

## Examination of Cr and S Speciation within Saltstone Monoliths

FY13 Final Report  
Task 1: Saltstone Redox Geochemistry

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## **Examination of Cr and S Speciation within Saltstone Monoliths**

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## **LIST of ACRONYMS**

ACS: American Chemical Society

AVS: Acid volatile sulfides

BFS: Blast furnace slag

DDI: Distilled deionized water

IC: Ion chromatography

ICP-MS: Inductively coupled plasma mass spectrometry

ISE: Ion specific electrode

Micro-XRF: Micro-X-ray Fluorescence Spectroscopy.

NIST: National Institute of Standards and Technology

PIPS: Passivated Implanted Planar Silicon

SAOB: Sulfate antioxidant buffer

SRR: Savannah River Remediation, LLC

SSRL: Stanford Synchrotron Radiation Laboratory

UV-Vis: Ultraviolet-Visible Spectroscopy

VSL: Vitreous State Laboratory

XANES: X-ray absorption near edge spectroscopy

XAS: X-ray absorption spectroscopy

## 1.0 Summary

This report describes measurements of chromium and sulfur concentrations and redox speciation taken from a series of saltstone monoliths which had been aged for approximately 3 weeks and 4 months after receipt from VSL (Vitreous State Laboratory) under an oxidizing, humid atmosphere at ambient pressure. The objective of saltstone waste forms is to maintain reducing conditions through the addition of sulfide bearing blast furnace slag (BFS). The reducing conditions are expected to maintain analytes, such as Tc, in a less soluble Tc(IV) state compared with Tc(VII). Due to the difficulty in working with radioactive Tc in most analytical laboratories, Cr was used in this study as a redox surrogate for Tc. The oxidation of Cr(III) to Cr(VI) is expected to provide an upper boundary for conditions in which Tc(IV) would be oxidized to Tc(VII) (i.e., if oxidation from Cr(III) to Cr(VI) is observed then it is expected oxidation of Tc(IV) to Tc(VII) would occur). The monoliths were provided by VSL at the Catholic University of America. Twelve monoliths were provided, and at each of the two sampling intervals four monoliths were sacrificed. Four monoliths remain and these will be characterized after an aging period of 18 months. The data associated with the 18 month samples will be included in a later report. Each of the four monoliths was subjected to various analyses including:

1. Batch chromium leaching tests in an anaerobic chamber using oxygenated and deoxygenated water in which Cr(VI) concentrations were measured using UV-Vis (ultraviolet-visible spectroscopy) and total Cr was measured using inductively coupled plasma mass spectrometry (ICP-MS)
2. Batch sulfur leaching tests in an anaerobic chamber using oxygenated and deoxygenated water in which sulfur speciation and total concentrations were determined using ion chromatography (IC).
3. Micro x-ray fluorescence (micro-XRF) microprobe analysis to determine Cr distribution within the cross-sectioned saltstone monolith and oxidation state speciation (only for first sampling interval as discussed in Section 2.0).
4. X-ray near edge spectroscopy (XANES) to determine S oxidation state distribution within the cross-sectioned saltstone monolith (only for first sampling interval as discussed in Section 2.0).

Samples for chromium and sulfur leaching were performed by segmenting the monoliths and determining the concentration of chromium or sulfur in the leachate solutions as a function of depth in the monolith. Sulfur and chromium speciation using ICP-MS, UV-Vis and IC techniques were determined by removing thin sections of the monolith and determining the speciation as a function of depth using a focused x-ray beam.

Overall the results indicate that the dominant oxidation state of sulfur within the leachate solutions and the monoliths is sulfate. The leaching tests indicated only a small fraction (<1%) of the total chromium leached under both oxidizing and reducing conditions. However, the degree of Cr leaching slightly (max. leaching: 1.4 to 10 mg/kg) increased with increasing aging time of saltstone. Cr(VI) was the dominant chromium oxidation state measured in the leachate from leaching tests using oxidizing and degassed waters. In contrast, the XANES and micro-XRF analysis indicated that Cr(III) was the dominant oxidation state within the saltstone. This bulk XANES analysis indicating Cr(III) as the dominant oxidation state is consistent with the low fraction of total Cr released during the leaching tests. The concentrations of sulfur and chromium in the leachate solutions were similar between the oxic and anoxic leachate solutions.

## **2.0 Material Preparation and Receipt**

Monoliths were received from VSL on 3/25/2013. The monoliths were cylindrical with an approximate 1 inch diameter and were 4 inches in height. Each sample was individually labeled by VSL with 500-X where “X” was a unique integer for each saltstone sample. The “500” within the sample name refers to the 500 ppm concentration of Cr(VI) as sodium chromate which was added to each monolith upon preparation. The source of sulfur in saltstone is predominantly from the BFS and cement. The concentration of sulfur in each monolith was not provided by VSL. Upon opening the package it was noticed that some monoliths had loose material on the top. After discussions with Savannah River Remediation, LLC (SRR) and VSL it was decided to remove this loose material by turning the vial upside down and lightly shaking. The removed material was weighed and accounted for only a few milligrams of material. Therefore, the loose material represented only a small fraction of the total monolith.

The monoliths were cured at VSL for 28 days prior to sending to Clemson. At Clemson University, the samples were stored in a vacuum desiccator chamber in which the desiccant was removed and replaced by ~500 mL of distilled deionized water (DDI) with a resistivity greater than 18 MΩ·cm. The vacuum valve was removed leaving a hole in the side of the chamber so that exchange between the chamber and the ambient atmosphere could take place. Therefore, high humidity oxidizing conditions were maintained. The presence of oxygen was visually verified through the use of an indicator solution which would change color in the absence of oxygen. Throughout the experiments oxic conditions were maintained. It was noticed that several monoliths would “pool” water on the surface presumably due to the high humidity environment within the chamber.

Monoliths were removed from the chamber for analysis after approximately one and five months of equilibration. To ensure all four samples taken during a sampling interval were exposed to the humid, oxidizing conditions to equal amounts of time, some monoliths were “quenched” by capping and sealing the vessel containing the monolith and placing the monolith in a -4°C freezer. These quenched monoliths were analyzed at a later date. Due to the need to secure time at synchrotron facilities and the amount of work involved to perform these measurements, it is not possible to time the experiments such that all four monoliths were analyzed on the same day. Table 1 lists the sample ID and treatment conditions for each monolith analyzed in this work. There are four monoliths which have not been quenched at this point and remain in the humid, oxidizing chamber at the time this report is being written. The current plan is to examine those monoliths after at least 18 months of aging.

Note that samples 500-11 and 500-12 were quenched on 07/19/2013 but were not analyzed with the other two samples quenched on that same date. These two samples are for Cr and S micro-XRF and XANES measurements. As described in the task plan for this project, synchrotron based analyses are based on availability of beam time. Since the synchrotron facility at the Stanford Synchrotron Radiation Laboratory (SSRL), Menlo Park, CA was not in operation on 07/19/2013 and the next cycle for beam time allocation does not start until after the FY13 fiscal year ends, it was not possible to analyze the five month aged samples using synchrotron techniques. These samples were quenched for analysis during FY14 if possible.



