New Formulation of Cast Stone for ^{99}Tc Immobilization in Sulfate Rich Secondary Waste Stream – 16098

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ABSTRACT

A low-temperature, cementitious waste form called Cast Stone (or grout) has been selected for solidification of the Effluent Treatment Facility (ETF)-treated wastes at the Hanford Site. Because the waste stream to be solidified may be relatively high in sulfate, the current Cast Stone dry blend formulation with ordinary Portland cement (OPC), fly ash (FA), and blast furnace slag (BFS) (47% BFS, 45% FA, and 8% OPC) may not be adequate. Thus a new formulation, called secondary waste grout, was proposed and tested. The secondary waste grout uses hydrated lime [$Ca(OH)_2$] to tie up the sulfate initially such that ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\bullet 26(H_2O)$] forms rapidly instead of forming as the cementitious waste form cures. Three different liquid waste simulants (242-A evaporator, Environmental Restoration Disposal Facility [ERDF] leachates, and Hanford Tank Waste Treatment and Immobilization Plant [WTP] off-gas condensates) were prepared and solidified using this new dry blend formulation. Baseline grout dry mixes were 20 wt% hydrated lime (HL), 35 wt% OPC, and 45 wt% BFS, and two different water-to-dry mix (w/dm) ratios (0.5 and 0.6) of free water mass to mass of dry blend were tested. After curing for a minimum of 28 days, the grout solidified waste forms were characterized and used for Tc leachability testing using the EPA 1315 Method. X-ray diffraction analysis confirmed that ~12-15% of ettringite was formed in early stage of 28-day curing for the grouts prepared with the high sulfate WTP simulant and HL addition. In addition, the new formulation of secondary waste grout prepared with HL (20%), OPC (35%), and BFS (45%) at either 0.5 or 0.6 water to dry mix ratio yields higher average Tc interval leachability index (LI) values (12.5 to 13.9) after 28 to 90 days of leaching using deionized water, which is higher than the desired ^{99}Tc LI value of 12 for grout destined for burial in the Integrated Disposal Facility at the Hanford Site.

INTRODUCTION

The Effluent Treatment Facility (ETF) at the Hanford Site currently treats aqueous waste streams including evaporator condensates from the 242-A evaporator, Environmental Restoration Disposal Facility (ERDF) leachates, and the future Integrated Disposal Facility (IDF) leachates, laboratory liquid wastes, and contaminated groundwater. When the Hanford Tank Waste Treatment and Immobilization Plant (WTP) begins operations, the WTP will generate secondary aqueous waste streams from primary and secondary off-gas capture systems that will be sent to the ETF for treatment and solidification. The solidification treatment unit will also be used to solidify the ETF process streams currently being fed to the rotary evaporator, which dries the ETF process liquid wastes, forming a powder. The resulting powders are currently placed in drums and are disposed of onsite at the ERDF. The ETF-treated wastes will be solidified into a low-temperature cementitious solid waste form that will be disposed in the IDF. Because additional information about the other wastes currently being treated in the ETF indicates that the waste streams to be solidified contain relatively high sulfate, the standard Cast Stone formulation with ordinary Portland cement (OPC), fly ash (FA), and blast furnace slag (BFS) may not be adequate. Thus, hydrated lime (HL) was added to the dry blend mix to tie up the sulfate such that ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}{\bullet}26(H_2O)$] forms rapidly before the waste form sets and cures. Late formation of ettringite can lead to undesired swelling and cracking of the waste form. Formulations different from the current Cast Stone formulation (47% BFS, 45% FA, and 8% OPC) are referred to as grouts herein. Such grouts were prepared and then tested for ^{99}Tc leachability for comparison to the original Cast Stone waste forms.

