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Hanford's Simulated Low Activity Waste Cast Stone Processing

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Abstract

Cast Stone is undergoing evaluation as the supplemental treatment technology for Hanford's (Washington) high activity waste (HAW) and low activity waste (LAW). This report will only cover the LAW Cast Stone. The programs used for this simulated Cast Stone were gradient density change, compressive strength, and salt waste form phase identification. Gradient density changes show a favorable outcome by showing uniformity even though it was hypothesized differently. Compressive strength exceeded the minimum strength required by Hanford and greater compressive strength increase seen between the uses of different salt solution The salt waste form phase is still an ongoing process as this time and could not be concluded.

Introduction

The Hanford site is about 586 square miles (374,934 acres) and the Savannah River site (SRS) is about 310 square miles (198,344 acres). From 1943-1964, about 149 single shell tanks were built at Hanford, and between 1968-1986 about 28 double shell tanks were built. The materials in the tank consist of liquids, gases, semi-solids, and solids. Although only liquid portion of the waste was transferred to double shell tanks leaving semi-solids and solids in the single shell tanks. These wastes including the liquids will be either processed as a High Activity Waste (HAW) or Low Activity Waste (LAW). Hanford is in process of building these facilities. There are four ways of processing the LAW under consideration for the supplemental treatment method to the primary LAW glass: One by forming it into a glass in a cylindrical canister like the primary treatment method, and another by mixing it into a grout form called Cast Stone. Here at Savannah River National Laboratory (SRNL), simulated Cast Stone goes through multiple tests before it becomes applicable for Hanford's LAW. The programs that were performed on the Cast Stone at SRNL were gradient density, compressive strength, and salt waste form phase identification.

Simulated Cast Stone

Gradient Density for Cast Stone

The purpose of this experiment was to find out the gradient change in density of the three sections (top, middle, and bottom) of each Cast Stone samples. The outcome that was expected from this was waste form liquids will potentially create a self-settling effect.

The equipment that was used was the multipycnometer. Multipycnometer as referred to by the Quantachrome Corporation Multipyncometer Instruction Manual measures the amount of

volume of a given object that can be used in a density calculation. It is much more accurate than water volume because it uses helium gas which is smaller than the water particles and can easily go in-between the pore spaces of the samples being analyzed. When using a pycnometer, it starts out with a 15 minute warm-up. "Gas in" and "Gas out" should be closed, and the helium value should be set on 20 psig. Anywhere above 25 psig will damage the multipycnometer pressure transducer. Then the machine must be purged for five minutes before calibration. During the calibration, "cell" is turned on, "Gas out" valve is open and "Gas in" valve is closed. This operational method defines

$P_a (V_{cell}-V_{sample}) = n_aRT_a$ which is the ideal gas law.

Where V_{cell} is the cell volume, V_{sample} is the sample volume, n is the ambient mole of gas, R is the gas constant, and T is the ambient temperature. Once the "Gas out" valve stabilizes, close the valve then set the psig display to 0 which is defined as P_a. Then set the valve to "REF", open the "Gas in" and close it when it reaches around 17 psi. This is expressed as

$P_1 V_{ref} = n_1RT_a$, where P_1 represents as 17 psi or 17 lbs/in^2 above ambient, and n_1 is the total number of moles in the reference volume (V_{ref}). P_2 is the second reading of pressure after P_1 which is done by selecting the "Cell" valve. The pressure decreases and is defined by

$P_2 (V_{cell}-V_{sample}+V_{ref}) = n_aRT_a+n_1RT_a$

By substitution the equation turns out to be

Step1: $P_2 (V_{cell}-V_{sample}+Vref) = P_a (V_{cell}-V_{sample}) + P_1V_{ref}$ or $(P_2-P_a)(V_{cell}-V_{sample}) =(P_1-P_2)V_{ref}$

Step2: $V_{cell}-V_{sample}= ((P_1-P_2)/ (P_2-P_a))\ V_{ref}$

Because P_a is equal to zero, it is ignored in the equation as shown on the next step.

Step3: $V_{cell}-V_{sample}= ((P_1-P_2)/P_2)$ VR or $V_{sample}=V_{cell}-V_{ref}$ $[(P_1/P_2)-1]$

The pressure was obtained from the pycnometer three times one representing 17 psi (P_1) and above and second by selecting to "Cell" valve (P_2).

And this is how the sample volume is obtained. To get the Vref and Vcell, initial calibration must be done on the pycnometer.

During the initial calibration, a standard large ball is placed into a cell, and the cell is placed into a cell holder making sure the vertical lines are aligned to side horizontal openings. The volume of the standard large ball is 56.5592 cm^3. This can be noted as $V_{cal}L$. However this time P_1 is represents as same as above, but with a large ball in the chamber and same is applied with P_2. P_3 is same as P_1 without a large ball in the chamber and P_4 is same as P_2 giving the second reading of pressure for P_3 by selecting the "Cell" valve.

