

Computational investigation of the formation of hyperstoichiometric uranium dioxide
(UO_{2+x})

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F.N. Skomurski¹, R.C. Ewing¹, and U. Becker¹

¹University of Michigan, Department of Geological Sciences, 1100 N. University Ave.
Ann Arbor, MI 48109, USA
fskomurs@umich.edu

The stability of spent nuclear fuel as a waste form depends upon the oxidation behavior of uranium dioxide (UO_2) under repository conditions. Because U^{6+} phases are more soluble than U^{4+} phases, understanding the formation of higher-oxidized UO_2 phases is important. While a variety of diffraction and spectroscopic studies have been used to investigate the oxidation behavior of UO_2 to U_4O_9 , questions still remain as to the effect of interstitial oxygen on the oxidation state of uranium in hyperstoichiometric UO_2 . In this study, computational techniques were used to investigate questions such as: Is the formation of U^{5+} or U^{6+} more energetically favorable upon the oxidation of UO_2 ? And, how do calculated activation energies for the diffusion of interstitial oxygen in UO_2 compare with experimental values?

A density functional theory (DFT) approach was used to investigate the structural location of interstitial oxygen, the energy associated with oxygen substitution into different interstitial sites, and the influence of interstitial oxygen on the redox chemistry of uranium dioxide. Two different quantum mechanical programs were used to perform these calculations, one based on planewaves (CASTEP) and another that uses atomic-like basis functions to describe the electronic structure of each atom (Dmol³). Preliminary results from planewave calculations suggest that the formation of one U^{6+} is favorable to

a more delocalized charge distribution resulting in the formation of two U^{5+} for every interstitial oxygen atom.

Experimental studies suggest that two symmetrically unique locations exist for the incorporation of interstitial oxygen in bulk UO_2 . Excess oxygen is thought to be incorporated along the perpendicular bisectors or the body diagonals of the unoccupied cubic sites created by lattice oxygen atoms in the UO_2 structure. Using a single unit cell starting model, quantum mechanical calculations allow us to compare the relative energies associated with placing oxygen on these incorporation sites. Activation energies for the diffusion of oxygen from one such local energy minimum site to another are also evaluated. Calculations are expanded to larger defect cluster formations within the computational limits of DFT methods.