Fluid Flow, Solute Mixing and Precipitation In Porous Media

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Theme:

Reactant Mixing

Precipitation

Modification of Permeability or Flow Paths

Prediction and Control of Subsurface Processes

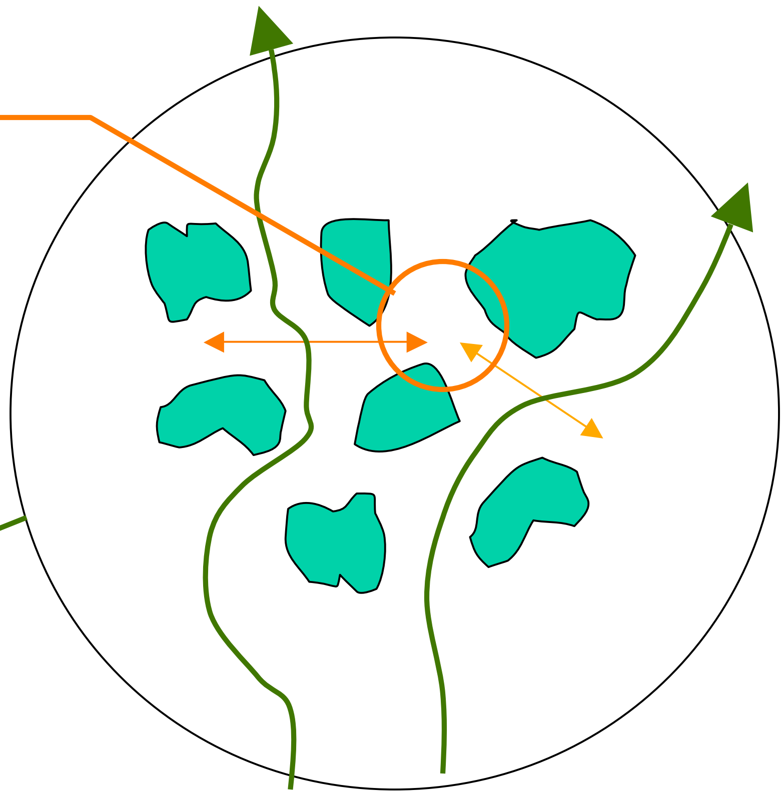
Mixing: Dispersion vs. Diffusion

- **Diffusion**
  - **Molecular-scale mixing → precipitation**

  Flux = -$D_{diff}(\nabla C)$

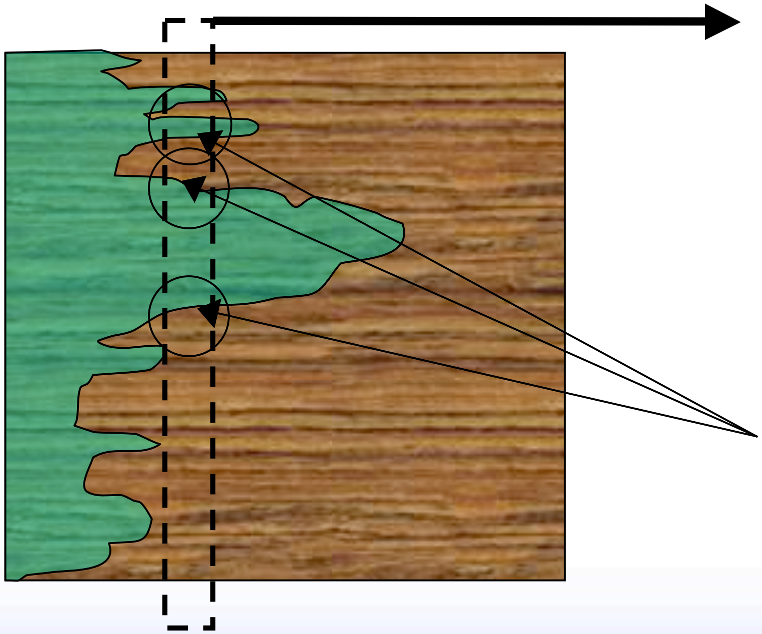
- **Dispersion**
  - **Macroscopic volume-averaged concentration**

  Flux = $\Theta D_{disp}(\nabla C)$



Issues and challenges:

- **Evolution of the spatial distribution of properties and processes**
- **Volume averaging of properties and processes in systems characterized by mixing zones (at all scales). For example:**

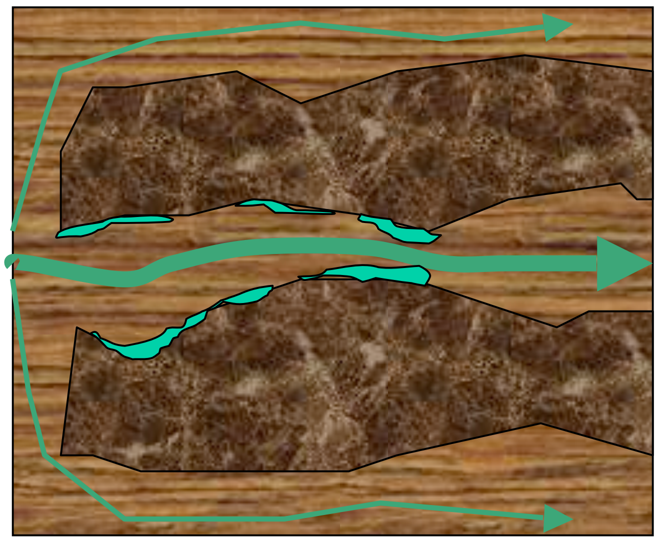


How should volume-averaged concentration be used to predict reaction rates?

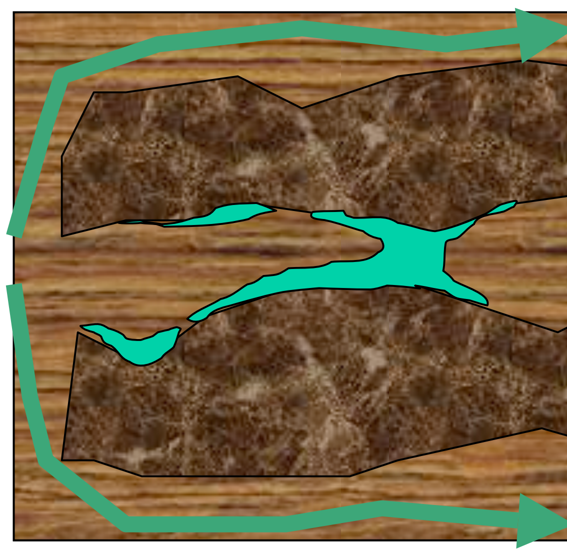
Averaged concentrations may exist only in mixing zones, which can be small and transient.

Issues and challenges:

- **Hysteresis**



Precipitation path
(advection > diffusion)



Dissolution path
(diffusion > advection)

Precipitation

- **Mineral precipitation**
- **Biomass growth**
- **Biofilm formation**
- **Colloid filtration**

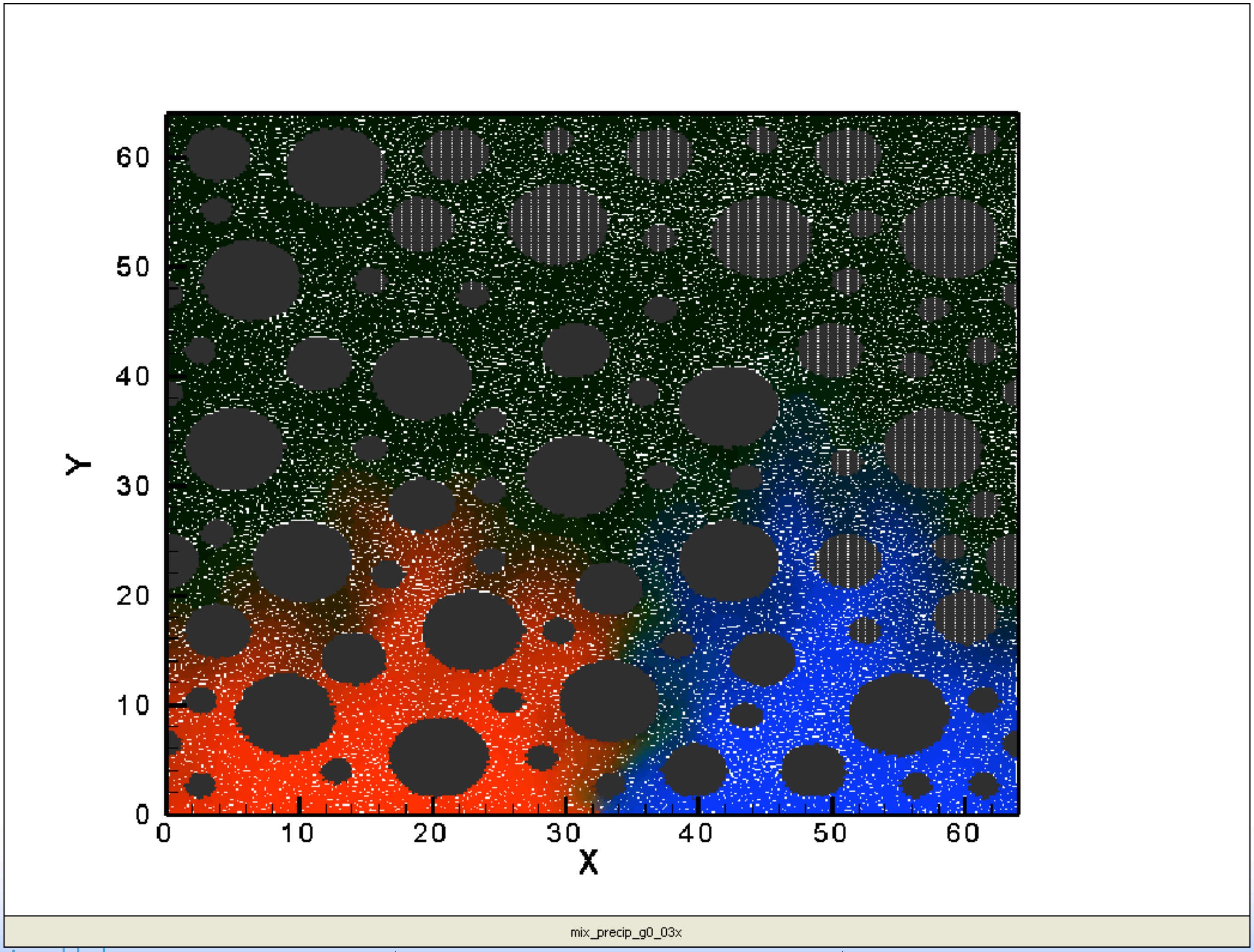
Impact:

- **Fate and transport, sequestration**
- **Field-scale kinetics vs. laboratory kinetics**
- **Understanding the evolution of subsurface properties (MNA)**
- **Developing amendment introduction strategies**
- **Understanding “Rapid” engineered events**

Flagship experiment:

- **Hypotheses**
  - **Precipitation can be induced in the mixing zone between solutions containing reactive substrate (intuitively obvious, but interested in possible deviation of flow paths)**
  - **Permeability of a mixing zone where mineral precipitation occurs does not go to zero. (If it did, both sides of the mixing zone would be undersaturated)**

Premodeling using Smoothed Particle Hydrodynamics: Parallel flow with mixing and precipitation



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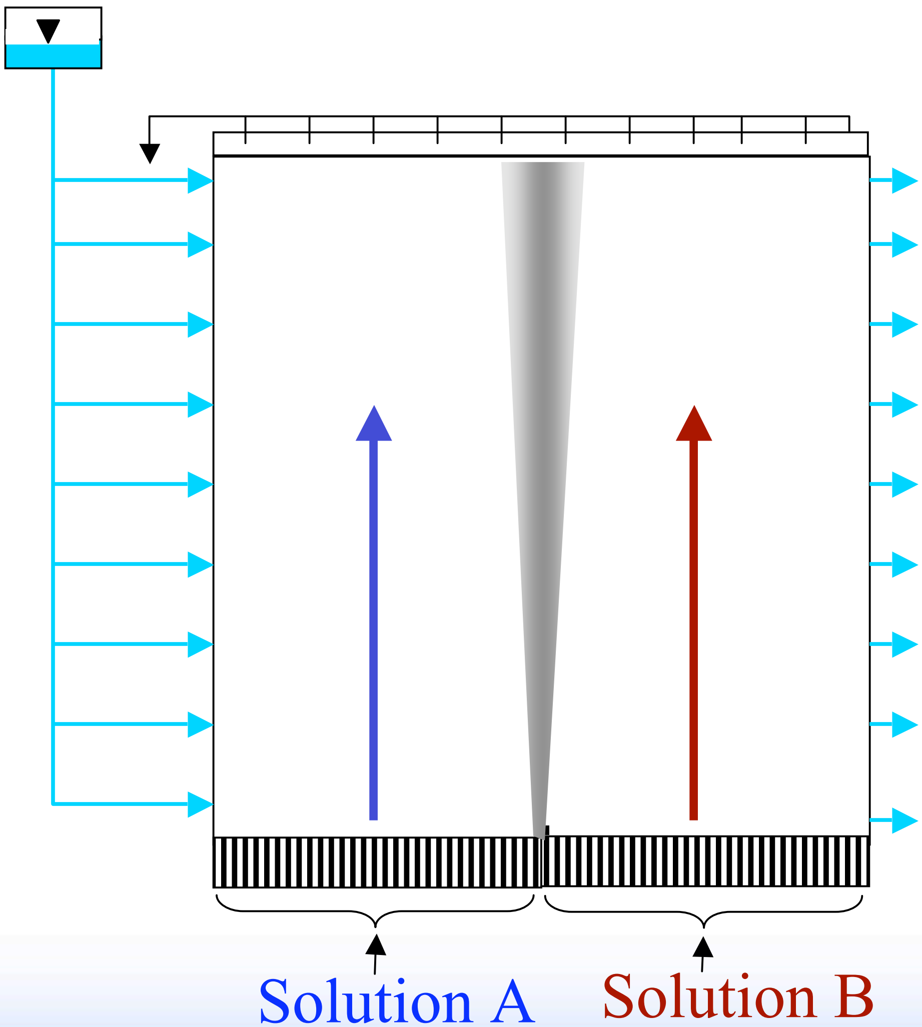
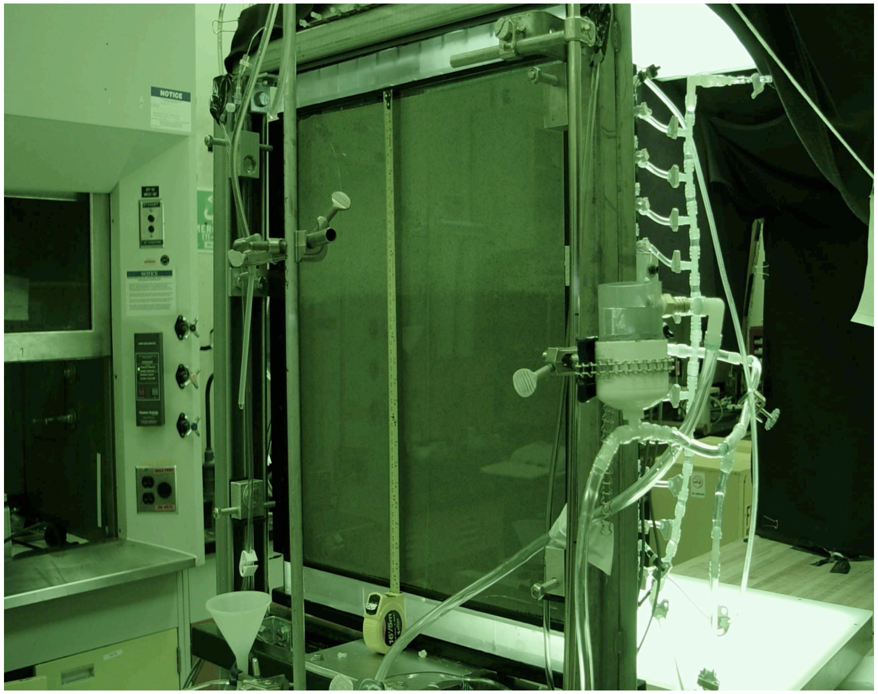
Experimental approach: Parallel flow, mixing and precipitation at a solution-solution interface, “2-D”





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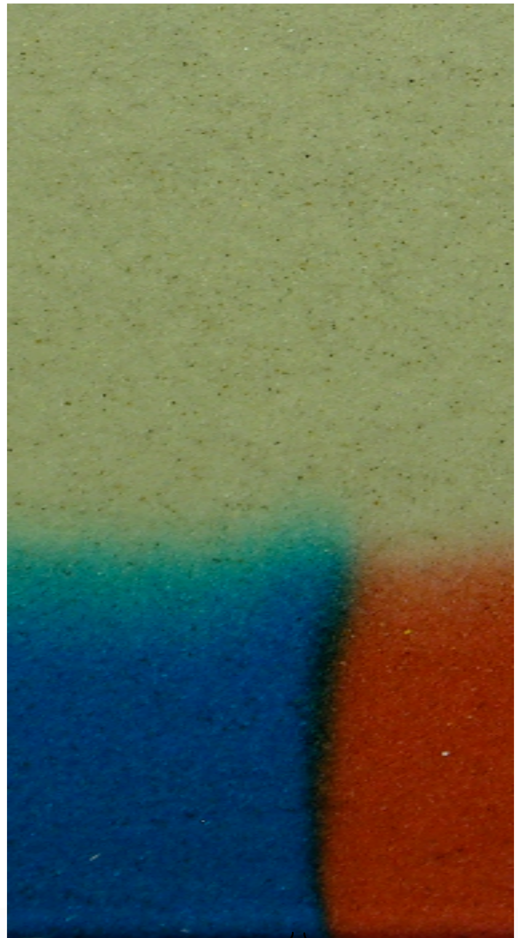
Tracer test showing fluid-fluid interface and mixing

Blue dye　　Red dye

Tracer test showing fluid-fluid interface and mixing

Blue dye Red dye

Tracer test showing fluid-fluid interface and mixing



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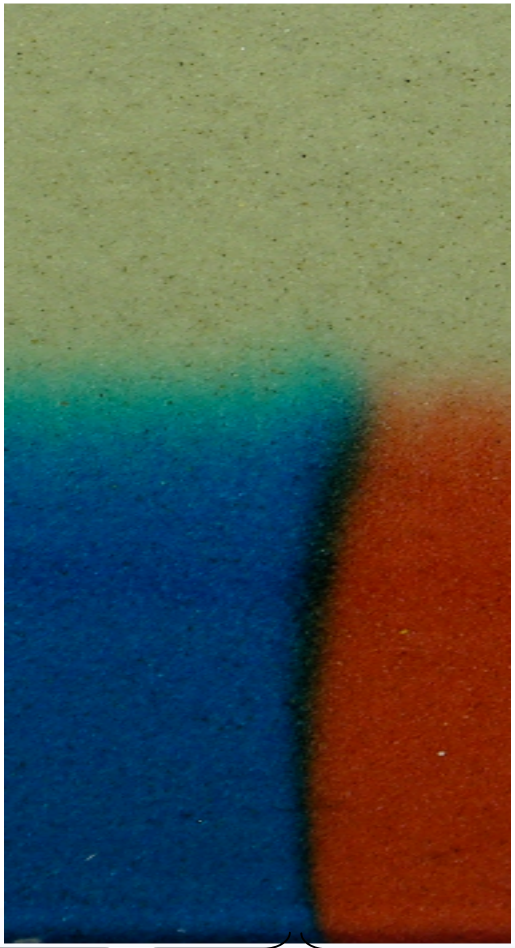

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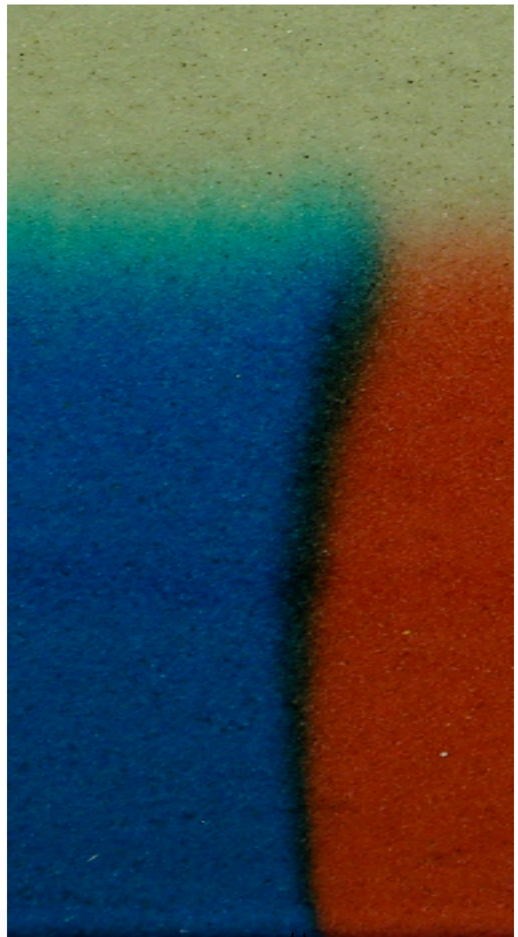

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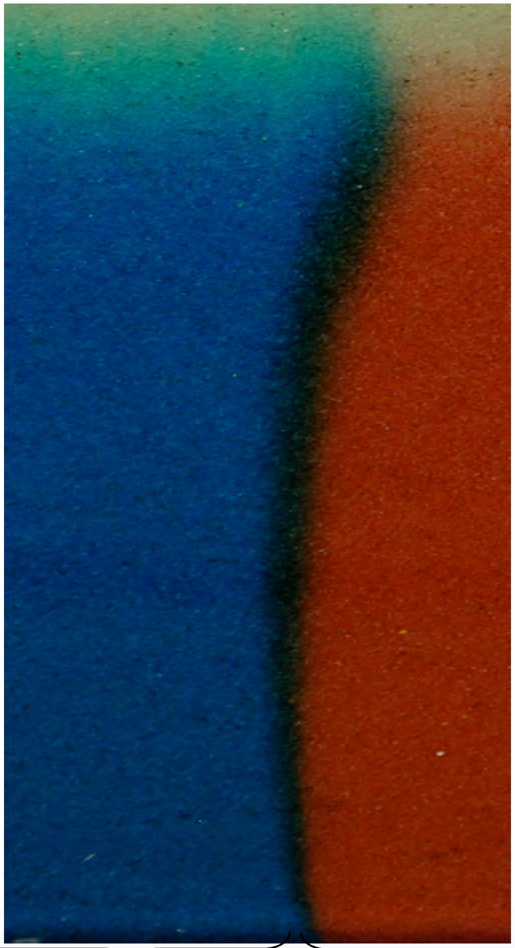

Blue dye Red dye

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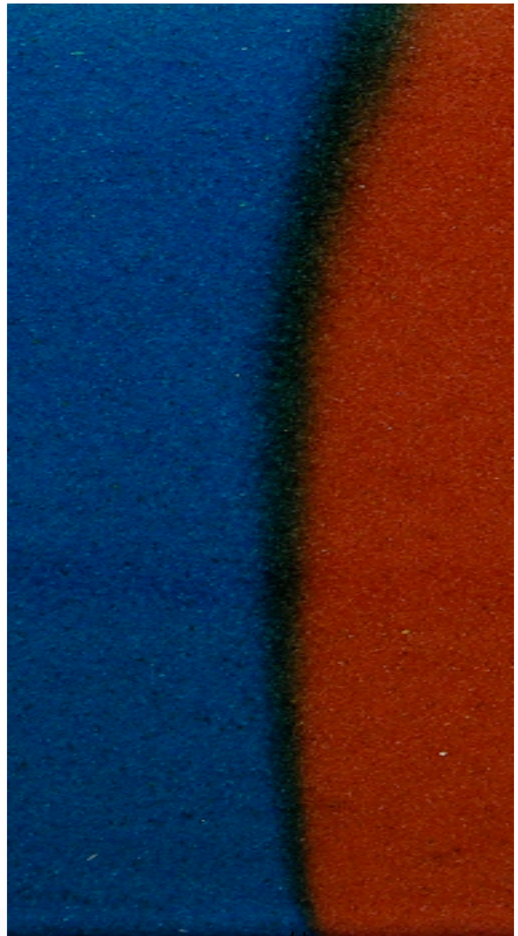

