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Fixation of Waste Materials in Grouts. Part I: Empirical Correlations of Formulation Data

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03; Microfiche A01

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ORNL/TM-9680/PI
Dist. Category UC-70

Chemical Technology Division

NUCLEAR AND CHEMICAL WASTE PROGRAMS
(Activity No. AR 05 10 05 K; ONL WN05)

FIXATION OF WASTE MATERIALS IN GROUTS. PART I: EMPIRICAL CORRELATIONS OF FORMULATION DATA

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Date of Issue - March 1986

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

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FIXATION OF WASTE MATERIALS IN GROUTS. PART I: EMPIRICAL CORRELATIONS OF FORMULATION DATA

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ABSTRACT

Data correlations have demonstrated systematic relationships between important variables in hydrofracture grout formulation. The data are taken from an investigation to determine conditions for eliminating drainable water from the grout system. The two most important variables affecting drainable water are the amounts of Attapulgite-150 clay in the dry-solid blends and the ratios in which the blends are mixed with the waste.

Empirical equations were developed relating the (1) vol % of drainable water, (2) time for free water adsorption, (3) wt % clay, (4) dry-blend liquid-waste mix ratio, (5) compressive strength, (6) wt % fly ash, and (7) pumping velocity required for turbulent flow through a 2-in.-ID pipe.

The equations allow predictions of properties within the compositional range of the investigation from which the data were obtained. They also provide a relatively simple method that can be used to improve future test design, eliminate superfluous testing, decrease costs, and increase overall efficiency of individual investigations.

1. INTRODUCTION

The hydrofracture process is a technique that has been used at Oak Ridge National Laboratory (ORNL) for many years* to dispose of low-level waste (LLW).[1-4] In this process, cement and other additives are mixed with a waste solution or sludge to form a grout suitable for injection into a deep shale bed that has been hydraulically fractured along a horizontal bedding plane. The primary objective of this investigation was to provide information to more accurately define conditions for the elimination of drainable water from grout systems used in the hydrofracture.

*Suspended in 1984.

process. Previously, requirements allowed the drainable water from grout to be $\leq$5.0 vol % after 2 h of cure time, whereas present suggested requirements are that there be 0 vol % drainable water after 28 d. Another purpose of this investigation was to define conditions for decreasing the drainable water as much as practicable throughout the grout curing period.

The development of the grout blend and the role of additives to the cement are described in the literature.[5,6] The two most important variables affecting the volume of drainable water appear to be (1) the amount of Attapulgite-150 clay in the dry solids blend and (2) the ratio at which the blend is mixed with the waste. To determine conditions for no drainable water after 28 d, tests were conducted with four dry-solid blends containing varying amounts of Attapulgite-150 clay at mix ratios of 6, 7, 8, and 9 lb/gal.* Changes in the Attapulgite-150 clay content and in the grout mix ratio affect properties other than the drainable water of the grout. Thus, compressive strength and rheological properties were determined in addition to drainable water in order to determine overall acceptability[6] of the grouts. A compressive strength of 60 psig is required, and the rheological properties must be such that the grout can be pumped in turbulent flow. Dry-shearing of the blends can be detrimental to the free water adsorption and beneficial to the rheological properties. Grouts, as designated, were prepared from both sheared and unsheared blends.

Two additional objectives of this study were: (1) to document and disseminate information in referenceable form on the experimental methods used in grout-waste formulation studies, and (2) to provide statistical data analyses to allow more complete utilization of data obtained in the studies. Both objectives seek to broaden the scope of waste-grout uses and to generally add credibility to grout-waste methods for waste disposal.

The tests discussed here were designed primarily to determine the workability of given grouts in the ORNL hydrofracture system. Thus, from a developmental standpoint, the data were obtained over a relatively narrow test range. The results are, nevertheless, typical of most of those obtained in hydrofracture studies during the last decade.

---

*To convert to SI units: 1 lb/gal = 0.12 kg/L.

2. TEST METHODS, EXPLANATIONS, AND DATA USES

2.1 WASTE COMPOSITION

The composition of the simulated W-7 waste used in the tests is shown in Table 1. The compounds present in this waste are representative of the principal chemical components of composite intermediate-level ORNL waste. Trace components were not included since leaching tests were not conducted on the grout samples. The waste solution was mixed with each of the four dry blends described in the next section.

Table 1. Composition of W-7 simulated waste solution

Compound	Concentration (mM)
$Al(NO_3)_3 \cdot 9H_2O$	7
NaCl	93
Na_2CO_3	190
$NaNO_3$	810
NaOH	180
Na_2SO_4	94
NH_4NO_3	3

2.2 COMPOSITION AND PREPARATION OF BLENDS

The compositions of four dry blends that were mixed with simulated W-7 waste to prepare grouts for testing are shown in Table 2. The amounts of Type I Portland cement and Indian Red pottery clay were kept constant at 42.0 and 8.0 wt %, respectively; however, the amounts of Kingston fly ash (ASTM class F) were decreased from 36.0 to 30.0 wt % as the amounts of Attapulgite-150 clay were increased from 14.0 to 20.0 wt %. Attapulgite-150 clay aids in the adsorption of drainable water, which occurs as a separate phase on top of a grout. The Indian Red pottery clay adsorbs trace materials (e.g., radioactive cesium) that are found in hydrofracture

process grouts even though they were not present in the test grouts. The fly ash has a favorable impact on the flow properties of the freshly mixed grouts. In most of the tests, the dry blends were tumbled in a V-blender for 1.0 h and then sheared in a commercial Waring blender (Model 91-186) at 5000 rpm for 2.0 h.

Table 2. Blends of solids used in grout mix

Material	Blend 1 (wt %)	Blend 2 (wt %)	Blend 3 (wt %)	Blend 4 (wt %)
Type I Portland cement	42.0	42.0	42.0	42.0
Kingston fly ash (class F)	36.0	34.0	32.0	30.0
Attapulgite-150 clay	14.0	16.0	18.0	20.0
Indian Red pottery clay	8.0	8.0	8.0	8.0

In a few of the early tests (as will be designated), the blends were mixed in the V-blender for 16 h and the shearing step was omitted. These blending procedures (with shearing) are considered to be representative of those used in the ORNL Hydrofracture Facility.

2.3 PHASE SEPARATION TESTS

Phase separation, as previously noted, refers to a separate liquid or water phase that collects at the top of freshly mixed grout. The volume of liquid is usually found to increase for a short period (~1 d) after the grout is mixed and then decrease and go to dryness with additional cure time. The volume of the liquid layer is determined by a settling test in a 1-L plastic bottle. In the test, a known volume of freshly mixed grout (usually 500 mL) is poured into the bottle; then the bottle is capped and allowed to stand for intervals up to 28 d. The phase separation, in vol %, is calculated as the volume of clear drainable surface liquid

(hereafter referred to as drainable water) divided by the total initial grout volume times 100.

The procedure[7,8] for preparing grouts for the drainable water test was as follows: The appropriate weight of a given dry blend was added to 500 mL of the waste solution while stirring (commercial Waring blender, Model 91-186) at 2000 rpm. The dry blend was added over a period of 15 s, after which the mix was stirred for 15 s at 5000 rpm. The mixes were then poured into plastic bottles for the drainable-water tests. The batches of Blend 1 used in the tests were not dry-sheared, whereas all batches of Blends 3 and 4 were sheared. The batches of Blend 2 were tested both ways (i.e., with and without shearing). This procedure takes into account the shearing that can be expected from pumping hydrofracture grouts.

2.4 COMPRESSIVE STRENGTH TESTS

Compressive strength is a measure of the structural integrity that grouts are expected to exhibit after injection underground into hydraulically fractured shale. Low compressive strength (allowing easy crushing) would result in increased grout surface area and the possibility of increased leaching. Therefore, compressive strength tests were conducted in triplicate on each grout.

The specimens for the compressive strength tests[9] were prepared by pouring freshly prepared grout into 2-in.-cube stainless steel molds and allowing the molds to stay in a humidity cabinet at room temperature for 28 d. Crushing strengths of the grout cubes were then determined using a Model 60,000, Super "L" Tinius-Olsen Testing Machine. The freshly mixed grouts were prepared by following the same procedure as that used for the drainable water tests. Again, the batches of Blends 1 and 2 used in the tests were not dry-sheared, whereas all batches of Blends 3 and 4 were sheared.

2.5 RHEOLOGICAL MEASUREMENTS

Rheological measurements were conducted primarily to determine those properties relating to the pumpability of the grouts. Grouts for the tests were prepared by mixing W-7 waste solution (Table 1) with Blends 1, 2, 3, and 4 (Table 2) at mix ratios of 6, 7, 8, and 9 lb/gal. The preparative procedure was the same as that used for the drainable-water tests

except that the stirring rate was maintained at 2000 rpm instead of being increased to 5000 rpm during the last 15 s of mixing. In these tests, all the blends were dry-sheared. The products obtained with this procedure are representative of grouts before pumping and are not as thoroughly mixed as pumped grouts. Duplicate tests were conducted, and rheology measurements were made using a Fann Direct-Reading Viscometer, Model 35A. Freshly prepared grouts were added to the viscometer, and the shear stress was measured at shear rates from 600 to 0.9 rpm.

The data obtained in the tests were used to calculate (1) Reynolds numbers, (2) critical velocity (flow rate required for turbulent flow), (3) 10-min gel strength, and (4) frictional pressure drop per 100 ft of 2-in-ID pipe.

Although grouts can be readily pumped in the laminar-flow regime, the turbulent-flow regime is preferred for pumping grouts over long distances because radial components of velocity are present in the latter. These components exert both resisting and driving forces and, therefore, promote mixing at the pipe wall. Pumping in the turbulent-flow regime will not eliminate caking at the pipe wall but should minimize it. This mode, in turn, minimizes the operational flushing requirements and excessive pressure drops.[10]

2.5.1 Fluid Consistency Index, n', and Flow Behavior Index, K'

For non-Newtonian grouts, shear stress is dependent on shear rate and is represented by the power-law model,[11]

$$\log S_s = \log K' + n' \log S_r \ , \qquad (1)$$

where

S_s = shear stress, lb_f/ft^2,*

K' = fluid consistency index, $lb_f s^{n'}/ft^2$,

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

n' = flow behavior index ($0 < n' < 1.0$), dimensionless.

Values of n' and K' are determined from the power-law model [Eq. (1)] for a given set of viscometer-shear-stress vs shear-rate data. A typical plot of such data (for Blend 2 with a mix ratio of 6 lb/gal) with a line slope,

*To convert to SI units: 1 lb_f/ft^2 = 47.9 N/m^2.

n', equal to 0.6571 and the intercept, K', equal to 0.0015 is shown in Fig. 1. Values for n' and K' were also determined for Blends, 1, 2, 3, and 4 for each mix ratio. The values of n' and K' were then used for calculating Reynolds numbers and the conditions for turbulent flow of the grouts.

2.5.2 Density

The density of each freshly mixed grout was directly measured, in lb/gal, at room temperature using a Baroid mud balance.

