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Fixation of Waste Materials in Grouts. Part III: Equation for Critical Flow Rate

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FIXATION OF WASTE MATERIALS IN GROUTS. PART III: EQUATION FOR CRITICAL FLOW RATE

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FIXATION OF WASTE MATERIALS IN GROUTS. PART III: EQUATION FOR CRITICAL FLOW RATE

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ABSTRACT

Critical flow rate data for grouts prepared from three distinctly different nuclear waste materials have been correlated. The wastes include Oak Ridge National Laboratory (ORNL) low-level waste (LLW) solution, Hanford Facility waste (HFW) solution, and cladding removal waste (CRW) slurry. Data for the three wastes have been correlated with a 0.96 coefficient of correlation by the following equation:

$$\log V_E = 0.289 + 0.707 \log \mu_E ,$$

where V_E and μ_E denote critical flow rate in m^3/min and apparent viscosity in Pa•s, respectively. The equation may be used to estimate critical flow rate for grouts prepared within the compositional range of the investigation.

1. INTRODUCTION

Waste disposal is rapidly becoming one of the most important technological endeavors of our time, and fixation of waste in cement-based materials is an important part of that endeavor. Many wastes can be adequately incorporated into grout, but each waste must be investigated separately. This requires numerous tests, with the result being that large quantities of data must be obtained. The purpose of this report, along with the two previous publications in this series,[1,2] is to extend the usages of the data. In the first report,[1] hydrofracture hydrofracture process variable data were correlated with phase separation, compressive strength, and critical velocity (or flow rate) grout product characteristics. In the second report,[2] data for three distinctly different wastes were correlated. In the current report, the possibility of

estimating the critical flow rate of freshly mixed grout from the measurement of apparent viscosity is examined. This report broadens the scope of previous work by correlating critical flow rate data for grouts prepared from three different waste forms: (1) ORNL LLW, (2)Hanford Facilities Waste (HFW), and (3) CRW from Rockwell Hanford Operations. Critical flow rate, defined as the flow rate at which a grout must be pumped through a pipe to obtain turbulent flow, is not only one of the most important determinations regarding grouted waste but, at present, is also one of the most tedious and difficult to obtain. Grout flow through a pipe needs to be turbulent since laminar flow allows the grout to cake on pipe walls and eventually plug the pipe. Critical velocity data are being evaluated based on the following equation:[3]

$$V^{(2-n')} = \frac{2100\ (96/D_i)^{n'}}{1.86\ \rho}\ , \qquad (1)$$

where

V = critical velocity, ft/s;

D_i = inside diameter of the pipe, in.,;

n' = flow behavior index, dimensionless;

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

ρ = fresh-mix density, lb/gal.

Because this equation is commonly applied in field operations, it is used here despite the mixed units. Its use is necessitated by the non-Newtonian characteristic of grouts. Values for n' and K' are determined based on the power law[3] relationship,

$$S_s = K' S_r^{\,n'}, \qquad (2)$$

S_s = shear stress, lb_f/ft^2

S_r = shear rate, s^{-1}

Typically, S_s values are measured using a Fann viscometer at rotation speeds of 600, 300, 200, 181, 100, 90, 60, and 30 rpm. Rotation speeds are multiplied by 1.703 to convert to shear rates (S_r) in s^{-1}. A fit of the S_s and S_r values to the power law equation is used to evaluate n'

and K' in Eq. (2). The density of the grout mix needed for Eq. (1) is determined using a Baroid mud balance. The critical velocity, V, calculated from Eq. (1), can be converted from ft/s (assuming that a "2-in. pipe" is 2.0 in. ID) to m^3/min units using a multiplication factor of 0.037. The method for estimating critical flow rate from apparent viscosity measurements at 300 rpm would be expected to reduce the extent to which the more-involved method, Eq. (1), must be used in waste grout work.

