Hydration of calcium sulfoaluminate cement by a zinc chloride solution

Application to nuclear waste conditioning

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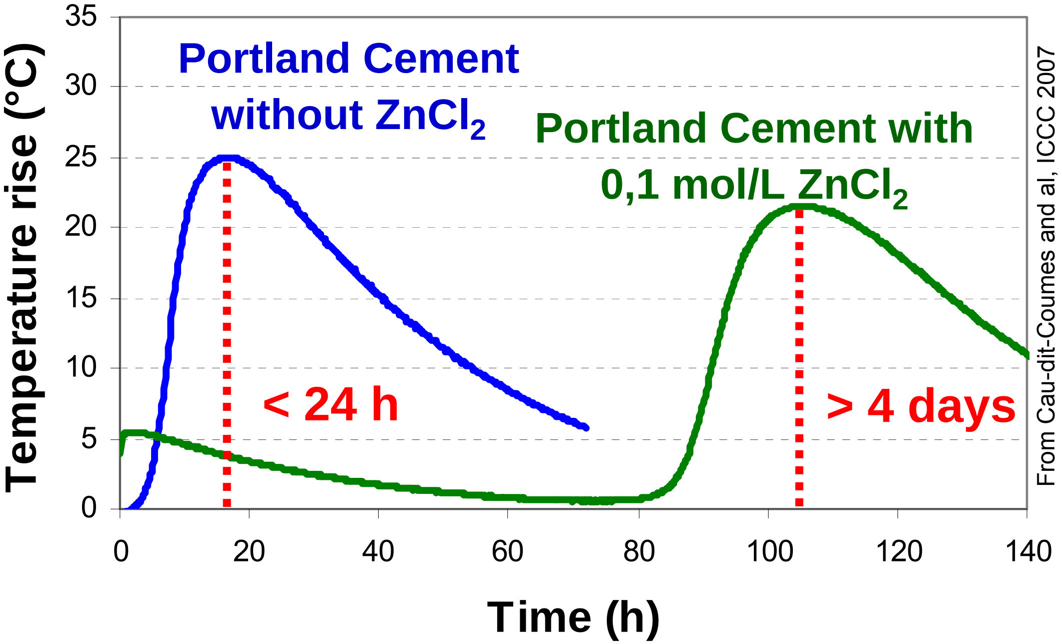
Context

Zinc chloride is a soluble salt contained in ashes resulting from the incineration of α radioactive wastes including neoprene and polyvinylchloride.

Deleterious effects on Portland cement:

- setting is strongly delayed and can be inhibited at high zinc chloride loading *(Arliguie 1985),*
- hydration and hardening are slowed down *(Ortego 1989)*.



Precipitation of β_2-$Zn(OH)_2$ or $Zn_2Ca(OH)_6.2H_2O$ over the cement grains has been postulated to explain the delay in cement hydration *(Arliguie 1985)*.

It is necessary to select a binder having a different chemistry, more compatible with the waste:
a calcium sulfoaluminate cement.

Objective: **to investigate the influence of zinc chloride on the hydration of CSA cements.**

Overview

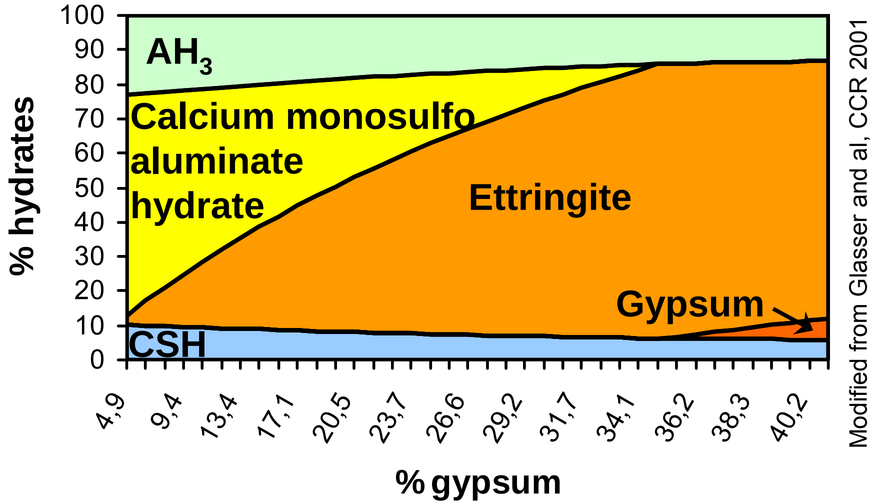
Materials:
cement composition and hydration

Mineralogical composition of the CSA clinker (KTS 100 provided by Bellitex):

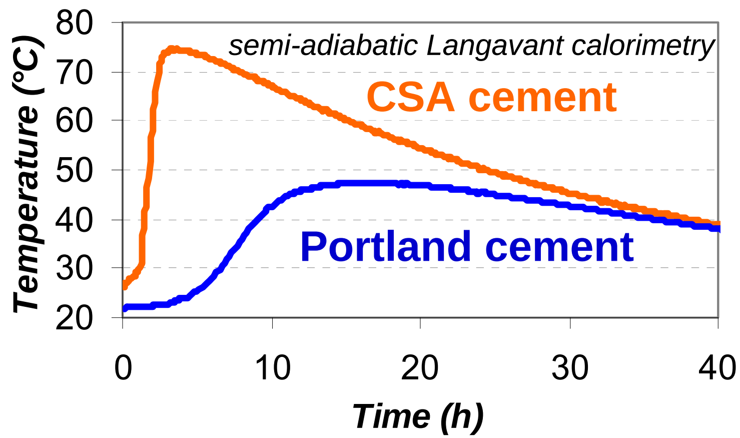
Minerals (% weight)						
$C_4A_3\bar{S}$	C_2S	C_3FT	$C_{12}A_7$	Periclase	$C\bar{S}$	Quartz
71	16	6.6	3.1	2.6	0.5	0.5

Two main features of CSA cement hydration:

Hydrates proportion depend of the amount of gypsum mixed with the clinker.



Major heat output



Influence of temperature and gypsum content has to be studied.

Materials and methods: preparation of specimens

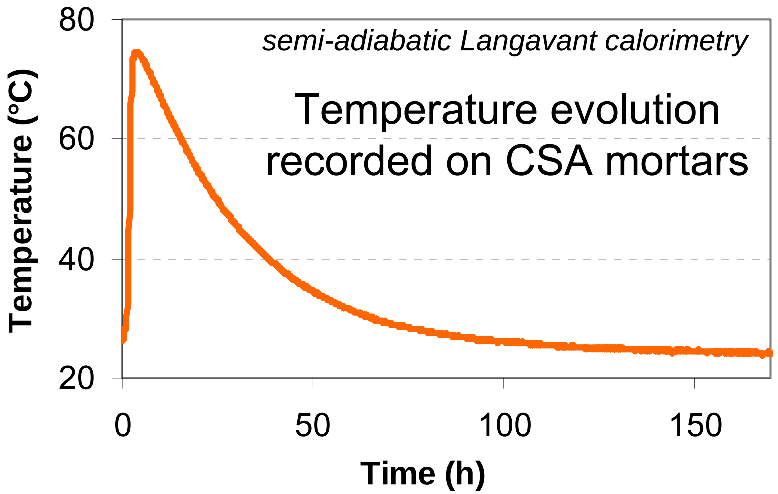
Two kinds of specimens were prepared:

- **pastes** for XRD analysis, (hydration stops at 5min, 1h, 2h, 5h, 24h, 7days,…)
- **mortars** for semi-adiabatic Langavant calorimetry.

- **CSA cements preparation:** mixing of ground CSA clinker with gypsum (0-10%, 20% and 35%).
- **Mixing solution:** dissolution of $ZnCl_2$ salt (0 or 0.5 mol/l) into distilled water.
- **Water to cement ratio:** 0.55 for pastes and mortars.
- **Sand to cement ratio :** 3, sand and cement pre-mixed.

