Gypsum products and investment materials

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Gypsum products

Indications: models, casts, dies

Preparation:

Thermal decomposition (**dehydratation**, calcination) of natural or artificial $CaSO_4 . 2H_2O$ (gypsum)

$$CaSO_4 . 2H_2O \xrightarrow{110\text{-}130^oC} CaSO_4 . 0.5H_2O + 1.5H_2O$$

Calcium sulfate dihydrate (monoclinic)

In an open reactor - calcium sulfate β-hemihydrate (orthorhombic)

130-200°C anhydrite

(producing a low strength gypsum)

Properties and types of gypsum products depend on dehydration conditions

*Dentistry - Types of gypsum products EN ISO 6873, **five types***

Decomposition in an open reactor: β-hemihydrate (**Plaster of Paris**, impression, model plaster), ***Type 1 and 2 gypsum products***

Decomposition in the presence of water steam under pressure: α-hemihydrate (model gypsum, hydrocal gypsum/**dental stone**/**stone**, ***Type 3 gypsum products***)

Decomposition in the presence of $CaCl_2$: α-hemihydrate (**die stone/high-strength dental stone/Densite**, ***Type 4 and 5 gypsum products***)

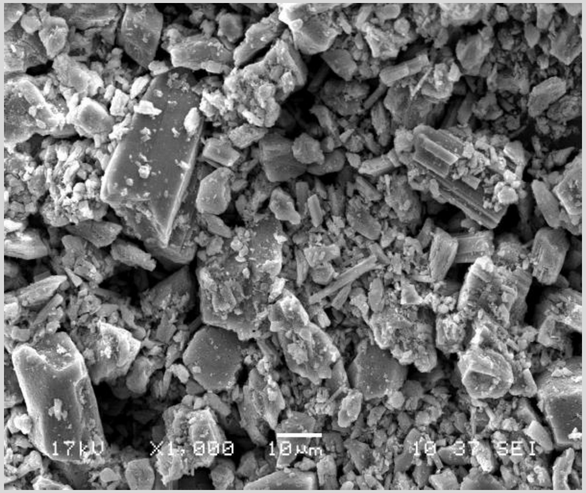
The same chemical composition, crystallographical modification, but differences in shape, size and porosity of crystals

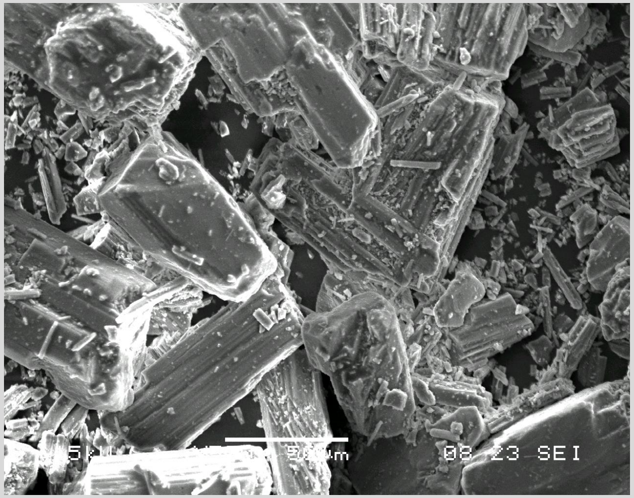
$CaSO_4 . 2H_2O$

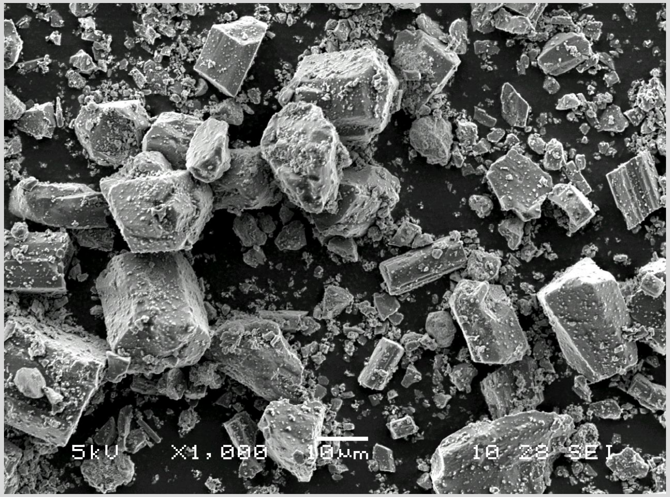
Open reactor*

Pressure, steam H_2O

Boiling, $CaCl_2$







$CaSO_4 . 0.5H_2O$

β-hemihydrate
Plaster of Paris
Small, irregular crystals, ***spongy***, *high porosity*
mixing ratio 50-60 mL H_2O /100 g powder

α-hemihydrate
Stone, hydrocal
Large prismatic, more regular, **low porosity** ***crystals***, mixing ratio 30-35 mL/100 g

α-hemihydrate
Die stone, high strength dental stone
Small, ***dense*** crystals of ***low porosity***
mixing ratio 19-24 mL/100 g

Setting reaction:

