Assessing Deterioration of Concrete Structures using Self-Sufficient Reactive-Transport Modeling

O. Burkan Isgor and W. Jason Weiss

Acknowledgements

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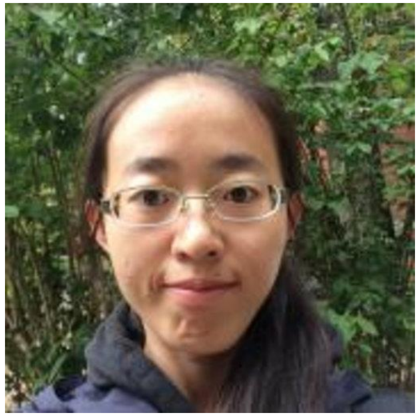
Dr. Deborah Glosser
Ph.D. student, Post-doctoral researcher
(currently, Assistant Professor at UWW)

Dr. Vahid Jafari Azad
Post-doctoral researcher
(currently Senior Engineer at WSP)



Dr. Qin Pang
Post-doctoral researcher
(currently Researcher at PNNL)

Dr. Keshav Bharadwaj
Ph.D. student, Post-doctoral researcher

Concrete sustainability

(Vector Corrosion Technologies)

Life Cycle Performance

Increase the service life of the structures

Performance-based mixture proportioning

Service life modeling

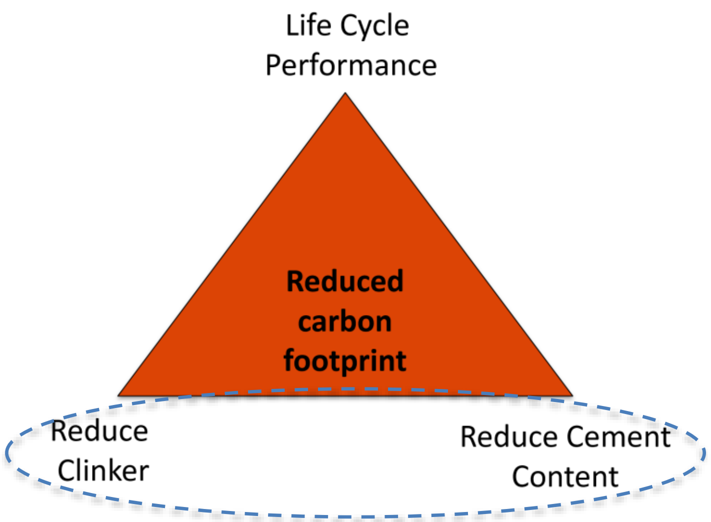
Reduced carbon footprint

Reduce Clinker

Reduce Cement Content

Increase the use of low-carbon footprint cementitious materials and powder extenders

Concrete sustainability



Increase the use of low-carbon footprint cementitious materials and powder extenders

- We have been using conventional (in-spec) SCMs, some limestone, etc.

- Time to consider

    - underutilized, novel, low-carbon footprint binders
        - ➢ Off-spec SCMs (off-spec fly ash, natural pozzolans, slag, etc.
        - ➢ Other types of ashes (bottom ash, reclaimed ash, agricultural ash, etc.)
        - ➢ Other industrial and natural products (pumice, clays, etc.)

    - Increased use of powder extenders
        - Larger limestone replacement
        - Synergies with binders (e.g., limestone + Al-containing binders)

Challenges

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OPC chemistry
C_3S, C_2S, C_3A, C_4AF, Na_2O, K_2O, etc

Other binder chemistry
SiO_2, Al_2O_3, CaO, Na_2O, K_2O, etc.

- **Do we know how these unconventional binders react?**
  - Maximum reactivity (portion of the reactive components)?
  - Reactions vs. time
- **Do we know how to proportion mixtures with these unconventional binders?**
  - For specified performance
  - For cost
  - For lowest carbon footprint
  - Etc.

Performance-based mixture proportioning
Bharadwaj et al. 2022

- **Can we perform service life modeling of concrete produced with these materials?**
  - Modeling transport of deteriorative species (e.g., chlorides, sulfates, etc.)
  - Modeling reactive processes (e.g., chloride binding, sulfate attack, salt damage, etc.)

Service life modeling
(this presentation)

Photo 44066082 © Luchschen | Dreamstime.com
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Service life modeling of concrete

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Moisture movement (e.g., wetting/drying, ponding, etc.)

+

Transport of ionic (e.g., chloride, sulfates, etc.), gaseous (e.g., CO_2,O_2) species

Diffusion + Electrical migration + Chemical activity + Advection

+

Reactions (e.g., chloride binding, sulfate attack, carbonation, etc.)

Service life modeling of concrete

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College of Engineering

Moisture movement (e.g., wetting/drying, ponding, etc.)

+

Transport of ionic (e.g., chloride, sulfates, etc.), gaseous (e.g., CO_2, O_2) species

Diffusion + Electrical migration + Chemical activity + Advection

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Reactions (e.g., chloride binding, sulfate attack, carbonation, etc.)

Service life modeling of concrete

Ionic flux = Diffusion + Electrical migration + Chemical activity + Advection

Service life modeling of concrete

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$$\underbrace{-\,\mathit{D}_{\mathrm{i}}\,\nabla \mathrm{c}_{\mathrm{aq,i}}} - \underbrace{\mathit{D}_{\mathrm{i}}\,\mathrm{c}_{\mathrm{aq,i}}\,\frac{\mathrm{Fz}}{\mathrm{RT}}\,\nabla\emptyset} - \underbrace{\mathit{D}_{\mathrm{i}}\,\mathrm{c}_{\mathrm{aq,i}}\,\nabla \mathrm{ln}\gamma_{\mathrm{i}}} + \underbrace{\mathrm{c}_{\mathrm{aq,i}}\,\mathrm{v}_{\mathrm{L}} + \mathrm{c}_{\mathrm{G},i}\,\mathrm{v}_{\mathrm{G}}}$$

Ionic flux = Diffusion + Electrical migration + Chemical activity + Advection

Reactive-transport modeling

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$$\frac{\partial\left[\varphi c_{aq,i}\right]}{\partial t}\frac{\partial c_{s,i}}{\partial t} = -\sum_{n_i} \nabla\cdot\left(\underbrace{-\,D_i \nabla c_{aq,i}}_{\text{diffusion}} - \underbrace{D_i\, c_{aq,i}\,\frac{Fz}{RT}\,\nabla\emptyset}_{\text{electrical migration}} - \underbrace{D_i\, c_{aq,i}\,\nabla \ln\gamma_i}_{\text{chemical activity}}\right)$$

Reactive-transport modeling

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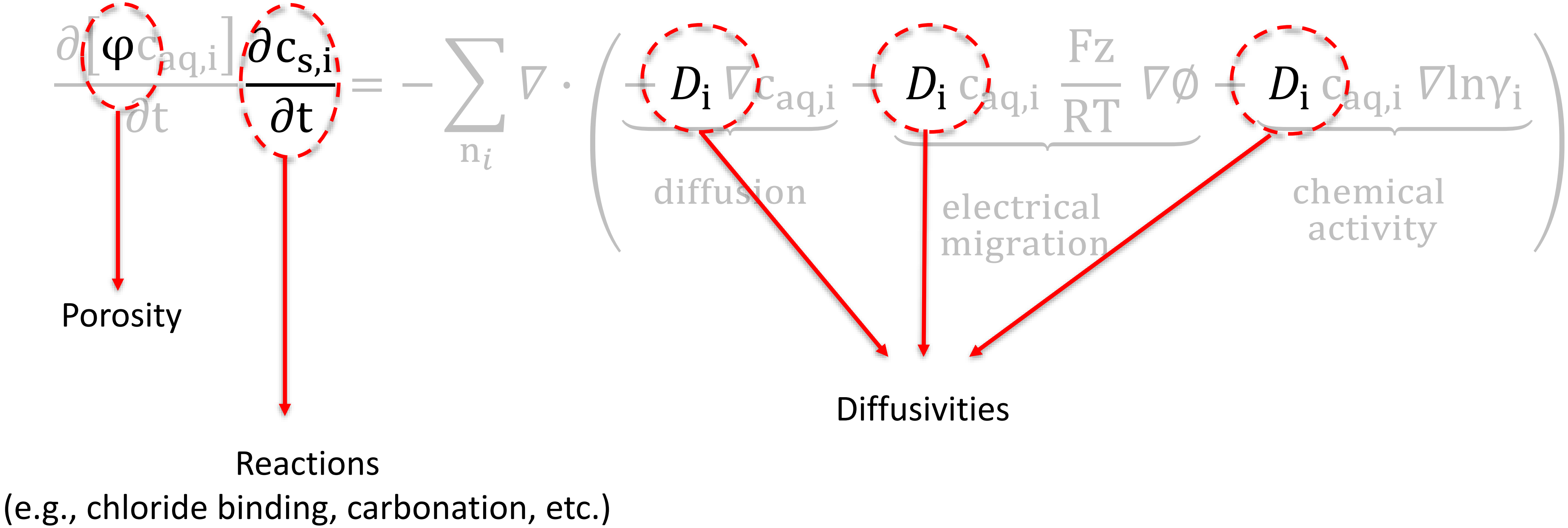

$$\frac{\partial[\varphi c_{\mathrm{aq,i}}]}{\partial t}\frac{\partial c_{\mathrm{s,i}}}{\partial t} = -\sum_{n_i} \nabla\cdot\left(\underbrace{-D_{\mathrm{i}}\nabla c_{\mathrm{aq,i}}}_{\text{diffusion}}\underbrace{-D_{\mathrm{i}}\, c_{\mathrm{aq,i}}\frac{\mathrm{Fz}}{\mathrm{RT}}\nabla\emptyset}_{\text{electrical migration}}\underbrace{-D_{\mathrm{i}}\, c_{\mathrm{aq,i}}\nabla\ln\gamma_{\mathrm{i}}}_{\text{chemical activity}}\right)$$

Porosity

Reactions
(e.g., chloride binding, carbonation, etc.)

Diffusivities

Reactive-transport modeling

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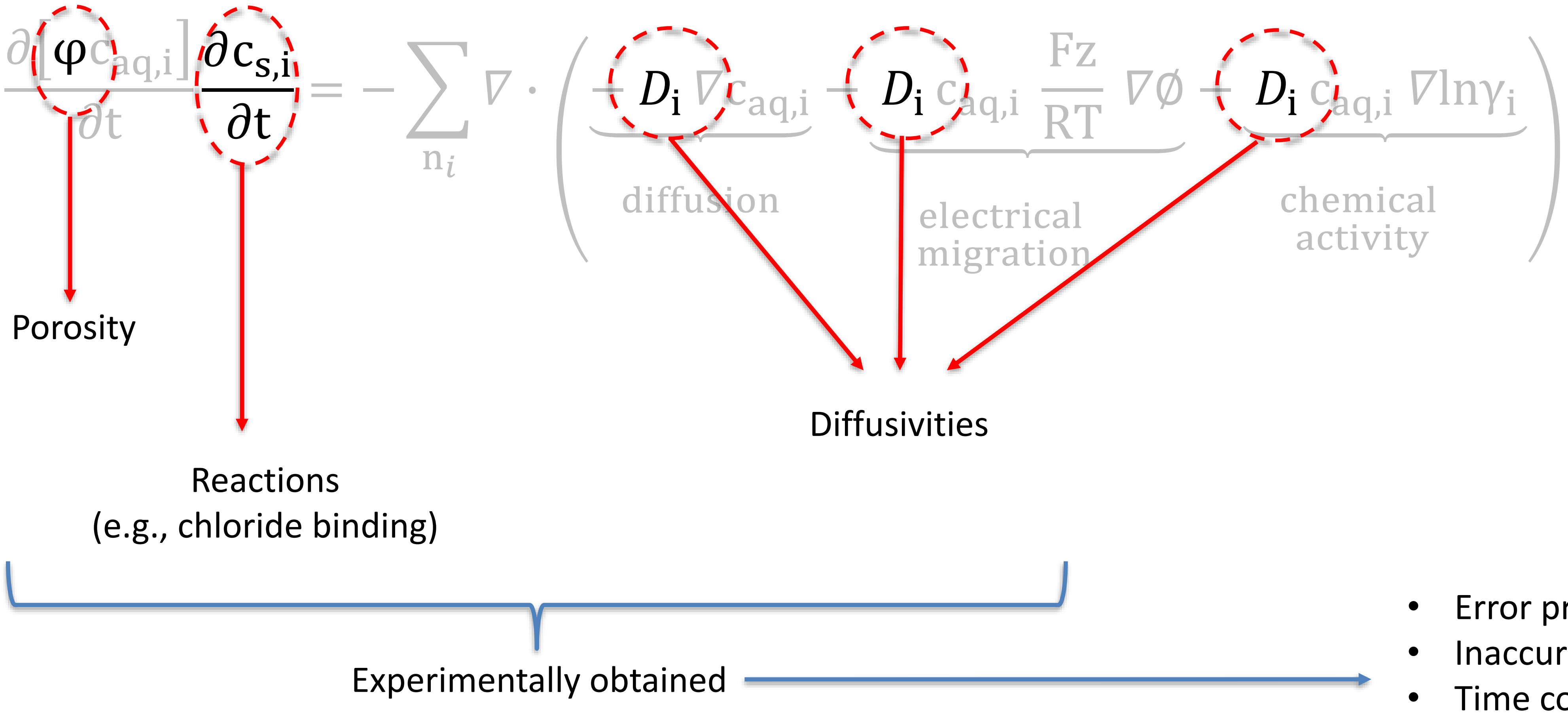

$$\frac{\partial[\varphi c_{aq,i}]}{\partial t} + \frac{\partial c_{s,i}}{\partial t} = -\sum_{n_i} \nabla \cdot \left(\underbrace{-D_i \nabla c_{aq,i}}_{\text{diffusion}} \underbrace{- D_i c_{aq,i} \frac{Fz}{RT} \nabla \emptyset}_{\text{electrical migration}} \underbrace{- D_i c_{aq,i} \nabla \ln \gamma_i}_{\text{chemical activity}} \right)$$

