

MAY 13 1987

ornl

ORNL/TM-9264

**OAK RIDGE
NATIONAL
LABORATORY**

MARTIN MARIETTA

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

**Weldon Spring, Missouri, Raffinate Pits
1, 2, 3, and 4: Preliminary Grout
Development Screening Studies for
In Situ Waste Immobilization**

**E. W. McDaniel
T. M. Gilliam
L. R. Dole
G. A. West**

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

CONTENTS

| | <u>Page</u> |
|--|-------------|
| ABSTRACT | 1 |
| 1. INTRODUCTION | 1 |
| 2. BACKGROUND | 2 |
| 3. PHASE I: SCREENING STUDIES | 6 |
| 4. PHASE II: GROUT DEVELOPMENT WITH ACTUAL WASTE | 10 |
| 5. PRELIMINARY CONCLUSIONS | 20 |
| 6. PHASE III: ADDITIONAL DATA NEEDS IN GROUT DEVELOPMENT | 21 |
| 7. REFERENCE | 25 |

WELDON SPRING, MISSOURI,
RAFFINATE PITS 1, 2, 3, & 4: PRELIMINARY GROUT DEVELOPMENT
SCREENING STUDIES FOR IN SITU WASTE IMMOBILIZATION

E. W. McDaniel
T. M. Gilliam
L. R. Dole
G. A. West

ABSTRACT

Results of Oak Ridge National Laboratory's initial support program to develop a preliminary grout formula to solidify in situ the Weldon Spring waste are presented. The screening study developed preliminary formulas based on a simulated composite waste and then tested the formulas on actual waste samples. Future data needs are also discussed.

1. INTRODUCTION

The Weldon Spring Department of Energy (DOE) Raffinate Pits Site is located in St. Charles County, Missouri, covers an area of approximately 50 acres, and contains four raffinate pits. The four raffinate pits contain an estimated 6-M ft³ of waste, including ~150 tons of uranium and 75 tons of thorium. Any other material residing in the pits is of unknown character.

As part of the Formerly Utilized Site Remedial Action Program (FUSRAP) for this site, one remedial action scenario proposal is the solidification in situ of these wastes in the existing pits. The most cost-effective means to solidify these wastes is with cement-based grouts.

This report presents the results of Oak Ridge National Laboratory's (ORNL's) initial support program to develop a preliminary grout formula that would solidify in situ the Weldon Spring waste sufficiently to (1) eliminate freestanding water and (2) support earth-moving equipment. The initial ORNL support consisted of two phases: Phase I was a screening study to develop a formula(s) based on a simulated composite waste, and Phase II applied the formula(s) from Phase I to samples of actual waste

from the Weldon Spring Pits. The future Phase III will attempt to develop a reference formula(s) that is compatible with the process design conditions and to show that the product(s) meets regulatory requirements. The scope of work for Phase III is also presented.

2. BACKGROUND

To fully characterize the mixability and the flow behavior of grouts, data are needed concerning the fluid consistency index, flow behavior index, density, and gel strength. To demonstrate compliance with the solid grout performance criterion of no freestanding water and to show the capability to support earth-moving equipment (Sect. 1.0), two other parameters must also be determined—phase separation and unconfined compressive strength.

Phase separation, a measurement of drainable water, is determined by a settling test in a 250-mL graduate cylinder. The freshly mixed grout is poured into the graduate and allowed to stand for 2 h, after which percent phase separation is calculated as the volume of clear, drainable surface water divided by the total initial grout volume × 100.

The industry standard for determining the grout's ability to withstand an axial load is the 28-d unconfined compressive strength test (ASTM C109-80). Generally, compressive strength measurements at cure times less than 28 d have little relationship to the 28-d value. Experience indicates that a 28-d unconfined compressive strength of 50 psi is adequate to meet the Weldon Spring performance criteria.

Also, rheological measurements are required to establish the mixability and pumpability of the fluid grout. Three parameters define the rheological properties of a simple fluid—density, flow rate, and viscosity. However, defining the rheological properties of a grout is more difficult than for a simple fluid because of its non-Newtonian behavior. For non-Newtonian grouts, shear stress is dependent on shear rate and can be represented by the power law model¹

$$S_S = k'(S_r)^n' , \quad (1)$$

where

$$\begin{aligned} S_s &= \text{shear stress, } \text{lb}_f/\text{ft}^2; \\ k' &= \text{fluid consistency index, } \text{lb}_f \cdot \text{s}^{n'}/\text{ft}^2; \\ S_r &= \text{shear rate, } \text{s}^{-1}; \\ n' &= \text{flow behavior index } (0 < n' < 1.0), \text{ dimensionless.} \end{aligned}$$

From Eq. (1), the viscosity can be calculated by

$$\mu = 47880 k' (S_r)^{n'-1}, \quad (2)$$

where

$$\mu = \text{viscosity, cP.}$$

It is a common practice to report an apparent viscosity at a shear rate of 511 s^{-1} (300 RPM on the Fann Viscometer). However, this apparent viscosity at the reference shear rate of 511 s^{-1} can satisfy an infinite combination of k' and n' in Eq. (2). Figure 1 shows two cases where the apparent viscosity of both is 35 cP at the reference shear rate of 511 s^{-1} . Case 1 has a $k' = 0.107 \text{ lb}_f \cdot \text{s}^{n'}/\text{ft}^2$ and a $n' = 0.2$, and case 2 has a $k' = 0.009 \text{ lb}_f \cdot \text{s}^{n'}/\text{ft}^2$ and an $n' = 0.6$. Thus, a single apparent viscosity at an arbitrary shear rate cannot be used to define k' and n' and the dynamic response of the grouts over the ranges of shear in mixing and pumping.

