

Weathering Effects on Technetium Leachability from Ceramicrete Waste Form

Jongkwon Choi^{a,*}, Syazwani Mohd Fadzil^a, Wooyong Um^{a,b}

^a Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), Pohang, South Korea

^b Pacific Northwest National Laboratory, Richland, Washington, United States

*Corresponding author: jjangcjk@postech.ac.kr

1. Introduction

Ceramicrete waste form was developed as part of the U.S. Department of Energy's (DOE's) Office of Environmental Management program to stabilize and contain volatile radioactive contaminant such as technetium (⁹⁹Tc). Ceramicrete processing technology has been demonstrated on various waste streams and has shown to retain both radioactive and hazardous contaminants effectively [1]. Radioactive Tc is highly soluble and mobile in the environment as pertechnetate anion [2]. Tc is also easily volatilized. Tc can be in the waste in two oxidation states – IV and VII. Tc is volatilized even during the evaporation stage when removing excess water from HLW that contains acidic solutions of Tc(VII) as pertechnetate (TcO₄⁻) [2].

Common chemical weathering process to occur within waste forms in the nuclear waste repository is carbonation [3]. In addition, since technetium (⁹⁹Tc) leachability is closely related with oxidation condition and the oxidized Tc species, pertechnetate (TcO₄⁻) shows much higher leachability, oxidative weathering pre-treatment of waste form is important, especially for the shallow-depth radioactive waste repositories. In 2011, an evaluation of weathering effects on Tc release from different waste forms (Cast Stone and DuraLith) was conducted in the environmental chamber with different gas mixtures to produce enhanced oxidizing or carbonation conditions [3].

Based on the technical literature and previous testing results, Ceramicrete waste form was also selected for further weathering testing to evaluate oxidizing or carbonation effects on Tc release after weathering [1]. Leachability Indexes (LI) of Tc from two waste forms (Cast Stone and DuraLith) without pre-treatment of O₂(g) or CO₂(g) are higher than those of waste forms with pre-treatment of the same gases to simulate enhanced oxidation and carbonation weathering conditions, respectively. The LI values of two waste forms with and without weathering are shown in Table 1.

Comparing Tc leachability from two waste forms (Cast Stone and DuraLith) with or without weathering pre-treatment, Tc diffusivity increased and the LI value of Tc decreased after weathering processes. Therefore, the objective of this study is to evaluate the weathering effects on Tc release from Ceramicrete waste form and compare the results with other data obtained from different waste forms.

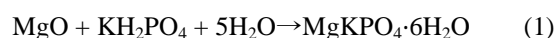
Table 1. Technetium LI of waste forms measured by the EPA 1315 method without pre-treatment and after CO₂/N₂ or O₂/N₂ chamber pre-treatment.

Waste form	LI without pre-treatment	Gas	LI with pre-treatment
Cast stone	10.3	CO ₂ /N ₂	9.34
		O ₂ /N ₂	10.2
DuraLith	10.6	CO ₂ /N ₂	9.80
		O ₂ /N ₂	9.62

2. Methods and Results

2.1 Preparation of Phosphate-Bonded Ceramicrete Waste Form

Chemical reaction of magnesium phosphate ceramics is represented in equation (1) and the method to form Ceramicrete is well developed.



To prepare Ceramicrete monoliths (2.5 cm by 5 cm), Hanford secondary waste simulant containing TcO₄⁻ and DIW were added to a mixing bowl containing tin chloride (0.2 gram) used as a reducing agent, and then mixed for 4 minutes at low speed with a planetary mixer. In a separate container, magnesium oxide, monopotassium phosphate and Class C fly ash were dry mixed using a wire whisk. The dry materials were added and mixed at medium speed for 20 minutes. When slurry was mixed, the resulting paste was poured into molds and vibrated in ultra cleaner for 1 minute to remove air bubbles. Then, the slurry was cured for 14 days before use. More details of Ceramicrete formation can be found in Mattigod et al. (2011) [1].

2.2 Weathering condition before EPA 1315 test

A mixture of 5% CO₂(g) and 95% N₂(g) or 22% O₂(g) and 78% N₂(g) in an environmental reaction chamber accelerates the carbonation or oxidation weathering reaction on Ceramicrete waste form. After exposure to the enhanced oxidation or carbonation condition for 14 days, Ceramicrete waste form monolith with Tc were subjected to EPA 1315 leaching test [3].

2.3 EPA 1315 method

The cylindrical monolith Ceramicrete waste form was

put into the center of a vessel and submerged in DIW solution to maintain a solid-to-solution ratio of 9 ± 1 mL of eluent per cm^2 of sample [4]. The leaching intervals in these experiments were 2 hours and 1, 2, 7, 14, 28, 42, 49, 63, 77, and 91 or 93 days. Samples collected during these intervals were used to measure pH, EC, and redox potential. Before chemical analyses for major cations, anions and Tc concentrations, the samples were filtered with a $0.45\text{-}\mu\text{m}$ syringe filter [1].

