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## **Examination of Tc, S, and Fe Speciation within Saltstone**

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### **FY14 Final Report**

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## **LIST of ACRONYMS**

ACS: American Chemical Society

APS: Advanced Photon Source

AVS: Acid volatile sulfides

BFS: Blast furnace slag

DDI: Distilled deionized water

EXAFS: Extended X-ray absorption fine structure spectroscopy

IC: Ion chromatography

ICP-MS: Inductively coupled plasma mass spectrometry

ISE: Ion specific electrode

LSC: Liquid Scintillation Counting

NIST: National Institute of Standards and Technology

PIPS: Passivated Implanted Planar Silicon

SDU: Saltstone Disposal Unit

SRR: Savannah River Remediation LLC

SSRL: Stanford Synchrotron Radiation Laboratory

UV-Vis: Ultraviolet-Visible Spectroscopy

XANES: X-ray absorption near edge spectroscopy

XAS: X-ray absorption spectroscopy

## Executive Summary

This report describes measurements of sulfur (S), iron (Fe), and technetium (Tc) concentrations and speciation for a series of saltstone grout samples. Saltstone samples were prepared at Clemson University using the method and formulation provided by Savannah River Remediation LLC (SRR). Saltstone is a cementitious material that is used to encapsulate and immobilize a low activity salt waste produced at the Savannah River Site (SRS). The salt waste is mixed with a dry feeds mixture consisting of 45 wt% blast furnace slag (BFS), 45 wt% fly ash, and 10 wt% cement. It is believed that the presence of reduced S and Fe species in the BFS help to maintain REDOX sensitive radionuclides, in particular  $^{99}\text{Tc}$ , in a reduced and immobile state. Samples were prepared with and without  $^{99}\text{Tc(VII)}$  amendments and aged in an oxic chamber under high relative humidity. Multiple samples were prepared from the same batch of saltstone to allow S, Fe, and Tc speciation analyses at 4 time-points over an 18 month period using X-ray absorption spectroscopy (XAS). This report describes the results from analysis of the first set of samples which were aged for 29 days. A second set of samples was frozen after 117 days and is awaiting analysis at the next available beamtime. Additional leaching tests for Fe and S were performed to support the XAS studies. The XAS analysis will indicate which reduced S/Fe species in solid phase contributed to the labile S/Fe in the leaching test. In this work, the oxidation state of S, Fe, and Tc was determined in samples aged for 29 days. The presence of the oxidized form of Tc (Tc(VII)) suggests the incomplete reduction of Tc(VII) during the 29-day curing duration.

Tc-amended samples were sent for bulk Tc K-edge XAS measurements to determine the chemical speciation of Tc. During the first sampling interval at 29 days, hydrated and as-received BFS were also examined. Two of the  $^{99}\text{Tc}$  free saltstone samples and the BFS were subjected to various analyses including:

1. Batch S and Fe leaching tests of aged saltstone samples and (un)hydrated BFS in an anaerobic chamber using deoxygenated water in which sulfate, sulfide, sulfite, and thiosulfate concentrations were measured using ion chromatography (IC) and ultraviolet-visible spectroscopy (UV-Vis) and total Fe was measured using ICP-MS.
2. Bulk Fe K-edge X-ray near edge spectroscopy (XANES) analysis in a saltstone monolith to understand the oxidation state as a function of depth.
3. S K-edge XANES to determine S oxidation state distribution as a function of depth.
4. Tc K-edge XANES to determine the Tc oxidation state distribution as a function of depth.

Samples for S/Fe leaching were performed by segmenting the samples and determining the concentration of S and Fe in the leachate solutions as a function of depth in the monolith. S speciation determination was conducted using UV-Vis and IC techniques, while Fe concentration was determined using inductively coupled plasma mass spectrometry (ICP-MS). The solid state chemical speciation of S, Fe and Tc was determined by removing bulk material from the samples and determining the speciation as a function of depth using XAS; this analysis provides the direct information of the local structure (< 3.5 ang.) of targeted atoms in heterogeneous materials. The XANES portion is sensitive to oxidation state of targeted elements whereas the extended portion (i.e., EXAFS) provides the local structural information of the X-ray absorber. Coordination number and radial distances can be obtained from the spectra analysis.

Overall the results indicate that the dominant oxidation state of S within the leachate solutions and the monoliths is sulfate ( $\text{SO}_4^{2-}$ ). The leaching tests of BFS indicated that sulfate was the dominant S species in the leachate solutions from as received BFS samples. This is an unexpected result as most of the S within the BFS is assumed to be reduced sulfide. Thus, after a few hours of hydration in a simulant solution, the BFS appears to lose significant reduction capacity. Interestingly, Fe speciation in BFS seems to be dominated by ferrous iron, suggesting that the ferrous ion might be a larger contributor in reducing Tc(VII) in saltstone. In the Tc spiked saltstone sample, there is both reduced Tc(IV) as well as unreduced Tc(VII). While the exact Tc speciation and its quantification require more reliable data from Tc(IV) reference compounds (e.g.,  $\text{TcS}_x$ ), it is clear that Tc(VII) is not completely reduced in this particular saltstone formulation, at least not at the Tc loading level required for XAS analysis. It is noteworthy that samples for Tc XAS analysis must be prepared at a significantly higher concentration than is expected in the saltstone facility. Due to detection limits with XAS, samples were prepared with 124 ppm Tc ( $\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$ ), which is significantly higher than the 0.4 ppm Tc ( $\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$ ) expected in the actual saltstone.

## 1.0 Introduction

A portion of low-level radioactive waste is disposed at the Savannah River Site (SRS) as saltstone, a cementitious waste form that is, and continues to be, disposed of in concrete disposal units in the SRS vadose zone. A key attribute of this waste form is that it chemically immobilizes some radionuclides through its strong chemical reducing potential. Of specific interest is technetium ( $^{99}\text{Tc}$ ), a long-lived radioactive constituent of saltstone, which when oxidized is highly soluble and thus potentially highly mobile. Several studies have demonstrated both the difficulty in reducing pertechnetate ( $\text{TcO}_4^-$ ; i.e.,  $\text{Tc(VII)}$ ), the oxidized form of Tc, and the rapid oxidation of reduced Tc (i.e.,  $\text{Tc(IV)}$ ) when exposed to even moderate levels of  $\text{O}_2$  (Cantrell and Williams, 2013; Kaplan et al., 2011; Kaplan et al., 2008; Almond and Kaplan, 2012; Lukens et al., 2005). Reducing agents such as BFS, which contain reductants, such as sulfide ( $\text{S}^{2-}$ ) and ferrous iron ( $\text{Fe}^{2+}$ ), are added to cementitious material formulations for waste stabilization as a means of enhancing the retention of redox sensitive  $^{99}\text{Tc}$ , though the mechanism by which  $^{99}\text{Tc}$  is reduced is not well understood. As such, the intent of the proposed study is to determine the efficacy and mechanism(s) of BFS in reducing (and immobilizing)  $^{99}\text{Tc}$ . Understanding and measuring the chemistry responsible for this immobilization may ultimately permit kinetic and thermodynamic modeling. As the oxidation state and speciation of Fe, S, and Tc are vital for understanding this work,  $E_{\text{H}}$ -pH diagrams for each species are provided in Appendix A. It is noteworthy that the reduced species considered in this work ( $\text{Tc(IV)}$ ,  $\text{Fe(II)}$ ,  $\text{S(-II)}$ , and  $\text{S(0)}$ ) are only thermodynamically stable at very low  $E_{\text{H}}$  values, particularly for the high pH range (10-13) of the pore water in most cementitious materials.

This project has two major objectives as follows:

1. Analyze unhydrated and hydrated blast furnace slag (BFS) with respect to total sulfur (S) and iron (Fe) content, and S and Fe speciation.
2. Process saltstone samples with and without technetium ( $^{99}\text{Tc}$ ) additions and:
  - a. Characterize S, Fe, and Tc speciation after curing durations in the range of 1 to 24 months.
  - b. Determine S, Fe, Tc phases present after curing durations in the range of 1 to 24 months.

## 2.0 Sample Preparation and Receipt

### *Preparation of Tc-free saltstone samples*

Saltstone monoliths without  $^{99}\text{Tc}$  addition were prepared at Clemson University on 3/28/2014.  $^{99}\text{Tc}$ -free monoliths were cylindrical with an approximate 1 inch diameter and were 4 inches in height. A dry feed mixture of 45% fly ash, 45% BFS, and 10% cement was used per SRR instructions as described in Appendix B. The fly ash, BFS, and cement were received from Steve Simner of SRR on 1/15/2014. Photographs of the as-received materials are shown in Appendix B, Figures B1 through B3. A description of the salt waste simulant solution, and instructions provided by SRR for preparation of the saltstone monoliths are provided in Appendix B. Briefly 50 g of cement, 225 g BFS, and 225 g of Fly Ash were mixed at 30 rpm in a plastic bucket for 10 minutes to produce the dry feed mixture (Note an 8.5 g aliquot of this mixture was removed to prepare the Tc-amended samples discussed below). Then 442 g of saltwaste simulant (Appendix B, Table B2) was added to the dry mixture. This corresponds to a water to dry feed ratio of 0.60. The wet slurry was stirred using an overhead stirrer at 250 rpm for 15 minutes. The

stirring was stopped at 5 and 10 minutes to check for aggregate formation. After mixing, the slurry was divided into 10 pre-weighed and labeled 1” diameter x 4” tall polypropylene centrifuge tubes. As noted above, the objective of this work is to determine Fe, S, and Tc speciation in cured saltstone using synchrotron based techniques for at least four time intervals over an 18 month period. A total of 10 saltstone samples were prepared for these tests and given the sample IDs “SS-I-24X” where X = A through J to represent the 10 samples. Samples aged in an oxic, humid chamber are shown in Figure 1. The chamber was a glass desiccator with standing water in the bottom to provide a high relative humidity atmosphere. The desiccator was left in an oven and the samples were subjected to a temperature profile representative of a Saltstone Disposal Unit (SDU) as indicated in Table 1.

As discussed below, Tc-amended samples were prepared in smaller tubes to minimize the radioactivity. These samples were approximately 1.7 cm<sup>3</sup> each. The Tc-amended samples were given the sample IDs “Tc-SS-I-26X” where X = A through G to represent the 7 samples. Figure 1 provides a visual comparison of the 2 different sample sizes. To verify that the smaller sample size had not produced any experimental artifacts (*e.g.*, increased oxygen diffusion due to the smaller surface area to volume ratio which could influence Fe, S, and Tc redox speciation), 10 replicate samples from the <sup>99</sup>Tc-free saltstone mixture were prepared on the smaller scale and analyzed for Fe and S speciation. The same wet slurry prepared above was used to make these samples. Thus, there are effectively two sets of samples for Fe and S XAS analysis (*i.e.* one in large tubes and one in small). The smaller Tc-free saltstone samples were given the sample IDs “SS-I-26X” where X = A through J to represent the 10 samples



**Figure 1: (Left) Saltstone monoliths within the oxic, humid chamber used for aging experiments. The glass chamber was placed inside an oven to provide temperature control. The temperature profile in use is listed in Table 1. The white wire shown in the picture is the temperature sensor. A relative humidity >99% was maintained by having standing water at the bottom of the chamber underneath the samples which are supported by a ceramic disc. (Right) Representative Tc-free and Tc-amended samples. The 50mL tube is the standard size for the Tc-free saltstone samples (Samples SS-I-24X). The two smaller 2 mL tubes to the right were made with and without Tc (Samples SS-I-26X and Tc-SS-I-26X).**

These saltstone samples were prepared on March 28, 2014. Two saltstone samples (SS-I-24A and SS-I-24F) were removed from the curing environment on April 1, 2014, effectively a few days after preparation (*i.e.*, one for Fe analysis and a second for S analysis). With the four expected time points, there are two “spare” Tc free monoliths available for additional time points if needed.

In a preliminary study that was begun in January 2014, a set of Tc-free saltstone samples were prepared to take advantage of X-ray synchrotron beamtime available to the investigators. A mistake was made in the preparation and these samples were prepared using a water to dry feed ratio of 0.5 instead of 0.6 as described above. This lower water/solids ratio is expected to result in a slightly denser sample. The influence of the lower water content on Fe or S speciation is unknown. Therefore, the samples were saved and analyzed using XAS to determine if changing the water to dry feed ratio has an impact on the Fe and S redox speciation. The samples were aged from 1/21/2014 to 1/31/2014 under the same oxic, humid conditions described above. Rather than discarding the samples and losing the available beamtime, the samples were removed from the chamber and shipped for XAS analysis on 1/31/2014. XAS data was collected for these samples and is presented in this report. These samples were given the sample IDs “SS-I-9X” where X = A through J to represent the 10 samples.

### ***Historical reducing grout samples for XAS analysis***

Fe and S XAS analysis was also performed on three historical samples. These samples were used in a previous study (Estes et al., 2011) examining Tc sorption to reducing grouts. They are described as Vault 2, TR547, and TR545 and have 17%, 45%, and 90% BFS content. These samples were prepared in early 2009 and received from Daniel Kaplan of SRNL to perform Tc sorption studies (Estes et al., 2011; Roberts and Kaplan, 2009). The samples were prepared from monoliths, ground, and stored in plastic bottles under atmospheric conditions. Therefore, these samples are proposed to represent fully oxidized reducing grouts. Comparison of the Fe and S oxidation states in these aged samples and the freshly prepared saltstone in this work is expected to provide some insight regarding the rate and extent of Fe and S oxidation.

### ***Preparation of hydrated BFS samples***

To examine the sulfur and iron speciation directly in BFS, additional samples were prepared by hydrating BFS with the saltwaste simulant. XAS analysis was performed on as-received dry BFS as noted in Table 3. Additional samples were hydrated with the saltwaste simulant using a 0.6:1 water to BFS ratio and aged prior to XAS analysis. These are samples BFS-I-11A and BFS-I-11B and were prepared on 1/28/2014 and 1/29/2014, respectively. The samples were shipped to UIUC for analysis on 1/29/2014. Sulfur XAS analysis was performed on 1/31/2014 and Fe XAS analysis was performed on 5/12/2014. The samples were frozen during the time period between S and Fe XAS analysis. These are intended for comparison with the dry as-received BFS and hydrated BFS samples listed in Table 3. The BFS was hydrated with the same salt simulant immediately prior to beamline analysis. Therefore, the set of BFS samples effectively represents the behavior of BFS as a function of time after hydration in the order:

- Zero hydration (i.e. dry BFS) – reference point
- XAS minutes after hydration (hydrated BFS)
- XAS 2 days after hydration (BFS-I-11B)
- XAS 3 days after hydration (BFS-I-11A).

### ***Preparation of Tc-amended saltstone samples***

Seven <sup>99</sup>Tc amended samples were prepared with 124 ppm (mg<sub>Tc</sub>/kg<sub>saltstone</sub>) <sup>99</sup>Tc for Tc XAS analysis to be performed at similar timepoints as the Fe and S analysis. The samples were prepared exactly as described above for the Tc-free saltstone except that <sup>99</sup>Tc(VII) was added to the simulant solution to

achieve a final concentration of 124 ppm  $^{99}\text{Tc}$  in the final saltstone samples (described in the following paragraph). Since there are four planned time-points for Fe and S XAS work, there are three additional  $^{99}\text{Tc}$  amended samples to use as needed in future testing. The 124 ppm  $^{99}\text{Tc}$  loading is significantly higher than the expected concentration in the SDU. However, this higher concentration is necessary to facilitate analysis using XAS as described below. Assuming a concentration of  $^{99}\text{Tc}$  in the salt solution currently being processed at SRS (Bannochie, 2013) of  $1.93 \times 10^4$  pCi/mL, the estimated  $^{99}\text{Tc}$  concentration within the saltstone is  $6.8 \times 10^6$  pCi/g or  $0.4 \text{ mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$  (0.4 ppm) This calculation assumed that a 0.6 water to dry feed ratio and a density of the salt solution of  $1.257 \text{ g}/\text{cm}^3$ , and a density of the saltstone product of approximately  $1.7 \text{ g}/\text{cm}^3$ . Accounting for the water contained within the chemicals used to make the saltwaste simulant, this ultimately corresponds to adding 0.885 g of saltwaste simulant to 1 g of dry feed materials.

