2F

Hanford Grout Technology Program

Variability in Properties of Grouted Phosphate/Sulfate N-Reactor Waste

R. O. Lokken
P. F. C. Martin
W. M. Bowen

H. Harty
R. L. Treat

February 1987

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

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government of any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or Battelle Memorial Institute.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

VARIABILITY IN PROPERTIES OF GROUTED
PHOSPHATE/SULFATE N-REACTOR WASTE

R. O. Lokken
P. F. C. Martin
W. M. Bowen
H. Harty
R. L. Treat

February 1987

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

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

A Transportable Grout Facility (TGF) is being constructed at the Hanford site in Washington State to convert various low-level liquid wastes to a grout waste form for onsite disposal. The TGF Project is managed by Rockwell Hanford Operations (Rockwell). Oak Ridge National Laboratory (ORNL) has provided a grout formulation for Phosphate/Sulfate N-Reactor Waste, the first waste stream scheduled for grouting beginning in late 1987. The formulation includes a blend of portland cement, fly ash, attapulgite clay, and an illitic clay. Grout will be produced by mixing the blend with Phosphate/Sulfate N-Reactor Waste. These wastes result from decontamination and ion-exchange regeneration activities at Hanford's N-Reactor. Pacific Northwest Laboratory (PNL) is conducting studies on grouted Phosphate/Sulfate N-Reactor Waste to verify that the grout can be successfully processed and, when hardened, that it will meet all performance and regulatory requirements.

As part of these studies, PNL is assessing the variability that may be encountered when processing Phosphate/Sulfate N-Reactor Waste grout. Sources of variability that may affect grout properties include the composition and concentrations of the waste and dry solids, temperature, efficiency of dry solids blending, and dry blend storage time. Significant conclusions of the variability studies follow.

- The expected variation in the grout solids-to-liquid ratio will not adversely affect grout rheological properties, although drainable liquid may be present on the surface of the grout after curing.
- Variation in the properties of attapulgite clay from different suppliers and different lots significantly affected rheological properties of grouts produced in the laboratory.
- Variation in the properties between lots of the other solid components of grout had negligible effects on grout properties.
- Variation in the composition and concentration of Phosphate/Sulfate N-Reactor Waste affected grout rheology and the formation of drainable liquid. The reference Phosphate/Sulfate N-Reactor Waste

contains 50% phosphate waste and 50% sulfate waste. The grout formulation may need to be adjusted in order to grout phosphate/sulfate wastes that deviate from the reference waste (50/50) composition.

- The pH (or hydroxide content) of the liquid waste prior to grouting had a large effect on grout rheology. Grouts made with 50/50 Phosphate/Sulfate N-Reactor Waste were most viscous when the initial pH of the waste was approximately 12.8.
- Variation in temperature did not adversely affect the rheological properties of Phosphate/Sulfate N-Reactor Waste grouts. Increased temperature accelerated setting rates and strength gain, however.
- Variation in the efficiency or degree of blending dry solids had a large effect on Phosphate/Sulfate N-Reactor Waste grout rheology. Prolonged blending times reduced the effectiveness of the attapulgite, resulting in thinner grouts and increased drainable liquids.
- Prolonged storage of blended solids in sealed containers resulted in thinner grouts (compared with grouts produced immediately after solids blending). Blended solids left open to the atmosphere for extended periods of time resulted in thicker grouts.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support provided by several people who helped make this report possible. Specifically, we want to thank R. S. Shirley, L. D. Vanselow, and R. H. Guymon of Rockwell Hanford Operations for their review of the report; D. A. Perez and J. A. Richelieu for word processing support; K. J. Defferding, D. F. Foley, and C. C. Harbour for graphics support; and Andrea McMakin for technical editing.

CONTENTS

SUMMARY	iii
ACKNOWLEDGMENTS	v
INTRODUCTION	1
MATERIALS	3
DRY SOLIDS	3
WASTE SOLUTIONS	4
EXPERIMENTAL PROCEDURES	9
DRY SOLIDS BLENDING	9
GROUT MIXING	9
MEASURING RHEOLOGICAL PROPERTIES	11
Fann Viscometer	11
Haake Viscometer	11
MEASURING DENSITY AND DRAINABLE LIQUIDS	12
COMPRESSIVE STRENGTH TESTING	13
RESULTS AND DISCUSSION	15
COMPOSITIONAL VARIABILITY	15
Effect of Dry Blend Compositional Variation	15
Effect of Waste Composition	24
Effect of Different Turco Solutions	25
Effect of Hydroxide Content	28
ATTAPULGITE VARIABILITY	32
PROCESSING VARIABILITY	34
Effect of Temperature	34

Effect of Dry Solids Blending Time	37
Effect of Dry Solids Blend Storage Time	37
CONCLUSIONS	41
REFERENCES	43
APPENDIX - STATISTICAL DESIGN AND ANALYSIS RESULTS FOR PHOSPHATE/SULFATE N-REACTOR WASTE GROUTS	A.1

FIGURES

1	Schematic of Fann Viscometer	12
2	Schematic of Haake Rotovisco RV100 Viscometer	13
3	Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends 1 and 15	18
4	Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends Containing Different Lots of Individual Materials	19
5	Volume Percent Drainable Liquid of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends Containing Different Lots of Individual Materials	20
6	Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Blends 33 to 37, and Blends 38 to 42	21
7	Comparison of Set Time of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Reference Blend and with a High-Cement Blend	22
8	Compressive Strength of Phosphate/Sulfate N-Reactor Waste Grouts as a Function of Waste/Cement Ratios	23
9	Volume Percent Drainable Liquid of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blend 8 and Varying Proportions of Phosphate/Sulfate Waste	25
10	Volume Percent Drainable Liquid of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blend 15 and Varying Proportions of Phosphate/Sulfate Waste	26
11	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends 8 and 15 and Varying Proportions of Phosphate/Sulfate Waste	27
12	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Waste Made with Different Lots of Turco	28
13	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Waste Made with Different Lots of Turco	29
14	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with 50% Phosphate/50% Sulfate Waste with Varying Initial pH Levels	30

15	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with 50% Phosphate/50% Sulfate Waste with Varying Degrees of Volume Reduction	31
16	Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends Containing 7, 9, and 11 wt% Attapulgite from Different Sources	33
17	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts as a Function of Temperature	35
18	Compressive Strength of Phosphate/Sulfate N-Reactor Waste Grouts as a Function of Temperature and Curing Time	36
19	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with the Components of Dry Blend 29 Blended for Various Time Periods	38
20	Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blend 43 Stored Under Different Conditions for Various Time Periods	39

TABLES

1	Dry Materials Used in Phosphate/Sulfate N-Reactor Waste Grout Variability Testing	3
2	Oxide Composition of Dry Materials Used for Variability Studies of Phosphate/Sulfate N-Reactor Waste Grouts, wt%	5
3	Physical Properties of Dry Materials Used for Variability Studies of Phosphate/Sulfate N-Reactor Waste Grouts	6
4	Nominal Composition of Phosphate and Sulfate Waste Solutions Used for Variability Studies of Phosphate/Sulfate N-Reactor Waste Grouts	6
5	Analyzed Composition of Four Lots of Turco Decontamination Solution	7
6	Target Composition of Dry Solids Blends Used for Variability Studies of Phosphate/Sulfate N-Reactor Waste Grouts, wt%	10
7	Reference Phosphate/Sulfate N-Reactor Waste Grout Formula	16
8	Flow Properties of Grouts Produced with Blend 1 in a 2-in.-Diameter Pipe	16
9	Flow Properties of Grouts Produced with Blends 2 - 7 in a 2-in.-Diameter Pipe	17

INTRODUCTION

A Transportable Grout Facility (TGF) is being constructed on the Hanford Site near Richland, Washington, to convert various low-level radioactive defense wastes to grout waste forms for onsite disposal. As used in this report, the term grout refers to a mixture of various dry solids and liquid wastes that harden into a solid mass through hydration reactions of the cementitious constituents. The dry solids blend used in grout preparation is composed of portland cement, fly ash, and two types of clay. The solids used for Hanford grouts are similar to those used in cement-based waste forms at Oak Ridge National Laboratory (ORNL) for disposal of low-level wastes using a high-pressure hydrofracture process (Weeren 1974, 1976, 1980). Savannah River Laboratory (SRL) is also investigating the use of cement-based waste forms for disposal of defense salt wastes (Langton and Dukes 1984). The TGF is scheduled to begin operating in late 1987 using a waste stream identified as Phosphate/Sulfate N-Reactor Waste. Rockwell Hanford Operations (Rockwell) manages the TGF program and will operate the facility. Oak Ridge National Laboratory is providing preliminary grout formulations for Phosphate/Sulfate N-Reactor Waste and other waste streams. Pacific Northwest Laboratory (PNL) is testing the grout and assessing its long-term performance to ensure that the grouts that will be produced and disposed meet all performance and regulatory requirements (Treat et al. 1985).

The purpose of this report is to document laboratory activities that were performed to assess the variability in grout properties that may be encountered during the processing of Phosphate/Sulfate N-Reactor Waste grout in the TGF. The initial formulations for Phosphate/Sulfate N-Reactor Waste grouts were developed for a reference 50/50 volume mixture of phosphate and sulfate waste, two waste streams that result from decontamination and fuel storage basin water cleanup operations at the N Reactor.

This report deals primarily with the variability that may be encountered when grouting the reference mixture of phosphate and sulfate wastes. Sources of variability that may affect grout properties--including the compositions and concentrations of the waste and dry solids, temperature of the waste and the

dry solids blend, efficiency and time of dry solids blending, and dry blend storage time--were evaluated and the results presented. Also discussed are the potential impacts of the variability in grout properties on grouting operations and on grout quality.

MATERIALS

Phosphate/Sulfate N-Reactor Waste grouts are prepared by mixing a four-component dry solids blend with liquid waste. The dry solids blend recommended by ORNL for Phosphate/Sulfate N-Reactor Waste includes 41 wt% type I-II-LA portland cement, 40 wt% Centralia, Washington, ASTM Class F fly ash, 11 wt% Attapulgate-150 drilling clay, and 8 wt% Indian Red Pottery Clay. These are mixed with a 50/50 volume mixture of phosphate and sulfate waste at a mix ratio of 7.5 pounds of dry solids per gallon of liquid waste (900 g/L).

DRY SOLIDS

The dry solids used in this study included those listed above plus additional attapulgate clays from other suppliers. Table 1 lists all of the dry solids used and their suppliers. The type I-II portland cement was manufactured at Durkee, Oregon, by the Ash Grove West Company. The fly ash was produced at the Centralia, Washington, coal-burning power plant and distributed by Pozzolanic International, Mercer Island, Washington. Indian Red Pottery Clay is distributed by the American Art Clay Company, Inc. of Indianapolis, Indiana.

TABLE 1. Dry Materials Used in Phosphate/Sulfate N-Reactor Waste Grout Variability Testing

<u>Material</u>	<u>Lot No.</u>	<u>Supplier</u>
Type I-II-LA Portland Cement	1,2,3 R1	Ash Grove West, Portland, OR Builder's Lumber, Kennewick, WA
Centralia, WA, Class F Fly Ash	1,3 R1	Ross Island Sand and Gravel Portland, OR Centralia, WA Power Plant Centralia, WA
Attapulgate-150 Drilling Clay	1 2	Engelhard Corp., Edison, NJ Agri Empressa, Midland, TX
Florigel H-Y (attapulgate)	1	T&T Trucking, Williston, ND
Indian Red Pottery Clay	2,3	American Art Clay Co., Indianapolis, IN

The attapulgite clays are from three sources: the Minerals and Chemical Division of Engelhard Corporation, Attapulgus, Georgia; Floridin Company, Quincy, Florida; and Milwhite Company, Inc., Houston, Texas. Table 2 lists the oxide composition of selected dry materials used for grouts discussed in this report. The compositions are based on analyses by inductively coupled plasma (ICP) spectroscopy. Physical properties of these materials are shown in Table 3.

WASTE SOLUTIONS

The formulation development studies for Phosphate/Sulfate N-Reactor Waste grout were based on a 50/50 mixture of phosphate/sulfate waste. The phosphate waste results from the decontamination of the N Reactor cooling system. The precursor of this waste is a commercial decontamination solution known as Turco 4512A, which is manufactured by Turco Products, Carson, California. Turco is composed of approximately 75% phosphoric acid and various organic compounds added to aid in decontamination and to inhibit corrosion. Diethylthiourea, which is an inhibitor added just prior to decontamination, was not used in the laboratory studies. Citric acid is the major organic species. The majority of the simulated phosphate waste solutions used in these studies were prepared with 36 mL of Turco, 905 mL of water, 65 mL 19 M of NaOH ($\text{pH} = 12.0 \pm 0.1$), and 0.88 g of NaNO_2 , on a 1-liter basis. A subsequent simulated phosphate waste was produced using 25.5 mL of Turco and no NaNO_2 . The sulfate waste, which results from the regeneration of ion exchange resin used in a cleanup process of water in spent fuel storage basins, is essentially a dilute solution of sodium sulfate. The nominal compositions of the phosphate and sulfate waste solutions are shown in Table 4. Four different Turco solutions have been used at PNL; their compositions are shown in Table 5. Turco lots 2, 3, and 4 were used in these studies.

