Development of pore solution chemistry and hydrate assemblages during hydration of calcium sulfoaluminate cements

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Outline

- Introduction
- Used cements
- Hydration of calcium sulfoaluminate cements

  - Isothermal heat flow calorimetry
  - X-ray diffraction analysis
  - Thermogravimetric analysis
  - Pore solution chemistry
  - Microstructure (SEM)
  - Thermodynamic modelling
- Conclusions

Comparison OPC - CSA

	OPC	CSA
main phases *	C_3S, C_2S, C_3A, C_4AF	C_4A_3s (= ye‘elimite)
raw materials	limestone & clay	limestone, bauxite & anhydrite
burning temperature	≈ 1450 °C	≈ 1250 °C
CO_2-release from raw materials **	C_3S: 1.80 g / ml C_3S	C_4A_3s: 0.56 g/ml C_4A_3s
grindability	medium	easy
gypsum addition	≈ 4-8 wt.-%	≈ 20-25 wt.-%
w/c total hydration	≈ 0.4	≈ 0.8
hydration products	C-S-H phases, CH, AFt, …	AFt, AFm, $Al(OH)_3$ gel

** Cement notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, H = H_2O, s = SO_3*

*** Gartner E., Cem. Concr. Res. 34 (2004), 1489.*

CSA-Cements …

… have attracted new interest during the climate debate as they:

- need lower burning temperatures,
- release less CO_2 from the raw meal (less limestone),
- yield a higher volume of hydrate phases (higher water/cement ratio)

compared to ordinary Portland cement.

Besides that, they are of interest concerning waste encapsulation.

But they have some drawbacks:

- environment (SO_2 release)
- risk of expansion (ettringite is main hydration product)

CSA-cements: risk of expansion

United States Patent 4409030, 1983:

Material for destroying concrete structures

… comprises a mixture of … coarse-grained quicklime … and … cement. The cement may contain calcium sulfoaluminate ... The material is blended with water and then injected into holes formed in the body to be destroyed, the material expanding as it hydrates to crack and fracture the body.

Basic research is needed to understand the hydration mechanisms of calcium sulfoaluminate based systems !

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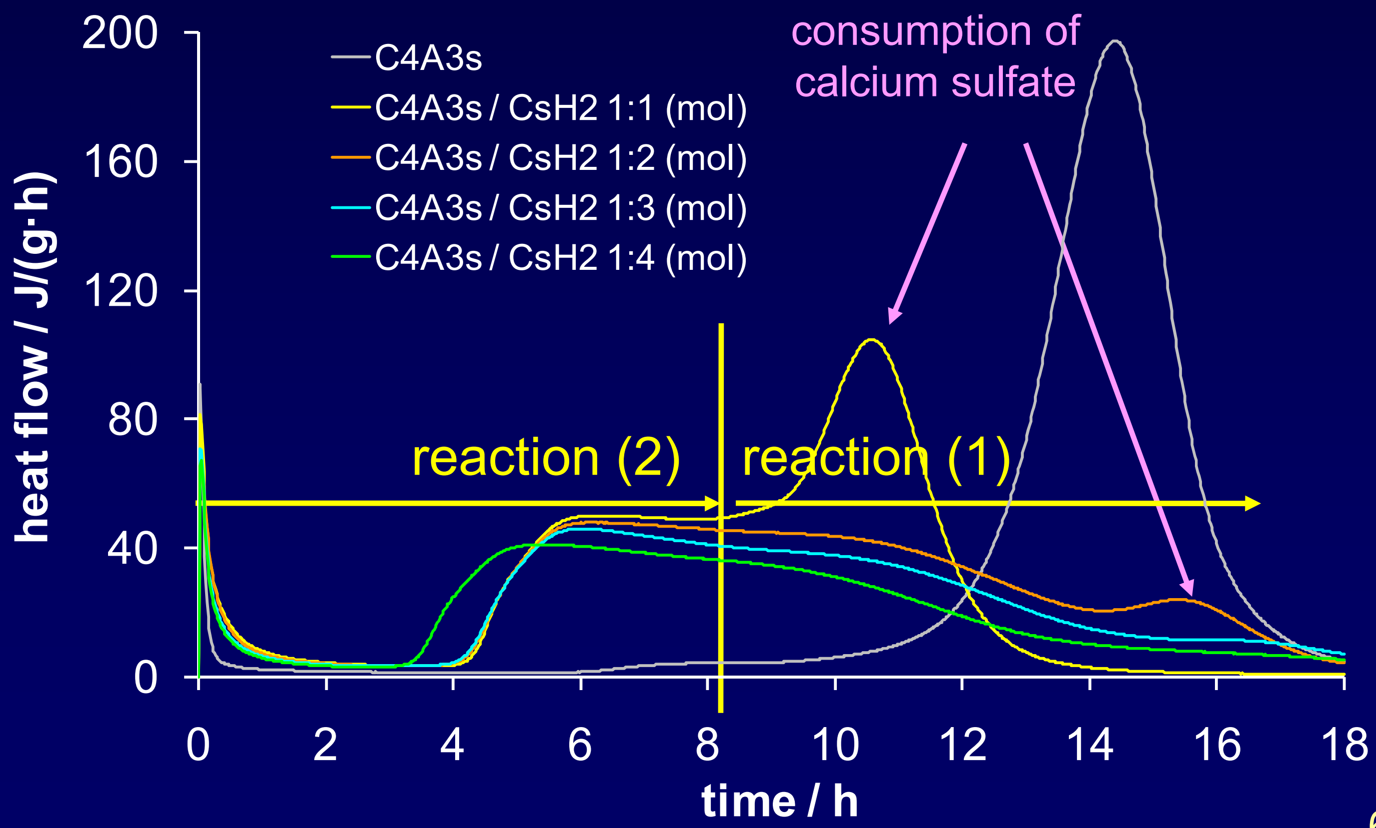
Hydration of pure ye‘elimite

(1) $C_4A_3s + 18\ H \longrightarrow C_3A{\cdot}CsH_{12} + 2\ AH_3$ **(monosulfate)**

(2) $C_4A_3s + 2\ CsH_2 + 24\ H \longrightarrow C_3A{\cdot}3CsH_{32} + 2\ AH_3$ **(ettringite)**

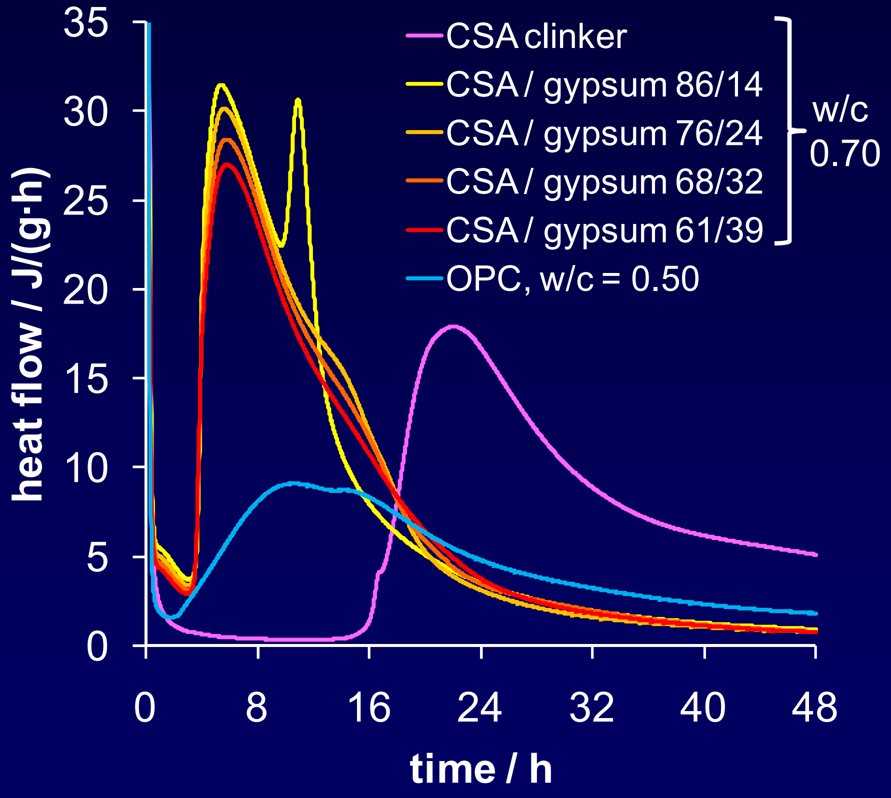
(3) $C_4A_3s + 6\ CH + 8\ CsH_2 + 74\ H \longrightarrow 3\ C_3A{\cdot}3CsH_{32}$

