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The setting of gypsum plaster

Part I *The hydration of calcium sulphate hemihydrate*

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The α- and β-forms of calcium sulphate hemihydrate, $CaSO_4 \cdot 1/2H_2O$, were characterized using thermal, X-ray diffraction, optical and electron microscopy techniques. The differences between the two forms arose from their mode of production, resulting in different crystal size and habit, and not from different crystal structures. The hydration of $CaSO_4 \cdot 1/2H_2O$ to $CaSO_4 \cdot 2H_2O$ was investigated using calorimetry, phase analysis and the changes in electrical resistance of the plaster slurries. The reaction occurred in three steps: dissolution, nucleation and precipitation, and finally completion due to depletion of reactants. The differences in reactivity of the α- and β-forms with water again appeared to be due to their different physical states.

1. Introduction

Calcium sulphate hemihydrate, $CaSO_4 \cdot 1/2H_2O$, is the major constituent of gypsum plasters which are used extensively in the building, ceramics and medical industries.

Hemihydrate has traditionally been given an "α" or "β" prefix, where the two modifications are defined according to the mode of preparation [1]; i.e. the α-form being prepared by wet methods (e.g. autoclaving) and the β-form by dry methods (e.g. calcining) from calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$ (gypsum) [2, 3]. Apart from the differences in the mode of preparation, the two forms differ in their reactivity with water and in the strength of the hydration products.

On mixing hemihydrate with water, the following reaction occurs

$$CaSO_4 \cdot 1/2H_2O + 3/2\ H_2O \xrightarrow{-\Delta H} CaSO_4 \cdot 2H_2O \qquad (1)$$

The hemihydrate is slightly soluble in water (0.65 g/100 ml, water at 20 °C) [3] and saturation is quickly reached. The solubility of the dihydrate (0.24 g/100 ml water at 20 °C) [3] is only a fraction of that of the hemihydrates, and needle-like dihydrate crystals nucleate and precipitate, growing rapidly to form a rigid interlocking crystalline mass [4].

Previous workers [5, 6] agree that for the same initial water/plaster (W/P) ratio the α-form produces a "set-plaster" which is stronger than that produced by the β-form, but disagree on which form sets more rapidly.

The two forms have been examined by various analytical techniques but the differences remain unclear and it is doubtful whether they constitute two distinct crystalline phases.

X-ray diffraction (XRD) studies [1] show no observable differences in peak position but slight changes in relative intensities were removed when the α-form was finely ground. The infrared spectra of the two forms have been studied by several workers [1, 7, 8] and showed no significant differences. This indicates that α- and β-hemihydrates have the same crystal structure and this has been studied in detail by Flörke [9].

Measurement of the ^1H nuclear magnetic resonance (NMR) signal from the two forms [7, 10] showed that water is present in two conditions, one of which is much more strongly bonded than the other. In each case most of the water is tightly bound and the only difference between the two forms is that adsorbed water in the β-form is more mobile than in the α-form.

Differential thermal analysis (DTA) has generally been utilized for differentiating between α- and β-forms on the basis of an exothermic peak corresponding to the soluble (hexagonal) to insoluble (orthorhombic) anhydrite transformation. Several workers [2, 11] have suggested that the differences in the DTA traces were due to the mode of preparation, the α-form having larger and more perfect crystals.

Goto *et al.* [12], on the basis of a kinetic and mechanistic study, proposed that the variation in DTA traces was the result of the operation of more than one mechanism for the phase change; differences in physical condition favouring one mechanism rather than the other. Support for two mechanisms was obtained from the DTA and XRD studies by Miyazaki and Matsuoaka [13].

Optical and electron microscopy studies [1, 7] have shown that α-hemihydrate consists mainly of single crystals and that the β-form particles are composed of a multiplicity of small crystals.

The hydration of hemihydrate, shown earlier, has

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been a source of disagreement between a "through-solution" or "gel-type" mechanisms. The work of Birss and Thorvaldson [14] and that of Ludwig and Singh [15] seemed to have settled the issue in favour of a "through-solution" mechanism. Ludwig and Singh's hydration study, using changes in electrical conductivity and temperature rise to follow the reaction, showed the reaction to be a three-stage process:

(i) an induction period during which nuclei form;
(ii) rapid growth of the dihydrate crystals;
(iii) completion due to depletion of reactants.

The kinetics of the reaction have been explained on the basis of seeded recrystallization [3]. However, the kinetic theories and rate equations are of limited value, in that they do not fit all the data and only apply to specific cases [16].