2. WASTE COMPOSITIONS AND DRY-SOLID BLENDS

Table 1 shows that the composition of the simulated ORNL LLW is characterized by the presence of NO_3^-, Cl^-, and CO_3^{2-} anions and NaOH. Each of the dry-solid blends listed in Table 2 was mixed with the LLW at ratios of 720, 840, 960, and 1080 kg/m^3. Major components and their maximum concentrations in the HFW are listed in Table 3. Aliquots of this waste solution were diluted to contain 0.50, 0.67, and 0.80 fractions of the concentrations shown in the table. Each of the dry-solid blends shown in Table 4 was mixed with one or more of the dilutions, along with the undiluted solution, at ratios of 720, 840, and 960 kg/m^3. Table 3 reveals that HFW is characterized by the presence of PO_4^{3-}, HPO_4^{2-}, SO_4^{2-}, and NO_2^- anions, as well as NaOH. Major components in the neutralized CRW from Rockwell-Hanford Operations are listed in Table 5. This waste is a slurry containing ~30 wt % solids, primarily $ZrO_2 \cdot xH_2O$. Samples of the waste slurry were diluted to contain 0.30, 0.50, 0.67, and 0.80 fractions of the concentrations shown in Table 5. These dilutions were mixed with the dry blends shown in Table 6 at mix ratios of 720 and 840 kg/m^3. As Table 5 reveals, the CRW is characterized by the presence of F^- and NH_4^+ ions, NaOH, and $ZrO_2 \cdot xH_2O$. The $Ca(OH)_2$ is included in the dry-solid blends to precipitate the fluoride as CaF_2. This action prevents the fluoride from acting as a set retarder in the grouts.

Table 1. Composition of simulated ORNL LLW solution

Component	Concentration (M)
$Al(NO_3)_3 \cdot 9H_2O$	0.007
NaCl	0.093
Na_2CO_3	0.190
$NaNO_3$	0.810
NaOH	0.180
Na_2SO_4	0.094
NH_4NO_3	0.003

Table 2. Blends of solids used in grout mix for ORNL LLW

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 (ASTM 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

Table 3. Maximum concentrations of major compounds in HFW

Component	Concentration (M)
Na_3PO_4	0.5
Na_2HPO_4	0.02
Na_2SO_4	0.02
NaOH	0.02
$NaNO_2$	0.02
Total carbon	(1.85 g/L)

Table 4. Dry-solid blends used in grout mix for HFW

Material	Blend 1 (wt %)	Blend 2 (wt %)	Blend 3 (wt %)	Blend 4 (wt %)
Type I-II-LA Portland cement	41.0	41.0	40.0	39.0
Centralia, Washington, fly ash (ASTM class F)	41.0	40.0	40.0	39.0
Attapulgite-150 clay	10.0	11.0	12.0	14.0
Indian Red pottery clay	8.0	8.0	8.0	8.0

Table 5. Major compound (element) concentration in neutralized CRW at Rockwell Hanford Operations

Component	Concentration (M)
$ZrO_2 \cdot xH_2O$ (undissolved)	1.03
NaF	2.27
$NaNO_3$	0.05
NaOH	0.91
NH_3	0.83
Uranium	<0.01

Table 6. Dry-solid blends used in grout mix for neutralized CRW

Material	Blend 1 (wt %)	Blend 2 (wt %)
Type III Portland cement	42.0	60.0
Centralia, WA, fly ash (ASTM class F)	42.0	19.0
Attapulgite-150 clay	5.0	5.0
$Ca(OH)_2$	10.0	15.0
$Ba(OH)_2$	1.0	1.0

3. TEST PROCEDURE

The mixing procedure[4,5] for both HFW and CRW consisted of adding the blended solids to the waste in a Model N-50 Hobart mixer for 30 s at a low stirring rate, ~139 rpm, and then increasing the stirring rate to ~285 rpm (medium-speed setting on mixer) for 30 s. The ORNL waste samples were prepared by a similar procedure using a Model 91-186 Waring blender (commercial type). The dry blend was added over a period of 15 s at 2000 rpm, after which the mix was stirred at 5000 rpm for an additional 15 s. The rheological measurements were made using a Fann Direct-Reading Viscometer, Model 35A SR-12. The apparent viscosity was determined directly from shear stress readings at a rotation speed of 300 rpm. The S_s and S_r data were fitted (power curve fit) to Eq. (2) to evaluate n' and K' values, which were then inserted in Eq. (1) to calculate the critical velocity. The densities of the grouts were measured using a Baroid mud balance. It was assumed that the grout would be pumped through an exactly 2.0 in. ID pipe when the critical flow rate was calculated.

