

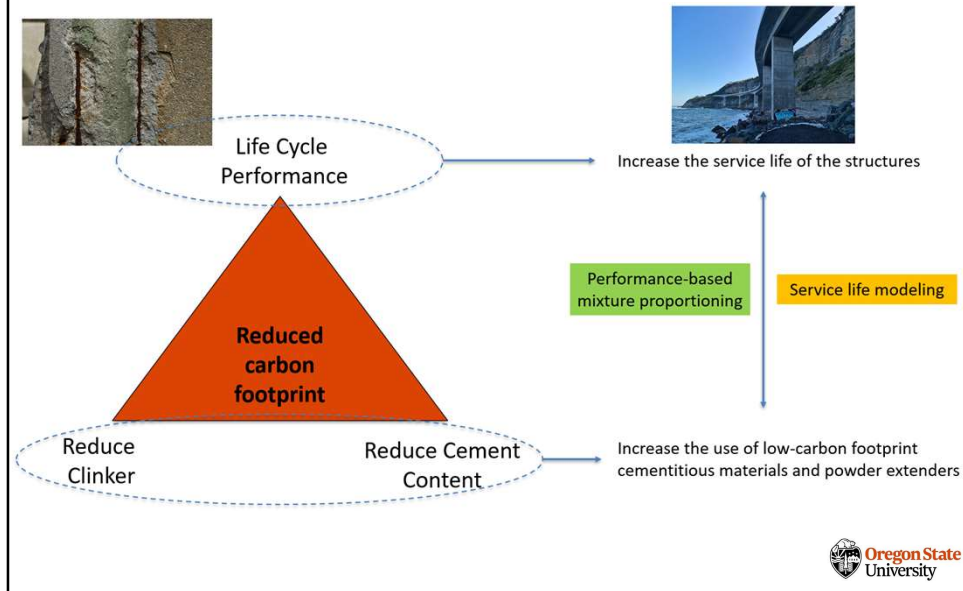
## Lecture 8 Reactive-Transport Modeling



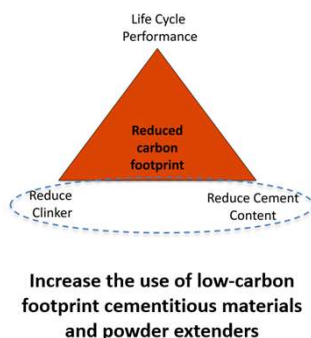
O. Burkan Isgor

Why do we need to model reactive  
transport (RT) processes?

## Why we model RT processes?

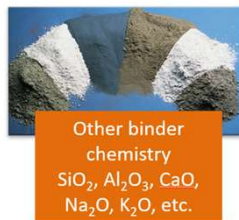


## Why we model RT processes?



- We have been using conventional (in-spec) SCMs, some limestone, etc.
- We have been increasing the use of
  - 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.)
  - powder extenders
    - Larger limestone replacement
    - Synergies with binders (e.g., limestone + Al-containing binders)

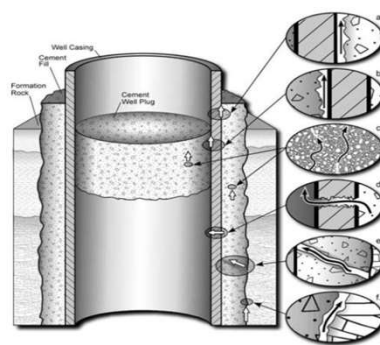
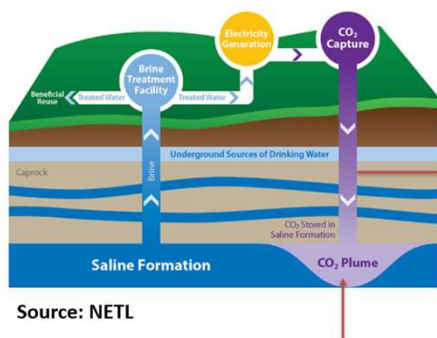
## Why we model RT processes?



- **Do we know how these unconventional binders react?**
  - Maximum reactivity (portion of the reactive components)?
  - Reactions vs. time
- **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, carbonation, etc.)

Photo 44066082 © Luchschen | Dreamstime.com  
Photo 43874974 © Alexander Levchenko | Dreamstime.com

## Why we model RT processes?



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

## Variability of cementitious materials

*A Literature-based Dataset Containing Statistical Compositions and Reactivities  
of Commercial and Novel Supplementary Cementitious Materials*

*Dataset Version 1.0*

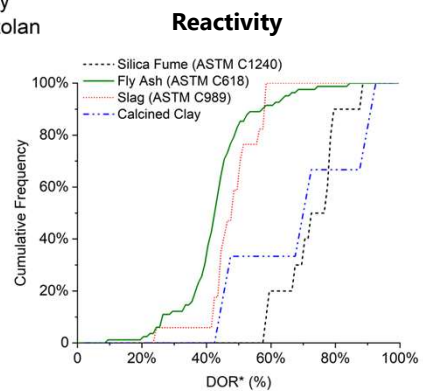
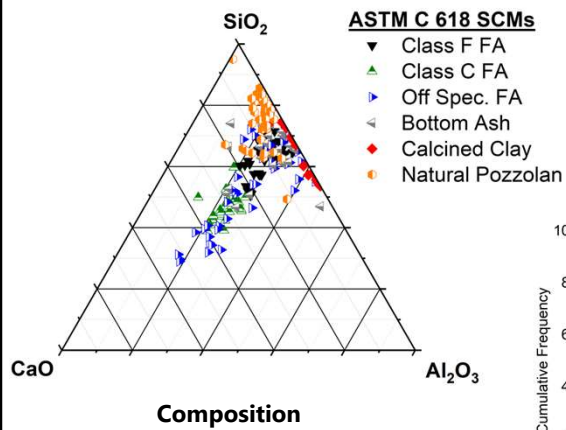
Keshav Bharadwaj, O. Burkan Isgor, W. Jason Weiss

Oregon State University  
School of Civil and Construction Engineering  
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<https://doi.org/10.7267/ft848z051>

May 20, 2022

## Variability of cementitious materials



## Variability of cementitious materials

### Reactive Pozzolanic Oxides (RPO)

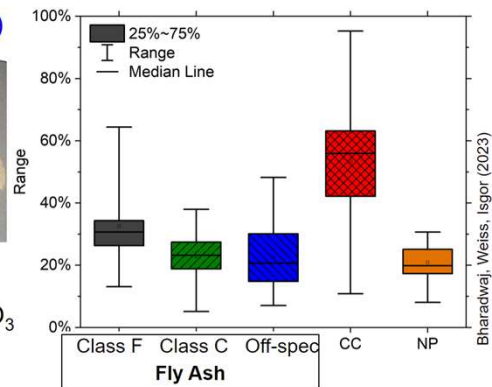
$$\text{RPO} = \text{DOR}^* \times (\text{SiO}_2 + \text{Al}_2\text{O}_3)$$



**Ground Quartz**  
 >95% SiO<sub>2</sub>  
 ~0% DOR\*  
**RPO = 0%**



**Avg. Fly Ash**  
 ~75% SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>  
 ~40% DOR\*  
**RPO = 30%**

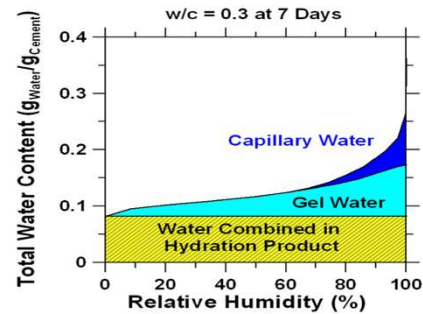
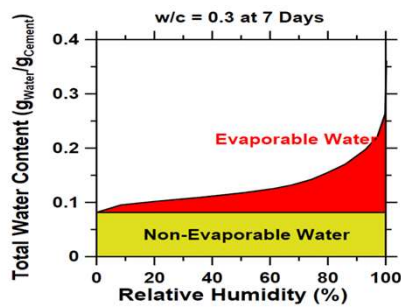


Some background on transport terminology...