2.5.3 Apparent Viscosity

Viscosity in a grout varies with shear rate. The apparent viscosities in these tests were measured at 511 s^{-1} (300 rpm on the Fann Viscometer), which is the common practice.[8]

2.5.4 Gel Strength (10-min)

The 10-min gel strength is indicative of the force required to restart the flow of grout in a pipe after it has been stopped for 10 min. The measurement is made in the Fann Viscometer with the same grout sample following the other rheological measurements. After the grout has been allowed to stand in the viscometer for 10 min without stirring, the instrument is turned on with the shear rate set at 3.0 rpm. The 10-min gel strength in lbs/100 ft^2 is read directly from the viscometer at the maximum deflection on the shear stress scale.

3. METHODS OF CALCULATION

3.1 REYNOLDS NUMBERS

Reynolds numbers were calculated from the following expression:

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

where

N_{Re} = Reynolds number, dimensionless,

V = fluid velocity, ft/s (reference condition, 20.4 ft/s),

n' = flow behavior index ($0 < n' < 1.0$),

d_i = inside pipe diameter, in. (reference condition, 2 in.),

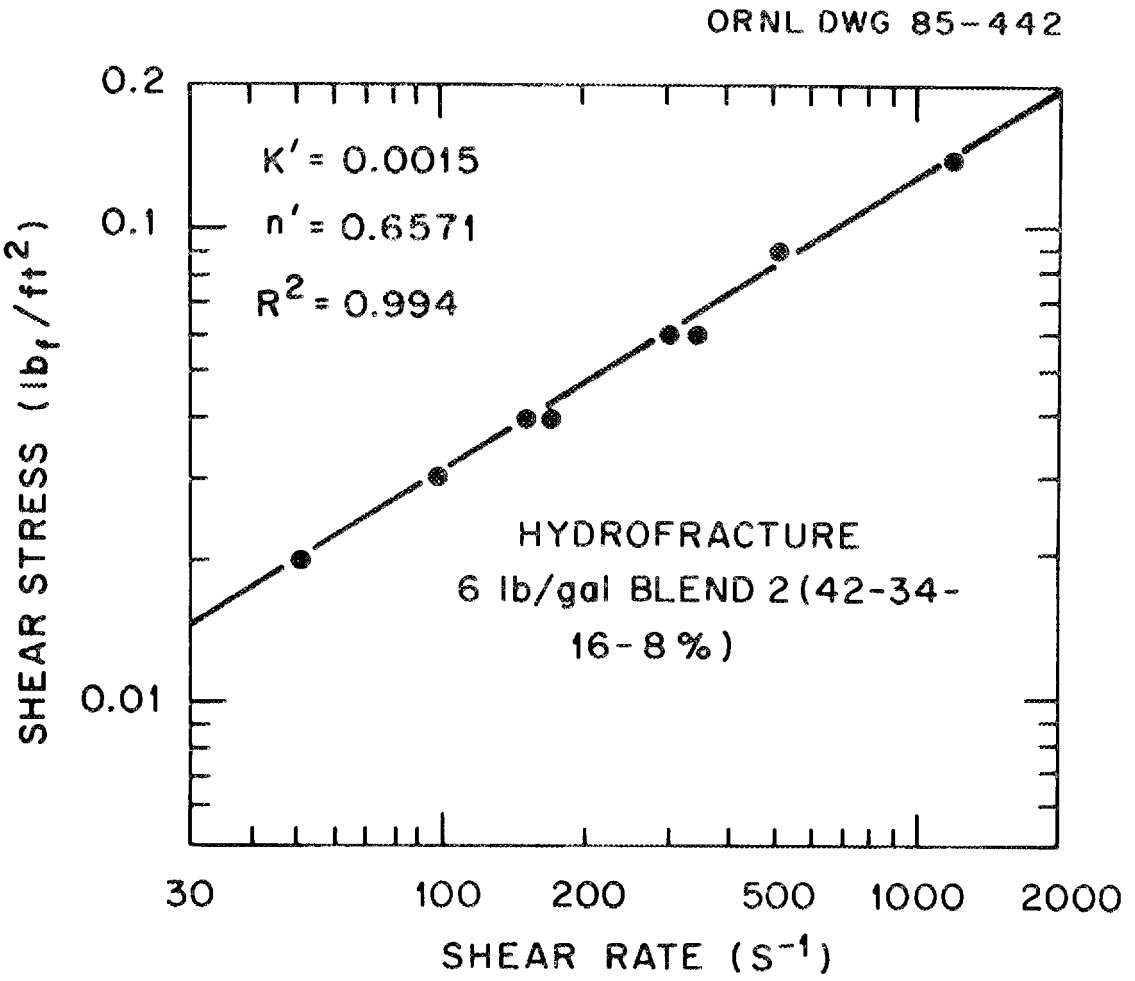

Fig. 1. Shear stress vs shear rate for grout with simulated W-7 waste.

ρ = fluid density, lb/gal, and

K' = fluid consistency index, $lb_f s^{n'}/ft^2$.

3.2 CRITICAL VELOCITY (VELOCITY FOR TURBULENT FLOW)

The critical velocity, V_c, is the velocity required for turbulent flow of a grout through a pipe — in this instance a 2-in.-diam pipe. Turbulent flow is assumed to occur at a Reynolds number $\geq$2100. The following expression for the critical velocity is obtained by rearranging Eq. (2) and setting $N_{Re} \geq 2100$:

$$V_c = \frac{2100K'(48)^{n'}}{1.86\ \rho}^{(2-n')^{-1}} \tag{3}$$

Values of V_c calculated from Eq. (3) are multiplied by 9.792 to convert the units from ft/s to gal/min in a 2-in.-diam pipe.

3.3 FRICTIONAL PRESSURE DROP

The frictional pressure drop for a grout during pumping can be defined as follow:

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

where

ΔP_f = frictional pressure drop through a straight pipe, psi,

L = pipe length, ft,

f = Fanning Friction Factor, dimensionless (f is a function of Reynolds number), and

ρ, V, and d_i represent the same variables as in Eq. (2). The value of L used in this case was 100 ft. The Fanning Friction Factor, f, decreases with increasing Reynolds number.[8] The f values used in this work were obtained by dividing 16 by the Reynolds number.

4. TEST RESULTS

4.1 DRAINABLE-WATER DEPENDENCE ON CURE TIME, MIX RATIO, ATTAPULGITE-150 CLAY CONTENT, AND BLEND SHEARING

As expected, test results show that the vol % drainable water collected over a grout decreases with increases in cure time, mix ratio, and Attapulgite-150 clay content. In general, shearing the dry blend before mixing with the waste to form the grout resulted in an increased vol % drainable water at a given cure time. The vol % drainable water as a function of cure time is plotted in Figs. 2 and 3, respectively, for Blends 1 and 2 (non-dry-sheared) and in Figs. 4, 5, and 6 for Blends 2, 3, and 4 (dry-sheared). The times plotted for zero-drainable water are less than or equal to ($\leq$) values. The general effect of decreasing the vol % drainable water while increasing the cure time and mix ratio can be seen individually in each of the figures. Other than the perturbations due to a change from nonshearing to shearing, it can be seen that the effect of increased Attapulgite-150 clay content was to decrease the volume of drainable water at a given time. The vol % drainable water for each of the 16 grouts listed in Tables 3, 4, 5, and 6 was 0.0 at cure times of $\leq$28 d. Data for Blend 2, not included in the tables, indicate that the drainable water for 6-lb/gal mixes of Blends 1 and 2 will not reach 0.0 vol % in 28 d if the blends are dry-sheared.

4.2 COMPRESSIVE STRENGTH DEPENDENCE ON MIX RATIO AND FLY-ASH CONTENT

The compressive strengths obtained from the tests are plotted in Fig. 7 as a function of mix ratio. It can be seen that the compressive strengths increase sharply as the mix ratio increases. Inspection of the figure also shows that for a given mix ratio the compressive strengths decrease slightly in going from Blend 1 to Blend 4, which apparently results from the decrease in the fly-ash content. All of the grouts had compressive strengths of >460 psig — significantly greater than the 50 psig required for an acceptable grout. Exact values of the compressive strengths obtained are listed in Tables 3, 4, 5, and 6 for grouts prepared from Blends 1, 2, 3, and 4, respectively.

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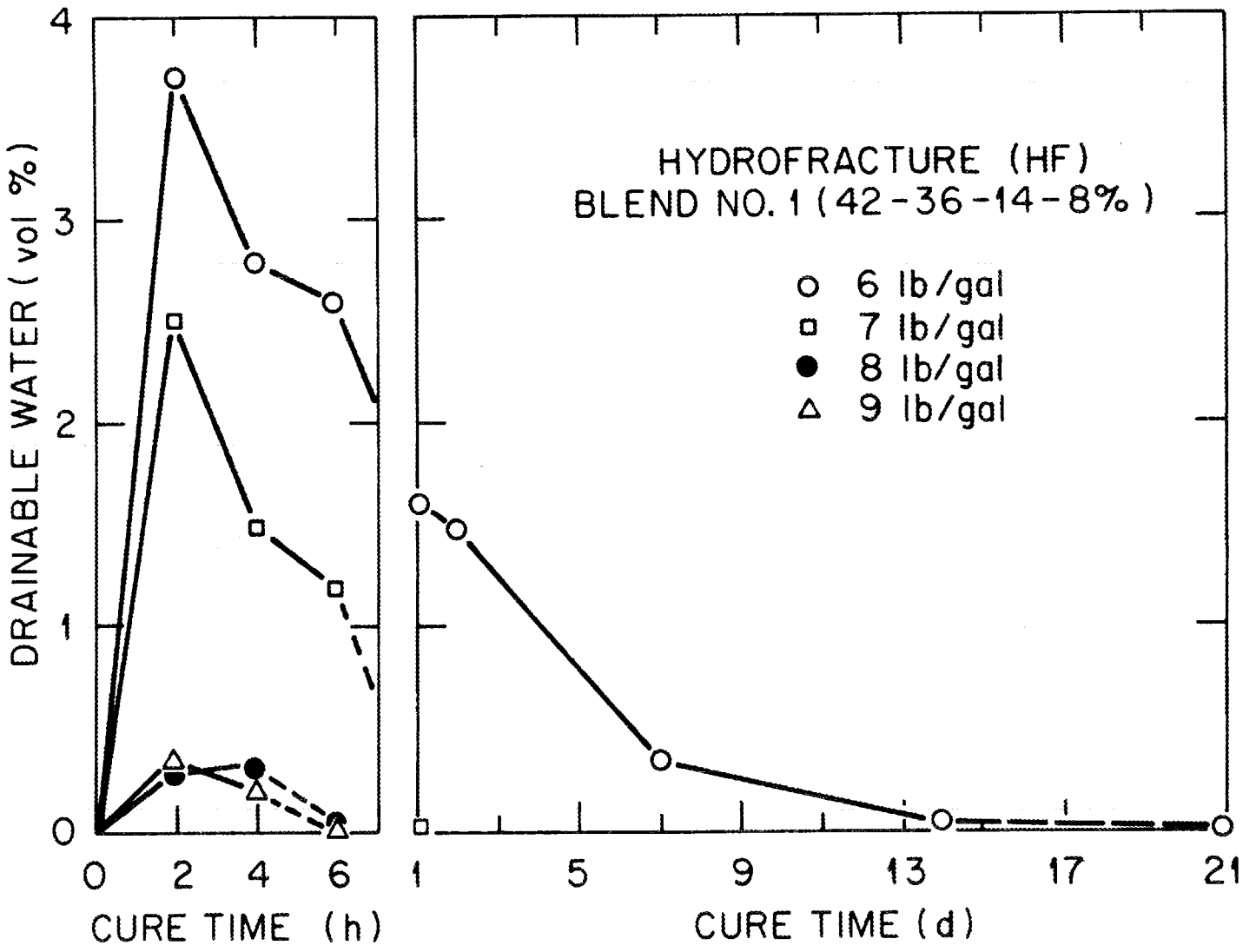

Fig. 2. Drainable water as a function of cure time for Blend 1 (Attapulgite-150 clay content, 14.0 wt %) with mix ratios of 6, 7, 8, and 9 lb/gal. Blend was not dry-sheared.