The initial aim of this work was to characterize fully the α- and β-hemihydrate reagents. This was followed by an investigation of the hydration process by calorimetry, phase analysis (XRD, thermal analysis) and changes in the electrical resistance of the reaction slurry.

2. Characterization of materials

The hemihydrate reagents were obtained from British Gypsum as commercial products and were characterized by XRD, thermal analysis, particle size, chemical analysis and optical/electron microscopy.

2.1. XRD and chemical analysis

The crystalline phases present in the reagents were determined using a Philips diffractometer and CuK_α radiation. The two hemihydrates showed no noticeable differences in peak positions but slight differences in intensities. On fine grinding of the α-form, it produced a pattern almost identical to that of the β. This indicated the same crystal structure but differences in the particle/crystallite size.

Quantitative chemical analysis was performed using a Jeol JSM-35 SEM fitted with an electron probe for micro-analysis (EPMA) facility. The energy dispersive analysis of X-rays (EDAX) system was used for the major elements calcium and sulphur, whilst the wavelength dispersion of X-rays (WDX) crystal spectrometer analysed for the trace elements sodium, potassium, magnesium and silicon.

The EDAX analysis showed that within experimental error the plasters had the expected stoichiometric molar ratio of 1:1 for Ca:S. The trace elements were shown by WDX to be present in quantities of less than 0.2 wt % each.

2.2. Thermal analysis

DTA traces of the two plasters were obtained using a specially designed thermal analyser [11] with crushed quartz as the inert thermal reference, static air as the furnace environment and a controlled heating rate of approximately 13 °C min^{-1} over the range 0–600 °C. The DTA traces are shown in Fig. 1 with the α-form having the exothermic soluble/insoluble anhydrite transformation at 225 °C. On grinding the α-form, the exotherm moved to 355 °C, the temperature at which the β-form shows this transition. This supports XRD finding that α/β differences are largely due to crystallite size and not to differences in the crystallographic structure.

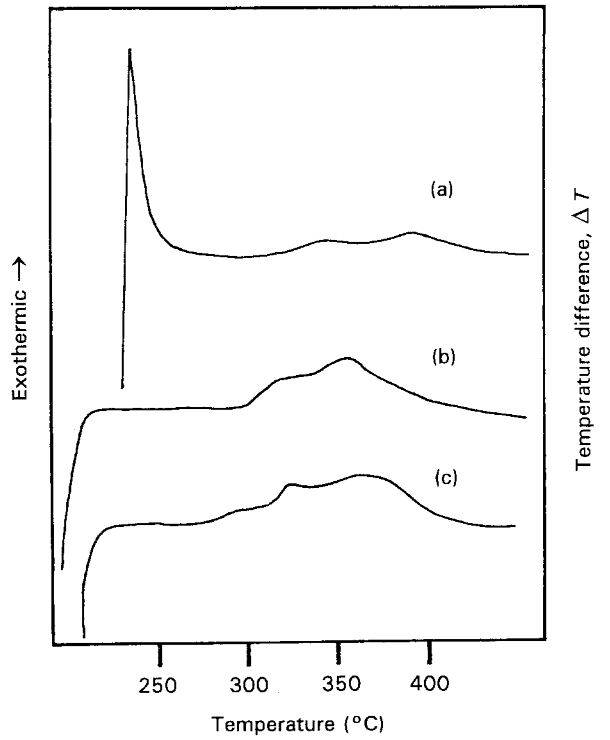

Figure 1 DTA traces from British Gypsum plasters: (a) α-hemihydrate; (b) β-hemihydrate; (c) ground α-hemihydrate.

Combined DTA/thermal gravimetric analysis (TGA) measurements were also made using a Stanton-Redcroft Series 780 simultaneous thermal analyser with the same conditions as above, except for a heating rate of 10 °C min^{-1} and alumina as the reference. Measurements obtained from the two hemihydrates are shown in Table I. The weak endotherm exhibited by the α-form is probably due to the presence of loosely bound water, while the strong endotherm shown by both is due to the loss of water from the

TABLE I TGA/DTA and the calculated percentage of $CaSO_4$ phases in British Gypsum hemihydrates

Plaster	TGA/DTA measurements (weight loss)[a]	Hemihydrate ($CaSO_4 \cdot 1/2\ H_2O$) (wt %)	Soluble anhydrite (δ $CaSO_4$) (wt %)
British Gypsum α	weak endotherm; 35 °C (0.1%) strong endotherm; 180 °C (6.05%)	97.6	2.4
British Gypsum β	strong endotherm; 180 °C (6.05%)	97.6	2.4

[a] The theoretical weight loss of water from pure hemihydrate is 6.21%; other commercial plasters showed anhydrite contents in the range 2–13 wt %.

hemihydrate crystal lattice. When the weight loss is less than the theoretical value of 6.21%, this is due to the presence of soluble anhydrite; the percentage of the $CaSO_4$ phase present has been calculated and is shown in Table I.

