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Fixation of Waste Materials in Grouts. Part II: An Empirical Equation for Estimating Compressive Strength for Grouts from Different Wastes

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FIXATION OF WASTE MATERIALS IN GROUTS.

PART II: AN EMPIRICAL EQUATION FOR ESTIMATING COMPRESSIVE STRENGTH FOR GROUTS FROM DIFFERENT WASTES

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FIXATION OF WASTE MATERIALS IN GROUTS.
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ABSTRACT

Compressive strength data for grouts prepared from three different nuclear waste materials have been correlated. The wastes include ORNL low-level waste (LLW) solution, Hanford Facility Waste (HFW) solution, and Hanford cladding removal waste (CRW) slurry. Data for the three wastes can be represented with a 0.96 coefficient of correlation by the following equation:

$$S = -9.56 + 9.27\ D/I + 18.11/C + 0.010\ R\ , \qquad (1)$$

where S denotes 28-d compressive strength, in mPa; D designates waste concentration, fraction of the original; I is ionic strength; C denotes Attapulgite-150 clay content of dry blend, in wt %; and R is the mix ratio, in kg/m^3. The equation may be used to estimate 28-d compressive strengths of grouts prepared within the compositional range of this investigation.

1. INTRODUCTION

Waste disposal is rapidly becoming one of the most important technologies of our time, and fixation of waste in cement-based materials is certainly an important part of the endeavor. Precise mechanisms by which waste is fixed in cement-based materials remain largely unknown despite widespread application of this waste disposal method. In the present state of development, many wastes can adequately be incorporated in concretes, but large numbers of scouting tests must be conducted on each individual waste to determine whether the final product will meet specification demands. The purpose of the statistical analysis reported here is to use data obtained in these tests to produce empirical equations that

correlate processing variables to the performance characteristics of the final product. Several of the important variables and tests used in waste-grout systems are described in Part I of this report.[1] Operator-controlled variables include the physical and chemical forms of the wastes, the dry blend composition, and the blend-waste mix ratio. Dependent-variable values were determined by various types of tests, including 28-d compressive strength, free water, and rheological properties. In the earlier report,[1] empirical equations were presented to relate variables for grouts prepared from ORNL LLW. This report broadens the scope of the previous work by correlating 28-d compressive strength data for grouts prepared from three different waste forms: (1) ORNL LLW, (2) HFW, and (3) CRW from Rockwell Hanford Operations. The rationale for using the various components in the dry-solid blends was presented in Part I.[1]

2. WASTE COMPOSITIONS AND DRY-SOLID BLENDS

Table 1 shows the composition of the simulated ORNL LLW. Each of the dry-solid blends listed in Table 2 was mixed with this waste at ratios of 720, 840, 960, and 1080 kg/m^3. Table 1 shows that this waste is characterized by the presence of NO_3^-, Cl^-, and CO_3^{2-} anions and NaOH. The ionic strength of the waste was calculated to be 1.93, assuming complete ionization of the ionic species.

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 these dilutions, along with the undiluted solution, at ratios of 720, 840, and 960 kg/m^3. Table 3 reveals that this waste is characterized by the presence of PO_4^{3-}, HPO_4^{2-}, SO_4^{2-}, and NO_2^- anions, as well as NaOH. The ionic strength of the waste (before dilution) was calculated to be 3.60.

Major components in the neutralized CRW from Rockwell Hanford Operations are listed in Table 5. This waste is a slurry containing

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
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, WA, 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)
$ZrO_2 \cdot xH_2O$	1.03
NaF	2.27
$NaNO_3$	0.05
NaOH	0.91
NH_3	0.83
Sn	Trace
U	<0.01

~30 wt % solids, primarily $ZnO_2 \cdot xH_2O$. 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. Each of the dry blends shown in Table 6 was mixed with these dilutions, along with the undiluted solution, at ratios of 720 and 840 kg/m^3. As Table 5 reveals, this waste 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. The ionic strength of the undiluted waste was calculated to be 4.50.

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

Material	Blend 9 (wt %)	Blend 10 (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 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 specimens for the tests were prepared by pouring freshly prepared grouts into 2-in.^{3} stainless molds and allowing the molds to stand 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. American Society for Testing and Materials (ASTM) procedures were used for reference.[2,3,4]

4. CORRELATION OF DATA

The statistical correlation included 50 data points: 16 from ORNL LLW, 22 from HFW; and 12 from CRW. The data were correlated by multilinear regression analyses. The data can be represented with a 0.96 coefficient of correlation by the following equation:

$$S = -9.56 + 9.27\ D/I + 18.11/C + 0.010\ R, \qquad (1)$$

where S denotes compressive strength, in MPa; D designates waste concentration, fraction of original; I is ionic strength; C denotes the Attapulgite-150 clay content of the dry solid blend, in wt %; and R is the mix ratio, in kg/m^3. The 0.96 coefficient of correlation is good, considering the number and nature of the variables. The compressive strength values predicted from Eq. (1) are listed in Table 7, along with the measured values. The predicted values are plotted vs the measured values in Fig. 1. The unbroken line in the figure represents a theoretical condition where the predicted values would be equal to the measured values. The broken lines are drawn to be $\pm$100 psig, or $\pm$0.689 MPa, from the theoretical condition line.