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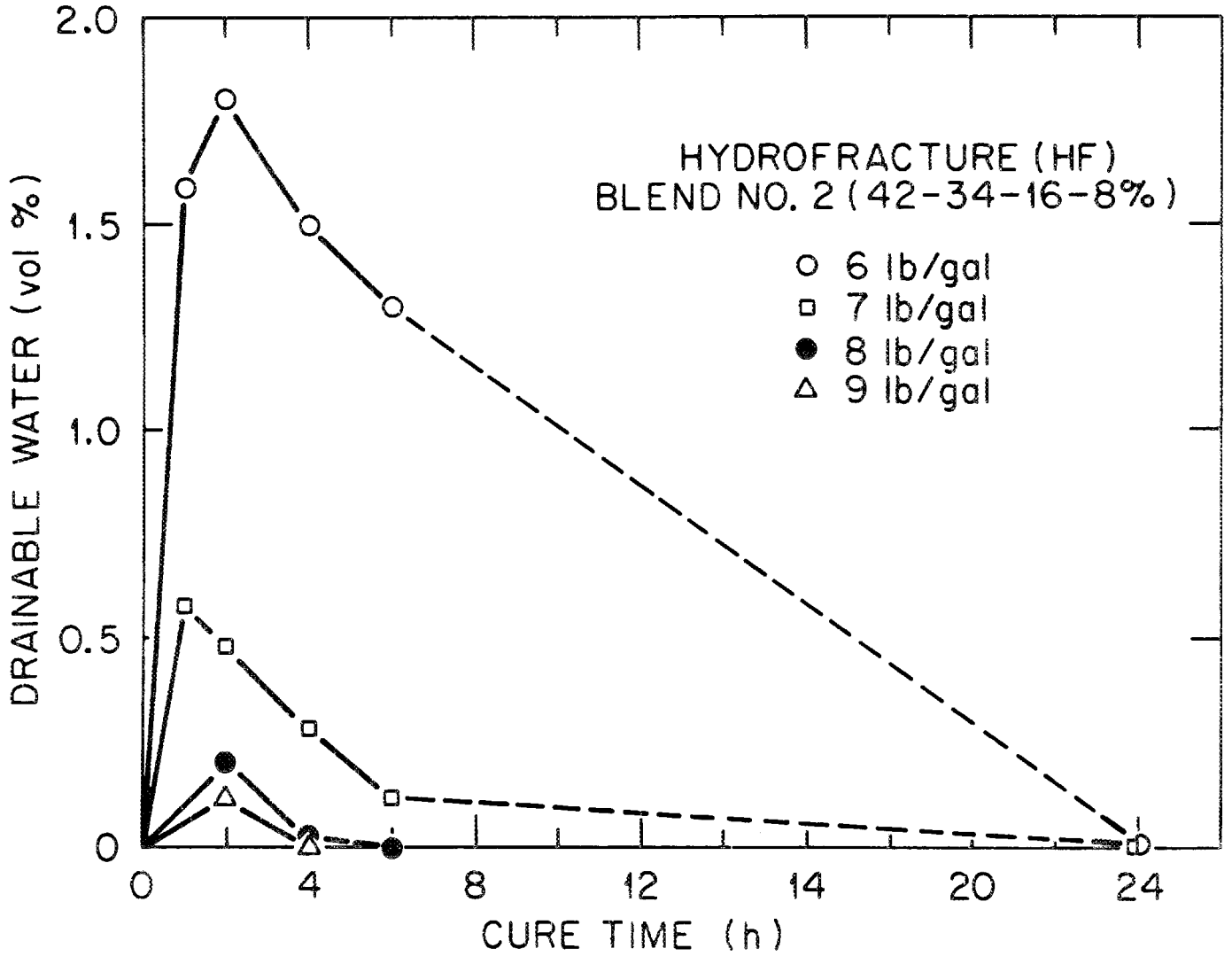

Fig. 3. Drainable water as a function of cure time for Blend 2 (Attapulgite-150 clay content, 16.0 wt %) with mix ratios of 6, 7, 8, and 9 lb/gal. Blend was not dry-sheared.

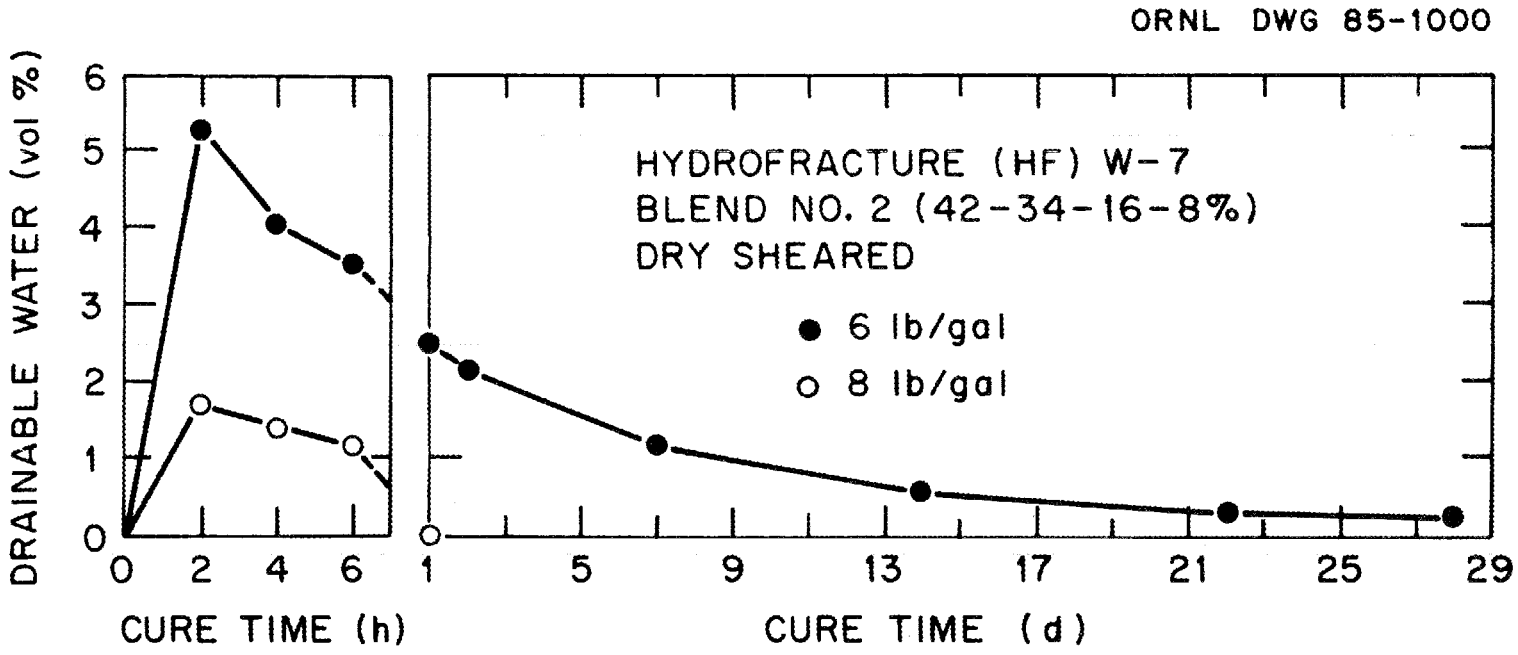

Fig. 4. Drainable water as a function of cure time for Blend 2 (Attapulgite-150 clay content, 16.0 wt %). Blend was dry-sheared.

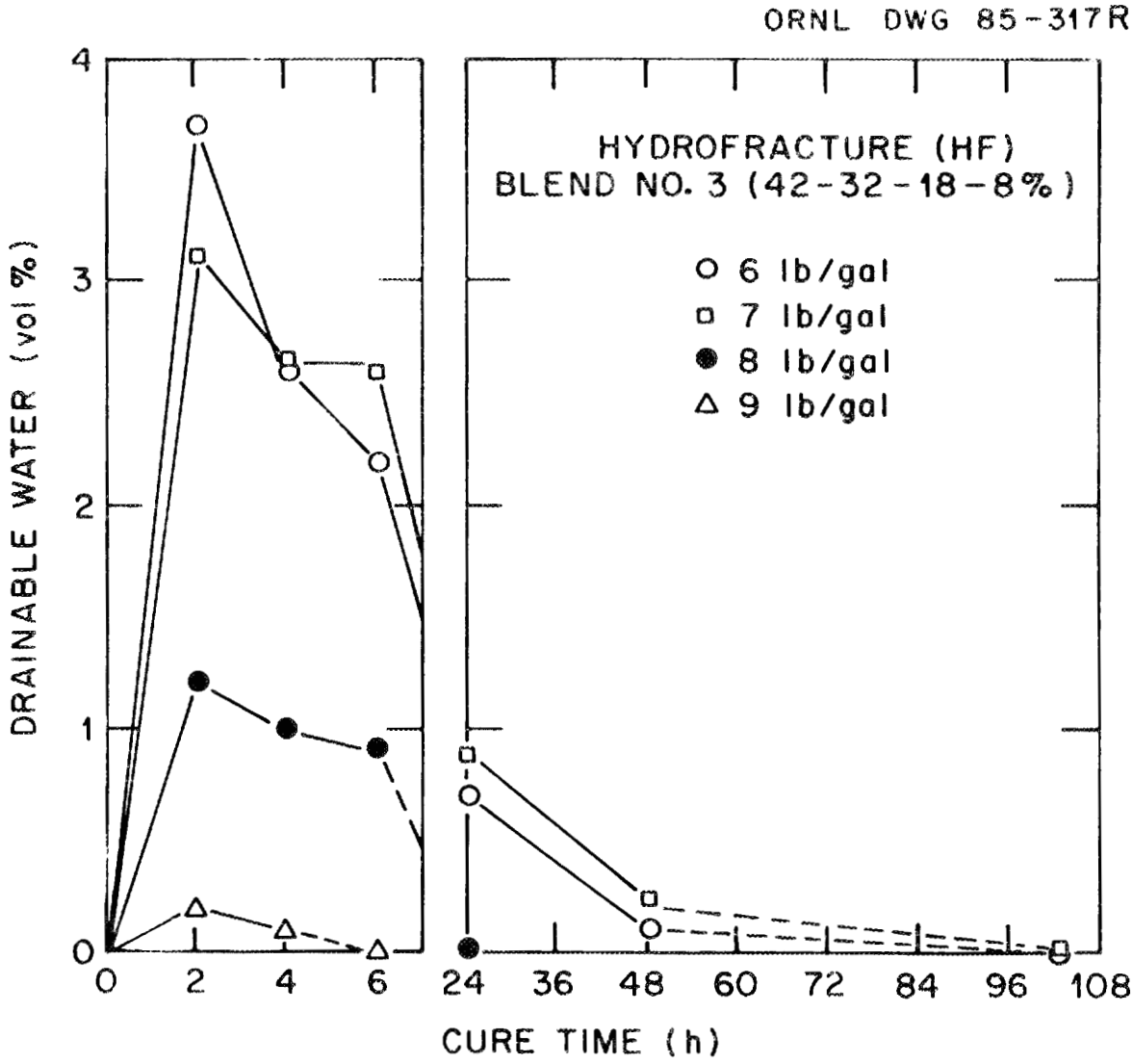

Fig. 5. Drainable water as a function of cure time for Blend 3 (Attapulgite-150 clay content, 18.0 wt %) with mix ratios of 6, 7, 8, and 9 lb/gal. Blend was dry-sheared.