It is necessary to define k' and n' because these characteristic parameters define the flow behavior of the grout. The flow calculations are

$$N_{Re} = \frac{1.86 v^{(2-n')} \rho}{k' (96/d_i)^{n'}}, \quad (3)$$

where

$$\begin{aligned} N_{Re} &= \text{Reynolds number, dimensionless;} \\ v &= \text{fluid velocity, ft/s;} \\ d_i &= \text{inside pipe diameter, in.;} \\ \rho &= \text{fluid density, lb/gal;} \end{aligned}$$

ORNL DWG 84-382

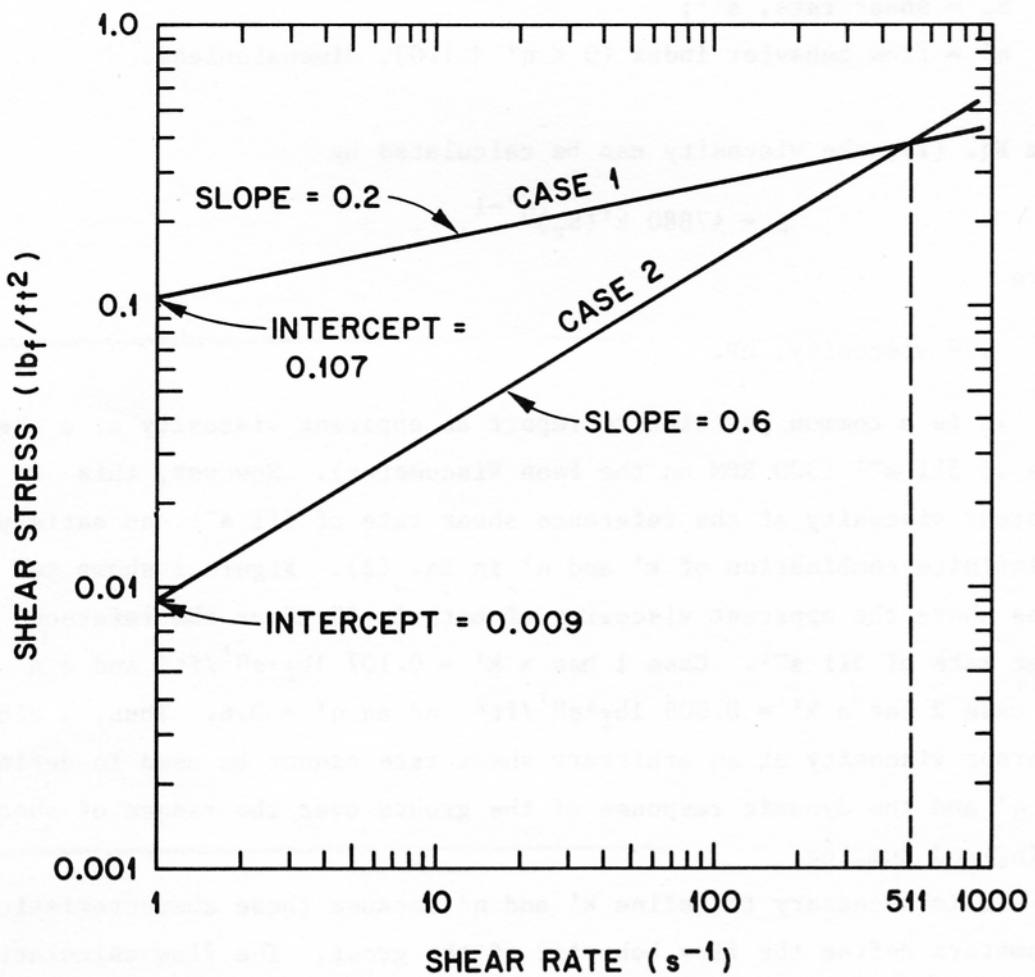


Fig. 1. Shear stress vs shear rate.

and

$$\Delta P_f = \frac{0.039 L \rho V^2 f}{d_i} , \quad (4)$$

where

ΔP_f = frictional pressure drop through a straight pipe, psi;

L = pipe length, ft;

f = fanning friction factor, dimensionless
(f is a function of Reynolds number).

Using the previous examples and assuming a grout density of 13.0 lb/gal and a reference flow rate of 5.1 ft/s (50 gal/min) through a 2-in.-ID pipe, the case 1 grout results in laminar flow ($N_{Re} = 1956$) with a ΔP_f of 5.4 psi/100 ft. In contrast, the case 2 grout results in turbulent flow ($N_{Re} = 2577$) with a ΔP_f of 4.4 psi/100 ft. Thus, differing values of k' and n' can have an impact on the flow behavior of the grout.

