

THE RELATIONSHIP BETWEEN THE MICROSTRUCTURE
AND MECHANICAL PROPERTIES OF SETTING GYPSUM PLASTERS

BY

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November 1987

*A thesis submitted for the degree of Doctor of Philosophy
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of the Imperial College*

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ABSTRACT

When calcium sulphate hemihydrate, $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ (plaster of Paris), is mixed with water it hydrates exothermally to form an interlocking mass of calcium sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ needles, known as gypsum. Widespread use is made of this plaster as a splinting material, where the requirement is for rapid setting and high set strength.

Commercial plasters are made from the mineral gypsum by dehydrating in an autoclave or by dry calcination; the products containing some soluble anhydrite ($\gamma - \text{CaSO}_4$). The processes give rise to two different products, known as ' α '- and ' β '- hemihydrate. Characterisation of the two products has shown that differences in properties is the result of crystal size and surface area. A plaster consisting totally of α - plaster has a higher initial and fully 'set' strength.

Microstructural and kinetic studies have shown that the strongest set plasters contain short, stubby dihydrate needles produced by the slow precipitation rate. Faster precipitation rates lead to branching, fibrous needles which give lower strengths due to the reduced inter-crystalline bonding.

The presence of the soluble anhydrite impurity reduces the strength of the set plaster by perturbing the microstructure.

Medical plaster formulations contain small additions of dihydrate and potassium sulphate (K_2SO_4), to act as a nucleating agent and accelerator respectively. The nucleating effect of the dihydrate is dependent on the surface area and 'roughness' of the particles. Increased nucleation results in a microstructure of finer, smaller dihydrate needles with a lower strength. The accelerating effect of potassium sulphate produced a microstructure of larger, stubbier needles and lower strength.

The use of KHSO_4 and Ca(OH)_2 to generate 'in-situ' microcrystalline nuclei in the presence of K_2SO_4 has been shown to be more advantageous than present commercial systems.

Hydroxypropylcellulose and polyvinylacetate, while efficient at binding plaster particles to the gauze, have an adverse effect on the mechanical properties; hydroxypropylcellulose in particular.

For Karen,

whose love and support made this task
much easier

In art, nothing worth doing can be done without genius; in science even a very moderate capacity can contribute to a supreme achievement.

(Bertrand Russell, *"Science and Culture",
Mysticism and Logic* (1917)).

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1. INTRODUCTION

Gypsum plaster is widely used throughout many branches of industry. As a building material it is applied to walls to give a smooth finish and provide decorative touches, in the ceramics industry it is used to make moulds for casting long objects and in the medical profession it is used for making cases for impressions and as a splinting material. For each application the basic plaster mix is modified to control either the rate at which the plaster sets or the properties of the final set material. Plasters for the building industry contain retarders which slow down the rate of setting thus giving a longer working period for the mix. As a splinting material accelerators are added to reduce the setting time and the formulation is aimed to give a high set strength.

This thesis is concerned primarily with gypsum plaster as used for splinting broken limbs. A reduction in the setting time allows the patient to leave the casualty area sooner, while the stronger the set plaster the less material which needs to be applied and hence the lighter the cast and reduced inconvenience.

The first reported use of gypsum plaster as a splinting material in Europe was in 1816 by Hubenthal¹, when he mixed equal parts of plaster of Paris with wet ground-up blotting paper. The resultant mixture was spread on the limb with a spatula.

In 1852, Anthonius Mathysen (1805-1879)², a Dutch Army surgeon, published a pamphlet on the use of plaster of Paris in the treatment of fractures. In it he discussed the preparation of plaster of Paris bandages, which consisted of a coarse cotton bandage with finely powdered plaster manually rubbed into it.

The commercial production of ready-made plaster of Paris bandages in Europe began in Germany in 1931 with the "Cellona" bandage.

Shortly afterwards a licence was secured by Smith and Nephew Ltd., U.K. to make and distribute "Cellona" in Great Britain. After making several improvements to the bandage the name "Cellona" was changed in 1947 to "Gypsona", and this trade name is still in use today.

The modern commercial bandage formulation of "Gypsona" is shown in Table 1.1³. The manufacture of the "Gypsona" bandage starts with the binders being dissolved in methylene chloride and the rest of the formulation is then added and mixed in a tank. A cotton gauze is then passed through the tank and coated with the plaster. The methylene chloride is then dried off and the bandage is wrapped around plastic formers.

In spite of their almost universal use, due mainly to the low cost and good moulding properties, plaster of Paris bandages are not the perfect splinting material. The application is very messy, 2-3 days are needed before the cast is completely cured and maximum strength is reached, and the finished casts are heavy, have a poor strength to weight ratio, are porous and are not water resistant.

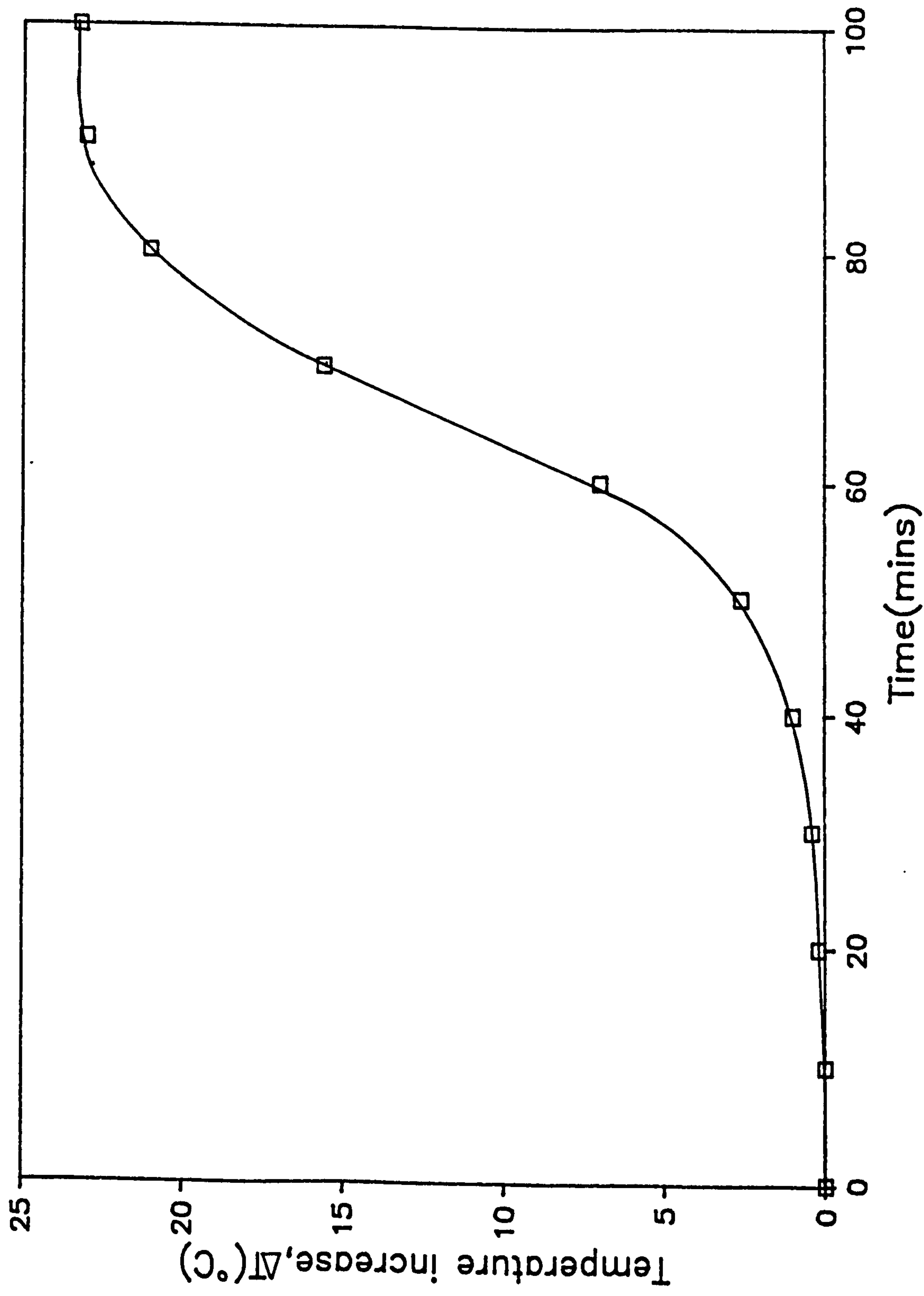
The calcium constituent of gypsum plaster is calcium sulphate hemihydrate, which on mixing with water reacts exothermally to form calcium sulphate dihydrate. The apparent simplicity of the reaction is deceptive, as can be seen by the manner in which the reaction rate changes with time. If the increase in temperature developed by a slurry of calcium sulphate hemihydrate and water is plotted against time, a sigmoidal curve with a well-defined induction period is obtained (see Figure 1.1).

Table 1.1: The commercial formulation of Gypsona plaster bandages.

Constituent		Wt%
Calcium sulphate hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (a mixture of the 'α' and 'β' forms in the ratio 1:2)	}	95
Calcium sulphate, soluble anhydrite, $\gamma\text{-CaSO}_4$ (up to a maximum of 10%)	}	
Calcium sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	.	2
Potassium sulphate		1
Binders	{ Polyvinylacetate	1
	{ and	
	{ hydroxypropylcellulose	1
Total:		100

Note: Soluble anhydrite is produced by overdehydration in the production of hemihydrate from dihydrate.

Figure 1.1: The temperature increase developed by a plaster/water slurry, W:P ratio = 0.6.
(after Ridge⁴).



This research project has been concerned primarily with the kinetics of the hydration reactions and the mechanical properties of the set plaster, with particular interest in those factors affecting the initial rate of build-up in strength as the setting processes progress. Strength development is one of the major factors determining the time which must be allowed before a load may be applied to a plaster cast, and therefore of great importance in medical applications.

Preliminary work⁵ carried out at Imperial College has shown that plaster of Paris from different suppliers show marked differences in the rates of hydration and full set strength. Therefore a full characterisation of these plasters was an essential starting point for this project, while the rate of hydration and relationships between mechanical properties and the microstructure of the set plaster formed a major part of the study. Finally, the effect on the hydration reaction and products by additions of the other constituents in commercial bandages (see Table 1.1) and by varying $\alpha:\beta$ hemihydrate ratios was investigated.

2. LITERATURE SURVEY

2.1 THE SYSTEM $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$

Figure 2.1 shows schematically the phases considered to exist in the $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ system.^{4,6,7} Calcium sulphate dihydrate, the hydration product of the hemihydrate, has a well established structure^{4,6,7} (see Figure 2.2). It consists of a layer lattice in which double layers of CaSO_4 alternate with double layers of water molecules bonded by hydrogen bonds.

There was for many years doubt as to whether hemihydrate was a precisely defined compound or better regarded as hydrated soluble anhydrite. The position regarding this is now fairly clear due to the work of Weiser et al.⁹. They investigated the isobaric dehydration of the hemihydrate and obtained a composition versus temperature curve with a sharp step indicating a 1st order phase change and considered the failure of previous workers to obtain this was because they did not obtain equilibrium. From this study, in conjunction with X-ray diffraction analysis, they concluded that the lattice type and unit cell size of the hemihydrate and soluble anhydrite were very similar and that the hemihydrate lattice does not change very much with the loss of the half molecule of water, but that there are distinct differences and the soluble anhydrite and hemihydrate should be regarded as distinct chemical species.

Florke⁷ advocated a structure for the hemihydrate which is permeated by wide channels (diam. $3\text{\AA}$) in which the water molecules are situated, the difference from soluble anhydrite (see Figure 2.3) being essentially the presence of water

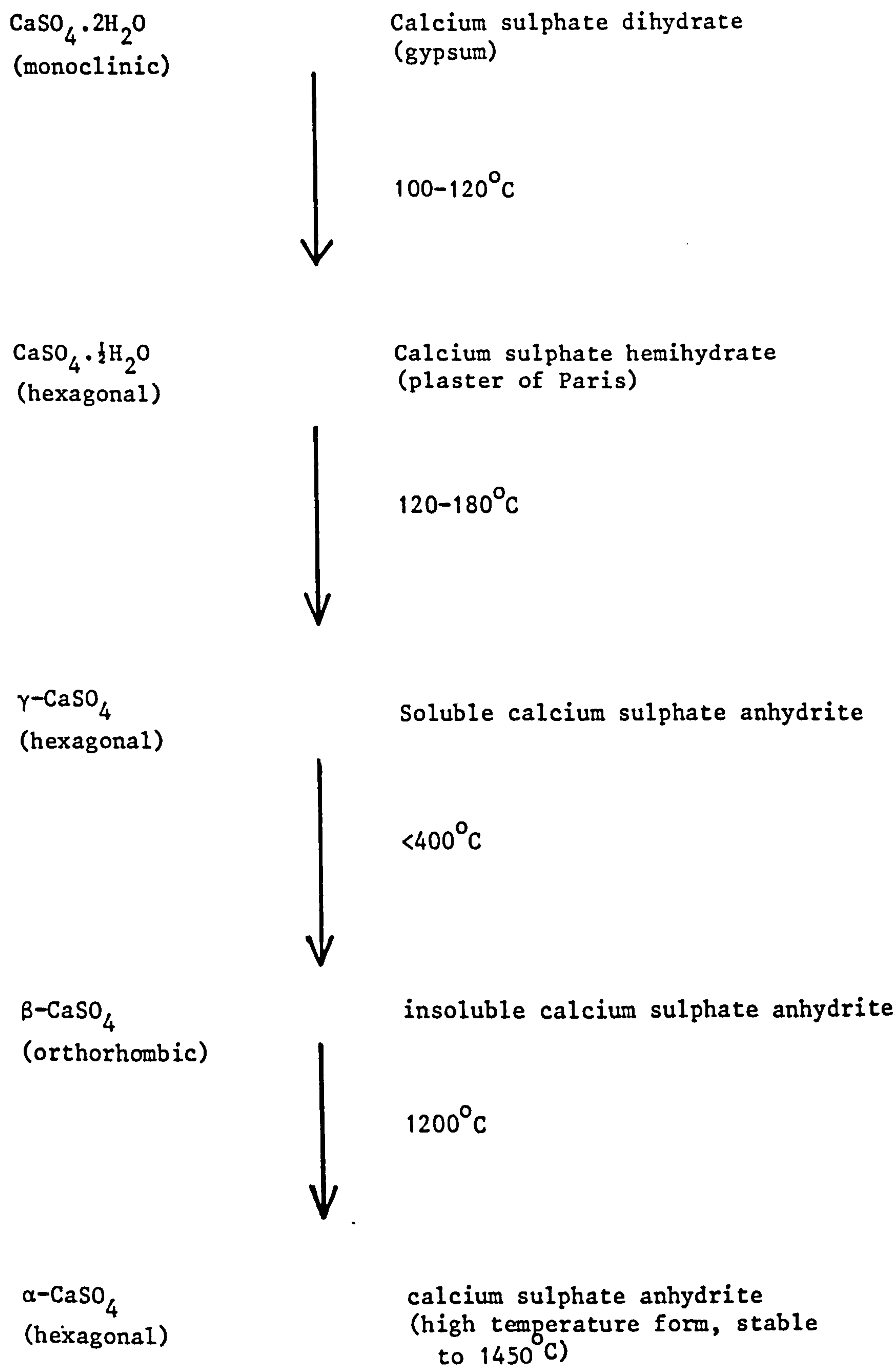


Figure 2.1: The $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ system.

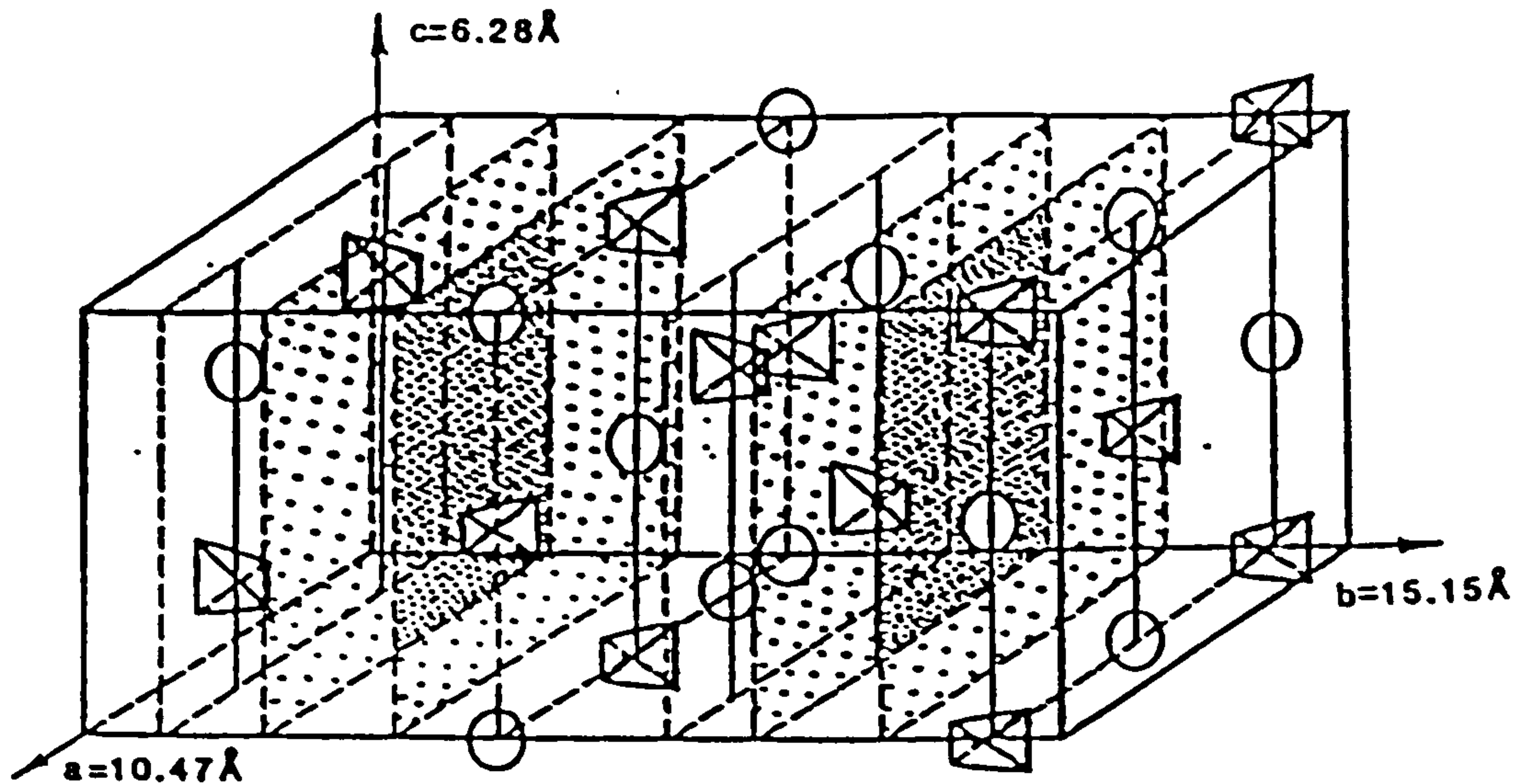


Figure 2.2: The structure of gypsum, where:

tetrahedron = SO_4

circle = Ca

The water molecules are in the dotted planes.

(after Florke⁸).

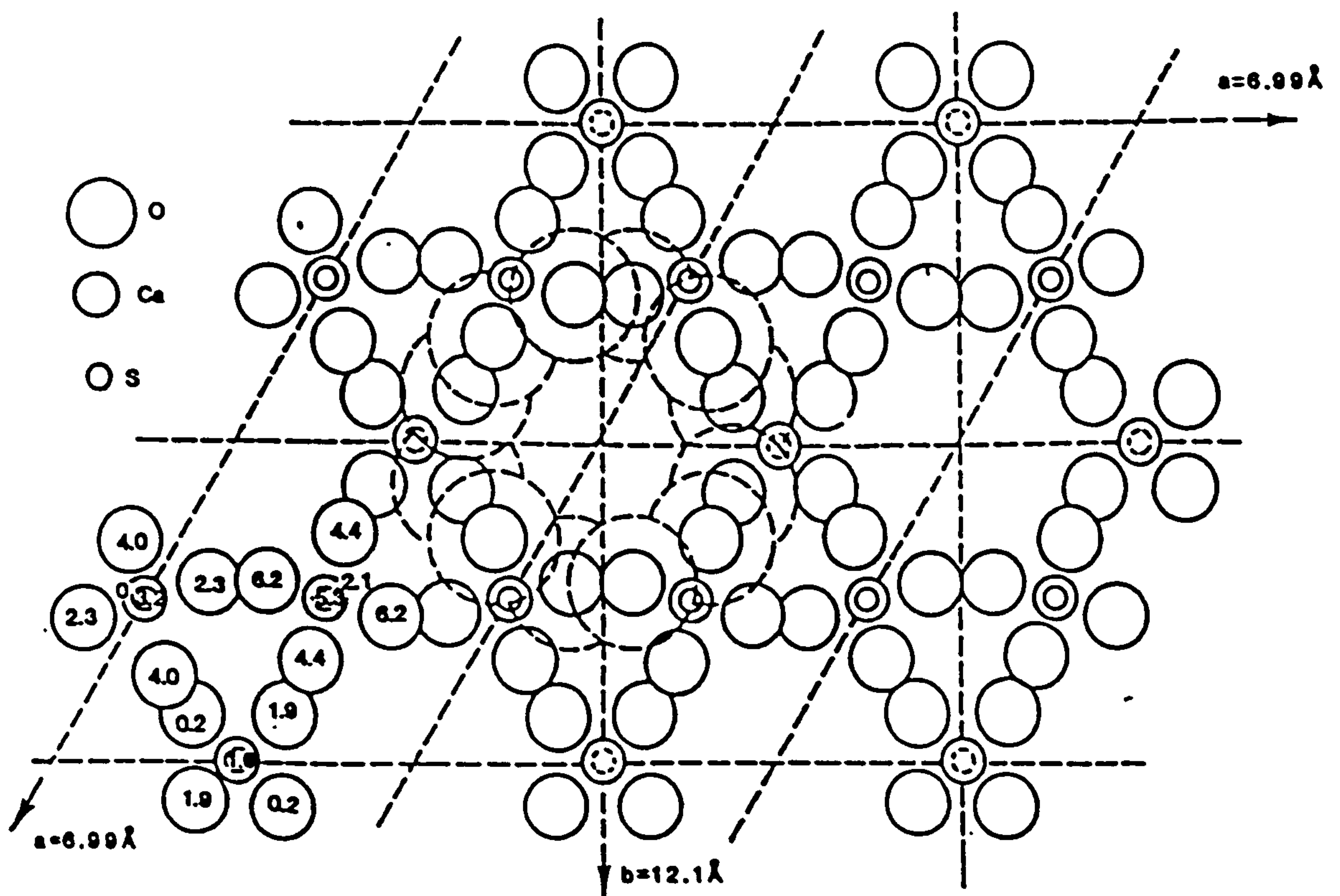


Figure 2.3: The structure of soluble anhydrite projected on the (001) plane. The figures give the position of the atoms on the C axis in Å. The large broken circles indicate the actual size of the O atoms.

(after Florke⁸).

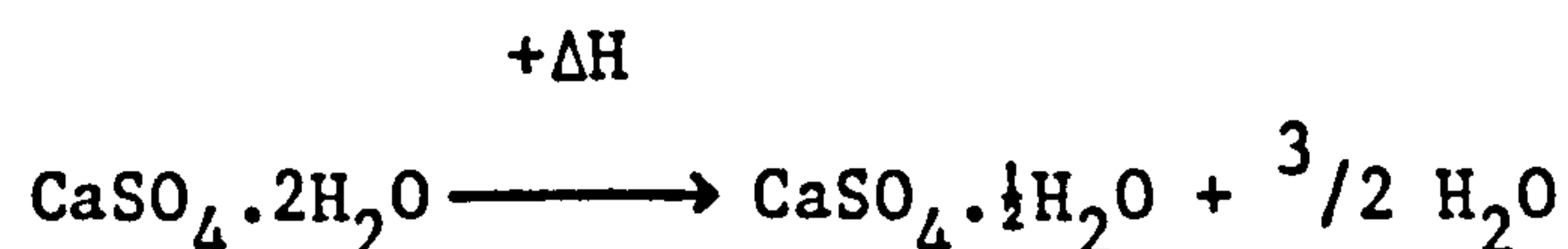
molecules bring about distortion and displacements in the position of the calcium atoms and SO_4 groups.

The crystal structure can be used to explain morphological investigations⁶ which show that macroscopically the hemihydrate crystals are rhombohedral in habit. Optical studies⁶ reveal that the crystals resolve into three biaxial orientations at room temperature and that these show undulous extinction. The formation of triplets creates pseudorhombohedral symmetry. When held at 70°C for some time the crystals become practically homogeneous between crossed nicols and uniaxial but extinction remains slightly undulous. On cooling the separation into fields occurs again. Using the Florke model (see Figure 2.3) based on soluble (hexagonal) calcium sulphate and the distortions caused by water molecules, the above observations can be explained, with the strains being relieved at higher temperatures.

2.2 CALCIUM SULPHATE HEMIHYDRATE ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)

2.2.1 Method of preparation

Calcium sulphate hemihydrate is usually prepared by the dehydration of the dihydrate in the form of the mineral gypsum; see below:



The methods for performing this reaction are summarised below:

(a) Gypsum is heated in an open kettle or rotary kiln at $110\text{--}130^\circ\text{C}$. This is the long established method and can be made more efficient by using continuous calcining processes instead of batch production,¹⁰ by simultaneous heating and

vibratory milling¹¹ or by fluidizing a bed of gypsum with a directly heated stream of air¹².

(b) Lump gypsum is heated by steam in an autoclave (120–147°C) giving a product known as "hydrocal".¹³

(c) Gypsum is heated in water, in the presence of a crystal modifier (e.g. sodium succinate), under steam pressure, between 125 and 165°C¹⁴.

(d) Gypsum can be heated in a solution of a salt (e.g. 30% calcium chloride or magnesium sulphate).¹⁵

In commercial practice all the plasters produced by the above methods are process products, containing impurities present in the original gypsum, and those introduced during the dehydration process, and the possibility of some unconverted dihydrate and/or anhydrite present due to non-homogeneous dehydration.

A more recent development (since 1970) is the use of byproduct gypsum¹⁶, mainly from phosphoric acid production but also from the process of desulphurising the exhaust gases from large combustion plants, as a replacement for natural gypsum in the plaster production processes described earlier. In Japan, for example, since 1976 natural gypsum production has been phased out in favour of the synthetically produced product.

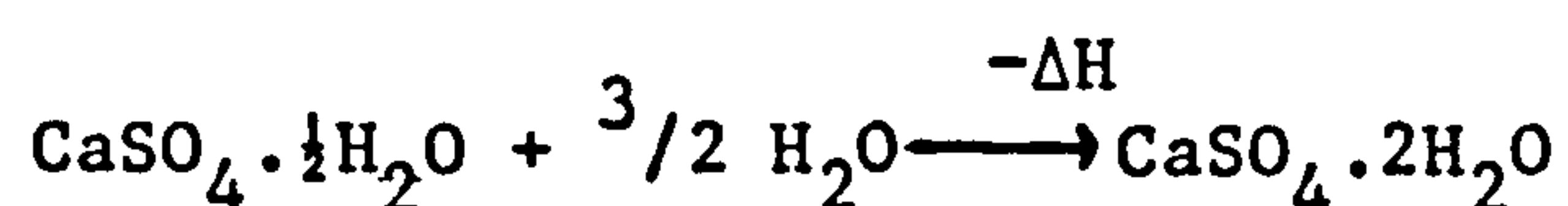
2.2.2. Differences between α - and β - hemihydrates

Calcium sulphate hemihydrate has traditionally been given a " α " or " β " nomenclature where the two modifications are defined according to the mode of preparation¹⁷; i.e. the α - form being prepared by wet methods (e.g. autoclaving)^{4,6} and the β - form by dry methods (e.g. calcining^{4,6}). Apart from the differences in mode of preparation, the two forms differ in

their reactivity with water and in the strength of the hydration product's structure. The two forms have been examined by various techniques but the differences remain unclear and it is doubtful if the two forms constitute two distinct crystalline phases. The results from various investigations are discussed in this section.

(a) Reactivity with water.

On mixing hemihydrate with water, the following reaction occurs:



The hemihydrate is slightly soluble in water and saturation is quickly reached. The solubility of the dihydrate is only a fraction of that of the hemihydrate and needle-like crystals of dihydrate nucleate and precipitate, growing rapidly to form a rigid interlocking crystalline mass¹⁸.

Previous workers^{19,20} agree that the α - form produces a "set plaster" which is stronger than that produced by the " β " form, but disagree on which form sets more quickly. Typical values are given in Table 2.1.

(b) X-ray diffraction analysis.

X-ray diffraction studies, made by Benstead and Varma¹⁷, showed no observable differences in the position of the diffraction peaks. Slight changes were observed in the relative intensities of some peaks in the α - form compared to those in the β - form but these differences decreased and finally disappeared when the α - form was finely ground.

Morris²¹ reported differences in the (212) reflection which he claimed indicated two forms existed, distinguished by the content of stacking fault imperfections. The criteria used

Table 2.1: The dry bending strength and the initial set times for plasters from α - and β - hemihydrates.

Measurement Plaster	after Lacheny ²⁰		after Enayetallah et al ¹⁹	
	Initial set-time	Bending strength; dry (7 days)	Initial set-time	Bending strength; dry (7 days)
α - hemihydrate	6-17 mins.	5-8 MN/m ²	6 mins.	7.0 MN/m ²
β - hemihydrate	3-13 mins.	3-5 MN/m ²	15 mins.	5.8 MN/m ²

hardly seems to warrant the distinction of separate crystalline forms and if the effects of line broadening due to particle size effects are considered^{4,17}, the two patterns may then be regarded as the same. This indicates that α - and β - hemihydrates have the same crystal structure and this has been studied in detail by Florke⁸ (see Section 2.1).

(c) Optical and electron microscopic studies.

These studies^{17,22} indicate that α -hemihydrate consists of larger crystals than the β -form, with the α - form showing sharp extinction in polarised light whereas the β - form showed shadowy extinction under similar conditions. This implies that the particles of β - hemihydrate are composed of a multiplicity of small crystals.

(d) Infra-red spectra.

Spectra of the two forms obtained by several workers^{17,22-24} show no significant differences.

The α -hemihydrate is more crystalline and has larger grains, so that there is more scattering from a sample of the α - form. Any differences in sharpness disappear when specimens of the α - form are well ground, as has been demonstrated by Benstead and Varma¹⁷ (see Figure 2.4).

Goto et al²² agreed that the spectra of the two forms were similar but noted that absorption by the β - form was more intense in the 2.85-3.05 μ m region of the spectrum. They attributed this to the β - form having a greater amount of absorbed water. The conclusion that can be drawn from this is that the α - and β - forms have the same type of structure.

(e) ^1H Nuclear Magnetic Resonance (N.M.R.) spectra.

Measurement of the derivative curves of the ^1H N.M.R. signal from water in the two forms, done by Saito²⁵ and by Goto et al²², showed that water is present in two different forms, one of which is much more tightly bound than the other.

The derivative curves obtained by Goto et al (see Figure 2.5) show that each curve consists of broad peaks whose peak to peak width of 9.5G remains constant, and narrower peaks whose width is dependent on the water content of the specimen.

The conclusions drawn from this were that the broad peaks are obtained from water that is tightly bound in the structure, whilst the narrower peaks are from adsorbed water that is more mobile, the mobility increasing with water content. In each case most of the water is in the tightly bound condition and the only difference between the two forms is that the adsorbed water in the β -form is more mobile than in the α -form.

(f) Differential Thermal Analysis. (D.T.A.)

D.T.A. has generally been utilized for differentiating between α - and β - hemihydrates on the basis of an exotherm corresponding to the soluble (hexagonal) to insoluble (orthorhombic) anhydrite transformation. Budnikov and Kosyreva²⁶ differentiated between the two forms on the basis that the α - form gave an endotherm at 190-210°C, while the β - form gave one at 170-185°C. It was also reported that the β - form had an exotherm at 360-370°C, which was not shown by the α - form. Powell²⁷

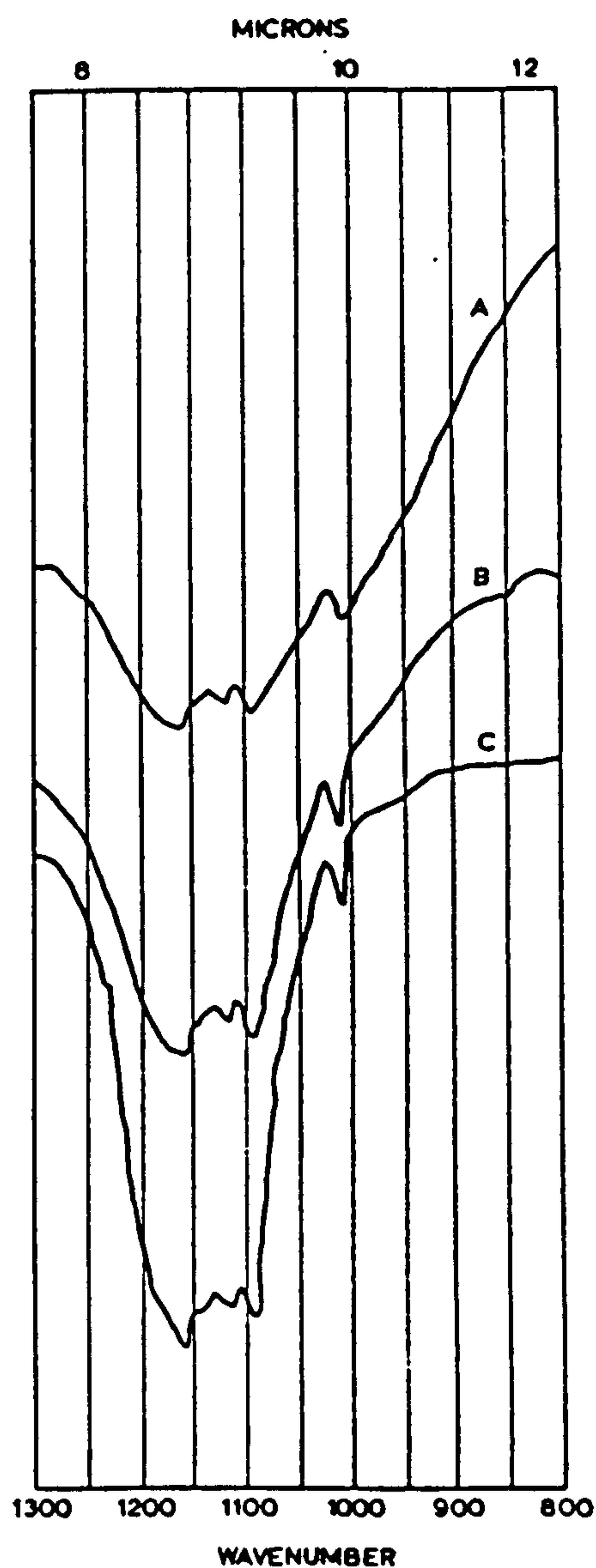


Figure 2.4: The infra-red spectra of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, where:

(A) α -

(B) β -

(C) the ground α - form.

(after Benstead and Varma¹⁷).

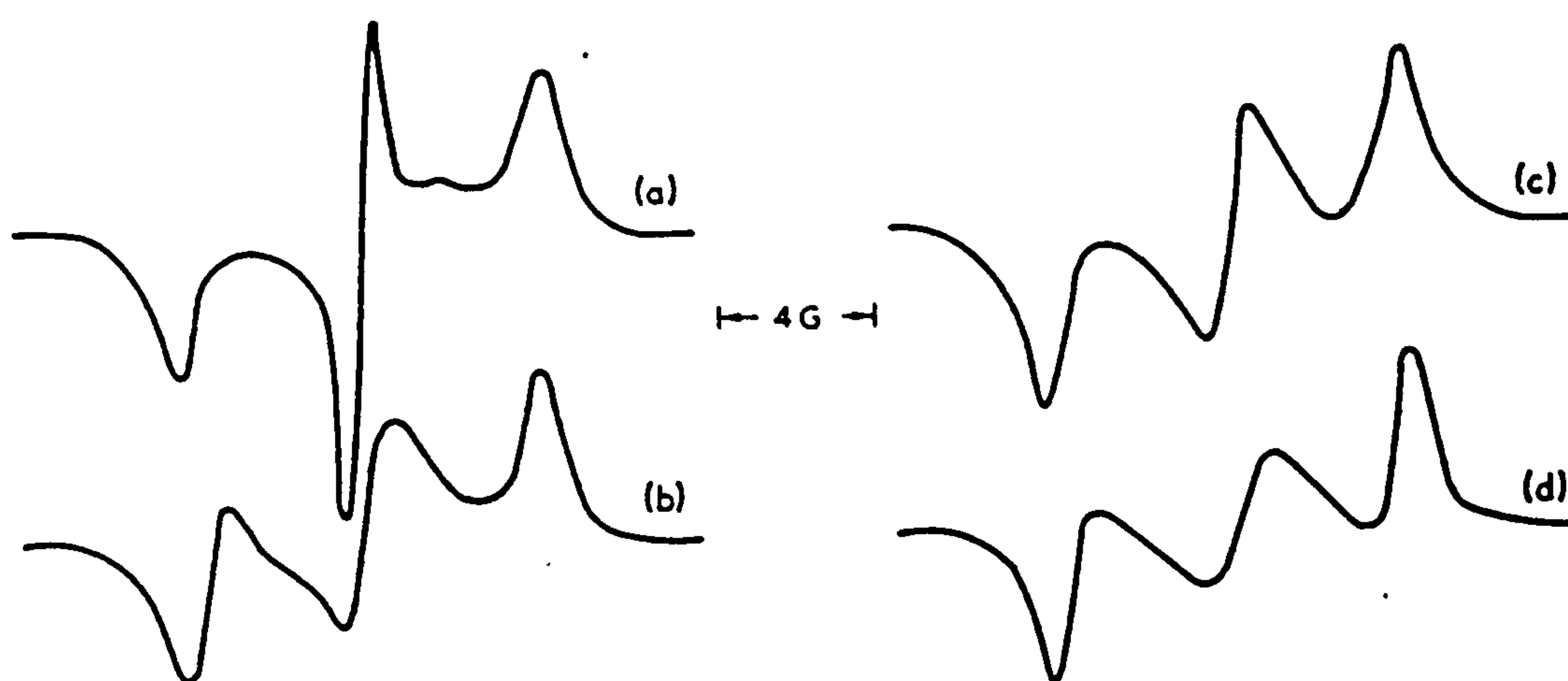


Figure 2.5: Derivative curves of the ^1H nuclear magnetic resonance signal from the water in $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$. (H_2O stoichiometric = 6.2%), where:

(a) β - (6.6% H_2O) (b) β - (5.8% H_2O)

(c) α - (6.4% H_2O) (d) α - (6.1% H_2O).

(after Goto et al²²).

observed that the α - form did have an exotherm which was very sharp and close to the preceding endotherm, suggesting that the dehydration product of the α - form (soluble anhydrite) changes more readily into insoluble anhydrite.

On the basis of D.T.A. studies it has been suggested that α - and β - hemihydrates are different forms, which may be differentiated by their exothermic effects corresponding to the soluble/insoluble anhydrite transformation. Ridge⁴, Mitsuki and Kita²⁸ disputed this conclusion suggesting that the difference in the D.T.A. traces was due to the preparation of the hemihydrates, in that the α - form has larger and more perfect crystals than the β - form. Evidence for this comes from Benstead and Varma¹⁷, who found that when the α - form was ground it gave a D.T.A. trace which was almost identical to that of the β - form (see Figure 2.6).

Goto et al²⁹, proposed that variation in the D.T.A. traces seem to be the result of variations in activity or the operation of more than one mechanism for phase change, the physical condition favouring one rather than the other. The kinetics and mechanistic study favours the latter explanation and they went on to explain:

"Soluble anhydrite from the β - form appears to change only by a "high temperature" mechanism involving nucleation and diffusion. Sintering is quite evident at 340°C and can only be due to diffusion or plastic deformation. The "high temperature" mechanism is catalysed by water vapour, which promotes mobility in solid systems and thus reduces the energy barrier for diffusion. Furthermore, the product occurs as numerous, compact, unoriented grains distributed throughout grains of soluble anhydrite and so supports the theory of random nucleation.

On the other hand, anhydrite from the α - form yielded less perfect crystallites and there is little evidence for sintering. The transformation is sharply suppressed by water vapour and the product from each single crystal has a common orientation. These facts, in conjunction with the low temperature coefficient ($<250^{\circ}\text{C}$), which is too low for surface diffusion to be a factor, indicates a diffusionless, low temperature mechanism. On the basis of the structures discussed by Flörke⁸, orthorhombic (insoluble) anhydrite can be derived from hexagonal (soluble) anhydrite by shearing parallel to the C-axis. The inhibition of the low temperature reaction by water can be understood as a result of hindering the co-operative movements producing the diffusionless transformation by water in crystallographic channels."

Further support for these two mechanisms is obtained from the D.T.A. and X-ray diffraction studies by Miyazaki and Matsuoka³⁰, who showed that the endothermic and exothermic peaks for the α - form were shifted to a lower temperature at pressures less than one atmosphere, whereas the exothermic peak for the β - form was not shifted (see Figure 2.7). Confirmation that these exothermic peaks correspond to the phase transition was also provided by X-ray diffraction analysis.

(g) Other properties.

