

Evaluating the Impacts of Reactive Gas (Carbon Dioxide and Oxygen) Ingress on Leaching from Cementitious Waste Forms -- 17482

J. L. Branch*, D.S. Kosson*, K.G. Brown*, A. C. Garrabrants* and H.A. van der Sloot**

*Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN

**Hans van der Sloot Consultancy, Langedijk, The Netherlands

ABSTRACT

Cementitious materials are currently being used as the waste forms for low-activity waste disposal (Saltstone) at the Savannah River Site. In addition, cementitious materials have been selected as the waste form (Cast Stone) for secondary wastes and are being investigated for use for supplemental low-activity waste treatment (Cast Stone) at the Hanford Site. These materials are subjected to numerous aging and degradation phenomena in the disposal environment that potentially impact their long-term durability and performance. One important phenomenon is the ingress of reactive gases (i.e., carbon dioxide and oxygen) that can react with and change the chemistry and pore structure and thus mass transport properties of the waste forms. The reaction of carbon dioxide (i.e., carbonation) reduces the pH of the waste form pore solution impacting the solubility of constituents of potential concern (COPCs). In Cast Stone and Saltstone, the reaction of oxygen (i.e., oxidation) impacts the solubility of redox-sensitive COPCs, notably the technetium-99 (Tc-99) and chromium. The objective of this research is to experimentally characterize the carbonation and oxidation impacts on chemistry and leaching behavior in cementitious waste forms using experimental techniques including United States Environmental Protection Agency (U.S. EPA) Method 1313 and U.S. EPA Method 1315. Results of experimental characterization will be used to parameterize reactive mass transport models to project leaching under a range of field scenarios in future applications.

INTRODUCTION

Cementitious materials are currently being used and investigated for use in nuclear waste forms or as barriers for nuclear waste in applications including high-level waste disposal, low-level waste disposal, reactor entombment, and dry cask storage. These materials are subjected to numerous environmental attack scenarios that could impact their long-term durability and performance. Specifically, the ingress of reactive gases (i.e., carbon dioxide and oxygen) is of concern because of the presence of these gases in the atmosphere and other contact media including soil or water and their ability to react with and change the chemistry of the cementitious materials and waste forms. The reaction of carbon dioxide (i.e., carbonation) reduces the pH of the material that impacts the solubility of constituents of potential concern (COPCs). For Cast Stone or Saltstone, a cementitious waste form, the reaction of oxygen (i.e., oxidation) affects the solubility of redox-sensitive COPCs, notably technetium (Tc-99) from the salt waste form contained in the Cast Stone.

Therefore, it is important to characterize the carbonation and oxidation reactions in cementitious materials to predict material performance and durability of these materials in the presence of these reactive gases and to mitigate the potential for environmental contamination.

The goal of this research is to investigate the effects of carbonation and oxidation on cementitious waste forms prepared using components from different sources. Fly ash and ground granulated blast furnace slag (GGBFS) are two supplemental cementitious materials used in the formulation of cementitious waste forms because they reduce the required amount of Portland cement (PC), improve the mechanical strength of the material, and in Cast Stone materials increase the reductive capacity of the material compared to plain PC mixtures. The effects of carbonation, oxidation, and coupled carbonation and oxidation on Cast Stone materials were investigated. Specifically, the impacts of carbonation and oxidation on the changes in solubility of COPCs, microstructural changes, chemical changes, and redox behavior under degradation scenarios were characterized using a variety of experimental techniques. Subsequently, this experimental work will be used for pH-dependent and mass transfer modeling to calibrate and verify modeling capabilities and provide understanding of the impact of carbonation and oxidation reactions waste disposal scenarios.

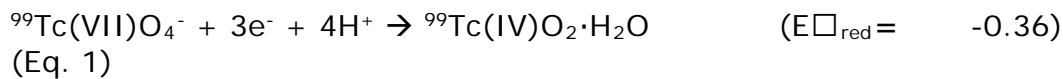
REACTION MECHANISMS

Impact of Carbonation in Cementitious Waste Forms and Barriers

Carbonation, the reaction of atmospheric or soil-gas CO₂ with the alkaline matrix of cementitious materials, is a key degradation method for cementitious materials in nuclear waste applications because it neutralizes the pore solution and alters the pore structure due to the formation of carbonated products. Prior studies have shown that these effects impact the time-dependent leaching of constituents [1-5], including the potential for release of radionuclides [6]. Therefore, leaching tests intended to characterize the liquid-solid partitioning of pH-dependent constituents can be used to identify changes in constituent solubility and concentration of constituents in the pore solution due to the phase changes associated with the carbonation reactions. These tests are also extended to characterize COPCs such as heavy metals or Tc-99 in Cast Stone materials.