**Figure 1: Saltstone monoliths within the oxic, humid chamber used for aging experiments. The oxygen indicator (RT Anaero Indicator, Fisher Scientific) solution is contained within the 50 mL Erlenmeyer flask.**

**Table 1: The record of saltstone samples used in the leaching tests and synchrotron based X-ray analysis.**

| Sample ID | Date Received | Date Quenched | Date of Analysis                    | Type of Analysis                        |
|-----------|---------------|---------------|-------------------------------------|---|
| 500-2     | 3/25/13       | 4/14/13       | 4/15/13 Cr Leaching<br>6/20/13 SSRL | Cr Leaching, Cr bulk XANES              |
| 500-3     | 3/25/13       | 4/14/13       | 6/20/13 analyzed at SSRL            | S bulk XANES, Cr XAS, Synch. microprobe |
| 500-4     | 3/25/13       | 4/14/13       | 7/22/13                             | S leaching, AVS                         |
| 500-7     | 3/25/13       | 4/14/13       | Transferred to Powell Lab 8/2/13    |   |
| 500-8     | 3/25/13       | 7/19/13       | 7/29/13                             | Cr leaching                             |
| 500-10    | 3/25/13       | 7/19/13       | 7/22/13                             | S leaching, AVS                         |
| 500-11    | 3/25/13       | 7/19/13*      | Transferred to Powell Lab 8/2/13    | -                                       |

|        |         |          |                                  |     |
|--------|---------|----------|----------------------------------|-----|
| 500-12 | 3/25/13 | 7/19/13* | Transferred to Powell Lab 8/2/13 |     |
| 500-13 | 3/25/13 | TBD      | Transferred to Powell Lab 8/9/13 | TBD |
| 500-17 | 3/25/13 | TBD      | Transferred to Powell Lab 8/9/13 | TBD |
| 500-18 | 3/25/13 | TBD      | Transferred to Powell Lab 8/9/13 | TBD |
| 500-21 | 3/25/13 | TBD      | Transferred to Powell Lab 8/9/13 | TBD |

\*Because of the last synchrotron beam time allocation in May-June, 2013, we were not able to conduct the XANES and synch. microprobe analysis on the ~5mo aged sample that was quenched in July 19, 2013. Samples have been transferred from Dr. Arai's laboratory to Dr. Powell's laboratory. Samples 500-11 and 500-12 remain quenched in a -4°C freezer and samples 500-13, 500-17, 500-18, and 500-21 remain in the humid, oxidizing chamber.

## 3.0 Methods

### 3.1 Saltstone Segmentation and Leaching Procedures

Saltstone samples spiked with 500 ppm ( $\text{mg}_{\text{Cr}}/\text{kg}_{\text{saltstone}}$ ) Cr were obtained from VSL. Depth dependent saltstone samples for both Cr and S leaching tests 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. The approximately 0.5g of material was divided and transferred into two Nalgene Oak Ridge High-Speed Centrifuge tubes. The exact mass of powder transferred was determined gravimetrically. To prepare degassed MilliQ water, MilliQ water was boiled for 20min, and then cooled to room temperature. It was kept in an anaerobic glove chamber for 5-7 days prior to the experiments. The first set of tubes was filled with degassed MilliQ water inside the glove bag while the second was transferred to an aerobic environment and then filled with oxygenated MilliQ water. All tubes were shaken on an end over shaker at 26 rpm for 24 hours. The samples were then removed and centrifuged at 10,500 rpm for 8 minutes; this is sufficient time for particles with a hydrodynamic radius greater than 100 nm to be removed from the supernatant (calculations based on Stokes' law). Approximately 10 mL of leachate was collected and filtered through a 0.45  $\mu\text{m}$  PVDF (Polyvinylidene fluoride) filter.

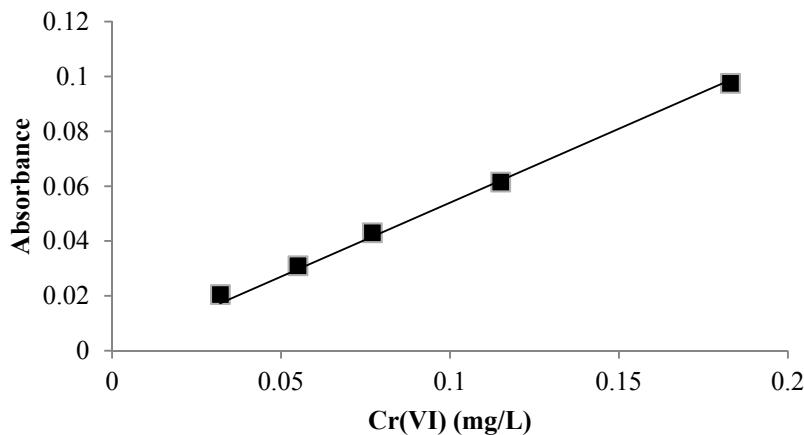
### 3.2 Chromium Leaching Sample Preparation

Saltstone sample 500-2 was quenched, by transferring into a freezer, on 14 April 2013 (3 weeks after being received on 03/25/2013) and sample 500-8 was quenched on 19 July 2013 (approximately 4 months after receipt). Sample 500-2 was drilled on 15 April 2013 while sample 500-8 was drilled on 29 July 2013 to represent two separate aging times. Note that attempts were also made to measure the Cr

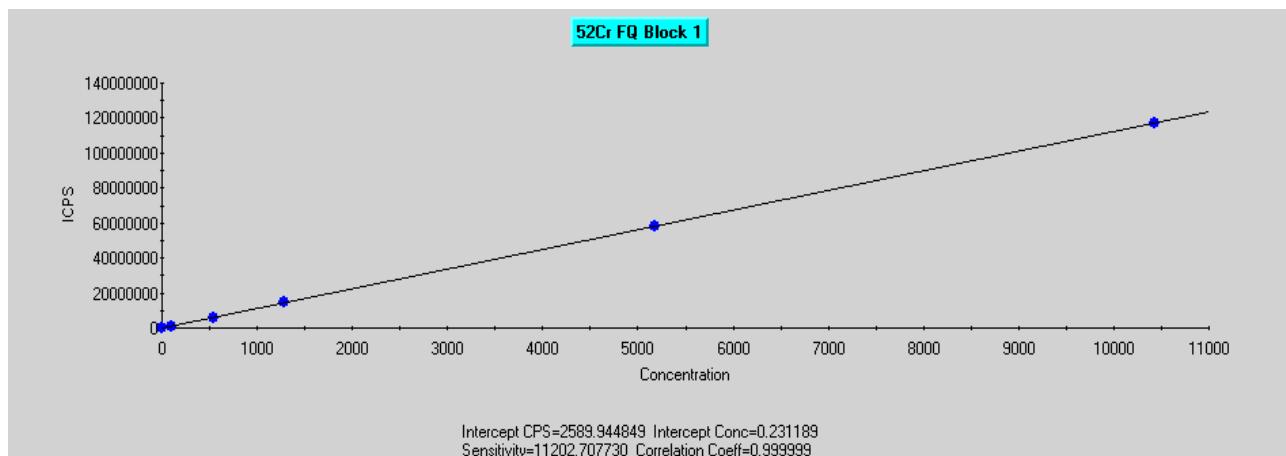
concentration in leachate solutions from monoliths 500-4 and 500-10 but no measurable quantity of Cr was measured as discussed below.