4. CORRELATION OF DATA

The statistical correlation (multiregression analysis) included 47 data points (Table 7): 16 from ORNL LLW, 18 from HFW, and 13 from CRW. The data are represented with a 0.96 coefficient of correlation by the following empirical equation:

Table 7. Critical flow rate as a function of important variables in waste grout formulation

Observation No.	Waste	Waste fraction concentration	Attapulgite-150 clay in blend (wt %)	Mix ratio (kg/m^3)	Portland cement in blend (wt %)	Fly ash in blend (wt %)	Viscosity (Pa•s)	Critical flow rate (m^3/min)
1	ORNL	1.00	14	720	42	36	0.008	0.057
2	ORNL	1.00	14	840	42	36	0.010	0.077
3	ORNL	1.00	14	960	42	36	0.013	0.093
4	ORNL	1.00	14	1080	42	36	0.023	0.131
5	ORNL	1.00	16	720	42	34	0.009	0.059
6	ORNL	1.00	16	840	42	34	0.013	0.092
7	ORNL	1.00	16	960	42	34	0.018	0.128
8	ORNL	1.00	16	1080	42	34	0.032	0.164
9	ORNL	1.00	18	720	42	32	0.010	0.071
10	ORNL	1.00	18	840	42	32	0.014	0.104
11	ORNL	1.00	18	960	42	32	0.024	0.152
12	ORNL	1.00	18	1080	42	32	0.045	0.229
13	ORNL	1.00	20	720	42	30	0.011	0.073
14	ORNL	1.00	20	840	42	30	0.015	0.093
15	ORNL	1.00	20	960	42	30	0.027	0.143
16	ORNL	1.00	20	1080	42	30	0.052	0.223
17	HFW	0.80	10	840	41	41	0.024	0.155
18	HFW	0.67	10	840	41	41	0.024	0.152
19	HFW	0.50	10	840	41	41	0.026	0.164
20	HFW	1.00	10	960	41	41	0.033	0.187
21	HFW	0.67	10	960	41	41	0.040	0.212
22	HFW	0.50	10	960	41	41	0.039	0.202
23	HFW	1.00	14	840	39	39	0.050	0.250
24	HFW	0.80	14	840	39	39	0.046	0.237
25	HFW	0.67	14	840	39	39	0.047	0.238

Table 7 (continued)

Observation No.	Waste	Waste fraction concentration	Attapulgite-150 clay in blend (wt %)	Mix ratio (kg/m^3)	Portland cement in blend (wt %)	Fly ash in blend (wt %)	Viscosity (Pa•s)	Critical flow rate (m^3/min)
26	HFW	0.50	14	840	39	39	0.048	0.242
27	HFW	1.00	12	960	40	40	0.036	0.191
28	HFW	0.80	12	960	40	40	0.050	0.244
29	HFW	0.50	12	960	40	40	0.051	0.212
30	HFW	0.80	10	840	41	40	0.036	0.189
31	HFW	1.00	11	960	41	40	0.078	0.295
32	HFW	0.80	11	720	41	40	0.015	0.109
33	HFW	0.80	11	840	41	40	0.028	0.170
34	HFW	0.80	5	840	42	42	0.036	0.189
35	CRW	0.67	5	840	42	42	0.051	0.247
36	CRW	0.67	5	840	42	42	0.072	0.271
37	CRW	0.50	5	840	42	42	0.040	0.190
38	CRW	0.30	5	840	42	42	0.054	0.233
39	CRW	0.50	5	720	42	42	0.030	0.150
40	CRW	0.30	5	720	42	42	0.021	0.140
41	CRW	0.80	5	720	60	19	0.085	0.304
42	CRW	0.67	5	720	60	19	0.057	0.235
43	CRW	0.50	5	720	60	19	0.037	0.186
44	CRW	0.30	5	720	60	19	0.048	0.221
45	CRW	0.67	5	840	60	19	0.095	0.320
46	CRW	0.50	5	840	60	19	0.071	0.382
47	CRW	0.30	5	840	60	19	0.081	0.305

$$\log V_E = 0.289 + 0.707 \log \mu_E \ , \qquad (3)$$

where V_E and μ_E denote critical flow rate in m^3/min and apparent viscosity in Pa•s, respectively. The logarithmic relationship between V_E and μ_E is shown graphically in Fig. 1. Figure 2 plots the critical flow rate values from Eq. (3) vs measured values. The line in Fig. 2 represents a theoretical condition in which the predicted values would be equal to the measured values.

