

# HEAT OF HYDRATION OF SALTSTONE MIXES – MEASUREMENT BY ISOTHERMAL CALORIMETRY

J. R. Harbour, V. J. Williams and T. B. Edwards  
Savannah River National Laboratory

May 2007

Process Science and Engineering  
Savannah River National Laboratory  
Aiken, SC 29808

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Prepared for the U.S. Department of Energy Under Contract Number  
DEAC09-96SR18500



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**Printed in the United States of America**

**Prepared For  
U.S. Department of Energy**

**Key Words:** *Fly Ash*  
*Portland Cement*  
*Blast Furnace Slag*

**Retention: Permanent**

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## REVIEWS AND APPROVALS

### AUTHORS:

---

J. R. Harbour, SRNL, Stabilization Science Research Date

---

V. J. Williams, SRNL, Stabilization Science Research Date

---

T. B. Edwards, SRNL, Computational and Statistical Science Date

### TECHNICAL REVIEWERS:

---

A. D. Cozzi, SRNL, Stabilization Science Research Date

### APPROVERS

---

D. A. Crowley, SRNL, Manager, Stabilization Science Research Date

---

R. E. Edwards, SRNL, Manager, Process Science and Engineering Date

---

J. E. Occhipinti, Manger, Waste Solidification Engineering Date

## EXECUTIVE SUMMARY

This report provides initial results on the measurement of heat of hydration of Saltstone mixes using isothermal calorimetry. The results were obtained using a recently purchased TAM Air Model 3116 Isothermal Conduction Calorimeter.

Heat of hydration is an important property of Saltstone mixes. Greater amounts of heat will increase the temperature of the curing mix in the vaults and limit the processing rate. The heat of hydration also reflects the extent of the hydraulic reactions that turn the fluid mixture into a 'stone like' solid and consequently impacts performance properties such as permeability. Determining which factors control these reactions, as monitored by the heat of hydration, is an important goal of the variability study.

Experiments with mixes of portland cement in water demonstrated that the heats measured by this technique over a seven day period match very well with the literature values of (1) seven day heats of hydration using the standard test method for heat of hydration of hydraulic cement, ASTM C 186-05 and (2) heats of hydration measured using isothermal calorimetry.

The heats of hydration of portland cement or blast furnace slag in a Modular Caustic Side Solvent Extraction Unit (MCU) simulant revealed that if the cure temperature is maintained at 25 °C, the amount of heat released over a seven day period is roughly 62% less than the heat released by portland cement in water. Furthermore, both the blast furnace slag and the portland cement were found to be equivalent in heat production over the seven day period in MCU. This equivalency is due to the activation of the slag by the greater than 1 Molar free hydroxide ion concentration in the simulant.

Results using premix (a blend of 10% cement, 45% blast furnace slag, and 45% fly ash) in MCU, Deliquification, Dissolution and Adjustment (DDA) and Salt Waste Processing Facility (SWPF) simulants reveal that the fly ash had not significantly reacted (undergone hydration reactions) after seven days (most likely less than 5%). There were clear differences in the amount of heat released and the peak times of heat release for the three different simulants. It turns out that SWPF simulant mixes give off greater heat than does MCU and DDA simulant mixes.

The temperature dependence of the heat of hydration was measured by carrying out these measurements at 25, 40 and 55 °C. In general, the peak times shifted to shorter times as the isothermal temperature increased and the amount of heat released was independent of temperature for DDA and MCU but slightly higher at higher temperatures for SWPF.

The goal of this study is to apply this technique to the measurement of the heat of hydration of mixes that will be made as part of the variability study. It is important to understand which variables will impact (and to what extent) the amount of heat generated and the peak times for the heat release. Those variables that can be controlled can then be tuned to adjust the heat of hydration as long as the other properties are still acceptable.

The first application of heat of hydration measurements to the variability study was completed and the results presented in this report. These measurements were made using Phase VI mixes

(SWPF simulants) following a statistical design that included variation in the compositional and operational variables. Variation in both the amount of heat released and the peak times for the heat release were observed. The measured ranges were 23 Joules per gram of premix for the heat release and 23 hours for the peak time of heat release at 25 °C.

Linear models with high  $R^2$  values and no statistical evidence for lack of fit were developed that relate the amount of heat release and the peak time for heat release for the Phase VI mixes to certain variables. The amount of heat released was a function of the aluminate and portland cement concentrations as well as the temperature of mixing. The peak time for heat release was a function of aluminate, portland cement and total nitrate plus nitrite concentrations.

A comparison was made of the measured values of heat release by isothermal calorimetry to a previous study of the measurement of the heat of hydration using adiabatic calorimetry by Steimke and Fowler. After 80 hours of reaction time, the two techniques provided heat release results that were roughly in the same range. However, additional experiments at higher isothermal temperatures will be required to see how well the two measurements agree for longer times. This is due to the higher temperatures that are experienced in adiabatic calorimetry (~105°C).

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**LIST OF ACRONYMS**

ACTL	Aiken County Technical Laboratory
ASTM	American Society for Testing and Materials
DDA	Deliquification, Dissolution and Adjustment
FA	Fly Ash
GGBFS	Ground Granulated Blast Furnace Slag
HoH	Heat of Hydration
MCU	Modular Caustic Side Solvent Extraction Unit
OPC	Ordinary Portland Cement
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SDF	Saltstone Disposal Facility
SPF	Saltstone Processing Facility
SWPF	Salt Waste Processing Facility
TR	Trial Run

## 1.0 INTRODUCTION

The hydration reactions of Saltstone mixes are responsible for producing the stone-like solid waste form (grout) that incorporates/immobilizes the low-level liquid waste at SRS. These hydration reactions are exothermic and consequently increase the temperature of the mix to levels that can limit the processing rates at Saltstone. The approach currently followed at SRS to control the temperature rise of the curing grout is to measure the amount and rate of heat production for a baseline mix [1] and use this information as input to a model [2] that can predict the temperature increase within the vaults as a function of pour schedule. A pour schedule is then selected for each batch (based on this baseline mix) to ensure that the maximum temperature is not exceeded.

In addition to impacting processing rates, the heat of hydration and associated temperature rise and temperature differential of the curing mix can affect the (1) performance properties, (2) durability and (3) degree of cracking of Saltstone. An upper temperature limit based on durability and a maximum temperature differential to prevent cracking are routine requirements in mass placements [3]. For example, maximum allowable temperature limits for concrete have been specified as low as 57 °C with a maximum allowable temperature difference of 19 °C [3]. The temperature dependence of curing on the performance properties of Saltstone such as permeability, diffusivity and porosity is still undetermined. Ultimately, a limit on the temperature of the mix is required that ensures compliance not only with the performance assessment requirements, but also the durability and degree of cracking of Saltstone. As part of this approach, the impact on the heat of hydration due to variations in the composition and operating parameters needs to be measured.