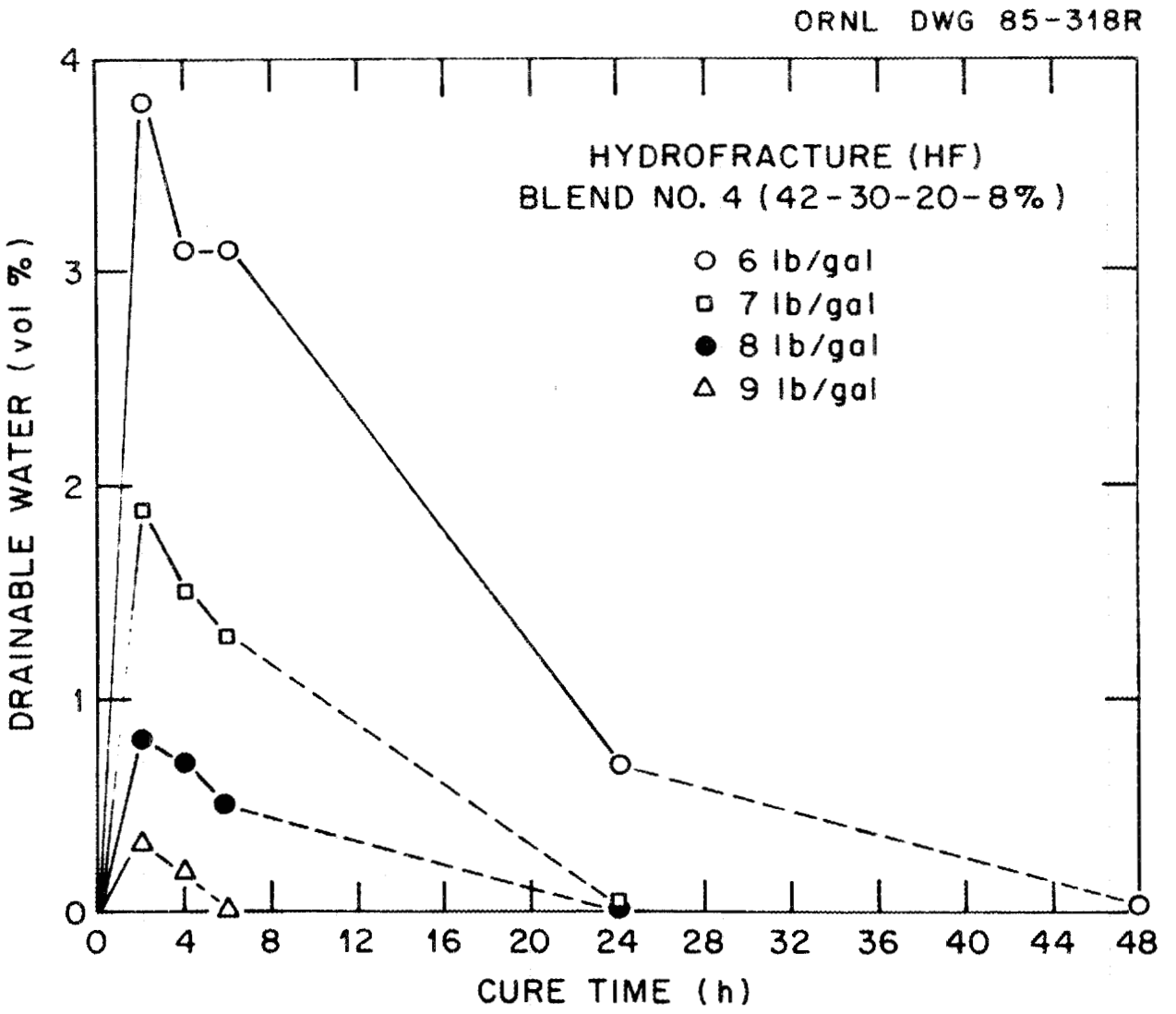

Fig. 6. Drainable water as a function of cure time for Blend 4 (Attapulgite-150 clay content, 20 wt %). Blend was dry-sheared.

Table 3. Properties of grouts prepared with dry solids Blend 1 and simulated W-7 waste

Parameter	Mix ratio (lb/gal) 6	7	8	9
28-d drainable water, vol %	0.0	0.0	0.0	0.0
28-d compressive strength, psig	534 ± 22	703 ± 16	920 ± 29	1182 ± 49
Fluid consistency index, K', $lb_f \cdot s^{n'}/ft^2$	0.0015 ± 0.0002	0.0042 ± 0.0001	0.0066 ± 0.0006	0.0121 ± 0.0004
Flow behavior index, n'	0.6511 ± 0.0198	0.5211 ± 0.0011	0.4866 ± 0.0011	0.4729 ± 0.0110
Density, lb/gal	11.7	12.0	12.2	12.6
Apparent viscosity, cP*	8.0	10.5	13.5	23.0
10-min gel strength, $lb_f/100\ ft^2$	40.5 ± 4.9	53.5 ± 9.2	69.0 ± 18.4	160.0 ± 2.8
At reference conditions:				
Reynolds number	68,157	61,117	50,350	30,994
Critical velocity, gal/min	15.1	20.4	24.4	34.8
Frictional pressure drop per 100 ft, psi	1.90	2.92	2.98	5.10

*1 cP = 1 mPa·s.

Table 4. Properties of grouts prepared with dry solids Blend 2 and simulated W-7 waste

Parameter	Mix ratio (lb/gal)			
	6	7	8	9
28-d drainable water, vol %	0.0	0.0	0.0	0.0
28-d compressive strength, psig	482 ± 33	703 ± 14	981 ± 16	1007 ± 32
Fluid consistency index, K', $lb_f \cdot s^{n'}/ft^2$	0.0015 ± 0.0001	0.0068 ± 0.0004	0.0175 ± 0.0052	0.0225 ± 0.0016
Flow behavior index, n'	0.6571 ± 0.0069	0.4744 ± 0.0118	0.3913 ± 0.0472	0.4250 ± 0.0126
Density, lb/gal	11.6	12.0	12.2	12.6
Apparent viscosity, cP*	9.0	13.0	18.5	32.0
10-min gel strength, $lb_f/100\ ft^2$	27.0 ± 0.0	27.5 ± 0.7	50.0 ± 2.8	245.0 ± 49.5
At reference conditions:				
Reynolds number	64,839	52,068	36,455	23,218
Critical velocity, gal/min	15.5	24.3	33.8	43.4
Frictional pressure drop per 100 ft, psi	1.88	2.92	3.96	7.16

*1 cP = 1 mPa·s.

Table 5. Properties of grouts prepared with dry solids Blend 3 and simulated W-7 waste

Parameter	Mix ratio (lb/gal)			
	6	7	8	9
28-d drainable water, vol %	0.0	0.0	0.0	0.0
28-d compressive strength, psig	469 ± 15	578 ± 22	788 ± 14	1003 ± 21
Fluid consistency index, K', $lb_f \cdot s^{n'}/ft^2$	0.0028 ± 0.0004	0.0086 ± 0.0039	0.0219 ± 0.0014	0.0981 ± 0.0186
Flow behavior index, n'	0.5746 ± 0.0263	0.4620 ± 0.0518	0.3928 ± 0.0218	0.2572 ± 0.0346
Density, lb/gal	11.7	11.9	12.3	12.6
Apparent viscosity, cP*	10.0	14.0	24.5	45.0
10-min gel strength, $lb_f/100\ ft^2$	26.5 ± 3.5	55.0 ± 0.0	85.5 ± 14.8	105.0 ± 63.6
At reference conditions:				
Reynolds number	61,836	44,653	29,021	16,913
Critical velocity, gal/min	18.6	27.3	39.9	60.3
Frictional pressure drop per 100 ft, psi	2.85	3.88	5.98	9.20

*1 cP = 1 mPa·s.

Table 6. Properties of grouts prepared with dry solids Blend 4 and simulated W-7 waste

Parameter	Mix ratio (lb/gal)			
	6	7	8	9
28-d drainable water, vol %	0.0	0.0	0.0	0.0
28-d compressive strength, psig	486 ± 13	572 ± 7	780 ± 38	1008 ± 32
Fluid consistency index, K', $lb_f \cdot s^{n'}/ft^2$	0.0023 ± 0.0002	0.0041 ± 0.0008	0.0125 ± 0.0000	0.0313 ± 0.0010
Flow behavior index, n'	0.6311 ± 0.0218	0.5848 ± 0.0247	0.4930 ± 0.0000	0.4531 ± 0.0037
Density, lb/gal	11.8	12.2	12.4	12.8
Apparent viscosity, cP*	11.5	15.5	27.0	52.5
10-min gel strength, $lb_f/100\ ft^2$	38.0 ± 2.8	44.5 ± 12.0	157.0 ± 15.6	>300
At reference conditions:				
Reynolds number	51,581	40,980	25,854	13,972
Critical velocity, gal/min	19.2	24.4	37.7	58.6
Frictional pressure drop per 100 ft, psi	2.88	3.95	6.06	11.43

*1 cP = 1 mPa s.

