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Summary Report on the Development of a Cement-Based Formula to Immobilize Hanford Facility Waste

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LIST OF ACRONYMS

ANS	American Nuclear Society
HFW	Hanford Facilities Waste
IRPC	Indian Red pottery clay
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PNL	Battelle Pacific Northwest Laboratories
RHO	Rockwell Hanford
TBP	tributyl phosphate
TGF	Transporatble Grout Facility
UNC	United Nuclear Corporation

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ABSTRACT

This report recommends a cement-based grout formula to immobilize Hanford Facility Waste in the Transportable Grout Facility (TGF). Supporting data confirming compliance with all TGF performance criteria are presented.

1. INTRODUCTION

This report develops a range of cement-based blended dry solids that may be mixed with Hanford Facility Waste (HFW) to produce grouts that are processible in off-the-shelf equipment and are compatible with the Transportable Grout Facility (TGF) design. In addition, the selected formula should also (1) optimize waste loading with minimum waste disposal volume increase, (2) use commercially available materials requiring no custom processing, and (3) result in a solid product which, after a reasonable (28-d) cure time, meets all state and federal requirements. These performance requirements have been identified and quantified by Battelle Pacific Northwest Laboratories (PNL) in Milestone 52 (5/30/84).

This report recommends a formula based on experiments with simulated HFW. Supporting processibility and solid performance data are included. The recommended formula will be applied to actual waste by PNL and results reported in PNL Milestone 70 (3-30-86).

2. HFW COMPOSITION

The waste stream for these studies is defined by Rockwell Hanford Operations (Rockwell Hanford)[1] as a 50:50 vol % mixture of sulfate and phosphate wastes. The major components of this waste are shown in Table 1. The development work presented in this report was aimed at producing acceptable grouts with a waste composition encompassing that in Table 1.

2.1 PHOSPHATE WASTE

The phosphate waste that makes up 50% of the reference HFW results from the United Nuclear Corporation (UNC) decontamination operations at the Hanford site using a TURCO decontamination solution. The TURCO solution contains the organics shown in Table 2 and up to 70-wt % H_3PO_4 prior to dilution. For a nuclear reactor decontamination 20,000 gal of TURCO were diluted with water to a total volume of 240,000 gal, resulting in an H_3PO_4 concentration of 8 wt %.

After the reactor decontamination was completed, the 240,000 gal were further diluted with water and "neutralized" with NaOH to pH 12. Sodium nitrite ($\geq$700 ppm) was added to meet a Rockwell tank farm specification, and the resulting 600,000 gal were then shipped to the Rockwell Hanford waste storage area.

Table 1. Possible major component concentrations of HFW

Component	$\underline{M}$
Na_3PO_4	0.15–0.5
Na_2HPO_4	0.01–0.02
Na_2SO_4	0.01–0.02
NaOH	0.01–0.02
$NaNO_2$	0.01–0.02

Table 2. Organic constituents of TURCO 4512-14A[a]

Sodium xylene sulfonate
N,N,N',N' tetrakis (2-hydroxypropyl) ethylene diamine
Ethylene glycol monobutyl ether
2-Mercaptobenzothiazole
Nonylphenoxy polyethoxy ethanol
Complex amine inhibitor[b]
2-Butyne-1,4-diol

[a]TURCO is a trade name of a range of products manufactured by TURCO Products Div. of Purex Corp., Carson, CA 90749.

[b]The complex amine inhibitor is a proprietary product for which the supplier will not disclose chemical composition. No concentrations are given.

The stored waste is defined as phosphate waste. The recipe for synthetic phosphate waste used in these studies is shown in Table 3. The actual waste's radionuclide content is shown in Table 4. Because phosphates act as set retarders for Portland cement, the phosphate concentration was a major consideration in the formulation development studies.

2.2 SULFATE WASTE

Sulfate waste, which makes up the other 50% of HFW, results from recharging ion-exchange columns. The sulfuric acid from this operation is neutralized with NaOH to a pH $\geq$12, as in the case of TURCO waste, and sent to underground tank storage.

This waste is defined as sulfate waste. Although the radionuclide content of this stream is unknown now, it is assumed by Rockwell Hanford to contain ^{137}Cs. The recipe for synthetic sulfate waste used in these studies is shown in Table 5. Sulfate also acts as a set retarder for Portland cement; therefore, its concentration became a major element to be addressed in the formulation studies.

3. PERFORMANCE CRITERIA

A successful grout formula is defined as one that, when mixed with HFW, meets all the performance criteria that are specified by Rockwell Hanford, PNL, and Oak Ridge National Laboratory (ORNL). Collectively, these criteria determine the grout formula recommended in this report.

3.1 ROCKWELL HANFORD PERFORMANCE CRITERIA

These are the Rockwell Hanford performance criteria:

1. The TGF is designed to operate at a nominal capacity of

Table 3. Recipe for ~ 1 L synthetic phosphate waste

Ingredient	Amount
Phosphoric acid decontaminant (TURCO 4512-14A)	36 mL
Water	905 mL
19-M NaOH, aqueous	65 mL
$NaNO_2$	0.88 g

Table 4. Radionuclide content of actual phosphate waste[a] (Determined by gamma energy analysis, except as noted)

Nuclide	Concentration (μCi/L)
^{60}Co	330
^{58}Co	25
^{59}Fe	50
^{51}Cr	36.5
^{54}Mn	28.4
^{103}Ru	5.8
^{137}Cs	not detectable
^{239}Pu	1.4[a]

[a]Calculated value.

Table 5. Recipe for ~ 1 L synthetic sulfate waste

Ingredient	Amount
Na_2SO_4	2.84 g
Water	1 L

50 gal/min, but it should be capable of operating within a range of 30 to 70 gal/min.

2. The grout distribution pump should be capable of supplying a continuous output pressure of 350 psi.
3. The grout should be pumped through 3000 ft of 2-in.-ID distribution pipe.
4. The maximum pressure available to overcome gel strength should be 500 psi.

To comply with the first three criteria, the grout's rheological properties must be tailored to result in a pressure drop <335 psi through 3000 ft of 2-in.-ID pipe at a nominal flow rate of 50 gal/min. The grout's compliance is determined by applying the following series of equations.[2] The first equation is the power law model of the relationship between shear stress and shear rate :

$$S_s = k'(S_r)^{\eta'}, \quad (1)$$

where

S_s = shear stress for non-Newtonian fluids, lb_f/ft^2;

k' = fluid consistency index, $lb_f \cdot s^{\eta'}/ft^2$;

S_r = shear rate, s^{-1};

η' = flow behavior index ($0 < \eta' < 1.0$), dimensionless.

From Eq. (1), the viscosity can be calculated by

$$\mu = 47880\ k'(S_r)^{n'-1}, \qquad (2)$$

where

μ = viscosity, cP.

Equation 2 is then used to calculate the Reynolds number,

$$N_{Re} = \frac{1.86\ V^{(2-n')}\rho}{k'(96/d_i)^{n'}} \qquad (3)$$

where

N_{Re} = Reynolds number, dimensionless;

V = fluid velocity, ft/s (5.1 ft/s at Rockwell Hanford design conditions);

d_i = inside pipe diameter, in. (2 in. at Rockwell Hanford design conditions);

ρ = fluid density, lb/gal.

From Eq. 3, frictional pressure drop can then be calculated:

$$\Delta P_f = \frac{0.039\ L\rho V^2 f}{d_i}, \qquad (4)$$

where

ΔP_f = frictional pressure drop through a straight pipe, psi (limited to $\leq$335 psi at Rockwell Hanford design conditions);

L = pipe length, ft (3000 ft at Rockwell Hanford design conditions);

f = fanning friction factor, dimensionless (f is a function of Reynolds number).

To demonstrate compliance with the fourth criteria, the pump head pressure necessary to overcome the gel strength of a grout, that has been static for 10 min in the distribution pipe, is calculated by

$$P_H = \frac{G \cdot A_W}{(1.44 \times 10^4)A_p} \quad , \tag{5}$$

where

P_H = pump head pressure, psi (limited to $\leq$500 psi at Rockwell Hanford design conditions);

G = 10-min gel strength, $lb_f/100\ ft^2$;

A_W = pipe inside surface area, $in.^2$;

A_p = inside pipe cross-sectional area, $in.^2$.

These calculations were performed assuming a pipe diameter of 2 in. ID and a length of 3000 ft. Thus, an acceptable grout would be tailored to result in $G \leq 100\ lb_f/100\ ft^2$.

3.2 PNL PERFORMANCE CRITERIA

These are the PNL performance criteria:

1. No drainable water should be present 28 d after a grout pour.
2. The grout should have an unconfined compressive strength of at least 50 psi, 28 d after a grout pour.
3. The discharged grout should exhibit an angle of repose $\leq$5°.
4. The solidified grout should exhibit an American Nuclear Society (ANS) 16.1 leachability index $\geq$6 for each radionuclide.

The measurement techniques required to demonstrate compliance with the first three criteria were not specified. Techniques used in the formulation development studies are detailed below.

3.2.1 Drainable Water

The Nuclear Regulatory Commission (NRC) standard recommended for determining drainable water is the ANS 55.1 test. This 55-gal drum test is not amenable to laboratory-scale work and is not representative of the proposed TGF disposal scenario. Consequently, in an attempt to simulate field conditions of covering fresh pours with plastic sheets, drainable water was measured by pouring fresh grout in a cylindrical mold and covering the grout with a water-saturated cloth. The covered grout was allowed to remain stationary for 28 d. Percentage drainable water was then determined as (100 × volume of water collected)(original grout volume)$^{-1}$.

An acceptable grout has no drainable water at 28 d or less.

3.2.2 Compressive Strength

The method suggested by the NRC for measuring unconfined compressive strength is ASTM C39-81. However, the cylindrical samples required by this method are more material- and cost-intensive than the comparable ASTM C109-80 method, which uses 2-in. cubes. Consequently, ASTM C109-80 was used in this study. It has been shown that values obtained by ASTM C109-80 are consistently 20% higher than those obtained by ASTM C39-81; therefore, the compressive strength criterion was set at 60 psi at 28 d with ASTM C109-80 for these studies.

3.2.3 Angle Of Repose

Angle of repose is a design-specific function of shear history, discharge velocity, and the design of both the distribution system and the trench. Consequently, this criterion was not directly applied to the formulation studies. Instead, to meet the intent of this requirement, an acceptable grout was one that would be characterized by an infinite slump as measured by ASTM C143-74. All grouts explored in these studies would be so characterized.

3.2.4 Leachability Index

Leachability index is defined as the inverse of the log of the effective diffusion coefficient as determined by the proposed ANS 16.1 test protocol. Thus, an acceptable grout would result in an effective diffusion coefficient $\leq 10^{-6}$ cm^2/s for each radionuclide. It was beyond the scope of this work to perform these measurements on all of the nuclides of interest; therefore, compliance with this criterion was determined for ^{90}Sr and ^{137}Cs, the two most mobile radionuclides. However, PNL will demonstrate compliance for all radionuclides and report results in Milestone 148 (7-30-86).

3.3 ORNL PERFORMANCE CRITERIA

These are the ORNL performance criteria:

1. Waste loadings should be optimized and waste disposal volume increases kept to a minimum.
2. Commercially available materials should be used that require no custom processing.
3. Grout should achieve turbulent flow below the TGF distribution pump operating limit of 70 gal/min.
4. Grouts made with reasonable deviations from the recommended formula, that are expected during routine TGF operation, should also meet all criteria.

3.3.1 Waste Loading

Target values were solid and liquid waste loading >50 wt % and increases over the original waste volume <30 vol %. To obtain a waste loading >50 wt %, the dry solids blend-to-waste ratio (mix ratio) must be less than the density of the waste (~9 lb/gal).

3.3.2 Materials

To reduce costs and minimize development time, the formulation studies were based on a dry solids blend consisting of components used routinely in the ORNL hydrofracture process for over 20 years.[3] Thus, the major dry solids blend components used in this study were limited to Portland cement, ASTM Class F fly ash, Attapulgite-150 drilling clay, and Indian Red pottery clay. These materials are commercially available in the Richland area.[4]

3.3.3 Turbulent Flow

ORNL experience has shown that grouts should be pumped in turbulent flow to minimize stagnant volumes in the pipe that can eventually result in excessive pressure buildups. This criterion further restricts an acceptable grout to be one that obtains a Reynolds number $\geq$2100 in the TGF distribution pipe at a pump rate less than 70 gal/min [Eq. (3)]. As such, this critical velocity [i.e., velocity at which a Reynolds number of 2100 is obtained using Eq. (3)] would be viewed as the minimum acceptable velocity.

3.3.4 Formula Deviations

Experience with the ORNL hydrofracture process has shown that it is unrealistic to expect the bulk solids blending to be performed at precisely the recommended formula. Reasonable deviations from the reference blend which can be expected are ± 5% relative variation for dry solids blend components. Thus, an acceptable formula with these deviations in the blend composition will also meet all performance criteria.

3.4 SUMMARY OF PERFORMANCE CRITERIA

Based on Rockwell Hanford, PNL, and ORNL performance criteria, an acceptable grout must result in

- frictional pressure drop < 11 psi/100 ft,
- 10-min gel strength < 100 $lb_f/100\ ft^2$,
- 0 vol % drainable water at 28 d,
- 28-d unconfined compressive strength > 60 psi,
- infinite slump,
- ANS 16.1 leachability index for ^{90}Sr and $^{137}Cs \geq 6$,
- solids-to-waste mix ratios ≤ 9,
- critical velocity < 70 gal/min,
- major dry solids blend components should be only component used in the ORNL process, and
- ± 5 % variation in dry solids blend composition.

4. FORMULATION DEVELOPMENT STUDIES

The dry solids blend components used in this study are cement, Indian Red pottery clay, Attapulgite-150, and fly ash. A detailed discussion of the role of each component has been reported previously.[4] In general, these components were chosen for their applicability to HFW, commercial availability, and use in the ORNL facility for ~20 years (Sects. 3.3.2 and

3.3.4). However, it is appropriate that some rationale for the range of components explored in the experimental studies be presented here.

4.1 CEMENT

The physical properties of hardened concrete or grout are determined by the quality of the cement paste (i.e, water and cement). Assuming proper mixing, etc., the quality is controlled by the water-to-cement ratio (w/c). For example, an oil well cement slurry typically contains ~73 wt % cement and has a w/c of 0.38.

In general, a w/c of only 0.25 is required for complete hydration of Portland cement; additional water fluidizes the mix and makes it more readily processible (more pumpable in the TGF). However, increased water content (i.e., higher w/c) also tends to reduce the quality of the final product. Specifically, increasing w/c tends to

- increase shrinkage and cracking;
- decrease creep relief with age, thus creating a tendency to crack; and,
- decrease the likelihood of resorption of drainable water.

The maximum w/c that can be applied to HFW before these tendencies become cause for concern is beyond the scope of this study. However, the ORNL facility routinely uses a w/c of ~3. Consequently, for HFW formulation studies the w/c was limited to ≤ 3.

4.2 INDIAN RED POTTERY CLAY

Indian Red pottery clay is added solely as an ion-exchange medium to retain ^{137}Cs. Because the exchange capacity is 0.1 meq ^{137}Cs per gram of clay, little clay should be needed.[5,6,7] However, experience at the ORNL facility has shown that the pottery clay content of the dry solids blend needs to be 8 wt % to ensure intimate contact with the ^{137}Cs. In addition, minor variations (± 5%) in the pottery clay content have been shown to have a negligible impact on the grout's rheological properties. Consequently, for HFW formulation development studies the pottery clay content of the dry solids blends was fixed at 8%.

The TGF should, at minimum, match the blending efficiency of the ORNL facility. However, because the TGF is newer, it may well be more efficient than the ORNL facility and need less pottery clay. The impact of using less pottery clay than the amount in the recommended formula is discussed in Appendix E.

4.3 ATTAPULGITE-150 CLAY

Attapulgite-150 clay is added primarily to reduce drainable water from the product. However, previous ORNL grout development experience has shown that when present at or above 0.7 lb/gal of water (waste) it also appears to reduce the leachability of the product. Consequently, HFW formulation development studies attempted to maintain the Attapulgite-150 content at or above this value.

4.4. FLY ASH

Fly ash is a cement extender, and its use should be maximized because of its low cost. However, because of the constraints on the other components, it must by necessity be the variable or slack component.

4.5 MIX RATIO

The dry solids blend-to-waste mix ratio is a key variable in the formulation studies. Experience has shown that if all criteria are met at mix ratios A and B, then all mix ratios between the two will also meet all criteria. Experience at the ORNL facility has also shown that mix ratios can be controlled to within ±0.5 lb/gal. Consequently, the increment in the mix ratio was 1 lb/gal in the formulation studies. Also, the lower and upper bounds of acceptable mix ratios would need to differ from the recommended value by at least 0.5 lb/gal. For example, if the lower and upper bounds of acceptable mix ratios were determined to be 7 and 8 lb/gal, respectively, then the recommended mix ratio would be 7.5 lb/gal.

As in the case of blending efficiency, the TGF may prove to be more efficient than the ORNL facility in controlling mix ratio. This would permit optimization of the mix ratio within the acceptable range. For example, in the case of the previous illustration, it might prove beneficial to operate at 7.2 ± 0.1 lb/gal. However, until this capability has been proven, it is assumed that the TGF can only match the efficiency of the ORNL facility.

4.6 SUMMARY OF FORMULATION CONSTRAINTS

Based on the discussions presented in this section, the formulation development studies are further constrained by

- Water(waste)-to-cement ratio ≤ 3,
- Indian Red pottery clay content of dry solids blend = 8 wt %,
- Attapulgite-150 content ≥ 0.7 lb/gal, and
- Mix ratio step size = 1 lb/gal.

5. EXPERIMENTAL PROCEDURES

5.1 SAMPLE PREPARATION

Dry solids were blended in 5.0-kg lots for 6 h at 30 rpm in a 7.6-L Patterson-Kelly twin-shell V-blender prior to grout preparation. Mixing of the dry solids blend and simulated waste was performed in a Hobart model N-50 mixer with a wire-loop whip mixer blade. Mixing is accomplished by adding solids to liquid during 8-15 s while stirring at low speed. Mixing is then continued at medium speed for a total mixing time of 30 s.

This laboratory blending and mixing technique was developed in support of the ORNL facility and is representative of grouts leaving the mixing tub from that facility. The ORNL facility contains a jet mixer and a mix tub that is equipped with a three-blade impeller. This design is similar to that envisioned for the TGF at the time the formulation studies began.

However, the current design of the TGF specifies a 15-gal Atcor in-line-intensive mixer. At a nominal pumping rate of 50 gal/min, the flow through the mixer is ~3.3 volumes per minute, resulting in a mixing time of 18 s. If it is assumed that a 15-gal pump feed tank is to be a part of the TGF mix module, then the mix times used in these laboratory experiments appear to be appropriate. However, the shear history may not be representative.

Grout properties are a function of shear history, and it is essential that mixing and blending procedures are standardized to ensure the consistency and reproducibility of data. We believe that the procedures used in these formulation studies are appropriate for the reasons given above.

5.2 RHEOLOGICAL MEASUREMENTS

Rheological measurements were made using a standard oil well cement-slurry method with a Model 35A/SR-12 Fann viscometer. Shear stress readings were taken as a function of shear rate, going from high to low shear rate.

Readings in $lb_f/100\ ft^2$ were taken in 12 steps ranging from 600 rpm to 0.9 rpm. RPMs are converted to reciprocal seconds (the standard shear rate unit) by multiplying by an instrument conversion factor. These data were used to determine the fluid consistency index and the flow behavior index, which, with density, are required for flow calculations. The method of data reduction is described in ORNL Milestone 30 and is based on the Ostwald-de Waele Model[8] more commonly referred to as the power law model.

Using the same measurement technique, the 10-min gel strength is determined as the maximum deflection of the dial (in $lb_f/100\ ft^2$) at 3 rpm, after the grout has been allowed to remain static for 10 min.

5.3 PHASE SEPARATION

Phase separation (drainable water) is determined by measuring clear fluid that collects on the freshly poured grout after a given time. It is a common observation that after grout, slurry, or concrete has been placed in position and while it is still plastic, bleed water appears on the surface (phase separation or drainable water). This is essentially a sedimentation phenomenon caused by the solids settling in the plastic mass. Phase separation is influenced by the plasticity of the mix, the amount of entrained air, and the motion or vibration the mix is subjected to during placement.

Phase separation can be beneficial to the final product because it provides the mechanism for proper hydration of the upper surface. If a source of moisture is not available to this surface, then it will crack and powder. Phase separation is the most economical means of supplying this source of moisture for the Rockwell Hanford application. However, one of the performance constraints is that no drainable water exists after 28 d (Sect. 3.2). It is anticipated that the trench design will include a means of surface water removal to allow both routine and emergency flushing of the TGF distribution piping directly to the trench. Therefore, this criterion may not have to be met by the grout.

Nonetheless, measurement of phase separation was an integral part of ORNL's formulation studies, and an acceptable grout as defined in Sect. 3.2.1 resulted in no phase separation at 28 d. For screening purposes, 2-h phase separation was measured by this same method. Grouts developed in the study that exhibited a 2-h phase separation >5% were arbitrarily eliminated from further consideration. Phase separation tests on selected grouts were also conducted in a closed system to determine maximum phase separation and percentage water actually resorbed by the grout.

6. PRELIMINARY SCOUTING STUDIES

There is an infinite combination of the four major dry solids blend components that can be applied to the grout formulation development studies. ORNL relied on previous experience to determine a meaningful starting point. This experience has shown that a 1.0 $\underline{M}$ $NaNO_3$ waste solution (pH $\geq$12), prepared with the dry solids blend shown in Table 6 and mixed at 8 lb/gal, produced grouts that achieved turbulent flow at 61 gal/min in a 2-in.-ID pipe.[9] Consequently, this became the basis for the Rockwell Hanford work.

However, as discussed in Sect. 2.0, a major concern was the effect of the set retarders PO_4 and SO_4 rather than the flow criteria of Sect. 3.0. Consequently, initial scouting studies focused on determining if these concentrations prohibited set (for a discussion on set, see Appendix B).

6.1 PHOSPHATE

Two phosphate solutions were prepared to obtain 5 and 8 wt % Na_2HPO_4 concentrations, respectively. These concentrations bracket the range expected in the Rockwell Hanford phosphate waste (Sect. 2.1). Data are shown in Table 7 for grouts prepared with these solutions at a mix ratio of 6 lb/gal and a dry solids blend consisting of 45 wt % Type I-II-LA Portland cement, 40 wt % ASTM Class F fly ash, and 15 wt % Attapulgite-150 drilling clay.

Both grouts achieved initial set (penetration resistance of 500 psi as per ASTM C-403) in less than 7 d and developed adequate 28-d compressive

Table 6. Composition of the dry solids blend used to prepare grouts with 1.0 M Na_2NO_3 solution

Material	Wt %
Type I Portland cement	38
Kingston fly ash	39
Attapulgite-150 drilling clay	15
Indian Red pottery clay	8

strength ($\geq$60 psi). Thus, when cement is present at levels $\geq$ 2.7 lb/gal (i.e., 45 wt %·6 lb/gal), the phosphate concentration appears to have no deleterious impact on set.

However, the 2-h phase separation exhibited by the grout prepared with the 8 wt % Na_2HPO_4 solution approaches the limit of permissible screening criterion (Sect. 5.3). Consequently, data were obtained for a dry solids blend with an increased attapulgite content (Table 8): 40 wt % Type I-II-LA Portland cement, 40 wt % ASTM Class F fly ash, and 20 wt % Attapulgite-150. Phase separation was within acceptable screening limits for both grouts. However, critical velocity would not be achieved within the TGF pumping conditions. Thus, the major effect of concern with these phosphate concentrations appears to be high phase separation and viscosity.

It is interesting to compare the strength development of the two blends. As seen in Table 8, the increase in attapulgite content results in a faster set and but not in a significantly higher 28-d compressive

Table 7. Effects of waste-stream phosphate concentration on grout properties[a]

Property	Na_2HPO_4 concentration (wt %)	
	5	8
10-min gel strength, $lb_f/100\ ft^2$	8 ± 1	5 ± 1
Fluid consistency index (k´), $lb_f \cdot s^{n'}/ft^2$	0.005 ± 0.001	0.002 ± 0.001
Flow behavior index (n´), dimensionless	0.60 ± 0.02	0.68 ± 0.04
Density, lb/gal	11.59 ± 0.03	11.48 ± 0.03
2-h phase separation, vol %	2.61 ± 0.94	4.97 ± 1.31
Apparent viscosity, cP	19.75	13.01
24-h penetration resistance, psi	0.0	532.5 ± 37.7
7-d penetration resistance, psi	1853.3 ± 295.7	1035.0 ± 166.8
28-d compressive strength, psi	1462.0 ± 208.9	836.7 ± 192.3
Reference conditions		
Reynolds number	4219.20	6114.00
Frictional pressure drop per 100 ft, psi	2.35	1.75
Critical velocity, gal/min	30.57	21.04

[a]Grouts were prepared at a mix ratio of 6 lb/gal; 0.2 mL tributyl phosphate waste was added to each liter of waste. The dry solids blend consisted of 45.0 wt % type I-II-LA Portland cement, 40.0 wt % ASTM Class F fly ash from Kingston, Tenn., and 15.0 wt % Attapulgite-150 clay.

Table 8. Effects of increased Attapulgite-150 content on grouts prepared with phosphate solutions[a]

Property	Na_2HPO_4 concentration (wt %)	
	5	8
10-min gel strength, $lb_f/100\ ft^2$	23 ± 6	61 ± 20
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.378 ± 0.249	0.843 ± 0.183
Flow behavior index (n´), dimensionless	0.15 ± 0.07	0.14 ± 0.01
Density, lb/gal	11.14 ± 0.04	11.58 ± 0.03
2-h phase separation, vol %	0.64 ± 0.17	0.21 ± 0.01
Apparent viscosity, cP	90.26	189.12
24-h penetration resistance, psi	580.0 ± 51.6	440.0 ± 57.2
7-d penetration resistance, psi	2000.0 ± 187.6	1880.0 ± 295.7
28-d compressive strength, psi	1578.0 ± 174.1	1079.0 ± 12.5
Reference conditions		
Reynolds number	620.72	307.57
Frictional pressure drop per 100 ft, psi	14.69	30.54
Critical velocity, gal/min	95.95	141.90

[a]Grouts were prepared at a mix ratio of 6 lb/gal; 0.2 mL tributyl phosphate waste was added to each liter of waste. The dry solids blend consisted of 40.0 wt % type I-II-LA Portland cement, 40.0 wt % ASTM Class F fly ash from Kingston, Tenn., and 20.0 wt % Attapulgite-150 clay.

strength than that shown in Table 7. Thus, the use of attapulgite to control phase separation appears to result in significant additional benefits because it alters the product's internal structure.

Organics such as those found in TURCO have also been known to act as set retarders. Consequently, experiments were performed on a 5 wt % Na_2HPO_4 solution with neutralized TURCO 4512-14A as the source of the phosphate. Data are shown in Table 9 for a grout prepared with this solution at 8 lb/gal with a dry solids blend consisting of 40 wt % Type I-II-LA Portland cement, 42 wt % ASTM Class F fly ash, 10 wt % Attapulgite-150 drilling clay, and 8 wt % Indian Red pottery clay. The composition of the attapulgite in this grout is similar to that reported in Table 7. For convenience, a comparison of the major component composition of grouts described in Tables 7 and 9 is highlighted below:

	Composition of grouts (lb/gal)	
Component	Table 7	Table 9
Cement	2.7	3.2
Attapulgite	0.9	0.8
Fly ash	2.4	3.36
Indian Red pottery clay	0	0.64

As shown by the data in Table 9, the grout containing TURCO-induced organics achieved initial set within 7 d, as did the grout reported in Table 7. The higher 7-d penetration resistance exhibited by the grout containing TURCO is due to the increase in cement content (3.2 vs 2.7 lb/gal) and is to be expected. Therefore, the presence of TURCO-induced organics does not appear to alter significantly the rate of

Table 9. Properties of a grout made with a 5 wt % Na_2HPO_4 solution with TURCO 4512-14A as the source of phosphate

	Measurement
	TURCO
Grout Property	
10-min gel strength, $lb_f/100\ ft^2$	18
Fluid consistency index (k´), $lb_f \cdot s^{n'}/ft^2$	0.016
Flow behavior index (n´), dimensionless	0.46
Density, lb/gal	12.25
2-h phase separation, vol %	1.28
Apparent viscosity, cP	26.41
24-h penetration resistance, psi	0.0
7-d penetration resistance, psi	4520.0
28-d compressive strength, psi	798.8 ± 59.8
Reference conditions	
Reynolds number	3112.22
Frictional pressure drop per 100 ft, psi	3.11
Critical velocity, gal/min	40.11

[a]Grout prepared at a mix ratio of 8 lb/gal. Dry solids blend consisted of 40 wt % Type I-II-LA Portland cement, 42 wt % ASTM Class F Fly ash, 10 wt % Attapulgite-150 drilling clay, and 8 wt % Indian Red pottery clay.

set compared with a Na_2HPO_4 solution. However, the presence of these organics does appear to affect the internal structure of the grout as illustrated by the reduction in the 28-d unconfined compressive strength (798 vs 1462 psi).

Another significant point is illustrated by comparing the rheological properties of the two grouts. The critical velocities and apparent viscosities are similar, indicating that Indian Red pottery clay has little effect on the grout's rheological properties, as stated in Sect. 4.2.

6.2 SULFATE

A grout was prepared with a 0.02 M Na_2SO_4 solution at 6 lb/gal and a dry solids blend consisting of 38 wt % Type I-II-LA Portland cement, 42 wt % ASTM Class F fly ash, 12 wt % Attapulgite-150, and 8 wt % Indian Red pottery clay. Data in Table 10 show that this grout failed to set within 28 d; however, the data also show that when the Na_2SO_4 solution is diluted by 50%, then set is achieved and adequate 28-d compressive strength is obtained. The effects of dilution are realized by mixing this solution with the high-viscosity-producing phosphate waste.

Data in Table 11 show that, when the cement content of grouts prepared with a 0.02 M Na_2SO_4 solution is increased, set is achieved. The grout was prepared at 8 lb/gal with a dry solids blend consisting of 40 wt % Type I-II-LA Portland cement, 42 wt % ASTM Class F fly ash, 10 wt % Attapulgite-150 clay, and 8 wt % Indian Red pottery clay. This in effect increased the cement content from 2.28 to 3.2 lb/gal.

