This online module will review the basic information about gypsum product structure and properties and then focus on the specific modifications that are required to make die stone and alternative die materials.
All gypsum products (plaster, stone, die stone (improved stone), impression materials, investment materials, etc. are all based on calcium sulfate hemihydrate (CaSO$_4$-$\frac{1}{2}$H$_2$O) crystals being mixed with water to form calcium sulfate dihydrate (CaSO$_4$-2H$_2$O) crystals. [CLICK] The reaction involves the dissolution of the original crystals into the water, reaction to the dihydrate form, and precipitation (nucleation and growth) of new crystals. [CLICK] The reaction is accelerated chemically by the addition of potassium sulfate or with calcium sulfate dihydrate crystals being used as nucleating agents. A variety of things can act as retarders, including blood and saliva (that might still be present on the surfaces of impression materials).

CaSO$_4$-½H$_2$O + 3/2H$_2$O $\rightarrow$ CaSO$_4$-2H$_2$O + HEAT
### MANUFACTURE

**of Dental Gypsum**

<table>
<thead>
<tr>
<th>Chemical Name:</th>
<th>β-calcium sulfate</th>
<th>α-calcium sulfate</th>
<th>α-calcium sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula:</td>
<td>CaSO₄·½H₂O</td>
<td>CaSO₄·½H₂O</td>
<td>CaSO₄·½H₂O</td>
</tr>
<tr>
<td>Powder Shape:</td>
<td>Irregular</td>
<td>Uniform</td>
<td>Uniform</td>
</tr>
<tr>
<td>Density:</td>
<td>Porous</td>
<td>Moderately dense</td>
<td>Dense</td>
</tr>
<tr>
<td>Production Steps:</td>
<td>Heat to 115°C in air.</td>
<td>Heat to 125°C with steam pressure.</td>
<td>Heat to 100°C in CaCl₂ solution.</td>
</tr>
<tr>
<td>Dental Products:</td>
<td>Plaster, Impression Plaster</td>
<td>Stone, Investment,</td>
<td>Improved Stone, Die Stone</td>
</tr>
<tr>
<td>Common Names:</td>
<td>Plaster of Paris</td>
<td>[eg, Hydrocal]</td>
<td>[eg, Densite]</td>
</tr>
</tbody>
</table>

Plaster, stone, and die stone are all chemically the same, calcium sulfate hemihydrate crystals. However, the crystals are slightly different in geometry and packing efficiency. Plaster crystals are produced by heating gypsum to 115°C in air. Crystals are irregular, porous, and do not pack well together. Therefore, making a useful mixture requires more water that for stone. Stone crystals are created by heating gypsum to 125°C under pressure. Their more regular shape allows better packing, requiring less water for mixing. Finally, die stone crystals are the most uniform of all, produced by heating at 100°C in CaCl₂ solution. These crystals require the least water for mixing. The strength of the set material is strongly related to the residual porosity of the solid. Plaster has more porosity because of the high level of water that was originally required for mixing.
For chemical reaction of 100 grams of calcium sulfate hemihydrate to dihydrate, 18 cc of water is required. Additional water is necessary to fill in all the spaces between the powder crystals and create a fluid consistency for mixing.

For plaster 50 cc of total water is normally used. For stone, 30 cc of water is used. For die stone, 24 cc of water is used. Average water-to-powder ratios (W/P) are shown above. Actual products may vary from these ideal ratios based on the presence of other additives for other reasons such as strength or color.

As the amount of water decreased, the amount of residual porosity is smaller, and the final strength is greater. This trend is emphasized in the next slide.
Gypsum products for all applications in dentistry come under a single ADA/ANS classification system for properties. The table above summarizes these relationships. Material for dies falls into the category called ADA Type IV. [CLICK]

Increasing porosity causes the strength of any material to exponentially decrease toward zero. From the image below it is apparent that, there is a great deal of porosity that remains between the individual reaction product crystals. [CLICK] In the figure at the right below, the effect of porosity is demonstrated in terms of the compressive strength (vertical axis) versus the water-to-powder ratio (W/P). Rectangles are placed in the graph to indicate the normal ranges for each of the ADA classifications of materials. [CLICK] Type IV gypsum product (used for die stone) is shown in red. It has much less porosity (~10%) and therefore has a relatively high compressive strength. Type II gypsum products (used for plaster) has more porosity (~35%) and is much weaker.
DIE SURFACE PROPERTIES
Effects of Impression and Die Stone Variables

A. IMPRESSION MATERIAL VARIABLES:
   1. Blood and Saliva
   2. Plasticizers
   3. Hydrophilicity
   4. Disinfection Procedures

B. STONE AND DIE STONE VARIABLES:
   1. W/P Ratio
   2. Disinfection Procedures
   3. Additives
      a. Accelerators: K₂SO₄; Gypsum Particles
      b. Retarders: Borax (Na₂B₄O₇·10H₂O); Colloids
      c. Fillers: Silica; Resin

Impression Material Variables: [CLICK] Gypsum products are in contact with the surfaces of impression materials during setting and may be influenced by the chemistry of those surfaces. (1) Blood or saliva should be carefully washed off of the internal surfaces of the impression before pouring with gypsum products. Otherwise the setting reactions of the gypsum will be retarded or interrupted, leaving the gypsum products soft and chalky. (2) Plasticizers in the impression materials, which are added to increased the flexibility of the impression and ease removal, may migrate into the gypsum products and soften the surfaces as well. (3) Newer impression materials have small concentrations of soap or other wetting agents added to decrease the contact angle with tooth structure and soft tissues, facilitate flow, eliminate bubbles, and increase the overall accuracy in critical regions such as margins. However, these same materials can alter the setting properties or final strength of gypsum products as well. (4) Disinfection procedures are notorious for softening the outer surfaces of impressions. General 5.25% hypochlorite or 2% glutaraldehyde solutions are recommended for most elastomer impression materials.

