3-4 are the plastic viscosity and the Bingham Plastic yield stress from Table 3-3 plotted with the results from the Screening Matrix testing.

**Table 3-3. Plastic Viscosity and Bingham Plastic Yield Strength for the Augmented Matrix Formulations**

| Mix Number | Water-to-Dry Blend Ratio | Admixture Added   | Plastic Viscosity (cP) | Yield Stress (Pa) |
|------------|--------------------------|-------------------|------------------------|-------------------|
| 51         | 0.5                      | None              | 157                    | 11.4              |
| 52         | 0.5                      | Xypex Admix C-500 | 154                    | 4.3               |
| 53         | 0.5                      | None              | 201                    | 6.6               |
| 54         | 0.6                      | None              | 98                     | 4.4               |
| 55         | 0.6                      | Xypex Admix C-500 | 95                     | 2.0               |
| 56         | 0.6                      | None              | 102                    | 3.0               |
| 57         | 0.5                      | None              | 192                    | 12.9              |
| 58         | 0.5                      | Xypex Admix C-500 | 213                    | 6.4               |
| 59         | 0.6                      | None              | 154                    | 6.2               |
| 60         | 0.6                      | Xypex Admix C-500 | 117                    | 2.1               |
| 61         | 0.5                      | Rheomac SF100     | 155                    | 10.0              |
| 62         | 0.6                      | Rheomac SF100     | 100                    | 4.3               |
| 63         | 0.5                      | Rheomac SF100     | 165                    | 10.6              |
| 64         | 0.5                      | None              | 223                    | 11.3              |
| 65         | 0.6                      | Rheomac SF100     | 125                    | 5.1               |
| 66         | 0.6                      | None              | 130                    | 5.5               |

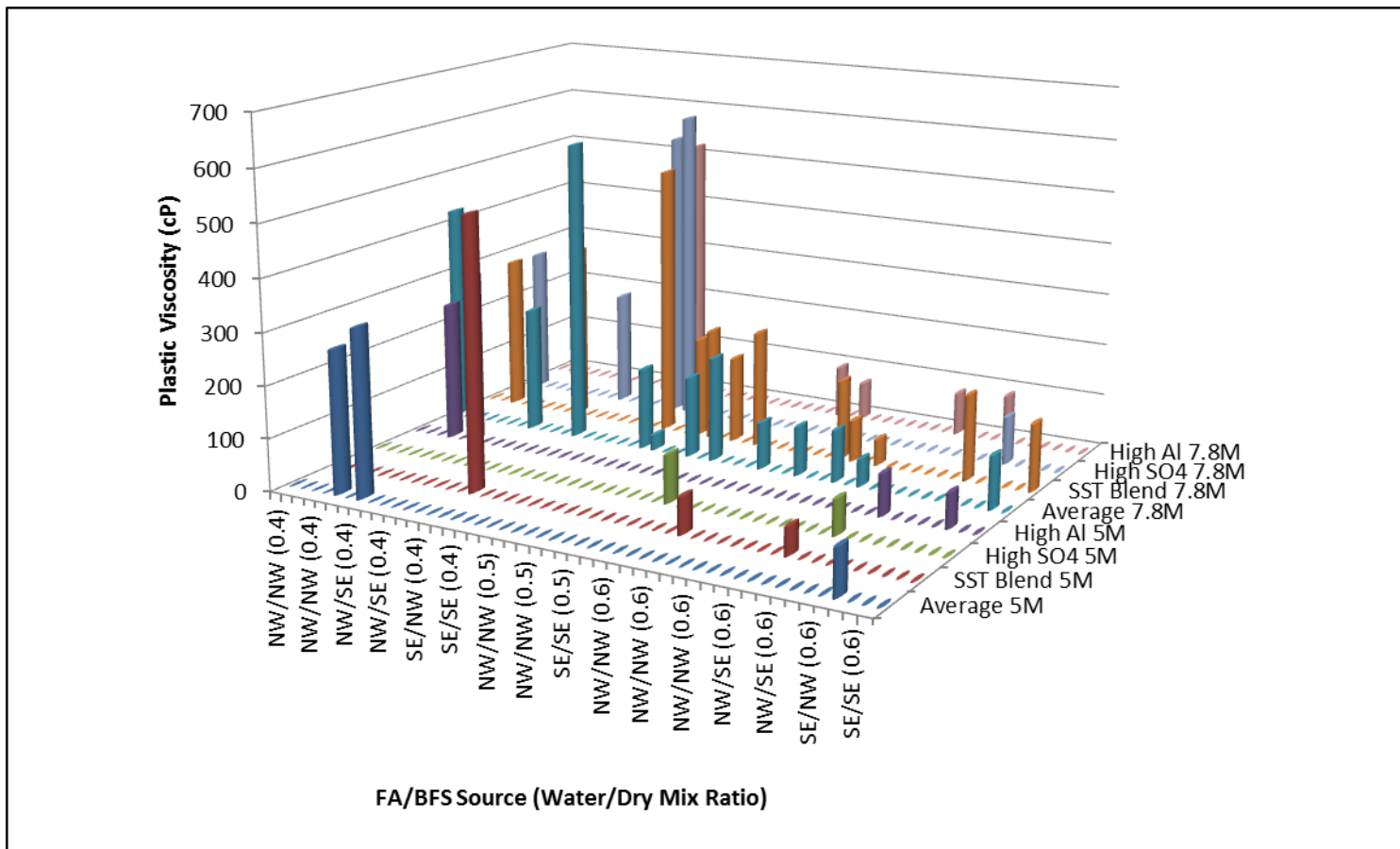


Figure 3-3. Plastic viscosity measurements for the 16 Augmented Matrix formulations plotted with the Screening Matrix mixes from Reference 1.