Other properties that have been used to distinguish between α - and β - hemihydrates are heat content, bulk volume, refractive index and yield value of suspensions in water. Zdanovski and Spiridonov³¹ measured the solubility of the α - and β - forms and found that the β - form had the higher solubility, but Ridge and Beretka⁶ just attributed this difference to the β - form's smaller crystallite size. They also found that by using the other properties, a sample could consist of the

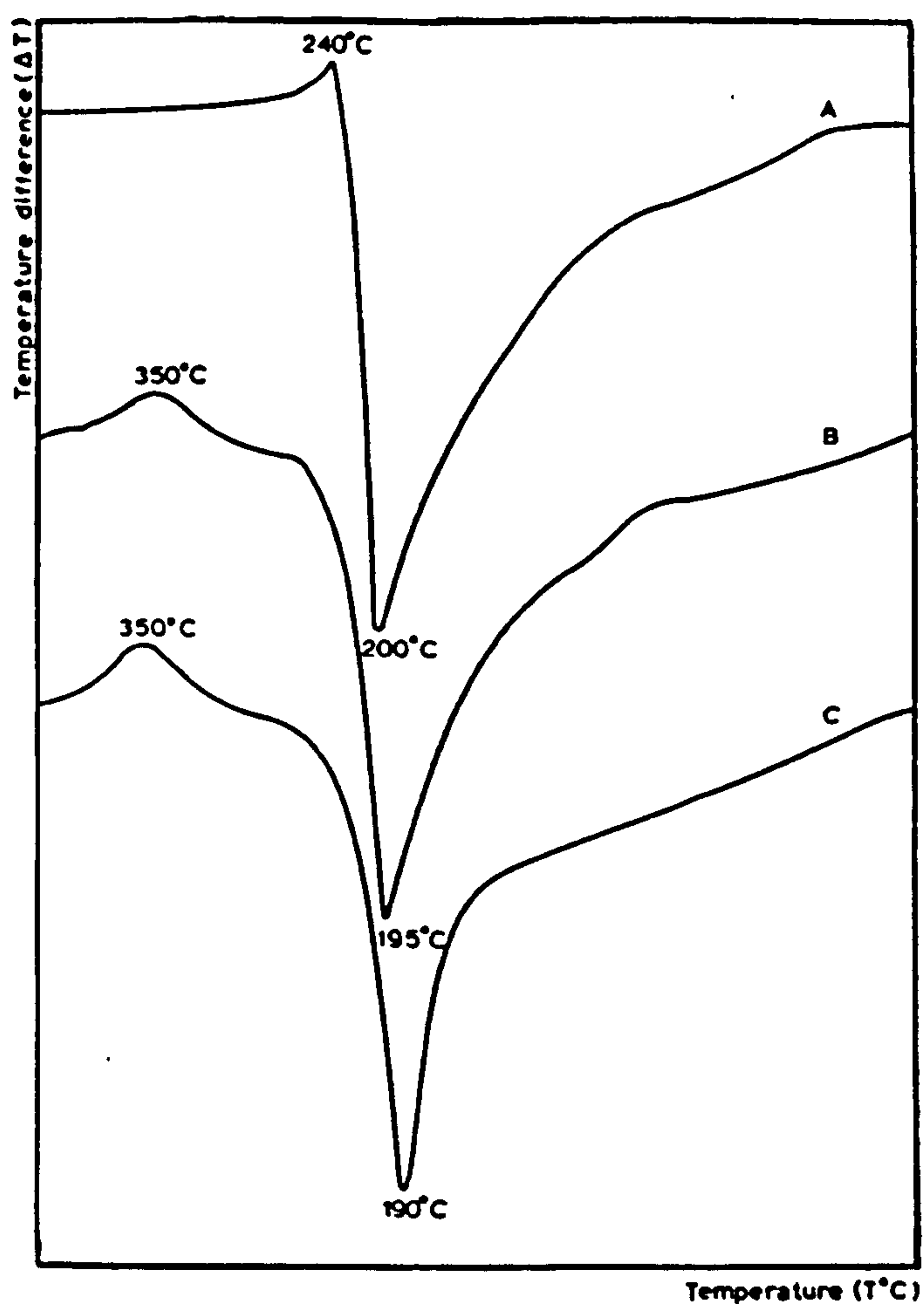


Figure 2.6: D.T.A. data for $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, where:

(a) α -

(b) β -

(c) ground α - form.
(after Benstead and Varma¹⁷)

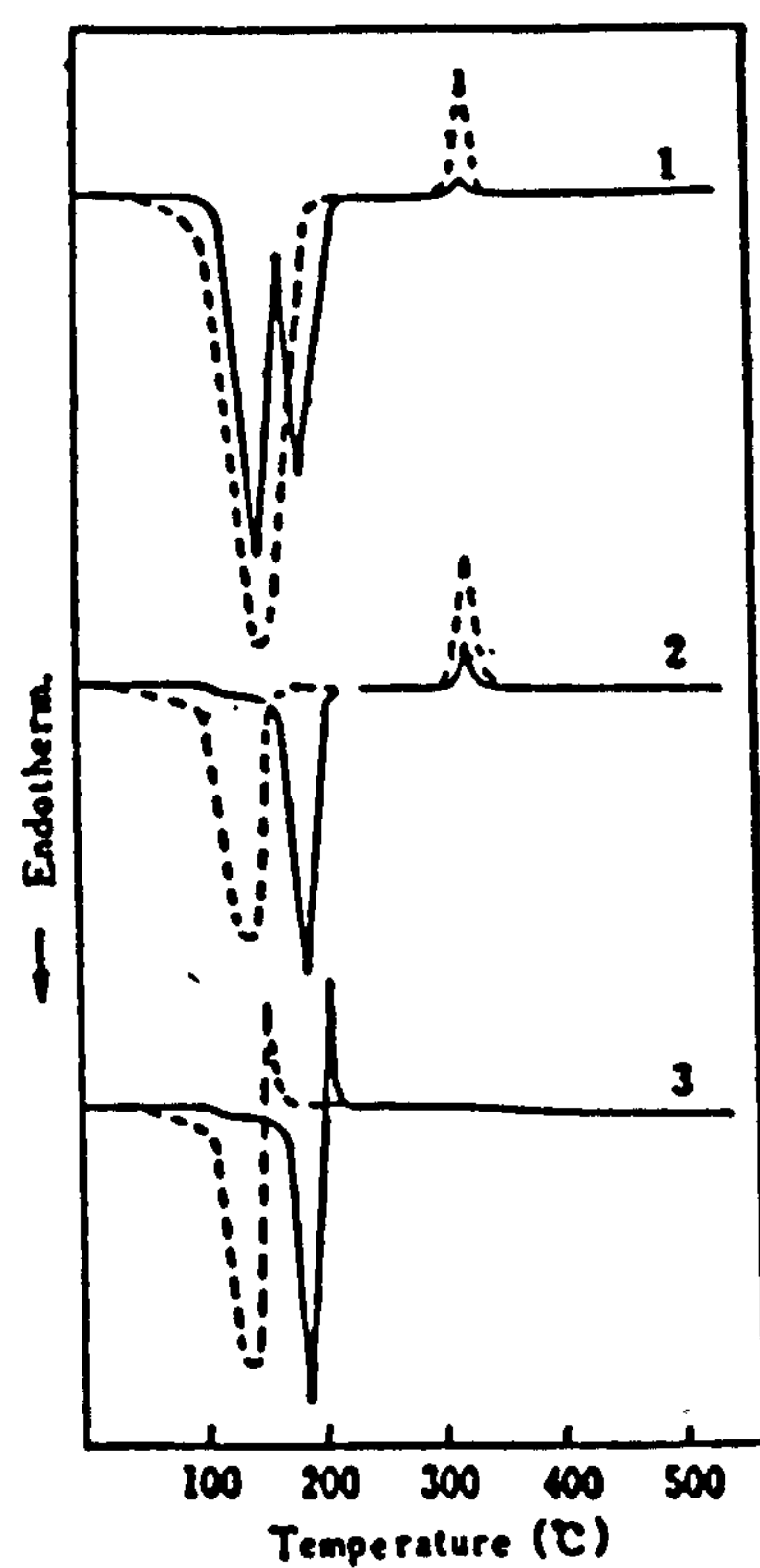


Figure 2.7: D.T.A. curves for calcium sulphates, where:

1. Dihydrate

2. β - hemihydrate

3. α - hemihydrate

— air

..... vacuum (20mmHg).

(after Miyazaki and Matsuoka³⁰)

α - form by one criterion and the β - form by another and came to the conclusion that this analysis was meaningless.

Lacheny²⁰, measured the absolute density of various α/β mixtures and proposed it was possible to determine α/β content in commercial plasters, the α - form having a greater density due to being more crystalline.

(h) Summary.

The tradition of having two forms has probably arisen from the fact that the material can be made by two processes, leading to products in distinctly different physical conditions.

The dry decomposition methods leading to a poorly crystalline, porous product, whilst hydrothermal methods result in well-formed crystals. As a result, the differences in properties are probably due to differences in habit, crystallite size, surface area and lattice perfection. The " α/β " nomenclature cannot therefore be justified on the basis of two distinct crystalline phases but can be in terms of convenience due to the different physical states and subsequent reaction with water.

2.3 CALCIUM SULPHATE HEMIHYDRATE IN DISPERSION

2.3.1 Properties in dispersion

Hemihydrate in the form of a powder is of considerable industrial importance and as a result the properties in dispersion deserve attention.

Significant properties of chemically active powders are bulk and sedimentation volumes, yield values of suspensions in specific liquids, the shapes, size and porosities of the component grains and the specific surface area. The first

three properties are determined by the surface condition of individual grains.

It has been shown by Ridge³² that the properties of dispersed hemihydrate are dependent on the mode of preparation. For example, the β -form's bulk volume is usually 40cm^3 per 100g higher than that of the α -form.

An important technical property of aqueous pastes of hemihydrate is the 'water requirement'. This is a measure of the amount of water that must be used to give a paste with a specified yield value, which in turn is related to the workability of the paste. This has industrial significance in that as much as 80ml of water per 100g of hemihydrate are needed whereas only about 18.3g of water are required for complete hydration. The porosity of the β -form's grains is approximately 20% (α -form approximately 0%) and 100g of hemihydrate has a volume of about 37ml^6 ; therefore this is not the main cause of difference in water requirement.

It is generally accepted that the bulk volume of a powder is determined by the strength of the adhesive forces between the particles³³ and Ridge³² obtained a good correlation between bulk volume and water requirement, which seems to indicate that the factors determining both are closely related.

2.3.2. Rheology of suspensions

The relationship between changes in the rheological properties of suspensions and the formation of structure within the system have been investigated by Reh binder³⁴. This work on the structures produced by crystallization from nucleation and growth of a new phase from supersaturated solutions is

particularly relevant to the hemihydrate hydration. When the hemihydrate is initially mixed with water, the primary dispersed phase (hemihydrate) gradually dissolves to give a solution which is supersaturated relative to the new phase (dihydrate).

The dihydrate is a product of the reaction with water and will be a crystal hydrate which is more thermodynamically stable under the given conditions and therefore less water-soluble. Fine crystals of the dihydrate grow from a solution which is kept supersaturated by continuing dissolution of the hemihydrate. The dihydrate crystals form junction contacts which lead to a rigid crystallisation structure.

Rehbinder has shown that the probability of formation of junction contacts when growing crystals come closer together increases with the degree of supersaturation and duration. Therefore, joining proceeds most intensively at the end of the induction period where the increasing degree of supersaturation attains its maximum value.

In the hardening structure internal stresses arise due to crystallisation pressure and the mechanical properties of the structure. These internal stresses increase with supersaturation as does the probability of the contact joining of crystals of the incipient new phase. Internal stresses reduce the strength of the hardening structure and therefore its maximum strength corresponds to a certain optimal degree of supersaturation.

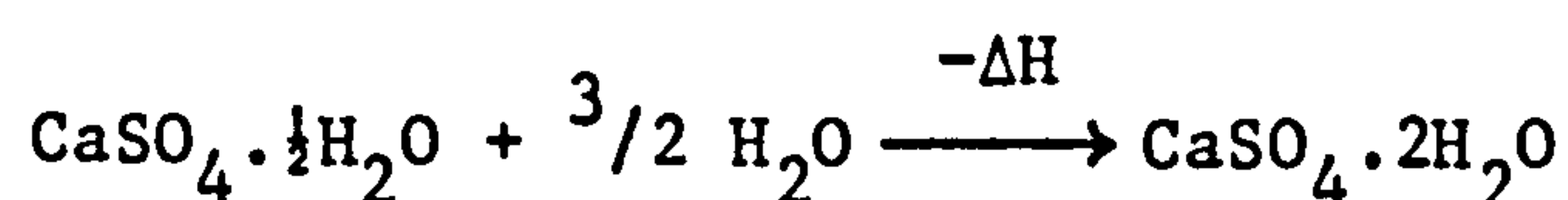
Chatterji and Kapse³⁵ made rheological measurements of dilute suspensions of hemihydrate and the effect of accelerators and retarders on the plastic viscosity. They explained the results on the assumption that the reaction between the hemi-

hydrate and water is a chemisorption process. When the water molecules are adsorbed on the surface they have their charged groups protruding outwards. These groups help orient the neighbouring water molecules and the layers of water surrounding the hemihydrate particles are stabilized.

Acceleration of the reaction leads to stabilization of the water structure in a larger volume than that expected if the reaction were allowed to proceed normally. This increased stabilization of the water lattice is probably responsible for the increased viscosity. The effect of the retarders is to reduce the coverage of the water molecules due to the retarder being preferentially chemisorbed. This leads to a reduction in the volume of the water structure and a lowering of viscosity is observed.

2.4 THE HYDRATION OF CALCIUM SULPHATE HEMIHYDRATE

When hemihydrate is mixed with water, the following reaction occurs:



Hemihydrate (solubility = 0.65g/100ml water at 20°C) is more soluble than the dihydrate (solubility = 0.24g/100ml water at 20°C) to which it hydrates.⁶ This difference in solubilities is probably the driving force for the reaction with the more thermodynamically stable dihydrate being formed. The reaction can occur in dilute suspensions, because of the very low solubilities involved, or in concentrated systems such as pastes, which set to a hard mass. The latter is of great technological importance and the reaction in this case is

strongly autocatalytic following an induction period. After this induction period, the reaction rate accelerates strongly until the depletion of the reactants takes effect and then the rate decays, finally reaching zero when the hemihydrate is totally depleted (see Figure 2.8). The small difference between adiabatic and isothermal results indicated that the accelerating rate of the reaction is not due to the effect of rising temperature and therefore the reaction may be followed by measuring temperature increase.

2.4.1 Mechanistic theories

The mechanism of the setting and hardening of plaster pastes was the subject of a scientific investigation by Lavoisier, in 1765³⁷, who proposed a theory which was later refined by Le Chatelier, in 1887⁴. The thickening and then hardening of mixtures of plaster and water were postulated as a direct result of the formation of microcrystals of gypsum. This was proposed as a "through solution" mechanism with the less soluble dihydrate precipitating on nuclei in the plaster as "needle-like" crystals.

After a few years Le Chatelier's theory began to be questioned and when Michaelis⁴ supported a colloidal theory for the hardening of cements, evidence began to appear which seemed to support the same approach for the hydration of plaster. In the intervening years to 1959 the arguments continued between the two theories, but the work was indirect in its approach. Ridge⁵ brought a more direct approach to the problem by examining samples of setting plaster in a reaction

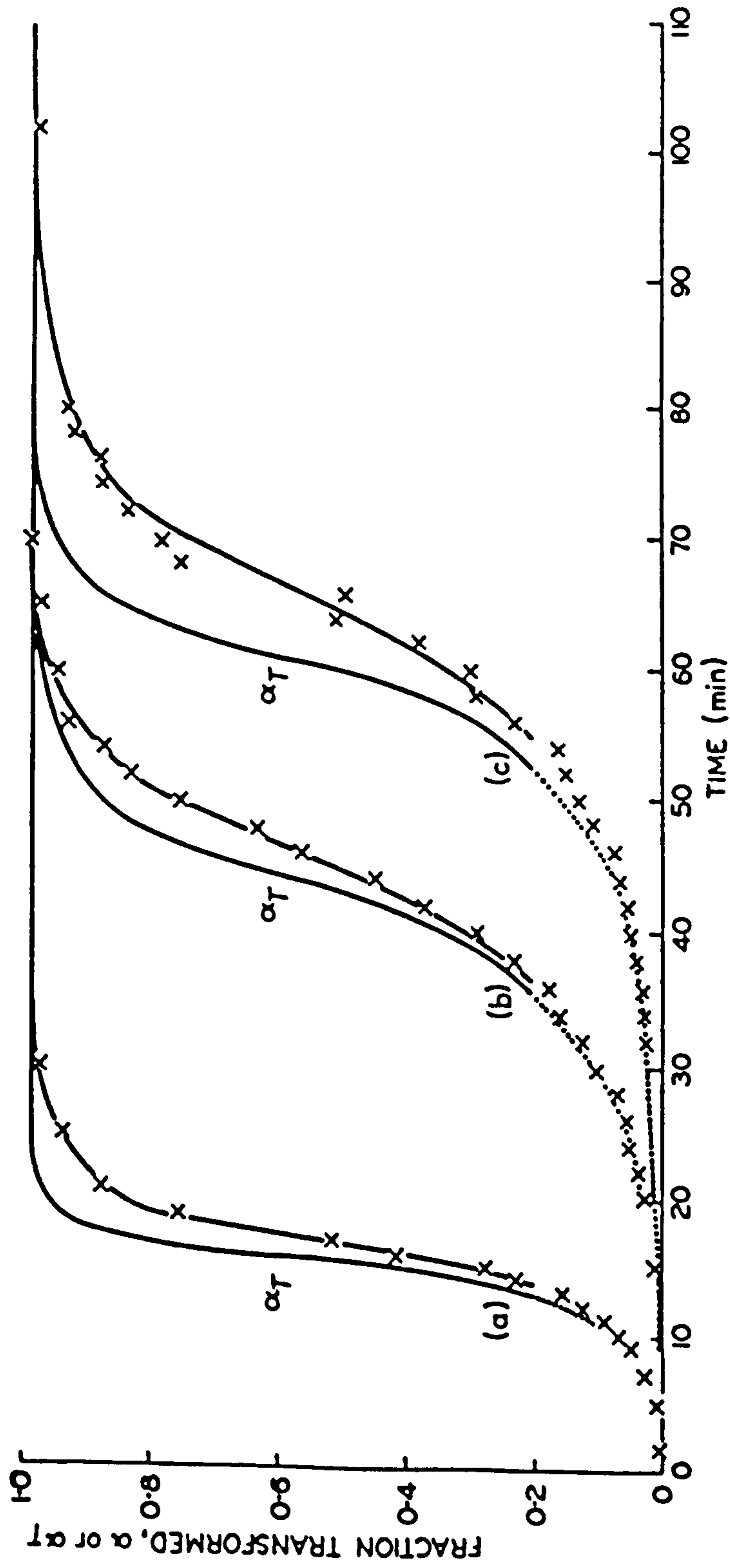


Figure 2.8: The fraction transformed plotted against time for hemihydrate/water reactions,

- (a) reaction accelerated by the addition of sodium chloride
- (b) unmodified reaction
- (c) reaction inhibited by the addition of di-sodium tetraborate.

Solid lines - the reaction has been carried out adiabatically and temperature increase has been taken as a measure of transformation. X- the reaction has been carried out isothermally and the course followed by chemical analysis of sample taken from time to time.

(after Ridge and Surkevicius³⁶).

vessel and of the set plaster's microstructure by using reflected light microscopy. He observed resolvable crystals of gypsum early in the setting process and found that the set plaster showed a fairly uniform grain size with no evidence of a finely divided fraction which would be expected if there was an intermediate gel stage.

Eipeltauer³⁸ made an optical study of the hydration reaction and observed that a clear zone appeared around the grains of hemihydrate and slowly moved inward to cover the entire grain. He interpreted this as a topotactic hydration to give a gel which then recrystallised as the dihydrate. Goto and Ridge³⁹ rejected this finding on the basis of their own investigations, which showed that the clear zone was anisotropic and continuous in orientation with the rest of the grain. They concluded that the grains of β -hemihydrate were porous and the observed phenomenon was a result of water slowly penetrating the pores and altering the light scattering properties. Complementary evidence for this effect was provided by α -hemihydrate grains which are not porous and in which this phenomenon has never been observed.

Hansen⁶ proposed another "gel-type" mechanism in which a layer forms on the surface of the grains hindering further hydration; this would result in the induction period. This layer then ruptures resulting in a sharp increase in the rate of reaction. This theory is supported by the rheological work of Chatterji and Kapse³⁵ (see Section 2.3.2) which indicated that the hemihydrate grains were covered with an adsorbed layer of water molecules.

Hansen's arguments though, have two drawbacks; firstly once the gel layer ruptures, why does the reaction proceed quickly rather than a new layer of gel being formed? Secondly, the layer of adsorbed water molecules would be expected to constitute the first step in the dissolution of the hemihydrate rather than to hinder it.

Further support for the "through solution" mechanism comes from the work of Biress and Thorvaldson⁴⁰ and that of Ludwig and Singh.⁴¹

Biress and Thorvaldson hydrated hemihydrate labelled with Ca^{45} or S^{35} isotopes in a supersaturated solution of calcium sulphate at 21°C . Their results were:

"In agreement with a mechanism which postulates a single passage of the structural units of the solid hemihydrate through solution and not consistent with one of direct hydration."

Ludwig and Singh's study of the hydration, using electrical conductivity and temperature rise as a means of following the reaction, showed that it is a 3-stage mechanism.

1. In the first stage, as soon as the hemihydrate comes into contact with water, it goes into solution, making it supersaturated with respect to dihydrate, and reaches a maximum conductivity. The conductivity, and thus the supersaturation, remains constant for a certain period of time, during which cluster and nuclei formation are taking place; this is the induction period.

2. The second stage begins once the nuclei have reached critical size, then rapid crystallisation occurs resulting in a suddenly decreasing conductivity.

3. In the third stage, as a result of depletion of the reactants, there is little crystallisation, resulting in little further change in the conductivity.

2.4.2. Kinetic theories

The kinetics of the reaction can be explained on the basis of seeded recrystallisation.⁶ Potential nucleating sites for the growth of dihydrate crystals exist on the grains of hemihydrate and crystals develop soon after the reactants are mixed. Microscopy reveals that the growing phase is in the form of plates and needles. Since growth occurs in only one or two dimensions the surface area of the growing phase is proportional to the mass rather than to 2/3 power of the mass, as in an ideal system.

The rate of hydration will be proportional to the surface area of the dihydrate and if the rate of diffusion from the dissolving phase to the growing phase is not the rate-determining step (unlikely because the two phases are so close), it will therefore also be proportional to the fraction hydrated; see Equation 1.

$$d\alpha/dt = K\alpha \quad (1)$$

where: α = fraction hydrated.
 t = time after reactants mixed.
 K = constant taking into account the rate of
 incorporation of the dissolved ions and water
 molecules into the growing dihydrate lattice.

$$\text{Hence } \alpha = Pe^{Kt} \text{ for } \alpha < \alpha_1 \quad (2)$$

where: P = effective fraction of dihydrate present at the
 beginning of the reaction (due to heterogenous
 nucleation).

α_1 = fraction transformed at the stage where depletion
 of reactants and mutual interference of growing
 centres takes effect.

The system described by Equation 1 is an idealized one, but
 despite this, Equation 2 has been shown by Ridge and
 Surkevicius³⁶ to represent the first half of the unmodified
 and accelerated hydration of the hemihydrate up to values of
 $\alpha_1 = 0.55$. However, with the inhibited reaction there are
 complications which have not been taken into account with
 this mathematical treatment.

Goto and Ridge³⁹ derived a theory to account for the
 latter stages of hydration by considering that the rate of
 growth of the dihydrate depended on both the rate of
 dissolution of hemihydrate and the surface area of the
 dihydrate. The rate of dissolution will be proportional to
 the surface area of the hemihydrate and because it occurs in
 approximately equiaxial grains, the surface area will be
 proportional to the $2/3$ power of the mass.

$$\text{Therefore } d\alpha/dt = K\alpha (1 - \alpha)^{2/3} \quad (3)$$

which leads to:

$$F(\alpha) = \frac{1}{2} \log \frac{[1 - (1 - \alpha)^{1/3}]^2}{1 + (1 - \alpha)^{1/3} + (1 - \alpha)^{2/3}} - \sqrt{3} \tan^{-1} \frac{[2(1 - \alpha)^{1/3} + 1]}{\sqrt{3}}$$

$$= Kt + P \text{ for } \alpha_0 < \alpha < 1 \quad (4)$$

where P = a measure of the extent of seeding of the reaction and is given by $F(\alpha_0)$.

α_0 = effective fraction of dihydrate present at the beginning of the reaction.

The effectiveness of Equation 4 can be seen in Figure 2.9; where $F(\alpha)$ is plotted against time for the isothermal hydration of hemihydrate accelerated by various amounts of added dihydrate and sodium chloride. Sodium chloride is believed to accelerate the hydration by increasing the rate of dissolution of the hemihydrate^{4,6}, whilst dihydrate accelerates by increasing nucleation^{4,6}. Therefore P should be unaffected by the presence of sodium chloride but K should increase and this is seen to be the case. In the case of dihydrate P should increase but K should be unaffected and this is again shown to be the case.

It has been shown by Goto and Ridge³⁹ that Equation 4 represents the accelerated or unmodified reaction for 93% of their course or for $\alpha < 0.93$; but it is still unsatisfactory with respect to inhibitors.

Goto and Ridge's theory has been criticised by Schiller⁶ who proposed his own equation using the same basic model, but this again was unsatisfactory in that it breaks down when accelerators are present.

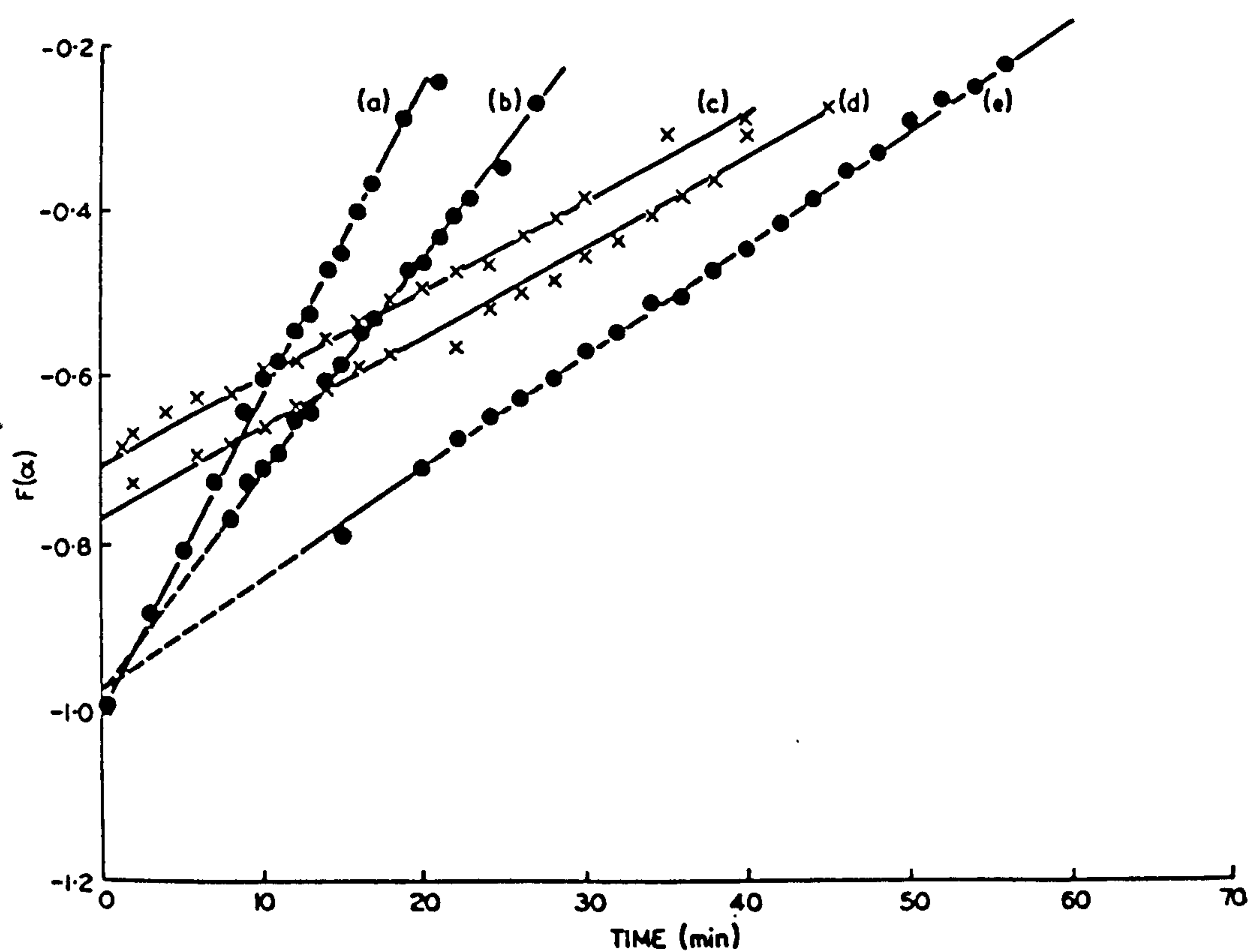


Figure 2.9: $F(\alpha)$ plotted against time for the isothermal hydration of hemihydrate (100g) by water (60g) at 20.5°C , where:

- (a) accelerated by 1.0g NaCl
- (b) accelerated by 0.5g NaCl
- (c) accelerated by 2.0g dihydrate
- (d) accelerated by 1.0g dihydrate
- (e) no accelerator.

(after Goto and Ridge³⁹).

Both theories have been shown by Combe⁴² to be unsatisfactory when applied to the hydration of α -hemihydrate, with and without additions of dihydrate; the previous theories being tested only on β -hemihydrate. Combe forwarded Braden's theory⁴² which considered the reaction to be diffusion controlled and gave the following equation:

$$\ln(1-\alpha) = -Kt^{2/3} \quad (5)$$

This has been shown to explain Combe's data but there was no work on accelerators or retarders.

Schiller⁴³ refined his theory to account for accelerators and retarders and proposed Equation 6:

$$t = K_1 v^{1/3} + K_2 (1 - \sqrt[3]{1-v}) \quad (6)$$

where: t = time since start of hydration at which fraction v has been transformed.

v = fraction transformed at time t .

K_1, K_2 = constants.

The theoretical approach is valid but the practical effectiveness of Equation 6 has yet to be verified.

A new rate equation has been proposed by Kim and Yoon⁴⁴:

$$dh/dt = K' (1-h)^{2/3} (1-0.186 h/x)^{-7} \quad (7)$$

where: h = the fraction hydrated.
 x = initial water to hemihydrate ratio.
 K' = rate constant independent of x .

Equation 7 is semi-empirical and a very high co-efficient of correlation is claimed.

2.4.3. The effect of additives

(a) Accelerators.

These are believed to work by two mechanisms:

- (i) Increasing nucleation by promoting seeding.
- (ii) Modifying the rate at which calcium sulphate is transported to, and built into, the lattice of the growing phase by increasing the rate of dissolution of the hemihydrate.

Ridge and Hill⁴⁵ have shown that dihydrate accelerates the hydration by mechanism (i) but also has an effect similar to mechanism (ii) when finely ground.

Ridge⁴⁶ has shown that neutral salts do not accelerate the hydration by mechanism (i) and proposed mechanism (ii) as a result of the kinetic effects observed (see Section 2.4.2.). This theory is supported by the rheological work of Chatterji and Kapse³⁵ (see Section 2.3.2.); which indicated that the hemihydrate grains were covered with an adsorbed layer of water molecules and that the amount of coverage was increased by the action of neutral salts. As this probably constitutes the first step in the dissolution of the hemihydrate, an increase in the coverage of an adsorbed water layer would increase the rate of dissolution.

Ridge et al⁴⁷ made a systematic study of the effects of various anions and cations on the hydration and analysed their results in terms of Ridge's partial kinetic theory (see Section 2.4.2.), taking the constant K as a measure of accelerating power. They found that univalent anions are equally effective, whilst the sulphate ion has more effect,

and in the case of the cations they found the order of effectiveness to be:



(b) Retarders (or inhibitors).

These are usually products of the hydrolysis of proteins but other materials such as borates, citrates, polyphosphates, tartrates and acetates are used.

Retarders are thought to act by processes which have been shown to have appreciable temperature coefficients, as indicated by the differences in the courses of the isothermal and adiabatic reactions (see Figure 2.8). The inhibited reaction is further complicated by the possible incorporation of the inhibitor into the growing phase and thus removed from the system as the reaction proceeds.

The theory that some retarders act by impeding the dissolution of hemihydrate is supported by the rheological work of Chattergi and Kapse³⁵ (see Section 2.3.2) which indicated that the hemihydrate grains were covered with an adsorbed layer of water molecules and that this coverage was reduced by the inhibitor being preferentially adsorbed (in the case of boric acid). As this probably constitutes the first step in the dissolution of the hemihydrate, a decrease in the adsorbed water layer coverage would decrease the dissolution rate.

Combe's work⁴² on the addition of lignosulphonate salts, indicated that the inhibitor in this case acted by "poisoning" nuclei for crystal growth rather than by effecting crystal growth rate, except at high concentration (5-10%) when the inhibitor modified the growth habit from spherulitic to small hexagonal crystals.



A practical problem in the gypsum industry is the variation of setting time from one batch to another and it would be advantageous to reduce this. In theory it is possible to achieve this by "poisoning" the existing dihydrate nuclei by use of a suitable inhibitor, and then to replace these nuclei with a stable nucleating agent. Work by Ridge et al⁶, with dihydrate as an accelerator and other selected inhibitors, and more recently with King⁴⁸, with calcium hydroxide as the accelerator have shown that this in principle is possible.

2.4.4. The reactivity of hemihydrate and the nucleation of dihydrate.

The reactivity, with respect to the hydration reaction, is dependant on the solubility, surface area, particle size and shape and the type and density of dihydrate nuclei present. Ridge et al⁴⁵ showed that the reactivity of commercial plasters is mainly dependent on the density and nature of seeding nuclei.

Although the effects of very high surface area are detectable, it was found that the particle size distribution for each sample was of the same order.

The nucleation of dihydrate in hemihydrate/water pastes appears to be heterogenous^{4,6}, and the nucleation sites are known to have the following features⁶:

- 1) Residual particles of dihydrate act as efficient nuclei.
- 2) Features on the surfaces of hemihydrate grains act as nuclei; and these are probably particular sites.
- 3) Areas of lattice damage or strain in the hemihydrate grains are known to be nucleation sites.

- 4) The nature of nuclei appear to be uncertain in that some are, and some are not, heat-resistant.

2.4.5. Summary

The hydration reaction of hemihydrate seems to be fairly well understood in most of its aspects. 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. In spite of this, the mechanisms of the unmodified, accelerated and inhibited reactions are understood.

Areas that require further elucidation are the nature of the nucleation sites and also their relationship with the kinetics. Further understanding in these fields could result in improved kinetic theories.

2.5 THE MICROSTRUCTURE OF SET PLASTERS

(a) Formation.

Hemihydrate hydrates to dihydrate in dilute suspensions, or in the form of pastes which set to hard masses (see Section 2.4). The hardened paste is not a compact solid, but a porous material with a relatively large internal surface, consisting of interlocking plates and needles.

(b) Microstructure .

The microstructure of hardened gypsum pastes affects most of the physical and engineering properties of the material, and in particular its rigidity⁴⁹ which is due to the skeleton of interlocking crystals⁴. The strength will depend on:

- (i) The size and shape of component crystals. The habit can be modified by addition of materials such as sodium hexametaphosphate such that equaxial grains are obtained; this results in less crystal-crystal contact and the hardened paste has little mechanical strength.
- (ii) The strength of the bond between the crystals, and as a result the mechanical strength, could be modified by the addition of materials which are adsorbed at the interface.
- (iii) It is possible that impurities built into the crystals will harden them or predispose them to fracture.
- (iv) The amount of empty space in the set mass will be determined by the water content of the mixture. It has been demonstrated^{4, 49} that strength increases as the water/plaster (W/P) ratio is reduced. In practice the water content is dependent on the nature of the plaster (see Section 2.3.1), and if this could be reduced the strength could be significantly increased.

(c) Effect of additives.

Combe⁴² studied the effect of lignosulphonate salts (see Section 2.4.3 (b)) on the microstructure and strength. He found that for a low concentration of the additive (0.5%), the additive reduced the water requirement, which resulted in a material of greater density and strength. However, at high concentrations (5-10%), the additive changes the crystal habit, resulting in a reduction in intercrystalline bonding and the formation of a denser, but weaker material.

(d) Examination of the pore structure.

Mikhail and Malek⁴⁹ studied the microstructure of set gypsum plasters by nitrogen adsorption and from the isotherms derived the pore size distribution and the specific surface area. The results showed that the microstructure from the unmodified reaction at low W/P ratios had a dual pore distribution, with small (S-) pores ($\bar{r} = 10 \text{ \AA}$) and large (L-) pores ($\bar{r} = 70-80 \text{ \AA}$). When the W/P ratio was increased, the S-pores size increased to $18 \text{ \AA}$ and the L- pores disappeared.

They concluded that S- pores were crystal pores, their size being a function of W/P ratio, and the L- pores were capillary pores, disappearing at high W/P ratios due to higher hydration rates which resulted in them being filled. This provides complementary evidence for a "through-solution" mechanism.

When a retarder (lignosulphonate salt) was added, the dual pore distribution was found for all W/P ratios and electron microscopy showed that this was due to a change in crystal habit.

With an accelerator (sodium chloride) it was found that the capillary pores were almost filled at every W/P ratio; this is probably due to the enhanced hydration rate.

(e) Microstructure and strength.

Mikhail and Malek⁴⁹ measured the compressive strength in conjunction with electron microscopy studies. In the case of the unmodified plaster they found that as the W/P ratio was reduced, the strength increased, and the grain size was reduced. They concluded that at high W/P ratios the larger

crystals grew at the expense of smaller crystals, which resulted in a loss of intercrystalline bonding.

In the case of the retarded reaction they drew the same conclusions as Combe⁴² (see Section 2.5(c)) and with the accelerated reaction just pointed out that the mechanism was different to the retarded reaction and the strength was reduced to approximately a quarter of that of the unmodified microstructure.

Phani⁵⁰ obtained an empirical expression relating the elastic modulus and porosity (see Equation 8), for four gypsum systems over the entire range of porosities.

$$E = E_0 (1 - ap)^n \quad (8)$$

where: E = Elastic (Young's) modulus at porosity p

E_0 = Elastic modulus at zero porosity.

a & n = material constants related to the packing geometry and pore structure of the material.

2.6 MEASUREMENT OF THE MECHANICAL PROPERTIES OF SETTING PLASTERS

The compressive strength of a set plaster (e.g. 70N/mm^2)¹⁸ is typically a factor of ten larger than the bending strength (e.g. 7N/mm^2)¹⁹ which in turn is typically a factor of two larger than the tensile strength (e.g. 3N/mm^2)¹⁹.

Not surprisingly, the mechanical failure of set plaster casts has been shown to be due to tensile stresses^{51,52}, which are caused by bending.⁵¹

The three-point bend test was chosen to measure the plaster's set strength. The relationship between the maximum stress (often referred to as the modulus of rupture), applied

force and specimen dimensions in the three-point bend test are shown in Figure 2.10. The disadvantages of this test are that only a small area of the specimen is subjected to the maximum stress (see Figure 2.11) and a stress gradient exists along the bar and also through the thickness of the test specimen. However, the test is simple and errors can be reduced by statistically analysing a large number of samples (typically 20 or more⁵⁵). Assuming the strengths fit a normal distribution, the mean value ($\bar{x}$) can be calculated and variation can be given as the standard error of the mean (see Equation 9):

$$\text{Standard error of mean} = \frac{\sigma_{n-1}}{\sqrt{n}} \quad (9)$$

where: σ_{n-1} = sample standard deviation
 n = number of specimens

Three-point test results are very useful in comparative work as long as the specimens geometry, surface finish and strain rate are kept constant, and in many cases is the closest approximation to the mode of failure in use.

2.7 THE ACOUSTIC EMISSION (A.E.) OF SETTING PLASTERS

(a) Principles of A.E.

When a dynamic process occurs in or on the surface of a material some of the energy, which is rapidly released, generates elastic stress waves. These waves propagate through the material as longitudinal and shear waves which are usually of low amplitude and high frequency.

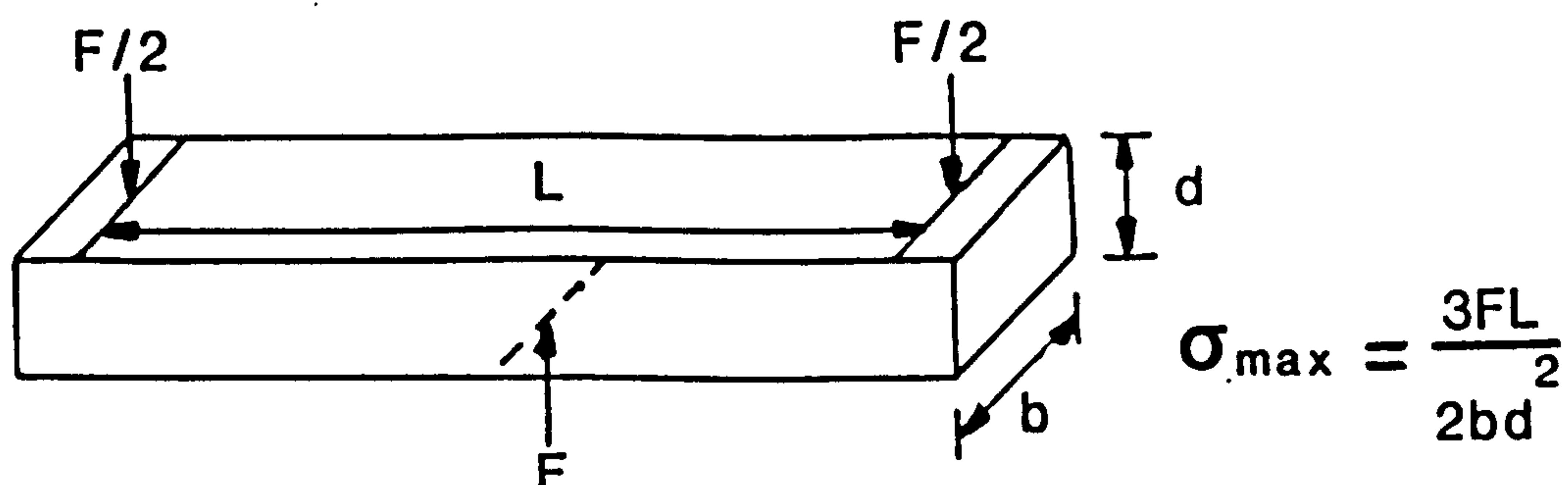


Figure 2.10: The three-point bend test and the relationship between maximum stress, applied force and specimen dimensions.

(after Davidge⁵³).

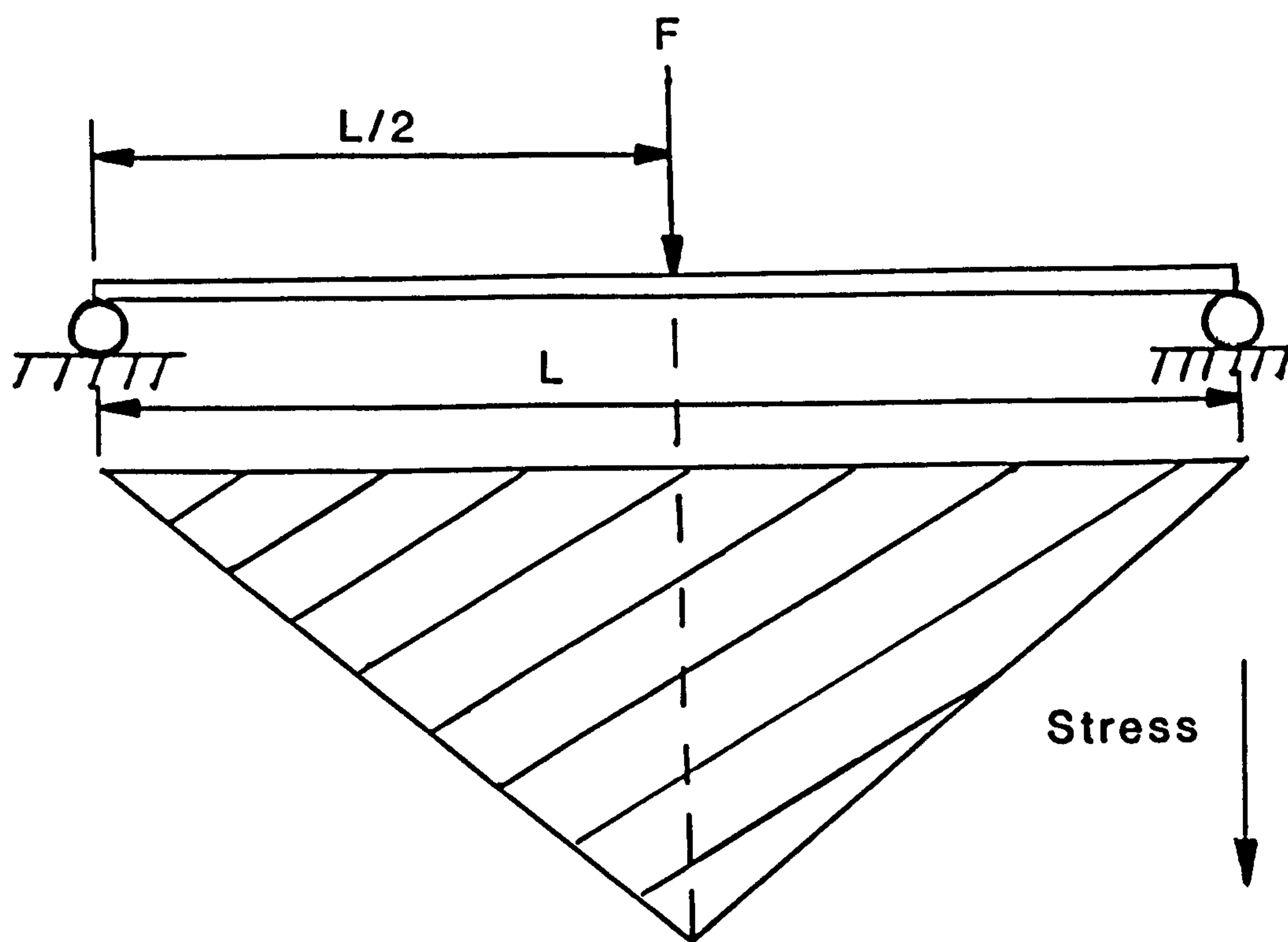


Figure 2.11: The tensile stress distribution for the three-point bend test.

(according to Benham as presented by Savage⁵⁴).

Sensitive transducers may be used to amplify the very small surface displacements associated with these waves. The transducers, which convert the displacements into electrical signals, must be coupled to the surface as efficiently as possible. The electrical signal is then amplified and in an idealised case the signal from a single displacement would be as shown in Figure 2.12.

The simplest method of obtaining an indication of A.E. activity is to count the number of amplified pulses (N_R) which exceed an arbitrary threshold voltage (V_t), a technique known as ring-down counting⁵⁷, and the signal in Figure 2.12(a) would give 12 ring-down counts (see Figure 2.12(b)). The threshold voltage is usually set at 1 volt and the total system amplification at about 90dB (approximately $\times 32,000$). The signal shown in Figure 2.12(a) is produced by a single surface displacement and it is convenient to call this "an event". This mode of analysis is known as "event counting" (see Figure 2.12(c)). The peak voltage (V_p) is a function of the acoustic energy (E) and the approximate relationship⁵⁸ is:

$$E \propto (V_p)^2$$

Elastic waves produced by a source event undergo significant modification before and during analysis and so complementary experiments, such as microscopy, are needed to assist in identification.