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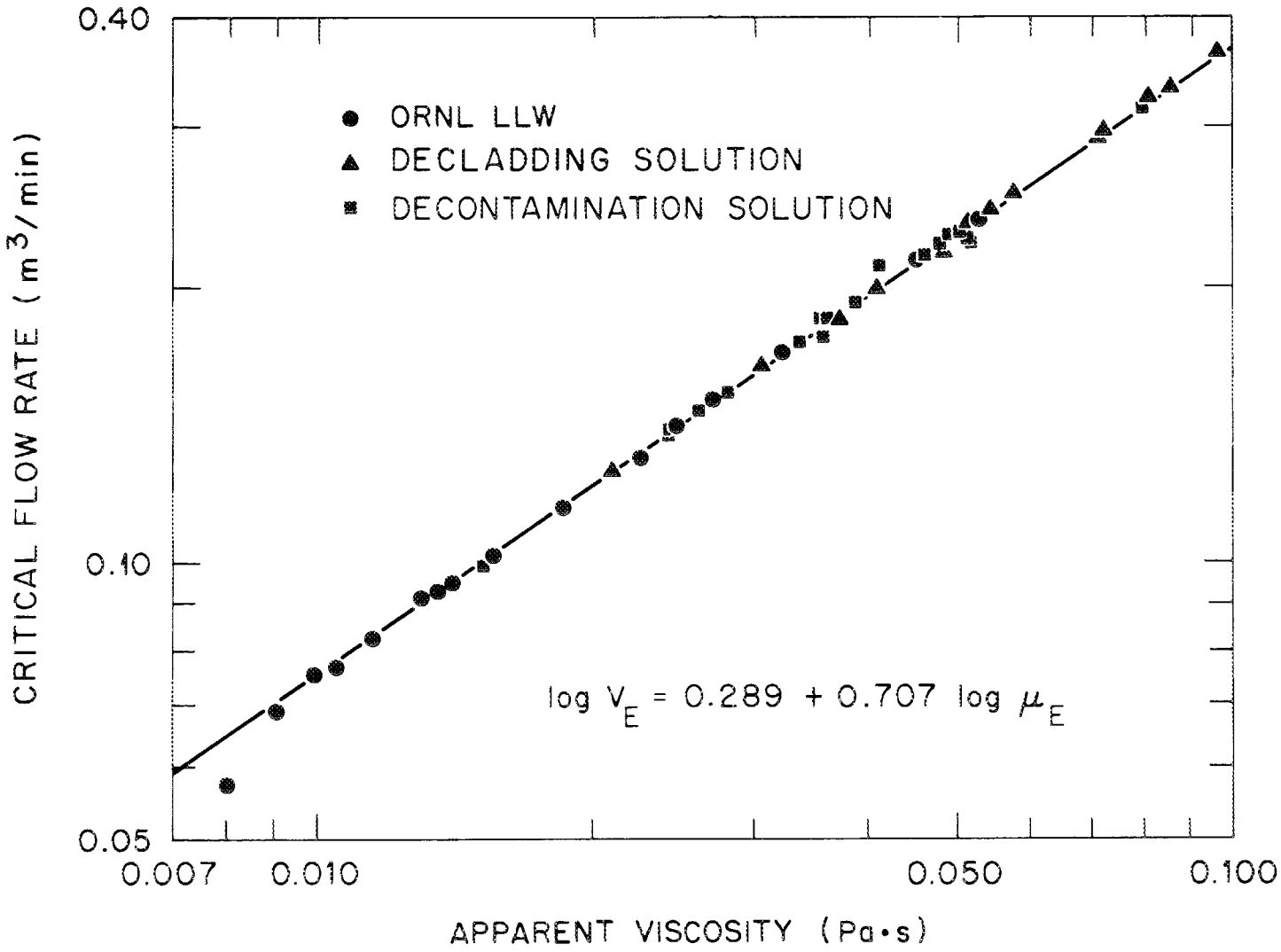

Fig. 1. Critical flow rate as a function of apparent viscosity for grouts prepared from three wastes.

