

CO₂ Foam Mobility Control and Adsorption with Nonionic Surfactant

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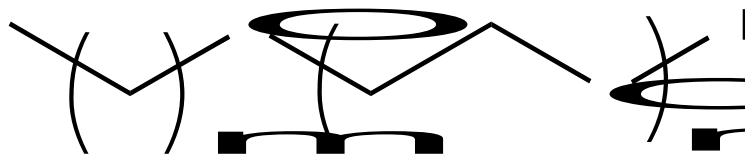
Core Flood at Reservoir Conditions

- **Composition of brine of East Seminole reservoir (TDS=34,180 ppm)**

Na_2SO_4 (mg/l)	KCl (mg/l)	$\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$ (mg/l)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (mg/l)	NaCl (mg/l)
5,236	458	5,825	2,760	22,796

- **Surfactant**

Linear alcohol ethoxylates SURFONIC[®]L24-22



$m=11\sim 13;$
 $n=22$

SURFONIC[®]L24-22, Huntsman Corporation



Core Flood at Reservoir Conditions

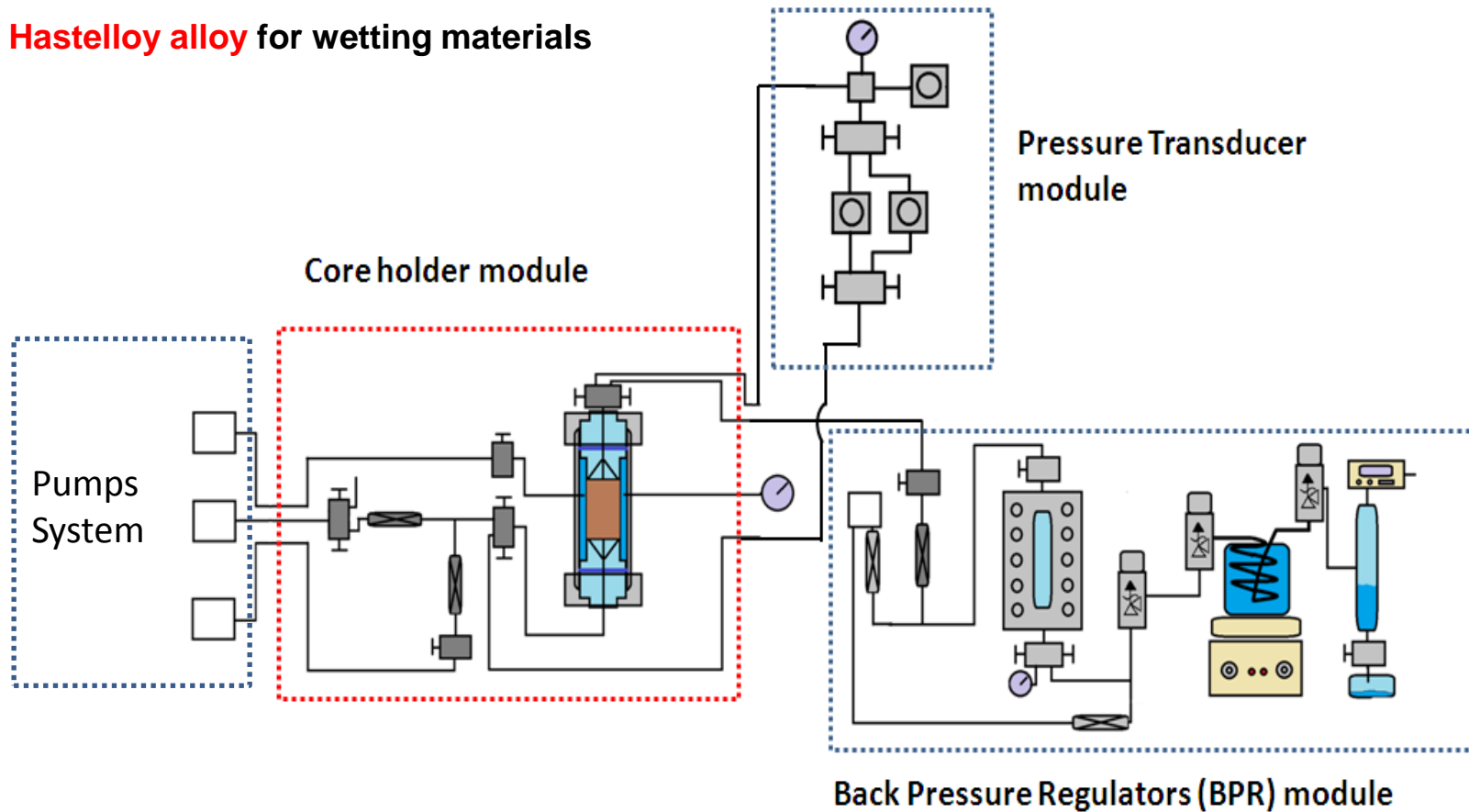
- **Core**
 - **Diameter: 1.50 inch**
 - **Length: 2.97 inch**
 - **Pore volume: 14.4 cm³**
 - **Lithology: Silurian dolomite core from Kocurek Industries**
 - **Porosity=16.7%**
 - **Permeability=91 mD**





