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IMPACT OF ALUMINATE IONS ON THE PROPERTIES OF SALTSTONE GROUT MIXES

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

INTRODUCTION

It is important to identify and control the operational and compositional variables that impact the important processing and performance properties of Saltstone grout mixes. The grout that is produced at the Saltstone Production Facility (SPF) is referred to as Saltstone and is a waste form that immobilizes low concentrations of radionuclides as well as certain toxic metals. The Saltstone will be disposed of in vaults at Savannah River Site (SRS). An effort referred to as the Saltstone Variability Study has been initiated to achieve this goal. The protocols developed in this variability study are also ideally suited as a tool to assess the impact of proposed changes to the processing flow sheet for Liquid Waste Operations at SRS. One such proposal that is currently under consideration is to introduce a leaching step in the treatment of the High Level Waste (HLW) sludge to remove aluminum prior to vitrification at the Defense Waste Processing Facility (DWPF). This leachate would significantly increase the soluble aluminate concentration in the salt feed that will be processed at the SPF. Consequently, an initial study of the impact of increased aluminate concentration on the Saltstone grout properties was performed. Prior work by Lukens (1) showed that aluminate in the salt solutions increases the amount of heat generation.

EXPERIMENTAL

The cementitious materials used in these tests were obtained from SPF and are listed in Table 1. The materials were transferred to 2-liter plastic bottles and tightly sealed. The mix design for Saltstone uses a combination of portland cement (OPC), blast furnace slag (BFS) and fly ash (FA) referred to as premix. The ratio of these cementitious materials in the premix blend is also provided in Table 1. The nominal water to cementitious materials ratio is 0.60.

Material	Category	Vendor	Premix Blend (wt%)
Portland cement (OPC)	Type II	Holcim	10
Blast Furnace slag (BFS)	Grade I	Holcim	45
Fly ash (FA)	Class F	SEFA	45

Table 1 Saltstone Cementitious Materials

The impact of aluminate was determined using a simulated salt solution (containing no radionuclides) that reproduces the current average projected composition of future batches. The composition of this simulant is provided in the first row of Table 2 (GVS74). The last three mixes contain increasing amounts of aluminate to determine the impact of aluminate on the grout properties. To keep the free hydroxide ion concentration constant, it was necessary to increase the sodium hydroxide concentration. A similar set of mixes with the same aluminate variation but a relatively constant nitrate concentration was also investigated and gave similar results to those obtained using the mixes presented in Table 2. In order to investigate the role of the individual cementitious components, additional mixes were batched using the mix designs for GVS74 and GVS76 with OPC, BFS or FA only. All testing was performed at ~25 ^oC.

Identifier	Aluminate	Free OH^-	w/cm	Nitrate	Nitrite	Carbonate	Sulfate
GVS74	0.11	2.4	0.60	2.31	0.38	0.12	0.06
GVS75	0.23	2.4	0.60	2.66	0.38	0.12	0.06
GVS76	0.34	2.4	0.60	2.99	0.38	0.12	0.06
GVS77	0.45	2.4	0.60	3.32	0.38	0.12	0.06

Table 2 Molarity of Salts in the Four Simulants used for the Mixes (Anions were Introduced as Sodium Salts)

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.

Rheological measurements were performed to characterize the flow properties of the Saltstone mixes by analyzing their flow curves (shear rate versus shear stress). Flow curve measurements were obtained using a cylindrical rotor and cup with a Haake RS600 rheometer. All of the down flow curves were analyzed as Bingham Plastic fluids.

RESULTS

Fresh Grout Properties

The fresh grout properties (and the cured grout density for comparison to the fresh grout density) for the four mixes presented in Table 2 are presented in Table 3.