2.3. Particle-size analysis

A Malvern 3600 particle-size analyser was used to determine both the particle size and size distribution of the plaster powders, using a dilute suspension of the hemihydrate in ethanol.

The β-form had a mean particle size of 8.6 μm whilst that of the α-form was 11.4 μm.

2.4. Optical and scanning electron microscopic studies

Samples were prepared for transmission optical microscopy by dispensing a small powder sample. The α-form consisted of larger particles than the β-form and showed a tendency to rhombohedral habit. The α-form was found to contain agglomerates and single crystals showing idiomorphic features and uniform straight extinction, while the β-particles showed fissures and pores with no discernible crystallographic facets. The β-form showed a range of orientations under polarized light and extinction was not complete; this indicated that the particles were composed of a multiplicity of small crystallites of varying orientation.

Scanning electron micrographs of the α- and β-particles (Figs 2 and 3) gave complementary evidence supporting the optical observations.

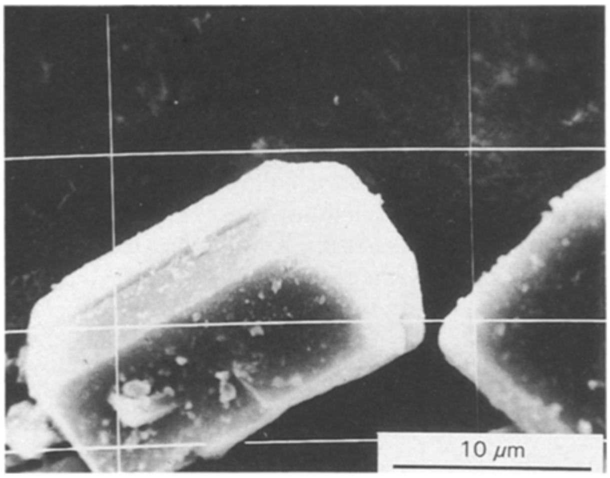

Figure 2 Scanning electron micrograph of a typical crystal of α-$CaSO_4 \cdot 1/2H_2O$.

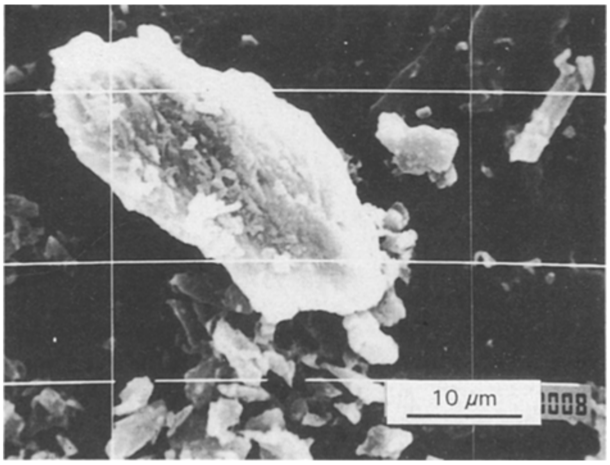

Figure 3 Scanning electron micrograph of a typical crystal of β-$CaSO_4 \cdot 1/2H_2O$.

3. Experimental procedure

When plaster is mixed with water the ensuing hydration reaction is exothermic (see earlier). The progress of the reaction could therefore be followed using calorimetry, in addition to phase analysis and changes in the electrical resistance of the reaction slurries. The reaction slurries were initially mixed at a water/plaster (W/P) ratio of 0.6 because this was found to be typical of that used in splinting applications [16].

3.1. Calorimetry of the hydration reaction

If the exothermic hydration of hemihydrate with water is performed under adiabatic conditions, the temperature rise, ΔT, will be proportional to the amount of calcium sulphate dihydrate formed.

The progress of the reaction was followed using a simple calorimeter with a chromel/alumel thermocouple inserted into the sample. The reaction rate was followed with ΔT as a function of time. A typical ΔT versus time curve and the parameters which can be derived from it is shown in Fig. 4.

