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Tool for quantification of chloride binding

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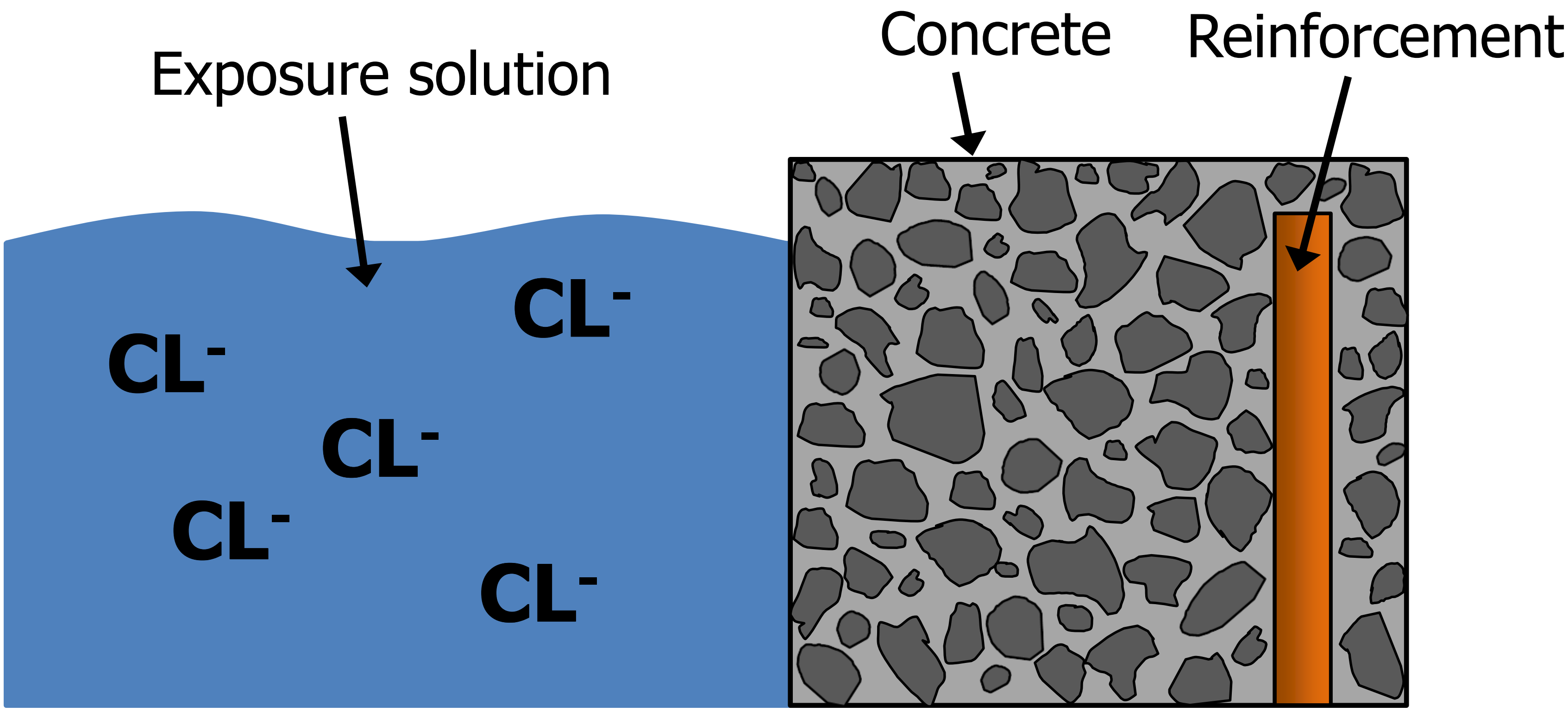
Chloride binding in concrete



