SYSTEMATIC APPROACH FOR THE DESIGN OF PUMPABLE CEMENT-BASED GROUTS
FOR IMMOBILIZATION OF HAZARDOUS WASTES

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ABSTRACT: Cement-based grouts have proven to be an economical and environmentally acceptable means of waste disposal. Costs can be reduced if the grout is pumped to the disposal site. This paper presents a systematic approach to guide the development of pumpable grouts.

KEY WORDS: Waste disposal; immobilization; cement-based grouts; grout formulation development; hazardous, radioactive and mixed wastes.

Introduction

Researchers at the Oak Ridge National Laboratory (ORNL) have developed versatile and inexpensive processes to solidify large quantities of radioactive (low- and intermediate-level) liquids, sludges, and fine solids (<0.6 mm diam) in cement-based grouts. Using standard "off-the-shelf" processing equipment, these batch or continuous processes are compatible with a wide range of disposal methods such as above-ground intermediate storage, shallow-land burial, deep geological disposal, and bulk in-situ solidification. The resulting grout monoliths have been shown to be less permeable than the surrounding host soil and resistant to (a) leaching by groundwater, (b) deterioration on exposure to radiation or thermal cycling, and (c) overburden subsidence. Disposal costs can be greatly reduced when these monoliths are formed on a large scale (e.g., in vaults or earthen trenches).

Research at ORNL has shown that cement-based grouts can be tailored to tolerate wide fluctuations in waste feed compositions and still maintain properties that are compatible with standard processing equipment and regulatory performance criteria. The 20-year operational history of the ORNL grouting program has demonstrated this resilience and reliability with a spectrum of waste feeds that bracket the developmental history of the nuclear fuel cycle. These wastes include ion-exchange media, evaporator bottoms, filter media, waste slags, incinerator ashes, waste calcines, shredded metallic pieces, basaltic glass frit, and contaminated pump oils. Research efforts have recently been expanded to address the solidification of hazardous chemical and mixed (i.e. radioactive and chemically hazardous) wastes.^{1,2,3}

Research personnel at ORNL develop grout formulas that are compatible with both the waste chemistry and the process and environmental (e.g. regulatory) constraints.^{4,5,6} In many cases, it is cost effective to formulate the grout to be sufficiently fluid so that it can be pumped to the disposal area where it hardens in-situ to form large grout monoliths, such as in the ORNL hydrofracture process⁷ and the Rockwell Hanford Operations Transportable Grout Facility.⁸ In these two applications, the disposal sites are situated some distance (300 and 1000m, respectively) from the grout facility, making the use of a fluid (i.e. pumpable) grout imperative. The development of pumpable grouts has long been considered an art; however, a systematic approach to developing these grouts has been applied at ORNL and is presented in this paper.

Basis for Rheological Limits

A typical grout facility consists of four major modules: (1) a dry solids blending and feed facility that prepares and delivers the solids blend (e.g. cement, fly ash, etc.); (2) a liquid/slurry waste feed system; (3) a mixing facility where the dry solids blend and the liquid waste are brought into contact with each other; and (4) a grout distribution system for pumping the fluid grout to the disposal area, where it hardens in situ. Of these four modules, the grout distribution system incurs the greatest limitations on the development of pumpable grouts because the non-Newtonian rheological behavior of the fluid grout must be tailored to be compatible with this system.^{4,8}

Typically, three parameters - density, flow rate, and viscosity - define the rheological behavior of a fluid. However, defining the rheological behavior of a cement-based grout is more difficult because of its non-Newtonian behavior. For non-Newtonian grouts, shear stress is dependent on shear rate as first described by the Ostwald-de-Waele model.⁹ Field experience has shown that the relationship between shear stress and shear rate is adequately represented by the power-law model¹⁰

$$S_s = \kappa' (S_r)^{n'} , \quad [1]$$

where

S_s = shear stress, Pa;

κ' = fluid consistency index, $\text{Pa} \cdot \text{s}^{n'}$;

S_r = shear rate, s^{-1} ; and

n' = flow behavior index ($0 < n' < 1.0$), dimensionless.

From Eq. [1], the Reynolds number for flow through a cylindrical pipe can be calculated by:

$$Re = \frac{8000 U^{2-\eta} \rho}{\kappa' (8/d_i)^\eta} , \quad [2]$$

where

Re = Reynolds number, dimensionless;

U = fluid velocity, m/s;

ρ = fluid density, g/cm³; and

d_i = inside pipe diameter, m.