TABLE 2. Oxide Composition of Dry Materials Used for Variability Studies
of Phosphate/Sulfate N-Reactor Waste Grouts, wt%

Oxide	Portland Cement I-II			Class F Centralia Fly Ash			Attapulgate 150		Florigel	Indian Red Pottery Clay	
	Lot 2	Lot 3	Lot R1	Lot 1	Lot 3	Lot R1	Lot 1	Lot 2	Lot 1	Lot 2	Lot 3
Al ₂ O ₃	3.40	3.03	2.96	23.10	22.90	23.94	8.70	8.30	10.02	19.40	19.00
B ₂ O ₃		0.11	0.06	0.44	0.47	0.45			0.09		0.33
BaO	0.10	0.11	0.09	0.17	0.18	0.16	0.02	0.02	0.02	0.06	0.07
CaO	63.00	62.40	63.20	8.60	7.92	8.04	5.30	4.39	2.17	0.68	0.63
Fe ₂ O ₃	5.10	4.85	4.61	5.00	6.06	6.20	2.80	2.67	3.25	6.50	6.30
K ₂ O	0.40		0.60	0.70	0.48	0.60	0.80		1.40	3.30	1.72
MgO	1.00	0.77	0.43	1.95	1.46	1.80	9.00	8.21	8.04	1.26	1.03
Na ₂ O	0.19	0.55	0.32	3.10	3.20	3.02	0.10	4.19	0.15	0.15	0.51
P ₂ O ₅	0.10				0.90	0.70	0.80	0.77	0.55		
SiO ₂	23.00	22.90	23.00	45.00	45.50	50.80	53.00	50.40	55.10	61.00	62.20
SO ₃	3.30		3.32	0.70		0.33					
SrO	0.05	0.05	0.04	0.26	0.31	0.28	0.37	0.01	0.01	1.10	0.02
TiO ₂	0.20	0.21	0.23	3.40	4.43	3.87	0.37	0.39	0.44	1.10	1.10
ZnO	0.03					0.04			0.03		
ZrO ₂		0.01	0.06		0.12	0.10		0.02	0.11		0.04
Totals	99.86	94.99	98.92	92.42	93.93	100.33	81.26	79.37	81.37	94.55	92.95

TABLE 3. Physical Properties of Dry Materials Used for Variability Studies of Phosphate/Sulfate N-Reactor Waste Grouts

Material	Lot No.	True Density, g/cm ³	BET Surface Area, m ² /g	Blaine Fineness, cm ² /g
Type I-II-LA Portland Cement	1	3.20	1.066	3600
	2	3.21	1.045	3680
	3	3.21	1.100	3715
	R1	3.21	1.120	3905
Centralia, WA, Class F Fly Ash	1	2.29	0.712	ND ^(a)
	3	2.56	0.568	ND
	R1	2.27	0.530	ND
Attapulgate-150 Clay	1	2.50	128.4	ND
	2	2.59	122.1	ND
Florigel H-Y (attapulgate)	1	2.57	143.9	ND
Indian Red Pottery Clay	2	2.80	20.20	ND
	3	2.77	20.77	ND

(a) ND = not determined.

TABLE 4. Nominal Composition of Phosphate and Sulfate Waste Solutions Used for Variability Studies of Phosphate/Sulfate N-Reactor Waste Grouts

Component	Concentration, moles/L	
	Phosphate	Sulfate
Na ⁺	1.11	0.11
OH ⁻	0.01	0.01
NO ₂ ⁻	0.01	0.01
PO ₄ ⁻³	0.36	--
SO ₄ ⁻²	--	0.04

TABLE 5. Analyzed Composition of Four Lots of Turco Decontamination Solution

Species	Concentration, g/L			
	Lot 1	Lot 2	Lot 3	Lot 4
Cr	0.02	<0.01	<0.01	0.04
Fe	0.07	<0.01	0.03	0.14
K	0.53	<0.1	<0.1	<0.3
Mg	0.58	<0.1	<0.1	<0.06
Mn	<0.002	<0.002	<0.002	0.003
Na	0.92	1.7	9.8	0.08
P	325	280	255	358
S	0.65	0.42	13.0	ND ^(a)
Si	0.03	0.01	0.02	0.02
TOC ^(b)	34.2	117	177	ND

(a) ND = Not determined

(b) Total organic carbon

EXPERIMENTAL PROCEDURES

This chapter describes the experimental procedures that were used to prepare the grouts. In some cases, procedures were modified to determine the effect of a procedural change on grout properties; these modifications are described in the chapter called "Results and Discussion."

DRY SOLIDS BLENDING

The dry solids blends used in this study were blended in twin-shell V-blenders^(a) for 23 hours. The blenders have 16-quart capacities; the nominal batch size was 12,000 grams of total dry blend. Following blending, the solids were sealed in plastic bags and stored in 5-gal metal containers. Thirty-two dry blends were used in the majority of the variability studies (see Table 6). In addition, 27 blends were prepared for assessing the effects of different attapulgite clays on the rheological properties of Phosphate/Sulfate N-Reactor Waste grouts. These blends contained 41 wt% cement (lot 3), 8 wt% pottery clay (lot 3), and 7, 9, or 11 wt% attapulgite, with fly ash (lot 3) making up the balance. Blending times of 1 h were used.

GROUT MIXING

Grouts were mixed in a Hobart Model N-50® mixer with a wire-loop whip. One liter of simulated waste solution and 0.2 mL tributyl phosphate were added to the mixer bowl and the mixer was turned on low speed (139 rpm). The dry solids blend was added during a 15-s period. After a total of 30 seconds of mixing, the mixer was stopped and the bowl was scraped with a rubber spatula. The grout was mixed for three additional minutes at low speed. A second mixing procedure involved mixing for 30 s at low speed, followed by 30 s at medium speed. This procedure was used when results were to be compared with those from formulation activities at ORNL.

(a) Manufactured by Patterson-Kelley, Stroudsburg, Pennsylvania.

® Manufactured by Hobart Corporation, Troy, New York.

TABLE 6. Target Composition of Dry Solids Blends Used for Variability Studies of Phosphate/Sulfate N-Reactor Waste Grouts, wt%

Dry Blend No.	Portland Cement (Lot #)	Centralia Fly Ash (Lot #)	Attapulgitte Clay (Lot #)	Indian Red Pottery Clay (Lot #)
1	41.0 (2)	40.0 (1)	11.0 (1)	8.0 (2)
2	41.0 (2)	41.0 (1)	10.0 (1)	8.0 (2)
3	41.0 (2)	39.0 (1)	12.0 (1)	8.0 (2)
4	43.0 (2)	38.0 (1)	10.0 (1)	9.0 (2)
5	38.0 (2)	42.0 (1)	12.0 (1)	8.0 (2)
6	42.0 (2)	38.0 (1)	12.0 (1)	8.0 (2)
7	39.0 (2)	42.0 (1)	10.0 (1)	9.0 (2)
8	40.0 (2)	48.0 (1)	12.0 (1)	0.0 (-)
12	41.0 (R1)	40.0 (1)	11.0 (1)	8.0 (2)
15	41.0 (3)	40.0 (3)	11.0 (2)	8.0 (3)
17	41.0 (3)	38.0 (3)	13.0 (2)	8.0 (3)
18	41.0 (3)	36.0 (3)	15.0 (2)	8.0 (3)
19	41.0 (3)	34.0 (3)	17.0 (2)	8.0 (3)
20	41.0 (3)	40.0 (3)	11.0 (1)	8.0 (3)
21	41.0 (3)	40.0 (3)	11.0 (Florigel)	8.0 (3)
22	41.0 (3)	40.0 (3)	11.0 (2)	8.0 (2)
23	41.0 (3)	40.0 (R1)	11.0 (2)	8.0 (3)
24	41.0 (R1)	40.0 (3)	11.0 (2)	8.0 (3)
25	41.0 (1)	40.0 (3)	11.0 (2)	8.0 (3)
28	39.0 (3)	38.0 (3)	15.0 (1)	8.0 (3)
29	41.0 (3)	40.0 (3)	11.0 (2C) (a)	8.0 (3)
33	41.0 (3)	40.0 (3)	11.0 (2C)	8.0 (3)
34	38.95 (3)	41.39 (3)	11.38 (2C)	8.28 (3)
35	43.05 (3)	38.61 (3)	10.62 (2C)	7.72 (3)
36	41.25 (3)	40.25 (3)	10.45 (2C)	8.05 (3)
37	40.75 (3)	39.75 (3)	11.55 (2C)	7.95 (3)
38	50.00 (3)	38.00 (3)	8.00 (2C)	4.00 (3)
39	47.50 (3)	39.90 (3)	8.40 (2C)	4.20 (3)
40	52.50 (3)	36.10 (3)	7.60 (2C)	3.80 (3)
41	50.22 (3)	38.16 (3)	7.60 (2C)	4.02 (3)
42	49.78 (3)	37.84 (3)	8.40 (2C)	3.98 (3)
43	41.0 (3)	42.0 (3)	9.0 (2C)	8.0 (3)

(a) Attapulgitte Lot 2C is a blend of clay from bags 2, 3, 10 and 11 of Lot 2. All previous Lot 2 blends were made with attapulgitte from bag 1.

MEASURING RHEOLOGICAL PROPERTIES

Rheological properties of the grouts were measured using two viscometers that employ rotational concentric cylinders in their designs. Grout rheological properties are required to determine process flow conditions, i.e., laminar or turbulent conditions, and pumping pressures. The two instruments included a Fann Model 35A® direct-reading viscometer and a Haake Rotovisco RV100®. These instruments allow the apparent viscosity to be measured at various shear rates. The Fann viscometer provides for fast viscosity measurements and allows for the determination of gel strengths. The Haake viscometer records shear stress as a function of shear rate and is used to determine the effects of time and shear rate on the rheological properties of grouts. Because grouts are non-Newtonian fluids, viscosity generally decreases with increasing shear rate.

Fann Viscometer

The Fann viscometer employs six preset speeds (3, 6, 100, 200, 300, and 600 rpm). A schematic of the Fann operating mechanism is shown in Figure 1. Grout is contained in the annular space between two cylinders. The outer cylinder, or rotor, is rotated by a motor at constant velocity. The rotation of the rotor in the grout produces a torque on the inner cylinder, or bob. A torsion spring attached to the bob restrains movement. The dial attached to the spring indicates the torque imparted as the rotor is rotated. The dial is calibrated to read directly in units of $\text{lb}/100 \text{ ft}^2$ with the proper combination of spring, bob, and rotor. Rheological measurements on grout are conducted using the highest four speeds of the instrument, starting at 600 rpm and working down to 100 rpm. As the speed of rotation changes, the momentum of the rotor causes the dial to oscillate. Once the oscillation is less than one dial unit, the reading is recorded and the speed is lowered to the next setting.

Haake Viscometer

Like the Fann viscometer, the Haake Rotovisco RV100 employs the rotational concentric cylinder principal. However, the Haake viscometer allows for continuous recording of flow curves (shear stress versus shear rate) through the

® Fann Instrument Corporation, Houston, Texas.

® Haake Buchler Instruments, Inc., Saddle Brook, New Jersey.

FIGURE 1. Schematic of Fann Viscometer

use of a programmable speed controller. This permits determination of thixotropy and yield stresses, properties that cannot be obtained using the Fann viscometer. Determining rheological properties of grout with this instrument requires that the sample be poured into the annulus between two coaxial cylinders (see Figure 2). A motor drives the inner cylinder. A viscosity-related torque, caused by the resistance of the sample to shearing, acts on the inner cylinder. This torque deflects a measuring spring placed between the motor and the inner cylinder. The magnitude of the spring deflection correlates linearly with the torque. The spring deflection is transformed into an electrical signal. The torque and tachometer signals are recorded. The majority of the grouts tested on the Haake viscometer were subjected to shear rates of up to 465 s^{-1} during 5 min of continuously changing shear rate.

MEASURING DENSITY AND DRAINABLE LIQUIDS

The density of freshly prepared grouts was determined by pouring approximately 240 mL of grout into a 250-mL graduated cylinder and measuring the

FIGURE 2. Schematic of Haake Rotovisco RV100 Viscometer

weight and the actual volume poured. The same sample was used to determine volume of drainable liquids and shrinkage as the grout solids settled and curing occurred. The presence of drainable liquids is undesirable because the liquid requires recycling in the grout process.

COMPRESSIVE STRENGTH TESTING

Compressive strength samples were poured into cylindrical molds, capped, and allowed to cure for a specified time period. They were subsequently removed from the molds and cut to provide flat, parallel faces using an abrasive saw. Testing was conducted with an Instron® test machine at a constant cross-head speed of 0.01 in./min. The load-to-failure was determined from the maximum point of a load-deformation curve. Cylindrical samples were chosen for

® Instron Corporation, Canton, Massachusetts.

testing because particle settling and the initial drainable liquid formed were not conducive to the preparation of precise 2-in. cubes as required by ASTM C-109 (American Society for Testing and Materials 1983). A minimum compressive strength of 50 psi is required.

FIGURE 2. Schematic of Waste Reduction Rotor System

weight and the actual volume poured. The test sample was used to determine volume of drainable liquid and shrinkage as the pour ended settled and compacted. The presence of drainable liquid is undesirable because the liquid reduces resistance to the pour process.

