Brine films in pores during geologic CO_2 sequestration; hypothesized behavior and experimental update

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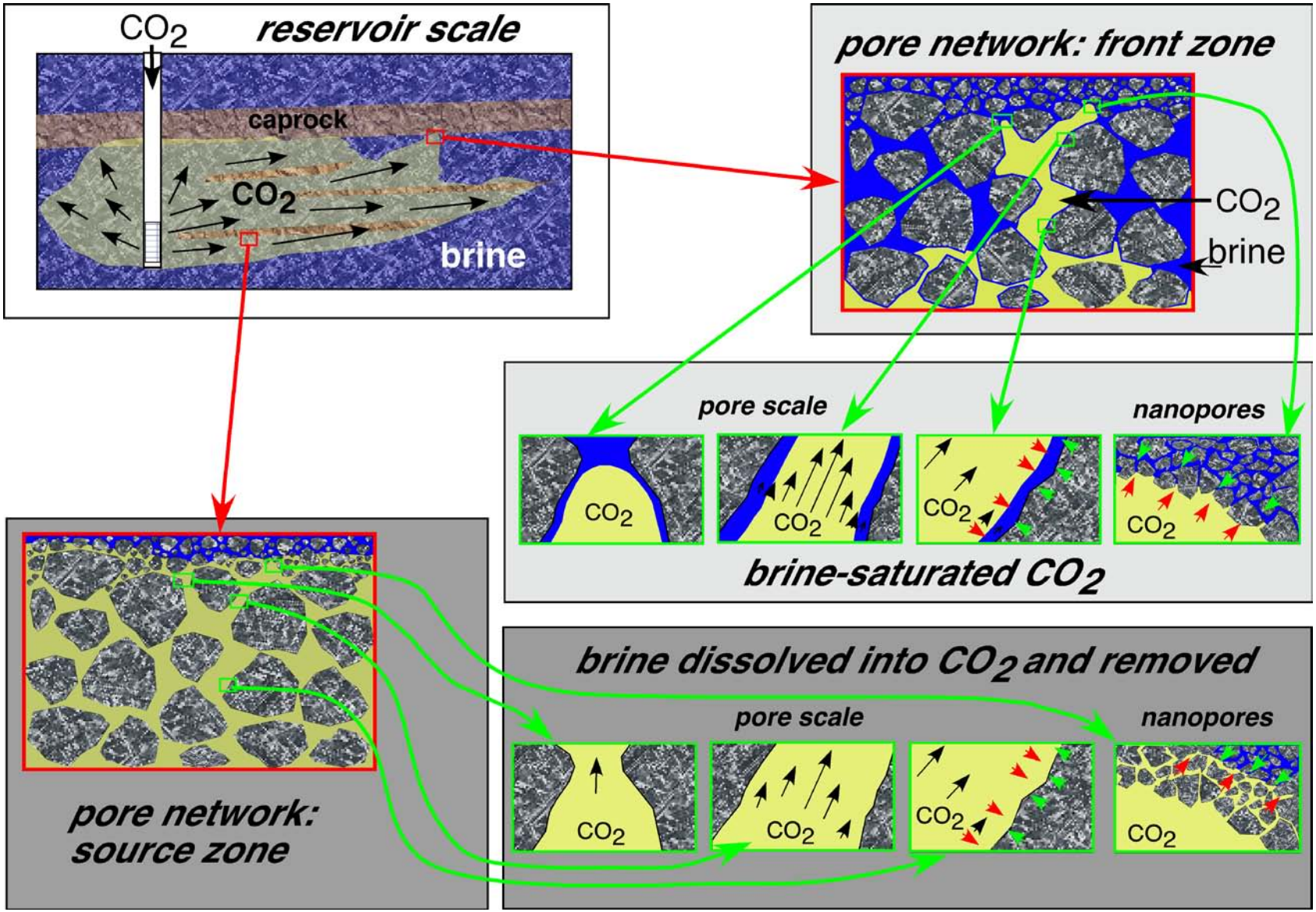
Workshop on Supercritical CO_2-Materials Interactions

Brookhaven National Laboratory. March 21-23, 2011

Many common minerals are hydrophilic, therefore brine films may persist within pores of deep formations used for geologic CO_2, sequestration.

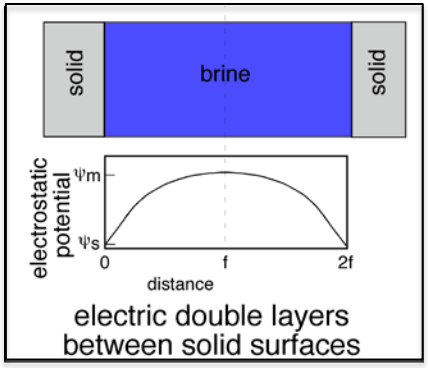


Categories of brine films

- Brine in nanopores
- Brine adsorbed on mineral surfaces
- Brine retained on mineral surfaces by capillarity

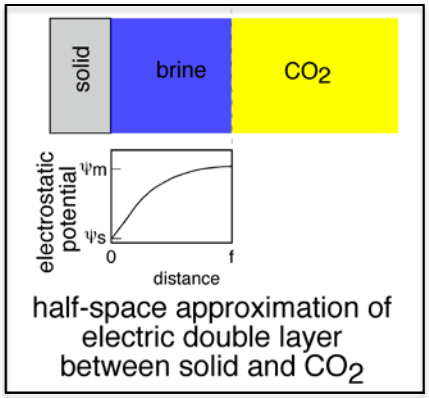
Common feature:
Strong interactions with interfaces

Brine films to be discussed in this presentation are those with direct interfacial contact with $scCO_2$.



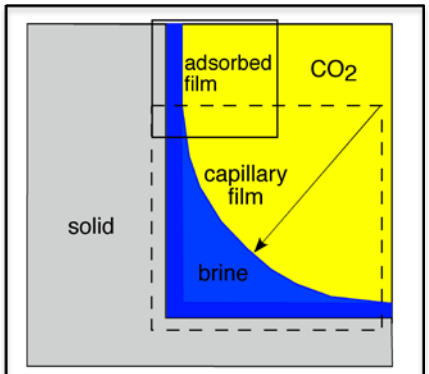
electric double layers between solid surfaces

