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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Characterization of Technetium Speciation in Cast Stone

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November 2013

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Pacific Northwest National Laboratory
Richland, Washington 99354

Executive Summary

This report describes the results from laboratory tests performed at Pacific Northwest National Laboratory (PNNL) for the U.S. Department of Energy (DOE) EM-31 Support Program (EMSP) subtask, “Production and Long-Term Performance of Low Temperature Waste Forms” to provide additional information on technetium (Tc) speciation characterization in the Cast Stone waste form. To support the use of Cast Stone as an alternative to vitrification for solidifying low-activity waste (LAW) and as the current baseline waste form for secondary waste streams at the Hanford Site, additional understanding of Tc speciation in Cast Stone is needed to predict the long-term Tc leachability from Cast Stone and to meet the regulatory disposal-facility performance requirements for the Integrated Disposal Facility (IDF). Characterizations of the Tc speciation within the Cast Stone after leaching under various conditions provide insights into how the Tc is retained and released. The data generated by the laboratory tests described in this report provide both empirical and more scientific information to increase our understanding of Tc speciation in Cast Stone and its release mechanism under relevant leaching processes for the purpose of filling data gaps and to support the long-term risk and performance assessments of Cast Stone in the IDF at the Hanford Site.

Various formulations of Cast Stone that include secondary waste simulants and different LAW simulants have been characterized previously. For this report, smaller Cast Stone monoliths were prepared with high Tc concentrations spiked into the 7.8 M Na overall average LAW simulant using dry ingredients from two different sources (referred to as NW and SE). These small Cast Stone monoliths were used for this Tc speciation characterization. The following subtasks are included within the Tc speciation characterization task:

1. Measure the reductive capacity of different types of dry ingredients, the 8 LAW simulants used in Westsik et al. (2013), and short-term cured Cast Stone before and after leaching with different leaching conditions.
2. Conduct the U.S. Environmental Protection Agency (EPA) 1315 leach test up to 90 days for Cast Stone monoliths prepared with high Tc concentration under different leaching conditions (air-equilibrated, elevated O_2-saturated, and fractured Cast Stone in O_2-saturated leaching solutions).
3. Determine Tc speciation and oxidation state changes in Cast Stone after leaching with additional O_2 exposure.

The reductive capacities of dry ingredients from NW and SE sources, various LAW simulants, and final Cast Stone before and after leaching tests were measured using two different methods, the Ce(IV) and Cr(VI) methods. One type of blast furnace slag (BFS) and the high-Ca fly ash were obtained from LaFarge North America Inc. in Pasco, Washington, and these materials are referred to as the NW slag and fly ash. The second BFS and the low-Ca fly ash are the same materials used in the Saltstone processing facility at the Savannah River Site in South Carolina and are referred to as the SE materials. Much more of the solids dissolve in the strong acid (pH ~1–2) environment created by the Ce(IV) method compared to circumneutral pH (~7.0) condition created by the Cr(VII) method. Among the dry ingredients, the reductive capacity measured by the Ce(IV) method was the highest for BFS (0.793 meq/g for NW slag and 0.800 meq/g for SE slag). The reductive capacity measured by the Ce(IV) method was 0.060 meq/g for NW fly ash and 0.288 meq/g for SE fly ash: the reductive capacity of the one Portland cement source used in the Cast Stone formulations was negligible, with a range of 0–0.042 meq/g by the Ce(IV) and

Cr(VI) methods. The reductive capacity of BFS measured by the Cr(VI) method was 0.078 meq/g for NW slag and 0.226 meq/g for SE slag, which were lower than the reductive capacities of NW slag and SE slag measured by the Ce(IV) method. Differences in the reductive capacities measured by these two methods could be attributed to the different pH conditions in the Ce(IV) and Cr(VI) methods. Moreover, the reduction of Cr(VI) in the Cr(VI) method could be less efficient and slower when the solution pH is buffered to alkaline pH by the reaction with BFS and cement samples. The reductive capacity measurements of different LAW liquid waste simulants by both Ce(IV) and Cr(VI) methods showed the highest reductive capacity for "High Al" simulant, followed by "Average" simulant, "High SO_4" simulant, and "SST Blend" simulant, whether the Na concentration was 5 M or 7.8 M. Higher reductive capacity found in 7.8 M Na simulants (1.025–2.146 meq/g) than in 5 M Na simulants (0.727–1.507 meq/g) are likely caused by the higher concentration of nitrite (NO_2^-) added in 7.8 M Na simulants than nitrite added to the 5 M Na simulants. The reductive capacity of simulants was strongly correlated with the concentrations of NO_2^-, which ranged from 0.085 to 0.194 mole-NO_2^-/mole Na in simulants. The measured reductive capacities of different LAW Cast Stone formulations before leaching followed similar trends for both Ce(IV) and Cr(VI) methods. The reductive capacities of LAW Cast Stones were highest for the "High Al" Cast Stone, followed by the "Average" Cast Stone, the "High SO_4" Cast Stone, and the "SST Blend" Cast Stone, similar to the trend of decreasing reductive capacities measured in these LAW simulants themselves. Cast Stones made with 7.8 M Na simulants consistently showed higher reductive capacity than Cast Stones made with 5 M Na simulants. This indicates that NO_2^- concentrations in LAW simulants exert a dominant role in determining a total reductive capacity of Cast Stones. However, because of the lower reduction potential of NO_2^-/NO_3^- redox couple (~0.01 V) compared to reduction potentials of the Fe^{2+}/Fe^{3+} (~ -0.5V), HS^-(or S^{2-})/SO_4^{2-} (~ -0.5 to -0.93V), and Tc^{4+}/Tc^{7+} (~ -0.36 V) redox couples at alkaline pH (~14) condition (Lukens et al. 2005), it is expected that most of the initial Tc(VII) species was not reduced to Tc(IV) by the nitrite in the simulants before mixing with dry ingredients to form Cast Stone. Aqueous S^{2-} and Fe^{2+} species slowly released from the BFS into the Cast Stone pore solution after mixing with the LAW waste simulants effectively reduced Tc(VII) to Tc(IV) and control Tc speciation in the final Cast Stone. The EPA 1315 leaching of LAW Cast Stone containing high concentrations of Tc in air-equilibrated deionized water leaching solution or elevated O_2-saturated deionized water decreased the reductive capacity of Cast Stone by ~30–70% after leaching compared to the measured reductive capacity before leaching. The reductive capacity of NW-Cast Stone and SE-Cast Stone decreased most significantly when they were fractured and leached under O_2-saturated leaching conditions because of the increased surface areas in contact with leaching solutions with elevated O_2 content. The results suggest that it is important to prevent the formation of fractures in Cast Stones, since O_2 diffusion can be faster through the fractures (or cracks) in Cast Stone and the O_2 facilitates reoxidation and remobilization of Tc.

The EPA 1315 leach test using different Cast Stones provided detailed information for the amount and release behavior of Tc under various leaching conditions. Previous EPA 1315 leachates collected up to 90 days for a secondary waste Cast Stone with high Tc concentration (~200 μg/g) showed that Tc diffusivity followed a general trend of slowly decreasing Tc diffusivity after initial increasing peaks due to the surface wash-off effect. Because of relatively high initial Tc concentration in Cast Stone compared to other previously tested Cast Stones in leaching tests, the average Tc diffusivity measured in high-Tc secondary waste Cast Stone was higher than others. However, after 60 days leaching, the Tc diffusivity dropped to almost 10^{-11} cm^2/s. The EPA 1315 leach tests also showed higher Tc release under elevated oxygen content leaching conditions using both NW- and SE-Cast Stones. Because of the potential reoxidation of the initially reduced less-mobile Tc(IV) species as the oxidized Tc(VII) species formed with increasing contact with the elevated oxygen content in leaching solution, enhanced Tc release is expected to occur in Cast Stone as the storage time increases even in suboxic conditions in the subsurface disposal site. In addition, the highest Tc release was found in the fractured Cast Stones among the three different leaching conditions for both NW- and SE-Cast Stones. Increased Tc releases due to the presence of fractures (or cracks) in both NW- and SE-Cast Stones are attributed to the increased surface areas in the fractured Cast Stone which can more easily contact and react with incoming oxygen. Between the two Cast Stones used in the Tc leaching test, the SE-Cast Stone showed relatively lower Tc release, which indicates slightly better Tc retention in SE-Cast Stone (or SE dry ingredients) compared to NW-Cast Stone (or dry ingredients) and agrees well with other testing results (reductive capacity and Tc speciation by x-ray absorption fine structure [XAFS] analysis).

The technetium speciation and oxidation state changes were estimated for both secondary waste Cast Stone (prepared earlier on a different project) and LAW NW- (or SE)-Cast Stones before and after leaching using XAFS spectroscopy. Secondary waste Cast Stone after 90 days leaching and an additional ~three years storage in air showed reoxidation of the reduced Tc(IV) species to Tc(VII) species. The percentage of Tc(VII) increased from 75% in Cast Stone cured for 60 days before leaching to 82% in the same Cast Stone after leaching and air exposure for about three years. Although the Tc(IV) contribution decreased from 25% in Cast Stone before leaching to 18% after leaching, some reduced Tc(IV) remains in the weathered Cast Stone. Because no Tc_2S_7 species contribution was found in Cast Stone after leaching or long-term storage in air, most of the Tc_2S_7 species reoxidized first to$TcO_2•2H_2O$, then some $TcO_2•2H_2O$ subsequently also reoxidized to TcO_4^- species during leaching and long-term storage in air. Due to the presence of sulfide and the higher reduction potential of S species redox couples than that of Fe^{2+}/Fe^{3+} redox couple (Lukens et al. 2005), reoxidation of Tc(IV) must start from Tc_2S_7 to $TcO_2•2H_2O$ followed by subsequent reoxidation from $TcO_2•2H_2O$ to TcO_4^-. It is not likely that Tc_2S_7 reoxidizes directly to TcO_4^-, even under highly oxidative conditions. However, the reoxidation rate of Tc(IV) to Tc(VII) in Cast Stone is controlled by the consumption rate of the remaining reductive capacity of Cast Stone and the diffusion rate of O_2 into Cast Stone, because oxygen is the only oxidant that effectively oxidizes Tc(IV) to Tc(VII) in Cast Stone in subsurface burial environments. For both LAW NW- and SE-Cast Stones made with the high concentration of Tc, due to the short curing time between Cast Stone preparation and XAFS sample collection dates, there was not much Tc(IV) species found, rather the Tc(VII) spiked into the LAW simulant still predominated in both Cast Stones before the leaching tests began. It appears that the reductants in the BFS have not had adequate time to reduce much of the originally spiked Tc(VII) within these short-term cured Cast Stone samples. Even after leaching under three different leaching conditions (air-equilibrated, elevated O_2-saturated, and fractured Cast Stone in O_2-saturated leaching solutions), no significant increase of Tc(VII) contribution was reported in the x-ray absorption near-edge structure (XANES) analysis for both leached LAW NW- and SE-Cast Stones. Because of the slow dissolution rate of BFS (the major reductant in Cast Stone), the total of 65 days of Cast Stone reaction (28 days curing for Cast Stone preparation, 28 days of leaching, and nine days of XAFS sample preparation and transportation) was insufficient for the BFS to release enough sulfide and ferrous iron ions to completely reduce Tc from Tc(VII) to Tc(IV). Although Tc reduction by dissolved ferrous iron and sulfide ions in Cast Stone was continuous even during the leaching process, a minor increase of Tc(VII) contribution was found in LAW NW-Cast Stone after O_2-saturated leaching. Higher O_2 content and contact in the leaching solution caused the Tc(VII) percentage in the bulk Cast Stone sample to increase through reoxidation from Tc(IV) in Cast Stone during leaching. Contributions of Tc(IV) decreased in LAW NW-Cast Stone after leaching in O_2-saturated solution as well. Also, lower Tc(VII) percentages were found in bulk samples of the LAW SE-Cast Stones in either the before or after leaching condition, consistent with the relatively higher reductive capacity of SE dry ingredients and 28 days cured Cast Stone. Even though time for extended x-ray absorption fine structure (EXAFS) sample collection was limited by the project schedule, the EXAFS analysis showed that there was no Tc-Tc scattering contribution found, indicating that Tc species were present without forming discrete precipitates in Cast Stone despite the high Tc concentration used to prepare the Cast Stone. The EXAFS analysis also showed that Tc(VII) species predominates in secondary-waste Cast Stone samples made in a previous project after leaching which is very consistent with the results from XANES analysis.

In summary, the measured reductive capacity of different Cast Stones decreased consistently after leaching, because of the consumption of reductive capacity in Cast Stone by O_2 during the leaching period. Consequently, the greatest amount of releasable Tc was found in Cast Stones when the fractured Cast Stone was tested in O_2-saturated deionized (DI) water, because the increase in surface areas exposed to O_2 in the fractured Cast Stones decreased the reductive capacity of the Cast Stone. In addition, Tc reoxidation increased noticeably in a secondary waste Cast Stone monolith after 90-day leaching and about three years storage in air. Therefore, the Tc reoxidation reaction is occurring under both water immersion and storage in air. The impacts of Tc reoxidation rate and O_2 diffusion into a monolithic Cast Stone can be limited by the size of waste form; however, the reoxidation reaction and formation of an oxidation front will occur at the exposed surfaces of the Cast Stone and along the outer layer or fractures. Wherever the reoxidation front exists in the Cast Stone, it can enhance Tc leachability. More quantitative and long-term measurements for Tc reoxidation and consequent Tc release should be performed to determine the long-term Tc reoxidation rate and to develop a robust predictive model for Cast Stone weathering with aging and subsequent Tc oxidation changes as well as amounts of Tc released in the Hanford IDF subsurface environment.

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Acronyms and Abbreviations

ANS	American Nuclear Society
ANSI	American National Standards Institute
BFS	blast furnace slag
DI	deionized
DOE	U.S. Department of Energy
EC	electrical conductivity
EMSP	DOE EM-31 Support Program
EPA	U.S. Environmental Protection Agency
EXAFS	extended x-ray absorption fine structure
HAW	high-activity waste
HTWOS	Hanford Tank Waste Operations Simulator
IDF	Integrated Disposal Facility
LAW	low-activity waste
LI	leachability index
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
RCRA	Resource Conservation and Recovery Act
SRNL	Savannah River National Laboratory
SST	single-shell tank
Tc	technetium
TOC	total organic content
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XAFS	x-ray absorption fine structure
XANES	x-ray absorption near-edge structure

Units of Measure

Å	Angstrom (10^{-10} m or 10^{-1} nm)
°C	temperature in degrees Celsius [T(°C) = T(K) – 273.15]
Ci	curie, 3.7×10^{10} disintegrations per second
cm	centimeter
eV	electron volt
g	gram(s)
in.	inch(es)
keV	kiloelectron volt
µ	micro (prefix, 10^{-6})
µm	micrometer
meq/g	milliequivalents per gram
mS/cm	millisiemens per centimeter (electrical conductance)
mM	millimole
M	molarity, mol/L
mL	milliliter
V	volt
wt%	weight percent

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1.0 Introduction

During the Cold War era, generation of fissile ^{239}Pu for use in America's atomic weapons arsenal yielded nearly 1,900 kg of technetium (Tc) at the Hanford Site, Washington State, USA (Darab and Smith 1996). A fraction of this inventory was intentionally released to the subsurface through ponds, trenches, and other excavations in the landscape, while a smaller fraction has been accidentally released through leaks from underground nuclear waste storage tanks and auxiliary equipment at the Hanford Site. The remainder, representing the bulk of the Tc generated at the Hanford Site, is present in fuel reprocessing wastes temporarily stored in 177 underground storage tanks awaiting retrieval, treatment, immobilization, and permanent disposal. After the wastes are retrieved from the storage tanks, current disposal plans call for separation of the waste into two fractions: a high-activity waste (HAW) and a low-activity waste (LAW) stream, which will be treated, vitrified, and disposed of separately. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed to treat the radioactive wastes and immobilize them in a glass waste form. At least a portion of (~35%) the LAW stream will be converted into a borosilicate glass waste form, which will be disposed of in a shallow burial facility at the Hanford Site, the Integrated Disposal Facility (IDF) (McGrail et al. 2001). The HAW stream will also be vitrified and stored until a deep-geologic repository is built to receive this defense radioactive waste as well as commercial spent nuclear fuel. Even with careful engineering controls, volatilization of a fraction of the Tc during the vitrification of both the HAW and LAW streams is expected. Although this volatilized Tc will be captured in melter off-gas scrubbers and returned to the melter, some of the Tc is expected to become part of the secondary waste stream from the vitrification process (Darab and Smith 1996).

Pacific Northwest National Laboratory (PNNL) has conducted laboratory testing for the U.S. Department of Energy (DOE) EM-31 Support Program (EMSP) with the subtask, "Production and Long-Term Performance of Low Temperature Waste Forms." To support the use of Cast Stone as a waste form for WTP secondary wastes and as a potential supplemental immobilization waste form for Hanford LAW, additional characterization and understanding of Tc speciation is needed to predict a long-term Tc leachability from Cast Stone and to meet the regulatory disposal-facility performance requirements for the IDF. To have confidence in the long-term performance of solidified waste forms such as Cast Stone, it is important to understand how Tc is retained in the waste form and how it can be released when exposed to water and/or air in the disposal environment. Characterization of the Tc species within Cast Stone provides insights into how the Tc is retained and released under conditions relevant to the IDF subsurface environment. This then enables extrapolating short-term leach testing results to long-term waste form performance.

Samples of both unleached and leached Cast Stone monoliths containing pertechnetate (TcO_4^-) were characterized for Tc speciation using reductive capacity measurement, additional leaching experiments with varying oxygen contents, and synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy. The results and data generated by the laboratory tests provide both empirical and more scientific information to increase our understanding of Tc speciation in Cast Stone and Tc release mechanisms under relevant leaching environments, which can also support filling data gaps and the long-term risk and performance assessments. This report addresses the laboratory results of the subtask, "Tc Speciation Characterization in Cast Stone." The specific objectives of this testing are as follows:

- Measure the reductive capacity of dry ingredients obtained from two sources, various LAW simulants, and various cured Cast Stones before and after leaching.

- Perform additional U.S. Environmental Protection Agency (EPA) 1315 leach test (EPA 2013) to determine Tc release with different leaching conditions, such as high starting Tc concentration, different O_2 contents in leaching solution, and presence of fractured surfaces in Cast Stones.
- Determine Tc speciation and oxidation state changes after leaching and air exposure.

The results generated from the subtasks above and included in this report will benefit the secondary waste Cast Stone and the LAW supplemental immobilization activities at the Hanford Site as well as other DOE sites where cementitious waste forms are considered for use as solidifying waste forms.

1.1 Report Content and Layout

Each of these subtasks is discussed in more detail in a separate section in this report. Section 2 describes the background and Cast Stone preparation details, including dry ingredients and waste simulants used for Cast Stone preparation. Section 3 provides reductive capacity measurements for dry ingredients, simulants, and different Cast Stone specimens before and after leaching using both Ce(IV) and Cr(VI) methods. Section 4 describes Tc releases from various Cast Stones using the EPA 1315 leach test under different leaching conditions. Section 5 describes the Tc speciation and oxidation-state changes in Cast Stone specimens after leaching using XAFS spectroscopy. Finally, Section 6 provides the summary and recommendations, and Section 7 lists the references cited in the report.

1.2 Quality Assurance

The PNNL Quality Assurance (QA) Program is based upon the requirements as defined in DOE Order 414.1D, “Quality Assurance” and 10 CFR 830, “Nuclear Safety Management”, Subpart A – “Quality Assurance Requirements.” The processes necessary to implement the requirements are documented through PNNL’s “How Do I?” (HDI) standards-based management system.

The work outlined in this report was performed in accordance with PNNL’s Quality Management System Description and associated Quality Assurance Program Description (QAPD), which are maintained electronically as part of the HDI system. Details of this project’s approach to assuring quality are contained in the PNNL QA plan for the EMSP. This alternative immobilization process test was conducted in accordance with QA-EMSP-1101, *Scientific Investigation for Basic Research*. The chemical analyses required as part of laboratory experiments and testing in this report were conducted in PNNL analytical laboratories. The Environmental Sciences Laboratory at PNNL operates under QA plans in compliance with *Hanford Analytical Services Quality Assurance Requirements Documents* (DOE/RL-96-68). Chemical analyses of these testing samples and materials were conducted under the respective analytical laboratory QA plans. All the data used in this report were reviewed by an independent technical reviewer for internal verification and validation.

2.0 Cast Stone Description and Preparation

Cast Stone specimens prepared in the laboratory for several purposes, including previous Cast Stone for WTP secondary waste (Pierce et al. 2010; Um et al. 2011), LAW Cast Stone, and new smaller monoliths made with one LAW simulant but two dry blend mixtures referred to as NW- and SE-Cast Stones with high Tc concentration were used for this Tc speciation characterization testing. Cast Stone is a low-temperature waste form that consists of a mixture of 47 wt% blast furnace slag (BFS), 45 wt% fly ash, and 8 wt% ordinary Type I/II Portland cement. A detailed description of simulant information and Cast Stone preparation follows.

