DEVELOPMENT OF A CEMENT-BASED GROUT FOR IMMOBILIZATION OF A LOW-LEVEL WASTE STREAM CONTAINING SODIUM SULFATE

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ABSTRACT

The use of cement-based grouts for immobilizing low-level liquid wastes has proven to be an economical and environmentally acceptable means of disposal. Formulation of grouts for such use often requires extensive research and development efforts. This paper discusses one of the methodologies currently being used by engineers at Oak Ridge National Laboratory. This approach uses statistical methods such as extreme vertices design and mixture experimental design to reduce development time and effort.

INTRODUCTION

Engineers in the Grout Technology Development Group (GTDG) at Oak Ridge National Laboratory (ORNL) have developed grout formulas for the immobilization of various waste streams. A unique approach to grout formulation, using statistical methods such as extreme vertices design and mixture experimental design, became the foundation for this developmental work. Using this approach, efforts were concentrated on immobilization of a waste stream containing sodium sulfate. This waste stream, which is approximately 0.03 M in sodium sulfate, is produced by the regeneration of ion-exchange resins that are used by commercial power plants and federal government facilities to treat contaminated wastewater before it is discharged to the environment. Development of a viable grout formula that would meet all pertinent criteria, processing, and regulatory requirements necessitated extensive experimental work. Thus, the work was divided into two phases: preliminary development and final process development.

The objective of the first phase of experimental work was to identify the principal components of the dry blend used to produce the grout. The components must be commercially available and should require little, or no, custom processing. Once the principal components were identified, the proper proportioning of dry-blend material to waste was investigated. After establishing these bounds, the final process development work was initiated.

The second phase of the work was focused on finding exact variations in the preliminary grout formula that could be used and still produce a grout that would meet all of the criteria. Statistical methodologies, such as extreme vertices design and mixture experimental design, were used in determining the boundary conditions. After completion of the experimental work and analysis of the data, a grout formula was developed for use in the immobilization of sodium sulfate waste streams. The chosen grout formula is processible, and the resulting waste form will meet current regulatory criteria. The statistical data that were acquired illustrate compliance with the regulatory criteria.

PERFORMANCE CHARACTERISTICS FOR AN ACCEPTABLE GROUT

A successful grout formulation for the 0.03 M sodium sulfate waste stream is defined as one that meets all pertinent regulatory and processing criteria. The following criteria were established for evaluation of grouts produced in this study and are very specific; it should be noted, however, that grouts can be formulated to meet a variety of criteria:

- No more than four dry-blend components can be used.
- The reference formula must be able to pass all criteria for $\pm 5\%$ relative variation for all dry-blend materials.
- The reference formula mix ratio must be ≤ 1.02 kg/L.
- The reference formula must be able to pass all criteria for a ± 0.06 kg/L variation in mix ratio.
- No more than three additives can be used in the reference formula.
- Maximum additive flow rate must be $\leq .03$ L/s.
- Frictional pressure drop must be ≤ 2.5 kPa per meter of 5-cm schedule 40 pipe.
- The grout must be able to achieve turbulent flow at rates ≤ 3.8 L/s.
- Maximum 10-min gel strength must be ≤ 47.9 Pa.
- Compressive strength ≥ 414 kPa using ASTM Test C109-80.
- Drainable liquid volume must be vol $\leq 5\%$ after 28 d in a closed laboratory test vessel.
- ANS 16.1 Leachability Index must be ≤ 6 for selected radionuclides.

CRITERIA FOR MATERIALS USED IN GROUT DEVELOPMENT

The ratio of dry-solids blend to waste is a key variable in the formulation studies. Experience has shown that if all criteria are met at mix ratios A and B, then any mix-blend variation between the two would also meet the criteria. Testing of various blending operations has shown that ratios can be controlled to within ±0.06 kg/L. Consequently, the increment in the mix ratio was 0.12 kg/L in the initial formulation studies. Also, the lower and upper bounds of acceptable ratios would have to vary 0.06 kg/L from the recommended value. For example, if the lower and upper bounds of acceptable mix ratios were determined to be 0.84 and 0.96 kg/L, respectively, then the recommended mix ratio would be 0.90 kg/L.

