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Non-diffusive Topochemical Transformation of Calcium Sulphate Hemihydrate into the Dihydrate

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The non-diffusive topochemical transformation of calcium sulphate hemihydrate into the dihydrate in an aqueous medium is described, together with the sensitivity of the transformation to the concentration of the medium and to the texture of the solid phase.

The transformation of $CaSO_4 \cdot 0.5H_2O$ (HH) into $CaSO_4 \cdot 2H_2O$ (DH) is a widely used industrial process and has been carefully investigated.[1–3] The classic work of Ridge[4,5] showed that the transformation took place in water by dissolution of the hemihydrate with simultaneous crystallization of the dihydrate (recrystallization mechanism). Since then an opinion has gradually been established that the recrystallization mechanism was the only one possible. However, the facts presented herein show that the transformation of HH into DH can also proceed *via* a rapid topochemical reaction. This conclusion is unusual and may have important technological applications.

Investigations were made into various HH samples (single crystals, polycrystal concretions, polydispersed phases) in 1.5 mol dm^{-3} H_3PO_4 solution with varying concentrations of HH at 40–80 °C.

(*i*) The needle-like HH crystals in the unsaturated (by HH) solution are transformed directly into DH with no changes in shape. As each single crystal dissolves pits are formed in its surface. The DH crystals nucleate in the pits and grow both normally to the surface into the solution (slowly) and into the bulk of the crystal (rapidly). The bulk growth rate is so large that the first crystal nucleated on one of the grains of the single crystal expands throughout its whole volume. For instance, a single crystal 0.1 cm long and 0.01 cm wide in solution at 60 °C dissolves without transformation for some minutes (induction period) and is then fully converted into DH within 1 s. The induction period, τ, increases with increasing sulphate concentration: $\tau \rightarrow \infty$ as $C \rightarrow C_{HH}$, where C_{HH} is the solubility of HH.

The HH crystals nucleate mainly on the (001) faces of the single crystal. Their growth rate in the solution direction increases with increasing C concentration but does not exceed 5×10^{-6} m s^{-1}. The growth rate W_s in the crystal bulk does not depend on C and exceeds 10^{-3} m s^{-1}. These facts were estimated by scanning electron microscopy (HH crystal nucleation) and by optical microscopy (crystal growth). Identification of the initial and final crystals was accomplished by X-ray structural analysis.

(*ii*) The transformation of HH concretions in solution takes place analogously with that in the single crystal, but with a shorter induction period. Some time after the introduction of concretions into the solution, a DH zone was formed on its surface, which spreads to the centre of each concretion. Fig. 1 shows a section through a prismatic concretion prepared by chemical crystallization of HH after a long immersion in the mother liquor. The concretion is connected with the substrate and introduced into the solution flow (6 mm s^{-1}). Experiments with many concretions (sizes from 50 to 150 μm) showed that

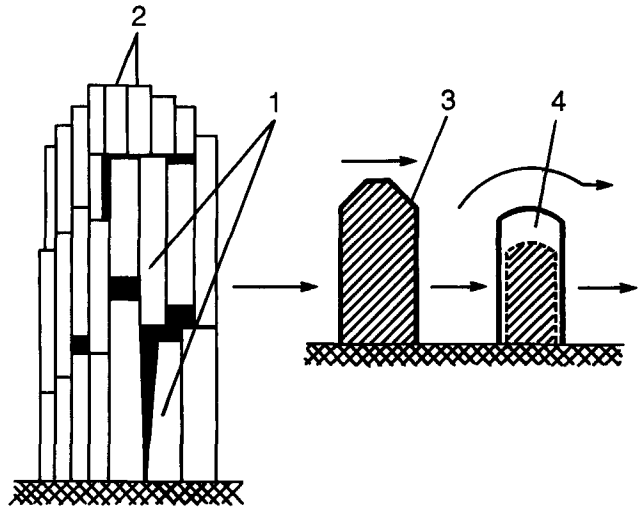

Fig. 1 Transformation of a concretion in the solution flow; 1: HH crystals, 2: (001) faces, 3: initial concretion, 4: DH zone

the induction period, τ, at $C/C_{HH} = 0.5$–0.95 could differ ten-fold from the mean value [eqn. (1)].

$$\tau = 21.0\,(1 - C/C_{HH})^{-1}\ \text{s} \qquad (1)$$

The zone movement takes place with mean rate W [eqn. (2)],

$$W = Bl\,(1 - C/C_{HH}) \qquad (2)$$

where $B = (8.6 \pm 0.4) \pm 10^{-2}\ s^{-1}$ and l is the mean size of crystals in the concretions. These facts were estimated from microscopic observation of 300 concretions in the flow chamber and by statistical treatment of the morphological data. The zone structure was studied by electron microscopy and X-ray methods.

