# The Effect of Ettringite on Cementitious Waste Form Development for Low-Activity Waste – 17170

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## ABSTRACT

The current Cast Stone formulation, with 8% ordinary Portland cement (OPC), 45% fly ash (FA), and 47% blast furnace slag (BFS), proposed for cementitious waste forms (CWFs) at the Hanford site has been shown to be inadequate for secondary liquid wastes sent to the Effluent Treatment Facility (ETF). This is due to the high sulfate concentrations and non-alkaline conditions present in the ETF waste stream that lead to the late formation of ettringite, $[Ca_6Al_2(SO_4)_3(OH)_{12} \bullet 26(H_2O)]$, which can consequently cause undesirable swelling and cracks in the CWF that facilitate $^{99}$Tc release. To overcome this challenge, hydrated lime (HL), $Ca(OH)_2$, can be used instead of FA to provide the Ca necessary to sequester sulfate early in the cast stone curing process through early formation of ettringite. Early ettringite formation minimizes the risk of localized disruptive action or harmful stress that lead to undesirable swelling and cracking of the CWF. Furthermore, early formation reduces the permeability of the CWF, further reducing the risk of $^{99}$Tc release and increasing structural stability.

Two liquid waste simulants, 1) WTP off-gas condensate (WTP) and 2) Effluent Management Facility (EMF) process condensate combined with low activity waste (LAW) caustic scrubber (labeled EMF/CS), were prepared and tested for ettringite formation effects on HL-containing CWF development and $^{99}$Tc leachability. After curing for 28 days, X-ray diffraction analysis revealed that ettringite was formed in the early stages of curing for the CWFs prepared using both simulants. However, because of the higher sulfate concentration in the EMF/CS simulant and limited Ca and Al sources, some sulfate did not form ettringite during the early stages of curing, resulting in significant monolith swelling and cracking during subsequent leaching tests. Despite observable cracking in monoliths prepared with the EMF/CS simulant, low $^{99}$Tc release from HL-based waste forms was measured in later leaching periods tested by the EPA Method 1315 in both simulants. Ettringite-$^{99}$Tc co-precipitation batch experiments support a possible chemical sequestration mechanism that is hypothesized to contribute to the observed low $^{99}$Tc leach rates, which are likely the result of an additional chemical reaction that sequesters $^{99}$Tc rather than simply physical factors such as reduced porosity and permeability (or tortuosity). Overall these findings quantitatively support the use of HL to overcome the deleterious effects of sulfate-rich conditions on CWFs through early formation of ettringite and provide evidence for $^{99}$Tc release rates that fall within low risk levels reported by the United States Department of Energy (US DOE).

## INTRODUCTION

The Hanford Site Effluent Treatment Facility (ETF) currently treats aqueous waste from sources including evaporator condensates from the 242-A Evaporator, miscellaneous laboratory liquid wastes, contaminated groundwater, and future Integrated Disposal Facility (IDF) leachates. When the Hanford Tank Waste Treatment and Immobilization Plant (WTP) comes on line, a secondary liquid waste stream composed of process condensates and the caustic scrubber solution from the low-activity waste (LAW) melter off-gas treatment system will also be sent to the ETF for treatment. Once treated, wastes will be solidified into a low-temperature cementitious waste form (CWF) that will be disposed of in the Integrated Disposal Facility (IDF). The projected ETF-treated WTP secondary liquid waste will have slightly low pH (5–6) and a high sulfate concentration because the ETF uses sulfuric acid to neutralize the alkaline waste stream. Without sequestering the sulfate, the environment under which the CWF cures is deleterious to the structural integrity of the CWF. To overcome this challenge, an excess of calcium, in the form of hydrated lime (HL) was added to the dry blend mix to promote the early formation of ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\bullet 26(H_2O)$], a sink for sulfate in solution, and increase pH for activating the binding of dry ingredients. The early formation of ettringite also reduces the permeability of the CWF, which will reduce $^{99}$Tc leach rates and improve structural stability of the waste form. However, should ettringite form later in the curing process, there is a greater risk of waste form swelling and cracking which is expected to lead to an increase in $^{99}$Tc release[1]. This effect of ettringite formation on CWF development and the impact on $^{99}$Tc leachability remains poorly understood and is thus the focus of this work.

