

## CALORIMETRIC EXAMINATION OF HYDROFRACTURE GROUTS<sup>a</sup>

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### ABSTRACT

A hydrofracture grout sample obtained during the SI-10 injection campaign was studied by calorimetry. The calorimetry curve of this grout was compared with laboratory-produced grout containing simulated wastes. Initiation of the cement-water reaction for the actual grout was delayed several days by the presence of a large quantity of boron in the waste. Although the hydration of cement was delayed, eventually the cement reacted with water and the grout hardened. This test indicates the potential need to analyze sludges for compounds known to retard cement hydration.

### INTRODUCTION

Low-level radioactive liquid and sludge wastes generated at Oak Ridge National Laboratory are solidified and permanently disposed of by shale fracturing. This process, termed the "hydrofracture process," immobilizes and isolates the radioactive liquids and sludges in a cementitious grout by injecting the grout into an impermeable shale formation 200 to 300 m below the earth's surface (Fig. 1) (refs. 1 and 2). Horizontal fractures are initiated within the shale formation by use of water at elevated pressures. During the actual injection, liquid or sludge wastes are blended with cement and other additives, and the resulting grouts are used to hydrofracture the shale and form a thin (<1-cm) horizontal sheet up to several hundred meters in diameter. The additives consist of fly ash and illitic clay. Fly ash is added as a partial substitute for cement to reduce the cost and to improve the retention of strontium. Illite is added for its high cesium retention. After the injection the well remains pressurized for several weeks to allow the grout to harden and to reduce bleedback (i.e., phase separation).

After many years of study, a grout composition that optimized the grout for low leachability, low bleedback (phase separation), and ease of pumping was selected.<sup>3-6</sup> The grout composition was also carefully selected for tolerance to wide variations of waste stream constituents. Characterization of hydrofracture grouts has been pursued for several years to verify that radionuclides are fixed within the grout and that they do not migrate into the surrounding shale. Additional studies of grouts produced in the laboratory have characterized the partitioning of simulated radionuclides in the cementitious phases.<sup>7</sup> The only study of grouts containing actual radionuclides was on core-drilled samples from experimental injections produced between 1959 and 1965 (ref. 8). No core-drilled samples or samples of actual grout have been examined from either the initial facility

operated from 1966 to 1980 or from the new facility operated since 1982. No studies had been performed on grouts from actual injections because it is difficult to obtain samples from process equipment located within hot cells and to handle samples containing significant levels of <sup>90</sup>Sr, <sup>137</sup>Cs, and other radionuclides. The objective of this study was to obtain a sample of the radionuclide-containing grout from the mixing tank during an actual injection and to observe by calorimetry the interaction of the radionuclide-containing sludge with the cementitious grout.

### EXPERIMENTAL PROCEDURE

A 150-mL sample of fresh grout was taken January 26, 1984, from the hydrofracture facility during the SI-10 injection campaign. The grout sample, which contained the equivalent of 0.75 kg solids per liter of sludge (~6 lb/gal), was taken during a scheduled shutdown of operations. The shutdown took place just before switching from an empty (20% remaining) to a full tank of sludge. The sample (sludge tank heel) represents a worst-case situation because the sludge thickens at the bottom of the tank and contains a larger fraction of radionuclides. The grout sample was immediately transported in a lead-lined container to a hot cell facility for examination.

Pseudoadiabatic calorimetry was performed on this sample to provide data on initiation of the cement-water reaction and to estimate the degree of reaction when the system is calibrated for heat loss (Fig. 2). The container of grout was placed in a dewar, and a glass tube containing a thermistor was inserted into the fresh grout. A thick styrofoam cork was used to close the dewar to minimize heat loss. The heat evolved during the exothermic reaction between portland cement and water was monitored as a function of time. Samples of laboratory-produced grouts containing simulated wastes were also examined by this technique for comparison.