nanopores



half-space approximation of electric double layer between solid and CO_2

planar surfaces

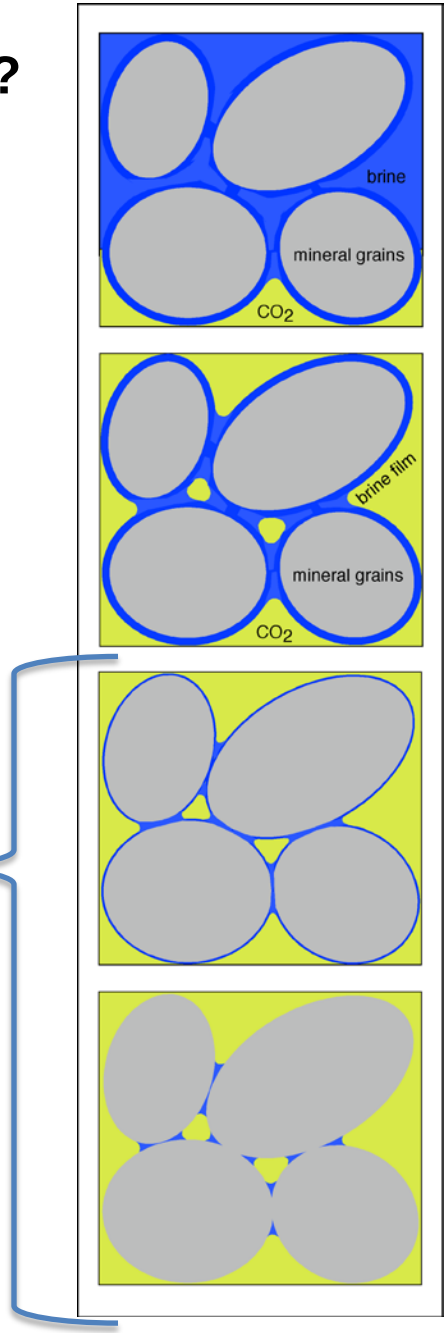


combined influences of adsorption and capillarity on CO_2-confined brine films

rough surfaces

Why are these brine films important to understand?

When CO_2 displaces brine from rock pores, films of residual brine may remain on mineral surfaces and mediate transport and reactions until they are depleted through dissolution into under-saturated CO_2, or displaced into local capillary minima.



Brine-wetted surface area within CO_2-invaded pores may be greatly changed, even with very small changes in brine saturation, depending on the stability of brine films.

- The extent to which mineral surfaces remain hydrated imposes controls on the extent of reactions at water-solid interfaces during CO_2 sequestration.

Factors Complicating Linkage of Basic Film Processes to the Field

- Heterogeneity and spatial variability of natural pore networks: Identify useful model systems from which general principles can be determined (rather than sample-specific results).

- High ionic strength of brines: Some conditions associated with $scCO_2$-brine films are beyond the limits of continuum treatments of electric double layers.

- Complex film topography: Films, when present, occur mostly on micro-topographically complex grain surfaces.

General Approach

- Identify hydraulic conditions (differential pressures between brine and CO_2 phases) where brine films could be present.

- Apply electric double layer and capillary film models to infer brine film properties.

- Experimentally measure brine film hydraulic properties.

    - Average film thickness versus brine chemical (matric, capillary, disjoining) potential.

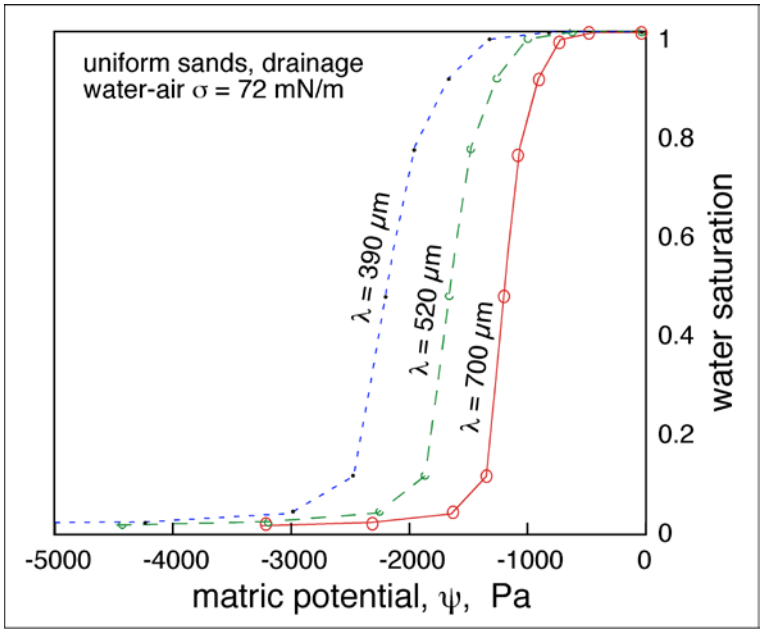
    - Transmissivity (hydraulic conductivity) of brine films.

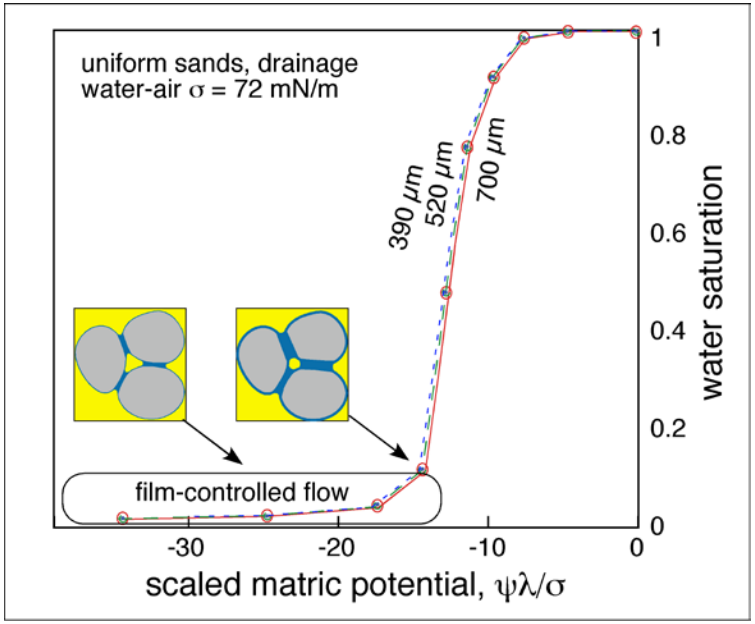
Estimating conditions for brine film formation using capillary scaling

Miller-Miller scaling with surface tension (σ) and grain-size (λ) predicts saturation versus matric (capillary, disjoining) potential (ψ) equilibrium between water and other immiscible fluids in geometrically similar porous media.

In homogeneous sands, drainage to scaled potentials $\psi\lambda/\sigma < -12$ leave the remaining water under film-controlled flow. Under these conditions, pores are drained, and pendular rings are stable.

Can capillary scaling be used to predict when brine films will coexist with $scCO_2$?