Impact of Oxidation in Cementitious Waste Forms and Barriers

In addition to carbonation, oxidation is a specific concern for Cast Stone and Saltstone because these materials contain Tc-99 from the salt waste. The Tc-99 is originally present as the more soluble and more mobile pertechnetate ion, ⁹⁹Tc(VII)O₄⁻, but reacts with the reductants in initial Cast Stone matrix during curing to form the less-soluble ⁹⁹Tc(IV)O₂·H₂O compound:



The high reductive capacity of the Cast Stone matrix provides an initial capacity to react with oxygen to keep the Tc-99 in its reduced form [7]. However, after continuous and prolonged exposure to oxygen-rich environments in scenarios expected for Cast Stone and Saltstone, the reduced Tc-99 reacts with oxygen to reform the more soluble ${}^{99}\text{Tc(VII)}\text{O}_4^-$. There are also other redox-sensitive contaminants (i.e., Cr, Se, and I) originating from the salt waste that can react with oxygen to form more soluble species after prolonged exposure to oxygen. Therefore, there is a greater potential for Tc-99 and these other redox-sensitive contaminants to leach from Cast Stone and Saltstone under extended timeframes [8].

APPROACH

Cast Stone materials were prepared with fly ashes of varying alkalinities and reductive capacities and exposed to oxidizing and carbonating conditions in coupled and decoupled conditions in an inert control condition (Table I). The Cast Stone composition was doped with chromium to serve as an oxidation indicator. These degradation scenarios were selected based on key degradation scenarios that are anticipated to compromise the structural, hydraulic, or chemical integrity of cementitious materials in nuclear waste applications, which could ultimately impact the environment and human health. The depth of carbonation was investigated by visual inspection and the pH-dependent and mass-transfer rate of constituents for all Cast Stone degradation scenarios were characterized using United States Environmental Protection Agency (U.S. EPA) Method 1313 and U.S. EPA Method 1315. Results from this study will be used in future applications to verify long-term prediction models for Cast Stone.

Cast Stone Samples Preparation and Aging

Cast Stone formulation. All Cast Stone samples were prepared with 45 % fly ash, 47 % GGBFS, 8 % ordinary Portland cement (OPC) on a dry weight basis, which is a typical Cast Stone formulation. During mixing, a salt waste simulant was added in amounts based on achieving a specified water-to-binder ratio (w/b). A w/b ratio of 0.48 was selected because it was the maximum w/b where no bleedwater was observed in the test samples after 3 days when de-molding occurred. The salt waste simulant composition was derived from the Hanford Tank Waste Operations Simulator (HTWOS) overall average final LAW simulants after charge balancing [9].

The simulant prepared for this study was not spiked with Resource Conservation and Recovery Act (RCRA) metals and Underlying Hazardous Constituents (UHCs) or radionuclides. Chromium (VI) was added as chromate as either sodium chromate and/or potassium chromate to achieve the desired chromium spiking levels of 0.1 wt%. The chromium spiking level is based on grams chromium per gram total Cast Stone mixture including the binders, water, and dissolved chemicals in the simulant. The 0.1 wt% chromium spiking level was achieved through the addition of sodium chromate.

The concentration of aluminum, chloride, fluoride, sulfate, phosphate, nitrite, carbonate, and TOC total remained fixed in each simulant and the reagents were added in amounts necessary to achieve the concentrations for the HTWOS overall average LAW composition. The 0.1 wt% simulant was prepared to match the concentration of sodium, potassium, and nitrate in the HTWOS overall average, with a slight increase in molarity of sodium due to the addition of sodium chromate. The recipe used for each simulant and the purity and manufacturer of each reagent is provided in Table II.

Cast Stone preparation. A total of 3 samples types were prepared (Table I). The amount of added simulant for the different spiking levels was adjusted based on the chromium spiking level to maintain the same w/b ratio in each mixture. The ratio of the dry mix ingredients remained constant for each batch, but the total amount of binders was adjusted slightly to prepare approximately 2.5 L of mix for each batch.

Molds consisted of 50-milliliter digitubes which had a 1-inch diameter with a less than 5% tapering from the top portion to the bottom portion of the tube. The mixture was poured to approximately the 50 ml mark corresponding to a height of approximately 7 cm. Each digitube was immediately sealed and lightly tapped on the counter surface 10 times to release air bubbles.

Samples were loaded onto a digitube rack and immediately placed in a 100% nitrogen chamber maintained at 100% relative humidity (RH). Samples were demolded after 3 days of curing in the chamber. Samples then were cured in the nitrogen chamber maintained at 100% RH for 100 days. The chamber contained oxygen scavenger packets (Oxy-Sorb, Harrisburg, NC) and a carbon dioxide scavenger that was prepared using a mixture of calcium hydroxide powder and water.