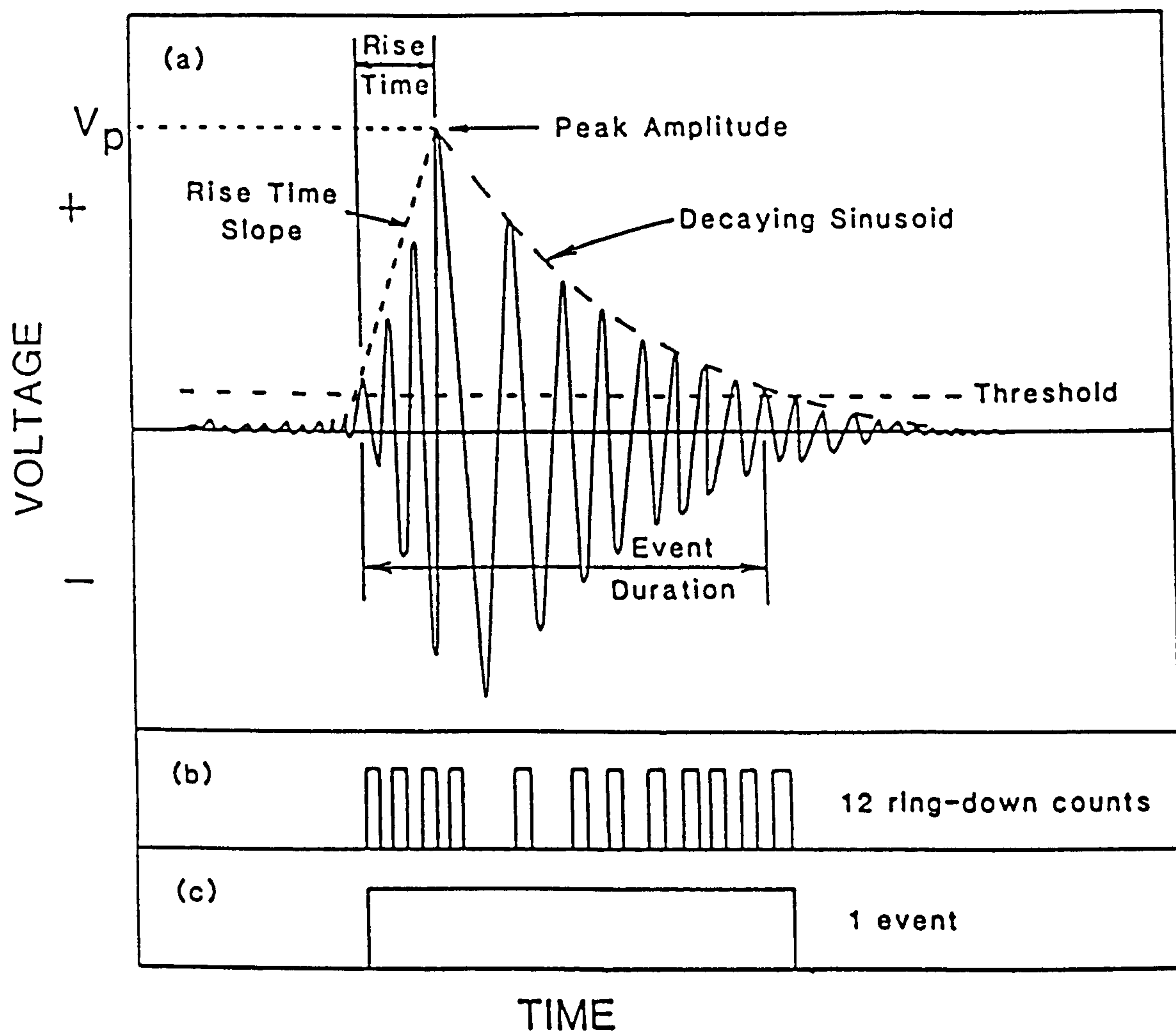


Figure 2.12: The idealised waveform showing some of the parameters used to characterise emissions.

(after Rawlings⁵⁶).

(b) Acousto-ultrasonic testing

A calibration technique used in A.E. studies, in which a pulsed transducer delivers a standard signal to the detector transducer, was discovered to be a sensitive way of monitoring the development of a setting cement structure⁵⁹. As a result this technique was a useful tool for studying the hydration of cement and may also be applicable to studies of the setting of gypsum plasters. This technique of monitoring artificially-induced waves by A.E. techniques is known as acousto-ultrasonics.

3. EXPERIMENTAL

3.1 CHARACTERISATION OF CALCIUM SULPHATES AND THEIR HYDRATES

The reagents were either commercial products or laboratory prepared, normally in the form of powders, and characterised by the following methods:

(a) X-ray powder diffraction analysis.

The crystalline phases present were determined using a Philips diffractometer using copper K_{α} radiation.

(b) Differential Thermal Analysis (DTA).

A standard DTA rig⁶⁰ was used using crushed quartz as the inert thermal reference, static air as the furnace environment and a controlled heating rate of approximately $13^{\circ}\text{C}/\text{min.}$ in the range $0\text{--}600^{\circ}\text{C}$. The chromel/alumel thermocouples were connected to a chart recorder such that the sample temperature and temperature difference were recorded simultaneously.

(c) Thermogravimetric Analysis (TGA) and water content.

Combined DTA/TGA measurements were made using 10 or 50g samples* of the reagent and a Stanton-Redcroft Series 780 simultaneous thermal analyser. Heating rates of $10^{\circ}\text{C}/\text{min.}$ and $15^{\circ}\text{C}/\text{min}^{\dagger}$ were used, with static air as the furnace environment. The combined DTA/TGA curves, in the range $0\text{--}600^{\circ}\text{C}$, were obtained by the use of a data-analysing package.

In some cases a static-temperature method was used in conjunction with the DTA/TGA method. Alumina crucibles, each containing an approximately 1g sample, were heated in a furnace at 400°C (for 8 hours) and the weight loss was found by reweighing the crucibles after allowing them to

cool in a desiccator to room temperature.

(d) Particle size analysis.

A Malvern 3600 particle size analyser was used to determine both the particle size and size distribution of the powders. The technique involves determining the distribution of diffracted light when a laser beam passes through a dilute suspension of the powders in ethanol⁶¹. Preparation of the suspension involved mixing 0.1g of the powder with ethanol (A.G., 200ml) in a beaker. The beaker was then placed in an ultra-sonic bath for 2 minutes, whilst being continuously stirred. A longer time in the ultra-sonic bath is thought to break-down the particles rather than to have the desired effect of inducing agglomerates to disperse. The suspension was then pipetted into the sample cell, which was already 90% full of dispersant (A.G. ethanol), until an observation ratio of approximately 0.25 was reached. The Malvern particle sizer then measured the diffraction angle θ ; the smaller the particle size, the greater the diffraction angle. By measuring the radial distribution of diffracted light, a data-analysing package calculated the distribution of particle sizes.

(e) Specific surface area measurements.

A standard nitrogen adsorption volumetric rig was used and the measurements were analysed using the Brunaver, Emmett and Teller (BET) theory to determine surface areas.⁶²

Note: The normal conditions for the DTA/TGA measurements were a ^{*}10mg sample and a heating rate of ⁺10°C/min.

(f) Optical and scanning electron microscopic studies.

The morphology of powders was examined by two methods:-

(i) Transmission optical microscopy.

Samples were prepared by dispersing a small amount of the powder with cedar wood oil on a glass slide. A cover slip was then placed on top and the samples were examined using a Reichert microscope.

(ii) Scanning electron microscopy.

Samples were prepared by dispersing a small amount of the powder with ethanol. A drop of the suspension was then pipetted onto the top of an aluminium stud. The ethanol was allowed to evaporate off and then the surface of the stud was gold coated to prevent charging under the electron beam. The samples were examined using the 'JEOL T-200' Scanning Electron Microscope (S.E.M.).

(g) Chemical analysis.

Quantitative analysis was conducted on the commercial plasters whilst qualitative analysis was performed on the other reagents using the following methods:

(i) Quantitative analysis.

This was performed by the Electron Probe Micro-Analyser (EPMA) using a 'JEOL JSM-35' SEM, fitted with an Energy Dispersive Analysis of X-rays (EDAX) system for the major elements Ca and S, and the Wavelength Dispersive X-ray (WDX) crystal spectrometer for analysis of the trace elements Na, K, Mg and Si.

Plaster samples were prepared by making a pellet, using 0.5g of plaster pressed in a 1/4" die with an applied force of 30KN. The pellet was then mounted in cold setting resin, and once set the surface was polished to a 1 micron finish and then carbon coated to prevent charging.

In both quantitative analysis techniques, the polished surface is bombarded with electrons, which leads to secondary emission of X-rays with wavelengths and energies characteristic of the elements present in the area under analysis^{63, 64}.

With EDAX, a data-analysing package compared the intensities of X-rays produced with those of a set of elemental standards. By applying corrections for atomic weight (Z), absorption (A), and fluorescence (F), known collectively as the ZAF corrections, the chemical composition of the surface was determined.

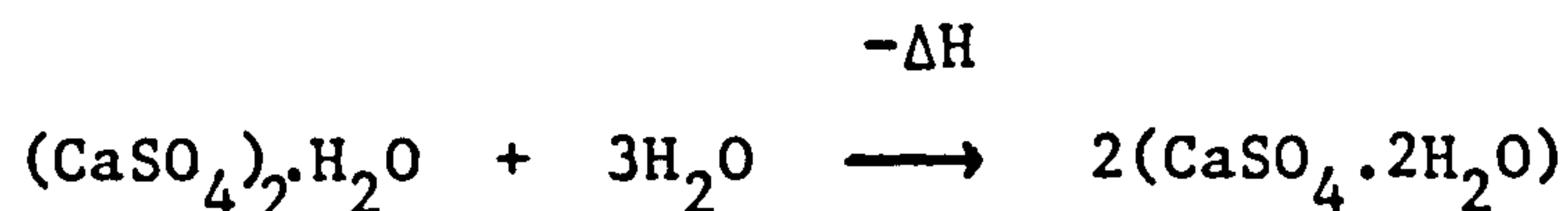
The WDX crystal spectrometer was used for trace element analysis because the chance of spectral overlap is reduced, and as a result the resolution is one or two orders of magnitude greater than EDAX^{63, 65}; although EDAX has the advantage of recording speed and the detection processes efficiency is three orders of magnitude greater.

(ii) Qualitative analysis.

This was performed using the EMPA of the 'JEOL T-200' SEM using EDAX, which scans qualitatively for all elements heavier than Na. Samples were prepared in the same manner as those used for the examination of the powder morphology (see Section 3.1.(f).(ii)).

3.2 THE HYDRATION OF CALCIUM SULPHATE HEMIHYDRATE

On mixing calcium sulphate hemihydrate with water, the following reaction occurs:



The hydration reaction (Section 2.4), and the microstructure and strength of the set pastes (Section 2.5) have been discussed previously.

A series of experiments were performed to provide a greater insight into the above phenomena.

3.2.1. Water : Plaster (W/P) ratio-determination in commercial products

Determination of the W/P ratio used in gypsum plaster application is important because of the pronounced effect on the hydration reactions and the mechanical properties and microstructure of the set plaster (Section 2.5). Thus the W/P ratios, in which experiments were to be conducted, were determined. The W/P ratio was determined using two types of plaster of Paris bandage: Gypsona (Smith and Newpew Ltd) and Cellona (Lohmann GmbH and Co.).

The commercial formulation is given in Table 1.1 and to calculate the W/P ratio, the water pick-up and amount of hemihydrate on each bandage were determined. This was done using the following methods:

(i) Water pick-up

The bandage was immersed in a large beaker containing tap water heated to 30°C and held until all trapped air bubbles were released. The bandage was then removed by hand and given a gentle squeeze (Note 1), and the water pick-up was found by reweighing. A number of separate determinations were made for each type of bandage.

(Note 1: A gentle squeeze is a subjective quantity and therefore the above method was used by two people to give an indication of the likely spread of results).

The plaster-loss from the gauze bandage due to handling was also determined.

(ii) Determination of hemihydrate content

A silica crucible, containing a plaster bandage with the plastic former removed, was heated for 1 hour in a furnace at 1000°C to burn off the gauze and binders, and to dehydrate the calcium sulphate hydrates. The residue was then cooled to room temperature in a desiccator and reweighed. The dehydration products from the bandage were confirmed by X-ray diffraction analysis (Section 3.1(a)) to be insoluble anhydrite, β -CaSO₄, and the hemihydrate content was calculated, assuming 98% hemihydrate in the initial plaster.

3.2.2 Calorimetry of the hydration reaction

When plaster is mixed with water the ensuing reaction is exothermic (Section 2.4). If this reaction is performed under adiabatic conditions, the temperature rise (ΔT) will be in proportion to ΔH which will, in turn, be in proportion to the mole fraction of calcium sulphate dihydrate.

The progress of the reaction was followed using a simple calorimeter consisting of a covered glass pot (ht. 50mm, dia. 22mm), placed in a beaker covered with aluminium foil and a lid, and containing cotton wool insulation. The plaster slurry was poured into the glass pot to a height of 40mm and a chromel/alumel thermocouple was placed in the slurry at a depth of 25mm. The thermocouple was connected to a chart recorder to monitor the temperature change (ΔT) as a function of time.

A typical ΔT versus time curve and the important parameters which can be derived from it are shown in Figure 3.1.

3.2.3 Phase analysis of the hydration products

(a) Hemihydrate/water slurries.

The degree of reaction was followed by stopping the reaction at various stages and determining the phases present using powder X-ray diffraction and thermal analysis.

The plaster slurry was poured into silicone rubber mould which was placed in a 'Vindon' salts humidity cabinet to

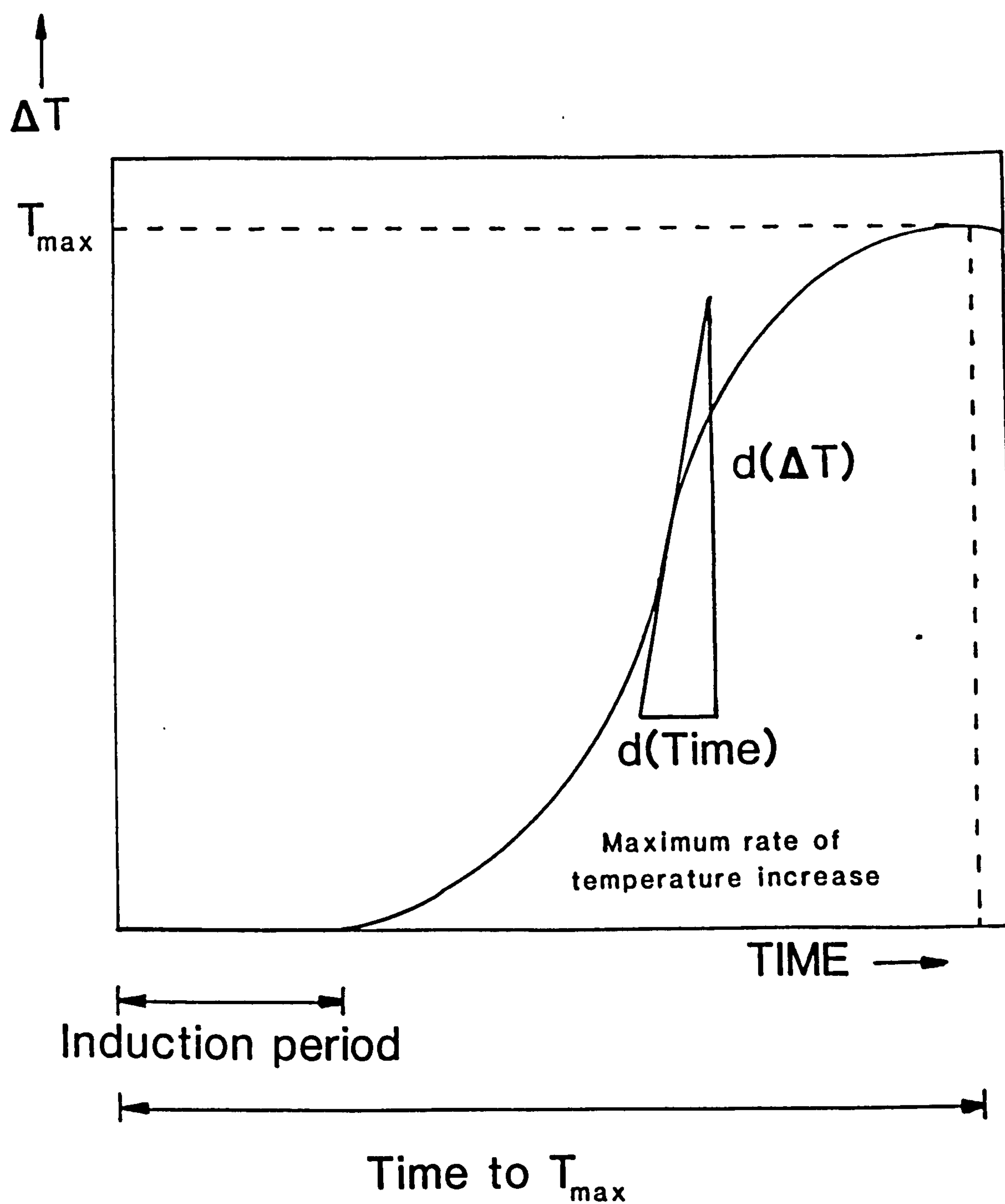


Figure 3.1: Typical $\Delta T/\text{Time}$ curve for the exothermic reaction of calcium sulphate hemihydrate with water.

keep temperature and humidity constant (30°C , 63%RH).

The chemical reaction was stopped by washing the specimen with excess ethanol (A.G.). To improve the efficiency of removal of the reaction solution the sample was crushed with a pestle while flushing with the ethanol.

(b) Soluble anhydrite/dihydrate solution reaction mixtures.

3g of soluble anhydrite was mixed with 3cm^3 of saturated dihydrate solution and then placed in a paper soxhlet thimble. The soxhlet was then placed in a sealed container to prevent loss of water by evaporation, with sufficient saturated solution to immerse the reaction mixture.

The mixtures were left to react for periods of 1, 10 and 100 hours at 30°C and 63%R.H. The reaction was stopped by removing the solution by washing with excess ethanol (AG) which was 'pulled through' the mixture held in paper soxhlet by a water pump. The remaining alcohol was allowed to evaporate off and the reaction products were then finely ground for x-ray powder diffraction and thermal analysis.

(c) Interpretation of the thermal analysis curves.

It is possible to calculate the amount of hemihydrate and dihydrate present in a mixture from the thermal analysis curves shown in Figure 3.2 and then in some experiments the combined percentage due to soluble and insoluble anhydrite was obtained by difference. The first weight loss (see Figure 3.2) corresponds to the loss of $3/4$ of the water present in the gypsum lattice to give hemihydrate:

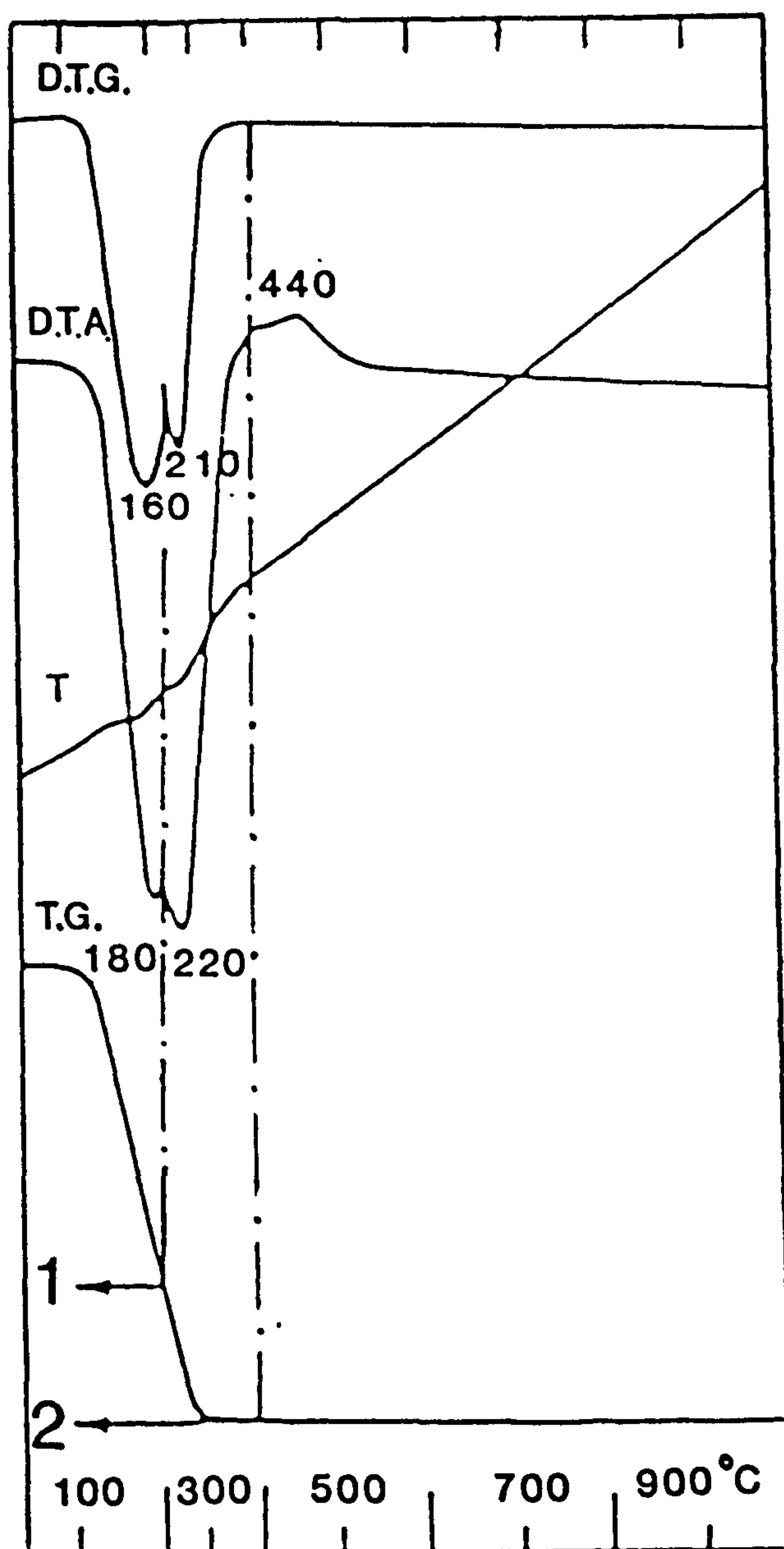


Figure 3.2: The thermal curves of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at a heating rate of 10°C per minute.

(after Todor⁶⁶).



(theoretical weight loss is 15.69%)

Thus the amount of dihydrate can be calculated. The second weight loss corresponds to the last half molecule of water lost from the hemihydrate:



The total amount of hemihydrate present is due to that produced from the dihydrate during the analysis (theoretical wt. loss is 5.23%) and that, if any, originally present in the reaction mixture (theoretical wt. loss is 6.21%). Thus the amount of hemihydrate can be calculated by difference.

Because of the close proximity of the two weight loss temperatures and the overlap of dihydration peaks, errors are easily introduced into this determination.

3.2.4 The electrical resistance of setting gypsum plasters

Ludwig and Singh⁴¹ used the electrical conductivity of plaster pastes to follow the hydration reaction and it was thought that this technique would provide a greater insight into the reactivity of the hemihydrate.

A cell consisting of a covered glass pot (ht. 50mm, dia. 22mm), in which the plaster slurry was poured to a depth of 40mm, contained two platinum wire electrodes (dia. 0.35mm) placed 1cm apart, inserted through the lid and placed to a depth of 15mm in the slurry. The electrodes

were connected to a Hewlett-Packard 4192A-L.F. AC impedance analyser. The frequency was set to 1000Hz and the resistance (in ohms) was measured as a function of time. Once the reaction was completed the set plaster was cracked open and the smallest distance between the electrodes was measured. Results were then quoted as resistance/electrode distance ($\Omega \cdot \text{cm}^{-1}$).

3.3 THE SETTING OF GYPSUM PLASTERS

Hemihydrate pastes hydrate to the dihydrate to form hard masses. The hardened paste is a porous solid consisting of interlocking dihydrate crystals. The microstructure and strength of set pastes (Section 2.5), and their relationship during the setting process are important, in that, if the microstructure can be modified to achieve certain mechanical properties an improved splinting material could result. This relationship was investigated in the following series of experiments.

3.3.1 The strength of setting plasters

The bend strength was measured by the three-point bend test (Section 2.6), within the range of W/P ratios found in gypsum plaster application.

(a) Specimen preparation.

The test specimens were in the form of bars (50 x 10 x 10mm) and were prepared in batches of five. Plaster was sprinkled on the surface of distilled water in a crystallisation dish, with a gentle mixing for the amount of plaster and water being adjusted to give the desired W/P ratio over a period of 10 secs.

The resulting mixture was then slowly stirred for a further 50 secs., making sure no air bubbles were entrapped. The slurry was then cast into bars in a silicone rubber mould, which had been lightly greased. The mould was then gently vibrated to remove any trapped air and left to 'set'. During 'setting', temperature and humidity were kept constant at 30°C and 63%RH. by placing the moulds in a 'Vindon' salts humidity cabinet. After 30 mins. any excess plaster was scraped off the surface of the mould, the bars were then removed and returned to the humidity cabinet until required for testing. Prior to testing, the surfaces were rubbed on fine silicon carbide paper to remove any surface irregularities. Exceptions to the above preparation were as follows:-

(i) For strength development tests.

When using α -hemihydrate the excess plaster was scraped off after 10 minutes and the specimens were removed from the mould after 20 minutes. For the β -hemihydrate excess plaster was removed after 20 minutes and the specimens were removed from the mould after 40 minutes. In neither case were the top surfaces of the bars dressed with SiC paper.

(ii) 'Wet' testing.

Test specimens were prepared as in (i) except that after the excess plaster was scraped off, a thin film of polyethylene was placed on top of the mould to minimise moisture loss. When the specimens were removed from the mould they were immersed in a saturated solution of dihydrate until required for testing.

(iii) With additions of dihydrate and/or potassium sulphate.

Tests were only performed on the α -hemihydrate and the difference in the technique, as described in (i), were that the excess plaster was scraped off after 5 minutes and specimens removed from the mould after 30 minutes.

(b) Determination of full set strength.

Full set strength was measured on bars which had been left to set for 200 hours. Three-point bend strength was measured on an Instron test machine, with:

(a) distance between lower rollers (L) = 35mm

(b) a strain rate of 0.2mm/min.

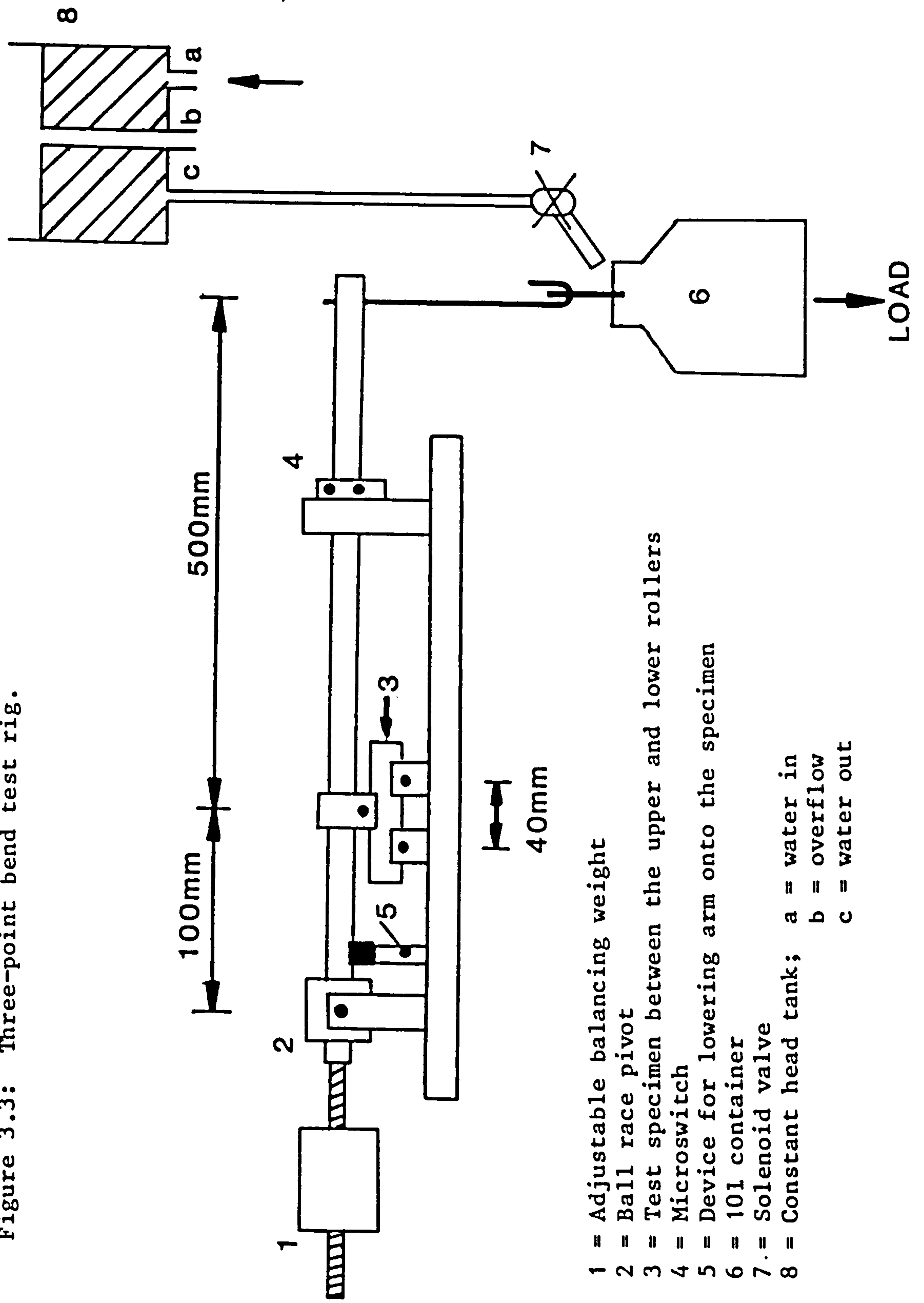
After each test, the breadth (b) and depth (d) of the bar were measured accurately with a micrometer gauge.

(c) Determination of strength build-up.

Because of the problems in transporting fragile specimens at frequent intervals to the Mechanical Testing laboratory a simple 3-point bend test rig was designed and built to use alongside the humidity cabinet (see Figure 3.3).

The rig was operated by placing a specimen on the lower rollers and the top roller was gently lowered onto the surface. A constant loading rate of 36N/min. was provided by adding water from a constant-head tank to a 10l container. When fracture occurred the arm operated a microswitch, which in turn closed a solenoid valve, thus cutting off the water supply. The load supplied to the end

Figure 3.3: Three-point bend test rig.



of the arm was then found by measuring the volume of water in the container. The failure load was then calculated taking moments around the central pivot (i.e. failure load (F) = 6 x applied load).

3.3.2. The microstructure of setting plasters.

(a) Scanning electron microscopy.

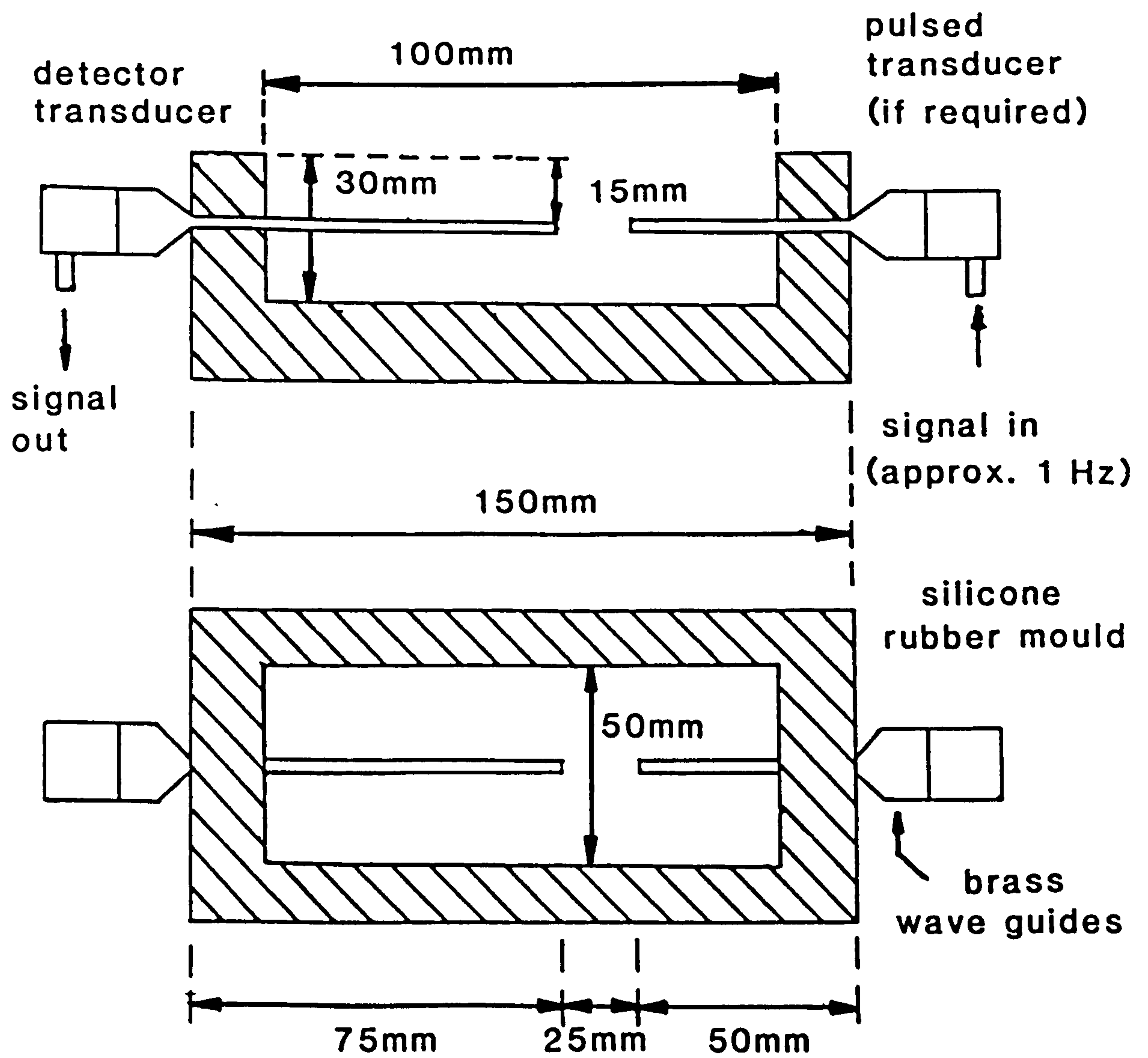
Samples were prepared by taking a thin section from the fractured surface of the bend test specimen (Section 3.3.1). These were attached to the top of aluminium studs by using "Durofix" or similar adhesive. To prevent charging the top surface of the specimen was gold coated and 'silver dag' was applied to the side of the sample to provide good electrical contact between fracture surface and the stud. The samples were then examined using the 'JEOL T-200' SEM.

To examine the microstructure during setting, samples <2mm thick were removed from the fractured specimen and washed with ethanol (A.G.) to remove the aqueous solution and "arrest" the reaction at that stage.

(b) Acoustic emission.

The experimental set-up is shown in Figure 3.4 but was used without the pulsed transducer, with the plaster slurry poured into the silicone rubber mould. The electrical signal from the detector transducer was then amplified and analysed by an electronics package. Total system amplification was set at 99dB and the threshold for the event measurements was set at 18dB. Ring counts and events were measured over 1 min. periods and quoted as rates.

CROSS SECTION



TOP VIEW

Figure 3.4: Experimental set-up used for the acoustic emission and acousto-ultrasonic testing of setting gypsum plasters.

(c) Acousto-ultrasonic testing.

The set-up is as shown in Figure 3.4 with the pulsed transducer transmitting a continuous signal of 1Hz frequency. Total system amplification was set at 93dB with the threshold for the event measurements set at 24dB. Ring counts, events and the amplification distribution of events were measured over 1 min. periods. Because one pulse is detected as one event, the results were quoted as ring counts per event (or pulse) and as the average amplitude of events.

3.3.3. The porosity of set plasters

The open porosity of set gypsum plasters was determined from the amount of toluene absorbed by a block of set plaster when immersed in a beaker of toluene placed in a vacuum desiccator. The test specimens in the form of blocks (18 x 18 x 18mm) were cast in a stainless steel mould in batches of five at a time. The blocks were prepared and treated during setting in exactly the same manner as the strength test specimens (see Section 3.3.1). The blocks were removed from the mould, weighed and then immersed in 200ml of toluene (A.G.) in a beaker. Saturation of the blocks with toluene was completed by placing the beaker in a desiccator which was evacuated until the pressure was near that of toluene at room temperature (22 mmHg at 20°C)⁶⁷. This process helped with the removal of trapped air from the pores. When the blocks were removed from the desiccator, surplus toluene on the surface was absorbed on a filter paper and the saturated block was reweighed in a sealed container to minimise loss of toluene by evaporation.

The volume of the blocks was determined by resaturating with toluene and weighing while suspended in a beaker of toluene using a wire of known weight.

The volume of the open pores and that of the saturated block were calculated taking the density of toluene to be 0.8669 g.cm^{-3} (20°C)⁶⁸.

The percentage open porosity is given by:

$$\frac{W_{\text{sat}} - W_{\text{unsat}}}{0.8669 \times V} \times 100$$

where: W_{sat} = weight of block saturated with toluene.

W_{unsat} = weight of unsaturated block.

V = volume of saturated block.

The bulk density of the block will be equal to W_{unsat}/V (g.cm^{-3}) and the density of dihydrate is 2.32 g.cm^{-3} . Therefore the calculated percentage of true porosity will be equal to:

$$[1 - (W_{\text{unsat}}/[2.32 \times V])] \times 100$$

The true porosity accounts for both open and closed pores present in the sample and therefore any difference between the calculated true and measured open porosity should be due to the closed pores present in the sample.

3.4 LABORATORY PRODUCTION OF PLASTER BANDAGES

A scaled down version of the industrial preparation of the Gypsona bandage was used for this process (See Section 1). The binders polyvinylacetate (10g) and hydroxypropylcellulose (10g) were dissolved in methylene chloride (800g) contained in a mixing tank (dia. 200mm, ht. 300mm) fitted with four baffles to prevent a vortex being formed during stirring. The mixture was stirred with a 6-bladed turbine impeller which was driven by a mechanical stirrer. The plaster (1006g), of known $\alpha:\beta$ hemihydrate ratio, was then added and stirred to ensure complete mixing. The slurry was then transferred to a spreading box, where pre-weighed 2m lengths of cotton gauze were evenly coated. The methylene chloride was then allowed to evaporate off in a fume cupboard and the bandage was then wrapped around a pre-weighed plastic former.

The completed bandage was then weighed to allow calculation of the hemihydrate content. The determination of water pick-up was performed as described earlier in Section 3.2.1(i).

The plaster remaining in the spreading tank was used for experiments to investigate the effect of the binders on the hydration reaction and products.

4. RESULTS

4.1 THE CHARACTERISATION OF THE HEMIHYDRATES

The hemihydrates were commercial products and obtained from three sources:

- (i) British Gypsum; α - and β - plasters
- (ii) "Bogardt; α - and β - plasters
- (iii) Lohmann; Guilini plaster.

(a) X-ray powder diffraction analysis

The five plasters showed no noticeable differences in the positions of the peaks in the diffraction patterns. Slight differences were noted in the intensity of some peaks from the α - and β - hemihydrates. On fine grinding of the α -hemihydrate a pattern almost identical to that of the β - hemihydrate was obtained. These results indicate that the α - and β - forms have the same crystal structure. The minor differences in the diffraction patterns are probably due to differences in crystallite as opposed to particle size.

(b) Differential Thermal Analysis (D.T.A.)

This method has been used by some workers to differentiate between the two forms of hemihydrate, on the basis of the position of an exothermic transition between 200°C and 400°C, where the soluble anhydrite transforms to insoluble anhydrite (see 2.2.2.(f)).

The results obtained with the commercial plasters are shown in Table 4.1.

Table 4.1: Position and size of the exothermic peak observed when examining hemihydrates by D.T.A.

Plaster Form	British Gypsum	" Bogardt	Guilini
α as received	large (225°C) small and broad (380°C)	large (225°C) small and broad (375°C)	-
β as received	large (355°C)	small (230°C) large and very broad (410°C)	-
Finely Ground α	large and quite broad (355°C)	large and very broad (380°C)	-
Plaster (α and β mixture)	-	-	small (225°C) large (380°C)

Because of the difficulty in measuring areas under the peaks, and also because part of the exotherm at 230°C is hidden by the much larger dehydration endothermic peak at 180°C , this technique is limited to a qualitative analysis of the hemihydrates.

When the British Gypsum α - form was finely ground the position of the exotherm moved from 225°C to 355°C , the temperature at which the β - form shows the transition (see Fig. 4.1). This supports the findings from X-ray diffraction that the difference between α and β is largely due to crystallite size and not crystallographic structure.

(c) Thermogravimetric analysis (T.G.A.) and water content

Measurements made on the five commercial plasters are shown in Table 4.2.

The weak endotherm exhibited in two of the samples is probably due to the loss of loosely bound water, while the strong endotherm exhibited by all of the samples is due to the loss of water from the crystal lattice (see Section 3.2.3.(c)). When the weight loss is lower than the theoretical value, this is probably due to the presence of soluble anhydrite, the percentage of the phases present in each sample has therefore been calculated and is shown in Table 4.3.

British Gypsum α and β and Guilini plaster have relatively low soluble anhydrite contents (approx. 2-3wt.%), but the Bogardt α and β have much higher anhydrite contents at 10 and 13wt.% respectively.

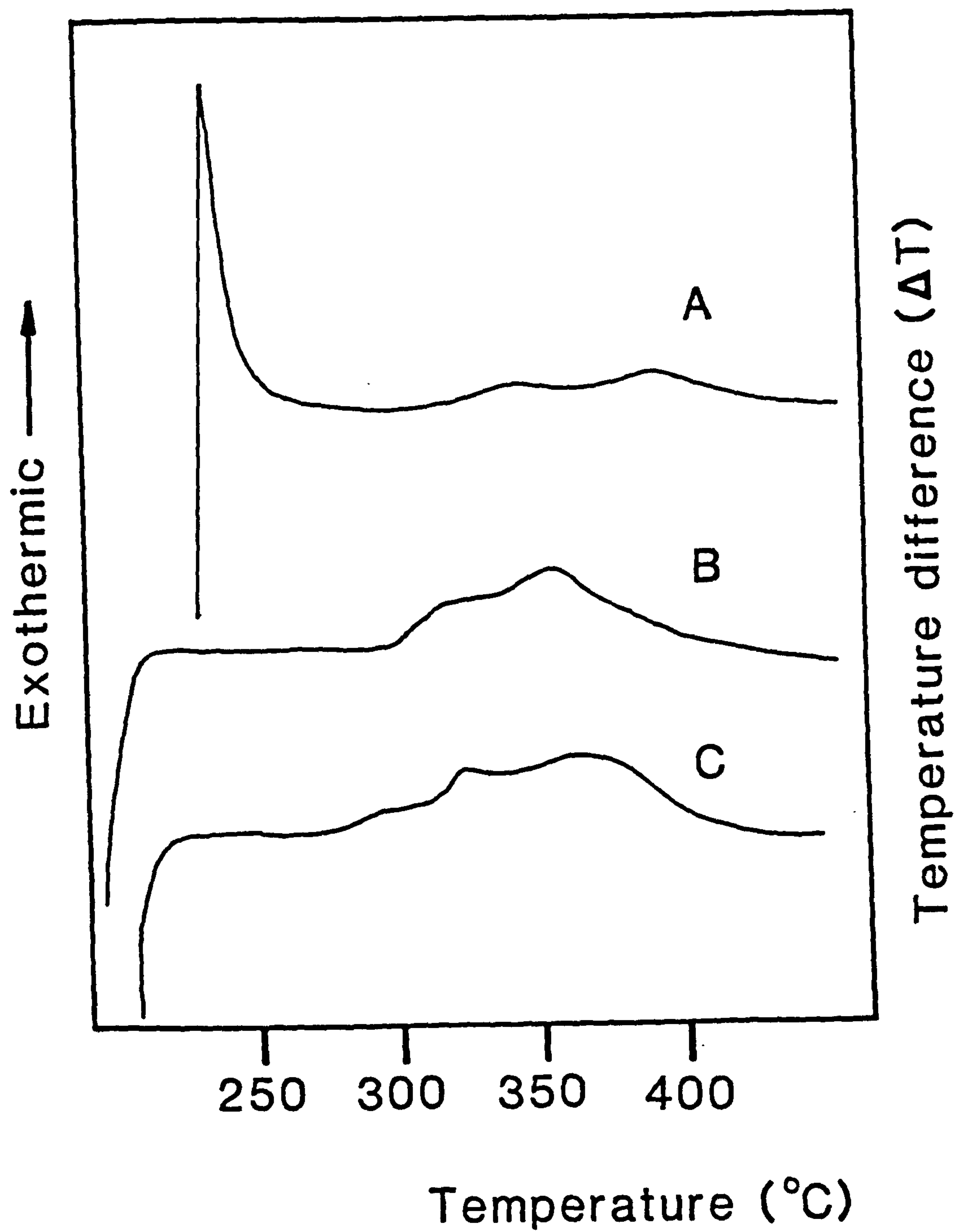


Figure 4.1: D.T.A. traces from British Gypsum plasters, where:

- (A) α - hemihydrate
- (B) β - hemihydrate
- (C) ground α - hemihydrate.