heat flow calorimetry
w/c = 2

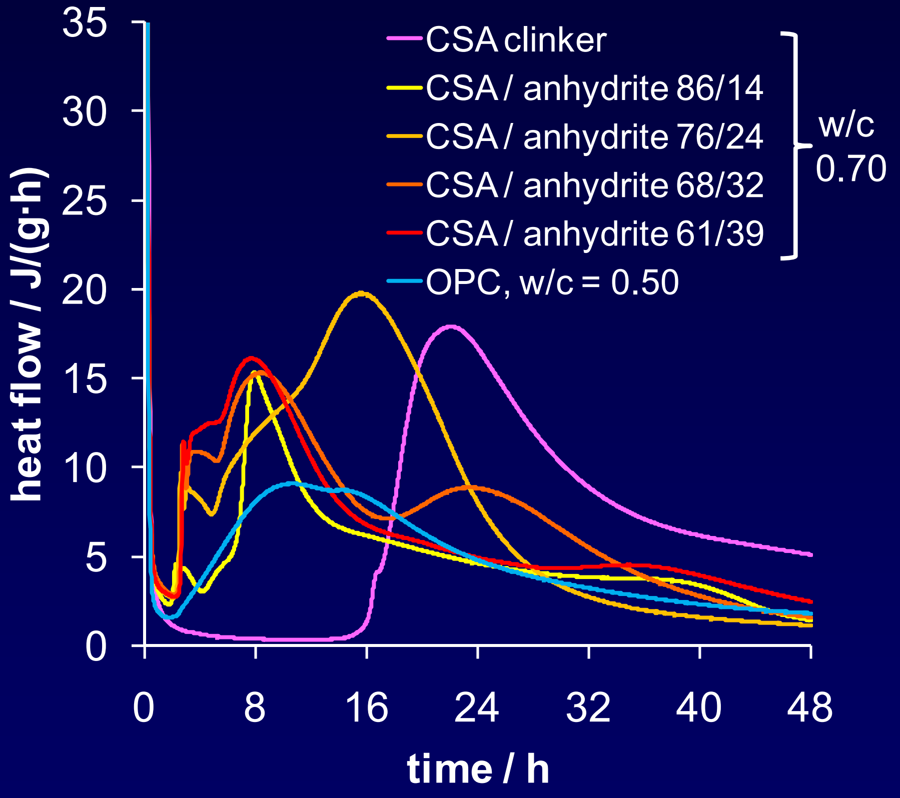


Hydration kinetics of CSA cements: influence of calcium sulfate

gypsum *



dead-burnt anhydrite



<u>reactive calcium sulfate:</u>
enables to control early hydration

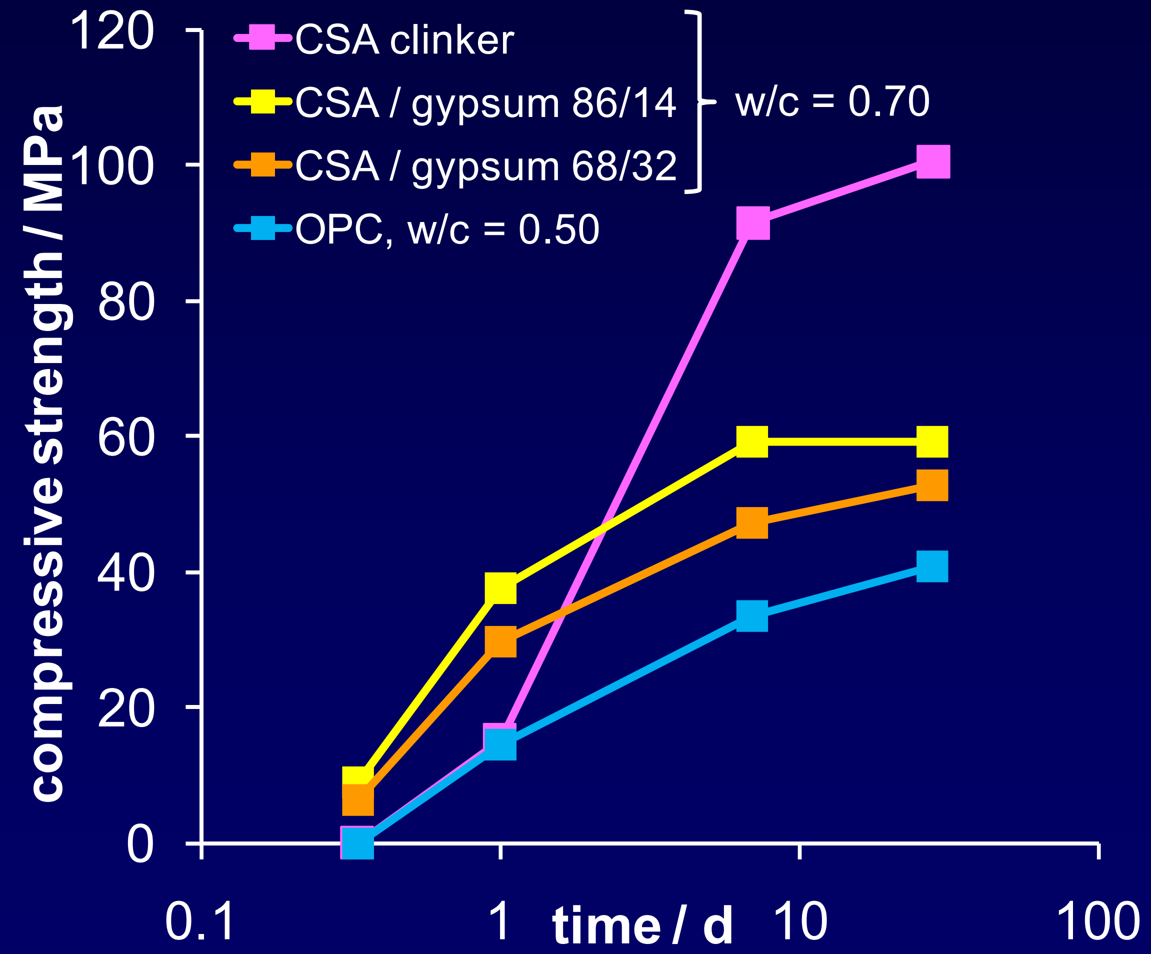
<u>calcium sulfate with poor reactivity:</u>
„chaotic“ early hydration

* amounts of gypsum given as anhydrous calcium sulfate

Strength development of CSA cements

- very high strength despite high water/cement-ratio
- gypsum increases early strength

