Preparation, Performance and Mechanism of Tc and I Getters in Cementitious Waste Forms – 17124

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ABSTRACT

Cementitious waste forms offer a low temperature, cost effective technology for the solidification of liquid wastes.   At the Department of Energy Hanford Site, 99-Tc and 129-I are radionuclides contained within low activity waste (LAW) which contribute significantly to environmental impacts associated with clean-up of the site.   Cast Stone, a cementitious waste form comprised of 47 wt% blast furnace slag, 45 wt% fly ash and 8 wt% ordinary Portland cement, has undergone investigation as a possible candidate technology for the solidification of LAW.   In screening tests using EPA Method 1315 leach testing of various mixes of Cast Stone with simulated LAW, Tc observed effective diffusivities (D_{obs}) had an average   of 5.3×10^{-11} cm^2/s and I D_{obs} had an average of 5.7×10^{-9} cm^2/s.   From these measurements, an opportunity exists to improve retention of Tc and I by Cast Stone.   One approach to accomplish this is through the incorporation of Tc and I getters to selectively sequester Tc and I in the waste stream and eventual waste form.   Initial testing conducted at PNNL identified potassium metal sulfide (KMS-2) and Sn(II)-apatite (Sn-A) as the strongest performing Tc getters and silver exchanged zeolite (Ag-Z) as the top performing I getter.   This research also demonstrated that the Tc and I getters, when added to solution simultaneously, can have deleterious interactions with one another and lower the Tc and I removal levels.   However, these interactions can be overcome through sequential treatment of solution with the getters.

Cast Stone samples were fabricated using a 6.5 M Na average LAW simulant spiked with Tc and I with the addition of various combinations of Tc and I getters. Through EPA Method 1315 and Method 1313 testing it was found that the KMS-2 Tc getter was most successful at lowering Tc D_{obs}.   The I getters were not effective, as apparent interference from sulfide components of the waste form may have led to dissociation of the AgI formed by the Ag-Z getter in sequestering the I from solution.

INTRODUCTION

Cementitious waste forms offer a low temperature, low cost option for the immobilization of liquid nuclear waste streams and encapsulation of solid secondary

wastes.   Cast Stone is a cementitious material comprised of a baseline dry mix of 8 wt. % Portland cement Type I/II, 45 wt. % Class F fly ash, and 47 wt. % Grade 100 or 120 blast furnace slag (BFS).   Cast Stone is considered the baseline technology for solidification of (1) aqueous secondary liquid effluents from the process condensates at the Hanford Tank Waste Treatment and Immobilization Plant and (2) melter off-gas caustic scrubber effluent low activity wastes (LAW)[1].   Recent research has also been focused on investigating Cast Stone as a possible candidate grout based technology for the solidification of LAW [2, 3].   The two radionuclides of highest importance expected in Hanford LAW are Tc-99 (commonly existing as pertechnetate, TcO_4^-; $t_{1/2}$ = 213 000 years, referred to as Tc from here on) and I-129 (commonly existing as iodide, I^-, and referred to as I from here on; $t_{1/2}$ = 15 700 000 years), both of which have high mobility in the subsurface.   EPA Method 1315 leach testing of Cast Stone fabricated with simulated LAW has given encouraging short term (63 d to 91 d) observed diffusivities for Tc and I.   However, the long term stability of these species within Cast Stone may be improved through the tailored addition of materials that specifically bind or retain the species of interest, termed getters.

Tc or I specific getters have been investigated previously in a range of environments with varying degrees of success in their Tc and I removal from solution [4-6].   The application of Tc and I getters in LAW presents challenges due to the high alkalinity, high ionic strength and presence of redox active species such as Cr(VI).   In terms of Tc getters, both Sn(II)-treated apatite (Sn-A) [7] and potassium metal sulfide (KMS-2) [8] have been shown to successfully sequester Tc from simulated LAW waste streams.   Both of these getters utilize redox processes to reduce Tc from its mobile $Tc(VII)O_4^-$ state to an immobile $Tc(IV)_2O \cdot xH_2O$ (Sn-A) or $Tc(IV)_2S_7$ (KMS-2) state.   Through generation of these Tc species it is plausible that upon inclusion of Tc-loaded getters in Cast Stone, additional stability will be imparted on the Tc and slow the re-oxidation to mobile $Tc(VII)O_4^-$.   The I getters that were found to have the most success toward removal from LAW function through an alternate mechanism.   Precipitation of I as a low solubility salt, such as AgI, is an effective approach at removing I from LAW [9].   Ag exchanged zeolite (Ag-Z) has been identified as a highly effective I getter in LAW.