## MATERIALS AND METHODS

### Liquid Waste Simulant Preparation

Based on WTP facility process stream model projections, two secondary liquid waste simulants were prepared to mimic possible chemical compositions of the WTP secondary liquid waste stream expected to be treated at the ETF. The two simulants included WTP-treated off-gas condensate (labeled WTP, pH = 5.6 and $SO_4^{2-}$ = 122 g/L) and the Effluent Management Facility (EMF) process condensate merged with low activity waste (LAW) caustic scrubber (CS) (labeled EMF/CS, pH = 6.2 and $SO_4^{2-}$ = 241 g/L). WTP simulant was prepared with 18 wt.% total (dissolved and suspended) solids based on projected limits on halide concentration in the salt solution and use of the existing ETF equipment; whereas the total solids content for the EMF/CS simulant was set at ~30 wt. % assuming potential ETF materials of construction upgrades. The projected composition of these two simulants are shown in Table 1. Final simulant concentrations were verified by charge-balanced compositions from chemical reagents. The prepared simulants were also analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) for cations, and ion chromatography (IC) for anions, the results of which confirmed that the target simulant composition was achieved within experimental error. Based on IC results, the measured sulfate concentrations were 122 g/L and 240 g/L for WTP and EMF/CS simulants, respectively, and within 5% of the target concentration. To understand the retention and release of the key radionuclide of concern, $^{99}$Tc was spiked into each simulant and used for all CWF batches prepared (See Table 1 for $^{99}$Tc concentration).

TABLE 1. Nominal Waste Compositions as Starting Point for Simulants

| **Chemical (relative molar amount)** | **WTP** | **EMF/CS** |
|---|---|---|
| $NH_4^+$ | 0.330 | 0.402 |
| $Cl^-$ | 0.006 | 0.0003 |
| $F^-$ | 0.001 | 0.0005 |
| $Na^+$ | 0.295 | 0.248 |
| $NO_3^-$ | 0.117 | 0.0384 |
| $NO_2^-$ | 0.001 | - |
| $SO_4^{2-}$ | 0.250 | 0.309 |
| Total Moles | 1.0 | 1.0 |
| $^{99}$Tc concentration (mg/L) | 15.0 | 13.5 |

## Preparation of Secondary Waste Cementitious Waste Forms

Secondary waste form monoliths were made using four primary dry ingredients that were blended together in different ratios. These primary dry ingredients consisted of HL ($Ca(OH)_2$), ordinary Portland cement (OPC, Type I/II), blast furnace slag (BFS, Grade 100), and fly ash (FA, Class F) [2]. For each of the CWF 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. The current Cast Stone formulation with OPC (8%), FA (45%), and BFS (47%) was also prepared using the WTP simulant (Test#3 in Table 2) to compare the effect of ettringite formation with two CWFs prepared with HL instead of FA in different simulants (Test# 1 and 2 in Table 2). The dry material components for each batch were weighed separately, combined into a large plastic bag, sealed, and then hand mixed to homogenize the contents for 5-10 minutes to ensure complete mixing.

Wet CWF mixing was performed with a Caframo BDC1850 variable speed “overhead stirrer,” joined to an impeller by a 3/8-inch shaft. The combined mixer apparatus was lowered into a 2-L plastic mixing beaker, containing the required volume of simulant, 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 to help minimize the creation of a central vortex, a major cause of 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 mix was slowly added to the simulant. A timer was used to ensure that all dry ingredients were added to the mixing beaker within approximately 5 minutes.

Table 2. CWF Test Matrix with Spiked $^{99}$Tc[a, b]

| **Test #** | **Simulant** | **Water-to-Dry Mix (w/dm) Ratio** | **Dry Blend Addition** | **Dry Materials** | **$^{99}$Tc Concentration (mg $^{99}$Tc/ Kg dry monolith)[c]** |
|---|---|---|---|---|---|
| 1 (T6-FY15) | WTP | 0.6 | 20%, 35%, 45% | HL, OPC, BFS | 7.98 |
| 2 (T1-FY16) | EMF/CS | 0.6 | 20%, 35%, 45% | HL, OPC, BFS | 7.46 |
| 3 (T13-FY15) | WTP | 0.6 | 45%, 8%, 47% | FA, OPC, BFS | 9.07 |

[a] 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.

