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FORMULATION VERIFICATION STUDY RESULTS FOR
241-AN-106 WASTE GROUT

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SUMMARY

Tests were conducted to determine whether the reference formulation and variations around the formulation are adequate for solidifying 241-AN-106 (106-AN) waste into a grout waste form. The reference formulation consists of 21 wt% type I/II Portland cement, 68 wt% fly ash, and 11 wt% attapulgite clay. The mix ratio is 8.4 lb/gal. Variations in dry blend component ratios, mix ratio, and waste concentration were assessed by using a statistically designed experimental matrix consisting of 44 grout compositions.

Grouts were also prepared with dry blends that contained attapulgite clay from two sources, Engelhard and Floridin. Attapulgite from Engelhard has been used in all laboratory studies, while attapulgite clay from Floridin was used in a recent pilot-scale test. The critical flow rates of grouts made with dry blend containing Floridin attapulgite were lower than those of grouts made with attapulgite from Engelhard. Grouts made with dry blends that had been stored for up to six weeks had critical flow rates that were slightly lower than grouts made with materials blended the same day as grout preparation; however, all grouts met the critical flow rate and drainable liquid criteria.

Compressive strength tests were conducted on 44 grout samples from the statistically designed matrix that were immersed for >90 days in deionized water. The post-immersion mean compressive strength was 1301 psi, which was 3.7% greater than the mean strength of the as-cured specimens.

After irradiating nine specimens to a total dose of $\sim 10^8$ rads, the compressive strengths were approximately 82 to 90% of the control specimens, indicating that irradiation had a measurable effect on the compressive strength of the 106-AN grouts. The strengths after irradiation, however, were greater than the 500 psi criterion.

Three 106-AN grout samples spiked with high levels of As, Ba, Cd, Cr, Pb, Ag, and Se were tested using the Toxicity Characteristic Leaching Procedure. The concentrations of all the heavy metals in the extract were below regulatory levels.

Three reference 106-AN grout specimens were subjected to the State of Washington Department of Ecology corrosivity test for solid materials. The average pH of the solutions was 11.6, which indicates that the grout is not considered corrosive because the pH was less than 12.5.

The thermal conductivity of a reference 106-AN grout sample averaged 0.47 BTU/h·ft·°F, which is greater than the minimum criteria of 0.45 BTU/h·ft·°F.

During curing, 106-AN grout samples exhibited an average linear shrinkage of 1.3 vol% due to settling of the solids before curing. Shrinkage beyond 28 days was not statistically significant. There was no evidence of radial shrinkage.

The effect of starting waste temperature on the adiabatic temperature rise was determined by preparing grouts with waste heated from 35°C to 55°C. Increased starting waste temperature resulted in higher reaction-rate peaks, with the peaks occurring at shorter times. The measured temperature rise exceeded 90°C for those grouts prepared with starting waste temperatures above 45°C.

Based on the results of the statistically designed variability study, the 106-AN grout formulations tested met all the formulation criteria except for the heat of hydration.

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INTRODUCTION

Current plans for disposal of the low-level fraction of selected double-shell tank (DST) wastes at the Hanford site include grouting. Grout disposal in this context is the process of mixing low-level liquid waste with cementitious powders, and pumping the resultant slurry to near-surface, underground concrete vaults. Once the slurry is in the vaults, the hydration reactions that occur result in the formation of a solid product of low permeability that binds and encapsulates the radioactive and hazardous constituents.

Cementitious materials have been or will be used at many places for the solidification and disposal of low-level radioactive wastes. Oak Ridge National Laboratory (ORNL) began disposing of low-level liquid wastes in 1966 using a process known as hydraulic fracturing (de Laguna 1966, Weeren 1976). This process involved mixing liquid wastes with a blend of cement, fly ash, pottery clay, and attapulgite clay, and pumping the slurry at 3000 to 5000 psi into shale formations underlying the ORNL site. The high pressures caused the shale to fracture, and the grout filled the resultant fissures. The Savannah River Plant (SRP) is planning to dispose of 400 million liters of a low-level salt solution using the "saltstone" process (Langton 1988, Wilhite et al. 1988). Saltstone is the name given to the product prepared by mixing the salt solution with a blend of fly ash, blast furnace slag, and cement. This process is very similar to the grouting process at Hanford (Guymon et al. 1988). At both sites, the major constituents in the waste solutions are the same (i.e., NaNO_3 , NaNO_2 , NaAl(OH)_4 and NaOH).

Westinghouse Hanford Company operates the Grout Treatment Facility (GTF) for the U. S. Department of Energy (DOE). The GTF includes the Dry Materials Facility (DMF), the Transportable Grout Equipment (TGE), and the grout disposal vaults. The DMF receives, stores, batches, and blends the individual dry materials for use in the grouting operation. The blended solids are transported to the site of the TGE where they are mixed with the liquid waste in a semi-continuous process at rates up to 70 gallons of grout per minute. The grout slurry is pumped to underground concrete vaults where it hardens and immobilizes the hazardous and radioactive constituents through chemical reactions and/or microencapsulation.

In July 1989, a Grout Disposal Program milestone was achieved with the production of over one million gallons of Phosphate/Sulfate Waste (PSW) grout. The phosphate waste originated from a commercial phosphoric-acid-based cleaning solution that was used in decontamination operations at the N Reactor. The remainder of the waste was generated during maintenance of the fuel storage basin, and consisted of a waste from the regeneration of ion-exchange resins with sulfuric acid, and sandfilter backwash. Details of the PSW campaign are reported in Cline et al. (1989).

Pacific Northwest Laboratory (PNL)^(a) sampled and tested the grout produced during the second half of the PSW campaign to support quality verification activities prior to grout vault closure. Samples of grout were obtained by inserting nested-tube samplers into the grout slurry in the vault. After the grout had cured, the inner tube of the sampler was removed and the grout samples extracted. Tests for compressive strength, sonic velocity, and leach testing were used to assess grout quality. Results of these tests were compared to results obtained from pilot-scale test grouts made with a simulated PSW (Martin and Lokken 1992). During 1991, five cores were obtained from the PSW grout vault. Testing and characterization results from the core samples are reported by Martin and Lokken (1993).

Grout formulations for subsequent double-shell tank wastes are being developed to meet criteria based on process, product, and disposal system requirements. The next waste that is scheduled to be disposed via grouting is from Tank 241-AN-106 (hereafter referred to as 106-AN). This waste will be transferred into a waste feed tank (Tank 241-AP-102) where it will be blended with the remaining contents of the feed tank.

Grout formulations must be developed that can be pumped in turbulent flow through 2-in.-diameter pipe using existing equipment. They must solidify into a solid with acceptable compressive strength, leach resistance, and other properties. The amount of drainable liquids must not be excessive. The maximum temperature within the vault must be less than 90°C. Previous studies

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RL0 1830.

have shown that other formulations tested for 106-AN waste grouts did not meet all applicable criteria (Lokken 1992a and 1992b). It was determined that the adiabatic temperature rise of 106-AN grouts made at 9 lb/gal with a dry blend nominally consisting of 40 wt% limestone flour, 28 wt% ground blast furnace slag, 28 wt% class F fly ash, and 4 wt% type I/II Portland cement exceeded the 90°C temperature limit (Lokken 1992b). Because of these high temperatures, the leach resistance and compressive strengths were lower than desired. Therefore, statistically designed experiments were conducted at ORNL and PNL using dry blend composition and mix ratio as variables to identify grout formulations for 106-AN waste. The individual dry materials included type I/II Portland cement, attapulgitic clay, class F fly ash, and a ground, air-cooled blast furnace slag. Based on the results of these studies, a reference grout formulation was selected for further testing to confirm that it will meet criteria defined in Riebling and Fadeff (1991). Pacific Northwest Laboratory recently conducted a pilot-scale test and laboratory studies on the reference formulation. Before routine operation begins, Westinghouse Hanford Company will conduct tests with samples obtained from the feed tank in their 222-S laboratory.

In the formulation development activity, ORNL measured density, critical flow rate, 10-min. gel strength, drainable liquids, NO₃/NO₂ leachability index, and compressive strength^(a). PNL measured the adiabatic temperature rise of the various grouts. After all data from the mixtures studies were collected, empirical modeling was conducted to provide a means for predicting the properties of grouts with any dry blend composition and mix ratio within the experimental range tested. "Optimum" grout formulations were estimated by modeling hundreds of combinations of dry blend ratios and mix ratios and eliminating those that had compressive strengths less than 500 psi, NO₃/NO₂ leach indices less than 6, drainable liquids greater than 3 vol%, and critical flow rates greater than 50 gpm. Adiabatic temperature rise was not used as a basis in the elimination process because nearly all the formulations that

(a) Spence, R. D., E. W. McDaniel, C. M. Anderson, R. O. Lokken and G. F. Piepel. 1992. Development of Grout Formulations for 106-AN: Mixtures Experiment Results and Analysis. Draft Letter Report. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

would result in a maximum grout temperature less than 90°C did not meet the compressive strength and leachability criteria. Furthermore, a decision was made to implement a staged pouring schedule to allow for grout cooling. Following the modeling exercise, two formulations were selected for further evaluation:

	Type I/II Portland Cement, wt%	Class F Fly Ash wt%	Attapulgate wt%	Mix Ratio lb/gal
Formulation 1	38	55	7	8.9
Formulation 2	20	66	14	8.7

Because of the high isothermal curing temperature used at ORNL (i.e. 90°C), the leachability index and compressive strengths were believed to be unrepresentative. Therefore, grout samples that were prepared during the adiabatic calorimetry study at PNL and cured at 75°C were tested for compressive strength and ANS 16.1 leachability. The results of these tests were modeled and the predictions showed that the formulation 2 listed above had a more favorable NO₃ leachability index, so it was chosen for pilot-scale testing. During the pilot-scale test, it was observed that formulation 2 became unacceptably thick during pumping resulting in critical flow rates exceeding the 60 gpm GTF criterion. A modified formulation, containing 11 wt% attapulgate and a mix ratio of 8.4 lb/gal, was tested during the latter stages of the pilot-scale test and found to have acceptable critical flow rates. This formulation was then chosen as the reference formulation to be tested in this study.

CONCLUSIONS

The purpose of these studies was to determine whether the reference grout formulation for 106-AN meets the criteria specified in Riebling and Fadeff (1991). The results show that all criteria, except for heat of hydration, are met as shown below:

<u>Criterion</u>	<u>Acceptable Value</u>	<u>Test Results</u>
NO ₃ /NO ₂ Leachability Index	> 6.0	NO ₂ : 7.5 - 8.3 NO ₃ : 6.8 - 7.5
TCLP	Non-toxic	Non-toxic
Corrosivity	pH $\leq$ 12.5	pH = 11.6
Drainable Liquids	$\leq$ 0.5 vol%	0
Compressive Strength (CS)	$\geq$ 500 psi	712 - 1993 psi
Homogeneity (Pilot-scale)	CS $\geq$ 500 psi	602 - 1438 psi ^(a)
Critical Flow Rate	< 60 gpm	17.3 - 32.9 gpm
10-min. Gel Strength	$\leq$ 100 lbf/100 ft ²	12 - 18 lbf/100 ft ²
Frictional Pressure Drop	$\leq$ 14 psi/100 ft	6.3 - 6.9 psi/100 ft
Heat of Hydration	T $\leq$ 90°C	T $\geq$ 90°C
Time/Temperature Effects	CS $\geq$ 500 psi	1250 - 2108 psi
Irradiation	Mean CS $\geq$ 500 psi	1221 psi
Immersion	Mean CS $\geq$ 500 psi	1301 psi
Thermal Conductivity	$\geq$ 0.78 W/mK	0.81 W/mK
Cure Time	< 28 days	< 28 days
Grout Expansion/Contraction	None after set	None after 28 days

(a) Lokken, R. O., L. M. Bagaasen, P. F. C. Martin, S. E. Palmer and C. M. Anderson. 1993. Characterization of 106-AN Grout Produced in a Pilot-Scale Test. Draft Letter Report, Pacific Northwest Laboratory, Richland, Washington.