Due to the high cost and high radioactivity associated with preparing  $^{99}\text{Tc}$  amended samples in 1" x 4" plastic molds, the  $^{99}\text{Tc}$  samples were smaller and prepared in 2mL (~0.25" diameter and 1" height) polypropylene centrifuge tubes yielding approximately  $1.7 \text{ cm}^3$  of saltstone per sample. A 8.5g aliquot of the dry feed mixture of BFS, cement, and fly ash prepared when making the Tc-free samples was removed and mixed with 7.55 g of simulant containing 260 ppm  $^{99}\text{Tc(VII)}$  ( $\text{mg}_{\text{Tc}}/\text{kg}_{\text{simulant}}$ ) (Table B3). Thus the final saltstone solid has a  $^{99}\text{Tc}$  solid phase concentration of  $124 \text{ mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$ . The wet mixture was stirred by hand for 15 minutes in a plastic vial then divided into seven aliquots as noted above. After preparation the samples were transferred to the oxic, humid chamber and aged with the Tc-free saltstone samples prepared above. These tubes have approximately the same height-diameter aspect ratio as the 1" x 4" molds used for the Tc-free saltstone samples discussed above.

All Tc-amended samples were prepared on March 28, 2014 at the same time as the Tc-free samples discussed above. The Tc-amended samples were given the sample IDs "Tc-SS-I-26X" where X = A through G to represent the 7 samples. In this report, data is shown for one Tc-amended sample (Tc-SS-I-26A) removed for Tc XAS analysis on April 22, 2014 (Table 3). To prepare sample Tc-SS-I-26A for Tc XAS analysis, the sample was transferred out of the oxic, humidity chamber and placed within an anaerobic chamber. Using a metal spatula, the first 0-0.5 cm of sample was removed and a second sample from the 0.5-1.5 cm section was removed and ground (separately) in an agate mortar. The ground samples were individually packed into cells of an Al holder backed with kapton tape. This holder was then sealed in kapton tape on all sides then transferred out of the anaerobic chamber where it was then mounted into the XAS sample holder for shipment to SSRL. This sample packing occurred on 5/1/14 and the sample was shipped to SSRL on 5/5/14 and analyzed on 5/9/14. Thus eight days passed between sample packing and analysis. The kapton tape has a low oxygen diffusion coefficient but the potential impacts of oxygen diffusion must be considered.

**Table 1: Temperature profile used in aging experiment started on 03/28/2014. This profile was provided by SRR and follows the measured temperatures within an Saltstone Disposal Unit (SDU).**

Days	Temperature (°C)	Date of temperature change
0	43	3/28/2014
0.63	47	3/28/2014
5	54	4/2/2014
15	61	4/12/2014
25	65.5	4/22/2014
35	65.5	5/2/2014
97	50	7/3/2014
160	39.5	9/4/2014
176	38	9/20/2014
200	38	10/14/2014
240	36.5	11/23/2014
350	35	3/13/2015
400	33	5/2/2015
450	29.5	6/21/2015

**Table 2: The record of saltstone, BFS and reference mineral samples used for preliminary studies to utilize beamtime allotted prior to the start of the project in March, 2013. These are historical samples available in the Powell and Arai research laboratories from previous work with saltstone and cementitious materials.**

Sample ID	Date Prepared	Date Received at UIUC	Sample Description	Date Quenched	Date of Analysis	Type of Analysis
Vault 2-1	Unknown <sup>a</sup>	3/25/2013	Ground cement using Vault 2 formulation. 17% BFS Used in previous studies <sup>a</sup>	NA	Dec 9, 2013 Fe XAS at ID5BM, APS	bulk Fe XAS
TR 545	1/16/2009 <sup>a</sup>	3/25/2013	Ground saltstone containing 90% BFS used in previous studies <sup>a</sup>	NA	Dec 9, 2013 Fe XAS at ID5BM, APS	bulk Fe XAS
TR 547	2/4/2009 <sup>a</sup>	3/25/2013	Ground saltstone containing 45% BFS used in previous studies <sup>a</sup>	NA	Dec 9, 2013 Fe XAS at ID5BM, APS	bulk Fe XAS
SS-I-9A	1/21/2014	1/31/2014	Saltstone samples prepared with a 0.5:1 water to dry feed ratio <sup>b</sup>	NA	Jan 31, 2014 S XAS at BL43, SSRL April 3, 2014 Fe XAS at ID13BM, APS	Bulk S and Fe XAS
SS-I-9C	1/21/2014	1/31/2014	Saltstone samples prepared with a 0.5:1 water to dry feed ratio <sup>b</sup>	NA	Jan 31, 2014 S XAS at BL43, SSRL	Bulk S XAS
SS-I-9H	1/21/2014	1/31/2014	Saltstone samples prepared with a 0.5:1 water to dry feed ratio <sup>b</sup>	NA	Jan 31, 2014 S XAS at BL43, SSRL	Bulk S XAS
SS-I-9I	1/21/2014	1/31/2014	Saltstone samples prepared with a 0.5:1 water to dry feed ratio <sup>b</sup>	NA	Jan 31, 2014 S XAS at BL43, SSRL	Bulk S XAS

<sup>a</sup>Roberts and Kaplan, 2009; Estes, et al., 2011

<sup>b</sup>Materials prepared using BFS, cement, and fly ash obtained from S. Simner on January 15, 2014. Samples were prepared using the procedure outlined in Appendix B and discussed above. Note an approximately 0.5:1 water to dry feeds ratio was used instead of the recommended 0.6:1 value. Photographs of this material are shown in Appendix B.

**Table 3: The record of saltstone, BFS and reference mineral samples used in the leaching tests and synchrotron based X-ray analysis. All BFS and saltstone samples were prepared using dry feed materials obtained from S. Simner on 1/15/2014 as discussed above.**

Sample ID	Date Prepared	Date Received at Univ. Illinois for XAS and leaching	Sample Description	Date Quenched	Date of Analysis	Type of Analysis
As-Received BFS	No preparation	4/1/2014	Dry as-received BFS <sup>a</sup>	NA	April 3, 2014 Fe XAS at ID13BM, APS	Leaching, Bulk Fe XAS
Hyd. As-received BFS <sup>a</sup>	4/1/2014 <sup>a</sup>	4/1/2014	BFS hydrated with saltwaste simulant at beamline <sup>a</sup>	NA	April 3, 2014 Fe XAS at ID13BM, APS	Leaching, Bulk Fe XAS
BFS-I-11A	1/28/2014	1/31/2014	BFS hydrated with saltwaste simulant	NA	Jan 31, 2014 S XANES at BL43, SSRL May 12, 2014 S XAS at BL43, SSRL	Bulk S/Fe XAS
BFS-I-11B	1/29/2014	1/31/2014	BFS hydrated with saltwaste simulant	NA	Jan 31, 2014 S XANES at BL43, SSRL May 12, 2014 S XAS at BL43, SSRL	Bulk S/Fe XAS
SS-I-24A	3/28/2014	4/1/2014	Saltstone sample	4/1/2014	April 3, 2014 Fe XAS at ID13BM, APS	Leaching, Bulk Fe XAS
SS-I-24F	3/28/2014	4/1/2014	Saltstone sample	4/1/2014	May 12, 2014 S XAS at BL43, SSRL	Leaching, Bulk S XAS
SS-I-26F	3/28/2014	4/1/2014	Saltstone sample	4/1/2014	April 3, 2014 Fe XAS at ID13BM, APS	Leaching, Bulk Fe XAS
Fe <sub>2</sub> O <sub>3</sub>	No preparation, stock chemical	NA, provided by Arai	Standard for Fe(III) XAS analysis	NA	April 3, 2014 Fe XAS at ID13BM, APS	Bulk Fe XAS
Fe <sub>2</sub> S	No preparation, stock chemical	NA, provided by Arai	Standard for Fe(II) XAS analysis	NA	April 3, 2014 Fe XAS at ID13BM, APS	Bulk Fe XAS

**Table 3:** Continued

<b>Sample ID</b>	<b>Date Prepared</b>	<b>Date Received at Univ. Illinois</b>	<b>Sample Description</b>	<b>Date Quenched</b>	<b>Date of Analysis</b>	<b>Type of Analysis</b>
Tc-SS-I-26A, bottom layer	3/28/2014	Removed from chamber on 4/30/14 and shipped to SSRL 5/5/14	Tc-amended saltstone sample containing 124 ppm <sup>99</sup> Tc (mg <sub>Tc</sub> /kg <sub>saltstone</sub> )	Sample processed 4/30/14 for XAS analysis	May 9, 2014 at BL11-2, SSRL	Bulk Tc XAS
Tc-SS-I-26A, upper layer	3/28/2014	Removed from chamber on 4/30/14 and shipped to SSRL 5/5/14	Tc-amended saltstone sample containing 124 ppm <sup>99</sup> Tc (mg <sub>Tc</sub> /kg <sub>saltstone</sub> )	Sample processed 4/30/14 for XAS analysis	May 9, 2014 at BL11-2, SSRL	Bulk Tc XAS
TcO <sub>2</sub> (am)	4/28/2014	shipped to SSRL 5/5/14	Standard for Tc(IV) XAS	NA	May 9, 2014 at BL11-2, SSRL	Bulk Tc XAS
NH <sub>4</sub> TcO <sub>4</sub> (aq)	4/28/2014	shipped to SSRL 5/5/14	Standard for Tc(VII) XAS	NA	May 9, 2014 at BL11-2, SSRL	Bulk Tc XAS
<sup>a</sup> Sample was hydrated with saltwaste simulant at the synchrotron beamline immediately before analysis using a 0.6:1 water:BFS ratio.						

## 3.0 Methods

### 3.1 Saltstone Segmentation and Leaching Procedures

Saltstone samples SS-I-24A, SS-I-24F, and SS-I-26A were prepared at Clemson University and shipped to UIUC for leaching tests and XAS analysis. Samples were drilled as described previously on May 12, 2014 to collect samples for leaching tests and for S XAS and April 3, 2014 for Fe XAS measurements at different synchrotron light sources. Note that all samples were kept in a freezer except for the drilling period. Samples were kept in a freezer until the further XAS measurements. In addition to saltstone samples, the leaching test was also performed on BFS before and after hydration with the saltstone simulant solution.

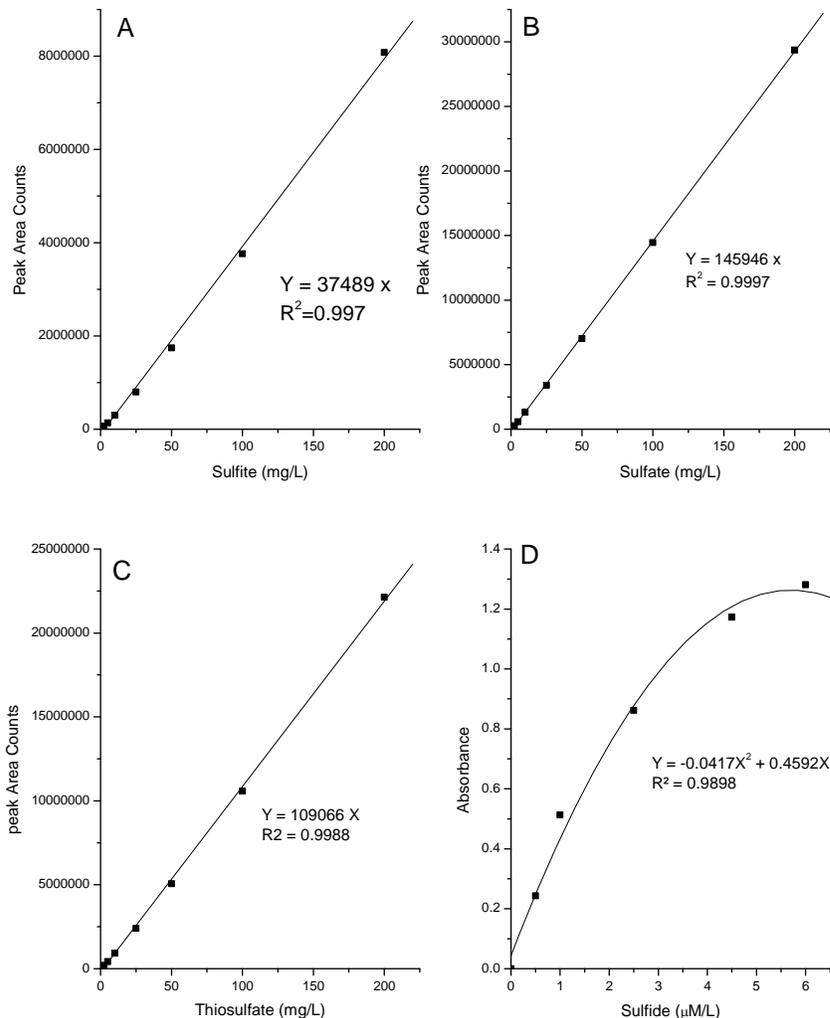
Depth dependent saltstone samples (SS-I-24A, SS-I-24F) for leaching tests and XAS analysis were collected inside an anaerobic glove bag by drilling in approximate millimeter increments using a Dremel 200 Drill (2 speed rotary tool) equipped with a tungsten carbide drill bit. The drill was vertically mounted on a Dremel factory stand (Dremel 220-01 Rotary Tool Work Station) to ensure the accuracy of drilling depth. Depth was measured by inserting a ruler into the hole and measuring from the top of the sample. A 1.5 cm diameter hole was drilled in the center of the samples to a depth of 3 cm. Ground powder was collected at each depth increment and subsequently ground using a Diamonite mortar and pestle. Approximately 0.5g of material was divided and transferred into two Nalgene Oak Ridge High-Speed Centrifuge tubes. The exact mass of powder transferred was determined gravimetrically. To prepare degassed MilliQ water, MilliQ water was boiled for 30min, and then cooled to room temperature and then sparged with nitrogen gas for 3 hrs. It was maintained in an anaerobic glove chamber for 5-7 days prior to the experiments. The first set of tubes was filled with degassed MilliQ water inside the glove bag. All tubes were shaken on an end over shaker at 20 rpm for 24 hours. The samples were then removed and centrifuged at 10,500 rpm for 8 minutes; this is sufficient time for particles with a hydrodynamic radius greater than 100 nm to be removed from the supernatant. Approximately 10 mL of leachate was collected and filtered through a 0.45  $\mu\text{m}$  PVDF (Polyvinylidene fluoride) filter.

### 3.2 Aqueous Sulfur Speciation Analysis

Oxygen free MilliQ (18.2 $\Omega$ ) water was prepared by boiling for 30min. After cooling to 30-35°C, it was sparged with N<sub>2</sub> gas for 3 hrs. The degassed water was kept in a N<sub>2</sub> filled glove bag until it was ready to be used. Using a Dremel drill, saltstone powder was sampled every 5mm in the glove bag as discussed previously. The sampling depth was up to 3cm. Any large fragments were ground in a mortar and a pestle prior to the leaching test. The mass of sample ranged from 0.52-0.86 g. Each depth sequence sample was transferred to a 15mL polycarbonate tube, and then 13 mL of degassed MilliQ water was added. The tubes were shaken at 10rpm at 22 °C  $\pm$  0.4. After 24hrs, tubes were centrifuged at 2000 rpm for 10 min, and aliquots were passed through 0.45  $\mu\text{m}$  polyvinylidene difluoride (PVDF) filters. Filtrates were immediately analyzed for S speciation using the following ion chromatography and spectrophotometric methods.

**ION CHROMATOGRAPHY:** Aqueous sulfur speciation was conducted using a Dionex DX-120 Ion Chromatograph unit. The following standards were used in instrument calibration: a 1000 ppm sulfate ICP-MS National Institute of Standard Technology (NIST) traceable standard, and 0.1N thiosulfate standardized solution (Alfa Aesar), a 100 ppm ISE sulfide standard (Cole-Parmer), and a sulfite Standard

Solution, 15 mg/L as SO<sub>3</sub> (Hatch products). Calibration curves for sulfate, sulfide, thiosulfate, and sulfite measurement are provided in Figure 2. The IC unit is equipped with a Dionex IonPac AS25 guard column (4mm × 250 mm), a Dionex ASRS 300 4 mm suppressor and an AS40 Automated Sampler. The following instrumental set-up was used: Flow Rate: 1.0 mL/min, current: 92 mA (recycle), oven temperature: 30 °C, Eluent Generation Modules: 36 mM KOH, Injection volume: 25 μL, and DS4 Detection Stabilizer: Model DS4-1. The peak area was estimated using a Dionex Software, PeakNet-SE 5.10d . Approximately 5mL of leachate filtrate solutions was used in the analysis.