Although grouts can be pumped in the laminar flow regime, the turbulent flow regime is preferred because radial components of velocity aid in keeping these particulate slurries well mixed. These radial flow components promote mixing at the pipe wall and, hence, minimize caking at the pipe wall. This, in turn, minimizes the operational process flushing requirements.

In general, turbulent flow begins at a Reynolds number greater than or equal to 2100.¹⁰ If one assumes that critical velocity (U_c) is achieved at a Reynolds number of 2100, then the minimum pumping velocity necessary to achieve turbulent flow in the grout distribution system can be calculated by:

$$U_c = \left[\frac{2100 \kappa' (8/d_i)^\eta}{8000 \rho} \right]^{\frac{1}{2-\eta}} . \quad [3]$$

For a given grout formula, κ' , η' , and ρ can be calculated from laboratory measurements using standard techniques⁵ to determine the minimum desired pumping velocity for onset of turbulent flow as described by Eq. [3].

The pressure drop resulting from pumping the fluid grout through the distribution pipe can be calculated by:

$$\Delta P_f = \frac{1000\rho U^2 f}{d_1} \quad [4]$$

where

ΔP_f = frictional pressure drop through a straight pipe, Pa/m; and

f = Fanning Friction Factor, dimensionless (f is a function of Reynolds number).

The maximum pumping velocity can be determined from Eq. [4] by comparing the calculated pressure drop with the discharge pressure rating for a given pump. Thus, for an established grout formula, Eqs. [3] and [4] can be used to determine the maximum and minimum pumping required for the grout distribution system.

However, the design criteria for the process facility are commonly selected independently of the grout's properties; for example, when facility design proceeds before the optimum grout formula has been determined or when use of an existing facility is desired. In such an instance, the grout formula must be tailored so that it will be compatible with an existing plant design. Then, Eqs. [3] and [4] establish rheological criteria for grout formulation development. As such, it is necessary to determine limits on κ' , η' , and ρ because these

characteristic parameters define the flow behavior of the grout and thereby determine the compatibility of the grout with the design of the grout distribution system.

In the past, an enormous number of experiments have been required to develop grouts compatible with the distribution system design due to the lack of a systematic approach to formulation development. However, experience at ORNL has led to the development of a systematic approach which greatly reduces the experimentation required to develop a grout formula compatible with an established design.

For a given grout distribution system design, three pertinent parameters have been established:

1. the inside diameter of the distribution pipe (d_1),
2. the maximum permissible pressure drop across the distribution pipe (ΔP_m), and
3. the maximum distribution pump throughput capacity (U_m).

These values in combination with Eq. [4] can be used to establish limits on fluid grout density:

$$\rho_m = \frac{\Delta P_m d_1}{1000 U_m^2 f} \quad [5]$$

where ρ_m is the maximum fluid grout density. Although the selection of an appropriate fanning friction factor (f) is somewhat arbitrary, experience at ORNL has shown that, 0.008, the value for smooth pipe at a Reynolds number of 2100,¹¹ is generally appropriate.^{4,8} Thus, Eq. [5] reduces to:

$$\rho_m = \text{constant} = C \quad [6]$$

The density of a fluid grout can be approximated by the following:

$$\rho_g = \frac{W_g}{\frac{W_s}{\rho_s} + \frac{W_w}{\rho_w}} = \frac{W_s + W_w}{\frac{W_s}{\rho_s} + \frac{W_w}{\rho_w}} \quad [7]$$

ρ_g = density of fluid grout;

W_g = total mass of grout;

W_s = mass of dry solids blend;

W_w = mass of waste;

ρ_s = true density of dry solids blend;

ρ_w = density of waste.

