

# Progress in the development of Ternocem

## A belite ye'elimite ferrite cement

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**HEIDELBERGCEMENT**

# Progress in the development of Ternocem

Formerly known as BCT

## Belite Calciumsulfoaluminate Ternesite (BCT) A new low carbon clinker technology

Wolfgang Dienemann, Dirk Schmitt, Frank Bullerjahn, Mohsen Ben Haha

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VDZ Düsseldorf



Slide 2 - September 28, 2018 – VDZ Congress 2018  
Progress in the development of Ternocem  
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# 1. Background: The CO<sub>2</sub> challenge and alternative binders

## ■ How to (further) reduce CO<sub>2</sub> impact of concrete production?

- Reduce concrete volumes
- Reduce clinker content in concrete
- Use of alternative fuels and raw materials
- Use of supplementary cementitious materials (SCMs)
- **Alternative binders**

## ■ A wide range of alternative binder concepts have been investigated and developed over the past decades

- Hydrothermal activated binders, Alkali activated systems, Mg-Si binders, etc...

**So far no alternative binder approach reached maturity  
to replace OPC based concrete in substantial volumes**

# 1. Background: Specific CO<sub>2</sub> emission from clinker phases

- Belite cement: only low reduction of CO<sub>2</sub>, low reactivity, hard to grind
- Calcium aluminate cement: high burning temperature (ca. 1700°C), low CO<sub>2</sub>
- CSA cement: low burning temperature (ca. 1250°C), low CO<sub>2</sub>, easy to grind
- Ternocem: low burning temperature 1150 – 1280°C, low CO<sub>2</sub>, easy to grind

Phase Chemical	Phase notation	Synthesis from	g CO <sub>2</sub> / g phase	% CO <sub>2</sub>	
3CaO·SiO <sub>2</sub>	C <sub>3</sub> S	Limestone + quartz	0.58	100	} OPC Belite
2CaO·SiO <sub>2</sub>	C <sub>2</sub> S	Limestone + quartz	0.51	88	
3CaO·Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A	Limestone + Al-source	0.49	85	} CAC
CaO·Al <sub>2</sub> O <sub>3</sub>	CA	Limestone + Al-source	0.28	48	
4CaO·3Al <sub>2</sub> O <sub>3</sub> ·SO <sub>3</sub>	C4A3\$	Limestone + Al-source + anhydrite	0.22	38	} CSA Ternesite
5CaO·2SiO <sub>2</sub> ·SO <sub>3</sub>	C5S2\$	Limestone + quartz + anhydrite	0.37	64	

**Ternocem reduces CO<sub>2</sub> emissions by 30%**



## 2. Ternocem clinker technology

### Raw materials

- Limestone / marl
- **Bauxite**
- Iron sources
- SiO<sub>2</sub> sources
- **Sulfate sources**
- Al-Si bearing minerals
- Pozzolana
- **Industrial by-products**



### Production / Technology

- Production similar to OPC clinker manufacturing
- **Lower energy demands in comp. to OPC**
  - 1250 -1350 °C
  - Friable clinker
- **Lower CO<sub>2</sub> emissions compared to OPC**
- **SO<sub>2</sub> emission mastered**



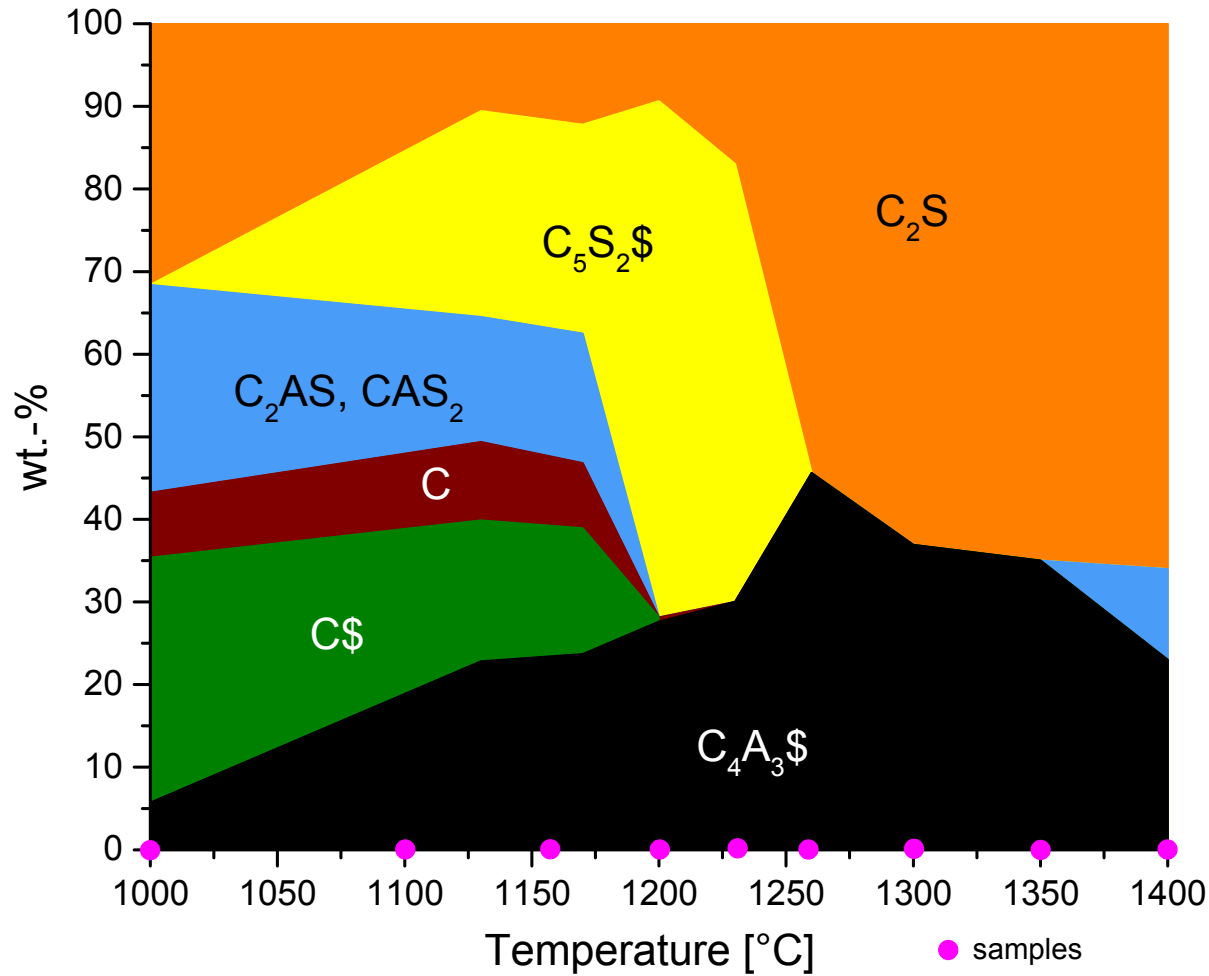
### Cement / Binder

- Based on
  - Ye'elimite C<sub>4</sub>(A<sub>x</sub>F<sub>1-x</sub>)<sub>3</sub>S
  - Belite C<sub>2</sub>S
  - Ferrite C<sub>2</sub>(AF)
  - Ternesite
  - Anhydrite / Gypsum C\$·nH<sub>2</sub>O
  - Minor phases



