Gypsum products and investment materials

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Gypsum products

Indications: models, master casts, dies

Preparation:

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

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

Calcium sulfate dihydrate
monoclinic

Calcium sulfate hemihydrate
(orthorhombic)+impurities, anhydrite

110-130°C	plaster (gypsum powder) ($CaSO_4.0.5H_2O$)
130-200°C	γ-anhydrite (soluble $CaSO_4$)
200-1000°C	β-anhydrite (insoluble $CaSO_4$)

Properties and types of gypsum products depend on dehydration conditions

Decomposition in an open reactor: β-hemihydrate (Plaster of Paris, Type I a II[1] gypsum products)

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

Boiling in the presence of $CaCl_2$: α-hemihydrate (die stone/ high-strength dental stone/Densite, Type IV a V gypsum p.)

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

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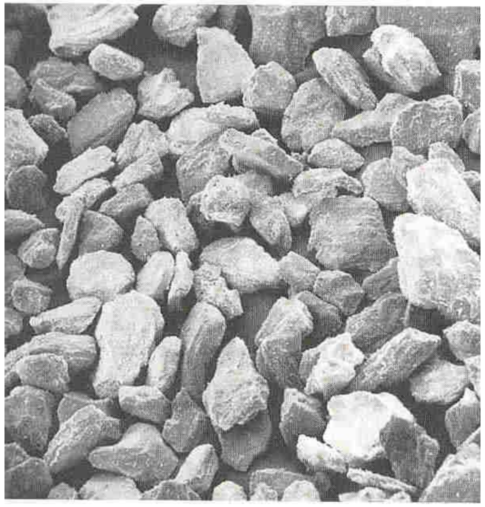
[1] *Dentistry - Types of gypsum products EN ISO 6873, five types*