Table 4.2: T.G.A./D.T.A. and H₂O content of the commercial plasters.

Method Plaster	D.T.A./T.G.A. (Wt. loss)	Static temperature (400°C) Wt. loss
British Gypsum α	weak endotherm; 35 °C (0.1%) strong endotherm: 180°C (6.05%)	6.2 (± 0.2)%
British Gypsum β	strong endotherm; 180°C (6.05%)	6.0 (± 0.2)%
" Bogardt α	strong endotherm; 180°C (5.6%)	5.7(± 0.1)%
" Bogardt β	strong endotherm; 180°C (5.4%)	5.5(± 0.1)%
Guilini plaster	weak endotherm; 60°C (0.65%) strong endotherm; 180°C (6.0%)	6.6 (± 0.1)%

Table 4.3: Calculated percentage of CaSO_4 phases in commercial plasters.

Plaster	% Wt. loss	Wt.% hemi- hydrate ($\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$)	Wt% soluble anhy- drite (γCaSO_4)
British Gypsum α	6.05	97.6	2.4
British Gypsum β	6.05	97.6	2.4
" Bogardt α	5.60	90.3	9.7
" Bogardt β	5.40	87.1	12.9
Guilini Plaster	6.00	96.8	3.2

N.B. The theoretical wt. loss for the water lost from hemihydrate is 6.21%.

(d) Particle size analysis.

The particle size distributions of the five plasters are shown in Figure 4.2. The β -hemihydrates have smaller particles than the α -hemihydrates.

British Gypsum β and Guilini plaster have almost identical distributions, with mean sizes of $8.6\mu\text{m}$ and $9.0\mu\text{m}$ respectively. The mean size of Bogardt β particles is $10.9\mu\text{m}$. Bogardt α has the largest particles with a mean size of $20.0\mu\text{m}$, whilst British Gypsum α has a mean size of $11.4\mu\text{m}$.

The effect of grinding British Gypsum α in the Tema-mill is shown in Figure 4.3. The mean size was reduced from $11.4\mu\text{m}$ to $5.3\mu\text{m}$. The particle size distribution of British Gypsum β is shown for comparison. The grinding effectively removes all the large particles, the largest size detected being reduced from approximately $50\mu\text{m}$ to $15\mu\text{m}$.

(e) Optical and scanning electron microscopic studies.

Transmission optical microscopy of the plasters indicated that the α -forms consisted of larger particles than the β -forms and that the α -forms showed a tendency to rhombohedral habit. The α -forms were found to contain agglomerates and single crystals showing idiomorphic features and uniform straight extinction, while the β -forms showed resolvable fissures and pores with no discernable crystallographic facets. The β -forms showed a range of orientations under polarised light and extinction was not complete. This indicated that the particles of the β -form were composed of a multiplicity of small

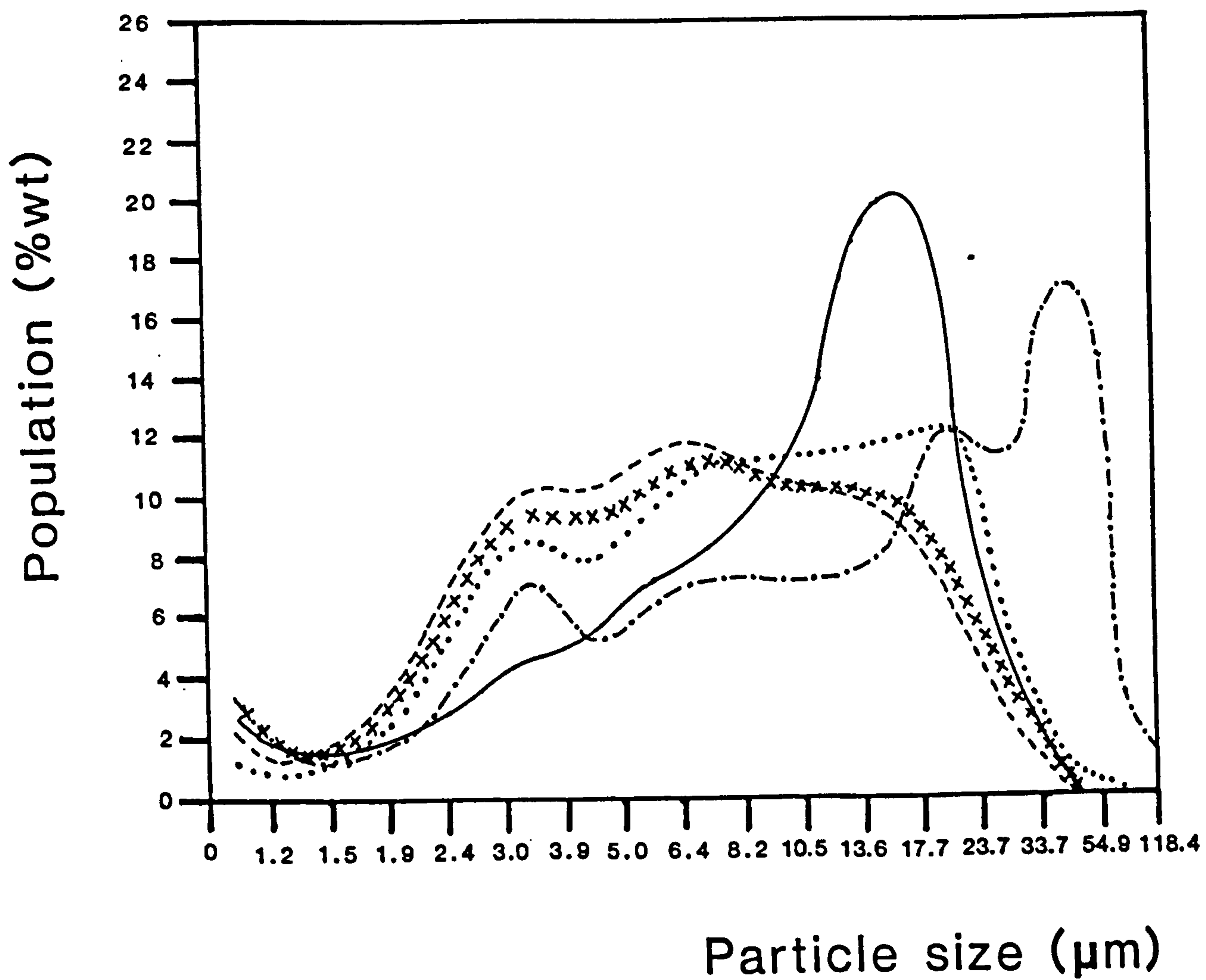


Figure 4.2: Particle size distributions of the commercial plasters, where:

- British Gypsum α
- British Gypsum β
- .- " Bogardt α
- ... " Bogardt β
- xxx Gypsum Plaster.

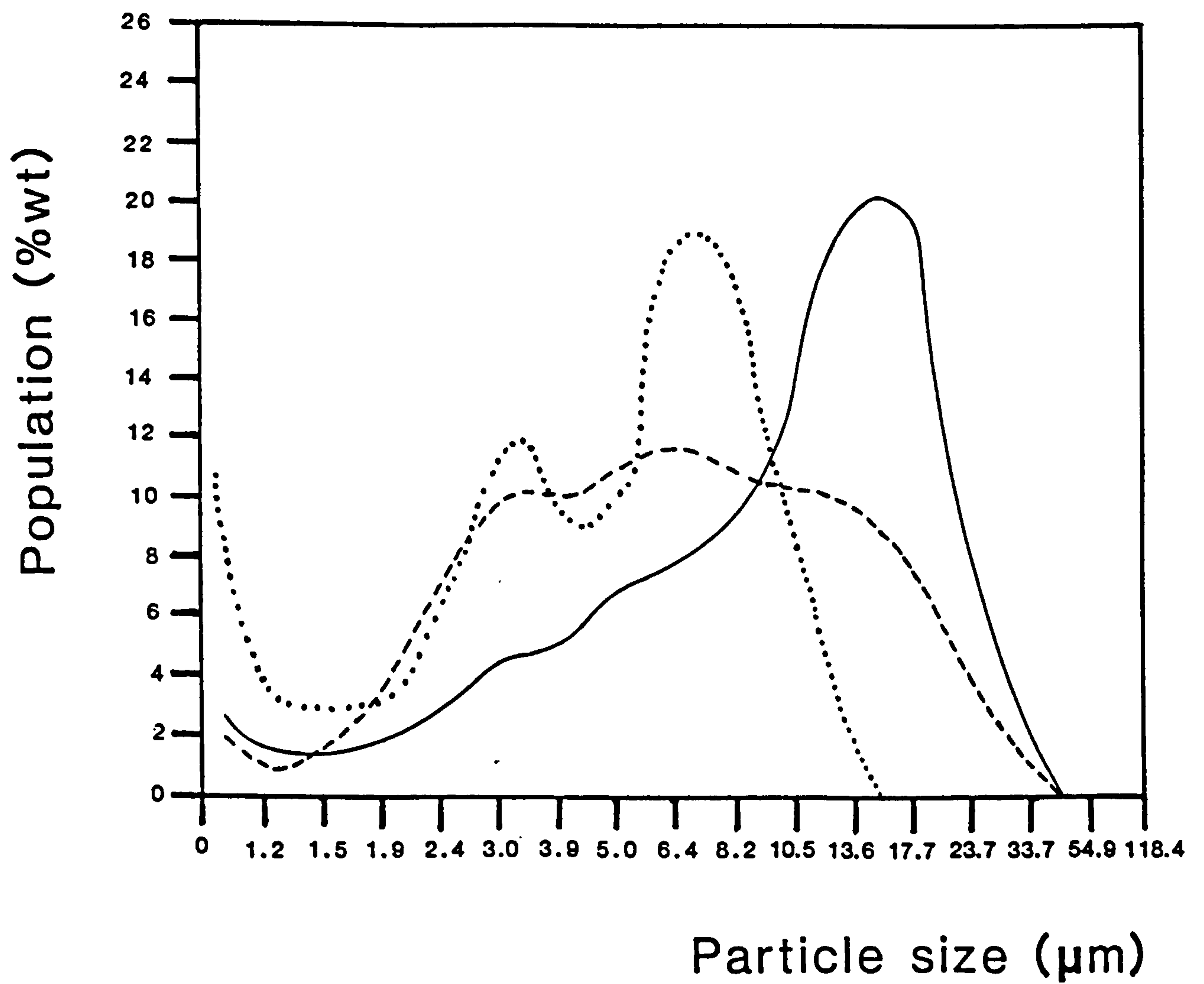


Figure 4.3: The particle size distributions of the British Gypsum hemihydrates, where:

- α
- - - β
- ... ground α.

crystallites of varying orientation.

Scanning electron micrographs of the α - and β - particles (Plates 4.1 and 4.2) gave complementary evidence supporting the optical observations.

(f) Chemical analysis

Quantitative analysis of the five plasters, with WDX. (see Section 3.1.(g).(i)), showed that the trace elements (Na, K, Mg and Si) are each present in quantities of less than 0.2 wt.% each.

Results of the analyses for the major elements (Ca and S), by EDAX, are shown in Table 4.4. Within the errors of the technique all the plasters have the expected stoichiometric molar ratio of 1:1 for Ca:S, except that of the Guilini plaster which appears to be slightly calcium deficient.

Please note that from this point onwards in this thesis α - and β - hemihydrates will refer to the British Gypsum products except where the other manufacturers products are specified.

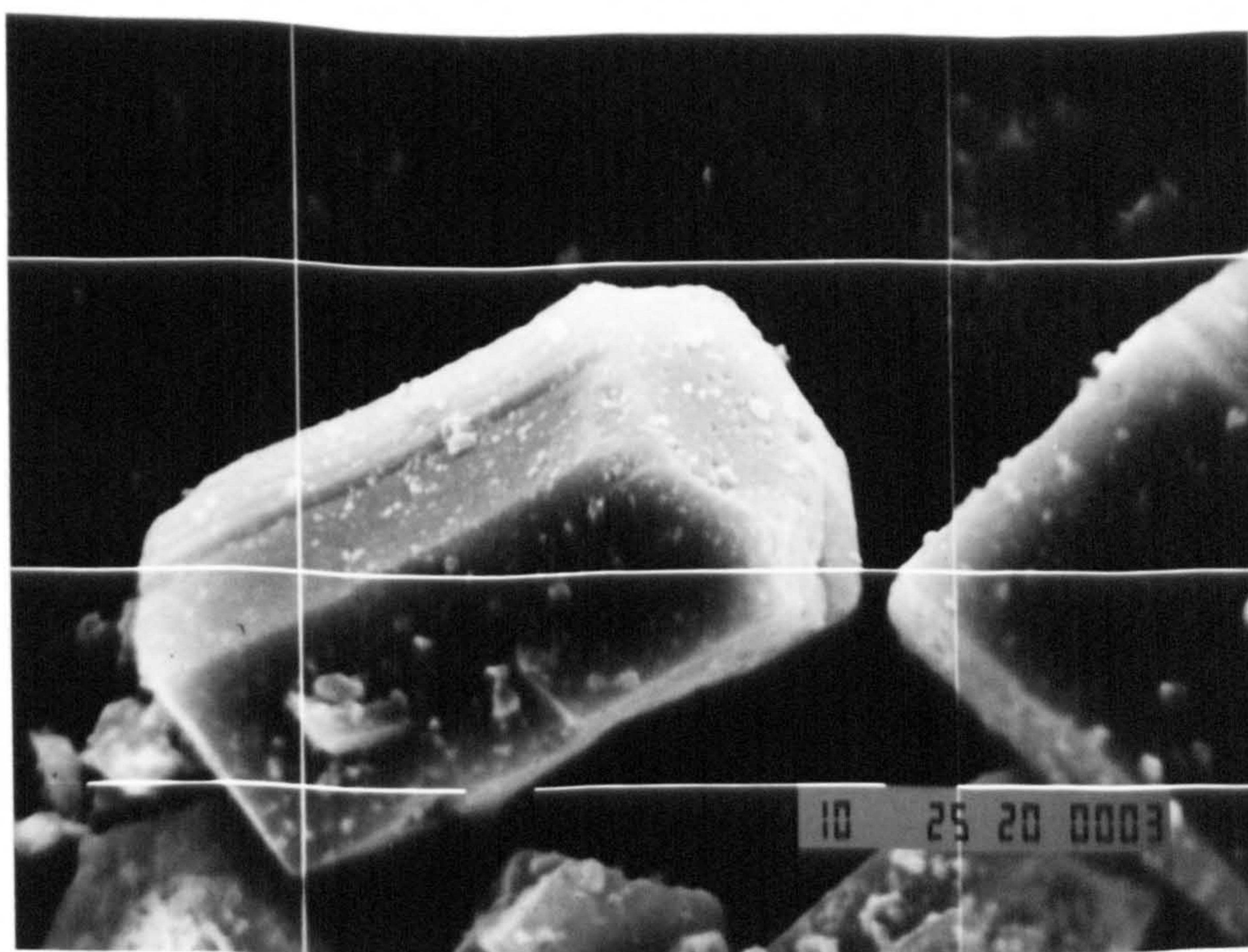


Plate 4.1: Scanning electron micrograph of a typical crystal of $\alpha\text{-CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, at x 3500.

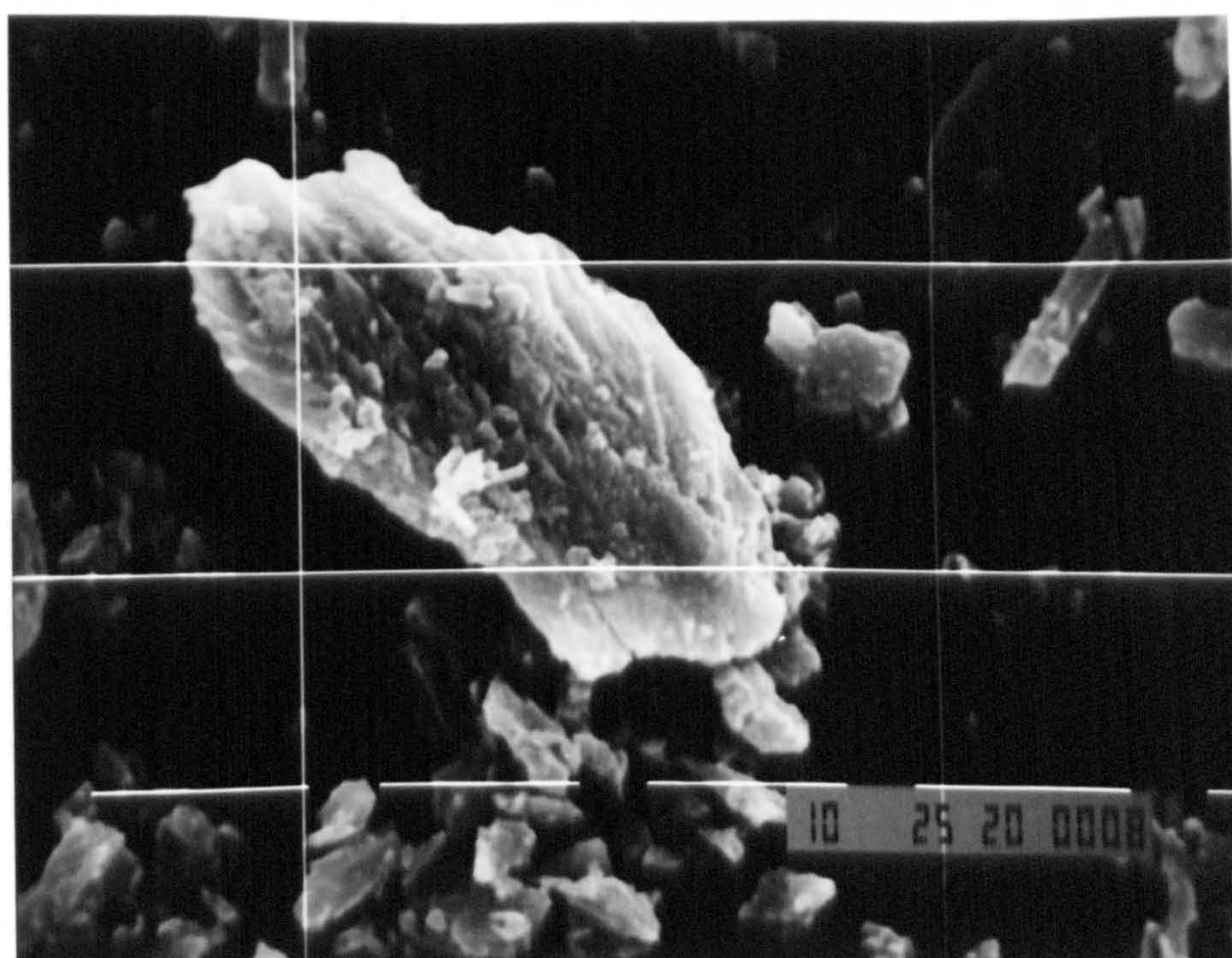


Plate 4.2: Scanning electron micrograph of a typical particle of $\beta\text{-CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, at x 2000.

Magnification: the length of the white marker is given in μm by the first number (e.g. $10\mu\text{m}$).

Table 4.4: Chemical analysis of the hemihydrates, by E.D.A.X., for Ca and S.

PLASTER	NORMALISED * WEIGHT PERCENTAGES		CaO/SO ₃ MOLAR RATIO
	CaO	SO ₃	
British Gypsum α	39.6 ± 1.1	54.4 ± 1.1	1.01 ± 0.05
British Gypsum β	38.0 ± 0.6	56.0 ± 0.6	0.97 ± 0.03
" Bogardt α	38.4 ± 0.3	55.6 ± 0.3	0.99 ± 0.01
" Bogardt β	38.0 ± 0.2	56.0 ± 0.2	0.97 ± 0.01
Guilini Plaster	37.0 ± 0.3	57.0 ± 0.3	0.92 ± 0.02

* Analysed oxide contents where lower than expected from CaSO₄.½H₂O due to charging of samples. Normalised figures based on 94% CaSO₄ in CaSO₄.½H₂O.

N.B. Analysis was performed on five areas of each sample to ensure a true bulk analysis.

4.2 THE HYDRATION OF HEMIHYDRATES

(a) Determination of Water/Plaster (W/P) ratio in commercial plasters.

The W/P ratio in plaster of Paris bandage was determined from the water pick-up and the amount of hemihydrate on the bandage (see Section 3.2.1).

$$\text{W/P ratio} = \frac{\text{water pick-up}}{\text{hemihydrate content}}$$

The range of W/P ratios found for Cellona and Gypsona bandages, with the percentage loss of plaster while handling, are shown in Table 4.5. The results indicated the wide range of W/P ratios over which work could be conducted. A W/P ratio of 0.6 was chosen for all studies on hydration and set strength, with the exception of the study of the variation of W/P ratio due to the α : β ratio of plasters.

(b) Calorimetry of the hydration reaction. Temperature changes during hydration are shown in Table 4.6(a) and represented graphically in Figure 4.4. In order to characterise the hydration curves derived parameters were used (Section 3.2.2) and these are shown in Table 4.6.(b)

The induction period for α - hemihydrate was about a quarter of that for the β - hemihydrate. Once the reaction was underway the maximum rate of temperature increase was far lower for the α - hemihydrate ($0.75^{\circ}\text{C}/\text{min.}$) compared with that of the β - hemihydrate ($2.9^{\circ}\text{C}/\text{min.}$). 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 after the induction period. Experimental errors and heat losses

Table 4.5: W/P ratios found in bandage applications.

W/P ratio Bandage	Average value	Maximum value	Minimum value	loss of plaster from bandages while handling (wt.%)
Gypsona (Smith and Nephew Ltd)	0.61	0.71	0.46	2
Cellona (Lohmann Gmbh)	0.41	0.53	0.30	25

Table 4.6(a): Calorimetric data for the hemihydrate/water reactions (W/P ratio = 0.6).

Reaction time (mins.)	Temperature rise ($^{\circ}\text{C}$)	
	α -hemihydrate	β -hemihydrate
10	1.5	0.0
20	6.8	0.2
30	12.4	1.6
40	19.4	9.3
50	23.1	28.3

Table 4.6(b): Parameters used to characterise the curves in Figure 4.4.

Hemihydrate Parameter	α	β
Induction period (mins.)	5.4	19.6
T_{max} ($^{\circ}\text{C}$)	23.3	28.5
Time to reach T_{max} (mins.)	52.5	50.2
maximum rate of temp. increase ($^{\circ}\text{C}/\text{min.}$)	0.75	2.9

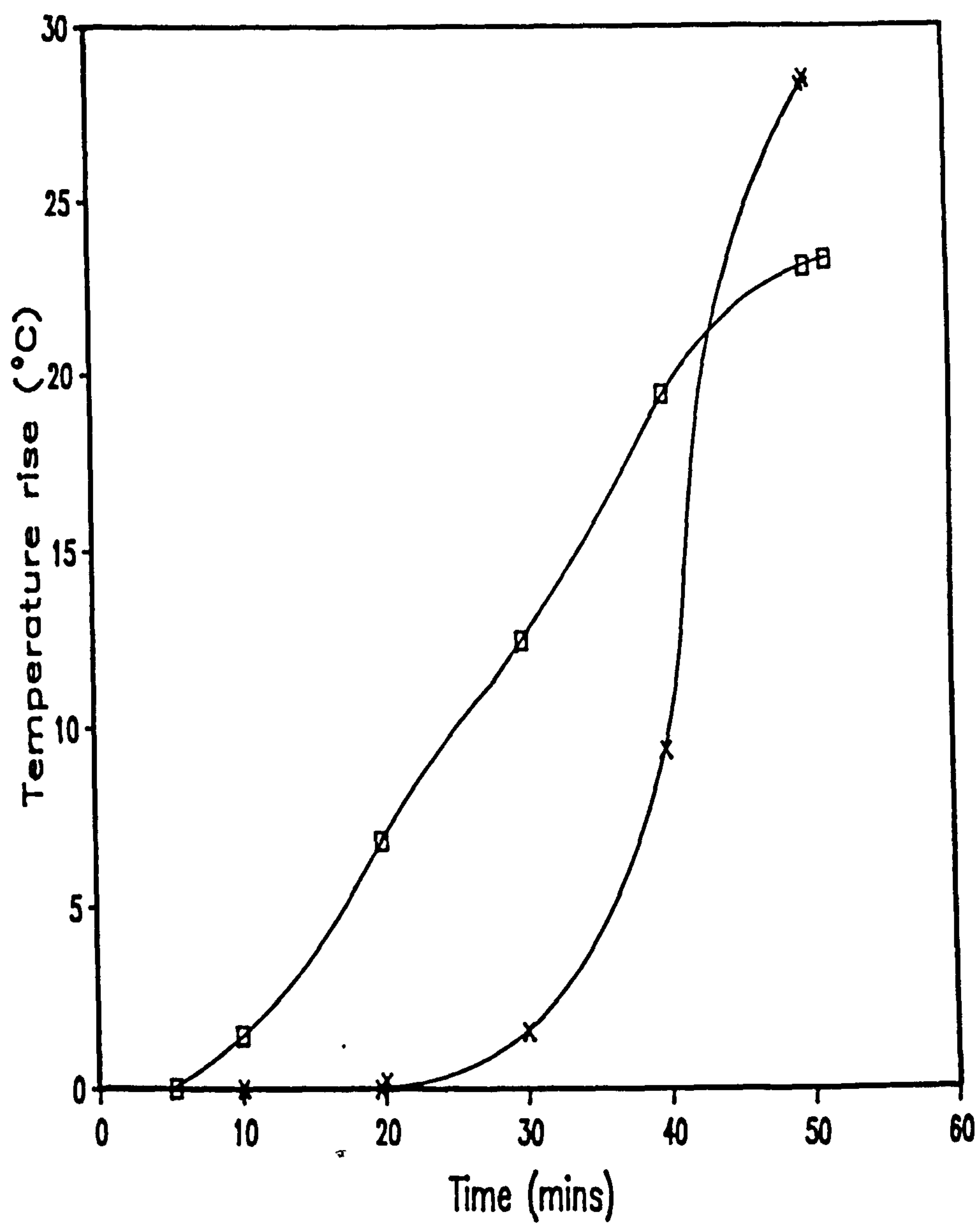


Figure 4.4: The hydration of α - and β - hemihydrates (W/P ratio = 0.6) as followed by the temperature change, where:

□ α

× β .

limit the technique to comparative work, unless complicated cooling curve corrections are performed on the temperature/time curves.

(c) Phase analysis of the hydration products.

(i) X-ray powder diffraction analysis.

Examination of the diffraction patterns of the α -hemihydrate/water reaction products showed a mixture of hemihydrate and/or dihydrate to be present. After 45 mins. dihydrate became the major phase and after 75 mins. no hemihydrate was detectable. Detection of small quantities of phases was difficult due to the close proximity of the diffraction peaks from the two phases. In the case of the β -hemihydrate/water reaction, there were approximately equal amounts of the two phases, after 45 mins. and the reaction appeared to be complete after 75 mins.

(ii) Thermal analysis

An analysis of the TGA data enabled the proportions of dihydrate and hemihydrate to be calculated (section 3.2.3 (c)); the results are shown in Table 4.7 and represented graphically in Figure 4.5.

The curves obtained are similar to those obtained by calorimetry (see Section 4.2(b)) and are more accurate provided that sufficient samples are taken. The calorimetric method does have the advantage of a continuous curve which would be more sensitive to small

Table 4.7: Phases present in partially reacted mixtures of hemihydrate and water (W/P ratio = 0.6).

Reaction time (mins.)	Hemihydrate (mole%)	Dihydrate (mole%)
α -hemihydrate		
10	94.4	5.6
20	81.5	18.5
30	60.9	39.1
45	29.3	70.7
60	3.2	96.8
75	1.1	98.9
≥ 120	< 1.0	> 99.0
β -hemihydrate		
20	99.7	0.3
30	92.8	7.2
45	46.0	54.0
60	1.4	98.6
75	0.9	99.1
≥ 120	$\ll 1.0$	$\gg 99.0$

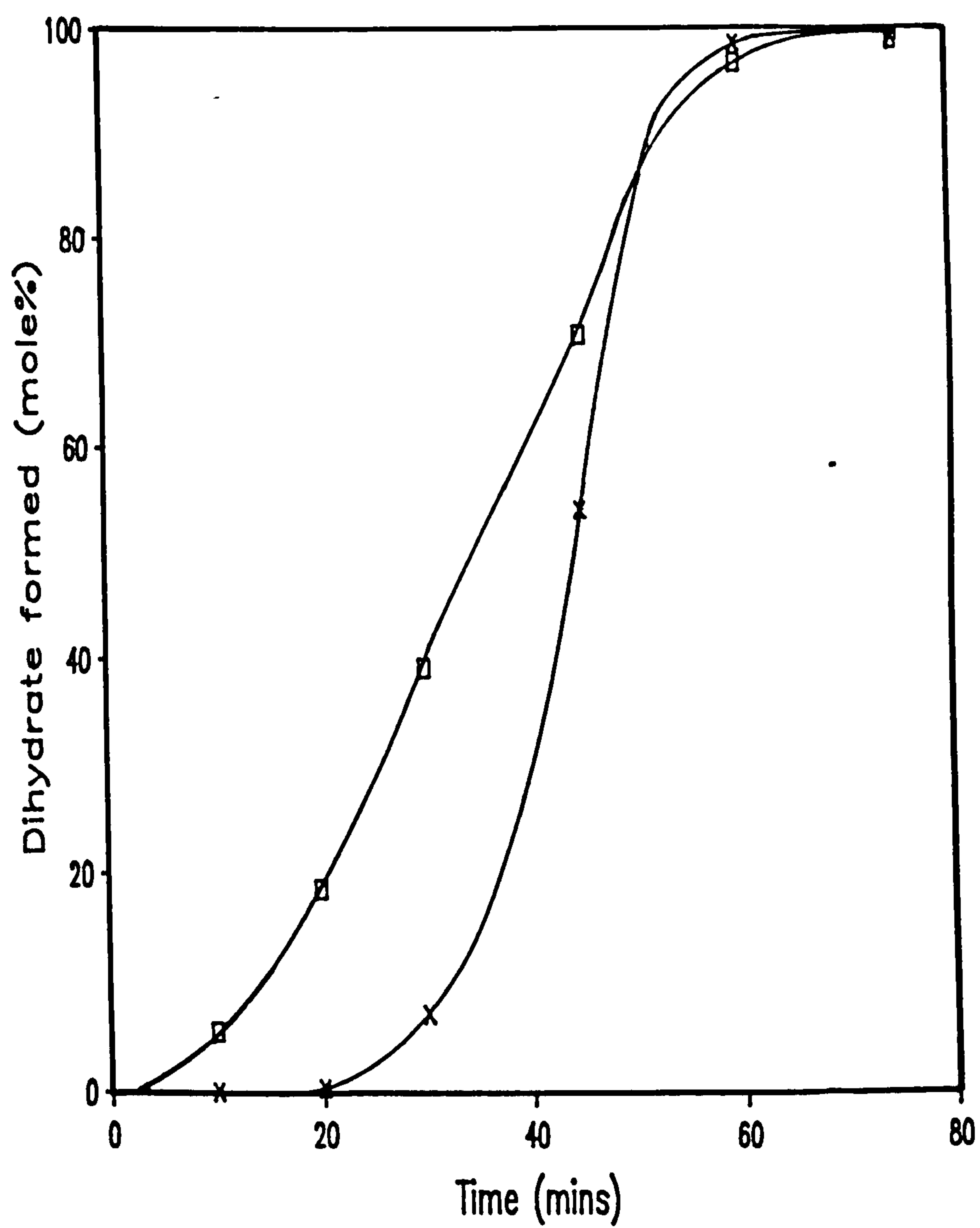


Figure 4.5: The amount of dihydrate formed in hemihydrate/water reaction mixtures as determined by thermal analysis, where:

$\square$ α -hemihydrate

$\times$ β -hemihydrate.

changes in the reaction rate.

(d) The electrical resistance of setting plaster

The results obtained are shown in Table 4.8 and represented graphically in Figures 4.6 and 4.7. Both setting plasters showed an initial minimum resistance in the first 10 mins., followed by a large increase in resistance over the next 100 mins., after which time the resistance levels out. The α - form reaches the initial minimum resistance point sooner than the β - form but the increase in resistance is slower when compared to the β - form. Both forms level out at approximately 120 mins. at a resistance of $7500\Omega.\text{cm}^{-1}$.

Table 4.8: The electrical resistance of setting plaster slurries (W/P ratio = 0.6).

Time (mins.)	Resistance/unit length ($\Omega \cdot \text{cm}^{-1}$)	
	α - hemihydrate	β - hemihydrate
4	784.2	-
5	776.6	-
6	781.4	-
7	792.8	844.7
8	821.6	839.3
9	835.2	836.3
10	854.4	843.1
15	951.0	878.6
20	1086.4	958.3
25	1275.0	1306.1
30	1598.4	1836.7
35	2009.0	2812.2
40	2486.4	4172.2
45	2990.0	4873.3
50	3490.0	5430.0
55	3988.0	5852.2
60	4572.0	6150.0
65	5090.0	6363.3
70	5562.0	6516.7
75	6002.0	6642.2
80	6384.0	6738.9
85	6892.0	6827.8
90	-	-
100	-	7192.6
105	7274.0	-
110	7346.0	-
115	7418.0	-
120	7452.0	7571.1
125	7486.0	7633.3

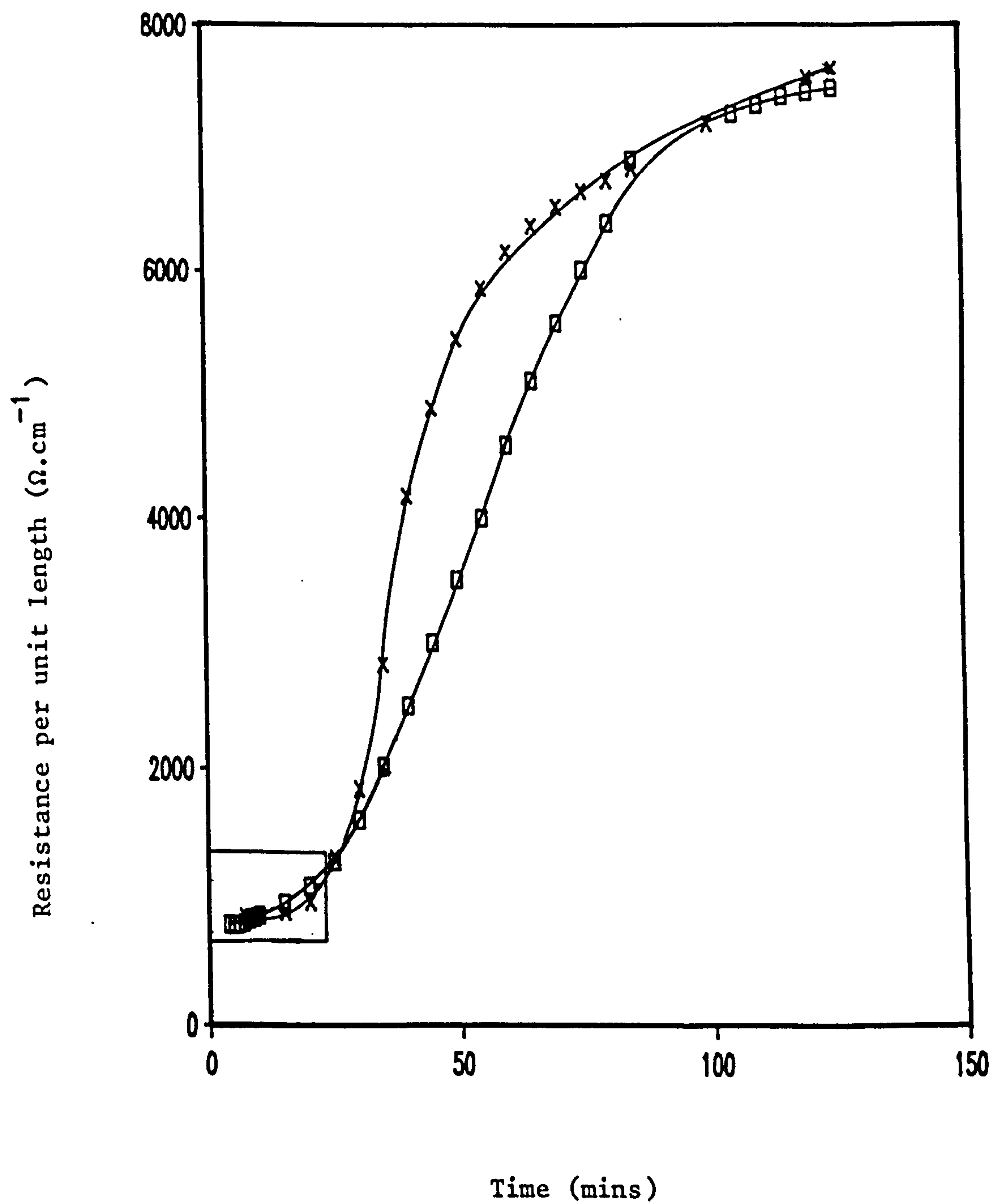


Figure 4.6: The electrical resistance of setting plaster slurries (W/P ratio = 0.6), where:

$\square$ α - hemihydrate

$\times$ β - hemihydrate.

N.B. Changes in resistance during the first 20 mins. are shown in Figure 4.7.

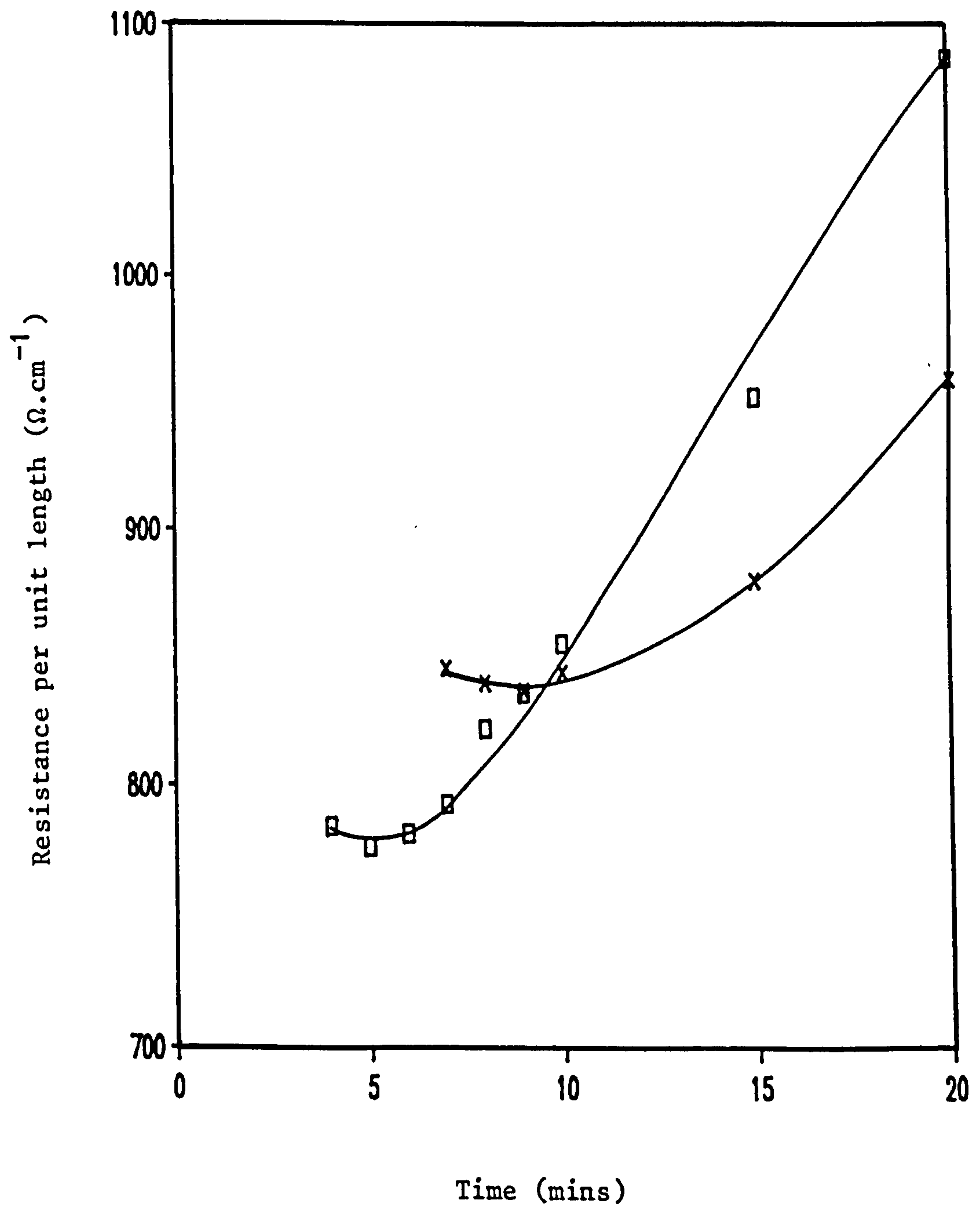


Figure 4.7: An expanded view of the boxed area shown in Figure 4.6.

4.3 MICROSTRUCTURAL AND STRENGTH DEVELOPMENT OF SETTING PLASTERS

(a) Full set commercial plasters.

Values for the fully set bend strength of the five plasters are shown in Table 4.9. British Gypsum α gave the strongest plaster with a modulus of rupture of 18MN/m^2 . The set plasters from British Gypsum β , Bogardt α and Guilini plaster all have approximately the same bend strength of 10MN/m^2 . The weakest plaster is from Bogardt β with a full set strength of only 5.8MN/m^2 .

The microstructure of the set plaster from British Gypsum α (Plate 4.3) consisted of relatively short stubby needles of dihydrate, in contrast to the β - plasters which have set plasters with branching fibrous needles growing from obvious nucleation sites (Plates 4.4 and 4.5). The set plaster from Bogardt α had a similar microstructure to that of the set plaster from British Gypsum β . The Guilini set plaster (Plate 4.6) shows an intermediate structure with some evidence of needles branching and clustering.

(b) The development of strength in setting plasters.

Strength measurements were made on the three-point bend test rig developed for this project (Section 3.2.1.(c)), for these and all subsequent tests.

The strength development of setting hemihydrates is shown in Table 4.10 and is represented graphically in Figure 4.8. With the α - hemihydrate the strength increased rapidly to a value of 6.3MN/m^2 after 1.25 hrs. and then declined to a value of 5.5Mn/m^2 after 2 hrs. After this time the strength increased slowly reaching

Table 4.9: The bend strength of fully set commercial plasters (W/P ratio = 0.6).

Plaster	British Gypsum α	British Gypsum β	" Bogardt α	" Bogardt β	Quilini Plaster
Modulus of rupture (MN/m ²)	18 $\pm$ 1	10 $\pm$ 1	11 $\pm$ 1	5.8 $\pm$ 0.3	10 $\pm$ 1

N.B. Specimens were tested using a three-point bending rig on an Instron test machine with a strain of 0.2mm/min.



Plate 4.3: Scanning electron micrograph, at x1000, of the microstructure of the fully set plaster from British Gypsum α (W/P ratio = 0.6).



Plate 4.4: Scanning electron micrograph, at x1000, of the microstructure of the fully set plaster from British Gypsum β (W/P ratio = 0.6).