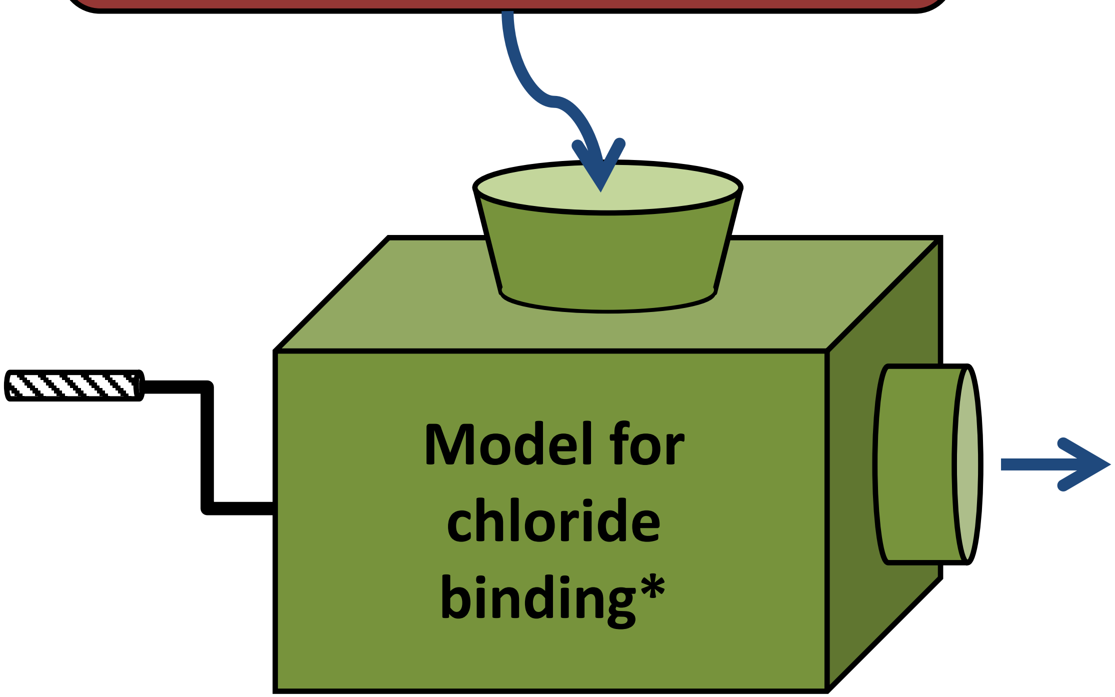
Chloride binding:

- Partial fixation of chloride ions by the hydrate phases
- Chloride ions are removed from the pore solution

Model for chloride binding

Input

- Chemical composition of system



Output

- Quantification of chloride binding.
- Chemical composition of pore solution: $[Cl^-]$, $[Na^+]$, $[OH^-]$, $[Ca^{2+}]$.
- Phase assemblage of hydrated system.

** Nielsen, E.P. The durability of white Portland cement to chemical attack. PhD thesis R-084, DTU·BYG, 2004.*

Model for chloride binding

- Thermodynamic model based on Gibb's Phase Rule

put

Chemical composition of system

- Model verified by chloride binding experiments carried out on six binder compositions + two 25 year-old pastes and experimental data from DTU projects