2.1 Waste Simulants

The liquid secondary-waste simulant composition was developed based on Hanford Tank Waste Operations Simulator (HTWOS) flowsheet modeling. Table 2.1 shows the four LAW simulants used for the LAW Cast Stone formulation as well as the simulant used in the Phase I testing of WTP secondary waste Cast Stone (Pierce et al. 2010; Um et al. 2011). The Na concentration of 2 M was used for WTP secondary waste Phase I simulant. More information and details of the secondary waste simulant preparation can be also found in Pierce et al. (2010) and Sundaram et al. (2011).

The LAW simulants consist of four chemical simulants, including a saltcake simulant used in previous testing of LAW immobilization technologies and three chemical simulants based on the HTWOS flowsheet modeling results of the LAW feed that is anticipated to be sent to a supplemental immobilization facility. A detailed description of the LAW simulant development work is provided in Russell et al. (2013). Saltcake is a predominant form of wastes in a large fraction of the single-shell tanks (SSTs) at the Hanford Site. The saltcake LAW simulant was developed based on a blend of real tank waste samples from SSTs S-101, S-110, S-111, U-106, and U-109 (Rassat et al. 2003). The first of the three LAW chemical simulants based on the HTWOS modeling is an overall average of the 1046 weeks of modeled waste feed over a 20-year mission. The second LAW chemical simulant is a high-Al, high-Cl simulant corresponding to 235 weeks in the HTWOS flowsheet simulation. The third LAW chemical simulant is a high-SO_4 simulant because sulfate and fluoride are at relatively high concentrations and phosphate is near its maximum. The Na concentrations of 5 M and 7.8 M were also selected to represent a range of possible LAW waste concentrations for processing. For comparison, the simulants in Table 2.1 have been normalized to 1 M Na and are expressed as moles/liter per mole Na.

In addition to the main components of the LAW simulant, the simulants used to make Cast Stone were spiked with hazardous chemicals and/or radionuclides of interest, mostly Tc, I and /or U (Table 2.1).

Table 2.1. Composition of Waste Simulants

Waste Constituents	**WTP Secondary Waste-Phase I (Pierce et al. 2010;Um et al. 2011)**	**SST Blend(a) Saltcake (Rassat et al. 2003)**	**HTWOS(a) Overall Average**	**HTWOS High Al(a)**	**HTWOS High SO_4(a)**
	Concentration (moles/liter per mole Na)				
Na	1.000	1.000	1.000	1.000	1.000
K	-	0.002	0.007	0.028	-
Al	0.115	0.013	0.061	0.112	0.047
Cl	-	0.009	0.008	0.018	0.007
F	-	0.006	0.006(b)	0.010	0.012(b)
SO_4	4.85E-03	0.018	0.017	0.004	0.030
PO_4	0.85E-02	0.010	0.010(b)	0.005	0.010(b)
NO_2	-	0.085	0.113	0.194	0.098
NO_3	0.345	0.502	0.324	0.287	0.367
CO_3	0.750E-06	0.095	0.055	0.040	0.035
TOC(c) Total	0.115	0.057	0.015	0.021	0.007
Free OH	0.600	0.097	0.312	0.293	0.306
RCRA Metals and Radionuclides	**WTP Secondary Waste-Phase I (Pierce et al. 2010;Um et al. 2011)**	**SST Blend(a) Saltcake (Rassat et al. 2003)**	**HTWOS(a) Overall Average**	**HTWOS(a) High Al**	**HTWOS(a) High SO_4**
	Concentration (moles/liter per mole Na)				
Ag	1.25E-04	-	-	-	-
Cd	2.50E-05	2.78E−06	2.78E−06	2.78E−06	2.78E−06
Cr	4.22E-03	2.42E−03	2.42E−03	2.42E−03	2.42E−03
Pb	3.95E-04	1.16E−05	1.16E−05	1.16E−05	1.16E−05
Ni	-	6.41E−05	6.41E−05	6.41E−05	6.41E−05
Hg	1.65E-05	-	-	-	-
Radionuclides	Ci/liter per mole Na (or µg/liter per mole Na)				
^{99}Tc	0.65E-05 (Ci/liter per mole Na)	1.13E−05 (Ci/liter per mole Na)	1.13E−05 (Ci/liter per mole Na)	1.13E−05 (Ci/liter per mole Na)	1.13E−05 (Ci/liter per mole Na)
^{99}Tc	-	(6.65E+02 µg/liter per mole Na)	(6.65E+02 µg/liter per mole Na)	(6.65E+02 µg/liter per mole Na)	(6.65E+02 µg/liter per mole Na)
^{129}I	-	1.44E−08 (Ci/liter per mole Na)	1.44E−08 (Ci/liter per mole Na)	1.44E−08 (Ci/liter per mole Na)	1.44E−08 (Ci/liter per mole Na)
^{127}I (stable)[d]	1.45E-06 (mole/liter per mole Na)	(8.14E+01 µg/liter per mole Na)	(8.14E+01 µg/liter per mole Na)	(8.14E+01 µg/liter per mole Na)	(8.14E+01 µg/liter per mole Na)
$^{232+233+234+235+236+238}$U	-	1.59E−08 (Ci/liter per mole Na)	1.59E−08 (Ci/liter per mole Na)	1.59E−08 (Ci/liter per mole Na)	1.59E−08 (Ci/liter per mole Na)

(a) After charge balancing.

(b) Concentration of F and PO_4^{3-} reduced from HTWOS values because of solids formation observed in preliminary simulants.

(c) TOC = total organic carbon.

(d) Stable iodide (^{127}I) was spiked into the simulants instead of using ^{129}I that is in the real wastes.

2.2 Cast Stone Preparation

Cast Stone specimens used in this Tc speciation characterization test include previous WTP secondary waste Cast Stone (Um et al. 2011), LAW Cast Stone, and a new smaller monolith LAW NW- and SE-Cast Stone with high Tc concentration (~150 µg/g).

For making secondary waste Cast Stone monoliths, the Portland cement (Type I/II) and Grade-120 BFS were obtained from LaFarge North America, Inc. (Herndon, Virginia), and the Class F fly ash was obtained from Lonestar (Seattle, Washington). The dry materials were blended for 5 minutes with a planetary mixer set at low speed. After the dry-solid mixture was homogeneous, the Tc-spiked Phase I simulant was added to the blended dry mixtures and mixed for 5 minutes to obtain a homogeneous slurry that could flow easily. Even though three different Tc concentrations (i.e., 100, 200, and 300 µg-Tc/g of the final solid form) were prepared for previous WTP secondary waste Cast Stone monoliths (Um et al. 2011), only one 200 µg-Tc/g of secondary waste Cast Stone was used in this Tc speciation characterization. A Tc stock solution with a concentration of ~10,000 ppm was prepared with $NaTcO_4$ as the Tc source. The waste loading was approximately 8 wt% on a dry-weight basis of final Cast Stone and the ratio of free water to dry solids mix was 0.4. Smaller-sized Cast Stone monoliths were cast in molds that were 1 inch in diameter by 2 inches high (2.5 cm by 5 cm). The molds were initially partially filled in the vertical orientation and vibrated until a significant decrease in the release of air bubbles was observed. Then, the molds were filled to capacity with additional wet slurry and vibrated until no air bubbles were observed. The molds were stored in a 100% relative humidity chamber at room temperature for a curing time of 28 days. More details on the Cast Stone used in WTP secondary waste Phases I and II are found in Pierce et al. (2010) and Um et al. (2011), respectively.

Two sources of BFS and fly ash materials were used as part of the dry ingredients for LAW Cast Stone preparation. One type of BFS and the high-Ca fly ash were obtained from LaFarge North America, Inc., in Pasco, Washington, and these materials are referred to as the NW slag and fly ash. The second BFS and the low-Ca fly ash are the same materials used in the Saltstone processing facility at the Savannah River Site in South Carolina. The product used for the second source of BFS is granulated BFS obtained from Holcim (US), Inc., in Waltham, Maine, and this product is referred to as the SE slag. The low-Ca fly ash was a thermally beneficiated Class F fly ash obtained from South Carolina Electric & Gas through the SEFA Group in Lexington, South Carolina; this product is referred to as SE fly ash. A single source of Portland cement (Type I/II) from the Pacific Northwest was used in the dry blend mixes. Prior to making the LAW Cast Stone monoliths, the dry materials were premixed and the ratios of 0.4 and 0.6 for the free water to dry solids mix were used to make LAW Cast Stones. The Cast Stone specimens were prepared by mixing aliquots of the simulant batches and the dry blend mixes. The beaker containing the simulant was placed under the overhead mixer. A Caframo model BDC1850 overhead mixer with a 3.5-in. (8.75 cm) outer diameter elliptical impeller was used to mix the simulants and blend the Cast Stone mixture. More details can be found in the LAW Cast Stone Screening Tests report (Westsik et al. 2013). After approximately 1 minute of agitation, the premixed dry materials were added to the beaker over a time period of 4.5 to 7 minutes with agitation. The wet slurry was continuously stirred for a total of 15 minutes from the start of addition of the dry blend, and the slurry material was poured into 2-in. × 4-in. (5 cm × 10 cm) plastic mold forms. The forms were agitated to release any potential entrained air and capped with a perforated lid to cure for 28 days before using. The components for LAW Cast Stone samples used in this test are identified in Table 2.2.

New LAW Cast Stone smaller monoliths with high Tc concentration (~150 µg-Tc/g) were prepared using Portland cement (Type I/II) with both the NW and SE dry materials (slag and fly ash). Both BFS and fly ash are the same materials as used for previously prepared LAW Cast Stone. The new Cast Stone monoliths were prepared using LAW 7.8 M Na HTWOS "overall average" simulant (see Table 2.1 for simulant information) with water-to-solids ratio of 0.5. The mixed LAW NW- and SE-Cast Stone slurries were poured into 0.404 in. × 0.808 in. (1.01 cm × 2.02 cm) plastic cylinders and cured for 28 days under 100% relative humidity before use.

Table 2.2. LAW Cast Stone Preparation

Sample #	**Simulant**	**Sodium Molarity**	**Portland Cement**	**Fly Ash Class F**	**Blast Furnace Slag**	**Water-to-Dry-Blend Solids Ratio**
1 (T1)	High SO_4	5.0	Type I/II	SE Low Ca	NW	0.40
2 (T2)	Average	5.0	Type I/II	SE Low Ca	SE	0.60
3 (T3)	Average	7.8	Type I/II	NW High Ca	SE	0.60
4 (T4)	High Al	5.0	Type I/II	NW High Ca	SE	0.40
5 (T5)	Average	7.8	Type I/II	NW High Ca	NW	0.40
6 (T6)	Average	7.8	Type I/II	SE Low Ca	NW	0.40
7 (T7)	High SO_4	7.8	Type I/II	SE Low Ca	SE	0.40
8 (T8)	SST Blend	5.0	Type I/II	SE Low Ca	NW	0.40
9 (T9)	Hi Al	7.8	Type I/II	NW High Ca	SE	0.60
10 (T10)	High SO_4	5.0	Type I/II	NW High Ca	NW	0.60
11 (T11)	High Al	7.8	Type I/II	SE Low Ca	NW	0.60
12 (T12)	SST Blend	5.0	Type I/II	NW High Ca	SE	0.60
13 (T13)	Average	5.0	Type I/II	SE Low Ca	SE	0.60
14 (T14)	High SO_4	7.8	Type I/II	SE Low Ca	SE	0.40
15 (T15)	High SO_4	7.8	Type I/II	NW High Ca	NW	0.40
16 (T16)	SST Blend	7.8	Type I/II	NW High Ca	NW	0.40
17 (T17)	High Al	5.0	Type I/II	SE Low Ca	SE	0.60
18 (T18)	SST Blend	7.8	Type I/II	SE Low Ca	SE	0.40
19 (T19)	High Al	7.8	Type I/II	SE Low Ca	NW	0.40
20 (T20)	Average	5.0	Type I/II	NW High Ca	SE	0.40
21 (T21)	High SO_4	7.8	Type I/II	SE Low Ca	NW	0.60
22 (T22)	Average	7.8	Type I/II	NW High Ca	SE	0.60
23 (T23)	SST Blend	7.8	Type I/II	SE Low Ca	NW	0.60
24 (T24)	High Al	5.0	Type I/II	NW High Ca	NW	0.60
25 (T25)	High SO_4	7.8	Type I/II	NW High Ca	NW	0.40
26 (T26)	High SO_4	7.8	Type I/II	SE Low Ca	NW	0.60
LAW-NW *	Average	7.8	Type I/II	NW High Ca	NW	0.50
LAW-SE *	Average	7.8	Type I/II	SE Low Ca	SE	0.50

* New LAW Cast Stone smaller monoliths (0.404 in. × 0.808 in.) with high Tc concentration (~150 µg-Tc/g) were prepared using Portland cement (Type I/II) with the NW and SE dry materials (slag and fly ash).

3.0 Reductive Capacity Measurement

3.1 Introduction

Technetium (^{99}Tc) in Cast Stone is of greatest concern because of its high solubility and mobility of Tc(VII), pertechnetate (TcO_4^-), which is the stable form of technetium in oxic environments such as found at IDF. Previous studies have shown that Cast Stone can more effectively stabilize ^{99}Tc if it contains additives that chemically reduce mobile TcO_4^- to immobile Tc(IV) species (Allen et al. 1997; Lukens et al. 2005; Um et al. 2011). However, Tc(IV) has the potential to reoxidize rapidly to Tc(VII) upon contact with oxygen thus transforming into highly mobile pertechnetate [$Tc(VII)O_4^-$]. Therefore, developing a waste form that retains a reduced environment, which minimizes reoxidation of reduced Tc(IV) even in contact with oxygen, is the key for successful Tc immobilization in Cast Stone for long-term storage.

In the Cast Stone waste form, ferrous iron and sulfide (S^{2-}) ions in BFS are considered the major reductants capable of reducing Tc from Tc(VII) to Tc(IV) (Atkins and Glasser 1992). Dissolution of BFS at alkaline pH releases sulfide species into the cement pore fluid, predominantly as S^{2-} and possibly with a small contribution from SO_3^{2-} and $S_2O_3^{2-}$ (Atkins and Glasser 1992), which impose a strong reduction potential in Cast Stone. Therefore, measuring the reductive capacity of Cast Stone, as well as the dry ingredients and simulants used to make Cast Stone, is needed to understand the Tc release for the long-term performance of the Cast Stone in the subsurface environment similar to the IDF.

Two different measurement techniques have been used to determine the reductive capacity in anthropogenic or natural materials (Angus and Glasser 1985; Lee and Batchelor 2003). The reductive capacity is determined as the amount of an oxidant that can be reduced when sufficient time is given for the reaction to proceed to its maximum extent (Lee and Batchelor 2003). The reductive capacity measurements are based on the difference between the oxidizing equivalent in Ce(IV) or Cr(VI) solution and the reducing equivalent of Fe(II) needed to neutralize excess Ce(IV) or Cr(VI) after reaction with the specimen. Angus and Glasser (1985) measured the amount of Ce (IV) reduced by BFS and Portland cement, while Lee and Batchelor (2003) measured the amount of Cr(VI) reduction by soil minerals and sediment. In this study, both Ce(IV) and Cr(VI) methods were used to measure the reductive capacity of Cast Stones, liquid waste simulants, and individual dry ingredients (e.g., Portland cement, BFS, and fly ash). In addition, the reductive capacity of Cast Stone after leaching was also determined and compared to unleached Cast Stone of the same formulation to estimate the change of reductive capacity in the Cast Stone between the unleached and leached states.

3.2 Materials and Methods

3.2.1 Materials

Cast Stone dry ingredients including Grade-120 BFS (NW slag and SE slag), Class-F fly ash (NW fly ash and SE fly ash), and Type I/II Portland cement were used for reductive capacity measurements. The SE slag contains less alumina (6.6–8.4% vs. 12.2%), less calcium oxide (35–38.5% vs. 43.4%), less SO_3 (0.3–2.08% vs. 4.9%), but more magnesium oxide (12.9–13.1% vs. 4.9%) than the NW slag (Serne and Westsik 2011). The SE fly ash contains significantly less calcium oxide (0.6–0.7% vs. 14.1%) and much more alumina (28.6% vs. 16.1%) than the NW fly ash.

A total of eight liquid waste simulants used to make different LAW Cast Stones were also tested for reductive capacity measurements. Four different LAW chemical compositions of simulants as shown in Table 2.1 with either 5 M or 7.8 M Na concentration represent a range of possible eight LAW compositions to be solidified in the LAW Cast Stones. Included are SST Blend Saltcake and three chemical simulants of HTWOS with overall average, High Al, and High SO_4 simulants (Table 2.1).

A total of 26 unleached LAW Cast Stone specimens with no Tc spike (see Table 2.2 for details) were measured for reductive capacity. Only three LAW Cast Stone samples (T2, T6, and T22 in Table 2.2) with Tc spike (~7 µg/g Tc) and after approximately 64 days of EPA 1315 method leaching were also measured for reductive capacity to compare the change of reductive capacity in LAW Cast Stone after leaching. In addition, new smaller LAW NW- and SE-Cast Stone monoliths with high Tc concentration (~150 µg-Tc/g) were used to determine reductive capacity changes between before leaching and after the EPA 1315 method leaching.

3.2.2 Ce(IV) Method

The Ce(IV) stock solution [$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$] was prepared in 10% H_2SO_4 with a concentration of 30–60 mM depending on the reductive capacity of the specimen. Approximately 0.5 g of crushed Cast Stone, dry ingredient, or liquid simulant was mixed with 15 mL of the Ce(IV) stock solution in a 20-mL quartz vial. Immediately after mixing, the vial was tightly closed and placed on a platform shaker. The sample was reacted at room temperature for seven days. After seven days reacting, the supernatant solution was filtered through a 0.45-µm syringe filter and 0.05 mL of ferroin solution [0.025 M Fe (o-phenanthroline)$_3^{2+}$] was added to 5 mL of the filtrate. The final solution was titrated using 20 mM ammonium ferrous sulfate prepared in 4% H_2SO_4 solution until the solution developed and retained a lilac color. The reductive capacity was calculated by determining the difference between the oxidizing equivalent in Ce(IV) solution [meq Ce(IV)] and the reducing equivalent of Fe(II) needed to neutralize excess Ce(IV) after reaction with the sample [meq Fe(II)]. The final reductive capacity per gram of sample was determined by dividing the reductive capacity (meq) by the mass of sample (g).

3.2.3 Cr(VI) Method

The Cr(VI) stock solution (30–50 mM K_2CrO_4) was prepared in 10 mM $NaHCO_3$ solution. The Cr(VI) solution was purged with N_2 gas for one hour and was moved into an anoxic chamber (Coy Laboratory Products, Inc.) containing a mixed gas atmosphere (4% H_2 and 96% N_2). Approximately 0.5 g of solid powdered Cast Stone, dry ingredient, or liquid simulant sample was placed in a 20-mL quartz vial and then the vial was introduced into the anoxic chamber. The sample vials and Cr(VI) stock solution were kept in the anoxic chamber for two days with lids off to remove atmospheric air present in the sample vials and Cr(VI) stock solution before use. After the 2-day air-purging period in the H_2/N_2 atmosphere, 10 mL of the Cr(VI) stock solution was added into the sample vial and the pH of the suspension was adjusted to 7±1 by adding a few drops of 1 M NaOH or 1 M H_2SO_4 solution. After closing the vials tightly, the vials were moved from the anoxic chamber to a platform shaker, and the samples were reacted at room temperature for seven days. After the 7-day reaction, the vials were moved to the anoxic chamber again, and 0.142 g of sodium sulfate was added into the vials. The vials were removed from the anoxic chamber and placed on the platform shaker for one more day in order to remove any potentially adsorbed Cr(VI) from the materials before the final supernatant was filtered through a 0.45-µm syringe filter. One mL of the filtrate was mixed with 1 mL of 10% H_2SO_4 solution (1:1 ratio in volume), and 0.05 mL of ferroin solution was added. The solution was titrated with 20 mM ammonium ferrous sulfate solution prepared in 4% H_2SO_4 solution until the solution became and remained lilac in color. The final reductive capacity per gram of sample was determined by dividing the reducing equivalent (meq) by the mass of sample (g).

