

PNL--7979

DE93 007179

CHARACTERIZATION OF DOUBLE-SHELL SLURRY FEED
GROUT PRODUCED IN A PILOT-SCALE TEST

R. O. Lokken
P. F. C. Martin
J. W. Shade

December 1992

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland Washington

UNCLASSIFIED

REPRODUCTION OF THIS DOCUMENT IS UNLIMITED *eb*

SUMMARY

Current plans for disposal of the low-level fraction of selected double-shell tank (DST) wastes at Hanford, Washington include grouting. Grout disposal in this context is the process of mixing low-level liquid waste with cementitious powders, and pumping the resultant slurry to near-surface, underground concrete vaults. Once the slurry is in the vaults, the hydration reactions that occur result in the formation of a highly impermeable solid product that binds and encapsulates the radioactive and hazardous constituents. Westinghouse Hanford Company (WHC) operates the Grout Treatment Facility (GTF) for the U. S. Department of Energy (DOE).

Pacific Northwest Laboratory^(a) (PNL) provides support to the Grout Disposal Program through laboratory support activities, radioactive grout leach testing, performance assessments, and pilot-scale tests. A pilot-scale test was conducted in November 1988 using a simulated Double-Shell Slurry Feed (DSSF) waste. The main objective of the pilot-scale test was to demonstrate the processability of a DSSF grout formulation that was developed using laboratory equipment and to provide information on scale-up. The dry blend used in this test included 47 wt% class F fly ash, 47 wt% blast furnace slag, and 6 wt% type I/II portland cement. The dry blend was mixed with the simulated waste at a ratio of 9 lb/gal and pumped to a 2800-gal, insulated tank at about 10.4 gpm.

Samples of simulated DSSF waste, dry blend, grout slurry, and cured grout were obtained during and after the pilot-scale test for testing and product characterization. Major conclusions of these activities are:

- Grout slurry samples collected at the discharge from the mixer during the pilot-scale test were frothy and considerably thicker than slurry samples prepared using laboratory samples.
- The grout slurry thinned during pumping, resulting in critical flow rates comparable to those of laboratory-prepared grouts.

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U. S. Department of Energy under contract DE-AC06-76RLO 1830.

- Curing simulated DSSF grouts in adiabatic calorimeters at atmospheric pressure resulted in peak temperatures of about 105°C. The calculated adiabatic temperature rise was 81°C.
- The moisture content (evaporable water) of pilot-scale grout cores averaged 33 wt%, approximately the same as grout samples cured under saturated conditions in the laboratory.
- The unconfined compressive strength of the pilot-scale grout cores averaged 1040 psi, compared to 1430 psi for lab-cured grout samples.
- The simulated DSSF grout cores were found not to be corrosive because the pH ranged from 11.3 to 11.7, compared to critical value of ≤ 12.5 .
- The simulated DSSF grout cores were not EP toxic.
- Grouts cured at higher temperatures were less resistant to leaching than those cured at lower temperatures. The total amount of nitrate leached from a sample cured at 71°C was 56% less than from a sample cured at 101°C.
- The thermal conductivity of the DSSF grout averaged 0.75 W/mK.

CONTENTS

SUMMARY..... iii

1.0 INTRODUCTION.....1

2.0 PILOT-SCALE TEST.....3

 2.1 GROUT FEED MATERIALS.....3

 2.2 PROCESS EQUIPMENT.....5

 2.3 OPERATION.....7

 2.4 SAMPLING.....8

 2.5 TEMPERATURE RISE.....8

3.0 EXPERIMENTAL PROCEDURES.....11

 3.1 GROUT SLURRY.....11

 3.1.1 Lab Grout Preparation and Curing.....11

 3.1.2 Adiabatic Calorimetry.....12

 3.1.3 Rheological Property Measurements.....13

 3.1.4 Density Measurements.....14

 3.2 CURED GROUT TESTS.....14

 3.2.1 Physical Property Testing.....14

 3.2.2 Corrosivity.....15

 3.2.3 Extraction Procedure Toxicity.....15

 3.2.4 American Nuclear Society (ANS 16.1) Leach Test....16

 3.2.5 Thermal Conductivity.....17

 3.2.6 X-Ray Diffraction.....19

 3.2.7 Thermal Analysis.....19

 3.2.8 Scanning Electron Microscopy.....19

4.0 RESULTS AND DISCUSSION.....21

 4.1 ADIABATIC CALORIMETRY.....21

 4.2 RHEOLOGICAL CHARACTERIZATION.....24

4.3	CORROSIVITY.....	25
4.4	EP TOXICITY.....	25
4.5	ANS 16.1 LEACHING.....	25
4.6	THERMAL CONDUCTIVITY.....	28
4.7	PHYSICAL PROPERTIES.....	31
4.8	X-RAY DIFFRACTION.....	33
4.9	THERMAL ANALYSIS.....	33
4.10	MICROSTRUCTURE.....	34
5.0	CONCLUSIONS.....	37
6.0	REFERENCES.....	39

FIGURES

2.1	Schematic of the Pilot-Scale Grout System.....	6
2.2	Temperature Rise in DSSF Grout Receiver Vessel.....	9
2.3	Maximum Temperature Distribution for the Three DSSF Grout Cores.....	10
3.1	Schematic of an Adiabatic Calorimeter.....	13
3.2	Schematic of a Thermal Conductivity Probe.....	18
4.1	Adiabatic Temperature Rise for Lab-Produced DSSF Grout Prepared with Waste Preheated to 35°C.....	22
4.2	Adiabatic Temperature Rise for Lab-Produced DSSF Grout Prepared with Waste Preheated to 45°C.....	22
4.3	Adiabatic Temperature Rise and Rate of Temperature Rise for Lab-Produced DSSF Grout.....	24
4.4	Density of Pilot-Scale DSSF Grout Slurries.....	26
4.5	Critical Flow Rates of Pilot-Scale DSSF Grout Slurries.....	26
4.6	Cumulative Fraction Nitrate Leached From Pilot-Scale Grout (Core A).....	29
4.7	Cumulative Fraction Nitrate Leached From Pilot-Scale Grout (Core B).....	29
4.8	Cumulative Fraction Nitrate Leached From Pilot-Scale Grout (Core C).....	30
4.9	Scanning Electron Micrographs of DSSF Grout Cores Taken Along the Centerline of the Receiver Vessel	35

TABLES

2.1	Composition of Simulated DSSF Waste used in the Pilot-Scale Test	4
2.2	Composition of Dry Blend Used in the Pilot-Scale Grout Test....	4
2.3	Oxide Composition of Dry Materials used in the Pilot-Scale Grout Test. Analyses were Conducted Using ICP.....	5
3.1	Extraction Procedure Toxicity Limits.....	16
3.2	Leach Intervals Used for the ANS 16.1 Leach Test.....	17
4.1	Extraction Toxicity Results for Pilot-Scale Grout Cores.....	27
4.2	Average Leach Indices (Li) for Nitrate, Sodium, and TOC Through 91-days for Pilot-Scale DSSF Grout Cores.....	30
4.3	In Situ Thermal Conductivity and Temperatures of Pilot-Scale Grout.....	31
4.4	Summary of Compressive Strength, Density, and Evaporable Water Content of DSSF Pilot-Scale Grout Samples.....	32

1.0 INTRODUCTION

Current plans for disposal of the low-level fraction of selected double-shell tank (DST) wastes at Hanford, Washington include grouting. Grout disposal in this context is the process of mixing low-level liquid waste with cementitious powders, and pumping the resultant slurry to near-surface, underground concrete vaults. Once the slurry is in the vaults, the hydration reactions that occur result in the formation of a highly impermeable solid product that binds and encapsulates the radioactive and hazardous constituents.

Cementitious materials have been or will be used at many places for the solidification and disposal of low-level radioactive wastes. Oak Ridge National Laboratory (ORNL) began disposing of low-level liquid wastes in 1966 using a process known as hydraulic fracturing (de Laguna 1966, Weeren 1976). This process involved mixing liquid wastes with a blend of cement, fly ash, pottery clay, and attapulgite clay, and pumping the slurry at 3000 to 5000 psi into shale formations underlying the ORNL site. The high pressures caused the shale to fracture and the grout filled the resultant fissures. The Savannah River Plant (SRP) is planning to dispose of 400 million liters of a low-level salt solution using the "saltstone" process (Langton 1988, Wilhite et al. 1988). Saltstone is the name given to the product prepared by mixing the salt solution with a blend of fly ash, blast furnace slag, and cement. This process is very similar to the grouting process at Hanford (Guymon et al. 1988). Both processes use the same type of dry solids, and the major constituents in the waste solutions are the same (i.e., NaNO_3 , NaNO_2 , NaAl(OH)_4 and NaOH).

Westinghouse Hanford Company (WHC) operates the Grout Treatment Facility (GTF) for the U. S. Department of Energy (DOE). The GTF includes the Dry Materials Facility (DMF), the Transportable Grout Equipment (TGE), and the grout disposal vaults. The DMF receives, stores, batches, and blends the individual dry materials for use in the grouting operation. The blended solids are transported to the site of the TGE where they are mixed with the low-level waste in a continuous process at rates up to 70 gallons of grout per minute. The grout slurry is pumped to underground concrete vaults where it hardens and immobilizes the hazardous and radioactive constituents through chemical reactions and/or microencapsulation.

Pacific Northwest Laboratory^(a) (PNL) provides support to the Grout Disposal Program at Hanford through laboratory support activities (Lokken et al. 1987), radioactive grout leach testing (Serne et al. 1987), performance assessments (Sewart et al. 1987), and pilot-scale tests (Fow et al. 1987). A major pilot-scale test was performed in 1986 with a simulated phosphate/sulfate waste (PSW) to assess the effectiveness of the grouting operations and to characterize the grout produced with pilot-scale equipment and cured in a large mass. The results of that test are presented in Fow et al. (1987), Lokken et al. (1988), and Lokken and Mitchell (1988). A second pilot-scale test was conducted in November 1988 using a simulated double-shell slurry feed (DSSF) waste. The main objective of that pilot-scale test was to demonstrate the processability of a DSSF grout formulation that was developed using laboratory equipment and to provide information on scale-up. The dry blend used in the test included 47 wt% class F fly ash, 47 wt% blast furnace slag, and 6 wt% type I/II portland cement. The dry blend was mixed with the simulated waste at a ratio of 9.0 lb/gal and pumped to a 2800-gal, insulated tank at about 10.4 gpm.

Samples of simulated DSSF waste, dry blend, grout slurry, and cured grout were obtained during and after the pilot-scale test for testing and product characterization. This report presents the results from these activities.

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U. S. Department of Energy under contract **DE-AC06-76RLO 1830**.

2.0 PILOT-SCALE TEST

The main objective of the pilot-scale test was to demonstrate the processability of a DSSF grout formulation that was developed using laboratory equipment and to provide information on scale-up. A second objective was to provide information on the behavior of grout following production, including: 1) an estimate of the heat of hydration during curing, 2) measurements of thermal conductivity, 3) measurements of volume changes during curing, 4) determination of possible effects from the 34-ft. fall into the grout receiver vessel during production, 5) observations of the amount of separated liquid occurring after placement, 6) determination of the restart pressures that can be expected if the pump operation is interrupted, and 7) provision of samples for characterizing the grout waste form. A description of the pilot-scale test operations and operational results are briefly discussed in this section.

2.1 GROUT FEED MATERIALS

The materials used in the pilot-scale test included simulated DSSF waste based on the composition given in Claghorn (1987) and a blend of dry materials that included blast furnace slag, class F fly ash, and type I/II portland cement.