## Transport of what?

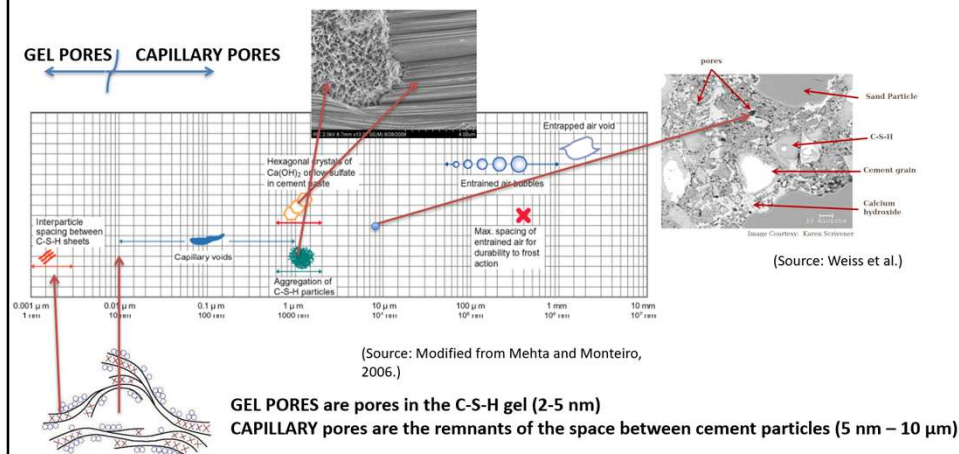
- Heat
- Moisture
- Ions (e.g.  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ , etc.)
- Gasses (e.g.  $\text{O}_2$ ,  $\text{CO}_2$ )

**ALL RELATED TO PORES  
AND WATER IN THE  
PORES!**



(Source: Weiss et al.)

## Water in pores

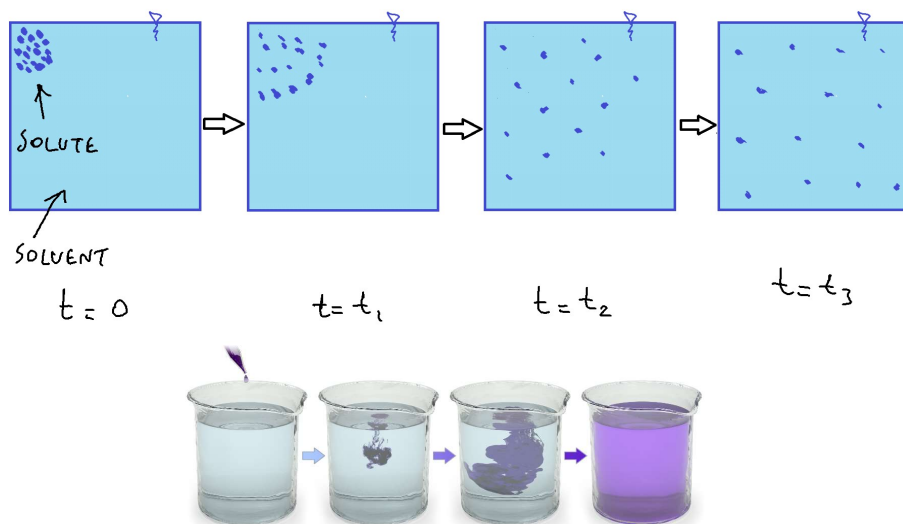


## Why do ions move?

- Diffusion
  - Ions move (in water) due to a concentration gradient
- Movement of ions with moving water
  - Ions move (with water) that is under hydraulic pressure gradient
  - Ions move (with water) due to moisture gradient
- (Electrical) Migration
  - Ions move due to electrical potential gradient
- Movement due to ionic interactions
  - Ions move due to interactions with other ions (activity)

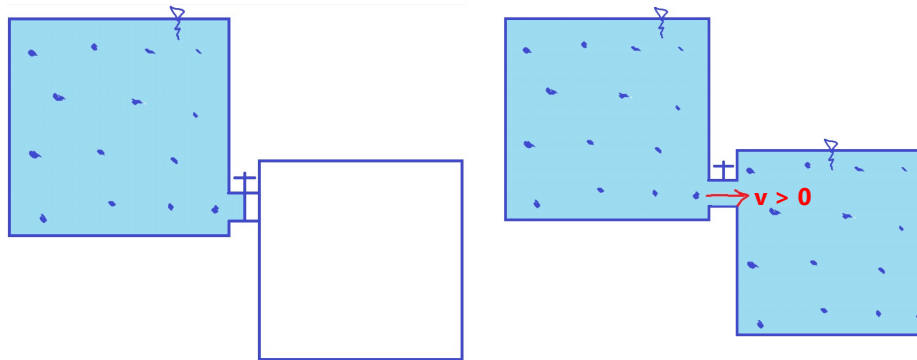
$$\text{Ionic flux} = \text{Diffusion} + \text{Electrical migration} + \text{Chemical activity} + \text{Advection}$$

## Ionic diffusion in water



"Blausen 0315 Diffusion" by BruceBlaus

## Advection – ionic movement with water



$v$  = rate of flow (m/s)

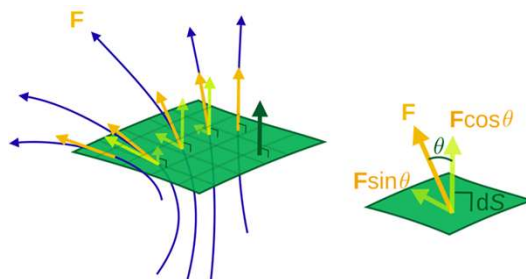
**Question:** Why would water move?

## Advection – ionic movement with water

**FLUX VECTOR ( $\mathbf{N}$ ,  $\mathbf{J}$ ,  $\mathbf{F}$ , etc.):**

Amount of substance (e.g. ion) passing through per unit area per unit time

**Unit:** MASS/AREA-TIME (e.g. mol/m<sup>2</sup>-s, g/cm<sup>2</sup>-s, etc.)





## Diffusion flux

### Fick's First Law

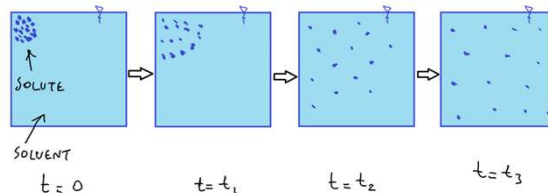
$$N_i = -D_i \frac{\partial c_i}{\partial x} \quad (1D)$$

$$N_i = -D_i \frac{\partial c_i}{\partial x} - D_i \frac{\partial c_i}{\partial y} \quad (2D)$$

$$N_i = -D_i \frac{\partial c_i}{\partial x} - D_i \frac{\partial c_i}{\partial y} - D_i \frac{\partial c_i}{\partial z} \quad (3D)$$

$$N_i = -D_i \nabla c_i \quad (1D, 2D, \text{ or } 3D)$$

$$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

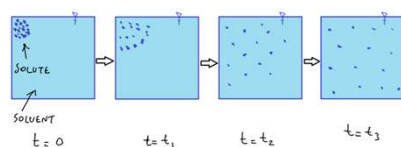


$c_i$  = Concentration of ion  $i$  (e.g. chloride) in solvent (e.g. water)

$D_i$  = Diffusion coefficient of ion  $i$  (e.g. chloride) in solvent (e.g. water)

(also called "the self diffusion coefficient")