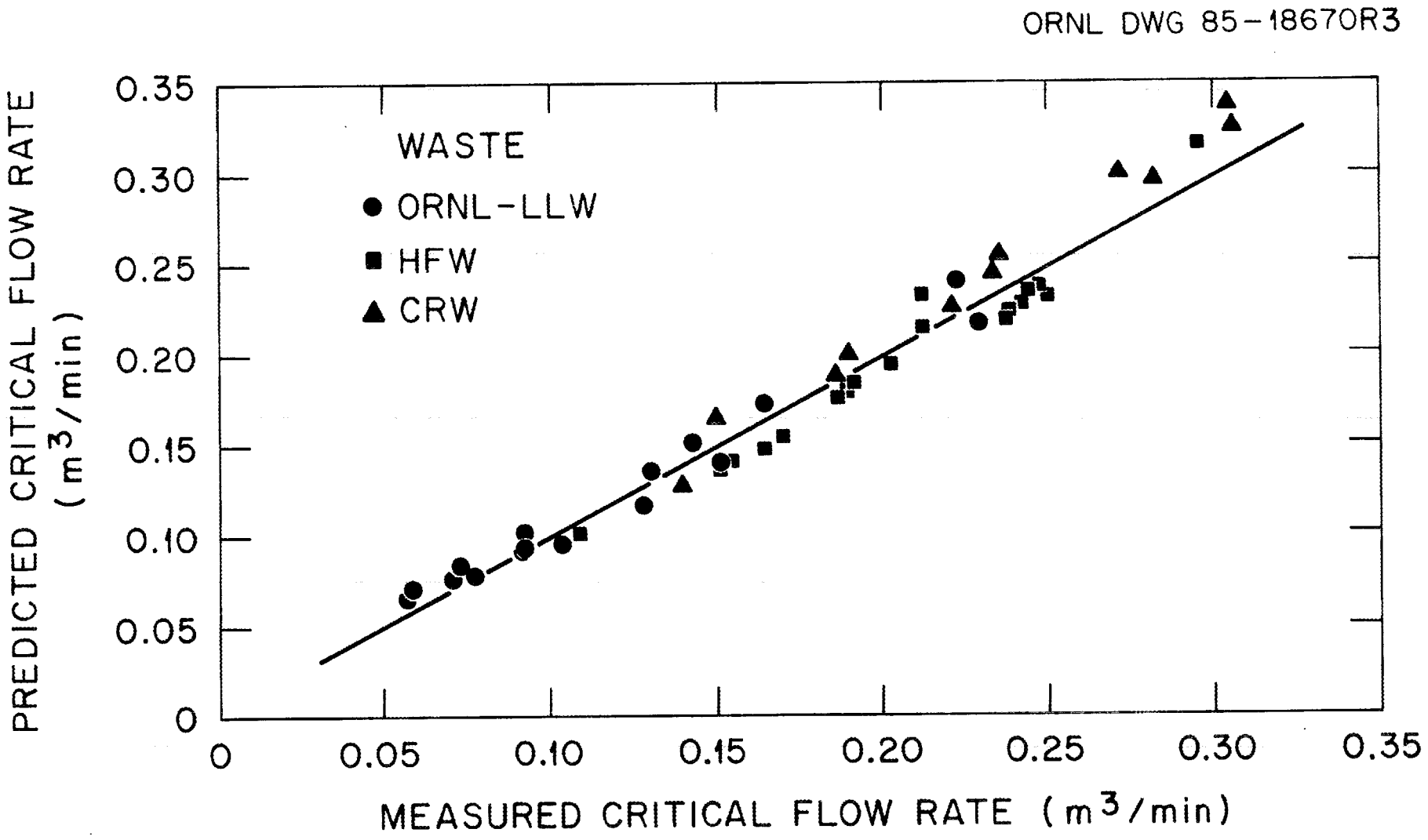

Fig. 2. Predicted vs measured critical flow rates for grouts prepared from three different wastes.

