Formulation Verification Study Results for Tank 106-AN Waste

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December 1992

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

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SUMMARY

Because of the excessive heat generated during hydration of double-shell tank waste grouts using a formulation that consisted of 47 wt% blast furnace slag, 47 wt% class F fly ash, and 6 wt% type I/II Portland cement, a modified formulation was recommended for testing of Tank 106-AN grout. The recommended dry blend proportions are shown below:

Agricultural Grade CaCO_3 (ground limestone)	40 wt%
Blast Furnace Slag	28 wt%
Fly Ash, ASTM Class F	28 wt%
Cement, Type I-II	4 wt%

Verification studies were conducted with the recommended dry blend and simulated Tank 106-AN waste to determine compliance with selected formulation criteria. The only criterion not met in all cases was for drainable liquid. The specific criteria and the acceptable and measured values are summarized below:

<u>Criterion</u>	<u>Acceptable Value</u>	<u>Result</u>
Critical Flow Rate, gpm	≤ 60	7.9 - 9.4
10-min Gel Strength, $\text{lb}_f/100\text{ft}^2$	≤ 100	5.0 - 6.5
28-d Drainable Liquids, vol%	≤ 3	2.5 - 5.2
Maximum Hydration Temperature, $^{\circ}\text{C}$	≤ 90	$\Delta T < 45$ (~500 hr)
Thermal Conductivity, $\text{BTU/hr/ft/}^{\circ}\text{F}$	≥ 0.45	0.53 ± 0.03
Compressive Strength, psi	≥ 50	440 ± 53
NO_3 and NO_2 Leachability Index	≥ 7	7.4 - 7.7

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INTRODUCTION

Most of the development and testing of double-shell tank (DST) waste grout has been conducted with a dry blend consisting of 47 wt% blast furnace slag, 47 wt% class F fly ash, and 6 wt% type I/II Portland cement (hereafter referred to as 47/47/6). The dry blend was mixed with simulated double-shell slurry feed (DSSF) waste at a mix ratio of 9 lb/gal. The resulting grout slurry met all processing criteria, and the cured grout surpassed most performance criteria. However, the adiabatic temperature rise due to hydration resulted in a grout temperature that exceeded the 90°C design limit. In an attempt to decrease the temperature rise, alumina powder, clinoptilolite, and ground limestone were added to the dry blend to decrease the amount of reactive solids. Replacement levels ranged from 30 wt% to 60 wt% in the dry blend. The measured adiabatic temperature rise of a grout prepared with simulated DSSF and a dry blend with 40 wt% ground limestone was less than 45°C. Based on this result, a reference dry blend for DST waste grouts was designated as 40 wt% ground limestone, 28 wt% blast furnace slag, 28 wt% class F fly ash, and 4 wt% type I/II Portland cement.

The addition of ground limestone to the dry blend reduces the total amount of reactive solids in the formulation, thereby decreasing the temperature rise due to hydration. Tests were conducted to determine the adequacy of this formulation for use with Tank 106-AN waste. Specific tests included adiabatic calorimetry, thermal conductivity, specific heat, rheology, compressive strength, leachability, and drainable liquid determinations. Results were compared with specific formulation criteria to determine whether the modified dry blend would produce grouts with acceptable properties.

The specific criteria included the following:

- 1) Critical flow rate ≤ 60 gpm,
- 2) Ten-minute gel strength ≤ 100 lb_f/100ft²,
- 3) 28-day drainable liquids ≤ 3 vol%,
- 4) Maximum grout temperature due to hydration $\leq 90^{\circ}\text{C}$,
- 5) Thermal conductivity ≥ 0.45 BTU/hr/ft/ $^{\circ}\text{F}$,
- 6) Unconfined compressive strength ≥ 50 psi, and
- 7) ANS 16.1 Leachability Index ≥ 7 for NO_3 and NO_2 .

GROUT PREPARATION

The dry blend, with the proportions listed above, was mixed in a V-blender for 23 hours. Simulated Tank 106-AN waste (Table 1) was heated to approximately 50°C and added to a Hobart mixer bowl. The dry blend (at a ratio of 9 lb/gal) was added while the mixer was operating at low speed. The resultant slurry was mixed for a total of 30 seconds on low speed and an additional 30 seconds on medium speed. Approximately 500 ml of grout slurry was poured into a stainless steel Dewar for calorimeter testing. Samples were also taken for rheology, density, and drainable liquid measurements and for 28-day compressive strength and leachability tests. These samples were cured at 50°C until they were tested.