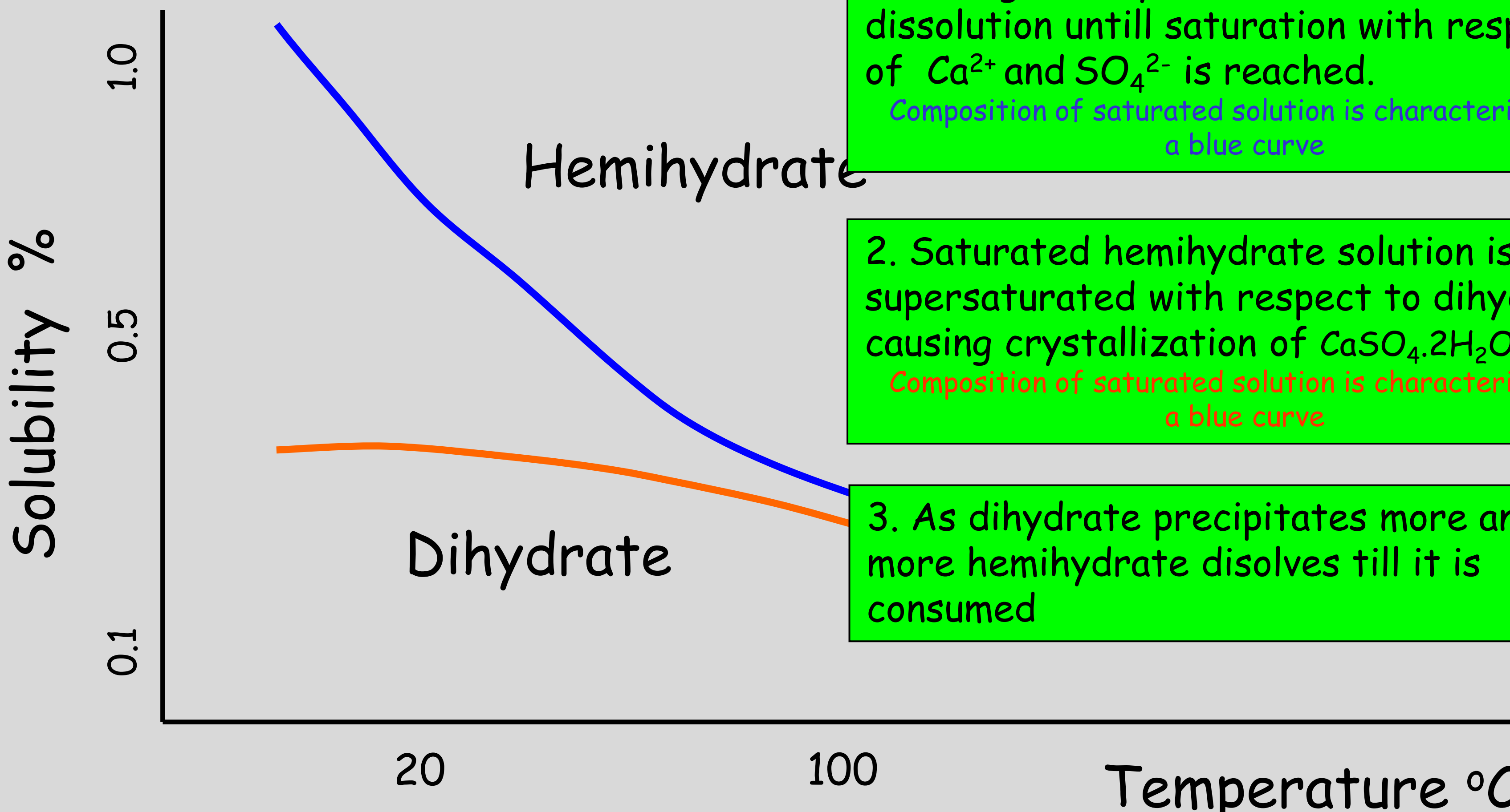
$$CaSO_4.0.5H_2O + 1.5H_2O \longrightarrow CaSO_4.2H_2O + heat$$

β,α-hemihydrate   dihydrate, gypsum

1. Mixing hemihydrate with water – its dissolution untill saturation with respect of Ca^{2+} and SO_4^{2-} is reached.
Composition of saturated solution is characterized by a blue curve

2. Saturated hemihydrate solution is supersaturated with respect to dihydrate causing crystallization of $CaSO_4.2H_2O$
Composition of saturated solution is characterized by a blue curve

