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SALTSTONE OXIDATION STUDY: LEACHING METHOD - #13092

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ABSTRACT

Cementitious waste forms can be designed to chemically stabilize selected contaminants, such as Tc^{+7} and Cr^{+6}, by chemically reduction to lower valance states, Tc^{+4} and Cr^{+3}, respectively, and precipitation of these species in alkaline media as low solubility solid phases. Data for oxidation of this type of cementitious waste form cured under field conditions as a function of time is required for predicting the performance of the waste form and disposal facility. The rate of oxidation (oxidation front advancement) is an important parameter for predicting performance because the solubilities of some radionuclide contaminants, e.g., technetium, are a function of the oxidation state.

A non-radioactive experiment was designed for quantifying the oxidation front advancement using chromium, as an approximate redox-sensitive surrogate (Cr^{+6} / Cr^{+3}) for technetium (Tc^{+7} / Tc^{+4}). Non-radioactive cementitious waste forms were prepared in the laboratory and cured under both laboratory and "field conditions." Laboratory conditions were ambient temperature and sealed sample containers. Field conditions were approximated by curing samples in open containers which were placed inside a plastic container stored outdoors at SRS. The container had a lid and was instrumented with temperature and humidity probes.

Subsamples as thin as 0.2 mm were taken as a function of distance from the exposed surface of the as-cast sample. The subsamples were leached and the leachates were analyzed for chromium, nitrate, nitrite and sodium. Nitrate, nitrite, and sodium concentrations were used to provide baseline data because these species are not chemically retained in the waste form matrix to any significant extent and are not redox sensitive.

"Effective" oxidation fronts for Cr were measured for samples containing 1000, 500 and 20 mg/kg Cr added as soluble sodium chromate, Na_2CrO_4. For a sample cured for 129 days under field conditions, leachable Cr (assumed to be the oxidized form, i.e., Cr^{+6} was detected in the top 15 to 20 mm of the sample spiked with 1000 mg/kg Cr. Below about 20 mm, the Cr concentrations in leachates were below the detection limit (< 0.010 mg/L) which indicates that the oxidation as the result of exposure to air was limited to the top 20 mm of the sample after exposure for 129 days and that the bulk of the waste form was not affected, i.e., the Cr was stabilized and insoluble.

For samples cured in the laboratory, leachable Cr was detected in the top 8 mm of the Cr 1000 sample cured in the laboratory for 37 days. Between 8 and 14 mm, the concentration Cr in the leachate dropped by a factor of about 20 to just above the detection limit. These depth of penetration results indicate that the rate of advancement of the oxidation front for samples spiked with 1000 mg/kg Cr cured under "field conditions" for 129 days is less than that for the sample cured in the laboratory for 37 days, i.e., 0.156 and 0.216 mm/day, respectively. Additional data are presented for samples spiked with 500 and 20 mg/kg Cr.

In summary, cementitious waste forms are porous solids with a network of interconnected pores ranging in diameter from 10E-10 m to greater than a few mm. The oxidation process is assumed to occur as the result of oxygen transport through the interconnected porosity which may be filled with air, aqueous salt solution, or both. Upon oxidation, the Cr becomes soluble and can be transported in solution through aqueous pore fluid or leachate.

INTRODUCTION

Objective

The objective of this work was to identify a method for determining the rate of oxidation front advancement for specific (individual) redox sensitive contaminants in saltstone as a function of time and to apply the method to samples cured under "field" conditions. More specifically, the objective was to evaluate leachability of depth-discrete samples for characterizing the oxidation front progression in the porous saltstone waste form cured in air. Chromium was used to develop the method because it is a stable and does not require radioactive facilities. The method was developed so it can be applied to radioactive redox sensitive contaminants, e.g., Tc^{+7}/Tc^{+4}, in future studies.

Background

In the current SRS liquid waste processing system, waste solutions from F and H Tank Farms are treated to remove actinides and fission products. The resulting decontaminated solution is a low-level aqueous sodium salt solution which is stored in Tank 50-H. Small volumes of sodium salt solutions from other SRS facilities (Effluent Treatment Project and H-canyon) are blended with the decontaminated salt solution in Tank 50-H before it is transferred to the Saltstone Production Facility (SPF) and mixed with preblended cementitious reagents: blast furnace slag, thermally beneficiated Class F fly ash, and Type I/II portland cement to produce the saltstone waste form.

The fresh grout slurry is pumped from the SPF to the Saltstone Disposal Facility (SDF) where it cures. The resulting solid waste form has an alkaline, chemically reducing chemistry which stabilizes (immobilizes) selected contaminants including redox sensitive contaminants, i.e., pertechnetate (TcO_4^-) and chromate (CrO_4^{2-}). Tc(VII) is reduced to Tc(IV) and forms one or more low solubility sulfide compounds, i.e., TcS_x or a hydrated oxide phases, e.g., $TcO_2 \bullet xH_2O$ [1]. Cr(VI) is reduced to is reduced to Cr(III) and precipitated as $Cr(OH)_3$.

Saltstone disposal units (engineered concrete barriers) are anticipated to degrade over a 10,000 year period of performance. Given the Tc-99 half-life of about 2.12E+05 years and that the chromium is stable (i.e., infinite half-life), understanding the oxidation rate of saltstone and in particular the effective oxidation rates of the redox sensitive contaminants in saltstone is important for predicting long-term performance.

EXPERIMENTAL METHOD

Details of the leaching method developed for determining effective oxidation fronts of redox sensitive contaminants in saltstone are described elsewhere [2, 3]. The method can be applied to both radioactive and stable contaminants provided that the solubilities of the oxidized or reduced species are distinctly different. The method was developed to be performed in radioactive hoods on actual production samples and will be extended to Tc in future studies. The experimental steps are as follows:

- Prepare samples with redox sensitive spikes
- Cure samples under representative conditions in open containers
- Observe macroscopic features of the samples
- Section samples and record macroscopic features as a function of distance from the surface
- Crush subsamples (to a standard sieve size if desired)
- Leach subsamples in deionized, deaerated water tumbled at 30 rpm for 18 ± 2 hr., EPA Method 1311
- Observe color of leachate and leached subsamples
- Filter leachates
- Analyze leachates for contaminants of concern
- Analyze data.

