GYPSUM

Gypsum ($CaSO4\text{-}2H_2O$, calcium sulfate dihydrate) is a mineral mined from the earth. It goes through a process called calcination where the water of crystallization (water of hydration) is driven off to produce calcium sulfate hemihydrate ($CaSO_4\text{-}½H_2O$). The method used for calcining determines the type of gypsum product produced. For example, if calcination occurs by heating the calcium sulfate dihydrate in an open kettle at 110 C to 120 C, the beta form of the hemihydrate is produced. This type has particles that are porous and irregular in shape and is found in impression plaster and, to a certain extent, model plaster. If calcination occurs by heating the dihydrate in an autoclave at 130 C, the alpha form of the hemihydrate is produced. This type is dense, regular, and needle-like and is found in model plaster and regular stone. Finally, if calcination occurs by boiling the dihydrate in a 30% calcium chloride solution, the alpha form of the hemihydrate is again produced. Its crystal shape, however, is stubby in addition to being regular and dense. This particle type is found in the high-strength stones.

Types of Gypsum Products

Type	**Expansion Rate (%)**	**Water/Powder Ratio**
Type I -- Impression Plaster	0.15	0.50
Type II -- Model Plaster	0.30	0.50
Type III -- Stone	0.20	0.30
Type IV -- High-Strength Stone	0.10	0.22
Type V -- High-Strength, High-Expansion Stone	0.30	0.22

Water powder (W/P) ratios are expressed in decimal form. For the high-strength stones, for example, the 0.22 W/P ratio means that 22 mLs or ccs of water are used for every 100 grams of the powder.

Setting Reaction of Gypsum

$CaSO_4\text{-}½H_2O + 1½H_2O \text{ ---> } CaSO_4\text{-}2H_2O + 3900$ cal/gm mole

As indicated, the reaction is an exothermic one.

Control of Setting Time

Control of the setting time is generally accomplished by altering one or more of the following factors:

1. Mixing Time: By increasing the mixing time (within practical limits) the setting time will be shortened. This occurs because more nuclei of crystallization per unit volume are created. The greater the number of nuclei of crystallization, the faster the dihydrate crystals will form and the faster the

material will set as the crystals intermesh.

2. W/P Ratio: By decreasing the W/P ratio, the setting time will be shortened, again because more nuclei of crystallization of dihydrate per unit volume are created.

3. Temperature: Increasing the temperature of the mixing water shortens the setting time because ion diffusion rates increase. This speeds the reaction rate. Above 50 C, however, the effect reverses because the solubility of hemihydrate compared to dihydrate decreases. Hemihydrate is normally 4.5 times as soluble as dihydrate at 20 C and this drives the reaction. Increasing the temperature above 50 C reduces this reaction factor. When the temperature of the mixing water exceeds 100 C, the reaction does not proceed because the solubility rates for hemihydrate and dihydrate are the same.

4. Retarders and Accelerators: This is the most practical method for controlling reaction rate and setting time. Accelerators include potassium sulfate (K_2SO_4) which acts by contributing sulfate ions to the reaction. Another accelerator is sodium chloride (NaCl) in a concentration of less than 20%. It acts by increasing the solubility of the hemihydrate. A well known retarder of gypsum is borax, which acts by forming a layer on the hemihydrate and dihydrate particles. This reduces their solubility and inhibits their growth, respectively.

5. Colloidal Materials: Blood, saliva, agar, and alginate act to lengthen the setting time by poisoning the nuclei of crystallization of the dihydrate particles.

6. Gypsum: Calcium sulfate dihydrate itself in the form of slurry water acts as a potent accelerator of the setting time because it provides nuclei of crystallization of the dihydrate.

<u>Control of Setting Expansion</u>

As noted earlier, gypsum materials expand during setting, primarily because the dihydrate crystals push against each other as they form. Several factors can be altered to affect setting expansion.

1. Mixing Time: Increasing the mixing time, within practical limits, increases expansion by increase the number of nuclei of crystallization of dihydrate particles.

2. W/P Ratio: Decreasing the W/P ratio increases expansion by also increasing the number of nuclei of crystallization of dihydrate particles.