## Diffusion flux



### Example: Ions in water at 25°C

Species	Mobility, $u_i$ ( $10^{-8}$ $\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ )	Diffusion coefficient, $D_i$ ( $\text{m}^2/\text{s}$ )
$\text{OH}^-$	20.56	$5.28 \times 10^{-9}$
$\text{Fe}^{3+}$	5.60	$0.72 \times 10^{-9}$
$\text{Ca}^{2+}$	6.17	$0.79 \times 10^{-9}$
$\text{Cl}^-$	7.92	$2.03 \times 10^{-9}$
$\text{Na}^+$	5.19	$1.33 \times 10^{-9}$
$\text{K}^+$	7.62	$1.96 \times 10^{-9}$
$\text{O}_2$	-	$2.20 \times 10^{-9}$

### Einstein's Equation

(Universal gas constant,  $8.3143 \text{ J/mol}\cdot\text{K}$ )

(Temperature, K)

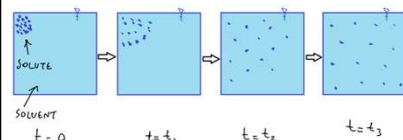
(Mobility of the ion at 25°C)

$$D_i = \frac{RTu_i}{z_i F}$$

(Valence # of the ion)

(Faraday's constant,  $96,488 \text{ C/mol}$ )

## Diffusion flux



Example: Ions in water at 25°C

Species	Mobility, $u_i$ ( $10^{-8}$ $\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ )	Diffusion coefficient, $D_i$ ( $\text{m}^2/\text{s}$ )
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### Einstein's Equation

(Universal gas constant, 8.3143 J/mol-K))

(Temperature, K)

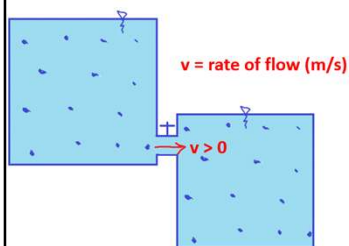
(Mobility of the ion at 25°C)

$$D_i = \frac{RTu_i}{z_iF}$$

(Valance # of the ion)

(Faraday's constant, 96,488 C/mol)

## Advective flux



$$\mathbf{N}_i = v c_i$$

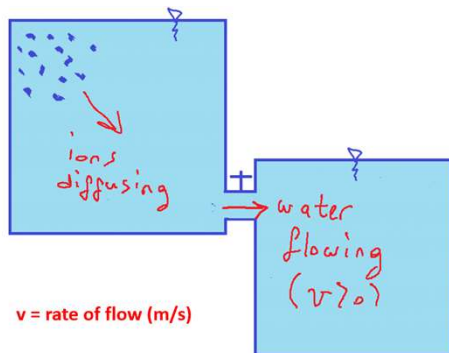
Question: Why would water move?  
(Or why do we have  $v$ ?)

$$v = -\left(\frac{K}{\mu}\right) \nabla h$$

Coef. of permeability      Viscosity      Pressure gradient

- Pressure head (positive pressure)
- Capillary suction (negative pressure)
- Wicking (moisture gradient)

## Advective-diffusion flux



**Advective flux:**  $N_i = v c_i$

**Diffusion flux:**  $N_i = -D_i \nabla c_i$

**Advective-diffusion flux:**  $N_i = v c_i - D_i \nabla c_i$

**Advective-diffusion flux (1D in x direction):**

$$N_i = v_x c_i - D_i \frac{\partial c_i}{\partial x}$$

## Migration flux

Ions move due to electrical potential gradient

$$N_i = -\frac{D_i z_i F}{RT} c_i \nabla \phi$$

$z_i$ : valance electron number for the ion (e.g. for  $\text{Cl}^-$ ,  $z=1$ )

$F$ : Faraday's constant (96,488 C/mol)

$R$ : Universal gas constant (8.3143 J/mol/K)

$T$ : Temperature (K)

$\phi$ : electric potential (V)

**Question:** What are some examples this might apply?

## Activity flux

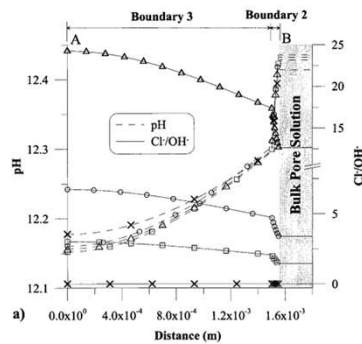
Ions move due to interactions with other ions

$$N_i = -D_i c_i \nabla \ln \gamma_i$$

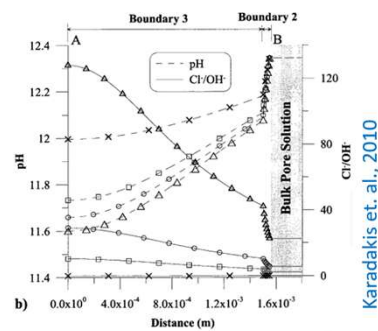
$\gamma_i$ : activity of ion  $i$

Question: How important is it?

With ionic interactions



Without interactions



Karadakis et. al., 2010

## Total flux in water

$$N_i = c_i v - D_i \nabla c_i - \frac{D_i z_i F}{RT} c_i \nabla \phi - D_i c_i \nabla \ln \gamma_i$$

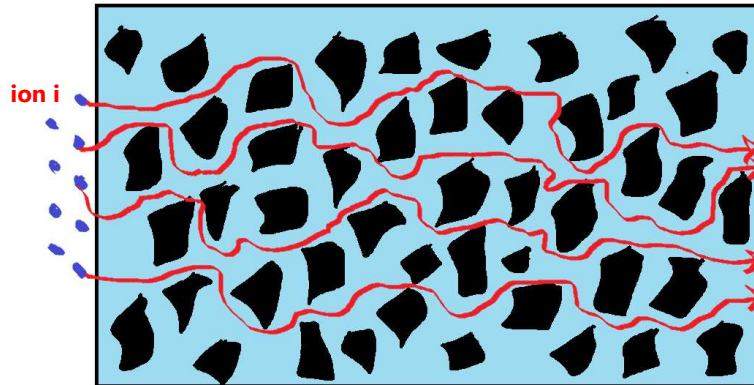
Ionic flux due to water movement

Ionic flux due to water movement

Ionic flux due to electrical potential gradient

Ionic flux due to interactions between ions (chemical activity)

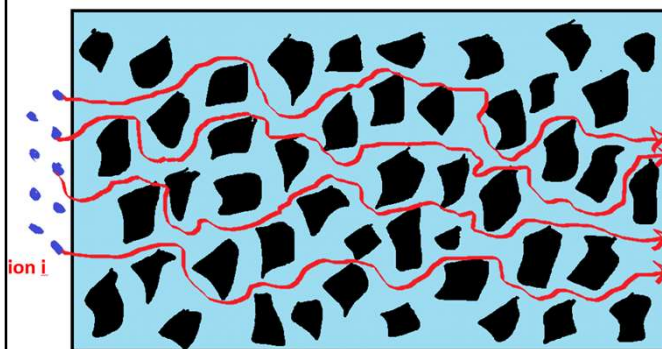
## Total flux in water



**Question:** Can we still use the self diffusion coefficient of the ion  $i$  in water?  
If not,  $D_{i,c} = ?$

$$D_i = \frac{RTu_i}{z_i F}$$

## Total flux in porous cementitious matrix



Formation factor

$$FF = \frac{r_{concrete}}{r_{ps}} = \frac{1}{\phi\beta}$$

$$\frac{D_{i,c}}{D_i} = \frac{r_{ps}}{r_{concrete}}$$

← (Electrical resistivity of pore solution)

← (Electrical resistivity of concrete)

## Total flux in porous cementitious matrix

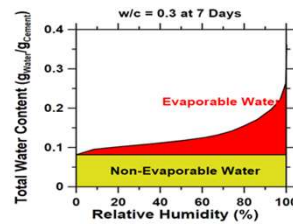
$$\mathbf{N}_i = c_i \mathbf{v} - D_{i,c} \nabla c_i - \frac{D_{i,c} z_i F}{RT} c_i \nabla \varphi - D_{i,c} c_i \nabla \ln \gamma_i$$

