

Evolution of ^{99}Tc Species in Cementitious Nuclear Waste Form

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1. Introduction

Technetium (Tc) is produced in large quantities as a fission product during the irradiation of ^{235}U -enriched fuel for commercial power production and plutonium genesis for nuclear weapons. The most abundant isotope of Tc present in the wastes is ^{99}Tc because of its high fission yield (~6%) and long half-life (2.13×10^5 years) [1,2]. During the Cold War era, generation of fissile ^{239}Pu for use in America's atomic weapons arsenal yielded nearly 1900 kg of ^{99}Tc at the U.S. Department of Energy's (DOE) Hanford Site in southeastern Washington State [3]. Most of this ^{99}Tc is present in fuel reprocessing wastes temporarily stored in underground tanks awaiting retrieval and permanent disposal. After the wastes are retrieved from the storage tanks, the bulk of the high-level waste (HLW) and low-activity waste (LAW) stream is scheduled to be converted into a borosilicate glass waste form that will be disposed of in a shallow burial facility called the Integrated Disposal Facility (IDF) at the Hanford Site. Even with careful engineering controls, volatilization of a fraction of Tc during the vitrification of both radioactive waste streams is expected. Although this volatilized Tc can be captured in melter off-gas scrubbers and returned to the melter, some of the Tc is expected to become part of the secondary waste stream from the vitrification process. The off-gas scrubbers downstream from the melter will generate a high pH, sodium-ammonium carbonate solution containing the volatilized Tc and other fugitive species. Effective and cost-efficient disposal of Tc found in the off-gas scrubber solution remains difficult. A cementitious waste form (Cast Stone) is one of the nuclear waste form candidates being considered to solidify the secondary radioactive liquid waste that will be generated by the operation of the waste treatment plant (WTP) at the Hanford Site. Because Tc leachability from the waste form is closely related with Tc speciation or oxidation state in both the simulant and the final waste forms, the identity of Tc species is necessary to understand its retention mechanism and long-term leachability.

2. Methods and Results

Both Eh-pH diagram calculation and x-ray absorption near edge structure (XANES) spectroscopy were used to investigate Tc species and oxidation state in Cast Stone

waste form prepared with a simulated secondary waste stream.

2.1 Tc Eh-pH Diagram Calculation

Eh-pH diagram for Tc in secondary waste simulant was developed at 25°C and 1 atm pressure using *The Geochemist's Workbench* software (version 8.0.9). The thermodynamic database originally was developed at Lawrence Livermore National Laboratory for use with the EQ3/6 geochemical model. Based on the measured Eh and the pH values for the simulant (pH:12-13), the dominant aqueous Tc species was oxidized $^{99}\text{Tc(VII)O}_4^-$ (Fig. 1).

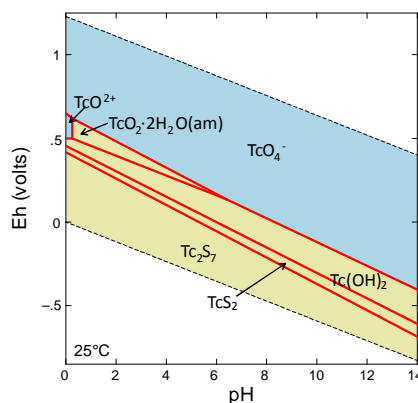


Fig. 1. Eh-pH diagram for dominant technetium species at 25°C for the caustic scrubber secondary waste simulant.

2.2 Preparation of Cast Stone Waste Form

The Cast Stone monoliths (2.5cm diameter x 5cm height) were prepared by mixing the dry materials in the following order: cement, fly ash, and blast furnace slag (BFS). The composition of the Cast Stone formulation is shown in Table I.

Table I: Dry reagent compositions used in Cast Stone

Ingredients	wt %
Portland Cement Type I/II	8
Fly Ash Class F	45
Blast Furnace Slag, Grade 120	47

The dry materials were blended for 5 minutes using a planetary mixer set at low speed. After the dry-solid mixture was homogenous, the Tc-spiked simulant and deionized water (DIW) were added to the blended dry mixture and mixed for 5 minutes to obtain a homogeneous slurry that flowed easily. The Tc

concentration of 100~150 $\mu\text{g-Tc/g}$ of the final solid form was used to prepare Cast Stone sample. The target waste loading was approximately 8 wt% on a dry-weight basis for each material.