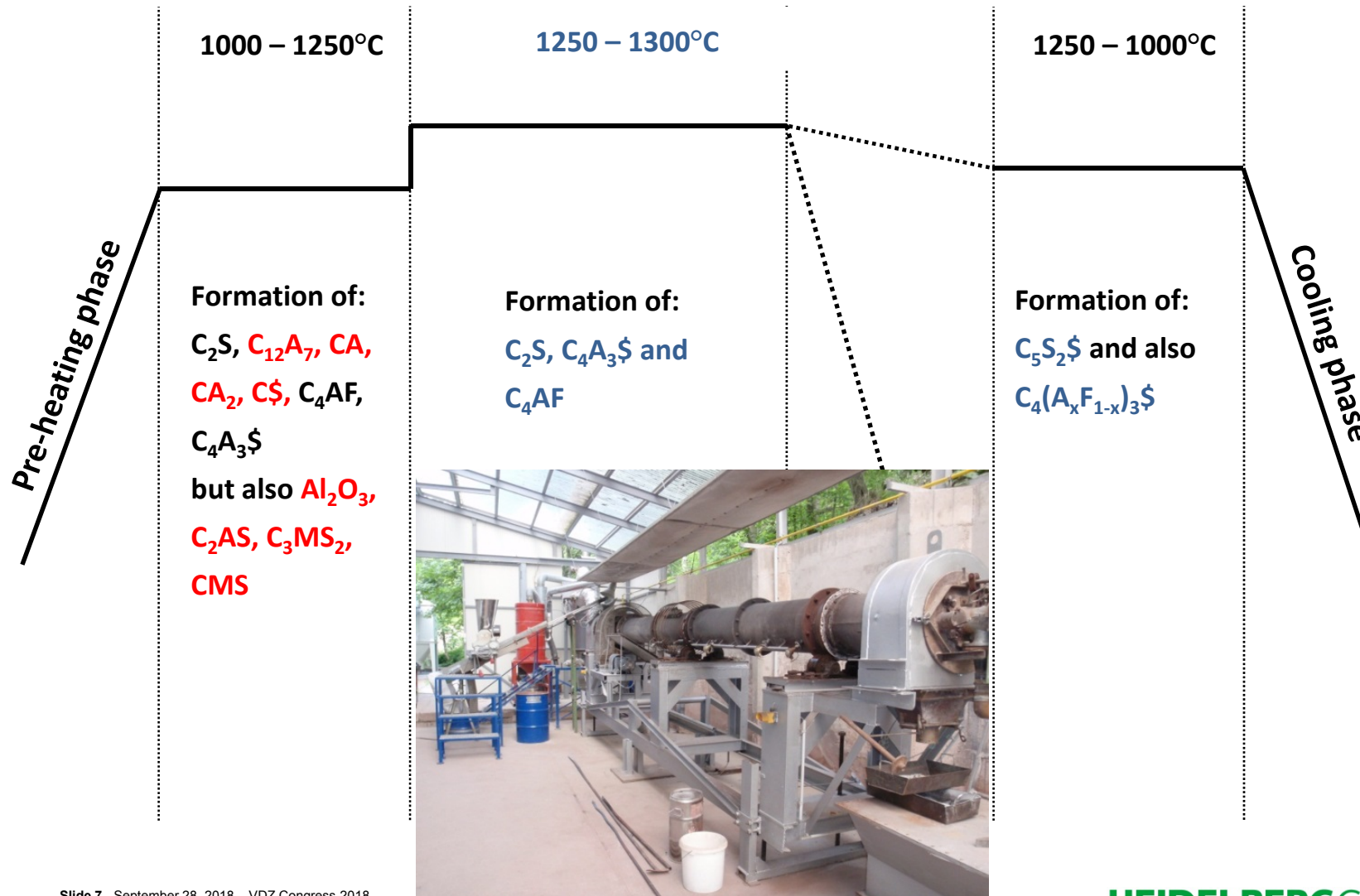
## 2. Ternocem clinker technology: Equilibrium phase composition

