A New Precipitation Pathway for Calcium Sulfate Dihydrate (Gypsum) via Amorphous and Hemihydrate Intermediates

YUNWEI WANG[1], YIYEOUN KIM[1], HUGO CHRISTENSON[2] AND FIONA MELDRUM[1]*

[1]Fiona Meldrum, Yunwei Wang, Yiyeoun Kim, University of Leeds, Email: F.Meldrum@leeds.ac.uk
[2]Hugo K. Christenson, University of Leeds, Email: H.K.Christenson@leeds.ac.uk

This work investigates the precipitation of calcium sulfate in aqueous solution at room temperature. The focus is on the stability and transformation of hemihydrate and gypsum (calcium sulfate dihydrate) and a new precipitation mechanism is revealed. It is widely known that gypsum is the most stable phase at low temperatures, and hemihydrate is metastable at all temperatures (MacDonald 1953; Freyer and Voigt 2003). The reported typical transition temperature for gypsum/hemihydrate is approximately 97 °C. (Ostroff 1964) To investigate this further, the early stages of calcium sulfate precipitation in bulk solution were studied by isolating precipitates and characterising them with a range of techniques including TEM, XRD and Raman microscopy. Interestingly, the existence of an amorphous calcium sulfate (ACS) was demonstrated, where this rapidly transforms to calcium sulfate hemihydrate before converting to the thermodynamically-stable phase calcium sulfate dihydrate (gypsum). This work therefore also provides the first report of the formation of calcium sulfate hemihydrate in solution at room temperature and the existence of amorphous calcium sulfate.

Interestingly, additives are also active in controlling the morphologies of the hemihydrate crystals, which can play a key role in defining properties such as porosity and mechanical strength. The results confirm the stepwise-precipitation of gypsum via amorphous and hemihydrate intermediates and suggest an alternative to the energy-intensive calcination processes which are currently widely used to prepare hemihydrate. A crossed-cylinder apparatus is also used to study this process at room temperature, focusing on the stability and transformation of amorphous calcium sulfate and hemihydrate at different surface separations.