GYPSUM PRODUCTS

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INTRODUCTION

- Gypsum is a naturally occuring white powdery mineral mined in various parts of the world, with chemical name calcium sulfate dihydrate ($CaSO_4.2H_2O$).
- Gypsum is derived from a greek word “Gypsas” (chalk).

FORMS

1. ROCK :- Dull coloured rock.

2. ALABLASTER :- Fine grained variety.

3. GYPCRETE(gypcrust) :- Hard layer formed on soil.

4. SELENITE

5. SATIN SPUR :- Fibrous with silky lustre.

USES

1. For construction purposes.
2. Used in industry for making pottery, moulds etc.
3. Used in orthopaedics to make plaster casts.

APPLICATION IN DENTISTRY

1. For cast preparation.
2. Models and dies.
3. Impression Material.
4. As Investment Material.
5. Mounting of Casts.
6. As a mold material for processing of complete dentures.

- DESIRABLE PROPERTIES:-

1. Accuracy
2. Dimensional Stability
3. Ability to reproduce fine detail.
4. Strength & resistance to abrasion.
5. Compatibility with the impression materials.
6. Colour
7. Biological safety
8. Ease of use
9. Cost.

CHEMICAL & PHYSICAL NATURE OF GYPSUM PRODUCTS

- Gypsum – Calcium Sulphate Dihydrate

$$CaSO_4.\ 2H_2O \xrightarrow{\text{on heating}} CaSO_4.\ \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O \quad (1)$$

(gypsum) (calcium sulphate hemihydrate) (water)

$$CaSO_4.\tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O \longrightarrow CaSO_4.\ 2H_2O + 3900 \quad (2)$$

(plaster of paris) (water) (gypsum) (cal)

- Reaction is exothermic.

MANUFACTURE OF DENTAL PLASTER & STONE

- Formed by calcining of gypsum .

$$CaSO_4 . 2H_2O \xrightarrow{110\text{-}130^{\circ}C} (CaSO_4)_2\ H_2O \xrightarrow{130\text{-}200^{\circ}C} CaSO_4 \xrightarrow{200\text{-}1000^{\circ}C} CaSO_4$$

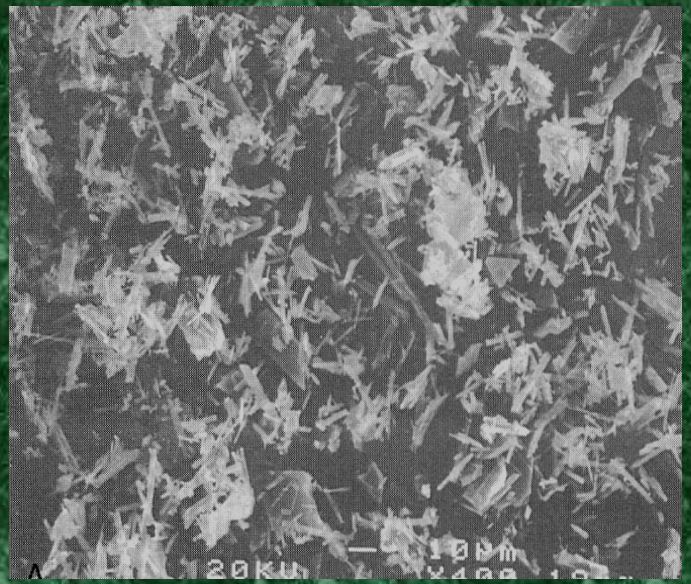
gypsum (calcium sulphate dihydrate)	plaster/stone (calcium sulphate hemihydrate)	hexagonal anhydrite	ortho-rhombic anhydrite

- β-hemihydrate(plaster)-

  - Gypsum is heated in a kettle, vat or rotatory kiln open to air.

  - Crystals – spongy & irregular.

Powder particles of plaster of paris



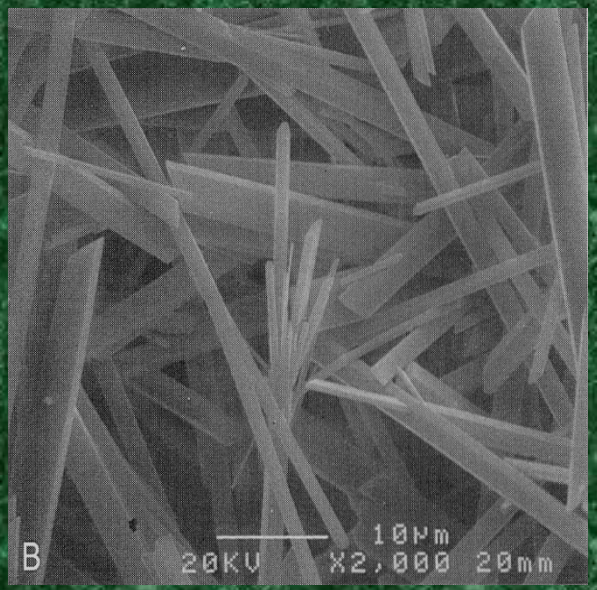
Scanning electron micrograph of dental plaster powder particles

- α-hemihydrate(stone)-

  - Gypsum is heated to 125^0c under steam pressure in an autoclave or boiled in a solution of $CaCl_2$.