- Ternesite only stable below 1250°C



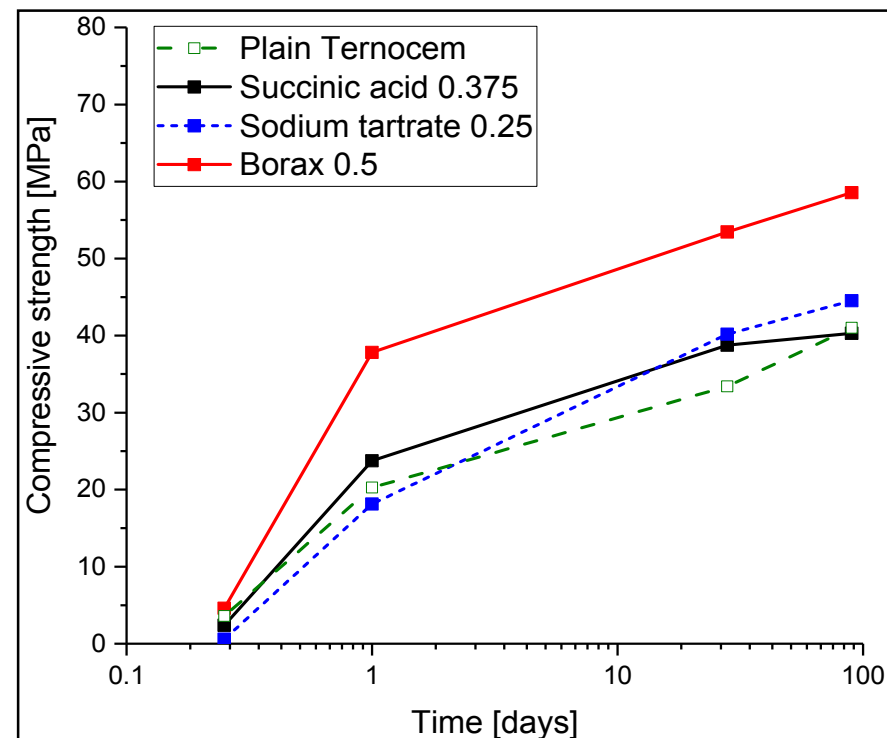
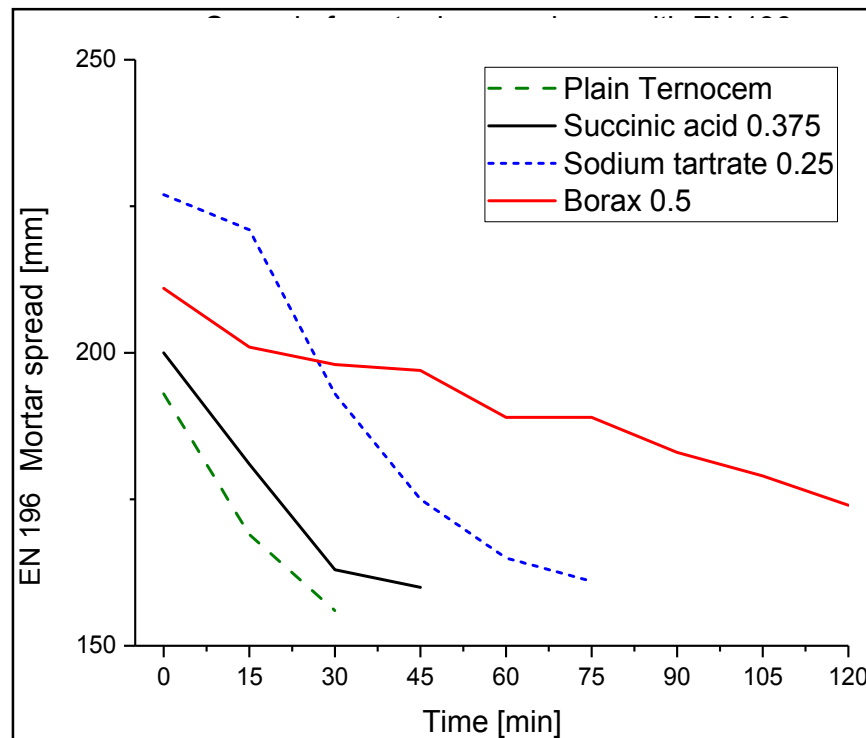
PhD Tilman Scholten 2017

## 2. Ternocem clinker technology: Clinker phase formation



## 2. Cement performance: Retarder development

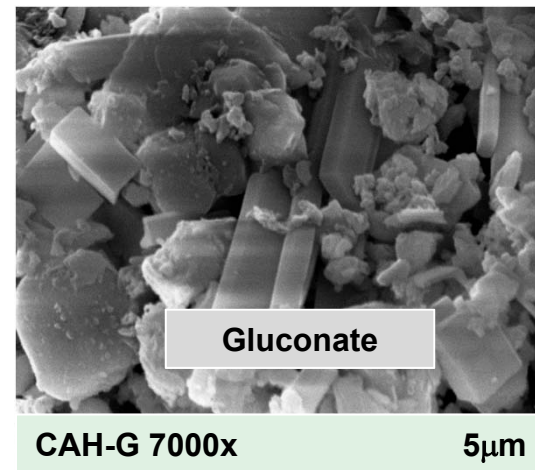
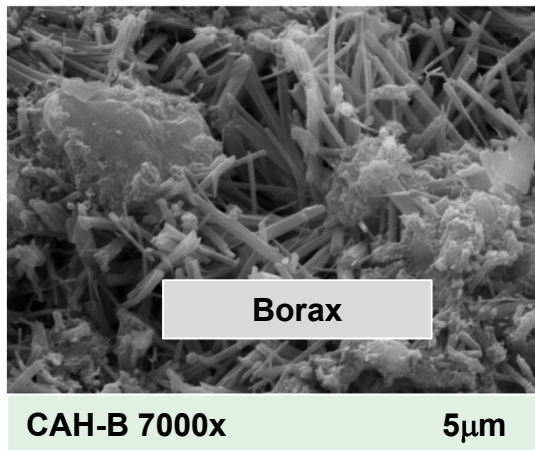
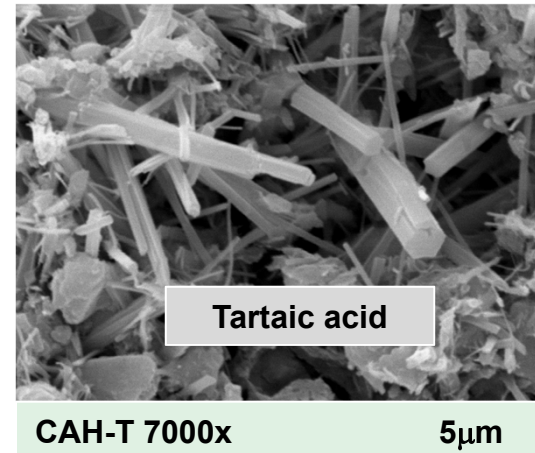
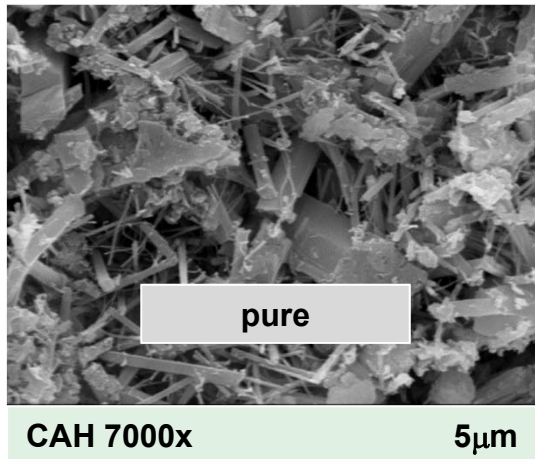
- Boron acid / salts are the optimal retarders for Ternocem
- Performance significantly better compared to other known solutions (e.g. organic acids)
  - Combination of retarding – microstructure optimization effect
- Similar results for borax and boric acid