3.2. Phase analysis of the hydration products

The degree of reaction was followed by stopping the reaction at various stages and determining the phases

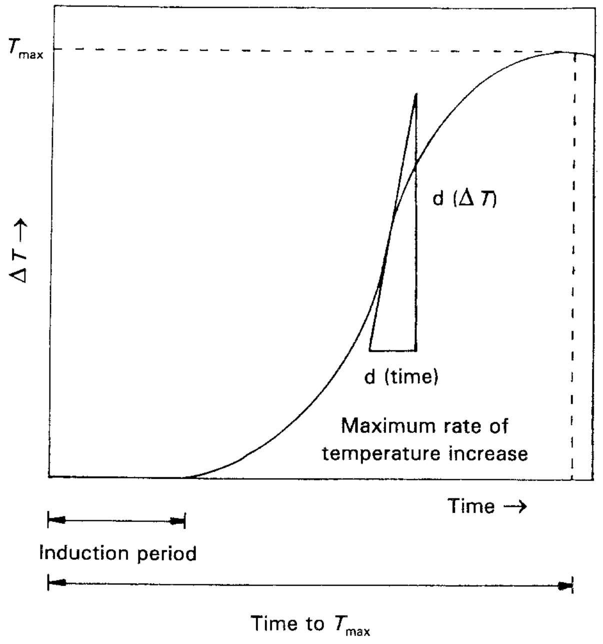

Figure 4 Typical ΔT/time curve for the exothermic reaction of calcium sulphate hemihydrate with water.

present using powder XRD and thermal analysis [16, 17].

The plaster slurry was poured into a silicone rubber mould which was placed in a humidity cabinet to ensure both constant temperature and humidity (30 °C, 63% RH) during setting. The chemical reaction was stopped by washing the specimen with excess ethanol.

3.3. Electrical resistance of setting gypsum plasters

A simple cell was constructed in which two platinum electrodes were inserted into the plaster slurry. These were then connected to a Hewlett–Packard 4192 A-LF a.c. impedance analyser. The frequency was set to 1000 Hz and the resistance, Ω, was measured as a function of time. The results were then quoted as resistance/electrode distance ($\Omega\ cm^{-1}$).

4. Results and discussion

4.1. α- and β-hemihydrates

The tradition of having two forms of hemihydrate has probably arisen from the fact that the material can be made by two processes, which give rise to products with distinctly different physical properties. Dry decomposition of the dihydrate gives a crystalline, porous product with particles consisting of randomly orientated small crystallites, whilst hydrothermal methods result in larger, well-formed crystals. This was confirmed by the SEM and optical transmission microscopy, but XRD showed no significant differences in the crystal lattice for the two forms. Thermal analysis, in particular DTA studies, showed a difference in the temperature of the soluble/insoluble phase transition but this was probably due to the effects crystallite size.

The "α", "β" nomenclature cannot, therefore, be justified on the basis of two distinct crystalline phases, but can be used for convenience to indicate different physical states and subsequent reactions with water.

4.2. Calorimetry of the hydration reaction

The temperature changes noted during the hydration of the α and β plasters during hydration are shown in Fig. 5. The induction period for α-hemihydrate (5.4 min) was about a quarter of that for the β-form (19.6 min). Once the reaction was underway the maximum rate of temperature increase was far lower for the α-form (0.75 °C min^{-1}) compared to that of the β-form (2.9 °C min^{-1}). The maximum temperature reached was higher in the case of the β-hemihydrate/water reaction, which was probably due to the much higher rate of temperature increase.

4.3. Phase analysis of the hydration products

Analysis of the DTA/TGA data enabled the proportions of dihydrate and hemihydrate to be calculated; the results are represented graphically in Fig. 6 and where confirmed semi-quantitatively by XRD.

