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Stability of uranium (VI) peroxide hydrates under ionizing radiation

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ABSTRACT

The uranyl peroxide, studtite ($UO_4 \cdot 4H_2O$, *C*2/*c*, $Z = 4$), is expected to form as a consequence of alpha radiolysis of water in contact with spent nuclear fuel (SNF) in a geologic repository. Investigation of its stability is, therefore, of critical importance because secondary U(VI) phases may incorporate trace amounts of radionuclides and thus retard their mobility away from a repository site. To examine the effect of ionizing radiation on uranyl peroxides, electron-beam irradiation experiments have been conducted on two synthetic uranyl peroxides: studtite and metastudtite ($UO_4 \cdot 2H_2O$, *Immm*, $Z = 2$). All experiments were done using a transmission electron microscope (TEM) with an acceleration voltage of 200 kV at room temperature. The fluence required to completely amorphize studtite was 0.51–1.54 $\times 10^{17}$ e/cm^2, which is equivalent to an absorbed dose of 0.73–1.43 $\times 10^7$ Gy. Metastudtite becomes amorphous at a higher absorbed dose (1.31×10^7 Gy) than studtite, most likely because it contains fewer water molecules in its structure. These uranyl peroxides partially amorphize at doses that are one-tenth of the dose required for complete amorphization. With continued irradiation, uraninite nanocrystals form that are a few nanometers in diameter, at 4–20 $\times 10^{10}$ Gy. In a geologic repository, for spent nuclear fuel, the estimated absorbed doses due to ionizing radiation may be as high as 10^8–10^{11} Gy after 10^6 years. This is well in excess of doses in the laboratory experiments that caused the uranyl peroxides to become amorphous and decompose.

Keywords: Ionizing radiation, TEM, uranyl peroxide, amorphization