Gypsum products

Introduction

Gypsum is a naturally occurring, white powdery mineral with the chemical name calcium sulphate dihydrate (CaSO4·2H2O). Gypsum products used in dentistry are based on calcium sulphate hemihydrate (CaSO4·1/2H2O). Their main uses are for casts or models, dies and investments.

Many dental restorations and appliances are constructed outside the patient’s mouth using models and dies which should be accurate replicas of the patient’s hard and soft tissues. The term model is normally used when referring to a replica of several teeth and their associated soft tissues or, to an edentulous arch. The term die is normally used when referring to a replica of a single tooth.

Many materials have been used for producing models and dies but the most popular are the materials based on gypsum products. The current ISO Standard for Dental Gypsum Products identifies five types of material as follows:

Type 1 Impression plaster

Type 2 Dental plaster

Type 3 Dental stone

Type 4 Dental stone, die, high strength, low expansion

Type 5 Dental stone, die, high strength, high expansion
Requirements of dental cast materials:

1. The main requirements of model and die materials are dimensional accuracy and adequate mechanical properties.
2. The material should, ideally, be fluid at the time it is poured into the impression so that fine detail can be recorded.
3. The set material should be sufficiently strong to resist accidental fracture and hard enough to resist abrasion during the carving of a wax pattern.
4. The material should be compatible with all the other materials with which it comes into contact.

Composition:
Gypsum products used in dentistry are formed by driving off part of the water of crystallization from gypsum to form calcium sulphate hemihydrate.

\[
\text{Gypsum} \rightarrow \text{Gypsum product} + \text{water} \\
2\text{CASO}_4\cdot2\text{H}_2\text{O} \rightarrow (\text{CaSO}_4)_2\cdot\text{H}_2\text{O} + 3\text{H}_2\text{O}
\]
Calcium sulphate   Calcium sulphate
dihydrate            hemihydrate

Applications of gypsum products in dentistry involve the reverse of the above reaction. The hemihydrate is mixed with water and reacts to form the dihydrate.

The various types of gypsum product used in dentistry are chemically identical, in that they consist of calcium sulphate hemihydrate, but they may differ in physical form depending upon the method used for their manufacture.

Dental plaster (plaster of Paris): Dental plaster is indistinguishable from the white plaster used in orthopaedics for stabilizing fractured limbs during bone healing. Plaster is produced
by a process known as calcination. Gypsum is heated to a temperature of about 120°C in order to drive off part of the water of crystallization. This produces irregular, porous particles which are sometimes referred to as β-hemihydrate particles.

**Dental stone:** Dental stones may be produced by one of two methods. If gypsum is heated to about 125°C under steam pressure in an autoclave a more regular and less porous hemihydrate is formed. This is sometimes referred to as an α-hemihydrate. Alternatively, gypsum may be boiled in a solution of a salt such as CaCl2. This gives a material similar to that produced by autoclaving but with even less porosity. Manufacturers normally add small quantities of a dye to dental stone in order that they may be differentiated from dental plaster, which is white.

**Manipulation:**

Plaster and stone powders are mixed with water to produce workable mix. Hydration of the hemihydrate then occurs producing the gypsum model or die.

Although a ratio of only 0.186 is required to satisfy the reaction, such a mix would be too dry and unworkable. In the case of the more dense material, dental stone, a ratio of about 0.30 is required to produce a workable mix, whereas for the more porous plaster a higher W/P ratio of 0.50 is required. The excess water is absorbed by the porosities of the plaster particles. Considerable quantities of air may be incorporated during mixing and this may lead to porosity within the set material. Air porosity maybe reduced either by vibrating the mix of plaster or stone in order to bring air bubbles to the surface or by mixing the material mechanically under vacuum, or both.
Setting characteristics:

The setting process begins rapidly after mixing the powder and water. The first stage in the process is that the water becomes saturated with hemihydrate, which has a solubility of around 0.8% at room temperature. The dissolved hemihydrate is then rapidly converted to dihydrate which has a much lower solubility of around 0.2%. The process continues until most of the hemihydrate is converted to dihydrate.

The crystals of dihydrate are spherulitic in nature and grow from specific sites called nuclei of crystallization. These may be small particles of impurity, such as unconverted gypsum crystals within the hemihydrate powder. If a thin mix of material is used, the formation of the supersaturated solution of dihydrate which is a precursor to crystallization is delayed and the centers of nucleation are more widely dispersed by the dilution effect. The set plaster is therefore less dense with greater spaces between crystals leading to a significant reduction in strength.