Therefore, the formulation development studies proceeded with the assumptions that (1) the phosphate waste would aid in alleviating the

Table 10. Properties of grouts[a] mixed in the ratio of 6 lb/gal with a 0.02 M Na_2SO_4 solution

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	14 ± 3	12 ± 2	14 ± 5	16 + 3
Fluid consistency index k´ $lb_f \cdot s^n/ft^2$	0.015 + 0.006	0.007 + 0.001	0.013 + 0.005	0.013 + 0.005
Flow behavior index n´, dimensionless	0.45 ± 0.03	0.49 ± 0.03	0.42 ± 0.04	0.42 ± 0.04
Density, lb/gal	11.30 ± 0.04	11.20 ± 0.04	11.19 ± 0.03	11.21 ± 0.07
2-h Phase separation, vol %	1.89 ± 0.42	5.78 ± 0.86	3.03 ± 0.68	3.47 ± 0.70
Apparent viscosity, cP	23.26	13.93	16.72	16.72
24-h penetration resistance psi	0	0	0	0
7-d penetration resistance, psi	0	0	0	28.0
28-d compressive strength, psi	0	0	0	79.56 ± 8.54
Reference conditions				
Reynolds number	2918.00	4877.40	3901.29	3908.24
Frictional pressure drop per 100 ft, psi	2.87	1.70	2.27	2.27
Critical velocity, gal/min	39.52	27.20	32.36	32.36

[a]0.4 mL TBP added per gallon waste solution. Dry solids blend contained 38 wt % Type I-II-LA Portland cement, 42 wt % ASTM Class F fly ash, 12 wt % Attapulgite-150 clay, and 8 wt % Indian Red pottery clay.

Table 11. Properties of grouts[a] mixed in the ratio of 8 lb/gal with a .02 M Na_2SO_4 solution

Property	Measurement
10-min gel strength, $lb_f/100\ ft^2$	7
Fluid consistency index (k´), $lb_f \cdot s^{n} /ft^2$	0.004
Flow behavior index (n´), dimensionless	0.57
Density, lb/gal	11.95
2-h Phase separation, vol %	3.42
Apparent viscosity, cP	13.11
24-h penetration resistance psi	0.0
7-d penetration resistance, psi	420.0
28-d compressive strength, psi	50.0 ± 14.5
Reference conditions	
Reynolds number	5710.25
Frictional pressure drop per 100 ft, psi	1.82
Critical velocity, gal/min	23.22

[a]Dry solids blend consisted of 40 wt % Type I-II-LA Portland cement, 42 wt % ASTM Class F fly ash, 10 wt % Attapulgite-150 clay, and 8 wt % Indian Red pottery clay.

deleterious effects of the SO_4 concentration in achieving set, and (2) the cement content should be greater than 2.28 lb/gal.

7. SELECTION OF DRY SOLIDS BLEND MATRIX FOR FORMULATION DEVELOPMENT STUDIES

7.1 LOWER BOUND OF THE DRY SOLIDS BLEND MATRIX

The scouting studies (Sect. 6.0) indicated that the cement content should be >2.28 lb/gal to ensure set, the attapulgite content should be $\geq$0.7 lb/gal, the Indian Red pottery clay content should be 8 wt %, and increments in mix ratio should be 1 lb/gal. These data provide the lower bound for the dry solids blend matrix studied.

The effects of a cement content greater than 2.28 lb/gal indicate that the minimum cement content in the solids blend necessary to ensure set is as follows:

Cement content (lb/gal)	Mix ratio (lb/gal)	Minimum cement content of solids blend (wt %)
2.28	6	38
2.28	7	33
2.28	8	29
2.28	9	25

However, as discussed in Sect. 4.1, another criterion for cement content is a water-to-cement ratio $\leq$3. If one assumes that a gallon of liquid waste contains 8.3 lb of water, then the minimum cement content is 2.77 lb/gal [i.e., (8.3 lb/gal)/3]. Thus, the minimum cement content becomes

Cement content (lb/gal)	Mix ratio (lb/gal)	Minimum cement content of solids blend (wt %)
2.77	6	46
2.77	7	40
2.77	8	35
2.77	9	31

Likewise, the criterion of an Attapulgite-150 content of at least 0.7 lb/gal indicates that the minimum Attapulgite-150 is as follows:

Attapulgite-150 content (lb/gal)	Mix ratio (lb/gal)	Minimum Attapulgite-150 content of solids blend (wt %)
0.7	6	12
0.7	7	10
0.7	8	9
0.7	9	8

7.2 UPPER BOUND OF THE DRY SOLIDS BLEND MATRIX

Data in Table 12 show the effects of compositional variations in the dry solids blend for a grout prepared at 6 lb/gal with an 8 wt % Na_2HPO_4 solution. From a blend of 40 wt % Type I-II-LA Portland cement, 40 wt % ASTM Class F fly ash, and 20 wt % Attapulgite-150 clay, a decrease of 10% in the fly ash content slowed the development of product strength but did not greatly affect the 28-d compressive strength. However, the flow regime changed from laminar to turbulent at reference conditions; therefore, increasing the fly ash content improves the grout's flow behavior. Lowering the clay content ~20% significantly lowered the gel strength, while increasing the 2-h phase separation and resulting Reynolds number. The clay content is a key variable in controlling these parameters.

Table 12. Effect of dry solids blend variations on a grout prepared with an 8 wt % Na_2HPO_4 solution

Property	Mix Ratio (lb/gal) 6	6	6	8
Cement, wt %	40	35	45	45
Fly ash, wt %	40	45	40	40
Attapulgite-150 clay, wt %	20	20	15	15
Apparent viscosity, cP	201	27.5	13.75	87
10-min gel strength, $lb_f/100\ ft^2$	60.5	13.8	5.0	28.8
Density, lb/gal	11.58	11.40	11.48	12.16
Fluid consistency index (k') $lb_f \cdot s^{\eta}/ft^2$	0.84	0.024	0.002	0.15
Flow behavior index (η')	0.14	0.43	0.68	0.30
2-h phase separation, vol %	0.2	1.72	4.97	0.86
24-h penetration resistance, psi	440	60	532	1150
7-d penetration resistance, psi	1880	1300	1035	3180
28-d compressive strength, psi	269	231	209	612
Reference conditions				
Reynolds number	310	2165	6611	756
Frictional pressure loss per 3000 ft of pipe, psi	910	122	104	393
Critical velocity, ft/s	14.3	5.0	2.1	9.3
Critical velocity, gal/min	140	49	21	91

Increasing the mix ratio from 6 to 8 lb/gal for a blend containing 45 wt % Type I-II-LA Portland cement, 40 wt % ASTM Class F fly ash, and 15 wt % Attapulgite-150 clay increased both compressive strength and critical velocity. Significantly, the 33% increase in mix ratio at a fixed blend resulted in increasing the grout's vertical velocity from 21 to 91 gal/min, which is well above the TGF's pumping capacity of 70 gal/min.

The discussion presented in this section illustrates an important point: Relatively minor composition variations have a major impact on grout rheological properties. There is no need to explore major variations in the dry solids blend composition and mix ratio. Based on all of the information in this section, the matrix shown in Table 13 was tested in the formulation development studies.

8. HANFORD FACILITY WASTE USED IN FORMULATION DEVELOPMENT STUDIES

The recipe for the reference synthetic HFW to be used in these studies has been defined by Rockwell Hanford (see Sect. 2.0). The concentrations of the major components of this waste are shown in Table 14. Scouting studies (Sect. 6.0) indicated that the sulfate content is the major concern because it can prevent set. These studies also showed that sulfate concentrations as high as 0.02 M can be tolerated with cement contents >2.28 lb/gal. These studies suggested that combining the sulfate waste with the phosphate waste might further mitigate the set, retard the action of the sulfate, and thus permit even higher sulfate concentrations. Therefore, in the formulation development studies the

Table 13. Weight percent of materials in dry solids blends used to develop grouts for HFW

	Blend number								
Material	1	2	3	4	5	6	7	8	9
Type I-II-LA Portland cement	40	41	42	42	40	38	37	39	41
Centralia, Wash. ASTM Class F fly ash	42	41	40	38	40	42	41	39	37
Attapulgite-150 clay	10	10	10	12	12	12	14	14	14
Indian Red pottery clay	8	8	8	8	8	8	8	8	8

Table 14. Major element concentrations of HFW composed of a 50 : 50 mixture of phosphate and sulfate waste

Component	M
Na_3PO_4	0.15
Na_2HPO_4	0.01
Na_2SO_4	0.01
NaOH	0.01
$NaNO_2$	0.006
TOC	0.92 g/L

Na_2SO_4 concentration was increased over the 0.1. M presented in Table 14 to 0.03 M. In addition, to assess the effects of dilution associated with anticipated waste retrieval schemes and, to a lesser extent, the effects of major component concentration variations, formulation studies were performed with four variations of the waste composition:

- No dilution. HFW as defined by the Rockwell recipe, in which the Na_2SO_4 content was increased to 0.03 M. Throughout the remainder of this report, this solution is referred to as the reference waste.
- 20% dilution (25% volume increase). A solution made by diluting 1 L of reference waste with 0.25 L of water.
- 33% dilution (50% volume increase). A solution made by diluting 1 L of reference waste with 0.5 L of water.
- 50% dilution (100% volume increase). A solution made by diluting 1 L of reference waste with 1 L of water.

The resulting anion concentrations are shown in Table 15.

Table 15. Concentration of anions in the four synthetic waste streams used in the formulation development studies

Anion	Concentration		
	0 vol % (M)	33 vol % (M)	50 vol % (M)
PO_4^{-3}	0.15	0.1	0.08
SO_4^{-2}	0.03	0.02	0.015
NO_2^{-1}	0.006	0.004	0.002
TOC, g/L	0.92	0.62	0.46

9. FORMULATION DEVELOPMENT STUDIES WITH REFERENCE WASTE

Data are presented on grout formulations with dry solids blends shown in Table 13 and synthetic wastes shown in Table 15. Data reported with a standard deviation are an average of four replicate samples unless otherwise noted. For convenience, the data are grouped by Attapulgite-150 content.

9.1 10 WT % ATTAPULGITE-150 DRILLING CLAY

Grouts were prepared at 7 lb/gal with reference wastes and blends 1, 2, and 3 (Table 13). Data are shown in Tables 16 and 17. As shown in Table 16, grouts prepared at 7 lb/gal with a blend consisting of 41 wt % Type I-II-LA Portland cement, 41 wt % ASTM Class F fly ash, 10 wt % Attapulgite-150 drilling clay, and 8 wt % Indian Red pottery clay met all of the major design criteria including:

- 10-min gel strength <100 $lb_f/100\ ft^2$,
- No 28-d phase separation,
- 28-d compressive strength >60 psi,
- Turbulent flow achieved at <70 gal/min and,
- Frictional pressure drop <11 psi/100 ft.

For waste dilutions up to 33%, initial set occurred in less than 7 d, while at 50% dilution initial set occurred after 7 d.

Properties of grouts prepared with blend 1 (cement content reduced to 40 wt % and fly ash increased to 42 wt %) and blend 3 (cement content increased to 42 wt % and fly ash decreased to 40 wt %) are shown in Tables 17 and 18, respectively. As with blend 2, these grouts met all of the

Table 16. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 2 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	27 ± 10	19 ± 3	18 ± 4	22 ± 5
Fluid consistency index (k′), $lb_f \cdot s^{n'}/ft^2$	0.020 ± 0.005	0.019 ± 0.007	0.019 ± 0.007	0.046 ± 0.007
Flow behavior index (n′),	0.41 ± 0.05	0.42 ± 0.04	0.40 ± 0.04	0.30 ± 0.02
Density, lb/gal	11.60 ± 0.04	11.61 ± 0.09	11.60 ± 0.04	11.53 ± 0.05
2-h phase separation, vol %	1.26 ± 0.49	1.99 ± 0.39	3.28 ± 1.78	1.59 ± 0.21
28-d phase separation	0	0	0	0
Apparent viscosity, cP	24.17	24.44	21.57	27.99
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1640.0	740.0	520.0	284.0
28-d compressive strength, psi	361.19 ± 15.13	390.49 ± 17.70	309.13 ± 8.66	205.50 ± 6.07
Reference conditions				
Reynolds number	2877.40	2833.40	3249.67	2281.00
Frictional pressure drop per 100 ft, psi	3.53	3.53	2.94	4.09
Critical velocity, gal/min	40.49	40.15	38.26	47.22

[a]0.4 mL TBP added per liter of waste

Table 17. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 1 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	17 ± 3	19 ± 2	26 ± 10	18 ± 3
Fluid consistency index (k'), $lb_f \cdot s^{n'}/ft^2$	0.010 ± 0.001	0.009 ± 0.003	0.020 ± 0.008	0.023 ± 0.008
Flow behavior index (n'),	0.49 ± 0.02	0.49 ± 0.03	0.39 ± 0.03	0.38 ± 0.06
Density, lb/gal	11.59 ± 0.03	11.60 ± 0.04	11.59 ± 0.03	11.54 ± 0.03
2-h phase separation, vol %	3.28 ± 0.54	3.07 ± 0.94	2.22 ± 0.81	2.94 ± 0.51
28-d phase separation	0	0	0	0
Apparent viscosity, cP	19.90	17.91	21.33	23.05
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1480.0	664.0	576.0	312.0
28-d compressive strength, psi	318.00 ± 11.63	327.63 ± 12.19	330.56 ± 18.23	246.06 ± 17.04
Reference conditions				
Reynolds number	3605.14	4209.67	3300.22	3006.00
Frictional pressure drop per 100 ft, psi	2.35	2.35	2.94	2.93
Critical velocity, gal/min	33.66	31.38	37.75	40.30

[a]0.4 mL TBP added per liter of waste.

Table 18. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 3 and different dilutions of reference waste[a]

Parameter	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	34 ± 4	36 ± 2	41 ± 2	32 ± 3
Fluid consistency index (k´) $lb_f \cdot s^{n} /ft^2$	0.030 ± .003	0.018 ± .003	0.029 ± .004	0.027 ± .004
Flow behavior index (η´)	.37 ± .02	.46 ± .03	.38 ± .02	.38 ± .02
Density, lb/gal	11.70 ± 0.00	11.75 ± 0.00	11.74 ± .03	11.71 ± .03
2-h phase separation, vol %	1.15 ± .21	1.06 ± .24	1.05 ± .25	1.06 ± .25
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	28.25	29.71	29.06	27.06
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	960.0	660.0	480.0	284.0
28-d compressive strength, psi	332.56 ± 16.38	353.94 ± 5.95	257.94 ± 10.47	208.12 ± 8.57
Reference conditions				
Reynolds number	2382.85	2442.36	2352.38	2541.83
Frictional pressure drop per 100 ft, psi	4.15	4.17	4.17	3.56
Critical velocity, gal/min	44.87	44.49	46.04	44.11

[a]0.4 mL TBP added per liter of waste.

major design criteria. In general, 28-d compressive strength and frictional pressure drop increased with cement content.

The average properties of grouts prepared with these blends are shown in Table 19. Therefore, grouts prepared at 7 lb/gal, with dry solids blends containing 8 wt % Indian Red pottery clay, 10 wt % Attapulgite-150, 40—42 wt % Type I-II-LA Portland cement, and 40—42 wt % ASTM Class F fly ash, are fluid and achieve turbulent flow below the nominal TGF pump rate of 50 gal/min. Phase separation in a closed system for the grout prepared with blend 3 is shown in Fig. 1. As indicated by Fig. 1, these grouts are characterized by a high bleed rate with little resorption of water by the grout. Therefore, operations in this range would be favored if processibility were the major concern. However, this would not be the case if resorption of the bleed water by the grout was desired.

To address resorption of bleed water, grouts were prepared with blends 1, 2, and 3 at 8 lb/gal. As seen in Fig. 2, the increase in mix ratio resulted generally in less bleed water and total resorption of the water by the grout in a closed system at waste dilutions $\lesssim$20%.

Other pertinent properties of these grouts are shown in Tables 20 through 22. As with grouts prepared at 7 lb/gal, all major design criteria were met. In general, the increase in mix ratio (in effect increasing the dry solids content, particularly the cement) resulted in harder (higher 28-d compressive strength) and more viscous (higher pressure drop and critical velocity) grouts.

The average properties of grouts made with these blends at 8 lb/gal are shown in Table 23. At this mix ratio, critical velocity is achieved

Table 19. Average properties of grouts prepared at 7 lb/gal with dry solids blends 1, 2, and 3

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	31 ± 5	25 ± 10	28 ± 12	24 ± 7
2-h phase separation, vol %	1.9 ± 1.2	2.0 ± 1.0	2.2 ± 1.1	1.9 ± 1.0
28-d phase separation, vol %	0	0	0	0
Density, lb/gal	11.63 ± 0.06	11.66 ± 0.08	11.59 ± 0.1	11.59 ± 0.1
Apparent viscosity, cP	24 ± 5	25 ± 5	24 ± 4	26 ± 3
28-d compressive strength, psi	337 ± 22	356 ± 33	299 ± 37	220 ± 23
<u>Reference conditions</u>				
Frictional pressure drop per 100 ft, psi	3.34 ± 0.91	3.35 ± 0.92	3.35 ± 0.71	3.53 ± 5.8
Critical velocity, gal/min	40 ± 6	39 ± 7	41 ± 5	44 ± 4

ORNL DWG 84-730

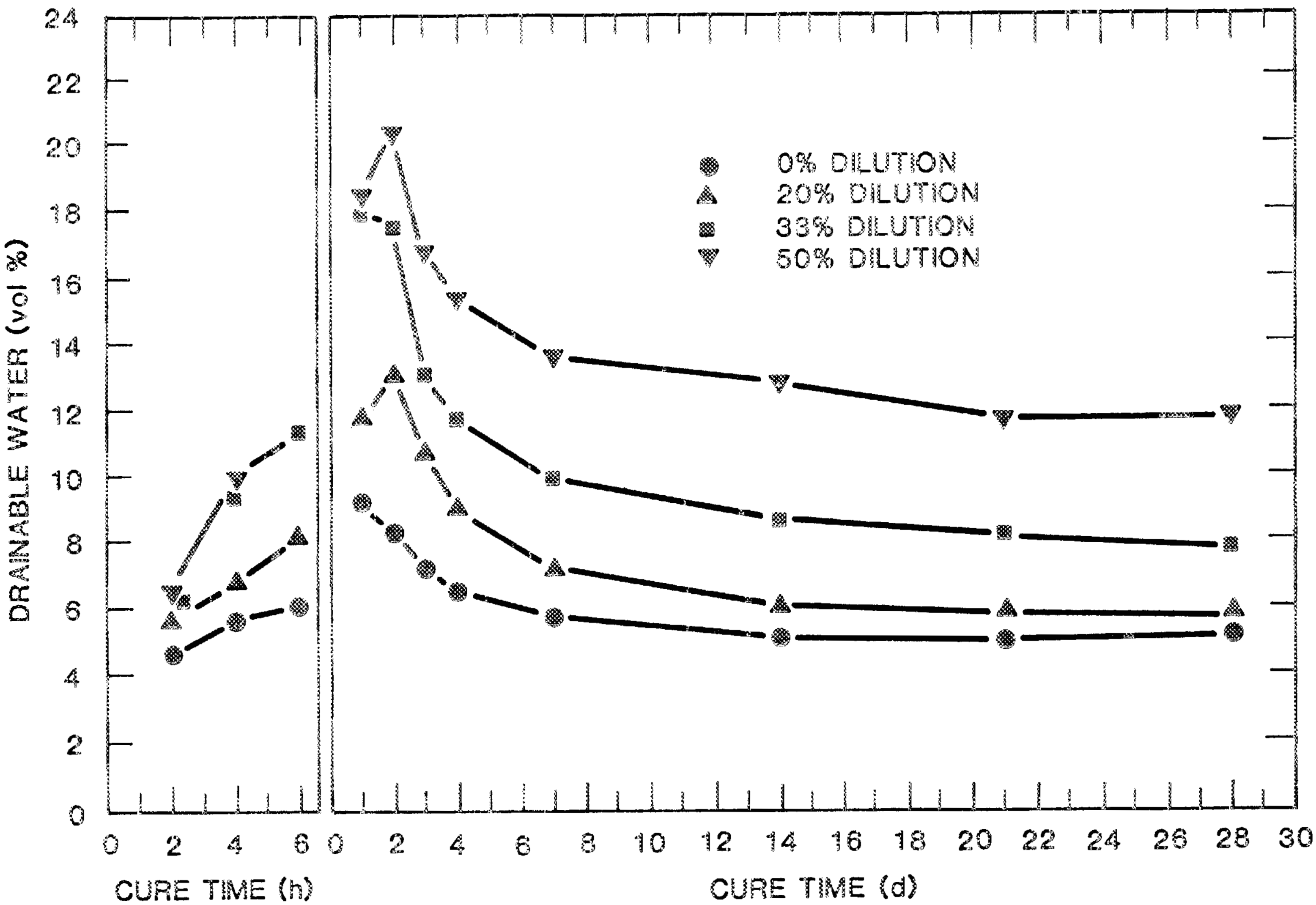

Fig. 1. Drainable water as a function of cure time in a closed system for grouts prepared at 7 lb/gal with blend 3.

ORNL DWG 84-733

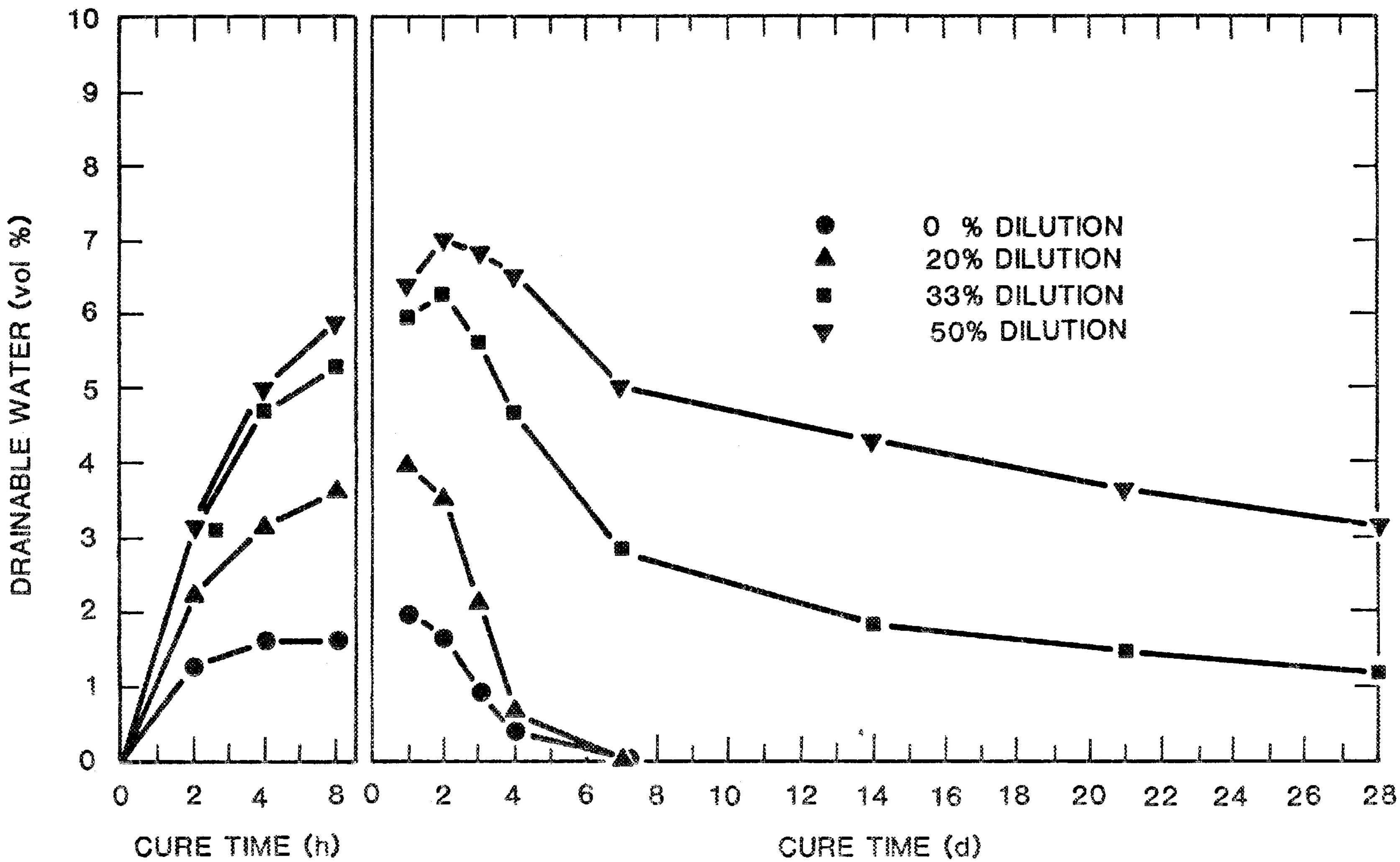

Fig. 2. Drainable waste water as a function of cure time in a closed system for grouts prepared at 8 lb/gal with blend 3.

Table 20. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 2 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	32 ± 6	35 ± 6	24 ± 3	17 ± 2
Fluid consistency index (k'), $lb_f \cdot s^{n'}/ft^2$	0.089 ± 0.008	0.059 ± 0.029	0.070 ± 0.022	0.034 ± 0.006
Flow behavior index (n'),	0.27 ± 0.01	0.35 ± 0.05	0.31 ± 0.02	0.40 ± 0.01
Density, lb/gal	11.90 ± 0.00	11.91 ± 0.03	11.90 ± 0.04	12.03 ± 0.16
2-h phase separation, vol %	0.74 ± 0.21	0.94 ± 0.63	1.26 ± 0.34	0.52 ± 0.21
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	44.92	49.04	45.33	38.60
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	3960.0	1300.0	490.0	280.0
28-d compressive strength, psi	676.38 ± 13.97	793.88 ± 41.54	237.75	297.00 ± 59.40
Reference conditions				
Reynolds number	1483.24	1416.39	1510.52	1895.69
Frictional pressure drop per 100 ft, psi	6.64	6.64	6.64	4.88
Critical velocity, gal/min	61.88	63.95	60.74	53.95

[a]0.4 mL TBP added per liter of waste.

Table 21. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 1 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	37 ± 4	37 ± 12	26 ± 5	20 ± 2
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.064 ± 0.012	0.050 ± 0.007	0.057 ± 0.004	0.038 ± 0.007
Flow behavior index (n´),	0.29 ± 0.03	0.34 ± 0.02	0.33 ± 0.02	0.42 ± 0.03
Density, lb/gal	11.86 ± 0.05	11.90 ± 0.07	11.85 ± 0.04	11.86 ± 0.06
2-h phase separation, vol %	1.15 ± 0.40	0.94 ± 0.20	1.68 ± 0.69	0.94 ± 0.21
28-d phase separation, vol%	0	0	0	0
Apparent viscosity, cP	36.59	39.05	41.82	48.87
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1620.0	1980.0	1220.0	1160.0
28-d compressive strength, psi	441.56 ± 21.06	488.56 ± 45.71	452.25 ± 1.37	310.94 ± 15.65
Reference conditions				
Reynolds number	1788.60	1741.32	1674.35	1523.37
Frictional pressure drop per 100 ft, psi	5.41	5.43	6.01	6.62
Critical velocity, gal/min	53.56	54.89	58.17	61.31

[a]0.4 mL TBP added per liter of waste.

Table 22. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 3 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	14	5	16	11
Fluid consistency index (k'), $lb_f \cdot s^{n'}/ft^2$	0.010	0.007	0.025	0.032
Flow behavior index (n'),	0.48	0.54	0.43	0.36
Density, lb/gal	12.15	12.01	12.25	12.05
2-h phase separation, vol %	5.79	5.58	4.96	2.97
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	18.70	19.03	34.22	28.31
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	3540.0	3480.0	1160.0	248.0
28-d compressive strength, psi	671.75 ± 83.09	672.25 ± 6.01	571.25 ± 69.30	356.75 ± 36.77
Reference conditions				
Reynolds number	4481.67	4017.50	2262.54	2494.46
Frictional pressure drop per 100 ft, psi	2.46	2.44	4.35	3.67
Critical velocity, gal/min	31.80	30.52	48.48	44.77

[a]0.2 mL TBP added per liter of waste.

Table 23. Average properties of grouts prepared at 8 lb/gal with dry solids blends 1, 2, and 3

Property	Waste dilutions (vol %) 0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	28 ±12	26 +18	22 ± 6	16 ±5
2-h phase separation, vol %	2.6 ± 2.8	2.5 ± 2.7	2.6 ± 2.0	1.5 ± 1.3
28-d phase separation, vol %	0	0	0	0
Density, lb/gal	11.97 ± 0.16	11.94 ± 0.06	12.0 ± 0.22	11.99 ± 0.10
Apparent viscosity, cP	33 ± 13	36 ± 15	40 ± 6	39 ± 10
28-d compressive strength, psi	596 ± 134	651 ± 154	420 ± 169	322 ± 31
Reference conditions				
Frictional pressure loss per 100 ft, psi	4.84 ± 2.15	4.84 ± 2.16	5.67 ± 1.18	5.06 ± 1.4
Critical velocity, gal/min	49 ± 16	50 ± 17	56 ± 7	53 ± 8

near the nominal TGF pumping rate (50 gal/min). Therefore, if water resorption were the major concern, operations in this range would be favored. However, some reduction in processibility would result.

9.2 12 WT % ATTAPULGITE-150 DRILLING CLAY

Scouting studies (Sect. 6.2) indicated that set was not achieved with a grout prepared at 6 lb/gal with blend 6 and a 0.02 M Na_2SO_4 solution. To assess the dilution effects of the phosphate addition, grouts were prepared at a mix ratio of 6 lb/gal with blends 4, 5, and 6. Data are shown in Tables 24 through 26. As seen by the data, set was achieved at cement contents $\geq$ 2.4 lb/gal (blends 4 and 5), which is only a slight increase above 2.28 lb/gal (blend 6). In addition, set was acheived with blend 6 and a waste dilution of 50%. Consequently, combining the phosphate and sulfate wastes (to produce HFW) appears to increase the permissible sulfate concentration.

Data are presented in Tables 27–29 for grouts prepared with these three blends at a mix ratio of 7 lb/gal. All performance criteria were met. Average properties are shown in Table 30. Data in Table 30 indicate that grouts prepared at 7 lb/gal, with a dry solids blend consisting of 8 wt % Indian Red pottery clay, 12 wt % Attapulgite-150, 38–42 wt % Type I-II-LA Portland cement, and 38–42 wt % Centralia, Wash. ASTM Class F fly ash, are fluid and achieve turbulent flow below the TGF nominal pump rate (50 gal/min). However, Fig. 3, which shows phase separation data in a closed system, indicates that water would be resorbed by grouts in this range only at 0% waste dilution. Thus, grouts prepared

Table 24. Properties of grouts mixed in the ratio of 6 lb/gal with dry solids blend 6 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	14 ± 3	12 ± 2	14 ± 5	16 + 3
Fluid consistency index (k′), $lb_f \cdot s^n/ft^2$	0.015 + 0.006	0.007 + 0.001	0.013 + 0.005	0.013 + 0.005
Flow behavior index (n′),	0.45 ± 0.03	0.49 ± 0.03	0.42 ± 0.04	0.42 ± 0.04
Density, lb/gal	11.30 ± 0.04	11.20 ± 0.04	11.19 ± 0.03	11.21 ± 0.07
Apparent viscosity, cP	23.26	13.93	16.72	16.72
24-h penetration resistance, psi	0	0	0	0
7-d penetration resistance, psi	0	0	0	28.0
28-d compressive strength, psi	0	0	0	79.56 ± 8.54
Reference conditions				
Reynolds number	2918.00	4877.40	3901.29	3908.24
Frictional pressure drop per 100 ft, psi	2.87	1.70	2.27	2.27
Critical velocity, gal/min	39.52	27.20	32.36	32.36

[a]0.4 mL TBP added per liter of waste.

