

Thermochemistry of Zr-containing Layered Double Hydroxides

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At an early stage of operation, repository systems for highly radioactive wastes are expected to feature elevated temperature conditions over a significant period of time due to the high decay heat of the waste. In the case of early canister failure, radionuclides then may come into contact with aquifers at elevated temperatures. Safety assessments therefore require an understanding of the retention properties of relevant mineral phases at these conditions.

Layered double hydroxides (LDH), consisting of positively charged octahedral brucite-type layers and interlayer anions, have been widely studied in the last decades because of their ability to control the mobility of various anions and cations in the environment. LDH may be relevant to the safety case of nuclear waste repositories due to their retention potential of anionic radionuclide species, for example of ¹²⁹I or ⁷⁹Se. Few studies were dedicated to Zr incorporation into Cl-bearing LDH, a relevant secondary phase due to the possible corrosion of zircaloy cladding and the presence of ⁹³Zr, a long-lived fission and activation product. In fact, the incorporation of tetravalent cations such as Zr^{IV} into the brucite sheets of LDH has been debated during the last years.

The focus of our study was to synthesize and characterize LDH with different Zr-content to evaluate their thermodynamic properties, especially their solubility as a function of temperature. By combining X-ray diffraction and scanning electron microscopy we show that Zr can be incorporated into the brucite sheets of MgAl-Zr-Cl-LDH up to an estimated limit of 5 mol %, which is lower than for Zr-CO₃-LDH. At higher synthesis temperatures (>300K), a segregated amorphous Zr-phase occurred besides the high-Zr LDH which can be explained by the decreasing solubility of hydrous Zr-oxides with temperature. A consistent thermochemical dataset for Zr-LDH has been derived experimentally by calorimetric methods and by theoretical considerations.