  - Crystals- more dense & prismatic.

Powder particles of dental stone



Scanning electron micrograph of dental stone powder particles

HYDRATES OF CALCIUM SULPHATE

Mineral source → Calcium Sulphate Dihydrate(gypsum) ← By product of other industries

Heat in an open vessel, 120ºc	Heat in autoclave under steam pressure, 120-130ºc	Heat ground gypsum in H_2O with small quantity, organic acid or salt, in an autoclave,140ºc	Heat in boiling30% aqueous solution of $CaCl_2$/ $MgCl_2$
↓	↓	↓	↓
Calcined $CaSO_4$ hemihydrate (β- hemihydrate)	Autoclaved $CaSO_4$ hemihydrate (HYDROCAL or α- hemihydrate)	Autoclaved $CaSO_4$ hemihydrate (α- hemihydrate)	$CaSO_4$ hemihydrate (DENSITE)

TYPES OF GYPSUM PRODUCTS

Classification:-

1. Depending on the method of calcination:-
   - Dental plaster or β- hemihydrate
   - Dental stone or α- hemihydrate or hydrocal
   - Dental stone, high strength or densite
2. Other Gypsum Products:-
   - Impression plaster
   - Dental Investments:-
     a) Gypsum bonded investments
     b) Phosphate bonded investments
     c) Silica bonded investments

Five types of gypsum products & their properties

Type	W/P ratio	Setting time (min)	2-Hr setting expansion (%)		1-Hr compressive strength†	
			Min	Max	(MPa)	(psi)
I. Plaster, impression	0.40–0.75	4±1	0.00	0.15	4.0	580
II. Plaster, model	0.45–0.50	12±4	0.00	0.30	9.0	1300
III. Dental stone‡	0.28–0.30	12±4	0.00	0.20	20.7	3000
IV. Dental stone, high strength§	0.22–0.24	12±4	0.00	0.10	34.5	5000
V. Dental stone, high strength, high expansion	0.18–0.22	12±4	0.10	0.30	48.3	7000

1. IMPRESSION PLASTER(Type 1)-

-They are composed of Plaster of Paris to which modifiers have been added to regulate setting time & setting expansion.

- Modifiers such as:-
  - -Potassium sulphate
  - -Borax
- Advantage:- Records excellent fine details.
- Disadvantages:- Small dimensional changes.
  Fracture on removal from undercuts
  Separating media is required
  Non toxic but causes dryness

2. MODEL PLASTER (Type 2):-

- β – hemihydrate
- Powder particles are porous & irregular.
-It is usually white in colour.
- Use:- For primary cast for complete dentures.
  For articulation purposes.
  For flasking in denture construction.
- Advantage:- Inexpensive
- Disadvantage:- Low strength
  Porosity

3. DENTAL STONE(Type 3):-

- Discovered in 1930
- α – hemihydrate or Hydrocal
- Powder particles are more dense & regular in shape.
- Comes in different colours, like yellow, green .
- Use:- - Making casts for diagnostic purposes & for complete or partial denture construction.
- Advantages:- Greater strength & surface hardness
- Disadvantage:- More expensive than plaster.

4. DENTAL STONE, HIGH STRENGTH(Type 4):-

- Modified α – hemihydrate, Densite or Die stone.
- Powder particles are very dense, cuboidal in shape & has reduced surface area.
- Use:- For making casts or dies for crown, bridge & inlay fabrication.
- Advantages:-
  - -High strength
  - -Surface hardness
  - -Abrasion resistant
  - -Minimum setting expansion

Powder particles of Type 4 & 5 stones

5. DENTAL STONE, HIGH STRENGTH, HIGH EXPANSION(Type 5):-

- Most recent gypsum product.
- Use:- When inadequate expansion has been achieved during the fabrication of cast crowns.
- Advantages:- Higher compressive strength
  Higher setting expansion(0.10-0.30%)

SYNTHETIC GYPSUM:-

- α & β- hemihydrates can also be made from the by products/ waste products of the manufacture of phosphoric acid.
- Synthetic product is more expensive than that made from natural gypsum.

SETTING

$$(CaSO_4)_2.H_2O + 3H_2O \longrightarrow 2CaSO_4.2H_2O$$

+

unreacted $(CaSO_4)_2.\frac{1}{2}H_2O$

+

heat

SETTING REACTION

- Gypsum is a unique material.

