

Model for binding of chlorides

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CONCRETE EXPERTCENTRE

Ingress of chloride in concrete

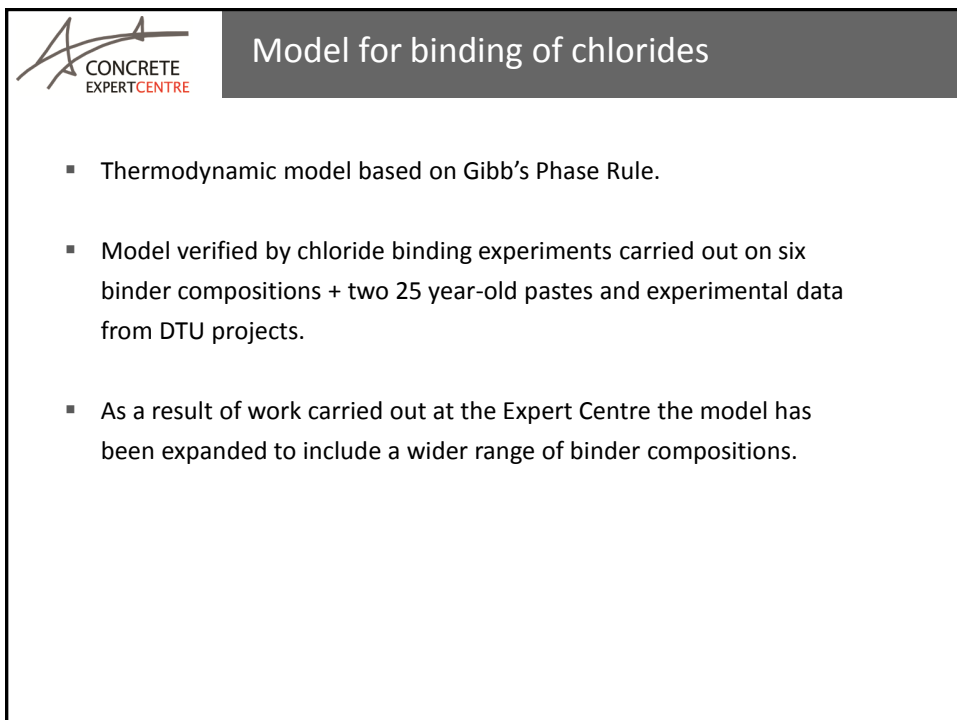
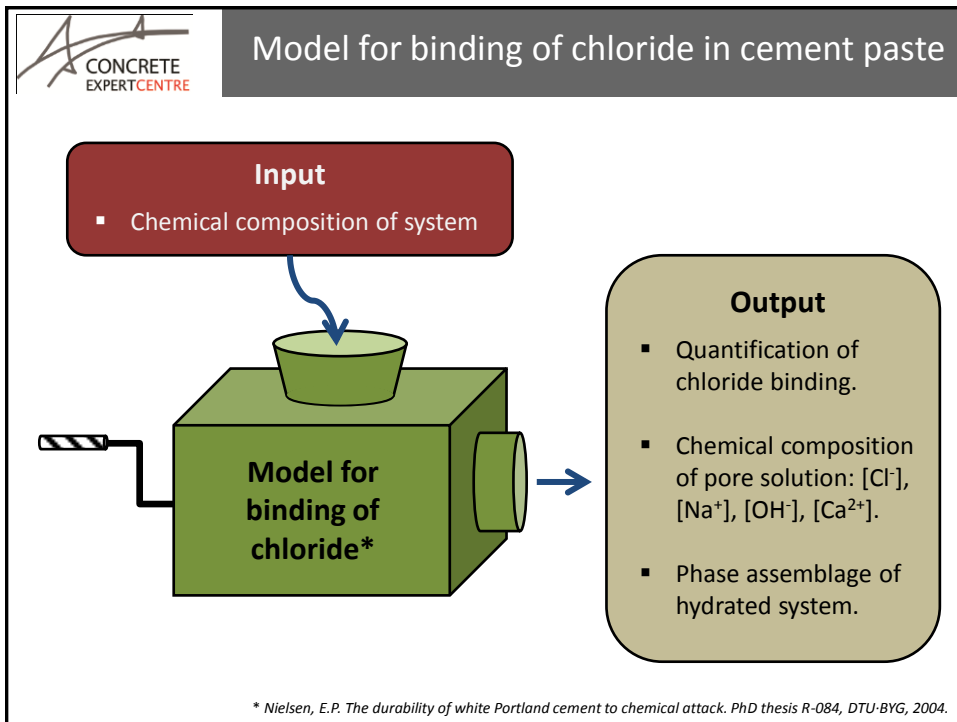
Exposure solution

Concrete

Rebar

Cl^-

- Partial fixation of chloride ions by the hydrate phases through processes collectively known as **chloride binding**.





