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RHEOLOGICAL CHARACTERIZATION OF CEMENTITIOUS GROUTS USED TO DISPOSE OF INTERMEDIATE-LEVEL RADIOACTIVE WASTE BY HYDROFRACTURING AT OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

The hydrofracturing process is a waste disposal process in use at the Oak Ridge National Laboratory for the permanent disposal of locally generated waste solutions. This process is now being modified for use in the disposal of sludge that results from the sodium hydroxide neutralization of acid waste solutions. In this process, the sludges will be slurried in a bentonite clay suspension and mixed with a solids blend of cement and other additives. The amount of dry solids required for each liter of waste slurry will be determined from a rheogram that relates the viscosity of the slurry with the grams per liter recommended for grouts with desirable flow properties.

A description of the process and the development of rheograms are included. Data are presented on the use of chemical additives to control the flow properties of grouts.

INTRODUCTION

At Oak Ridge National Laboratory (ORNL), intermediate-level waste (ILW) solutions (wastes with a specific activity between 1.5×10^4 and 2.0×10^{10} Bq/L) are currently being disposed of by the hydrofracturing process. In this process, the waste solution is mixed with cement and injected into an impermeable shale formation at a depth of about 300 m. Here the waste grout sets, fixing the radionuclides in the cement matrix. Subsequent injections form new grout sheets adjacent and parallel to the earlier grout sheets. This process is described in refs. 1 and 2.

The existing hydrofracturing disposal facility was built in 1963 for a series of four experimental injections. It was modified in 1966 for the routine disposal of the Laboratory's ILW solutions and has since been used for the disposal of over one million gallons of waste solution containing about 500,000 Ci of various radionuclides. This facility has worked quite well for the disposal of ILW but cannot handle either slurries or wastes with a specific activity higher than 2.0×10^{10} Bq/L. A disposal system for these types of waste has been designed and is being built. When the new facility has been completed, the sludge that is now in the Gunite waste tanks at ORNL will be suspended and pumped to the new ILW storage tanks in Melton Valley. Subsequently, this suspended sludge will be pumped to the new fracturing facility and mixed with a cement mix base to form a grout. This grout will then be injected underground by the hydrofracturing technique (Fig. 1). The grout-containing sludge must have properties not greatly dissimilar from those of current shale fracturing grouts.[3] It must be fluid and remain fluid for at least 24 h, exhibit phase separation of less than 5%, and have an acceptable compressive strength and leach rate. The amount of dry solids required for each liter of waste slurry will be determined from a rheogram that relates the viscosity of the slurry with the grams per liter recommended for grouts with desirable flow properties.

EXPERIMENTAL

The grout used at the hydrofracture facility to dispose of the waste supernate was made by combining the solution with a predetermined weight of dry solids. This procedure was modeled in the laboratory by preparing simulated waste solutions based on chemical analyses of actual waste solutions in the ORNL waste storage tanks.[4] Mixing was performed by adding dry solids slowly to the waste solution during a 15-s period while stirring followed by continued stirring for an additional 15 s at the same mix speed. A speed of 2000 rpm was used to simulate grout mixed in the plant mixer tub.

The grout resulting from mixing dry solids with a sludge-slurry suspension should have properties not greatly dissimilar from those used in the disposal of ILW solutions.

The experimental objective is to establish a rheogram that relates the apparent viscosity* of a slurry of simulated radioactive sludge to the dry blend/slurry ratio required to produce a grout similar to a grout prepared with waste solution. Previous work has shown that even though the individual flow properties [fluid consistency index (K'), flow behavior index (n'), viscosity, and density] of grouts may vary greatly, they could exhibit similar pumping properties and phase separation.[5,6,7] For example, in calculating the flow rate required for turbulence (critical velocity), the quotient K'/D of two completely different values could be equal.

Dry solids slurry mixing experiments were conducted in the laboratory using only those physical properties that can be determined on the actual sludge-mix. These include, for example, the slurry viscosity and density. The underlying assumption which formed the basis of the measurements was that a dry solids blend could be added to a sludge-slurry suspension of a given viscosity until the power required to mix the grout at a predetermined speed was equal to that of a reference mix. It was felt that the resulting grout would have a viscosity, critical velocity, and phase separation similar to the reference grout.