### 3.3 Chromium Analysis

Aliquots from sample 500-2 were analyzed using the s-diphenyl carbazide UV-Vis spectrophotometric method described by Bartlett and James (Bartlett and James, 1979) for total hexavalent Cr. A standard curve was made using a 1000 ppm Cr ICP-MS National Institute of Standard Technology (NIST) traceable standard (Figure 2). However, Cr(VI) was not detectable using the UV-Vis method for the leachate aliquots from monolith 500-8, possibly due to changes in the pore water chemistry of saltstone over the different aging times causing an interference with the spectrophotometric method. It is also possible that the detection limits of the UV-Vis method (0.62  $\mu\text{mol/L}$ ) were above the concentration of Cr in the samples. Therefore, aliquots from sample 500-8 were diluted with 2% Aristar Plus nitric acid and analyzed for total soluble Cr using an ICP-MS Thermo Scientific X Series 2. The ICP-MS was calibrated using Cr ICP-MS NIST traceable standard (Figure 3). The calibration curve intercept concentration of 0.23 ppb ( $\mu\text{g/L}$ ) is the detection limit. Note that the ICP-MS measurement is that of total Cr. Therefore, oxidation state speciation cannot be determined as it can with the UV-Vis method. Cr was measured in the aliquots from 500-8 above this detection limit and those results are reported in Figure-5. It is noteworthy that the leachate solutions from monoliths 500-4 and 500-10 were also analyzed for Cr and none of the leachate samples had Cr concentrations above the detection limit.



**Figure 2: Cr(VI) calibration curve analysis using Cr ICP-MS NIST traceable standard and MilliQ water.**



**Figure 3: Cr calibration curve using Cr ICP-MS NIST traceable standard in 2% nitric acid.**

### 3.4 Sulfur Leaching Sample Preparation

Sample 500-4 was quenched, by transferring into a freezer, on 14 April 2013 (20 days after receipt from VSL) and sample 500-10 was quenched on 19 July 2013 (approximately 4 month after receipt from VSL). Both samples were analyzed on 22 July 2013. One mL of each leachate was analyzed by IC using sulfate, thiosulfate, and sulfide American Chemical Society (ACS) grade standards.

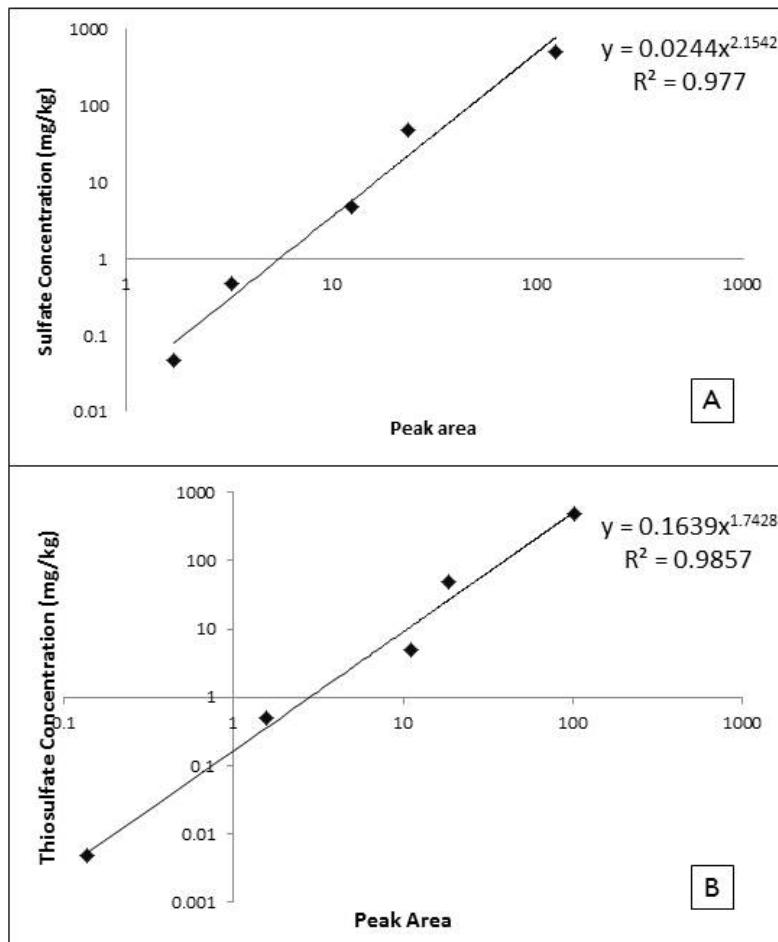
### 3.5 Acid Volatile Sulfide (AVS) Measurements

A portion of the 0.5 mg saltstone powder was transferred into a third set of centrifuge tubes under anaerobic conditions. The exact mass of powder transferred was determined gravimetrically. These tubes were capped and transferred outside the glove bag. They were weighed to determine the mass of saltstone. Then 50 mL of 1M HCl and a magnetic stir bar were added to a 250 mL Corning Biometer flask. Sulfide antioxidant buffer (SAOB) was added to the attached glass reservoir in a 6:1 ratio with the mass of saltstone powder and capped. The centrifuge tube containing saltstone powder was uncapped and quickly added to the volumetric flask and then immediately capped. The contents of the flask were stirred briskly for approximately 60 minutes. The SAOB solution was removed and the sulfide content was measured using an ion-selective electrode (ISE) to determine the molar concentration of AVS within each sample.

### 3.6 Sulfur Speciation Measurements using Ion Chromatography

Aliquots of the leachate solutions were measured to determine sulfate, thiosulfate, and sulfide concentrations using ion chromatography. Unfortunately, it was found that the SAOB solution that is commonly used to preserve sulfur redox states in environmental sampling campaigns also interferes with separation of sulfur species using IC. Therefore the samples were only diluted with degassed DDI water instead of a mixture of water and SAOB solution. Furthermore, the IC effluent peaks for thiosulfate and sulfide significantly overlap at approximately 21.2 and 22.3 minutes, respectively. Therefore in order to report quantitative measurements the peak areas for both sulfide and thiosulfate have been combined and are reported as a sulfide/thiosulfate concentration. However, as will be discussed in the subsequent text

this has a minimal effect on the data since the vast majority of sulfur was found to be present as sulfate. Calibration curves for sulfate and the combined sulfide/thiosulfate measurement are provided in Figure 4.



**Figure 4:** A. Sulfate calibration curve for IC analysis with a peak area at approximately 11 minutes. B. Sulfide/Thiosulfate calibration curve for IC analysis with a peak area at approximately 21 minutes.

### 3.7 Synchrotron Based X-ray Analysis

Macro- and micron-scale chemical speciation of Cr was evaluated at beam lines 4-3 and 2-3 at the SSRL. For the bulk analysis, segmented saltstone powder samples were used. All samples were loaded in x-ray absorption spectroscopy (XAS) sample holders in an anaerobic glove chamber. Samples were sealed with kapton/polypropylene film. They were kept in mylar bags with 30 cc oxygen scrubber packs (IMPAK Corporation, CA), until the analysis. Incident of energy was calibrated with respect to the pre-edge peak of sodium chromate. In order to assess the % Cr(VI) fraction in saltstone samples, a calibration curve was constructed using the Cr XANES pre-edge peak features. Different Cr(VI) and Cr(III) salt mixtures were prepared using ACS grade  $K_2Cr(VI)O_4$  and  $Cr_2(III)O_3$ . A depth discrete saltstone chip cut vertically from the center of the saltstone core (1 x 2mm) was also analyzed using microfocused XANES and micro XRF spectroscopy. The XRF compositional maps of Cr were collected at 5993 eV for Cr(VI),