$\swarrow$  Ionic flux due to water movement  
 $\downarrow$  Ionic flux due to water movement  
 $\swarrow$  Ionic flux due to electrical potential gradient  
 $\swarrow$  Ionic flux due to interactions between ions (chemical activity)

$$D_{i,c} = \frac{D_i}{FF}$$

## Mass conservation equation

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\mathbf{N}_i) = 0$$



Without chemical reactions:

Evaporable water

$$\phi S_L \frac{\partial c_i}{\partial t} + \phi S_L \nabla \cdot (c_i \mathbf{v} - D_{i,c} \nabla c_i - D_{i,c} c_i \nabla \ln \gamma_i - \frac{D_{i,c} z_i F}{RT} c_i \nabla \varphi) = 0$$

With chemical reactions:

$$\frac{\phi S_L \partial c_i}{\partial t} + \phi S_L \nabla \cdot \left( c_i \mathbf{v} - D_{i,c} \nabla c_i - D_{i,c} c_i \nabla \ln \gamma_i - \frac{D_{i,c} z_i F}{RT} c_i \nabla \varphi \right) + \frac{\partial c_{i,r}}{\partial t} = 0$$

## Multiphysics problem

**Ionic transport:** 
$$\frac{\phi S_L \partial c_i}{\partial t} + \phi S_L \frac{\partial c_{is}}{\partial t} + \nabla \cdot (-D_{i,e} \nabla c_i - D_{i,e} c_i \nabla \ln \gamma_i - \frac{D_{i,e} z_i F}{RT} c_i \nabla \phi + c_i v) = 0$$

- Solve for  $\text{Cl}^-$ ,  $\text{Ca}^{+2}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{-2}$ , etc. concentrations

**Electrical potential:** 
$$\nabla \cdot \left( \frac{1}{\rho} \nabla \phi \right) = 0$$

- Solve for  $\phi$

**Heat transfer:** 
$$\rho_{co} c_q \frac{\partial T}{\partial t} + \nabla \cdot (\lambda \nabla T) = 0$$

- Solve for temperature profiles

**Moisture transfer:** 
$$\frac{\partial w_e}{\partial h} \frac{\partial h}{\partial t} + \nabla \cdot (D_h \nabla h) = 0$$

- Solve for RH and moisture profiles

At every point in domain and at every time step of the analysis

**Boundary Conditions**

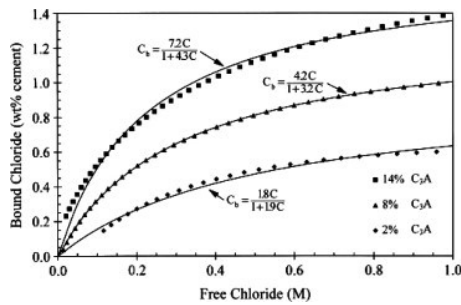
Modeling reactions during transport of species in a cementitious system...

## Method 1: Explicit integration into PDE

Reaction term

$$\frac{\phi S_L \partial c_i}{\partial t} + \phi S_L \nabla \cdot \left( c_i v - D_{i,c} \nabla c_i - D_{i,c} c_i \nabla \ln \gamma_i - \frac{D_{i,c} z_i F}{RT} c_i \nabla \varphi \right) + \frac{\partial c_{i,r}}{\partial t} = 0$$

Example: chloride binding



Yuan et al. 2009

$$c = c_f + c_b$$

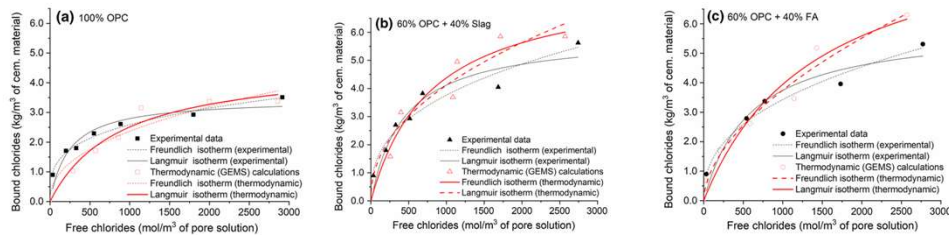
$$c_b = \frac{\alpha c_f}{1 + \beta c_f}$$

Langmuir Isotherm

$$\frac{\partial c_{i,r}}{\partial t} = \frac{\partial c_b}{\partial t}$$

## Method 1: Explicit integration into PDE

Thermodynamically calculated chloride binding isotherms:



(Isgor and Weiss, Materials and Structures, 2019)

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



## Group work: Chloride binding isotherms



**Calculate chloride binding isotherms for hydrated Portland cement paste**



## Method 2: Operator splitting



**Transport PDE does not have an reaction term:**

$$\frac{\phi S_L \partial c_i}{\partial t} + \phi S_L \nabla \cdot (c_i \mathbf{v} - D_{i,c} \nabla c_i - D_{i,c} c_i \nabla \ln \gamma_i - \frac{D_{i,c} z_i F}{RT} c_i \nabla \varphi) = 0$$

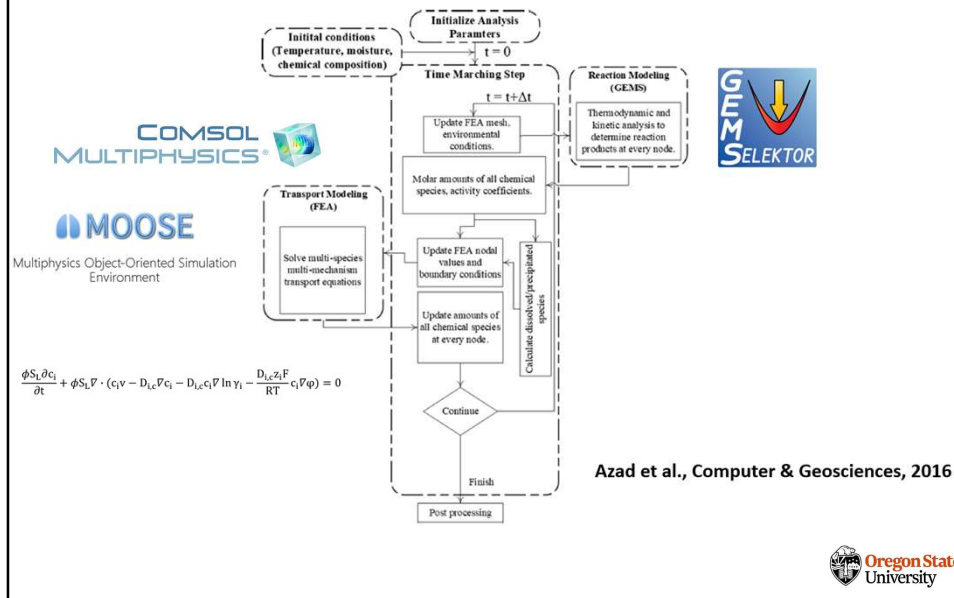
**Reactive processes are solved externally using thermodynamic calculations:**



**Note:** This approach requires small time steps; therefore, it is computationally intensive...



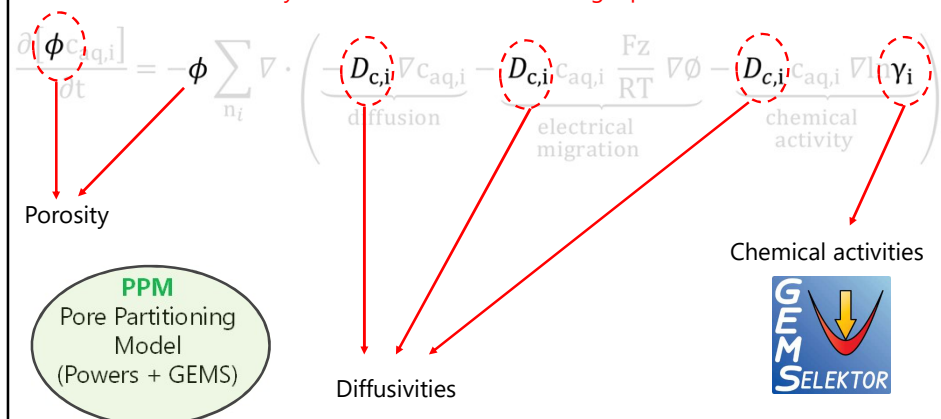
## Method 2: Operator splitting



## Method 2: Operator splitting

### Simplified system

Fully saturated, no advection, single phase flow...