Blue dye Blue dye

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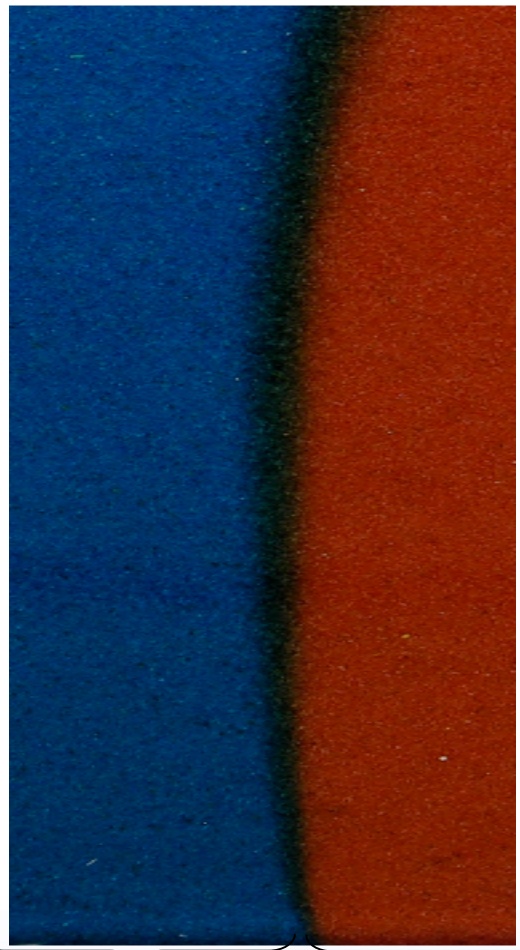
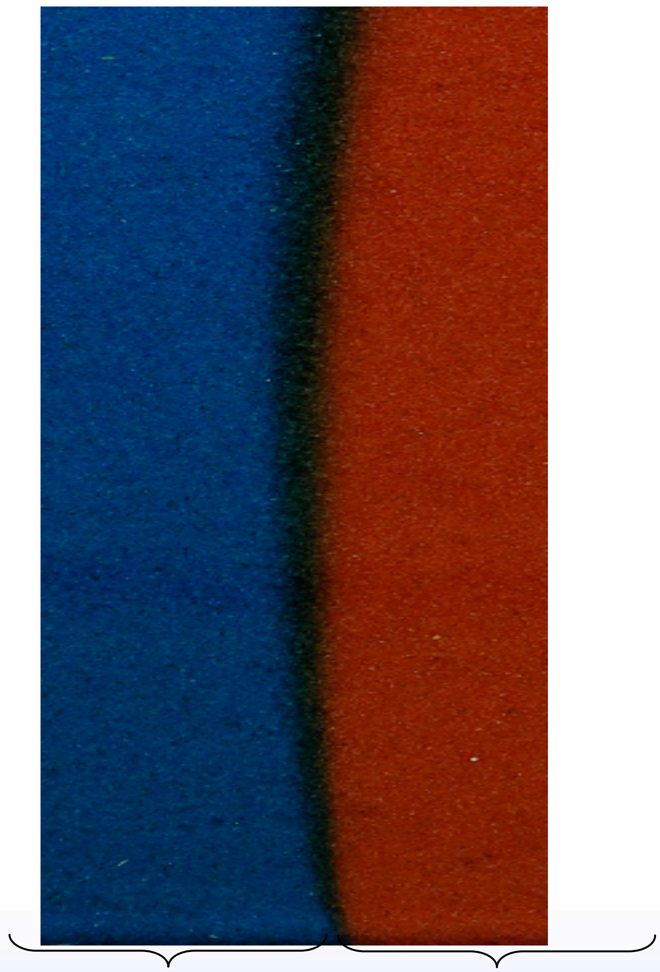
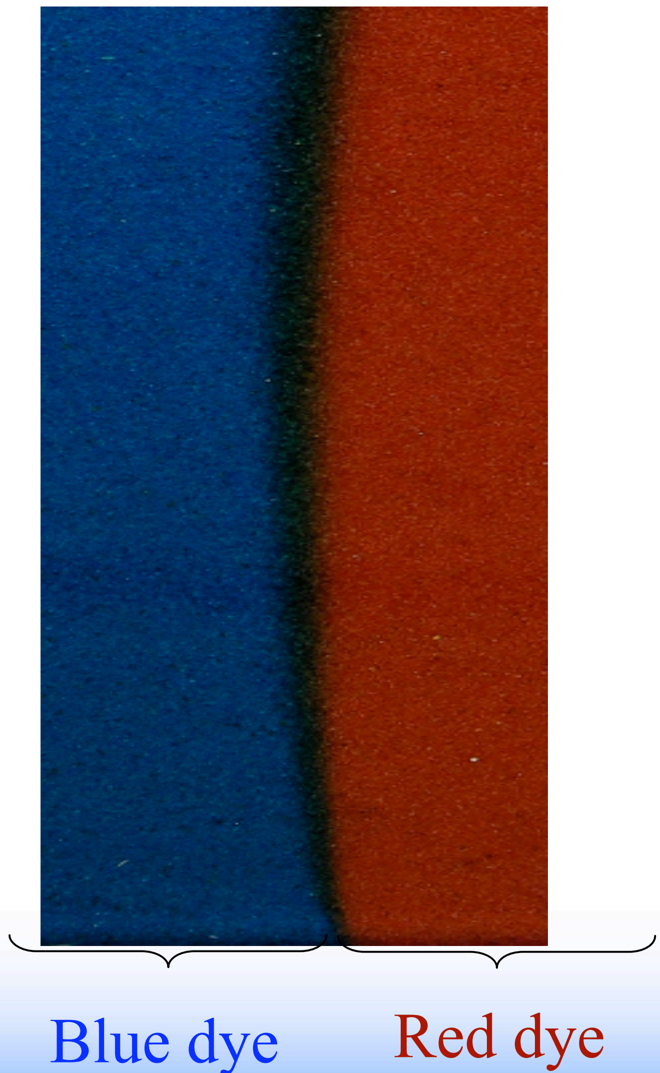


Tracer test showing fluid-fluid interface and mixing

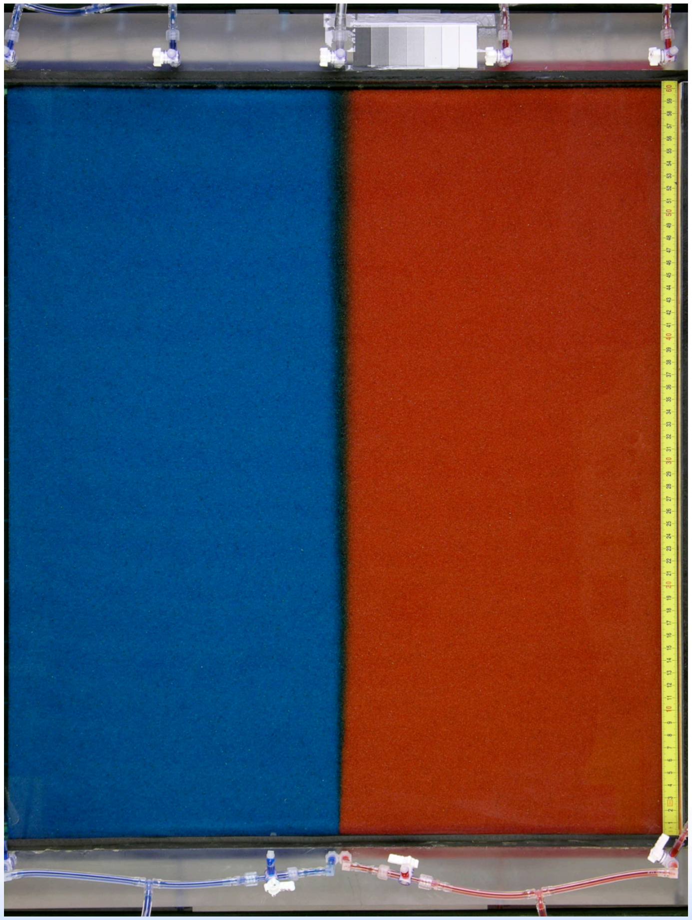


Blue dye Red dye

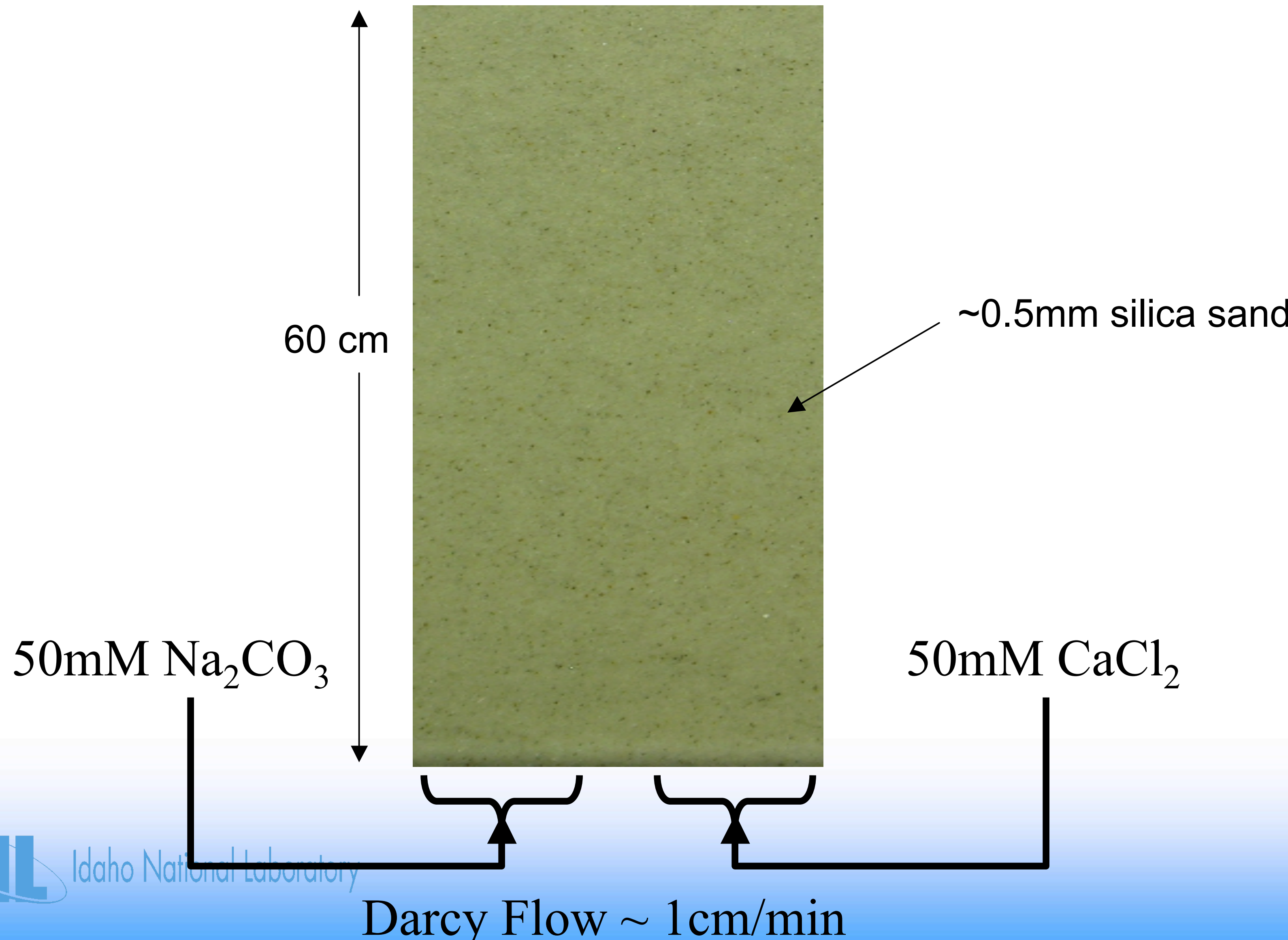
Tracer test showing fluid-fluid interface and mixing



Tracer test showing fluid-fluid interface and mixing (second attempt)



Propagation of calcium carbonate



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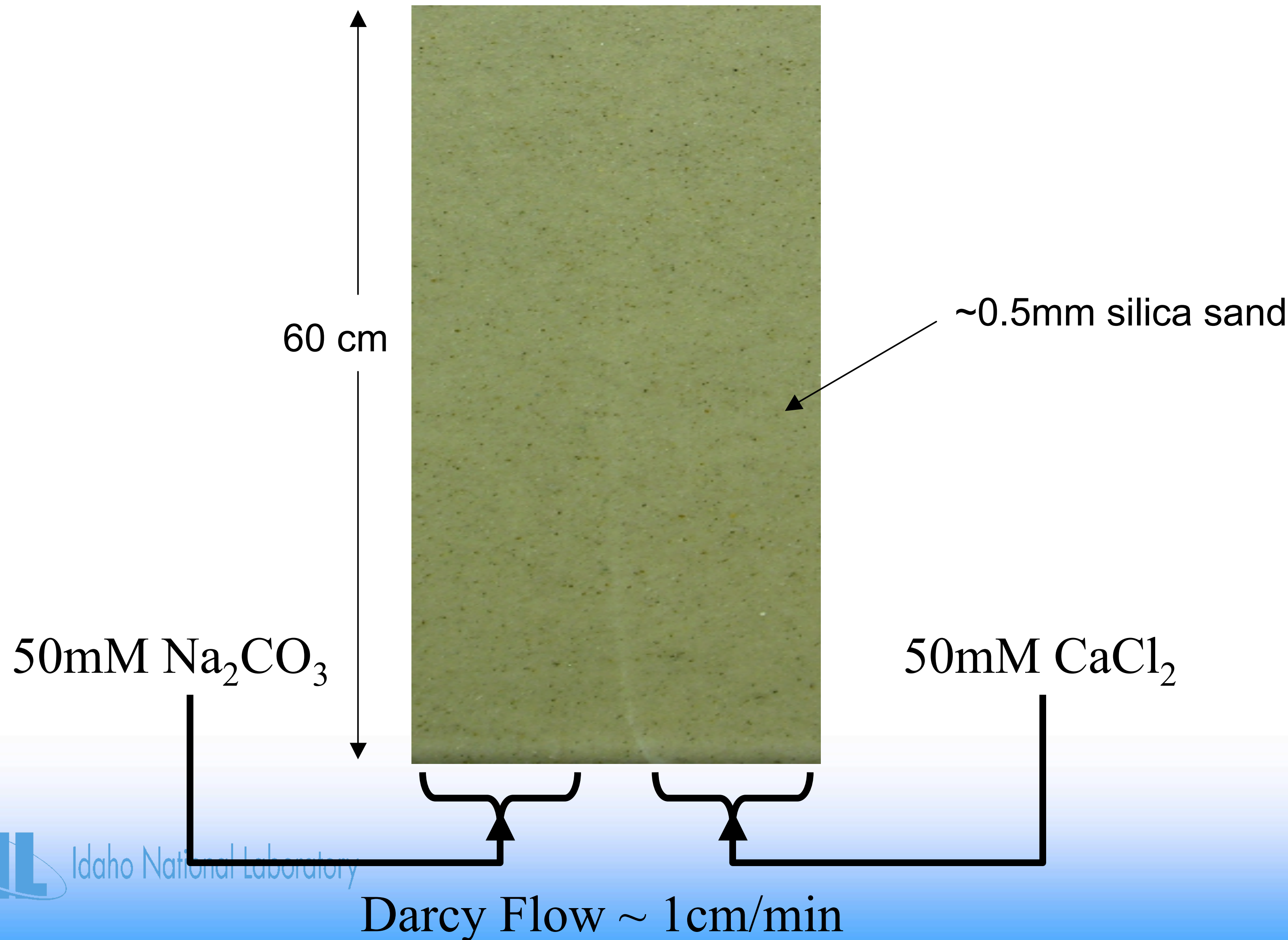

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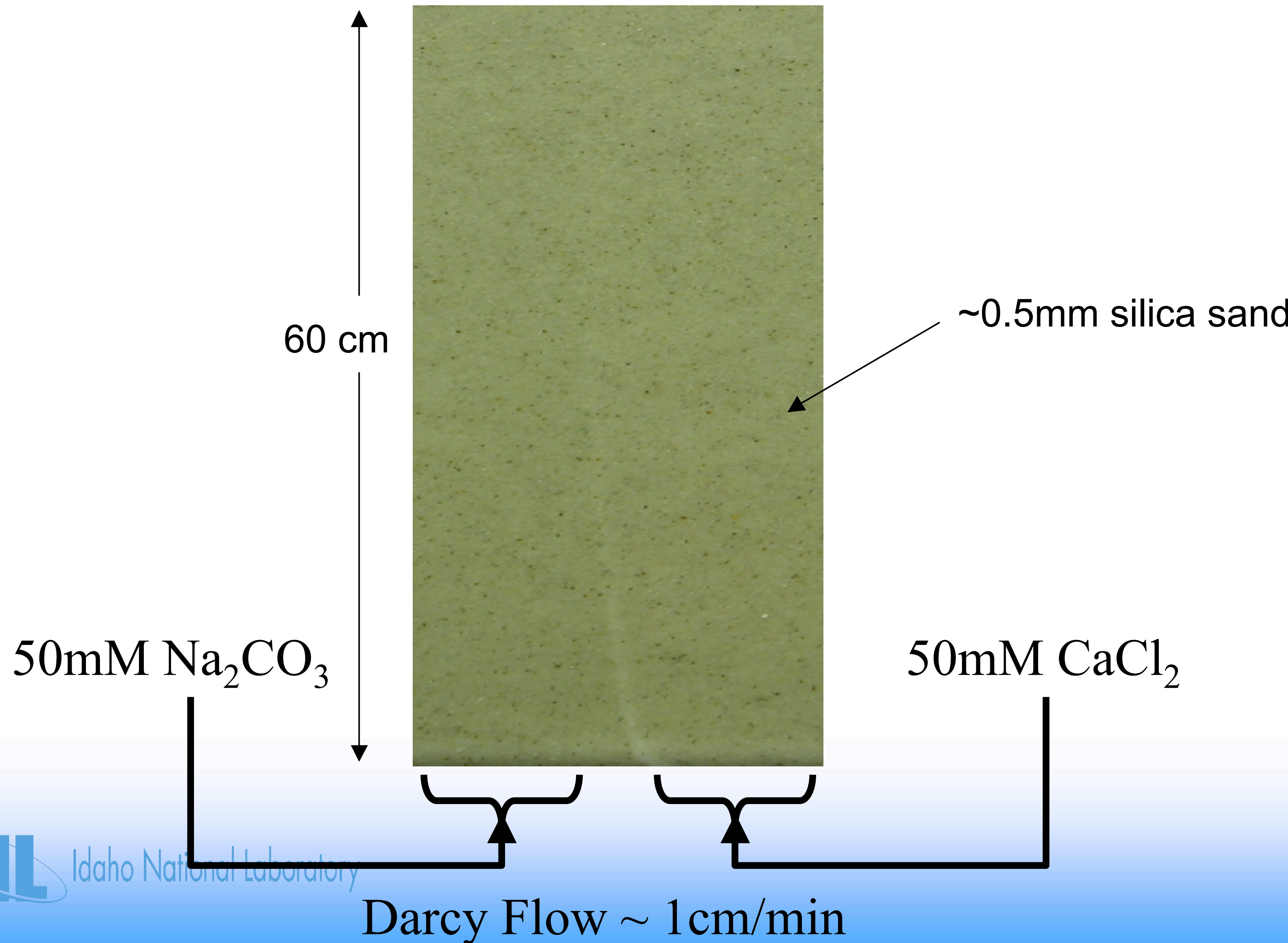

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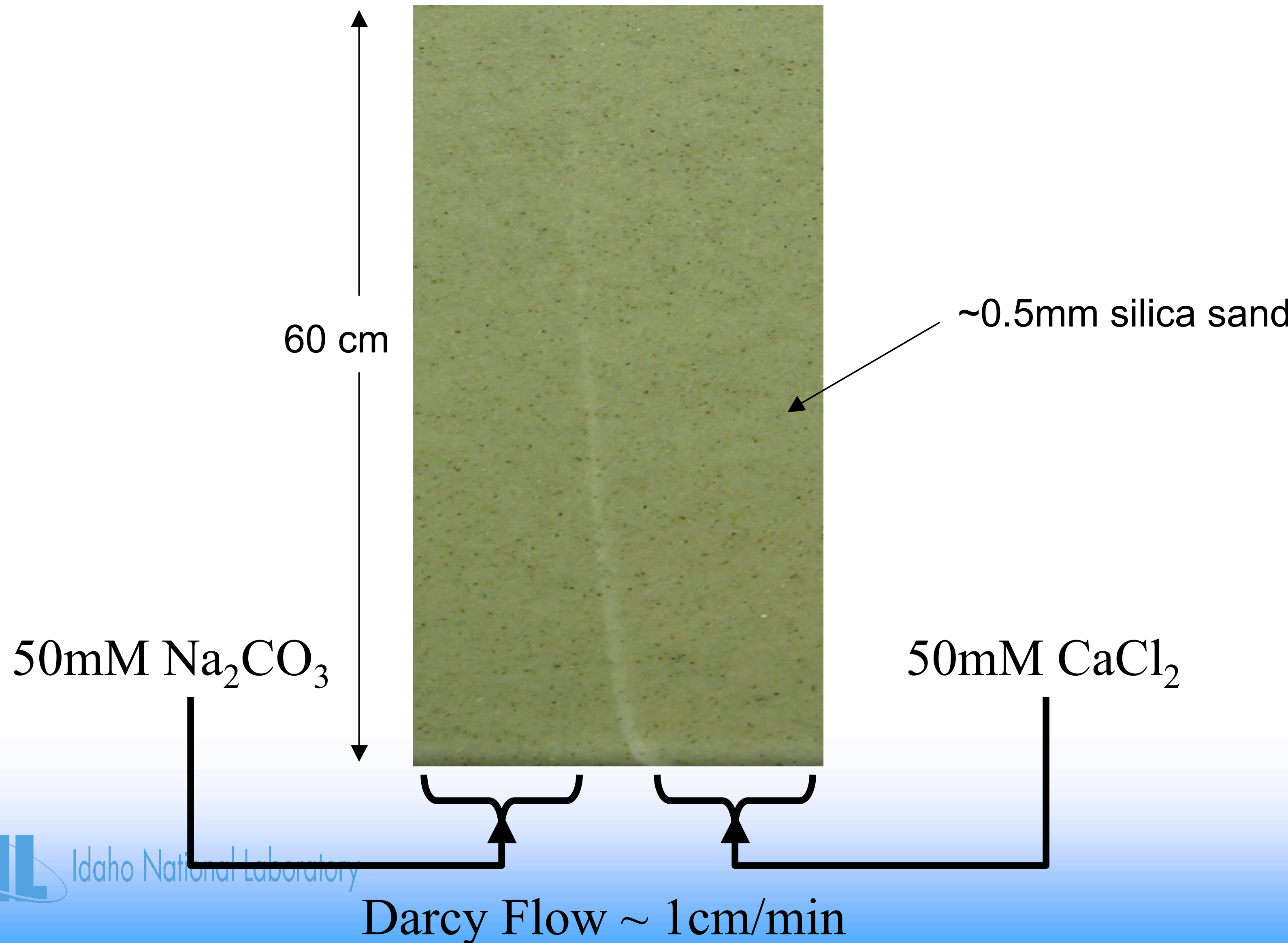

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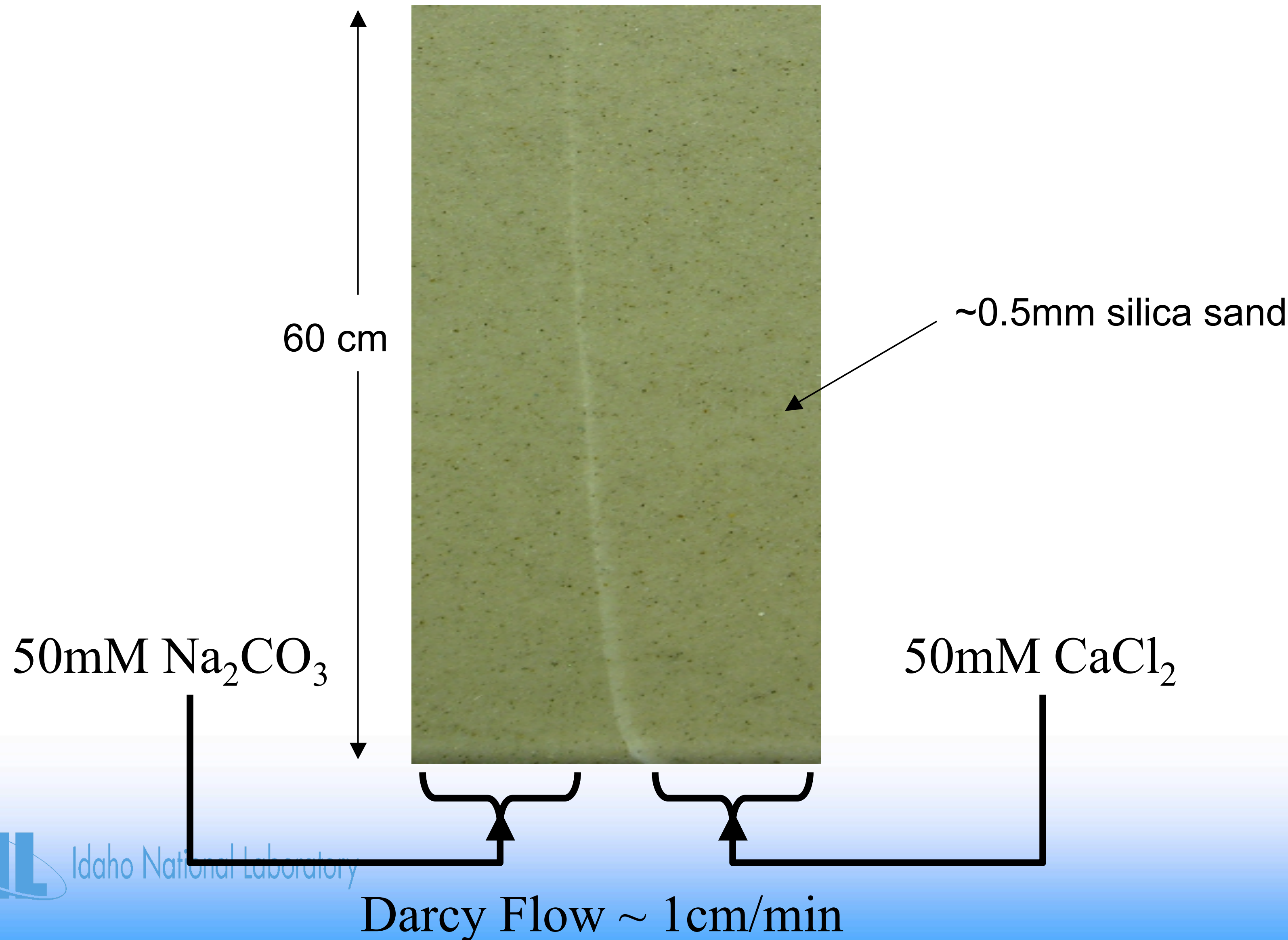