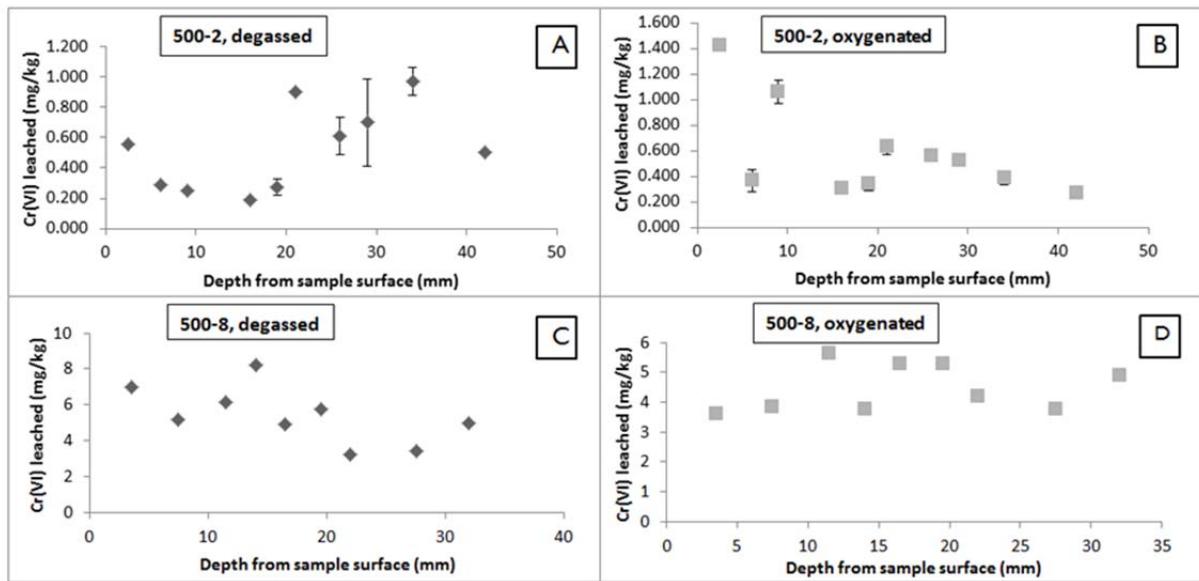
6003 eV for Cr(III), 6010 eV for total Cr in each pixel using a Canberra SL30165 Si(Li) detector. Once areas of Cr abundance were identified around grains, synchrotron microbeam (5(H) x 3(V)  $\mu\text{m}$ ) XANES structure spectra were collected up to 200 eV above the Cr K edge absorption energy in fluorescence mode using a Canberra 9-element Ge Array detector.

The S XANES analysis was performed using beamline 4-3 at the SSRL. The monochromator consists of crystal pairs of Si(111) with a wavelength resolution of 0.2 eV at the S K-edge energy (2472 eV). Fresh (<2 hrs after drilling) saltstone powder samples were sealed in XAS sample holders with polypropylene film in an anaerobic box and kept in a mylar bag with oxygen scrubber prior to analysis. The first white line peak of thiosulfate was used to calibrate the incident of energy at 2472.02eV. The S XANES spectra were recorded in fluorescence mode using a Passivated Implanted Planar Silicon (PIPS) detector in He atmosphere at room temperature. Samples were scanned by incident X-ray energy over the range of 2460 to 2570 eV using a quick scan mode. Average spectra consist of 1-3 individual scans.

## 4.0 Results and Discussion

### 4.1 Results from Cr leaching tests

Results from the Cr leaching tests of monolith 500-2 are shown in Figure 5. The concentration of Cr in the leachate solution was used to calculate a “leachable” concentration of Cr within the saltstone. This allows direct comparison with the total Cr concentration of 500 ppm ( $\text{mg}_{\text{Cr}}/\text{kg}_{\text{saltstone}}$ ) in the monoliths. The 500-2 leaching test has extremely low concentrations (0.19 to 1.42  $\text{mg}_{\text{Cr}}/\text{kg}_{\text{saltstone}}$ ) of Cr in both degassed and oxygenated systems. Leaching tests using oxygenated and degassed solutions from monolith 500-2 and monolith 500-8 show a similar range of Cr concentrations. Two leaching solutions were used to verify if the samples handling may have impacted the data in terms of artificially oxidizing Cr(III) under aerobic conditons. The depth discrete drilling and sample collection was performed in a glovebox to ensure reducing conditions (oxygen content less than 1 ppm) in the event that the core of a monolith contained a reduced zone that would oxidize upon exposure to air. The similar results from the two types (oxygenated and degassed) of leaching tests provide circumstantial evidence that artificially induced oxidation of Cr did not occur. If the oxidation was occurring, one should observe near 100 % Cr recovery during the leaching tests. The leaching tests with monolith 500-8 exhibit higher Cr concentrations (3.60 to 8.23  $\text{mg}_{\text{Cr}}/\text{kg}_{\text{saltstone}}$ ) relative to the 500-2 monolith leaching tests performed at an earlier time. For the 500-2 oxygenated and 500-8 degassed systems, there is an overall decrease in Cr concentration with increasing sample depth. The 500-2 degassed system shows an increase with increasing sample depth, while the 500-8 oxygenated test shows only a slight increase with increasing sample depth. All samples indicate spikes in the Cr concentration, possibly indicative of heterogeneous distribution of Cr throughout the monolith. Thus the variations in concentration as a function of depth may be statistical fluctuation based on localized Cr concentrations. It is noteworthy that there is an average 4.4% increase in the overall average Cr leached with increasing aging time. This is an interesting result and indicates that measurement of the remaining 4 monoliths after an extended aging time will provide useful data regarding the release of redox active ions from saltstone under humid, oxidizing conditions.



**Figure 5:** A. Cr leaching test results for 500-2 segmented 14 April 2013 under degassed conditions. B. Cr leaching test results for 500-2 segmented 14 April 2013 under oxygenated conditions. C. Cr leaching test results for 500-8 segmented 29 July 2013 under degassed conditions. Standard deviation (hidden within data markers) is  $\leq 0.061$ . D. Cr leaching test results for 500-8 segmented 29 July 2013 under oxygenated conditions. Standard deviation (hidden within data markers) is  $\leq 0.061$ .