A laboratory mixer with an electronic speed control was used for all mixes. A sensitive ampmeter was used to detect changes in current required to maintain constant mixing speed. The argument made here is that the power required to maintain constant speed is proportional to the viscosity of the mix. The current change (increase) for a given dry solids ratio as solids were added to a simulated waste solution was used as a reference point for mixing more-viscous slurries that required less dry solids addition to yield an equal current increase. Reference grouts made with simulated waste solution were made in the ratios 719.0 g/L (6.0 lb/gal) and 758.0 g/L (8.0 lb/gal) respectively. Grout properties are listed in Table 1; dry solids compositions used in grout mixing are listed in Table 2.

The grout rheological properties were measured with a Fann viscometer. The power law model was used to determine all grout flow properties. The power law model is based on the assumption that the fluid (grout) exhibits a proportionality between the logarithm of the pressure loss and the logarithm of the flow rate in the region of laminar flow.[5] A log-log plot of shear stress vs

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*Apparent viscosity is the viscosity that a fluid appears to have at a stated shear rate. It is a function of the plastic viscosity (resistance to flow caused by friction between suspended particles and by the viscosity of the liquid phase) and the yield point, which is a measure of the forces that cause a gel structure to develop when the slurry is at rest.

shear rate is constructed to obtain the two parameters required to define the power law model. The intercept of this line at unit shear rate is called the "consistency index." The index is denoted by K'. The slope of the line, n', is referred to as the "flow behavior index" and is a measure of the non-Newtonian behavior of the fluid.

Fifteen weight percent metal oxides suspended with 2.0 wt % commercial-grade bentonite clay in a 0.1 M $NaNO_3$ solution were used as a simulated sludge slurry. Bentonite, a more predictable clay than Attapulgite, was found to be an effective suspender in dilute $NaNO_3$ solutions.

An area of interest in sludge-slurry grout compatibility testing is the effect of surface area and particle size on viscosity and settling rate. Even though no detailed study was made, the trend was for the smaller particles to produce more viscous suspensions. This was used as an advantage when slurries of equal solids contents but different viscosity were needed.

Sludge-slurry grouts were prepared by adding a dry solids blend (Table 2) to slurries of different viscosities until the power required for mixing equaled that of the reference grout. Grouts were referenced to 719.0 g/L and 958.0 g/L respectively. Data are listed in Tables 3 and 4. From these data, a rheogram (Fig. 2) was established. The rheogram relates the viscosity of the slurry with the grams per liter of dry solids recommended for grouts with desirable flow properties.

It is obvious from data listed in Tables 3 and 4 that the individual flow parameters differ greatly from those of the reference grouts. The mixing power is not represented on the rheogram. The only significance is that the mixer required the same power to mix the slurry grout as was required to mix the reference grout.

As an additional check of grout similarity, critical velocities (velocity where flow changes from laminar) were compared. The following equation is used to calculate the velocity (flow rate) at a specific Reynolds number.[4]

$$V = {\frac{N_{re} K'(96/d_i)^{n'}}{1.86D}}^{\frac{1}{2-n'}} , \qquad (1)$$

V = velocity (ft/s),*
D = fluid density (lb/gal),
d_i = 4 times area of flow/wetted perimeter (in.),
N_{re} = Reynolds number (dimensionless),
n' = flow behavior index (dimensionless),
K' = consistency index ($lbf \cdot s^{n'}/ft^2$).

A Reynolds number of 2100 is the accepted value for the start of turbulence in cement slurry flow calcualtions. This N_{re} is used in all calculations presented in this report.

THE USE OF CHEMICAL ADDITIVES TO CONTROL FLOW PROPERTIES OF SLUDGE-SLURRIES AND CEMENTITIOUS GROUTS

There are several types of chemical compounds that may be used to change the flow properties of non-Newtonian liquid. For example, tannins, lignites, polyphosphates, and lignosulfonates are the compounds that the oil industry has found to be the most effective "thinners." Each of these materials has its optimum effectiveness under certain conditions and within

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*To convert from ft/s to m/s multiply by 0.3048.

a definite pH range. Polyphosphates are rarely used if the pH exceeds 10. Tannins are effective if the pH is >8, and lignites work best between a pH of 8.5 and 9.5. The action of these compounds when added to a fluid to lower the velocity required for turbulent flow is thought to be that they complete broken valence bonds, thus reducing interparticle forces.