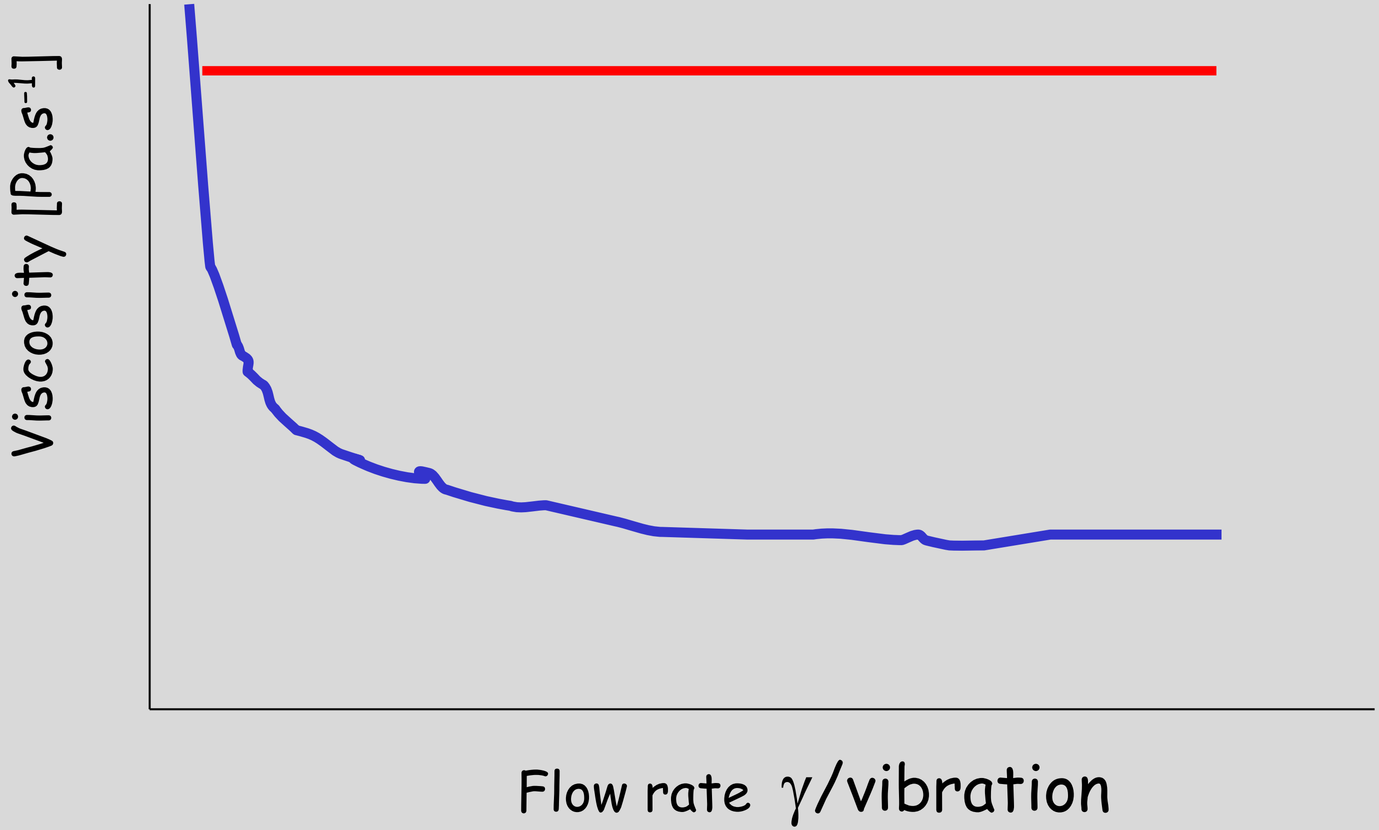
3. As dihydrate precipitates more and more hemihydrate disolves till it is consumed



Important properties of gypsum products

1. Pseudoplasticity (shear thinning)

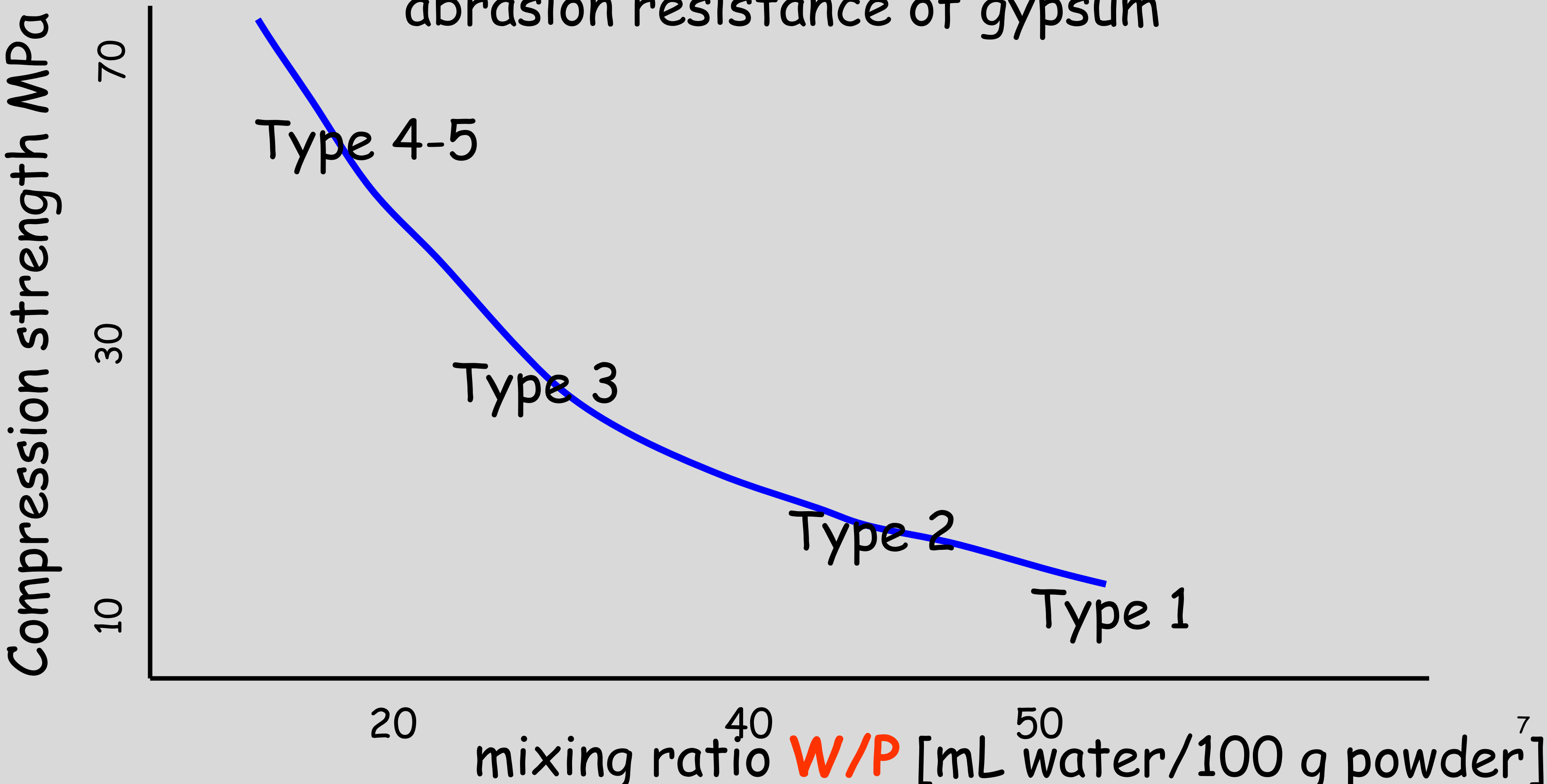
A decrease in viscosity with shear rate e.g - mixing, vibrations, flow with the aim to increase the ability of mixed plaster to flow into the impresion details