The simulated DSSF waste was prepared in two batches -- a 200-gal batch and a 2500-gal batch. The smaller batch was prepared to verify the adequacy of the waste makeup procedure and to identify and correct any problems with the procedure before preparing the larger batch. After both batches were complete, the two were combined and stored in a heated, insulated tank that was maintained near 45°C. The analyzed and target composition of the simulated DSSF waste is listed in Table 2.1.

The dry blend was prepared by weighing individual materials in the proportions: 47 wt% blast furnace slag, 47 wt% class F fly ash, and 6 wt% type I/II portland cement (Table 2.2). The materials were placed into a concrete mixer and mixed for 900 revolutions. Two batches were prepared in this manner, with each batch emptied into steel hoppers for storage. The oxide composition of the dry materials is listed in Table 2.3.

TABLE 2.1. Composition (g/L) of Simulated DSSF Waste Used in the Pilot-Scale Test

<u>Species</u>	<u>Analyzed</u>	<u>Calculated</u>
Al	22.4	20.3
B	0.136	0.105
Ba	0.6	0.623
Ca	0.573	0.2
Cr	1.26	1.15
Fe	1.49	1.41
K	11.5	9.72
Mg	0.32	
Mn	3.01	2.75
Mo	0.068	0.049
Na	122	121.8
P	2.02	1.84
Si	0.502	0.56
Zn	2.93	1.63
Cl ⁻	5.36	3.86
NO ₂ ⁻	27.2	23.0
PO ₄ ⁻³	5.4	5.65
NO ₃ ⁻	186	154.4
SO ₄ ⁻²	5.1	5.05
TOC	1.556	1.28

TABLE 2.2. Composition of Dry Blend Used in the Pilot-Scale Test

<u>Component</u>	<u>Amount, wt%</u>
Blast Furnace Slag ^(a)	47
Class F Fly Ash ^(b)	47
Type I/II Portland Cement ^(a)	6

(a) From Ash Grove Cement West, Inc., Seattle, Washington

(b) From Centralia, Washington Power Plant

TABLE 2.3. Oxide Composition of Dry Materials Used in the Pilot-Scale Test. Analyses were Conducted Using ICP.

<u>Oxide</u>	<u>Slag</u>	<u>Fly Ash</u>	<u>Cement</u>
Al ₂ O ₃	13.4	23.5	3.3
B ₂ O ₃		0.5	0.105
BaO	0.117	0.169	0.084
CaO	43.4	8.05	65.4
Fe ₂ O ₃	0.377	5.73	4.08
K ₂ O	0.89	0.98	0.65
MgO	5.42	1.57	1.38
MnO ₂	1.03	0.088	0.072
Na ₂ O	0.401	3.02	0.32
P ₂ O ₅		0.94	
SiO ₂	33.3	47.8	22.2
SrO	0.078	0.31	0.035
TiO ₂	1.08	4.43	0.22
<u>Total</u>	<u>99.693</u>	<u>97.087</u>	<u>97.846</u>

2.2 PROCESS EQUIPMENT

A schematic of the pilot-scale process is shown in Figure 2.1. The process equipment consisted of four main units: a dry blend transfer and feed system, a liquid waste storage tank and transfer system, a grout mixer, and a grout pump. Piping and an insulated receiver vessel completed the system.

Dry blend was transferred by vacuum to a storage bin that was located directly above the active bin. During production, the dry blend was gravimetrically fed using an auger to an 18-in. vibrating screen and then into the grout mixer. The screen removed particles greater than 0.2 in. from the dry blend.

The simulated waste solution was pumped from the storage tank to the grout mixer using a centrifugal pump. The flow rate of the waste was controlled with a gate valve.

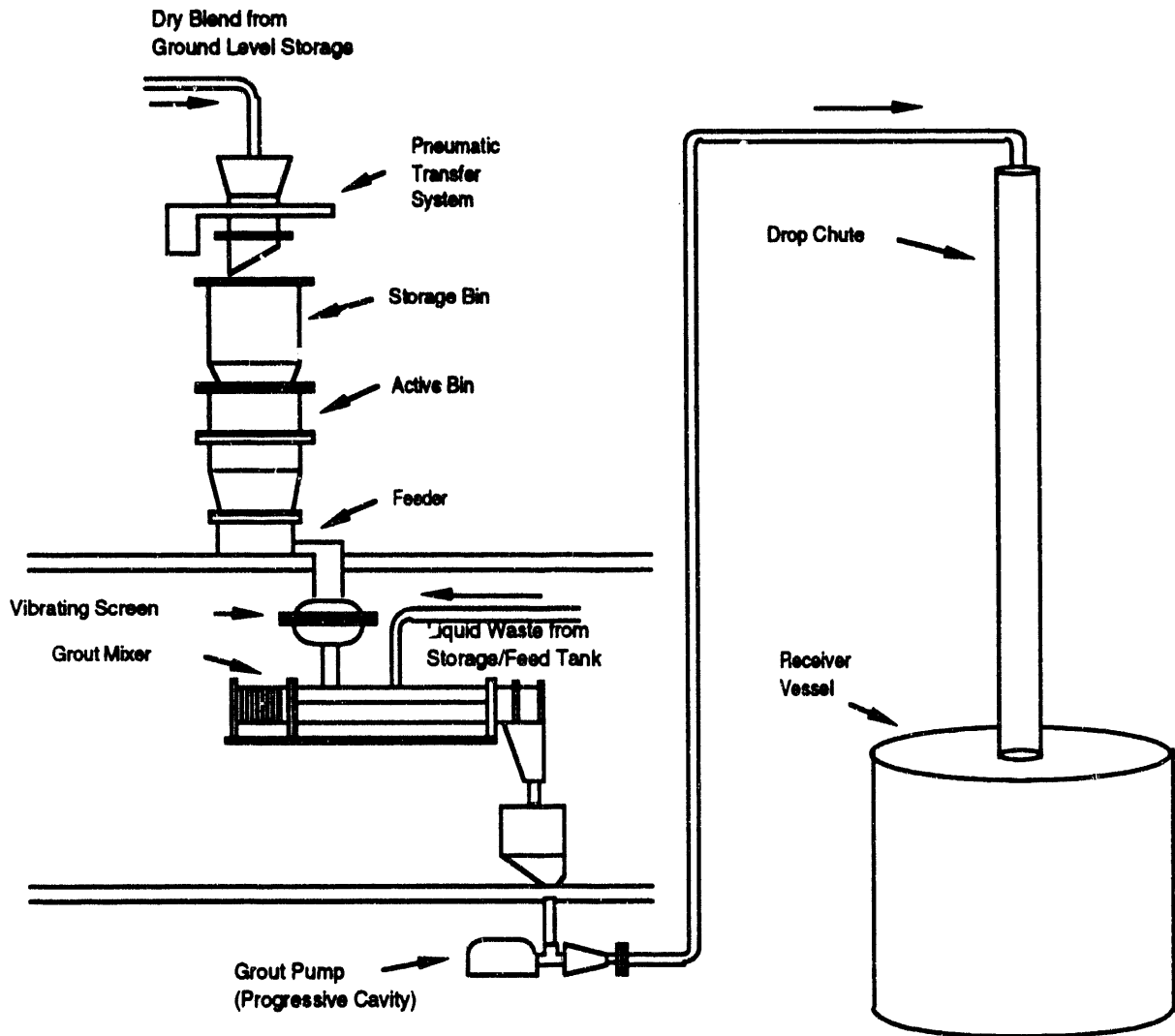


FIGURE 2.1. Schematic of the Pilot-Scale Grout System

The mixer was a Teledyne Readco 5.25-in. twin-shaft continuous processor. The dry blend and waste entered the top of the mixer, and grout slurry discharged at the opposite end into a surge tank right above the pump inlet. Mixing was conducted at 250 rpm.

The grout transfer system consisted of a grout pump and steel piping. The grout pump consisted of a two-stage progressive cavity pump with an ethylene-propylene-diene-monomer (EPDM) stator. The pump speed was manually controlled to maintain a constant grout level in the surge tank. Grout was pumped through 3/4-in. Schedule 40 carbon steel pipe to the vessel. The total length of the piping was approximately 170 feet.

The grout receiver vessel consisted of an 8-ft-dia, 7.5-ft-high corrugated steel culvert with a welded steel bottom. A 2-ft.-dia., 27.5-ft.-long polypropylene pipe (drop chute) was mounted vertically over the center of the vessel lid. This pipe allowed the incoming grout to fall 34 ft before hitting the bottom of the vessel, which is equivalent to the maximum distance the grout would fall in the full-scale vaults. The main body of the vessel was insulated with a 6-in. layer of fiberglass. Following the test, the drop chute was removed and the opening was sealed and insulated. A tarp was placed over the entire vessel to protect it from the elements and to further reduce heat loss.

2.3 OPERATION

The pilot-scale DSSF grout test was conducted over a 5.5-hr period, with an actual grout production time of about 4.5 hours. During the course of the test, only one major operational problem was encountered. Approximately 80 minutes into the test, the inlet supplying the DSSF delivery pumps became blocked, forcing a temporary shutdown of the process. The DSSF delivery lines were backflushed to remove the blockage, and the pumps tested to ensure proper flow. The process was restarted after about 50 minutes. During restart, an incorrect valve position resulted in the production of grout with process water rather than the DSSF. It was estimated that during this 6-min period, about 40 gal of water grout was pumped to the receiver vessel. After correcting the valve position, the process ran without upset.

The mix ratio during the run deviated from the average of 9.08 lb/gal by only ± 0.3 lb/gal. The target mix ratio was 9.0 lb/gal with an allowable deviation of ± 0.5 lb/gal^(a). The average instantaneous grout flow rate throughout the test was 10.44 gpm.

(a) Riddelle, J. G. 1987. Formulation Criterion for the Hanford Grout Disposal Program. Internal Report SD-WM-SS-004, Westinghouse Hanford Company, Richland, Washington.

2.4 SAMPLING

During the course of the pilot-scale test, several samples of simulated DSSF waste, dry blend, and grout slurry were taken. The dry blend and waste were sampled hourly; the slurry was sampled twice an hour. Dry blend samples were collected from the active bin of the solids feed system. Simulated DSSF was sampled near the mixer, just upstream from the flow meter and control valve.

Grout slurry samples were collected every half hour of operation. Samples were collected from the surge tank just above the grout pump and from the discharge to the vessel at the bottom of the drop chute. The slurry samples from the surge tank were obtained by holding a plastic bucket in the grout slurry stream exiting the mixer. The bucket of grout slurry was immediately delivered for rheological testing and sample casting. The samples from the discharge point were collected by holding a bucket at the bottom of the drop chute and allowing the grout slurry to enter the bucket. These samples were also delivered for rheological testing and sample casting.

After about three months of curing, the grout was core drilled at three locations within the vessel. The cores were designated "A", "B", and "C". Core A was drilled 5 inches from the wall of the vessel, core B was 20 inches from the wall, and core C was drilled along the centerline. Samples from three sections (top, middle, and bottom) of each core were used for various tests as described in the next section.

2.5 TEMPERATURE RISE

The grout receiver vessel was instrumented with 40 thermocouples to monitor the temperatures within the grout as a function of curing time and position within the vessel. The temperatures were recorded hourly for the first two weeks after production, and every eight hours for the next 44 days. The measured temperature rise near the center of the vessel and the estimated adiabatic rise are shown in Figure 2.2. An adiabatic temperature rise of 83°C was estimated by heat loss calculations. This value is higher than the temperature rises measured in the laboratory because of the sensitivity and accuracy of the laboratory calorimeters at very slow heat release rates and

some of the heat generated by the grout was used to heat the container. Section 4.1 provides a discussion on laboratory calorimetry tests. The estimated maximum temperatures for each of the three cores as a function of position in the vessel are shown in Figure 2.3.