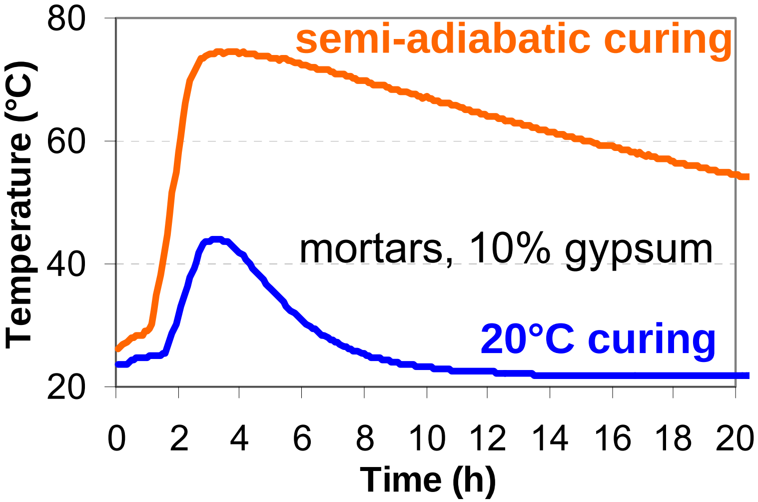
After mixing, samples were cured 7 days in sealed plastic bag at 20°C or were submitted to a thermal cycle in an oven.

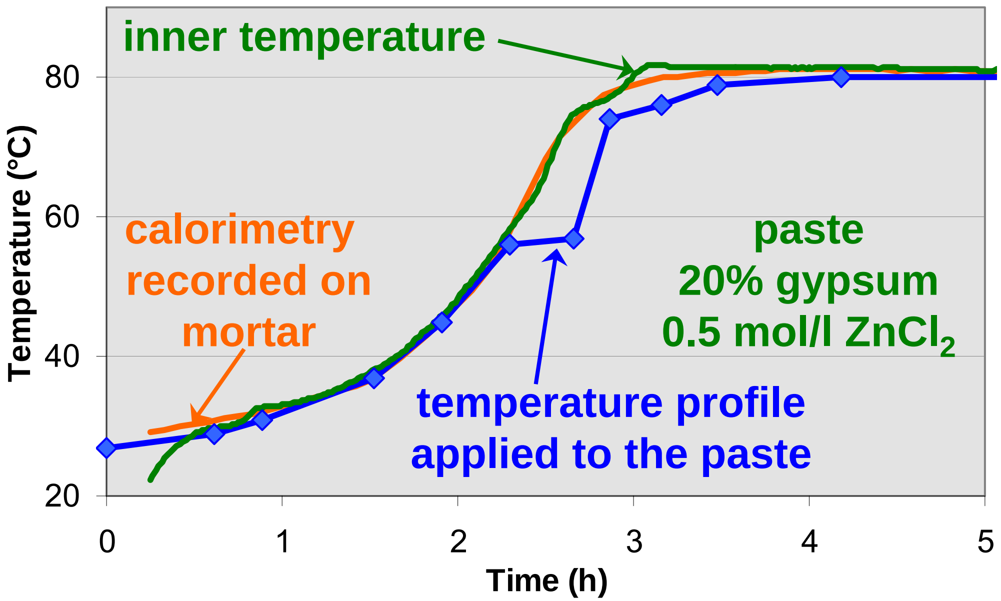
Thermal cycles: temperature profiles made from the temperature evolution of mortars under semi-adiabatic conditions and applied on pastes to reproduce the temperature rise and decrease which may occur in a massive structure during cement hydration.



Materials and methods:
preparation of specimens

Differences between the thermal evolution of two mortar samples cured at 20°C or under semi-adiabatic conditions were very significant.

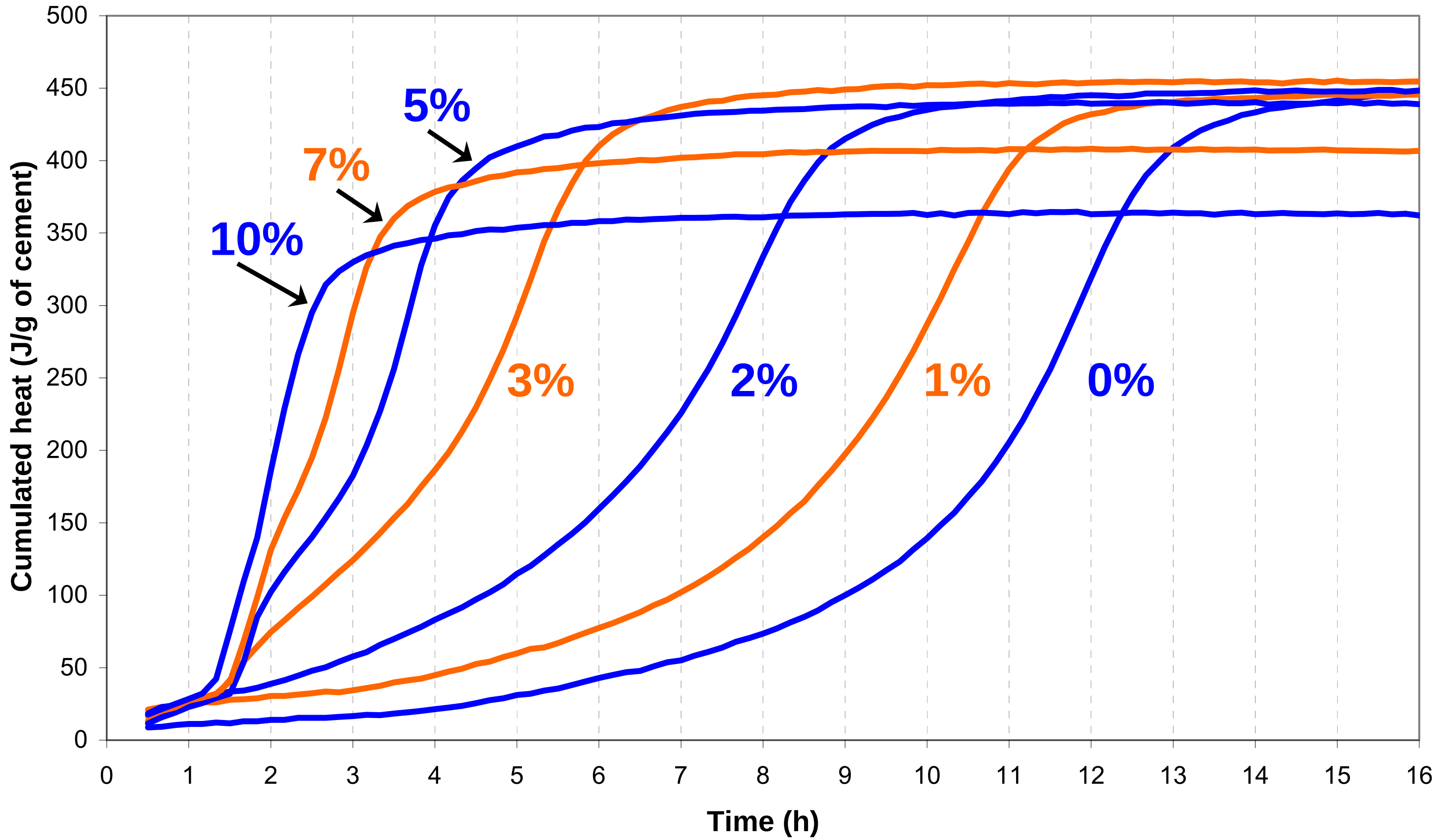




Temperature profiles were defined by interpolating in 20-40 segments the curves recorded on mortars.

Some corrections were required to keep the inner temperature of the paste near that of the mortar under semi-adiabatic curing.