In addition to k' , n' , and ρ , the other grout rheological characteristic of concern is gel strength. When dry solids blend and waste come in contact with each other, the resulting mix must remain in motion during processing. If the mix becomes stationary due to a temporary process shutdown, the mix will begin to assume a colloidal gel state and develop gel strength. The measured gel strength (API RP 13 B) of the fluid is the maximum deflection taken from a direct-reading viscometer on the fluid after it has been static for 10 min. This reversible gel strength must be overcome before flow can begin again. The pump head pressure necessary to overcome this gel strength in pipe can be calculated by:

$$P_H = \frac{G \cdot A_W}{(1.44 \times 10^4) A_p} , \quad (5)$$

where

P_H = pump head pressure, psi;

G = gel strength, $\text{lbf}/100 \text{ ft}^2$;

A_W = pipe inside surface area, in.²;

A_p = inside pipe cross-sectional area, in.².

For a straight pipe, Eq. (5) can be reduced to

$$P_H = \frac{G \cdot L}{300 \cdot d_i} . \quad (6)$$

Grouts with a 10-min gel strength of 50 lb_f/100 ft² are common in oil-well cementing practice.

3. PHASE I: SCREENING STUDIES

Initial grout-screening studies were performed with a surrogate composite waste (Tables 1 and 2) that was based on analyses of composite samples of residues from pits 1, 2, 3, and 4. Grouts were prepared in a high-shear mixer to ensure solid components were dispersed uniformly throughout the mix. Rheological measurements were taken with a Fann 35A/SR-12 direct-reading viscometer.

Three dry solids blends were tested: (1) 20-wt % lime and 80-wt % ASTM Class F fly ash, (2) 20-wt % Type I Portland cement and 80-wt % ASTM Class F fly ash, and (3) ASTM Class C fly ash. These blends were mixed with the surrogate waste at various solids-to-liquid waste ratios (mix ratios). Pertinent data are shown in Tables 3 and 4. Because all of the lime-fly ash waste mixes had an unacceptable 28-d-unconfined compressive strength (<50 psi), no experimental data are reported for these mixes.

The data shown in Tables 3 and 4 are for those mix ratios that resulted in no phase separation. Thus, both blends meet the criterion of having no drainable water. A lower mix ratio is adequate for Class C fly ash than for Class F fly ash because Class C fly ash is more efficient in reducing phase separation.

In addition to the parameters identified in Sect. 2.0, penetration resistance and volume increase are reported. The penetration resistance is a measure of the set, or the stiffening, of the grout. Initial set (the point at which the grout begins to stiffen) is defined as the point at

Table 1. Composition of simulated Weldon Spring waste

| Material | Concentration (wt %) |
|---------------------------------|-------------------------|
| Fe ₂ O ₃ | 15.17 |
| SiO ₂ | 2.53 |
| Al ₂ O ₃ | 1.01 |
| CaCO ₃ | 1.01 |
| MgCO ₃ | 0.51 |
| NaNO ₃ | 3.54 |
| Na ₂ SO ₄ | 0.3 |
| NaCl | 0.1 |
| Water | 75.83 |

Table 2. Properties of simulated Weldon Spring waste

| | |
|---|------|
| Density, lb/gal | 9.68 |
| Apparent viscosity, ^a cP | 5.5 |
| 10-min gel strength, lb _f /100 ft ² | 1 |
| 2-h phase separation, vol % | 30 |
| pH | 9-11 |

^aViscosity data were taken at a shear rate of 511 s⁻¹.

Table 3. Properties of grouts made with simulated Weldon Spring waste using a dry solids blend of 20-wt % Portland Type I cement and 80-wt % ASTM Class F fly ash

| Grout characteristics | Mix ratio (lb/gal) | | |
|---|-----------------------|-----------------------|-----------------------|
| | 8 ^a | 9 | 10 |
| Apparent viscosity, cP | 42 | 45 | 84 |
| 10-min gel strength, 1bf/100 ft ² | 30 | 29 | 32 |
| Density, lb/gal | 13.2 | 13.4 | 13.5 |
| 24-h penetration resistance, psi | 630 | 1040 | 1200 |
| 7-d penetration resistance, psi | 5200 | 6480 | 8000 |
| Volume increase, vol % | 37 | 40 | 43 |
| Fluid consistency index (k'), 1bf \cdot s $^{n'}$ /ft ² | 4.77×10^{-2} | 7.06×10^{-2} | 9.72×10^{-2} |
| Flow behavior index (n'), dimensionless | 0.35 | 0.30 | 0.34 |

^aMinimum solid/simulated waste ratio necessary to eliminate freestanding water.

Table 4. Properties of grouts made with simulated Weldon Spring waste using a dry solids blend of ASTM Class C fly ash

| Grout characteristics | | Mix ratio (1b/gal) | | | |
|--|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|
| | 6a | 7 | 8 | 9 | 10 |
| Apparent viscosity, cp | 25 | 36 | 39 | 52 | 69 |
| 10-min gel strength, 1bf/100 ft ² | 56 | 79 | 168 | 147 | 127 |
| Density, 1b/gal | 12.0 | 12.5 | 12.9 | 13.3 | 13.5 |
| 24-h penetration resistance, psi | 20 | 28 | 37 | 780 | 644 |
| 7-d penetration resistance, psi | 1000 | 1720 | 2600 | 3920 | 5840 |
| Volume increase, vol % | 30 | 33 | 37 | 40 | 43 |
| Fluid consistency index ('k'), 1bf•s ⁿ /ft ² | 4.10×10^{-2} | 8.40×10^{-2} | 9.51×10^{-2} | 1.65×10^{-1} | 2.5×10^{-1} |
| Flow behavior index ('n'), dimensionless | 0.30 | 0.24 | 0.23 | 0.19 | 0.22 |

aMinimum solid/simulated waste ratio necessary to eliminate freestanding water.

which the penetration resistance as measured by an Acme Penetrometer is 500 psi (ASTM C403-80). For example, at a mix ratio of 8 lb/gal the cement-Class F fly ash grout begins to set up within 24 h (Table 3) due to the reactive nature of cement, whereas the Class C fly ash grout takes between 1 and 7 d (Table 4).

