Thermodynamic modeling of hydrated Portland cement – SCM systems:

Implementation of hydration kinetics based on ^{29}Si MAS NMR spectra

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Implementation of hydration kinetics

based on ^{29}Si MAS NMR spectra

Why implement kinetic aspects into your modelling?

Kinetic aspects might **modify or prevent** that a phase assemblage reaches its **thermodynamic equilibrium** within the experimental time.

To model these aspects, further **boundary conditions** need to be implemented.

This presentation is going through such an **example** for a binder consisting of:

white Portland cement (**wPc**),
metakaolin (**MK**)
limestone (**LS**)

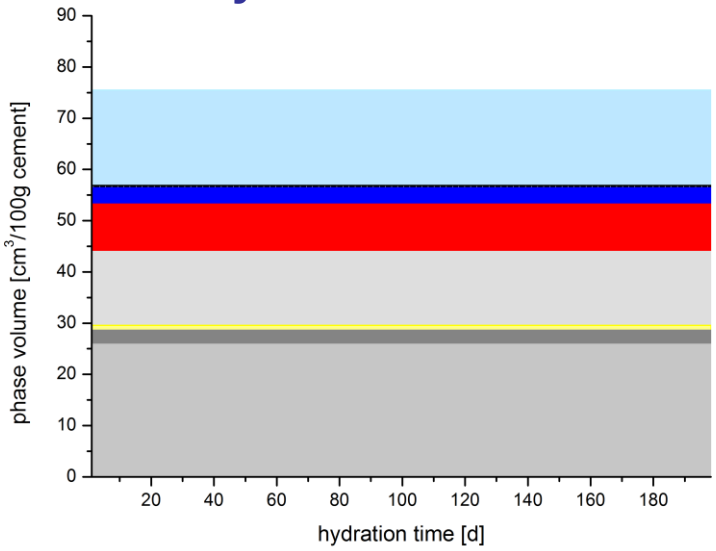
Implementation of hydration kinetics

Common approaches:

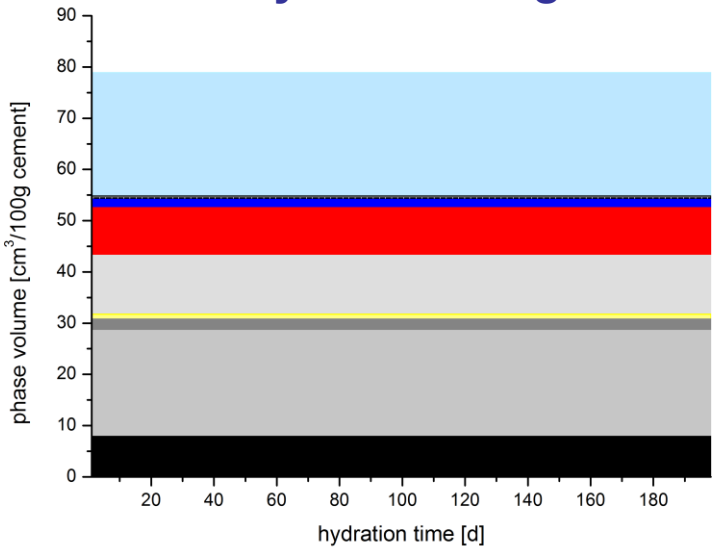
- **No hydration kinetics** = phase diagrams
- **Fixed hydration degree** = for one specific hydration time
- **Using empirical models**
- **Using experimental data** collected at different times

