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Heat of Hydration of Low Activity Cementitious Waste Forms

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ABSTRACT

During the curing of secondary waste grout, the hydraulic materials in the dry mix react exothermally with the water in the secondary low-activity waste (LAW). The heat released, called the heat of hydration, can be measured using a TAM Air Isothermal Calorimeter. By holding temperature constant in the instrument, the heat of hydration during the curing process can be determined. This will provide information that can be used in the design of a waste solidification facility.

At the Savannah River National Laboratory (SRNL), the heat of hydration and other physical properties are being collected on grout prepared using three simulants of liquid secondary waste generated at the Hanford Site. From this study it was found that both the simulant and dry mix each had an effect on the heat of hydration. It was also concluded that the higher the cement content in the dry materials mix, the greater the heat of hydration during the curing of grout.

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I. INTRODUCTION

The Department of Energy's Hanford Site contains millions of gallons of nuclear waste in large storage tanks which were primarily intended for short term use. The tanks have past their life cycles and many have started to leak. The nuclear waste must be contained in a long term storage form that will prevent further environmental contamination. Currently, the waste is processed into high-level waste (HLW) and low-activity waste (LAW). The HAW contains most of the radioactive material concentrated in a small volume. The LAW contains little radioactive material, but is a large percentage of the total volume. The HAW and some of the LAW undergoes a process called vitrification, where the radioactive material is immobilized in glass. The waste from these processes is a LAW form called secondary waste. A method of immobilizing the secondary waste in the form of grout is being explored as a long term storage solution with the aid of the Savannah River National Laboratory (SRNL). Grout can be formed by mixing the liquid secondary waste with dry materials. The secondary waste was simulated using nonradioactive chemicals to make it easier and safer to handle.

Currently at the SRNL, various dry material ratios as well as different simulant to dry-mix ratios are being tested for the physical properties to decide the formula for the best disposal method of the secondary waste. One property of the grout that was tested was the heat of hydration. The heat of hydration is the amount of heat that is given off during the exothermic hydration reaction. In this study, the reaction was water reacting with the components in ordinary Portland cement (OPC). By allowing the grout to cure inside a calorimeter, the heat of hydration data was gathered for each mix. The data from this study could be used in the design of a waste solidification plant and relationships between the heat of hydration and the materials used to make the grout could be identified.

II. EXPERIMENTAL PROCEDURE

A. Creating the secondary waste simulant

There were three secondary waste streams at the Hanford Site that were being tested at the SRNL. These were from the 242-A evaporator, the Environmental Restoration Disposal Facility (ERDF), and the Waste Treatment and Immobilization Plant (WTP). In order to simulate these waste streams for this study, various chemicals were stirred together with water using a mixer. The concentrations of chemicals in each simulant are found in **Table 1**, **Table 2**, and **Table 3**. Each simulant was tested for density, pH, weight percent solids, and weight percent dissolved solids.

Species	Mol Fraction	Component	g/L
SO_4^{2-}	0.324	Na_2SO_4	7.3
NH^{4+}	0.541	$CaSO_4$	7.3
Na^+	0.075	$(NH_4)_2SO_4$	84
Ca^{2+}	0.023	$MgSO_4 \cdot 7H_2O$	5.2
Cl^-	0.013	NaCl	1.4
SiO_4^{2-}	0.011	KCl	0.5
Mg^{2+}	0.009	$Na_2SiO_3 \cdot 5H_2O$	5.5
K^+	0.003	H_2O	~943
Total	0.999	--	--

Table 1: Target Concentrations for 242-A Brine Simulant[1]

Species	Mol Fraction	Component	g/L
SO_4^{2-}	0..250	Na_2SO_4	55
NH^{4+}	0.330	$(NH_4)_2SO_4$	100
Na^+	0.295	NaCl	1.6
Cl^-	0.006	NaF	0.2
NO_3^-	0.117	$NaNO_3$	45
NO_2^-	0.001	$NaNO_2$	0.3
F^-	0.001	H_2O	~923
Total	1.000	--	--

Table 2: Target Concentration for WTP Simulant[1]

Species	Mol Fraction	Component	g/L
SO_4^{2-}	0.235	Na_2SO_4	33.0
Na^+	0.222	$CaSO_4$	9.1
Cl^-	0.162	$Ca(NO_3)_2 \cdot 4H_2O$	29.6
NO_3^-	0.117	$CaCl_2$	18.8
Ca^{2+}	0.171	$MgSO_4 \cdot 7H_2O$	47.8
Mg^{2+}	0.092	H_2O	~941
Total	0.999	--	--

Table 3: Target Concentration for ERDF Simulant[1]

B. Batching dry materials

Four different dry materials were used to form the grout. These materials were hydrated lime (HL), ordinary Portland cement (OPC), blast-furnace slag (BFS), and fly ash (FA). In some of the dry mixes, Xypex C-500, a crystalline admix, was also added so the mix contained 5% Xypex C-500. Different blends of these dry materials in specific ratios that were to be tested were batched by weighing each component on a balance and mixing them together in a large plastic bag. These ratios can be found in **Table 4**.

Premix	Hydrated Lime	Ordinary Portland Cement	Blast Furnace Slag	Fly Ash	Admix
Secondary 1	**20**	**35**	**45**	**0**	**--**
Secondary 3	**20**	**10**	**70**	**0**	**--**
Secondary 4	**0**	**20**	**45**	**35**	**Xypex**
Supplemental 1	**0**	**8**	**45**	**47**	**--**

Table 4: Dry Material Mass Percent

C. Mixing dry materials and simulant

Once the dry mixes and simulants were prepared, the next step was to mix the dry mixes and simulants together in specific ratios. The formulations can be found in **Table 5**. The samples had either a 0.5 or 0.6 water to dry mix ratio. In order to use the correct amount of simulant needed, the weight percent solid value collected when creating the simulant was used. Before beginning to mix, the tare weight of the vial was measured and recorded. The appropriate amounts of simulant and dry mix were weighed out and poured into a vial. The vial was capped and then put in a LabRAM Mixer to mix for one minute. Once done mixing, the mass of the sample was recorded.

