

Characterization of vandenbrandeite: A potential alteration product of spent nuclear fuel

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ABSTRACT

The use of copper canisters in the Swedish KBS-3 concept for spent nuclear fuel disposal could result in the formation of copper-bearing uranyl phases should a canister suffer from defects or if the containment were to fail before reducing conditions are established in the repository. Most uranyl species would be expected to display higher solubility than the original uranium(IV) dioxide fuel, leading to enhanced release, though this would depend on the phase and prevailing groundwater conditions. Secondary alteration products may also be poorly crystalline or even amorphous, making characterization difficult during the pre-closure period owing to the high radiation field close to the canister. Vandenbrandeite, [CuUO₂(OH)₄], is a rare mineral in nature but known to form by alteration of primary uraninite through interaction with oxidizing groundwater containing dissolved copper. Consequently, an attempt has been made to characterize two vandenbrandeite specimens of varying crystallinity by luminescence and multiple-laser Raman spectroscopy; techniques amenable to remote, robotic deployment and which have proved useful in discriminating other uranyl oxy-hydroxides, silicates, and phosphates. The first reported luminescence emission and excitation spectra for vandenbrandeite revealed near-negligible luminescence, with a slightly enhanced signal for the specimen displaying poorer crystallinity. This observation agrees well with density functional theory calculations. The simulated projected density of state and band structure show an unlikely transition from the U f-orbitals to Cu d-orbitals, or O states, would be required for luminescence to be detectable; this probably improves for poorly crystalline specimens as the spatial overlap between the orbitals increases. Furthermore, negligible differences in the number of peaks and peak positions were detected in the laser wavelength-dependent Raman spectra although again, variation in background noise and peak shape was observed based on the degree of crystallinity. Good agreement was obtained between experimental and simulated Raman spectra, particularly with the environmentally sensitive axial uranyl stretching modes, validating the crystal system derived in this study. The findings of this study suggest luminescence spectroscopy, when combined with Raman spectroscopy, may be able to both identify vandenbrandeite and distinguish between crystalline and amorphous forms based on their relative luminescence intensity.

Keywords: Raman spectroscopy, time-resolved laser fluorescence spectroscopy, density functional theory Raman simulation, projected density of states