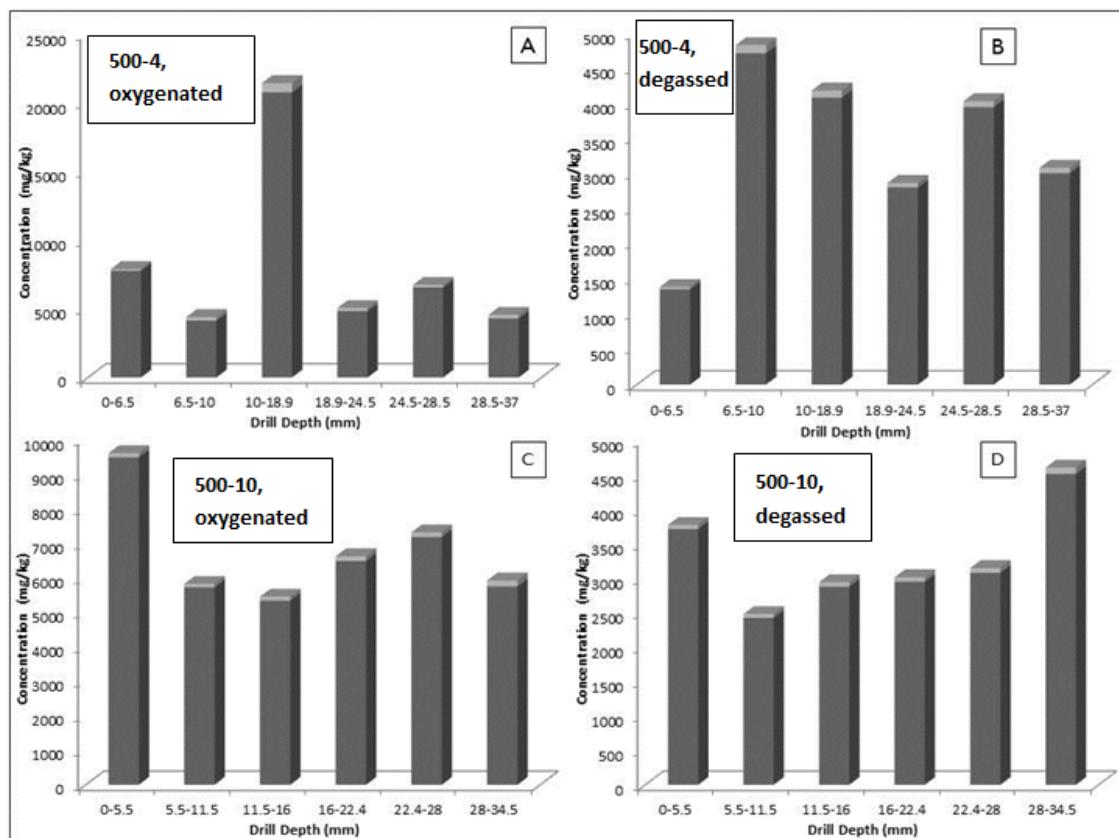
#### 4.2 Results from Sulfur Leaching Tests

The sulfate concentrations for 500-4 and 500-10 in Figure 6 show variability as a function of depth. In general, the concentration of sulfate was much greater than the concentration of thiosulfate/sulfide. For the sample measured after approximately 3 weeks of aging (500-4), the average measured sulfate concentration under degassed conditions is 41% of the same value under oxygenated conditions. For thiosulfate/sulfide this value is only 27%. The sulfate concentrations for 500-10 under degassed conditions are 48.9% of the same value under oxygenated conditions, while for thiosulfate/sulfide the value is 52.5%. Therefore, there appears to be more sulfate in oxygenated leachate solutions compared with that in the degassed leachate solutions. In general, the thiosulfate/sulfide concentrations were much smaller than sulfate concentrations in leachate from both oxidizing and degassed systems. However, there were higher concentrations of thiosulfate/sulfide measured under oxygenated conditions for both 500-4 and 500-10. There was more of a difference between oxygenated and degassed average thiosulfate/sulfide concentrations for sample 500-4 than 500-10 (294 and 79 mg<sub>S</sub>/kg<sub>saltstone</sub> vs. 132 and 69 mg<sub>S</sub>/kg<sub>saltstone</sub>, respectively).

Sample 500-4 has a very high sulfate concentration at the 10-18.9 sample depth, but otherwise has comparable concentrations under oxygenated conditions with 500-10. The corresponding average thiosulfate/sulfide values are higher for 500-4 than 500-10 (294 vs. 132 mgs/kg<sub>saltstone</sub>). Under degassed

conditions, the average sulfate concentrations are similar between the two samples ( $3317 \text{ mg}_S/\text{kg}_{\text{saltstone}}$  for 500-4 vs.  $3256 \text{ mg}_S/\text{kg}_{\text{saltstone}}$  for 500-10), as are the thiosulfate/sulfide concentrations ( $79 \text{ mg}_S/\text{kg}_{\text{saltstone}}$  for 500-4 vs.  $69 \text{ mg}_S/\text{kg}_{\text{saltstone}}$  for 500-10).

For the AVS measurements of the saltstone powders, the sulfide captured in SAOB was  $\leq 0.032 \text{ mg/L}$  (32 ppm), which was below the linear detection range of the ISE. These values corresponded to  $\leq 0.2 \text{ mg/kg}$  sulfide from the saltstone powder. Therefore, it appears that the majority of sulfur contained within the monolith is present as sulfate. This is consistent with the high sulfate concentrations observed in the leaching tests and the results of S XANES analysis. This evidence supports the theory that oxidation of sulfide to sulfate is not responsible for the observed difference between the oxygenated and degassed leaching experiments discussed above. As will be discussed in the subsequent text, the observation of relatively little sulfide and high sulfate concentrations within the saltstone monolith is consistent with S XANES measurements.



**Figure 6: A. Oxygenated sulfur leaching test for 500-4.\*** Dark grey indicates sulfate; light grey indicates cumulative thiosulfate/sulfide concentration. **B. Degassed sulfur leaching test for 500-4.** **C. Oxygenated sulfur leaching test for 500-10.** **D. Degassed sulfur leaching test for 500-10.\***Sulfate and thiosulfate/sulfide speciation analyzed with IC while AVS was below detection limit ( $\leq 0.03 \text{ ppm}$ ).

There was an overall trend in the  $E_h$  values becoming less negative with increasing saltstone depth as shown in Table 2. The pH increased with sample depth and overall the oxygenated leaching samples had higher pH values. It is noteworthy that the highest measured  $E_h$  (10-18.9 cm depth for sample 500-4) also had the highest sulfur released during the leaching experiments. This may indicate that the higher  $E_h$  conditions facilitated greater release of sulfate.

**Table 2: Measurements of  $E_h$  in DG (degassed) leaching analysis and pH in DG and O (oxygenated) leaching analysis for 500-4 and 500-10.**

|               | Drill Depth<br>(mm) | $E_h$ (mV)-<br>DG System | pH - DG<br>system | pH - O<br>system |
|---------------|---------------------|--------------------------|-------------------|------------------|
| <b>500-4</b>  | 0-6.5               | -20                      | 10.72             | 11.17            |
|               | 6.5-10              | 46.5                     | 11.32             | 11.58            |
|               | 10-18.9             | 68.6                     | 11.33             | 11.58            |
|               | 18.9-24.5           | 27.5                     | 11.31             | 11.2             |
|               | 24.5-28.5           | 42.2                     | 11.38             | 11.58            |
|               | 28.5-37             | 39.7                     | 11.31             | 11.74            |
| <b>500-10</b> | 0-5.5               | -93.7                    | 10.47             | 10.9             |
|               | 5.5-11.5            | -51                      | 11.36             | 11.69            |
|               | 11.5-16             | 1                        | 11.42             | 11.58            |
|               | 16-22.4             | 38.3                     | 11.47             | 11.56            |
|               | 22.4-28             | -4.3                     | 11.43             | 11.6             |
|               | 28-34.5             | -35.9                    | 11.45             | 11.81            |