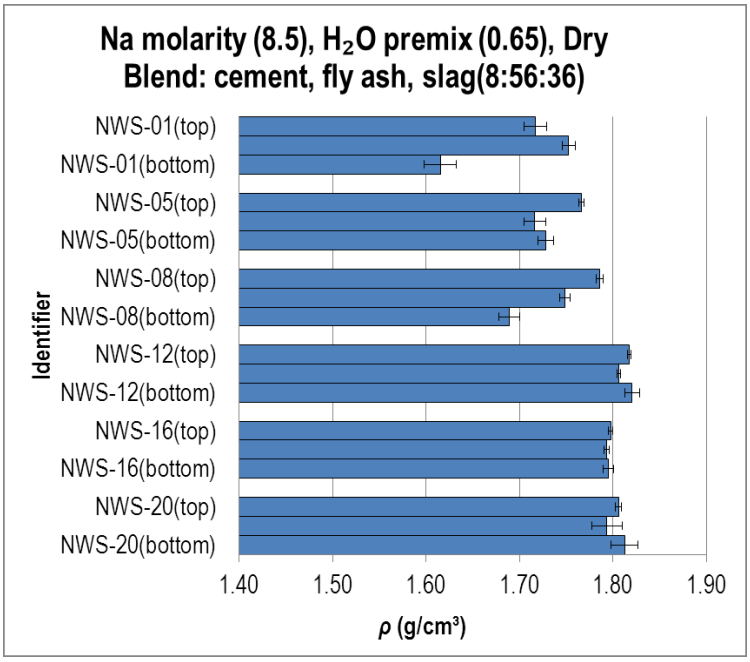
The equation can be defined as

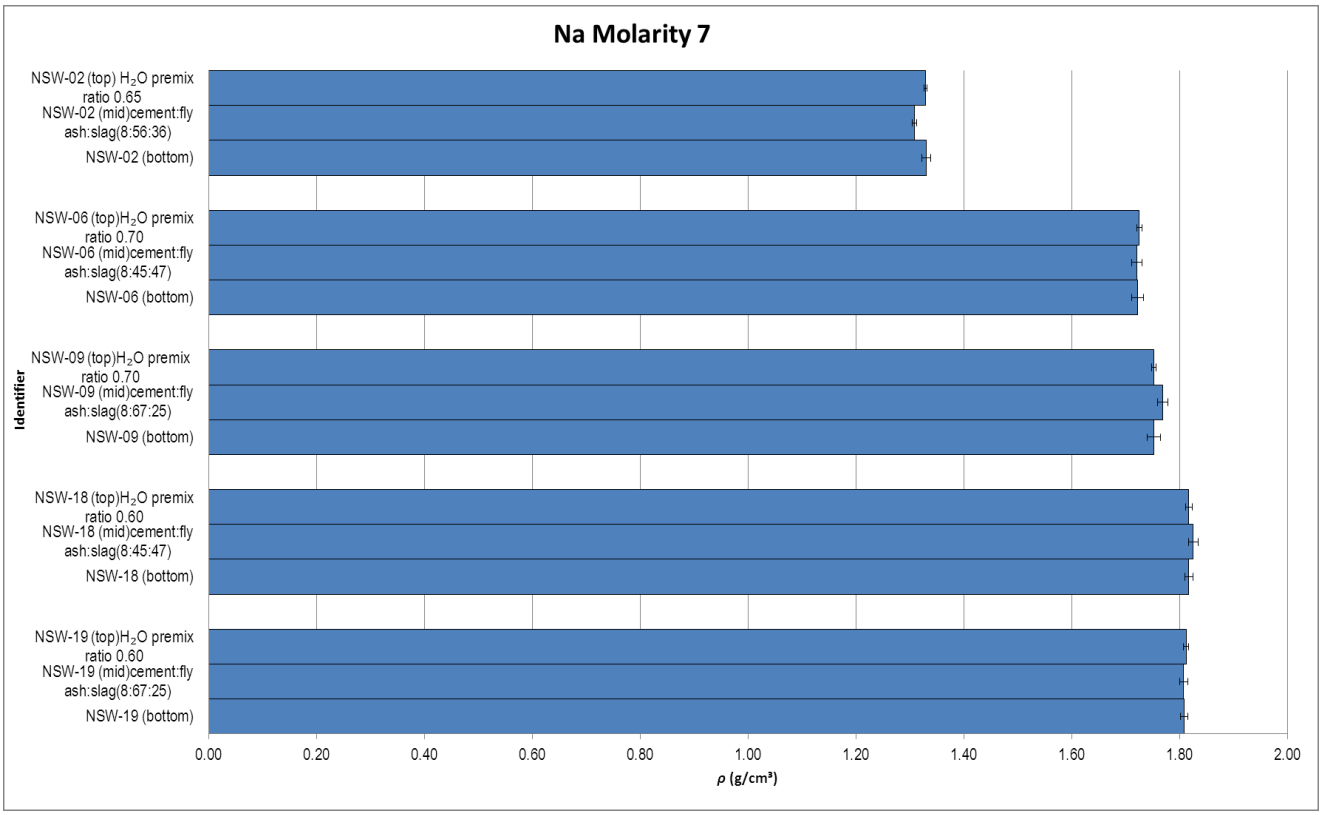
$V_{ref} = V_{cal}L/ [(P_3L/P_4L)-1]-[(P_1L/P_2L)-1]$

$V_{cell} = V_{cal}L +V_{ref}L * [(P_1L/P_2L)-1]$

Other equations that were applied to the Cast Stone samples were geometric density and standard deviation to determine the errors. Using the geometric density, Cast Stonesample density can be compared to determine if the values come in close to each other.

*The term Na Molarity this does not mean only sodium is contained as added solution, it identifies the concentration of sodium in the salt solution. Similarly, the H_2O to premix ratio indicated the water content in the salt solution ratio to the dry materials .

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NSW-02 (bottom)
NSW-06 (top)H2O premix ratio 0.70
NSW-06 (mid)cement:fly ash:slag(8:45:47)
NSW-06 (bottom)
NSW-09 (top)H2O premix ratio 0.70
NSW-09 (mid)cement:fly ash:slag(8:67:25)
NSW-09 (bottom)
NSW-18 (top)H2O premix ratio 0.60
NSW-18 (mid)cement:fly ash:slag(8:45:47)
NSW-18 (bottom)
NSW-19 (top)H2O premix ratio 0.60
NSW-19 (mid)cement:fly ash:slag(8:67:25)
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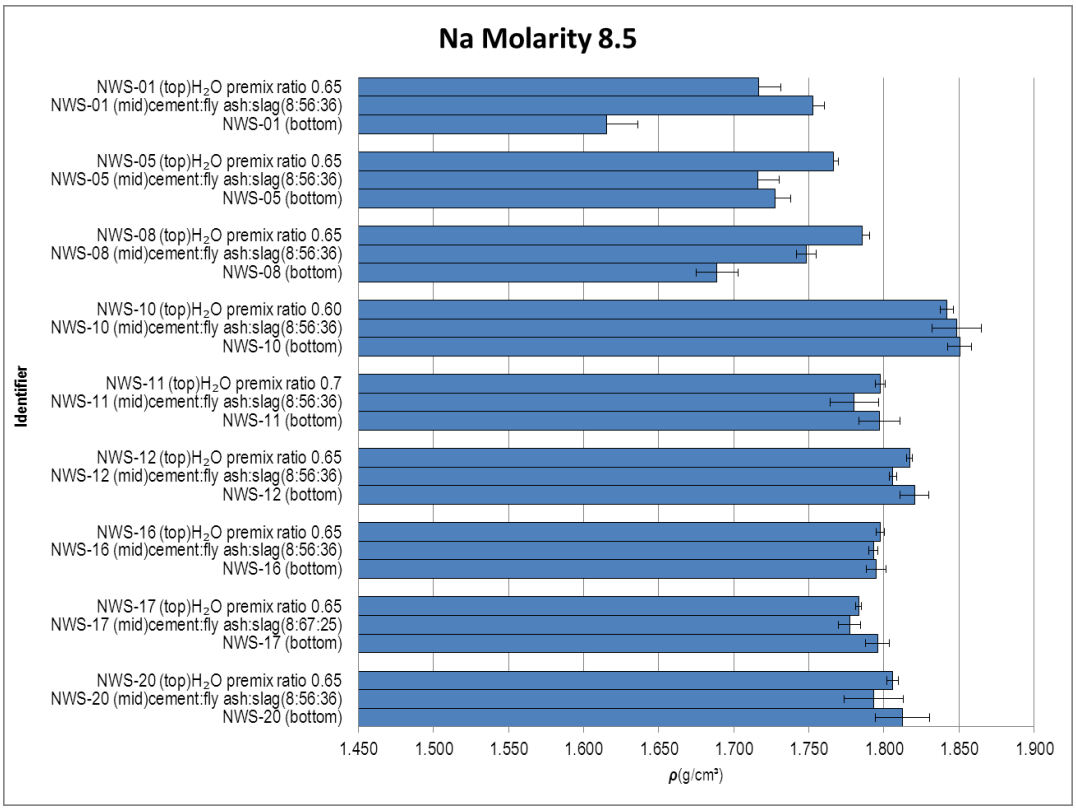
ρ (g/cm³)