Table I. Summary of Cast Stone materials, curing conditions, exposure conditions, and material characterization. Entries are listed in order of their conditioning.

Material ID ^(a)	Fly ash type	Cr loading (wt%)	100 % RH cure, 100 % N ₂	65 % RH, 100 % N ₂	65 % RH, 21% O ₂ , 79% N ₂	65 % RH, 5% CO ₂ , 95 % N ₂	65 % RH, 5% CO ₂ , 95 % air
CS-FAF-0S-N	Low Ca, low Fe	0.1	100 days	60 days	-	-	-
CS-FAF-0S-O	Low Ca, low Fe	0.1	100 days	-	60 days	-	-
CS-FAF-0S-C	Low Ca, low Fe	0.1	100 days	-	-	60 days	-
CS-FAF-0S-OC	Low Ca, low Fe	0.1	100 days	-	-	-	60 days
CS-NFA02-0S-N	Low Ca, high Fe	0.1	100 days	60 days	-	-	-
CS-NFA02-0S-O	Low Ca, high Fe	0.1	100 days	-	60 days	-	-
CS-NFA02-0S-C	Low Ca, high Fe	0.1	100 days	-	-	60 days	-
CS-NFA02-0S-OC	Low Ca, high Fe	0.1	100 days	-	-	-	60 days
CS-NFA18-0S-N	Moderate Ca, low Fe	0.1	100 days	60 days	-	-	-
CS-NFA18-0S-O	Moderate Ca, low Fe	0.1	100 days	-	60 days	-	-
CS-NFA18-0S-C	Moderate Ca, low Fe	0.1	100 days	-	-	60 days	-
CS-NFA18-0S-OC	Moderate Ca, low Fe	0.1	100 days	-	-	-	60 days

Following the 100-day cure, the ends of each cylinder were removed by dry cutting with a diamond saw to account for possible settling effects and to create a completely flat exposure surface. Half of the monoliths from each Cast Stone type were sealed in epoxy on all surfaces except the top surface, which remained exposed to the gaseous atmosphere to allow for one-dimensional (1-D) diffusion of the reactive gases. This procedure simplifies the characterization and modeling of degraded materials. These monolithic materials were used for testing in U.S. EPA Method 1315 and will be used in future characterization work including scanning electron microscopy and microCT characterization.

The remaining half of the monoliths from each Cast Stone type were crushed to particle size < 2 mm to satisfy the geometric conditions required for pH dependent leaching tests and to increase the surface area exposed to degradation. These granular materials were used for testing in U.S. EPA Method 1313 and will be used in future characterization work including x-ray diffraction and measurement of the reductive capacity.

Table II. Simulant recipe and reagent type per 1L of simulant

Reagent	Reagent Formula	Manufacturer	Purity (%)	0.1 wt% batch (g)
Milli-Q water	H ₂ O	-	-	729.40
Aluminum nitrate nonahydrate	Al(NO ₃) ₃ ·9H ₂ O	Fisher Scientific	99.2	114.44
Sodium sulfate	Na ₂ SO ₄	Fisher Scientific	99.8	12.15
Sodium chloride	NaCl	Fisher Scientific	99.3	2.47
Sodium fluoride	NaF	Fisher Scientific	99.9	1.33
Sodium hydroxide	NaOH·H ₂ O	Fisher Scientific	N/A	222.96
Sodium phosphate dodecahydrate	Na ₃ PO ₄ ·12H ₂ O	Fisher Scientific	100.5	18.70
Sodium carbonate	Na ₂ CO ₃	Fisher Scientific	99.7	29.05
Sodium nitrite	NaNO ₂	Fisher Scientific	98.9	38.97
Sodium acetate trihydrate	NaCH ₃ COO·3H ₂ O	Fisher Scientific	> 99	5.11
Potassium nitrate	KNO ₃	Fisher Scientific	100.4	3.31
Sodium nitrate	NaNO ₃	Fisher Scientific	99.4	56.86
Sodium chromate	Na ₂ CrO ₄	Sigma Aldrich	98	9.74
		Total Na+K Molarity (mol/L)		5.15
		Mean % Water (g. H ₂ O/g. simulant)		72.6
		Mean Measured Density (g/L)		1.237
		Mean Mixing Time (mins)		31

Each material type and geometry (i.e., granular or monolithic) was divided equally among four different chambers under different gaseous conditions for carbonation, oxidation, oxidation and carbonation, or no carbonation or oxidation for the control (Table I). Each chamber was maintained at 65% relative humidity (RH) and the appropriate scavenger for each condition was placed in the respective chamber.