EN 196-1 - mortars



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Used CSA-cements - composition

chemical analysis

wt.-%	CSA-1	CSA-2
CaO	35.4	41.2
SiO_2	3.2	6.9
Al_2O_3	35.5	26.8
Fe_2O_3	0.88	0.88
MgO	0.76	0.75
Na_2O	0.05	0.13
K_2O	0.21	0.40
TiO_2	1.8	1.2
SO_3	16.8	19.5
L.O.I.	5.1	1.84

potential phase content

wt.-%	CSA-1	CSA-2
C_4A_3s	50	54
CA	8	-
C_2AS	15	-
C_2S	-	17
Cs	-	22
CsH_2	22	-
others *	5	7

* mainly titanium containing phases

water/cement ratio

- CSA-1: 0.72
- CSA-2: 0.80

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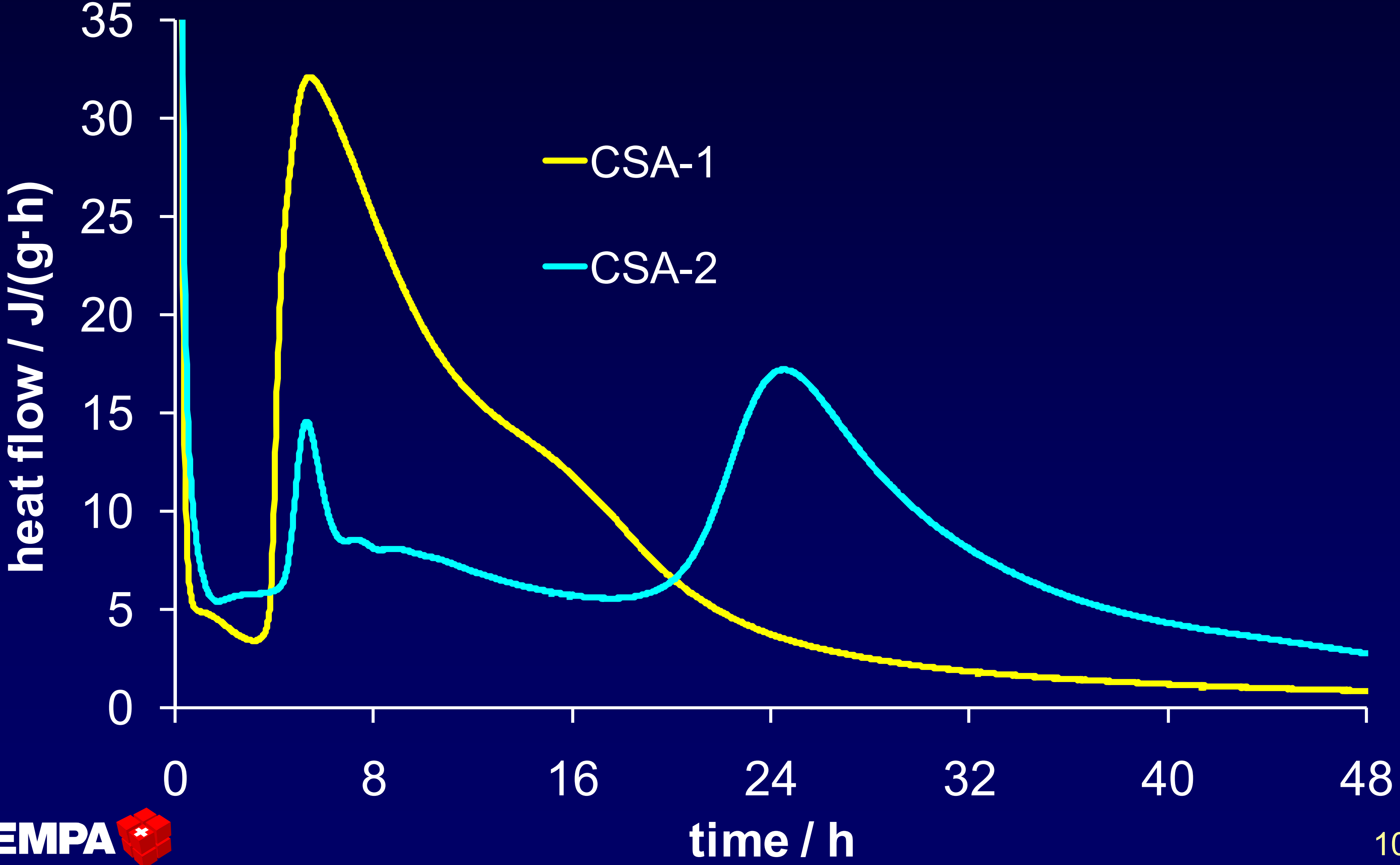
Isothermal heat flow calorimetry



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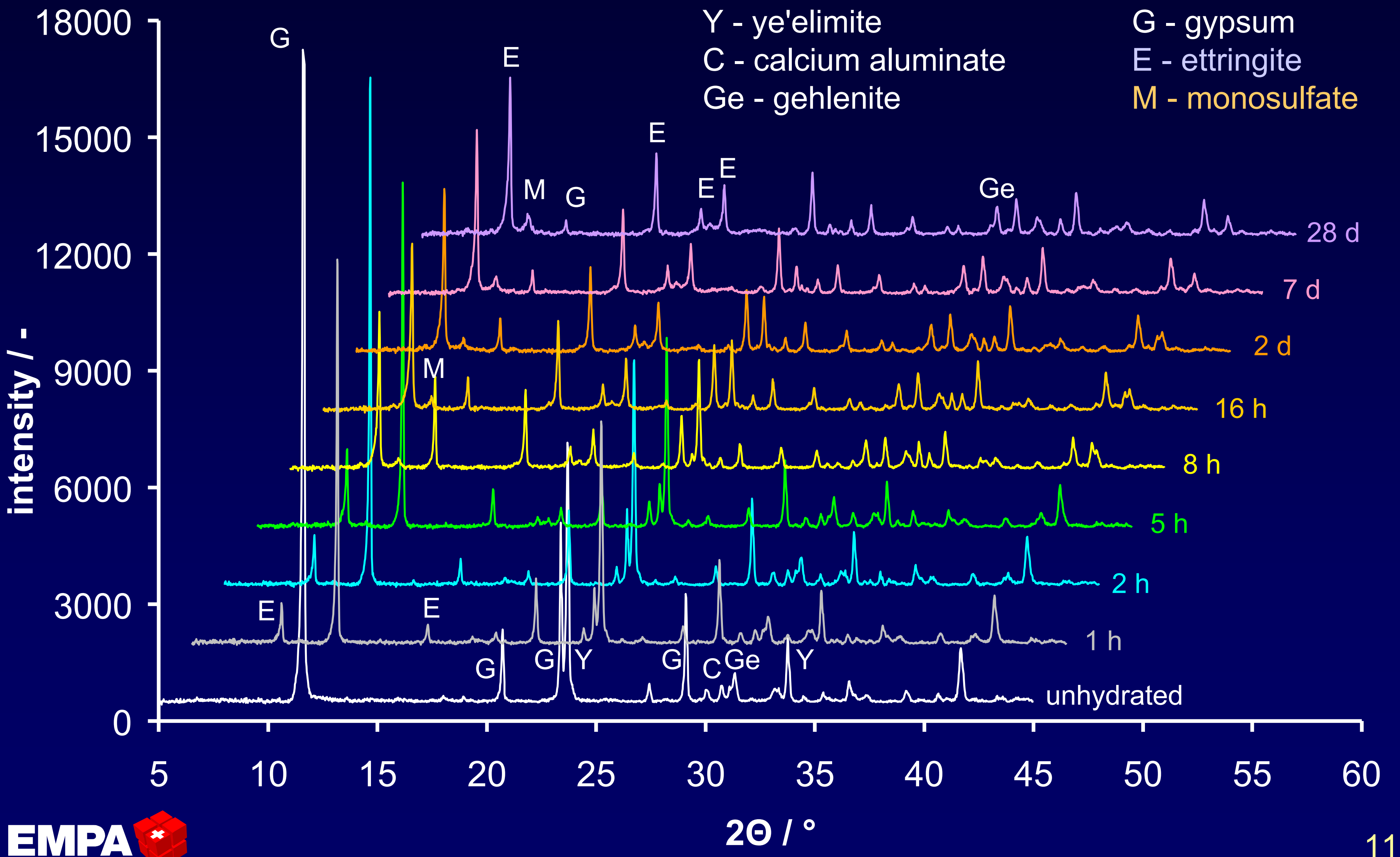
Hydration (XRD) of CSA-1



