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NATURAL RESOURCES AND ENVIRONMENTAL SCIENCES
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Examination of Tc, S, and Fe Speciation within Saltstone

Yuji Arai and Brian A. Powell

FY15 Final Report

SRR Project Title: SRR Technical Support Provided by Clemson University

SRR PO Number: SRRA042328

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LIST of ACRONYMS

ACS: American Chemical Society

AVS: Acid volatile sulfides

BFS: Blast furnace slag

CN: Coordination number

DDI: Distilled deionized water

EXAFS: Extended X-ray absorption fine structure spectroscopy

FY: Fiscal year

IC: Ion chromatography

ICP-OES: Inductively coupled plasma optical emission spectrometry

ISE: Ion specific electrode

LSC: Liquid Scintillation Counting

NIST: National Institute of Standards and Technology

PIPS: Passivated Implanted Planar Silicon

SDU: Saltwaste Disposal Unit

SRR: Savannah River Remediation LLC

SRS: Savannah River Site

SSRL: Stanford Synchrotron Radiation Laboratory

UIUC: University of Illinois at Urbana-Champaign

UV-Vis: Ultraviolet-Visible Spectroscopy

XANES: X-ray absorption near edge structure 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}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 for over 450 days. 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 primarily describes the results from samples aged between 117 to 453 days but also includes a re-evaluation of samples described in the previous years report which were aged for 3 to 29 days. Additional leaching tests for Fe, S, and Tc were performed to support the XAS studies. The XAS analysis will indicate which reduced Tc/S/Fe species in solid phase contributed to the labile Tc/S/Fe in the leaching test. In this work, the oxidation state of S, Fe, and Tc was determined in samples aged for up to 453 days.

Tc-amended samples were sent for bulk Tc K-edge XAS measurements to determine the chemical speciation of Tc alongside Tc-free samples which were prepared to determine Fe and S speciation. The analysis could not be performed on the same samples because of the regulations at the Stanford Synchrotron Radiation Laboratory (SSRL) which do not allow analysis of radionuclide bearing samples on the beamline required for Fe and S speciation. The Tc-free bearing samples were subjected to the following analyses:

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 Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).
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.

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 ICP-OES. 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 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., Extended X-ray Absorption Fine Structure Spectroscopy) 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. However, a significant amount of thiosulfate is also present but appears to decrease as a function of time and increase as a function of depth. Thus, it appears the oxidation front moving through the saltstone facilitates oxidation of the sulfide originally present in the saltstone. In the first years effort of this project (reported in the FY14 report, Arai and Powell, 2014) pure BFS was analyzed in addition to the saltstone samples. It was determined that a significant amount of sulfide (present in the unhydrated BFS) is oxidized to sulfate upon hydration (i.e. within a few hours after hydration with the salt waste simulant solution). Both ferrous and ferric iron were still present in the saltstone samples after 3 days of preparation. Thus it appears that initially both ferrous iron and some sulfide remain within the saltstone. Upon continued aging to 117 days, no ferrous iron was detected in any sample but small amounts of sulfide persisted. Furthermore, measureable amounts of thiosulfate were observed in leaching studies. Thus it appears that over longer time scales (i.e. >100 days) reduced sulfur species continue to provide reducing capacity within the saltstone.

In the Tc-spiked saltstone sample, both reduced Tc(IV) as well as unreduced Tc(VII) were observed after 29 days. However, after 117 days, no Tc(VII) was observed in the saltstone using XAS measurements. The saltstone samples (both Tc-amended samples and Tc-free samples) accumulated water on the surface of the monolith while aging in the high humidity, oxic atmosphere chamber used in this work. The concentration of Tc within the water increased over time up to $35\% \pm 5\%$ (2σ uncertainty) of the total Tc added to the samples after 453 days. The leaching of Tc from the saltstone into the pooled water reduced the fraction of Tc(VII) within the saltstone and is hypothesized to be the reason that Tc(VII) was not observed in XAS analysis of samples after 117 days (thought Tc(IV) phases remained in the saltstone as discussed below). The pooled water was removed prior to preparation of XAS samples so that only the pore water within the saltstone (which may contain small amounts of Tc(VII)) remained. The leaching of Tc into the pooled water was unexpected and is hypothesized to be associated with the incomplete reduction of Tc(VII) upon preparation of the saltstone. This could be due to the relatively high loading of Tc in this work (14 mg_{Tc}/kg_{saltstone} relative to 0.4 mg_{Tc}/kg_{saltstone} expected in real samples) which may have overcome the capacity of the saltstone reducing capacity or induced a kinetic limitation on the reduction of Tc(VII) to Tc(IV).

The Tc speciation within saltstone samples aged over 117 days could not be determined using the XANES data alone collected in this work. Attempts were made to fit the observed

XANES data using reference compounds TcO_4^- , TcO_2 , and TcS_x . However, fitting the XANES data using these standards (i.e., linear combination of XANES spectra fit) was not able to reproduce the observed data. The inability of the standard compounds to reproduce the observed spectra indicates that additional reactions were occurring. Based on qualitative changes in the EXAFS spectra and the leaching data, it appears that after reduction of Tc(VII), Tc(IV) first hydrolyzes then undergoes a sulfidization step to form TcS_x based on the three reactions listed below. Over time, reaction with sulfide causes some hydrolyzed species to become partially sulfidized (step 2) with the reaction progressing to a fully sulfidized species (TcS_2) over time (step 3).

- Step 1. Reduction of $\text{Tc(VII)}\text{O}_4^-$ by ferrous iron and or sulfides to form $\text{Tc(IV)}\text{O}_6 \rightarrow$ hydrolysis to form $\text{Tc(IV)}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3$
- Step 2. $\text{Tc(IV)}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3 \rightarrow$ partial sulfidation $\rightarrow \text{Tc(IV)}\text{O}(\text{H}_2\text{O})_{5-x}\text{S}_x^{2-}$ (This step 2 is limited by low sulfide activity in saltstone)
- Step 3. Polymerization of sulfidized species $\rightarrow \text{Tc(IV)}\text{S}_2$ like species at where high sulfide and Tc activity is present

While the partially/fully sulfidized Tc(IV) species at each point in time were observed in this work, the data show that there was no/near negligible Tc(VII) in aged saltstone samples.

1.0 Introduction

1.1 Overview

This work is a continuation of a project started in Fiscal Year (FY) 2014 under the same name and SRR PO Number (SRRA042328). In this work saltstone samples were prepared with and without a Tc amendment. The samples were aged in a high humidity, oxic chamber following a temperature profile provided by Savannah River Remediation LLC (SRR). Multiple samples were prepared and subsequently tested at various time intervals. Samples were taken to the Stanford Synchrotron Radiation Laboratory (SSRL) for x-ray absorption spectroscopy (XAS) to determine the Fe, S, and Tc speciation. In the FY14 report associated with this effort, samples aged up to 30 days were discussed along with several long term (>5 years) samples taken from an archive of reducing grout samples at Clemson University (Arai and Powell, 2014). The data in this report describes samples aged from 117 to 453 days.

1.2 Background

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}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 (TcO_4^- ; i.e., Tc(VII)), the oxidized form of Tc, and the rapid oxidation of reduced Tc (i.e., Tc(IV)) when exposed to even moderate levels of 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 blast furnace slag (BFS), which contain reductants, such as sulfide (S^{2-}) and ferrous iron (Fe^{2+}), are added to cementitious material formulations for waste stabilization as a means of enhancing the retention of redox sensitive ^{99}Tc , though the mechanism by which ^{99}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}Tc . Understanding and measuring the chemistry responsible for this immobilization may ultimately permit kinetic and thermodynamic modeling. As the oxidation state speciation of Fe, S, and Tc are vital for understanding this work, E_{H} -pH diagrams for each species are provided in Appendix A. It is noteworthy that the reduced species considered in this work (Tc(IV), Fe(II), S(-II), and S(0)) are only thermodynamically stable at very low E_{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}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

2.1 Preparation of Tc-free saltstone samples

Saltstone monoliths without ^{99}Tc addition were prepared at Clemson University on 3/28/2014. ^{99}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 the task plan associated with this work (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 agglomerate 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. Figure 1 indicates samples aging in an oxic, humid chamber. 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 the Saltstone Disposal Unit (SDU) as indicated in Table 1.

As discussed below, Tc-amended samples were prepared in smaller tubes to minimize the amount of radioactivity used in the experiments. These samples were approximately 1.7 cm^3 each as discussed below. 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 ^{99}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 the ceramic disc shown in the picture above. (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).

Table 1: Temperature profile used for curing and aging of saltstone samples started on 03/28/2014. This profile was provided by SRR and follows the measured temperatures within a 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

These saltstone samples were prepared on March 28, 2014. The samples were then removed at various times and utilized for XAS and Fe/S leaching studies. The exact sampling dates for each sample are provided in Table 2 along with additional data (relevant to sample analysis) in Table 4.

Table 2: Listing of preparation date and sampling date for Tc-free saltstone monoliths in 50mL (Samples SS-I-24X) and 2mL tubes (Samples SS-I-26X)

Event	Date	Total # of aging days	Sample IDs sacrificed
Preparation date	3/28/2014		
Sampling Event 1	4/1/2014	4	SS-I-24A, SS-I-26A, SS-I-24F, SS-I-26F
Sampling Event 2	7/23/2014	117	SS-I-24B, SS-I-26B, SS-I-24G, SS-I-26G
Sampling Event 3	1/3/2015	281	SS-I-24C, SS-I-26C, SS-I-24H, SS-I-26H
Sampling Event 4	6/29/2015	458	SS-I-24D, SS-I-26D, SS-I-24H, SS-I-26H

2.2 Preparation of Tc-amended saltstone samples

Seven ^{99}Tc amended samples were prepared with 124 ppm ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$) ^{99}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 $^{99}\text{Tc(VII)}$ was added (in a soluble form as TcO_4^- from a NH_4TcO_4 solution) to the simulant solution to achieve a final concentration of 124 ppm ^{99}Tc in the final saltstone samples (described in the following paragraph). There were four planned timepoints for analysis in the original experimental design. Thus, there were three additional ^{99}Tc amended samples to use as needed in future testing. One sample was sacrificed for a H_2O_2 reactivity test described in the subsequent text. At the time of this report, the additional two samples have been frozen and archived at Clemson University to be used in future experiments beyond the scope of this project if needed. The 124 ppm ^{99}Tc loading is significantly higher than the expected concentration in the SDU. However, this higher concentration is necessary to facilitate XAS analysis as described below. Assuming a concentration of ^{99}Tc in the salt solution currently being processed at SRS (Bannochie, 2013) of $1.93 \times 10^4 \text{ pCi/mL}$, the estimated ^{99}Tc concentration within the saltstone is $6.8 \times 10^6 \text{ pCi/g}$ or 0.4 $\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$. This calculation assumed a 0.6 water to dry feed ratio, a salt solution density of 1.257 g/cm^3 , and a saltstone product density of approximately 1.7 g/cm^3 .

Due to the high cost and high amount of radioactivity required to prepare ^{99}Tc amended samples in 1" x 4" plastic molds, the ^{99}Tc samples were smaller and prepared in 2 mL (~0.25" diameter and 1" height) polypropylene centrifuge tubes yielding approximately 1.7 cm^3 of saltstone per sample. An 8.5 g aliquot of the dry feed mixture of BFS, cement, and fly ash prepared when making the Tc-free samples above was removed and mixed with 7.55 g of simulant (Table B3) that was spiked with $^{99}\text{Tc(VII)}$ to achieve a concentration of 0.26 ppm $^{99}\text{Tc(VII)}$ ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{simulant}}$). 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 samples aged for 117 to 453 days. A listing of the sampling dates or the Tc-bearing samples is provided in Table 3 along with additional detail for each sample provided in Table 4.

Table 3: Listing of preparation date and sampling date for Tc-amended saltstone monoliths in 2mL tubes (Samples Tc- SS-I-27X)

Event	Date	Total # of aging days	Sample IDs sacrificed
Preparation date	3/28/2014		
Sampling Event 1	4/30/2014	33	Tc-SS-I- 27A
Sampling Event 2	7/23/2014	117	Tc-SS-I-27B
Sampling Event 3	1/3/2015	281	Tc-SS-I-27C
Sampling Event 4	2/25/2015	334	Tc-SS-I-27D
Sampling Event 5	6/24/2015	453	Tc-SS-I-27E

Table 4: The record of saltstone samples used in the leaching tests and synchrotron based X-ray analysis. All 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
SS-I-24B	3/28/2014	9/1/2014	Saltstone sample	7/23/2014	Ran at NSLS in Sept 6, 2014, detector issue. No usable data	Fe XAS
SS-I-26B	3/28/2014	9/1/2014	Saltstone sample	7/23/2014	Ran at NSLS in Sept 6, 2014, detector issue. No usable data	Fe XAS
SS-I-24G	3/28/2014	9/1/2014	Saltstone sample	7/23/2014	Jan 6, 2015 S XAS at BL43, SSRL	Leaching, S and Fe XAS
SS-I-26G	3/28/2014	9/1/2014	Saltstone sample	7/23/2014	Sept 6, 2014 Fe XAS NSLS	S and Fe XAS
SS-I-24C	3/28/2014	12/22/2014	Saltstone sample	1/4/2015	Jan 6, 2015 S XAS at BL43, SSRL	Leaching, Fe XAS
SS-I-26C	3/28/2014	12/22/2014	Saltstone sample	14/2015		Fe XAS
SS-I-24H	3/28/2014	12/22/2014	Saltstone sample	1/4/2015		S XAS
SS-I-26H	3/28/2014	12/22/2014	Saltstone sample	1/4/2015		S XAS
SS-I-24D	3/28/2014	6/22/2015	Saltstone sample	6/29/2015	July 6, 2015 S XAS at BL43, SSRL	Leaching, Fe XAS
SS-I-26D	3/28/2014	6/22/2015	Saltstone sample	6/29/2015		Fe XAS
SS-I-24I	3/28/2014	6/22/2015	Saltstone sample	6/29/2015		S XAS
SS-I-26I	3/28/2014	6/22/2015	Saltstone sample	6/29/2015		S XAS
FeO and Fe ₂ O ₃	None, stock chemical	NA, provided by Arai	Fe(II) and Fe(III) standards	NA	Provided by Arai	Fe XAS

Table 4: Continued

Sample ID	Date Prepared	Date Received at Univ. Illinois	Sample Description	Date Quenched	Date of Analysis	Type of Analysis
Tc-SS-I-27B	3/28/2014	Removed from chamber on 7/23/14 and shipped to SSRL 1/6/2015	Tc-amended saltstone sample containing 124 ppm ^{99}Tc ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$)	7/23/14	Jan 7, 2015 at BL11-2, SSRL	Bulk Tc XAS
Tc-SS-I-27C	3/28/2014	Removed from chamber on 1/3/15 and shipped to SSRL 1/6/2015	Tc-amended saltstone sample containing 124 ppm ^{99}Tc ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$)	1/3/15	Jan 7, 2015 at BL11-2, SSRL	Bulk Tc XAS
Tc-SS-I-27D	3/28/2014	Removed from chamber on 2/25/15 and shipped to SSRL 3/2/2015	Tc-amended saltstone sample containing 124 ppm ^{99}Tc ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$)	2/25/15	March 2, 2015 at BL11-2, SSRL	Bulk Tc XAS
Tc-SS-I-27E	3/28/2014	Removed from chamber on 6/24/15 and shipped to SSRL 6/26/2015	Tc-amended saltstone sample containing 124 ppm ^{99}Tc ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$)	6/24/15	June, 26, 2015 at BL11-2, SSRL	Bulk Tc XAS

3.0 Methods

3.1 Tc-free Saltstone Segmentation and Leaching Procedures

Tc-free saltstone samples SS-I-24B, SS-I-26B, SS-I-24G, SS-I-26G, SS-I-24C, SS-I-26C, SS-I-24H, SS-I-26H, SS-I-24D, SS-I-26D, SS-I-24I, and SS-I-26I were prepared at Clemson University and shipped to the University of Illinois at Urbana-Champaign (UIUC) for leaching tests and XAS analysis. Samples were drilled 3 days prior to the allocated beamtime described in Table-2. Leaching tests were conducted in April, 2015 for SS-I-24B and SS-I-24C and July, 2015 for SS-I-24D. Note that all samples were kept in a freezer except for the drilling period. Samples were kept in a freezer until required for further XAS measurements.

Depth dependent saltstone samples for leaching tests and XAS analysis were obtained 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 water, MilliQ water (18.2Ω) was boiled for 30min, and then cooled to room temperature and 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 13 mL of degassed MilliQ water inside the glove bag. All tubes were shaken on an end over shaker at 20 rpm for 24 hours at $22^{\circ}\text{C} \pm 0.4^{\circ}\text{C}$. 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 $0.45\text{ }\mu\text{m}$ PVDF (Polyvinylidene fluoride) filter.

3.2 Aqueous Sulfur and Iron Speciation Analysis

Oxygen free MilliQ (18.2Ω) was prepared by boiling for 30 min. After cooling to $30\text{-}35^{\circ}\text{C}$, it was sparged with N_2 gas for 3 hrs. The degassed water was kept in a N_2 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 above. The sampling depth was up to 3cm. Any large fragments were ground with a mortar and pestle prior to the leaching test. The mass of samples ranged from 0.22-0.96 g. Each depth sequence sample was transferred to a 15 mL polycarbonate tube, and then 13 mL of degassed MilliQ water was added. The tubes were shaken at 10 rpm at $22^{\circ}\text{C} \pm 0.4$. After 24 hrs, tubes were centrifuged at 2000 rpm for 10 min, and aliquots were passed through $0.45\text{ }\mu\text{m}$ PVDF filters. Filtrates were immediately analyzed for S speciation using the following ion chromatography and spectrophotometric methods described below.