The ingredients and proportions in the simulated salt solution used for preparing the saltstone samples are provided in Table 1. The simulated salt solution is based on a recent Tank 50 WAC Analysis [4, 5] and was prepared by dissolving the ingredients listed in Table 1 in ASTM Type I deionized water. Na_2CrO_4 was added to the simulated salt solution for the Cr spike.

Table 1. Simulated Salt Solution Composition [4, 5].

Compound	Molarity (moles / liter)	Molecular Wt. (grams / mole)	Amount (g / L)
Water (ASTM Type 1)	0	18.015	819.50
$Al(NO_3)_3 \cdot 9\ H_2O$	0.110	375.129	41.26
50% by Weight NaOH	1.551	39.998	124.07
Na_2SO_4	0.059	142.042	8.32
Na_2CO_3	0.148	105.990	15.64
$NaNO_3$	2.116	84.995	179.86
$NaNO_2$	0.336	68.996	23.20
Total Salt mass	--	--	312.47
Total Na Molarity	4.42	--	--
Density	1.2084		
Wt.% Solids	25.6		

The ingredients in the saltstone samples are listed in Table 2. Samples were spiked with 20, 500 and 1000 mg/kg Cr. The dry premix consisted of 10 wt. % portland cement (Type I/II), 45 wt. % blast furnace slag (Hlocim US Grade 100) and 45 wt. % thermally beneficiated Class F fly ash. All samples had a water to premix ratio of 0.60. The premix was added to the salt solution and mixed for three minutes after all of the powder was added. Samples were cast into 1 x 4 inch cylindrical plastic containers with lids. The lids were closed for the first 7 days while the samples set at laboratory ambient temperature and 65% to 70% relative humidity. See Figure 1.

Table 2. Ingredients and Proportions in Samples Prepared for the Leach Method Development.

Sample Description	Batch Number	Premix Batch 1 (g)	Premix Batch 2 (g)	Na_2CrO_4 (g)	Salt solution (g)	Water/ pre-mix
Saltstone w/ Slag, 1000 mg / kg Cr	11	249.1	--	1.402	200.9	0.60
Saltstone w/ Slag, 500 mg / kg Cr	10	--	249.1	0.7009	200.9	0.60
Saltstone w/ Slag, 20 mg / kg Cr	9	--	249.1	0.0280	200.9	0.60

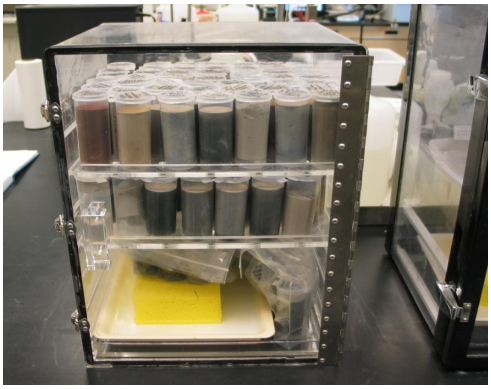

Figure 1. Curing cabinet in which "field cured" samples were stored prior to being relocated to Z-Area.

After setting, the samples were transported to the SPF (Z-Area) and placed in an un-insulated plastic container located under the cementitious reagent silos. Trays containing the samples were stacked in two layers. The lids were opened when the containers were placed plastic trays and remained open for the duration of the exposure time. See Figure 2.

Figure 2. Curing container in Z-Area and samples with open lids arranged in the container.

The Cr-spiked 1000, 500, and 20 mg/kg samples were retrieved from Z-Area after curing a total time of 129, 111, and 111 days, respectively. Temperature and humidity data inside the container were recorded. Macroscopic differences among the samples spiked with 1000, 500, 20 mg/kg Cr after they were retrieved from the curing container are illustrated in Figure 3. The surface of 1000 mg/kg Cr sample was a medium tan color and the top ~5 mm was light tan. The exterior surfaces of the 500 and 20 mg/kg Cr spiked samples were dark to medium gray. The top ~ 5 mm of both samples was light gray. The sample containers were completely filled and the color change was apparent before removing the samples from the containers.

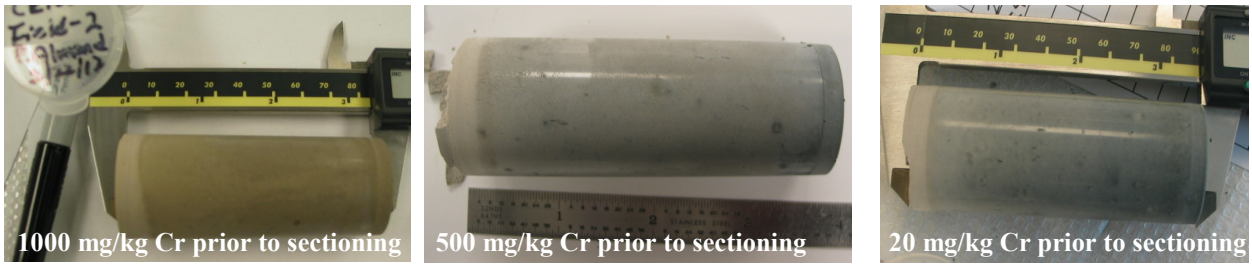

Figure 3. Appearance of the 3 Cr-spiked field-cured saltstone samples leached in this study.

