Pore-Scale Investigation of Wettability Alteration through Chemically-tuned Waterflooding in Oil-wet Carbonate Rocks using X-ray Micro-CT Imaging

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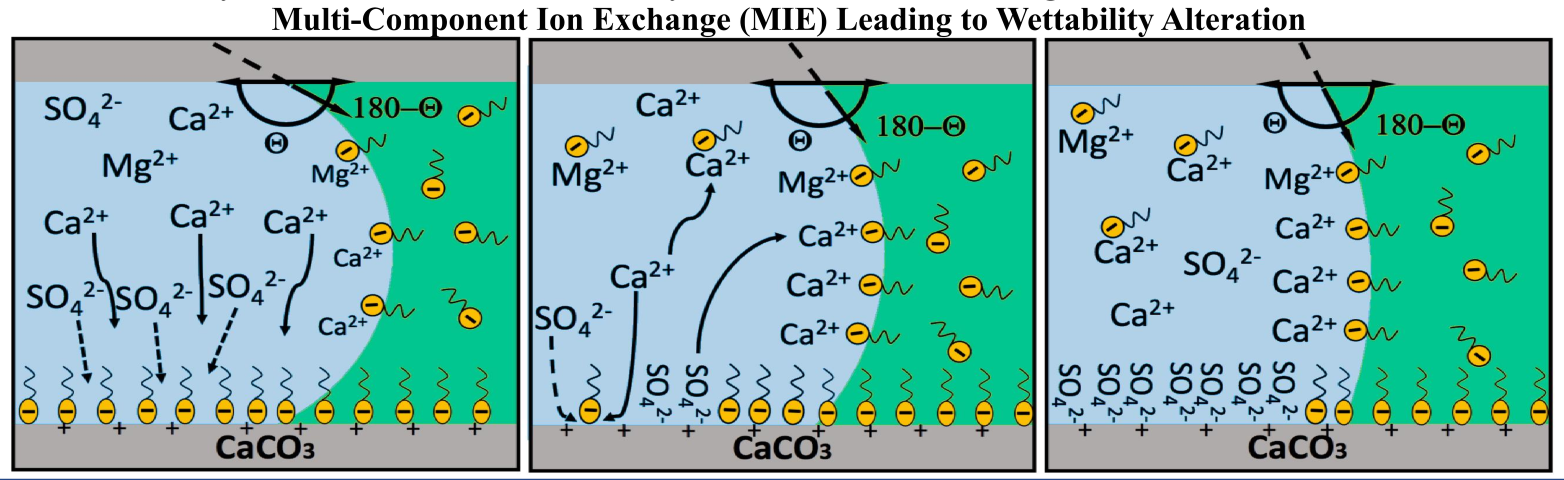
1. Background

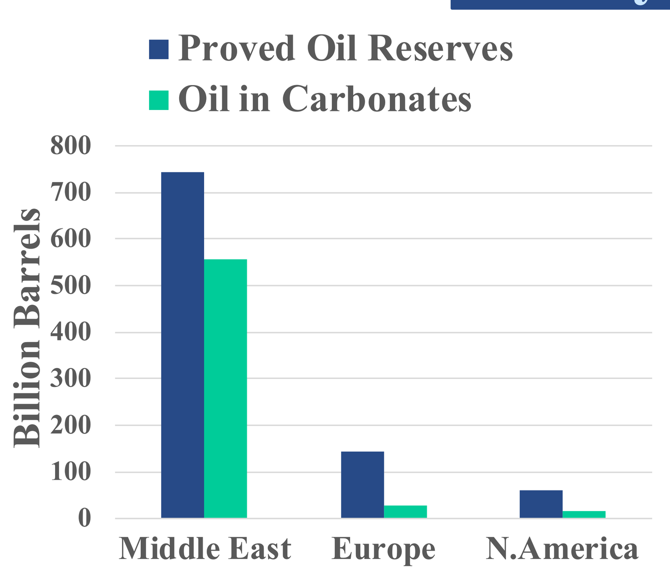
Carbonate reservoirs host more than half of the remaining oil reserves worldwide. Due to their unique wetting characteristics and complex pore structure, it is difficult to produce from these formations through conventional primary and secondary oil recovery schemes. Alternatively, chemically-tuned waterflooding (CTWF) has gained momentum as a feasible option to extend the productive life of these reservoirs. CTWF is an enhanced oil recovery technique where brines of tailored salinity and ion composition are injected into oil reservoirs. CTWF has been reported to cause wettability alteration in carbonate rocks, from preferentially oil-wet to a more water-wet state, thus promoting oil displacement. Several studies have shown that the overall reduction in injected brine salinity and increase in the concentration of potential determining ions: Mg^{2+}, Ca^{2+} and SO_4^{2-} can lead to an increase in oil recovery of up to 30% via wettability alteration (Zhang, P. et al., 2007; Fathi, S.J. et al., 2010). Conversely, other studies reported no additional oil recovery due to CTWF (Zhang, Y. et al., 2006; Hamouda, A.A. et al., 2014).