## Pore Partitioning Model (PPM)

## Citations for PPM

**Advances in Civil Engineering  
Materials**



V. Jafari Azad,<sup>1</sup> P. Suraneni,<sup>1,2</sup> O. B. Isgor,<sup>3</sup> and W. J. Weiss<sup>4</sup>

<http://dx.doi.org/10.1520/ACEM20160038>

Interpreting the Pore Structure of Hydrating Cement  
Phases Through a Synergistic Use of the Powers-  
**Brownyard** Model, Hydration Kinetics, and  
Thermodynamic Calculations

ACI MATERIALS JOURNAL TECHNICAL PAPER

Title No. 116-M86

**Extension of Powers-Brownyard Model to Pastes  
Containing Supplementary Cementitious Materials**

by Deborah Glosser, Vahid Jafari Azad, Prannoy Suraneni, O. Burkan Isgor, and W. Jason Weiss

<https://doi.org/10.14359/51714466>



Cement and Concrete Research  
Volume 124, October 2019, 105820

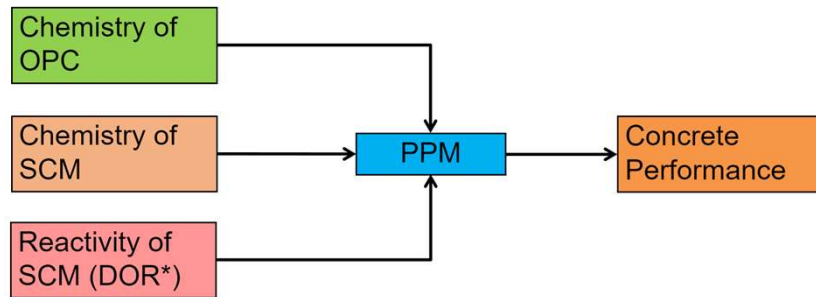


Toward the prediction of pore  
volumes and freeze-thaw  
performance of concrete using  
thermodynamic modelling

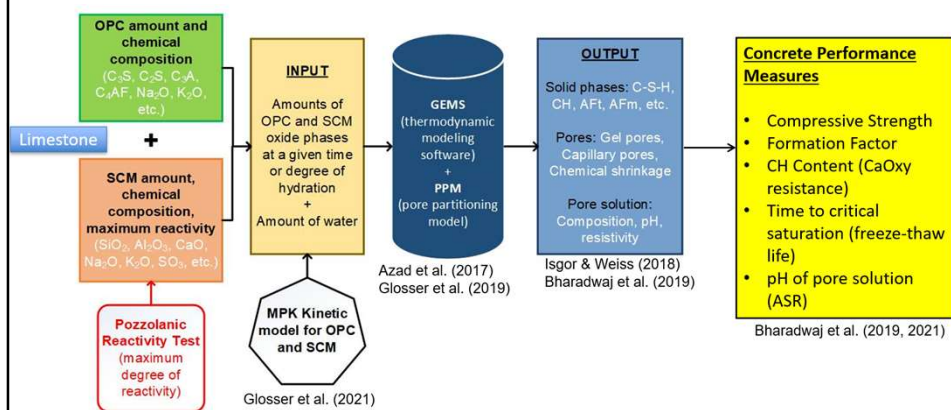
<https://doi.org/10.1016/j.cemconres.2019.105820>

Keshav Bharadwaj, Deborah Glosser, Mehdi Khanzadeh Moradillo,  
O. Burkan Isgor, W. Jason Weiss 

## Pore partitioning model (PPM)



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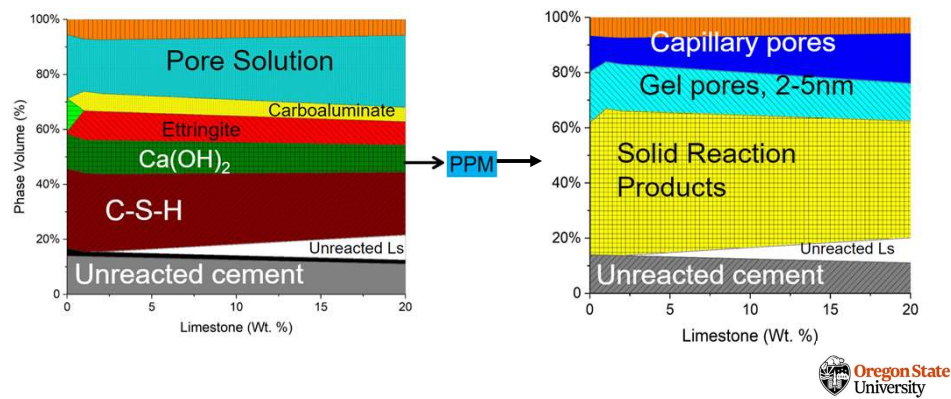


### ACI MATERIALS JOURNAL TECHNICAL PAPER

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## Pore partitioning model (PPM)