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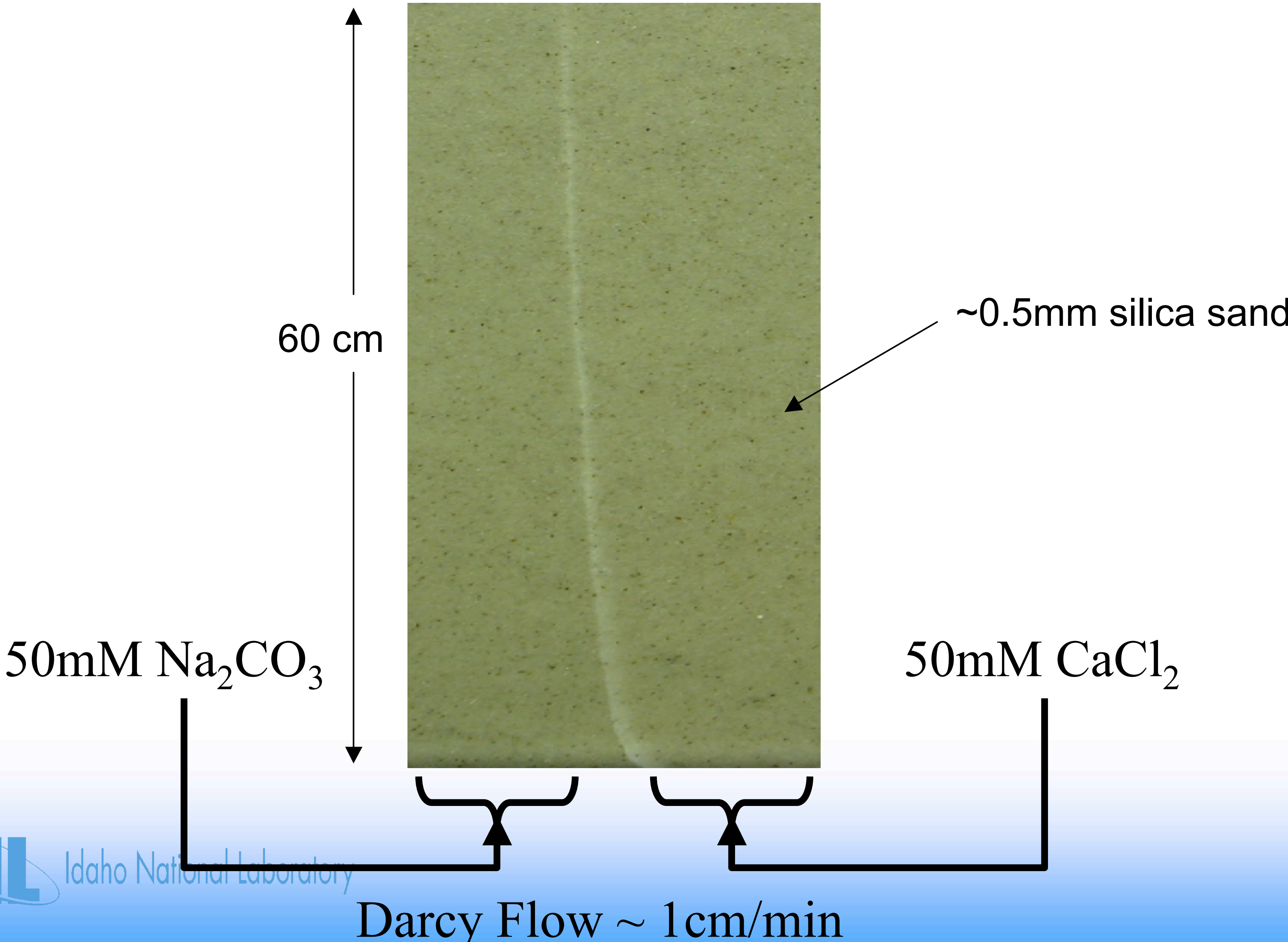

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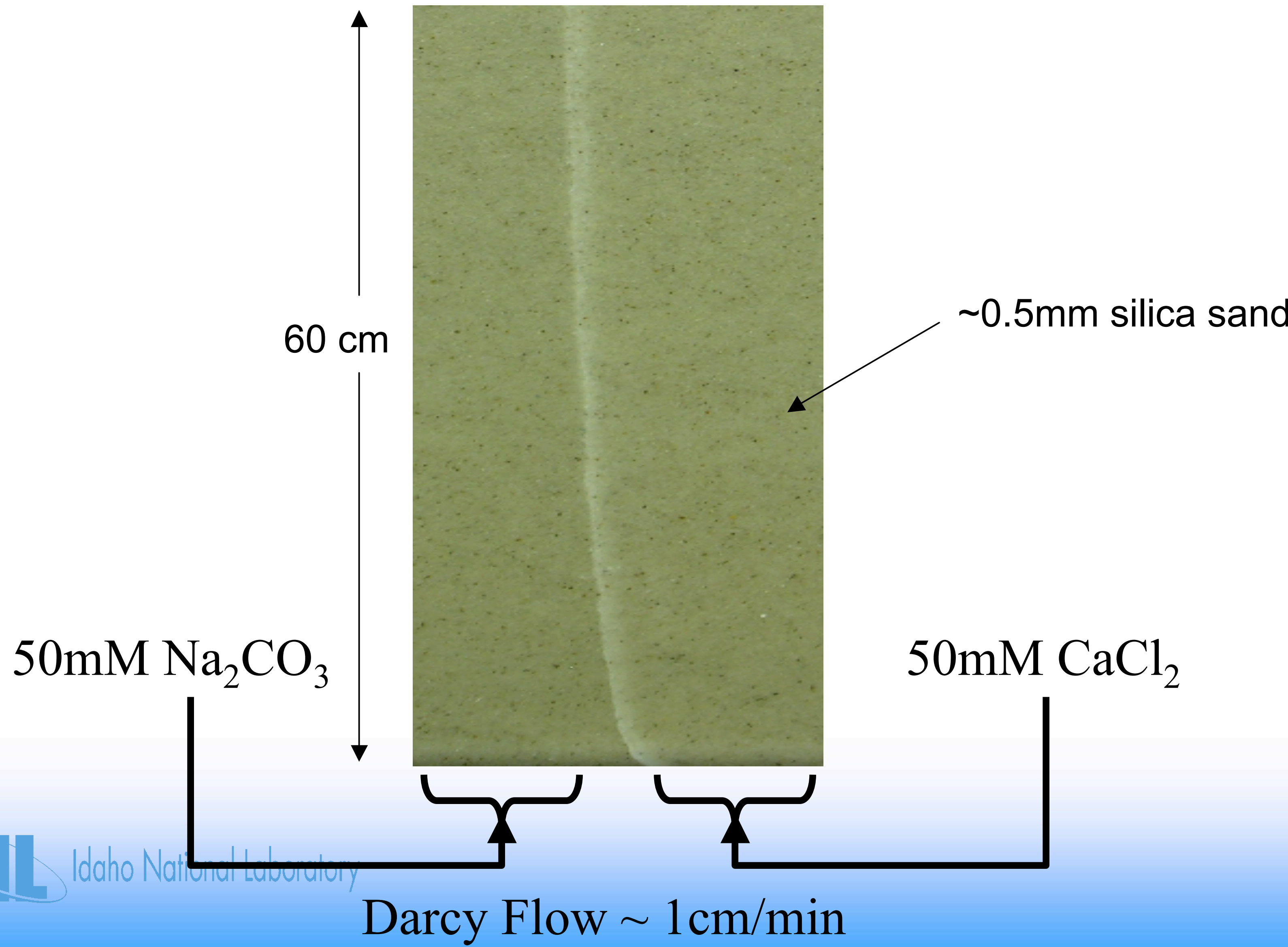

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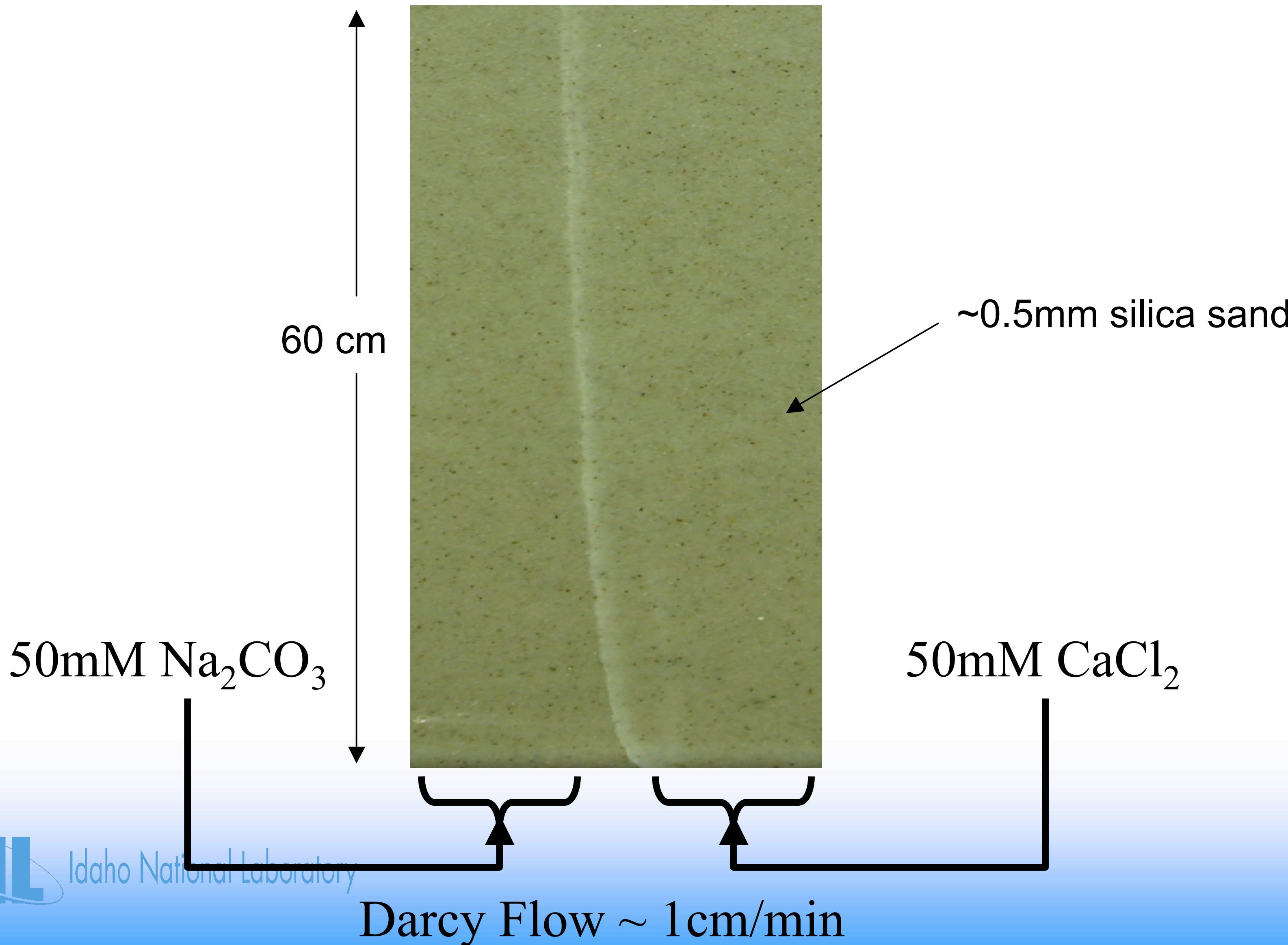

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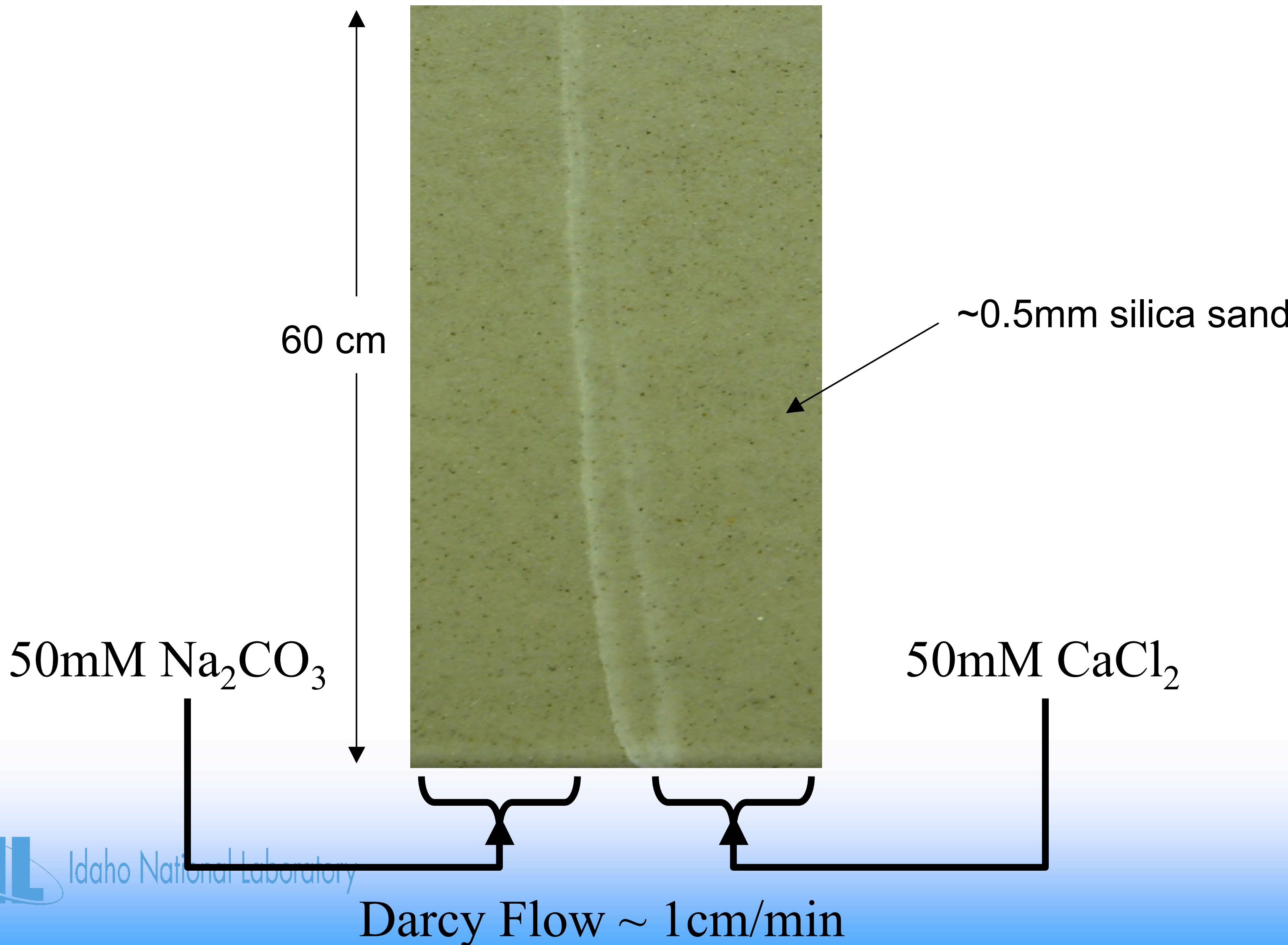

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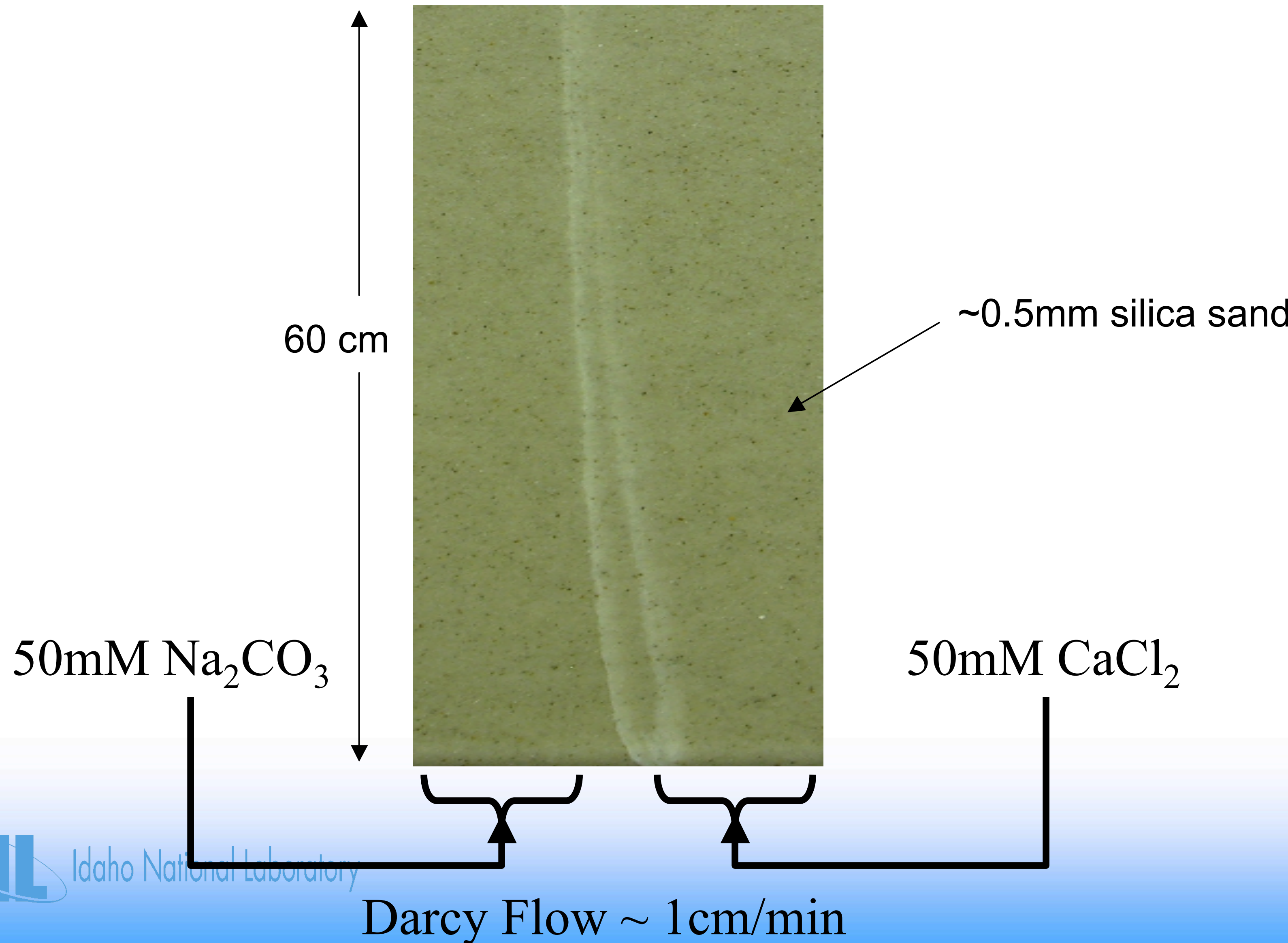

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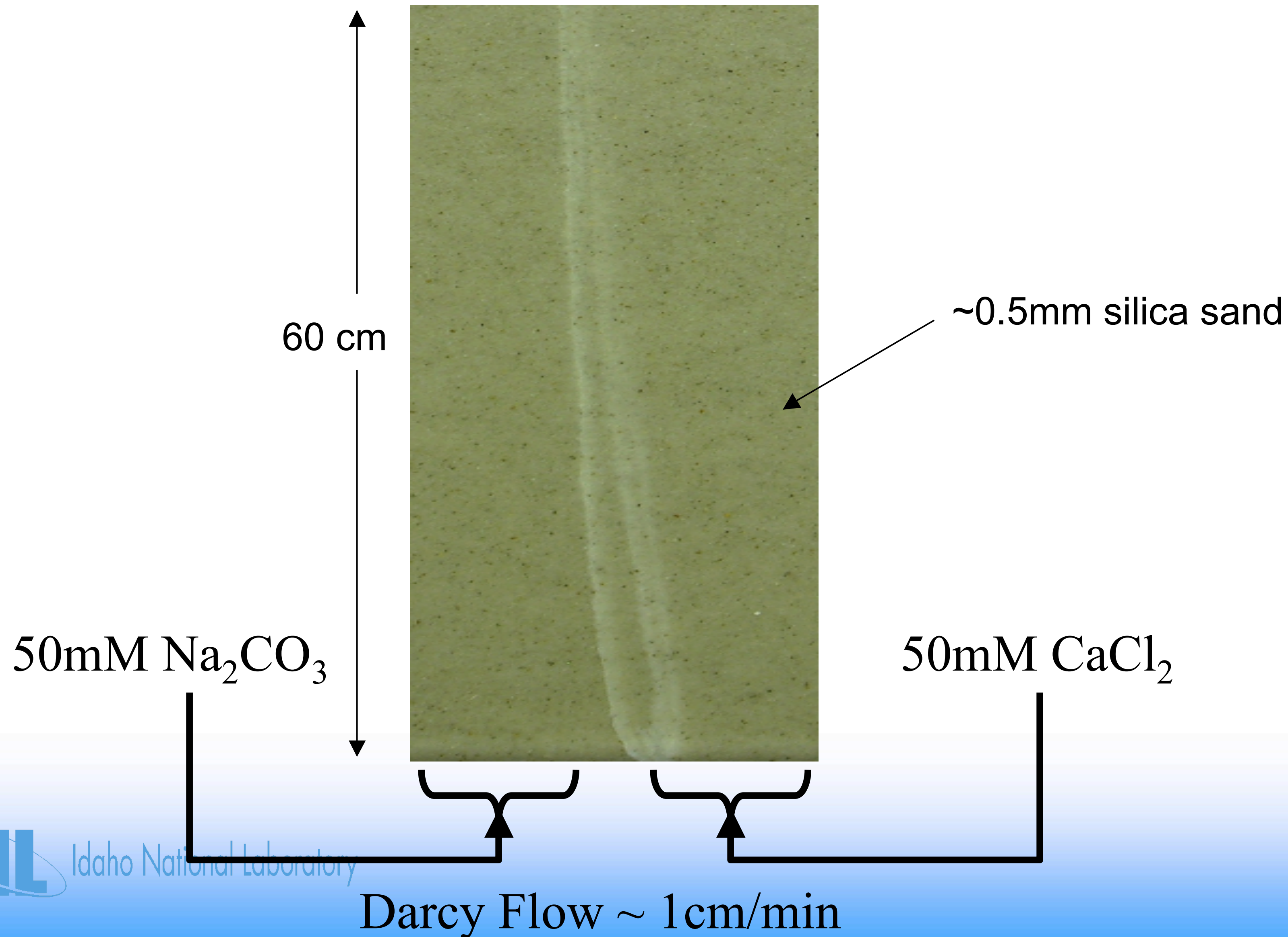

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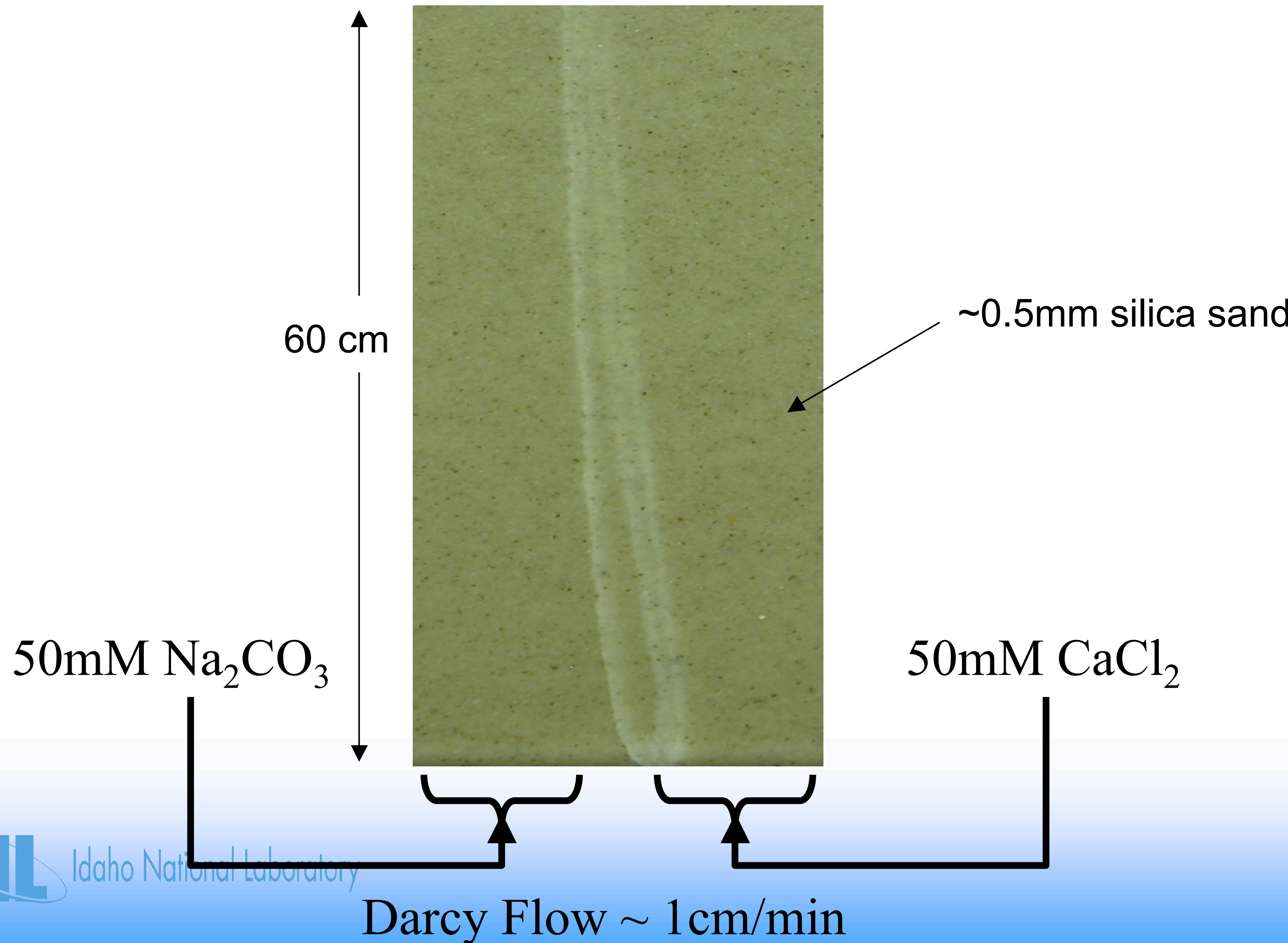