The volume increase caused by adding the dry solids blend to the waste would be a consideration as a formula selection criterion if there were stringent limits on available disposal area. However, the volume increases with both blends are low (30-45%). Since field operations indicate that laboratory tests consistently show higher volume increases than are actually experienced in the field, these volume increases, shown in Tables 3 and 4 and Fig. 2, should be viewed as maximum values.

4. PHASE II: GROUT DEVELOPMENT WITH ACTUAL WASTE

Two sludge samples labeled 1-1 and 3-2 were received from Bechtel. Pertinent properties of the samples are shown in Table 5. These properties are significantly different from those of the surrogate waste used in Phase I, which had a density of 9.7 lb/gal, viscosity of 5.5 cP, and 2-h phase separation of 30 vol % (Tables 1 and 2). Thus, it is possible that these samples are not representative of the bulk of the pit waste. The samples were chocolaty and gelatinous (see Fig. 3). The required loosening by hand stirring (with a paddle) prior to agitation. Agitation resulted in a stiff slurry (Fig. 4), indicating that some shear thinning occurred.

After agitation, the waste was allowed to settle for 24 h. The resulting surface liquid was decanted, and both the liquid and settled solids were analyzed. Results of the analysis are shown in Tables 6 and 7.

The same experimental procedures detailed in Phase I were followed using these waste samples. However, all the resulting grouts were too viscous for rheological properties to be determined with the Fann 35 A/SR-12 direct-reading viscometer. Therefore, the characteristic parameters necessary for flow behavior calculations (k' and n') could not be obtained.

ORNL DWG 84-197

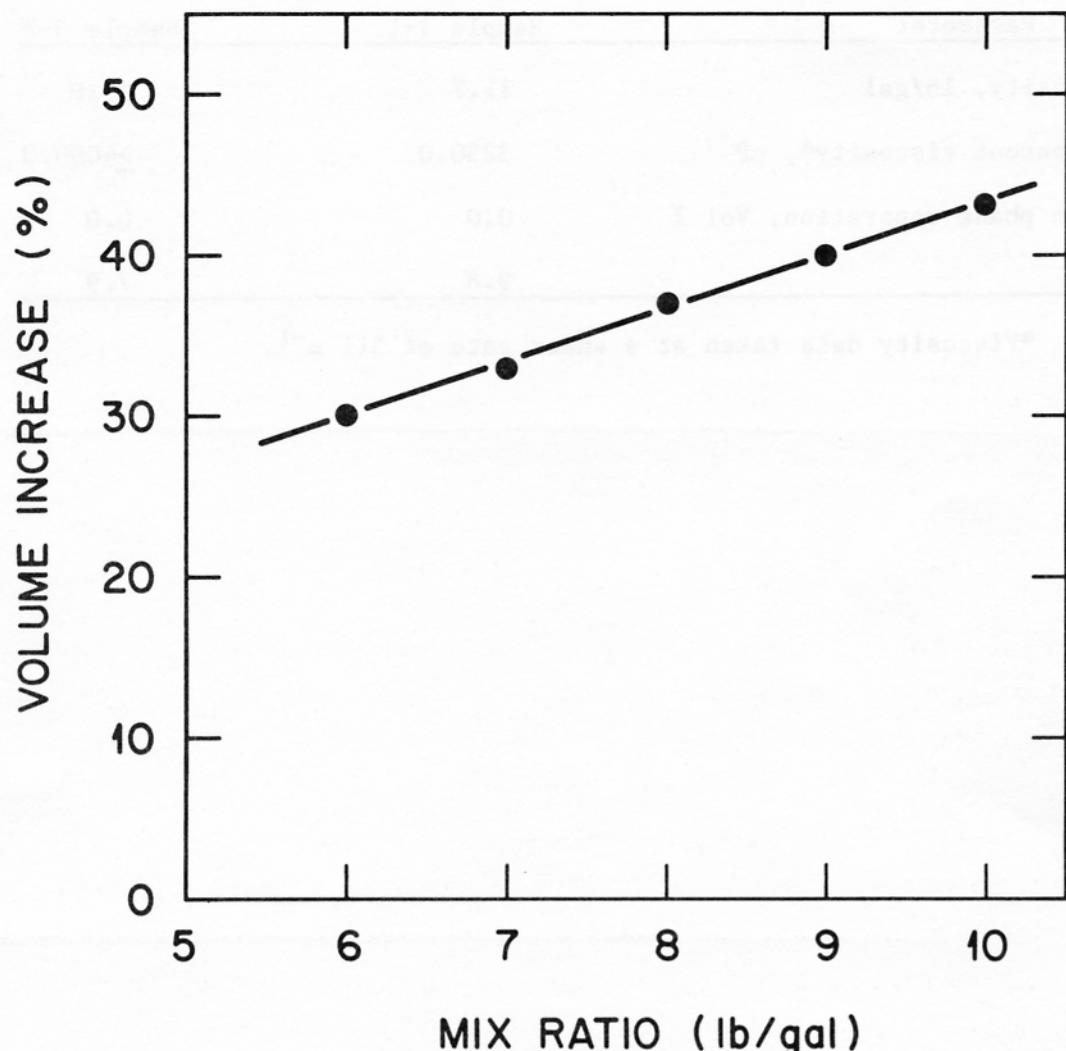


Fig. 2. Volume increase created by adding dry solids mix to the waste vs mix ratio using simulated Weldon Spring waste.