COMPRESSION STRENGTH TESTING

Compressive strength samples were prepared from cylindrical water, capped, and allowed to cure for a specified time period. They were subsequently removed from the mold and cut to provide flat, parallel faces using an abrasive saw. Testing was conducted with an Instron test machine at a constant cross-head speed of 0.01 in./min. The load-time curve was determined from the maximum value of a load-time curve. Cylindrical samples were chosen for

Instron Corporation, Canton, Massachusetts.

RESULTS AND DISCUSSION

This chapter includes results of compositional variability, attapulgite clay variability, and processing variability.

COMPOSITIONAL VARIABILITY

Because the dry materials used in producing grouts are either naturally occurring or are derived from naturally occurring materials, variations in composition and properties are inevitable. Additional compositional variability is introduced due to the inability of the process to precisely weigh and blend the dry solids. The efficiency in the dry solids blending operation is currently specified to result in a maximum relative variation of $\pm 5\%$. In addition, the waste streams that will be grouted may also vary in composition. Work is being conducted to identify a compositional range. The effects of changes in grout composition on various grout properties are presented in the following five sections.

Effect of Dry Blend Compositional Variation

The efficiency of the Dry Materials Receiving and Handling Facility (DMRHF) in batching and mixing the dry solids is $\pm 5\%$ of the targeted composition for each component. Therefore, all grouts produced with dry solids blends within this range must meet performance criteria in order to be deemed acceptable. The reference Phosphate/Sulfate N-Reactor Waste grout formulation is shown in Table 7. Grouts were produced with the reference dry blend, number 1, and modifications of the reference blend, numbers 2 through 7 as listed in Table 6. These grouts were mixed for 30 s at low speed and 30 s at medium speed. The Fann viscometer data were evaluated using the power law model according to Smith (1976) for determination of Reynolds number and critical flow rates. The results of these evaluations, shown in Tables 8 and 9, indicate that all of the grouts produced with mix ratios between 7 and 8 lb/gal had acceptable flow properties, i.e., turbulent flow would be maintained at pumping rates greater than the nominal flow rate of 50 gpm. Grouts produced with the reference blend at 8.5 lb/gal meet the formulation criterion, which allows critical flow rates of up to 65 gpm. However, drainable liquids were present after 28 days on

TABLE 7. Reference Phosphate/Sulfate N-Reactor Waste Grout Formula

Material	Amount, wt%
Type I-II-LA portland cement	41
Centralia, WA, ASTM Class F fly ash	40
Attapulgate-150 drilling clay	11
Indian Red Pottery Clay	8

Mix Ratio:

7.5 pounds of dry solids blend/gal of Phosphate/
Sulfate N-Reactor Waste. 0.02 vol% tributyl
phosphate (TBP) is added to the Phosphate/Sulfate
N-Reactor Waste as a defoaming agent.

TABLE 8. Flow Properties of Grouts Produced with Blend 1 in a
2-in.-Diameter Pipe

Property	Mix Ratio, lb/gal							
	7		7.5		8		8.5	
	(a)	(b)	(c)	(b)	(a)	(b)	(a)	(b)
Density	11.63	0.10	11.71	0.10	11.99	0.01	12.04	0.16
Gel Strength, lb/100 ft ²	15.7	1.5	15.5	1.6	27.3	2.1	32.7	9.5
Apparent Viscosity, cP	15.6	0.8	20.6	2.4	32.8	6.9	54.8	5.0
Reynolds Number at 50 gpm	5800	500	4300	500	3000	600	1700	100
Critical Flow Rate, gpm ^(d)	22.4	2.0	28.6	2.7	38.4	5.9	59.1	3.3
28-d Drainable Liquids, vol%	0.53	0.23	1.55	1.60	0		0	

- (a) Average of three mixes.
(b) One standard deviation.
(c) Average of four mixes.
(d) At a Reynolds Number of 2100.

TABLE 9. Flow Properties of Grouts Produced with Blends 2 - 7 in a 2-in.-Diameter Pipe^(a)

Dry Blend Number	Mix Ratio, lb/gal	Density, lb/gal	Gel Strength, lb/100 ft ²	Apparent Viscosity, cP	Reynolds Number at 50 gpm	Critical Flow Rate, gpm	28-Day Drainable Liquids, vol%
2	7.0	11.76	12.8	9.2	10050	14.4	4.0
	7.5	11.89	14.0	14.1	6550	20.6	1.6
	8.0	11.98	14.3	18.0	5320	23.6	1.3
3	7.0	11.72	14.0	14.7	6280	21.1	0
	7.5	11.91	15.5	18.1	5160	25.0	0.2
	8.0	12.08	28.3	34.4	2700	41.7	0
4	7.0	11.64	12.5	11.3	8360	17.2	2.2
	7.5	11.88	13.5	14.4	6680	20.8	2.6
	8.0	12.05	15.0	19.6	5040	25.8	0.2
5	7.0	11.69	11.8	13.6	6840	19.4	2.0
	7.5	11.86	19.0	24.4	3780	32.5	0
	8.0	11.97	22.3	33.5	2680	41.6	0
6	7.0	11.72	16.0	16.1	5960	22.4	0.4
	7.5	11.91	21.5	25.6	3660	33.5	0
	8.0	12.00	32.5	39.9	2320	47.2	0
7	7.0	11.70	13.3	10.7	8530	16.8	2.0
	7.5	11.85	14.8	12.5	8290	17.1	1.9
	8.0	12.06	15.0	19.8	4740	26.6	0.2

(a) Average of two mixes.

grouts produced with blends 2, 4, and 7 at all mix ratios. These blends contained 10 wt% attapulgite. A subsequent decision by Rockwell to remove and process any drainable liquid on Phosphate/Sulfate N-Reactor Waste grout alleviates concern about the presence of liquids in these tests.

Dry solids purchased to support pilot-scale grout tests became the reference materials for all laboratory tests at the start of FY-85. These solids are listed in Table 1 as lot numbers 3, 3, 2, 3, for the cement, fly ash, attapulgite, and Indian Red Pottery Clay, respectively. Dry blend 15 represents the reference dry solids formulation (as shown in Table 7) using these materials. During initial tests with this dry blend, differences were noted in the rheological properties and the amount of drainable liquids of these grouts compared with the properties of grouts produced with dry blend 1. Dry blend 1 represents the reference formulation prepared with different lots of dry solids. The critical flow rates for Phosphate/Sulfate N-Reactor Waste grouts produced at different mix ratios with these two dry blends are shown in Figure 3.

FIGURE 3. Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends 1 and 15 (Waste solution was 50% phosphate/50% sulfate.)

Critical flow rate is defined as the flow rate through a 2-in. diameter pipe that results in a Reynolds number equal to 2100. Grout is considered to be in turbulent flow at Reynolds numbers greater than 2100. The calculations were performed according to Smith (1976) using the power law model. The critical flow rate for blend 1 grouts increases almost exponentially with increasing mix ratio, whereas the critical flow rate for blend 15 grouts increases only slightly with increasing mix ratio. The differences between these two dry blends are believed to result from the lesser suspending or thickening ability of the second lot of attapulgate clay. Additional discussion on the effects of different attapulgate clays is presented later in the report.

The effect of different lots of the other dry materials (cement, fly ash, and pottery clay) were tested with dry blends 22 through 25. In these tests,

the components of blend 15 were substituted with material from other lots on a one-at-a-time basis to determine relative variability between lots. Attapulgate clay used in blend 15 was used in all the blends. Figures 4 and 5 show the variation in critical flow rate and 28-d drainable liquids for grouts produced with the various dry solids blends at a mix ratio of 8.5 lb/gal. These grouts were mixed for 3-1/2 min. at low speed. In these figures, the data shown for blend 15 represent the average results of 11 grout mixes; three mixes were evaluated for each of blends 22 through 25. The error bars represent one standard deviation from the average. Although slight differences exist between the different blends, the overall effect of different lots of individual materials does not appear to be significant when a single lot of attapulgate clay is used. Hence, variability between lots of the Portland cement, fly ash, and pottery clay is not likely to result in processing difficulties.

FIGURE 4. Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends Containing Different Lots of Individual Materials (Waste solution was 50% phosphate/50% sulfate with a mix ratio of 8.5 lb/gal.)

FIGURE 5. Volume Percent Drainable Liquid of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends Containing Different Lots of Individual Materials (Waste solution was 50% phosphate/50% sulfate with a mix ratio of 8.5 lb/gal.)

To address the concern that grout at the low points on large grout monoliths may exhibit longer set times because of increased liquid/cement ratios, dry blends containing larger proportions of cement and lesser amounts of attapulgite and pottery clay were tested. A dry blend of reference composition (blend 33) was compared with the modified blend (blend 38) to address effects of changes in blend composition and mix ratio on rheological properties. Each dry blend was varied by adjusting the amount of cement or attapulgite by ± 5 wt% while keeping the relative ratios of the other ingredients constant. The dry blends are shown in Table 6 as numbers 33 to 42.

Because the attapulgite content in blend 38 was lower than in the reference blend, the mix ratio was adjusted to yield a grout that possessed rheological properties the same as the reference Phosphate/Sulfate N-Reactor Waste grout. A mix ratio of 8.5 lb/gal for blend 38 was found to result in a grout that had nearly the same critical flow rate as one prepared with the reference

dry blend at 7.0 lb/gal. The critical flow rates for these grouts were 46.9 and 46.2 gpm, respectively, calculated with the power law model using a Reynolds number of 2100. Grouts were prepared with dry blends 33 to 37 at 6.5, 7, and 7.5 lb/gal and blends 38 to 42 at mix ratios of 8, 8.5, and 9 lb/gal to determine relative sensitivity of variations in dry blend composition and mix ratio to critical flow rate.

The critical flow rates of the grouts produced with these blends for each mix ratio are depicted in Figure 6. The error bars in the figure represent one standard deviation from the average values of critical flow rate calculated from grouts produced with the reference dry blend and the variations. Comparing the data from the two "reference" grouts and their variations, two conclusions can be drawn: 1) mix ratio has less of an effect on the critical flow

FIGURE 6. Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Blends 33 to 37, and Blends 38 to 42

rate of high-cement/low-attapulgitite grouts, and 2) at a given mix ratio, changes in critical flow rates due to variations in blend composition are nearly the same for the two cases.

The main purpose of comparing the reference blend with one higher in cement was to determine whether more favorable setting properties could be achieved with the latter blend. Penetration resistance measurements were conducted to determine setting rates of grouts produced with blends 33 and 38. The tests were conducted according to ASTM C403 (ASTM 1985); results are shown in Figure 7. Both grouts showed slow setting rates through the first 24 h and even though the blend 38 grout had a higher cement/liquid ratio, the time for initial set (500 psi) was longer than with the reference grout. After three

FIGURE 7. Comparison of Set Time of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Reference Blend (No. 33) and with a High-Cement Blend (No. 38)

days, however, the penetration resistance of the blend 38 grout exceeded the reference grout and increased at a higher rate.

The increased cement content and higher mix ratios of the blend 38 grouts resulted in higher 28-d compressive strengths, as shown in Figure 8. In this figure, the compressive strength is plotted as a function of the waste-to-cement ratio. The relationship of compressive strength and water/cement ratios in conventional concrete and mortars is approximated by a hyperbolic function at equivalent void volumes and degrees of hydration (Neville 1981). However, as evidenced by the discontinuity in the curves in Figure 8, the compressive strengths of grouts produced with blends 33 and 38 are influenced by other factors such as the degree of hydration, the volume fraction of hydrated phases, and/or the proportions of other solids (fly ash and clays). Additionally,

FIGURE 8. Compressive Strength of Phosphate/Sulfate N-Reactor Waste Grouts as a Function of Waste/Cement Ratios

because the simulated waste solution contains chemicals that affect the hydration of cement and may alter the nature of the hydration products (Neville 1981, Lea 1971), the relative concentration of these species for a given amount of cement may influence the strength development.

Effect of Waste Composition

The preliminary Phosphate/Sulfate N-Reactor Waste grout formulation is based on a 50/50 mixture of phosphate and sulfate waste; however, the exact ratio of wastes will likely vary due to varying generation and collection rates. The phosphate waste is generated on a batch basis with approximately 600,000 gal produced per decontamination. The sulfate waste is generated on a semicontinuous basis with yearly generation rates estimated at 720,000 gal. Recent concern over the regulatory aspects of nitrite, which is added to the liquid wastes for corrosion control of the waste storage tanks, has resulted in a decision to eliminate this additive from grout feed streams. New flow sheet data have also resulted in a revised phosphate waste composition and the inclusion of sandfilter backwash waste in the sulfate waste. The sandfilter backwash is an inorganic sludge generated during periodic filter flushing to remove accumulated solids. The following subsections present data from tests of grouts produced with: 1) various proportions of the nominal phosphate and sulfate wastes, and 2) 50/50 mixtures of phosphate/sulfate solutions of different concentrations.