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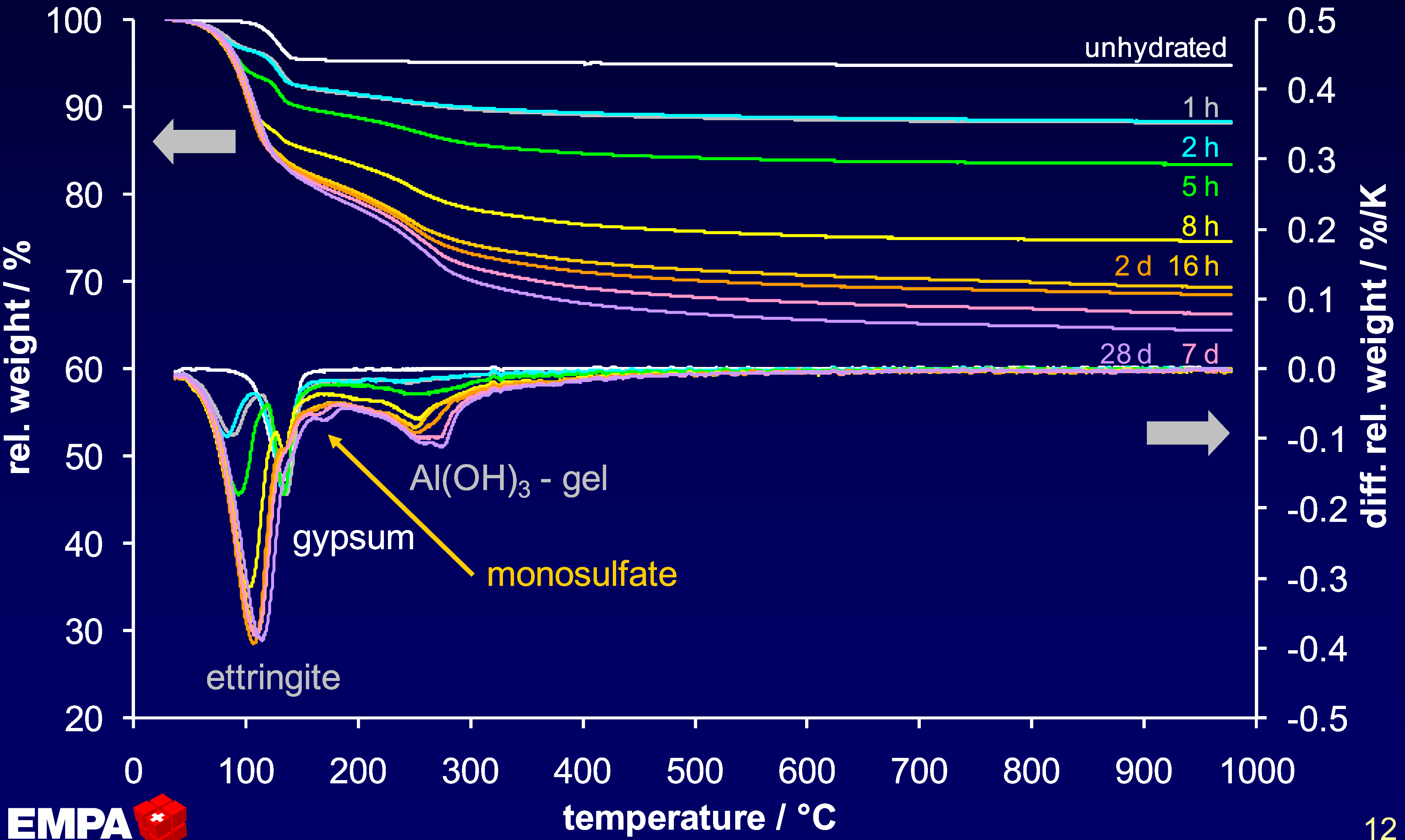
Hydration (TGA) of CSA-1