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

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

As the dry mix was added, the mixer rpm was increased to maintain obvious surface movement with minimal creation of a central vortex. As soon as all of the dry 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 wet cementitious material 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 from the start of dry mix addition. Over the course of mixing, time was spent ensuring CWF 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 the wet cementitious material shear properties changed over time.

At the end of the mixing period, the wet cementitious material was poured into 2-inch x 4-inch cylindrical forms constructed from thin-walled plastic mailing tubes and push-on plastic caps. The forms were initially filled about three-quarters full. This allowed mechanical agitation to achieve de-airing with minimal risk of spillage. Not all wet CWFs 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 CWF. The forms were then filled completely, 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°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. Moisture contents and geometric surface areas were measured for the CWF specimens after curing and before leaching.

## Solid Characterization of Cementitious Waste Forms

Cured $^{99}$Tc-spiked CWF specimens were characterized using X-ray diffraction (XRD) analysis to determine mineralogy within the waste form. The final cured solids were homogenized by grinding in an agate mortar with pestle and mounted onto a small circular sample holder before scanning from 2 to 75 degrees (2-theta) using a Rigaku Miniflex II XRD unit equipped with a Cu K-alpha radiation (40 kV, 15 mA) source. About 10 wt. % of a reference ($TiO_2$) powder was added to obtain a semi-quantitative analysis of major mineral phases. Data reduction and mineral identification were completed using Topas or Jade analysis software with references sourced from the International Centre for Diffraction Data database.

## EPA Method 1315 Leaching Test

EPA Method 1315 [3] is a semi-dynamic leach test that consists of submerging a 28-day cured monolithic sample in deionized water (DI) leachant at a fixed liquid-volume to solid-geometric-surface-area ratio. Duplicate monoliths of each composition were leached and sampling completed at pre-determined fixed cumulative leach times of 0.08, 1, 2, 7, 14, 28, 42, 49, and 63 days. Two additional samplings were conducted at cumulative leaching times of 90 and 140 days for Tests # 1 and 3, while one additional 100 day leachate was collected for Test #2. At each sampling interval, all the leachate was removed and replaced with fresh fluid, while the monolith mass was recorded at each sampling time. 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. Leachate pH and electrical conductivities were measured on a small aliquot of unfiltered leachate at each sampling interval. Then, a larger aliquot of leachate was removed from the leach container and split into various analytical aliquots for chemical analyses. Methods used include ICP-OES for cations, ICP-MS for $^{99}$Tc concentration, and IC for anion concentrations in the leachates. The observed effective diffusivity for $^{99}$Tc was calculated using Eq. 1 and the term observed effective diffusion coefficient, $D_{obs}$, was used to account for all physical and chemical retention factors influencing mass transfer.

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

where $D_{obs(i)}$ = 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 at the end of the previous leaching interval, *i-1,* (s)

$C_o$ = initial concentration of constituent in the dry starting material (mg/kg dry)

$\rho$ = monolith dry bulk density (kg-dry/m$^3$).