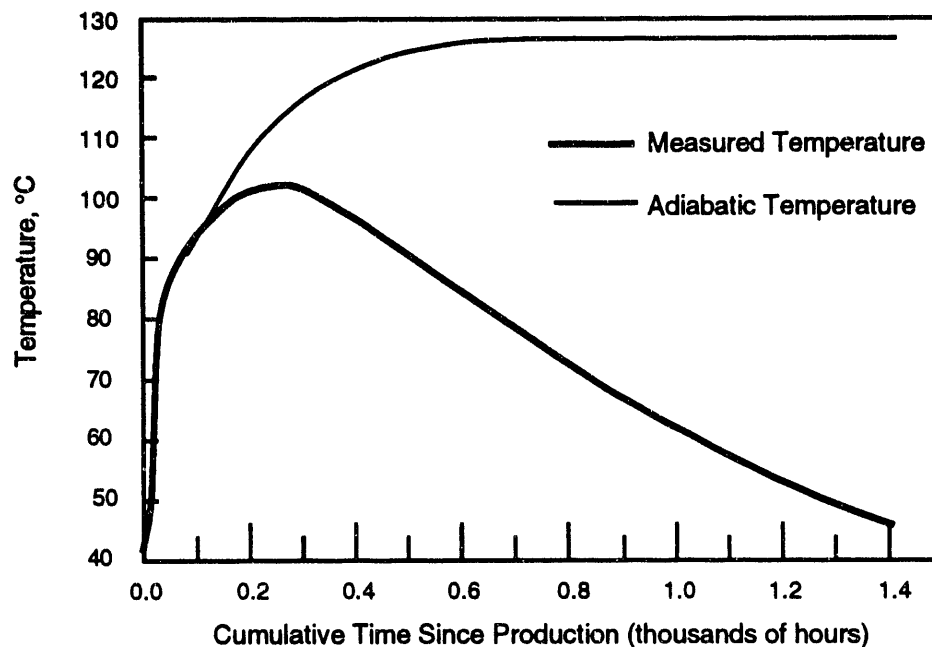


FIGURE 2.2. Temperature Rise in DSSF Grout Receiver Vessel

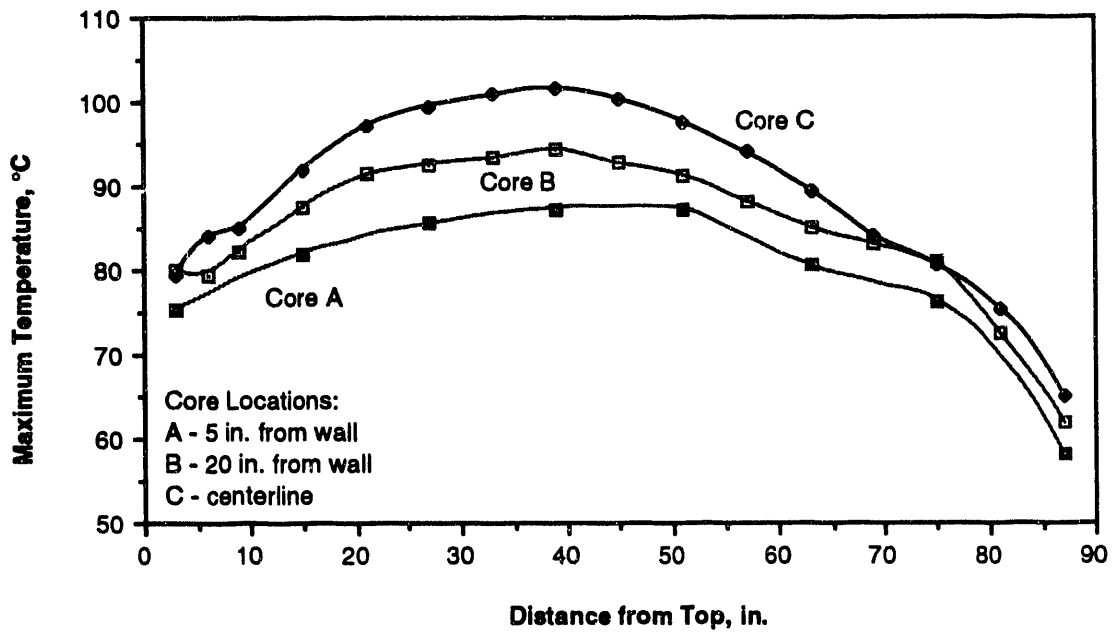


FIGURE 2.3. Maximum Temperature Distribution for the Three DSSF Grout Cores

3.0 EXPERIMENTAL PROCEDURES

This chapter describes the experimental procedures used to test the grout slurry and cured grout samples.

3.1 GROUT SLURRY

Grout slurry samples were collected at two locations during the pilot-scale test: at the surge tank leading to the pump and at the discharge nozzle to the receiving vessel. In addition, grout samples were also produced in the laboratory with waste solution and dry blend samples collected during the test. The properties of grout slurry measured included the rheological properties and density.

3.1.1 Laboratory Grout Preparation and Curing

Laboratory grout samples were prepared using dry blend and simulated DSSF waste collected during the run to compare properties with those prepared using the pilot-scale equipment. Laboratory grouts were prepared at a mix ratio of 9 lb/gal (1.08 kg/L) using a Hobart^(a) N-50 mixer equipped with a wire whip. The simulated waste was preheated to 45°C and added to the mixer bowl. With the mixer on slow speed, the dry blend was added over a 15-sec period. Mixing continued on slow speed for an additional 15 seconds, after which time the speed was increased and the grout slurry mixed for 30 seconds on medium speed. Following mixing, the grout slurry was poured into cylindrical molds that were capped and weighed. Four batches of lab grouts were prepared, with seven samples cast from each batch.

Three samples from each batch were placed into plastic containers containing water to maintain 100% relative humidity. The others were placed into containers without any additional water to approximate the curing conditions of the samples collected during the pilot-scale test. The lids were replaced and the containers placed in a 60°C oven the following day. The temperature of the oven was subsequently increased to 90°C over a period of six days. Twenty-eight days following preparation, the oven was turned off and the sam-

(a) Hobart Corporation, Troy, Ohio

ples allowed to cool to room temperature. The samples remained in their containers at room temperature until the time that they were tested.

3.1.2 Adiabatic Calorimetry

Adiabatic calorimetry was conducted on DSSF grout using computer-controlled calorimeters to monitor heat generation during curing. A schematic of an adiabatic calorimeter is shown in Figure 3.1. Freshly prepared grout slurry was poured into a 1/2-L stainless steel dewar. The dewar was sealed with a stopper, and a thermocouple or thermistor was inserted through the stopper to about the midpoint of the grout. The dewar was then placed into an oil bath with oil completely surrounding the dewar.

Two different calorimeters were used in these studies. The principle of operation of the two calorimeters is the same even though the physical arrangement and method of control was different. The first calorimeter, which is depicted in the schematic shown in Figure 3.1, consisted of an oil bath, a recirculating programmable temperature controller, and a thermistor for temperature display and control. The thermometer displays the current temperature, and outputs an analog voltage equivalent to 10 mV/°C. The output voltage is connected to the computer data acquisition system and to the temperature controller, which accepts an analog voltage input of 10 mV/°C. Therefore, the temperature of the bath is continually adjusted to equal the temperature of the grout.

The second calorimeter consisted of a recirculating programmable temperature bath connected to a stainless steel tempering beaker. The temperature measuring instrument for this calorimeter was a type T thermocouple. Because of impedance mismatches between the thermometer output and the controller input, the output voltage was not suitable for direct control of the temperature controller. The temperature of the grout was read by the computer, the value converted into the proper voltage, and a voltage of 10 mV/°C was applied to the controller through a digital-to-analog conversion card.

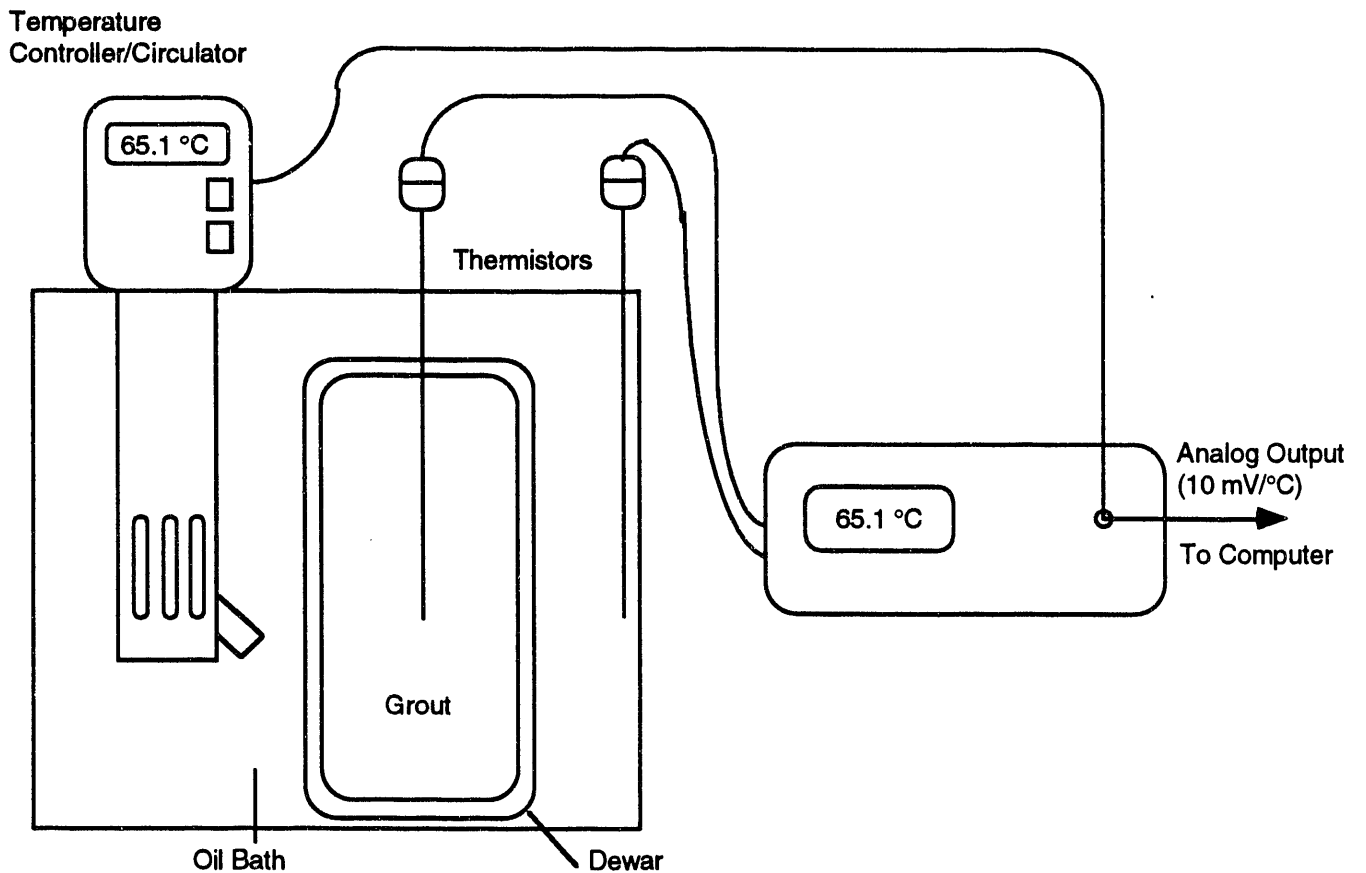


FIGURE 3.1. Schematic of an Adiabatic Calorimeter Using Thermistors for Temperature Measurement and Control.