The 0.96 coefficient of correlation for Eq. (1) was essentially unchanged when data for the cement and fly ash (Table 7) in the dry-solid blends were included. Inclusion of the cement and fly ash data and deletion of the Attapulgite-150 clay data decreased the coefficient of the correlation to 0.91.

5. DISCUSSION

The compressive strength test is only one of many tests routinely conducted during waste-grout formulation studies; however, it is an important one and is conducted in almost all waste-grout formulation studies. Frequently, a compressive strength of 0.445 MPa (50 psi) is considered acceptable, although it has recently been suggested that the acceptable value for ORNL hydrofracture be increased to ~2.85 MPa (400 psi). The empirical relationship shown in Eq. (1) can be used to estimate 28-d compressive strengths of waste grouts based on operator-controlled variables within the compositional range of this investigation. This range includes three distinctly different waste solutions (Tables 1, 3, and 5), with blends having Attapulgite-150 clay contents of 5, 10, 11, 12, 14, 16, 18, and 20 wt % and mix ratios of 720, 840, 960, and 1080 kg/m^3. Equation (1) should be useful to optimize conditions within this operational range and to help set conditions for future investigations. The equation, although empirical, demonstrates an inherent systematics that, if found demonstrable for other waste-grout variable relationships, should add immeasurably to the credibility and usefulness of waste-grout systems.

Table 7. Compressive strength (28-d) as a function of important variables in waste grout formulation

Observation No.	Waste	Waste fraction conc.	Attapulgite-150 clay in blend (wt %)	Portland cement in blend (wt %)	Fly ash in blend (wt %)	Mix ratio (kg/m^3)	Compressive strength (MPa)	
							Predicted	Measured
1	ORNL	1.00	14	42	36	720	3.68	3.68
2	ORNL	1.00	14	42	36	840	4.82	4.85
3	ORNL	1.00	14	42	36	960	6.05	6.34
4	ORNL	1.00	14	42	36	1080	7.25	8.15
5	ORNL	1.00	16	42	34	720	3.49	3.32
6	ORNL	1.00	16	42	34	840	4.69	4.85
7	ORNL	1.00	16	42	34	960	5.89	6.76
8	ORNL	1.00	16	42	34	1080	7.09	6.94
9	ORNL	1.00	18	42	32	720	3.36	3.23
10	ORNL	1.00	18	42	32	840	4.57	3.98
11	ORNL	1.00	18	42	32	960	5.77	5.43
12	ORNL	1.00	18	42	32	1080	6.97	6.91
13	ORNL	1.00	20	42	30	720	3.26	3.35
14	ORNL	1.00	20	42	30	840	4.46	3.94
15	ORNL	1.00	20	42	30	960	5.67	5.38
16	ORNL	1.00	20	42	30	1080	6.87	6.95
17	HFW	0.80	10	41	41	840	2.62	2.45
18	HFW	0.67	10	41	41	840	2.29	2.06
19	HFW	0.50	10	41	41	840	1.85	1.52
20	HFW	1.00	10	41	41	960	4.34	4.11
21	HFW	0.67	10	41	41	960	3.49	2.90
22	HFW	0.50	10	41	41	960	3.05	2.22
23	HFW	1.00	14	39	39	840	3.62	3.06
24	HFW	0.80	14	39	39	840	2.11	2.84
25	HFW	0.67	14	39	39	840	1.77	2.25

Table 7 (continued)

Observation No.	Waste	Waste fraction conc.	Attapulgite-150 clay in blend (wt %)	Portland cement in blend (wt %)	Fly ash in blend (wt %)	Mix ratio (kg/m^3)	Compressive strength (MPa)	
							Predicted	Measured
26	HFW	0.50	14	39	39	840	1.44	1.34
27	HFW	1.00	12	40	40	960	4.50	4.04
28	HFW	0.80	12	40	40	960	3.17	3.53
29	HFW	0.50	12	40	40	960	2.06	2.75
30	HFW	1.00	11	41	40	720	1.93	1.78
31	HFW	1.00	11	41	40	840	2.93	2.98
32	HFW	1.00	11	41	40	960	3.87	4.18
33	HFW	0.80	11	41	40	720	2.01	1.26
34	HFW	0.80	11	41	40	840	2.58	2.46
35	HFW	0.80	11	41	41	960	3.78	3.66
36	HFW	1.00	10	41	41	840	3.14	2.30
37	HFW	0.80	10	41	41	960	3.83	4.49
38	CRW	0.67	12	41	40	960	3.34	3.19
39	CRW	0.67	5	41	40	840	3.76	3.76
40	CRW	0.50	5	42	42	840	3.41	3.59
41	CRW	0.30	5	42	42	840	2.99	3.13
42	CRW	0.50	5	42	44	720	2.21	2.38
43	CRW	0.30	5	42	42	720	1.79	2.07
44	CRW	0.80	5	60	19	720	2.82	2.07
45	CRW	0.67	5	60	19	720	2.56	2.09
46	CRW	0.50	5	60	19	720	2.21	2.09
47	CRW	0.30	5	60	19	720	1.79	2.40
48	CRW	0.67	5	60	19	840	3.76	3.36
49	CRW	0.50	5	60	19	840	3.41	3.57
50	CRW	0.30	5	60	19	840	3.00	3.48