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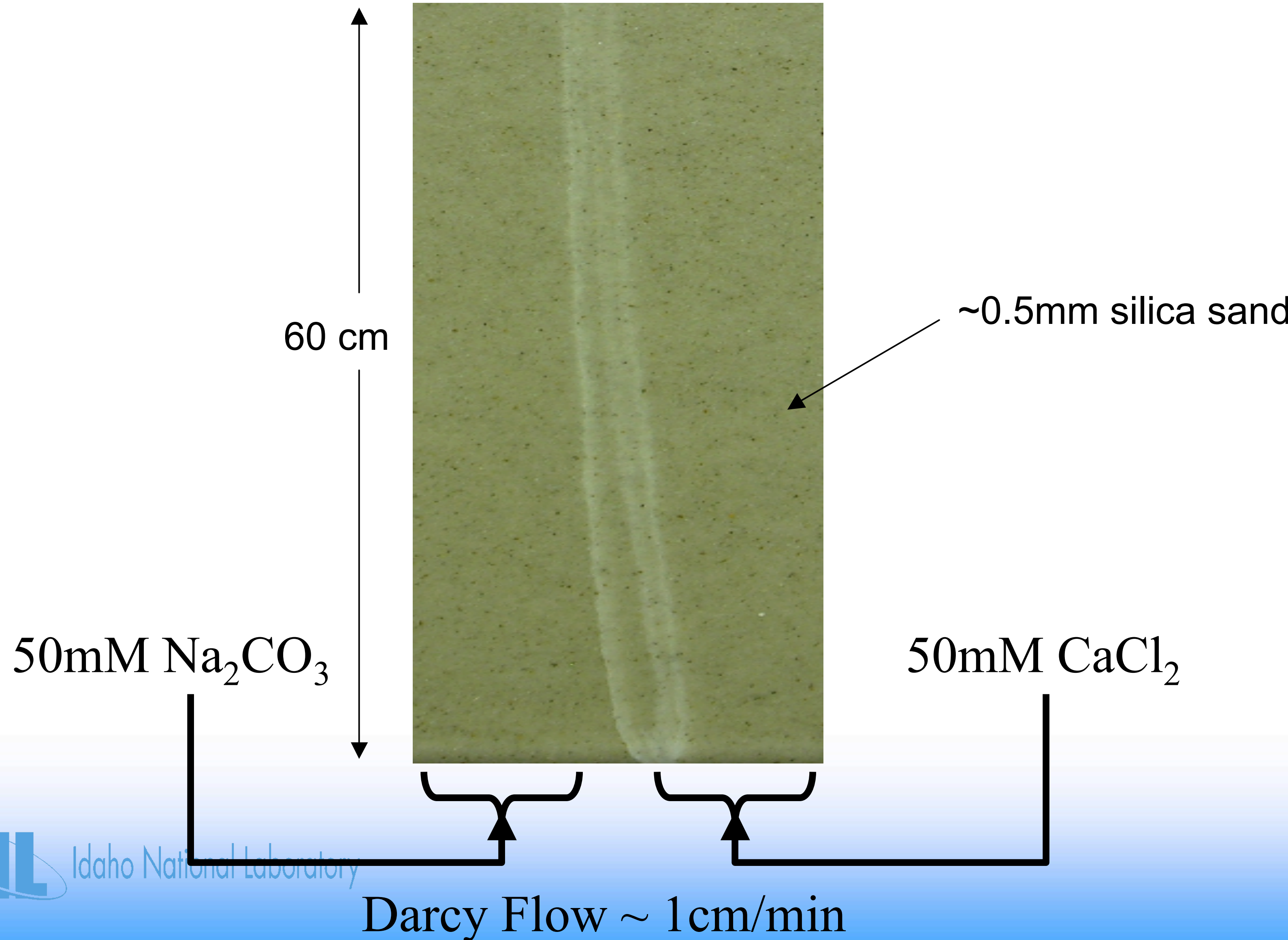

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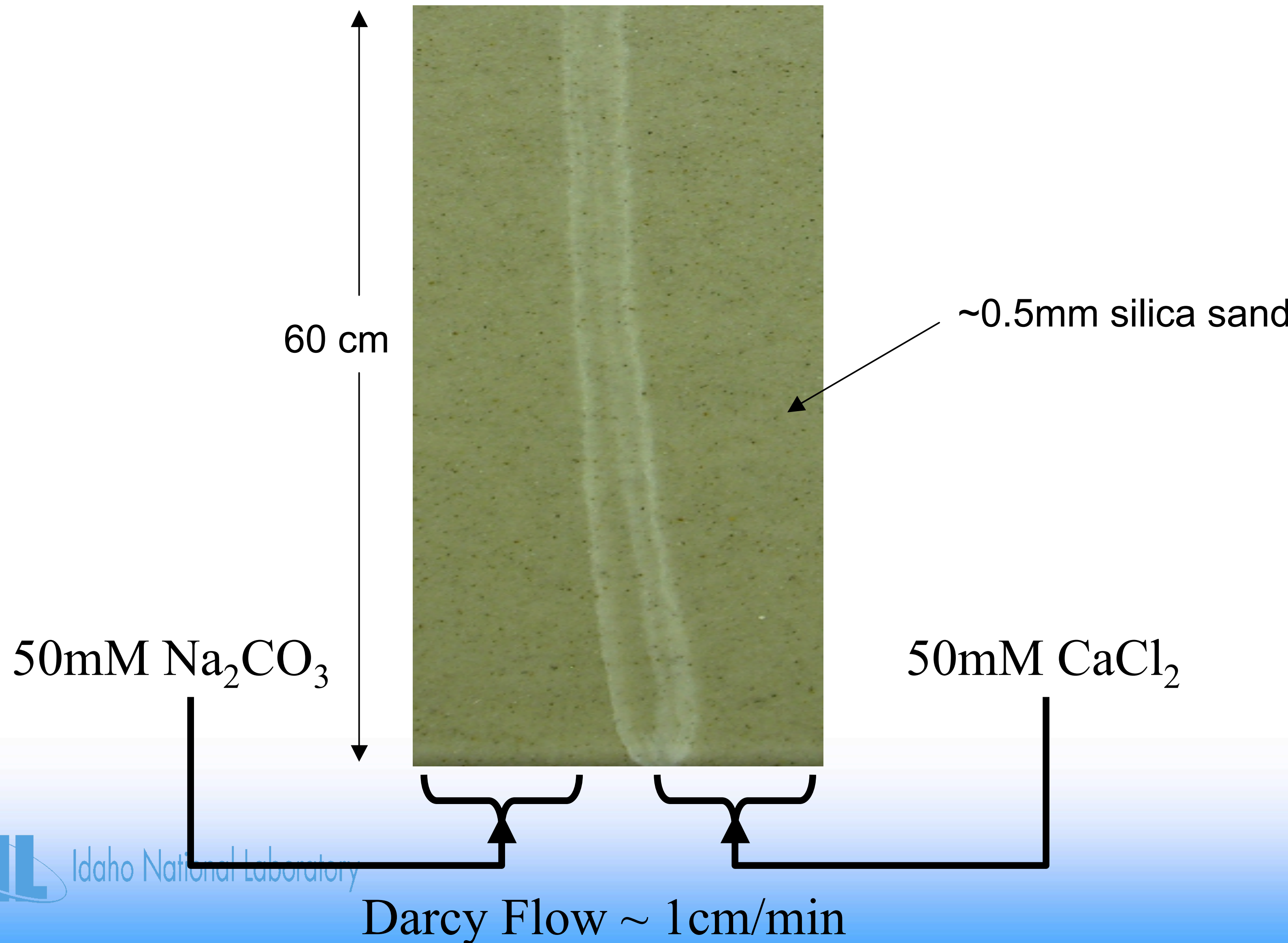

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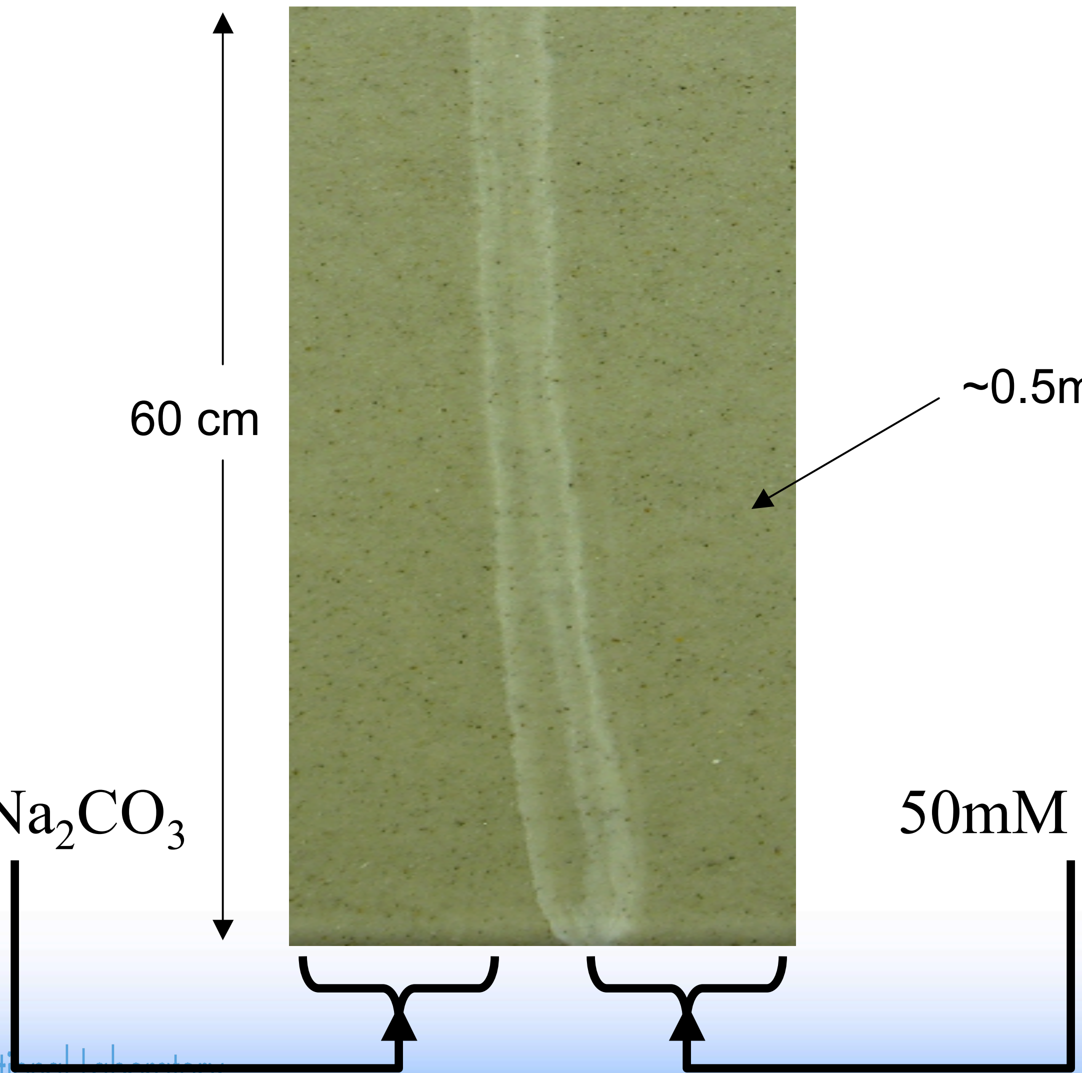

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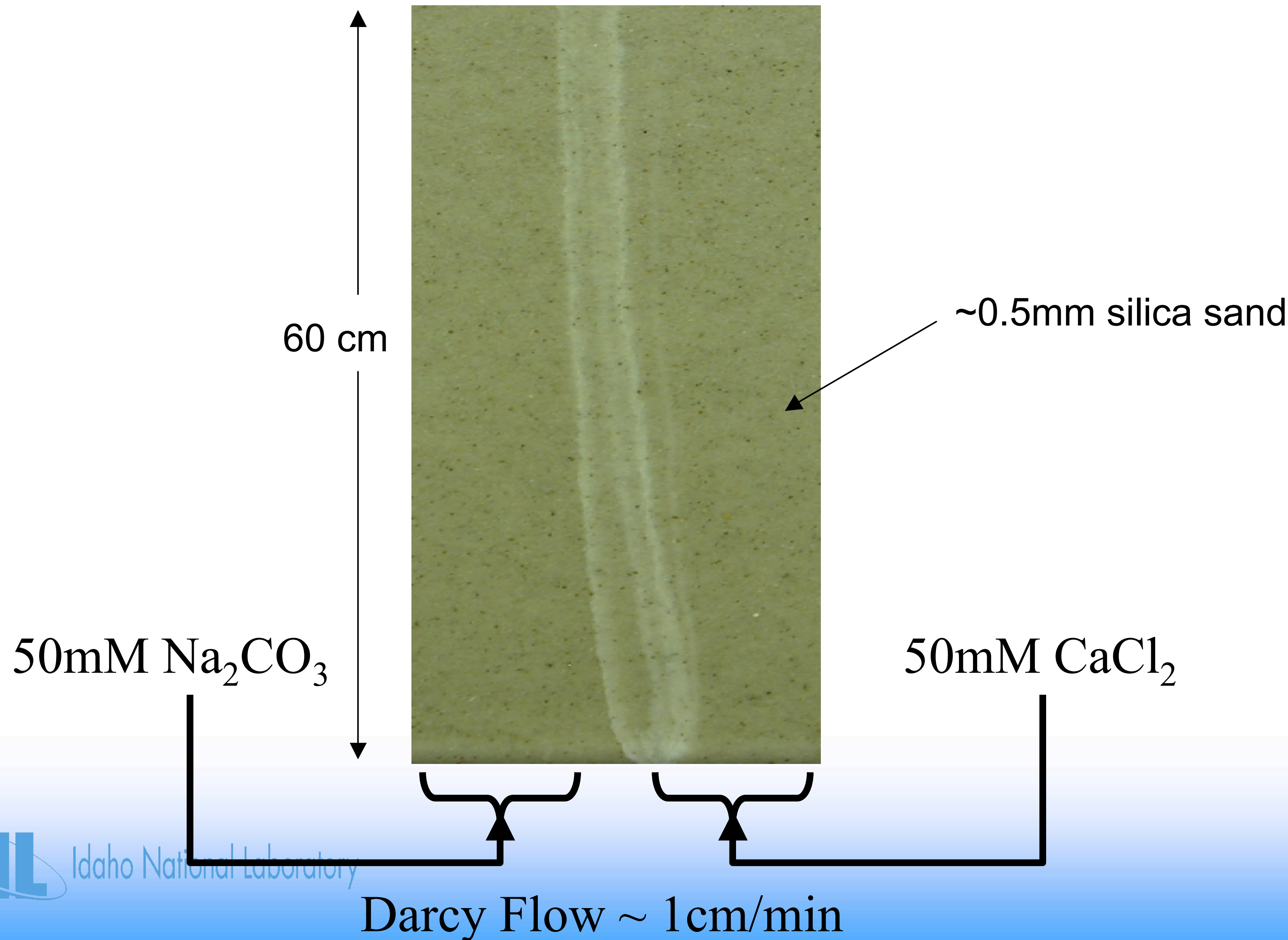

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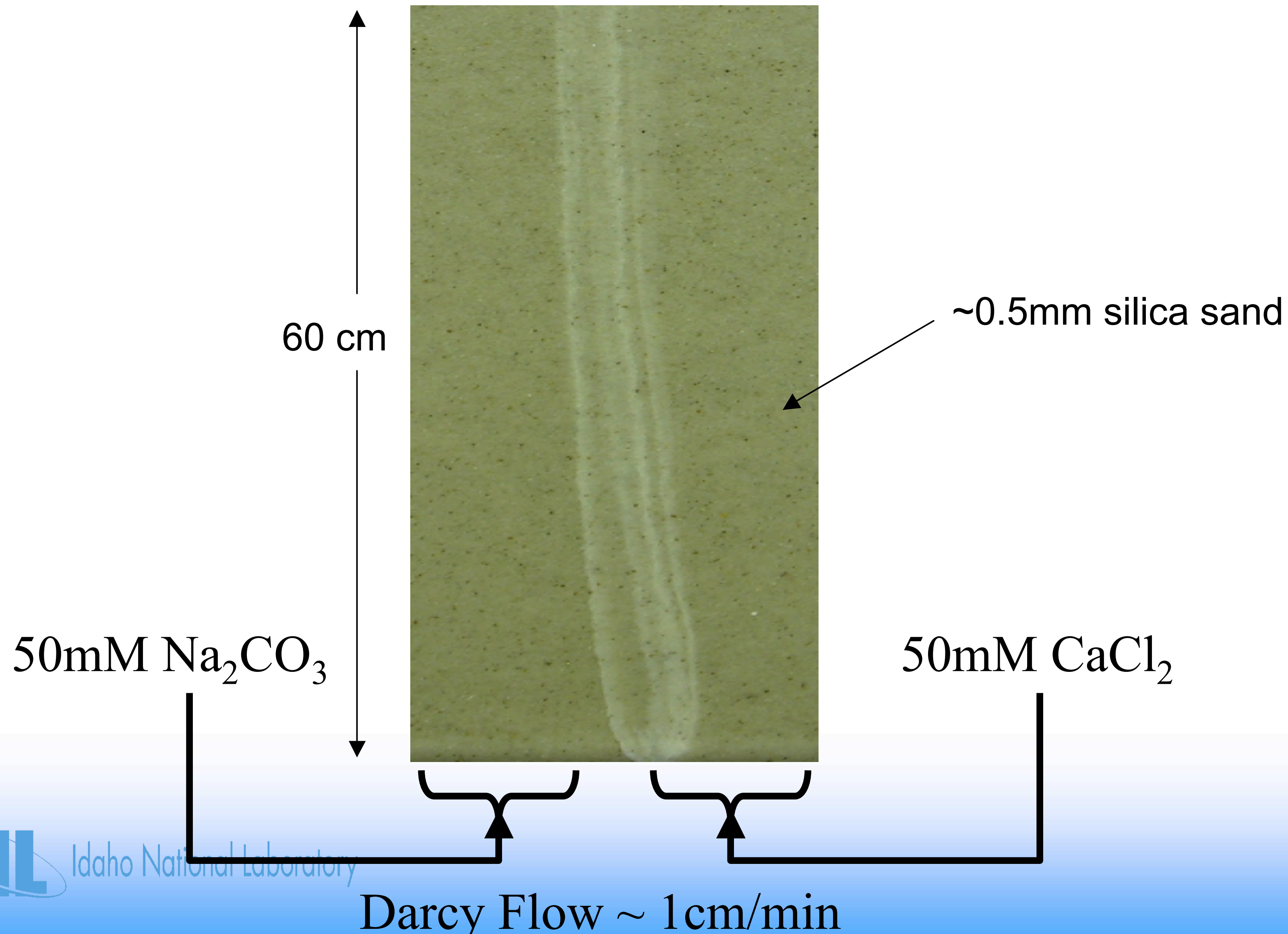

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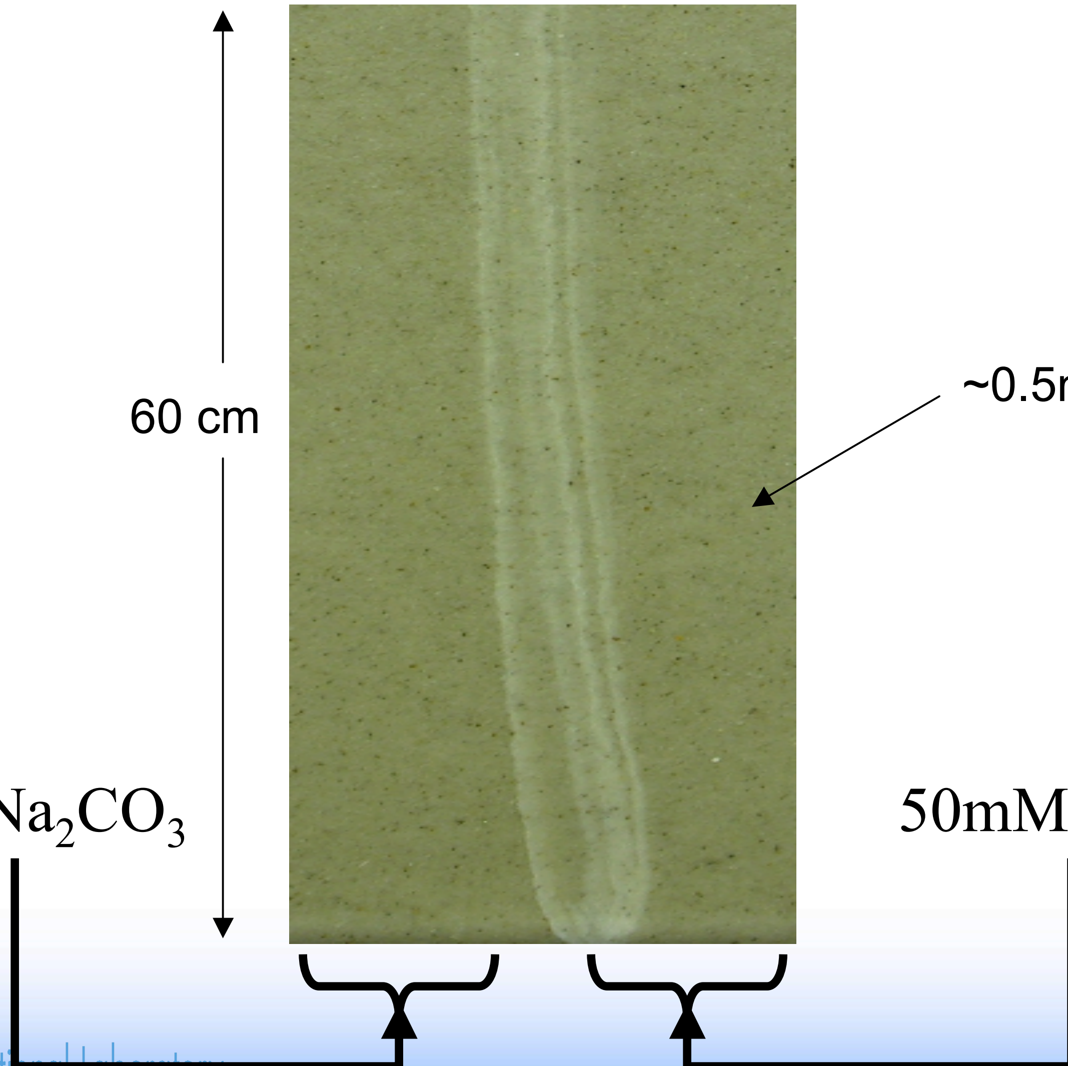

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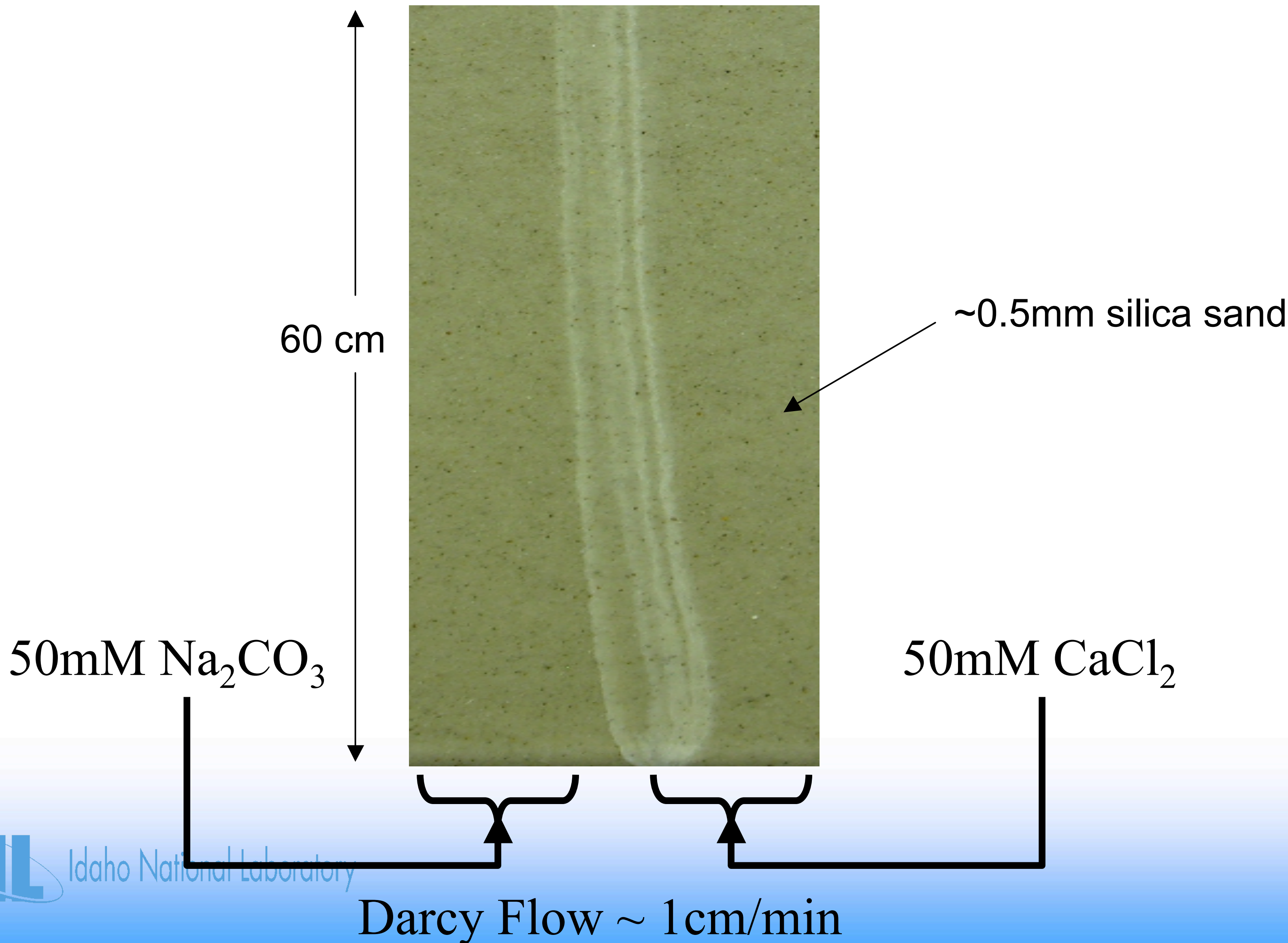