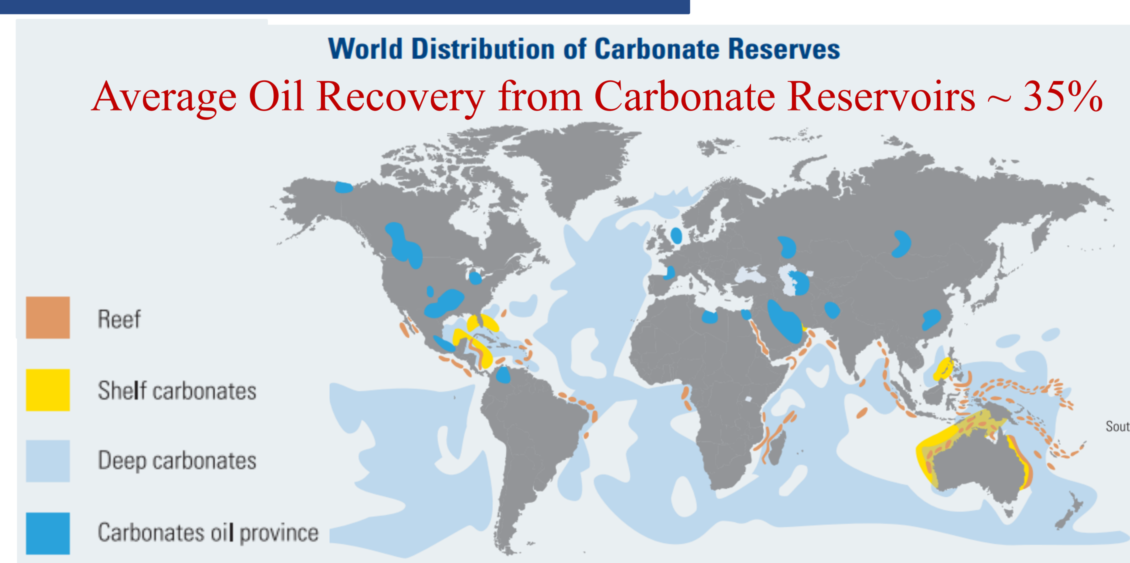
There is insufficient experimental evidence to effectively correlate brine chemistry to wettability alteration and ultimate recovery under dynamic flow conditions, such as those encountered during enhanced oil recovery applications. Our ability to successfully implement CTWF at the field scale is currently limited by inadequate understanding of the physico-chemical mechanisms affecting fluid-solid interactions at the pore-scale and their impact on fluid displacement and oil recovery at the macro-scale. Therefore, we propose an integrated experimental and numerical investigation to integrate in-situ pore-scale observations of wettability alteration, core-scale measurements of oil recovery and chemical analyses of selected brine-oil-solid samples to propose a physico-chemical model for wettability alteration via chemically-tuned waterflooding in carbonate rocks.

Multi-Component Ion Exchange (MIE) Leading to Wettability Alteration



2. Why Carbonate Reservoirs?





Modified from Schlumberger Market Analysis, 2007

3. Objectives

1. Investigate the effect of salinity, ion composition, and temperature on oil recovery from oil-wet carbonate rocks.
→ **How?** Coreflood Experiments.

2. Investigate the effect of salinity, ion composition, and temperature on wettability alteration using In-situ 3D contact angle measurements.
→ **How?** Micro-Coreflood Experiments.

