

A new uranyl oxide hydrate sheet in vandendriesscheite: Implications for mineral paragenesis and the corrosion of spent nuclear fuel

PETER C. BURNS*

Department of Geology, University of Illinois at Urbana-Champaign, 245 Natural History Building,
1301 West Green Street, Urbana, Illinois 61801, U.S.A.

ABSTRACT

The structure of vandendriesscheite, $Z = 8$, $\text{Pb}_{1.57}[(\text{UO}_2)_{10}\text{O}_6(\text{OH})_{11}](\text{H}_2\text{O})_{11}$, orthorhombic, $a = 14.1165(6)$, $b = 41.378(2)$, $c = 14.5347(6)$ Å, $V = 8490$ Å³, space group *Pbca*, has been solved by direct methods and refined by full-matrix least-squares techniques to an agreement factor (*R*) of 12.1% and a goodness-of-fit (*S*) of 1.28 using 4918 unique observed reflections ($|F_o| \geq 4\sigma F$) collected with MoK α X-radiation and a CCD (charge-coupled device) detector. The structure contains ten unique U⁶⁺ positions, each of which is part of a nearly linear (UO₂)²⁺ uranyl ion that is further coordinated by five equatorial (O²⁻, OH⁻) anions to form pentagonal bipyramidal polyhedra. There are two unique Pb positions; one is fully occupied, but site-scattering refinement gives an occupancy factor of 0.573(8) for the other. The Pb positions are coordinated by O atoms of the uranyl ions and by H₂O groups. There are 11 unique H₂O groups; five are bonded to Pb and the other six are held in the structure by hydrogen bonds only. The U polyhedra link by the sharing of equatorial edges to form sheets parallel to (001). The sheet of U polyhedra is not known from another structure and is the most complex yet observed in a uranyl oxide hydrate. The sheets are structurally intermediate to those in schoepite and becquerelite and are linked by bonds to the interlayer Pb cations and the H₂O groups. The extensive network of hydrogen bonds that link adjacent sheets is derived on the basis of crystal-chemical constraints.

The high mobility of U⁶⁺ in oxidizing fluids, as opposed to Pb²⁺, causes the alteration products of Precambrian uraninite deposits to become progressively enriched in Pb relative to U. In the case of lead uranyl oxide hydrate minerals, there is a continuous sequence of crystal structures that involves a systematic modification of the sheets of U polyhedra and that corresponds to increasing sheet charge and increasing Pb content. Thus, a clear relationship exists between the crystal structures of lead uranyl oxide hydrates and their paragenesis, and this is relevant to the disposal of spent nuclear fuel.