Because of the presence of both Tc and I in LAW, simultaneous application of Tc and I getters must be possible without deleterious interactions between added getters.   Herein we present investigations into the interactions between select Tc and I getters and approaches to overcome these interactions from batch testing.   However, the potential for interference affecting getters is not limited to the treatment of the LAW simulant.   Cementitious waste forms have complex chemical makeups and the potential exists for interactions, both beneficial and deleterious, to occur between the grout matrix and the getters.   An investigation into the impact of getter inclusion in Cast Stone will also be presented.

METHODS

Getter Materials

The getters studied were selected based on previous work conducted by our group at PNNL [5, 7-9].   The following getters were utilized in testing in this study:

Sn(II)-treated apatite ($Sn_xCa_y(PO_4)(OH,Cl,F)$) (Sn-A) – the Sn-A was synthesized by the RJ Lee group using a previously published method [10], then stored in a desiccator during transport and until its use in Cast Stone fabrication.

Potassium Metal Sulfide (KMS-2) – This work utilizes KMS-2 fabricated using a solid state approach.   Details of the synthesis can be found in Neeway et al. (2016).   The approximate chemical formula for the KMS-2 is $K_{1.3}Mg_{0.95}Sn_{2.1}S_6$.

Silver exchanged zeolite (Ag-Z) – In the previous getters screening tests and work presented in other publications, [5, 9], Ag-Z has consistently removed the highest amount of I in the shortest time from LAW environments.   The Ag-Z was purchased from Sigma-Aldrich Corporation (St. Louis, MO) and received as > 840 μm pellets.   The pellets were crushed with a mortar and pestle to a size < 300 μm to increase the surface area and to achieve a homogenous distribution of Ag-Z in the Cast Stone mix.

Solutions

Three main solutions were utilized in this study:

1) *Distilled deionized water* (18.2 MΩ·cm, DDI)

2) *LAW simulant:* 6.5 M Na average LAW simulant was fabricated following the description listed in a previous report [11].   No solids were present in the LAW simulant following fabrication.   The measured composition of the LAW simulant is listed in Table 1.

3) *Simulated Hanford vadose zone pore water* (VZPW): VZPW was fabricated with distilled water and is based on analysis of Hanford sediments relevant to the disposal location (Integrated Disposal Facility (IDF)) on the Hanford site [12].   A full description of the VZPW fabrication can be found elsewhere [11].

Table 1 – Measured composition of the LAW simulant used in this study.   The average Na concentration was 6.5 M.

Anion/Cation	Measured Concentration (g/L)	Concentration (mol/mol Na)
Na	153.33	1.000
Al	11.75	0.065
Cl	3.47	0.015
NO_3	140.00	0.339

NO$_2$	37.04	0.121
SO$_4$	11.58	0.018
K	2.08	0.008
PO$_4$	1.47	0.002
Free OH	35.39	0.312

Batch Testing

Batch contact experiments containing getters were performed in an anaerobic chamber (N$_2$ atmosphere with 0.7 % H$_2$) in either distilled deionized water (DDI, 18.2 MΩ·cm) or LAW simulant in polytetrafluoroethylene bottles.   The solutions were spiked with a 10 400 ppm Tc (as TcO$_4^-$) or 10 000 ppm I (as NaI) solutions to achieve starting concentrations of 46 ppm Tc or 6 ppm I.   The concentrations were developed based on Hanford Tank Waste Operations Simulator (HTWOS) model runs to support the River Protection Project System Plan Revision 6 [13].   The concentrations used represent 10 × the concentrations of both Tc and I based on the HTWOS model. These concentrations were selected to provide an indication of overall capacity of the getters. Prior to addition of the getters, a sample was collected from the bottle to determine starting concentrations.   The getters were then added at 1 g : 100 mL solid : solution ratio.   Upon sampling, the collected aliquot was filtered with a 0.22 µm syringe filter.   Tc and I concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) with matrix determined detection limits of 4.1 ppb for Tc and 0.5 ppb for I in DDI, and 41 ppb for Tc and 50 ppb for I in the LAW simulant.   In sequential addition batch experiments, any filtration was performed using a 0.45 µm vacuum filter.