(*iii*) If the number of concretions, described above, is introduced into a 1.5 mol dm^{-3} H_3PO_4 solution (solid:liquid = 1:10) and this suspension is stirred the concentration of calcium sulphate in the solution changes as shown in Fig. 2. When the concentration is rising or is constant at C_{HH}, the DH phase is absent in the concretions, but the DH crystals nucleate in the solution volume and grow owing to the dissolution of HH *i.e.*, producing an excess by the recrystallization mechanism. As the concentration of the solution decreases to $C = 0.9C_{HH}$ DH zones appear in some concretions. The frequency of appearance of such concretions rises as the concentration of the solution decreases. This was established by

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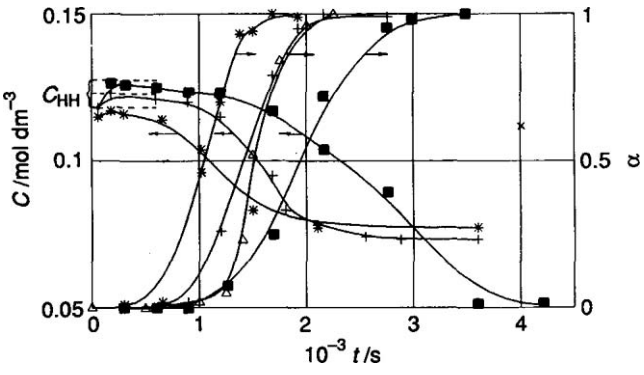

Fig. 2 Time dependence of the solution concentration (C) and molar fraction (α) of the DH solid phase. Solution volume 100 cm^3, stirrer rate 400 rpm, Reynolds number 170. ■: 40, +: 60, *: 80 °C; △: calculated for 60 °C.

comparison of chemical composition data for the solution with phase composition and morphological data for the solid phase.

The facts presented show that the transformation of HH into DH depends on the sensitivity of the phenomenon to the texture of the solid phase. Both the phase consisting of single crystals (untextured) and the phase consisting of concretions (textured) are transformed with all the indications of a topochemical process but at different rates. The transformation front for the single crystal phase is formed near the surface and expands at a rate $W_s > 10^{-3}$ m s^{-1}, significantly exceeding the diffusion rate of the reagents through the single crystal. The diffusion coefficient for water through a single crystal of DH at 60 °C is about 4×10^{-13} m^2 s^{-1},[6] therefore the diffusion-limited transformation of a crystal 0.01 cm long would continue for about 3×10^4 s. In fact it continues for 1 s. Perhaps the high rate of movement of the front is supported by cracks in the single crystal arising from the structural discrepancy between the DH and HH lattices. Water could be supplied to the front *via* these cracks. The front in the textured phase appears near the surface of each concretion and spreads over its volume (Fig. 1) at a rate W [eqn. (2)] which is 10^4 times lower than the rate for the single crystal. In the concretion the front moves rapidly through the volume of each crystal, stopping on the borders between them. These stops [eqn. (1)] are so long that $W \ll W_M$. The crystal size is greater in the concretions, therefore there are fewer borders and W is higher [eqn. (2)]. It follows from eqns. (1) and (2) that if the transformation takes place in a medium where $C \sim C_{HH}$ ($t \to \infty$, $W \to 0$) the recrystallization mechanism will dominate. If the concentration of the medium is close to the solubility of DH then the topochemical mechanism will dominate. In a closed system where the concentration of the medium is changed during the transformation (Fig. 2) the recrystallization mechanism dominates at the start and the topochemical process then takes over. The results of a calculation of the degree of transformation α, assuming that the topochemical process is the only one, are presented in Fig. 2. The difference between the calculated and experimental curves $\alpha(t)$ represents the contribution of the recrystallization process to the transformation.

The topochemical mechanism has not been observed previously[1–5] because of the concentration and textural sensitivity of the transformation.

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