It is realistic to expect that the blended bulk solids would not be prepared at precisely the recommended formula in plant operations. The recommended reference formula would be such that a ±5% relative variation in the dry-solids blend components could be tolerated. With these deviations in dry-blend composition, an acceptable grout formula would continue to meet all other performance requirements.

Dry-Blend Components

The processing criteria state that no more than four dry materials can be used in a dry blend. These components consist of Portland cement, ASTM class F fly ash, Attapulgite-150 drilling clay, and Indian Red pottery clay (IRPC). The dry-blend components chosen are readily and commercially available.

An acceptable grout must have certain physical properties that meet or exceed performance criteria. Physical properties of the hardened and the wet grout are partially determined by the amount of cement in the blend. The amount of cement used is typically described in the waste/cement ratio (w_s/c). In general, a w_s/c of only 0.25 is required for complete hydration of Portland cement, with additional water serving to fluidize the mix, making it more readily processible. Cement serves as a binder, and materials are bound by cement during the formation of hydration products within the waste form. Hydration occurs over a period of time and produces a solid matrix of material.

Although several types of Portland cement are available, only Types I, II, and III were chosen for use in this study. Type III cement was ultimately chosen for use with this particular waste stream because it reduced the amount of drainable liquid.

IRPC is added solely as an ion-exchange medium, primarily to retain ^{137}Cs. With an exchange capacity of 0.1 meq ^{137}Cs per gram of clay, little clay should be needed (1,2,3). However, experience at the ORNL facility has shown that the pottery clay content of the dry-solids blend needs to be 8 wt % to ensure intimate contact with the ^{137}Cs. In addition, minor variations (±5%) in the pottery clay content have been shown to have a negligible impact on the rheological properties of the grout.

Fly ash is a cement extender, and its use should be maximized because of its low cost. The addition of fly ash improves the fluid properties of the grout and the adsorption of water; it also decreases the leachability of strontium by incorporating it into the cementitious matrix.

Attapulgite-150 is added primarily to reduce drainable water from the product. However, previous ORNL grout-development experience has shown that when this material is present at concentrations ≤0.08 kg/L of water (waste), it appears to reduce the leachability of the product. Consequently, our formulation-development studies attempted to maintain the Attapulgite-150 content at or above this value. Attagel, a trade name for Attapulgite-150, was used in this study.

Tributyl phosphate (TBP), a defoaming agent that helps reduce the entrainment of air in the grout during mixing, was added to the waste before the dry-solids blend was added. The TBP was added at 0.04 vol % of the liquid waste, a flow rate less than that stipulated by the criteria.

TEST RESULTS AND ANALYSIS

The initial phase of this work concentrated on the establishment of upper and lower bounds for the dry materials as well as the mix ratio. Table I shows the initial blends studied. The amounts of each dry material used in this preliminary study were based on both experience and standard statistical techniques (4,5,6). The acceptability of a grout mixture was defined in the previous section, and the following discussion concentrates on factors affecting each of the performance criteria. All grouts produced during the preliminary study and the experimental design passed the compressive strength criteria. Because these criteria presented no problem to formulation, further discussion is restricted. The major criteria of concern are those involving processibility, which include critical flow rate, 10-min gel strength, and frictional pressure drop. The amount of drainable water is another important criterion. The effects of both mix ratio and dry-material content on each of the criteria are discussed. These effects are described in greater detail in another publication (7).

Factors Affecting Critical Flow Rate

The first factor affecting critical flow rate is the speed at which the grout must be pumped to achieve turbulent flow.