Table 25. Properties of grouts mixed in the ratio of 6 lb/gal with dry solids blend 5 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	5 ± 1	7 ± 1	6 ± 2	8 ± 3
Fluid consistency index (k´), $lb_f \cdot s^{n´}/ft^2$	0.003 ± 0.001	0.004 ± 0.002	0.002 ± 0.001	0.003 ± 0.001
Flow behavior index (n´),	0.63 ± 0.02	0.58 ± 0.07	0.66 ± 0.03	0.61 ± 0.04
Density, lb/gal	11.60 ± 0.09	11.48 ± 0.03	11.46 ± 0.13	11.40 ± 0.11
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	14.29	13.95	11.50	12.62
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	980.0	560.0	336.0	176.0
28-d compressive strength, psi	249.63 ± 18.07	242.02 ± 12.65	249.75 ± 23.08	198.63 ± 3.51
Reference conditions				
Reynolds number	6702.33	5397.00	6305.67	6805.00
Frictional pressure drop per 100 ft, psi	1.18	1.75	1.74	1.16
Critical velocity, gal/min	23.65	24.54	19.68	22.38

[a]0.4 mL TBP added per liter of waste.

Table 26. Properties of grouts mixed in the ratio of 6 lb/gal with dry solids blend 4 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	14 ± 2	14 ± 3	17 ± 6	11 ± 2
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.005 ± 0.001	0.008 ± 0.001	0.011 ± 0.005	0.014 ± 0.005
Flow behavior index (n´),	0.54 ± 0.02	0.48 ± 0.01	0.44 ± 0.03	0.41 ± 0.04
Density, lb/gal	11.59 ± 0.07	11.24 ± 0.03	11.26 ± 0.14	11.25 ± 0.07
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	13.59	14.96	16.03	16.92
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1660.0	832.0	500.0	132.0
28-d compressive strength, psi	308.18 ± 19.40	260.64 ± 36.13	293.87 ± 15.10	176.19 ± 27.2
Reference conditions				
Reynolds number	5815.50	4975.20	4433.17	3986.57
Frictional pressure drop per 100 ft, psi	1.76	1.71	2.28	2.28
Critical velocity, gal/min	24.88	28.89	31.01	32.97

[a]0.4 mL TBP added per liter of waste.

Table 27. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 4 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	16 ± 3	21 ± 5	15 ± 5	13 ± 2
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.019 ± 0.011	0.0107 ± 0.003	0.0077 ± 0.0037	0.009 ± 0.001
Flow behavior index (n´),	0.43 ± 0.07	0.502 ± 0.038	0.541 ± 0.043	0.507 ± 0.018
Density, lb/gal	11.90 ± 0.00	11.7 ± 0	11.71 ± 0.06	11.66 ± 0.03
2-h phase separation, vol %	2.68 ± 0.90	2.77 ± 1.06	3.78 ± 0.47	4.66 ± 1.09
28-d phase separation, vol %	0.0	0	0	0
Apparent viscosity, cP	24 ± 5	24 ± 2	21 ± 3	21 ± 2
24-h penetration resistance, psi	0.0	0	0	0
7-d penetration resistance, psi	1640	680	416	252
28-d compressive strength, psi	459 ± 6	407 ± 10	328 ± 9	221 ± 6
Reference conditions				
Reynolds number	2857.20	3344	3750	3868
Frictional pressure drop per 100 ft, psi	3.62	2.84	2.53	2.45
Critical velocity, gal/min	38.58	36.6	33.5	33.2

[a]0.4 mL TBP added per liter of waste.

Table 28. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 5 and different dilutions of reference waste[a]

Property	Waste dilutions vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	21 ± 7	39 ± 8	35 ± 16	35 ± 10
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.019 ± 0.016	0.068 ± 0.038	0.039 ± 0.011	0.051 ± 0.023
Flow behavior index (n´),	0.44 ± 0.08	0.29 ± 0.06	0.33 ± 0.03	0.29 ± 0.05
Density, lb/gal	11.75 ± 0.00	11.69 ± 0.06	11.71 ± 0.03	11.73 ± 0.03
2-h phase separation, vol %	2.32 ± 0.88	1.28 ± 0.62	1.48 ± 0.22	1.59 ± 0.22
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	27.68	38.88	28.61	29.16
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1360.0	960.0	340.0	136.0
28-d compressive strength, psi	430.7 ± 21.3	379.9 ± 27.2	291.2 ± 6.0	162.3 ± 17.6
Reference conditions				
Reynolds number	2775.6	1679.00	2363.64	2211.25
Frictional pressure drop per 100 ft, psi	3.58	5.93	4.16	4.16
Critical velocity, gal/min	42.82	55.94	46.65	47.25

[a]0.4 mL TBP added per liter of waste.

Table 29. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 6 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	20 ± 4	29 ± 11	37 ± 15	31 ± 8
Fluid consistency index (k′), $lb_f \cdot s^{n'}/ft^2$	0.014 ± 0.004	0.024 ± 0.012	0.034 ± 0.020	0.035 ± 0.013
Flow behavior index (n′),	0.46 ± 0.03	0.40 ± 0.05	0.36 ± 0.07	0.34 ± 0.04
Density, lb/gal	11.75 ± 0.00	11.75 ± 0.06	11.79 ± 0.03	11.65 ± 0.00
2-h phase separation, vol %	1.69 ± 0.36	1.48 ± 0.24	1.47 ± 0.26	1.69 ± 0.60
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	23.11	27.25	30.08	27.33
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1480.0	800.0	360.0	120.0
28-d compressive strength, psi	466.7 ± 19.2	342.6 ± 11.1	297.9 ± 10.6	165.4 ± 15.1
Reference conditions				
Reynolds number	3358.25	2693.18	2266.29	2491.54
Frictional pressure drop per 100 ft, psi	2.98	3.58	4.19	3.55
Critical velocity, gal/min	37.78	43.97	47.08	44.89

[a]0.4 mL TBP added per liter of waste.

Table 30. Average properties of grouts prepared at 7 lb/gal with blends 4, 5, and 6

Property	Waste Dilution (vol %) 0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	19	30	29	26
2-h phase separation, vol %	2.2	1.8	2.2	2.7
28-d phase separation, vol %	0	0	0	0
Density, lb/gal	11.8	11.7	11.7	11.7
Apparent viscosity, cP	25	30	27	26
28-d compressive strength, psi	452	377	306	183
Reference conditions				
Frictional pressure loss per 100 ft, psi	3.39	4.12	3.63	3.39
Critical velocity, (gal/min)	40	46	42	42

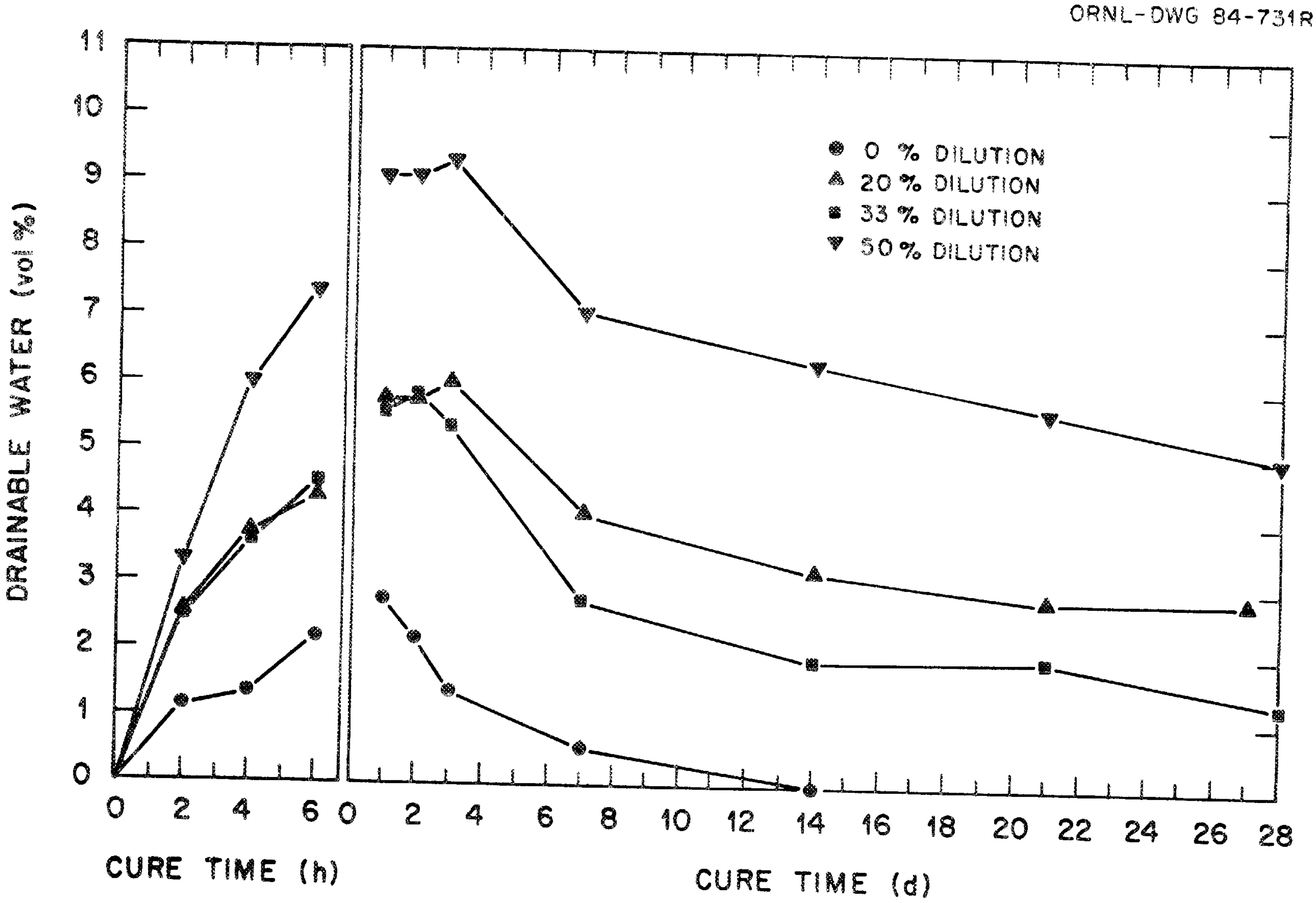

Fig. 3. Drainable water as a function of cure time in a closed system for grouts prepared at 7 lb/gal with blend 5.

in this range would be favored if processibility were the primary concern.

Data in Tables 31–33 show the effects of increasing the mix ratio to 8 lb/gal. Grouts prepared with blend 4 met all performance criteria, except for the 50% diluted reference waste. In this case, critical velocity was not achieved at $\leq$70 gal/min. Grouts prepared with blend 5 met all performance criteria; critical velocity was achieved near 50 gal/min. This is to be expected since increasing the fly ash content while simultaneously decreasing the cement content typically results in less-viscous, more-fluid grouts. However, as seen in Table 33, it is difficult to predict grout behavior. These grouts prepared with blend 6 were significantly more viscous than those prepared with blend 5 even though the cement content decreased and the fly ash content increased. For these grouts, waste dilutions of 20 and 33% did not achieve critical velocity within the desired range, and 10-min gel strengths were excessive (>100 lb_f/100 ft^2) for dilutions of 0 and 20%.

However, as seen in Table 34, on the average, grouts prepared with these three blends met all performance criteria. However, both 10-min gel strength and critical velocity are approaching the design limits of the TGF distribution pump. Therefore, it appears that 0.96 lb/gal (8 lb/gal × 12 wt %) may be approaching the maximum Attapulgite-150 content of grouts that are compatible with TGF performance criteria. However, even with this clay content, drainable water is not resorbed by the grout with 50% waste dilution (Fig. 4).

Table 31. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 4 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	49 ± 1	37 ± 5	31 ± 6	32 ± 6
Fluid consistency index (k'), $lb_f \cdot s^{n'}/ft^2$	0.079 ± 0.015	0.114 ± 0.017	0.116 ± 0.049	0.095 ± 0.014
Flow behavior index (n'),	0.27 ± 0.03	0.26 ± 0.04	0.24 ± 0.07	0.32 ± 0.02
Density, lb/gal	12.18 ± 0.03	12.21 ± 0.11	12.16 ± 0.04	12.20 ± 0.06
2-h phase separation, vol %	0.94 ± 0.22	0.60 ± 0.47	0.43 ± 0.01	0.47 ± 0.35
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	39.87	54.05	48.55	65.49
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	0.0	460.0	200.0	148.0
28-d compressive strength, psi	498	444.0 ± 27.6	297.3 ± 8.8	186.5 ± 0.7
Reference conditions				
Reynolds number	1725.18	1247.50	1372.07	1061.88
Frictional pressure drop per 100 ft, psi	5.56	8.05	7.40	9.28
Critical velocity, gal/min	56.97	66.54	65.45	75.88

[a]0.2 mL TBP was added per liter of waste.

Table 32. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 5 and different dilutions of reference waste[a]

Parameter	Waste dilutions (vol %) 0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	11 ± 2	13 ± 3	22 ± 4	30 ± 9
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.006 ± 0.001	0.030 ± 0.003	0.035 ± 0.019	0.022 ± 0.011
Flow behavior index (n´),	0.60 ± 0.02	0.39 ± 0.01	0.41 ± 0.11	0.46 ± 0.08
Density, lb/gal	12.14 ± 0.05	11.79 ± 0.10	12.16 ± 0.14	12.09 ± 0.05
2-h phase separation, vol %	3.36 ± 0.03	2.99 ± 0.50	1.16 ± 0.94	1.67 ± 1.02
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	23.70	32.00	42.30	36.31
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	2360.0	340.0	1060.0	400.0
28-d compressive strength, psi	710.6 ± 26.1	271.3 ± 6.3	521.8 ± 36.4	270.1 ± 17.8
Reference conditions				
Reynolds number	3682.83	2158.14	1774.35	2126.46
Frictional pressure drop per 100 ft, psi	2.46	4.19	5.55	4.91
Critical velocity, gal/min	33.67	48.03	55.92	49.75

[a]0.4 mL TBP was added per liter of waste.

Table 33. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 6 and different dilutions of reference waste[a]

Propterty	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	209 ± 43	190 ± 37	71 ± 38	18 ± 2
Fluid consistency index (k´), $lb_f \cdot s^{n} /ft^2$	0.100 ± 0.009	0.352 ± 0.132	0.118 ± 0.079	0.066 ± 0.015
Flow behavior index (n´),	0.25 ± 0.02	0.11 ± 0.03	0.28 ± 0.17	0.34 ± 0.02
Density, lb/gal	12.14 ± 0.07	12.10 ± 0.12	12.06 ± 0.05	12.08 ± 0.03
2-h phase separation, vol %	0.63 ± 0.24	0.72 ± 0.21	0.94 ± 0.19	0.83 ± 0.02
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	44.55	65.49	63.38	51.54
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	2580.0	1680.0	580.0	364.0
28-d compressive strength, psi	598.6 ± 13.3	668.0 ± 20.2	634.2 ± 37.6	445.7 ± 18.3
Reference conditions				
Reynolds number	1503.15	906.17	1056.37	1343.40
Frictional pressure drop per 100 ft, psi	6.77	11.05	9.18	7.35
Critical velocity, gal/min	60.6	78.09	73.96	64.26

[a]0.4 mL TBP added per liter of waste.

Table 34. Average properties of grouts prepared at 8 lb/gal with blends 4, 5, and 6

Properties	Waste dilution (vol %) 0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	90	80	41	27
2-h phase separation, vol %	1.6	1.4	0.8	1.0
28-d phase separation, vol %	0	0	0	0
Density, lb/gal	12.15	12.03	12.13	12.12
Apparent viscosity, cP	36	50	51	51
28-d compressive strength, psi	655	461	484	301
Reference conditions				
Frictional pressure loss per 100 ft, psi	493	7.76	7.38	7.18
Critical velocity, gal/min)	51	64	65	63

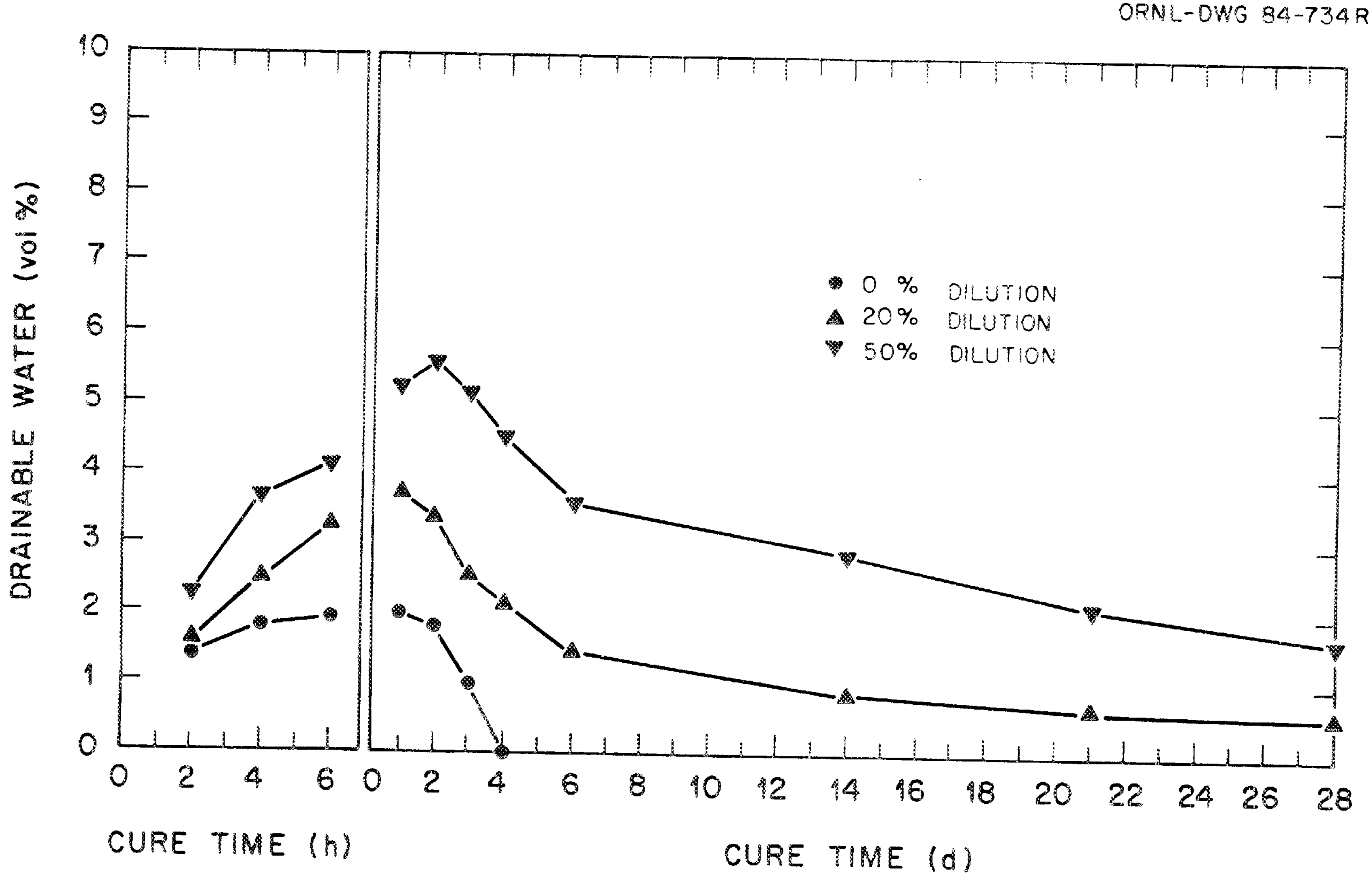

Fig. 4. Drainable water as a function of cure time in a closed system for grouts prepared at 8 lb/gal with blend 5.

9.3 14-WT-% ATTAPULGITE-150 DRILLING CLAY

Data in the previous section indicates that grouts containing 0.96 lb/gal Attapulgite-150 approach the upper bound of processibility in the TGF. To verify this, grouts were prepared at 7 lb/gal with dry solids blends 7, 8, and 9 containing 0.98 lb/gal Attapulgite-150. Data are shown in Tables 35–37.

Data for blend 7 (Table 35) show that 10-min gel strength exceeds TGF distribution pump design limits (<100 $lb_f/100\ ft^2$) for all waste dilutions except 50%. Data in Table 37 for blend 9 show critical velocity was not achieved at design conditions (<70 gal/min) for 0% waste dilution. Thus, if grouts with Attapulgite-150 contents >0.96 lb/gal are only slightly varied, they will fail to meet TGF performance requirements. Indeed, a grout made at 8 lb/gal with blend 8 (Attapulgite-150 content of 1.12 lb/gal) was too viscous to obtain rheological measurements using the Fann Viscometer. Therefore, the Attapulgite-150 content of blends to be used with HFW in the TGF must be $\leq$ 0.96 lb/gal.

10. RECOMMENDED FORMULA

Based on grout development studies with simulated sulfate, phosphate, and HFW (Sect.6–9), the following formula is recommended for HFW:

Dry solids blend[a]

Material	Amount (wt %)
Type I-II-LA Portland cement	41
Centralia, Wash. ASTM Class F Fly ash	40

Table 35. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 7 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %) 0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	134 ± 51	152 ± 39	192 ± 25	29 ± 5
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.104 ± 0.062	0.082 ± 0.069	0.114 ± 0.063	0.107 ± 0.014
Flow behavior index (n´),	0.24 ± 0.05	0.27 ± 0.09	0.22 ± 0.07	0.26 ± 0.04
Density, lb/gal	11.80 ± 0.04	11.76 ± 0.09	11.70 ± 0.08	11.69 ± 0.05
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	43.53	41.38	42.12	50.73
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1280.0	1580.0	900.0	310.0
28-d compressive strength, psi	485.5 ± 10.9	481.5 ± 12.7	396.7 ± 33.0	246.7 ± 14.6
Reference conditions				
Reynolds number	1485.08	1593.26	1464.89	1276.72
Frictional pressure drop per 100 ft, psi	6.58	5.96	6.53	7.71
Critical velocity, gal/min	61.61	59.41	60.42	65.72

[a]0.4 mL TBP added per liter of waste.

Table 36. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 8 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	71 ± 30	38 ± 5	27 ± 11	24 ± 5
Fluid consistency index (k´), $lb_f \cdot s^{n'}/ft^2$	0.045 ± 0.022	0.087 ± 0.022	0.053 ± 0.018	0.060 ± 0.016
Flow behavior index (n´) ,	0.36 ± 0.05	0.30 ± 0.09	0.36 ± 0.04	0.33 ± 0.02
Density, lb/gal	11.76 ± 0.06	11.85 ± 0.07	11.76 ± 0.09	11.71 ± 0.15
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	39.81	52.94	46.89	44.02
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1460.0	790.0	470.0	212.0
28-d compressive strength, psi	403.4 ± 38.5	420.6 ± 3.9	309.1 ± 15.9	225.7 ± 10.8
Reference conditions				
Reynolds number	1758.17	1255.86	1507.00	1504.14
Frictional pressure drop per 100 ft, psi	5.37	7.81	6.56	6.53
Critical velocity, gal/min	55.94	67.66	61.81	60.41

[a]0.4 mL TBP added per liter of waste.

Table 37. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 9 and different dilutions of reference waste[a]

Parameter	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	73 ± 18	39 ± 11	19 ± 2	20 + 1
Fluid consistency index (k´), $lb_f \cdot s^n\ ft^2$	0.204 + 0.223	0.081 + 0.045	0.044 + 0.003	0.057 + 0.015
Flow behavior index (n´),	0.20 ± 0.10	0.28 ± 0.07	0.41 ± 0.02	0.36 ± 0.04
Density, lb/gal	11.85 ± 0.07	11.83 ± 0.06	11.80 ± 0.07	11.75 ± 0.11
28-d phase separation, vol %	0	0	0	0
Apparent viscosity, cP	66.54	43.51	53.17	50.43
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi		332.0	144.0	136.0
28-d compressive strength, psi	420	335.0 ± 6.11	276.50	156.44 ± 7.65
Reference conditions				
Reynolds number	940.6	1511.15	1330.50	1374.78
Frictional pressure drop per 100 ft, psi	10.22	6.60	7.18	7.15
Critical velocity, gal/min	79.58	60.13	65.83	64.65

[a]0.4 mL TBP added per liter of waste.

Attapulgite-150 drilling clay	11
Indian Red pottery clay	8

[a]Mix ratio = 7.5-lb dry solids blend per gallon HFW. (However, 0.02 vol % tributyl phosphate (TBP) must be added to HFW as a defoaming agent).

10.1 VARIATIONS IN DRY SOLIDS BLEND COMPOSITION

The recommended mix meets all performance criteria; reasonable deviations from the recommended reference formula also meet these criteria. Specifically, these deviations are limited to ±5% in individual component compositions of the dry solids blend and variations of ±0.5 lb/gal in the mix ratio. The range of compositions that result in an acceptable grout are shown in Table 38.

10.2 RANGE IN GROUT PROPERTIES

In reality, the recommended formula is a target value. During routine TGF operation the formula will be a composite, dependent upon the capability of the blending (± 5%) and mixing (assumed to be ± 0.5 lb/gal) equipment. The range in the average grout properties prepared with this composite can be obtained by averaging the data at 7 and 8 lb/gal with blends 1 through 6 (Sect. 9). The average values thus obtained are shown in Table 39 for 0% diluted reference waste. As the data in Table 39 shows, grouts prepared with the reference formula meet all performance criteria listed in Sect. 3.4, including:

- Frictional pressure drop — <11 psi/100 ft
- 10-min gel strength — <100 $lb_f/100\ ft^2$
- 28-d drainable water — 0 vol %

Table 38. Ranges in blend composition that result in acceptable grouts

Parameter	Acceptable ranges
Dry solid blend component	
Type I-II-LA Portland cement	38 to 43 wt %
Centralia, Wash; ASTM Class F fly ash	38 to 42 wt %
Attapulgite-150 drilling clay	10 to 12 wt %
Indian Red pottery clay	8 wt %
Solid blend-to-waste mix ratio	7 to 8 lb/gal

• 28-d unconfined compressive strength	>60 psi
• ANS 16.1 leachability for ^{90}Sr and ^{137}Cs	≥6 (see Sect. 11.2)
• Solid-to-waste mix ratios	≤9
• Critical velocity	<70 GPM
• Major dry solid blend components	Only components used in ORNL process
• Dry solid blend composition	Tolerate ± 5% variation in reference formula components

Properties of grouts prepared at 7 and 8 lb/gal with the recommended dry solids blend and 0% diluted HFW are shown in Table 40. A comparison between data in Tables 39 and 40 shows that properties of grouts prepared with the recommended blend and undiluted HFW are similar to the average properties of the composite.

10.3 POTENTIAL MODIFICATIONS TO THE RECOMMENDED MIX RATIO

As discussed in Sect. 4.5, the formulation development studies were performed assuming the TGF would be capable of controlling the mix

Table 39. Average properties of grouts encompassing the blend compositions shown in Table 38 with 0% diluted reference waste

Parameter	Mix ratio (lb/gal) 7	8
10-min gel strength, $lb_f/100\ ft^2$	23	59
2-h phase separation, vol %	2.1	2.1
28-d phase separation, vol %	0	0
Density, lb/gal	11.72	12.06
Apparent viscosity, cP	24	35
28-d compressive strength, psi	395	620
Reference conditions		
Frictional pressure loss per 100 ft, psi	3.37	4.88
Critical velocity, GPM	40	50

ratio to within ± 0.5 lb/gal; however, being newer the facility might be capable of closer control. If this proves to be the case, then modifications to the recommended mix ratio may be appropriate.

10.3.1 Increasing Mix Ratio

Drainable water (i.e., phase separation) as a function of cure time is shown in Fig. 5 for a grout prepared with undilutied HFW and the recommended dry solids blend. At mix ratios above 6 lb/gal, all bleed water is resorbed by the grout. However, as indicated in previous sections this is not true for all deviations from the recommended formula, particularly at increased waste dilutions. In general, the ability of a grout to resorb bleed water is directly proportional to mix ratio. Thus,

Table 40. Properties of grouts prepared with undiluted Hanford Facility Waste (HFW) and mixed in the ratio of 7 and 8 lb/gal, respectively, with a dry solids blend that contains 41.0 wt % Type I-II-LA Portland cement, 40 wt % Centralia, Wash. ASTM Class F fly ash, 11.0 wt % Attapulgite-150 clay, and 8.0 wt % Indian Red pottery clay

Property	Dry solids addition (lb/gal)	
	7	8
10-min gel strength, $lb_f/100\ ft^2$	36.50 ± 5.80	37.50 ± 3.70
Fluid consistency index (k´), $lb_f \cdot s^{n'}/ft^2$	0.027 ± 0.016	0.082 ± 0.001
Flow behavior index (n´),	0.342 ± 0.019	0.354 ± 0.003
Density, lb/gal	11.81 ± 0.13	12.04 ± 0.02
28-d phase separation, vol %	0	0
Apparent viscosity, cP	39.25 ± 16.52	78.50 ± 1.29
24-h penetration resistance, psi	0	0
7-d penetration resistance, psi	2640	3360
28-d compressive strength, psi	424.75 ± 9.50	561.58 ± 36.25
Reference conditions		
Reynolds number	3225	1921
Frictional pressure drop per 100 ft, psi	2.97	5.13
Critical velocity, gal/min	39	53

if resorption becomes a desirable performance criterion, then mix ratios closer to 8 lb/gal would be preferred.