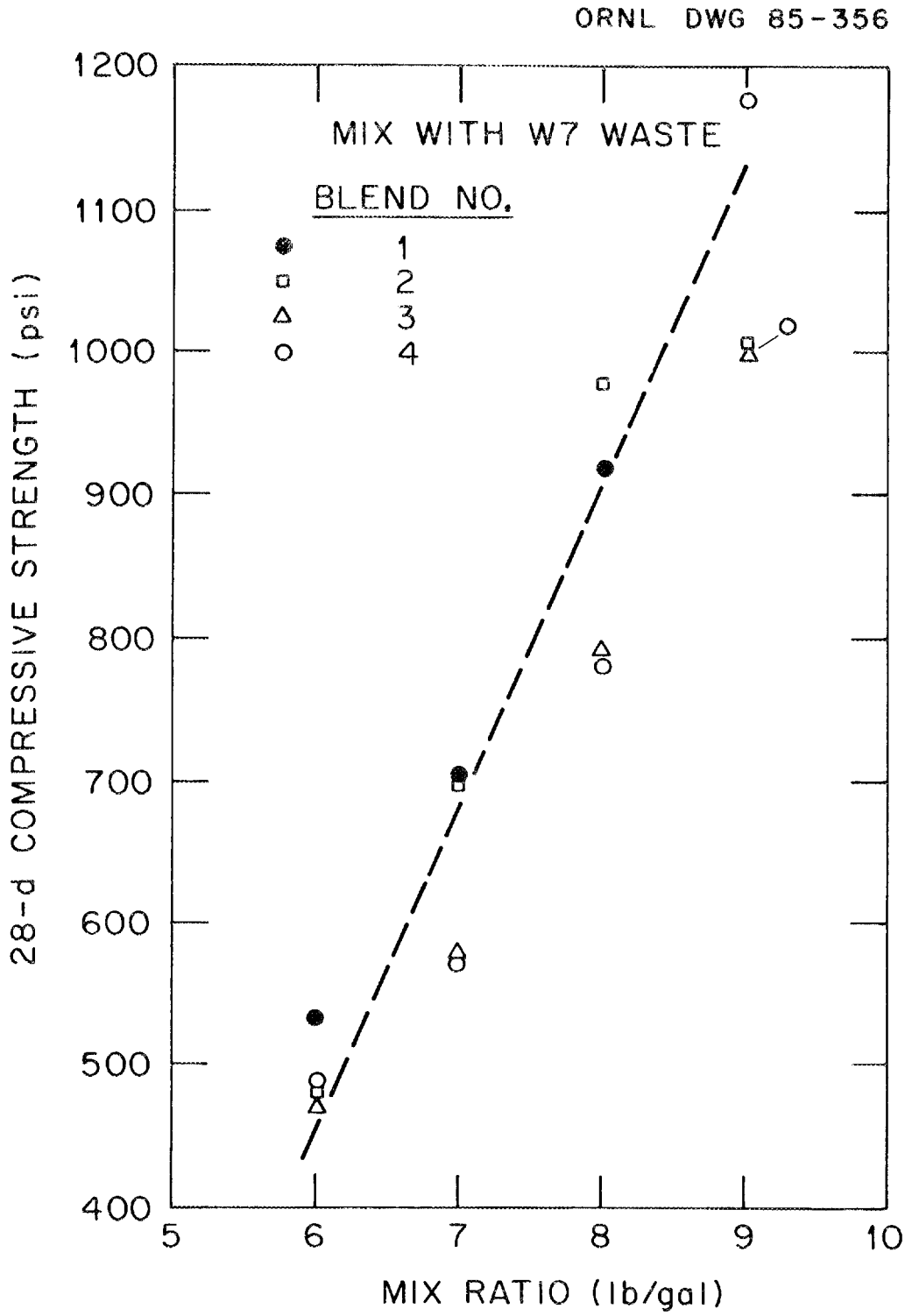

Fig. 7. Compressive strengths of grouts prepared from simulated W-7 waste and four dry blends as a function of mix ratio.

4.3 RHEOLOGICAL PROPERTY DEPENDENCE ON MIX RATIO AND FLY ASH AND/OR ATTAPULGITE-150 CLAY CONTENT

Rheological data are listed in Tables 3, 4, 5, and 6 for grouts prepared using Blends 1, 2, 3, and 4, respectively. Three of the most important rheological properties of the grouts are: (1) 10-min gel strength, (2) critical velocity, and (3) frictional pressure drop.

4.3.1 Ten-minute Gel Strength

Plots of 10-min gel strength vs mix ratio for the four blends are shown in Fig. 8. The results show that the 10-min gel strength for a given blend increases sharply as the mix ratio increases. Differences, if any, due to the usage of different blends (i.e., due to differences in the Attapulgite-150 clay or fly ash content) are not readily apparent. The 10-min gel strength for Blend 4 with a mix ratio of 9 lb/gal was >300 $lb_f/100\ ft^2$. The remaining values ranged from a low of 26.5 $lb_f/100\ ft^2$ for Blend 3 (mix ratio, 6 lb/gal) to a high of 40.83 $lb_f/100\ ft^2$ for Blend 2 (mix ratio, 9 lb/gal).

4.3.2 Critical Velocity

Plots of critical velocity vs mix ratio for the four blends are shown in Fig. 9. The critical velocity for a given blend increases sharply as the mix ratio is increased. Slight increases in the critical velocity at a given mix ratio due to usage of blends (Table 2) with decreasing fly-ash content or increasing Attapulgite-150 clay content are apparent from an inspection of the plots. Overall, the critical velocities ranged from a low of ~15.5 gal/min for a mix ratio of 6 lb/gal (Blends 1 and 2) to a high of 60.3 gal/min for a mix ratio of 9 lb/gal.

4.3.3 Frictional Pressure Drop

The frictional pressure drop per 100 ft (2-in. pipe) was 11.43 psi for Blend 4, which had a mix ratio of 9 lb/gal. The frictional pressure drops per 100 ft for the remaining grouts ranged from a low of 1.90 psi for Blends 1 and 2, each with a mix ratio of 6 lb/gal, to a high of 9.2 psi for Blend 3, with a mix ratio of 9 lb/gal.

5. EMPIRICAL RELATIONSHIPS

The equations presented below apply to grouts prepared from the simulated low-level ORNL waste (Table 1) mixed with blend compositions

ORNL DWG 85-458

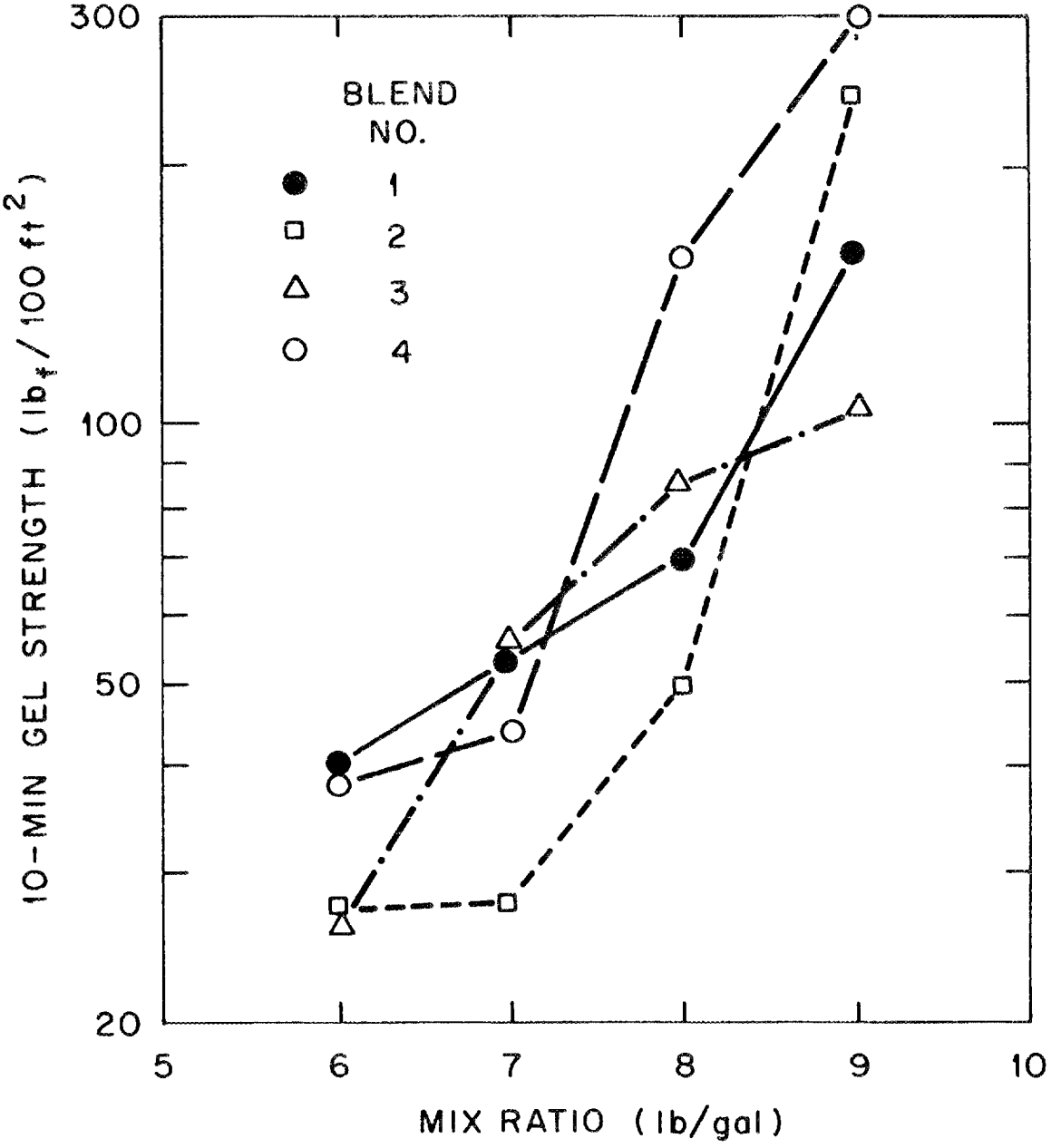

Fig. 8. Ten-minute gel strengths of grouts prepared from simulated W-7 waste and four dry blends as a function of mix ratio.

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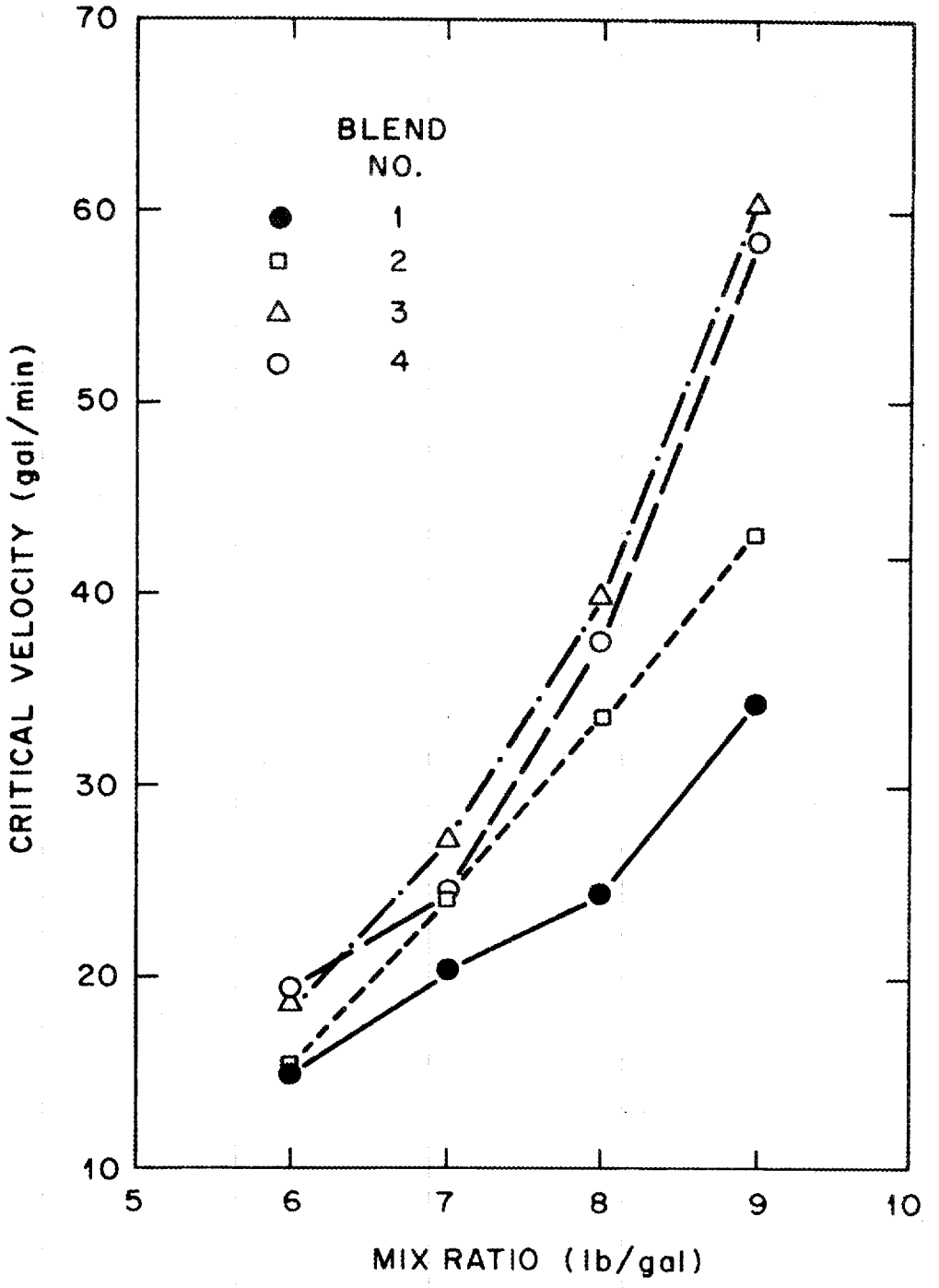