Na Molarity 8.5
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NWS-05 (mid)cement:fly ash:slag(8:56:36)
NWS-05 (bottom)
NWS-08 (top)H2O premix ratio 0.65
NWS-08 (mid)cement:fly ash:slag(8:56:36)
NWS-08 (bottom)
NWS-10 (top)H2O premix ratio 0.60
NWS-10 (mid)cement:fly ash:slag(8:56:36)
NWS-10 (bottom)
NWS-11 (top)H2O premix ratio 0.7
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NWS-12 (top)H2O premix ratio 0.65
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NWS-16 (mid)cement:fly ash:slag(8:56:36)
NWS-16 (bottom)
NWS-17 (top)H2O premix ratio 0.65
NWS-17 (mid)cement:fly ash:slag(8:67:25)
NWS-17 (bottom)
NWS-20 (top)H2O premix ratio 0.65
NWS-20 (mid)cement:fly ash:slag(8:56:36)
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Identifier
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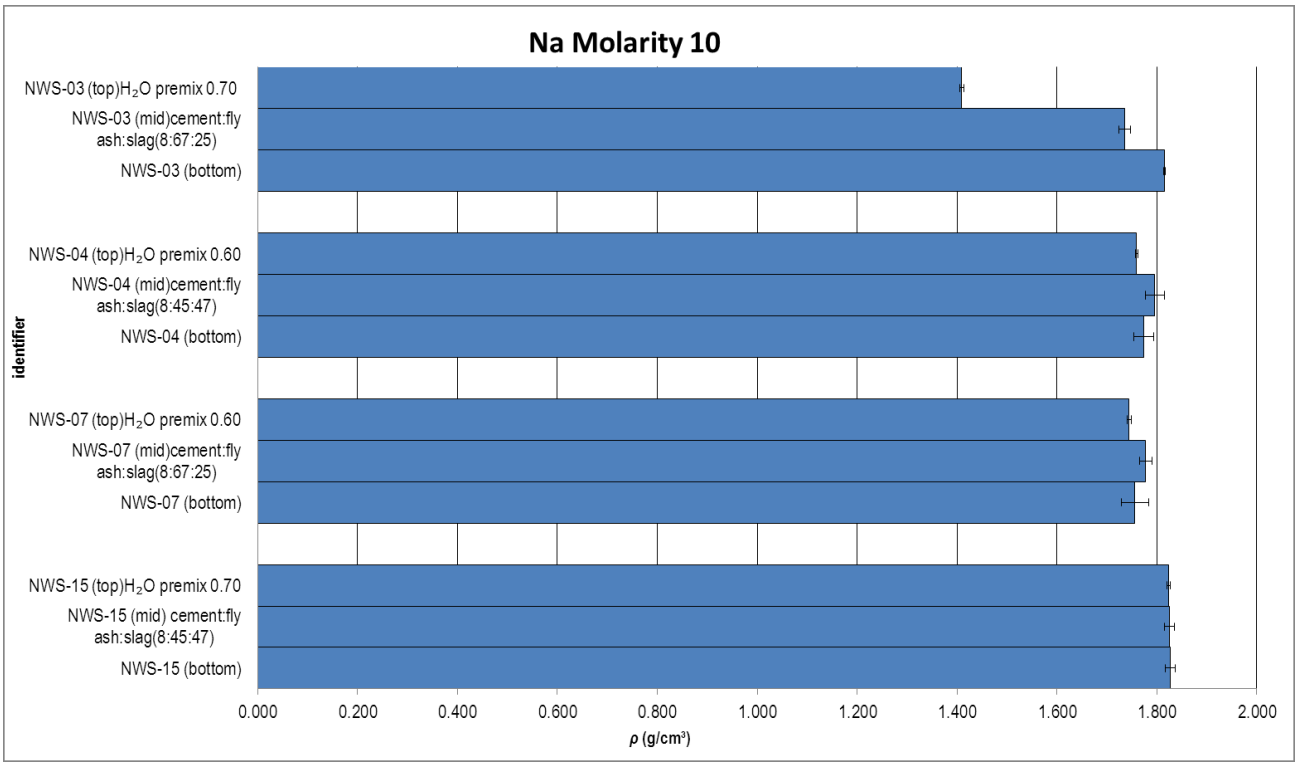
ρ(g/cm³)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NWS-04 (bottom)
NWS-07 (top)H2O premix 0.60
NWS-07 (mid)cement:fly ash:slag(8:67:25)
NWS-07 (bottom)
NWS-15 (top)H2O premix 0.70
NWS-15 (mid) cement:fly ash:slag(8:45:47)
NWS-15 (bottom)
identifier
0.000
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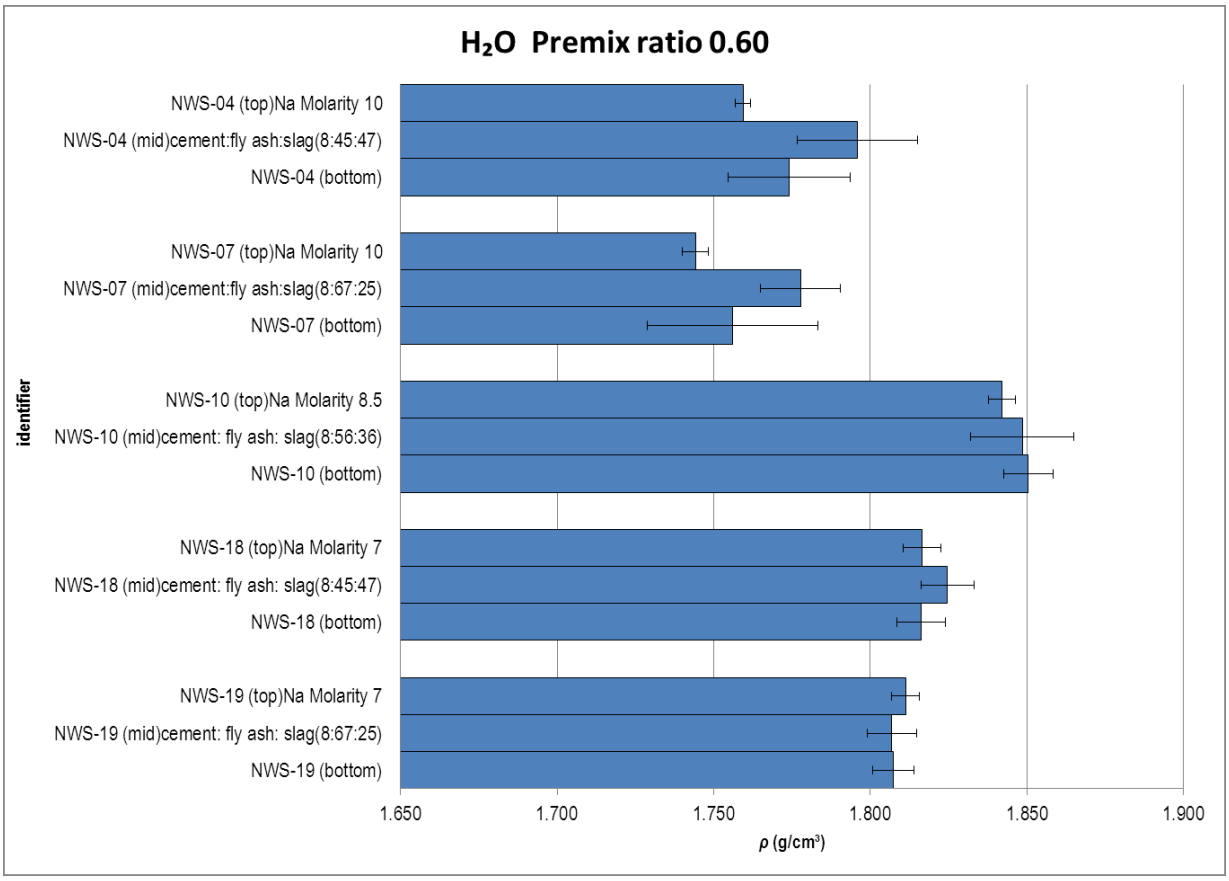
0.600
0.800
1.000
1.200
1.400
1.600
1.800
2.000
ρ (g/cm3)