Color differences were also observed in the saltstone samples after they were removed from the 1x4 inch plastic containers. Because of the noticeable color change in the top 0.5 to 1 cm of the samples, relatively thin subsample slices were collected in this region. Thicker slices were taken deeper in the samples where the color was more uniform. The leaching profile over the entire length of the sample containing 500 mg/kg Cr was characterized. Only the upper portions of the samples containing 1000 and 20 mg/kg Cr were characterized.

The cured saltstone samples were sectioned perpendicular to the long axis immediately after they were removed from the containers. A sample holder was fabricated to enable sectioning of slices as thin as 0.1 to 0.2 mm. The samples were crushed to a powder and leached in de-aerated, deionized ASTM Type I water for 18 hr. ± 2 hr. Leaching was performed using a modified EPA Method 1311 [6].

Leachates were filtered (0.45µmfilter) and analyzed for Al, Ca, Cr, Fe, K, Na, NO_2^-, NO_3^-, and SO_4^{2-} concentrations, as well as pH. Photos of the leached saltstone samples in the leaching solution, filtered leachates, and crushed saltstone residues after the leaching solution was decanted are provided in Figure 4. Color differences in the filtered leachates as a function of distance from the exposed surface were very noticeable in the Cr-1000 and Cr-500 samples. Leachates for subsamples taken to a depth of ~12 mm

from the surface were clear. Leachates generated by samples further from the exposed surfaces were yellow. All of the leachates from the sample spiked with 20 mg/kg Cr were clear regardless of distance from the top surface. The color differences appear to correlated to oxidized versus reduced subsamples and to the subsample mass/leachate mass ratios. Surprisingly, the yellow color was not correlated to chromate concentration.

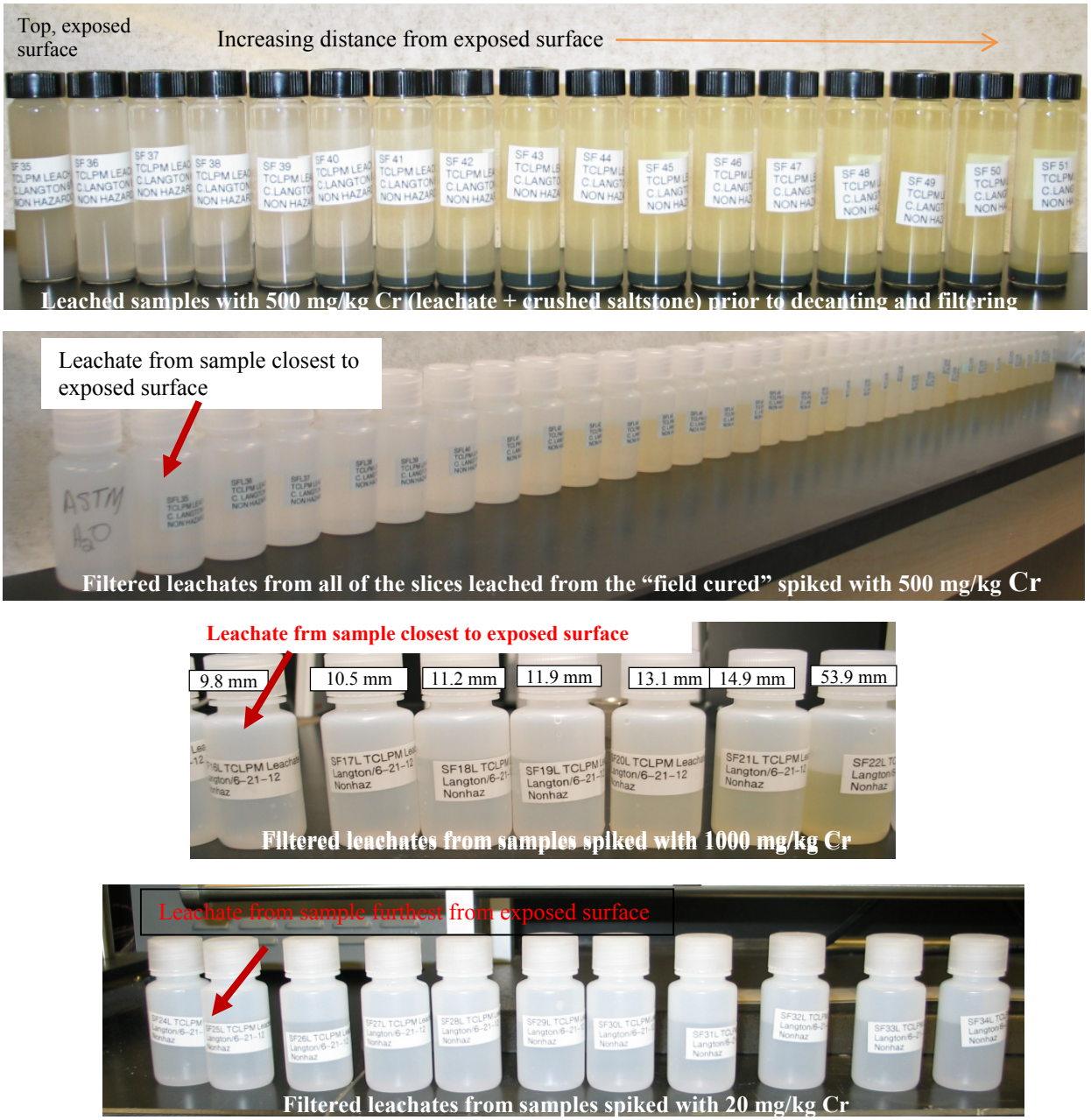

Figure 4. Unfiltered and Filtered leachates from "field cured" subsamples.