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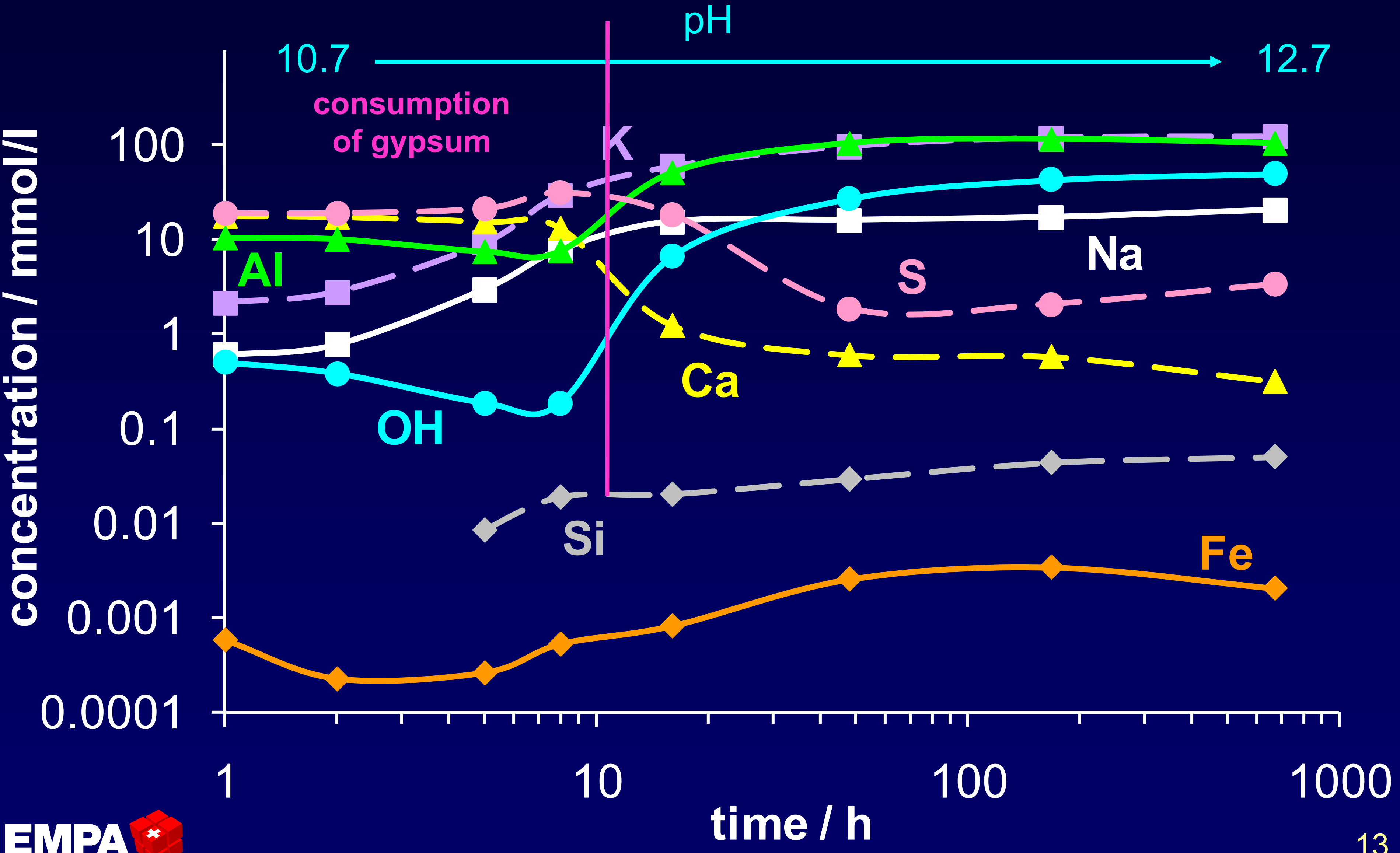
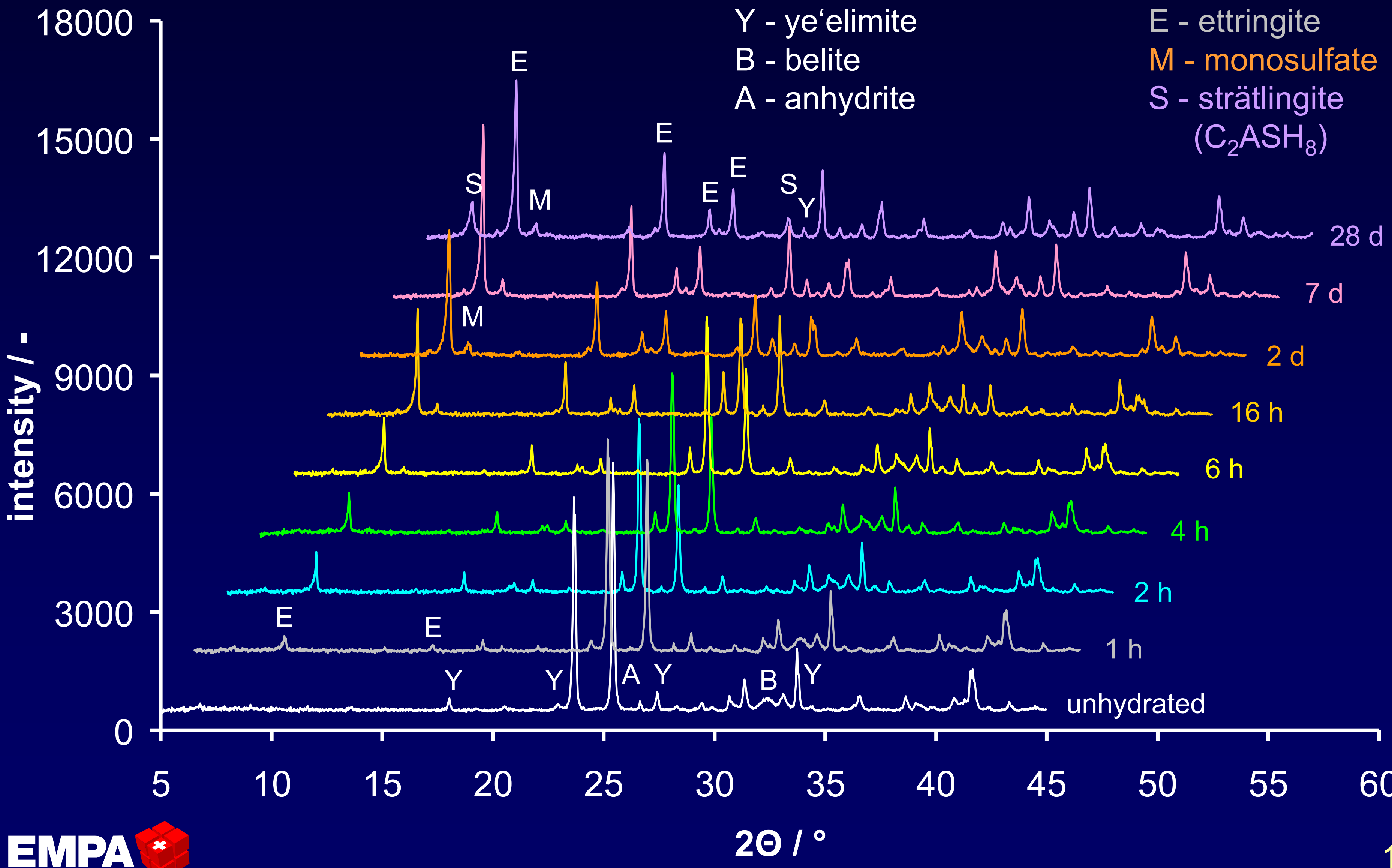
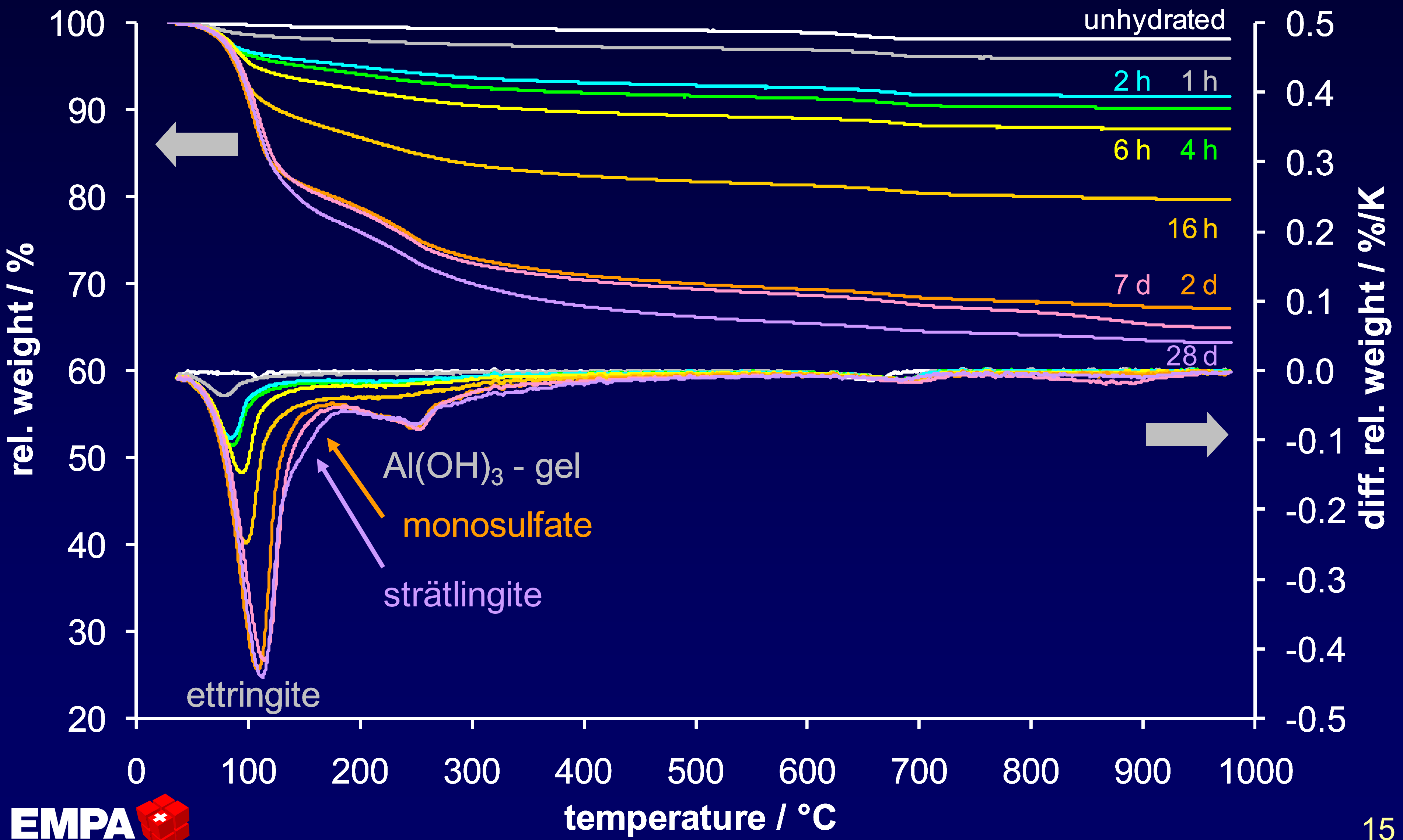
Pore solution composition of CSA-1



