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STRONTIUM LEACHABILITY OF HYDROFRACTURE GROUTS FOR SLUDGE-SLURRIES*

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ABSTRACT

This paper summarizes a series of experiments to determine the strontium leachability of cement-based sludge-slurry hydrofracture grouts.

The hydrofracture process has been used at ORNL since 1966 for the routine disposal of intermediate-level waste (ILW) solutions. In this process, cement and other additives are mixed with a waste stream to form grout, which is then injected into a shale bed at a pressure sufficient to cause fracturing along the horizontal bedding planes. This injected grout soon hardens, fixing the radionuclides between layers of the massive Conasauga shale formation.

Modified IAEA dynamic leach tests on hydrofracture grout specimens showed improved leach resistance (by a factor of 3 to 5) as the curing time increased from 28 d to 91 d. A weak trend toward lower leachability with increased amounts of dry solids was observed.

The moving boundary-plus-diffusion leach model fits the dynamic leach data successfully in most cases. An apparent diffusion coefficient of $5 \times 10^{-12} \text{ cm}^2/\text{s}$ and a moving boundary coefficient of $1 \times 10^{-7} \text{ s}^{-1}$ were obtained when one of the best grout compositions was leached in distilled water. Assuming that vertical fractures produce the leachable

surfaces in a grout sheet, the release rate of strontium calculated with these coefficients is well below the NRC maximum of 10^{-5} fraction per year.

1. INTRODUCTION

This study of the leachability of strontium from hydrofracture grouts is part of a continuing program at ORNL to develop cementitious waste forms for the disposal of radioactive wastes. The grouts used in these experiments simulate those that will be used in the hydrofracture process to dispose of the radwaste sludges now stored at ORNL.

The sludges from the ORNL tanks will be slurried with bentonite clay and pumped about 1.600×10^3 m (1 mile) to holding tanks at the hydrofracture site. (Previous work has shown that bentonite clay is an effective suspending agent for the sludge.¹) Then the sludge-slurry will be blended with the dry solids mix to produce grouts for injection into the underlying Conasauga shale formation.²⁻⁵ The addition of dry solids will be regulated to control the viscosity and pumpability of the grouts.⁶ The leachability of certain radioactive nuclides from the grout sheet after injection and solidification is a major concern. These nuclides include ^{90}Sr and actinides that precipitate with other sludge-forming materials generated during neutralization of acid waste streams.

Past work has shown that the immobilized actinides have very low leach rates from these cement-based grouts.^{7,8} This report addresses only the ^{90}Sr leachability from such grouts.

2. EXPERIMENTAL PROCEDURE

Slurries of different viscosities were prepared by using 15.0 wt % metal oxides and/or metal particles suspended with 2.0 wt % bentonite clay in a 0.1 M NaNO_3 solution. The viscosity variations, measured at a given shear rate, were obtained by changing the stabilization process shear rate and the pH. The NaNO_3 was included to simulate the liquid phase that separates and stands above actual waste sludges. A dry-solids blend composed of 46.0 wt % Type I Portland cement, 46.0 wt % Kingston fly ash, and 8.0 wt % Indian Red pottery clay was added to the slurries. The amount of dry solids added was regulated by using the mixing power (as indicated by a meter connected to the blender) to match the viscosity of each mix with that of a pumpable reference grout at a given shear rate. The two reference grouts had dry-solids-to-liquid ratios of 719 g/L (6 lb/gal) and 958 g/L (8 lb/gal). Sludge-slurry grouts within the rheological boundaries of these two reference grouts will have parameters similar to grouts which have been shown to be pumpable. The slurries were subsequently poured into the molds and vibrated to remove air bubbles. The mixing procedure conformed to the requirements of ASTM Standard Procedure C109-73.*

The composition and properties of grouts used in the leach studies are given in Table 1. Each ingredient contained an inherent amount of

*C109-73, "Standard Method of Test for Compressive Strength of Hydraulic Cement Mixtures," Annual Book of ASTM Standards, Part 14 (1975).