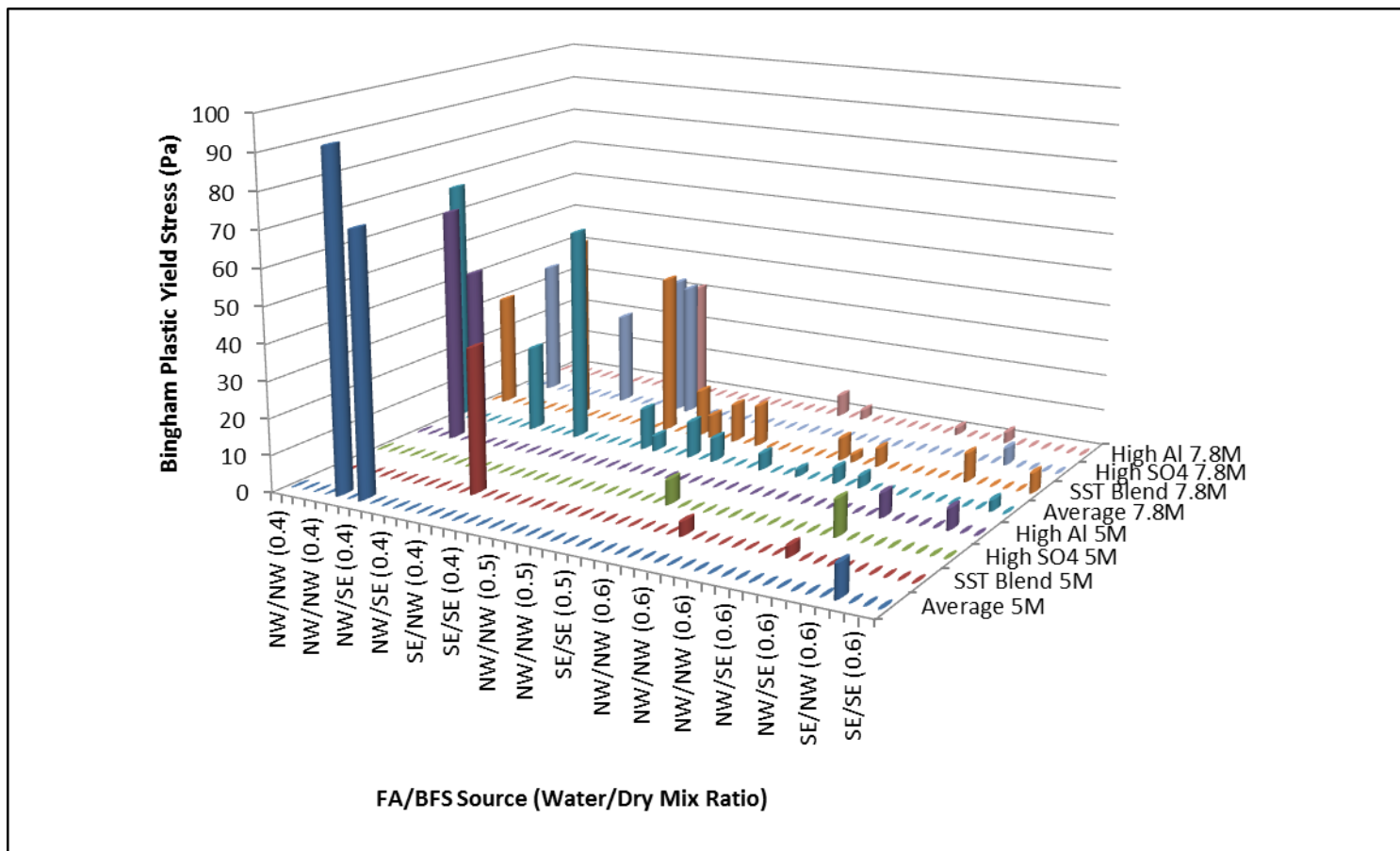


Figure 3-4. Bingham Plastic yield stress for the 16 Augmented Matrix formulations plotted with the Screening Matrix mixes from Reference 1.

### 3.4 Heat of Hydration

The isothermal heat of hydration for the Augmented Matrix formulations was measured as described in Section 6.5 of Reference 1. The total energy produced, normalized per gram of dry blend material, was determined at 300 hours. The elapsed time to attain the peak heat generation rate was also determined. Table 3-4 shows both the heat generated per gram over 300 hours and the time at which the heat generation rate peaked for each of the formulations tested. Figure 3-5 includes plots of the heat generated per gram of dry blend material in the formulation for the data in this study along with the Screening Matrix data. The time (in hours) to peak heat generation rate is for this study and the Screening Matrix are plotted in Figure 3-6. In this study, the cumulative heat generated in each of the mixes was similar over the formulations tested. Total heat generation is an indicator of the extent of hydration reaction in the mix. Peak heat generation is an indication of how the temperature might rise in a larger scale monolithic pour. Although the time to peak heat generation varied across the mixes, the cause of the shift in the timing of heat release in this system is not well understood.

**Table 3-4. Total Heat Generated after 300 h and the Time to Maximum Heat Generation Rate for the Augmented Matrix Formulations**

| Mix Number | Water-to-Dry Blend Ratio | Admixture Added   | 300 h Heat Generation (J/g) | Time to Peak Heat Generation (h) |
|------------|--------------------------|-------------------|-----------------------------|----------------------------------|
| 51         | 0.5                      | None              | 328.3                       | 44.03                            |
| 52         | 0.5                      | Xypex Admix C-500 | 356.6                       | 52.35                            |
| 53         | 0.5                      | None              | 376.8                       | 68.05                            |
| 54         | 0.6                      | None              | 337.3                       | 54.20                            |
| 55         | 0.6                      | Xypex Admix C-500 | 368.0                       | 64.45                            |
| 56         | 0.6                      | None              | 390.2                       | 103.05                           |
| 57         | 0.5                      | None              | 338.7                       | 94.10                            |
| 58         | 0.5                      | Xypex Admix C-500 | 346.2                       | 73.55                            |
| 59         | 0.6                      | None              | 341.2                       | 125.54                           |
| 60         | 0.6                      | Xypex Admix C-500 | 351.5                       | 129.34                           |
| 61         | 0.5                      | Rheomac SF100     | 327.4                       | 54.50                            |
| 62         | 0.6                      | Rheomac SF100     | 333.2                       | 66.32                            |
| 63         | 0.5                      | Rheomac SF100     | 312.7                       | 108.27                           |
| 64         | 0.5                      | None              | 374.5                       | 47.59                            |
| 65         | 0.6                      | Rheomac SF100     | 328.9                       | 135.30                           |
| 66         | 0.6                      | None              | 389.7                       | 56.47                            |