## Batch Co-precipitation Experiment

Batch experiments were carried out under oxidizing and reducing conditions to determine whether $^{99}$Tc may be removed from solution through co-precipitation with ettringite. The oxidizing condition samples were prepared in duplicate using $^{99}$Tc spiked into 0.12 M $Ca(OH)_2$ solution (1 mL of 100 mg/L $NaTcO_4$ stock solution spiked into 24.5 mL 0.12 M $Ca(OH)_2$) outside the anoxic chamber. Then, 0.02 M $Al_2SO_4 \cdot 18H_2O$ solution (24.5 mL) was reacted with the $^{99}$Tc spiked $Ca(OH)_2$ solution in a 1:1 ratio at room temperature followed by 48 hours agitation on a shaker. The reducing condition samples were prepared inside an anoxic chamber filled with a mixture of $N_2$ (98%) and $H_2$ (2%) gases. The chamber was also equipped with a palladium catalyst that converts $O_2(g)$ to water via reaction with $H_2(g)$. A reductant, 100 mg of $SnCl_2$ was added to a 100 ppm $NaTcO_4$ stock solution and allowed to equilibrate overnight inside the anoxic chamber. This solution containing $^{99}TcO_2(aq)$ species was subsequently filtered and used as a $^{99}$Tc spike for preparing the reducing condition samples. The reducing condition samples were prepared in duplicate by adding 1 mL of the reduced-$^{99}$Tc-spike to a $Ca(OH)_2$ solution (24.5 mL) followed by the addition of an $Al_2SO_4 \cdot 18H_2O$ solution (24.5 mL) before mixing for 48 hours inside the anoxic chamber. After mixing 48 hours for both oxidizing and reducing condition samples, the final slurry was removed from the shaker and the supernatant (2 mL) was separated using a 0.22 μm syringe filter. The filtered supernatant was submitted for $^{99}$Tc concentration using ICP-MS and the filtered solid was analyzed for mineralogy using XRD.

# RESULTS AND DISCUSSION

The XRD patterns collected for the three cured radioactive CWFs showed the presence of ettringite as the primary crystalline phase, within the range of 12 to 27 wt. %, before leach testing. The pre-leaching XRD patterns collected are very similar for Test #1 and #2 that were prepared with HL (Table 3). Test #3, prepared with FA, OPC, and BFS did not show the presence of portlandite, while Tests #1 and #2 CWF monoliths formed portlandite as a second major mineral ranging from 7 to 10 wt. %. Other major mineral phases are calcite and larnite. Quartz was only found in Test #3 because of FA addition. Most of the pre-leached CWFs are amorphous (61-78 wt. %) and attributed to non-crystalline calcium-silicate-hydrate (CSH) gel in cured CWFs. After 100 or 140 days of leaching in DI water using EPA Method 1315, the ettringite content increased in all test samples, indicating continuous formation of ettringite from phase transformation of portlandite and calcium silicate hydrate (CSH) reacting with remaining sulfate from the liquid simulants present in CWF pores.

Table 3. XRD Analysis for Mineral Content

| Test Batch # | XRD Analysis (wt. %)[(a)] | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ettringite | Portlandite | Calcite | Larnite | Hydro-calumite | Quartz | Amorphous |
| 1 (T6-FY15) before leaching | 17 | 9.7 | 5.4 | 4.5 | - | - | 63 |
| 1 (T6-FY15) after leaching | 21 | 9.3 | 6.7 | 4.5 | | | 59 |
| 2 (T1-FY16) before leaching | 21 | 6.6 | 3.4 | 5.1 | 0.6 | - | 61 |
| 2 (T1-FY16) after leaching | 27 | 1.6 | 9.2 | 3.4 | 0.4 | 0.1 | 58 |
| 3 (T13-FY15) before leaching | 12 | - | 4.2 | 2.0 | - | 4.1 | 78 |
| 3 (T13-FY15) after leaching | 16 | | 3.0 | 3.0 | | 3.1 | 75 |

(a) chemical formulas of minerals: ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\bullet 26H_2O$], portlandite [$Ca(OH)_2$], calcite [$CaCl_2$], larnite [$Ca_2SiO_4$], hydrocalumite [$Ca_4Al_2(OH)_{12}(OH)_2\bullet 6H_2O)$], and quartz [$SiO_2$]. Wt. % error for reported values between ≤ 2 wt. %.

The $^{99}$Tc observed effective diffusivity coefficients ($D_{obs}$) for Test #1 and #3 CWFs calculated through 140 days and Test #2 CWF up to 100 days are shown in Fig. 1. The $^{99}$Tc diffusivities for CWF formulations with HL addition (Test #1 and #2) were compared with the current Cast Stone formulation prepared with FA, OPC, and BFS dry ingredients (Test #3). Test #1 CWF showed lower $^{99}$Tc diffusivity values in DI water for the 140-day cumulative leaching than Test #3 CWF prepared for the same WTP simulant. The current Cast Stone formulation, Test #3 CWF, showed noticeably higher $^{99}$Tc diffusivity values (at least two orders of magnitude higher; ~$10^{-11}$ vs. $10^{-13}$ $cm^2/s$) than Test #1 and #2 CWFs prepared with HL addition. At diffusivity levels of ~$10^{-13} cm^2/s$, these HL-based CWFs would no longer be considered a dominant risk contributor to groundwater at the Core Zone Boundary, assuming an infiltration rate of 3.5 mm per year, according to US DOE Environmental Impact Statement [4].