Samples were also created using water, instead of simulant, with each dry mix in 0.5 and 0.6 water to dry mix ratios. These were mixed in the same manner as the samples created with the simulated secondary waste.

Test ID	Simulant	W/DM	HL/OPC/BFS/FA Blend	Admix
1	242-A	0.5	20/35/45/0	None
2	ERDF	0.5	20/35/45/0	None
3	WTP	0.5	20/35/45/0	None
4	242-A	0.6	20/35/45/0	None
5	ERDF	0.6	20/35/45/0	None
6	WTP	0.6	20/35/45/0	None
7	ERDF	0.5	20/35/45/0	None
8	WTP	0.6	20/35/45/0	None
9	242-A	0.5	20/10/70/0	None
10	WTP	0.5	20/10/70/0	None
11	WTP	0.6	0/20/45/35	Xypex
12	242-A	0.6	0/20/45/35	Xypex
13	WTP	0.6	0/8/45/47	None
14	242-A + ERDF	0.5	0/20/45/35	None

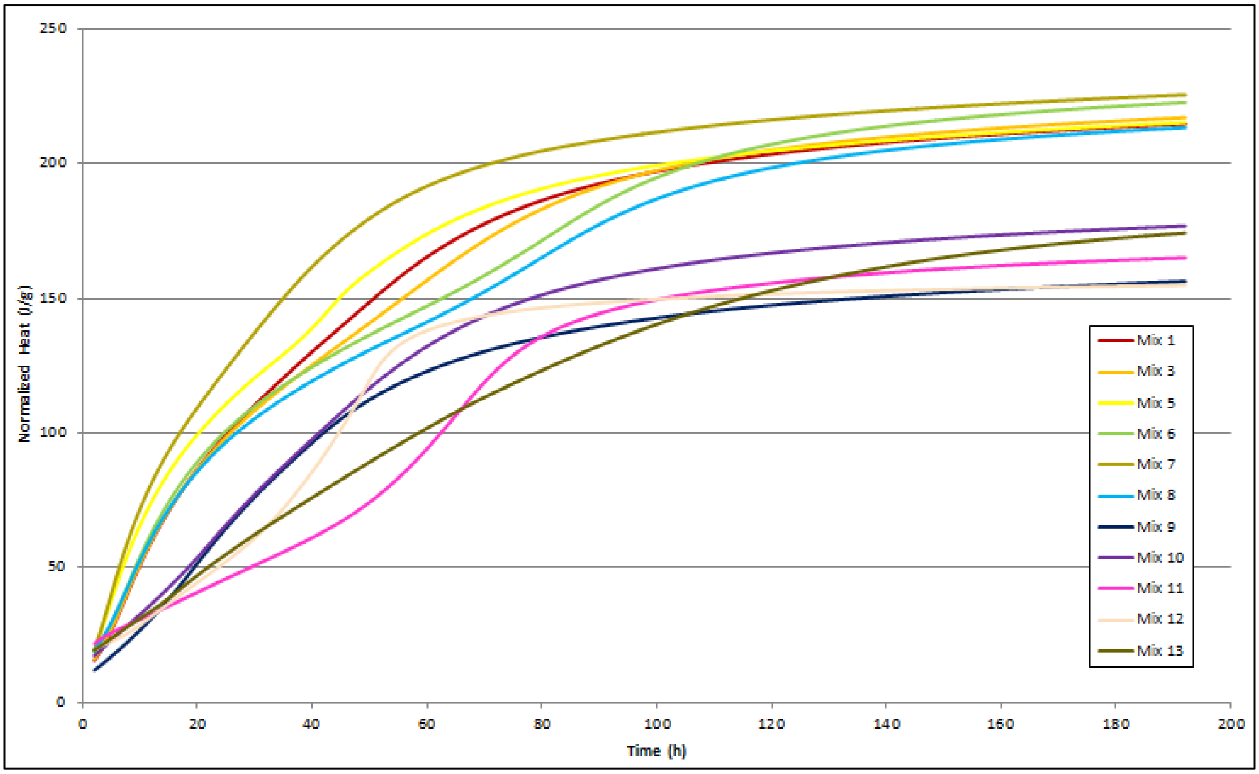
Table 5: Matrix of Formulation for this Study[1]

D. Calorimeter testing of simulated grout

Immediately after mixing, the vials were lowered into a TAM Air Isothermal Calorimeter. By keeping temperature at a constant 25.0^{o} C, the calorimeter measured the amount of heat that was given off during the curing of the grout. After being left in the calorimeter for eight days for the mixes made with simulant or three days for the samples made with water, the samples were removed from the machine. The heat of hydration data that was collected was recorded on a computer attached to the calorimeter.