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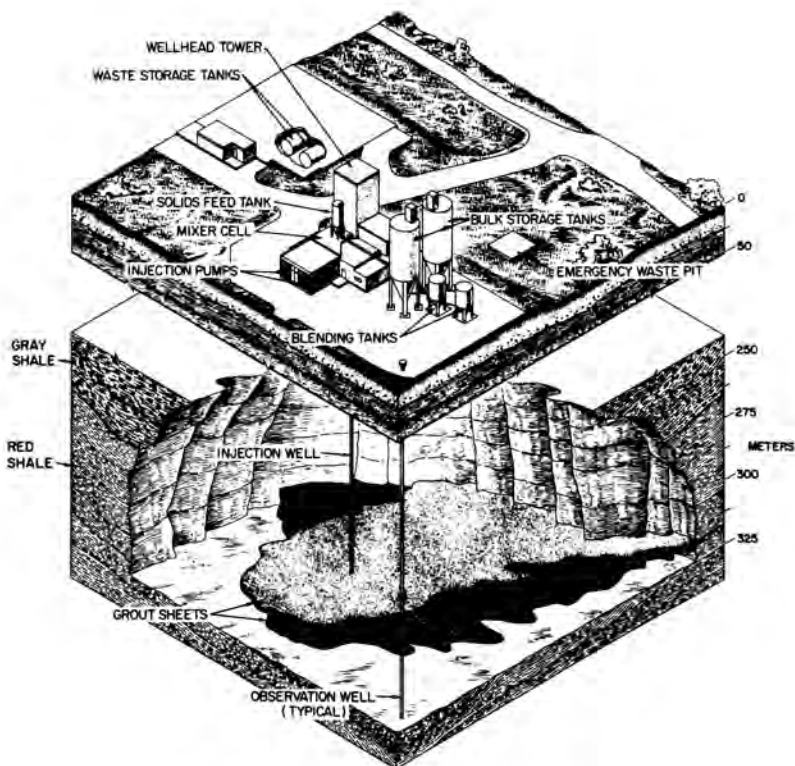


Fig. 1. Hydrofracture facility.

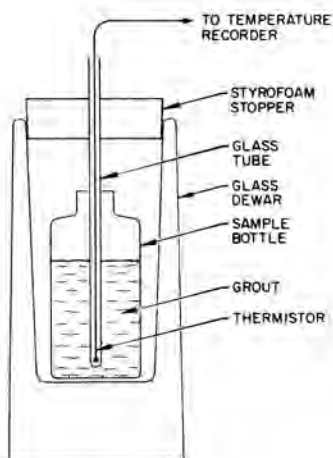


Fig. 2. Calorimeter used to measure heat evolved during cement hydration.

#### RESULTS AND DISCUSSION

Hydrofracture grouts are composed of cementitious phases produced from the hydration of portland cement. However, the phases present are complicated by the addition of fly ash and illite to control the properties of the grout. The nominal composition of the SI-10 grout sample used in this work is shown in Table I. Note the high water-to-cement ratio (typical of all grouts) required to pump the grout into the fractured shale at rates up to about 760 L/min (200 gal/min).

The radioactivity of the 150-mL sample measured 4 rem on contact with the outside of the plastic bottle containing the grout. This was somewhat higher than expected, probably because the sludge was taken from the bottom of the waste tank (the heel). Radiochemical analysis of the sludge (Table II) showed that the activity was primarily from  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ .

TABLE I  
Nominal composition of SI-10 hydrofracture grout sample

Grout mixture	Content	
	(wt %)	(vol %)
Cement	16.3	8.1
Fly ash	16.3	10.1
Illite	2.8	1.7
Retarder	0.005	
Air detrainin	0.005	
Sludge solids	16.2	10.0
Dissolved salts	2.1	
Water	46.3	70.1
Total	100.0	100.0

Control grouts containing simulated intermediate-level waste solutions were hydrated in the calorimeter at room temperature to observe the cement-water reaction. A typical calorimetry curve of a control grout is shown in Fig. 3. Because the calorimeter was not calibrated for the heat loss of the system, arbitrary