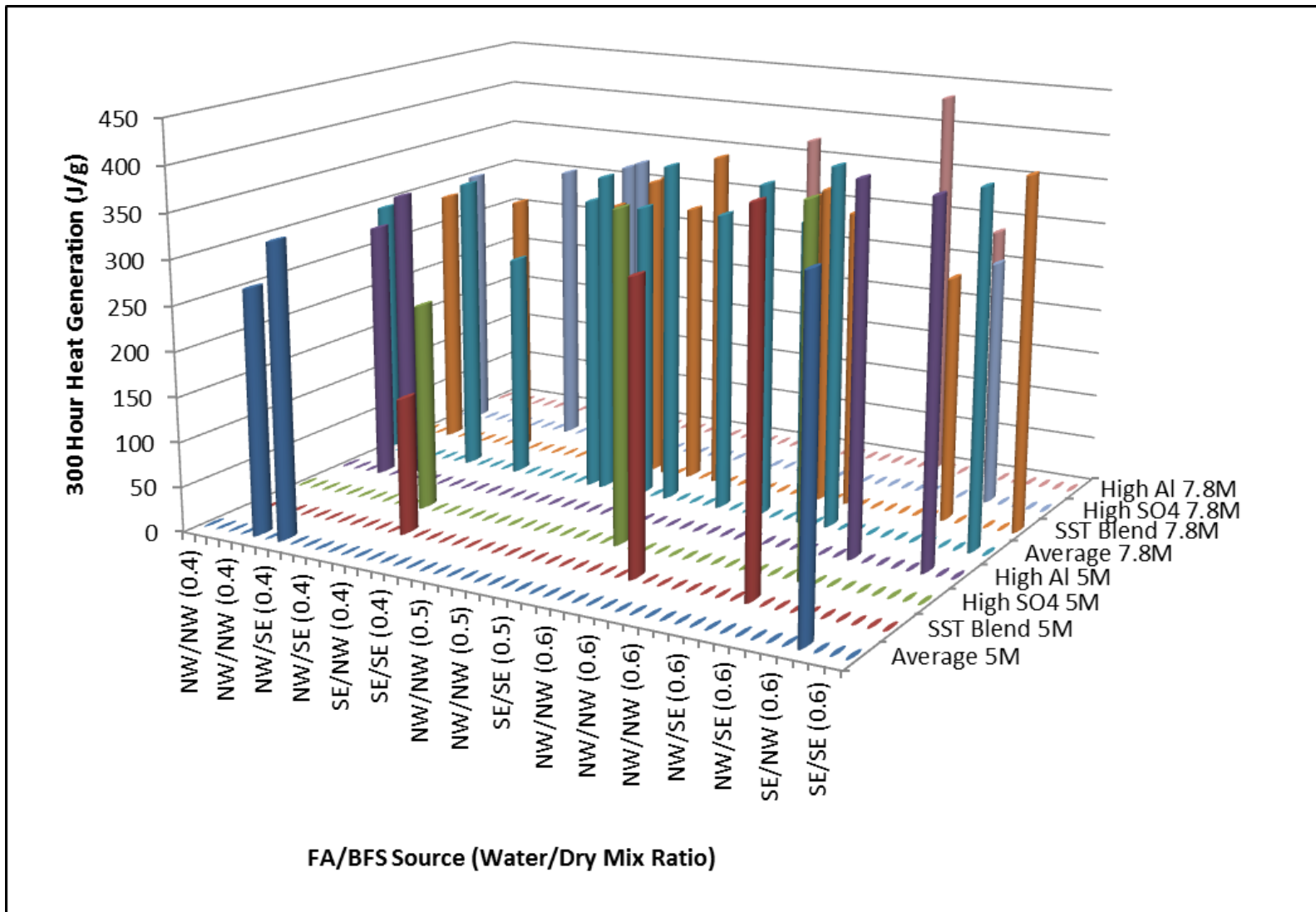


Figure 3-5. Heat generation after 300 hours for the 16 Augmented Matrix formulations plotted with the Screening Matrix mixes from Reference 1.

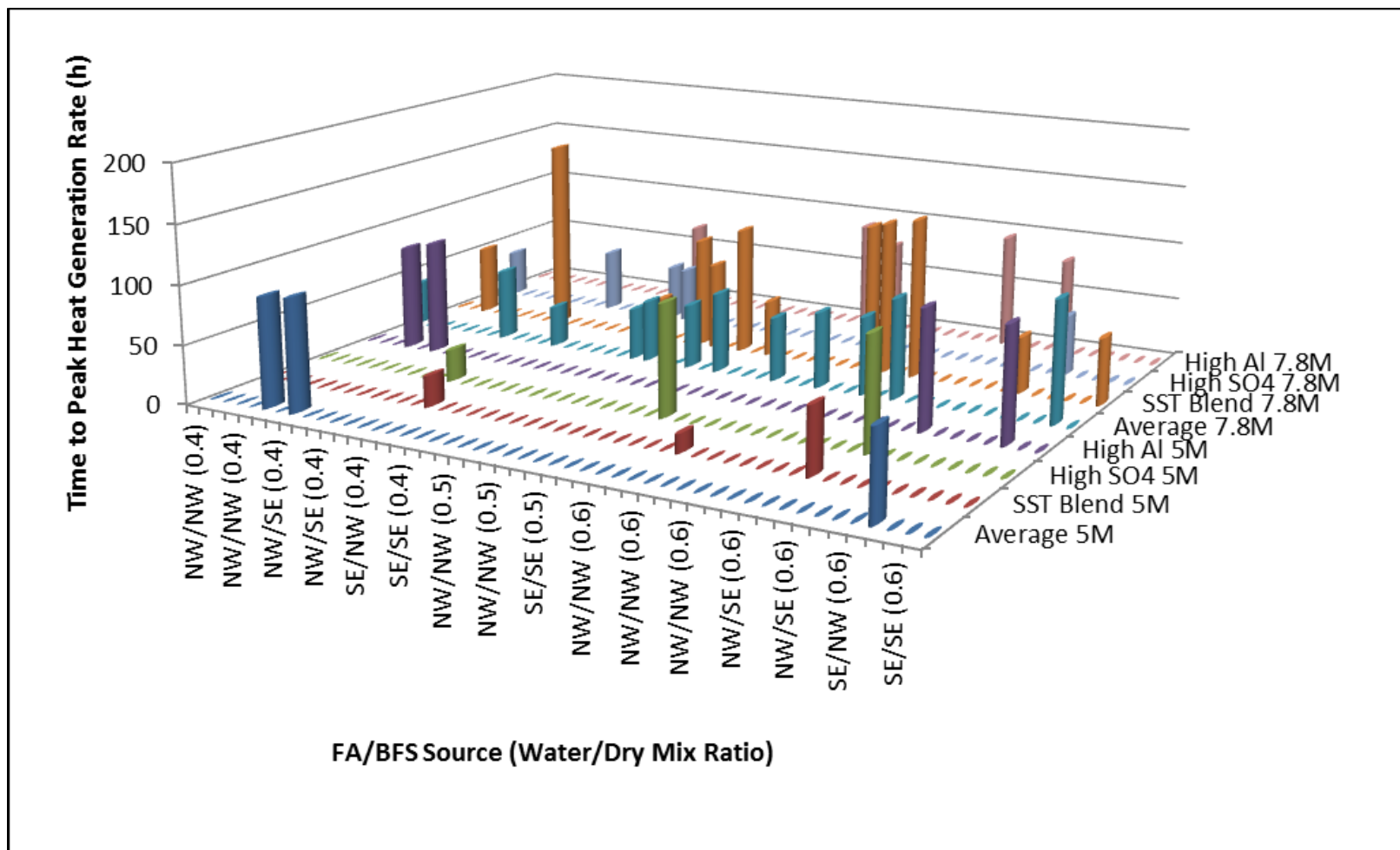


Figure 3-6. Time to peak heat generation rate for the 16 Augmented Matrix formulations plotted with the Screening Matrix mixes from Reference 1.