Porosity

Reactions
(e.g., chloride binding)

Diffusivities

Experimentally obtained

- Error prone
- Inaccurate / unrepresentative
- Time consuming
- Expensive

“Self-sufficient” model

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$$\frac{\partial[\varphi c_{aq,i}]}{\partial t}\frac{\partial c_{s,i}}{\partial t} = -\sum_{n_i} \nabla \cdot \left(\underbrace{-D_i \nabla c_{aq,i}}_{\text{diffusion}} \underbrace{-D_i c_{aq,i} \frac{Fz}{RT} \nabla \emptyset}_{\text{electrical migration}} \underbrace{-D_i c_{aq,i} \nabla \ln \gamma_i}_{\text{chemical activity}} \right)$$

Porosity

Theoretical
(using MPPM)

Reactions
(e.g., chloride binding)

Theoretical
(using kinetic/thermodynamic modeling)

Diffusivities

Theoretical
(using MPPM)

Isgor and Weiss, Materials & Structures, 2019
Azad et al., Computer & Geosciences, 2016

MPPM: Modified Pore Partitioning Model (Powers + GEMS) up-scaled to concrete

Time marching

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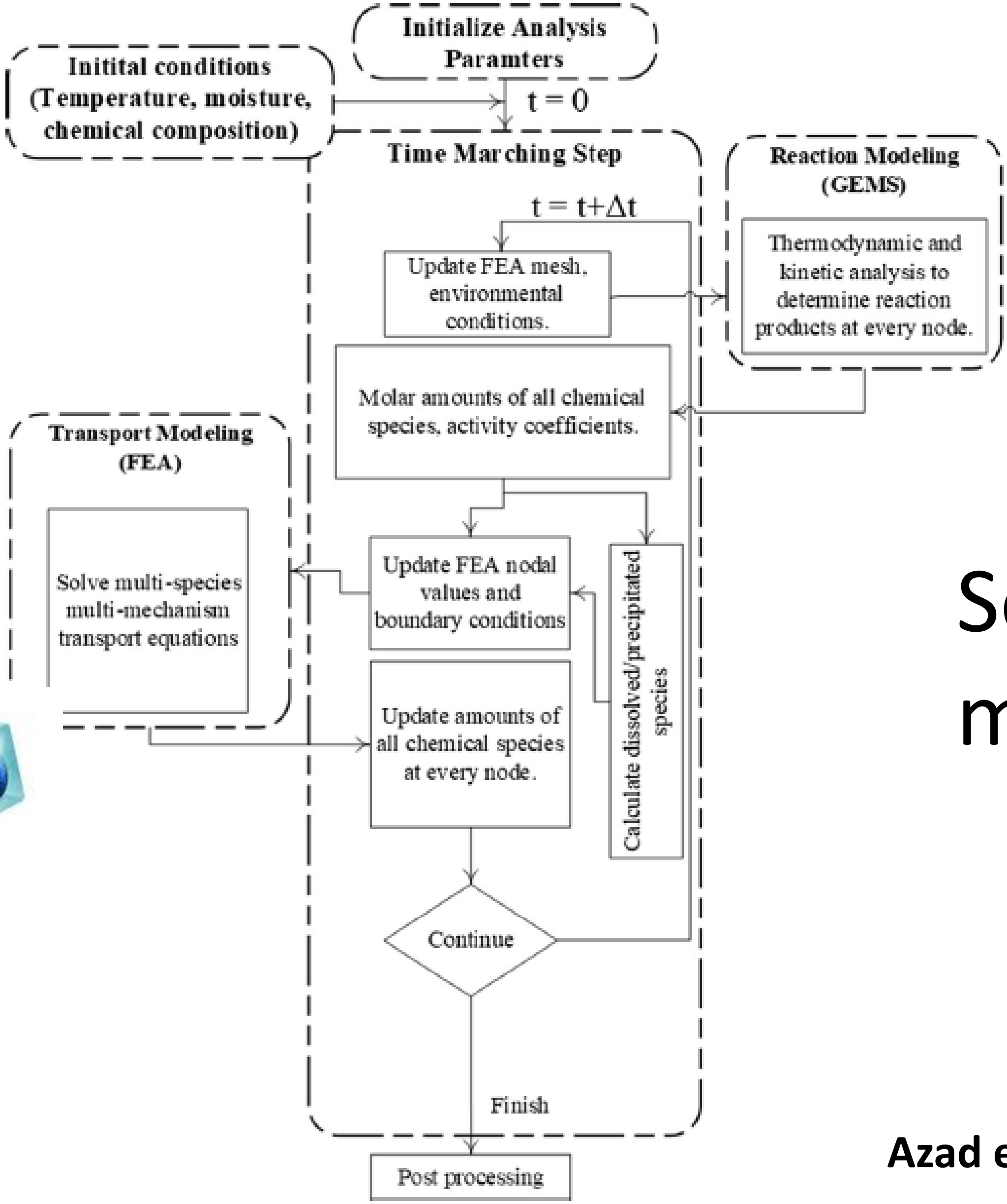
MOOSE

Multiphysics Object-Oriented Simulation Environment

COMSOL MULTIPHYSICS®



GEMS3K

Self-sufficient modeling algorithm

Azad et al., Computer & Geosciences, 2016

How do we move from “empirical” to “self-sufficient”?

Gibbs energy minimization (GEM)

EXAMPLE:

INPUT

1000 g OPC + 400 g H_2O →

425 g C_3S
325 g C_2S
80 g C_3A
70 g C_4AF

30 g Na_2O
20 g K_2O

50 g gypsum ($CaSO_4$)

Etc.

OUTPUT

??? g of C-S-H

C-S-H-1, C-S-H-2, etc.

??? g of CH

??? g of AFm

AFm1, AFm2, etc.

??? g of AFt

AFt1, AFt2, etc.

??? pore solution

Ca+2, Na+, K+, etc.

} 1,400 g

Gibbs energy minimization (GEM)

EXAMPLE:

INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
325 g C_2S
80 g C_3A
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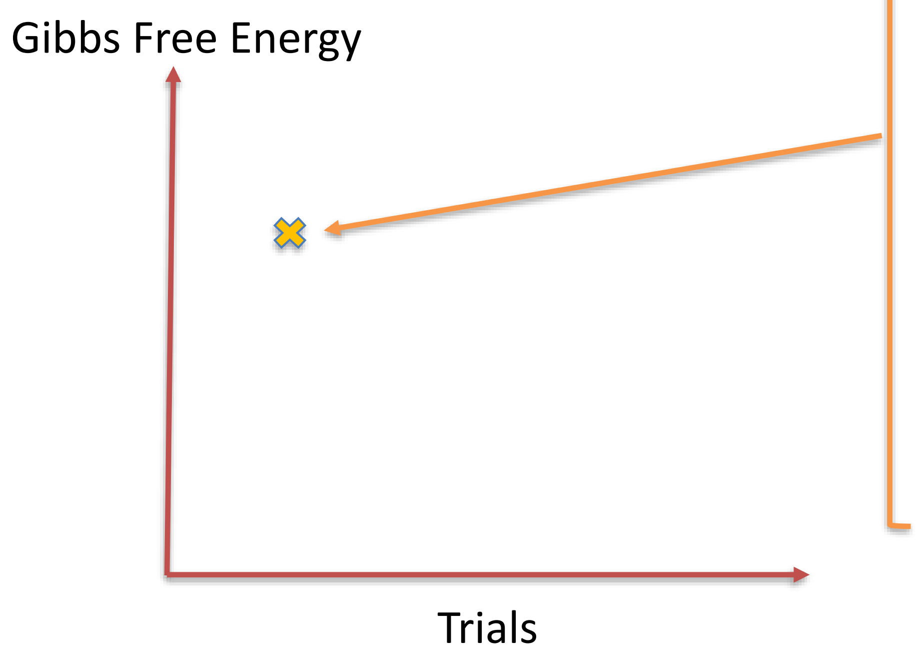

OUTPUT 1

500 g of C-S-H
C-S-H-1, C-S-H-2, etc.
400 g of CH
200 g of AFm
AFm1, AFm2, etc.
200 g of AFt
AFt1, AFt2, etc.
100 g pore solution
Ca+2, Na+, K+, etc.

1,400 g

Gibbs energy minimization (GEM)

EXAMPLE:

INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
325 g C_2S
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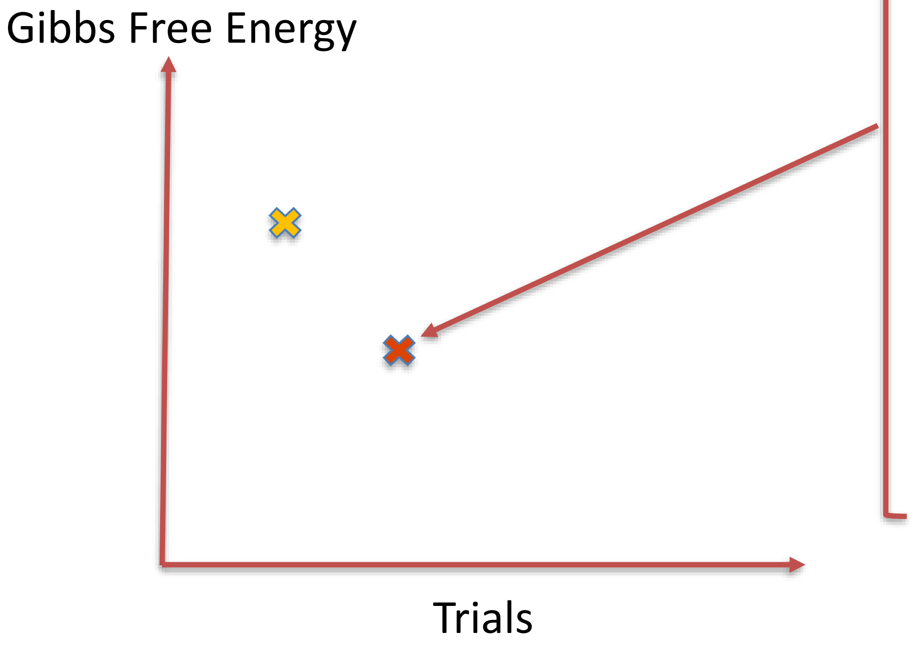

OUTPUT 2

550 g of C-S-H

C-S-H-1, C-S-H-2, etc.

350 g of CH

175 g of AFm

AFm1, AFm2, etc.

225 g of AFt

AFt1, AFt2, etc.

100 g pore solution

Ca+2, Na+, K+, etc.