- The setting reaction of gypsum occurs by:-

1. Dissolution of calcium sulphate hemihydrate.
2. Formation of saturated solution of calcium sulphate.
3. Subsequent aggregation of less soluble calcium sulphate dihydrate.
4. Precipitation of the dihydrate crystals.

- THEORIES FOR SETTING REACTION:-

1. Colloidal/ Gel Theory.
2. Hydration Theory.
3. Crystalline Theory.
4. Dissolution- precipitation Theory.

1. Colloidal/ Gel Theory:-

- Originated in 1893 by M. Michaelis.
- When plaster is mixed with water, plaster enters into the colloidal state through a sol- gel mechanism.
- In the sol state, hemihydrate particles are hydrated to form dihydrate, thereby entering into an active state.
- As the measured amount of water is consumed, the mass converts to a solid gel.

2. Hydration Theory:-

- The rehydrated plaster particles join together through hydrogen bonding to the sulfate groups to form the set material.

3. Crystalline Theory:-

- Originated in 1887 by Henry Louis Le Chatelier
- In 1907, supported by Jacobus Hendricus van't Hoff
- The difference in the solubilities of calcium sulphate dihydrate & hemihydrate causes setting differences.
- Dissolved $CaSO_4$ precipitates as calcium sulphate dihydrate, since it is less soluble than hemihydrate.
- X-ray diffraction studies – not all hemihydrate is converts to dihydrate.

- In a setting mass of plaster 2 types of centers are there:-

  a) Dissolution center- around $CaSO_4$ hemihydrate

  b) Precipitation center- around $CaSO_4$ dihydrate

4. Dissolution- Precipitation Theory:-

- Based on dissolution of plaster & instant recrystallization of gypsum ⟶ interlocking of crystals

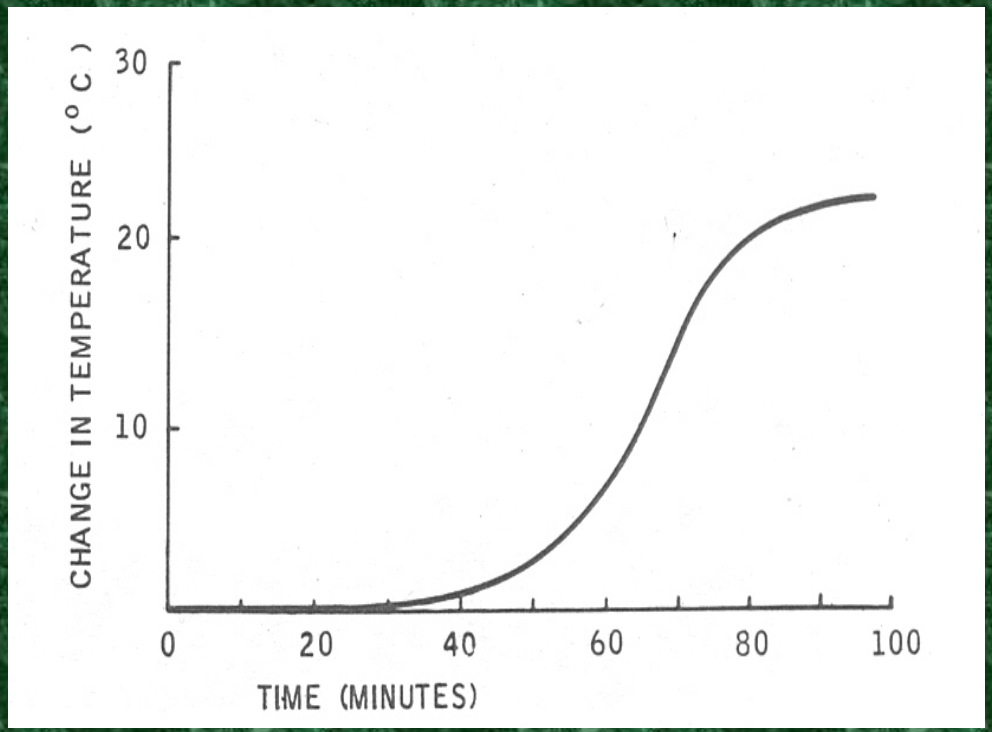
Solubility of gypsum & gypsum products

TYPE	FORMULA	SOLUBILITY, GM/100 ML
Dihydrate	$CaSO_4 \cdot 2H_2O$	0.2
Hemihydrate	$(CaSO_4)_2 \cdot H_2O$	0.9
Anhydrite	$CaSO_4$	*0.3*

