75 Years of experience with high dosed blast furnace slag cement

Mario de Rooij

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TNO in brief

*The **N**etherlands **O**rganization for Applied Scientific Research*

- Owner: Dutch Government
- Mission:
  TNO connects people and knowledge to create innovations that boost the sustainable competitiveness of industry and well-being of society
- 4,400 people
- **576 M€** turn over in 2009; ± 30 % through government funding
- Active in 7 areas:
  - Safety, security and defense
  - Healthy living
  - Industrial innovation
  - Energy
  - Mobility
  - Built Environment
  - Information society

Content

- **Slag as product**
  - No waste product, but quality control tool
  - Long history
  - Standard for slag
- **Slag as binder material**
- **Properties of slag based concrete**
  - Low heat of hydration, strength development, freeze-thaw, resistance against chloride and ASR
- **Sales and use**
- **Conclusions**

What is slag?

The production process

Table: *Composition range of main components in slag* ***(mass %)***

Component	Europe	NL
CaO	30 – 45	~ 37
SiO_2	30 – 44	~ 33
Al_2O_3	5 – 16	~ 15
MgO	4 – 17	~ 11

Production:

100 ton pig iron results in
20 – 25 ton slag

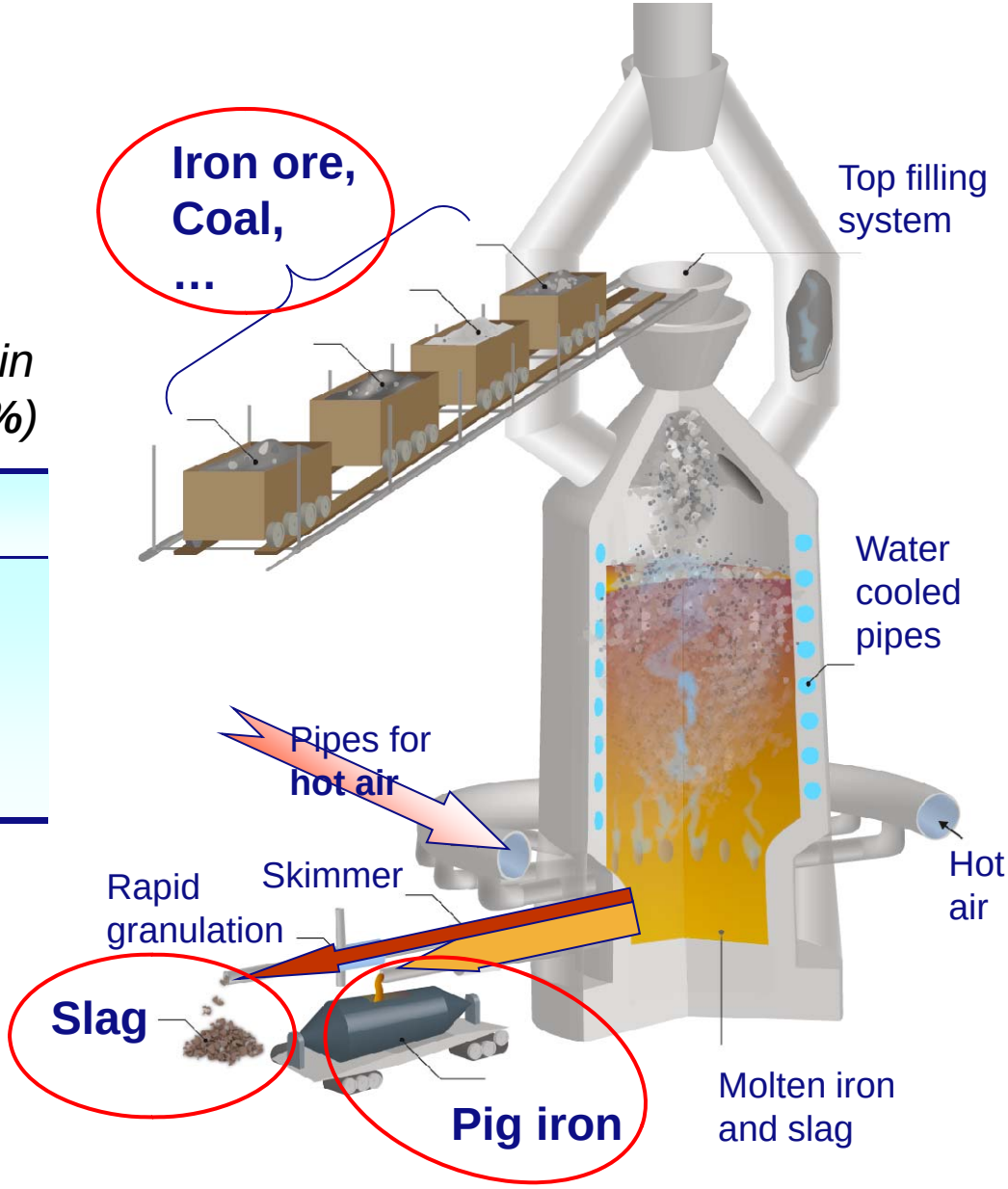


Fig.: *Schematic of a blast furnace*

Slag: Not a waste product!

But a quality control tool

Quality demand to produce **steel**:
Low sulfur content in pig iron (< 0.035%)

- **Achieved by moving sulfur to the slag**
  - Controlled by chemical composition of slag

$$Alkalinity = \frac{CaO + MgO}{SiO_2}$$

NL: ~ 1.48

- **Slag solidifies sooner than iron**
  - Solidification in blast furnace ruins process
  - Controlling liquidus temperature of slag
  - Liquidus temperature depends on CaO, MgO, Al_2O_3 and SiO_2
  - Same components as first point, but work in opposite direction

- **Blast furnace process is controlled via above two points**

Distinctive blue colour of slag cement

- **A main purpose of slag is to remove sulfur (S) from iron**
- In cement reaction the S reacts with present Fe and Mg to form FeS_2 and MgS, both blue coloured products
- Upon reaction with oxygen reaction continuous to form $FeSO_4$ and $MgSO_4$, which are both colourless

History line

From slag to binder

- 384 – 322 BC Aristotle first notes on making and using slag

- **1728** Patent of John Payne (UK); cast slag to produce blocks to build chimneys
- 1737 Bélidor (France) suggest using slag aggregates in ‘concrete’
- ***1824*** *Patent Portland cement by Joseph Aspdin*

Germany:

- 1853 ‘Discovery’ of latent hydraulic action of slag by a German blast furnace process operator (water cooling)
- 1862 Emil Langen has first results to activate slag
- **1888** Opening of first blast furnace cement works