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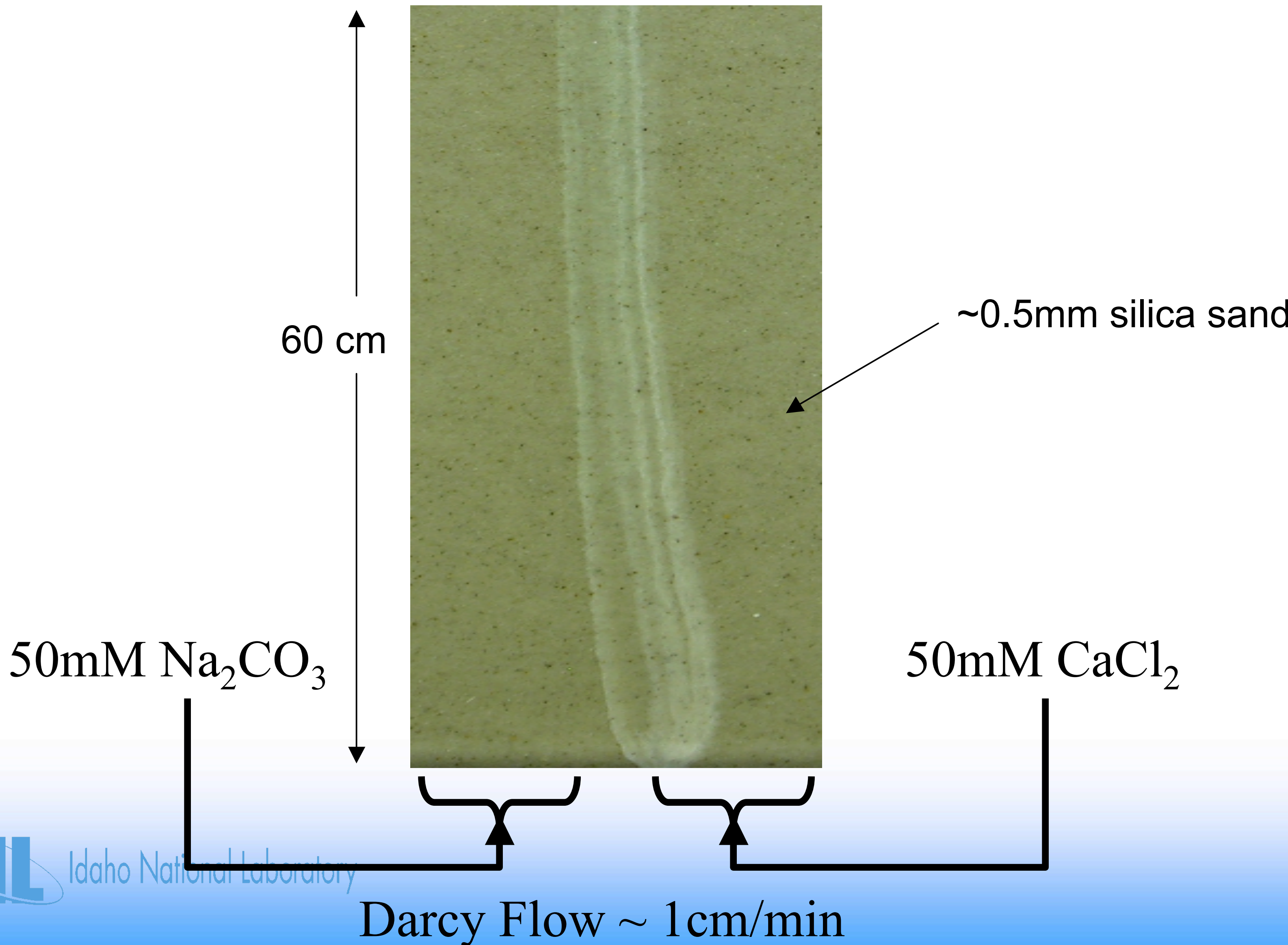

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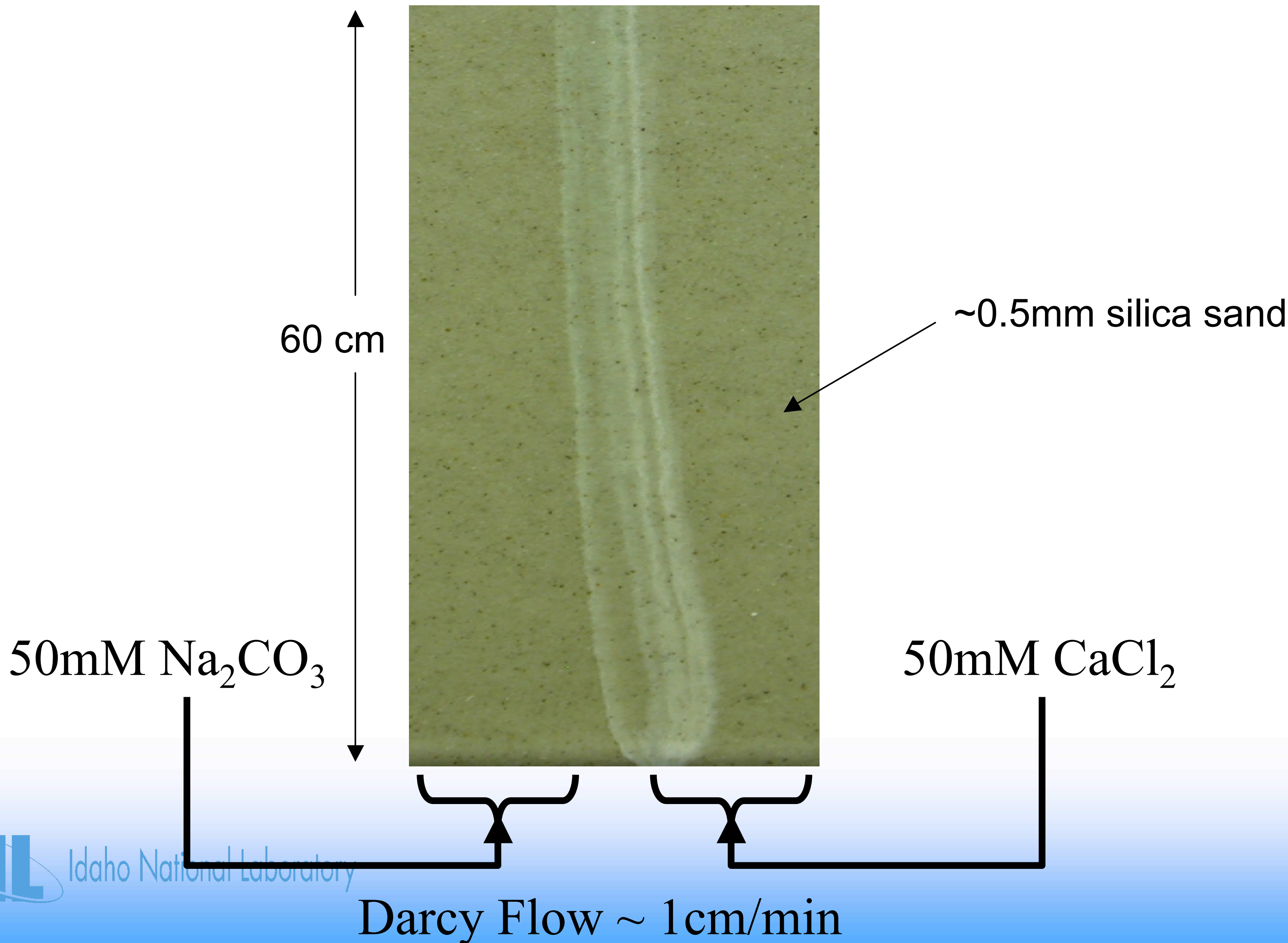
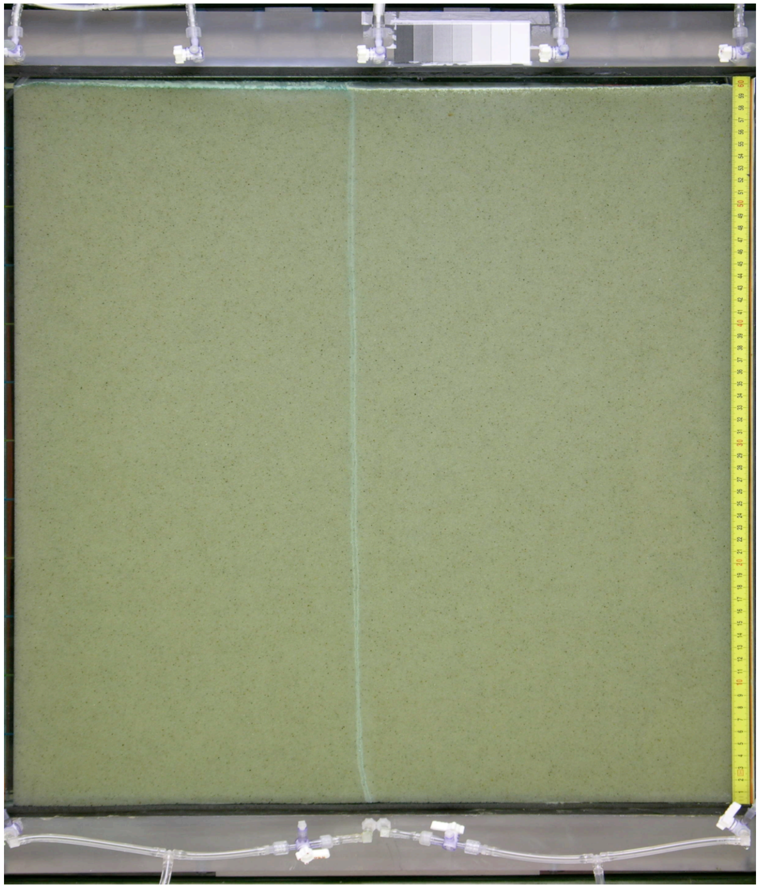
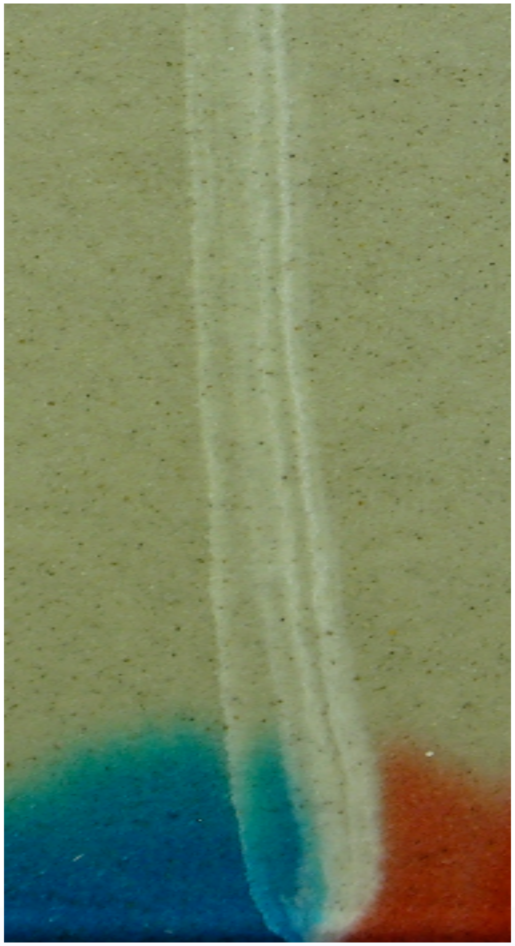


Propagation of calcium carbonate (second attempt)



And Biofilms…?

Tracer test following precipitation



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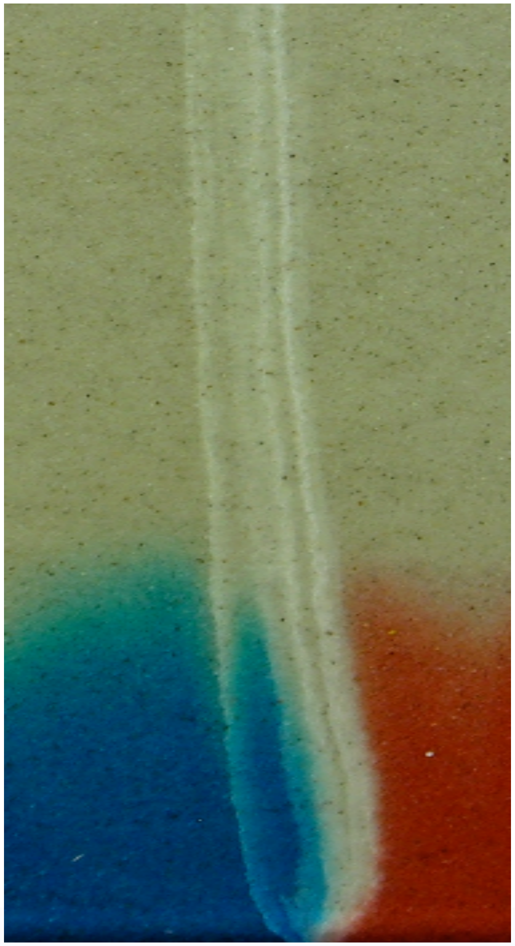

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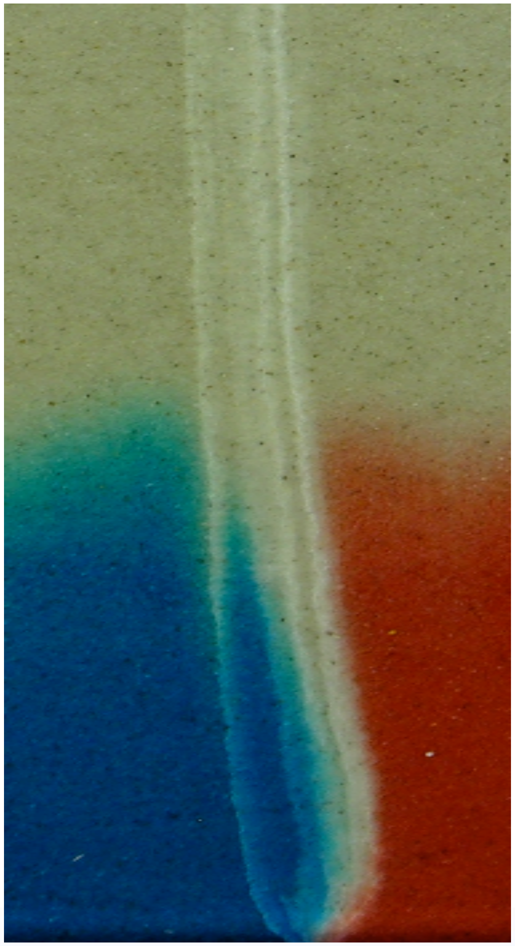

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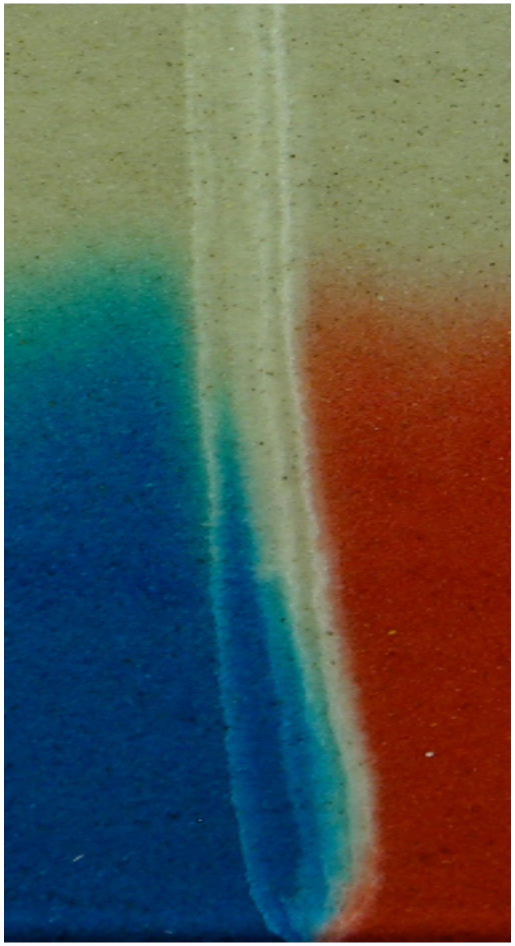

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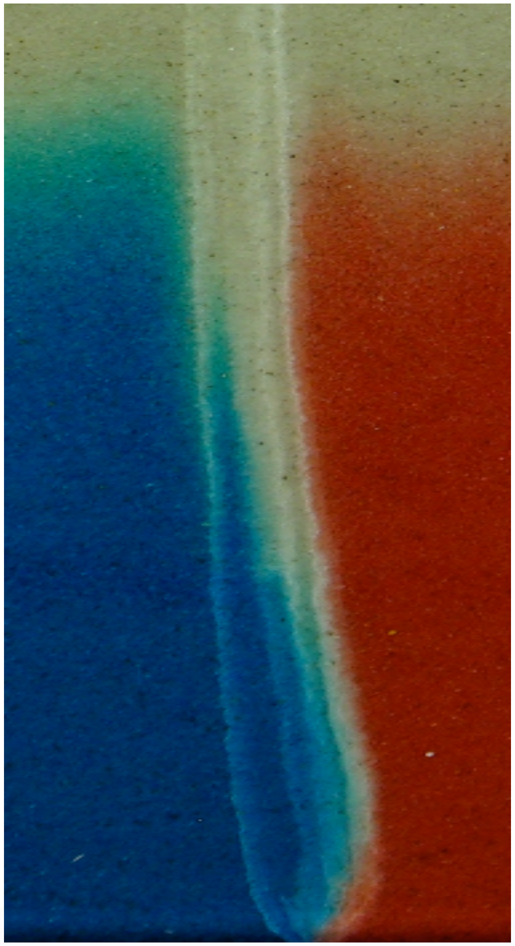

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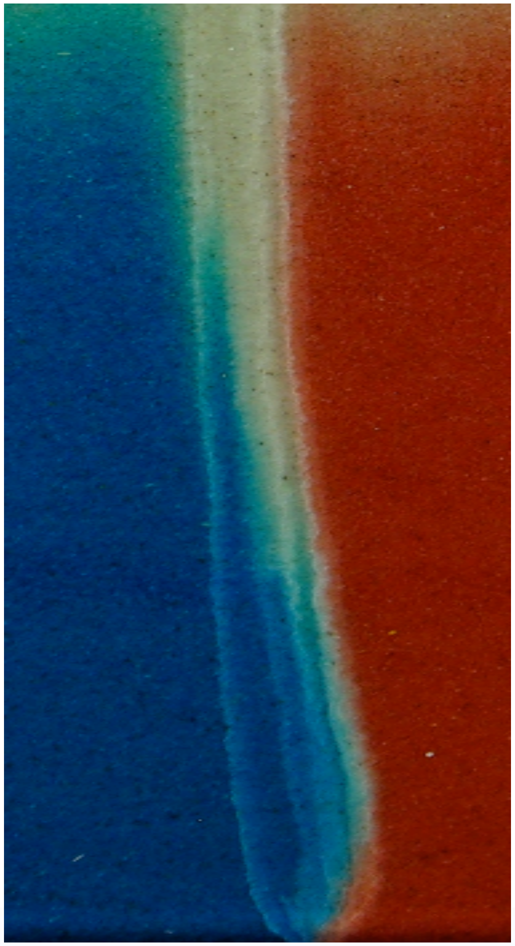

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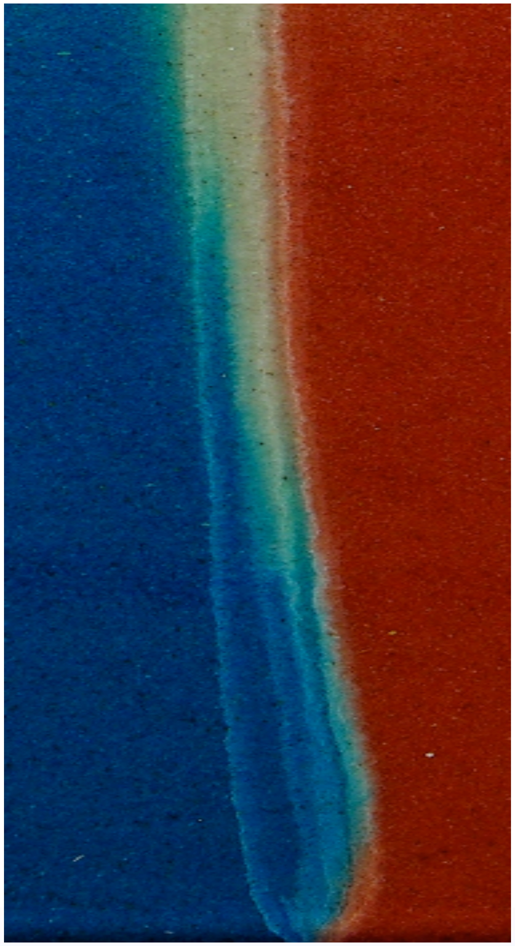

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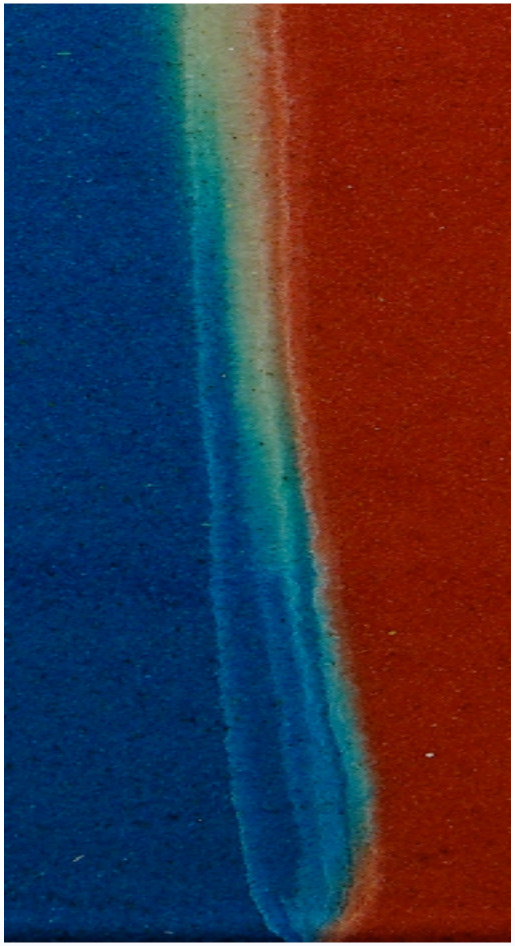

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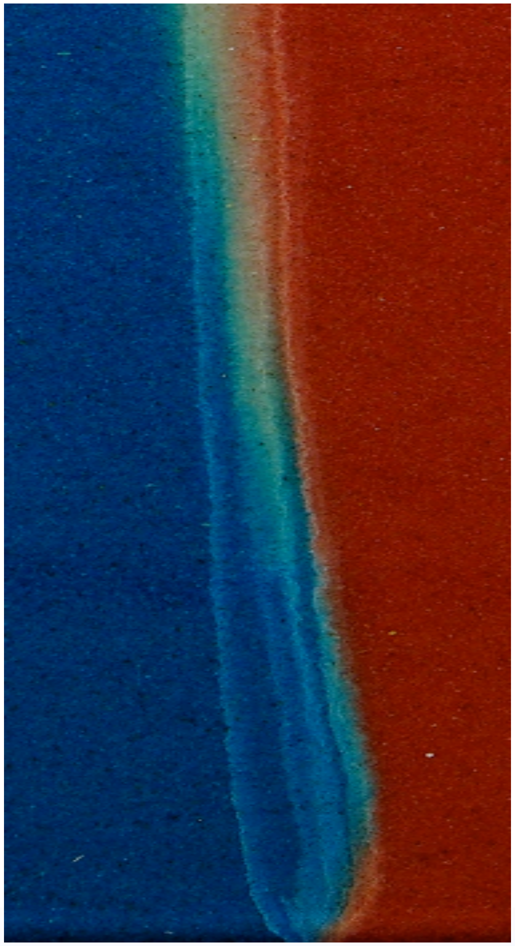

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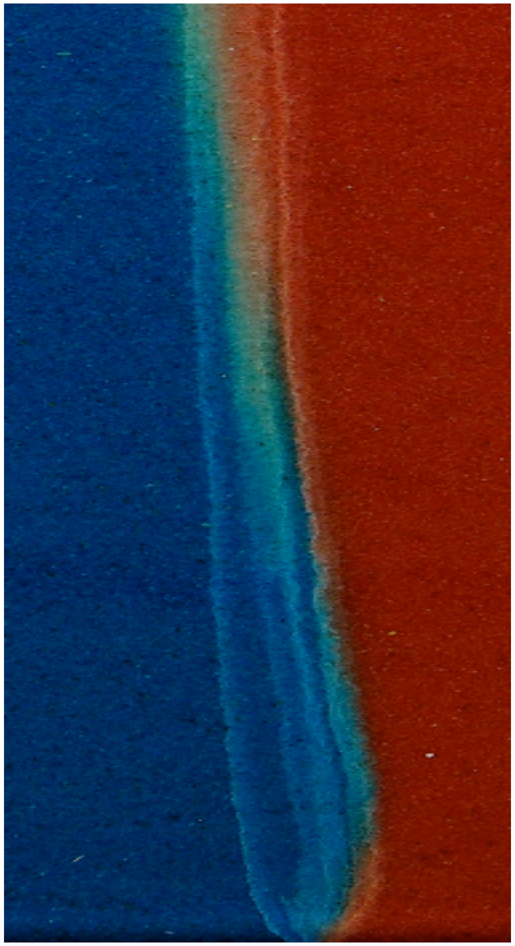

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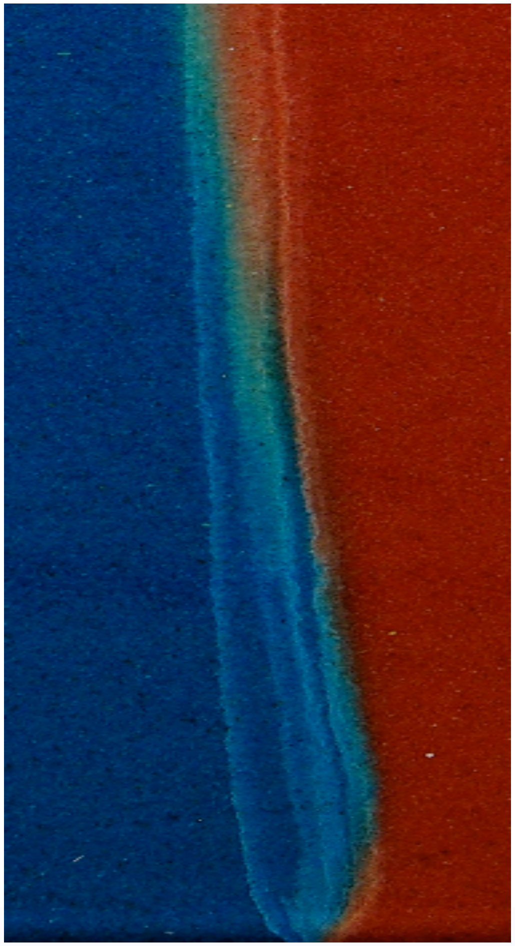