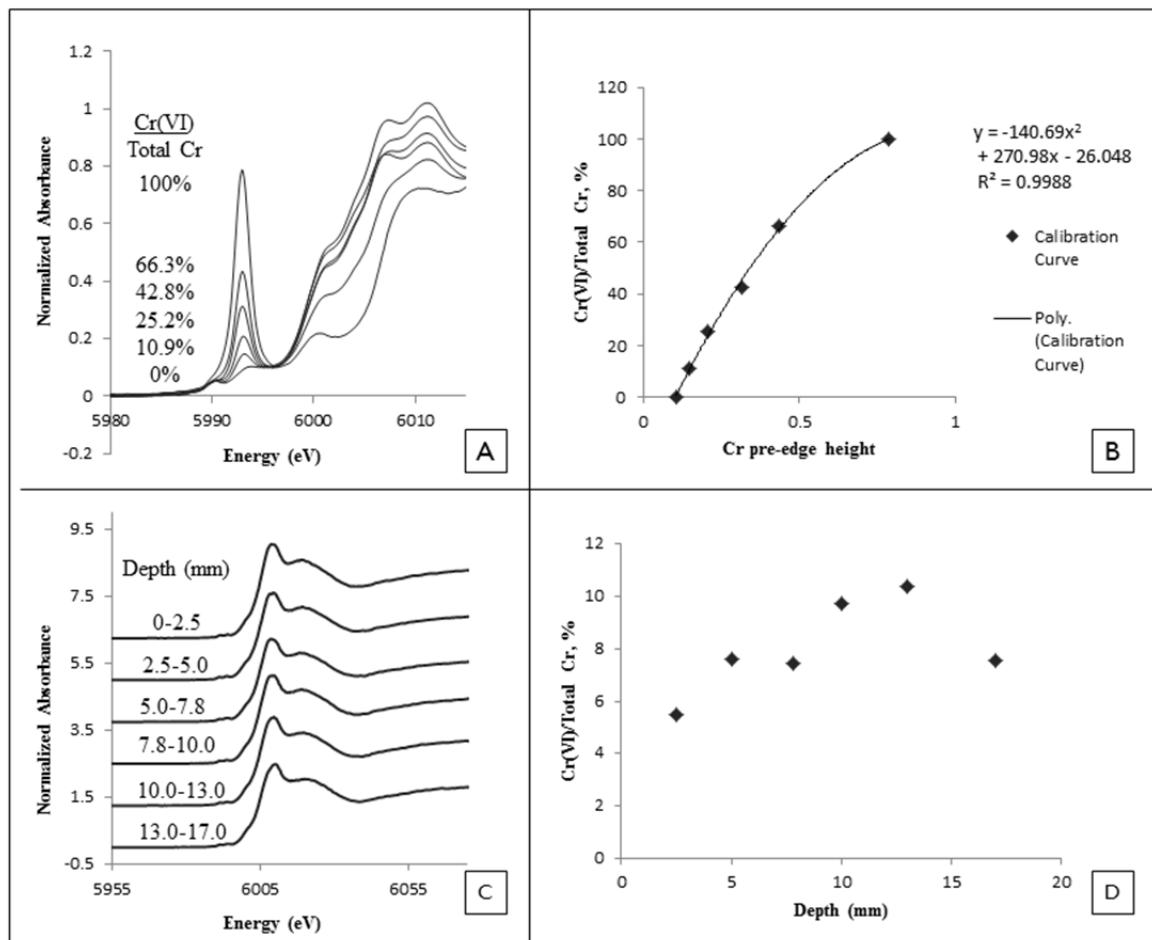
#### **4.3 Bulk XANES Cr Analysis:**

A Cr valence state calibration curve and corresponding reference spectra are shown in Figures 7A and 7B. The intensity of pre-edge peak increases with increasing the content of Cr(VI) in samples. All of Cr XANES spectra in Figure 7C indicate lack of Cr(VI) pre-edge feature, suggesting that Cr is predominantly Cr(III). Using the Cr XANES calibration curve and the pre-edge peak intensity of XANES spectra in Figure 7C, the fraction of Cr(VI) within the saltstone was estimated. The results show 1) no clear trend in Cr(VI) distribution as a function of depth and 2) the content of Cr(VI) is between 5.8-10.5% at the depth of 0-17mm. These results are consistent with the leaching tests described previously in which little Cr was leached into either oxidizing or degassed leachate solutions.

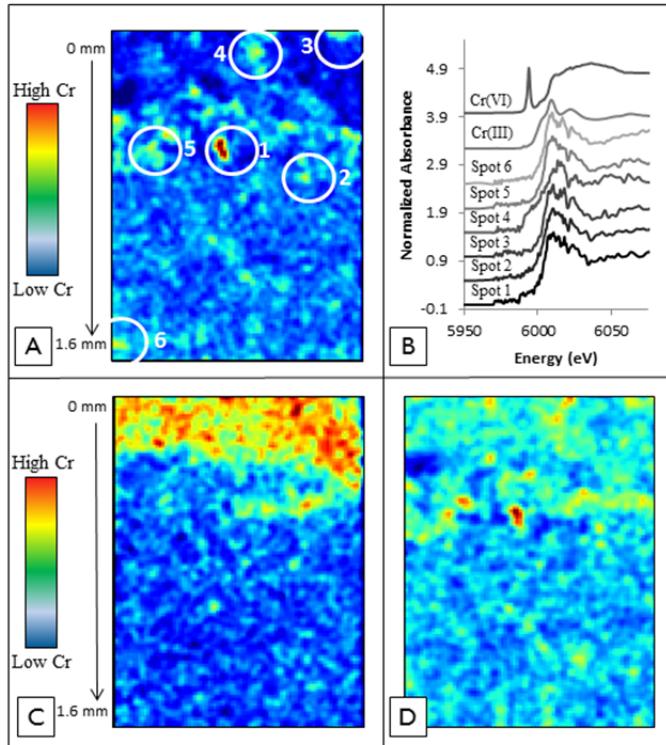
#### **4.4 Microfocused XANES analysis:**

Figure 8A shows that total Cr XRF map in a saltstone chip. When Micro-XANES spectra at Cr hotspots are compared with Cr(III) and Cr(VI) reference spectra (Figure 8B), it is clear that the pre-edge peak is near negligible except for spot 4. Using the intensity of pre-edge peak in each pixel, we further analyzed the distribution of Cr(VI) with respect to the large Cr(III) background. The results are shown in Figure 8C and 8D. The trace level of Cr(VI) is concentrated at near surface (0- ~2mm) while Cr(III) is

distributed throughout the sample.