TABLE II  
Radiochemical analysis of sludge

Element	Content ( $\mu\text{Ci/mL}$ )	Element	Content ( $\mu\text{Ci/mL}$ )
$^{90}\text{Sr}$	210	$^{244}\text{Cm}$	3.1
$^{137}\text{Cs}$	21	$^{60}\text{Co}$	1.4
$^{237}\text{Pu}$	0.5	$^{95}\text{Nb}$	<0.01
$^{239-240}\text{Pu}$	0.3	$^{152}\text{Eu}$	0.3
$^{238}\text{U}$	$3 \times 10^{-3}$	$^{154}\text{Eu}$	0.4
$^{235}\text{U}$	$2 \times 10^{-3}$	$^{155}\text{Eu}$	0.1
$^{233}\text{U}$	0.06	$^{95}\text{Zr}$	0.06
$^{241}\text{Am}$	0.3		

units of temperature are plotted versus time. The rapid reaction of tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ , a major component of cement) with water begins after about 7 h (point A). Rapid cement hydration continues for an additional 12 h until the maximum temperature is reached (point B). At that point all the tricalcium silicate is surrounded by a hydrated layer.<sup>9</sup> The reaction then becomes diffusion controlled, and the rate of hydration decreases significantly. Measurable reaction in the calorimeter occurs for about 60 h.

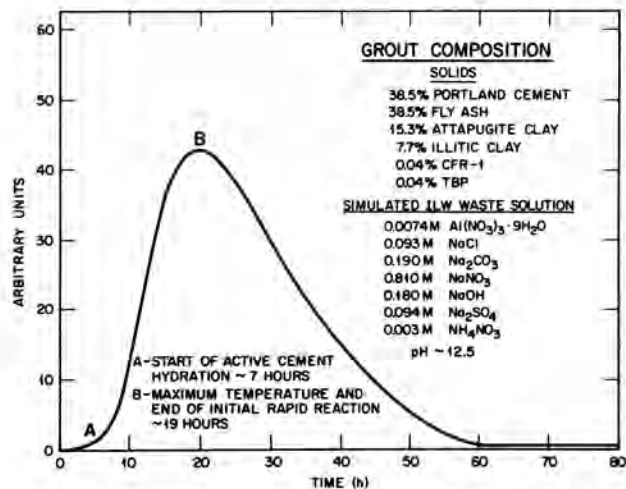


Fig. 3. Calorimetry curve of control grout [0.96 kg solids per liter (8 lb/gal)].

Calorimetry of the actual hydrofracture grout was performed at room temperature. However, the initial temperature of the grout was lower because the sludge is stored underground. The calorimetry curve of the hydrofracture grout is shown in Fig. 4. About 1.5 d was required for the grout to reach room temperature inside the calorimeter. The unanticipated slow reactivity of the grout allowed the equilibration to room temperature to be distinguished from the subsequent active cement hydration. To verify that no reaction had occurred during the first 1.5 d, the glass tube containing the thermistor was removed from the grout. Soft grout dripped from the glass tube, indicating that no appreciable reaction had occurred. The thermistor was replaced and the test continued. After about 3.5 d, the temperature began to increase more

rapidly, indicating the initiation of active cement hydration (point A). Rapid hydration continued for about 2.5 d until the maximum temperature was reached (point B). Measurable reaction continued in the calorimeter for about 12 d.

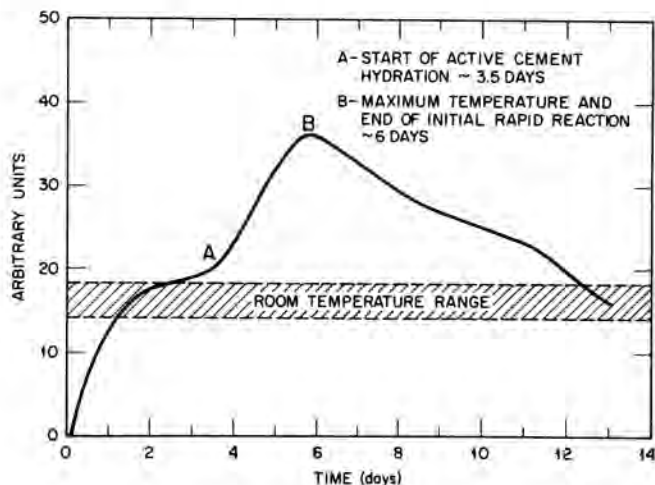


Fig. 4. Calorimetry curve of actual hydrofracture grout [0.75 kg solids per liter (~6 lb/gal)].