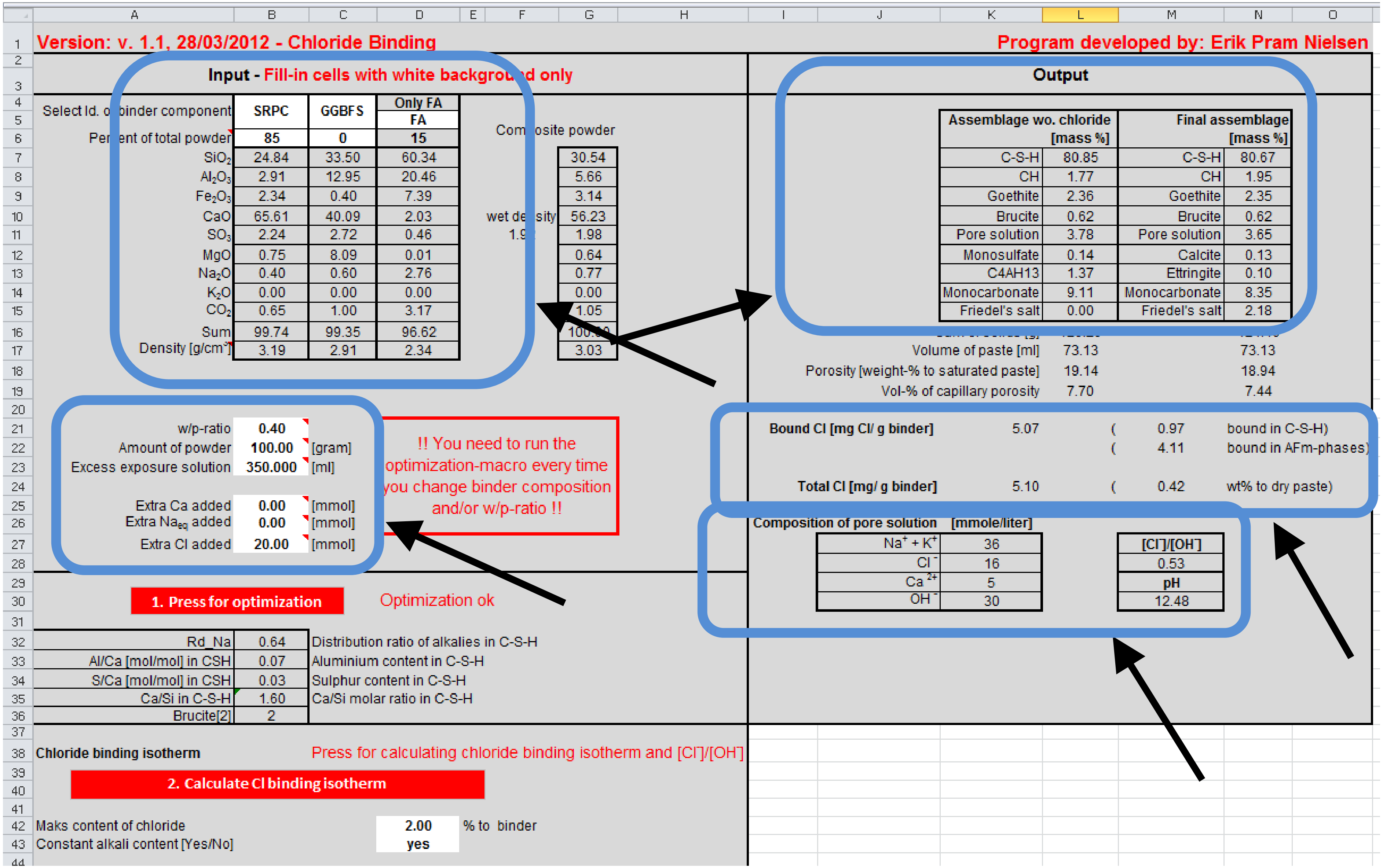
- As a result of work carried out at the Expert Centre the model has been expanded to include a wider range of binder compositions

- Binding of chlorides in:
  - C-S-H phase
  - Afm solid solution phase: Monocarbonate – Fridel's salt

Model for chloride binding

- In binders containing significant amounts of slag, fly ash or micro-silica: Ca/Si in C-S-H < 1.75
- The Ca/Si ratio in the C-S-H phase 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