10.3.2 Decreasing Mix Ratio

As indicated in Tables 39 and 40, increasing the mix ratio measurably decreases the grout's processibility in the TGF. This is

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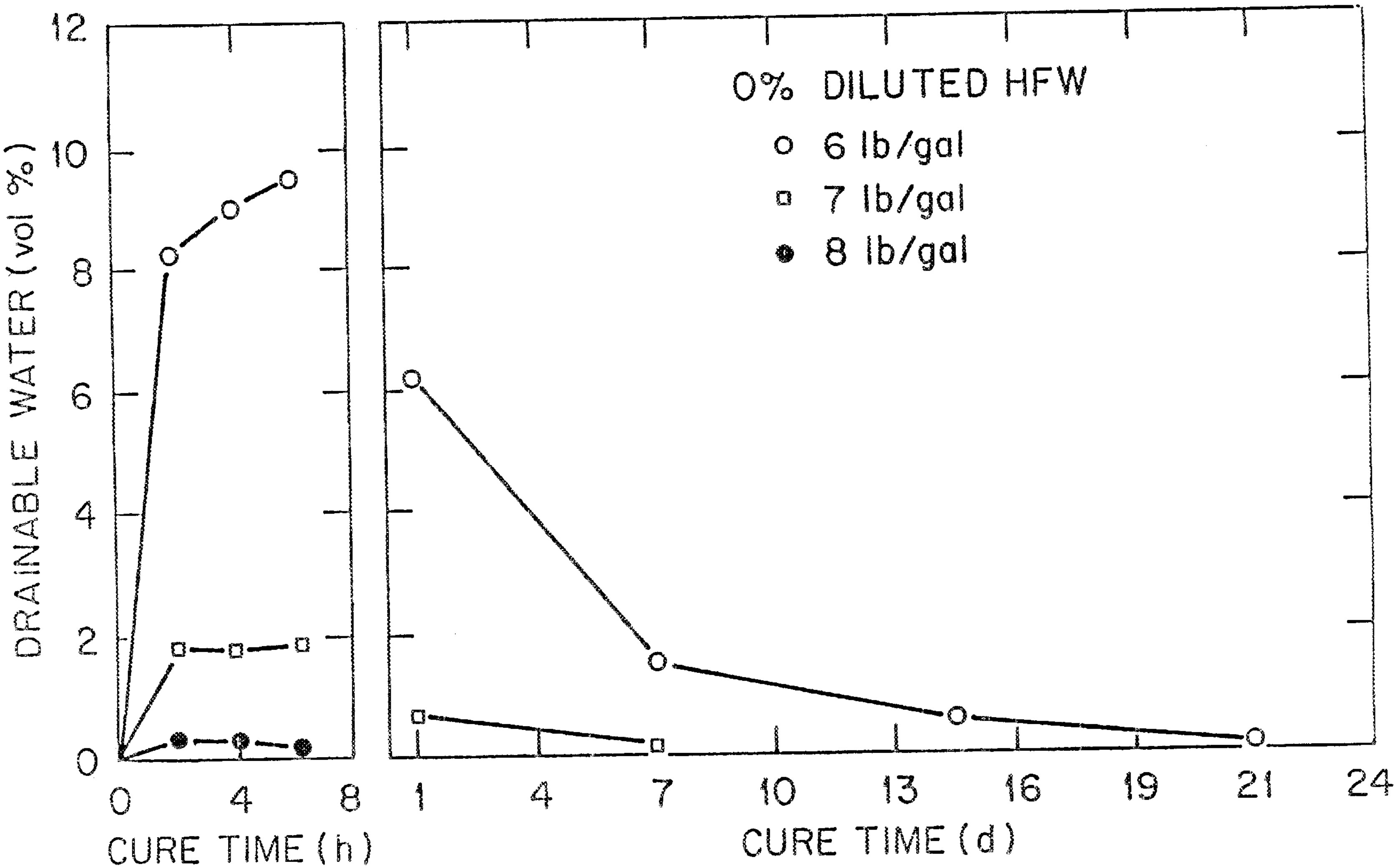

Fig. 5. Drainable water as a function of cure time in a closed system for grouts prepared at various mix ratios with the recommended blend.

reflected in the critical velocity and, in particular, the 10-min gel strength. At lower mix ratios, grouts are more readily processible in the TGF and result in greater flexibility during operation. Thus, if processibility was the major criterion of concern, then mix ratios closer to 7 lb/gal would be favored.

10.4 USE OF WATER WITH RECOMMENDED DRY SOLIDS BLEND

It is anticipated that during routine or emergency shutdown the TGF will be f ushed with water. Experiments were performed to determine if substitution of HFW with water would be compatible with the recommended dry solids blend and TGF performance criteria. This compatibility is essential if this "clean" grout is to be flushed directly to the disposal trench, thereby eliminating the need for a separate dump trench or separate dry solids blend storage silos. In general, grouts containing water are expected to display lower viscosity and higher phase separation than grouts prepared with HFW.

Grouts were prepared with water at mix ratios of 7, 8, 9, and 10 lb/gal with blend 5. Blend 5 was chosen because its high Attapulgite-150 clay content (12 wt %) should minimize phase separation and maximize viscosity. The 28-d phase separation values obtained in a closed system are shown in Table 41. It can be seen that 28-d phase separation decreases from 19 vol % at 7 lb/gal to 1 vol % at 10 lb/gal. Values as a function of cure time are shown in Fig. 6. Rheological data on the grout prepared at 10 lb/gal are shown in Table 42.

The data indicate that subsitution of water for HFW results in more-fluid grouts. The critical velocity, even at a mix ratio as high as

Table 41. The 28-d phase separation values obtained in a closed system for grouts prepared with water and blend 5

Mix ratio (lb/gal)	Phase separation (vol %)
7	19
8	12
9	7
10	1

Table 42. Properties of grouts prepared at a ratio of 10 lb/gal with dry solids blend 5 and water[a]

Property	Measurement
Grout Property	
10-min gel strength, $lb_f/100\ ft^2$	20 ± 2
Fluid consistency index (k′), $lb_f \cdot s^{\eta}/ft^2$	0.047 ± .040
Flow behavior index (η′),	0.37 ± .01
Density, lb/gal	12.36 ± .02
Apparent viscosity, cP	63.09
24-h penetration resistance, psi	152
7-d penetration resistance, psi	850
28-d compressive strength, psi	71
Reference conditions	
Reynolds number	1168.71
Frictional pressure drop per 100 ft, psi	8.78
Critical velocity (gal/min)	70.83

[a]0.4 mL TBP added per liter of water.

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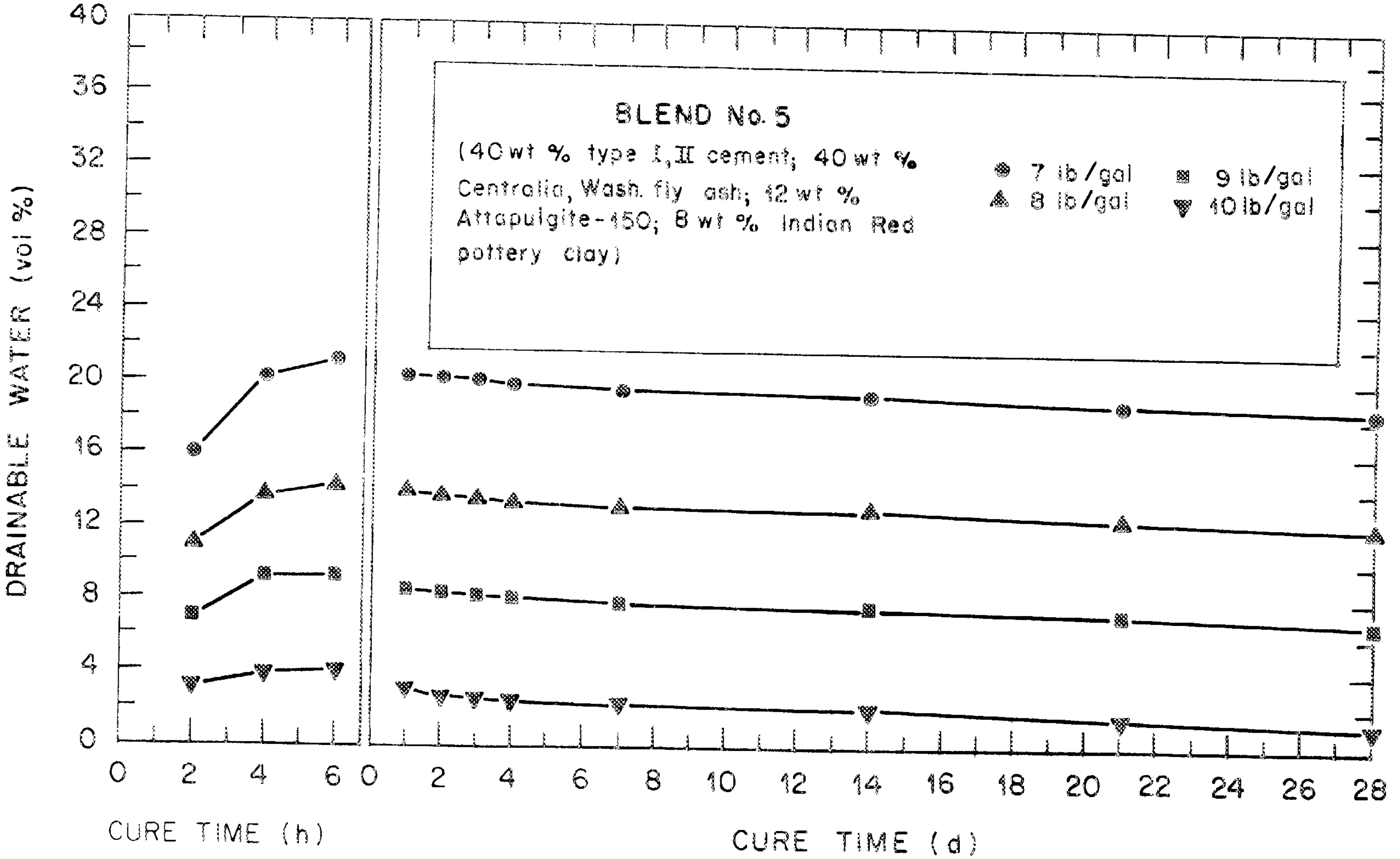

Fig. 6. Drainable water as a function of cure time in a closed system for grouts prepared with blend 5 and water at mix ratios of 7, 8, 9, and 10 lb/gal.

10 lb/gal, is near the TGF distribution pump limit (70 gal/min). Thus at mix ratios between 7 and 8 lb/gal, the resulting grouts will be readily processable in the TGF. However, the data further indicate that these grouts will be characterized by a high bleed rate and will be incapable of resorbing all of the bleed water.

11. SOLID PERFORMANCE DATA

This section presents data pertinent to the performance evaluation of the solidified grout product. Data presented include ^{90}Sr and ^{137}Cs leachability, thermal conductivity, heat capacity, porosity, and liquid permeability. It was beyond the scope of this study to obtain data on all grouts considered in the previous section. Therefore, the data presented here are representative of grouts prepared with the recommended formula. The data are sufficient for use in modeling studies involving risk, environmental, and technical assessment.

11.1 STRONTIUM-90 AND CESIUM-137 LEACHABILITY

Leachability is a property often used in assessing the retention of nuclides in solidified waste forms. Leachability as presented in this section is based on the proposed ANS 16.1 standard test for the measurement of the leachability of solidified low-level radioactive wastes. It is important to note that this test does not attempt to simulate the site-specific environment of the disposal trench; rather, it provides reproducible laboratory conditions so that comparisons with generic studies are possible. In addition, the results of the ANS 16.1 test protocol are generally more conservative than site-specific tests.

11.1.1 Sample Preparation

A total of 6 right-circular cylindrical grout samples were subjected to the ANS 16.1 abbreviated (5-day) leach test. The grouts were prepared at 7 lb/gal with synthetic HFW and the dry solids blends shown in Table 43. As indicated previously, it was beyond the scope of this study to perform a series of comprehensive leach tests. Consequently, the composition of the grout samples was chosen to result in conservative leach rates as compared with grouts prepared with the recommended formula. This conservatis is due to the minimizing of ingredients that restrict leaching such as fly ash content, attapulgite-150 clay content, cement content, and dry solids loading.

Amounts measuring 4.53 μCi of radiotracer ^{90}Sr and 5.53 μCi radiotracer ^{137}Cs were added to three individual samples of each dry solids blend. All samples were poured in Teflon molds and cured for 30 d.

11.1.2 Leach Test Vessels

All leach tests were conducted in 500-mL Teflon containers and cleaned by the MCC-1 Teflon cleaning procedure as follows:

- New containers shall be heated in a 200 C oven for one week prior to cleaning.
- New and used containers are subjected to the following cleaning procedure:

  1. Soak for 1 h in 6 M HNO_3 and 0.2 M HF.
  2. Rinse with three container vol mes of deionized water.
  3. Soak in 6 M HNO^3 for 4 h at 50°C.

  3a. Rinse with three container volumes o deionized water.

Table 43. Grouts tested in leach studies

Parameter	Case 1	Case 2
Type I-II-LA Portland cement, wt %	44	38
Centralia, Wash. ASTM Class F fly ash wt %	38	44
Attagel-150, wt %	10	10
Indian Red pottery clay, wt %	8	8
Solids blend-to-waste mix ratio	7	7

4. Soak for 30 min in >60°C deionized water by full immersion.
5. Soak for at least 8 h in fresh deionized water at 80°C by full immersion.
6. Boil for 30 min in fresh deionized water by full immersion.
7. Rinse with 3 container volumes of deionized water.

7a. Attach matching container cleaning number to matching lids and containers.

8. Clean containers that are not to be used immediately must be sealed and stored in plastic bags.

11.1.3 Leachant

The leachant was deionized water with an electrical conductivity <2 μmho/cm at 24°C and total organic carbon (TOC) <1 ppm.

The leachant volume (cm^3) used in each leach interval was equal to 10 ± .02 cm times the surface area of the specimen (cm^2).

11.1.4 Leaching Procedure

1. The specimen was rinsed by immersion in a volume of distilled water equal to the leachant volume for 30 s.
2. The sample mold was rinsed with a distilled water volume equal to the volume of the mold. This mold rinse and the specimen rinse in step 1 were combined and saved for analysis of rinse-off material.
3. The grout sample was suspended from the top of the leach containers with a nylon monofilament in the leachant. This began the test clock.
4. The leachants were left undisturbed for each time interval. Test temperature was maintained at ambient temperature (20 to 25°C).
5. At the end of the various time intervals (see Table 44), the specimen was transferred immediately in its support to a new container with fresh leachant.
6. The resulting leachate was acidified with 3 mL concentrated nitric acid and stored for analysis. No particulates were discernable in the leachates.

Table 44. Standard intervals for ANS 16.1 leach test

Cumulative time (h)	Time interval (h)
2	2
7	5
24	17

Table 44. Standard intervals for ANS 16.1 leach test (contd)

Cumulative time (h)	Time interval (h)
48	24
72	24
96	24
120	24

11.1.5 Leachate Analysis

The leachates were stored in the Teflon containers until a representative aliquot was taken for anlysis. The ^{137}Cs content was determined using the LKB Wallac CompuGamma Model 1282 gamma counter, while the ^{90}Sr content was determined using the LKB Wallac RackBeta Model 121 liquid scintillation counter.

11.1.6 Experimental Results

The results of this study are reported as

- plot of quantity (cumulative fraction of radioactivity times sample volume-to-surface area) leached vs time,
- effective diffusivity, and
- ANS 16.1 Leachability Index (L_i).

Leach test results reported as only the cumulative fraction leached are applicable only to the particular sample because this is dependent upon the volume-to-surface ratio of the sample. Thus, as a normalizing factor the fraction is multiplied by the volume-to-surface ratio of the sample. Examples of these plots for ^{90}Sr and ^{137}Cs are shown in

Figures 7–10. These include samples of both Case 1 and Case 2 dry solids blends. If the leaching is purely diffusion controlled, a linear relationship exists between cumulative fraction leached and the square root of time. The data consistently show that, after the initial wash-off periods, the leaching is diffusion controlled. In the first few leach intervals, the fraction of isotope leached was seemingly low due to the initial presence of insoluble salts on the surface of the samples. Then, after sufficient time, these salts dissolved and allowed diffusion-controlled leaching to occur.

Using the cumulative fraction leached in the diffusion-coefficient calculation has one major disadvantage: the data points all depend on each other. That is, any error or bias is carried into subsequent data points. Thus, the ANS 16.1 procedure suggest calculating the diffusivities at each leach interval.

If less than 20% of a species is leached from a diffusion-controlled environment, the effective diffusivity for the nth leach interval can be calculated by the expression

$$D_e = \pi \left[\frac{a_n/A_o}{(\Delta t)_n}\right]^2 \left[\frac{V}{S}\right]^2 T , \qquad (6)$$

where

D_e = effective diffusivity, cm^2/s;

V = volume of specimen, cm^3;

S = geometric surface area, cm^2;

T = $\left[1/2 \left[(t_n)^{1/2} + (t_{n-1})^{1/2}\right]\right]^2$ representing the mean time of the leaching interval, s;

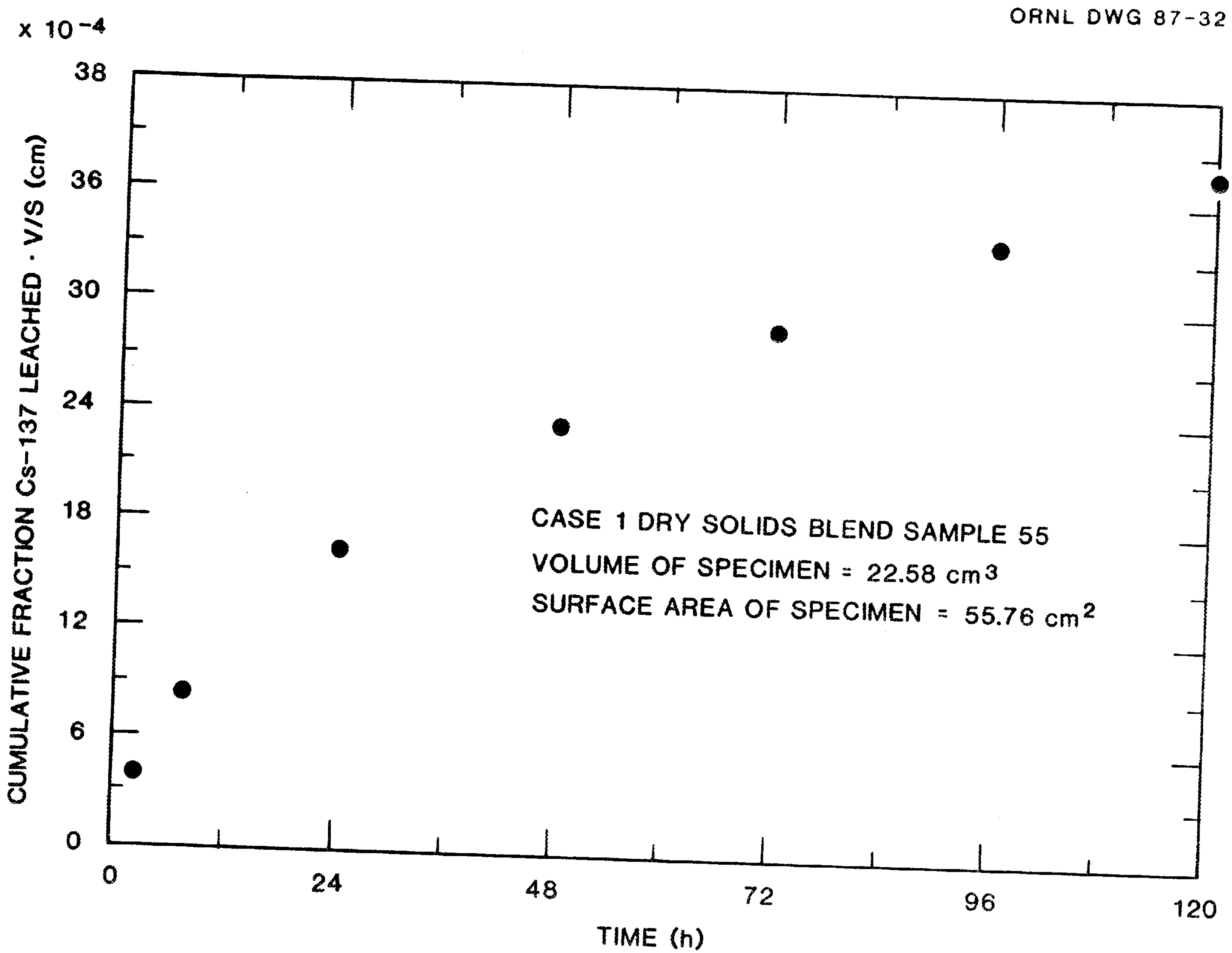

Fig. 7. Cumulative fraction ^{137}Cs leached as a function of time for a Case 1 grout.

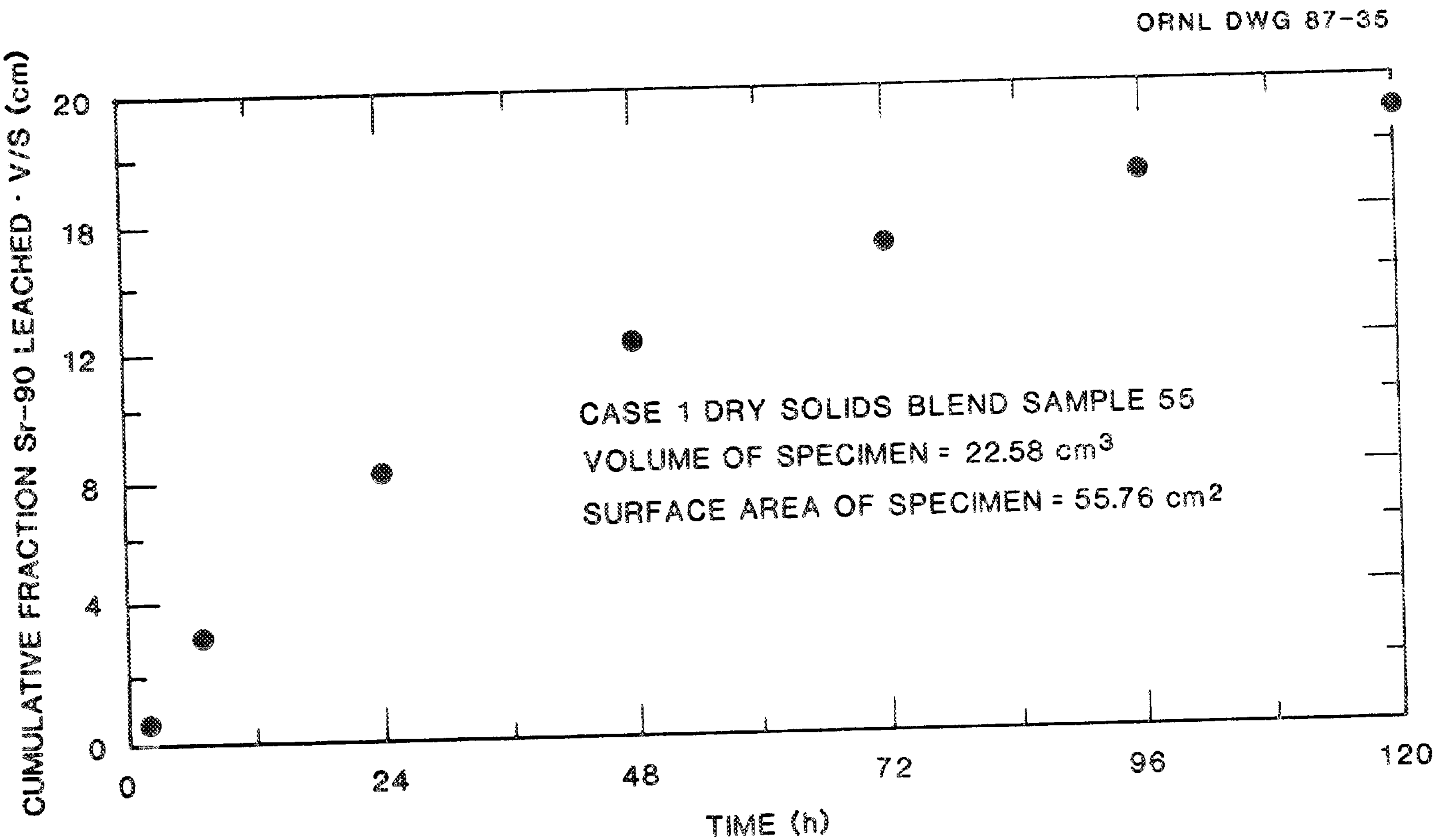

Fig. 8. Cumulative fraction ^{90}Sr leached as a function of time for a Case 1 grout.

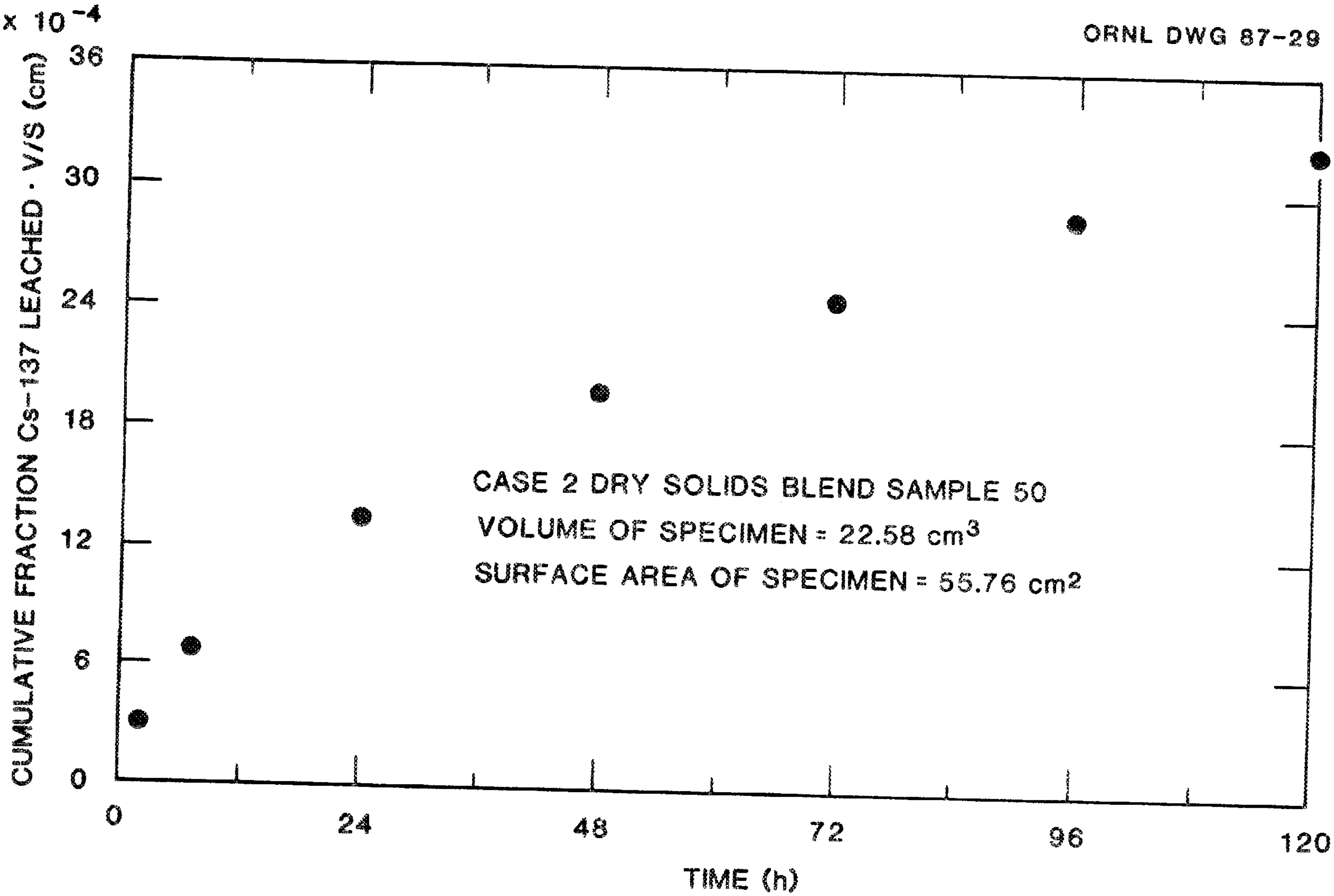

Fig. 9. Cumulative fraction ^{137}Cs leached as a function of time for a Case 2 grout.

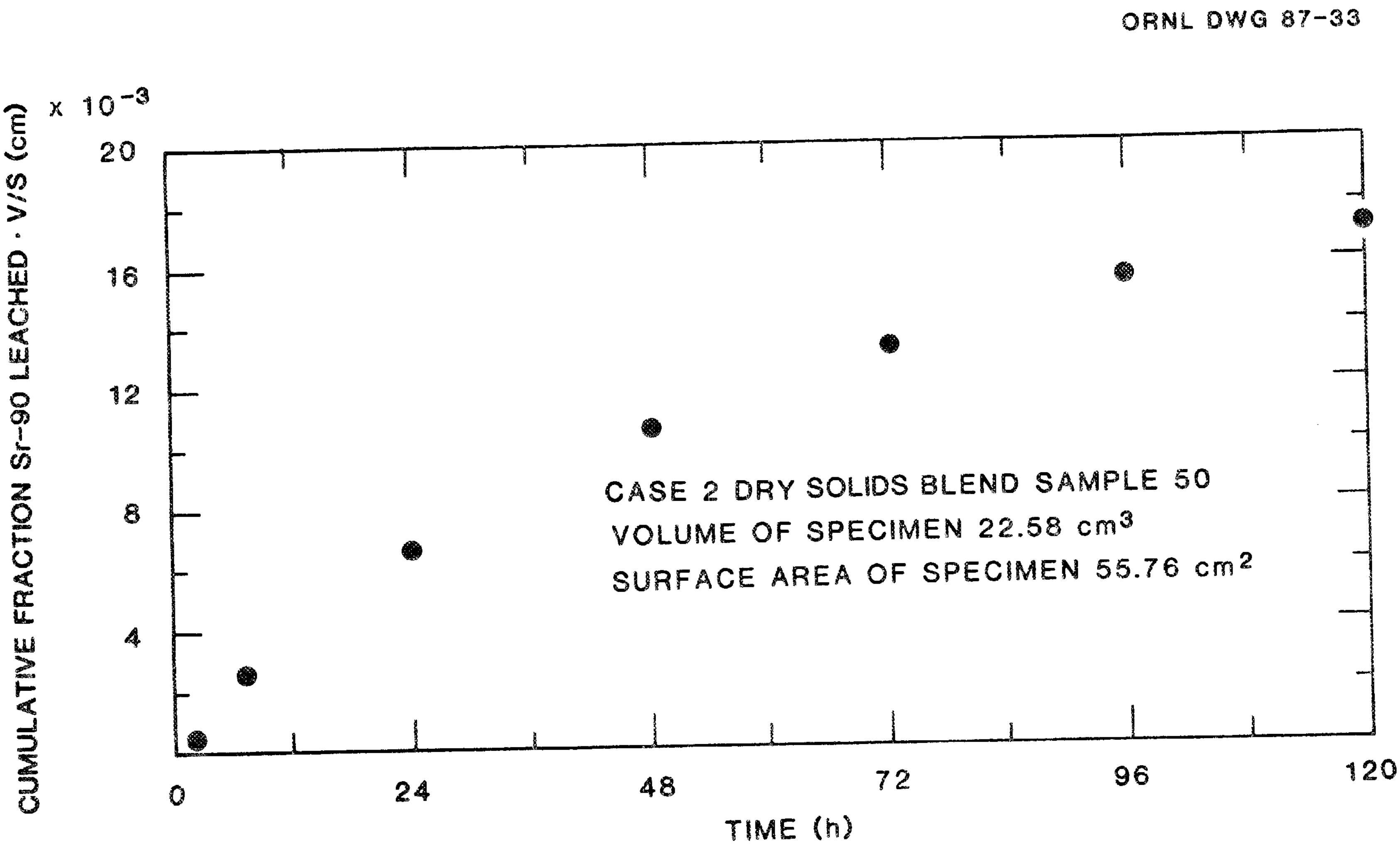

Fig. 10. Cumulative fraction ^{90}Sr leached as a function of time for a Case 2 grout.

t_n = cumulative leaching time, s;

$(\Delta t)_n$ = duration of the nth leaching interval, s;

a_n = activity of a nuclide released from the specimen during the nth leaching interval;

A_o = total activity of a given radionuclide in the specimen at the beginning of the leach test (i.e., after the initial 30-s rinse).