MATERIALS AND METHODS

Liquid Waste Simulant Preparation

Three liquid waste simulants (242-A Evaporator, ERDF leachate, and WTP off-gas condensate) were prepared to mimic the chemical composition of three primary waste streams that are expected to be treated at the ETF. The projected compositions of these three waste streams are shown in Table 1. For these secondary waste grout formulation tests, chemical simulants of each of the three different waste streams were used in preparing the grout specimens. The simulants were prepared with 10 wt% total (dissolved and suspended) solids for 242-A evaporator and ERDF leachates simulants, while the total solids content of WTP off-gas condensate simulant was set at 18 wt%. The final concentrations were selected based on charge-balanced compositions verified by simulant preparation from chemical reagents. See Russell et al. [1] for details. To understand the retention and release of the key radionuclide of concern, ^{99}Tc was spiked into each simulant and used for all grout batches prepared (See Table 1 for ^{99}Tc concentration).

TABLE 1. Nominal Waste Compositions as Starting Point for Simulants

Chemical (relative molar amount)	**242-A Evaporator**	**ERDF Leachates**	**WTP Off-gas Condensates**
NH_4^+	0.541	-	0.330
Ca^{2+}	0.023	0.171	-
Cl^-	0.013	0.162	0.006
F^-	-	-	0.001
Na^+	0.075	0.222	0.295
K^+	0.003	-	-
Mg^+	0.009	0.092	-
NO_3^-	-	0.117	0.117
NO_2^-	-	-	0.001
SO_4^{2-}	0.324	0.235	0.250
Si^{4+}	0.011	-	-
Total Moles	1.0	1.0	1.0
^{99}Tc concentration	14.2 mg/L	15.1 mg/L	15.0 mg/L

"-" = not reported, and therefore not added to the simulants.

Preparation of Secondary Waste Grouts

Secondary waste grout monoliths were made using four primary dry ingredients that were blended together in different ratios. These primary dry ingredients consisted of slaked or HL ($Ca(OH)_2$), OPC (Type I/II), BFS (Grade 100), and FA (Class F). In each case, these specific materials were selected 1) because they are commercially available in high volumes and 2) to provide continuity with previous experimental work. Detailed characterization of the OPC, BFS, and FA can be found in Westsik et al. [2] and Serne et al. [3]. The hydrated lime (HL) was sourced from the Graymont Rivergate facility in Portland, Oregon. At this time, the source limestone is mined in Utah and processed in Portland to produce a high-calcium product that assays at 92-100 %wt calcium hydroxide. Published data from Graymont states that 95% of this $Ca(OH)_2$ passes through a 0.600-mm sieve, and we used it without further particle size reduction. For each of the secondary waste grouts formulations (described in Table 2), the necessary liquid and dry material aliquots were prepared ahead of time so that all of the monoliths would begin curing at approximately the same time. In the case of the dry materials, the different components for each batch were weighed separately and then combined into one large plastic bag. The large plastic bag was then sealed and hand mixed to homogenize the contents. Homogeneity was determined visually, but all were homogenized for 5-10 minutes to facilitate complete mixing. Wet grout mixing was performed with a Caframo BDC1850, variable speed, "overhead stirrer." The impeller and mixer head were joined by a 3/8-inch shaft. The combined mixer apparatus was supported by a Caframo A210 heavy duty stand and A120 heavy duty clamp. The mixer shaft was lowered into a 2-L plastic mixing beaker until the bottom of the impeller was between 0.75 to 1.25 inches from the bottom of the beaker. The beaker was offset from the mixer shaft so that the impeller was between 0.25 to 0.5 inches from one sidewall. This offset helped to minimize the creation of a central vortex, and thus air entrainment, during wet slurry mixing. With the beaker of simulant in place under the mixer, the mixer was started at about 200 rpm. Then, with the mixer turning at about 200 rpm, the homogenized bag of dry pre-mix was slowly added to the simulant. To facilitate clean transfer from the bag to the beaker, a 2-inch diagonal cut was made across one corner of the bag. This corner opening funnels the pre-mix into the desired location and allows for good control during addition to the beaker. A timer was used to ensure that all dry ingredients were added to the mixing beaker within approximately 5 minutes.