3. Relate pore-scale measurements (i.e.: contact angles) to core-scale oil recovery.
→ **How?** Modeling wettability alteration as a manifestation in changes in relative permeability (Kr).

4. Scientific Impact

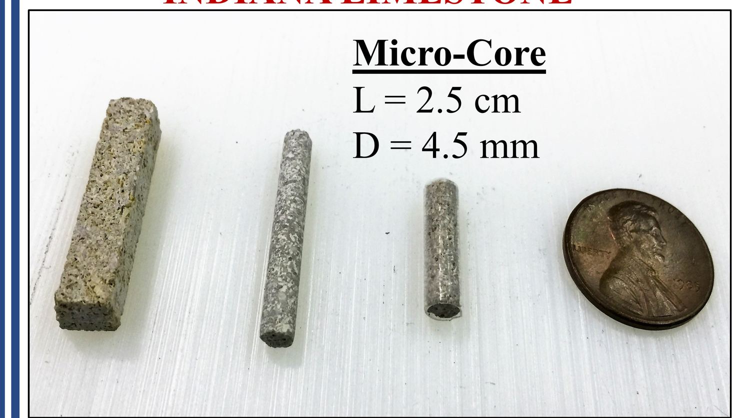
- Direct pore-scale measurement of wettability alteration.
- Kr and Pc Equation of State
- Macro-scale effect on oil recovery.

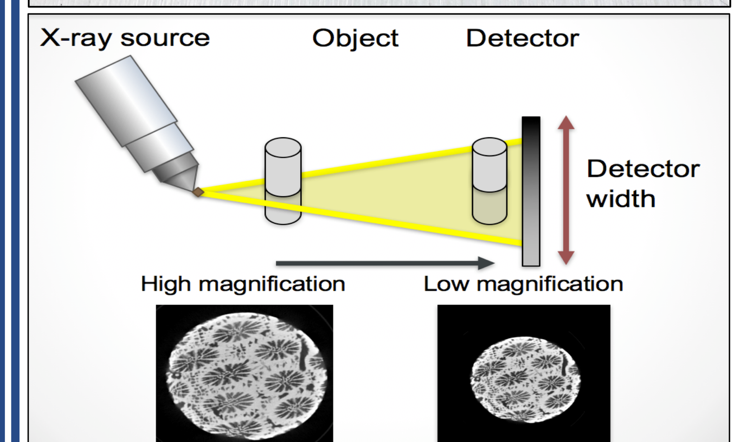
→ Better understanding of oil-brine-rock interactions.

→ Optimum brine design. | Better predictive capability.