### 3.5 Fresh Density

The density of the freshly prepared Cast Stone mixes were measured as described in Section 6.6 of Reference 1. Table 3-5 is the measured fresh density and the density calculated from the formulation for the mixes prepared in this study. The density was calculated from the measured densities of the salt solutions and dry blends in Reference 1. As was noted in Reference 1, the density was related to the water to dry blend ratio, with the lower dry blend ratio producing mixes with higher densities. The calculated densities reflect the measured densities. The fresh density of freshly prepared Cast Stone for the 16 augmented matrix formulations are plotted with the Screening Matrix mixes from Reference 1, Figure 3-7. The small difference between actual and calculated densities may be an indication of air entrainment in the mixing process.

**Table 3-5. Measured and Calculated Density for Freshly Prepared Mixes**

| <b>Mix Number</b> | <b>Water-to-Dry Blend Ratio</b> | <b>Fresh Density (g/ml)</b> | <b>Calculated Density (g/ml)</b> | <b>Difference (%)</b> |
|-------------------|---------------------------------|-----------------------------|----------------------------------|-----------------------|
| 51                | 0.5                             | 1.863                       | 1.877                            | -0.75%                |
| 52                | 0.5                             | 1.877                       | 1.861                            | 0.86%                 |
| 53                | 0.5                             | 1.858                       | 1.833                            | 1.36%                 |
| 54                | 0.6                             | 1.818                       | 1.803                            | 0.83%                 |
| 55                | 0.6                             | 1.818                       | 1.808                            | 0.55%                 |
| 56                | 0.6                             | 1.802                       | 1.780                            | 1.24%                 |
| 57                | 0.5                             | 1.873                       | 1.862                            | 0.59%                 |
| 58                | 0.5                             | 1.873                       | 1.844                            | 1.57%                 |
| 59                | 0.6                             | 1.815                       | 1.809                            | 0.33%                 |
| 60                | 0.6                             | 1.815                       | 1.789                            | 1.45%                 |
| 61                | 0.5                             | 1.877                       | 1.847                            | 1.62%                 |
| 62                | 0.6                             | 1.818                       | 1.789                            | 1.62%                 |
| 63                | 0.5                             | 1.873                       | 1.834                            | 2.13%                 |
| 64                | 0.5                             | 1.854                       | 1.820                            | 1.87%                 |
| 65                | 0.6                             | 1.815                       | 1.782                            | 1.85%                 |
| 66                | 0.6                             | 1.799                       | 1.758                            | 2.33%                 |

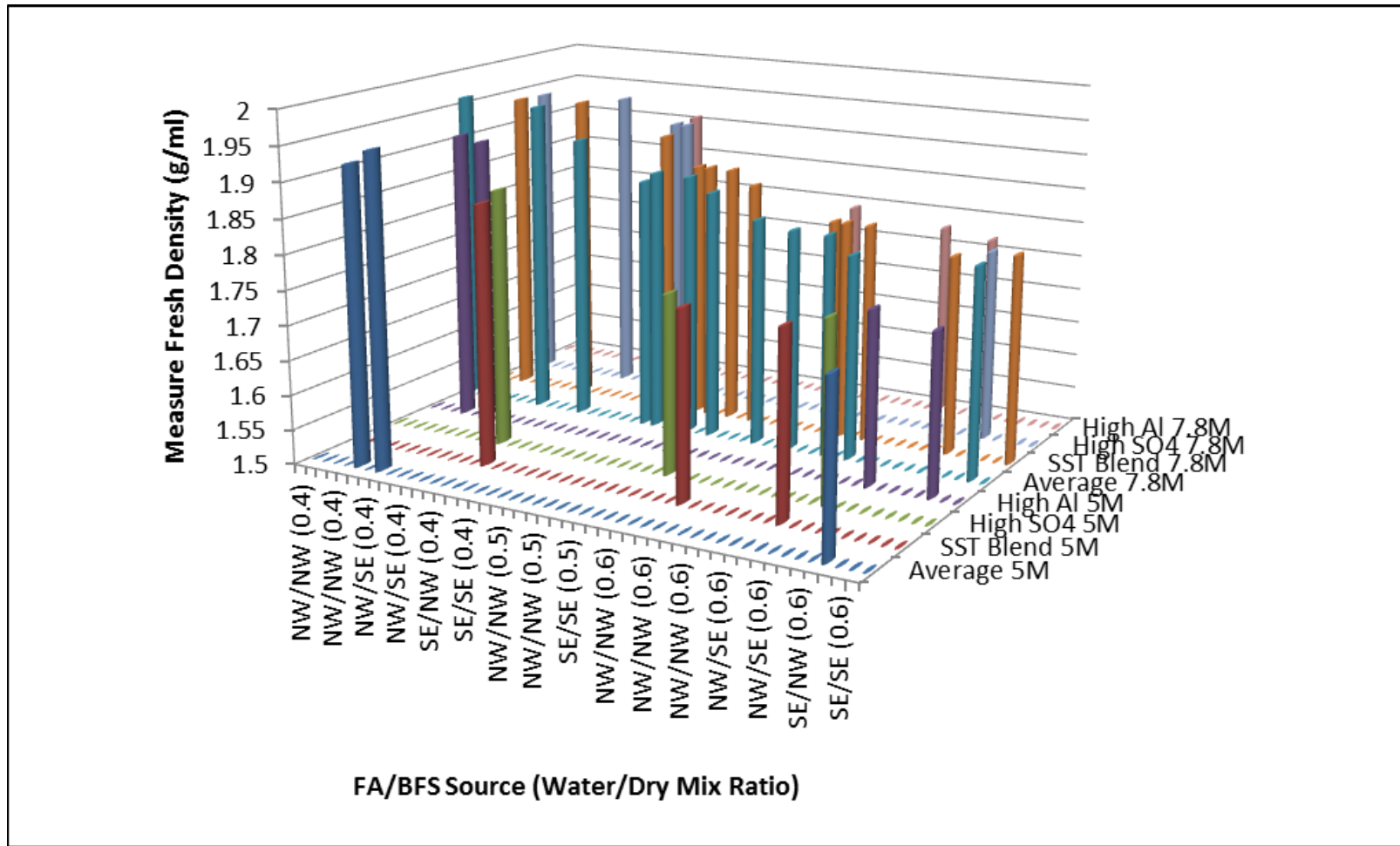


Figure 3-7. Density of freshly prepared Cast Stone for the 16 Augmented Matrix formulations plotted with the Screening Matrix mixes from Reference 1.

