The crystal chemistry of uranyl peroxide nanospheres

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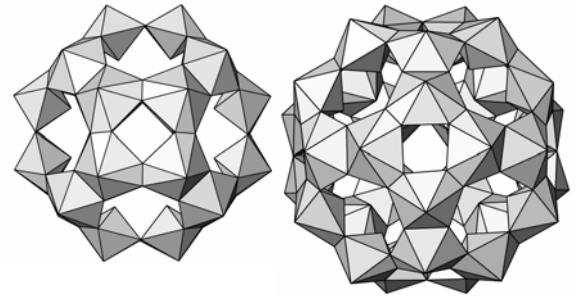
Basis for Research

Studtite is the only inorganic compound known to contain polymerized uranyl peroxide polyhedra. Peroxide defines an equatorial edge of the polyhedra, resulting in a shortening of equatorial edges to ~1.4 Å. The potential for novel uranyl peroxide structure types under alkaline conditions, as well as the significance of such phases in nuclear waste management, provides the impetus for study of this system.

Figure 1: 24-polyhedral and 32-polyhedral peroxide nanospheres.



Results and Discussion

Synthesis experiments using alkaline solutions provided several uranyl peroxide compounds with unprecedented structures. Polymerization of distorted uranyl peroxide polyhedra apparently precludes formation of the many sheet topologies typical of uranyl compounds. Details of the most remarkable of these new structures will be presented. Three uranyl peroxide nanospheres, based on the polymerization of 24, 28 and 32 uranyl polyhedra, have been characterized. Small angle X-ray scattering experiments have determined the presence of these clusters in solution, and analogous nanospheres have been formed from Np^{6+}. Actinyl nanospheres may impact the mobility of higher-valence actinides in the environment under alkaline conditions associated with nuclear waste storage and disposal.

The epsilon phase in the UO_2 of the Oklo natural reactors

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In spent nuclear fuel (SNF), the metal epsilon phase consists of an alloy of Mo-Ru-Pd-Tc-Rh, occurring at a micron to sub-micron scale. ^{99}Tc has a long half life (2.13 x 10^5 years) and can be an important contributor to dose in safety assessments of nuclear waste repositories. Under oxidizing conditions, TcO_4^- is the predominant species of Tc. In this form, Tc is highly soluble and weakly adsorbed onto mineral surfaces. Because the Oklo reactors are 2.0 billion years old, a majority of the ^{99}Tc has decayed to ^{99}Ru. Thus, this study is focused on Ru and the other constituents of the epsilon phase in order to investigate the occurrence and the fate of epsilon phase elements during the corrosion of this natural SNF.

Samples from reactor zone (RZ)-10 (836, 819, 687); from RZ-13 (864, 910); from Okélobondo (943) were studied. High resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) were completed on thin foil specimens of uraninite from each reactor zone.

A Bi-Pd particle (40-60 nm), froodite, $PdBi_2$, occurs with trace amounts of As, Fe, and Te surrounded by an amorphous Pb-rich area (#864). A Ru-As particle (~300nm) occurs surrounded by Pb-rich inclusion (400-500nm) in uraninite (#819). Based on EDX analysis the composition is: As, 59.9: Co, 2.5: Ni, 5.2; Ru, 18.6; Th, 8.4; Pd, 3.1; Sb, 2.4 in atomic%. The Ru-As phase is an aggregate of 100-200 nm-sized ruthenarsenite, (Ru,Ni)As, particles. Another Ru-particle (600-700 nm) shows that Pb occurs at the core, and the rim portion consists of Ni, Co, and As without Ru (#819). Ru-particles, ruthenarsenite, occur with Ni between the core and the rim. A Mo-particle (<50 nm) is embedded in a galena (#836). A Ru-particle occurs in a Pb-inclusion in the presence of two phases within the particle: Ru; As-rich part and Pd; Rh-rich area. The Pd-Rh-rich area occupies the center of the particle, and Ru-rich region occurs at the edge of the particle. Semi-quantitative analysis gives: 16.0 As, 5.8 Ru, 26.7 Rh, 39.2 Pd, 2.8 Sn, and 9.4 Sb in atomic%. The phase is either palladodymite or rhodarsenide, both of which are $(Pd, Rh)_2As$.

All of the Ru-phases are associated with polycrystalline galena. There is a wide variation in the composition of the Ru-phase. The Ru-particles are, in most cases, ruthenarsenite, and do not contain detectable amounts of Mo, although the Mo-concentration for the epsilon phase in SNF is reported to be as high as 40 atomic %.