INDUSTRIAL PILOT PROJECT

Synchrotron SAXS for investigating structural behaviour in montmorillonite clays for improved nuclear waste disposal

THE INDUSTRIAL CHALLENGE

Bentonite clay is proposed as barrier material for nuclear waste disposal concepts in copper canisters due to its sealing properties and ability to attain a high osmotic pressure, which in turn suppresses sulphate-reducing bacteria and a corrosive environment. Clay Technology Lund AB has for 30+ years conducted research for nuclear waste management organisations and provided accurate measurements and modelling of bentonite and its main component montmorillonite (Mt). Mt is a layered mineral with negatively charged 10 Å thick lamellae, charge-compensated by cations. Such structure has high affinity for water uptake between the layers, resulting in the build-up of an osmotic pressure. The relationship between pressure and structure of sodium-based Mt (Na-Mt) is well known, but in calcium (Ca)-rich groundwater an ion exchange will occur, and the system evolve towards Ca-Mt, which is poorly understood and less homogenous. Therefore, increased knowledge and ability to model the system is important.

WHY USING A LARGE-SCALE FACILITY

Structural analyses of Mt can be obtained with X-ray diffraction, but only small angle X-ray scattering (SAXS) experiments at a synchrotron would allow for the q-range $5 \cdot 10^{-3} \leq q \leq 1$ Å^{-1} necessary to detect structures of sufficient size, and to secure robust information on how the structure vary upon exposure to various aqueous solutions and amount of water.

HOW THE WORK WAS DONE

The CoSAXS beamline at MAX IV offers a suitable setup to perform SAXS measurement in the required q-range. A sandwich cell with mica windows, with room for a ~2 mm thick Mt sample, was used (Fig.1). To relate structure to pressure, eight samples with different cations (Na, Ca, and also K as reference) with Mt volume fractions of $0.28<\phi<0,54$ were prepared for osmotic pressure tests and subsequent SAXS measurements. In addition, 16 reference samples of Na- and Ca-Mt with ϕ between 0.15 and 0.54 were prepared by mixing dried Mt with deionised water.

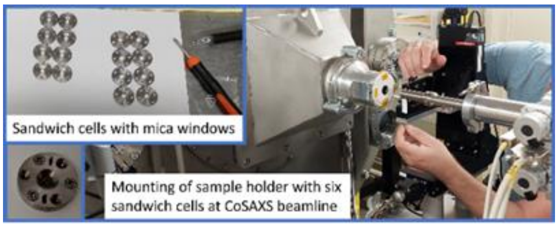

Figure 1. Sandwich cells (left) and the experiment setup at CoSAXS beamline (right).

THE RESULTS AND EXPECTED IMPACT

For $\phi > 0.5$, the SAXS data showed that Na- and Ca-Mt have very similar homogeneous lamellar structures and their osmotic pressures were comparable. At lower ϕ, e.g., 0.28 (Fig. 2) the three systems behave differently. The more homogeneous a system is, the higher the osmotic pressure. Na-Mt remains homogeneous with increasing amount of water in the inter-lamellar space. In K-Mt the water appears distributed in two interlamellar regions of different size. In Ca-Mt the maximum layer separation is 9.5 Å, with no indication of a second separation as in K-Mt. This suggests that for Ca-Mt, water exists both as interlamellar and non-lamellar regions. Synchrotron SAXS has provided a unique opportunity to show unequivocally the structural differences between Na-, K-, and Ca- Mt, and was able to demonstrate that Ca-Mt at low ϕ definitely has both lamellar and non-lamellar regions.

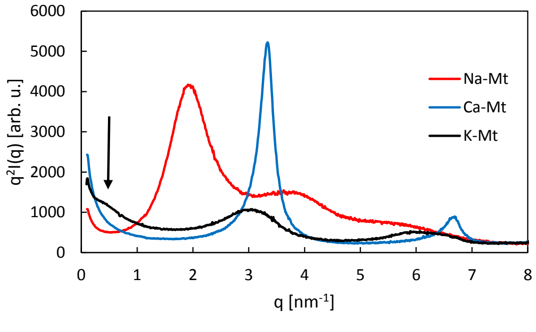

Figure 2. Kratky plot illustrating the differences between Na-, Ca-, and K-Mt at Mt volume fraction ϕ= 0.28. The main peaks correspond to interlamellar distances of 23.1, 9.5, and 11.4 Å, respectively. The arrow indicates an additional separation of K-Mt layers by 119 Å. The measured osmotic pressures of these samples were 600, 40, and 120 kPa, respectively.

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