

SOLIDIFICATION/STABILIZATION OF TECHNETIUM IN CEMENT-BASED GROUTS*

T. MICHAEL GILLIAM¹ and ROGER D. SPENCE

Oak Ridge National Laboratory Oak Ridge, TN 37831 (U.S.A.)

and

WILLIAM D. BOSTICK and J.L. SHOEMAKER

Oak Ridge Gaseous Diffusion Plant, Oak Ridge, TN 37831 (U.S.A.)

Summary

Mixed low-level radioactive and chemically hazardous process treatment wastes from the Portsmouth Gaseous Diffusion Plant are stabilized by solidification in cement-based grouts. Conventional portland cement and fly-ash grouts have been shown to be effective for retention of hydrolyzable metals (e.g., lead, cadmium, uranium, and nickel) but are marginally acceptable for retention of radioactive ⁹⁹Tc, which is present in the waste as the highly mobile pertechnetate anion. Addition of ground blast furnace slag to the grout is shown to reduce the leachability of technetium by several orders of magnitude. The selective effect of slag is believed to be due to its ability to reduce Tc(VII) to the less soluble Tc(IV) species.

Introduction

Solidification/stabilization techniques using cement-based grouts are the most widely used technology for the treatment and ultimate disposal of both radioactive and chemically hazardous waste because of their low processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements. Grouts, which meet all applicable regulatory requirements for the disposal of heavy metals [1], selected organics [2], and radionuclides [3], have been developed. In general, the performance of these grouts in sequestering the waste constituents of concern is most successful when the constituent of interest is relatively insoluble in the high pH of the grout pore water. Grouts, particularly neat cement-paste grouts, have proven less successful in sequestering species such as technetium and nitrates, which are readily soluble in pore water.

*Paper presented at the GCHSRC Second Annual Symposium: Mechanisms and Applications of Solidification/Stabilization, Lamar University, Beaumont, TX, U.S.A., February 15-16, 1990.

¹To whom correspondence about this paper should be sent at Martin Mariette Energy Systems Inc., P.O. Box 2003, Oak Ridge, TN 37831-7273.

Technetium is one of four radionuclides (^{99}Tc , ^3H , ^{14}C , and ^{131}I) of particular concern to the U.S. Nuclear Regulatory Commission (NRC), because of their mobility and biological activity [4]. The mobility of technetium results in large part from the movement of the pertechnetate anion (prevalent in low-level radioactive waste [LLW]) through soil and geologic strata with little or no interaction with the surrounding matrix. Ground blast furnace slag has been shown to improve the leach resistance of cement-based waste forms, particularly in regard to technetium [5,6]. This improved performance has been attributed to fewer and smaller pores in the solidified slags (versus a neat cement paste) and to the reduction of the pertechnetate ion to a less soluble form.

This paper presents preliminary results of a grout development effort to identify grout formulas that can satisfactorily sequester ^{99}Tc contained in an existing Portsmouth Gaseous Diffusion Plant waste.

Experimental

Waste characterization

The LLW examined in this study originates from the treatment of an aqueous effluent, or "raffinate", from uranium recovery and equipment decontamination operations at the Portsmouth Gaseous Diffusion Plant in Portsmouth, Ohio. The acidic raffinate is diluted and the pH adjusted to a value of 8.2 to 8.5. The pH adjustment results in the precipitation of metal hydroxides, which are further concentrated by paper filtration to yield a filter cake designated as heavy metals sludge (HMS) and an HMS filtrate. Although the sludge is basically a soft solid, it contains a significant amount of liquid (~65 wt. %). It has also been shown to be characteristically hazardous according to the U.S. Environmental Protection Agency (EPA) EP-Toxicity test [7,8] for both cadmium and lead and, hence, is mixed waste. Typical concentrations of selected constituents for both the sludge and filtrate are shown in Table 1. The high concentrations of technetium and nitrate remaining in the sludge filter cake are due primarily to incomplete dewatering.