Table 45 shows a sample calculation of the diffusivities at each leach interval for ^{137}Cs in a sample containing Case 2 dry solids blend. Table 46 summarizes the average diffusivities for ^{137}Cs and ^{90}Sr in the grout samples tested.

The ANS 16.1 procedure defines a figure-of-merit for the leachability of radionuclides in solidified waste forms. This leachability index (L_i) is defined as

$$L_i = 1/J \sum_{n=1}^{J} [\log (B/D_i)]_n \quad , \tag{7}$$

where B is a defined constant (1 cm^2/s), D_i is the effective diffusivity of nuclide i calculated from the test data, and J is the number of leach intervals. Table 47 summarizes the leachability index calculations for ^{137}Cs and ^{90}Sr in the samples tested. As indicated by the data, grouts representative of those prepared with the recommended formula are characterized by a leachability index significantly above the required performance criterion of 6 (see Sect. 3.2) for both ^{90}Sr and ^{137}Cs.

Table 45. Sample calculation of diffusivities of ^{137}Cs

Sample 55	(a_n/A_o)	$(V/S)^2$	$[1/(\Delta t)_n]2$	T	D
2 h	9.83×10^{-7}	0.240	1.93×10^{-8}	1,800	2.57×10^{-11}
7 h	1.23×10^{-6}	0.240	3.09×10^{-9}	14,835	4.24×10^{-11}
24 h	3.93×10^{-6}	0.240	2.67×10^{-10}	51,231	4.05×10^{-11}
48 h	3.06×10^{-6}	0.240	1.34×10^{-10}	125,894	3.89×10^{-11}
72 h	1.80×10^{-6}	0.240	1.34×10^{-10}	213,818	3.89×10^{-11}
96 h	1.38×10^{-6}	0.240	1.34×10^{-10}	300,849	4.20×10^{-11}
120 h	9.81×10^{-7}	0.240	1.34×10^{-10}	387,596	3.84×10^{-11}

Table 46. Summary of average diffusivity of ^{137}Cs and ^{90}Sr in immobilized Hanford Facility Waste

Sample No.	Dry solids blend case No.	Average diffusivity of ^{137}Cs (cm^2/s)	Average diffusivity of ^{90}Sr (cm^2/s)
55	1	3.81×10^{-11}	1.02×10^{-9}
56	1	2.70×10^{-11}	6.15×10^{-10}
57	1	3.83×10^{-11}	9.48×10^{-10}
50	2	2.81×10^{-11}	8.10×10^{-10}
51	2	2.79×10^{-11}	7.72×10^{-10}
52	2	2.71×10^{-11}	6.61×10^{-10}

Table 47. Leachability index for ^{90}Sr and ^{137}Cs in immobilized Hanford Facility Waste

Sample No.	Dry solids blend case No.	Leachability index of ^{137}Cs	Leachability index of ^{90}Sr
55	1	10.4	9.1
56	1	10.6	9.3
57	1	10.4	9.3
50	2	10.6	9.2
51	2	10.6	9.3
52	2	10.6	9.3

11.2 THERMAL PROPERTIES

A parametric sensitivity analysis which addressed the hypothetical conditions which lead to maximum grout temperature in shallow earthen trenches has been reported previously (ORNL Milestone 76). In this analysis, soil and grout thermal conductivity, grout specific heat, waste loading and disposal geometries were varied in a computer model. Since the grout specific heat and thermal conductiviy had the greatest impact on the calculated maximum grout temperatures, experimental values of these two parameters were obtained for grouts representative of those discussed in Section 9 and 10. The results of the thermal measurement study has been reported previously (ORNL Milestone 123). Only the highlights of that study are presented here.

11.2.1 Thermal Conductivity

The computer simulation study indicated that a wide range in grout thermal conductivity (λ) had no significant deleterious effect on trench peak temperature (Fig. 11). Based on this analysis, acceptable values of thermal conductivity appear to be $\geq$ 0.1 Btu/hr · ft · °F.

Experimental values of thermal conductivity were determined using a Dynatech Corporation model TCFM-N20 comparative thermal conductivity analyzer in conjunction with a Hewlett Packard model 3052A automatic data acquisition and control system (Fig. 12). Data were obtained over the temperature range ambient to 90°C.

The data showed that there is a weak relationship between thermal conductivity and temperature. For example, the relationship between thermal conductivity and temperature is shown in Fig. 13 for a grout prepared at 7 lb/gal and blend 1 (Table 13) with 33% diluted reference waste. Consequently, the data were averaged over the entire temperature range, with results shown in Fig. 14. The data show that thermal conductivity decreases with increasing mix ratio. However, the range of mix ratios over the operational limits of the TGF (7 and 8 lb/gal) is small (0.51 to 0.46 Btu/h · ft · °F, respectively).

The average of all 317 thermal conductivity measurements obtained for these grouts is 0.46 Btu/h · ft · °F $\pm$ 0.07. Thus, with a 99% confidence level, the average thermal conductivity of the grouts studied is 0.46 $\pm$ 3%. More importantly, one can state with 95% confidence that the thermal conductivities of these grouts are within the range 0.29–0.60 Btu/h · ft · °F. Therefore, the thermal conductivities of these grouts are well above the minimum acceptable value of 0.1 Btu/h · ft · °F.

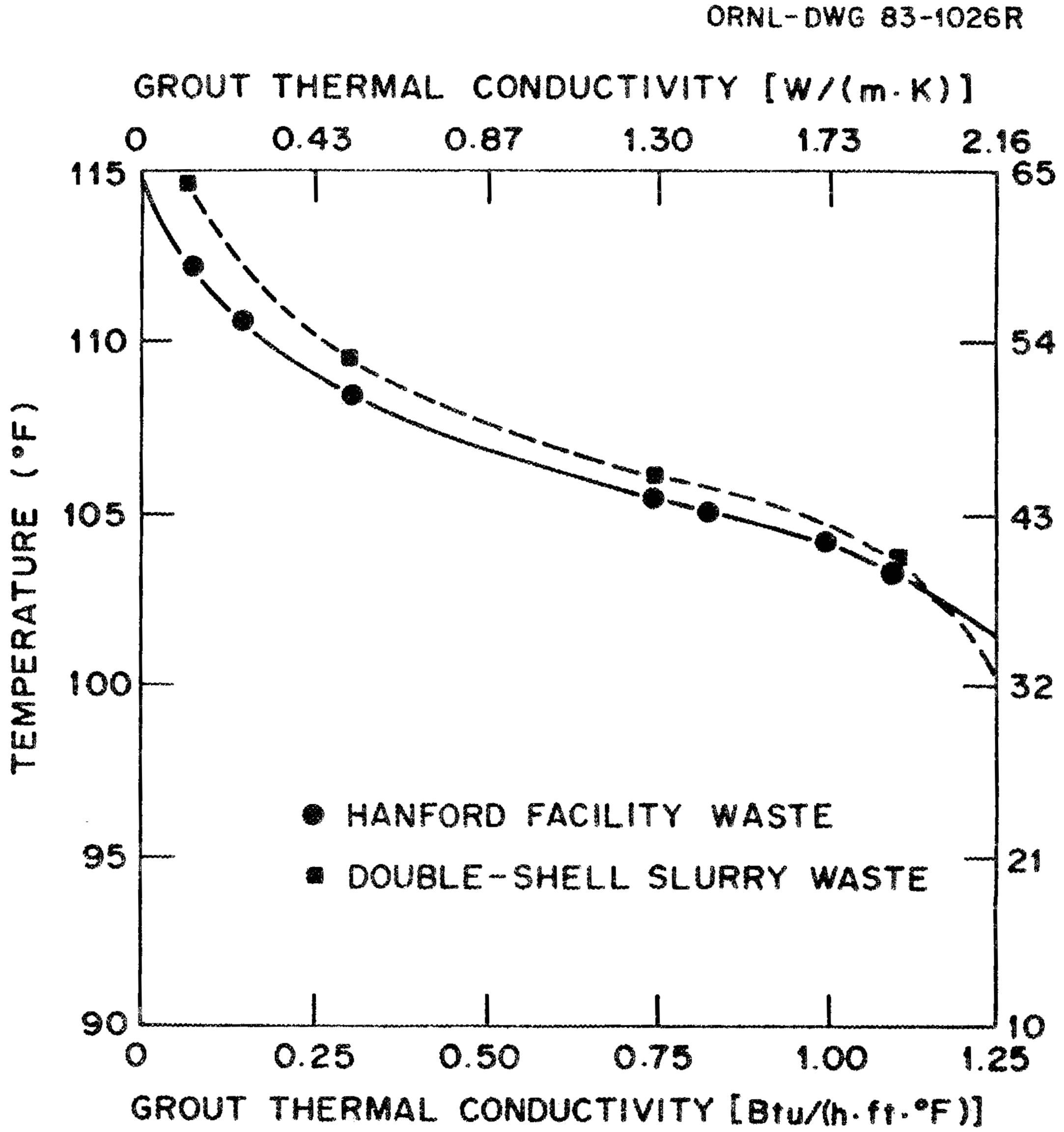

Fig. 11. Peak trench temperature as a function of grout thermal conductivity.

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Fig. 12. Thermal conductivity equipment.

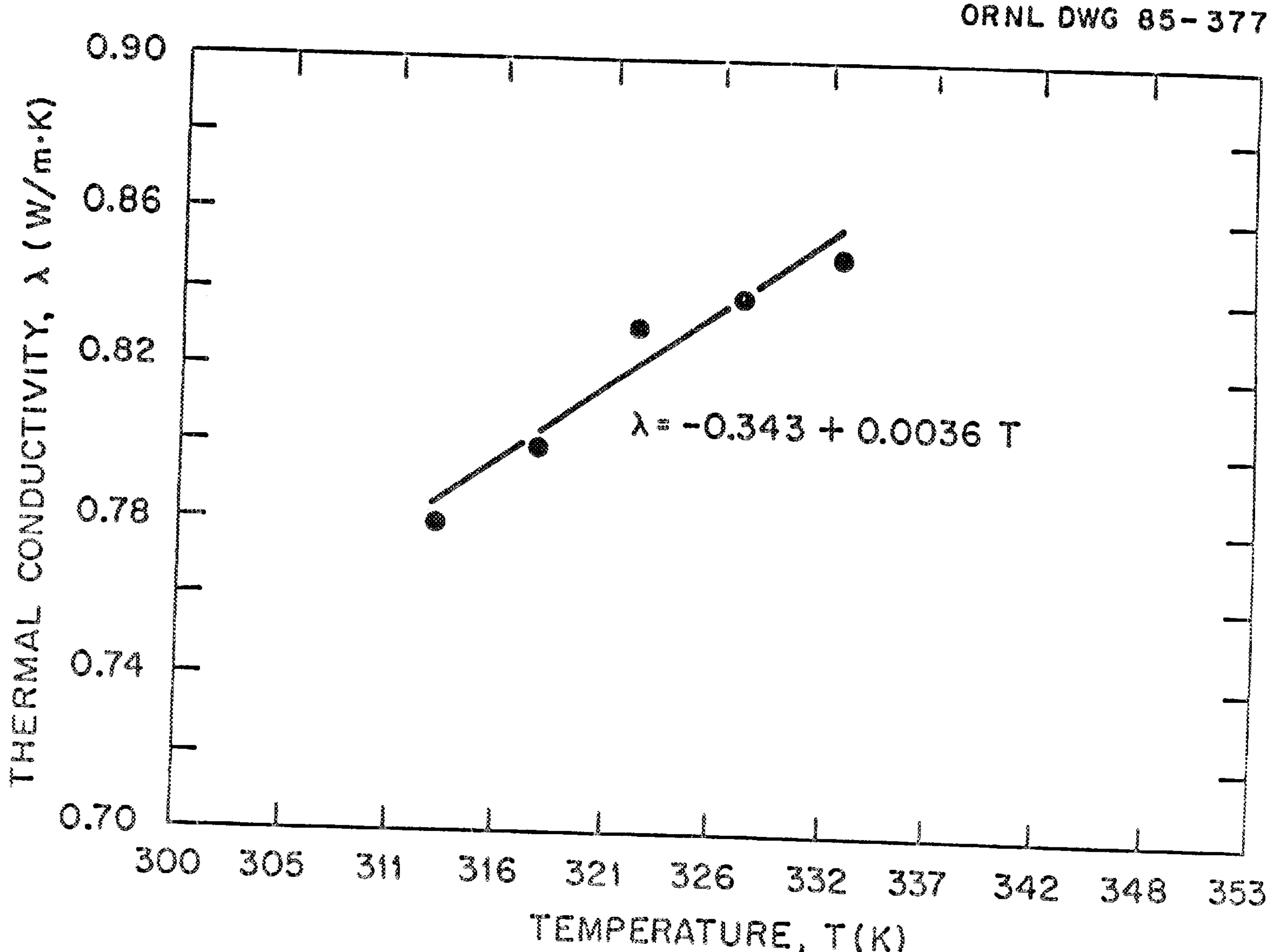

Fig. 13. Therm l conductivity as a function of temperature for a grout prepared at 7 lb/gal with blend 1 and 33% diluted reference waste.

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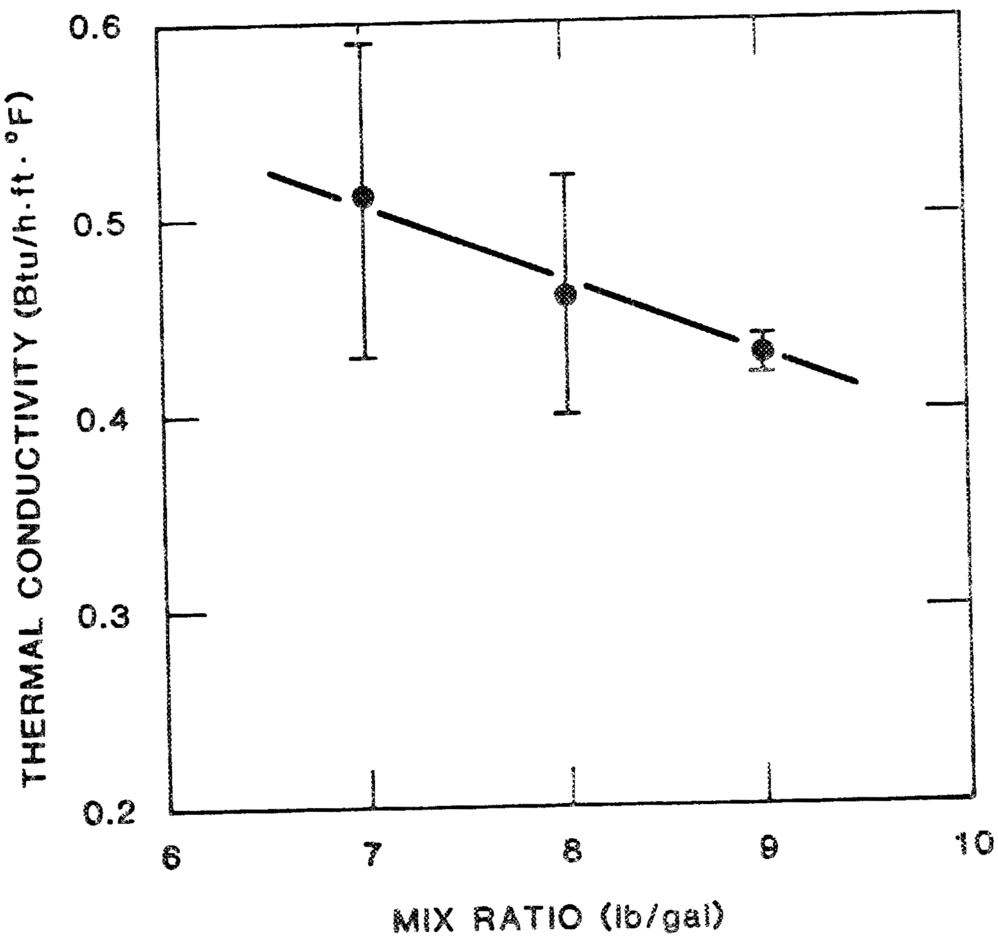

Fig. 14. Average thermal conductivity as a function of mix ratio for grouts containing reference waste.

11.2.2 Heat Capacity

As with thermal conductivity, the computer simulation study indicated that a wide range in grout heat capacity has no significant deleterious effect on trench peak temperature (Fig. 15). Based on the analysis, acceptable values of heat capacity appear to be $C_p \geq 0.25$ Btu/lb • °F.

Experimental values of heat capacity were determined using a DuPont model 1090 Differential Scanning Calorimeter. Data were obtained over the temperature range ambient to 100°C.

As with thermal conductivity, the relationship between heat capacity and temperature is weak. Data for grout prepared at 7 lb/gal and blend 1 (Table 13) with 33% diluted reference waste are shown in Fig. 16. In general, the relationship between heat capacity and temperature follows Debye's law, which states that heat capacity is a function of temperature cubed. Consequently, the data were averaged over the entire temperature range, with results shown in Fig. 17. The data show that the heat capacity of these grouts is well above the minimum acceptable value of 0.25 Btu/lb • °F. Also shown is the predicted value of heat capacity using a weighted average of individual component heat capacities (Table 48). The predicted values are in good agreement with measured values, but are consistently 10% higher.

Table 48. Heat capacity of individual grout components

Component	Heat Capacity (Btu/lb • °F)
Cement	0.186
Clay	0.224

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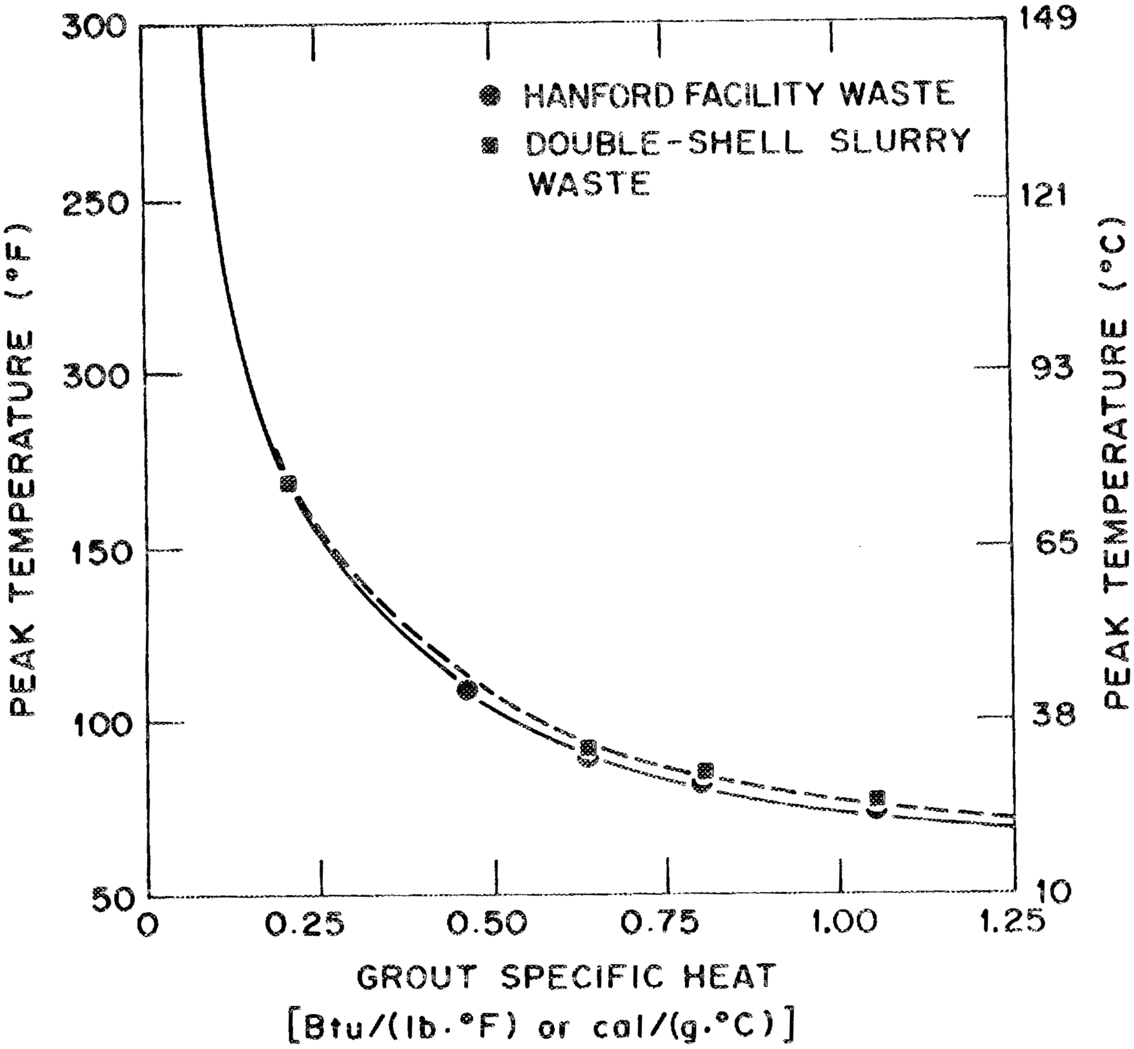

Fig. 15. Peak trench temperature as a function of grout heat capacity.

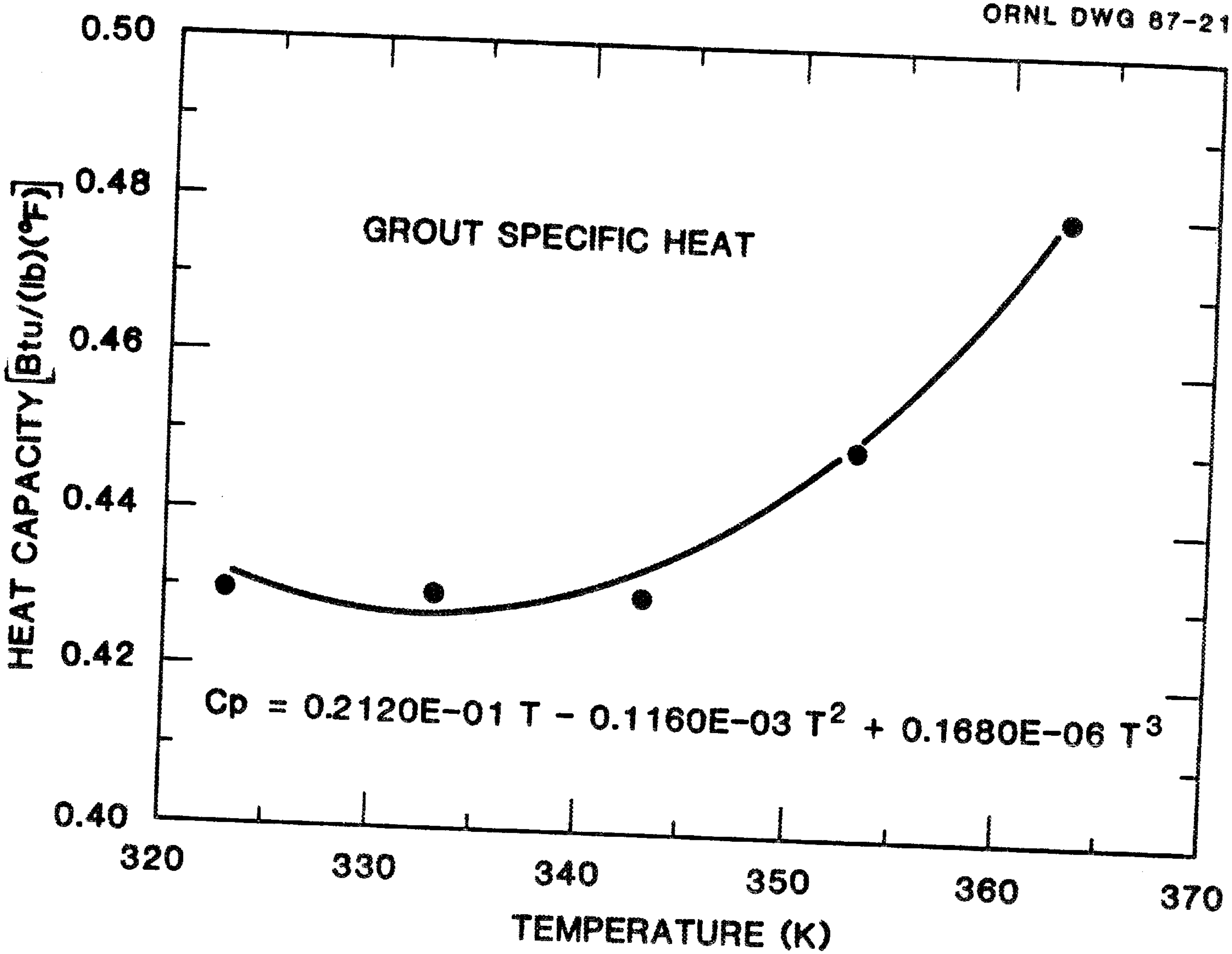

Fig. 16. Heat capacity as a function of temperature for a grout prepared at 7 lb/gal with blend 1% and 33% diluted reference waste.

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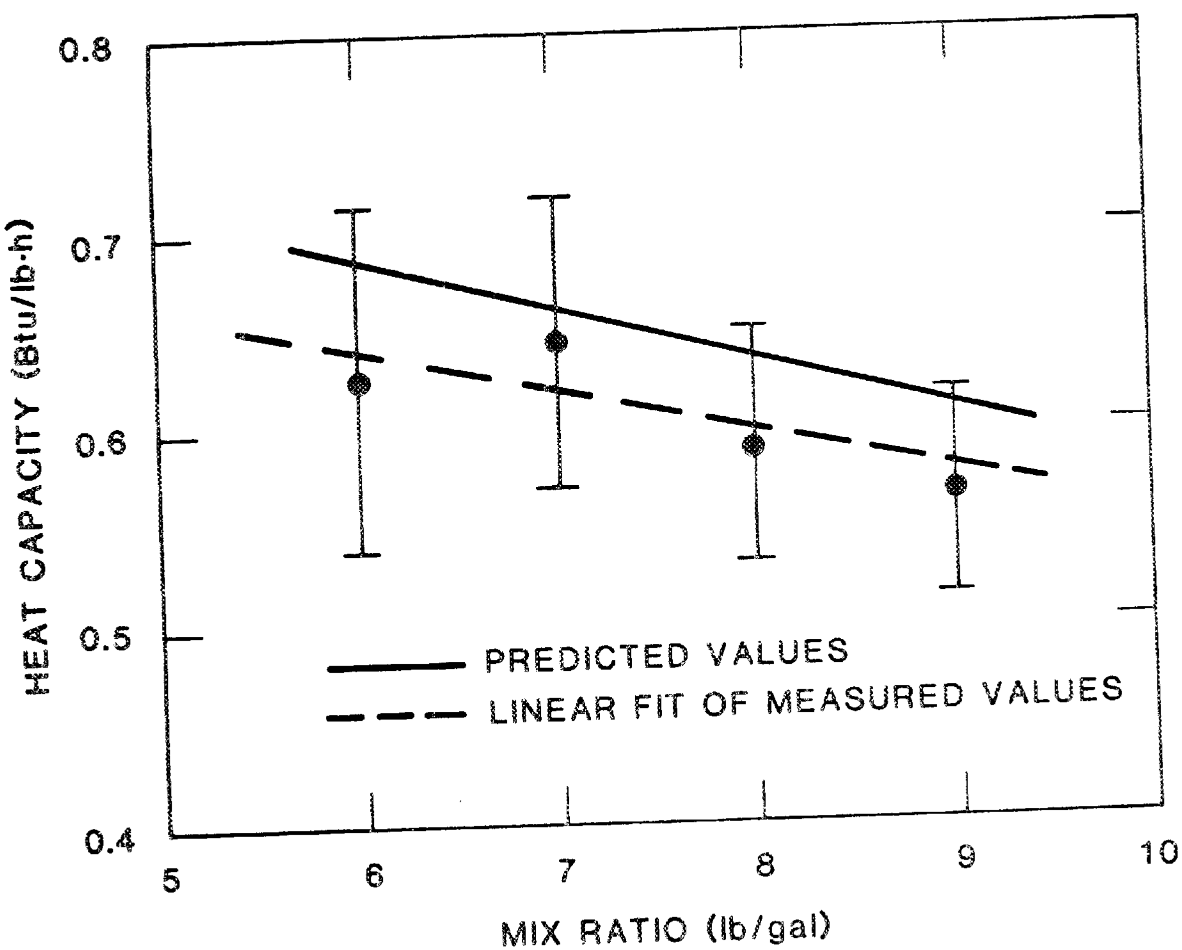

Fig. 17. Average heat capacity as a function of mix ratio for grouts containing reference waste.

Table 48. Heat capacity of individual grout components (contd)

Component	Heat Capacity (Btu/lb · °F)
Fly Ash	0.316
Waste	1.0

11.3 POROSITY AND LIQUID PERMEABILITY

In evaluating the long-term behavior of the disposal trench after closure, two grout parameters of interest are porosity and liquid permeability. These two parameters are germane to predicting water percolation through the disposal trench.

11.3.1 Liquid Permeability

11.3.1.1 Experimental Procedure. A schematic of the test apparatus used for measuring liquid permeability is shown in Fig. 18. A 2.5-cm-diam grout sample, cured for a minimum of 28 d, was cut to length (approximately 0.02 cm) by a wet cutting wheel. The exact diameter and length of each specimen was measured with calipers. The specimen was then rinsed with water and loaded into the sample chamber after the heavy-wall rubber tube was pulled back by a vacuum exerted through the Hassler opening (See Fig. 18). The line and inner cell chamber were then filled with water from the stainless steel reservoir. A sealing pressure of approximately 300 psi was exerted on the sample by the heavy-wall rubber tubing, by filling the space between the outer walls of the Hassler cell with water, and by the rubber tubing. A differential water pressure of 2–4 atms was exerted across the sample.