- The Setting Reaction is as follows:-

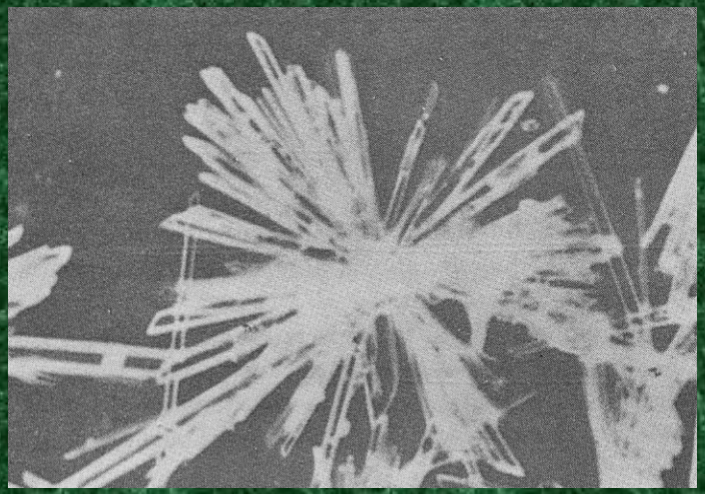
1. When the hemihydrate is mixed with water, a suspension is formed that is fluid & workable.
2. The hemihydrate dissolves until it forms a saturated solution.
3. This saturated solution of hemihydrate, supersaturated in dihydrate, precipitates out dihydrate.
4. As the dihydrate precipitates, the solution is no longer saturated with the hemihydrate, so it continues to dissolve. Dissolution of hemihydrate & precipitation of dihydrate as either new crystals or further growth on the already present. The reaction continues until no further dihydrate precipitates out of solution.

- The reaction rate is followed by the exothermic heat evolved as shown in fig.

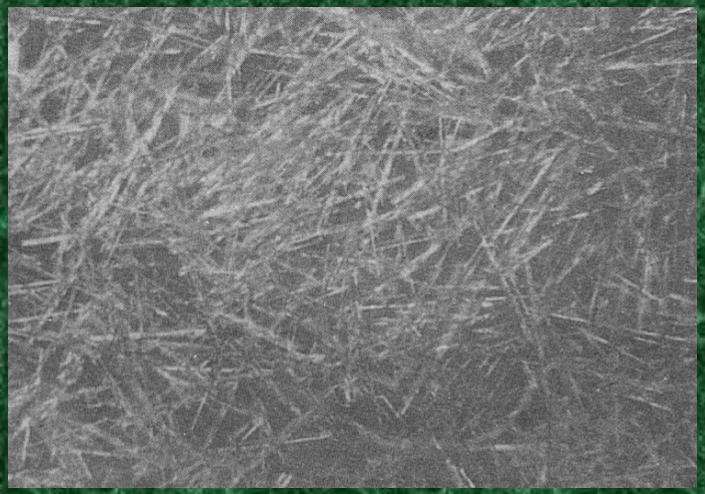


Temperature increases during the setting of plaster of paris

- As the gypsum forming increases, mass hardens into needle- like clusters called SPHERULITES.
- The intermeshing & entangling of crystals lead to a strong, solid structure.



Clusters of needle like crystals



Dark- field photomicrograph of set plaster

- **W: P ratio:-**

-The amount of water & hemihydrate should be gauged accurately by weight.

-W: P ratio is an important factor in determining the physical & chemical properties of the final gypsum product.

↑ed W: P ratio ⟶ ↑ ed Setting Time
↓ ed Strength
↓ ed Setting Expansion

-Typical recommended ranges are:-

	W: P ratio
Type 2 plaster	0.45-0.50
Type 3 stone	0.28-0.30
Type 4 stone	0.22-0.24

- **Temperature:-**

2 main effects on setting reaction:-

1. Change in temperature causes change in the relative solubilities of hemihydrate & dihydrate, which alter the rate of the reaction.

Solubility of hemihydrate & dihydrate at different temperatures

Temperature (° C)	$CaSO_4 \cdot \frac{1}{2}H_2O$ (g/100 g water)	$CaSO_4 \cdot 2H_2O$ (g/100 g water)
20	0.90	0.200
25	0.80	0.205
30	0.72	0.209
40	0.61	0.210
50	0.50	0.205
100	0.17	0.170

- Temperature ↑es ⟶ Solubility ratio ↓ es
- Solubility ratio ↓ es ⟶ Setting Reaction ↓ es& Setting Time ↑es
- Solubility ratio ↑ es ⟶ Setting Reaction ↑ es & Setting Time ↓es

2. There is change in ion mobility with temperature.

↑ in temperature ⟶ ↑ in the mobility of Ca & SO_4 ions ⟶

↓ed setting time ⟵ ↑ in rate of reaction ⟵

Practically the effects of these 2 phenomena are superimposed, & the total effect is observed.