Table 2. Grout Test Matrix with Spiked ^{99}Tc

Test #	**Simulant**	**Water-to-Dry Mix (w/dm) Ratio**	**Dry Blend Addition**[a]	**Dry Materials**	**WRA**[b]	**Leachant**[c]	**^{99}Tc conc. (mg-^{99}Tc/Kg-dry monolith)**[d]
1(T1)	242-A	0.5	20%, 35%, 45%	HL, OPC, BFS	3030	DIW	6.43
2(T2)	ERDF	0.5	20%, 35%, 45%	HL, OPC, BFS	3030	DIW	6.85
3(T3)	WTP	0.5	20%, 35%, 45%	HL, OPC, BFS	3030	DIW	6.63
4(T4)	242-A	0.6	20%, 35%, 45%	HL, OPC, BFS	3030	DIW	7.73
5(T5)	ERDF	0.6	20%, 35%, 45%	HL, OPC, BFS	3030	DIW	8.15
6(T6)	WTP	0.6	20%, 35%, 45%	HL, OPC, BFS	3030	DIW	7.98
7(T13)	WTP	0.6	45%, 8%, 47%	FA, OPC, BFS	3030	DIW	9.07

[a] The three dry blend materials were mixed together by placing the dry ingredients into a single plastic bag and manipulating the bag until the dry mixture appeared to be homogenous.

[b] Water-reducing additive (WRA): MG 3030 (BASF Corp.) was used to enhance the cement rheology based on 0.6 mL of MG 3030 per 100 g of dry mix.

[c] One leachant, de-ionized water (DIW) was used for EPA 1315 leaching test on duplicate cured monoliths.

[d] Initial concentration ($C_{(0)}$ inventory) of ^{99}Tc used in EPA 1315 leaching tests.

As dry pre-mix was added, the mixer rpm was increased to maintain obvious surface movement with minimal central vortex and associated air entrainment. As soon as all of the pre-mix had been added to the mixing beaker, water reducing additive (MG 3030) was slowly added near the vortex. The MG 3030 significantly reduced viscosity and allowed the grout to be “burped” to release entrained air by stopping the mixer for 15 to 30 seconds and tapping the beaker on the benchtop. Mixing continued until 15 minutes had elapsed since the beginning of pre-mix addition. This time was spent ensuring grout homogeneity by scraping the beaker sides and mixer shaft with a plastic spatula as needed. Mixer speed was adjusted to the highest possible level without risking air entrainment. This speed varied from batch to batch and was occasionally decreased during mixing as grout shear properties changed over time. At the end of the mixing period, the grout was poured into 2-inch x 4-inch cylindrical forms. These forms consist of relatively thin-walled plastic mailing tubes with push-on plastic caps. These mailing tubes were sourced from Icon Plastics in Cost Mesa, California. Each batch of grout was expected to fill approximately six forms. The forms were initially filled about three quarters full. This allowed mechanical agitation to achieve de-airing with minimal risk of spillage. Not all grouts appeared to have entrained air, but all monoliths were agitated to ensure that minimal entrained air remained in the wet monoliths. De-airing required 1 minute or less per monolith. De-airing was considered complete when visual inspection detected the cessation of new bubbles rising to the surface of the wet grout. The forms were then filled, gently de-aired, and covered with perforated caps. The caps were left a few millimeters higher than the upper surface of the grout to allow the grout surface to find its own level and minimize surface imperfections induced by contact with the cap. The filled and capped forms were placed into racks, which were then stacked into 5-gallon buckets. Before the racks were installed, the buckets were pre-loaded with 1 to 2 inches of water to maintain a humid environment at 21^{o}C (~80% relative humidity) inside the sealed bucket. Monoliths were allowed to cure at room temperature and high humidity for 28 days inside the sealed buckets before testing. A non-radioactive grout that had the same preparation condition as Test# 6 in Table 2 was also prepared, cured, and then used for solid characterizations. Moisture contents and geometric surface areas were also measured for the grout specimens after curing and before leaching.

Characterization of Grout Samples

The ^{99}Tc-spiked grout specimens after curing and before leaching were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS) analysis to determine the sample mineralogy and to gain insight into the distribution of elements within the waste form. The final solid products were first characterized using a Rigaku Miniflex II XRD unit equipped with a Cu K-alpha radiation (40 kV, 15 mA) source. The bulk samples were homogenized by grinding in an agate mortar and pestle and mounted onto a small circular sample holder before scanning from 2 to 75 degrees 2-theta. About 10 wt% of a reference (TiO_2) powder was also added and run for XRD pattern to obtain a semi-quantitative analysis of major mineral phases. Data reduction and mineral identification were done by Jade software with PDF XRD database.