Additives more closely related to cementing are the friction reducers and plasticizers. Friction reducers are essentially dispersing agents which reduce the apparent viscosity of the slurry with no change in flow rate. A lower apparent viscosity gives a higher Reynolds number and therefore a lower Fanning friction factor and a lower critical velocity.[4] Plasticizers increase the fluidity of a cement slurry for a given water-to-solids ratio. Friction reducers and plasticizers may be conveniently added to a dry solids blend. Data related to those chemicals are well covered in the literature.[5,8] Caution must be exercised in using chemicals to control flow properties of radioactive sludge-slurries and grouts because of the uncertainity of slurry composition.

RESULTS AND CONCLUSIONS

The rheogram presented in this paper describes grout pumping parameters that can be used by field personnel to mix dry solids to sludge-slurries of different viscosities. The grouts referenced to 719 g/L exhibit critical velocities twice that of the reference grout when the calculations are based on a 5.08-cm-ID tube. The calculations become more accurate with increasing dry solids per liter and smaller tube diameters. Addition of dry solids can be based solely on the viscosity of the slurry.

Chemical additives can be used to control the flow properties of sludge-slurries and grouts. These chemicals should not be used unless necessary since they would add to the complexity of the grout and increase operating costs.

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TABLE I
Properties of reference grouts

Property	719 g/L	958 g/L
Fluid consistency index (*K*')	4.43×10^{-3}	5.56×10^{-2}
Flow behavior index (*n*')	0.59	0.35
Viscosity (Pa·s)	0.015	0.045
Density (g/cm^3)	1.40	1.48
Phase separation (vol %)	4.52	0.60
Critical velocity in 5.08-cm-diam pipe (m/s)	0.8	1.8

TABLE II
Composition of dry solids used in grout mixing studies

Material	Waste solution reference (wt %)	Sludge-slurry (wt %)
Type I portland cement	38.5	46.0
Kingston TVA fly ash	38.5	46.0
Attapulgite clay	15.3	-
Indian Red clay	7.7	8.0

TABLE III
Flow properties of grouts referenced to 6.0 lb/gal (719.0 g/L) dry solids in simulated waste solution-reference velocity of 2.8 ft/s (0.8 m/s)

Slurry[a] viscosity		Grout viscosity		Dry solids added		Grout density		Critical velocity[b]		Phase sep. vol	Flow parameters	
											Fluid consistency index	Flow behavior index
(Pa·s)	(cP)	(Pa·s)	(cP)	(g/cm^3)	(lb/gal)	(g/cm^3)	(lb/gal)	(m/s)	(ft/s)	(%)	(K')	(n')
0.035	3.5	0.270	27.0	0.66	5.5	1.43	11.96	1.33	4.40	3.64	4.81×10^{-2}	0.27
0.045	4.5	0.270	27.0	0.66	5.5	1.40	11.65	1.43	4.72	2.01	6.60×10^{-2}	0.23
0.075	7.5	0.375	37.5	0.60	5.0	1.39	11.60	1.74	5.71	1.82	1.22×10^{-1}	0.18
0.085	8.5	0.335	33.5	0.54	4.5	1.37	11.40	1.57	5.16	1.42	1.19×10^{-1}	0.16
0.090	9.0	0.330	33.0	0.54	4.5	1.36	11.35	1.60	5.26	2.10	1.03×10^{-1}	0.18
0.120	12.0	0.260	26.0	0.30	2.5	1.28	10.65	1.45	4.75	4.96	5.48×10^{-2}	0.25
0.130	13.0	0.270	27.0	0.24	2.0	1.27	10.60	1.50	4.91	4.10	5.48×10^{-2}	0.25
							$\bar{X}$ = 11.31	1.52	4.98		8.11×10^{-2}	0.22
							S = 0.51	0.13	0.43		0.03	0.04

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[a] Slurry composed of 15.0 wt % Fe_3O_4 suspended with 2.0 wt % bentonite clay in 0.1 M $NaNO_3$ solution. Viscosity was varied by stabilizing at slightly different shear rates and slight variations in pH.

[b] Critical velocity for flow in a 2-in.-ID (5-cm) tube. Flow rate would be approximately 50 gal/m (3.2 L/s). A hydrofracture injection is normally made at a flow rate of 250–275 gal/m (16–17 L/s).