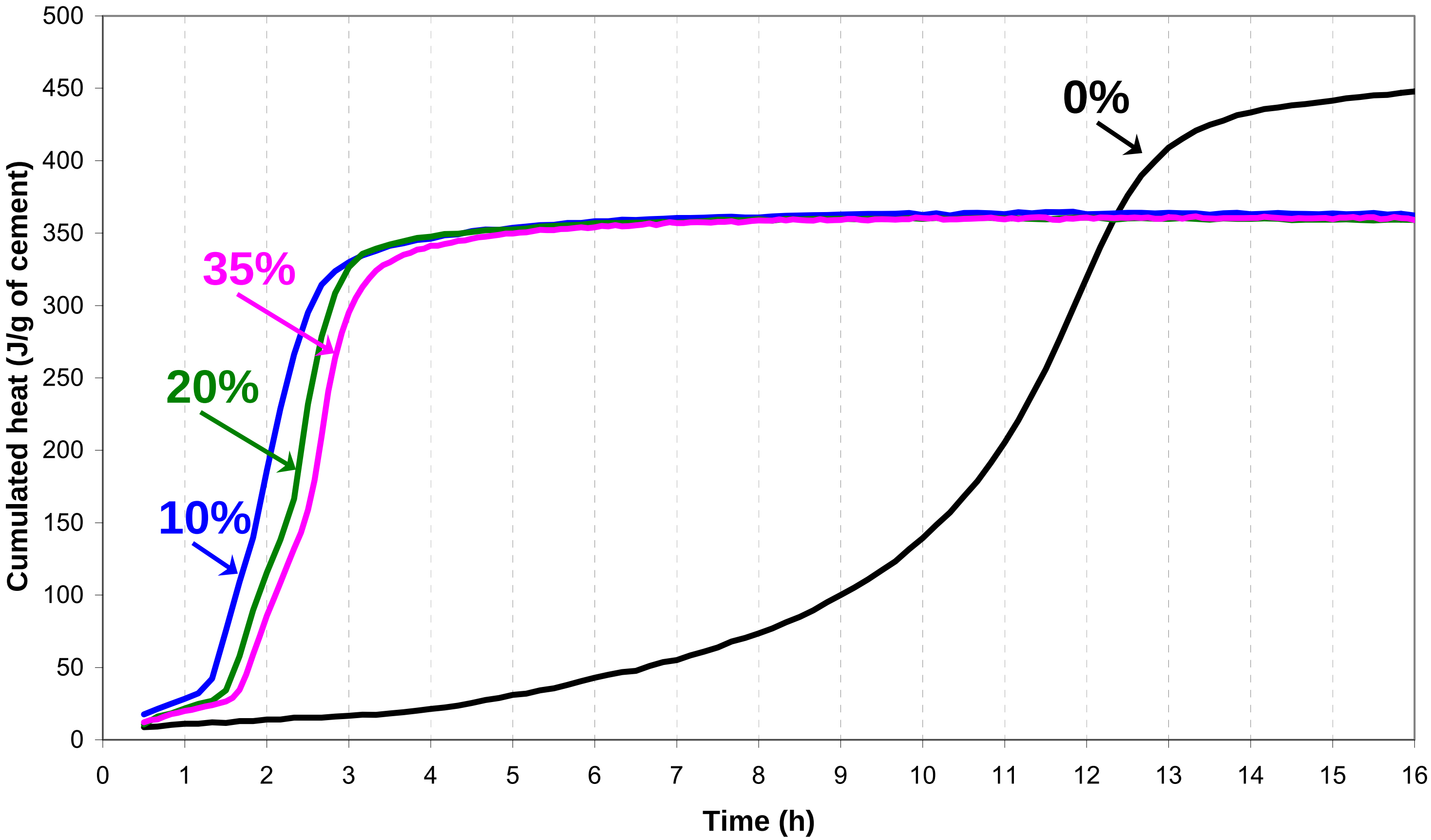
Kinetics of hydration:
influence of gypsum content



Two effects were observed when the gypsum content increased from 0 to 10%:

- the cumulated heat output was reduced when the gypsum content exceeded 5%,
- the induction period decreased strongly especially at low gypsum contents.

Kinetics of hydration:
influence of gypsum content



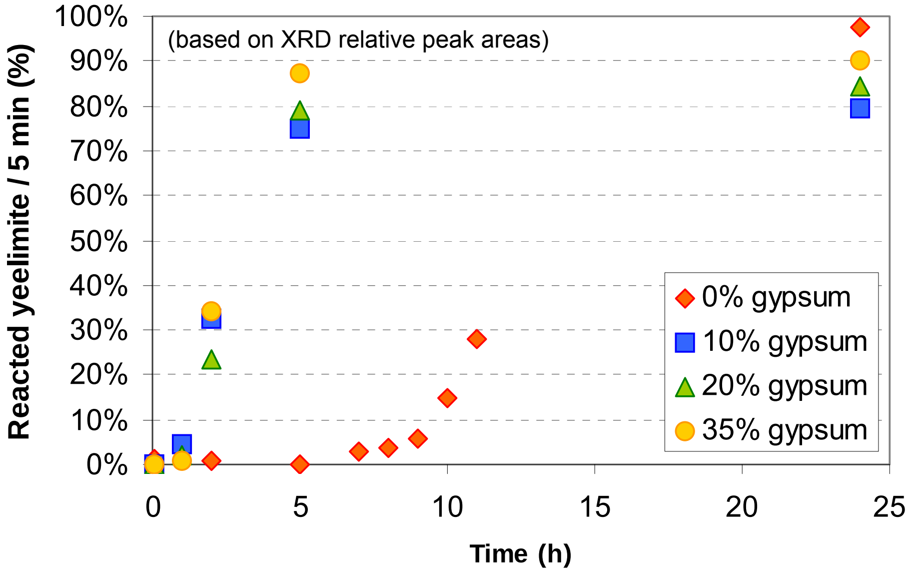
Beyond a gypsum content of 10%, heat output and induction period did not vary anymore.

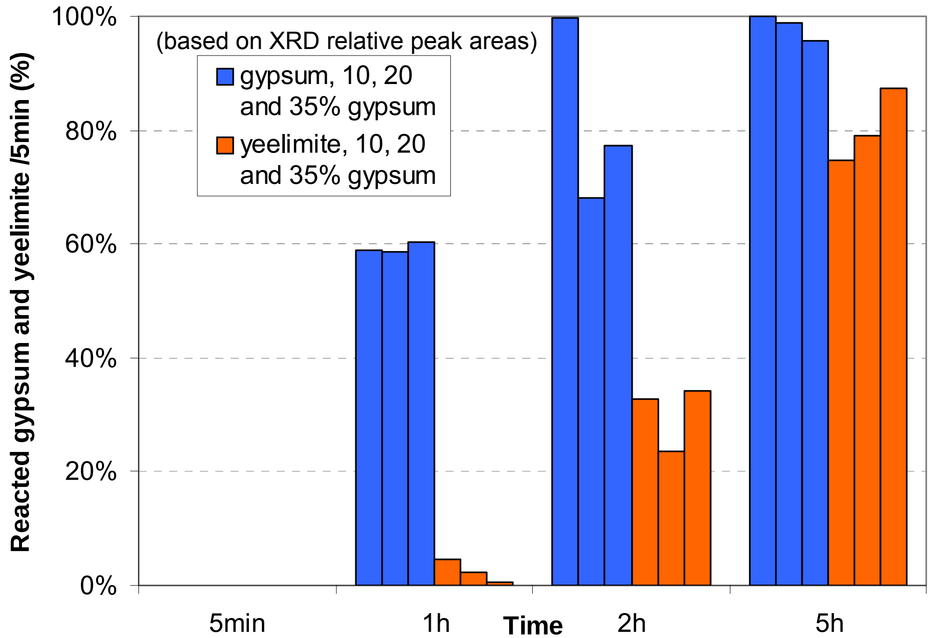
Kinetics of hydration:
influence of gypsum content

Mineralogical study on pastes with thermal cycles :

Without gypsum:

- yeelimite started to react much later, in agreement with the long induction period previously observed.
- Yeelimite was almost totally depleted at 24h while with gypsum, 10 to 20% were still unreacted.