**Figure 2: Standard curves of aqueous S speciation in ion chromatography and spectrophotometric analysis. A) Sulfite, B) Sulfate, C) Thiosulfate and D) sulfide.**

**UV-VIS:** For sulfide, a methylene blue method was used to analyze dissolved sulfide since the previous attempts to measure sulfide using acid volatile sulfide analysis resulted in non-detectable level of sulfide. A N,N-dimethyl-*p*-phenylene-diamine dihydrochloride·2HCl solution (Sigma Aldrich; 0.48 g in a SRR PO: SRRA042328SR, FY14 Final Report, page 17

100 mL of 6M HCl) and ferric chloride solution (Fisher scientific; 1.6 g in a 100 mL of 6M HCl) were prepared from ACS grade chemicals. The mixture of chemicals were used as described previously (Sakamoto-Arnold et al., 1986). Both chemicals were kept in brown polyethylene bottles. The absorbance of samples was read at 670nm.

**ICP-MS Analysis for Fe:** Dissolved Fe from the leaching test was measured using a Thermo X Series II ICP-MS. A Sc internal standard was simultaneously aspirated with the samples and used to correct for variations in flow. The instrument was calibrated using a 1000 ppm NIST Fe standard. Note that this method does not differentiate between Fe(II) and Fe(III). As discussed below, Fe concentrations were below the detection limits. Therefore, no additional analysis to differentiate between Fe(II) and Fe(III) was performed.

### **3.3 Preparation of $TcO_4^-$ and $TcO_2(am)$ Standards for XAS Analysis**

For XAS analysis, Tc(VII) and Tc(IV) standards are required and were prepared as aqueous  $TcO_4^-$  and solid  $TcO_2(am)$ . A 50 microCi  $^{99}Tc$  in water stock was obtained from Eckerdt and Zeigler. The solution was purified on a Eichrom TEVA resin column. Briefly the column was wet packed with a 5mL bed volume. The  $^{99}Tc$  stock solution was diluted into 0.01 M  $HNO_3$  and loaded on the column (after a 5 column volume (CV) pre-equilibration with 0.01 M  $HNO_3$ ). The column was washed with an additional 5 CV of 0.01 M  $HNO_3$ . Then the  $^{99}Tc$  was eluted in three 5 mL aliquots of 12 M  $HNO_3$ . The  $^{99}Tc/12$  M  $HNO_3$  solution was then evaporated to dryness slowly over 120 °C heat on a hotplate. The eluted reconstituted in 1 mM  $NH_4OH$  dissolving Tc as the  $TcO_4^-$  ion and creating a 3.5 g/L  $^{99}Tc$  working solution. The exact concentration was verified using liquid scintillation counting (LSC). The Tc(VII) XAS standard was prepared by pipetting a 100 uL aliquot of this working solution onto a piece of filter paper within the XAS sample holder. The  $TcO_2(am)$  solid was prepared using the method described by Hess et al., (2004). Briefly, a 0.5 mL aliquot of the 3.5 g/L  $^{99}Tc(VII)$  working solution was mixed with 5 mL of 0.2 M  $Na_2S_2O_4$ . A black precipitate indicative of  $TcO_2(am)$  immediately formed. The solid was isolated using centrifugation then a wet slurry was pipetted onto a dry filter paper packed into the XAS sample holder.

### **3.4 Fe XAS Analysis**

All XAS samples were transferred from a freezer to a  $N_2$  filled glove bag prior to the measurements. Saltstone samples were ground and loaded in polycarbonate XAS sample holders sealed with Kapton tape in the glove bag. The hydration for BFS in a simulant solution was also carried out ~1.5 hrs prior to the measurements (noted as sample “Hyd. As-received BFS” in Table 3). Beamlines ID5BM and ID13BM at the Advanced Photon Source (APS), Argonne, IL were used to collect XAS spectra in fluorescence mode for all samples and in transmission mode for reference compounds. Each beamline is equipped with a channel-cut Si(111) double-crystal monochromator. Sample holders were oriented at 45° to the unfocused incident beam. The incident of X-ray energy was calibrated at the inflection point of the first derivative of a Fe foil at 7112 eV. All samples were run at room temperature. The following detectors were used, a Vortex-ME 4 (Hitachi High-Tech Science America, Inc.) at ID5 and a GE13 element detector at ID13. Spectra were recorded in three regions: 5 eV steps at 6962 eV- 7100 eV with 2sec. dwell, 0.25 eV steps over the XANES (7100eV – 7137eV) at 2 sec. dwell, and 0.44 eV steps at 7137eV -7600 eV with 2sec. To monitor the change in Fe valence state in saltstone and its materials, Fe pre-edge peaks of Fe reference compounds (Fe(II)sulfide, hematite( $Fe(III)_2O_3$ )) were also collected. The

data reduction of XAS spectra was performed using the SixPACK/IFEFFIT interface (Webb, 2005) and Athena (Ravel and Newville, 2005). To prevent beam induced damage, only one to four spectra were collected per sample. The following data normalization was carried out at approximately 6962-7600 eV so the data were not affected by synchrotron X-ray. A Gaussian/linear function was used for normalization of the pre-edge region and a quadratic function was used for the post-edge region.

### ***3.5 Sulfur XAS Analysis***

Sulfur K-edge XANES measurements were conducted at beamline 4-3 Stanford synchrotron Radiation Laboratory (Menlo Park, CA). A monochromator consisting of double crystal Si (111)  $\Phi=0^\circ$  with an entrance slit of 0.5 mm and minimum energy resolution of 104 at the S K-edge (2472eV) was used. Saltstone samples were ground and homogenized using a mortar and pestle and packed into a 1.2 mm layer on 28 X 32 mm polycarbonate sample holders with a 0.2 mm XRF film (SPEX sample prep Inc. Metuchen, NJ) and S-free scotch tape. The measurements were performed under ambient and He purged conditions. Spectra were collected in fluorescence mode using a one-element passivated implanted planar silicon (PIPS) detector. Spectra were recorded from 2440 to 2575 eV with five regions: 2 eV steps from 2440 to 2460eV with 1sec. dwell, 0.08 eV steps over the pre-edge from 2460 to 2478 eV at 1sec. dwell, 0.2eV steps from 2478 to 2490 eV with 1sec., 0.5eV steps from 2490 to 2525 eV with 1sec. and 5eV steps from 2525 to 2575 eV with 1sec. Incident of X-ray energy was calibrated using a thiosulfate powder every 24hr. The first peak was set at 2472.02eV. Minimum of three spectra were recorded for each sample. Acquiring multiple spectra across time allows us to quantitative evaluation of reproducibility including beam induced reduction. The background was subtracted, and the step-edge height normalized to unity for all samples prior to data processing.

### ***3.6 Technetium K-edge XAS Measurements***

Technetium K-edge XAS measurements of saltstone were performed at beam line 11-2 at Stanford Synchrotron Radiation laboratory (SSRL), Menlo Park, CA. Due to limited  $^{99}\text{Tc}$  source, a small scale monolith was prepared at Clemson University. Top and bottom layer were used for the measurements in addition to bulk  $\text{TcO}_2(\text{am})$  precipitates and a ammonium pertechnetate solution sample. All measurements were performed in fluorescence mode at 77K using the radioactive sample cryogenic sample holder and hatch set-up. XAS measurements were conducted using a 100-element Ge solid-state detector. The energy calibration was performed at 20,000 eV using a Mo foil. Spectra were recorded in three regions: 5 eV steps at 2089.9 eV-21009.9 eV with 2sec. dwell, 0.2 eV steps over the XANES (21009.9 eV – 21069 eV) at 2 sec. dwell, and 1 eV steps at 21069.7eV - 22011 eV with 2sec. Chemical composition maps and XANES spectra were processed up to  $11.5 \text{ \AA}^{-1}$  using Sixpack software (Webb, 2005).

## **4.0 Results and Discussion**

### ***4.1 Results from S and Fe Leaching Tests***

Results from the S leaching tests of BFS in degased MilliQ water are shown in Figure 3 and listed in Appendix C. Sulfite ( $\text{SO}_3^{2-}$ ) was not detected in any analysis (detection limit: 1mg/L). After the hydration in a simulant solution, the release of sulfate and thiosulfate increased (Figure 3A). The concentration of sulfate was as high as  $\sim 3900\text{mg/kg}$  in the hydrated sample while it was below 500 mg/kg in the unhydrated BFS. Evaluation of the sulfate leaching of hydrated samples is complicated as sulfate was

added to the BFS as a part of the saltwaste simulant and sulfur is present in the BFS. Based on the 0.059 M concentration of  $\text{SO}_4^{2-}$  in the saltwaste simulant, the sulfate added from the simulant will generate 3300 ppm sulfate ( $\text{mg SO}_4^{2-}$  per kg of hydrated BFS). The exact sulfur concentration of the BFS received from SRR is unknown but an average value of 2.5% by weight sulfur is expected. Furthermore, it is expected that the majority of sulfur in BFS is initially present as reduced sulfide. Therefore, assuming 2.5% by weight sulfur in BFS, the hydrated BFS will contain approximately 6000 ppm sulfur. This is twice the sulfur concentration contributed by the saltwaste simulant. It is unclear if the sulfate observed in the leachate solution is from the saltwaste simulant or from the dry BFS.

The release of thiosulfate was ~7 times greater after hydrating the BFS, suggesting the oxidation of reduced sulfur species in a alkaline pH simulant solution. This oxidation reaction can also be supported by the sulfide data (Figure-3B). Although the sulfide release is much lower than that of thiosulfate and sulfate, one can observe that the concentration of sulfide is greater in the as-received (unhydrated) BFS.

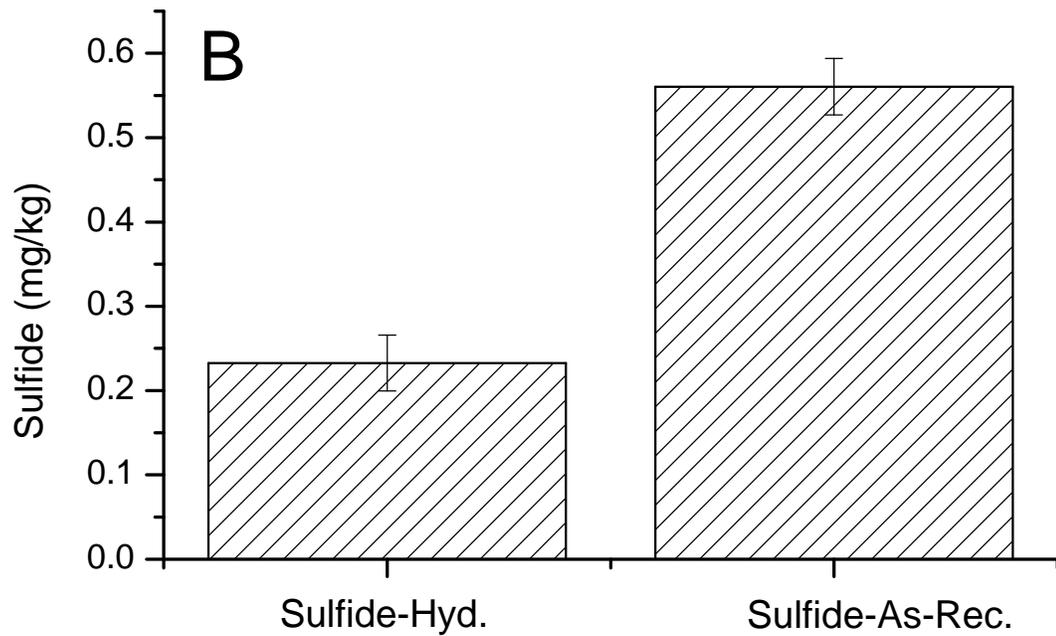
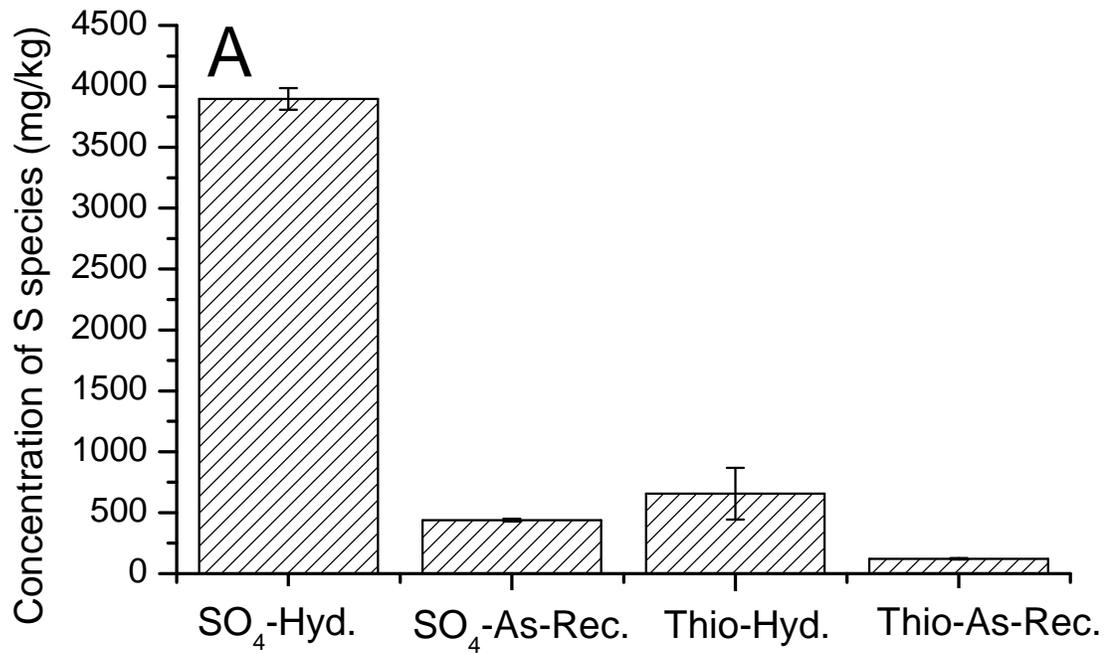
Results from the S leaching tests of saltstone monoliths I-24A and I-26A are shown in Figure 4 and listed in Appendix D. There was no detectable level of sulfide and sulfite in these saltstone samples (detection limit for sulfite: 1 mg/L, detection limit for sulfide 0.5 $\mu\text{M/L}$ ). The release of sulfate in the two saltstone samples is much greater than that of thiosulfate. While the level of sulfate release ranges from ~5000 to 7000  $\text{mg}_{\text{SO}_4}/\text{kg}_{\text{saltstone}}$ , the concentration of thiosulfate was ~1000 mg/kg throughout all depths. As discussed above for the BFS samples, the sulfate added from the saltwaste simulant solution will add 3300 ppm sulfate to the samples. This is lower than the observed range of sulfate concentrations from samples SS-I-24A and SS-I-26A indicating that some sulfate was leaching from the BFS, fly ash, or cement. The sulfur content of the cement and fly ash have not been characterized. The depth discrete drilling and sample collection was performed in a glovebox to ensure anoxic conditions (oxygen content < 1 ppm) in the event that the core of a monolith contained a reduced zone that would oxidize upon exposure to air. All samples indicate spikes in the S concentration, possibly indicative of heterogeneous distribution of S throughout the monoliths. Thus the variations in concentration as a function of depth may be statistical fluctuation based on localized S concentrations from saltstone components (e.g., BFS and cement). The high sulfate concentrations observed in the leaching tests are consistent with the results of S XANES analysis (discussed in Section 4.3 below). Although the impact of the sulfate addition by way of the saltwaste simulant solution is unclear, the sulfate leaching from saltstone samples represents more sulfate than was added in the simulant. Therefore, some sulfate is being leached in the system. It is unclear if this is coming from cement, BFS, or fly ash. However, the data do indicate that some oxidation of sulfide to sulfate occurs readily upon hydration of the dry materials. This is supported by the S XAS analysis discussed in Section 4.3 below.