H₂O Premix ratio 0.60
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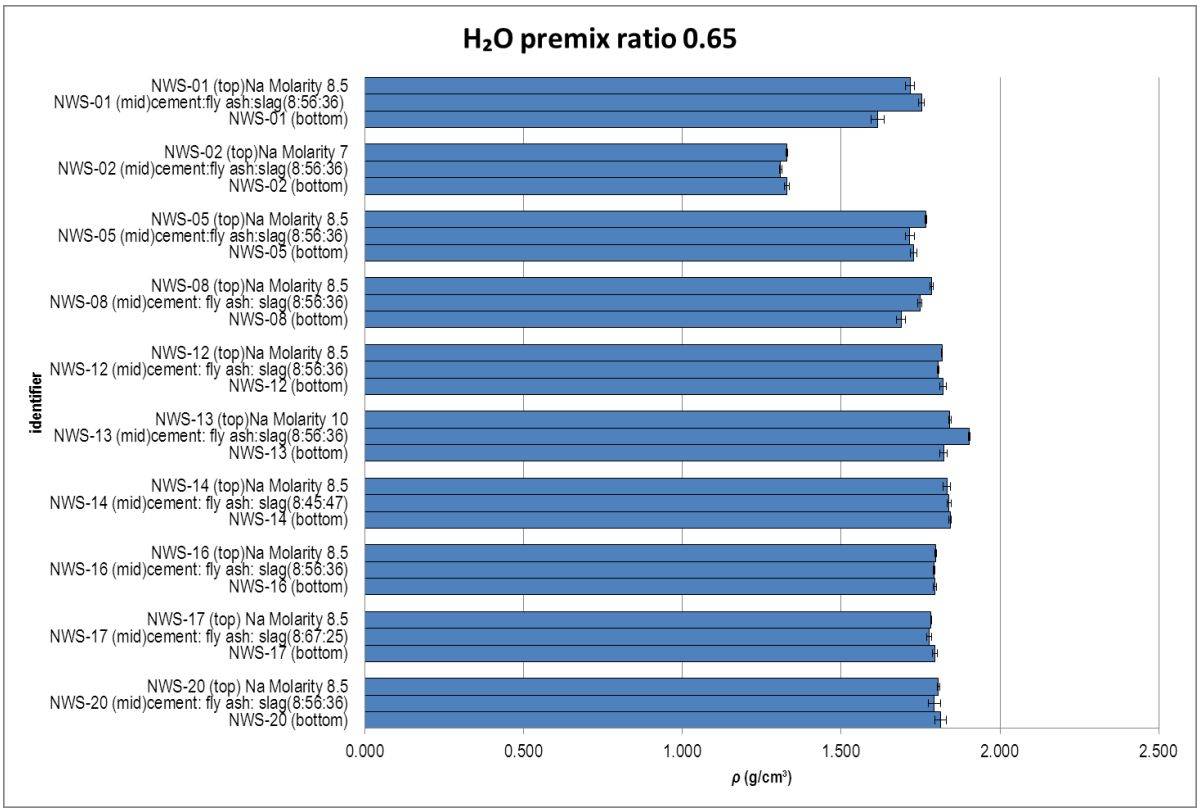
NWS-07 (mid)cement:fly ash:slag(8:67:25)
NWS-07 (bottom)
NWS-10 (top)Na Molarity 8.5
NWS-10 (mid)cement: fly ash: slag(8:56:36)
NWS-10 (bottom)
NWS-18 (top)Na Molarity 7
NWS-18 (mid)cement: fly ash: slag(8:45:47)
NWS-18 (bottom)
NWS-19 (top)Na Molarity 7
NWS-19 (mid)cement: fly ash: slag(8:67:25)
NWS-19 (bottom)
1.650
1.700
1.750
1.800
1.850
1.900
ρ (g/cm³)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NWS-01 (mid)cement:fly ash:slag(8:56:36)
NWS-01 (bottom)
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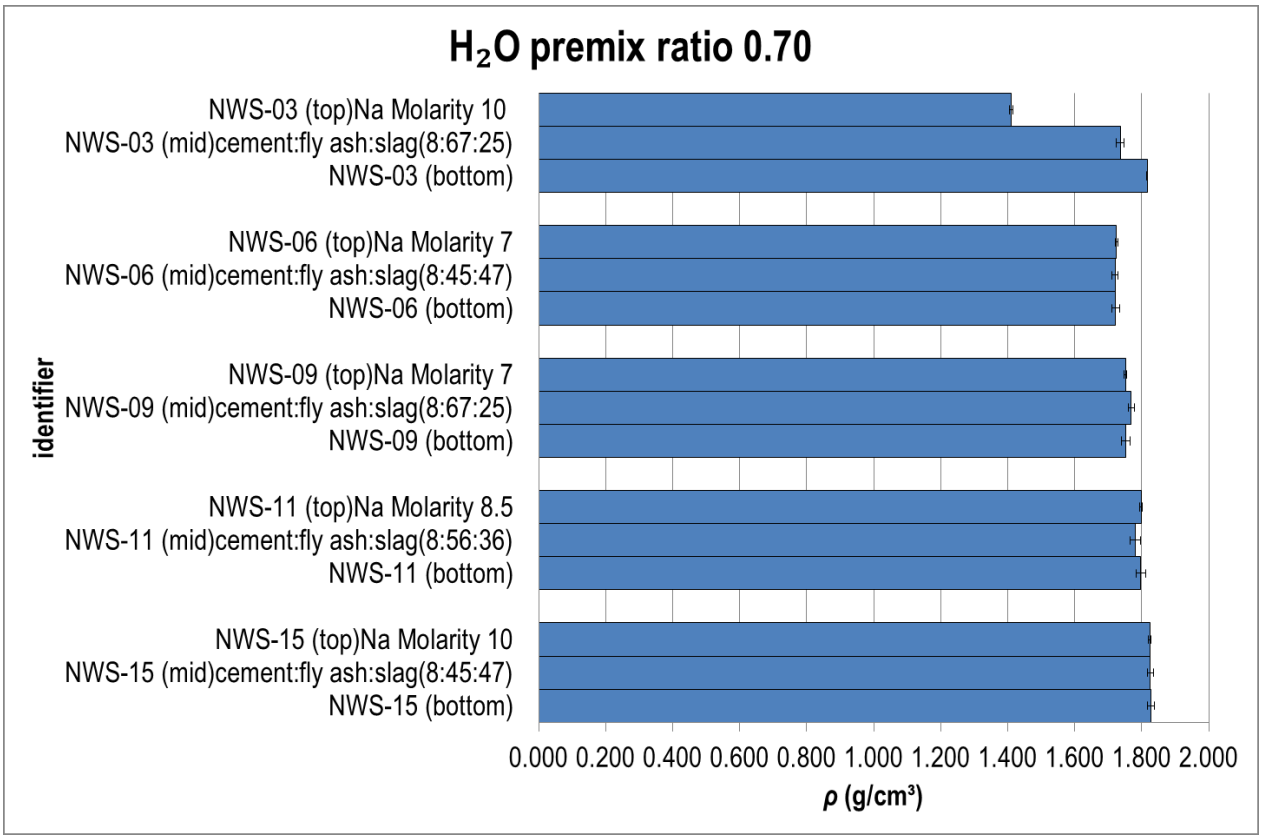
NWS-02 (mid)cement:fly ash:slag(8:56:36)
NWS-02 (bottom)
NWS-05 (top)Na Molarity 8.5
NWS-05 (mid)cement:fly ash:slag(8:56:36)
NWS-05 (bottom)
NWS-08 (top)Na Molarity 8.5
NWS-08 (mid)cement: fly ash: slag(8:56:36)
NWS-08 (bottom)
NWS-12 (top)Na Molarity 8.5
NWS-12 (mid)cement: fly ash: slag(8:56:36)
NWS-12 (bottom)
NWS-13 (top)Na Molarity 10
NWS-13 (mid)cement: fly ash:slag(8:56:36)
NWS-13 (bottom)
NWS-14 (top)Na Molarity 8.5
NWS-14 (mid)cement: fly ash: slag(8:45:47)
NWS-14 (bottom)
NWS-16 (top)Na Molarity 8.5
NWS-16 (mid)cement: fly ash: slag(8:56:36)
NWS-16 (bottom)
NWS-17 (top) Na Molarity 8.5
NWS-17 (mid)cement: fly ash: slag(8:67:25)
NWS-17 (bottom)
NWS-20 (top) Na Molarity 8.5
NWS-20 (mid)cement: fly ash: slag(8:56:36)
NWS-20 (bottom)
identifier
0.000
0.500
1.000
1.500
2.000
2.500
ρ (g/cm³)