Leachates were analyzed for Cr, Na, NO_3^-, NO_2^-, and SO_4^{2-} concentrations (components of the salt solution)[1] and Al, Ca, and K concentrations (components in the premix) using methods described elsewhere [1 and 2]. Leachate analyses were run in duplicate. Values were averaged and used to

[1] The premix also contains K, Na, Cr, and SO_4^{2-}. The contribution of these species from the premix was not taken into account in the percent leached calculations. Consequently this calculation was limited to Cr, nitrate and sodium.

calculate the fraction leached (percent leached). This report is limited to Cr, $NO3^-$ and Na^+ data. The entire data set is presented elsewhere [2 and 3]. The percent of the selected ions leached from the crushed subsamples was determined using Equation 1.

Equation 1. $$\%Leached = 100 * (\frac{m_{i-leachate}}{m_{i-solid}})$$

Where: $m_{i\text{-leached}}$ = mass of species *i* leached (mg). The leachate was filtered prior to analysis using a 0.45 μ filter.

$M_{i\text{-total}}$ = mass of species *i* in the subsample leached (mg). The total amount in the waste form was approximated and only reflects the contribution to the waste form from the spiked mixing solution.

RESULTS

Leachate concentrations and subsample and leachate mass information are tabulated elsewhere [2 and 3]. The fractions leached as a function of sample distance from the exposed top surface are plotted for NO_3^-, Na^+, and Cr in Figures 5-7, respectively. These three samples are identical with respect to ingredients except for the amount of Cr added as a spike.[2]

The NO_3^- mass fractions leached as a function of distance from the top of the sample are similar for all three samples cured under "field conditions." The mass fractions of Na leached as a function of distance from the top of the samples are also similar to those for nitrate although the Na profiles, as a function of depth from the top, are not as sharp and well defined as those for NO_3^-. For both of these species, about 10 % of the total amount in the top subsample was extracted in the 18 hour test. The percentages extracted increased for subsequent subsamples up to 20 to 25 % of the total in the salt solution. The locations of the subsamples with the highest mass fractions leached were between 5 and 6 mm from the top surface. The percentages extracted from subsamples below 5 to 6 mm decrease to about 15 % at about 12 mm from the top surface and remained at about 15 % throughout the remainder of the sample. About 9 percent of the total Na was extracted from a subsample cut from the middle of the sample spiked with 1000 mg/kg Cr. This single data point supports the general pattern but more data are required to better characterize the leaching behavior of Na.

The leaching behavior for Cr as a function of distance from the top exposed surface has the same pattern as described for NO_3^- and Na, i.e., a spike in the percentage leached for subsamples collected about 3 to 5 mm from the top surface followed by a sharp decrease in the percentages of Cr extracted between 5 and 10 to 15 mm from the top surface. The percentages of Cr leached as a function of depth from all three "field cured" samples (Cr spikes of 1000, 500, and 20 mg/kg) are significantly lower than the percentages of NO_3^- and Na leached from the corresponding subsamples.

The maximum percentage of Cr leached from the sample spiked with 1000 mg/kg Cr was 5.8 % compared to 22.4, 19.4, and 24.3 %, the maximum percentages of NO_3^- leached from samples spiked with 1000, 500, and 20 mg/kg Cr, respectively. In addition between 10 and 20 mm from the exposed top surface, the amount of Cr detected in the leachates from samples spiked with 500 mg/kg were below the limit of detection, 0.01 mg/L. All of the leachates from the sample spiked with 20 mg/kg Cr were below the Cr detection level of 0.01 mg/L. Consequently the percentages reported and plotted are over estimates of the actual values.

[2] Some differences that were encountered include: the samples were cured for slightly different times (111 vs. 129 days) which should not affect the results and they were made from different batches of premix materials.

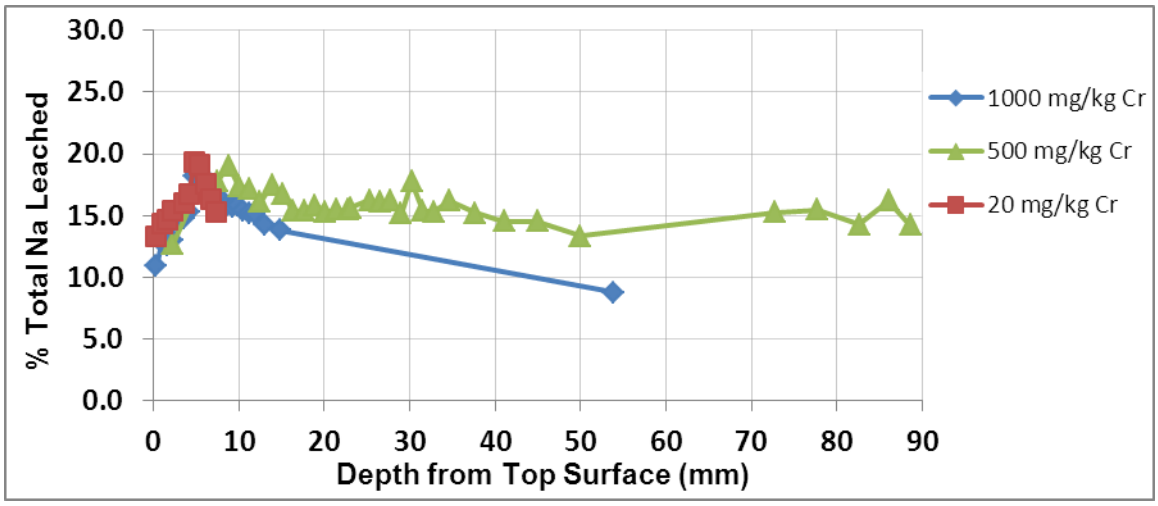

Figure 5. Sodium Leached from "Field Cured" Saltstone Spiked with Cr.