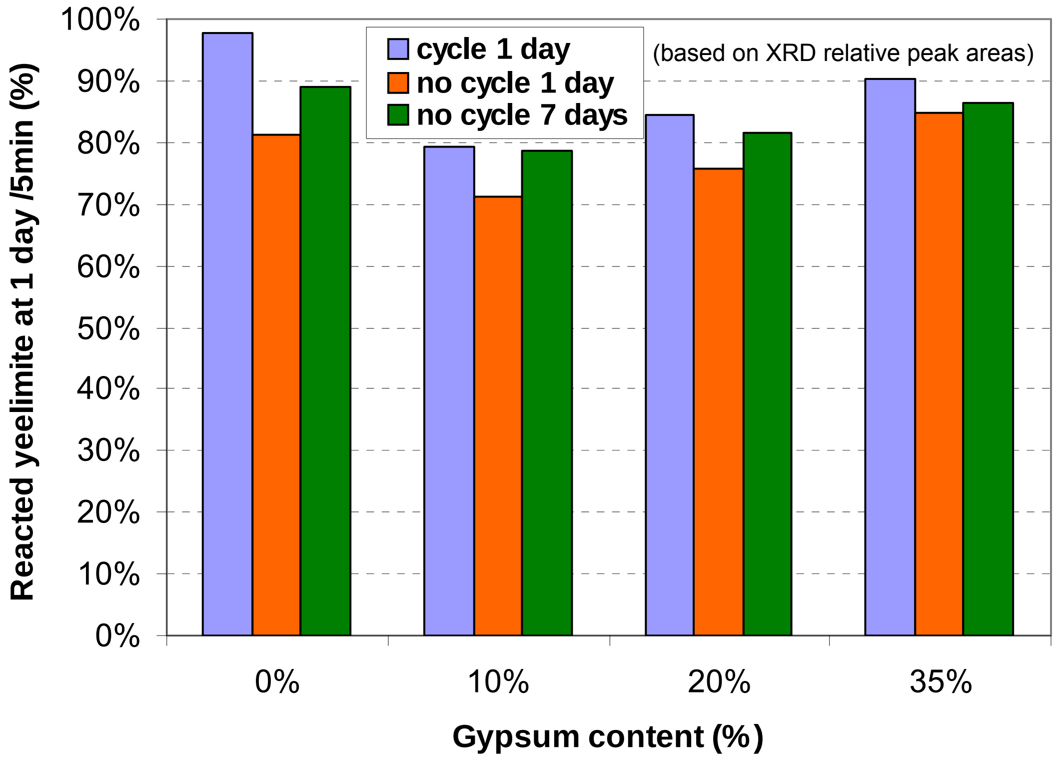




Gypsum reactivity:

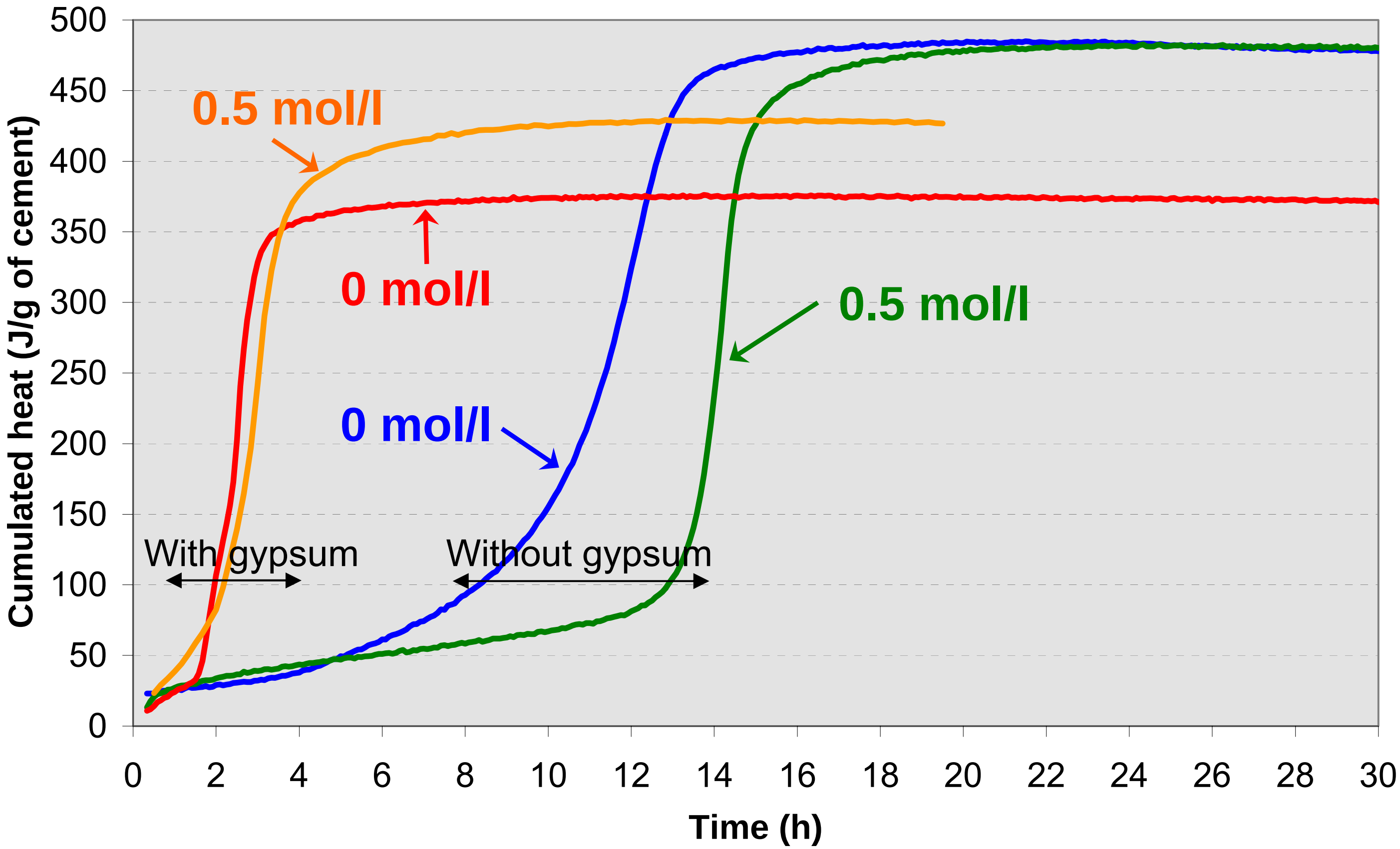
- gypsum dissolution before that of yeelimite,
- almost total depletion at 5h.

Kinetics of hydration:
influence of thermal cycle



The thermal cycle promoted the dissolution of yeelimite: amount of yeelimite consumed at 1 day higher than that depleted at 7 days when curing is performed at 20°C.

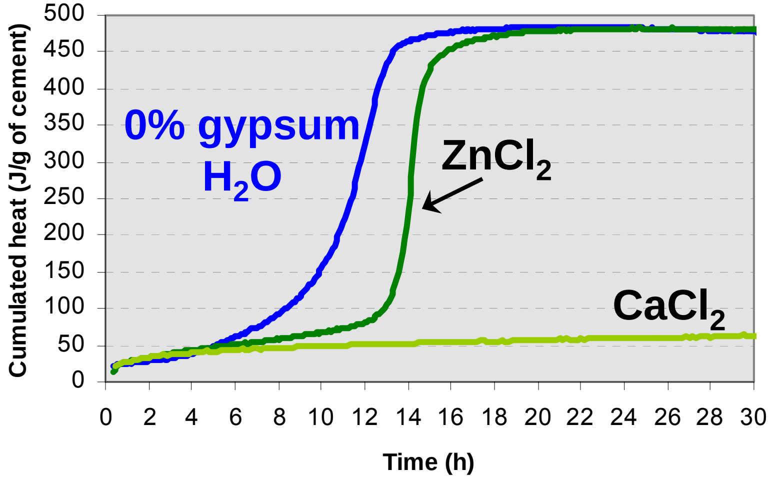
Kinetics of hydration:
influence of zinc chloride addition