5. THEORETICAL RELATIONSHIP BETWEEN CRITICAL AND APPARENT VISCOSITY

Equations reported previously[1,2] for correlating drainable water, compressive strength, and critical velocity to operator-controllable variables were either empirical or semi-empirical. The apparent viscosity measurements required for use of Eq. (3) (Fig. 1) are not directly operator controllable but are easily made in the laboratory or in the field. In contrast to the previous equations, a partial theoretical basis can be shown for the Eq. (3) relationship. This is demonstrated by starting with two fundamental equations:

$$V^{(2-n')} = \frac{2100\ (96/D_i)^{n'}}{1.86\ \rho}\ , \tag{1}$$

and

$$\mu = 47{,}880K'S_r^{(n'-1)} \tag{4}$$

where V, n', K', D_i, ρ, and S_r have the same designations as previously indicated and μ is the viscosity in cP. Dividing Eq. (1) by Eq. (4) and rearranging terms gives the following expression:

$$V^{(2-n')} = \frac{2100\ (96/D_i)^{n'}}{1.86\ \rho} \cdot \frac{\mu}{47880K'S_r^{(n'-1)}} \tag{5}$$

Within a given family of mixes, the value of ρ (the mix density) changes only a small amount and, for the purposes of this work, may be considered constant at 12 lb/gal. Substituting 2 in. for D_i, 510 s^{-1} for S_r, and 12 lb/gal for ρ yields:

$$V^{(2-n')} = \frac{(1.96 \times 10^{-3})(48)^{n'}(\mu)}{510^{(n'-1)}} \tag{6}$$

When rearranged in logarithmic form, Eq. (6) becomes:

$$\log V = \frac{-1.02n'}{2.00-n'} + \frac{1}{2.00-n'} \log \mu , \qquad (7)$$

where the units for V are ft/s, or

$$\log V_m = -1.43 - \frac{1.02n'}{2.00-n'} + \frac{3.00}{2.00-n'} + \frac{1}{2.00-n'} \log \mu_m \qquad (8)$$

where the units for V_m are m^3/min, and for μ_m are Pa•s.

Terms for both n' and μ_m occur in Eq. (8), while the use of n' in the empirical expression, Eq. (3), was unnecessary. Therefore, the extent to which the variance of n' affects V_m values calculated from Eq. (8) was examined. The frequency distribution of n' values for the 47 grout mixes shown in Fig. 3 (listed in Table 7) reveals that the values range from 0.250 to 0.650, with greater than 89% of the values lying between 0.300 and 0.600. In Fig. 4, the area between the lines represents the maximum variance of V_m for n' values between 0.300 and 0.600 based on Eq. (8). The variance decreases from 0.026 m^3/min (6.8 gal/min) at μ = 0.01 Pa•s to zero at μ_m = 0.09 Pa•s. Figure 4 shows that, while both μ and n' are variables in Eq. (7), variations in n' have a relatively limited effect on the V_m values calculated using the equation and the data obtained in this investigation. It is, thus, not surprising that the V_E and μ_E data correlate well in Eq. 3 (the empirical equation) with n' excluded from the correlation.

6. DISCUSSION

The major purpose of this report and the two previous publications in this series[1,2] is to extend usages of the large quantities of data currently being obtained in grout formulation work. A second purpose is to to provide referenceable reports describing the experimental methods and techniques used in waste grout formulation work. Equation (3) mathematically relates grout apparent viscosity, which is easily measured, to grout critical velocity, a quantity that is considerably more difficult to