Spreadsheet for model calculations



Version: v. 1.1, 28/03/2012 - Chloride Binding

Program developed by: Erik Pram Nielsen

Input - Fill-in cells with white background only

Select Id. of binder component	SRPC	GGBFS	Only FA FA	Composite powder
Percent of total powder	85	0	15	
SiO_2	24.84	33.50	60.34	30.54
Al_2O_3	2.91	12.95	20.46	5.66
Fe_2O_3	2.34	0.40	7.39	3.14
CaO	65.61	40.09	2.03	56.23
SO_3	2.24	2.72	0.46	1.98
MgO	0.75	8.09	0.01	0.64
Na_2O	0.40	0.60	2.76	0.77
K_2O	0.00	0.00	0.00	0.00
CO_2	0.65	1.00	3.17	1.05
Sum	99.74	99.35	96.62	[illegible]
Density [g/cm^3]	3.19	2.91	2.34	3.03

wet density 1.9[illegible]

w/p-ratio	0.40
Amount of powder	100.00 [gram]
Excess exposure solution	350.000 [ml]
Extra Ca added	0.00 [mmol]
Extra Na_{eq} added	0.00 [mmol]
Extra Cl added	20.00 [mmol]

!! You need to run the optimization-macro every time you change binder composition and/or w/p-ratio !!

1. Press for optimization

Optimization ok

Rd_Na	0.64	Distribution ratio of alkalies in C-S-H
Al/Ca [mol/mol] in CSH	0.07	Aluminium content in C-S-H
S/Ca [mol/mol] in CSH	0.03	Sulphur content in C-S-H
Ca/Si in C-S-H	1.60	Ca/Si molar ratio in C-S-H
Brucite[2]	2	

Chloride binding isotherm

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

2. Calculate Cl binding isotherm

Maks content of chloride 2.00 % to binder

Constant alkali content [Yes/No] yes

Output

Assemblage wo. chloride [mass %]		Final assemblage [mass %]	
C-S-H	80.85	C-S-H	80.67
CH	1.77	CH	1.95
Goethite	2.36	Goethite	2.35
Brucite	0.62	Brucite	0.62
Pore solution	3.78	Pore solution	3.65
Monosulfate	0.14	Calcite	0.13
C4AH13	1.37	Ettringite	0.10
Monocarbonate	9.11	Monocarbonate	8.35
Friedel's salt	0.00	Friedel's salt	2.18
Volume of paste [ml]	73.13		73.13
Porosity [weight-% to saturated paste]	19.14		18.94
Vol-% of capillary porosity	7.70		7.44

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]

$Na^+ + K^+$	36
Cl^-	16
Ca^{2+}	5
OH^-	30

[Cl⁻]/[OH⁻]
0.53
pH
12.48

Experimental testing of the model

- Crushed concrete samples exposed to artificial pore solutions with different concentrations of chloride
- Purpose: Testing of the models ability to predict the binding of chloride in concrete
- Two experimental test series have been carried out:
  - Adjustment of the model as a result of the first test series

Experimental testing of the model

- Five types of concrete
  - Low-alkali sulphate-resistant Portland cement (SRPC)
  - SRPC + 15% fly ash
  - SRPC + 25% fly ash
  - SRPC + 12% fly ash + 4% microsilica
  - Rapid Portland cement (RCP) + 70% slag
- Age: 2.5 years

