THE RELATIONSHIP BETWEEN THE VISCOSITY OF
THE MIX AND THE TENSILE STRENGTH OF
CAST GYPSUM

ALEX SELBY, B.D.S.

A THESIS SUBMITTED IN PARTIAL
REQUIREMENT FOR THE DEGREE OF
MASTER OF DENTAL SURGERY

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Peter Sell

1979
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CHAPTER 1

LITERATURE REVIEW

1.1 INTRODUCTION

Gypsum is a naturally occurring mineral mined in many parts of the world and has been in use for many centuries, in one form or another\(^1\). It is one of the softest minerals known (1.5 to 2 on Moh's Scale) and therefore it lent itself to carving with primitive tools\(^2\). In fact it is one of the oldest building materials, and alabaster (a form of gypsum) was allegedly used in the construction of King Solomon's temple in the Old Testament\(^1,2\).

Gypsum products, the results of the calcining of gypsum, are used today in a number of industries, such as the manufacture of phosphoric acid, pottery, ceramics and portland cement\(^3\). They are widely used in the building industry and are of course invaluable to the dental profession. The importance of gypsum products in dentistry, particularly in the prosthetic field, is emphasized by the many diversified uses for the material which include:

- taking impressions of the oral anatomy
- use as an investment or mould material for the processing of dentures
- use as a cast, model or die material which duplicates the oral anatomy when poured into an impression
- use as a binding material for the silica refractory in investments used for the casting of gold restorations or for precision soldering.
1.2 THE FORMS OF CALCIUM SULPHATE

The products used in dentistry are chemically almost in a pure state\(^{(1)}\); however raw gypsum, after being mined or quarried contains many impurities, which vary not only between deposits, but also within individual deposits\(^{(2)}\). The main impurities are calcium carbonate and clay\(^{(2)}\), although other carbonates, iron minerals and quartz may be found, and sometimes traces of compounds of such elements as strontium, barium, potassium, magnesium and aluminium\(^{(4,5)}\).

The raw gypsum is washed to remove gross superficial contamination such as salt and clay, however impurities which are intimately associated with the gypsum (often occurring as impurity atoms incorporated in the gypsum crystal structure) are not removed this way and subsequently remain in the end product after the gypsum has been converted to plaster and dental stone\(^{(6)}\). For highly specialized needs, such as that of the dental profession, the manufacturers rely on careful selection of the original rock, to minimize contamination of their products\(^{(4)}\).

Gypsum is, in fact, calcium sulphate dihydrate (\(\text{CaSO}_4\cdot2\text{H}_2\text{O}\)). Gypsum products are obtained by heating gypsum to drive off some or all of the water of crystallization. This process of dehydration is called calcination. Ridge and Beretka\(^{(3)}\) recognize the following combinations of calcium and sulphate ions and water as constituting individual chemical species:

1) one form of calcium sulphate dihydrate (\(\text{CaSO}_4\cdot2\text{H}_2\text{O}\)) crystallographically identical with the mineral gypsum.
ii) one form of calcium sulphate hemihydrate (CaSO$_4$·$\frac{1}{2}$H$_2$O).

iii) two forms of anhydrous calcium sulphate (CaSO$_4$):
    a) hexagonal calcium sulphate
    b) orthorhombic calcium sulphate - which is crystallographically identical with the naturally occurring mineral anhydrite.

Calcium sulphate hemihydrate is the principal constituent of all dental plasters and stones$^{(6)}$. Hexagonal calcium sulphate has, in the past literature, also been called soluble anhydrite, and orthorhombic calcium sulphate has been known as insoluble anhydrite or "dead-burnt" gypsum$^{(3)}$.

The relationships between the different forms of calcium sulphate are summarized in Table 1.1.
<table>
<thead>
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<th>Transformation</th>
<th>Reaction Details</th>
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<tr>
<td>Calcium sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (monoclinic)</td>
<td>Dehydration probably involving topotaxy. Recrystallization without topotaxy.</td>
</tr>
<tr>
<td>Calcium sulphate hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$</td>
<td>Quasi-zeolitic loss of water from lattice without recrystallization. Water absorbed from vapour without recrystallization. Quasi-zeolitic reaction.</td>
</tr>
<tr>
<td>Hexagonal calcium sulphate, $\text{CaSO}_4$</td>
<td></td>
</tr>
<tr>
<td>Orthorhombic calcium sulphate, $\text{CaSO}_4$</td>
<td>Transformation can occur even at room temperature.</td>
</tr>
</tbody>
</table>
1.3 CALCINATION

When gypsum is heated in a kettle, vat or rotary kiln, open to the air, the product is referred to as dry-calcined hemihydrate, otherwise known as gypsum plaster or plaster of Paris\(^{(2, 6-8)}\). If gypsum is heated in the presence of liquid water or steam under pressure, then the product is autoclaved or wet-calcined hemihydrate\(^{(7)}\). These materials are high-strength gypsum plasters and are known in dentistry as dental stones and die stones\(^{(9, 10)}\).

The methods of hemihydrate production may be summarized as follows\(^{(11)}\):

i) gypsum is heated in an open kettle, pan or rotary kiln at 110-130°C. This is a long established method;

ii) lump gypsum is heated by steam in an autoclave at 120-147°C (a typical product is 'Hydrocal');

iii) ground gypsum is heated in water in the presence of a crystal modifier (for example sodium succinate) under steam pressure between 125°C and 165°C. (A typical product is 'Crystocal' Base);

iv) lump gypsum can be heated in a solution of a salt, for example, 30 per cent calcium chloride or magnesium sulphate. (A typical product is 'Densite').

Dental stones are produced by method (ii). Methods (iii) and (iv) produce hemihydrate crystals which are relatively larger and more perfect than those of stone and hence have a lower surface area per unit weight in the final
product. These materials are known as die stones. Dental stones and die stones are chemically identical and physically very similar, with little difference in their mechanical properties\(^{(12)}\). I shall hereafter collectively refer to both materials as stone (that is, dental stone) or as wet-calcined hemihydrate, unless otherwise specified.

In commercial manufacture, conversion of the entire dihydrate to hemihydrate is rarely achieved. A small amount of gypsum (due to under-calcination) or orthorhombic calcium sulphate (due to over-calcination) is usually present in the product\(^{(13)}\).

If calcination is prolonged or carried out at higher temperatures, the remaining water of crystallization is driven off and anhydrous calcium sulphate is produced\(^{(14)}\). The hexagonal form is produced first, and if heating is continued at higher temperatures then there is a slow conversion to the orthorhombic form\(^{(4,15)}\).

The dehydration stages of calcium sulphate dihydrate are summarized in Equation 1.1.

\[
\begin{align*}
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} & \xrightarrow{T_1} \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} & \xrightarrow{T_2} \text{CaSO}_4 & \xrightarrow{T_3} \text{CaSO}_4 \\
\text{gypsum (dihydrate)} & \text{plaster or stone (hemihydrate)} & \text{hexagonal anhydrite} & \text{orthorhombic anhydrite} \\
\end{align*}
\]

... Equation 1.1\(^{(7)}\)

where \(T_1, T_2, T_3\) represent temperatures of transformation.

The temperatures at which the three transformations take place are variable, and may vary according to heating rate and size of the sample. The transformations are very
susceptible to ambient conditions, especially temperature and humidity. Humid conditions are present when calcination takes place in closed vessels, and this necessitates the use of higher temperatures, or alternatively, longer periods of time for dehydration, because the higher partial pressure of water vapour present makes conditions relatively less favourable for the release of water molecules from the gypsum lattice\(^{(4,15)}\).

Phillips\(^{(7)}\) quotes the following temperatures for the transformations in Equation 1.1:

\[
T_1 = 110-130^\circ C \\
T_2 = 130-200^\circ C \\
T_3 = 200-1,000^\circ C
\]

However many different temperatures have been reported in the literature. For instance, the following examples represent some of the temperatures at which dehydration of dihydrate to hemihydrate \((T_1)\) supposedly takes place:

a) 98\(^\circ\)C\(^{(16)}\)

b) 110\(^\circ\)-120\(^\circ\)\(^{(17)}\)

c) 128\(^\circ\)\(^{(18)}\)

d) approximately 97\(^\circ\)C\(^{(19)}\)

e) temperatures above 70\(^\circ\)C\(^{(4)}\)

Although higher temperatures achieve faster conversion of dihydrate to hemihydrate, under equilibrium conditions the reaction occurs at a much lower temperature. Weiser et al.\(^{(20)}\) achieved complete dehydration to hemihydrate within weeks, at a temperature somewhat above 50\(^\circ\)C.
And Andrews (21) found that over a period of two and a half years, a specimen of gypsum stored in dried air at 50°C lost just about that amount of water needed to convert it to hemihydrate, whereas another specimen stored at 40°C showed evidence of virtually no dehydration at all.

Furthermore, Van't Hoff et al. (reported by Jorgensen (22)) have shown that in an atmosphere with a water vapour pressure equivalent to 50 per cent saturation (that is, the humidity level which, although subject to fluctuation, is usually found in room atmosphere), above 43°C dihydrate will give off water vapour to the atmosphere and be converted into hemihydrate (see Figure 1.1).

Below approximately 40°C the dihydrate is the only stable form of calcium sulphate and will not undergo transformation (14, 16).
Figure 1.1
Curves showing water vapour pressure against temperature.
Curve A: Pressure of saturated water vapour between 0-70°C.
Curve B: Equilibrium vapour pressure in the system dihydrate - hemihydrate - water vapour.
Curve C: Water vapour pressure of the atmosphere at a saturation value of 50 per cent (after Jorgensen (22) after Van't Hoff et al.).

Differences in the conditions under which calcination is carried out bring about variations in the properties of the hemihydrate; for instance, the reactivity of the resultant hemihydrate may vary (23). One important property which is sensitive to such differences is the proportion of
water needed to give a mixture of hemihydrate with a defined viscosity. This water requirement is much greater for dry-calcined than for wet-calcined hemihydrate \(^{(7, 24)}\).
1.4 DIFFERENCES BETWEEN DRY-CALCINED HEMIHYDRATE
AND WET-CALCINED HEMIHYDRATE

For many years it was believed that hemihydrate existed in two distinct forms: $\alpha$ and $\beta$ (stone and plaster respectively). The tradition of two forms probably arose because the material can easily be made by two processes, leading to products in distinctly different physical conditions. Plaster is made up of particles which are irregular in shape and show evidence of being soft with many voids, cracks and other deficiencies. On the other hand, stone consists of crystals which are denser and more regular in shape; often in the shape of rods and prisms\(^{(7,8)}\).

Evidence for the existence of two varieties was largely based on differences in density, specific heat, heats of solution and hydration\(^{(14)}\). Other properties reportedly used to distinguish the two forms are\(^{(3)}\): bulk volume, refractive index, yield value of suspensions in water, and the position of the exothermic peak obtained by differential thermal analysis during transformation of hexagonal to orthorhombic calcium sulphate. Differential thermal analyses have been used as a means of determining the proportions of dry-calcined and wet-calcined hemihydrate in a given sample\(^{(4,15)}\).

However, Ridge and Beretka\(^{(3)}\) state that these properties are not necessarily associated, in principle or in experimental fact, and are not definitive means of identification of different forms. Analysis for the two forms ($\alpha$ and $\beta$) is meaningless unless the terms designate
distinct crystallographic species, if for no other reason than that no unambiguous standards of reference exist in principle.

Most evidence up to the present time does not warrant the differentiation of different forms of hemihydrate. Studies by x-ray and electron diffraction, infra-red absorption and proton magnetic resonance absorption have so far failed to reveal significant differences between dry-calcined and wet-calcined hemihydrate.

It is true that Morris has reported differences in x-ray diffraction patterns, but Ridge and Beretka feel that differences of this type result only from differences in the perfection of the crystal structure and are scarcely such as to warrant the distinction of two crystallographic forms.

It now appears that there are no mineralogical or chemical differences between the two forms of hemihydrate. The differences in the properties of calcium sulphate hemihydrate prepared by wet and by dry methods of calcination are merely the result of differences in habit, crystallite size, surface area and lattice perfection. Therefore the use of the prefixes α and β should be discontinued. Instead, the adjective is used which describes the process by which the material is manufactured; that is "wet-calcined" or "dry-calcined".

Dry-calcination represents a rapid disruptive type of dehydration, which is responsible for the characteristics of the product (plaster). Ordinary commercial pan or kettle calcination usually produces a mixture of the
two types of hemihydrate, since the water of crystallization, which is liberated from the dihydrate, provides an atmosphere partially enriched by steam. Pure dry-calcined hemihydrate can only be produced by dehydration in a vacuum or in a nearly dry atmosphere\(^{(14)}\). Wet-calcined calcium sulphate hemihydrate (dental stone) is the more stable form, at normal temperatures, and is always formed if calcination occurs in the presence of water or steam\(^{(14)}\).
1.5 STRUCTURE OF CALCIUM SULPHATE COMPOUNDS

1.5.1 Calcium Sulphate Dihydrate

Gypsum from various sources may yield plaster with different properties and may require different calcination temperatures\(^{1}\). However, Kelley, Southard and Anderson\(^{14}\) have shown that the heats of solution of rock gypsum, set plaster, precipitated calcium sulphate dihydrate and hydrated hemihydrate show no significant variation. The x-ray diffraction patterns also exhibit no significant variation indicating that these materials are all the same chemical compound.

The identity and structure of this compound has been established for many years. Flörke\(^{5}\) has made an impressive x-ray and crystallographic study of the calcium sulphates, and Hass and Sutherland\(^{29}\) have investigated the structure of gypsum using infra-red absorption spectroscopy. Calcium sulphate dihydrate consists of a layer lattice in which double layers of calcium sulphate alternate with double layers of water bonded by hydrogen bonds. Within the layers, sulphate tetrahedra and calcium form parallel chains (Figure 1.2).

Morphologically, the dihydrate crystal structure is monoclinic with four or eight molecules in the unit cell. Removal of a substantial part of the water in gypsum will destroy the lattice. However investigations of the transformations of the different calcium sulphates into one another have shown that the "calcium sulphate chains" which occur in all of the lattices must be an important
Figure 1.2
Schematic illustration of the layer structure of gypsum. Solid circles denote the positions of Ca; open circles denote those of water molecules and the tetrahedrons represent SO₄ (from Goto and Ridge³⁰).

structural element. Even if the lattice connection is destroyed to a large extent, the "chains" remain preserved and direct the growth of newly forming crystallites in a uniform direction⁵.

1.5.2 Calcium Sulphate Hemihydrate
Many years ago doubts were held as to whether calcium sulphate hemihydrate was a definite chemical species³¹, and many felt it could best be regarded as a hydrous hexagonal calcium sulphate¹⁵. However most of the
evidence to date favours treating the hemihydrate as an individual species \((20,32)\).