Binding of chlorides

- Binding of chlorides in:
 - C-S-H phase.
 - AFm solid solution phase: Monocarbonate – Fridel’s salt.

- Well-defined distribution between the content of chloride bound by the C-S-H phase and that bound by the AFm solid solution phase.

- The content of alkalis in the binder has a pronounced effect on its chloride binding capacity: Decrease in alkali content → increased chloride binding capacity.



Expansion of model for chloride binding

- Typical Ca/Si ratio of C-S-H in plain Portland cement paste: 1.75.

- In binders containing significant amounts of slag, fly ash or silica fume: $\text{Ca/Si} < 1.75$.

- The Ca/Si ratio in the C-S-H phase has a significant effect on the distribution of alkalis between the pore solution and the C-S-H phase, which consequently affects the chloride binding capacity of the C-S-H.

- Expanded version of the model, which takes the variation of Ca/Si in the C-S-H phase into account: Ca/Si ratio is allowed to vary between: 0.8 and 1.75.

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Model for binding of chloride

Version: v. 1.0, 10/02/2012 - Chloride Binding

Program developed by: Erik Pram Nielsen

Input - Fill-in cells with white background only

Select id.	binder component	SRPC	GGBS	Only FA
6	percent of total powder	85	0	15
7	SiO ₂	24.84	33.50	60.34
8	Al ₂ O ₃	2.91	12.95	20.46
9	Fe ₂ O ₃	2.34	0.40	7.39
10	CaO	65.61	40.09	2.03
11	SO ₃	2.24	2.72	0.46
12	MgO	0.75	8.09	0.01
13	Na ₂ O	0.40	0.60	2.76
14	K ₂ O	0.00	0.00	0.00
15	CO ₂	0.65	1.00	3.17
16	sum	99.74	99.35	96.62
17	density, g/cm ³	3.19	2.91	2.34

Composite powder: 30.54
wt density: 1.92, 1.98, 0.64, 0.77, 0.00, 1.05, 3.05

Output

Assemblage wo. chloride	Final assemblage
mass %	mass %
C-S-H	80.85
CH	1.77
Goethite	2.36
Brucite	0.62
Pore solution	3.78
monosulfate	0.14
C ₄ AH ₃	1.37
monocarbonate	5.11
Friedels salt	0.00
calcite	0.13
ettringite	0.10
monocarbonate	8.35
Friedels salt	2.38

volume of binder, g: 73.13
volume of water, g: 73.13
volume of paste, ml: 19.14
porosity, weight-% to saturated paste: 19.14
vol-% of capillary porosity: 7.70

Bound Cl, mg Cl/g binder: 5.07 (0.97 bound in C-S-H, 4.11 bound in AFm-phases)
Total Cl, mg/g binder: 5.10 (0.42 wt% to dry paste)

Composition of pore solution mmole/liter, mM

Na ⁺ + K ⁺	Cl ⁻	Ca ²⁺	OH ⁻	Cl/OH, mM/mM	pH
36	16	5	30	0.53	12.48

1. Press for optimization Optimization ok

2. Calculate Cl binding isotherm

Maks content of chloride: 2.00 % to binder
Constant alkali content [Yes/No]: yes


Chloride binding isotherm: Press for calculating chloride binding isotherm and [Cl]/[OH]

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Crushed concrete in artificial pore solution

- Crushed concrete samples (grain size $\phi < 4$ mm) exposed to artificial pore solutions.
- The test method allows a raking of different binders with regard to resistance against chloride induced reinforcement corrosion.
- [Na⁺] in the artificial pore solution was adjusted to that expected in the "unexposed" concrete by adding NaOH to the solution. Calculated by the model.
- [Cl⁻] was set at 6 levels covering an interval around the expected chloride threshold value, based on the assumption that a [Cl⁻]/[OH⁻] \approx 0.6 triggers reinforcement corrosion. Calculated by the model.