GROUT FORMULATION CRITERIA

The primary purpose of the Grout Disposal Program is to immobilize low-level mixed wastes currently stored in double-shell tanks at Hanford. A set of grout formulation criteria has been developed to ensure the grouts can be effectively processed and, once cured, perform as required (Riebling and Fadeff 1991). The criteria are grouped into three categories based on regulatory and engineering requirements. The three categories include:

- Category I: Criteria required for technical and environmental reasons. These criteria are governed by local, state, and federal laws, regulations, and recommendations.
- Category II: Processing criteria required to mix and pump the grout safely and economically within the vaults.
- Category III: Criteria that are necessary either to yield an acceptable product or to improve processing.

The specific criteria from each of the three categories are described below.

CATEGORY I

The following criteria must be met to show compliance with environmental and regulatory requirements:

- Leachability: A leachability index greater than 6.0 for NO_3 and NO_2 when tested according to the ANS 16.1 procedure.
- Toxicity: The toxicity characteristic leaching procedure (TCLP) shall be conducted on radioactive and simulated waste grouts and the results shall indicate that the grouts are non-toxic.
- Hazard Class: The grout shall be within acceptable limits for the corrosivity characteristic (i.e., $2 \leq \text{pH} \leq 12.5$).
- Free-Standing Liquid at Cure: Free-standing liquid shall be less than 0.5 vol% at cure.
- Unconfined Compressive Strength: The grout shall be classified as a solid, with a recommended goal being a mean unconfined compressive strength ≥ 500 psi.
- Grouted Waste Homogeneity and Pilot-Scale Testing: Core samples from pilot-scale grouts must meet minimum compressive strength (≥ 500 psi) when maximum and minimum thermal curing conditions are compared.

CATEGORY II

Category II criteria specify the desirable grout slurry processing properties that allow effective, safe, and economical placement of the grout slurry into the disposal vault. These include:

- Critical Flow Rate: To provide reasonable operating range and to ensure turbulence, the critical flow rate shall be attained at less than 60 gpm.
- Ten-Minute Gel Strength: This property must be ≤ 100 lb_f/100 ft².
- Frictional Pressure Drop: The pressure drop must be ≤ 14 psi/100 ft of 2-in. schedule-80 pipe.
- Adiabatic Heat of Hydration Temperature Rise: The maximum temperature of the grout must be $\leq 90^{\circ}\text{C}$ due to heat of hydration.

CATEGORY III

Category III criteria specify the qualities or attributes that are necessary to yield a better product or improve processing. These include:

- Time/Temperature Effects: The grouts shall exhibit microstructural stability beyond the initial cure period with respect to the influence of temperature (specifically, the compressive strength shall remain ≥ 500 psi).
- Irradiation: After exposure to 100 Mrad, the mean compressive strength must be ≥ 500 psi and not less than 75% of the mean strength of the as-cured grouts.
- Immersion: After immersion in deionized water for a period of ≥ 90 days, the mean compressive strength must be ≥ 500 psi and not less than 75% of the mean strength of the as-cured grouts.
- Thermal Conductivity: The thermal conductivity must be >0.45 BTU/h/ft/ $^{\circ}\text{F}$ (0.78 W/mK).
- Slurry Cure Time: The grout slurry shall solidify within a period of 28 days.
- Grout Expansion/Contraction: The grout shall not expand or contract after the initial cure period (28 days).

NEED FOR FORMULATION QUALIFICATION/VERIFICATION

Four main variables make up the grout formulation process. These include the dry blend composition, the waste composition, the mix ratio, and the waste feed temperature. Each of these has a variability associated with it that can affect grout properties. The variation in the batching and blending of the dry materials in the Dry Materials Facility (DMF) is expected to be less than 5 wt%, which should not have a large impact on most grout properties (Lokken et al. 1987). Variability in the waste comes from uncertainty in the actual composition used as the basis for the reference simulant composition and possible nonuniformity of the waste in the tank during the grouting operations. Variability in the mix ratio (i.e., dry blend to waste ratio, lb/gal) depends on the accuracy of the dry blend and waste feed systems. The design accuracy of the grout process equipment is specified at $\pm 5\%$ of the mix ratio (Harris 1988).

Time is another important variable associated with property changes in grout properties. Previous studies (Lokken et al. 1987) have shown a large impact of storage time (i.e., the time between blending of the dry materials and grout production) on the rheological properties of phosphate/sulfate waste (PSW) grouts. The effects on the physical properties were not determined, however. Blending time of dry materials also affected the rheological properties of PSW grouts that contained attapulgite. Studies conducted in preparation for the 106-AN pilot-scale test showed that V-blending for one hour resulted in grouts that had similar rheological properties as grouts prepared with dry blend from the DMF. Time will also affect the waste feed temperature because of the heat generated by the in-tank mixer. During a grouting campaign, the mixer will be operated to keep the waste homogeneous and to keep any particulates suspended within the tank.

Although the variables discussed above can all affect the grout slurry and final grout properties, the studies conducted at ORNL varied only the dry blend ingredient ratios, which also changed the mix ratios. The waste composition, dry blending time, initial waste temperature, and grout mixing time were held constant. Also, because no data existed on the temperatures attained during curing, two isothermal curing temperatures were used: 40°C for

determining drainable liquids, and 90°C for samples tested for leachability and compressive strength. These temperatures were believed to be conservative because the lower temperatures usually result in larger amounts of drainable liquids and the higher temperatures result in lower leach resistance and strengths. The actual maximum grout temperatures when cured in a 90°C oven may have exceeded 90°C because of the heat of hydration.

Qualification/verification activities are needed to ensure that the chosen reference formulation, and the variability associated with the process, meet all applicable criteria (Riebling and Fadeff 1991). The specific activities that were addressed for the 106-AN grout formulation qualification include determining the effects of 1) dry blend composition variability, 2) waste composition variability, 3) mix ratio variability, 4) attapulgite source, and 5) curing time and curing temperature. The specifics of these items are discussed in this report.

DRY BLEND, MIX RATIO, AND WASTE COMPOSITION VARIABILITY

The effects of variations in dry blend composition, mix ratio, and waste composition were addressed by adjusting the level of each variable and determining the effect on rheological properties, compressive strength, and leachability. The nominal dry blend composition was 21 wt% cement, 68 wt% fly ash, and 11 wt% attapulgite. The nominal mix ratio was 8.4 lb/gal. A statistically designed matrix was developed to address the variability. This approach allows quantification of the effects of the different variables. The amount of cement, fly ash and attapulgite were varied by ± 0.5 lb/gal to yield the following ranges in the variables:

Variable	Range	Nominal
Cement	1.64 to 1.84 lb/gal	1.75 lb/gal
Fly Ash	5.44 to 6.04 lb/gal	5.74 lb/gal
Attapulgite	0.84 to 1.00 lb/gal	0.92 lb/gal
Mix Ratio	7.92 to 8.88 lb/gal	8.40 lb/gal
Waste Concentration	-15% to +15% of nominal	

The experimental design strategy was to include all 16 of the extreme vertices, several centroids of faces, and six true replicates to make up a total of 44 runs. The experimental design that resulted from this activity is given in Table 1. The following steps were used:

- 1) A 2^3 factorial design for the dry material components was generated at the "low" (-15%) and "high" (+15%) levels of concentration for the waste. This determined the 16 extreme vertices.
- 2) The 2^3 factorial design for the dry materials was also generated at the nominal waste concentration to add eight more formulations.
- 3) The nominal levels for cement, fly ash, and attapulgite clay were combined with the "low" and "high" concentrations of the waste for two more formulations.
- 4) The overall nominal formulation is included six times.
- 5) At each nominal value of the dry materials, a 2^2 factorial was identified for each of the other dry materials. This effectively defines a face centroid for the dry material that is fixed at the nominal value. This produced 12 additional formulations. The waste concentration was assigned for these twelve formulations such that all levels were represented within each 2^2 factorial.

TABLE 1. Test Matrix for Determining the Effects of Dry Blend and Waste Variability

<u>Random</u> <u>Run Order</u>	<u>Test</u> <u>Number</u>	<u>Cement</u> <u>lb/gal</u>	<u>Fly Ash</u> <u>lb/gal</u>	<u>Attapulgate</u> <u>lb/gal</u>	<u>Waste</u>
1	33	1.75	5.44	0.84	L
2	3	1.64	6.04	0.84	L
3	41	1.64	5.44	0.92	H
4	9	1.64	5.44	0.84	N
5	16	1.84	6.04	1.00	N
6	42	1.64	6.04	0.92	L
7	7	1.64	6.04	1.00	L
8	19	1.64	6.04	0.84	H
9	20	1.84	6.04	0.84	H
10	24	1.84	6.04	1.00	H
11	5	1.64	5.44	1.00	L
12	36	1.75	6.04	1.00	L
13	43	1.84	5.44	0.92	N
14	38	1.64	5.74	1.00	H
15	21	1.64	5.44	1.00	H
16	44	1.84	6.04	0.92	H
17	30	1.75	5.74	0.92	N
18	23	1.64	6.04	1.00	H
19	14	1.84	5.44	1.00	N
20	8	1.84	6.04	1.00	L
21	29	1.75	5.74	0.92	N
22	13	1.64	5.44	1.00	N
23	26	1.75	5.74	0.92	N
24	28	1.75	5.74	0.92	N
25	32	1.75	5.74	0.92	N
26	1	1.64	5.44	0.84	L
27	11	1.64	6.04	0.84	N
28	4	1.84	6.04	0.84	L
29	34	1.75	5.44	1.00	N
30	40	1.84	5.74	1.00	N
31	17	1.64	5.44	0.84	H
32	18	1.84	5.44	0.84	H
33	10	1.84	5.44	0.84	N
34	25	1.75	5.74	0.92	L
35	6	1.84	5.44	1.00	L
36	2	1.84	5.44	0.84	L
37	27	1.75	5.74	0.92	H
38	35	1.75	6.04	0.84	H
39	15	1.64	6.04	1.00	N
40	39	1.84	5.74	0.84	L
41	22	1.84	5.44	1.00	H
42	37	1.64	5.74	0.84	N
43	31	1.75	5.74	0.92	N
44	12	1.84	6.04	0.84	N

EXPERIMENTAL PROCEDURES

This section describes the waste makeup, dry blend preparation, curing conditions, and experimental procedures used in these studies^(a).

SIMULATED 106-AN WASTE

The composition of the simulated waste is based on the estimated contents of the 102-AP grout feed tank, which includes waste from 106-AN and the heel currently in 102-AP. Most of the simulated waste was prepared in 20- to 40-liter batches according to the recipe listed in Table 2 for the reference composition. The target and analyzed composition of the reference simulated waste feeds are shown in Table 3. Tables 2 and 3 refer to 106-AN/102-AP which most closely reflects the expected composition of the waste feed (Hendrickson and Welsh 1992). Throughout the remainder of this report, the waste is referred to as "106-AN." The reference waste was diluted with deionized water for the "low" concentration and a separate solution was prepared at 15% greater concentrations of all species for the "high" concentration in the variability study matrix (i.e., the waste was prepared with the recipe shown in Table 2 using 15% more of the compounds in the same amount of water). Waste for making grouts for the Toxicity Characteristic Leaching Procedure (TCLP) was prepared in a one-liter batch. The waste for TCLP used the reference composition with the heavy metals As, Ba, Cd, Cr, Pb, Ag, and Se added in the concentrations shown in Tables 2 and 3.

DRY BLEND

Dry blends were prepared with type I/II Portland Cement from Ash Grove Cement West, Class F fly ash from the Centralia, Washington plant, and attapulgite clay from either Engelhard or Floridin. The oxide composition of these materials is shown in Table 4. The dry materials were blended in a V-blender for 1 h prior to grout preparation. The 1-h blending time was based on results of tests conducted to correlate V-blending time with DMF blending. Previous studies had shown that excessive V-blending resulted in grouts with

(a) These studies were conducted according to Test Plan HGTP-92-0301-01 Rev. 0 and Quality Assurance Plan WTC-015 Rev. 5.

lower critical flow rates (Lokken et al. 1987). Normally, the dry blend was prepared the same day as the grouts were prepared; however, some dry blends were stored in sealed plastic bags for later tests to determine the effects of storage time on grout properties.