Proportions of Phosphate/Sulfate Waste

The effects of various proportions of phosphate and sulfate wastes on grout properties were determined using dry blends 8 and 15. The range of waste proportions ranged from 0 to 100 vol% phosphate waste for blend 8 and from 20 to 80 vol% phosphate waste for blend 15. Figures 9 and 10 illustrate the effect of waste proportions on the amount of drainable liquids at various time periods for grouts made with blends 8 and 15, respectively. As shown in the figures, the phosphate/sulfate ratio has a marked effect on drainable liquids, with increasing sulfate contents resulting in considerably more liquids. The critical flow rates, however, are not influenced as much with changing proportions, as shown in Figure 11. The maximum critical flow rate for grout produced with blend 15 occurs at a phosphate content of 50%, whereas the critical

FIGURE 9. Volume Percent Drainable Liquid of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blend 8 and Varying Proportions of Phosphate/Sulfate Waste (Mix ratio was 7.0 lb/gal.)

flow rates for grouts with blend 8 increase continually with increasing phosphate contents. These results show that waste mixtures containing low fractions of phosphate waste may require adjustments in the reference formulation if the quantity of drainable liquids is to be reduced.

Effect of Different Turco Solutions

Since the start of the grout project, four lots of Turco decontamination solution have been used at PNL for preparation of simulated phosphate waste. The first lot (250 mL) was obtained from Rockwell in the early stages of the project. This lot was used in the initial scoping studies. Subsequently, three additional lots were obtained and used to prepare the simulated phosphate waste. The chemical analyses of the different Turco solutions were shown in

FIGURE 10. Volume Percent Drainable Liquid of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blend 15 and Varying Proportions of Phosphate/Sulfate Waste (Mix ratio was 8.5 lb/gal.)

Table 5. The amount of phosphorus, sodium, and sulfur in these solutions account for most of the differences in composition. The higher sodium and sulfur values of lot 3 suggest a higher concentration of sodium xylene sulfonate, which is an organic constituent of the Turco solutions. Lot 4 Turco was obtained from UNC Nuclear Industries (UNC).

The effect of the different Turco solutions on the critical flow rate of grouts made with dry blend 15 is illustrated in Figure 12. At all mix ratios, the critical flow rate of grouts made with lot 3 Turco were lower than the others. This is believed to be due to the lower phosphorus and higher sulfur concentrations. This is consistent with the effect of lowering the phosphate/sulfate waste ratios as discussed in the previous section.

FIGURE 11. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends 8 and 15 and Varying Proportions of Phosphate/Sulfate Waste (Mix ratios were 7.0 and 8.5 lb/gal, respectively, for dry blends 8 and 15.)

Figure 13 shows the effect of different Turco solutions on critical flow rate of grouts made with three different dry solids blends at a mix ratio of 7 lb/gal. The same trends are seen for blends 15 and 21 with the order of increasing critical flow rate being lot 4 > lot 2 > lot 3. However, with blend 20, the critical flow rate is highest for grouts produced with lot 3 Turco. The same was seen for blend 1, which contains the same lot of attapulgate clay.

Because only a single source of Turco will be involved in a grouting campaign, these effects could occur only between campaigns. Studies of samples of actual Phosphate/Sulfate N-Reactor Waste collected prior to a grout campaign may identify a need for minor adjustments in the grout formulation.

FIGURE 12. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Waste Made with Different Lots of Turco (Grouts were produced with dry blend 15 with 50% phosphate/50% sulfate.)

Effect of Hydroxide Content

The liquid wastes to be grouted will have hydroxide contents of approximately 0.01 M (pH = 12) for protection against tank corrosion during storage. The exact amount of hydroxide, however, will likely vary with different waste streams as a result of variations in the neutralization process. In the laboratory preparation of the simulated phosphate and sulfate waste solutions, the amount of sodium hydroxide used in the neutralization process was kept constant, i.e., the pH was maintained at slightly greater than 12. To determine the effect of varying hydroxide contents in phosphate/sulfate waste on grout properties, a series of grouts were produced with 50/50 Phosphate/Sulfate N-Reactor Waste and dry blend 29 at a mix ratio of 7.5 lb/gal. The wastes were prepared by adding additional sodium hydroxide to a 50/50 mixture of the initial waste solutions in amounts ranging from 0.01 M to 0.5 M excess.

FIGURE 13. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Waste Made with Different Lots of Turco (Grouts were produced with dry blends 15, 20, and 21 with 50% phosphate/50% sulfate at a mix ratio of 7.0 lb/gal.)

Figure 14 illustrates the effect of pH on the critical flow rate. As shown in the figure, the critical flow rate increases up to pH values of approximately 12.8 and then decreases with higher pH. The increases are extreme at the lower and higher pH ranges tested. The addition of 0.01 mole of sodium hydroxide to the starting Phosphate/Sulfate N-Reactor Waste solution results in an increase in the critical flow rate from 39 gpm to 60 gpm. The magnitude of this relatively small changes suggests that careful adjustment of the pH in the waste feed tank is needed to achieve desired grout rheological properties.

Concentration of Waste

Because waste storage space may be limited, concentration of the wastes may be required. However, at the time this report was written, no plans to concentrate Phosphate/Sulfate N-Reactor Waste existed since there would be no way to segregate the wastes. The effect of concentrated Phosphate/Sulfate

FIGURE 14. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with 50% Phosphate/50% Sulfate Waste with Varying Initial pH Levels (Grouts were produced with dry blend 29 at a mix ratio of 7.5 lb/gal.)

N-Reactor Waste on grout properties was determined using three concentrated solutions. The solutions included one in which the phosphate fraction was concentrated by evaporation to half its original volume, and one in which the phosphate was prepared by neutralizing Turco diluted to a 1:11 ratio with water. (The reference phosphate waste specifies a 1:27 dilution.) The sulfate concentration in these solutions was doubled by adding additional sodium sulfate. Grouts were prepared with these solutions at a mix ratio of 8.5 lb/gal using dry blend 15. The third solution was a 50/50 mixture of phosphate/sulfate waste that was evaporated to 27% of its original volume (73% volume reduction). This solution was mixed with dry blend 20 at a mix ratio of 7.5 lb/gal.

The critical flow rates of these grouts and reference waste grouts are shown in Figure 15. The critical flow rates of grouts produced with blend 15 are essentially identical, indicating no adverse effects on the flow properties of grouts produced with concentrated Phosphate/Sulfate N-Reactor Waste. The amount of drainable liquids on the concentrated waste grouts was less than that on the reference grouts, suggesting that concentration of Phosphate/Sulfate N-Reactor Waste may be beneficial with dry blend 15. The difference in critical flow rates of grouts produced with blend 20 is more pronounced than of those produced with blend 15. In this case, waste concentration resulted in

FIGURE 15. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with 50% Phosphate/50% Sulfate Waste with Varying Degrees of Volume Reduction
 Solution 1 - phosphate evaporated to 50% original volume with double molarity sulfate
 Solution 2 - phosphate was neutralized Turco diluted 1:11 with water; double molarity sulfate
 Solution 3 - 50% phosphate/50% sulfate evaporated to 27% original volume

increasing the critical flow rate from 40 to 54 gpm. Each of the concentrated-waste grouts reabsorbed the drainable liquids within 24 hours. These results indicate that phosphate/sulfate waste that is more concentrated than the reference composition is probably compatible with the current formulation.

ATTAPULGITE VARIABILITY

Attapulgate clays obtained from various sources were studied to determine their effects on rheological properties of Phosphate/Sulfate N-Reactor Waste grouts. In these tests, dry blends were prepared with 41 wt% cement, 8 wt% pottery clay, either 7, 9, or 11 wt% attapulgate, with the balance being fly ash. The dry blends were blended for one hour in V-blenders just prior to producing the grouts. Grouts were produced in triplicate at mix ratios of 7.0, 7.5, and 8.0 lb/gal using simulated 50% phosphate/50% sulfate N-Reactor Waste. Grout mixing was conducted for 3-1/2 min according to the procedure described previously. The grouts were tested for rheological properties using both Fann and Haake viscometers.

The attapulgate clays used in these studies were purchased directly from three producers and from various vendors listed by the American Petroleum Institute as authorized suppliers of attapulgate for use in salt water drilling fluids (American Petroleum Institute 1980). Procuring the clay from these "middlemen" allowed an evaluation of the variability of properties of clay from the three producers. Based on information obtained from the vendors, two clays were manufactured by Milwhite, two by Engelhard, four by Floridin, and one was unknown (i.e., the supplier would not divulge his source).

Large differences were observed in the rheological properties of grouts produced in this study. Clays from Floridin resulted in grouts with high critical flow rates. The two clays from Milwhite resulted in grouts with the largest difference in critical flow rates.

Formulation criteria for Phosphate/Sulfate N-Reactor Waste grouts permit a maximum critical flow rate of 65 gpm. Figure 16 shows the critical flow rates calculated from the data obtained with the Fann viscometer for grouts prepared with blends containing 7, 9 and 11 wt% attapulgate. Seven of the clays resulted in grouts that were thicker than those that were produced during most

FIGURE 16. Critical Flow Rates of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blends Containing 7, 9, and 11 wt% Attapulgite from Different Sources

of the variability testing described in this report. Grouts produced at a mix ratio of 8 lb/gal with 11 wt% of four of the attapulgite clays were too thick to adequately measure rheological properties. However, using lower contents of these clays in the blend and lowering the mix ratio would result in acceptable properties.

The differences in grout properties between the different clays is likely due to differences in clay processing. The processing methods and conditions used to produce attapulgite clays suitable for use in drilling fluids have a significant impact on their properties (Haden and Schwint 1967, Sawyer 1983). Factors that are detrimental to the thickening ability of the attapulgite include fine grinding, grinding when the clay is dry, and high-temperature drying. Additives may be added to the clay, either during processing or during use, to improve its thickening or viscosity development properties.

PROCESSING VARIABILITY

Processing variability is another factor that may affect the properties of grouts. Variations in temperature may arise from seasonal changes and variation in the temperature of the waste fed to the grout process. Changes in grout properties may also occur due to variations in the efficiency of dry solids blending and the time between blending and grout production. These latter two factors may influence the homogeneity of the blend and result in changes in physical properties of the solids during blending or storage.

Effect of Temperature

Temperature variations may result from several factors. The temperature of stored waste can be affected by decay heat, agitation, and length of storage time. Other sources of temperature variations are seasonal variations and the chemical reactions that occur between the waste and the dry solids. The effect of temperatures from 15 to 40°C on calculated critical flow rates was determined for grouts produced with dry blend 8 at a mix ratio of 7 lb/gal. Figure 17 shows the effect of temperature on the critical flow rates calculated from flow curves recorded immediately after mixing, and after 5 min of additional shearing at 1170 s^{-1} . Temperature is shown to have a significant effect on the critical flow rates of those grouts that were subjected to the increased

FIGURE 17. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts as a Function of Temperature (Grouts were produced with dry blend 8 with 50% phosphate/50% sulfate at a mix ratio of 7.0 lb/gal.)

shear but very little effect when measured immediately after mixing. Based on these results, changes in temperature will have very little effect on grout rheology during operation of the TGF because shear rates less than 600 s^{-1} are expected during mixing and pumping.

The effect of curing temperature on the compressive strength of Phosphate/Sulfate N-Reactor Waste grouts was determined at temperatures from 5 to 70°C. These grouts were prepared with 50/50 Phosphate/Sulfate N-Reactor Waste and dry blend 43 at a mix ratio of 7.5 lb/gal. For grouts that were cured at temperatures above the ambient temperature, the waste was preheated to the desired temperature prior to producing the grouts. The lower-temperature grouts were produced with Phosphate/Sulfate N-Reactor Waste that was cooled to

0°C. Curing at 10 to 20°C was conducted in water baths maintained at the desired temperatures. Refrigerators were used for curing temperatures of 0 and 5°C. The effect of curing temperature on compressive strength at various time periods is shown in Figure 18. Phosphate/Sulfate N-Reactor Waste grouts cured at temperatures of 50 to 70°C reached between 70 and 90% of their 28-day strengths after only 3 days of curing. At temperatures of 15 and 20°C, curing times of seven days were required to achieve adequate strength to allow sample preparation for compressive strength testing. Although the strength

FIGURE 18. Compressive Strength of Phosphate/Sulfate N-Reactor Waste Grouts as a Function of Temperature and Curing Time

development of grout is considerably slower at decreased temperatures, the 28-day compressive strength of Phosphate/Sulfate N-Reactor Waste grout cured at 5°C was 70 psi, which exceeds the minimum 50 psi criteria for formulation development. Curing temperatures of at least 10°C are expected.

Effect of Dry Solids Blending Time

The dry solids used in the preparation of most laboratory grouts were blended in twin-shell V-blenders for 23 h to ensure a homogeneous blend and to minimize variations in composition. This blending technique, while providing a well-mixed, homogeneous blend, may not be representative of the blending in the Dry Materials Receiving and Handling Facility (DMRHF) which will provide the solids blend for the grout process. The effect of dry solids blending time on the critical flow rates of Phosphate/Sulfate N-Reactor Waste grout is shown in Figure 19. The reference laboratory blending conditions (23 h) result in grouts that have the lowest critical flow rate (30 gpm), while grouts made with solids that were not preblended had the highest critical flow rate (64 gpm). The changes in critical flow rate were minimal for blending times between 5 min and 2 h, but decreased by 60% between 2 and 23 h. Subsequent testing of dry blends produced by the DMRHF indicate that V-blending times of approximately 1 h result in grouts with comparable rheological properties. However, the uncertainty in component ratios in the DMRHF blended solids needs to be addressed in order to more accurately determine equivalent blending.

