

Weathering Effect on ^{99}Tc Leachability from Cementitious Waste Form

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1. Introduction

Changes in the physical properties of the waste forms, namely pore structure parameters such as porosity, pore diameter, pore throat size and shape, pore connectivity, total pore volume, and pore size distribution, can have a significant impact on the transport of water, gas, and solutes into and out of the waste forms during physical and chemical weathering processes. The mass transfer of contaminants from the solid phase to the waste form pore water, and subsequently out of the solid waste form, is directly related to the number and size distribution of pores as well as the microstructure (i.e., the pore tortuosity and connectivity) of the waste form. Because permeability (or diffusivity) and porosity are controlled by pore apertures (or pore diameter) size, pore volume, and pore distribution, it is important to have some indication of how these characteristics change in the waste form during weathering. Knowledge of changes in these key parameters can be used to develop predictive models that estimate diffusivity or permeability of radioactive contaminants from waste forms for long-term performance assessment. It is known that dissolution or precipitation of amorphous/crystalline phases within waste forms alters their pore structure and controls the transport of contaminants out of waste forms. One very important precipitate is calcite, which is formed as a result of carbonation reactions in cement and other high-alkalinity waste forms. Calcite precipitation and the related calcium leaching process on the surface and within micropores in waste forms can significantly affect the microstructure by changing the size, number, volume, and distribution of pores within these high-alkalinity waste forms. In addition, enhanced oxidation can also increase Tc leachability

from the waste form. To account for these changes, weathering experiments were conducted in advance to increase our understating of the long-term Tc leachability, especially out of the cementitious waste form (Cast Stone).

2. Methods and Results

2.1 Carbonation Reaction in Waste Form

The possible mechanism that is controlling the change in the pore structure of cementitious waste form during carbonation is formation of calcite in the capillary pores. The Ca^{2+} ion is supplied by dissolution of $\text{Ca}(\text{OH})_2$ (Portlandite or CH), which is formed during the hydration reactions of the dry blend. Other cementitious solids such as C-S-H and C-A-S-H can also supply ample concentrations of Ca^{2+} ions to the Cast Stone pore water. The $\text{CO}_2(\text{g})$ is continually supplied by diffusion of air and/or bicarbonate/carbonate ions in percolating recharge waters into the subsurface.

2.2 Environmental Chamber Reaction

An environmental humidity chamber was configured to allow the atmosphere composition to be controlled. A $\text{CO}_2(\text{g})$ chamber was made by modifying a polycarbonate vacuum desiccator. A hole was drilled ~2.5 cm below the O-ring seal in the base of the desiccator and a Swagelok bulkhead with neoprene gaskets was installed. A piece of Teflon tubing was installed on the inside of the bulkhead fitting, run through a hole in the desiccator plate, and placed into approximately 800 mL of DIW. A zero to 60 mL/min flow meter was connected to the outside portion of the bulkhead fitting to control the gas flow. After the

waste form cylindrical samples were added to the desiccator, the two halves were taped together. For the carbonation weathering tests, the chamber was continually refreshed with an atmosphere mixture of 5-percent CO_2 and 95-percent N_2 gases. For the oxidation weathering tests, the waste forms were bathed in a mixture of 22-percent O_2 and 78-percent N_2 gases (with no CO_2). After exposure to the CO_2 or O_2 atmospheres for 14 days, the monolith samples were taken out and tested for Tc leachability with the EPA 1315 method.

3. Conclusions

Pore structure analysis was characterized using both $\text{N}_2(\text{g})$ absorption analysis and XMT techniques, and the results show that cementitious waste form is a relatively highly-porous material (less dense) compared to other waste forms studied in this task. Detailed characterization of Cast Stone chunks and monolith specimens indicate that carbonation reactions can change the Cast Stone pore structure, which in turn may correlate with Tc leachability. Short (14-day) carbonation reaction times for the Cast Stone causes pore volume and surface area increases, while the average pore diameter decreases. Based on the changes in pore volumes measured using gas absorption analysis, the total porosity was changed from 8.6 percent to 10.7 or 12.0 percent after carbonation. The accelerated weathering reactions produced with exposure to elevated $\text{CO}_2(\text{g})$ or $\text{O}_2(\text{g})$ condition were performed on cast stone monoliths and the resulting water leachates for the carbonated Cast Stone using the EPA 1315 method showed significantly decreased pHs, but increased Tc diffusivities for the entire 90-day period when compared to Cast Stone monoliths that were not weathered. The increased Tc diffusivity for Cast Stone after reacting with $\text{CO}_2(\text{g})$ resulted from increased porosity as found in previous pore structure analyses. However, the increased Tc diffusivity in carbonated Cast Stone gradually decreased (Fig.1), and the decreased pH in effluents also gradually increased as leaching times increased, suggesting that calcite precipitate and pore

structure changes might affect Tc diffusivity under long-term leaching conditions.

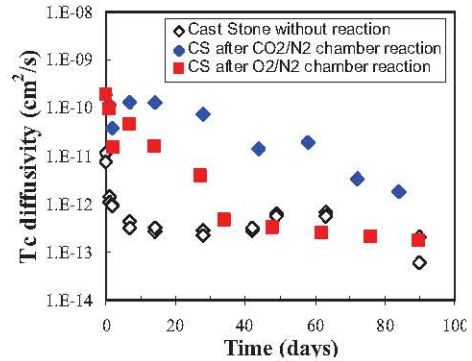


Fig. 1. Diffusivity of Tc and Measured pHs for Cast Stone Leachates Before and After Reaction Inside CO_2/N_2 or O_2/N_2 Chamber using the EPA 1315 Method [1].

The Cast Stone monolith reacted in the enhanced $\text{O}_2(\text{g})$ environment generated leachates with pH values that were the same as leachates for Cast Stone that were not weathered. However, the Tc diffusivity for the oxidized Cast Stone increased significantly during early leaching times, most likely because $\text{O}_2(\text{g})$ is a strong oxidant that re-oxidized the reduced Tc(IV) species found near the surface of the monolith. Increased Tc diffusivity in oxidized Cast Stone also decreased as the leaching times increased and showed the same Tc diffusivity as unreacted Cast Stone after leaching for 50 days.

4. REFERENCES

- [1] Um, RJ Serne, MM Valenta, KE Parker, C-WChung, G Wang, JS Yang, KJ Cantrell, MH Engelhard and JH Westsik, Jr., Radionuclide Retention Mechanisms in Secondary Waste-Form Testing: PhaseII, PNNL-20753, 2011.