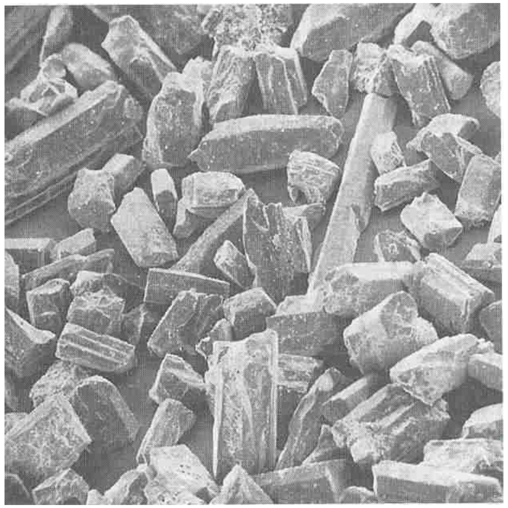
$CaSO_4 . 2H_2O$

Open reactor



Pressure, 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

Prismatic, more regular, low porosity crystals, mixing ratio 30-35 mL/100 g

α-hemihydrate

Die stone, high-strength dental stone

Large, dense crystals of low porosity

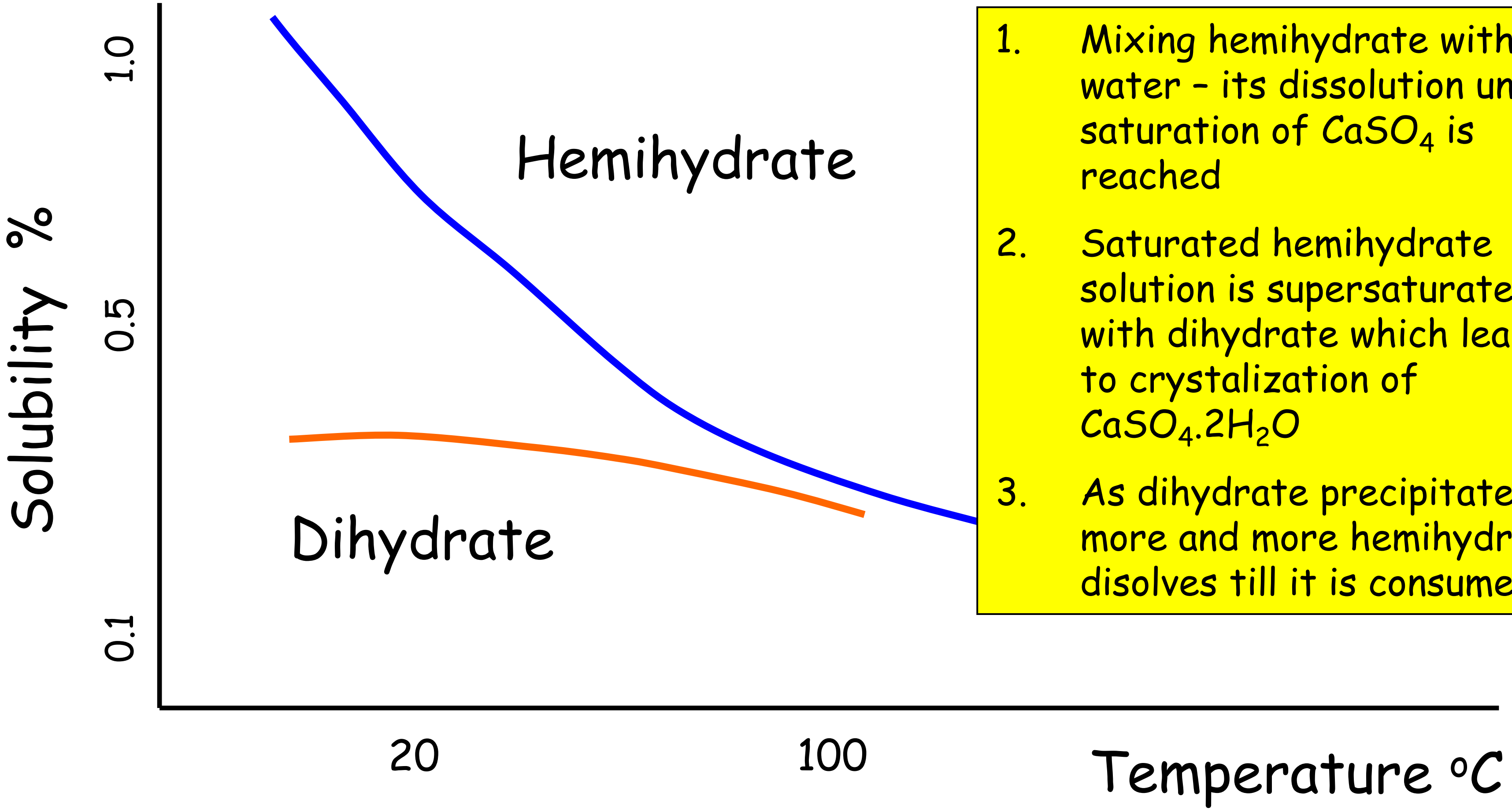
mixing ratio 19-24 mL/100 g

Phillips´ Science of Dental Materials, 11th. edition

Setting reaction:

$$CaSO_4.0.5H_2O + 1.5H_2O \rightarrow CaSO_4.2H_2O + \text{heat}$$

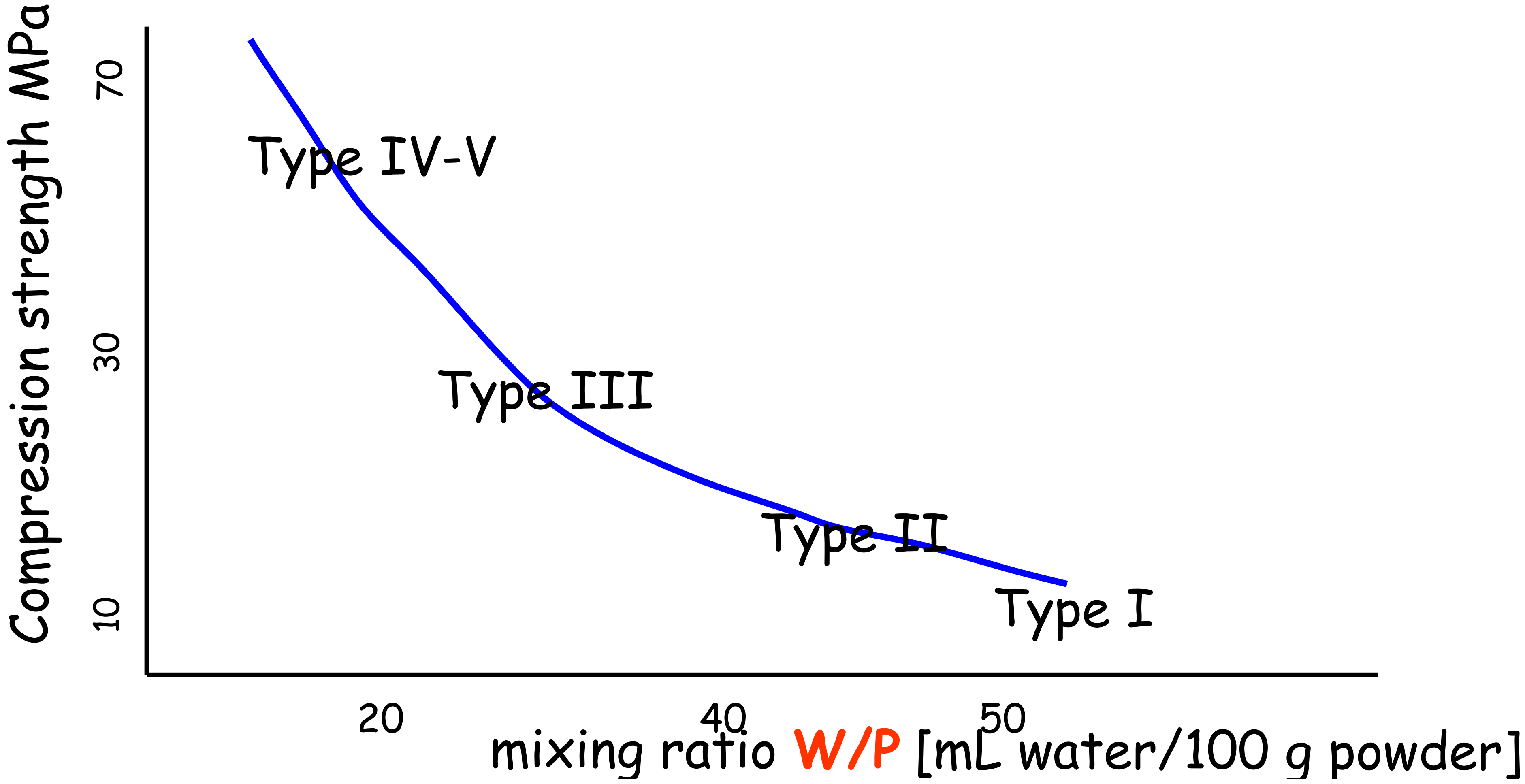
β,α-hemihydrate dihydrate, gypsum



1. Mixing hemihydrate with water – its dissolution untill saturation of $CaSO_4$ is reached
2. Saturated hemihydrate solution is supersaturated with dihydrate which leads to crystalization of $CaSO_4.2H_2O$
3. As dihydrate precipitates more and more hemihydrate disolves till it is consumed

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

Excess of water evaporates leaving voids and porosity which decreases the strength and abrasion resistance of gypsum