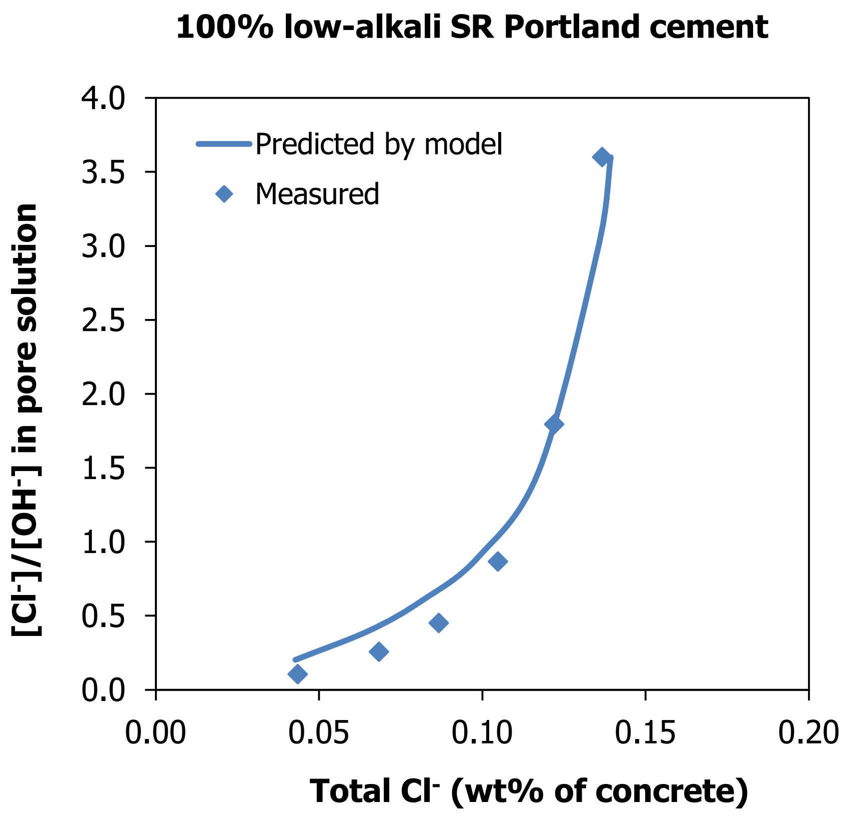
Experimental testing of the model

- Preparation of artificial pore solutions:
  - For each concrete type the [Cl^-] was set at 6 different levels.
  - [Na^+] adjusted to that expected in the “unexposed” concrete by adding NaOH to the solution. Calculated by model.

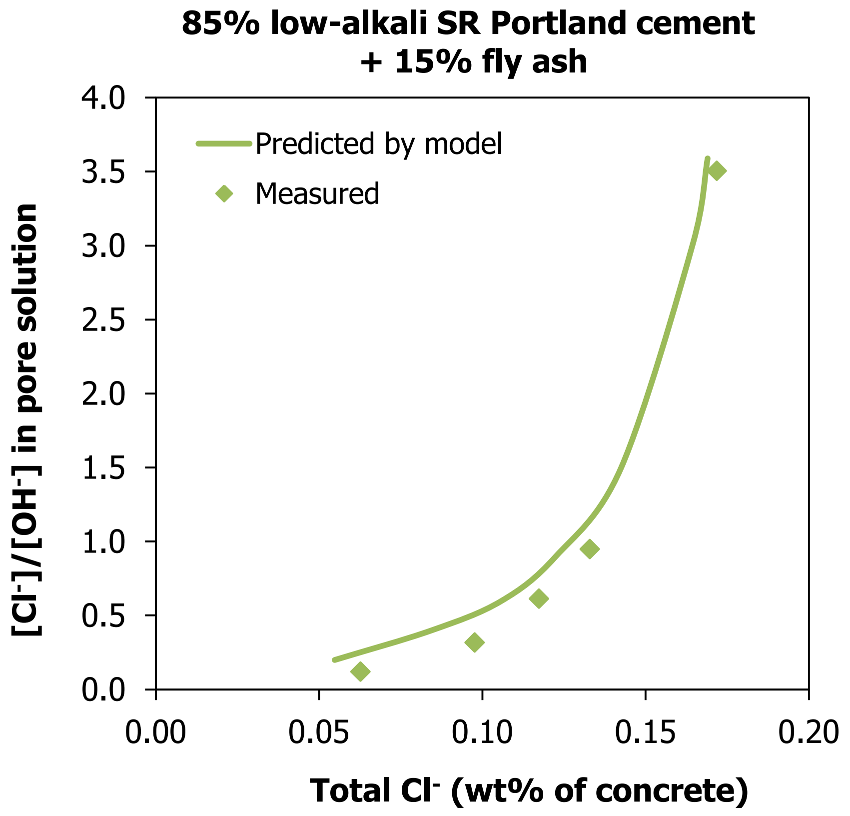
Experimental testing of the model

- 1000 g crushed concrete + 350 ml solution in each plastic container
- Specimens kept sealed and stored at 20°C for three months in order to obtain equilibrium conditions
- After storing the solutions were analyzed for [Cl^-] and [OH^-]