The observed diffusivity value for each sample was calculated by Equation 2.

$$D_i = \pi \left[\frac{M_{ti}}{2\rho C_0 (\sqrt{t_i} - \sqrt{t_{i-1}})} \right]^2 \quad (2)$$

where D_i =observed diffusivity of the constituent for leaching interval, i [cm^2/s]

M_{ti} =mass of constituent released during leaching interval, i [$\mu\text{g}/\text{m}^2$]

t_i = cumulative contact time after leaching interval, i [s]

t_{i-1} = cumulative contact time after leaching interval, $i-1$ [s]

C_0 = initial leachable content of constituent ($\mu\text{g}/\text{g}$)

ρ = sample density (g/cm^3)

The mean observed diffusivity for each sample can be determined by taking the average of the interval observed diffusivity with the standard deviation. The LI value can be calculated as the negative logarithm of the observed diffusivity as shown in Equation (3).

$$LI = -\log(D_{\text{observed}}) \quad (3)$$

The LI value of Tc from Ceramicrete without reaction was about 9.4. The Tc LI value from Ceramicrete after oxidation or carbonation weathering was similar to or even higher than that obtained from without weathering unlike Cast Stone and DuraLith showed.

As shown in Fig.1., Cast Stone showed the largest pore volume, indicative of relatively high porosity among different waste forms tested. The DuraLith showed smaller pore volume than Cast Stone, and Ceramicrete waste form showed the smallest pore volume. This indicates that the overall porosity of Ceramicrete waste form is lower than other waste forms [3]. Therefore, when weathering (oxidation or carbonation) was progressed, gas diffusion, especially for oxygen would not be fast enough to make Tc reoxidation due to the smaller pores present in Ceramicrete waste form. In other words, Tc release from Ceramicrete was scarcely affected by weathering, especially oxidation reaction.

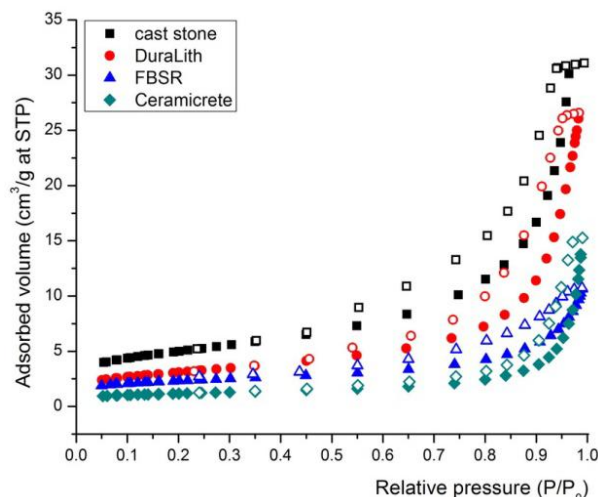


Fig.1. $\text{N}_2(\text{g})$ gas adsorption and desorption isotherms of Cast Stone, DuraLith, FBSR, and Ceramicrete waste forms before carbonation or oxidation reaction. Closed and open symbols represent adsorption and desorption of $\text{N}_2(\text{g})$, respectively [3].

3. Conclusions

From previous tests using EPA 1315, diffusivity and leachability index of Tc in Cast Stone and Duralith waste forms showed higher diffusivity and lower LI values after weathering in the environmental chamber simulating enhanced carbonation and oxidation condition. Nevertheless, after treating the same way for Ceramicrete waste form, Tc release was not significantly affected by weathering pre-treatment, because of low porosity found in Ceramicrete which may delay the gas diffusion through Ceramicrete waste form structure.

ACKNOWLEDGEMENTS

This work was supported by World Class University (WCU) (R31-30005) Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology

REFERENCES

- [1] SV Mattigod, MJ Lindberg, JH Westsik, Jr., KE Parker, CW Chung, Waste Acceptance Testing of Secondary Waste Forms: Cast Stone, Ceramicrete and DuraLith, PNNL-20632, 2011
- [2] MI Ojovan and WE Lee, An Introduction To Nuclear waste immobilization, Elsevier, Amsterdam, Vol. 1, p. 246
- [3] W Um, RJ Serne, MM Valenta, KE Parker, C-W Chung, G Wang, JS Yang, KJ Cantrell, MH Engelhard and JH Westsik, Jr., Radionuclide Retention Mechanisms in Secondary Waste-Form Testing: Phase II, PNNL-20753, 2011
- [4] DRAFT EPA METHOD 1315, 2009