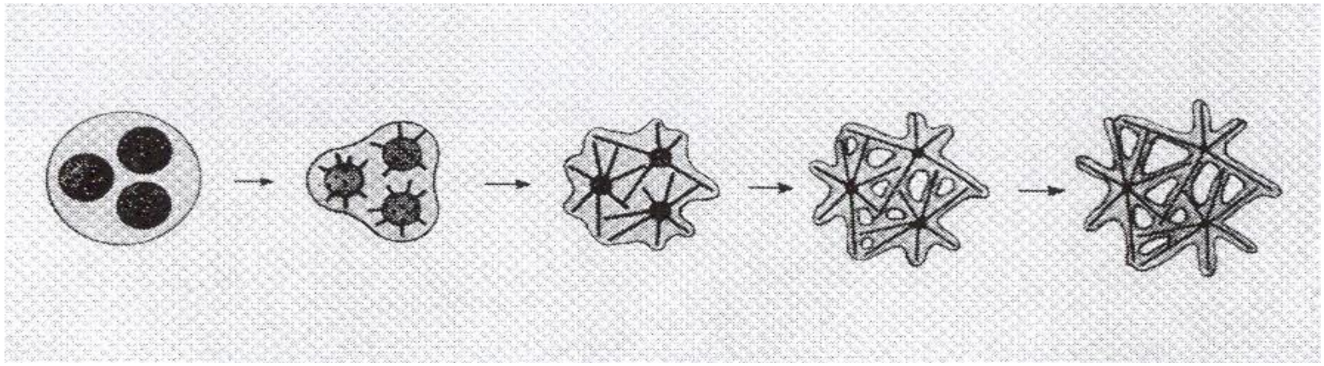


Theoretical setting shrinkage: 6.9 vol. %

In reality setting expansion: from 0.1 to 0.3 vol. %

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

Normal setting conditions



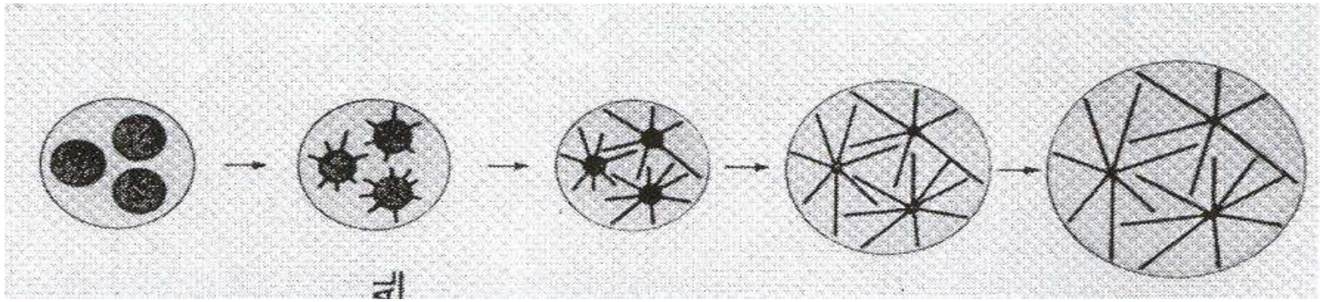
initial mix — crystal growth — close contact of crystals — expansion — termination

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

Hygroscopic expansion:

An increase in the expansion when dihydrate crystalizes under water - hygroscopic expansion – (e.g. from 0.15 % to 0.30 vol. %) as a result of not constrained crystal growth by the surface tension

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
- chemical additives in the produts:

Accelerators:

Inorganic salts - potassium sulfate (concentration >2 wt.%), NaCl (<2 wt.%), Na_2SO_4 (<3.5 wt. %), sodium/potasium tartrate by increasing hemihydrate dissolution

Retarders:

Alginates, agar, borax, citric acid – usually by forming protective layers on hemihydrate particles which inhibit their dissolution and inhibit growth of gypsum crystals

2. Control of setting rate – in the cabinet:

Faster setting:

1. Rest of $CaSO_4.2H_2O$ in the powder from the calcination process or gypsum debries in the mixing bowl – act as nuclei of crystallization

2. Prolonged and rapid mixing – accelerate hemihydrate dissolution

3. Small particle size – increases rate of hemihydrate dissolution

Slower setting:

1. More water – less nuclei formed and less supersaturation

3. Improvement of gypsum strength and abrassion resistance:

1. Drying a gypsum model
2. Using colloidal sols of SiO_2 (contain up to 30 % SiO_2 in water) to mix the gypsum powder

Investment materials

Indications: casting mould preparation

Main requirements:

1. Compensation of metal solidification shrinkage by the mould expansion

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

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 Co-Cr-Mo, Ag-Pd etc alloys, melting point app. 1500°C
3. Ethyl silicate-bonded investment

Types of refractories:

Allotropic modifications of SiO_2 (quartz, cristobalite, tridymite)

1. Cristobalite – transformation from β to α modification at 270°C
2. Quartz – β to α tranformation at 575°C

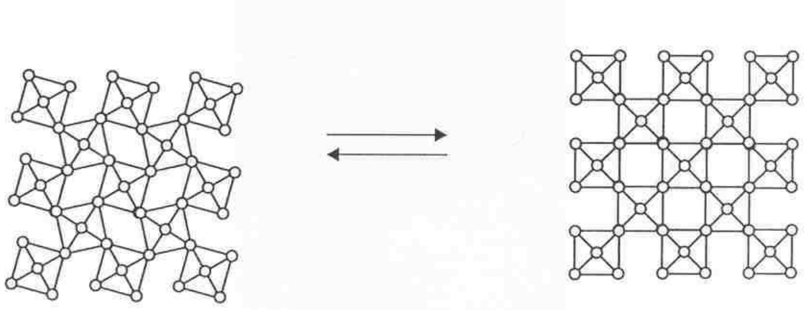
Modification of SiO_2	Crystal system	Temperature of transformation [°C]	Density [g/cm^3]
β-cristobalite	tetragonal	220-270	2.33
α-cristobalite	cubic	270-1700	2.20
β-quartz	trigonal	<575	2.65
α-quartz	hexagonal	575-1050	2.53

Low to high temperature transformation of SiO_2

β low quartz

575°C

α high quartz



a)

b)