H2O premix ratio 0.70
NWS-03 (top)Na Molarity 10
NWS-03 (mid)cement:fly ash:slag(8:67:25)
NWS-03 (bottom)
NWS-06 (top)Na Molarity 7
NWS-06 (mid)cement:fly ash:slag(8:45:47)
NWS-06 (bottom)
NWS-09 (top)Na Molarity 7
NWS-09 (mid)cement:fly ash:slag(8:67:25)
NWS-09 (bottom)
NWS-11 (top)Na Molarity 8.5
NWS-11 (mid)cement:fly ash:slag(8:56:36)
NWS-11 (bottom)
NWS-15 (top)Na Molarity 10
NWS-15 (mid)cement:fly ash:slag(8:45:47)
NWS-15 (bottom)
identifier
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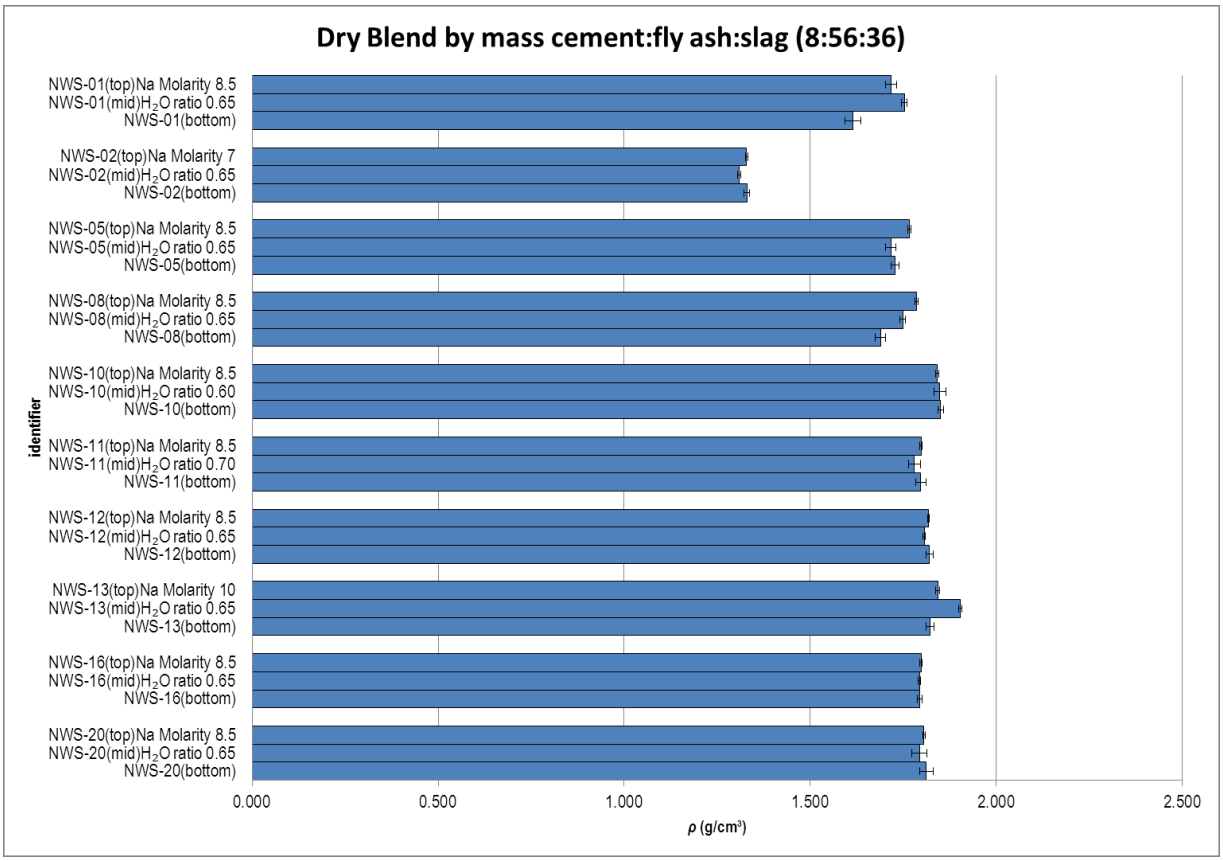
ρ (g/cm³)


Dry Blend by mass cement:fly ash:slag (8:56:36)
identifier
NWS-01(top)Na Molarity 8.5
NWS-01(mid)H2O ratio 0.65
NWS-01(bottom)
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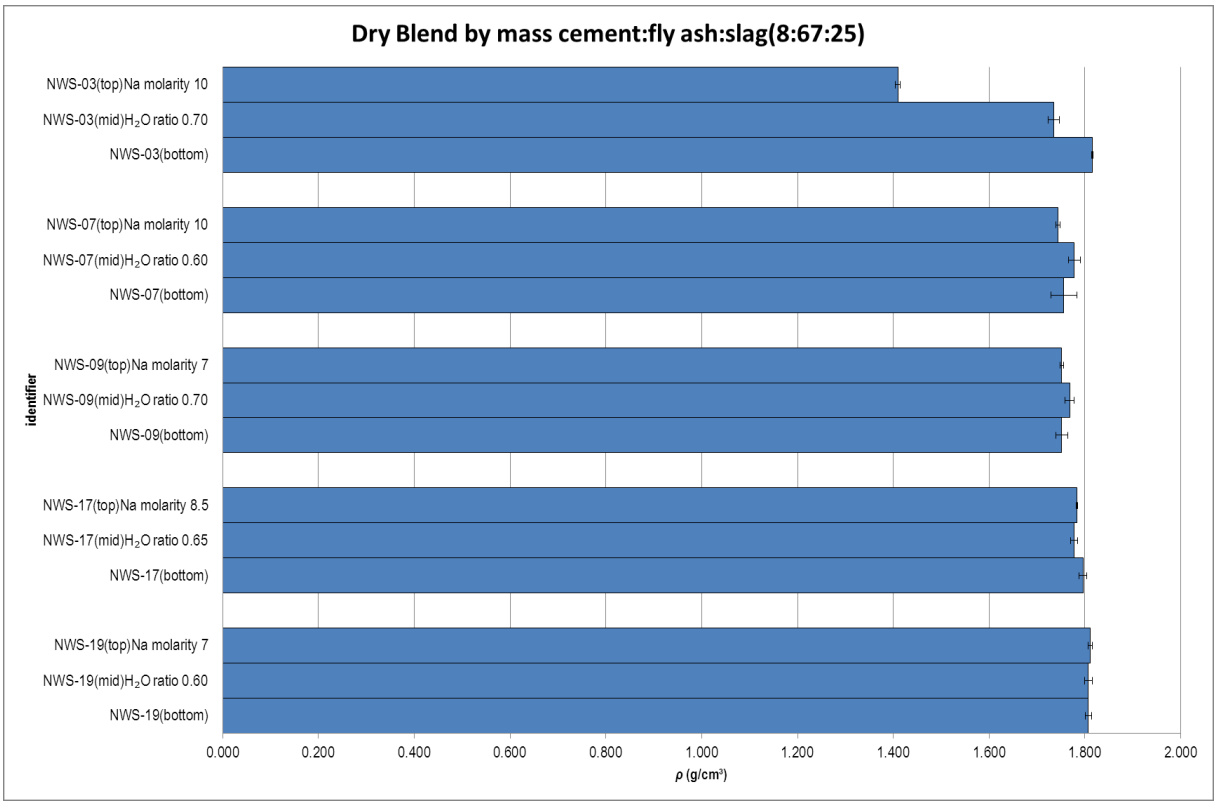
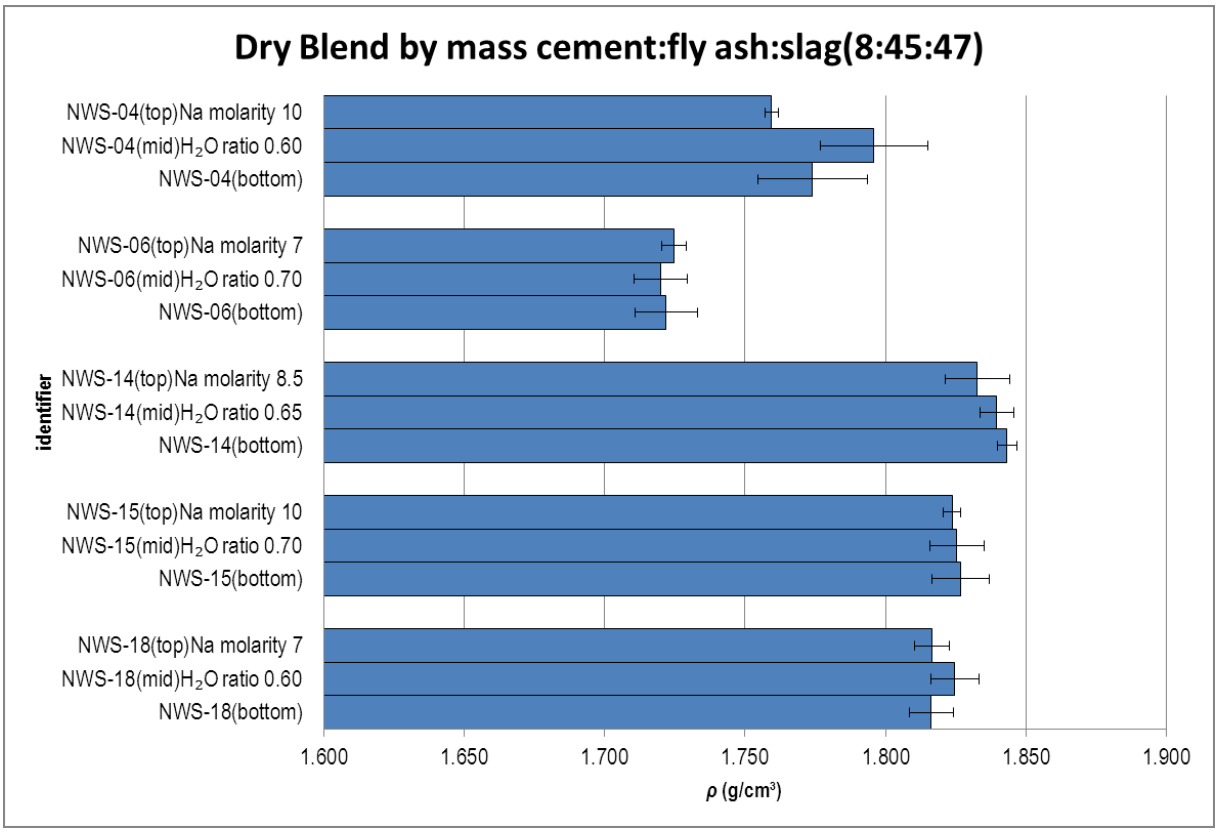
NWS-02(mid)H2O ratio 0.65
NWS-02(bottom)
NWS-05(top)Na Molarity 8.5
NWS-05(mid)H2O ratio 0.65
NWS-05(bottom)
NWS-08(top)Na Molarity 8.5
NWS-08(mid)H2O ratio 0.65
NWS-08(bottom)
NWS-10(top)Na Molarity 8.5
NWS-10(mid)H2O ratio 0.60
NWS-10(bottom)
NWS-11(top)Na Molarity 8.5
NWS-11(mid)H2O ratio 0.70
NWS-11(bottom)
NWS-12(top)Na Molarity 8.5
NWS-12(mid)H2O ratio 0.65
NWS-12(bottom)
NWS-13(top)Na Molarity 10
NWS-13(mid)H2O ratio 0.65
NWS-13(bottom)
NWS-16(top)Na Molarity 8.5
NWS-16(mid)H2O ratio 0.65
NWS-16(bottom)
NWS-20(top)Na Molarity 8.5
NWS-20(mid)H2O ratio 0.65
NWS-20(bottom)
0.000
0.500
1.000
1.500
2.000
2.500
ρ (g/cm3)