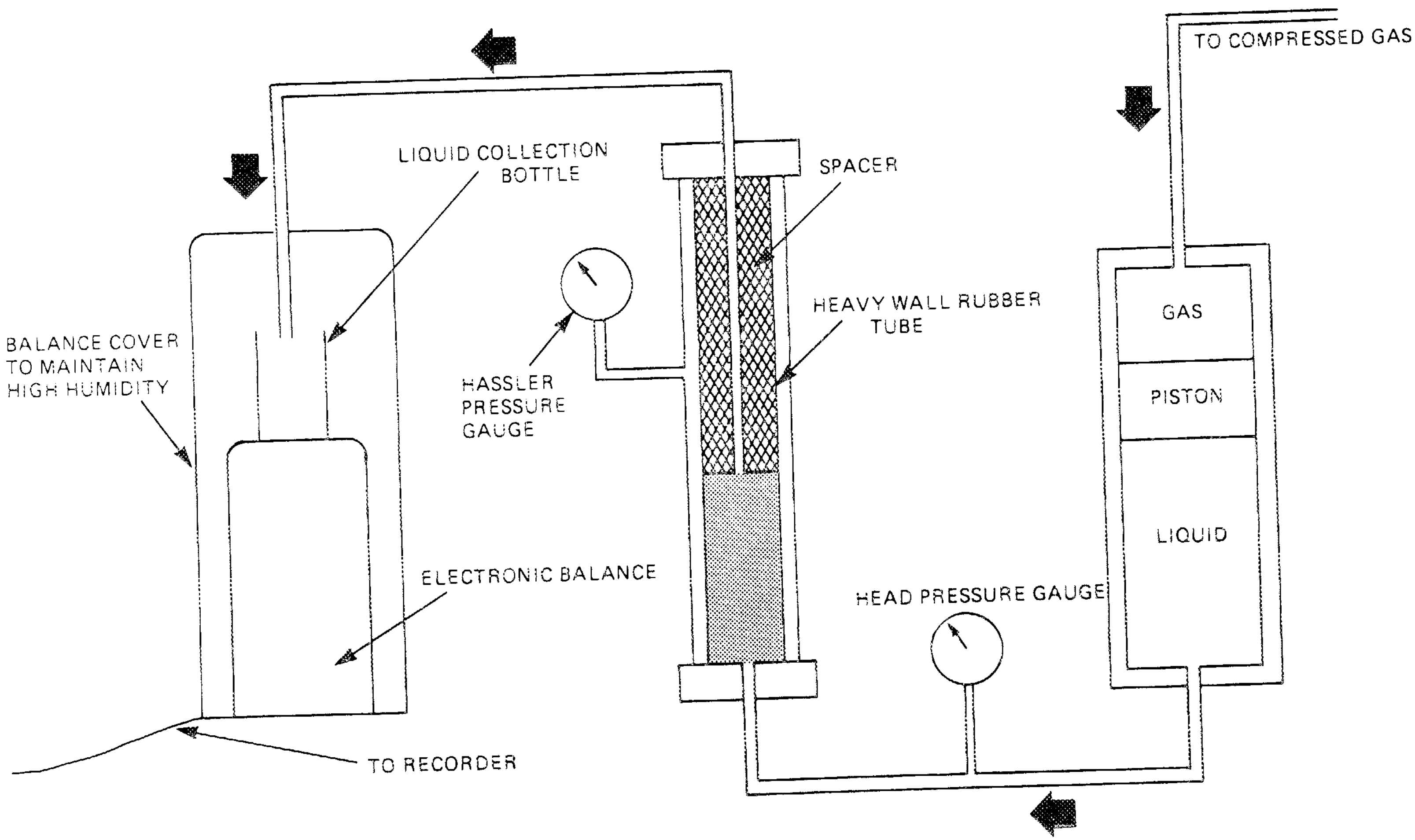

Fig. 18. Schematic of permeability equipment.

11.3.1.2 Data Reduction. The flow rate was calculated by weighing the amount of water flowing through the sample per unit time on an electronic balance. The balance was enclosed in a shield with a wet paper towel inside to saturate the surrounding air with water.

The permeability was calculated from a plot implementing Darcy's law, expressed as:

$$k = \frac{\mu Q L}{\Delta P A} \tag{8}$$

where

k = permeability, darcy;

μ = viscosity of the working fluid, cP;

Q = flow rate, cm^3/s;

L = length of the sample, cm;

ΔP = pressure gradient ($P_1 - P_2$), atm;

A = cross section of the sample, cm^2.

The unit most widely used to measure permeability is the darcy. This unit is defined as the permeability that results in a flow rate of 1 cm^3/s of fluid with a viscosity of 1 cP through a cube having sides 1 cm in length at a pressure differential of 1 atm. Thus,

$$1 \text{ darcy} = \frac{1\ (cm^3/s) \times 1\ (cP)}{1\ (cm^2) \times 1\ (atm/cm)}$$

The permeability of the grout samples was determined from a plot of Q/A vs $\Delta P/L$. Three points at pressure gradients of 2, 3, and 4 atmospheres were plotted, and the slope of the resulting straight line was taken as the permeability. Examples of these plots are shown in Figs. 19–24 for grouts prepared at 7 lb/gal with several dry solids blends from Table 13. The R-square value given for each plot is the square of the multiple correlation coefficient, sometimes called the coefficient of determination. It represents the fraction of the total variation in Q/A explained by the linear relationship to $\Delta P/L$, where a value of 1 represents a perfect fit. The F value is also included for each plot.

11.3.1.3 Experimental Results. Permeability measurements were made of grout specimens composed of blends 1–9 (Table 13) with 0 and 100% dilutions of reference waste at mix ratios of 7 and 8 lb/gal. Additional permeability measurements were made of grout specimens prepared with blend 5 at a mix ratio of 6 and 9 lb/gal and 0, 25, 50, and 100% dilutions of reference waste. Also, two specimens containing water instead of reference waste were tested.

The resulting permeability values are tabulated in Table 49. No correlation between permeability and mix ratio could be ascertained. However, there is a noticeable difference between mix ratios of 6 and 9 lb/gal for blend 5. These data indicate that the more solid per volume of waste, the more impermeable the grout, which is to be expected.

The greatest difference in permeabilities was noted between specimens made from reference waste and those made with water. The specimens made with water were much more permeable than those made from reference waste. A measurement of 1.3×10^{-3} darcy was made for the specimens containing water, and $<3 \times 10^{-8}$ for a comparable specimen was made with reference

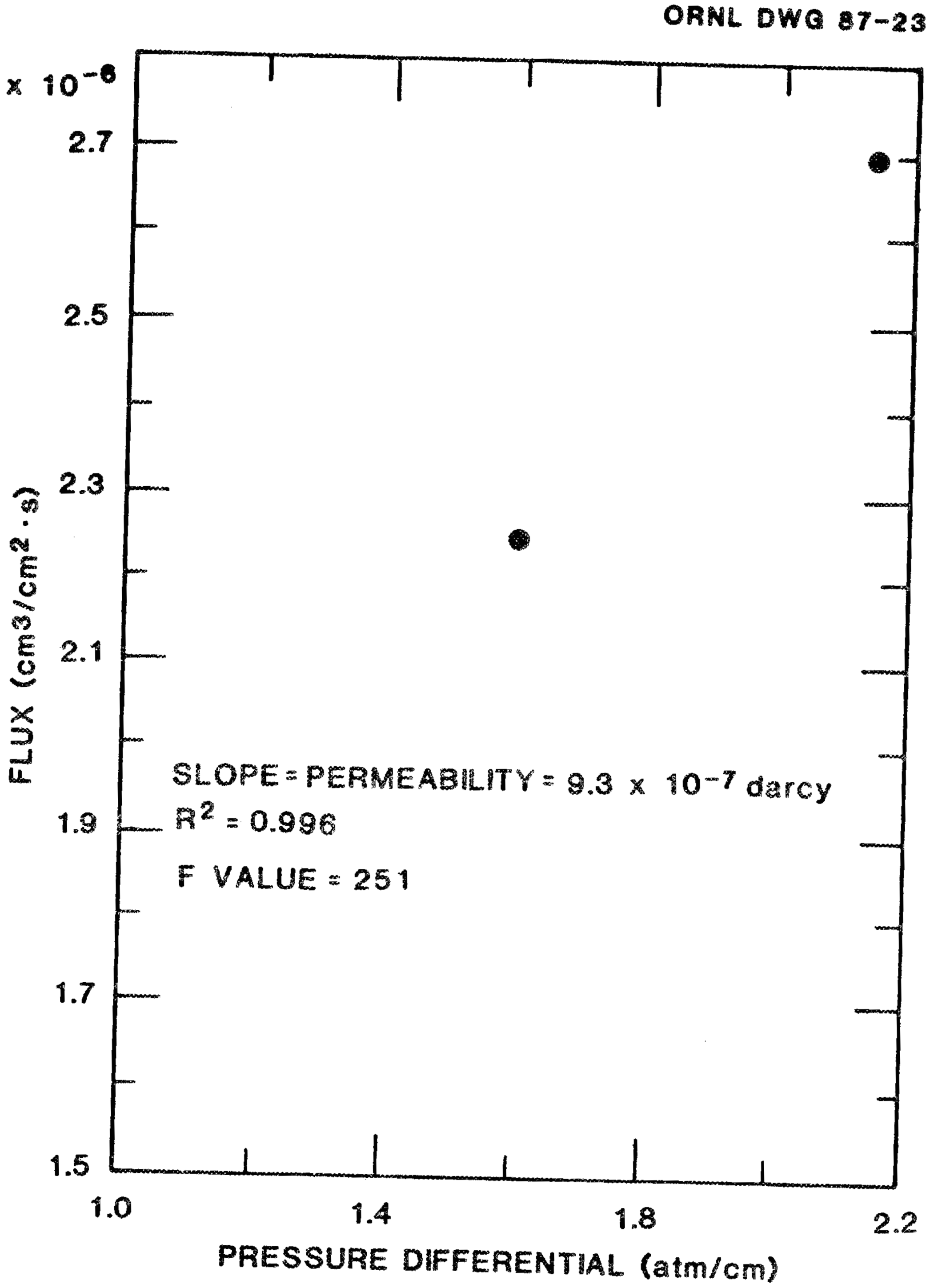

Fig. 19. Plot of flux (Q/A) vs pressure differential ($\Delta P/L$) for a grout prepared at 7 lb/gal with blend 1 and 0% diluted reference waste.

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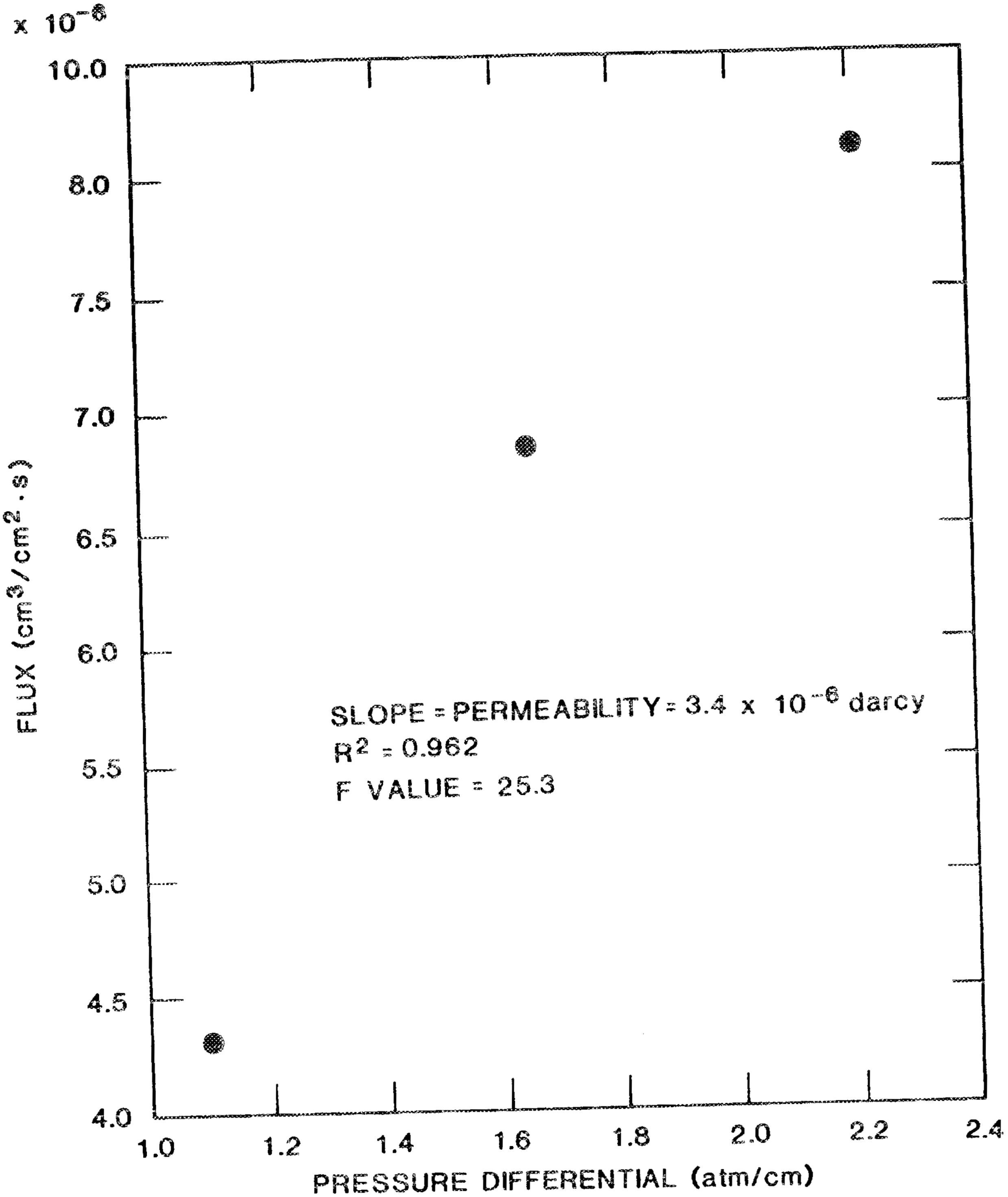

Fig. 20. Plot of flux (Q/A) vs pressure differential (ΔP/L) for a grout prepared at 7 lb/gal with blend 2 and 0% diluted reference waste.

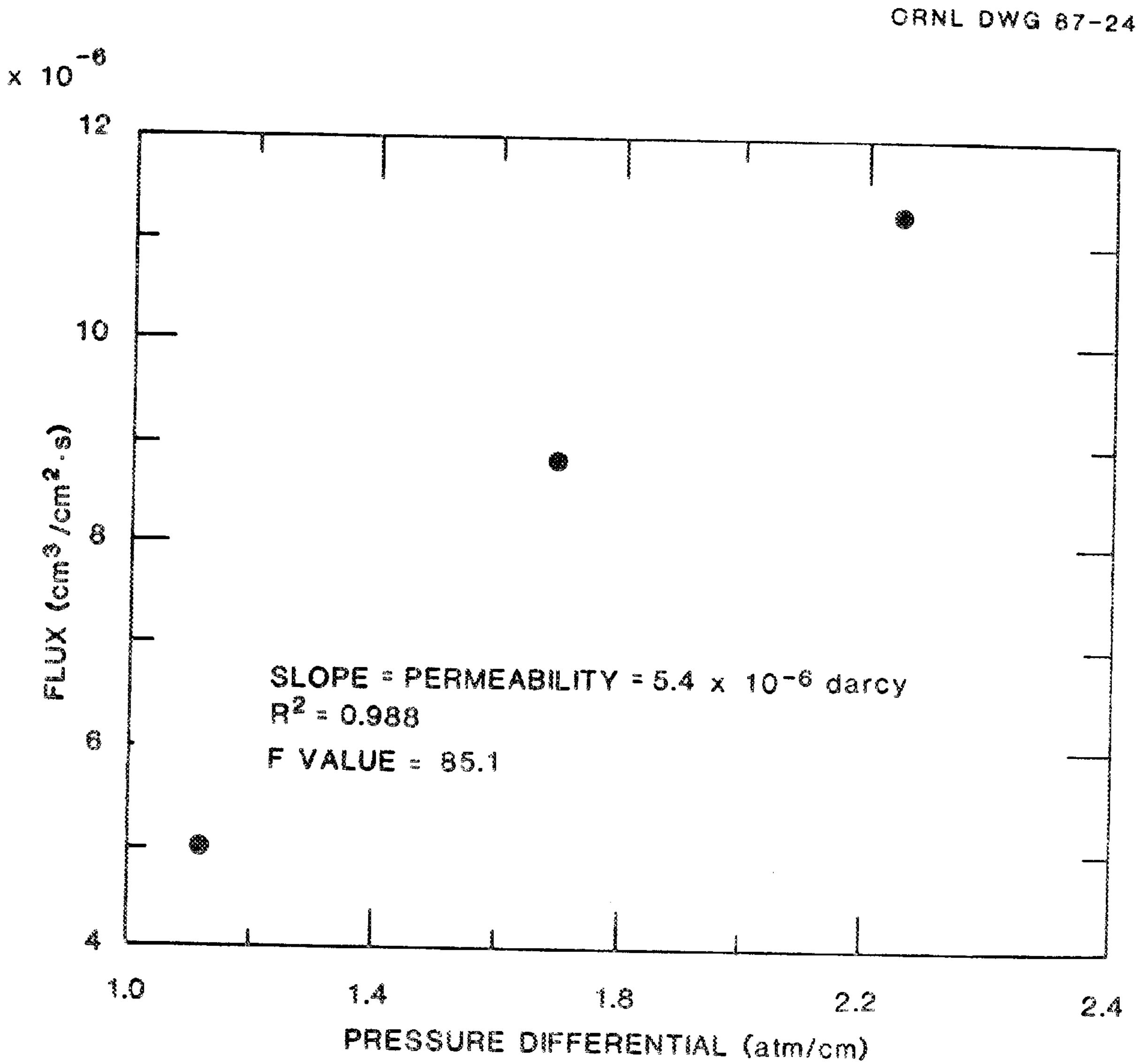

Fig. 21. Plot of flux (Q/A) vs pressure differential ($\Delta P/L$) for a grout prepared at 7 lb/gal with blend 4 and 0% diluted reference waste.

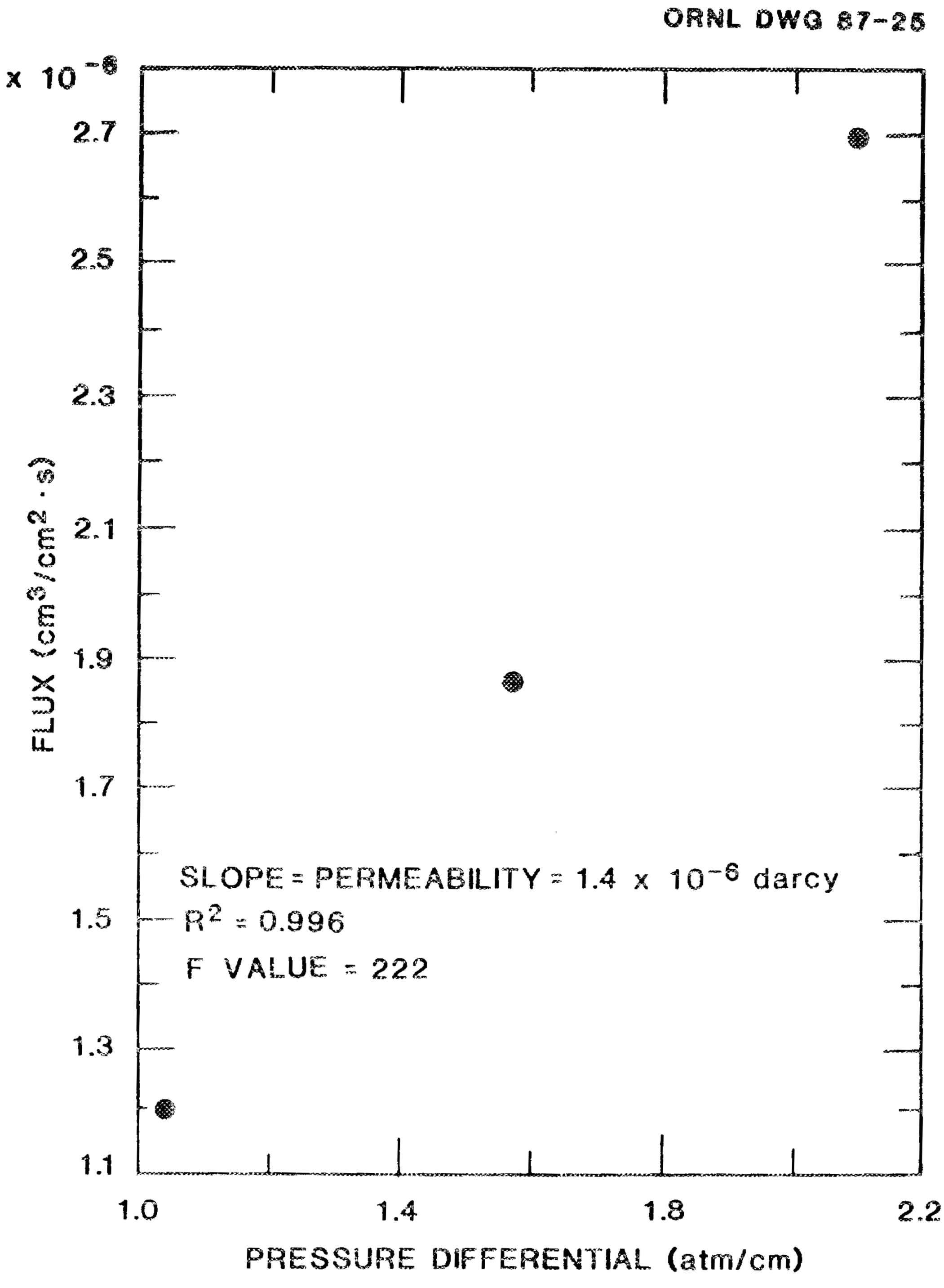

Fig. 22. Plot of flux (Q/A) vs pressure differential ($\Delta P/L$) for a grout prepared at 7 lb/gal with blend 5 and 0% diluted reference waste.

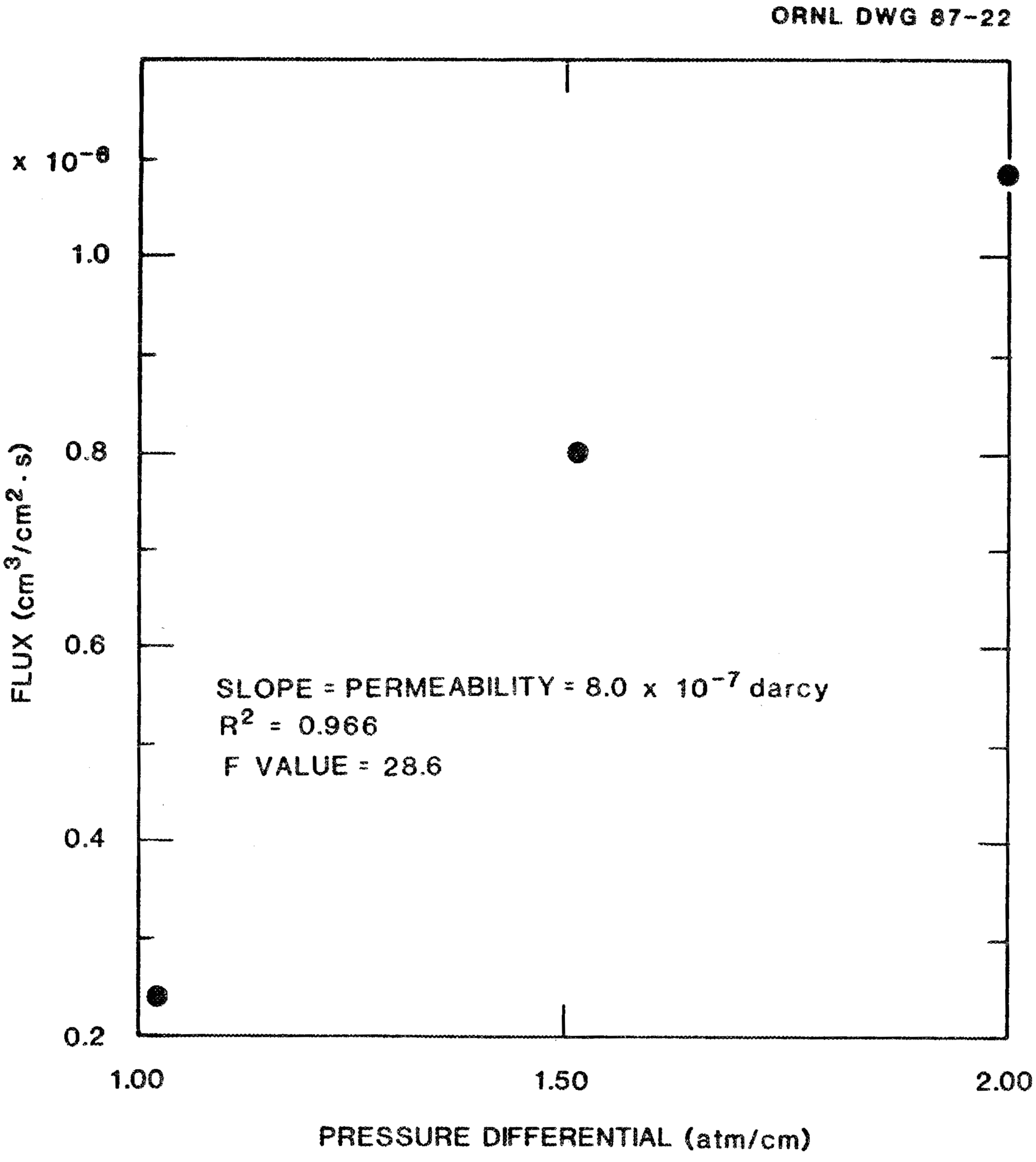

Fig. 23. Plot of flux (Q/A) vs pressure differential ($\Delta P/L$) for a grout prepared at 7 lb/gal with blend 9 and 0% diluted reference waste.

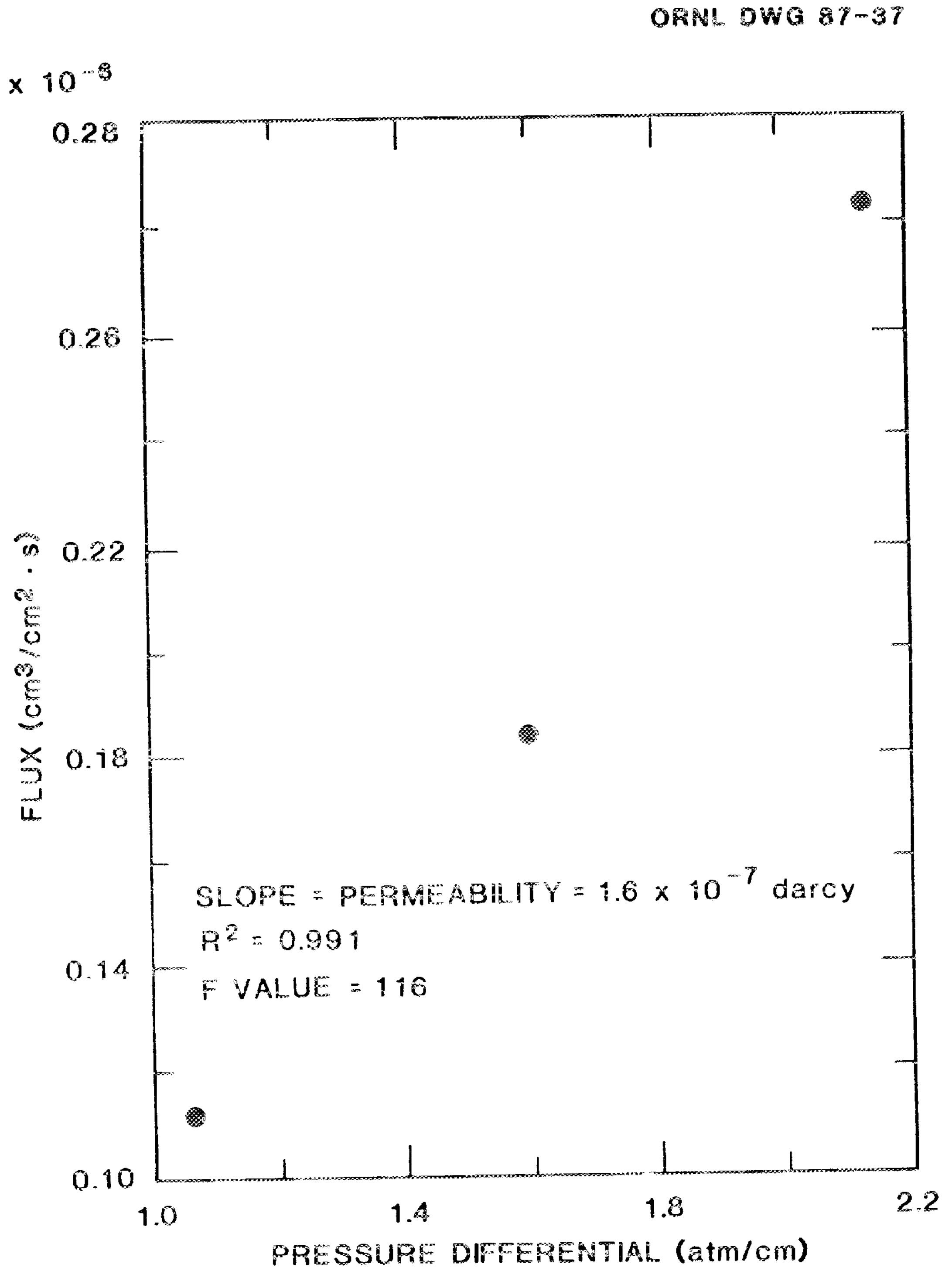

Fig. 24. Plot of flux (Q/A) vs pressure differential (ΔP/L) for a grout prepared at 7 lb/gal with blend 9 and 100% diluted reference waste.

Table 49. Liquid permeabilities of grouts containing reference waste

Mix ratio (lb/gal)	Dilution of reference waste (%)	Liquid permeabilities (darcy) of grouts prepared with blend 1	2	3	4	5	6	7	8	9
6	0					3.2×10^{-6}				
	25					8.0×10^{-7}				
	50					6.5×10^{-6}				
	100					4.9×10^{-6}				
7	0	9.3×10^{-7}	3.4×10^{-6}	7.7×10^{-7}	5.4×10^{-6}	1.4×10^{-6}	2.2×10^{-7}	5.3×10^{-8}	6.0×10^{-8}	8.0×10^{-7}
	25					5.2×10^{-7}				
	50					8.1×10^{-7}				
	100	6.1×10^{-7}	6.9×10^{-7}	4.5×10^{-8}	1.7×10^{-7}	8.0×10^{-8}	1.7×10^{-7}	1.5×10^{-7}	4.1×10^{-7}	1.6×10^{-7}
8	0	1.4×10^{-6}	1.3×10^{-6}	2.9×10^{-7}	1.0×10^{-7}	$<3.2 \times 10^{-8}$	4.5×10^{-8}	$<3.2 \times 10^{-8}$	$<3.0 \times 10^{-8}$	3.1×10^{-6}
	25					1.2×10^{-7}				
	50					$<5.5 \times 10^{-8}$				
	100	2.2×10^{-7}	5.8×10^{-7}	2.4×10^{-7}	1.8×10^{-7}	3.6×10^{-6}	$<1.7 \times 10^{-8}$	4.5×10^{-7}	5.5×10^{-7}	3.6×10^{-5}
9	0					$<5.3 \times 10^{-8}$				
	25					2.7×10^{-7}				
	50					$<3.0 \times 10^{-8}$				
	100					$<3.0 \times 10^{-8}$				
9	H_2O[a]					1.3×10^{-3}				
10	H_2O[a]					1.0×10^{-3}				

[a]Water was substituted for reference waste.

waste. This is to be expected as substitution of waste results in less-viscous grouts (Sect. 10.4).