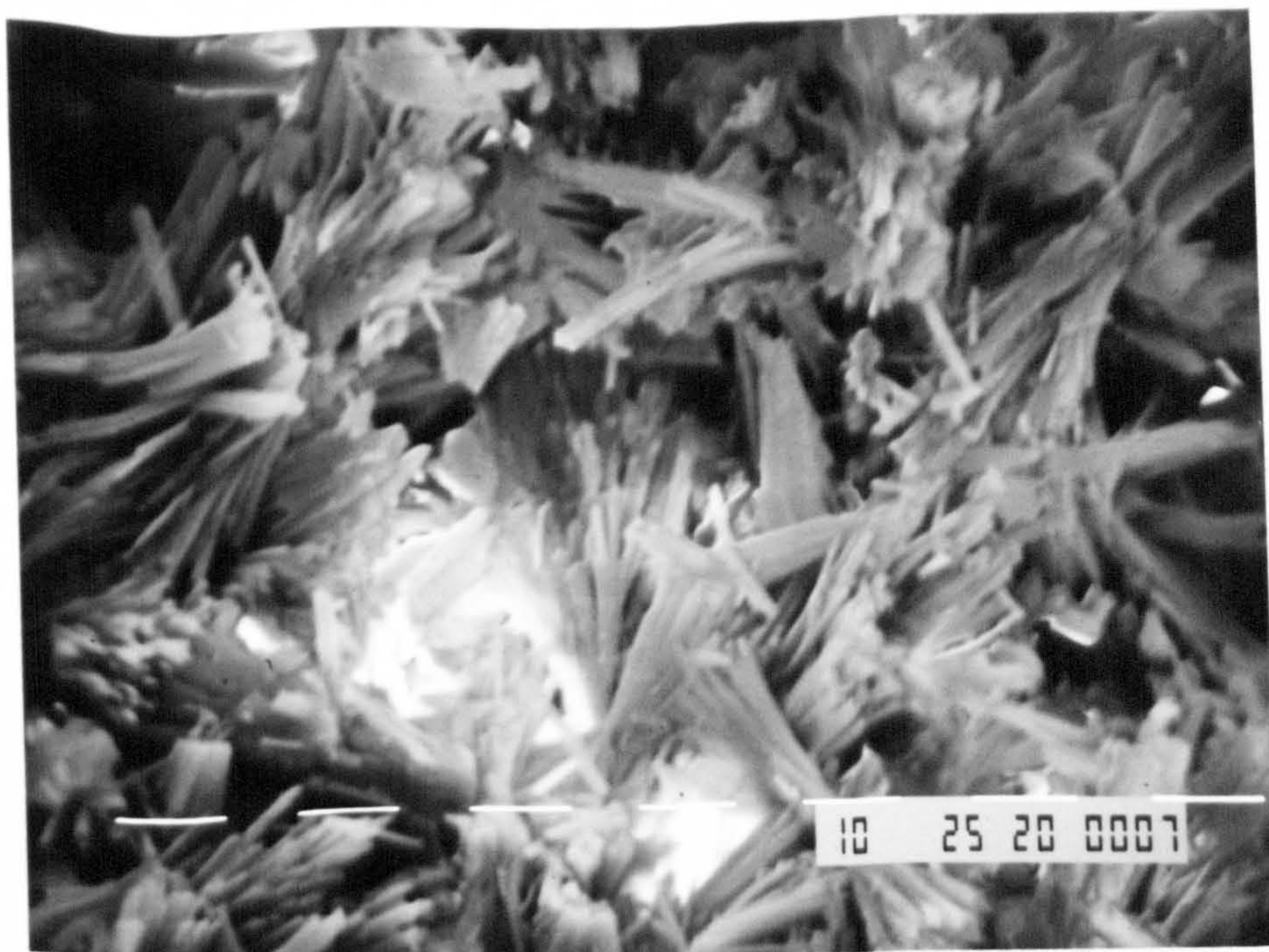


Plate 4.5: Scanning electron micrograph at x1000, of the microstructure of the fully set plaster from Bogardt β (W/P ratio = 0.6).



Plate 4.6: Scanning electron micrograph, at x1000, of the microstructure of the fully set plaster from Guilini plaster (W/P ratio = 0.6).

Table 4.10: The development of strength as the α - and β -hemihydrates set (W/P ratio = 0.6).

Time (hrs.)	Modulus of rupture (MN/m^2)	
	α - hemihydrate	β - hemihydrate
0.33	1.4 $\pm$ 0.1	-
0.5	3.6 $\pm$ 0.1	-
0.75	5.4 $\pm$ 0.2	3.1 $\pm$ 0.3
1	6.2 $\pm$ 0.1	4.6 $\pm$ 0.1
1.25	6.3 $\pm$ 0.2	4.8 $\pm$ 0.1
1.50	6.1 $\pm$ 0.2	4.3 $\pm$ 0.1
2	5.5 $\pm$ 0.2	4.5 $\pm$ 0.1
5	5.9 $\pm$ 0.3	4.8 $\pm$ 0.1
7.5	9.5 $\pm$ 0.9	-
10	10.8 $\pm$ 0.4	6.7 $\pm$ 0.3
15	11.8 $\pm$ 0.5	8.3 $\pm$ 0.2
20	11.6 $\pm$ 0.2	9.8 $\pm$ 0.2
25	12.5 $\pm$ 0.4	9.8 $\pm$ 0.2
200	12.6 $\pm$ 0.5	10.0 $\pm$ 0.2

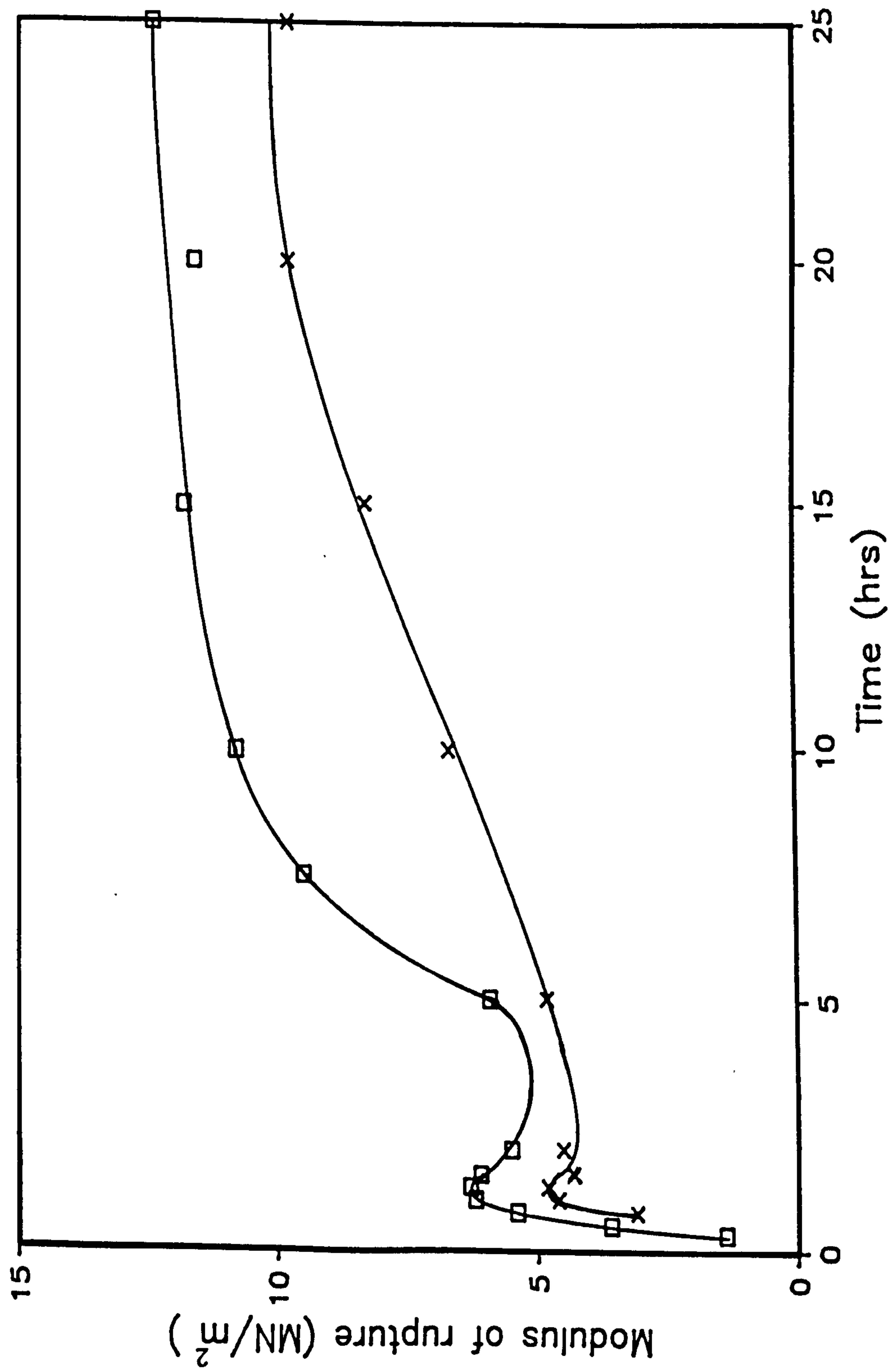


Figure 4.8: The development of strength as the hemihydrates set, where:

a limiting value of approximately 12.4 MN/m^2 after 25 hrs. The setting β - hemihydrate shows a similar trend to the α - hemihydrate. After a rapid initial increase a first maximum of 4.8 MN/m^2 was reached after 1.25 hrs., followed by a drop to 4.3 MN/m^2 after 1.5 hrs; the strength then increased to a limit of approximately 10 MN/m^2 after 25 hrs.

(c) The 'wet' strength of setting plasters.

To provide a greater insight into the setting processes the specimens were prevented from drying out by allowing them to set in a saturated solution of dihydrate (Section 3.3.1. (a) (ii)). The bend strength was then measured for each specimen, which was effectively 'wet'.

The results for the 'wet' strength of α - and β - hemihydrates are shown in Table 4.11 and graphically in Figure 4.9. Both curves are similar, with an initial rapid increase in strength reaching a maximum after 1hr. This was followed by a decline in strength reaching a limiting value after 5hrs. The setting α - hemihydrate reached a maximum strength of 6.1 MN/m^2 declining value of approximately 5 MN/m^2 . The setting β - hemihydrate had maximum and limiting strengths of 4.4 and 3.4 MN/m^2 respectively.

Comparison of the strength versus time curves obtained from the 'dry' and 'wet' setting plasters showed that both curves had an initial strength increase to a maximum which was followed by a decrease. The difference between them was that after this strength decrease no subsequent increase in strength was observed for 'wet' test specimens.

Table 4.11: The strength development of setting hemihydrates when the test specimens are kept wet (W/P ratio = 0.6).

Time (hrs.)	Modulus of rupture (MN/m^2)	
	α - hemihydrate	β - hemihydrate
0.33	0.9 $\pm$ 0.1	-
0.50	2.6 $\pm$ 0.2	-
0.75	5.3 $\pm$ 0.1	2.5 $\pm$ 0.2
1	6.1 $\pm$ 0.1	4.4 $\pm$ 0.1
1.25	5.8 $\pm$ 0.1	4.0 $\pm$ 0.1
1.50	5.4 $\pm$ 0.1	3.7 $\pm$ 0.1
2	5.2 $\pm$ 0.1	3.5 $\pm$ 0.1
5	5.1 $\pm$ 0.1	3.4 $\pm$ 0.1
10	5.1 $\pm$ 0.1	3.6 $\pm$ 0.1
15	5.1 $\pm$ 0.1	3.4 $\pm$ 0.1
20	4.9 $\pm$ 0.1	3.3 $\pm$ 0.1
25	5.0 $\pm$ 0.1	3.5 $\pm$ 0.1
200	5.1 $\pm$ 0.1	3.5 $\pm$ 0.1

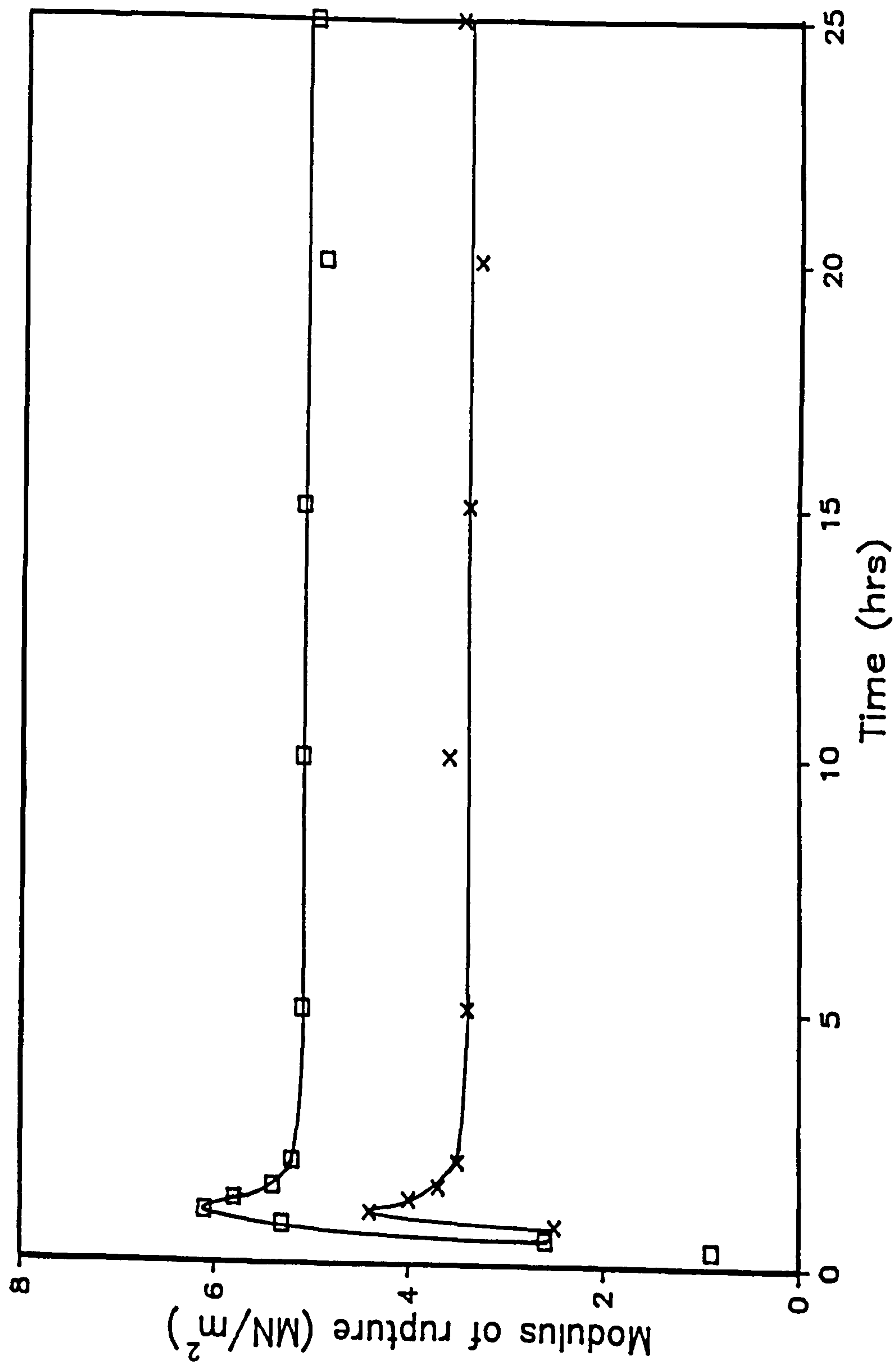


Figure 4.9: The development of 'wet' strength as the hemihydrates set, where:

□ α

-x- β.

(d) Microstructural formation during the setting of plasters.

(i) Scanning electron microscopy studies.

Plates 4.7 and 4.8 show the development of the microstructure in partially reacted mixtures of α -hemihydrate and water. After 45 mins. (Plate 4.7) large needles of dihydrate had nucleated and grown on particles of hemihydrate. After 60 mins. (Plate 4.8) the microstructure consisted of a mass of interlocking, stubby dihydrate needles and there appeared to be no further change after this time (see Plate 4.3).

Plates 4.9 and 4.10 show the microstructure of the β -hemihydrate/water reaction mixtures after 45 and 60 mins. respectively. After 45 mins. (Plate 4.9), needles of dihydrate had nucleated on the surface of the hemihydrate particles and had grown to form a microstructure of interlocking, branching and fibrous dihydrate needles after 60 mins. (Plate 4.10). No further changes were detected for longer setting times (see Plate 4.4) and thus the differences between a set α - and β -plaster are quite marked.

(ii) The acoustic emission studies

No acoustic emission signals were detected, above the background electronic noise, during the first 24 hours of setting. It was therefore concluded that there was no process which involved rapid release of energy.



Plate 4.7: Scanning electron micrograph, at x500, of the solid phases present in a partially reacted mixture of α -hemihydrate and water after 45 mins. (W/P ratio = 0.6).



Plate 4.8: As in Plate 4.7 except at x1000 and after 60 mins.



Plate 4.9: Scanning electron micrograph, at x500, of the solid phases present in a partially reacted mixture of β -hemihydrate and water after 45 mins. (W/P ratio = 0.6).



Plate 4.10: As in Plate 4.9 except at x1000 and after 60 mins.

(iii) Acousto-ultrasonic testing.

The acoustic transmittance of the setting plasters can be seen in Tables 4.12 and 4.13, and graphically in Figures 4.10 and 4.11. Both setting plasters showed an initial rapid increase in acoustic transmittance up to approximately 70 - 80 mins. After this the α -plaster showed no significant increase for the next 23 hours, while the β plaster increase by 25 - 50 percent. This technique has demonstrated that full microstructural development in the β - plaster takes 24 hrs as compared to approximately $1\frac{1}{2}$ hrs for the α - plasters.

Table 4.12: The acoustic transmittance of setting α - hemihydrate (W/P ratio = 0.6).

Time (mins.)	Ring counts/event (or pulse)	Average amplitude of events. (dB)
5	0	0
10	0	0
15	0	0
20	0	0
25	0	0
30	0	0
35	18.9	33.3 $\pm$ 0.1
40	40.8	44.1 $\pm$ 0.2
45	42.3	44.0 $\pm$ 0.1
50	49.2	47.0 $\pm$ 0.0
55	67.5	50.1 $\pm$ 0.1
60	67.6	52.0 $\pm$ 0.0
75	70.8	54.6 $\pm$ 0.4
90	80.9	54.1 $\pm$ 0.1
120	82.2	55.0 $\pm$ 0.0
135	80.5	55.2 $\pm$ 0.1
165	85.3	56.0 $\pm$ 0.0
180	83.4	56.1 $\pm$ 0.1
300	85.2	56.0 $\pm$ 0.0
1440	90.2	58.0 $\pm$ 0.0

Table 4.13: The acoustic transmittance of setting β - hemi-
hydrate (W/P ratio = 0.6).

Time (mins.)	Ring counts/event (or pulse)	Average amplitude of events (dB)
10	0	0
20	0	0
30	0	0.
40	0	0
50	8.0	30.0 $\pm$ 0.1
55	10.1	31.1 $\pm$ 0.1
60	13.7	33.2 $\pm$ 0.1
65	18.9	32.9 $\pm$ 0.1
70	20.1	32.6 $\pm$ 0.1
75	23.4	33.2 $\pm$ 0.1
90	21.5	33.2 $\pm$ 0.1
105	22.0	34.0 $\pm$ 0.1
120	21.4	33.9 $\pm$ 0.1
150	19.5	33.3 $\pm$ 0.1
195	24.2	33.5 $\pm$ 0.1
300	26.1	35.4 $\pm$ 0.1
1440	46.7	45.5 $\pm$ 0.1

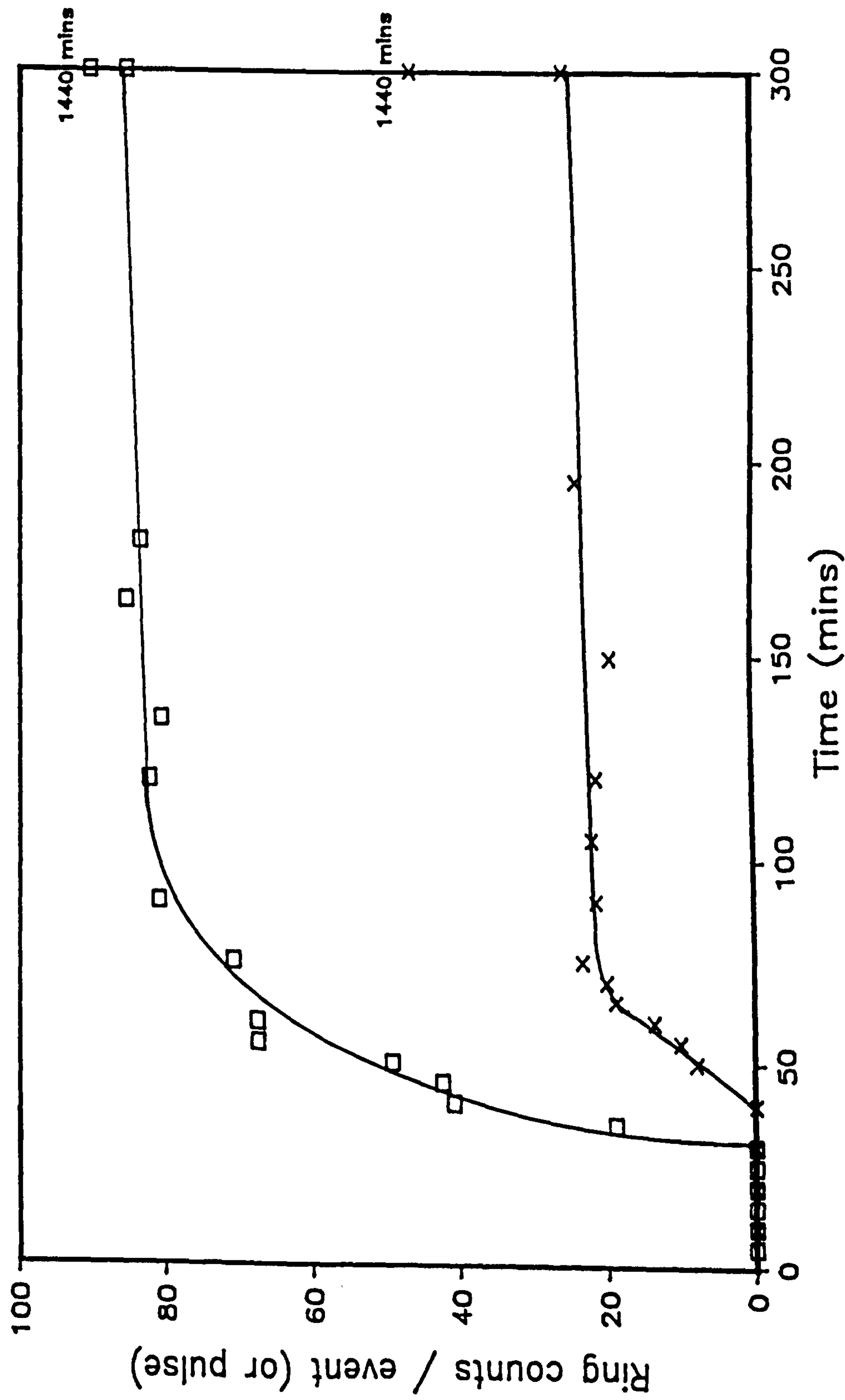


Figure 4.10: The acoustic transmittance (measured as ring counts/event) of setting hemihydrates (W/P ratio = 0.6), where:

□ α
× β.

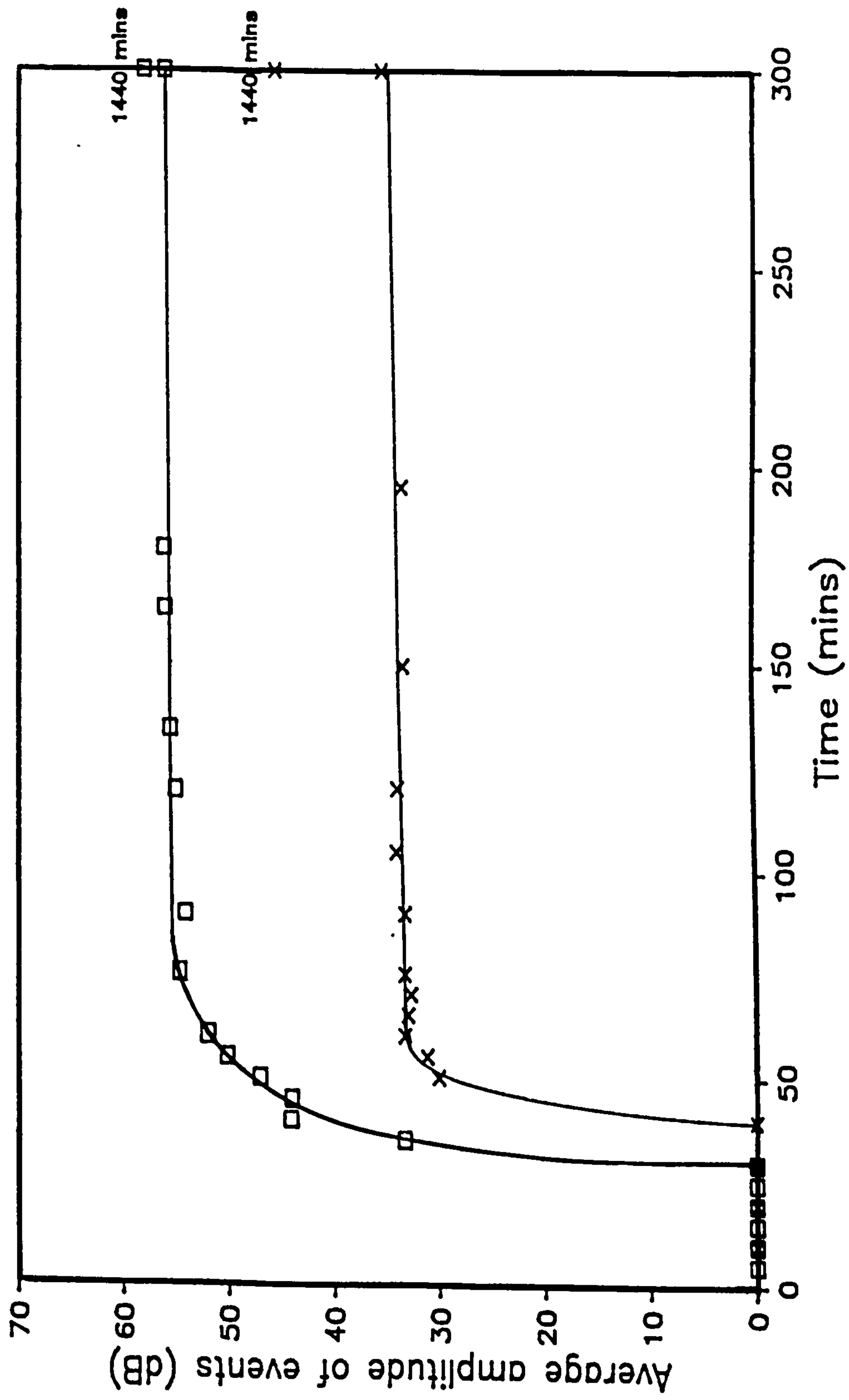


Figure 4.11: The acoustic transmittance (measured as the average amplitude of events) of setting hemihydrates (W/P ratio = 0.6), where:

$\square$ α
 $\times$ β .

4.4 THE PREPARATION AND CHARACTERISATION OF SOLUBLE ANHYDRITE

γ - (CaSO_4)

4.4.1 Preparation of Soluble Anhydrite

Since soluble anhydrite was found to occur in small amounts in the commercial α - and β - plasters (see Section 4.1(c)), and is produced by over-dehydrating hemihydrate, it was decided that the effect of the presence of two soluble anhydrites should be further investigated.

' β '- soluble anhydrite was prepared by dehydrating a flat bed of British Gypsum β - plaster in an oven at 140°C for 4 days.

When ' α '- soluble anhydrite was prepared by the same method it was found by powder x-ray diffraction that a substantial amount of insoluble anhydrite (β - CaSO_4) was present. Reduction of the dehydration temperature to 120°C resulted in the production of a negligible amount of the insoluble anhydrite impurity.

4.4.2 The Characterisation of Soluble Anhydrite

(a) X-ray powder diffraction analysis

The position of the peaks in the diffraction patterns of the ' α ' and ' β '- soluble anhydrites were found to be identical to those of the starting material, i.e. α - and β - hemihydrates, except for the small amount of insoluble anhydrite detected in the ' α '- soluble anhydrite. This suggests that the removal of water molecules from the hemihydrate lattice does not perturb the crystal

lattice in any way (see Section 2.1)

(b) DTA.

The data obtained from the soluble anhydrites is shown in Table 4.14.

The DTA traces are similar to those of the starting materials (see Section 4.1.(b)) apart from the following:

- (i) The endotherm due to the loss of water was shifted to a lower temperature.
- (ii) In ' α '- soluble anhydrite the exotherm, due to the soluble/insoluble anhydrite phase change, was shifted to a lower temperature.

The first effect was probably due to only small amounts of hemihydrate being present. The second effect gives complementary evidence to the theory that the phase change in α - hemihydrate is suppressed by water (see Section 2.2.2(f)), the reduction in water content resulting in a lowering of the transformation temperature.

(c) Water content

The results obtained from the soluble anhydrites are shown in Table 4.15. These indicated that the soluble anhydrite reagents prepared were approximately 90wt% pure.

Table 4.14: D.T.A of the soluble anhydrite reagents.

FORM	D.T.A.
α	strong endotherm (159°C) strong exotherm (199°C) weak and broad exotherm (380°C)
β	strong endotherm (145°C) strong exotherm (360°C)

Table 4.15: Water content and the calculated percentage of hemihydrate present in the soluble anhydrites.

FORM	% Wt. loss	wt % hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)
α	0.45	7.3
β	0.70	11.2

(d) Particle size analysis

The particle size distributions of α - hemihydrate and soluble anhydrite, and of β - hemihydrate and soluble anhydrite, are shown in Figures 4.12 and 4.13.

' α '- soluble anhydrite has a similar distribution to α - hemihydrate except the mean particle size has been reduced from 11.4 to 9.4 μ m.

The distributions of β - hemihydrate and soluble anhydrite are almost identical with average particle sizes of 8.6 and 9.6 μ m respectively.

The above observations support the x-ray diffraction evidence that the crystal lattice was unperturbed by dehydration.

The reduced particle size in the ' α '- soluble anhydrite can be explained by the presence of the insoluble anhydrite impurity which is formed from soluble anhydrite by shearing parallel to the C-axis (see Section 2.2.2(f)). This would result in two small particles being formed from a large particle; the result being a reduction in the overall particle size.

(e) SEM studies

Plate 4.11 shows that ' α '- soluble anhydrite consists of single crystals showing idiomorphic features whilst ' β '- soluble anhydrite particles (Plate 4.12) show no discernable crystallographic facets.

The above observations indicate that there is little morphological change when compared to the starting

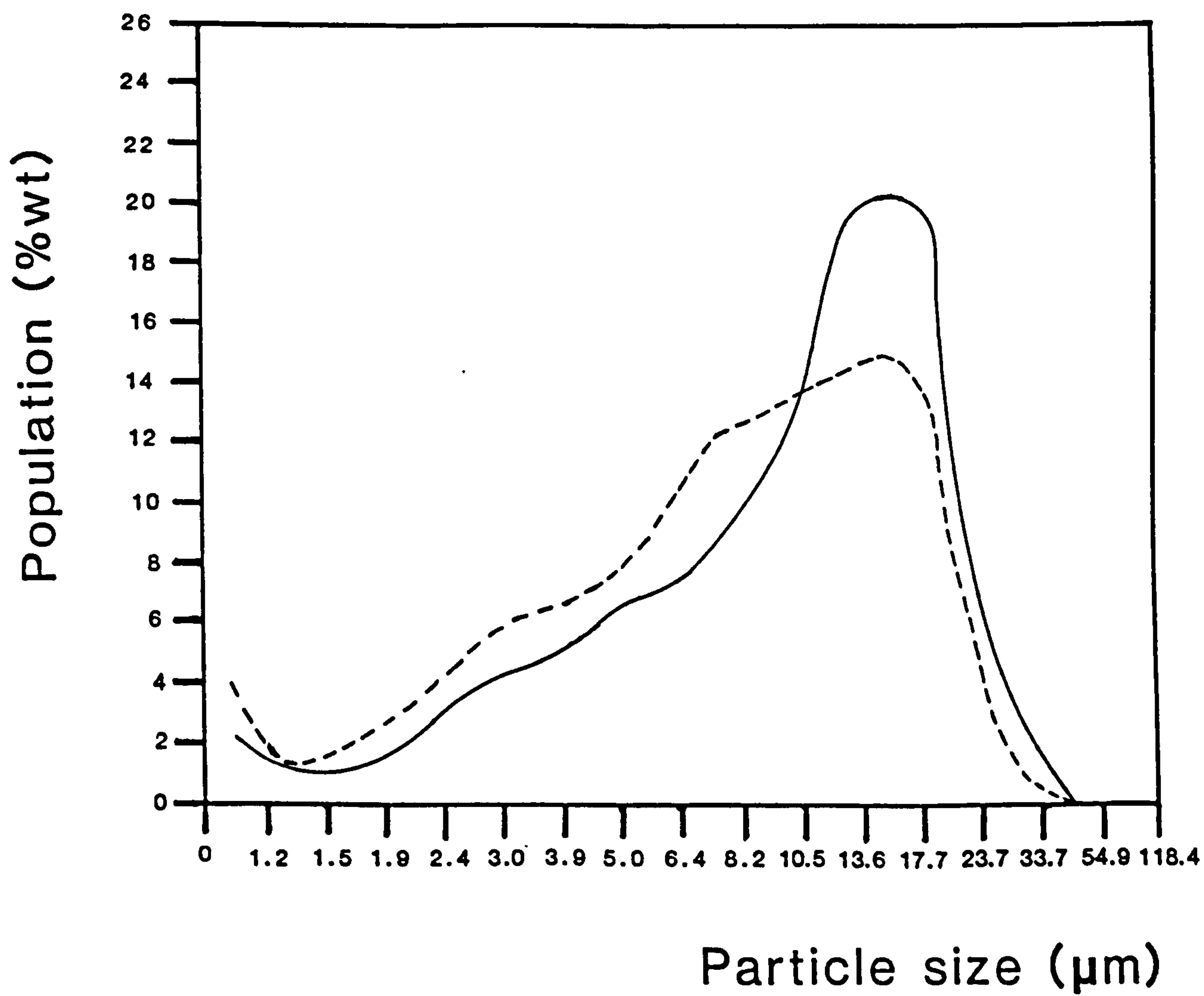


Figure 4.12: The particle size distributions of α - hemihydrate and soluble anhydrite, where:

—— hemihydrate
----- soluble anhydrite.

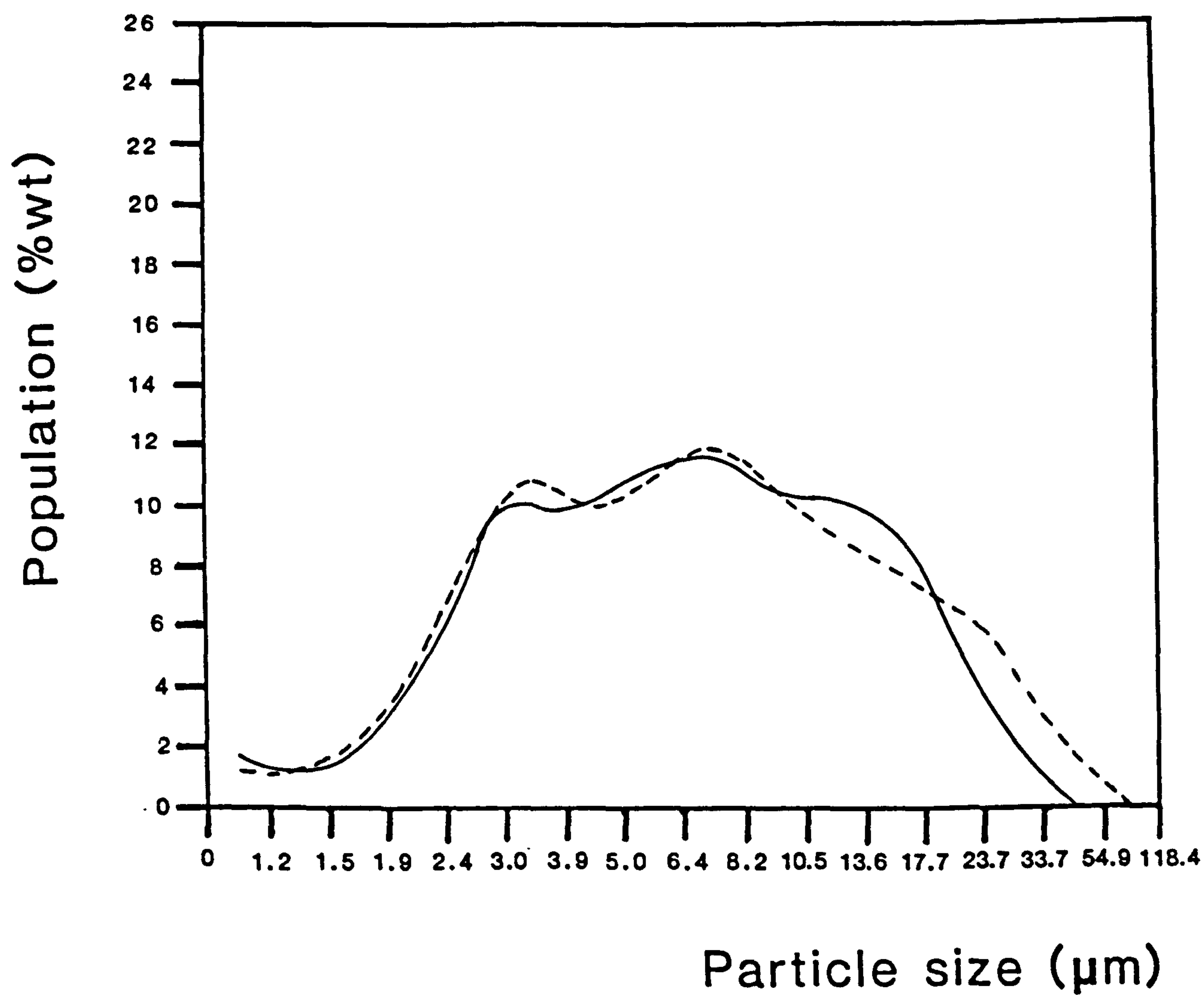


Figure 4.13: Particle size distributions of β - hemihydrate and soluble anhydrite, where:

—— hemihydrate

----- soluble anhydrite.

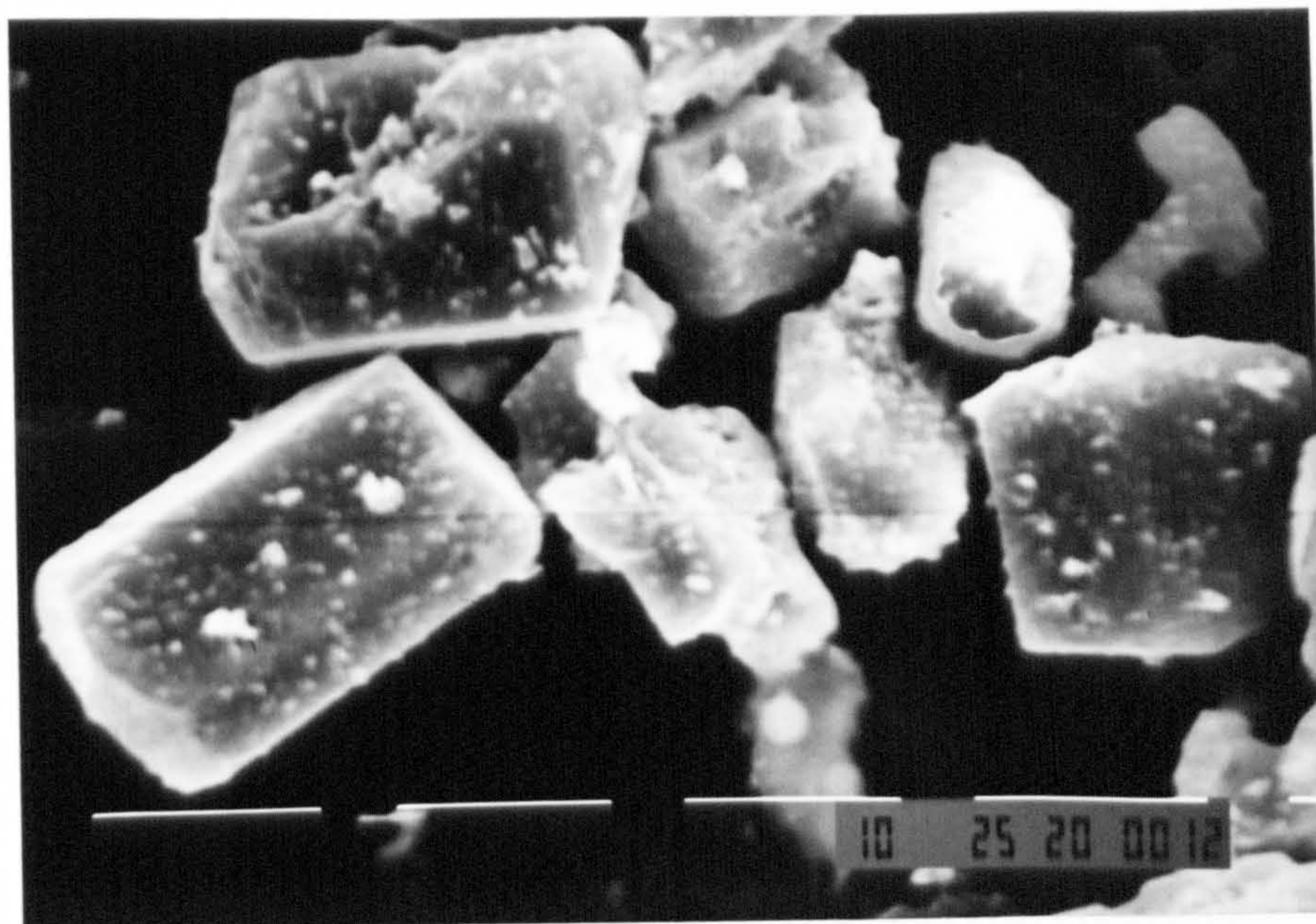


Plate 4.11: Scanning electron micrograph, at x2000, of typical ' α '-soluble anhydrite particles.

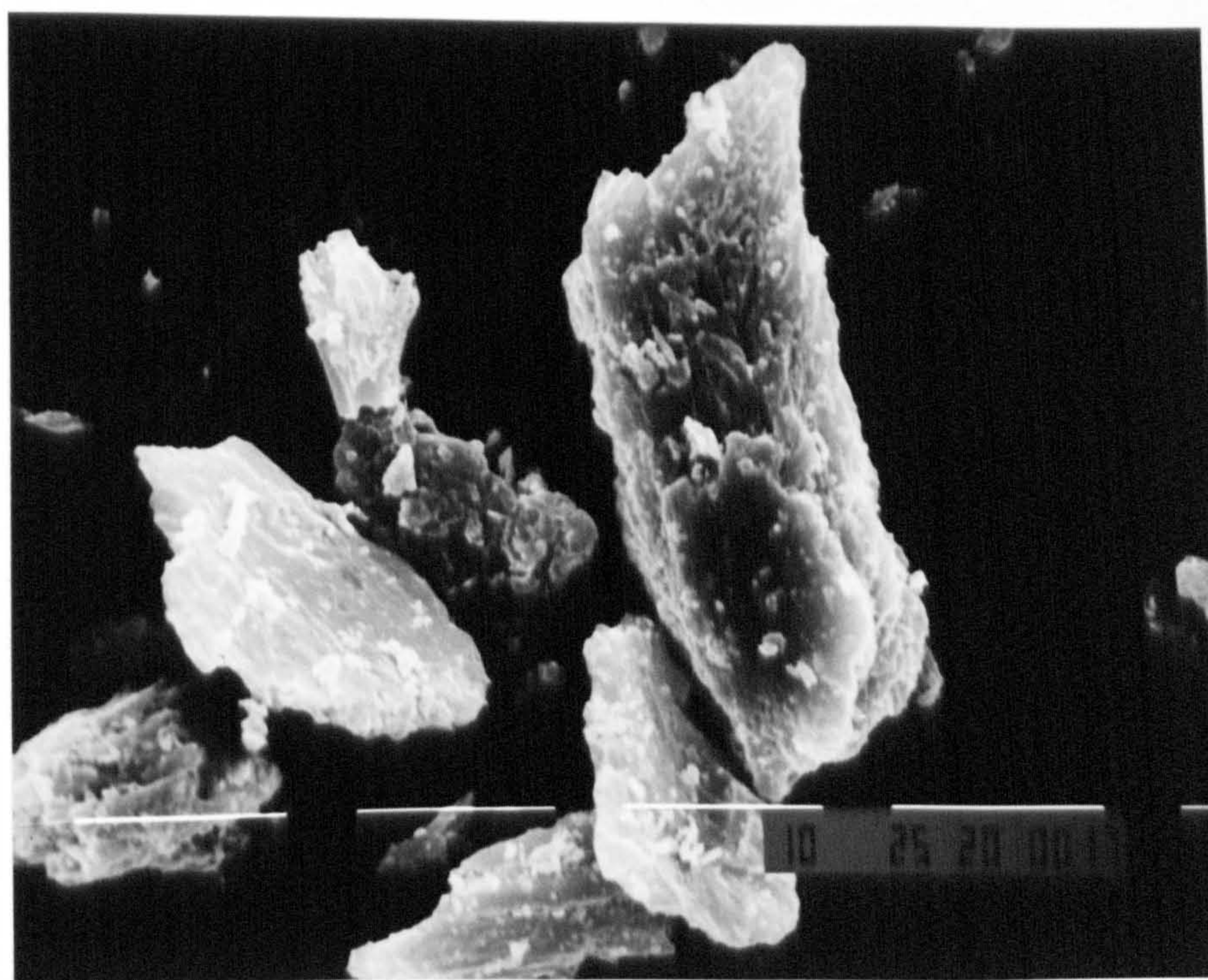


Plate 4.12: Scanning electron micrograph, at x2000, of typical ' β '-soluble anhydrite particles.

materials (Plates 4.1 and 4.2) and supports the hypothesis that the crystal lattice was not changed by the dehydration reaction.