Florke \((5)\) advocates for the hemihydrate a structure permeated by wide channels (diameter three angstroms) in which the water molecules are situated. He considers that the lattice of the hemihydrate differs from hexagonal calcium sulphate essentially by the fact that water molecules are present and bring about slight distortions and displacements in the calcium, oxygen and sulphate groups. It is a loosely packed lattice; water is relatively far from the cations and is probably bound mainly by hydrogen bonds to the oxygen atoms of the sulphate group. The energy of the hydrogen bond linkage is relatively low, and removal of the water molecules (that is, dehydration of the hemihydrate) leaves the lattice virtually unchanged. On the other hand, during the reaction with water to yield dihydrate, the hemihydrate lattice undergoes complete reconstruction.

There has been some disagreement about the morphology of the crystal lattice. Florke \((5)\) came to the conclusion that the hemihydrate lattice is rhombohedral as it originates and on transition to lower temperatures it suffers rhombic deformation through the increasing strength of the water linkage. Gay's \((26)\) findings however led him to believe that the hemihydrate has a monoclinic crystal structure.

Although there is evidence to suggest that the hemihydrate lattice will accommodate greater or lesser amounts of water than required by the formula \(\text{CaSO}_4\cdot\frac{1}{2}\text{H}_2\text{O}\)
without serious disorganization\textsuperscript{(14)}, hemihydrate is the only hydrate of calcium sulphate (apart from CaSO\textsubscript{4}·2H\textsubscript{2}O) whose identity has been established with any degree of certainty.

1.5.3 Anhydrous Calcium Sulphate

Unlike the case of hemihydrate, there is no denying that two polymorphic forms of anhydrous calcium sulphate exist, with hexagonal and orthorhombic crystal structures\textsuperscript{(3,33)}. Details of the structure of the orthorhombic form are well established\textsuperscript{(33)}, and Florke\textsuperscript{(5)} has proposed a structure for the hexagonal form. Gay\textsuperscript{(33)} found untwined hexagonal crystals of anhydrous calcium sulphate which roughly conformed to Florke's proposed form, however Ridge and Beretka\textsuperscript{(3)} feel that the structure of hexagonal calcium sulphate is still open to revision.

Orthorhombic calcium sulphate, occurring naturally as anhydrite, has four molecules per unit cell of the crystal lattice. This lattice has the closest packing, highest density and most stable arrangement of any of the forms of calcium sulphate\textsuperscript{(14)}.

The transformation of hexagonal to orthorhombic calcium sulphate was studied by Goto, Molony and Ridge\textsuperscript{(34,35)} and Gay\textsuperscript{(33)}. When the hexagonal calcium sulphate is derived from dry-calcined hemihydrate, it appears that the transformation takes place by the formation of nuclei, the growth of which is fed by diffusion. However, the transformation of hexagonal calcium sulphate formed from
wet-calcined gypsum is interpreted as being a diffusionless process. According to Goto, Molony and Ridge\(^{34,35}\) the dependence of the behaviour of anhydrous calcium sulphate upon the method of preparation does not indicate the existence of two forms of hexagonal calcium sulphate but the occurrence of two mechanisms for the transformation. It seems that samples of calcium sulphate derived from wet-calcined and from dry-calcined gypsum represent end members of a series. In some samples the two mechanisms take place simultaneously, the physical condition of some particles favouring one rather than the other\(^{35,36}\).

Hexagonal calcium sulphate is extremely unstable at room temperatures and hydrates rapidly to give hemihydrate\(^{35,37}\).
1.6 THE WATER REQUIREMENT

A property of considerable technical interest in the preparation of aqueous pastes of calcium sulphate hemihydrate is the "water requirement" (38,39). This is a measure of the amount of water that must be used to give a paste with a specified viscosity. The latter determines the plasticity ("workability") of the paste.

From the chemical reaction (Equation 1.2 in Section 1.7) it can be calculated that only 18.6 per cent of water by weight is required for complete hydration (40,41). However, water must be in excess so that the particles will move over one another with ease during manipulation. Consequently as much as 60g water/100g hemihydrate may be needed.

The importance of the water requirement lies in the fact that, all things being equal, the strength and hardness of the cast gypsum varies inversely with the water content of the mixture used (42), since water that is mixed in excess of that required for chemical combination exists in the final mass without being chemically bound, thereby contributing to the volume but not to the strength (43).

The water requirement varies greatly depending upon the origin and method of manufacture of the hemihydrate (42). The products of dry methods of calcination have a much higher water requirement than the products of wet methods of calcination (42) (Table 1.2).
### TABLE 1.2

<table>
<thead>
<tr>
<th>METHOD OF MANUFACTURE</th>
<th>PRODUCT</th>
<th>TYPICAL W/P RATIO (APPROX.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Heat:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotary Calcined</td>
<td>Plaster</td>
<td>0.5</td>
</tr>
<tr>
<td>Kettle Calcined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pan Calcined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet Heat:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Autoclaved</td>
<td>Dental Stone (Hydrocal)</td>
<td>0.3</td>
</tr>
<tr>
<td>(b) Autoclaved with</td>
<td>Dental Die Stone (Crystocal)</td>
<td>0.25</td>
</tr>
<tr>
<td>Sodium Succinate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Boiled in 30%</td>
<td>Dental Die Stone</td>
<td>0.25</td>
</tr>
<tr>
<td>Calcium Chloride Solution</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 1.6.1 Factors Affecting the Water Requirement

i) **Relative Surface**

ii) Bulk Volume, determined by:

   a) surface condition,
   b) particle shape,
   c) particle size distribution.

i) **Relative Surface** (surface area/unit weight)

Plaster particles, in addition to being very porous, are large and highly irregular in shape. Consequently plaster materials have a very high surface area per unit weight. Stone particles, although much smaller than plaster particles, have a much more regular shape which results in a large reduction in overall surface area. The die stones
have particles which are still more perfectly formed than those of the Hydrocal type of dental stones, and so have an even lower relative surface in the final ground product\(^{(24)}\).

Combe and Smith\(^{(24)}\) found wet-calcined materials have a surface area per unit weight of 4,000-6,000 cm\(^2\)/g compared with about 8,000 cm\(^2\)/g for dry-calcined hemihydrate, and state this difference in surface area per unit weight permits the use of a lower water to powder ratio for a given viscosity of mix.

ii) **Bulk Volume**

The bulk volume is the volume occupied by a given mass of the powder, subject to a standard amount of compaction. Ridge\(^{(39)}\) found that variations in surface area, and in the porosity of the particles were not the main cause of differences in the water requirement. He found a close relationship between water requirement and bulk volume of the dry powder (Figure 1.3).

ii,a) **Surface condition:**

The surface condition, and in particular the surface charge, determines the strength of the adhesive forces between the particles. If these forces are strong the particles tend to stick at the points of first contact giving bulky powders with open structures.

The evidence suggests\(^{(39)}\) that the water requirement is largely determined by the amount of water necessary to fill the voids in the compacted powder, and that the
factors determining the bulk volume of the powder persist much the same in aqueous suspensions as in the dry powder.

But if the adhesive forces are weak, the particles can slip over one another to find the positions of closest packing and produce dense powders.

![Graph](image)

**Figure 1.3**
The water requirement of a number of samples of calcined gypsum plotted against bulk volumes (after Ridge).

Ridge and Boell have shown that suspensions of dry-calcined hemihydrate in water assumed a flocculated nature (that is, the particles are bound together at the points of contact forming a loose aggregate in which the voids are filled with water). It was noted however, that the sample of wet-calcined hemihydrate exhibited far lower sedimentation volumes, than the dry-calcined hemihydrates, and would be expected to show a lesser degree of flocculation.
The important role played by surface forces is emphasized by the large reduction in the water requirement achieved by small additions (a fraction of one per cent) of active materials such as mixtures of gum arabic and calcium oxide \(^{(44,45)}\), or calcium lignosulphate \(^{(44,46)}\). The additives only act by changing the condition of the surface of the particles and the strength of the forces between the particles.

ii,b) **Particle shape:**

Greater effects on water requirement are produced by mechanical processes such as grinding the dry powder \(^{(10,39)}\).

The surfaces of particles produced by dry calcination have the same irregular shape as the original particles of gypsum. The effect of light grinding is probably to remove the asperities and projections inherited from the crushed gypsum \(^{(38)}\). Such resurfaced particles do not show so great a tendency to adhere as the 'pseudomorphs' of the original particles of gypsum and hence the particles fit together more compactly and there is a drop in bulk volume \(^{(39)}\). In the case of wet-calcined hemihydrate, where the particles are regular prismatic crystals, often long and rod-like, light grinding breaks these into shorter more equi-axial crystals and also "rounds off" the corners allowing more effective packing.

ii,c) **Particle size distribution:**

Grinding also provides a proportion of finer particles, and a wider range of particle sizes. This also allows
better packing of the powder and the bulk volume is reduced. The effect is very marked with wet-calcined materials which before grinding consist of well formed prismatic crystals with a fairly uniform particle size and so a relatively high bulk volume.

Eberl and Ingram (10) found, however, that continued or excess grinding causes an increase in water requirement and bulk volume. This may be explained by the enhanced fluffing or powdering attributable to an undesirable over-production of fine particles, and so to the increase in relative surface.

Ridge and Boell (38) also believe a small amount of water (approximately two to four ml/100g powder) is necessary to give an adsorbed layer on the surface of the particles. Therefore, overall, the water requirement of calcined gypsum is made up of (38):

a) water required to fill the open pores in the particles themselves;

b) water required to give an adsorbed layer on the external surface of the particles;

c) water required to fill the voids in the compacted powder;

d) excess water necessary to give mixtures the required flow properties.
1.7 HYDRATION OF CALCIUM SULPHATE HEMIHYDRATE

The terms "hydration" and "setting" must be clearly distinguished. Setting is the change in flow properties of the aqueous paste of hemihydrate and water, whereas hydration is the reversion to gypsum\(^{(21)}\). The rapidity of set is very sensitive to small changes in the proportion of water (that is, the water/powder ratio), but provided enough water is present to produce an aqueous phase throughout the whole reaction, the rate of hydration is unaffected\(^{(47-50)}\).

At first sight, the reaction between water and calcium sulphate hemihydrate to yield calcium sulphate dihydrate appears to be a very simple chemical reaction:

\[ \text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{heat} \]

... Equation 1.2\(^{(22,51)}\)

The reaction is exothermic, and the heat evolved is equivalent to the heat used originally for calcination\(^{(37)}\). However, the temperature coefficient of the heat and rate of the reaction are not large and it was found that the reaction followed a similar course whether it was carried out at a constant temperature, or whether it was carried out under adiabatic conditions. In the latter case the progress of the reaction could be followed by monitoring the changes in temperature\(^{(52,53)}\). It is in fact far simpler to follow the progress of hydration in this way, than to follow the kinetics of the reaction isothermally\(^{(32)}\).
If the increase in temperature developed by a paste of hemihydrate and water is plotted against time, a sigmoidal curve is developed\(^{(6)}\), and it may be seen from the manner in which the rate of hydration changes with time that the apparent simplicity of Equation 1.2 is deceptive (see Figure 1.4).

![Graph showing change in temperature over time](image)

**Figure 1.4**
A characteristic curve of temperature rise occurring during the hydration of calcium sulphate hemihydrate (from Phillips, Skinner's Science of Dental Materials\(^{(37)}\)).

A typical hydration curve has the following characteristics:

i) When the hemihydrate is added to water there may be an initial small, but sharp rise in temperature\(^{(54, 55)}\).

ii) There is a well-defined induction period throughout which there is a comparatively small but gradual increase in temperature\(^{(56)}\). Ridge\(^{(53)}\) defines the induction
period as to the "time taken for the rate of rise in
temperature to exceed 0.1°C/min."

iii) The induction period is followed by an increase in
the rate of rise in temperature up to a maximum, and
thereafter decays until -

iv) The temperature finally levels off to a substantially
constant value (54).

The hydration reaction is strongly self-accelerating (57). The period of induction is not a period
of rest, although reaction during this time is slight (56). However the induction period is followed by a period of
rapid acceleration of the reaction and then a period of
decay, during which the rate of hydration falls away to
zero (57).

Lautenschläger, Harcourt and Ploszaj (48) have
confirmed that while the reaction progresses, the actual
amount of hemihydrate decreases whilst the amount of
dihydrate increases. The transformations are shown to be
smooth and continuous (Figure 1.5).
Figure 1.5
Hydration of calcium sulphate hemihydrate and formation of calcium sulphate dihydrate examined using the x-ray diffraction peaks of the materials (after Lautenschlager, Harcourt and Ploszaj(48)).

1.7.1 Mechanism of Hydration

1.7.1.1 EARLIER THEORIES OF HYDRATION

The mechanism of the setting of pastes of plaster was an early subject of scientific investigation. Early work led to the view that thickening and then hardening of mixtures of plaster and water were the direct result of the formation of microscopic crystals of gypsum(6).

It has been recognized since the 19th century that the hemihydrate is more soluble than the dihydrate(16). It is in fact four to five times more soluble at ordinary room temperatures(40,55)(Figure 1.6). Moreover, below about 40°C gypsum is the only stable hydrate of calcium sulphate(14). The hemihydrate, although it exists at room temperature, is actually in a metastable state.
Figure 1.6
Solubility diagram showing relative solubilities of calcium sulphate dihydrate (A), orthorhombic calcium sulphate (B) and calcium sulphate hemihydrate (C) at different temperatures (after Kelley, Southard and Anderson(14)).

Knowing that the hemihydrate was more soluble than the dihydrate, Le Chatelier proposed the following simple mechanism in 1887 (as reported by Jorgensen(22) and Ridge(6)):

Upon being mixed with water, the hemihydrate passes into solution. The solution so formed is supersaturated with respect to the less soluble dihydrate, and consequently the dihydrate is precipitated as needle-like crystals. The mechanical strength of the product was supposedly due to the interlocking of the spikes and needles of dihydrate.

A few years later Michaelis (1893) questioned this theory and put forth a colloidal theory of setting (reported by Ridge(6,32)). This concept gained popularity
as various evidence was produced over the years by a number of different authors\(^{(6)}\).