Although no correlation could be determined for predicting permeability, several general trends are apparent that provide useful information for modeling.

- Liquid permeabilities of grouts representative of those prepared with the recommended formula are on the order of 10^{-6} to 10^{-7} darcy.
- Liquid permeabilities of grouts representative of those prepared with the recommended formula and flush water substituted for waste are on the order of 10^{-3} darcy.
- Liquid permeability is inversely related to mix ratio, but the relationship is sufficiently weak and has little effect over the range 7 to 8 lb/gal.
- Liquid permeability is inversely related to waste salt content. This relationship should also hold for the percolation water. Thus, the values presented here should be conservative.

11.3.2 Porosity

11.3.2.1 Experimental Procedure. The grout samples were cured for at least 28 d before measurements were started. Then, the grout specimens (approximately 2.5-cm-diam and 3.8-cm-long) of the various compositions were weighed in air and also weighed suspended under water. The specimens were then dried in an oven at 50 to 55°C overnight and further dried in a vacuum drying oven between 90 to 100°C for 9 to 14 d. The dried specimens were then weighed after cooling in a dessicator containing Drierite. The samples were then evacuated in a dessicator for approximately 2.5 h and submerged in toluene overnight without contacting air. The samples were then weighed while being suspended in toluene.

The porosity, saturation density, dry density, and percent water were calculated using the following equations:

Volume of specimen = Weight in air − weight in water,

$$\text{Percentage porosity} = 1 - \frac{\text{dry weight} - \text{weight in toluene}}{\text{density of toluene } (0.866) \times \text{volume of specimen } (\text{cm}^3)} \times 100,$$

$$\text{Saturation Density} = \frac{\text{dry weight} \times \text{density of toluene } (0.866)}{\text{dry weight} - \text{weight in toluene}},$$

$$\text{Dry density} = \frac{\text{dry weight}}{\text{volume of specimen}},$$

$$\text{Percentage of } H_2O = \frac{\text{weight in air} - \text{dry weight}}{\text{weight in air}} \times 100.$$

11.3.2.2 Experimental Results. The porosity, dry density, saturation density, and percentage of water were measured for grout specimens prepared at 6 to 9 lb/gal with blends 1–9 and reference waste diluted at 0 and 100%. Some specimens were made with water instead of reference waste. The various measurements of the specimens are reported in Table 50.

The porosity varied from 57.8 to 73.4% (Table 50) for these samples. A porosity value of 52.5% was obtained for a sample containing 7 lb/gal of blend 3 with a waste dilution factor of 100%. However, a measurement of another specimen of the same composition gave a porosity value of 66.4%, indicating a significant variation among samples.

Table 50. Porosities of grouts containing reference waste

Blend	TURCO solution	lbs/gal	Dry density	porosity	Saturation density	H_2O (%)
3	0.50	9	0.8422	61.77	2.2030	42.10
1	0.50	9	0.8267	61.79	2.1630	43.54
1	1.00	9	0.8485	61.85	2.2240	42.75
5	1.00	9	0.8826	62.38	2.3460	42.37
5	0.00	9	0.8735	62.59	2.3350	42.29
2	1.00	9	0.8456	62.62	2.2620	42.74
2	0.50	9	0.8176	62.65	2.1890	43.54
6	1.00	9	0.8742	62.93	2.3582	43.75
5	0.25	9	0.8710	63.41	2.3810	42.18
6	0.25	9	0.8417	63.42	2.3010	43.68
2	0.00	9	0.8571	63.48	2.3470	42.38
4	1.00	9	0.8352	63.48	2.2840	42.31
9	1.00	8	0.8302	64.76	2.3560	42.32
8	0.25	8	0.7761	64.80	2.2050	45.88
7	0.25	8	0.7740	64.80	2.1990	46.28
9	0.00	8	0.8339	65.12	2.3910	43.10
7	1.00	8	0.7881	65.25	2.2678	44.99
4	0.25	8	0.7756	65.29	2.2350	45.57
5	1.00	8	0.8054	65.48	2.3330	44.41
6	1.00	8	0.7625	67.20	2.3240	46.60
2	0.50	8	0.7729	67.25	2.3600	46.78
1	0.00	8	0.7535	67.30	2.3042	46.94
3	0.50	8	0.7710	67.30	2.3570	47.23
4	1.00	8	0.7775	67.31	2.3781	46.90
2	0.25	8	0.7742	67.34	2.3700	46.81
3	0.00	8	0.7675	67.46	2.3583	46.84
1	1.00	7	0.7291	68.72	2.3308	50.02
7	0.50	7	0.6976	68.73	2.2310	50.04
6	0.00	7	0.7248	68.77	2.3210	49.30
2	0.00	7	0.7263	68.78	2.3265	48.94
2	0.25	7	0.7296	68.86	2.3430	49.93
8	0.25	7	0.7041	68.93	2.2660	49.66
3	0.00	7	0.7280	68.93	2.3427	49.86
4	0.50	7	0.7200	68.99	2.3220	48.97
9	0.00	7	0.7501	69.02	2.4210	47.25
1	0.50	7	0.7235	69.12	2.3430	49.81
1	0.25	7	0.7216	69.22	2.3440	49.97
4	0.00	6	0.6946	70.74	2.3740	51.97
4	1.00	6	0.7055	70.93	2.4270	51.31
4	0.50	6	0.6786	71.71	2.3980	52.59

Table 50. Porosities of grouts containing reference waste (continued)

Blend	TURCO solution	lbs/gal	Dry density	porosity	Saturation density	H_2O (%)
5	1.00	6	0.6591	72.17	2.3690	52.92
5	0.00	6	0.6676	72.22	2.4300	52.83
5	0.25	6	0.6535	72.88	2.4100	53.59
5	0.50	6	0.6383	73.38	2.3980	53.91

The porosity appears to vary inversely with mix ratio (as shown in Table 50). No correlations could be found for porosity variations among the various blends or the reference waste dilution factor.

The dry density varied from 0.638 to 0.885 g/mL for the samples containing reference waste. Those samples made with water instead of reference waste had a dry density as great as 0.921 g/mL.

The dry density varied directly with the mix ratio. No correlations could be found in the variations of the dry densities due to either the blends or the waste dilution factor.

The saturation density of the samples appeared to vary from 2.16 to 2.43 g/mL. A value of 1.88 g/mL was calculated for a sample composed of blend 3 prepared at 7 lb/gal solids and 100% waste dilution, and a value of 1.99 g/mL was calculated for another sample composed of blend 3 prepared at 9 lb/gal and 0% dilution. However, reruns of these two specimens gave values of 2.25 and 2.28 g/mL, respectively. No correlations for the variations in saturation density could be found with either the different blends, the weight of solids per volume of liquid, or the waste dilution factor.

The water percentage varied inversely with mix ratio. The samples prepared with reference waste contained 41.5 to 53.9% water. No correlations for the percentage of water could be found between either the blend used or the waste dilution.

Collectively, these data illustrate an important characteristic of fluid grouts: Although the fluid grouts are highly porous, they are relatively impermeable.

12. CONCLUSIONS

Based on studies of grout development with synthetic waste, it is recommended that the following formula be used for the immobilization of Hanford Facility Waste in the Transportable Grout Facility:

Dry Solids Blend

Material	Amount (wt%)
Type I-II-LA Portland cement	41
Centralia, Wash. ASTM Class F, fly ash	40
Attapulgite-150 drilling clay	11
Indian Red pottery clay	8

Mix Ratio

7.5 lb dry solids blend per gallon of Hanford Facility Waste. However, 0.02 vol % TBP must be added to HFW as a defoaming agent.

The data show that grouts prepared in the TGF with the recommended formula will be characterized by:

- Frictional pressure drop <11 psi/100 ft
- 10-min gel strength $<100\ lb_f/100\ ft^2$
- 28-d unconfined compressive strength >60 psi

• ANS 16.1 leachability index for ^{90}Sr and ^{137}Cs	≥ 6
• Critical velocity	<70 gal/min
• Dry solids blend compostion	Tolerate ± 5% variation in recommended composition
• Thermal conductivity	~0.46 Btu/h•ft•°F
• Heat capacity	~0.59 Btu/lb•°F
• Permeability	10^{-6} to 10^{-7} darcy
• Porosity	58 to 74%

Data from the recommended operating range of mix ratios between 7 and 8 lb/gal indicate that grouts are more processible at mix ratios approaching 7 lb/gal. The average properties of a grout prepared with the recommended dry solids blend at 7 lb/gal include a 10-min gel strength of 23 $lb_f/100\ ft^2$ and a critical velocity of 40 gal/min. Conversely, at 8 lb/gal, the average 10-min gel strength is 59 $lb_f/100\ ft^2$.

At mix ratios approaching 8 lb/gal, the ability of the grout to resorb bleed water is increased significantly. However, substitution of flush water for HFW in the recommended formula results in a grout with increased bleed water and little ability to resorb it. Consequently, in order to flush clean grout directly to the disposal trench, it is necessary to remove trench water.

The Attapulgite-150 clay content appears to have the tightest concentration restrictions, with a minimum of 0.7 lb/gal and a maximum of 0.96 lb/gal. The narrowness of this range is attributable directly to the capacity of the TGF distribution pump. A larger capacity pump would provide greater operating flexibility and greater formula applicability to other waste streams.

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APPENDIX A

FORMULATION SCOUTING STUDIES ON PHOSPHATE WASTE

As indicated in Sect. 6.1 of this report, the starting point for formulation development was a dry solids blend consisting of 38 wt % Type I Portland cement, 39 wt % ASTM Class F fly ash, 15 wt % Attapulgite-150 drilling clay, and 8 wt % Indian Red pottery clay. This blend is used routinely at ORNL for a 1 M Na_2NO_3 waste solution. The resulting grouts are characterized by a 28 d phase separation (in a closed system) of ~10%. Higher attapulgite concentrations may be required to meet the TGF criterion of 0% 28-d phase separation. Consequently, the blends shown in Table A.1 were used in initial scouting studies with a 5 wt % Na_2HPO_4 solution. The resulting data are presented in Tables A.2 through A.8.

Data in Tables A.2 and A.3 describe a blend containing 15 wt % Attapulgite-150 clay mixed at 6 lb/gal. The blend (Table A.2) containing 45 wt % cement met the 2-h phase separation (in an open system) screening criterion of ~3% while the blend containing 40 wt % did not. Both grouts were processible (critical velocity <70 gal/min) in the TGF. Therefore, the former blend is in or near the range of interest for the Rockwell Hanford application.

Data in Tables A.4 and A.5 show the effects of increasing the attapulgite content to 20 wt %. The blend containing 35 wt % cement met the 2-h phase separation and processibility criteria. However, increasing the cement content to 40 wt % (Table A.5) produced a grout that was not processible in the TGF (critical velocity was greater than 70 gal/min). Data in Tables A.6 and A.7 indicate that at a mix ratio of 8 lb/gal, blends with 20 wt % Attapulgite-150 clay containing both 35 and 40 wt % cement produce grouts that are not processible in the TGF.

Table A.1. Dry solids blends used in initial scouting studies with an Na_2HPO_4 solution

Component	Amount (wt %)				
Type I-LA Portland cement	45	40	35	40	35
ASTM Class F fly ash, Kingston, Tenn.	40	45	45	40	40
Attapulgite-150 drilling clay	15	15	20	20	25

Table A.2. Properties of grouts prepared at 6 lb/gal with a 5 wt % Na_2HPO_4 solution and a dry solids blend consisting of 45 wt % cement, 40 wt % fly ash, and 15 wt % attapulgite clay

Property	Concentration (vol %)
10-min gel strength, $lb_f/100\ ft^2$	8 ± 1
Fluid consistency index (k′), $lb_f \cdot s^{n'}/ft^2$	0.005 ± 0.001
Flow behavior index (n′)	0.60 ± 0.02
Density, lb/gal	11.59 ± 0.03
2-h phase separation, vol %	2.61 ± 0.94
Apparent viscosity, cP	19.75
24-h penetration resistance, psi	0.0
7-d penetration resistance, psi	1990.0 ± 262.0
28-d compressive strength, psi	1462.0 ± 208.9
Reference conditions	
Reynolds number	4219.20
Frictional pressure drop per 100 ft, psi	2.35
Critical velocity, gal/min	30.57

Table A.3. Properties of grouts prepared at 6 lb/gal with a 5 wt % Na_2HPO_4 solution and a dry solids blend consisting of 45 wt % cement, 40 wt % fly ash, and 15 wt % attapulgite clay

Property	Concentration (wt %)
10-min gel strength, $lb_f/100\ ft^2$	5 ± 1
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.003 ± 0.001
Flow behavior index (n´)	0.62 ± 0.05
Density, lb/gal	11.30 ± 0.00
2-h phase separation, vol %	6.63 ± 3.35
Apparent viscosity, cP	13.42
24-h penetration resistance, psi	0.0
7-d penetration resistance, psi	1510.0 ± 160.4
28-d compressive strength, psi	923.7 ± 85.0
Reference conditions	
Reynolds number	6636.00
Frictional pressure drop per 100 ft, psi	1.15
Critical velocity, gal/min	23.15

Table A.4. Properties of grouts prepared at 6 lb/gal with a 5 wt % Na_2HPO_4 waste solution and a dry solids blend consisting of 35 wt % cement, 45 wt % fly ash, and 20 wt % attapulgite clay

Property	Concentration (wt %)
10-min gel strength, $lb_f/100\ ft^2$	14 ± 3
Fluid consistency index (k´), $lb_f \cdot s^{n'}/ft^2$	0.019 ± 0.006
Flow behavior index (n´)	0.47 ± 0.04
Density, lb/gal	11.53 ± 0.03
2-h phase separation, vol %	1.50 ± 0.81
Apparent viscosity, cP	33.37
24-h penetration resistance, psi	142.5 ± 17.1
7-d penetration resistance, psi	1620.0 ± 154.9
28-d compressive strength, psi	1260.0 ± 99.9
Reference conditions	
Reynolds number	2161.42
Frictional pressure drop per 100 ft, psi	4.09
Critical velocity, gal/min	47.83

Table A.5. Properties of grouts prepared at 6 lb/gal with Na_2HPO_4 waste solutions and a dry solids blend consisting of 40 wt % cement, 40 wt % fly ash, and 20 wt % attapulgite clay

Property	Na_2HPO_4 Concentration (wt %)	
	5	8
10-min gel strength, $lb_f/100\ ft^2$	23 ± 6	61 ± 20
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.378 ± 0.249	0.843 ± 0.183
Flow behavior index (n´)	0.15 ± 0.07	0.14 ± 0.01
Density, lb/gal	11.14 ± 0.04	11.58 ± 0.03
2-h phase separation, vol %	0.64 ± 0.17	0.21 ± 0.01
Apparent viscosity, cP	90.26	189.12
24-h penetration resistance, psi	580.0 ± 51.6	440.0 ± 57.2
7-d penetration resistance, psi	2000.0 ± 187.6	1880.0 ± 295.7
28-d compressive strength, psi	1578.0 ± 174.1	1079.0 ± 12.5
Reference conditions		
Reynolds number	620.72	307.57
Frictional pressure drop per 100 ft, psi	14.69	30.54
Critical velocity, gal/min	95.95	141.90

Table A.6. Properties of grout prepared at 8 lb/gal with a 5 wt % Na_2HPO_4 solution and a dry solids blend consisting of 35 wt % cement, 45 wt % fly ash, and 20 wt % attapulgite clay

Property	Concentration (wt %)
10-min gel strength, $lb_f/100\ ft^2$	Off scale
Fluid consistency index (k´), $lb_f \cdot s^n\ /ft^2$	
Flow behavior index (n´)	
Density, lb/gal	
2-h phase separation, vol %	0
Apparent viscosity, cP	
24-h penetration resistance, psi	1380.0 ± 76.6
7-d penetration resistance, psi	4200.0 ± 477.8
28-d compressive strength, psi	2611.3 ± 631.3

Table A.7. Properties of grouts prepared at 8 lb/gal with Na_2HPO_4 solutions and a dry solids blend consisting of 40 wt % cement, 40 wt % fly ash, and 20 wt % attapulgite clay

Property	Concentration (wt %)	
10-min gel strength, $lb_f/100\ ft^2$	Off Scale	Off Scale
Fluid consistency index (k'), $lb_f \cdot s^{n'}/ft^2$		
Flow behavior index (n')		
Density, lb/gal	12.01	12.25
2-h phase separation, vol %	0	0.0
Apparent viscosity, cP		
24-h penetration resistance, psi	2340.0 ± 285.7	2210.0 ± 509.5
7-d penetration resistance, psi	5310.0 ± 465.8	3850.0 ± 270.1
28-d compressive strength, psi	4668.7 ± 140.6	2623.5 ± 256.5

Data in Table A.8 indicate that increasing the attapulgite content to 25 wt % results in a nonprocessible grout even at a mix ratio of 6 lb/gal with a blend containing 35 wt % cement.

Based on these studies, it appears that a blend containing 15 wt % Attapulgite-150 clay prepared at a mix ratio of 6 lb/gal will result in acceptable grouts. Increasing the clay content significantly results in grouts that are unprocessible in the TGF or extremely sensitive to variations in the other blend components. A 15 wt % clay at a mix ratio of 6 lb/gal has a clay content of 0.9 lb/gal. Table A.9 shows the clay content of the blend required to achieve 0.9 lb/gal at various mix ratios. Therefore, it appears that a reasonable range of attapulgite concentrations to be explored in the formulation studies is 10 to 15 wt %.

Table A.8. Properties of grouts prepared at 6 lb/gal with an 8 wt % Na_2HPO_4 solution and a dry solids blend consisting of 35 wt % cement, 40 wt % fly ash, and 25 wt % attapulgite clay

Property	Concentration (wt %)
10-min gel strength, $lb_f/100\ ft^2$	Off Scale
Fluid consistency index (k'), $lb_f \cdot s^{n'}/ft^2$	
Flow behavior index (n')	
Density, lb/gal	
2-h phase separation, vol %	0
Apparent viscosity, cP	
24-h penetration resistance, psi	440.0 ± 36.5
7-d penetration resistance, psi	1200.0 ± 126.5
28-d compressive strength, psi	1093.0 ± 97.9

Table A.9. Weight percent of Attapulgite-150 in the dry solids blend required to achieve 0.9 lb/gal of waste

Mix ratio (lb/gal)	Attapulgite-150 clay content of blend (wt %)
6	15
7	13
8	11

APPENDIX B

QUALITY ASSURANCE TESTING OF GROUT PRODUCT

B.1 INTRODUCTION

The majority of the performance criteria are measured 28 d after pouring the grout. During operation of the TGF, some waste component may be introduced that was not in the synthetic waste but that affects the quality of the grout. Therefore, a QA/QC test should be performed during operations to indicate the quality of the final product prior to 28 d. Predicting product quality with complex waste streams based on the grouts' initial properties is very difficult. Once the grout has been produced, the main criterion of interest becomes the 28-d compressive strength. Although predicting compressive strength development has not proved reliable, one point is clear: In order to obtain the desired compressive strength, the grout must begin to set. Therefore, one possible method of predicting product quality is to measure set time.

B.2 SETTING OF CEMEMT

When Portland cement and water are mixed, there is an immediate rapid reaction that forms a supersaturated solution. The reaction slows down because a film of microcrystalline or gel-like calcium sulfoaluminate forms around the cement particles. A period of slow reaction follows, termed the induction period, during which the amount of hydration products gradually builds up with time and slowly involves the plastic viscosity of the paste. The process of structure formation begins immediately when the cement is mixed with water. Strength development is divided into two stages, low strength and high strength.

During the first stage, a structure coagulates that is characterized by the presence of a three-dimensional network formed by disordered coupling of the finest particles in the disperse phase through thin layers of the dispersion medium. At this stage, only individual crystals form. The period of low strength comes to an end at a certain critical time and is followed by a rapid growth in strength. During this second stage, there is more intense crystal formation resulting in a strong crystal network.

The critical time, while not fixed, represents the point in time at which any further mechanical deformation of the setting mix becomes detrimental to its ultimate strength. This critical time phenomenon is used to advantage in the ORNL process if emergency dumping of the grout is required. During emergency shutdown, the contents of the mix tub can be routed to a stirred tank. Mechanical agitation eliminates the formation of a strong crystal network by stopping the second stage of strength development. The result is an aqueous solution containing fine particles that can be used subsequently as waste feed at the facility.

B.2.1 Set Time

At ORNL, the ACME Laboratory Penetrameter is used to measure the rate of set in accordance with ASTM C-403-70 Time of Setting of Concrete Mixtures by Penetration Resistance. This procedure determines the rate of set by measuring the rate of hardening. Initial set is defined as achieving a penetration resistance of 500 psi; final set is the point at which a penetration resistance of 4000 psi is achieved. Thus, a penetration resistance of 500 psi is taken to mean that the second stage of strength development has begun, while a penetration resistance of 4000 psi indicates the time at which performance objectives are met (in this case a compressive strength >60 psi).

B.2.2 Hanford Facility Waste

Penetration resistance as a function of cure time is shown in Figs. B.1 through B.4 for various dilutions of reference waste using blends 3, 5, and 8 (Sect. 7.2). In all cases, the mix ratio was 7 lb/gal. The data show that set is inversely related to cement content. Thus, these set times should be conservative and are probably slower than at a mix ratio of 8 lb/gal (i.e., a higher cement content). The data indicate that for the four dilutions of the synthetic HFW initial set occurs within 6 d and within 3 d for the undiluted waste. Final set is achieved in all cases within 28 d.

Based on the data, it appears that a penetration resistance test could predict in less than one week the quality (strength) of the final product and compare its behavior to development work using synthetic waste. Data based on actual waste may alter the time of initial set and should be the final basis for comparison.

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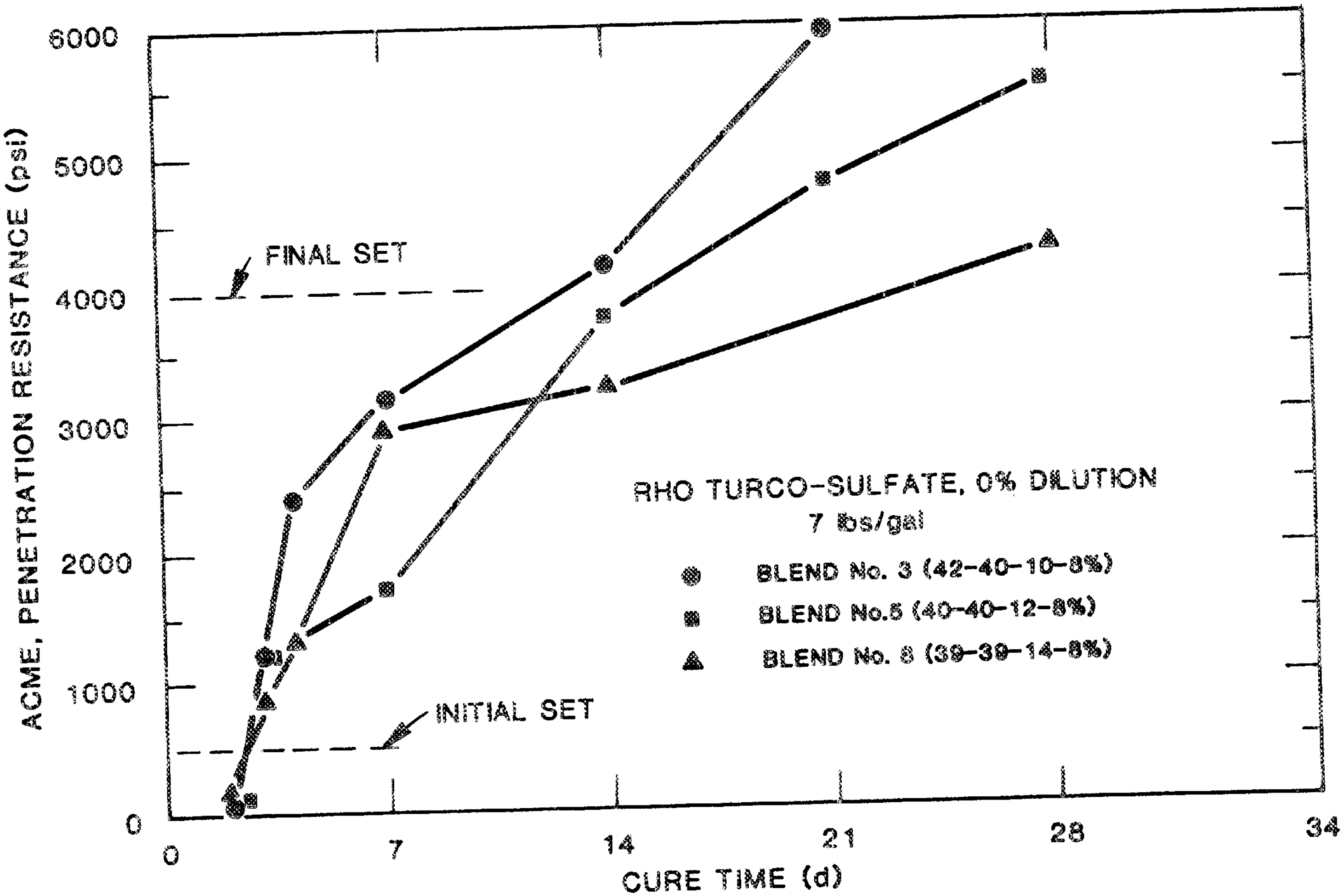

Fig. B.1. Rate of set of grouts prepared at 7 lb/gal with 0 wt % diluted reference waste and dry solids blends 3, 5, and 8.

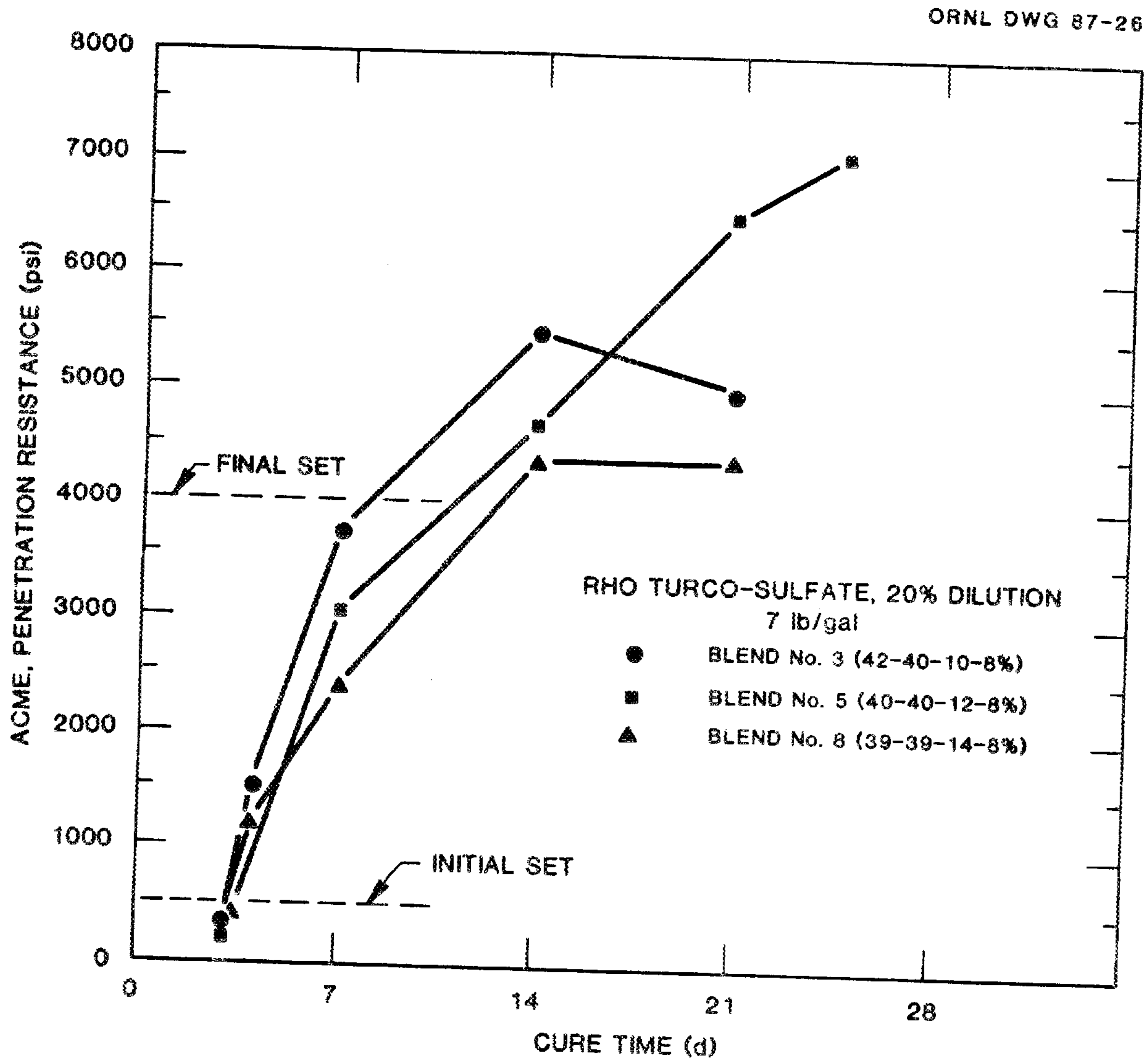

Fig. B.2. Rate of set of grouts prepared at 7 lb/gal with 20 wt % diluted reference waste and dry solids blends 3, 5, and 8.