### 3.6 Free Liquids

The presence and amount of free liquids present in freshly prepared Cast Stone mixes were measured as described in Section 6.7 of Reference 1. Four of the formulations exhibited free liquid after one day. The free liquid present in the samples remained after three days for all four formulations, increasing in mixes 63 and 65. Table 3-6 shows the four formulations that produced free liquid. The table also contains the mix formulation and select fresh properties that could be used to substantiate the presence of free water. cursory review of the formulation and properties does not provide a clear cause of the free liquid in these samples.

**Table 3-6.Free Liquid Measured after Three Days**

| Mix # | Free Water (%) | Salt Solution | FA/BFS Source | Admix             | W/DM | Gel Time (min) | Flow Diameter (mm) | Bingham Plastic Yield (Pa) |
|-------|----------------|---------------|---------------|-------------------|------|----------------|--------------------|----------------------------|
| 55    | 2.5            | Average       | NW/NW         | Xypex Admix C-500 | 0.6  | 105            | 319                | 2.0                        |
| 57    | 3.4            | SST Blend     | NW/NW         | None              | 0.5  | 45             | 187                | 12.9                       |
| 63    | 3.3            | SST Blend     | NW/NW         | Rheomac SF100     | 0.5  | 85             | 208                | 5.6                        |
| 65    | 6.6            | SST Blend     | NW/NW         | Rheomac SF100     | 0.6  | >51            | 230                | 5.1                        |

### 3.7 Compressive Strength

The compressive strength of triplicate Cast Stone mixes were measured as described in Section 7.1 of Reference 1. The average compressive strength of the formulations used in this augmented matrix study ranged from 1443 psi (Mix 54) to 5757 psi (Mix 63), Table 3-7. The compressive strength of samples in this study were bounded by the compressive strength of the Screening Matrix 850-8990 psi.<sup>1</sup> Average compressive strength of triplicate Cast Stone for the 16 augmented matrix formulations are plotted with the Screening Matrix mixes from Reference 1 in Figure 3-8.

**Table 3-7.Average Compressive Strength of Triplicate Samples in this Study**

| Mix # | Salt Solution | FA/BFS Source | Admix             | W/DM | Compressive Strength (psi) |
|-------|---------------|---------------|-------------------|------|----------------------------|
| 51    | Average       | NW/NW         | None              | 0.5  | 2557                       |
| 52    | Average       | NW/NW         | Xypex Admix C-500 | 0.5  | 2657                       |
| 53    | Average       | SE/SE         | None              | 0.5  | 3172                       |
| 54    | Average       | NW/NW         | None              | 0.6  | 1443                       |
| 55    | Average       | NW/NW         | Xypex Admix C-500 | 0.6  | 1611                       |
| 56    | Average       | SE/SE         | None              | 0.6  | 2057                       |
| 57    | SST Blend     | NW/NW         | None              | 0.5  | 4980                       |
| 58    | SST Blend     | NW/NW         | Xypex Admix C-500 | 0.5  | 3880                       |
| 59    | SST Blend     | NW/NW         | None              | 0.6  | 2457                       |
| 60    | SST Blend     | NW/NW         | Xypex Admix C-500 | 0.6  | 2768                       |
| 61    | Average       | NW/NW         | Rheomac SF100     | 0.5  | 4989                       |
| 62    | Average       | NW/NW         | Rheomac SF100     | 0.6  | 2706                       |
| 63    | SST Blend     | NW/NW         | Rheomac SF100     | 0.5  | 5757                       |
| 64    | SST Blend     | SE/SE         | None              | 0.5  | 5230                       |
| 65    | SST Blend     | NW/NW         | Rheomac SF100     | 0.6  | 4383                       |
| 66    | SST Blend     | SE/SE         | None              | 0.6  | 4390                       |