GROUT MIXING

Grout slurries were prepared using a Hobart mixer and a wire whip. The waste was preheated to approximately 45°C, except for the adiabatic calorimetry tests where the waste temperature ranged from 35°C to 55°C. Room-temperature dry blend was added and the grout slurry was mixed for a total of 60 seconds (30 seconds on low and 30 seconds on medium). Upon completion of mixing, the mixer was reset to low speed while samples were taken from a spigot near the bottom of the bowl.

RHEOLOGICAL PROPERTIES

The rheological properties of grout slurry samples were determined with a Fann Model 35A viscometer. The Fann viscometer employs six preset speeds (3, 6, 100, 200, 300, and 600 rpm). Grout slurry is contained in the annular space between two cylinders. The outer cylinder (or rotor) is rotated by means of a motor at constant velocity (shear rate). The rotation of the rotor in the grout produces a torque on the inner cylinder (bob). A torsion spring attached to the bob restrains movement. The dial attached to the spring indicates the torque imparted through the grout as the rotor is rotated. The dial is calibrated to read shear stress directly in units of $\text{lb}_f/100 \text{ ft}^2$. Rheological measurements on grout slurries use the highest four speeds of the instrument, starting at 600 rpm and working down to 100 rpm.

TABLE 2. Simulated 106-AN/102-AP Waste Recipe

<u>Compound</u>	<u>Amount, g/l</u>
NaNO ₃	8.58
NaOH (50%)	149.7
Al(NO ₃) ₃ •9H ₂ O	128.0
Na ₃ (PO ₄)•12H ₂ O	74.4
NaNO ₂	36.9
Na ₂ CO ₃	36.2
KCl	1.83
NaCl	2.50
Na ₃ (Citrate)•2H ₂ O	2.50
Na ₂ B ₄ O ₇	0.131
Ni ₂ SO ₄	3.89
Ni(NO ₃) ₂ •6H ₂ O	0.302
Ca(NO ₃) ₂ •4H ₂ O	0.438
Na ₄ (EDTA)•2H ₂ O	1.415
Na ₃ (HEDTA)	5.293
Glycolic acid	0.645
Mg(NO ₃) ₂ •6H ₂ O	0.028
Na ₂ CrO ₄ •4H ₂ O(a)	2.4377
Ba(NO ₃) ₂ (a)	1.9069
Pb(NO ₃) ₂ (a)	0.1752
Cd(NO ₃) ₂ •4H ₂ O(a)	0.2805
Ag(NO ₃)(a)	0.3260
Se (10.00 mg/ml)(a)	11.23 (10 ml)
As (10.00 mg/ml)(a)	10.64 (10 ml)

(a) Compounds added to waste for TCLP grouts. The concentrations of the heavy metals were levels much higher than would be expected in actual waste for the purpose of setting upper limits on concentration

TABLE 3. Target and Analyzed Composition of the Reference Simulated 106-AN/102-AP Waste

Species	Concentration, moles/L		
	Target	Analyzed ^(a)	Analyzed ^(b)
NO ₃	1.13	1.18	1.17
OH	0.497	-(c)	-
Al	0.341	0.345	0.328
PO ₄	0.196	0.115	0.196
NO ₂	0.534	0.550	0.509
CO ₂	0.341	-	-
Na	3.95	3.75	3.87
K	0.0246	<0.005 ^(d)	<0.005
Cl	0.0675	-	-
B	0.0026	0.0029	0.0031
SO ₄	0.0273	-	-
Ni	0.00104	0.00095	0.00095
Ca	0.00186	0.00142	0.00174
Si	0.00158	<0.0004	0.00053
Mg	0.000107	<0.002	<0.002
TOC	0.238	-	-
Cr	0.0104 ^(e)	<0.00002	0.010
Ba	0.00730 ^(e)	<0.000006	0.0048
Pb	0.00053 ^(e)	<0.000048	0.00043
Cd	0.00091 ^(e)	<0.000009	0.00088
Ag	0.00192 ^(e)	<0.000009	0.00008
Se	0.00127 ^(e)	<0.00013	0.00127
As	0.00133 ^(e)	<0.00007	0.00148

(a) Reference composition from 40-L batch with no heavy metals

(b) Reference composition with heavy metals added for TCLP

(c) Not analyzed

(d) "Less than" values are analytical detection limits

(e) Target values for the waste prepared for TCLP testing

TABLE 4. Oxide Composition (wt%) of Dry Materials used in 106-AN Grout Formulation Verification Tests.

Oxide	Type I/II Portland Cement	Class F Fly Ash	Engelhard Attapulgate	Floridin Attapulgate
Al ₂ O ₃	2.83	24.56	7.75	8.31
BaO	0.11	0.18	0.01	0.01
CaO	64.36	8.95	4.76	3.50
Fe ₂ O ₃	4.43	5.00	2.43	2.72
K ₂ O	0.60	0.48	0.36	0.60
MgO	0.93	1.82	8.95	9.29
MnO ₂	0.07	0.04	0.05	0.04
Na ₂ O	0.22	3.37	0.05	0.05
P ₂ O ₅	0.21	0.80	0.78	0.69
SiO ₂	21.39	44.92	47.06	47.06
SrO	0.05	0.35	0.01	0.01
TiO ₂	0.20	4.17	0.32	0.35
V ₂ O ₃	0.01	0.10	0.01	0.01
ZrO ₂	0.01	0.15	0.00	0.00
Total	95.42	94.92	72.55	72.65

The shear rate/shear stress values are used to calculate flow properties according to the power law model described by Smith (1976). In this analysis, turbulent flow is assumed to begin at a Reynolds number of 2100. Grout is required to be pumped in turbulent flow to minimize particle settling that could result in flow restrictions. The parameter used in this report to describe the flow properties of grout slurries is the critical flow rate (CFR). The CFR is defined as the minimum flow rate that must be maintained through a given pipe diameter such that the calculated Reynolds number is 2100. Critical flow rate is calculated by

$$CFR = \left[\frac{1129 K' (96/d)^{n'}}{\rho} \right]^{\frac{1}{2-n'}} \frac{\pi d^2 / 4}{0.3208} \quad (1)$$

where, CFR = critical flow rate, gpm

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

n' = flow behavior index, dimensionless

ρ = grout slurry density, lb/gal

d = inside pipe diameter, in.

The density of freshly prepared grout slurry was determined by pouring approximately 250 ml of grout into a 250-ml graduated cylinder and measuring the weight and the actual volume poured.

ADIABATIC CALORIMETRY

The adiabatic calorimeter system used in these studies consists of eight individual calorimeter cells and a common temperature measurement and control system. Figure 1 shows a schematic of a cell. The calorimeter cells consist of a 6-liter stainless steel Dewar, a water circulation pump, an immersion heater, and a 1-liter stainless steel Dewar to contain the grout slurry. The heater is controlled with a solid-state relay connected to the control system. The data acquisition system consists of a relay multiplexer, a thermocouple amplifier/conditioner, and a 16-bit analog-to-digital converter.

Adiabatic calorimetry testing of grout hydration is based on the premise that all the heat generated by the grout is retained within the grout, thereby increasing the grout temperature. For the large grout disposal vaults, near adiabatic curing conditions are expected, particularly near the center of the vault. In the laboratory, adiabatic conditions are achieved by placing freshly prepared grout slurry into a stainless steel Dewar. A thermocouple is then inserted into the grout slurry. The Dewar containing the grout slurry is then placed into a second, larger Dewar containing water preheated to the initial grout temperature. A heater in the larger Dewar maintains the temperature of the water bath at the same temperature as the grout. In an ideal system, no heat transfer between the grout and the surroundings can occur because the temperatures within the grout and the water are the same at all times. Although this system is designed to simulate adiabatic conditions,

FIGURE 1. Schematic of the Adiabatic Calorimeter System

the temperatures measured in the calorimeter would be less than those experienced in a large vault because some of the heat generated by the hydration reactions is used to heat the Dewar walls. Therefore, the heat capacity of the calorimeter system is determined and the measured grout temperatures are adjusted to give the "true" adiabatic temperature rise. The heat capacity is determined by inserting a resistive thermal device (RTD) with known resistance/temperature relationship into a known amount of water in the small Dewar and then the Dewar is placed into the calorimeter. A known current is applied to the heater and the temperature recorded with time. The theoretical rate of temperature rise is calculated by

$$^{\circ}\text{C}/\text{h} = \frac{I^2 R \cdot (3600)}{(4.184) \cdot g_w} = \text{Rate}_{\text{theoretical}} \quad (2)$$

where, I = current, amps
 g_w = weight of water in Dewar
 R = heater resistance calculated by

$$R = \frac{T_{\text{max}} + T_{\text{min}}}{2} \cdot 0.385 + 100 \quad (3)$$

where, T_{max} = final water temperature
 T_{min} = starting water temperature.

The actual rate of temperature rise ($\text{Rate}_{\text{actual}}$) of the water in the Dewar is determined by either plotting temperature vs. time and measuring the slope or by performing linear regression analysis.

The heat capacity of the calorimeter (C_{pcal}) can then be calculated by

$$(C_{\text{pcal}}) = \frac{\text{Rate}_{\text{theoretical}} - \text{Rate}_{\text{actual}}}{\text{Rate}_{\text{actual}}} \cdot g_w. \quad (4)$$

GROUT CURING

After mixing, grout samples were cast into 250-ml polypropylene graduated cylinders. The weight of the grout was measured and the cylinders were capped with rubber stoppers and placed into copper tubes. Each end of the copper tube was capped with a copper end cap and the sample mold weighed and placed into small, programmable curing ovens. The ends of the copper tubes were secured to ensure a moisture-tight seal. The temperature of the ovens was programmed to approximate the adiabatic temperature rise of the nominal grout formulation as given in Table 5 and Figure 2.

The ovens were set to final curing temperatures of 55°C, 65°C, 70°C, or 85°C. Figure 3 shows the measured grout temperature of a sample and the programmed temperature of the oven set to a maximum of 70°C. The initial decrease in temperature of the grout sample is due to heat loss during the

TABLE 5. Programmed Temperature Profile for the Initial Curing of 106-AN Grout Samples

<u>Temperature</u>	<u>Time Increment</u>	<u>Equivalent Rate, °C/h</u>
40°C to 45°C	1 h	5.0
45°C to 47°C	1.5 h	0.67
47°C to 55°C	2 h	4.0
55°C to 65°C	9 h	1.11
65°C to 70°C	4.5 h	1.11
70°C to 75°C	5 h	1.0
75°C to 80°C	10 h	0.5
80°C to 85°C	20 h	0.25

time period between sample preparation and insertion into the oven. As seen in the figure, the temperature of the grout sample was lower than the oven until shortly after the 70°C setting had been reached.

When the temperature of the samples reached the required temperature (i.e., either 55°C, 65°C, 70°C, or 85°C), the samples were removed from the small ovens and secured in curing frames (See Figure 4) and then placed into larger ovens set at the same temperature and allowed to cure. After curing, the samples were removed from the large ovens and placed into preheated, programmable ovens and cooled to room temperature over a 20-h period.

In addition to the curing profiles described above, additional samples were cured according to two different temperature profiles that were predicted in the grout vault. These profiles, shown in Figure 5, were obtained by thermal modeling^(a). The two curves in the figure represent two lift/pour scenarios. The upper curve represents the peak temperature location for grout poured in eight lifts with 515 h between lifts. The lower curve in the figure shows the peak temperature for grout in the vault after pouring 48 lifts and waiting 97 h between lifts.

(a) Letter from R. Valdiviez to R. O. Lokken, Results of the Grout Vault Thermal Modeling to Support PNL Testing, Westinghouse Hanford Company, No. 9259443, December 18, 1992.

FIGURE 2. Initial Curing Schedule for 106-AN Grout Samples

FIGURE 3. Measured Grout Temperature and Programmed Oven Temperature for 106-AN Grout Sample.

FIGURE 4. Schematic of Grout Curing Assembly

FIGURE 5. Temperature History of Two Lift/Pour Scenarios for 106-AN Grout at the Highest Temperature Location in the Vault as Predicted by Thermal Modeling

THERMAL CONDUCTIVITY

Thermal conductivity measurements were conducted on the reference 106-AN grout formulation utilizing a specially constructed probe that is particularly suited for determining the thermal conductivity of multiphase materials or materials that are not suited for conventional, steady-state measurement methods. The operation is based on the line heat source method (Tye, 1969). A schematic of the probe is shown in Figure 6. The probe consists of a 6-in.-long heated section that is composed of bifilar-wound constantan thermocouple wire. The heating coil was inserted into a 1/8-in.-diameter stainless steel tube. A type K thermocouple was inserted into the assembly at the midpoint of the coil. Electrical connections were made inside a stainless steel connector and the voids were filled with a plastic resin. The resistance of the heater was 134.5 Ω .