RESULTS AND DISCUSSION

Carbonation Ingress

Fig. 1 provides the visual differences apparent among different Cast Stone samples after 6 months aging. Most prominent is the reactive front associated with carbonation. Previous research has suggested that 65% RH is within the RH range for most rapid carbonation. If the rate of ingress is assumed proportional to the external CO₂ partial pressure and atmospheric CO₂ is approximately 0.04%, then

maximum carbonation ingress rates of 1.18, 0.83 and 0.49 mm/y for CS-FAF, CS-FA02 and CS-FA18, respectively, are obtained. These rates highlight the importance of material alkalinity in reducing the rate of carbonation ingress.

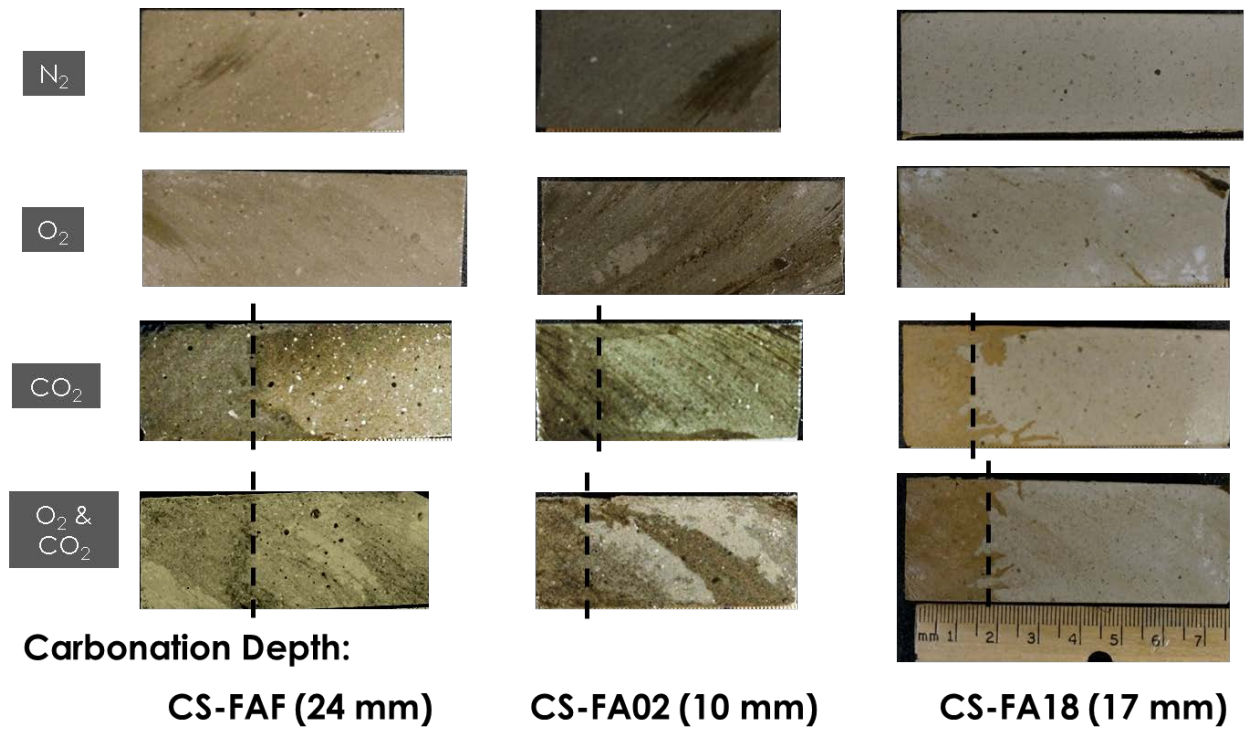


Fig. 1. Cross-section pictures of the extent of visually apparent reactive front ingress for 0.1 wt% Cr spiked samples after 100 days curing under 100% nitrogen followed by 60 days of aging under designated conditions. Exposed face of each sample was on the left of each picture.

Liquid-solid partitioning as function of pH

The pH-dependent leaching for the four exposure conditions for each material revealed differences in the solubility and leaching as a function of pH for the different exposure conditions. Leaching of select elements (i.e., Ca, Mg, S, and Cr) as a function of pH and the pH as a function of acid addition are compared in Fig. 2 for the CS-NFA02-OS materials. All pH-dependent leaching results for CS-NFA02-OS are representative of the other materials made with different fly ash types.

The release of chromium increased slightly in the oxidized material (-O) compared to the control material (-N) at the natural pH of the materials. The release of chromium was reduced in the carbonated and oxidized/carbonated materials compared to the control and oxidized at the natural pH of the materials and for pHs greater than 3.5. A significant decrease in the release of chromium was observed near the pH point of 6 in the carbonated and oxidized/carbonated materials which suggests the dominance of a less-soluble chromium species near pH of 6 for carbonated materials. In addition, the oxidized/carbonated material had a slightly higher release of chromium at its natural pH compared to the carbonated material at its natural pH. This suggests that, as expected, more soluble chromium species

and phases form during oxidation and less soluble chromium species and phases form during carbonation.