2.3 XANES Spectroscopy Analysis

Cast Stone waste-form monolith prepared with different curing times was crushed and ground to make powder samples for mounting on Teflon sample holders and sealing with Kapton tape. XANES data collection was conducted at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using beamline X11A. A Si(220) double flat crystal monochromator was used, and the energy was calibrated by using the first inflection point of the Tc K-edge spectrum of Tc(VII) standard defined as 21.044 keV. The Tc solid standards (KTcO_4 , NaTcO_4 , TcO_4^- adsorbed on Reillex-HPQ resin, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, and Tc_2S_7) were also collected in transmission mode at room temperature using a 7-element (NSLS) Ge detector. XAFS spectrum processing (i.e., calibration, alignment, background subtraction, normalization, and averaging) was performed with Athena software using the software IFEFFIT and ATHENA/ARTEMIS after correction for detector dead-time. The XANES spectra for the Tc waste form samples were fit using a linear combination of the XANES spectra using TcO_4^- adsorbed on Reillex HPQ resin as the Tc(VII) standard spectrum and both $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and Tc_2S_7 in grout as the standard spectra for Tc(IV) [4].

The XANES spectra of Tc standards [TcO_4^- adsorbed on Reillex-HPQ resin for Tc(VII) and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ for Tc(IV)] and Tc-Cast Stone samples are shown in Fig. 2. The spectrum of TcO_4^- (VII) standard is characterized by a strong pre-edge feature because of the 1s to 4d transition, which is allowed for the tetrahedral TcO_4^- anion. The XANES spectrum of Tc(IV) standard, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ is very different and is characteristic of Tc(IV) coordinated by six oxygen atoms in an octahedral geometry. Using a linear combination model in which three Tc species (TcO_4^- , $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, and Tc_2S_7) are considered to be plausible, the summation of spectra contributions from these three Tc species matched the measured Tc XANES spectra well. The contribution of the Tc_2S_7 species increased as reaction (storage) time increased from 3 days to 76 days, even though its contribution was small when compared to the overall species distribution. Intensity of the pre-edge peak present around 21,047 eV also decreased as the storage time (slow continued hydration reaction in Cast Stone) increased. In addition, absorption peaks around 21,065 eV moved relatively to lower energy regions for the Cast Stone samples cured for 60 days compared to those cured for 3 days storage, indicating a greater contribution from Tc(IV) species as the storage time increased. For Tc-Cast Stone sample prepared with 76 days reaction times, the pre-edge peak, typical of Tc(VII) species, essentially disappeared in this sample.

Although a small weak-hump can still be found in low-energy regions between 21,040 eV and 21,050 eV, there appears to be increased contributions of Tc_2S_7 species (22 percent) in the Tc-Cast Stone samples after 76 days reaction compared to other Tc-Cast Stone samples (0 to 3 percent) reacted between 3 days to 60 days. The increase of Tc_2S_7 and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ contributions as the reaction time increases is considered to result from more dissolved concentrations of sulfide and other reductants like ferrous iron from the BFS used in preparing Cast Stone.

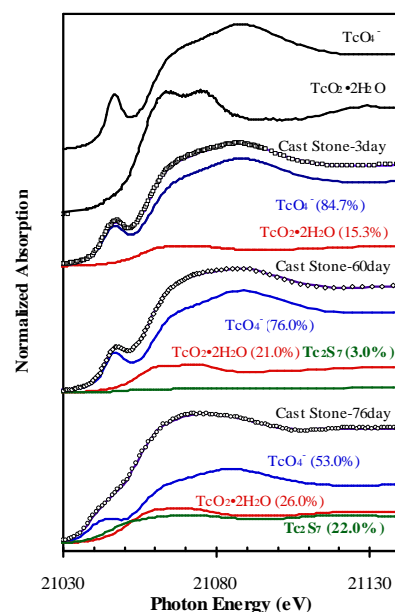


Fig. 2. Normalized Tc XANES spectra and Fits for Cast Stone samples prepared with different cured times. Data are represented by symbols, and the fit is represented by the solid black line. The contribution of each Tc species and percentage are shown with different colors.

3. Conclusions

Although the initial Tc species and oxidation states in the simulant were estimated to be solely TcO_4^- or the Tc(VII) oxidation state, the Tc species in the final Cast Stone waste forms varied depending the reaction (or storage) times because of the slow dissolution kinetics for the BFS used as one of dry ingredients. Different Tc species controls Tc leachability from the solidifying waste form.

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