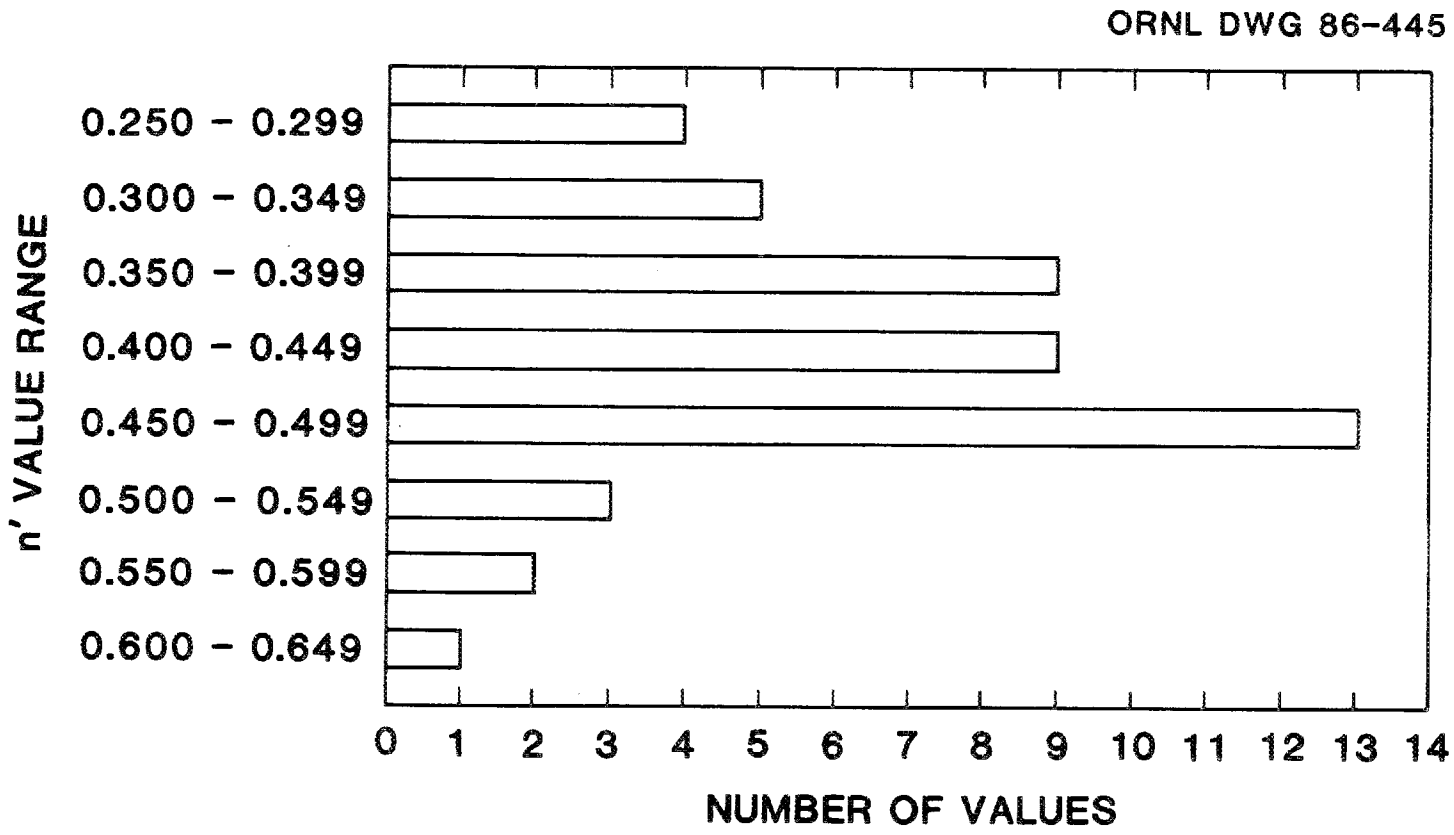

Fig. 3. Frequency distribution of fluid index values, n'.