Isothermal conduction calorimetry is one method used to measure the heat of hydration of grout and concrete mixes [4-6]. In this method, the heat of hydration (which includes both the time dependence and quantity of heat generated) is obtained at a fixed temperature and can be measured at a number of different temperatures to provide the temperature dependence of the heat of hydration.

Another method of measurement of the heat of hydration uses adiabatic calorimetry [7]. In this method, the fresh grout sample is thermally insulated from its surroundings and the increase in temperature of the mix is measured as the grout cures. This data can be used with an independent measurement of the specific heat (the amount of heat needed to raise the temperature of one gram of a substance by 1°C) of the grout to determine the total amount of heat generated by a given mix. It has been demonstrated that the heat of hydration determined adiabatically can be reproduced by measuring the heat of hydration isothermally at several different temperatures and using a model to predict the adiabatic response [8].

A third method for measurement of heat of hydration is through dissolution of a cured sample using concentrated hydrofluoric acid and 2 M nitric acid following ASTM C 186-05 [9]. The time dependence of the heat of hydration can be determined by dissolving samples at various stages of curing (typically 7 or 28 days).

It is a goal of the Saltstone variability study [10] to determine the impact of process (including compositional) variation on the processing and performance properties of interest at Saltstone. Heat of hydration impacts both processing and performance properties. For example, the hydraulic conductivity of the grout is dependent on the curing temperature. The isothermal conduction calorimetric method of measurement of heat of hydration was selected for the variability study since it is possible to collect data on eight samples simultaneously and to control the maximum temperature of the mixes.

This report provides the first heat of hydration data obtained from a TAM Air Microcalorimeter (isothermal conduction calorimeter). This instrument will be used as part of the Saltstone variability study and for a task on the reduction of the heat of hydration for Saltstone.

## 2.0 EXPERIMENTAL

### 2.1 Materials

The cementitious materials were obtained from Saltstone. These materials were specified in a WSRC contract for Saltstone cementitious materials and arrived with the delivery of the cementitious materials to Saltstone. The materials were transferred to 2 liter plastic bottles at ACTL and tightly sealed. The seal limits the amount of exposure the materials get to the air and associated humidity.

Portland cement (OPC)	Type II	Holcim
Blast Furnace slag (GGBFS)	Grade I or II	Holcim
Fly ash (FA)	Class F	The SEFA Group (Cross Station)

The DDA, MCU and SWPF simulants were batched to the compositions presented in a previous report [11]. The SWPF simulants for Phase VI of the variability study were batched according to the design provided in Table 2-1. Samples GVS63 and GVS73 were duplicate samples batched at different times. GVS68 is also a replicate but the heat of hydration was not measured for this sample.

Table 2-1 Design for Phase VI of the Saltstone Variability Study

Grout Variability Study Phase 6									
Run Number	Simulant	Temp	Water/Premix	Cement	Added OH	Free OH	Nitrate plus Nitrite	Phosphate	Aluminate
Run Order	Number	°C	Ratio	Wt %	Molarity	Molarity	Molarity	Molarity	Molarity
GVS63	43	22	0.60	10	2.87	2.41	2.457	0.0073	0.1144
GVS64	44	14	0.62	8	2.21	1.91	2.957	0.0113	0.0744
GVS65	45	14	0.62	8	3.49	2.91	1.957	0.0033	0.1444
GVS66	46	14	0.58	12	2.49	1.91	1.957	0.0113	0.1444
GVS67	47	14	0.58	12	3.21	2.91	2.957	0.0033	0.0744
GVS68	43	22	0.60	10	2.87	2.41	2.457	0.0073	0.1144
GVS69	48	30	0.58	8	3.21	2.91	1.957	0.0113	0.0744
GVS70	49	30	0.62	12	3.49	2.91	2.957	0.0113	0.1444
GVS71	50	30	0.62	12	2.21	1.91	1.957	0.0033	0.0744
GVS72	51	30	0.58	8	2.49	1.91	2.957	0.0033	0.1444
GVS73	52	22	0.60	10	2.87	2.41	2.457	0.0073	0.1144

The mixing was performed as previously described using a paddle blade mixer with a three minute mixing duration [11].

## 2.2 Isothermal Calorimetry

The heat of hydration measurements were performed using a TAM Air Isothermal Calorimeter, Model Number 3116 that was manufactured in Sweden and distributed by TA Instruments (previously distributed by Thermometrics, which was bought out by TA Instruments during the purchase process).

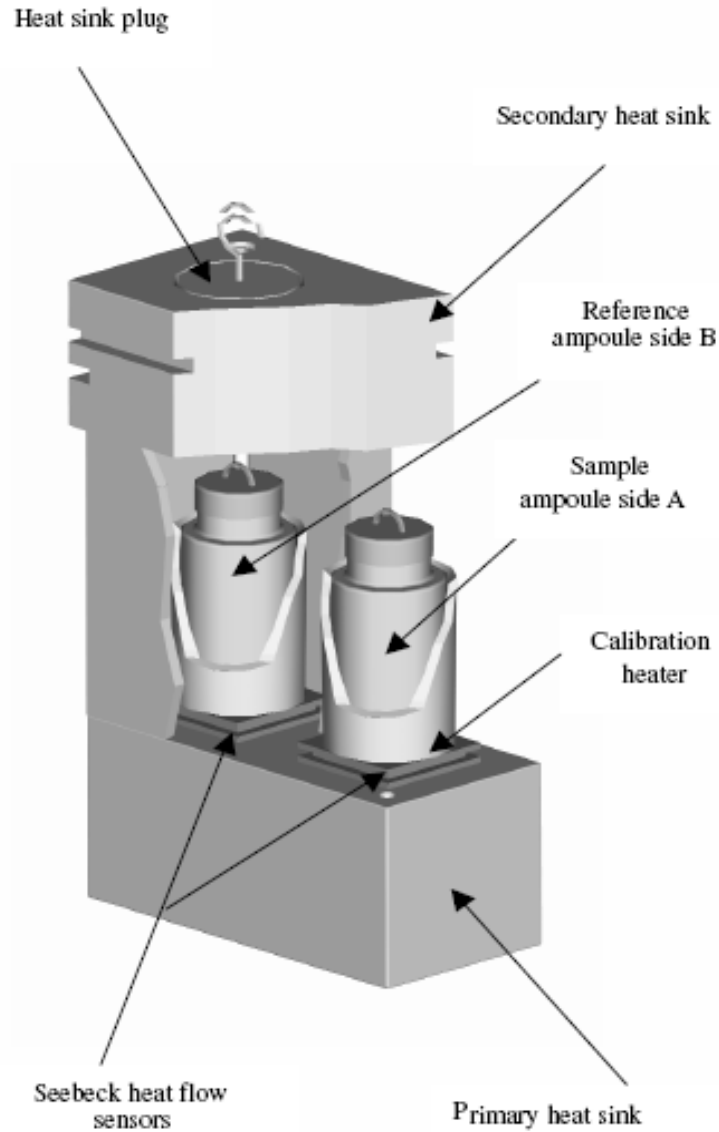
A photograph of the isothermal calorimeter is shown in Figure 2-1. It has 8 channels with each channel having both a sample and reference port. This allows for eight different samples to be measured simultaneously at a given temperature. The temperature range is from 5 to 90°C +/- 0.02°C.