AgI dissolution experiments were performed by adding ~ 0.05 g of AgI to 50 mL of solution.   Care was taken to limit exposure of AgI to light prior to its addition to solution.   The solutions used were prepared with DDI and using NaOH or HNO$_3$ to adjust the pH and NaNO$_3$ to maintain equal ionic strength for all solutions.   In experiments spiked with Na$_2$S, a 0.1 mol/L Na$_2$S solution was used to add S^{2-} in an equimolar amount to the I present.   In BFS spiked experiments, 0.1 g of BFS was added to the solution.

Cast Stone Fabrication

Cast Stone samples were prepared with 6.5 M Na average LAW simulant spiked with 16 ppm Tc-99 and 6 ppm I-127 (stable I-127 was used to allow ease of experimental work).   A mix of 47 wt% blast furnace slag (BFS), 45 wt% class F fly ash (FA) and 8 wt% ordinary Portland cement (OPC) was used as a dry mix.   The Cast Stone had a "water to dry mix" ratio of 0.55.   In the incorporation of getters to the Cast Stone mix, the getters were added to either the LAW simulant or the dry mix ingredients.   The mass of getter added was subtracted from the total mass of the dry ingredients and the remaining dry mix mass was divided in the ratio of BFS, FA, and OPC listed above.   Full details on the Cast Stone formation can be found elsewhere [11].   The alterations from the standard Cast Stone recipe used in the getter containing Cast Stone are as follows:

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Cast Stone with Sn-A and Ag-Z: Sn-A (50 g) was added to the LAW simulant (1 L) and allowed to react for 24 h.   After this period the Ag-Z (8.75 g) was added and 24 h taken to react before adding the Cast Stone dry mix ingredients.

Cast Stone with KMS-2 and Ag-Z: KMS-2 (2.35 g) was added to the LAW simulant (1 L) and allowed to react for 48 h.   The Ag-Z (1.45 g) was added directly to the dry mix ingredients.   After the 48 h KMS-2 contact, the Cast Stone was fabricated.

Cast Stone with AgI: prior to Cast Stone fabrication 0.0198 g of AgI was added to the LAW simulant (1 L), equivalent to 20 ppm I.

