# THE EFFECT OF USING DIFFERENT SOURCES OF DRY MATERIALS ON WASTE-FORM GROUT PROPERTIES

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## ABSTRACT

A reference grout formulation had been developed for a liquid low-level radioactive waste using the following dry materials: ground limestone, ground granulated blast furnace slag, fly ash, and cement. The effect of varying the sources of these dry materials was tested. Two limestones, two fly ashes, two cements, and eight slags were tested. Varying the source of dry materials significantly affected the grout properties, but only the 28-d free-standing liquid varied outside of the preferred range. A statistical technique, Tukey's paired comparison, can be used to ascertain whether a given combination of dry materials resulted in grout properties significantly different from those of other combinations of dry materials.

## INTRODUCTION

Stabilization/solidification (S/S) technology is one of the most widely used techniques for the treatment and disposal of both radioactive and chemically hazardous wastes. Cementitious products, commonly referred to as grouts, are the predominant materials of choice because of their associated low processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements. This technology is being used to dispose of caustic aqueous solutions of low-level radioactive waste at Department of Energy (DOE) sites. The waste solution is mixed with a dry-solids blend and pumped through a few thousand feet of pipe into an underground concrete vault. Thus, the rheology of the freshly mixed grout, as well as the final cured properties, were of interest for this study. The reference grout formulation developed for this application consisted of a dry-solids blend with 40, 28, 28, and 4 wt %, respectively, of ground limestone, ground granulated blast furnace slag (GGBFS), Class F fly ash, and Type II-LA Portland cement. This paper reports that varying the source of the dry solids significantly affected the properties of interest and describes which properties varied outside the preferred range.

## GROUT PROPERTIES OF INTEREST

The grout properties of interest measured in the laboratory were critical flow rate, 10-min gel strength, 28-d free-standing liquid, 28-d unconfined compressive strength, and nitrate leachability index. The critical flow rate was defined as the flow rate necessary for a Reynold's number of 2100. The Reynold's number was that for a non-Newtonian fluid. The grout was assumed to be a simple power-law fluid and the power-law model equations were used to calculate the critical flow rate from Fann viscometer measurements of the shear stress at different shear rates. For the existing pump, pipelines, and grout facility, the critical flow rate is preferred to be less than 3.79 L/s (60 gal/min).

The 10-min gel strength was the force necessary to break the grout gel loose from the Fann viscometer wall after sitting quiescent for 10 min. The 10-min gel strength was preferred to be less than 47.9 Pa (100 lb/100 $ft^2$).

The 28-d free-standing liquid was the volume of liquid that could be drained or siphoned from a sample after curing for 28 d relative to the initial volume (0.00025 $m^3$ or 250 mL) of grout. The 28-d free-standing liquid was preferred to be less than 5 vol %.

The 28-d unconfined compressive strength was the unconfined compressive strength of the blocks of grout cast into 2-in. cube molds and cured for 28 d. Since some solids settling occurred, leaving free-standing liquid, the blocks were not perfect 2-in. cubes, but the actual area compressed was measured for calculating the unconfined compressive strength. The 28-d unconfined compressive strength was preferred to be greater than 0.414 MPa (60 psi).

The nitrate leachability index was a measure of the leach resistance of the cured waste forms and was defined as the negative logarithm of the effective diffusion coefficient in units of $cm^2/s$. The index was estimated for samples that had been cured 28 d and leached using a modified ANSI/ANS-16.1-1986 procedure (1). The nitrate leachability index was preferred to be less than 6.

## EXPERIMENTAL

A surrogate waste solution made in the laboratory was used to mix the grouts. This surrogate waste solution consisted of an aqueous solution of 0.421, 0.031, 0.15, 0.0081, 0.002, 0.675, 1.29, 0.758, 0.382, 0.019, 0.0044, 0.042, 0.155, and 0.03 *M*, respectively, of sodium aluminum hydroxide, sodium sulfate, sodium chloride, sodium fluoride, calcium nitrate, sodium hydroxide, sodium nitrate, sodium nitrite, sodium carbonate, n-(2-hydroxyethyl)ethylenedinitrilotriacetic acid (HEDTA), tetrasodium salt of ethylenediaminetetraacetic acid (EDTA), glycolic acid, sodium phosphate, and sodium citrate. This solution was a surrogate of the supernatant from one of the tanks of waste at a DOE site.