The release of sulfur was largest in the oxidized material at its natural pH compared to the release of sulfur at the other materials' natural pH values. The release of sulfur was lower in the carbonated and oxidized/carbonated materials at their natural pH compared to the release of sulfur in the control material at its natural pH. The release of sulfur increased slightly in the oxidized/carbonated material compared to carbonated material at their respective natural pHs. There were no significant trends in the sulfur release across the measured pH domain for all materials. This suggests that a more soluble sulfur phase forms during oxidation, consistent with reduced sulfur species being the primary reducing mechanism for Cast Stone, but the solubility is not a function of pH.

The release of calcium and magnesium decreased as the pH increased for pH values greater than 6 in all materials. The release of calcium and magnesium increased in the carbonated materials (-C and -OC) compared to the non-carbonated materials (-N and -O) at the natural pH of each material. However, the release of calcium and magnesium decreased in the carbonated materials compared to the non-carbonated materials between pH of 6 and 12. These results suggest that carbonation decreases the release of calcium and magnesium, possibly due to formation of magnesium carbonate, which becomes less soluble under increasing alkaline conditions. However, the reduction of natural pH in the carbonated materials indicates a greater release of calcium and magnesium in the carbonated materials will be observed compared to the non-carbonated materials.

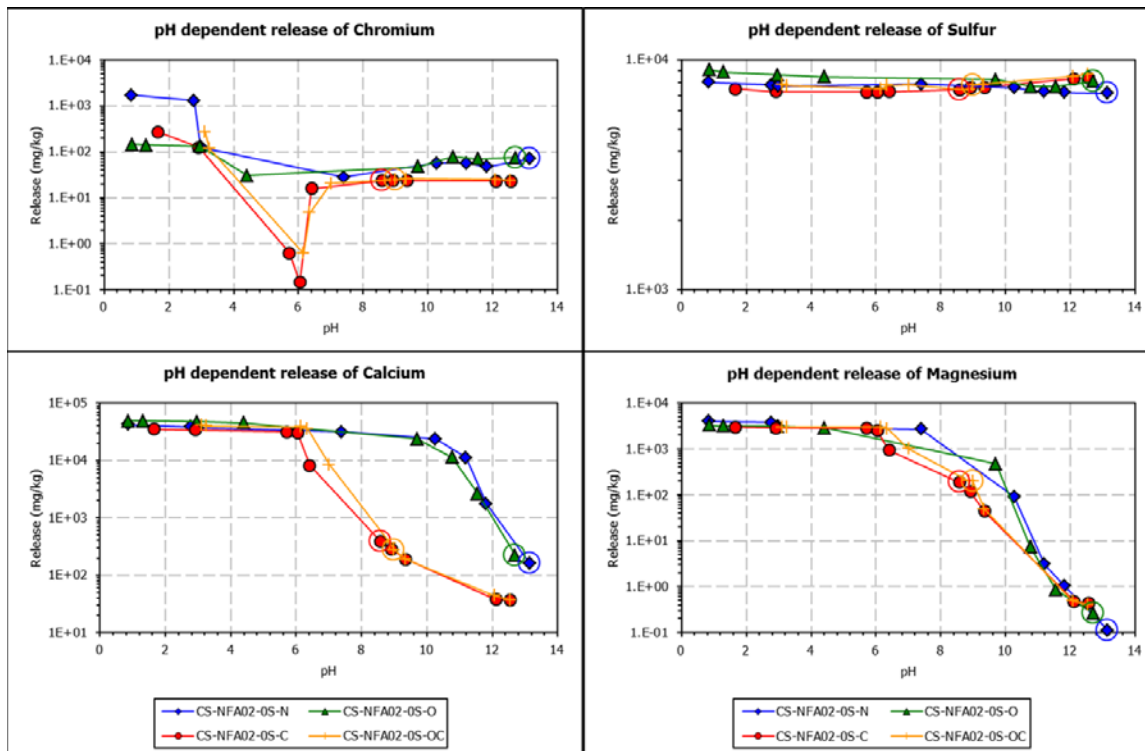


Fig. 2. Comparison of the pH-dependent releases for Cr, S, Ca, and Mg in the four degradation scenarios for CS-NFA02-0S Cast Stone

Mass-transfer

The mass flux and cumulative release rates for the four exposure conditions for each material revealed differences in the mass flux and cumulative release rates in select elements based on exposure condition. Select elements (i.e., Ca, Mg, S, and Cr), pH, and oxidation-reduction potential (ORP) are compared in Fig. 3 and Fig. 4 for the NFA02-OS materials. All trends between the different exposure conditions for the NFA02-OS materials were also observed in the other Cast Stone materials prepared with different fly ash types.