Ion Chromatography (IC): 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 ion specific electrode (ISE) sulfide standard (Cole-Parmer), and a sulfite Standard Solution, 15 mg/L as SO₃ (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 solution was used in the analysis.

Ultraviolet-Visible Spectroscopy (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 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 was 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.

Inductively coupled plasma optical emission spectrometry (ICP-OES) Analysis for Fe: Dissolved Fe from the leaching test was measured using a Perkin Elmer Optima 8000 Series ICP--OES 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 in the latter text, Fe concentrations were below the detection limits. Therefore, no additional analysis to differentiate between Fe(II) and Fe(III) were performed.

3.3 Tc leaching into pore water from Tc-amended samples

The Tc amended samples were prepared on March 28, 2014 and placed uncapped in the oxic, humidity chamber for aging. It was noticed that in the oxic, humidity chamber, there was pooled water building over each of the Tc-amended and Tc-free saltstone samples. It was presumed that this was due to water condensing over the samples. A discussion was held with SRR staff to assess the potential impact of the water. It was determined that it was necessary to have the samples open to the atmosphere. Therefore, in an attempt to limit the amount of water

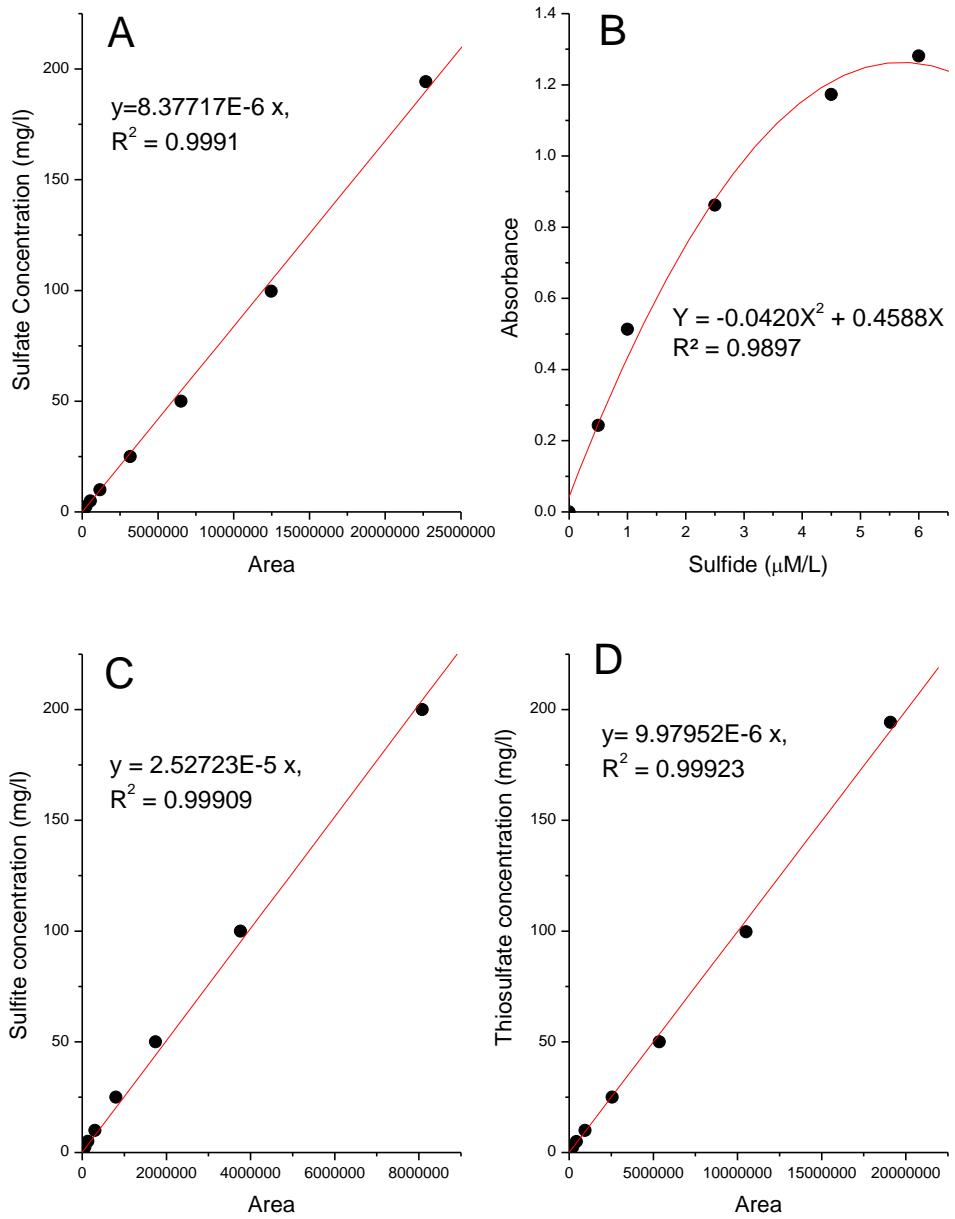


Figure 2: Standard calibration curves of aqueous S speciation in ion chromatography and spectrophotometric analysis. A) Sulfate, B) sulfide, C) sulfite and D) Thiosulfate.

building up over each sample, the caps were placed on top of each sample and two holes were drilled in the side through the cap and the walls of the vial. This allowed for atmospheric exchange but minimized the amount of water pooling over the samples. Therefore, on April 29th year (approximately one month after sample preparation) holes were drilled into the side/cap of

each sample. The water buildup slowed but did not stop. Therefore, it was determined that the pooled water would be used to monitor the release of Tc into the aqueous phase. It is important to note that this is not a controlled diffusion experiment because the amount of water continually changed. The water was periodically monitored and removed. At several sampling intervals, a 100 to 300 μ L aliquot of the water was removed and mixed with 20 mL of HiSafe 3 liquid scintillation cocktail and counted on a Hidex 300SL scintillation counter. The exact volume of water in each sample was determined gravimetrically.

3.4 Preparation of XAS samples from Tc-amended saltstone monoliths

To prepare samples for Tc XAS analysis, the sample was transferred out of the oxic, humidity chamber and placed within an anaerobic chamber (2% H₂ and 98% N₂) The exact height of the sample was measured with a plastic ruler with mm resolution. Then using a metal spatula, depth discrete sections were ground out of the sample. The depth of sampling was recorded for each sample. After removal from the tube, larger particles were ground using an agate mortar. The ground samples were individually packed into cells of an aluminum (Al) holder backed with kapton tape. In many cases a few drops of degassed, ultrapure H₂O which had been stored in the anaerobic chamber were added to the sample to facilitate transfer to the Al holder. The Al holder was then sealed in kapton tape on all sides, and transferred out of the anaerobic chamber where it was then mounted into the XAS sample holder for shipment to SSRL. A photograph of the kapton sealed Al sample holder is provided in Figure 3. Because the samples had to be shipped to SSRL, sampling usually occurred two days prior to the start of the XAS beamtime. The samples were cored and packed into the XAS cell on day one then shipped first thing in the morning on the second day to SSRL. The samples were received on the third day and placed into a cryogenic sample holder for the XAS analysis. In most cases, the analysis took three days. Therefore, the samples were removed from the monolith for between 3 and 5 days prior to analysis. There is thus a potential for oxygen diffusion into the cell and artificial oxidation of the sample. However, this potential artifact was minimized because 1) the kapton tape has a low oxygen diffusion coefficient and 2) the sample was shipped with ice packs and placed into a cryogenic system at the beamline. Thus, while the potential impacts of oxygen diffusion cannot be discounted, they have been minimized in this work.

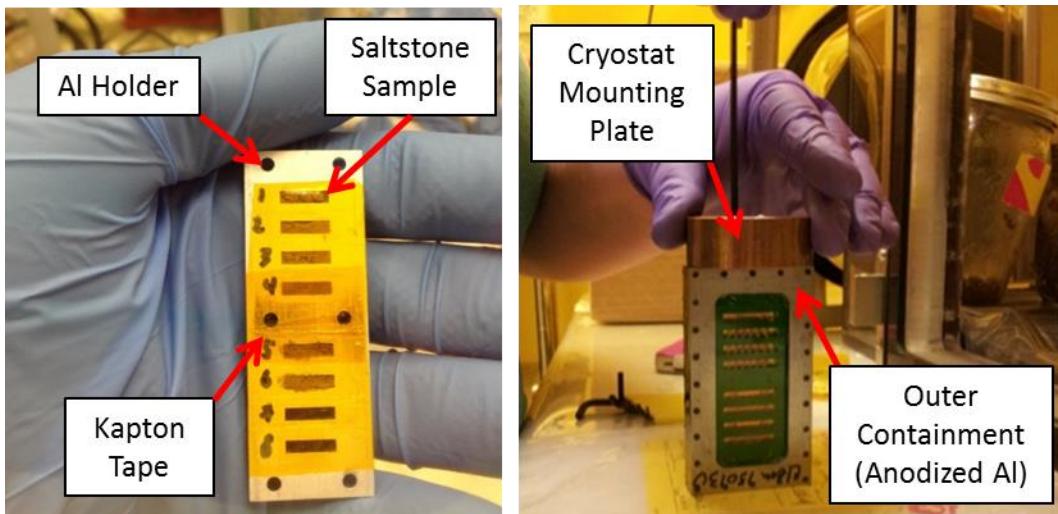


Figure 3: Photograph of Al XAS sample holder (left, sample Tc-SS-I-27E) within the anaerobic chamber and sample contained within secondary housing being mounted onto the cryostat base (right).

This sampling protocol was modified for the Tc-amended sample Tc-SS-I-27D. It was hypothesized that sulfide groups were maintaining Tc in a reduced state. Therefore, the sample was reacted with hydrogen peroxide under the hypothesis that the H₂O₂ would oxidize sulfur to sulfur and potentially alter the Tc speciation within the sample. As a control, the sample was prepared by coring a 1 cm section from the top of the monolith inside an anaerobic chamber as described above. The sample was homogenized by grinding in an agate mortar. Then half the sample was packed into an Al XAS sample holder as described above. The remaining half of the sample was placed in a 2 mL vial and reacted with 1.0 mL of 30% H₂O₂ for twelve hours. After 12 hours, the sample was washed with degassed, ultrapure H₂O then centrifuged 20 minutes at 8000 rpm in an Allegra 22R centrifuge. The washed sample was transferred to the Al XAS holder.

3.5 Tc leaching studies

For the preparation of XAS samples, saltstone monoliths were segmented into depth discrete samples as discussed above. The sampling event where the highest number of individual, depth discrete samples was collected took place for the 453 day aged sample (Tc-SS-I-27E). To allow for comparison with the Tc behavior observed using XAS, tests were performed under anoxic then oxic conditions to examine the leaching of Tc into the aqueous phase. Aliquots of the ground monoliths were transferred into pre-weighed 15 mL polypropylene centrifuge vials in the anaerobic chamber. The vials were weighed to determine the mass of sample transferred, and then a 5 mL aliquot of degassed and deionized water, which had been stored in the anaerobic chamber for over 6 months, was added to each sample (the exact volume was determined gravimetrically). The vials were then transferred out of the chamber and mixed end-over-end at 8 rpm for 24 hours. Then a 0.5 mL sub-sample was removed with a transfer pipette, centrifuged at 8000 rpm for 20 minutes (Allegra 1015 Rotor), and a 0.4 mL aliquot of the supernatant

transferred to a 7 mL liquid scintillation counting (LSC) vial containing 5 mL of Perkin Elmer HiSafe 3 scintillation cocktail, and measured on a Hidex 300 LSC. The remaining saltstone suspensions were left uncapped for 30 minutes to allow for oxygen exchange then capped and placed back on the end-over-end mixer. The sampling protocol was performed again after 13 days and 51 days to examine the impact of transferring the samples into an oxic environment.

Due to leaching of Tc into the pooled water above each monolith, the Tc concentration as a function of depth in the monolith was not known after the 453 days of aging. Therefore, the data are reported as a fraction Tc leached into the aqueous phase relative to the total Tc in the sample (after correcting for the activity of Tc leached into the pore water). The mass of saltstone within each fraction was calculated by taking the fractional volume of each depth discrete sample and multiplying by the total mass of the sample. Then the total Tc within the depth discrete sample was calculated as:

$$f_{Tc,depth} = \frac{[Tc]_{solid} mass_{solid}}{A_{monolith}}$$

where $f_{Tc,depth}$ is the fraction of Tc within the depth discrete sample relative to the total Tc in the monolith, $[Tc]_{solid}$ is the concentration of Tc leached into the aqueous phase relative to the mass of the solid suspended in the aqueous phase (units: Bq/g), $mass_{solid}$ is the mass of the solid monolith within the depth discrete sample in g, and $A_{monolith}$, is the activity of Tc in the monolith in Bq. The value of $[Tc]_{solid}$ was calculated from the LSC data as:

$$[Tc]_{solid} = \frac{A_{Tc} V_{sample}}{V_{LSC} mass_{saltstone}}$$

where A_{Tc} is the activity of Tc measured in the LSC sample (Bq), V_{sample} is the total volume of the leaching suspension, V_{LSC} is the volume of the leachate used to prepare the LSC sample, and $mass_{saltstone}$ is the mass of the powdered saltstone monolith in the suspension.

3.6 Fe XAS Analysis

All XAS samples were transferred from a freezer to a N₂-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. Beamline 4-3 at SSRL was used to collect XAS spectra in fluorescence mode for all samples and in transmission mode for reference compounds. The 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. A Passivated Implanted Planar Silicon (PIPS) detector was used. Spectra were recorded in three regions: 5 eV steps at 6960 eV- 7100 eV with 2 sec. dwell, 0.25 eV steps over the XANES (7100 eV – 7137 eV) at 2 sec. dwell, and 0.44 eV steps at 7137 eV -7600 eV with 2 sec. dwell. To monitor the change in Fe valence state, Fe pre-edge peaks of Fe reference compounds (Fe(II)O and hematite (Fe(III)₂O₃) 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 three spectra were collected per sample. A Gaussian/linear function was used for normalization of the pre-edge region and a quadratic function was used for the post-edge region. Data normalization was carried out at approximately 6962-7600 eV so the data were not affected by synchrotron x-rays.

3.7 Sulfur XANES Analysis

Sulfur K-edge XANES measurements were conducted at beamline 4-3 SSRL.A monochromator consisting of double crystal Si (111) Phi=0° with an entrance slit of 0.5 mm and minimum energy resolution of 104 at the S K-edge (2472 eV) 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 PIPS detector. Spectra were recorded from 2440 to 2575 eV with five regions: 2 eV steps from 2440 to 2460 eV with 1sec. dwell, 0.08 eV steps over the pre-edge from 2460 to 2478 eV at 1 sec. dwell, 0.2 eV steps from 2478 to 2490 eV with 1sec., 0.5 eV steps from 2490 to 2525 eV with 1 sec. and 5 ev steps from 2525 to 2575 eV with 1 sec. dwell. The first peak was set at 2472.02 eV. A minimum of three spectra were recorded for each sample. Acquiring multiple spectra across time allowed for the evaluation of reproducibility including beam induced reduction. The background was subtracted, and the step-edge height was normalized to unity for all samples prior to data processing.

3.8 Technetium K-edge XAS measurements

Technetium K-edge XAS measurements were performed at beam line 11-2 at SSRL. All measurements were performed in fluorescence mode at 77 K using the radioactive sample cryogenic sample holder and hatch set-up indicated in Fig. 3. XAS measurements were conducted using a 100-element Ge solid-state detector. The energy calibration was performed at 20,000 eV using a molybdenum (Mo) foil. Spectra were recorded in three regions: 5 eV steps at 2089.9 eV-21009.9 eV with a 2 sec. dwell, 0.2 eV steps over the XANES (21009.9 eV – 21069 eV) at 2 sec. dwell, and 1 eV steps at 21069.7 eV - 22011 eV with 2 sec. dwell. Chemical composition maps and XANES spectra were processed up to ~11 Å⁻¹ using Sixpack software (Webb, 2005). Using the best integer method, the coordination number (CN) for Tc-Tc was fixed at 1. The coordination number is the number of its near neighboring atoms of a central atom in a molecule. The Debye-Waller factor of a short Tc-O distance (~1.7Å) was fixed at 0.001 that was an average value. The Debye-Waller factor of Tc-S was fixed at 0.0115 according to the parameters reported for the Tc-S shell in grout (Lukens et al., 2005). Because of large noise in 481 d samples (Tc-SS-I-27E), Debye-Waller factor of a longer Tc-O had to be fixed at 0.009 using the parameter from previous saltstone samples.

4.0 Results and Discussion

4.1 Results from S and Fe leaching tests

The subsequent discussion focuses only on sulfur leaching tests. Iron leaching tests were performed but all samples were below the iron detection limit for the ICP-OES method used. All pH values of the leachate solutions remained around 12 and did not change with depth (Appendix C). 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-OES analysis of the leachate.