Stone and Die Stone Variables: [CLICK] Even if the impression surfaces do not alter the gypsum product surfaces, there are still other things that may keep those surfaces from achieving their ultimate hardness. (1) An improper W/P ratio, on either side of the correct one, will weaken the surface. (2) Disinfectants can be added to the gypsum products as well to impart long term resistance to growth of contaminant bacteria from the impression. (3) Other additives to the power are important as well. Accelerators (e.g., potassium sulfate) will help to more rapidly harden the surfaces. Retarders will slow the setting reaction and amplify the effects of hydrocolloid contamination (e.g., blood and saliva). Fillers (e.g., silica or polymer powder) will fill in the spaces between the calcium sulfate dihydrate crystals, improve the strength, and improve the abrasion resistance.
The key dies onto which restorations are to be fabricated for crowns, bridges, or partials generally see much more duress. These require special properties. Therefore, they are generally made out of a stronger gypsum product (die stone) and are made as removable dies.

Dies should be highly accurate and dimensionally stable replicas. They should be resistant to fracture and wear. Gypsum products are already very accurate and dimensionally stable, but not fracture or wear resistant. Thus, the formulation needs to be changed to improve the durability of dies.

[CLICK] Normal die stone can be unmodified, filled with some polymer (e.g., Resinrock, Milestone, Vel-Mix, or Die-Keen) and/or formulated with disinfectant (e.g., Steri-Die-A). In all these cases, the formulation is still just die stone. [CLICK] However, the gypsum surfaces can be hardened or [CLICK] the dies can be made from different materials altogether using polymer or investment.

All of these processes are summarized in the following diagram.
[CLICK] Die Stone with Die Hardener: [CLICK] Die hardeners are liquids that can be painted on the surface of dies that interact with the die stone (accelerator, K2SO4) that promote formation of more product and help to fill in the spaces between the initial die stone crystals with more reaction product crystals. Ideally, the new crystals contribute only to a denser surface and do not produce crystals sticking out of the surface that might increase the surface roughness and distort a wax pattern during removal.
DIET MATERIALS
Types of “Surface-Hardened” Die Materials

[CLICK] Cyanoacrylate (or Super Glue or Krazy Glue): Cyanoacrylate in this form is really α-methyl cyanoacrylate whose polymerization is initiated by the presence of moisture in the air. However, moisture also can depolymerize the polymer as well. Thus, it only has strength for a limited period of time. Most cyanoacrylate products suffer from the problem of slow and insidious contamination by moisture after the tube is opened. Therefore, these can be quick thick by the time that they are used a second or third time from a freshly opened tube. Thick material can actually lay on the die surfaces and increase the die dimensions in a negative manner.
[CLICK] Cu-Plating or Ag-Plating: With gypsum as the main die material, it is possible to coat the surfaces with Cu or Ag in a small film, both of which are more wear resistant. This is done using an electrochemical bath to immerse the original impression material and electro-deposit Cu or Ag. After the impression is coated, the gypsum is poured into the plated impression. When the impression is separated, the electroplated surface sticks to the newly formed cast stone dies creating a much better surface for wear resistance. In addition, the surface is extremely smooth and produces a highly accurate representation of the original impression. Unfortunately there is also a tendency for this process to increase the actual dimensions (thickness) of the die. Fabricated prostheses are thinner in the same dimension and require more cement or other luting agents for final intra-oral attachment.
[CLICK] All of the materials above improve the wear resistance but do not necessarily improve the fracture resistance. In this case, die stone can be replaced with a polymer potting compound that are significantly stronger. However, these materials must undergo setting reactions that include some shrinkage.

[CLICK] Epoxy: Generically, epoxies are linear or cross-linked polymers formed by alternating sections of acid/amine structures. A hardener is mixed with a pre-polymer to complete the polymerization reaction (e.g., Epoxy-Die or Epoxy-Dent). However, shrinkage still takes place. To counteract shrinkage and even further enhance the mechanical properties, epoxies can be filled as well.

Urethane: Urethanes are produced by reactions of -CNO functional components with any active hydrogen (acids, alcohols, amines, or water) to produce monomers connected together by urethane linkages. This class of materials typically has very good wear resistance and excellent fracture resistance due to its high toughness. There is still some shrinkage during polymerization and so filled versions are more dimensionally accurate.

Cu-Plated Epoxy: Just as copper plated impressions can but used to create copper-coated gypsum dies, one can also produce copper-coated epoxy dies.
As an alternative to a hardened surface and coated surface (cyanoacrylate or Cu-plating/Ag-plating, it is possible to create a much smoother and more dense surface using gypsum-bonded investment material.

**[CLICK] Investment Dies:** Gypsum-bonded investment (GBI) has a much more carefully formulated particle size distribution of powder than regular gypsum. In addition, GBI is two-thirds silica filler particles. Therefore, the final surface is much denser and smoother. There are several advantages here. There is much less possibility of wax distortion since the wax cannot penetrate into the surface. The surface is much harder than with gypsum. The material is intermediate in wear and fracture resistance to gypsum-based materials and polymer-based materials.
More sophisticated laboratories tend to use more expensive or elaborate die fabrication methods.

THANK YOU.