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R. O. Lokken

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Pacific Northwest Laboratory
Richland, Washington 99352

EFFECT OF ALUMINATE IONS ON THE HEAT OF HYDRATION OF CEMENTITIOUS WASTE FORMS

R. O. Lokken, Pacific Northwest Laboratory[(a)], Richland, Washington

INTRODUCTION

During the hydration and setting of high-salt content liquid waste grouts, considerable heat is generated by exothermic reactions within the grout. These reactions include hydration reactions of cementitious solids and reactions between waste constituents and the solids. Adiabatic temperature rises exceeding 80°C have been estimated for grouts prepared with a dry blend of 47 wt% fly ash, 47 wt% blast furnace slag, and 6 wt% type I/II Portland cement (1). Performance criteria for grout disposal specify that the temperature of the grout waste form must not exceed 90°C (2). To counter the increase in temperature, inert solids were added to the "47/47/6" dry blend to reduce the amount of heat-generating solids, thereby decreasing the temperature rise. Based on preliminary results from adiabatic calorimetry, a dry blend consisting of 40 wt% limestone flour, 28 wt% class F fly ash, 28 wt% ground blast furnace slag, and 4 wt% type I/II Portland cement was selected for further testing.

Even with the limestone added, the temperature of the grouts approached the 90°C limit. Therefore, a series of experiments were conducted using simulated waste to determine which factors contribute most to the generation of heat. The ultimate goal of these and subsequent tests was to identify a suitable grout formulation that minimizes temperature rise while still meeting all other applicable criteria. Minimizing the temperature rise during curing is desirable for reducing thermal stresses and for limiting the detrimental effects on grout leach resistance (3). The results showed the heat generation of the grouts was greatly influenced by the waste composition.

PROCEDURES

A series of tests was conducted to determine the effects of waste composition and dry blend materials on heat generation during the curing of the grouts. This section describes the operation of the adiabatic calorimeter sys-

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tem, the waste compositions, the dry blend ingredients, and grout preparation procedures.

Adiabatic Calorimetry

The adiabatic calorimeter system consists of eight individual calorimeter cells and a common temperature measurement and control system. Figure 1 shows a schematic of a cell. The calorimeter cells consist of a 6-liter stainless steel Dewar, a water circulation pump, an immersion heater, and a 1-liter stainless steel Dewar for the grout slurry. The heater is controlled with a solid-state relay connected to the control system. The data acquisition system consists of a relay multiplexer, a thermocouple amplifier/conditioner, and a 16-bit analog-to-digital converter.

Grout hydration testing using adiabatic calorimetry is based on the premise that all the heat generated by the grout is maintained within the grout, thereby increasing the grout temperature. For the large grout disposal vaults, adiabatic curing conditions are expected, particularly for grout near the center of the vault. In the laboratory, adiabatic conditions are achieved by placing freshly prepared grout slurry into a stainless steel Dewar. A thermocouple is then inserted into the grout slurry. The Dewar containing the grout slurry is then placed into a second, larger Dewar containing water preheated to the initial grout temperature. A heater in the larger Dewar maintains the temperature of the water bath at the same temperature as the grout. The temperature of the grout is recorded every half hour during operation of the calorimeter. The data presented in this paper are the measured temperatures; "true" adiabatic temperatures are approximately 15% higher due to the heat capacity of the Dewar walls.