RESULTS

Getter Interaction with Spiked DDI and LAW Simulant Batch Experiments

With getters identified to be successful at the removal of both Tc (Sn-A and KMS-2) and I (Ag-Z) from LAW, simultaneous batch contact experiments with combinations of these getters were performed in a simplified system (DDI) and LAW simulant spiked with Tc and I, with getters for both added simultaneously. The resulting Tc removal is shown in Figure 1.   In DDI, Figure 1 a), the Sn-A (blue) and KMS-2 (pink) when present individually in solution removed > 99.9 % and 44.0 % of the original Tc (46 ppm), respectively.   However, neither the Sn-A nor KMS-2 were capable of removing Tc from solution when the Ag-Z I getter was added along with the Tc getters.   Similar behavior was observed in the LAW simulant, Figure 1 b).   The KMS-2 was highly effective, as expected, in terms of Tc removal in the harsh LAW environment removing >94 % of the Tc (46 ppm). The Tc removal was hindered in the presence of Ag-Z as no measurable Tc removal was attained during the 15 d batch experiment.
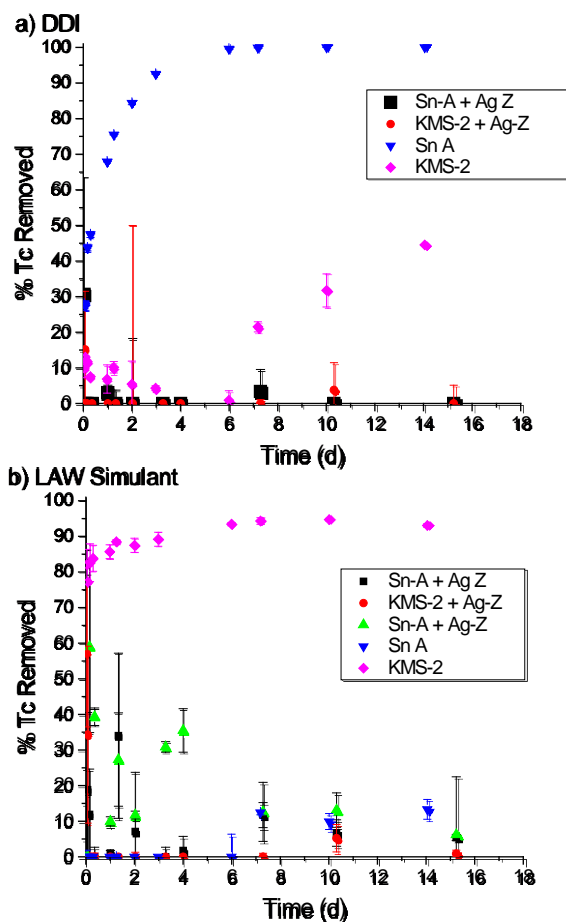
Figure 1 – measured % Tc removed from solution in batch contact experiments in a) DDI and b)LAW simulant spiked with 46 ppm Tc and 6 ppm I.   Experiments were performed in an anaerobic chamber and each getter was added at a 1 g : 100 mL ratio.

It is clear that the presence of the I getter simultaneously with the Tc getter negatively effects the Tc getter.   Figure 2 displays the I removal by the Ag-Z I getter during the same batch contact experiments.   In DDI, the Ag-Z was not affected by the presence of the Sn-A or KMS-2 in DDI, Figure 2 a), and was able to remove > 99.9 % of the initial I (6 ppm) at 15 d contact.   In the LAW simulant, Figure 2 b), the Sn-A had no observable impact on the Ag-Z ability to remove I as it removed > 99.9 % of the I immediately both with and without Sn-A present. Contrarily, the KMS-2 had a direct effect on I removal by the Ag-Z.   At 2 d when both KMS-2 and Ag-Z were present, 48.5 % of the I was removed from solution by the Ag-Z.   After this point, all of the I was released back into solution and no further removal occurred.
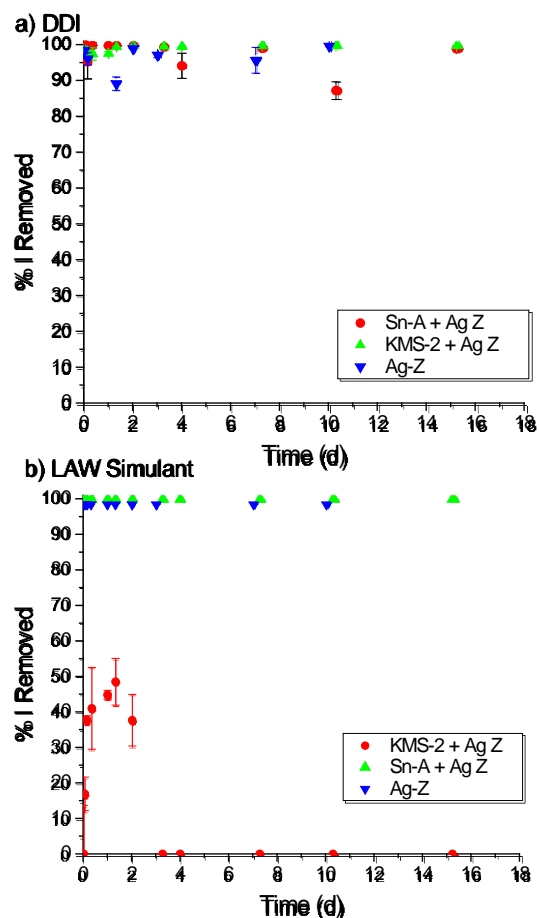
Figure 2 - measured % I removed from solution in batch contact experiments in a) DDI and b) LAW simulant spiked with 46 ppm Tc and 6 ppm I.   Experiments were performed in an anaerobic chamber and each getter was added at a 1 g : 100 mL ratio.