1,400 g

Gibbs energy minimization (GEM)

EXAMPLE:

INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
325 g C_2S
80 g C_3A
70 g C_4AF

30 g Na_2O
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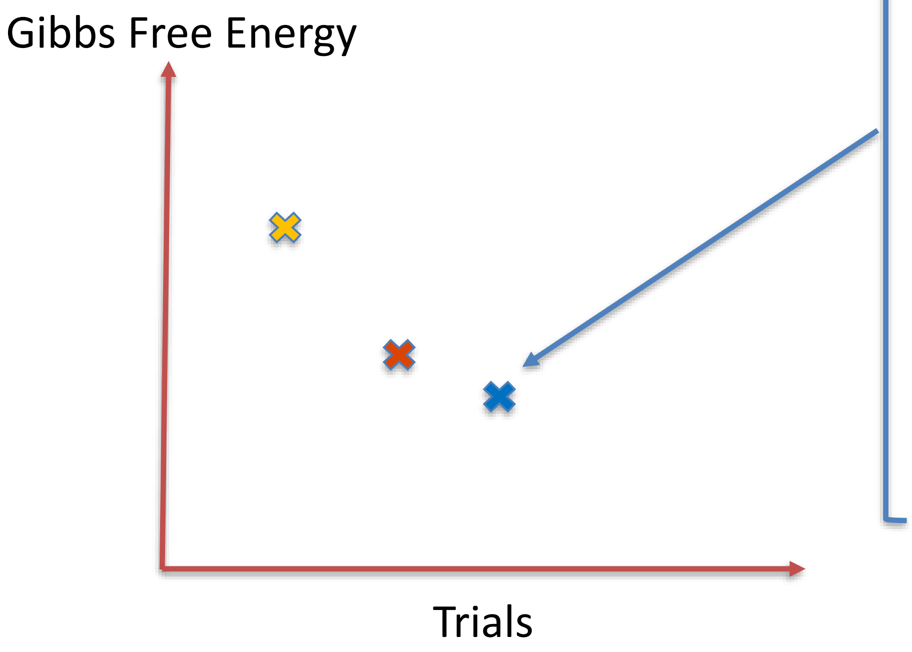
50 g gypsum ($CaSO_4$)

Etc.



OUTPUT n

555 g of C-S-H

C-S-H-1, C-S-H-2, etc.

345 g of CH

180 g of AFm

AFm1, AFm2, etc.

210 g of AFt

AFt1, AFt2, etc.

110 g pore solution

Ca+2, Na+, K+, etc.

1,400 g

Gibbs energy minimization (GEM)

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EXAMPLE:

INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
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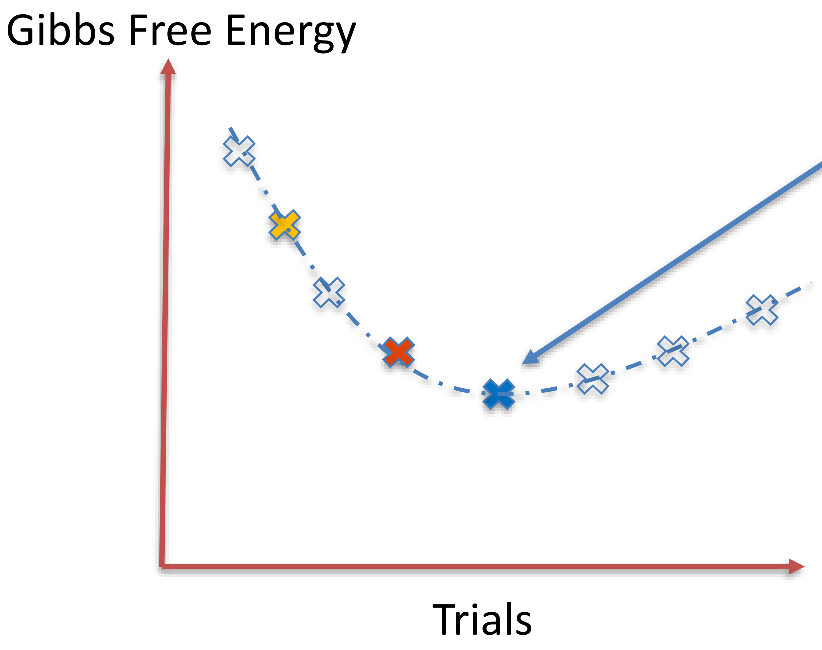

SOLUTION

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C-S-H-1, C-S-H-2, etc.

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AFm1, AFm2, etc.

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110 g pore solution

Ca+2, Na+, K+, etc.

1,400 g

Kinetic/thermodynamic modeling

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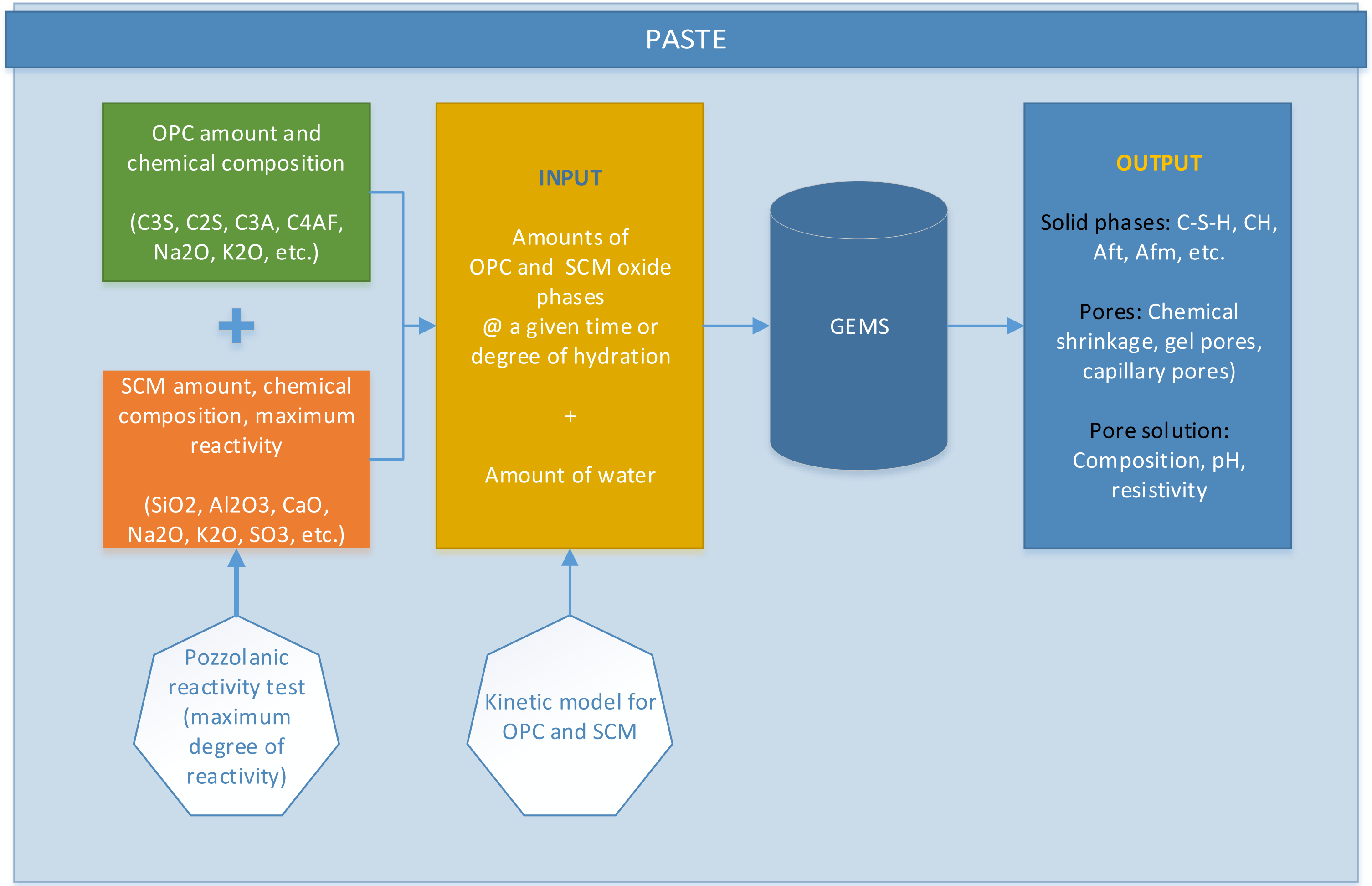


PASTE

OPC amount and chemical composition

(C3S, C2S, C3A, C4AF, Na2O, K2O, etc.)

+

SCM amount, chemical composition, maximum reactivity

(SiO2, Al2O3, CaO, Na2O, K2O, SO3, etc.)

Pozzolanic reactivity test (maximum degree of reactivity)

INPUT

Amounts of OPC and SCM oxide phases @ a given time or degree of hydration

+

Amount of water

Kinetic model for OPC and SCM

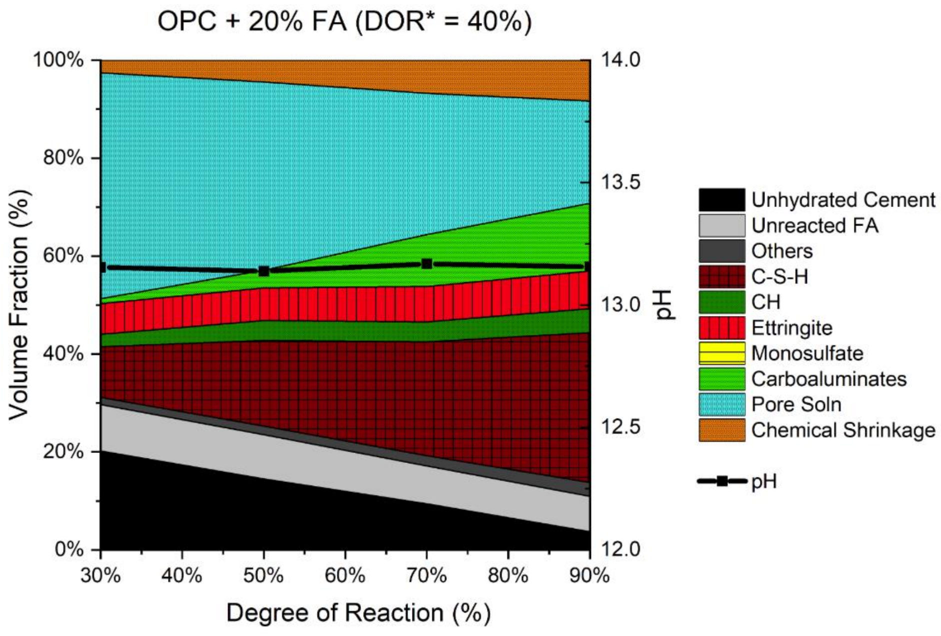
GEMS

OUTPUT

Solid phases: C-S-H, CH, Aft, Afm, etc.

Pores: Chemical shrinkage, gel pores, capillary pores)

Pore solution: Composition, pH, resistivity



(Simulation by K. Bharadwaj)

Reactivity

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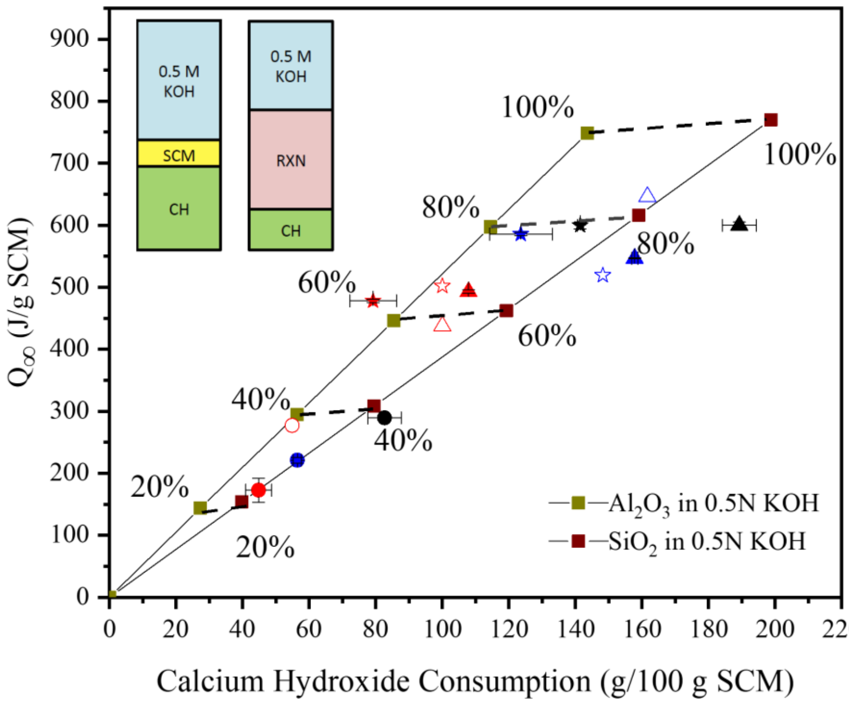