Implementation of hydration kinetics

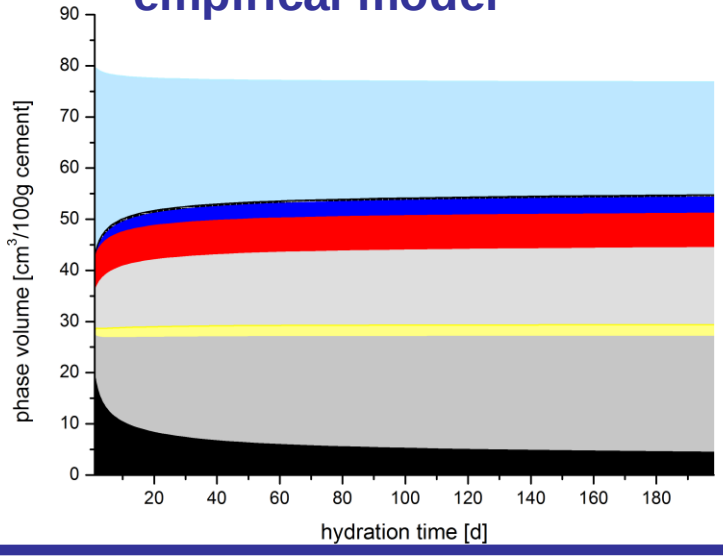
no hydration kinetics



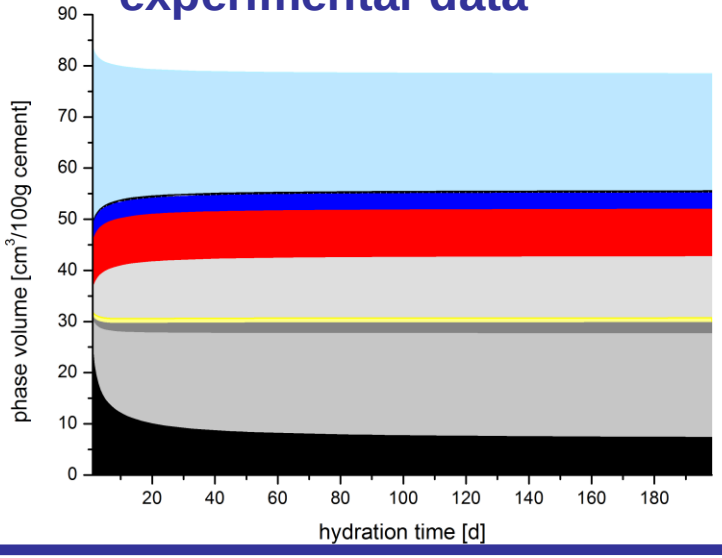
fixed hydration degree



empirical model



experimental data



Implementation of hydration kinetics

- **Empirical models** e.g. Parrott and Killoh*
    1. Based on sets of experimental data
    2. Imply the independence of hydration of different phases
    3. Surface area, w/c
    4. No input for non-clinker-phases

- **Experimental data** collected at different times
    1. Imply the independence of hydration of different phases
    2. Based on experimental data
    3. Tailored for your binder
    4. Include possibly rates for hydration of SCM´s

***L.C. Parrott & D.C. Killoh.**
"Prediction of cement hydration"
British Ceramic Proceedings 35 (1984), 41-53

Implementation of hydration kinetics

Based on empirical models

Here: Parrott and Killoh (1984)*

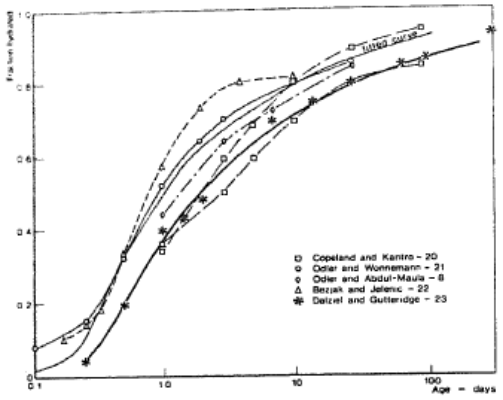


Fig. 1: Hydration of alite by x-ray diffraction

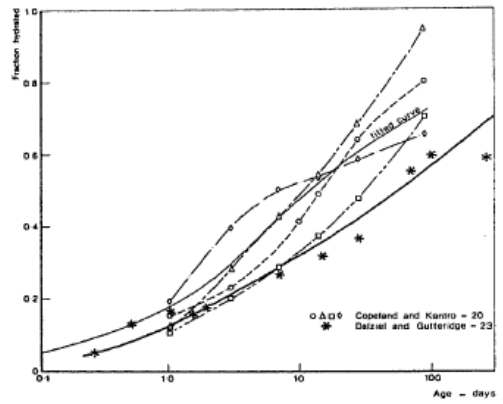
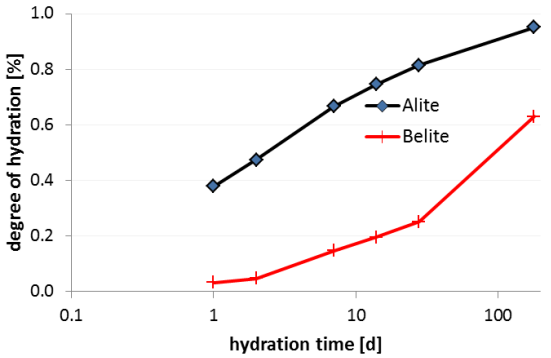
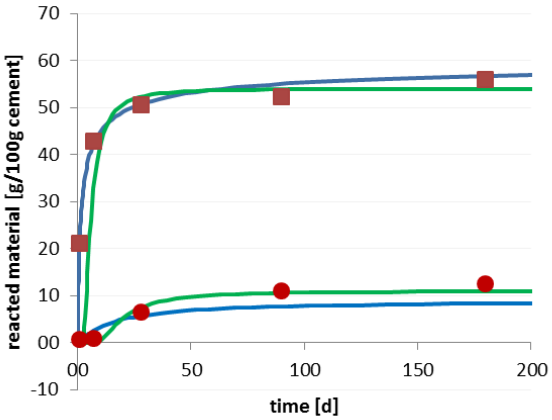