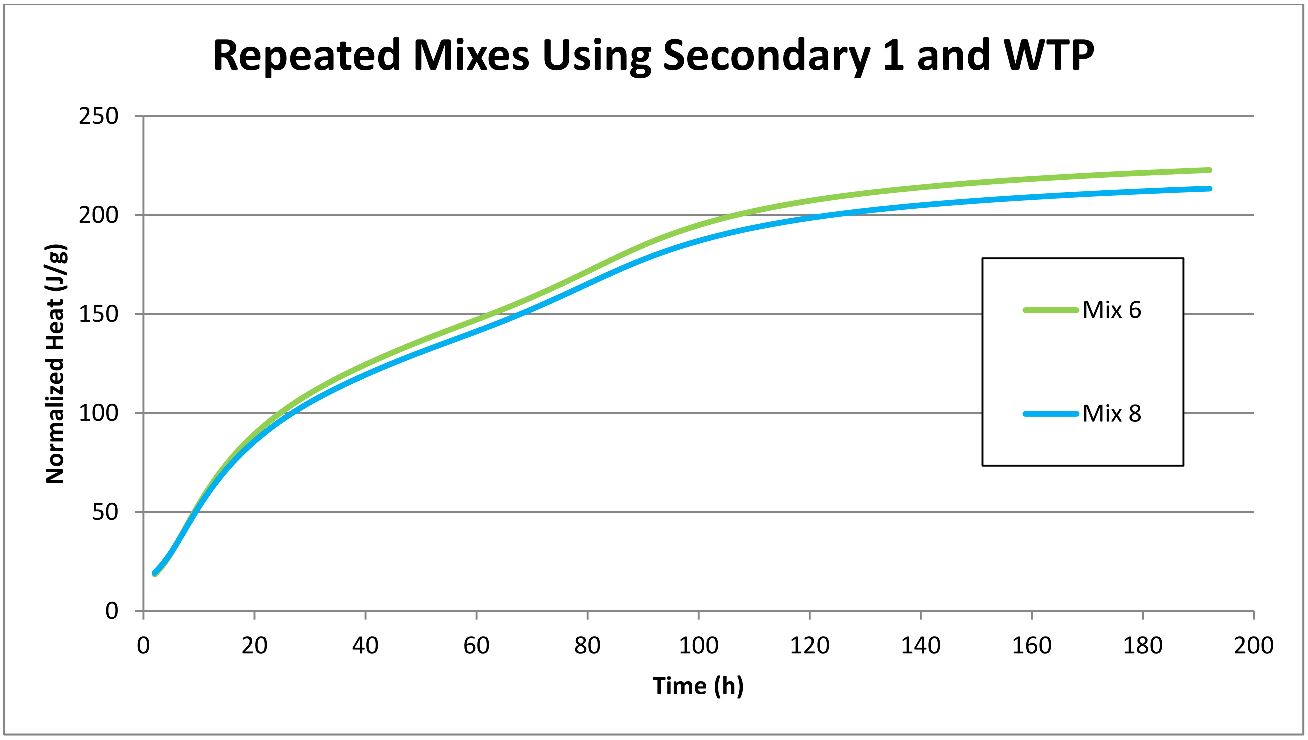
III. RESULTS

The heat of hydration data from the mixes was gathered from the calorimeter, and the heat and heat flow of each sample were normalized with the mass of dry mix in each sample. Data from Mix 2, Mix 4, and Mix 14 was either lost or unusable and must be re-run. All the normalized heat data was graphed together on **Graph 1**, and the normalized heat flow data was graphed together on **Graph 2**, but it is more beneficial to divide the data to compare specific mixes.

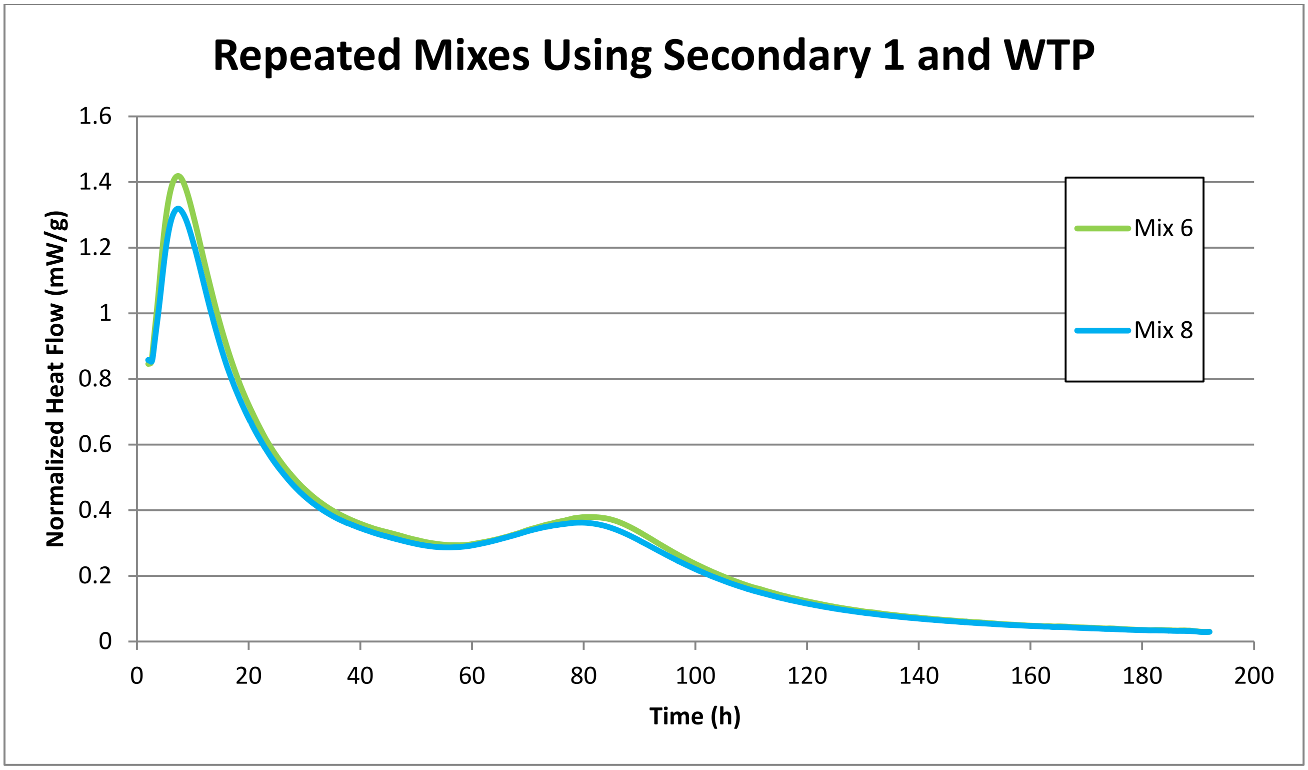


Graph 1: Normalized Heat of all Mixes

On **Graph 3** and **Graph 4**, Mix 6 and Mix 8 were compared. These two samples used the WTP simulant and the Secondary 1 dry mix, both having the same water to dry mix ratio of 0.6. On each graph, the pair of mixes has the same shape and do not vary much from each other. The difference between the two are miniscule enough that it can be concluded that this method of testing heat of hydration is replicable, and samples only need to be run one time to obtain accurate data.