FIGURE 6. Schematic of a Thermal Conductivity Probe

In operation, the probe is inserted into a material, constant heat is applied, and the temperature rise within the probe is recorded with time. The thermal conductivity of the material is related to temperature rise, time, and heat input by the following relationship:

$$\Delta T = \frac{Q}{4 \pi \lambda} \ln \left(\frac{(t_2 - t_c)}{(t_1 - t_c)} \right) \quad (5)$$

where, ΔT = temperature change, K

Q = heat flow, W/m

λ = thermal conductivity, W/mK

t_2, t_1 = time, s

t_c = time factor constant, s.

The time factor constant is an empirically determined value that depends on contact resistance, thermocouple position, and the thermal properties of the probe materials. The time factor constant was determined during the calibration of the probe as described below.

The heat flow is determined by applying the following equation:

$$Q = V^2 / (R * L) \quad (6)$$

where, V = volts

R = heater resistance, ohms

L = probe length, m

Q = heat flux, W/m.

For ideal behavior, a plot of temperature vs. $\ln(t)$ would give a straight line with a slope of $Q / (4\pi\lambda)$. Thermal conductivity is then determined by the following equation:

$$\lambda = \frac{Q}{4 \pi \text{ Slope}} \quad (7)$$

The experimental data were analyzed by performing a linear regression of temperature rise and the logarithm of time. The thermal conductivity of the solid phase was then calculated from the above equation.

The probe was calibrated using a packed bed of glass beads in deaerated distilled water. The beads were 3 mm diameter with a density of 2.5 g/cm³. The beads were placed in a 0.5-liter stainless steel Dewar and the interstices filled with water. The packing density of the beads was calculated to be 62 vol%. The probe was inserted along the centerline of the beads, power was applied, and the temperature rise recorded with time. A constant voltage of 16 volts was applied for a total time of five minutes. The thermal conductivity of the mixture was calculated using the preceding equation and the thermal conductivity of the glass was calculated with the following equation:

$$\lambda_g = \lambda_m(1/1-f) + \lambda_w(f/1-f) \quad (8)$$

where, λ_g = thermal conductivity of the glass
 λ_m = thermal conductivity of the mixture
 λ_w = thermal conductivity of water
 f = volume fraction water in the mixture.

A typical plot of temperature vs. time is shown in Figure 7 and the corresponding plot of temperature vs. logarithm of time is shown in Figure 8. Data analyses were conducted using temperature values observed between 120 and 240 seconds after applying power to the heater. The time factor constant, t_c , was determined using iterative calculations to obtain a thermal conductivity of the glass beads of 1.072 W/mK, as reported by Tanaka and Miyazawa (1979).

Figure 7. Typical Plot of Temperature Rise vs. time for Glass Beads in Water

Figure 8. Typical Plot of Temperature Rise vs. ln Time for Glass Beads in Water. (Large data points were used for linear regression analysis)

POST-CURING SAMPLE PREPARATION

After the samples had cured and cooled to room temperature, the curing tubes (i.e., the copper tubes and the graduated cylinders containing grout) were weighed to determine the amount of weight loss that had occurred during curing. The graduated cylinder was then removed from the copper tube and the amount of drainable liquid and the final volume of grout were recorded. The graduated cylinders containing the cured grout were cut to produce samples for compressive strength and ANS 16.1 leach tests. The samples were cut on a band saw and the faces were milled parallel on a lathe. The locations of the samples are shown in Figure 9. For those samples where only compressive strengths were conducted, three specimens were cut from near the top, middle and bottom. When ANS 16.1 leach tests were performed, the leach specimen was obtained from the middle of the cylinder. After cutting and milling, the specimens were stored at room temperature in plastic bags until tested.

COMPRESSIVE STRENGTH

Compressive strength testing was conducted on an Instron test machine using a constant cross-head speed of 0.05 in./min. The load-to-failure was determined from the maximum point on the load-deformation curve. Compressive strength values were calculated by dividing the maximum load by the average cross-sectional surface area of the cylinders which had a length-to-diameter ratio of two.

FIGURE 9. Location of Grout Specimens Cut From Graduated Cylinders for Compressive Strength and ANS 16.1 Leach Testing.

AMERICAN NUCLEAR SOCIETY (ANS 16.1) LEACH TEST

The ANS 16.1 leach test (ANS 1986) was conducted on specimens from the variability matrix and several other specimens. This test is an intermittent leachate exchange test designed to simulate a dynamic leaching situation. The leachate exchange intervals used in these tests are shown in Table 6.

The samples used in these tests were right circular cylinders, with nominal dimensions of 3.36-cm dia. by 4.6-cm high. The samples, with a surface area of approximately 66 cm², were suspended by nylon monofilament in approximately 660 ml of deionized water within polyethylene containers. After the elapsed time periods, the samples were removed from the leachates and placed into a second set of containers containing fresh leachant. The pH of the leachates was measured after removing the samples and filtered aliquots of leachate were submitted for NO₃ and NO₂ analysis by ion chromatography (IC).

The ANS 16.1 leach test is designed to determine a "figure of merit" parameter called the leachability index (L). The leachability index for a given species is defined as the negative logarithm (base 10) of the effective diffusion coefficient (D) of that species. The effective diffusivity is given by (ANS 1986)

$$D = \pi \left[\frac{(a_n/A_0)}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T \quad (9)$$

where, D = effective diffusivity, cm²/s

TABLE 6. Leach Intervals Used for the ANS 16.1 Leach Test

Leach Interval No.	Time Between Intervals	Cumulative Time
1	7 h	7 h
2	17 h	1 d
3	24 h	2 d
4	48 h	4 d
5	72 h	7 d

- a_n = concentration of ion released from the specimen during the leaching interval n
- A_0 = total amount of species in the specimen at the beginning of the leach test
- $(\Delta t)_n = t_n - t_{n-1}$, duration of the n -th leaching interval, s
- V = volume of specimen, cm^3
- S = geometric surface area of specimen, cm^2
- $T = [1/2 (\sqrt{t_n} + \sqrt{t_{n-1}})]^2$, representing the "mean time" of the leaching interval, s.

When greater than 20% of the total inventory of a species is leached, the effective diffusivity is calculated by

$$D = \frac{Gd^2}{t} \quad (10)$$

where, D = effective diffusivity, cm^2/s

G = dimensionless time factor for cylinder

d = cylinder diameter, cm

t = elapsed leaching time from beginning of test, s.

The treatment of the data from this type of leach test assumes that the release of ions from the waste form is controlled by diffusion. For pure diffusional release, the cumulative amount of species released from the sample plotted as a function of the square root of time would yield a straight line passing through the origin at time zero.

The leach specimens from the variability study were allowed to remain in deionized water for a total of >90 d to determine the effects of immersion on compressive strength.

TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

The TCLP (U.S. EPA 1990) was conducted on three samples of simulated 106-AN grout. The grout samples were crushed and sieved through a screen with 3/8-in. openings. One hundred grams of grout that had passed through the screen and 2000 g of extraction fluid were added to 2-L glass bottles. The extraction fluid was an acetic acid solution with an initial pH of 2.88. The

vessels were tumbled in a rotary extractor at 30 rpm for 18 ± 2 h. Following the extraction, the solutions were filtered and aliquots were submitted for chemical analysis.

CORROSIVITY

The corrosivity of three reference 106-AN grout samples was determined using the State of Washington Department of Ecology (WDOE) Method 83-13 (WDOE 1984). Approximately 50 grams of grout were combined with an equal weight of distilled water and agitated on a shaker table for 30 minutes. The pH of the solution was then measured. According to this procedure, a solid is considered corrosive if the average pH of the solutions is less than or equal to 2, or greater than or equal to 12.5. The average is calculated using the antilog of pH and taking the log of the average.

IRRADIATION

Nine specimens prepared for compressive strength testing were placed into a stainless steel container that was sealed and purged with argon gas and then irradiated with ^{60}Co to a total dose of $\sim 10^8$ Rad in approximately 66 h. The samples were During the irradiation, the pressure and temperature were monitored. Gas samples taken before and after irradiation were analyzed by mass spectroscopy. Control samples were prepared at the same time and were tested for compressive strength the same day as those that were irradiated.

RESULTS

This section presents and discusses the results of the studies conducted to determine the acceptability of the reference formulation for grouting 106-AN waste. Variability in dry blend composition, waste composition, and the effects of using two different attapulgite clays were addressed. The effects of curing time and temperature, and of irradiation on compressive strength are discussed.

CRITICAL FLOW RATE AND SLURRY DENSITY

Critical flow rate is defined as the minimum flow rate required to obtain a Reynolds number of 2100. The formulation criteria for critical flow rate is <60 gpm. This section describes the effects of several parameters on the critical flow rate of 106-AN grout slurries.

Effects of Dry Material and Waste Variability

Table A1 (see Appendix) lists the critical flow rate and slurry density data for the variability study grouts. The general method of analysis for these data started with the calculation of summary statistics. These statistics include the overall mean and standard deviation, the minimum, maximum, and range, and the number of observations (N). The normality of the data was assessed and possible outliers were identified using an outlier test found in ASTM Standards (ASTM 1969). These investigatory calculations are an important first indication of the underlying structure of the data. For both critical flow rate and slurry density the data appeared to be approximately normally distributed. One outlier was identified for slurry density (test number = 5, slurry density = 1.4914 g/cm³) and was omitted from the analysis. The summary statistics for critical flow rate (gpm) and slurry density (g/cm³) are given below.

	Critical Flow Rate (gpm)	Slurry Density (g/cm ³)
Mean	24.2825	1.5409
Standard Deviation	3.9379	0.0142
Minimum	17.3000	1.5154
Maximum	32.8600	1.5740
Range	15.5600	0.0586
N	44	43

In addition, summary statistics were calculated within each waste concentration. A fundamental statistical method (F-test) was used to test if the variances across waste concentration were equal (Weisberg 1985). In general, if the variances test to be significantly different, then the overall standard deviation does not appropriately represent the true variability. For critical flow rate there were no significant differences in the variances across waste concentration. For slurry density, the difference between the "low" concentration and the nominal concentration variance was statistically significant, but was determined to be not practically different. Consequently, the overall standard deviations presented above can be used to represent the overall variability.

Statistical confidence and tolerance intervals have been calculated for these data to provide probability statements about the location of the mean and the individual observations from the underlying distribution. For example, 95% confidence intervals (Steel and Torrie 1980) allow statements which say that "we have 95% confidence that the true mean of the underlying distribution lies between these interval limits". A statement for a 95/95 tolerance interval (Owen 1963) says "we have 95% confidence that for 95% of the operating conditions bracketed in this design, the property of interest will be above (or below) the interval limit". The 95/95 tolerance interval is of most interest for the purposes of this experiment. The 95% confidence intervals and the 95/95 upper tolerance interval value for critical flow rate are given below.

	<u>Critical Flow Rate (gpm)</u>
Lower 95% Confidence Limit	23.0853
Upper 95% Confidence Limit	25.4798
Upper 95/95 Tolerance Limit	32.5487

These values indicate that we have 95% confidence that the mean critical flow rate is between 23 and 25 gpm and that we have 95% confidence that 95% of the bracketed operating conditions will produce a grout with a critical flow rate less than 33 gpm.

Effects of Attapulgite Source and Dry Blend Storage Time

Attapulgite clay used at ORNL and PNL in laboratory formulation studies was obtained from Engelhard. The pilot-scale test used attapulgite purchased from Floridin. Although both clays meet the applicable criteria set forth in the American Petroleum Institute's Bulletin (API 1980) for drilling clay, the properties of grouts made with the different clays can be quite variable as reported by Lokken et al. (1987). Studies were conducted to determine the effects of the different sources of attapulgite clay and to see whether acceptable properties can be achieved with both clays. In addition, the effects of dry blend storage time were studied. Dry blend storage times from four to six weeks are likely because of the need to pour the grout in lifts to allow the grout to cool. Table A4 lists the critical flow rate data for these grouts.