Following the lead of Michaelis, Cavazzi (reported by Gibson and Johnson\(^{(51)}\)) concluded that a colloidal calcium sulphate gel is produced as an intermediate product from which crystals of dihydrate are deposited. Baykoff, Neville and Budnikoff (reported by Weiser and Moreland\(^{(55)}\)) came out definitely in support of the formation of a gel as an intermediate stage in the setting process:

- Baykoff was able to produce what he considered to be a "gypsum gel" and decided that the initial thickening of the hemihydrate paste was due to gelation;

- Neville attributed the period of induction to the formation of a gel or adsorption complex between plaster and water;

- Budnikoff concluded that a layer of gel forms on the particles of hemihydrate and protects them from the action of water, thus producing the induction period, which presumably ended by crystallization of the enclosing gel allowing water to once again act on the hemihydrate. But, as pointed out by Weiser and Moreland\(^{(55)}\), the disappearance of a first gel layer would merely be followed by the formation of a new one, giving rise to a second induction period, and so on.

Weiser and Moreland\(^{(55)}\) published, in 1932, a study on the hydration of plaster using thermometric and optical observations. They vigorously rejected the colloidal theories for setting and hydration, noting that there was
an absence of any direct evidence of gel formation. Baykoff's "gypsum gel" was shown to be a "false gel" consisting of a mass of interlacing crystals of gypsum.

They concluded that the period of induction is not due to the formation of an adsorption complex between water and hemihydrate. The delay in precipitation from a supersaturated solution was the result of a scarcity of gypsum nuclei and could be eliminated by the addition of less than one per cent of finely ground gypsum to the hemihydrate. Many years later Guha and Sen\(^{(58)}\), using conductivity measurements, came to the same conclusion.

More recently, Fischer\(^{(59)}\) has claimed that the initial setting of the paste is caused by the formation of a gel structure and that hydration only occurs afterwards. However, using thermogravimetric, differential thermal and x-ray analyses, Powell\(^{(50,56)}\) detected increasing amounts of crystals during the gradual thickening of slurries of hemihydrate and water and his results indicated that gypsum crystal formation is really the main cause of initial thickening.

Using a more direct approach, Ridge\(^{(60)}\) examined samples of setting plaster by microscopy using reflected light and detected fine crystals of gypsum very early in setting process. There was no evidence of any non-crystalline material. Microscopic examination of plaster after hardening and drying revealed a fairly uniform crystal size with no evidence of a finely divided fraction which might be expected if the crystals of gypsum emerged from an intermediate gel stage\(^{(6)}\). The fairly even crystal
size suggested to Ridge that the growth of all the crystals began at about the same time; that is, shortly after the hemihydrate was mixed with water\textsuperscript{(53)}.

Even more recently Eipeltauer\textsuperscript{(61)} (also reported by Ridge and Beretka\textsuperscript{(3)}) has observed that under the microscope a clear zone appears around the periphery of particles of hemihydrate immersed in water, and that this zone slowly moves towards the centre to cover the whole particle. This was interpreted as being a solid-state reaction to yield a gel. Goto and Ridge\textsuperscript{(62)} have shown in a study by microscopy that the clear zone is anisotropic and is continuous in orientation with other parts of the particle. They believe this phenomenon is probably the result of water slowly penetrating the pores of the hemihydrate particles and altering its light scattering properties. This explanation gains support from the fact that such changes in optical properties were not observed with hemihydrate prepared by wet methods\textsuperscript{(32)}; the powder particles in this case consist of individual crystals which are free from pores\textsuperscript{(38)}. The results of Goto and Ridge\textsuperscript{(62)} confirmed that hydration is not topotactic.

Hansen\textsuperscript{(63)} postulated that reaction between hemihydrate and water yields a layer of dihydrate, which he calls G.A., on the surface of the hemihydrate grains. The layer of G.A. hinders further hydration and is responsible for the induction period. On reaching a critical thickness, the layer ruptures and provides fresh nuclei for crystallization. This theory is in fact very similar to that propounded by Budnikov (as reported by Weiser and
Moreland\(^{55}\) and suffers from the same deficiency; namely, that the disappearance of the first layer would logically be followed by the formation of a second layer on the fresh hemihydrate surface, thus producing a second induction period, and so on.

Hansen's view received some support from Chatterji and Kapse\(^{64}\), whose work indicated that the surfaces of the hemihydrate crystals immersed in water are covered with a layer of adsorbed water molecules. But this condition would really be the first step in the ionization of calcium sulphate, and one would expect this to happen in the natural course of events\(^{3}\).

1.7.1.2 CURRENT CONCEPT OF HYDRATION

It is now widely accepted that Le Chatelier's concept of hydration was basically correct, and that the mechanism involved is one of solution and recrystallization\(^{11,22,32,37,50,65,66}\).

A saturated solution of calcium sulphate is formed almost immediately after the hemihydrate is mixed with water. An induction period follows, the length of which is determined by the nature of the hemihydrate and the presence of any accelerating or retarding substances. Crystallization of calcium sulphate dihydrate occurs, because the dihydrate is the only stable form of calcium sulphate at temperatures below approximately 40°C. Calcium and sulphate ions diffuse through the solution from the hemihydrate to the dihydrate nuclei where further
crystallization takes place. The dihydrate crystals continue to grow at the expense of the hemihydrate. Their growth is fed by the calcium and sulphate ions which are supplied by progressive dissolution of the hemihydrate. The reaction rate is strongly auto-catalytic, and after the induction period the reaction gathers pace at an increasingly accelerating rate, until the effects of depletion of the reactants make themselves felt. The rate then decays and finally falls to zero, at which time all the hemihydrate has been spent.

For the crystals to develop, a stable nucleus of crystallization must have formed. Nuclei may develop spontaneously in saturated solutions by the chance aggregation of sufficient calcium and sulphate ions and water molecules to give a volume of gypsum lattice which is sufficiently large to have a high chance of continued growth\(^{(6)}\). Below a critical size the aggregates of calcium and sulphate ions and water will tend to redissolve\(^{(67)}\).

However, hemihydrate pastes are heterogeneous systems and homogeneous nucleation is said to be unimportant\(^{(20, 68)}\). Residues of foreign particles are capable of acting as favourable sites for the development of gypsum nuclei, and it is well accepted that residual gypsum particles which remain after calcination act as nuclei for crystallization\(^{(6)}\). Guha and Sen\(^{(58)}\) showed that a solution saturated with respect to hemihydrate, takes approximately 100 minutes to attain the maximum rate of concentration drop due to spontaneous nucleation of
dihydrate. The addition of a small quantity of gypsum caused this maximum to be reached almost instantaneously.

In addition, regions of damage or imperfection in the hemihydrate crystals may serve as nucleation sites for the growth of the new phase from solution, and may be present as cracks, stains or dislocations in the hemihydrate lattice\(^{(5,68)}\). These potential nuclei may be created by grinding the hemihydrate particles after calcination\(^{(6)}\). They can be removed by heating the hemihydrate (annealing) and recreated by further grinding. These changes may be observed experimentally as an increase in the reactivity after grinding and a subsequent loss of reactivity on reheating the material. This cycle can be repeated several times (Figure 1.7)\(^{(69)}\).

**Figure 1.7**
The effect of alternate grinding and heating treatments on the setting time of gypsum plaster (after Waters, Way and Lewis\(^{(69)}\)).
A number of factors have been suggested as determining the rate of setting of gypsum (that is, reactivity) but by far the greatest effect on the kinetics was found to be due to the density and effective surface area of the nuclei present in suspension\(^{20}\). Furthermore, the experiments of Waters et al.\(^{69}\) on grinding and reheating indicate that the residual gypsum is much less effective as an accelerating agent than areas of strain or damage on the hemihydrate crystals; and indeed it would appear that these active areas of hemihydrate lattice are the major sites for nucleation of dihydrate crystals.

In any case, there is general agreement that the crystallization which occurs during hydration is heterogeneously nucleated\(^{52,53,69,70}\). The nuclei for crystallization can be regarded as being available at the very beginning of the reaction\(^{71}\). Optical examination indicates that a crop of nuclei begins to develop shortly after or perhaps even immediately the reactants are brought together\(^{32}\).

1.7.1.3 INTERPRETATION OF HYDRATION KINETICS

Since the mechanism of hydration is by a process of solution-recrystallization, the following factors may assume importance in determining the rate of reaction\(^{72}\):

i) rate of solution of hemihydrate (which is proportional to surface area);

ii) rate of diffusion of calcium and sulphate ions
through the solution, from the hemihydrate to the 
nuclei of crystallization;

iii) rate of precipitation.

A concentration gradient will be established between 
the dissolving hemihydrate and the growing dihydrate phase, 
providing a more or less steady supply of calcium and 
sulphate ions to the growing crystals\(^{6}\). The capacity of 
the system to supply calcium sulphate will be determined 
by the surface area of the hemihydrate and the distance 
over which diffusion must occur. Because of the close 
proximity of the two phases in the system, both Ridge and 
Beretka\(^{3}\) and Schiller\(^{71}\) believe diffusion to be 
quantitatively unimportant as a rate controlling factor.

Ridge, and fellow workers have, over a number of 
years, developed a theoretical model to explain the kinetics of hydration\(^{3,6,32,52,53,57,62,73-75}\). He proposed 
the equation:

\[
\frac{d\alpha}{dt} = K\alpha(1-\alpha)^{2/3}
\]

where \(\alpha\) is the fraction of hemihydrate transformed to 
gypsum in time \(t\).

\(\frac{d\alpha}{dt}\) is therefore the rate of hydration and 

\(K\) is a constant.

This equation was shown to describe the reaction well for 
93 per cent of its course in the unmodified and accelerated system\(^{3,32}\). The inhibited reaction apparently 
involves complications which are not taken into account in
these mathematical treatments. It seems that the retarder is consumed by the growing phase as the reaction proceeds\(^{(52)}\).

Schiller\(^{(47,66,71,76)}\) also developed a basic model for hydration and has proposed an equation of the type:

\[
t = B\left[V^{1/3} + 1 - (1-V)^{1/3}\right]
\]

where \(V\) is the percentage volume of dihydrate formed in time \(t\), and \(B\) is a constant.

There has been much disagreement between Ridge and Schiller in the literature over each other's interpretation of hydration kinetics\(^{(57,77,78)}\); however Schiller's equation has been reported not to be in accord with experimental results for either dry-calcined or wet-calcined hemihydrates\(^{(3,49,79)}\).

Combe, Smith and Braden\(^{(49)}\) noted that most of the work of previous authors was performed with dry-calcined hemihydrate. They followed the kinetics of autoclaved materials by an essentially isothermal method, and concluded that the theories and equations of both Schiller and Ridge were inadequate in describing the kinetics of hydration of wet-calcined materials. They, in turn, put forward an alternative theory:

\[
\alpha = 1 - \exp(-kt^{3/2})
\]

This was based on the Avrami theory of crystallization and assumes the reaction to be diffusion controlled.
They found this accounted well for the hydration kinetics of the autoclaved materials studied, below about 50°C.
1.8 SETTING OF CAST GYPSUM

1.8.1 Measurement of Setting

Setting is a continuous process of thickening and hardening. The main process of thickening is the formation of an interlocking network of crystals of dihydrate which interfere with the free flow of the mix\(^{(50,65,74)}\). The viscosity of the slurry gradually increases until it looses its ability for plastic flow. It then becomes a brittle solid and thereafter continued setting brings about increasing strength until hydration is completed\(^{(80)}\). Any figure for setting time only identifies a particular stage in this continuous process.

Two stages of hardening have been arbitrarily recognized, called the initial set and the final set:

a) The initial set may be considered to be a stage at which the new gypsum crystals have grown to sufficient length to interfere with one another and with the neighbouring hemihydrate particles, and hence confer some structure and rigidity upon the mass\(^{(47,65)}\).

b) The final set stage represents the formation of a relatively rigid, three-dimensional framework of gypsum crystals\(^{(65)}\). At this stage however, the hydration reaction is still far from being completed, and at most only 70 per cent of the hemihydrate has been converted to dihydrate\(^{(48)}\).

It is impossible to get a true measurement of setting. The laboratory methods used do not measure the amount of chemical reaction\(^{(49)}\), but give measurements
which vary, according to the particular parameter upon which the test is based. The initial set (or final set) can represent many different degrees of hardness, according to how it is measured.

Many methods have been established over the years, to measure particular stages in setting:

i) Loss of Gloss Test,

ii) Knife-Cut Test,

iii) Temperature Measurement,

iv) Vicat Initial Set,

v) Vicat Final Set,

vi) Gillmore Initial Set,

vii) Gillmore Final Set.

i) Loss of Gloss Test\(^{(24,80)}\)

This test was specifically developed to assess the time at which fluidity was lost. The free water on the surface of the paste is drawn into the mass, causing disappearance of the surface gloss, and this was found to correspond to the point at which loss of fluidity occurred. Both phenomena are said to occur at the time when the dihydrate crystals begin to interact.

ii) Knife-Cut Test\(^{(81)}\)

In this test, the time is measured which elapses before a knife-cut, made in the surface of the paste, ceases to heal. This test is also close to the change from the fluid to plastic state.
iii) **Temperature Measurement**\(^{6,60}\)

This involves the measurement of the increase in temperature of the paste. This is really a measure of the rate of hydration, and not of actual stiffening. The time required for the rate of increase of temperature to exceed 0.1° C per minute may be defined as the time to reach the end of the induction period.

iv) **Vicat Initial Set**\(^{82-85}\)

A needle of specified dimensions is allowed to penetrate a volume of the paste under a weight of 300gf. The apparatus has a scale to show the depth of penetration and the paste is contained within a mould. The mould usually has a height of 40mm\(^{82,84,85}\) however the ADA\(^{83}\) specification for dental gypsum products requires the mould to be 25mm high. The specifications for the Vicat needle also vary. The needle may be round with a 1mm diameter\(^{82,83}\) or a 1.13mm diameter\(^{85}\) or it may be 1mm square in section\(^{84}\).

The ASTM\(^{82}\) and ADA\(^{83}\) specifications for gypsum products define the initial setting time as the time (measured from the commencement of mixing) at which the indenter fails to penetrate to the bottom of the plaster or stone sample. However the Australian specification for Portland cement\(^{84}\) defines the initial set as "the time elapsing between the addition of the water and the first refusal of the needle to penetrate the paste to within 1mm" of the bottom of the mould; and the British specification for testing cement\(^{85}\) stipulates that initial
setting time is determined when the needle reaches a point approximately 5mm from the bottom of the mould.

v) **Vicat Final Set** (84,85)

This is the time elapsing between the commencement of mixing and the first refusal of the needle to penetrate more than 0.5mm when applied gently to the surface of the paste. In the Australian Standard (84) the same needle is used for measuring both initial and final setting times. The British Standard (85) specifies the use of a round needle, 1.13mm in diameter, with a metal attachment which permits only 0.5mm of the needle to project beyond the edge of the attachment.

vi) **Gillmore Initial Set** (40,86)

The Gillmore apparatus consists of two standardised indenters. The smaller one is used to determine the initial set. It weighs ¼lb and has a tip diameter 1/12 inch in diameter. The Australian Standards Association have adopted a metric equivalent to the Gillmore needle which weighs 100g and has a tip diameter of 2mm. The test is said to be completed when the needle may rest on the surface of the plaster or stone sample without making a complete impression.

vii) **Gillmore Final Set** (40,87)

This is determined in the same way as the Gillmore Initial Set, however the larger of the two indenters is used. This weighs 1 lb and has a tip diameter of 1/24 inch.
The present Australian equivalent weighs 400g and has a tip diameter of 1mm.