Table 1. Properties of typical sludge-slurry grouts^a

Reference grout (g/L)	Sample No.	Slurry visc. (Pa·s)	Grout ingredients (wt %) ^b					Density (g/cm ³)
			Type I cement	Fly ash	Pottery clay	Sludge (dry)	B. clay mix	
719	280002	0.0040	17.41	17.41	3.03	9.51	52.64	1.41
	280003	0.0070	15.33	15.33	2.70	10.21	56.44	1.37
	280004	0.0095	13.28	13.28	2.31	10.89	60.24	1.25
958	280005	0.0040	24.26	24.26	4.22	7.23	40.03	1.63
	280006	0.0090	21.97	21.97	3.82	8.00	44.24	1.54
	280007	0.0155	17.41	17.41	3.03	9.51	52.64	1.46

^aPrepared by mixing a dry solids blend consisting of 46.0 wt % Type I cement, 46.0 wt % Kingston fly ash, and 8.0 wt % pottery clay with a 15 wt % sludge-slurry. The sludge-slurry was made by suspending 45.18 g of dried sludge in 250 mL of a 2.0 wt % bentonite clay-0.1 M NaNO₃ solution with pH adjusted to 11.0.

^bApproximately 0.04% of tributyl phosphate (TBP) was added to prevent foaming. CFR-1, added as a chemical retarder to setting, amounts to about 0.05 wt %.

Table 2. Cold strontium^a contents of grout components

Material	Strontium concentration (mg Sr/g material)
Type I cement	1
Fly ash	0.8
Indian Red pottery clay	0.4
Bentonite	1
Sludge (dry)	1

^aAnalyzed by dc spark emission spectroscopy.

natural strontium (Table 2). In these experiments, the fraction of strontium leached out is based on the total strontium contained in the grout. This paper assumes that the leaching behavior of this cold strontium is the same as that of radioactive strontium, which would be supplied only by the sludge in actual practice. This assumption should be verified by additional experiments. The specimens were cured for 28, 91, or 182 d in a closed bottle which was immersed in water at ambient temperature. The leach tests began immediately after curing.

A modified IAEA leaching procedure⁹ was used with specimens that were right-circular cylinders 1.6 cm in diameter by 2.2 cm long. The leachant volume was 150 mL. The leach solutions were automatically changed on a daily basis. The contents of the mixes and leachates were measured by inductively coupled plasma (ICP) spectrometry.

3. RESULTS AND DISCUSSION

The strontium leach data of selected grouts were fitted by a non-linear least-squares method to the Codbee-Joy equation:¹⁰

$$F \cdot V / SA = (R \cdot D)^{1/2} [(t + 1/2R) \operatorname{erf}(R \cdot t)^{1/2} + (t/\pi R)^{1/2} \exp(-R \cdot t) + t],$$

where

F = fraction released at time t ;

V = volume of sample, cm^3 ;

SA = surface area of sample, cm^2 ;

$R = U^2/4D$, apparent moving boundary constant, s^{-1} ;

D = apparent diffusion coefficient, cm^2/s ;

t = time, s ;

U = apparent moving boundary velocity or degradation rate, cm/s ;

$\text{erf } u$ = error function = $2/\pi^{1/2} \int_0^u e^{-z^2} dz$.

The apparent diffusion and moving boundary coefficients obtained and the physical properties of the grouts are listed in Table 3. These results show that strontium leach rates decreased with curing time. However, the rate of decrease leveled off after the 91-d interval. Also, there is a weak trend toward decreasing leach rates as increased amounts of dry solids were added. More complete results have been previously reported.¹¹

A diffusion coefficient of $5 \times 10^{-12} \text{ cm}^2/s$ and a moving boundary coefficient of $1 \times 10^{-7} \text{ s}^{-1}$ were obtained for the best grout cured at 182 d. The worst case produced a diffusion coefficient of $1 \times 10^{-9} \text{ cm}^2/s$ and a moving boundary coefficient of $2 \times 10^{-21} \text{ s}^{-1}$. Plots of the fraction released vs time show a linear relation for the best grout, indicating that dissolution or erosion predominated (Fig. 1). A decreasing rate with time for the worst grout indicates diffusion-controlled release (Fig. 2).