Fig. 2: Hydration of belite by x-ray diffraction

Based on ^{29}Si MAS NMR data



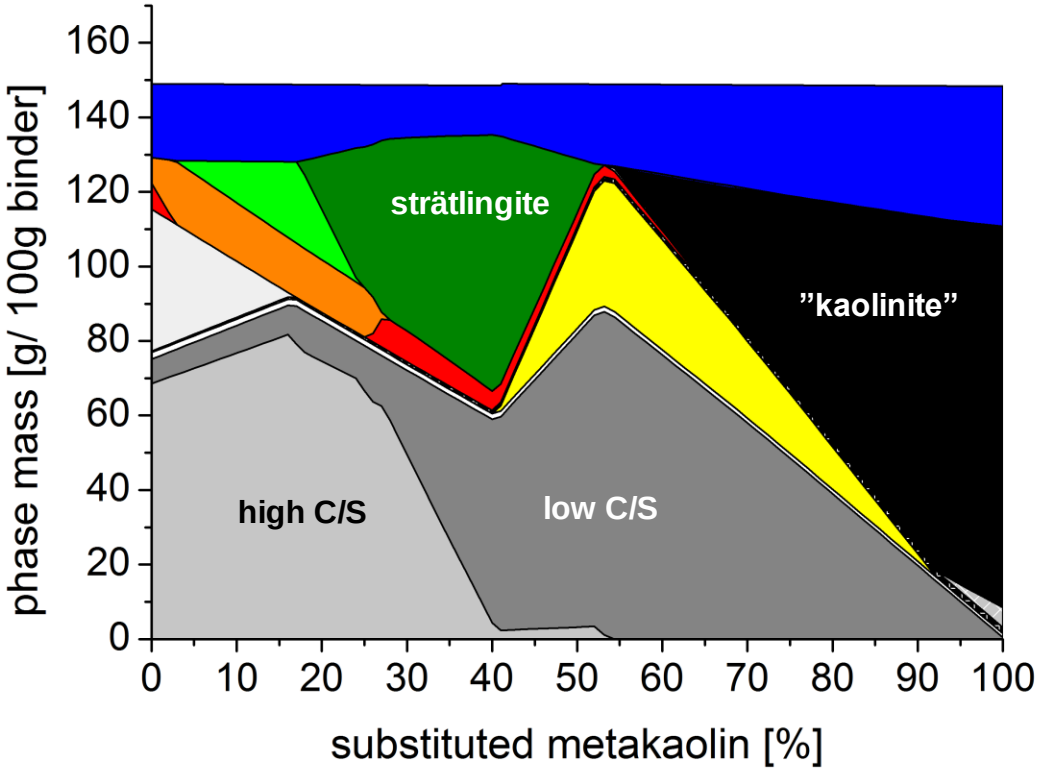
Comparison:



Motivation:

How to implement metakaolin hydration?