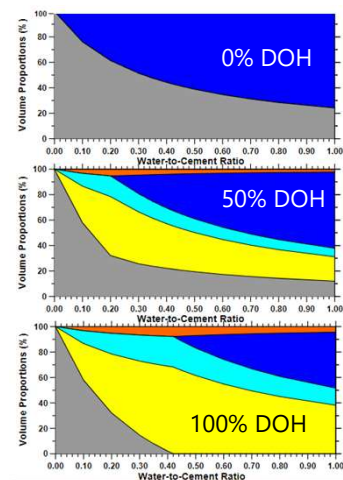


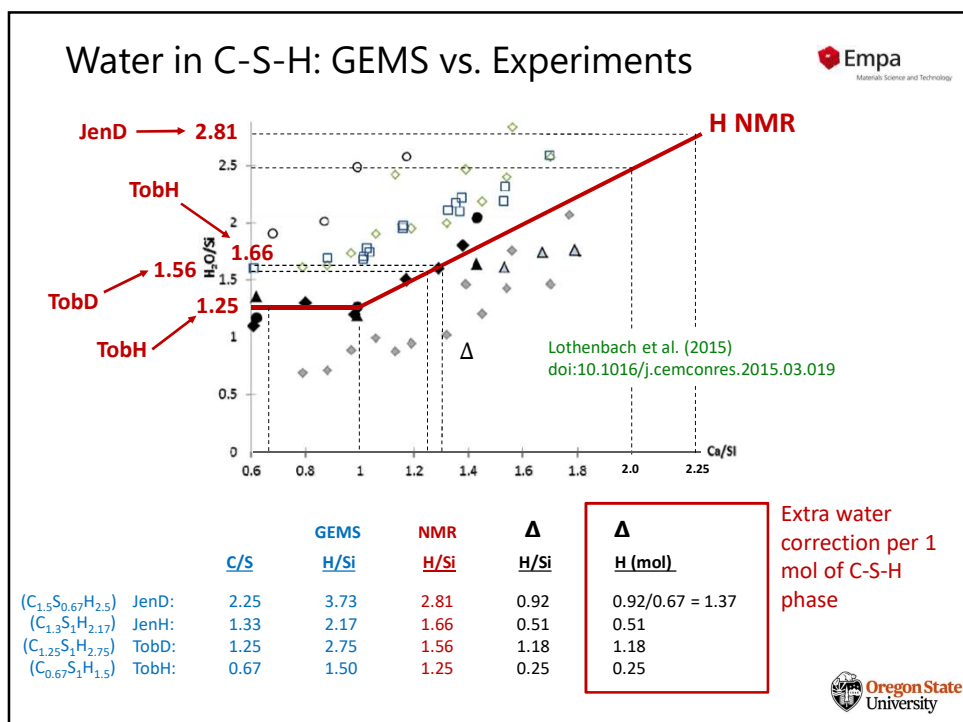
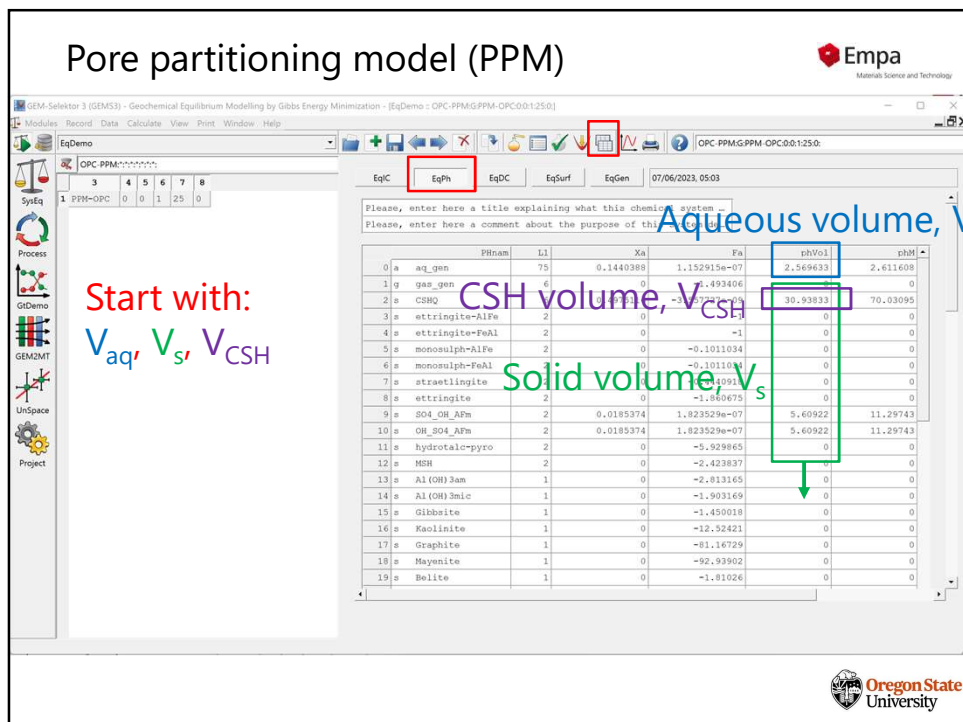
### Powers' Model

$$\begin{aligned}
 V_{c,s} &= 0.2 \cdot (1-p) \cdot \alpha &= \rho_c \cdot 6.4 \cdot 10^{-5} \cdot (1-p) \cdot \alpha \\
 V_{c,w} &= p - 1.3 \cdot (1-p) \cdot \alpha &= p - (\rho_c / \rho_w) \cdot (0.19 + 0.23) \cdot (1-p) \cdot \alpha \\
 V_{g,w} &= 0.6 \cdot (1-p) \cdot \alpha &= (\rho_c / \rho_w) \cdot 0.19 \cdot (1-p) \cdot \alpha \\
 V_{g,s} &= 1.5 \cdot (1-p) \cdot \alpha &= (1 - \rho_c \cdot 6.4 \cdot 10^{-5} + (\rho_c / \rho_w) \cdot 0.23) \cdot (1-p) \cdot \alpha \\
 V_c &= (1-p) \cdot (1-\alpha)
 \end{aligned}$$

$$p = \frac{w/c}{w/c + \rho_w / \rho_c} \quad \rho_w = 1000 \text{ kg/m}^3 \quad \rho_c = 3150 \text{ kg/m}^3$$

Jensen 2005





Corrections for  $V_{aq}$ ,  $V_s$ ,  $V_{CSH}$

Extra water in CSH:

$$\Delta H_2O_{CSH} = \sum n_i \times \Delta H_2O_i$$

Correct volume fractions:

Aqueous:

$$v_{aq} = (V_{aq} + \Delta H_2O_{CSH}) / V_{in}$$

Solid volume:

$$v_s = (V_s - \Delta H_2O_{CSH}) / V_{in}$$

CSH volume:

$$v_{CSH} = (V_{CSH} - \Delta H_2O_{CSH}) / V_{in}$$

Pore partitioning model (PPM)

Gel water:

$$v_{gw} = k_{CSH} v_{CSH} + \sum n_{ph} n_{gwph} \bar{V}_{H_2O}$$

Diagram illustrating the components of the equation:

- $v_{CSH}$ : Volume of C-S-H (from GEMS)
- $k_{CSH}$ : Water associated with C-S-H
- $\sum n_{ph} n_{gwph}$ : Moles of phase (from GEMS) multiplied by Moles of gel water associated with phase
- $\bar{V}_{H_2O}$ : Molar vol. of water

On the left, a vertical stack of volume fractions is shown:  $v_{CS}$ ,  $v_{CW}$ ,  $v_{gw}$  (highlighted in red),  $v_{gs}$ , and  $v_{ub}$ .

Gel water in hydrated paste

Calculated as sum of water associated with C-S-H and gel-water released when certain phases are heated to 105°C

## Pore partitioning model (PPM)

### Determine $k_{CSH}$

Obtain  $k_{CSH}$  from OPC data from Powers & Brownnyard (1946):

1. Run thermodynamic model with PB's OPC composition  
(NOTE: Ls must be under 0.5 wt. %)

2. Calculate  $k_{CSH}$  as follows:

$$k_{CSH} \approx 0.42$$

(You can use this for most cases...)

$$k_{CSH} = \frac{v_{gw,PB} - \sum n_{ph} n_{gwph} \bar{V}_{H_2O}}{v_{CSH}}$$

From thermodynamics and calculations shown previously

$$v_{gw,PB} = 0.60(1 - \phi_0)DOH$$

Degree of hydration

$$\phi_0 = \frac{w/c}{w/c + \rho_w / \rho_{cem}}$$

Ratio of specific gravity of water to cement


## Pore partitioning model (PPM)

Other gel water containing phases

Phase	RH State (at 23°C)	Composition	Water released from 100%RH	Reference
OH-AFM	100%	C <sub>4</sub> AH <sub>13</sub>	-N/A-	[27, 28]
	80%	C <sub>4</sub> AH <sub>13</sub>	6	[28]
	50%	C <sub>4</sub> AH <sub>13</sub>	6	[28]
	Oven Dry	C <sub>4</sub> AH <sub>7</sub>	12	[28]
Monosulfate	100%	C <sub>4</sub> AsH <sub>14</sub>	-N/A-	[28]
	80%	C <sub>4</sub> AsH <sub>12</sub>	2	[28]
	50%	C <sub>4</sub> AsH <sub>12</sub>	2	[28]
	Oven Dry	C <sub>4</sub> AsH <sub>6</sub>	6	[28]
Hemicarbonate	100%	C <sub>4</sub> Ac <sub>0.5</sub> H <sub>12</sub>	-N/A-	[28]
	80%	C <sub>4</sub> Ac <sub>0.5</sub> H <sub>12</sub>	0	[28]
	50%	C <sub>4</sub> Ac <sub>0.5</sub> H <sub>12</sub>	0	[28]
	Oven Dry	C <sub>4</sub> Ac <sub>0.5</sub> H <sub>4.5</sub>	5.5	[28]
Monocarbonate	100%	C <sub>4</sub> AcH <sub>11</sub>	-N/A-	[28]
	80%	C <sub>4</sub> AcH <sub>11</sub>	0	[28]
	50%	C <sub>4</sub> AcH <sub>11</sub>	0	[28]
	Oven Dry	C <sub>4</sub> AcH <sub>5</sub>	3	[28]
Ettringite	100%	C <sub>6</sub> As <sub>3</sub> H <sub>12</sub>	-N/A-	[28]
	80%	C <sub>6</sub> As <sub>3</sub> H <sub>12</sub>	0	[29]
	50%	C <sub>6</sub> As <sub>3</sub> H <sub>12</sub>	0	[29]
	Oven Dry	C <sub>6</sub> As <sub>3</sub> H <sub>12</sub>	20	[28]
CAH <sub>10</sub>	100%	CAH <sub>10</sub>	-N/A-	[28]
	80%	CAH <sub>10</sub>	0	[28]
	50%	CAH <sub>8</sub>	2	[28]