The pH was reduced for both carbonating conditions (-C and -OC) compared to the control (-N) and oxidizing condition (-O). The pH increased throughout the duration of the leaching test in all materials due to the penetration of the leaching front into unreacted regions containing higher alkalinity. The ORP was reduced in both non-carbonating conditions (-N and -O) with a slightly higher initial increase in ORP for the oxidized material compared to the control. ORP values for all samples converged as the leaching times approached 100 days.

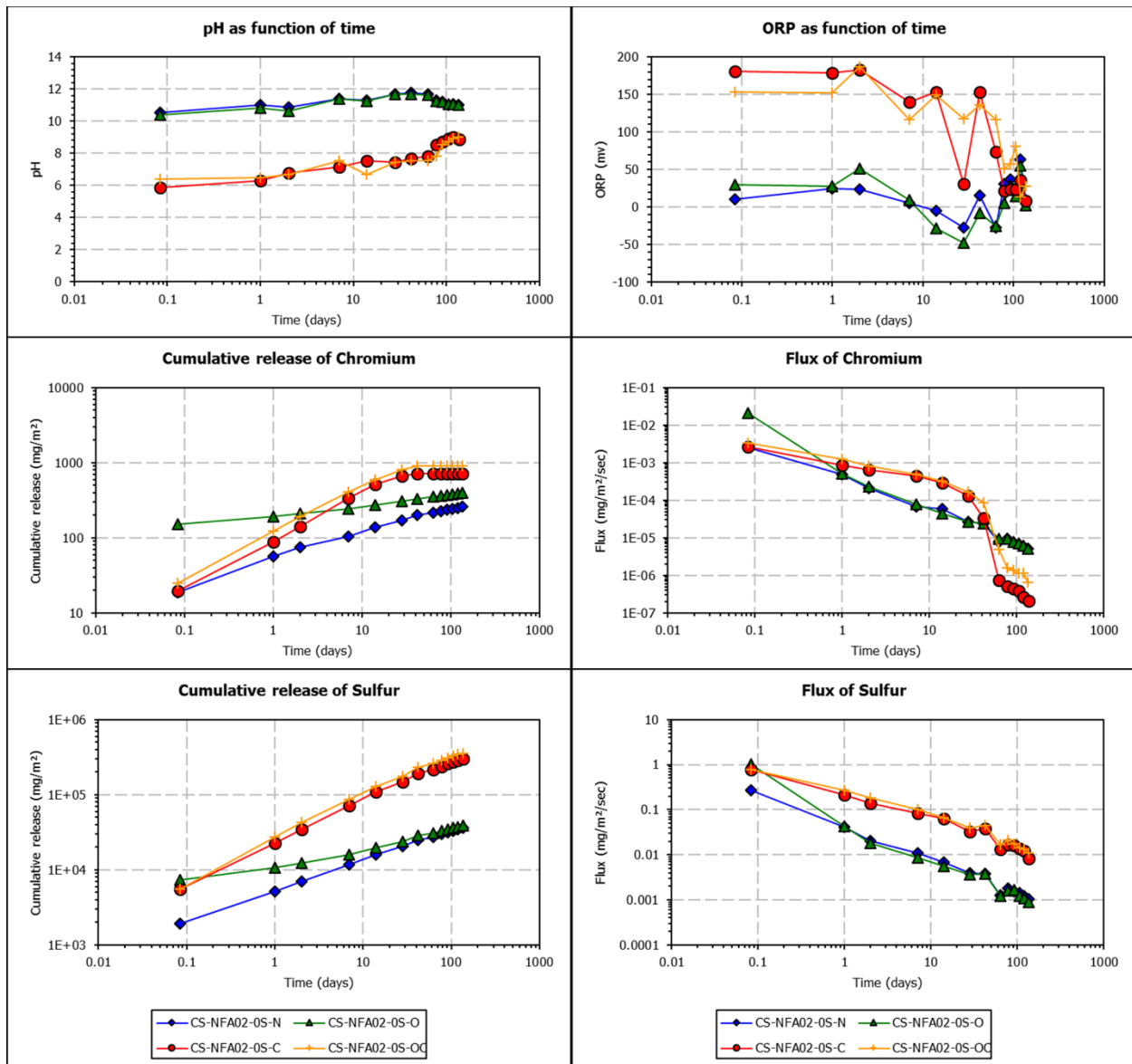


Fig. 3. pH as a function of time, ORP as a function of time, cumulative release rates of Cr and S, and the mass flux of Cr and S from U.S. EPA Method 1315 for the four degradation scenarios of NFA02-0S Cast Stone