- 1901 Request for cement standard with up to 30% slag
- 1907 Request for cement standard with up to 85% slag
- 1909 Cement standard with up to 30% slag
- 1917 Cement standard with up to 85% slag
- **1917** Blast furnace-cement has equal performance to Portland cement

Slag history in the Netherlands

From slag to binder

- 1921 - 1929 Noordersluis IJmuiden using German blast furnace cement

Locks of IJmuiden

Building periods

- 1876

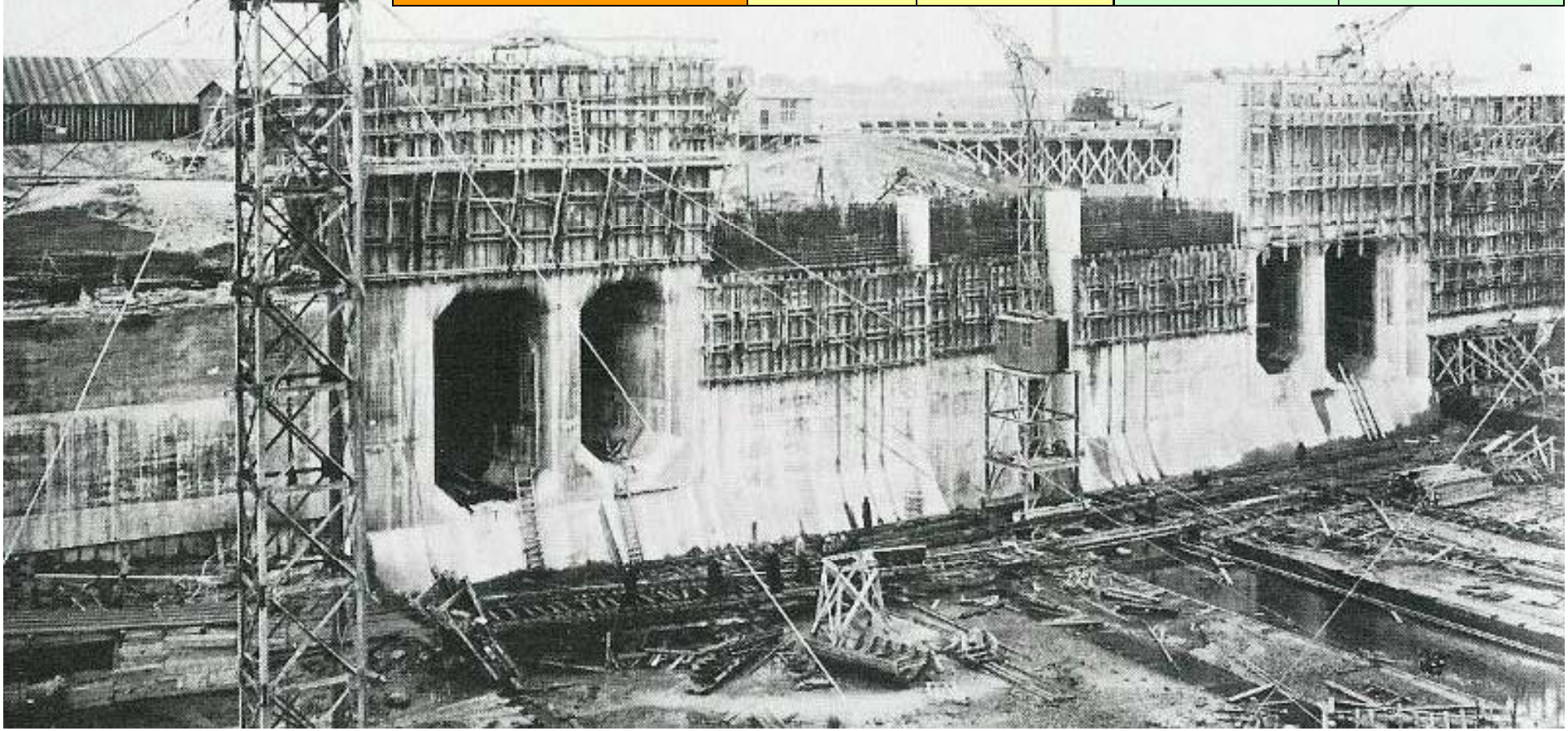
- 1896

1921 - 1929

Northern

400 x 50 m

Constituents	Typical Mix Design			
	Lock head		**Chamber walls and floors**	
	Liters	Ratio (V/V)	Liters	Ratio (V/V)
OPC (CEM I)	225	1		
Tras (pozzolanic)	56	¼		
GGBFS (CEM III)	--	--	240	1 1/8
Fine sand	193	0,85	193	0,9
Coarse sand	387	1,7	387	1,8
Gravel	700	3,1	700	3,3
Water	??	??	??	??



Slag history in the Netherlands

From slag to binder

- 1921 - 1929 Noordersluis IJmuiden using German blast furnace cement

- 1924 Production of steel in Netherlands using blast furnace
- 1931 Production of first blast furnace slag cement in Netherlands IJmuiden (CEMIJ)

- 1966 Opening of blast furnace slag cement plant Rozenburg (ROBUR)

- 1970s Blast furnace slag > 50% of cement market in Netherland

- 1996 Introduction CEM III/A 52,5 for faster strength development

European standard for slag: EN 15167 (2006)

'Ground granulated blast furnace slag for use in concrete, mortar and grout'

Main requirements:

Table: *Chemical requirements slag*

Component	Requirement
$CaO + MgO + SiO_2$	≥ 2/3
$(CaO + MgO)/ SiO_2$	≥ 1.0
MgO	≤ 18 % (m/m)
Sulfide	≤ 2.0 % (m/m)
Sulfate	≤ 2.5 % (m/m)
LOI	≤ 3.0 % (m/m)
Moisture content	≤ 1.0 % (m/m)

Table: *Physical requirements slag*

Component	Requirement
Blaine	≥ 275 m^2/kg
Start binding	≤ Twice of ref cement
Activity coefficient *	
• 7 days	≥ 45 %
• 28 days	≥ 70 %