3. Accelerators and Retarders: Accelerators and retarders not only affect setting time, but also affect expansion of the gypsum. Both decrease expansion by changing the shape of the developing dihydrate crystals.

Summary of factors that influence setting time and expansion of the gypsum materials:

*Increasing the mixing time or decreasing the W/P ratio shortens the setting time and increases expansion by creating more nuclei of crystallization of calcium sulfate dihydrate per unit volume. They also increase strength by producing a more dense product.

*Accelerators and retarders will either shorten or lengthen the setting time (depending upon which material is added), but both decrease the compressive strength and expansion by changing the shape of the dihydrate crystals that are formed.

*Colloidal materials not only lengthen the setting time but result in a weaker product because they poison the nuclei of crystallization.

*Slurry water acts as a potent accelerator of the setting reaction but does not affect expansion or strength.

Theory of Hygroscopic Expansion

Hygroscopic expansion, the setting of gypsum under water, results in a greater amount of expansion than if the expansion is allowed to occur in air. The reason is that when gypsum sets in air, the water of hydration exerts surface tension forces on the developing dihydrate crystals, which prevents them from expanding to the degree that they would if surface tension were not a factor. By placing the setting gypsum in contact with a lot of excess water, these forces are significantly reduced, which allows the dihydrate to expand to a much greater degree than normal.[1]

Gypsum Strength

The strength of set calcium sulfate dihydrate is not an inherent property of the material but is based upon the W/P ratio. This, in turn, is dependent on the type of hemihydrate particle. Type II gypsum (model plaster) has a higher W/P ratio than does Type IV gypsum (high-strength stone) because the hemihydrate particles in the plaster are more porous and irregular and require more water to provide a workable mix than those in the stone. This means that the set plaster product will be softer since the spaces occupied by the water of hydration between the crystals of dihydrate are larger.

Excess Water

If the approximately 8.8% excess water in a cast is driven off, the cast will double in strength and hardness. This is because the excess water adds mobility to the dihydrate crystals. Also, when the water evaporates form the plaster or stone, fine dihydrate crystals form that reinforce the larger dihydrate crystals and strength the mass.[2] These forces have their greatest effect on the cast as the final 2% of the water is lost. The drying process can take up to a week at normal room temperature and humidity. It may be accelerated by heating the cast, but this should be done cautiously because if the cast is heated above 60 C, the water of hydration will also be driven off and the cast will be weakened.

Gypsum Storage

Gypsum materials should not be left open to the air in storage bins because if the relative humidity exceed 70%, hemihydrate will convert to dihydrate and the crystals will act as accelerators when the mixing water is added. This will shorten the setting time greatly. If gypsum is stored for a longer period of time under high humidity conditions, more conversion will occur and lead to a lengthening of the setting time because the dihydrate crystals will surround the hemihydrate making it difficult for the mixing water to reach and react with the hemihydrate.

<u>General Information</u>
Casts should not be rinsed under water because they will erode. To rinse debris from a cast, rinse it in a saturated solution of calcium sulfate. This can be prepared by placing a broken cast in a container of water for 12 hours.

Do not model trim a wet cast because even though it is soft and easy to trim in that condition, it is also quite soluble because of the high percentage of hemihydrate present.

Type IV gypsum materials are frequently incompatible with alginate impression materials because the alginate produces a soft surface on the cast. Often, fluoride is added to the impression material as a strengthening agent to prevent this.

Type IV and V gypsum materials are used for final casts and dies because they have a lower expansion rate, are harder, stronger, and more wear resistant than the other gypsum products.

The Type V (high-strength, high-expansion stone) products were developed in a way that makes it possible for them to be mixed at a lower W/P ratio than the Type IV products. This gives them greater strength, but produces a greater degree of expansion. The greater expansion is desirable, however, because newer alloys contract more during casting and the stone s expansion helps to compensate for this.

<u>References</u>
1. Mahler DB, Ady AB. An explanation for the hygroscopic setting expansion of dental gypsum products. J Dent Res 1960;39:578-589.
2. Fairhurst CW. Compressive properties of dental gypsum. J Dent Res 1960;39:812-824.