The detection limit is 4 microwatts. The sample vial will hold up to 24 mL of sample. Immediately after the three minute mixing period, a portion of the mix was transferred to the 24 mL sample vial (typically 10 mL), weighed and then placed within the calorimeter. There is an equilibration time required after placement of the sample in the calorimeter which is typically 45 minutes. The heat produced during this time is not included in the overall heat of hydration.



**Figure 2-1 A photograph of the TAM Air 3116 Isothermal Calorimeter from reference [12]**

Figure 2-2 provides a cutaway view of the sample and reference ports for the TAM Air 3116 Calorimeter [12].



**Figure 2-2 Cutaway diagram of the location of the sample and reference ampoules for a given channel of the TAM Air Calorimeter**

### 3.0 RESULTS AND DISCUSSION

Heat of hydration measurements were first conducted using either ordinary portland cement (OPC), ground granulated blast furnace slag (GGBFS) or Class F fly ash (FA) in water and MCU simulant to provide insight into the individual contributions of these materials to the heat of hydration. This was followed by measurements using the normal premix material with a mass ratio of 45% GGBFS, 45% FA and 10% OPC mixed with simulants of DDA, MCU and SWPF.

#### 3.1 OPC and GGBFS in Water

Mixes of (1) OPC in water and (2) GGBFS in water were prepared using a conventional paddle blade mixer for three minutes at a mixing temperature of ~ 25 °C. It is noted that the temperature of the mix increases several degrees during this mixing due to the initial heat generation when the cementitious materials were added to water. The water to OPC or GGBFS ratio was 0.60.

Figure 3-1 shows the normalized (to grams of OPC) response for heat flow and the normalized response for total heat (integral of the normalized heat flow) for the OPC in water mix.

- Signal, Ch 1, TR293-1, Normalized heat flow
- Signal, Ch 1, TR293-1, Normalized heat

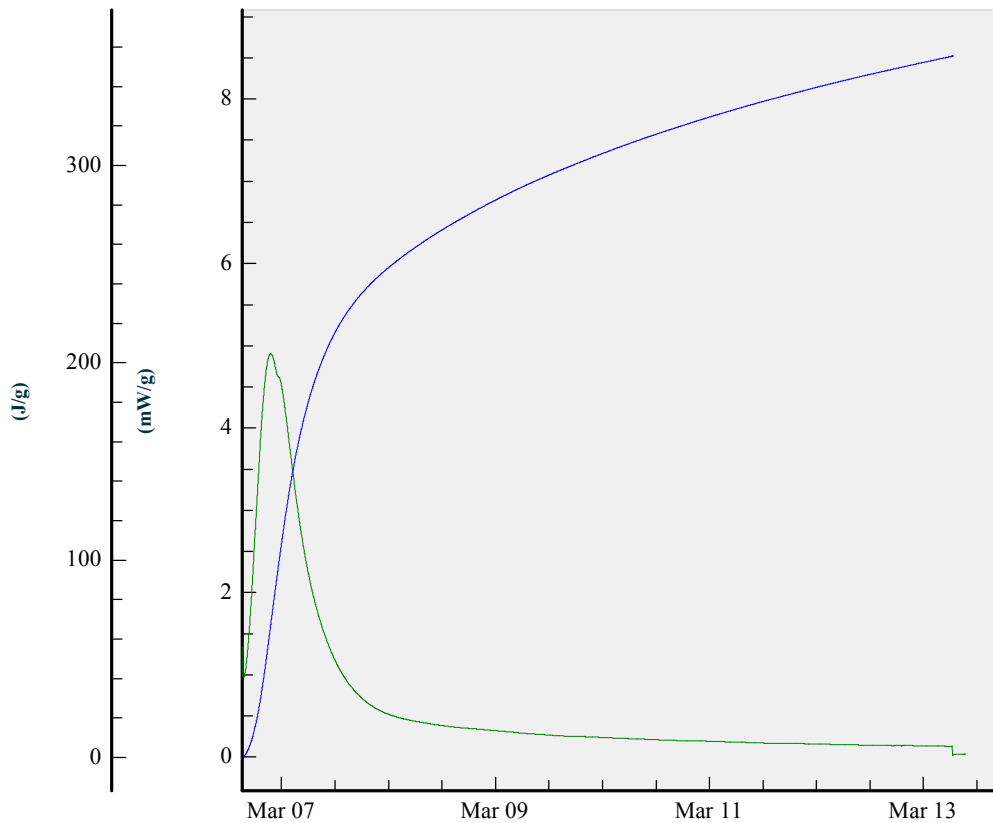


Figure 3-1 Normalized heat flow and thermal output for OPC in water at 25°C



From the heat flow curve, the peak time for the maximum output in mW per gram of OPC can be measured (in this case it was ~7.1 hours). There is also a shoulder evident on the peak of the heat flow curve at ~9 hours. This peak has been observed and associated with conversion of ettringite to the mono-sulfate phase [5]. Integration of this heat flow curve provides the heat output in Joules/gram of OPC as a function of time (this curve is shown in blue in Fig. 3-1).

Table 3-2 presents the normalized heat production and peak time of maximum heat flow time for two samples of OPC in water and two samples of GGBFS in water. The data were collected on all four samples simultaneously in four of the eight channels available in the TAM Air calorimeter. Data collection continued over seven days.