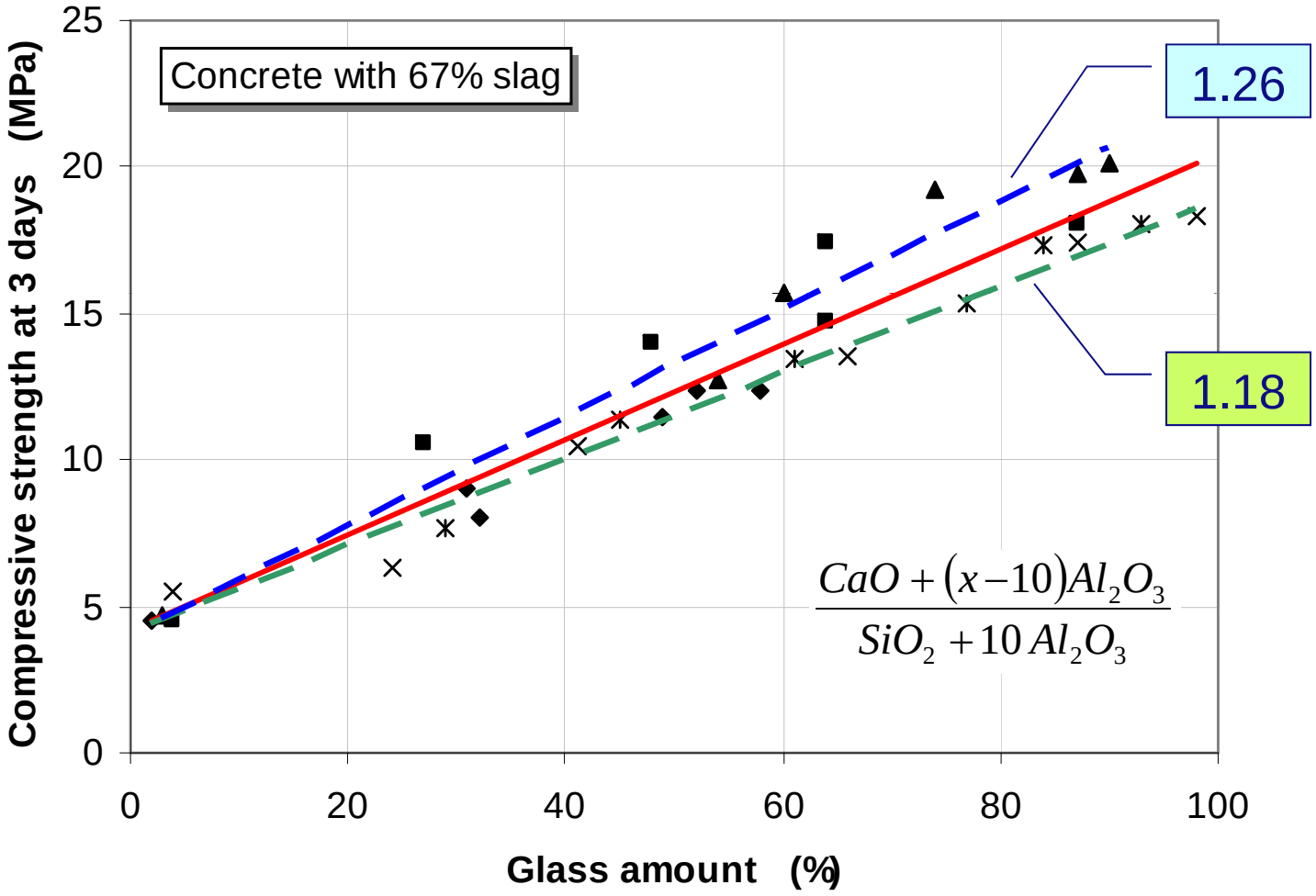
Blast furnace controlled on:

NL: ~ 1.48

* Activity coefficient based on 50% ref cement and 50% slag

Effect of glass phase

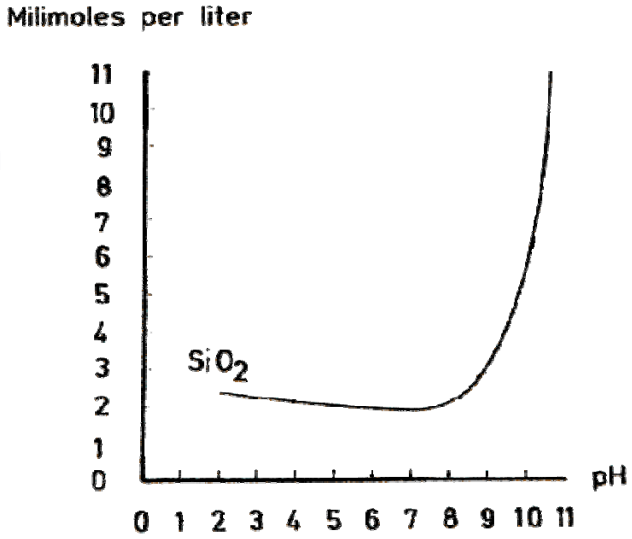
on strength development (Dölber, 1961)