Specimens for SEM-EDS were mounted on an aluminum stub with carbon tape and sputter coated with Pt (Polaron Range SC7640, Quorum Technologies Ltd., East Sussex, England). The samples were analyzed using a JSM-7001F field emission gun scanning electron microscope (SEM, JEOL USA, Inc. Peabody, MA), and the EDS analysis was done using a Bruker xFlash 6|60 silicon drift detector (Bruker AXS, Inc., Madison, WI). The acceleration voltage during the analysis was 15 kV. For all of the analyses, Kα positions were considered for the calculations. The EDS spectra were collected for 20 s each at 80k to 100k counts/s. Background noise subtraction and the estimation of atomic ratios were done using ESPRIT (v1.9, Bruker AXS, Inc.) software.

EPA Method 1315 Leaching Test

EPA Method 1315 [4] is a semi-dynamic leach test that consists of submerging a monolithic sample in leachant (DIW) at a fixed liquid-volume to solid-geometric-surface-area ratio. Duplicates monoliths were leached and the sampling was done at fixed periods at cumulative leaching times of 0.08, 1, 2, 7, 14, 28, 42, 49, and 63 days. An additional sampling was conducted at cumulative leaching times of 90 days. At each sampling interval, all the leaching fluid was removed and replaced with fresh fluid, while the monolith mass was recorded. The cylindrical monoliths were placed into the centers of leaching vessels containing sufficient leachant to maintain a solution-to-solid geometric surface area ratio of 9 ± 1 mL of leachant per square centimeter of sample geometric surface area. Sample stands and holders were used to maximize the contact area of the monolith with the leaching solution. Solution pH and electrical conductivities were measured on a small aliquot of unfiltered leachate at each leaching interval. Then, a larger aliquot of leachate was removed from the leach container and split into various analytical aliquots for chemical analyses. Methods include inductively coupled plasma-optical emission spectroscopy (ICP-OES) for cations, ICP-mass spectroscopy (ICP-MS) for ^{99}Tc concentration, and ion chromatography (IC) for anions concentrations in the leachates. The observed effective diffusivity for ^{99}Tc was calculated using the analytical solution for Fick's second law using Eq. 1, for simple radial diffusion from a cylinder into an infinite bath as used in EPA Method 1315.

$$D_{eff(i)} = \pi\left[\frac{M_{ti}}{2\rho C_0\,(\sqrt{t_i}-\sqrt{t_{i-1}})}\right]^2 \qquad \text{Eq. 1}$$

where $D_{eff(i)}$ = observed effective diffusivity of a specific constituent for leaching interval, i (m^2/s)
M_{ti} = mass of specific constituent released during leaching interval i (mg/m^2)
t_i = cumulative contact time after leaching interval, i (s)
t_{i-1} = cumulative contact time after leaching interval, $i-1$ (s)
C_o = initial concentration of constituent in the dry Cast Stone (mg/kg dry)
ρ = Cast Stone dry bulk density (kg-dry/m^3).

The leachability index (LI), a unitless parameter derived from the interval effective diffusion coefficient values is calculated using Eq. 2. A low diffusivity results in a larger LI.

$$LI = -\log(\frac{D_{effective}}{cm^2 s}) \quad \text{Eq.2}$$

RESULTS AND DISCUSSION

The XRD patterns collected for the non-radioactive grout prepared as the same conditions as Test #6 showed that 15 wt% of ettringite formed before and during curing (Fig. 1). Other major mineral phases are 8.0 wt% of portlandite [$Ca(OH)_2$] and 4.4 wt% of larnite (Ca_2SiO_4). Most of amorphous phase (73 wt%) is attributed to calcium-silicate-hydrate (CSH) gel in grout.