**Table 3-1 Normalized (per Gram of Cementitious Material) Heat Release (J/g) and Peak Times (hrs) for Heat Flow for Duplicate Mixes of OPC in Water and GGBFS in Water Over a Seven Day Period.**

ID #	WATER	Water/Cementitious Ratio	Normalized Heat		Peak of Heat Flow
			J/g grout	J/g cementitious material	Hours
TR293-1	OPC	0.60	222	355	7.1
TR293-2	OPC	0.60	221	353	7.1
TR294-1	GGBFS	0.60	44	70	21.2
TR294-2	GGBFS	0.60	45	72	21.3

The seven day total heat output for the Type II OPC used for Saltstone can be compared to literature values for Type I and Type II portland cements provided in Table 3-3 [13]. This comparison reveals that the seven-day heat output for Saltstone Type II OPC measured in this study using the isothermal conduction calorimeter is reasonably close to the average value of Type I or Type II OPC reported in the literature and is within the ranges provided. The data in Table 3-1 are also consistent with published isothermal calorimetric data with OPC in water [5].

**Table 3-2 Normalized (per gram of OPC) heat release (J/g) for Type I and Type II OPC in water mixes at 25 °C [13]**

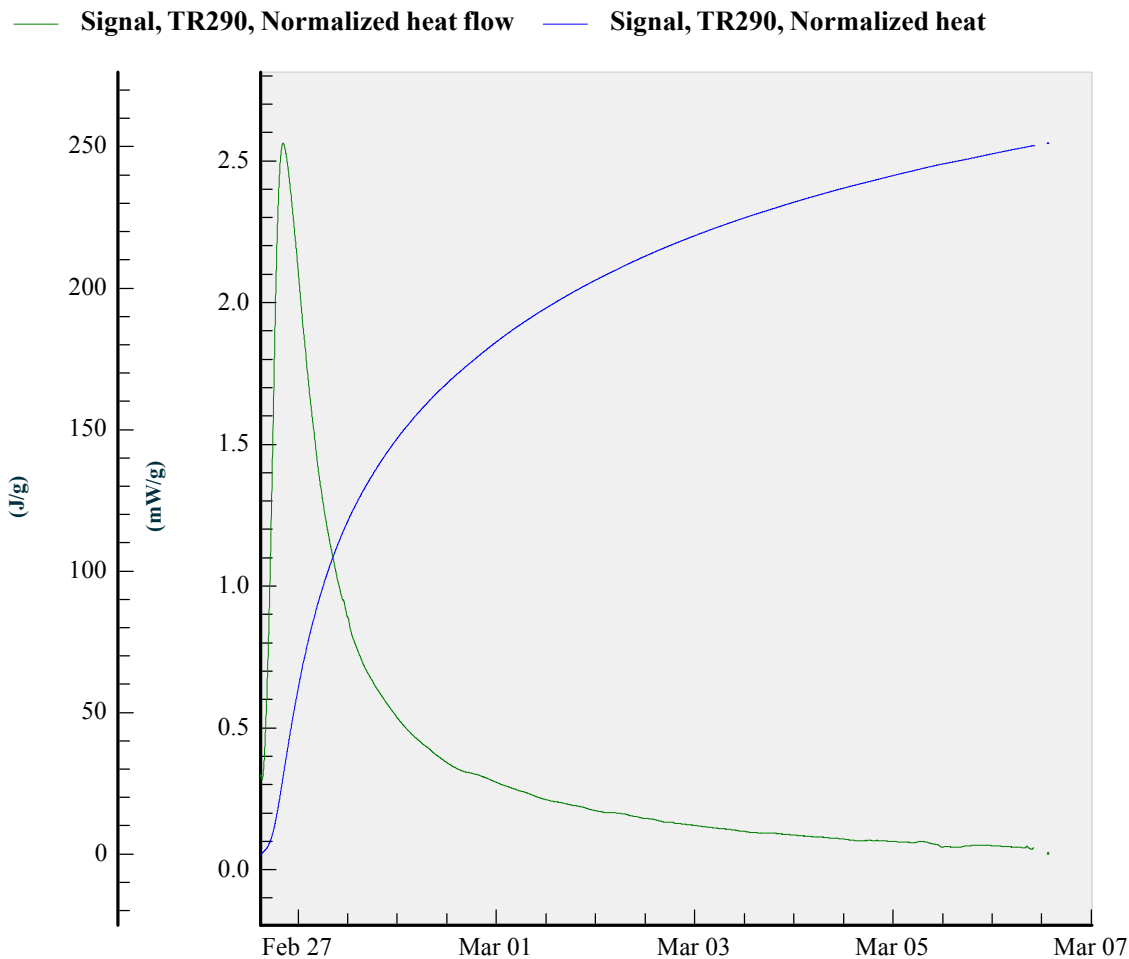
	Average 7 day heat of hydration	Range of heat of hydration
	Joules/gram	Joules/gram
Type I Portland cement	349	320 to 372
Type II Portland cement	344	308 to 371

On the other hand, at 25 °C the GGBFS does not hydrate as rapidly as the OPC and overall has a normalized heat release approximately 5 times less than the value observed for OPC. The peak time of heat flow for the GGBFS sample occurred 13 hours later than the peak time for OPC.

Ultimately, it is the heat produced per gram of grout that is important since this will determine the temperature increase of the mixture. This heat output normalized to the mass of grout is also included in Table 3-1. For example, the amount of heat released by OPC in water at a 0.60 water to cement ratio can be translated into an increase in the temperature of the mix if the mix were perfectly insulated. Assuming that it requires 1.25 joules to increase the temperature of 1 gram of grout by 1 °C [1], a release of 222 joules per gram of grout would increase the temperature of the mix by 178 °C.

### 3.2 OPC, GGBFS and FA in MCU Simulant

The heats of hydration were also measured for three mixes made using OPC, GGBFS or FA in the MCU simulant at a water-to-cementitious material ratio of 0.60 at 25 °C. For example, Figure 3-2 shows the normalized heat flow and heat release/gram of GGBFS in the MCU simulant.



**Figure 3-2 Normalized heat production and normalized heat/gram of GGBFS in MCU (TR290) at 25 °C.**

The values for all three cementitious components in MCU are provided in Table 3-4. These data reveal that the GGBFS is now as reactive as OPC in the basic simulant solution. Evidently, the

high concentration of base activates/accelerates the dissolution of the GGBFS which leads to the hydration reactions. However, the heat produced after seven days for either OPC or GGBFS (251 and 245 J/g) is ~ 100 J/g less than the amount of heat released by OPC in water (see Table 3-2). Finally, the amount of heat produced by FA in MCU is only 7 J/g after seven days.