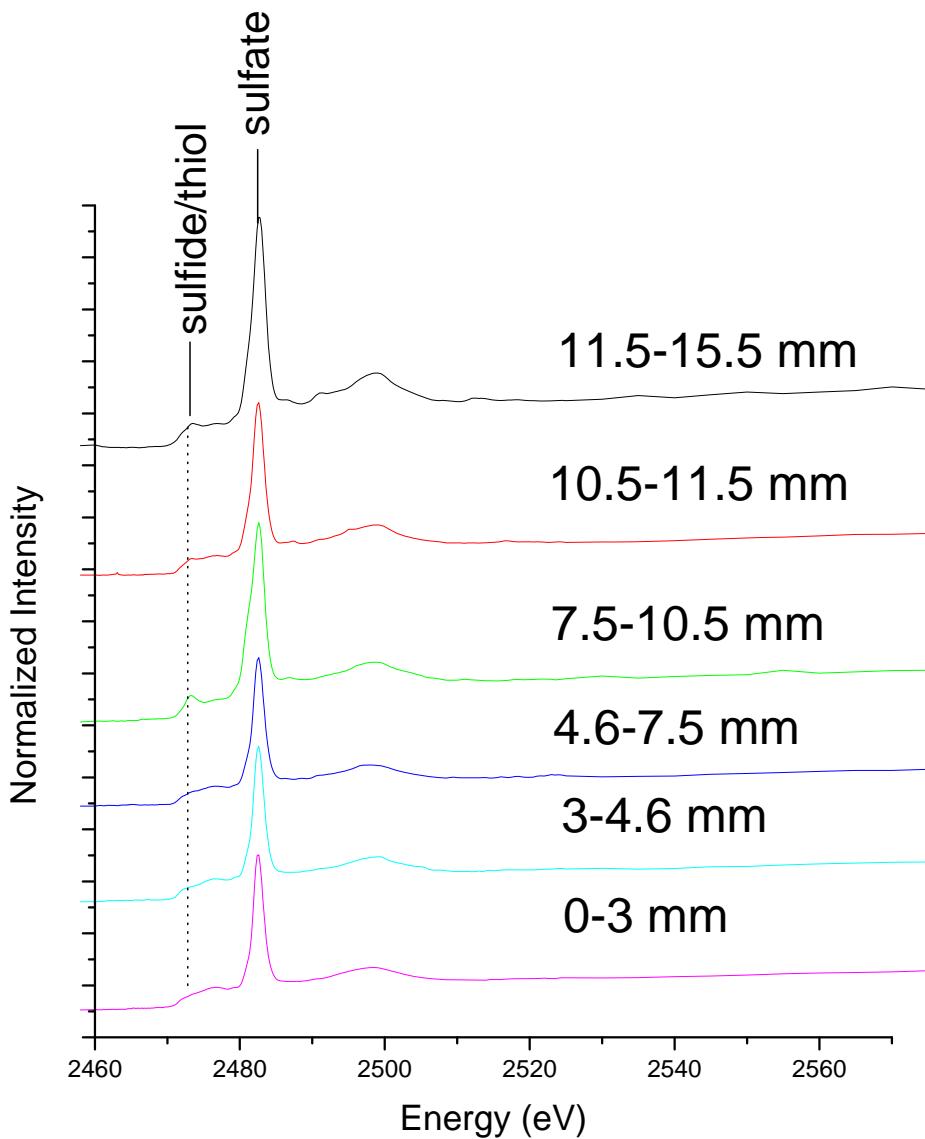
**Figure 7:** A). Bulk XANES calibration spectra created with ACS grade  $K_2Cr(VI)O_4$  and  $Cr_2(III)O_3$ . B). A calibration curve of  $Cr(VI)/Total\ Cr\ (%)$  created using  $Cr(VI)$  pre-edge height of reference spectra shown in A. C). Bulk XANES spectra from STS-CLS 500-2 segmented 14 April 2013 (2 days after received). D).  $Cr(VI)/Total\ Cr\ (%)$  through depth of saltstone sample STS-CLS 500-2 using XANES pre-edge height.



**Figure 8:** A. Total Cr map (H:1.6mm X W:0.33 mm) from surface (0 mm) to subsurface (1.6 mm). Higher intensity (red) correlates to higher Cr content. B. Normalized bulk Cr K-edge XANES spectra of saltstone segment with Cr(VI) and Cr(III) standard spectra. C. Cr(VI) saltstone valence state map. D. Cr(III) saltstone valence state map.

#### 4.5 Bulk S XANES Analysis:

The S XANES spectra as a function of depth are shown in Figure 9. All spectra are dominated by sulfate that is indicated by the large whiteline peak at 2482.6 eV. There was a small peak at 2472-2474 eV at the depth of 7.5-15.5 mm that corresponds to disulfides and could be contributed from thiol functional group. Due to lack of resolution, it cannot be clearly quantified. However, the intensity of peak appears after 7.5 mm, suggesting the presence of more oxidized zone at shallower depth (< 7.5 mm). This can be also supported by the leaching data in Figures 5A and 5B.



**Figure 9:** Depth profile of Sulfur K-edge XANES spectra in 3 week aged saltstone (Cr 500-3) since received. Two reference lines at 2472.4 and 2482.6 eV represent sulfide and sulfate, respectively.

## 5.0 Summary

In this work, the chemistry of sulfur and chromium was examined in saltstone monoliths exposed to oxidizing, high humidity conditions. The monoliths were amended with Cr(VI) which was used as an indicator of redox activity. After approximately 3 weeks and 4 months of aging under oxidizing, high humidity conditions, only a small fraction of Cr leached into both oxygenated and degassed solutions. Thus the saltstone appears to maintain Cr in a trivalent state after exposure to oxidizing conditions. This observation was supported by synchrotron based oxidation state speciation analysis (XANES). Characterization of sulfur speciation using leaching tests, solid phase AVS measurements, and XANES

analysis indicated that the oxidized sulfate ion is the dominant sulfur species within the saltstone monoliths.

## 6.0 References

1. Bartlett, R.; James, B. Behavior of Chromium in Soils: III. Oxidation. *Journal of Environmental Quality* **1979**, 8, 31-35.

## Appendix A: Cr Leaching Data

Sample Event: STS-CLS 500-2 and 500-8 Cr leaching test using 15 mL degassed water.

Note: To produce the solid phase concentrations in terms of  $\text{mg}_{\text{Cr}}/\text{kg}_{\text{saltstone}}$  as shown in Figure 5, the concentration of Cr reported in the leachate below were multiplied by the total volume of leachate (15mL) and divided by the mass of saltstone.

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

| Sample ID    | Drill Depth<br>(mm) | Saltstone<br>(g) | [Cr] in<br>leachate,<br>mg/L | Fraction<br>of Cr<br>leached |
|--------------|---------------------|------------------|------------------------------|------------------------------|
| ST-CLS 500-2 | 2.5                 | 0.248            | 0.009                        | 4.96E-04                     |
| ST-CLS 500-2 | 6.1                 | 0.293            | 0.006                        | 5.86E-04                     |
| ST-CLS 500-2 | 9.0                 | 0.549            | 0.009                        | 1.10E-03                     |
| ST-CLS 500-2 | 16.0                | 0.589            | 0.007                        | 1.18E-03                     |
| ST-CLS 500-2 | 19.0                | 0.360            | 0.006                        | 7.20E-04                     |
| ST-CLS 500-2 | 21.0                | 0.215            | 0.013                        | 4.30E-04                     |
| ST-CLS 500-2 | 26.0                | 0.319            | 0.013                        | 6.38E-04                     |
| ST-CLS 500-2 | 29.0                | 0.338            | 0.016                        | 6.76E-04                     |
| ST-CLS 500-2 | 34.0                | 0.214            | 0.014                        | 4.28E-04                     |
| ST-CLS 500-2 | 42.0                | 0.329            | 0.011                        | 6.58E-04                     |
| ST-CLS 500-8 | 3.5                 | 0.406            | 0.190                        | 3.80E-04                     |
| ST-CLS 500-8 | 7.5                 | 0.871            | 0.302                        | 6.04E-04                     |
| ST-CLS 500-8 | 11.5                | 0.364            | 0.149                        | 2.98E-04                     |
| ST-CLS 500-8 | 14.0                | 0.323            | 0.177                        | 3.54E-04                     |
| ST-CLS 500-8 | 16.5                | 0.619            | 0.203                        | 4.05E-04                     |
| ST-CLS 500-8 | 19.5                | 0.701            | 0.268                        | 5.37E-04                     |
| ST-CLS 500-8 | 22.0                | 1.022            | 0.219                        | 4.38E-04                     |
| ST-CLS 500-8 | 27.5                | 1.116            | 0.254                        | 5.08E-04                     |
| ST-CLS 500-8 | 32.0                | 1.045            | 0.347                        | 6.93E-04                     |

Sample Event: STS-CLS 500-2 and 500-8 Cr leaching test using 15 mL oxygenated water.