The values provided by the different tests do not usually correspond. The end of the induction period as determined by temperature measurements corresponds approximately with the time given by the Knife-Cut Test\(^6\), and is about 15 minutes before the Gillmore Initial Set, although the two parameters run more or less parallel\(^8\). The loss of glass also precedes the Gillmore and Vicat Initial Set by several minutes\(^9\). Furthermore, the initial set determined by the Vicat method occurs approximately one or two minutes earlier than that determined by the Gillmore method\(^{40}\). The setting mass is relatively strong at the Gillmore Initial Set; the Gillmore Final Set occurs quite late in the setting process.

### 1.8.2 Control of Setting Time

The setting time of a mixture of hemihydrate and water is influenced by a number of factors:

i) Calcination

ii) Particle size of hemihydrate powder

iii) Grinding the hemihydrate

iv) Mixing

v) Water/Powder ratio

vi) Temperature

vii) Addition of chemical modifiers:
   a) accelerators
   b) retarders.
i) **Calcination**: *(23, 36, 69, 90)*

If calcination is incomplete and residual gypsum remains then the induction period is shortened and setting time is reduced. If, on the other hand, calcination is prolonged or completed at excessively high temperatures then hexagonal or orthorhombic anhydrite may be formed (Section 1.3). Hexagonal anhydrite, if present, will decrease the induction period (and hence the setting time), and orthorhombic anhydrite may also influence the reactivity of the hemihydrate. Furthermore the conditions of calcination have an effect on the presence and abundance of the potential nucleation sites which may play an important role in the initiation of hydration.

ii) **Particle size of hemihydrate powder**: *(90)*

Smaller particles of hemihydrate provide an overall increase in surface area, which allows an increased rate of dissolution of the hemihydrate. Therefore the rate of the reaction is accelerated.

iii) **Grinding the hemihydrate**: *(69, 90)*

Grinding (for instance, during manufacture) damages the crystals of hemihydrate. The number of nucleation sites is increased, thereby accelerating the setting reaction. Grinding also reduces the size of the hemihydrate particles, which in turn also causes an increase in the setting rate.
iv) **Mixing**: (90-92)

Both the amount and speed of stirring affects the setting time. Spatulation causes the initially formed crystals of dihydrate to be broken up and distributed throughout the mixture and thus provides an increased supply of nucleation sites. Consequently an increase in mixing time and speed of spatulation, within practical limits, results in a reduction in the setting time of gypsum products.

v) **Water/Powder ratio**: (48, 90)

An increase in the water/powder (W/P) ratio results in an increase in the setting time. This occurs because the reaction products, although still forming at the same rate, are diluted with respect to one another, and therefore more product must be formed to produce a sufficiently rigid network of crystals.

vi) **Temperature**: (6, 88, 90, 92)

Although the effects of temperature upon setting time tend to be erratic, temperature changes exert a comparatively small effect on the reaction rate and setting time of gypsum products. Greener, Harcourt and Lautenschlager (92) report that as the temperature increases from 0 to 30°C there is a slight acceleration; in the vicinity of 30 to 50°C, the setting rate is essentially constant and above 50°C the reaction rate is progressively retarded until at about 95°C setting does not occur.
vii) Addition of chemical modifiers\(^{(93)}\)

Probably the most effective and practical method for the control of setting time is by the use of modifying chemicals. If the chemical added decreases the setting time it is known as an accelerator; if the setting time is increased it is called a retarder. In addition to affecting the setting time, these chemical modifiers are also known to have an effect on other properties such as setting expansion\(^{(93)}\) and strength of the cast gypsum\(^{(94)}\).

a) Accelerators:

Accelerators act by modifying the rate at which calcium sulphate is transported to and built into the lattice of the growing phase. This is probably achieved by increasing the rate of dissolution of hemihydrate\(^{(6)}\).

Neutral salts, such as sodium chloride and potassium chloride, are generally very effective accelerators of setting\(^{(3)}\), and most soluble sulphates, such as potassium sulphate, are potent accelerators\(^{(92)}\). However, the concentration of these chemical additives is an important factor in their effect on setting time. Although acting as powerful accelerators in dilute solutions, they may actually increase the setting time in higher concentrations\(^{(95)}\). For instance, sodium chloride in concentrations less than five per cent is an effective accelerator, but in concentrations of 20 per cent or greater it acts as a retarder. Sodium sulphate solutions act in a similar way.

The probable explanation of this phenomenon is as follows: as precipitation occurs the remaining solution becomes supersaturated with the accelerator, which in turn
may crystallize on the growing gypsum nuclei and thus interfere with further crystallization\(^{(92)}\). This process is known as nuclei "poisoning"\(^{(95)}\).

Potassium sulphate is the most commonly used and most reliable accelerator, and is effective in all concentrations. In low concentrations its action is the same as that of sodium chloride, but above two or three per cent the reaction product is syngenite \((K_2Ca(SO_4)_2\cdot H_2O)\) which crystallizes very rapidly, markedly reducing the setting time\(^{(92,95)}\).

b) Retarders:

Any material which adsorbs onto the surface of the hemihydrate particles or the growing gypsum crystals will form a barrier and thereby impede the dissolution of hemihydrate or the crystallization of the gypsum. Colloidal materials such as gelatin, glue, agar, and gum arabic cause retardation in this manner\(^{(96)}\). Many colloids are also effective in "poisoning" the nuclei of crystallization\(^{(97)}\).

Borax is one of the most effective retarders, and acts by forming insoluble calcium borate as a product of its reaction with calcium sulphate. The insoluble calcium borate is deposited on the growing dihydrate nuclei and then interferes with further crystallization\(^{(95)}\). Citrates and acetates act in a similar fashion\(^{(96)}\).

The action of retarders is complicated by the fact that the retarder can be incorporated into the growing crystals of dihydrate and so be removed from the system as
the reaction proceeds. The rate of consumption of the retarder therefore probably influences the period of retardation (73).
1.9 SETTING EXPANSION OF CAST GYPSUM

During hydration, the chemical reaction is accompanied by a considerable contraction in volume. The expected contraction is estimated to be seven per cent by volume\(^{22,51}\); however in the case of unmodified hemihydrates during setting an actual linear expansion in external dimensions of up to 0.5 per cent can be observed\(^{6,98}\).

The apparent expansion may be explained in the following way\(^{6,43}\): During the setting process, the crystals of dihydrate encounter one another as they grow. It is known that a growing crystal exerts a force against a surface with which it comes into contact\(^{65,99}\). The integrated effect of the thrusting of the individual crystals results in an expansion of the skeletal framework of interlocking crystals, producing the observed expansion of the mass as a whole. The expansion depends on the size and shape of the dihydrate crystals\(^{91}\), as well as the presence of excess water during setting and the water/powder ratio used in the mix\(^{22}\).
1.10 POROSITY OF CAST GYPSUM

The occurrence of a true volumetric contraction of the reactants during setting, in a mass which shows an observed expansion, implies that there is a development of internal porosity\(^{(22)}\). The apparent volume of the set mass really represents the true volume of gypsum plus the volume of all the porosity within the mass.

Porosity may originate in a number of ways:

i) Air-bubble porosity\(^{(100)}\): which is due to the incorporation of air during mixing procedures, and may be markedly reduced by the use of vacuum-mixing methods. Air-bubble porosity is not related to setting expansion, in any way.

ii) Porosity caused by excess water\(^{(101)}\): that is, caused by the evaporation of gauging water present in excess of that required for the actual hydration reaction (18.6g/100g hemihydrate; Section 1.6).

iii) Porosity caused by crystal growth\(^{(101)}\): supposedly the result of the outward thrust of impinging crystals during expansion, creating voids within the skeletal framework. Lautenschlager and Corbin\(^{(101)}\) designate this as "microporosity", however it is difficult to justify their selective use of the term because the pores formed by evaporation of unreacted water are also microscopic.
Total porosity increases with increasing water/powder ratios, however porosity caused by crystal growth decreases since there is a reduction in expansion with increases in the water/powder ratio (101). Therefore the presence of excess water in the mix appears to be the dominant factor in pore formation (Figure 1.8).

**Figure 1.8**
Porosity versus water/powder ratio for dental stone. Total porosity is divided into its components of excess water porosity and porosity caused by crystal growth (labelled "micropores") (after Lautenschlager and Corbin (101)).
For all practical purposes air-bubble porosity has been found to be independent of water/powder ratio, except with very thick mixes. However porosity is markedly reduced when mixing is carried out under vacuum (Figure 1.9(100)).

Figure 1.9
Relationship between water/powder ratio and air-bubble porosity of cast gypsum. A = vacuum-treated. B = not vacuum-treated (after Jorgensen and Kono(100)).
The reduction in porosity achieved by vacuum treatment achieves a moderate increase in the compressive strength. The increase in strength is greater, at lower water/powder ratios, with a maximum difference of about 20 per cent (Figure 1.10\(^\text{100}\)).

Figure 1.10
Relationship between water/powder ratio and compressive strength of cast gypsum. A = vacuum-treated. B = not vacuum-treated (after Jorgensen and Kono\(^\text{100}\)).
1.11 VISCOSITY

Viscosity may be defined as a property of fluids or mobile materials, which appears as a dissipative resistance to flow (that is, to irreversible deformation)\(^{(102)}\). Fluidity is the reciprocal of viscosity\(^{(103)}\).

The generally recognized form of flow is in shear, with the rate of flow being a function of the stress. For purposes of quantitative evaluation, viscosity is measured by determining the ratio of applied shear stress to the rate of shear. This ratio is called the coefficient of viscosity or is simply referred to as viscosity\(^{(103)}\). The S.I. unit for viscosity is the pascal.second.

For an ideal viscous body, a Newtonian fluid, the coefficient of viscosity, \(\eta\), is a constant and shear stress is proportional to shear rate\(^{(103)}\).

\[
\eta = \frac{\tau}{\dot{\gamma}} \quad \text{... Equation 1.3}\(^{(104)}\)
\]

where \(\eta\) = coefficient of viscosity
\(\tau\) = shear stress
\(\dot{\gamma}\) = shear rate

But for several classes of fluids the shear stress is not proportional to the shear rate and hence the viscosity varies with changing rate of shear (or with changing shear stress). Such materials are called non-Newtonian fluids; the viscosity for such materials is called the apparent viscosity\(^{(103, 104)}\).
Typical flow curves for Newtonian and non-Newtonian fluids are presented in Figure 1.11.

Figure 1.11
Flow curves for various ideal rheological bodies.
A is a Newtonian fluid;
B is a pseudoplastic fluid;
C is a dilatant fluid;
D is a Bingham plastic;
E is a pseudoplastic material with a yield value;
F is a dilatant material with a yield value;
\( \psi \) is the yield value. The dotted lines represent the apparent viscosities corresponding to point \( x \) on Curve B and point \( y \) on Curve F (from Von Wazer, Lyons, Kim and Colwell, Viscosity and Flow Measurements).
Line A represents the Newtonian body for which viscosity is constant. When rate of shear increases more than in proportion to the shear stress, the material is called a pseudoplastic or shear-thinning fluid. Such a material exhibits a flow curve shaped like Line B. When rate of shear is less than in proportion to the shear stress the material is called dilatant or shear-thickening and this is demonstrated by Line C\(^{(103)}\).

The apparent viscosity is the ratio of total shear stress to total rate of shear of a given point on a curve\(^{(103)}\). It is represented by the slope of the dotted lines in Figure 1.11 for the point x on Curve B and the point y on Curve F.

More complex materials, which flow readily when subjected to a sufficiently high shear stress, will not flow at all if the shear stress is reduced below a certain level, called the yield value. Once the yield value has been exceeded the rate of shear may be proportional to the stress, as is the case with Newtonian liquids. Such materials are called plastic substances or Bingham bodies and have a flow curve similar to Line D in Figure 1.11. However if the material exhibiting a yield value behaves in a non-linear manner, then it may behave as a pseudoplastic material or a dilatant material (Lines E and F respectively in Figure 1.11)\(^{(105)}\).

The yield value is due to interference between the dispersed particles under static conditions, forming a "house-of-cards" structure. As the concentration of the
dispersed phase is reduced the yield value decreases until it reaches zero\(^{(106)}\).

### 1.11.1 Viscosity of Gypsum Pastes

Gypsum slurries or pastes, resulting from the mixing of calcium sulphate hemihydrate powder with water, exhibit the rheological properties of pseudoplastic fluids with a yield value; that is, they resist small stresses but flow at higher stresses. This phenomenon is readily observed with a fresh mix of putty-like consistency. It will maintain its shape under the influence of gravity (that is, at a relatively low shear stress) but will flow easily when subjected to the greater shear stresses provided by a dental vibrator.

#### 1.11.1.1 IMPORTANCE OF VISCOSITY

It has already been noted that the proportion of water used for mixing has a great effect on the properties of gypsum products. A decrease in the water/powder ratio produces an increase in setting rate, setting expansion, strength and hardness of the set material. Although an increase in setting rate and expansion may sometimes be undesirable, an increase in strength and hardness is certainly an advantage. Just a small change in the water/powder ratio can dramatically improve the strength of the set gypsum, by as much as 100 per cent in some instances\(^{(107)}\).

Since setting expansion and setting rate are controlled by the addition of chemical modifiers in most
commercial products, it is obviously desirable to use as low a water/powder ratio as is practicable. The limiting factor however is the ability of the mix to be manipulated, and its capacity to conform easily and accurately to an impression or pattern. This in turn is governed by the viscosity of the mix.

1.11.1.2 NEED FOR TESTING VISCOSITY

Different brands and often even different batches of the one brand of calcium sulphate hemihydrate powder will vary in viscosity if all mixed with the same proportion of water. In turn, if all are mixed to the same viscosity there is a wide variation in the properties of the set casts (24,108).

Rather than mixing to an actual water/powder ratio, most dentists and dental technicians generally mix gypsum plasters to a viscosity which is convenient and suits their individual preferences, without regard to the resultant variation in properties. The viscosities employed may range from that of a stiff paste to that of cream (40,107). It is therefore important that if the relative merits of different products and materials are to be assessed in the testing laboratory, then they should be evaluated at a comparable or "standard" viscosity.

