Efficient and Selective Uptake of TcO_4^- by Cationic Metal-Organic Framework Material

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^{99}Tc is one of the most problematic radioisotopes in used nuclear fuel owing to its combined features of high fission yield, long half-life, and high environmental mobility. Cationic inorganic or polymer based materials are widely investigated to remove TcO_4^- from aqueous solution, but previous results showed that the inorganic ion exchangers held poor stability, low capacity, or slow kinetic, which significantly limits their applications in the real technetium spills situations. We reported an 8-fold interpenetrated three-dimensional cationic metal-organic framework material, SCU-100, which is assembled from a tetradentate neutral nitrogen-donor ligand and two-coordinate Ag^+ cations as potential open metal sites. SCU-100 maintains its crystallinity in aqueous solution over a wide pH range from 1 to 13 and exhibits excellent β and γ radiation-resistance. Anion exchange studies show that SCU-100 is able to both quantitatively and rapidly remove TcO_4^- from water within 30 min. The exchange capacity for the surrogate ReO_4^- reaches up to 541 mg/g and the distribution coefficient K_d is up to 1.9×10^5 mL/g. More importantly, SCU-100 can selectively capture TcO_4^- in presence of large excess of competitive anions (NO_3^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}) and remove as much as 87% of TcO_4^- from the Hanford low-level waste melter off-gas scrubber simulant stream within 2 hours. The sorption mechanism is well elucidated by single crystal X-ray diffraction, showing that the sorbed ReO_4^- anion is able to selectively coordinate to the open Ag^+ sites forming Ag-O-Re bonds and a series of hydrogen bonds. This work represents a practical case of TcO_4^- removal by Cationic MOF material and demonstrates the promise of using this type of material as a scavenger for treating anionic radioactive contaminants during the nuclear waste partitioning and remediation processes.

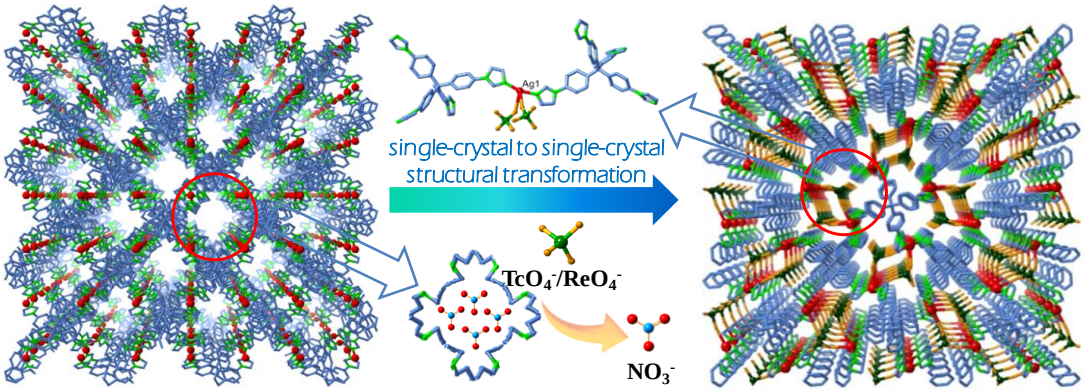

Fig.1. Crystal structures of SCU-100 and SCU-100-Re showing a single-crystal to single-crystal transformation mechanism .

TABLE I. ReO_4^- adsorption capacity of SCU-100 in the presence of different concentration of SO_4^{2-} as studied by ICP-OES ($C_{ReO4-}=7.92\times10^{-5}$M).

Sample	Mole ratio of n(ReO_4^-) : n(SO_4^{2-})	%ReO_4^- removal
SCU-100	1:0.1	99.7%
	1:1	99.6%
	1:10	99.2%
	1:100	98.6%
	1:1000	97.5%
	1:6000	97.1%