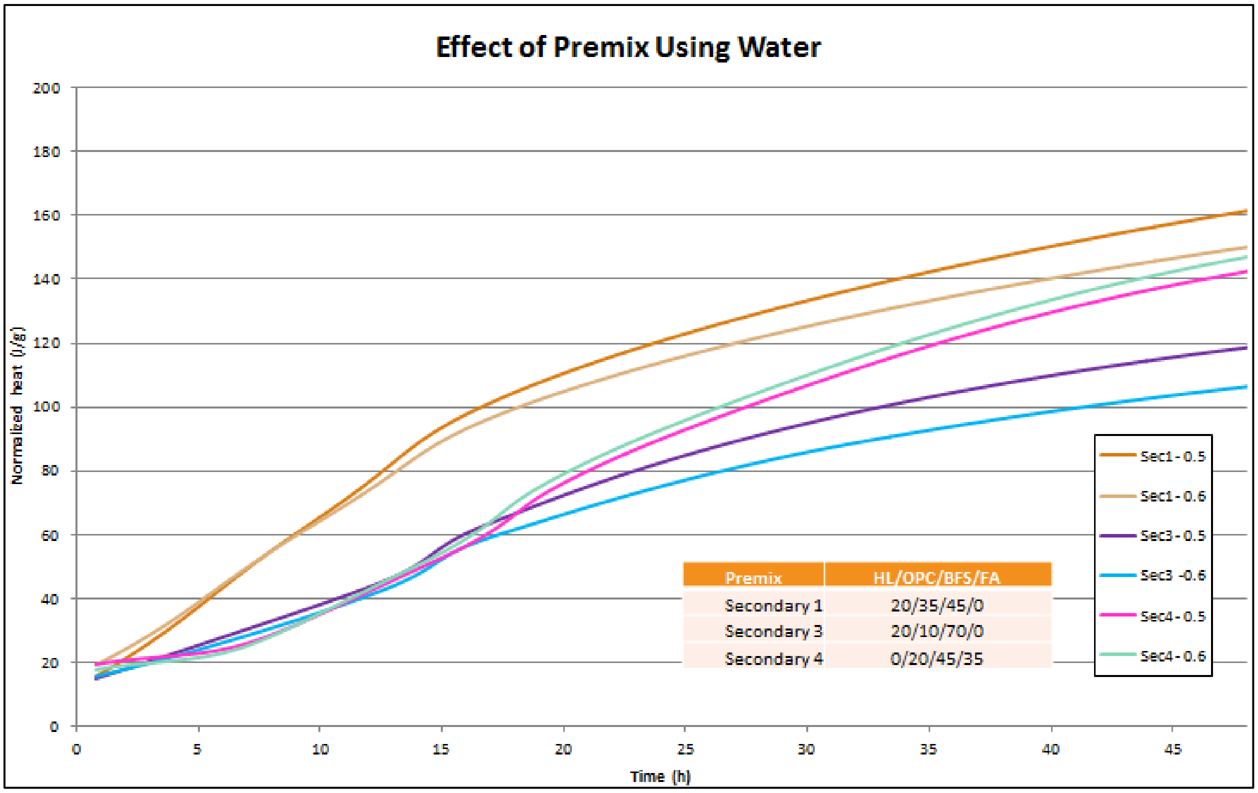


Graph 3: Normalized Heat of Mix 6 and Mix 8

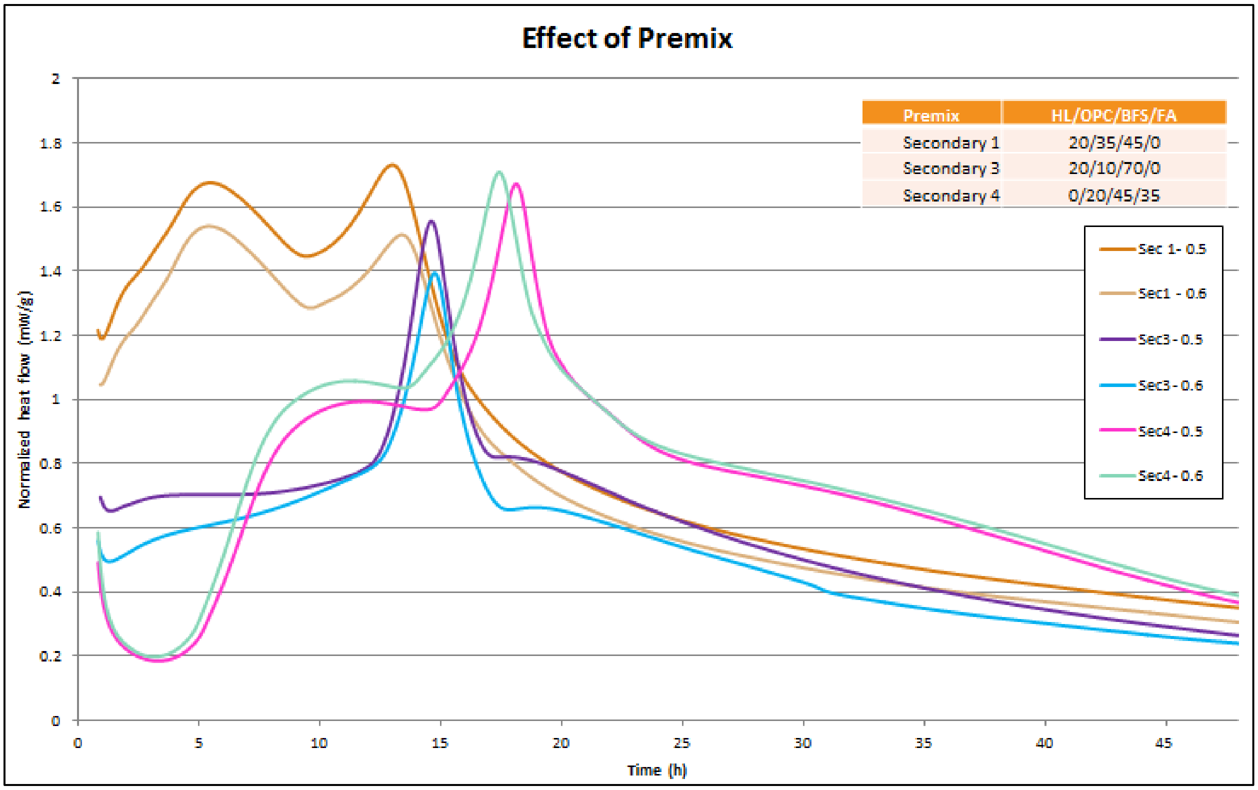


Graph 4: Normalized Heat Flow of Mix 6 and Mix 8

Using the data from the samples made with water instead simulant, the effects of the premixes on the heat of hydration can be identified. In **Graph 5**, it can be seen that Secondary 1 releases the most amount of heat, followed by Secondary 4, and Secondary 3 releases the least amount of heat. Between **Graph 5** and **Graph 6**, it can be seen that the composition of the dry mix does has an effect on the heat generated in the grout.