↑in Temperature(20-30ºC) ⟶ ↓ in solubility ratio ⟶ ↓rate of Rx

↑in mobility of ions ⟶ ↑setting reaction

Experimentation has shown,

↑in Temperature(20-37ºC) ⟶ ↑ in rate of reaction & ↓ in ST.

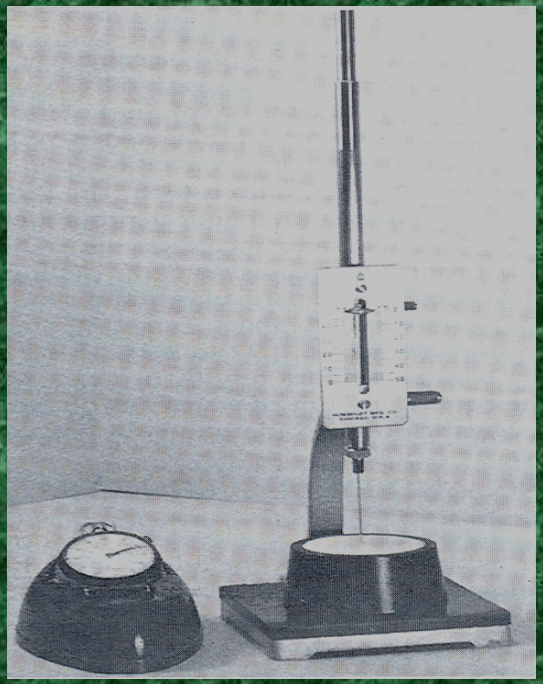
- **pH:-**

Liquids with low pH(saliva) ⟶ ↓ in setting reaction

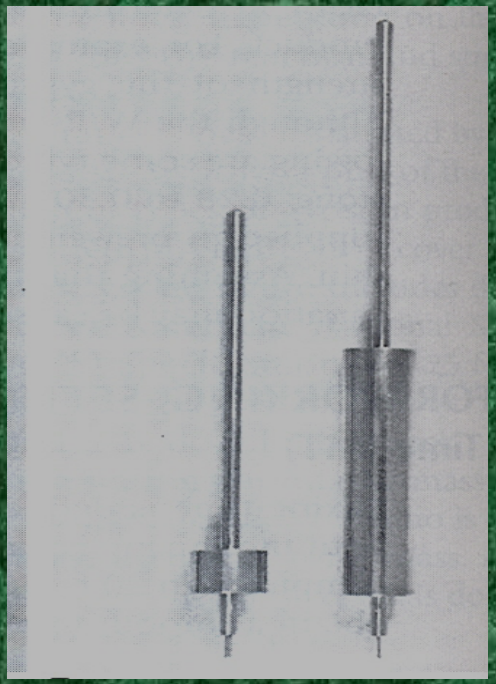
Liquids with high pH ⟶ ↑ in setting reaction

SETTING TIME

- Measured by "Penetration Test"(time taken from the start of mix until the needle no longer penetrates to the bottom) with the help of Vicat & Gillmore needles.



VICAT NEEDLE



SET OF GILLMORE NEEDLES

- There are number of stages in the setting of a gypsum product:-

- MIXING TIME:- The time from the addition of powder to the water until the mixing is completed.

  Mechanical mixing – 20-30 secs.

  Hand spatulation - 1 min.

- WORKING TIME:- The time available to use a workable mix.

  Working time – 3min.

- LOSS OF GLOSS TEST FOR INITIAL SET:- Some of the excess water is taken up in forming the dihydrate so that the mix loses its gloss.

- INITIAL GILLMORE TEST FOR INITIAL SET:- The mixture is spreadout, & the needle is lowered onto the surface. The time at which it no longer leaves an impression is called the "Initial Set."

  This is marked by a definite increase in strength.