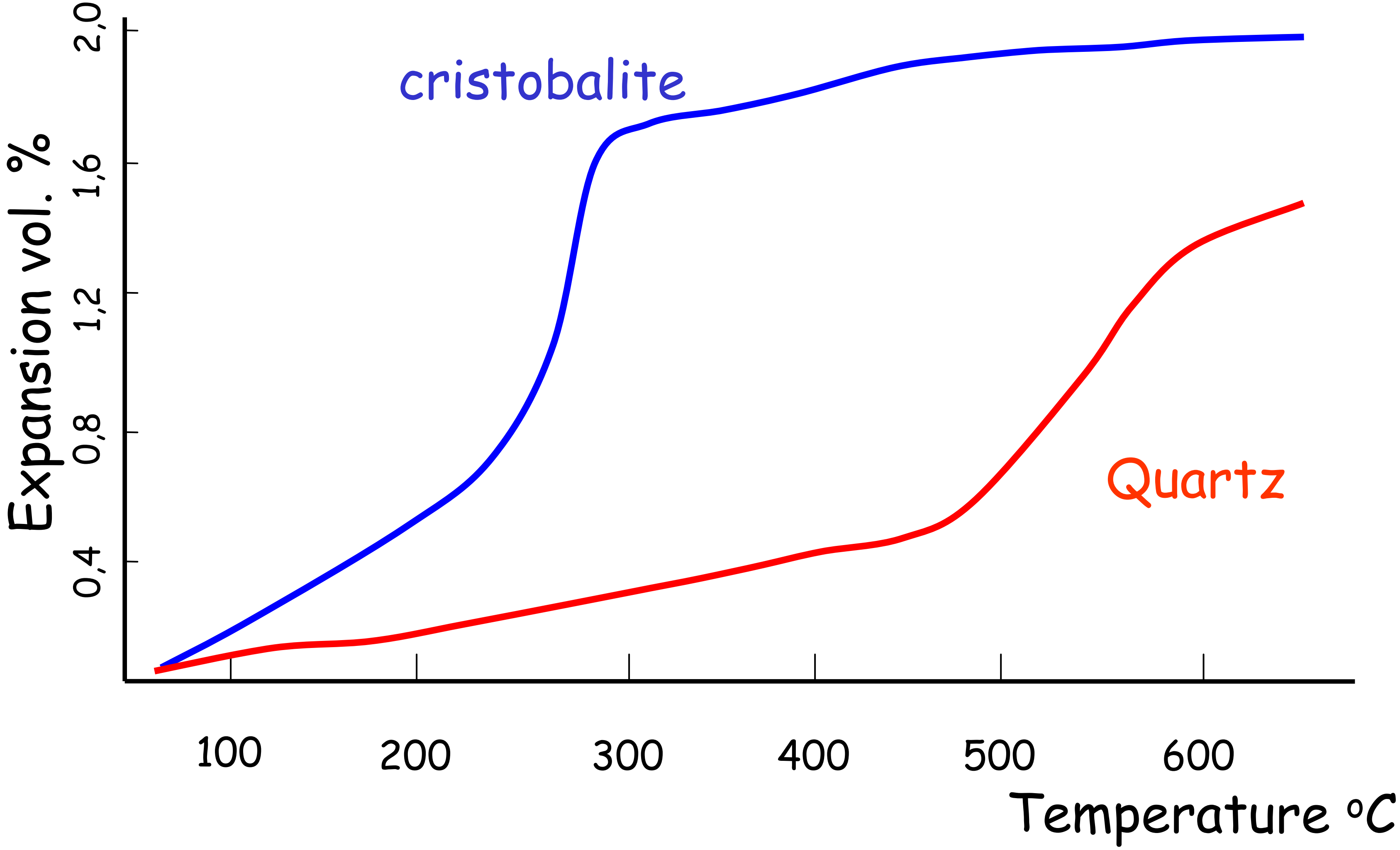
Fast reversible transformation

Increase in volume:

Quartz - by 4.7 vol. %

Cristobalite – by 5.9 vol. %

Thermal expansion of cristobalite and quartz



Gypsum-bonded investment materials

Composition:

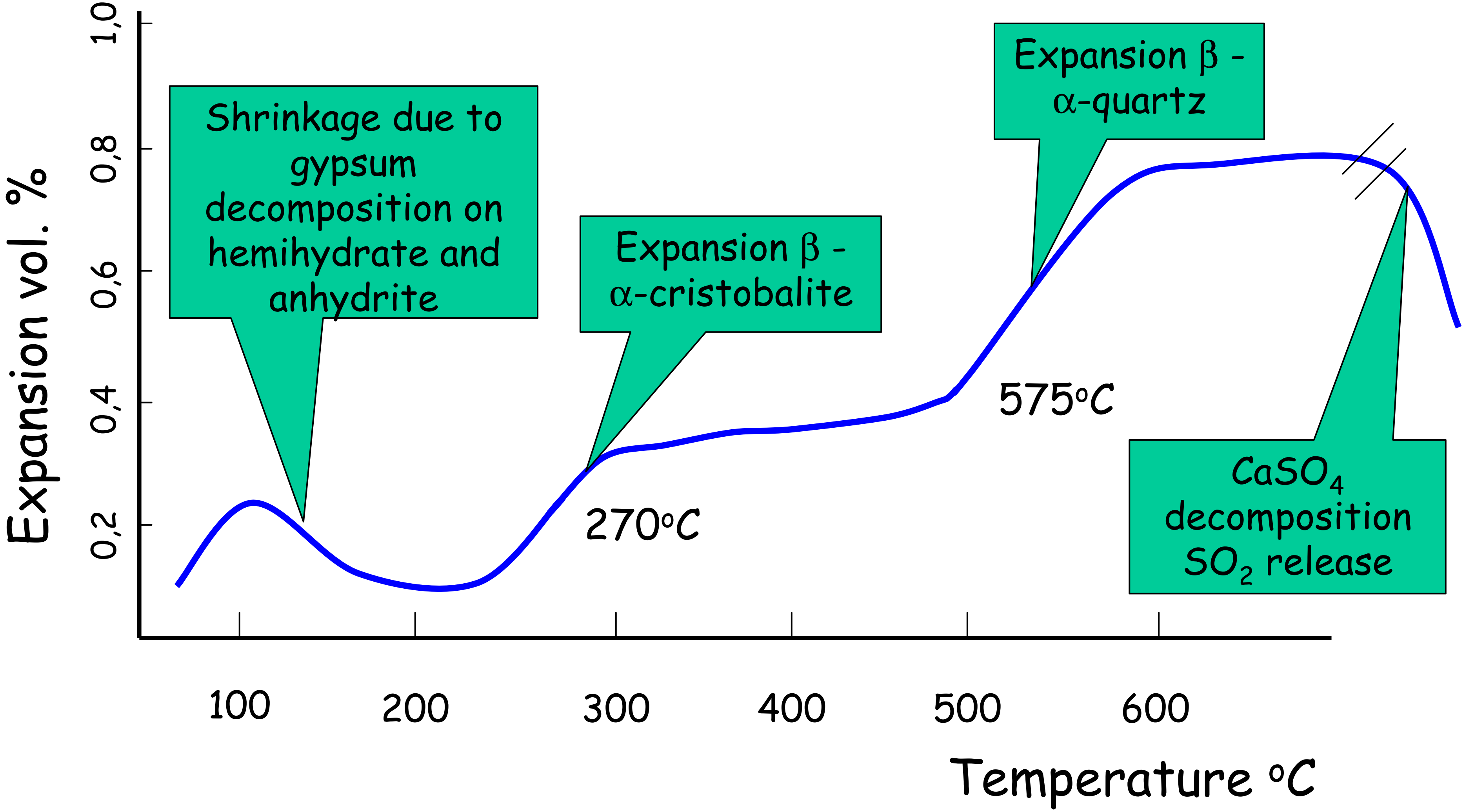
- α-hemihydrate $CaSO_4.0.5H_2O$
- Quartz, cristobalite (broader range of expansion temperatures to reduce internal stresses during mold preheating)
- Setting regulators of gypsum

Setting reaction (mixing with water):

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

α-hemihydrate gypsum

Typical volume changes of gypsum-bonded investment materials during heating



Phosphate-bonded investment materials:

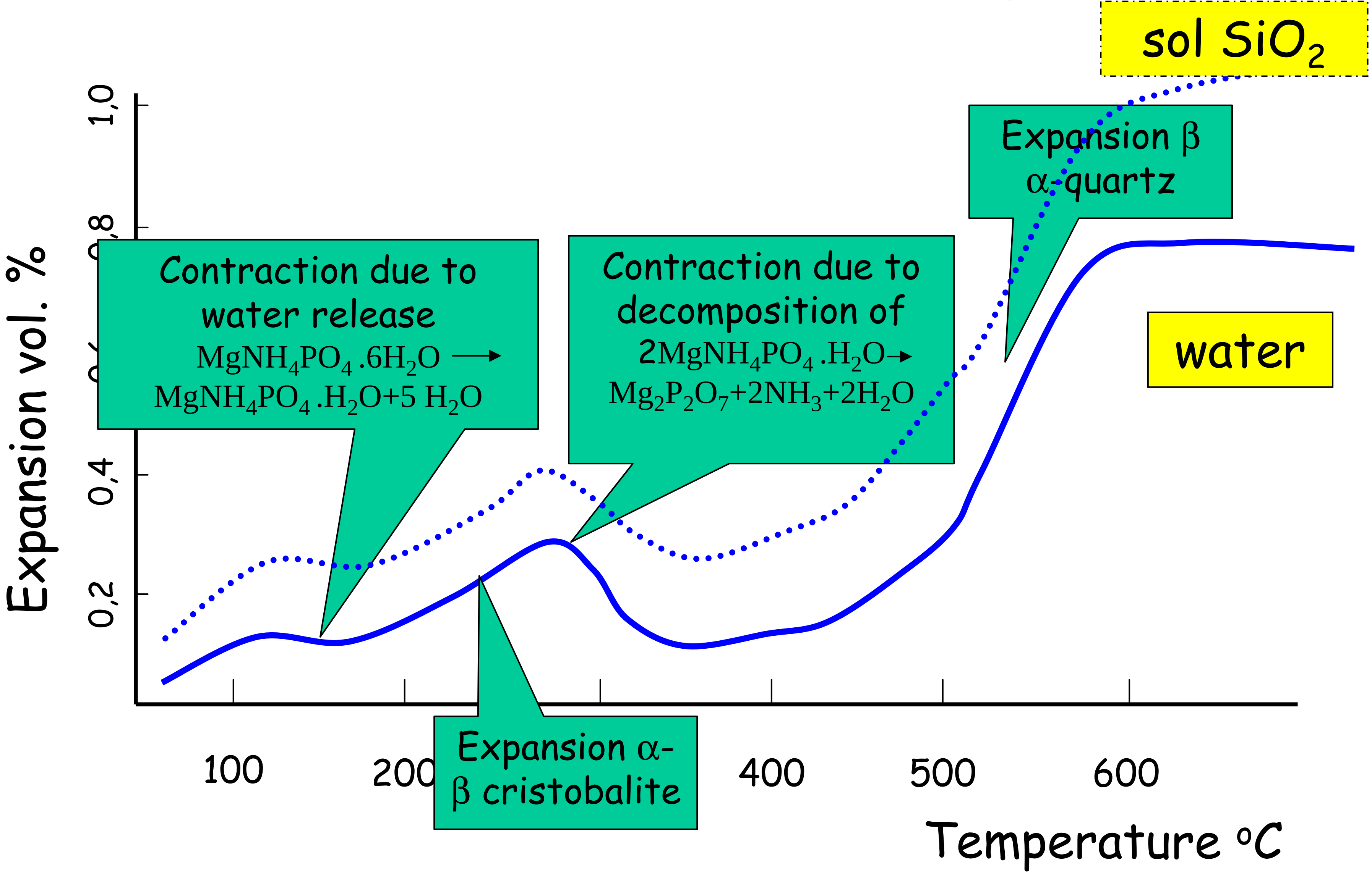
Composition:

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

Setting reaction after mixing with water:

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

Typical volume changes of phosphate-bonded investment materials during heating



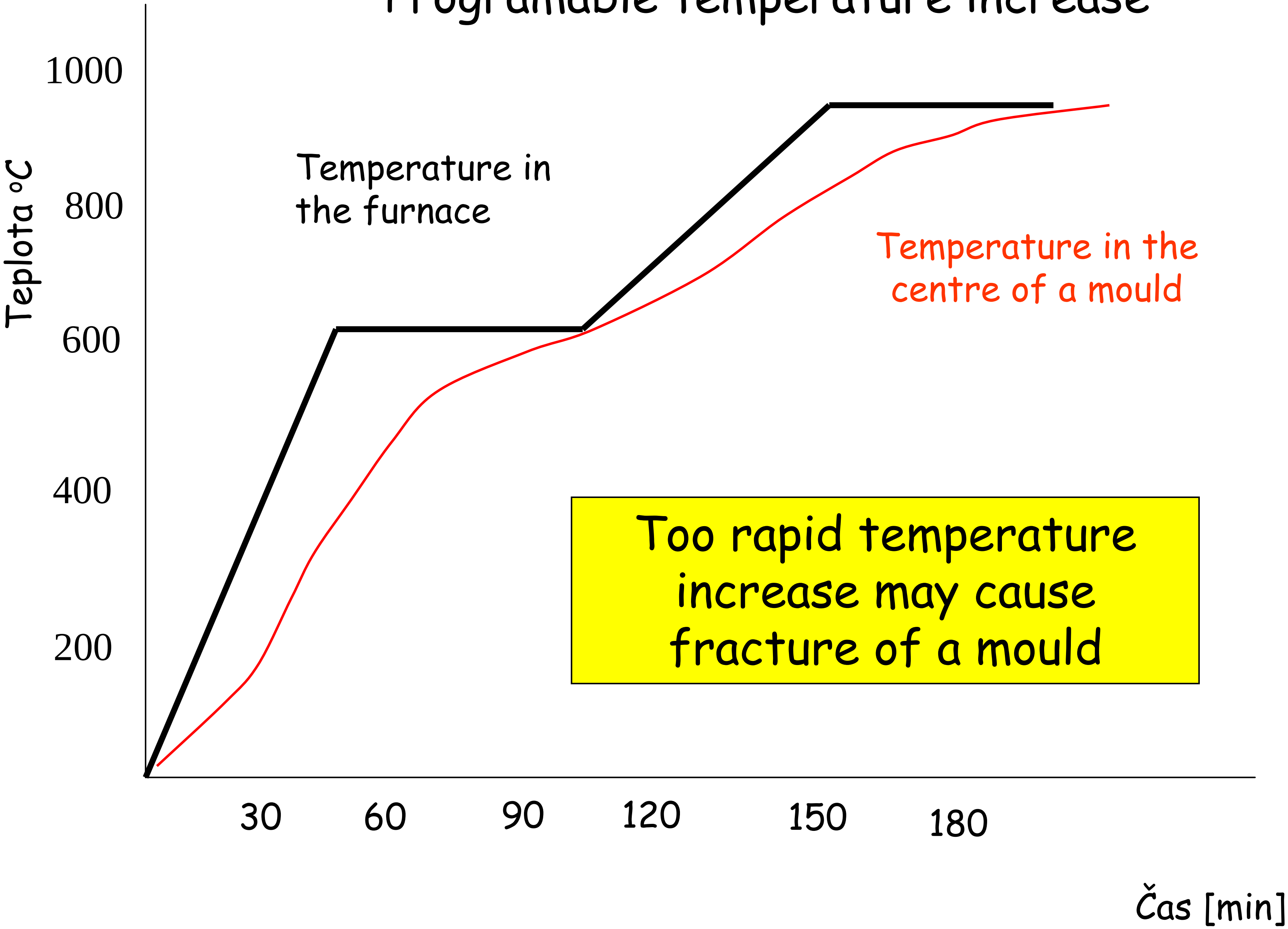
Contraction due to water release
$MgNH_4PO_4 . 6H_2O \longrightarrow MgNH_4PO_4 . H_2O + 5 H_2O$