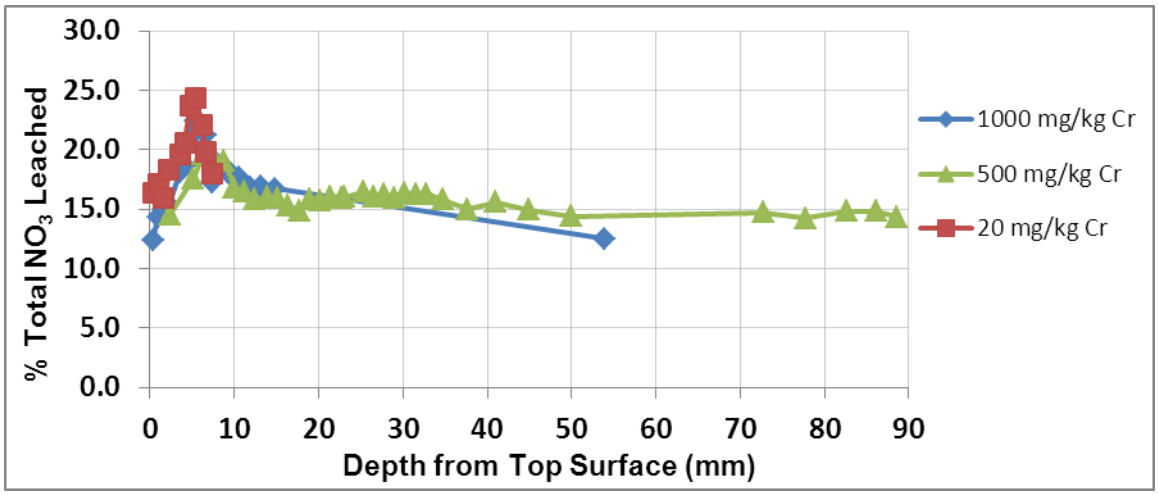

Figure 6. Nitrate Leached from "Field Cured" Saltstone Spiked with Cr.

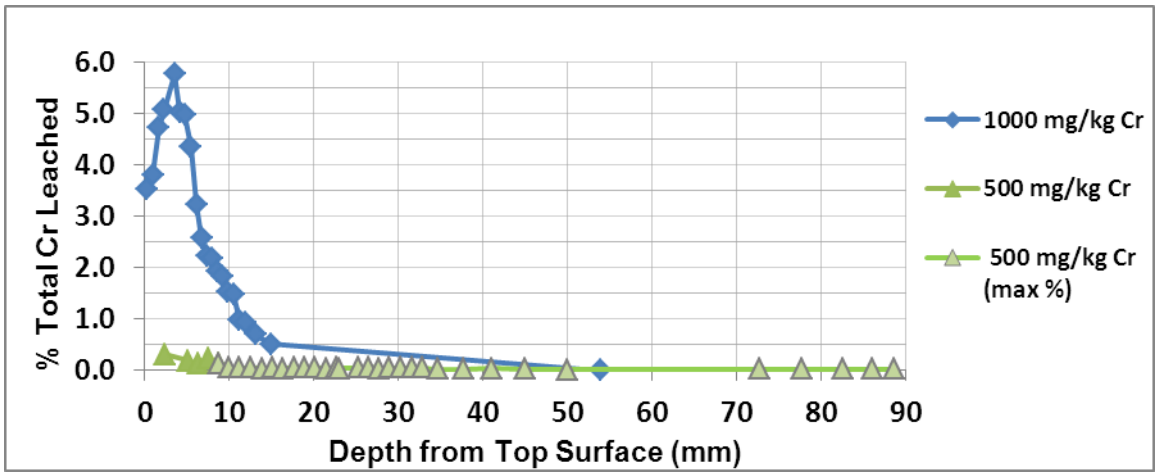

Figure 7. Chromium Leached from "Field Cured" Saltstone Spiked with Cr.

DISCUSSION

Contaminant Stabilization in Saltstone as a Function of Distance from Top Surface

Bulk Sample: About 15 % of the total nitrate was extracted from each crushed (powdered) "field cured" subsample collected more than about 15 mm below the top surface.[3] Consequently, the bulk unaltered material was considered to be represented by subsamples collected from 15 to 90 mm below the exposed surface. (The entire sample was about 90 mm.)

In comparison, only about 0.05 % of the Cr added to the samples was extracted from subsamples more than about 15 mm below the top surface (bulk material not exposed to air) for samples spiked with 500 and 1000 mg/kg Cr. These results are illustrated in the semi-log graph shown in Figure 8. Leachate results for the sample spiked with 20 mg/kg Cr were all below the detection level, < 0.01 mg/L. Consequently meaningful percentages or mass fractions extracted could not be calculated.

The mass fraction of nitrate leached from bulk saltsotne was more than 300 times the Cr mass fraction leached from the bulk material which indicates that the stabilization mechanisms for NO_3^- and Cr are very different. Nitrate is assumed to be physically entrapped in the saltstone pore solution and possibly matrix as very soluble precipitates. Low solubility nitrate phases have not been identified in saltstone.[3] On the other hand; Cr appears to be chemically stabilized as a low solubility solid phase(s) in the bulk saltstone matrix unless exposed to air (oxygen) during "field curing" in which case it oxidized back to soluble chromate.