Because of the nature of the freshly mixed slurry of gypsum, it is very difficult and impracticable to measure the viscosity using conventional rheological apparatus (107). Although it would be useful to be able to measure its viscosity in absolute units (pascal.second),
it is however not truly necessary. It is only necessary to be able to make comparative determinations with a test which is simple, accurate, reproducible and does not involve wide departures from clinical and dental laboratory conditions.

1.11.1.3 VISCOSITY TESTS

In 1943 Worner(107) outlined three methods for testing the viscosity of fresh mixes of dental and surgical plasters and casting investments. The tests involved:

i) flow of the slurry down a steeply sloping surface;

ii) penetration of a weighted, cylindrical rod into the mix and measurement of the depth of penetration;

iii) slump tests -

a) from a ring container, in which the change in form produced by the action of gravity on a given volume of the material, is measured after removal of the containing vessel. The diameter of the slump is the variable usually measured;

b) using a steadily applied weight on a glass plate to cause spreading of a given volume of the material. The diameter of the spread is measured.

Worner(107) noted that, in general, the slump tests seemed to show the greatest range of applicability. The American Society for Testing Materials originally adopted the method for testing viscosity which involved penetration of a weighted cylindrical rod into the mix(109). A modification of the penetration test was developed by Kuntze(110), in which a modified Vicat apparatus with a
conical penetrator is used instead of a cylindrical rod.

The American Society for Testing Materials now uses this test for the determination of "normal consistency" in its specification for testing gypsum products\(^{(82)}\).

The American Dental Association has also adopted this method for the determination of standard testing viscosity of model plaster, dental stones and high-strength dental stones in its specification for dental gypsum products\(^{(83)}\).

The American Dental Association specifies the use of a slump test under the influence of gravity as the testing method for determining a standard testing viscosity for impression plaster\(^{(83)}\) and for dental casting investments\(^{(111)}\).

The British Standards Institution in its specifications for impression plaster\(^{(112)}\) and laboratory plaster\(^{(113)}\), prescribes the use of a slump test in which a plate, on which rests the cylindrical mold containing the fresh mix, is allowed to fall away from the cylinder at a constant rate, allowing slumping to occur.

Another method for the determination of a standard testing viscosity is described by the British Standards Institution as the "dropping ball penetrometer". In this test a ball of acrylic resin, 25.4mm in diameter and weighing 10.25g is allowed to fall freely from a height of 254mm into a fresh mix of gypsum. The depth of penetration is then measured. This method is specified in the British Standard for dental artificial stones\(^{(114)}\), as well as for building plasters\(^{(115)}\).
All of the above methods for determination of a standard testing viscosity, with the exception of the slump test for dental casting investments in the American Dental Association specifications (111), prescribe the use of a retarding solution in place of water for the preparation of the gypsum slurries. Sodium citrate is generally specified as the retarding to be used.

However, Chatterji and Kapse (64) in a study on the rheology of suspensions of calcium sulphate hemihydrate found that the chemical modifiers used in their experiments produced changes in the viscosity of the mixture. Ridge and Boell (44) found that some retarders caused an increase in viscosity whilst still others varied in their effect on different types of plasters. They also showed that sodium citrate consistently reduced the viscosity of slurries of various gypsum plasters.

Earnshaw (108) also found that the decrease in viscosity obtained using the retarding sodium citrate varied amongst the different materials tested. He therefore concluded that the use of a sodium citrate solution for the testing of viscosity of dental gypsum products should be avoided.

1.11.1.4 VISCOSITY TESTS INVOLVING VIBRATION

As already pointed out, slurries of freshly mixed gypsum have the rheological characteristics of a pseudoplastic material with a yield value. Therefore a decrease in viscosity can be achieved by the use of vibration, which in turn permits the use of a much thicker mix, and
hence results in a denser and stronger set product. For this reason, dentists and dental technicians in practice routinely use vibrators in the manipulation of these materials.

Any method for testing viscosity for the purposes of comparison of the properties of different types and brands of gypsum products should resemble as closely as possible the practical application of these products. Therefore, the viscosity test should involve vibration as an integral part of the procedure.

Jorgensen(116) found that the change in viscosity produced by vibration varied greatly with different products. Certain mixes which were very viscous during stirring became quite fluid under slight vibration, whereas other products were less viscous during spatulation but showed only slight improvement in fluidity when subjected to vibration. He called this the "vibration effect".

None of the previously mentioned viscosity tests involve vibration as part of the testing procedure. Static tests such as these do not reproduce practical conditions of use of the materials, and in view of the differing vibration effect observed from product to product, these tests could not be expected to give valid results.

Jorgensen and Kono(117) developed a method for determining the viscosity of dental stones under the influence of vibration. They found scarcely any correlation between the results obtained using vibration and those obtained using a static viscosity test (the cone
penetration test as specified in the American Dental Association specifications).

Their apparatus consisted of a horizontal, semi-cylindrical trough with a diameter and length of 10mm, and an inclined plane with a 60° gradient sloping away from the trough. When released from the trough, a freshly mixed slurry was able to flow down the incline. The entire apparatus was screwed onto a dental vibrator, which was switched on, simultaneously with the release of the slurry, for twenty seconds. The length of the stone or plaster tongue on the inclined plane was taken as the measure of the viscosity. This test was made using unretarded mixes.

Combe and Smith\(^{24,118}\) used a simple method for the determination of viscosity under vibration which they found to yield consistent results. A standard volume of an unretarded mix was allowed to spread on a glazed tile resting on a vibrator during a fixed period of vibration. The length of the slump was measured and the square of this dimension was taken to be the measure of viscosity, since it was felt that the ability of the material to flow under vibration was related to the area of the slump. Earnshaw\(^{108}\) modified this basic method in an attempt to improve the reproducibility of the results. Two vibrators were used for testing. The first was used only for mixing and specimen preparation. The second was carefully calibrated and connected to a regulated power supply and was the vibrator used for the execution of the actual slump test. Furthermore, the glazed tile was
screwed directly to the vibrator platform and the calibration of the vibrator gave the actual peak-to-peak displacement of the surface of the tile. Earnshaw found that the test, in this modified form, gave a satisfactory evaluation of viscosity.
1.12 STRENGTH OF CAST GYPSUM

The strength of cast gypsum is an important physical property and has usually been expressed in terms of compressive or "crushing" strength (119). A high strength is desirable for most of its applications in dentistry.

The strength depends on the quantity of solid material (mostly calcium sulphate dihydrate) packed into a given volume (120). That is, it depends on the apparent density of the mass, which is based on the volume suggested by the external dimensions of the set material (but not taking into consideration porosity which is the result of manipulative conditions). This apparent volume is in turn determined by the amount of gauging water used for a given quantity of calcium sulphate hemihydrate powder (43), since water in excess of that required for chemical combination ultimately results in empty space (Section 1.10) (see Figure 1.12).
Figure 1.12
Relationship between water/powder ratio and density of set gypsum without air-bubble porosity. The broken line indicates the theoretically calculated density (after Jorgensen and Kono\textsuperscript{100}).

Therefore, since excess guaging water contributes to the external volume, but not to the strength, the strength of cast gypsum is ultimately determined by the water/powder ratio used\textsuperscript{(22,43)}.

In addition, the free water content of set gypsum products affects their strength. Consequently, strength is conventionally expressed as either wet or dry strength\textsuperscript{(119)}:

a) Wet Strength:
The test is conducted whilst the set mass contains water in excess of that required for complete hydration.
b) **Dry Strength:**

The test is conducted when the gypsum mass has been dried completely free of that excess water.

The strength of cast gypsum increases rapidly during the setting process, but then levels off and remains fairly constant once hydration is completed. Relatively small gains in strength occur thereafter, whilst water is being lost to the ambient atmosphere, until a point is reached when almost all of the excess water has been removed. There is then a rapid increase in strength, of about 100 per cent as the last of the excess water is removed\(^{(40,43)}\). This represents the dry strength.

The wet strength prevails whilst most of the excess water is present. The average wet strength level is reached after only a one to two per cent increase in weight due to excess water in a formerly dry specimen. Fairhurst\(^{(121)}\) has shown that even a weight increase as small as 0.1 - 0.2 per cent produces a significant reduction in all instances (Figure 1.13).
Figure 1.13
The per cent of dry compressive strength of cast gypsum specimens plotted against the per cent excess water contained in the specimen. The scatterband shown in the diagram represents the general characteristics exhibited by the experimental values (after Fairhurst(121)).

It is believed that the transition in strength from wet to dry conditions is probably the result of structural change at the inter-crystalline boundaries; these areas are the last locations to lose water on drying and the first to receive it during wetting. At some critically low water...
content most of the water is located only in the smaller crystal boundary areas. The water is actually in the form of a concentrated solution of calcium sulphate dihydrate, which is continually increasing in concentration as the water evaporates. Consequently there is continual precipitation of calcium sulphate dihydrate in this region, forming an inter-crystalline union which consolidates as all the water is evaporated. On entry of water these areas are the first to be attacked. The junctional union dissolves and strength is decreased (121-123) (Figure 1.14). This suggests that the wet strength is the result of the mechanical structure of the specimen and is dependent on the interlocking nature of the large gypsum crystals.

Figure 1.14
Diagrammatic representation of the drying out of cast gypsum materials. (a) Water causing solution of the surface of dihydrate crystals in contact. (b) More rigid structure after complete drying (from Anderson, Applied Dental Materials(122)).
Wet and dry strengths are both influenced in a similar manner by variations in water/powder ratio (Figure 1.15).

Figure 1.15
Compressive strength of cast gypsum plotted against the water/powder ratio for wet and dry specimens (after Fairhurst[121]).

Surface hardness is very closely related to strength and behaves similarly in response to alterations in water/powder ratio and the presence of excess moisture. It is however, more prone to variation and is more susceptible to ambient atmospheric conditions (40, 116, 124).
Strength is also affected by other variables:

i) **Mixing**

An increase in spatulation produces an increase in strength up to approximately one minute of hand mixing. However over-mixing caused a decrease in strength, probably due to disruption of the freshly forming crystal structures.

ii) **Presence of chemical modifiers**

Accelerators and retarders produce a decrease in wet and dry strength. This may be partly caused by decreased inter-crystalline cohesion, and in some cases may also be the result of altered crystal morphology.

1.12.1 Tensile Strength

Tensile strength may be defined as the maximum tensile stress that a structure will withstand before rupture.

Most of the research into the strength of gypsum products has involved compressive strength measurements only. The compressive strength of brittle materials is normally much greater than the tensile strength. The tensile strength of gypsum, as a brittle material, is only 10-25 per cent of the corresponding compressive strength and the relationship between the two is non-linear and varies with differences in the water/powder ratio.

Because of the comparatively low tensile strength of such materials, failure in practical usage frequently occurs in tension and not in compression. Therefore,
measurements of the tensile strength provide a valuable index of the strength for practical purposes \(128,130\).

1.12.2 Tensile Tests

Three tests which have been used for the measurement of tensile strength of brittle materials are:

i) the direct or uniaxial tensile test;

ii) the flexural or bend test;

iii) the diametral compression test.

Unfortunately the first two tests suffer from serious disadvantages and drawbacks, whereas the diametral test is free of these and gives more uniform results than the other two tests \(131-133\).

i) The direct tensile test:

The test specimen, usually dumb-bell shaped, is held at both ends in the testing machine and subjected to increasing tensile loads until fracture occurs \(126,128\). It is essential for the success of the test that the tensile grips holding the enlarged end-portions of the specimens are aligned axially. The capacity of ductile materials to flow allows for "self-correction" of slight misalignments; however brittle materials have virtually no capacity for plastic flow. Thus even small misalignments add a bending component to the load on the specimens and seriously reduce the measured strength \(131\).
Furthermore, the specimen must break near the middle of its length for the results to be accurate\(^{(134)}\). But, because of large stress concentrations at the loading grips, as well as difficulty in ensuring completely axial alignment, fracture often occurs away from the central cross-section\(^{(133)}\).

ii) The bend test:

A specimen, in the form of a beam of rectangular cross-section, supported at each end, is subjected to either central point loading or symmetrical two-point loading causing flexure and eventual failure\(^{(135,136)}\).

With brittle materials failure is initiated on the convex side of the beam, which is essentially in a state of pure tension. The calculated modulus of rupture could therefore be regarded as a measure of the tensile strength of the specimen. However the stress distribution throughout the beam is non-uniform. It varies from zero at the neutral axis within the specimen to a maximum at the outer surface. This makes the test very sensitive to the specimen's surface condition\(^{(131)}\). The surface of a material which sets in a confined mould can be expected to be denser and stronger than elsewhere within the specimen\(^{(128)}\). Consequently, the test can yield results considerably in excess of the tensile strength measured by other means\(^{(132,136)}\). Berenbaum and Brodie\(^{(137)}\) demonstrated this fact experimentally with cast gypsum prepared from plaster of Paris.
1.12.3 The Diametral Compression Test

This test, also referred to as the indirect tensile test and the Brazilian test, has become popular in recent years for determining the tensile strength of brittle materials. It has been used for the testing of concrete\(^{(132,133,138)}\), coal\(^{(137)}\) and ceramics\(^{(131)}\). And, since 1965 it has been used with increasing frequency for determining the tensile strengths of many brittle dental materials\(^{(130,139-144)}\). The test has been shown to be applicable to the testing of cast gypsum and has been used successfully for this purpose\(^{(128,137)}\).

In the diametral compression test a cylindrical specimen is compressed diametrically between two flat platens. Tensile stresses are generated along the diametral plane normal to the loading direction, that is, across the loaded diameter joining the two lines of contact between specimen and platens\(^{(131)}\). (Figure 1.16).

Under proper conditions, this tensile stress causes splitting of the cylinder along the diametral plane. It is proportional to the applied load and reaches its maximum value across the diametral plane\(^{(145)}\). Furthermore, in the idealized model, this maximum tensile stress is uniform along the whole of the loaded diameter\(^{(133)}\). (See Figure 1.17).
Figure 1.16
Diagrammatic representation of the diametral compression test. Compressive load, $P$, produces a tensile stress, $\sigma$, across the diametral plane of the specimen, indicated by the dotted line A-B; $d$ is the diameter of the specimen.