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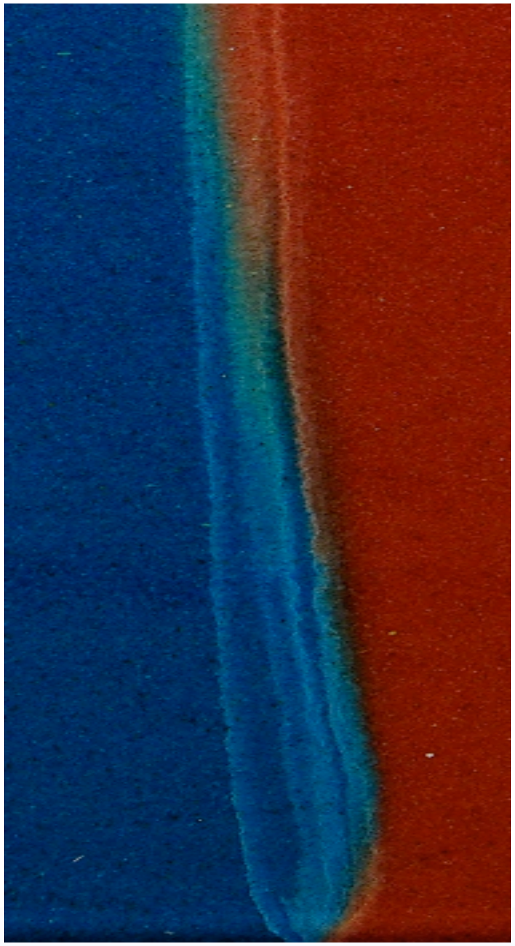
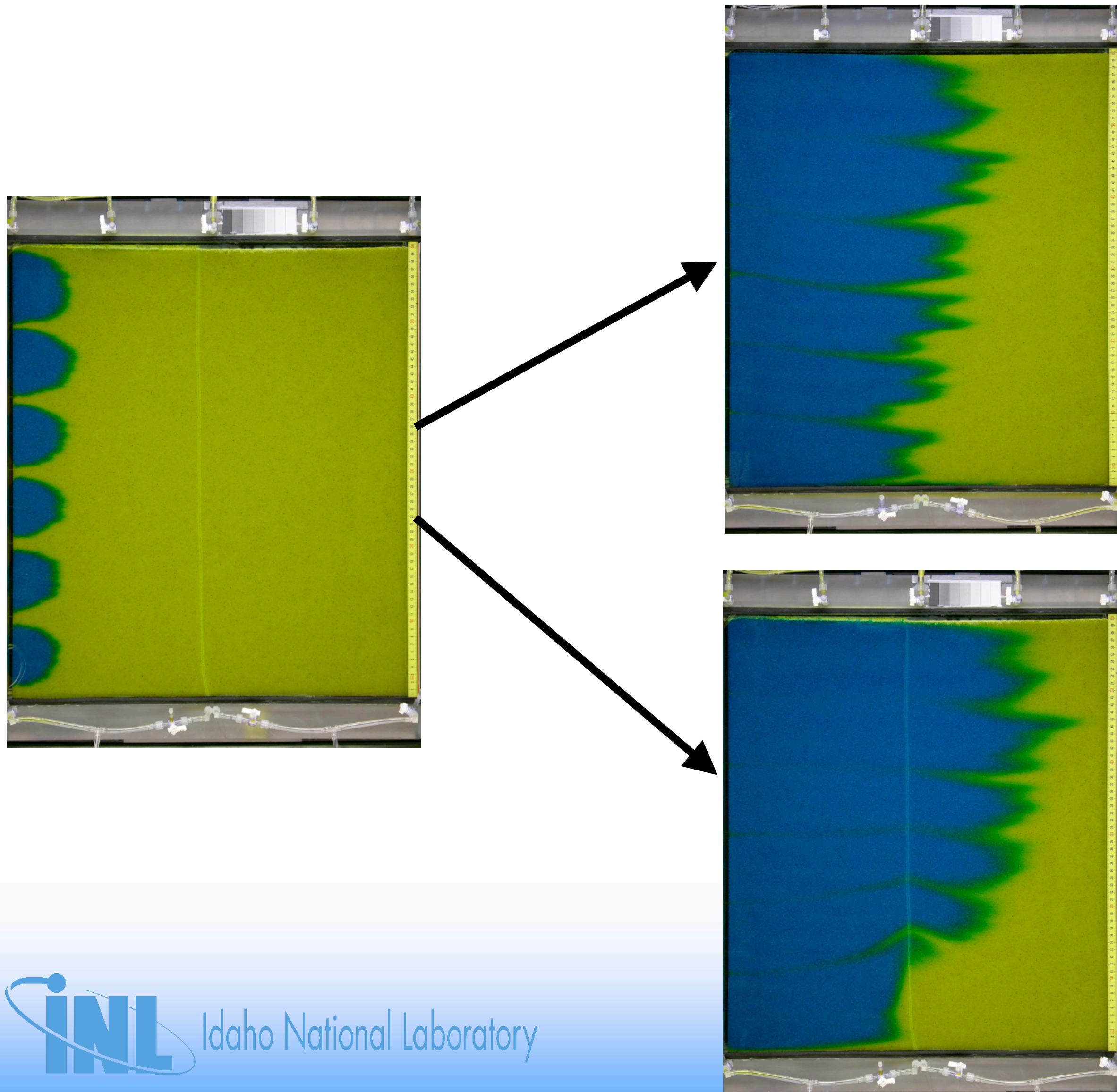
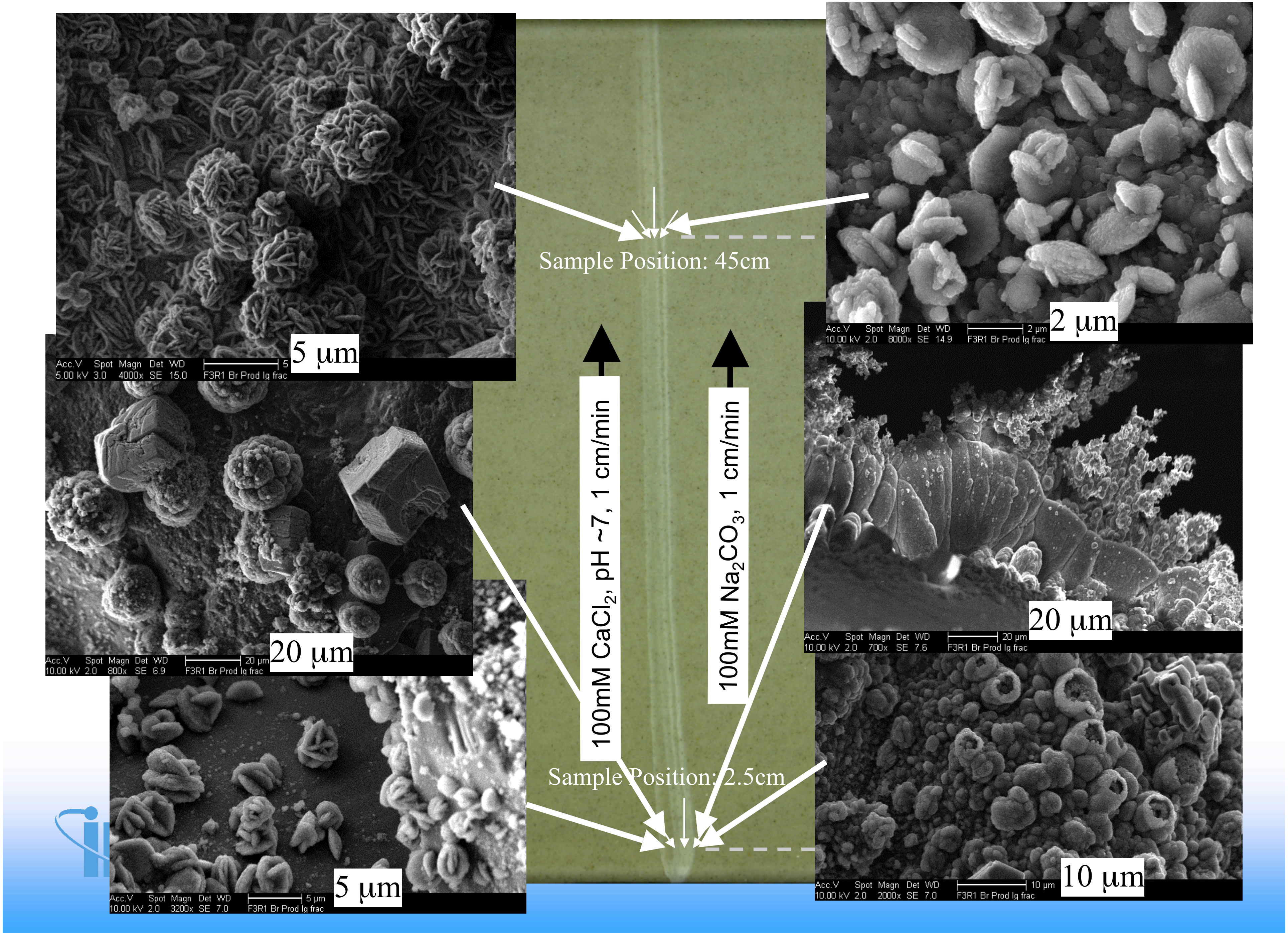


Impact on permeability



Before carbonate precipitation

After carbonate precipitation: Average permeability decreased by ~ 100



Sample Position: 45cm
Sample Position: 2.5cm
100mM $CaCl_2$, pH ~7, 1 cm/min
100mM Na_2CO_3, 1 cm/min
5 µm
2 µm
20 µm
20 µm
5 µm
10 µm
Acc.V Spot Magn Det WD
5.00 kV 3.0 4000x SE 15.0
F3R1 Br Prod lg frac
10.00 kV 2.0 8000x SE 14.9
10.00 kV 2.0 800x SE 6.9
10.00 kV 2.0 700x SE 7.6
10.00 kV 2.0 3200x SE 7.0
10.00 kV 2.0 2000x SE 7.0

Plans:

- Precipitation Kinetics
  - Extend outside conventional conditions
  - Ion ratios
  - Correlation to Sr uptake and speciation
- 2-D flow experiments
  - Full characterization
  - propagation of precipitates in physically heterogeneous systems
    - Low permeability inclusions
    - High permeability flow paths
  - propagation of precipitates in chemically heterogeneous systems
    - calcite seeds
    - clay on sand
- SPH and continuum-scale model refinement

Precipitation Kinetics

(see A.E. Nielsen (1983))

- $R = k'(\Omega-1)$ *Adsorption (linear)*
- $R = k''(\Omega-1)^2$ *Spiral growth (parabolic)*
- $R = [k_{ex}\ \Omega^{7/6}(\Omega-1)^{2/3}(\ln\Omega)^{1/6}]\ \exp(-K_{ex}/\ln\Omega)$ *Surface nucleation*

  $\sim (\Omega-1)^{5/6}\ \exp(-K_{ex}/\ln\Omega)$

  $\sim \exp(-K_{ex}/\ln\Omega)$
- $R = k'''(\Omega-1)^n$ …Practical

Where:

ks are rate constants

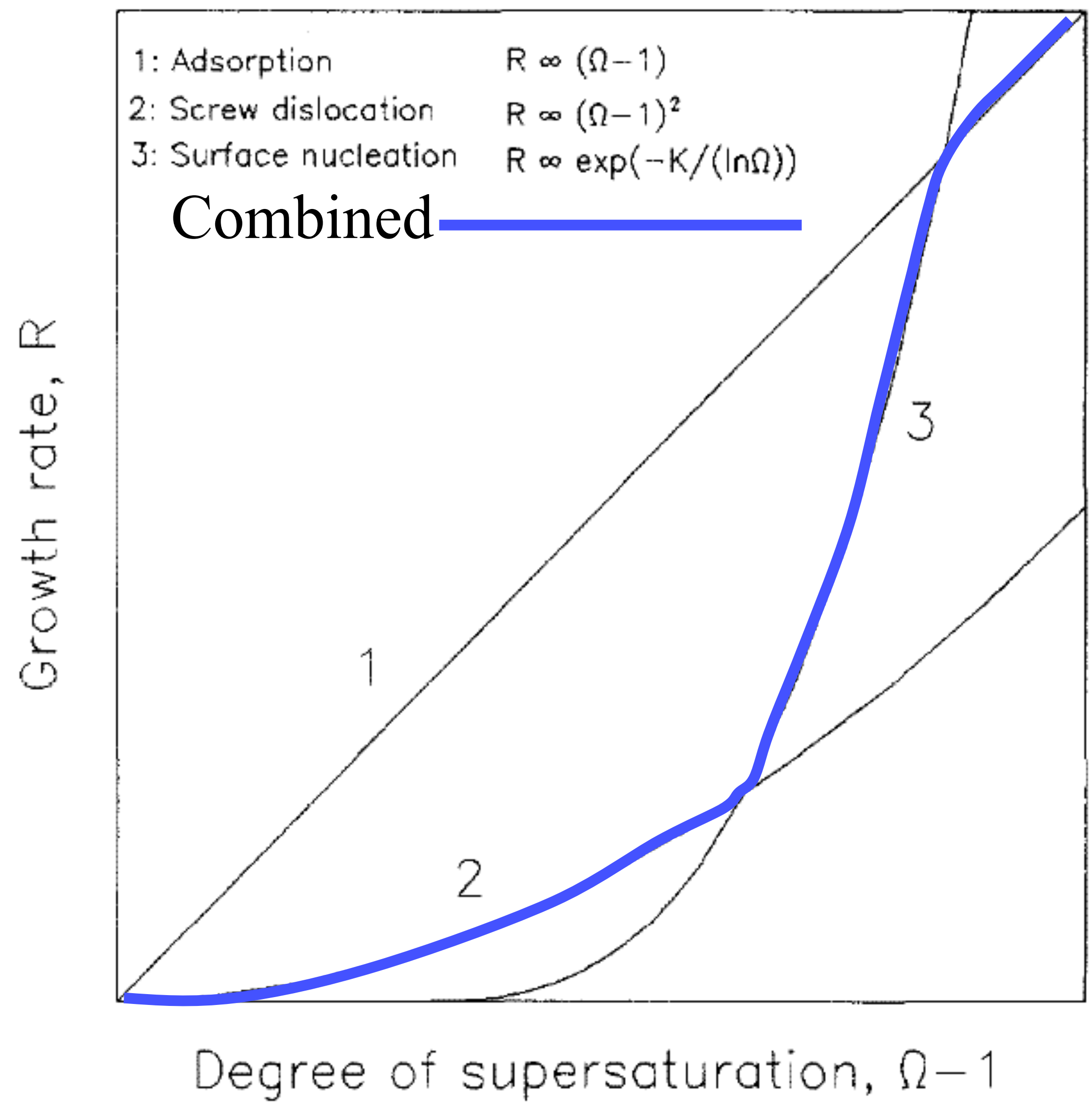
$\Omega = [\Pi(a_i^{\nu})]/K_{sp}$ (saturation ratio)

a_i^{ν} is the activity of component i with stoichiometry ν

K_{sp} = solubility product

- Also, Ostwald Ripening, Ostwald Step Rule
- Colloid filtration? Biomass growth?

Precipitation Kinetics



From Shiraki and Brantley (1995, GCA, vol. 59, pp. 1457-1471).

Precipitation Kinetics and Sr^{2+} sequestration: Experimental Approach

- Goals:
  - Test growth rate functions – apply in models
  - Test influence of ion ratios and modifiers
  - Morphologies, modes, products – interpretive
  - Sr^{2+} uptake and speciation
- Method - constant composition
  - *Batch reactors*
  - *Seeding* – to confine the role of homogeneous nucleation
  - *Stirring* - maintain uniform concentrations and reduce the influence of diffusive transport to surface layers.
  - *Maintain chemical composition* (as opposed to "free drift") - to prolong the state of supersaturation.

Precipitation Kinetics: Relevant to Field?

- Will these relationships help predict what happens in the field?
  - Subsurface mixing zones are not stirred reactors. Diffusion will influence precipitation kinetics and, subsequently, distributions of saturation states.
  - Relative rate at which solutes are replenished or consumed – can result in non-stoichiometric, varying ion ratios
    - $R = k_f(Ca^{2+})^p(CO_3^{2-})^q - k_b$ (Zhong and Mucci, 1993, GCA, vol. 57; Lin and Singer, 2005, GCA, vol. 69)

Pre-modeling: Simulating pore-scale precipitation using Smoothed Particle Hydrodynamics

- **Lagrangian, gridless, particle-based**
- **Used to establish a basis for parameters and conceptual basis for continuum approach**
  - Continuity: $d\rho / dt = \rho \nabla \cdot \mathbf{v}$
  - Conservation of momentum:
    $$d\mathbf{v} / dt = 1/\rho \nabla P + \mu / \rho \nabla^2 \mathbf{v} + \mathbf{F}^{ext}$$
  - Diffusion/reaction:
    $$dC^A / dt = D_A \nabla^2 C^A - k_{AB} C^A C^B$$
    $$dC^B / dt = D_B \nabla^2 C^B - k_{AB} C^A C^B$$
    $$dC^C / dt = D^C \nabla^2 C^C + k^{AB} C^A C^B$$
- **Precipitation of A and B via $C_{intermediate}$**

Hypothetical intermediate:

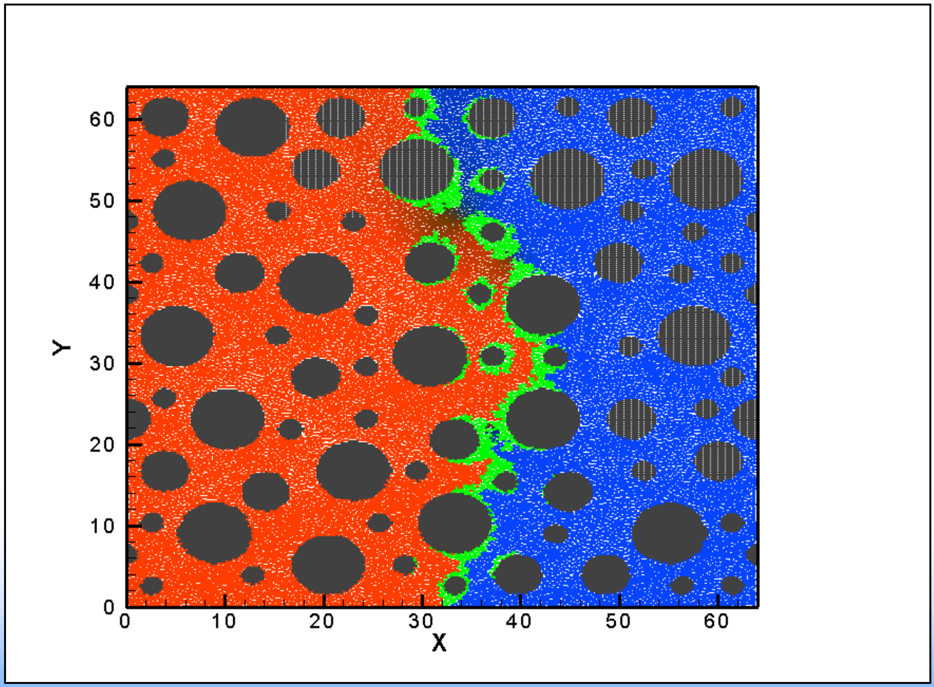
$A + B = C_{intermediate}$

$C_{intermediate} = C_{solid}$, driven by $(C - C_{eq})$

Irreversible formation of $C_{intermediate}$:

$$dC^A / dt = D_A \nabla^2 C^A - k_{AB} C^A C^B$$

Irreversible formation of $C_{intermediate}$:



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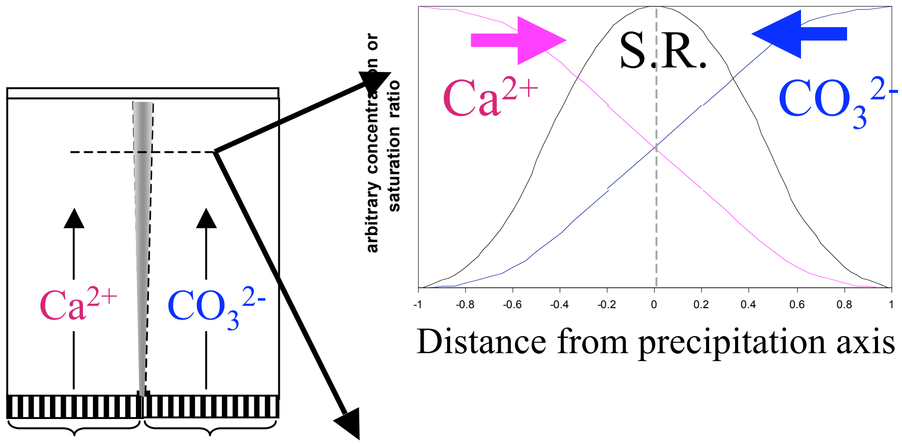
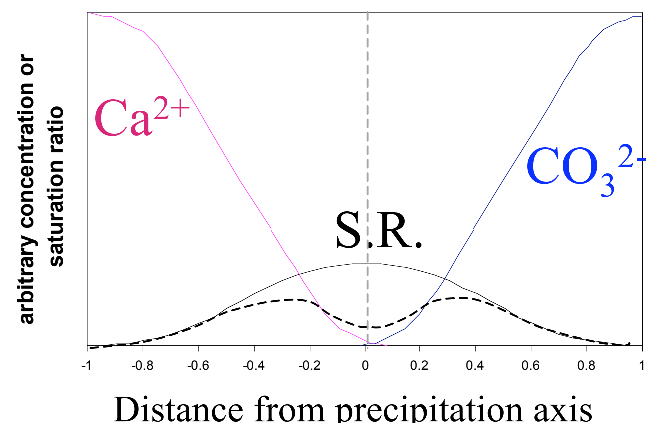
- **Initial Saturation index**



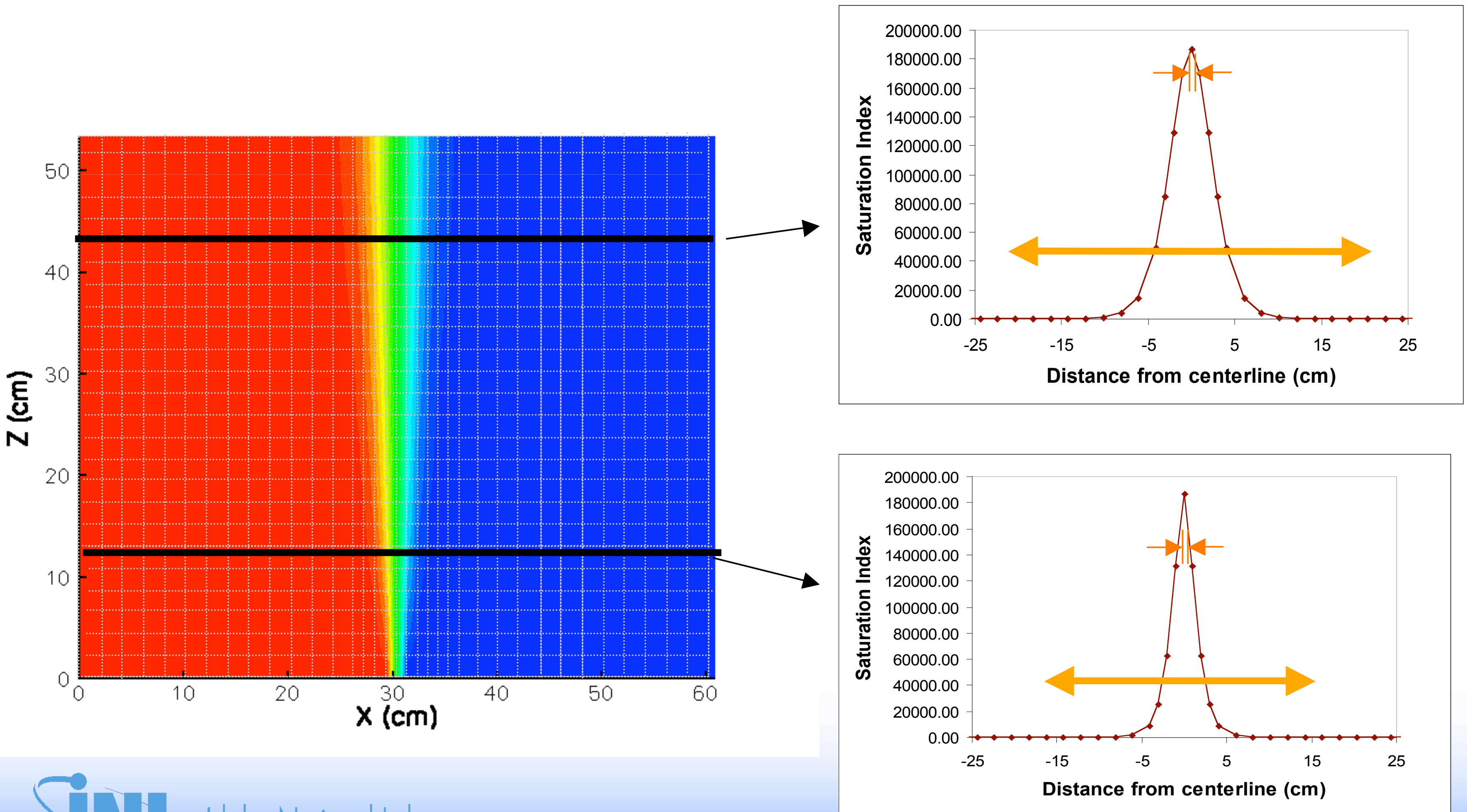
- **Saturation index during precipitation**



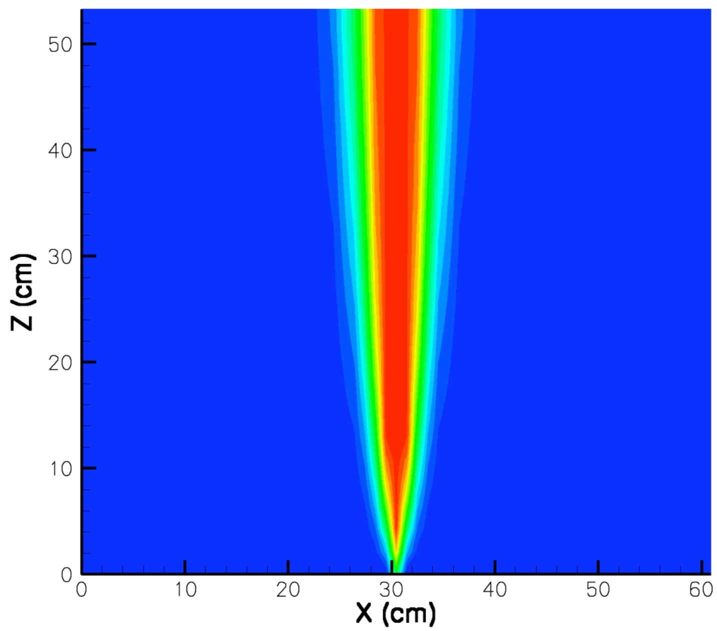
- **Steady-state condition at solution-solution interface**
  - **Preservation of less stable solid phases**
  - **Co-existence of multiple phases**