The mass flux and cumulative release of chromium were initially higher in the oxidized material (-O) compared to the control (-N) and carbonated materials (-O and -OC). However, the flux of chromium in the oxidized material was nearly equivalent to the flux of chromium in the control and carbonated materials after 1 day of contact time. After a contact time of 2 days, the cumulative release of chromium in the oxidized material was nearly equivalent to the cumulative releases of chromium in the carbonated materials. From a contact time of 2 days to 63 days, the flux of chromium in the oxidized and control were equivalent and both were significantly lower than the flux of chromium in the carbonated materials. In parallel, the mass transfer rate of sulfur was initially higher in the oxidized materials and carbonated materials and after 1 day of contact time the mass

transfer rate of sulfur in the oxidized material became nearly equivalent to the mass transfer rate of sulfur in the control material. The mass transfer rate of sulfur remained higher in the carbonated materials compared to the oxidized and control material for the remainder of the test. This result is consistent with chromium and sulfur becoming more soluble under oxidizing conditions and carbonating conditions. In addition, these data suggest a relatively small oxidized front in the oxidized materials since the mass transfer rates of chromium and sulfur in the oxidized material when compared to the non-oxidizing materials are higher only in the first exchange. The data also suggest a much larger carbonation front compared to the oxidation front and that the leaching front surpasses the carbonation front around 42 days of contact time based on the rapid decrease in the flux of chromium at 42 days.

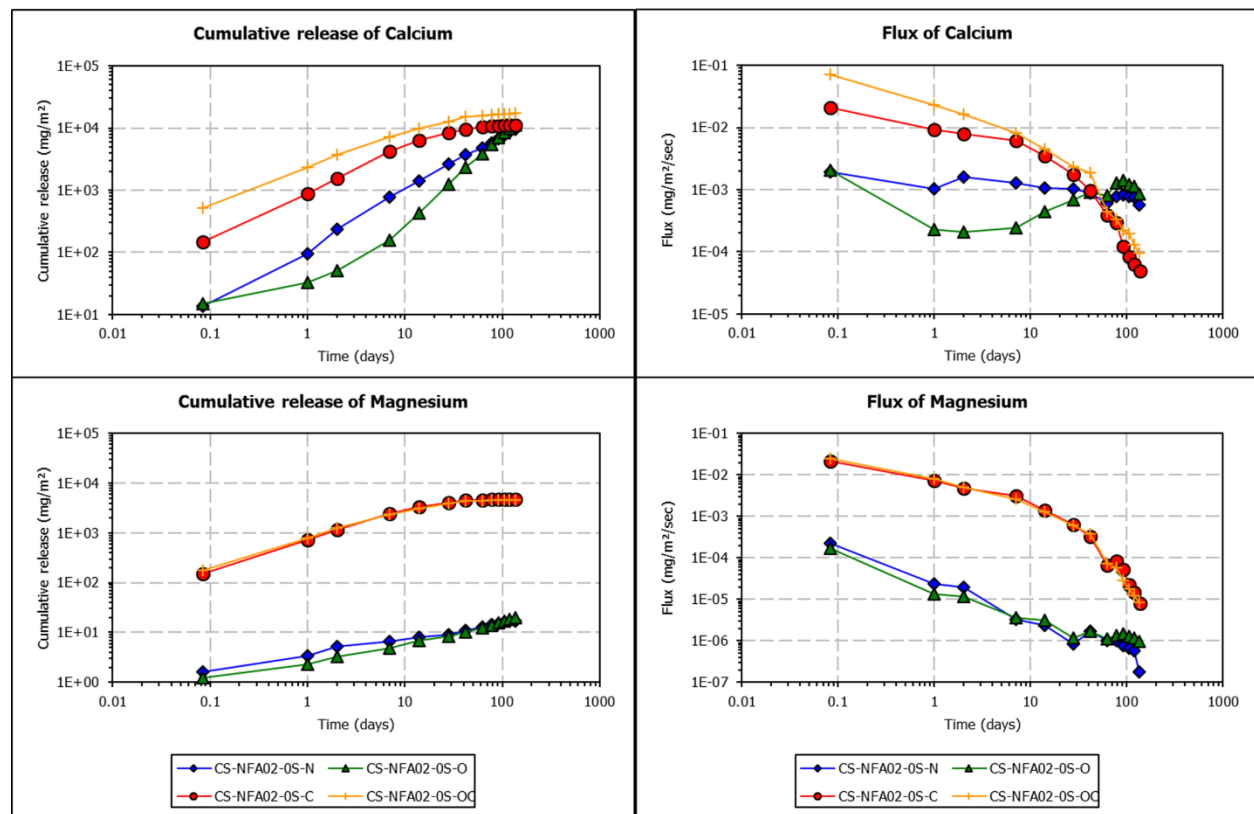


Fig. 4. Cumulative release rates of Ca and Mg and the mass flux of Ca and Mg from U.S. EPA Method 1315 for the four degradation scenarios of NFA02-OS Cast Stone.