3.3 Results and Discussion

3.3.1 Reductive capacity of dry ingredients

The measured reductive capacity results for the dry ingredients using both the Ce(IV) and Cr(VI) methods are given in Table 3.1. The reductive capacities of BFS measured by the Ce(IV) method were 0.793 meq/g and 0.800 meq/g for NW slag and SE slag, respectively. This result is consistent with previously reported reductive capacity results for BFS by the Ce(IV) method (Kaplan et al. 2005; Um et al. 2011). Um et al. (2011) reported that the reductive capacity of NW slag measured by the Ce(IV) method was 0.799 meq/g, while the reductive capacity of SE slag measured by the Ce(IV) method ranges from 0.817 to 0.832 meq/g by others (Kaplan et al. 2005; Lukens et al. 2005; Kaplan et al. 2008; Roberts and Kaplan 2009). The reductive capacity of fly ash determined by the Ce(IV) method was higher for SE fly ash, at 0.288 meq/g, than for NW fly ash, at 0.060 meq/g (Table 3.1). The reductive capacities of fly ash measured in this study are in agreement with previously reported reductive capacities, which are 0.299 meq/g for SE fly ash (Roberts and Kaplan 2009) and 0.077 meq/g for NW fly ash (Um et al. 2011). Portland cement showed the lowest reductive capacity of 0.042 meq/g by the Ce(IV) method. This is also comparable to the reductive capacity (0.079 meq/g) of Portland cement reported by Um et al. (2011), but is lower than the reductive capacity (0.198 meq/g) of Portland cement reported by Roberts and Kaplan (2009). Among the dry ingredients used to make the Cast Stone, the BFS showed significantly higher reductive capacity than the Portland cement (a calcium silicate mineral phase) and the fly ash because BFS contains both Fe^{2+} and various forms of sulfides (e.g., CaS) (Roy 2009), which are major chemical reductants.

Table 3.1. Reductive Capacity (meq/g) of Dry Ingredients Measured by the Ce(IV) and Cr(VI) Methods

Dry Ingredient	Reductive Capacity by Ce(IV) (meq/g)	Reductive Capacity by Cr(VI) (meq/g)
NW slag	0.793	0.078
SE slag	0.800	0.226
NW fly ash	0.060	0.007
SE fly ash	0.288	0.000
Portland Cement (Type I/II)	0.042	0.349

The reductive capacities of dry ingredients measured by the Cr(VI) method were lower than those measured by the Ce(IV) method except that of Portland cement (Table 3.1). The reductive capacity of BFS determined by the Cr(VI) method was 0.078 meq/g for NW slag and 0.226 meq/g for SE slag. The reductive capacity of fly ash measured by the Cr(VI) method was negligible for both NW fly ash and SE fly ash. Um et al. (2011) also reported that the reductive capacity of NW slag was significantly lower when it was measured by the Cr(VI) method than by the Ce(IV) method. The lower reductive capacity measured by the Cr(VI) method was attributed to different pH conditions between the two methods (Um et al. 2011). The Ce(IV) method uses 10% sulfuric acid, and thus the Ce(IV) method can measure almost total reductive capacity of the solid samples because most of the solids dissolve in the strong acid. In contrast, because the Cr(VI) method uses 10 mM $NaHCO_3$ solution and the solution pH should be adjusted to around 7 before reductive capacity measurement, the Cr(VI) method can measure only the surface (or readily available) reductive capacity of the solid samples. Moreover, the solution pH could have increased to alkaline pH during the 7-day reaction even after the pH was adjusted to ~7, because the pH could have been buffered to ~8–10 by the BFS and cement samples. The Cr(VI) reductive capacity measurement method has been reported to be less efficient and slower at alkaline pH (Eary and Rai 1988; Zouboulis et al. 1995; Graham and Bouwer 2010), which probably caused lower reductive capacity measurements for BFS compared to results using the Ce(IV) method. In addition, the reduced Cr(III) could react with Fe(III) from BFS (e.g., 0.89 wt% Fe_2O_3 for NW slag and 0.33 wt% Fe_2O_3 for SE slag) and form a passivation layer of [Fe(III) and Cr(III)] hydroxide (Richard and Bourg 1991; He and Traina 2005). This layer also could prevent further chromate, Cr(VI) reduction by BFS, which would have caused relatively lower reductive capacity. On the other hand, the reductive capacity of Portland cement measured by the Cr(VI) method was 0.349 meq/g, which was an order of magnitude higher than the reductive capacity measured by the Ce(IV) method. This high reductive capacity of Portland cement determined by the Cr(VI) method could result from the coprecipitation of Cr(VI) with $CaCO_3$ formed at alkaline pH during the 7-day reaction with Portland cement powder (Hua et al. 2007; Tang et al. 2007), not from the reduction of Cr(VI) to Cr(III) only. A previous study also reported that Cr-bearing phases such as $CaCrO_4$ and $CaCrO_4 \cdot 2H_2O$ were formed at alkaline pH (10.5–12.2) during the reaction of Portland cement with high-Cr-concentration solution (15,000–50,000 mg/L) (Laforest and Duchesne 2005), suggesting that the high reductive capacity of Portland cement determined by the Cr(VI) method could be overestimated by the precipitation of Cr-bearing phases. A previously reported reductive capacity of Portland cement measured by the Cr(VI) method was 0.035 meq/g (Um et al. 2011) which is lower than the 0.349 meq/g in this study. However, the difference in the measured reductive capacities of Portland cement might result from varying Ca contents even in the same Portland cement samples.

Both the Ce(IV) and Cr(VI) methods showed that BFS possesses the highest reductive capacity of the dry ingredients used for Cast Stone preparation. A major source of sulfide in BFS is CaS phase (Oldhamite), in which the sulfide can reduce Tc(VII) and react to form a stable Tc(IV) sulfide compound (TcS_x) (Allen et al. 1997; Lukens et al. 2005; Fan et al. 2013). Therefore, both the Ce(IV) and Cr(VI) methods were attempted to determine the reductive capacity of calcium sulfide (CaS) that was purchased from Sigma-Aldrich. Before using the purchased CaS, an x-ray diffraction analysis was conducted and the CaS was identified as crystalline Oldhamite (Figure 3.1). Although only ~0.1 g of CaS was reacted with 50 mM of Ce(IV) or Cr(VI) stock solution, the Ce(IV) and Cr(VI) were completely reduced to Ce(III) and Cr(III), respectively. This suggests that CaS phase present in BFS has a reduction capacity much higher than others, consistent with BFS being the main contributing source to the reductive capacity in Cast Stone. Therefore, the measured reductive capacities of CaS using smaller amount of ~0.02 mg were 18.16 meq/g and 39.22 meq/g for Ce(IV) and Cr(VI) method, respectively. Higher reductive capacity of CaS measured by Cr(VI) method than Ce(IV) is also considered to overestimate due to $CaCrO_4$ and $CaCrO_4 \cdot 2H_2O$ precipitates as described above for Portland cement by Cr(VI) method.

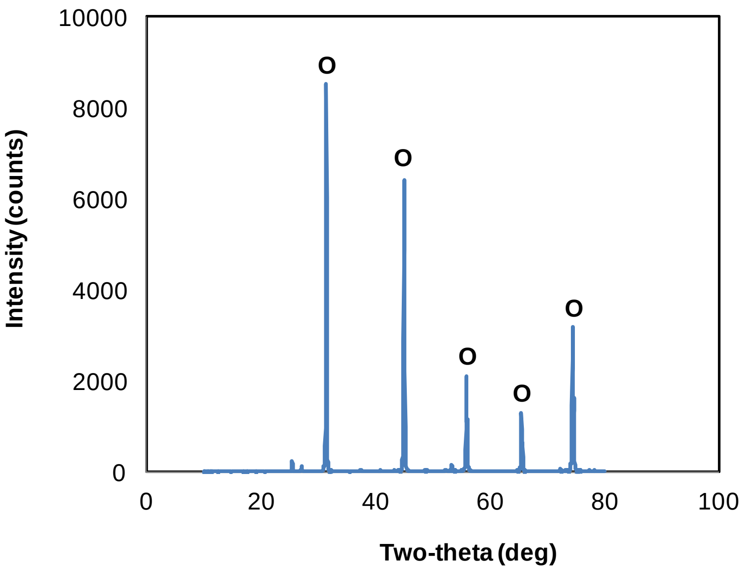


Figure 3.1. X-Ray Diffraction Patterns of CaS. The Letter O Represents the Standard Peaks for Oldhamite (CaS)

3.3.2. Reductive Capacity of Simulants

Reductive capacities of various LAW simulants at a constant Na concentration measured by both the Ce(IV) and Cr(VI) methods were very similar. Both the Ce(IV) and Cr(VI) methods indicate that the reductive capacities of simulants were the highest for “High Al” simulant, followed by “Average” simulant, “High SO_4” simulant, and “SST Blend (Saltcake)” simulant, whether the Na concentration was 5 M or 7.8 M (Table 3.2). The reductive capacity was consistently higher for 7.8 M Na simulants (1.025-2.146 meq/g) than for 5 M Na simulants (0.727–1.507 meq/g) (Figure 3.2). This is attributed to a higher concentration of NO_2^- added in 7.8 M Na simulants than the nitrite present in 5 M Na simulants. The average reductive capacities of eight simulants measured by both the Ce(IV) and Cr(VI) methods showed a good correlation (correlation coefficient, $R^2 = 0.99$ in Figure 3.3) with the concentrations of NO_2^- in simulants ranging from 0.085 to 0.194 mole-NO_2/mole Na. However, nitrate (NO_3^-), a potential oxidizing agent also present in simulants, showed no correlation with reductive capacity values measured for those simulants by either the Ce(IV) or Cr(VI) methods, while nitrite is considered to be a major contributor in simulant as a reductant (Figure 3.3). This suggests that Ce(IV) or Cr(VI) was reduced to Ce(III) or Cr(III) by NO_2^- in simulants during the 7-day reaction with simulants according to the following reactions:

$$Cr_2O_7^{2-} + 7NO_2^- = 2Cr^{3+} + 7NO_3^- \qquad (3\text{-}1)$$

$$Ce^{4+} + NO_2^- + H_2O = Ce^{3+} + NO_3^- + 2H^+ \qquad (3\text{-}2)$$

Table 3.2. Reductive Capacity (meq/g) of LAW Simulants Measured by the Ce(IV) and Cr(VI) Methods

Simulants	Composition	Reductive Capacity by Ce(IV) (meq/g)	Reductive Capacity by Cr(VI) (meq/g)
S1	5 M Na Average	0.871	0.943
S2	5 M Na High SO$_4$	0.752	0.817
S3	5 M Na High Al	1.516	1.507
S4	5 M Na SST Blend	0.681	0.727
S5	7.8 M Na Average	1.279	1.296
S6	7.8 M Na High SO$_4$	1.121	1.134
S7	7.8 M Na High Al	2.207	2.146
S8	7.8 M Na SST Blend	0.930	1.025

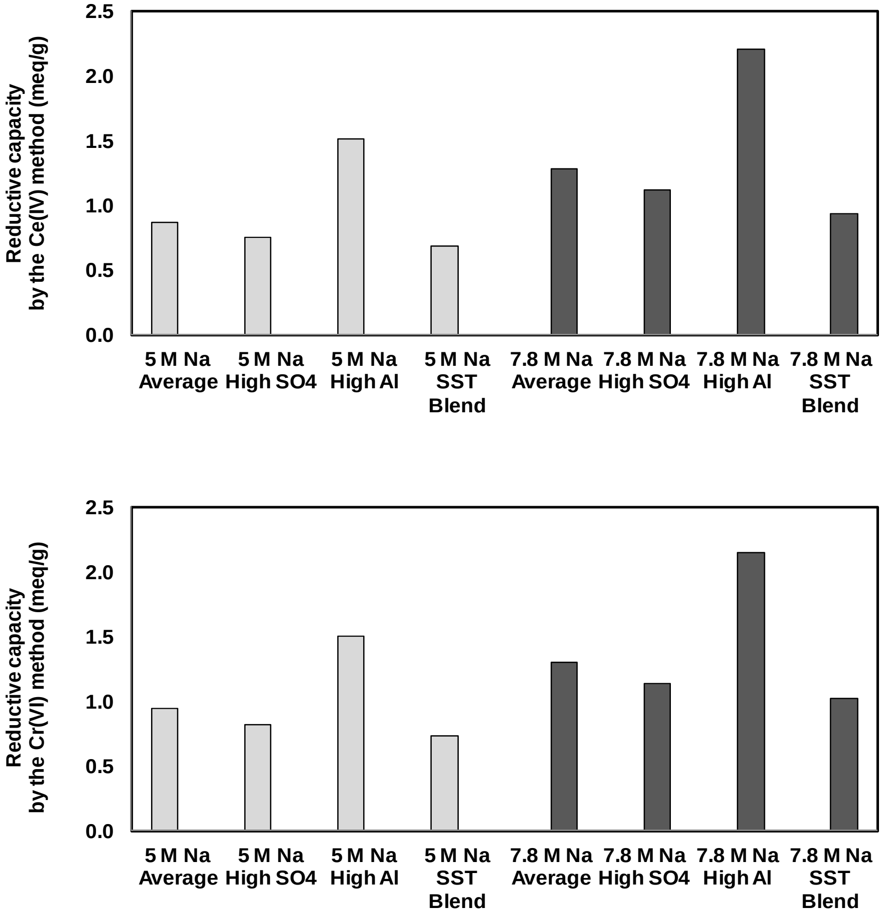


Figure 3.2. Reductive Capacity of Eight Different Liquid Waste Simulants with 5 M and 7.8 M Na Concentrations

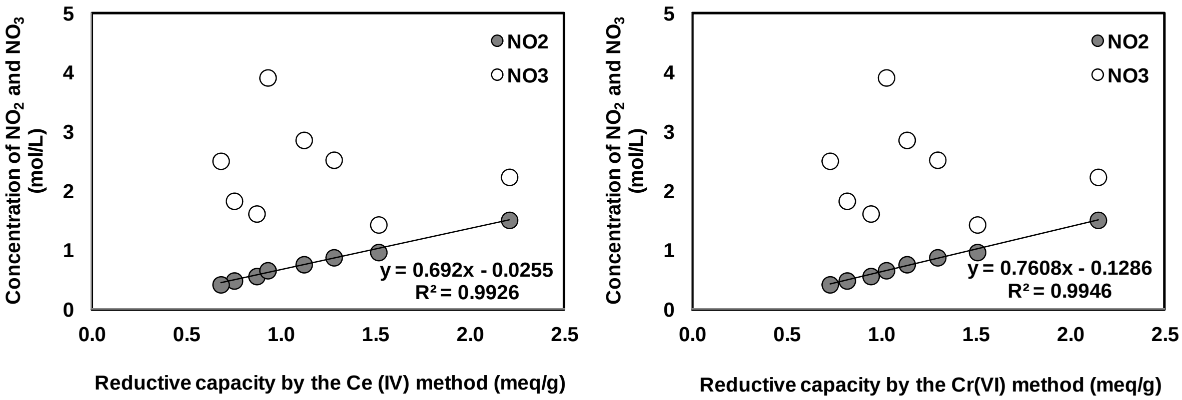


Figure 3.3. Relationship Between Average Reductive Capacity of Eight Different Simulants Measured by the Ce(IV) and Cr(VI) Methods and the Concentrations of NO_2^- and NO_3^- in Simulants

3.3.3. Reductive Capacity of Cast Stone Before Leaching

The reductive capacities of LAW Cast Stone samples measured before leaching using the Ce(IV) and Cr(VI) methods were also in good agreement, with $R^2 = 0.91$ (Table 3.3 and Figure 3.4). Generally, the reductive capacity measured by the Ce(IV) method was slightly higher than that by the Cr(VI) method. This could also be attributed to the different pH conditions between the Ce(IV) and Cr(VI) methods as mentioned in Section 3.3.1. The Ce(IV) method can measure nearly all the reductive capacity of the solid materials under an acidic pH condition because most of the solids dissolve, while the Cr(VI) method is likely to measure only the reductive capacity of the solids' surface and any internal surfaces that the oxidant can reach in the available contact time at neutral pH or alkaline pH due to pH buffering during the reaction with powdered Cast Stone. That is little of the solid's mass dissolves during the Cr(VI) reduction capacity measurement.

The reductive capacity measured by the Ce(IV) method was the highest for the Cast Stone made with "High Al" simulant, which was on average 1.040 meq/g for 5 M Na Cast Stone and 1.390 meq/g for 7.8 M Na Cast Stone (Figure 3.5). Higher reductive capacity was also found in the 7.8 M Na than in 5 M Na simulants because of the higher nitrite concentration added in the 7.8 M Na simulant. Cast Stone samples made with the "Average" simulant showed the second highest reductive capacity (0.609 meq/g for 5 M Na and 0.763 meq/g for 7.8 M Na), followed by the Cast Stones made with the "High SO_4" simulant (0.578 meq/g for 5 M Na and 0.667 meq/g for 7.8 M Na), and the "SST Blend" simulant (0.575 meq/g for 5 M Na and 0.659 meq/g for 7.8 M Na). The reductive capacity measured by the Cr(VI) method exhibited the same pattern, with the highest reduction capacity for the "High Al" Cast Stone, followed by the "Average" Cast Stone, the "High SO_4" Cast Stone, and the "SST Blend" Cast Stone (Figure 3.5). The reductive capacities of Cast Stone samples measured by both the Ce(IV) and Cr(VI) methods thus show a good correlation ($R^2 = 0.96$) with the reductive capacities of simulants measured by the Ce(IV) or Cr(VI) method (Figure 3.6).

Table 3.3. Reductive Capacity (meq/g) of Cast Stones Measured by the Ce(IV) and Cr(VI) Methods

Cast Stone	Composition	Na (mol/L)	Fly Ash	Slag	Water-to-Dry Blend Solids Ratio	Reductive Capacity by Ce(IV) (meq/g)	Reductive Capacity by Cr(VI) (meq/g)
T1	High SO_4	5.0	SE	NW	0.4	0.591	0.554
T2*	Average	5.0	SE	SE	0.6	0.672	0.646
T3	Average	7.8	NW	SE	0.6	0.784	0.847
T4	High Al	5.0	NW	SE	0.4	1.470	1.389
T5	Average	7.8	NW	NW	0.4	0.699	0.726
T6*	Average	7.8	SE	NW	0.4	0.750	0.686
T7	High SO_4	7.8	SE	SE	0.4	0.693	0.685
T8	SST Blend	5.0	SE	NW	0.4	0.603	0.404
T9	High Al	7.8	NW	SE	0.6	1.449	1.346
T10	High SO_4	5.0	NW	NW	0.6	0.565	0.545
T11	High Al	7.8	SE	NW	0.6	1.490	1.330
T12	SST Blend	5.0	NW	SE	0.6	0.546	0.583
T13	Average	5.0	SE	SE	0.6	0.612	0.606
T14	High SO_4	7.8	SE	SE	0.4	0.663	0.664
T15	High SO_4	7.8	NW	NW	0.4	0.601	0.705
T16	SST Blend	7.8	NW	NW	0.4	0.578	0.667
T17	High Al	5.0	SE	SE	0.6	0.841	0.766
T18	SST Blend	7.8	SE	SE	0.4	0.678	0.482
T19	High Al	7.8	SE	NW	0.4	1.231	1.007
T20	Average	5.0	NW	SE	0.4	0.541	0.443
T21	High SO_4	7.8	SE	NW	0.6	0.702	0.686
T22*	Average	7.8	NW	SE	0.6	0.819	0.837
T23	SST Blend	7.8	SE	NW	0.6	0.720	0.606
T24	High Al	5.0	NW	NW	0.6	0.810	0.929
T25	High SO_4	7.8	NW	NW	0.4	0.614	0.645
T26	High SO_4	7.8	SE	NW	0.6	0.732	0.808

* Cast Stones of T2, T6, and T22 were also tested for reductive capacity after leaching.

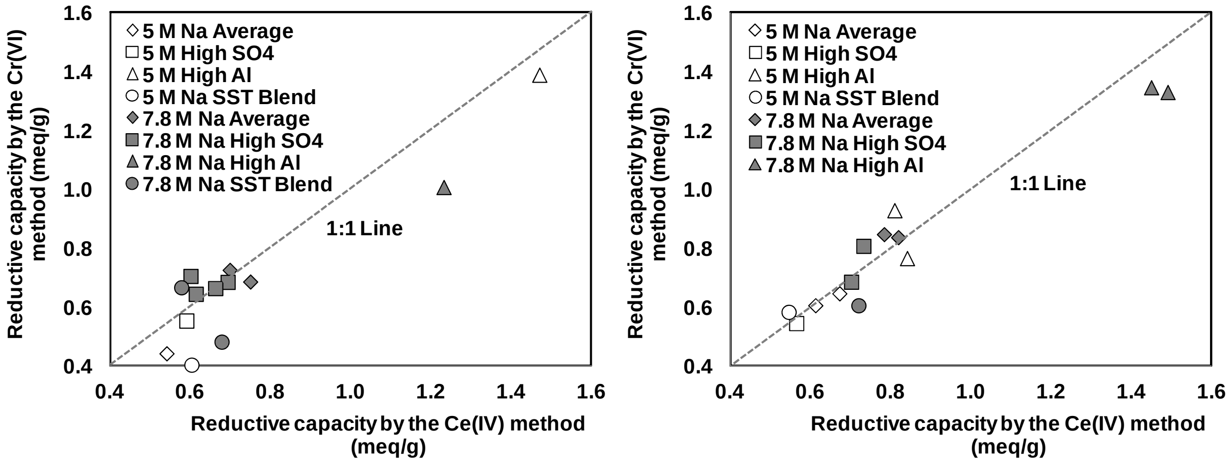
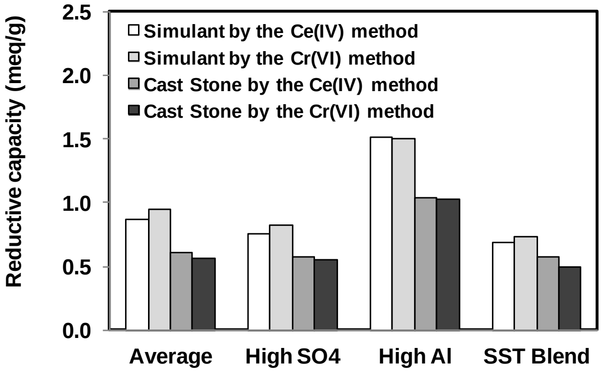
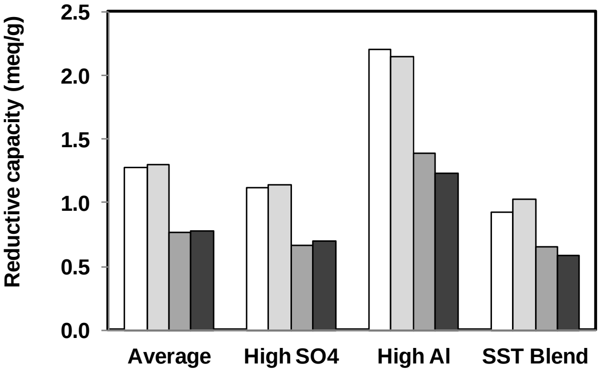


Figure 3.4. Comparison Between Reductive Capacities of LAW Cast Stones Before Leaching Measured by the Ce(IV) Method and the Cr(VI) Method. Cast Stone Water to Dry Blend Ratio of 0.4 (Left) and 0.6 (Right).