2. Strength

Theoretical water requirement: 19 mL/100 g $CaSO_4 . 0.5H_2O$

Excess of water (above theoretical value and necessary to prepare workable mass which can be poured into an impression) **evaporates** leaving **voids and porosity** which decrease strength and abrasion resistance of gypsum

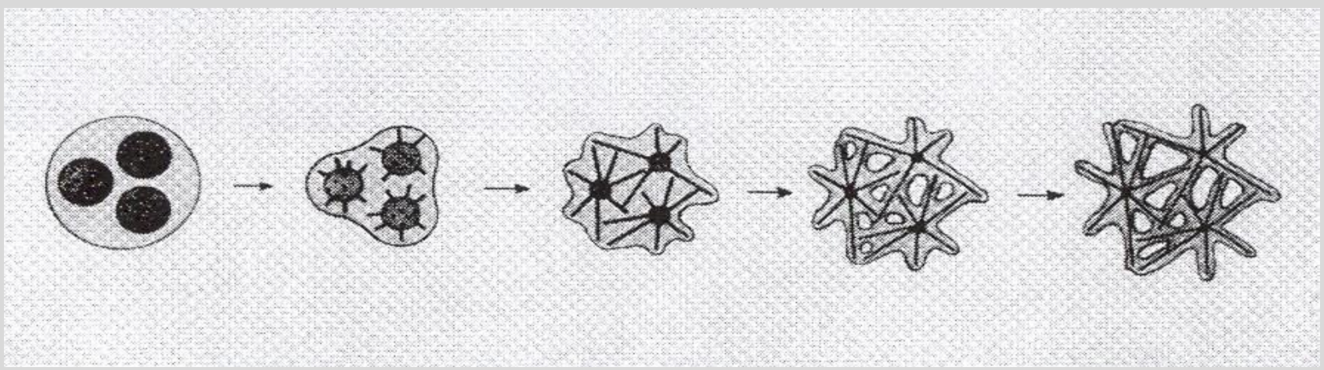


3. Setting expansion

Theoretical setting shrinkage is app. 2.4 lin. % (6.9 vol. %) but in reality gypsum expands during its setting from 0.1 to 0.3 lin. %

Needle-like crystals grow freely – crystals push each other from a nucleation centre and increase the volume occupied resulting in **setting expansion**. Their size is, however, constrained by surface tension of water

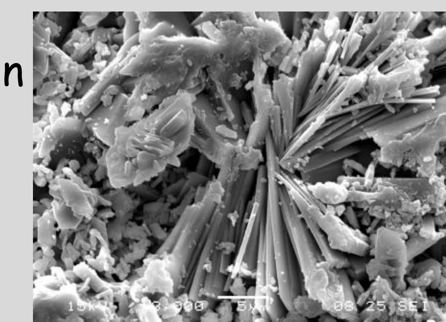
Normal setting conditions - crystals are pushed from each other



Plaster – max. 0.2-0.3 lin. %

Stones - max 0.08-0.15 lin. %

initial mix | crystal growth | close contact of crystals | expansion | Termination of crystal growth