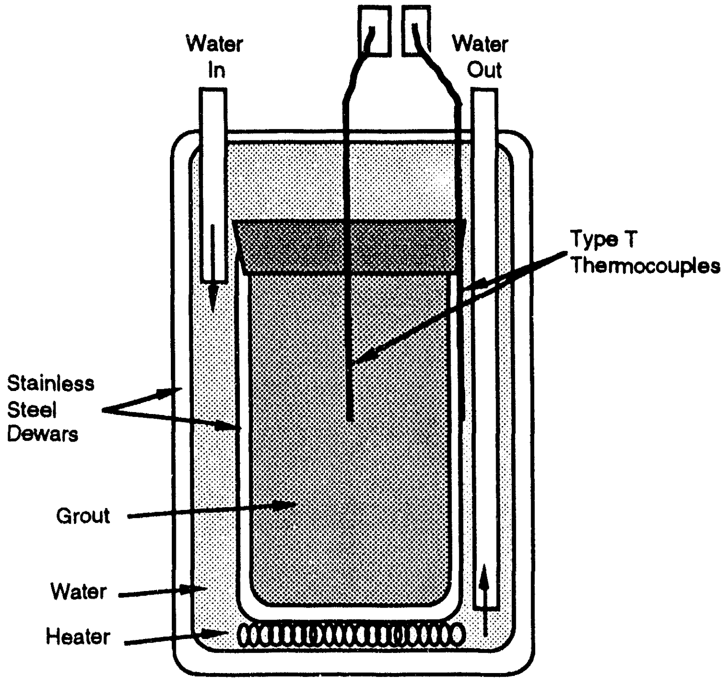

Figure 1 Schematic of an Adiabatic Calorimeter Cell

Simulated Waste

A simulated radioactive waste was used ,with the composition listed in Table 1. In addition to the simulated waste, other solutions were also used in some tests to determine the effects of several ions on the heat generation. The nominal composition of the solutions is shown in Table 2.

Table 1. Concentration of Major Species in Simulated Waste

Species	Concentration, g/L
Al	7.36
K	10.1
Na	115
P	1.26
Cl	4.34
NO_2	18.0
NO_3	162
SO_4	5.14
pH	~13.8

Table 2. Compositions of Solutions Used in Calorimetry Studies

Solution No.	Compound	Concentration, M/L
1	NaOH	1.0
2	NaOH	0.1
3	NaOH	1.5
	$NaNO_3$	3.0
	$NaAlO_2$	0.85
4	NaOH	1.5
	$NaNO_3$	3.0
5	$Al(NO_3)_3$	0.85
	NaOH	0.01 (pH = 12)
6	$Al(NO_3)_3$	0.85
	NaOH	1.0 (pH = 14)

Dry Blends

The simulated waste grouts were prepared with blends that consisted of 40 wt% limestone flour, 28 wt% class F fly ash, 28 wt% ground blast furnace slag, and 4 wt% type I/II Portland cement. Two other dry blends were used with the $NaOH/Al(NO_3)_3$ solutions (solutions 5 and 6) listed in Table 2. These included 50 wt% limestone flour and either 50 wt% fly ash or 50 wt% slag.

Grout Preparation

Grout slurries were prepared using a Hobart mixer and a wire whip The solutions were preheated to 45°C or 50°C and placed in the mixer. Room temperature dry blend was added at a ratio of 1.08 kg of solids per liter of solution. After mixing, approximately 1 liter of grout slurry was poured into a stainless steel Dewar, and the Dewar was placed into a calorimeter cell.

RESULTS AND DISCUSSION

Results of previous adiabatic calorimetry tests showed a great effect of simulated waste concentration on the heat of hydration of grouts (4). The temperature rise of a grout made with waste diluted 100 times was more than 30°C less than the grout made with undiluted waste. These results indicated that constituents in the waste were reacting with the solids from the dry blend to generate additional heat.

Calorimetry of Grouts Made with Simple Solutions

Several tests using the dry blend ingredients and simple solutions (Table 2) were conducted to determine the effects of various constituents present in the simulated wastes on the adiabatic temperature rise. The first tests were conducted to determine the effects of hydroxide ion on the heat generation. The results of these tests are compared with a reference grout in Figure 2. Although slight differences are seen in the rate of heat generation of the two sodium hydroxide solutions, the overall temperature rise of the two grouts was within about 5°C of each other after 250 hours of hydration. The total heat generated by these two grouts is less than half that of the reference grout. These results suggest that constituents other than the hydroxide in the waste contribute to the total heat generation.