Table 5. Properties of Weldon Spring sludge samples 1-1 and 3-2

| Parameter | Sample 1-1 | Sample 3-2 |
|--------------------------------------|------------|------------|
| Density, lb/gal | 11.7 | 11.0 |
| Apparent viscosity ^a , cP | 3250.0 | >4000.0 |
| 2-h phase separation, Vol % | 0.0 | 0.0 |
| pH | 9.8 | 7.9 |

^aViscosity data taken at a shear rate of 511 s⁻¹.



Fig. 3. Weldon spring sludge sample 1-1 as received. (Photo 5574-83).



Fig. 4. Weldon Spring sludge sample 3-2 after agitation. (Photo 5575-83).

Table 6. Trace analysis of Weldon Spring sample 1-1 after agitation and setting for 24 h.

| Element | Concentration | |
|---------|--------------------------------|------------------------------|
| | Liquid ($\mu\text{g/mL}$) | Solid ($\mu\text{g/g}$) |
| U | <0.3 | 2,000 |
| Th | <0.3 | 100 |
| Pb | <0.1 | <10 |
| Hg | <0.1 | <10 |
| Ba | - | 30 |
| Cd | <0.5 | <20 |
| Mo | 1 | 5,000 |
| Zr | - | 20 |
| Sr | 2 | 50 |
| As | - | 100 |
| Zn | 0.6 | 1,000 |
| Cu | 0.2 | 100 |
| Ni | <0.1 | - |
| Co | <0.5 | <10 |
| Fe | 1 | 10,000 |
| Y | - | 20 |
| Mn | <0.03 | 500 |
| Cr | 0.6 | 30 |
| V | 0.1 | 10,000 |
| Ca | >100 | >100,000 |
| K | 50 | 500 |
| Cl | 10 | 1,000 |
| S | 100 | 10,000 |
| P | 0.4 | 2,000 |
| Si | <2 | <200 |
| Al | 0.2 | 500 |
| Mg | 5 | 10,000 |
| Na | >100 | 8,000 |
| F | <0.2 | >100,000 |
| B | 0.3 | >100,000 |
| Ce | - | <4 |

Table 7. Trace analysis of Weldon Spring sample 3-2 after mixing and settling for 24 h

| Element | Concentration | |
|---------|--------------------------------|------------------------------|
| | Liquid ($\mu\text{g/mL}$) | Solid ($\mu\text{g/g}$) |
| U | 0.6 | 8000 |
| Th | ≤ 0.2 | 10,000 |
| Pb | ≤ 0.05 | 50 |
| Hg | ≤ 0.1 | ≤ 20 |
| Ba | - | 400 |
| Sn | - | 70 |
| Cd | ≤ 0.1 | ≤ 50 |
| Mo | 5 | 600 |
| Nb | - | ≤ 20 |
| Zr | ≤ 0.02 | 200 |
| Y | - | 60 |
| Sr | 0.7 | 50 |
| Se | 0.3 | - |
| As | - | 200 |
| Zn | 0.2 | 50 |
| Cu | 0.1 | 600 |
| Co | 0.2 | ≤ 5 |
| Fe | 0.3 | $>100,000$ |
| Mn | 0.04 | 500 |
| Cr | 0.1 | 100 |
| V | 0.4 | 4,000 |
| Ca | 200 | $>100,000$ |
| K | 40 | 500 |
| Cl | 4 | 700 |
| S | 100 | 700 |
| P | 0.04 | 7,000 |
| Si | ≤ 1 | ≤ 100 |
| Al | >100 | $>100,000$ |
| Mg | >100 | $>100,000$ |
| Na | >100 | $>100,000$ |
| F | ≤ 0.2 | $>100,000$ |
| B | 0.7 | $>100,000$ |
| Ce | - | 20 |

Pertinent data are shown in Tables 8 and 9 with mix ratios that eliminate phase separation. The data clearly indicate that both dry solids blends developed in Phase I meet the solid performance criterion of no drainable water. However, due to the nature of the actual sludges, lower solid-to-sludge mix ratios (i.e., leaner mixes) are sufficient to meet this criterion.

The 28-d compressive strength values using both blends were significantly less for sample 3-2 than for sample 1-1, indicating that variations in the waste compositions are affecting the cementitious reactions. A comparison of samples 1-1 and 3-2 shows that sample 3-2 possesses a higher Al content (Tables 6 and 7). This suggests the possibility of forming a calcium aluminate sulphate hydrate such as $C_3A \cdot 3CaSO_4 \cdot 31-32H_2O$ (i.e., ettringite). The formation of this salt, with its large amount of water of crystallization and consequently large increase in volume, can be destructive to the grout product. If the ettringite is formed while the grout paste is still plastic, then the grout can accommodate the expansive salt. However, if the ettringite forms after the grout has become rigid and "less forgiving," cracking will occur, which can significantly reduce the strength of the product.