4.5 THE REACTIVITY OF SOLUBLE ANHYDRITE AND THE EFFECT ON HYDRATION PRODUCTS

4.5.1 The Reactivity of Soluble Anhydrite

The reactivity of soluble anhydrite in a saturated solution of dihydrate was investigated to provide information on the effect on the hydration of hemihydrate.

(a) Phase analysis of the hydration products.

(i) X-ray powder diffraction analysis

Examination of the diffraction patterns of the ' α '- soluble anhydrite reaction products showed that each contained a mixture of soluble anhydrite/hemihydrate^{*}, dihydrate and possible traces of insoluble anhydrite. After 1 hour dihydrate was the minor phase and soluble anhydrite/hemihydrate the major, so the reaction was still proceeding. After 10 hours, dihydrate was the major phase and only a small amount of soluble anhydrite/hemihydrate remained. The reaction was complete after 100 hours with dihydrate and a small amount of insoluble anhydrite present.

In the case of the ' β '- soluble anhydrite reaction products, the reaction appeared to be over after 1 hour with only a small amount of soluble anhydrite detected thereafter. While these

* NB As pointed out in Section 4.4.2(a), the crystal structure is identical and cannot be distinguished by X.R.D.

experiments provide an insight into the relative degree of reaction, quantitative data was obtained and is shown in the next section.

(ii) Thermal analysis.

The calcium sulphate phases in the reaction products were calculated from the thermal analysis curves (see Section 3.2.3.(c)) and are shown in Table 4.16. ' α '- soluble anhydrite appears to react with water to first form hemihydrate which then reacts further to give dihydrate. After 1 hour the second reaction had just started and was almost completed after 10 hours. The almost constant anhydrite content was probably due to the soluble anhydrite impurity in the starting material which reacts very slowly.⁷

The ' β '- soluble anhydrite reaction appeared almost complete after 1 hour, with 92% dihydrate present. The remaining anhydrite was slow to react with traces still present after 100 hours.

(b) Microstructure of hydration products

Plates 4.13 and 4.14 show the microstructural development of the solid phases in the ' α '- soluble anhydrite/saturated dihydrate solution reaction mixture.

After 1 hour (Plate 4.13) large particles can be seen to have small needle shaped crystals of dihydrate

Table 4.16: Solid phases present in partially reacted soluble anhydrite/saturated dihydrate solution reaction mixtures.

Reaction time (hrs.)	Dihydrate (wt%)	Hemihydrate (wt%)	soluble and insoluble anhydrite (wt%)
<u>'α'-form</u>			
1	7.8	82.3	9.9
10	92.2	0	7.8
100	93.7	0	6.3
<u>'β'-form</u>			soluble anhydrite (wt%)
1	92.0	0	8.0
10	96.1	0	3.9
100	99.4	0	0.6

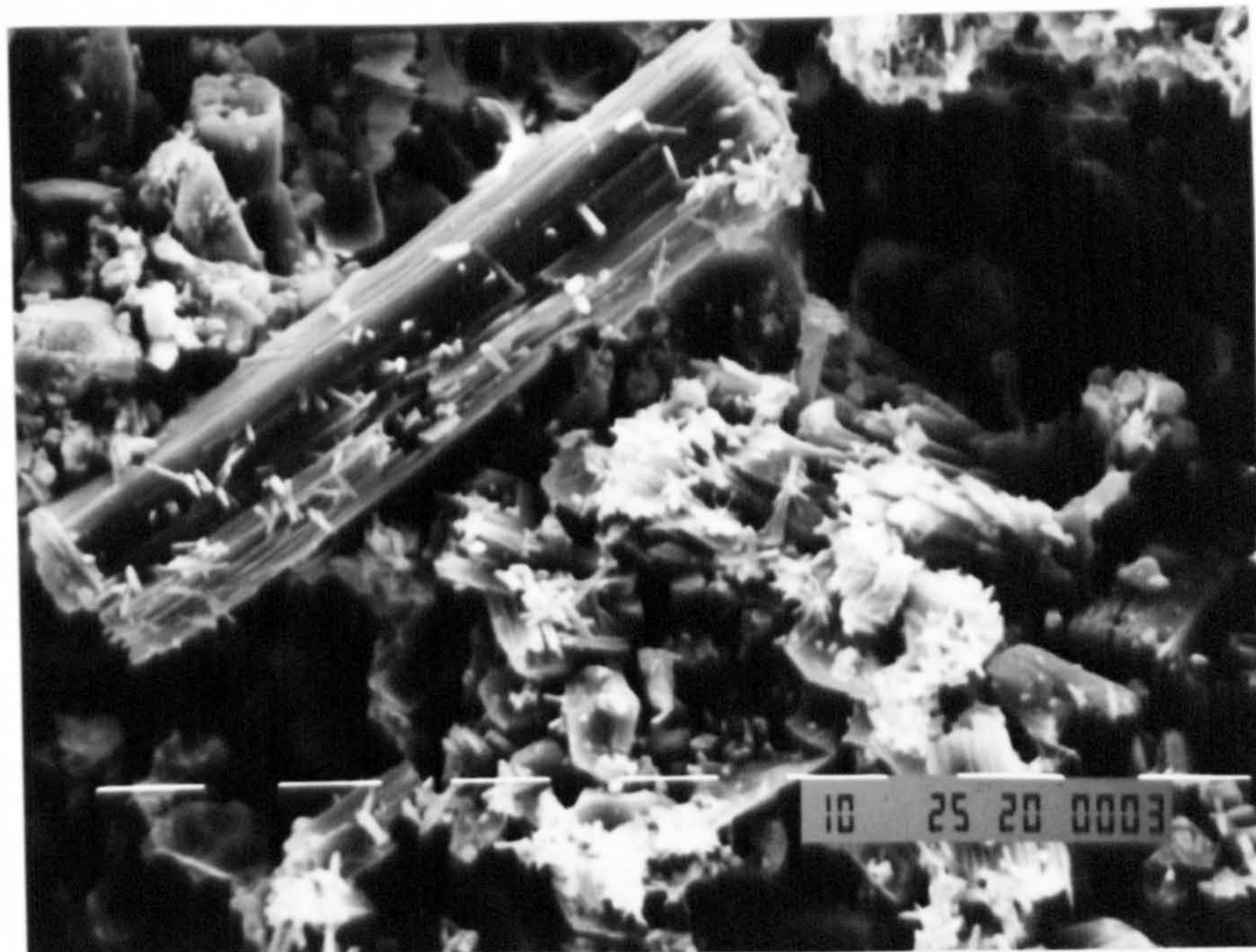


Plate 4.13: Scanning electron micrograph, at x1000, of the solid phases in the ' α '- soluble anhydrite/saturated dihydrate solution reaction mixture after 1 hour.



Plate 4.14: As Plate 4.13, except after 10 hours.

nucleating on the surface. Plate 4.14 shows the microstructure after 10 hours which consisted of a mass of interlocking stubby needles of dihydrate and little change was observed after this time.

The microstructure of the ' β '- soluble anhydrite reaction mixture after 1 hour is shown in Plate 4.15. The microstructure changes very little after this time, consisting of branching, fibrous needles of dihydrate growing from nucleation points.

4.5.2. The Effect of Soluble Anhydrite on the Hydration Products.

The effect of soluble anhydrite on the microstructure, full set strength and porosity of set gypsum plasters was investigated.

(a) Reaction conditions.

If the "water requirement" of the solids is considered, which is dependent on the nature of the grains (see Section 2.3.1), the hemihydrate and soluble anhydrite will have similar water requirements. This is because dehydration has been shown to have little effect on the crystal structure and morphology, or particle size. (see Section 4.4.2). Therefore to ensure constant hydration reaction conditions, the Water/Solid (W/S) ratio was kept constant. Thus the weight percentage of soluble anhydrite added was equal to:

$$\frac{\text{weight (soluble anhydrite)}}{\text{total weight of solids}} \times 100$$



Plate 4.15: Scanning electron micrograph, at x1000, of the solid phases in the ' β '-soluble anhydrite/saturated dihydrate solution reaction mixture after 1 hour.

Note that ' α '- soluble anhydrite was only added to α - hemihydrate and similarly, with ' β '- soluble anhydrite to β - hemihydrate.

(b) Full set and strength.

The variation in full set strength obtained with soluble anhydrite additions is shown in Table 4.17 and graphically in Figure 4.14.

The trend with both hemihydrates is one of decreasing strength with increasing addition of soluble anhydrite. With α - hemihydrate, a 10% addition of anhydrite gave a decrease in strength of approximately 15%. The β - hemihydrate's strength decreased by approximately 20% for the same addition.

(c) Microstructure

Plate 4.16 shows the microstructure of a fully set plaster from α - hemihydrate with 10% wt% of ' α '- soluble anhydrite added. When compared to that of set α - hemihydrate (see Plate 4.3), there is no observable difference in the microstructure.

Microstructures of the set β - hemihydrate, with (Plate 4.17) and without (Plate 4.4) anhydrite additions also showed no difference.

Table 4.17: Variation in the full set strength of hemihydrates with increasing amounts of soluble anhydrite (W/S ratio = 0.6).

Soluble an- hydrite added (wt%)	Modulus of Rupture (MN/m ²)	
	α-hemihydrate	β-hemihydrate
0.0	12.2 ± 0.7	9.8 ± 0.3
2.5	11.2 ± 0.4	8.2 ± 0.2.
5.0	10.8 ± 0.3	8.2 ± 0.3
7.5	10.9 ± 0.4	8.1 ± 0.3
10.0	10.4 ± 0.6	7.7 ± 0.3

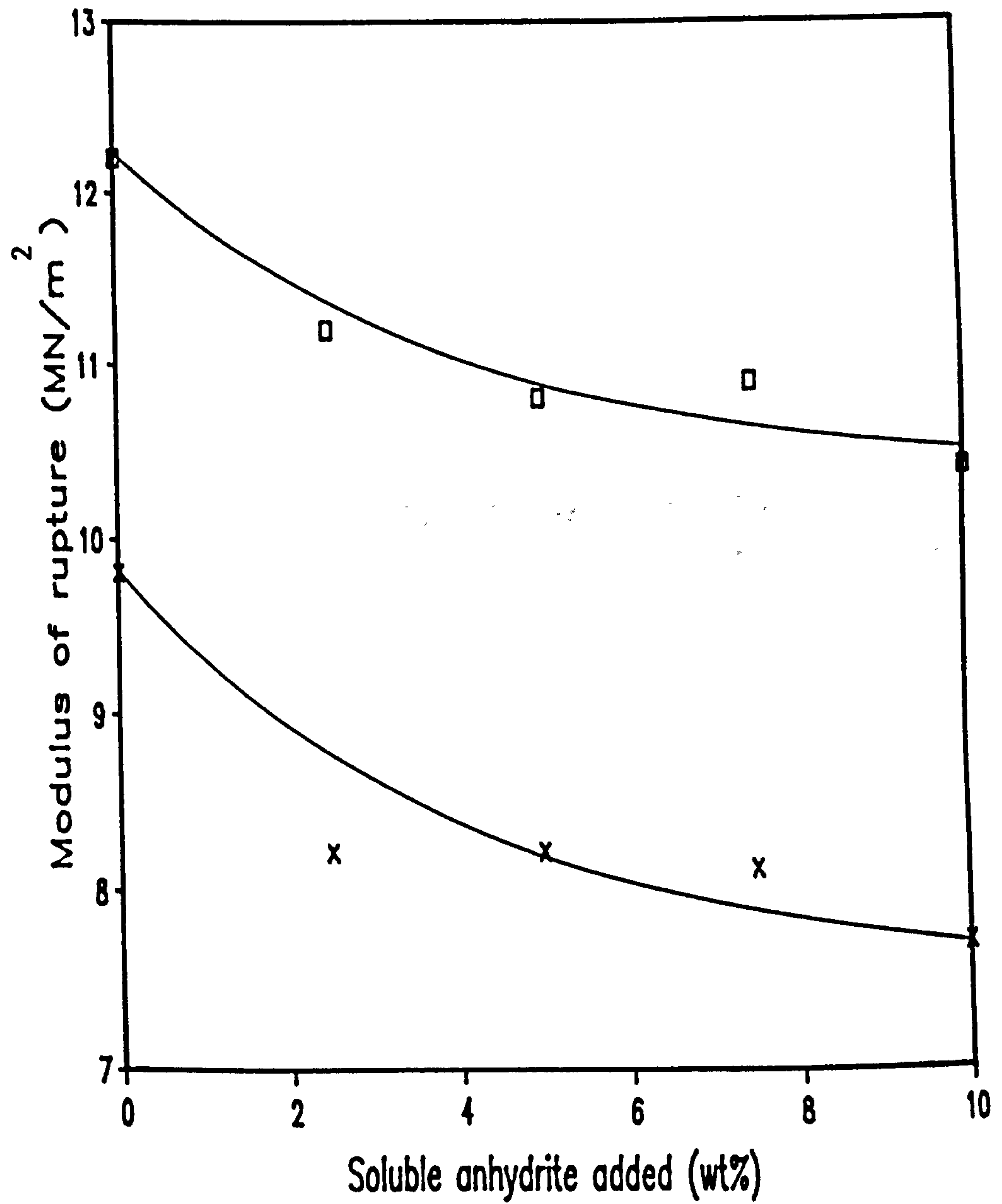


Figure 4.14: Variation in the full set strength of hemihydrates with increasing amounts of soluble anhydrite (W/S ratio = 0.6), where:

- α - hemihydrate
- × β - hemihydrate.



Plate 4.16: Scanning electron micrograph, x1000, of the microstructure of set plaster from 90wt% α -hemihydrate/10wt% α -soluble anhydrite (W/S ratio = 0.6).



Plate 4.17: Scanning electron micrograph, x1000, of the microstructure of set plaster from 90wt% β -hemihydrate/10wt% β -soluble anhydrite (W/S ratio = 0.6).

(d) Porosity.

The variations in the open and true porosities of hemihydrate to which various amounts of soluble anhydrite have been added are shown in Table 4.18. The variation in open porosity is represented graphically in Figure 4.15. Both hemihydrates show almost constant porosity with increasing additions of anhydrite, but it should be noted that the scatter of points and the error bars are reasonably large. These large data variations make the calculation of the closed porosity, from the difference between true and open porosities, meaningless because the value of the difference was much smaller than the magnitude of the errors. However the set β - plaster shows a consistently higher open porosity compared to set α - plaster.

Table 4.18: Variation in the porosity of set hemihydrates with increasing amounts of soluble anhydrite (W/S = 0.6).

Soluble anhydrite added (wt%)	Experimentally determined open porosity (%)	Calculated true porosity (%)
α -hemihydrate		
0.0	43.6 ± 2.8	43.8 ± 2.7
2.5	45.1 ± 0.2	46.0 ± 0.3
5.0	42.8 ± 1.2	45.0 ± 0.6
7.5	43.8 ± 0.9	45.4 ± 0.5
10.0	43.2 ± 0.5	45.2 ± 0.3
β -hemihydrate		
0.0	45.4 ± 0.8	45.4 ± 0.9
2.5	45.5 ± 0.8	45.5 ± 0.8
5.0	46.2 ± 0.6	46.3 ± 0.6
7.5	45.7 ± 1.0	45.7 ± 1.0
10.0	45.4 ± 0.8	45.5 ± 0.8

N.B. Error quoted is the range of the results.

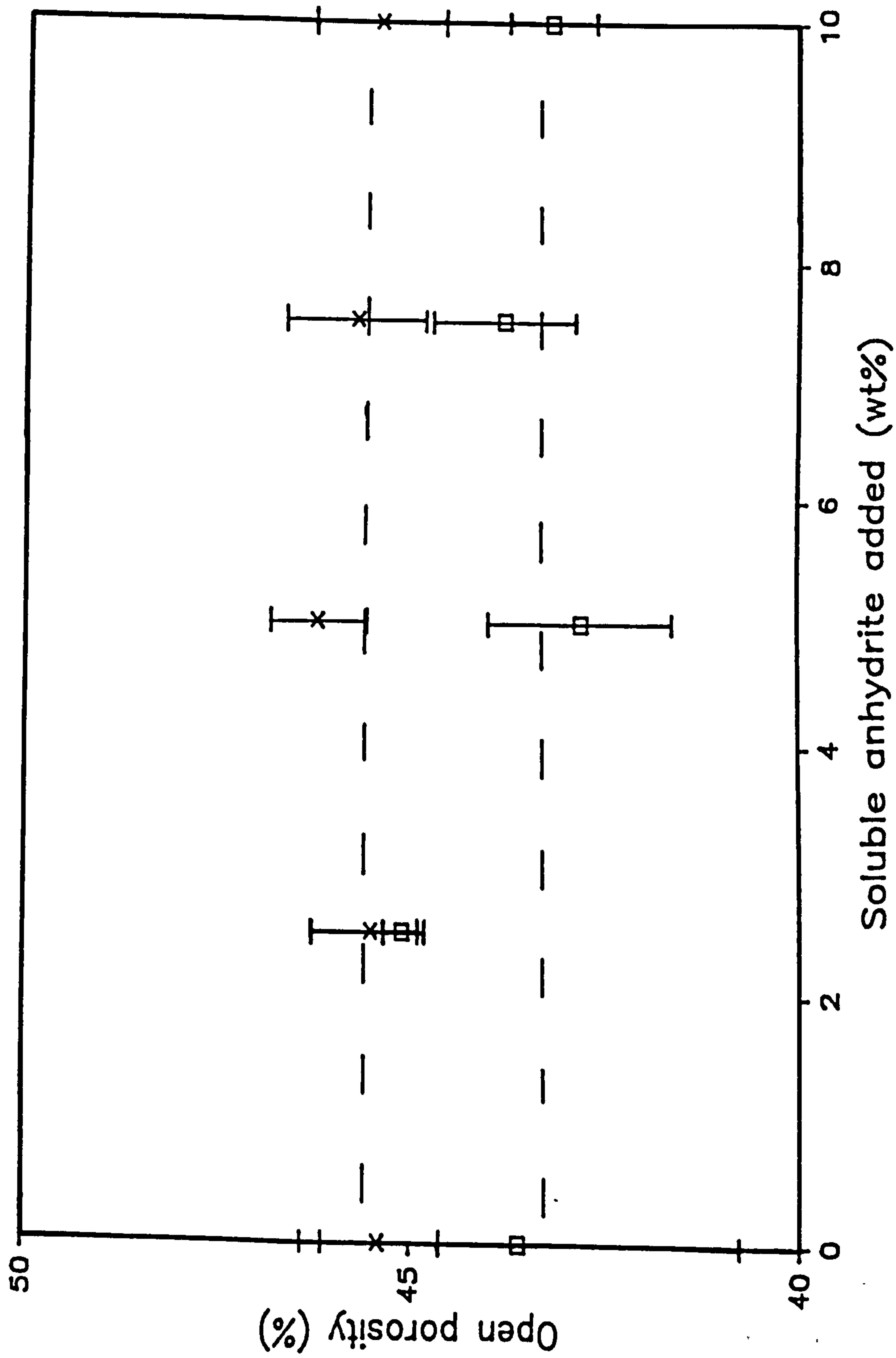


Figure 4.15: Variation in the open porosity of hemihydrates with increasing amounts of soluble anhydrite (W/S ratio = 0.6), where:

□ α

X β .

4.6 CHARACTERISATION OF THE DIHYDRATE REAGENTS

The materials were obtained from two sources:

- (i) BDH - Analar (99%)
- (ii) British Gypsum - washed, ground and then passed a 200 mesh (75 μ m) sieve.⁷¹

Both materials were then ground in either a Tema mill (dry or ethanol slurry) or in a ball mill (ethanol slurry),

- (a) X-ray powder diffraction analysis.

The diffraction patterns of the BDH and British Gypsum reagents showed peaks corresponding to the dihydrate crystal structure with no additional phases detected.

- (b) Thermal analysis.

The data obtained from the dihydrate reagents is shown in Table 4.19 and was typical of Gypsum (see Section 3.2.3.(c)). The amount of dihydrate present can be calculated from these thermal curves and the results are shown in Table 4.20. Both reagents contain over 98% dihydrate.

- (c) Particle size and specific area measurements.

Particle size distributions of the ground reagents were obtained by the laser analysis method (Section 3.1(d)) and the results were quoted as the statistical mean ($\bar{x}$). These results, with the specific surface area measurements,

Table 4.19: T.G.A./D.T.A. of the dihydrate reagents.

Source	D.T.A./T.G.A.	(wt. loss)
British Gypsum	strong endotherm, 137°C } medium endotherm, 157°C } weak exotherm, 358°C	(20.59%) (0.00%)
B.D.H.	strong endotherm, 147°C } medium endotherm, 187°C } weak exotherm, 388°C	(20.62%) (0.00%)

Table 4.20: Calculated percentage of dihydrate in the reagents.

Reagent	% wt. loss	wt% dihydrate (CaSO ₄ .2H ₂ O)
British Gypsum	20.59	98.4
B.D.H.	20.62	98.5

are quoted in Table 4.21. Both reagents show a decrease in particle size and increase in specific surface area on grinding. A point to note is that the BDH ball-milled product has a smaller particle size than the BDH Tema milled (7 mins.) product (6.3 as opposed to 6.7 μ m) and also has a smaller specific surface area (5.9 compared with 7.4 m².g⁻¹).

(d) Chemical analysis.

Qualitative EDAX (see Section 3.1 (g)(ii)) for all elements above Na showed that Ca and S were present in the dihydrate reagents.

(e) S.E.M. studies

The BDH material (Plate 4.18) which had been lightly ground consisted of well formed crystals. The result of dry grinding in Tema mill (Plate 4.19) was to alter the particle shape to nearly spherical and introduced surface roughness. The observed surface roughness was probably responsible from the BDH (6.7 μ m) reagents especially high specific surface area. The ball-milled product (Plate 4.20) was produced by a shearing action which resulted in smaller but still well formed crystals. The 'as received' British Gypsum material consisted of well formed crystal with a relatively rough surface, probably caused by the manufacturer's grinding (Plate 4.21).

Table 4.21: The particle size and specific surface area of the ground reagents.

Reagent	Mode of grinding	Average particle size (μm)	Specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)
BDH.	Tema mill		
	1 min. (dry)	7.2	3.5
	7 min. (dry)	6.7	7.4
	25 min. (ethanol slurry)	10.7	1.6
	Ball mill		
British Gypsum	5 days (ethanol slurry)	6.3	5.9
	as received	54	0.9
	7 days (ethanol slurry)	4.7	15.1

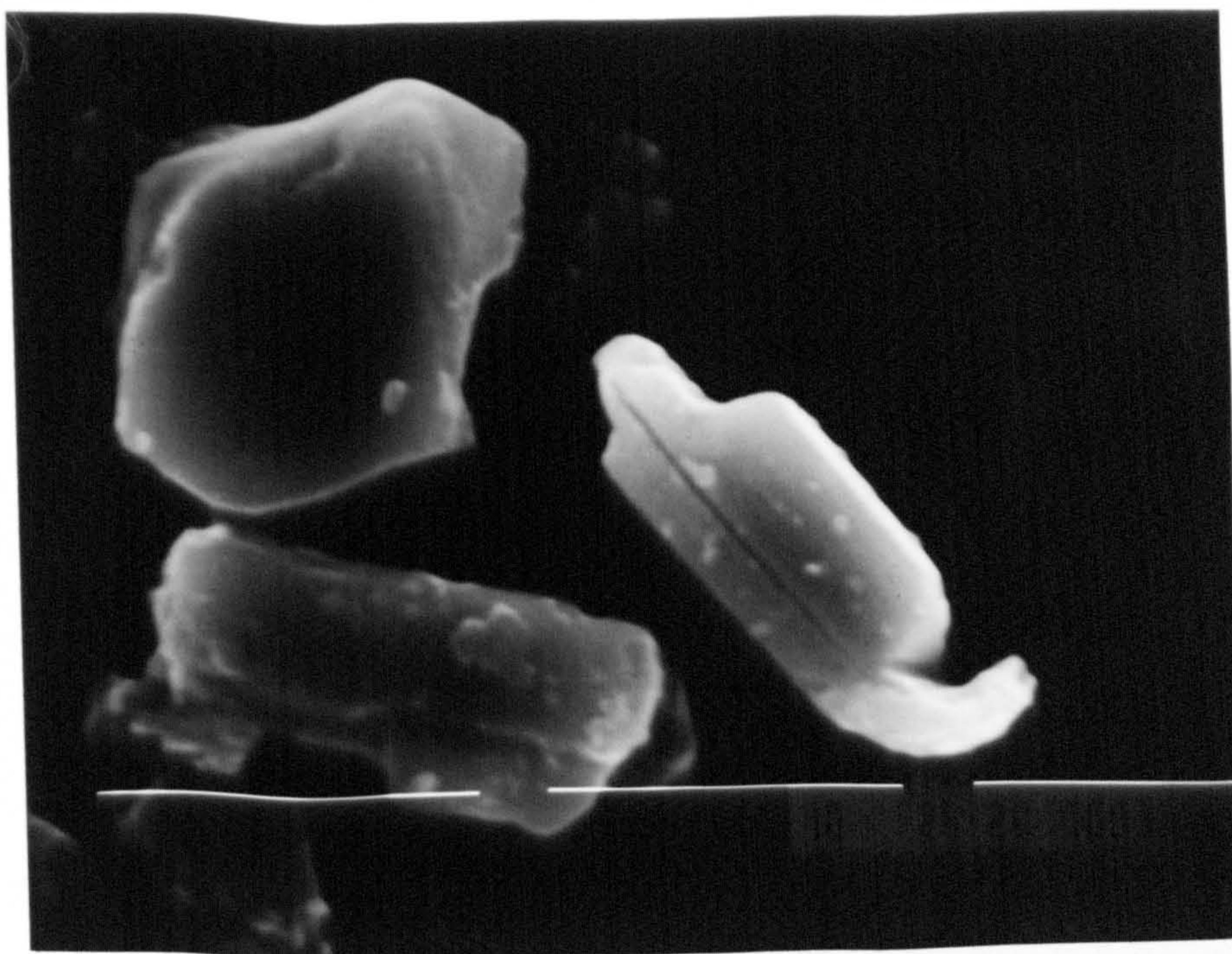


Plate 4.18: Scanning electron micrograph, at x3500, of the BDH (10.7 μ m) dihydrate reagent.

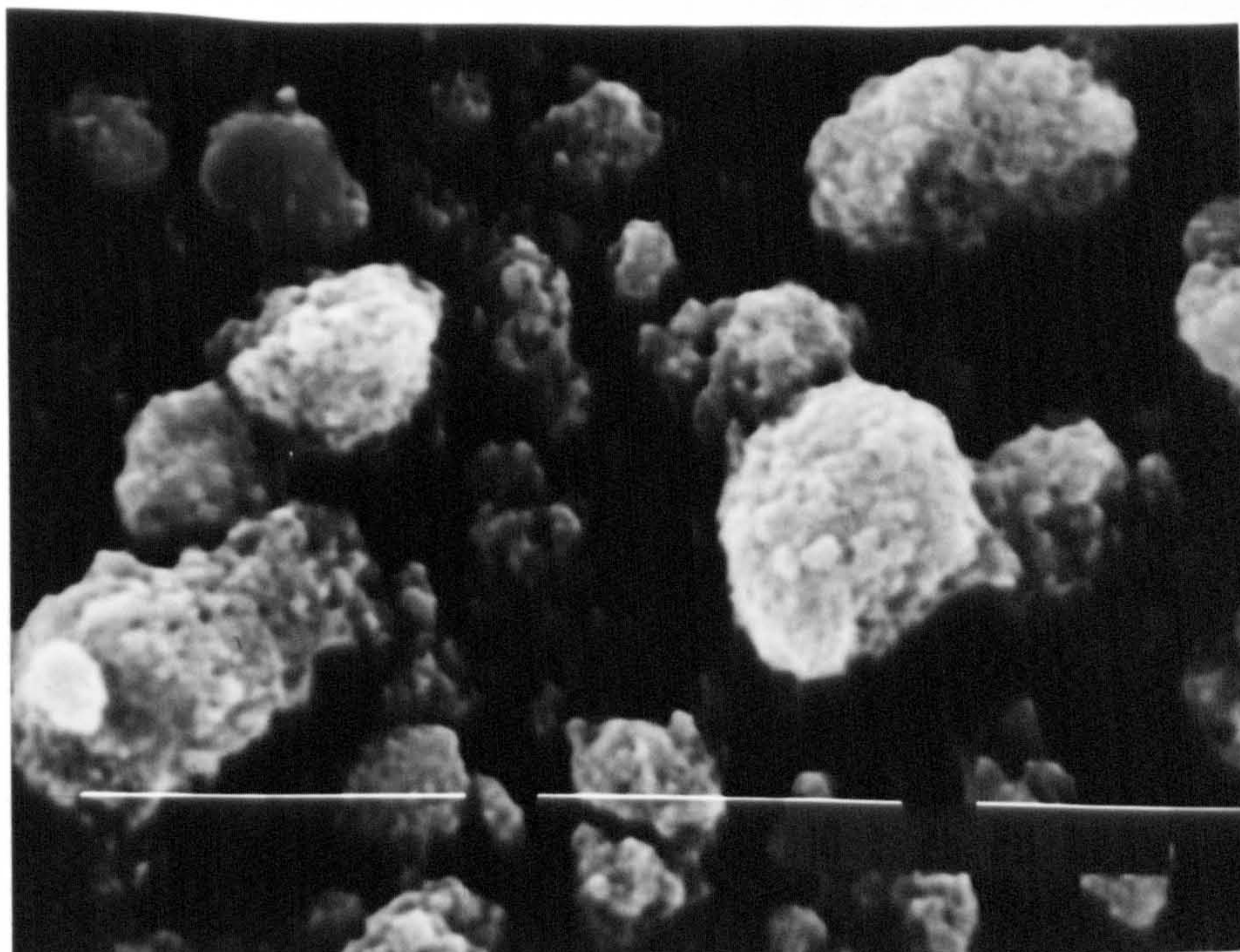


Plate 4.19: Scanning electron micrograph, at x3500, of the BDH (6.7 μ m) dihydrate reagent.

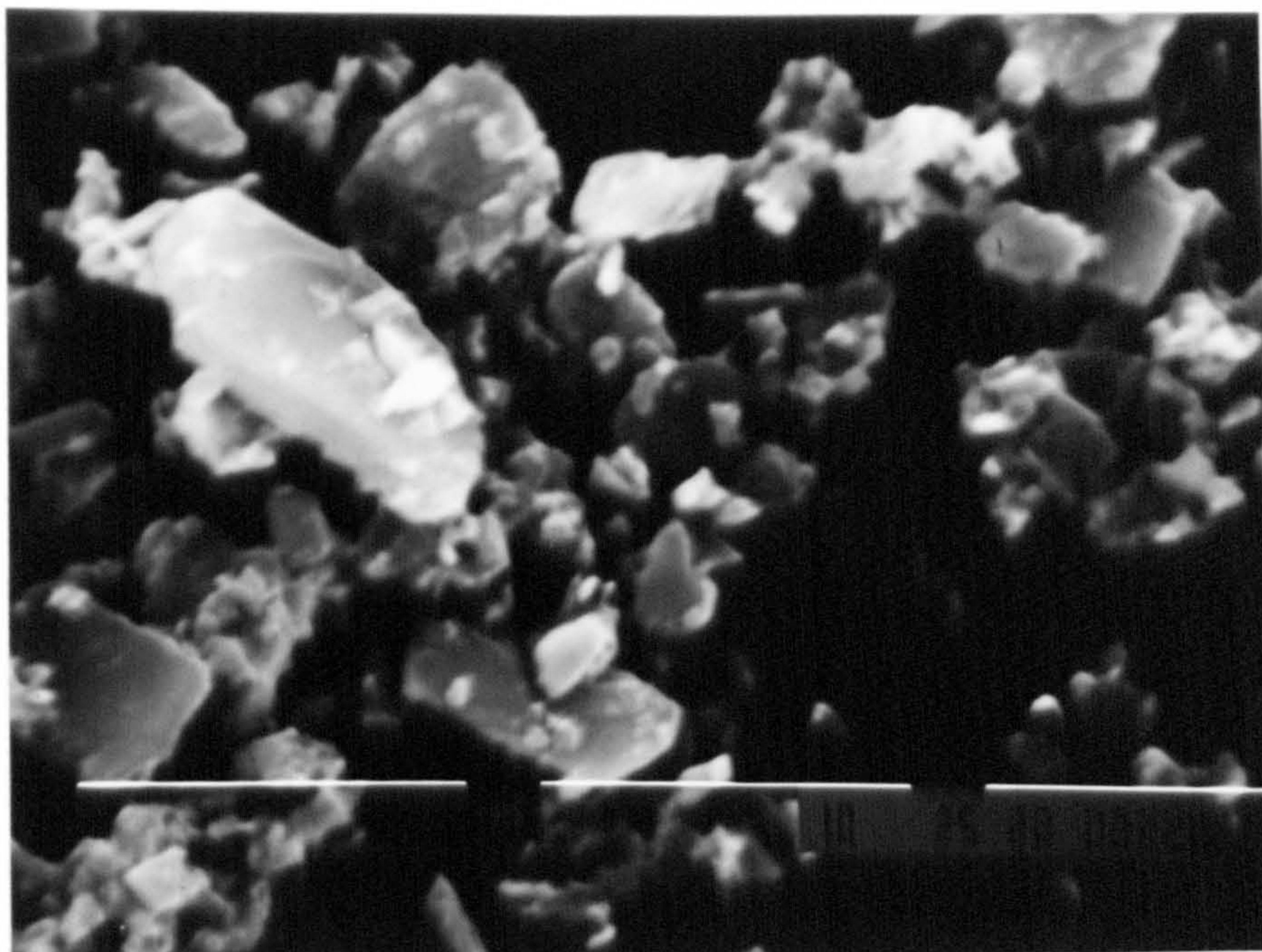


Plate 4.20: Scanning electron micrograph, at x3500, of the BDH (6.3 μ m) dihydrate reagent.

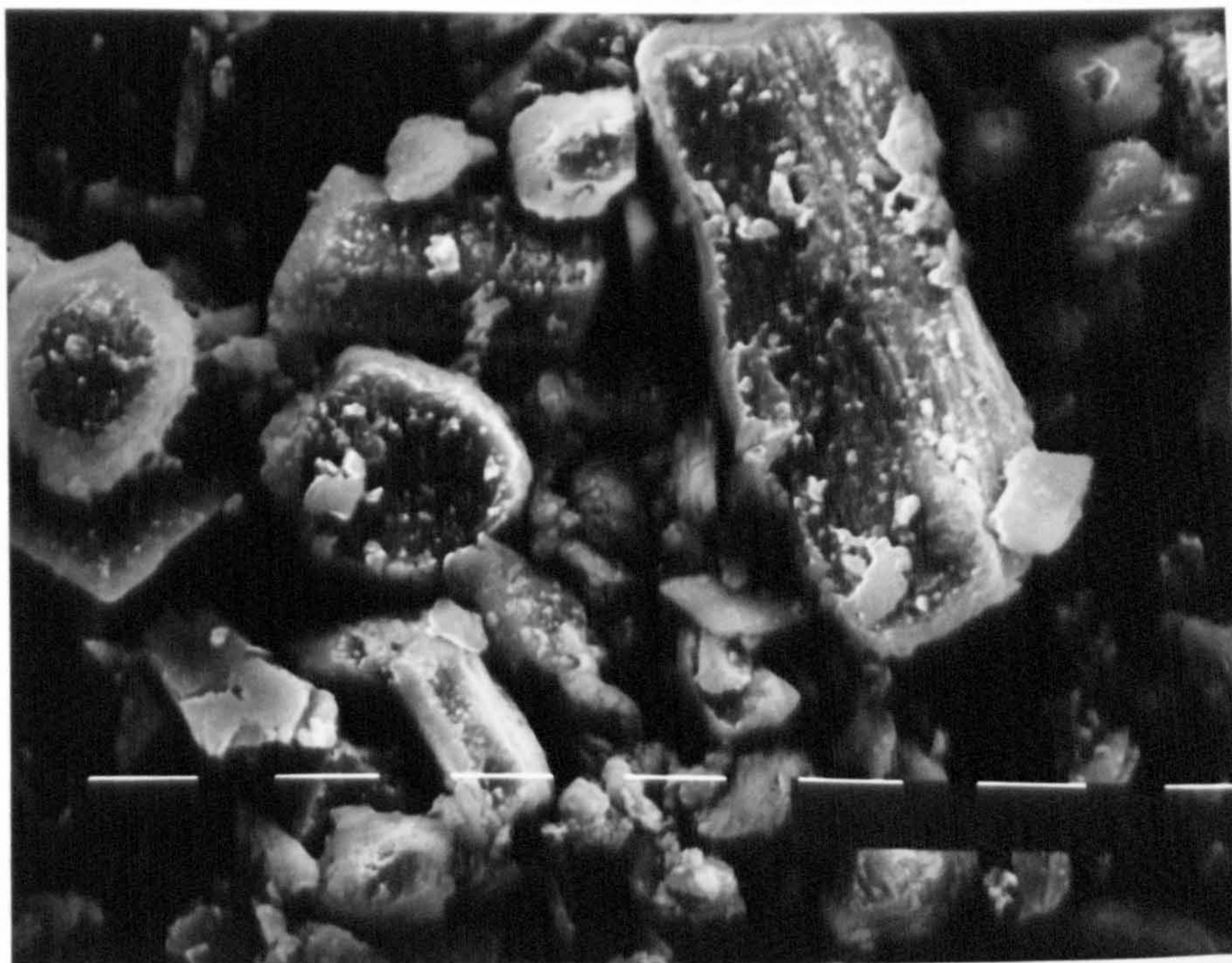


Plate 4.21: Scanning electron micrograph, at x1000, of the British Gypsum (54 μ m) dihydrate reagent.

4.7 THE EFFECT OF DIHYDRATE ADDITIONS ON THE HYDRATION AND REACTION PRODUCTS

(a) The hydration reaction.

The progress of the reaction was followed by simple calorimetry and the results were obtained as ΔT versus time curves. These curves were characterised by the use of derived parameters (see Section 3.2.2.).

The effect of dihydrate additions, of various weight % and particle size, on the hydration reaction is shown in Table 4.22. The W/S ratio of the reaction slurry was kept constant at 0.6 to ensure constant reaction conditions.

The results showed that dihydrate additions accelerated the hydration of hemihydrate and two trends were observed; the smaller the particle size and larger the addition, the faster the reaction. The notable exception to this was the British Gypsum 54 μ m reagent which accelerated the reaction to a greater extent than the BDH 10.7 μ m reagent.

(b) Hydration products.

(i) Full set strength

The effect of 2wt% additions of dihydrate, with various particle sizes, on the full set strength of α - hemihydrate is shown in Table 4.23. Any addition resulted in a reduction in full set strength. The observed trend was for increasing strength to be associated with decreasing dihydrate particle size.

Table 4.22: The effect of dihydrate additions on the hydration of α -hemihydrate (W/S ratio = 0.6).

Dihydrate addition (wt.%)	T _{max} (°C)	Time to T _{max} (mins.)	Max. dT/dt (°C/min.)	Induction period (min.)
No addition	23.3	52.5	0.75	5.4
BDH.				
10.7 μ m (10)	28.8	34.3	1.13	<1
(5)	30.0	44.4	0.97	<1
(2)	30.0	48.5	0.97	1.7
7.2 μ m (2)	30.3	35.6	1.42	<1
(1)	28.2	39.0	1.09	2.6
($\frac{1}{2}$)	25.0	44.6	0.83	3.2
6.7 μ m (2)	30.9	34.9	1.43	<1
(1)	30.0	38.7	1.24	1.7
6.3 μ m (5)	30.6	31.7	1.67	<1
(2)	32.1	32.8	1.53	<1
(1)	30.0	35.5	1.39	<1
($\frac{1}{2}$)	29.2	40.8	1.11	1.6
British Gypsum				
54 μ m (2)	28.8	40.4	1.28	1.32
4.7 μ m (2)	31.4	25.1	2.36	<1

Table 4.23: The effect of dihydrate additions on the full set strength of α -hemihydrate (W/S ratio = 0.6).

Dihydrate addition (2wt%)	Modulus of rupture (MN/m^2)
No addition	12.5 $\pm$ 0.4
BDH.	
10.7 μm	11.5 $\pm$ 0.6
7.2 μm	11.2 $\pm$ 0.5
6.7 μm	10.9 $\pm$ 0.3
6.3 μm	10.7 $\pm$ 0.5
British Gypsum	
54 μm	12.2 $\pm$ 0.2
4.7 μm	11.0 $\pm$ 0.4

(ii) Microstructure

The microstructure of the set α - plaster (Plate 4.22) consisted of an interlocking mass of relatively stubby needles of dihydrate (approximately $15 \times 1 \times 1 \mu\text{m}$).

When 2wt.% dihydrate, of various particle sizes, was added the microstructure changed (Plate 4.23) to shorter, thinner needles of dihydrate (approximately $10 \times \frac{1}{2} \times \frac{1}{2} \mu\text{m}$).



Plate 4.22: Scanning electron micrograph at x2000, of the set plaster from α -hemihydrate (W/S ratio = 0.6).

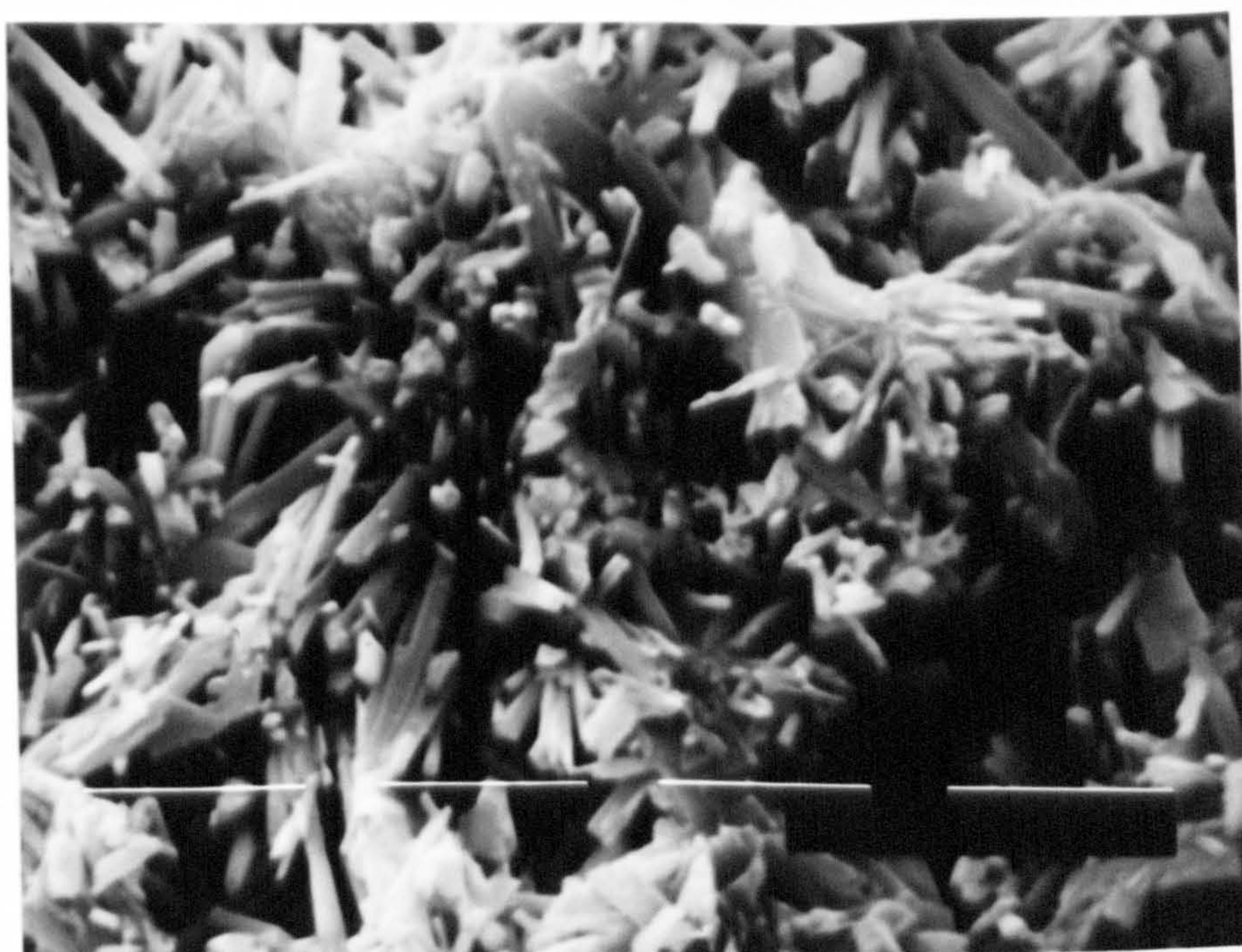


Plate 4.23: Scanning electron micrograph, at x2000, of the set plaster from α -hemihydrate plus 2wt% BDH, (6.7 μ m) dihydrate (W/S ratio = 0.6).