There are two very important points with regards to the measured thiosulfate concentrations.

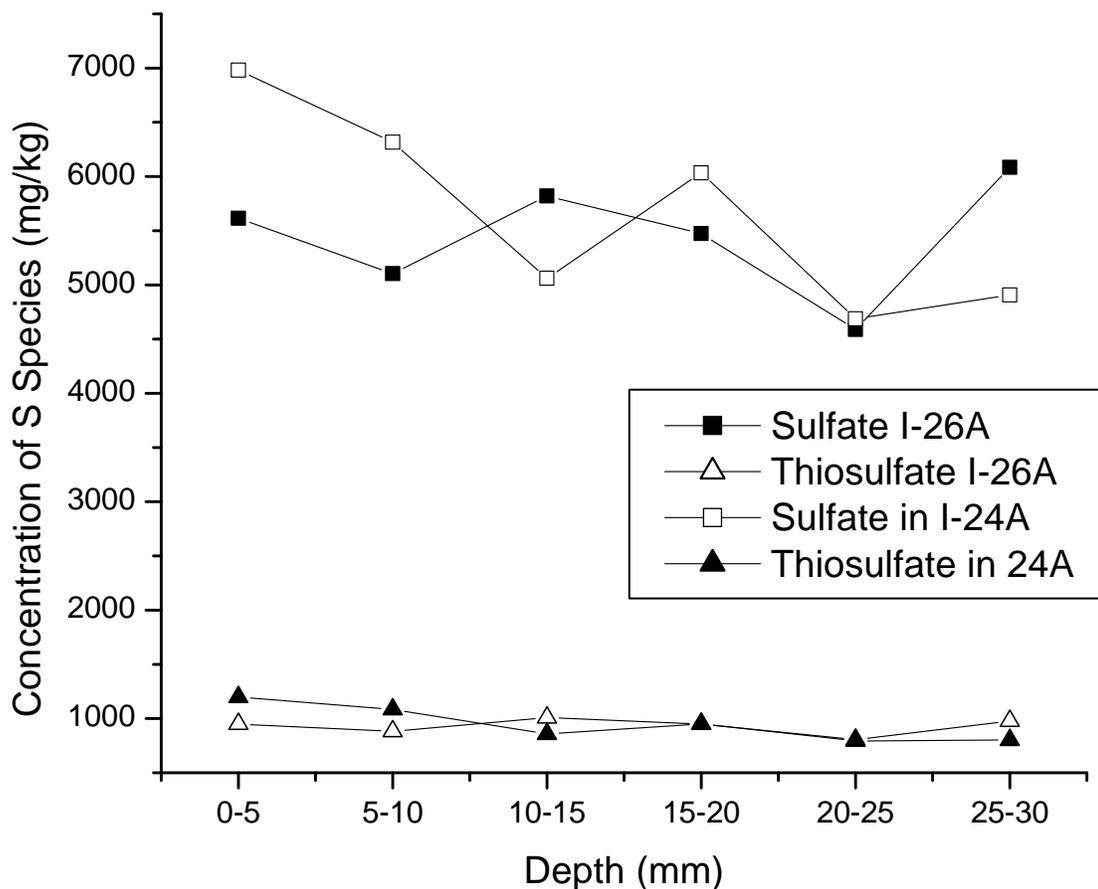
1. Some reducing capacity remains within the saltstone matrix after the samples have been prepared and aged for a short period of time. The persistence of these reduced sulfur species will be something to monitor carefully as the replicate samples age.
2. There is essentially no difference in the sulfate and thiosulfate concentrations between samples SS-I-24A and SS-I-26A. This is important because these samples are two different sizes. As discussed in Section 2 above, sample SS-I-26A is significantly smaller than sample SS-I-24A but is the same size as the Tc-amended samples. The smaller Tc-free sample (SS-I-26A) was

prepared to perform S and Fe speciation analysis and verify that the smaller sample size did not artificially influence the redox speciation (*e.g.*, increased oxygen diffusion due to the smaller surface area to volume ratio which could influence Fe, S, and Tc redox speciation). The similarity between the two samples indicates that the smaller sample size indeed does not introduce any experimental artifacts and that the smaller size is representative of the larger size. This conclusion is also supported by the Fe XAS analysis discussed in Section 4.2 below.

All pH values of the leachate solutions remained around 12 and did not change with depth (Appendix D). There was also no iron detected in the leachate for any sample. It is noteworthy to mention that all of dissolved iron is hydrolyzed, and could have precipitated out as iron oxyhydroxides during the leaching process. This may explain why no soluble iron was detected in the ICP-MS analysis of the leachate.



**Figure 3: A) The results of sulfate (SO<sub>4</sub>) and thiosulfate (Thio) leaching test from hydrated (Hyd.) BSF in a simulant solution and as-received(As-Rec.) BFS, and B) the result of sulfide leaching test from hydrated (Hyd.) and as-received (As-Rec.)**



**Figure 4: The results of sulfate and thiosulfate leaching test from two 29 days old saltstone samples (I-24A and I-26A). Sulfite was below detection limit.**

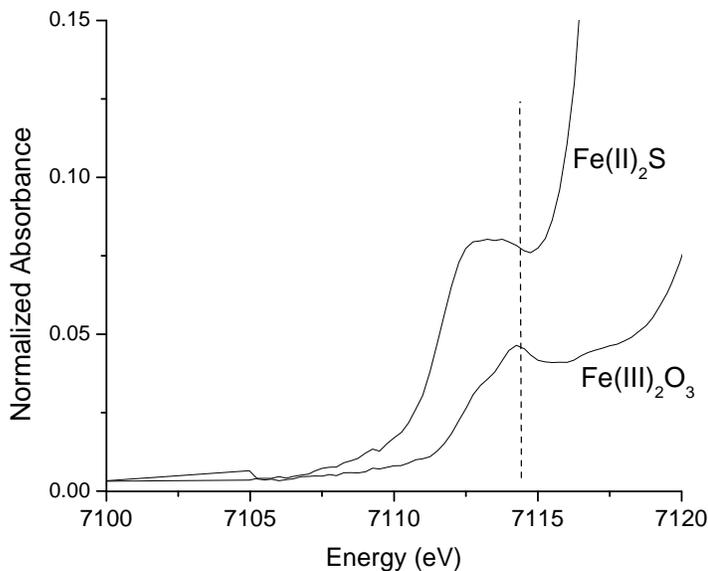
#### 4.2 Fe XANES Analysis

In Figure 5, Fe K-edge XANES of Fe reference compounds (Fe(III) oxide and Fe(II)sulfide) show the distinctive pre-edge features corresponding to the  $1s \rightarrow 3d$  transition that are sensitive to Fe oxidation state (Calas and Petiau, 1983; Waychunas et al., 1983). In general, oxidized forms of Fe show the pre-edge feature at higher energy. The vertical dotted line shows the peak of hematite ( $\text{Fe}_2\text{O}_3$ ). The position of pre-edge feature of Fe reference compounds can be used to identify the valence state in unknown samples. The overall XAS spectra of various saltstone samples are shown in Figure 6. Prior to detailed EXAFS analysis that will be performed in FY15, it is important to identify the predominant oxidation state in unknown phases. For this reason, the comparison of pre-edge feature was a focus of this study. Figure 7 shows the pre-edge feature of Fe K-edge XAS spectra of various saltstone samples and components as a zoomed in region from Figure 6. Based on the position of the pre-edge feature, the iron within as-received BFS and hydrated BFS appears to be dominated by Fe(II). The position of the pre-edge feature shifts to higher energy in the fresh saltstone samples SS-I-24A, SS-I-26A and SS-I-9A. This indicates that in younger saltstone samples, reduced Fe (ferrous species) appear to still be present as

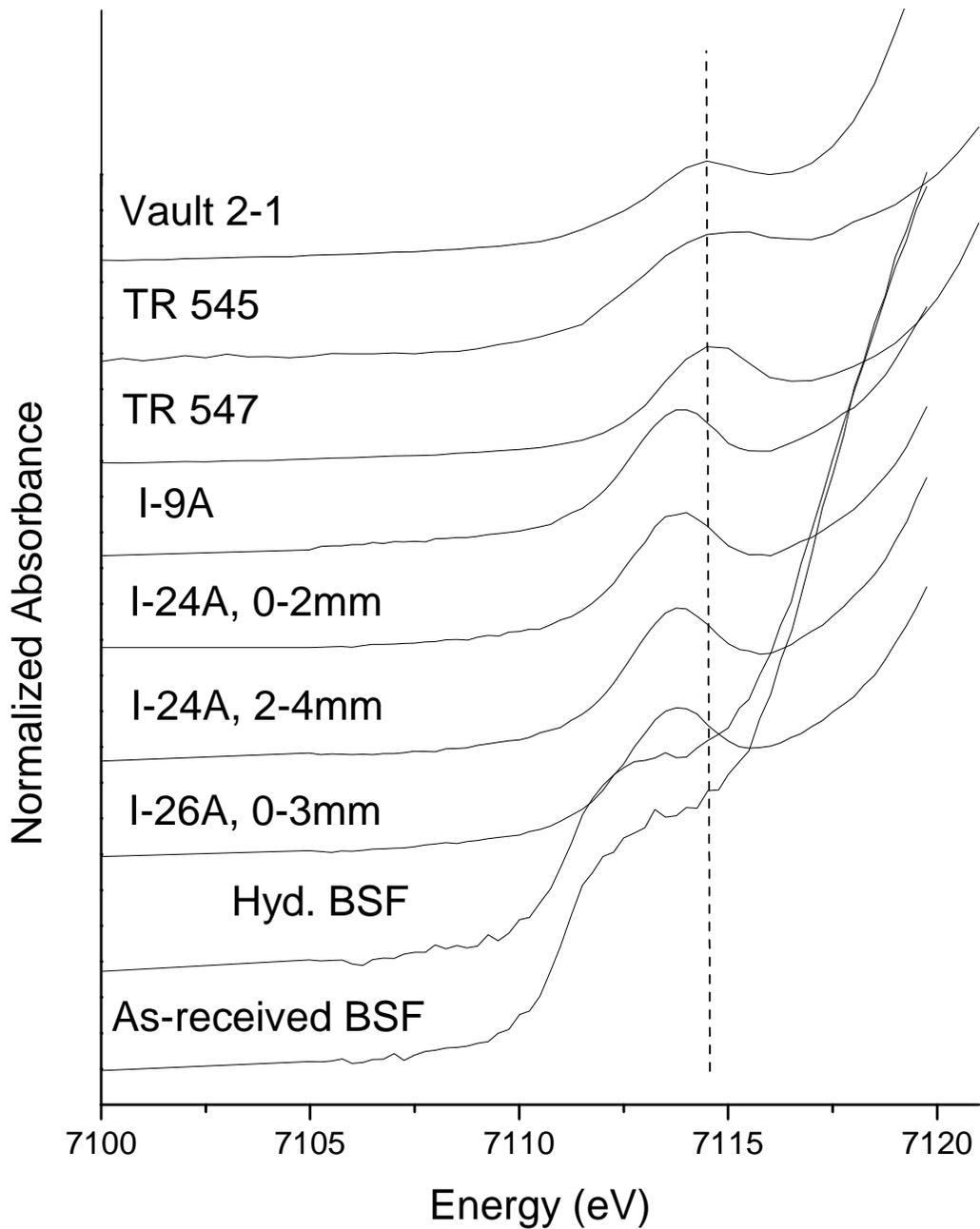
indicated by the pre-edge feature. The older cement and saltstone samples that had been powdered and stored since 2009 under atmospheric conditions (TR547, TR545, and Vault 2) all show Fe(III) features and no pre-edge feature corresponding to reduced Fe. This suggests that all Fe compounds were oxidized in Vault 2, TR547, and TR545. This is an important observation as it demonstrates that the Fe(II) initially present in the new saltstone samples will undergo complete oxidation on the order of years under atmospheric conditions. Comparison of the younger saltstone samples also provides two important pieces of information:

1. Comparison of the small (SS-I-26F) and large (SS-I-24F) saltstone samples indicates that the Fe oxidation state is similar between the two samples. The similarity between the two samples indicates that the smaller sample size indeed does not introduce any experimental artifacts and that the smaller size is representative of the larger size. This conclusion is also supported by the S leaching tests discussed previously in Section 4.1.
2. Samples SS-I-9A and SS-I-24A also show similar Fe XAS spectra indicating the iron speciation within these two samples is similar. The samples were prepared with a 0.5:1 water:dry feed ratio and a 0.6:1 water:dry feed ratio, respectively. Therefore, it does not appear that the lower water content in the preparation of sample SS-I-9A has altered the iron speciation.

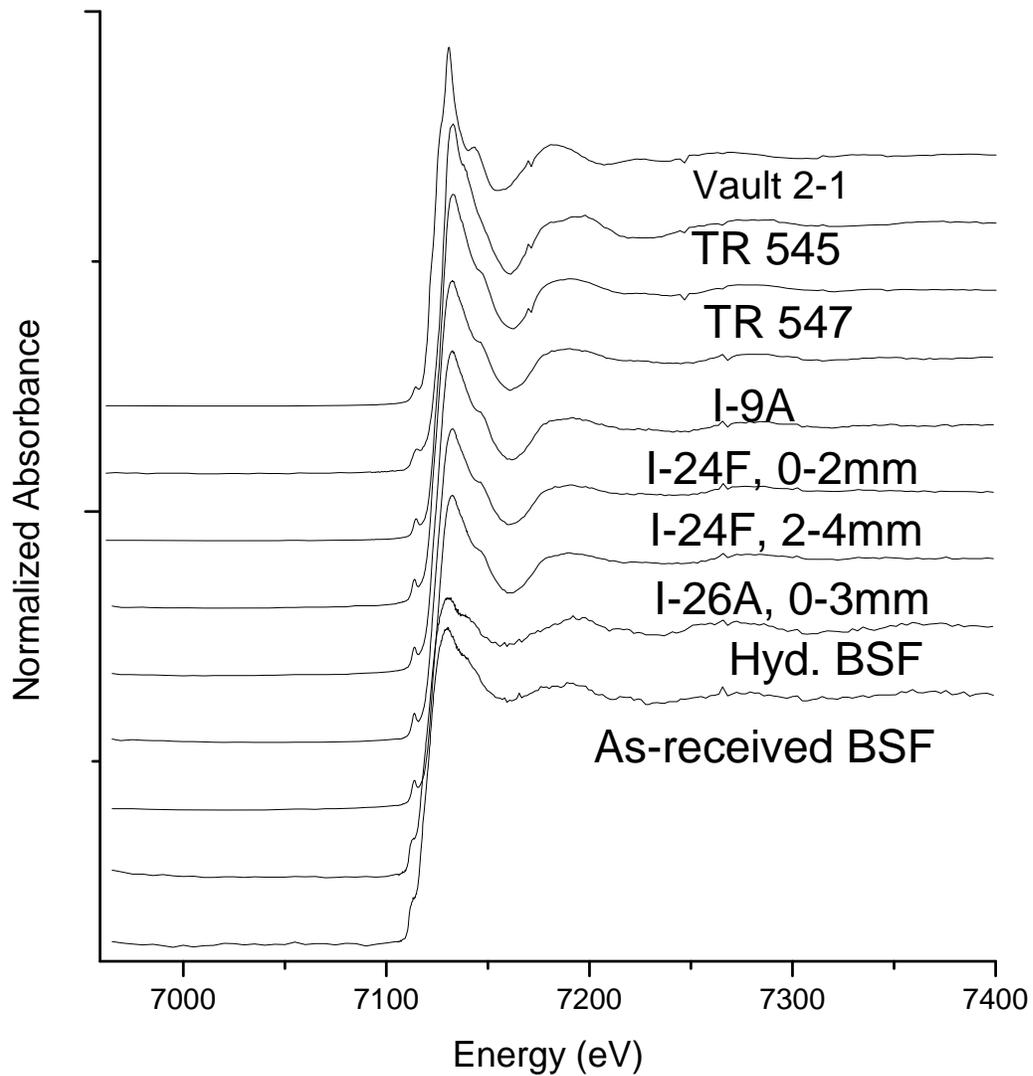
It is noteworthy that the discussions of iron speciation above are mainly qualitative and are primarily focused on comparing the shape of the spectra. In FY15, the primary focus will be to collect data on samples aged for longer times and provide quantitative fits to the XAS data.