Figure 1.17
Stress distribution across the loaded diameter for a cylinder compressed between two line loads. $P = \text{load}$; $\sigma_1 = \text{tensile stress}$, $\sigma_2 = \text{compressive stress}$, $\tau = \text{shear stress}$ (after Rudnick, Hunter and Holden\textsuperscript{131}).
Compressive and shear stresses are also generated within the specimen along the loaded diameter. They vary from minimal values at the centre to a maximum at either end. In the ideal model, compressive and shear stresses at points A and B on the specimen (Figure 1.17) are infinitely large. But fracture must be initiated by failure in tension, if the test is to yield valid results. Therefore certain precautions need to be taken in practice to ensure that these infinitely high compressive and shear stresses are reduced, so that in fact only the tensile stress will be large enough to cause failure\(131,133\).

The direction of failure clearly establishes if failure does occur in tension. There is always a primary fracture along the diametral plane, which begins in the central portion of the specimen (Figure 1.18). A "triple-cleft" fracture pattern is sometimes found with stronger specimens. Here the initial diametral fracture is immediately followed by symmetrical secondary fractures on either side. This has been shown to be a variation of the normal tensile fracture\(131\).

Very occasionally, with still stronger specimens (for instance, with the strongest dental gypsum products in their dry condition), asymmetrical complex fracture modes are found (Figure 1.18). However, examination always reveals one fracture in the diametral plane which may be assumed to be the initial site of failure. Hence this fracture mode may also be considered a valid sign of tensile failure\(128\).
Figure 1.18
Different modes of fracture demonstrated with specimens reassembled after fracture. Specimen A shows a classical diametral fracture and is typical of the weakest specimens tested. Specimen B shows a "triple-cleft" fracture pattern. Specimen C shows a complex fracture pattern, in which the initial diametral fracture is clearly demonstrated. This mode of fracture is only observed with high-strength gypsum products in the dry condition(128).
(Photographs courtesy of Dr. R. Earnshaw).

The tensile stress across the diametral plane is given by Equation 1.4(131,145,146).

\[ \sigma = \frac{2P}{\pi dt} \]

... Equation 1.4

where \( \sigma \) = maximum tensile stress
\( P \) = applied load
\( d \) = specimen diameter
\( t \) = specimen thickness
This equation is derived from a theoretical treatment of the test which assumes certain ideal conditions\(^{(147)}\). In practice, although there are some departures from the ideal, the test still maintains its validity.

Ideally, the specimen is assumed to be homogeneous and isotropic and behave in a purely elastic manner under load up to the point of fracture\(^{(132,133,146)}\). Cast gypsum does not completely meet these requirements. Concrete however is even further removed from the ideal and yet the diametral test is widely used and considered reliable for testing concrete\(^{(132,133,138,148)}\).

Furthermore, in the theoretical model, loading occurs along lines of contact between specimen and platen. In practice, the load is distributed over a small area of contact. However, the tensile stresses along the diametral plane remain virtually unaffected except in the regions close to the areas of load application (see Figure 1.19). Hence, as long as the areas of contact remain small in relation to the over-all specimen size the test results remain unaffected\(^{(133,137,145)}\).

The relative size of the contact area is specified by the ratio \(2a/d\), where \(a\) is half the width of the contact area and \(d\) is the specimen's diameter.

The areas of contact are in fact an important consideration in the application of the diametral compression test. If the area of loading is indeed very small, then the compressive and shear stresses become extremely high immediately next to the loading platens (that is, at A and B in Figure 1.17), and fracture will not be initiated
by failure in tension. This effect can be prevented by distributing the load over a wider area as demonstrated in Figure 1.19.}

Figure 1.19
Stress distribution across the loaded diameter for a cylinder compressed between deformable plates. \( P \) = load, \( \sigma_1 \) = tensile stress, \( \sigma_2 \) = compressive stress, \( \tau \) = shear stress. The stress distribution shown assumes uniform contact pressure, with \( \frac{2a}{d} = 0.10 \), where \( 2a \) is width of contact area and \( d \) is diameter of specimen (after Rudnick, Hunter and Holden).}

However, if the ratio \( \frac{2a}{d} \) is too large, that is, if the load is distributed over too great an area, then the stresses closer to the central portion of the specimen become affected. As the area of contact is increased, progressively less material along the diametral plane is
subjected to the maximum tensile stress calculated by Equation 1.4 and over-estimation of the tensile strength occurs (131). Peltier (145) came to the conclusion that the tensile stresses can be held uniform over a reasonable proportion of the loaded diameter if the width of the load bearing area is controlled so that \( \frac{2a}{d} \) does not exceed 0.20 or 0.25.

Load distribution may be controlled by the use of narrow packing strips of relatively soft material interposed between the specimen and the platens, as in Figure 1.19 (131). Strips of plywood of suitable width are recommended as packing pieces in the testing of concrete (132, 138, 148).

In the case of cast gypsum localized plastic deformation or crushing causes flattening of the specimen at the areas of contact, resulting in a certain degree of load distribution. Earnshaw (128) considered that this degree of flattening present without packing strips was sufficient to ensure that failure always occurred in tension. And Addinall and Hacket (149) found the lowest and most consistent values for tensile strength of a cast gypsum were obtained without the use of packing pieces.

However, in more recent studies comparing the direct tensile test to the diametral compression test for the measurement of tensile strength of gypsum products, Mori (150) and Mori and Earnshaw (151, 152) make specific recommendations regarding the desirable contact area for load distribution.
They found that the area of load distribution resulting from localized deformation of the gypsum specimens varied with changes in the strength of the specimens. Furthermore, the desirable contact area calculated by Peltier to ensure that tensile stresses remained constant over a large proportion of the loaded diameter (that is, $2a/d = 0.20$) was found to be unrealistic in the case of gypsum materials. The deformation of cast gypsum is too large and does not conform to this limitation. Mori (150) and Mori and Earnshaw (151, 152) suggested $2a/d = 0.24$ as a more practical limitation for the contact area. Packing strips of a suitable material, such as cardboard, can provide this desirable contact area for most dental stones mixed at or near their recommended water/powder ratios. As long as $2a/d = 0.24$ prevails, the actual tensile stresses over $2/3$ of the loaded diameter are maintained at 89-96 per cent of the value given by Equation 1.4. Furthermore, the localized fracture in the vicinity of the loading area is often prevented and thus the fracture on the diametral plane tends to reach the ends of the plane. This degree of load distribution will result in slightly higher measured values for tensile strength, however it has been shown that the use of packing strips in this fashion results in a more constant relationship between the results of the diametral compression test and those of direct tensile measurements (150-152).
CHAPTER 2

PURPOSE AND SCOPE OF THE INVESTIGATION

An important prerequisite for dental gypsum products is that they achieve optimal strength in the set state. Although it is obvious that the lower the water/powder ratio, the greater the strength, a point may be reached beyond which further decreases in water/powder ratio do not produce corresponding improvements in strength, and may in fact produce decreases in strength\(^{(24,120)}\). Earnshaw and Smith\(^{(128)}\) found that below a certain water/powder ratio the strength of cast gypsum levelled off at its maximum value in the form of a plateau, whereas Overberger and Samay\(^{(153)}\) found that the maximum value was generally followed by a decline in strength.

Furthermore, decreases in water/powder ratio produce corresponding increases in viscosity. The viscosity of freshly mixed slurries of dental plasters and stones determines the ease with which the slurries can be poured and manipulated; in other words it determines the "workability" of the mix.

The manufacturers of various gypsum products usually state an optimum or recommended water/powder ratio for their product that is considered to give an optimal mix with high strength and good workability. An examination of these figures shows that the manufacturers have widely different ideas of what is to be considered as optimum. Furthermore, there are considerable differences between the viscosities of many materials when mixed to a standard
water/powder ratio. Conversely, there is a wide variation in water/powder ratios between different products which are mixed to a standard viscosity; however one would expect the highest strength to be exhibited by the material which has the lowest water/powder ratio at that viscosity.

The workability, and hence the viscosity, may be the limiting factor in attempts to achieve maximum strength properties in the cast material\(^{(107)}\). On the other hand, marked falling off in strength may perhaps occur before the material reaches the unworkable stage\(^{(120)}\).

The purpose of this investigation was to examine the relationship that exists between the viscosity of freshly mixed gypsum and its strength upon setting, particularly concentrating on materials mixed at water/powder ratios in the region of, and lower than, those recommended by the manufacturers; and also to compare the viscosity characteristics of different products, especially in the regions of maximum strength and at the manufacturers' recommended water/powder ratios. In addition, the strength of cast gypsum was examined at water/powder ratios approaching the theoretical combining value (18.6g water/100g hemihydrate), to determine whether the strength continues to rise, develops a plateau or reaches a maximum value and drops off again.

It was hoped that as a result of this investigation one optimum viscosity could be recommended, which would correspond to the maximum strength of the different materials and yet still be within the range of a workable mix.
CHAPTER 3
MATERIALS TESTED

The tests were conducted using the materials listed in Table 3.1. The batch numbers are listed wherever possible.

All except Densite K5 are dental products commercially available in Australia and comply with the Australian Standards for dental stones, die stones and laboratory plasters (86). Densite K5 is a high-strength gypsum plaster used as the base material for many dental die stones.

All materials were kept sealed and stored under controlled atmospheric conditions.

<table>
<thead>
<tr>
<th>Product</th>
<th>Classification</th>
<th>Recommended W/P</th>
<th>Manufacturer</th>
<th>Batch No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellowstone</td>
<td>dental stone</td>
<td>0.33</td>
<td>Investo Mfg.Co. Pty.Ltd.Aust.</td>
<td>61077</td>
</tr>
<tr>
<td>Calestone</td>
<td>dental stone</td>
<td>0.30</td>
<td>Amalgamated Dental Trade Distributors Ltd. England</td>
<td>35769</td>
</tr>
<tr>
<td>Velmix</td>
<td>die stone</td>
<td>0.22-0.25</td>
<td>Kerr Dental Mfg. Co.Ltd., USA</td>
<td>6533H</td>
</tr>
<tr>
<td>Densite K5</td>
<td>die stone</td>
<td>used at 0.24</td>
<td>Georgia Pacific Corp., USA</td>
<td>30775</td>
</tr>
<tr>
<td>Art Plaster</td>
<td>laboratory plaster</td>
<td>0.50</td>
<td>Investo Mfg.Co. Pty.Ltd. Aust.</td>
<td>-</td>
</tr>
</tbody>
</table>
CHAPTER 4

EXPERIMENTAL METHODS

4.1 AMBIENT CONDITIONS

Except where otherwise specified all experiments, including mixing, specimen preparation and testing, were carried out in ambient atmospheric conditions maintained at 21 ± 1°C and relative humidity (R.H.) 50 ± 5 per cent.

4.2 MIXING AND CASTING OF GYPSUM PRODUCTS

Each material was mixed according to Australian Standards (86) and all mixing and casting of specimens took place on a dental vibrator.

Distilled water at room temperature and calcium sulphate hemihydrate powder were carefully proportioned by weight to obtain the desired water/powder ratio for each test. The water was placed into the mixing bowl, and the powder was sifted into the water over approximately 15 seconds. Vibration was then commenced and continued until completion of mixing. Another 15 seconds was allowed for continued wetting of the powder and elimination of entrapped air. Then the mix was spatulated by hand for a further 30 seconds.

Because of the extremely high viscosity of the pastes at the very low water/powder ratios being investigated, the vibrator was used on maximum, or near to maximum settings.
at all times. At the lowest range of water/powder ratios, most of the materials were too thick to be effectively spatulated. In these instances the material was mixed for the prescribed length of time by using a kneading action with the spatula. In all cases the mixed paste appeared to be homogeneous and uniformly mixed.

Casting of the slurry or paste was performed with the aid of a vibrating spatula (E. Mettler, Zurich), without which effective manipulation of the thick mixes would have been nearly impossible (Figure 4.1).

![Vibrating spatula being used to cast a specimen. The mould rests on the platform of a dental vibrator, which is in operation throughout the procedure.](image-url)
4.3 MEASUREMENT OF TENSILE STRENGTH

The tensile strength of cast gypsum specimens at different water/powder ratios was measured by the diametral compression test using packing strips as recommended by Mori (150) and Mori and Earnshaw (151, 152).

At the completion of mixing the slurry or paste was cast into brass moulds (Figure 4.2). Six specimens were cast from each mix, and the moulds were covered with glass plates and left until 30 minutes had elapsed from the start of mixing. The specimens were then removed from the moulds and stored at 100 per cent R.H. and 21 ± 1°C. Testing was performed two hours after the beginning of mixing.

Figure 4.2
Brass mould for fabrication of specimens used in the diametral compression test.
The specimens were cylinders of diameter 25.0 ± 0.1 mm and length 25.2 ± 0.2 mm. The dimensions of each specimen were measured and recorded to the nearest tenth of a millimeter (Figure 4.3).

Figure 4.3
Typical specimens used in the diametral compression test.

Twelve specimens were tested for each water/powder ratio, and in most cases a minimum of ten results were used to obtain a mean value. However, some experiments on Art Plaster are reported, in which only six specimens were tested. All six results were then used in each case.

The tensile tests were performed using a Hounsfield Tensometer at a crosshead speed of 0.2 mm per minute, using the 5 kN and 10 kN beams.

Cardboard strips of 0.3 mm thickness were used as packing pieces. The strips were 6 mm wide, as this corresponded with the ratio $\frac{2a}{d} = 0.24$ for load distribution.
Figure 4.4
Jig used for the alignment of specimen and packing strips in the diametral compression test. (A) Viewed from above. (B) Oblique view. Specimen is shown located centrally between loading platens of Hounsfield Tensometer with cardboard packing strips aligned in the vertical plane passing through the axis of the specimen. The arms on either side of the specimen are rotated out of the way before testing.
A jig was employed to ensure correct alignment of the specimen and packing strips between the platens of the testing machine (Figure 4.4).

The breaking load of the specimens in the Hounsfield Tensometer was recorded to the nearest 0.01 kN, and the tensile strength of each specimen was determined using Equation 1.4 (Section 1.12.3).

4.4 MEASUREMENT OF VISCOSITY

Viscosity measurements were made using a slump test under vibration. The test itself was the same as that described by Earnshaw(108).

The apparatus consisted of two dental vibrators, a glazed ceramic tile 15cm square, a brass cylinder 25mm I.D. and 30mm high, and two glass plates 4cm square. The first vibrator was the one used for all mixing and specimen preparation. The second vibrator was connected to a stabilized power supply, calibrated, and only used for the actual performance of the slump test. It was therefore only run for 30 seconds at a time and always allowed at least five minutes between successive tests. The glazed tile was directly attached to the platform of the second vibrator, and the vibrator was adjusted to give a peak-to-peak displacement of 0.2mm.