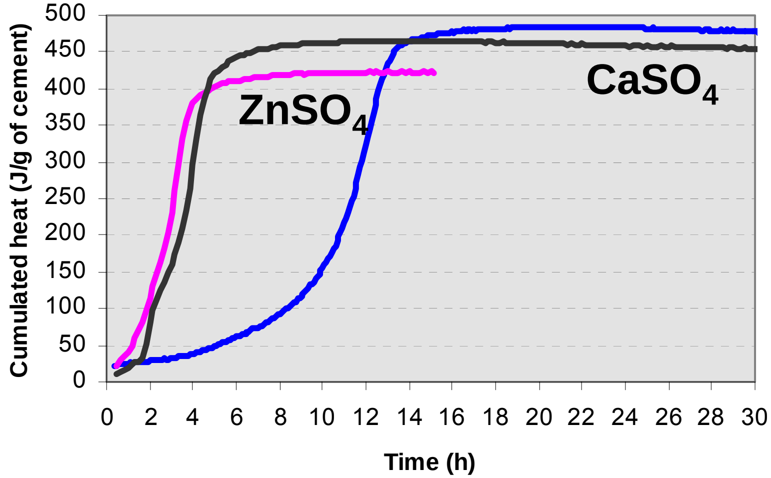


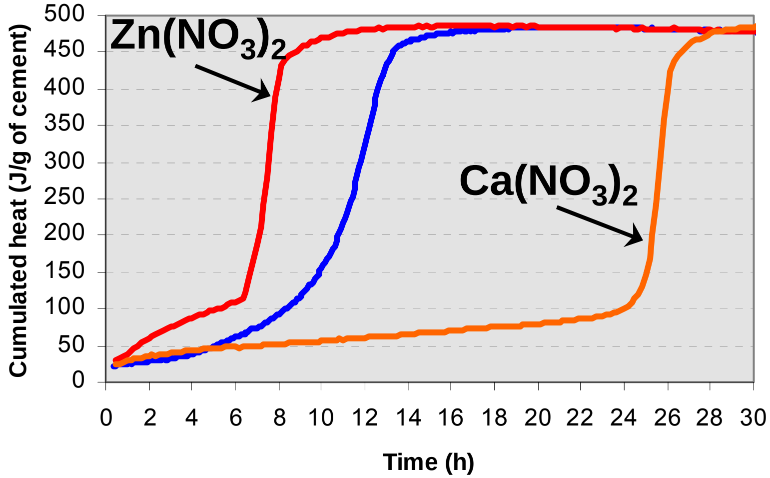
- A retardation was observed, but its magnitude was much smaller than that recorded with OPC.
- Setting inhibition was never observed: setting occurred in less than 2h with gypsum, and in less than 24h without it.

Kinetics of hydration:
influence of zinc chloride addition

Investigating the reactivity of zinc cations and chloride anions







Temperature of the mixing solution: 20°C

Salt concentration : 0.5 mol/l

acceleration $Zn^{2+} > Ca^{2+}$ delay

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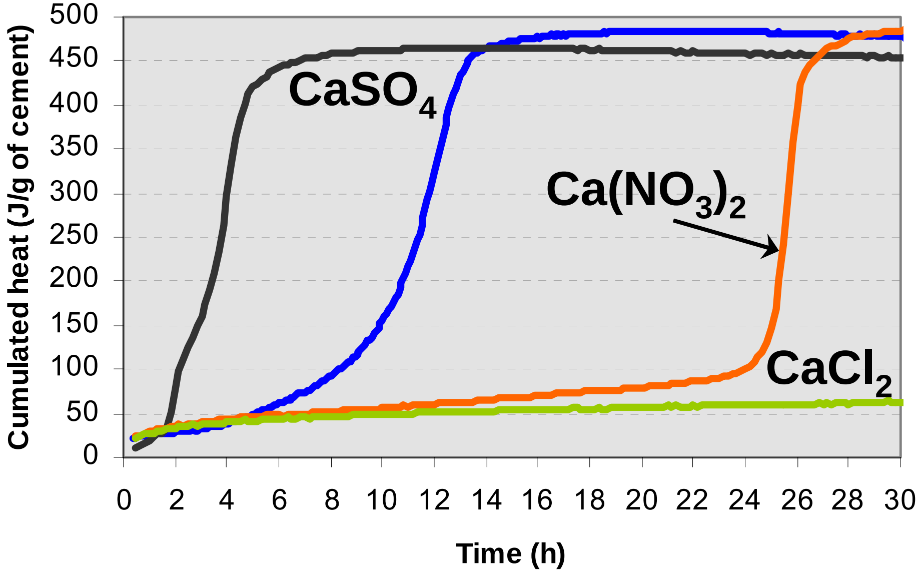
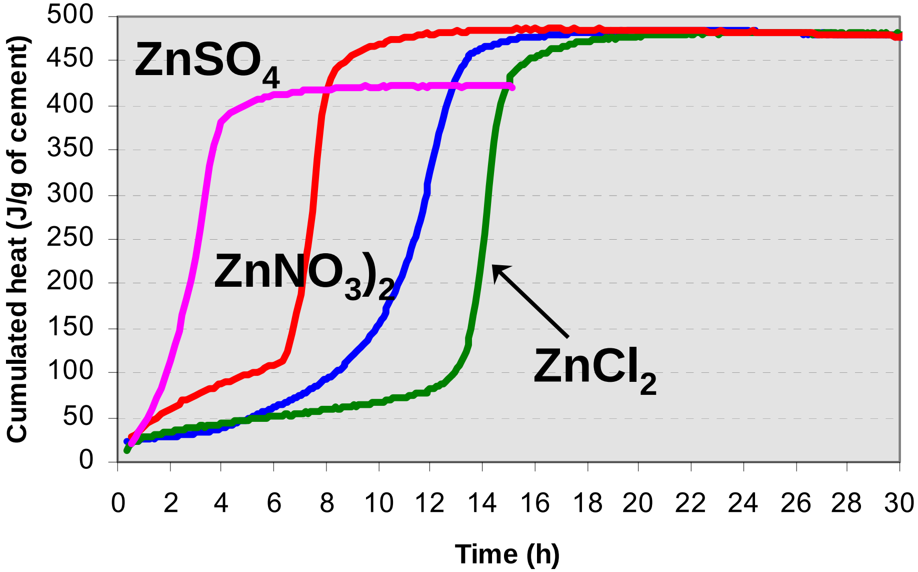
Kinetics of hydration:
influence of zinc chloride addition

Investigating the reactivity of zinc cations and chloride anions





Temperature of the mixing solution: 20°C

Salt concentration : 0.5 mol/l

acceleration SO_4^{2-} >> 2 NO_3^- > 2 Cl^- delay

Chloride anions strongly slowed down hydration but zinc cations accelerated it.