**Figure 5: Normalized pre-edge features of Fe K-edge XAS spectra of hematite ( $\text{Fe}^{\text{III}}_2\text{O}_3$ ) and iron sulfide ( $\text{Fe}^{\text{II}}\text{S}$ ). A vertical dotted line is at the peak of whiteline of hematite.**



**Figure 6: Normalized Fe K-edge XAS spectra of various saltstone samples and their components (BFS: Blast furnace slag). Spectra for duplicate samples of Vault 2, TR545, and TR547 are available and are identical to the spectra shown here.**



**Figure 7: Normalized pre-edge features of Fe K-edge XAS spectra of saltstone samples and its components. A vertical dotted line is at the peak of whiteline of hematite.**

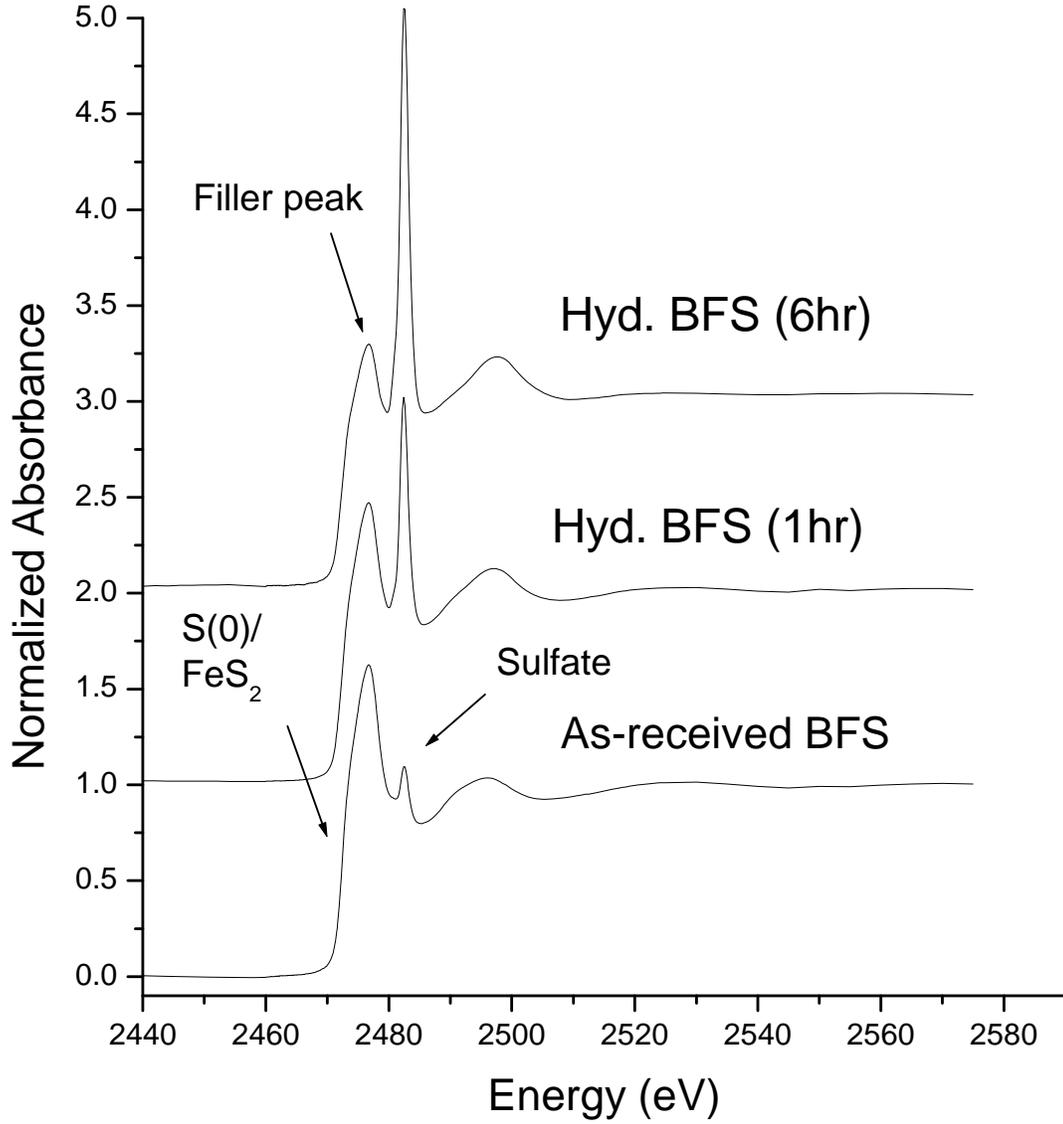
#### **4.3 S XANES Analysis**

Sulfur XANES analysis was conducted in normalized XANES spectra using the following energies that corresponds to the whiteline peaks (sulfide: 2470 eV, pyrite or elemental sulfur 2472 eV, sulfite: 2478.8eV, and sulfate: 2483eV). In most of spectra, there is an intermediate peak at 2476.5 eV. It is a filler energy that does not correspond to any specific compound.

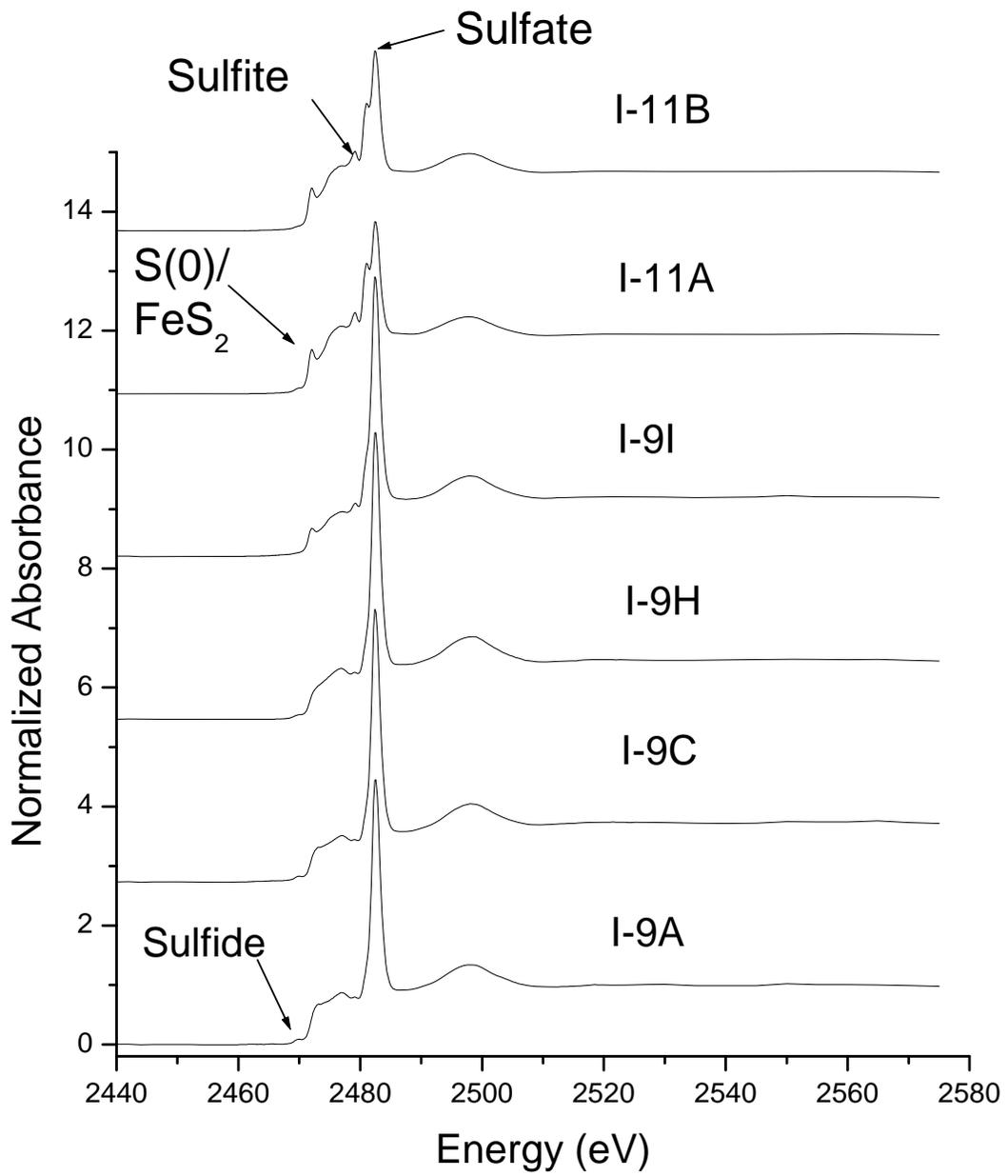
Figure 8 shows the S K-edge XAS spectra of BFS analyzed as a dry sample and as a hydrated sample 1 and 6 hours after hydration with a salt simulant solution at the beamline. While reduced S species are

present in untreated BFS, there is a clear shift in sulfur speciation with increasing time in a simulant solution. Some of this shift may be due to the sulfide added from the saltwaste simulant used to hydrate the BFS. As discussed in Section 4.1 above, this added sulfide would produce approximately a 3300 ppm sulfate ( $\text{mg SO}_4^{2-}$  per kg of hydrated BFS). The exact sulfur concentration of the BFS received from SRR is unknown but assuming a value of 2.5% by weight sulfur, the as received BFS will contain approximately 6000 ppm sulfur. This is twice the sulfur concentration contributed by the saltwaste simulant. From the XAS spectra of the as received (dry) BFS, it is clear there is both sulfide and sulfate in the solid phase. However, the distributions have not yet been quantified. This will be a focus of the FY15 effort. However, since the BFS clearly contains sulfide and has approximately 2x the total sulfur concentration than that provided by the saltwaste simulant solution which was added as sulfate, it can be assumed that the sulfide contribution is from the BFS. The increase in the sulfate peak height relative to the sulfide peak height in the XAS spectra for BFS sample hydrated for 1 hour to 6 hours in Figure 8 indicate that sulfide and or S(0) species of the BFS are being oxidized to sulfate over time. The height of the reduced sulfur peak in Samples BFS-I-11A and BFS-I-11B shown in Figure 9 are further reduced relative to the sulfate peak. Samples BFS-I-11A and BFS-I-11B are hydrated BFS that had been aged for 2 and 3 days, respectively, prior to the XAS measurements. Therefore, in comparing the as received BFS, and the hydrated BFS after analysis at 1 hour and 6 hours with the data from samples BFS-I-11A and BFS-I-11B, a timeline can be constructed to observe the change in ratio of the reduced sulfur peak to the sulfate peak. Since the total S content in these samples is the same, the changing ratio is further indication that reduced S (i.e. sulfide or elemental sulfur) is being oxidized to sulfate in these systems on the order of days. Similar to the Fe XAS discussion above, this discussion is mainly qualitative and is primarily focused on comparing the shape of the spectra. In FY15, the focus will be to collect data on samples aged for longer times and provide quantitative fits to the XAS data.

The freshly prepared hydrated BFS (Samples BFS-I-11A and BFS-I-11B) and saltstone (sample SS-I-24F, Figures 9 and 10) have obvious peaks corresponding to the presence of reduced S species (sulfide, S(0) and sulfite). Unfortunately, sufficient beamtime was not available to analyze any of the historical samples (TR545, TR547) or the smaller saltstone sample (SS-I-26F). It is noteworthy that in sample SS-I-24F, there are differences in samples collected at different depths. At the surface -2 mm, sulfate is the dominant species. The S species are more reduced with increasing depth. This suggests the reducing conditions may persist with decreasing depth. It is suspected that this phenomena is caused by limited  $\text{O}_2(\text{g})$  diffusion into the deeper parts of the sample. As  $\text{O}_2(\text{g})$  infiltrates the sample, it is expected that Tc(IV), S(-II,0), and Fe(II) will be oxidized. Thus, further analysis of samples aged for longer time periods in FY15 may be used to determine an oxygen diffusion rate through saltstone based on the observed oxidation.



**Figure 8: Normalized S K-edge XAS spectra of blast furnace slag before and after hydration in simulant solution.**



**Figure 9: Normalized S K-edge XAS spectra of various saltstone and BFS samples.**

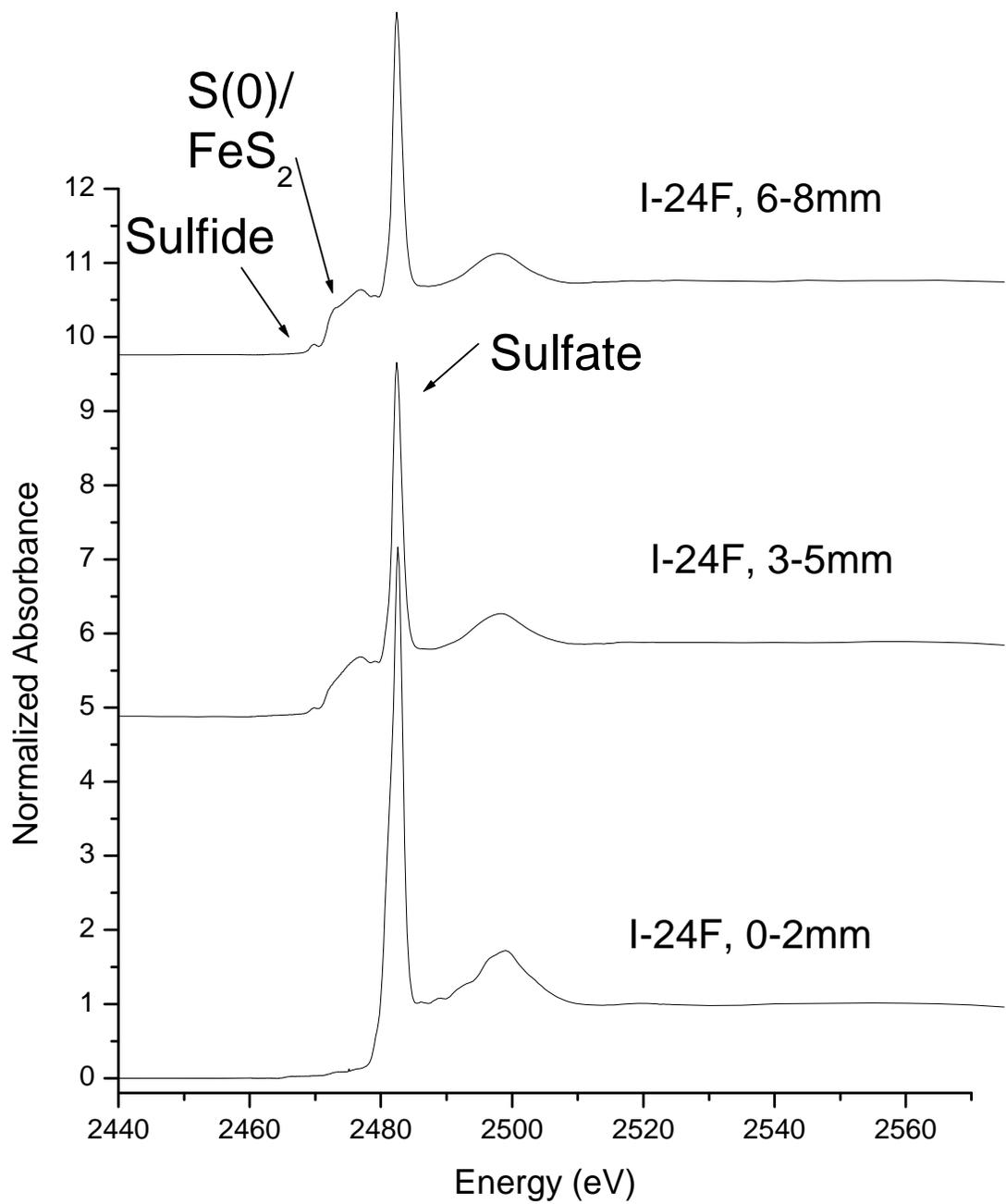


Figure 10: Normalized S K-edge XAS spectra of aged saltstone samples as a function of depth.

