The role of anion (Cl^-, SO_4^{2-} and CO_3^{2-}) ratio and concentration on reformation of calcined hydrotalcite

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Layered double hydroxides (LDH) are widely investigated because of their unique structural properties, their simple, low cost and non-toxic synthesis and their high tunability. While LDH formation mechanisms in single anion solutions are fairly well understood, the structure and composition of LDH formed in complex solutions, with multiple anions at varyious ratios and concentrations is basically unknown. This knowledge is particularly important for tuning LDH properties, to optimize them for specific applications such as sorbents, exchangers, delivery shuttles as well as cleaning agents in groundwaters and soils.

In this study, hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) was synthesised, calcined and then reformed back to a layered structure (using the so-called "memory effect") in a suite of mixed anion solutions to quantify the affinities of chloride, sulphate and carbonate for intercalation. X-ray diffraction and infrared spectroscopy show that if there is any dissolved carbonate (as low as 1 mM), it is always incorporated in the LDH interlayer. Chloride can compete with carbonate for intercalation (i.e., they have similar size and interlayer coordination), while sulphate cannot. Instead two separate LDH phases form. In solutions with equal chloride and sulphate concentrations, LDH affinity for sulphate is higher than for chloride, even if chloride is in molar excess. In solutions with unequal chloride and sulphate concentrations, intercalation affinity depends on anion concentration. At concentrations <100 mM, sulphate always outcompetes chloride, even if chloride is in molar excess. At concentrations ≥100 mM, the most abundant anion has the highest affinity. The results bring us closer to a clear description of the structure, composition and behavior of Mg, Al LDH that form in multi ion solutions.