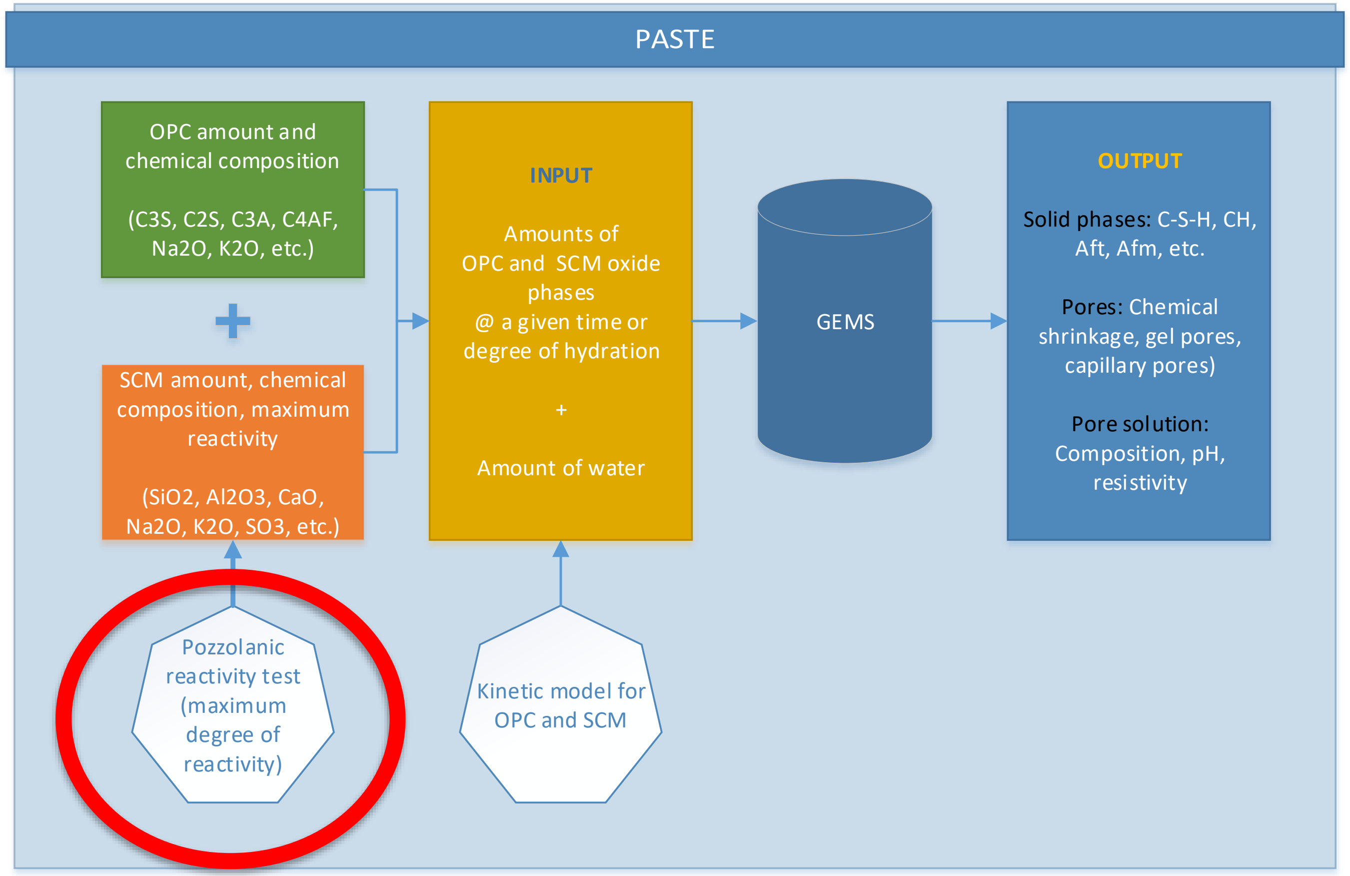

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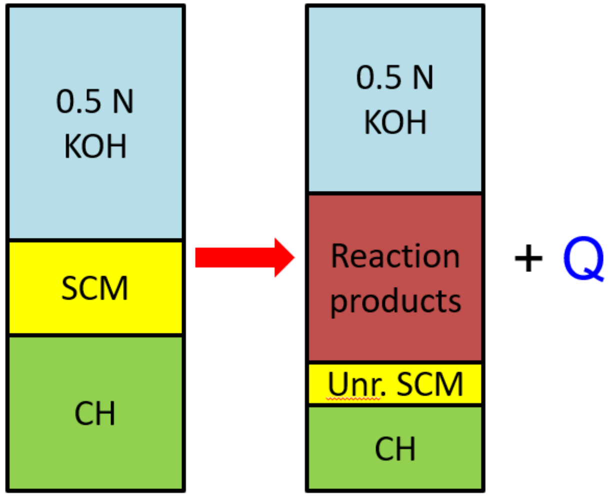
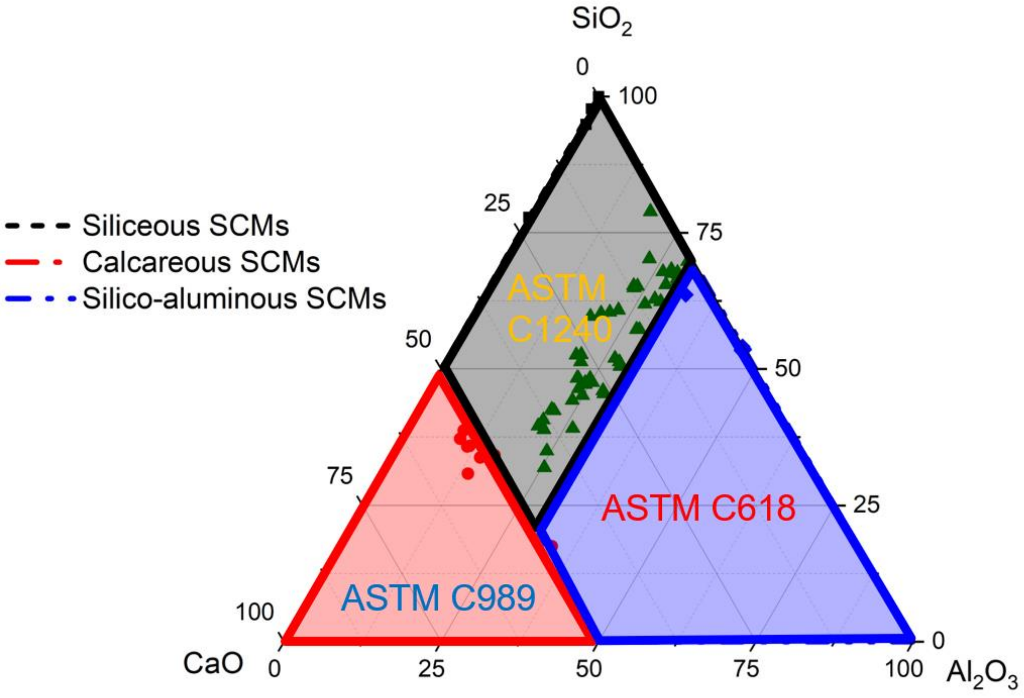
Pore solution: Composition, pH, resistivity

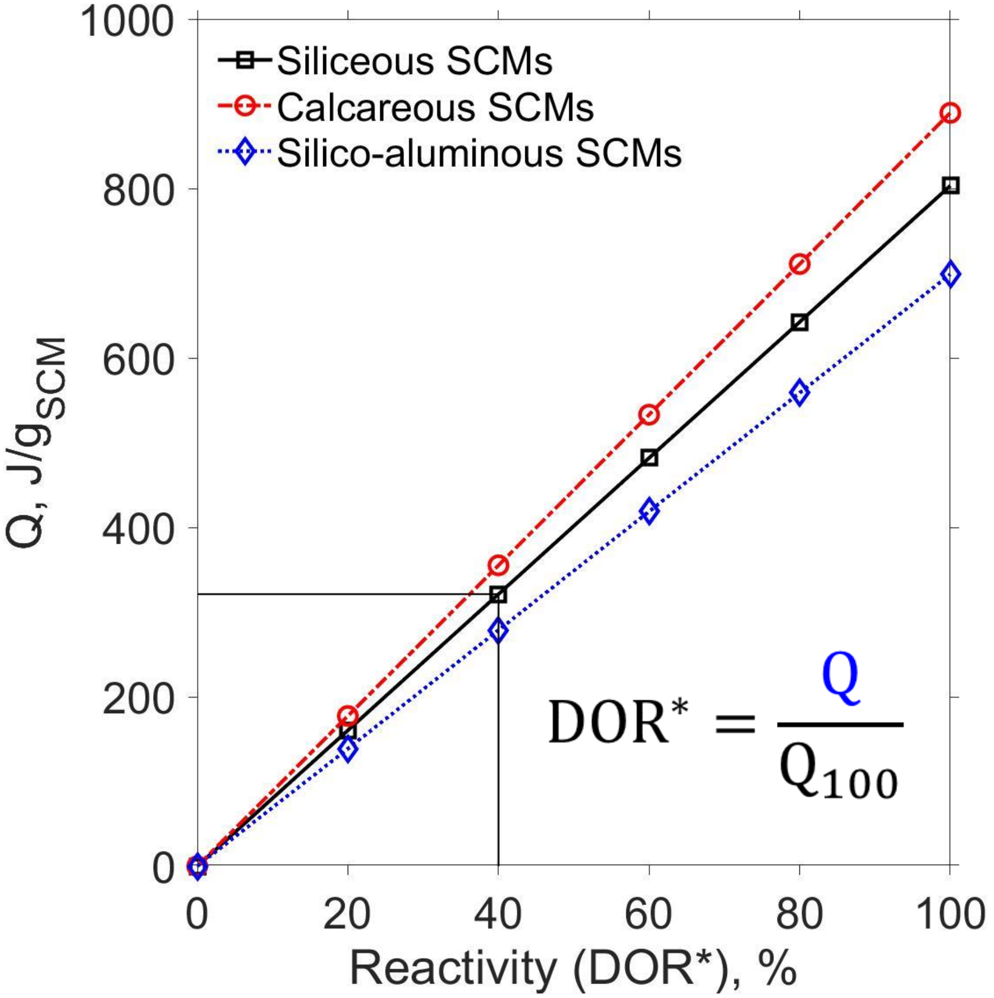
Pozzolanic Reactivity Test (PRT)

Glosser et al. 2019, 2020, 2021

PRT



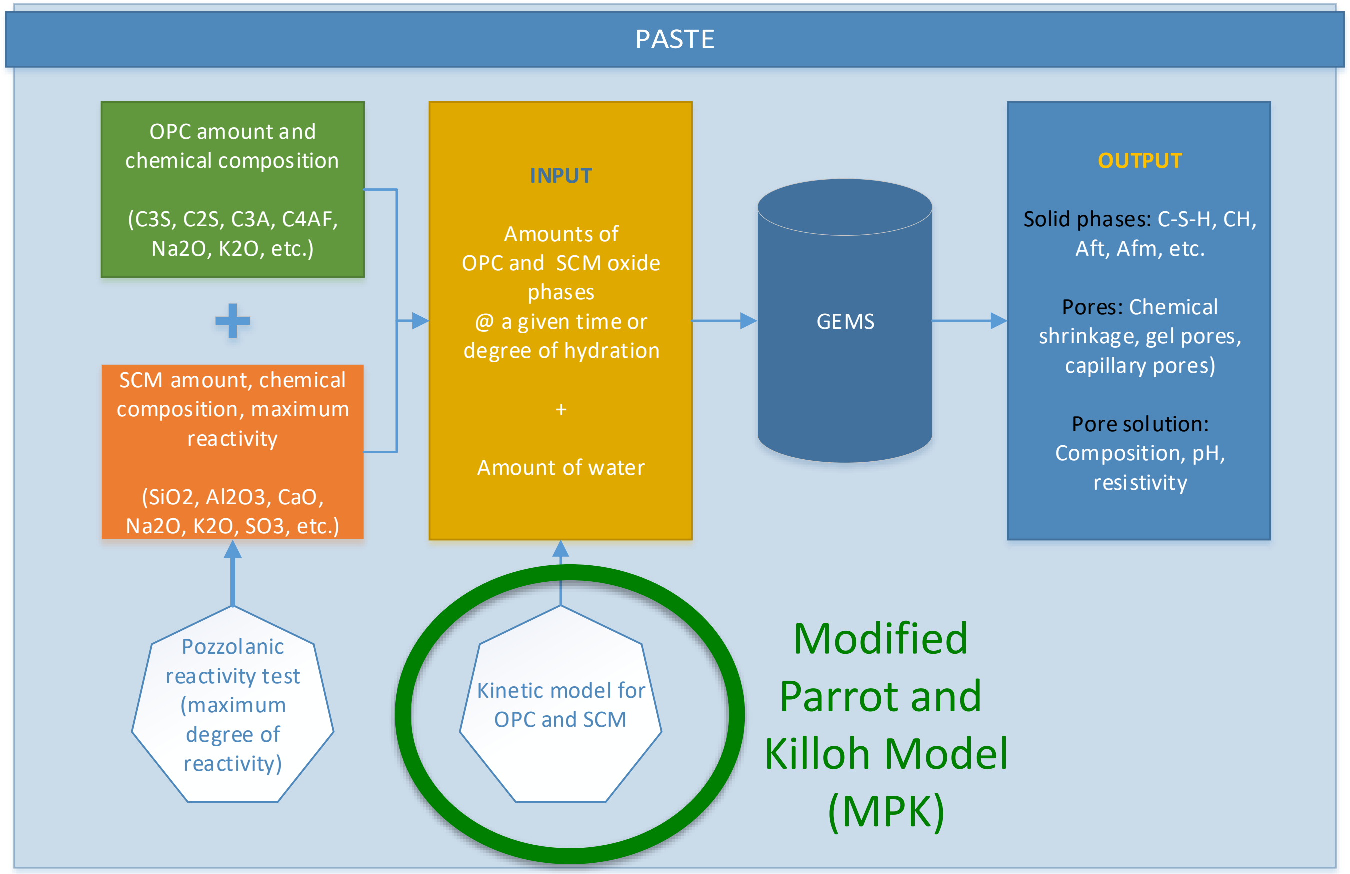




$$DOR^{*} = \frac{Q}{Q_{100}}$$

Bharadwaj et all. 2022

Kinetics



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(C3S, C2S, C3A, C4AF, Na2O, K2O, etc.)