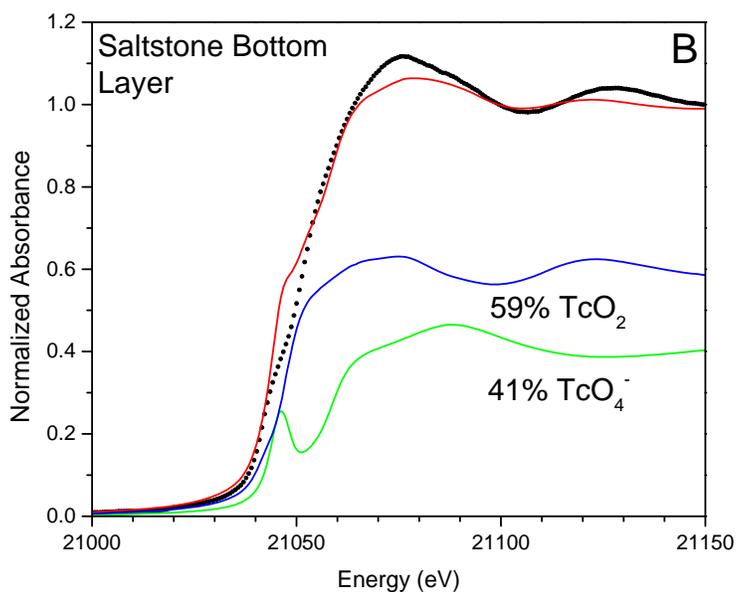
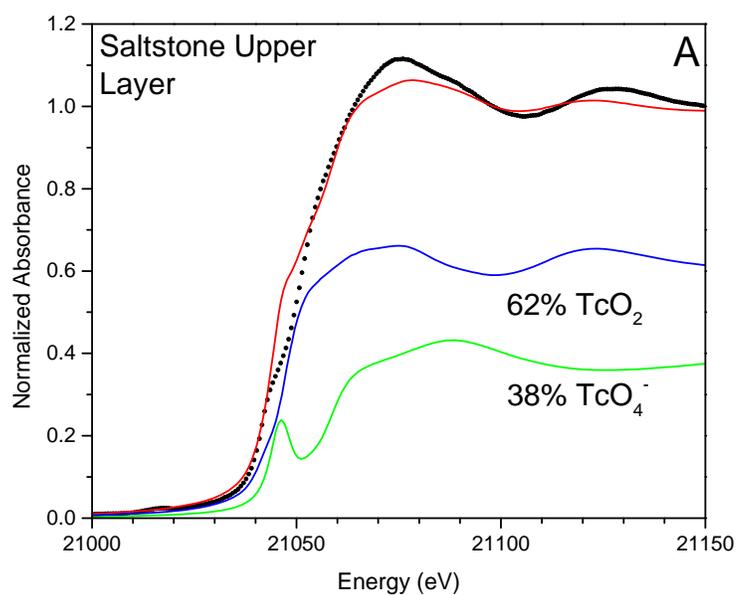
#### 4.4 Tc XAS Analysis

Figures 11 and 12 show Tc K-edge XANES and EXAFS spectra, respectively. To understand the Tc speciation in saltstone samples, we first conducted a linear combination (LC) fit of the Tc amended saltstone XANES spectra using two reference spectra ( $\text{Tc(IV)O}_2$  (am) and  $\text{Tc(VII)O}_4^-$ ). It is important to note the major assumption in LC fit analysis is that the reference compounds represent major chemical species in unknown samples. This analysis indicated that the top layer of saltstone contained ~62% ( $\pm 4.8\%$ ) Tc(IV) and ~38% ( $\pm 4.8\%$ ) Tc(VII). The bottom layer of saltstone contained, ~59% Tc(IV) ( $\pm 4.8\%$ ) and ~41% ( $\pm 4.8\%$ ) Tc(VII). The goodness of fit (R-factor) was 0.00184, suggesting reasonable fit. However, both fits slightly over-estimated the pre-edge region, possibly suggesting the presence of another reduced Tc(IV) phases (e.g.,  $\text{Tc(IV)S}_x$ ). In FY15, additional reference standards (i.e.  $\text{TcS}_x$ ) will be prepared for analysis of these data using the same LC approach.

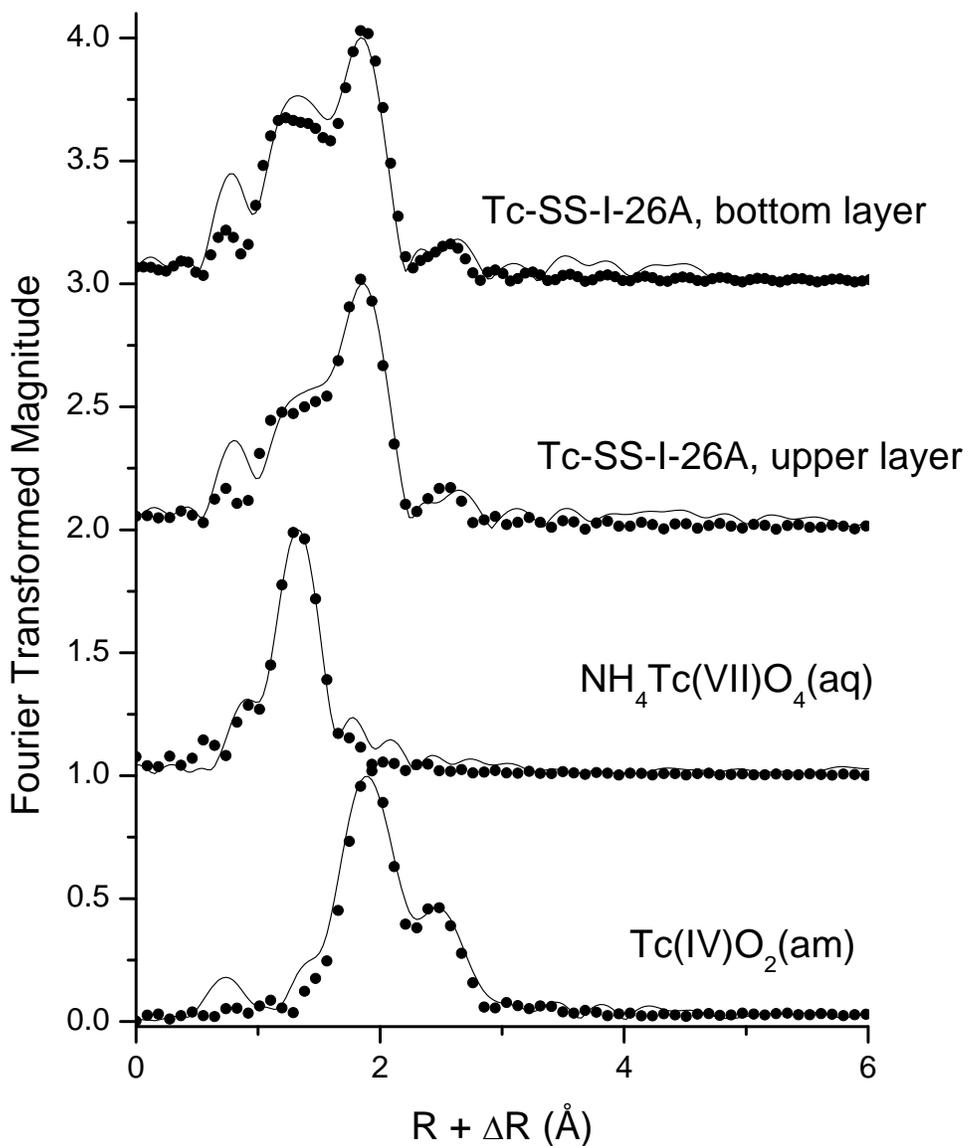
In the  $\text{TcO}_2$ (am) EXAFS spectra, there were two Tc-O distances at ~2.2 Å and ~2.8Å (Table 4, Figure 12). A shorter Tc-O distance at ~2.2 Å was slightly longer than the reported value in the crystalline  $\text{TcO}_2$ (cr) phases, 2.0 Å. (McKeown, et al., 2007). It is likely that highly disordered nature of freshly precipitated, amorphous  $\text{TcO}_2$  is influencing the Tc-O distance. In the aqueous  $\text{TcO}_4^-$  sample, both Coordination number (CN) and radial distance (R) represent the theoretical Tc tetrahedral structure, the interatomic distance for Tc-O is ~1.72Å and CN is 4.5( $\pm 0.5$ ).

In the EXAFS analysis of saltstone samples, the contribution of these phases was considered. Two Tc(IV) and Tc(VII) oxo species were initially considered without constraining any fitting parameters. A reasonable fit (R-factor <0.04) was obtained but the CN of Tc(VII)-O is significantly lower than the theoretical values (~4). For this reason, the best integer approach was used to constrain the CN of Tc(VII)-O shell at 4, and this led to the following fitting procedure to explain large Fourier Transform (FT) features. When  $\text{Tc(IV)O}_2$  species were considered with  $\text{Tc(VII)O}_4^-$ , CN and R of Tc(IV)-O was ~6 and 2.2Å for both samples. The fit quality in R-factor was 0.08 for the top layer and 0.089 for the bottom layer, suggesting good XAS fit. This is consistent with the LC fit analysis. Table 4 shows that the results of structural parameter of least square fit of EXAFS spectra.

In summary, it is clear that un-reduced Tc(VII) is present in both samples. At this stage of XAS analysis, we were limited with one Tc(IV) species,  $\text{Tc(IV)O}_2$  (am). To explain the large FT feature at 1.95 Å (uncorrected for the phase shift), it is possible to incorporate the Tc-S at 2.3 Å from  $\text{TcS}_x$  (Lukens et al., 2005) since it is close to the Tc(IV)-O of 2.2Å. In the next FY, a additional  $\text{Tc(IV)S}_x$  phases will be synthesized and used to fit the data. The intent will be to fit the observed XAS spectra using a combination of either pure  $\text{TcS}_x$  and  $\text{TcO}_2$  phases and/or solid solutions of Tc within  $\text{FeS}_x$  phases.



**Figure 11: Normalized Tc K-edge XANES spectra of Tc reacted saltstone samples (Tc-SS-I-26A) in upper (A) and bottom (B) layers. Linear combination fit was performed using  $\text{TcO}_2(\text{am})$  (blue) and  $\text{TcO}_4^-(\text{aq})$  (green), and fit is shown in filled black circles.**



**Figure 12: Tc K-edge EXAFS spectra of Tc reacted saltstone samples (Tc-SS-I-26A) in upper and bottom layers with two reference compounds ( $\text{TcO}_2(\text{am})$  and ammonium pertechnetate). Raw spectra and fit are shown in black solid lines and filled black circles, respectively.**

**Table 4: The results of least square fit of Tc EXAFS analysis shown in Figure-12. The number in parentheses is the standard deviation of the parameter obtained by EXAFS fit. \*Fixed parameter. CN: coordination number, R(Å): interatomic distance,  $\sigma^2$  (Å<sup>2</sup>): Debye-Waller factor. So2 of 0.9 was used in the fit.**

Sample		Tc(IV)-O	Tc(VII)-O	Tc-O	R factor
TcO <sub>2</sub> (am)	CN	6(1)		16(3)	0.103
	R(Å)	2.28(1)		2.90(1)	
	$\sigma^2$ (Å <sup>2</sup> )	0.005(1)		0.01*	
NH <sub>4</sub> TcO <sub>4</sub> (aq)	CN		4.5(4)		0.024
	R(Å)		1.716(4)		
	$\sigma^2$ (Å <sup>2</sup> )		0.0021(5)		
Saltstone upper layer	CN	6(1)	4*		0.080
	R(Å)	2.21(1)	1.68(1)		
	$\sigma^2$ (Å <sup>2</sup> )	0.005(1)	0.011(2)		
Saltstone bottom layer	CN	6(1)	4*		0.089
	R(Å)	2.22(1)	1.68(1)		
	$\sigma^2$ (Å <sup>2</sup> )	0.006(1)	0.009(1)		

## 5.0 Conclusion

In this work, the chemistry of S, Fe and Tc was examined in saltstone monoliths exposed to oxidizing, high humidity conditions. The oxidation state of S, Fe, and Tc within the saltstone matrix was monitored using XAS techniques and complimentary leaching tests were performed to evaluate the amount of Fe and S leachable from the saltstone. After approximately 7 days of aging under oxidizing, high humidity conditions, sulfate appears to be the dominant S species in leached degassed solutions as well as in the solid phase. However, the true amount of reduced S (sulfur, sulfide) oxidation to sulfate is somewhat occluded by the fact that sulfate was added to the systems in the hydrating saltwaste simulant solution. Furthermore, the initial oxidation state of S within the cement and BFS is currently unknown. Spectra for additional standards will be collected in FY15 and used to quantify the S speciation from the XAS data. Despite being unable to quantify the speciation in this report, comparison of the XAS spectra of hydrated BFS samples aged between 1 hours and 3 days indicate that reduced S is indeed oxidizing to sulfate over time. Furthermore, the S XAS data of a saltstone sample aged 3 days indicated that the amount of reduced S species increased with depth. The first 2 mm were dominated by sulfate but reduced S species were observed from 2 mm to 8 mm.

As shown in the Fe K-edge XAS analysis, ferrous ions in BFS might be a major contributor to the reducing conditions within the saltstone. It may be that reduced iron phases are the major contributor to maintaining Tc in the reduced tetravalent state (e.g., TcS<sub>x</sub>, TcO<sub>2</sub>). This will be investigated in the upcoming synchrotron beam time. This observation was supported by synchrotron based oxidation state speciation analysis of the Tc in two monoliths aged for 29 days (XANES). In FY15 the oxidation state of Fe, S, Tc in monoliths aged for longer time periods (i.e. samples discussed above prepared on March 28, 2014) will be monitored over time using XAS.

A noteworthy aspect of this work is that the concentration of Tc in these saltstone samples is 124 ppm ( $\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$ ) which is significantly higher than the 0.4 ppm ( $\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$ ) targeted in the SDU. Thus it is possible that the Tc loading was sufficiently high to overcome the reducing capacity of the saltstone thus resulting in unreduced Tc(VII). The high concentration was necessary for XAS measurements performed in this work. Accurate measurements of the reducing capacity of the saltstone would be useful in determining the total Tc that could be sequestered in a reduced form. However, those reducing capacity measurements must be done over time since the oxidation of reduced S and Fe(II) over time will change the reducing capacity.

## **6.0 Future Work**

In FY15 we will continue monitoring the oxidation state speciation of Fe, S, and Tc in the saltstone samples prepared on March 28, 2014. Based on the observed data, reduced S(0), S(-2), Fe(II), and Tc(IV) species are all present. Monitoring changes in the oxidation state distribution over time is considered the most important part of this work. Samples are already quenched for a second time-point and are awaiting analysis. Samples from a third and fourth data point after approximately 6 months and 12 months of aging will be analyzed. Also, a major effort will be made to quantify the oxidation state distribution from XAS spectra rather than qualitatively discussing the data. This will include preparation of  $\text{TcS}_x$  solid phases for use as XAS standards.