Results from the S leaching tests of aged saltstone in degased MilliQ water are shown in Figure 4 and listed in Appendix C. The analytical procedure was calibrated to measure sulfide (S^{2-}), sulfite (S^-), thiosulfate ($S_2O_3^{2-}$), and sulfate (SO_4^{2-}) which represent sulfur oxidation states ranging from -2 to 6. The sulfur Eh-pH diagrams in Appendix A indicate that sulfide and sulfate are the dominant thermodynamically stable oxidation states. Thus full oxidation of sulfide to sulfate is expected as the redox potential increases. However, it is noteworthy that sulfite and thiosulfate are transient species which may persist within the saltstone. There was no detectable level of sulfide and sulfite in these saltstone samples (detection limit for sulfite: 1 mg/L, detection limit for sulfide 0.2 mg/L). The overall sulfate concentration was nearly doubled in sample Tc-SS-I-24D (458 day aged) compared to Tc-SS-I-24B/C (117/281 day aged), suggesting that the monolith is gradually becoming oxidized. In the 258 day aged sample, interestingly, there was less sulfate near the surface and more sulfate below the surface. It is possible that labile sulfate at the surface might have diffused out during the dewatering process. The release of sulfate in 24B and 24C fluctuated between ~100-240 mg/kg with no discernible trend with respect to depth. These data should not be attributed to the oxidization of sulfide and thiosulfate species by air contamination since all experiments were performed in a glovebox to ensure anoxic conditions (oxygen content < 1 ppm). It is likely that it is due to heterogeneous distribution of S throughout the monoliths.

While the level of sulfate release was less than $350 \text{ mg SO}_4/\text{kg}_{\text{saltstone}}$ in all three samples, the concentration of thiosulfate from these samples was greater than 600 mg/kg in all samples. The concentration of thiosulfate seems to decrease with increasing aging time. While youngest sample (24B, 117 day) released ~1400-2000 mg/l, the rest of two samples (24C, 281d and 24D, 458d) released only ~600-1500 mg/l. While the release of thiosulfate fluctuated at different depths in 24B, the release of thiosulfate in the other aged two samples (24C and 24D) increased with increasing depth, suggesting the presence of more reduced environment below the surface at 15-35 mm depth. The presence of reduced sulfur compounds in the pore waters of the saltstone monolith could maintain technetium in a reduced tetravalent state. However, the specific sulfur speciation appears to be a major factor. Lukens et al., attempted to reduce Tc(VII) with thiosulfate in a high ionic strength alkaline but saw no reaction up to 14 days (Lukens et al., 2005).

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

1. With increased aging time, the release of thiosulfate decreases while the release of sulfate increases. The progression of oxidation within the upper 25 mm could be established after 458 days.
2. Based on thiosulfate data, the depth dependent sulfur speciation is more pronounced in the sample aged 458 days which suggests the presence of a reduced zone below the sample surface.

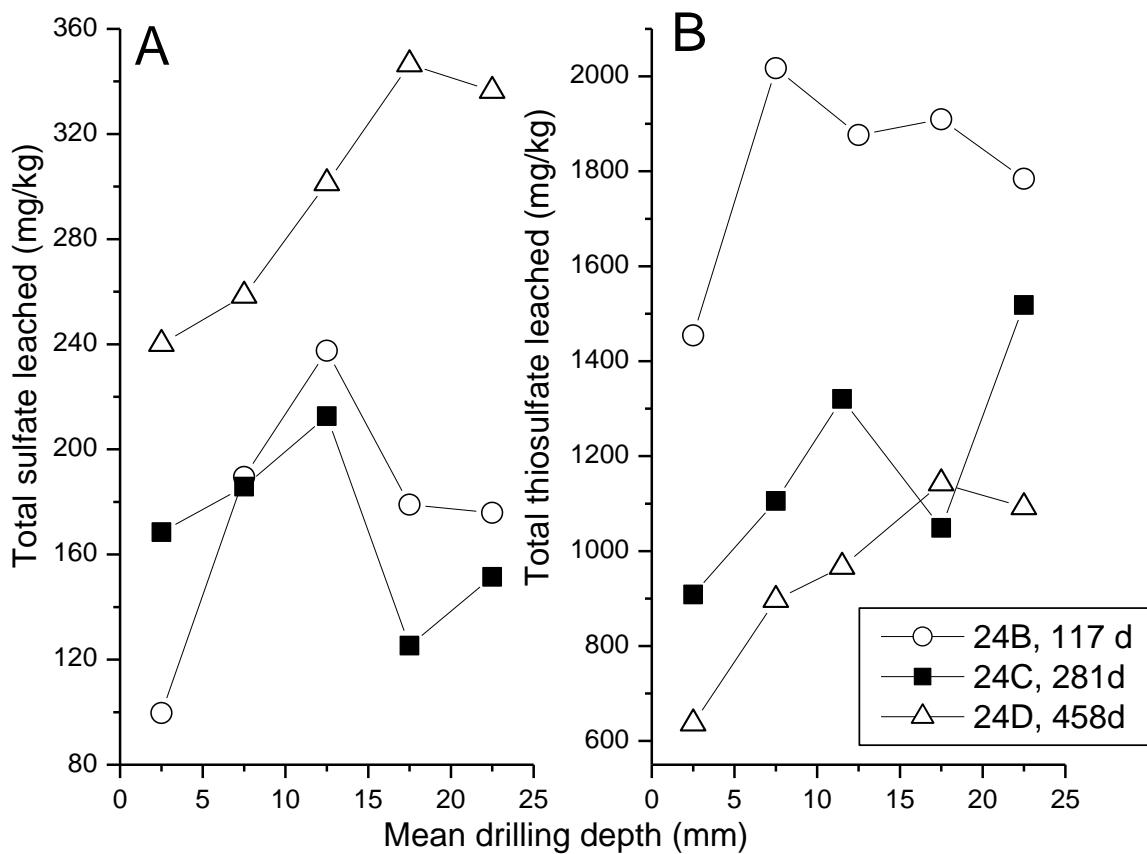


Figure 4: The results of (A) sulfate (SO_4) and (B) thiosulfate leaching test from saltstone samples aged 117 to 458 days (SS-I-24B, SS-I-24C and SS-I-24D). Error bars are hidden within symbols (<0.1% for both sulfate and thiosulfate). Sulfite and sulfide were below detection limit.

4.2 Leaching of Tc into pooled water above saltstone monoliths.

Monitoring the release of Tc(VII) into the water pooling above the Tc amended saltstone samples gives some important information regarding release and mobilization of Tc(VII). The

fraction of Tc released into the pooled water is shown in Figure 5. The data points represent the average of all Tc amended samples available at that time point. Initially there were 6 samples which were present after the pooled water started to accumulate. Sampling was performed periodically when the water level approached the holes in the vials and at times when a sample was removed for XAS analysis. Thus, the number near each point represents the number of samples averaged for that point. A significant fraction of Tc is being released into solution and the release increases with time and the relatively low standard deviations indicate the samples are fairly consistent. Thus it does not appear the Tc measured is only that contained at the top of the saltstone monolith; rather Tc is being released from further down into the monolith. There are two possible explanations for the observed behavior. First, Tc(IV) may be oxidized to Tc(VII) as oxygen diffused into the sample through the infiltrating water. Recall the vials have holes in the lids to allow exchange with atmospheric oxygen. Then Tc(VII) is diffusing out of the sample into the pooled water. A second explanation is that all of the Tc was not reduced to Tc(IV) within the saltstone matrix. The concentration of Tc in these saltstone samples is 124 ppm ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$) which is drastically 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 prevent the complete reduction of Tc(VII) to Tc(IV). The high concentration was necessary for XAS measurements performed in this work. Experiments are proposed in the Future Work section below to examine this potential reduction capacity in detail.

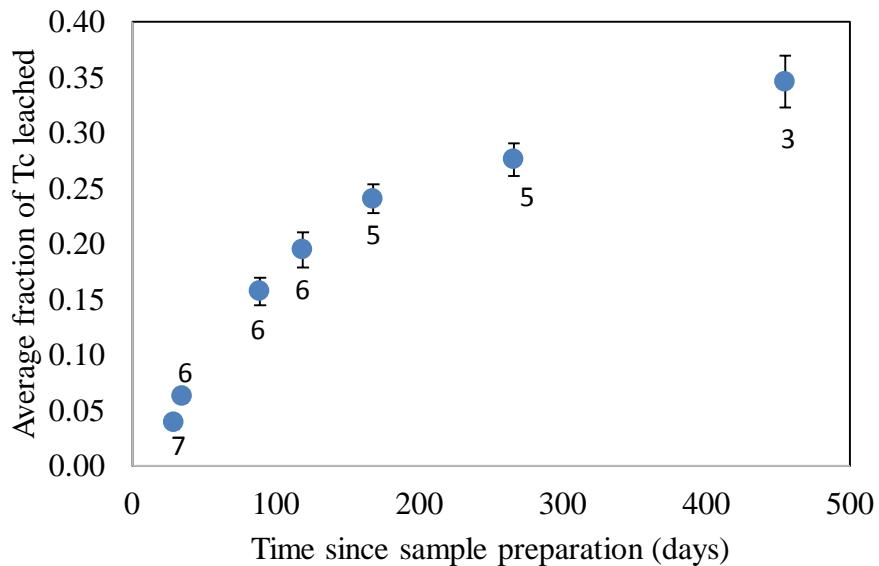


Figure 5: Cumulative fraction of Tc leached into pooled water standing over Tc amended saltstone monoliths as a function of time. Note that the volume of water was changing as new water condensed from the humid atmosphere and water was removed for sampling. The values represent the average of replicate samples (with the number of samples noted near each datapoint). The error bars represent standard deviation of the averaged samples.

4.3 Leaching of Tc from saltstone into anoxic and oxic waters

Tc leaching from the depth discrete subsamples from the Tc monolith aged for 117, 281, and 453 days (Samples: Tc-SS-I-27B, Tc-SS-I-27C, and Tc-SS-I-27E, respectively) indicate a significant fraction Tc leaching into the aqueous phase (Figure 6). The leaching data indicate that 38%, 56%, and 38% of the total Tc remaining in the saltstone at the time of leaching (i.e. after subtraction of the Tc leached into the pooled water during aging) for the 117, 281, and 453 day aged samples, respectively. The amount of Tc leached into the aqueous phase is relatively consistent for all samples aged from 117 to 453 days. This implies that the Tc speciation is not significantly changing over this time period or that any changes in speciation do not result in the formation of a more labile Tc species. The XAS data discussed below indicate that the latter is likely occurring. As discussed below, the XAS spectra indicate that while Tc is remaining as Tc(IV), there appears to be a transition from a Tc(IV) hydroxide to a Tc(IV) sulfide phase. Thus, these data indicate that despite a potential change in Tc speciation over time, there is not a significant difference in the lability of Tc.

In Figure 6, data for samples aged 117 and 281 days are only available for a 13 day leaching period. Therefore, the figure also contains only the 13 day leaching data from the 453 day aged sample. Data for additional leaching periods from the 453 day aged sample are provided in Figure 7. Note that the data in Figure 7 are reported as a function of the total Tc in the monolith (corrected for the leaching observed in Figure 5). A specific depth discrete calculation could not be performed because the total concentration of Tc as a function of depth is unknown due to the potentially heterogeneous leaching of Tc into the pooled water discussed above. The leaching tests were started under anoxic conditions and were transferred to atmospheric conditions after 24 hours to examine the impact of the oxic atmosphere. There was relatively little change in the leaching profile under oxic and anoxic conditions but the total Tc leached slightly increased as 30.1%, 36.5%, and 38.7% for the 1 day, 13 day, and 51 day leaching periods, respectively. These data indicate that there is a relatively large fraction of labile/soluble Tc which can be mobilized from powdered saltstone samples after aging 453 days under oxic/humid conditions. It is noteworthy that there appears to be a decrease with the fraction of labile Tc as a function of depth. This is consistent with the presence of reduced sulfur at depth and a reducing zone which may keep Tc in a less labile, reduced state. As discussed below, the Tc is predominantly in a tetravalent state but not present as any specific ordered crystalline phase. Therefore, the labile Tc fraction may be part of a highly disordered phase which is easily oxidized under these conditions. Oxidation state analysis of the dissolved Tc was not conducted to determine if the dissolved species was Tc(IV) or Tc(VII). A detailed study of this could be included in future work.

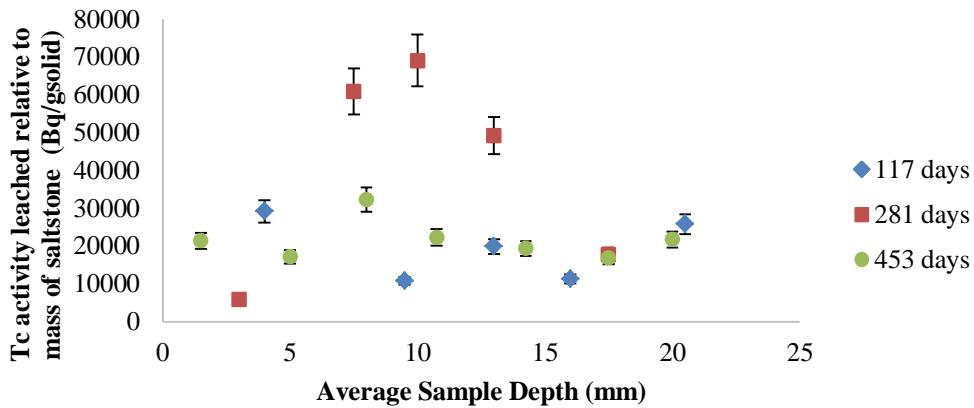


Figure 6: Tc concentration in leachate solutions after a 13 day leaching period (normalized to the saltstone mass being leached) as a function of depth in samples aged for 117, 281, and 453 days. Since the solids were transferred to the tubes for leaching contained some water, there is an inherent error in the mass of sample. Thus, a conservative error estimate of 10% on the y-axis should be considered. This is represented by the error bars shown above.

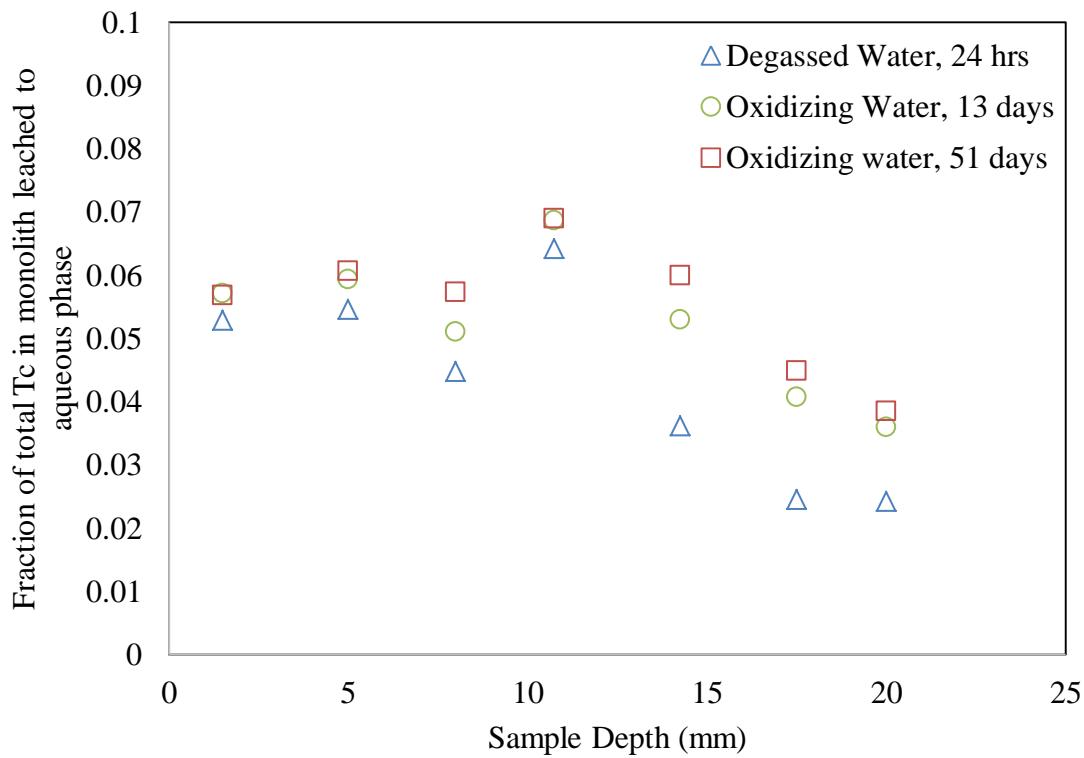


Figure 7: Tc leaching as a function of sample depth. Suspensions were made of the ground, depth discrete samples and leached under oxic and anoxic conditions as noted in the figure legend. Data are reported as a function of the total Tc in the monolith (corrected for the leaching observed in Figure 5).

4.4 Fe XANES Analysis

In Figures 8-10, Fe K-edge XANES of Fe reference compounds (Fe(III) oxide (as Fe_2O_3) and Fe(II)O) 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 (Fe_2O_3). The position of the 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 Figures 8-10. Based on the position of the pre-edge feature, the iron in all aged (117-458 day) saltstone is dominated by Fe(III). There was no depth dependent relationship of iron oxidation state. The position of the pre-edge feature in the 24 series (i.e., large 50 ml saltstone samples) was also same as those in 26 series (small 2 ml tubes), suggesting that ferrous iron in both saltstone series was oxidized under atmospheric conditions. This suggests that reduction capacity by ferrous iron was no longer present in aged saltstone samples after 117 day. As discussed by Arai and Powell (2014), ferrous iron was present in both saltstone samples as well as hydrated blast furnace slag aged for only 3 days. Thus, it appears oxidation of Fe(II) to Fe(III) is occurring in the saltstone which is consistent with the prediction of Fe(III) as the dominant iron species under the pH and E_H conditions in this work.