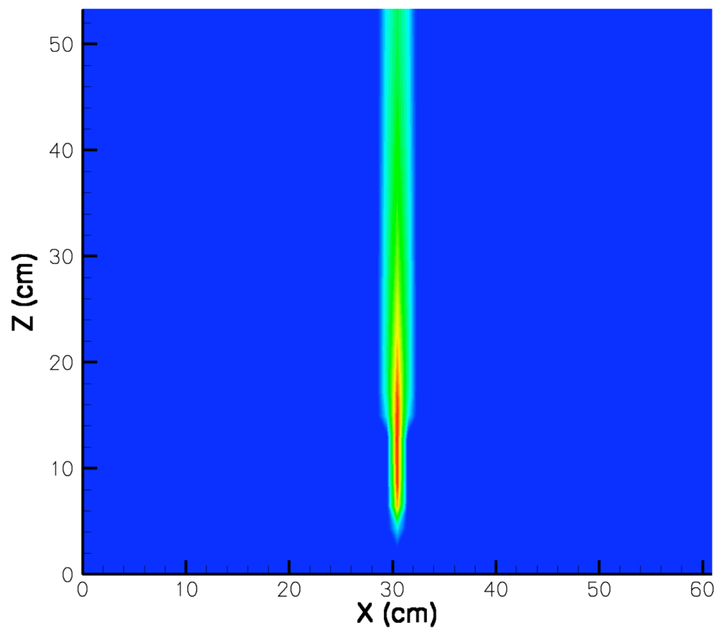
- **Flow variations**
  - **Velocities and ratios**
  - **Changing map of Damköhler (reaction rate vs. advection), and Peclet (advection vs. diffusion) numbers**

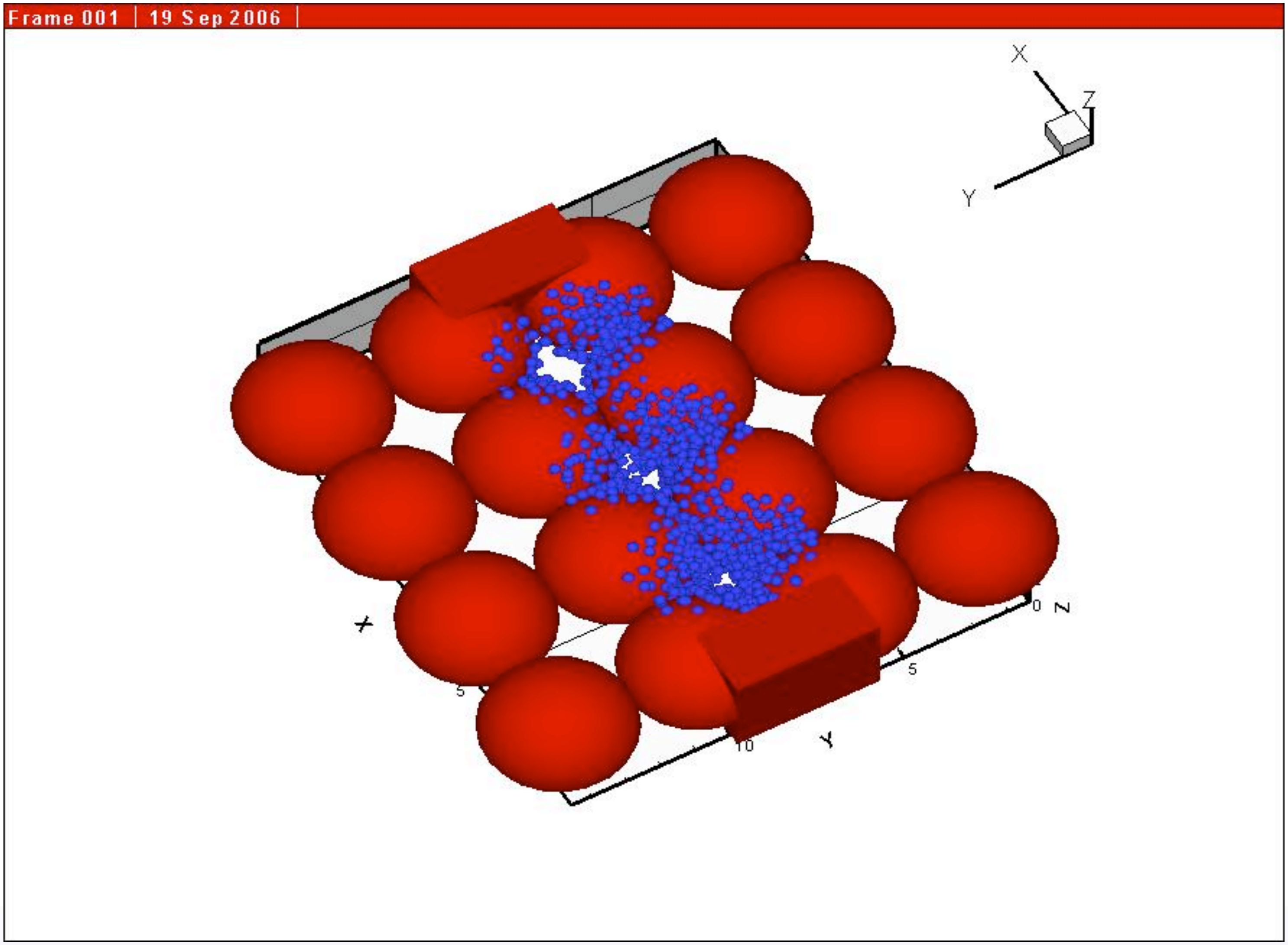
Continuum-scale simulation: mixing



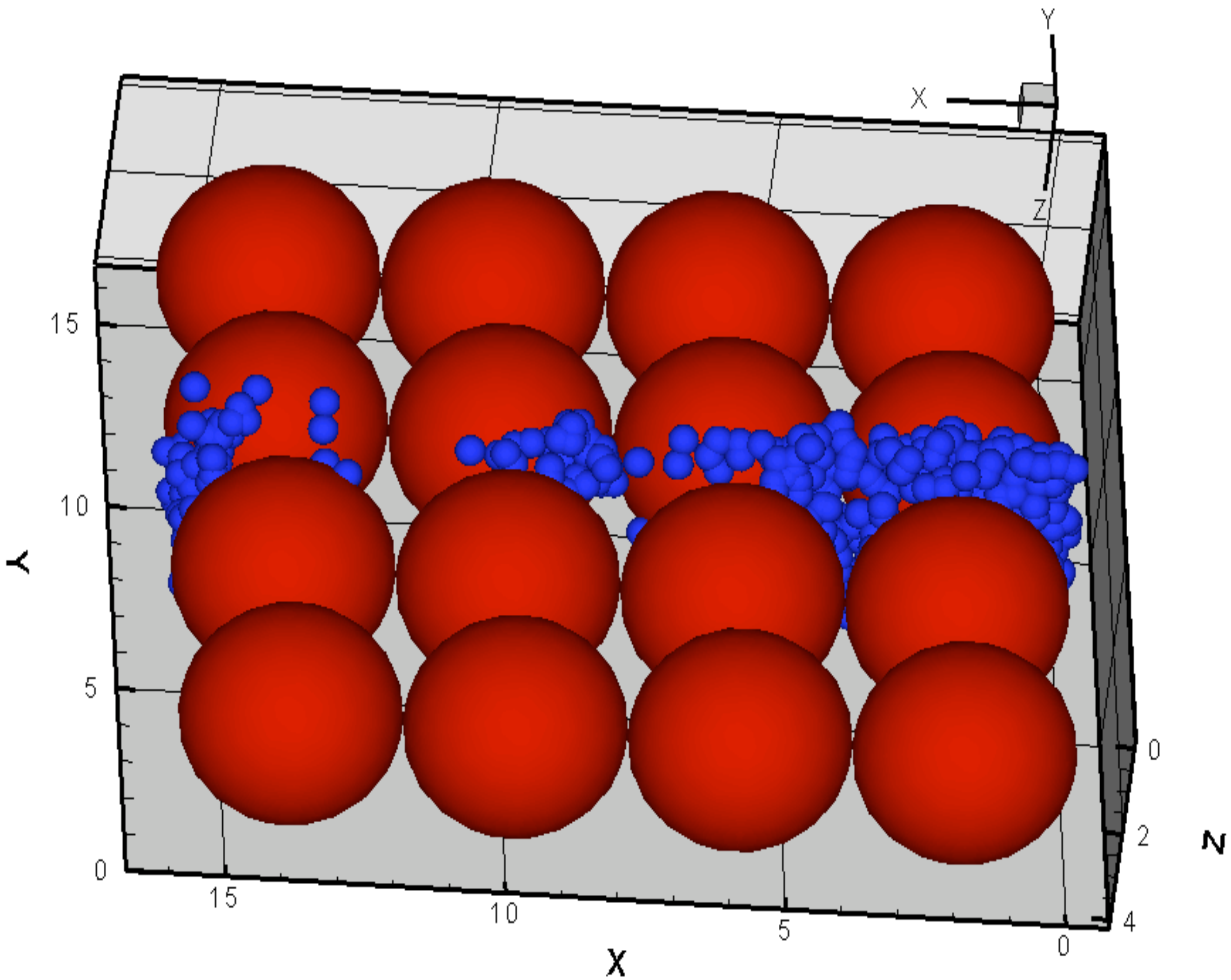
Mixing without and with precipitation

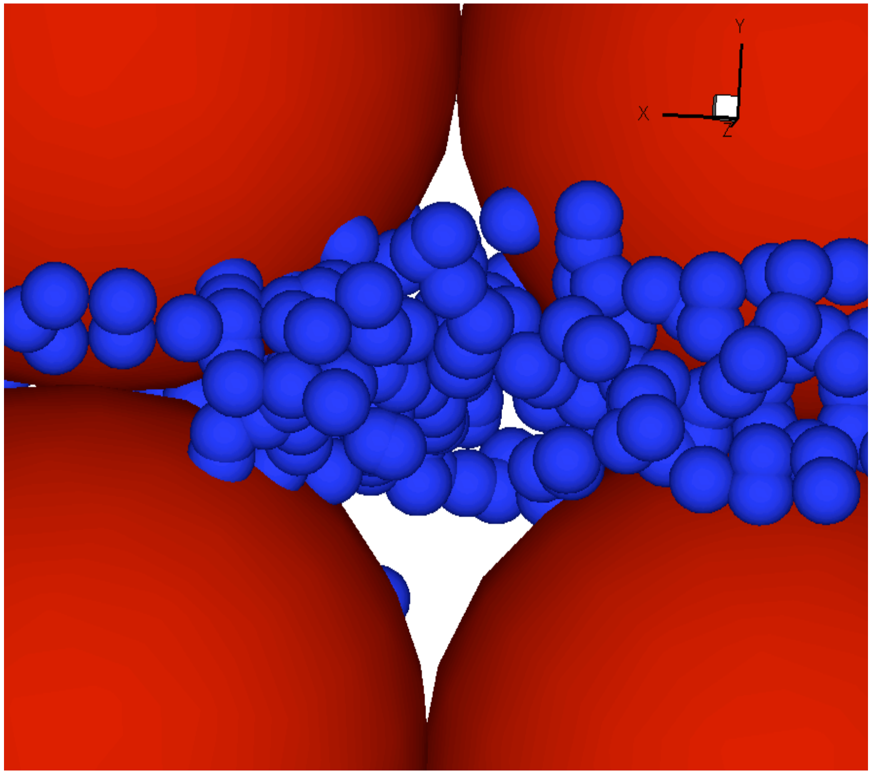


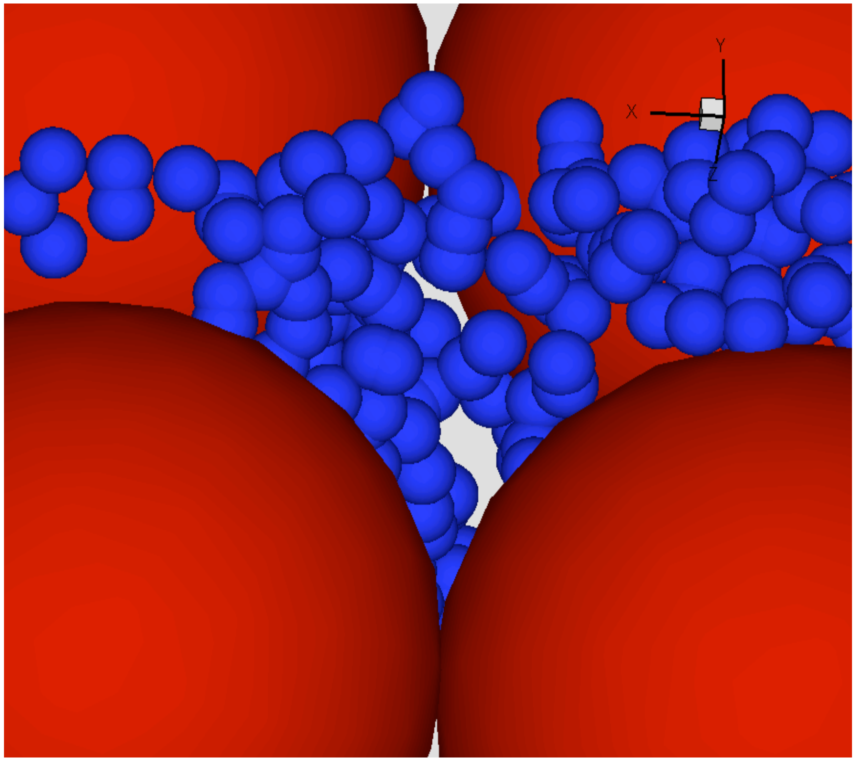




Frame 001 | 19 Sep 2006
X
Y
Z
5
10
5
0


Y
X
Z
15
10
5
0
Y
15
10
5
0
X
0
2
4
Z


Y
X
Z


Y
X
Z

Presentations, Publications:

Redden, G. and A. M. Tartakovsky (2006). Merging Experiments, Sensing, and Modeling for Predicting Coupled Biogeochemical Process Behavior Posters. American Geophysical Union 2006 Fall Meeting, San Francisco, American Geophysical Union.

Redden, G. D., Y. Fang, T. Scheibe, A. Tartakovsky, D. T. Fox, T. A. White, Y. Fujita and M. E. Delwiche (2005). Calcium carbonate precipitation along solution-solution interfaces in porous media. American Geophysical Union 2005 Fall Meeting, San Francisco, CA.

Redden, G. D., Y. Fang, T. Scheibe, A. Tartakovsky, D. T. Fox, T. A. White, Y. Fujita and M. E. Delwiche (2005). "Calcium carbonate precipitation along solution-solution interfaces in porous media." EOS Trans. AGU **86**(52): Abstract B33C-1042.

Redden, G. D., Y. Fang, T. Scheibe, A. M. Tartakovsky, D. T. Fox and T. A. White (2006). Metal precipitation and mobility in systems with fluid flow and mixing: Illustrating coupling and scaling issues. American Chemical Society, 231st ACS National Meeting, Atlanta, GA, American Chemical Society.

Redden, G. D., Y. Fang, T. D. Scheibe, A. M. Tartakovsky, D. T. Fox, Y. Fujita and T. A. White (2006). Fluid Flow, Solute Mixing and Precipitation in Porous Media. INRA 2006 Environmental Subsurface Science Symposium, Moscow, ID.

Scheibe, T. D., Y. Fang, A. M. Tartakovsky and G. Redden (2006). Hydrogeologic controls on subsurface biogeochemistry: field-scale effects of heterogeneous coupled physical and biogeochemical processes. 2006 Philadelphia Annual Meeting (22–25 October 2006). Geological Society of America. Philadelphia, Geological Society of America.

Scheibe, T. D., A. M. Tartakovsky, Y. Fang and G. D. Redden (2006). Models of Coupled Flow, Transport and Mineral Precipitation at a Mixing Interface in Intermediate-Scale Experiments. American Geophysical Union 2006 Fall Meeting, San Francisco, American Geophysical Union.

Scheibe, T. D., A. M. Tartakovsky, G. Redden, P. Meakin and Y. Fang (2006). Pore-scale simulations of reactive transport with smoothed particle hydrodynamics. Society for Industrial and Applied Mathematics Annual Meeting, Boston, MA.

Tartakovsky, A., T. Scheibe, G. Redden, Y. Fang, P. Meakin and P. Saripalli (2006). Smoothed particle hydrodynamics model for pore-scale flow, reactive transport and mineral precipitation. CMWR XVI - Computational Methods in Water Resources conference, XVI International Conference, Copenhagen, Denmark.

Tartakovsky, A., T. Scheibe, G. Redden and P. Meakin (2006). "Pore-scale smoothed particle hydrodynamics model of the mixing induced precipitation.", submitted to Water Resources Research

Tartakovsky, A. M., T. D. Scheibe, P. Meakin, G. Redden and Y. Fang (2006). Multiscale Lagrangian Particle model for Reactive Transport and Mineral Precipitation in Porous Media. American Geophysical Union 2006 Fall Meeting, San Francisco, American Geophysical Union.

Tartakovsky, A. M., T. D. Scheibe, G. Redden, Y. Fang, P. Meakin and K. P. Saripalli (2006). Smoothed particle hydrodynamics model for pore-scale flow, reactive transport and mineral precipitation. XVI International Conference on Computational Methods in Water Resources, Copenhagne, Denmark.

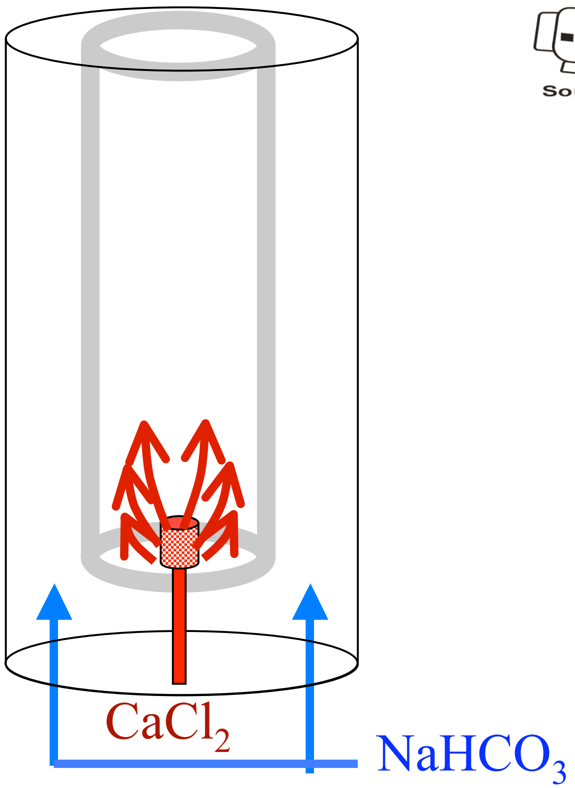
Connections:

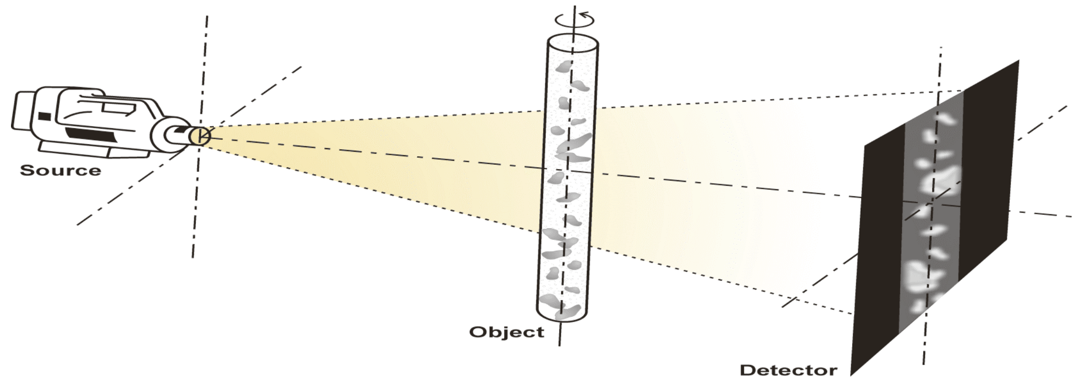
- Field Investigations of Microbially Facilitated Calcite Precipitation for Immobilization of Strontium-90 and Other Trace Metals in the Subsurface
  - University of Idaho; Robert W. Smith, PI

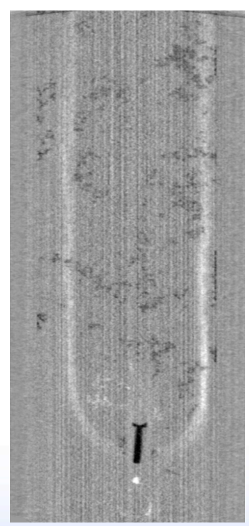
- Hybrid Numerical Methods for Multiscale Simulations of Subsurface Biogeochemical Processes
  - PNNL; Tim Scheibe, PI

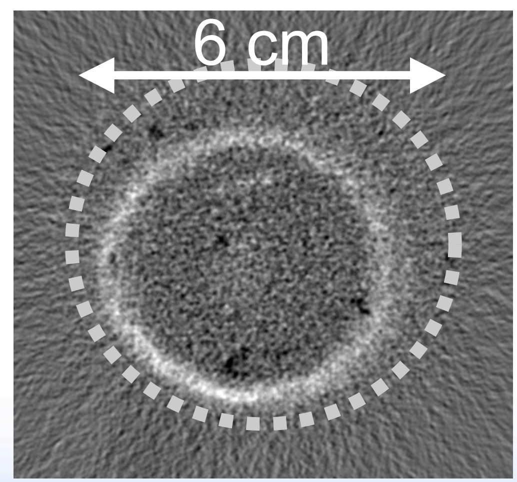
- Collaboration opportunities for:
  - Microbial characterization methods
  - Geotechnical properties

Parallel flow: mixing and precipitation at a solution-solution interface, 3-D, X-ray tomography