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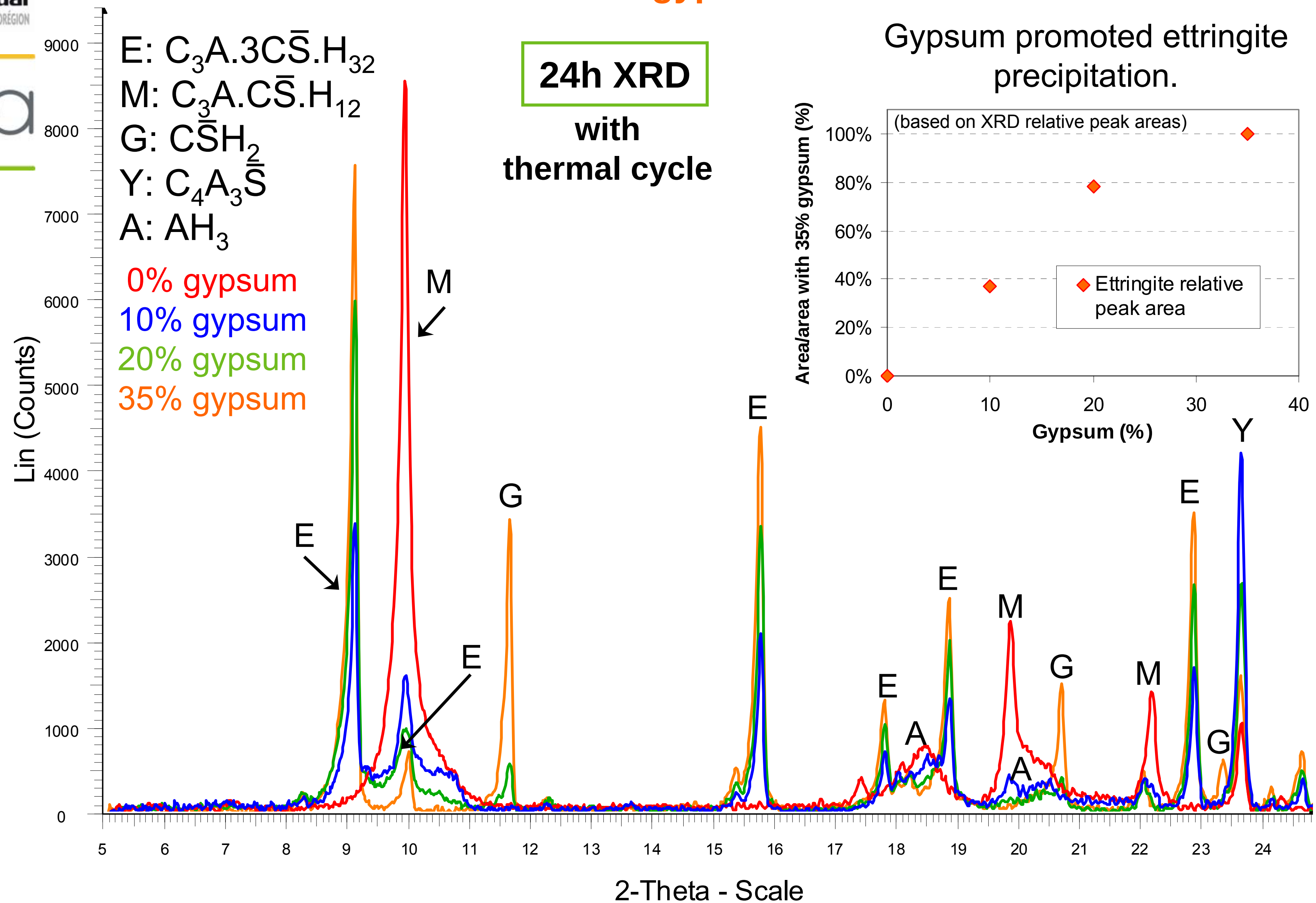
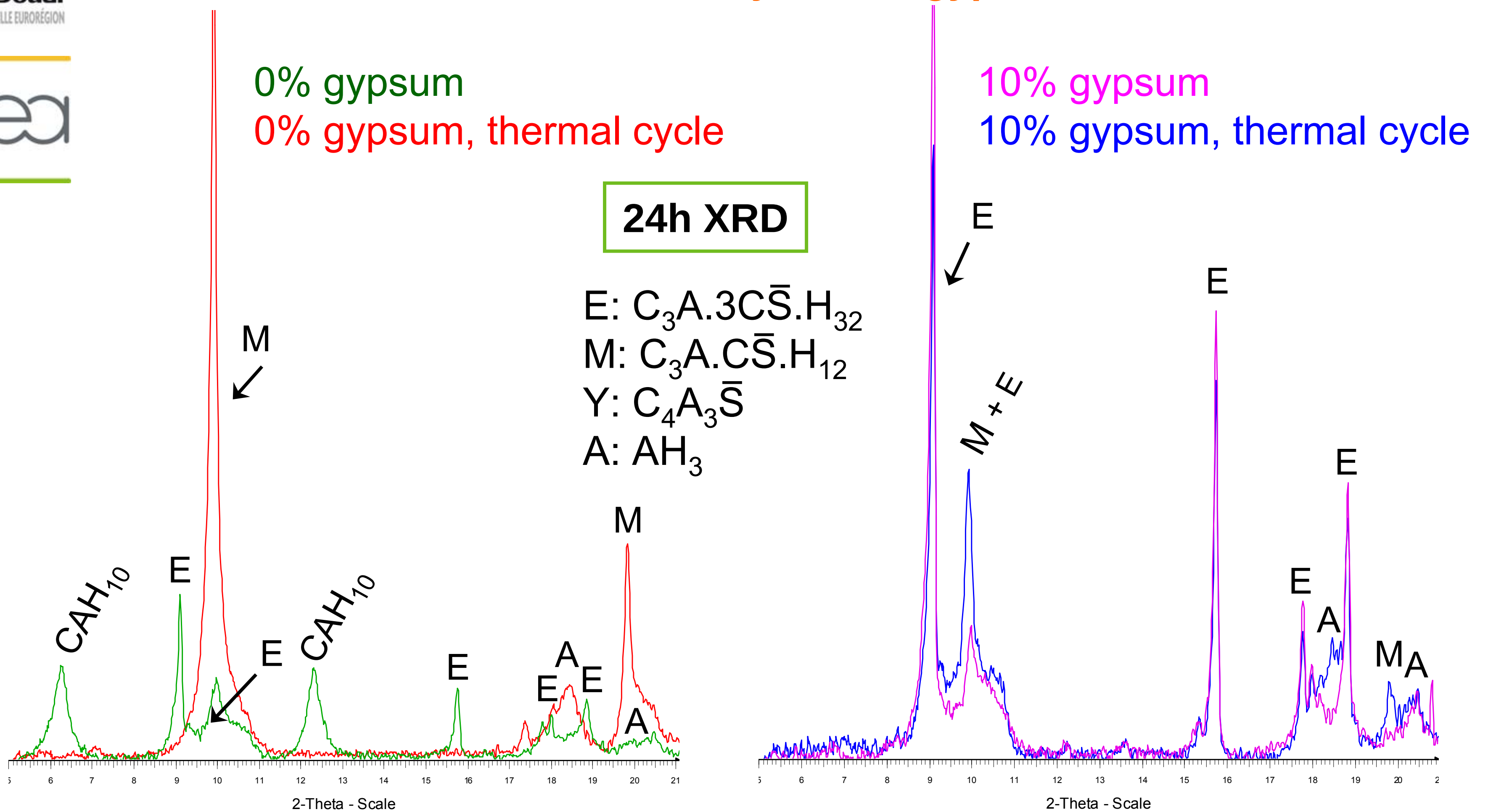
Mineralogical evolution: influence of gypsum



Mineralogical evolution:
influence of thermal cycle and gypsum content

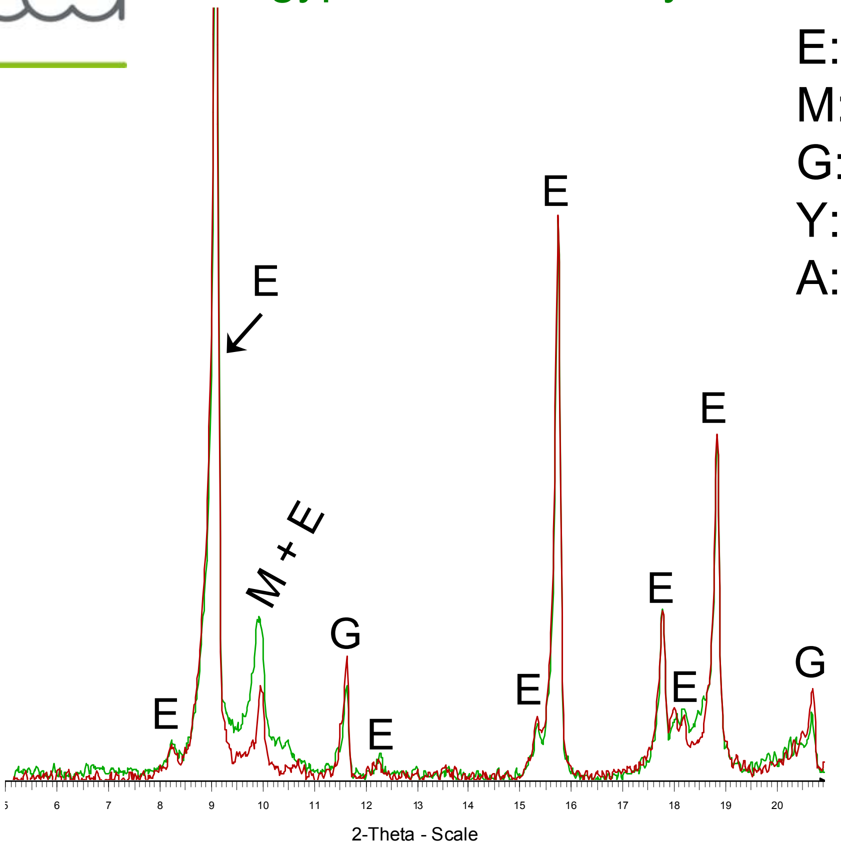


Thermal cycle promoted precipitation of calcium monosulfoaluminate hydrate instead of ettringite. This effect was enhanced in absence of gypsum. CAH_{10} was unstable with gypsum and/or temperature rise.