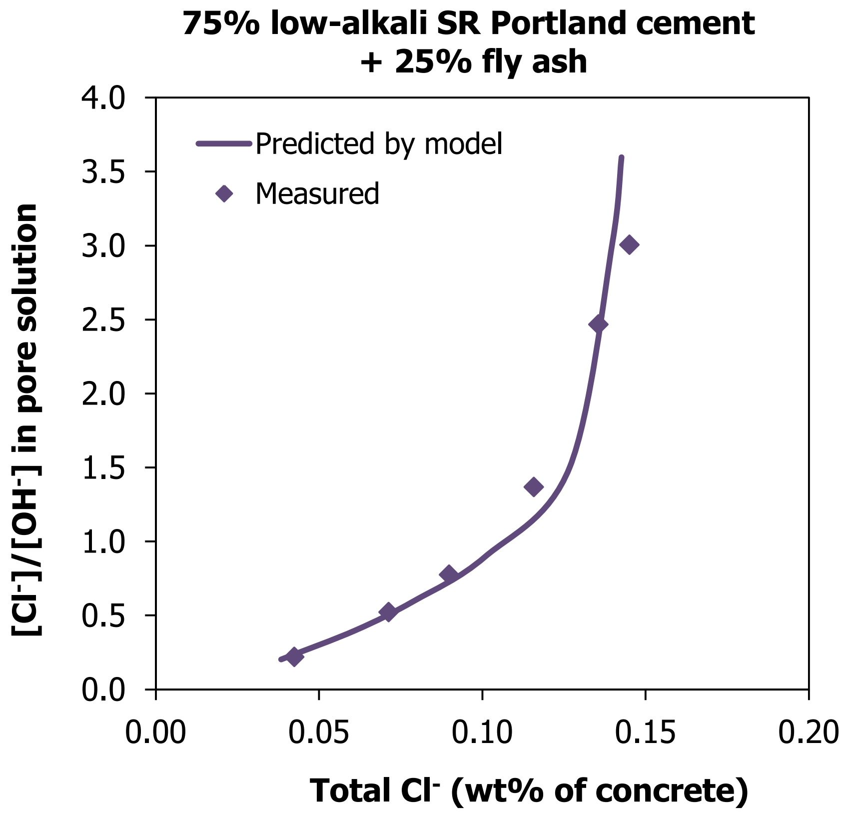
Measured data vs. model predictions



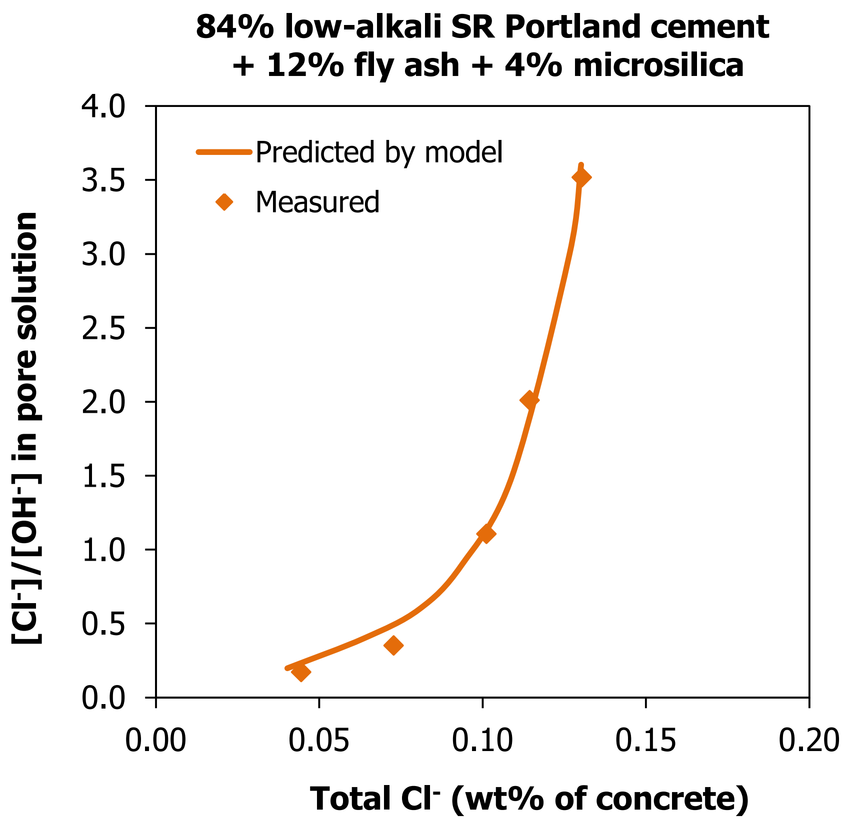
Measured data vs. model predictions



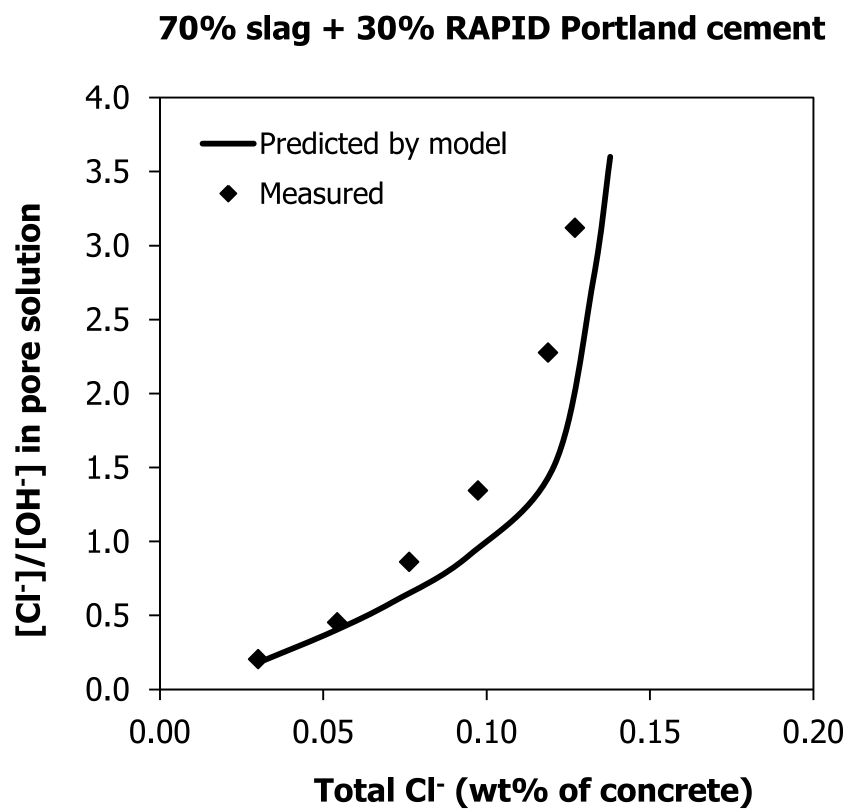
Measured data vs. model predictions



Measured data vs. model predictions