**Table 3-3 Normalized Heat Release (per Gram of Cementitious Material) and Peak Times for Heat Flow for Mixes of OPC, GGBFS and FA in MCU Over a Seven Day Period.**

ID #	Cementitious Material	Water/Cementitious Ratio	Normalized Heat		Peak of Heat Flow Hours
			J/g of grout	J/g of cementitious material	
TR289	OPC	0.60	134	251	9.3
TR290	GGBFS	0.60	130	245	6.0
TR295	FA	0.60	4	7	NA

The peak time for heat flow for the OPC in MCU was increased to 9.3 hours relative to 7.1 hours in water while the GGBFS in MCU peak time was shortened considerably from 21.3 hours to 6.0 hours in water at 25 °C.

The amount of heat released by OPC or GGBFS in MCU simulant can be translated into an increase in the temperature of the mix if the mix were perfectly insulated. Assuming that it requires 1.25 joules to increase the temperature of 1 gram of grout by 1 °C, a release of 134 joules per gram of grout would increase the temperature of the mix by 107 °C.

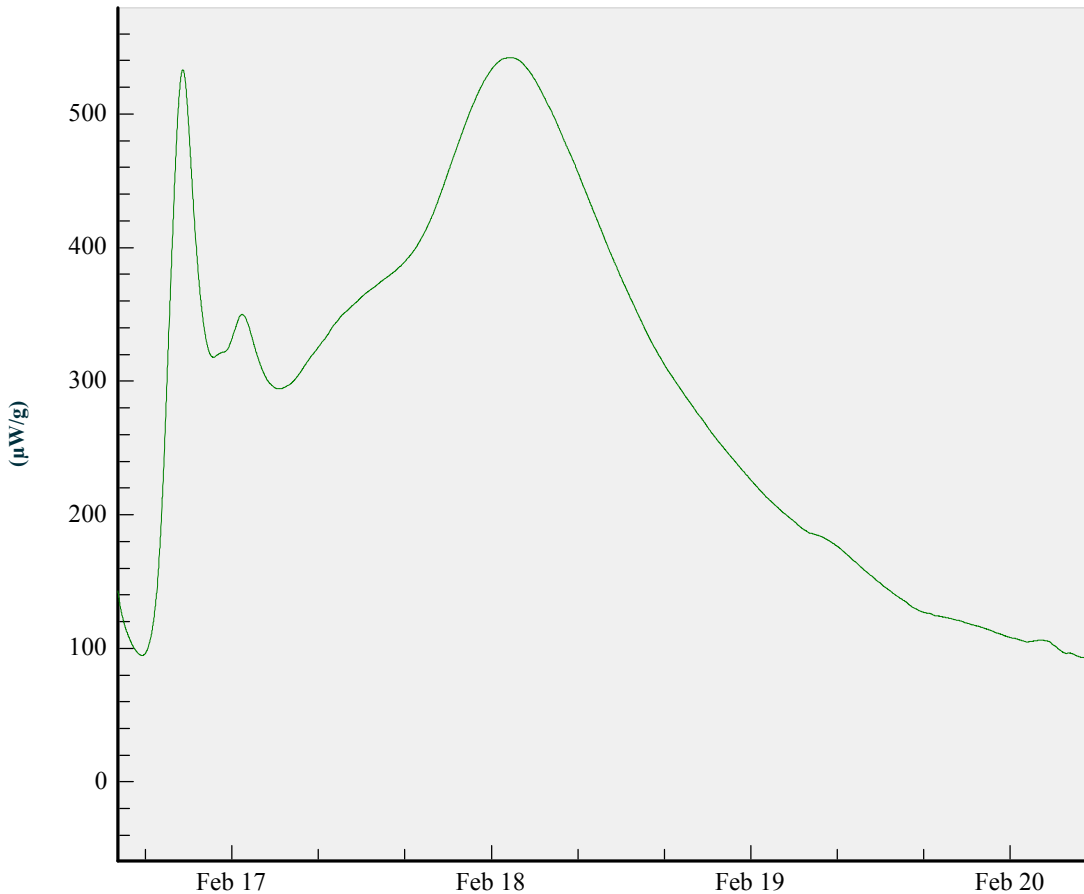
### 3.3 Premix in DDA, MCU and SWPF Simulants

The grout formulations for Saltstone mixes typically use a cementitious material mixture (premix) made up of 45% GGBFS, 45% FA and 10% OPC at 25 °C. The heat flow and heat release were measured using premix and simulants for DDA, MCU and SWPF. These data for all three mixes are presented in Table 3-4.

**Table 3-4 Results of the Heat Release and Peak Time for Heat Flow for Mixes Made from Premix and the Simulants at 25°C.**

ID	Cementitious Material	Water/Cementitious material Ratio	Normalized Heat		Peak of Heat Flow Hours
			J/g grout	J/g cementitious material	
DDA	Premix	0.60	64	114	6 / 36
MCU	Premix	0.60	64	120	2.5 / 5.5
SWPF	Premix	0.60	75	138	7

These data reveal that the amount of heat given off for a seven day period is greatest for the SWPF simulant and least for the DDA simulant. The time dependence of the heat generation is also significantly different for these three simulants. The DDA simulant has several peaks with the largest one peaking at 36 hours (Figure 3-3). It is also interesting to note that the amount of heat generated is roughly half that produced with either OPC or GGBFS by itself in MCU. These results suggest that the FA (which contributes 45% by mass of the premix) is contributing very little to the heat of hydration over this initial seven day period at 25 °C.



**Figure 3-3 The normalized heat flow and heat release for premix in DDA at 25°C.**

The amount of heat released by premix in these simulants can be translated into an increase in the temperature of the mix if the mix were perfectly insulated. Assuming that it requires 1.25 joules to increase the temperature of 1 gram of grout by 1 °C, a release of 64 to 75 joules per gram of grout would increase the temperature of the mix by 51 to 60 °C.

### 3.4 Temperature Dependence of Heat of Hydration

The temperature dependence of the heat of hydration was measured for OPC in water and premix in DDA, MCU and SWPF simulants at a water to cementitious material ratio of 0.60. For this study, the heats of hydration were measured at 25, 40 and 55 °C.

#### OPC in H<sub>2</sub>O

For OPC in H<sub>2</sub>O a more rapid release of heat (shorter peak time) was observed as the isothermal temperature increased. The overall amount of heat released in a seven day period increased slightly. The results are summarized in Table 3-5.