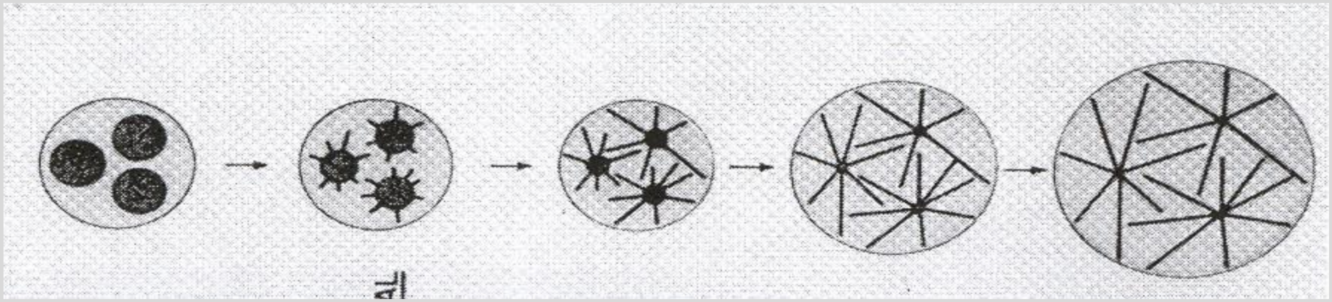


Mahler DB, Ady AB. Explanation for the hygroscopic setting expansion of dental gypsum products. J Denr Res 1960, p. 578

4. Hygroscopic expansion

An increase in the expansion when dihydrate crystalizes under water - hygroscopic expansion – (5-6 higher compared to setting expansion) as a result of not constrained crystal growth by the surface tension of hemihydrate solution.

Hygroscopic setting conditions



initial mix | crystal growth | close contact of crystals | expansion | termination

Mahler DB, Ady AB. Explanation for the hygroscopic setting expansion of dental gypsum products. J Denr Res 1960, p. 578

How physical and mechanical properties of gypsum produts can be controlled?

1. Control of setting rate using chemicals:

a) gypsum manufacturer

Accelerators:

Potassium sulfate increases the rate of dihydrate crystallization and decreases setting expansion

Retarders:

Borax, NaCl, citric acid – cover hemihydrate particles with calcium salts less soluble than the sulfate – **reduce** hemihydrate dissolution - prolongs setting time and lowers gypsum expansion

Alginates, agar - usually form layers on hemihydrate particles inhibiting their dissolution and inhibiting growth of dihydrate crystals

b) by a technician/dentist

1. Gypsum debries in the mixing bowl – act as nuclei of crystallization – accelerate setting

2. Alginate debries in the mixing bowl – act as nucleation inhibitor - usually form layers on hemihydrate particles inhibiting their dissolution and inhibiting growth of dihydrate crystals-decrease setting rate

3. Prolonged and rapid mixing – accelerate hemihydrate dissolution – accelerate setting (more dihydr. nuclei)

4. More water – nuclei are formed slowly – setting is prolonged, higher porosity - decreased strength

2. Improvement of gypsum strength and abrasion resistance:

- Drying a gypsum model
- Using ***special*** colloidal sols of SiO_2 (contain app. 30 % SiO_2 in water) to mix the gypsum powder

3. Decreasing the gypsum setting expansion

- decreased mixing ratio W/P (water/powder)

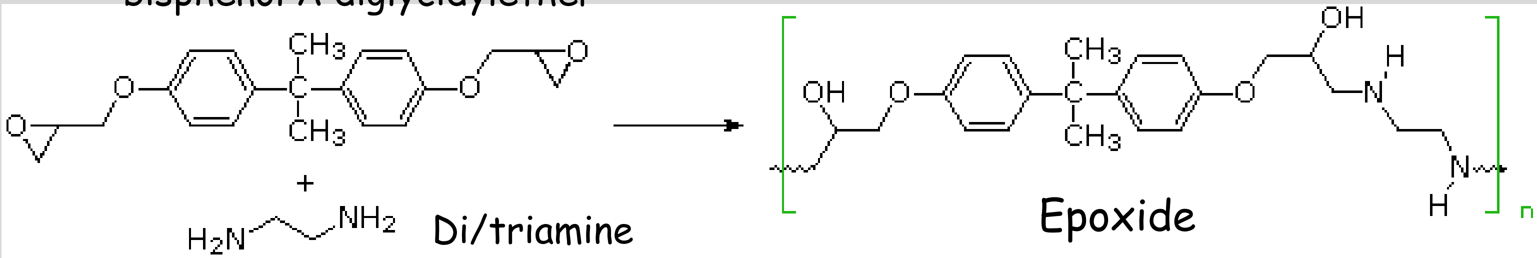
- by reducing hygroscopic expansion - after initial setting **avoid** contact of a model with water stimulating growth of needle-like dihydrate crystals and volume expansion

Remember: more intensive and longer mixing increases number of nucleation centres and thus mutual interaction between crystalls and **supports the setting** expansion - negative effect on model accuracy