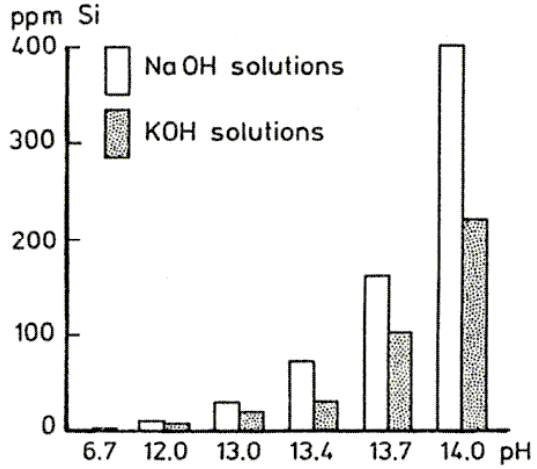


Activation of slag reaction

Two principle routes

- **Increase pH**
  - Dependency on dissolution of the glass phase

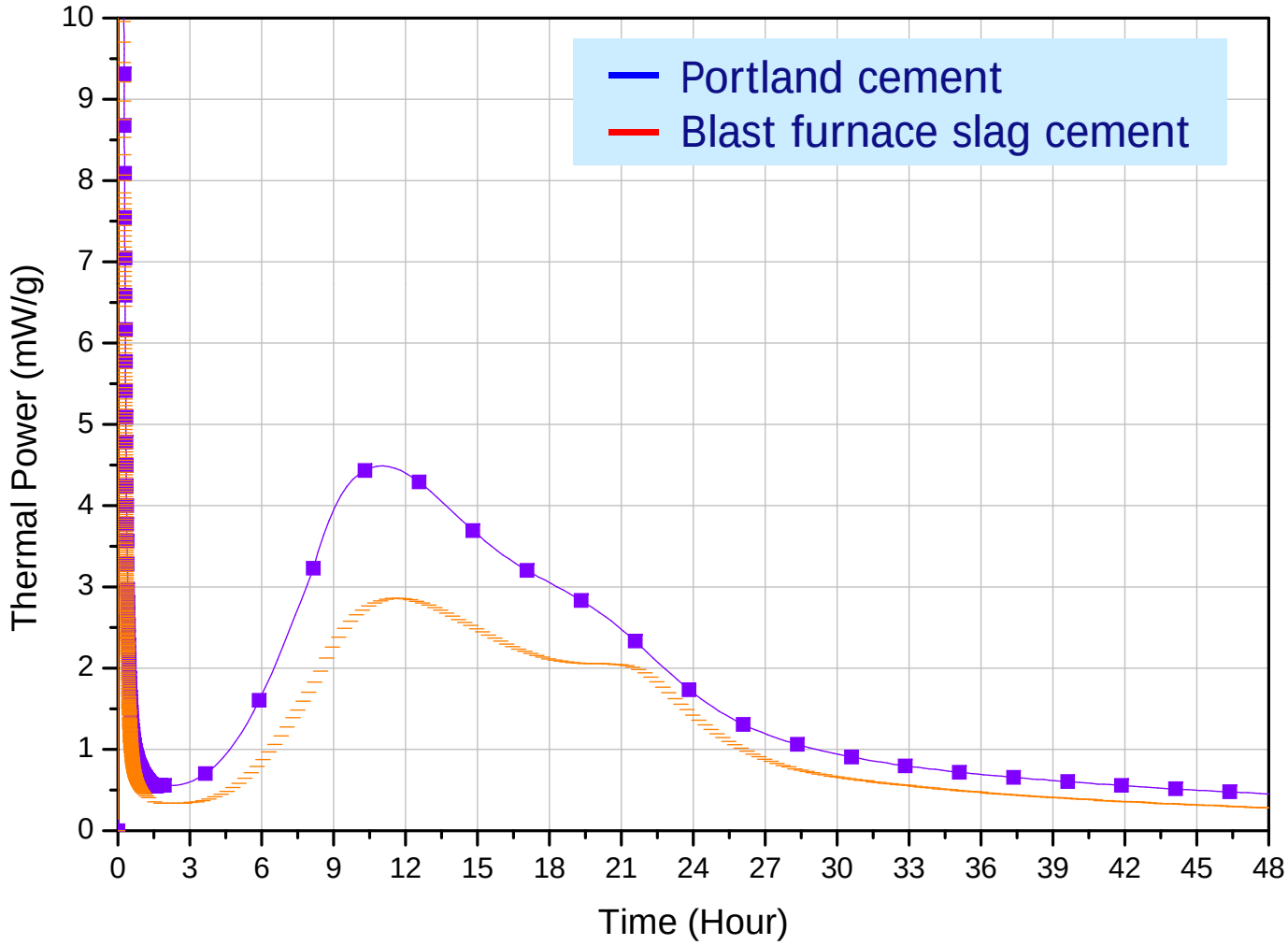




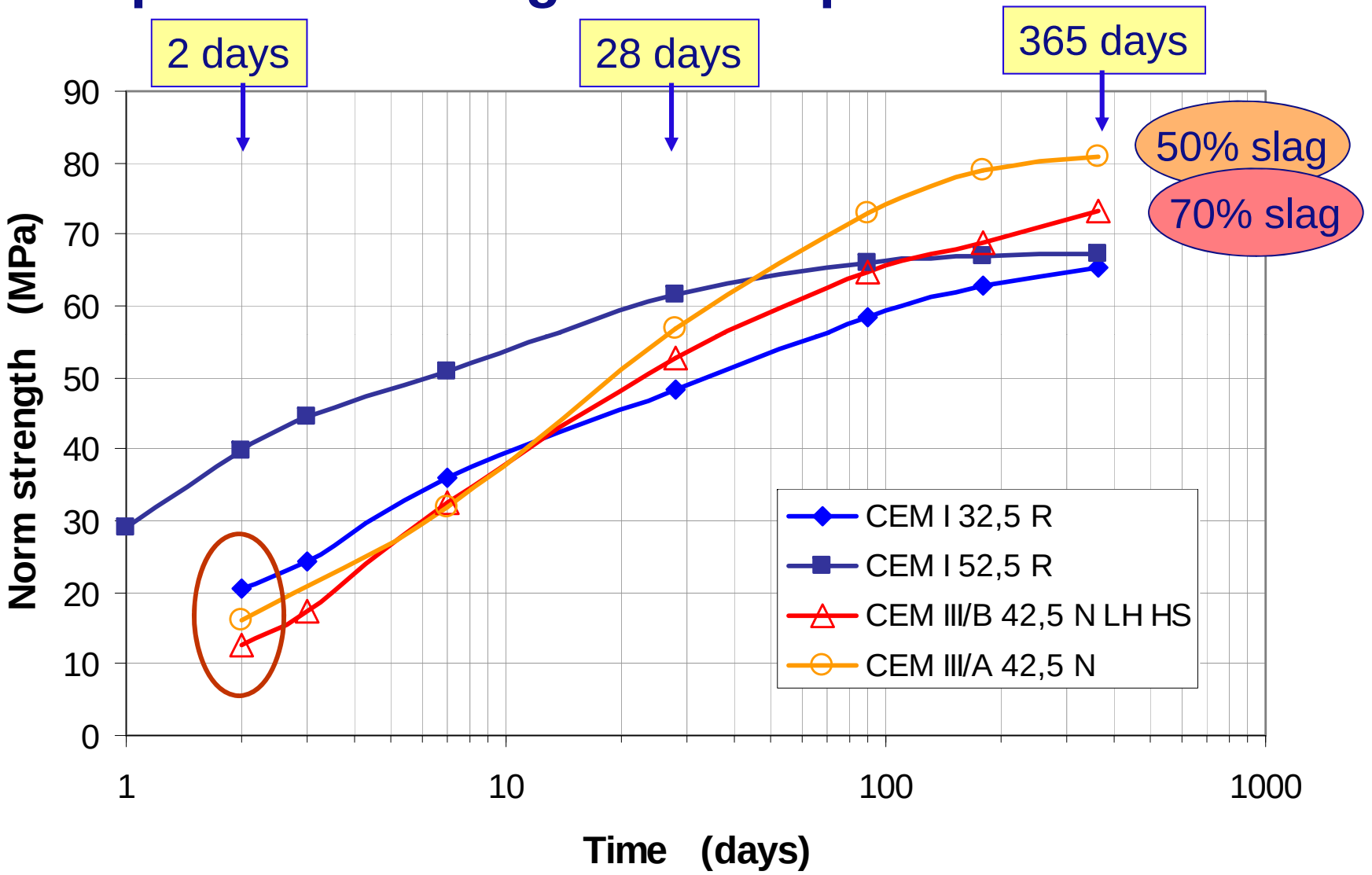
- **Sulphate**
  - Reaction of sulphate with aluminum fraction to form needle structures like ettringite;
  - Build up structure quickly