| Sample ID    | Drill Depth (mm) | Saltstone (g) | [Cr] in leachate, mg/L | Fraction of Cr leached |
|--------------|------------------|---------------|------------------------|------------------------|
| ST-CLS 500-2 | 2.5              | 0.196         | 0.019                  | 3.92E-04               |
| ST-CLS 500-2 | 6.1              | 0.455         | 0.013                  | 9.10E-04               |
| ST-CLS 500-2 | 9.0              | 0.223         | 0.017                  | 4.46E-04               |
| ST-CLS 500-2 | 16.0             | 0.406         | 0.009                  | 8.12E-04               |
| ST-CLS 500-2 | 19.0             | 0.366         | 0.007                  | 7.32E-04               |
| ST-CLS 500-2 | 21.0             | 0.331         | 0.013                  | 6.62E-04               |
| ST-CLS 500-2 | 26.0             | 0.350         | 0.013                  | 7.00E-04               |
| ST-CLS 500-2 | 29.0             | 0.317         | 0.011                  | 6.34E-04               |
| ST-CLS 500-2 | 34.0             | 0.400         | 0.009                  | 8.00E-04               |
| ST-CLS 500-2 | 42.0             | 0.567         | 0.011                  | 1.13E-03               |
| ST-CLS 500-8 | 3.5              | 0.592         | 0.142                  | 2.84E-04               |
| ST-CLS 500-8 | 7.5              | 1.154         | 0.296                  | 5.93E-04               |
| ST-CLS 500-8 | 11.5             | 0.888         | 0.334                  | 6.67E-04               |
| ST-CLS 500-8 | 14.0             | 0.590         | 0.149                  | 2.97E-04               |
| ST-CLS 500-8 | 16.5             | 0.630         | 0.222                  | 4.45E-04               |
| ST-CLS 500-8 | 19.5             | 0.697         | 0.247                  | 4.93E-04               |
| ST-CLS 500-8 | 22.0             | 0.820         | 0.230                  | 4.60E-04               |
| ST-CLS 500-8 | 27.5             | 1.031         | 0.259                  | 5.18E-04               |
| ST-CLS 500-8 | 32.0             | 0.835         | 0.272                  | 5.44E-04               |

## Appendix B: Sulfur Leaching and AVS Data

Sample Event: STS-CLS 500-4 and 500-10 sulfur leaching test using 15 mL degassed water.

Note: To produce the solid phase concentrations in terms of  $\text{mg}_{\text{Sulfur}}/\text{kg}_{\text{saltstone}}$  as shown in Figure 6, the concentration of sulfur reported in the leachate below were multiplied by the total volume of leachate (15mL) and divided by the 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) | Saltstone (g) | $[\text{SO}_4]$ (mg/L) | $[\text{S}_2\text{O}_3/\text{S}]$ (mg/L) | pH    | $E_h$ (mV) |
|----------------|------------------|---------------|------------------------|--|-------|------------|
| STS-CLS 500-10 | 5.5              | 0.375         | 92.78                  | 1.53                                     | 10.47 | -313.7     |
| STS-CLS 500-10 | 11.5             | 0.818         | 132.03                 | 3.12                                     | 11.36 | -271.0     |
| STS-CLS 500-10 | 16.0             | 0.521         | 99.8                   | 2.32                                     | 11.42 | -219.0     |
| STS-CLS 500-10 | 22.4             | 0.874         | 171.68                 | 3.93                                     | 11.47 | -181.7     |
| STS-CLS 500-10 | 28.0             | 0.563         | 115.49                 | 2.63                                     | 11.43 | -224.3     |
| STS-CLS 500-10 | 34.5             | 0.631         | 189.66                 | 3.93                                     | 11.45 | -255.9     |
| STS-CLS 500-4  | 6.5              | 0.174         | 15.73                  | 0.36                                     | 10.72 | -240.0     |
| STS-CLS 500-4  | 10.0             | 0.477         | 149.78                 | 3.77                                     | 11.32 | -173.5     |
| STS-CLS 500-4  | 18.9             | 0.402         | 109.26                 | 2.65                                     | 11.33 | -151.4     |
| STS-CLS 500-4  | 24.5             | 0.386         | 72.19                  | 1.68                                     | 11.31 | -192.5     |
| STS-CLS 500-4  | 28.5             | 0.396         | 104.10                 | 2.22                                     | 11.38 | -177.8     |
| STS-CLS 500-4  | 37.0             | 0.348         | 69.81                  | 1.75                                     | 11.31 | -180.3     |

Sample Event: STS-CLS 500-4 and 500-10 sulfur leaching test using 15 mL oxygenated water.

| Sample ID      | Drill Depth (mm) | Saltstone (g) | $[\text{SO}_4]$ (mg/L) | $[\text{S}_2\text{O}_3/\text{S}]$ (mg/L) | pH    |
|----------------|------------------|---------------|------------------------|--|-------|
| STS-CLS 500-10 | 5.5              | 0.586         | 370.17                 | 4.78                                     | 10.90 |
| STS-CLS 500-10 | 11.5             | 0.741         | 281.95                 | 4.95                                     | 11.69 |
| STS-CLS 500-10 | 16.0             | 0.650         | 230.62                 | 5.19                                     | 11.58 |
| STS-CLS 500-10 | 22.4             | 0.655         | 282.98                 | 5.93                                     | 11.56 |
| STS-CLS 500-10 | 28.0             | 0.622         | 297.25                 | 5.66                                     | 11.60 |
| STS-CLS 500-10 | 34.5             | 0.795         | 303.79                 | 9.42                                     | 11.81 |
| STS-CLS 500-4  | 6.5              | 0.483         | 250.12                 | 4.07                                     | 11.17 |
| STS-CLS 500-4  | 10.0             | 0.796         | 218.87                 | 14.36                                    | 11.58 |
| STS-CLS 500-4  | 18.9             | 0.172         | 238.49                 | 7.68                                     | 11.58 |
| STS-CLS 500-4  | 24.5             | 0.763         | 245.92                 | 11.51                                    | 11.20 |
| STS-CLS 500-4  | 28.5             | 0.599         | 261.21                 | 7.93                                     | 11.58 |
| STS-CLS 500-4  | 37.0             | 0.968         | 276.61                 | 17.55                                    | 11.74 |

Sample Event: STS-CLS 500-4 and 500-10 AVS measurements.

| Sample         | Drill Depth (mm) | Saltstone (g) | SAOB (mL) | [S] (mg/L) |
|----------------|------------------|---------------|-----------|------------|
| STS-CLS 500-10 | 5.50             | 1.57          | 9.46      | 0.0015     |
| STS-CLS 500-10 | 11.50            | 2.01          | 12.13     | 0.0039     |
| STS-CLS 500-10 | 16.00            | 2.57          | 15.50     | 0.0015     |
| STS-CLS 500-10 | 22.40            | 2.69          | 16.14     | 0.0304     |
| STS-CLS 500-10 | 34.50            | 2.07          | 12.42     | 0.0275     |
| STS-CLS 500-4  | 10.00            | 3.00          | 18.00     | 0.0390     |
| STS-CLS 500-4  | 18.90            | 2.28          | 13.69     | 0.0270     |
| STS-CLS 500-4  | 24.50            | 2.85          | 17.15     | 0.0345     |
| STS-CLS 500-4  | 28.50            | 2.66          | 15.91     | 0.0266     |
| STS-CLS 500-4  | 37.00            | 3.38          | 20.08     | 0.0119     |