Dry Blend by mass cement:fly ash:slag(8:67:25)
NWS-03(top)Na molarity 10
NWS-03(mid)H2O ratio 0.70
NWS-03(bottom)
NWS-07(top)Na molarity 10
NWS-07(mid)H2O ratio 0.60
NWS-07(bottom)
NWS-09(top)Na molarity 7
NWS-09(mid)H2O ratio 0.70
NWS-09(bottom)
NWS-17(top)Na molarity 8.5
NWS-17(mid)H2O ratio 0.65
NWS-17(bottom)
NWS-19(top)Na molarity 7
NWS-19(mid)H2O ratio 0.60
NWS-19(bottom)
identifier
0.000
0.200
0.400
0.600
0.800
1.000
1.200
1.400
1.600
1.800
2.000
ρ (g/cm³)



As for the results, when a Na concentration of 7 molar was added to the Cast Stone, uniformity in density gradients existed for all three parts of each sample; however, NSW-02 shows a lower density when compared to other samples. Similarly, uniformity is seen for Na concentration of 10 molar except for sample NWS-03, it shows the solids have settled. Also, the more H_2O premix ratio shows uniformity than having less liquid solution. This is true with the dry blend mix of cement, fly ash, and slag with a ratio of 8:67:25. However, both show that sample NWS-03 have settled just like the one seen for Na concentration with 10 molarity.

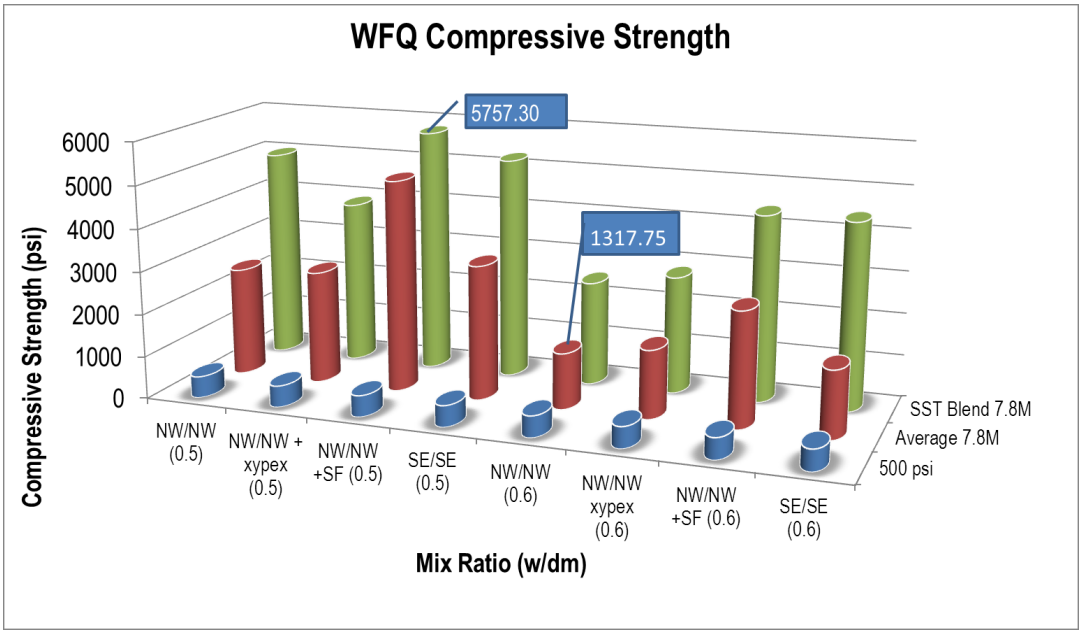
This concludes that having more liquid salt solution and fly ash in the dry blend mix shows uniformity. These tests were performed three consecutive times on the pycnometer. The

accuracy of the data was less than 1 standard deviation. Although NWS-03 did not show those signs, further studies needs to be done on this sample including NSW-02.

Compressive Strength Testing

In accordance with the ASTM C39/C39M-10 the strength test of the cylindrical specimen is determined by compressive load applied to the Cast Stone at a rate where failure will occur. This calculation can be expressed by maximum load divide by cross-sectional area of a given sample. When using the compression tester, instructions on using the equipment must be followed carefully or the result would be inaccurate. Each step must be done in order shown by instruction in the procedure ITS-0169 manual number L29. The results of the test can be determined by various size, shape, mixing, batching, temperature, moisture, and age during the curing process. Use the proper platen for the sample to be placed into a load frame. Make sure the sample is parallel and evenly aligned with the compressor and leave off about 1.5 mm air gap between the sample and the compressor by using the hydraulic load control valve. This will

ensure the pressure is evenly applied to the sample. Other processes were using the compression test software to record the results.



The compressive strength SST Blend 7.8M salt solution tends to have more effect on the compressive strength than the mix ratio, which is the dry blend of the Cast Stone. The highest compressive strength which is SST Blend 7.8M was about 5757.30 psi and the lowest was the Average 7.8M salt solution which is about 1317.75 psi. All the Cast Stone samples exceeded 500 psi.

This concludes that the type of salt solution can make a big difference on the compressive strength than the type of dry blend mix of cement, fly ash, and slag. Also, all of the Cast Stone samples passed its minimum psi level.

Salt Waste form Phase Identification in cement, slag, fly ash

The purpose here is to identify and characterize amorphous crystalline phase, and identify poor crystalline phase in the Cast Stone. This information will be useful in helping identify mechanism for contaminant stabilization, projecting evolution of phases over time and condition, designing waste forms, and selecting phase assemblages for thermodynamic modeling in which equilibrium is assumed. There are two types of methods in identifying the phase for salt waste which is direct method and two indirect methods. One of the indirect methods will be mentioned in this report.