The four dry powders were blended for 23 h in a laboratory V-blender. The surrogate was heated to 50°C and then mixed with the dry blends using a Hobart mixer with a wire whisk. The rheology, density, and 10-min gel strength of the freshly mixed grouts were measured. The fluid grouts were poured into plastic graduated cylinders for the free-standing liquid measurements, 5.1-cm (2-in.) cubical molds for the compressive strength measurements, and 2.51-cm diam. by 4.65-cm high cylindrical molds for leachability index measurements and cured for 28 d at 50°C under humid conditions. One rheology measurement, one density measurement, one 10-min gel- strength measurement, three free-standing liquid measurements, and three unconfined compressive strength measurements were made for each grout mixed for the matrix of dry solids from different sources and varied in composition to test field variability of blending and mixing. Three leachability index measurements were made for each matrix grout, but only with the reference composition.

The modifications to the ANSI/ANS-16.1-1986 5-d procedure consisted of using double-distilled water as the leachant, leaching for 72 h during the last interval for a total of 7 d of semi-dynamic leaching, and using an integral technique to estimate the effective diffusion coefficient (2). Details of the experimental equipment, procedures, and results can be found in the laboratory reports (3,4).

## SOURCES OF DRY MATERIALS

All of the dry blends consisted of the following four dry powders: Type II-LA Portland cement, Class F fly ash, ground limestone, and GGBFS. Cement was obtained from two sources, Ash Grove Cement West, Inc., and Lafarge Corp. Fly ash was obtained via Pozzolanic International from two coal-burning power plants, Jim Bridger and Centralia. Two different grindings of limestone-titled "ground limestone" and "limestone flour"-were obtained from Ash Grove Cement West, Inc. The particle size distribution of these two grindings were similar with the former being slightly more coarse than the latter. The following eight different GGBFS were obtained either from different sources or as different grinds from the same source.

| Sources of GGBFS | Blaine Fineness, $m^2$/kg |
|---|---|
| The Standard Slag Co.<br>(Std Slag) | 518 & 627 |
| Ash Grove Cement West, Inc.<br>(Ash Grove) | 567 |
| Blue Circle Atlantic, Inc.<br>(Blue Circle) | 402 & 566 |
| C. T. Takahashi & Co., Inc.<br>(Takahashi) | 428 |
| Standard Slag Cement<br>(Slag Cement) | 419 & 592 |

## COMBINATIONS IN BLENDS

The grouts selected tested both the effect of varying the source of the dry powders and the normal variation in grout composition expected during field operation. To do this, thirteen different combinations of the above dry powders were used in matrices of blends. Each matrix consisted of the same composition and was a quarter factorial for the following five variables: blend weight percent of cement, fly ash, ground limestone, and GGBFS and mix ratio of mass of blend to volume of surrogate. Each matrix tested the variation in grout composition and the different matrices tested the variation in dry materials source. Table I lists the grout compositions used for each matrix and Table II lists the sources of dry materials.

## RESULTS AND DISCUSSION

Table III summarizes the results by listing the means of the critical flow rates, 10-min gel strengths, 28-d free-standing liquids, and 28-d unconfined compressive strengths for all of the grout mixes tested in each matrix, including replicates. The nitrate leachability index was measured in triplicate for the reference grout formulation of each matrix, but not for the quarter factorial set of grout formulations. The means of these triplicate measurements are listed in Table III. The 95% confidence limits of these means are given inside of parentheses with the means in Table III. The upper or lower 95% confidence limits were obtained by simply adding or subtracting, respectively, the value in parentheses to/from the mean, giving a two-tailed interval.