Comparison of the aged (117-458 day) saltstone samples provides three important pieces of information:

1. During the aging time, all ferrous iron was oxidized to ferric iron in saltstone.
2. No depth dependent trend of iron oxidation state was observed in aged saltstone.
3. Comparison of the small (26 series in 2 mL tubes) and large (24 series in 50 mL tubes) saltstone samples indicates that the Fe(III) oxidation state is similar between the two samples. The similarity between these samples indicates that the smaller sample size does not introduce any experimental artifacts related to Fe speciation and that the smaller size is representative of the larger size. Note this was not the case for S speciation as discussed below.

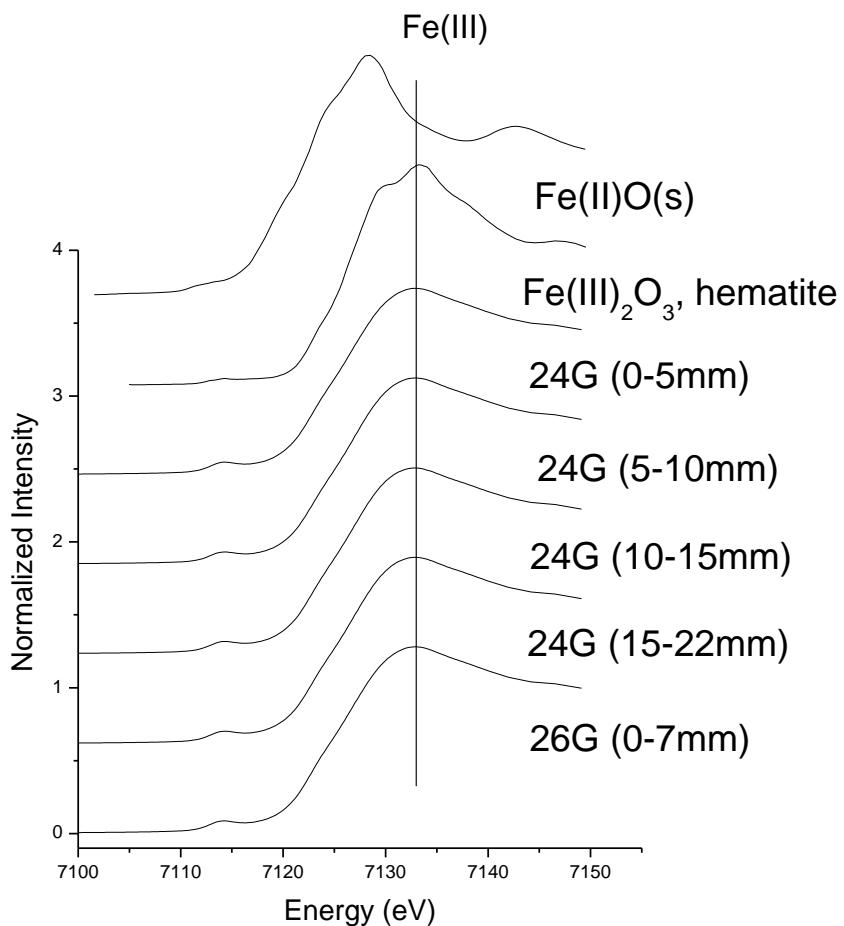


Figure 8: Normalized pre-edge features of Fe K-edge XAS spectra of 177 day old saltstone samples (24G and 26G) with hematite ($\text{Fe}^{\text{III}}_2\text{O}_3$) and iron oxide ($\text{Fe}^{\text{II}}\text{O}$). A vertical dotted line is at the peak of whiteline of Fe(III) in hematite.

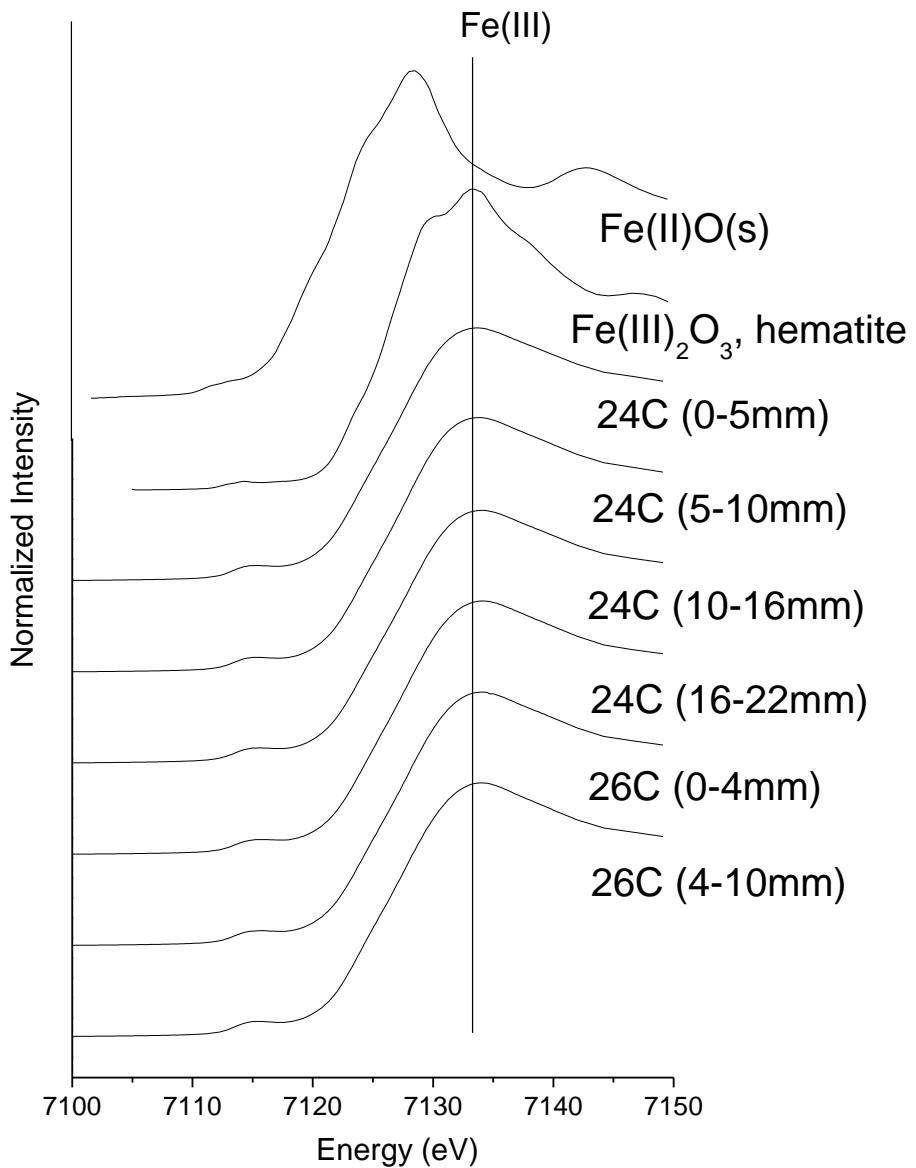


Figure 9: Normalized pre-edge features of Fe K-edge XAS spectra of 281 day old saltstone samples (24C and 26C) with hematite ($\text{Fe}^{\text{III}}_2\text{O}_3$) and iron oxide ($\text{Fe}^{\text{II}}\text{O}$). A vertical dotted line is at the peak of whiteline of Fe(III) in hematite.

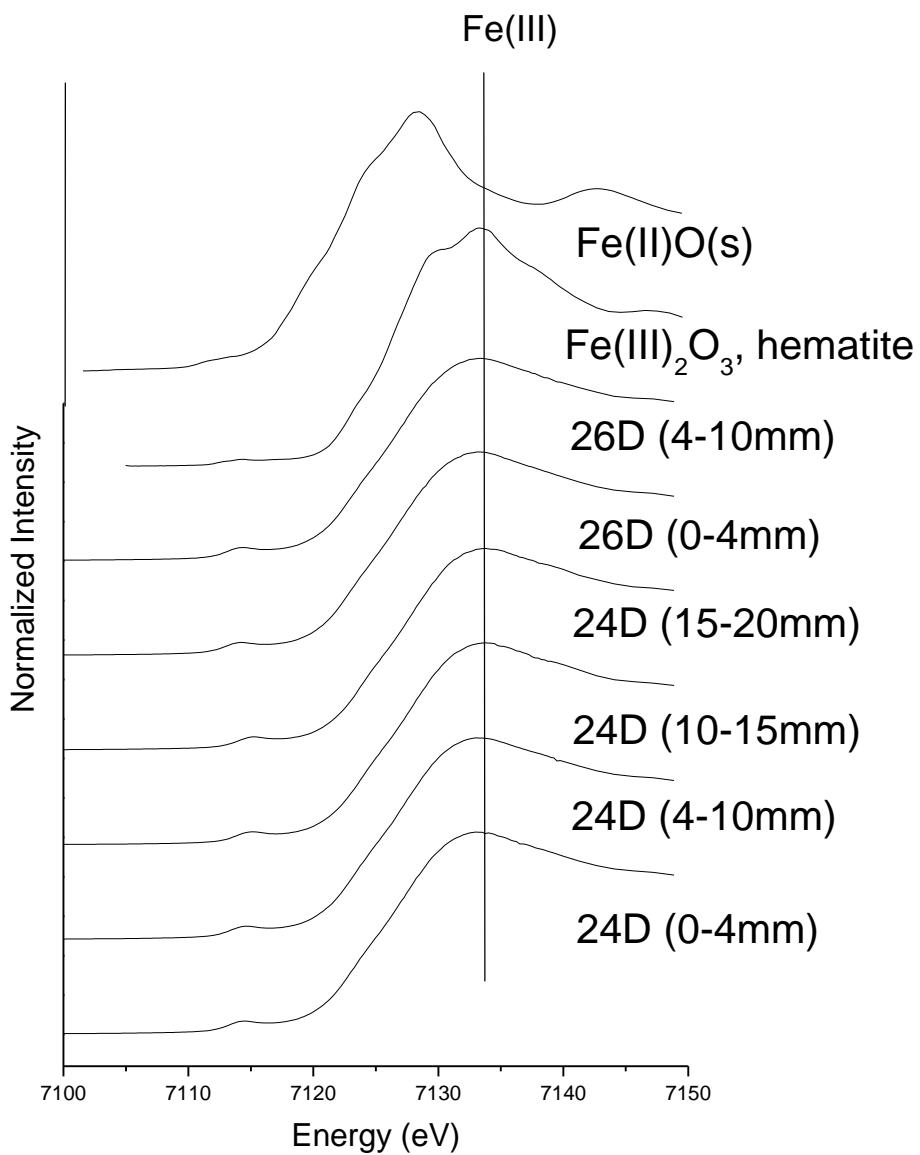


Figure 10: Normalized pre-edge features of Fe K-edge XAS spectra of 458 day old saltstone samples (24D and 26D) with hematite ($\text{Fe}^{\text{III}}_2\text{O}_3$) and iron oxide ($\text{Fe}^{\text{II}}\text{O}$). A vertical dotted line is at the peak of whiteline of Fe(III) in hematite.

4.5 S XANES Analysis

Sulfur XANES analyses were 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: 2478.8 eV, and sulfate: 2483 eV). In most of the spectra, there is an intermediate peak at 2476.5 eV. This is a background signal that does not correspond to any specific compound. As noted above, sample IDs containing “24” correspond to larger samples in 50 mL tube and samples containing “26” correspond to samples in smaller 2 mL tubes.

Figure 11 and 12 show the S K-edge XAS spectra of 117 day and 281 day aged saltstone samples, respectively. At the depth up to 1 mm in the 117 day aged sample, sulfate is the dominant species and there is a trace of S(0)/FeS₂ at depths <10 mm. The distribution of S valence state is similar to 4 day old samples (SS-I-24A) in an earlier report (Arai and Powell, 2014). At the depth of 0-5 mm, only sulfate was present, and a small quantity of S(0)/FeS₂ and sulfides were present at the depth of 6-8 mm. While sulfate remains dominant, in samples aged 281 days (SS-I-24H and SS-I-26H), S(0)/FeS₂ is only present in all depth in the larger sample (SS-I-24H). The peaks present at 2470 and 2472 keV corresponding to S(0)/FeS₂ are absent in the smaller samples (26 series). Thus it appears there may be oxidation occurring in the smaller sample tubes that is not occurring in the larger samples for the 281 day aged samples. While this is an experimental concern, it is noteworthy that sample SS-I-24H which was aged for 281 days shows the strongest signal for S(0)/FeS₂. There appears to be a lower amount of reduced sulfur species in the sample aged for 117 day (SS-I-24G). Samples SS-I-24G and SS-I-26G were shipped for analysis soon after their removal from the aging chamber (7/23/2014). However, due to a detector problem at the beamline, the samples were not analyzed until several months later during the January 2015 beamtime. The samples were frozen during this time and assumed to be dormant. However the redox stability of the samples cannot be confirmed. The observation of reduced sulfur species in the samples aged for 3 days discussed in the previous year’s report (Arai and Powell, 2015) and the observation of reduced sulfur species in sample SS-I-24H aged for 281 d indicates that freezing the samples may not have fully preserved the redox conditions. After aging 458 days, the peak corresponding to S(0)/FeS₂ was absent in SS-I-26I. This sample was never frozen and analyzed as soon as possible (within two weeks) after removal from the aging chamber. Thus, if freezing the samples did introduce an experimental artifact in the 117 day aged sample, it would not have influenced the 458 day sample. The majority of sulfur in the 458 day aged sample in the larger tube was predominantly sulfate with a small amount of sulfide at the lower depth (9-20 mm) as shown in Figure 13. In the smaller tube also aged 458 day, sulfate was the only observed sulfur species, confirming that oxidation of sulfur was more rapid in samples prepared in the smaller tubes.

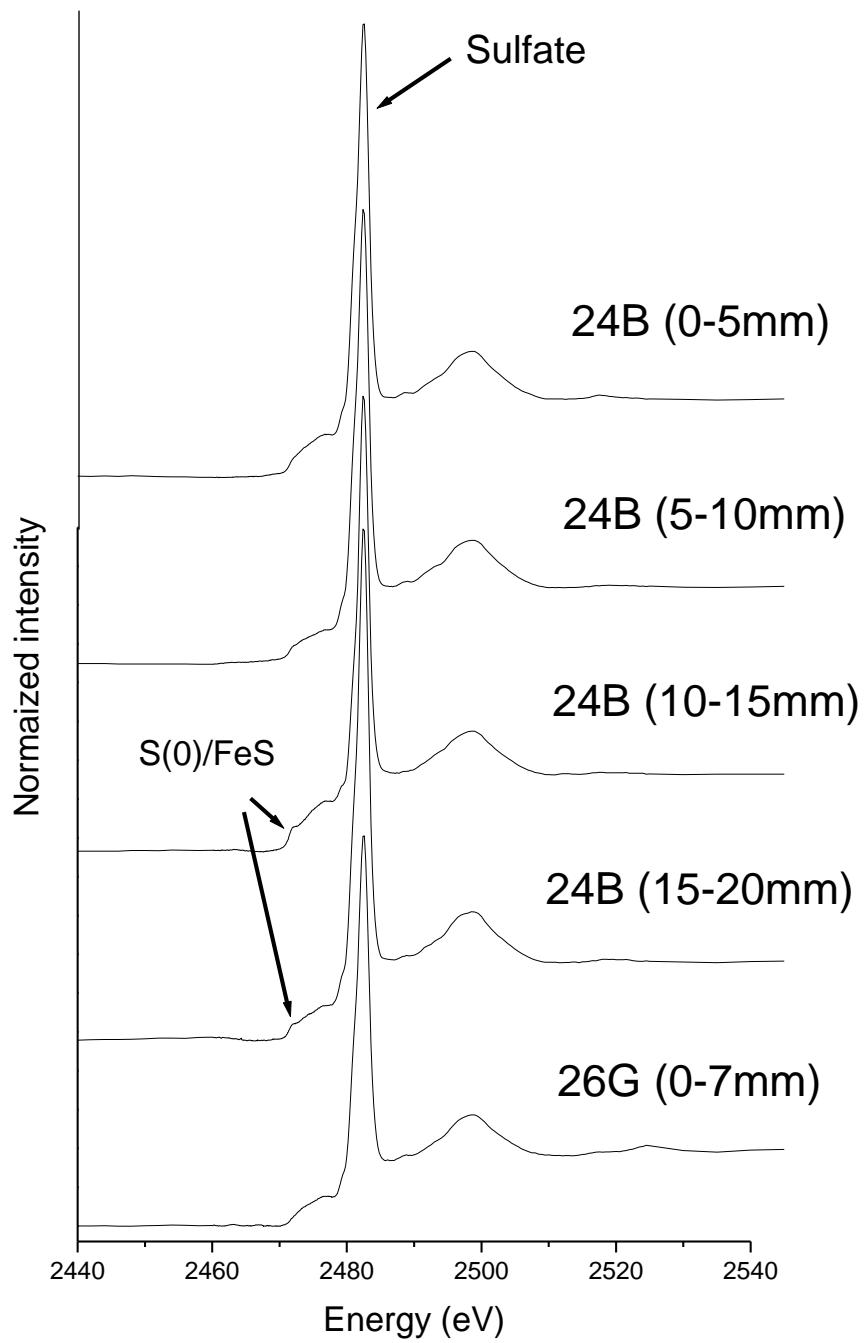


Figure 11: Normalized S K-edge XANES spectra of 117 day old saltstone samples (SS-I-24B and SS-I-26G) as a function of depth.