3.1.3 Rheological Property Measurements

The rheological properties of grout samples were determined with a Fann^(a) Model 35A viscometer. The Fann viscometer employs six preset speeds (3, 6, 100, 200, 300, and 600 rpm). Grout slurry is contained in the annular space between two cylinders. The outer cylinder (or rotor) is rotated by means of a motor at constant velocity (shear rate). The rotation of the rotor in the grout produces a torque on the inner cylinder (bob). A torsion spring attached to the bob restrains movement. The dial attached to the spring indicates the torque imparted through the grout as the rotor is rotated. The dial is calibrated to read shear stress directly in units of $lb_f/100\text{ ft}^2$.

(a) Fann Instrument Corporation, Houston, Texas

Rheological measurements on grout are conducted using the highest four speeds of the instrument, starting at 600 rpm and working down to 100 rpm.

The shear rate/shear stress values are used to calculate flow properties according to the power law model described by Smith (1976). In this analysis, turbulent flow is assumed to begin at a Reynolds number of 2100. Grout is required to be pumped in turbulent flow to minimize particle settling that could result in flow restrictions. The parameter used in this report to describe the flow properties of grout slurries is the critical flow rate (CFR). The CFR is defined as the minimum flow rate that must be maintained through a given pipe diameter such that the calculated Reynolds number is 2100.

3.1.4 Density Measurements

The density of freshly prepared grout slurry was determined by pouring approximately 240 ml of grout into a 250-ml graduated cylinder and measuring the weight and the actual volume poured.

3.2 CURED GROUT TESTS

Properties of cured grout samples were determined using various test methods. Tests were conducted on grout samples collected during the pilot-scale test, samples prepared and cured in the laboratory, and core samples from the vessel.

3.2.1 Physical Property Testing

Grout slurry collected during the run and slurry produced in the laboratory was poured into 1.3-in.-diameter cylindrical molds, capped, and placed in an oven. The oven temperature was periodically adjusted to approximate the maximum temperature of the grout in the vessel. After six days, the temperature was set at 90°C and remained there until 28 days after the test. At the end of 28 days, the ovens were turned off and the samples allowed to cool to room temperature.

Immediately prior to testing, the grout samples were removed from the molds and the ends of the samples were trimmed to provide flat, parallel

faces. Samples were used for bulk density measurements, compressive strength testing, and moisture content determinations.

Compressive strength testing was conducted with an Instron^(a) test machine at a constant cross-head speed of 0.05 in./min. The load-to-failure was determined from the maximum point of a load-deformation curve. Compressive strength values were calculated by dividing the maximum load by the cross-sectional surface area of the cylinders. The length-to-diameter ratio of these samples was one.

The moisture content, or evaporable water content, of the grouts was determined by drying the samples to constant weight at 105°C.

3.2.2 Corrosivity

The corrosivity of grout samples from the pilot-scale test was determined using the Washington Department of Ecology (WDOE) Method 83-13 (WDOE 1984). Approximately 50 grams of grout were combined with an equal weight of distilled water and agitated on a shaker table for 30 minutes. The pH of the solution was then measured. According to this procedure, a solid is considered corrosive if the solution has a pH of less than or equal to 2, or greater than or equal to 12.5.

3.2.3 Extraction Procedure Toxicity

The extraction procedure (EP) toxicity test is a laboratory test designed to simulate the leaching conditions a waste may encounter in a sanitary landfill (U. S. EPA 1982). The EP toxicity tests were conducted on nine grout core samples taken from the vessel. In the test, samples of grout cores were extracted with a mixture of deionized water and 0.5 M acetic acid/sodium acetate buffer maintained at a pH of 5. The samples and acid solution were added to glass jars and the jars placed in a rotary extractor that rotated at 30 rpm. At periodic intervals, the pH of the solution was measured and, if necessary, adjusted to 5 ± 0.2 . The adjustments continued for 24 hours, or until the maximum amount of acid (4 ml/g of waste) had been added. Following

(a) Instron Corporation, Canton, Massachusetts

the extraction period, the solutions were allowed to settle for a few hours, and aliquots of the solutions were filtered through 0.45- μm filters. The filtrates were submitted for analyses of the eight metals listed in Table 3.1.

TABLE 3.1. Extraction Procedure Toxicity Limits

<u>Metal</u>	<u>Maximum Concentration, mg/l</u>
As	5
Ba	100
Cd	1
Cr	5
Pb	5
Hg	0.2
Se	1
Ag	5

3.2.4 American Nuclear Society (ANS 16.1) Leach Test

The ANS 16.1 leach test (ANS 1986) was applied to nine grout core samples to determine whether position within the vessel had any effect on the leachability. The test is an intermittent leachate exchange test designed to simulate a dynamic leaching situation. The leachate exchange intervals used in these tests are shown in Table 3.2.

The samples used in these tests were right circular cylinders, with approximate dimensions of 4.5-cm dia. by 3.5-cm high. The samples, with a surface area of approximately 80 cm^2 , were suspended by nylon monofilament in approximately 800 ml of deionized water within polyethylene containers. After the elapsed time periods, the samples were removed from the leachates and placed into containers containing fresh leachant. The pH of the leachates was measured immediately after removing the samples. Aliquots of leachate were submitted for cation analysis by inductively coupled argon plasma (ICP) spectroscopy, for anion analysis by ion chromatography (IC), and for total organic carbon (TOC) analysis.

TABLE 3.2. Leach Intervals Used for the ANS 16.1 Leach Test

Leach Interval No.	Time Between Intervals	Cumulative Time
1	7 hr	7 hr
2	17 hr	1 d
3	24 hr	2 d
4	48 hr	4 d
5	72 hr	7 d
6	7 d	14 d
7	14 d	28 d
8	28 d	56 d
9	35 d	91 d

3.2.5 Thermal Conductivity

In situ thermal conductivity measurements were taken using four probes that were inserted into the vessel prior to grout production. A schematic of a typical probe is shown in Figure 3.2. The probes were constructed using 12-in.-long, 0.375-in.-dia. cartridge heaters. A 0.063-in. diameter type K thermocouple was attached near the midpoint of the heater sheath. The assemblies were then connected to pieces of pipe with a compression fitting.

This method of measuring thermal conductivity is a variant of the line-heat-source method (Tye 1969). With the probe inserted in the grout, a constant current is applied to the probe, and the temperature rise is recorded with time. The thermal conductivity of the material is related to temperature rise, time, and heat input by the following relationship (Tye 1969):

$$\Delta T = \frac{Q}{4 \pi \lambda} \ln \left[\frac{(t_2 - t_c)}{(t_1 - t_c)} \right] \quad (1)$$

where, ΔT = temperature change, K
 Q = heat flow, W/m
 λ = thermal conductivity, W/mK
 t_2, t_1 = time, sec
 t_c = time-factor constant

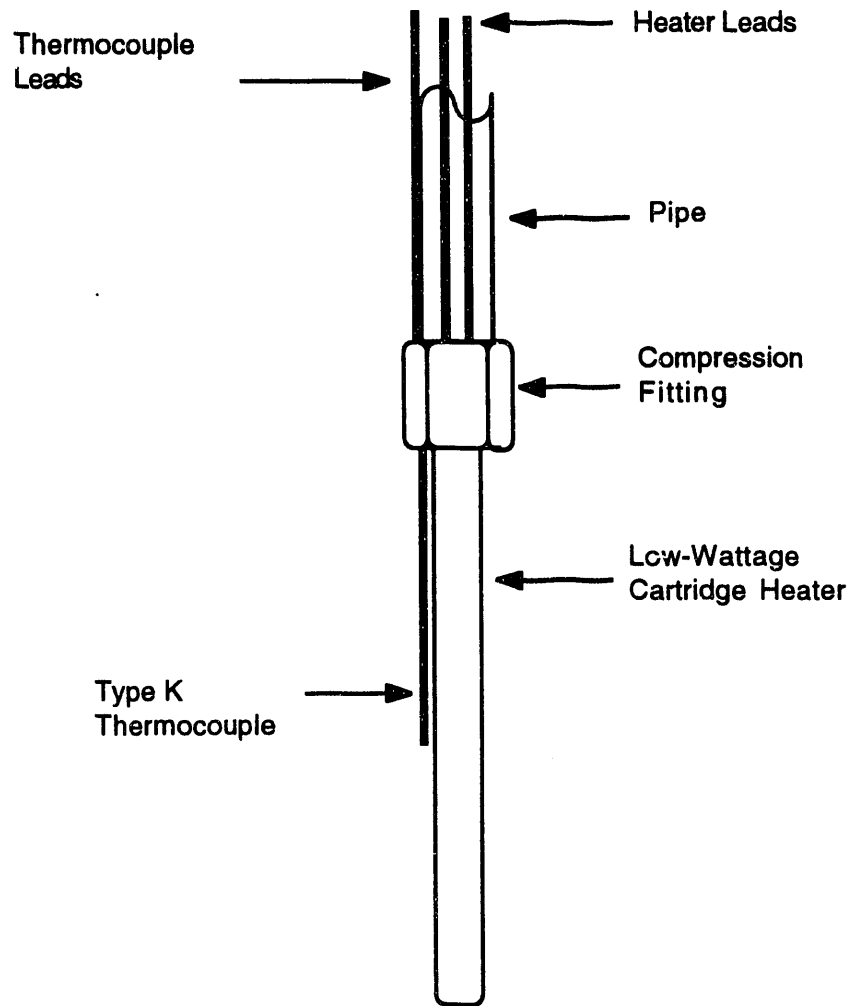


FIGURE 3.2. Schematic of a Thermal Conductivity Probe

The time-factor constant is an empirically determined value that depends on contact resistance between the grout and the probe, thermocouple position, and the thermal properties of the probe materials.

The heat flow is determined by applying the following equation:

$$Q = V^2 / (R * L) \quad (2)$$

where, Q = heat flux, W/m
 V = volts
 R = heater resistance, ohms
 L = probe length, m

A plot of T vs. $\ln(t-t_c)$ gives a straight line with a slope of $Q/(4\pi\lambda)$. The data were analyzed by performing a linear regression on the temperature rise, $\ln(t-t_c)$ data pairs. The thermal conductivity was then calculated using the following equation:

$$\lambda = \frac{Q}{4 \pi \text{ Slope}} \quad (3)$$

3.2.6 X-Ray Diffraction

X-ray diffraction was used to characterize and to compare relative crystallinity of the grout core samples. Dried grout samples were analyzed with a Philips^(a) APD 3600 automated powder diffractometer. Powdered samples were packed in standard X-ray powder mounts with reasonable care taken to obtain uniform density. $\text{CuK}\alpha$ radiation, obtained with a graphite monochromator, was used at 40 kV and 25 mA.

3.2.7 Thermal Analysis

Simultaneous differential thermal analyses (DTA) and thermal gravimetric analyses (TGA) of grout samples were made using a Netzsch^(b) model STA 409 DTA/TGA system. Samples of about 100 mg were heated in air to 960°C at a rate of 300°C/hr and cooled at 600°C/hr. Alumina powder was used as the reference material. Alumina crucibles were used for both the grout samples and for the reference material.

3.2.8 Scanning Electron Microscopy

Fracture surfaces of dried grout cores were examined by scanning electron microscopy (SEM) using an ISI^(c) Model SX-30 using an accelerating voltage of 15kV.

(a) Philips Electronics, Mahwah, New Jersey

(b) Netzsch Incorporated, Exton, Pennsylvania

(c) International Scientific Instruments, San Mateo, California

4.0 RESULTS AND DISCUSSION

4.1 ADIABATIC CALORIMETRY

Laboratory adiabatic calorimetry tests were conducted to monitor temperature rise caused by hydration reactions in DSSF grouts as a function of curing time. The dry blend used in these tests consisted of three reactive solids, i.e., the solids reacted with the simulated waste to form hydrated compounds with the accompanying liberation of heat. Adiabatic calorimetry was used to simulate the conditions within the center of a large mass of grout. Under these conditions, it is assumed that all the heat generated by the hydration reactions is used to heat the grout and that none is lost to the surroundings. In the laboratory tests, however, some of the heat generated is used to heat the inside of the dewar (~ 20 cal/°C), and some of the heat may be lost to the oil bath because of heat transfer through the thermocouple or thermistor. The latter possibility is greatest at very slow heat generation rates and is dependant on the overall accuracy of the temperature measurements. The electronic thermometers had an accuracy of $\pm 0.1^\circ\text{C}$ and the data acquisition had an overall resolution of $\pm 0.12^\circ\text{C}$. Therefore, at long times, even a 0.1°C difference between the actual grout temperature and the bath temperature would result in a net heat transfer between the grout and the bath.