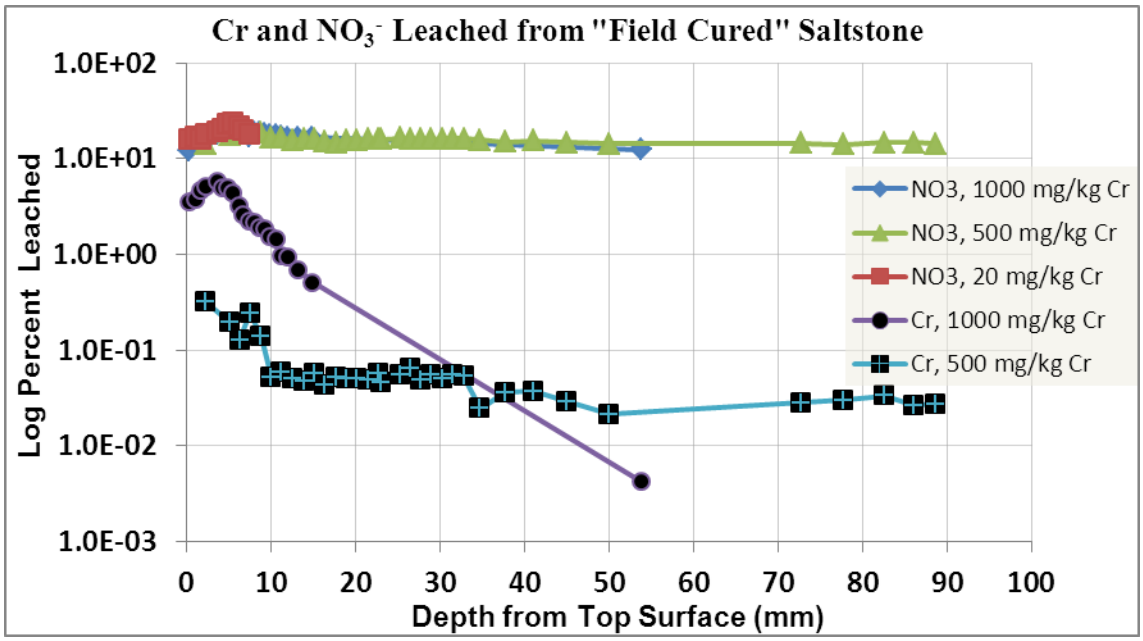

Figure 8. Semi-log plot of percentages of Cr and NO_3^- leached as a function of subsample distance from the exposed top surface.

Exposed Surface and Near Surface: The percentages of Cr and NO_3^- leached as a function of distance from the exposed surface to a depth of 10 to ~12 mm showed similar patterns in the three "field cured"

[3] Higher percentages of nitrate are expected to leach from these samples for longer exposure times; however, this has not been experimentally confirmed. Deionized, de-aerated water was used as the extraction fluid and the leaching test was performed for 18 ± 2 hr..

samples analyzed.[4] The pattern can be described as follows: lower percentages leached from the top followed by a spike in the percentages leached between about 3 and 10 mm from the top surface depending on the sample. The concentration spikes dropped to consistent values between 10 and 20 mm below the exposed top surfaces. This pattern is illustrated in the semi-log plot in Figure 8 and also in Figures 5 to 7.

Higher percentages of NO_3^- were leached from the near surface material to a depth of about 10 to 15 mm. The same pattern was observed for Cr in the sample spiked with 1000 mg/kg Cr. This pattern was not apparent for the "field cured" sample spiked with 500 mg/kg Cr. However, this "field cured" sample had an irregular exposed surface and was longer than the sample holder used to prepare the leaching sections. Consequently, some material was lost and the first few subsamples were not totally representative of distance from the exposed surface.

These results coupled with the mass fractions of Cr leached from the bulk material indicate that part of the Cr added to the samples has been solubilized between 10 and 20 mm after curing under "field conditions" for 111 to 129 days. The distance into which soluble (leachable) Cr was detected is referred to as the "effective Cr oxidation front."

The extracted Cr profile suggests that the effective Cr oxidation front advances through the sample by preferential pathway, and the front advances ahead of complete oxidation and dissolution of the Cr at any given distance from the surface. This is reasonable given that saltstone has a high porosity, 40 to 60 volume percent [7]. Additional characterization is required to further understand the chemistry responsible for the observed leaching results as a function of distance from the exposed surface.[5]

Chromium Stabilization as a Function of Chromium Concentration

The fraction of Cr leached from the top 20 to 30 mm appears to be a function of the Cr concentration in the sample. The percentages of Cr leached from samples spiked with 1000 mg/kg Cr were about 10X higher than the percentages of Cr leached from samples spiked with 500 mg/kg Cr over this depth. (Comparisons were not possible for samples prepared with 20 mg/kg Cr because the amount of Cr leached was below the detection level of 0.01 mg/L and less than values resulted in false percentages that overstate the true values.)

The relationship between the concentration of Cr spiked into the sample and the percentage of Cr that leached as a function of distance from the exposed top surface may be related to the availability of oxygen. Consequently the "effective Cr oxidation" rate may also be a function of the amount of Cr in the salt solution/saltstone waste form. Additional characterization is planned to further evaluate this correlation.

Comparison of Lab and Field Cured Sample Results

Laboratory cured samples were initially used to develop the method for sectioning saltstone specimens as a function of distance from an exposed surface and for developing a leaching method. A comparison of the NO_3^- and Cr leached from a laboratory cured (37 days) and from a "field cured" (129 days) sample is provided in Figure 9. Both samples were spiked with 1000 mg/kg Cr and contain identical proportions of ingredients.[6]

[4] The surfaces of these samples were exposed to moist air in the "cooler" under the premix silos in Z-Area.

[5] Regardless of the chemistry reflected in this leaching profile, the top 10 to 15 mm of the samples are not representative of the bulk based on the nitrate profiles.

[6] The samples spiked with 1000 mg/kg Cr were prepared form the same batch of premix. The samples spiked with 500 and 20 mg/kg Cr were prepared with a different batch of premix.

This spike pattern in the mass fraction leached near the exposed surface is present but less well defined for NO_3^- in the laboratory cured sample. The pattern was not observed for Cr in the laboratory cured sample [2]. The different exposure times, 37 days (lab cured sample) versus 129 days (field cured sample), or the variability in temperature and humidity between field and laboratory cured samples may account for some or all of the observed differences. Additional information is required to understand the differences in the field and laboratory cured samples and to determine whether the field conditions were more oxidizing than the laboratory conditions.