5. Materials

INDIANA LIMESTONE

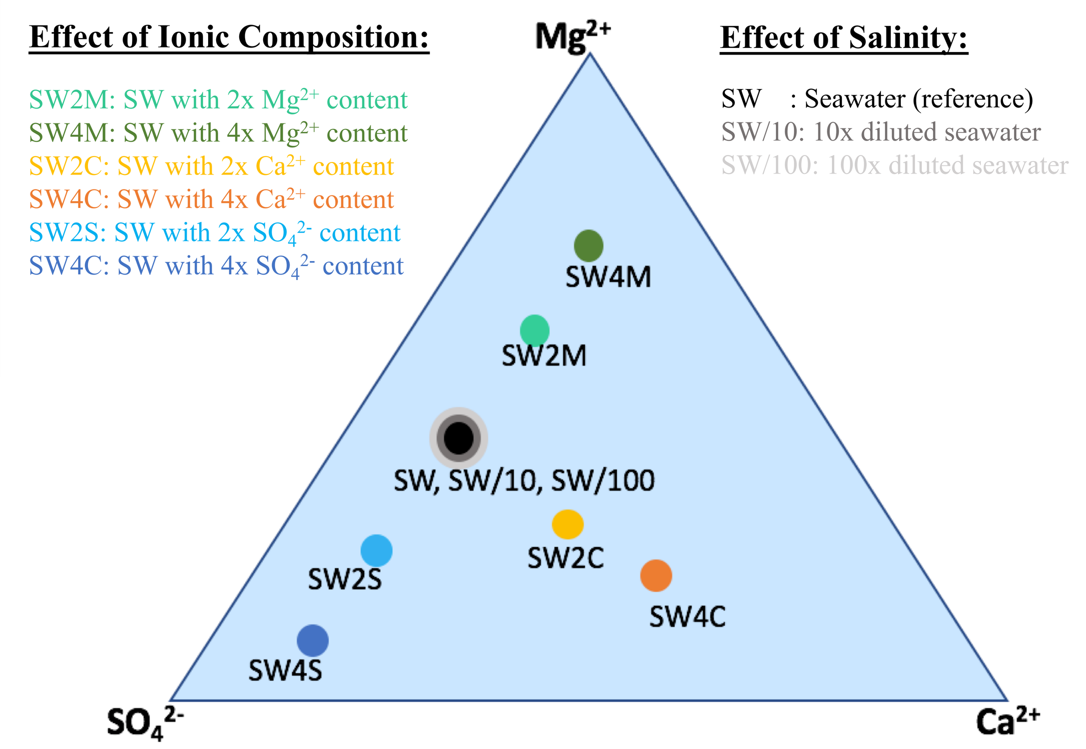




CRUDE OIL

Oil Density, g/cc	0.82
API Gravity	41
Oil Viscosity, cp (at 22 C)	9.06
Total acid no. (TAN), g KOH/g oil	0.62

