Alteration of dehydrated schoepite and soddyite to studtite, [(UO$_2$)(O$_2$)(H$_2$O)$_2$](H$_2$O)$_2$

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ABSTRACT

The oxidation of used nuclear fuel in a geologic repository has important implications for the mobility of radionuclides and fission products in the environment. Hexavalent uranium (uranyl) minerals, including oxyhydroxides and silicates, form as alteration phases on the surface of fuel pellets in laboratory simulations. However, alpha-radiolysis of water forms hydrogen peroxide in solution, which may favor the alteration of these secondary phases to the uranyl peroxide mineral studtite. This study investigates the alteration of dehydrated schoepite, UO$_2$(H$_2$O)$_2$, and soddyite, [(UO$_2$)$_2$(SiO$_3$)](H$_2$O)$_2$, in the presence of aqueous solutions containing hydrogen peroxide. Crystalline samples were reacted with various concentrations of hydrogen peroxide and the resulting material was analyzed by powder X-ray diffraction. Both dehydrated schoepite and soddyite readily convert to studtite in the presence of hydrogen peroxide following the reaction stoichiometry. These results indicate that the possible impact of peroxide buildup on the stability of alteration phases in a repository setting should not be overlooked.

**Keywords:** Soddyite, studtite, schoepite, nuclear waste, geologic repository

INTRODUCTION

Studtite, [(UO$_2$)(O$_2$)(H$_2$O)$_2$](H$_2$O)$_2$, and metastudtite, (UO$_2$)(O$_2$)(H$_2$O)$_2$, are the only known peroxide minerals (Walenta 1974). The peroxide contained in studtite is likely formed due to the alpha-radiolysis of water, and the buildup of peroxide in thin films of water on uranium minerals can reach levels required to form studtite (Kubatko et al. 2003). Despite the relatively restricted conditions that appear to be necessary for studtite formation, it has been reported to occur in more than a dozen localities. Peroxide in studtite was confirmed when Burns and Hughes (2003) reported the structure that contains chains of uranyl peroxide polyhedra.

The structure of studtite is particularly intriguing because it is the first inorganic compound found to contain linked uranyl peroxide polyhedra. Each uranyl hexagonal bipyramid in the structure contains two peroxide groups that form equatorial edges of the bipyramid, and adjacent bipyramids form a chain by sharing peroxide edges. Following our report of these new linkages of polyhedra in studtite (Burns and Hughes 2003), we have created a family of nano-structured uranyl peroxide clusters with similar linkages between uranyl polyhedra (Burns et al. 2005; Forbes et al. 2008; Sigmon et al. 2009).

Our interest in studtite stems not only from its unusual composition, structure, and mineralogical origins, but also from its potentially important role in the interactions between nuclear waste and the environment. Studtite has been found as an alteration product of used fuel in cooling basins at the Hanford, Washington site (Abrefah et al. 1998), and on Chernobyl “lava” that formed during the nuclear accident that occurred in 1986 (Burakov et al. 1997). Room-temperature studies of used fuel alteration in de-ionized water showed that studtite forms over the course of two years, and that it replaces earlier formed uranyl oxide hydrate minerals such as schoepite or metaschoepite (McNamara et al. 2002; Hanson et al. 2005). Other studies have emphasized the importance of the formation of studtite where UO$_2$ is altered in the presence of peroxide or a radiation field that creates peroxide by radiolysis (e.g., Corbel et al. 2006; Clarens et al. 2005, 2004; Amme 2002). Incorporation of Np into studtite has also been examined (Douglas et al. 2005).

The studies mentioned above suggest that studtite may be important in a geologic repository for nuclear waste. As a repository ages and waste canisters are breached, used fuel, which is mostly UO$_2$, may be exposed to a moist, oxidizing environment. Studies of natural analogues (Finn and Ewing 1992; Peary et al. 1994), unirradiated UO$_2$ (Wronkiewicz et al. 1992, 1996), and used fuel (Finn et al. 1996; Finn et al. 1999) all indicate that UO$_2$ is unstable in such an environment, that alteration rates may be appreciable, and that the main products of alteration are uranyl minerals such as schoepite, dehydrated schoepite, uranophane, boltwoodite, soddyite, and compeigneacite. Studies of unirradiated UO$_2$ (Wronkiewicz et al. 1992, 1996) and used fuel (Finn et al. 1999) were conducted at 90 °C, which likely would preclude formation of studtite because of the decrease in peroxide stability that occurs with increasing temperature.

Used nuclear fuel is much more radioactive than uranium ore, and will remain so for a very long time. As a consequence, peroxide may begin to accumulate in a geological repository where water contacts used fuel and the temperature has cooled sufficiently. Studtite could then become an important mineral in the paragenetic sequence that forms where waste is altered in a geological repository.

We hypothesize that the buildup of peroxide in water that occurs as films on used fuel or its alteration products in a repository could not only cause the formation of studtite, but also result in the alteration of previously formed uranyl minerals. The focus of