Four DSSF grouts were subjected to adiabatic calorimetry tests. Two were prepared with waste preheated to $\sim 35^\circ\text{C}$ and two with waste preheated to $\sim 45^\circ\text{C}$. The first two were tested using thermistors and the latter with type T thermocouples. The results of four calorimeter runs are summarized in Figures 4.1 and 4.2. The tests were conducted in duplicate to determine repeatability of the calorimeters. Both calorimeters appear to have good repeatability, as shown in the figures.

The data in Figure 4.1 show the effect of a small difference in starting temperature on the early heat generation rate. The upper curve during the first 50 hours resulted from a grout that started about 2°C higher than the starting temperature of the other. The two curves cross at about 100 hours and eventually reach the same peak temperature of about 104°C . The temperature increase for these grouts ranged from 68°C to 70°C .

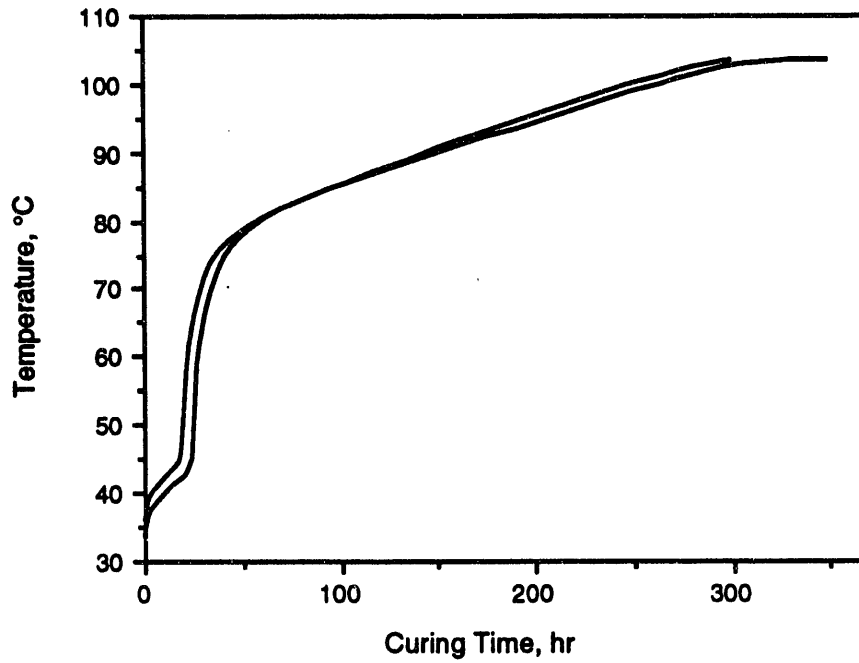


FIGURE 4.1. Adiabatic Temperature Rise for Laboratory-Produced DSSF Grout Prepared with Waste Preheated to 35°C

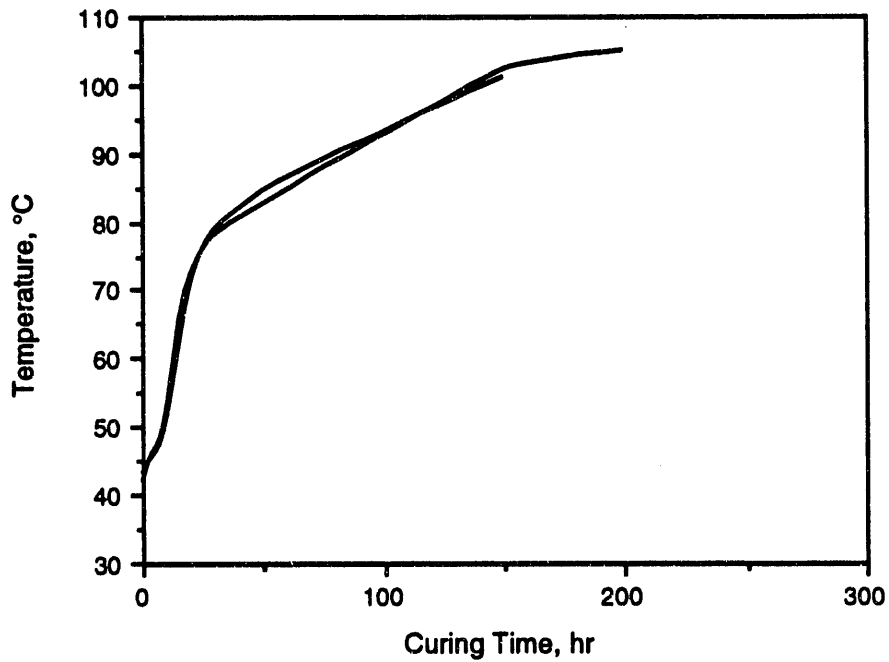


FIGURE 4.2. Adiabatic Temperature Rise for Laboratory-Produced DSSF Grout Prepared with Waste Preheated to 45°C

At starting temperatures of about 45°C, the rate of heat generation of DSSF grouts at early time periods is increased compared to that for the 35°C grouts. The maximum temperature of these grouts was also 104°C-105°C. Because all the grouts tested reached the same maximum temperature during the calorimetry testing, it appears that they have reached the "boiling" point of the pore solution. For the temperatures to increase any further, the grouts must be cured in a pressurized system.

Figure 4.3 shows the temperature rise and rate of rise during the first 60 hours of hydration. This figure depicts various stages of hydration. Immediately after placing the grout in the calorimeter, the rate of temperature rise was fairly high. The high initial rate is due to surface hydration reactions and to the reaction between the solids and the highly alkaline waste solution. The rate then decreased and remained relatively constant up to about 10 hours. This period corresponds to the dormant period found in portland cement hydration. At the end of the dormant period, the rate of temperature rise increased to greater than 12°C/hr as the hydration reaction progressed. Following the rapid rate, there was a broadening in the rate curve which corresponds to the fly ash reactions. After about 30 to 40 hours, the rate slowed as the reactions became controlled by diffusion of the reactants through the hydrated phases.

An electrical heating element was used to determine the heat capacity of the first calorimeter system. A teflon-coated wire was suspended in a known amount of water in a dewar. The dewar was placed in the calorimeter and a constant current was passed through the heater. The temperature rise in the water was monitored and used to control the bath. The analyses of the data resulted in a heat capacity of the calorimeter of approximately 74 cal/°C. This takes into account the heat absorbed by the dewar and an average heat loss from the grout. Using this value, a calculated adiabatic temperature rise for the grout with the highest measured rise is approximately 81°C. This rise corresponds to a heat of hydration value of 52 cal/g of grout and a specific heat of 0.64 cal/°C. The calculated value is very close to the estimated 83°C adiabatic temperature rise. As discussed above, however, the maximum temperature that can occur at atmospheric pressure is around 105°C.

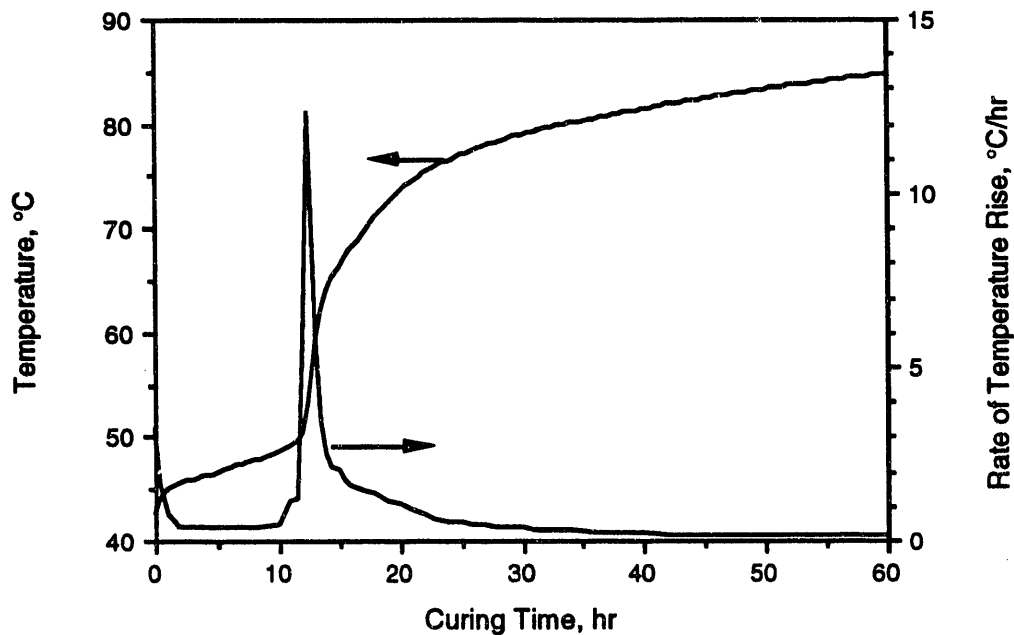


FIGURE 4.3. Adiabatic Temperature Rise and Rate of Temperature Rise for Laboratory-Produced DSSF Grout

4.2 RHEOLOGICAL CHARACTERIZATION

Several samples of grout slurry were collected during the pilot-scale test for rheological characterization. Slurry samples were collected from the grout surge tank immediately above the pump and from the discharge at the bottom of the drop chute leading to the receiver vessel. Figures 4.4 and 4.5 show the results of the density measurements and critical flow rate calculations, respectively. With the exception of the first and fourth sample from the discharge, the densities of the slurries were relatively constant throughout the run, with a standard deviation of less than one percent of average. Although the measured density values are nearly the same for the samples collected at the different locations, the samples of slurry from the surge tank were frothy and less dense than the discharge samples. The process of pouring the slurry into cylinders allowed the larger air bubbles to escape, resulting in densities higher than actual.

The critical flow rates of the slurries are shown in Figure 4.5. The critical flow rates of the surge tank samples are considerably higher than those of the discharge samples, i.e., the grout slurry got thinner with pumping. This is just opposite of what was observed in the PSW test, where the

grout slurry got thicker (higher critical flow rates) as the grout was pumped (Lokken et al. 1988). The reason for the thicker grout in the surge tank may be due to an initial reaction between the dry blend and the highly alkaline waste that resulted in a viscous gel. As the grout slurry was pumped and flowed through the piping, the gel was broken, resulting in a less viscous slurry.

4.3 CORROSIVITY

The WDOE test method for determine the pH of solutions in contact with solids was applied to the core samples to determine whether the grouts would be considered corrosive. For this test, equal weights of sample and deionized water were combined and agitated for 30 minutes, and the resultant pH of the solution was measured. The pH ranged from 11.3 to 11.7 for the core samples, indicating that these samples are not corrosive by definition because the pH is below the maximum permissible pH of 12.5.

4.4 EP TOXICITY

Core samples were tested for EP toxicity using the procedure discussed in Section 3.2.3. All nine samples behaved similarly throughout the 24-hour extraction period. The samples required the maximum acid addition allowed by the procedure (4 ml/g). The final pH of samples ranged from 6.06 to 6.87, averaging 6.27 ± 0.24 . All EP toxic metal concentrations in the extract were below regulatory limits as shown in Table 4.1; therefore, the samples are not EP toxic.