Hydration (XRD) of CSA-2



Hydration (TGA) of CSA-2



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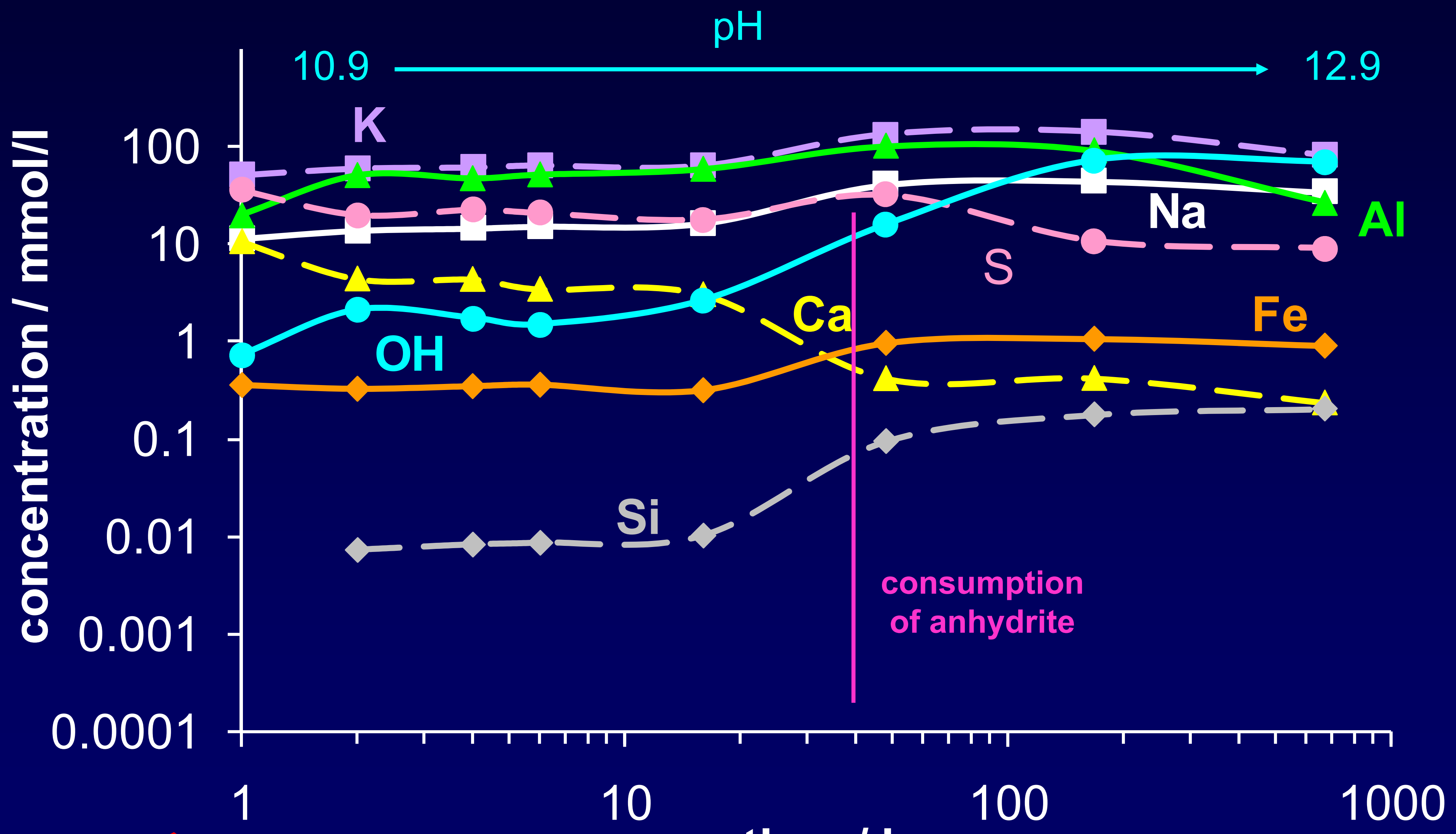
Pore solution composition of CSA-2