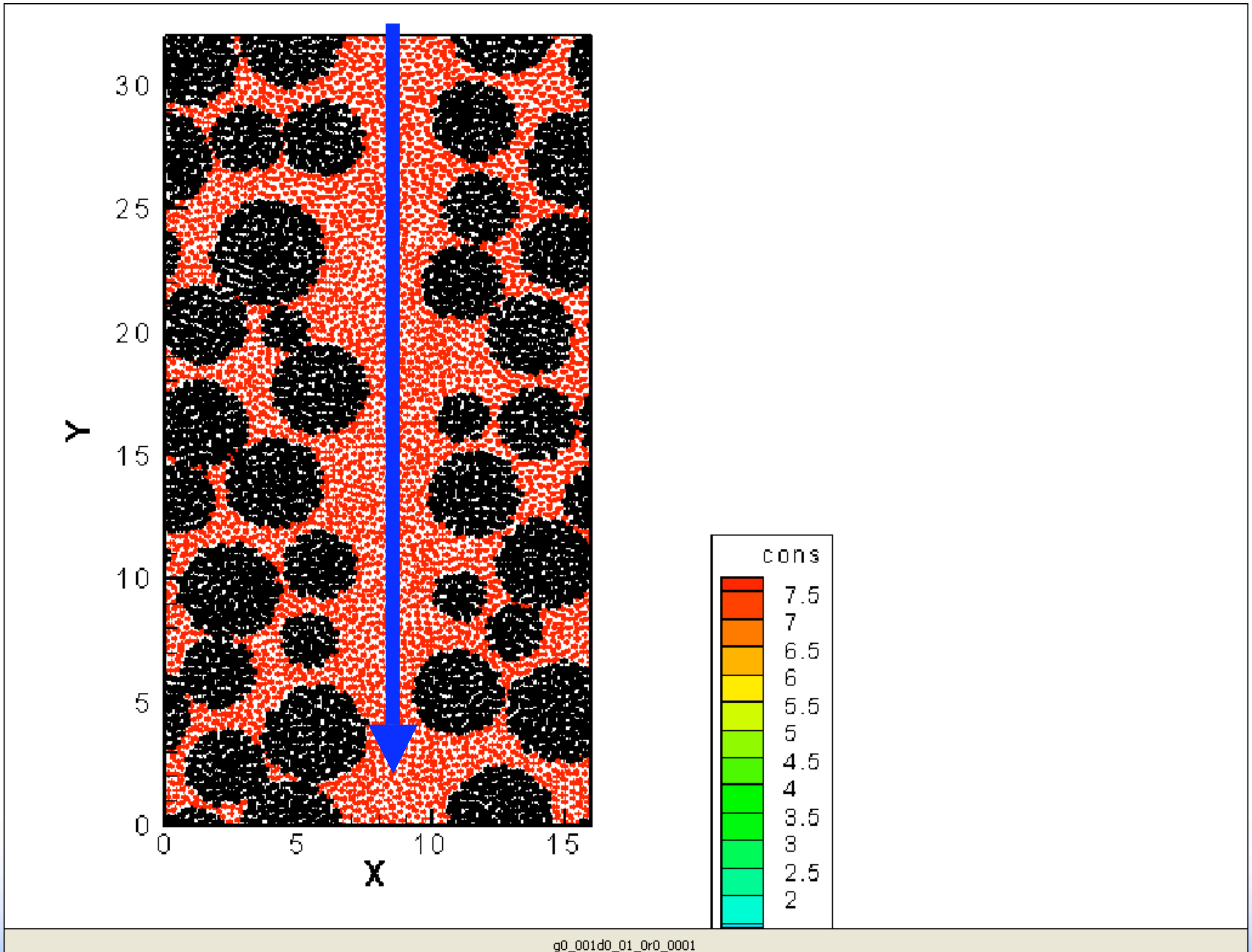


Calcium carbonate

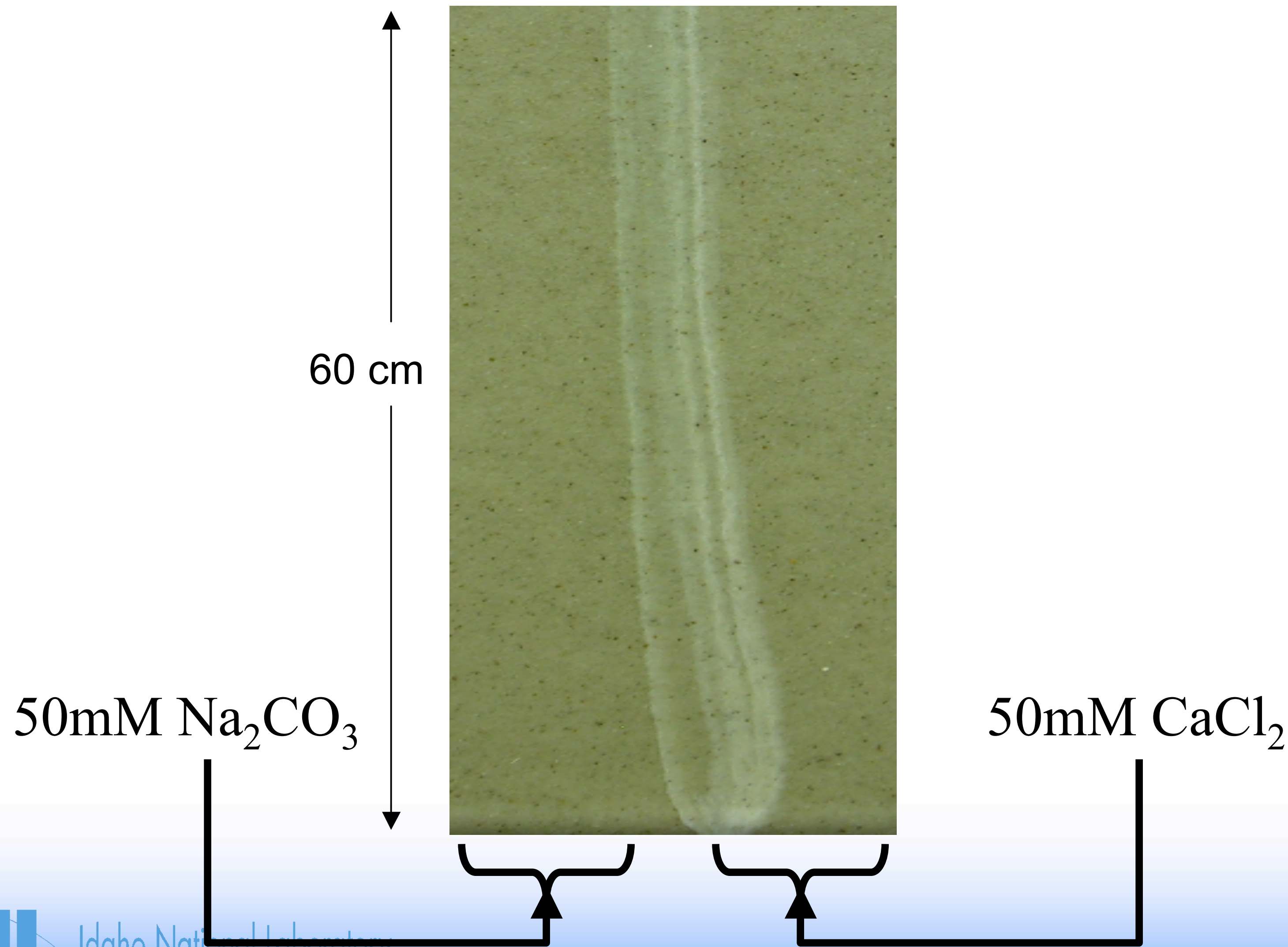
Inner perimeter of column

Injection of a supersaturated solution

Direction of Flow

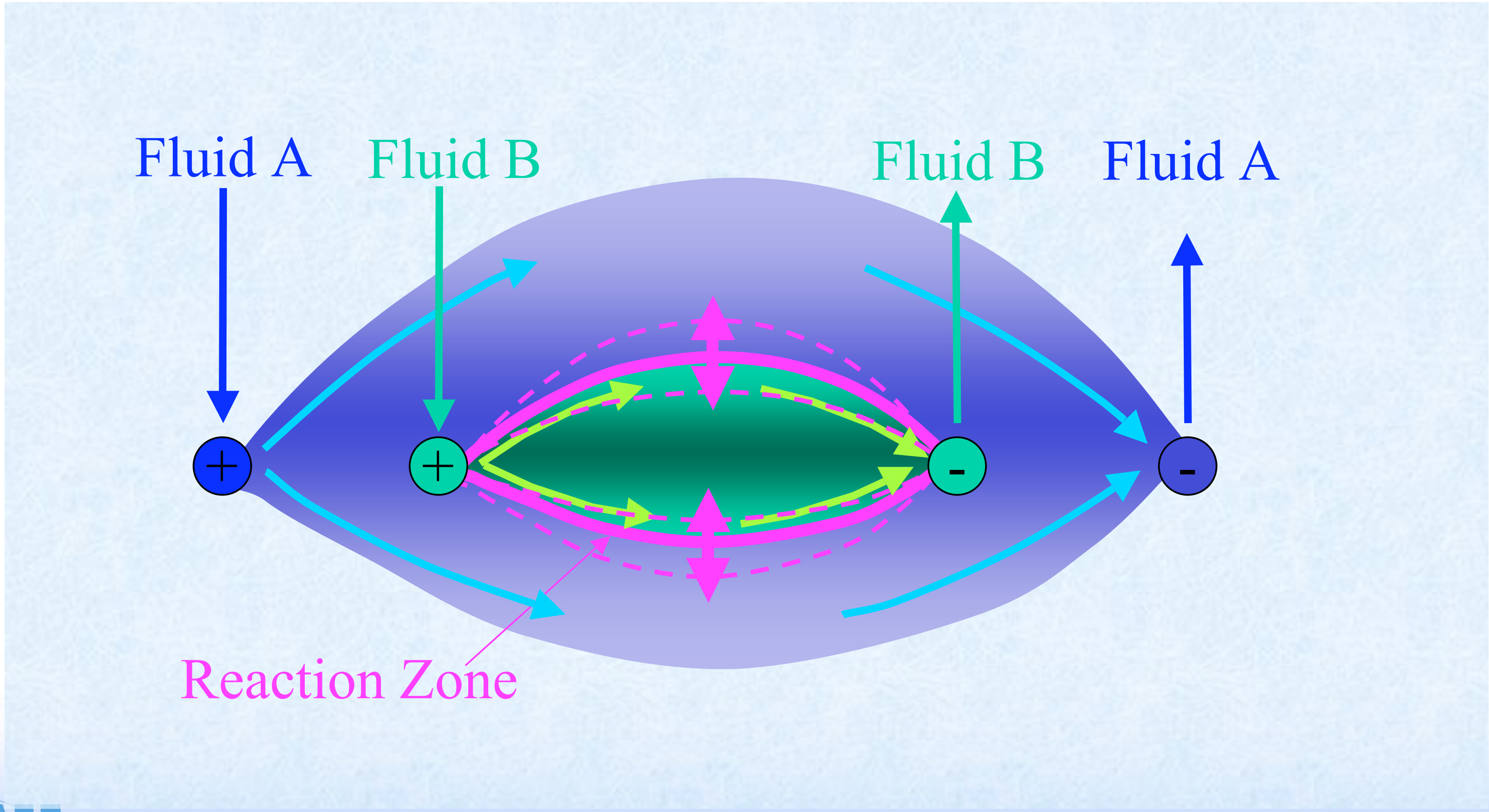


Propagation of calcium carbonate



Darcy Flow ~ 1cm/min

Application: nested dipole application



Example 1: *In situ* generation and mixing of reactants and geophysical monitoring

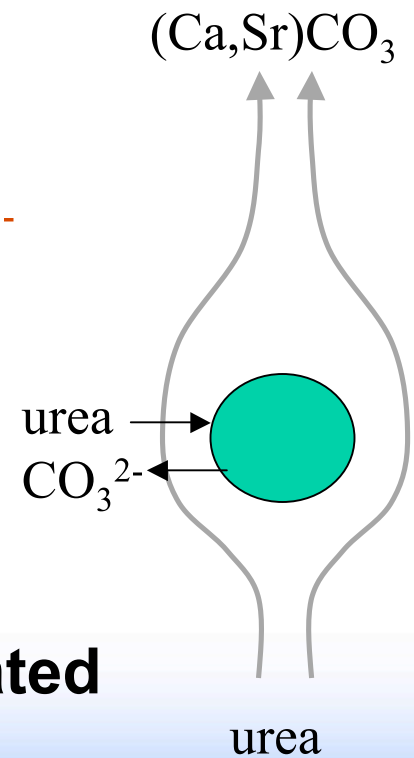
- **Application: Formation of calcium carbonate and co-precipitation (immobilization) of strontium**
- **Reactions (simplified):**

$$(NH_2)_2CO + 3H_2O \xrightarrow{\text{urease}} HCO_3^- + 2NH_4^+ + OH^-$$

$$HCO_3^- + Ca^{2+} \rightarrow CaCO_3(s) + H^+$$

$$HCO_3^- + Ca^{2+} + Sr^{2+} \rightarrow (Ca,Sr)CO_3(s) + H^+$$

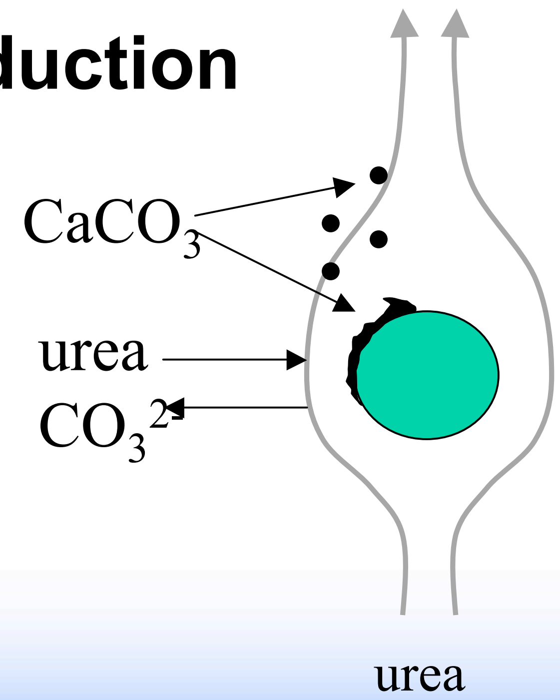
$$\mathbf{K_{sp}\ calcite = (Ca^{2+})(CO_3^{2-}) \sim 10^{-8.4}}$$



- **An abiotic analog to a microbially mediated process**

Questions:

- Impact of flow rate
  - Location of pecipitation
  - Efficiency of reaction = f(mixing)
- Impact of premeability reduction
  - Constant flow
  - Constant gradient



Ultimate Modeling Objective

Prefer a macroscopic continuum scale description

- Practical
- Can simulate larger systems

Perform pore-scale modeling to:

- Validate continuum approach
- Provide basis for empirical or effective parameters used in continuum approach

- → Reduce level of detail as much as possible

Continuum model

$$\mathrm{A} + \mathrm{B} = \mathrm{C}_{\mathrm{solid}}$$

Continuity: $d\rho / dt = \rho \nabla \cdot \mathbf{v}$

- Conservation of momentum:

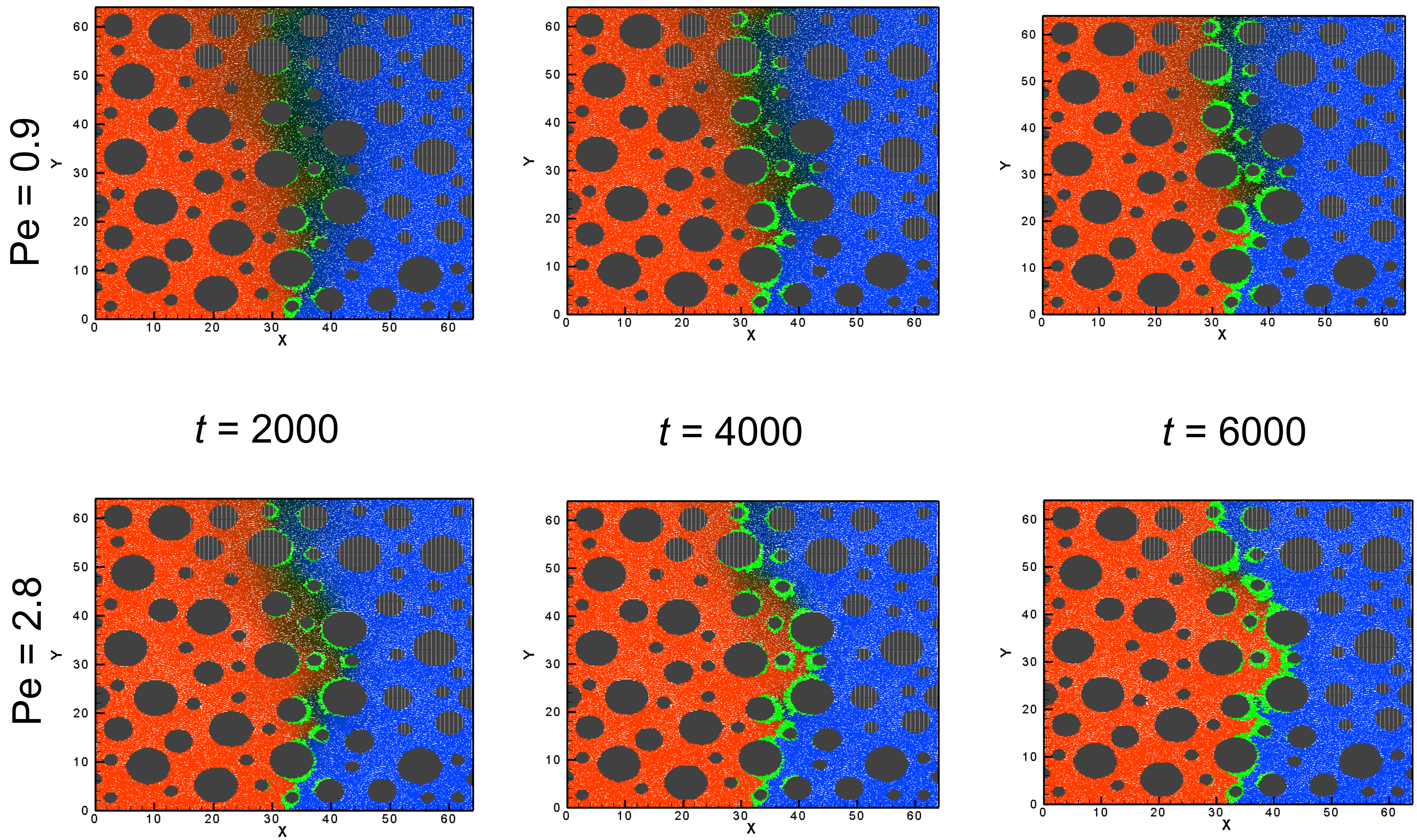
$$d\mathbf{v} / dt = 1 / \rho \nabla P + \mu / \rho \nabla^2 \mathbf{v} + \mathbf{F}^{ext}$$

- Diffusion/reaction:

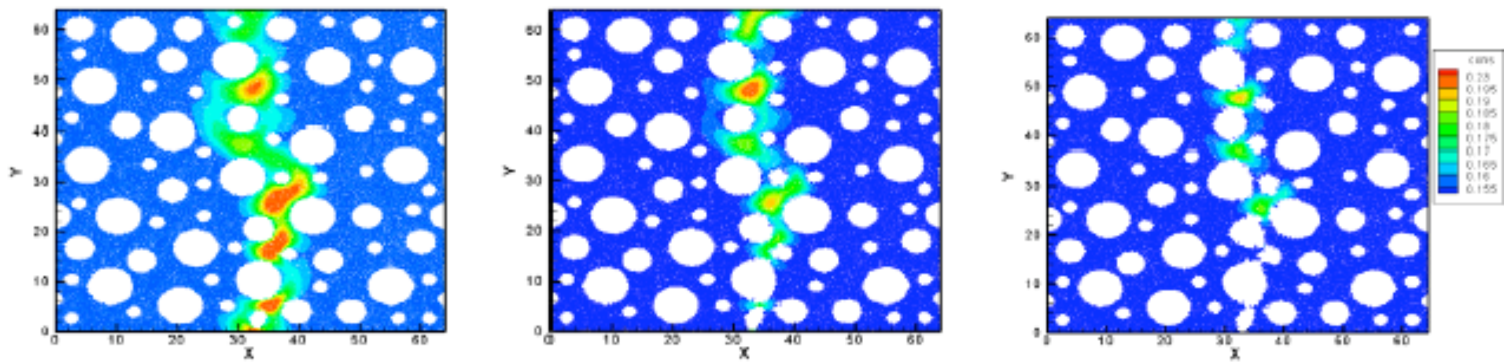
$$dC^A / dt = D_A \nabla^2 C^A - k_{AB} C^A C^B$$

$$dC^B / dt = D_B \nabla^2 C^B - k_{AB} C^A C^B$$

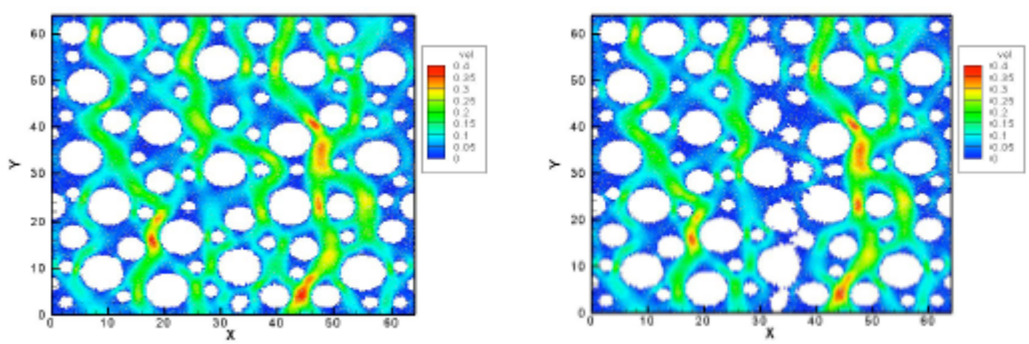
$$dC^C / dt = D^C \nabla^2 C^C + k^{AB} C^A C^B$$


Pe = 0.9
Pe = 2.8
t = 2000
t = 4000
t = 6000
X
Y

Supersaturation and velocity profiles

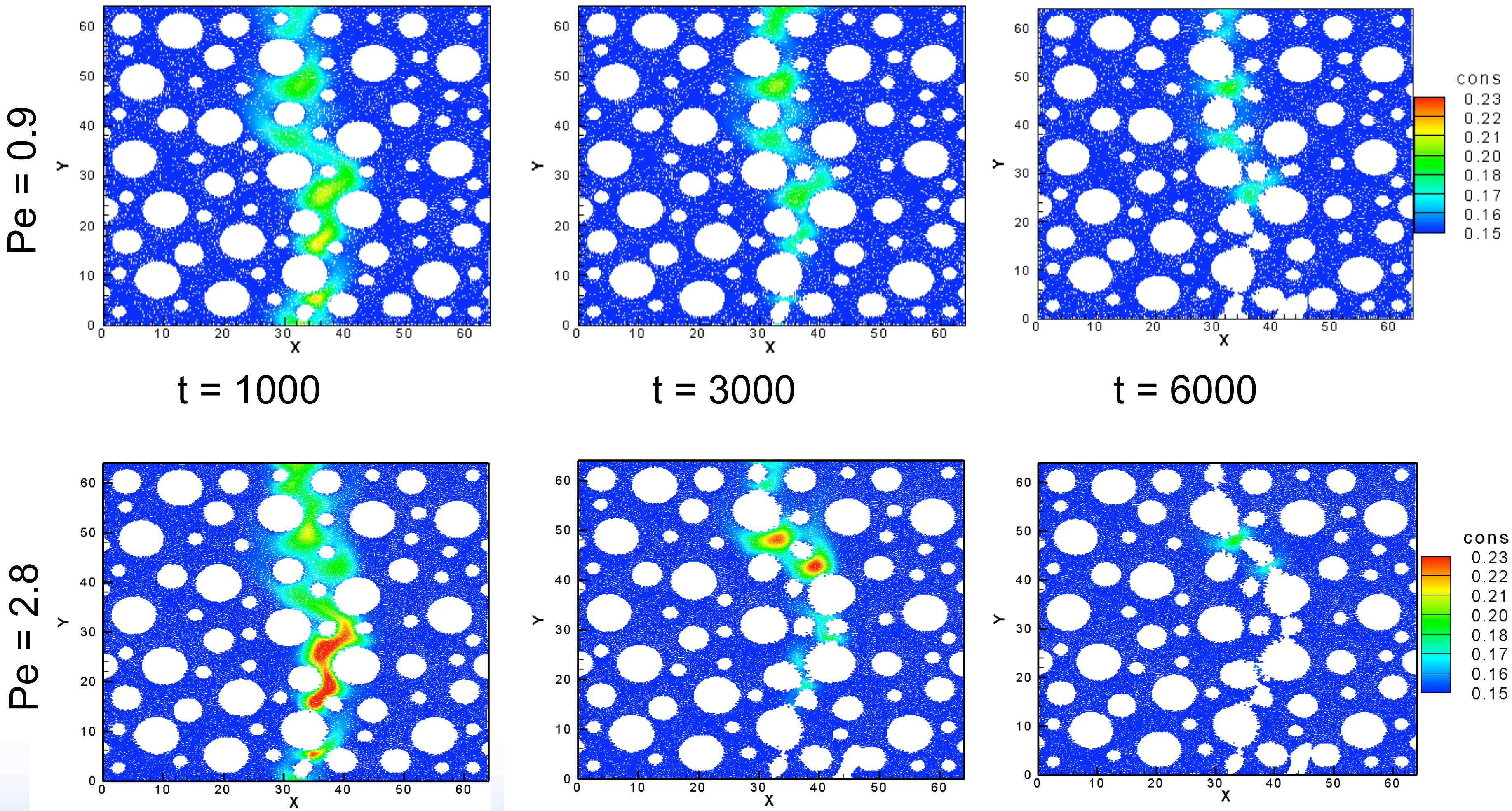


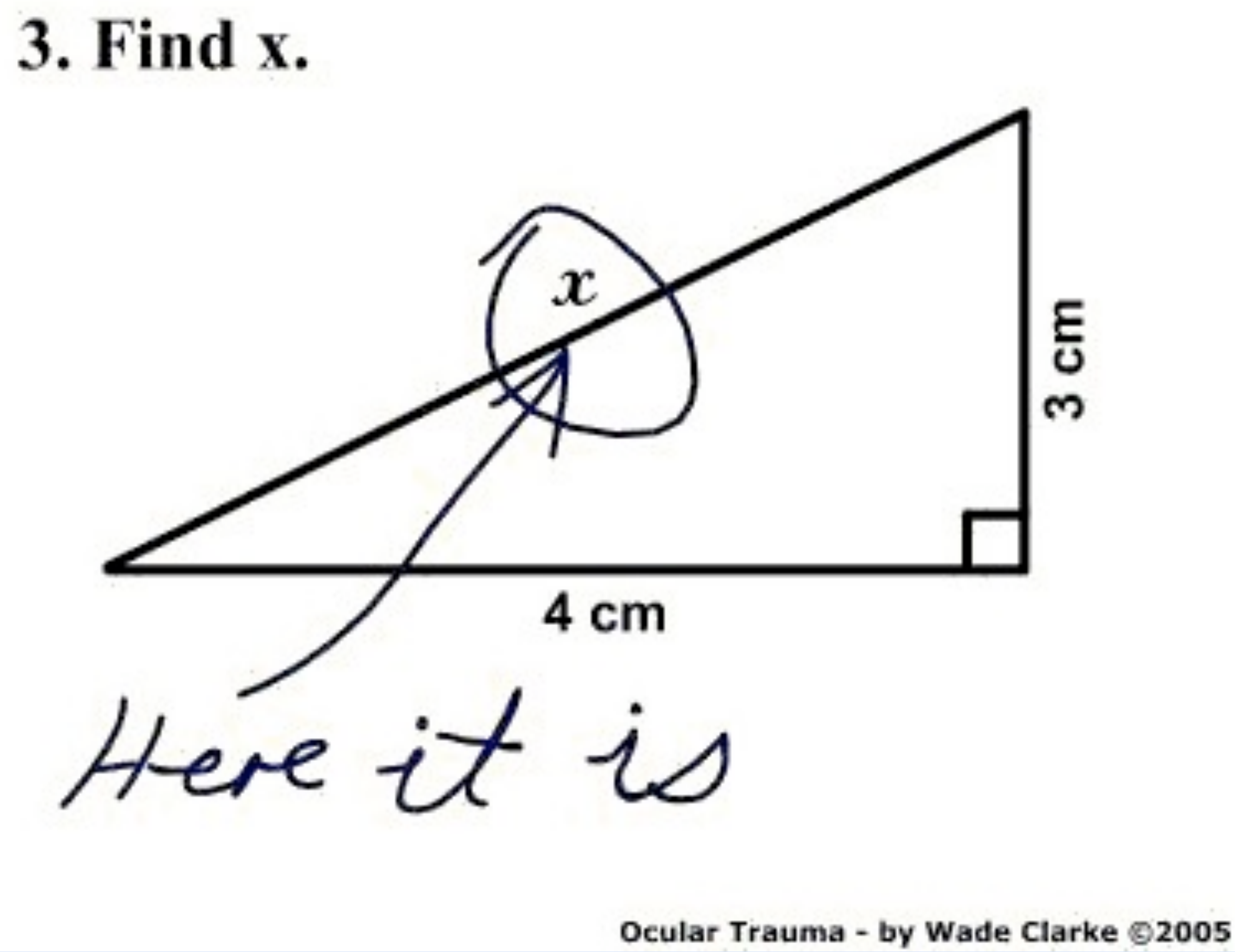
t = 1000 t = 3000 t = 6000



t=1000 *t*=6000

Impact of Peclet number (advection/diffusion)




3. Find x.
x
3 cm
4 cm
Here it is
Ocular Trauma - by Wade Clarke ©2005

After explaining to a student through various lessons and examples that:

$$\lim_{x \to 8} \frac{1}{x-8} = \infty$$

I tried to check if she really understood that, so I gave a different example. This was the result:

$$\lim_{x \to 5} \frac{1}{x-5} = 5$$

- anon