NEUP Nuclear Energy University Programs

U.S. Department of Energy

Thermodynamic and Microstructural Mechanisms in the Corrosion of Advanced Ceramic Technetium-bearing Waste Forms and Thermophysical Properties

PI: Thomas Hartman – University of Nevada, Las Vegas

Collaborators: Steven Frank – Idaho National Laboratory

Program: Separations and Waste Forms

ABSTRACT

The isolation of technetium-99 from the environment is critical to the mission of the Office of Nuclear Energy of the US-DOE in order to move forward on used nuclear fuel recycling. The management of nuclear waste containing Tc-99 is highly challenging because of the high mobility of Tc- 99 at its highest oxidation level (Tc+7) in aqueous environments. Therefore we are proposing to incorporate the fission product Tc-99 as Tc4+cations into advanced ceramic structures. This will significantly reduce the mobility of technetium in the environment and might effectively isolate fission technetium from the biosphere. The objective of this project is to harvest fundamental thermodynamic and microstructural data on the leaching- and corrosion mechanism of advanced ceramic waste forms to evaluate their potential to stabilize and to isolate Tc-99. We further intend to determine thermophysical properties of the proposed advanced waste form candidates to structurally stabilize Tc-99 as Tc4+cation.

We believe that the research work as proposed here strongly supports the goals of the Fuel Cycle R&D program and could lay the foundation to advance the state-of-the-art of the methodology in stabilization and isolation of fission technetium from high-level waste streams. Within the last two years in our related research activities, we were successful in fabricating novel and promising waste form candidates to incorporate fission technetium into ceramic matrices and crystalline structures such as cubic pyrochlores with lanthanides (Ln2Tc2O7), orthorhombic perovskites with strontium (SrTcO3), and tetragonal layered perovskites with strontium (Sr2TcO4). The incorporation of fission technetium into the crystalline pyrochlore- and perovskite structure types has significant advantages compared with the fabrication of vitrified Tc-containing borosilicate glass in terms of thermodynamics and corrosion resistance, but also in regard to efficiency of the technical scale process.

The main objective of this project is to compare thermodynamic and kinetics aspects of (1) Tc-leaching, (2) matrix corrosion, and (3) microstructural corrosion mechanism of the advanced ceramic Tc-waste form candidates Ln2Tc2O7, A2+TcO3, and A2+ 2TcO4 (Ln = Ce, Nd, Sm, and A2+ = Ca, Sr, Ba) against a Tcbearing borosilicate-based reference glass. Therefore we propose five tasks for a period of 3 years: (1) Fabrication of dense, single phase, Tc-bearing ceramic monoliths. We will build a compact Hot Uniaxial Press (HUP) for fabricating crystalline, dense, gram-size, single phase, Tc-bearing waste forms. The HUP design is subject of a current senior design project at UNLV. (2) Thermodynamics and kinetics of Tc-leaching. ASTM C1285-02 (PCT-B) and ASTM C1220-10 (MCC-1) will be used to evaluate the thermodynamics and kinetics of Tc leaching. Tc-leaching from the waste-form candidates will be compared to a reference Tc-bearing borosilicate glass. The fabrication of Tc-containing borosilicate glasses is subject of a current PhD student research work at UNLV. (3) Thermodynamics and kinetics of Tc waste form matrix corrosion. ASTM 1662-10 (SPFT) will be applied to understand matrix corrosion, and ASTM 1663-09 (VHT) to determine the accelerate formation of altered and secondary phase on the surface of the waste forms. (4) Microstructural waste form corrosion mechanism. In autoclave-type corrosion experiments test specimens will be corroded (e.g. 200 °C, 10 MPa) to mimic near-field conditions of a generic geological repository. Microstructure and secondary phase formation will be characterized. (5) Thermophysical properties of advanced Tc waste forms. Basic thermophysical properties of the advanced waste forms will be determined. Data can not only be used in performance assessment of a generic geological repository but also can provide new avenues for potential technical applications. The waste forms SrTcO3, and Sr2TcO4 are superconductors at 7.8 and 7 K.