Properties: ‘Heat of hydration’

Compared to Portland cement low heat of hydration



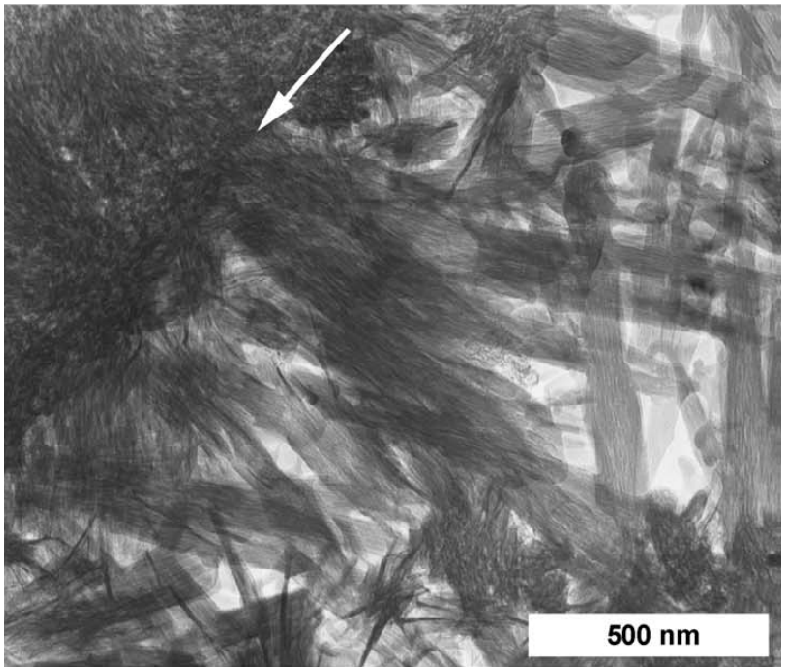
Properties: 'Strength development'