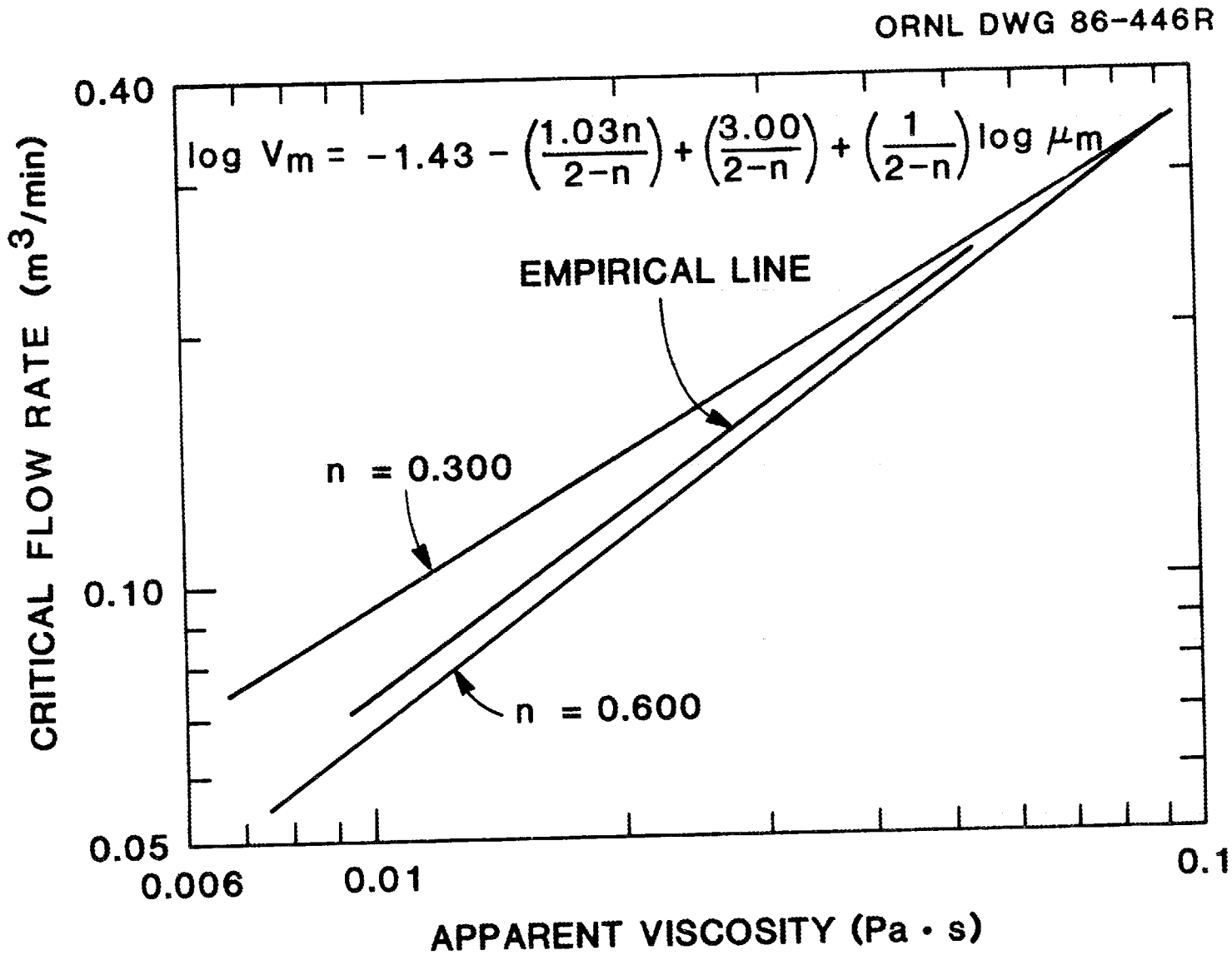

Fig. 4. Effect of varying the fluid behavior index, n', from 0.300 to 0.600 in Eq (8).

measure. As grout formulation work moves from the development stages into applied field applications, it is expected that utilization of such facile measurement methods as the apparent viscosity method will become a necessity. The equations, both in this report and in the previous documents[1,2], are largely empirical; nevertheless, they demonstrate the existence of an inherent and underlying state of order and predictability in mechanisms controlling waste grout formulation. Thus, the credibility and usefulness of grout formulation systems are increased. The utility of the equations is in the prediction of properties within the compositional range of the investigation from which the data were obtained. Such equations provide a relatively simple method that is 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, the equations provide a means of examining suspect data and pinpointing unusual occurences.

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