Effect of Dry Solids Blend Storage Time

The effects of storage time of dry blends on the rheological properties of Phosphate/Sulfate N-Reactor Waste grouts was assessed to determine whether prolonged storage times adversely affect grout properties. Dry blends of composition number 43 in Table 6 were prepared in the usual manner and stored under three conditions: 1) sealed in a plastic bag, 2) sealed in a plastic bag with Drierite®, and 3) open to the atmosphere. (Blends produced in the laboratory are normally sealed in plastic bags.) Grouts were prepared with these dry blends at 1, 7, 14, 28, 56, and 84 days after blending.

® W. A. Hammond Drierite, Xenia, Ohio.

FIGURE 19. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with the Components of Dry Blend 29 Blended for Various Time Periods (Grouts were produced with 50% phosphate/50% sulfate at a mix ratio of 7.5 lb/gal.)

The effect of storage time under the three storage conditions are shown in Figure 20. The critical flow rate of grouts produced with blends that had been sealed (1 and 2) decreased with increased storage time throughout the period, whereas the dry blend that was left open to the atmosphere yielded grouts that had critical flow rates that were higher after seven days of dry blend storage.

FIGURE 20. Critical Flow Rate of Phosphate/Sulfate N-Reactor Waste Grouts Produced with Dry Blend 43 Stored Under Different Conditions for Various Time Periods

FIGURE 20. Change in weight percentage of open, dimer, and monomer components of polybutadiene-1,2 stored under nitrogen.

CONCLUSIONS

Based on the results of the variability testing of Phosphate/Sulfate N-Reactor Waste grouts, the following conclusions were drawn:

- The expected variation in the grout solids-to-liquid ratio will not adversely affect grout rheological properties, although drainable liquid may be present on the surface of the grout after curing. The critical flow rates of grouts produced with a reference blend at mix ratios of 7 to 8.5 lb/gal ranged from 22 to 59 gpm, which are below the upper limit of 65 gpm.
- Variation in the properties of attapulgite clay from different suppliers and different lots significantly affected rheological properties. However, grouts possessing acceptable properties can be produced by adjusting the attapulgite content in the dry blend prior to operation, and by adjusting the mix ratio during operation.
- Variation in the properties between lots of the other solid components of grout had negligible effects on grout properties. Only minor differences were seen in the critical flow rates of grouts produced with different lots of cement, fly ash, and pottery clay when the same attapulgite clay was used in the dry blends. This indicates that the properties of the attapulgite clay dominate the viscosity and flow characteristics of Phosphate/Sulfate N-Reactor Waste grouts.
- Variation in the composition and concentration of Phosphate/Sulfate N-Reactor Waste affected grout rheology and the formation of drainable liquid. The reference Phosphate/Sulfate N-Reactor Waste grout formulation may require adjustments when wastes other than the reference 50/50 (phosphate/sulfate) waste are grouted, particularly when the phosphate waste content is low or absent. The need for any adjustments to the formulation will be identified through laboratory tests with dry blend and waste prior to the startup of the grouting process. Since the contents of the waste feed tank will be homogenized throughout the grouting campaign, changes in grout properties due to compositional variation should be minimal.

- The pH (or hydroxide content) of the liquid waste prior to grouting had a large effect on grout rheology. Grouts made with 50/50 N-Reactor Waste were most viscous when the initial pH of the waste was approximately 12.8. These effects are expected to be minimal during operation of the TGF since the pH of the waste during a grouting campaign will remain relatively constant.
- Variation in temperature does not adversely affect the critical flow rates of Phosphate/Sulfate N-Reactor Waste grouts. However, increased temperature accelerated setting rates and strength gain. Grouts cured at temperatures as low as 5°C attained compressive strengths greater than 50 psi after 28 d.
- Variation in the efficiency or degree of blending dry solids had a large effect on Phosphate/Sulfate N-Reactor Waste grout rheology. Prolonged blending times reduced the effectiveness of the attapulgate, resulting in thinner grouts and increased drainable liquids. The effectiveness of the attapulgate clay is reduced by extended blending. Preliminary tests on grouts produced with materials blended at the DMRHF and with the same materials blended for various time periods in laboratory V-blenders indicate that V-blending times of 1 to 2 hours produce dry blends equivalent to those produced in the blender of the DMRHF.
- Prolonged storage of blended solids in sealed containers resulted in thinner grouts (compared with grouts produced immediately after solids blending). Blended solids left open to the atmosphere for extended periods of time resulted in thicker grouts.

REFERENCES

- American Petroleum Institute (API). 1980. API Bul 13D: The Rheology of Oil-Well Drilling Fluids, American Petroleum Institute, Washington, D.C.
- American Society for Testing and Materials (ASTM). 1983. 1983 Annual Book of ASTM Standards. Vol. 04.01 Cement; Lime; Gypsum, American Society for Testing and Materials, Philadelphia, Pennsylvania.
- American Society for Testing and Materials (ASTM). 1985. 1985 Annual Book of ASTM Standards. Vol. 04.02 Concrete and Mineral Aggregates, American Society for Testing and Materials, Philadelphia, Pennsylvania.
- Haden, W. Linwood, Jr. and Ira A. Schwint. 1967. Industrial and Engineering Chemistry, Vol. 59, No. 9, pp. 59-69.
- Langton, C. A. and M. D. Dukes. 1984. "Defense Waste Salt Disposal at the Savannah River Plant," Waste Management '84, Proceedings of the Symposium on Waste Management, March 11-15, 1984, Tucson, Arizona.
- Lea, F. M. 1971. The Chemistry of Cement and Concrete. Third Edition. Chemical Publishing Company, Inc. New York, New York.
- Neville, A. M. 1981. Properties of Concrete. Third Edition. Pitman Publishing Inc., Marshfield, Massachusetts.
- Sawyer, Edgar W., Jr. 1983. The Characterization and Use of Clays for Gelling Salt Water Drilling Fluids, presented at the SME-AIME Annual Meeting, Atlanta, Georgia, March 6-10, 1983. Society of Mining Engineers of AIME, Caller No. D, Littleton, Colorado.
- 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.
- Treat, R. L., R. O. Lokken, S. L. Stein and C. A. Geffen. 1985. "Operational and Long-Term Performance Assessment for Hanford Grout", Waste Management '85, Proceedings of the Symposium on Waste Management, March 24-28, 1985, Tucson, Arizona, pp. 497-501.
- Weeren, H. O. 1974. Shale Fracturing Injections at Oak Ridge National Laboratory - 1972 Series, ORNL/TM-4467, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Weeren, H. O. 1976. Shale Fracturing Injections at Oak Ridge National Laboratory - 1975 Series, ORNL/TM-5545, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Weeren, H. O. 1980. Shale Fracturing Injections at Oak Ridge National Laboratory - 1977-1979 Series, ORNL/TM-7421, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

APPENDIX

STATISTICAL DESIGN AND ANALYSIS RESULTS FOR PHOSPHATE/SULFATE N-REACTOR WASTE GROUTS

APPENDIX - STATISTICAL DESIGN AND ANALYSIS RESULTS
FOR PHOSPHATE/SULFATE N-REACTOR WASTE GROUTS

CONTENTS

INTRODUCTION	A.3
EXPERIMENTAL SPECIFICATIONS	A.3
STATISTICAL DESIGN METHODS	A.4
MODELING PROCEDURES	A.9
Analysis of Variance	A.9
Property Modeling	A.10
Lack of Fit	A.10
Effects Plots	A.11
MODELING AND ANALYSIS OF VARIANCE RESULTS	A.14
Results for the Reynolds Number	A.16
Results for Penetration Resistance	A.16
Results for Drainable Liquids	A.22
OPTIMIZATION/SIMULATION RESULTS	A.24
REFERENCES.....	A.30

FIGURES

A.1	Effects Plots for Reynolds Number with Mix Ratios 7, 10 and 13 lb/gal	A.17
A.2	Effects Plots for Reynolds Number with Mix Ratios 7, 7.5 and 8 lb/gal	A.18
A.3	Effects Plots for Penetration Resistance at 7 Days with Mix Ratios 7, 7.5 and 8 lb/gal	A.21
A.4	Effects Plots for Drainable Liquids with Mix Ratios 7, 7.5 and 8 lb/gal	A.25

TABLES

A.1	Experimental Ranges of Dry Blend Components	A.4
A.2	Optimal Set of Dry Blends	A.7
A.3	Analysis of Variance and Pseudo-Coefficients for Log N_{Re}	A.15
A.4	Analysis of Variance and Pseudo-Coefficients for Log Penetration Resistance at 24 Hours	A.19
A.5	Analysis of Variance and Pseudo-Coefficients for Log Penetration Resistance at 7 Days	A.20
A.6	Analysis of Variance and Pseudo-Coefficients for Log Drainable Liquids at 24 Hours	A.22
A.7	Analysis of Variance and Pseudo-Coefficients for Log Drainable Liquids at 7 Days	A.23
A.8	Results of Optimization/Simulation with Objective of Simultaneously Maximizing Predicted Reynolds Number and Predicted Penetration Resistance at 7 Days	A.28

INTRODUCTION

This appendix contains results of a statistically designed study of Phosphate/Sulfate N-Reactor Waste grouts. In many experimental studies, one-at-a-time variation of a parameter or component in a mixture is used in an attempt to determine the effect on the properties under study. This technique may be effective if the mixture is relatively simple and the parameters under investigation are limited. However, using the one-at-a-time variation technique would be extremely time-consuming and expensive for grout formulation development and variability studies that encompass a large compositional space. An alternative technique uses statistically designed experiments that yield the maximum amount of useful information for the time and resources spent on experimentation. Moreover, if properly designed, such an experiment will lead to sound, defensible conclusions about the effects of varying the individual parameters or components and their interaction effects on the properties being studied. Prediction models fitted to the data from a designed experiment can be used to explore parameter and component combinations that were not included in the experiment but are inside the region defined by the experimental ranges of the parameters and components. This strategy can be used to great advantage in identifying parameter and component combinations that yield desirable values of the properties being studied.

EXPERIMENTAL SPECIFICATIONS

Simulated Phosphate/Sulfate N-Reactor Waste was mixed with each of 21 distinct dry solids blends at three mix ratios: 7, 10, and 13 pounds of dry solids per gallon of waste. The experimental ranges of the dry solids blend components are shown in Table A.1.

When performing an experiment of this type, careful control of materials composition is essential. Both the liquid and the dry solids were prepared in sufficiently large, well homogenized batches so that the same batch could be used throughout the study. Thus, a 100 L batch of the synthetic

TABLE A.1. Experimental Ranges of Dry Blend Components

<u>Component</u>	<u>Minimum Wt%</u>	<u>Maximum Wt%</u>
Cement	30	80
Fly Ash	20	70
Attapulgate Clay	0	20
Indian Red Pottery Clay	0	20

Phosphate/Sulfate N-Reactor Waste and 12-kg batches of each dry solids blend were prepared. This eliminated batch-to-batch variations that could have obscured important information in the experimental data.

Each of the dry blends was prepared in a twin-shell V-blender for 23 hours and stored in plastic bags until used. In all cases, grouts were prepared using one liter of simulated waste solution. The solution and 0.2 mL tributylphosphate were added to a Hobart mixer prior to the solids addition. Tributylphosphate was added as a defoaming agent. The grouts were mixed for three minutes at the low speed of the mixer using a wire whip. The rheological properties of the grouts were measured with a Rotovisco RV100 viscometer. Shear stress was determined at 10% increments in shear rate up to 1170 per second. In addition to the rheological property measurements, density, vol% drainable liquids, and penetration resistance were measured. The percent drainable liquids was determined at 1, 2, and 24 hours and 7 days by visual observation of the grouts in 250-mL graduated cylinders and 9.5-cm diameter by 15.2-cm-high cylinders. The respective length-to-diameter ratios for these cylinders were 8.1 and 1.6. Penetration resistance was measured at 24 h and 7 days using an Acme Penetrometer.^(a)

STATISTICAL DESIGN METHODS

This study differs from a typical mixtures study, because the liquid waste was not treated as a component in the overall mixture. Instead, each dry-solids blend was mixed with the simulated liquid waste at the three mix ratios: 7, 10 and 13 lb/gal.

(a) Manufactured by Humboldt Manufacturing Company, Norridge, Illinois.

The experimental design strategy was to determine an optimal set of dry blends to include in the experiment in order to obtain data for fitting a special cubic polynomial model (Cornell 1981), assuming initially that there is only one mix ratio. This optimal set of dry blends would then be mixed with the liquid at each of the three mix ratios. The special cubic polynomial model has the form:

$$y = \sum_{i=1}^4 \beta_i X_i + \sum_{i < j} \beta_{ij} X_i X_j + \sum_{i < j < k} \beta_{ijk} X_i X_j X_k + e \quad (1)$$

where y = property (or its logarithm)

X_i = i th dry-blend pseudo-component (defined below)

e = Residual error including pure error and lack of fit

and where the β_i , β_{ij} and β_{ijk} are unknown coefficients.

For a particular dry blend, the pseudo-components X_i in Equation (1) are given by

$$X_i = \frac{C_i - a_i}{1 - \sum_{i=1}^4 a_i} \quad (2)$$

where C_i is the proportion of the i th component in the dry blend and a_i is the lower bound for the i th component as given in Table A.1. Pseudo-components are used rather than the original component proportions for computational reasons.