The material should be used as soon as possible after mixing since its viscosity increases to the stage where the material is unworkable within a few minutes. Two stages can be identified during setting. The first is the time at which the material develops the properties of a weak solid and will not flow readily. At this time, often referred to as the initial setting time, it is possible to carve away excess material with a knife. The materials continue to develop strength for some time after initial setting and eventually reach a stage when
the models or dies are strong and hard enough to be worked upon. The time taken to reach this stage is referred to as the final setting time, although this term is misleading since it implies that the material has reached its ultimate strength. This may not be reached until several hours after mixing.

**Control of setting time:**

Setting time must be controlled for different applications. Theoretically, at least three methods can achieve such control:

1. The solubility of the hemihydrate can be increased or decreased. For example, if the solubility of the hemihydrate is increased, super saturation of the calcium sulfate increases, and the rate of crystalline deposition is also increased.

2. The number of nuclei of crystallization can be increased or decreased. The greater the number of nuclei of crystallization, the faster the gypsum crystals form and the sooner the hardening of the mass occurs because of crystalline intermeshing.

3. The setting time can be accelerated or retarded by increasing or decreasing the rate of crystal growth, respectively.

In practice, these methods have been incorporated into the commercial products available. Thus the operator can vary the setting time within reason by changing the W/P ratio and mixing time.

**Factors Affecting the Setting time:**

1. **Impurities**

   If the calcination is not complete and gypsum particles remain, or if the manufacturer adds gypsum, the setting time is shortened because of the increase in potential nuclei of crystallization.
2-Fineness
The finer the particle size of the hemihydrate, the faster the mix hardens, particularly if the product has been ground during manufacture. Not only is the rate of the hemihydrate dissolution increased, but the gypsum nuclei are also more numerous. Therefore a more rapid rate of crystallization occurs.

3-W/P Ratio
The more water used for mixing, the fewer nuclei there are per unit volume. Consequently, the setting time is prolonged.

4-Mixing
Within practical limits, the longer and the more rapidly the plaster is mixed, the shorter is the setting time. Some gypsum crystals form immediately when the plaster or stone is brought into contact with the water. As the mixing begins, the formation of these crystals increases. At the same time, the crystals are broken up by the mixing spatula and are distributed throughout the mixture, resulting in the formation of more nuclei of crystallization. Thus the setting time is decreased.

5-Effect of Temperature
The temperature of the water used for mixing, as well as the temperature of the environment, has an effect on the setting reaction of gypsum products. The setting time probably is affected more by a change in temperature than by any other physical property. Evidently the temperature has two main effects on the setting reaction of gypsum products. The first effect of increasing temperature is a change in the relative solubility of calcium sulfate
hemihydrate and calcium sulfate dihydrate, which alters the rate of the reaction. The second effect is the change in ion mobility with temperature. In general, as the temperature increases, the mobility of the calcium and sulfate ions increases, which tends to increase the rate of the reaction and shorten the setting time.

6-The use of additives.
The easiest and most reliable way to change the setting time is to add different chemicals. Potassium sulfate, K2SO4, is known as an effective accelerator, and the use of a 2% aqueous solution of this salt rather than water reduces the setting time of model plaster from approximately 10 minutes to about 4 minutes. On the other hand, sodium citrate is a dependable retarder. The use of a 2% aqueous solution of borax to mix with the powder may prolong the setting time of some gypsum products to a few hours.

Setting Expansion
When set, all gypsum products show a measurable linear expansion. The percentage of setting expansion, however, varies from one type of gypsum material to another. Under ordinary conditions, plasters have 0.2% to 0.3% setting expansion, low- to moderate-strength dental stone about 0.15% to 0.2 %5 and high-strength dental stone only 0.08 % to 0.1 %. The setting expansion of high-strength/high-expansion dental stone ranges from 0.10% to 0.20%. Typically, over 75% of the expansion observed at 24 hours occurs during the first hour of setting. The setting expansion may be controlled by different manipulative conditions and by the addition of some chemicals. Mechanical mixing decreases setting expansion., a vacuum-mixed high-strength stone expands less at 2
hours than when mixed by hand. Power mixing appears to cause a
greater initial volumetric contraction than is observed for hand
mixing. The W/P ratio of the mix also has an effect, with an
increase in the ratio reducing the setting expansion. The addition of
different chemicals affects not only the setting expansion of
gypsum products, but may also change other properties. For
example, the addition by the manufacturer of sodium chloride
(NaCl) in a small concentration increases the setting expansion of
the mass and shortens the setting time. The addition of 1%
potassium sulfate, on the other hand, decreases the setting time but
has no effect on the setting expansion. If during the setting process,
the gypsum materials are immersed in water, the setting expansion
increases. This is called hygroscopic expansion. A typical, high-
strength dental stone has a setting expansion of about 0.08%. If
during the setting process the mass is immersed in water, it
expands about 0.10%. Increased expansion is observed when
dental stone hardens as it comes in contact with a hydrocolloid
impression.