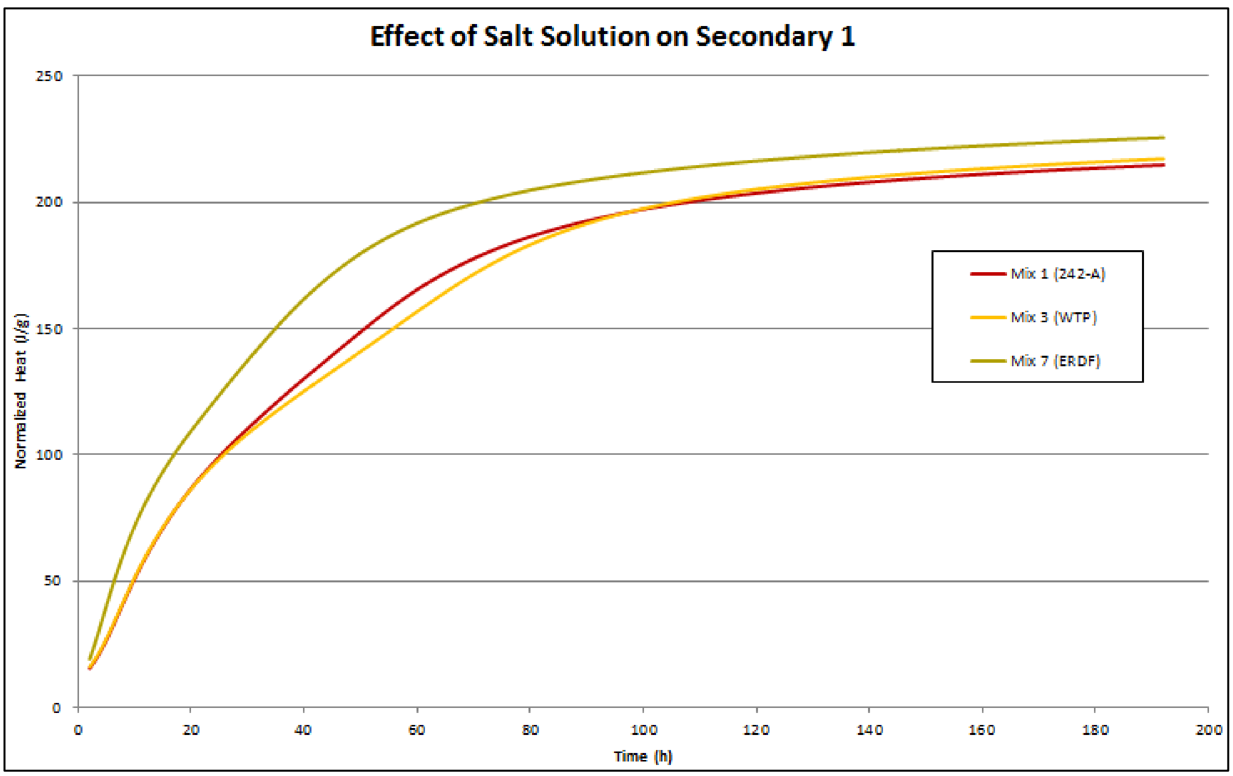


Graph 5: Normalized Heat using Premix and Water

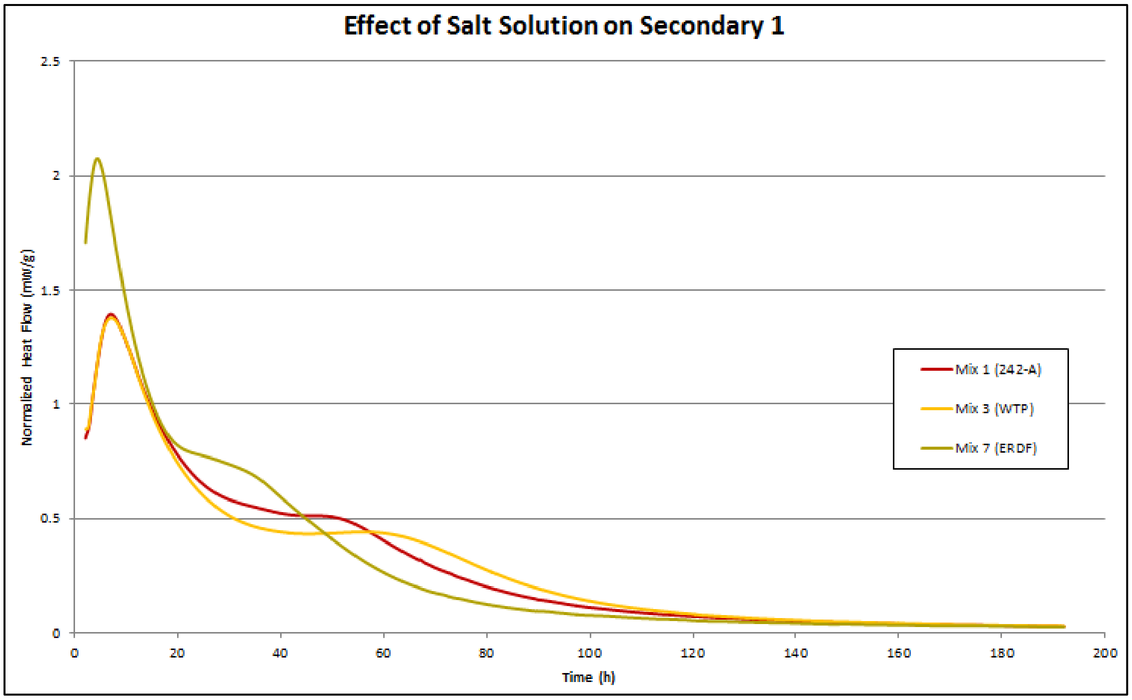


Graph 6: Normalized Heat Flow using Premix and Water

Next, the effects of the simulants were analyzed. On **Graph 7**, it can be seen that the ERDF simulant released a noticeably more amount of heat than the other two simulants. On **Graph 8,** the variance in the heat flow can be seen. Complementary work at Pacific Northwest National Laboratory (PNNL) showed that there is ettringite formation in the making of grout. Knowing this, from **Table 8**, it can be seen that ERDF has a large amount of undissolved solids in the liquid. Calcium sulfate was suspected to be a component of the solids because this reacts with the tricalcium aluminate that is found in the cement. This is an exothermic reaction that produces ettringite. It was concluded that the formation of ettringite in the ERDF simulant was the reason it had a greater initial heat of hydration.