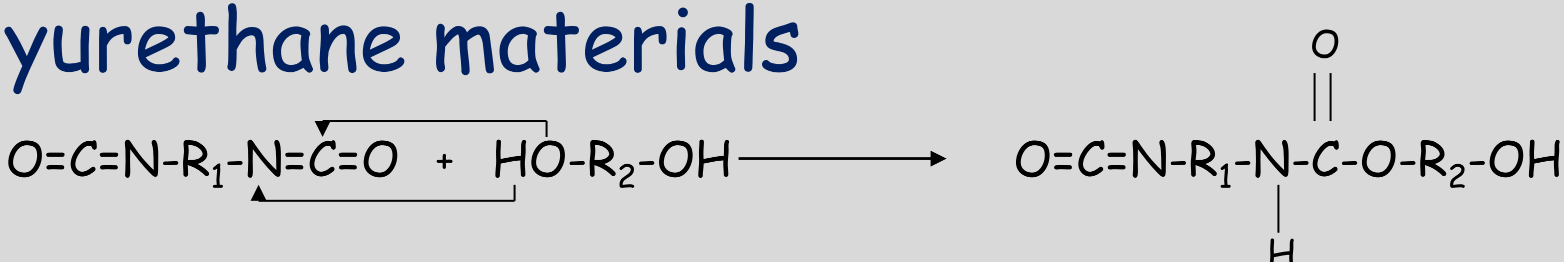
Other types of model materials

Epoxid-based materials

bisphenol A diglycidylether



Polyurethane materials



Alkyl, aryl diisocyanate Diol

uretane

Higher strength and abrasion resistance, excellent surface quality but higher polymerization shrinkage.

Investment materials

Indications: casting mould preparation

Main requirements:

1. Resistance to high temperatures of molten metals, mechanical strength to resist pressures during preheating and casting, permeability to gasses

2. Compensation of metal solidification shrinkage by the mould expansion

Composition:

1. Refractory component (filler)
2. Inorganic binder

Types of investment materials

1. Gypsum-bonded investment materials – casting of Au alloys melting point <1000°C

2. Phosphate-bonded investment materials – casting of Cr-Co/Cr-Ni, Ag-Pd etc alloys, melting point app. 1500°C, but also Au alloys

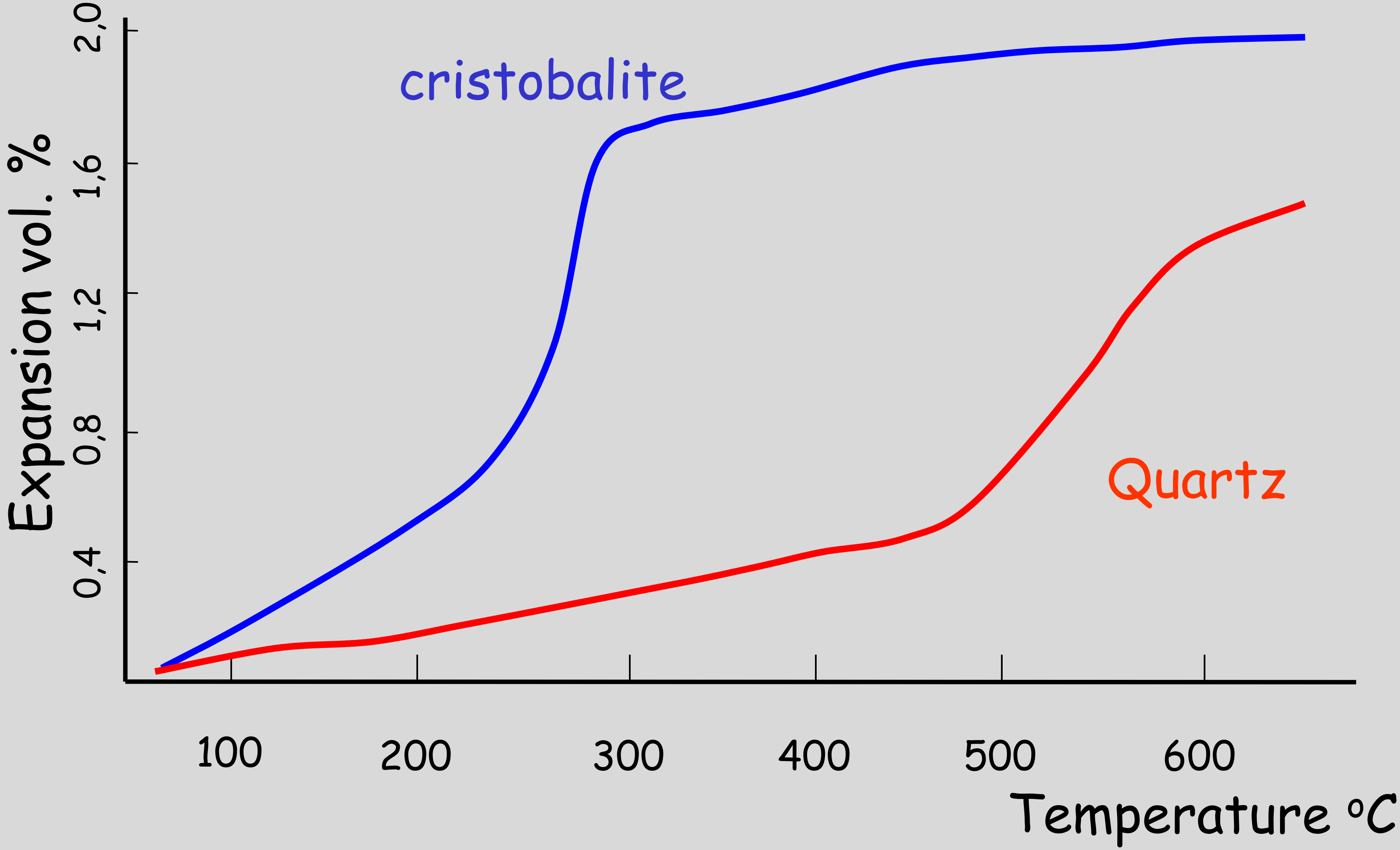
Types of refractories:

Allotropic modifications of SiO_2 (quartz, cristobalite, tridymite)

1. Cristobalite – transformation from α to β modification at 275°C
2. Quartz – α to β tranformation at 575°C

Modification of SiO_2	Crystal system	Transformation temperature [°C]	Density [g/cm³]
α-cristobalite	tetragonal	220-270	2.33
β-cristobalite	cubic		2.20
α-quartz	trigonal	App. 550-570	2.65
β-quartz	hexagonal		2.53

Thermal expansion of cristobalite and quartz



Gypsum-bonded investment materials

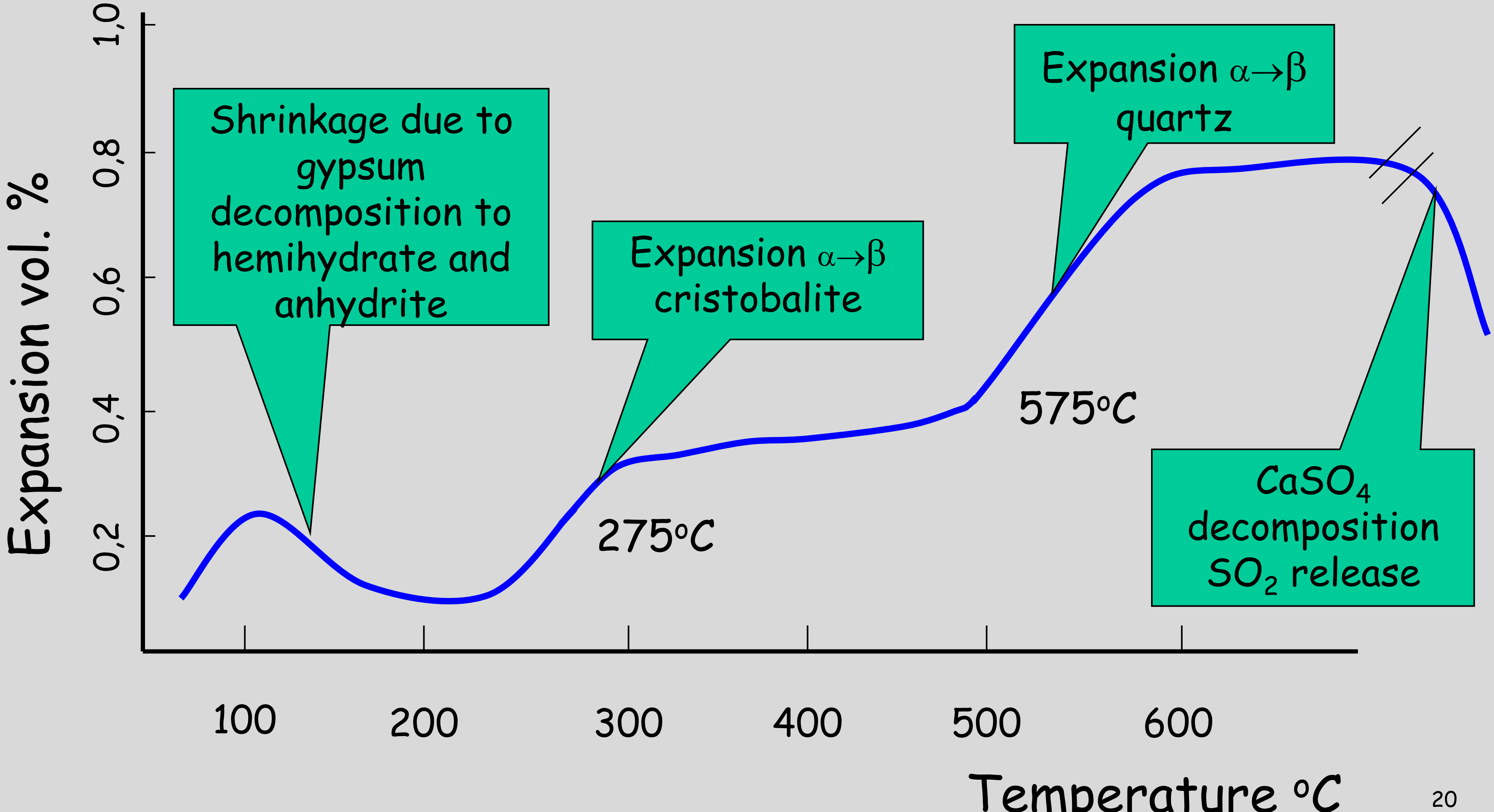
Composition:

- α-hemihydrate $CaSO_4.0.5H_2O$
- Quartz, cristobalite (broader range of expansion temperatures to reduce internal stresses during the mold preheating)
- Setting regulators of gypsum

Setting reaction (mixing with water):

$$\underset{\alpha\text{-hemihydrate}}{CaSO_4.0.5H_2O} + 1.5H_2O \longrightarrow \underset{\text{gypsum}}{CaSO_4.2H_2O} + \text{heat}$$

Typical volume changes of gypsum-bonded investment materials during heating



Phosphate-bonded investment materials:

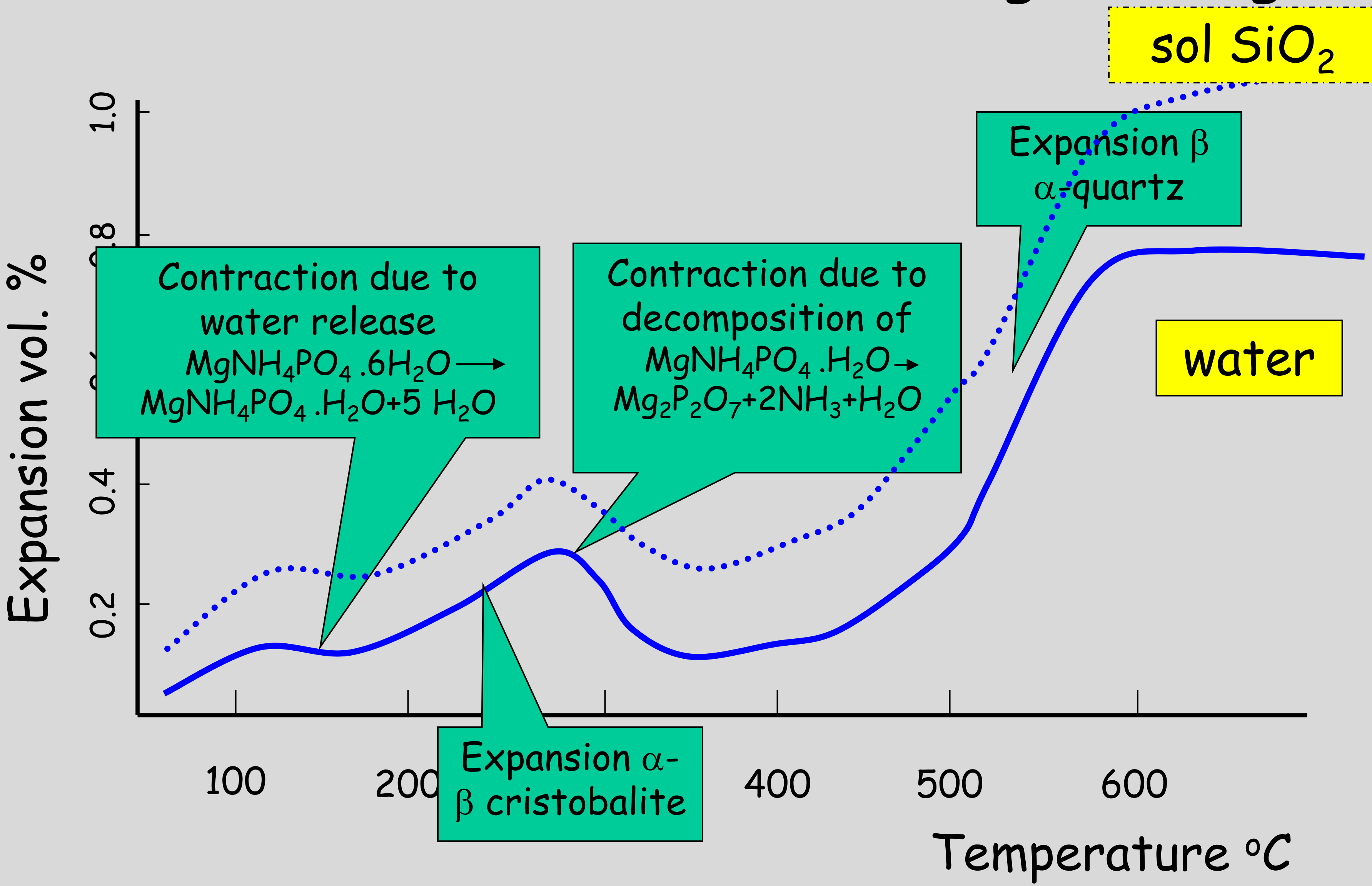
Composition:

- MgO, $NH_4H_2PO_4$
- Quartz, cristobalite
- Adittives – graphite (reduction of metal surface oxidation

Setting reaction after mixing with water:

$$MgO + NH_4H_2PO_4 + 5H_2O \longrightarrow MgNH_4PO_4 \cdot 6H_2O + \text{heat}$$

Typical volume changes of phosphate-bonded investment materials during heating



Expansion control:

- By using mixtures of cristobalite and quartz (also to decrease expansion stresses during molds heating and risk of mold fractures)
- Mixing with SiO_2 sols