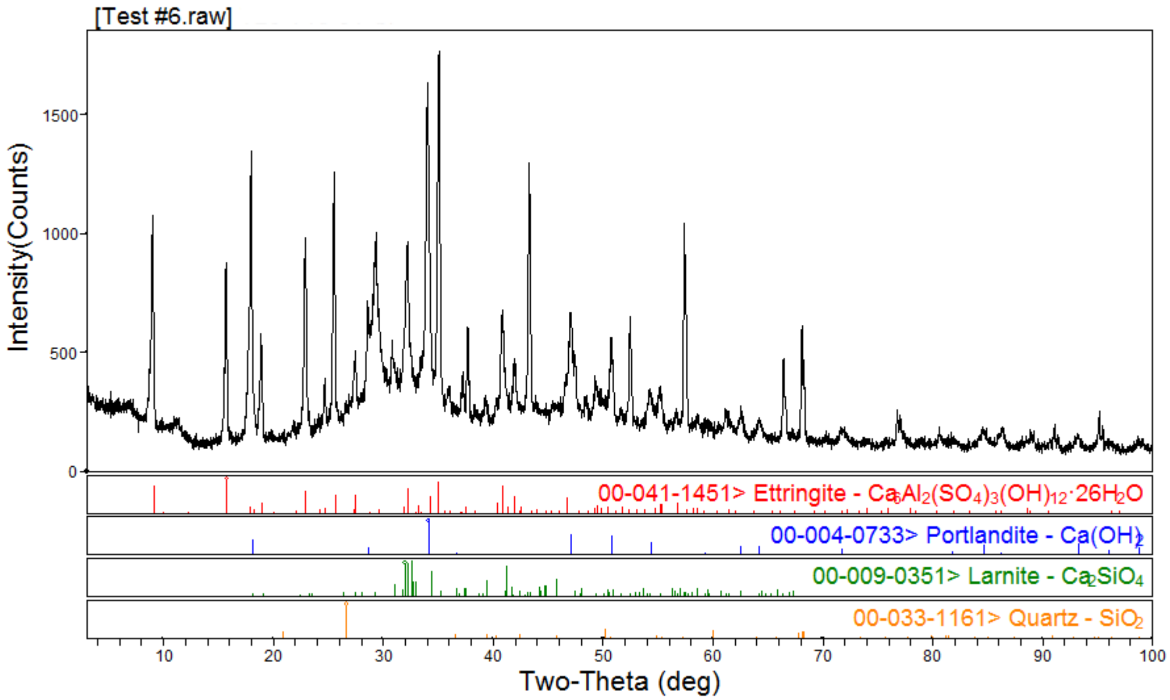


Fig. 1. XRD pattern of non-radioactive grout prepared under the same condition as Test #6 in Table 1.

Analysis by SEM-EDS for the same powdered non-radioactive grout (#6) as was used for XRD analysis provided chemical composition and morphology data. SEM images and EDS data are shown in Fig. 2. As found in the XRD analysis, needle-shaped ettringite was found and the major elements in the selected area were identified as Ca, S, Al, Si, and Na.