**Table 3-5 Temperature Dependence of the Normalized Heat Release and the Peak Time of Heat Flow for OPC in water**

Temperature	Water/OPC Ratio	Normalized Heat		Peak Time Hours
		J/g of grout	J/g of OPC	
		25°C	0.60	
40°C	0.60	236	377	3.8
55°C	0.60	244	390	2.7

For premix in DDA, MCU and SWPF, the results showed that the peak time for heat flow decreased as the temperature increased (Table 3-6, Table 3-7 and Table 3-8). On the other hand, the total amount of heat was generally independent of the temperature except for SWPF in which case the total amount of heat released increased with temperature. This increase in heat release with temperature for SWPF corresponds to a new peak that emerges at 22 hours for the 55 °C isothermal condition (Figure 3-4).

**Table 3-6 Temperature Dependence of the Normalized Heat release and the Peak time of Heat Flow for Premix in DDA**

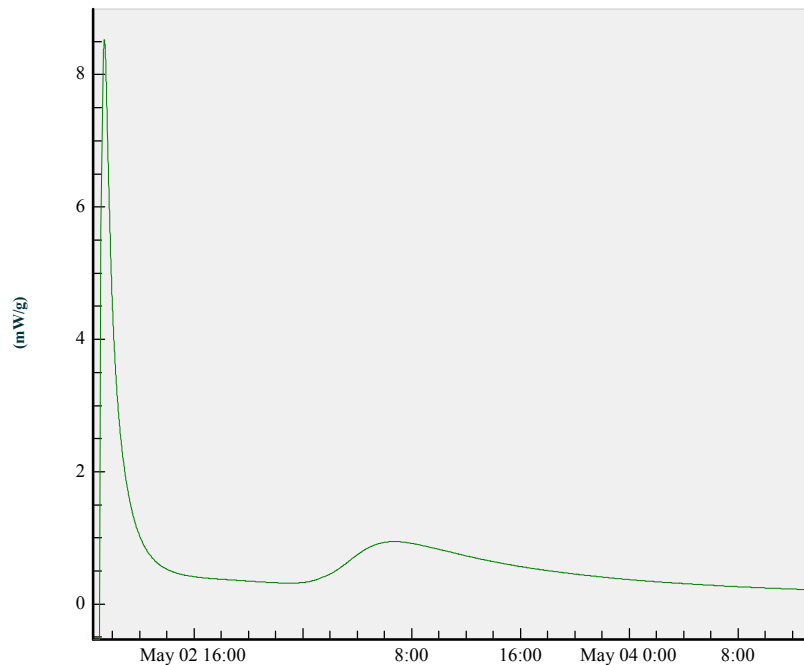
Temperature	Water/Premix Ratio	Normalized Heat		Peak Time Hours
		J/g of grout	J/g of Premix	
		25°C	0.60	
40°C	0.60	67	119	2.5 / 3.5 / 11.5
55°C	0.60	63	112	1.5 / 3.0

**Table 3-7 Temperature Dependence of the Normalized Heat release and the Peak time of Heat Flow for Premix in MCU**

Temperature	Water/Premix Ratio	Normalized Heat		Peak Time Hours
		J/g of grout	J/g of Premix	
		25°C	0.60	
40°C	0.60	59	110	1.0
55°C	0.60	67	126	0.7

**Table 3-8 Temperature Dependence of the Normalized Heat release and the Peak time of Heat Flow for Premix in SWPF**

Temperature	Water/Premix Ratio	Normalized Heat		Peak Time Hours
		J/g of grout	J/g of Premix	
		25°C	0.60	
40°C	0.60	75	138	2.0
55°C	0.60	127	150	0.8 / 22



**Figure 3-4 Normalized heat flow for premix in SWPF at 55 °C (note peak at 22 hours)**

### 3.5 Variability in SWPF Feed – Phase VI

The objective for measurement of the heat of hydration is to determine the sensitivity of the heat of hydration to the projected chemical and processing variations experienced under normal operating conditions at SPF. Phase VI of the Saltstone Variability Study focused on the variation in the SWPF feed to the Saltstone Production Facility. As part of this study, the heats of hydration of 10 of the 11 samples produced in Phase VI were measured. These measurements were performed at 25 °C for a duration of seven days. The results are provided in Table 3-9.

**Table 3-9 Total Heat Release Normalized to Grams of Premix and Peak Time of the Heat Flow for Mixes Made During Phase VI of the Variability Study ( the Heat Release in Joules per Gram of Grout is also Provided for Each Sample)**

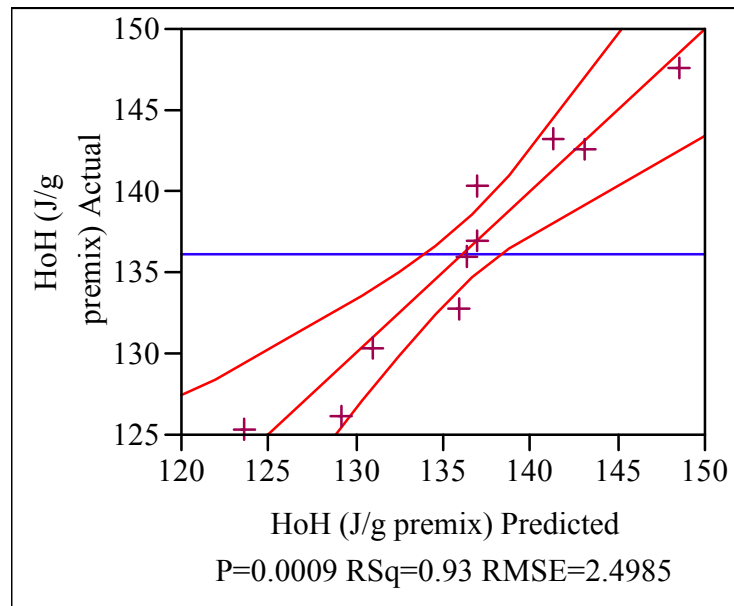
Identifier	Heat of Hydration at 25°C		
	J/g premix	J/g grout	Peak time (minutes)
GVS63	140	76	431
GVS64	136	72	398
GVS65	148	79	727
GVS66	143	80	454
GVS67	126	68	214
GVS69	130	73	227
GVS70	133	69	605
GVS71	125	69	0
GVS72	143	77	1281
GVS73	137	74	470

The average value and standard deviation for the total heat release (in J/gram of premix) at 25 °C were 136 J/g premix and 7.5 J/g premix respectively with a range of 23 J/g premix. One of the next phases of the variability study will extend the processing and compositional variations and the range of values will increase over those of this first stage for SWPF. The peak time for heat of hydration was more sensitive to the chemical and processing variations with an average peak time of 481 minutes with a standard deviation of 349 minutes. The range was 1281 minutes (~21 hrs).