Fig. 9. Critical velocities of grouts prepared from simulated W-7 waste and four dry blends as a function of mix ratio.

intermediate to, or near, those listed in Table 2. Thus, the equations are applicable to blends with Attapulgite-150 clay compositions ranging from ~13.5 to ~20.5 wt % at mix ratios from ~5.5 to ~9.5 lb/gal. Potentially of more importance, the equations demonstrate a systematic method for representing grout-waste data which may be applicable to other systems.

5.1 DRAINABLE WATER

The drainable-water data used in the correlation for Eq. (5) below were obtained from tests in which the blends were dry-sheared (data plotted in Figs. 4, 5, and 6). Results for Blend 1 were excluded since this blend was not dry-sheared. The data points for 0.0 vol % drainable water were also excluded since the times recorded for those points represent $\leq$ values. The remaining points (39) are represented with a 0.94 coefficient of correlation by the equation

$$W = 11.222 + 3.070 \log T - 0.328\ C \log T - 1.010\ R\ , \qquad (5)$$

where W, T, C, and R, respectively, denote drainable water, in vol %; time, in h; Attapulgite-150 blend content, in wt %; and mix ratio. These symbols, when used in later equations, designate the same variables. The data for Eq. (5) did not correlate as well as all of the other analyses; nevertheless, the 0.94 value is reasonably good, considering the number and nature of the variables. The time required for the drainable water in a given grout to reach 0.0 vol % can be estimated by making appropriate substitutions in Eq. (5) for C and R and setting W equal to zero. A list of estimated times, along with measured $\leq$ times, for 0.0 vol % drainable water is shown in Table 7. In most instances, the estimated times are less than the measured times; however, the estimated values are probably more nearly correct in this case since the measured values are $\leq$ values. The data (Table 7) can be represented by the following equation:

$$\log T_o = -3.026 + 0.089\ C \log T_o + 0.296\ R\ , \qquad (6)$$

where T_o denotes the time, in h, at which the drainable water reaches 0.0 vol %.

Table 7. Measured times compared with estimated[a] times for grouts[b] to reach 0 vol % drainable water

Mix ratio (lb/gal)	Blend Attapulgite-150 clay (wt %)	Time (h) to reach zero 0 vol % drainable water	
		Measured	Estimated
6	16 (Blend 2)	>648	936
7	16 (Blend 2)	N.D.[c]	182
8	16 (Blend 2)	24	35
9	16 (Blend 2)	N.D.[c]	7
6	18 (Blend 3)	108	122
7	18 (Blend 3)	108	39
8	18 (Blend 3)	24	12
9	18 (Blend 3)	6	4
6	16 (Blend 4)	48	40
7	16 (Blend 4)	24	17
8	16 (Blend 4)	24	7
9	16 (Blend 4)	6	3

[a]Estimates are based on Eq. (5).

[b]All blends were dry-sheared.

[c]N.D. = not determined.

5.2 COMPRESSIVE STRENGTH

The compressive strength data for the 16 grouts (Tables 3, 4, 5, and 6) can be represented with a 0.96 coefficient of correlation by the following equation:

$$S = -918.87 + 190.00\ R + \frac{6423.78}{F}\ , \qquad (7)$$

where S denotes the compressive strength, in psig, and F the amount of ASTM Class F fly ash in the dry blend, in wt %.

Plots of the compressive strength vs mix ratio are shown in Fig. 10 for grouts prepared from Blends 1 and 2 and in Fig. 11 for grouts prepared from Blends 3 and 4. The lines drawn in the figures represent values estimated from Eq. (7); the data points plotted with error bars are the measured values. The error bars were determined by repeated measurements. It is obvious that the lines represent the measured data very well.

There is a question as to how many of the compressive strength data are actually needed for this type of investigation. In this regard, a correlation was made based on results from one-half of the tests (8 data points), i.e., from only the 6- and 8-lb/gal tests. The data from these tests are represented with a 0.95 coefficient of correlation by the following equation:

$$S = -839.85 + 187.15\ R + \frac{5319.77}{F}\ . \qquad (8)$$

Plots of the compressive strength vs mix ratio are shown in Fig. 12 for grouts prepared from Blends 1 and 2 and in Fig. 13 for Blends 3 and 4. The lines drawn in the figures represent values determined from Eq. (8) based on 8 instead of the entire 16 data points. As seen, the lines represent the measured data plotted in the figures very well. Again, this result is interesting and the extent to which such tests could be decreased in number in future work is undetermined without significant future study.

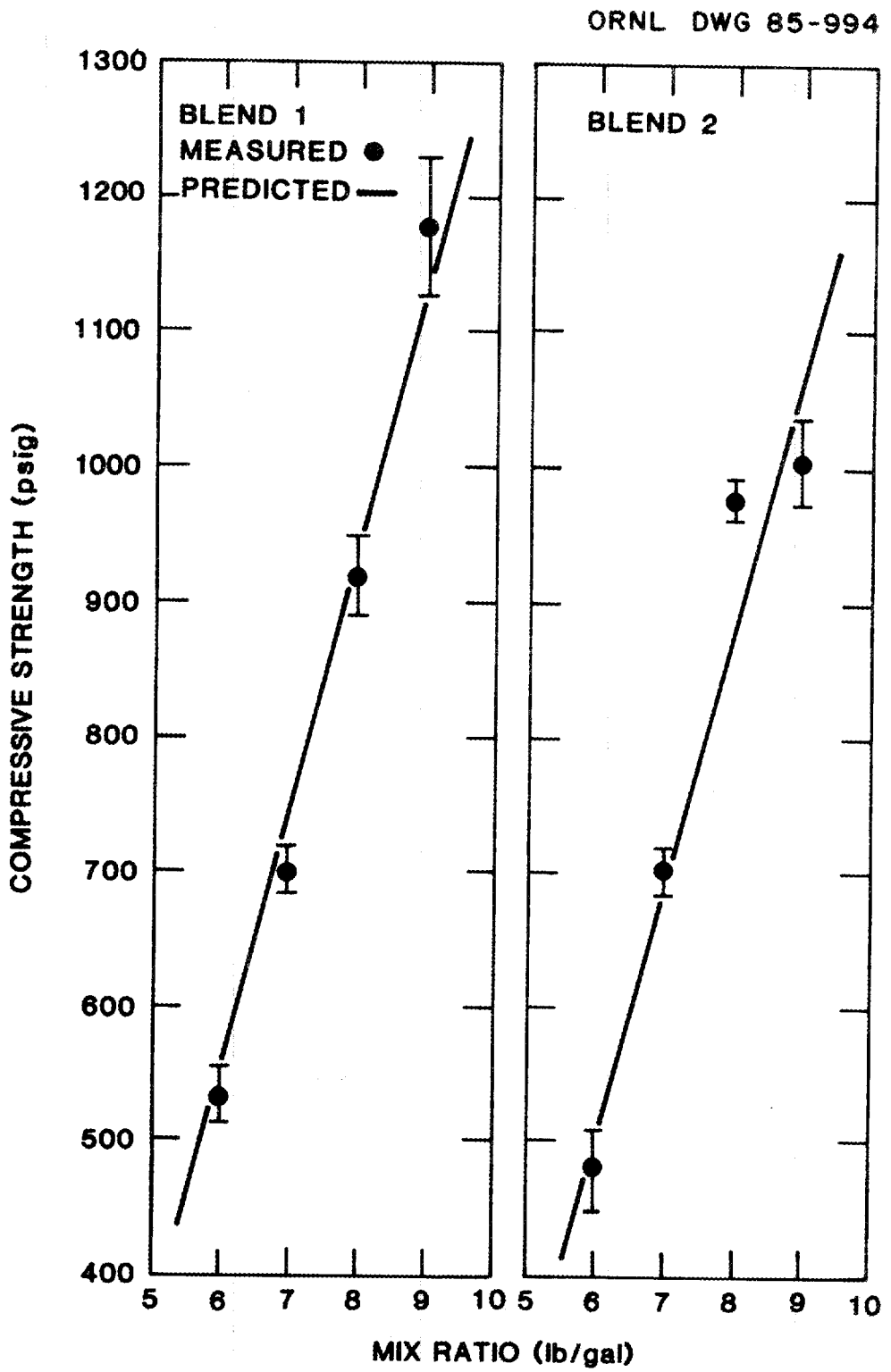

Fig. 10. Measured compressive strength values compared with value lines predicted from Eq. (7) for Blends 1 and 2.