4.8 THE EFFECT OF POTASSIUM SULPHATE ON THE HYDRATION AND REACTION PRODUCTS

The potassium sulphate used was a BDH, analar (99.5%) grade reagent and XRD, showed this to be the only phase present.

(a) Hydration reaction.

The effect of various weight % additions of potassium sulphate on the hydration of *hemihydrate* is shown in Table 4.24. The results showed that potassium sulphate accelerated the hydration reaction and the rate increased with the amount of K_2SO_4 added up to 2wt.%. Above 2wt.% very little change in the degree of acceleration was observed.

(b) Hydration products.

(i) Full set strength

The effect of potassium sulphate additions on the full set strength of α - hemihydrate is shown in Table 4.25. The observed trend was for increasing amounts of K_2SO_4 to progressively decrease the full set strength.

(ii) Microstructure

The effect of K_2SO_4 additions on the set plasters microstructure is shown in Plates 4.24 and 4.25. When compared to that of set α - hemihydrate (Plate 4.22) the effect of K_2SO_4 addition was to increase the size of the dihydrate crystals. With no addition the size was approximately $15 \times 1 \times 1 \mu m$, with 1wt.%

Table 4.24: The effect of potassium sulphate additions on the hydration of α -hemihydrate (W/P ratio = 0.6).

K_2SO_4 added (wt.%)	T_{max} ($^{\circ}C$)	Time to T_{max} (mins.)	Max.dT/dt ($^{\circ}C/min.$)	Induction period (mins.)
0	23.3	52.5	0.75	5.4
$\frac{1}{2}$	35.0	27.1	2.48	3.4
1	34.0	19.4	3.40	2.2
2	37.9	13.9	5.23	< 1
5	39.4	13.8	5.33	< 1

Table 4.25: The effect of potassium sulphate additions on the full set strength of α -hemihydrate (W/P ratio = 0.6).

K_2SO_4 added (wt.%)	Modulus of rupture (MN/m^2)
0	12.6 ± 0.5
$\frac{1}{2}$	11.5 ± 0.1
1	11.2 ± 0.3
2	10.5 ± 0.3
5	9.6 ± 0.3



Plate 4.24: Scanning electron micrograph, at x2000, of the set plaster from α -hemihydrate plus 1wt% K_2SO_4 (W/P ratio = 0.6).

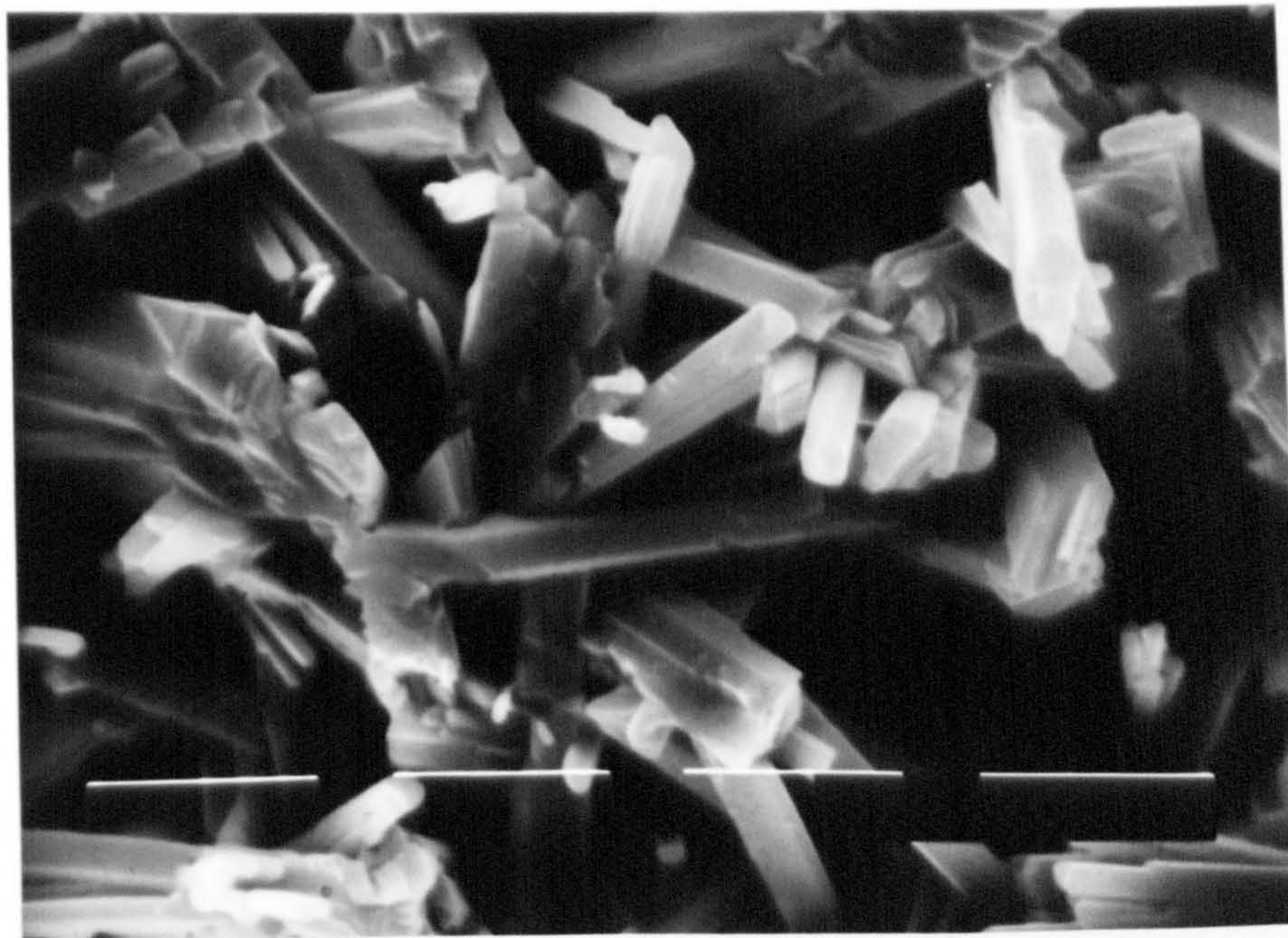


Plate 4.25: As Plate 4.24, except 2wt% K_2SO_4 .

K_2SO_4 the size was $20 \times 2 \times 2 \mu m$ and finally with
2wt.% K_2SO_4 the size increased to $25 \times 3 \times 3 \mu m$.

4.9 THE EFFECT OF AN 'IN-SITU' NUCLEATION/ACCELERATION AGENT ON THE HYDRATION AND REACTION PRODUCTS

It was proposed that the following reaction:

$2\text{KHSO}_4 (\text{aq}) + \text{Ca}(\text{OH})_2 (\text{aq}) \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} (\text{s}) + \text{K}_2\text{SO}_4 (\text{aq})$ could be used to generate 'in-situ' microcrystalline nuclei of the dihydrate in the presence of K_2SO_4 , a known accelerating agent. This would hopefully result in a fast setting plaster of higher strength.

(a) *Conformation of the 'in-situ' reaction.*

Potassium hydrogen sulphate (1.58g, A.G.) and calcium hydroxide (0.43g, A.G.) were mixed together and then added to water (30g) with stirring. If the stoichiometry of the above reaction was correct this would result in the formation of 1g of dihydrate and 1.01g of potassium sulphate. After 1½ mins. the above suspension was filtered and any dissolved solids were precipitated with ethanol (A.G.). Examination of the solids in suspension by XRD showed the phases present to be $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (estimated approximately 70%) and $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (estimated approximately 30%). The solids from solution were found to contain only K_2SO_4 .

(b) *Nucleation/acceleration systems*

It was decided to compare four systems; two using the 'in-situ' generated reagents and two using the commercial reagents K_2SO_4 (A.G.) and British Gypsum (54µm) dihydrate. The systems were as follows:

(i) 'In-situ' systems.

System 1; Ca(OH)_2 (0.86g) and KHSO_4 (3.16g) were added to α -hemihydrate (100g) and mixed in a ball-mill for 24 hours. The plaster was then added to water (60g) with stirring. The W/P ratio was kept constant at 0.6 and if the nucleation/acceleration reaction was stoichiometric 2g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 2.02g of K_2SO_4 would be produced.

System 2; As system 1 except Ca(OH)_2 (0.43g) and KHSO_4 (0.58g) were used to produce 1g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 1.01g of K_2SO_4 'in-situ'.

(ii) Reference systems.

System 3; As System 1 except the Ca(OH)_2 and KHSO_4 were replaced by K_2SO_4 (2g) and 2g of British Gypsum (54 μm) dihydrate.

System 4; As system 3 except that the weight added of the reagents was changed to 1g of each

(c) Hydration reaction.

Table 4.26 shows that all four systems accelerated the hydration of α -hemihydrate. The 'in-situ' systems had greater accelerating power than the reference systems;

Table 4.26: The effect of the nucleation/acceleration systems on the hydration of α -hemihydrate (W/P ratio = 0.6).

System	$T_{\max}$ ($^{\circ}\text{C}$)	Time to $T_{\max}$ (mins.)	Max. dT/dt ($^{\circ}\text{C}/\text{min.}$)	Induction period (mins.)
No addition	23.3	52.5	0.75	5.4
1	45.0	6.42	9.38	< 1
2	38.8	9.84	6.37	< 1
3	35.4	11.5	5.71	< 1
4	35.4	14.4	4.87	< 1

Table 4.27: The effect of the nucleation/acceleration systems on the full set strength of α -hemihydrate (W/P ratio = 0.6).

System	Modulus of rupture (MN/m^2)
No addition	12.6 ± 0.5
1	— *
2	11.8 ± 0.5
3	10.5 ± 0.3
4	11.1 ± 0.3

* The plaster set too rapidly to allow production of strength test specimens.

both 'in-situ' systems accelerated the reaction to a greater degree than the addition of 2wt.% K_2SO_4 and 2wt.% (54 μ m) dihydrate.

(d) *Hydration products*

(i) Full set strength

Table 4.27 shows the effect of the four systems on the full set strength of α - hemihydrate.

The 'in-situ' reagents reduced the strength by a lesser degree than the commercial additives.

(ii) Microstructure

Plates 4.26 and 4.27 show the microstructure of the set plasters for systems 2 and 4 respectively.

The crystal habit of the dihydrate changed very little compared to that of the set α - hemihydrate (Plate 4.3).



Plate 4.26: Scanning electron micrograph, at x1000, of the set plaster from α -hemihydrate (50g) plus $\text{Ca}(\text{OH})_2$ (0.22g) and KHSO_4 (0.79g) (W/P ratio = 0.6).

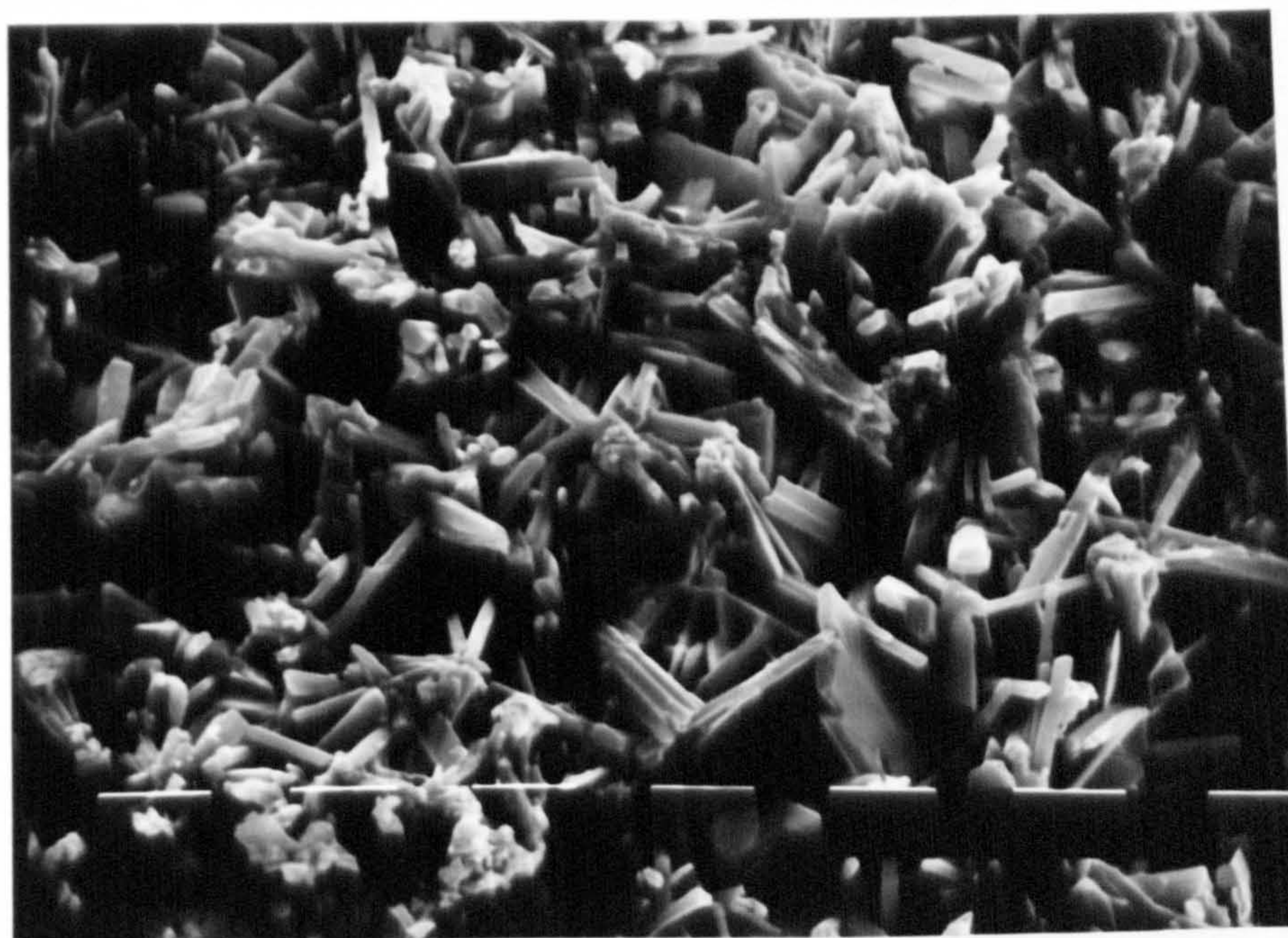


Plate 4.27: Scanning electron micrograph, at x1000 of the set plaster from α -hemihydrate plus 1wt% K_2SO_4 and 1wt% British Gypsum (54 μm) dihydrate (W/P ratio = 0.6).

Table 4.28: The effect of $\alpha:\beta$ hemihydrate ratio on the W/P ratio of bandages.

Weight fraction of α ($\alpha/[\alpha + \beta]$)	Experimentally determined W/P ratio	Least squares fitted values of W/P ratio
1	0.45	0.45
0.75	0.49	0.51
0.5	0.59	0.56
0.25	0.61	0.62
0	0.68	0.68

Table 4.29: The effect of $\alpha:\beta$ hemihydrate ratio, at the determined W/P ratio, on the full set strength of plasters.

Weight fraction of α ($\alpha/[\alpha + \beta]$)	W/P ratio*	Modulus of rupture (MN/m^2)
1	0.45	14.6 ± 0.3
0.75	0.51	12.0 ± 0.2
0.5	0.56	11.1 ± 0.3
0.25	0.62	9.9 ± 0.1
0	0.68	7.3 ± 0.1

* Note that this is the least squares fitted value.

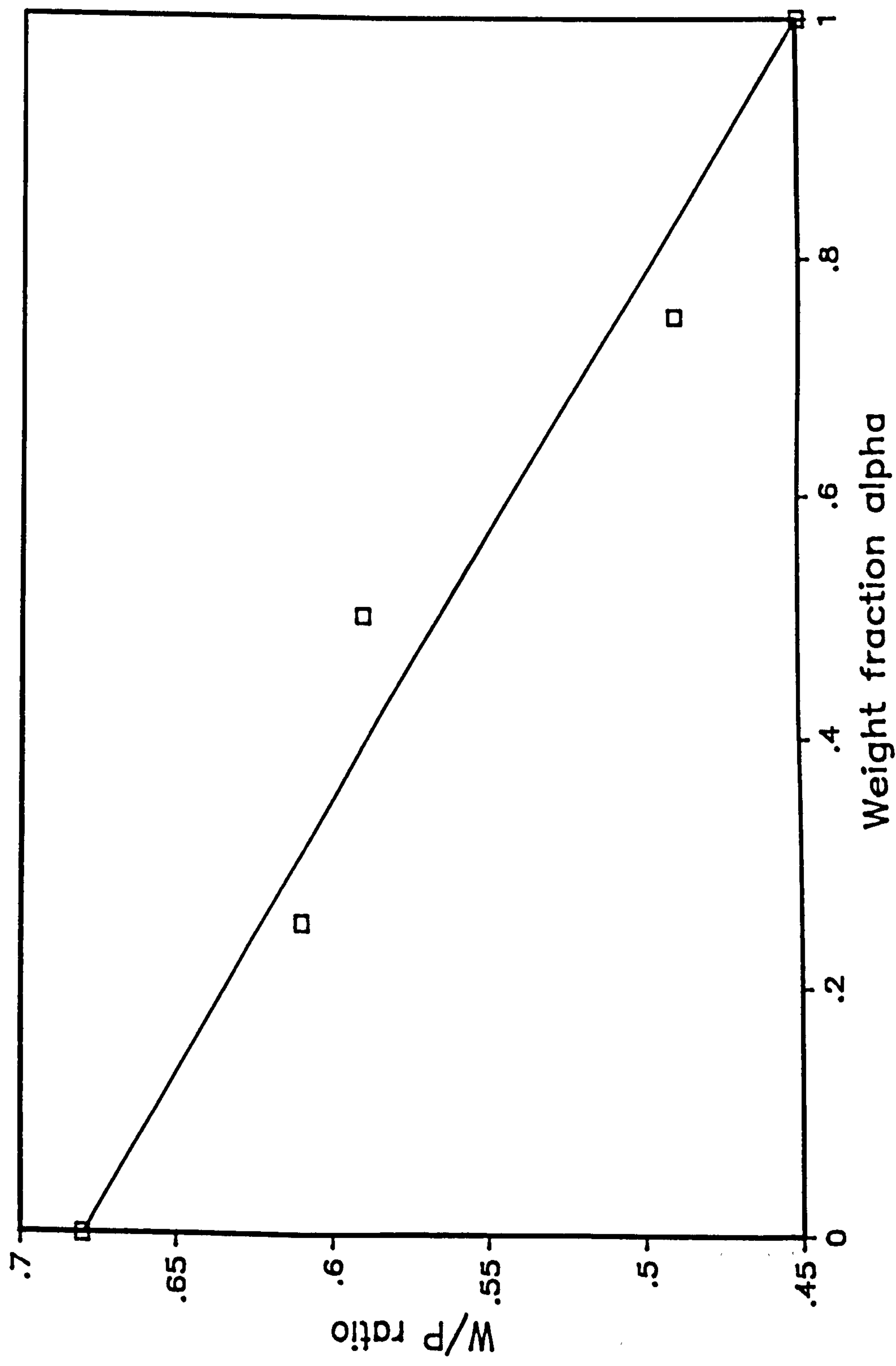


Figure 4.16: The effect of $\alpha : \beta$ hemihydrate ratio on the W/P ratios of bandages.

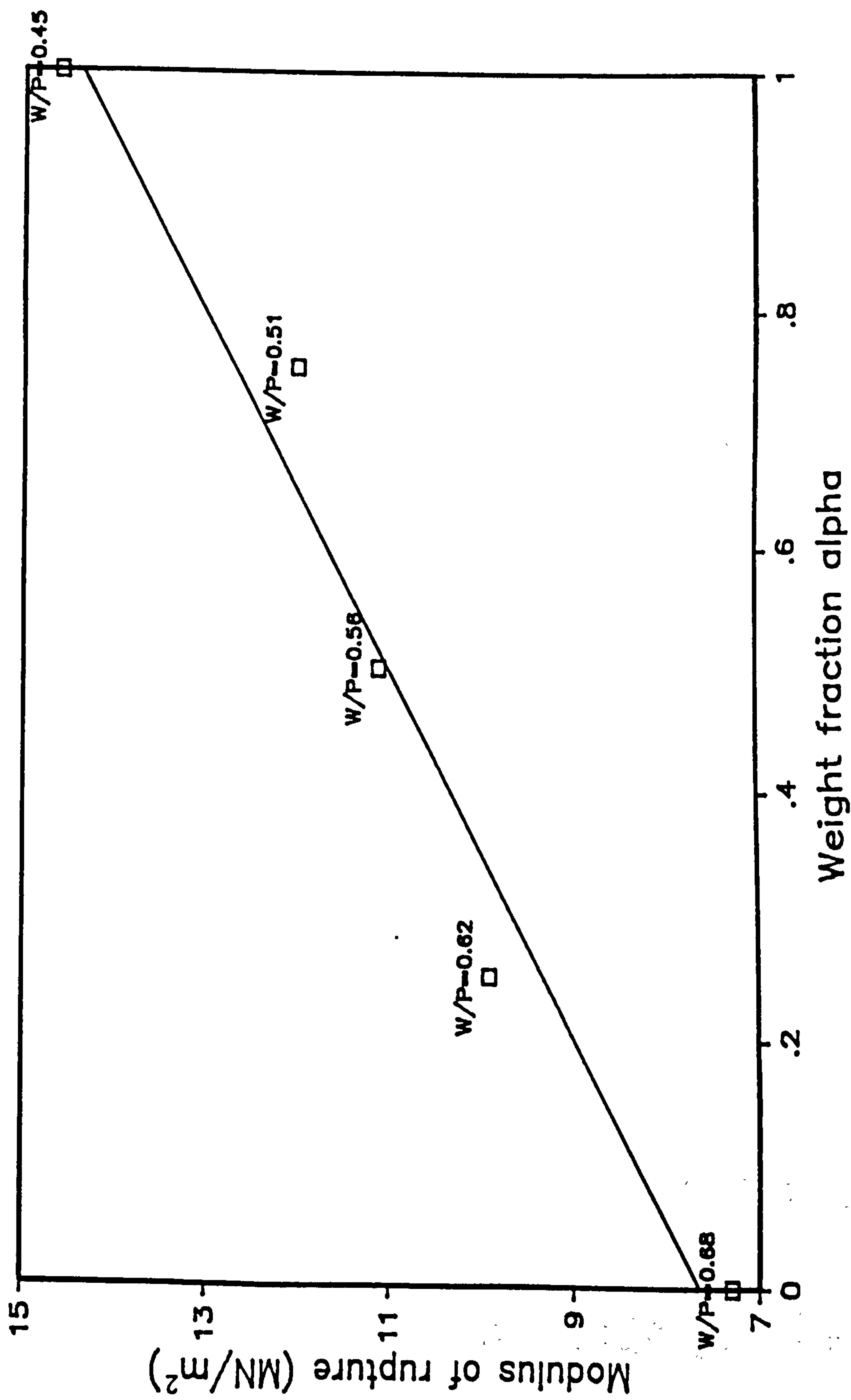


Figure 4.17: The effect of α : β hemihydrate ratio, at the determined W/P ratio, on the full set strength of plasters.



Plate 4.28: Scanning electron micrograph, at x1000, of the set plaster from 100wt% α -hemihydrate. (W/P ratio = 0.45).



Plate 4.29: Scanning electron micrograph, at x1000, of the set plaster from 75wt% α /25wt% β -hemihydrates (W/P ratio = 0.51).



Plate 4.30: Scanning electron micrograph, at x1000, of the set plaster from 50wt% α /50wt% β -hemihydrates (W/P ratio = 0.56).

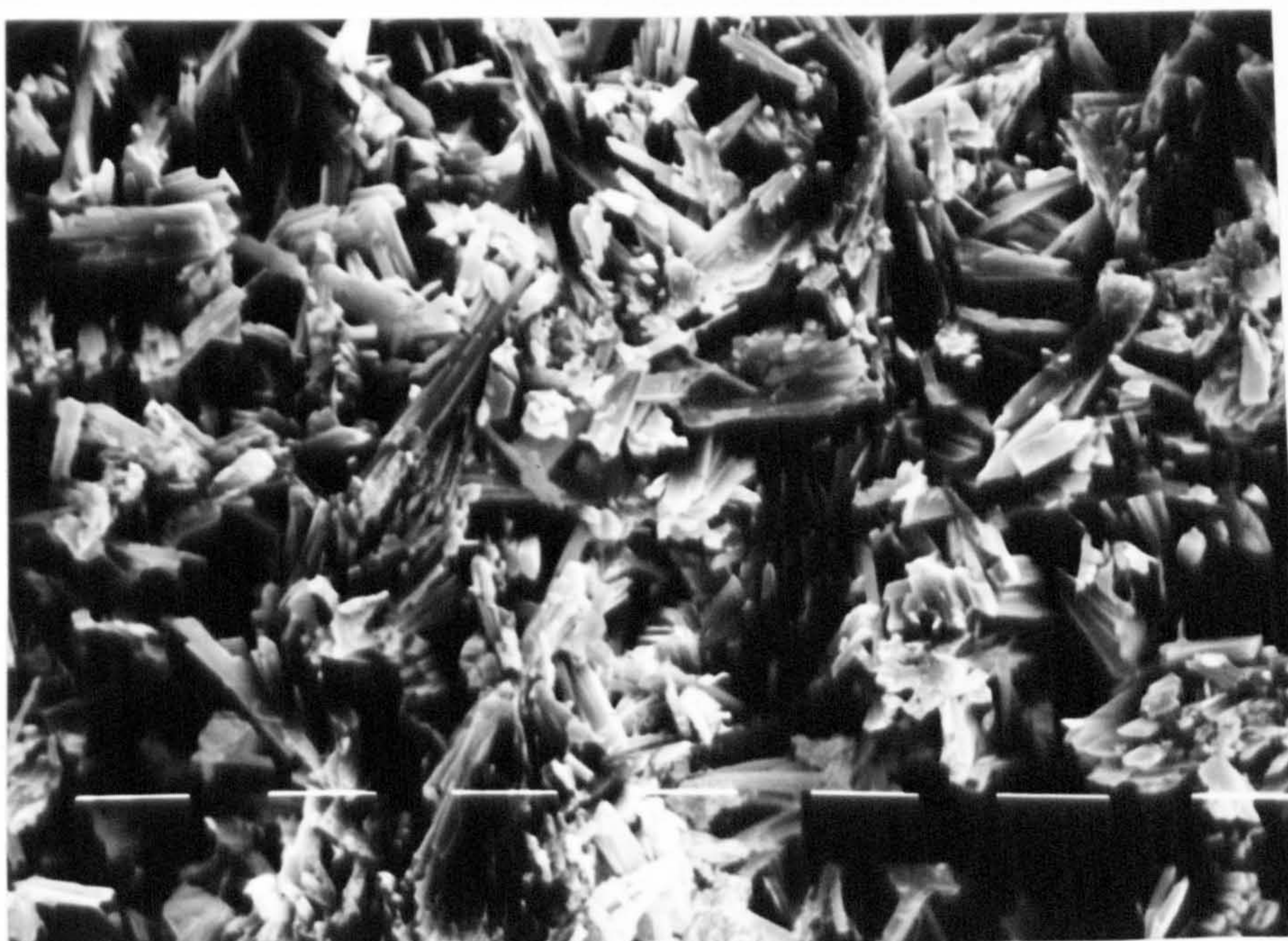


Plate 4.31: Scanning electron micrograph, at x1000, of the set plaster from 25wt% α /75wt% β -hemihydrate (W/P ratio = 0.62).



Plate 4.32: Scanning electron micrograph, at x1000, of the set plaster from 100wt% β -hemihydrate (W/P ratio = 0.68).

4.10 THE EFFECT OF α : β HEMIHYDRATE RATIO ON THE PROPERTIES OF SET GYPSUM PLASTERS

(a) W/P ratio determination for various α : β ratios.

Bandages were produced with plasters of various α : β hemihydrate ratios (see Section 3.4) and the W/P ratio of these bandages was determined (see Section 4.2(a)). The results of these determinations are shown in Table 4.28 and represented graphically in Figure 4.16. The trend was for decreasing W/P ratios with increasing α - hemihydrate content.

(b) Properties of set gypsum plasters with varying α : β ratios.

(i) Full set strength

The effect of α : β hemihydrate ratio, at the least squares fitted W/P ratio value, on the full set strength of plaster is shown in table 4.29 and graphically in Figure 4.17. The trend was for increasing strength with increased α - hemihydrate content and as a result decreasing W/P ratio.

(ii) Microstructure

Plates 4.28 to 4.32 show the change in microstructure of set plasters with decreasing α - hemihydrate content and as a result increasing W/P ratio. The microstructure of set α - hemihydrate (W/P ratio = 0.45) consisted of an interlocking mass of relatively short, stubby

needles of dihydrate (Plate 4.28). At the other extreme, the microstructure of set β -hemihydrate (W/P ratio = 0.68) consisted of more fibrous, branching needles of dihydrate forming sheafs which have grown radially from nucleation sites (Plate 4.32). Plates 4.29 to 4.31 show intermediate structures.

4.11 THE EFFECT OF THE COMMERCIAL BINDING AGENTS ON THE HYDRATION REACTION AND PRODUCTS

The α - hemihydrate with 1 wt.% polyvinyl acetate and 1 wt.% hydroxypropylcellulose was recovered in the form of a plaster/methylene chloride slurry from the mixing stage of bandage production (see Section 3.4). The solvent was allowed to evaporate off resulting in a compacted solid, which was then lightly ground to produce a powder.

(a) *The effect on the hydration reaction.*

The effect of the binders on the hydration of α - hemihydrate is shown in Table 4.30. The results show that at a fixed W/P ratio the binders slightly accelerate the hydration reaction.

(b) *The effect on the hydration products.*

(i) Full set strength

Table 4.31 shows the effect of binders on the full set strength of α - hemihydrate. The binders decrease the strength by 24%; from 12.6 to 9.6 MN/m²

(ii) Microstructure

Plate 4.33 shows the microstructure of set α - hemihydrate plus the commercial binders. When compared to the microstructure of set α - hemihydrate (Plate 4.3), the dihydrate needles appear to have become finer with a higher aspect ratio in the presence of these binders.

Table 4.30: The effect of binders on the hydration of α -hemihydrate (W/P ratio = 0.6).

Binders (wt%)	$T_{\max}$ ($^{\circ}\text{C}$)	Time to $T_{\max}$ (mins.)	Max.dT/dt ($^{\circ}\text{C}/\text{min}$)	Induction period (mins)
No binders	23.3	52.5	0.75	5.4
P.V. Acetate (1%) + hydroxypropyl-cellulose (1%)	22.8	47.7	0.77	5.2

Table 4.31: The effect of binders on the full set strength of α -hemihydrate (W/P ratio = 0.6).

Binders (wt%)	Modulus of rupture (MN/m^2)
No binders	12.6 $\pm$ 0.5
P.V. Acetate (1%) + hydroxypropylcellulose (1%)	9.6 $\pm$ 0.2

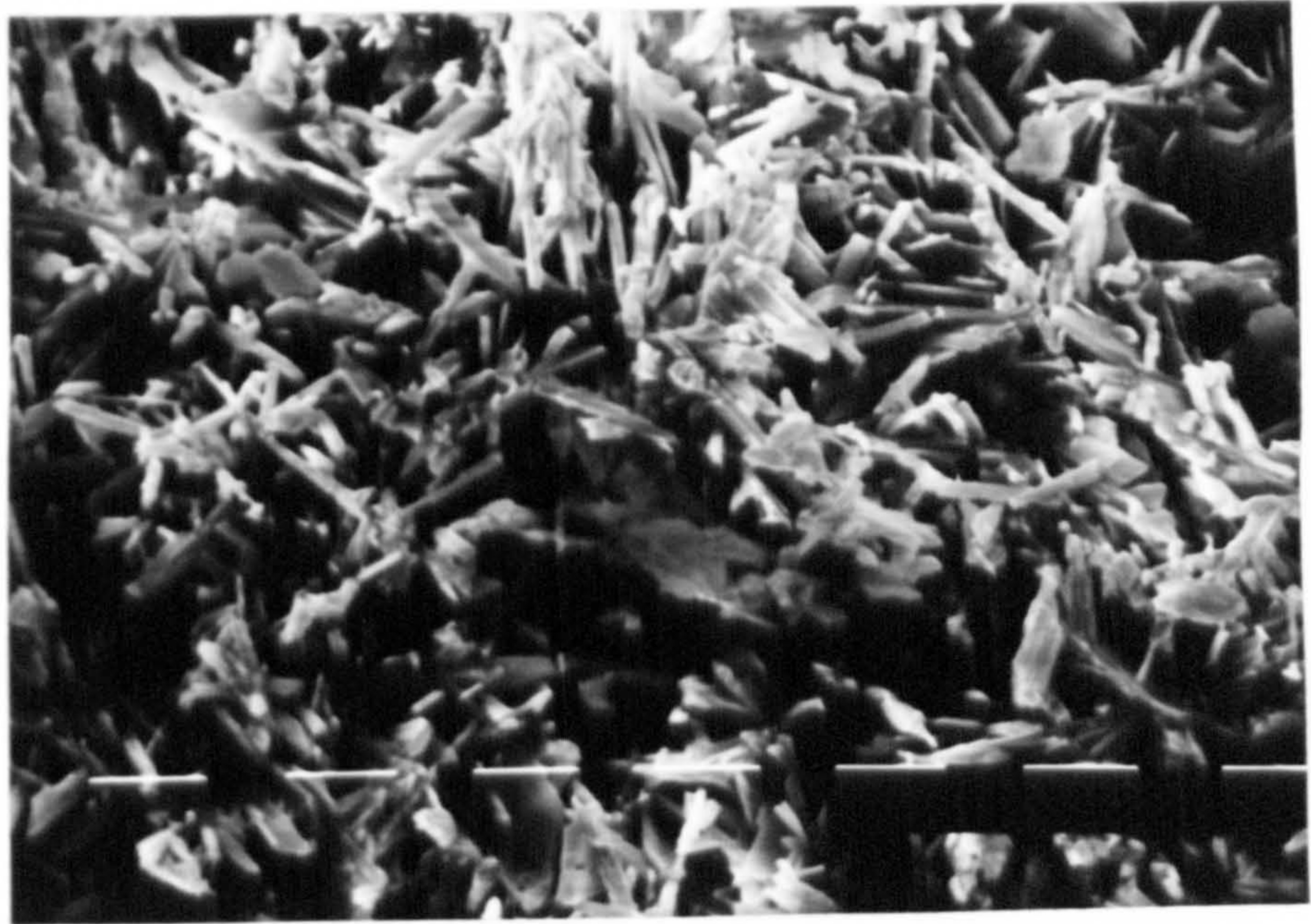


Plate 4.33: Scanning electron micrograph, at x1000, of the set plaster from α -hemihydrate plus the commercial binders; 1wt% polyvinyl acetate and 1wt% hydroxypropyl-cellulose (W/P ratio = 0.6).

5. DISCUSSION

5.1 COMMERCIAL BANDAGES

Medical applications require a plaster that will initially be plastic so that the bandage can be moulded around the fractured limb. This should be followed by a fast initial build-up of strength so that the patient may depart as soon as possible. Finally the cast should have a high set strength allowing a lighter cast and reducing the inconvenience to the patient.

The commercial formulation of Gypsona (Section 1) contains dihydrate as a nucleating agent, potassium sulphate as an accelerator to control the initial strength build-up, while the hemihydrate in the plaster is an α/β mix, in the ratio 1:2, to give high set strength. Finally the plaster is bound to gauze by polyvinylacetate and hydropropylcellulose to reduce plaster loss during handling thus effectively reducing the mess during application.

5.2 α - AND β -HEMIHYDRATES

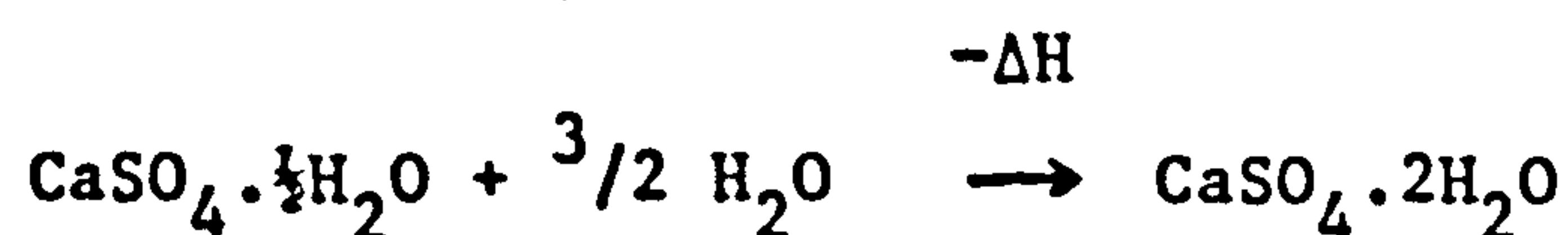
The tradition of having two forms has probably arisen from the fact that the material can be made by two processes, leading to products in distinctly different physical conditions. Dry decomposition methods give a poorly crystalline, porous product with particles consisting of randomly orientated small 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 the D.T.A. studies showed a difference in the temperature of the soluble/insoluble phase transition but this was probably due to the effects of crystallite size and habit rather than to differences in crystal structure.

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 reaction with water, the 'α- hemihydrate' being produced by hydrothermal methods whilst 'β- hemihydrate' is produced by dry decomposition methods.

5.3 THE HYDRATION OF HEMIHYDRATE

When hemihydrate is mixed with water, the following reaction occurs:



The hemihydrate (solubility = 0.65g/100ml water at 20°C) is more soluble than the dihydrate (solubility = 0.24g/100ml water at 20°C) to which it hydrates. The difference in solubilities is the driving force for the reaction with the more thermodynamically stable dihydrate being formed. When the reaction occurs in pastes it is strongly autocatalytic following an induction period, the reaction occurring by a "through solution" mechanism in 3-stages:

- (a) Hemihydrate in contact with water, goes into solution, making it supersaturated with respect to the dihydrate. The supersaturation remains constant for a period of time, during which nuclei formation take place; this is the induction period.
- (b) Once the nuclei have reached critical size, then rapid crystallisation takes place.
- (c) With depletion of hemihydrate, crystallisation slows down and finally stops.

If the hydration reaction is performed under adiabatic conditions, the temperature rise (ΔT) will be proportional to ΔH which in turn will be proportional to the mole fraction of dihydrate formed.

Thermal analysis and XRD of the reaction products at various stages has been used to determine the proportions of dihydrate and hemihydrate. This would provide an initial check that the accelerating rate of reaction was not due to the effect of rising temperature and therefore the reaction may be followed by measuring temperature increase.

The results obtained from calorimetry and phase analysis both showed a three-stage reaction, both techniques showing the reaction to be complete at approximately the same time. This indicated that calorimetry could be used to follow the reaction, but because of heat losses and experimental errors was limited to a comparative study. On the other hand, phase analysis by

thermal techniques was more accurate provided sufficient samples were taken, but the technique was time consuming and did not have the advantage of producing data continuously which would be sensitive to small changes in the reaction rate. It was therefore decided that, despite the drawbacks, calorimetry should be used for comparative rate studies.

The induction period for the β - hemihydrate was longer than that for the α - hemihydrate. This was difficult to explain due to the fact that the particle size of β - hemihydrate is smaller, 8.6 μm as compared to 11.4 μm , and β - hemihydrate particles consisted of small crystallites. This suggested that processes other than the rate of dissolution determine the length of the induction period.

Following the induction period, the rate of precipitation of dihydrate 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 (see Plates 4.7 and 4.9). This suggests that because the β - form has a smaller crystallite size and hence a higher specific surface area, it will have a larger number of nucleation sites. This could result in a faster dihydrate precipitation rate and implies that nucleation controlled the rate of precipitation rather than the rate at which the hemihydrate reached saturation. To throw further light on the processes which controlled the length of the induction period it was decided to investigate the degree of supersaturation of the solution by measuring the changes in the electrical resistance. The electrical resistance of plaster slurries developed in three stages:

- (i) A minimum resistance was obtained after 5 to 10 mins.

This was probably the point of maximum saturation of the solution with calcium and sulphate ions.

- (ii) The resistance then increased steadily during the next 100 mins., and this was due to the precipitation of dihydrate. This can be explained by considering the densities of reactants and products⁶⁹, and the expansion of the slurry during setting, which is of the order of 1%¹⁸. The density of hemihydrate is 2.78g.cm^{-3} , while that of dihydrate is 2.32g.cm^{-3} , a difference of 16.5%. Therefore, the increase in the volume of solid per unit volume of slurry is approximately 42%.

$$\text{Since resistance, } R = \frac{\rho l}{A},$$

(where ρ = resistivity, l = length and A = area) the area of pathway between needles for the ions in solution decreased with crystallisation, this would lead to an increase in measured resistance.

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

The α - plaster reached maximum saturation in 5 mins., about half the time taken by the β - plaster. This suggested that the length of the induction period was dependant 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 different crystal habit resulting in more preferential sites for the chemisorption of water leading to a faster dissolution rate.

5.4 MICROSTRUCTURE AND STRENGTH

When hemihydrate in the form of a paste hydrates to the dihydrate, it sets to a hard porous mass consisting of interlocking plates and needles. The microstructure controls most of the engineering properties of the material and in particular the rigidity which is due to the skeleton of interlocking crystals. The strength of the plaster will depend on a number of factors, including:

- (i) The morphology of component crystals.
- (ii) The degree of intercrystalline bonding.
- (iii) The porosity of the set mass.
- (iv) Impurity atoms built into the crystal matrix.

The porosity of the set mass is due to excess water in the initial reaction slurry evaporating off, thus leaving voids or pores. Reducing the W/P ratio of the initial slurry has been shown to substantially increase the strength of the set plaster. The minimum W/P ratio is governed by the 'water requirement' of the hemihydrate, i.e. the amount of water used to give a paste with a specified yield value. This has been shown to depend on the surface condition of individual grains and the specific surface area of the powder. β -hemihydrate, due to its mode of preparation, has a rougher surface and a

smaller crystallite size. This results in a greater water requirement and as a consequence the set plaster had a higher porosity and lower strength. It is unclear from the literature which form has the faster rate of setting.

Examination of the microstructure of the set commercial plasters (Section 4.3(a)), using a constant W/P ratio to ensure porosity of the plasters did not vary, showed that high strength was associated with a crystal habit of short, stubby dihydrate needles. The set α - plasters exhibit this microstructure and have high strength. In comparison, set β - plasters show branching fibrous needles growing from nucleation sites and the strengths are much lower.

The faster precipitation rate of the β - hemihydrate resulted in faster crystal growth of a uniaxial nature. This has resulted in a microstructure of lower strength.

The habit of crystals growing from solution is known to depend on the rate of growth of the close packed faces⁷². The gypsum structure (Figure 2.2) has Ca and O ions most closely packed in the [001] direction⁷³, which is perpendicular to the direction of the layered lattice arrangement. This is where double layers of CaSO_4 alternate with double layers of water molecules. Since β - hemihydrate has a faster precipitation rate and therefore a faster crystal growth rate, it will be energetically more favourable for growth to take place along the [001] direction, resulting in the observed uniaxial growth.

5.5 THE DEVELOPMENT OF STRENGTH IN SETTING PLASTERS AND THE RELATED SETTING PROCESSES

From examination of the literature, topics which needed further investigation are the setting processes of plaster slurries and the difference in the setting rates of α - and β - plasters.

(a) Development of Strength

Strength development in setting plasters has been shown to occur in three stages (see Figure 5.1):

(i) The strength increases steadily for the first 60 - 75 mins. reaching a maximum. This period coincides with the formation of the interlocking dihydrate crystal matrix. The hydration reaction which is responsible for the formation of the crystal matrix has been shown to be complete after approximately one hour, and provides complementary evidence for the above hypothesis.