In comparing the 24-h penetration resistance of the cement-Class F fly ash and Class C fly ash blends at identical mix ratios with the sample 3-2 waste (Tables 8 and 9), the penetration resistances for the Class C mixes are generally higher than those for the cement-Class F fly ash mixes. This indicates that the Class C fly ash mixes are hardening (i.e., losing their plasticity) at a faster rate. The data in Table 9 further illustrate that the compressive strength of the product is lessening with time, supporting the hypothesis that ettringite is being formed. It should be noted that some of the calcium and aluminum in Class C fly ash is present as calcium aluminates (C_xA_y). Thus, the possibility exists that more ettringite is being formed in the Class C fly ash mixes than in the cement-Class F fly ash mixes.

The data show that the waste composition can have a major impact on grout performance. This illustrates why ORNL tests a range of waste compositions in detailed grout-formulation studies.

Table 8. Properties of grout made with Weldon Spring sludge and a dry solids blend of 20 wt % Portland Type I cement and 80 wt % ASTM Class F fly ash

| Grout characteristics | Mix Ratio of waste sample 1-1 (lb/gal) | | | Mix Ratio of waste sample 3-2 (lb/gal) | | |
|---|--|------|-------|--|-------|-------|
| | 4 ^a | 6 | 8 | 4 ^a | 6 | 8 |
| Density, lb/gal | 13.4 | 13.4 | 14.0 | 12.6 | 12.8 | 13.2 |
| 10-min gel strength, 1bf/100ft ² | >300 | >300 | >300 | >300 | >300 | >300 |
| 24-h penetration resistance, psi | 16 | 180 | 500 | 40 | 120 | 100 |
| 7-d penetration resistance, psi | 260 | 940 | 2,300 | 280 | 1,000 | 3,000 |
| 7-d compressive strength, psi | 22 | 157 | 650 | 39 | 145 | 225 |
| 28-d compressive strength, psi | 562 | 235 | 977 | 147 | 119 | 951 |
| Volume increase vol % | 24 | 30 | 36.5 | 24 | 30 | 36.5 |

^aMinimum solid/sludge ratio to eliminate freestanding water.

Table 9. Properties of grout made with Weldon Spring sludge and a dry solids blend of ASTM Class C fly ash

| Grout characteristics | Mix Ratio of waste sample 1-1 (1b/gal) | | | Mix Ratio of waste sample 3-2 (1b/gal) | | |
|--|---|------|-------|---|------|----------------|
| | 4 ^a | 6 | 8 | 4 | 6 | 8 ^b |
| Density, lb/gal | 12.6 | 13.4 | 14.1 | 12.6 | 13.2 | 13.8 |
| 10-min gel strength, 1bf/100ft ² | >300 | >300 | >300 | >300 | >300 | >300 |
| 24-h penetration resistance, psi | 120 | 420 | 2,040 | 0 | 300 | 1,360 |
| 7-d penetration resistance, psi | 260 | 700 | 1,400 | 160 | 680 | 1,520 |
| 7-d compressive strength, psi | 39 | 72 | 257 | 45 | 123 | 212 |
| 28-d compressive strength, psi | 65 | 148 | 195 | 15 | 44 | 107 |
| Volume increase vol % | 24 | 30 | 36.5 | 24 | 30 | 36.5 |

^aMinimum solid/sludge ratio to eliminate freestanding water.

^bMinimum solid/sludge ratio to meet minimum 28-day compressive strength requirements.

5. PRELIMINARY CONCLUSIONS

These scouting studies were performed with surrogate and actual waste from the Weldon Spring Pits. Two dry solids blends, (1) 20-wt % Type I Portland cement and 80-wt % ASTM Class F fly ash, and (2) ASTM Class C fly ash, were identified that resulted in solid grouts that had no drainable water and could support earth-moving equipment. When these blends were applied to samples of actual waste, the solid grout performance criterion of no drainable water was also met. Because the actual wastes had a higher viscosity and lower phase separation than the surrogate waste, lower solid-to-waste ratios (i.e., leaner mixes) could be used to meet this criterion.

Therefore, the data obtained at the same mix ratios for surrogate and actual wastes were not similar, particularly with waste sample 3-2 and the Class C fly ash blend, illustrating that the waste composition can have a major impact on the processability and quality of the resulting grout product. This finding also illustrates why ORNL prefers to perform detailed formulation studies on a range of expected waste compositions rather than one or two samples.

When two blends are acceptable, the preference is usually determined by cost. The raw material costs are estimated to be: Type I Portland cement at \$60/ton (Knoxville, Tennessee), ASTM Class F fly ash at \$6/ton (Knoxville, Tennessee), and ASTM Class C fly ash at \$10/ton (Amarillo, Texas). Solid transportation costs in bulk will depend on the distance and the method of delivery, which are not included here. However, transportation costs can add significantly to the cost of these materials.

Using these raw material costs, the minimum material costs (per 1000 gal of sludge) for the cement-Class F fly ash blend at 4 lb/gal would be \$34, and for the Class C fly ash blend at 8 lb/gal, \$40. Within the accuracy of the data, these costs are identical. The use of only Class C fly ash eliminates the capital and operating costs associated with the solids blending that is necessary for the cement-Class F fly ash blend.