Dry-solids blend components

Dry-solids blend components of the grouts tested were: (a) Type I-II LA portland cement obtained from the Dixie Cement Company in Knoxville, Tennessee; (b) ASTM Class F fly-ash from Centralia, Washington, obtained from Pozzolan International in Mercer Island, Washington; and (c) granulated blast furnace slag (BFS). Blast furnace slag is produced when the molten slag from a blast furnace is cooled quickly to minimize crystallization and is a blend of amorphous silicates and aluminosilicates of calcium and other bases. Because of the presence of ferrous iron and reduced sulfur compounds, BFSs may impart a selective retention for mobile species such as Tc(VII) by reduction to a less soluble valence state such as Tc(IV). Four sources of BFS were eval-

TABLE 1

Characterization of heavy metal sludge and filtrates

| Constituent | Sludge concentration ($\mu\text{g/g}$) | Filtrate concentration (mg/L) |
|-------------|---|--|
| Arsenic | 4.5 | - |
| Barium | 35 | 0.47 |
| Cadium | 970 | <0.03 |
| Chromium | 490 | <0.1 |
| Lead | 52,300 | <0.5 |
| Mercury | <1 | 0.92 |
| Selenium | <0.5 | - |
| Silver | 5.7 | <0.06 |
| Aluminum | 96,000 | 8.5 |
| Copper | 1,900 | <0.04 |
| Iron | 36,000 | <0.04 |
| Nickel | 6,000 | <0.1 |
| Uranium | 310 | <0.01 |
| Zinc | 1,300 | |
| Nitrate | 117,000 | 94,000 |
| Technetium | 5.13 | 13.7 |

uated: (I) a material originating from Japan and obtained from Ash Grove Cement West, Inc., in Kennewick, Washington; (II) a material originating from Cleveland Republic Furnace No. 6 and obtained from Standard Slag Company in Canfield, Ohio; (III) the Cleveland slag with gypsum added at 3 wt.%; and (IV) material originating from Sparrow's Point, Maryland, obtained from Blue Circle Atlanta, Inc., in Atlanta, Georgia.

Test and sample preparation procedures

The dry-solids blend components for each grout formula were placed in a V-blender and tumbled for 4 h. The resulting blend was added to the waste over a 30-s period in a Model N-50 Hobart mixer, which was set at a low stirring rate (~ 285 rpm), and the blend was allowed to mix for an additional 30 s. The resulting freshly prepared grouts were then poured into cylindrical Teflon[®] molds (2.55-cm diameter by 4.80-cm length) and allowed to cure at 100% humidity for 28 days [9]. The resulting monolithic samples were then leached following the abbreviated ANSI/ANS-16.1-1986 procedure [10]. This procedure produces a figure of merit designated as a leachability index (*LI*), which can be used to compare the leach resistance of different grout formulas. This *LI* is the basis for comparison of performance for the formulas tested in this preliminary study. It should be noted that unless otherwise specified, all in-

dices reported in this paper are the average obtained from three replicate samples.

Results

Effect of slag source

A single right circular cylindrical sample (3.3-cm diameter by 7.1-cm length) was prepared with HMS and a reference grout formula used at the Oak Ridge Gaseous Diffusion Plant (ORGDP) Concrete Fixation Facility for stabilization of waste treatment pond sludges. The grout matrix composition, in percent, was 38.3% HMS, 11.7% added water (for a total water content of 35.5%), 25.0% Type I-II-LA portland cement, and 25.0% ASTM Class F fly-ash. A commercially available (Master Builders, Cleveland, Ohio) air entrainment admixture, MB-AE-10, was added to the dry-solids blend at 0.12 wt.%. This admixture is used at the ORGDP Concrete Fixation Facility to improve processibility for large batch pours.

An EP-Toxicity test was performed on the sample, and, as expected, the grout rendered the waste nonhazardous per this characteristic. The resulting leachate concentrations of all of the eight metals addressed in this test (As, Ba, Cd, Cr, Pd, Hg, Se, and Ag) were below EPA primary drinking water standards, with the possible exception of total Cr, Pb, and Ag, which were <0.1, <0.5, and <0.06 ppm, respectively. An ANSI/ANS-16.1-1986 leach test performed on this sample yielded *LI* values for ⁹⁹Tc and nitrate of 6.1 and 5.9 ppm, respectively.