These deleterious interactions between the getters occur for different reasons.   The loss of Sn-A - Tc removal capability by the Ag-Z is likely a result of redox interactions between the two getters.   Sn-A requires Sn(II) to facilitate the reduction of Tc(VII), however, in the presence of Ag(I) from the Ag-Z, the Ag(I) will be preferentially reduced and in turn oxidizes the Sn(II) to Sn(IV).   This process does not impact the Ag-Z due to the excess stoichiometry of Ag to I in the solution. The KMS-2 and Ag-Z have a different interaction.   KMS-2 was developed for the removal of cations from solution and has shown a high affinity for Ag(I) in previous testing [14].   The Ag will primarily interact with the sulfur component of the KMS-2.   The sulfur is the redox active component of the KMS-2, and by interacting with the Ag, is no longer capable of being utilized to reduce Tc.   As well, the Ag will no longer be available to remove I from solution.   After initially forming AgI in the LAW simulant in the first two days, the KMS-2 will pull the Ag from the AgI complex, releasing the I back into solution, as has been previously observed with Ag-containing solids [14].

Sequential Addition of Tc and I Getters to Spiked DDI and LAW Simulant

The deleterious interactions experienced between the Tc and I getters when present simultaneously in solution can be overcome through sequential addition of the getters.   Sequential addition testing was performed in batch experiments with 46 ppm Tc and 6 ppm I in DDI at a 1 g : 100 mL getter to solution ratio for each getter.

Figure 3 a) shows the % Tc and % I removed in experiments where Sn-A and Ag-Z were added in varying orders.   When the Sn-A and Ag-Z were added simultaneously in DDI, the Sn-A removed 23 % of the initial 46 ppm Tc and the Ag-Z removed > 99% of the I at 48 h contact.   By adding the Ag-Z to solution first for 24 h contact followed by Sn-A, the Ag-Z removed > 99 % of the I while the Sn-A removed 26 % of the Tc, 24 h after introducing the Sn-A.   The performance becomes much more promising when the Sn-A was added first for 24 h followed by the Ag-Z.   The Sn-A removed 70 % of the Tc and the Ag-Z removed 91 % of the I, 24 h after introduction of the Ag-Z.   This result confirms that in use of Sn(II) containing getters with Ag containing getters, the Sn(II) getter should be introduced first to solution to sequester Tc, followed by treatment with the Ag containing getter.