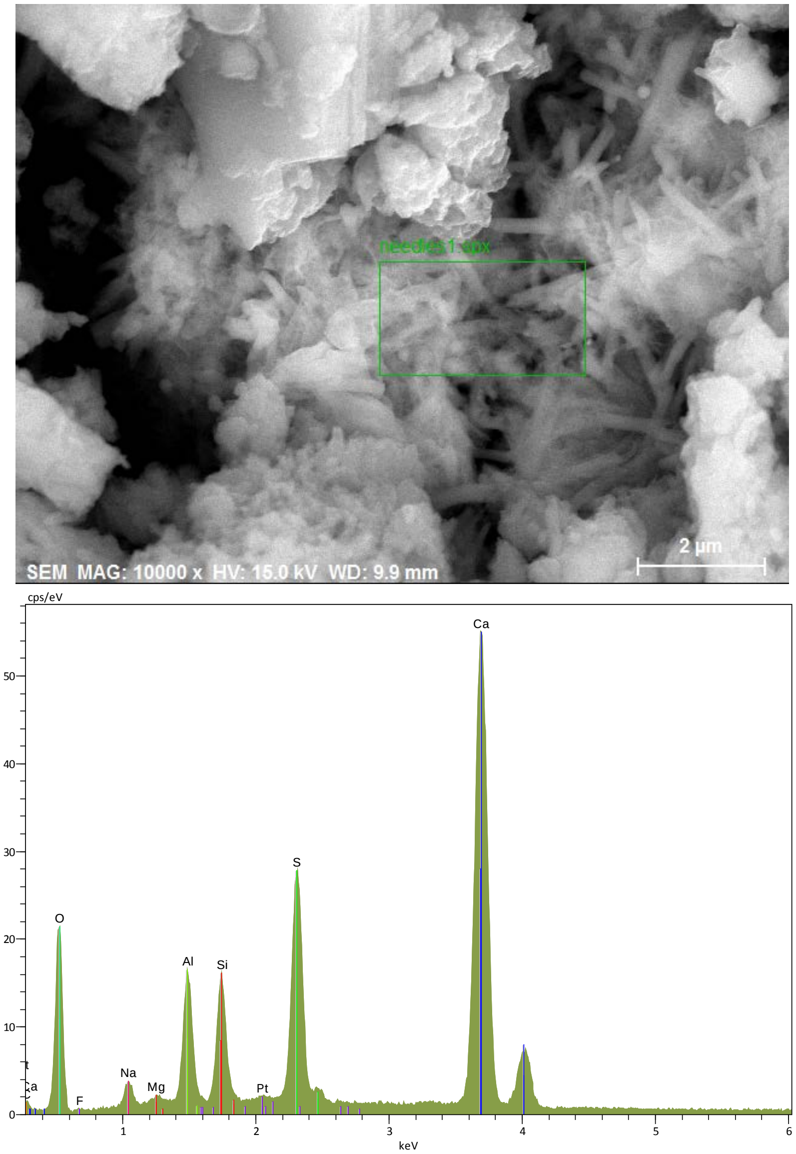
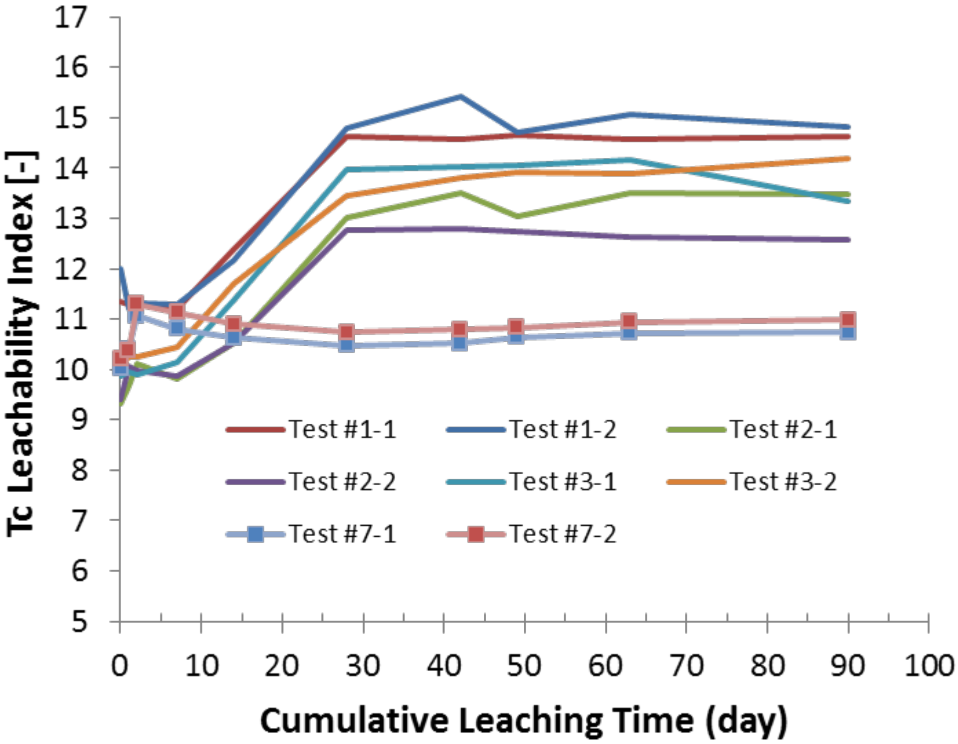


Fig. 2. SEM image of non-radioactive grout (Test #6) showing needle shape of ettringite (left) and EDS result (right) showing different atomic % of Ca (25.5%), S (7.4%), Al (4.5%), Si (4.1%), Na (1.5%), F (0.7%), Mg(0.2%), and O (56.1%) on the selected area.