4.5 ANS 16.1 LEACHING

The American Nuclear Society (ANS) 16.1 leach test was conducted on nine samples of grout obtained from the cores. The grout had cured about 15.5 weeks prior to the start of the leach tests. The tests continued through 91

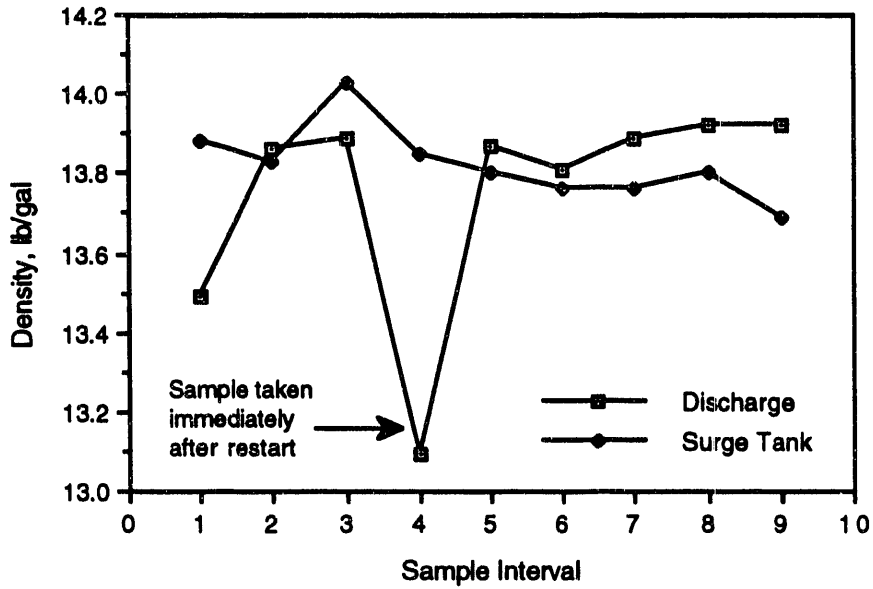


FIGURE 4.4. Density of Pilot-Scale DSSF Grout Slurries

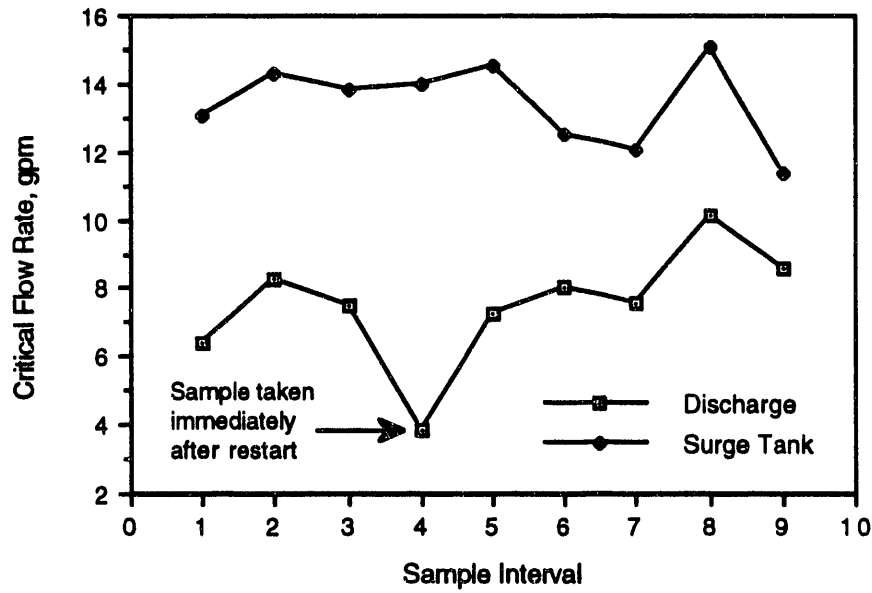


FIGURE 4.5. Critical Flow Rates of Pilot-Scale DSSF Grout Slurries

TABLE 4.1. Extraction Procedure Toxicity Results for Pilot-Scale Grout Cores

Sample ID	Concentration, mg/L							
	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
A-b	<1.0	1.1	<0.1	0.3	<1.0	<0.03	<0.1	0.07
A-m	<1.0	0.6	<0.1	0.2	<1.0	<0.03	<0.1	0.10
A-t	<1.0	0.7	<0.1	0.2	<1.0	<0.03	<0.1	0.07
B-b	<1.0	0.6	<0.1	0.2	<1.0	<0.03	<0.1	0.13
B-m	<1.0	0.5	<0.1	0.1	<1.0	<0.03	<0.1	0.11
B-t	<1.0	0.7	<0.1	0.3	<1.0	<0.03	<0.1	0.06
C-b	<1.0	1.3	<0.1	0.3	<1.0	<0.03	<0.1	0.05
C-m	<1.0	0.5	<0.1	0.2	<1.0	<0.03	<0.1	0.16
C-t	<1.0	0.5	<0.1	0.2	<1.0	<0.03	<0.1	0.15
Limit	5	100	1	5	5	0.2	1	5.00

days. Although this test is intended for use on low-level radioactive waste forms, it was applied here to determine the relative leaching resistance of major cations and anions, and to determine homogeneity of the grout within the vessel. The ANS 16.1 leach test is designed to determine a "figure of merit" parameter called the leachability index (L). The leachability index for a given species is defined as the negative logarithm (base 10) of the effective diffusion coefficient (D) of that species. The effective diffusivity is given by (ANS 1986):

$$D = \pi \left[\frac{(a_n/A_0)}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T \quad (4)$$

- where,
- D = effective diffusivity, cm²/sec
 - a_n = concentration of ion released from the specimen during the leaching interval n
 - A₀ = total amount of species in the specimen at the beginning of the leach test
 - (Δt)_n = t_n - t_{n-1}, duration of the n-th leaching interval, sec
 - V = volume of specimen, cm³
 - S = geometric surface area of specimen, cm²
 - T = [1/2 (√t_n + √t_{n-1})]², representing the "mean time" of the leaching interval, sec.

The treatment of the data from this type of leach test assumes that the release of ions from the waste form is controlled by diffusion. For pure diffusional release, the cumulative amount of species released from the sample plotted as a function of the square root of time would yield a straight line passing through the origin at time zero. This type of plot is shown in Figures 4.6 through 4.8 for the cumulative fraction of nitrate released from the three pilot-scale grout cores. The nitrate curves are relatively straight up through 28 days; however, after about 20% of the nitrate was leached, the curves began to curve downward. The curvature is typical of cylindrical samples when greater than 20% of the original inventory has been leached (ANS 1986).

Table 4.2 lists the average leach indices for nitrate, sodium, and total organic carbon for each of the nine samples through 91 days of leaching, plus the estimated maximum temperature the samples reached during curing. The nitrate leach indices ranged from a low of 7.5 to a high of 8.4. It is apparent that increased curing temperatures resulted in a more leachable grout. This is particularly evident by the results for core C as shown by the leach indices listed in Table 4.2, and by the cumulative fraction leached (Figure 4.8). The total amount of nitrate leached after 91 days from sample that had reached 71°C was 56% less than from the sample that reached 101°C.

4.6 THERMAL CONDUCTIVITY

Table 4.3 shows the thermal conductivity values and the grout temperatures at each of the four probes. Based on an estimated accuracy of $\pm 10\%$, there appears to be little difference in the measured values as a function of time or position within the vessel. Averaging all the values results in a thermal conductivity of 0.75 W/mK (0.43 BTU/hr·ft·°F).

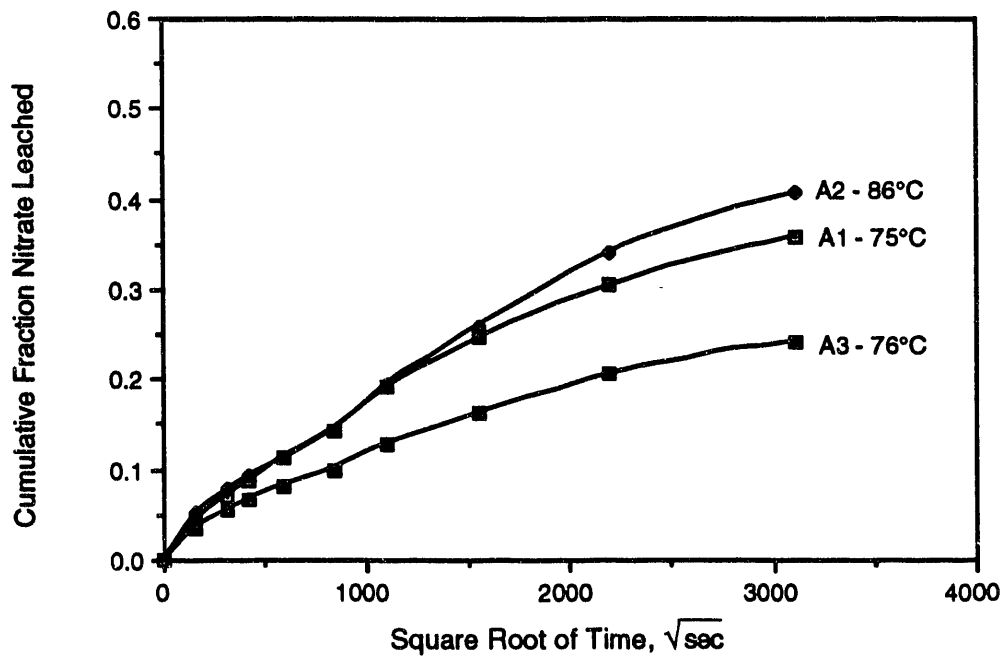


FIGURE 4.6. Cumulative Fraction Nitrate Leached From Pilot-Scale Grout (Core A)

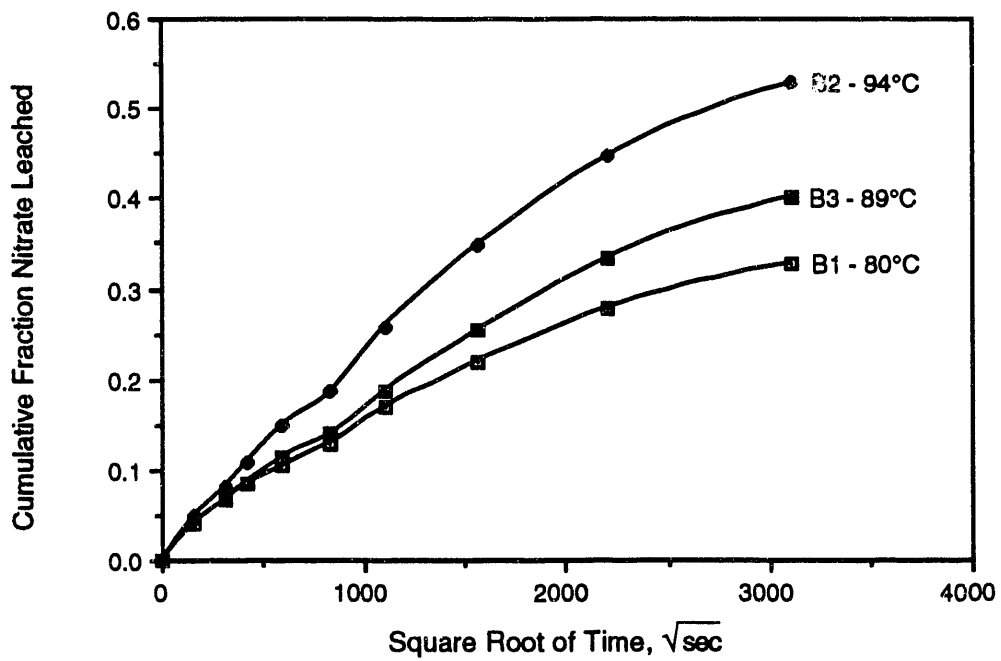


FIGURE 4.7. Cumulative Fraction Nitrate Leached From Pilot-Scale Grout (Core B)