Qualitatively speaking, each blend component affects the response in varying degrees and direction. Generally, increasing the amount of cement or attapulgite resulted in

TABLE I

Dry-Solids Blend Variations for Sulfate Waste[a]

Material	Amount (wt %), blend number								
	1	2	3	4	5	6	7	8	9
Cement, Type III	40	40	40	45	45	45	50	50	50
Fly ash, class F	38	38	38	33	33	33	28	28	28
Attapulgite-150	16	14	12	16	14	12	16	14	12
IRPC[b]	6	8	10	6	8	10	6	8	10

[a]Mix ratios studied: 0.84, 0.96, and 1.08 kg/L.
[b]IRPC = Indian Red pottery clay.

an increase in the critical flow rate. The cement appeared to have a more pronounced effect, and the amount of fly ash had the opposite effect. The critical flow rate increased as the amount of fly ash decreased; this response was consistent with the fact that fly ash can improve the fluidity of the grout. The addition of IRPC appeared to have the least effect on critical flow rate.

Factors Affecting 10-min Gel Strength

The 10-min gel strength is a measure of the force necessary to restart grout flow after a stagnant period of time. The majority of grouts produced during this experimental design passed this criterion, and the principal controlling component appeared to be the cement. Increasing the amount of cement generally increased the 10-min gel strength. This would be expected since the cement was undergoing hydration. The other three components appeared to have only a slight effect on this particular response. Both the fly ash and the attapulgite contents appeared to have a slight inverse effect on the 10-min gel strength.

Factors Affecting Drainable Water

The drainable water criteria was the most troublesome area in this development study. It appeared that there were two controlling components, cement and fly ash, for this response; however, their effects were in opposing directions. An increase in cement content appeared to decrease the amount of drainable water, whereas an increase in fly ash content appeared to increase the amount of drainable water. Decreasing the amount of attapulgite had a slight effect on increasing the amount of drainable water, and the IRPC appeared to have an insignificant effect on the drainable water. These trends are general and were investigated further in the final development work.

EXPERIMENTAL DESIGN

The results of the previously discussed experimental matrix indicated that an acceptable grout could be produced at cement contents of 45 to 50 wt %.

A matrix of experiments was then set up to develop a reference formula for the sulfate waste. This matrix (Table II) was performed in triplicate, and the results for both phases of this work were summarized in another publication (7).

TABLE II

Experimental Matrix for 100% Sulfate Waste Formulation[a]

Material	Amount (wt %), blend number		
	10	11	12
Cement, Type III	44.5	47.0	49.5
Fly ash, class F	34.5	30.0	25.5
Attapulgite-150	14	15	16
IRPC[b]	7	8	9

[a]Mix ratios = 0.96, 1.02, and 1.08 kg/L.
[b]IRPC = Indian Red pottery clay.

Drainable water was a problem area, as it was in the previous matrix. However, the grouts produced using the sulfate waste were acceptable throughout the matrix. As such, the data were analyzed and a reference formula was developed. The reference formula follows:

Portland cement, Type III	47 ± 2.5 wt %
Class F fly ash,	30 ± 2.5 wt %
Centralia, Washington	
Attapulgite-150	15 ± 4.5 wt %
IRPC	8 1.0 wt %
Mix ratio	0.96 ± 0.06 kg/L

The mix ratio from the three blends (10, 11, and 12) was treated as a single, independent variable with the variations in blend components considered unknown. For example, at a mix ratio of 0.90 kg/L, for blends 10, 11, and 12, the nine mixes (each mix performed in triplicate) were combined and the mean was determined. The mean for the 0.90-kg/L mixes was then plotted along with the 95% confidence interval. This method assumes that if the reference formula is being used, then uncontrollable variations in the blend composition are taken into consideration for production of an acceptable grout. Figures 1 through 4 show the results of this matrix of experiments.