More detailed cost estimates based on local Weldon Spring conditions must be performed since these raw material costs are dependent on both the source of material and the associated shipping charges. Also, a local ven-

dor might preblend the cement and fly ash for a minor fee. It should be noted that in the case of a vendor supplying the preblended solids, the user must maintain a quality assurance program to ensure that the blend meets the specifications.

The cement-Class F fly ash blend is tentatively recommended because grouts made with waste sample 3-2 and Class C fly ash showed decreasing compressive strength with time, suggesting the formation of ettringite. If ettringite formation continues, then the compressive strength will decrease further. The preliminary nature of this study, with its associated budget and time constraints, precluded performing the necessary analyses to quantify the formation of ettringite. However, it should be noted that further study may show the Class C fly ash blend to be acceptable.

The viscous nature of these grouts indicates that a desirable processing method is in situ mixing and solidification. An example of an in situ processing scheme (i.e., a grouting gun) is shown in Figs. 5 and 6. The grouting gun is mounted on a backhoe, and the solid feed is pneumatically transferred to the gun directly from the delivery trucks. The gun injects the solids directly into the waste pit with waste-solids mixing being accomplished by the movement of the gun arm. This technique has been successfully demonstrated recently on the in situ solidification of oil field sludge pits in Oklahoma.

For this technique to be applied to radioactive wastes, however, concerns over product homogeneity and the elimination of dusting and aerosol formation must be resolved.

6. PHASE III: ADDITIONAL DATA NEEDS IN GROUT DEVELOPMENT

The scouting studies performed in Phases I and II developed two dry solids blends based on the limited rheological data from two samples of Weldon Spring sludge. These studies showed that the two principal solid grout performance criteria can be met and recommended a dry solids blend and a suggested disposal technique that can be used in preliminary cost estimates.

However, these data also show that the character of the pits' waste can have a major impact on the character of the resulting grout. Experience at

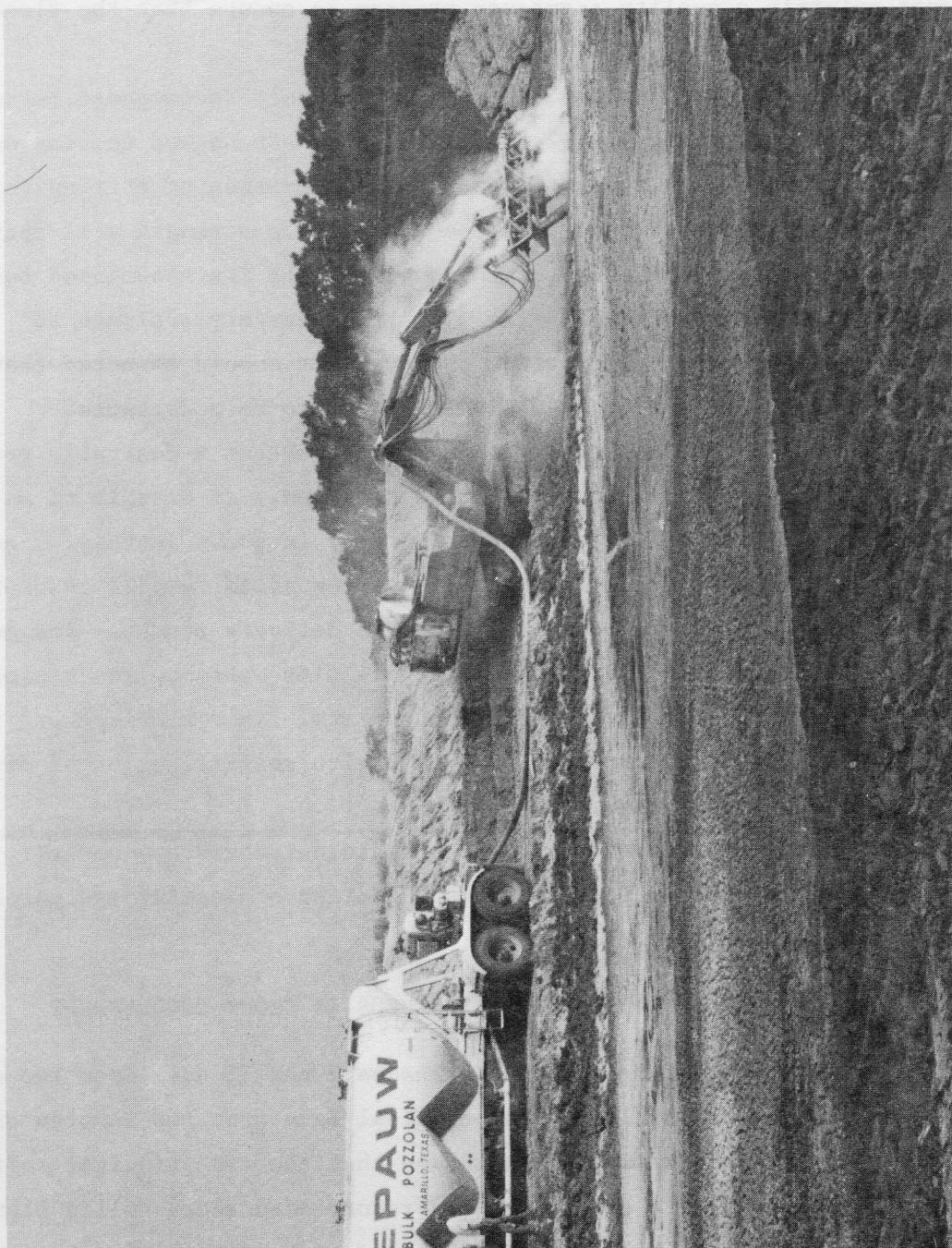


Fig. 5. Overview of grouting gun. (Photo 4128-83).