Measured data vs. model predictions

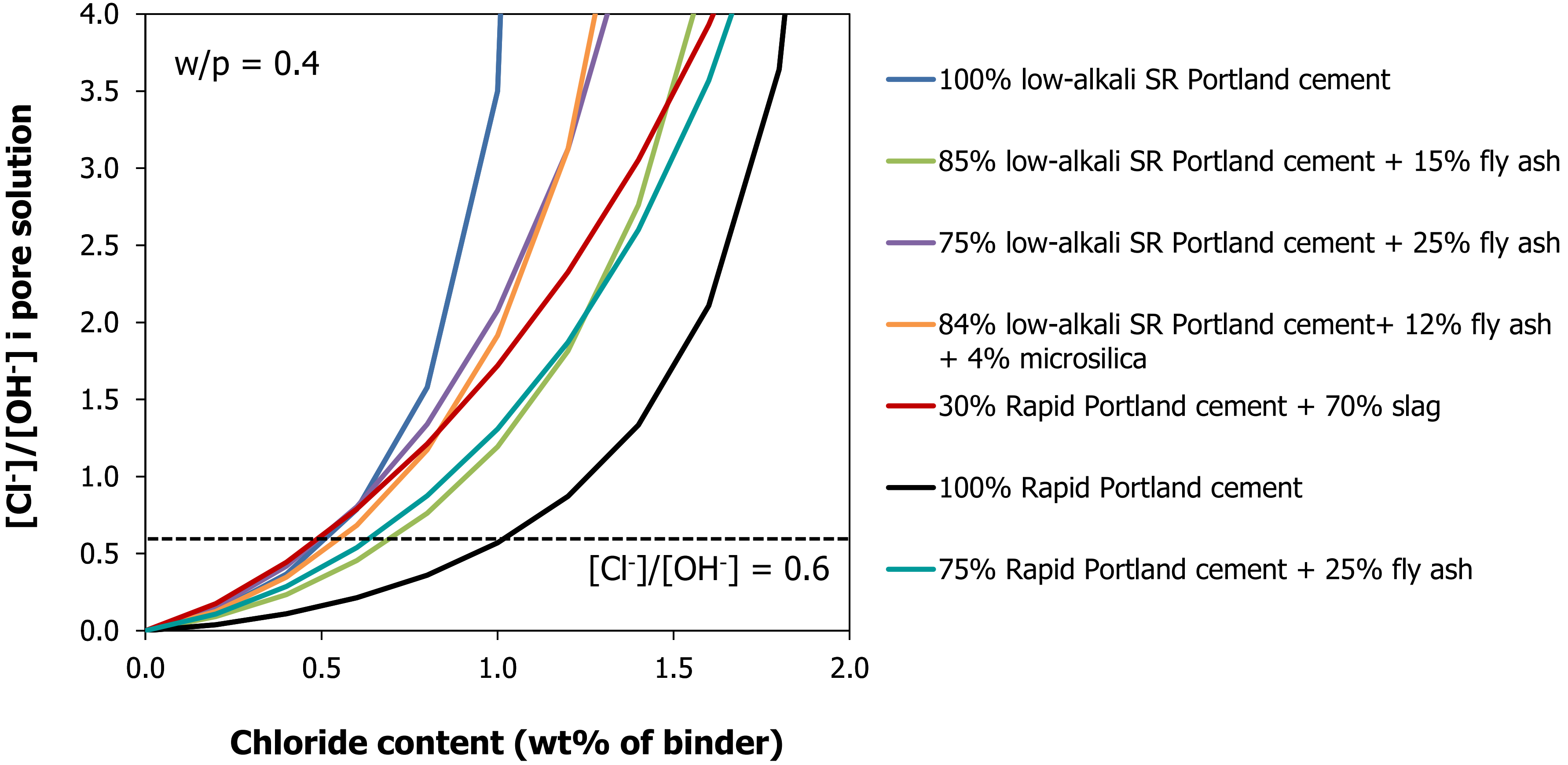


Application of the model

- The performance of different binders in terms of chloride binding can be evaluated without having to carry out time-consuming experimental investigations

- Ranking of binders in terms of the ability to ensure a low $[Cl^-]/[OH^-]$ ratio in the pore solution

Model predictions



Future work

- New test series on the same concretes, but at a lower temperature (the model was developed for conditions at 20°C)

- New tests on binders with different slag content

Thank you

for your attention!