Table 7 summarizes the results of critical flow rate calculations for 106-AN grouts made with dry blend containing attapulgite clay from Engelhard and from Floridin. The table shows that the critical flow rate of grouts made with Floridin attapulgite were less viscous, i.e., a lower critical flow rate, than grouts made with Engelhard attapulgite. A lower critical flow rate usually means more drainable liquid. However, there were no drainable liquids on any of the samples after curing for 28 days at 70°C. Storage time did not have an appreciable effect on the critical flow rates and, because there were no drainable liquids, grouts with acceptable critical flow rates were produced with dry blends stored for up to six weeks.

TABLE 7. Effect of Dry Blend Storage Time on the Critical Flow Rate (gpm) of 106-AN Grouts Made with Dry Blend Containing Attapulgite Clay From Engelhard and From Floridin

Attapulgite Source	Storage Time, weeks					
	0	1	2	3	4	6
Engelhard(a)	29.4 ± 0.7 ^(b)	30.2	28.2	28.2	25.9	25.9
Engelhard(c)	27.2 ± 0.7		26.0 ± 0.2		25.8 ± 0.1	
Floridin(c)	19.6 ± 0.1		19.3 ± 0.2		19.3 ± 0.1	

(a) Grout slurry made using one liter of waste

(b) ± values are one standard deviation from the mean of a minimum of three mixes

(c) Grout slurry made using one half liter of waste

COMPRESSIVE STRENGTH AND BULK DENSITY

The formulation criterion for unconfined compressive strength is >500 psi. This property can be influenced by numerous factors, many of which are discussed below. Tables A2 and A5 list compressive strength data for the grouts.

Effects of Dry Material and Waste Variability

Table A2 lists the compressive strength and bulk density data for the variability study grouts. Compressive strength and bulk density measurements were made on two grout specimens taken from each sample. Consequently, 88 values are reported for these properties. However, the 88 values cannot be considered to be 88 independent measurements because measurements from the same sample will be more alike than measurements from different samples. If measurements from the same sample are averaged together and the overall variability is assessed based on those averages, then the variability due to repeated measurements on the same sample will be appropriately incorporated. It is possible to independently assess the variability due to repeated measurements on the same sample, but that was not done for this report. The results presented in this report were calculated using the average of the measurements from the same sample.

Summary statistics for compressive strength and bulk density are presented below. The normality of the data was assessed and possible outliers were identified using an outlier test found in ASTM Standards. The overall data for compressive strength did not appear to be distributed normally. For bulk density the data appeared to be distributed approximately normally. One outlier was identified for compressive strength (test number = 4, compressive strength = 2873 psi) and was omitted from the analysis.

	<u>Compressive Strength (psi)</u>	<u>Bulk Density (g/cm³)</u>
Mean	1235.08	1.5525
Standard Deviation	372.77	0.0156
Minimum	712.00	1.5215
Maximum	1992.50	1.5940
Range	1280.50	0.0725
N	43	44

In addition, summary statistics were calculated within each waste concentration. A fundamental statistical method (F-test) was used to test if the variances across waste concentration were equal. In general, if the variances test to be significantly different, then the overall standard deviation does not appropriately represent the true variability. For bulk density there were no significant differences in the variability across waste concentrations. For compressive strength the "low" waste concentration variability tested to be significantly different from the variability in the other concentrations. Consequently, the data from the "low" waste concentration must be treated separately from the other two concentrations. Summary statistics for the "low" waste concentration and for the combined nominal/high waste concentrations are presented below. Within these two groups, the data appear to be distributed approximately normally. Summary statistics for compressive strength are shown below:

	Compressive Strength (psi)	
	Low Waste Concentration	High/Nominal Waste Concentration
Mean	1753.88	1034.26
Standard Deviation	188.01	179.57
Minimum	1427.50	712.00
Maximum	1992.50	1356.00
Range	565.00	644.00
N	12	31

Using the definition for confidence and tolerance intervals provided in the previous section, those intervals are given below for compressive strength:

	Compressive Strength (psi)	
	"Low" Waste Concentration	"High"/Nominal Waste Concentration
Lower 95% Confidence Limit	1634.42	968.39
Upper 95% Confidence Limit	1873.33	1100.12
Lower 95/95 Tolerance Limit	1239.46	637.91

These values indicate that we have 95% confidence that the mean compressive strength for "low" waste concentrations is between 1634 and 1873 psi and between 968 and 1100 psi for nominal and "high" waste concentrations. We have 95% confidence that 95% of the bracketed operating conditions will produce compressive strengths greater than 1239 psi for "low" waste concentrations and greater than 638 psi for nominal and "high" waste concentrations.

Effect of Immersion

The 44 grout samples that were tested for ANS 16.1 leachability remained in deionized water for >90 d. Afterwards, the effects of immersion on the compressive strengths of the specimens were determined. The results of the compressive strength tests are listed in Table A3 of the Appendix. According

to the Nuclear Regulatory Commission's Waste Form Technical Procedure (NRC 1991), the post-immersion mean compressive strength of the specimens should be greater than or equal to 500 psi and not less than 75% of the as-cured specimens. The mean compressive strength of the as-cured specimens was 1272 psi, while the mean strength of the post-immersion specimens was 1301 psi, which corresponds to a 3.7% increase in strength.

Effects of Attapulgite Source and Dry Blend Storage Time

After the grout slurries were made for determining the effects of storage time and attapulgite clay source on the critical flow rates, samples were poured and cured at 70°C for 28 days. Compressive strength tests were conducted to determine whether the source of attapulgite (Engelhard or Floridin) and storage time had any effect on the strengths. The results of these tests are shown in Table 8. The data in the first line of the table suggest increasing compressive strengths for samples made with dry blends and stored for increasing time periods up to four weeks; a decrease in strength is indicated after the dry blend is stored for six weeks. The second two sets of data, however, indicate no significant changes in the compressive strengths. Whether the effects are real are of no particular significance, because the primary purpose of these tests was to determine whether grouts made with either attapulgite clay would have acceptable (i.e., >500 psi) compressive strengths, and the results show that acceptable strengths are obtained in all cases.

Effects of Curing Time and Temperature

Previous studies have shown that high-temperature curing for long time periods can affect the compressive strength of grout samples (Lokken 1992c). Tests were conducted to determine the effects of these variables on the reference 106-AN grout samples by curing from approximately 8°C to 85°C for up to 91 days. The effects of these conditions on the compressive strengths of the grout specimens are shown in Figure 10. Each value in the figure is the average of two measurements. The two lowest temperatures will not exist within the vaults; however, they were included for comparative purposes. The strengths of the specimens cured at 55°C, 70°C, and 85°C were all greater than

TABLE 8. Effect of Dry Blend Storage Time on the Compressive Strengths (psi) of 106-AN Grouts Made with Dry Blends Containing Attapulgite Clay from Engelhard and from Floridin

Attapulgite Source	Storage Time, weeks					
	0	1	2	3	4	6
Engelhard ^(a)	1178 ± 24 ^(b)	1141 ± 50	1261 ± 29	1499 ± 26	1598 ± 34	1064 ± 28
Engelhard ^(c)	1158 ± 39 ^(d)				1123 ± 33	
Floridin ^(c)	1812 ± 290 ^(d)				2079 ± 124	

(a) Grout slurry made using one liter of waste

(b) ± values in the first row are one standard deviation from the mean of two specimens

(c) Grout slurry made using one half liter of waste

(d) ± values in rows two and three are one standard deviation from the mean of nine specimens (three specimens from each of three samples)

1000 psi after curing for 28 days. Grout strengths after 56 and 91 days of curing were greater than the strengths after 28 days. The grouts cured at 70°C had lower strengths than those cured at either 55°C or 85°C for up to 56 days. The strength after 91 days of curing, however, was about the same as the strength of samples cured at 85°C.

The last two bars in Figure 10 represent samples that had cured for 28 days under two predicted time/temperature histories within the vault as seen in Figure 5. These grouts were cured at a slower rate than the other high-temperature cured samples (see Figures 2 and 5). These results suggest that curing at slower rates may be beneficial for improved microstructural development and subsequent increases in compressive strengths.

FIGURE 10. Effect of Curing Temperature and Curing Time on the Compressive Strength of Reference 106-AN Grouts (Note: Values are average strengths from two specimens from the same sample; V1 and V2 refer to the top and bottom curves in Figure 5, respectively.)

Effects of Heavy Metals in Waste

The samples that were prepared for TCLP testing were tested for compressive strength prior to testing, mainly to facilitate obtaining the required particle sizes. The only difference between these grout samples and those of the control grouts was the presence of heavy metals in the waste. The strengths of these grouts was consistently higher than the strengths of comparably prepared and cured grouts, with an average strength of 1774 psi, compared with 1220 for the control grout samples cured under the same conditions. It should be noted, however, that the concentration of heavy metals added to the waste was extremely high because the primary purpose for making these grouts was to confirm the compositional limits in Hendrickson (1991).

Effects of Position in Cylinder

Specimens used for compressive strength testing were obtained from different positions within the graduated cylinder molds (see Figure 9). The position within the cylinder was shown to have a significant effect on the compressive strength and bulk density of the specimens. In general, the higher compressive strengths and greater bulk densities were found for the specimens taken from the bottom of the cylinder. These results suggest that the grout slurry exhibited preferential particle settling prior to setting, which may have resulted in a compositional gradient within the cylinder; the bottom appears to be more concentrated in cement, which is approximately 40% more dense than the fly ash or attapulgite. Figures 11 and 12 illustrate a typical trend in the relationship of position within the cylinder to the compressive strength and bulk density for three cylinders from the same grout mix.

Effects of Irradiation

Nine specimens of 106-AN grout were irradiated in a ^{60}Co radiation field to a total dose of $\sim 10^8$ rad to determine the effects of irradiation on the compressive strength. The specimens were obtained from three graduated cylinders, two made with dry blend containing Engelhard attapulgite clay and one containing Floridin attapulgite clay. Control specimens that were subjected to identical conditions, except for irradiation, were included in the tests. All samples were cured for 28 days at 70°C and an additional 25 days at room temperature before they were irradiated. During irradiation, the temperature of the samples was about 38°C. Control samples were also subjected to a 38°C temperature. Compressive strengths were measured the same day after removing the samples from the radiation field. Table 9 summarizes the results of these tests. The values shown in the table are the average and standard deviation for three specimens from the same sample. There were statistically significant differences between the control (non-irradiated) and the irradiated samples; however, all strengths were greater than the desired 500 psi. The lower strengths are likely due to small cracks that developed either by drying or by internal pressures caused by gas generation during the irradiation.

FIGURE 11. Relationship Between Compressive Strength and Position Within the Graduated Cylinder

FIGURE 12. Relationship Between Bulk Density and Position Within the Graduated Cylinder

TABLE 9. Effects of Irradiation on the Compressive Strength of 106-AN Grouts

	Compressive Strength, psi
Engelhard Clay Grout	
Irradiated	1093 ± 49(a)
Irradiated	1054 ± 46
Control	1198 ± 26
Floridin Clay Grout	
Irradiated	1515 ± 108
Control	1831 ± 105
Control	1881 ± 95

(a) ± values are one standard deviation from the mean of three specimens

ANS 16.1 LEACH TESTS

Leach tests are conducted on grout samples to determine the diffusion coefficients and corresponding leachability indices as a measure of how well the soluble species are contained within the grout structure. The grout formulation criteria dealing with leachability specifies that the leachability index for NO₂ and NO₃ must be greater than 6.0. This section describes the results of the ANS 16.1 leach tests and some of the factors that affect leachability.

Effects of Dry Material and Waste Variability

Table A6 lists the NO₃ and NO₂ leachability indices for the variability study grouts. Summary statistics have been calculated for NO₂ and NO₃ leachability index and are presented below. The data do not appear to be normally distributed. No outliers were detected in the data.

	<u>NO₂ Leachability</u>	<u>NO₃ Leachability</u>
Mean	7.9027	7.1825
Standard Deviation	0.2591	0.2194
Minimum	7.4723	6.8239
Maximum	8.3345	7.5491
Range	0.8622	0.7252
N	44	44

There were no significant differences between variances of "low", nominal, and "high" waste concentrations. However, the data appear to be approximately normal within each waste concentration. Consequently, the confidence and tolerance intervals are presented below for each waste concentration level.