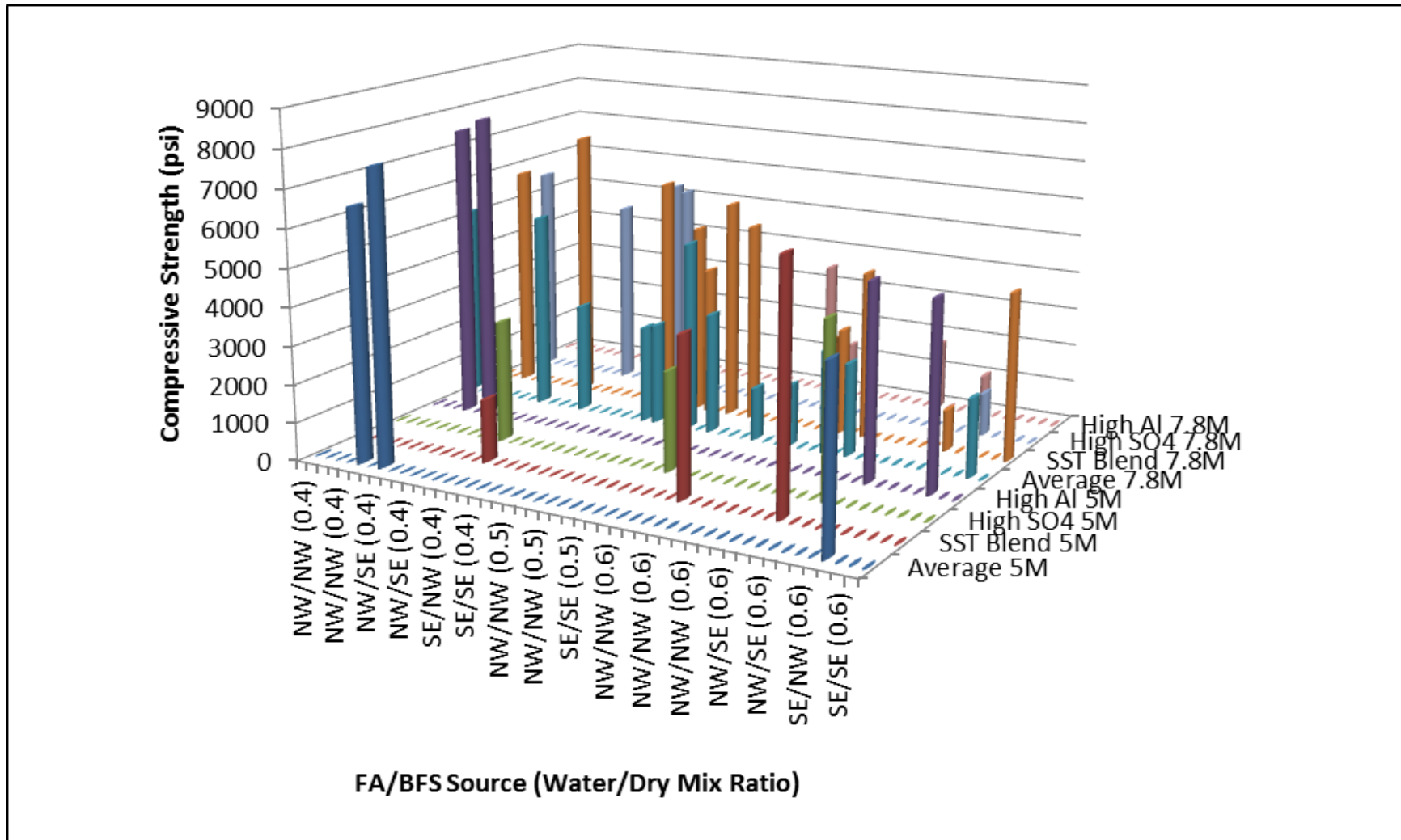


Figure 3-8. Average compressive strength of triplicate Cast Stone cylinders for the 16 Augmented Matrix formulations plotted with the Screening Matrix mixes from Reference 1.

### 3.8 Chemical Composition

In previous work, compositional analysis of the cured Cast Stone did not consistently mass balance to within 95-105 mass%.<sup>1,6</sup> Attaining complete mass balance is troublesome because the grouts are made up of water with dissolved salts and refractory oxides, which made sample preparation and analysis difficult. An accurate initial composition ( $C_0$ ) of components that will be used for subsequent calculations is critical. To calculate the composition, the formulations in Table 2-5 were used to calculate the mass fraction of salt solution and dry materials in each mix. The compositions of the salt solutions and dry blends used the measured chemical compositions of the salt simulants in Section 3.0 of Reference 2 and the three dry blend materials in Section 4.0 of Reference 1. For the salt solution composition, calculated values were used for the analytes that were not analyzed, iodine, technetium, and hydroxide. The water content of the mixes were determined by drying triplicate samples. Table 3-8 provides the calculated chemical compositions of the formulations prepared in this study. The Tc-99 concentration is reported in dpm Tc-99/kg Cast Stone for use in leach testing calculations.

**Table 3-8. Calculated Chemical Compositions of the Cured Test Mixes (wt %)**

| Analyte                        | Mix#     |          |          |          |          |          |          |          |
|--------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
|                                | 51       | 52       | 53       | 54       | 55       | 56       | 57       | 58       |
| Al <sub>2</sub> O <sub>3</sub> | 8.34     | 8.34     | 9.88     | 7.80     | 7.80     | 9.21     | 7.57     | 7.57     |
| BaO                            | 0.15     | 0.15     | 0.04     | 0.13     | 0.13     | 0.04     | 0.14     | 0.14     |
| CaO                            | 17.04    | 17.04    | 12.09    | 15.63    | 15.63    | 11.09    | 16.70    | 16.70    |
| CdO                            | 8.0E-04  | 8.0E-04  | 8.0E-04  | 8.8E-04  | 8.8E-04  | 8.8E-04  | 8.5E-04  | 8.5E-04  |
| Cr <sub>2</sub> O <sub>3</sub> | 0.09     | 0.09     | 0.10     | 0.10     | 0.10     | 0.10     | 0.04     | 0.04     |
| Fe <sub>2</sub> O <sub>3</sub> | 1.78     | 1.78     | 2.16     | 1.64     | 1.64     | 1.98     | 1.75     | 1.75     |
| K <sub>2</sub> O               | 0.57     | 0.57     | 0.78     | 0.54     | 0.54     | 0.73     | 0.50     | 0.50     |
| MgO                            | 2.20     | 2.20     | 3.63     | 2.02     | 2.02     | 3.33     | 2.16     | 2.16     |
| Na <sub>2</sub> O              | 9.16     | 9.16     | 8.47     | 9.92     | 9.92     | 9.29     | 8.95     | 8.95     |
| NiO                            | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     |
| P <sub>2</sub> O <sub>5</sub>  | 0.17     | 0.17     | 0.17     | 0.18     | 0.18     | 0.18     | 0.18     | 0.18     |
| PbO                            | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     |
| SO <sub>4</sub>                | 2.17     | 2.17     | 1.30     | 2.07     | 2.07     | 1.27     | 2.16     | 2.16     |
| SiO <sub>2</sub>               | 22.30    | 22.30    | 25.22    | 20.46    | 20.46    | 23.15    | 21.86    | 21.86    |
| SrO                            | 0.10     | 0.10     | 0.05     | 0.09     | 0.09     | 0.05     | 0.10     | 0.10     |
| TiO <sub>2</sub>               | 0.31     | 0.31     | 0.38     | 0.28     | 0.28     | 0.35     | 0.30     | 0.30     |
| ZnO                            | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     |
| ZrO <sub>2</sub>               | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     | 0.02     |
| NO <sub>3</sub> <sup>-</sup>   | 5.10     | 5.10     | 5.10     | 5.61     | 5.61     | 5.61     | 8.15     | 8.15     |
| NO <sub>2</sub> <sup>-</sup>   | 1.14     | 1.14     | 1.14     | 1.25     | 1.25     | 1.25     | 0.84     | 0.84     |
| Cl <sup>-</sup>                | 0.08     | 0.08     | 0.08     | 0.08     | 0.08     | 0.08     | 0.08     | 0.08     |
| F <sup>-</sup>                 | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     |
| I                              | 8.3E-04  | 8.3E-04  | 8.3E-04  | 9.2E-04  | 9.2E-04  | 9.2E-04  | 8.5E-04  | 8.5E-04  |
| Free OH <sup>-</sup>           | 1.38     | 1.38     | 1.38     | 1.52     | 1.52     | 1.52     | 0.44     | 0.44     |
| Subtotal                       | 72.11    | 72.11    | 72.01    | 69.39    | 69.39    | 69.30    | 71.98    | 71.98    |
| Water                          | 24.41    | 23.80    | 24.49    | 27.46    | 27.61    | 26.69    | 24.45    | 24.48    |
| Total                          | 96.52    | 95.90    | 96.50    | 96.86    | 97.00    | 95.99    | 96.43    | 96.45    |
| Tc-99 dpm/kg                   | 2.38E+05 | 2.38E+05 | 2.38E+05 | 2.62E+05 | 2.62E+05 | 2.62E+05 | 2.42E+05 | 2.42E+05 |