The curves obtained are similar to those obtained by calorimetry (see Fig. 5) and will be more accurate provided sufficient samples are taken. This shows that calorimetry can be used to follow the reaction's progress because the accelerating rate of reaction appears not to be due to the rising temperature. Calorimetry also has the advantage of producing data continu-

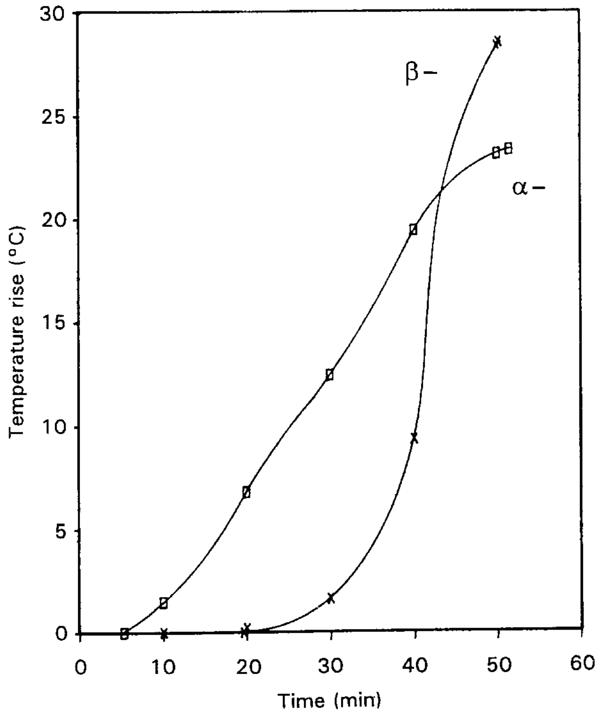

Figure 5 The hydration of α- and β-hemihydrates (W/P ratio = 0.6) as followed by the temperature change.

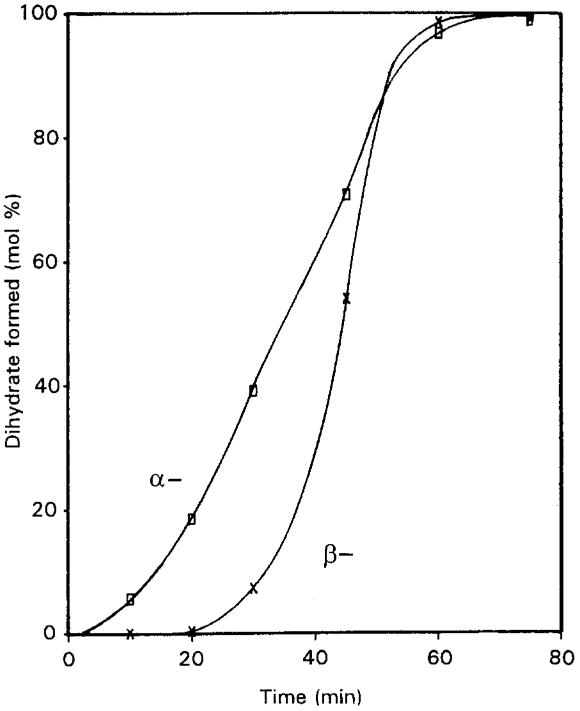

Figure 6 The amount of dihydrate formed in hemihydrate/water reaction mixtures as determined by thermal analysis.

ously and would therefore be sensitive to small changes in the reaction rate.

The induction period for β-hemihydrate was longer than that for the α-form. Because the β-form particles are smaller and consist of small crystallites, this suggests that processes other than the dissolution rate determine the length of the induction period.

Following the induction period, the rate of dihydrate precipitation from the β-hemihydrate/water reaction mixture is faster than that of the α-form. The hemihydrate particles have been shown to act as heterogeneous nucleation sites for dihydrate growth [16]. Because the β-form has a smaller crystallite size and hence higher specific surface area, it will have a larger number of nucleation sites. This probably results in a faster dihydrate precipitation rate and implies the process is nucleation controlled. This aspect is treated in more detail in a following paper [18].

To investigate further the factors controlling the induction period, the solubility of hemihydrate was investigated by measuring changes in the electrical resistance of the slurries.

4.4. Electrical resistance of setting gypsum plasters

The change in electrical resistance with time of setting plaster slurries, is shown in Figs 7 and 8. These graphs indicate that the reaction takes place in three stages.

(i) A minimum resistance was obtained after 5–10 min. This represents the point of maximum solubility of the calcium and sulphate ions.

(ii) The resistance then increased steadily over the next 100 min and this was due to dihydrate precipitation. This can be explained by considering the densities of reactants and products [19], and the expansion of the slurry during setting, which is of the order of 1% [4]. The density of hemihydrate is 2.78 g cm^{-3}, while that of dihydrate is 2.32 g cm^{-3}, a difference of 16.5%. Therefore, the increase in the volume of solid per unit volume of slurry is approximately 42%.

