Influence of hydroxyl-water interaction on structural transformations during Cs^+ exchange in microporous H-CST

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Crystalline silicotitanate (CST) molecular sieve is being tested as an ion exhanger for targeted removal of Cs^+ from high level radioactive nuclear waste solutions. CST is resistant to high radiation fields and highly alkaline/acidic solutions which make it an ideal sequestration canidate. The mechanisms and dynamics of the crystallographic structural changes involved are the fundamental properties of selectivity in this material, and have not been studied previously.

This study investigates the molecular processes of ion exchange in real time using neutron and X-ray diffraction as well molecular dynamics (MD) simulations. These techniques in unison have provided the most complete description of the Cs^+ exchange process in hydrogen form of CST (H-CST).

In the H-CST structure, the elliptical channels cannot accommodate Cs^+ due to unacceptable short Cs-O bond distances. From time-resolved X-ray diffraction studies, the elliptical channels in H-CST transform to circular geometry after ≈8 wt.% Cs^+ exchange. Although structural transformations were observed and thte symmetry changed from space group **P**4_2/*mbc* to **P**4_2/*mcm*, the mechanisms were still unknown. Identifing all atom types and postions in the CST structure will ultimately explain the mechanisms of selectivity for Cs^+ in H-CST.

Time-resolved and static neutron diffraction studies added the proton positions on the water moleuces and hydroxyl units to the model derived from X-ray scattering. The results show that as Cs^+ diffuses through the structure, water molecules must change orientations and positions to hydrate Cs^+ and maintain the hydrogen bond network. The new configuration of the proton on the water sites are closer to the framework and force close proton-proton repulsion with the framework hydroxyl. This repulsison bends the hydroxyl and drives the transformation of the CST structure.

Hydroxyl bending and water dynamics have been confirmed using MD simulations. The short time scales of MD simulations is ideal to study these fast molecular motions and emphsizes the important role hydrogen has in CST toward Cs^+ selectivity.