	<u>NO₂ Leachability</u>		
	<u>Concentration</u>		
	<u>Low</u>	<u>Nominal</u>	<u>High</u>
Lower 95% Confidence Limit	7.8669	7.7088	7.7281
Upper 95% Confidence Limit	8.1334	7.9955	8.0222
Lower 95/95 Tolerance Limit	7.4113	7.1450	7.2254

These values indicate that we have 95% confidence that the mean NO₂ leachability index is between 7.87 and 8.1 for "low" waste concentrations and that the mean NO₂ leachability index is between 7.7 and 8.0 for nominal and "high" waste concentrations. We have 95% confidence that 95% of the bracketed operating conditions will produce an NO₂ leachability index greater than 7.41, 7.15, and 7.23 for "low", nominal, and "high" waste concentrations, respectively.

The tolerance intervals for NO₃ leachability are:

	NO ₃ Leachability		
	Concentration		
	Low	Nominal	High
Lower 95% Confidence Limit	7.1531	7.0172	7.0361
Upper 95% Confidence Limit	7.3826	7.2595	7.2805
Lower 95/95 Tolerance Limit	6.7610	6.5405	6.6186

These values indicate that we have 95% confidence that the mean NO₃ leachability index is between 7.15 and 7.38 for "low" waste concentrations and that the mean NO₃ leachability index is between 7.0 and 7.3 for nominal and "high" waste concentrations. We have 95% confidence that 95% of the bracketed operating conditions will produce an NO₃ leachability index greater than 6.76, 6.54, and 6.62 for "low", nominal, and "high" waste concentrations, respectively.

Effects of Curing Temperature

The effect of curing temperatures from 8°C to 85°C on the NO₂ and NO₃ leachability indices for the 106-AN grouts was determined after curing for 28 days. Figure 13 illustrates the effect of curing temperature on the leachability indices. The leachability index for NO₂ is greater than 6 for all curing temperatures while the NO₃ leachability index is greater than 6 only at the higher temperatures. Although the two lower temperatures are not possible in the vault, they were included for comparison purposes. As seen before, the leachability indices decrease with increasing curing temperatures between 55°C and 85°C (Lokken et al. 1992c).

Comparing the leach data above for NO₂ and NO₃, it appears that the NO₃ leaches more than the NO₂. The differences could be to conversion of some NO₂ to NO₃. The concentrations of NO₂ and NO₃ in the original waste were used in the calculations, and if some conversion occurred, the leach indices would change (i.e., the NO₂ leach index would decrease and the NO₃ leach index would increase).

FIGURE 13. Effect of Curing Temperature on NO₂ and NO₃ Leachability Index of Reference 106-AN Grouts Cured for 28 days

SHRINKAGE

During curing, the grout samples exhibited linear shrinkage that averaged 1.3 vol% with a standard deviation of 0.3 vol%. These values were based on volume measurements within 42 graduated cylinders before and after curing for 28 days. The shrinkage is due to settling of the solids prior to setting. Any drainable liquids that formed were reabsorbed during the hydration process. There was no evidence that the grouts shrunk radially, i.e., pulled away from the walls of the graduated cylinders. No statistically significant additional shrinkage occurred after 28 days.

THERMAL CONDUCTIVITY

The thermal conductivity of the reference 106-AN grout was determined after curing for two months. Five replicate measurements were taken with an average value of 0.81 W/mK (0.47 BTU/h.ft.°F) and a standard deviation of 0.01 W/mK. This value is just slightly higher than the criteria of 0.45 BTU/h.ft.°F (Riebling and Fadeff 1991).

TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

The TCLP was conducted to determine whether the 106-AN grouts would be considered a characteristically hazardous waste. The reference 106-AN simulated waste was spiked with high levels of seven heavy metals. After curing for 28 days at 70°C, three samples were tested by the TCLP. Analyses of the extracts, shown in Table 10, indicate that the concentration of all species in the extract were below the regulatory limits.

CORROSIVITY

The corrosivity of three reference 106-AN grout samples was determined using the WDOE Method 83-13 (WDOE 1984). The logarithmic average pH of the three solutions was 11.6. According to this procedure, a solid is considered corrosive if the solution has a pH of less than or equal to 2, or greater than or equal to 12.5. Therefore, the reference 106-AN grout is not considered corrosive.

TABLE 10. Results of the Toxicity Characteristic Leaching Procedure on Three Reference 106-AN Grout Samples

Metal	Extract Concentration, mg/l			Regulatory Limit
	#1	#2	#3	
As	<0.05 ^(a)	<0.05	<0.05	5
Ba	0.9	0.9	0.9	100
Cr	0.02	(0.01) ^(b)	<0.01	1
Cd	0.8	0.8	0.8	5
Pb	<0.1	<0.1	<0.1	5
Se	0.2	0.2	(0.1)	1
Ag	<0.01	<0.01	<0.01	5

(a) "less than" values are analytical detection limits

(b) values in parentheses are near detection limits

EFFECT OF STARTING WASTE TEMPERATURE

Adiabatic calorimetry was conducted on grouts prepared with the nominal formulation discussed above using simulated waste starting at temperatures of 35°C to 55°C. These tests were conducted to supply information about reaction rates at various temperatures and stages of hydration for improved thermal modeling.

Figure 14 shows the calculated adiabatic temperatures of grouts prepared with starting waste temperatures of 35, 40, 45, 50, and 55°C. As expected, the magnitude of temperature rise and the rate of rise are direct functions of the starting waste temperature. The temperature of the grout made with waste heated to 55°C reached 98°C after only 50 h of hydration, whereas the samples prepared with waste heated to 35°C and 40°C had not reached 90°C after 200 h.

The initial reaction rates for these five grouts is shown in Figure 15, which depicts the rate of temperature rise for the first ten hours of hydration. The figure illustrates the effect of starting waste temperature on both the magnitude and the time at which the second major hydration peak occurs. The magnitude of the first hydration peak is impossible to determine because

the initial reactions begin when the waste and dry blend are first mixed in the Hobart blender. Therefore, some of the heat is not accounted for in these measurements because time "zero" is the time when the grout is placed into the calorimeter cell.

GAS GENERATION DURING IRRADIATION

Nine grout specimens were placed into a gas-tight stainless steel vessel as three groups of three specimens bound together with stainless steel wire. A total of five packs of radiachromic film dosimeters were attached to the stack; they were positioned to measure both longitudinal and outside-to-center dose rates. The internal volume of the system had been determined previously as 1604 cm³ by measuring gas volume released and the associated pressure drop. A type K thermocouple was centered in the vessel to measure internal temperatures and the system was connected to a calibrated pressure transducer.

FIGURE 14. Adiabatic Temperature Rise for 106-AN Grouts Prepared with Waste at Different Starting Temperatures (Note: Temperatures are corrected for Dewar heat capacity)

FIGURE 15. Rate of Temperature Rise for 106-AN Grouts Prepared with Waste at Different Starting Temperatures (Note: Values are corrected for Dewar heat capacity)

Figure 16 shows the internal vessel temperature and pressure as a function of irradiation time over the 66.2 h the specimens were irradiated. The internal vessel temperature rose to about 38°C within the first 8 h of irradiation due to the gamma heating; it remained fairly constant throughout the remainder of the time. The gas pressure inside the vessel increased only slightly during the irradiation, from a starting value of 9.42 psig to 11.14 psig. Part of this increase is attributable to the temperature increase inside the vessel, but this amounts to only 0.46 psig.

The gas composition before and after irradiation was analyzed to determine the relative amount of radiolytically produced gases. The results of these analyses are shown in Table 11. The normalized values were calculated by subtracting the argon content. Before irradiation, the normalized gas composition was that of air. After irradiation, however, significant amounts of nitrogen, hydrogen, and nitrous oxide were found.

FIGURE 16. Pressure Rise and Inside Vessel Temperature During Irradiation of 106-AN Grout Specimens

TABLE 11. Gas Composition Before and After Irradiating 106-AN Grout Samples (mole percent)

Gas	Before Irradiation		After Irradiation	
	As-Measured	Normalized	As-Measured	Normalized
Ar	98.93	-	94.08	-
O ₂	0.206	19.32	0.33	5.62
N ₂	0.85	79.74	3.523	59.98
H ₂	0	0.00	0.958	16.31
N ₂ O	0	0.00	1.063	18.10
CO ₂	0.01	0.94	-	0.00
Total	99.996	100.00	99.954	100.01

Upon disassembly of the vessel following irradiation, a yellow fluid was found. The estimated volume of this fluid was ~50 ml. At first, it was believed to be pore solution that was expelled from the grout due to internal gas pressures generated during the irradiation. However, chemical analyses of the fluid showed the concentration of sodium and NO_3 to be about 22 times lower in the fluid than would be expected if the fluid were pore solution. Further investigation into the conditions during irradiation suggested that the fluid resulted from condensation of water vapor and subsequent leaching of the grout samples at the bottom of the vessel. Expulsion of a small quantity of pore fluid cannot be ruled out, however. The internal vessel temperature was about 38°C , high enough to evaporate a significant amount of water from the grout samples. The temperature outside the vessel was about 17°C . The colder temperature of the vessel walls acted as a condensor and basically acted like a reflux condensor with the liquid collecting at the bottom the vessel. It was estimated that the depth of the liquid was 1 in.

The radiachromic dosimeters used in the first experiment were damaged by the fluid and were not readable. Another irradiation was conducted for 1 h using an empty vessel to obtain dosimetry values. The dose rate calculated from the measured dose was 1.742 Mrad/h at 3 in. off the bottom, 1.772 Mrad/h at 6 in. off the bottom, and 1.416 Mrad/h at 9 in. Assuming no significant shielding effects of the grout, the grout samples were irradiated to a dose between 0.94 and 1.17×10^8 rad, which is close to the 1×10^8 rad target.

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APPENDIX

DATA TABLES FOR 106-AN FORMULATION VERIFICATION TESTS

TABLE A1. Slurry Density and Critical Flow Rate Data for 106-AN Formulation Verification Study (Note: Table is sorted by increasing critical flow rate)

Cement, lb/gal	Fly Ash, lb/gal	Attapulgate, lb/gal	Waste, Relative Concentration	Density g/cm ³	Critical Flow Rate gpm
1.64	5.74	0.84	1.00	1.533	17.30
1.84	6.04	0.84	0.85	1.539	17.59
1.84	5.44	0.84	0.85	1.523	17.83
1.84	5.74	0.84	0.85	1.533	18.09
1.64	5.44	0.84	1.00	1.528	18.88
1.75	5.44	0.84	0.85	1.524	18.95
1.64	5.44	0.92	1.15	1.545	20.73
1.64	6.04	0.84	0.85	1.522	20.94
1.64	5.44	1.00	0.85	1.491	21.37
1.84	5.44	0.92	1.00	1.545	21.63
1.64	6.04	0.84	1.00	1.535	21.65
1.84	6.04	0.84	1.00	1.549	21.91
1.64	5.44	0.84	1.15	1.549	21.93
1.84	5.44	1.00	0.85	1.530	22.04
1.84	5.44	0.84	1.00	1.528	22.14
1.64	5.44	0.84	0.85	1.515	22.40
1.84	5.44	0.84	1.15	1.545	22.67
1.64	6.04	0.92	0.85	1.521	22.99
1.75	5.74	0.92	0.85	1.519	23.37
1.75	6.04	0.84	1.15	1.574	23.37
1.84	6.04	0.84	1.15	1.562	23.43
1.64	6.04	0.84	1.15	1.563	23.63
1.75	5.74	0.92	1.00	1.541	23.63
1.75	5.74	0.92	1.00	1.551	24.00
1.75	5.74	0.92	1.00	1.546	24.06
1.75	5.74	0.92	1.00	1.535	24.25
1.75	5.74	0.92	1.00	1.543	24.80
1.75	5.44	1.00	1.00	1.541	25.23
1.64	5.44	1.00	1.00	1.535	26.23
1.84	5.44	1.00	1.00	1.535	26.32
1.75	5.74	0.92	1.00	1.528	26.42
1.75	6.04	1.00	0.85	1.540	27.01
1.64	5.44	1.00	1.15	1.547	27.10
1.84	6.04	0.92	1.15	1.571	27.58
1.84	5.44	1.00	1.15	1.552	28.00
1.75	5.74	0.92	1.15	1.562	28.01
1.84	5.74	1.00	1.00	1.542	28.30
1.64	6.04	1.00	0.85	1.518	28.60
1.84	6.04	1.00	0.85	1.535	29.09
1.84	6.04	1.00	1.15	1.564	29.83
1.64	5.74	1.00	1.15	1.547	30.16
1.64	6.04	1.00	1.00	1.543	30.25
1.84	6.04	1.00	1.00	1.549	31.86
1.64	6.04	1.00	1.15	1.550	32.86