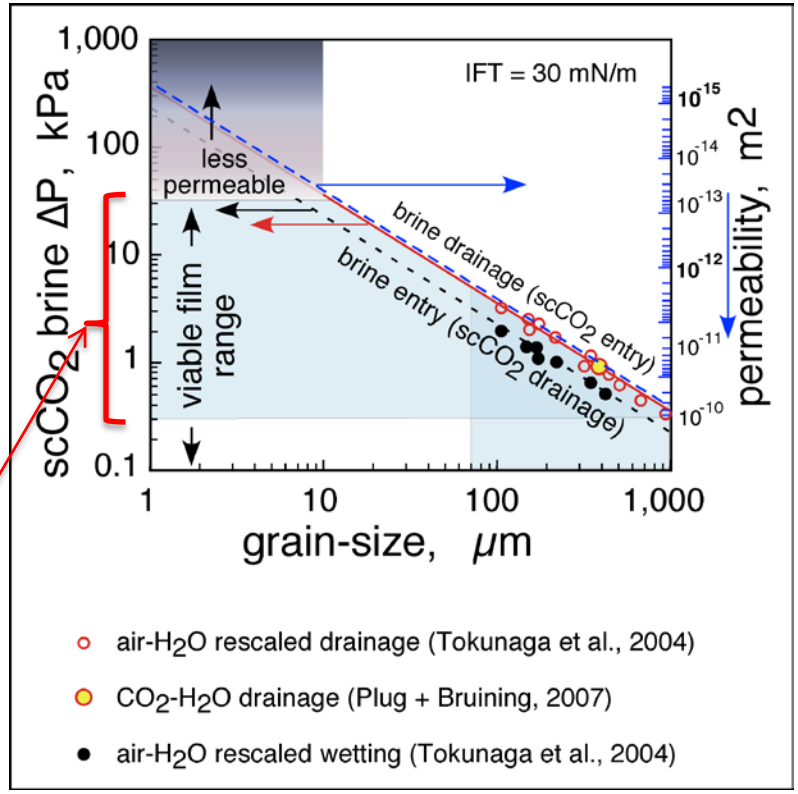
Scaling applied to predict ranges of capillary potentials for films

Abundant data supporting Miller-Miller scaling exist for water-air systems (some summarized in Tokunaga et al., 2004).

Results from Plug and Bruining (2007) indicate that capillary scaling may be used to identify ranges of capillary potential where brine films might be stable.

From Miller-Miller scaling, film capillary potentials will be in the range of ≈300 to ≈30,000 Pa during $scCO_2$ entry.

Much higher ΔP are associated with low permeability zones which exclude $scCO_2$ entry.

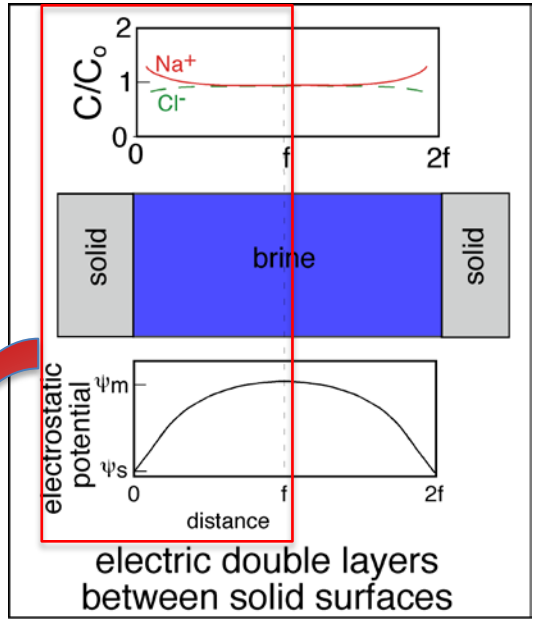


Predicting hydraulic properties of brine films within the capillary-constrained potentials

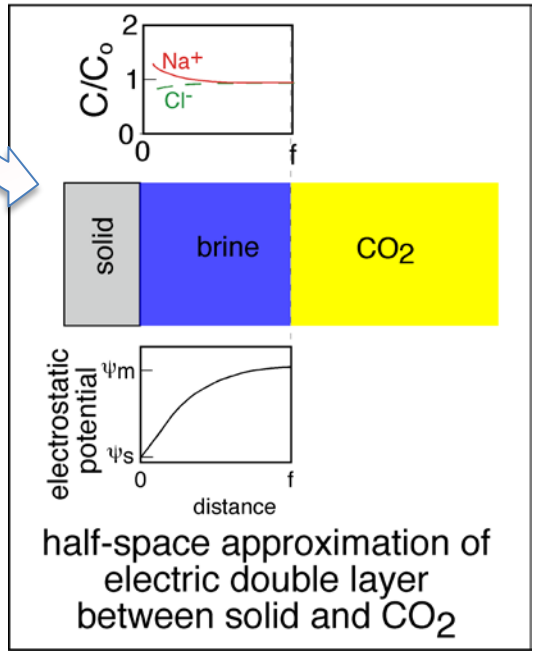
Film thicknesses only need to be determined for (matric, disjoining, capillary) potentials corresponding to desaturation of the reservoir pores (300–30,000 Pa).

Electric double layer models may provide useful constraints on brine film thicknesses on smooth surfaces (limiting case).

Langmuir (Science, 1938) developed a model for adsorbed water film thicknesses based on double layer pressure between identical solid surfaces. The model approximates adsorbed films as being half-spaces between opposing electric double layers.



electric double layers between solid surfaces



half-space approximation of electric double layer between solid and CO_2

Langmuir scaling within capillary limits

Below $\psi_c \approx -12\sigma/\lambda$, adsorbed films of low ionic strength have ψ and λ dependent thickness *f* predicted by our capillary-scaled Langmuir film equation to be