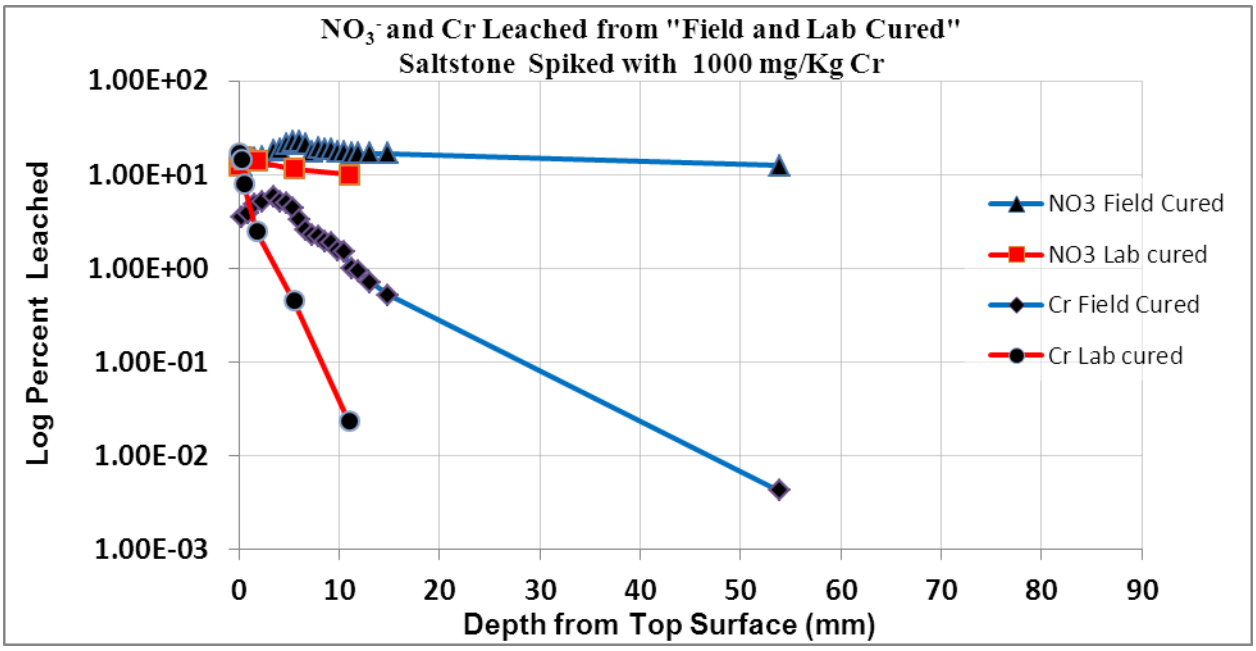

Figure 9. Comparison of NO_3^- and Cr leached for Cr-1000 field and laboratory cured samples.

Discussion of Visual Appearance of Saltstone Samples

The appearance of the saltstone sample spiked with 1000 mg/kg Cr was fairly uniform except that the top 5 mm of the sample was a buff color and the exterior surfaces of the rest of cylinder were tan to brown. The top 5 mm of the saltstone samples spiked with 500 and 20 mg/kg Cr was light gray and the rest of the exterior surfaces were medium to dark gray. The top 15 mm of both samples also had a mottled appearance characterized by tan lines surrounding gray areas. This pattern was not apparent at deeper locations in the samples. Only the top portion (11 mm) of the sample containing 20 mg/kg Cr was evaluated so no observations were made further from the exposed surface.

The cause of the color change in the top 5 mm may be due to drying, segregation/bleed, oxidation, some other chemical change, or to a combination of these phenomena. Additional testing is required to more fully characterize the cause of the color change.

Leachate Color as an Indicator of Cr Leachability

The color of the leachates generated in this study ranged from clear to yellow. The source of the yellow color is not known at this time but appears to be related to the sample mass-leachate mass ratio and to the amount of Cr in the leachate. Leachates containing < 0.01 mg/L Cr were yellow provided that the sample mass to leachate mass was at least 1.5 : 40. In addition, filtered leachates that were initially yellow turned clear upon re-examination 2 days after being analyzed. (No attempt was made to keep the leachates in a de-aerated condition after analysis.) Additional characterization work is required to understand these observations. The initial color of the leachates generated in a zero head space vessel using de-aerated

ASTM Type I water may be a useful and inexpensive method of approximating the depth of oxygen ingress / infiltration.

Leaching Results in Relation to Distribution Ratios (R_{ds})

The leaching experiments performed in this study did not result in equilibrium partitioning of any chemical species between the liquid and solid phases. Leachate concentrations from only one relatively short time interval, 18 hr., were evaluated. Therefore, distribution ratios, $R_{ds,}$ are reported rather than equilibrium distribution coefficients. Distribution ratios are calculated according to Equation 2.

$$\textbf{Equation 2.} \quad R_d = \frac{\text{[Concentration of species in the solid phase] (mg/kg)}}{\text{[Concentration of species in the liquid phase] (mg/L)}}$$

The relationship between percentage leached and distribution ratio is provided in Equation 3. Percentages of NO_3^- and Cr extracted from "field cured" saltstone were converted into distribution ratios (non-equilibrium) to illustrate the difference between physical stabilization and chemical stabilization in the saltstone matrix and should not be used for PA modeling. See Figure 10.

$$\textbf{Equation 3.} \quad R_d = \frac{\text{[100 – \% leached into the liquid phase]}}{\text{\% leached into the liquid phase}}$$