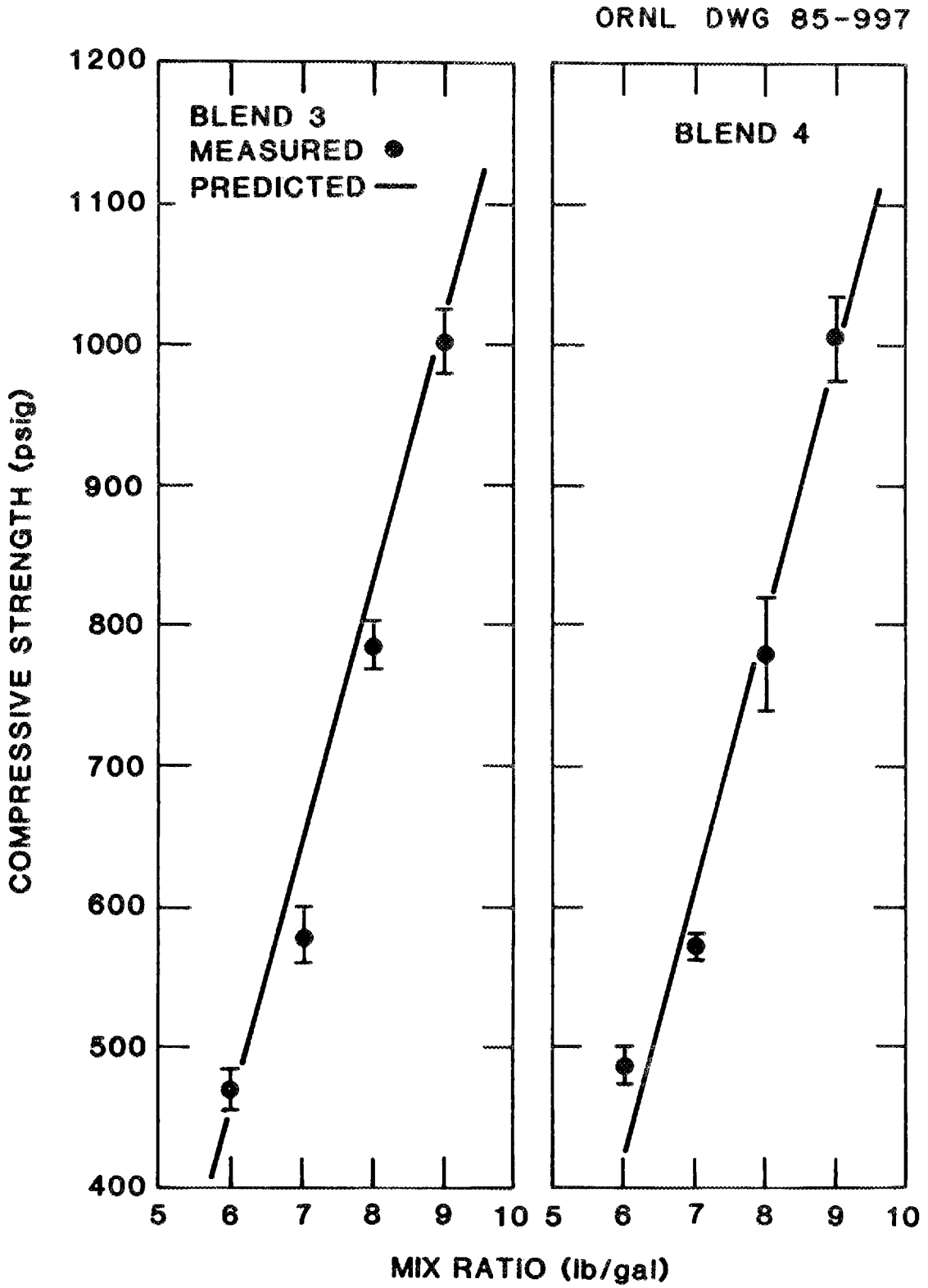

Fig. 11. Measured compressive strength values compared with value lines predicted from Eq. (7) for Blends 3 and 4.

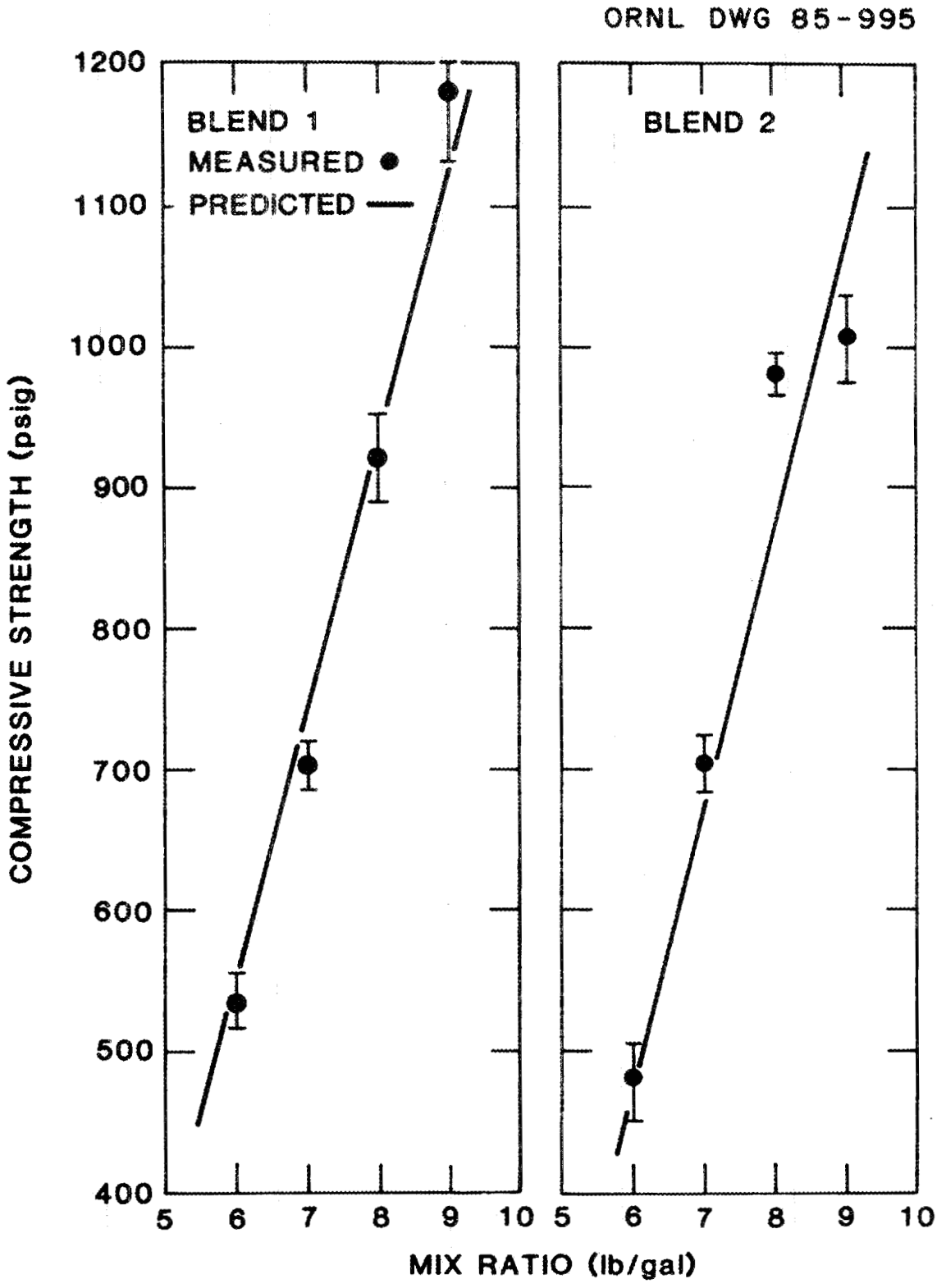

Fig. 12. Comparison of measured compressive strength values with predicted value lines from Eq. (8) for Blends 1 and 2.

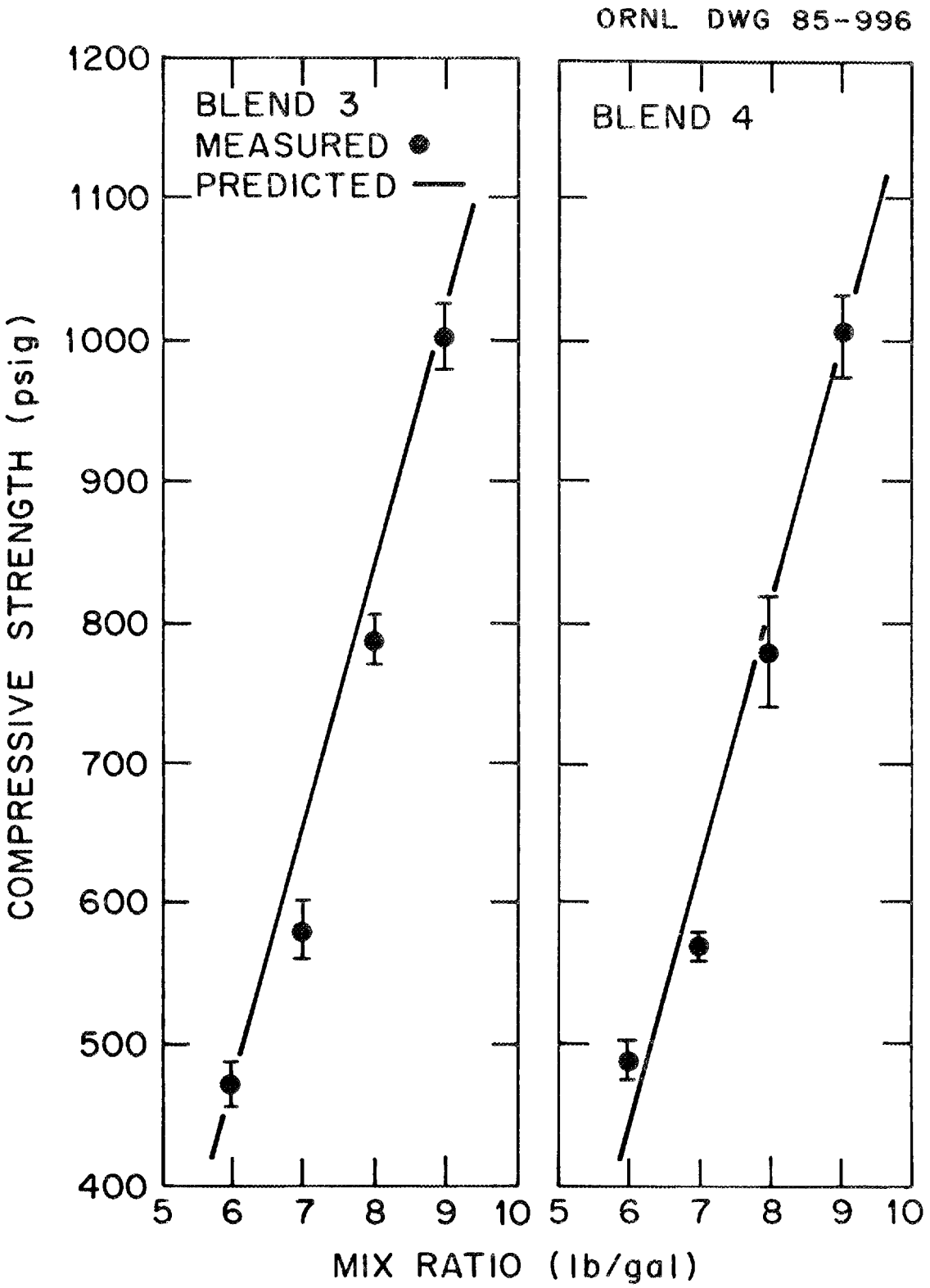

Fig. 13. Comparison of measured compressive strength values with predicted value lines from Eq. (8) for Blends 3 and 4.

5.3 CRITICAL VELOCITY

The critical velocity data for the 16 grouts (Tables 3-6) can be represented with a 0.96 coefficient of correlation by the following equation:

$$\log V_{cr} = 2.406 + 0.198\ R - \frac{8.828}{C} - 0.157\ \rho\ , \qquad (9)$$

where R and C have the usual designations and V_{cr} and ρ, respectively, denote critical velocity, in gal/min, and density, in lb/gal. The blend compositions (Table 2) are such that C = 50 - F; thus, 50 - F may legitimately be substituted for C in this equation and in Eq. (10). Since the equations are empirical, either form may be used. Plots of the log of the critical velocity vs mix ratio are shown in Fig. 14 for grouts prepared from Blends 1, 2, 3, and 4. The lines drawn in the figure represent values estimated from Eq. (9), while the plotted data points designate actual measurements. As with the compressive strength data, the lines represent the measured data very well.