## 7.0 References

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**Appendix A: E<sub>H</sub>-pH diagrams for Fe, S, and Tc generated using Geochemist Workbench.**

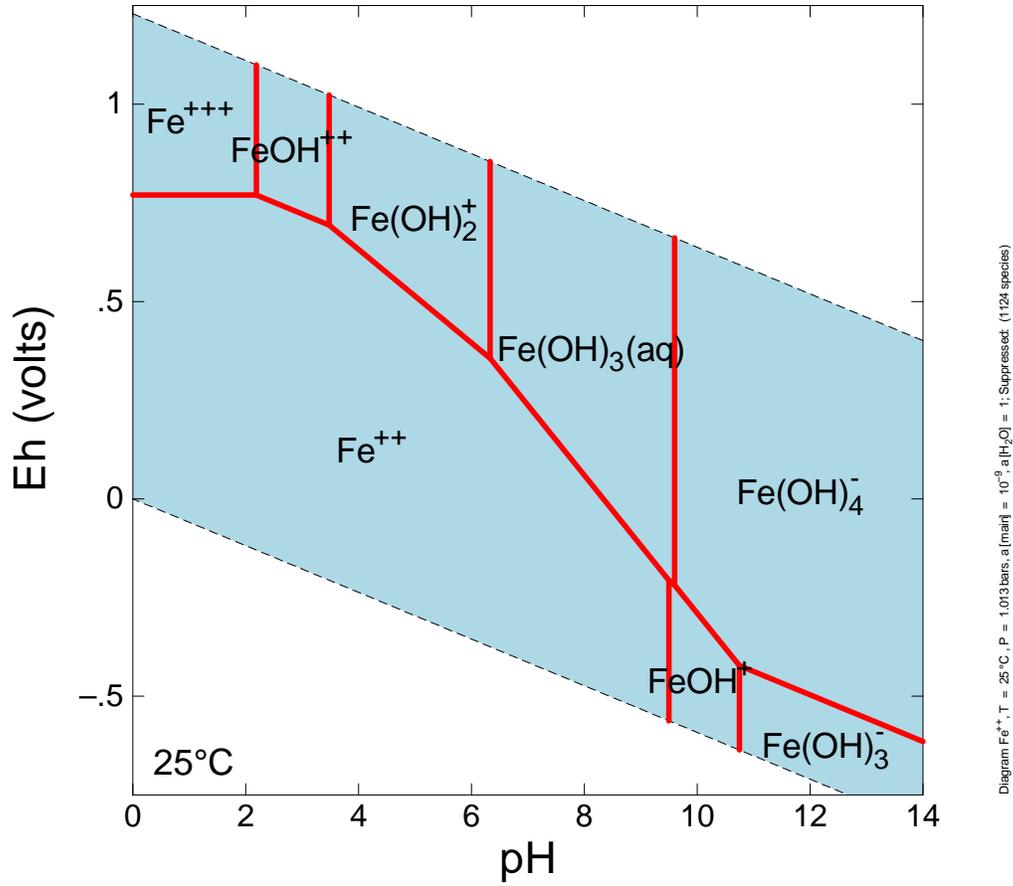


Figure A1: E<sub>H</sub>-pH diagram of iron modeled using Geochemist Workbench and the thermo.com.v8.r6+\_modNEA.dat database.

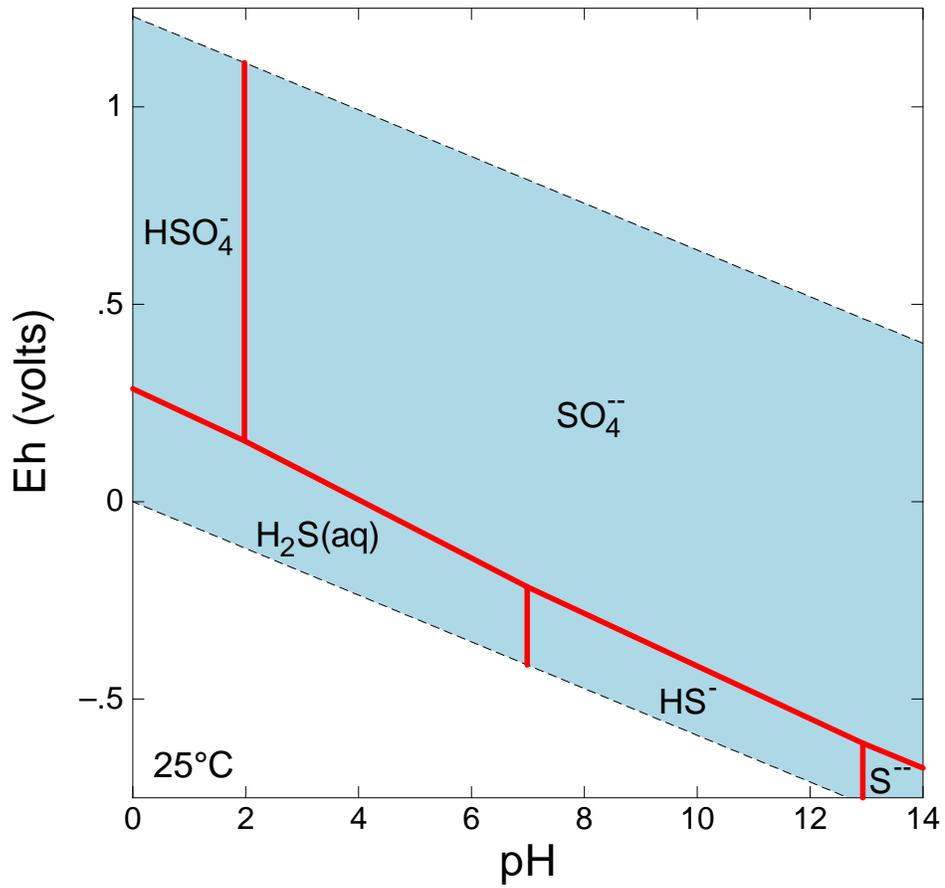


Diagram  $\text{SO}_4^-$ , T = 25°C, P = 1.013 bars, a[ $\text{H}_2\text{O}$ ] =  $10^{-7}$ , a[ $\text{H}_2\text{O}$ ] = 1; Suppressed: (1124 species)

Figure A2:  $E_{\text{H}}$ -pH diagram of sulfur modeled using Geochemist Workbench and the thermo.com.v8.r6+\_modNEA.dat database.

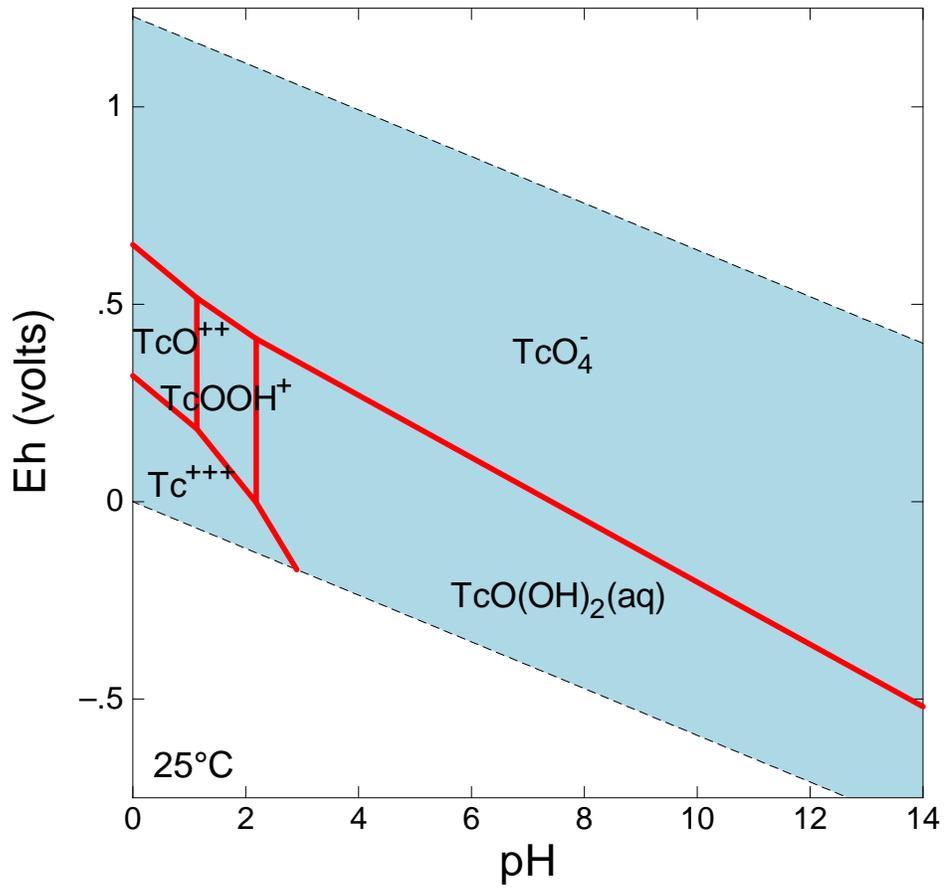


Figure A3:  $E_{\text{H}}$ -pH diagram of technetium modeled using Geochemist Workbench and the thermo.com.v8.r6+\_modNEA.dat database.

## **Appendix B: Procedure for production and aging of salt simulant solution and saltstone samples provided by SRR.**

### **Saltstone Preparation and Curing**

#### **Materials and Equipment**

1. Secure laboratory notebook dedicated to documenting all laboratory efforts associated with the preparation and curing of saltstone monoliths.
2. Deionized water, 18.2 M $\Omega$  cm at 25 °C
3. Laboratory Balance, max. 5100 g,  $\pm$  0.01 g, calibration verified
4. Graduated cylinders
5. Dry powdered materials delivered from SRR
  - a. Class F fly ash (The SEFA Group, Inc. Lexington, SC 29073)
  - b. Grade 100/120 blast furnace slag (Holcim US, Inc. Birmingham, AL 35221)
  - c. Type II Portland cement (Holcim US, Inc. Birmingham, AL 35221)
6. Concrete Molds: Standard 1" ID x 4" plastic concrete molds
7. Humidity-Controlled Curing Oven
8. Laboratory Mixer
9. Salt Waste Simulant Solution

#### **Salt Waste Simulant Solution for making Saltstone (Standard Method for 1 kg dry feed batch)**

Prepare a day in advance of grout processing.

1. Record all pertinent details per preparation log (Table B2).
2. Weigh an empty 1 L polycarbonate volumetric flask, plus cap.
3. Weigh all chemicals in Table B1 other than the NaOH soln. and combine in 1 L polycarbonate flask with about half of the total volume of DI water. Stir.
4. Weigh and add the NaOH as a 50% soln.
5. Fill flask with DI water up to a little less than 1 L.
6. Add magnetic stirring bar and cap the flask. Stir the solution overnight. Proceed with caution; the dissolution of Salt Waste Solution components is exothermic.
7. Add contaminant spike solution as necessary just before making to final volume.
8. Remove the magnetic bar from the flask, and add DI water to make 1 L. Put the magnetic bar back in and stir the solution. Remove the bar, and verify the final volume as 1 L. Repeat the process if necessary.
9. Weigh the flask containing the solution plus the cap. Calculate the solution density and the mass of water per unit mass of salt solution

Note for step 7  $^{99}\text{Tc}$  will be added as the contaminant. As discussed above to facilitate XANES and EXAFS analysis, the concentration in experimental samples may be higher than the concentration used in the real saltstone facility. Conversion between the mass concentration of ppm ( $\text{mg}_{\text{Tc-99}}/\text{kg}_{\text{saltstone}}$ ) to an activity concentration for Tc in  $\text{pCi}_{\text{Tc-99}}/\text{kg}_{\text{saltstone}}$  can be performed using equation 1.

$$A \left( \frac{pCi}{kg} \right) = \frac{[Tc] \left( \frac{mg_{Tc}}{kg_{saltstone}} \right) A \left( \frac{atom}{mol} \right) \lambda (s^{-1})}{MW \left( \frac{g}{mol} \right)} * 27 \frac{pCi}{Bq} * \frac{1g}{1000mg} \quad (\text{Equation 1})$$

In equation 1, [Tc] is the Tc-99 concentration in  $mg_{Tc}/kg_{saltstone}$ , A is Avogadro's number ( $6.022 \times 10^{23}$  atoms per mol),  $\lambda$  is the decay constant ( $1.04 \times 10^{-13} s^{-1}$ ), MW is the molecular weight of Tc (99 g per mol), and  $A_{Tc}$  is the activity concentration of Tc-99 in saltstone in  $pCi_{Tc-99}/kg_{saltstone}$ .

### **Methods for Preparation of Simulant Saltstone (Standard Method for 1 kg dry feed batch)**

1. Record all pertinent details per cementitious paste preparation log (Table B3).
2. Weigh each of three dry powdered materials into 5QT disposable pails using plastic scoops.
  - a. Class F fly ash - 450 g (Mixing Pail 1)
  - b. Grade 100/120 blast furnace slag - 450 g (Mixing Pail 2)
  - c. Type II Portland cement - 100 g (Mixing Pail 3)
    - Caution: These materials are very fine powders. Wear proper PPE and a dust mask while handling these materials!
3. Slowly pour the weighed materials in Pails 2 and 3 into Pail 1 while in the hood. Mix them with a mechanical mixer at low rpm (30-50 rpm). While mixing, move the pail around the mixing arm to make sure the materials are thoroughly homogenized. Occasionally, stop the mixer, and scrape the bottoms and sides of the pail to homogenize any unmixed materials.
4. Calculate the necessary salt solution mass for 1 kg of dry materials. The water to dry feeds ratio should be 0.6. Calculate the actual mass of salt waste simulant solution containing 0.6 kg water, and weigh the salt solution using Pail 3.
5. Move Pail 1 and the mixer from the hood to a bench top. While slowly mixing the powders, add the required simulant salt solution in small increments. Use the solution to rinse any remaining dry materials in Pails 2 and 3 into Pail 1.
6. Increase mixer speed to approximately 250 rpm. Stop the mixing occasionally, and check the mixture for aggregate formation. Finish the mixing process within 20 min.
7. Pour the grout into the standing molds in one increment, and then cap immediately.
8. Transfer the saltstone molds into the humidity controlled curing oven and cure at a high degree of humidity (> 95 %) following a curing temperature profile provided by SRR.
9. All cured samples (i.e., cores, core sections, etc.) will be stored under an inert atmosphere (i.e., N<sub>2</sub>) at ambient temperature and high humidity.

**Table B1. Base composition of ARP/MCU Saltwaste Simulant**

<b>Material</b>	<b>ARP/MCU Salt Simulant</b>	
	<b>Molarity (moles/L)</b>	<b>Mass (g/L)</b>
Sodium Hydroxide, NaOH (50 wt.% by weight)	1.594	127.50
Sodium Nitrate, NaNO <sub>3</sub>	3.159	268.48
Sodium Nitrite, NaNO <sub>2</sub>	0.368	25.39
Sodium Carbonate, Na <sub>2</sub> CO <sub>3</sub>	0.176	18.65
Sodium Sulfate, Na <sub>2</sub> SO <sub>4</sub>	0.059	8.37
Aluminum Nitrate, Al(NO <sub>3</sub> ) <sub>4</sub> .9H <sub>2</sub> O	0.054	20.33
Sodium Phosphate, Na <sub>3</sub> PO <sub>4</sub> .12H <sub>2</sub> O	0.012	4.67

**Table B2. Saltstone Waste Simulant and Permeant Preparation Log**

Logbook:				Requested by:			
Recipe ID:				Date:			
Sample #:				Task #:			
Order of Addition	Chemical	Assay	#	Target Mass (g)	Actual Mass (g)	Balance ID	Date and Initials
1	$\text{NaNO}_3$	1		268.48	102.41	II	5/1/20
2		2			105.13	II	5/1/20
3		3			60.94	II	5/1/20
4	$\text{NaNO}_2$	1		25.39	25.40	II	5/1/20
5	$\text{Na}_2\text{CO}_3$	1		18.65	18.65	II	5/1/20
6	$\text{Na}_2\text{SO}_4$	1		8.37	8.38	II	5/1/20
7	$\text{Al(NO}_3)_3$	1		20.33	20.36	II	5/1/20
8	$\text{Na}_2\text{PO}_4$	1		4.67	4.68	II	5/1/20
9	$\text{H}_2\text{O}$	1			~200 mL		5/1/20
10	$\text{NaOH } 50\%$	1		127.50g	127.42	II	5/1/20
Total Batch (g):							
Reviewed by:				Date:			

Water source - Elyon Purilab Flex 18.2 MPa-cm, < 1ppb TOL

Table B3. Saltstone Cementitious Paste Preparation Log

Logbook: <i>Tc-Saltstone-2014-I</i>		Requested by: <i>—</i>					
Recipe ID: <i>—</i>		Date: <i>3/26/14</i>					
Sample #: <i>—</i>		Task #: <i>—</i>					
Order of Addition	Chemical	Assay	#	Target Mass (g)	Actual Mass (g)	Balance ID	Date and Initials
	<i>P3-PL</i>			<i>50g</i>	<i>50.14g</i>	<i>II</i>	<i>3/26</i>
	<i>P2-BFS</i>			<i>225g</i>	<i>223.17g</i>	<i>II</i>	<i>3/26</i>
	<i>P1-FA</i>			<i>225g</i>	<i>224.99g</i>	<i>II</i>	<i>3/26</i>
	<i>Simulant</i>			<i>442g</i>	<i>442.65g</i>	<i>II</i>	<i>3/26</i>
Total Mass (g)					<i>942.95g</i>		
Reviewed by: <i>Pendall</i>		Date: <i>3/26/14</i>					
Mixing Parameters				Comments			
Container: <i>Plastic bucket</i>				<i>- stirred dry feed 10min @ 20rpm</i>			
Mixing method: <i>overhead</i>				<i>- slowly added simulant and stirred @ 250rpm for 15 minutes</i>			
Start mixing time: <i>10:00</i>				<i>- stirring stopped @ 5min + 10min to check for lumps.</i>			
End mixing time: <i>10:25</i>							
Total mixing time: <i>25min</i>							
Measured density: <i>not measured</i>							
Reviewed by: <i>Pendall</i>		Date: <i>3/26/14</i>					