Identifier	Gel Time	Bleed (vol%)		Density (g/mL)		Bingham Plastic	
	(minutes)	1 day	3 Day	Fresh	Cured	Yield Stress	Plastic Viscosity
GVS74	115	2.5	1.9	1.74	1.80	2.7	69.7
GVS75	52	1.2	1.0	1.75	1.80	2.0	66.5
GVS76	40	1.2	1.2	1.76	1.80	1.6	61.5
GVS77	50	0.6	1.0	1.77	1.81	1.4	67.2

Table 3 Fresh Grout Properties of Mixes as a Function of Aluminate Concentration (0.11 to 0.45 M)

As the aluminate concentration increased from 0.11 M (GVS74) through 0.45 M (GVS77), the gel time, bleed volume and yield stress decreased. The plastic viscosity was essentially unchanged as a function of aluminate ion concentration. Figure 1 contains all the flow curves, which show little difference in the flow properties.

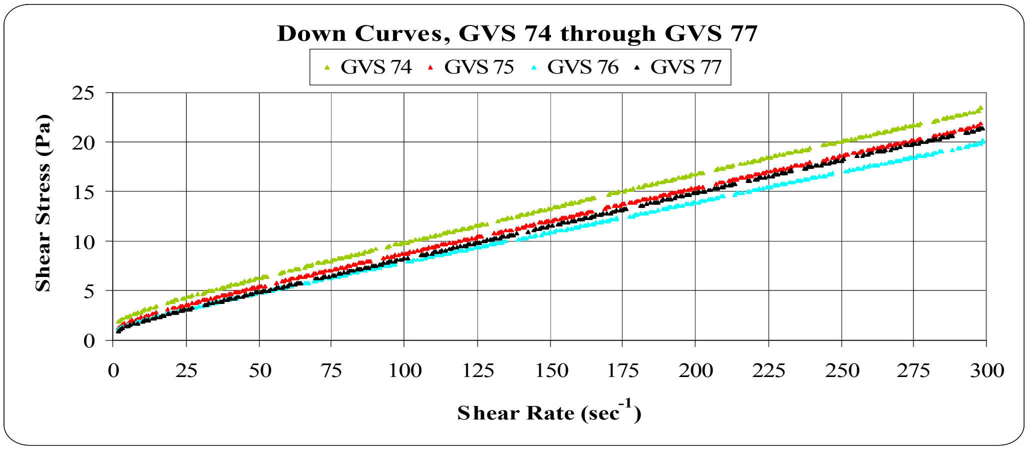

Figure 1 Superposition of the flow curves for GVS74 through GVS77

Set Time and Heat of Hydration

The set time and the 7-day heat of hydration data for these mixes are presented in Table 4. The data in this table reveal that an increase in the aluminate concentration increased the 7-day heat of hydration of the grout mix and significantly increased the induction period, quantified as the peak time for heat flow (the amount of time, starting with mixing, until heat generation from the hydration reactions is a maximum). It turns out that the increase in heat production for the mixes containing higher levels of aluminate is approximately 30 % greater than for the GVS74 mix at two weeks.

Identifier	Set Time (Days)	7-Day Heat of Hydration (J/g)		Peak Time
		premix	grout	Hours
GVS74	1	141	76	6
GVS75	3	163	87	47
GVS76	4	162	85	57
GVS77	4	158	81	57

Table 4 Set Time, 7-Day Heat of Hydration and Peak Times for Heat Flow for the Four Mixes

The peak time for heat flow correlates with the set times measured for these grouts. That is, the set time increased as the peak time for heat flow increased. This is explained by the fact that a threshold for the degree of hydration (the fraction of cementitious material that reacts or hydrates) must be exceeded prior to a proper set of the grout. The heat of hydration data for GVS74 are provided in Figure 2 and the corresponding data for GVS76 with a higher aluminate concentration (0.34 M) are provided in Figure 3.