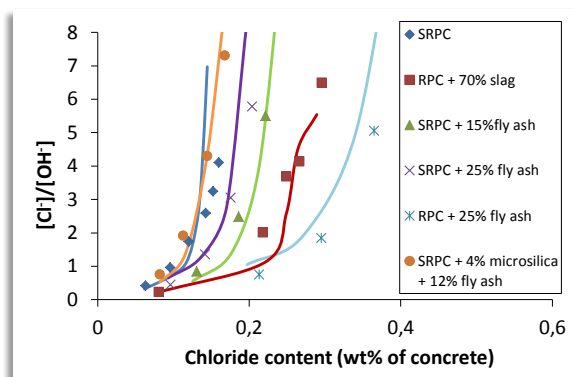
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Crushed concrete in artificial pore solution

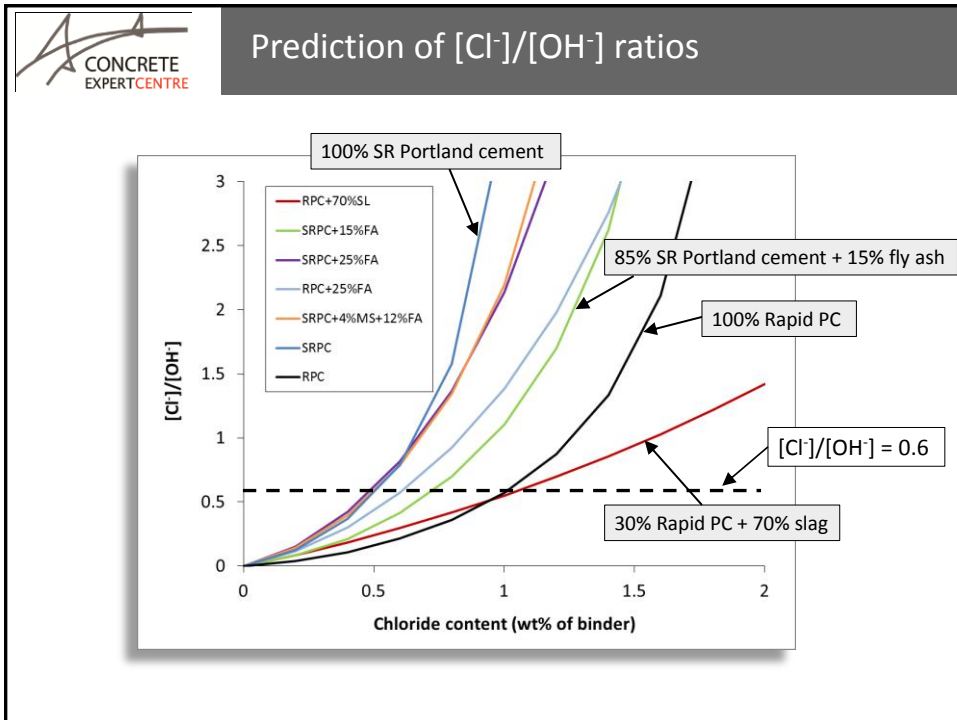
- 6 types of concrete:
 - Sulfate resistant Portland cement (SRPC)
 - SRPC + 15% fly ash
 - SRPC + 25% fly ash
 - SRPC + 12% fly ash + 4% microsilica
 - Rapid Portland cement (RCP) + 70% slag
 - RCP + 25% fly ash
- Age of concretes: 1.5 years.
- 1000 g crushed concrete + 350 ml solution in each plastic container.
- Specimens kept sealed and stored at 20°C for 3 months in order to obtain equilibrium.
- After storing the solutions were analyzed for $[Cl^-]$ and $[OH^-]$.



Crushed concrete in artificial pore solution



- The artificial pore solutions were prepared with too much alkali for the binders containing slag and fly ash. Apparently, only a minor proportion of the alkalis in the fly ash and the slag becomes available during hydration.
- Data was used to modify the model.



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Crushed concrete in artificial pore solution

- Small pieces of reinforcement steel have been exposed to artificial pore solutions to test the ability of the solutions to initiate corrosion.
- The steel was cleaned in citric acid and passivated in saturated $Ca(OH)_2$ solution prior to the exposure.
- No signs of reinforcement corrosion in any of the specimen containers after 4 weeks of exposure.
- It appears that even very high $[Cl^-]/[OH^-]$ ratios will not necessarily result in the onset of reinforcement corrosion. Other triggering factors?



New test series with crushed concrete

- New test series with crushed concretes in artificial pore solutions will be carried out. Same procedure and same concretes, but with correct concentration of alkalis in the artificial pore solutions.
- This was developed for conditions at 20°C. New test series on the same concretes, but at a lower temperature.



Thank you for your attention