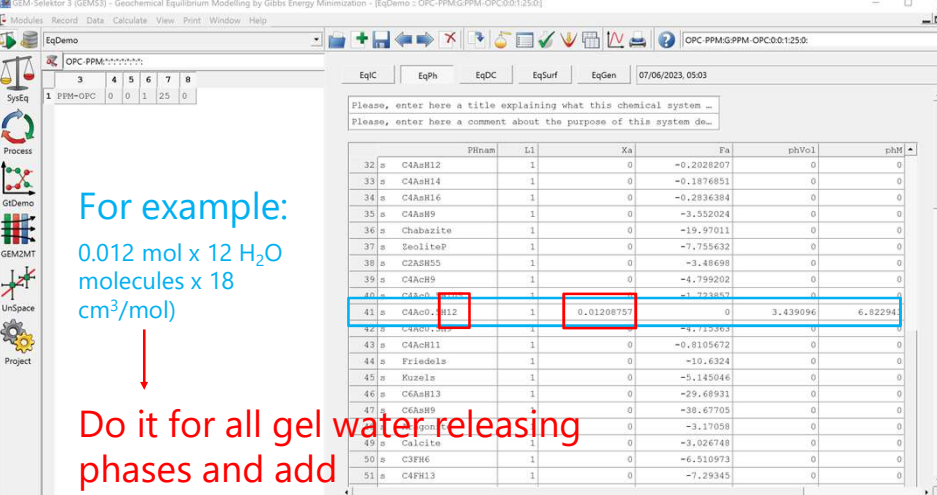



## Pore partitioning model (PPM)




**For example:**  
 0.012 mol x 12 H<sub>2</sub>O  
 molecules x 18  
 cm<sup>3</sup>/mol)

Do it for all gel water-releasing  
phases and add





## Pore partitioning model (PPM)




Capillary water:

$v_{cs}$   
 $v_{cw}$   
 $v_{gw}$   
 $v_{gs}$   
 $v_{ub}$

$$v_{cw} = v_{pore\ soln} - k_{CSH}v_{CSH}$$

Volume of capillary water in hydrated paste

Equals total volume of pore solution from GEMS  
 ( $v_{pore\ soln}$ ) minus the water associated with the C-S-H  
 ( $=k_{CSH}v_{CSH}$ )



## Pore partitioning model (PPM)



### Gel solids:

$v_{cs}$
$v_{cw}$
$v_{gw}$
$v_{gs}$
$v_{ub}$

$$v_{gs} = v_{solids} - \sum n_{ph} n_{gwph} \bar{V}_{H_2O}$$

Volume of gel solids ( $v_{solids}$ ) in hydrated paste

Calculated as the difference between total volume of solid reaction products from GEMS and gel water from water releasing phases.



## Pore partitioning model (PPM)



### Chemical shrinkage:

$v_{cs}$
$v_{cw}$
$v_{gw}$
$v_{gs}$
$v_{ub}$

$$v_{cs} = 1 - v_{gw} - v_{cw} - v_{gs} - v_{ub}$$

Total volume reduction due to chemical reaction



## Group work X: Pore partitioning model

Paste porosity:

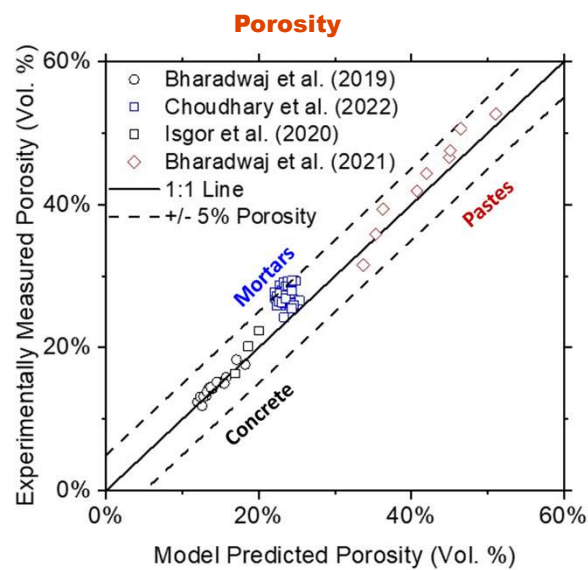
$$p = v_{gw} + v_{cw} + v_{cs}$$

Non-evaporable water:

$$v_{w,NE} = (V_{w,in} / V_{in}) - v_{gw} - v_{cw}$$

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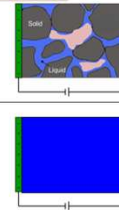
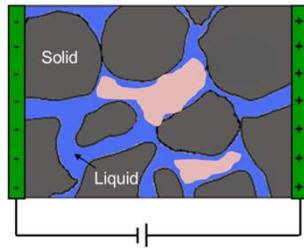
## Pore partitioning model (PPM)



## Pore partitioning model (PPM)

### Formation Factor

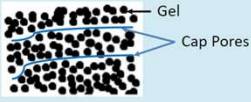
- Related to porosity ( $\phi$ )
- Related to pore connectivity ( $\beta$ )



$$F = \frac{1}{\phi \cdot \beta} = \frac{\rho_{bulk}}{\rho_0}$$

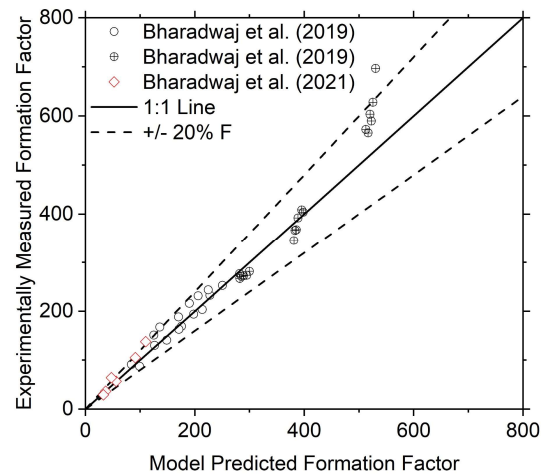
## Pore partitioning model (PPM)

### Formation Factor

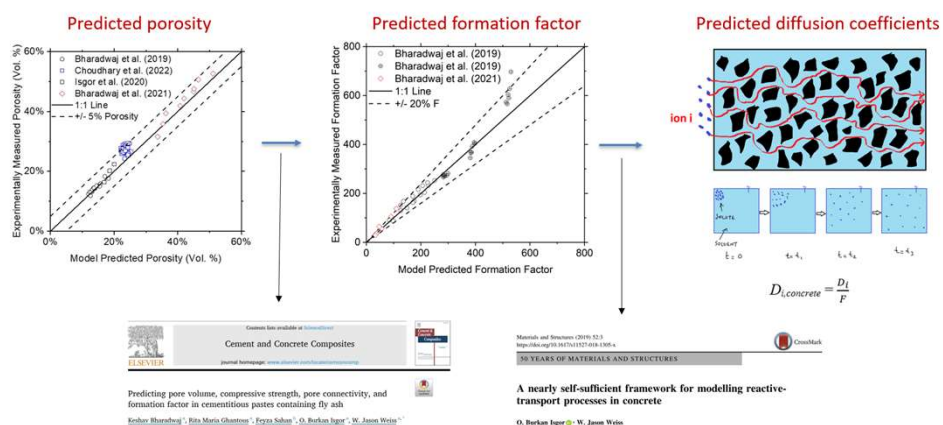
Gel	Paste
<p>From Garboczi &amp; Bentz (1992),</p> $F_{gel} = 400$ $\beta_{gel} = \frac{1}{\phi_{gel} F_{gel}}$ 	<p>From Koponen et. al. (1997),</p> $\beta_{cap} = \frac{1}{\left(1 + b_1 \frac{1 - \phi_{paste}}{(\phi_{paste} - \phi_{thres})^{b_2}}\right)^2}$ $\beta_{paste} = \beta_{gel} + \beta_{cap}$ $F_{paste} = \frac{\rho_{paste}}{\rho_{ps}} = \frac{1}{\phi_{paste} \cdot \beta_{paste}}$