The variety of responses and process variables studied do not lend themselves well to analysis. Because the true variance of the population of data is not known and the variance of a random sample of size n fluctuates considerably, the distribution of the random variable $(X-u)/(S/n^{1/2})$ is no longer a standard normal distribution. Recognition of this fact forces one to deal with the distribution of a statistic called T, where

$$T = \frac{\bar{X} - u}{S / n^{\frac{1}{2}}}$$

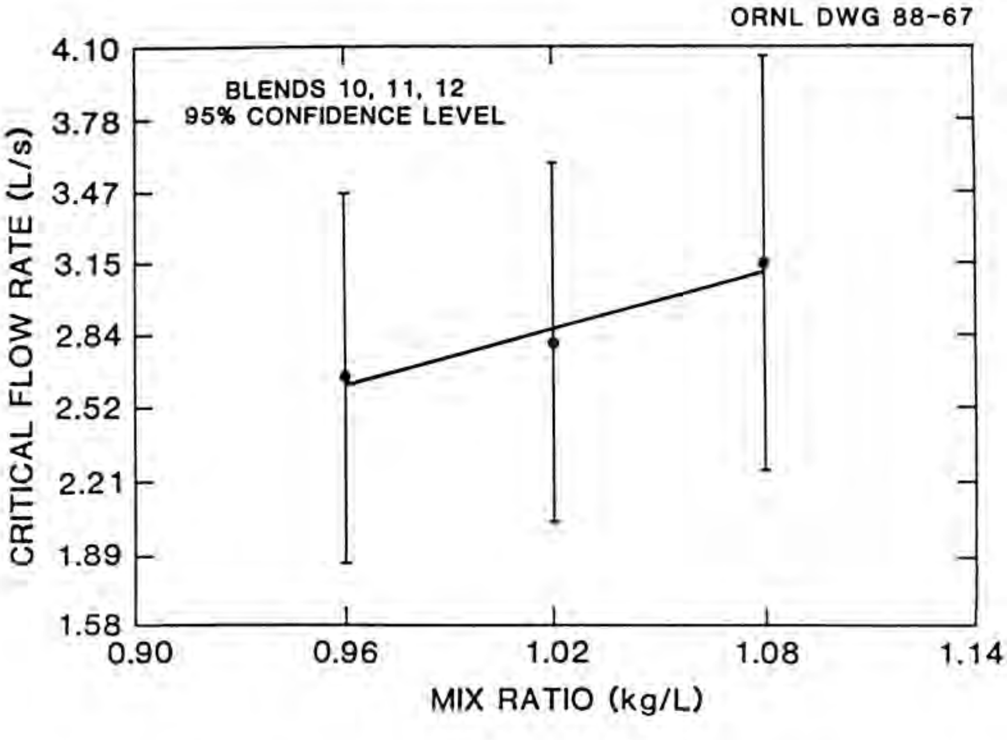

Fig. 1. Critical Flow Rate vs Mix Ratio for Blends 10,11,12.