Although the release of $^{99}$Tc from the HL-based CWF (Test #1) showed lower $^{99}$Tc diffusivity, $^{99}$Tc release did not follow a pure diffusion trend as found in Test #3 (Fig. 2). The $^{99}$Tc release in DI water from Test #1 CWF showed two different linear slopes: an initial linearity with high slope up to 14 days leaching, and another linearity with slope lower than 0.5 between the 28 and 140 days leaching intervals. Initial $^{99}$Tc release through 14 days leaching followed a diffusion-controlled release of $^{99}$Tc, even though a small deviation from the slope range of 0.5 ± 0.15 was found. However, $^{99}$Tc release after 28 days leaching was linear with a slope lower than 0.5, which suggests that additional effects from either physical and/or chemical processes retarded $^{99}$Tc release during these relatively later leaching periods. Although the mechanism for this low $^{99}$Tc release in the later leaching periods for the HL-based CWFs is not clear, the low $^{99}$Tc leach rate is considered to result from some chemical reaction that sequesters $^{99}$Tc rather than physical factors such as reduced porosity and permeability (or tortuosity). More details on the decreased $^{99}$Tc release were discussed previously in Um et al [5].

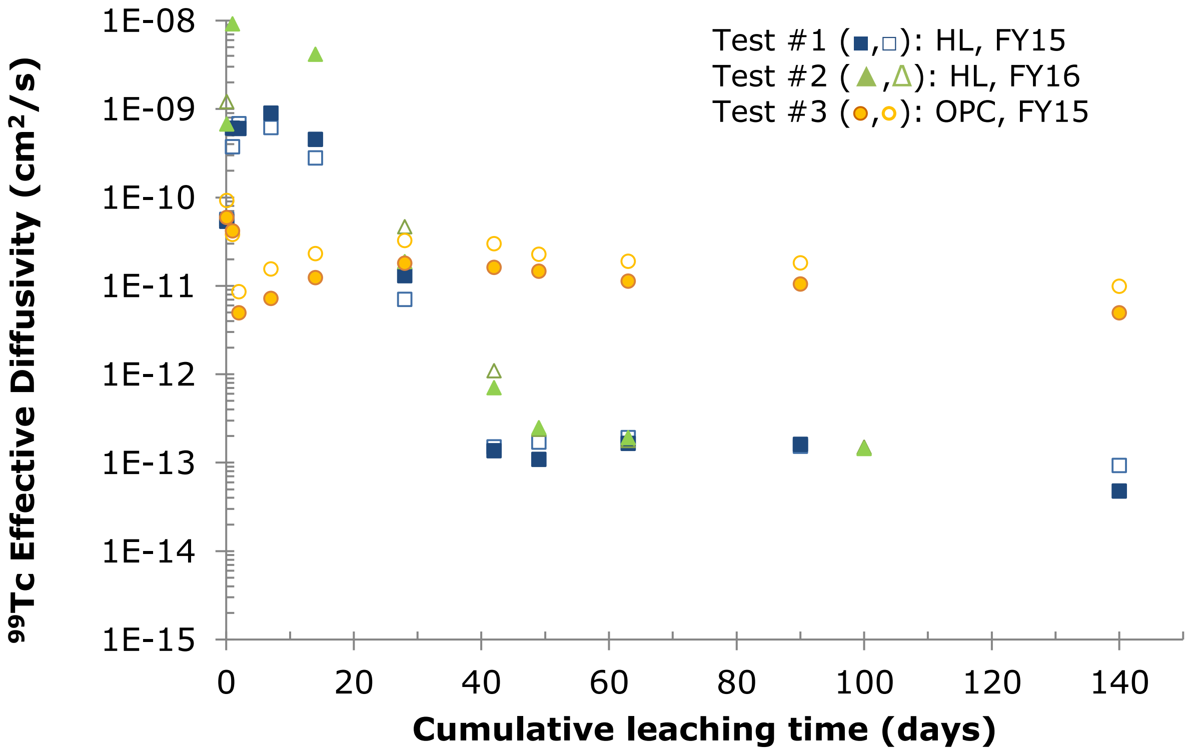

Fig. 1. $^{99}$Tc effective diffusivity values of EPA 1315 leaching test up to 140 days for Tests #1 and #3, and 100 days for Test #2. Duplicates are differentiated by open and closed variations of each test symbol (Test #1, squares; Test #2, triangles, and Test #3 circles).

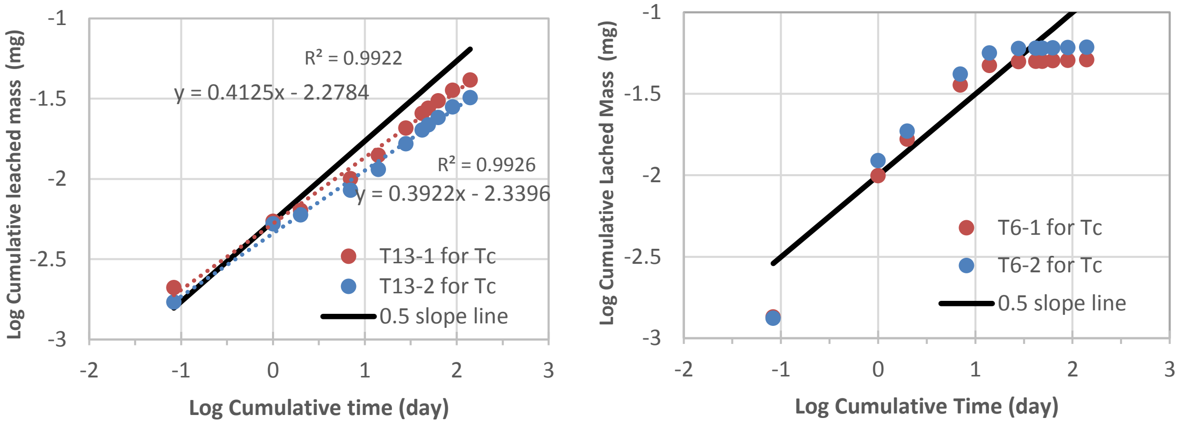

Fig. 2. Logarithm of the cumulative $^{99}$Tc release plotted vs. the logarithm of cumulative time for Test #3(T13-FY15) CWF (left) and Test #1(T6-FY15) CWF (right) along with a 0.5-slope line; $R^2$ is the correlation coefficient.