This test verified that in a regulatory context, the metals were not of major concern to this study. Furthermore, this test allowed the visual observation that waste constituents, particularly lead, had no deleterious effects on the rate of set of the grout. Thus, the developmental effort could concentrate on improving the retention of technetium and nitrates using a surrogate to minimize nonhomogeneity concerns for the small sample size used.

Using HMS filtrate as a surrogate, ANSI/ANS-16.1-1986 samples were prepared with the following composition: 40 wt.% HMS filtrate, 20 wt.% BFS, 20 wt.% ASTM Class F fly-ash, and 20 wt.% Type I-II-LA portland cement. Four sources of BFS were tested, and their resulting *LIs* are shown in Table 2. An additional test was performed on the formula containing BFS from Japan with the addition of an air entrainment admixture that is used routinely at the ORGDP Concrete Fixation Facility.

The data in Table 2 show the improved retention of ⁹⁹Tc over the reference ORGDP formula by 4.4 units (10.5 versus 6.1) as measured by the *LI*. Nitrate retention was also improved, although only by 1.4 units (7.3 versus 5.9). It should be noted that, assuming diffusion-controlled release, an increase in *LI* of one unit corresponds to a reduction in the effective diffusion coefficient by a factor of 10. In addition, the indices for the various formulas tested are quite

TABLE 2

Leachability indices for technetium and nitrate from grouts containing granulated BFS^a

| Slag source | Leachability/Index | |
|------------------------|--------------------|------------------------------|
| | ⁹⁹ Tc | NO ₃ ⁻ |
| Cleveland | 11.12 ± 0.33 | 7.40 ± 0.21 |
| Japan | 9.99 ± 0.62 | 7.22 ± 0.03 |
| Japan ^b | 10.45 ± 0.44 | 7.43 ± 0.15 |
| Cleveland ^c | 10.97 ± 0.25 | 7.23 ± 0.13 |
| Cleveland | 9.91 ± 0.16 | 7.19 ± 0.03 |
| Sparrow Point | 10.41 ± 0.17 | 7.23 ± 0.18 |
| Average | 10.50 ± 0.50 | 7.30 ± 0.10 |

^aNumbers are the mean and standard deviation for three replicates measured after nominal 30-day cure.

^bMB-AE-10 added to final dry-solids at 0.12 wt. %.

^cGypsum added to slag at 3 wt. %.

TABLE 3

Stabilization of HMS in grout effects of miscellaneous additives

| Constituent added to as-poured wet grout | Grout composition (wt.%) | | |
|--|--|--------|------------|
| | B-174-3 | B174-4 | 1361-162-3 |
| Raw HMS ^a | | | |
| As total | 13.9 | 13.9 | 13.9 |
| As solids | 4.5 | 4.5 | 4.5 |
| Water | | | |
| As diluent | 36.1 | 36.1 | 36.1 |
| As total ^b | 45.5 | 45.5 | 45.5 |
| Portland cement | | | |
| Type I-II LA | 23.2 | 25.0 | 24.0 |
| Fly-ash, ASTM Class F | 23.2 | 25.0 | 24.0 |
| Other additives | | | |
| Iron fillings (~40 mesh) | 3.7 | | |
| FeSO ₄ | | | 2.0 |
| | ANSI/ANS-16.1-1986 Leachability Index ^c | | |
| ⁹⁹ Tc | 8.1 | 7.7 | 9.3 |

^aRaw HMS contains 32.6 wt. % solids and 67.4 wt. % water.

^bTotal water is the sum of that added as diluent and from sludge.

^cSamples were cured for 30 days prior to leach test.

similar, averaging 10.5 ± 0.5 for ^{99}Tc and 7.3 ± 0.1 for nitrate, indicating that both the source of the BFS and the use of the admixture do not measurably change the retention performance for technetium and nitrate.

Effects of selected additives

In a companion study, several additives (iron metal, ferrous sulfide, and ferrous sulfate) were found to be effective in the removal of ^{99}Tc and heavy metals from the HMS filtrate [11]. The effects of two of these additives on the grout matrix containing HMS were studied. It should be noted that the comparisons discussed in this section were from single samples.