Figure 3 b) shows the % Tc and % I removed in experiments where KMS-2 and Ag-Z were added using steps to avoid their interactions with one another in LAW simulant.   In the first test, the KMS-2 was added first to the LAW simulant and after 24 h of reaction time the Ag-Z was added.   The KMS-2 removed 96 % of the Tc while the Ag-Z only removed 25 % of the I when measured 24 h after introduction of the Ag-Z.   From the previous batch testing, it can be expected that the I would be released at longer contact time, as suggested in Figure 2 b).   In order to avoid any contact between the KMS-2 and Ag-Z, a filtration step was attempted to remove the first getter added before treatment with the second getter.   When the KMS-2 was added first it removed 98 % of the Tc at 24 h and was then filtered out of solution.   The filtered LAW simulant was then treated with the Ag-Z and 91 % of the I was removed after 24 h.   This is a marked improvement from both getters being present in solution.   The slight decrease in Ag-Z I removal capability may be due to residual KMS-2 or sulfide containing particles passing through the 0.45 µm filter.   Reversing the addition order is not as beneficial.   Treatment with Ag-Z first prior to filtering removed > 99 % of the I. Following this, treatment of the filtered LAW with KMS-2 only led to a removal of 61 % of the Tc after 24 h.   This decrease is due to dissolved Ag from the Ag-Z being present in the LAW simulant and interfering with the KMS-2.   Thus, it can be suggested that getter treatments with sulfide containing Tc getters and Ag containing I getters is best suited for initial treatment with the sulfide containing material, followed by removal of the sulfide containing getter and treatment with the I getter or incorporation of the I getter into the cementitious dry mix ingredients.
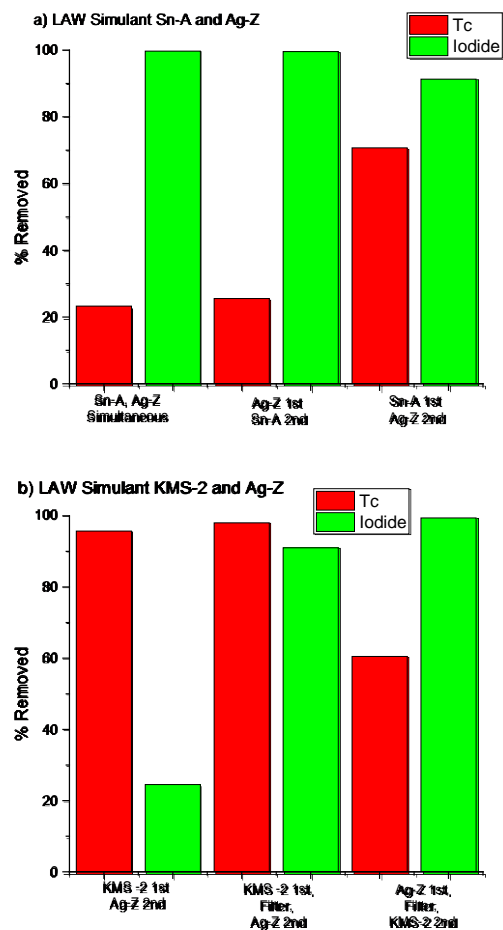
Figure 3 – the % Tc and % I removed in batch experiments containing a) Sn-A and Ag-Z in DDI or b) KMS-2 and Ag-Z in LAW simulant.   The getters were added in varying orders listed in the figure.   A 1 g : 100 mL solid : solution ratio was used for both getters, with a 24 h reaction allowance after each addition.   The starting Tc concentration was ~ 46 ppm and the starting I concentration was ~ 6 ppm.

Getter Interactions within Cast Stone

Cast Stone samples were fabricated using combinations of Tc and I getters added in the suggested methods from the sequential addition tests.   The Tc getters performed well in their pre-fabrication contact, and in EPA Method 1315 leach testing of the getter containing Cast Stone in VZPW, it was found that a minimal addition of KMS-2 (equivalent to 0.1 wt% of the overall waste form mass) was able to induce an order of magnitude decrease in Tc D_{obs} compared to a getter-free control Cast Stone [11].   It should also be noted that filtration of the KMS-2 prior to I getter treatment had little impact on Tc D_{obs} compared to Cast Stone fabricated with KMS-2 remaining in the LAW simulant and the I getter added to the dry mix.   Further details can be found in a recent report [11].
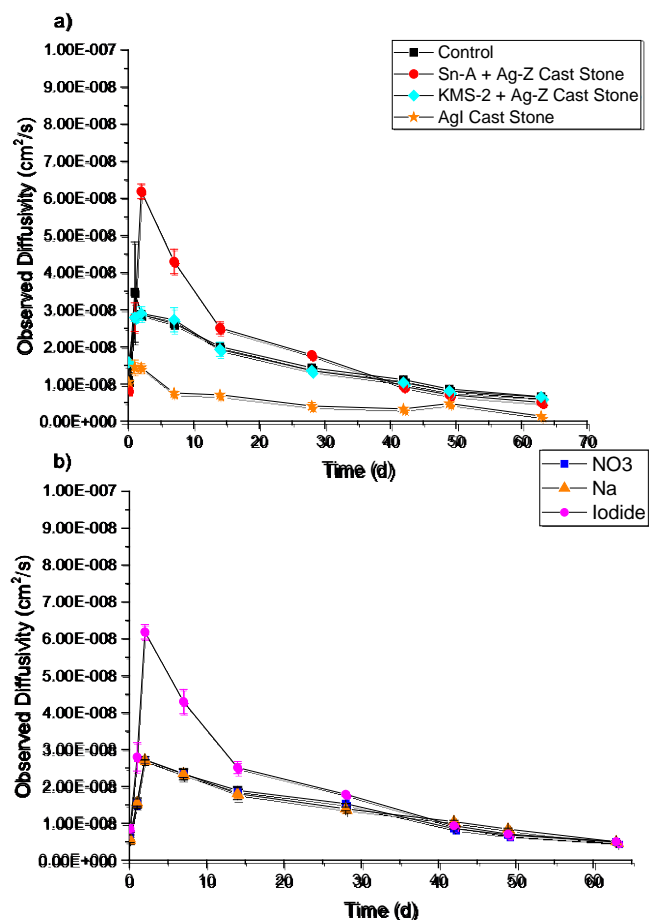
Figure 4 – a) iodide D_{obs} from the various Cast Stone samples in VZPW and b) comparison between the D_{obs} values for the mobile constituents Na and NO_3 with I for the Sn-A + Ag-Z Cast Stone from leaching in VZPW.