Direct methods

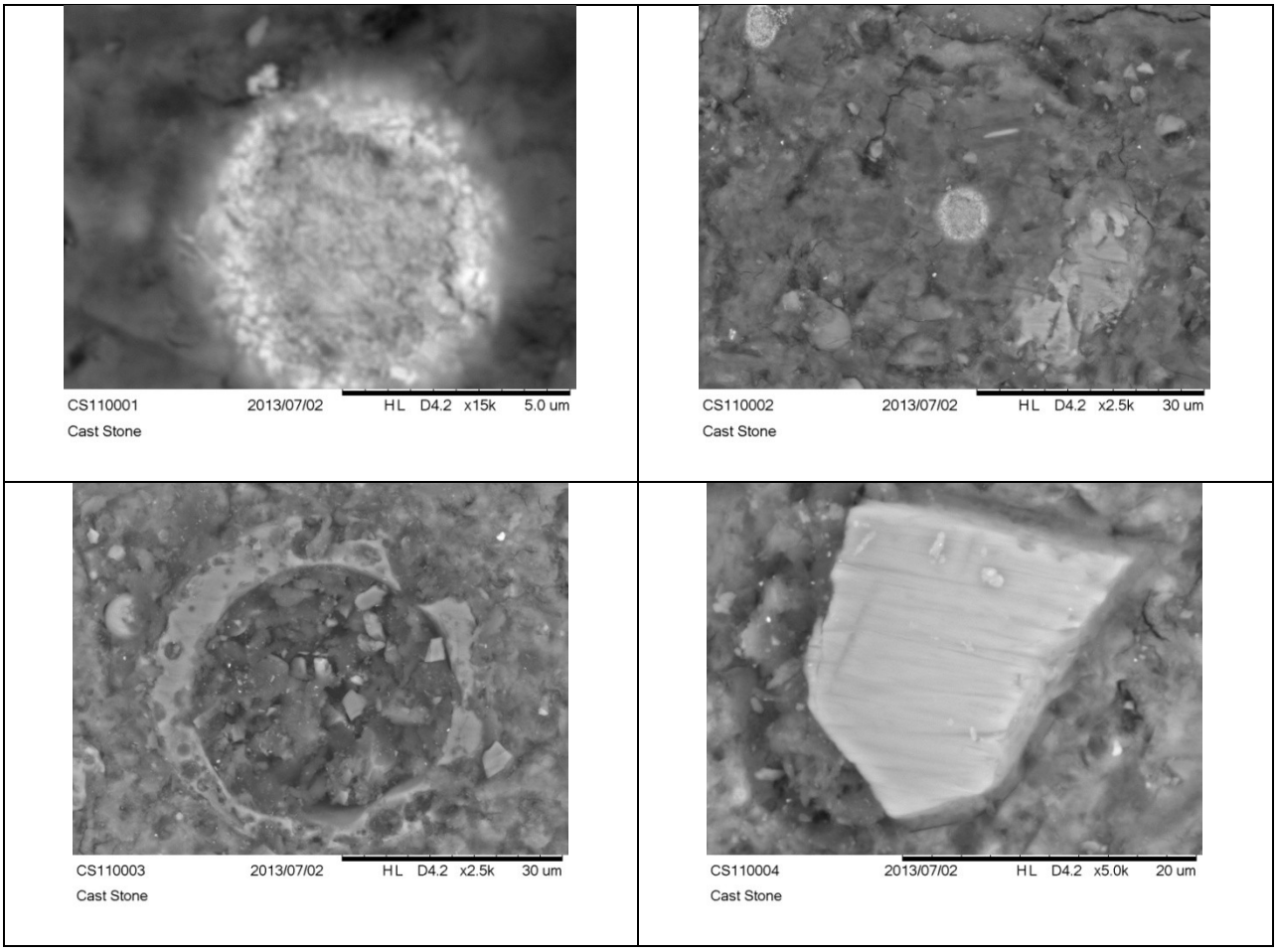
Sample Run-18 was cut and polished with sandpaper. This was done to get a focused view on the light microscope using 40X magnification. The second method was to mount the same sample on the glass to level the surface. A hot plate was used to melt the mounting material onto the glass. However, the Cast Stone sample dried out quicker when it was placed on the hot plate and showed fractures that were not there before and made the sample no good. A stereo microscope was used to capture images at lower magnifications than the previous one. The image run18_001 format with the scale bar of 100µm was much clearer than the previous images. Then we decided to use another method by cutting sample run12 instead of run18. We decided to cut the sample into four small pieces. A smaller sample piece than the one before was used for preparation. We add 2 parts (5 ml) Resin to 1 parts (2.5 ml) Hardener of Epoxy to the small piece of sample of run 12 under the vent hood. If the sample is mixed properly it will harden within 1 hour, if not the process must be repeated. Then we used the vacuum for 1 hour to get the air and moisture out of the sample.

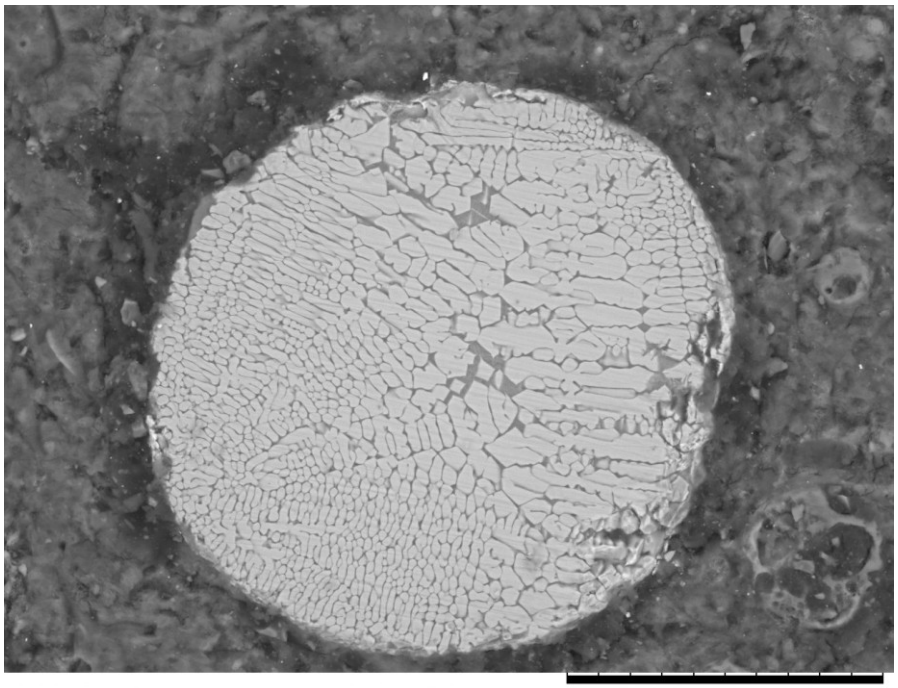
Data results

Epoxy run 11 was polished with a 180 grit silicon carbide paper. Light microscope BX41 was used to see if the image became clear and if the polish is acceptable. Each time the polish was acceptable, the grit level of the silicon carbide paper increased from 180 – 1200 grit. The magnification was use as the image of the sample became clearer, however, the image at 40X was somewhat clear and the image 100X was not clear.

The light microscope can only magnify to a certain extent, so a Scanning Electron Microscope (SEM) was used for additional images. Photos of the sample run 11 on the SEM microscope. The images were labeled as CS110001, CS110002, CS110003, CS110004, and CS 110005. CS 110001, CS110003, and CS110004 were sent in for observation, but when the results came back CS110001 was considered not important, and CS110004 needed further

observation typical chemical data. CS 110005 as we predicted it is in fact a fly ash with reacted particles inside.





New sample using run 4 was prepared just like sample run 11. Sample run 4 was cut and made into two samples one for the light microscope and the other for the SEM. To prepare the sample for SEM, release agent was applied to the interior of the small cylindrical container that the sample and the epoxy were to be placed. Epoxy was prepared using two parts (5 ml) resin and one part (2.5 ml) hardener were mixed and poured into the container with the sample. Then it was placed into the vacuum to take the air out of the sample, and this can be seen if the vacuum is doing its job by bubbles showing up on the epoxy. Due to the extent of time it takes to prepare a sample an indirect approach was used instead of continuing with this method.