Iron fillings (~ 40 mesh or $420 \mu\text{m}$) were added to a simple cement/fly-ash blend, and the *LI* was determined. As shown in Table 3, the *LI* obtained from a grout containing iron fillings (B-174-3) increased only slightly from that exhibited by the cement/fly-ash grout (B-174-4).

The addition of FeSO_4 to the simple cement/fly-ash grout (1361-162-3) had a more positive effect. As shown in Table 3, *LI* increased from 7.7 to 9.3, which approaches values obtained for grouts containing BFS.

TABLE 4

Leach performance of HMS in ordinary portland cement-fly-ash grouts: effect of added sodium sulfide

| Constituent added to as-poured grout | Blend composition (wt.%) | | | |
|---|--------------------------|---------------|---------------|----------------|
| | KS | KS+S | MH | MH+S |
| Raw HMS ^a | | | | |
| As total | 30.0 | 30.0 | 13.9 | 13.9 |
| As solids | 9.8 | 9.8 | 4.5 | 4.5 |
| Water | | | | |
| As diluent | 20.0 | 20.0 | 36.1 | 36.1 |
| As total ^b | 40.2 | 40.2 | 45.5 | 45.5 |
| Portland cement (Type I-II) | 25.0 | 24.6 | 25.0 | 24.6 |
| Fly-ash (Class F) | 25.0 | 24.6 | 25.0 | 24.6 |
| Sodium sulfide ^c | | 0.9 | | 0.9 |
| ANSI/ANS-16.1-1986 Leachability Index (30-day cure) | | | | |
| ^{99}Tc | 6.8 ± 0.3 | 9.4 ± 0.1 | 7.2 ± 0.2 | 10.0 ± 0.5 |

^aRaw HMS contains 32.6 wt. % solids and 67.4 wt. % water.

^bTotal water is the sum of that added from the sludge and diluent.

^cTechnical grade sodium sulfide ($\text{NaS} \cdot 9\text{H}_2\text{O}$, $\sim 80\%$ pure, from PPG Industries, Pittsburgh, PA).

Effect of soluble sulfide ion

The work of Angus and Glasser [12] suggests that the addition of $\sim 4.5 \times 10^{-4}$ mol Na_2S per gram of cement produced a cement paste with pore water redox potential (E_h) comparable to that of a grout paste prepared with BFS. In Table 4, the effect of using technical-grade sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $\sim 80\%$ pure) as an additive to grout dry-solids blend is shown. The reductive soluble sulfide (added to $\sim 6 \times 10^{-5}$ mol per gram of dry-solids blend) is observed to significantly improve retention of ^{99}Tc as evidenced by the increase in the *LI* value.

Discussion

The results presented indicate that the source of granulated BFS does not measurably affect retention of technetium and nitrate for the four grouts tested. Indeed, the slag characteristics were similar, with gross chemical composition generally falling within industry averages as reported in brochures from the National Slag Association [8]. Bulk densities of the slags ranged from 2.85 to 2.98 g/cm³, and surface area measurements (calculated from nitrogen adsorption measurements and Brunauer–Emmett–Teller theory [BET]) ranged from 1.80 to 2.4 m²/g. It should be noted that the BFS from Japan (as received) contained 1 wt.% gypsum added as a grinding agent. Thus, it can be concluded that for this application, the source of BFS would be driven by economics rather than by performance.

The results presented also clearly demonstrate the improved retention of technetium and, to a lesser extent, nitrates by the addition of granulated BFS. As stated earlier, this improvement has been attributed to the reduction of the slag and to the resulting less porous grout product. To access the redox potential of the slags, E_h was measured on aqueous samples of the grout matrix materials, which were prepared by adding 5 g of each matrix material to 10 mL of 0.1 N NaOH and shaken overnight before E_h measurement. Relative E_h values for the slags were -250 mV compared with ~ 450 mV for fly-ash and cement.

It can be hypothesized that porosity reduction and tortuosity increase in the grout matrix can be qualitatively observed by the *LI* for nitrate. As nitrates are readily soluble in grout pore water, any significant improvement in their retention may be attributed to these factors. As shown in Table 2, the use of granulated BFS improved nitrate retention but by a relatively small amount compared with technetium. Thus, it can be concluded that the principal mechanism of improved technetium retention is a result of the redox potential of the BFS and not of the resulting improved physical properties of the grout.