In addition, the release of $^{99}$Tc from Test #2 prepared with EMF/CS simulant and addition of HL showed a similar leaching trend to Test #1 (Fig. 1), in that minimal changes in $^{99}$Tc release was observed at later stages of leaching. Even though significant cracks were formed in Test #2 monoliths, in as early as 7 days leaching in DI water, no noticeable increase in the calculated $^{99}$Tc diffusivity was found in later leaching periods (after 28 days). Slightly increased $^{99}$Tc diffusivity of Test #2 monoliths in early leaching periods (< 14 days) results from the initial crack formation. The crack size increased with increasing leaching time in Test #2 monoliths, and large-sized cracks were formed around the entire circumference of the monolith top (Fig. 3). Additional small broken pieces were observed from the monolith top. However, Test #1 monoliths prepared with the same formulation (20% HL, 35% OPC, and 45% BFS) as Test #2 monoliths, but using different simulants (Test #1 for WTP simulant and Test #2 for EMF/CS simulant) did not show any cracks even after 140 days leaching in DI water (Fig. 3). Because of the higher sulfate concentration in the EMF/CS simulant, it is likely that some sulfate did not react with the limited sources of Ca and Al to form ettringite in Test #2 monoliths during the early curing stage and set period, resulting in a significant swelling of monoliths during the subsequent leaching test. As described above, an additional chemical process is considered to have enhanced $^{99}$Tc sequestration in HL-based Test #1 and #2 CWFs during the later leaching periods, but this process has not yet been identified.