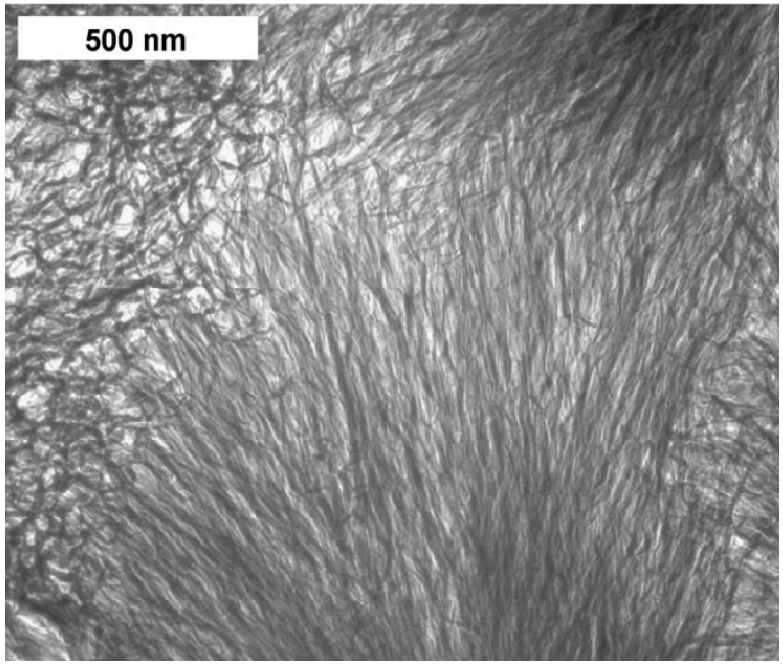
A different hardened cement structure

Portland matrix is less dense than slag matrix

Portland



Blast furnace slag



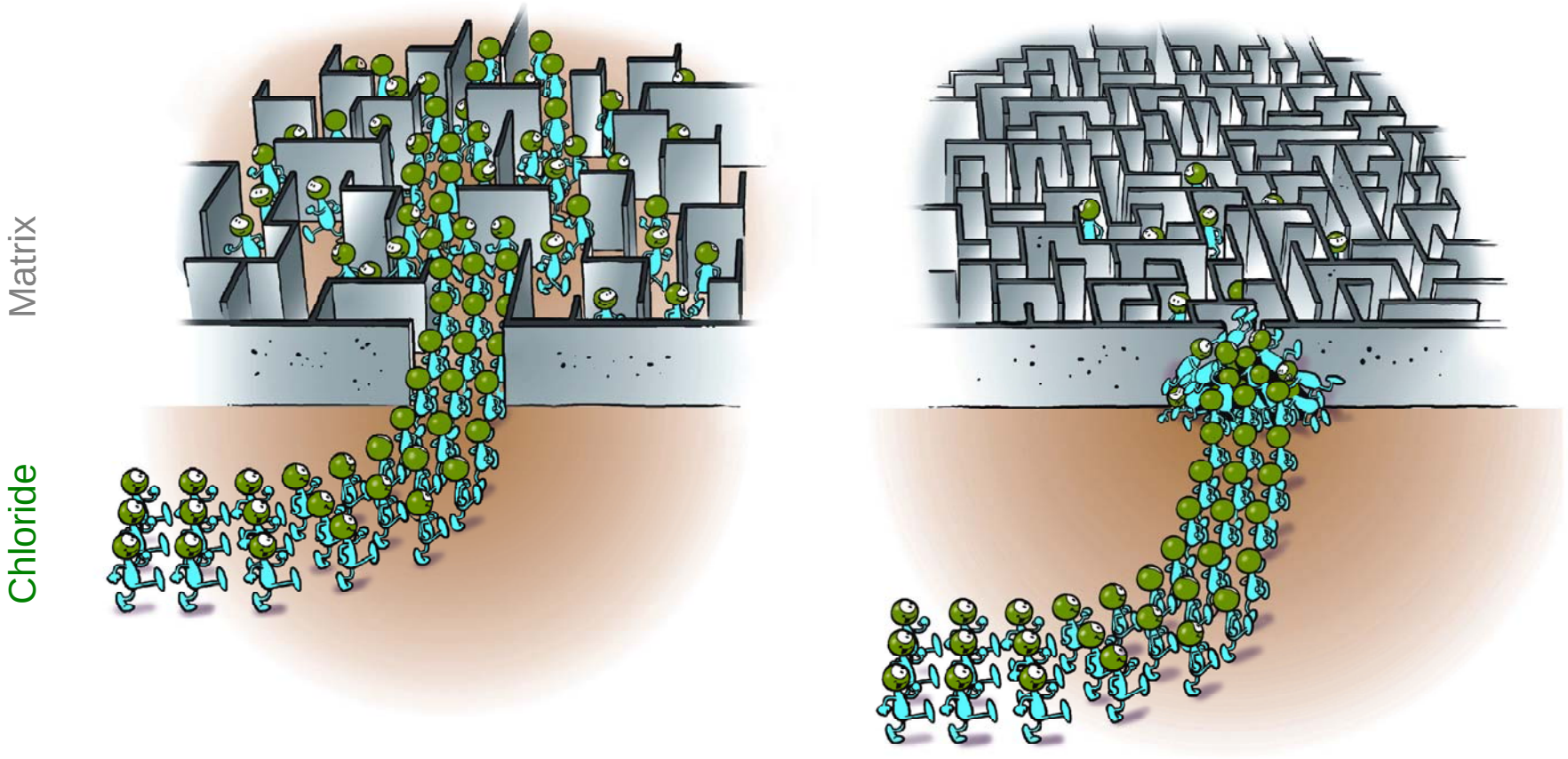
8 year old C_3S paste;
w/c = 0.5

1 year old blast furnace slag 70%;
w/c = 0.5

Pictures credits: I.G. Richardson

Dense matrix results in

High durability of slag cement

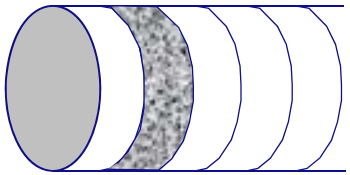


CEM I (Portland cement)

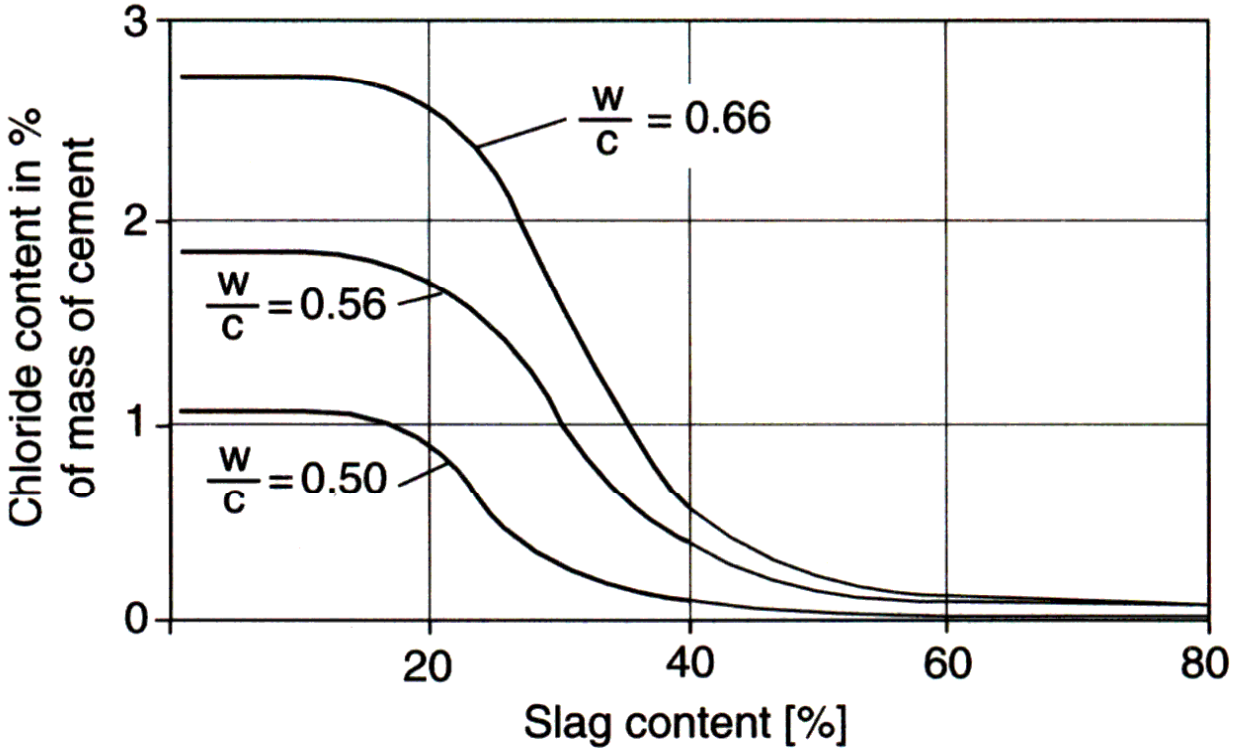
CEM III (Blast furnace slag cement)

Slag effect on chloride ingress

- Concrete sample kept 1 year in 3 M NaCl bath
- Next analyzed the slice at 20-40 mm depth
- Plot total chloride content