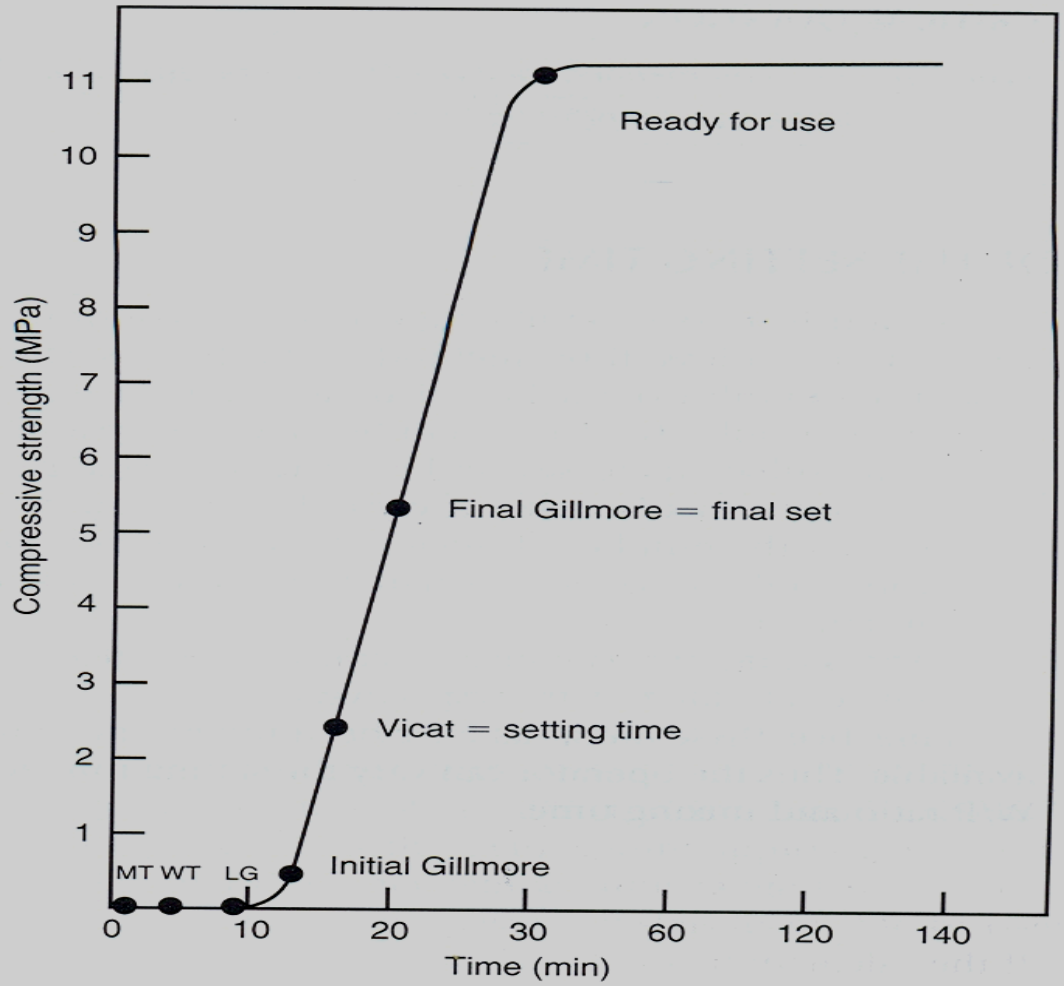


Fig. 10-5 Compressive strength of a Type-II model plaster during setting. The W/P ratio was 0.50. The various stages in the setting reaction are indicated by the particular instruments used in measuring the hardening of the mix. *MT,* mixing time; *WT,* working time; *LG,* loss of gloss from the surface of the mix.

- VICAT TEST FOR SETTING TIME:- Vicat Penetrometer is used.

The needle with a weighed plunger rod is supported & held just in contact with the mix. After the gloss is lost, the plunger is released.

The time elapsed until the needle no longer penetrates to the bottom of the mix is known as the "Setting Time."

- GILLMORE TEST FOR FINAL SETTING TIME:-

Heavier Gillmore Needle is used.

The time elapsed at which this needle leaves only a barely perceptible mark on the surface is called the "Final Setting Time."

- READY- FOR- USE CRITERION:- The subjective measure of the time at which the set material may be safely handled in the usual manner.

Ready for use state is reached in approx. 30 min.

CONTROL OF SETTING TIME

- The setting time depends on :-

1. Temperature
2. W:P ratio
3. Fineness
4. Humidity

- Factors that control setting time :-

  a) Factors controlled by the operator:-

  1. W:P ratio
  2. Mixing time

W/P ratio	Mixing time (min)	Setting time (min)
0.45	0.5	5.25
0.45	1.0	3.25
0.60	1.0	7.25
0.60	2.0	4.50
0.80	1.0	10.50
0.80	2.0	7.75
0.80	3.0	5.75

Effect of W:P ratio & Mixing time on the Setting time of plaster of paris

b) Factors controlled by the manufacturer:-

1. By the addition of Accelerators & Retarders:-

Accelerators:-

- Gypsum (<20%) - ↓es setting time

  The set gypsum used as an accelerator is called "Terra Alba."

- Potassium Sulphate(conc. 2-3%)

- Sodium Chloride(<28%)

Retarders:-

- Organic materials – glue, gelatin & some gums.

- Potassium citrate, borax, sodium chloride(20%), sodium citrate

SETTING EXPANSION

- Expansion may vary from 0.06% to 0.5%
- Volume of dihydrate formed is less than equal volume of hemihydrate & water.

  i.e. actually a volumetric contraction should occur during setting reaction, but instead a setting expansion is observed.

- PHENOMENON:-

  Based on crystallization mechanism.

- RESULT:-

  The set material must be porous.