Substituting Eq. [6] into Eq. [7] and rearranging yields:

$$\frac{W_s}{W_w} = \frac{\rho_s (\rho_w - C)}{\rho_w (C - \rho_s)} \quad [8]$$

Thus Eq. [8] establishes the upper limit of dry solids blend per unit of waste for formulation development studies. This ratio expressed in units of kilograms dry solids blend per liter of waste is typically referred to as the mix ratio (M). The minimum mix ratio is determined by product performance criteria such as minimum required compressive strength¹² and rate of set.¹³ The determination of this minimum is still somewhat of an art, and one generally relies on the experience of the researcher. However, in the absence of other guidance, civil engineering applications of grouting technology have shown that the minimum mix ratio must result in a fluid-grout water to cement ratio (wt/wt) of at least 0.38.¹⁴

At this point, both the minimum and maximum mix ratios for the dry solids blend under study have been established. However, guidance on limits for κ' and η' are still required. This guidance is supplied by another parameter of an established distribution system: the nominal throughput. Assuming turbulent flow is desired at or below this throughput, and substituting the throughput for critical velocity in Eq. [3] results in a three parameter equation involving κ' and η' , and ρ . However, Eq. [3] is relatively insensitive to density.¹⁵ Consequently, the waste density can be substituted into Eq. [3] and it then becomes a two parameter equation which can guide formulation development efforts.

For example, if a distribution system is characterized by:

(1) 0.05m inside diameter of the grout distribution pipe, (2) a nominal throughput of 3.15 L/s, and (3) a waste density of 1 g/cm³, then Eq. [3] becomes:

$$1.61 > \left[\frac{2100\kappa' (160)\eta'}{8000} \right]^{\frac{1}{2-\eta'}} \quad [9]$$

Equation 9 is shown graphically in Fig. 1. The combinations of κ' and η' values which satisfies Eq. [9] lies on or below the straight line (Fig. 1) and bounds the area representing an acceptable window of grout flow characteristics.

This window, coupled with limits on mix ratio, becomes the basis for developing grout formulas with acceptable flow behavior. This systematic approach greatly reduces the amount of experimentation required to develop a grout with acceptable flow characteristics. In addition, measurements

Fig. 1. Combination of k' and n' which result in turbulent flow at reference design conditions.

required by this approach are performed on freshly prepared grouts. Thus, this phase of grout formulation requires no waiting on the grout cure period.

ANS 16.1 Leach Procedure

Once a grout with the proper flow characteristics has been developed, desired product performance characteristics (e.g. compressive strength) are, in general, a minor concern. This is due to the fact that the minimum mix ratio used in the development of a grout with acceptable flow characteristics was chosen to meet the desired product characteristics. The major exception to this is product leachability, particularly in regards to the Environmental Protection Agency Extraction Toxicity Procedure (EP-Tox).¹⁶

In formulation development studies involving hazardous or mixed wastes, the synthetic waste solution used is, in general, spiked with excessive amounts of the chemical pollutants. This is done for two reasons: (1) to assess deleterious effects of the pollutants on the rate of set of the cement-based product and (2) to facilitate analytical detection limits for determining leachability of the species of interest from the solidified product. This, in turn, requires a means of relating the EP-Toxicity¹⁶ of the product containing the synthetic solution to that containing the actual waste concentration. The relationship is provided by the ANS 16.1 Leach Procedure.¹⁷

The ANS 16.1 Leach Procedure is designed to determine the effective solid diffusion coefficients for species of interest. In general, solid-diffusion controlled leaching represents the maximum release rates for the species of interest.¹⁸

The ANS 16.1 procedure utilizes periodic leachant replacement to simulate a continuous-flow system. The procedure is designed so that the

results can be modeled by the fundamental mass transport equation:

$$\left(\frac{\Sigma a_n}{A_0}\right)\left(\frac{V}{S}\right) = 2\left(\frac{D_e}{\pi}\right)^{1/2} t^{1/2} , \quad [10]$$

where

Σa_n = cumulative mass of species released through cumulative time, t ;

A_0 = original mass of species in the waste form;

V = external volume of the waste form;

S = external surface area of the waste form;

D_e = effective solid diffusion coefficient.

The Leachability Index, $\bar{L}$, of a species is defined as:

$$\bar{L} = -\log(D_e) .$$

For this theory to be valid, a plot of $[(\Sigma a_n/A_0)(V/S)]$ vs $\sqrt{t}$ must result in a straight line which passes through the origin. Effective diffusivities have been reported from data which, through linear with the square root of time, did not go through the origin.¹⁹ A positive intercept may represent a surface phenomena where salts are washed off over a relatively short period of time. A negative intercept may correspond to a delay in leaching caused by a passive surface layer.