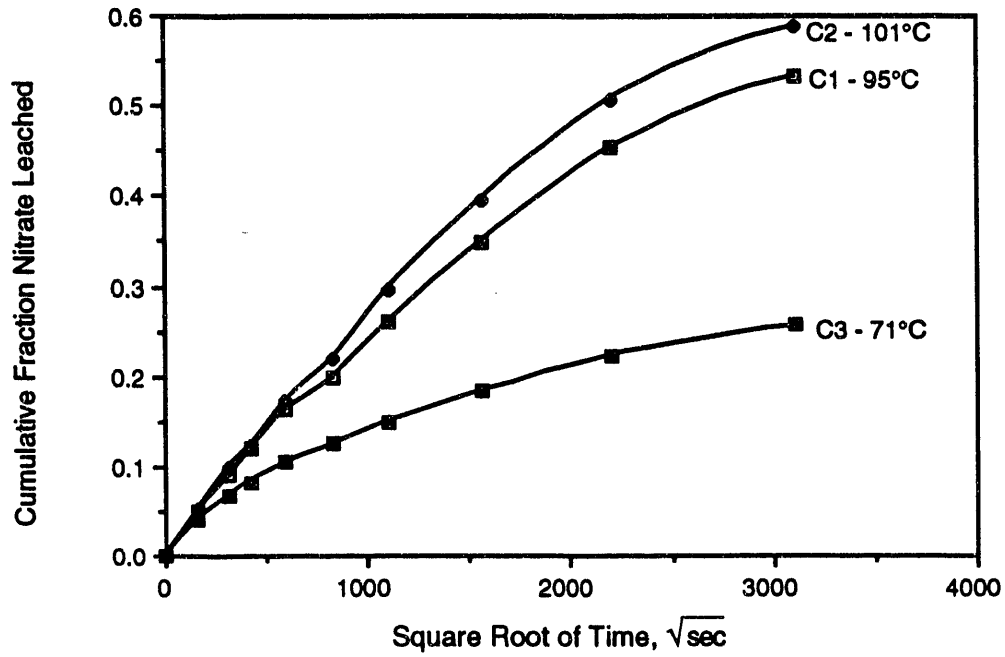


FIGURE 4.8. Cumulative Fraction Nitrate Leached From Pilot-Scale Grout (Core C)

TABLE 4.2. Average Leach Indices (L) for Nitrate, Sodium, and Total Organic Carbon (TOC) Through 91 Days for Pilot-Scale DSSF Grout Cores

Core Sample	Estimated Maximum Temperature, °C	Leachability Index		
		Nitrate	Sodium	TOC
A1	75	8.0	8.2	8.0
A2	86	8.0	8.2	8.2
A3	76	8.4	8.5	8.3
B1	80	8.1	8.3	8.0
B2	94	7.7	8.0	7.9
B3	89	8.0	8.2	8.0
C1	95	7.6	8.0	7.8
C2	101	7.5	7.9	7.8
C3	71	8.3	8.4	8.2

TABLE 4.3. In Situ Thermal Conductivity and Temperatures of Pilot-Scale Grout

<u>Probe No.</u>	<u>Thermal Conductivity, W/mK</u>				
	<u>2d</u>	<u>4d</u>	<u>7d</u>	<u>14d</u>	<u>28d</u>
1	0.76	0.76	0.76	0.76	0.77
2	0.76	0.76	0.78	0.80	0.81
3	0.77	0.77	0.76	0.72	0.67
4	0.73	0.75	0.76	0.66	--(a)

<u>Probe No.</u>	<u>Temperature, °C</u>				
	<u>2d</u>	<u>4d</u>	<u>7d</u>	<u>14d</u>	<u>28d</u>
1	85.0	89.3	90.0	86.9	44.5
2	84.7	89.8	92.3	89.3	45.7
3	73.0	69.1	63.1	55.1	28.5
4	73.2	70.0	62.8	54.6	28.5

(a) Probe had an erratic response.

4.7 PHYSICAL PROPERTIES

Samples of DSSF grout from the cores and samples that were collected from the surge tank and from the pipe discharge were tested for compressive strength, density, and moisture content. The surge tank and discharge samples were collected during the pilot-scale test and were cured at temperature up to 90°C for the first 28 days, and at ambient temperature thereafter. All the samples had cured about 4 months at the time of testing. The results of these tests are summarized in Table 4.4. The average compressive strength of the pipe discharge samples was slightly higher than the surge tank samples, even though the density and moisture content were nearly the same. The higher values are attributed to the additional mixing that occurred during the flow through the piping. The average strength of the core samples was appreciably

lower than the strengths of the other samples. However, these strength values are considerably larger than the formulation criteria of 50 psi^(a).

Most of the samples cured under unsaturated conditions in the ovens were cracked, with some cracks extending the length of the sample. The cracking was due to drying shrinkage, since the samples lost about 10% to 20% of their original moisture during curing. The samples that were cured under saturated conditions in the laboratory actually gained about 1% to 2% moisture during curing. The average moisture content in the core samples was about the same as the as-cast and moist-cured laboratory samples, indicating that no significant moisture loss occurred during the curing of the core samples. The lower bulk densities and evaporable water contents of the surge tank and pipe discharge samples were caused by partial drying during the initial 28-day curing times. The samples were placed in a convection oven with no additional source of moisture (i.e., very low relative humidity in the oven). The evaporable water content of the cores was about the same as that for the laboratory samples cured in 100% relative humidity.

TABLE 4.4. Summary of Compressive Strength, Density, and Evaporable Water Content of DSSF Pilot-Scale Grout Samples^(a)

Sample Location	Compressive Strength (psi)	Bulk Density (g/cm ³)	Evaporable Water Content (wt%)
Surge Tank	1320 ± 150	1.52 ± 0.06	23.8 ± 2.7
Discharge	1490 ± 180	1.51 ± 0.05	23.6 ± 4.4
Lab-Cured (Dry)	1160 ± 110	1.51 ± 0.05	23.7 ± 3.0
Lab-Cured (Moist)	1430 ± 140	1.69 ± 0.00	33.6 ± 0.2
Cores	1040 ± 210	1.66 ± 0.02	32.5 ± 0.5
Cores (After Leaching)	1100 ± 120	1.62 ± 0.01	36.9 ± 0.9

(a) These results are based on the as-received grout samples.

(a) Riddelle, J. G. 1987. Formulation Criterion for the Hanford Grout Disposal Program. Internal Report SD-WM-SS-004, Westinghouse Hanford Company, Richland, Washington.

4.8 X-RAY DIFFRACTION

X-ray diffraction analyses were conducted on grout samples from cores A and C to qualitatively assess relative crystallinity between samples. There were no attempts made to quantify the amount of crystalline phases present in these samples. The diffraction patterns for the samples from core A were essentially identical, each showing a moderate degree of crystallinity. The maximum curing temperature of these samples ranged from 74°C to 86°C. The samples of core C that reached the highest temperatures (C1 - 95°C and C2 - 101°C) appeared to have the highest degree of crystallinity. The diffraction patterns of these samples were similar to those of the samples from core A with the addition of small peak around $7^{\circ} 2\theta$. This peak could correspond to tobermorite, a crystalline calcium silicate hydrate that forms at high temperatures, although absolute identification could not be made because of several overlapping peaks at the higher angles. The overall intensities in the diffraction pattern for the sample C3 (71°C maximum temperature) were lowest of all the samples tested suggesting larger proportions of x-ray amorphous materials. The curing temperatures of this sample may have been sufficiently low to preclude formation of the crystalline phases present in the other samples.

The major peaks in the diffraction patterns were compared with standard powder diffraction files for possible identification. Based on the comparison, six phases were identified whose patterns generally fit the peaks. These include hydrated calcium silicate, tricalcium aluminate hydrate, various hydrated calcium aluminum silicates, tobermorite, and sodium silicate. Another crystalline phase that may be present is pectolite, although its presence was not verified. Pectolite, a sodium calcium silicate hydrate, was found in hydrothermal treatment of several mixtures in the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ system by Xi and Glasser (1984).

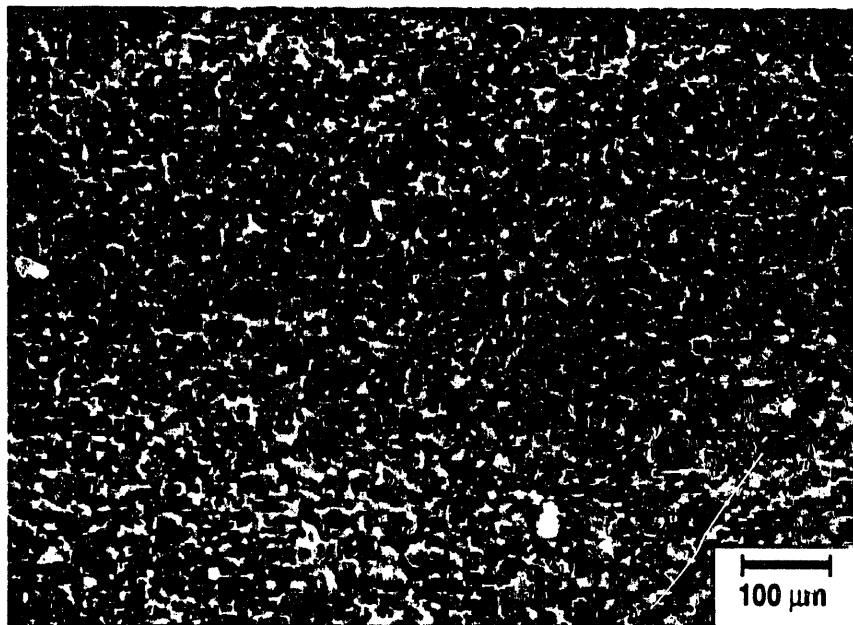
4.9 THERMAL ANALYSIS

Simultaneous DTA/TGA was conducted on grout powders to monitor weight loss over an extended temperature range to assess how tightly the moisture is bound within the grout porosity. The DTA/TGA results for the six samples tested (cores A and C) were all about the same. The samples had previously been

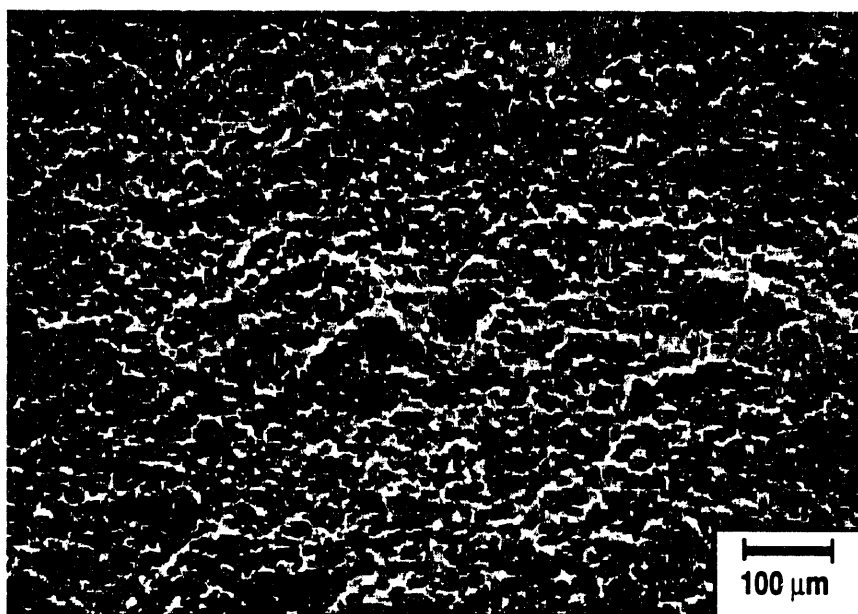
dried at 105°C, pulverized, and stored in plastic bags prior to testing. Weight loss began at about 100°C and continued at a fairly steady rate with a slight inflection at 300°C and 440°C. The initial weight loss is from adsorbed and free water in the larger pores. Water bound in the capillaries, gel pores, and hydrated phases is lost at the higher temperatures. The presence of a small endothermic peak was observed around 580°C which falls in the range where decomposition of calcium hydroxide occurs (Kesselouri et al. 1983 and Fordham and Smalley 1985). The presence of calcium hydroxide suggests that additional hydration products may form at longer times by reaction with the silica in the fly ash and blast furnace slag.