Calorimetry curves of the control grout and the hydrofracture grout are plotted together in Fig. 5. Obviously, the hydration of the actual grout was retarded several days when compared with the control grout. Measurable reaction in the control grout was complete before the hydration of the actual grout began. Retardation of the cement hydration could be caused by any one of several factors. Initially, we suspected that the start of cement hydration was retarded by the addition of excess set retarder (Delta Gluconoactone). A small amount of set retarder is routinely added to the grout mixture to extend the set

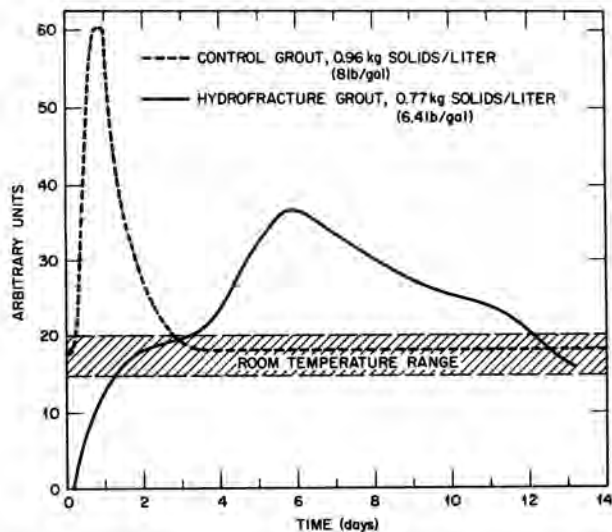


Fig. 5. Calorimetry curve comparing control grout with hydrofracture grouts.

time to ensure that the grout remains fluid during the injection process. In laboratory tests, the addition of 0.04% set retarder to a grout-waste solution mixture extends the time to the initiation of cement hydration from 5.6 to 8.0 h. About 0.3% Delta Gluconoactone would have been required to retard the initiation of active cement hydration to 3.5 d (Table III). Therefore, it is very unlikely that 7 or 8 times the normal amount of retarder was added. The most likely cause of the extended set time was the presence of some element in the sludge that delayed the reaction. The most common cationic set retarders are  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$ . However, many set retarders like fluorides; borates; and complexing organics such as hydroxycarboxylic acids, citric acid, tartaric acid, benzoic acid, and phenol are frequently found in waste streams from nuclear facilities.<sup>10</sup> An analysis of the sludge remaining in the bottom of the tank (Table IV) shows a very large unanticipated amount of boron present. Sludges are normally analyzed for only the solids content and radionuclide activity. Therefore, the presence of set retarders or set

accelerators such as  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{La}^{3+}$  would go unnoticed.

### CONCLUSIONS

Calorimetry of the hydrofracture grout sample obtained from the SI-10 injection campaign showed that the cement-water reaction was abnormally delayed several days. Although the reaction was delayed, the cement eventually hydrated and the grout hardened. Because the temperature at the injection depth is 5 to 10°C lower than that at room temperature, the hydration of the grout would be retarded even further.

Because waste streams are widely fluctuating complex mixes of elements whose concentrations may vary by one or two orders of magnitude between waste tanks, the results from this work cannot be extrapolated. However, the test does indicate a potential need for analyses to determine the presence of compounds known to retard or accelerate cement hydration. Experimentation with the waste stream compositions will likely be necessary because of the combined effects of the accelerators and retarders present in the waste.

TABLE III

Effect of retarder addition on grout hydration

(Grout contained 0.77 kg solids per liter mixed with an intermediate-level waste solution)

Retarder <sup>a</sup> (%)	Initiation of rapid cement hydration (h)	Maximum heat evolution (h)
0	5.6	15.2
0.02	6.8	16.4
0.04	8.0	18.6
0.10	12.9	25.6
0.20	33.0	46.0
0.40	288.0	336.0
<sup>b</sup>	84	144

<sup>a</sup>Delta Gluconoactone.

<sup>b</sup>Hydrofracture grout.

TABLE IV

Mass spectroscopy analysis of sludge

Element	Content (µg/mL)	Element	Content (µg/mL)
Al	5000	Na	5000
B	Major <sup>a</sup>	Ni	2000
Ca	1000	P	1000
Cl	700	Pb	100
Co	10	S	1000
Cr	100	Si	100
Cu	80	Sr	10
Fe	3000	Th	5000
K	1000	U	9000
Mg	1000	V	10
Mn	90	Zn	30

<sup>a</sup>Estimated to be about 10% or 100,000 µg/mL.

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