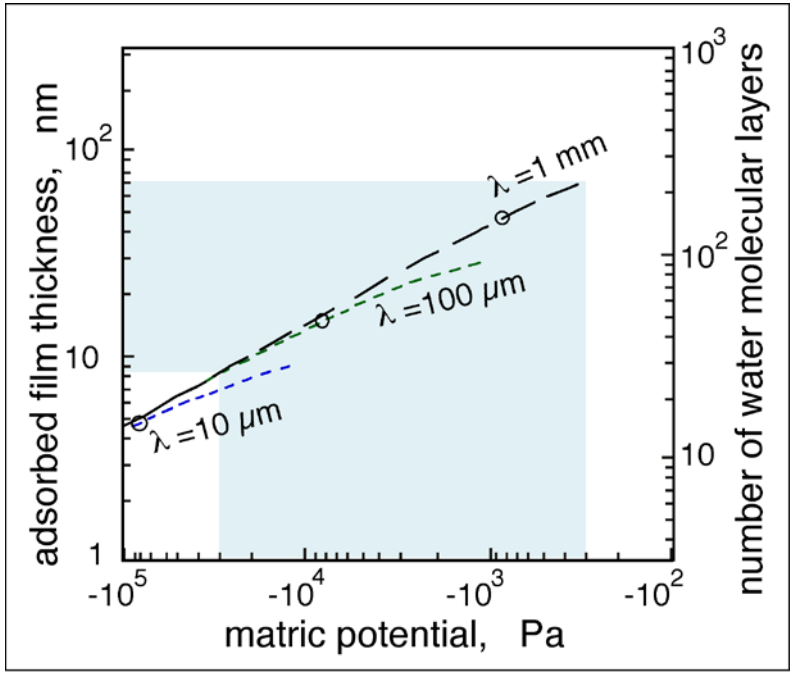
$$f = \sqrt{\frac{\varepsilon\varepsilon_0}{2}}\left(\frac{\pi k_B T}{ze}\right)\left(\frac{2\sigma}{\lambda} - \psi\right)^{-0.5}$$

where ε is the water dielectric, ε_o is the vacuum permittivity, k_B is the Boltzmann constant, T is the Kelvin temperature, z is the ion valence, and *e* is the electron charge (Wan & Tokunaga, Environ. Sci. Technol. 1997).

Capillary + Langmuir scaling: hydrostatics

- From Miller-Miller scaling, film capillary potentials will be in the range of ≈ 300 to ≈30,000 Pa during drainage ($scCO_2$ entry).

- In the Langmuir limit, film thicknesses for dilute 1:1 salt solutions are predicted to be in the range of 8 to 70 nm upon drainage. This is the <u>upper limit</u> of thickness for adsorbed films in permeable porous media.



(modified from Tokunaga, Water Resour. Res., 2009)

Some limitations of the Langmuir equation:

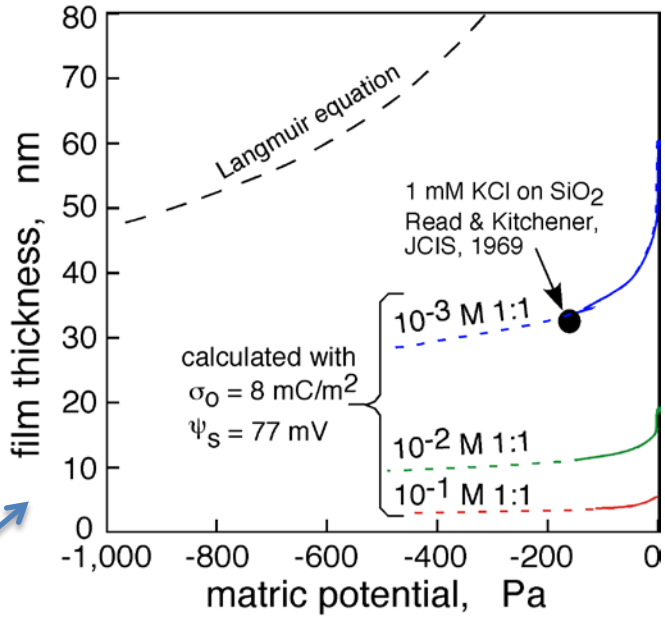
- Developed for dilute solutions, <u>unlike brines</u>.
- Assumes a high electrostatic potential at the water-solid interface, <u>unlike SiO_2</u>.

Getting a little closer to brines on weakly charged surfaces:

The "weak overlap approximation" of the Gouy-Chapman equation for pressure within opposing double layers, is only applicable for $f > \kappa^{-1}$,

$$f = -\frac{1}{2}\kappa^{-1}\ln\left(\frac{\varepsilon\varepsilon_o}{2\sigma_o^2}|\psi|\right)$$

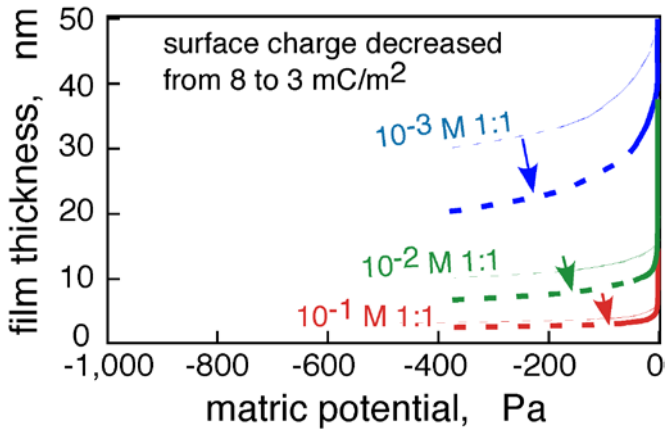
where σ_o is the surface charge density and κ^{-1} is the Debye length, $[\varepsilon\varepsilon_o kT/(2e^2z^2n_o)]^{1/2}$. However, it can be used to deduce impacts of salinity and surface charge over broader ranges of conditions.



- Higher salinity solutions substantially compress films.

- Decreased surface charge density is predicted to also compress aqueous films.

- Therefore, high salinity (brine) films on low charge density surfaces (quartz, especially at acidic pH) will be displaced by CO_2.



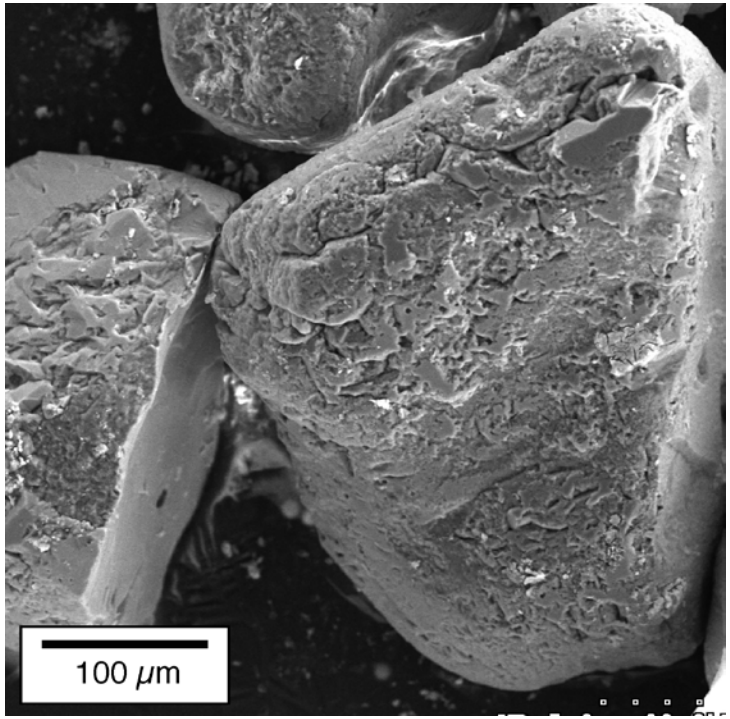
Grain surface microtopography enhances retention of wetting fluid phase by surface capillarity