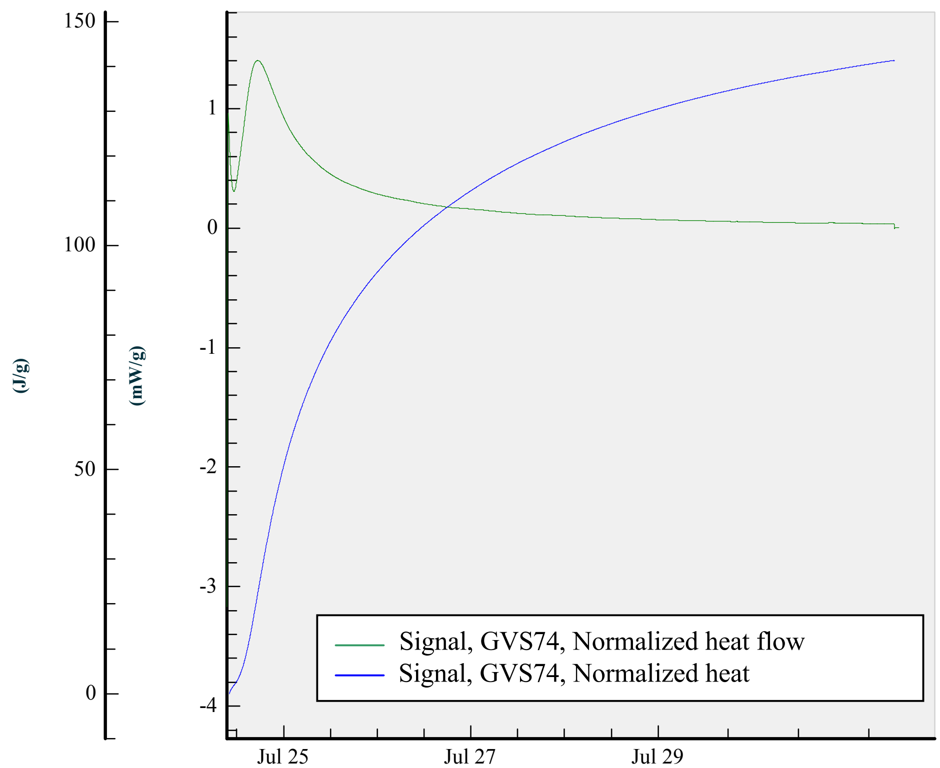

Figure 2 Normalized heat flow and normalized heat for GVS74

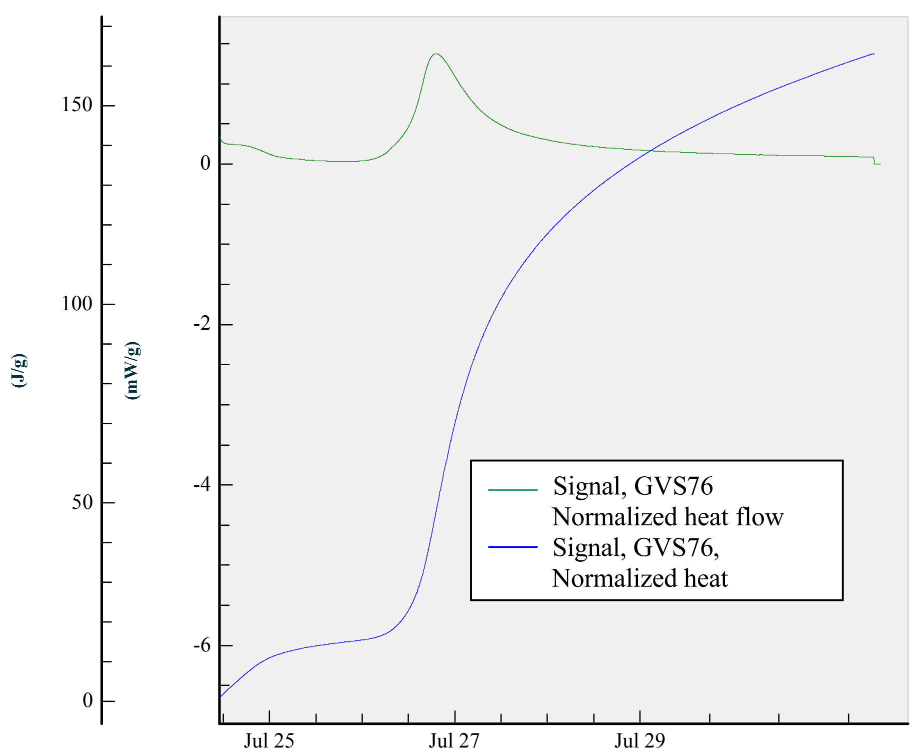

Figure 3 Normalized heat flow and normalized heat for GVS76

Role of Cementitious Material

Mixes were made using the GVS74 mix design (0.11 M aluminate) and GVS76 mix design (0.34 M aluminate) with OPC, BFS or FA only. The results for the fresh grout properties are provided in Table 5. The OPC mixes gelled quickly, had no bleed water, and exhibited relatively high yield stress and plastic viscosity. For BFS mixes, the gel time, yield stress and plastic viscosity decreased with increasing aluminate concentration. The FA-only mixes gelled in less than 1 day, had very large bleed volumes, and had low yield stress and plastic viscosity.

Cementitious Material	Aluminate Molarity	Identifier	Gel Time (minutes)	Bleed (vol%)		Density (g/ml)		Bingham Plastic	
				1 Day	3 Day	Fresh	Cured	Yield Stress (Pa)	Plastic Viscosity (cP)
OPC	0.11	GVS74-1	5	0	0	1.89	1.914	12.6	181.7
	0.34	GVS76-1	5	0	0	1.87	1.916	11.5	138.5
BFS	0.11	GVS74-2	20	0	0	1.79	1.822	9.1	99.2
	0.34	GVS76-2	10	0.4	0	1.8	1.883	5.9	86.5
FA	0.11	GVS74-3	> 600	NM	20	1.683	NM	0.2	56.8
	0.34	GVS76-3	>600	NM	17	1.687	NM	0.3	51

Table 5 Fresh Grout Properties of Mixes Containing OPC, BFS or FA

The set time and the 7-day heat of hydration data for these mixes are presented in Table 6. For the OPC mixes, the induction period (peak time) actually decreased from 2 to 0.4 hours with an increase in aluminate concentration and the set time was 1 day for both mixes (set times were monitored every 24 hours). On the other hand, the set time and heat of hydration of BFS mixes were similar to the properties of the mixes prepared with the premix blend. The peak time increased from 6 to 32 hours and the set time increased to 