+

SCM amount, chemical composition, maximum reactivity

(SiO2, Al2O3, CaO, Na2O, K2O, SO3, etc.)

INPUT

Amounts of OPC and SCM oxide phases @ a given time or degree of hydration

+

Amount of water

GEMS

OUTPUT

Solid phases: C-S-H, CH, Aft, Afm, etc.

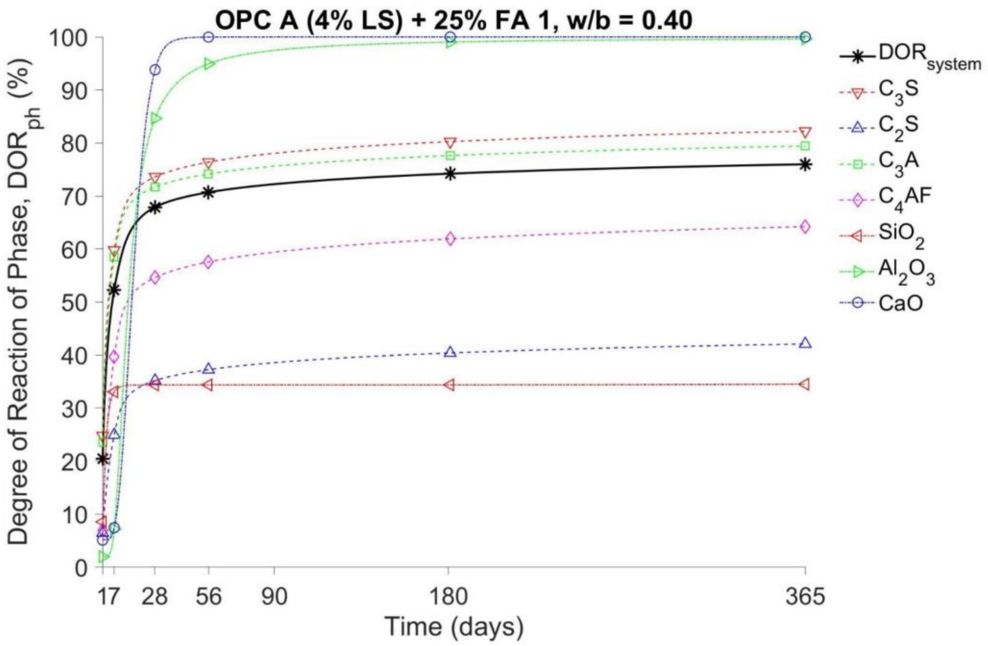
Pores: Chemical shrinkage, gel pores, capillary pores)

Pore solution: Composition, pH, resistivity

Pozzolanic reactivity test (maximum degree of reactivity)

Kinetic model for OPC and SCM

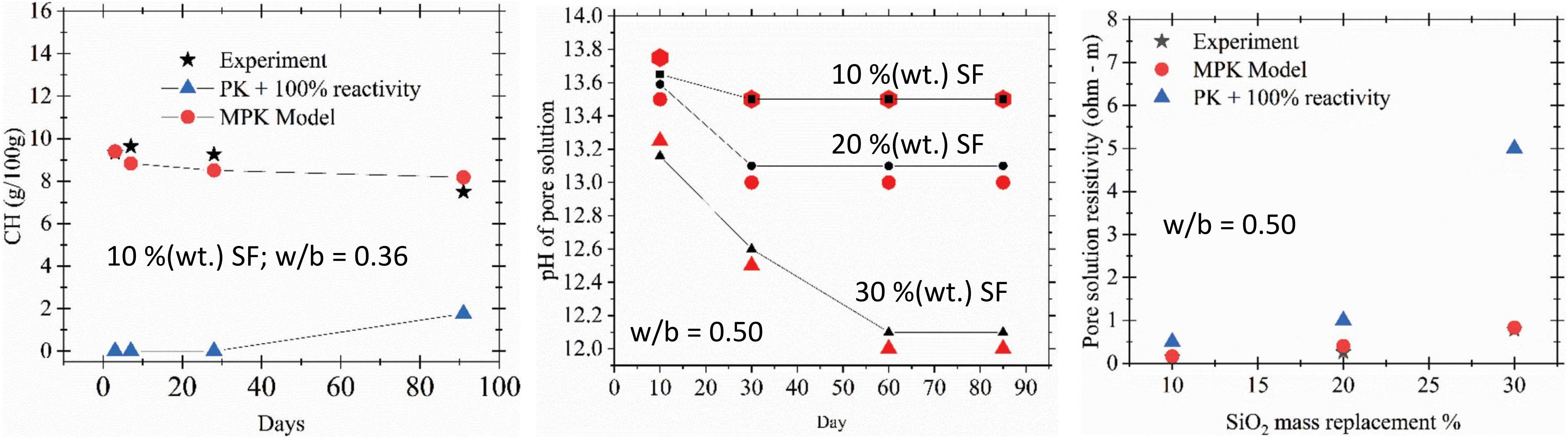
Modified Parrot and Killoh Model (MPK)



Glosser et al. 2019, 2020, 2021

Kinetics

OPC + Silica fume



Glosser et al. (2020) “Non-Equilibrium Thermodynamic Modeling Framework for Ordinary Portland Cement/Supplementary Cementitious Material Systems,” ACI Mat. J., 117(6): 111-123

Modified Pore Partitioning Model for Concrete

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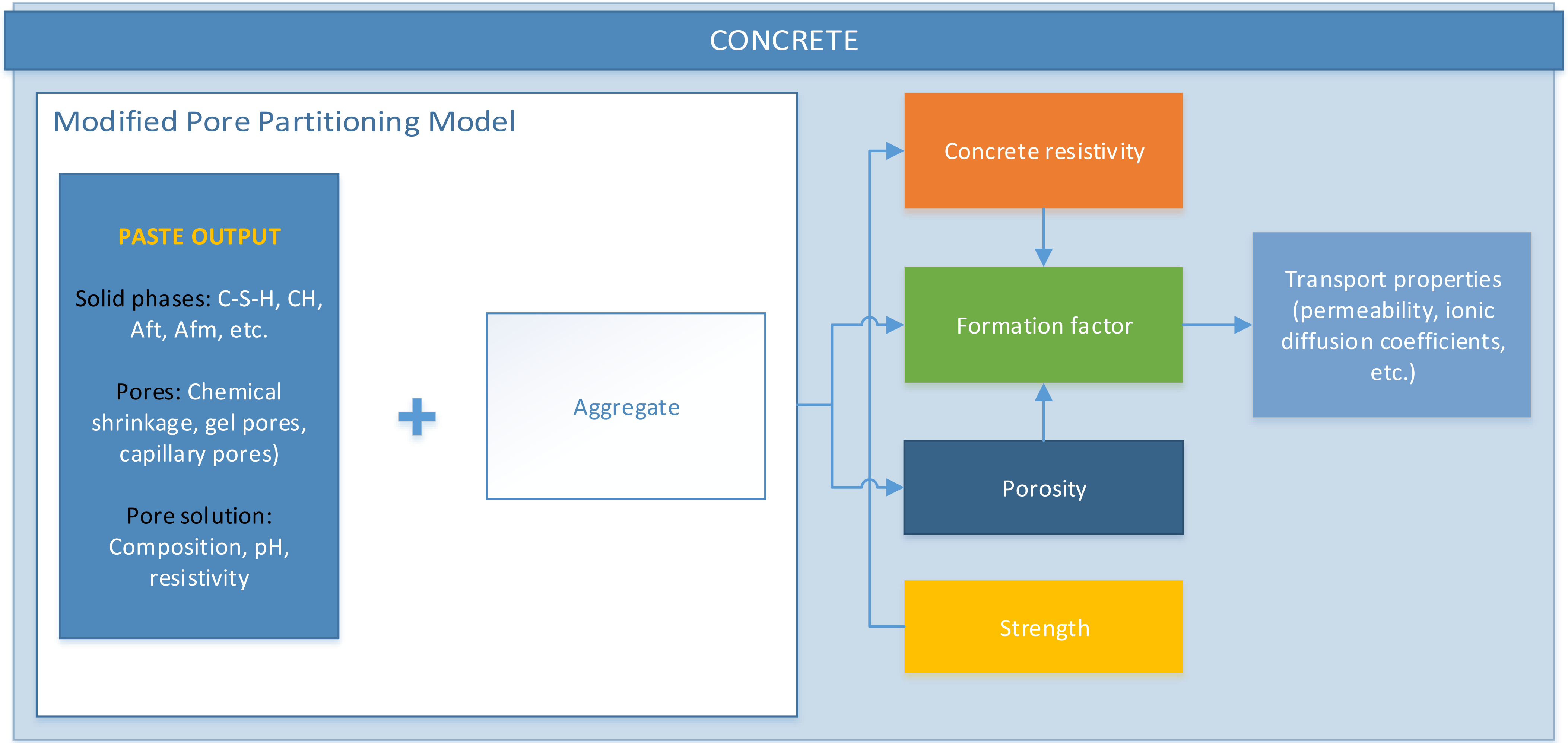

CONCRETE

Modified Pore Partitioning Model

PASTE OUTPUT

Solid phases: C-S-H, CH, Aft, Afm, etc.

Pores: Chemical shrinkage, gel pores, capillary pores)

Pore solution: Composition, pH, resistivity

\+

Aggregate

Concrete resistivity

Formation factor

Porosity

Strength

Transport properties (permeability, ionic diffusion coefficients, etc.)