5 M Na cast stone composition



7.8 M Na cast stone composition

Figure 3.5. Reductive Capacities of Simulants and Cast Stone Samples Prepared with 5 M Na Simulants (top) and 7.8 M Na Simulants (bottom)

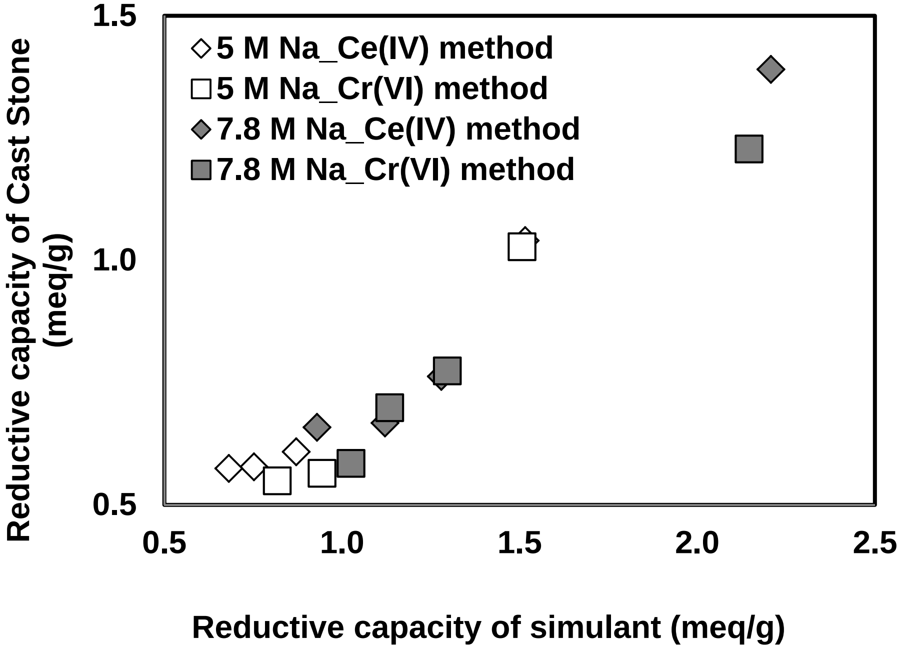


Figure 3.6. Relationship Between the Reductive Capacity of Simulants Measured by the Cr(VI) Method and the Reductive Capacity of Cast Stones Measured by the Ce(IV) and Cr(VI) Methods

Based on the reductive capacities of individual dry ingredients (47% BFS, 45% fly ash, and 8% Portland cement) determined by the Ce(IV) method, the reductive capacity of Cast Stone was predicted to range from 0.403 meq/g to 0.509 meq/g if the dry ingredients were the only sources for reductive capacity on the basis of individual dry ingredient wt% used for Cast Stone preparation. However, the measured reductive capacity by the Ce(IV) or Cr(VI) method was slightly higher, by a factor of ~1.5–3, than these predicted reductive capacity values. This suggests that a significant fraction of the reductive capacity of Cast Stone samples is contributed by simulant in addition to dry ingredients because the ratios of water to dry blend for the preparation of Cast Stones are 0.4–0.6 (Table 3.3). As the reductive capacity of simulants is proportional to the concentration of NO_2^- (Figure 3.3), dissolved NO_2^- in the simulant that is mixed with dry ingredients to make a Cast Stone is also a dominant component in determining the total reductive capacity of Cast Stones. The increasing reductive capacity of Cast Stones with higher concentration of NO_2^- in simulants has been also reported by Um et al. (2011). Um et al. (2001) found that as the Na concentration in secondary waste simulants that were used to make Cast Stones increased from 2 M to 10 M, the reductive capacity of the cured Cast Stones increased systematically from 0.399 meq/g to 0.596 meq/g. This was also attributed to the NO_2^- concentration increasing from 0.024 M to 0.120 M with increasing Na concentration in simulants from 2 M to 10 M.

The source of BFS (i.e., NW or SE) seems to have only a minor effect on the reductive capacity of Cast Stones because the measured reductive capacity is similar for NW slag (0.793 meq/g) and SE slag (0.800 meq/g). When the reductive capacities of Cast Stones prepared with the same types of simulant and BFS are compared, the Cast Stones made with SE fly ash generally show higher reductive capacity by ~0.03–0.15 meq/g compared to the Cast Stones made with NW fly ash (Table 3.3) probably because the reductive capacity is higher for SE fly ash (0.288 meq/g by the Ce(IV) method) than for NW fly ash (0.060 meq/g by the Ce(IV) method).

In summary, the concentration of NO_2^- in simulants plays an important role in determining the reductive capacity of Cast Stones. However, the reduction potential of the NO_3^-/NO_2^- redox couple at pH = 14 (~0.01 V) is relatively weak compared to the $TcO_4^-/TcO_2{\bullet}2H_2O$ redox couple (~ -0.36 V) (Lukens et al. 2005) so that most of the initially oxidized Tc(VII) species spiked in simulants seems to remain as oxidized species, TcO_4^-. Although the measured reductive capacity of BFS is lower than the reductive capacity of most of the LAW simulants measured by either the Ce(IV) or Cr(VI) method, aqueous ferrous iron and sulfide ions are slowly released from BFS as the Cast Stone is cured and aged. These two species are likely the major reductants in Cast Stone that effectively reduce Tc(VII) to Tc(IV) because they are the stronger reducing agents (e.g., reduction potentials of SO_4^{2-}/SO_3^{2-}, SO_4^{2-}/S^{2-}, SO_3^{2-}/S^{2-}, and Fe^{3+}/Fe^{2+} redox couples are ~ -0.5 to -0.93 V at pH = 13–14) than the NO_3^-/NO_2^- redox couple

3.3.4. Reductive Capacity of Cast Stone After Leaching

The reductive capacities of LAW Cast Stone samples (samples T2, T6, and T22) all with ~7 µg-Tc/g of cured Cast Stone, see details in Table 3.3, that had been previously leached by the EPA 1315 method leach test for 63 days were measured using both the Ce(IV) and Cr(VI) methods. In addition, newly prepared high-Tc LAW NW- and SE-Cast Stone samples containing (~150 µg/g Tc) before and after leaching about 64 days were also measured for reductive capacities by both the Ce(IV) and Cr(VI) methods. After subjecting Cast Stone to the EPA 1315 method leach test for ~60 days, the reductive capacities of Cast Stones decreased in compared to those of Cast Stone before leaching (Table 3.4).

The reductive capacities of LAW Cast Stones that were leached for 63 days measured by the Ce(IV) method decreased from 0.672 meq/g to 0.467 meq/g for T2 (5 M Na average), from 0.750 meq/g to 0.442 meq/g for T6 (7.8 M Na average), and 0.819 meq/g to 0.374 meq/g for T22 (7.8 M Na average) (Table 3.4). The measurements by the Cr(VI) method also showed a consistent decrease, as much as approximately 62%, in reductive capacity of LAW Cast Stones after leaching (Table 3.4). The reductive capacities of LAW Cast Stones T2, T6, and T22 measured by the Cr(VI) method decreased from 0.646 meq/g, 0.686 meq/g, and 0.837 meq/g to 0.354 meq/g, 0.363 meq/g, and 0.315 meq/g, respectively. The reductive capacity of high-Tc LAW NW- and SE-Cast Stones also decreased after 64 days of leaching by the EPA 1315 method. While the reductive capacity measured by the Ce(IV) method was 0.602 meq/g for NW-Cast Stone and 0.731 meq/g for SE-Cast Stone before leaching, it decreased to 0.171–0.211 meq/g for NW-Cast Stone and 0.241–0.262 meq/g for SE-Cast Stone after leaching, depending on the various leaching conditions (Table 3.4). The reductive capacity measurements by the Cr(VI) method also exhibited a consistent decrease in reductive capacity from 0.735 meq/g to 0.131-0.156 meq/g for NW-Cast Stone and from 0.752 meq/g to 0.163–0.210 meq/g for SE-Cast Stone, respectively. The decrease in the measured reductive capacity of Cast Stones by both the Ce(IV) and Cr(VI) methods after leaching is attributed to the consumption of reductive capacity (e.g., BFS and NO_2^-) in Cast Stone by O_2 during the leaching period (63–64 days). Assuming that the decrease in reductive capacity is caused solely by O_2 diffusion into Cast Stone and there is a 50% decrease in the reductive capacity of Cast Stone after 10^6-second (or 11.6-day) leaching, the thickness of the oxidized layer after leaching will be approximately 1414.2 times to the thickness of the oxidized layer at t=0 based on the following equation modified from a shrinking core model (Smith and Walton, 1993; Lukens et al. 2005):

$$d = \sqrt{\frac{8C_{O2}tD_{m(O2)}}{N_m C_{red}}} \tag{3-3}$$

where d = the thickness of the oxidized layer [cm], t = leaching time [s], C_{O2} is the concentration of O_2 in water [$2.7\text{x}10^{-7}$ mol/cm^3], $D_{m(O2)}$ is the diffusion coefficient of O_2 in water [$2.0\text{x}10^{-5}$ cm^2/s], C_{red} is the concentration of reducing equivalents in the Cast Stone sample [mol/cm^3=reductive capacity of sample divided by sample density], and N_m is the MacMullin number of O_2 in water defined as the tortuosity of porous sample divided by the porosity of sample ranging from 300 to 11800 [-] (Lukens et al. 2005).

However, the relative impact of the oxidized layer thickness on the volume of the waste from that becomes oxidized can be limited by the size of cementitious waste form. The larger the size of the waste form the smaller the overall impact of the oxidation front thickness, because of a lower surface area to volume ratio of large waste forms and the longer pathway for O_2 diffusion.

Table 3.4. Reductive Capacity (meq/g) of Cast Stone Samples Containing Tc Before and After the EPA 1315 Method Leach Test

Samples	Leaching Conditions	Reductive Capacity by Ce(IV) (meq/g)	Reductive Capacity by Cr(VI) (meq/g)
Before Leaching			
T2 (LAW with ~7 µg/g Tc)	—	0.672	0.646
T6 (LAW with ~7 µg/g Tc)	—	0.750	0.686
T22 (LAW with ~7 µg/g Tc)	—	0.819	0.837
NW-Cast Stone (150 µg/g Tc)	—	0.602	0.735
SE-Cast Stone (150 µg/g Tc)	—	0.731	0.752
After Leaching*			
T2 (LAW with ~7 µg/g Tc)	air equilibrated	0.467	0.354
T6 (LAW with ~7 µg/g Tc)	air equilibrated	0.442	0.363
T22 (LAW with ~7 µg/g Tc)	air equilibrated	0.374	0.315
NW-Cast Stone (150 µg/g Tc)	air equilibrated	0.211	0.156
	O_2 saturated	0.194	0.178
	fractured and O_2saturated	0.171	0.131
SE-Cast Stone (150 µg/g Tc)	air equilibrated	0.260	0.210
	O_2 saturated	0.261	0.190
	fractured and O_2 saturated	0.241	0.163

*Air-equilibrated leaching condition indicates the traditional EPA 1315 method leach testing condition where the leaching container with DI water leaching solution was prepared open to the atmosphere. Oxygen-saturated leaching condition was prepared by saturating the DI water leaching solution with O_2 by pure O_2 gas sparging. See Section 4.2.2 and Figure 4.6 for details.

Different leaching conditions affected the reductive capacity change in Cast Stone samples after leaching. For both NW- and SE-Cast Stones, the reductive capacity decreased most significantly when the Cast Stone was fractured and leached under oxygen-saturated conditions (Table 3.4). This leaching condition was prepared to simulate leaching Cast Stone with cracks and fractures after long-term disposal. For the NW-Cast Stones without fractures, the measured reductive capacity by the Ce(IV) method after leaching under the O_2-saturated condition (0.194 meq/g) was slightly lower than that of samples leached under the air-equilibrated conditions (0.211 meq/g) that exist in the EPA 1315 method leach test. However, the reductive capacity measurements by the Cr(VI) method showed slightly higher reductive capacity in the NW-Cast Stone even after leaching under the O_2-saturated condition (0.178 meq/g) than under the air-equilibrated condition (0.156 meq/g). In contrast, the reductive capacity of SE-Cast Stones measured by the Ce(IV) method was similar whether they were leached under the air-equilibrated condition (0.260 meq/g) or the O_2-saturated condition (0.261 meq/g), while it was higher for the air-equilibrated condition (0.210 meq/g) than for the O_2-saturated condition (0.190 meq/g) when measured by Cr(VI) method. There was only a minor difference in the measured reductive capacities of both NW- and SE-Cast Stones after leaching between air-equilibrated and O_2-saturated leaching conditions because the elevated oxygen content in the O_2-saturated condition was higher only in the early stage of leaching intervals, right after the leaching solution was replaced by freshly O_2-saturated leaching deionized (DI) water. Since O_2-saturated leaching solution was not continuously replenished by O_2 gas sparging during the leaching periods, O_2 content even in O_2-saturated leaching solution became similar to O_2 content in air-equilibrated leaching solution after 7 days leaching (See Section 4.0 for O_2 content changes in O_2-saturated leaching solution with reaction times). In general, however, both NW- and SE-Cast Stones showed noticeable decreases in the measured reductive capacity after leaching under air-equilibrated and O_2-saturated leaching conditions. Also after leaching, the SE-Cast Stones showed slightly higher reductive capacities than the NW-Cast Stones, consistent with the higher reductive capacities of SE BFS and fly ash than NW ingredients.

3.4 Conclusions

The reductive capacities of dry ingredients (e.g., BFS, fly ash, and Portland cement), LAW simulants, and Cast Stones before and after leaching were measured using both the Ce(IV) and Cr(VI) methods. Among the dry ingredients, the reductive capacity measured by the Ce(IV) method was the highest for BFS (0.793 meq/g for NW slag and 0.800 meq/g for SE slag). The reductive capacities measured by the Ce(IV) method were 0.060 meq/g for NW fly ash and 0.288 meq/g for SE fly ash, while the reductive capacity of Portland cement was negligible at 0.042 meq/g based on the Ce(IV) method. Among the Cast Stone dry ingredients, the BFS is a main contributing source to the reductive capacity of Cast Stone because of Fe^{2+} and various forms of sulfides (e.g., CaS), which are strong reductants in the BFS. The reductive capacity of BFS measured by the Cr(VI) method was 0.078 meq/g for NW slag and 0.226 meq/g for SE slag, which were lower than the reductive capacities of NW slag and SE slag measured by the Ce(IV) method. Differences in the reductive capacities measured by these two methods are attributed to different pH conditions used for the Ce(IV) and Cr(VI) methods. The Ce(IV) method can measure nearly all the reductive capacity of the solid samples because significant portions dissolve under the highly acidic pH condition in H_2SO_4 solution, while the Cr(VI) method is likely to measure only the reductive capacity of the solids' surface and near-surface open porosity under the neutral to slightly alkaline pH conditions. Moreover, the reduction of Cr(VI) in the Cr(VI) method could be less efficient and slower when the solution pH is buffered to alkaline pH by reaction with the BFS sample. In contrast, the reductive capacity of Portland cement measured by the Cr(VI) method was an order of magnitude higher than that measured by the Ce(IV) method. This result could be attributed to the precipitation of Cr-bearing phases or coprecipitation of Cr(VI) with $CaCO_3$ formed at alkaline pH during the reaction with Portland cement powder with the bicarbonate buffer solution used in the Cr(VI) method (Hua et al. 2007; Tang et al. 2007). The removal of Cr(VI) by such precipitation mechanism, rather than the "pure" reduction of Cr(VI) to Cr(III), results in overestimated reductive capacity. This suggests more careful interpretation of the measurement is required when the Cr(VI) method is used for reductive capacity measurement of alkaline solid samples.

The reductive capacity measurements of liquid waste simulants by both Ce(IV) and Cr(VI) methods showed the highest reductive capacity for "High Al" simulant, followed by "Average" simulant, "High

SO_4" simulant, and "SST Blend" simulant, whether the Na concentration was 5 M or 7.8 M. Higher reductive capacity was also found in 7.8 M Na simulants (1.025–2.146 meq/g) than in 5 M Na simulants (0.727–1.507 meq/g) due to the higher concentration of NO_2^- added in 7.8 M Na simulants than added in 5 M Na simulants. The reductive capacity of simulants was strongly correlated with the concentrations of NO_2^-, which ranged from 0.085 to 0.194 mole-NO_2/mole Na in simulants. The measured reductive capacities of cured Cast Stones were similar for both the Ce(IV) and Cr(VI) methods. The reductive capacities of Cast Stones were the highest for the "High Al" Cast Stone, followed by the "Average" Cast Stone, the "High SO_4" Cast Stone, and the "SST Blend" Cast Stone, which is similar to the trend of decreasing reductive capacities in these simulants. Cast Stones made with 7.8 M Na simulant consistently showed higher reductive capacity than Cast Stones made with 5 M Na simulants. This indicates that NO_2^- in simulants exerts a dominant role in determining the reductive capacity of Cast Stones. However, because of the weak reduction potential for the NO_3^-/NO_2^- redox couple, the presence of aqueous S^{2-} and Fe^{2+} species from slowly dissolving BFS in the Cast Stone can effectively reduce Tc(VII) to Tc(IV) and control Tc speciation in hardened Cast Stone waste form.

The reductive capacity of LAW Cast Stone, both those prepared previously (see Westsik et al. 2013) and newly prepared LAW NW- and SE-Cast Stones with high Tc concentration that had been leached using the EPA 1315 leach test of Cast Stone under air-equilibrated or O_2-saturated leaching conditions decreased by ~30–70% after leaching compared to the same Cast Stones before leaching. The reductive capacity of both NW- and SE-Cast Stones decreased most significantly when they were fractured and leached under an O_2-saturated condition because of the increased exposed surface areas from the fractures. The results suggest that it is important to prevent the formation of fractures in Cast Stones, since O_2 can diffuse faster through the fractures (or cracks) and facilitate reoxidation and remobilization of Tc.

4.0 Additional EPA 1315 Method Leach Tests with Varying Oxygen Contents and High Tc Concentration

4.1 Introduction

The leachability or diffusivity of Tc from Cast Stone is one of the criteria used to evaluate long-term performance of Cast Stone in the IDF at the Hanford Site. Previous testing conducted by PNNL (Um et al. 2011) and reductive capacity measurements previously described in Section 3 have proved that some of Tc(VII) present in the liquid waste simulants could be reduced to the Tc(IV) species in the cured Cast Stone, because the BFS serves as the key reductant. The mobility or leachability of Tc in Cast Stone is expected to be significantly lower when present as the reduced state Tc(IV) compared to the oxidized state Tc(VII). However, over time, Cast Stone that is buried in the IDF will encounter weathering conditions similar to being partially open to the atmosphere which contains 20% oxygen and partially in contact with oxygen from infiltrating vadose zone pore water. Thus oxygen is expected to penetrate into Cast Stone through pores and/or cracks, which increases reoxidation of Tc(IV) to the more mobile Tc(VII) species and results in a subsequent increase of Tc release into the environment. Because Tc leachability from Cast Stone is closely related to the Tc speciation and oxidation state change, additional understanding of Tc leachability in the Cast Stone under different leaching conditions is necessary to estimate Tc retention and release mechanisms in the final long-term performance of Cast Stone in the IDF disposal environment.