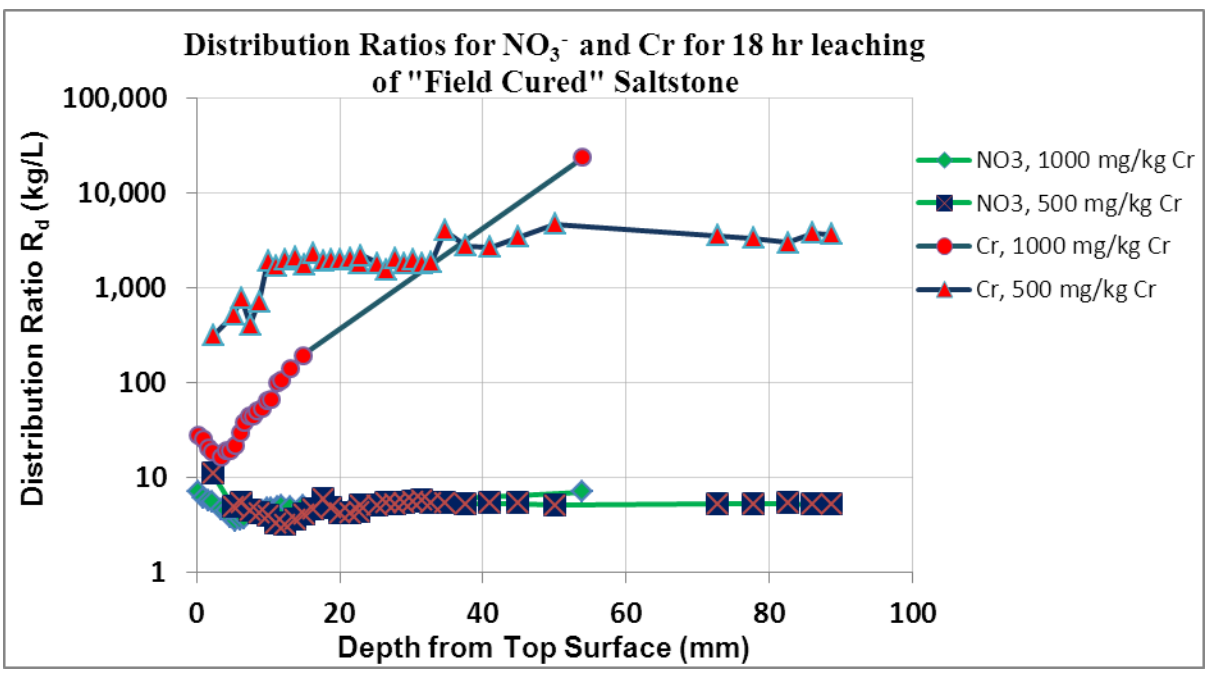

Figure 10. Comparison of NO_3^- and Cr Distribution Ratios for the 18 hr. extraction of crushed saltstone (powdered) in de-aerated ASTM Type I water.

CONCLUSIONS AND RECOMMENDATIONS

Quantification of contaminant retention in saltstone cured under "field conditions" as a function of time is required for predicting the performance of the waste form and disposal facility. The rate of oxidation is an important parameter for predicting performance because the solubilities of some contaminants, e.g.,

technetium, are a function of the oxidation state. TcO_4^- in the salt solution is reduced to Tc^{+4} which reacts with ingredients in the saltstone to precipitate a low solubility sulfide compound (TcS). Upon exposure to oxygen, the compounds containing Tc^{+4} oxidize to form pertechnate ion (TcO_4^-) which is very soluble. Consequently the rate of oxidation front advancement is important to saltstone performance and ground water concentration predictions.

An approach for measuring an "effective" oxidation front based on Cr leaching was developed. Cr speciation and solubility is also redox sensitive and was selected so that the method could be developed on the bench top before being transferred to a rad hood. The leaching method was one of five methods investigated for oxidation front studies in field cured simulated saltstone samples [8].

Based on leaching results presented in this report, Cr can be used as a non-radioactive redox indicator for saltstone. Leaching is a viable characterization method for determining "effective" chromium oxidation front progression in saltstone cured under laboratory or "field" conditions. The details of the leaching method have been provided elsewhere [2, 3]. In addition to measuring the Cr in the leachates collected from depth-discrete samples, the color of the leachates immediately after filtering may be a redox indicator for the samples. Additional testing is required to evaluate the unexpected observations made with respect to leachate color. Samples with Cr concentrations below the detection level or near the detection level were yellow, whereas samples containing low but detectable levels of Cr^{6+} were clear.

Results of this method can be used to model release of these contaminants from a waste disposal facility. The leaching method does not address total reduction capacity. Additional testing is recommended to correlate total reduction capacity as a function of depth to the fraction of Cr leached (oxidized) as a function of depth and exposure time.

Based on characterization of samples collected for one exposure time (111 to 129 days) and for two different levels of Cr spike, the oxidation front appears to have advanced from the as-cured exposed surface to a depth of 15 to 20 mm for the "field cured" sample spiked with 1000 mg/kg Cr and to a depth of 5 to 10 cm for the "field cured" sample spiked with 500 mg/kg Cr. These samples were prepared at different times and different batches of premix were used. In addition, the appearance (color and mottling) of the air exposed surface and sides of these two samples was not the same.

The as-cast surface and near surface region of the sample may not be representative of the bulk material. Consequently the rate of oxidation of the exposed surface may not be representative of the oxidation rate of the bulk material. More testing is required to determine whether the depth-discrete Cr leaching profiles are a function of sample preparation or a combination of phenomena that could have occurred under field curing conditions. Wet-dry cycling in addition to oxidation, carbonation, and other environmental conditions may have contributed to the depletion-spike profiles observed for the fraction of Cr leached from the near surface region of the samples.

In order to apply the leaching method described in this report to oxidation front measurements for actual saltstone samples, which contain about 20 mg/kg Cr, improvements in the leachate analytical method(s) is required. The detection level for technetium concentrations in the leachates may be lower than that for Cr and therefore should be evaluated for applicability to actual radioactive saltstone.
Finally, the color (oxidized corresponds to clear, reduced corresponds to yellow) of the leachate initially after filtering appears to correlate to oxidation-reduction state of the leachate. Additional testing is required to identify the inorganic or organic species responsible for the color. Additional testing is also required to correlate the "effective" Cr oxidation front to total reduction capacity.

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