Impeding ^{99}Tc(IV) mobility in novel waste forms

MAL-SOON LEE[1*], WOOYONG UM[2, 3], GUOHUI WANG[2], ALBERT A. KRUGER[4], WAYNE W. LUKENS[5], ROGER ROUSSEAU[1], AND VASSILIKI-ALEXANDRA GLEZAKOU[1]

[1]Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA (*correspondence: mal-soon.lee@pnnl.gov)

[2]Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA

[3]Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POTECH), Pohang, South Korea

[4]United States Department of Energy, Office of River Protection, Richland, WA 99352, USA

[5]Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^{99}Tc is a long-lived radioactive fission product whose mobility in the subsurface is largely governed by its oxidation state. Migration of Tc from a waste repository may be prevented by immobilizing Tc(IV) in durable glass forms. Thus, efficient incorporation and high retention of Tc by glasses is very important for radioactive waste management and environmenta remediation. Tc(IV) oxidation to higly volatile Tc(VII) (TcO_4^-) at glass vitrification temperatures results in poor Tc retention in the final waste glass. Retention of Tc in the glass is generally improved by reducing conditions since Tc(IV) is not volatile. However, experiments with Tc-magnetite under high temperature and oxic conditions showed re-oxidation of Tc(IV) to volatile pertechnetate.[2] Experiments also showed that magnetite transforms to maghematite resulting in disproportionation and re-oxidation of Tc. This transformation can be suppressed through incorporation of trace elements such as Co, Ni, Zn into magnetite forming spinel.[3]

In this talk, we will present results from *ab initio* molecular dynamics simulations and experiments on the structural and electronic properties of Tc-incorporation in magnetite. We will discuss the temperature effect on Tc mobilization and changes of Tc retention in magnetite. Theory predictions indicated enhanced Tc retention in the presence of 1st row transition metal dopants in Tc-incorporated magnetite, that was confirmed by followup eperiments.

[1] Lee, M.-S. et al, Nature Communications, in press. [2] Marshall, T. A., et al. Incorporation and Retention of 99-Tc(IV) in Magnetite under High pH Conditions. Environ. Sci. Technol. 48, 11853-11862 (2014); [3] Sidhu, P. S., Gilkes, R. J., Posner, A. M. Mechanism of the low temperature oxidation of synthetic magnetites. J. lnorg. Nucl. Chem. 39, 1953-1958 (1977).