Fig. 6. Close-up of solids injection barrels. (Photo 4124-83).

ORNL with the hydrofracture process has shown that variations in the compositions of the waste and dry solids can also have a major impact on the resulting grout's mixing and solid performance characteristics.

Consequently, the following additional work is recommended:

1. Characterize grouts with more samples of Weldon Spring sludge.
2. Prepare grouts with local materials from several potential Weldon Spring suppliers.
3. Assess the effects of composition variations in the waste and solids blend on the grout(s). Measured variables should include unconfined compressive strength, phase separation, rate of strength development, ettringite formation, and leachability.
4. Modify the reference grout formula as required.

It should be noted that the recommendations in Phases I and II are based on only two performance criteria: (1) absence of drainable water, and (2) capability of supporting earth-moving equipment. Leachability, another critical criterion, was not addressed due to budget and time restraints. The leachability of the solidified grout determines the source term of potential contamination in most risk assessment scenarios.

It is generally agreed that the most likely means of contaminant transport from a disposal site is through leaching by groundwater. The applicable leach test is not generally agreed upon, however. Three potentially applicable leach tests that reflect DOE, Nuclear Regulatory Commission (NRC), and Environmental Protection Agency (EPA) regulatory requirements are

1. Modified MCC-1 for porous solids that can be used to determine leachate saturation. The saturated concentration may be used as a conservative source term for release-modeling studies.
2. ANS 16.1 that is being considered by the NRC as an applicable test for low-level waste. This test can result in a solid diffusion coefficient that can be used to predict long-term release from large monoliths.
3. EPA Toxicity Test that may be required by the Missouri EPA. These leach tests (or others, as determined by Bechtel) should be added to the list of measurements in item three in the list of recommended additional work above.

Phase III would result in a formula that ensures safe and reliable processing and waste disposal. The data would be directly applicable to process operations, risk assessments, and demonstrations of regulatory compliance. The resulting formula would then be used in a demonstration of the in situ disposal scheme. Indeed, such a demonstration could well be Phase IV of this program.

Phase IV, a demonstration, is essential to answer the unresolved questions of applying this in situ mixing and solidification with a grouting gun. First, while not a radiological hazard, the dusting that has accompanied the oil field demonstrations may become an Occupational Safety and Health Administration (OSHA) issue for some locations. Second, the use of compressed air to transport the dry solids blend through the grout gun may cause a radiological hazard from the aerosol transport of radioactive pit material.

Finally, none of the previous demonstrations have addressed the quality assurance issues associated with the proof of product homogeneity in this process. Monitoring methods need to be developed and product performances need to be determined in order to establish the potential reliability and regulatory compliance of this cost-effective waste disposal method.

If the efficiency of this in situ method cannot be established, then a much more elaborate and expensive disposal scenario could include (1) dredging and diluting, (2) mixing and pumping, and (3) in situ solidification and capping.

7. REFERENCE

1. D. K. Smith, Cementing, Society of Petroleum Engineers of AIME, New York, 1976.

ORNL/TM-9264
Dist. Category UC-70B

INTERNAL DISTRIBUTION

- | | |
|-----------------------|--------------------------------|
| 1. J. T. Bell | 29. K. M. McKeehan |
| 2. C. H. Brown | 30. L. W. McMahon |
| 3. R. M. Canon | 31. J. E. Mrochek |
| 4. L. R. Dole | 32. F. R. Mynatt |
| 5. C. P. East | 33. D. J. Naus |
| 6. C. W. Forsberg | 34. W. W. Pitt |
| 7. C. E. Francis | 35. M. E. Reeves |
| 8-12. T. M. Gilliam | 36-40. T. L. Sams |
| 13. R. W. Glass | 41. J. L. Shoemaker |
| 14. H. W. Godbee | 42. R. D. Spence |
| 15. M. V. Helfrich | 43. J. H. Stewart, Jr. |
| 16. F. J. Homan | 44. M. G. Stewart |
| 17. J. R. Horton | 45. D. P. Stinton |
| 18. E. K. Johnson | 46. S. H. Stow |
| 19. M. J. Kania | 47. O. K. Tallent |
| 20. C. W. Kimbrough | 48. R. G. Wymer |
| 21. R. E. Leuze | 49. Central Research Library |
| 22. A. J. Mattus | 50. Document Reference Section |
| 23-27. E. W. McDaniel | 51. Laboratory Records-RC |
| 28. C. P. McGinnis | 52-53. Laboratory Records |
| | 54. ORNL Patent Section |

EXTERNAL DISTRIBUTION

- 55. Office of Assistant Manager, Energy Research & Development,
DOE-ORO, P. O. Box E, Oak Ridge, TN 37831
- 56-442. Given distribution as shown in TIC-4500 under UC-70B,
Low-Level Radioactive Waste Management Category.