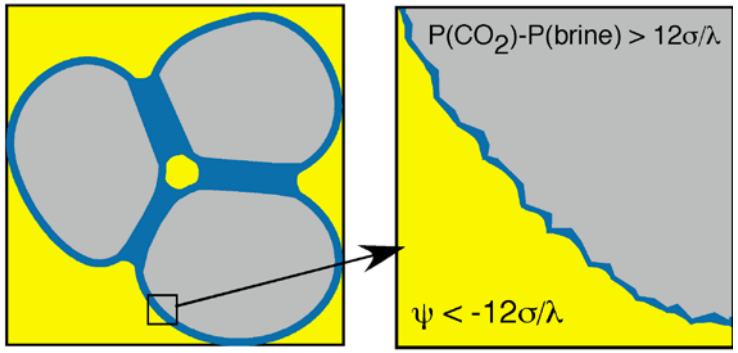
Smooth surface models provide lower limits for effective film thicknesses.

Films on natural mineral surfaces are stabilized by both adsorption and capillarity.

Therefore, potential-dependent retention of brine on rough surfaces is important to determine.

Grain size and capillary entry criteria (pore size) constrain upper roughness scale limit for capillary films.





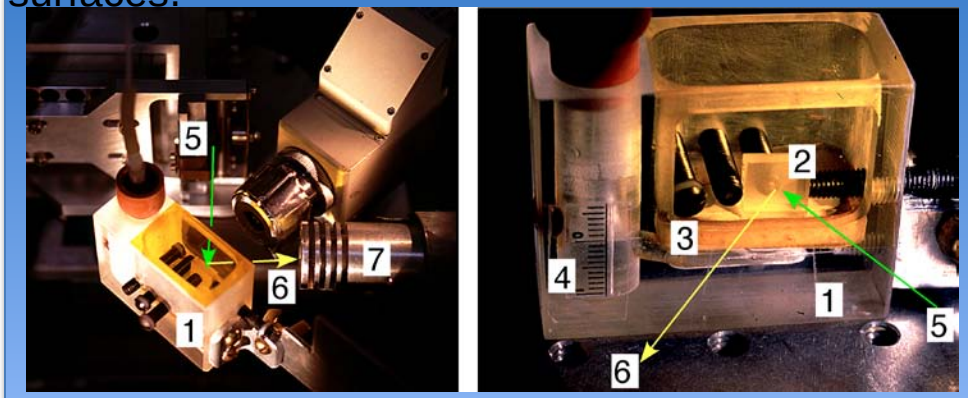
Requirements for measuring brine film hydraulic properties

- An approach that can be applied on variably rough surfaces.
- An approach that permits rapid equilibration of films to imposed ΔP.
- An approach that permits control of very small ΔP (10 Pa) relative to very large absolute P (10 MPa), i.e., $1{:}10^6$.

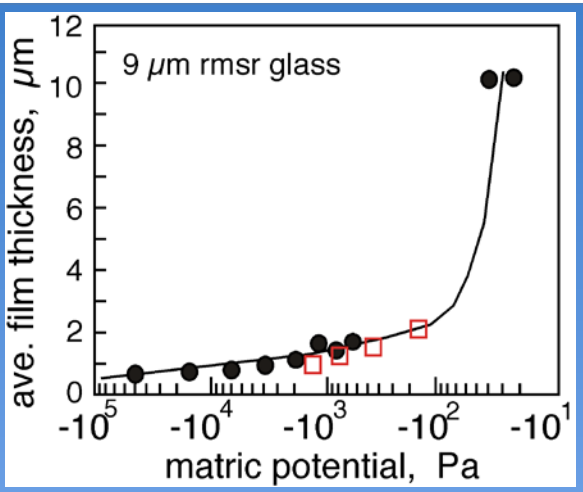
For other studies, we developed several experimental cells for measuring water film thicknesses on variably rough surfaces, under atmospheric pressure. These earlier designs helped in developing our high P film cell.

Measurements of films on variably rough surfaces

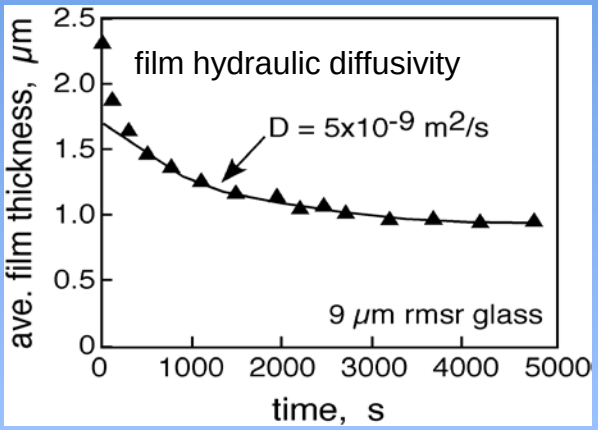
We adapted approaches from soil physics, combined with synchrotron X-ray fluorescence of solute tracers, to measure the film thickness dependence on matric potentials (pressure plate outflow-inflow). This earlier design was suitable for films on very rough surfaces.



Water film chamber, at beamline X26A, National Synchrotron Light Source. (1) sample chamber, (2) sample, (3) porous ceramic, (4) pressure-controlled tracer reservoir, (5) monochromatic X-ray beam, (6) fluorescent X-rays, (7) detector.



Film thickness vs. potential, on rough glass on using Se(VI) tracers.



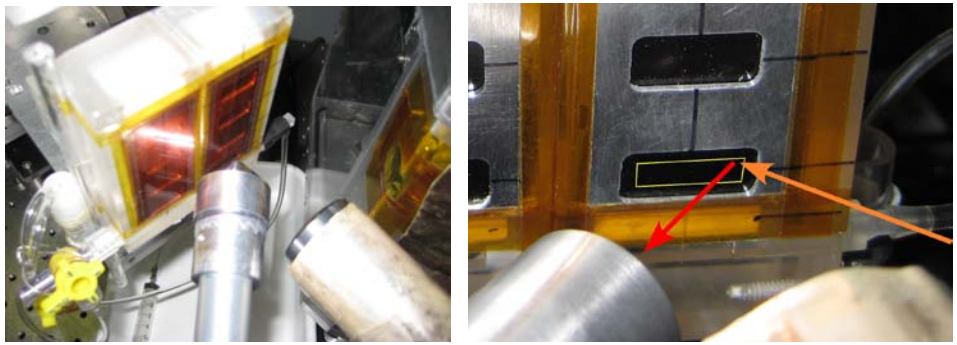
Film thinning in response to step-change in boundary reservoir suction yields D(f).