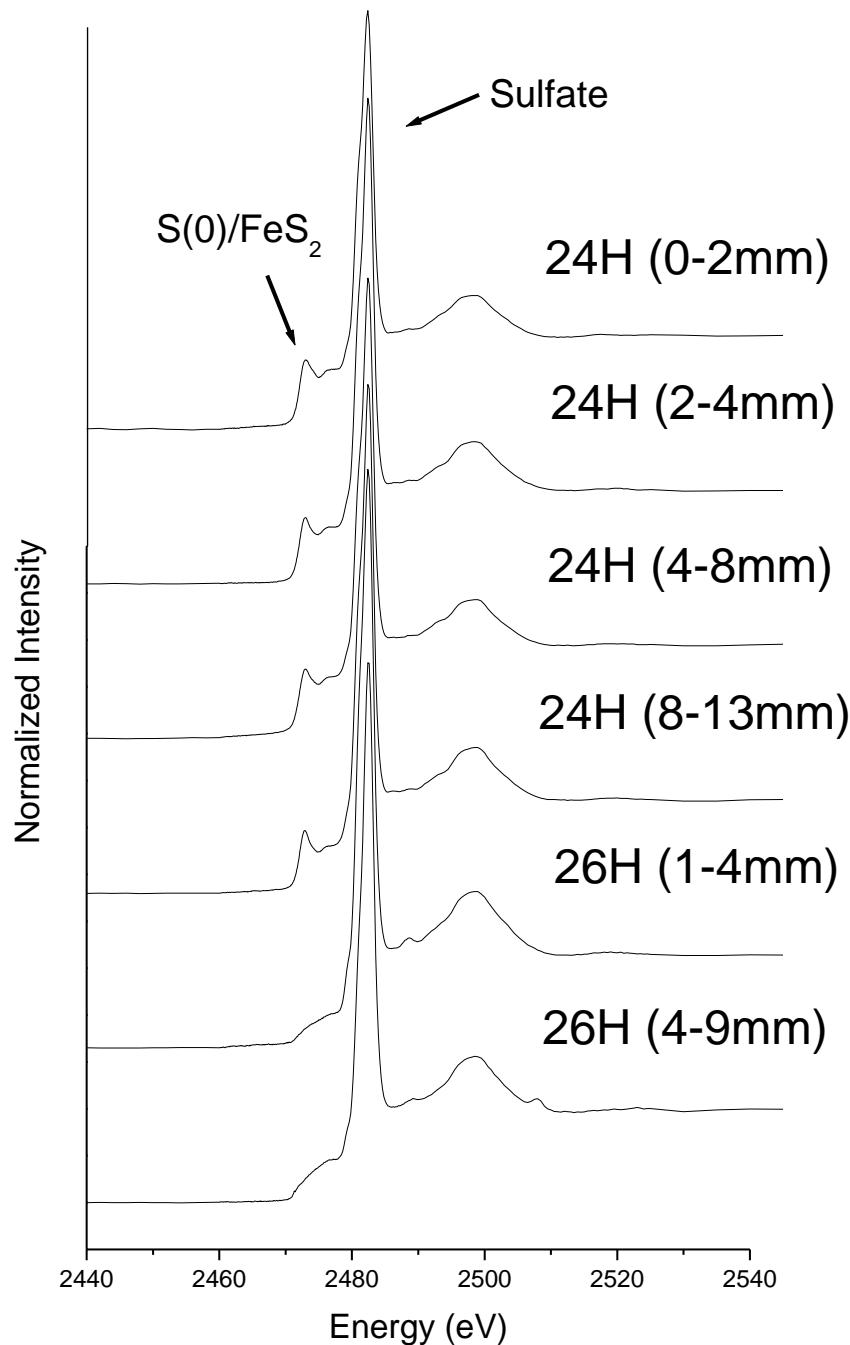


Figure 12: Normalized S K-edge XANES spectra of 281 day old saltstone samples(24H and 26H) as a function of depth.

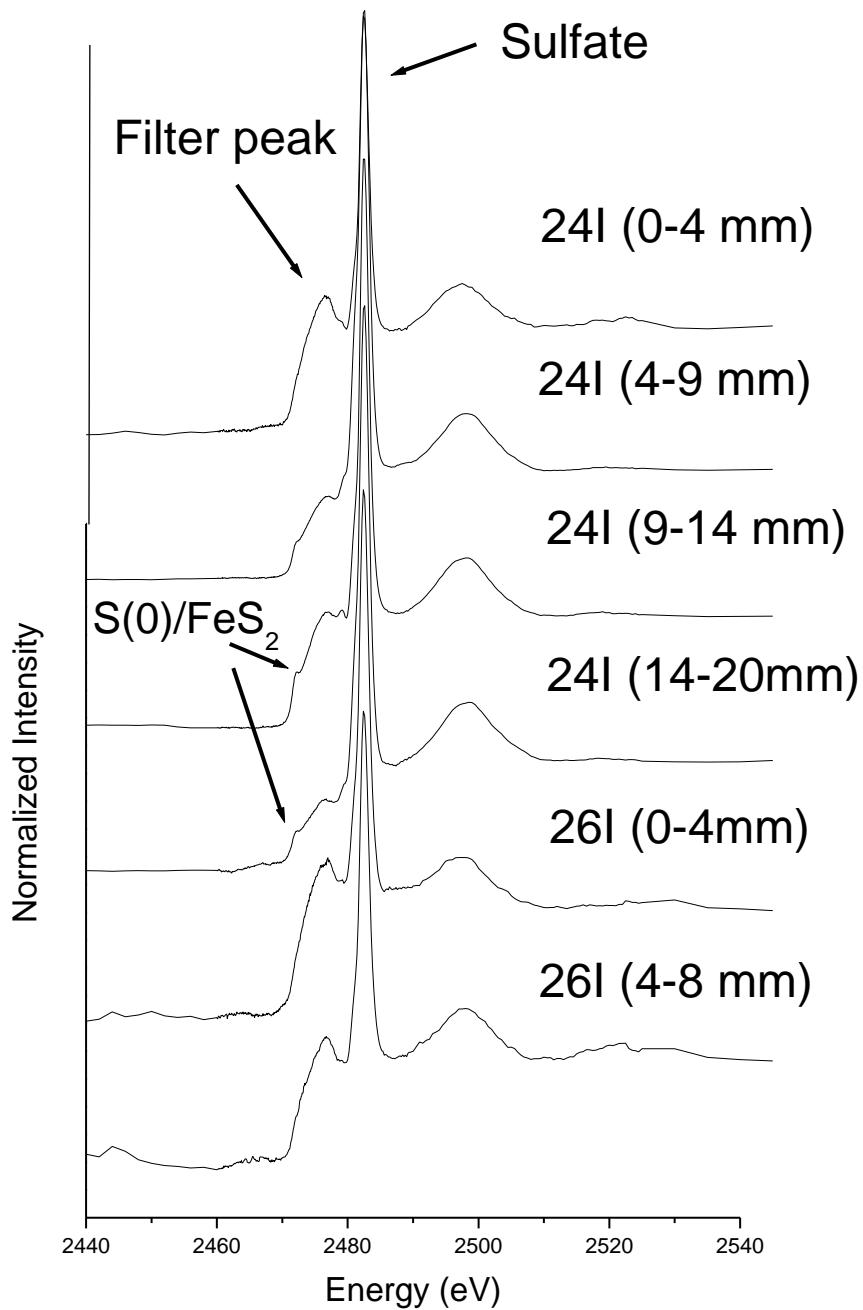


Figure 13: Normalized S K-edge XAS spectra of 458 day old saltstone samples as a function of depth.

4.6 Tc XANES Analysis

XANES spectra of reference compounds and Tc spiked aged saltstone samples are shown in Figure 14. It is clear that pre-edge feature of Tc(VII) species (indicated by a curved arrow) was not present in any saltstone spectra, suggesting that there is no or little contribution from Tc(VII) in saltstone aged for 29 to 453 days. However, leaching of Tc into the pore waters overlying the samples is proposed to have mobilized Tc(VII) and reduced the Tc(VII) signal in the samples. The amount of Tc leaching into the overlying water increased over time for all samples. The total Tc leached over the ~450 day experiments described here was approximately equal to the ~35% TcO_4^- content observed in the initial XANES analysis of the 29 day aged sample (Figure 5). In the $\text{TcO}_2(\text{am})$ reference spectrum, there is a split white line peak feature (indicated by an arrow). The feature is absent in saltstone spectra. This suggests that $\text{TcO}_2(\text{am})$ is not the major component in saltstone. A vertical line is aligned at the peak maxima of Tc_2S_7 . All saltstone samples seem to share the similar peak position. However, a broad oscillation (indicated by an arrow) in Tc_2S_7 is absent in saltstone samples. This suggests Tc_2S_7 is not the major component in aged saltstone samples. It is unlikely that Tc(VII), $\text{TcO}_2(\text{am})$, and Tc_2S_7 are present in aged saltstone. To assure the interpretation of XANES analysis, EXAFS analyses were conducted.

4.7 Tc EXAFS Analysis

EXAFS spectra (k^3 -weighted) of aged, Tc-spiked saltstone samples are shown in Figures 15-17. XRD/XAS fit parameters of reference compounds are compared with fit results of saltstone samples in Tables 5 and 6. Interatomic distances mentioned in this section are corrected for phase shift. Overall, there are four interatomic distances: a short Tc-O at $\sim 1.7\text{\AA}$, a long Tc-O at $\sim 2.1\text{\AA}$, Tc-S at $\sim 2.4\text{\AA}$, and Tc-Tc at $\sim 2.9\text{\AA}$. Oxygen atoms belong to distorted $\text{Tc(IV)}\text{O}_2$ in an octahedral structure. Sulfur atoms are from sulfidized $\text{TcO}_{x}\text{S}_{6-x}$ (potential Tc species in saltstone are discussed in detail below) and/or TcS_2 -like species. A Tc-Tc distance is indicative of a polymeric species within either sulfidized $\text{TcO}_{x}\text{S}_{6-x}$ and/or distorted hydrolyzed Tc(IV). Using the reductive elimination method, potential solid state Tc species are discussed below.

Excluding $\text{Tc(VII)}\text{O}_4^-$ species:

As seen in the XANES spectra, there are no pre-edge features corresponding to pertechnetate species. This suggests that the Tc(VII) species is not a major component in these samples. Using the fitting parameters from the analysis of other $\text{TcO}_4^-(\text{aq})$ species (McKeown et al. 2007), four oxygen atoms at $\sim 1.7\text{\AA}$ were considered. The results showed that the Tc-O linkage at this distance was not associated with four oxygen atoms. Therefore it is unlikely that $\text{Tc(VII)}\text{O}_4^-$ is present.

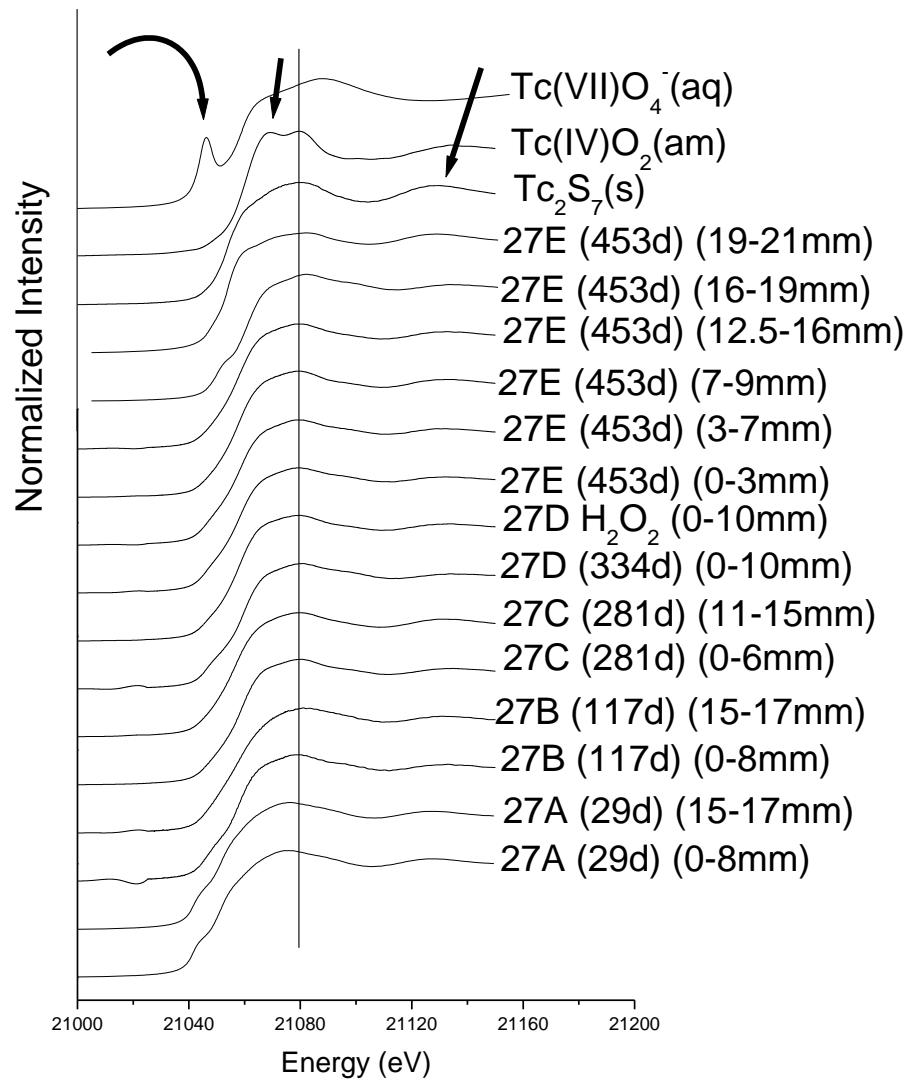


Figure 14: Normalized Tc K-edge XANES spectra of aged (33, 117, 281, 334, and 453 days) Tc reacted saltstone samples (27A, 27B, 27C, 27D, and 27E) as a function of depth. Spectra of $\text{Tc(IV)}\text{O}_2(\text{am})$. and TcS_x were provided by Dr. W. Lukens from Lawrence Berkeley National laboratory (Berkeley, CA). A vertical line is aligned at the whiteline peak maxima of TcS_x (Lukens et al., 2003). A curved arrow points out the pre-edge feature of Tc(VII). An arrow in a $\text{Tc(IV)}\text{O}_2(\text{am})$ spectrum points out the 1st whiteline peak. An arrow in a TcS_x spectrum points out a broad post-edge feature.

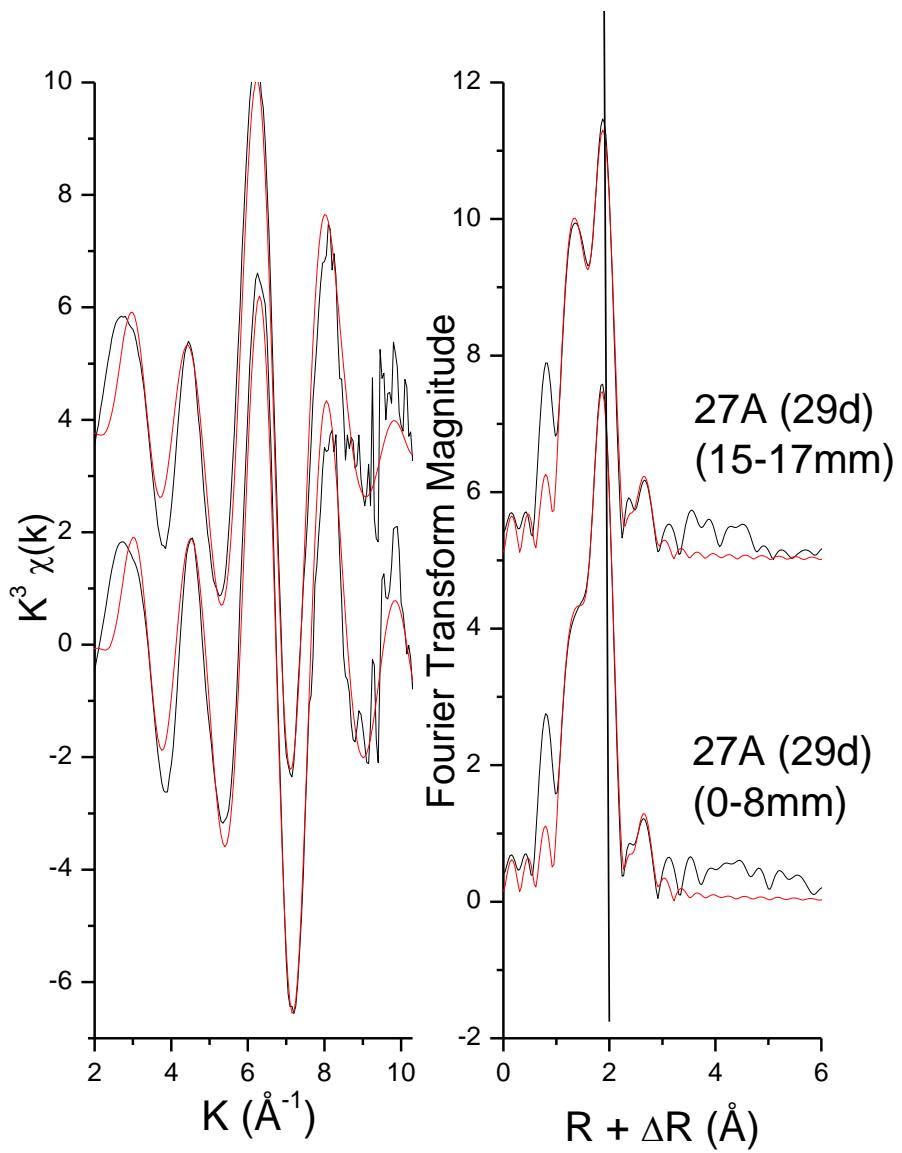


Figure 15: Least-squares analyses of k^3 -weighted $\chi(k)$ (left) and Fourier transform (right) Tc K-edge EXAFS spectra of aged (29 day) Tc reacted saltstone samples (27A) as a function of depth. A vertical line is at 2\AA of $R + \Delta R$ that corresponds to the FT peak maxima of TcSx (Lukens et al. 2003). Raw spectra and fit are shown in black solid lines and red solid lines, respectively.