In this subtask, the effects of oxygen on Tc leaching from various Cast Stones were investigated by leaching new LAW NW- and SE-Cast Stone small intact and fractured monoliths using the EPA 1315 leach test with varied O_2 contents at room temperature (20°C). In addition, following the Phase II secondary waste form testing program, secondary waste Cast Stone prepared with a Phase I secondary waste simulant (See Table 2.1) and high Tc concentration (~200 µg-Tc/g) was also tested for Tc leaching using the EPA 1315 leach test for 90 days. Through the EPA 1315 test procedure, the leachability and diffusivity of Tc from the Cast Stones were determined as a function of oxygen exposure. In addition, the leached Cast Stone samples were tested for Tc oxidation state change (Section 5) and reductive capacity change (Section 2) by comparing the measured values with the same data collected from unleached Cast Stone. More details for Tc oxidation state and speciation changes before and after leaching using a spectroscopic method are described in Section 5, XAFS spectroscopy for Tc oxidation state changes.

4.2 Materials and Methods

4.2.1 Materials

Both NW- and SE-Cast Stone mini-monoliths (0.404 in. × 0.808 in. or 1.03 cm diameter by 2.05 cm height) were prepared and used for this additional Tc leaching subtask. As mentioned in Sections 2 and 3, two different sources of BFS and fly ash materials, referred to as NW-fly ash/slag or SE-fly ash/slag, and a single source of Portland cement (Type I/II) from the Pacific Northwest were used as the dry ingredients to prepare the NW- and SE-Cast Stone with a dry blend recipe of 8% cement, 45% flay ash, and 47% slag. The thoroughly mixed homogeneous dry blends were mixed with the 7.8 M Na overall average simulant at a water-to-solid ratio of 0.5 (See Table 2.1 for simulant information). In addition, an artificially fractured Cast Stone monolith, (sliced vertically into two equal halves using a tile saw in the absence of water and put back together with a string), was used to simulate a cracked Cast Stone with increased surface area that is subjected to enhanced oxygen contact in O_2-saturated DI water for the EPA 1315 method leach test (Figure 4.1).

The WTP secondary waste Cast Stone monolith was 1 inch in diameter by 2 inches high (2.5 cm by 5.0 cm) and the dry blend was Portland cement (Type I/II) and Grade-120 BFS obtained from LaFarge North America, Inc. (Herndon, Virginia) and Class F fly ash from Lonestar (Seattle, Washington) in the standard ratio of 8:47:45 by weight. The dry blend was mixed for 5 minutes with a planetary mixer set at low speed. After the dry-solid mixture was homogeneous, the Tc-spiked Phase I secondary waste simulant was added to the blended dry mixture at a free-water-to-dry-solids mix ratio of 0.4 and mixed for 5 minutes to obtain a homogeneous slurry. The homogeneous slurry was placed in plastic molds and cured for 28 days at room temperature in a 100% relative humidity chamber. Even though three different high-Tc concentrations (i.e., 100, 200, and 300 μg-Tc/g of the Cast Stone) were prepared for previous WTP secondary waste Cast Stone monoliths (Um et al. 2011), only one 200 μg-Tc/g of secondary waste Cast Stone was used this time. More details on the Cast Stone used in WTP secondary waste Phase II are found in Um et al. (2011).

Figure 4.1. The Cast Stone Monoliths Without and With Fracture (left), Leaching Vessels of 125 mL Poly Bottles (middle), and Preparation of O_2-Saturated Leaching Solution by Pure O_2(g) Bubbling Used for the EPA 1315 Method Leach Test (right)

4.2.2 EPA Method 1315

The EPA 1315 method is a 63-day semi-dynamic leach test that consists of submerging a monolithic sample in DI water at a fixed liquid volume-to-solid surface area ratio and sampling at fixed periods of leaching time (EPA 2013). The cumulative leaching time may be extended beyond the standard 63 days. All the leachate data for the various sampling times are then used to calculate diffusivity values. The geometric surface area used in this EPA 1315 method is calculated based on the cylindrical dimensions of the monolith sample. At each of predetermined leaching intervals (nine in the standard 63-day test protocol), the sample mass is recorded, and the leaching solution is changed. This method is similar to American National Standards Institute/American Nuclear Society (ANSI/ANS)-16.1, but the leaching intervals in the EPA 1315 method are modified, and the process of mass transfer can be interpreted by more complex release models.

The cylindrical Cast Stone monoliths were placed into the center of a leaching vessel hung from a nylon string and leached in DI water with varied O_2 contents. A solution-to-monolith surface area ratio of 9±1 cm (mL of leachant-to-cm^2 of Cast Stone monolith) is held constant during each leaching interval.

Including both small LAW NW- and SE-Cast Stone monoliths and the one Phase II secondary waste Cast Stone monolith, a total of seven monolith samples were used for this Tc leaching subtask. After the leachate sampling at the 28-day interval, slices about 4–9 mm thick were cut from one end of all the small LAW NW- and SE-Cast Stone monoliths for preparation of samples for XAFS analysis to determine the change in Tc oxidation state after leaching. After cutting, the remaining main portions of the NW- and SE-Cast Stone monoliths were returned to the leaching vessels for continued leaching. The new monolith dimension was recalculated based on the monolith weight change and known density; the DI water leachant volume (~60 mL) was adjusted correspondingly to meet a fixed solution-to-monolith surface area ratio of 9 ±1 mL/cm^2. The one WTP secondary waste Cast Stone monolith (~200 µg-Tc/g) had been leached for 90 days and then stored about three years in air before being used to prepare an XAFS sample. Details on these Tc leaching experiments are given in Table 4.1.

Table 4.1. EPA 1315 Method Leach Test Conditions with Various Cast Stone Monoliths

Cast Stone Leaching Conditions	Monolith Weight [(a)] (g)	Monolith Height [(a,b)] (cm)	DI Water Volume [(a)] (mL)	O_2 Content in DI Water (mg/L)	Ratio of solution to surface area (mL/cm^2)
NW-air	2.67/2.24	2.08/1.74	70.7/62	9.8	8.7
NW-O_2	2.83/2.30	2.21/1.79	70.7/60	30.8	8.3
NW-O_2-fracture	2.45/1.41	2.19/1.26	70.7/47	30.8	9.0
SE-air	2.80/2.32	2.03/1.68	70.7/61	9.8	8.9
SE-O_2	2.92/2.42	2.12/1.76	70.7/61	30.8	8.6
SE-O_2-fracture	2.40/1.93	2.00/1.60	70.7/60	30.8	9.8
WTP secondary waste	32.0	5.0	455	9.8	8.9

(a) The numbers after "/" indicate the new dimensions for the NW- and SE-Cast Stone monoliths after the cut for XAFS sample preparation at the 28-day leaching interval.
(b) The monolith height was measured and confirmed by calculation using monolith weight and the cured monolith wet densities of 1.63 and 1.75 g/cm^3 for NW- and SE-Cast Stone monoliths, respectively; the Cast Stone monolith dry density (1.22 and 1.35 g/cm^3 for NW- and SE-Cast Stone monoliths, respectively) was also determined after 24 hours of oven drying at 105°C and used for Tc diffusivity calculation as well.

Between each sampling and leaching solution replacement interval, each leaching test vessel was covered by a lid and sealed with tape to minimize the O_2 (g) exchange between the inside and outside of the leaching vessel. Photos of the leaching vessels and the O_2 gas bubbling system in DI water leaching solutions are shown in Figure 4.1. The leaching intervals used for the Tc leaching experiments were 2 hours and 1, 2, 7, 14, 28, 42, 49, 63, and 90 days for the WTP secondary waste Cast Stone monolith, while the leaching intervals for new LAW Cast Stone monoliths prepared with NW and SE dry ingredients were 1, 2, 7, 14, 28, and 64 days. Two different O_2 contents in DI water leaching solutions were prepared and used as the different leaching solutions: (1) air-equilibrated DI water without additional O_2 saturation treatment, which has a measured O_2 concentration of 9.8 mg/L at ~20°C under 1 atm; this measured O_2 concentration is quite close to the reported value of 9.1 mg/L in "the Engineering Tool Box";[1] (2) additionally pure O_2-sparged DI water solution was prepared by bubbling the DI water for 15 minutes using pure O_2 gas inflow in the leaching vessels, resulting in an average O_2

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[1] http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html.

concentration of ~31 mg/L in the O_2-saturated DI water leaching solution.[1] The dissolved O_2 concentration in the DI water leaching solution was continuously monitored by a Golden Scientific Fiber Optic Oxygen Sensor D0400. A constant O_2 content (~31 mg/L) could be obtained after O_2(g) sparging at least for 15–20 minutes in either 60 or 71 mL DI water leaching solution using the current bubbling treatment protocol (Figure 4.2). At each leaching collection interval, a new O_2-saturated DI water leaching solution was prepared and used as the leaching solution without continuous O_2 bubbling for each leaching interval. The blue line in Figure 4.2 shows the O_2 content (~9.1–9.8 mg/L) in DI water leaching solution without additional O_2-saturation treatment.

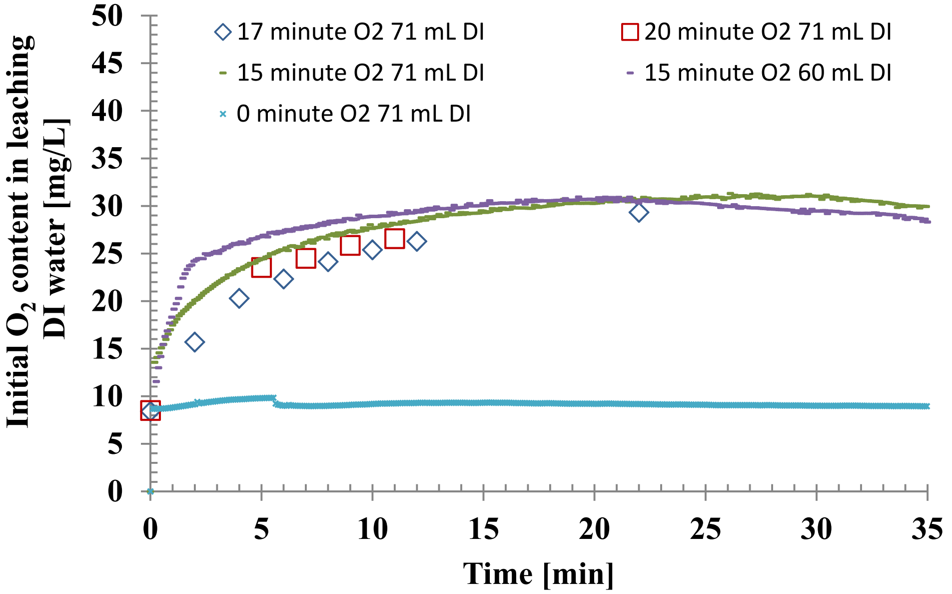

Figure 4.2. The Constant Initial O_2 Content (~31 mg/L) in 60–71 mL DI Water Leaching Solutions After 15–20 Minutes with Additional O_2(g)-Saturation Treatment. The blue curve represents the O_2 content in DI water leaching solution without additional O_2-saturation treatment.

Leachate samples collected at each leaching interval were analyzed for pH and the released Tc concentration. The leachates were filtered with a 0.45-µm syringe filter before chemical analyses. The pH of the solution samples was measured using a solid-state pH electrode and a pH meter (Hanna, Model HI 4521). Before measurement, the pH probe was calibrated with National Institute of Standards and Technology (NIST)-traceable buffers (pH = 10.0 and 12.0 at 21°C). The precision of the pH measurement was ±0.1 pH units. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the concentration of Tc in solution samples. These measurements were performed following the PNNL-AGG-415 method (PNNL 1998), which is similar to EPA Method 6020 (EPA 2000). To determine the Tc concentration in the cured Cast Stone monolith, microwave-assisted strong-acid digestion was conducted using 0.05 g of ground monolith materials. The composition of the strong acid was 16 M HNO_3 (~17 wt%), 12 M HCl (7 wt%), 32 M HF (3.3 wt%), and DI water (72.7%). The digestion was performed at 210°C for 60 minutes using a MARSXpress microwave unit. About 0.5 g of

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[1] The water solubility of pure oxygen at 20°C and 1 atm is ~44 mg/L from http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html

H_3BO_3 was also added to the acid leachate at the end of the digestion to neutralize residual HF before the analysis for total Tc concentration.

The observed diffusivity of Tc was calculated for each leach interval using the analytical solution, Equation (4.1), for simple radial diffusion from a cylinder into an infinite bath as presented by Crank (1986).

$$D_i = \pi \left[\frac{M_{t_i}}{2\rho C_o \left(\sqrt{t_i} - \sqrt{t_{i-1}} \right)} \right]^2 \tag{4.1}$$

where D_i = observed diffusivity of the constituent for leaching interval i (m^2/s)
M_{ti} = mass 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 leachable content (mg/kg)
ρ = sample density (kg/m^3).

The mean observed diffusivity for Tc can be determined by taking the average of the diffusivities observed for each interval. A leachability index (LI) for each leach interval can then be calculated as the negative logarithm of the observed diffusivity in cm^2/s as shown in Equation (4.2). A low diffusivity means a larger LI according to Equation (4.2). The average LI is then calculated using all the individual interval LI values and often used in performance assessment predictions.

$$LI = -\log\left(\frac{D_{effective}}{cm^2 s}\right) \text{ and } LI_{(\text{average})} = \frac{\sum_{i=1}^{n} LI_i}{n} \tag{4.2}$$

4.3 Results and Discussion

4.3.1 Diffusivity (or Leachability Index) of Tc in Secondary Waste Cast Stone

The Tc diffusivity coefficient for the secondary waste Cast Stone with high Tc concentration (~200 µg/g) was calculated using the EPA 1315 leach test after leaching for 90 days (Figure 4.3). Although the initial Tc concentration was much higher than those of other Cast Stones previously tested, the Tc diffusivity results in Figure 4.3 showed a trend similar to the all previous Cast Stone leaching tests, with higher Tc diffusivity observed at beginning and gradually decreasing Tc diffusivity as the cumulative leaching time increased, as reported by others (Pierce et al. 2010; Sundaram et al. 2011; Um et al. 2011). However, both the early and average Tc diffusivity values (2×10^{-9} cm^2/s vs. 4.3×10^{-10} cm^2/s) after 90 days leaching were higher than previous Cast Stones, because a relatively higher Tc initial concentration was spiked in a small volume of simulant with limited amounts of dry ingredients for preparing the smaller sized secondary waste Cast Stone monolith. As Um et al. (2011) showed before, most of the Tc still existed as oxidized Tc(VII) species in secondary waste Cast Stone even after 60 days curing time before being used for leaching, which could cause higher Tc releases in early stages of the leaching test by the surface wash-off effect (Figure 4.3). However, after 50–60 days leaching, Tc diffusivity seemed to reach a steady state, and there was no discernible increase of Tc diffusivity even after the extended 90-day leaching.

Other 90-day leachate results including pH, electrical conductivity (EC), alkalinity, and calculated LI values are also given in Table 4.2. The pH ranged from 8.0 to 11.0, and there was no noticeable increase of EC and alkalinity values measured during 90-day leaching, indicting no broken debris generated from secondary waste Cast Stone during the leaching periods.

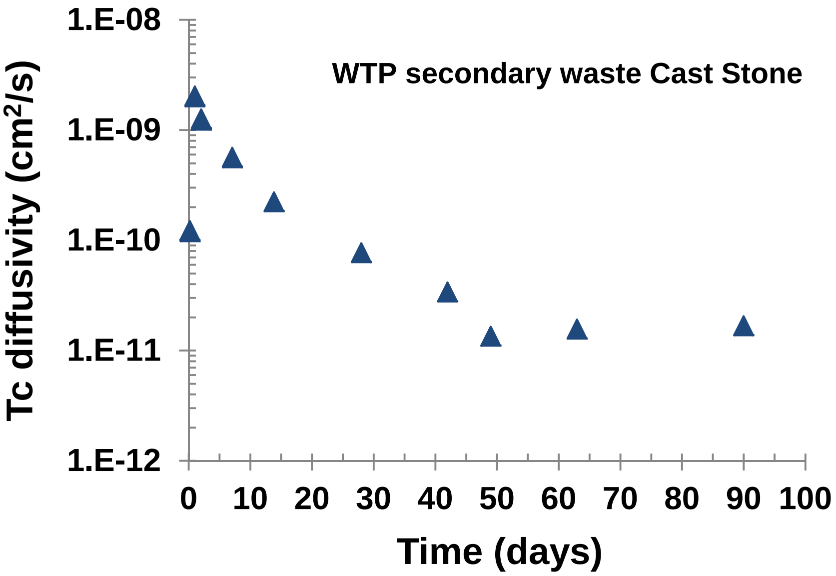

Figure 4.3. Diffusivity of Tc from Secondary Waste Cast Stone with High Tc Concentration Measured Using EPA 1315 Method Leach Test up to 90 Days Leaching

Table 4.2. Tc Diffusivity, Tc LI, pH, EC, and Alkalinity Results of Secondary Cast Stone During 90-Day Leaching Using EPA 1315 Method Leach Test

Leaching Times	Tc Diffusivity (cm^2/s)	Tc Leachability Index(LI)	pH	EC (mS/cm)	Alkalinity (mg/L as $CaCO_3$)
2 hours	1.23E-10	9.91	8.04	0.104	43.7
	1.20E-10	9.92	9.16	0.103	45.6
1 day	2.05E-09	8.69	8.30	0.161	74.1
	2.00E-09	8.70	8.48	0.163	76.7
2 days	1.27E-09	8.90	7.95	0.117	56.2
	1.23E-09	8.91	8.50	0.117	54.5
7 days	5.70E-10	9.24	9.57	0.148	69.9
	5.60E-10	9.25	9.93	0.146	69.7
14 days	2.24E-10	9.65	10.4	0.171	65.4
	2.24E-10	9.65	11.0	0.174	65.6
28 days	7.72E-11	10.1	8.41	0.178	75.6
	7.74E-11	10.1	8.38	0.178	76.0
42 days	3.39E-11	10.5	8.44	0.132	58.6
	3.42E-11	10.5	8.38	0.133	60.5
49 days	1.36E-11	10.9	9.66	0.0644	33.4
	1.35E-11	10.9	9.68	0.0636	33.2
63 days	1.57E-11	10.8	8.24	0.122	60.5
	1.56E-11	10.8	8.22	0.123	61.5
90 days	1.68E-11	10.8	9.33	0.103	42.6
	1.69E-11	10.8	9.34	0.101	44.3
Two values were obtained from duplicate measurements and analyses for each collection interval.					

4.3.2 Cumulative Tc Releases in LAW NW- and SE-Cast Stones Under Different Leaching Conditions

Cumulative Tc mass released from both NW and SE small Cast Stone monoliths for the 64-day leaching using the EPA 1315 method leach test were calculated, and the results are shown in Figure 4.4. The released Tc mass percentage based on initial Tc concentration (~150 µg-Tc/g) and the measured pH values are also listed in Table 4.3. For both the NW- and SE-Cast Stone specimens, it is clear that Tc release was higher in O_2-saturated leaching solution than in air-equilibrated DI water, indicating that a more oxidized leaching condition facilitates Tc release from the Cast Stones. For both leaching tests with O_2-saturated DI water leaching solutions, more Tc mass was released from the fractured Cast Stone than from non-fractured Cast Stone (65 µg/g compared to 35 µg/g for NW-Cast Stone and 25 µg/g compared to 12 µg/g for SE-Cast Stone). This result was attributed to larger surface area exposed to the leaching solution in the fractured Cast Stones.