Mineralogical evolution:
influence of thermal cycle and gypsum content

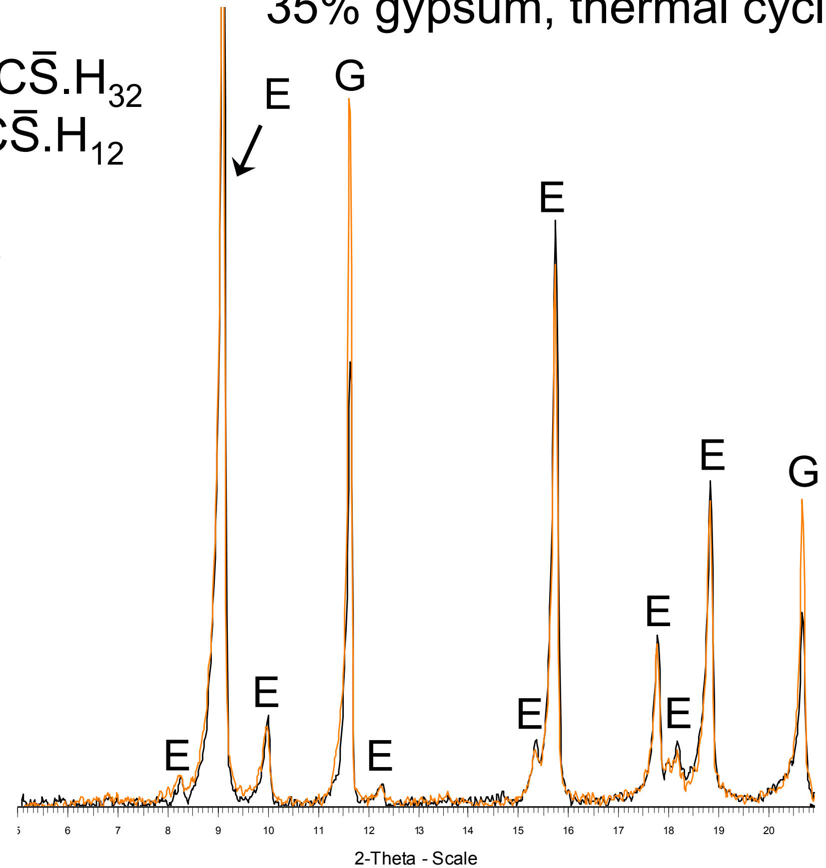
24h XRD

20% gypsum
20% gypsum, thermal cycle



E: $C_3A.3C\bar{S}.H_{32}$
M: $C_3A.C\bar{S}.H_{12}$
G: $C\bar{S}H_2$
Y: $C_4A_3\bar{S}$
A: AH_3

35% gypsum
35% gypsum, thermal cycle



With 20% and more of gypsum, the thermal cycle had no significant effect on the mineralogy: gypsum stabilized ettringite in spite of the temperature increase. Gypsum influence seemed to prevail over temperature effect.

Mineralogical evolution: influence of zinc chloride addition

7 days XRD

Chloride-containing minerals were identified:

- **Kuzel's salt, K:** $3CaO\text{-}Al_2O_3\text{-}0.5CaCl_2\text{-}0.5CaSO_4\text{-}12H_2O$
- **Friedel's salt, F:** $3CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}10H_2O$

0% gypsum

0% gypsum, **0.5 mol/l**

E: $C_3A.3C\bar{S}.H_{32}$

M: $C_3A.C\bar{S}.H_{12}$

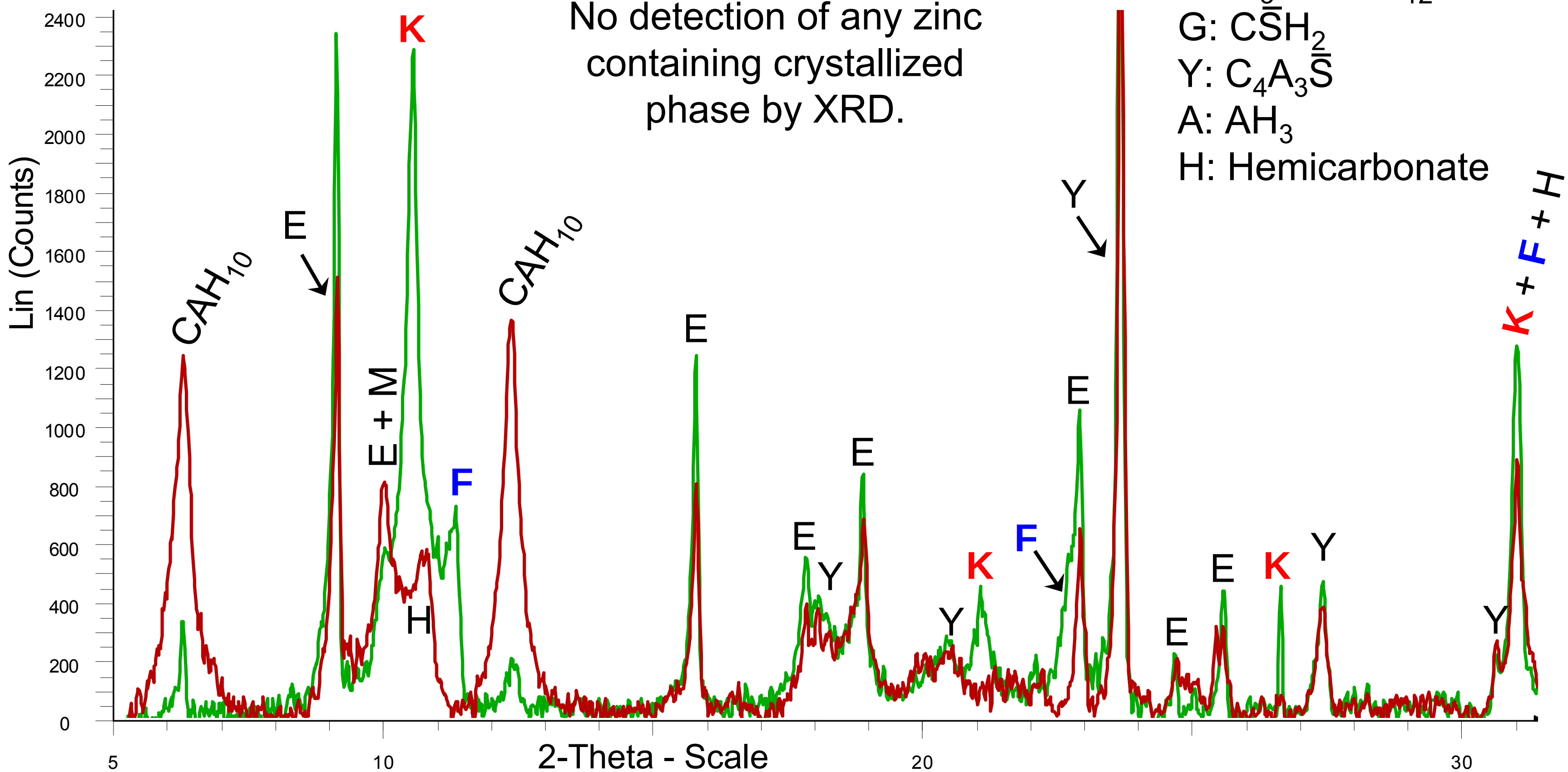
G: $C\bar{S}H_2$

Y: $C_4A_3\bar{S}$

A: AH_3

H: Hemicarbonate

No detection of any zinc containing crystallized phase by XRD.