## Pore partitioning model (PPM)

### Formation Factor



## Pore partitioning model (PPM)



## Group work: Pore partitioning model



### Calculate paste properties from GEMS solution

#### Task:

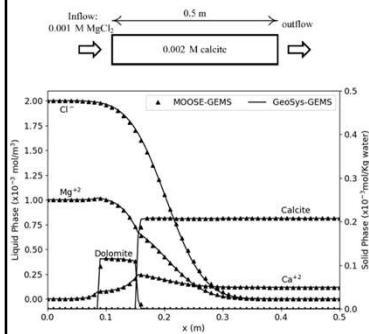
1. Use the PPM\_OPC file from lecture 8
2. Make a new single file:
  - Hydrated cement paste at 100% DoH
    - 100 g PC (assume full reaction)
    - 50 g water (mixing water)
3. Calculate the equilibrium
4. Follow the PPM steps described in the lecture to calculate the volume fractions of gel water, capillary water, gel solids, chemical shrinkage; porosity; non-evaporable water content; paste resistivity; formation factor (assuming pore solution resistivity); and ionic diffusion coefficients for  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{+2}$ ,  $\text{OH}^-$ , etc.



Some RT modeling exercises...



## Validation / benchmarking

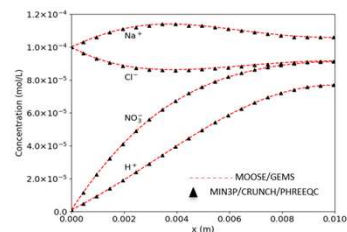


WATER RESOURCES RESEARCH, VOL. 26, NO. 10, PAGES 202-240, OCTOBER 1992

A Geochemical Transport Model for Redox-Controlled Movement of Mineral Fronts in Groundwater Flow Systems: A Case of Nitrate Removal by Oxidation of Pyrite

PETER ENGEHARD

### Tracer isotope diffusion



Computer Geosciences 19:525-533

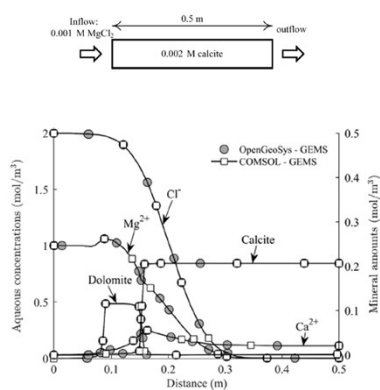
DOI 10.1007/s10596-015-9483-z

ORIGINAL PAPER

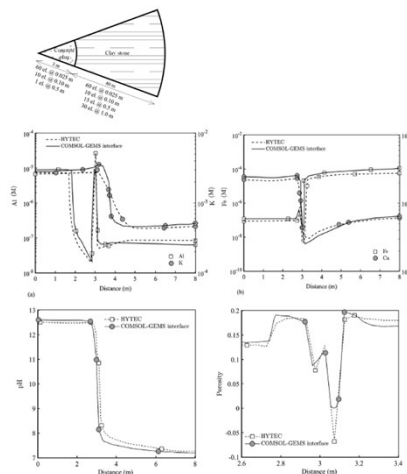
Benchmarks for multicomponent diffusion and electrochemical migration

Pijmen Ranzani<sup>1</sup> · Carl L. Steefel<sup>1</sup> · K. Ulrich Mayer<sup>2</sup> · Massimo Rolle<sup>3</sup>

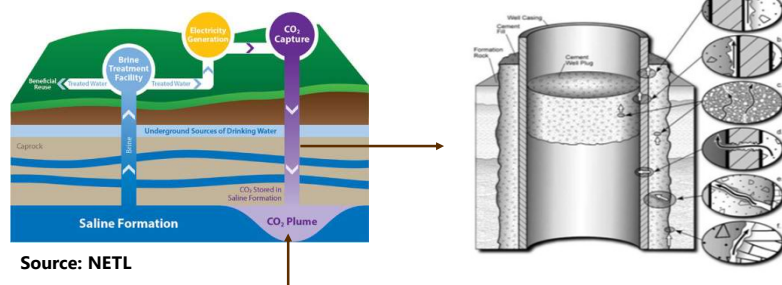
## Validation / benchmarking



Azad et al., Computer & Geosciences, 2016



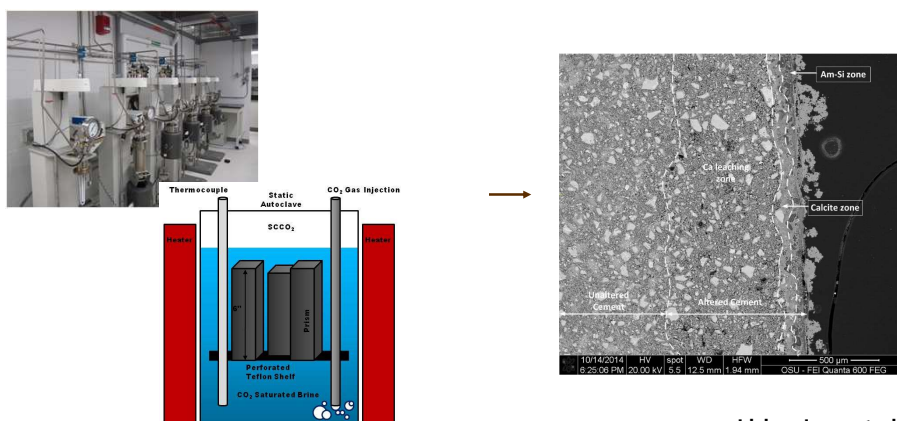
## CO<sub>2</sub> storage in old oil reservoirs



Source: NETL

High temperature (85°C), high pressure (14.7 psi),  
supercritical CO<sub>2</sub>, complex brine chemistry

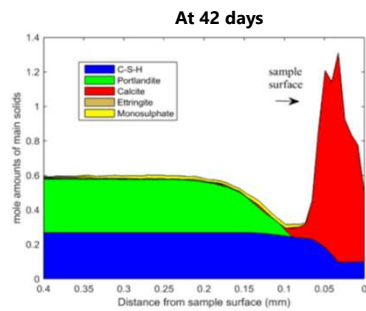
## CO<sub>2</sub> storage in old oil reservoirs



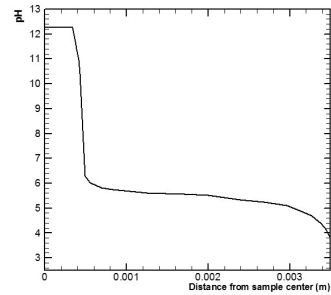
Ideker, Isgor, et. al. (201)



## CO<sub>2</sub> storage in old oil reservoirs



~1000 years to achieve ~1 m of deterioration



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

**Azad et al., Computer & Geosciences, 2016**



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Post-doctoral researcher  
(currently Researcher at PNNL)



Prof. Jason Weiss

Dr. Keshav Bharadwaj  
Ph.D. student, Post-doctoral researcher  
(incoming professor at IIT, Delhi)



Thank you...



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