Tokunaga et al., Water Resour. Res, 2000.

Tokunaga et al., Vadose Zone J., 2001.

Tokunaga, Water Resour. Res., 2009.

New methods are needed to obtain hydraulic properties of thinner films

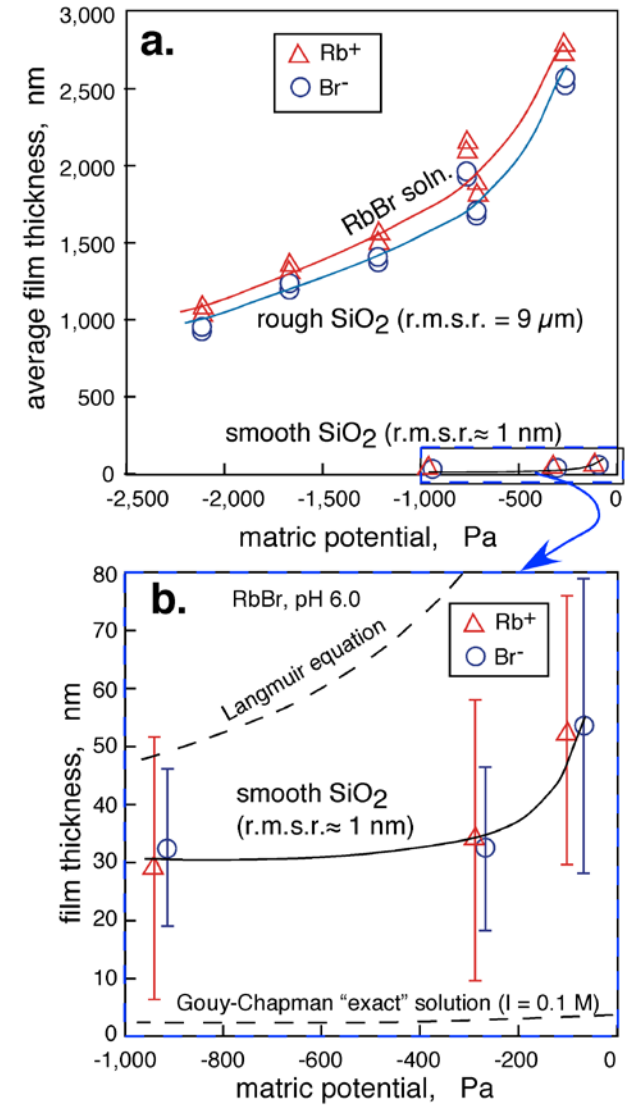


New, multi-sample film cell (atmospheric P), at Beamline X26A, National Synchrotron Light Source, Brookhaven National Laboratory

Our earlier film chambers were only capable of quantifying thick films (1- 15 µm) on rough surface.

We are working on improvements to allow us to measure finer film thicknesses, currently to 10s of nm.

Our X-ray fluorescence microprobe approach is complementary to X-ray microtomography because it achieves high resolution for film thickness, by integrating over large areas (0.5 to 1 mm^2).



Matric potential dependence of 2 M RbBr brine films (**a**) on smooth versus rough SiO_2 surface. (**b**) smooth surface measurements compared with calculations.

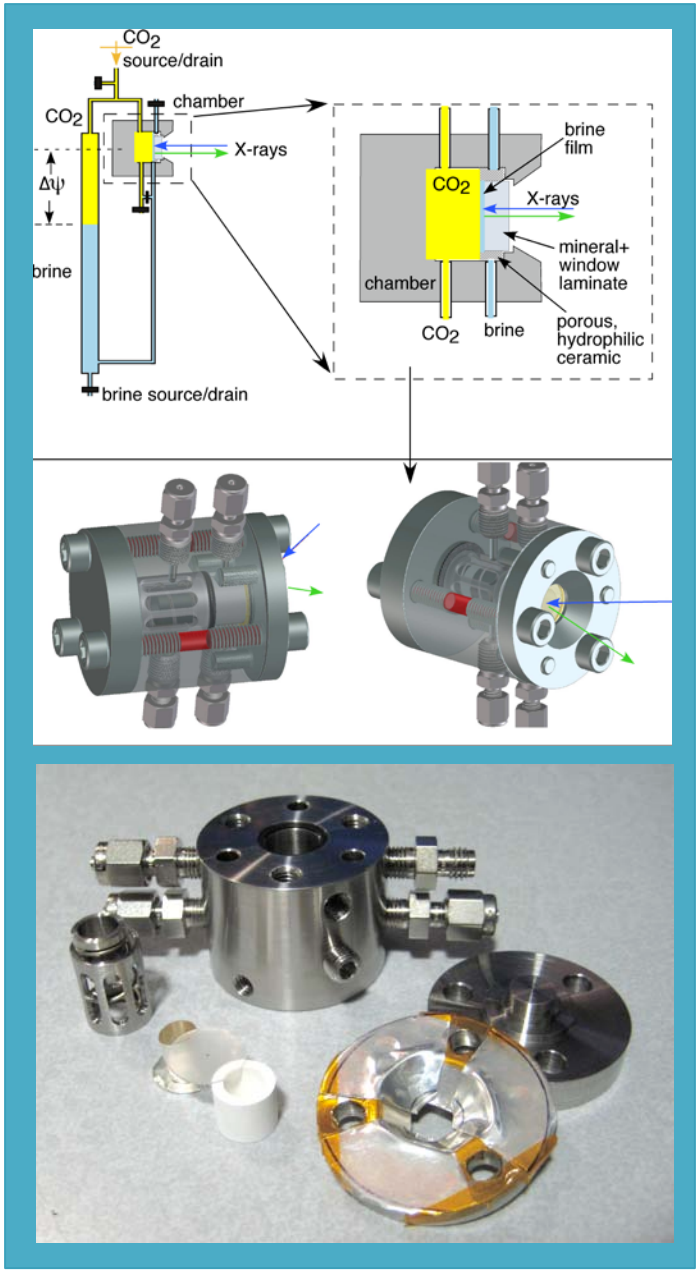
Measuring Hydraulic Properties of Brine Films Under $scCO_2$ Confinement

- Pressure regulation needed to operate at high total P (> 8 MPa) and elevated T.

- Hydraulic properties of brine films need to be determined on both smooth and rough surfaces.