Graph 7: Normalized heat of the three simulants with Secondary 1

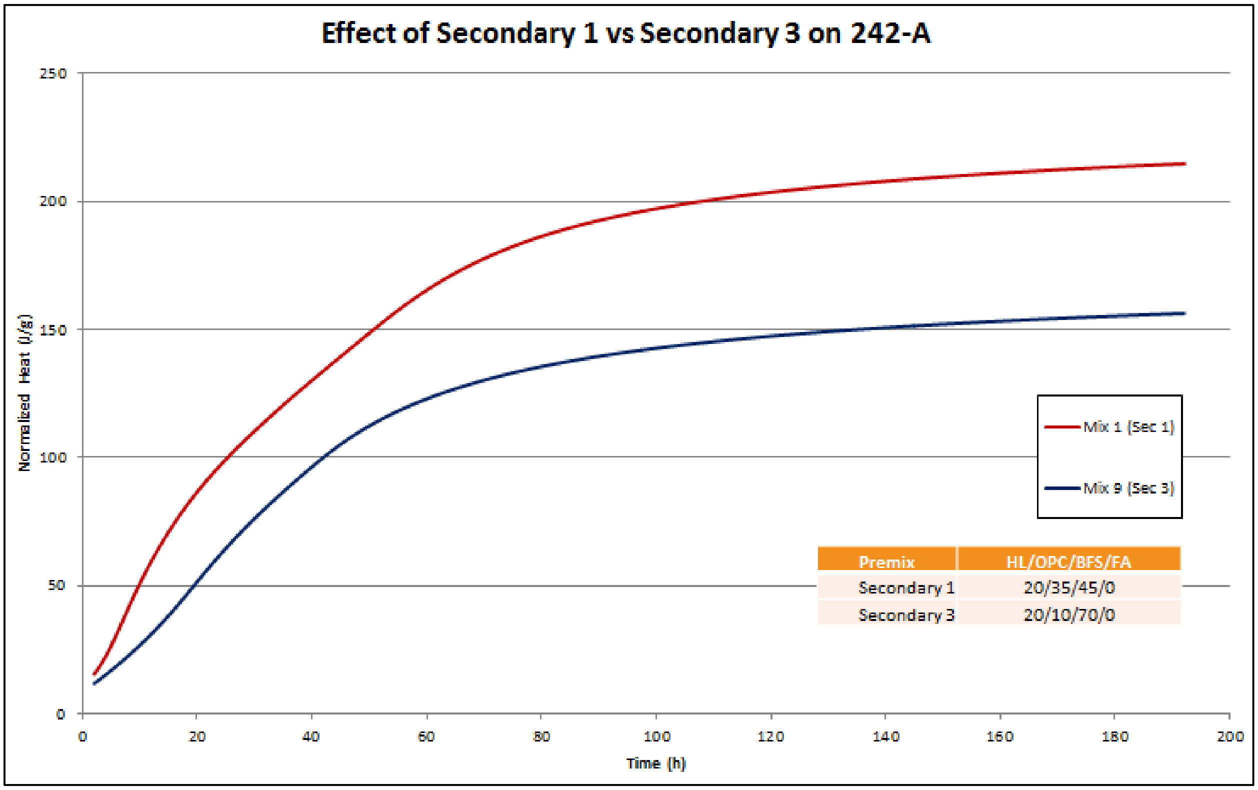


Graph 8: Normalized Heat Flow of the three simulants with Secondary 1

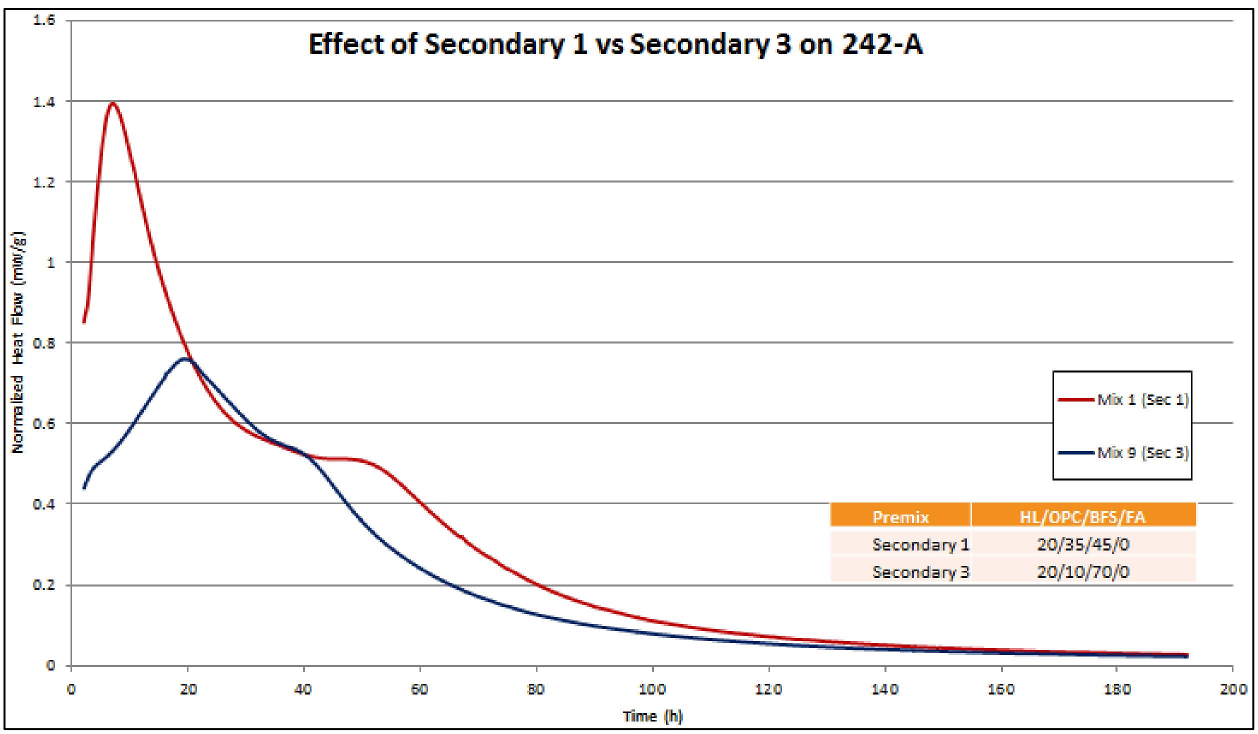
Simulant	Density (g/mL)	pH	Wt % Solid	Wt % Dissolved Solids
242-A	1.05930	8.57	9.75	9.53
WTP	1.12515	6.49	18.09	18.00
ERDF	1.08739	6.76	11.15	6.28

Table 6: Measured Properties of Each Simulant

Next, the effects that the ratio of materials has on the heat of hydration were analyzed. On **Graph 9**, it can be seen that Secondary 1, the premix with a higher OPC, released a greater amount of heat than that of Secondary 3. On **Graph 10** it can be seen that the major difference in the heat flow occurs in the initial reaction peak. It can be concluded from this, that the greater the concentration of OPC in the dry mix, the greater the heat of hydration.