Again, the question arises as to how much data is actually needed. A second correlation was made, based on one-half the critical velocity data (8 data points) from the 6- and 8-lb/gal tests. The data are represented with a 0.97 coefficient of correlation by the following equation:

$$\log V_{cr} = 0.796 + 0.146\ R - \frac{7.417}{C}\ . \qquad (10)$$

Plots of log V_{cr} vs R are shown in Fig. 15. The lines drawn in the figure represent values estimated from Eq. (10) based on 8 instead of the entire 16 data points. As seen, the lines represent the measured data plotted in the figure very well. While this result is interesting, the extent to which such tests could be decreased in number in future work is undetermined without significant further study.

6. DISCUSSION

One objective of this study (see Sect. 1) was to provide a referenceable document describing the experimental methods and techniques used

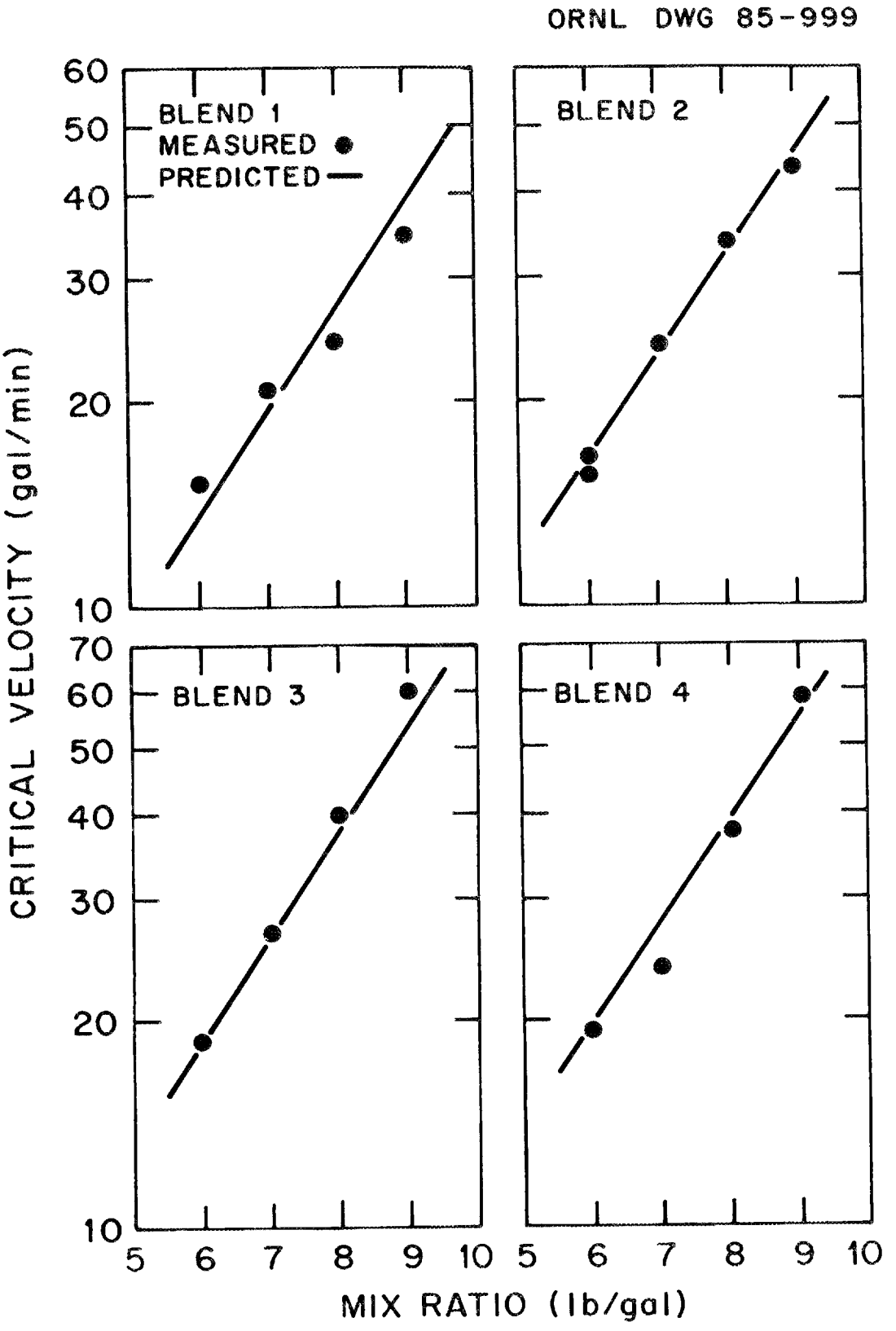

Fig. 14. Measured critical velocity values compared with predicted value lines from Eq. (9).

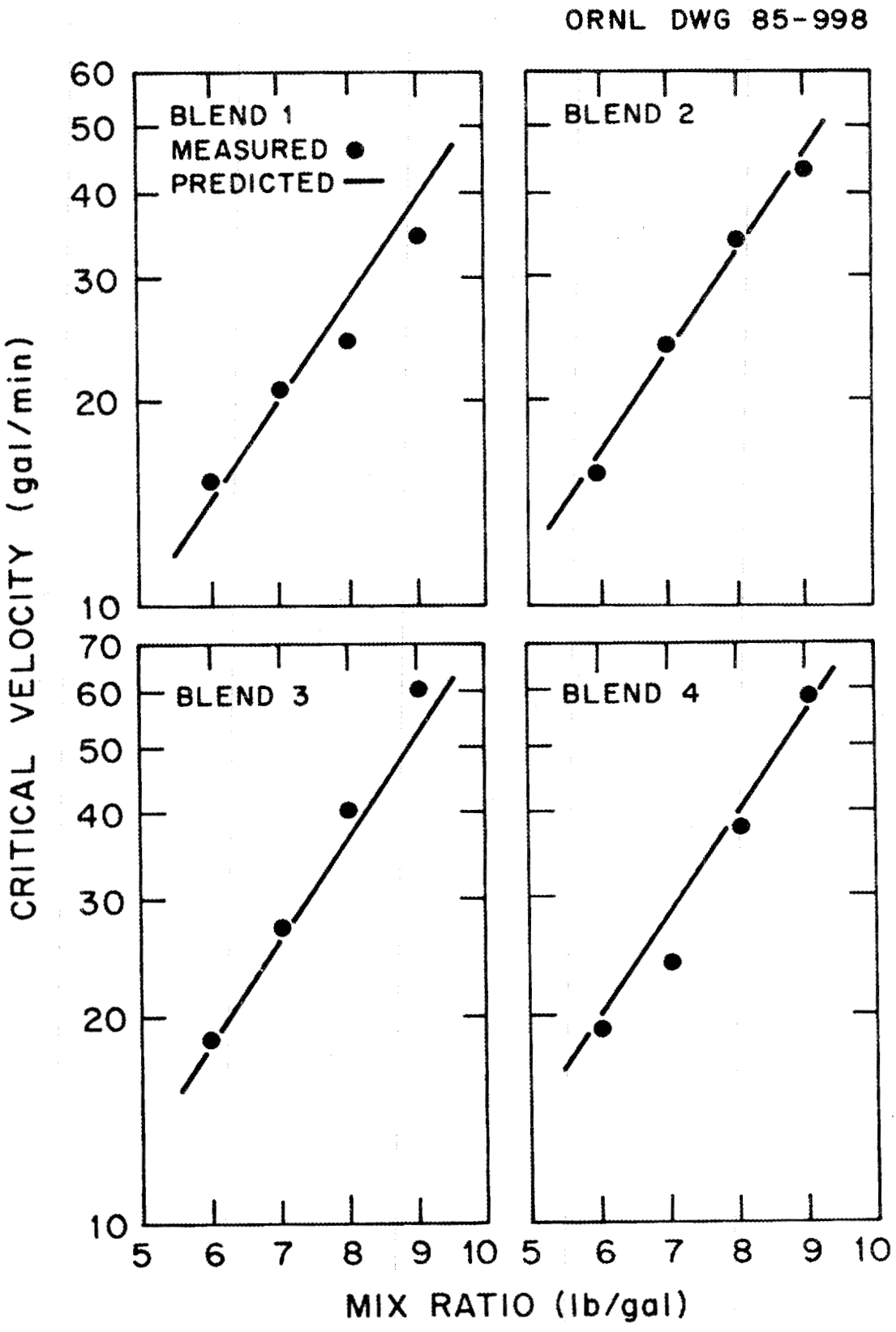

Fig. 15. Measured critical velocity values compared with predicted value lines from Eq. (10).

in studies of waste grout formulation. The phase separation, compressive strength, and rheological tests described here are used in most formulation studies for the fixation of wastes in cement-based grouts. Many data points are obtained every year from tests such as these and reported in internal documents. A penetration resistance test, which measures grout thickening or settling rate and is usually performed on grouts to be poured in trenches, drums, etc. is also frequently used in similar investigations. It was not conducted on the grouts for this study.

A second objective was to demonstrate statistical analysis methods that would ultimately broaden the scope of grout-waste uses and generally add credibility to grout-waste treatment methods. The equations in Sect. 5 mathematically relate several of the important variables involved in ORNL Hydrofracture grout-waste formulation. Although empirical, the equations demonstrate an inherent systematics which, if found to be demonstratable in other grout-waste systems, should increase the credibility and usefulness of the systems. One advantage of the empirical approach is that only a superficial understanding of the chemical reactions and mechanisms occurring in the system is required. This aspect is particularly important in grout-waste work since the chemistry of cement is, at best, complex and difficult to understand and the chemistry of grouts containing waste substances is even more so. The utility of the empirical equations [Eqs.(5)-(10)] is in the prediction of properties within the compositional range of the investigation from which the data were obtained. These equations provide a relatively simple method applicable to (1) improved future test design, (2) elimination of superfluous testing, (3) decreased costs, and (4) greater overall efficiency of individual investigations. For quality assurance purposes, they provide a means of searching out suspect data and pinpointing unusual occurrences.

7. ACKNOWLEDGEMENT

The technical advice and information provided by G. A. West,* of the ORNL Chemical Technology Division, are gratefully acknowledged.

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*Now retired.

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NOMENCLATURE

C = Attapulgite-150 clay content in dry blend, wt %

d_i = inside pipe diameter (reference condition, 2 in.)

F = Class F fly-ash content in dry blend, wt %

f = Fanning Friction Factor, dimensionless

K' = fluid consistency index, $lb_f\ s^{n'}/ft^2$

L = pipe length, ft

n' = flow behavior index ($0 < n' < 1.0$), dimensionless

N_{Re} = Reynolds number, dimensionless

ρ = fluid density, lb/gal

ΔP_f = frictional pressure drop through a straight pipe, psi

R = solids/liquid mix ratio, lb/gal

S = compressive strength, psig

S_r = shear rate, s^{-1}

S_s = shear stress, lb_f/ft^2

T = time, h

V = fluid velocity, ft/s (reference condition, 20.4 ft/s)

V_{cr} = pumping velocity required for turbulent flow under reference conditions, gal/min

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