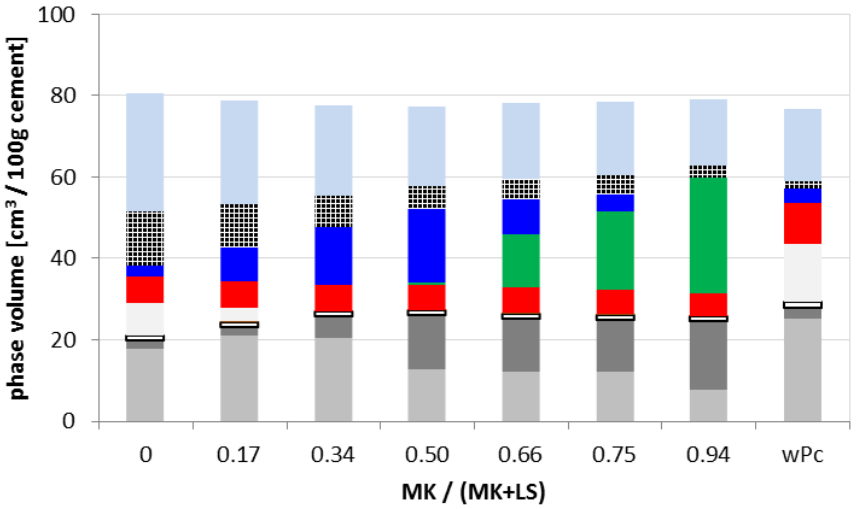
White PC + metakaolin (no hydration kinetics)



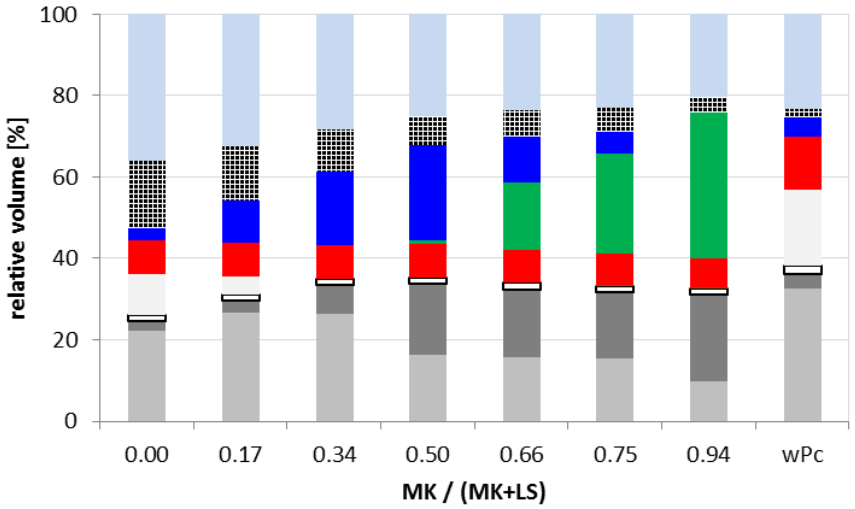
Initial calculations (100% reaction)