Diagram of the High Temperature and High Pressure Core Flooding Setup

- Specially designed heating coil, core holder and back pressure regulator system.
- Harsh Conditions: **2,600 psi**, **T=110 °F**, **moderate salinity** and **low pH (≈ 4)**
- **Hastelloy alloy** for wetting materials





Core flooding: Apparent Viscosity

- Apparent viscosity is used to describe the foam strength, which is calculated by **Darcy's law**:

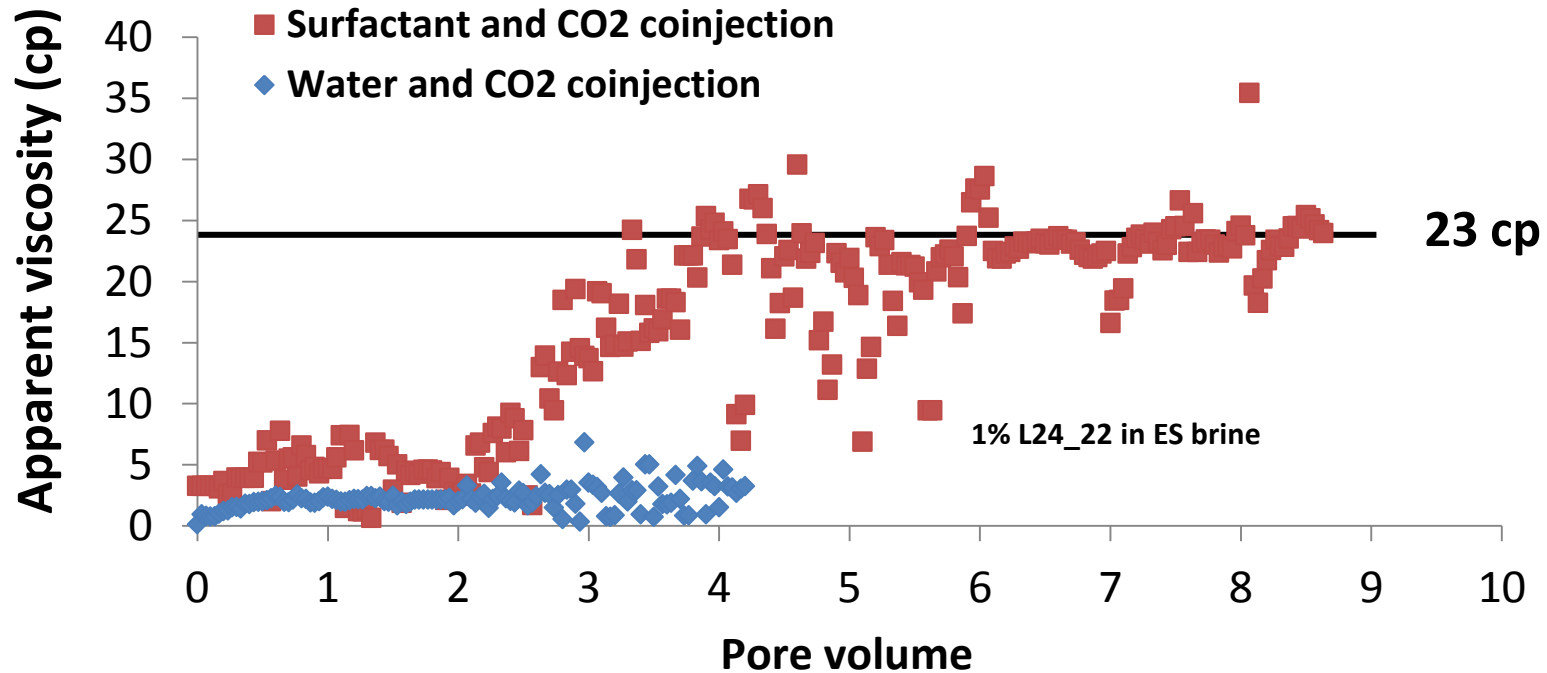
$$\mu_{app} = -\frac{k}{u_t} \cdot \nabla p$$

where μ_{app} is foam apparent viscosity, k is core permeability, u_t is the total superficial velocity and ∇p is the pressure gradient.