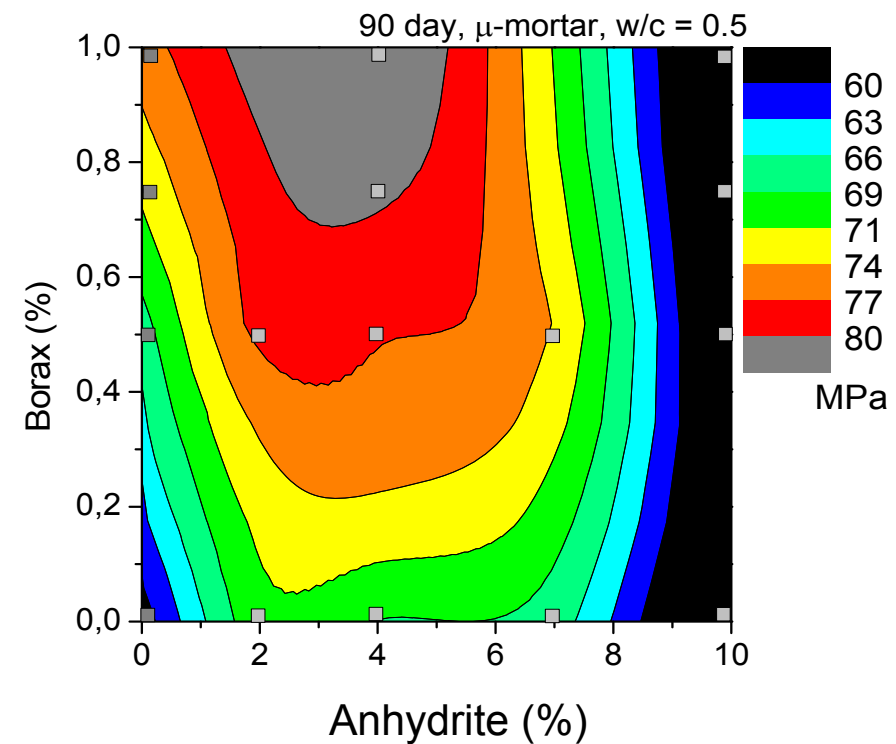
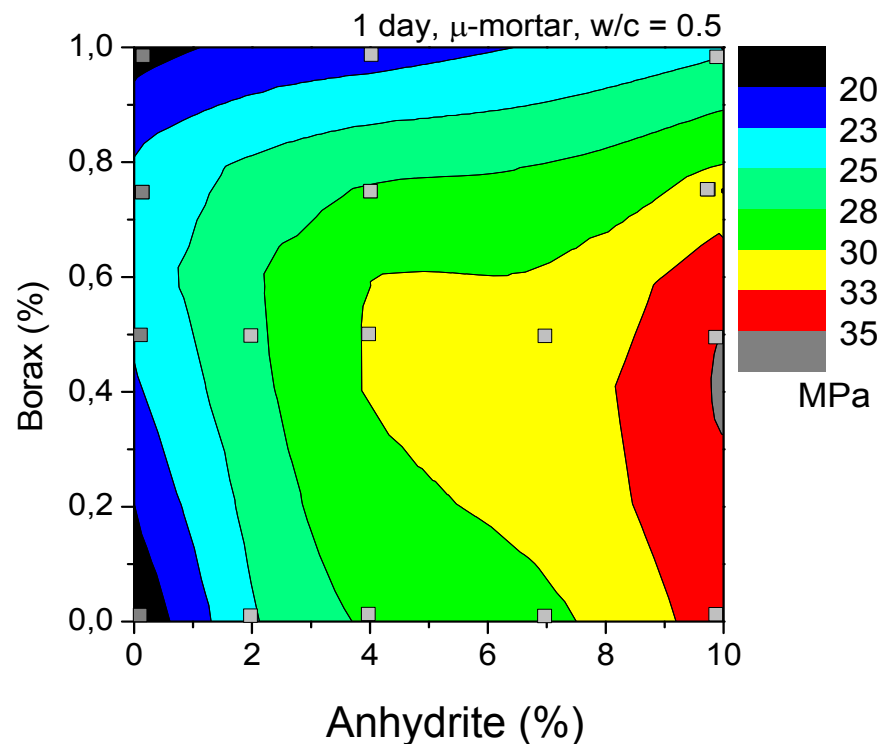
## 2. Cement performance – Effect of retarders

- Ettringite morphology / microstructure identical to pure system when Borax is used



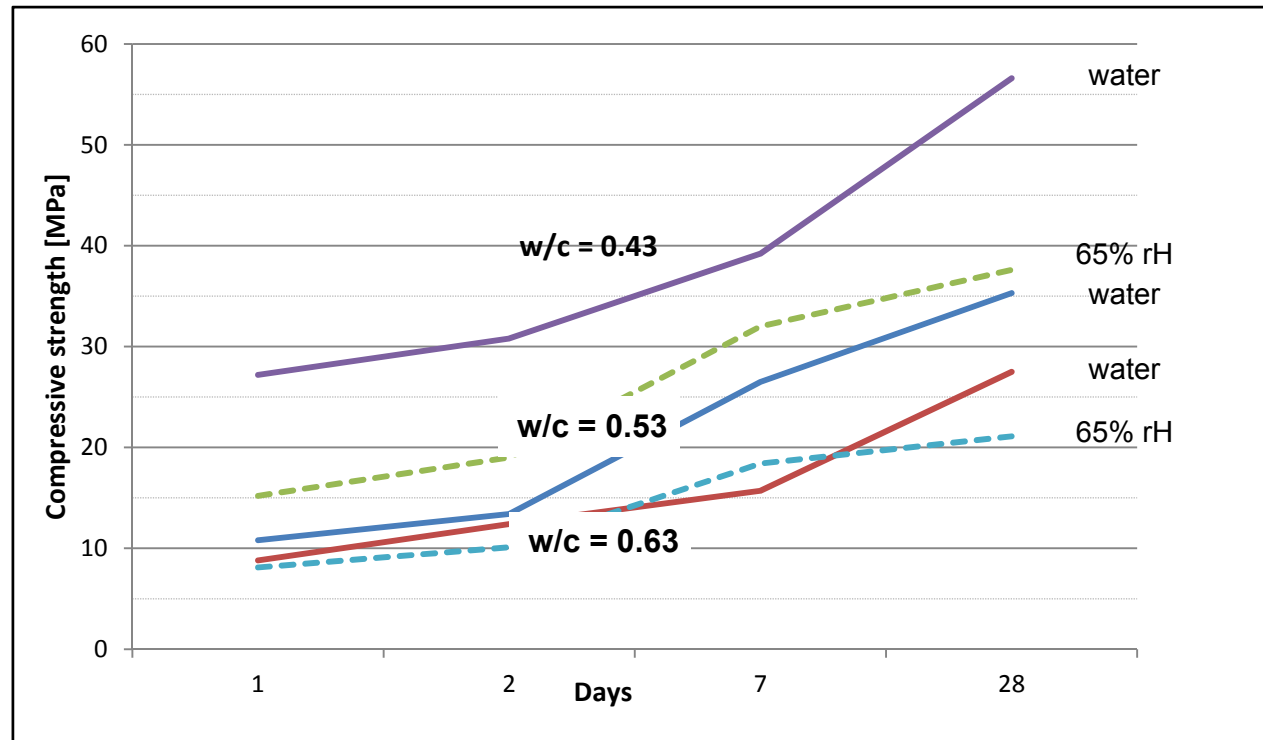
## 2. Cement performance: Strength development flexibility