RESULTS

Results for density, drainable liquids, and rheological measurements for duplicate mixes are listed in Table 2. The slurries were very "thin," as indicated by the low critical flow rates. The measured critical flow rates are well below the upper limit of 60 gpm. Ten-minute gel strengths were also very low. One of the samples met the drainable liquid criterion of ≤ 3 vol% after 28 days, while the amount of liquid present on the other was 5.2 vol%. By comparison, after 40 days of curing actual Tank 106-AN waste grout prepared with the 47/47/6 blend, the amount of drainable liquid was about 7 vol% (Serne et al. 1989). Curing temperature has a great effect on the amount of drainable liquids. One sample prepared and

TABLE 1. Composition of Simulated Tank 106-AN Waste

<u>Compound</u>	<u>Moles/Liter</u>
NaAl(OH) ₄	0.421
Na ₂ SO ₄	0.031
NaCl	0.15
NaF	0.0081
Na ₃ PO ₄ ·12H ₂ O	0.155
Ca(NO ₃) ₂ ·4H ₂ O	0.002
Na ₂ B ₄ O ₇ ·10H ₂ O	0.0005
Cu(NO ₃) ₂ ·3H ₂ O	0.00004
Fe(NO ₃) ₃ ·9H ₂ O	0.0002
NaOH	0.675
NaNO ₃	1.29
NaNO ₂	0.758
Na ₂ CO ₃	0.382
HEDTA	0.019
Na ₄ EDTA	0.0044
Na ₃ Citrate·2H ₂ O	0.03
Glycolic Acid	0.042
SiO ₂ (Ludox) (30%)	0.0002
Na ₂ CrO ₄ ·4H ₂ O	0.012
AgNO ₃	0.000051
BaNO ₃	0.0008
Cd(NO ₂) ₂ ·4H ₂ O	0.0000098
Ni(NO ₃) ₂ ·6H ₂ O	0.001
Pb(NO ₃) ₂	0.000027
As (10,000 µg/ml)	0.000037
Se (10,000 µg/ml)	0.000014
Hg (10,000 µg/ml)	0.0000011

cured at room temperature had over 18 vol% drainable liquid. Oak Ridge National Laboratory (ORNL) has also shown the effect of curing temperature on drainable liquids. Tallent et al. (1988)¹ report

¹ Tallent, O. K., E. W. McDaniel, G. D. Del Cul, K. E. Dodson, and D. R. Trotter. 1988. Formulation Verification Studies for 106-AN and 101-AW Wastes, ORNL Milestone Report, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

drainable liquid values of 11.6 vol% at 35°C and 0 vol% at 60°C. These results were from Tank 106-AN grouts prepared at 8 lb/gal with the 47/47/6 blend. The amount of drainable liquids could be reduced or eliminated by either increasing the reaction rates or by increasing the slurry viscosity. Reaction rates may be increased by replacing the cement with hydrated lime, adding set accelerators, or by increasing the initial temperature. Each of these may have deleterious effects on other properties, however. Adding hydrated lime may result in 10-minute gel strengths that exceed the 100 lbf/100ft² limit. Increasing the initial temperature sufficiently to eliminate drainables may cause the temperature due to hydration to exceed 90°C. Attapulgate clay may also be added to increase the viscosity of the grout slurry and prevent significant particle settling.

Adiabatic calorimetry was conducted to determine the temperature rise of the grout during hydration. The calorimeter test was conducted for up to 20 days. Figure 1 shows the average temperature of two grout samples as a function of curing time. The temperature rise for these samples ranged from 38 to 43°C after curing 15 and 20 days, respectively. The upper value is near the limit of 45°C, which is based on a 45°C starting temperature and a maximum grout temperature of 90°C. As shown by the curves in Figure 1, the temperature of the grouts is still increasing. During post-run thermocouple calibration checks, small temperature differences were observed between the bath and the grout (i.e., the bath was slightly warmer than the grout). Correcting the measured grout temperature for this difference results in the lower curve in the figure. Determining the best estimate for the true adiabatic temperature rise requires another correction for heat loss to the inner Dewar walls and stopper. The results of this correction are shown by the middle curve in Figure 1.

Results of tests for compressive strength, bulk density, thermal conductivity, and specific heat are shown in Table 3. The compressive strengths exceed the 50 psi criterion and the average

thermal conductivity is greater than the criterion of 0.78 W/mK (0.45 BTU/hr/ft/°F). There are no specific criteria for density or specific heat.