Bharadwaj et al. 2019, 2020

MPPM - Porosity

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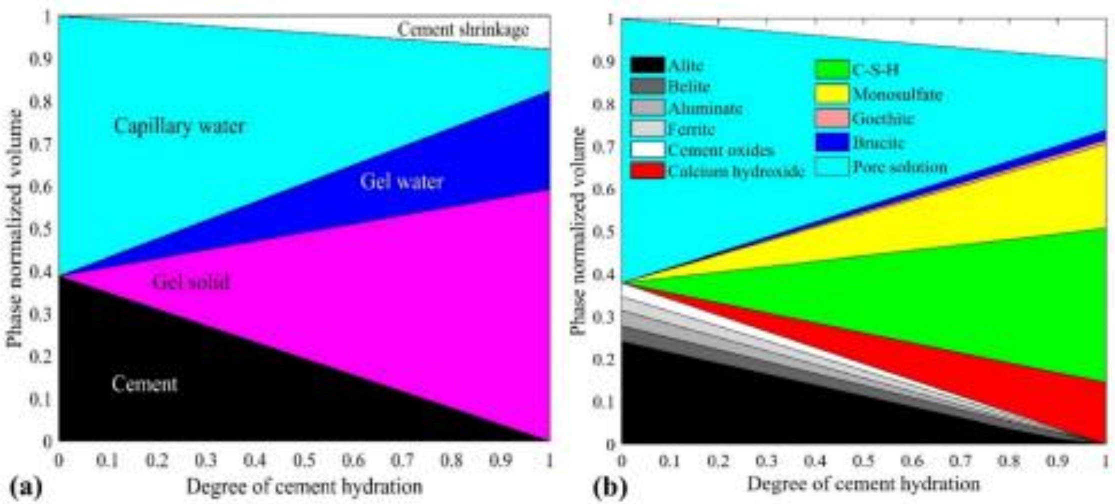
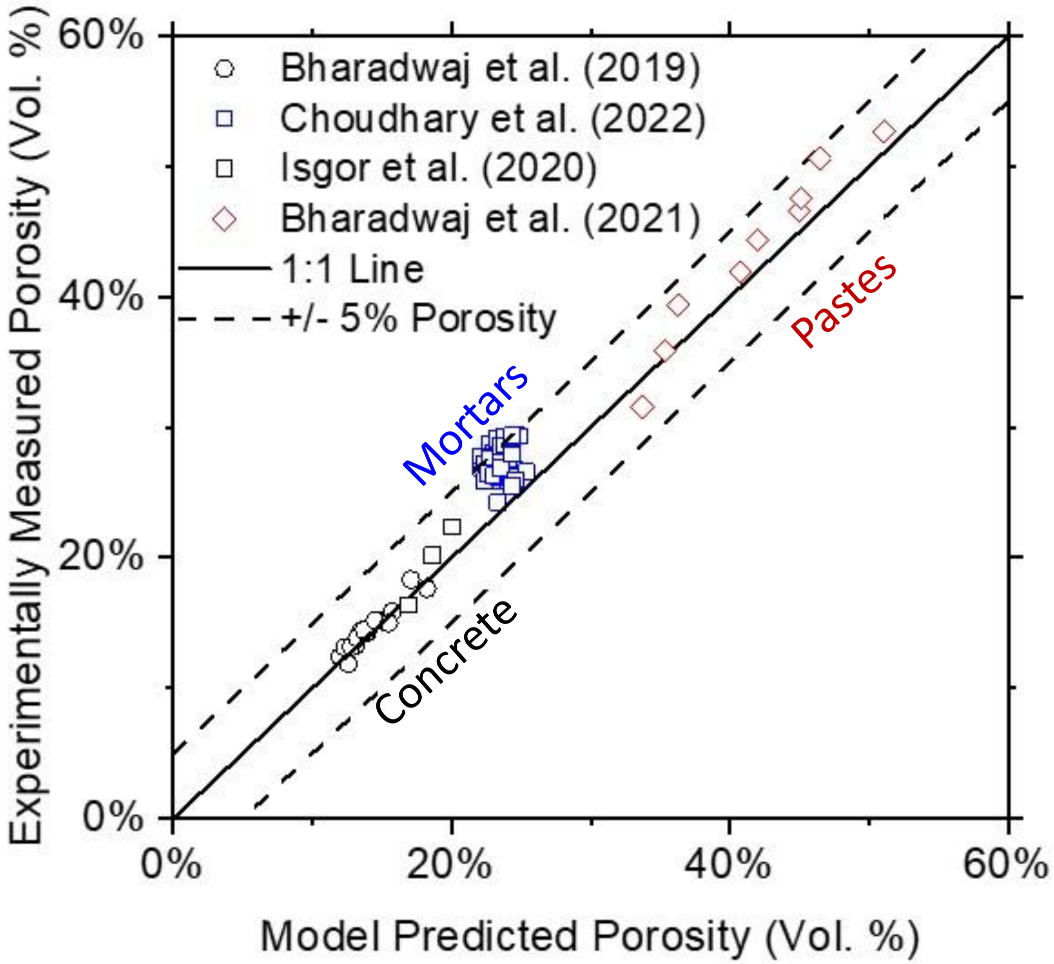
$$\phi_{paste} = V_{air} + \underbrace{\left(v_{gw} + v_{cw} + v_{cs}\right)}_{\text{From GEMS and Powers Model}} \cdot V_{paste}$$





MPPM - Formation Factor

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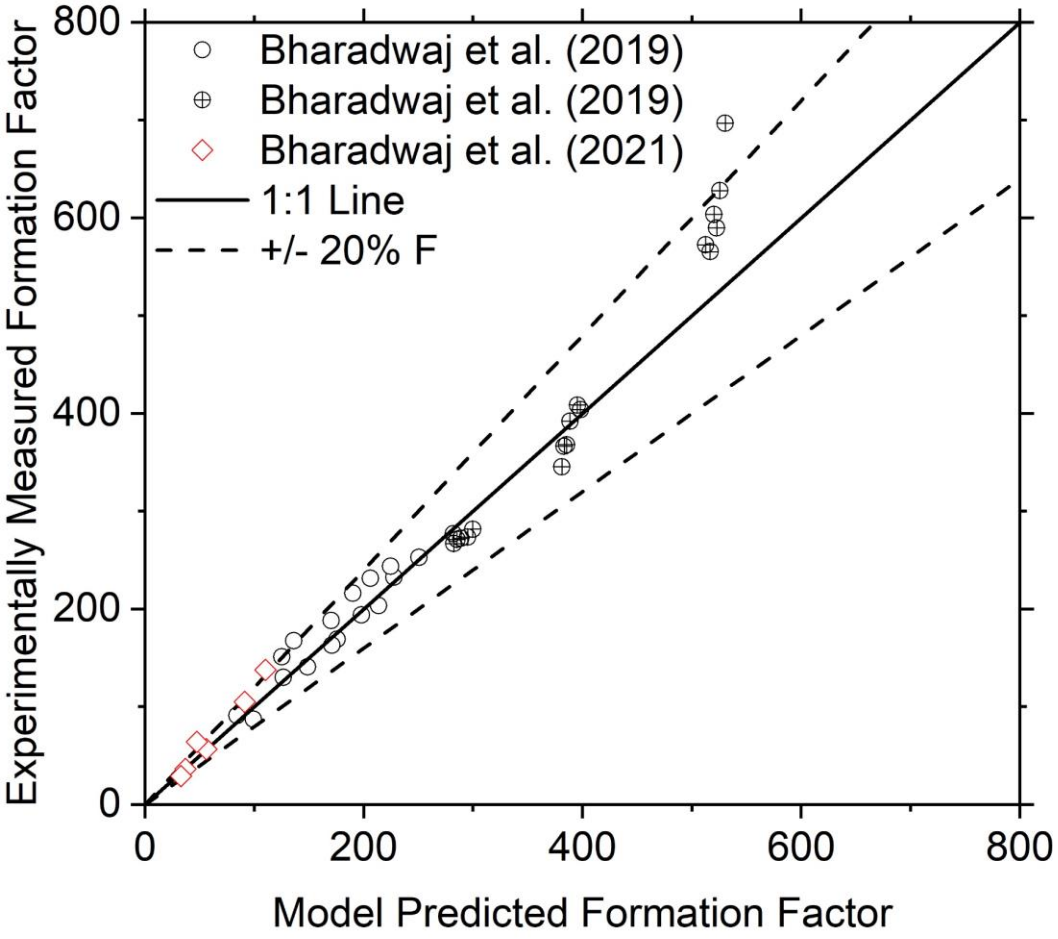

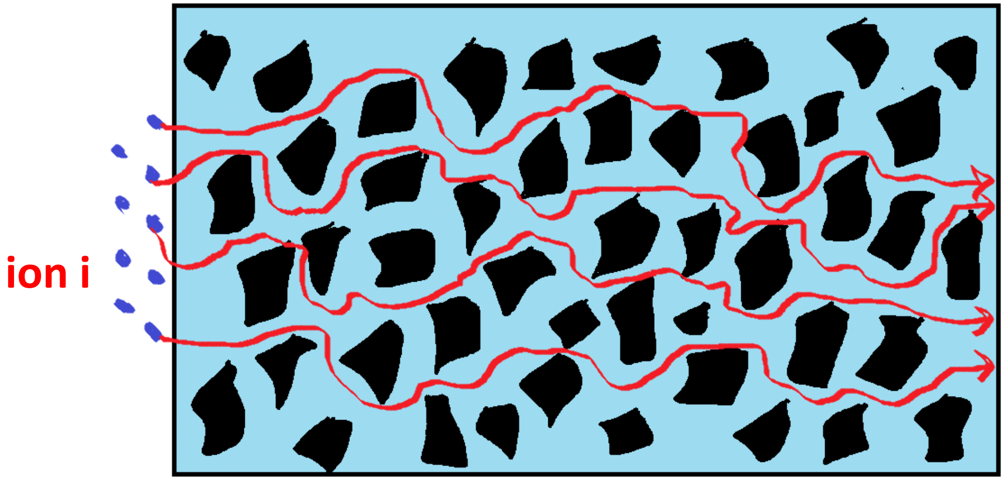

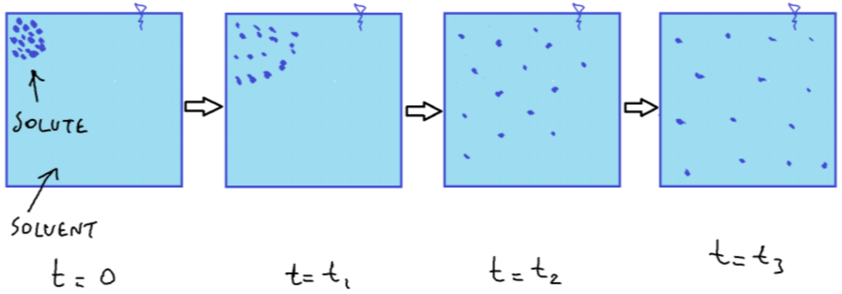

$$D_{i,concrete} = \frac{D_i}{F}$$

Summary

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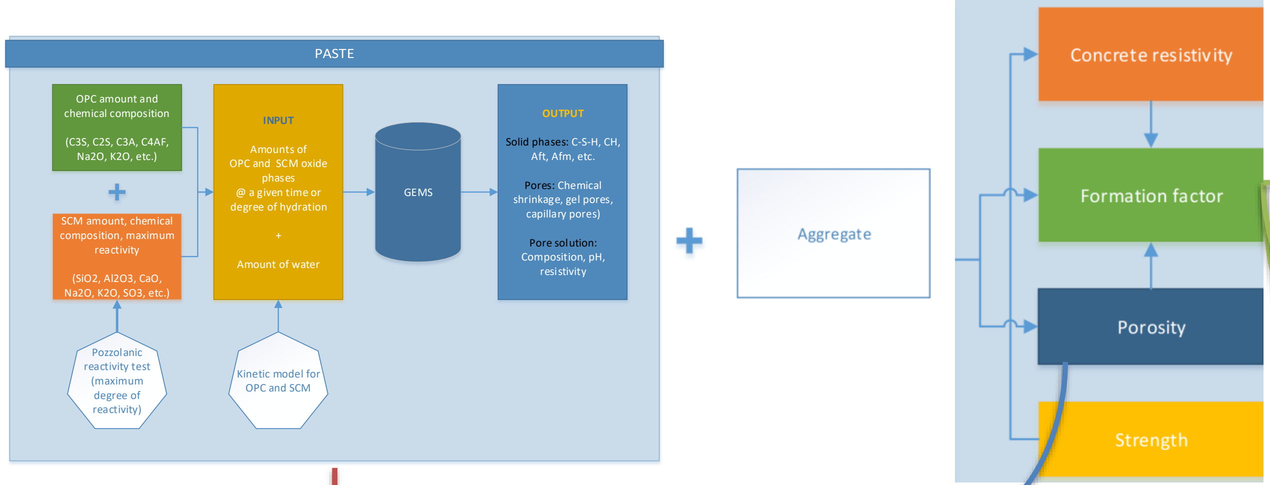

PASTE

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(C3S, C2S, C3A, C4AF, Na2O, K2O, etc.)

+

SCM amount, chemical composition, maximum reactivity

(SiO2, Al2O3, CaO, Na2O, K2O, SO3, etc.)

Pozzolanic reactivity test (maximum degree of reactivity)

INPUT

Amounts of OPC and SCM oxide phases @ a given time or degree of hydration

+

Amount of water

Kinetic model for OPC and SCM

GEMS

OUTPUT

Solid phases: C-S-H, CH, Aft, Afm, etc.