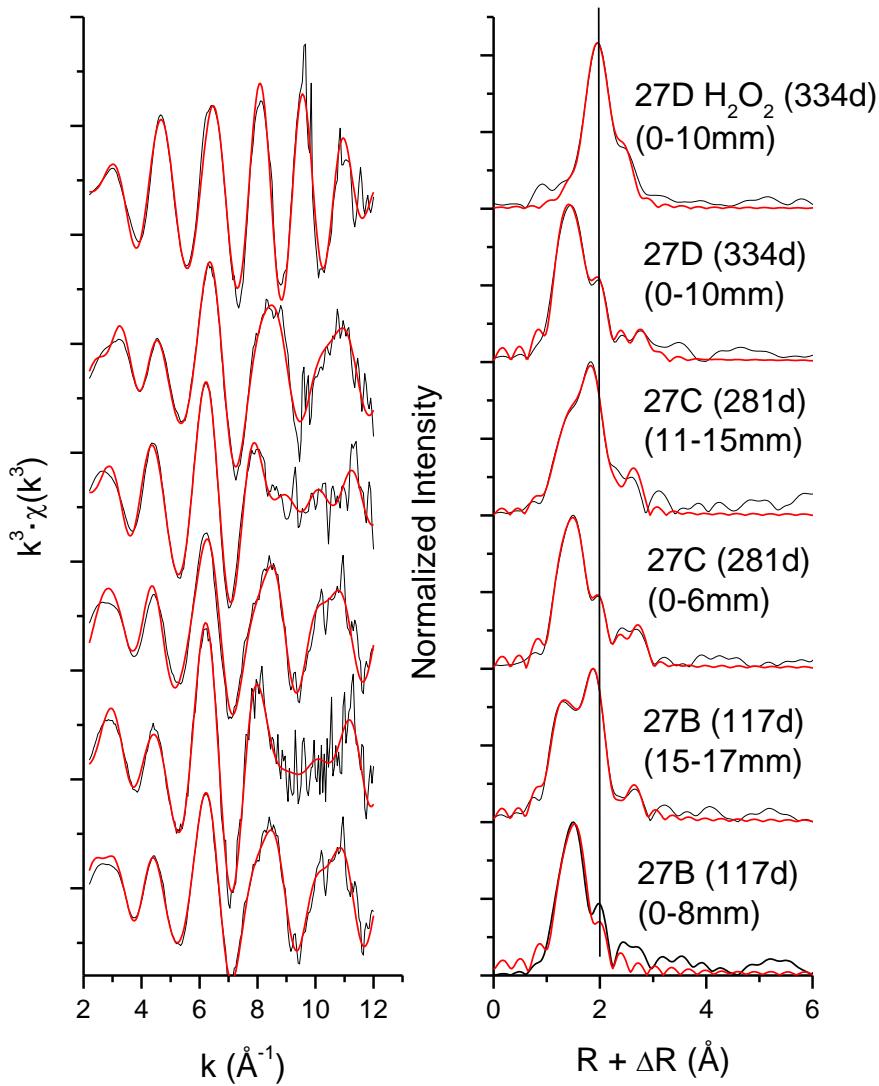


Figure 16: Least-squares analyses of k^3 -weighted $\chi(k)$ (left) and Fourier transform (right) Tc K-edge EXAFS spectra of aged (117, 281, and 334 days) Tc reacted saltstone samples (27B, 27C, 27D) as a function of depth. “27D H_2O_2 ” indicates that the samples were exposed to hydrogen peroxides. A vertical line is at 2 \AA of $R + \Delta R$ that corresponds to the FT peak maxima of TcSx (Lukens et al. 2003). Raw spectra and fit are shown in black solid lines and red solid lines, respectively.

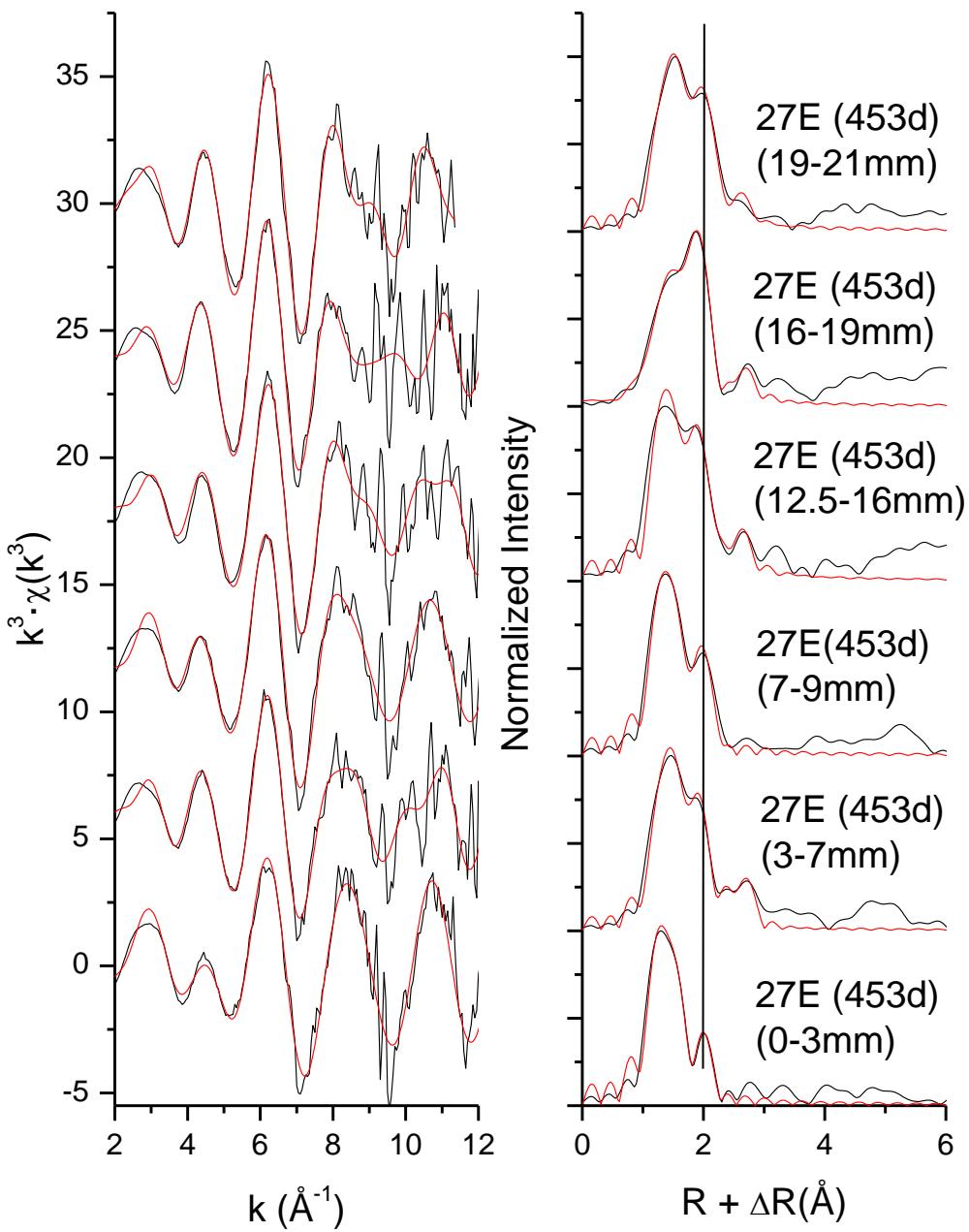


Figure 17: Least-squares analyses of k^3 -weighted $\chi(k)$ (left) and Fourier transforms (right) of Tc K-edge EXAFS spectra of aged (453 day) Tc reacted saltstone samples (Tc-SS-I-27E) as a function of depth. A vertical line is at 2\AA of $R + \Delta R$ that corresponds to the FT peak maxima of TcS_x (Lukens et al. 2003). Raw spectra and fit are shown in black solid lines and red solid lines, respectively.

Excluding the presence of amorphous TcO₂(s) and Tc₂S₇(s):

EXAFS was conducted for saltstone samples using the fitting parameters reported by Lukens' co-workers (2005) for Tc₂S₇ (reported as TcS_x) and by McKeown et al. (2007) for amorphous TcO₂(am). For oxygen atoms, amplitude and oscillation from amorphous TcO₂ reported in Allen et al. (1997) were not able to simulate the saltstone samples from the current work.

In considering a TcS_x phase, there are discrepancies in the fit. Most of saltstone samples contain a Tc-S distance at >2.4 Å that was slightly longer than a Tc-S distance in TcS_x reported by Lukens et al (2005). The coordination number (CN) was approximately 2-3, except for a few samples (Tc-SS-I-27B (15-17mm) and Tc-SS-I-27D H₂O₂), that were much smaller than the experimental value (~7) of TcS_x reported by Lukens et al. (2005). It is unlikely that the exact TcS_x phase observed by Lukens et al., (2005) is present in our samples. This hypothesis is supported by a FT spectra comparison. In all samples, the largest Fourier transform features appear at ~1.5 Å (R + ΔR) (Figures 15-17). However, Lukens et al., (2005) reported that the first FT feature occurs at ~2 Å (R + ΔR) in TcS_x species in sulfide amended grout samples. **It is clear that the predominant first scattering atoms in the samples prepared by Lukens et al., (2005) are different in the samples examined in this work. This difference is proposed to be due to the fact that Lukens et al, (2005) added sulfide to the grout which provided a higher activity of sulfide.** The saltstone monoliths prepared in the current work did not receive any additional sulfides during preparation.

Excluding surface adsorbed Tc(IV) species

A Tc-Fe/Al distance at ~2.7-3.1 Å was also considered for adsorbed Tc(IV)O₆ on Fe/Al octahedral. Several molecular configurations of octahedrally coordinated Mo(IV)O₂ (analog of Tc(IV)O₂) were considered according to the work by Arai (2010). When the path was included without a Tc-Tc path, the Tc-Fe/Al amplitude and oscillation do not simulate the spectra feature. Appropriate amplitude and oscillations for Tc-Fe/Al do not seem to be present in this sample. For this reason, a heavier scattering atom such as Tc was considered at this longer distance and it was confirmed that Tc(IV) was not present as a sorbed mononuclear species.

Suggested Tc species in aged saltstone:

Based on the results of Tc XANES and EXAFS analysis, the following reactions are proposed to describe the evolution of Tc chemistry in the saltstone samples prepared in this work. Due to the observed short Tc-O distance at ~1.7 Å, it is clear that **a distorted Tc(V)O₂ in an octahedral coordination is present. Owing to the high pH of the system and the propensity of tetravalent ions to strongly hydrolyze, a hydrolyzed Tc(IV) species like Tc(IV)O(OH)₂(H₂O)₃ (step 1)** is a reasonable candidate. This can be seen in a sample Tc-SS-I-27B (0-8mm) which was aged for 117 days. The sum of coordination numbers for short Tc-O and long Tc-O bonding is ~6. Over time, reaction with sulfide causes some hydrolyzed species to become partially

sulfidized (step 2) with the reaction progressing to a fully sulfidized species (TcS_2) over time (step 3).

- Step 1. Reduction of $Tc(VII)O_4^-$ by ferrous iron and or sulfides to form $Tc(IV)O_6 \rightarrow$ hydrolysis to form $Tc(IV)O(OH)_2(H_2O)_3$
- Step 2. $Tc(IV)O(OH)_2(H_2O)_3 \rightarrow$ partial sulfidation $\rightarrow Tc(IV)O(H_2O)_{5-x} S_x^{2-}$
(This step 2 is limited by low sulfide activity in saltstone)
- Step 3. Polymerization of sulfidized species $\rightarrow Tc(IV)S_2$ like species at where high sulfide and Tc activity is present

The extent of the reaction will be dependent on the time of the reaction which controls the oxidation rate of sulfide to thiosulfate and sulfate and the local concentrations of reactive sulfur in the systems. As discussed above, the scatter in the concentration of sulfur species as a function of depth is proposed to be due to a heterogeneous distribution of sulfur species within the monolith. The degree of heterogeneity will be dependent on the particle size of the fly ash, BFS, and cement used in the preparation and the solubility of various sulfur bearing species in the pore waters. A complete analysis of the impact of particle size and mobility of dissolved sulfur species is beyond the current scope of this work. However, the impact of heterogeneity in these systems should be considered in the design of future experimental efforts.

In most of the saltstone samples, except for Tc-SS-I-27B (0-8mm) and Tc-SS-I-27D H_2O_2 , CN for a short Tc-O is ~1, CN for Tc-S is ~2-3, CN for a long Tc-O is ~2-3 and CN for Tc-Tc is 1 (Table 5). The sum of coordination numbers for each sample is approximately 6. This suggests that the partially sulfidized $Tc(IV)O(OH)_2(H_2O)_3$ species like $Tc(IV)O(H_2O)_{5-x} S_x^{2-}$ is a reasonable candidate. However, the peroxide treated sample aged for 334 day (Tc-SS-I-27D- H_2O_2) might provide a clue to better understand the solid state Tc species in saltstone.

Interestingly, after reacting with peroxide, all of the short Tc-O distances are lost with ~6 sulfur atoms at $\sim 2.4\text{\AA}$ and one Tc atom at 2.9\AA . These parameters are close to the structural parameter of TcS_2 reported by Allen et al. (1997). It is unclear why H_2O_2 would result in formation of a TcS_2 phase. The experimental hypothesis was that the peroxide would oxidize any labile Tc to $Tc(VII)O_4^-$. One possibility is that the H_2O_2 did indeed cause formation of TcO_4^- in the sample which then leached into the pore waters and was removed from the sample during the washing step. Thus, the observed TcS_2 could represent a Tc bearing phase which is resistant to oxidation by H_2O_2 . Unfortunately, the residual Tc concentrations in the saltstone samples were not measured to support this hypothesis.

It is reasonable to assume that there are more than one Tc species in aged saltstone and that one species is more susceptible to oxidation and/or speciation changes than the others. It is likely

that there were simple hydrolyzed species ($\text{Tc(IV)O(OH)}_2(\text{H}_2\text{O})_3$) and partially or fully sulfidized species. Hydrolyzed $\text{Tc(IV)O(OH)}_2(\text{H}_2\text{O})_3$ (aq) should oxidize first prior to the oxidation of polymerized sulfidized species. A mixture of these species still supports that structural parameters for one oxygen atom at $\sim 1.7\text{\AA}$, $\sim 2\text{-}3$ oxygen atoms for a long Tc-O at 2.1\AA , $\sim 2\text{-}3$ sulfur atoms and one Tc atoms at $\sim 2.9\text{\AA}$.

Table 5: The results of least square fit of Tc EXAFS and XRD analysis of known reference compounds. CN: coordination number, R(\AA): interatomic distance, σ^2 (\AA^2): Debye-Waller factor.

Sample	Tc-O	Tc-O	Tc-O	Tc-O/S	Tc-Tc	references
$\text{NH}_4\text{Tc(VII)O}_4$ (aq)	CN R(\AA) σ^2 (\AA^2)	4.5(4) 1.716(4) 0.0021(5)				Mckeown et al., 2007)
TcS_2	CN R(\AA) σ^2 (\AA^2)		6 2.24- 2.55		3 2.55-2.92	(Allen et al., 1997) XRD
TcSx	CN R(\AA) σ^2 (\AA^2)		7-7.4 2.38 0.013	1.7-1.9 2.77-2.78 0.007		(Lukens et al., 2005)
$\text{Tc(IV)O(OH)}_2(\text{H}_2\text{O})_3$	CN R(\AA)	1 1.728	2 1.966	2 2.198	1 2.511	(Breynaert et al., 2009)
am. Tc(IV)O_2 (s)	CN R(\AA)	4 2.01			1.4 2.49	(Mckeown et al., 2007) XRD

Table 6: The results of least square fit of Tc EXAFS analysis of aged saltstone shown in Figures 12-14. The number in parentheses is the standard deviation of the parameter obtained by EXAFS fit. *Fixed parameter. CN: coordination number, R(Å): interatomic distance, σ^2 (Å²): Debye-Waller factor. So² of 0.9 was used in the fit.