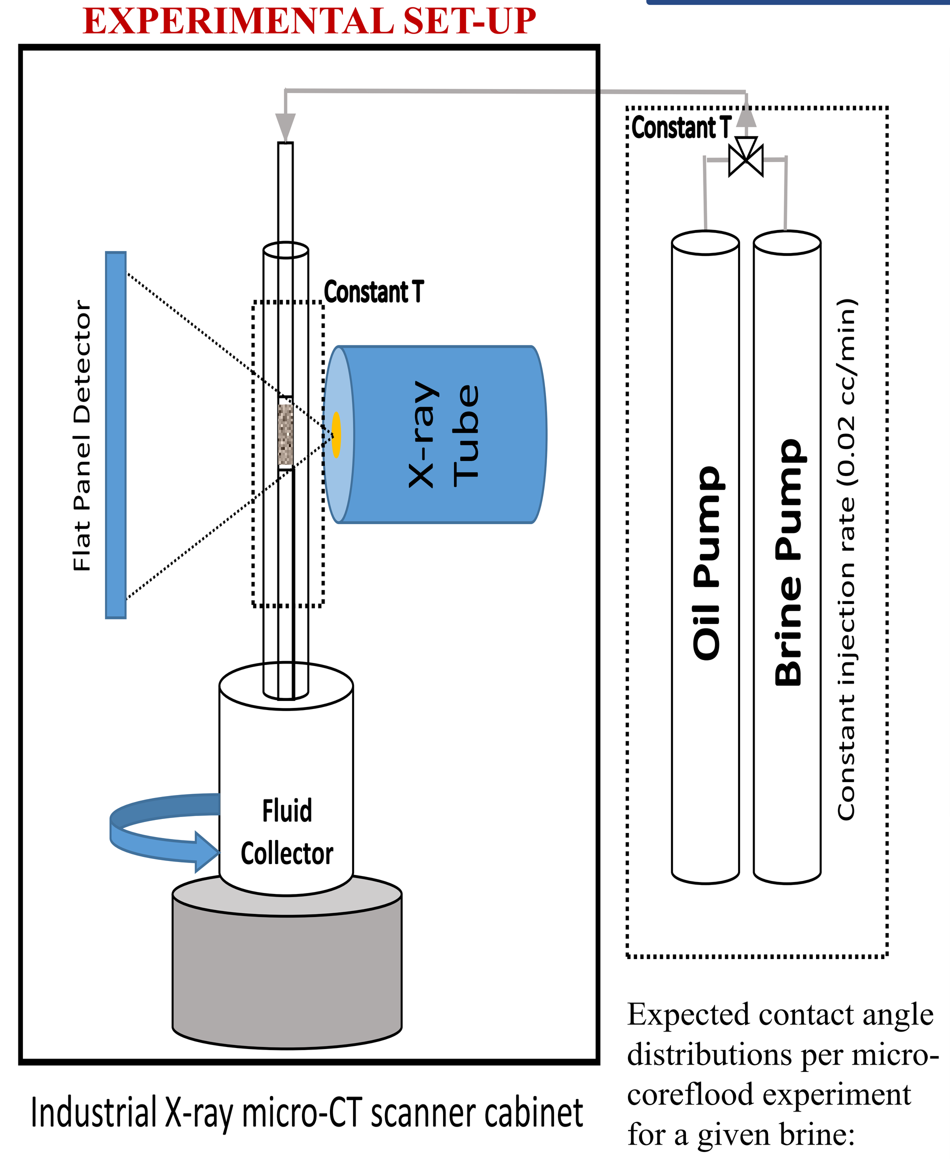
CHEMICALLY-TUNED INJECTION BRINES



Six brines are prepared in-house to investigate the effect of injected brine ion composition on the performance of CTWF. The reference brine is seawater (SW). The overall salinity is kept constant among all brines. This is achieved by increasing the concentrations of potential determining ions (PDIs) – Mg^{2+}, Ca^{2+}, and SO_4^{2-} that participate in the MIE process on the expense of non-participating ions – Na^{+} and Cl^{-}. The effect of salinity is investigated using two additional brines SW/10 and SW/100 which represent 10 and 100 times dilutions of SW.

6. Methodology

EXPERIMENTAL SET-UP



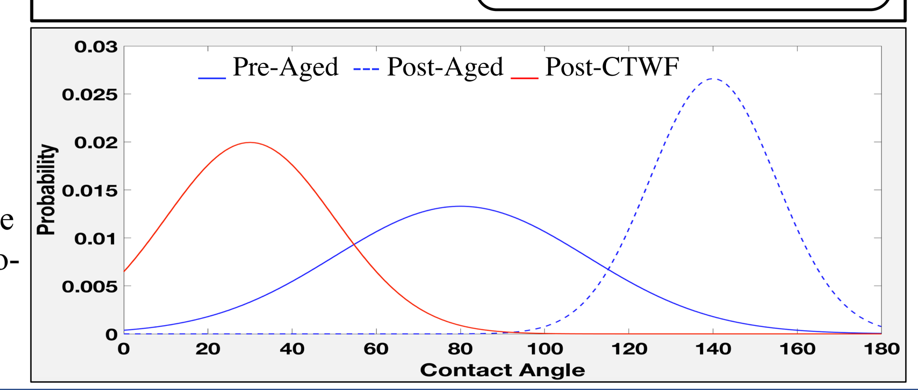
Industrial X-ray micro-CT scanner cabinet

MICRO-COREFLOOD WORKFLOW

1. Dry micro-CT Scan
2. Vacuum Saturate micro-core with Formation Water (100% S_w)
3. Inject Crude oil until S_{wirr}
4. Pre-aging Scan → Pre-aging Contact Angle Distribution (at S_{wirr})
5. Age for 12 days at T = 90°C
6. Post-aging Scan → Post-aging Contact Angle Distribution (at S_{wirr})
7. Inject chemically-tuned Brine until S_{orw}
8. Post-CTWF Scan → Post-CTWF Contact Angle Distribution (at S_{orw})

Deliverables: Pre-aging Contact Angle Distribution (at S_{wirr}); Post-aging Contact Angle Distribution (at S_{wirr}); Post-CTWF Contact Angle Distribution (at S_{orw})

Expected contact angle distributions per micro-coreflood experiment for a given brine:



9. Work in Progress

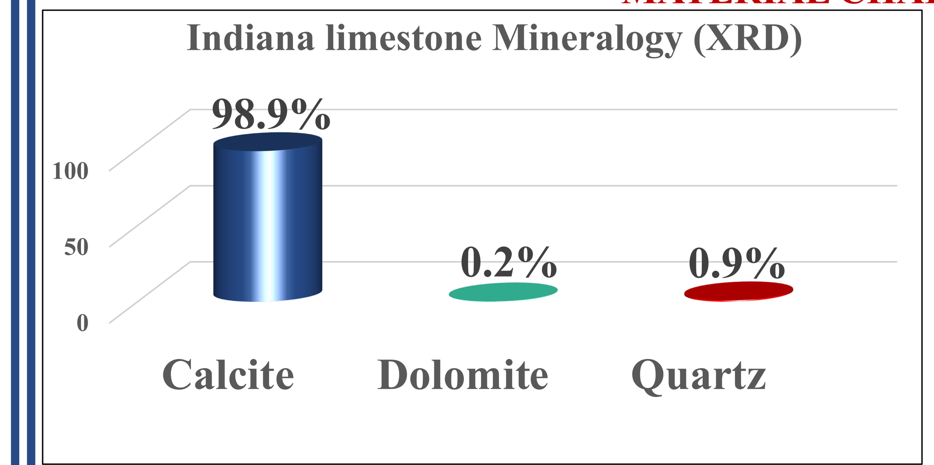
1- Develop the contact angle calculation algorithm to accommodate complex carbonate pore structures.
2- Produce contact angle distributions for CTWF using different brine compositions, and relate to core-scale oil recoveries.
3- Model wettability alteration as a manifestation in relative permeability using a Kr state function approach:

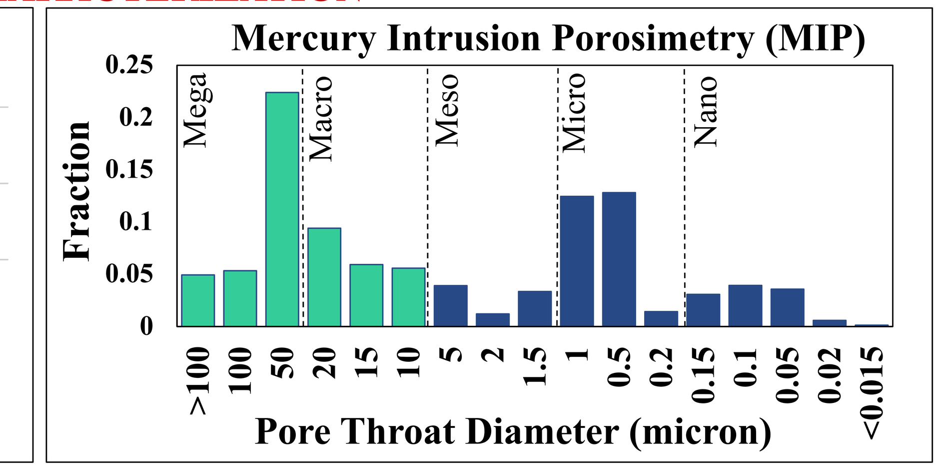
$$dk_r = \frac{\partial k_r}{\partial S}dS + \frac{\partial k_r}{\partial \hat{\chi}}d\hat{\chi} + \frac{\partial k_r}{\partial I}dI + \frac{\partial k_r}{\partial N_C}dN_C + \frac{\partial k_r}{\partial \lambda}d\lambda$$

(Phase distribution; Wettability; Capillary number; Rock structure) Khorsandi et al. (2017)