4.10 MICROSTRUCTURE

Scanning electron microscopy was used to examine fracture surfaces of the DSSF grout core samples. Figure 4.10 compares the microstructure of samples taken from a core along the centerline of the vessel. The top micrograph is of a sample near the bottom of the core where the maximum temperature during curing was approximately 71°C. The bottom micrograph is of a sample near the center of the core where the maximum temperature was 101°C. Both samples exhibit very dense microstructures. The major difference between the two samples is the surface morphology. The surface of the sample cured at the lower temperature appeared grainy, with several spherical fly ash particles present. The surface of the sample cured at the higher temperature was covered with gelatinous hydration products. The fly ash particles in this sample were covered with the gelatinous coating, whereas in the other sample, most of the fly ash spheres appeared as distinct particles.



Core C - Maximum Curing Temperature 71°C



Core C - Maximum Curing Temperature 101°C

FIGURE 4.9. Scanning Electron Micrographs of DSSF Grout Cores Taken Along the Centerline of the Receiver Vessel

5.0 CONCLUSIONS

Based on the results of the tests and characterization activities performed on simulated DSSF grout samples, the following conclusions can be drawn:

- Grout slurry samples collected at the surge tank during the pilot-scale test were frothy and considerably thicker than slurry samples prepared using laboratory samples.
- The grout slurry thinned during pumping, resulting in critical flow rates comparable to those of laboratory-prepared grouts.
- Curing simulated DSSF grouts in adiabatic calorimeters at atmospheric pressure resulted in peak temperatures of about 105°C. The calculated adiabatic temperature rise was 81°C.
- The moisture content (evaporable water) of pilot-scale grout cores averaged around 33 wt%, the same as grout samples cured under saturated conditions in the laboratory.
- The unconfined compressive strength of the grout cores averaged 1040 psi, compared to 1430 psi for lab-cured grout samples.
- The simulated DSSF grout cores were found not to be corrosive because the pH ranged from 11.3 to 11.7, compared to the critical value of ≤ 12.5 .
- The simulated DSSF grout cores were not EP toxic.
- Grouts cured at higher temperatures were less resistant to leaching than those cured at lower temperatures. The total amount of nitrate leached from a sample that reached 71°C was 56% less than from a sample that reached 101°C.
- The thermal conductivity of the DSSF grout averaged 0.75 W/mK.

6.0 REFERENCES

- American Nuclear Society (ANS). 1986. Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure. ANSI/ANS 16.1-1986, American Nuclear Society, LaGrange Park, Illinois.
- Claghorn, R. D. 1987. Compositional Limits for Grout Feed: Double-Shell Slurry and Retrieved Double-Shell Slurry Formulation Experiments. RHO-RE-EV-96, Rockwell Hanford Operations, Richland, Washington.
- de Laguna, W. 1966. "Disposal of Radioactive Wastes by Hydraulic Fracturing: Part I," Nuclear Engineering and Design, 3, pp. 338-352.
- Dubovoy, V. S., S. H. Gebler, P. Klieger and D. A. Whiting. 1986. "Effects of Ground Granulated Blast-Furnace Slags on Some Properties of Pastes, Mortars, and Concretes, in Blended Cements, G. Frohnsdorff, ed. ASTM STP 897, American Society for Testing and Materials, Philadelphia, Pennsylvania.
- Fordham, C. J. and I. J. Smalley. 1985. "A Simple Thermogravimetric Study of Hydrated Cement", Cement and Concrete Research, Vol. 15, No. 1, pp. 141-144, Pergamon Press, New York.
- Fow, C. L., D. H. Mitchell, R. L. Treat, and C. R. Hymas. 1987. Pilot-Scale Grout Production Test with a Simulated Low-Level Waste. PNL-6148. Pacific Northwest Laboratory, Richland, Washington.
- Guymon, R. H., L. D. Vanselow, and G. D. Campbell. 1988. "The Grout Treatment Facility -- Processing Facilities for Low-Level Waste Immobilization and Disposal", in Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, SPECTRUM '88, held September 11-15, 1988, Pasco, Washington. American Nuclear Society, Inc., La Grange Park, Illinois. pp. 95-98.
- Kasselouri, V., Ch. Ftikos, and G. Parissakis. 1983. "DTA-TG Study on the $\text{Ca}(\text{OH})_2$ - Pozzolan Reaction in Cement Pastes Hydrated up to Three Years". Cement and Concrete Research, Vol. 13, No. 5, pp. 649-654, Pergamon Press, New York.
- Langton, C. A. 1988. "Metal Toxicity Evaluation of Savannah River Plant Saltstone - Comparison of EP and TCLP Test Results", in Proceedings of Waste Management '88, held February 28 - March 3, 1988, Tucson, Arizona.
- Lokken, R. O. and D. H. Mitchell. 1988. "Pilot-Scale Grout Production using a Simulated Low-Level Waste: Process Description and Product Characterization", in Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, SPECTRUM '88, held September 11-15, 1988, Pasco, Washington. American Nuclear Society, Inc., La Grange Park, Illinois. pp. 234-236.
- Lokken, R. O., M. A. Reimus, P. F. C. Martin and S. E. Geldart. 1988. Characterization of a Simulated Low-Level Waste Grout Produced in a Pilot-Scale Test. PNL-6396. Pacific Northwest Laboratory, Richland, Washington.

Lokken, R. O., P. F. C. Martin, W. M. Bowen, H. Harty, and R. L. Treat. 1987. Variability in Properties of Grouted Phosphate/Sulfate N-Reactor Waste. PNL-6030, Pacific Northwest Laboratory, Richland, Washington.

Serne, R. J. et al. 1987. Laboratory Leach Tests of PSW Grout and Leachate Adsorption Tests using Hanford Sediment. PNL-6019, Pacific Northwest Laboratory, Richland, Washington.

Sewart, G. H., W. T. Ferris, D. H. Huizenga, A. H. McMakin, G. P. Streile, and R. L. Treat. 1987. Long-Term Performance Assessment of Grouted Phosphate/Sulfate Waste From N Reactor Operations. PNL-6152, Pacific Northwest Laboratory, Richland, Washington.

Smith, D. K. 1976. Cementing. Monograph Volume 4 of Henry L. Doherty Series, Henry L. Doherty Memorial Fund of AIME and Society of Petroleum Engineers of AIME, New York.

State of Washington Department of Ecology (WDOE). 1984. "Chemical Testing Methods for Complying with the Dangerous Waste Regulation," Chapter 173-303, Washington Administration Code, State of Washington, Olympia, Washington.

Tye, R. P. 1969. Thermal Conductivity, Volume 1. Academic Press, London and New York.

U. S. Environmental Protection Agency (U.S. EPA). 1982. "Test Methods for the Evaluation of Solid Waste." Physical/Chemical Properties. SW-846. GPO Stock No. 055-002-8100-2. Washington, D.C.

Weeren, H. O. 1976. An Evaluation of Waste Disposal by Shale Fracturing. ORNL-TM-5209, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Wilhite, E. L., C. A. Langton, H. F. Sturm, R. L. Hooker, and E. S. Occhipinti. 1988. "Saltstone Processing Startup at the Savannah River Plant", in Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, SPECTRUM '88, held September 11-15, 1988, Pasco, Washington. American Nuclear Society, Inc., La Grange Park, Illinois. pp. 99-101

Yaozhong Xi and L. S. Dent Glasser. 1984. "Hydrothermal Study in the System $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ at 300°C", Cement and Concrete Research, Vol. 14, No. 5, pp. 741-748, Pergamon Press, New York.

DISTRIBUTION

<u>No. of Copies</u>		<u>No. of Copies</u>
	<u>OFFSITE</u>	
12	DOE/Office of Scientific and Technical Information C. Frank, EM-50 DOE Office of Technology Development Trevion-II 12800 Middlebrook Rd. Germantown, MD 20874	M. Fuhrmann Brookhaven National Laboratory Upton, NY 11973 T. C. Johnson Nuclear Regulatory Commission MS-623SS Washington, DC 20555 M. McFadden DOE Albuquerque Operations Office P.O. Box 5400 Albuquerque, NM 87115
4	DOE Office of Waste Operations Trevion-II 12800 Middlebrook Rd. Germantown, MD 20874 ATTN: J. A. Coleman, EM-35 M. W. Frei, EM-34 H. Harmon, EM-32 J. E. Lytle, EM-30	R. M. Neilson, Jr. EG&G P.O. Box 1625 Idaho Falls, ID 83415
	J. C. Haugen DOE Chicago Operations Office 9800 South Cass Avenue Argonne, IL 60439	3 Oak Ridge National Laboratory P.O. Box X Oak Ridge, TN 37831 ATTN: T. M. Gilliam E. W. McDaniel R. D. Spence
	F. Bazan Lawrence Livermore National Laboratory University of California P.O. Box 808 Livermore, CA 94550	E. B. Peacock Wastech, Inc. P.O. Box 1213 Oak Ridge, TN 37831-1213
5	Westinghouse Savannah River Company Savannah River Site Aiken, SC 29808-0001 ATTN: C. A. Langton R. M. Wallace E. Wilhite E. Stevens M. Hay	D. M. Smith University of New Mexico Chemical and Nuclear Engineering Department Albuquerque, NM 87131

No. of
Copies

No. of
Copies

FOREIGN

19 Westinghouse Hanford Company

A. Atkinson
Atomic Energy Research
Establishment
HARWELL
Didcot
Oxfordshire, OX 11 0RA
UNITED KINGDOM

L. P. Buckley
Atomic Energy of Canada Ltd.
Chalk River, Ontario KOJ 1J0
CANADA

P. Cote
Environment Canada
Canada Centre for Inland
Waters
Burlington, Ontario LTR 4A6
CANADA

R. Dayal
Ontario Hydro
800 Kipling Ave.
Toronto, Ontario MBZ 5S4
CANADA

C. L. Farmer
Atomic Energy Establishment
WINFRITH
Dorchester, Dorset DT2 8DH
UNITED KINGDOM

ONSITE

3 DOE Richland Field Office

K. W. Bracken
G. H. Sanders
L. A. Huffman

K. W. Bledsoe
J. M. Connor
J. L. Epstein
A. P. Hammitt
D. W. Hendrickson
A. A. Kruger
D. J. Newland
W. J. Powell
T. V. Rebagay
E. F. Riebling
J. L. Scott
J. W. Shade
J. E. Van Beek
J. A. Voogd (4)
T. L. Welsh
G. F. Williamson

31 Pacific Northwest Laboratory

L. M. Bagassen
K. A. Borgeson
R. E. Einziger
D. K. Kried
R. O. Lokken (5)
P. F. C. Martin
J. L. McElroy
G. W. McNair
G. L. McVay
J. E. Mendel
R. K. Quinn
P. A. Scott
R. J. Serne
P. Sliva
J. H. Westsik, Jr. (5)
G. A. Whyatt
K. D. Wiemers
Publishing Coordination
Technical Report Files (5)

END

**DATE
FILMED
5/26/93**