- Sulfate level strongly determines early and late strength
- Strength development can be adapted to type of application



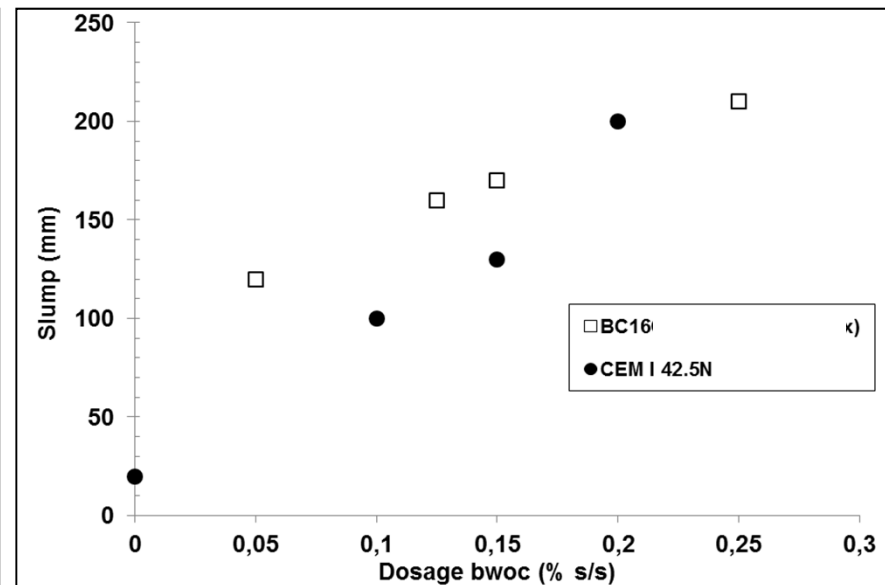
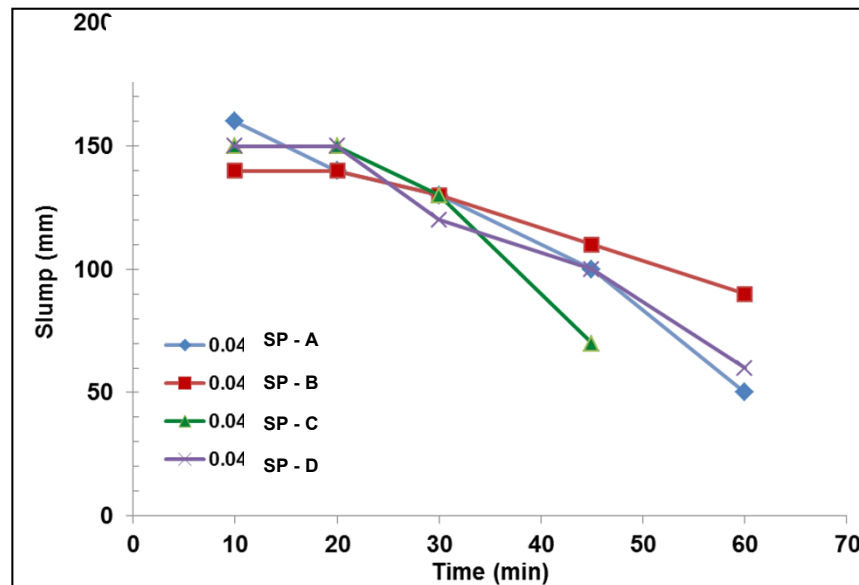
### 3. Concrete technology: Effect of w/c ratio and storage

- Strength not very sensitive to curing (under water / 65 % rH)
- Strength development and its dependence on w/c roughly comparable to CEM I



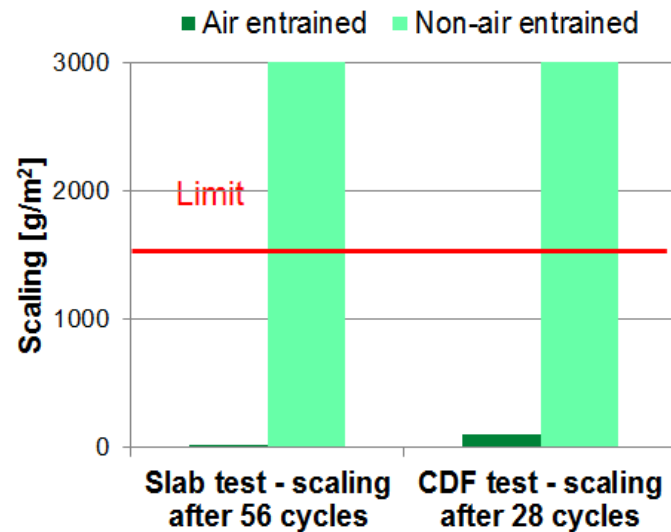
### 3. Concrete technology: Workability

- Performance of conventional superplasticizers (SP) similar to OPC concrete
- Ternocem concrete less sensitive to variations in SP dosage
- Open time seems well controlled by retarder

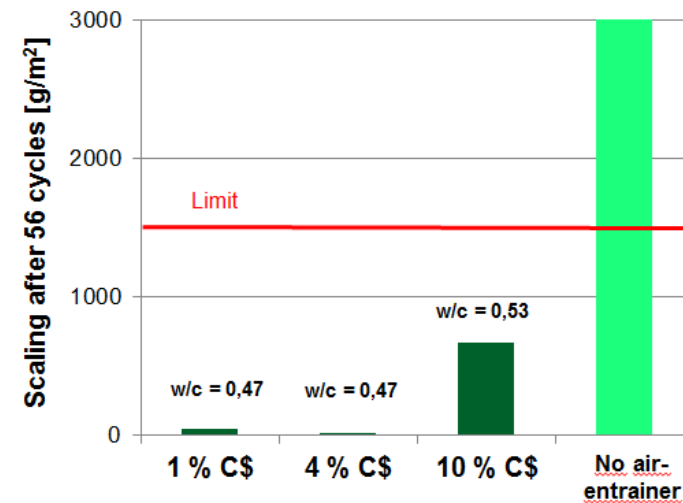


### 3. Concrete technology: Freeze-thaw & de-icing salt resistance

- Air-entrained concrete has excellent scaling resistance
- Existing air-entraining agents are suitable
- Slab tests and CDF tests give comparable results
- Excellent resistance even for high w/c for all sulfate levels