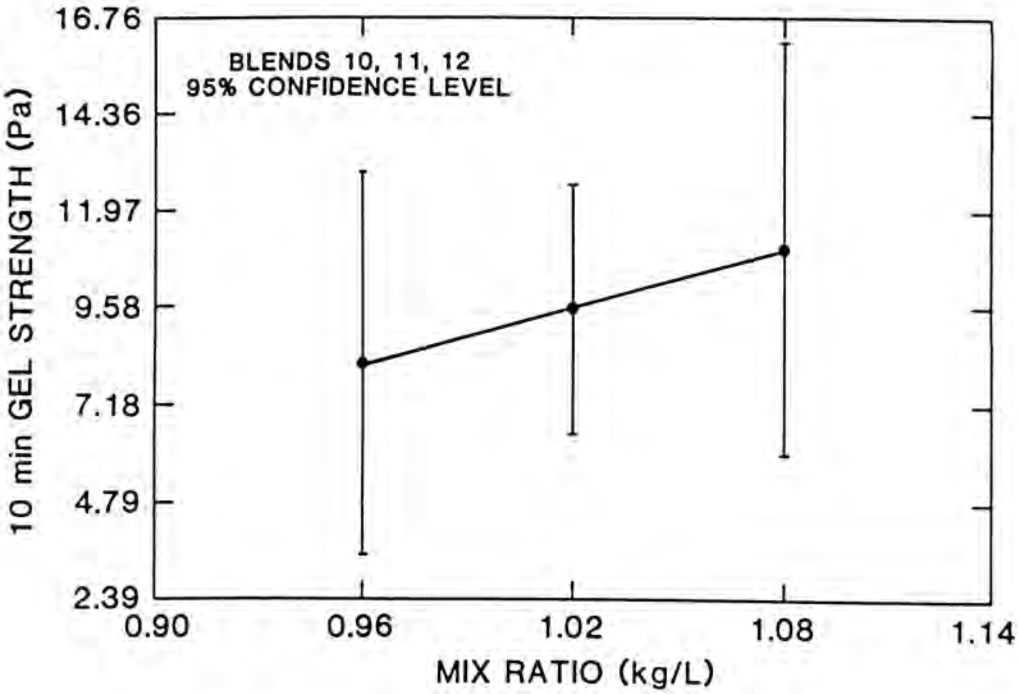

Fig. 2. Gel Strength vs Mix Ratio for Blends 10, 11, 12.

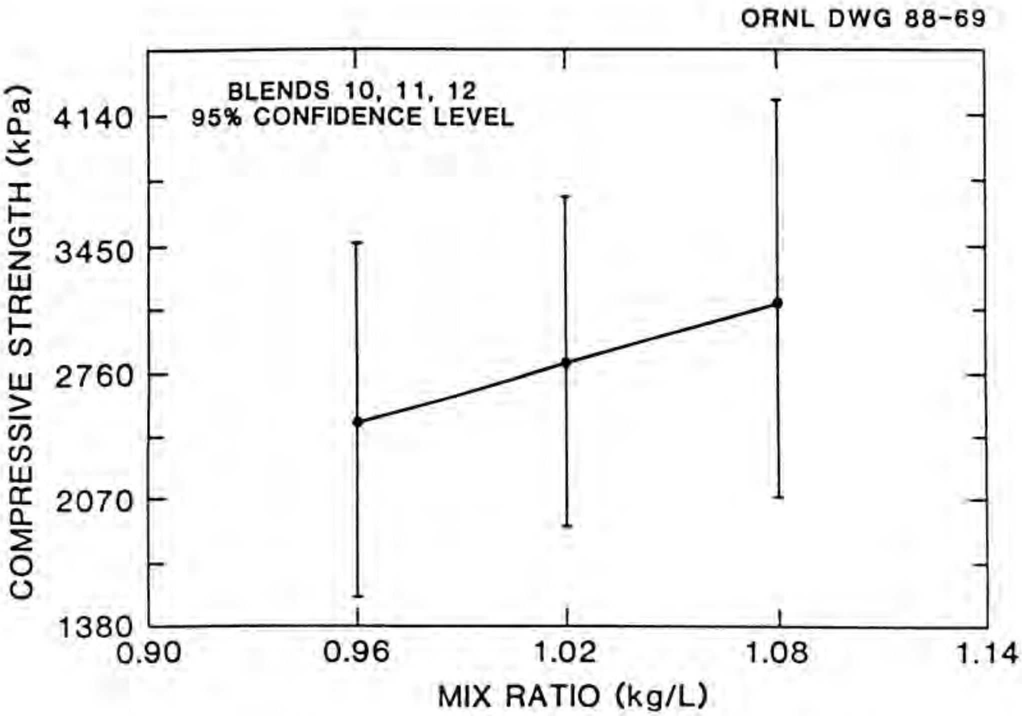

Fig. 3. Compressive Strength vs Mix Ratio for Blends 10,11,12.