Pores: Chemical shrinkage, gel pores, capillary pores)

Pore solution: Composition, pH, resistivity

+

Aggregate

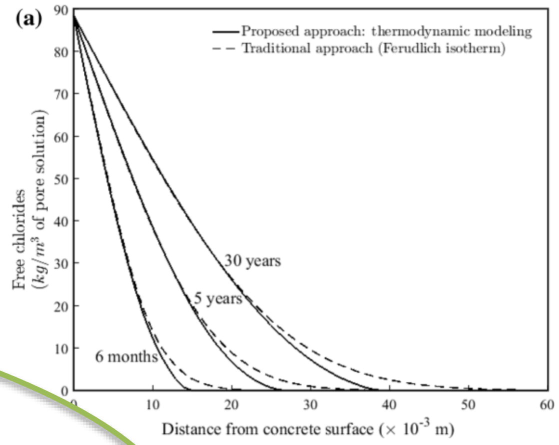
Concrete resistivity

Formation factor

Porosity

Strength

$$\frac{\partial[\varphi c_{aq,i}]}{\partial t}\frac{\partial c_{s,i}}{\partial t} = -\sum_{n_i}\nabla\cdot\left(\underbrace{-D_i\,\nabla c_{aq,i}}_{\text{diffusion}} - \underbrace{D_i\,c_{aq,i}\,\frac{Fz}{RT}\,\nabla\emptyset}_{\text{electrical migration}} - \underbrace{D_i\,c_{aq,i}\,\nabla\ln\gamma_i}_{\text{chemical activity}}\right)$$



Validation

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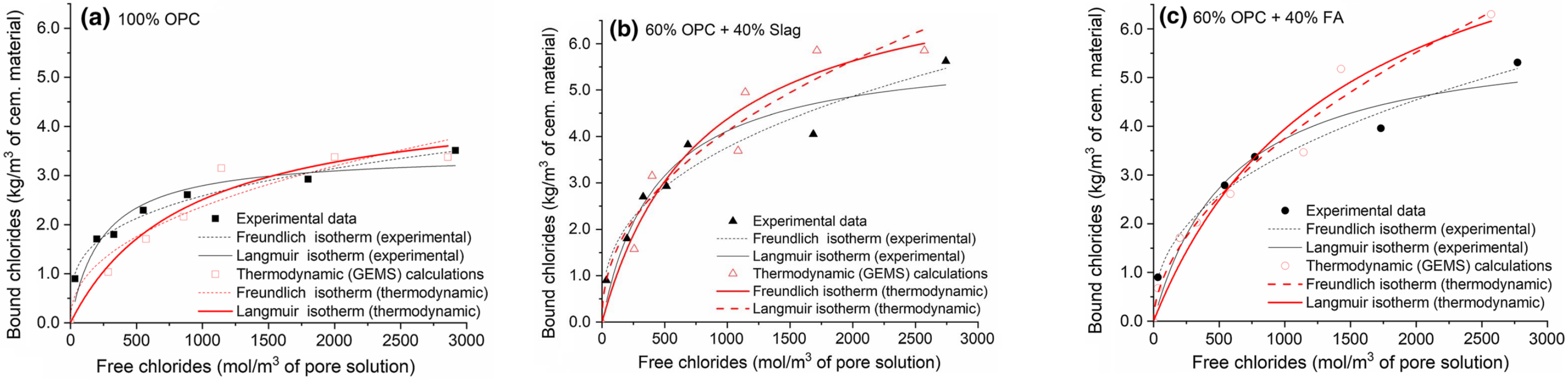
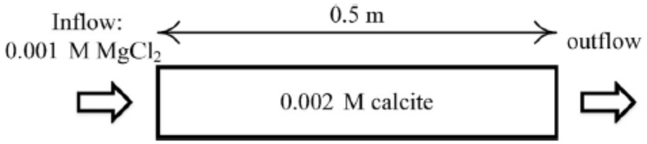
Thermodynamically calculated chloride binding isotherms:

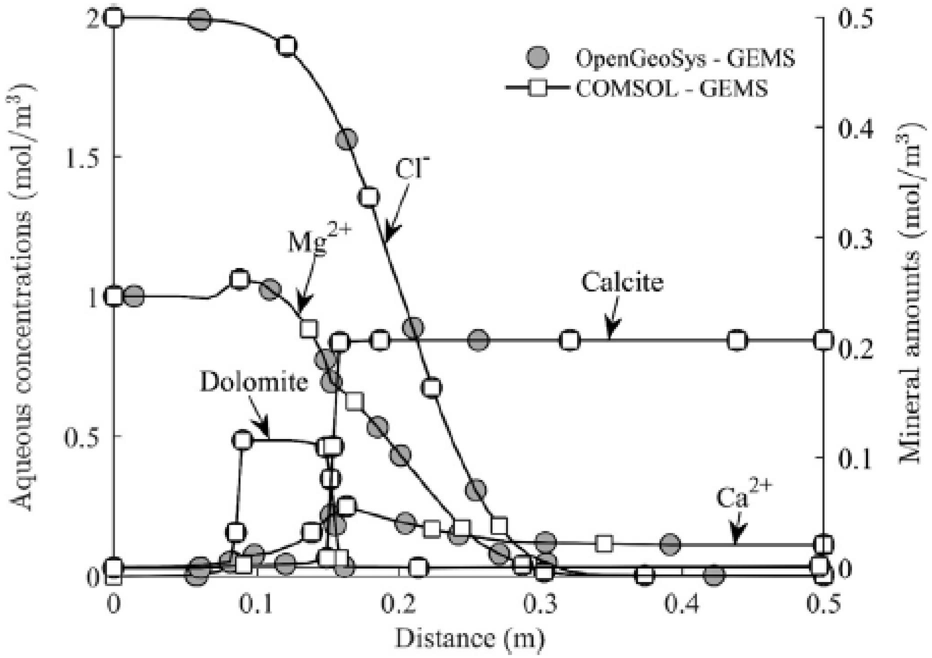


(Isgor and Weiss, Materials and Structures, 2019)

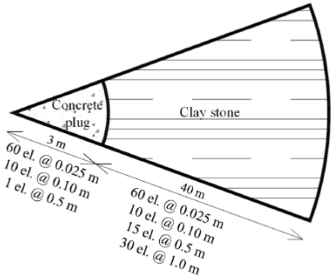
(Azad et al., Computer & Geosciences, 2016)

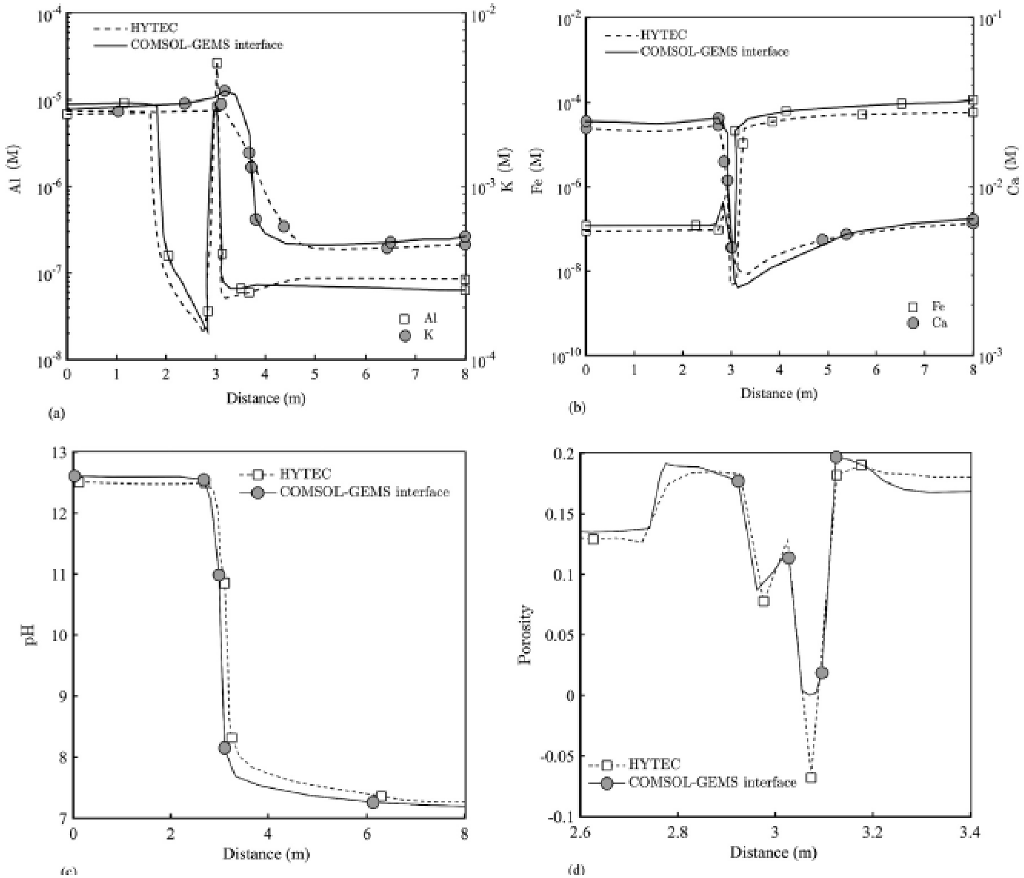
Validation / benchmarking



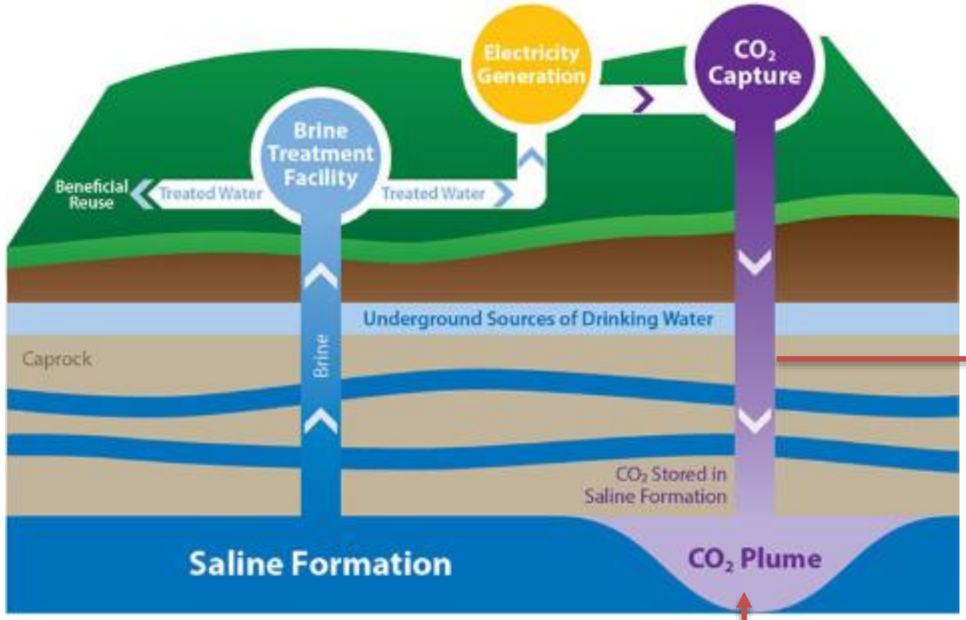


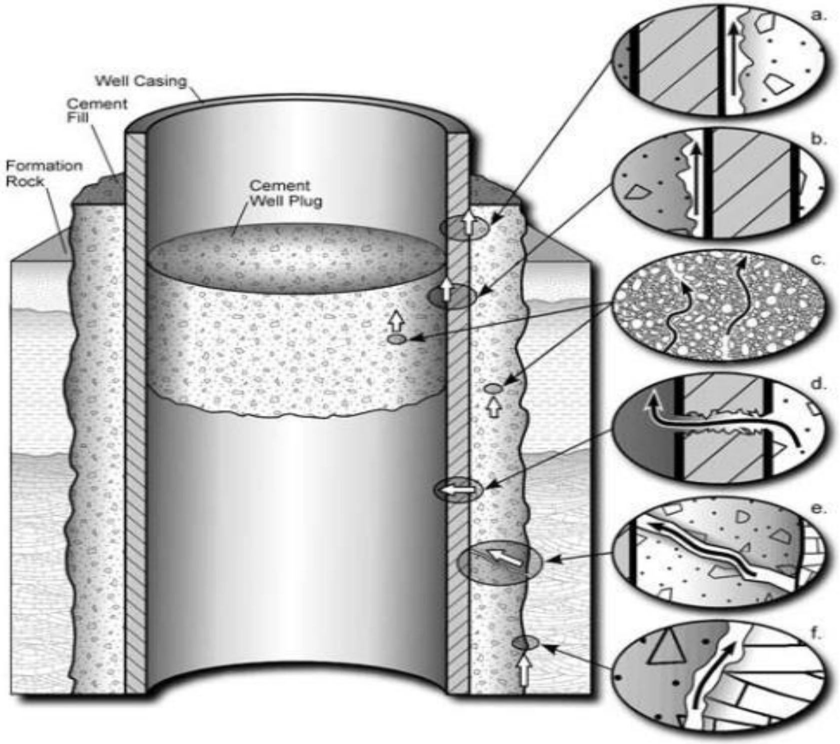
Azad et al., Computer & Geosciences, 2016