$c = 390 \text{ kg/m}^3$   
 $w/c = 0.43$

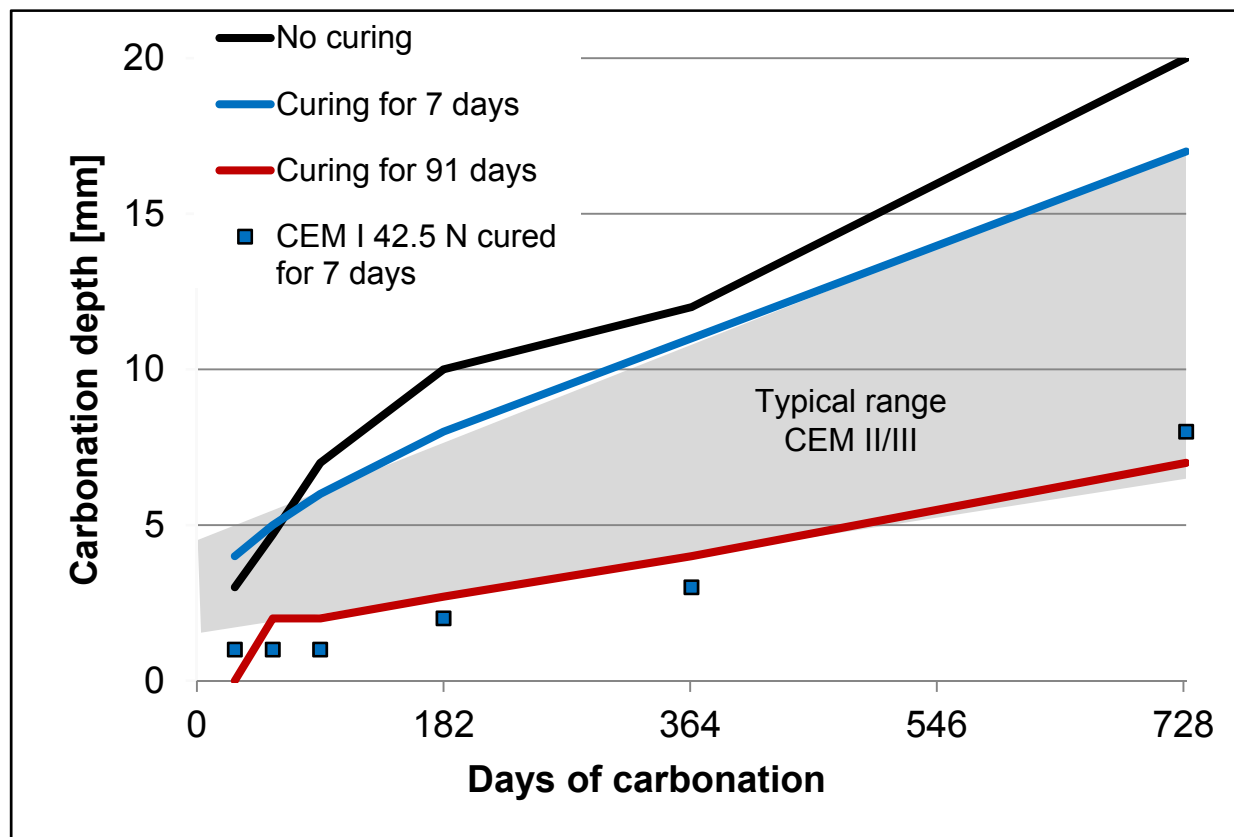


$c = 325-350 \text{ kg/m}^3$   
 $w/c = 0.47-0.53$



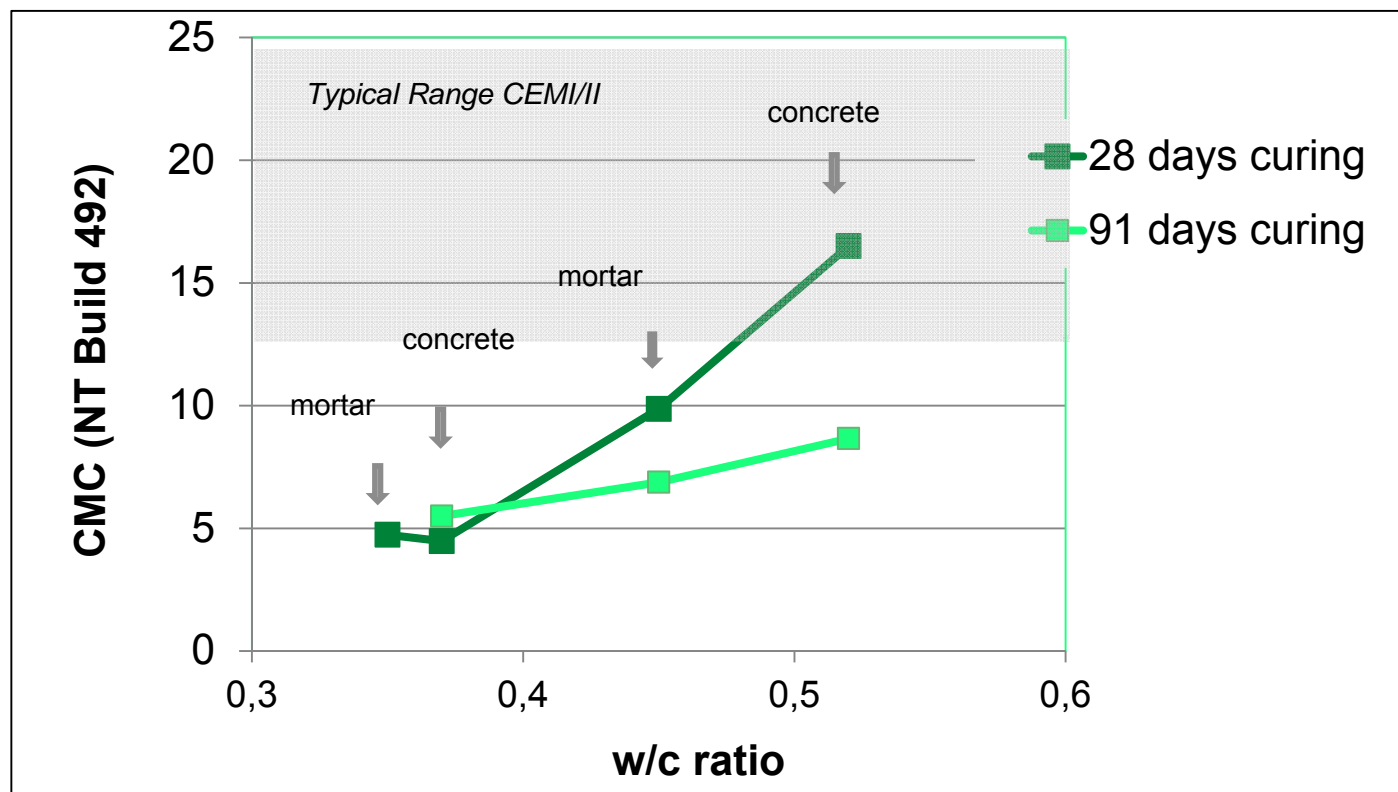
### 3. Concrete technology: Carbonation

- Carbonation rates generally higher than OPC cements, comparable to composite cements
- Belite reactivity is important to have a good carbonation resistance
- Carbonation resistance improved by increased curing time or lowered w/c ratio