The behavior of Ag-Z as an I getter within Cast Stone is more complex.   In Cast Stone samples fabricated with a sequential Sn-A then Ag-Z treatment, the Ag-Z removed, as expected, was > 99% of the initial I prior to Cast Stone formation. A separate batch of Cast Stone was fabricated with the Ag-Z added to the dry blend ingredients with treatment of the LAW simulant with KMS-2.   Following fabrication, the getter containing Cast Stone was leached under EPA Method 1315 testing in VZPW along with a getter-free control.   The resulting I D_{obs} measurements from these systems are shown in Figure 4 a).   Little difference exists between the I D_{obs} measured for the control Cast Stone and the KMS-2 + Ag-Z Cast Stone where the Ag-Z was added to the dry blend.   The Sn-A + Ag-Z Cast Stone measured higher I D_{obs} in the first 28 d of leach testing before measuring the same as the other two systems.   This is despite the Ag-Z sequestering the complete inventory of I in the LAW simulant prior to fabrication.   Also, no effect was observed from having the I getter contained within the Cast Stone dry mix.   When comparing the I D_{obs} from the Sn-A + Ag-Z Cast Stone with the D_{obs} for the mobile constituents of the Cast Stone, Na and NO_3 (since they have limited chemical interaction with the waste

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form), little difference was observed, Figure 4 b).   After 28 d the D_{obs} values are identical for I, Na, and NO_3.   This is a result of there being no chemical or physical restriction on I release within the Cast Stone.

When the Ag-Z removes the I from the LAW simulant, it does so by forming AgI.   An additional test was performed in which AgI was added directly to the LAW simulant prior to fabricating the Cast Stone.   In this system, also shown in Figure 4 a) only a slight decrease in I D_{obs} was observed measuring 1.3×10^{-9} cm^2/s at 63 d compared with ~ 5×10^{-9} cm^2/s for the other Cast Stone systems.   As no large decrease in I D_{obs} was observed from the direct addition of AgI, it is likely that interference within the Cast Stone on the AgI is occurring.
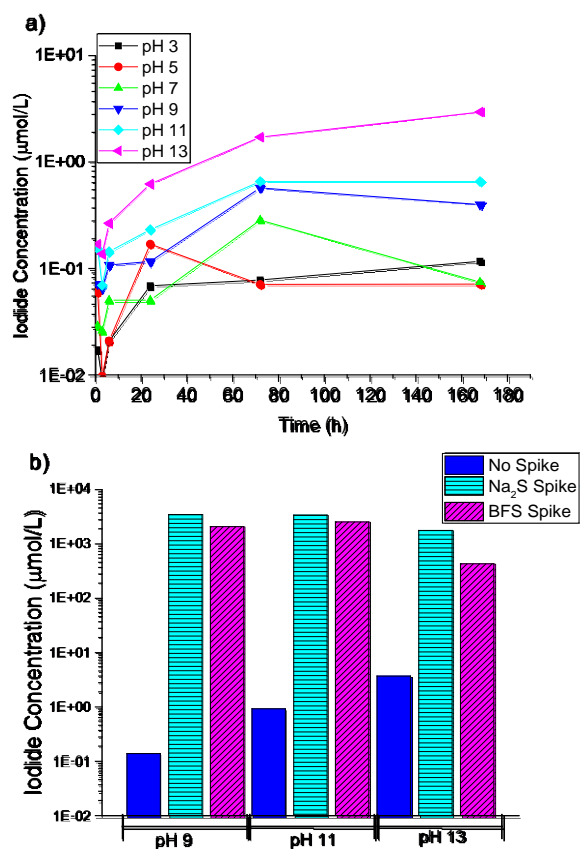
Figure 5 – a) change in concentration of I in solution over time at various pH levels following the addition of 0.05 g of AgI to 50 mL of solution and b) change in the concentration of I after 7 d of AgI dissolution in the presence of Na_2S and BFS.   The Na_2S was added at an equimolar amount to the I and 0.1 g of BFS was added.