- We incorporated aspects of our earlier cells into a high P cell design developed by Diefenbacher et al. (Rev. Sci. Instrum., 2005). The new film cell has been designed (Derek Shuman, LBNL) and constructed (Andrew Mei, LBNL).

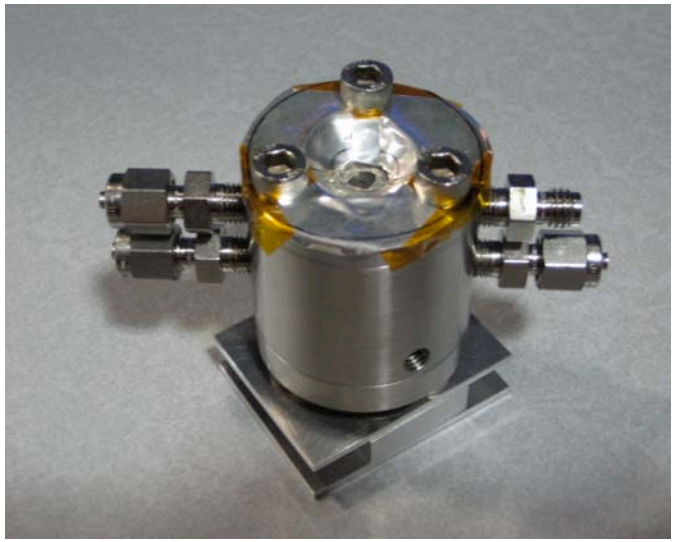
- New pressure regulation system invented to control capillary pressures to within 10 Pa, while maintaining very high total P (> 8 MPa).



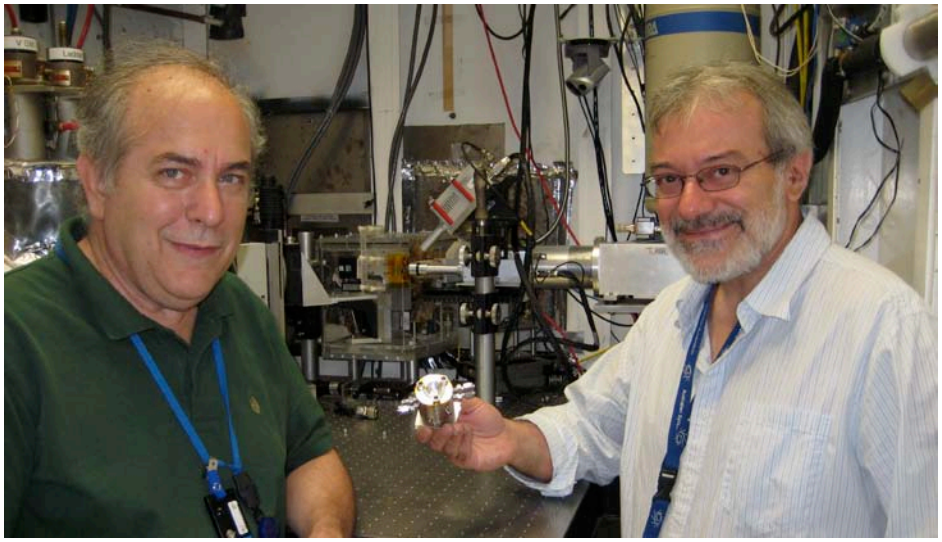
Trial run of new brine film chamber

Goals:

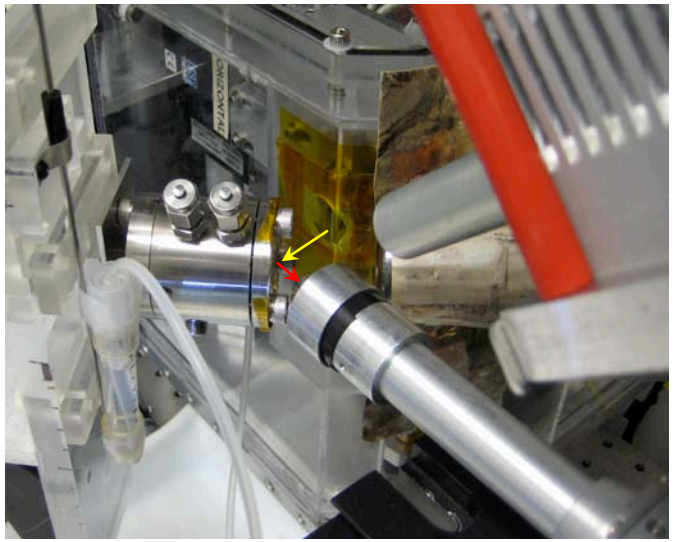
- Evaluate functioning of chamber under simpler conditions of brine-air at atmospheric P.
- Identify improvements to implement.



Assembled high pressure brine film cell.



Bill Rao and Tony Lanzirotti, NSLS X26A.



Film cell, atmospheric P test, NSLS X26A.