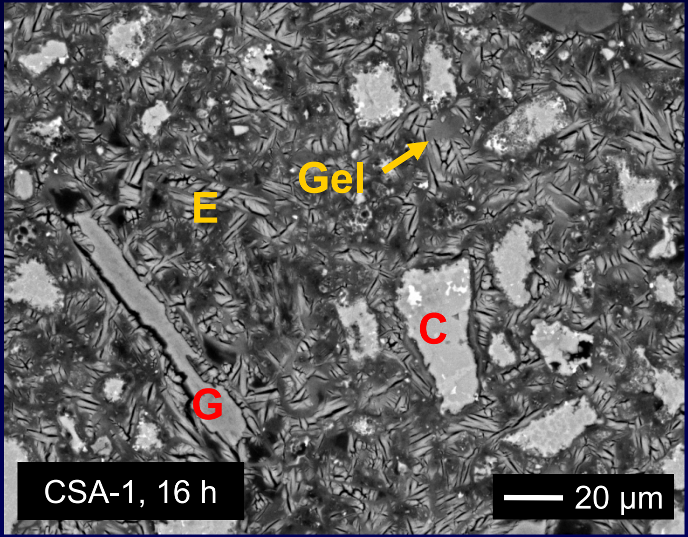
Microstructure of CSA-1 and CSA-2

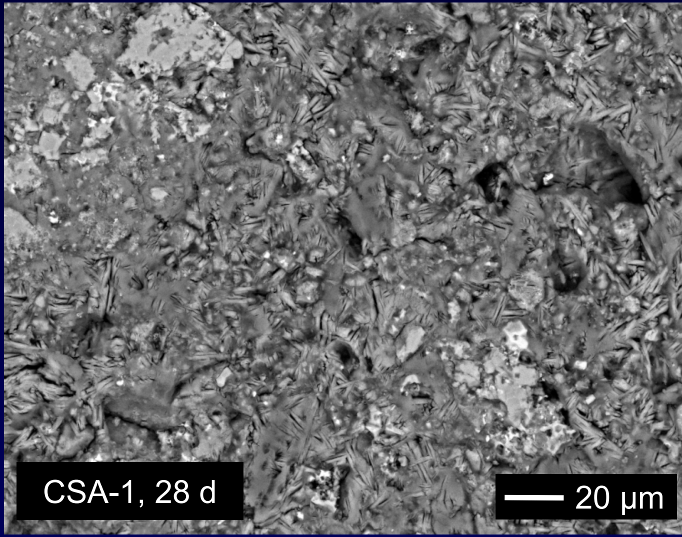
16 h

28 d

CSA-1

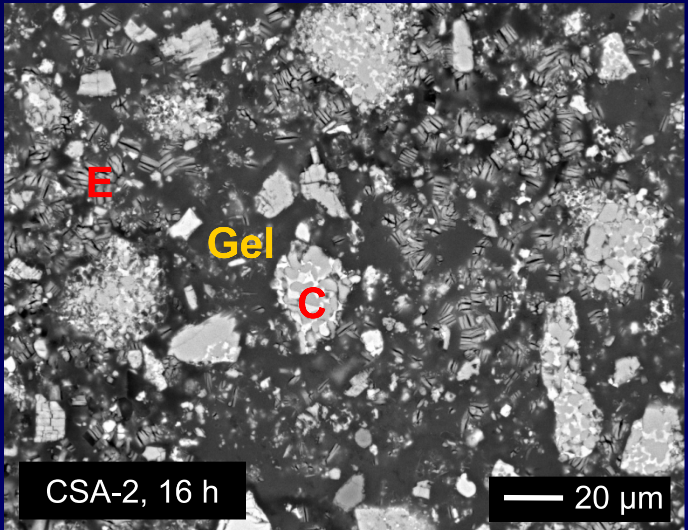
E = ettringite
C = clinker
G = gypsum
Gel = gel-like phases