The selection of the optimal set of dry blends was performed in three stages. First, the dry solids component ranges were used in specialized computer algorithms to generate a set of 35 candidate dry blends that included the extreme vertices, overall centroid, face and edge centroids, and centroid variants of the experimental region.

These candidate dry blends were used in ADDEXC, a computer-aided experimental design algorithm developed in accordance with the methods described by Wynn (1970) and St. John and Draper (1975). The eight centroid variants and the overall centroid were forced into the design (i.e., they were never allowed

to leave the design). These were augmented with the eight extreme vertices for use as a 17-blend starting design. The "exchange" and "add" options in ADDEXC were then applied in an alternating sequence until very little improvement could be achieved by continuing. No replicates were allowed to enter the design at this stage. This process yielded a 23-blend design. This design was then modified by forcing three additional replicates of the overall centroid into it. The resulting design was then entered as a starting design in ADDEXC and design points were allowed as candidates. This resulted in the addition of one replicate of each of four dry blends that were already in the design.

There were a total of 30 dry blends in the design. These include the 21 distinct dry blends, shown in Table A.2, and nine additional replicates. The overall centroid, blend M9, is replicated four times and blends M1, M2, M5, M7, M8 and M18 are each replicated twice. Note that blends M1 and M8 are both extreme vertices and centroid variants.

Assuming that the special cubic model, given by Equation (1), is an adequate approximation model for the properties of interest, data obtained from this design will yield a fitted model with maximum prediction variance $0.82 \sigma^2$ over the experimental region, where σ^2 is the experimental error variance. This design also has global efficiency of 57% with respect to the special cubic model and the full set of candidate blends. The criteria for a good design are a maximum prediction variance no larger than σ^2 and a global efficiency of at least 50%. Thus, the chosen design can be classed as a good design for obtaining data to fit the special cubic model.

The 30 dry blends in Table A.2 were mixed with the simulated liquid waste at each of the three mix ratios (7, 10 and 13 lb/gal). However, the resulting 90 dry blend/mix ratio combinations were mixed and tested in a completely random order.

Because the liquid waste is not treated as a component of the blend in the usual mixture experiment context, the appropriate methods of statistical

TABLE A.2. Optimal Set of Dry Blends

Blend No.	Cement	Fly Ash	Attapulgate	IRPC(a)	
M1	80.00	20.00	0.00	0.00	Extreme Vertices
M2	60.00	20.00	0.00	20.00	
M3	55.00	20.00	25.00	0.00	
M4	35.00	20.00	25.00	20.00	
M5	30.00	50.00	0.00	20.00	
M6	30.00	25.00	25.00	20.00	
M7	30.00	45.00	25.00	0.00	
M8	30.00	70.00	0.00	0.00	
M9	45.30	35.30	10.61	8.79	Overall Centroid
M10	30.00	57.50	12.50	0.00	Face and Edge Centroids
M11	30.00	37.50	12.50	20.00	
M12	67.50	20.00	12.50	0.00	
M13	47.50	20.00	12.50	20.00	
M14	55.00	45.00	0.00	0.00	
M15	45.00	35.00	0.00	20.00	
M1	80.00	20.00	0.00	0.00	Centroid Variants
M16	30.00	42.05	15.29	12.67	
M17	52.05	20.00	15.29	12.67	
M8	30.00	70.00	0.00	0.00	
M18	49.42	39.42	0.00	11.16	
M19	39.71	29.71	25.00	5.58	
M20	48.56	38.56	12.87	0.00	
M21	41.14	31.14	7.72	20.00	

(a) Indian Red Pottery Clay.

analysis and modeling are different than those used with typical mixtures data. Let the standardized mix ratio be denoted by

$$z = \frac{(\text{Mix Ratio}) - 10}{3} \quad (3)$$

Then at the i th distinct dry blend ($i=1,2,\dots,21$), the property response (or its logarithm) at the j th mix ratio is approximated by a second-order polynomial model of the form

$$y_{ij} = \gamma_{i0} + \gamma_{i1}z_j + \gamma_{i2}z_j^2 + \delta_{ij} \quad (4)$$

where γ_{i0} , γ_{i1} and γ_{i2} are unknown coefficients specific to the ith dry blend, and δ_{ij} is the residual error.

If the models given by Equations (1) and (4) are "crossed," the resulting model can be algebraically reduced to the form

$$\begin{aligned}
 y = & [b_{(1)0} + b_{(1)1} Z + b_{(1)2} Z^2] x_1 \\
 & + [b_{(2)0} + b_{(2)1} Z + b_{(2)2} Z^2] x_2 \\
 & + [b_{(3)0} + b_{(3)1} Z + b_{(3)2} Z^2] x_3 \\
 & \cdot \\
 & \cdot \\
 & \cdot \\
 & + [b_{(13)0} + b_{(13)1} Z + b_{(13)2} Z^2] x_1 x_2 x_4 \\
 & + [b_{(14)0} + b_{(14)1} Z + b_{(14)2} Z^2] x_2 x_3 x_4 \\
 & + \epsilon
 \end{aligned}
 \tag{5}$$

where y is the response property (or its logarithm) at any dry blend in the experimental region applied at any mix ratio between 7 and 13 lb/gal. The $b_{(k)j}$ are unknown coefficients (there are 42 of them), and ϵ is the residual error. Note that Equation (5) has the same basic structure as Equation (1), except that the unknown β_i , β_{ij} and β_{ijk} in Equation (1) are expressed as second-order polynomial functions of Z in Equation (5). That is, at a given mix ratio, the property model is a special cubic polynomial as given in Equation (1), but the coefficients β_i , β_{ij} and β_{ijk} depend on the value of the mix ratio. The 90 dry blend/mix ratio combinations described above provided

adequate data to fit the model given by Equation (5), estimate the experimental error variance, and test for lack of fit. The modeling process and results are described below.

MODELING PROCEDURES

Five properties were modeled after the results from the experiments were obtained. These properties were the Reynolds number, penetration resistance at 24 hours, penetration resistance at 7 days, drainable liquid at 24 hours, and drainable liquid at 7 days. Drainable liquid data from the smaller L/D cylinders were used for modeling.

Analysis of Variance

The experimental data for each property were initially analyzed by applying the two-way analysis of variance method, where the "factors" were dry solids blend ($i=1,2,\dots,21$) and mix ratio ($j=1,2,3$). This preliminary analysis revealed that the experimental error standard deviation (the square root of the experimental error variance) for each property is proportional to the measured property value. However, the least squares regression method to be used in fitting property models assumes that the experimental error variance is constant over the experimental region. In an attempt to satisfy this assumption, it was found that for each property the logarithm has a much more constant experimental error variance than the property itself. Thus, the modeling process was carried out using the logarithm of each property as the "property" variable.

For each set of log property data, the two-way analysis of variance method was applied to obtain an estimate of the experimental error (pure error) sum of squares, degrees of freedom and mean square. This analysis indicated that each log property is strongly affected by changes in the dry blend and by changes in the mix ratio. It also indicated that the effect of changing the mix ratio is strongly dependent on the dry solids blend (i.e., there is an interaction effect). The presence of these significant effects indicates that fitting a prediction model of the form given by Equation (5) to each set of log property data could potentially account for a major portion of the total variability.

Property Modeling

A stepwise regression algorithm, specially adapted for this study, was used to select a subset of terms from Equation (5) for each log property and to estimate the unknown coefficients. The property modeling process was the same for each property, but a different set of terms was selected for each of the property models. The stepwise regression algorithm proceeds by adding terms one at a time to the model until further additions do not improve the fit of the model to the data. Because the dry blend component fractions and their two-way and three-way cross-products are inherently correlated, bringing a term into the model can reduce the significance of other terms that are already in the model. Thus, at each step in the model building process, the stepwise regression algorithm automatically checks the statistical significance of each term in the model and eliminates any terms that have become insignificant.

Lack of Fit

In the above brief explanation of the modeling process, the question arises as to whether the resulting fitted model adequately characterizes the log property data or whether the model has a significant lack of fit (LOF). This question is resolved as follows. A set of log property data has a certain amount of variability, and an attempt is made to account for as much of this variability as possible with a predictive model that is fitted to the log property data. If a large portion (approximately 90%) of the variability is explained by the fitted model, and the remaining variability is essentially due to experimental error, then the model fits well. The proportion of the total variability explained by the fitted model is denoted by R^2 . Because adding terms to a model always increases R^2 , R_A^2 is considered instead, where the "A" implies adjustment for the number of terms in the model. R_A^2 is always between 0 and 1, and values above 0.90 generally indicate a satisfactory fit. However, R_A^2 does not take into account the estimate of the experimental error variance. Even if a fitted model explains a large portion of the total variability in the log property data, it still has a significant LOF if the variability that is not accounted for is much larger than the experimental error variance.

To test for a significant lack of fit, the ratio

$$\text{LOF-F} = \frac{\text{LOF Mean Square}}{\text{Pure Error Mean Square}} \quad (6)$$

is computed, using quantities from the analysis of variance and the stepwise regression analysis for a particular property. If this ratio is larger than the appropriate F-distribution table value, the fitted log property model is said to have a statistically significant lack of fit.

Care must be taken when considering the result of an LOF-F test, because it is strongly influenced by the estimate of the experimental error variance obtained from replicating several dry blend/mix ratio combinations in the experiment. If the estimate of the experimental error variance is large, indicating that the data have limited reproducibility, the LOF may be statistically insignificant, but R_A^2 will tend to be lower. On the other hand, when the estimate of the experimental error variance is very small (for example, from replicates with zero property values), the LOF-F test may indicate a statistically significant LOF when none exists or when the LOF is too small to be of practical concern. Hence, in assessing the fit of the model, R_A^2 and the LOF-F test must be considered together with the experimental error variance estimate.

Effects Plots

The effects on the grout properties that result from varying the proportion of a given component of the dry solids and/or varying the mix ratio are of great value in formulation development. The ability to calculate the effect of variations in the formulation on the final grout properties eliminates costly and time-consuming experimental work that would normally be performed to determine grout properties for a range of compositions. Grout properties are modeled to aid in understanding and predicting these effects, and the fitted models can be used to construct a meaningful and easily understandable display of these effects.

In some fitted model applications, the effect of a particular variable (e.g., amount of fly ash) on a property (e.g., Reynolds number) is characterized by changing the variable of interest while holding all other variables in the fitted model at fixed levels. However, this is not possible with a

mixtures experiment because of the restriction that the sum of the proportions of the dry blend components must equal one. Thus, when one component is changed, the others cannot remain fixed. Therefore, the technique described below was used for estimating and graphically displaying component and mix ratio effects from the fitted models in this study. This technique is an adaptation of the methodology introduced by Piepel (1982) for use with typical mixtures experiments.

At a particular mix ratio, a component effect is defined as the change in the predicted property value (e.g., Reynolds number) when the proportion of a component (e.g., fly ash) is changed. Because the fitted property models have cross-product terms that introduce curvature in the predicted "response surfaces," it is necessary to consider both total component effects (change in predicted values due to the maximum possible change in a component) and partial component effects (changes in predicted values due to small incremental changes in a component). The technique involves choosing a "line" through the experimental region for each component along which the component of interest varies from its lower to its upper bound. The proportions of the other components are held fixed relative to each other, but their cumulative proportion increases or decreases to offset changes in the component being studied.

For this study, the "effects line" for a particular component is defined by starting at the reference dry blend (41% cement, 40% fly ash, 11% attapulgite clay, and 8% Indian Red Pottery Clay) transforming to pseudo-components, holding the other three components at that proportion relative to each other, and then moving in small increments along the pseudo-component axis towards the lower bound of the component of interest (the total amount of the blend of the other three components is incrementally increased to offset the incremental decreases in the component of interest). The procedure is repeated in reverse to move in small increments along the pseudo-component axis from the reference dry blend to the upper bound of the component of interest. The total amount of the blend of the other three components is incrementally decreased to offset the incremental increases in the component of interest.)

In the presentation of results for each property, the fitted model is used to predict along each component "effect line." Graphical presentation of these

predicted values provides an easily interpreted illustration of the effect of changing each dry blend component over its experimental range while holding the mix ratio at a fixed level. For a given mix ratio and a given property, plotting these component effects for all components on the same graph allows easy comparison of their effects relative to each other. This graph is called an "effects plot" for the property of interest at a given mix ratio. Because these plots "intersect" at the reference dry blend, an effects plot illustrates how deviations from the reference dry blend will affect the property of interest. Each graph shows the predicted property values along the component effect lines for the four components plotted versus wt% change in the components from the reference dry blend. This graph is called an "effects plot" for the property of interest at a given mix ratio. Comparing the effects plots for a given property at different mix ratios provides a means for visually assessing the effect of varying the mix ratio.

MODELING AND ANALYSIS OF VARIANCE RESULTS

This section discusses the modeling results for each log property. The results include an ANOVA table, R_A^2 value, the LOF-F test result, the estimated pseudo-coefficients and their standard deviations. Note that each model was fitted in terms of the pseudo-components and standardized mix ratios computed from Equations (2) and (3). A pseudo-component term in a fitted model is indicated by the first letter of the corresponding dry solids component (i.e., C, F, A or I). Also, ZL indicates the standardized mix ratio, and ZQ represents the square of ZL. For example, in Table A.3, the first term in the fitted model is 4.26283(C), and the last term is -7.30598(P)(A)(I)(ZQ).