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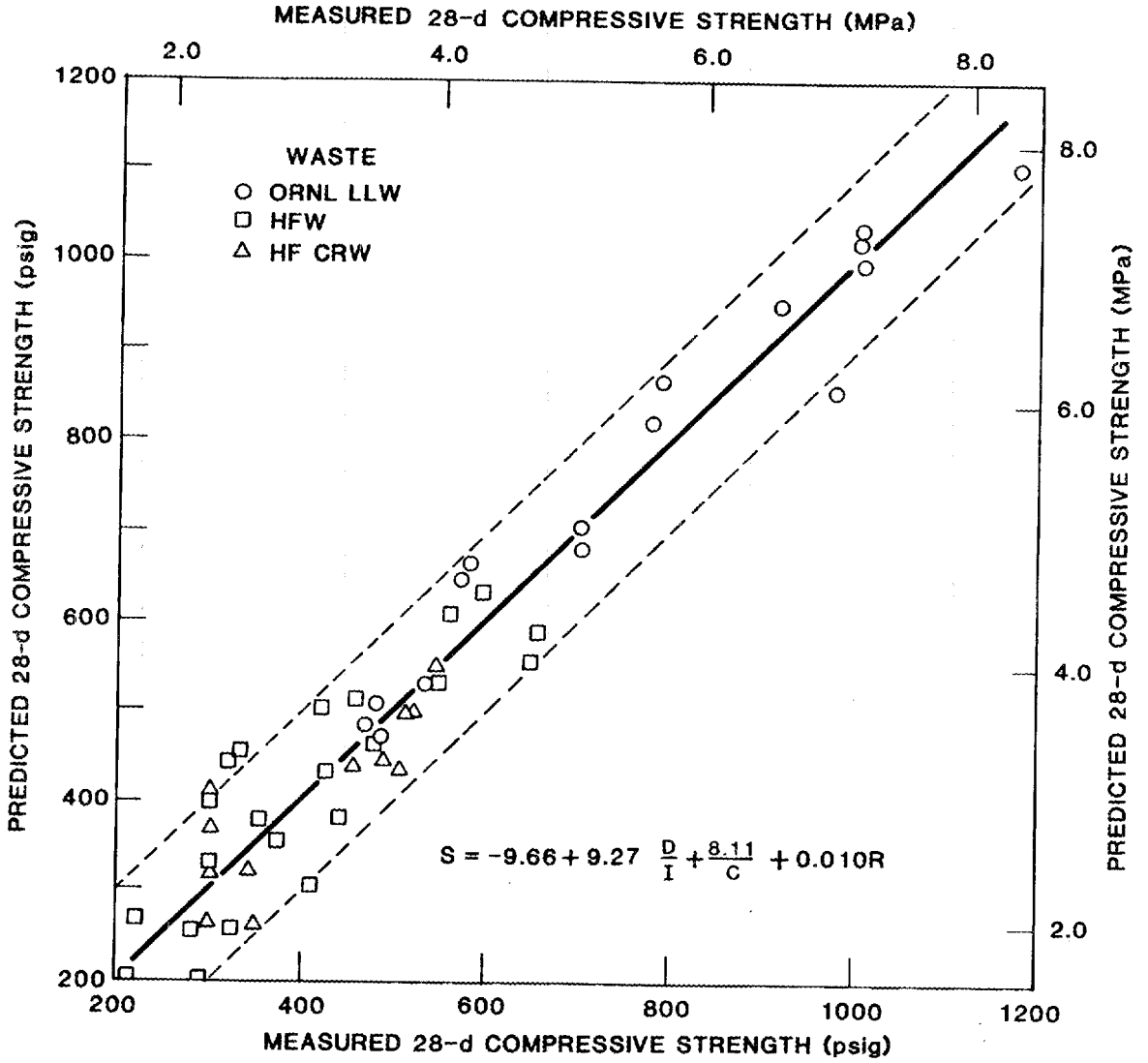

Fig. 1. Plot of compressive strength predicted from Eq. (1) vs measured compressive strength.

A detailed discussion of chemical and/or physical mechanisms by which the compressive strength of the grouts might be decreased by the presence of the Attapulgite-150 clay is beyond the scope of this report. Because Eq. (1) is empirical, the relationship between the compressive strength and the clay may be indirect and obscure. One possible explanation might be that it is not the clay but, rather, the increased retention of water by the clay in the grout which produces the decrease in compressive strength.

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