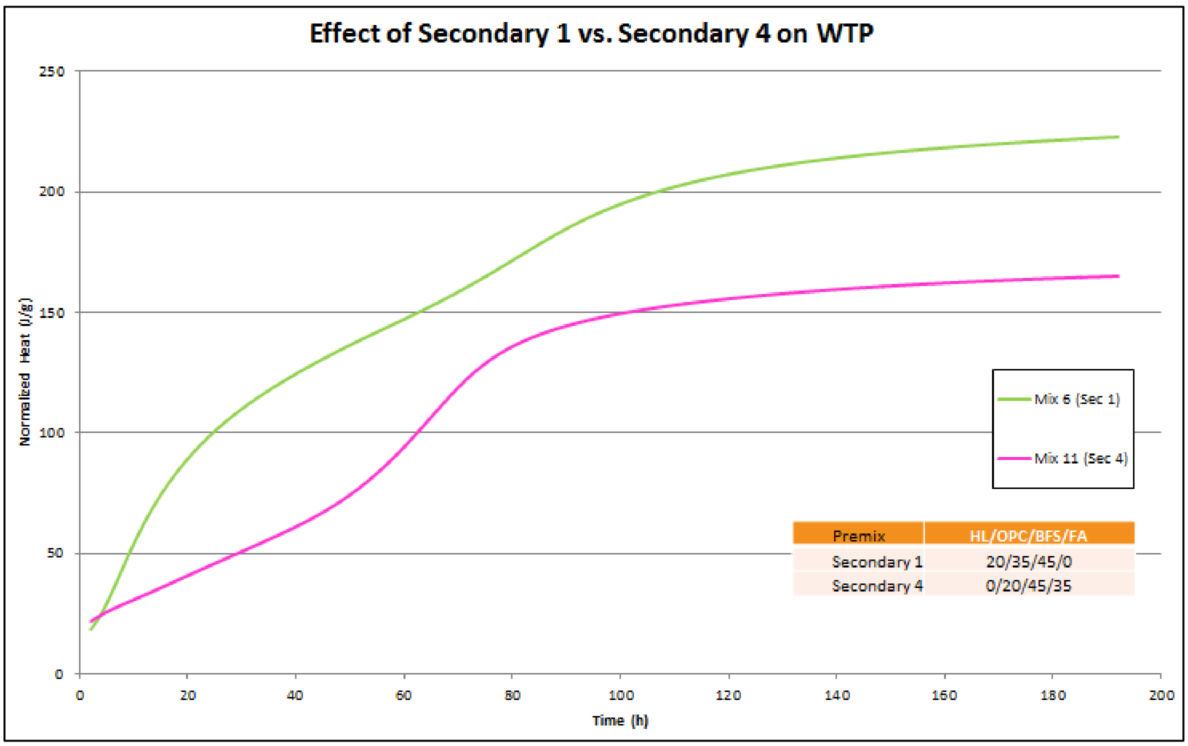


Graph 9: Normalized Heat of Secondary 1 and Secondary 3 with 242-A

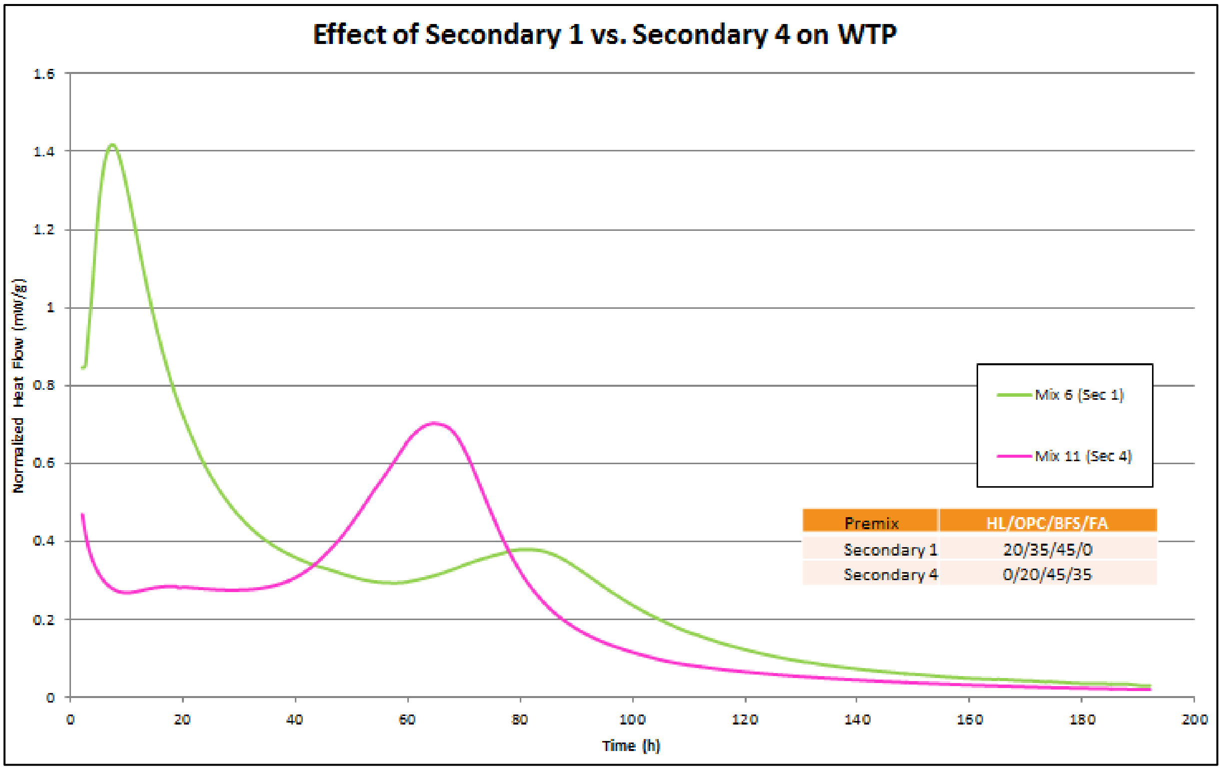


Graph 10: Normalized Heat Flow of Secondary 1 and Secondary 3 with 242-A

In **Graph 11**, Secondary 1 and Secondary 4 are compared. Secondary 4 contains less OPC and more FA than Secondary 1. It can be seen that Secondary 1, the mix that contains more OPC, releases more heat than Secondary 4, a mix with less OPC. On **Graph 12**, it can be seen that the heat flows of each mix vary greatly from one another. This was concluded to be because of the addition of fly ash.



Graph 11: Normalized Heat of Secondary 1 and Secondary 4 with WTP



Graph 12: Normalized Heat flow of Secondary 1 and Secondary 4 with WTP

Table 7 provides values that can be used in the design of a waste solidification facility. This contains the maximum heat flow values and the times that the peaks occur at. These peaks must be accounted for in the design of a waste solidification facility.

Mix #	*Temperature rise during Mixing (^{o}C)	Time to first normalized heat flow peak (h)	First normalized heat flow peak (mW/g)	Time to second heat flow peak (h)	Second normalized heat flow peak (mW/g)	Normalized heat ~192 hours (J/g)
1	7.3	6.97	1.394320	46.15000	0.513159	214.758
2	4.4	--	--	--	--	--
3	7.0	7.10	1.377090	56.05000	0.441485	217.189
4	5.8	--	--	--	--	--
5	3.2	4.52	1.791840	42.93333	0.670928	215.320
6	5.2	7.38	1.419820	80.93333	0.382060	222.753
7	4.1	4.32	2.076180	--	--	225.585
8	4.8	7.40	1.320060	79.66667	0.364305	213.397