To illustrate application of the fitted models for predicting property values, suppose that it is of interest to predict N_{Re} at dry blend 1 (in Table A.2) when the mix ratio is 9 lb/gal. The pseudo-component quantities C, A, F and I are computed from Equation (2) as follows:

$$C = (0.80 - 0.30)/(1.0 - 0.50) = 1.0$$

$$F = (0.20 - 0.20)/(1.0 - 0.50) = 0.0$$

$$A = (0.0 - 0.0)/(1.0 - 0.50) = 0.0$$

$$I = (0.0 - 0.0)/(1.0 - 0.50) = 0.0$$

The quantities ZL and ZQ are computed from Equation (3) as follows:

$$ZL = (9.0 - 10)/3 = -0.33333$$

$$ZQ = (ZL)(ZL) = 0.11111$$

TABLE A.3. Analysis of Variance (ANOVA) and Pseudo-Coefficients for Log N_{Re}

Analysis of Variance

Source	DF	SS	MS
Total	70	0.39221E+02	
Regression	15	0.38345E+02	0.25564E+01
Error	55	0.87510E+00	0.15911E-01
LOF	32	0.66230E+00	0.20697E-01
Pure Error	23	0.21280E+00	0.92521E-02

Adjusted R-Squared = 0.9716

Lack of Fit F Test $F = 2.24$, significant at the 0.05 level

Component				Pseudo Coeff	Std Dev
C				4.26283	0.08380
P				4.31359	0.12545
A				-4.57106	0.90157
I				3.81475	0.16975
C	X A			5.99435	1.40050
P	X A			5.21325	1.70141
A	X I			8.35994	1.89810
P	X A	X I		-9.13182	6.41426
C	X ZL			-0.32945	0.08506
P	X ZL			-0.29660	0.08295
I	X ZL			-0.46129	0.16231
C	X A	X ZL		-0.92365	0.59894
A	X I	X ZL		-2.87161	1.00558
P	X ZQ			-0.07631	0.09499
P	X A	X ZQ		3.19560	1.33167
P	X A	X I	X ZQ	-7.30598	6.66414

The predicted value of $\log N_{Re}$ is

$$\begin{aligned}
 \log N_{Re} &= 4.26283(1.0) + 0.0 + 0.0 + 0.0 + 0.0 + 0.0 + 0.0 + 0.0 \\
 &\quad + (-0.32945)(-0.33333) + (\text{all remaining terms are } 0.0) \\
 &= 4.26283 + 0.10982 = 4.37265
 \end{aligned}$$

The predicted value of N_{Re} is then computed by taking the antilog of 4.37265 which gives

$$N_{Re} = 23,856$$

Results for the Reynolds Number (N_{Re})

The log N_{Re} modeling results from the stepwise regression algorithm are displayed in Table A.3. The resulting fitted model has 16 terms, with $R_A^2 = 0.97$, and the lack-of-fit (LOF) is statistically significant at the 0.05 level. Although the LOF is statistically significant, the value $R_A^2 = 0.97$ indicates that this model should be quite useful for predicting the major trends in log N_{Re} (and thus N_{Re}) as the dry blend and mix ratio are varied within the experimental region.

Effects plots for N_{Re} at mix ratios of 7, 10 and 13 lb/gal are displayed in Figure A.1. At all three mix ratios, cement (C) and fly ash (F) have strong positive effects; that is, increasing cement or fly ash in the dry blend increases the predicted N_{Re} . Attapulgite (A) shows a strong negative effect at all mix ratios; that is, increasing attapulgite in the dry blend decreases the predicted N_{Re} . Indian Red Pottery Clay (I) shows a noticeable positive effect at the 7 lb/gal mix ratio, but this decreases to a negligible effect as the mix ratio increases to 13 lb/gal. Increasing the mix ratio from 7 to 13 lb/gal decreases the overall magnitude of the predicted N_{Re} values, thus decreasing the size of the dry blend component effects.

Effects plots for N_{Re} at mix ratios of 7, 7.5 and 8 lb/gal are displayed in Figure A.2. The plots are very similar; the main difference is that increasing the mix ratio from 7 to 8 lb/gal decreases the overall magnitude of the predicted N_{Re} values. The reference grout has predicted N_{Re} values of 5509 at 7 lb/gal, 4241 at 7.5 lb/gal, and 3327 at 8 lb/gal. Although these differences have practical significance, they are not readily discernible by a visual comparison of the plots.

Results for Penetration Resistance

Penetration resistance was measured at 24 h and at 7 days. The modeling results from the stepwise regression algorithm for log penetration resistance

FIGURE A.1. Effects Plots for Reynolds Number with Mix Ratios 7, 10 and 13 lb/gal

are displayed in Tables A.4 and A.5 for 24 h and 7 days, respectively. The model fitted to the 24-h data has 14 terms, with $R_A^2 = 0.78$, and the lack of fit (LOF) is statistically significant at the 0.05 level. The model fitted to the 7-day data has 24 terms, with $R_A^2 = 0.91$, and the lack of fit (LOF) is not statistically significant at the 0.05 level.

FIGURE A.2. Effects Plots for Reynolds Number with Mix Ratios 7, 7.5 and 8 lb/gal

TABLE A.4. Analysis of Variance (ANOVA) and Pseudo-Coefficients for Log Penetration Resistance at 24 Hours

Analysis of Variance

Source	DF	SS	MS
Total	75	0.52809E+02	
Regression	13	0.43380E+02	0.33369E+01
Error	62	0.94293E+01	0.15209E+00
LOF	37	0.75860E+01	0.20503E+00
Pure Error	25	0.18433E+01	0.73731E-01

Adjusted R-Squared = 0.7840

Lack of Fit F Test F = 2.78, significant at the 0.05 level

Component				Pseudo Coeff	Std Dev
C				0.01731	0.29708
P				0.07987	0.43576
A				2.42799	0.73617
I				0.29139	0.75764
C	X P			-1.43451	1.34996
C	X A			-4.36533	2.34914
P	X ZL			-0.79508	0.27412
I	X ZL			-1.29084	0.52123
C	X P	X ZL		1.73119	1.42515
C	X P	X A	X ZL	-16.33631	12.67618
C	X P	X I	X ZL	-8.79501	10.73899
P	X A	X I	X ZL	14.07412	10.41074
P	X ZQ			0.57239	0.33982
I	X ZQ			0.90708	0.59508

The model fitted to the 24-h data has both a statistically significant LOF and a low R_A^2 value; thus, it was not used in the optimization/sensitivity analysis or to construct effects plots. However, the model fitted to the 7-day data should be quite useful for predicting the major trends in log penetration resistance at 7 days (and thus penetration resistance at 7 days) as the dry blend and mix ratio are varied within the experimental region.

Effects plots for penetration resistance at 7 days at mix ratios of 7, 7.5 and 8 lb/gal are displayed in Figure A.3. The major difference among the three plots is that the overall magnitude of the predicted penetration resistance

TABLE A.5. Analysis of Variance (ANOVA) and Pseudo-Coefficients for Log Penetration Resistance at 7 Days

Analysis of Variance

Source	DF	SS	MS
Total	73	0.60284E+01	
Regression	23	0.56639E+01	0.24525E+00
Error	50	0.36457E+00	0.72914E+02
LOF	25	0.60061E+01	0.24024E+02
Pure Error	25	0.30451E+00	0.12180E-01

Adjusted R-Squared = 0.7840

Lack of Fit F Test F = 2.78, significant at the 0.05 level

Component				Pseudo Coeff	Std Dev
C				3.91251	0.07880
P				2.99052	0.08159
A				4.02268	0.33027
I				2.89066	0.19464
C	X P			1.79066	0.38072
C	X A			-0.67192	0.62639
P	X A			1.85576	0.75648
C	X I			0.84952	0.50227
C	X P	X A		-10.14066	3.27000
C	X ZL			0.17967	0.04324
P	X ZL			0.14217	0.04802
A	X ZL			0.61507	0.14634
C	X P	X ZL		0.45165	0.23539
P	X I	X ZL		-0.30116	0.23151
C	X P	X A	X ZL	-3.18601	2.09349
P	X A	X I	X ZL	1.92477	1.91361
C	X ZQ			-0.13118	0.06320
P	X ZQ			0.27269	0.06717
C	X P	X ZQ		-1.03680	0.31000
P	X A	X ZQ		-1.38866	0.46760
C	X I	X ZQ		0.40060	0.27311
P	X I	X ZQ		0.57911	0.28180
C	X P	X A	X ZQ	6.61162	2.62509
P	X A	X I	X ZQ	-2.27053	1.64264

FIGURE A.3. Effects Plots for Penetration Resistance at 7 Days with Mix Ratios 7, 7.5 and 8 lb/gal

values increases as the mix ratio increases. The reference dry blend has predicted penetration resistance values of 2103 psi at 7 lb/gal, 2263 psi at 7.5 lb/gal and 2441 psi at 8 lb/gal.

Results for Drainable Liquids

Drainable liquids were measured at 24 h and at 7 days. The modeling results from the stepwise regression algorithm for log drainable liquids are displayed in Tables A.6 and A.7 for 24 h and 7 days, respectively. For the purpose of working in terms of log drainable liquids, all zero values were replaced by 0.05. The model fitted to the 24-h data has 14 terms, with $R_A^2 = 0.95$, and the lack of fit (LOF) is statistically significant at the

TABLE A.6. Analysis of Variance (ANOVA) and Pseudo-Coefficients for Log Drainable Liquids at 24 Hours

Analysis of Variance			
Source	DF	SS	MS
Total	74	0.67621E+02	
Regression	13	0.64834E+02	0.45690E-01
Error	61	0.27871E+01	0.69339E-01
LOF	37	0.25655E+01	0.69339E-01
Pure Error	24	0.22153E+00	0.92306E-02

Adjusted R-Squared = 0.9500

Lack of Fit F Test F = 7.51, significant at the 0.05 level

Component				Pseudo Coeff	Std Dev
C				1.48755	0.15068
P				1.20781	0.14167
A				-6.60351	0.72377
I				1.24990	0.29061
C	X A			5.84380	1.64252
C	X P	X A		12.43053	6.49234
P	X A	X I		5.62912	7.75413
C	X ZL			-0.13748	0.14803
A	X ZL			-1.99655	0.65887
I	X ZL			-0.31446	0.29011
C	X A	X ZL		2.48554	1.51780
C	X A	X I	X ZL	-4.76515	7.21575
P	X A	X I	X ZL	7.88622	7.51875
C	X A	X I	X ZQ	5.15946	5.29526

TABLE A.7. Analysis of Variance (ANOVA) and Pseudo-Coefficients for Log Drainable Liquids at 7 Days

Analysis of Variance

Source	DF	SS	MS
Total	75	0.10998E+03	
Regression	18	0.10568E+03	0.58712E+01
Error	57	0.42947E+01	0.75345E-01
LOF	32	0.41488E+01	0.12965E+00
Pure Error	25	0.14588E+00	0.58354E-02

Adjusted R-Squared = 0.9486

Lack of Fit F Test F = 22.22, significant at the 0.05 level

Component				Pseudo Coeff	Std Dev
C				1.52949	0.15881
P				1.12935	0.15939
A				-3.17704	1.49000
I				0.84208	0.33815
P	X A			-6.56920	2.70913
A	X I			-5.26020	3.04236
C	X P	X A		-26.65382	11.57866
C	X A	X I		-24.59097	11.37492
C	X ZL			-0.14014	0.14895
A	X ZL			-1.25122	0.58387
I	X ZL			-0.35183	0.34428
C	X P	X A	X ZL	-18.82803	8.27807
C	X P	X I	X ZL	-5.17195	5.92488
C	X A	X I	X ZL	-15.33914	8.13398
P	X A	X I	X ZL	8.14154	7.79643
C	X A	X ZL		-3.00174	1.80006
P	X A	X ZL		1.14538	1.51128
C	X P	X A	X ZL	18.63526	10.60343
C	X A	X I	X ZL	27.49229	9.51335

0.05 level. The model fitted to the 7-day data has 19 terms, with $R_A^2 = 0.95$, and the lack of fit (LOF) is statistically significant at the 0.05 level.

Although both models have statistically significant LOF, the values $R_A^2 = 0.95$ indicate that these fitted models should be quite useful for predicting the major trends in log drainable liquids (and thus drainable liquids) at both 24 hours and 7 days as the dry blend and mix ratio are varied within the experimental region. However, only the model fitted to the 7-day data was used in the optimization/sensitivity analysis or to construct effects plots.

Effects plots for drainable liquids at 7 days at mix ratios of 7, 7.5 and 8 lb/gal are displayed in Figure A.4. The major differences in the three plots are that with mix ratios of 7.5 or 8 lb/gal, small deviations from the reference dry blend have less effect on the predicted drainable liquids than when the mix ratio is 7 lb/gal. The overall magnitude of the predicted drainable liquids decreases as the mix ratio increases from 7 to 8 lb/gal. The reference dry blend has predicted drainable liquids values of 1.22 vol% at 7 lb/gal, 0.62 vol% at 7.5 lb/gal, and 0.34 vol% at 8 lb/gal.