7. Preliminary Results

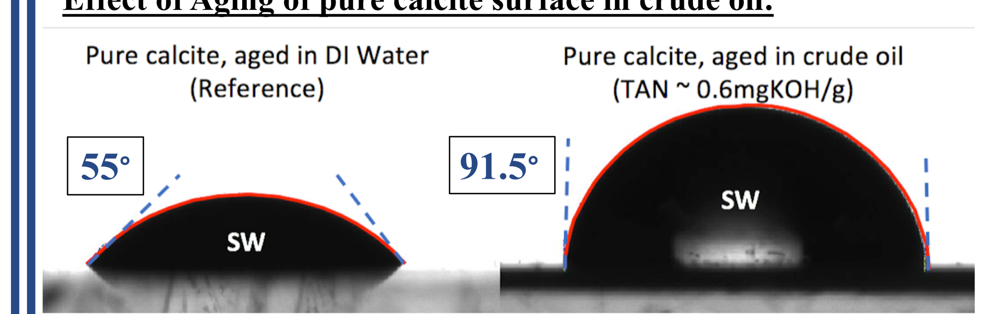
MATERIAL CHARACTERIZATION



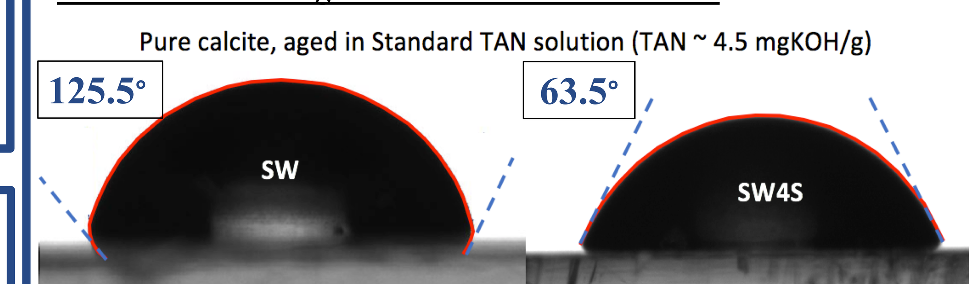


SESSILE-DROP CONTACT ANGLES

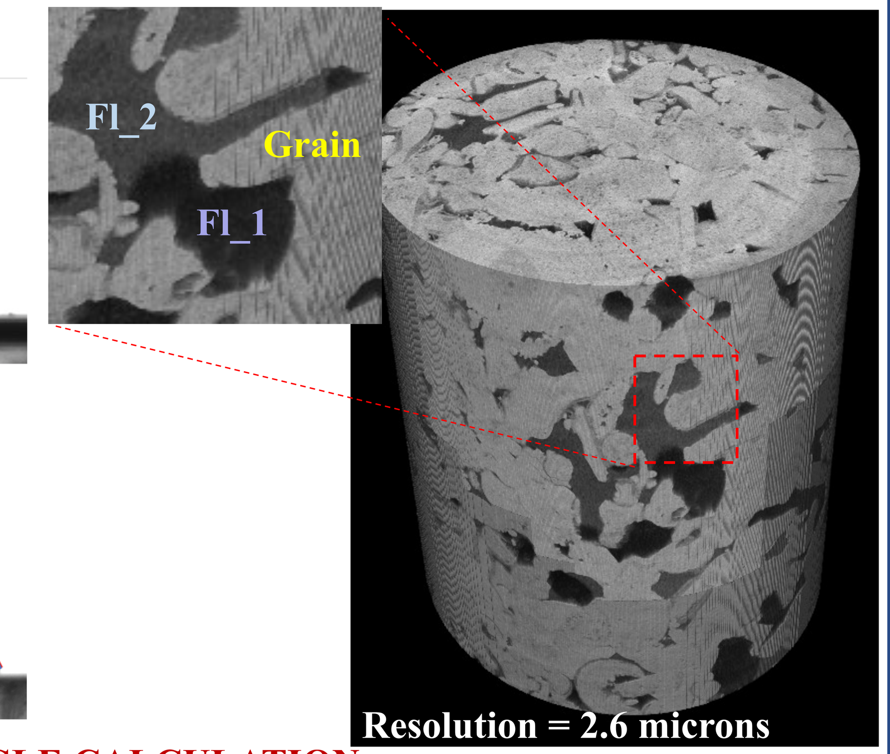
Effect of Aging of pure calcite surface in crude oil:



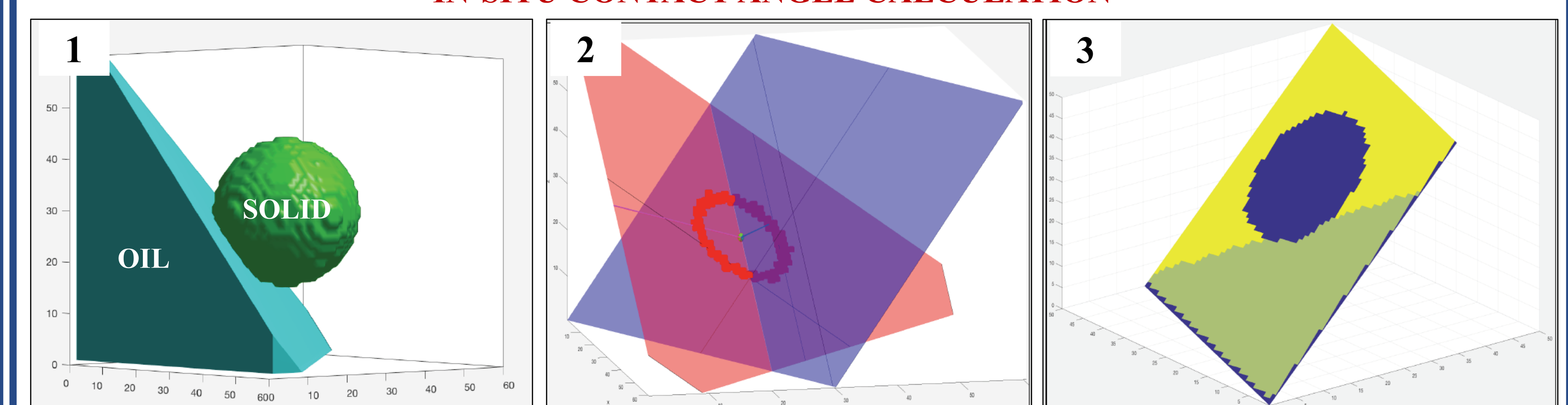
Effect of increasing Sulfate ions concentration:

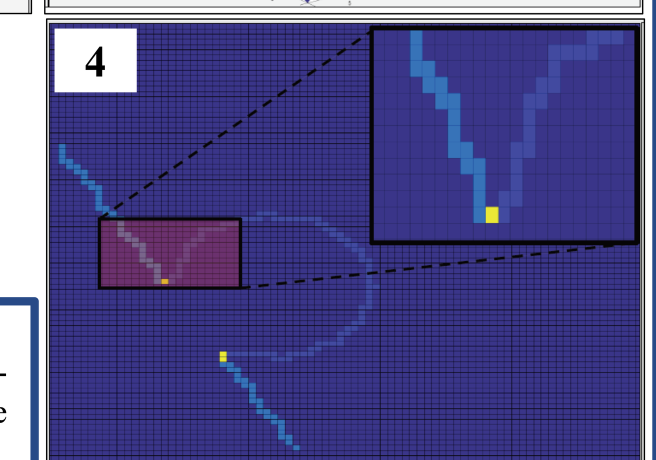


MICRO-CT IMAGING OF CARBONATES



IN-SITU CONTACT ANGLE CALCULATION

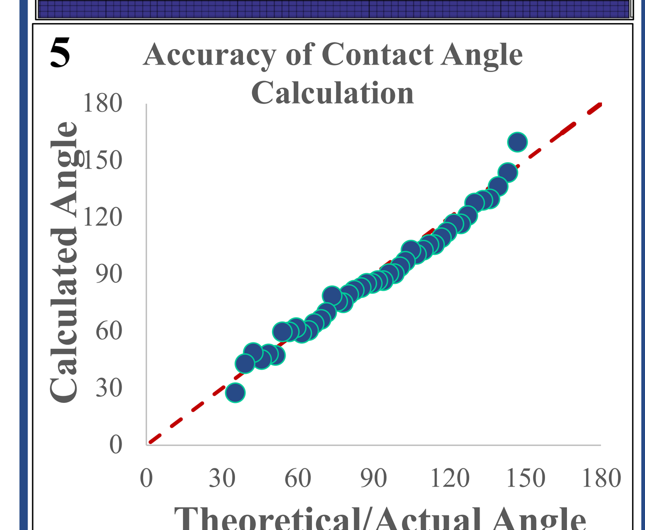




Validation Case: Given solid sphere diameter = 0.78 mm
Theoretical contact angle at each plane is known:

$$\theta = \frac{\pi}{2} + Sin^{-1}\left(1 - \frac{(i-1)}{r}\right)$$

Where i = number of voxel layers through the sphere.



8. Findings

- Mineralogy of the micro-core is consistent with the mineralogy of the macro-core, as evident from the XRD results. This allows mapping of pore-scale observations to core-scale recoveries.
- Indiana limestone is a good candidate for implementing the proposed integrated experimental study, due to the large fraction of pores of diameters >10 microns as evident from the mercury intrusion porosimetry (MIP) results.
- Aging process successfully changes the wettability of carbonates to a more oil-wet state as evident from the sessile drop contact angle measurements. In addition, higher TAN oil leads to more oil-wetness due to aging.
- Adding 4x the amount of sulfate to seawater leads to wettability alteration to a more water-wet state compared to seawater (as shown in the sessile drop contact angle measurements).
- The validation case shows that the in-situ contact angle algorithm successfully captures the contact angles as shown on the right [5]. This is promising since the validation case has a resolution which can be achieved using the current micro-coreflood experimental setup (~ 2.5 microns).

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