Two factors may be primarily influencing the instability of the AgI getter product in the Cast Stone: the alkalinity of the environment and the interference of sulfides.   Tests were performed to monitor the dissolution of AgI in solutions of varying pH and with the addition of sulfide sources.   Figure 5 a) shows the change

in I concentration in solution resulting from AgI dissolution at different pH levels. It can clearly be seen that increasing pH leads to an increased dissolution of AgI with the dissolution in pH 13 being ~ 6 × higher than pH < 11.   A more dramatic release of I from AgI was observed in the presence of sulfides.   AgI was added to solution along with one of two sulfide sources, a spike with 0.1 M Na_2S solution (at an equimolar level to the amount of I in the AgI) or the addition of blast furnace slag.   Figure 5 b) compares the resulting I concentration in solution after 7 d of spiking.   At all pH levels, the Na_2S spike led to the highest release of I, a maximum 3.4 ×10^3 μmol/L (maximum release would be ~ 4 × 10^3 μmol/L) at pH 9, compared to the dissolution of AgI without a sulfide spike, maximum 3.7 μmol/L at pH 13.   A similar magnitude release of I was also observed when BFS was present in the system with a maximum release of 2.5 × 10^3 μmol/L induced at pH 11. From the dissolution experiments, it is likely that the instability of the AgI within the Cast Stone is most likely caused by the sulfide component of the BFS with the alkalinity of the LAW simulant and grout playing a minor role in the dissolution. The sulfide can displace the I, leading to release, as also suggested by Inagaki et al. [15].   It is unlikely that the Fe component of the BFS plays a role in the dissolution [16].   This example does not represent a failure of Ag based getters for I retention in Cast Stone, as previous examples of incorporating Ag based materials in cementitious waste forms fabricated with less aggressive waste streams at much higher loadings (up to 10 wt% compared with < 0.1 wt % here) have showed improvements in I D_{obs}.   However, we have identified processes which will ultimately interfere with AgI stability, and thus alternate encapsulation technologies should be considered as well.

CONCLUSIONS

This study examined the complex interactions possible in the treatment of LAW with getters in cementitious waste forms.   Clear deleterious interactions were identified between Sn-A and Ag-Z, limiting Tc removal, and between KMS-2 and Ag-Z, hindering both Tc and I removal.   These interactions were overcome through sequential addition of the getter materials to LAW simulant and limiting their simultaneous contact in solution.   In leach testing of Cast Stone containing getters, the Ag-Z was found to be ineffective in lowering I D_{obs} when the Cast Stone was leached in VZPW.   When adding AgI directly as the I source to Cast Stone, again little improvement in I D_{obs} was observed.   The instability of AgI in Cast Stone is likely the result of the competition from sulfide species and the alkaline environment of the waste form, with the sulfide competition having a larger impact on the AgI.

ACKNOWLEDGEMENTS

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