4. CONCLUSIONS

The following conclusions can be drawn from the results obtained in this study:

Table 3. Results from dynamic leaching experiments on sludge-slurry hydrofracture grouts in distilled water

No. ^a	Cure time (d)	Slurry visc. (cP)	Dry solids conc. (g/L)	Effective diffusion coefficient (cm ² /s)	Apparent moving boundary coeff. (cm/s)	Zero-time Intercept (cm)	F ₈₀ ^b	Density (g/cm ³)
1	91	4.0	719	1.7 x 10 ⁻¹⁰	5.9 x 10 ⁻¹⁰	0.00	0.146	1.401
2	91	7.0	599	5.8 x 10 ⁻¹²	5.8 x 10 ⁻⁷	0.00	0.097	1.280
3	91	9.5	479	1.8 x 10 ⁻¹⁰	5.4 x 10 ⁻⁹	0.00	0.161	0.908
4	28	4.0	1258	1.1 x 10 ⁻⁹	3.5 x 10 ⁻¹³	1.00	0.328	1.284
5	91	4.0	1258	5.1 x 10 ⁻¹³	4.4 x 10 ⁻⁶	0.00	0.077	1.257
6	182	4.0	1258	5.3 x 10 ⁻¹²	9.9 x 10 ⁻⁸	0.05	0.039	1.341
7	28	9.0	1078	1.2 x 10 ⁻⁹	2.2 x 10 ⁻¹⁹	0.02	0.344	1.191
8	91	9.0	1078	1.5 x 10 ⁻¹¹	2.0 x 10 ⁻⁷	0.00	0.095	1.137
9	182	9.0	1078	1.3 x 10 ⁻¹¹	2.8 x 10 ⁻⁷	0.00	0.103	1.031
10	28	15.5	719	1.3 x 10 ⁻⁹	1.8 x 10 ⁻²¹	3.00	0.506	1.125
11	91	15.5	719	2.4 x 10 ⁻¹⁰	2.6 x 10 ⁻⁸	0.00	0.228	1.151
12	182	15.5	719	2.2 x 10 ⁻¹⁰	2.8 x 10 ⁻⁸	0.00	0.195	1.052

^aSamples 1 through 3 were matched to a reference grout with a solids-to-liquid ratio of 719 g/L. Samples 4 through 12 were matched to a grout with a ratio of 958 g/L.

^bF₈₀ is the fraction leached in 80 d. These values are dependent on the S/V ratios and would be much smaller in the hydrofracture geometry sealed between layers of shale.

Fig. 1. Fraction of strontium leached vs time from sample 280005.3, cured 182 d.

Fig. 2. Fraction of strontium leached vs time from sample 280007.1, cured 28 d.

1. Using the modified IAEA leach procedure and the Godbee-Joy model, an apparent diffusion coefficient of $5 \times 10^{-12} \text{ cm}^2/\text{s}$ and a moving boundary coefficient of $1 \times 10^{-7} \text{ s}^{-1}$ were obtained for one of the best grout formulations in distilled water. The Godbee-Joy equation shows that release by both diffusion and surface degradation is proportional to SA/V , where SA is the surface area and V is the volume of the solid. The effective surface area of a grout sheet inserted in a horizontal fracture of a shale bed will be very small compared to the volume since the horizontal surfaces will be sealed by impervious shale under pressure. Vertical fractures will expose only small edges of the grout sheet. In a typical hydrofracture injection, the grout sheet may be 1600 ft (5000 cm) in diameter by 0.5 in. (1.3 cm) thick. If we assume a uniform thickness, an exposed circumference, and a single vertical fracture across the center, the SA/V ratio will be $1 \times 10^{-4} \text{ cm}^{-1}$. Although additional fractures would increase the exposed area, the SA/V ratio would still be considerably less than that for exposed cylindrical waste forms. Under such conditions, best values represent a release rate of 2×10^{-6} fraction per year, which meets the NRC requirement for nuclear waste of less than 1×10^{-5} fraction per year.

2. Results showed only a slight dependence of strontium leachability on grout composition variations within the range of acceptable pumpability. In hydrofracture, pumpability is a necessary requirement.
3. The leach resistance improved by a factor of 3 to 5 as curing time was increased from 28 d to 91 d. A very slight trend toward increased leach resistance was noted with increased solids addition.

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