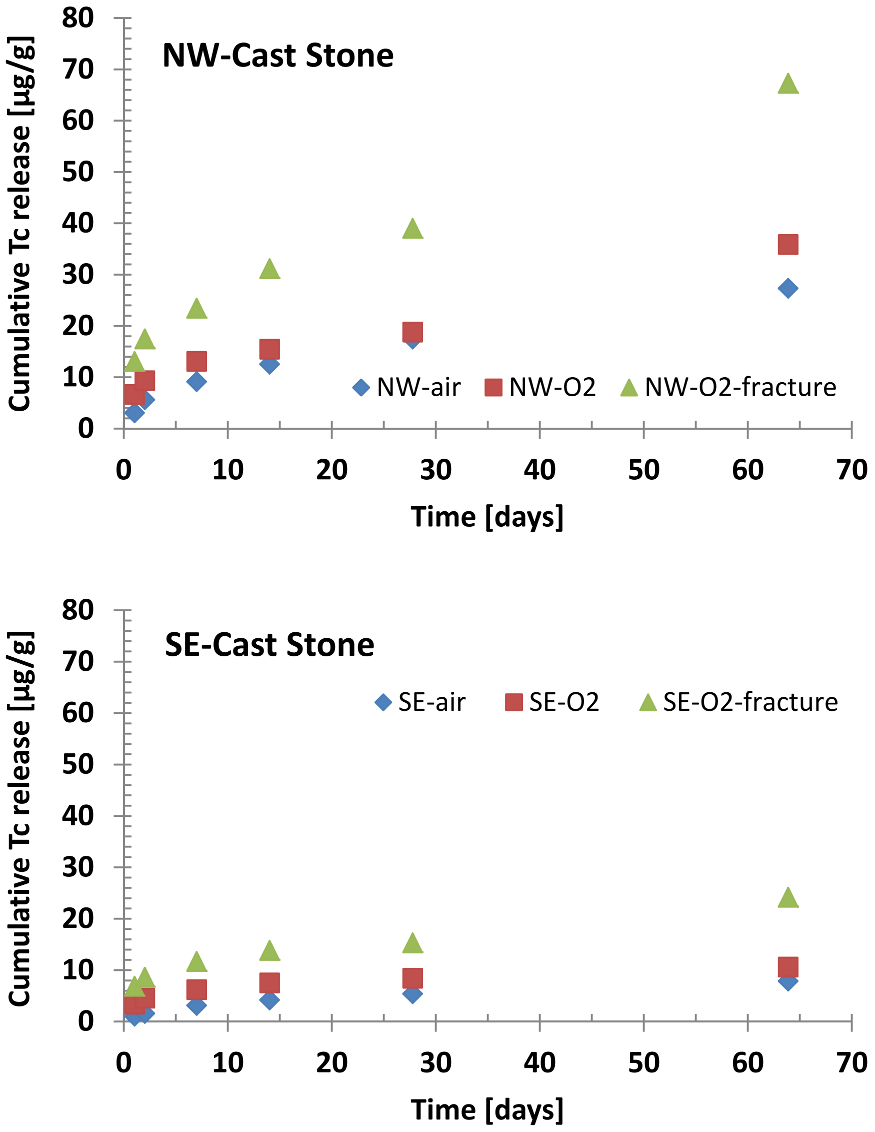

Figure 4.4. Cumulative Tc Mass Released from NW-Cast Stone (top) and SE-Cast Stone (bottom) Monoliths During 64-Day Leaching Using EPA 1315 Method Leach Tests Under Different Leaching Conditions

Between NW- and SE-Cast Stones, more Tc (by a factor of ~3) was released from the NW-Cast Stone in all leaching conditions, implying different Tc retention capacities between these two Cast Stones. The SE-Cast Stone seems to have higher Tc retention capacity than the NW-Cast Stone. In terms of the cumulative mass percentage of Tc released from Cast Stone, defined as [cumulative released Tc mass per Cast Stone monolith dry weight (µg-Tc/g) / initial leachable Tc content (C_o) in dry Cast Stone, µg-Tc/g], the released Tc mass percentages are 23.6%, 31.0%, and 58.1% for NW-Cast Stone and 6.0%, 8.1%, and 18.4% for SE-Cast Stone under the three different leaching conditions of air-equilibrated, O_2-saturated, and O_2-saturated with fractures, respectively (See Table 4.3). This result is also consistent with the measured reductive capacity results previously discussed in Section 2, where higher reductive capacity was reported for SE dry ingredients (and SE-Cast Stone) compared to NW dry ingredients (and NW-Cast

Stone). Nearly constant pH values between 11.7 and 11.8 were also observed in all leaching experiments (Table 4.3) during the entire 64-day leaching period.

Table 4.3. Average Tc Diffusivity and LI Values, pH, and Percentage of Released Tc Mass in the NW- and SE-Cast Stone Monoliths after 64 Days Leaching Using EPA 1315 Method Leach Test

Cast Stones Leaching Conditions	Tc Diffusivity (cm^2/s)	Tc LI	Tc release (%)	pH
NW-air	4.10E-10	9.4	23.6%	11.8
NW-O_2	6.64E-10	9.2	31.0%	11.8
NW-O_2-fracture	8.13E-10	9.1	58.1%	11.8
SE-air	2.40E-11	10.6	6.0%	11.7
SE-O_2	8.62E-11	10.1	8.1%	11.8
SE-O_2-fracture	1.12E-10	10.0	18.4%	11.7

4.3.3 Diffusivity (or Leachability Index) of Tc with Varying O_2 Contents

The diffusivity and LI for Tc were calculated for both NW- and SE-Cast Stone monoliths with different O_2 contents or with fractures and the results are shown in Table 4.3 as well as in Figure 4.5. The fracture surface areas were also considered in Tc diffusivity calculations. For NW-Cast Stone, the average Tc diffusivity values ranged between 4.1E-10 cm^2/s for NW-air to 8.13E-10 cm^2/s for NW-O_2-fracture, while the LI ranged from 9.4 to 9.1 correspondingly. In the case of SE-Cast Stone, the average Tc diffusivity values ranged from 2.4E-11 cm^2/s for SE-air to 1.12E-10 cm^2/s for SE-O_2-fracture, while the LI ranged from 10.6 to 10.0 correspondingly. In both Cast Stones, the highest Tc mass releases were from the fractured Cast Stone monoliths under the O_2-saturated leaching condition.

The Tc diffusivity values for the SE-Cast Stone were typically one order of magnitude lower than those calculated for NW-Cast Stone (Table 4.3). This also agrees well with the measured reductive capacity results where SE-Cast Stone shows higher reductive capacity than NW-Cast Stone, which can cause more Tc reduction and thus slow Tc release even in oxidized leaching conditions. Compared to the later collection intervals (7, 14, and 28 days leaching), much higher Tc diffusivity values were observed in the early stage of leaching (e.g., 1- and 2-day leaching intervals) for both NW- and SE-Cast Stones in all leaching conditions, except SE-Cast Stone in the air-equilibrated leaching condition. This can be also explained by the initial “surface wash-off effect” in which the release of the Tc located on or near the fresh Cast Stone monolith surfaces could be accelerated by both water and O_2 molecules. This mechanism is again confirmed by the increased Tc diffusivity values collected at the 64-day leaching interval; these were measured after returning the main parts of the Cast Stones after XAFS sample preparation at 28 days leaching. As mentioned in Section 4.2.2, a small slice from one end of the Cast Stone monoliths was cut after the 28-day leaching interval for XAFS sample preparation to determine Tc oxidation state changes, and the remaining main part of the Cast Stone monoliths were submerged again into the leaching solutions for up to 64 days. The fresh surface areas produced by removal of a slice from one end of the Cast Stone monolith also increased the Tc diffusivity at 64-day leaching intervals (Figure 4.5).

Much more Tc mass was released from the fractured Cast Stone monoliths than from the ones without fractures (see Figure 4.4), and the calculated Tc diffusivities are slightly higher in the fractured Cast Stones. This is logical because more surface area is exposed to the leaching solution in the fractured Cast Stone monoliths, resulting in increasing Tc mass release into the leaching solution. Therefore, for the Tc diffusivity calculation, the increased Tc mass release was compensated by the increased surface area of Cast Stone exposed to O_2, and the Tc mass release per surface area of Cast Stone could be constant or similar in the Cast Stones tested under these different leaching conditions.

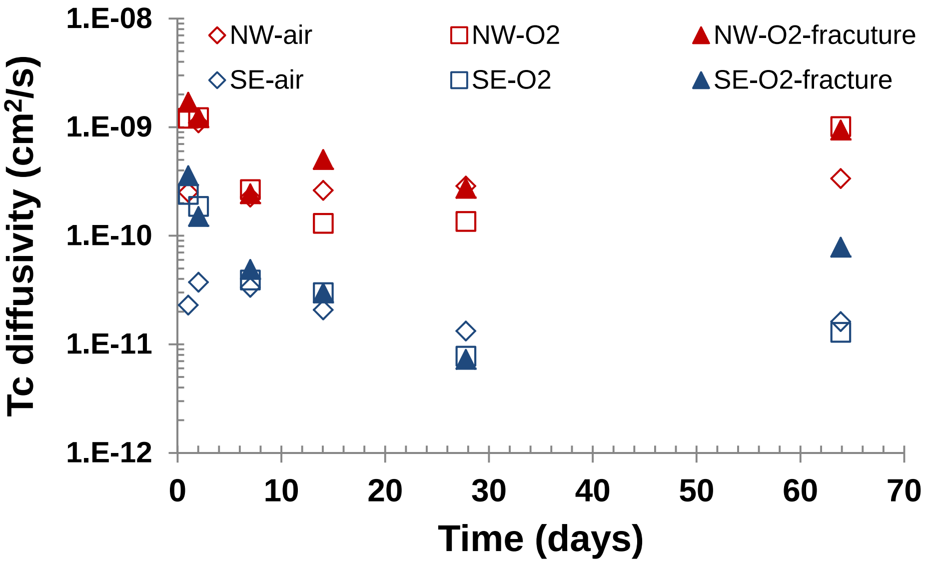

Figure 4.5. Tc Diffusivity Values Measured in LAW NW- and SE-Cast Stones Using the EPA 1315 Method Leach Test up to 64 Days Reaction

It is expected that more Tc release occurs in the leaching solutions with elevated O_2 content because initially reduced and less-mobile Tc(IV) species can be easily reoxidized to more soluble Tc(VII) species due to the enhanced O_2 diffusion into the Cast Stone monolith. For both NW- and SE-Cast Stone leaching experiments, this is absolutely true for the Tc leaching at the early stage of 1-to-7-day intervals, while the magnitude of the difference in Tc diffusivity between the air-equilibrated and O_2-saturated leaching conditions was dramatically reduced as the leach test proceeded beyond the 7-day interval. The difference ratio of the Tc diffusivity (Tc diffusivity in O_2-saturated solution divided by Tc diffusivity in air-equilibrated solution) changed from 4.8 at the 1-day interval to 1.2 at the 7-day interval for NW-Cast Stone, and from 10.5 at the 1-day interval to 1.2 at the 7-day interval for SE-Cast Stone, because of $O_2(g)$ exsolution back to the atmosphere after 5–7 days even in the prepared O_2-saturated solution. At the later collection intervals, the Tc diffusivity difference ratio became close to 1.0. When the relationship was opposite (e.g., the Tc diffusivity in air-equilibrated solution was higher than that of O_2-saturated solution at a certain collection interval) the ratio of the Tc diffusivity difference was less than 1.0 (Figure 4.5). This unexpected observation might result from the less sensitive measurement method for O_2 concentration in solution and/or any minor potential for an analytical artifact in the laboratory experiments.

Decreasing O_2 contents in solution with the increasing time in control solutions (without Cast Stone included), even in a solution prepared and tape-sealed in the same 125-mL poly bottle as was used for Cast Stone leaching, are shown in Figure 4.6. It is evident that the O_2-gas-bubbling process can elevate

O_2 content up to ~31 mg/L initially after 15–20 minute O_2 sparging in solution (Figure 4.2). However, the poly bottle used as the leaching vessel cannot maintain the elevated O_2 content in solution for long times. The initially elevated O_2 content dropped dramatically even after 1–2 days of reaction to a value of 10.7 mg/L, which is similar to the O_2 contents measured in the air-saturated leaching solution (~9.8 mg/L in Table 4.1). The elevated O_2 contents in the current leaching vessel after O_2-saturation can only hold for short leaching times (Figure 4.6), thus the oxygen content effect on the Tc leaching in Cast Stone can only be reliably observed at the short leaching intervals of 1–2 days or the first 1–2 days of each collection interval right after replacing the leaching solution with a freshly O_2-saturated DI water leaching solution at each leaching interval. The poly bottles used for Tc leaching in Cast Stones are not impermeable to $O_2(g)$ exchange, so the elevated O_2 inside the vessel could easily diffuse to the outside atmosphere through the air-permeable poly bottle materials. A better leaching vessel that is completely impermeable for gas exchange (e.g., glass) even for a long-leaching leaching intervals or a continuous O_2-bubbling system should be adopted in future experiments.

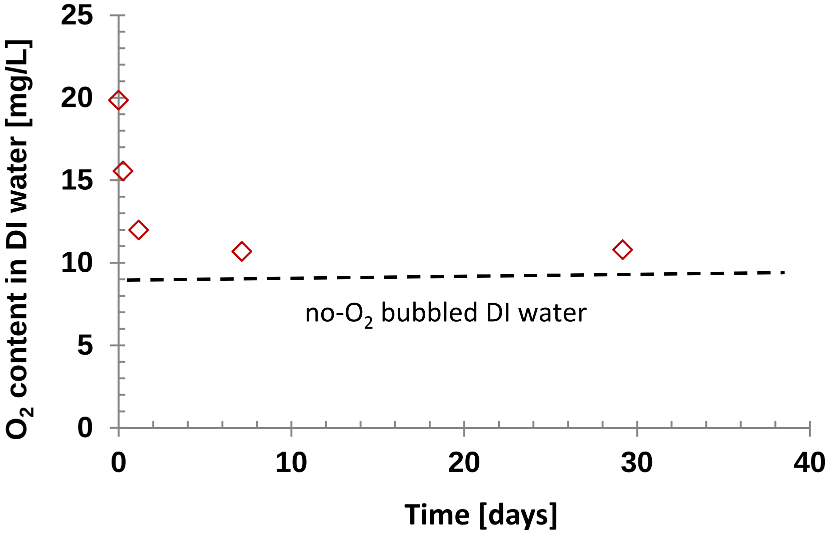

Figure 4.6. Oxygen Content Changes in O_2-Saturated DI Water Solution Over Time

4.4 Conclusions

The EPA 1315 leach test, similar to ANSI/ANS-16.1 testing, is intended here to measure the Tc diffusivity (or leachability index) as it leaches out of Cast Stone. The EPA 1315 leach test results using different Cast Stones in this study provide detailed information on the amount and release behavior of Tc in Cast Stone under various oxygen conditions. The EPA 1315 leachates collected up to 90 days for secondary waste Cast Stone with high Tc concentration (~200 µg/g) showed that Tc diffusivity followed a general trend of slowly decreasing Tc diffusivity after an initial peak increase due to the surface wash-off effect as well as high total Tc concentration loading. Because of the relatively higher initial Tc concentration in high-Tc Cast Stone compared to other previously tested Cast Stones, the average Tc diffusivity measured in high-Tc Cast Stone was higher than others Cast Stone leach tests with lower Tc contents. However, after 60-day leaching, the Tc diffusivity in secondary waste Cast Stone dropped to almost 10^{-11} cm^2/s.

The EPA 1315 leach test of both LAW NW- and SE-Cast Stones also showed higher Tc releases and diffusivity under higher oxygen content conditions in leaching solution. Because of the potential reoxidation of the initially reduced less-mobile Tc(IV) into the soluble oxidized species Tc(VII) with increasing contact with the elevated solution oxygen contents through diffusion, the Tc release and diffusivity are expected to increase in Cast Stone as the storage time increases, even in the subsurface IDF disposal site. In addition, the highest Tc release was found in the fractured Cast Stones among the three different leaching conditions for both NW- and SE-Cast Stones. Increased Tc release due to the presence of fractures (or cracks) in both NW- and SE-Cast Stones are attributed to the increased surface areas in the fractured Cast Stone, which provide more contact with oxygen. Between the two Cast Stones used in the Tc leaching test, the SE-Cast Stone showed lower Tc release, which indicates slightly better Tc retention in SE-Cast Stone (or SE dry ingredients) than in NW-Cast Stone (or dry ingredients).

5.0 XAFS Spectroscopy for Tc Oxidation State Changes

5.1 Introduction

One of the radioactive fission products, technetium-99, has been released into the environment as the result of nuclear weapons testing and radioactive waste disposal. A large fraction of the Hanford radioactive waste currently stored in the underground storage tanks contains nearly 1,900 kg of Tc, which will be treated, solidified, and disposed of as LAW at the Hanford Site. The highly soluble and oxidized pertechnetate oxyanion, $Tc(VII)O_4^-$, does not sorb onto sediments and solid surfaces, so TcO_4^- migrates at nearly the same velocity as groundwater under common subsurface conditions (i.e., at pH levels close to neutral or slightly alkaline and under suboxic conditions). However, under reducing conditions, Tc can precipitate as $Tc(IV)O_2{\bullet}2H_2O$, sorb more strongly to mineral phases, and be retained in different natural environments and engineered waste forms. One of the key approaches to immobilize Tc in waste forms such as Cast Stone is to preserve the reducing conditions required to keep Tc reduced as Tc(IV) because oxidized Tc, pertechnetate [$Tc(VII)O_4^-$], is very mobile under oxidizing conditions.

Our past work has shown that Tc(VII) can be reduced to Tc(IV) in Cast Stone because one of the dry ingredients, the BFS, works as reductant, releasing ferrous iron and sulfide ions into Cast Stone pore solutions through BFS dissolution during Cast Stone formation, curing, and/or storage. Although reduced Tc(IV) can persist in Cast Stone for a time even after being exposed to the oxidized Hanford pore water (due to the limited diffusion of oxygen available for contact with reduced Tc(IV) in Cast Stone), no one knows how long this reduced Tc(IV) will exist within the Cast Stone waste form under repository conditions. While the tortuous nature of pathways in Cast Stone pores and the existence of reducing agents such as BFS can help retain Tc as the reduced species Tc(IV) initially, the cracks or fractures that may be generated in the cementitious waste form during the aging and storage period can allow oxygenated water or oxygen gas to access the pores present in the Cast Stone. In addition, preliminary studies of the impacts of oxygen and carbon dioxide ingress into Cast Stone formed with Tc present in the liquid waste also showed increased rates of Tc reoxidation and release out of the Cast Stone (Um et al. 2011). Therefore, reduced technetium Tc(IV) can be reoxidized to become the oxidized species Tc(VII), making it difficult to stabilize Tc within Cast Stone over the long term. At the Hanford Site, solidified low-level waste form disposal at the IDF is being planned as a landfill trench type; it is being constructed at shallow depth in the 200 East Area where oxidizing conditions prevail naturally through diffusive oxygen mass transfer. In addition, because Tc leachability from Cast Stone is closely related to the Tc speciation and oxidation state change in the Cast Stone after being exposed to an oxidative environment in long-term storage, reoxidation and subsequent release of Tc out of the Cast Stone should be fully understood; this information can be used to develop the predictive Tc release model that is required to evaluate long-term environmental impacts of LAW (or secondary waste) Cast Stone and for safety analysis of the repository. Previous sections already showed that reductive capacity of Cast Stone decreased and Tc leachability increased after leaching or being exposed to elevated oxygen in leaching conditions. However, there was no proof that those changes in reductive capacity and Tc releases are related to different Tc speciation and Tc oxidation state changes after leaching. Therefore, XAFS spectroscopy was used to investigate Tc speciation and oxidation state changes in various Cast Stones between the unleached and leached states.

5.2 Materials and Methods

5.2.1 Cast Stone Specimens

Different Cast Stone monolith samples were characterized to determine the Tc oxidation state (Tc[VII] vs. Tc[IV]) and nearest neighbors using XAFS before and after EPA 1315 method leach testing. For WTP secondary waste Cast Stone, a Cast Stone monolith (1-in. diameter by 2-in. high) prepared with secondary waste Phase I simulant (see Table 2.1 for simulant information and Section 2 for Cast Stone preparation) with high Tc concentration of ~200 µg-Tc/g was tested to investigate the change of Tc oxidation state after leaching for 90-days and about three years of air exposure. After long-term leaching and air exposure, the secondary waste Cast Stone monolith was broken into chunks with a hammer and the Cast Stone chunks were immediately ground using a ball mill (or mortar and pestle) to make powder for the XAFS sample. In addition, the new smaller LAW NW- and SE-Cast Stone monoliths (0.404 in. × 0.808 in.) with Tc concentration of ~150 µg-Tc/g prepared using NW dry ingredients or SE dry ingredients were also used for XAFS analysis before and after leaching. After a certain time of leaching in solution, each Cast Stone monolith was removed from the leaching DI water solution, and one end of LAW NW- and SE-Cast Stone monoliths was sliced by a saw. Then, the LAW NW- and SE-Cast Stone fragments were also immediately ground using a mortar and pestle to make powder XAFS samples. The powder samples of both secondary waste and LAW Cast Stones were mounted on Teflon® sample holders and sealed with Kapton® tape to collect Tc XAFS spectra.

5.2.2 XAFS Spectroscopy Analysis

XAFS data were collected at the Stanford Synchrotron Radiation Laboratory beamline 11-2. Fluorescence data were collected using a 100 pixel high purity Ge detector and corrected for detector dead time, while transmission data were obtained using Ar filled ion chambers. A Si(220) double-flat-crystal monochromator was used and detuned 50% to reduce the harmonic content of the incoming beam. The energy was calibrated by using the first inflection point of the Tc K edge spectrum of the Tc(VII) standard defined as 21.044 keV. Tc x-ray absorption near-edge structure (XANES) data were obtained from 200 eV below the edge to 1,000 eV above the edge; the data from 75 eV below the edge to 200 eV above the edge was obtained with 0.35 eV spacing, while the rest of the data points were widely spaced (50 eV) and were used for the pre- and post-edge correction. Tc extended x-ray absorption fine structure (EXAFS) data were obtained with the same pre-edge energy spacing, and the spacing above the edge was obtained with a k-spacing of 0.05 and the collection time was weighted by k^3. Three Tc solid standards ($KTcO_4$, TcO_2•$2H_2O$, and Tc_2S_7) were also collected in transmission mode at room temperature. The latter two Tc standards represent the Tc(IV) oxidation state with varying degrees of disorder in the first shell of six oxygen atoms. In TcO_2•$2H_2O$, there are four oxygen atoms at 2.0 Å from the Tc center and two oxygen atoms at ~2.4 Å in an octahedral geometry. In Tc_2S_7, there are three disulfides (S_2^{2-}) so that the right chemical formula is $Tc_2(S_2^{2-})_3S$, resulting in the Tc(IV) oxidation state. The collected XAFS data were converted from raw data to spectra using SixPack software (Newville 2001). Spectra were normalized using Artemis and normalized XANES spectra were fit using standard spectra. The Tc-XANES spectra were fit in the following way. Initially, all three standard spectra were used to fit each spectrum. Any Tc(IV) standard spectrum for which the contribution was less than other standard deviations was removed, and the fitting process was repeated. If more than one Tc(IV) standard is used, the standard deviation of each becomes very large since their contributions are strongly correlated.