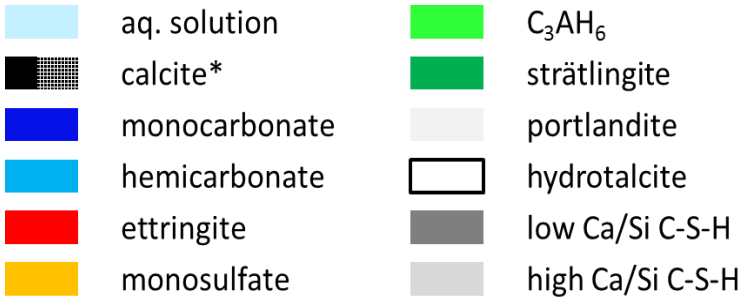
White PC + metakaolin + limestone

phase volumes



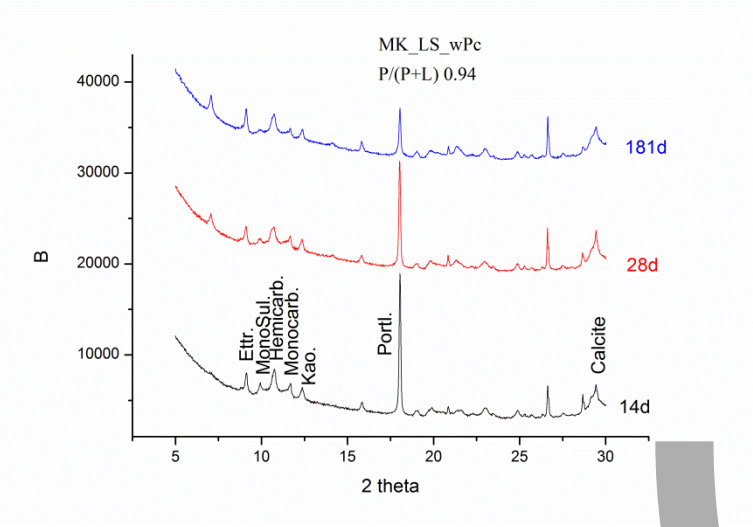
relative phase volumes



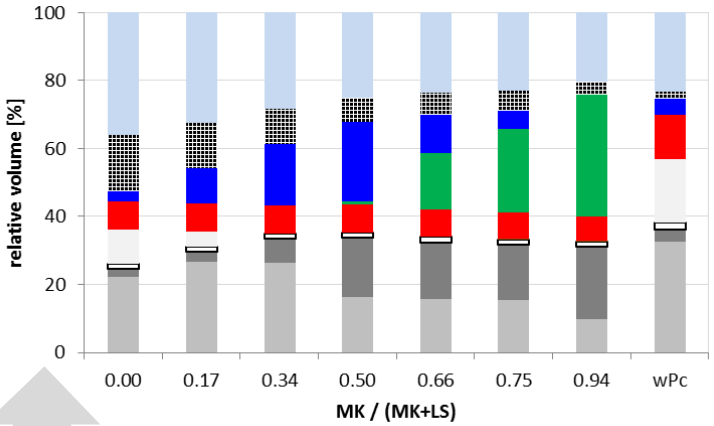


Reality check: phase characterization

XRD:



modeled:



	35% LS			0.171			0.34			0.5			0.66			0.75			0.94			wPc		
	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d
Calcite																								
Monocarbonate																								
Hemicarbonate																								
Strätlingite																								
Ettringite																								
Monosulfate																								
Portlandite																								

Experimental data from Zhuo Dai´s PhD project*

Or "how to use a by-product"

6 mixes + 2 references (wPc, 35%LS)

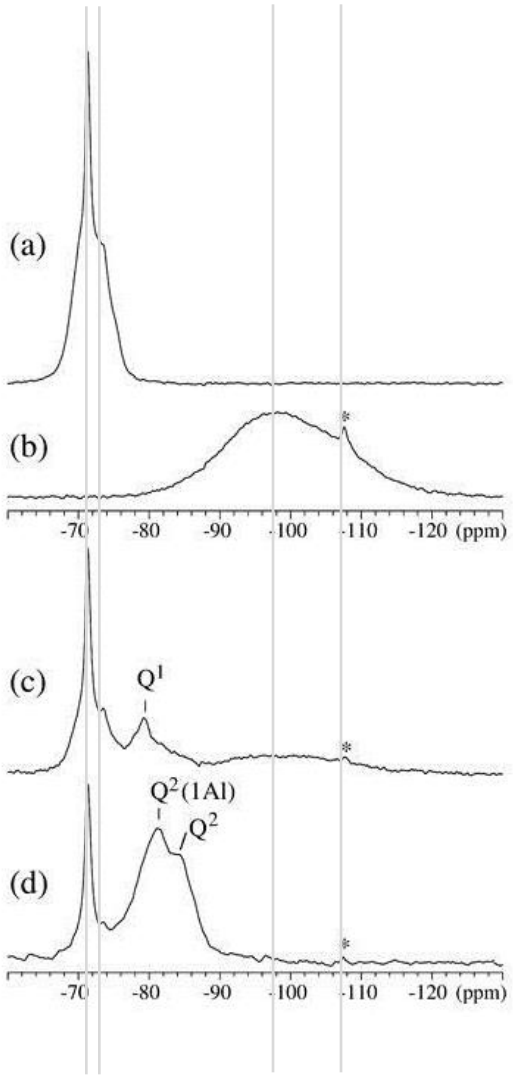
MK+LS:

^{29}Si MAS NMR (1d, 2d, 7d, 14d, 28d, 63d, 182d)
^{27}Al MAS NMR (14d, 28d, 182d)
XRD (14d, 28d, 182d)

→ *hydration degree*
→ *phase characterization*

* First publication:
Z. Dai, T.T. Thuan and J. Skibsted.
"Aluminum incorporation in the C–S–H phase of white Portland cement – metakaolin blends studied by ^{27}Al and ^{29}Si MAS NMR spectroscopy,"
J. Am. Ceram. Soc. (accepted)

