Thermal Behavior of Polyhalite: A Mineral Relevant to Salt Repository

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Salt repository is an attractive option for permanent disposal of used nuclear fuel (UNF) and high-level waste (HLW), as salt has several advantageous attributes, including impermeability, self-sealing (plasticity) and good thermal conductivity, at repository conditions. However, small amounts of water occur in salt formations in the form of fluid inclusions contained in salt grains or as water molecules and/or hydroxyl units in hydrous minerals coexisting with salt. Since radionuclides in UNF/HLW undergo decays to daughter elements with various half-lives and many of the decays generate high heat outputs, the surrounding salt and its associated water will be heated, causing water liberation and migration. These processes will have marked effects on salt behavior and thus on the overall performance of salt repository.

An important hydrous mineral coexisting with salt is polyhalite, $K_2MgCa_2(SO_4)_4{\cdot}2H_2O$. Like other hydrous phases, polyhalite dehydrates on heating, where the released water will interact with its neighboring salt. In this work, a polyhalite sample containing a small amount of halite was collected from the Salado formation at the WIPP site in Carlsbad, New Mexico. To characterize its thermal behavior, in-situ high-temperature synchrotron X-ray diffraction was conducted from room temperature to 1066 K with the sample powders sealed in a silica-glass capillary. At about 506 K, polyhalite started to decompose into anhydrite ($CaSO_4$), triple salt ($K_2SO_4{\cdot}MgSO_4{\cdot}CaSO_4$) and water vapor. XRD peaks of the minor halite disappeared, presumably due to its dissolution by water vapor. With further increasing temperature, the triple salt decomposed into two langbeinite-type phases along the $K_2SO_4{\cdot}2MgSO_4$–$K_2SO_4{\cdot}2CaSO_4$ join. Rietveld analyses of the synchrotron data allow determination of structural parameters of polyhalite and its decomposed phases as a function of temperature. From these results, the thermal expansion coefficients have been derived, and the mechanisms of polyhalite decomposition been discussed. In addition, to determine stability relations, standard enthalpies of formation of polyhalite from constituent oxides and elements were measured using high-temperature oxide-melt drop-solution calorimetry.