Typically, this intercept represents a small fraction of the total amount released during the experiment. As such, it can be ignored for comparisons of competing waste forms or for predicting long-term release. However, for predicting a 24-h release, as in the EP-Toxicity Procedure, it may become significant. Consequently, the fundamental mass transport equation [Eq.10] must be modified to:

$$\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = \left[\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right)\right]_o + 2\left(\frac{D_e}{\pi}\right)^{1/2} t^{1/2}, \quad [11]$$

or

$$\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = I_o + 2\left(\frac{D_e}{\pi}\right)^{1/2} t^{1/2}. \quad [12]$$

Substituting EP-Tox boundary conditions, Eq. 12 becomes

$$\frac{a_n}{A_o} = 1.49 I_o + 494.19 \sqrt{D_e} \quad [13]$$

For pumpable grouts, it can be shown that Eq. 13 can be expressed as^{5,20}

$$\frac{C}{C_o} = \frac{0.093 I_o}{M + \rho_w} + \frac{(31) 10^{-\bar{L}/2}}{M + \rho_w} \quad [14]$$

where

C = EP-Tox leachate concentration, mg/l;

C_o = original waste concentration, mg/l;

M = grout mix ratio, kg/l;

ρ_w = density of waste solution, g/cm³.

Although the EP-Tox Procedure requires an acetic acid solution as the leachant, previous laboratory experience at ORNL has shown that, generally, results from leaching in distilled water are similar for grouts that pass the structural integrity test.²⁰ Therefore, both the leachability index ($\bar{L}$) and the intercept (I_o) used in Eq. [14] can be obtained using distilled water, the ANS 16.1 standard leachant.

Because Leachability Indices are insensitive to relatively large variations in trace element waste concentration, Eq. [14] in conjunction with ANS 16.1 leach data provides a means to assess waste composition variations on EP-Tox results. Thus, the relationship provides a powerful tool which can guide formulation development. That is, with ANS 16.1 data obtained on a grout product containing synthetic waste, the EP-Tox concentration on the product containing actual waste can be predicted.

Conversely, the relationship can guide formulation development efforts by quickly establishing a minimum Leachability Index. Assuming the intercept in Eq. [14] to be zero, the equation reduces to:

$$\frac{C}{C_0} = \frac{(31)(10^{-L/2})}{M + \rho_w} \quad [15]$$

Prior to initiating formulation development efforts, both the waste concentration (C_0) and density (ρ_w) are known. Using Eq. [15], the minimum leachability index required to achieve the desired EP-Tox leachate concentration (C) for the mix ratio (M) under study can be calculated. Efforts would then be directed toward formulating a product characterized by an Index greater than the calculated minimum. This concept is illustrated graphically in Fig. 2.

Summary

Versatile and inexpensive processes to solidify large quantities of radioactive liquids, sludges, and fine solids in cement-based grouts have been developed and used routinely for the ultimate disposal of radioactive wastes. Using standard "off-the-shelf" processing equipment, these batch

Fig. 2. Fraction released in EP-Tox test versus Leachability Index.

or continuous processes are compatible with a wide range of disposal methods such as above-ground intermediate storage, shallow-land burial, deep geological disposal, and bulk in-situ solidification. The resulting grout monoliths have been shown to be less permeable than the surrounding host soil and resistant to (a) leaching by groundwater, (b) deterioration on exposure to radiation or thermal cycling, and (c) overburden subsidence. Recent studies have shown that similar product performance can be obtained upon application of these processes to the disposal of chemically hazardous or mixed wastes.

Disposal costs can be further reduced if the cement-based grout is formulated to be sufficiently fluid so that it can be pumped to the disposal area where it hardens in-situ to form large grout monoliths. The development of pumpable grouts has long been considered an art; however, a systematic approach to developing these grouts has been applied at ORNL and presented in this paper. The approach greatly reduces the experimentation required for grout formulation development. As such, both the cost and time for formulation development is reduced. In addition, the approach provides a tool for application of quality control/assurance to the development process. Thus, the approach is a powerful tool which can be used to rapidly extend the application of grout technology to the ultimate disposal of chemically hazardous waste.