Sample		Tc-O	Tc-O	Tc-S	Tc-Tc	R-factor	
27A (0-8mm)	CN	1.1(1)	1.72(7)	4.2(5)	1*	0.011	
	R(Å)	1.718(2)	2.18(1)	2.37(2)	2.90(2)		
	σ^2 (Å ²)	0.001*	0.001(2)	0.0115*	0.011(2)		
27A (15-17mm)	CN	1.3(1)	1.3(8)	4(1)	1*	0.016	
	R(Å)	1.717(9)	2.18(2)	2.39(2)	2.92(3)		
	σ^2 (Å ²)	0.001*	0.002(3)	0.0115*	0.010(3)		
27B (0-8mm)	CN	1.7(2)	7(2)	-----		0.025	
	R(Å)	1.77(1)	2.20(4)	-----			
	σ^2 (Å ²)	0.001*	0.016(6)	-----			
27B (15-17mm)	CN	1.2(8)	-----		5.2(4)	1*	
	R(Å)	1.72(1)	-----		2.37(1)	2.87(1)	
	σ^2 (Å ²)	0.005(3)	-----		0.0115*	0.008(2)	
27C (0-6mm)	CN	1.31(1)	3(2)	2.9(7)	1*	0.0079	
	R(Å)	1.74(6)	2.13(4)	2.45(2)	2.92(2)		
	σ^2 (Å ²)	0.001*	0.009(7)	0.0115*	0.009(1)		
27C (11-15mm)	CN	0.73(9)	1.5(7)	2.92(2)	1*	0.0219	
	R(Å)	1.71(1)	2.17(2)	2.45(3)	2.92(2)		
	σ^2 (Å ²)	0.001*	0.01(2)	0.015*	0.009(2)		
27D (0-10mm)	CN	1.44(9)	3(2)	2.0(6)	1*	0.015	
	R(Å)	1.75(8)	2.17(3)	2.45(3)	2.99(2)		
	σ^2 (Å ²)	0.001*	0.009(5)	0.0115*	0.009(1)		
27D H ₂ O ₂ (0-10mm)	CN	-----		5.8(6)	1*	0.023	
	R(Å)	-----		2.40(1)	2.76(1)		
	σ^2 (Å ²)	-----		0.0115*	0.002(3)		
27E (0-3mm)	CN	1.9(1)	2.4(4)	1.9(3)	-----		
	R(Å)	1.718(5)	2.14(2)	2.41(2)	-----		
	σ^2 (Å ²)	0.001*	0.009	0.0115*	-----		
27E (3-7mm)	CN	1.1(1)	2.4(5)	2.1(5)	1*	0.022	
	R(Å)	1.73(1)	2.15(2)	2.44(3)	2.96(2)		
	σ^2 (Å ²)	0.001*	0.009*	0.0115*	0.007(1)		
27E (7-9mm)	CN	1.55(9)	1.9(4)	2.5 (4)	1*	0.015	
	R(Å)	1.728(6)	2.12(2)	2.44(2)	2.91(4)		
	σ^2 (Å ²)	0.001*	0.009*	0.0115*	0.014(5)		
27E (12.5-16mm)	CN	1.2(1)	2.1(7)	2.5(6)	1*	0.026	
	R(Å)	1.72(1)	2.16(3)	2.41(3)	2.89(2)		
	σ^2 (Å ²)	0.001*	0.009*	0.0115*	0.008(1)		
27E (16-19mm)	CN	0.7(1)	3(1)	3(1)	1*	0.0185	
	R(Å)	1.71(2)	2.21(4)	2.42(2)	2.95(3)		
	σ^2 (Å ²)	0.001*	0.009*	0.0115*	0.009(2)		
27E (19-21mm)	CN	1.17(8)	2.5(5)	2(1)	1*	0.024	
	R(Å)	1.735(7)	2.14(2)	2.40(3)	2.86(2)		
	σ^2 (Å ²)	0.001*	0.009*	0.0115*	0.008(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. Regardless of aging time (i.e., between 4 - 458 days), there is no Fe leaching into solution and the oxidation state of Fe within the saltstone monoliths appears to be ~100% Fe(III). Thus, ferrous iron appears to have been oxidized relatively rapidly in these samples and would provide little additional reduction capacity.



Sulfur speciation determined using XAS indicated that sulfate is the dominant species within the solid phase after 458 days. However, reduced sulfur species (sulfide or elemental sulfur) was observed in most samples and appeared to have an increasing fraction with depth in the monolith. This is consistent with the data in 4 days old samples previously reported (Arai and Powell, 2014). Samples aged up to 458 days under oxic, humid conditions still maintained a small amount of elemental sulfur or sulfide below 9 mm depths in the sample. Leaching tests indicated no sulfide or sulfite in the aqueous phase between 4 and 458 days. Rather sulfate and thiosulfate were the dominant aqueous species within the leachate. While the release of thiosulfate was between several hundreds to ~1,000 mg/kg in 4-281 days old samples, it increased to 1,400-2,000 mg/kg after 458 days. Sulfate leaching was initially (after 4 days of aging) at several thousands (5,000-7,000) mg/kg. However, it drastically decreased to ~100 mg/kg after 117 and 281 days, and then increased to a few hundred mg/kg after 458 days. While there was significant scatter in the data proposed to be due to the heterogenous distribution of sulfur leaching in the samples, as the sampling depth increased, the amount of thiosulfate generally increased and the amount of sulfate decreased in 458 days samples. The observation of a thiosulfate/sulfate gradient in the leaching experiments along with the observation of reduced sulfur species at depth by XAS indicate that a redox gradient persists in these samples and that a reducing zone is maintained below ~1 cm after 458 days of aging.



The Tc XAS experiments have demonstrated that Tc is likely not a single species within the saltstone formulation at 4-458 days. However, it was confirmed that all Tc was present in the tetravalent state. The XAS analysis has helped formulate a working hypothesis that Tc initially forms disordered hydrolyzed species which undergo continuous sulfidation over time.



Such a reaction will be highly dependent on the local concentration of reduced sulfur species in a sample which will be influenced by the aging time (i.e. oxidation of sulfide to sulfate), particle size of the dry feed materials, and the mobility of sulfur species within the pore waters. It is noteworthy that no pertechnetate species were observed in the XAS spectra after 117 days of aging. Thus, TcO_4^- does not appear to persist within the monolith and either 1) leaches into the



pore water or 2) is re-reduced by the saltstone. Additional studies to differentiate between these processes are proposed for the future work.

6.0 Future Work

One of the key findings in this work is the observation that Tc does not appear to be a single species within the saltstone monolith. This is proposed to be due to the heterogeneous distribution of reducing species, mainly sulfide, within the monolith and the evolution of Tc speciation over time from a hydrolyzed to sulfidized species. XAS analysis of iron speciation indicated that ferrous iron which was initially present as a component of the BFS was fully oxidized to ferric iron after 117 days. Similar analysis of the sulfur speciation indicated that a small but measureable amount of sulfur was present as sulfide or elemental sulfur which persisted for up to 458 days. Thus, it appears that the reduction capacity of the saltstone is predominantly provided by reduced sulfur species rather than ferrous iron. However, the scatter in sulfur leaching data and the range of observed Tc compounds indicates that the sulfur distribution within the system is relatively heterogeneous. Understanding the impact of this heterogeneity is crucial for understanding the specific chemical reactivity of Tc in saltstone. If the length scale associated with the heterogeneity is under the grid size of a reactive transport model, it is likely that the model will capture the bulk data and it may not be an important parameter to consider. However, if the heterogeneity of the system extends beyond the model grid resolution, then the influence of these reactions would not be captured.

Also, the observation of TcO_4^- in the initial samples and the leaching of TcO_4^- into the pooled water standing above the monoliths introduces some uncertainty regarding the initial reduction of Tc(VII) to Tc(IV). In this work, Tc was amended into samples at 125 ppm ($\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$). This is well above the expected loading level of approximately 0.4 ppm in the Saltstone Production Facility. Thus, it is possible that the TcO_4^- observed in the initial systems and the Tc leached into the pore waters was a result of incomplete reduction of Tc(VII) to Tc(IV) during the initial formation of the saltstone monolith. Thus, experiments which examine the relative amount of Tc(VII) remaining as a function of total Tc concentration in a monolith are needed. The presence of residual Tc(VII) in these sample may be due to the higher Tc concentration which could overwhelm the reduction capacity, particularly given the potentially heterogeneous distribution of sulfur species, in the local environment which would result in incomplete reduction to Tc(IV). Conversely, if a similar fraction of Tc(VII) persists after forming monoliths containing different total Tc concentrations, then the Tc(VII) fraction is a thermodynamically consistent quantity which would persist across a range of scales. To study this would require preparation of samples with a range of Tc concentrations from 0.1 to 100 $\text{mg}_{\text{Tc}}/\text{kg}_{\text{saltstone}}$ with a constant volume of water over each sample for monitoring the release of Tc as a function of concentration. The range of Tc concentrations will allow for the determination of an “effective” reducing capacity of the saltstone (i.e. determination of how much Tc(VII) can be reduced). The oxidation state in the solid phase for all samples cannot be determined using XAS

in this experiment because of the lower solid phase concentration. However, oxidation of Tc(IV) can be inferred by the concentration of Tc in the water overlying the saltstone in each sample.

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Appendix A: Eh-pH diagrams for Fe, S, and Tc generated using Geochemist Workbench.

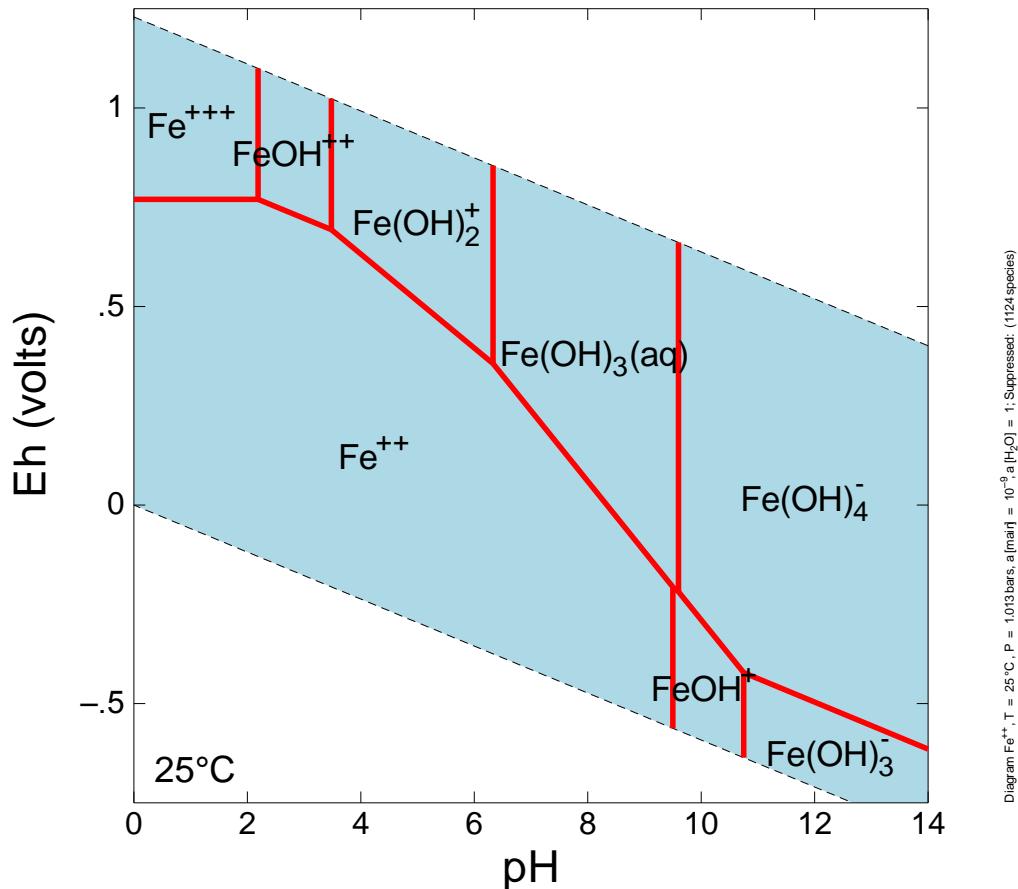


Figure A1: Eh-pH diagram of iron modeled using Geochemist Workbench and the thermo.com.v8.r6+_modNEA.dat database.

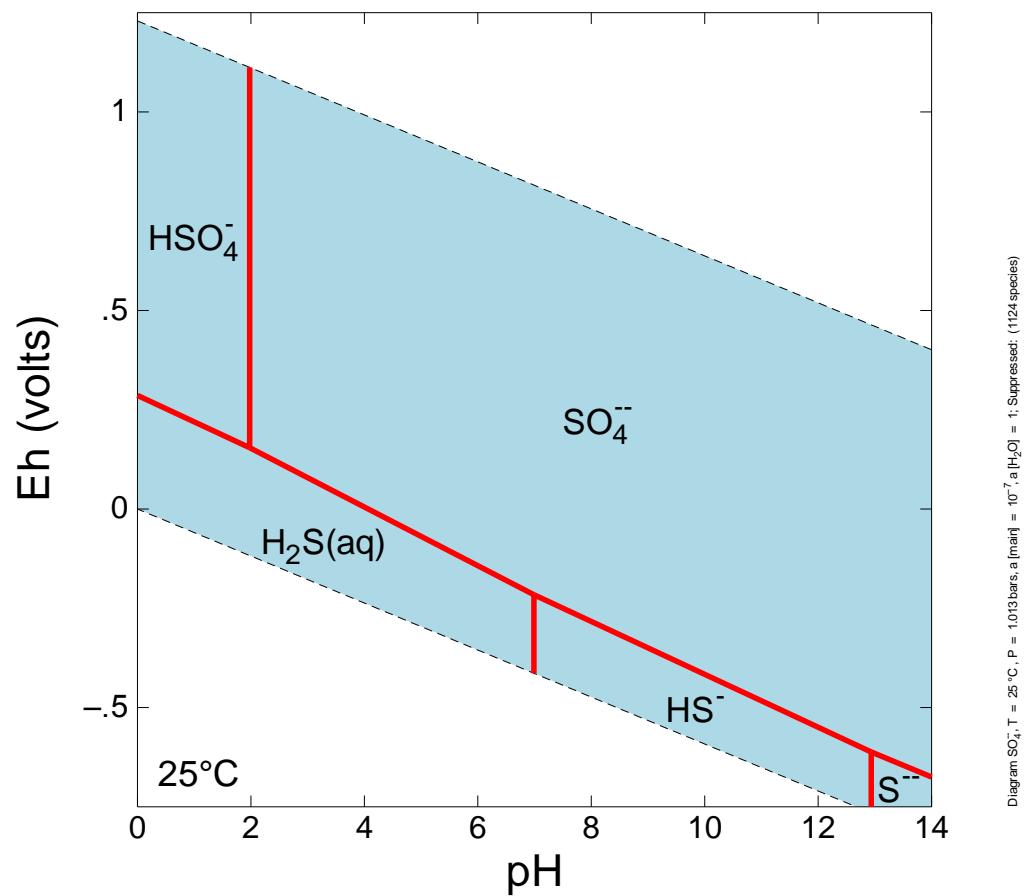


Figure A2: Eh-pH diagram of sulfur modeled using Geochemist Workbench and the thermo.com.v8.r6+_modNEA.dat database.

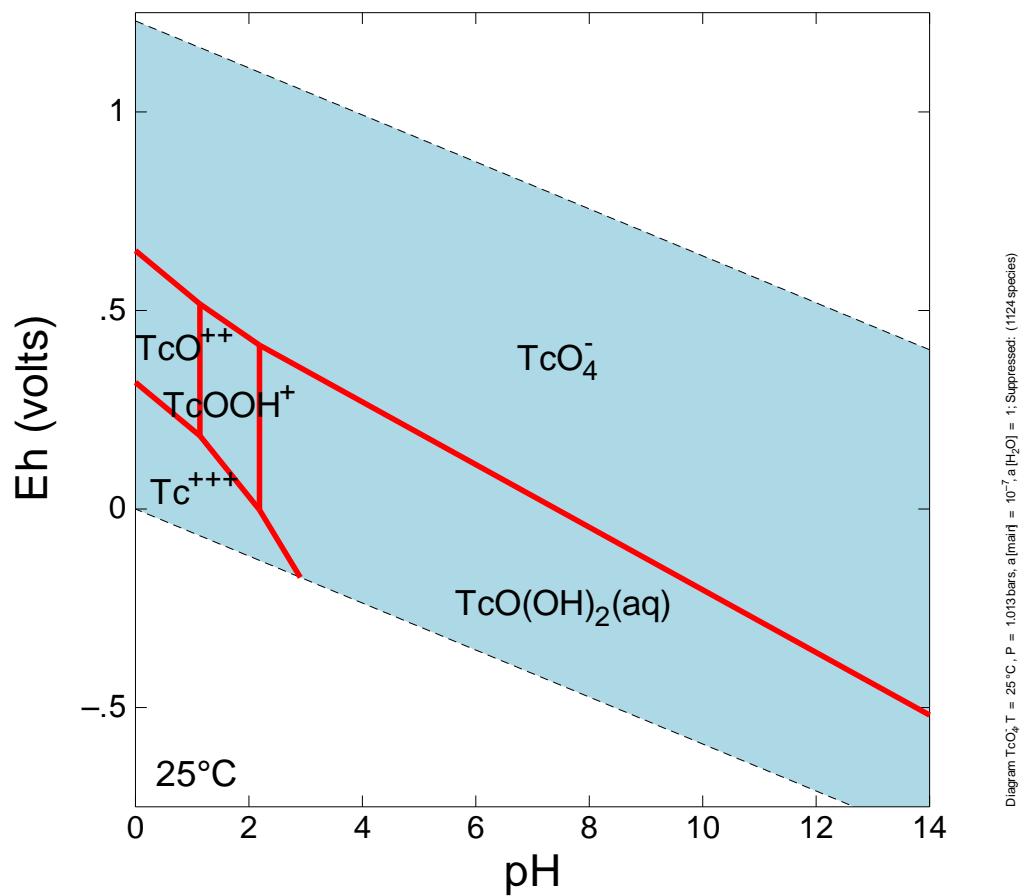


Figure A3: Eh-pH diagram of technetium modeled using Geochemist Workbench and the thermo.com.v8.r6+_modNEA.dat database.