The ^{99}Tc diffusivity coefficient and LI values up to 90 days were calculated, and ^{99}Tc LI values are shown along with the cumulative leaching times in Fig. 3. The calculated ^{99}Tc LI values of the new grout formulation (Tests #1-6) prepared with HL (20%), OPC (35%), and BFS (45%) at either 0.5 or 0.6 water-to-dry mix (w/dm) ratio showed much higher ^{99}Tc LI values (or lower ^{99}Tc effective diffusivity) than those for original secondary waste Cast Stone formulation, OPC (8%), FA (45%), and BFS (47%) of Test #7. ^{99}Tc LI values for Test #1, prepared with 242-A simulant at 0.5 w/dm ratio ranged from 11.34 to 16.98 with an average value of interval LIs from 28 to 90 days of 14.8. Average values of interval LIs from 28 to 90 days for Test #2 and #3 prepared with ERDF and WTP simulant at 0.5 w/dm ratio were 13.0 and 13.9, respectively. A higher w/dm ratio, 0.6 compared to the 0.5 w/dm ratio, also decreased ^{99}Tc LI values for Tests #4 and 6 prepared with 242-A and WTP simulant to 13.4 and 12.5, respectively. Lower ^{99}Tc LI values (or higher ^{99}Tc diffusivities) at a higher w/dm ratio, 0.6 compared to grouts prepared at 0.5 w/dm, are likely related to higher moisture contents of Tests #4, 5, 6 (29.5% to 30.7%) compared to those of Tests #1, 2, and 3 (25.0% to 27.1%). However, average ^{99}Tc LI values of grouts (Tests #2 and 5) prepared with ERDF simulant were 13.0 and 13.1, which are also very similar irrespective of w/dm ratio between 0.5 and 0.6 because of low concentration of the chemical constituents in ERDF simulant compared to the other two simulants, 242-A and WTP. New formulation of secondary liquid waste grout (Test #6) prepared with WTP simulant at 0.6 w/dm ratio showed ^{99}Tc LI values ranging from 9.05 to 12.96, with average interval Tc LI value of 12.5 for the leach intervals between 28 and 90 days. Initial low ^{99}Tc LI values for Test #6 grout ranging from 9.05 to 10.3 resulted from a wash-off effect of ^{99}Tc at early (before 28 days) leaching times. However, the average interval ^{99}Tc LI value (12.5) from 28-day and 90-day collection for new formulation grout (Test #6) was much higher than average interval ^{99}Tc LI value (10.7) of Test #7 prepared based on original Cast Stone formulation, OPC (8%), FA (45%), and BFS (47%) as shown in Fig. 3. Initially higher ^{99}Tc LI values in grout (Test #7) before 28-day leaching was likely caused by the lower moisture content of Test #7 (26.6%) compared to Test #6 (29.7%) prepared with new formulation containing hydrated lime.