ANS 16.1 leach tests were conducted on four samples of simulated Tank 106-AN grout prepared with the modified formulation. The average leachability indices for sodium, chloride, nitrite, nitrate, and sulfate are listed in Table 4. The values are compared with those obtained with actual Tank 106-AN waste using the earlier dry blend (Serne et al. 1989) and with data from ORNL (Tallent et al. 1988)¹.

TABLE 2. Critical Flow Rate, Drainable Liquid, and Density Results for Tank 106-AN Grouts Prepared with Modified Dry Blend Formulation at a Mix Ratio of 9 lb/gal

Property	Mix Number	
	M106-1	M106-2
Critical Flow Rate, gpm	9.4	7.9
10-min Gel Strength lb _f /100ft ²	5.0	6.5
28-day Drainable Liquid, vol%	5.2	2.5
Density, lb/gal	13.7	13.8

¹ Tallent, O. K., E. W. McDaniel, G. D. Del Cul, K. E. Dodson, and D. R. Trotter. 1988. Formulation Verification Studies for 106-AN and 101-AW Wastes, ORNL Milestone Report, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

TABLE 3. Properties of Tank 106-AN Grouts Prepared with Modified Dry Blend Formulation at a Mix Ratio of 9 lb/gal

Property	Average	S.D. (a)	No. Samples
Compressive Strength, psi	440	53	4
Bulk Density, g/cm ³	1.67	0.01	4
Evaporable Water, wt%	36.0	0.6	4
Specific Heat cal/g/°C	0.49	0.01	4
Thermal Conductivity, W/mK	0.92	0.05	14(b)

(a) S.D. = one standard deviation from the average

(b) Number of measurements taken on same sample

TABLE 4. Average Leachability Index Through 28 Days of ANS 16.1 Leach Tests (ANS 1986) for 106-AN Grouts^(a)

Sample No.	Average Leachability Index				
	Na	Cl	NO ₂	NO ₃	SO ₄
1	7.9 ± 0.2	7.5 ± 0.2	7.6 ± 0.2	7.6 ± 0.2	8.1 ± 0.2
2	7.8 ± 0.2	7.4 ± 0.2	7.5 ± 0.2	7.5 ± 0.2	8.1 ± 0.2
3	7.9 ± 0.2	7.5 ± 0.2	7.6 ± 0.2	7.7 ± 0.2	8.2 ± 0.2
4	7.7 ± 0.1	7.3 ± 0.2	7.4 ± 0.2	7.5 ± 0.2	8.0 ± 0.1
PNL ^(b,d)	9.0 ± 0.1	7.6 ± 0.1	7.9 ± 0.1	8.0 ± 0.0	-----
ORNL ^(c,d)	-----	7.7 ± 0.2	8.0 ± 0.1	8.0 ± 0.1	-----

(a) Dry blend consisted of 40 wt% limestone, 28 wt% slag, 28 wt% fly ash and 4 wt% cement

(b) Data from Serne et al. (1989)

(c) Data from Tallent et al. (1988)¹

(d) Dry blend consisted of 47 wt% slag, 47 wt% fly ash and 6 wt% cement

¹ Tallent, O. K., E. W. McDaniel, G. D. Del Cul, K. E. Dodson, and D. R. Trotter. 1988. Formulation Verification Studies for 106-AN and 101-AW Wastes. ORNL Milestone Report, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

FIGURE 1. Adiabatic Temperature Rise for Simulated Tank 106-AN Grouts Prepared at 9 lb/gal with a Dry Blend of 40 wt% Limestone, 28 wt% Blast Furnace Slag, 28 wt% Class F Fly Ash, and 4 wt% Type I/II Portland Cement

CONCLUSIONS

A series of tests have been conducted to determine the adequacy of a modified dry blend for producing acceptable grouts with tank 106-AN waste. The results of these tests indicate that the only criterion that was not met in all cases was for drainable liquids. One grout tested had 5.2 vol% drainable liquids after 28 days, with an allowable value of 3 vol%. All other tests resulted in acceptable results. The specific criteria and the acceptable and measured values are summarized below:

<u>Parameter</u>	<u>Acceptable Value</u>	<u>Result</u>
Critical Flow Rate, gpm	≤ 60	7.9 - 9.4
10-min Gel Strength, $\text{lb}_f/100\text{ft}^2$	≤ 100	5.0 - 6.5
28-d Drainable Liquids, vol%	≤ 3	2.5 - 5.2
Hydration Temperature, °C	≤ 90	$\Delta T < 45$ (~500 hr)
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Compressive Strength, psi	≥ 50	440 ± 53
NO_3 and NO_2 Leachability Index	≥ 7	7.4 - 7.7

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