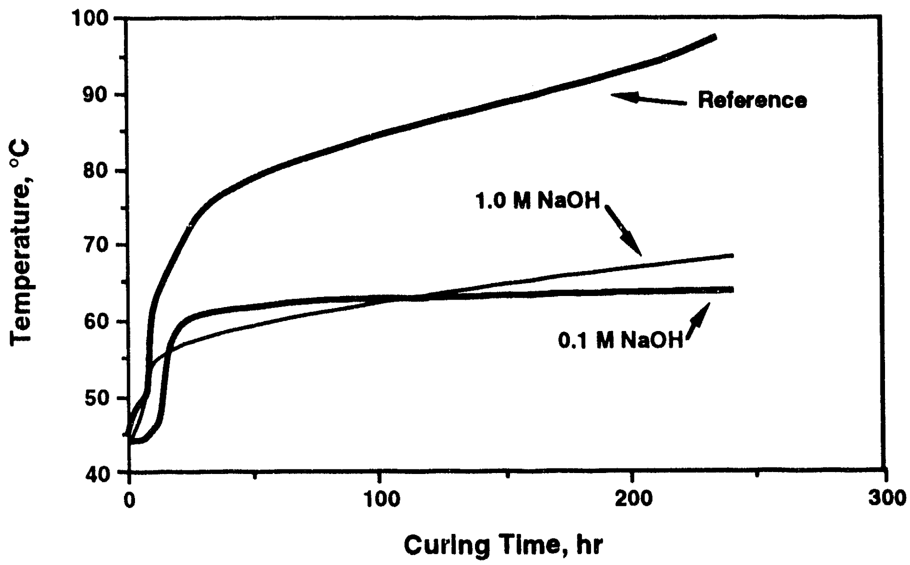

Figure 2. Measured Adiabatic Temperature Rise for Grouts Prepared with NaOH Solutions

The second set of tests investigated the effects of aluminum on the heat generation. Both solutions included 1.5 M NaOH and 3 M $NaNO_3$ and one contained 0.85 M $NaAlO_2$. The calorimeter results for grouts prepared with these solutions are shown in Figure 3. The temperature rise of the grout containing aluminum exceeded 45°C after only 150 hours of hydration, while the temperature rise of the grout without aluminum was only about 20°C after the same time period. These results strongly suggest that the aluminum reacts with the dry blend components to generate considerable amounts of heat. Because the hydroxide concentration of these solutions, and of the simulated wastes, are very high, most of the aluminum would be expected to be in solution as the aluminate ion.

Another series of tests was conducted to measure the heat generation of grouts prepared with solutions containing equal amounts of total aluminum but with different concentrations of sodium hydroxide. Figure 4 shows the temperature rise of grouts prepared with the reference dry blend and with solutions containing 0.85 M $Al(NO_3)_3$ and either 1 M or 0.01 M excess OH^-. The temperature rise of the grout containing 1.0 M OH^- was greater than 50°C after about 160 hours, while the temperature rise of the grout with the 0.01 M OH^- was less than 20°C. Based on these data, and on the data from Figures 2 and 3, it appears that the majority of the heat generation in grouts produced with these dry materials is from reactions between the soluble aluminum and the dry blend materials.

Four additional grouts were made to determine the relative reactivity of the slag and the fly ash in the latter solutions. Figure 5 shows the adiabatic calorimetry results of these tests. As shown by the lower two curves, neither the slag nor the fly ash are very reactive in the 0.85 M $Al(NO_3)_3$ solutions at a pH of 12 (i.e., 0.01 M OH^-) with temperature increases less than 4°C after about 200 hours. However, the solutions at a pH of 14 were very reactive with the slag and moderately reactive with the fly ash. The temperature rise after about 200 hours was nearly 50°C for the slag blend and about 30°C for the fly ash blend. Comparing the bottom two curves from Figure 6 and the lower curve of Figure 5 illustrates the interactions that occur during the hydration process of blends containing cement, fly ash, and slag. Figure 5 presents data for grouts prepared with the reference dry blend that contains limestone flour, cement, fly ash and slag. The temperature rise for the grout prepared