CONTROL OF SETTING EXPANSION

1. W: P ratio:-

W/P ratio	Mixing time (min)	Setting expansion (%)
0.45	0.6	0.41
0.45	1.0	0.51
0.60	1.0	0.29
0.60	2.0	0.41
0.80	1.0	0.24

Effect of W:P ratio & Mixing time on Setting expansion of plaster of paris

2. Accelerators & Retarders:-

Accelerators:-

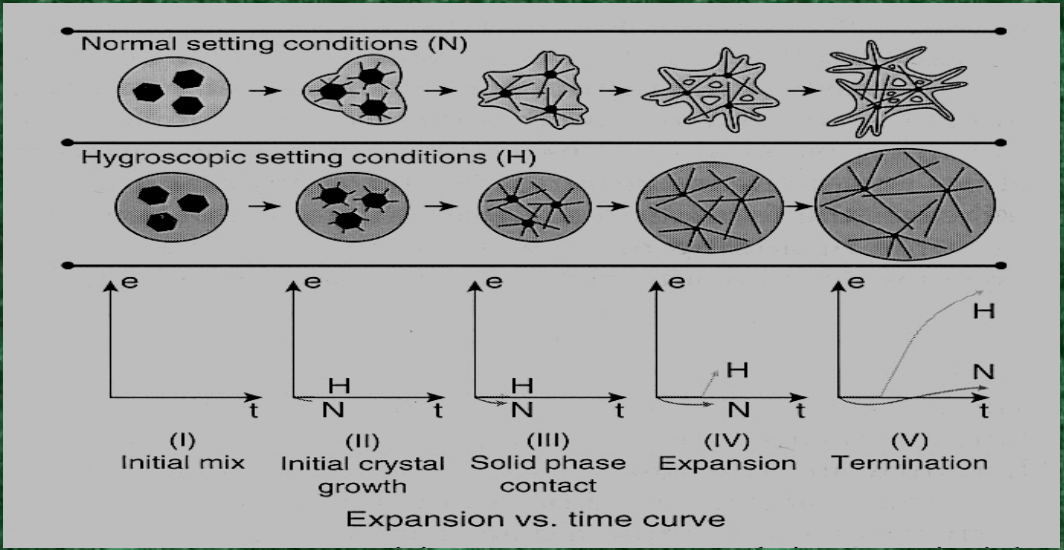
- Sodium Chloride (upto 2% of hemihydrate)
- Sodium Sulfate (max. effect at 3.4%)
- Potassium Sulfate (>2%)
- Potassium Tartrate

Retarders:- Citrates, acetates & borates

HYGROSCOPIC SETTING EXPANSION

- Setting expansion that occurs under water is called as "Hygroscopic Setting Expansion."
- Setting expansion without water immersion is called "Normal Setting Expansion."

Stages of Hygroscopic setting expansion:-



Expansion vs. time curve

STRENGTH

- 2 Strength properties of gypsum are:-

  1. WET STRENGTH (Green Strength):-

  Strength obtained when the water in excess of that required for hydration of the hemihydrate is left in the test specimen.

  2. DRY STRENGTH:-

  Strength obtained when the excess water in the specimen has been driven off by drying.

- Strength depends upon:-

1. Addition of Accelerators & Retarders.
2. W:P ratio

Effect of W:P ratio & Mixing time on the Compressive Strength of plaster of paris

W/P ratio	Mixing time (min)	Compressive strength (MPa)	Compressive strength (psi)
0.45	0.5	23.4	3400
0.45	1.0	26.2	3800
0.60	1.0	17.9	2600
0.60	2.0	13.8	2000
0.80	1.0	11.0	1600

- COMPRESSIVE STRENGTH:-

- Compressive strength is inversely related to the W:P ratio of the mix.

Effect of W:P ratio on the Compressive Strength of different materials

Material	W/P Ratio (ml/g)	Compressive Strength (MPa)
Model plaster	0.45	12.5
	0:50	11.0
	0.55	9.0
Dental stone	0.27	31.0
	0.30	20.5
	0.50	10.5
High-strength dental stone	0.24	38.0
	0.30	21.5
	0.50	10.5

- After final setting time the hardened gypsum material appears dry & has maximum strength.

Effect of Drying on the Compressive Strength of plaster of paris

Drying period (hr)	Compressive strength (MPa)	Compressive strength (psi)	Loss in weight (%)
2	9.6	1400	5.1
4	11.7	1700	11.9
8	11.7	1700	17.4
16	13.0	1900	—
24	23.3	3400	18.0
48	23.3	3400	18.0
72	23.3	3400	—

- Effect of drying is reversible, soaking a dry cast in water reduces its strength to the original level.