^{29}Si MAS NMR & the degree of hydration



(a) the anhydrous white Portland cement

(b) metakaolin

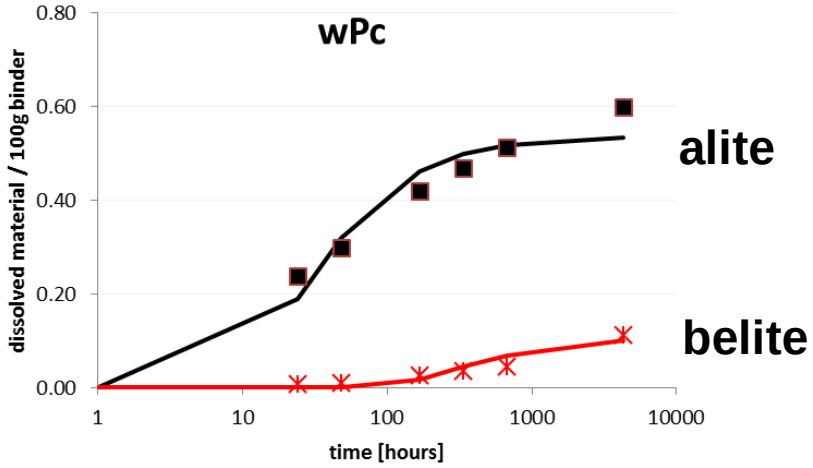
(c) wPc-MK blend hydrated for one day

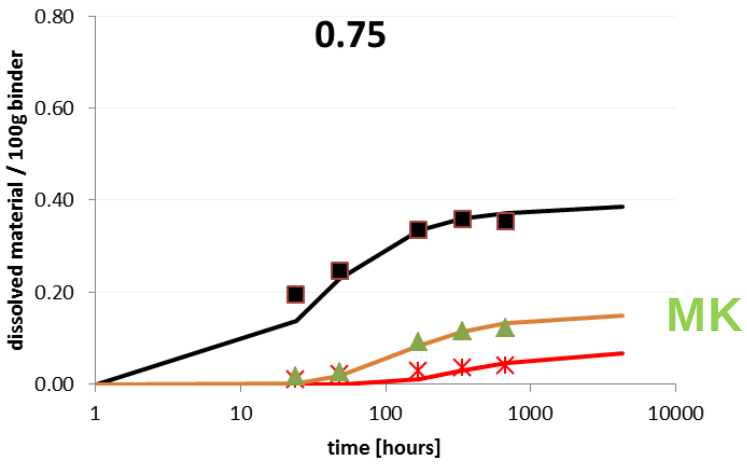
(d) wPc-MK blend hydrated for 180 days

The asterisks (*) indicate the resonances from a quartz impurity in the metakaolin.

Z. Dai, T.T. Thuan and J. Skibsted.
"Aluminum incorporation in the C–S–H phase of white Portland cement – metakaolin blends studied by ^{27}Al and ^{29}Si MAS NMR spectroscopy,"
J. Am. Ceram. Soc. (accepted)

Converted into alite, belite, MK reaction kinetics



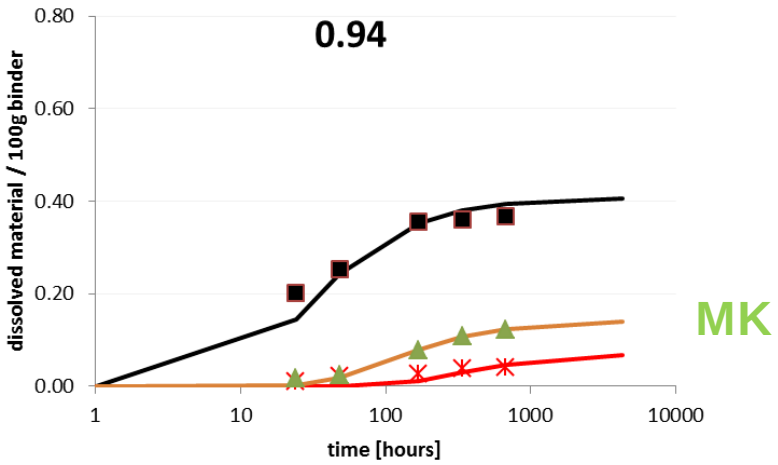


Best fit with a dissolution equation:

$$Q(t) = ke^{-(\frac{n}{t})}$$

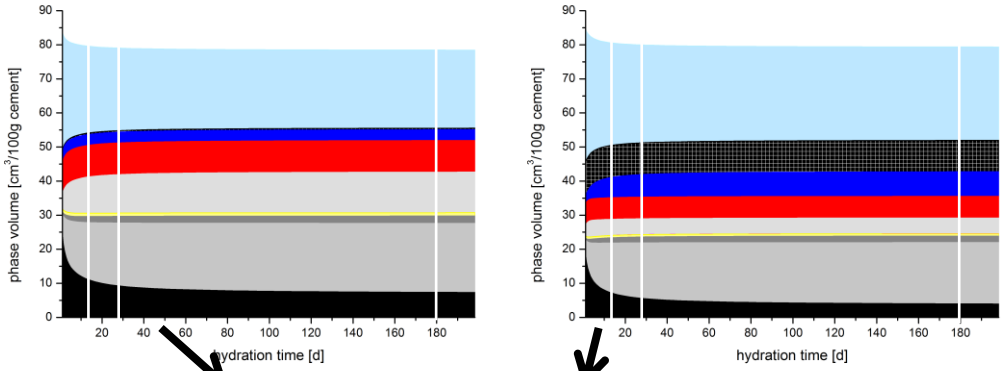
k= dissolved material

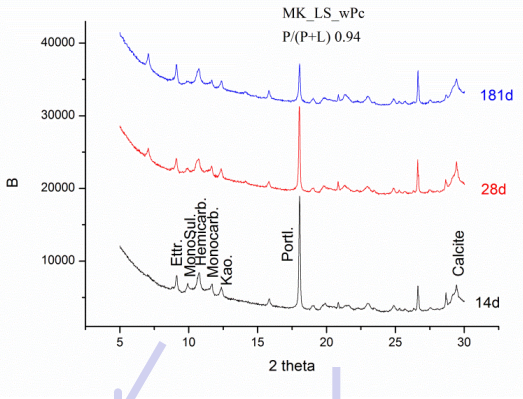
n = rate constant



		wPc	0.00	0.17	0.34	0.50	0.66	0.75	0.94
unreacted	alite	9%	1%	3%	4%	4%	4%	4%	2%
unreacted	belite	7%	2%	4%	5%	5%	5%	5%	5%
unreacted	MK			1%	3%	5%	8%	10%	18%

Hydration modelling in GEMS with kinetics





	wPc			0.00			0.17			0.34			0.5			0.66			0.75			0.94		
	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d	14 d	28 d	181 d
Calcite																								
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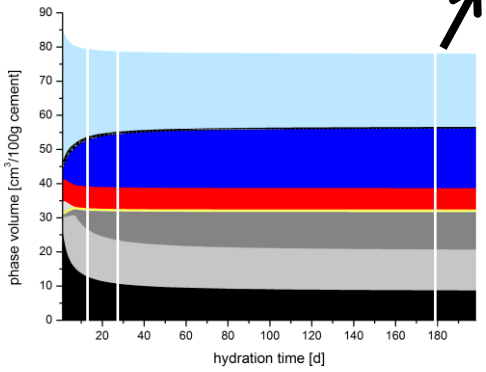
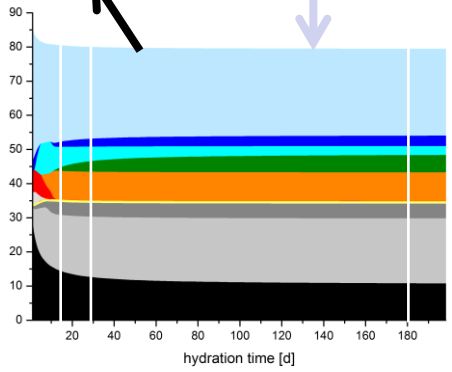
Monosulfate																								
Ettringite																								
Portlandite																								

aq. solution
calcite
monocarbonate
hemicarbonate
ettringite
monosulfate
C_3AH_6
strätlingite
portlandite
hydrotalcite
low Ca/Si C-S-H
high Ca/Si C-S-H
unreacted





XRD data show a **good agreement** with the predicted phases!

Summary

*The predicted **phase assemblages** in real systems **might differ** from equilibrium conditions (full hydration).*

*In those cases can the **implementation of hydration kinetics** improve the predicted phase assemblage significantly.*

***^{29}Si MAS NMR** can be utilized as technique to determine the degree of hydration.*

*In this example was the reacted material implemented into GEMS via a simple exponential **"dissolution" function**. This equations introduces two parameters - **one rate** and **one mass** parameter - which were fitted to represent the experimental data.*

*The **suppression of strätlingite** formation could be modeled successfully, including the complex AFm phase assemblage at high MK substitutions.*