**Table 3-8. Calculated Chemical Compositions of the Cured Test Mixes (wt %) (continued)**

| Analyte                        | Mix#            |                 |               |               |               |               |               |               |
|--------------------------------|-----------------|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                                | 59              | 60              | 61            | 62            | 63            | 64            | 65            | 66            |
| Al <sub>2</sub> O <sub>3</sub> | 6.96            | 6.96            | 8.34          | 7.80          | 7.57          | 9.07          | 6.96          | 8.34          |
| BaO                            | 0.13            | 0.13            | 0.15          | 0.13          | 0.14          | 0.04          | 0.13          | 0.04          |
| CaO                            | 15.29           | 15.29           | 17.04         | 15.63         | 16.70         | 11.85         | 15.29         | 10.85         |
| CdO                            | 9.3E-04         | 9.3E-04         | 8.0E-04       | 8.8E-04       | 8.5E-04       | 8.5E-04       | 9.3E-04       | 9.3E-04       |
| Cr <sub>2</sub> O <sub>3</sub> | 0.05            | 0.05            | 0.09          | 0.10          | 0.04          | 0.05          | 0.05          | 0.05          |
| Fe <sub>2</sub> O <sub>3</sub> | 1.60            | 1.60            | 1.78          | 1.64          | 1.75          | 2.12          | 1.60          | 1.94          |
| K <sub>2</sub> O               | 0.47            | 0.47            | 0.57          | 0.54          | 0.50          | 0.71          | 0.47          | 0.66          |
| MgO                            | 1.98            | 1.98            | 2.20          | 2.02          | 2.16          | 3.56          | 1.98          | 3.26          |
| Na <sub>2</sub> O              | 9.67            | 9.67            | 9.16          | 9.92          | 8.95          | 8.27          | 9.67          | 9.05          |
| NiO                            | 0.01            | 0.01            | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          |
| P <sub>2</sub> O <sub>5</sub>  | 0.20            | 0.20            | 0.17          | 0.18          | 0.18          | 0.18          | 0.20          | 0.20          |
| PbO                            | 0.01            | 0.01            | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          |
| SO <sub>4</sub>                | 2.06            | 2.06            | 2.17          | 2.07          | 2.16          | 1.31          | 2.06          | 1.28          |
| SiO <sub>2</sub>               | 20.02           | 20.02           | 22.30         | 20.46         | 21.86         | 24.72         | 20.02         | 22.64         |
| SrO                            | 0.09            | 0.09            | 0.10          | 0.09          | 0.10          | 0.05          | 0.09          | 0.04          |
| TiO <sub>2</sub>               | 0.28            | 0.28            | 0.31          | 0.28          | 0.30          | 0.38          | 0.28          | 0.34          |
| ZnO                            | 0.01            | 0.01            | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          |
| ZrO <sub>2</sub>               | 0.02            | 0.02            | 0.02          | 0.02          | 0.02          | 0.02          | 0.02          | 0.02          |
| NO <sub>3</sub> <sup>-</sup>   | 8.96            | 8.96            | 5.10          | 5.61          | 8.15          | 8.15          | 8.96          | 8.96          |
| NO <sub>2</sub> <sup>-</sup>   | 0.93            | 0.93            | 1.14          | 1.25          | 0.84          | 0.84          | 0.93          | 0.93          |
| Cl <sup>-</sup>                | 0.09            | 0.09            | 0.08          | 0.08          | 0.08          | 0.08          | 0.09          | 0.09          |
| F <sup>-</sup>                 | 0.01            | 0.01            | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          | 0.01          |
| I <sup>-</sup>                 | 9.3E-04         | 9.3E-04         | 8.3E-04       | 9.2E-04       | 8.5E-04       | 8.5E-04       | 9.3E-04       | 9.3E-04       |
| OH <sup>-</sup>                | 0.48            | 0.48            | 1.38          | 1.52          | 0.44          | 0.44          | 0.48          | 0.48          |
| <b>Subtotal</b>                | <b>69.31</b>    | <b>69.31</b>    | <b>72.11</b>  | <b>69.39</b>  | <b>71.98</b>  | <b>71.88</b>  | <b>69.31</b>  | <b>69.22</b>  |
| <b>Water</b>                   | <b>26.50%</b>   | <b>26.77%</b>   | <b>24.37%</b> | <b>27.15%</b> | <b>24.98%</b> | <b>24.51%</b> | <b>26.34%</b> | <b>26.99%</b> |
| <b>Total</b>                   | <b>95.81</b>    | <b>96.08</b>    | <b>96.47</b>  | <b>96.54</b>  | <b>96.95</b>  | <b>96.39</b>  | <b>95.65</b>  | <b>96.21</b>  |
| <b>Tc-99<br/>dpm/kg</b>        | <b>2.66E+05</b> | <b>2.66E+05</b> | <b>0</b>      | <b>0</b>      | <b>0</b>      | <b>0</b>      | <b>0</b>      | <b>0</b>      |

### 3.9 Leach Testing

Duplicate samples of the simulant formulations and Tc-99 containing formulations were subjected to the United States EPA Manual SW-846 Method 1315 leach test.<sup>7</sup> Leach indices for simulant samples were determined for sodium, nitrate, chromium, and iodine. Tc-99 was the only leach index calculated for the Tc-99 containing samples.

#### 3.9.1 Leach Testing – non-radioactive samples

After curing for approximately 28 days, cylindrical samples of each of the test mixes were removed from their molds and leached following the EPA 1315 procedure as described in Reference 6. The testing was performed on duplicate samples. The leachates were analyzed via Inductively Coupled Plasma – Optical

Emission spectroscopy for sodium and chromium—an ultrasonic nebulizer was also used in the chromium analysis, Ion Chromatography for nitrate, and Gas Chromatography – Mass Spectroscopy (GC-MS) for iodine. In this testing, iodine was measured in the leachate samples following the method described by Zhang et al.<sup>8</sup> For this analysis, an internal standard (2,4,6 tribromoaniline) was added to each aqueous sample as a yield monitor. The iodide was oxidized followed by iodination of an organic compound (N,N-dimethylamine). The iodinated derivative, 4-iodo-N,N-dimethylaniline was measured on a gas chromatograph- mass spectrometer (GC-MS). Typical analyses are for iodine-127, but using the GC-MS software it is possible to specify the mass of the iodinated compound thereby allowing for distinction between iodine-127 and iodine-129. Analytical separations were carried out on a Hewlett Packard 6890 gas chromatograph, equipped with a 25 m DB-5 column, with 0.20 mm diameter and 0.33 um film thickness. Quantitation was performed using a Hewlett Packard 5973 mass selective detector. Initial concentrations of the contaminants in the waste form were calculated as described in Section 3.8. The target iodine concentrations were used as the initial concentrations of iodine since the preparation for chemical analysis of the cured Cast Stone samples resulted in a significant loss of iodine. Leachability indices were determined for nitrate, iodine, chromium, and sodium. The average of the two duplicate leachability indices for each contaminant is reported, Table 3-9. 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. Although an ultrasonic nebulizer was used for the chromium analysis, 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 sodium and nitrate were generally similar. The addition of the Xypex, Admix C-500 may have improved the iodine leach index in formulations prepared with the HTWOS Average salt solution, Mixes 52 and 55, with respect to the corresponding mixes that did not contain the admixture, Mixes 51 and 54. No noticeable difference in leach indices were noted among the samples prepared with Rheomac SF100.