To test the hypothesis that the grout properties for a given matrix were in the preferred range, the mean added to the value in parentheses for the critical flow rate, 10-min gel strength, and 28-d free-standing liquid would have to be less than the preferred upper limits of 3.79 L/s, 47.9 Pa, and 5 vol %, respectively; and the mean subtracted by the value in parentheses for the 28-d unconfined compressive strength and nitrate leachability index would have to be greater than the preferred lower limits of 0.414 MPa and 6.0, respectively. This was a single-tailed hypothesis test, meaning that using the values in parentheses in Table III gave 97.5% of a t-distribution above or below the calculated value; in other words, a

TABLE I

Grout Compositions for Each Matrix

| Mix No. | Dry blend composition (wt %) | | | | Mix ratio $(kg/m^3)$ |
|---|---|---|---|---|---|
| | Limestone | Fly ash | GGBFS | Cement | |
| 1 | 39.6 | 27.8 | 27.8 | 4.8 | 1020 |
| 2 | 37.7 | 26.4 | 32.2 | 3.8 | 1139 |
| 3 | 37.7 | 32.2 | 26.4 | 3.8 | 1139 |
| 4 | 35.3 | 30.2 | 30.2 | 4.3 | 1020 |
| 5 | 44.5 | 25.5 | 25.5 | 4.5 | 1139 |
| 6 | 42.5 | 24.4 | 29.7 | 3.5 | 1020 |
| 7 | 42.5 | 29.7 | 24.4 | 3.5 | 1020 |
| 8 | 40.0 | 28.0 | 28.0 | 4.0 | 1139 |
| 9[a] | 40.0 | 28.0 | 28.0 | 4.0 | 1080 |

[a] Reference grout formulation

**TABLE II**

Dry materials Source for the Matrices

| Matrix No. | Limestone | Fly ash | GGBFS[a] | Cement |
|---|---|---|---|---|
| 1 | Flour | Centralia | Ash Grove (567) | Ash Grove |
| 2 | Flour | Centralia | Blue Circle (402) | Ash Grove |
| 3 | Flour | Centralia | Blue Circle (566) | Ash Grove |
| 4 | Flour | Centralia | Std. Slag (518) | Ash Grove |
| 5 | Flour | Centralia | Std. Slag (627) | Ash Grove |
| 6 | Flour | Centralia | Slag Cement (592) | Ash Grove |
| 7 | Flour | Bridger | Slag Cement (592) | Ash Grove |
| 8 | Flour | Bridger | Std. Slag (627) | Ash Grove |
| 9 | Flour | Bridger | Slag Cement (419) | Ash Grove |
| 10 | Ground | Centralia | Std. Slag (518) | Ash Grove |
| 11 | Ground | Bridger | Slag Cement (419) | Ash Grove |
| 12 | Flour | Centralia | Ash Grove (567) | Lafarge |
| 13 | Flour | Centralia | Takahashi (428) | Lafarge |

[a] Blaine fineness ($m^2/kg$) in parentheses for GGBFS.

97.5% level of confidence that the mean lay above or below the given value. This hypothesis test made it clear that all of the grout properties, except free-standing liquid, were well within the preferred range regardless of the source of dry materials or variation in composition.

Matrices 1 and 3 were not included in the estimation of either the F-ratios or the Q-values listed in Table III, because the surrogate used to make these grouts appeared different. A difference in the surrogate may have contributed to the observed variance in grout properties for these two matrices. Including these two matrices may have led to incorrect conclusions about the effect of varying the source of dry materials.

The hypothesis that varying the source of dry materials causes a significant variation in the grout properties is accepted using the Table III F-ratios in the F-test of the analysis of variance technique. The F-ratio is the ratio of the variance between matrices to the variance within the matrices (5). The F-ratios in Table III can be compared to the F-values with the same degrees of freedom compiled in statistical tables at different levels of confidence. The degrees of freedom were 2 and 12 for the leachability index and 8 and 10 for the other grout properties. The F-values for these degrees of freedom at a 99.9% level of confidence were 12.97 and 9.20, respectively. Thus, the hypothesis that varying the source of dry materials causes significant variation in the grout properties is accepted with greater than a 99.9% level of confidence.