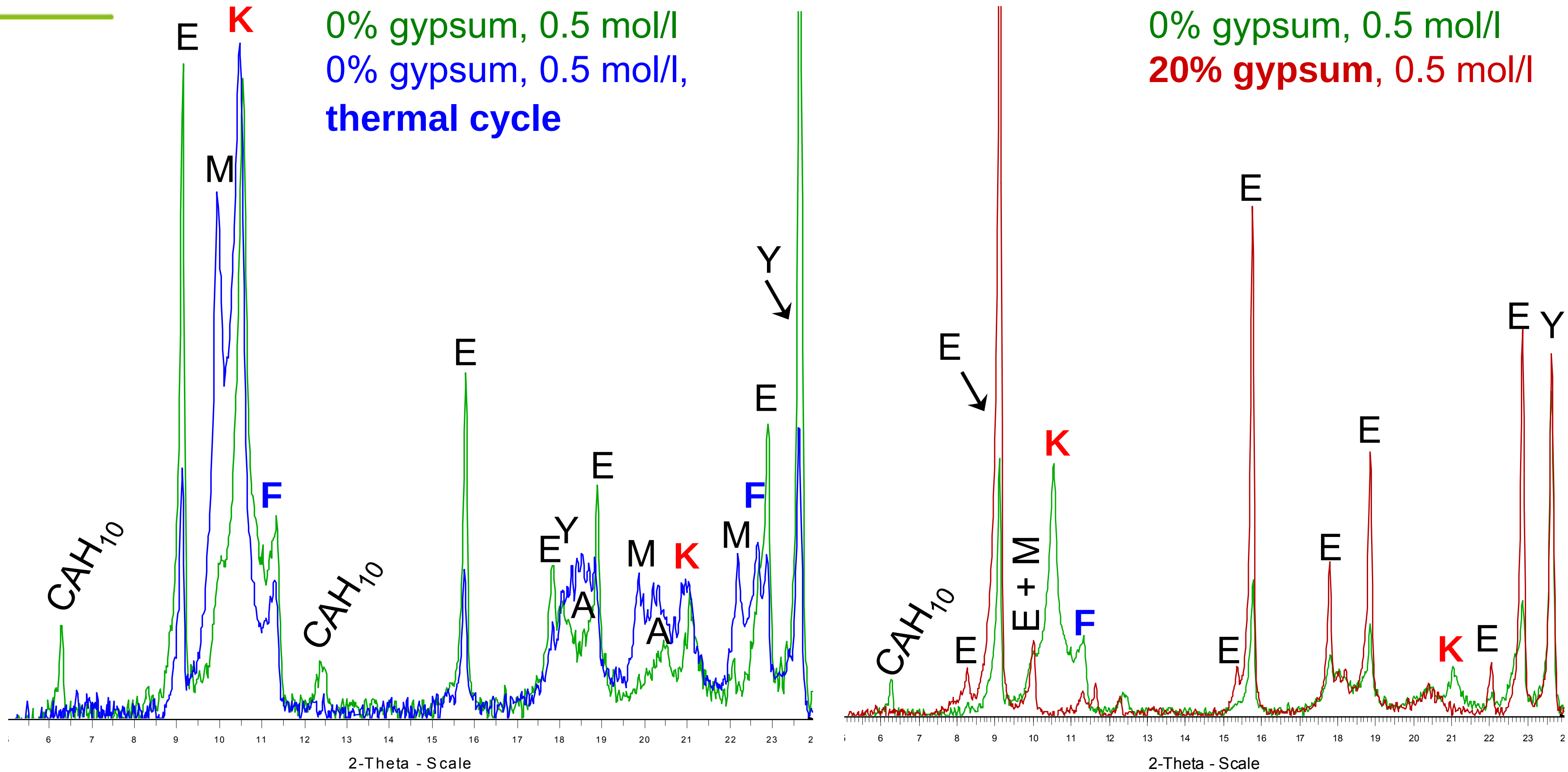


Mineralogy evolution: influence of zinc chloride addition

Influence of thermal cycle

7 days XRD

Influence of gypsum (20%)



K: $3CaO\text{-}Al_2O_3\text{-}0.5CaCl_2\text{-}0.5CaSO_4\text{-}12H_2O$; **F:** $3CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}10H_2O$

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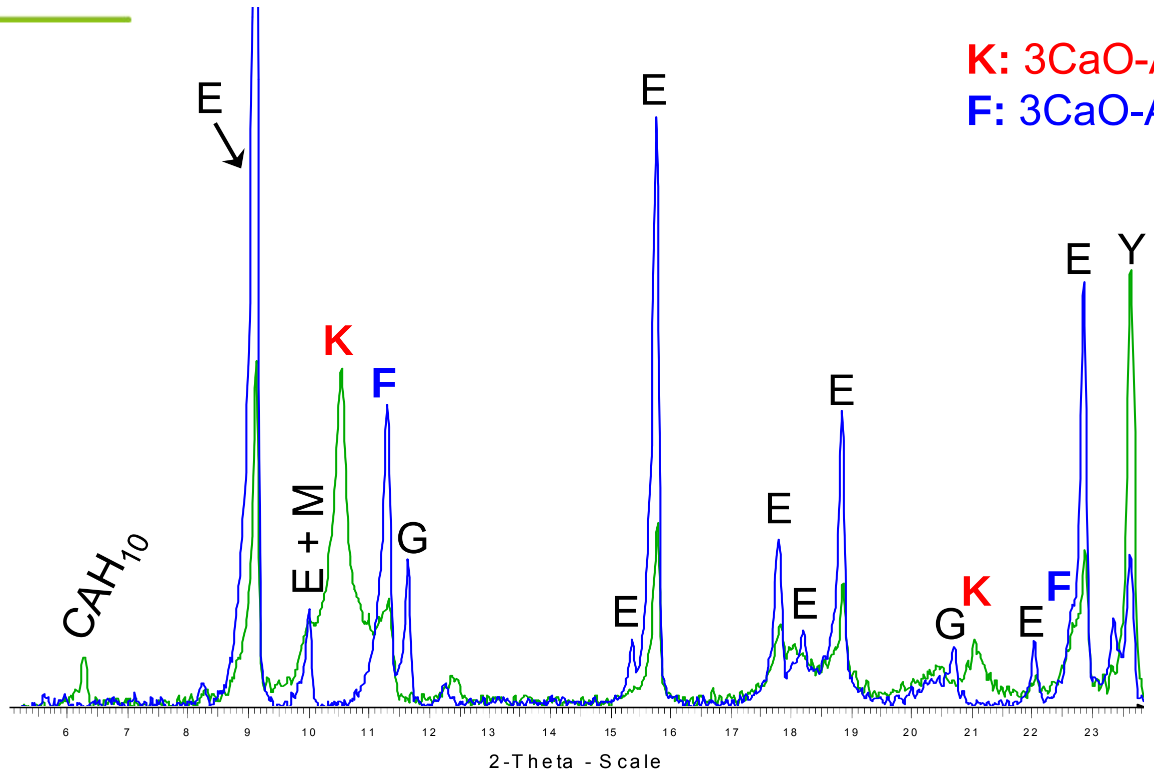
Mineralogical evolution:
influence of zinc chloride addition

7 days XRD

With thermal cycle and 20% gypsum



K: $3CaO\text{-}Al_2O_3\text{-}0.5CaCl_2\text{-}0.5CaSO_4\text{-}12H_2O$

F: $3CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}10H_2O$

0% gypsum, 0.5 mol/l

20% gypsum, 0.5 mol/l, **thermal cycle**

Gypsum promoted ettringite precipitation instead of all AFm phases. However, Friedel's salt seemed to be stabilized by a temperature rise and a strong chloride concentration.

Conclusion

CSA cements showed a much better compatibility with zinc chloride than OPC: hydration was slightly slowed down but setting inhibition was never observed.

Chloride anions induced a strong retardation, but this effect was balanced by zinc cations and sulfate anions from gypsum.

In the presence of zinc chloride, the mineralogy observations revealed the precipitation of chloro-AFm such as Kuzel's salt and Friedel's salt.

The thermal history of the samples proved to be a key parameter since a temperature rise accelerated the rate of hydration and modified the nature of the hydrates, particularly with a low gypsum content.

Prospects

- to find the location of zinc cations,
- to identify the mechanisms which inhibit or accelerate the hydration,
- to investigate the influence of zinc chloride and temperature on the properties of the hardened materials (porosity, compressive strength, length change, durability,…).