**Table 3-9. Leachability Indices (LI) for the Augmented Matrix Formulations**

| Mix # | Salt Solution | FA/BFS Source | Admix             | Na  | NO <sub>3</sub> | Cr  | I   |
|-------|---------------|---------------|-------------------|-----|-----------------|-----|-----|
| 51    | Average       | NW/NW         | None              | 8.1 | 8.3             | >13 | 8.3 |
| 52    | Average       | NW/NW         | Xypex Admix C-500 | 8.1 | 8.4             | >13 | 9.1 |
| 53    | Average       | SE/SE         | None              | 8.3 | 8.4             | >13 | 8.1 |
| 54    | Average       | NW/NW         | None              | 8.1 | 8.3             | >13 | 8.1 |
| 55    | Average       | NW/NW         | Xypex Admix C-500 | 8.0 | 8.2             | >13 | 9.1 |
| 56    | Average       | SE/SE         | None              | 8.1 | 8.2             | >13 | 9.1 |
| 57    | SST Blend     | NW/NW         | None              | 8.1 | >8.5            | >13 | 7.9 |
| 58    | SST Blend     | NW/NW         | Xypex Admix C-500 | 8.4 | >8.9            | >13 | 8.1 |
| 59    | SST Blend     | NW/NW         | None              | 8.2 | 8.3             | >13 | 8.4 |
| 60    | SST Blend     | NW/NW         | Xypex Admix C-500 | 8.1 | 8.3             | >13 | 8.1 |
| 61    | Average       | NW/NW         | Rheomac SF100     | 8.2 | 8.3             | >13 | 8.6 |
| 62    | Average       | NW/NW         | Rheomac SF100     | 8.1 | 8.3             | >13 | 8.4 |
| 63    | SST Blend     | NW/NW         | Rheomac SF100     | 8.3 | 8.4             | >13 | 8.5 |
| 64    | SST Blend     | SE/SE         | None              | 8.4 | 8.6             | >13 | 8.3 |
| 65    | SST Blend     | NW/NW         | Rheomac SF100     | 8.1 | 8.3             | >13 | 8.5 |
| 66    | SST Blend     | SE/SE         | None              | 8.1 | 8.2             | >13 | 8.2 |

### 3.9.2 Leach Testing –radioactive samples

Duplicate samples of Mixes 51-60 were prepared with Tc-99 additions as shown in Table 2-5. Leach testing was carried out as described in Section 3.9.1. Leachate analysis was limited to Tc-99 by liquid scintillation method. In cases where the concentration of the Tc-99 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. Values are reported in Table 3-10, below.

**Table 3-10. Leachability Indices (LI) for the Augmented Matrix Formulations Spiked with Tc-99**

| Mix # | Salt Solution | FA/BFS Source | Admix             | Tc-99 Leach Index |
|-------|---------------|---------------|-------------------|-------------------|
| 51    | Average       | NW/NW         | None              | >10.9             |
| 52    | Average       | NW/NW         | Xypex Admix C-500 | >11.8             |
| 53    | Average       | SE/SE         | None              | >10.7             |
| 54    | Average       | NW/NW         | None              | >10.8             |
| 55    | Average       | NW/NW         | Xypex Admix C-500 | >11.6             |
| 56    | Average       | SE/SE         | None              | 10.4              |
| 57    | SST Blend     | NW/NW         | None              | 9.7               |
| 58    | SST Blend     | NW/NW         | Xypex Admix C-500 | 10.8              |
| 59    | SST Blend     | NW/NW         | None              | 9.5               |
| 60    | SST Blend     | NW/NW         | Xypex Admix C-500 | 10.5              |

The values indicate that for both the HTWOS Average and SST Blend stimulants, Xypex addition increases the leachability index by nearly one unit corresponding to a nearly tenfold decrease in effective diffusivity.

## 4.0 Conclusions

Sixteen formulations were prepared to augment the statistically constructed Screening Matrix in Reference 1. The Augmented Matrix series introduced an intermediate water-to-dry-blend ratio and two admixtures intended to reduce the leachability of the waste form. The results for properties that were influenced by the W/DM ratio in the Screening Matrix; flow diameter, plastic viscosity, density, and compressive strength, showed consistent behavior in this study with respect to W/DM. The properties of formulations with a W/DM of 0.5 were bounded by the results of the Screening Matrix. The admixtures evaluated in this study, Xypex Admix C-500 and Rheomac SF100, did not noticeably influence these properties. Properties that rely on reaction rate and extent of reaction, gel time, free liquid, and heat of hydration, did not follow a recognizable pattern with changing formulation—W/DM, salt simulant, or admixture. As was noted in Reference 1 and Reference 6, the leach index for highly soluble components, sodium and nitrate, were not influenced by changes in formulation. The leach index for both iodine and Tc-99 show an influence from the addition of the admixture, Xypex Admix C-500, with the Leach Index for Tc-99 being nearly one unit higher for both the HTWOS Average stimulant and SST Blend formulations with Xypex added. This may be the result of reduced effective porosity as Xypex is marketed to the commercial concrete industry as a waterproofing admixture.



## 5.0 Recommendations

The results of this study indicate an influence of additions of the admixture, Xypex Admix C-500, on the leach index of both iodine and Tc-99. Additional testing to determine the relationship between the admixture concentration and leach index for a range of formulations should be considered. This would help determine if the effect of the admixture was dependent on other variables in the matrix of formulations tested. To date, leach indices have been measured on samples that have been cured for short times, 28 days, in ambient conditions. Actual curing and storage of any waste form will involve temperature variations and material interactions. The effects of these conditions with respect to the current sample curing and storage prior to testing is not well known. Testing should be performed to evaluate if there is an improvement that persists for longer curing times under different storage conditions. Properties that look to be influenced by hydration kinetics, gel time, free water, and heat of hydration, have varied greatly over the matrix of formulations investigated. Additional testing is required to identify interactions between formulation components to identify items that influence these properties.

## 6.0 References

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- <sup>8</sup>Zhang, S., Schwehr, K.A., Ho, Y.-F., Xu, C. Roberts, K.A., Kaplan, D.I., Brinkmeyer, R. Yeager, C.M., and Santschi, P.H. 2010. A novel approach for the simultaneous determination of iodide, iodate, and organo-iodine for 127I and 129I in environmental samples using gas chromatography – Mass Spectrometry. *Environ. Sci & Technol.*, 44, 9042-9048.

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