2 days from 1 day with an increase in aluminate concentration. Finally, over the 7 day period, the FA mixes did not produce much heat relative to OPC and BFS mixes. These data suggest that the impact of aluminate on set time and heat of hydration involves the alkali activation of BFS (2-4).

Cementitious	**Identifier**	**Set Time**	**7-Day Heat of Hydration (J/g)**		**Peak Time**
Material		Days	cm	grout	Hours
OPC	GVS74-1	1	223	120.9	2
	GVS76-1	1	227	118.6	0.4
BFS	GVS74-2	1	282	152.8	6
	GVS76-2	2	286	149.5	32
FA	GVS74-3	>7	16.3	8.5	None
	GVS76-3	>7	13.8	7.5	None

Table 6 Set Time, 7-Day Heat of Hydration and Peak Times for Heat Flow

CONCLUSIONS

The addition of aluminate to the salt solutions significantly increased the set times from 1 to 4 days for the simulated mixes. Heat of hydration measurements were consistent with the increased set times in that the induction periods were extended to several days as aluminate concentration increased in the salt solution. The overall heat generation was greater in the mixes containing higher concentrations of aluminate. The induction period at higher aluminate concentrations is evidently associated with hydration reactions of the BFS since OPC alone speeds up the rate of heat generation whereas the BFS mixes exhibited an increased induction period at higher aluminate concentrations similar to that observed with mixes prepared using premix.

The increased induction periods and greater amounts of heat evolution observed with increasing aluminate concentrations must be addressed by Saltstone operations in determining pour schedule. Saltstone Operations uses a model to limit temperature in the vaults and this model includes as inputs both the amount and time dependence of heat produced by the grout.

REFERENCES

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