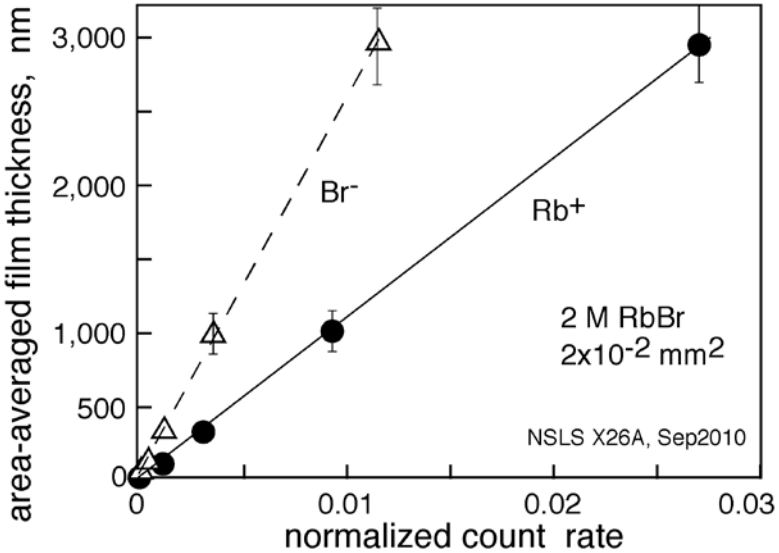
Trial run of new brine film chamber

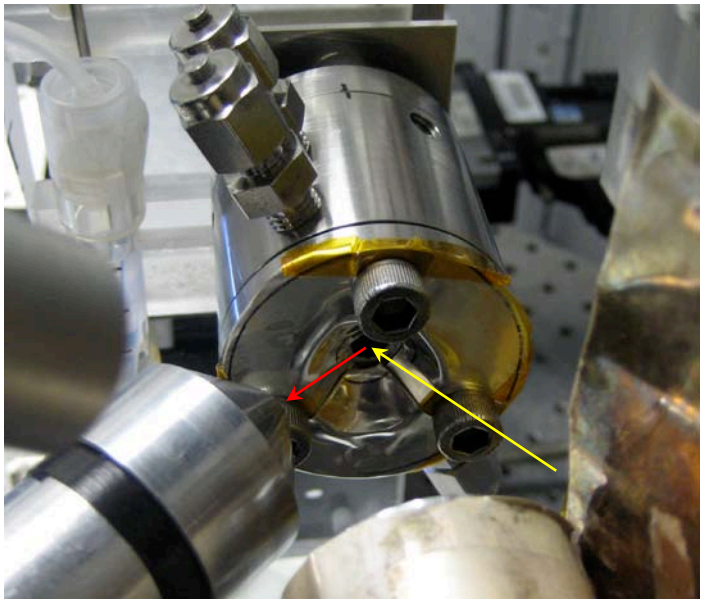
Results of Sep. 2010 test at NSLS X26A:

- Demonstrated practically linear response to film thickness calibration samples over the range of 30 to 3,000 nm. Finer film thickness resolution anticipated at APS and at the future NSLS-II.

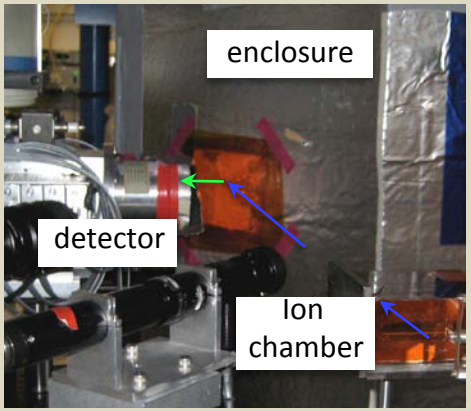
- Confirmed functioning of new capillary pressure regulation design (under atm P).

- Identified improvements to implement; X-ray window mounting.

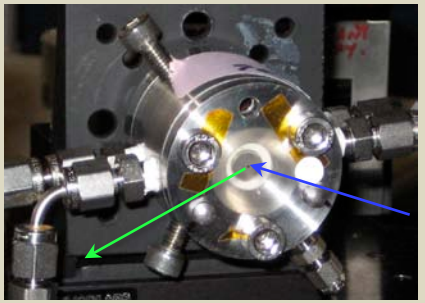




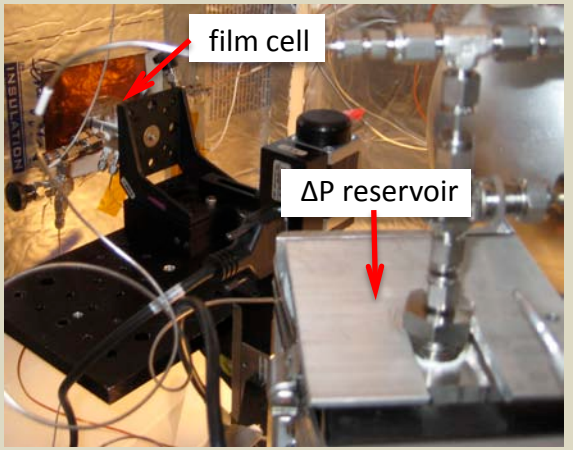
First $scCO_2$-brine film experiment:
APS-GSECARS beamline 13BM-D. March 4-8, 2011



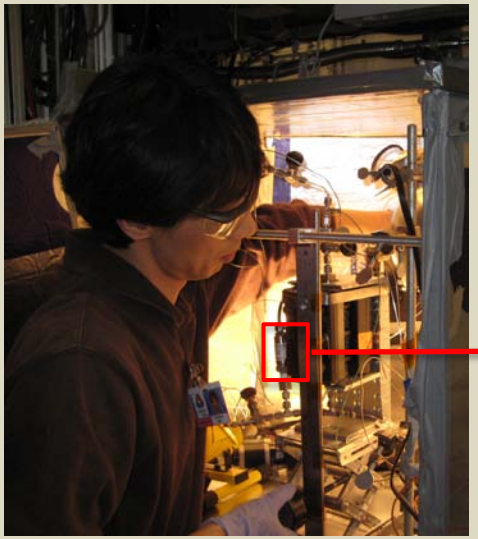
Insulated (40˚C) enclosure on 13BM-D endstation table



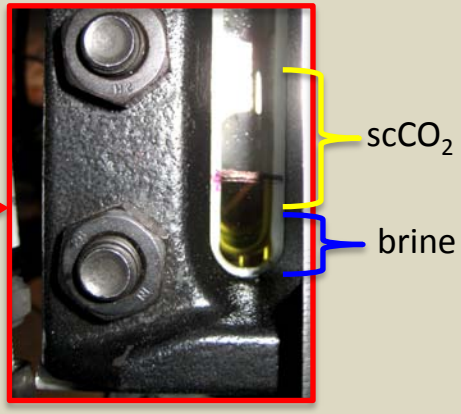
scCO2-brine film cell on 13BM-D sample stage



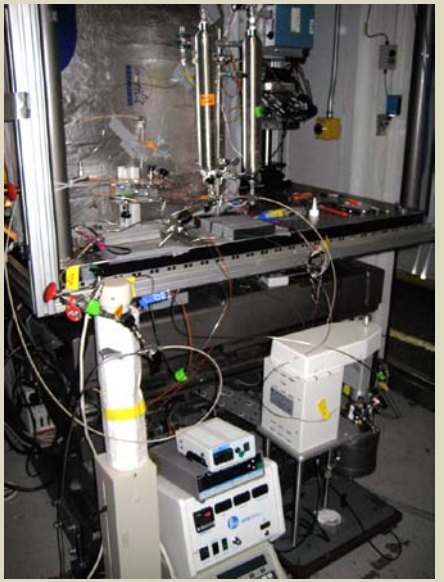
scCO2-brine film cell and ΔP reservoir inside 13BM-D insulated enclosure



Tae Wook Elliot Kim adjusting ΔP reservoir height



View into sight window of ΔP reservoir (∑P = 8 MPa)



$scCO_2$-brine equilibration

Summary

- Identified practical capillary potential ranges for studying CO_2-confined brine films.

- Designed a new film chamber for studies at elevated P and T.

- Designed a new ΔP regulating system capable of 10 Pa resolution at a total P of 8 MPa.

- Conducted initial tests of a new high pressure chamber for measuring hydraulic relations of $scCO_2$-confined brine films on variably rough surfaces.

Acknowledgments

Thanks very much to DOE BES EFRC, LBNL, NSLS, APS, GSECARS.