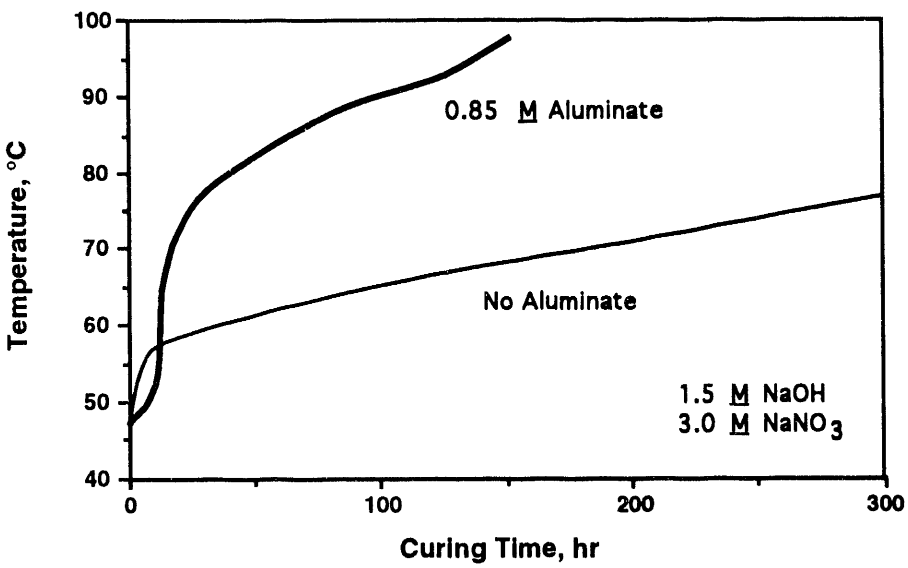

Figure 3. Measured Adiabatic Temperature Rise for Grouts Prepared with NaOH and $NaNO_3$ Solutions With and Without $NaAlO_2$

with the pH 12 solution was about 17°C after 200 hours (Figure 5), while the rise for the slag/limestone and fly ash/limestone blends was less than 4°C (Figure 6). The differences can be attributed to the presence of cement in the former grouts. Pozzolanic reactions of the fly ash require a source of Ca, which is produced during the hydration of cement as $Ca(OH)_2$. Also, slag will not undergo significant reactions without being "activated." The slag can be activated by the $Ca(OH)_2$ produced during cement hydration or by high concentration of alkali hydroxides (as illustrated by the pH 14 curves). At the low waste pH values, and without any cement in the blend, insufficient $Ca(OH)_2$ is available for the reactions, resulting in lower heat generation.

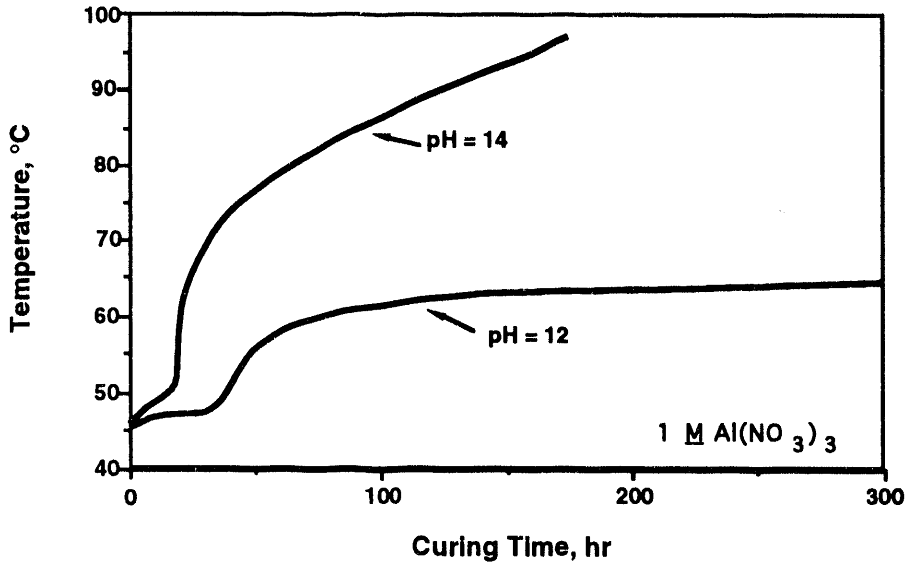

Figure 4. Measured Adiabatic Temperature Rise for Grouts Prepared with $Al(NO_3)_3$ Solutions at Different pH Values