SURFACE HARDNESS & ABRASION RESISTANCE

- Surface hardness of gypsum materials is related to their compressive strength.
- Surface hardness increases at a faster rate than the compressive strength.
- Abrasive Resistance of gypsum product is ↑ ed by impregnating the set gypsum with epoxy resins.
- Surface hardness of set gypsum is improved by mixing stone with a hardening solution containing colloidal silica(about 30%).

VISCOSITY

- It is the resistance of a fluid to flow.

Viscosity of several High Strength Dental Stones & Impression Plaster

Material	Viscosity (cp)
High-strength dental stone*	
A	21,000
B	29,000
C	50,000
D	54,000
E	101,000
Impression plaster	23,000

REPRODUCTION OF DETAIL

- Gypsum dies do not reproduce surface detail as well as electroformed or epoxy dies.
- Air bubbles are formed at the interface of impression & gypsum cast.
- Contamination of the impression(by saliva or blood) in which the gypsum die is poured can also affect the detail reproduction.

PROPORTIONING, MIXING & CARING FOR GYPSUM PRODUCTS

- PROPORTIONING:-

  - Strength of a stone is inversely proportional to the W:P ratio.

- MIXING:-

  - Trapping of air should be avoided while mixing to avoid porosity – weak spots & surface inaccuracies.

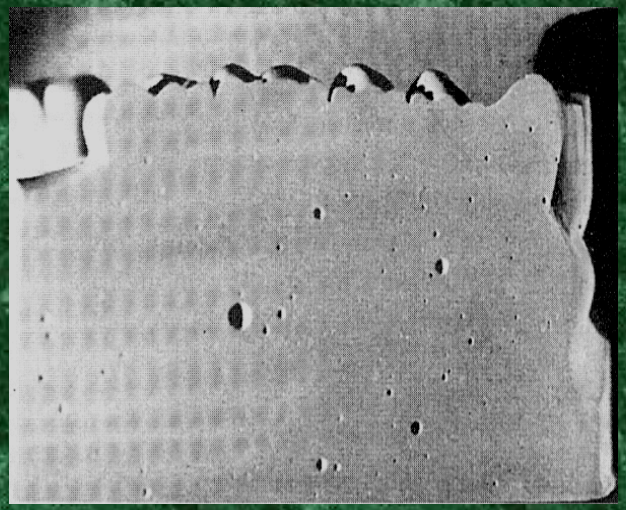
  - Longer spatulation ⟶ ↓es working time

  - Method of mixing:-

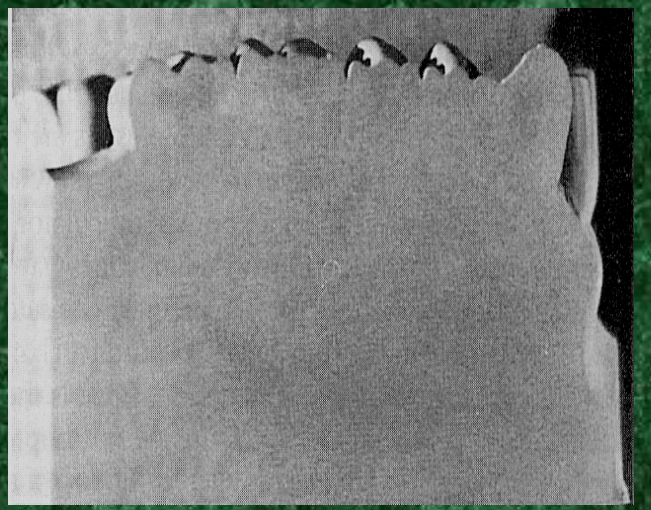
Add measured water

↓

Gradual addition of the preweighed powder



Section through a cast of a set stone that was improperly mixed



Section through a cast of a set stone that was properly proportioned & mixed

- CARING FOR THE CAST:-

  - Once the setting reaction in the cast is completed, its dimensions remain constant under room temperature & humidity.

  - If stone cast is immersed in running water, its linear dimensions may ↓ 0.1% for every 20min. of immersion.

  - If storage temperature is raised to 90º &110ºC – shrinkage occurs

- SPECIAL GYPSUM PRODUCTS:-

  - White stone or plaster – longer working time

  - Gypsum products used for mounting casts are called as "mounting stones or plasters"- fast setting & ↓ ed setting expansion.

- ## CARING FOR GYPSUM PRODUCT:-

- All types of gypsum products should be stored in a dry atmosphere.
- Products should be sealed in a moisture proof metal container.

- ## INFECTION CONTROL:-

- If an impression has not been disinfected, it is necessary to disinfect the stone cast.
- Disinfection solutions that do not adversely affect the quality of the gypsum product can be used.
- Dental stone containing a disinfectant may also be used.
- Useful disinfectants for stone casts include spray disinfectants, hypochlorites, & iodophores.

CONCLUSION

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