These data were statistically evaluated to determine whether a linear model could be developed for the total heat release as a function of the variables tracked. Figure 3-5 shows the linear model that was developed with an  $R^2$  of 0.93 and no statistical evidence for a lack of fit. The equation corresponding to this empirical fit is:

$$\text{Total heat release (J/g premix)} = 142.5 - 0.34T - 1.8 [\text{OPC}] + 174.0 [\text{Al(OH)}_4^-]$$

where T is the temperature in degrees C at which the mix was prepared, [OPC] is the concentration of OPC in wt %, and  $[Al(OH)_4^-]$  is the aluminate concentration in moles/liter.

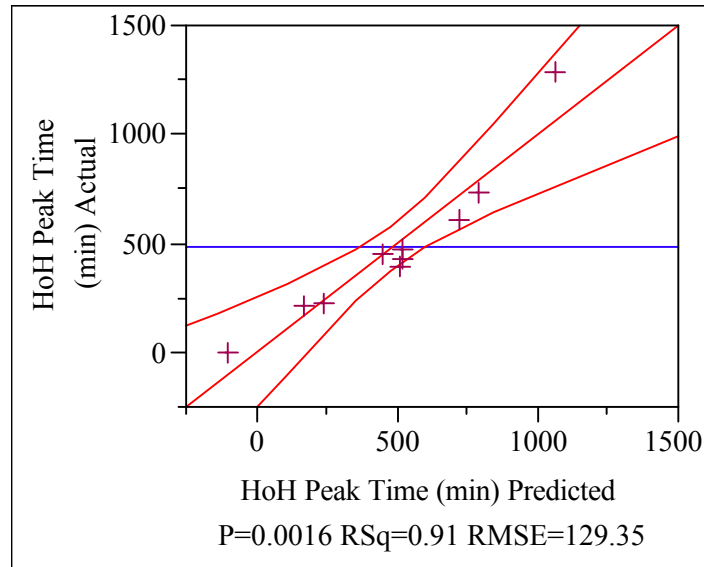


**Figure 3-5 Linear model for the total heat release as a function of temperature, aluminate concentration and wt % OPC in SWPF measured at 25°C**

A similar analysis (Figure 3-6) was performed for the peak time for heat generation with the development of a linear model with an R2 of 0.91 and no statistical evidence for a lack of fit:

$$\text{Peak time (minutes)} = -210.3 - 8.5 [\text{OPC}] + 7894.1 [Al(OH)_4^-] + 272.5 [NO_3^- + NO_2^-]$$





**Figure 3-6 Linear model for the total heat release as a function of temperature, aluminate concentration and wt % OPC in SWPF measured at 25 °C**

Both the total heat release and the peak time for heat flow are significantly dependent on the aluminate concentration as has been previously noted by Lokken [5]. The option for aluminum removal from HLW sludge will increase aluminate concentration in the feed to SPF. Therefore, a study is underway to determine the impact of increased aluminate on heat of hydration as well as the other properties of fresh and cured Saltstone.

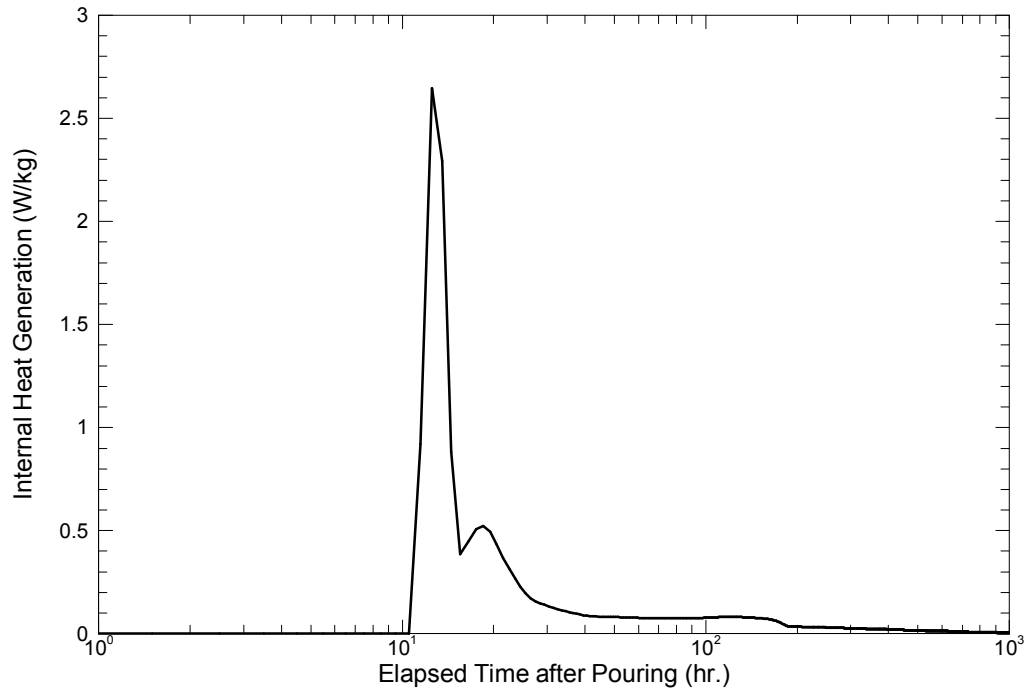
### 3.6 Additional Contributions to the Heat of Hydration

It turns out that there is an initial temperature rise of the mix that occurs during the three minutes of mixing that is not captured in the overall heat of hydration. Typically the temperature rise is on the order of 2 °C. Assuming that the specific heat for the mix is 1.25 Joules per degree per gram, a temperature increase of 2 °C corresponds to an additional 2.5 J/g of premix. However, under the conditions where the grout has yet to form, the specific heat could be higher which increases the 2.5 J/g premix to 3.9 J/g premix. The contribution from this early stage exothermic reaction has not been added to the overall heats of hydration of these mixes.

There is always a competition between the time needed for the sample to equilibrate in the calorimeter and the time at which initiation of the hydration reactions begin. Typically, with OPC, the delay in hydration is such that equilibration in the calorimeter is achieved before hydration begins. However, as the temperature at which the test is performed increases, the time for hydration to begin decreases and therefore, some of the evolved heat will not be captured before equilibration is achieved (~45 minutes). Estimates on some of the samples indicate that heat values up to 5 - 10 J/g of premix may not be recorded. This estimated heat production was not added back to any of the values in this report.

### 3.7 Comparison of Isothermal to Adiabatic Calorimetry

Steimke and Fowley [1] measured the temperature increase of a Saltstone mix using adiabatic calorimetry. Their data, presented as the heat of hydration (watts/kg of grout), are provided in Figure 3-7 for reference.