Fig. 3. Photographs of CWF Test #1 (T6-FY15) after 140 days of cumulative leaching in DI water (left) and Test #2 (T1-FY16) after 100 days of cumulative leaching in DI water (right).

The batch results for $^{99}$Tc removal using co-precipitation with formation of ettringite showed that much higher $^{99}$Tc removal from solution was possible under reducing conditions than under oxidizing conditions (Fig. 4). No other mineral, other than ettringite, was found in the filtered co-precipitate. Removal of $^{99}$Tc by co-precipitation with ettringite is considered to occur as long as reducing conditions exist. Because both Test #1 and #2 CWFs were prepared with 45% BFS in the dry blend, slow dissolution of BFS could be releasing more reductants, such as ferrous iron and sulfide ions, that maintain a reducing environment in CWF pores for long-time periods.

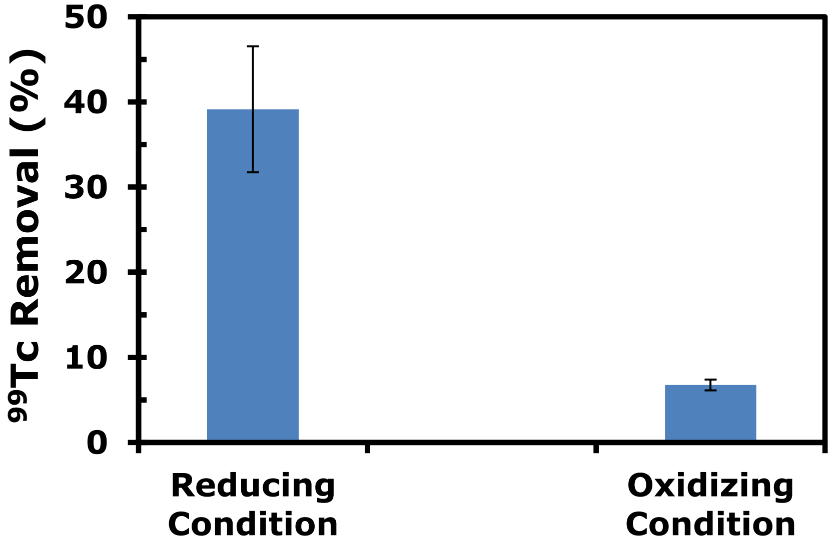

Fig. 4. Removal of $^{99}$Tc from solution likely by co-precipitation with ettringite under oxidizing or reducing conditions.

## CONCLUSIONS

Solid phase characterization showing a 5-9 wt. % increase in ettringite presence within cementitious materials formed with HL, rather than FA, indicate successful early formation of ettringite during the waste form curing process. As previously mentioned, early sequestration of sulfate in the form of ettringite is beneficial to the treatment of sulfate-rich secondary liquid waste at the Hanford site and in the process creates a less permeable CWF for achieving long-term waste storage objectives. These results also suggest that ettringite formation may increase $^{99}$Tc sequestration under reducing conditions thus limiting the release of $^{99}$Tc from CWFs. This is evident from extended leach testing results showing a decrease in $^{99}$Tc observed effective diffusivity coefficients of at least two orders of magnitude for leach periods greater than 28 days, despite the presence of cracks in the monolith material. In accordance with the US DOE Environmental Impact Statement, these observed $^{99}$Tc diffusion coefficients, ~$10^{-13}$ cm$^2$/s, would remove these HL-based waste forms from the list of dominant risk contributors to groundwater, assuming an infiltration rate of 3.5 mm per year [4]. Furthermore, based on ettringite-$^{99}$Tc co-precipitation batch experiments, continued chemical sequestration of $^{99}$Tc is proposed to contribute to the sustained low release in $^{99}$Tc. Overall these findings support the use of HL to overcome the deleterious effects of sulfate-rich conditions on CWFs through early formation of ettringite and support a dynamic chemical environment that can be leveraged to enhance $^{99}$Tc sequestration and long-term storage. Continued formulation development for preventing crack formation in EMF/CS CWFs is expected to improve $^{99}$Tc release rates beyond what is reported here, improving the efficacy of this approach to sulfate-rich secondary waste streams.

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