For EXAFS analysis, the Tc EXAFS spectra were obtained from the raw Tc absorption data using Athena/Artemis software (Ravel and Newville 2005). Theoretical phase and amplitude scattering factors were calculated using Feff 8 and EXAFS data were fit using Artemis software (Ravel and Newville 2005). The amplitude reduction factor (S_o) was fixed at 0.9 or 1.0 for all the EXAFS fits. The E_o parameter was allowed to vary during fitting, but was constrained to be the same for all scattering shells for a given fit.

5.3 Results and Discussion

5.3.1 XANES Spectroscopy Analysis of Secondary Waste Cast Stone

The XANES spectra of Tc standards and Tc Cast Stone samples prepared with secondary waste Phase I simulant are shown in Figure 5.1. The XANES spectrum of the TcO_4^-(VII) standard is characterized by a strong pre-edge feature found at around the 21,046 eV energy region because of the 1s-to-4d electron transition, which is allowed for the tetrahedral TcO_4^- coordination. The XANES spectra for the Tc(IV) standards from TcO_2•$2H_2O$ and Tc_2S_7 are very different from the Tc(VII) standard spectrum, and are characteristic of Tc(IV) coordinated by oxygen (or sulfur) atoms in an octahedral geometry showing no pre-edge feature. The oxidation state of Tc in Cast Stone after 90-day leaching and about three years of air exposure was determined by fitting the XANES spectra using a linear combination model in which three Tc species (TcO_4^-, TcO_2•$2H_2O$, and Tc_2S_7) are considered to be plausible. The summation of spectra contributions from these three Tc species matched the measured Tc XANES spectra well. For comparison, the XANES spectra of Tc in the same secondary waste Cast Stone before leaching were obtained from Um et al. (2011) and are shown together with new XANES result for the leached Cast Stone in Figure 5.1. The XANES fit results and the contributions of each of the three different Tc species are also provided in Table 5.1.

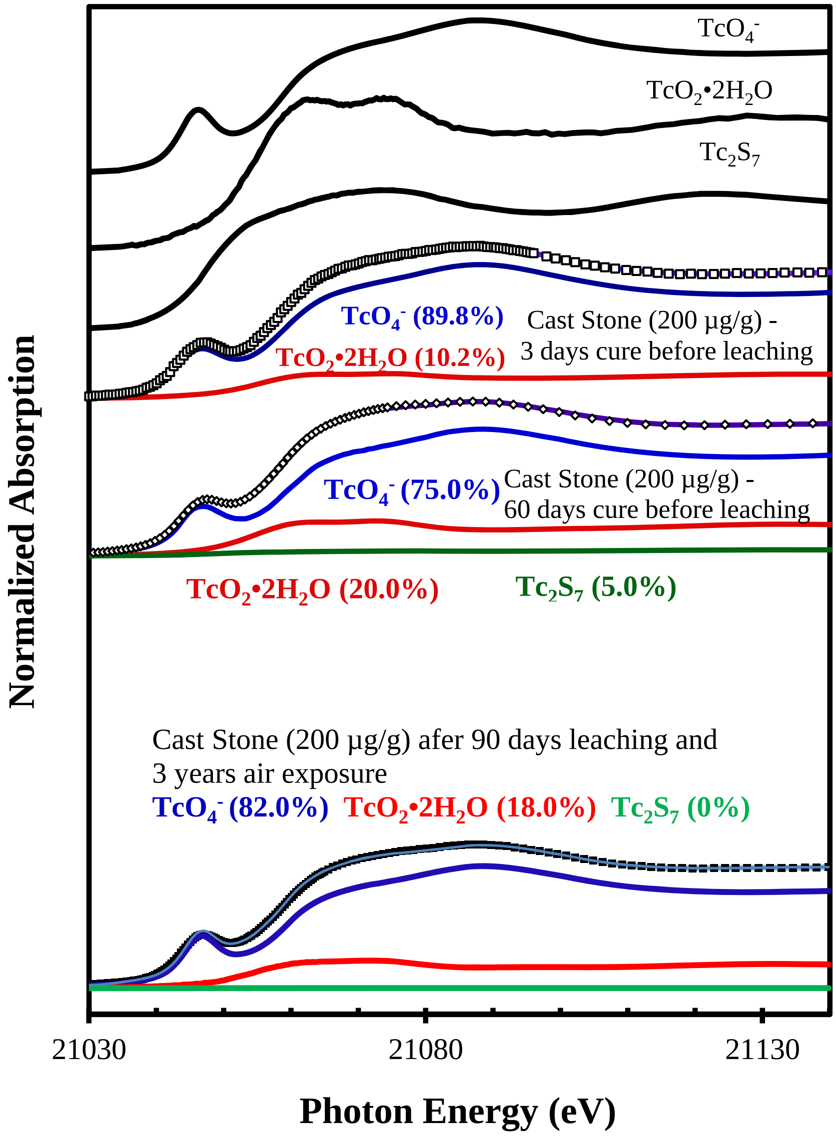

Figure 5.1. Normalized Tc XANES Spectra and Fits for WTP Secondary Waste Cast Stone Prepared with Phase I Simulant Before Leaching and After 90 Days Leaching and Three Years Air Exposure. Data are represented by symbols, and the fits are represented by the solid lines. The contributions of each Tc species and their percentages are shown with different colors for TcO_4^-, TcO_2•$2H_2O$, and Tc_2S_7, respectively.

Table 5.1. XANES Fit Results for Tc Species in Different Cast Stones

Samples	Tc conc. (µg/g)	Time(a) (days)	Tc_2S_7 (b) (%)	p(F)(c)	$TcO_2\cdot 2H_2O$(b) (%)	p(F)(c)	TcO_4^- (b) (%)	p(F)(c)	Conditions
Secondary waste Cast Stone-3 days cured before leaching	200	3	0.0	NC	10.0	1E-6	90.0	1E-6	Secondary waste Phase- I simulant
Secondary waste Cast Stone-60 days cured before leaching	200	60	5.0	0.1	20.0	3E-5	75.0	7E-10	Secondary waste Phase- I simulant
Secondary waste Cast Stone after 90-day leaching	200	1095	0.0	NC	18.0	1E-4	82.0	1E-4	Secondary waste Phase- I simulant
New LAW Cast Stone with NW ingredients before leaching	150	37	10.0	1E-4	0.0	0.833	90.0	1E-4	LAW 7.8 M average simulant +NW ingredients
New LAW Cast Stone with SE ingredients before leaching	150	37	9.0	1E-4	3.0	0.100	88.0	1E-4	LAW 7.8 M average simulant +SE ingredients
New LAW Cast Stone with NW ingredients after 28-day leaching	150	65	8.0	1E-4	4.0	0.006	88.0	1E-4	LAW 7.8 M average simulant +NW ingredients
New LAW Cast Stone with NW ingredients after 28-day leaching with saturated oxygen	150	65	7.0	1E-4	2.0	0.064	91.0	1E-4	LAW 7.8 M average simulant +NW ingredients
New LAW Cast Stone with NW ingredients after 28-day leaching with fracture surfaces	150	65	11.0	1E-4	6.0	1E-4	83.0	1E-4	LAW 7.8 M average simulant +NW ingredients
New LAW Cast Stone with SE ingredients after 28-day leaching	150	65	13.0	1E-4	4.0	0.001	83.0	1E-4	LAW 7.8 M average simulant +SE ingredients
New LAW Cast Stone with SE ingredients after 28-day leaching with saturated oxygen	150	65	13.0	1E-4	3.0	0.047	84.0	1E-4	LAW 7.8 M average simulant +SE ingredients
New LAW Cast Stone with SE ingredients after 28 day leaching with fractured surfaces	150	65	15.0	1E-4	5.0	0.001	80.0	1E-4	LAW 7.8 M average simulant +SE ingredients

(a) Time indicates "total time" between sample preparation including 28-day curing and XAFS data collection in units of days. Secondary waste Cast Stone after 90 days leaching was stored open to the atmosphere.

(b) These values represent the percentage of the total Tc assumed to be present as the designated species. The sum of all species is 1.0. Average standard deviation of the fit is 2%.

(c) p(F) is the probability that the improvement to the fit result including this component is due to random error. If p(F) <0.05, the component can be considered to be present. NC indicates "not conducted," because the other two possible Tc species contribute significantly to the fits, so adding the third species is not necessary.

For the secondary waste Cast Stone, the fraction of TcO_4^- species decreased from 90% after 3-day curing to 75% after 60-day curing, because of slowly dissolving BFS and reaction with simulant in the cement hydration process (Um et al. 2011). The contribution of the Tc_2S_7 species increased as the reaction (curing) time in Cast Stone increased from three days to 60 days before starting leaching and additional air exposure. However, the same Cast Stone that has been leached for 90 days using the EPA 1315 method (see Section 4.0) and stored in a container open to the atmosphere for approximately three years showed the fraction of TcO_4^- increased from 75 to 82% compared to the Tc oxidation state before leaching (Table 5.1). The increased fraction of TcO_4^- after leaching and long-term storage open to the atmosphere indicates Tc reoxidation in Cast Stone with increasing contact with oxygen in solution or the atmosphere. Fractions of Tc(IV) compounds also decreased in Cast Stone after leaching and long-term air exposure, confirming reoxidation of Tc in Cast Stone after being exposed to more oxygen contact in long-term storage. Because no Tc_2S_7 contribution was found in Cast Stone after leaching and long-term storage, the Tc_2S_7 species readily reoxidized to $TcO_2{\bullet}2H_2O$, then some $TcO_2{\bullet}2H_2O$ also reoxidized to TcO_4^- species during solution leaching and long-term storage with extended air contact. Due to the presence of sulfide and the higher reduction potential of sulfur species than the Fe^{2+}/Fe^{3+} redox couple (Lukens et al. 2005), reoxidation of Tc(IV) species would be expected to start from Tc_2S_7 to $TcO_2{\bullet}2H_2O$ followed by subsequent reoxidation of $TcO_2{\bullet}2H_2O$ to TcO_4^-. It is not likely for Tc_2S_7 to reoxidize directly to TcO_4^-, even under highly oxidative conditions. However, the reoxidation rate of Tc from Tc(IV) to Tc(VII) in Cast Stone must be controlled by the consumption rate of the remaining reductive capacity of Cast Stone and the diffusive rate of O_2 into Cast Stone.

5.3.2 XANES Spectroscopy Analysis of New LAW Cast Stone

The XANES spectra of Tc standards and new LAW mini Cast Stone monoliths prepared with 7.8 M LAW average simulant spiked with high Tc concentration and using either the NW (or SE) dry ingredients are shown in Figure 5.2. The XANES spectra of the TcO_4^- (VII) standard and Tc(IV) standard compounds are also given for comparison with the Cast Stone Tc XANES spectra in Figure 5.2. The pre-edge peak present around 21,047 eV, a typical feature of Tc(VII), was found in both new Cast Stone prepared with LAW average simulant and NW (or SE) dry ingredients before leaching and after leaching. Two new LAW Cast Stone samples before leaching contained mainly TcO_4^- species (88–90%), because the total curing and storage time (~30 days) between Cast Stone preparation and XAFS data collection was relatively short (Table 5.1). Previous secondary waste Cast Stone before leaching also showed that the Tc(VII) contribution dropped from 90% at three days of reaction to 75% after 60 days curing time because of slow dissolution of BFS and subsequent reduction of TcO_4^- in Cast Stone. In addition, the smaller size (0.404 in. × 0.808 in. or 1.01 cm × 2.02 cm) of the new LAW Cast Stone monoliths compared to secondary waste Cast Stone (1.0 in. × 2.0-in. or 2.5 cm × 5.0 cm) might result in relatively high Tc(VII) contribution in these two new LAW NW- and SE-Cast Stones even after 30 days of curing, because of the relatively smaller amounts of BFS and larger surface area to volume ratio for the smaller monoliths. That is, there was more opportunity of air (oxygen) to diffuse into the smaller monoliths during curing. Although both new LAW NW- and SE-Cast Stones showed very similar contributions from each of the three Tc species, the Cast Stone prepared with SE dry ingredients before leaching contained slightly less Tc(VII) species (88%) compared to the NW-Cast Stone (90%), indicating stronger reductive capacity due to the slightly higher reductive capacity of SE dry ingredients than NW dry ingredients, which agrees well with previous reductive capacity and Tc leaching results.

The new LAW NW- and SE-Cast Stone samples were tested for Tc oxidation change after leaching for 28 days in three different conditions (air equilibrated DI water, DI water saturated with oxygen, and fractured monolith in DI water saturated with oxygen). The Tc(VII) percentage in Cast Stones after 28-day leaching was similar to or less than the Tc(VII) percentage found in LAW Cast Stone before leaching (Figure 5.2 and Table 5.1). Only LAW NW-Cast Stone that was leached with saturated oxygen showed slightly increased Tc(VII) contribution, from 90% before leaching to 91% after leaching. This small change and increased Tc(VII) contribution in NW-Cast Stone after leaching with DI water saturated with oxygen might result from reoxidation of Tc(IV) (mostly from TcO_2•$2H_2O$) because of increased oxygen content during leaching. In addition, the Tc(VII) contribution in NW-Cast Stone after leaching in the saturated oxygen condition was the highest among the three Tc(VII) contributions in different leaching conditions. Even though LAW SE-Cast Stone leached with O_2-saturated leaching solution showed that the Tc(VII) species still dominated in the Cast Stone, the Tc(VII) contribution in LAW SE-Cast Stone after leaching was lower than before leaching, which agrees well with the Tc leaching data presented in Section 4. Less Tc leached from the SE-Cast Stone in comparison to the NW-Cast Stone because of the higher reductive capacity measured in SE dry ingredients than the NW dry ingredients.

Because of relatively short 28-day leaching time, all of the leached LAW NW- and SE-Cast Stone samples still contained some (2 to 6 %) TcO_2 and (7 to 15%) Tc_2S_7 Tc(IV) species. The total contribution of Tc(IV) from the summation of Tc_2S_7 and TcO_2•$2H_2O$ species in LAW SE-Cast Stone increased from 12% before leaching to 16–20% even after 28-day leaching, while the total Tc(IV) contribution increased in LAW NW-Cast Stone from 10% before leaching to 12–17% after leaching except in the O_2-saturated leaching condition, which showed decreased Tc(IV) contribution from 10% before leaching to 9% after leaching. These results suggest that the BFS slags continued to slowly dissolve in the Cast Stone and promoted additional slow reduction of Tc(VII) inside the monoliths. However, because the measured differences in Tc(VII) vs. Tc(IV) species percentages are small and likely within the uncertainty level of the XANES analysis, additional XAFS data collection and analysis with longer-reacted Cast Stone samples are required to support the understanding of Tc oxidation state changes. There is still a high percentage of Tc(IV) contribution, about 17–20%, in LAW SE-Cast Stone even after 28-day leaching, suggesting that there is still strong reductive capacity in SE-Cast Stone to keep some of the Tc(IV) resistant to reoxidation to Tc(VII). Continuous oxygen diffusion into the small Cast Stone monoliths may eventually consume the residual reduction capacity of the BFS and then promote reoxidation of residual Tc(IV) species. The short period of oxidized leaching tested to date needs to be extended for longer time periods to fully quantify the kinetics of reoxidation.

Even though larger masses of Tc leached from LAW Cast Stone with fracture surfaces (Section 4), a relatively lower residual percentage of Tc(VII) was found in both LAW NW- and SE-Cast Stones after leaching. This might be because we prepared XAFS samples using one slice off the end of each leached Cast Stone. The XAFS analysis can measure bulk information on the Tc oxidation state on the powder sample prepared in this study. If we had scraped only material from along the fractured surfaces, the XANES Tc speciation results for the fractured surface itself may have shown much higher percentages of Tc(VII) species in the surface scrapings which were exposed to oxygen more.

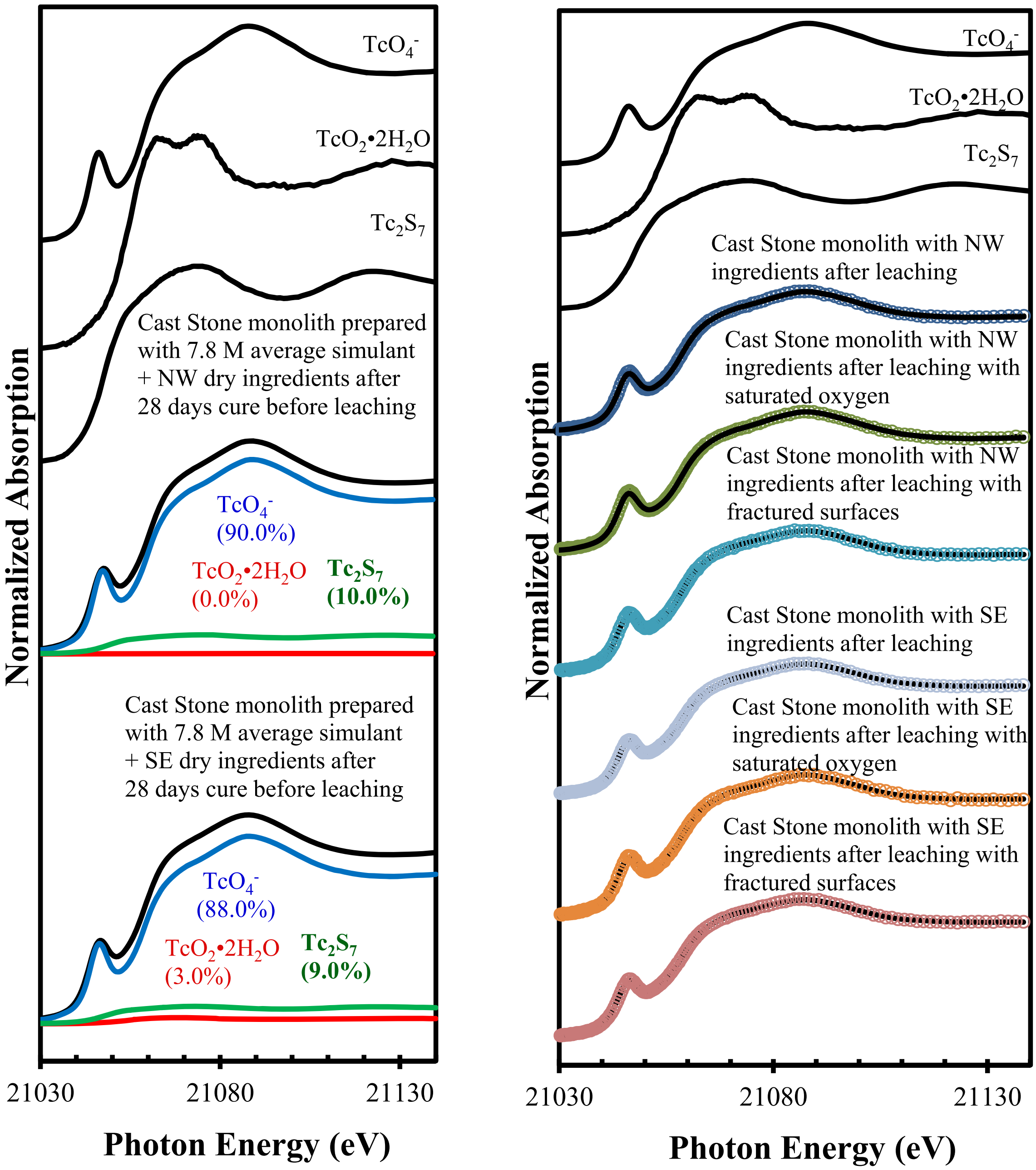

Figure 5.2. Normalized Tc XANES Spectra and Fits for New Small LAW Cast Stone Prepared with 7.8 M Average Simulant with NW (or SE) Dry Ingredients Before (left) and After (right) Leaching Using the EPA 1315 Method. The three different leaching conditions, including normal leaching in air equilibrated DI water, leaching with saturated oxygen, and leaching with fractured surfaces, were described in Section 4.0. Data are represented by symbols, and the fit is represented by the solid black line. The contributions of each Tc species and the percentages are shown with different colors for Cast Stone samples.