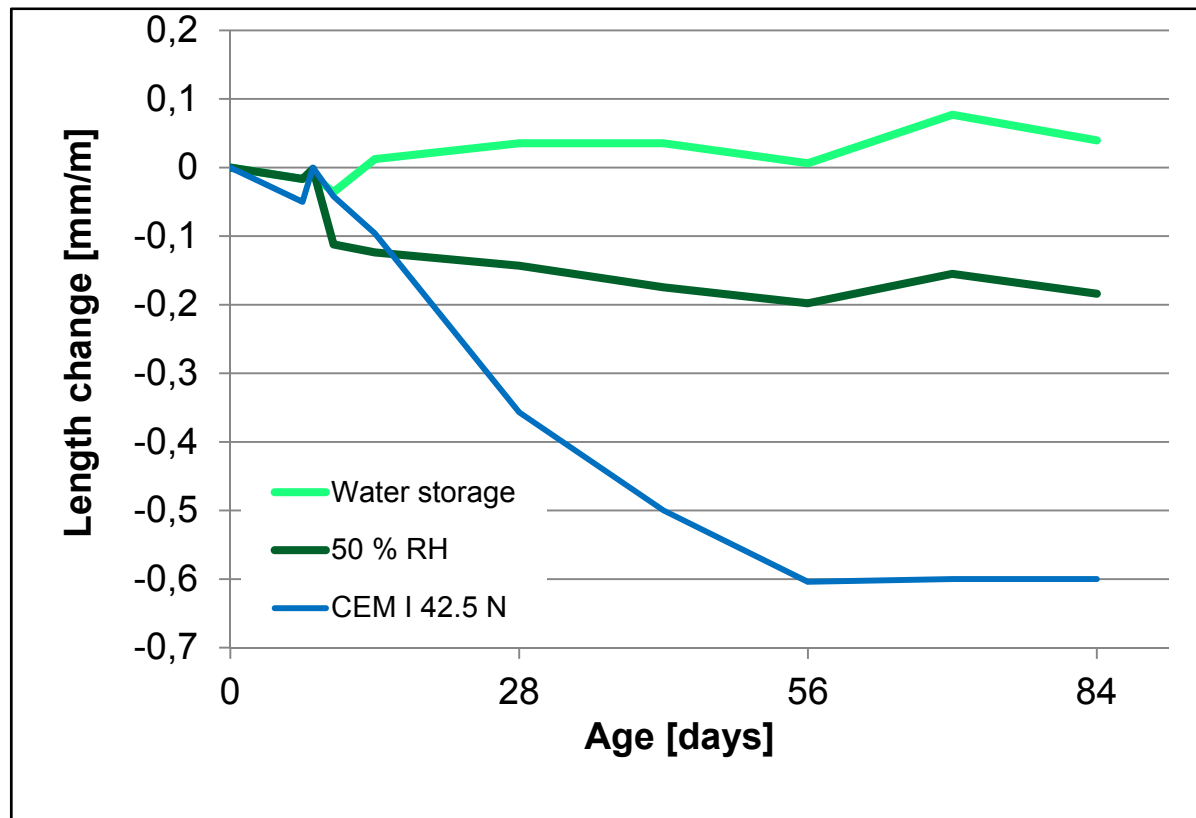
### 3. Concrete technology: Chloride ingress

- Migration coefficients within common range
- Significant impact of w/c and curing time / aging
- Chloride profiles different than common concretes – under investigation



### 3. Concrete technology: Shrinkage

- Excellent volume stability at all ages and exposures
- Independent of w/c curing time conditions
- Low risk of cracking



## 4. Ternocem applications: Concrete field trial, Germany 2014

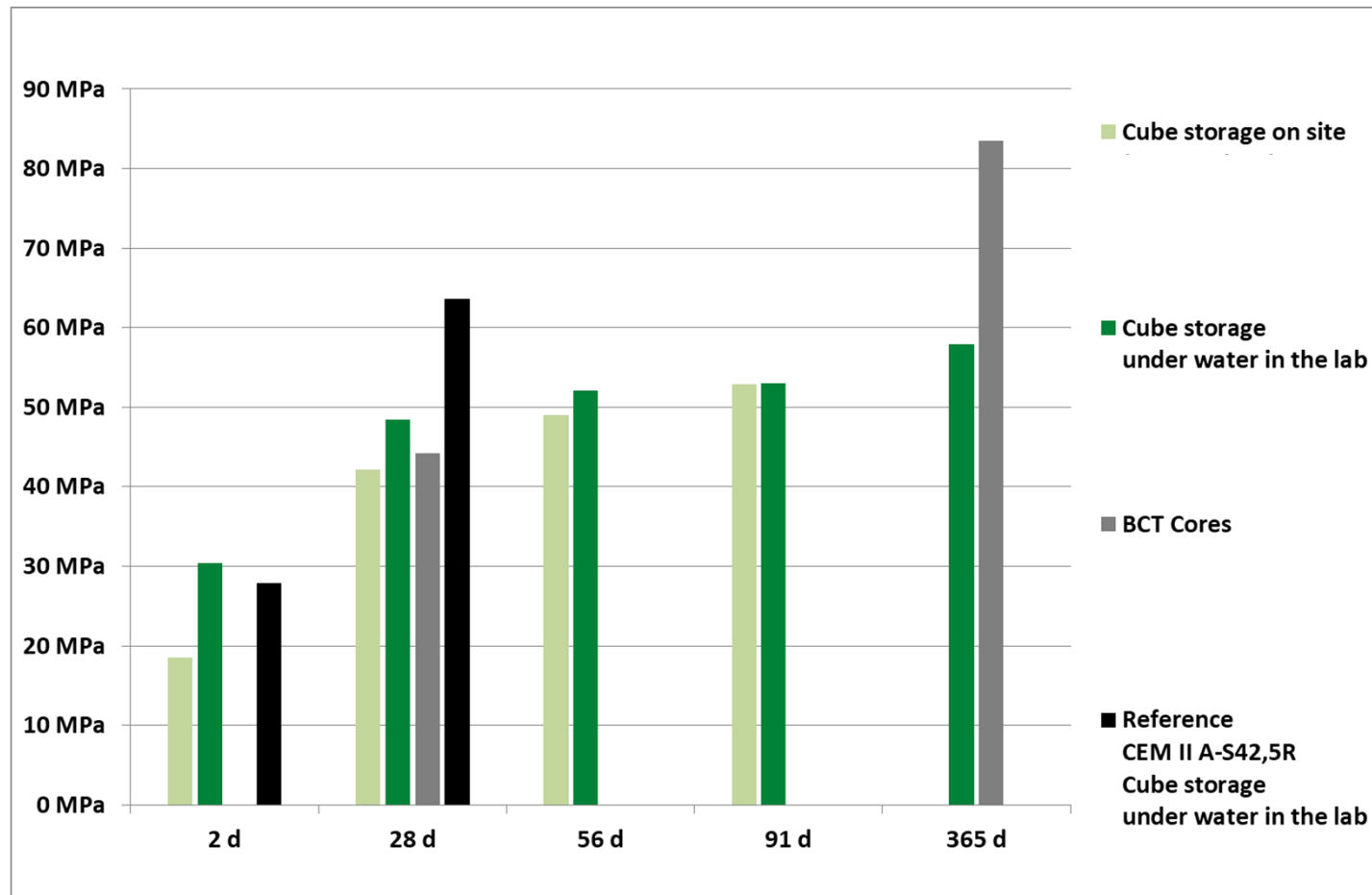
### ■ The first concrete slab with Ternocem casted in 2014