OPTIMIZATION/SIMULATION RESULTS

The fitted models can be used to predict the properties of any hypothetical dry blend/mix ratio combination in the experimental region. This accommodated a simulated search of the experimental region to locate a range of dry blend/mix ratio combinations that yield processible grouts with desirable predicted properties. Because the cost per ton of the dry blend components is known, the cost of the dry blend required to process a gallon of liquid waste was computed for each simulated dry blend/mix ratio combination. Also, the volume of each simulated grout was computed as the mix ratio divided by the composite density of the dry blend. The cost and volume were then included in the optimization, and tradeoffs were evaluated between minimizing cost and volume, maximizing Reynolds number, and maximizing penetration resistance.

The process of searching the experimental region began by densely "filling" the experimental region with 7,392 distinct simulated dry blends. Each of the 7,392 simulated dry blends was evaluated at mix ratios of 7, 8, 9, 10, 11, 12, and 13 lb/gal. The predicted property values, cost and volume were computed for each of the resulting 51,744 dry blend/mix ratio combinations.

The properties of a processible grout must satisfy the following criteria:

- Reynolds number larger than 2100
- pressure drop less than 11 psi/100 ft of 2-in. pipe
- no drainable liquids.

FIGURE A.4. Effects Plots for Drainable Liquids with Mix Ratios 7, 7.5 and 8 lb/gal

Two additional recommendations were added to the criteria for screening the simulated grouts:

- The proportion of each dry blend component must be at least 5 wt%.
- The mix ratio should not exceed 10 lb/gal.

For each of 51,744 simulated grouts, the predicted properties, dry blends and mix ratios were examined, and all grouts that did not satisfy the above criteria were eliminated. This left 6,584 simulated grouts in the data base; that is, about 87% of the experimental region was eliminated on the basis of these criteria.

To allow for error in predicting drainable liquids, predicted values greater than 1.0 were eliminated. It is quite possible that a grout with a predicted drainable liquids value between 0.0 and 1.0 could have a true drainable liquids value larger than 1.0; however, for the purposes of this study, this was not considered to be a serious concern.

The next objective was to search the remaining 6,584 cases to determine whether a range of grouts exist that simultaneously maximize the predicted Reynolds number and penetration resistance while minimizing cost and volume. The 6,584 cases were analyzed in various ways to aid in identifying tradeoffs that might affect this optimization. Based on these analyses, the following observations were made:

- Mix ratio and volume were highly correlated; i.e., minimizing volume also minimized mix ratio.
- There was no indication of a tradeoff between minimizing cost and maximizing predicted Reynolds number when volume and penetration resistance were ignored.
- An obvious tradeoff existed between minimizing cost and maximizing predicted penetration resistance.
- There was no indication of a tradeoff between minimizing volume and maximizing predicted Reynolds number when cost and penetration resistance were ignored.

- An obvious tradeoff existed between maximizing predicted penetration resistance and minimizing volume.
- There was no indication of a tradeoff between maximizing predicted penetration resistance and maximizing Reynolds number when cost and volume were ignored.

Because a tradeoff exists between maximizing predicted penetration resistance and minimizing volume and cost, the optimization search was conducted in stages. The results are displayed in Table A.8. The first stage of the optimization involved searching all 6,584 cases to locate the simulated grout compositions with maximum predicted values of both Reynolds number and penetration resistance. The resulting grout compositions all had mix ratios of 10 lb/gal. The "best" four of these compositions are displayed in the bottom section of Table A.8, with the reference grout (41% C, 40% F, 11% A and 8% I) for comparison.

At the next stage of the optimization, grouts with a mix ratio of 10 lb/gal were eliminated from the 6584 cases, and the procedure described in the previous paragraph was repeated. All resulting grouts had mix ratios of 9 lb/gal. The optimization continued by eliminating the cases with mix ratios of 9 lb/gal and then 8 lb/gal. The "best" four grouts from each stage (i.e., for each mix ratio) are displayed in Table A.8 together with the reference dry blend at each mix ratio for comparison. The reference dry blend at the reference mix ratio, 7.5 lb/gal, is also displayed for comparison. The results displayed in Table A.8 emphasize that increasing penetration resistance requires increases in volume and cost.

Note that the reference dry blend at 7 lb/gal would have been eliminated from the processible grout data base because it has a predicted drainable liquids value larger than 1.0. However, its other predicted properties and its cost and volume compare very favorably with the four "best" grouts at 7 lb/gal. At a mix ratio of 8 lb/gal, the reference dry blend has predicted values of both Reynolds number and penetration resistance that are much lower than the "best" four grouts at 8 lb/gal. Note also that for the about the same cost and volume as the reference grout at 7.5 lb/gal, the predicted Reynolds number and penetration resistance could both be substantially increased by switching to a

TABLE A.8. Results of Optimization/Simulation with Objective of Simultaneously Maximizing Predicted Reynolds Number and Predicted Penetration Resistance at 7 Days

Dry Blend Components, wt%				Mix Ratio	Cost	Vol.	Pres. Drop	Drain Liq.	Rey. Num.	Pene. Res. 7 d
C	F	A	I							
40.08	42.58	11.56	5.79	7.	0.266	0.310	3.98	0.94	5168.	2088.
39.85	42.35	11.40	6.39	7.	0.269	0.310	3.96	0.96	5219.	2069.
39.03	44.66	11.31	5.00	7.	0.258	0.311	3.73	0.88	5636.	2058.
37.50	44.26	10.07	8.17	7.	0.272	0.311	3.49	0.98	6378.	1946.
41.00	40.00	11.00	8.00	7.	0.280	0.308	3.87	1.22	5509.	2103.
41.00	40.00	11.00	8.00	7.5	0.300	0.330	4.39	0.62	4241.	2263.
50.89	34.64	9.47	5.00	8.	0.309	0.343	3.80	0.98	5586.	3049.
50.00	35.63	9.38	5.00	8.	0.307	0.344	3.78	0.95	5648.	2997.
49.12	24.85	10.07	15.96	8.	0.393	0.338	3.06	0.90	5829.	2945.
48.05	26.18	9.38	16.40	8.	0.391	0.339	3.01	1.00	6383.	2856.
41.00	40.00	11.00	8.00	8.	0.320	0.352	4.95	0.34	3327.	2441.
57.78	24.03	8.18	10.00	9.	0.399	0.374	3.36	0.99	5705.	4402.
55.00	31.02	7.64	6.34	9.	0.358	0.380	3.61	0.86	5873.	4126.
55.51	25.51	7.64	11.34	9.	0.403	0.376	3.28	0.94	6137.	4165.
52.65	32.14	7.04	8.17	9.	0.366	0.382	3.50	0.90	6399.	3908.
41.00	40.00	11.00	8.00	9.	0.360	0.395	6.26	0.12	2167.	2854.
59.28	29.28	6.43	5.00	10.	0.388	0.418	3.70	0.99	5652.	5613.
58.46	29.71	6.25	5.58	10.	0.391	0.418	3.67	0.98	5799.	5524.
58.13	30.63	6.25	5.00	10.	0.385	0.419	3.67	0.95	5818.	5502.
55.70	31.33	5.78	7.20	10.	0.397	0.421	3.62	0.93	6112.	5163.
41.00	40.00	11.00	8.00	10.	0.400	0.439	7.82	0.06	1523.	3360.

dry blend with approximately 50.5% C, 35% F, 9.5% A and 5% I at a mix ratio of 8 lb/gal. At 10 lb/gal, the reference dry blend would have been eliminated from the processible grout data base because the predicted Reynolds number is less than 2,100.

An additional optimization exercise was conducted to first maximize the predicted Reynolds number while minimizing cost and volume, and then try to maximize predicted penetration resistance. The "best" grouts selected from this approach are the same as those displayed in the third and fourth rows of the 7 lb/gal section of Table A.8.

REFERENCES

- Cornell, J. A. 1981. Experiments with Mixtures. John Wiley and Sons, New York.
- Piepel, G. F. 1982. "Measuring Component Effects in Constrained Mixtures Experiments." Technometrics. 24:29-39.
- St. John, R. C., and N. R. Draper. 1975. "D-Optimality for Regression Designs: A Review." Technometrics. 17:15-23.
- Wynn, H. P. 1970. "The Sequential Generation of D-Optimum Experimental Designs." Annals of Mathematical Statistics. 41:1655-1664.

DISTRIBUTION

<u>No. of Copies</u>	<u>No. of Copies</u>
<u>OFFSITE</u>	
30 DOE Technical Information Center	P. G. Hagan Joint Integration Office Bldg. 3, 2nd Floor 2201 San Pedro N.E. Albuquerque, NM 87110
3 DOE Office of Defense Waste & Transportation Management GTN Washington, DC 20545 ATTN: T. C. Chee, DP-123 G. H. Daly, DP-124 J. E. Lytle, DP-12	E. Maestas DOE West Valley Operations Office P.O. Box 191 West Valley, NY 14171
4 DOE Office of Remedial Action and Waste Technology GTN Washington, DC 20545 ATTN: J. A. Coleman, NE-24 T. W. McIntosh, NE-24 W. R. Voigt, NE-20 H. F. Walter, NE-24	2 DOE Idaho Operations Office 550 Second Street Idaho Falls, ID 83401 ATTN: J. P. Hamric S. T. Hinschberger
A. T. Clark Division of Fuel Material Safety Nuclear Regulatory Commission Washington, DC 20555	F. T. Fong DOE San Francisco Operations 1333 Broadway Oakland, CA 94612
V. Stello Office of the Executive Director for Operations Mail Station 62D9 Nuclear Regulatory Commission Washington, DC 20555	M. R. Jugan DOE Oak Ridge Operations Office P.O. Box E Oak Ridge, TN 37830
G. L. Sjoblom Environmental Protection Agency Office of Radiation Programs 401 M Street, S.W. Washington, DC 20460	W. J. Brumley DOE Savannah River Operations Office P.O. Box A Aiken, SC 29801
J. M. McGough DOE Albuquerque Operations Office P.O. Box 5400 Albuquerque, NM 87185	M. J. Steindler Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60439
	C. S. Abrams Argonne National Laboratory P.O. Box 2528 Idaho Falls, ID 83401

No. of
Copies

- 3 Battelle Memorial Institute
Project Management Division
505 King Avenue
Columbus, OH 43201
ATTN: W. A. Carbeiner
W. S. Madia
B. Rawles
- L. D. Ramspott
Lawrence Livermore National
Laboratory
University of California
P.O. Box 808
Livermore, CA 94550
- D. T. Oakley, MS 671
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM 87544
- 7 Oak Ridge National Laboratory
P.O. Box Y
Oak Ridge, TN 37830
ATTN: J. O. Blomeke
W. D. Burch
R. T. Jubin
E. W. McDaniel
L. J. Mezga
T. L. Sams
O. K. Tallent
- 4 Sandia Laboratories
P.O. Box 5800
Albuquerque, NM 87185
ATTN: D. R. Anderson
R. W. Lynch
W. Weart
Technical Library
- J. R. Berreth
Westinghouse Idaho Nuclear
Co., Inc.
P.O. Box 4000
Idaho Falls, ID 83401

No. of
Copies

- 9 E. I. du Pont de Nemours
& Company, Inc.
Savannah River Laboratory
Aiken, SC 29801
ATTN: M. D. Boersma
J. G. Glasscock
E. J. Hennelly
J. R. Knight
C. A. Langton
M. J. Plodinec
C. T. Randall
H. F. Sturm, Jr.
E. Wilhite
- E. A. Jennrich
EG&G Idaho
P.O. Box 1625
Idaho Falls, ID 83415
- R. Shaw
Electric Power Research
Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94304
- 5 West Valley Nuclear Services
Company
P.O. Box 191
West Valley, NY 14171
ATTN: C. C. Chapman
J. C. Cwynar
J. E. Krauss
S. J. Marchette
J. M. Pope
- J. L. White
Energy Research & Development
Authority
Empire State Plaza
Albany, NY 12223

No. of
Copies

ONSITE

8 DOE Richland Operations Office

E. A. Bracken
C. E. Collantes
C. R. DeLannoy
R. E. Gerton
R. D. Izatt
N. T. Karagianes
M. W. Shupe
J. D. White

18 Rockwell Hanford Operations

T. B. Bergman (2)
L. C. Brown
C. DeFigh-Price
J. E. Riddelle
R. S. Shirley (5)
J. E. Van Beek
L. Vanselow
T. B. Venziano
G. F. Williamson
D. D. Wodrich
R. D. Wojtasek
D. E. Wood
L. L. Zahn

UNC United Nuclear Industries

T. E. Dabrowski/W. J. Kyriazis

2 Westinghouse Hanford Company

R. E. Lerch
J. D. Watrous

No. of
Copies

53 Pacific Northwest Laboratory

R. P. Allen
W. W. Ballard, Jr.
W. F. Bonner
W. M. Bowen
D. J. Bradley
L. A. Bray
J. B. Brown
L. R. Bunnell
H. C. Burkholder
D. G. Coles
W. T. Farris
T. E. Gates
M. S. Hanson
H. Harty
D. G. Huizenga
G. V. Last
R. O. Lokken (10)
P. F. C. Martin
D. McCarthy
J. L. McElroy
T. J. McLaughlin
A. H. McMakin
G. B. Mellinger
D. H. Mitchell
L. G. Morgan
R. J. Serne
J. W. Shade
D. R. Sherwood
S. L. Stein
J. L. Straalsund
D. M. Strachan
L. E. Thompson
R. L. Treat (5)
Publishing Coordination (2)
Technical Report Files (5)