Significant variation between any two matrices was tested using Tukey's paired comparison procedure (5). The Q-values in Table III were calculated using this procedure, excluding Matrices 1 and 3. If the means of two matrices differed by more than the Q-value, then the two means were significantly different with a 95% level of confidence. Thus, it can be tested whether the change in dry materials source between two matrices led to a significant change in grout properties. For example, the critical flow rate, 10-min gel strength, 28-d free-standing liquid and 28-d unconfined compressive strength differed significantly between Matrices 2 and 6. The only difference between these two matrices was the source and fineness of the GGBFS, 402 $m^2/kg$ from Blue Circle for Matrix 2 and 592 $m^2/kg$ from Slag Cement for Matrix 6. Matrices 4 and 5 had no significant differences in grout properties between them. The only difference between these two matrices was the fineness of the GGBFS (518 $m^2/kg$ for Matrix 4 and 627 $m^2/kg$ for Matrix 5) both from Standard Slag.

In summary, changing the source of dry materials had a significant effect on the grout properties, but only the free-standing liquid varied outside the preferred range. All of the other properties were well within their preferred ranges, notwithstanding the significant effects caused by changing the dry-materials source. Only three-Matrices 1, 6, and 7- passed the t-test hypothesis of having 28-d free-standing liquid of less than 5.0 vol %. The surrogate used in Matrix 1 had an abnormal appearance. Since it was not clear whether a difference in the surrogate for Matrix 1 contributed to its superior 28-d free-standing liquid performance, the Matrix 1 results were not used for evaluating dry materials source effects. Matrices 6 and 7 used the 592 $m^2/kg$ GGBFS from Slag Cement, and none of the other matrices used this particular GGBFS. It is not clear from the data why this particular GGBFS gave such good results. All of the other dry materials used in these two matrices were tested in the other matrices without success. Also, a finer ground GGBFS (627 $m^2/kg$) from Standard Slag was tested and another grind (419 $m^2/kg$) of GGBFS from Slag Cement was tested, neither one resulting in acceptable 28-d free-standing liquids.

Not surprisingly, finer powders do appear to give better free-standing liquid performance, but the effect appears weak compared to the observed variation in results. It would be a mistake to attach too much importance to the performance of this one GGBFS. For example, the reference grout formulation (Mix 9 in Table I) results for Matrices 6 and 7 gave 28-d free-standing liquid means (and 95% confidence limits) of 4.7 (± 2.0) and 3.5 (± 1.5) vol %, respectively. The t-test hypothesis of being significantly less than 5 vol % would not be accepted for either of these.

TABLE III

Means and Statistics of the Measured Properties

| Matrix No. | Means (95% confidence limits) | | | | |
|---|---|---|---|---|---|
| | Critical flow rate (L/s) | 10-min gel strength (Pa) | 28-d Free-Standing Liquid (vol %) | 28-d unconfined Compressive Strength (MPa) | Nitrate Leachability Index[a] |
| 1 | 0.92 | 3.06 | 3.6 | 2.97 | 8.8 |
| | (0.04) | (0.24) | (0.6) | (0.10) | (0.05) |
| 2 | 0.86 | 1.87 | 9.1 | 2.41 | 8.5 |
| | (0.03) | (0.14) | (1.2) | (0.07) | (0.5) |
| 3 | 0.95 | 7.37 | 9.5 | 2.56 | 8.6 |
| | (0.03) | (0.86) | (1.4) | (0.08) | (0.3) |
| 4 | 0.95 | 2.63 | 5.8 | 2.99 | 8.9 |
| | (0.03) | (0.19) | (1.2) | (0.13) | (0.1) |
| 5 | 1.01 | 2.63 | 4.7 | 2.93 | 8.7 |
| | (0.03) | (0.19) | (0.9) | (0.12) | (0.2) |
| 6 | 1.03 | 2.68 | 3.1 | 3.26 | 8.8 |
| | (0.04) | (0.24) | (0.8) | (0.14) | (0.1) |
| 7 | 1.08 | 2.82 | 2.8 | 2.60 | 8.3 |
| | (0.03) | (0.19) | (0.8) | (0.12) | (0.08) |
| 8 | 1.04 | 2.82 | 5.1 | 2.66 | 8.4 |
| | (0.03) | (0.72) | (0.8) | (0.13) | (0.2) |
| 9 | 0.99 | 2.20 | 7.0 | 2.68 | 7.8 |
| | (0.03) | (0.19) | (0.8) | (0.09) | (0.2) |
| 10 | 0.97 | 1.87 | 8.2 | 2.97 | 8.3 |
| | (0.03) | (0.10) | (0.9) | (0.17) | (0.2) |
| 11 | 0.95 | 1.96 | 8.1 | 3.99 | 7.9[a] |
| | (0.02) | (0.19) | (0.6) | (0.28) | (0.1) |
| 12 | 0.99 | 3.35 | 4.5 | 3.63 | 8.3 |
| | (0.03) | (0.34) | (0.5) | (0.11) | (0.08) |
| 13 | 0.94 | 2.39 | 8.0 | 2.96 | 8.2 |
| | (0.03) | (0.19) | (0.8) | (0.11) | (0.09) |
| F-ratio[b] | 18.1 | 10.7 | 21.9 | 14.2 | 26.3 |
| Q-value[b] | 0.06 | 0.65 | 2.0 | 0.57 | 0.8 |