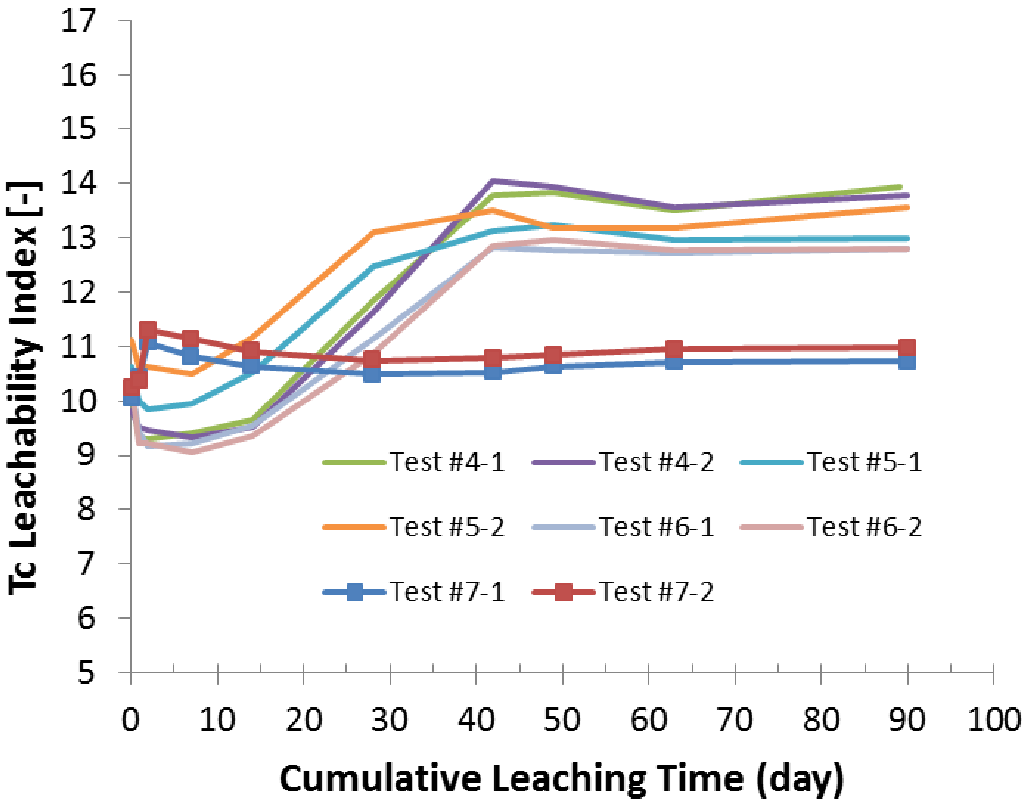


Fig. 3. ^{99}Tc leachability index of EPA 1315 leaching test up to 90 days. Duplicates are shown as Test #1-1 and Test #1-2. Tests #1 to 3 prepared with 0.5 w/dm ratio (top) and Tests #4 to 6 prepared with 0.6 w/dm ratio (bottom) are plotted with Test # 7 prepared without hydrated lime addition.

The highest ^{99}Tc LI values (or lowest ^{99}Tc diffusivities) found for the new formulation secondary waste grout after 90 days may be the result of continued carbonation reactions or increasing reduction of ^{99}Tc(VII) to ^{99}Tc(IV) species caused by the continued slow dissolution of the BFS reductant present in the dry blend. The slow dissolution of BFS and continued reduction of ^{99}Tc was discussed previously by Um et al [5]. In addition, hydrated lime addition in the new formulation for these secondary wastes can provide enough Ca for formation of both early stage ettringite and portlandite, while the original Cast Stone formulation doesn't have enough Ca to form both ettringite and portlandite during 28-days curing. Because portlandite plays a role in limiting the amount of shrinkage that occurs when the grout monolith is dried, the new formulation of grout monolith with addition of HL can provide a more durable and less permeable waste form for burial in the IDF in which unsaturated conditions prevail.

CONCLUSIONS

This study shows that the new dry blend formulation with hydrated lime for secondary waste simulants containing high sulfate, especially for the WTP waste stream, results in robust, low ^{99}Tc-leachable cured cementitious waste forms. The original Cast Stone formulation prepared with OPC (8%), FA (45%), and BFS (47%) does not provide the acceptable ^{99}Tc leach results, a leachability index (>12) for the high-sulfate WTP simulant. However, the new formation of secondary waste grout prepared with lime (20%), OPC (35%), and BFS (45%) at either 0.5 or 0.6 w/dm ratio provides acceptable (higher) average ^{99}Tc interval LI values than 12.0 from 28-day to 90-day cumulative leach times in the EPA 1315 leaching test using DIW.

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