(ii) Strength then decreased and reached a minimum between 1.25 - 2 hrs; three possible reasons for this have been considered. Firstly, once the reaction is complete, test specimens will start to lose excess water by evaporation. This would occur initially on the surface and could possibly result in shrinkage of a surface layer and with the formation of cracks. From the Griffith equation⁷⁴;

$$\text{fracture stress, } \sigma_f = (2 \gamma E / \pi a)^{1/2}$$

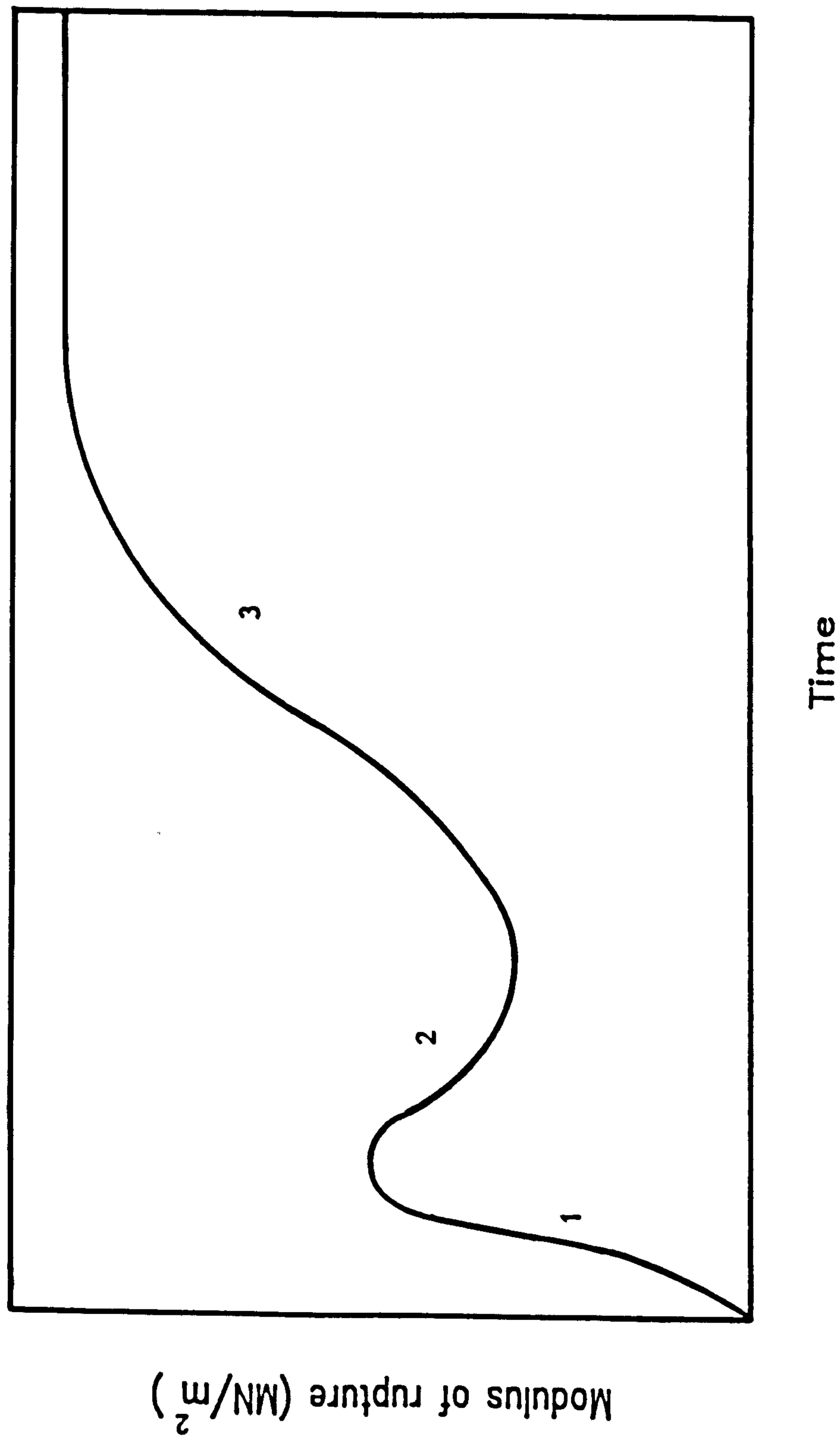


Figure 5.1: The three-stages in the strength build-up of plasters during setting, where:

- 1 - Formation of microstructure.
- 2 - Internal stress or microcracking.
- 3 - Drying out.

(where E = Young's modulus, γ = surface energy per unit area, $a = \frac{1}{2}$ x crack length) it can be seen that the stress necessary to cause crack propagation varies inversely as the square root of the crack length. Because set plaster fails as a brittle material,¹⁸ when the strength was measured by the three-point bend test* the introduction of surface microcracks would reduce the failure stress, resulting in a reduced strength. The second possible reason was that because a large amount of heat is generated by the hydration reaction, temperatures up to 30°C have been generated adiabatically, resulting in thermal gradients across the specimen. Because the interior and exterior would expand by different amounts this could lead to surface microcracking. Finally, during the growth of dihydrate needles it is possible that internal stress could be built up due to the crystals from different growth centres 'pushing' against each other. When the specimens were tested the internal stress would be relieved, resulting in a lower applied stress for failure and as a consequence lower strength.

*N.B. The stress/strain curves, when set plasters were tested by three-point bending on the Instron testing machine (Section 3.3.1(a)), were linear up to the point of failure. This indicated that the mode of failure was by brittle fracture.

(iii) Finally the strength increased slowly again to reach a maximum after approximately 15 - 20 hrs and this is almost certainly due to loss of lubricating solution between the dihydrate crystals as the specimen dried out. The remaining dihydrate would then precipitate from the saturated solution between the needles in the interlocking crystal matrix 'cementing' them together and making the structure rigid. Evidence to support these ideas was sought from a comparison of the strength tests of wet and dry plaster. Wet plaster has been shown to creep near the breaking strength whilst dry plaster acts as brittle material¹⁸, thus indicating a lubricating effect is present in wet plaster.

(b) The development of strength in setting α - and β - hemihydrates.

Medical applications require a plaster to have a fast initial strength build-up and high set strength. A comparison of the strength/time curves of setting α - and β - hemihydrates shows that both forms reach the initial maximum strength of the first stage of setting after 75 mins. This is due to precipitation of the dihydrate crystal matrix from the hydration reaction and was to be expected because both hemihydrates have been shown to complete the hydration reaction in the same time. However, the strength of setting α - hemihydrate at this stage (6.3MN/m^2) was appreciably higher than that of β -

hemihydrate (4.8MN/m^2) indicating that with respect to initial strength build-up the α - hemihydrate is the better material for medical applications.

During the third stage of setting, which coincides with the specimen drying out, the α - form dries out more quickly than β - form. The reason for this remains unclear as both plasters had the same initial W/P ratio of 0.6, with therefore the same quantity of excess water to evaporate from the pores. A possible reason for this difference could be different pore size distributions. However, lack of time prevented this aspect being explored further. The α - form reaches a final set strength of 11.8MN/m^2 after 15 hrs, compared to the β - form which gives 9.8MN/m^2 after 20 hrs. A consequence of this is that the α - plaster gives a higher initial set strength at the 75 mins. mark and reaches a higher full set strength in a shorter period. The α - plaster fits the requirements for a splinting material much better than the β - plaster.

(c) The 'wet' testing and acoustic emission of setting plasters.

The setting of plasters is a three-stage process but the mechanism of the strength loss in the second stage is unclear. Three explanations have been proposed; micro-cracking due to surface shrinkage or thermal gradients, or internal stress due to crystallisation pressure. The following investigations were performed to provide a greater insight into the mechanism of strength loss.

(i) 'Wet' testing.

The test specimens were immersed in a saturated solution of dihydrate until tested effectively keeping them 'wet'. This would prevent the surface and bulk drying, thus preventing surface microcracking due to shrinkage. If this was the mechanism for the strength loss the resulting strength/time curve for 'wet' testing would be similar to that shown in Figure 5.2. In Figure 5.2 the strength is shown to increase continuously with microstructural formulation. A constant strength is then reached with no strength decrease due to surface shrinkage and no strength increase due to the bulk drying of the specimens.

On the other hand, if the strength loss of the second stage was due to microcracking because of thermal gradients or internal stress, 'wet' testing would not prevent the loss in strength. This would result in a strength/time curve similar to that shown in Figure 5.3., where initial increase in strength to a maximum is due to microstructural formation. This is followed by a loss in strength due to thermal gradient microcracking or internal stress reaching a constant value. No final increase in strength was observed due to the prevention of bulk drying.

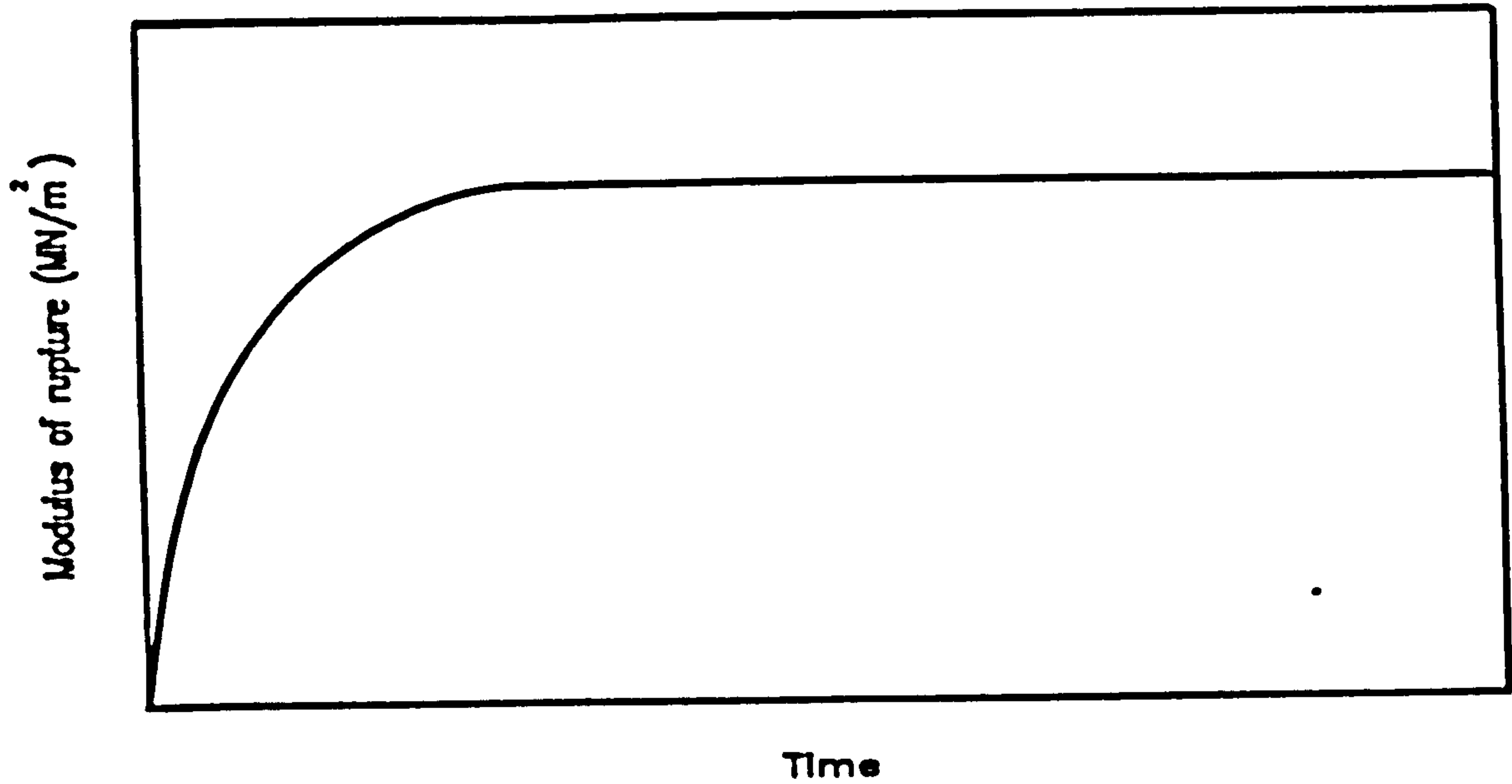


Figure 5.2: Schematic strength/time curve for the 'wet' testing of plaster if the second stage is due to surface microcracking because of shrinkage.

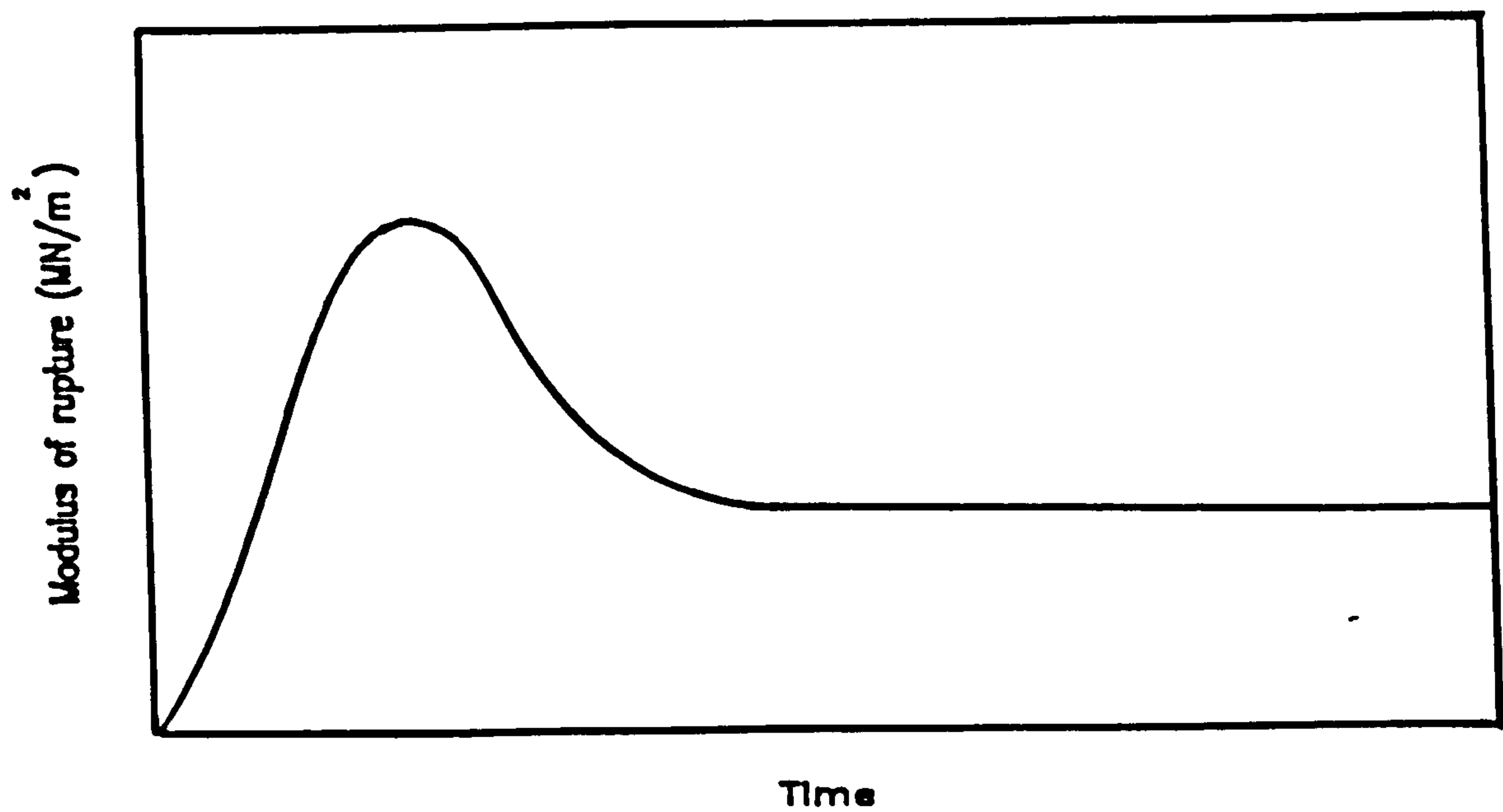


Figure 5.3: Schematic strength/time curve for the 'wet' testing of plaster if the second stage is due to internal stress or microcracking because of thermal gradients.

The strength/time curves for the 'wet' testing of setting α - and β - hemihydrates (Section 4.3(c)) were similar to the predictions in Figure 5.3, indicating that strength fall off during the second stage of setting is due to internal stress or microcracking because of thermal gradients within the specimen. Further evidence that the third stage of setting was due to bulk drying has also been obtained.

(ii) Acoustic emission (A.E.)

Since no acoustic emission signals were detected during setting it seems unlikely that surface microcracking, with its release of energy, occurs during the second stage of setting. It is possible that the equipment used was not sensitive enough to detect a weak signal, but this is unlikely. It would therefore appear that internal pressure due to crystallisation is responsible for the loss in strength observed during the second stage.

(d) Microstructural development in setting plaster.

S.E.M. studies, which were discussed earlier, have shown that microstructure of a set ' β '- plaster consists of fine, needle-shaped dihydrate crystals, while that of the set ' α '- plaster consists of relatively short, stubby crystals. The latter crystal habit is associated with high strength and porosity was not a factor because the W/P ratio was kept constant for each plaster. What was

unclear is whether the higher strength was linked to the crystal habit, which is controlled by the rate of precipitation, or whether the degree of intercrystalline bonding is also a factor. Acousto ultrasonic testing of the setting plasters was used to follow microstructural development; where acoustic transmittance is a measure of the rigidity of the structure. Both setting plasters gave an initial maximum acoustic transmittance after 90 minutes, indicating that the formation of the interlocking crystal matrix was then complete. However, the acoustic transmittance of the α - plaster was double that of the β - plaster, suggesting the degree of intercrystalline bonding is far greater in the structure of the α - plaster. This suggested that the faster rate of precipitation observed with the β - hemihydrate not only altered the crystal habit of dihydrate to give finer, branching needles but also decreased the degree of intercrystalline bonding. Both factors are probably responsible for the lower strength observed in set β - plasters.

Both plasters showed a significant increase in the acoustic transmittance during the next 23 hrs, with the effect being more marked with the β - plaster. This gave complementary evidence for the theory that the increase in strength during the third stage of setting was due to the loss of lubricating water and the 'cementing' of the structure by precipitated 'in-solution' dihydrate.

This effect is more marked with β - hemihydrate because the initial degree of intercrystalline bonding is far less

and therefore the precipitation of dihydrate between the sheafs of needles would result in a larger gain in inter-crystalline bonding.

5.6 THE ROLE OF SOLUBLE ANHYDRITE IMPURITIES

Soluble anhydrite is present in plasters due to the over-dehydration of gypsum during the production process. Commercial plasters with a high soluble anhydrite content (10 - 13wt.%) had a lower strength than counterparts with a relatively low anhydrite content of 2 to 3 wt.%. The effect of soluble anhydrite on the properties of set α - and β - plasters was to decrease strength, but with little effect on the open porosity and microstructure.

The mechanism by which soluble anhydrite reduced the set strength was unclear from the above observation so the reactivity in a saturated solution of dihydrate was investigated. Soluble anhydrite was shown to hydrate to the dihydrate by a two stage process. Firstly, water is absorbed by the anhydrite particles to form hemihydrate, this then reacts by a 'through solution' mechanism to precipitate dihydrate needles. Evidence for the first stage was gained by consideration of the reverse reaction. When soluble anhydrite is produced by dehydration of the hemihydrate, the loss of the half molecule of water does not disturb the crystal lattice. This was indicated by identical X.R.D. patterns and particle size distributions (see Section 4.4.2). The gain of water by hydrating soluble anhydrite would probably also result in little disturbance of

the crystal lattice. S.E.M. and X.R.D. analysis of the reaction products confirmed this theory. The soluble anhydrite hydrates to dihydrate more slowly than the hemihydrate forms dihydrate but it must be pointed out that soluble anhydrite prepared from β - hemihydrate hydrated faster than anhydrite prepared from α - hemihydrate. This suggests that the rate determining step in the soluble anhydrite to hemihydrate reaction was the absorption of water by the soluble anhydrite grains. The ' β - soluble anhydrite' particles are far more porous resulting in a faster absorption rate.

If we consider a hemihydrate/soluble anhydrite mixture reacting with water, the hemihydrate will hydrate to form dihydrate, whilst the anhydrite is hydrating to hemihydrate. Thus an interlocking crystal matrix of dihydrate will be formed containing hemihydrate particles. The next stage would be for these hemihydrate particles to hydrate further to dihydrate. This would result in disruption of the original crystal matrix reducing the overall set strength. Since both reactants will eventually form dihydrate, little change will be observed in the microstructure or open porosity of the fully set plaster.

5.7 NUCLEATION OF THE HYDRATION REACTION BY ADDITIONS OF DIHYDRATE

Commercial medical bandage formulations contain small amounts of dihydrate (approximately 2wt.%) added to provide nucleation sites for the growth of dihydrate needles. Dihydrate is said to accelerate the hydration reaction by increasing nucleation and promoting seeding⁶. Experimental work has shown that dihydrate additions did accelerate the hydration of gypsum

plaster. Decreasing the particle size or increasing the amount of dihydrate added resulted in a greater degree of acceleration. This indicated that the addition of dihydrate accelerated the hydration reaction by providing suitable sites on which the dihydrate grew from solution.

The chemical activity of powders is dependent on the shape and size of component grains, and the specific surface area³³. Because the amount of dihydrate added was varied and dihydrate of various specific surface areas was used, the effective surface area of the dihydrate will be the Wt. added multiplied by the specific surface area. The relationships between the effective (or relative) surface area of the dihydrate additions and reaction rate parameters (maximum dT/dt and time to T_{max}) are shown in Table 5.1 and graphically in Figures 5.4 and 5.5. Increasing the relative surface area leads to increased acceleration of the hydration reaction as one would expect if the dihydrate acted as a nucleating agent. The spread of results, marked by the two limits in Figures 5.4 and 5.5, was more difficult to account for. A possible explanation could be the difference in surface roughness of the dihydrate particles produced during grinding, as observed by S.E.M. (Section 5.4). The greater the degree of surface roughness, the larger the number of nucleation sites per dihydrate particle and subsequently the faster the reaction rate.

One exception to the above observations was the acceleration produced by the British Gypsum products. Possible reasons for this are a larger degree of surface roughness due to the manufacturer's processing or a more favourable crystal habit

Table 5.1: The effect of the surface area of dihydrate additions on the nucleation of the hydration reaction.

Dihydrate addition (wt%)	Specific surface area (m ² /g)	Relative surface area (m ²)*	max. dT/dt (°C/min)	Time to T _{max} (mins.)
<u>B.D.H.</u>				
10.7 μ m (10)	1.6	16	1.13	34.3
(5)	"	8.0	0.97	44.4
(2)	"	3.2	0.97	48.5
7.2 μ m (2)	3.5	7	1.42	35.5
(1)	"	3.5	1.09	39.0
($\frac{1}{2}$)	"	1.75	0.83	44.6
6.7 μ m (2)	7.4	14.8	1.43	34.9
(1)	"	7.4	1.24	38.7
6.3 μ m (5)	5.9	29.5	1.67	31.7
(2)	"	11.8	1.53	32.8
(1)	"	5.9	1.39	35.5
($\frac{1}{2}$)	"	2.95	1.11	40.8
<u>British Gypsum</u>				
54 μ m (2)	0.9	1.8	1.28	40.4
4.7 μ m (2)	15.1	9.4	2.36	25.1
No addition	0	0	0.75	52.5

* Relative surface area = Specific surface area x wt. of added dihydrate (units:m²).

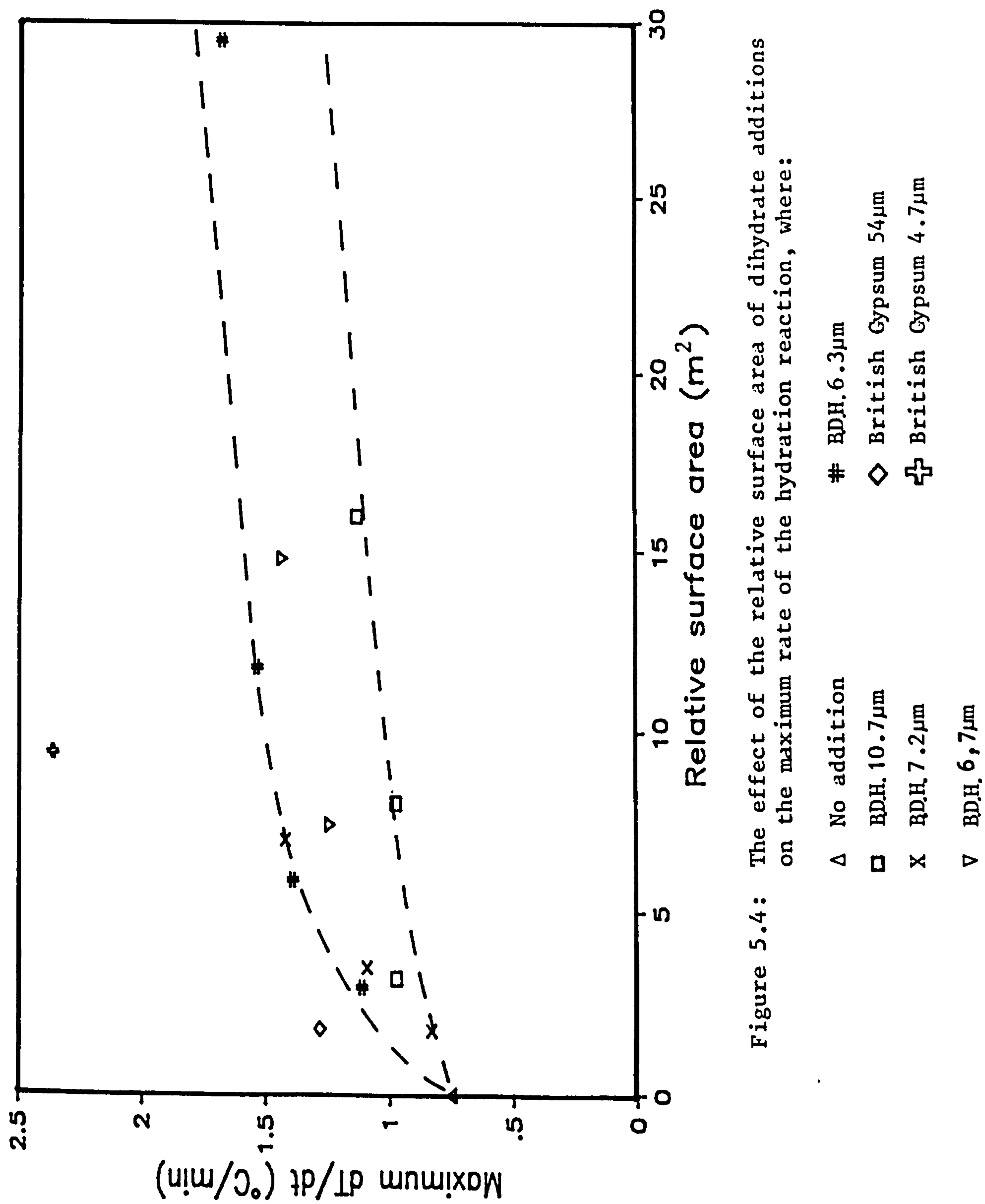


Figure 5.4: The effect of the relative surface area of dihydrate additions on the maximum rate of the hydration reaction, where:

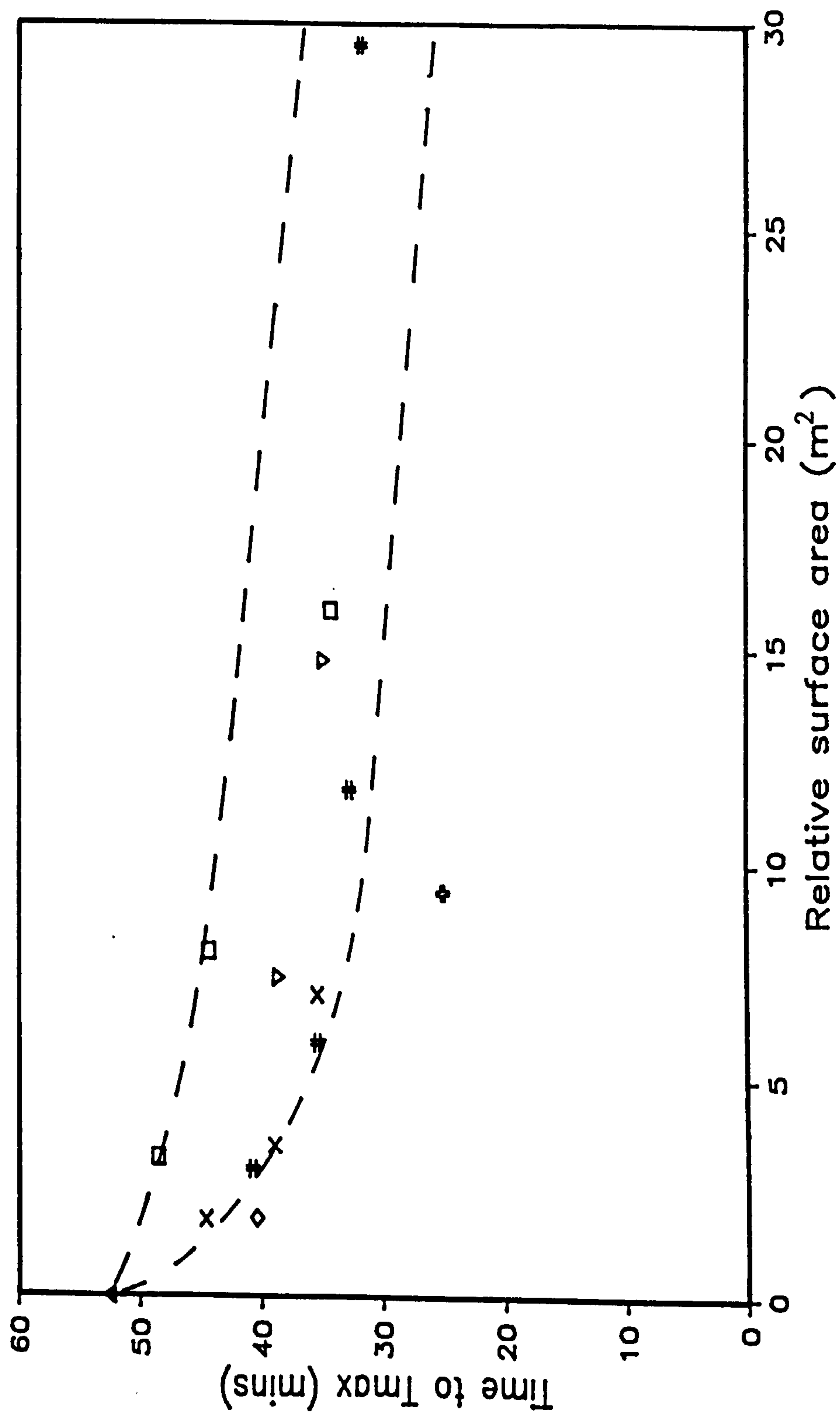


Figure 5.5: The effect of the relative surface area of dihydrate additions on the hydration reaction time, where:

- | | | | |
|---|--------------|---|----------------------|
| Δ | No addition | # | BDH. 6.3µm |
| □ | BDH. 10.7 µm | ◇ | British Gypsum 54µm |
| x | BDH. 7.2µm | ⊞ | British Gypsum 4.7µm |
| ▽ | BDH. 6.7µm | | |

for nucleation.

The effect of dihydrate additions on the microstructure was to reduce the needle size, as might be expected if the density of nuclei was increased. The aspect ratio of the needles was also increased which was probably due to the increased precipitation rate and as shown earlier, this probably results in a reduction in the degree of intercrystalline bonding. The overall effect should be a reduction in strength and this was observed.

5.8 ACCELERATION OF THE HYDRATION REACTION BY ADDITIONS OF POTASSIUM SULPHATE

Commercial bandages contain K_2SO_4 to increase the rate of initial strength build-up. Neutral salts, such as K_2SO_4 , are believed to increase the rate of reaction by increasing the rate of dissolution of the hemihydrate⁶. A mechanism to account for the behaviour of neutral salts has been proposed by Chatterji and Kapse³⁵, on the basis of rheological studies. These indicated that the hemihydrate grains were covered with an adsorbed layer of water molecules. Neutral salts stabilize the layer of water molecules and orientate the neighbouring water molecules, resulting in a multilayer water structure around each hemihydrate grain. As this probably constitutes the first step in the dissolution of hemihydrate, an increase in the area and depth of coverage of the adsorbed water would increase the rate of dissolution. Ridge et al⁴⁷ made a systematic study of the accelerating effect of various anions and cations which indicated that K^+ and SO_4^{2-} constitute the

best accelerating anion/cation pair.

Potassium sulphate additions were shown to accelerate the rate of hydration with the reaction rate increasing with the amount of added K_2SO_4 up to 2wt.%. Additions greater than this showed very little change in the degree of acceleration. The limit of the accelerating effect can be explained in terms of Chatterji and Kapse's mechanism. A 2wt.% addition of K_2SO_4 results in a stabilised multilayer water structure and greater additions would result in a greater number of water layers. These extra layers will be a relatively large distance from the surface of the hemihydrate grain and therefore would not contribute as much to the dissolution rate as those most closely bound to the surface. The result of this will be a limiting effect on the degree of acceleration observed.

Increasing amounts of K_2SO_4 progressively increased the rate of dihydrate precipitation and decreased the strength of the set plaster. It was also observed that the size of the dihydrate needles was increased and the aspect ratio lowered. Earlier it was seen that a higher precipitation rate results in lower strength, mainly due to reduced intercrystalline bonding with a microstructure consisting of needles of a higher aspect ratio.

The K_2SO_4 additions increased the precipitation rate and the expected result would be an increase in the rate of crystal growth in the [001] direction producing longer needles. This was observed, but K_2SO_4 also enhanced growth in directions perpendicular to the [001] direction and in this respect acted as a crystal modifier. This enhanced growth was possible due to

a decrease in the edge energy of the lattice step cause by adsorption of K^+ and SO_4^{2-} , which has been observed with other systems⁷² (e.g. LiF with 10^{-3} mole % addition of FeF_3).

The reduction in strength was probably due to the loss of intercrystalline bonding due to the higher precipitation rate, but additions of K_2SO_4 above 2wt.% did not increase the precipitation rate significantly but reduced the strength. The K_2SO_4 therefore appears to weaken the structure by an additional mechanism which could possibly be by either being built into the dihydrate needles and/or weakening the cementing action of residual dihydrate by being precipitated with it.

5.9 THE USE OF 'IN-SITU' ACCELERATION/NUCLEATION SYSTEM

Medical applications of gypsum plasters require a rapid build-up in initial strength and a high fully set strength. Commercial plasters such as Gypsona contain 2wt.% K_2SO_4 and 2wt.% (British Gypsum 54 μ m) dihydrate added as an accelerator and nucleating agent respectively. Their combined effect is to increase the rate of hydration but produce a plaster of lower set strength, the reduction in strength amounting to approximately 17%.

In this study, $KHSO_4$ and $Ca(OH)_2$ were used to generate 'in-situ' microcrystalline dihydrate nuclei in the presence of K_2SO_4 . This system reduced the reaction time to less than 70% of the commercial formulation and the reduction in strength was limited to 6%, as compared to 17% for the commercial formulation. The $KHSO_4/Ca(OH)_2$ system has several advantages

over the commercial system since it increased the initial rate of strength build by a greater degree but reduced the set strength by a lesser degree.

Microstructure of the plasters with the nucleation systems showed little change to that of set α - plaster. This was probably because dihydrate has been shown to reduce the size of dihydrate needles, while K_2SO_4 increased the size of the needles; the overall effect of both showing no apparent change.

5.10 OPTIMISATION OF THE $\alpha:\beta$ RATIO AND THE ROLE OF COMMERCIAL BINDERS

- (a) The effect of $\alpha:\beta$ ratios on the properties of set gypsum plasters.

When bandages are used for splinting fractured limbs, the technician immerses the bandage in water, which has been heated to 30°C , and holds it until all the trapped air bubbles are released. The bandage is then given a gentle squeeze to remove excess water and wrapped around the limb. The water picked up by the bandage in the above method will govern the W/P ratio of the plaster slurry and as a result the porosity of the set plaster. The factors controlling the 'water pick-up' are probably the surface condition of the hemihydrate grains and its specific surface area. If these were the only factors it would be expected that α - hemihydrate with its larger and more perfect crystals would have a lower water pick-up and as a result a lower W/P ratio. Bandages also have polyvinyl acetate and hydroxypropylcellulose in their formulation to act as

binding agents between the plaster particles and the gauze.

The plaster grains are coated with binding agents by mixing with a solution of the binders in methylene chloride. The resulting slurry is then used to coat the gauze to produce bandages.

Since the binders are a surface coating it is possible that these will have an effect on the water-pick of the bandage.

The trend observed is for decreasing W/P ratio (or water pick-up) with increasing α - hemihydrate content of the plaster.

This appears to indicate that the controlling factors are the surface condition and surface area of the hemihydrate particles and that the binders have little or no effect.

When the strength of plasters with varying α - hemihydrate content, at the pre-determined W/P ratio, was measured, the trend was for increased strength with increased α - hemihydrate content of the plaster. This was due to two factors:

(i) Microstructure.

The microstructure of set α - plaster has been shown to be stronger than that of the set β - plaster at the same W/P ratio, due to the greater degree of intercrystalline bonding with the slower precipitation rate during hydration.

(ii) Porosity.

The porosity of the set plaster is determined by the W/P ratio. The lower the W/P ratio, the lower the resulting porosity of the set plaster and as a result the higher the strength. As pointed out earlier in this section; increasing the α - hemihydrate content of the plaster

reduced the W/P ratio. This would result in a set plaster of lower porosity and therefore higher strength.

(b) Optimisation of the α : β ratio.

Gypsum plasters require rapid strength build-up and a high set strength. α - hemihydrate has been shown to have a faster strength build-up and also a higher set strength. Therefore in terms of mechanical properties, α - hemihydrate is a superior splinting material to β - hemihydrate but is more expensive to produce³. A cost evaluation involving more detailed specification for use is needed but if a plaster with greater α content is used then less plaster need be applied to the gauze to keep the cost constant and a bandage with the same mechanical properties would result. The advantage from the patient's point of view would be a lighter cast.

(c) The role of commercial binders.

The commercial binders, polyvinylacetate and hydroxypropyl-cellulose, have been shown to effectively bind the plaster to the gauze minimising plaster loss during handling.

However, the binders have been shown to slightly accelerate the hydration reaction. From earlier discussions it has been seen that increasing the precipitation rate has the effect of increasing the aspect ratio of the dihydrate needles reducing the degree of intercrystalline bonding and as a result decreasing the full set strength. The aspect ratio of the dihydrate needles was increased by the accelerating

effect of the binders but mechanical strength was reduced by 24%. This was out of proportion with the small loss of intercrystalline bonding.

The hydroxpropylcellulose was thought to cause the accelerating effect due to its solubility in water⁷⁵, reducing the saturation limit of the dihydrate. It was also thought to cause the unusually large reduction in strength by being precipitated with the residual dihydrate, thus reducing the cementing action. Polyvinyl acetate is insoluble in water⁷⁶ and is therefore thought to be relatively inert.

6. CONCLUSIONS

- (a) Five commercial plasters have been chemically analysed and characterised using thermal, phase and particle size analyses, supplemented with SEM and optical studies to determine particle morphology. The plasters have been shown to consist of essentially calcium sulphate hemihydrate with small but varying amounts of anhydrite.
- (b) Thermal analysis, XRD and SEM studies suggest that 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.
- (c) Both α - and β - hemihydrates react 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 matrix.
 - (iii) The final stage is depletion of hemihydrate.
- (d) The first stage of hydration involves an induction period of several minutes, being longer for β - hemihydrate than α - hemihydrate. Following this the rate of precipitation of dihydrate needles is faster for β - hemihydrate than α . This

results in uniaxial growth of dihydrate needles along the [001] direction.

(e) The setting or development of strength is also a three-stage process.

(i) The first stage is the development of an interlocking matrix of dihydrate needles which is the result of the hydration reaction.

(ii) The second stage is the relief of internal stress caused by the build-up of pressure as needles advance against each other. This stage is accompanied by a period of reduced strength.

(iii) The final stage involves the removal of water in excess of that required for the chemical reaction. The strength increases as the lubricating solution is removed, the final structure containing a large amount of open porosity. Salts in solution precipitate out at this stage "cementing" the matrix together.

(f) Set α - and β - plasters exhibit very different microstructures, the α - plaster consisting of relatively short stubby needles, while the β - plaster consists of longer, fibrous, branching sheaves.

- (g) Reduced intercrystalline bonding in set β - plasters is the result of faster precipitation rates and gives lower mechanical strengths.
- (h) The porosity of a set plaster, and consequently the set strength, are largely controlled by the Water:Plaster ratio. Since crystals of α - plasters are considerably larger than those of β - plasters, the water pick-up is less and hence the porosity of the set plaster was reduced.
- (i) Soluble anhydrite, which is present in all commercial plasters, has been shown to rehydrate in two stages, going first to the hemihydrate and then to dihydrate. It has been shown to reduce the strength of set plasters by disrupting the crystal matrix.
- (j) Additions of dihydrate to the plasters has been shown to nucleate the hydration reaction, the effectiveness increasing with surface area and roughness.
- (k) Increased nucleation rates gave finer and smaller dihydrate needles with reduced intercrystalline bonding and as a consequence lower mechanical strengths.
- (l) K_2SO_4 additions have been shown to accelerate the hydration reaction by increasing the rate of hemihydrate dissolution. The accelerating effect increased up to 2wt.% additions, further additions having a negligible effect.

- (m) K_2SO_4 increased the rate of crystal growth in both the [001] direction and directions normal to the needle axis. The resulting dihydrate needles were larger, had a lower aspect ratio and reduced intercrystalline bonding. Consequently the set plaster had reduced mechanical strength. Additions of K_2SO_4 in excess of 2wt.% produced further reductions in set strength.
- (n) The production of in-situ nucleation sites through the use of $KHSO_4$ and $Ca(OH)_2$ additions provided microcrystalline dihydrate nuclei in the presence of K_2SO_4 . This gave a rapidly setting plaster with a smaller reduction in set strength than present commercial formulations.
- (o) Varying the proportions of α - and β - hemihydrates in plasters has shown that for medical applications, an all α - plaster has the greatest build-up of initial strength and the best set strength.
- (p) Since the cost of α - hemihydrate is greater than that of β - hemihydrate, the technical advantage of an all α - plaster would have to be reconciled with increased production costs.
- (q) Polyvinylacetate and hydroxypropylcellulose are effective binding agents for holding the plaster particles onto the cotton gauze. Hydroxypropylcellulose has been shown to have a deleterious effect on the mechanical properties of the set plaster; polyvinylacetate would appear to be relatively inert.

7. FURTHER WORK

This study has concentrated on trying to understand the relationship between the microstructure of a plaster and the mechanical properties. It has involved a close examination of the role of each component in a commercial bandage formulation, of the hydration reactions and the resulting microstructure. Time has prevented a number of unexplored avenues to be pursued, each of which may lead to the further optimisation of the mechanical properties of a set plaster.

(a) The preparation of α -hemihydrate with closely defined ranges of crystallite size to provide quantitative data on:

- (i) rate of hydration
- (ii) initial strength build-up
- (iii) development of microstructure
- (iv) final set strength and microstructure

(b) Since porosity is known to have a marked effect on the mechanical properties, an investigation into the factors controlling the rate at which a plaster dries out and the effect of pore size distribution may lead to enhanced understanding.

(c) Further work on the role of surface active agents, e.g. calcium lignosulphonate, may well lead to a reduction in water pick-up and hence lower final porosity.

- (d) The generation of "in-situ" nucleation sites with the addition of KHSO_4 and Ca(OH)_2 to the plasters produced $\text{K}_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O}$ as part of the reaction. Since the 'in-situ' reaction was a notable improvement over the use of K_2SO_4 and dihydrate in accelerating the hydration reaction, a study of the effect of $\text{K}_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O}$ should be regarded as of great importance.
- (e) One major, unexplained finding from this study has been the effectiveness of British Gypsum dihydrate particles as nucleation sites for the growth of dihydrate needles. A study of the effect of surface roughness, crystal habit and possible impurities in this material could be extremely beneficial.
- (f) Polyvinylacetate and hydroxypropylcellulose are effective binding agents for retaining plaster particles on the cotton gauze. However, even small additions have a profound effect in reducing the strength of the set plaster. An investigation of other binding agents may well lead to further improvements of the formulation.

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9. ACKNOWLEDGEMENTS

The author would like to thank all the members of the *Nuffield Research Group* for their friendship and support over the last three years. My particular gratitude goes to *Dr. J. Williamson* for his advice and encouragement.

Mr. J. Wright, *Mr. L. Leake* and *Mr. A.J. Tipple* must be thanked for their technical assistance, *Miss J. Bowring* for typing the thesis text and *Mr. H. Hamilton* for proof-reading the text.

The financial support of *Smith and Nephew Ltd*, the supply of samples, technical information and valuable discussions with *Mr. P. Winterbottom*, *Miss C. Forsyth* and *Mr. J.J. Smith*, are gratefully acknowledged.

A special thankyou to *Dr. J.F. Bell* for all his help at the last minute.