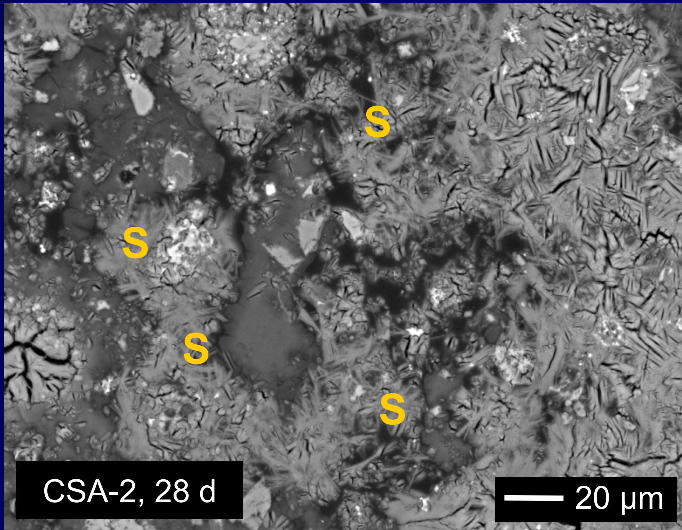




CSA-2

S = strätlingite





Thermodynamic modelling

Composition of cement

I Slowly soluble solids

C_4A_3s, CA, C_2S *K_2O*

=> Dissolution kinetics *Na_2O*

(XRD) *MgO*

II Rapid soluble solids

K_2SO_4 **gypsum**

Na_2SO_4 **anhydrite**

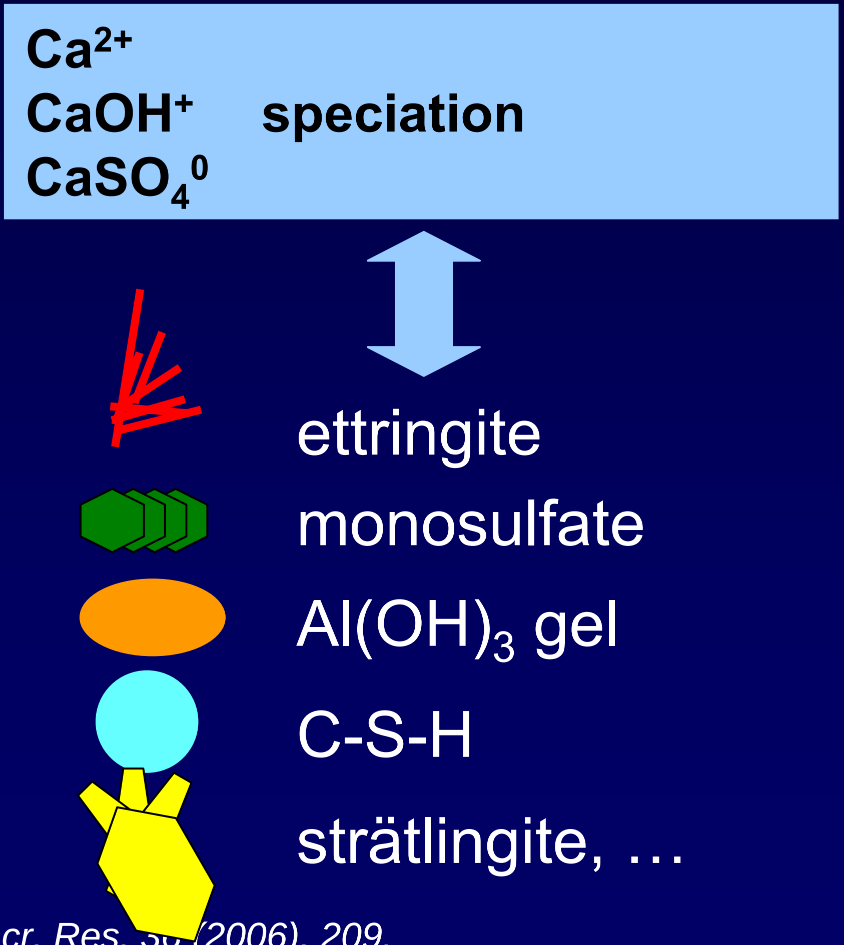
CaO

III Water

H_2O

thermodynamic modelling

GEMS-PSI



Ca^{2+}

$CaOH^+$ **speciation**

$CaSO_4^0$

ettringite

monosulfate

$Al(OH)_3$ gel

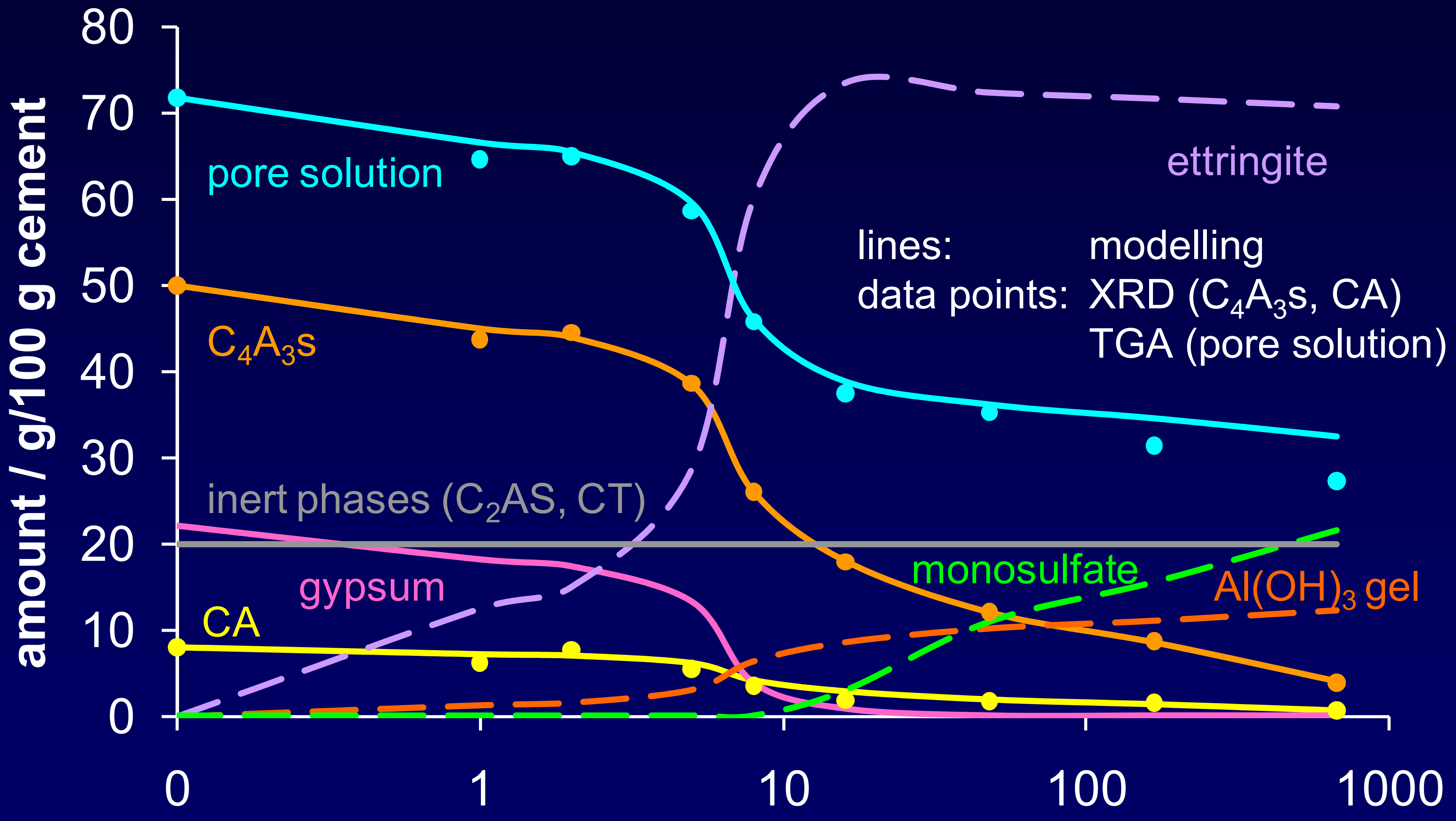
C-S-H

strätlingite, …

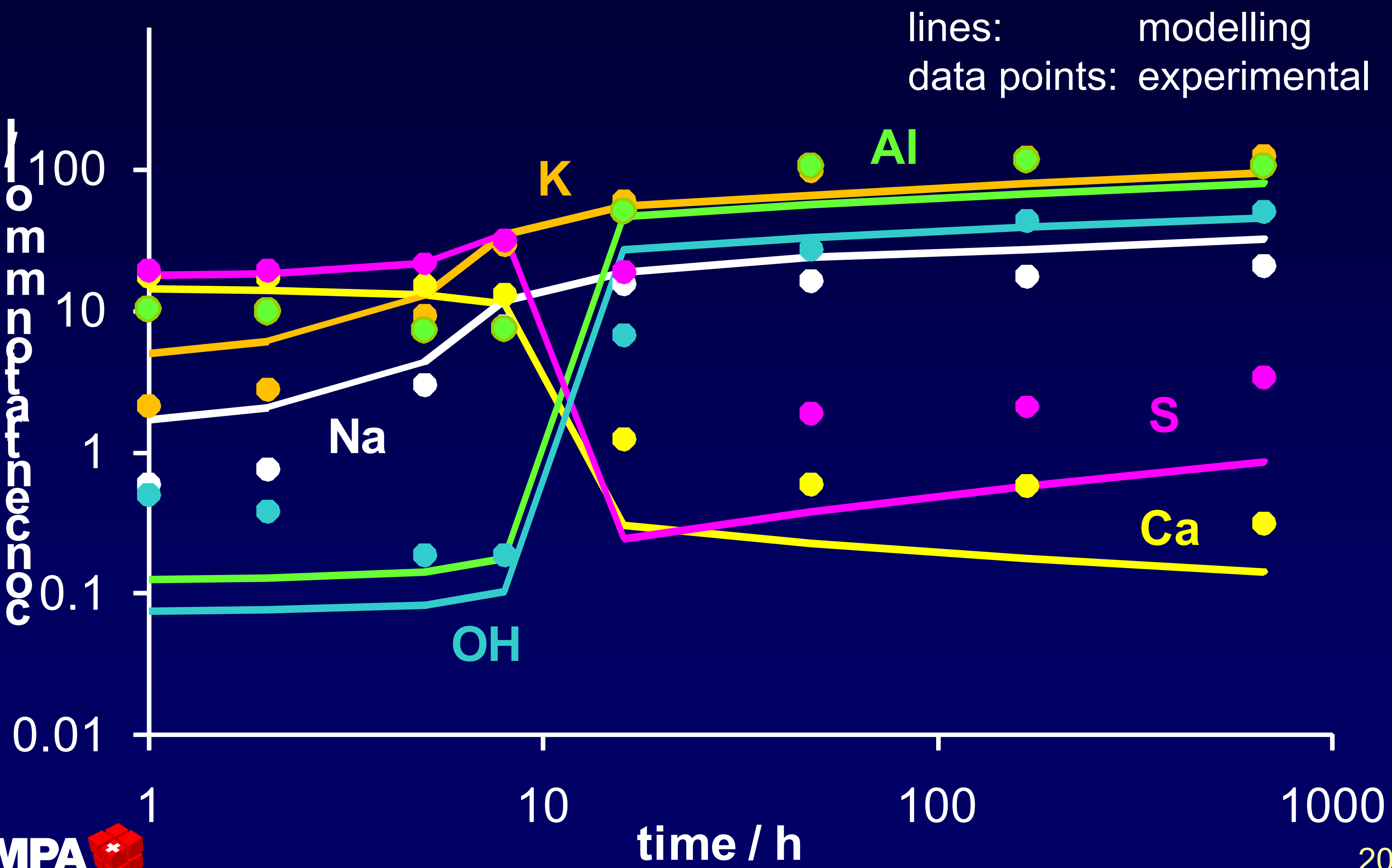
www.empa.ch/cemdata

Lothenbach B., Winnefeld F., Cem. Concr. Res. 36 (2006), 209.

Modelling: solid phases of CSA-1



Modelling: liquid phases of CSA-1



lines: modelling
data points: experimental

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Modelling: solid and liquid phase of CSA-2

Up to now, the hydration has been modelled only with insufficient accuracy (poor correlation with experimental data, especially with pore solution composition),

mainly due to:

- some uncertain thermodynamic data (e. g. CAH_{10})
- kinetic restraints (slow dissolution of anhydrite)

=> work in progress

Conclusion – hydration of CSA cements (I)

Solid phases:

- ettringite formation until $CaSO_4$ is (almost) used, then monosulfate occurs
- $Al(OH)_3$ gel forming by-product of hydration
- with C_2S als minor phase (CSA-2) strätlingite forms after 28 d
- dissolution of calcium sulfates hindered

Pore solution:

- first hours: dominated by alkalis, calcium and sulfate
  pH 10.5 - 10.8
- when $CaSO_4$ (almost) used: mainly alkalis, OH and Aluminum
  pH 12.5 - 12.8 after 28 d

Conclusion – hydration of CSA cements (II)

Microstructure:

- CSA-1: quite dense already after 18 hours,
  very dense after 28 days despite high w/c of 0.72
- CSA-2: dense, but inhomogeneous
  large strätlingite crystals after 28 days

Application:

- binder for various applications (e. g. „plaster“boards)
- acceleration of OPC or slag hydration in ternary blends also incorporatng gypsum or anhydrite
- shrinkage reducing / expansive agent
- waste encapsulation