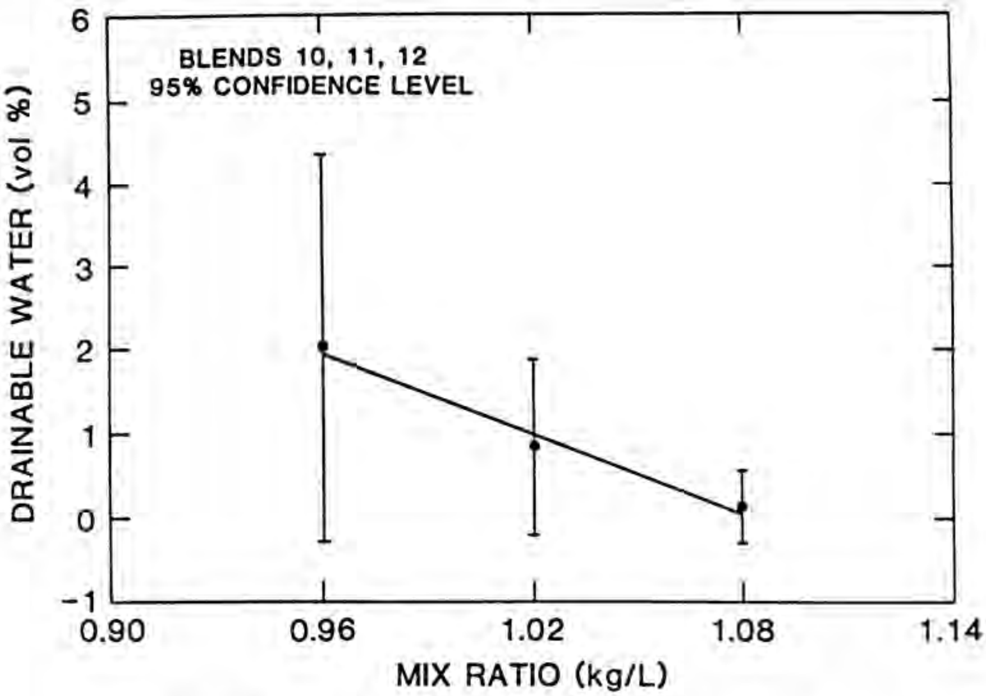

Fig. 4. Drainable Water vs Mix Ratio for Blends 10, 11, 12.

where

$\overline{X}$ = mean of a random sample of a size n,

u = mean of the population,

S = sample standard deviation,

n = population size.

In deriving the sampling distribution of T, it is assumed that the random sample was selected from a normal population. Although this appears to be a restrictive assumption, it has been shown that abnormal populations with bell-shaped distributions still provide values of T that very closely approximate the t distribution (5,6,8).

The probability that a random sample produces a t-value falling between two specified values is equal to the area under the curve of the t- distribution between the two ordinate values. Tables are used giving t-values above which a specified area ϕ can be found, where ϕ is 0.1, 0.05, 0.025, 0.01, or 0.005 (5). The t-value above which the area equal to ϕ is found, is normally represented by t_ϕ. Once this value is known, it can be determined whether the population mean falls significantly below the critical value of the response being studied.

The results of the T-test can be summarized as follows:

Cement	46.0 3.4 wt %
Fly ash	32.73.4 wt %
Attapulgite-15013.5	1.4 wt %
IRPC 7.9	0.8 wt %
Mix ratio1.06	0.04 kg/L
Gel strength7.1	1.7 Pa
Drainable water1.5	0.9 vol %
Compressive strength3.54	0.85 mPa
Critical flow rate2.6	0.3 L/s
Frictional pressure drop0.8	0.1 kPa/m

These limits represent a 99% confidence interval, and the comparison of these results with the actual data yields the reference formula.

CONCLUSIONS

This formulation development work encompassed a variety of responses and variables. The reference grout formula, as presented, should produce acceptable grouts that are processible and durable. The reference formula is such that variations in the dry-solids blend components will not adversely affect the grout properties, and the data were treated in such a manner as to verify this statement. This study is typical of the viability of cement-based grouts as a means of waste immobilization.

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