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 MΩ cm at 25 °C
3. Laboratory Balance, max. 5100 g, ± 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 C2).
2. Weigh an empty 1 L polycarbonate volumetric flask, plus cap.
3. Weigh all chemicals in Table C1 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 ⁹⁹Tc 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.

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

In equation 1, [Tc] is the Tc-99 concentration in mg_{Tc}/kg_{saltstone}, A is Avogadro's number (6.022 x 10²³ atoms per mol), λ is the decay constant (1.04 x 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
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 the 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., N₂) at ambient temperature and high humidity.

Table B1. Base composition of ARP/MCU Saltwaste Simulant

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

Table B2. Saltstone Waste Simulant and Permeant Preparation Log

Logbook:				Requested by:			
Recipe ID:				Date:			
Sample #:				Task #:			
<hr/>							
Order of Addition	Chemical	Assay	#	Target Mass (g)	Actual Mass (g)	Balance ID	Date and Initials
1	NaNO_3	1		268.48	102.41	II	4/1/20
2		2			105.13	II	4/1/20
3		3			60.44	II	4/1/20
4	NaNO_2	1		25.39	25.40	II	4/1/20
5	Na_2SO_4	1		18.65	18.65	II	4/1/20
6	Na_2SiO_4	1		8.37	8.38	II	4/1/20
7	$\text{Al}(\text{NO}_3)_3$	1		20.33	20.36	II	4/1/20
8	Na_2PO_4	1		4.67	4.68	II	4/1/20
9	H_2O	1			~800 mL		4/1/20
10	NaOH 50%	1		127.50	127.42	II	4/1/20
<hr/>							
Total Batch (g):							
Reviewed by:				Date:			

Water source Elgin Purelab Flex 18.2 MΩ·cm, 41 μS TDS

Table B3. Saltstone Cementitious Paste Preparation Log

Logbook:	Tc-Saltstone-2014-I	Requested by:	—				
Recipe ID:	—	Date:	3/26/14				
Sample #:	—	Task #:	—				
<hr/>							
Order of Addition	Chemical	Assay	#	Target Mass (g)	Actual Mass (g)	Balance ID	Date and Initials
	P3-PC			50g	50.14g	II	3/26/14
	P2-BFS			225g	225.17g	II	3/26/14
	P1-FA			225g	229.49g	II	3/26/14
	Silica fume			492g	492.65g	II	3/26/14
<hr/>				Total Mass (g)		942.95g	
Reviewed by:	Rawell	3/26/14	Date:	3/26/14			
<hr/>				<hr/>			
Mixing Parameters				Comments			
Container: Plastic beaker				- stirred dry feed 10min @ 30 rpm			
Mixing method: overhead				- slowly added sandblast and			
Start mixing time: 10:00				stirred @ 250 rpm for 15 minutes			
End mixing time: 10:25				- stirring stopped @ 5 min + 10 min			
Total mixing time: 25min				to check for lumps.			
Measured density: not measured				<hr/>			
Reviewed by:	Rawell	3/26/14	Date:	3/26/14			

$$\text{Silica fume by hand} \frac{942.65}{(50.14 + 225.17 + 229.49)} = 0.899$$

- note 8.5g of dry mix and 20g sandblast was held back for Tc99 sample preparation.

Continued on Page 26

Broadband Underreamer RV

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

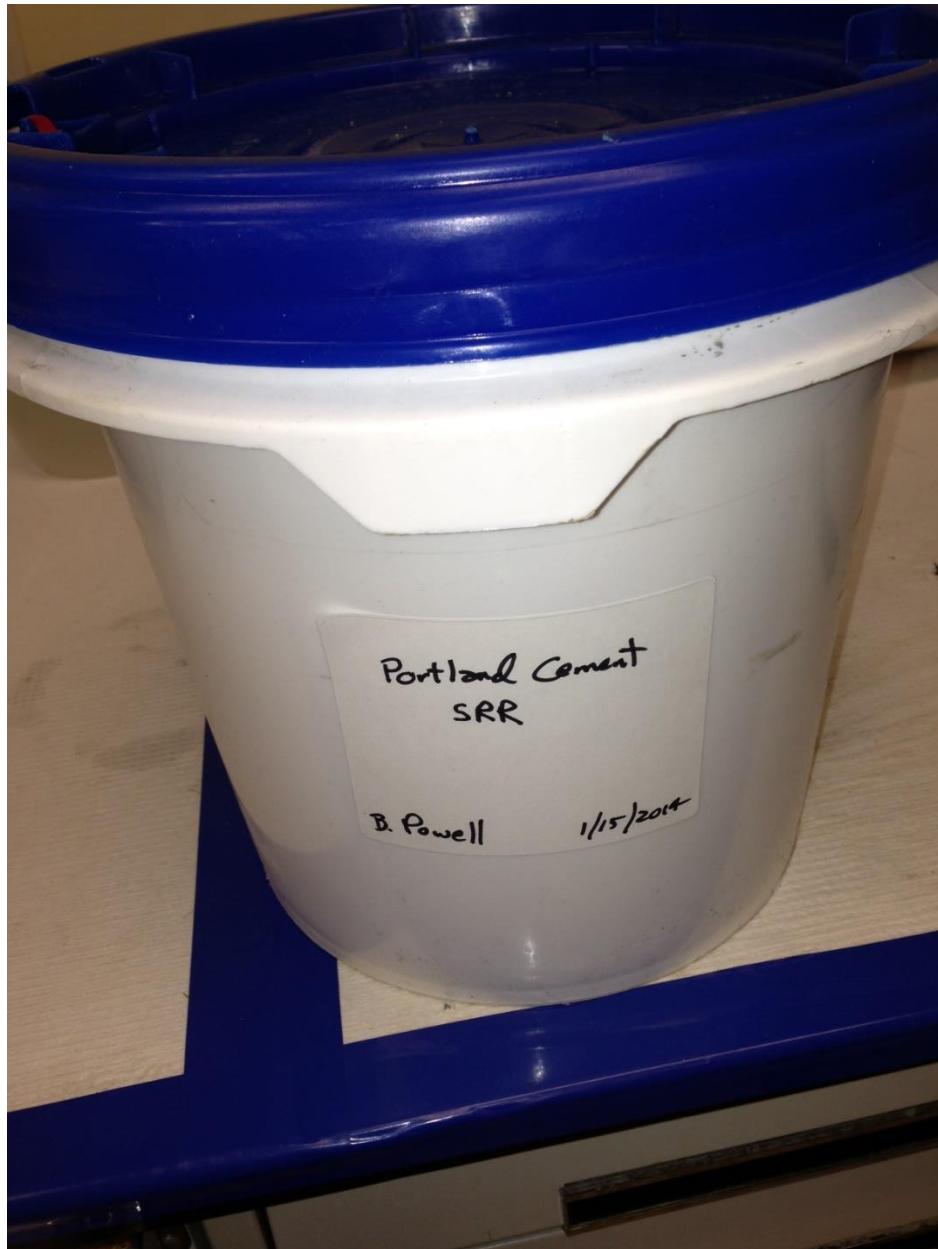


Figure B1: Photograph of bucket containing Portland cement received from S. Simner on 1/15/2014.

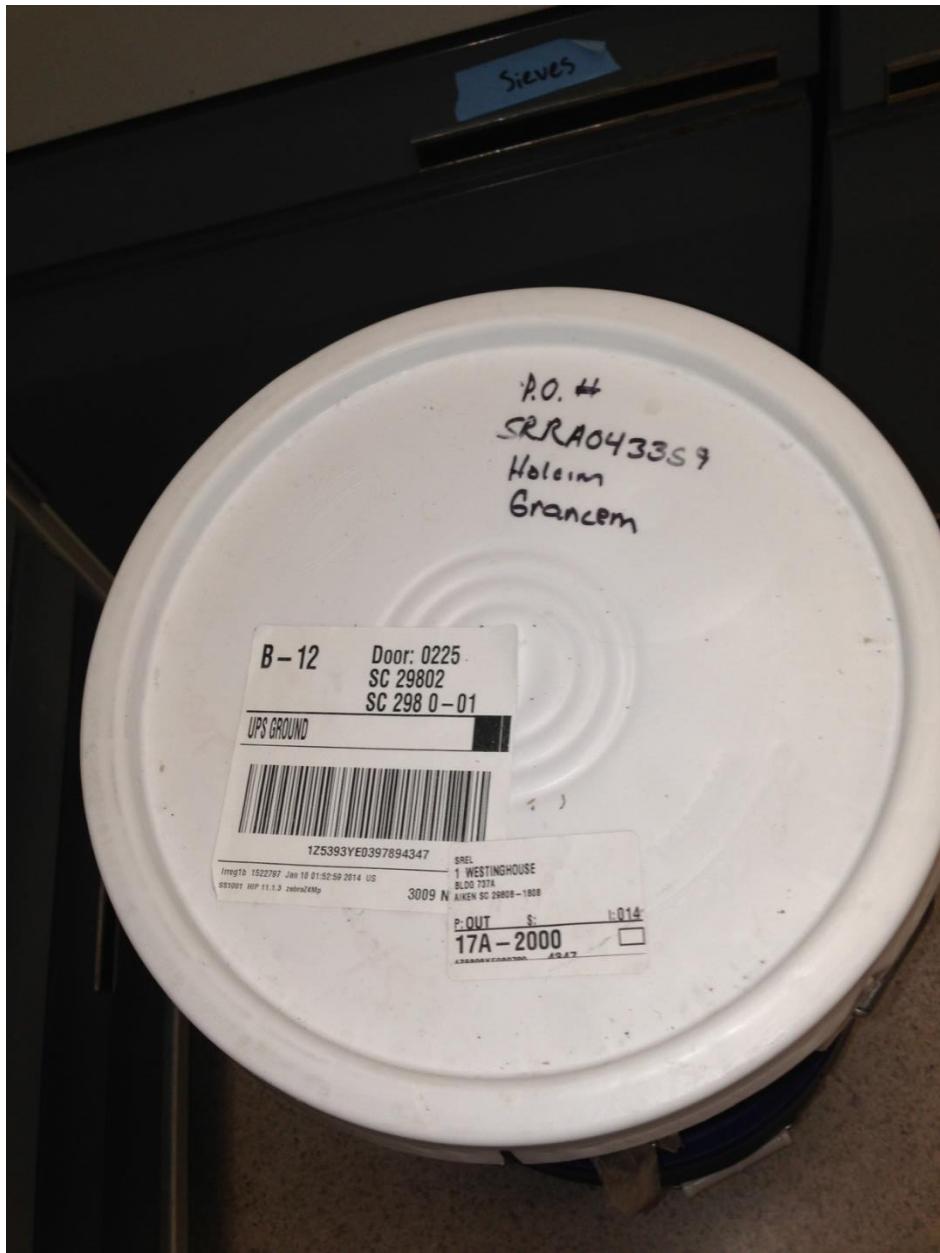


Figure B2: Photograph of bucket containing blast furnace slag received from S. Simner on 1/15/2014.

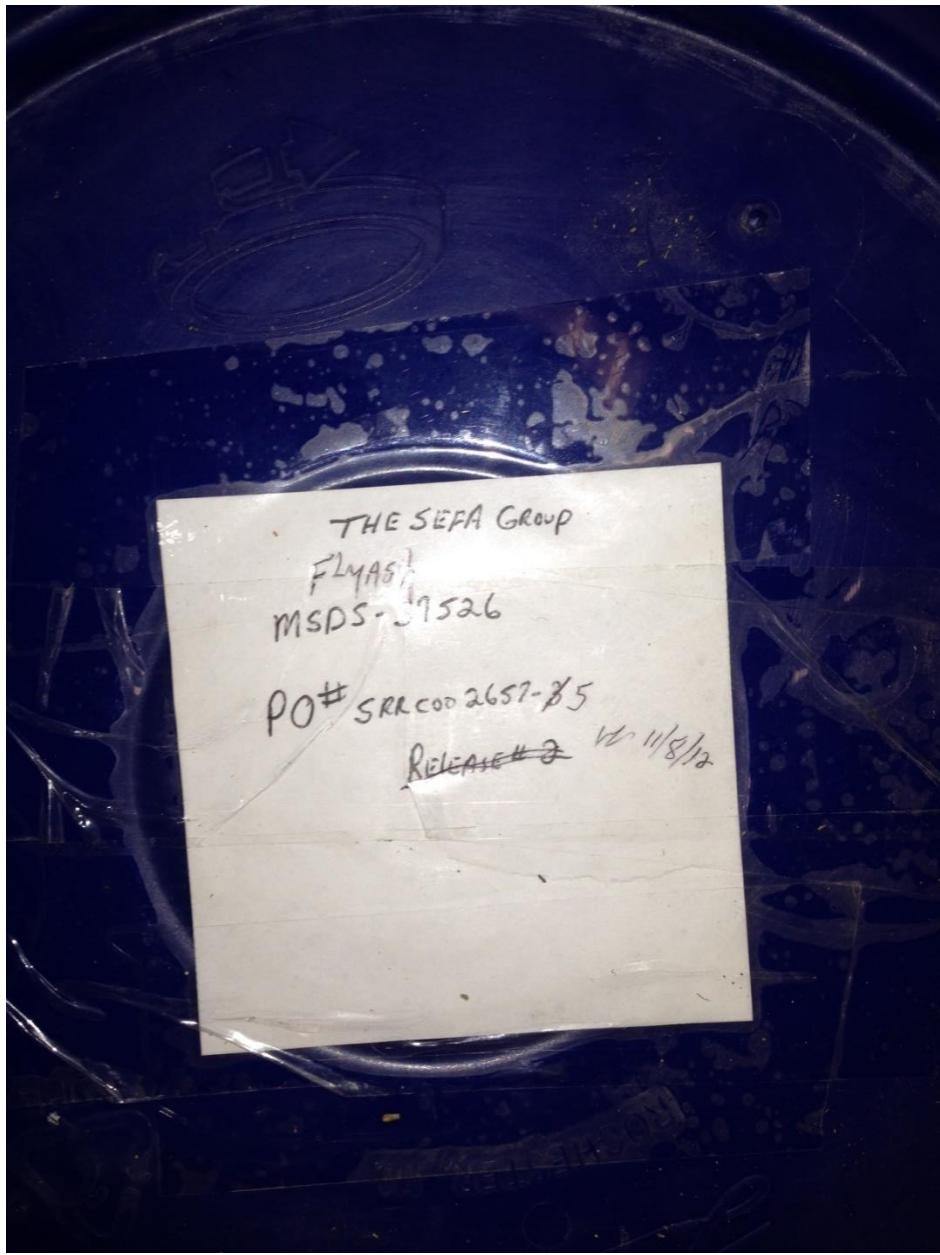


Figure B3: Photograph of bucket containing fly ash received from S. Simner on 1/15/2014.

Appendix C: Sulfur and Fe Leaching Data from 117-458 day aged saltstone

Sample Event: sulfur and iron leaching test using 13 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 (13mL) 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 ₂ O ₃] (mg/L)	[sulfite] (mg/L)	[sulfide] (mg/L)	Fe (mg/L)	pH
24B sample 11	0-5	0.96	417.60	107.4	BD	BD	BD	12.04
24B sample 12	5-10	0.47	268.32	72.93	BD	BD	BD	12.05
24B sample 13	10-15	0.37	205.96	59.18	BD	BD	BD	12.03
24B sample 14	15-20	0.51	264.74	74.91	BD	BD	BD	12.01
24B sample 15	20-25	0.51	252.46	70.0	BD	BD	BD	12.00
24C sample 1	0-5	0.53	164.81	37.04	BD	BD	BD	12.01
24C sample 2	5-10	0.48	149.47	40.81	BD	BD	BD	12.03
24C sample 3	10-15	0.42	139.28	42.66	BD	BD	BD	12.04
24C sample 4	15-20	0.75	212.72	60.52	BD	BD	BD	12.14
24C sample 5	20-25	0.60	252.73	70.08	BD	BD	BD	12.02
24D sample 1	0-5	0.45	108.05	22.04	BD	BD	BD	12.05
24D sample 2	5-10	0.50	129.24	34.5	BD	BD	BD	12.10
24D sample 3	10-15	0.40	120.51	29.76	BD	BD	BD	11.98
24D sample 4	15-20	0.24	83.16	21.10	BD	BD	BD	12.03
24D sample 5	20-25	0.34	114.39	28.58	BD	BD	BD	12.11