

Sequestration of a Pertechnetate analog – Perrhenate – in Mixed Anionic Sodalite

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Predicting and managing the fate and transport of long-lived radionuclides, such as technetium (Tc-99), after being released from caustic nuclear waste forms contained in a geologic disposal system represents a key component of the overall safety evaluation and is critical to closing the nuclear fuel cycle. Tc-99, a long-lived by-product of the nuclear fuel cycle, has a long half-life (211,000 y) and high mobility in oxidized subsurface environments. For example, Tc-99 contamination has occurred at select DOE waste sites and in sediments beneath the high-level waste (HLW) storage tanks at the Hanford Site in Washington

State. Over the years, these storage tanks have leaked caustic, Al-rich, and high ionic strength (mainly NaNO₃ salt) HLW solutions to the environment. Modeling the migration of known Tc-99 releases (5.31x10³ Ci) to ground water at Hanford led to prediction of its groundwater concentrations in excess of the 0.4 nmol/L MCL [4]. However, nearly half a century after the release, most of the Tc-99 persists in the deep subsurface sediment in non-labile phases. Previous studies demonstrated Sr-90 and Cs-137 incorporation into feldspathoid minerals, such as sodalite [Na₈(Al₆Si₆O₂₄)(X)_n, where X is an anion], that form when Hanford primary silicate minerals react with HLW solutions [1, 2]. The potential to immobilize pertechnetate (TcO₄⁻) in the subsurface or in engineered waste stream reactors is the subject of this investigation. We use perrhenate (ReO₄⁻) as a chemical analog for TcO₄⁻ because of the similarity in ionic radius and chemical behavior under oxic conditions [3].

To elucidate the influence of competing anions contained in the HLW solution, specifically Cl⁻, CO₃²⁻, NO₃⁻, SO₄²⁻, MnO₄⁻ and WO₄²⁻ on ReO₄⁻ incorporation into sodalite, we synthesized mixed sodalites with equivalent concentrations of the two anions. The resulting solids were characterized. Data showed that Re was immobilized in the mixed anion sodalites as Re(VII) and only those anions possessing similar valency, electronegativity and a difference in ionic radii of ≤15% are expected to foster significant ReO₄⁻ incorporation into the mixed sodalite lattice. Therefore, Tc-99 released under the Hanford tanks with high concentrations of NO₃⁻ and other small anions is unlikely to be sequestered into sodalite.

[1] Chorover, J., Choi, S., Rotenberg, P., Serne, R.J., Rivera, N., Strepka, C., Thompson, A., Mueller, K.T., O'Day, P.A., 2008, *Eochemica et Cosmochimica Acta* **72**, 2024-2047 [2] Deng, Y., Harsh, J.B., Flury, M., Young, J.S., and Boyle, J.S. 2006, *Applied Geochemistry*, **21**, 1392-1409 [3] Icenhower, J.P., NP Qafoku, JM Zachara, and WJ Martin. (2010). *American Journal of Science*, **310**, p.721-752 [4] USDOE. Vadose zone characterization project at the Hanford tank farms: AX tank farm report; 1997.