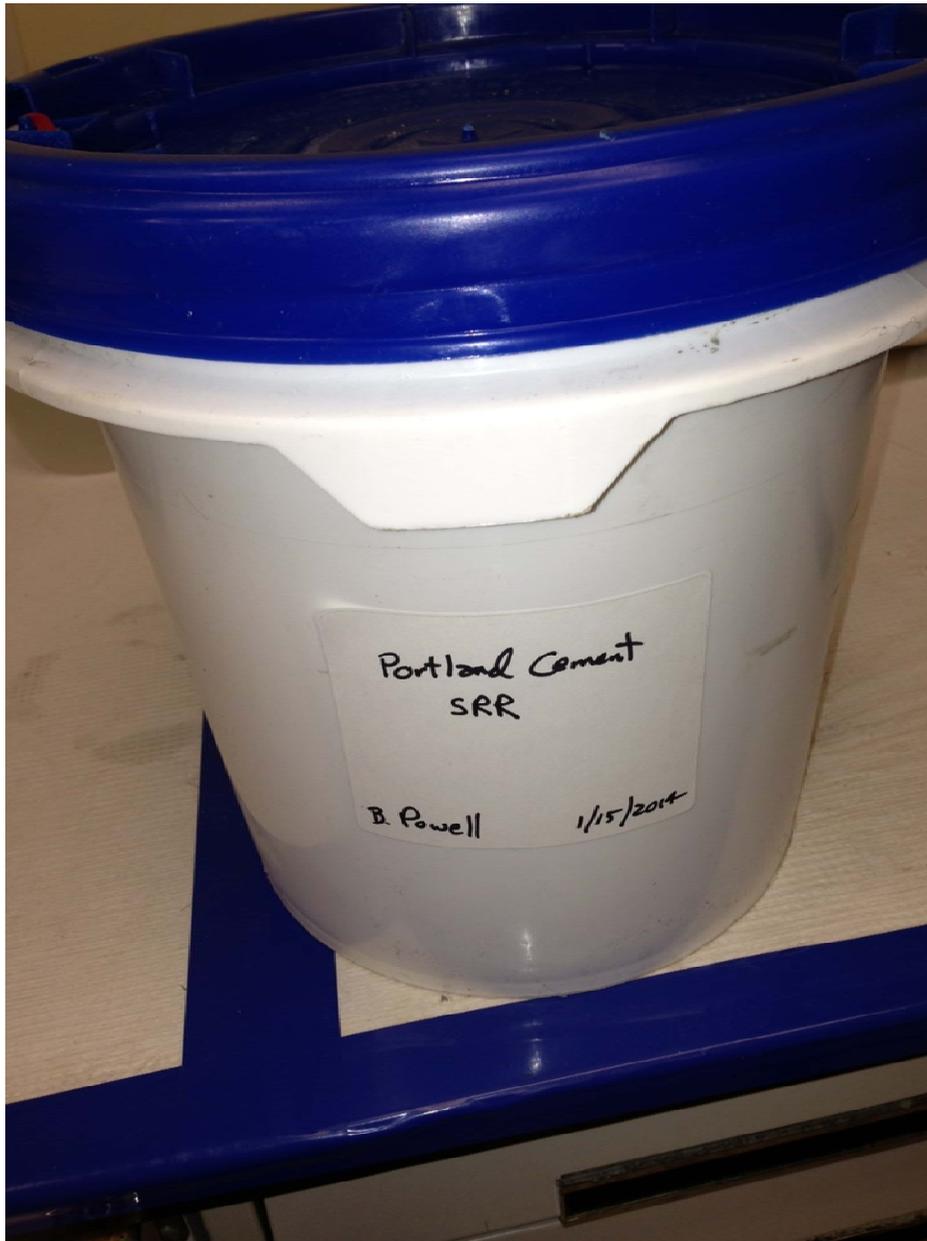
*Simulant to dry feed 442.65g (50.14 + 223.17 + 224.99) = 0.504*

*- note 8.5g of dry mix and 3g simulant was held back for Tc99 sample preparation.*

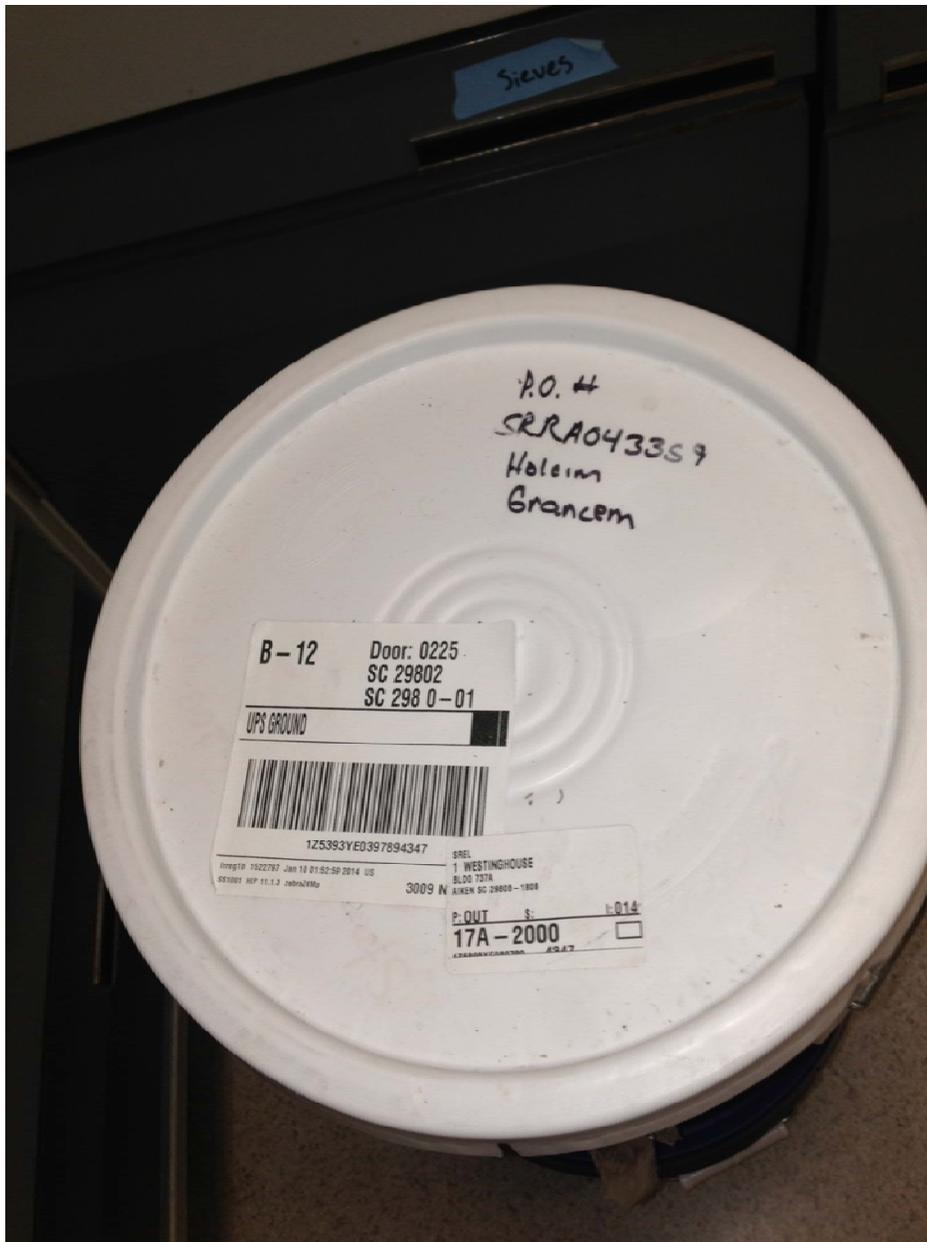
Continued on Page 26

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Photographs of the Blast Furnace Slag, Fly Ash, and Cement received from S. Simner on 1/15/2014.



**Figure B1: Photograph of bucket containing Portland cement received from S. Simner on 1/15/2014.**



**Figure B2: Photograph of bucket containing blast furnace slag received from S. Simmer on 1/15/2014.**

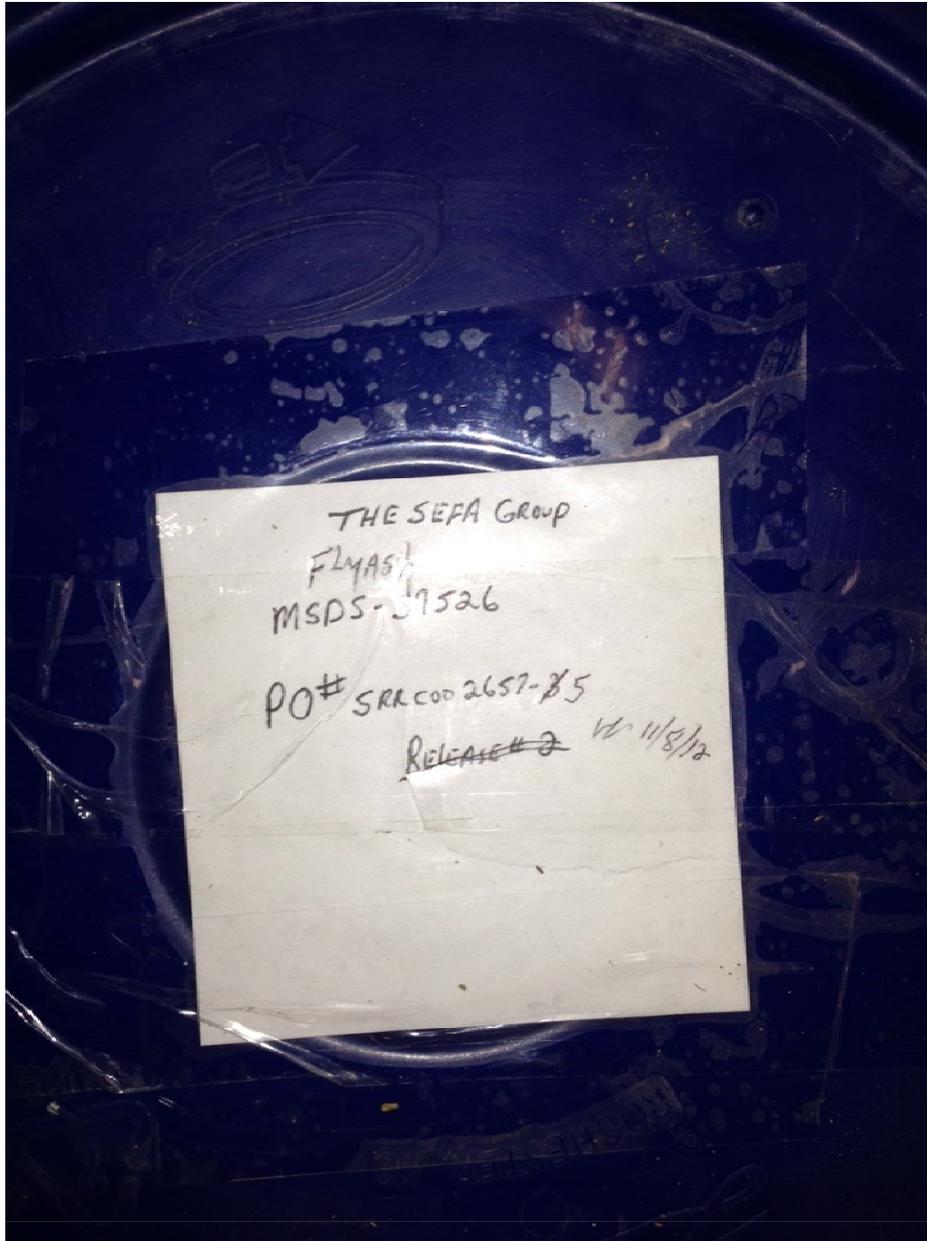


Figure B3: Photograph of bucket containing fly ash received from S. Simner on 1/15/2014.

## Appendix C: Sulfur and Fe Leaching Data from BFS

Sample Event: BFS S and Fe leaching test using 15 mL degassed MiliQ water.

Note: To produce the solid phase concentrations in terms of  $\text{mg}_{\text{Sulfur}}/\text{kg}_{\text{saltstone}}$  as shown in Figure 3, the concentration of sulfur reported in the leachate below were multiplied by the total volume of leachate (15mL) and divided by the dry mass of BFS.

$$[S] \left( \frac{\text{mg}_S}{\text{kg}_{\text{BFS}}} \right) = [S]_{\text{leachate}} \left( \frac{\text{mg}}{\text{L}} \right) * \frac{V_{\text{leachate}} (\text{mL})}{m_{\text{BFS}} (\text{g})} * \frac{1 \text{ L}}{1000 \text{ mL}} * \frac{1000 \text{ g}}{1 \text{ kg}}$$

Sample	Dry mass (g)	Sulfide (mg/L)	[Sulfate] (mg/L)	[S2O3] (mg/L)	[sulfite] (mg/L)	Fe (mg/L)	pH
Hyd BFS 1	0.336	0.27	98.42	11.50	BD	BD	10.37
Hyd BFS 2	0.356	0.20	109.13	23.74	BD	BD	10.74
BFS 1	0.193	0.53	6.70	1.88	BD	BD	10.84
BFS 2	0.216	0.59	7.09	1.93	BD	BD	10.94

## Appendix D: Sulfur and Fe Leaching Data from 29 d aged saltstone

Sample Event: SS-I-24A and SS-I-24F sulfur and iron leaching test using 15 mL degassed MiliQ water.

Note: To produce the solid phase concentrations in terms of  $\text{mg}_{\text{Sulfur}}/\text{kg}_{\text{saltstone}}$  as shown in Figure 4, the concentration of sulfur species reported in the leachate below were corrected for dilution factor and then multiplied by the total volume of leachate (15mL) and divided by the dry mass of saltstone.

$$[S] \left( \frac{\text{mg}_S}{\text{kg}_{\text{saltstone}}} \right) = [S]_{\text{leachate}} \left( \frac{\text{mg}}{\text{L}} \right) * \frac{V_{\text{leachate}} (\text{mL})}{m_{\text{saltstone}} (\text{g})} * \frac{1 \text{ L}}{1000 \text{ mL}} * \frac{1000 \text{ g}}{1 \text{ kg}}$$

Sample ID	Drill Depth (mm)	Dry mass (g)	[Sulfate] (mg/L)	[S <sub>2</sub> O <sub>3</sub> ] (mg/L)	[sulfite] (mg/L)	[sulfide] (mg/L)	Fe (mg/L)	pH
SS-I-24F_1	0-5	0.52	224.55	37.98	BD	BD	BD	12.02
SS-I-24F_2	5-9.5	0.64	251.30	43.37	BD	BD	BD	12.09
SS-I-24F_3	9.5-15	0.49	219.39	38.02	BD	BD	BD	12.01
SS-I-24F_4	15-19.8	0.55	231.53	40.12	BD	BD	BD	12.08
SS-I-24F_5	19.8-25.2	0.81	285.93	50.12	BD	BD	BD	12.14
SS-I-24F_6	25.2-30	0.39	182.54	29.32	BD	BD	BD	11.99
SS-I-24A_1	0-5	0.55	295.33	50.17	BD	BD	BD	11.99
SS-I-24A_2	5-10	0.46	223.50	38.35	BD	BD	BD	12.05
SS-I-24A_3	10-14.8	0.55	214.11	36.23	BD	BD	BD	12.05
SS-I-24A_4	14.8-20.2	0.45	208.81	32.91	BD	BD	BD	12.02
SS-I-24A_5	20.2-25	0.86	310.06	52.44	BD	BD	BD	12.08
SS-I-24A_6	25-30.3	0.65	245.35	40.11	BD	BD	BD	12.06