References

1. T. M. Gilliam and J. A. Loflin, "Leachability Studies of Hydrofracture Grouts," ORNL/TM-9879, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory (1986).
2. J. E. Mrochek, T. M. Gilliam, E. W. McDaniel, J. F. Land, and T. T. Godsey, "Grout Formulation and Leaching for the Immobilization of Sludges from the F-1 Tank at Y-12," ORNL/TM-9843, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory (in press).
3. T. Michael Gilliam, Leslie R. Dole, and Earl W. McDaniel, "Waste Immobilization in Cement-Based Grouts," Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933 (1986).
4. "Immobilization of Hanford Facility Decontamination Waste in a Cement-Based Grout," T. M. Gilliam, E. W. McDaniel, T. L. Sams, O. K. Tallent, and L. R. Dole, Proceedings of Spectrum '86, American Nuclear Society, Sept 14-18, 1986, (in press).
5. T. M. Gilliam, T. L. Sams, and W. W. Pitt, Testing Protocols for Evaluating Monolithic Waste Forms Containing Mixed Waste," Ceramic Advances 20, 220 (1986).
6. A. J. Mattus, T. M. Gilliam, and L. R. Dole, "A Review of EPA, DOE, and NRC Regulations Regarding Establishment of Solid Waste Performance Criteria." ORNL/TM-9322, Martin Marietta Energy Systems, Inc.
7. W. de Laguna et al., "Engineering Development of Hydraulic Fracturing As A Method For Permanent Disposal of Radioactive Wastes," ORNL-4259, August 1968.

References continued

8. "Immobilization of Neutralized Cladding-Removal Waste in a Cement-Based Grout," T. L. Sams, E. W. McDaniel, and T. M. Gilliam, Proceedings of the Second International Conference on Radioactive Waste Management, ISBN: 0-919784-08-9, Canadian Nuclear Society, Sept 7-11, 1986.
9. R. B. Bird, W. E. Stewar, and E. N. Lightfoot, Transport Phenomena, John Wiley & Sons, Inc., NY. 1960, pp 10-15.
10. D. K. Smith, "Cementing," Society of Petroleum Engineers of AIME, New York, 1976.
11. N. P. Cheremisinoff, "Fluid Flow, Pumps, Pipes, and Channels," Ann Arbor Science Publishers, Ann Arbor, Michigan, 1982.
12. ASTM C109-80 "Compressive Strength of Hydraulic Cement Mortars," Annual Book of ASTM Standards: Cement; Lime; Gypsum, Section 4, Volume 04.01 (1984).
13. ASTM (403-80, "Time of Setting of Concrete Mixtures By Penetration Resistance," Annual Book of ASTM Standards: Concrete and Mineral Aggregates, Section 4, Volume 04.02 (1984).
14. T. M. Gilliam, E. W. McDaniel, L. R. Dole, H. A. Friedman, J. A. Loflin, A. J. Mattus, I. L. Morgan, O. K. Tallent, and G. A. West, "Summary Report on the Development of a Cement-Based Formula to Immobilize Hanford Facility Waste," ORNL/TM-xxxx, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory (1987).
15. T. M. Gilliam, E. W. McDaniel, L. R. Dole, and G. A. West, "Preliminary Data on Rheological Limits for Grouts in the Transportable Grout Facility," ORNL/TM-9117, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory (1987).

References Continued

16. R. M. Hall, T. Watson, J. J. Davidson, D. R. Case, and N. S. Bryson, RCRA Hazardous Wastes Handbook, 6 ed., Government Institutes, Inc., Rockville, Md., 1985.
17. American Nuclear Society, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes," Draft prepared by the ANS Standards Committee, Working Group ANS 16.1, La Grange Park, Ill., Feb. 6, 1986.
18. A. Atkinson, "The Influence of Waste Form Permeability on the Release of Radionuclides From a Repository," Nucl. Chem. Waste Manage. Vol. 5, No. 203, 1985.
19. H. W. Godbee and D. S. Joy, "Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part 1: Theory," ORNL/TM-4333, Oak Ridge National Laboratory (1974).
20. T. Michael Gilliam, "Immobilization of Mixed Waste," Proceedings of the Waste Management '87 Conference, Tucson, AZ, March 1987.

LIST OF FIGURES

Fig. 1. Combination of K' and η' which result in turbulent flow at reference design conditions.

Fig. 2. Fraction released in EP-Tox test versus Leachability Index.