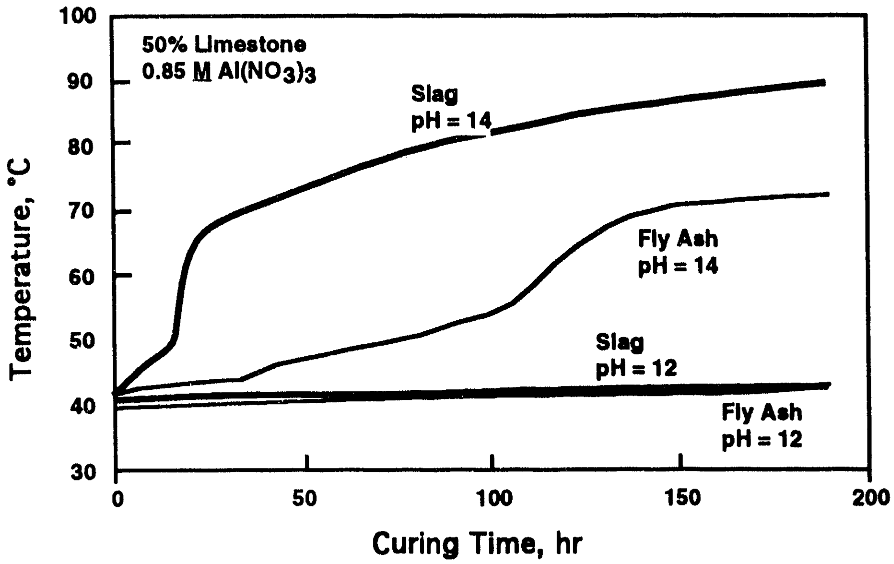

Figure 5. Measured Adiabatic Temperature Rise for Grouts Prepared with $Al(NO_3)_3$ Solutions at Different pH Values

Effect of Acid Addition

Tests were also conducted on grouts to determine the effect of nitric acid-treatment on the heat generation. Nitric acid was added to simulated waste to decrease the pH to 12.5. At this pH, the aluminum concentration in solution decreased from 7.4 g/L to 2 g/L with the precipitation of $Al(OH)_3$. Figure 7 shows the temperature rise of grouts made with untreated and treated wastes. The treated waste grout had a much lower heat of hydration, with temperatures after 250 hours up to 20°C less than the reference grout indicating that lower heat of hydration can be achieved by lowering the pH and precipitating some of the aluminum from solution.

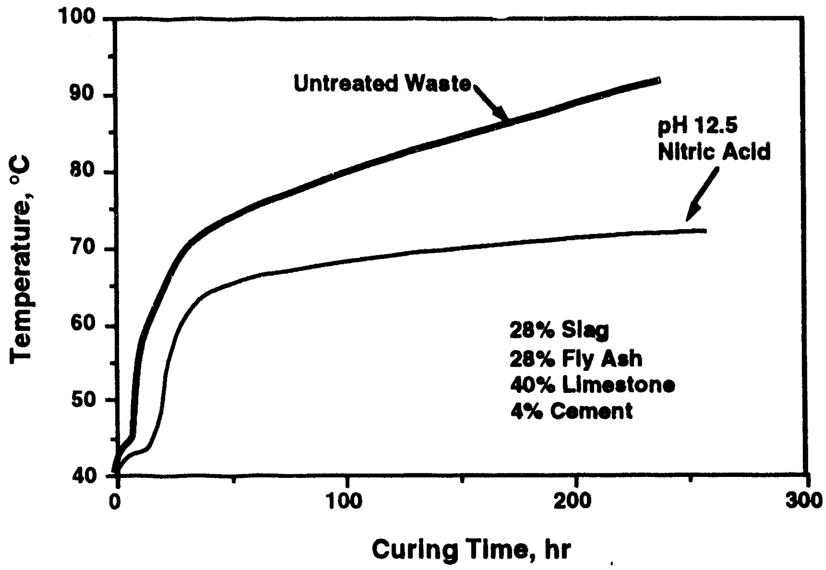

Figure 6. Measured Adiabatic Temperature Rise for Grouts Prepared with Untreated and Nitric Acid-Treated Simulated Waste

CONCLUSIONS

Based on the results of these studies, the following can be concluded:

- High concentrations of aluminum in solution contribute a significant amount of heat in grouts with dry blends containing reactive solids, including fly ash, slag, and cement.
- Decreasing the pH of simulated wastes to 12.5 lowers the aluminum concentration to ~2 g/L and decreases the temperature rise in the grouts by more than 20°C.

REFERENCES

1 Lokken, R. O., P. F. C. Martin and J. W. Shade. 1991. Characterization of Double-Shell Slurry Feed Grout Produced in a Pilot-Scale Test, PNL-7979, Pacific Northwest Laboratory, Richland, Washington.

2 Riebling, E. F. and J. G. Fadeff. 1991. Grout Formulation Standard Criteria Document, WHC-SD-WM-CSD-003, Westinghouse Hanford Company, Richland, Washington.

3 Lokken, R. O., P. F. C. Martin and J. W. Shade. 1991. Durability of Double-Shell Tank Waste Grouts, PNL-7835, Pacific Northwest Laboratory, Richland, Washington.

4 Lokken, R. O. 1991. Heat of Hydration of Double-Shell Slurry Feed Grouts, PNL-7860, Pacific Northwest Laboratory, Richland, Washington.

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