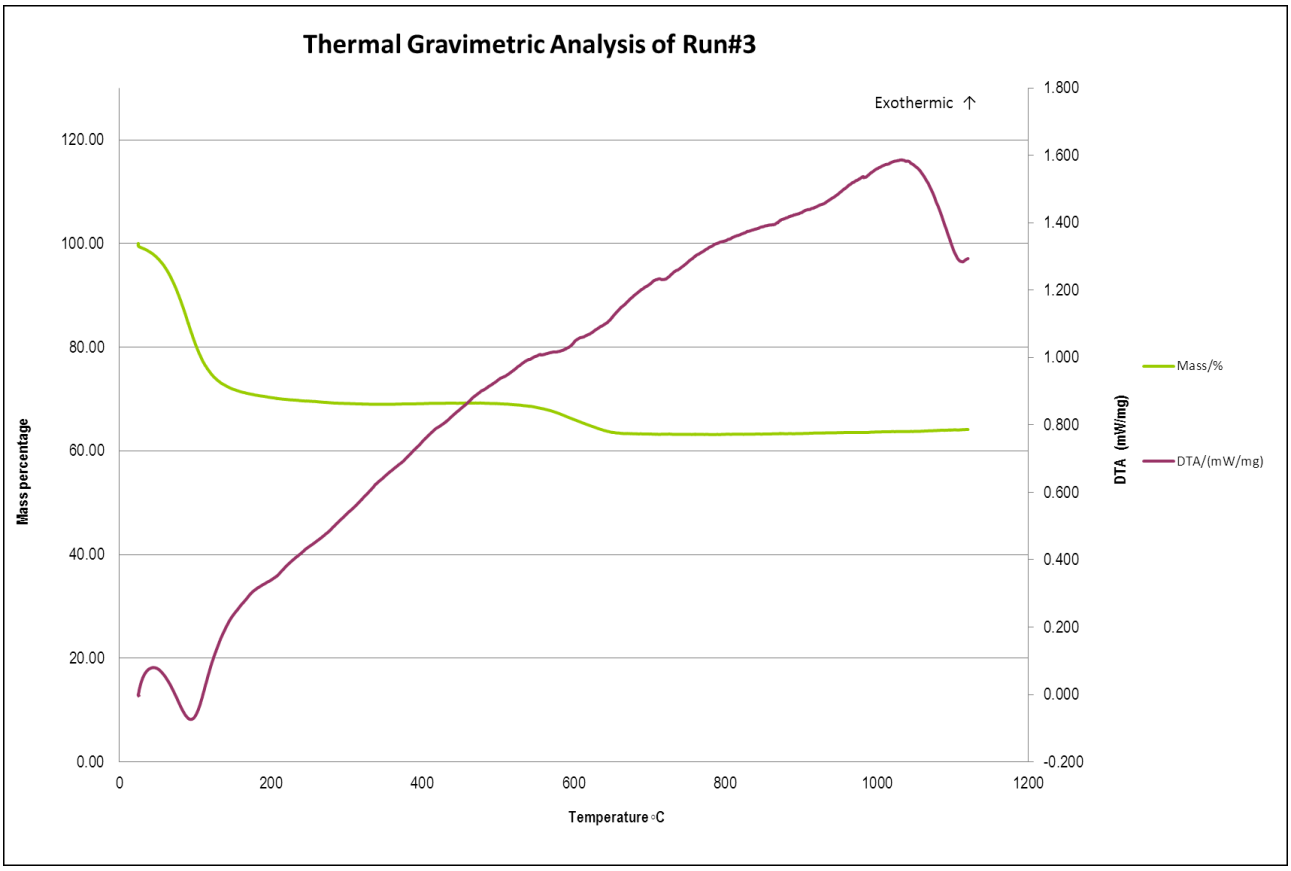
Indirect method

The purpose is if the composition is identified we can assign oxide bulk analyses to vary phases. If the Bogue method turns out useful, then we can predict hydrated phases from oxide analysis. This can tie into what phases are in the Cast Stone.

The Cast Stone was ground up into a powder form and divided into eight parts. 32 Cast Stone samples including the controls; one for dry sample and another for distilled water. Three were divided for dry and three were for distilled water that would be placed into the oven. The samples with the distilled water were rinsed and the water was added to be placed into a tumbler for a day. The rinsing and placing it into the tumbler would help get rid of excessive salt from the sample.

Thermal Gravimetric Analysis (TGA) was done on one of the sample run#3 controls.

TGA measures the weight loss or gain by heating the sample in air. It also identifies the exothermic and endothermic reaction overtime by heating. This was done in order to know what temperature the sample must be set. The equipment is very sensitive, so precautions on how to operate the equipment must be into consideration. The graph at the bottom was obtained from the TGA; it shows the criteria on what the three temperatures should be at. The temperature needed to be set and for how long is shown on the table below the TGA graph.



Test ID	Sample	Description	Temp.(◦C)	Mass (g)	Date begin heating	Date finish heating	Time	Duration
1	Run#3		1100	9.1	7/24/2013	7/25/2013	13:35	1 day
2	Run#3W		1100	9.3	7/24/2013	7/25/2013	13:35	1 day
3	Run#5		1100	9.7	7/24/2013	7/25/2013	13:35	1 day
4	Run#5W		1100	8.9	7/24/2013	7/25/2013	13:35	1 day
5	Run#10		1100	9.2	7/24/2013	7/25/2013	13:35	1 day
6	Run#10W		1100	9.0	7/24/2013	7/25/2013	13:35	1 day
7	WP 004		1100	9.3	7/24/2013	7/25/2013	13:35	1 day

8	Run#3		250	9.2	7/24/2013	7/31/2013	13:35	1 week
9	Run#3W		250	9.1	7/24/2013	7/31/2013	13:35	1 week
10	Run#5		250	9.0	7/24/2013	7/31/2013	13:35	1 week
11	Run#5W		250	9.1	7/24/2013	7/31/2013	13:35	1 week
12	Run#10		250	8.8	7/24/2013	7/31/2013	13:35	1 week
13	Run#10W		250	8.9	7/24/2013	7/31/2013	13:35	1 week
14	WP 004		250	9.3	7/24/2013	7/31/2013	13:35	1 week
15	WP 004W		1100	9.2				1 day
16	WP 004W		250	9.4				1 week
17	Run#3		650	9.2	7/29/2013	7/31/2013	8:50	2 days
18	Run#3W		650	9.3	7/29/2013	7/31/2013	8:50	2days
19	Run#5		650	9.0	7/29/2013	7/31/2013	8:50	2days
20	Run#5W		650	8.8	7/29/2013	7/31/2013	8:50	2days
21	Run#10		650	9.2	7/29/2013	7/31/2013	8:50	2days
22	Run#10W		650	9.1	7/29/2013	7/31/2013	8:50	2days
23	WP 004		650	9.0	7/29/2013	7/31/2013	8:50	2days
24	WP 004W		650	9.1	7/29/2013	7/31/2013	8:50	2days
25	Run#3 C		20-25	9.2	n/a	n/a	n/a	n/a
26	Run#3WC		20-25	9.9	n/a	n/a	n/a	n/a
27	Run#5 C		20-25	8.9	n/a	n/a	n/a	n/a
28	Run#5WC		20-25	9.1	n/a	n/a	n/a	n/a

29	Run#10 C		20-25	9.2	n/a	n/a	n/a	n/a
30	Run#10WC		20-25	9.3	n/a	n/a	n/a	n/a
31	WP004 C		20-25	9.1	n/a	n/a	n/a	n/a
32	WP004WC		20-25	9.4	n/a	n/a	n/a	n/a

*C-control WC- with distilled H_2O control W- with distilled H_2O

Once the sample was taken out of the oven it was placed into a desiccator, so the air would not change the sample.

The result was not able to be obtainable due to time it takes for the X-ray diffraction results to be generated and sent back to the lab.

Discussions

There are several additional programs that are not mentioned here. From the tests and experiments done so far, the result and the conclusion generated from these few programs for the simulated Cast Stone seems favorable. Acknowledgements

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SRS Insite- where we Are

http://www.srs.gov/general/about/where1.htm

Tank Farms- Hanford Site

http://www.hanford.gov/page.cfm/TankFarms