TABLE A2. Bulk Density and Compressive Strength Data for 106-AN Formulation Verification Study (Note: Table is sorted by increasing compressive strength)

Cement, lb/gal	Fly Ash, lb/gal	Attapulgate, lb/gal	Waste, Relative Concentration	Bulk Density, g/cm ³	Compressive Strength, psi
1.64	5.44	0.92	1.15	1.542	704
1.64	5.44	0.84	1.15	1.548	717
1.64	5.44	0.92	1.15	1.550	720
1.64	5.44	1.00	1.15	1.550	733
1.84	6.04	1.00	1.15	1.569	735
1.64	5.44	1.00	1.15	1.548	735
1.64	5.44	0.84	1.15	1.555	756
1.84	5.44	1.00	1.15	1.561	768
1.84	5.44	1.00	1.15	1.557	797
1.64	5.74	1.00	1.15	1.561	804
1.64	5.74	0.84	1.00	1.547	804
1.64	5.74	1.00	1.15	1.563	851
1.64	5.74	1.00	1.15	1.562	863
1.64	6.04	1.00	1.15	1.569	868
1.75	5.74	0.92	1.15	1.550	887
1.64	6.04	0.84	1.15	1.569	891
1.84	5.44	0.84	1.15	1.569	891
1.64	5.74	0.84	1.00	1.543	903
1.75	6.04	0.84	1.15	1.569	910
1.64	6.04	1.00	1.15	1.564	911
1.75	5.74	0.92	1.15	1.567	921
1.75	6.04	0.84	1.15	1.575	950
1.84	5.44	0.84	1.15	1.570	952
1.64	6.04	0.84	1.15	1.551	960
1.84	6.04	0.84	1.15	1.578	962
1.84	6.04	0.84	1.15	1.570	1003
1.84	6.04	0.84	1.15	1.565	1003
1.84	6.04	1.00	1.15	1.565	1003
1.64	5.44	0.84	1.00	1.548	1012
1.84	6.04	0.92	1.15	1.608	1034
1.84	5.44	0.84	1.00	1.543	1037
1.64	5.44	0.84	1.00	1.551	1043
1.84	6.04	0.92	1.15	1.580	1054
1.75	5.44	1.00	1.00	1.541	1058
1.64	5.44	1.00	1.00	1.586	1067
1.64	5.44	1.00	1.00	1.544	1082
1.75	5.44	1.00	1.00	1.551	1117
1.75	5.74	0.92	1.00	1.550	1123
1.84	5.44	0.84	1.00	1.549	1136
1.84	5.44	0.92	1.00	1.551	1146
1.75	5.74	0.92	1.00	1.551	1147
1.84	5.74	1.00	1.00	1.549	1156
1.75	5.74	0.92	1.00	1.550	1157
1.75	5.74	0.92	1.00	1.593	1159
1.75	5.74	0.92	1.00	1.548	1160
1.75	5.74	0.92	1.00	1.552	1160
1.64	6.04	0.84	1.00	1.555	1162
1.75	5.74	0.92	1.00	1.551	1165

TABLE A2. (contd)

Cement, lb/gal	Fly Ash, lb/gal	Attapulgate, lb/gal	Waste, Relative Concentration	Bulk Density g/cm ³	Compressive Strength, psi
1.84	5.44	1.00	1.00	1.553	1168
1.64	6.04	1.00	1.00	1.552	1180
1.75	5.74	0.92	1.00	1.555	1182
1.84	5.44	1.00	1.00	1.552	1183
1.84	5.44	0.92	1.00	1.546	1184
1.75	5.74	0.92	1.00	1.552	1213
1.64	6.04	0.84	1.00	1.559	1214
1.84	5.74	1.00	1.00	1.550	1214
1.75	5.74	0.92	1.00	1.556	1220
1.75	5.74	0.92	1.00	1.561	1223
1.84	6.04	0.84	1.00	1.568	1271
1.75	5.74	0.92	1.00	1.557	1275
1.64	6.04	1.00	1.00	1.553	1285
1.84	6.04	0.84	1.00	1.569	1317
1.84	6.04	1.00	1.00	1.615	1345
1.84	6.04	1.00	1.00	1.570	1367
1.64	5.44	1.00	0.85	1.359	1375
1.64	6.04	0.92	0.85	1.551	1475
1.64	5.44	1.00	0.85	1.522	1480
1.75	5.44	0.84	0.85	1.519	1489
1.84	5.44	1.00	0.85	1.532	1525
1.84	5.44	0.84	0.85	1.530	1571
1.75	5.44	0.84	0.85	1.536	1616
1.75	5.74	0.92	0.85	1.533	1626
1.84	5.44	1.00	0.85	1.537	1652
1.84	5.44	0.84	0.85	1.536	1655
1.75	5.74	0.92	0.85	1.531	1683
1.75	6.04	1.00	0.85	1.536	1811
1.64	6.04	0.84	0.85	1.540	1831
1.84	5.74	0.84	0.85	1.537	1838
1.84	5.74	0.84	0.85	1.540	1844
1.64	5.44	0.84	0.85	1.534	1852
1.64	6.04	1.00	0.85	1.514	1856
1.64	6.04	0.92	0.85	1.543	1911
1.75	6.04	1.00	0.85	1.537	1938
1.84	6.04	1.00	0.85	1.547	1947
1.64	6.04	0.84	0.85	1.543	1976
1.64	5.44	0.84	0.85	1.538	2033
1.84	6.04	1.00	0.85	1.551	2038
1.64	6.04	1.00	0.85	1.543	2071
1.84	6.04	0.84	0.85	1.549	2778
1.84	6.04	0.84	0.85	1.549	2968

TABLE A3. Comparison of Compressive Strengths of 106-AN Grout
Formulation Study Samples Before and After 90 days Immersion

Run No.	28-d(a) Curing	28-d Curing, 90-d Immersion	Percent Change
1	1553	1505	-3.1
2	1904	1839	-3.4
3	712	813	14.1
4	1027	1121	9.1
5	1356	1417	4.5
6	1693	1794	5.9
7	1964	1947	-0.8
8	923	951	3.0
9	982	1125	14.5
10	869	1089	25.4
11	1427	1334	-6.5
12	1875	1909	1.9
13	1165	1175	0.9
14	827	915	10.6
15	734	801	9.0
16	1044	1185	13.5
17	1187	1270	7.0
18	887	795	-10.4
19	1175	1015	-13.6
20	1993	1997	0.2
21	1173	1224	4.3
22	1074	1090	1.4
23	1159	1210	4.3
24	1140	905	-20.6
25	1183	1207	2.0
26	1942	1924	-0.9
27	1188	1234	3.9
28	2873	2774	-3.4
29	1087	1130	3.9
30	1185	1260	6.3
31	736	934	26.9
32	922	1006	9.2
33	1086	1227	13.0
34	1654	1707	3.2
35	1589	1542	-3.0
36	1613	1357	-15.9
37	894	959	7.2
38	930	1012	8.9
39	1233	1299	5.4
40	1841	1779	-3.4
41	782	843	7.7
42	854	881	3.1
43	1249	1332	6.6
44	1294	1414	9.3

(a) Values are average of two samples

TABLE A4. Slurry Density and Critical Flow Rate Data for 106-AN Grouts

Mix No.	Slurry Density lb/gal	Critical Flow Rate gpm	Comments
1	12.93	29.6	#1-5 are replicates, same dry blend, different grout batches made the same day
2	12.93	29.8	
3	12.82	28.3	
4	12.74	30.0	
5	12.69	29.3	
6	12.77	29.3	#6 is same as 1-5 except different batch of dry blend and made different day
7	12.90	26.0	#7 used same dry blend as #6, but different batch of waste that contained heavy metals
8	12.84	26.1	#8 same as #6
14	12.89	28.1	#14 - Engelhard attapulgate - 0-wk storage
14	12.86	27.1	#14 - Engelhard attapulgate - 0-wk storage
14	12.87	28.0	#14 - Engelhard attapulgate - 0-wk storage
15	12.79	19.7	#15 - Floridin attapulgate - 0-wk storage
15	12.83	19.6	#15 - Floridin attapulgate - 0-wk storage
15	12.84	19.6	#15 - Floridin attapulgate - 0-wk storage
16	12.76	26.5	#16 from first batch of multiple batches
19	12.76	26.2	#19 from last batch of multiple batches
20	12.81	30.2	Same dry blend as #1-5; 1 week storage time
21	12.90	28.2	Same dry blend as #1-5; 2 week storage time
22	12.89	28.2	Same dry blend as #1-5; 3 week storage time
23	12.87	25.9	Same dry blend as #1-5; 4 week storage time
26	12.93	25.9	Same dry blend as #1-5; 6 week storage time
24	12.90	25.8	#14 - Engelhard attapulgate - 2-wk storage
24	12.86	26.1	#14 - Engelhard attapulgate - 2-wk storage
24	12.89	26.2	#14 - Engelhard attapulgate - 2-wk storage
25	12.82	19.3	#15 - Floridin attapulgate - 2-wk storage
25	12.89	19.5	#15 - Floridin attapulgate - 2-wk storage
25	12.90	19.2	#15 - Floridin attapulgate - 2-wk storage
27	12.84	25.9	#14 - Engelhard attapulgate - 4-wk storage
27	12.90	25.8	#14 - Engelhard attapulgate - 4-wk storage
27	12.91	25.7	#14 - Engelhard attapulgate - 4-wk storage
28	12.88	19.2	#15 - Floridin attapulgate - 4-wk storage
28	12.82	19.3	#15 - Floridin attapulgate - 4-wk storage
28	12.89	19.4	#15 - Floridin attapulgate - 4-wk storage

Note: All grouts were made with the 21/68/11 dry blend
at a mix ratio of 8.4 lb/gal with waste preheated to 45°C

TABLE A5. Bulk Density, Compressive Strength, and Sonic Velocity Data for 106-AN Grouts

Specimen Number	Curing Temp., °C	Curing Time days	Relative Position(a)	Bulk Density g/cm ³	Compressive Strength psi	Notes
93-01-1	8	28	80	1.565	326	
93-01-1	8	28	220	1.563	319	
93-01-2	8	56	60	1.573	365	
93-01-2	8	56	190	1.577	363	
93-01-3	8	91	60	1.563	601	
93-01-3	8	91	190	1.594	601	
93-02-1	18	28	80	1.548	405	
93-02-1	18	28	220	1.538	397	
93-02-2	18	56	60	1.556	731	
93-02-2	18	56	190	1.506	701	
93-02-3	18	91	60	1.555	983	
93-02-3	18	91	190	1.556	932	
93-03-1	55	28	50	1.551	1552	
93-03-1	55	28	160	1.543	1488	
93-03-2	55	56	50	1.543	1730	
93-03-2	55	56	160	1.537	1620	
93-03-3	55	91	50	1.569	1877	
93-03-3	55	91	160	1.554	1769	
93-04-1	70	28	50	1.543	1195	
93-04-1	70	28	160	1.541	1161	
93-04-2	70	56	50	1.546	1403	
93-04-2	70	56	160	1.550	1381	
93-04-3	70	91	50	1.551	1545	
93-04-3	70	91	160	1.548	1500	
93-05-1	85	28	50	1.547	1525	
93-05-1	85	28	160	1.542	1457	

(a) Relative position is the volume mark on the graduated near the center of the specimen

TABLE A5. (contd)