9	5.7	19.32	0.760464	--	--	156.330
10	5.4	3.88	0.552944	22.26667	0.683372	176.883
11	7.0	17.93	0.285884	64.71667	0.704388	165.030
12	6.9	12.00	0.453636	49.15000	1.062470	154.875
13	5.8	4.37	0.443272	17.01667	0.481198	174.286
14	5.7	--	--	--	--	--

*Temperature rise during cured properties mixing

Table 7: Heat flow data that can be used in facility design

IV. FUTURE STUIDES

For future studies, the ERDF simulant needs to be analyzed to see if the calcium sulfate is actually present in the liquid simulant to confirm that the forming of ettringite accounts for the additional heat of hydration. Also, Mixes 2, 4, and 14 need to be run again to complete this set of heat of hydration data. The other testing for Mixes 1-14 need to be finished. The data from these other tests can be used to draw identify relationships between each test. X-ray diffraction could be used to identify the various components in each solid waste sample. The structural and compositional differences between each mix could be identified.

V. ACKNOWLEDGEMENTS

The author would like to acknowledge Dr. Alex Cozzi for his guidance in this project and for answering my constant stream of questions. Katie Hill helped everyday with the experiments and information processing. Dr. Elizabeth Hoffman and Natalie Ferguson welcomed me and kept me on track throughout my time at SRNL.

VI. REFERENCES

1. A.D. Cozzi, C.L. Crawford, K.A. Roberts, “Task Technical and Quality Assurance Plan for the Secondary Waste Cast Stone Formulation and Waste Form Qualification,” SRNL-RP-2015-00235, Revision 0, June 2015.