Contraction due to decomposition of
$2MgNH_4PO_4 . H_2O \rightarrow Mg_2P_2O_7 + 2NH_3 + 2H_2O$

Expansion β α-quartz

Expansion α-β cristobalite

Programable temperature increase



Too rapid temperature increase may cause fracture of a mould

Possibilities of expansion control:

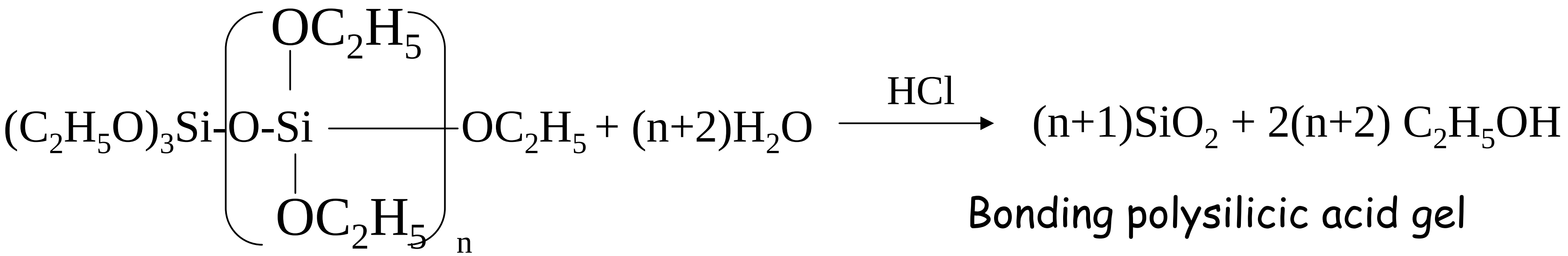
- Special liquids of SiO_2 colloidal sols to increase setting expansion

Ethylsilicate-bonded investment

Composition:

- Ethylsilicate (tetraethoxysilane)
- Quartz, cristobalite
- HCl or acidic solution to start hydrolyzation of ethylsilicate

Setting reaction:



$$(C_2H_5O)_3Si-\left[O-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}\right]_n-OC_2H_5 + (n+2)H_2O \xrightarrow{HCl} (n+1)SiO_2 + 2(n+2)\,C_2H_5OH$$

Bonding polysilicic acid gel

$n=0, 1, 2 .. 5$

Ethyl silicate – mixture of tetraethylsilicate and poly(ethyl silicates)

- Most frequently ethylsilicate containing 28 a 40 % of SiO_2

Properties:

- On heating pure and highly thermoresistant SiO_2 is produced - high quality casts surfaces

- Low stability of the hydrolyzate – investment should be prepared just before its use

Currently used as the industrial investment materials