As soon as mixing was completed, the cylinder was placed onto one of the glass plates on the vibrator
platform, and filled with the fresh mix, whilst still under vibration. The second glass plate was then placed on top of the cylinder and vibration was discontinued. Surplus material was removed and the filled cylinder with glass plates at either end was then transferred to the second vibrator, and placed on its side on the glazed tile. Precisely two minutes 30 seconds from the start of mixing the glass plates were withdrawn and the vibrator simultaneously switched on. Vibration was continued for 30 seconds, during which time the cylinder was gently held steady by the operator's fingers (Figure 4.5).

The total length of the slump along the axis of the cylinder was measured to the nearest 0.5mm and recorded. The square of the length was taken as a measure of the material's viscosity, and the test was repeated six times for each water/powder ratio investigated (Figure 4.6).
Figure 4.5
The viscosity test used in this investigation:
(A) The specimen before the start of vibration.
(B) Glass plates are removed and vibration is commenced simultaneously. *(Figure 4.5 continued on next page)*
Figure 4.5 (continued)

(C) Vibration is continued for 30 seconds allowing the slump to spread, while the cylinder is steadied by the operator's finger.

(D) The specimen at the end of the test. The length of the slump, squared, gives a measure of the relative viscosity of the mix, when subjected to vibration.
Figure 4.6
Measurement of the overall length of the slump at the completion of the viscosity test.
4.5 PREPARATION AND TESTING OF ART PLASTER

Difficulty was experienced during the preliminary experiments with Art Plaster. The material began to set so soon after mixing that there was inadequate time to prepare specimens. It was therefore decided that the experiments with Art Plaster would be conducted using a retarded mix.

In 1929 Johnson and Gibson\(^{(154)}\) described a retarding solution which they called "R2" solution. The use of "R2" solution in place of water allowed the plaster to be mixed with water/powder ratios as low as 0.35, whilst still remaining workable. Johnson\(^{(155)}\) reported that the use of this solution to produce thicker mixes resulted in casts with increased surface hardness and compressive strength. The "R2" solution had the following composition: four per cent Rochelle salts (sodium potassium tartrate) and 0.2-0.4 per cent borax (sodium tetraborate) in water. This solution was prepared for use in the present investigation, by dissolving 80g of Rochelle salts and 6g of borax in two litres of water.

Because of the delay in setting, the specimens for the diametral compression test were not removed from the brass moulds until at least one hour had elapsed from the start of mixing. These specimens were then stored under conditions approaching 100 per cent R.H. and were tested four days after preparation.

Before the tensile tests were begun with Art Plaster consideration was given to the applicability of the
diametral compression test. As already pointed out (Section 1.12.3), if the diametral compression test is to produce valid results the contact width between the specimen and the loading platens must not exceed the value specified by: $2a/d = 0.24$ (where "2a" is the width of the contact area, and "d" is the specimen's diameter). This corresponds with a width of 6mm for the specimens used in these experiments.

It was feared that plaster, because it is more easily deformed than dental stones and die stones, might exhibit flattening under load in excess of 6mm. But a preliminary survey revealed the width of flattening to be approximately 6mm for specimens mixed with water at the water/powder ratio 0.50. All the specimens mixed with the "R2" solution were observed to have a narrower zone of flattening under testing conditions. It is therefore assumed that the diametral compression test gave reliable results for Art Plaster in this investigation.
CHAPTER 5

RESULTS

5.1 TENSILE TEST RESULTS

These results are shown in Tables 5.1 to 5.5 and have been presented graphically together with their standard deviations in Figures 5.1 to 5.5.

5.2 VISCOSITY TEST RESULTS

These results are also shown in Tables 5.1 to 5.5 and have been presented graphically in Figures 5.6 to 5.10. The total range of results is shown for each mean value plotted on the graphs. A result for Art Plaster at water/powder ratio 0.32 is not available because extreme difficulty was experienced in manipulating the material at this viscosity.

5.3 COMPARISON OF RESULTS

For purposes of comparison results for the dental stone and die stone, materials have been combined in Figures 5.11 to 5.13 without the standard deviation or range. Figures 5.14 and 5.15 illustrate the differences in strength and viscosity found at the manufacturers' recommended water/powder ratios and at those water/powder
ratios which give the maximum tensile strength for these materials.

It should be noted that Yellowstone appeared to reach its maximum strength at a water/powder ratio intermediate between 0.24 and 0.25. Consequently, both water/powder ratios are represented in Figures 5.14 and 5.15.
TABLES OF RESULTS

The tensile strength and viscosity of the materials at different water/powder ratios is shown in Tables 5.1 to 5.5. The tables show mean values, standard deviations and the number of results averaged in each case for the tensile strength. For viscosity they show the mean of the results of six different tests and the total range of results in each case. In addition Table 5.5 shows whether or not a retarding solution was used.

**TABLE 5.1 VELMIX**

<table>
<thead>
<tr>
<th>W/P Ratio</th>
<th>No. of Results Averaged</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation</th>
<th>Viscosity (cm²)</th>
<th>Range of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16</td>
<td>10</td>
<td>4.88</td>
<td>0.39</td>
<td>30.2</td>
<td>27.6- 35.4</td>
</tr>
<tr>
<td>0.17</td>
<td>12</td>
<td>5.14</td>
<td>0.32</td>
<td>41.7</td>
<td>38.4- 43.6</td>
</tr>
<tr>
<td>0.18</td>
<td>12</td>
<td>4.97</td>
<td>0.38</td>
<td>46.7</td>
<td>42.9- 50.4</td>
</tr>
<tr>
<td>0.19</td>
<td>10</td>
<td>4.80</td>
<td>0.30</td>
<td>54.9</td>
<td>52.6- 57.8</td>
</tr>
<tr>
<td>0.20</td>
<td>10</td>
<td>4.63</td>
<td>0.32</td>
<td>59.4</td>
<td>57.8- 62.4</td>
</tr>
<tr>
<td>0.21</td>
<td>10</td>
<td>4.53</td>
<td>0.28</td>
<td>69.6</td>
<td>63.2- 73.1</td>
</tr>
<tr>
<td>0.22</td>
<td>10</td>
<td>4.45</td>
<td>0.16</td>
<td>78.4</td>
<td>73.1- 81.0</td>
</tr>
<tr>
<td>0.23</td>
<td>10</td>
<td>4.01</td>
<td>0.31</td>
<td>85.4</td>
<td>81.9- 89.3</td>
</tr>
<tr>
<td>0.24</td>
<td>12</td>
<td>3.85</td>
<td>0.31</td>
<td>89.8</td>
<td>82.8- 96.0</td>
</tr>
<tr>
<td>0.25</td>
<td>12</td>
<td>3.82</td>
<td>0.27</td>
<td>101.0</td>
<td>97.0-104.0</td>
</tr>
<tr>
<td>0.26</td>
<td>12</td>
<td>3.57</td>
<td>0.27</td>
<td>104.1</td>
<td>98.0-110.3</td>
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</tbody>
</table>
### TABLE 5.2  DENSITE K5

<table>
<thead>
<tr>
<th>W/P Ratio</th>
<th>No.of Results Averaged</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation</th>
<th>Viscosity (cm²)</th>
<th>Range of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>12</td>
<td>4.80</td>
<td>0.48</td>
<td>21.1</td>
<td>19.4-22.1</td>
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<td>0.18</td>
<td>11</td>
<td>4.83</td>
<td>0.36</td>
<td>26.2</td>
<td>24.0-29.7</td>
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<tr>
<td>0.19</td>
<td>12</td>
<td>5.03</td>
<td>0.38</td>
<td>27.9</td>
<td>25.5-31.9</td>
</tr>
<tr>
<td>0.20</td>
<td>10</td>
<td>4.80</td>
<td>0.37</td>
<td>34.9</td>
<td>31.9-40.3</td>
</tr>
<tr>
<td>0.22</td>
<td>12</td>
<td>4.56</td>
<td>0.22</td>
<td>45.4</td>
<td>41.6-49.0</td>
</tr>
<tr>
<td>0.24</td>
<td>11</td>
<td>4.46</td>
<td>0.20</td>
<td>58.3</td>
<td>53.3-60.8</td>
</tr>
<tr>
<td>0.26</td>
<td>12</td>
<td>4.21</td>
<td>0.25</td>
<td>65.6</td>
<td>62.4-68.1</td>
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</tbody>
</table>

### TABLE 5.3  YELLOWSTONE

<table>
<thead>
<tr>
<th>W/P Ratio</th>
<th>No.of Results Averaged</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation</th>
<th>Viscosity (cm²)</th>
<th>Range of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>12</td>
<td>3.49</td>
<td>0.42</td>
<td>20.8</td>
<td>19.4-23.0</td>
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<td>0.24</td>
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<td>3.88</td>
<td>0.22</td>
<td>29.9</td>
<td>26.0-32.5</td>
</tr>
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<td>0.25</td>
<td>12</td>
<td>3.89</td>
<td>0.21</td>
<td>35.3</td>
<td>33.6-37.2</td>
</tr>
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<td>12</td>
<td>3.73</td>
<td>0.23</td>
<td>41.7</td>
<td>34.8-44.9</td>
</tr>
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<td>0.27</td>
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<td>3.71</td>
<td>0.22</td>
<td>45.1</td>
<td>42.3-46.9</td>
</tr>
<tr>
<td>0.28</td>
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<td>3.54</td>
<td>0.21</td>
<td>55.1</td>
<td>52.6-57.8</td>
</tr>
<tr>
<td>0.30</td>
<td>11</td>
<td>3.51</td>
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<td>64.2</td>
<td>60.1-68.9</td>
</tr>
<tr>
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<td>12</td>
<td>3.07</td>
<td>0.18</td>
<td>82.1</td>
<td>77.4-86.5</td>
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<tr>
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<td>12</td>
<td>2.85</td>
<td>0.13</td>
<td>89.3</td>
<td>84.6-93.1</td>
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</table>
### TABLE 5.4 CALESTONE

<table>
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<th>W/P Ratio</th>
<th>No. of Results Averaged</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation</th>
<th>Viscosity (cm²)</th>
<th>Range of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>12</td>
<td>3.55</td>
<td>0.38</td>
<td>37.5</td>
<td>36.6-38.4</td>
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<td>0.22</td>
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<td>3.70</td>
<td>0.33</td>
<td>43.6</td>
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<td>12</td>
<td>3.58</td>
<td>0.15</td>
<td>48.5</td>
<td>46.2-51.8</td>
</tr>
<tr>
<td>0.24</td>
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<td>3.47</td>
<td>0.20</td>
<td>50.0</td>
<td>48.3-52.6</td>
</tr>
<tr>
<td>0.25</td>
<td>12</td>
<td>3.20</td>
<td>0.12</td>
<td>56.9</td>
<td>51.8-60.1</td>
</tr>
<tr>
<td>0.26</td>
<td>12</td>
<td>2.99</td>
<td>0.19</td>
<td>62.0</td>
<td>60.1-65.6</td>
</tr>
<tr>
<td>0.27</td>
<td>12</td>
<td>2.80</td>
<td>0.28</td>
<td>65.2</td>
<td>64.0-67.2</td>
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<tr>
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<td>2.26</td>
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<tr>
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<td>1.94</td>
<td>0.12</td>
<td>99.5</td>
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### TABLE 5.5 ART PLASTER

<table>
<thead>
<tr>
<th>W/P Ratio</th>
<th>Mixed With R2 Solution</th>
<th>No. of Results Averaged</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation</th>
<th>Viscosity (cm²)</th>
<th>Range of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>Yes</td>
<td>6</td>
<td>2.12</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.34</td>
<td>Yes</td>
<td>12</td>
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<td>0.18</td>
<td>21.1</td>
<td>18.1-22.1</td>
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<tr>
<td>0.36</td>
<td>Yes</td>
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<td>1.63</td>
<td>0.13</td>
<td>29.4</td>
<td>27.0-32.5</td>
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<tr>
<td>0.38</td>
<td>Yes</td>
<td>12</td>
<td>1.43</td>
<td>0.16</td>
<td>34.0</td>
<td>30.8-36.6</td>
</tr>
<tr>
<td>0.40</td>
<td>Yes</td>
<td>12</td>
<td>1.14</td>
<td>0.18</td>
<td>42.5</td>
<td>41.6-42.9</td>
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<tr>
<td>0.50</td>
<td>Yes</td>
<td>6</td>
<td>0.71</td>
<td>0.07</td>
<td>72.3</td>
<td>70.6-74.0</td>
</tr>
<tr>
<td>0.50</td>
<td>No</td>
<td>6</td>
<td>2.12</td>
<td>0.13</td>
<td>16.6</td>
<td>14.4-18.1</td>
</tr>
</tbody>
</table>
Figure 5.1
The effect of water/powder ratio on the tensile strength of Velmix. The height of each vertical bar represents the standard deviation of the mean value plotted.
Figure 5.2
The effect of water/powder ratio on the tensile strength of Densite K5. The height of each vertical bar represents the standard deviation of the mean value plotted.
Figure 5.3
The effect of water/powder ratio on the tensile strength of Yellowstone. The height of each vertical bar represents the standard deviation of the mean value plotted.
Figure 5.4
The effect of water/powder ratio on the tensile strength of Calestone. The height of each vertical bar represents the standard deviation of the mean value plotted.
Figure 5.5
The effect of water/powder ratio on the tensile strength of retarded Art Plaster. The retarder ("R2" solution) was a solution of 4 per cent Rochelle salts and 0.3 per cent borax in water. The tensile strength of unretarded Art Plaster at water/powder ratio 0.50 is also shown. The values plotted represent the mean of twelve results except for water/powder ratios 0.32 and 0.50, where the values represent the mean of six results. The height of the vertical bars represents the standard deviation of the mean in each case.
Figure 5.6
The effect of water/powder ratio on the viscosity of Velmix. Each vertical bar shows the total range of results for the mean value plotted.
Figure 5.7
The effect of water/powder ratio on the viscosity of Densite K5. Each vertical bar shows the total range of results for the mean value plotted.
Figure 5.8
The effect of water/powder ratio on the viscosity of Yellowstone. Each vertical bar shows the total range of results for the mean value plotted.
Figure 5.9
The effect of water/powder ratio on the viscosity of Calestone. Each vertical bar shows the total range of results for the mean value plotted.
Figure 5.10
The effect of water/powder ratio on the viscosity of retarded mixes of Art Plaster. The retarder ("R2" solution) was a solution of 4 per cent Rochelle salts and 0.3 per cent borax in water. The result of viscosity tests on unretarded mixes of Art Plaster at water/powder ratio 0.50 is also shown. Each vertical bar shows the total range of results for the mean value plotted.
Figure 5.11
The relationship between water/powder ratio and tensile strength for the four wet-calcined materials in this study.
Figure 5.12
The relationship between water/powder ratio and viscosity for the wet-calcined materials in this study.