- Good workability and good surface finishing
- Acceptable strength levels at 28 days
- Extremely high strength levels beyond



## 4. Ternocem applications: Concrete field trial, Germany 2014

### Strength development





## ■ 4. Ternocem applications: Railways sleepers production 2016

### ■ Key requirements on concrete for pre-stressed sleepers

- Workable for about 30 – 40 Min.
- High early strength  $\geq 30$  MPa at 6 h
- Frost resistant

### ■ Pilot production

- Abetong, Vislanda, Sweden
- August 2016

### ■ Results

- Strength 33,0 MPa at 6h in lab
- In production 32,3 MPa after 9 h (cutting)
- 28 days strength: 58,6 MPa (lab); 61,3 MPa (sleepers)

## 4. Ternocem applications: Railways sleepers production 2016

- Good flow and compactable concrete despite low w/c ratios ( $w/c \triangleq 0.36$ ) used for the production



## 4. Ternocem applications: Railways sleepers production 2016

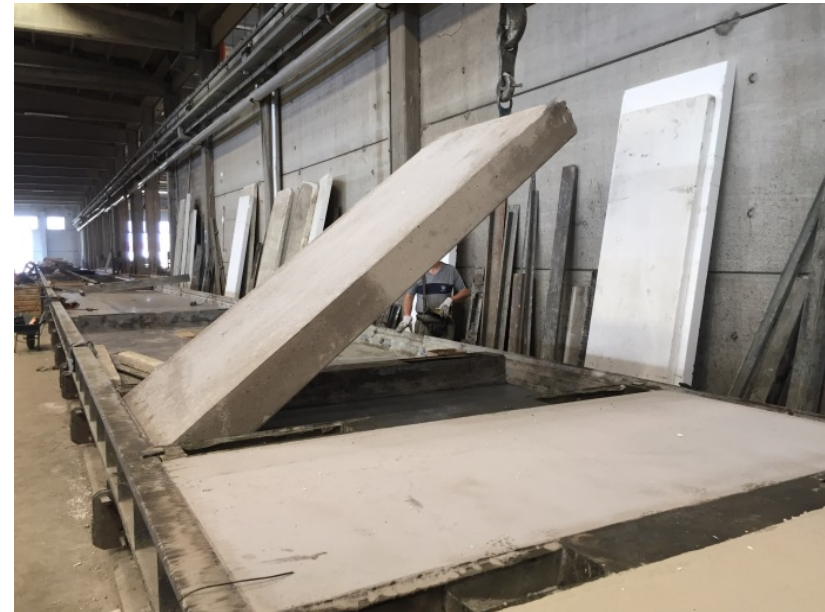
- Good finishing surfaces
- No deleterious reactions observed at contact zone to OPC concrete





## 4. Ternocem applications: ECO-Binder - Test at precast, Italy 2017

- Despite high temperatures ( $>30^{\circ}\text{C}$ ) slump stable at  $21\pm 2$  cm over 2 hours
- Open time - around 4 hours
- Compressive strength reached
  - 30 MPa after 20 hours
  - 35 MPa after 3 days
  - 46 MPa at 28 days



## ■ 4. Ternocem applications: Pre-cast wall elements, Sweden 2017

- Good workability
- Open time – between 1.5 and 2 hours
- Easy finishing
- Compressive strength reached
  - 20 to 23 MPa after 6 hours
  - 30 to 35 MPa after 1 day





## 4. Ternocem application: Road in Lixhe plant, Belgium 2018

■ Concreting at  $-2^{\circ}\text{C}$ , frost in first nights



## 4. Ternocem application: Road in Lixhe plant, Belgium 2018

■ Strength results:	20°C	outside
2d (MPa):	34,4	1,2
7d (MPa):	44,5	37,7
28d (MPa):	53,4	53,7

- 60 m no joints, no cracks
- In use since March



## 4. Ternocem application: mortar formulations

### ■ Promising characteristics and benefits for building chemistry

- More simple „single“ binder formulations can be used

Cement ( <i>what can be achieved</i> )	BYF - Low sulphate	BYF - High sulphate
Early strength	> 10 MPa after <b>4 hours</b> > 20 MPa with accelerator	> 15 MPa after <b>4 hours</b> > 30 MPa with accelerator
Workability time	From 15 to > 120 minutes	From 15 to > 120 minutes

### ■ Typical properties

- Formulation of low to zero shrinkage or expansive cements
- Normal to fast setting and high early strength
- Resistance to sulfate attack and against weak acids
- No efflorescence tendency
- Excellent finishing surfaces and abrasion resistance

## ■ 5. Outlook

**The Ternocem technology is in an advanced development stage but still several hurdles need to be overcome before commercialization.**

- Mastering of concrete technology – workability in various applications
- Establish / optimize durability and long-term performance of concrete
- Technical approval / standardization prerequisite on cement and concrete level
- Market launch, acceptance by customers

**Pilot market introduction ongoing in Sweden**