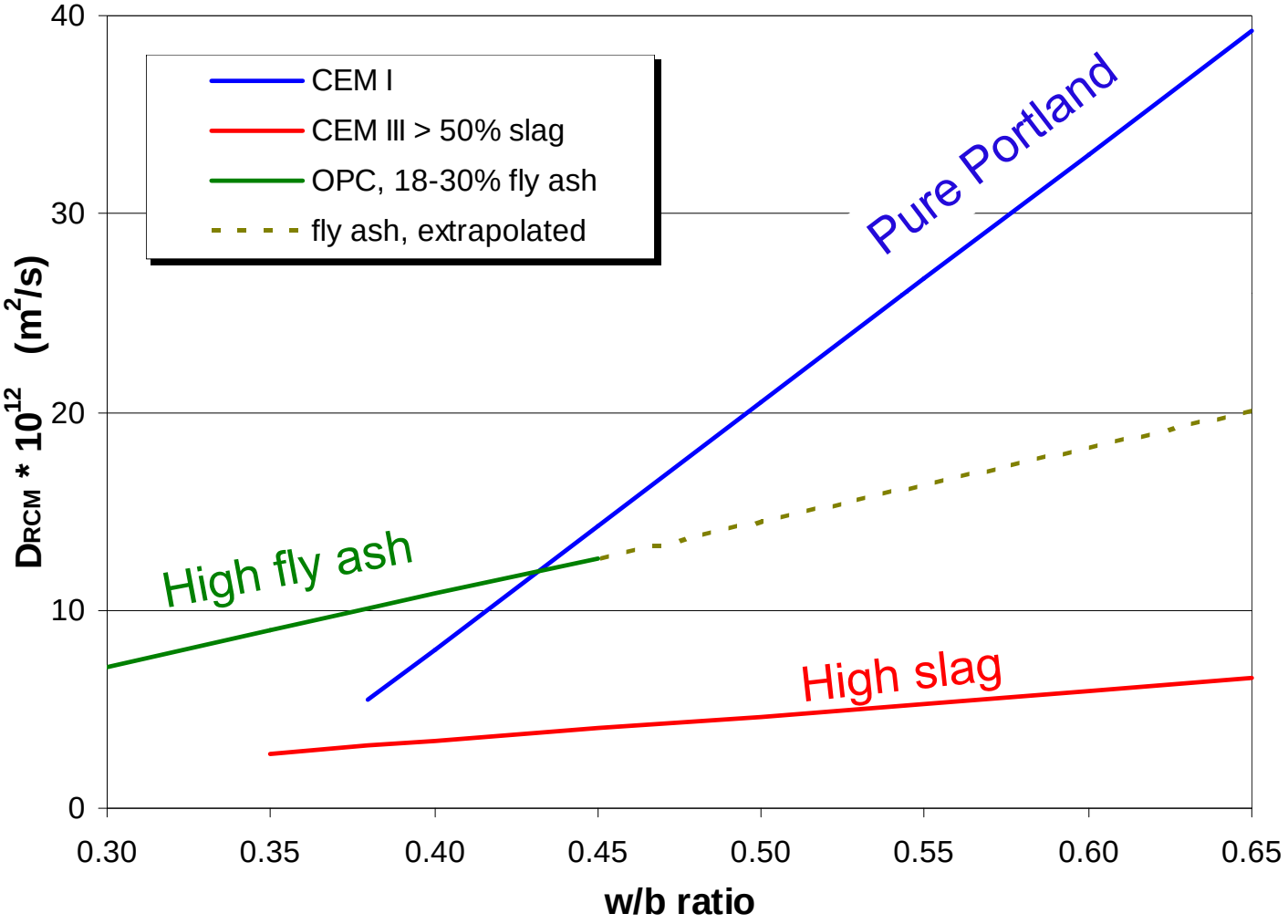


Slice of a core



Graph from durability performance doc.

Based on rapid chloride migration data (RCM)



Very good ASR resistance

- **The dense microstructure is complement with**:
  - A reduced pore size
  - Reduced mobility of the alkalis
- **Using slag reduces the total alkalis in the system**
  - There are less alkalis to start with (compared to Portland cement)
  - Creates a lower pH
  - Causes a slower dissolution rate of silica
- **Slag consumes alkalis in the hydration process**
  - Making them unavailable for the alkali silica reaction
- Dutch Department of Transportation / Army corps of engineers (RWS)
  → ***demands use of CEM III/B*** *in all important structures.*

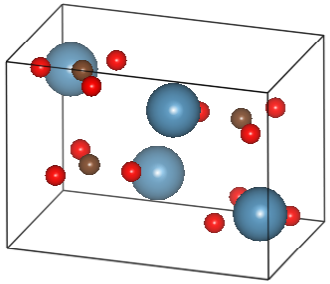
Spalling of slag concrete (freeze/thaw)

Seems related to carbonation of slag concrete

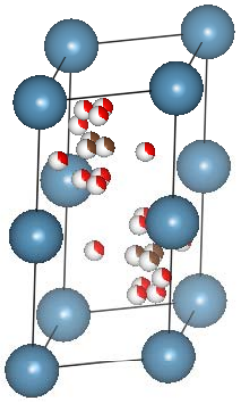
- **Calcium source:**
  - Portland cement → reaction with $Ca(OH)_2$ *(volume expansion)*
  - Slag cement → reaction with Ca from C-S-H *(volume reduction)*

- **$CaCO_3$ product formed:**

  - **Metastable forms:**

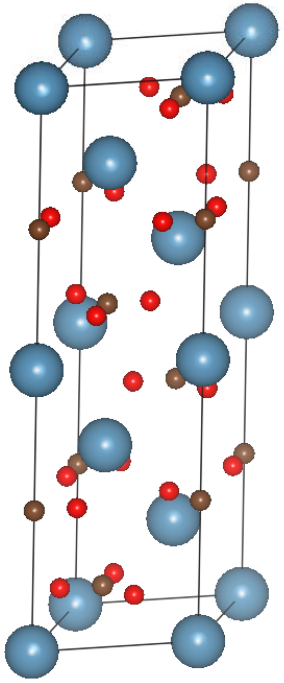


Aragonite



Vaterite

Stable form:

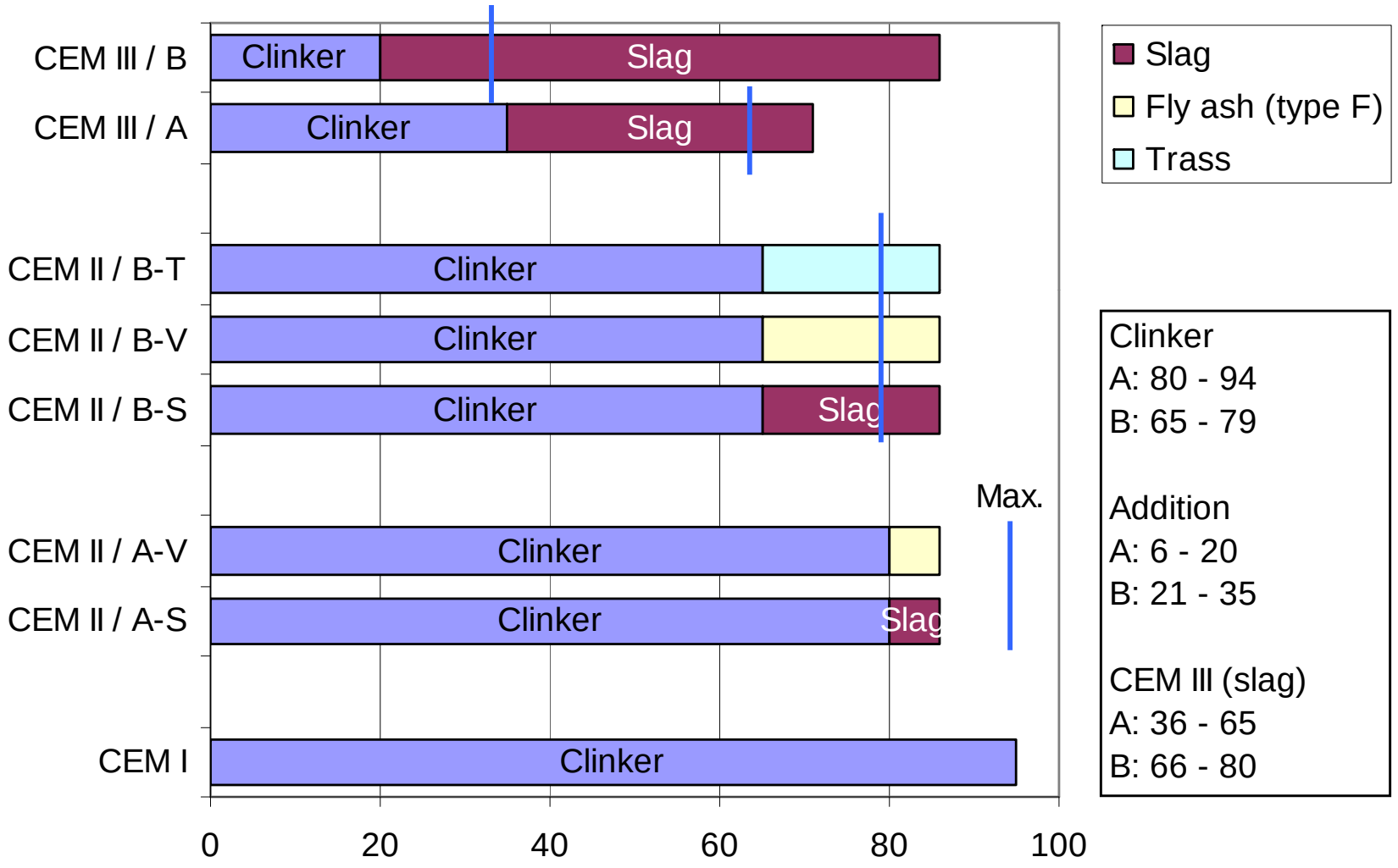


Calcite

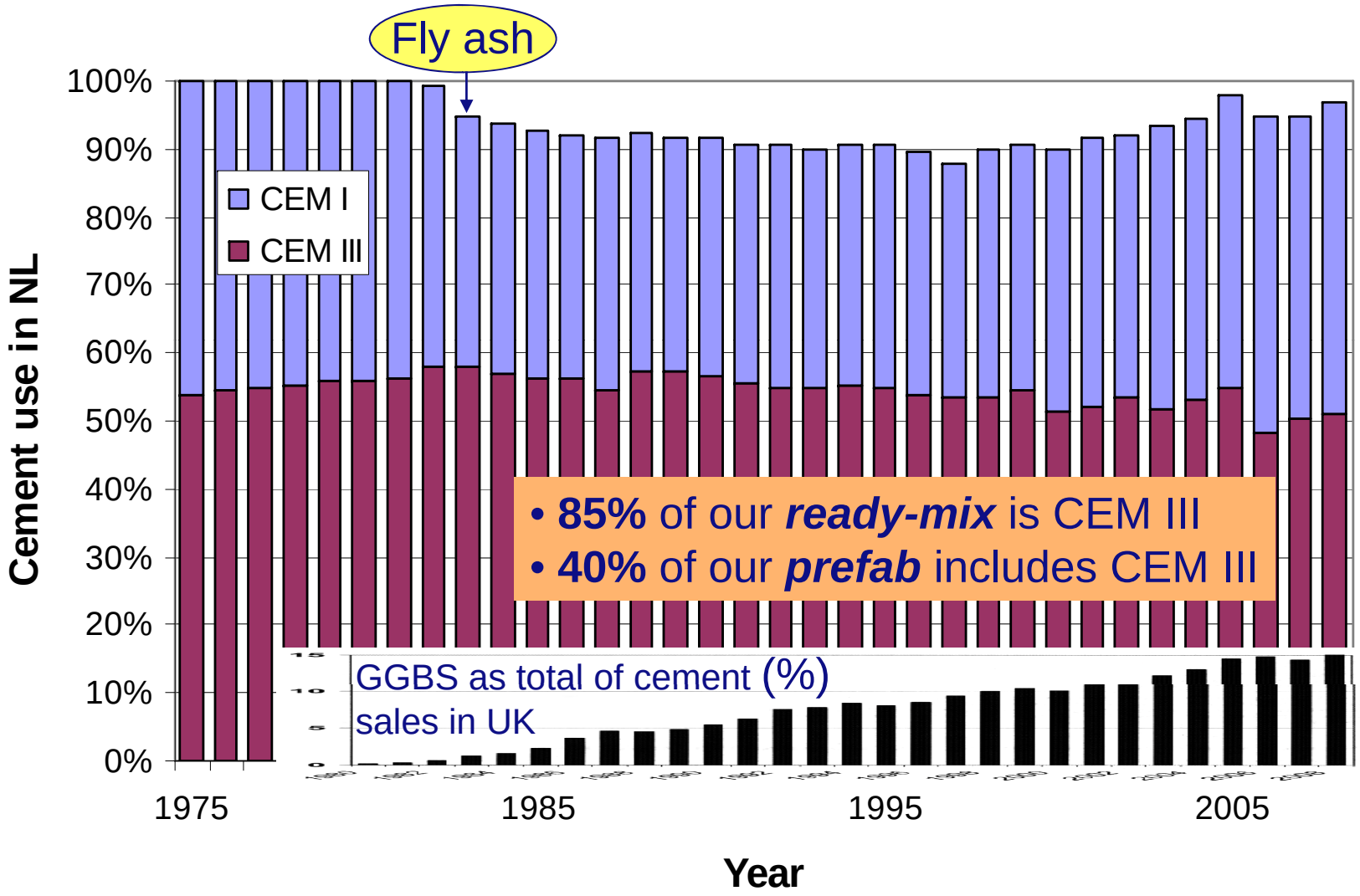
- **In (Dutch) practice**
  - Much less damage than in freeze/thaw tests

Slag in the cement code: EN 197-1 (2000)

Composition ranges of constituents



Use of cements in Netherlands



Conclusions

High dosed slag cement

- **Don't** consider it a waste product
  - Selling a product → quality control
- **Properties**
  - Low heat of hydration
  - Early strength is much better than generally percieved
  - Creates very dense concrete microstructure
  - Good durability resistance
- **Sales and practice show**
  - It is used over many decades
  - In large quantities
  - With great success