Specimen Number	Curing Temp, °C	Curing Time days	Relative Position	Bulk Density g/cm ³	Compressive Strength psi	Notes
93-05-2	85	56	50	1.545	1503	
93-05-2	85	56	160	1.537	1530	
93-05-3	85	91	50	1.559	1537	
93-05-3	85	91	160	1.546	1549	
93-06-1	70	28	50	1.554	1285	
93-06-1	70	28	110	1.551	1216	
93-06-1	70	28	180	1.549	1184	
93-06-2	70	28	50	1.556	1261	
93-06-2	70	28	110	1.556	1136	
93-06-2	70	28	180	1.550	1198	
93-06-3	70	28	30	1.566	1347	
93-06-3	70	28	90	1.555	1222	
93-06-3	70	28	150	1.553	1131	
93-07-1	70	28	50	1.557	1894	TCLP
93-07-1	70	28	110	1.557	1805	TCLP
93-07-1	70	28	180	1.554	1751	TCLP
93-07-2	70	28	50	1.565	1923	TCLP
93-07-2	70	28	110	1.564	1639	TCLP
93-07-2	70	28	180	1.558	1412	TCLP
93-07-3	70	28	50	1.568	1925	TCLP
93-07-3	70	28	110	1.567	1856	TCLP
93-07-3	70	28	180	1.565	1765	TCLP
93-14-1	70	28	50	1.557	1191	Engelhard - 0 week
93-14-1	70	28	110	1.552	1161	Engelhard - 0 week
93-14-1	70	28	180	1.551	1134	Engelhard - 0 week

TABLE A5. (contd)

Specimen Number	Curing Temp. °C	Curing Time days	Relative Position	Bulk Density g/cm ³	Compressive Strength psi	Notes
93-14-2	70	28	50	1.557	1221	Engelhard - 0 week
93-14-2	70	28	110	1.556	1163	Engelhard - 0 week
93-14-2	70	28	180	1.552	1092	Engelhard - 0 week
93-14-3	70	28	50	1.553	1189	Engelhard - 0 week
93-14-3	70	28	110	1.552	1147	Engelhard - 0 week
93-14-3	70	28	180	1.550	1124	Engelhard - 0 week
93-15-1	70	28	50	1.552	1443	Floridin - 0 week
93-15-1	70	28	110	1.551	1431	Floridin - 0 week
93-15-1	70	28	180	1.547	1403	Floridin - 0 week
93-15-2	70	28	50	1.555	1992	Floridin - 0 week
93-15-2	70	28	110	1.552	2006	Floridin - 0 week
93-15-2	70	28	180	1.550	1996	Floridin - 0 week
93-15-3	70	28	50	1.553	2020	Floridin - 0 week
93-15-3	70	28	110	1.996	2032	Floridin - 0 week
93-15-3	70	28	180	1.549	1981	Floridin - 0 week
93-16-1	20/85	28/28	50	1.579	3170	Floridin - 0 week
93-16-1	20/85	28/28	160	1.561	3036	
93-18-1	55/85	28/28	50	1.551	1764	
93-18-1	55/85	28/28	160	1.561	1706	
93-20-1	70	28	50	1.537	1182	1 week storage
93-20-1	70	28	110	1.547	1161	1 week storage
93-20-1	70	28	180	1.547	1150	1 week storage
93-20-2	70	28	50	1.546	1195	1 week storage
93-20-2	70	28	110	1.545	1118	1 week storage
93-20-2	70	28	180	1.545	1159	1 week storage
93-20-3	70	28	50	1.560	1173	1 week storage
93-20-3	70	28	110	1.552	1093	1 week storage

TABLE A5. (contd)

Specimen Number	Curing Temp., °C	Curing Time days	Relative Position	Bulk Density g/cm ³	Compressive Strength psi	Notes
93-20-3	70	28	180	1.551	1039	1 week storage
93-21-1	70	28	50	1.555	1291	2 week storage
93-21-1	70	28	110	1.551	1248	2 week storage
93-21-1	70	28	180	1.550	1222	2 week storage
93-21-2	70	28	180	1.550	1227	2 week storage
93-21-2	70	28	110	1.555	1251	2 week storage
93-21-2	70	28	50	1.558	1297	2 week storage
93-21-3	70	28	50	1.559	1296	2 week storage
93-21-3	70	28	110	1.558	1272	2 week storage
93-21-3	70	28	180	1.553	1244	2 week storage
93-22-1	70	28	50	1.572	1133	3 week storage
93-22-1	70	28	110	1.566	1097	3 week storage
93-22-1	70	28	180	1.565	1073	3 week storage
93-22-2	70	28	180	1.564	1095	3 week storage
93-22-2	70	28	110	1.562	1069	3 week storage
93-22-2	70	28	50	1.559	1023	3 week storage
93-22-3	70	28	50	1.574	1136	3 week storage
93-22-3	70	28	110	1.572	1097	3 week storage
93-22-3	70	28	180	1.568	1062	3 week storage
93-23-1	70	28	50	1.571	1206	4 week storage
93-23-1	70	28	110	1.575	1178	4 week storage
93-23-1	70	28	180	1.578	1157	4 week storage
93-23-2	70	28	50	1.580	1212	4 week storage
93-23-2	70	28	110	1.546	1150	4 week storage
93-23-2	70	28	180	1.557	1147	4 week storage
93-23-3	70	28	50	1.568	1211	4 week storage

TABLE A5. (contd)

Specimen Number	Curing Temp, °C	Curing Time days	Relative Position	Bulk Density g/cm ³	Compressive Strength psi	Notes
93-23-3	70	28	110	1.555	1110	4 week storage
93-23-3	70	28	180	1.535	1080	4 week storage
93-24-1	70	28	50	1.523	1150	Engelhard - 2 week (Irradiation)
93-24-1	70	28	110	1.419	1060	Engelhard - 2 week (Irradiation)
93-24-1	70	28	180	1.463	1067	Engelhard - 2 week (Irradiation)
93-24-2	70	28	50	1.573	1227	Engelhard - 2 week (Control)
93-24-2	70	28	110	1.551	1194	Engelhard - 2 week (Control)
93-24-2	70	28	180	1.526	1175	Engelhard - 2 week (Control)
93-24-3	70	28	50	1.517	1106	Engelhard - 2 week (Irradiation)
93-24-3	70	28	110	1.427	1039	Engelhard - 2 week (Irradiation)
93-24-3	70	28	180	1.456	1018	Engelhard - 2 week (Irradiation)
93-25-1	70	28	50	1.527	1419	Engelhard - 2 week (Irradiation)
93-25-1	70	28	110	1.474	1492	Floridin - 2 week (Irradiation)
93-25-1	70	28	180	1.500	1632	Floridin - 2 week (Irradiation)
93-25-2	70	28	50	1.564	1714	Floridin - 2 week (Control)
93-25-2	70	28	110	1.557	1860	Floridin - 2 week (Control)
93-25-2	70	28	180	1.562	1918	Floridin - 2 week (Control)
93-25-3	70	28	50	1.550	1772	Floridin - 2 week (Control)
93-25-3	70	28	110	1.564	1921	Floridin - 2 week (Control)
93-25-3	70	28	180	1.567	1948	Floridin - 2 week (Control)
93-26-1	70	28	50	1.570	1087	6 week storage
93-26-1	70	28	110	1.565	1055	6 week storage
93-26-1	70	28	180	1.565	1033	6 week storage
93-26-2	70	28	50	1.579	1089	6 week storage
93-26-2	70	28	110	1.569	1056	6 week storage
93-26-2	70	28	180	1.568	1035	6 week storage

TABLE A5. (contd)

Specimen Number	Curing Temp, °C	Curing Time days	Relative Position	Bulk Density g/cm ³	Compressive Strength psi	Notes
93-26-3	70	28	50	1.615	1117	6 week storage
93-26-3	70	28	110	1.559	1063	6 week storage
93-26-3	70	28	180	1.574	1045	6 week storage
93-27-1	70	28	60	1.566	1158	Engelhard - 4 week
93-27-1	70	28	160	1.606	1110	Engelhard - 4 week
93-27-2	70	28	60	1.564	1132	Engelhard - 4 week
93-27-2	70	28	160	1.557	1078	Engelhard - 4 week
93-27-3	70	28	60	1.572	1162	Engelhard - 4 week
93-27-3	70	28	160	1.553	1099	Engelhard - 4 week
93-28-1	70	28	60	1.577	1855	Engelhard - 4 week
93-28-1	70	28	160	1.622	2069	Floridin - 4 week
93-28-2	70	28	60	1.557	2131	Floridin - 4 week
93-28-2	70	28	160	1.555	2063	Floridin - 4 week
93-28-3	70	28	60	1.551	2220	Floridin - 4 week
93-28-3	70	28	160	1.547	2138	Floridin - 4 week
93-29-1	(a)	28	50	1.558	1846	Vault temperature conditions
93-29-1	(a)	28	160	1.559	1745	Vault temperature conditions
93-29-2	(a)	28	50	1.562	1814	Vault temperature conditions
93-29-2	(a)	28	160	1.567	1786	Vault temperature conditions
93-30-1	(b)	28	50	1.558	2142	Vault temperature conditions
93-30-1	(b)	28	160	1.563	2097	Vault temperature conditions
93-30-2	(b)	28	50	1.555	2111	Vault temperature conditions
93-30-2	(b)	28	160	1.565	2083	Vault temperature conditions

(a) Cured according to top curve in Figure 5 (8 lifts, 515 hr between lifts)

(b) Cured according to bottom curve in Figure 5 (48 lifts, 97 hr between lifts)

TABLE A6. Average NO₂ and NO₃ Leachability Indices for 106-AN Grout Formulation Verification Study

Cement, lb/gal	Fly Ash, lb/gal	Attapulgate, lb/gal	Waste, Relative Concentration	LiNO ₂	LiNO ₃
1.64	5.44	0.84	0.85	8.3	7.5
1.84	5.44	0.84	0.85	8.2	7.5
1.64	6.04	0.84	0.85	7.6	6.9
1.84	6.04	0.84	0.85	7.8	7.1
1.64	5.44	1.00	0.85	8.0	7.2
1.84	5.44	1.00	0.85	8.2	7.4
1.64	6.04	1.00	0.85	8.2	7.4
1.84	6.04	1.00	0.85	7.8	7.2
1.64	5.44	0.84	1.00	7.6	7.0
1.84	5.44	0.84	1.00	7.7	7.1
1.64	6.04	0.84	1.00	8.3	7.5
1.84	6.04	0.84	1.00	8.2	7.5
1.64	5.44	1.00	1.00	7.7	7.0
1.84	5.44	1.00	1.00	7.7	7.0
1.64	6.04	1.00	1.00	7.6	6.9
1.84	6.04	1.00	1.00	7.6	7.0
1.64	5.44	0.84	1.15	7.9	7.1
1.84	5.44	0.84	1.15	7.7	7.0
1.64	6.04	0.84	1.15	7.8	7.0
1.84	6.04	0.84	1.15	8.2	7.5
1.64	5.44	1.00	1.15	7.9	7.1
1.84	5.44	1.00	1.15	7.8	7.0
1.64	6.04	1.00	1.15	7.9	7.1
1.84	6.04	1.00	1.15	7.8	7.1
1.75	5.74	0.92	0.85	8.1	7.4
1.75	5.74	0.92	1.00	8.3	7.5
1.75	5.74	0.92	1.15	8.1	7.4
1.75	5.74	0.92	1.00	7.7	7.0
1.75	5.74	0.92	1.00	7.8	7.1
1.75	5.74	0.92	1.00	7.9	7.2
1.75	5.74	0.92	1.00	7.6	6.9
1.75	5.74	0.92	1.00	7.5	6.9
1.75	5.44	0.84	0.85	7.8	7.1
1.75	5.44	1.00	1.00	8.2	7.5
1.75	6.04	0.84	1.15	8.3	7.5
1.75	6.04	1.00	0.85	8.2	7.5
1.64	5.74	0.84	1.00	7.6	6.9
1.64	5.74	1.00	1.15	7.6	7.0
1.84	5.74	0.84	0.85	8.0	7.3
1.84	5.74	1.00	1.00	8.3	7.4
1.64	5.44	0.92	1.15	7.5	6.8
1.64	6.04	0.92	0.85	7.8	7.1
1.84	5.44	0.92	1.00	7.9	7.2
1.84	6.04	0.92	1.15	8.1	7.3

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