**Figure 3-7 Heat generation for Saltstone as measured using adiabatic calorimetry (from Steimke and Fowley [1])**

Their data show a sharp peak starting at about 10 hours and a second peak with a maximum at ~ 20 hours. No apparent temperature rise was observed in the first 10 hours.

Steimke and Fowley [1] measured the specific heat of Saltstone to be 0.304 calories/ g or 1.27 J/g. From the temperature rise of the grout mix as a function of time it is possible to calculate the heat of hydration at any time. For example, after 80 hours, the temperature of their simulated Saltstone mix had increased by 47 °C which translates to a heat release of 59.8 J/g of Saltstone or 105 J/g of premix. This heat release of 105 J/gram of premix determined adiabatically can be compared to heat release determined isothermally from DDA, MCU and SWPF mixes after 80 hours:

DDA	95 J/g of premix
MCU	102 J/g of premix
SWPF	120 J/g of premix

Therefore, the values determined by adiabatic and isothermal measurements are generally consistent at 80 hours. However, additional experiments at higher isothermal temperatures will be required to see how well the two measurements agree for longer times. This is due to the higher temperatures that are experienced in adiabatic calorimetry (~105 °C).

### 3.8 Extent of Reaction

The extent of hydration reactions can be estimated from the heat of hydration measurements. The theoretical amount of heat generated for cementitious materials is generally between 375 - 420 J/g. This maximum amount of heat generated may take up to a year or so to be achieved. For example, if the maximum amount of heat possible from Type II OPC is 400 J/g of OPC, then a measurement of 300 J/g of OPC indicates that 75% (extent of reaction) of the OPC has reacted.

For the measurements of OPC in water performed in this study, ~350 J/g of OPC was liberated after seven days corresponding to 88% of the OPC having reacted in this time period (again, assuming a maximum amount of heat of 400 J/g of OPC). For the case of an MCU mix, OPC and GGBFS both released ~250 J/g of OPC or GGBFS at 25 °C after seven days. This implies that only 63% of the OPC or GGBFS reacted after a week period in MCU.

When premix is added to MCU, the amount of heat released after seven days at 25 °C was further reduced to 120 J/g of premix. In this case the premix is composed of 55% by mass of GGBFS and OPC and the heat generated by these two components should equal  $0.45 \times 245 + 0.10 \times 251$  or 135 J/g of OPC and GGBFS. Comparing this 135 J/g of premix value to the measured 120 J/g of premix indicates that very little fly ash reacts during this seven day period. Similar results were obtained with DDA and SWPF again consistent with very little reaction of the fly ash over this period at 25 °C.

The temperature dependence of the heat of hydration demonstrates that the total amount of heat released by the premix in DDA and MCU does not significantly change with temperatures up to 55 °C. However, the amount of heat released by SWPF mixes at 55 °C does increase slightly from 135 to 150 J/g of premix due to an emergent peak at 22 hours. It is tempting to attribute this increase for SWPF to activation of the FA at higher temperatures and increased hydroxide ion concentration but the proof of that association will require additional experimentation at higher temperatures.

Degrees of reaction of portland cement and portland cement blended with reactive mineral admixtures (fly ash and slag) measured by Feng et al. [14] provides a reference to the data presented above even though their measurements used mixes containing distilled water rather than salt solutions. Using a point counting procedure with scanning electron micrographs of grout samples cured as a function of time, these authors were able to measure the degree of reaction of not only portland cement but also slag and fly ash. After 4 days of curing, a portland cement based mix showed that the hydration reactions of portland cement were ~53% complete. For the blended cement pastes, the degree of hydration of portland cement was roughly the same as it was in the portland cement only paste. In contrast with the blended systems, slag was only ~8% reacted after 4 days and only 30% reacted after 40 days. Class F fly ash was even less

reactive in this system with only 1 to 2% of the fly ash hydrated after 4 days and 11% reacted after 28 days. The high base content of Saltstone simulants activates the slag and can account for the increased reaction rate and heat evolution from GGBFS.

## 4.0 CONCLUSIONS

This report presents the heat of hydration measurements of Saltstone mixes using isothermal calorimetry. The conclusions from this study are:

- Both OPC and GGBFS produce heat over a 7 day period at 25 °C in a simulated MCU salt solution which is approximately 100 J/g of cementitious material less than the amount of heat generated for OPC in water. This reduction in the heat of hydration in a concentrated salt solution benefits the goal of reducing the amount of heat generated in the grout mix.
- Fly ash does not appear to contribute significantly to the heat of hydration of a grout mix made using premix. This means that the hydration reactions of fly ash have not occurred to a significant extent (most likely less than 5% over this seven day period at 25 °C).
- The amount of heat generated by premix at 25 °C is dependent on the simulant used. SWPF mixes generated 138 J/g of premix, MCU mixes 120 J/g of premix and DDA mixes 114 J/g of premix. The different amounts of heat generated in these three mixes may be due to the free hydroxide ion concentration (SWPF > MCU > DDA).
- The kinetics of release of the heat of hydration also depends significantly on the salt solution. MCU mixes have a peak releases at 2 and 5 hours whereas SWPF has a single peak at 7 hours. DDA mixes have a number of peaks that extend out to 36 hours.
- The temperature at which the isothermal measurement is made also impacts the results. The peak times all decreased as the temperature was increased to 55 °C. The amount of heat was generally the same for three temperatures studied except for SWPF. A new peak of heat flow was observed at 55 °C at ~ 22 hours. This peak may be due to activation of fly ash or additional activation of the GGBFS.
- The application of heat of hydration measurements as part of the variability study was initiated. In Phase VI of the variability study, only limited variations in the variables of interest were introduced. In spite of this, the results showed a range in the total amount of heat released of 23 J/g of premix whereas the peak times showed a range of 21 hours.
- The amount of heat released and the peak times produced could be empirically fit to linear relationships. These models revealed a dependence of the heat released to aluminate and OPC concentrations and temperature of mixing while peak times were dependent on aluminate, OPC, and total nitrate plus nitrite concentrations.
- A comparison of earlier studies using adiabatic calorimetry to the current isothermal calorimetry results shows a reasonable correlation after 80 hours of reaction time. However, longer times were not considered in this comparison and may diverge due to the differences in maximum temperature of the mix (55 °C for isothermal measurements vs. 105°C for the adiabatic measurements).
- The measurement of the heat of hydration can provide information on the extent of the hydration reactions by comparing heat release to maximum heat release potential of the cementitious materials. After seven days, roughly 60% of the OPC and GGBFS have reacted while essentially none of the FA has reacted.

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