[Graph showing the relationship between Viscosity (cm²) and W/P ratio for different materials: VELMIX, CALESTONE, DENSITE K5, and YELLOWSTONE.]
Figure 5.13
The relationship between tensile strength and viscosity for the wet-calcined materials studied.
Figure 5.14
The relationship between the maximum tensile strength and the tensile strength of the individual materials at their respective recommended water/powder ratios. The appropriate water/powder ratios are shown alongside each column. Densite K5 does not have a recommended water/powder ratio, however 0.24 is a commonly used water/powder ratio for this material. The manufacturers of Velmix recommend a range of water/powder ratios and so both ends of the range have been represented. The maximum tensile strength of Yellowstone was achieved at two water/powder ratios, 0.24 and 0.25; consequently both water/powder ratios are shown. The height of each black bar represents the standard deviation of the mean value shown. The approximate strength of Caestone, Yellowstone and Velmix at viscosity 60cm$^2$ was determined from Figure 13, and is shown alongside the asterisk.
Figure 5.15
The relationship between the viscosity of the recommended water/powder ratio and the viscosity at the water/powder ratio which provides maximum tensile strength, for the different materials shown. The appropriate water/powder ratios are shown alongside each column. Densite K5 does not have a recommended water/powder ratio, however 0.24 is a commonly used water/powder ratio for this material. The manufacturers of Velmix recommend a range of water/powder ratios and so both ends of the range have been represented. The maximum tensile strength of Yellowstone was achieved at two water/powder ratios, 0.24 and 0.25; consequently both water/powder ratios are shown. The black bars represent the total range of results for each mean value shown.
CHAPTER 6
DISCUSSION OF RESULTS

6.1 TENSILE STRENGTH

All of the wet-calcined materials tested responded very similarly to alterations in water/powder ratios. Figure 5.11 illustrates the similar nature of all of the curves. Characteristically the rise in strength which occurs with decreasing water/powder ratios becomes progressively steeper until a maximum value is reached, after which there is a sharp decline in strength. The dental stones tested reached their maxima in the range of water/powder ratios from 0.22 to 0.25, whereas the die stones reached theirs in the range 0.17 to 0.19.

These findings are contrary to earlier published studies. Overberger and Samay (153), in a study on the strength properties of dental stone and die stone, found that all but one of the die stones tested reached their maximum strengths in the range of water/powder ratios from 0.21 to 0.23. The exception in their study (which may have been Velmix, although this is not clearly expressed in the report) continued to rise in strength without reaching a maximum value. Their experiments were not carried out at water/powder ratios below 0.19. It is true however, that their experiments involved the measurement of compressive and not tensile strength and this may have been responsible for the observed difference. Earnshaw and Smith (128) also found the maximum compressive
strength of a die stone occurred at the water/powder ratio 0.21. The only dental stone tested by Overberger and Samay (153) reached its maximum compressive strength at the water/powder ratio 0.25, which does however, coincide with the corresponding results for maximum tensile strength presented in this study.

Earnshaw and Smith (128) also found in their investigation that the tensile strength of die stone did not improve below a water/powder ratio of 0.23 but that the strength remained at a plateau level. Their results are most certainly incorrect in this respect, because the plateau effect was undoubtedly an artefact of their testing method. At these low water/powder ratios the specimen in the diametral compression test does not deform readily and the resulting contact area under the loading platens is therefore very small. This subsequently results in early failure of the specimen due to high compressive and shear stresses and there is consequent under-estimation of the tensile strength (see Section 1.12.3). This can be avoided by using relatively soft packing strips between specimen and platen however the investigations of Earnshaw and Smith (128) were performed without the use of packing strips and consequently were subject to such errors at low water/powder ratios.

It is very interesting to note that in this investigation the die stones Densite K5 and Velmix were found to reach their maximum tensile strengths at water/powder ratios of 0.19 and 0.17 respectively, since theoretically 18.6 per cent (41) water is necessary for conversion of all
the available hemihydrate into dihydrate. At these low water/powder ratios a substantial proportion of the hemihydrate would in fact remain unreacted in the set material, since not all of the water used in mixing is necessarily available for conversion. In fact, Donnison, Chong and Docking(156) have shown that incomplete conversion of hemihydrate occurs with water/powder ratios as high as 0.50 and that the proportion of unconverted hemihydrate increases as the water/powder ratio decreases.

Figures 6.1 and 6.2 demonstrate the presence of large areas of exposed hemihydrate on the fracture surface of specimens of Densite K5 and Velmix mixed at water/powder ratios of 0.19 and 0.17 respectively. Yet despite this, and contrary to expectations, these specimens showed the highest recorded strengths.

An examination of Figures 5.11 and 5.14 reveals that the two dental stones tested in this study had approximately the same maximum tensile strength. Calestone, however, was generally much weaker than Yellowstone at any given water/powder ratio, and so there was a considerable difference noted in strengths at the recommended water/powder ratios.
Figure 6.1
Electron micrographs of fractured surface of Densite K5 specimen at water/powder ratio 0.19. Large areas of unreacted hemihydrate can be seen on the exposed surface. (A) Magnification x 1,000. (B) Magnification x 500.
Figure 6.2
Electron micrographs of fractured surface of Velmix specimen at water/powder ratio 0.17. Large areas of unreacted hemihydrate can be seen on the exposed surface. (A) Magnification x 1,000. (B) Magnification x 500.
Similarly, the die stones exhibited virtually identical maximum strengths. Velmix however showed a large variation in strength over the range of water/powder ratios recommended by the manufacturer (0.22 to 0.25). When mixed at the lowest of these water/powder ratios, the strength of Velmix was equivalent to that of Densite K5 mixed to the water/powder ratio 0.24. (Because Densite K5 is not a commercial product it does not have a recommended water/powder ratio. The ratio 0.24 was used in its place.) At the upper end of its range of recommended water/powder ratios, the strength of Velmix was relatively low, and in fact was similar to the maximum tensile strength of the dental stones.
6.2 VISCOSITY

The relationship between the viscosity under vibration and the water/powder ratio for the different wet-calcined materials is shown in Figures 5.6 to 5.9 to be essentially linear.

Figure 5.12 reveals that the slope of all the curves is very similar. The lines representing the viscosity of Densite and Calestone appear parallel and hence their viscosities respond alike to changes in water/powder ratios. The curve for Yellowstone is slightly steeper, but the curve for Velmix has the steepest gradient of all. This means that the viscosity of Velmix is most sensitive to changes in the water/powder ratio; that is, there is a greater change in the viscosity of Velmix with each change in water/powder ratio, than there is for the other materials.

Figure 5.12 shows Velmix to be the most fluid of the materials tested, whilst Yellowstone was found to be the most viscous, at comparable water/powder ratios. Velmix showed considerable variation in viscosity over the range of water/powder ratios recommended by the manufacturer and the upper end of the range proved to be very fluid.

It is interesting to note that the three commercial products, when mixed at their recommended water/powder ratios (Velmix at 0.22), displayed almost the same viscosity. Their mean viscosities, as shown in Figure 5.15, all lie within the range 78-84cm². It is an interesting
coincidence that the manufacturers seem to have arrived at a "standard" or desirable viscosity. It is unlikely that they perform their own viscosity tests under vibration when they measure the viscosity of their products at the respective recommended water/powder ratios. Static viscosity tests of the different products would most certainly provide differing results (see Sections 1.11.1.3 and 1.11.1.4).
6.3 RELATIONSHIP BETWEEN VISCOSITY AND TENSILE STRENGTH

Figure 5.15 shows that Calestone and Velmix have approximately the same viscosity at the respective water/powder ratios which give maximum tensile strength. Yellowstone however, is more viscous and Densite K5 is most viscous at this point. It is therefore evident that there is not an optimum viscosity which provides maximum strength for the different materials.

Furthermore, in all cases maximum tensile strength was achieved with viscosities at or below the figure of 44 cm$^2$. Mixes this viscous are relatively difficult to handle, and would not be suitable for general use in practice.

The viscosity of all the materials was substantially lower at the recommended water/powder ratios than that found at the water/powder ratio which provided the maximum strength. Figure 5.15 illustrates the magnitude of the differences.

Commercial products contain chemical additives used as retarders and accelerators. Many chemical additives affect the surface forces on the particles of hemihydrate and ultimately result in decreased viscosity in the fresh mix (39, 44). Densite K5, because it is a base material, does not contain the additives found in commercial products. Consequently one might expect it to be more viscous than a commercial die stone and this was confirmed by the experiments in this investigation. An examination of
Figure 5.12 reveals that Densite K5 is far more viscous than Velmix at all water/powder ratios. And, for most water/powder ratios Densite K5 is also stronger than Velmix which is not surprising since a thicker mix usually produces a stronger product. But Figure 5.13 shows that even at equivalent levels of strength, Densite K5 is still more viscous than Velmix.

In fact, comparison between Figures 5.11 and 5.13 reveals that although Densite K5 is stronger than Velmix at most water/powder ratios, the opposite is true at any given viscosity. In other words, the commercial product is much more manageable or workable, without any sacrifice in strength. This improvement appears to be an additional benefit gained from the use of chemical additives, in addition to their value in controlling setting time and setting expansion.

On the other hand, Figures 5.11 to 5.13 reveal that Yellowstone is not only stronger and more viscous than Calestone at most water/powder ratios, but in fact it is generally stronger at any given viscosity also.

The studies of Overberger et al. (153) and Earnshaw et al. (128) led them to believe that increasingly thicker mixes of die stones cease to show continuing improvements in strength, and for this reason they discouraged the use of mixes which are more viscous than those recommended by the manufacturer. Although these conclusions may be correct with respect to compressive strength, they do not appear to be true of tensile strength. The results of this investigation suggest that although a peak level of
tensile strength is reached, beyond which the strength declines, it occurs at such low water/powder ratios that the corresponding mixes are too viscous for practical use.

The compressive strength of dental gypsum products when mixed at or below recommended water/powder ratios is approximately ten times larger than the comparative tensile strength \(^{(128)}\). This is generally the reason why gypsum products in practice fail more often in tension than in compression (Section 1.12.1). Consequently, an improvement in tensile strength would be an advantage, even at the expense of a lowered compressive strength.

Therefore, it seems that the use of water/powder ratios lower than that recommended by the manufacturer may be of practical advantage when considering the overall strength of set gypsum. And so, it appears that in practice the limiting factor in achieving optimal strength properties continues to be the viscosity of the mix.

It was felt, from subjective impressions, that the limit for practical usefulness would be a viscosity of about 60cm\(^2\); this roughly corresponded with the viscosity of Densite K5 at water/powder ratio 0.24. From Figure 5.14 it may be seen that the strength of Velmix is only improved slightly at this relatively thick viscosity. It is only an improvement of approximately four per cent upon the strength of Velmix at water/powder ratio 0.22. However, a more substantial improvement can be noted with the dental stones, and particularly with Calestone. The improvement in strength beyond that found at the
recommended water/powder ratios was approximately 15 per cent and 35 per cent for Yellowstone and Calestone respectively.

Therefore, although it would appear that there is little advantage in using die stones below the recommended water/powder ratios, there is however some benefit to be gained in the use of dental stones at water/powder ratios lower than that recommended by the manufacturers. Nevertheless one must always temper this with the knowledge that there will be a concomitant increase in setting expansion, a decrease in setting time, and a decrease in the ease of manipulation.
6.4 TESTS ON ART PLASTER

Because a retarding solution ("R2" solution) was used, a direct comparison can not be made between the results of the tests on Art Plaster and those of the other materials. However the general behaviour of the material was observed to be the same.

The viscosity seemed to bear a linear relationship with the water/powder ratios (Figure 5.10). The viscosity figure for the unretarded mix (water/powder ratio 0.50) does not give a true indication of its viscosity however. During spatulation this mix was very fluid but by the time the actual slumping of the material was allowed to take place (two minutes 30 seconds after commencement of mixing), considerable thickening of the paste had already occurred.

The tensile strength (Figure 5.5) continued to rise with decreasing water/powder ratios and a maximum level was not reached. However only at the very low water/powder ratio of 0.32 did the material achieve the same tensile strength that was shown with unretarded specimens mixed at the water/powder ratio of 0.50 (Figure 5.5). At this low water/powder ratio the paste was extremely viscous and virtually unusable.

It is clear that the use of "R2" solution resulted in a marked decrease in tensile strength which was not offset by the use of lower water/powder ratios. The claims made by Johnson(155) of superior strength in casts prepared with "R2" solution were based on tests of compressive strength, which is a less important property
(Section 1.12.1). Furthermore, Worner\textsuperscript{157} found that the use of such a solution, containing four per cent Rochelle salts, was detrimental to the compressive strength and he advocated the use of solutions containing only two per cent Rochelle salts and 0.1 per cent borax to improve the properties of plaster casts.
CHAPTER 7
SUMMARY AND CONCLUSIONS

The relationship between the viscosity of fresh gypsum slurries and the strength of cast gypsum was examined in the hope of determining an optimum viscosity which would provide maximum strength for the different products whilst also providing a workable mix. In addition the strength of cast gypsum was examined at very low water/powder ratios to determine the nature of the changes in strength which take place as the water/powder ratio approaches the theoretical combining value (18.6g water/100 g hemihydrate).

Five materials were tested. These were:

a) a high strength gypsum plaster used as the base material for many dental die stones,
b) a commercial die stone,
c) two commercial dental stones,
d) a laboratory plaster.

A retarding solution was used with the plaster to allow sufficient working time for the tests to be performed.

A slump test involving vibration was employed to determine the relative viscosity. The tensile strength was measured by the diametral compression test, with cardboard packing strips interposed between the specimen and the loading platens to provide load distribution.

The following conclusions were drawn:
i) a) The tensile strength of cast gypsum improves as the viscosity of the mix increases until a peak is reached beyond which the strength declines. The maximum strength occurs at such low water/powder ratios that the corresponding mixes are too thick for convenient manipulation; hence the limiting factor in achieving optimal strength properties in practice is the viscosity of the mix.

b) There is no optimum viscosity which provides maximum strength for all materials.

c) There is little advantage in using die stones below the recommended water/powder ratio, however it is suggested that the use of dental stones at water/powder ratios below that recommended by the manufacturers will result in products with significantly higher tensile strengths. One must nevertheless keep in mind that a decrease in the gauging water will affect other variables such as the setting expansion, the setting time and the ease of manipulation.

ii) The die stones studied reach a peak tensile strength at, or below, the theoretical combining value.

iii) The use of a retarding solution composed of four per cent Rochelle salts (sodium potassium tartrate) and 0.3 per cent borax (sodium tetraborate) in water results in a markedly weaker gypsum cast.
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