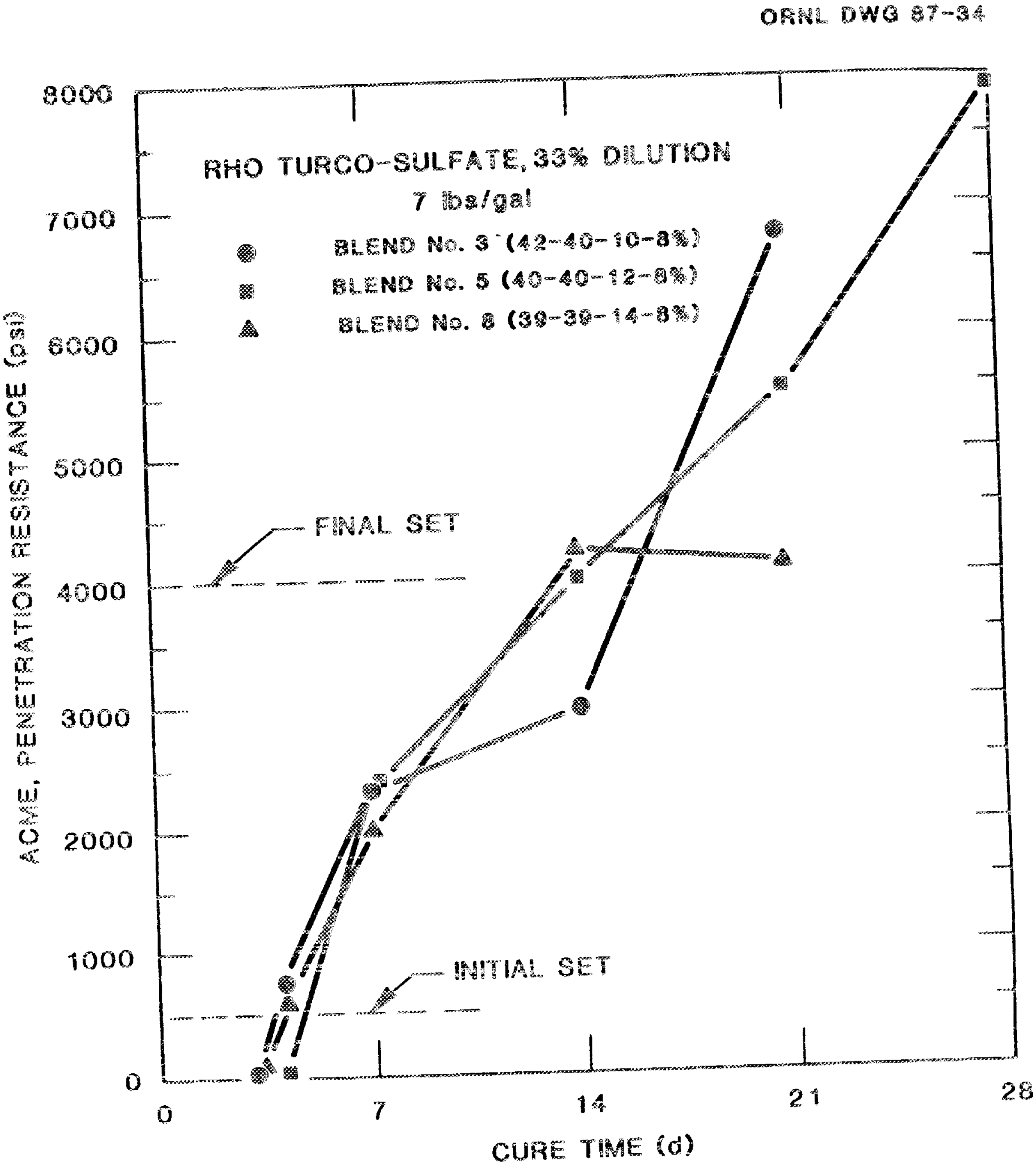

Fig. B.3. Rate of set of grouts prepared at 7 lb/gal with 33 wt % diluted reference waste and dry solids blends 3, 5, and 8.

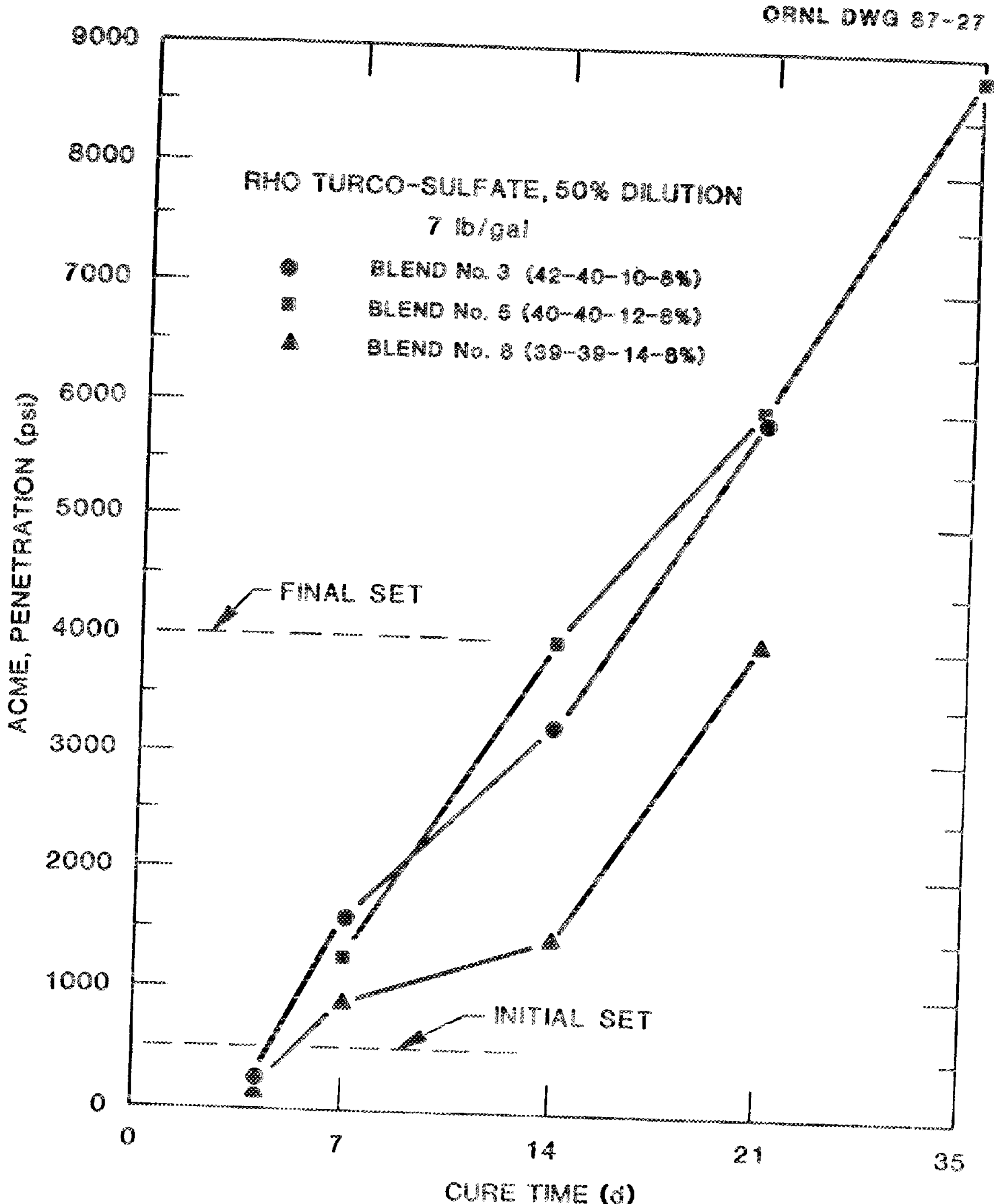

Fig. 8.4. Rate of set of grouts prepared at 7 lb/gal with 50 wt % diluted reference waste and dry solids blends 3, 5, and 8.

APPENDIX C

TYPICAL ANALYSIS OF TYPE I-II-LA PORTLAND CEMENT

AND

CENTRALIA, WASH. CLASS F FLY ASH

Table C.1. Typical analysis of Type I-II-LA cement

Chemical composition	Concentration (wt %)
Silicon dioxide (SiO_2)	22.78
Aluminum dioxide (Al_2O_3)	3.40
Ferric oxide (Fe_2O_3)	4.96
Magnesium oxide (MgO)	0.91
Sulfur trioxide (SO_3)	2.05
Loss on ignition	1.31
Insoluble residue	0.30
Tricalcium silicate (C_3S)	52.7
Tricalcium aluminate (C_3A)	0.6
Total alkalies (As Na_2O)	0.40
Physical properties	
Blaine fineness	3640 cm^2/g

Table C.2. Typical analysis of ASTM class F fly ash

	Source		
	Centralia, Wash.		Kingston, Tenn.
Chemical compositon	Concentration (wt %)		
Silicon dioxide (SiO_2)	46.02	49.2	48.57
Aluminum dioxide (Al_2O_3)	23.2	22.7	28.5
Ferric oxide (Fe_2O_3)	7.42	5.88	9.00
Calcium oxide (CaO)	10.1	8.40	1.32
Magnesium oxide (MgO)	1.72	1.70	1.31
Phosphorus pentoxide (P_2O_5)	.75	.77	0.99
Carbon (C)	.057	.028	0.27
Sulfur trioxide (SO_3)	0.001	.005	0.37
Sodium oxide (Na_2O)	3.75	4.61	0.33
Potassium oxide (K_2O)	0.70	0.52	3.14
Loss on ignition	0.52	0.58	2.84
Moisture	0.20	0.13	0.09
Physical Properties			
Density	2.32 g/cm^3	2.17 g/cm^3	2.36 g/cm^3
Surface area	0.68 m^2/g	0.49 m^2/g	1.34 m^2/g

APPENDIX D

FORMULATION SCOUTING STUDIES USING SET ACCELERATORS

D.1 INTRODUCTION

The majority of the performance criteria applied to the grout formulation studies must be achieved within 28 d. Preliminary experiments were performed to assess the use of set accelerators to achieve the grout performance objectives earlier than 28 d. To this end, two common set accelerators ($CaCl_2$ and Na_2SiO_3) were added to blends discussed in Sect. 7.2 of this report and then mixed with various dilutions of reference waste. As the accelerators were added to the blends (after they had been prepared according to Sect. 7.2), an explanation of the nomenclature used in this section is necessary. For example, a grout prepared at 8 lb/gal with blend 1 and 0.5 wt % $CaCl_2$ added would be interpreted as follows: The grout would be prepared at 8 lb/gal with blend 1. However, 0.04 lb of $CaCl_2$ (0.5 wt %) is added to the mixture. The following sections discuss the effects of this addition both as a solid and a liquid.

D.2 EFFECTS OF $CaCl_2$ ADDITION

Data for grouts prepared at 8 lb/gal with blend 1 and 0.5 wt % $CaCl_2$ added to the blend prior to mixing with the reference waste are shown in Table D.1. Data for a similar grout with no $CaCl_2$ added are shown in Table D.2. A comparison of the two illustrates an important point: The results of set accelerators are sensitive to the amount added. Indeed, a comparison of the 7-d penetration resistance shows that in this case the $CaCl_2$ acts as a set retarder, delaying initial set beyond 7 d. The grout

Table D.1. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 1 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	21	10	9	8
Fluid consistency index (k'), $lb_f \cdot s^{n'}/ft^2$	0.072	0.010	0.010	0.008
Flow behavior index (n')	0.31	0.50	0.49	0.53
Density, lb/gal	12.20	12.15	12.15	12.15
2-h Phase separation, vol %	0.43	3.39	4.60	0.86
Apparent viscosity, cP	46.63	21.18	19.9	20.43
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	0.0	0.0	0.0	0.0
28-d compressive strength, psi	2852.5 ± 30.4	3743.5 ± 14.8	2010.0 ± 66.5	987.5 ± 37.5
Reference conditions				
Reynolds number	1484.08	3718.29	3779.43	4131.17
Frictional pressure drop per 100 ft, psi	6.81	2.46	2.46	2.46
Critical velocity, gal/min	60.86	34.10	32.62	32.30

[a]0.5 wt % $CaCl_2$ added to dry solids blend prior to mixing.

Table D.2. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 1 and different dilutions of reference waste

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	37 ± 4	37 ± 12	26 ± 5	20 ± 2
Fluid consistency index (k´), $lb_f \cdot s^{n´}/ft^2$	0.064 ± 0.012	0.050 ± 0.007	0.057 ± 0.004	0.038 ± 0.007
Flow behavior index (n´)	0.29 ± 0.03	0.34 ± 0.02	0.33 ± 0.02	0.42 ± 0.03
Density, lb/gal	11.86 ± 0.05	11.90 ± 0.07	11.85 ± 0.04	11.86 ± 0.06
Phase separation, vol %	1.15 ± 0.40	0.94 ± 0.20	1.68 ± 0.69	0.94 ± 0.21
After 10 min in an atmospheric pressure consistometer				
Density, lb/gal	11.98 + 0.03	11.95 ± 0.07	11.93 ± 0.03	11.91 ± 0.06
Phase separation, vol %	1.49 ± 0.25	1.57 ± 0.39	1.91 ± 0.41	2.30 ± 0.27
Apparent viscosity, cP	36.59	39.05	41.82	48.87
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1620.0	1980.0	1220.0	1160.0
28-d compressive strength, psi	441.56 ± 21.06	488.56 ± 45.71	452.25 ± 1.37	310.94 ± 15.65
Reference conditions				
Reynolds number	1788.60	1741.32	1674.35	1523.37
Frictional pressure drop per 100 ft, psi	5.41	5.43	6.01	6.62
Critical velocity, gal/min	53.56	54.89	58.17	61.31

containing $CaCl_2$ is further characterized by a greater fluidity (as measured by critical velocity) and a higher bleed (as measured by 2-h phase separation). However, the addition of $CaCl_2$ had a major positive effect because it dramatically increased the 28-d compressive strength.

The effects of increasing the $CaCl_2$ content were assessed by adding 1 wt % $CaCl_2$ to a grout prepared at 8 lb/gal with blend 5. Data are shown in tables D.3 through D.5. Comparision between grouts prepared with 1 wt % $CaCl_2$ (Table D.3) and grouts with no additives (Table D.4) shows that the increase in $CaCl_2$ content did not have a positive effect on the rate of set. Indeed, the 7-d penetration resistance of the grout with no additives is ~2 times that of the grout containing 1 wt % $CaCl_2$, and there is no significant change in 28-d compressive strength. It appears that the effects of this $CaCl_2$ content are primarily negative, with both the 10 min gel strength and critical velocity increasing significantly.

However, Table D.5 shows that adding 1 wt % $CaCl_2$ as a liquid does not result in grouts characterized by the high viscosity and gel strengths exhibited in Table D.3. Therefore, addition of $CaCl_2$ in liquid form is the preferred method. Conversely, the addition of $CaCl_2$ does not appear to be an appropriate set accelerator.

To assess the effects of Na_2SiO_3 as a set retarder, 1 wt % Na_2SiO_3 was added (both as a solid and liquid) to grouts prepared at 8 lb/gal with blend 5. Data are shown in Tables D.6 and D.7. A comparison of data in Tables D.6 and D.4 shows that adding 1 wt % Na_2SiO_3 in solid form has a negligable effect on properties of interest. The lack of an increase in gel strength and critical velocity in grouts containing $CaCl_2$ shows that

Table D.3. Properties of a grout mixed in the ratio of 8 lb/gal with dry solids blend 5 and 0% dilution of reference waste[a]

Property	
10-min gel strength, $lb_f/100\ ft^2$	60 ± 35
Fluid consistency index (k'), $lb_f \cdot s^{n} / ft^2$	0.124 ± 0.079
Flow behavior index (n')	0.32 ± 0.11
Density, lb/gal	12.29 ± 0.11
2-h Phase separation, vol %	0.43 ± 0.00
Apparent viscosity, cP	85.48
24-h penetration resistance, psi	0.0
7-d penetration resistance, psi	1160.0
28-d compressive strength, psi	505.4 ± 23.4
Reference conditions	
Reynolds number	820.95
Frictional pressure drop per 100 ft, psi	11.84
Critical velocity, gal/min	88.64

[a]1.0 wt % $CaCl_2$ added to dry solids blend prior to mixing.

Table D.4. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 5 and different dilutions of reference waste

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	11 ± 2	13 ± 3	22 ± 4	30 ± 9
Fluid consistency index, (k') $lb_f \cdot s^n/ft^2$	0.006 ± 0.001	0.030 ± 0.003	0.035 ± 0.019	0.022 ± 0.011
Flow behavior index, (n')	0.60 ± 0.02	0.39 ± 0.01	0.41 ± 0.11	0.46 ± 0.08
Density, lb/gal	12.14 ± 0.05	11.79 ± 0.10	12.16 ± 0.14	12.09 ± 0.05
Phase separation, vol %	3.36 ± 0.03	2.99 ± 0.50	1.16 ± 0.94	1.67 ± 1.02
After 10 min in an atmospheric pressure consistometer				
Density, lb/gal	12.33 + 0.03	11.86 ± 0.10	12.29 ± 0.15	12.16 ± 0.03
Phase separation, vol %	2.84 ± 0.38	2.99 ± 0.45	1.69 ± 0.93	2.75 ± 1.46
Apparent viscosity, cP	23.70	32.00	42.30	36.31
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	2360.0	340.0	1060.0	400.0
28-d compressive strength, psi	710.6 ± 26.1	271.3 ± 6.3	521.8 ± 36.4	270.1 ± 17.8
Reference conditions				
Reynolds number	3682.83	2158.14	1774.35	2126.46
Frictional pressure drop per 100 ft, psi	2.46	4.19	5.55	4.91
Critical velocity, gal/min	33.67	48.03	55.92	49.75

Table D.5. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 5 and different concentrations of reference waste[a]

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	30 ± 6	13 ± 3	14 ± 1	14 ± 3
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.121 ± 0.059	0.030 ± 0.003	0.025 ± 0.010	0.025 ± 0.005
Flow behavior index (n´)	0.22 ± 0.05	0.39 ± 0.01	0.41 ± 0.03	0.41 ± 0.02
Density, lb/gal	11.85 ± 0.07	11.79 ± 0.10	11.70 ± 0.08	12.02 ± 0.02
2-h Phase separation, vol %	1.46 ± 0.24	2.99 ± 0.50	2.65 ± 0.23	3.05 ± 0.79
Apparent viscosity, cP	44.71	32.00	30.21	30.21
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	-	340.0	232.0	316.0
28-d compressive strength, psi	-	271.3 ± 6.3	258.4 ± 14.9	195.8 ± 10.9
Reference conditions				
Reynolds number	1430.71	2158.14	2418.58	2484.69
Frictional pressure drop per 100 ft, psi	6.61	4.19	4.15	3.66
Critical velocity, gal/min	62.03	48.03	46.35	45.57

[a]1.0 wt % $CaCl_2$ (dissolved in 20 mL of H_2O) added to waste prior to mixing.

Table D.6. Properties of a grout mixed in the ratio of 8 lb/gal with dry solids blend 5 and 0% diluted reference waste[a]

10-min gel strength, $lb_f/100\ ft^2$	15 ± 1
Fluid consistency index (k´), $lb_f \cdot s^n\ /ft^2$	0.015 ± 0.004
Flow behavior index (n´)	0.46 ± 0.03
Density, lb/gal	11.86 ± 0.03
2-h Phase separation, vol %	2.22 ± 0.40
Apparent viscosity, cP	24.76
24-h penetration resistance, psi	0.0
7-d penetration resistance, psi	2520.0
28-d compressive strength, psi	625.4 ± 21.4
Reference conditions	
Reynolds number	3013.11
Frictional pressure drop per 100 ft, psi	3.01
Critical velocity, gal/min	39.28

[a]1 wt % Na_2SiO_3 added to dry solids blend prior to mixing.

Table D.7. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 5 and different dilutions of reference waste[a]

Property	Waste dilutions (vol %) 0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	51 ± 9	33 ± 7	21 ± 4	32 ± 5
Fluid consistency index (k´), $lb_f \cdot s^{n} /ft^2$	0.064 ± 0.034	0.035 ± 0.015	0.045 ± 0.043	0.064 ± 0.005
Flow behavior index (n´)	0.32 ± 0.05	0.37 ± 0.06	0.36 ± 0.08	0.38 ± 0.03
Density, lb/gal	12.08 ± 0.09	11.90 ± 0.00	11.84 ± 0.07	12.03 ± 0.05
2-h Phase separation, vol %	1.55 ± 0.21	1.27 ± 0.33	1.69 ± 0.01	0.84 ± 0.02
Apparent viscosity, cP	44.12	32.96	39.81	64.13
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	-	2200.0	1600.0	1840.0
28-d compressive strength, psi	-	567.0 ± 21.7	529.1 ± 21.5	473.4 ± 10.5
Reference conditions				
Reynolds number	1577.14	2100.43	1770.11	1119.14
Frictional pressure drop per 100 ft, psi	6.13	4.83	5.40	8.54
Critical velocity, gal/min	60.22	48.78	55.71	74.08

[a]1.0 wt % Na_2SiO_3 (dissolved in 20 mL of H_2O) added to waste prior to mixing.

Na_2SiO_3 may be a more viable candidate. Indeed, adding Na_2SiO_3 as a liquid (Table D.7) results in a significant increase in rate of set (as measured by the 7-d penetration resistance), causing no major deleterious effects on grout flow properties. The critical velocity at 50 wt % dilution (74 gal/min) indicates that additional work is needed to optimize the Na_2SiO_3 concentration. However, the data are sufficient to indicate that (1) Na_2SiO_3 is a viable candidate for use as an accelerator and (2) addition as a liquid is the preferred method (the TGF is designed to have liquid addition capabilities).

APPENDIX E

FORMULATION SCOUTING STUDIES WITHOUT INDIAN RED POTTERY CLAY

Indian Red pottery clay (IRPC) is added to the dry solids blend as a cost effective ion exchange medium to reduce the leachability of ^{137}Cs. Based on ORNL experience, the IRPC blend content was fixed at 8 wt %. However, as discussed in Sect. 4.2 of this report, the TGF may be capable of operating with a reduced IRPC content. To assess the effects of this reduction, experiments were performed with a dry solids blend containing 40 wt % Type I-II-LA Portland cement, 48 wt % Centralia, Wash. ASTM Class F fly ash, and 12 wt % Attagel-150 (Tables E.1 through E.3) and compared with grouts prepared with a blend consisting of 40 wt % Type I-II-LA Portland cement, 40 wt % Centralia, Wash. ASTM Class F fly ash, 12 wt % Attagel-150, and 8 % IRPC (Tables E.4 through E.6). Fly ash was substituted for IRPC due to its low cost. The trends identified in Tables E.1 through E.6 are consistant with those identified in the main body of this report and are as follows: Increasing fly ash content tends to (1) increase 28-d compressive strength, (2) increase rate of set (7-d penetration resistance), (3) increase 10-min gel strength, and (4) decrease fluidity as illustrated by the critical velocity and frictional pressure drop. Therefore, decreasing the IRPC content appears to be a viable option, with the performance criterion of greatest concern being the critical velocity. This concern indicates that more extensive formulation scouting studies should be performed prior to lowering the IRPC content in the TGF.

Table E.1. Properties of grouts prepared with different dilutions of reference waste at 6 lb/gal and a dry solids blend consisting of 40 wt % Type I-II-LA Portland cement, 48 wt % Centralia, Wash. ASTM Class F fly ash, and 12 wt % Attagel-150

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	15 ± 2.94	14 ± 2.16	18 ± 0.96	16 ± 0.82
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.010 ± 0.0006	0.008 ± 0.0006	0.0148 ± 0.0020	0.0178 ± 0.0029
Flow behavior index (n´)	0.463 ± 0.004	0.484 ± 0.010	11.31 ± 0.025	11.23 ± 0.029
Density, lb/gal	11.43 ± 0.029	11.41 ± 0.048	11.31 ± 0.025	11.23 ± 0.029
28-d Phase separation, vol %	0	0	0	0
Apparent viscosity, cP	17	15.50	19.25	19.50
24-h penetration resistance, psi	0	0	0	0
7-d penetration resistance, psi	2000	1400	960	328
28-d compressive strength, psi	362.± 1.97	285.0 ± 22.38	344.07 ± 17.64	266.78 ± 9.29
Reference conditions				
Reynolds number	4332	4816	3730	32672
Frictional pressure drop per 100 ft, psi	2.14	1.92	2.46	2.48
Critical velocity, gal/min	31.14	28.89	34.57	35.35

Table E.2. Properties of grouts prepared with different dilutions of reference waste at 7 lb/gal and a dry solids blend consisting of 40 wt % Type I-II-LA Portland cement, 48 wt % Centralia, Wash. ASTM Class F fly ash, and 12 wt % Attagel-150

Parameter	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	31.50 ± 1.07	20.75 ± 2.86	21.75 ± 4.35	17.25 ± 2.99
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.027 ± 0.008	0.0165 ± 0.008	0.014 ± 0.0005	0.054 ± 0.011
Flow behavior index (n´)	0.393 ± 0.029	0.456 ± 0.039	0.460 ± 0.010	0.297 ± 0.026
Density, lb/gal	11.68 ± 0.23	11.69 ± 0.09	11.74 ± 0.05	11.69 ± 0.025
28-d Phase separation, vol %	0	0	0	0
Apparent viscosity, cP	30.25	26.5	24.75	34.5
24-h penetration resistance, psi	0	0	0	0
7-d penetration resistance, psi	2800	2320	1470	690
28-d compressive strength, psi	546.13 ± 17.24	492.31 ± 38.86	456.44 ± 5.99	353.69 ± 13.14
Reference conditions				
Reynolds number	2409.51	42790.53	3231.02	2044.55
Frictional pressure drop per 100 ft, psi	3.93	3.40	2.95	4.64
Critical velocity, gal/min	45.83	31.35	37.75	50.72

Table E.3. Properties of grouts prepared with different dilutions of reference waste at 8 lb/gal and a dry solids blend consisting of 40 wt % Type I-II-LA Portland cement, 48 wt % Centralia, Wash. ASTM Class F fly ash, and 12 wt % Attagel-150

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	23.25 ± 0.96	21.25 ± 0.96	20.25 ± 0.96	18.50 ± 1.29
Fluid consistency index (k'), $lb_f \cdot s^n/ft^2$	0.0032 ± 0.0904	0.044 ± 0.008	0.030 ± 0.003	0.0195 ± 0.004
Flow behavior index (n')	1.0 ± 0.02	0.468 ± 0.026	0.499 ± 0.014	0.562 ± 0.028
Density, lb/gal	12.05 ± 0.04	11.93 ± 0.03	11.86 ± 0.048	12.05 ± 0.04
Apparent viscosity, cP	253	84.75	86.75	72.75
24-h penetration resistance, psi	0	0	0	0
Reference conditions				
Reynolds number	744.18	999.72	1229.14	1358.61
Frictional pressure drop per 100 ft (psi)	13.14	9.68	7.83	7.20
Critical velocity, gal/min	140.92	81.07	71.35	67.60

Table E.4. Properties of grouts mixed in the ratio of 6 lb/gal with dry solids blend 5 and different dilutions of reference waste

Property	Waste dilutions (vol %) 0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	5 ± 1	7 ± 1	6 ± 2	8 ± 3
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.003 ± 0.001	0.004 ± 0.002	0.002 ± 0.001	0.003 ± 0.001
Flow behavior index (n´)	0.63 ± 0.02	0.58 ± 0.07	0.66 ± 0.03	0.61 ± 0.04
Density, lb/gal	11.60 ± 0.09	11.48 ± 0.03	11.46 ± 0.13	11.40 ± 0.11
Phase separation, vol %	5.70 ± 0.56	9.47 ± 6.41	10.95 ± 4.48	9.72 ± 4.19
After 10 min in an atmospheric pressure consistometer				
Density, lb/gal	11.86 ± 0.03	11.53 ± 0.36	11.63 ± 0.26	11.63 ± 0.12
Phase separation, vol %	9.89 ± 5.38	11.16 ± 6.97	10.33 ± 7.91	12.68 ± 6.78
Apparent viscosity, cP	14.29	13.95	11.50	12.62
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	980.0	560.0	336.0	176.0
28-d compressive strength, psi	249.63 ± 18.07	242.02 ± 12.65	249.75 ± 23.08	198.63 ± 3.51
Reference conditions				
Reynolds number	6702.33	5397.00	6305.67	6805.00
Frictional pressure drop per 100 ft, psi	1.18	1.75	1.74	1.16
Critical velocity, gal/min	23.65	24.54	19.68	22.38

Table E.5. Properties of grouts mixed in the ratio of 7 lb/gal with dry solids blend 5 and different dilutions of reference waste

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	21 ± 7	39 ± 8	35 ± 16	35 ± 10
Fluid consistency index (k´), $lb_f \cdot s^n/ft^2$	0.019 ± 0.016	0.068 ± 0.038	0.039 ± 0.011	0.051 ± 0.023
Flow behavior index (n´)	0.44 ± 0.08	0.29 ± 0.06	0.33 ± 0.03	0.29 ± 0.05
Density, lb/gal	11.75 ± 0.00	11.69 ± 0.06	11.71 ± 0.03	11.73 ± 0.03
Phase separation, vol %	2.32 ± 0.88	1.28 ± 0.62	1.48 ± 0.22	1.59 ± 0.22
After 10 min in an atmospheric pressure consistometer				
Density, lb/gal	11.80 ± 0.00	11.79 ± 0.07	11.78 ± 0.03	11.80 ± 0.04
Phase separation, vol %	2.63 ± 0.69	1.48 ± 0.43	2.32 ± 0.40	2.76 ± 0.23
Apparent viscosity, cP	27.68	38.88	28.61	29.16
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	1360.0	960.0	340.0	136.0
28-d compressive strength, psi	430.7 ± 21.3	379.9 ± 27.2	291.2 ± 6.0	162.3 ± 17.6
Reference conditions				
Reynolds number	2775.6	1679.00	2363.64	2211.25
Frictional pressure drop per 100 ft, psi	3.58	5.93	4.16	4.16
Critical velocity, gal/min	42.82	55.94	46.65	47.25

Table E.6. Properties of grouts mixed in the ratio of 8 lb/gal with dry solids blend 5 and different dilutions of reference waste

Property	Waste dilutions (vol %)			
	0	20	33	50
10-min gel strength, $lb_f/100\ ft^2$	11 ± 2	13 ± 3	22 ± 4	30 ± 9
Fluid consistency index (k′), $lb_f \cdot s^{n}/ft^2$	0.006 ± 0.001	0.030 ± 0.003	0.035 ± 0.019	0.022 ± 0.011
Flow behavior index (n′)	0.60 ± 0.02	0.39 ± 0.01	0.41 ± 0.11	0.46 ± 0.08
Density, lb/gal	12.14 ± 0.05	11.79 ± 0.10	12.16 ± 0.14	12.09 ± 0.05
Phase separation, vol %	3.36 ± 0.03	2.99 ± 0.50	1.16 ± 0.94	1.67 ± 1.02
After 10 min in an atmospheric pressure consistometer				
Density, lb/gal	12.33 + 0.03	11.86 ± 0.10	12.29 ± 0.15	12.16 ± 0.03
Phase separation, vol %	2.84 ± 0.38	2.99 ± 0.45	1.69 ± 0.93	2.75 ± 1.46
Apparent viscosity, cP	23.70	32.00	42.30	36.31
24-h penetration resistance, psi	0.0	0.0	0.0	0.0
7-d penetration resistance, psi	2360.0	340.0	1060.0	400.0
28-d compressive strength, psi	710.6 ± 26.1	271.3 ± 6.3	521.8 ± 36.4	270.1 ± 17.8
Reference conditions				
Reynolds number	3682.83	2158.14	1774.35	2126.46
Frictional pressure drop per 100 ft, psi	2.46	4.19	5.55	4.91
Critical velocity, gal/min	33.67	48.03	55.92	49.75

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