An application

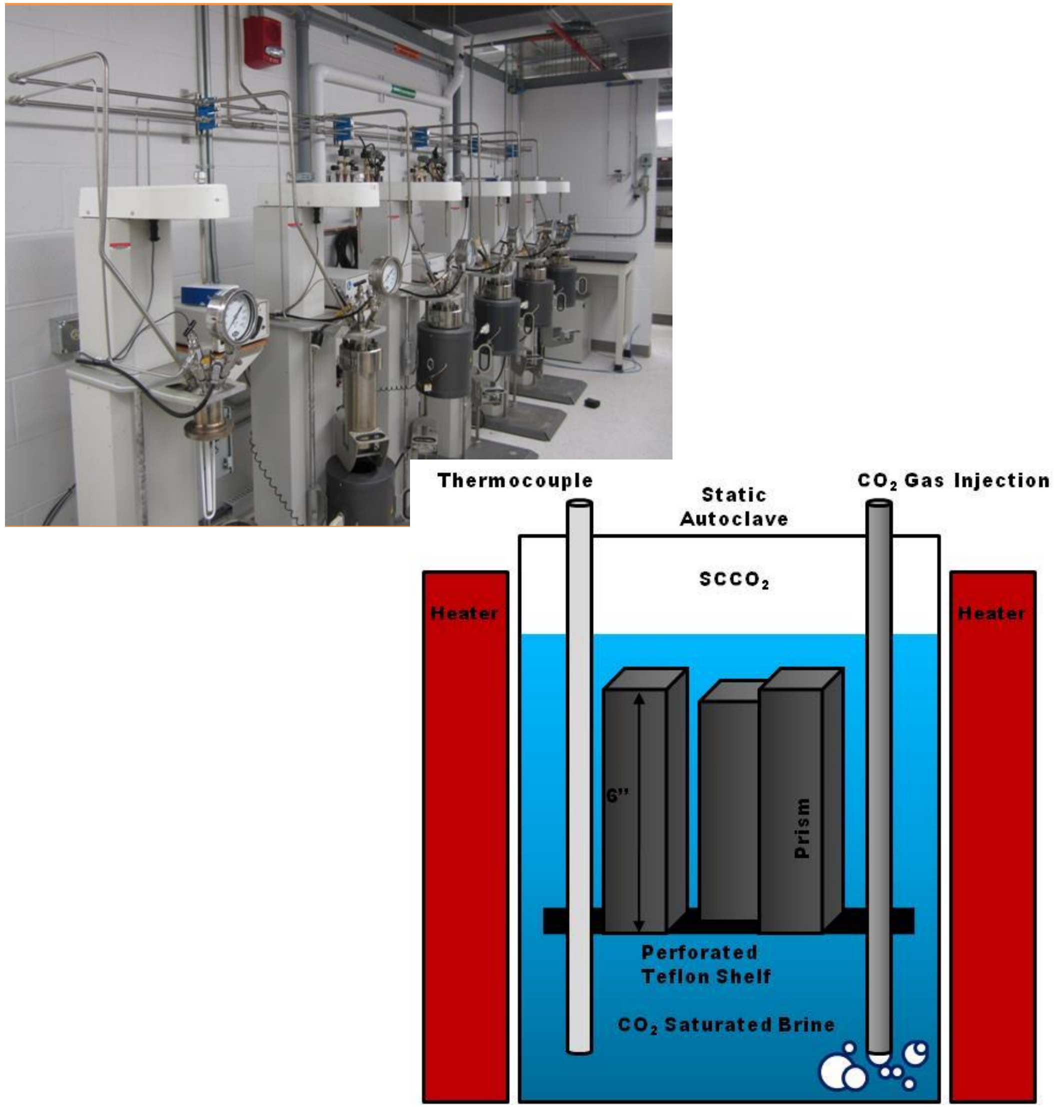


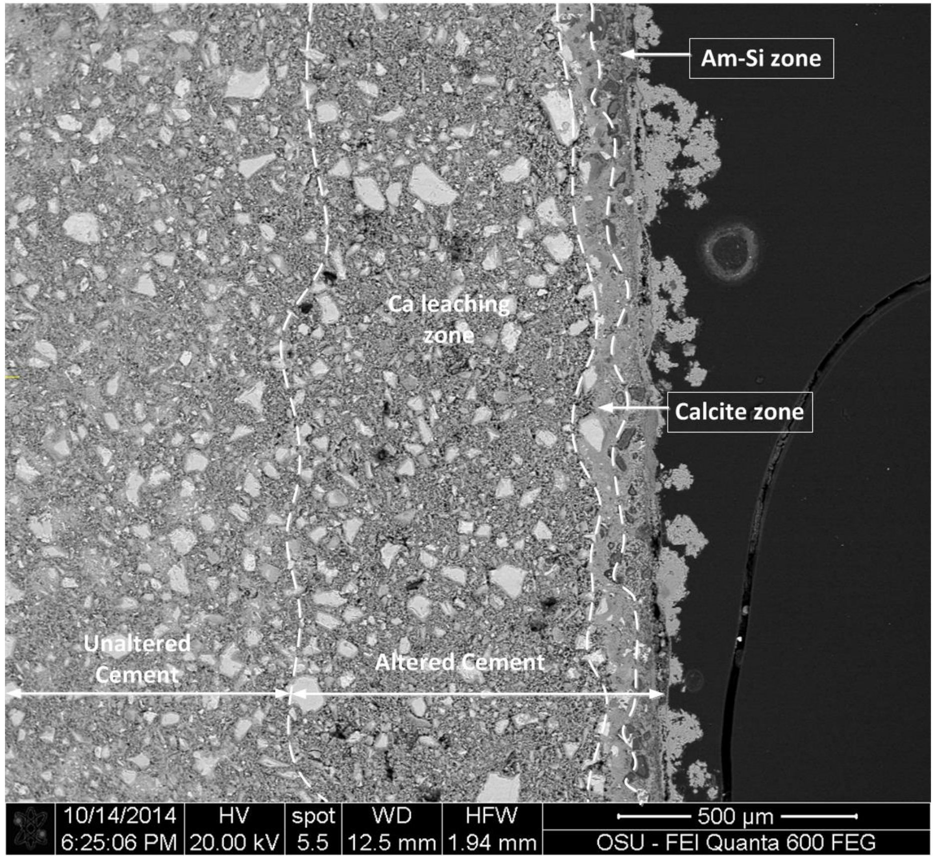


High temperature (85°C), high pressure (14.7 psi), supercritical CO_2, complex brine chemistry

Source: NETL

An application





Ideker,. Isgor, et. al. (2014)

An application

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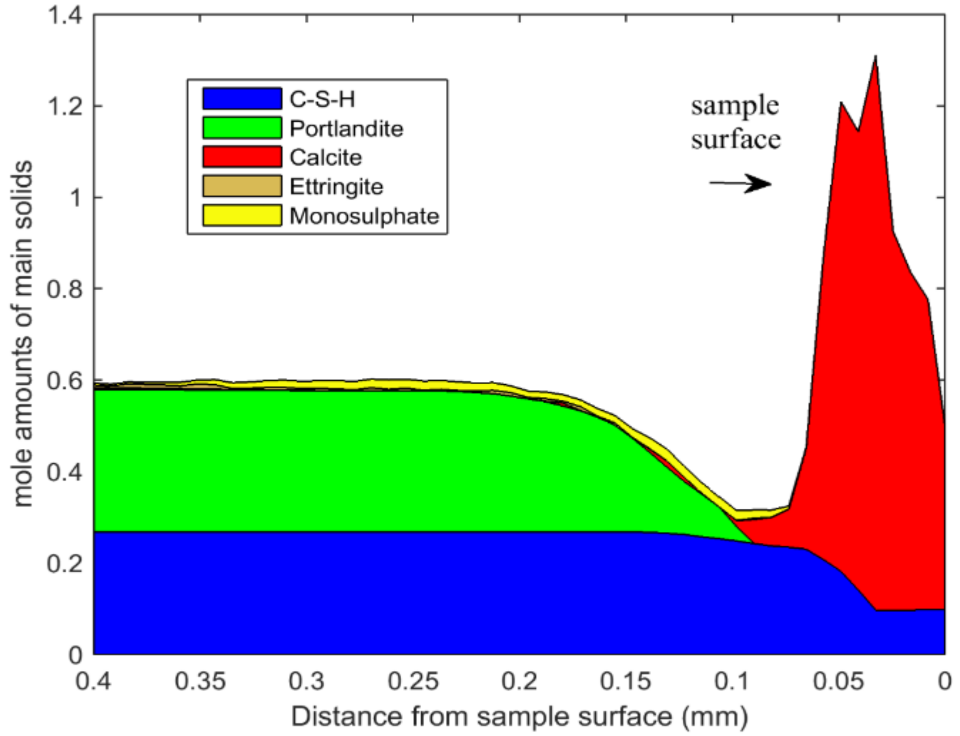
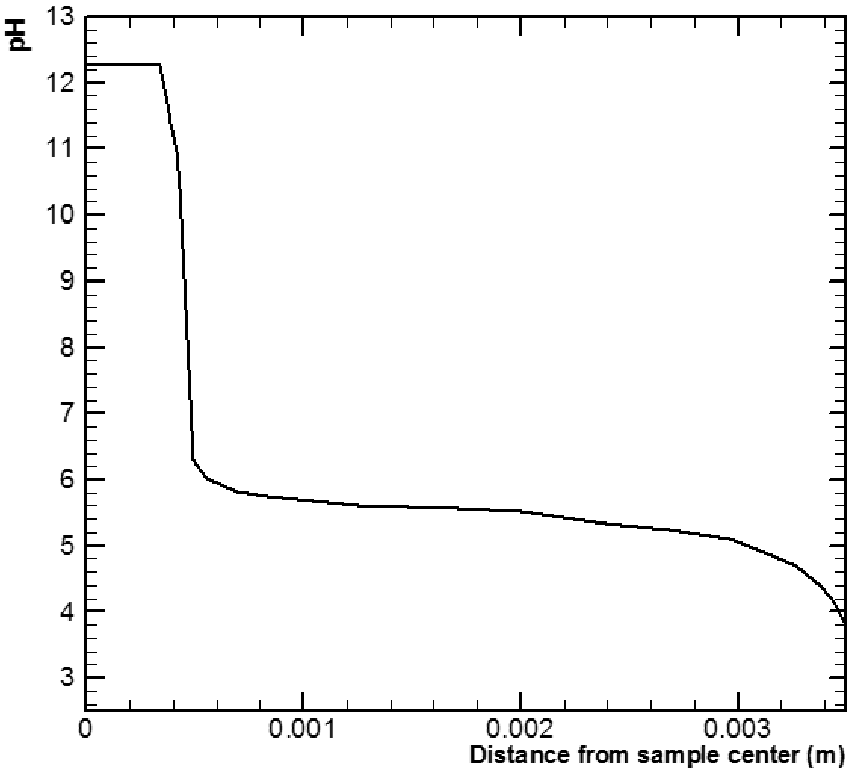
At 42 days



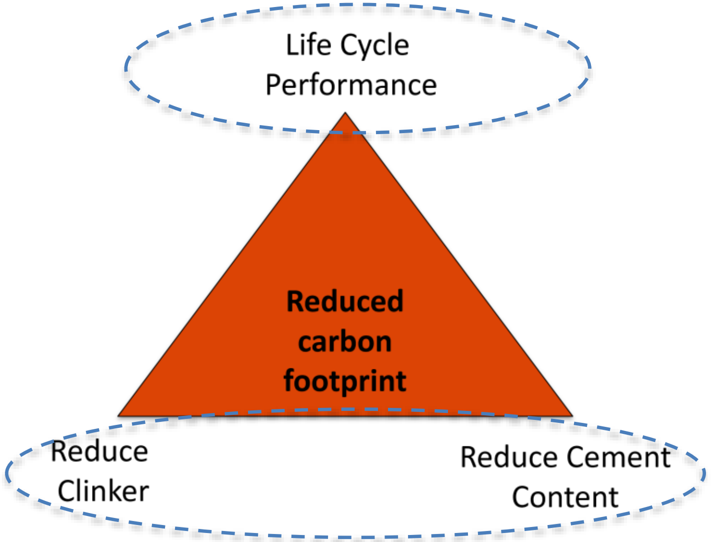


~1000 years to achieve ~1 m of deterioration

Corrosion of the casing and the leakage though cement-plug/steel interface is the main concern

Azad et al., Computer & Geosciences, 2016

Conclusion



Increase the use of low-carbon footprint cementitious materials and powder extenders

- Modeling reactive transport processes in concrete for predicting service life is possible irrespective of
  - Chemical composition of the materials
  - Reactivity of the materials

- We can do this using a coupled approach in which we model reactive processes using thermodynamic / kinetic algorithms and transport processes using finite element analysis.

- This approach eliminates the need to experimentally characterize every concrete mixture for modeling, hence it is dubbed “self-sufficient”.

- This approach allows the modeling of concrete produced with underutilized, novel, low-carbon footprint binders and powder extenders.

Thank you

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