[a] The leachability index was measured for the reference grout formulation in triplicate, but not for the entire matrix.
[b] Calculated excluding Matrices 1 and 3.

It is possible that finely ground (about 600 $m^2/kg$) GGBFS from Slag Cement would enable the free-standing liquid to fall within the preferred range, but it is not known what makes the Slag Cement GGBFS special and, therefore, what to specify to guarantee performance. It is also possible that there is nothing special about the Slag Cement GGBFS, that the observed performance was a fluke within the normal performance variation and cannot be reproduced; or, that interaction with other dry materials might be important.

Despite the apparent success of these two matrices, it is obvious that the reference grout formulation had problems attaining the desired free-standing liquid performance. At present, there are no dry-materials specifications that can be made to guarantee the desired performance. Certainly, specifying the finest grinds of these dry materials will improve their free-standing liquid performance.

## CONCLUSIONS

Changing the source of dry materials significantly affected the properties of the grout formulation. The resulting variation in grout properties was well within the preferred range, even taking into account the composition variation expected during field operation, for critical flow rate, 10-min gel strength, 28-d unconfined compressive strength, and nitrate leachability index. The grout formulation had trouble attaining the desired 28-d free-standing liquid performance, although one GGBFS in two combinations of dry materials apparently did. It was not clear why this GGBFS succeeded where the others failed. The Tukey paired comparison technique can be used to determine which changes in dry materials source were significant.

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## REFERENCES

1. ANSI/ANS-16.1-1986, "An American National Standard, Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure," American Nuclear Society, 555 North Kensington Avenue, La Grange Park, Illinois 60525 (April 1986).
2. C. W. NESTOR, JR., H. W. GODBEE, and D. S. JOY, "NEWBOX: A Computer Program for Parameter Estimation in Diffusion Problems," ORNL/TM-10910, Oak Ridge National Laboratory (in preparation).
3. T. M. GILLIAM, S. C. OSBORNE, C. L. FRANCIS, and T. C. SCOTT, "Evaluation of Dry-Solids-Blend Material Source for Grouts Containing 106-AN Waste: September 1990 Progress Report," ORNL/TM-11867, Oak Ridge National Laboratory (in preparation).
4. R. D. SPENCE, T. M. GILLIAM, S. C. OSBORNE, C. L. FRANCIS, and D. R. TROTTER, "Evaluation of Dry-Solids-Blend Material Source for Grouts Containing 106-AN Waste: Final Report," ORNL/TM-11785, Oak Ridge National Laboratory (in preparation).
5. G. E. P. BOX, W. G. HUNTER, and J. S. HUNTER, Chapter 6 in *Statistics for Experimenters*, John Wiley & Sons, Inc., New York, (1978).