Data from grouts prepared with FeSO_4 and Na_2S indicate that the effectiveness of BFS may be due to the presence of readily soluble sulfur compounds. Addition of these additives did not appear to have deleterious effects on ^{99}Tc

retention. Thus, trace additives can be used as a pretreatment step to reduce and precipitate the ^{99}Tc (thereby reducing the volume for disposal) and then can be incorporated into a grout with no reduction in observed leach behavior. In addition, grouts prepared with relatively small quantities of FeSO_4 and Na_2S showed similar ^{99}Tc retention compared to grouts prepared with BFS. Further formula optimization studies may show that sulfur compounds can be substituted for the BFS.

Although this paper focuses on ^{99}Tc , the results are believed to be applicable to other constituents which are pH sensitive. For example, chromium, with its highly mobile form $\text{Cr}(\text{VI})$, is a prime candidate for treatment and stabilization using granulated BFS or soluble sulfur compounds.

Acknowledgements

This research was sponsored by the Enrichment Technology Programs and Office of Defense Waste and Transportation Management, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References

- 1 T.M. Gilliam, Leach testing of hydrofracture grouts containing hazardous waste, J. Under-ground Injection Practice Council, 1 (1986) 192.
- 2 T.M. Gilliam, L.R. Dole and E.W. McDaniel, Waste Immobilization in Cement-based Grouts, Hazardous and Industrial Solid Waste Testing and Disposal: ASTM Special Technical Publication, Vol. 933 (6), 1986, pp. 295. ASTM Philadelphia, PA.
- 3 T.L. Sams, E.W. McDaniel and T.M. Gilliam, Immobilization of neutralized cladding-removal waste in a cement-based grout. In: Proc. 2nd Int. Conf. Radioactive Waste Management. Canadian Nuclear Society, Sept. 7-11, 1986.
- 4 10 CFR 20, U.S. Nuclear Regulatory Commission, Standards for Protection Against Radiation. Federal Register, Vol. 47, No. 248, December 27, 1982. Government Printing Office, Washington, DC, 1982.
- 5 O.K. Tallent, E.W. McDaniel, G.D. Del Cul, K.E. Dodson and D.R. Trotter, Immobilization of technetium and nitrate in cement-based materials, Paper presented at Materials Research Society Symposium (R.E. Wessterman, Ed.), November 30-December 3, 1987, Boston, MA, MRS, Pittsburgh, PA.
- 6 R.L.A. Malek, D.M. Roy, M.W. Barnes and C.A. Langton, Slag-Cement-Low Level Waste Forms at the Savannah River Plant, Report DP-MS-85-9, Savannah River Laboratory, Aiken, SC, 1985.
- 7 R.M. Hall, T. Watson, J.J. Davidson, D.R. Case and N.S. Bryson, RCRA Hazardous Wastes Handbook, 6 edn., Government Institutes, Inc., Rockwell, MD, 1985.
- 8 W.D. Bostick, J.L. Shoemaker, R.L. Fellows, R.D. Spence, T.M. Gilliam, E.W. McDaniel and B.S. Evans-Brown, Blast Furnace Slag-Cement Blends to Immobilization of Technetium-Containing Wastes, Report K/QT-203, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, TN, 1988.
- 9 T.M. Gilliam and J.A. Loflin, Leachability Studies of Hydrofracture Grouts, Report ORNL/TM-9879, Oak Ridge National Laboratory, Oak Ridge, TN, 1988.

- 10 ANSI/ANS-16.1-1986. Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure, American Nuclear Society, La Grange Park, IL, 1986.
- 11 W.D. Bostick and B.S. Evans-Brown, Sorptive Removal of Technetium from Heavy Metals, Sludge Filtrate Containing Nitrate Ion, K/QT-160, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, TN, 1988.
- 12 J.J. Angus and F.P. Glasser, The chemical environment in cement matrices, In: L.O. Werme (Ed.), Materials Research Society Symp. Proc., 50, MRS, Pittsburgh, PA, 1986, p. 547.