TABLE IV
Flow properties of grouts referenced to 8.0 lb/gal (959.0 g/L) dry solids in simulated waste solution-reference velocity of 6.2 ft/s (1.8 m/s)

Slurry viscosity[a]		Grout viscosity		Dry solids added		Grout density		Critical velocity[b]		Phase sep. vol.	Flow parameters: Fluid consistency index	Flow parameters: Flow behavior index
(Pa·s)	(cP)	(Pa·s)	(cP)	(g/cm³)	(lb/gal)	(g/cm³)	(lb/gal)	(m/s)	(ft/s)	(%)	(*K'*)	(*n'*)
0.030	3.0	0.505	50.5	1.32	11.0	1.62	13.5	1.89	6.21	0.84	1.28×10^{-1}	0.23
0.060	6.0	0.660	66.0	1.17	9.8	1.60	13.35	2.16	7.10	1.10	1.40×10^{-1}	0.25
0.095	9.5	0.365	36.5	0.96	8.0	1.57	12.60	1.76	5.79	1.10	9.07×10^{-2}	0.24
0.120	12.0	0.465	46.5	0.9	7.5	1.51	12.65	1.85	6.09	0.48	1.25×10^{-1}	0.21
0.160	16.0	0.480	48.0	0.63	5.25	1.42	11.85	1.97	6.47	3.30	1.56×10^{-1}	0.18
0.17	17.0	0.550	55.0	0.60	5.0	1.41	11.80	2.17	7.12	2.0	1.92×10^{-1}	0.17
0.19	19.0	0.580	58.0	0.48	4.0	1.37	11.40	2.07	6.79	2.70	1.85×10^{-1}	0.16
							$\bar{X}$ = 12.45	1.98	6.51		1.45×10^{-1}	0.21
							S = 0.80	0.16	0.51		0.04	0.04

[a] Slurry composed of 15.0 wt % Fe_3O_4 suspended with 2.0 wt % bentonite clay in 0.1 M $NaNO_3$ solution. Viscosity was varied by stabilizing at slightly different shear rates and slight variations in pH.

[b] Critical velocity for flow in a 2-in.-ID (5-cm) tube. Flow rate would be approximately 64 gal/m (4.0 L/s).

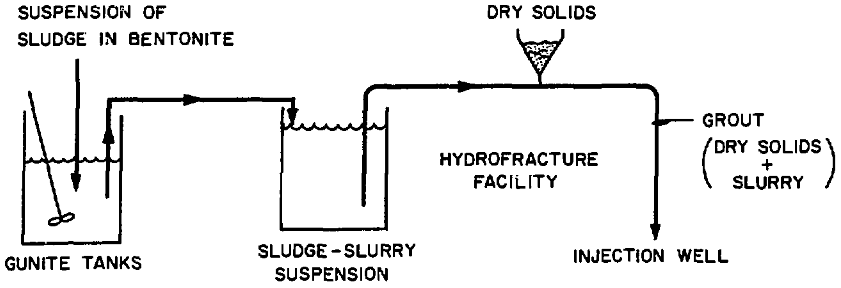

Fig. 1. Flow diagram of sludge disposal process.

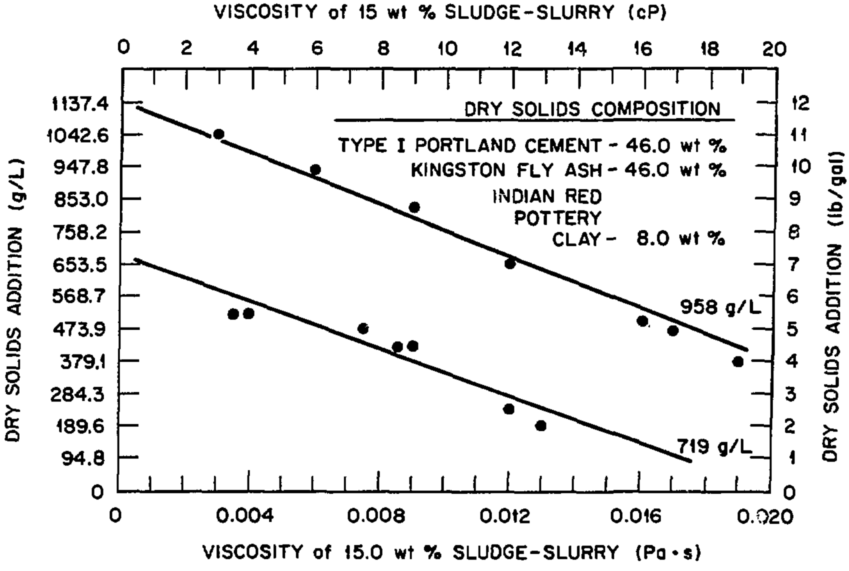

Fig. 2. Rheogram relating flow properties of sludge-slurry grouts to grouts made with ILW solutions.