The cumulative release rate and mass flux of calcium and magnesium were higher in the carbonated materials (-C and -OC) until 42 days of contact time. This result agrees with the pH-dependent leaching for the materials because of a reduction in the natural pH of the carbonated materials where the calcium and magnesium releases were higher at the carbonated conditions. Initially elevated calcium flux for the oxidized and carbonated case (-OC) relative to the carbonated only case (-C) is hypothesized to be attributed to migration of calcium to the oxidized zone to charge balance the conversion of Cr^{+3} to $(CrO_4)^{-2}$. By a similar charge-balancing

mechanism, the early decrease in calcium flux from the oxidized case (-O) compared to the nitrogen control (-N) may be the result of structure densification in the oxidized zone, slowing release at low calcium solubility conditions below the outermost surface. After day 42, the flux of calcium was lower in the carbonated materials compared to the non-carbonated materials, which suggests the carbonated calcium phase had been depleted in the carbonated region and supports that leaching front had surpassed the carbonation front around 42 days of contact time. At the end of the leaching period, the cumulative release of calcium was nearly equivalent for all materials. Contrarily, the flux and cumulative release of magnesium in the carbonated materials were higher for the entire duration of the leaching period.

CONCLUSIONS

Carbonation and oxidation have been shown to be important processes that affect the chemical performance and leaching mass transfer rates from cementitious materials. Further evaluations of the experimental results and simulations that account for the processes are needed to understand the potential impact on long-term disposal performance.

ACKNOWLEDGEMENTS

This document is partially based on work supported by the U. S. Department of Energy, under Cooperative Agreement Number DE-FC01-06EW07053 entitled 'The Consortium for Risk Evaluation with Stakeholder Participation III awarded to Vanderbilt University, David S. Kosson, principal investigator and Charles W. Powers [retired], co-principal investigator. The opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily represent the views of the Department of Energy or Vanderbilt University.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof.

REFERENCES

1. Q. YU, S. NAGATAKI, J. LIN, T. SAEKI, M. HISADA, The leachability of heavy metals in hardened fly ash cement and cement-solidified fly ash, *Cement and Concrete Research*, 35 (2005) 1056-1063.
2. T. VAN GERVEN, G. CORNELIS, E. VANDOREN, C. VANDECASTEELE, A.C. GARRABRANTS, F. SANCHEZ, D.S. KOSSON, Effects of progressive carbonation on heavy metal leaching from cement-bound waste, *AIChE Journal*, 52 (2006) 826-837.
3. A.C. GARRABRANTS, D.S. KOSSON, R. DELAPP, H.A. VAN DER SLOOT, Effect of coal combustion fly ash use in concrete on the mass transport release of constituents of potential concern, *Chemosphere*, 103 (2014) 131-139.
4. F. SANCHEZ, C. GERVAIS, A.C. GARRABRANTS, R. BARNA, D.S. KOSSON, Leaching of inorganic contaminants from cement-based waste materials as a result of carbonation during intermittent wetting, *Waste Management*, 22 (2002) 249-260.
5. J.L. BRANCH, D.S. KOSSON, A.C. GARRABRANTS, P.J. HE, The impact of carbonation on the microstructure and solubility of major constituents in microconcrete materials with varying alkalinities due to fly ash replacement of ordinary Portland cement, *Cement and Concrete Research*, 89 (2016) 297-309.
6. J.C. WALTON, L.E. PLANSKY, R.W. SMITH, Models for estimation of service life of concrete barriers in low-level radioactive waste disposal, 1990, pp. Medium: ED; Size: Pages: (38 p).
7. K.A. ROBERTS, D.I. KAPLAN, Reduction Capacity of Saltstone and Saltstone Components, in: S.R.N. Laboratory (Ed.) Aiken, SC, 2009.
8. C.A. LANGTON, ALMOND, P.M., Cast Stone Oxidation Front Evaluation: Preliminary Results for Samples Exposed to Moist Air, Savannah River National Laboratory, November 2013.
9. R. RUSSELL, J. JH WESTSIK, D. SWANBERG, R. EIBLING, A. COZZI, M. LINDBERG, G. JOSEPHSON, D. RINEHART, Letter Report: LAW Simulant Development for Cast Stone Screening Tests, Pacific Northwest National Laboratory, Richland, WA, March 2013.