5.3.3 EXAFS Spectroscopy Analysis of Cast Stones

Because of the limited availability of synchrotron beam time, the EXAFS spectra were collected and analyzed only for the secondary waste Cast Stone after leaching and new LAW NW- and SE-Cast Stones before leaching. The EXAFS spectra of previously analyzed secondary waste Cast Stone with 60-day curing before leaching were also included to compare the Tc coordination environment in Cast Stone before and after leaching (Um et al. 2011). The EXAFS spectra with the best fits are shown in Figure 5.3 and the final fitting parameters are given in Table 5.2 including the EXAFS result for secondary waste Cast Stone (~200 µg-Tc/g) from Um et al. (2011).

The best fit for the secondary waste Cast Stone after leaching showed results similar to those for Cast Stone before leaching, even though the coordination number (CN) may have decreased slightly after leaching. The EXAFS spectra for the secondary waste Cast Stone after leaching had more noise in the data because the Tc concentration in the Cast Stone decreased after leaching. Even after leaching, the EXAFS analysis of secondary waste Cast Stone still showed a contribution from oxygen neighbors at 2.0 Å and contained about 26 ±2% Tc(IV). From the XANES fitting, the secondary waste Cast Stone after leaching also contains 18% Tc(IV) species (Table 5.1).

Unlike the secondary waste Cast Stone EXAFS spectra, the best fits for both LAW NW- and SE-Cast Stones before leaching were obtained for a structure with about four oxygen atoms at ~1.7 Å from the Tc atom. This coordination is closest to that observed for TcO_4^- species. Because the contribution from Tc(IV) in LAW NW- and SE-Cast Stones before leaching was low (~10–12% see Table 5.1), no additional oxygen scattering was observed in this sample. A high contribution of Tc(VII) species in LAW Cast Stones before leaching as found from the EXAFS data agrees well with the XANES analysis, and is considered to result from only minor dissolution of BFS during the relatively short time between Cast Stone preparation and XAFS data collection as mentioned before. That is more curing time would likely allow larger amounts of BFS dissolution that results in reduction of the spiked Tc(VII) species immobilized in the Cast Stone.

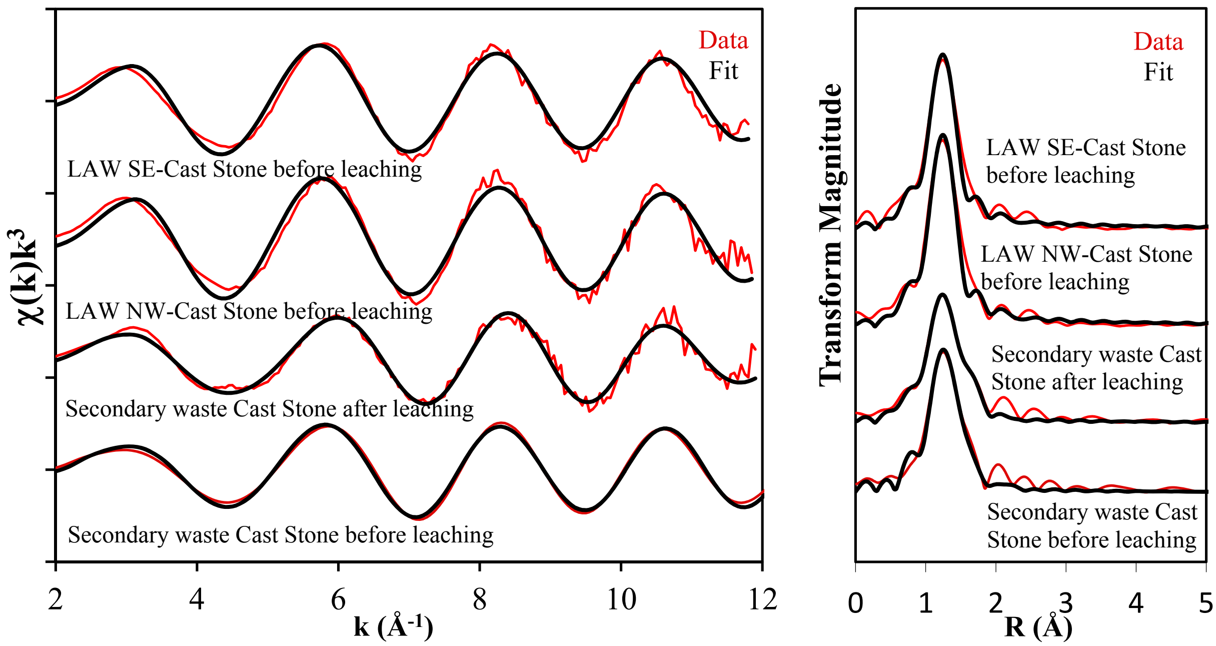

Figure 5.3. EXAFS Spectra (left) and their Fourier Transforms (right) for Secondary Waste Cast Stone Samples Before and After Leaching and for LAW NW- and SE-Cast Stones. The measured data and the fits are shown in red and black color, respectively.

Table 5.2. Best Fit Parameters for Cast Stones from EXAFS Analysis

Cast Stone Samples	**Neighboring Atoms**	**CN of Neighbors**	**Interatomic Distance (Å)**	**σ^2 (Å^2)$^{(a)}$**	**F(p)$^{(b)}$**	**R$^{(c)}$**
Secondary waste before leaching$^{(d)}$	O O	3.6(2)$^{(e)}$ 0.6(3)	1.71(1) 2.07(1)	0.0024(3) 0.0024(3)	0.017 0.056	0.009
Secondary waste after leaching$^{(f)}$	O O	3.0(1) 1.5(1)	1.71(7) 2.05(9)	0.0035(3) 0.0035(3)	0.012 0.001	0.030
LAW NW Cast Stone$^{(g)}$	O	3.4(9)	1.72(2)	0.002(2)	0.02	0.037
LAW SE Cast Stone$^{(h)}$	O	3.1(8)	1.72(1)	0.002(2)	0.02	0.037

(a) Debye-Waller factor constrained to equal to that of the previous shell.
(b) F(p) is the significance of the improvement to the fit created by adding an additional set of atoms. If the p-value is less than 0.05, the additional atoms have significantly improved the fit and can be considered "observed" in the EXAFS experiment.
(c) Goodness-of-fit parameter (R-factor) is described by $[\Sigma(y_{observed}-y_{calculated})^2/\Sigma(y_{obs})^2]^{1/2}$, where the sum is over all data. Lower value of R indicates a better fit.
(d) Fit range: 2 <k (photo-electron wavenumber) <12 and 0.8 <R (interatomic distance) <2 with amplitude reduction factor $S_o^2 = 0.9$ and energy shift (ΔE_o) = -5(3) eV from Um et al. (2011).
(e) The number in parentheses is the standard deviation in the same units as the last digit in the number [e.g., 0.17(1) is 0.17 with a standard deviation of 0.01].
(f) Fit range: 2 < k < 12 and 0.8 < R (interatomic distance) < 2 with $S_o^2 = 1.0$ and $\Delta E_o = 4(4)$ eV.
(g) Fit range: 2 < k < 12 and 0.8 < R (interatomic distance)< 1.8 with $S_o^2 = 1.0$ and $\Delta E_o = 5(5)$ eV.
(h) Fit range: 2 < k < 12 and 0.8 < R (interatomic distance) < 1.8 with $S_o^2 = 1.0$ and $\Delta E_o = 4(4)$ eV.

5.4 Conclusions

The technetium speciation and oxidation state changes were estimated for both secondary waste Cast Stone and LAW Cast Stones prepared with both NW and SE dry ingredients before and after leaching using XAFS spectroscopy. Secondary waste Cast Stone after 90-day leaching and about three years additional storage in atmospheric air showed reoxidation of the reduced Tc(IV) species to Tc(VII) species. The contribution of Tc(VII) increased from 75% in Cast Stone with 60-day cure before leaching to 82% in the same Cast Stone after leaching and air exposure for more than three years. Although the Tc(IV) contribution decreased from 25% before leaching to 18% after leaching, a certain amount of reduced Tc(IV) still remained in the Cast Stone. Because oxygen is the only oxidant that effectively oxidizes Tc(IV) to Tc(VII) in Cast Stone after leaching and air exposure, both the mass diffusive rate of oxygen into Cast Stone and the total reductive capacity of Cast Stone can control the reoxidation rate of Tc in Cast Stone in long-term storage and disposal environments. For the IDF facility and most other shallow land burial facilities, there will be a continuous source of oxygen in contact with the buried waste forms once any metallic canister corrodes.

For both LAW NW- and SE-Cast Stones, due to the short reaction time between Cast Stone preparation and XAFS sample collection, the percentages of Tc(IV) species observed in the Cast Stone were small, and Tc(VII) species still predominated. Even after leaching under three different leaching conditions, no significant increase of Tc(VII) contribution was reported in the XANES analysis for both LAW NW- and SE-Cast Stones. Because of the slow dissolution rate of BFS, a major reductant in Cast Stone, the total of 65 days of Cast Stone reaction (28 days of curing for Cast Stone, 28 days of leaching, and nine days of XAFS sample preparation and transportation) was not long enough for the slow dissolving BFS to completely reduce Tc from Tc(VII) to Tc(IV). Because Tc reduction by dissolved ferrous iron and sulfide ions from the BFS in Cast Stone continues even during the water leaching process, only a minor increase in Tc(VII) contribution was found in the LAW NW-Cast Stone after O_2-saturated leaching. Apparently the higher reductive capacity and perhaps faster dissolution kinetics of the SE BFS kept the Tc(IV) species even in the leached Cast Stone from converting to all Tc(VII). That is the SE BFS slag has a larger inherent reductive capacity and may dissolve more quickly thus promoting more reduction of Tc(VII) to Tc(IV) species that were not completely reoxidized as quickly during the 28-day leach tests under air equilibrated and elevated O_2 leaching conditions. Higher O_2 content in the leaching solutions should have increased the Tc(VII) contribution through reoxidation from Tc(IV) but the continual slow release of reductants from the BFS essentially "neutralized" or kept pace with the reoxidation. The contribution of Tc(IV) may have decreased only in LAW NW-Cast Stone after 28 days of leaching in O_2-saturated solution. The fact that lower Tc(VII) percentages were found in LAW SE-Cast Stones both before and after leaching is consistent with the higher reductive capacities measured for SE dry ingredients and 28-day cured Cast Stone made with SE dry blend.

Because available synchrotron beam time for EXAFS sample collection was limited, only the secondary waste Cast Stone after leaching and LAW Cast Stones before leaching were tested with EXAFS analysis. There was no Tc-Tc contribution scattering found in the EXAFS spectra, indicating the Tc species in these Cast Stone were not present as discrete precipitate phases in Cast Stone even though a high Tc concentration was used to prepare the Cast Stone. The EXAFS analysis also showed that Tc(VII) species still predominates in secondary waste Cast Stone even after leaching, which is very consistent with the results from XANES analysis.

6.0 Summary and Recommendations

The Tc speciation characterization in Cast Stone task for the EMSP subtask of “Production and Long-Term Performance of Low Temperature Waste Forms” consisted of the following subtasks to understand Tc speciation changes in Cast Stone after long-term storage and accelerated leaching with water containing elevated O_2(g):

- Measure the reductive capacity of dry ingredients obtained from two sources, various LAW simulants, and various cured Cast Stones before and after leaching.
- Perform additional EPA 1315 leach test to determine Tc release with different leaching conditions, such as high starting Tc concentration, different O_2 contents in leaching solution, and presence of fractured surfaces in Cast Stones.
- Determine Tc speciation and oxidation state changes after leaching and air exposure.

Various Cast Stones from previous secondary waste Cast Stone studies, LAW Cast Stone with varying simulants, and new smaller monolith-sized Cast Stone with high Tc concentration and NW (or SE) dry ingredients in 7.8 M Na overall average simulant were used for this Tc speciation characterization task.

The measured reductive capacity values of the various dry ingredients, different LAW simulants, and final Cast Stones before and after leaching were obtained with two methods, one based on Ce(IV) as the oxidant and another based on Cr(VI) as the oxidant. The Ce(IV) method subjects the solids to a strong acid (low pH) condition using H_2SO_4 that dissolves much more of the solids than are dissolved by the Cr(VI) method, which relies on a neutral pH condition. Among the dry ingredients tested, BFS (either NW or SE slag) showed the highest reductive capacity compared to the others (fly ash and Portland cement). Many of the LAW simulants showed higher reductive capacity than the BFS, because of NO_2^- present in the simulants. Nitrite in the simulants dominates their measured reducing capacity, thus increasing NO_2^- concentration in the 7.8 M Na simulants show higher reductive capacities than the 5 M Na simulants. However, because of the lower reduction potential of NO_2^-/NO_3^- redox couples (~0.01 V) than the reduction potentials of Fe^{2+}/Fe^{3+} (~ -0.5V), HS^-(or S^{2-})/SO_4^{2-} (~ -0.5 to -0.93V), and Tc^{4+}/Tc^{7+} (~ -0.36 V) redox couples at alkaline pH (~14) condition (Lukens et al. 2005), it is expected that the initial Tc(VII) species, pertechnetate, spiked into the simulants was not reduced to Tc(IV) by the nitrite in the simulants before mixing with dry ingredients to form Cast Stone. The major reductant in Cast Stone is still considered to be the BFS, even if the BFS dissolves slowly to release sulfide and ferrous iron ions in Cast Stone pore solutions after formation and during curing/storage. In addition, due to the higher reduction potential of S^{2-}/SO_4^{2-} than that of the Fe^{2+}/Fe^{3+} redox couple, the presence of sulfide from slowly dissolving BFS, can accelerate TcO_4^- reduction to form Tc_2S_7 as Cast Stone cures and ages. Cast Stones prepared with different simulants showed varying reductive capacity values according to the different reductive capacities measured in simulants. However, all the Cast Stone measured for the reductive capacity after leaching showed decreased reductive capacity compared to that of Cast Stone before leaching due to the consumption of reductive capacity with increasing O_2 contact. Significant decreases in reductive capacity was found for fractured Cast Stones prepared with 7.8 M Na average simulant and either the NW or SE dry ingredients, after a short 28-day EPA 1315 leaching test. This result suggests that it is important to minimize fracture formation (or crack genesis) in Cast Stone and limit its exposure to oxygen in order to decrease the loss of reductive capacity of Cast Stone and maintain efficient long-term reduction of Tc(VII) to Tc(IV) for immobilization of Tc in Cast Stone.

The EPA 1315 leach test on secondary waste Cast Stone from the secondary waste Phase II project that was prepared with higher Tc concentration (~200 μg/g) was performed for extended leaching times up to 90 days. Additional new LAW NW- and SE-Cast Stone monoliths were tested for Tc release under three different leaching conditions. The results showed that the Tc diffusivity for the Cast Stones followed a trend of gradual decrease in Tc diffusivity with time after an initial peak of Tc diffusivity at an early stage because of the surface-wash off effect. However, the average Tc leachability indices for secondary waste Cast Stone after 90-day leaching was higher than 11. The EPA 1315 method leach tests of both LAW NW- and SE-Cast Stones under O_2-saturated leaching solution increased the released Tc amounts compared to normal air-equilibrated leaching condition. The highest amount of releasable Tc was reported in both NW- and SE-Cast Stones when the fractured Cast Stone was tested in O_2-saturated DI water, which is due to the decreased reductive capacity of Cast Stone with the increased surface areas in the fractured Cast Stones. Slightly greater amounts of Tc released from NW-Cast Stone under all three different leaching conditions than from SE-Cast Stone, consistent with the higher reductive capacity measured in SE than in NW dry ingredients.

The technetium speciation and oxidation state changes were estimated for both secondary waste Cast Stone and LAW Cast Stones before and after leaching using XAFS spectroscopy. Secondary waste Cast Stone after 90-day leaching and about three years storage in the air showed noticeable changes in Tc oxidation state and speciation. Technetium reoxidation from the reduced Tc(IV) species to the Tc(VII) species was found in the aged secondary waste Cast Stone (after 90-day leaching and 3-year air exposure). Oxidized Tc(VII) is considered to be the species of Tc released into solution during leaching. Although the Tc(IV) percentage decreased from 25% before leaching to 18% after leaching in the 90-day leached secondary waste Cast Stone, some reduced Tc(IV) species still remain even after additional three years of storage in air after leaching. Because oxygen is the only oxidant that effectively oxidizes Tc(IV) to Tc(VII) in the aging Cast Stone, both the mass diffusive rate of oxygen into Cast Stone and the total residual reductive capacity of Cast Stone can control the Tc reoxidation rate.

Unfortunately, Tc reduction was not completely obtained in newly prepared smaller LAW NW- and SE-Cast Stone monoliths because of the relatively short curing time (~28 days) and short (~nine days) between preparing the cured Cast Stone for XAFS spectra collection. Further, the small amount of BFS used to make the small Cast Stone monoliths that contained higher than “normal” Tc(VII) concentrations in the simulant to facilitate Tc detection by XAFS analysis may also have skewed the percentage of spiked Tc(VII) reduced to Tc(IV) species within the Cast Stone monolith. On the other hand, fractures induced in some Cast Stone monoliths and the higher O_2 content present in most of the leaching solutions should have caused increased Tc(VII) percentages to be found in the leached Cast Stones through reoxidation from Tc(IV) after leaching. However, for the LAW NW-Cast Stone samples, the percentage of Tc(VII) increased in only one leach test (after leaching for 28 days in O_2-saturated solution) and the increase was only 1% (from 90% before leached Cast Stone to 91% after leaching). Regardless of different leaching conditions, lower Tc(VII) contributions were found in LAW SE-Cast Stones either before or after leaching, consistent with higher reductive capacity and lower Tc releases found in SE-Cast Stone than in NW-Cast Stone as reported in previous sections.

Although the results obtained from this subtask increase our understanding of Tc speciation and oxidation state changes in Cast Stone during prolonged curing, exposure to air, and leaching in various O_2 environments, more quantitative measurements after longer curing and leaching times under more various conditions should be performed. Additional recommendations for works to continued Tc speciation changes and development of predictive Tc releases using the aged Cast Stone are listed below:

1. Measurement of residual reductive capacity change should be conducted with varying accelerated O_2 exposure as a function of reaction time. The kinetics of how soon the reductants or reductive capacity in Cast Stone can lose its total reductive capacity by reacting with O_2 is a key data gap that we need to understand and need to address for evaluating long-term performance of Cast Stone disposed in the Hanford IDF. The changes in reductive capacity over time as a function of oxygen influx for Cast Stone need to be measured to improve our understanding and to predict the potential reoxidation rate for Tc. Such quantitative Tc reoxidation rate measurements and estimation of decrease in overall reductive capacity of Cast Stone and BFS are needed for long-term performance assessment calculation when Cast Stone is exposed to the IDF storage condition.
2. Continuous LAW Cast Stones long-term leaching tests (longer than 90 days) should be conducted to quantify the total releasable Tc amounts in Cast Stone under different leaching conditions. For O_2-saturated leaching condition, a constant O_2-saturated solution should be prepared that provides continuous $O_2(g)$ inflow into the leaching solution. In addition, more quantitative monitoring methods should be used to analyze dissolved O_2 concentration changes in the leaching solutions. New leaching experiments should be performed to obtain a quantitative amount of O_2 consumption and diffusive inflow of O_2 into the Cast Stone as it ages for more than a few years. Oxygen transport in pores and in any cracks that develop in Cast Stone may occur in the long-term storage so additional studies and calculations of correct O_2 contents and correlation between O_2 and Tc release are needed to predict the timing and impact of limited oxygenated water and air access to the stabilized Tc in the Cast Stone.
3. Continuous XAFS spectroscopic measurement for Tc speciation and oxidation state changes should be conducted along with the suggested tasks listed above. In addition, a special XAFS sample designed in the shape of a wafer (1 cm in diameter and 2–3 mm thick) should be prepared and leached in $O_2(g)$-saturated leaching solution. Before and after leaching at various leaching intervals, Tc speciation and oxidation state should be monitored by collecting XAFS data for at least five different locations (the center and two circumference edges, and two middle points between the center and edges). So far, our XAFS results only provided bulk information for Tc speciation and oxidation state changes after leaching and with varying O_2 contact. Even though the results from bulk sample analysis of XAFS spectroscopy have increased our understanding of Tc speciation and oxidation state changes in general, we could not obtain more quantitative depth of O_2 penetration and scientific information of Tc speciation changes at both location and time. This new information will be very useful to help develop a predictive model for Tc reoxidation rate with incoming diffusive O_2 transfer and changes of O_2 contents in the IDF disposal environment.
4. Additional leaching tests for Tc-laden Cast Stone monoliths surrounded with Hanford formation vadose zone sediments at various moisture contents should be conducted to monitor the release of Tc as a function of time and space into the IDF sediments and pore water.
5. Development of a predictive model for Cast Stone weathering with aging and subsequent Tc speciation and oxidation changes as well as Tc released amounts should be also considered for a long-term performance and safety assessment of Cast Stone in the Hanford IDF subsurface environment.

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