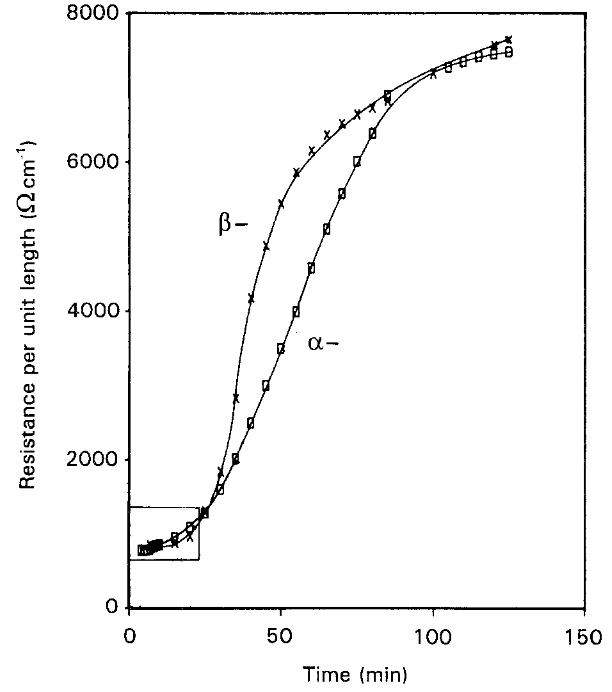

Figure 7 The electrical resistance of setting plaster slurries (W/P = 0.6).

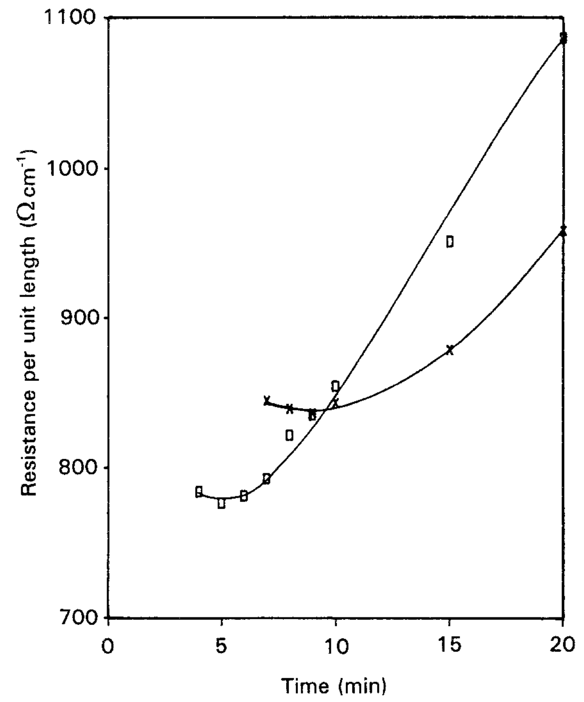

Figure 8 An expanded view of the boxed area shown in Fig. 7.

Because resistance, $R = \varepsilon l/A$, where ε is the resistivity, l the length and A the area, the area of pathway between the solid particles for the ions in solution decreases with crystallization, this would lead to an increase in measured resistance.

(iii) Finally, the resistance reached a relatively constant value at the end of the hydration process and a slight further increase was due to the drying-out process.

The α-plaster reached a maximum saturation in 5 min, about half the time taken by the β-plaster. This suggested that the length of the induction period was dependent on the rate of dissolution of the hemihydrate. The rate of dissolution, however, does not seem to depend on crystallite size and specific surface area but is possibly related to crystal habit and lattice perfection. A crystal habit with more preferential sites for the chemisorption of water would be expected to give a product with a faster dissolution rate.

5. Conclusions

1. The differences between α- and β-hemihydrates are due to crystal size and habit. These differences arise from the method of production and are not due to differences in crystal structure.

2. Calcium sulphate hemihydrate reacts with water to form calcium sulphate dihydrate, the reaction occurring in three stages:

(i) the first stage involves the dissolution of the hemihydrate to form a solution which is supersaturated with respect to dihydrate;

(ii) the second stage is the nucleation and growth of dihydrate needles to form an interlocking crystal/mass;

(iii) the final stage is completion due to depletion of hemihydrate.

3. α- and β-hemihydrate both completed the hydration reaction in approximately the same time, but the α-form has a shorter induction period and a slower rate of dihydrate precipitation.

4. The induction period appears to be controlled by the rate of hemihydrate dissolution whilst the rate of dihydrate precipitation is controlled by nucleation.

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