Core flooding

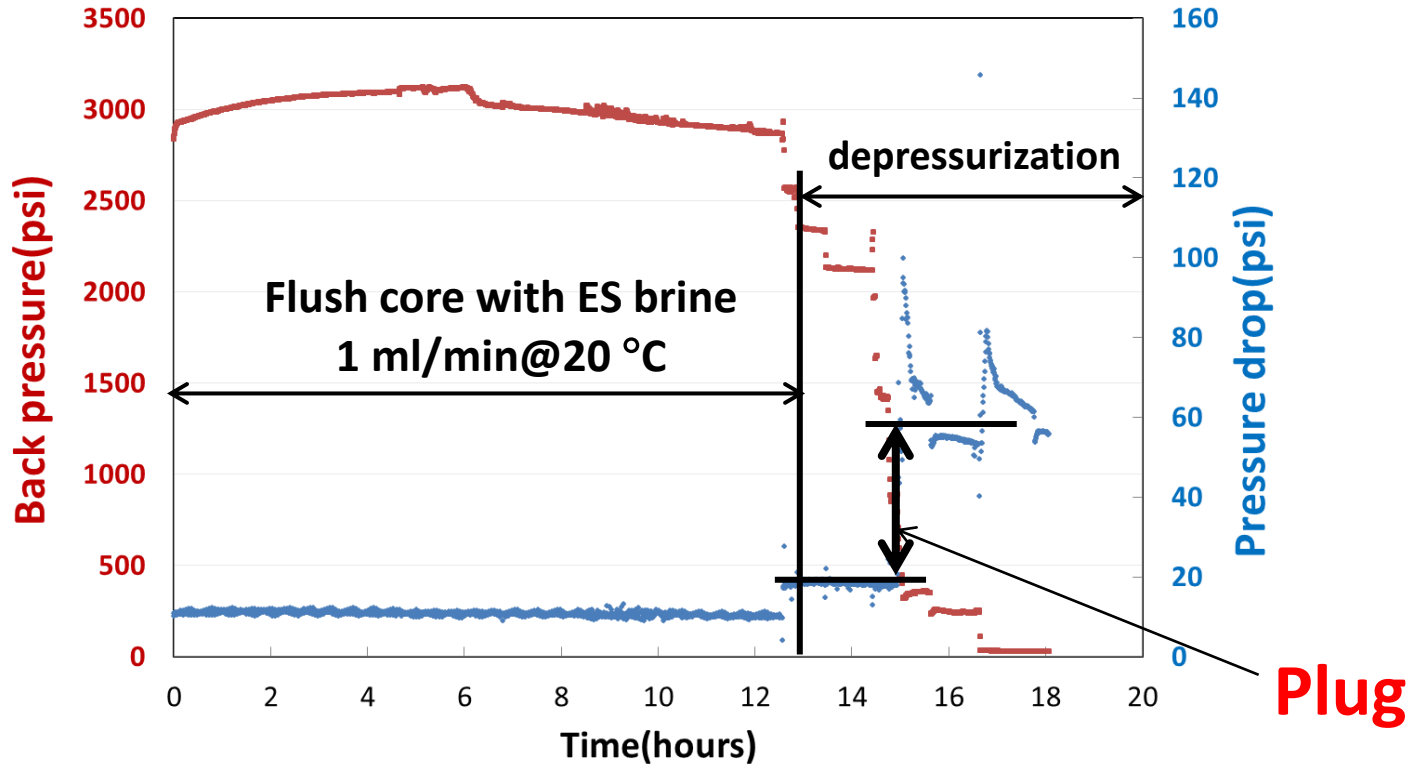
80% foam quality, Injection rate=4 ft/day,
T=110 °F(43.3 °C), Injection pressure=2600 psi.



- Equilibrium average apparent viscosity by co-injection of surfactant and CO₂ is **23 cp**



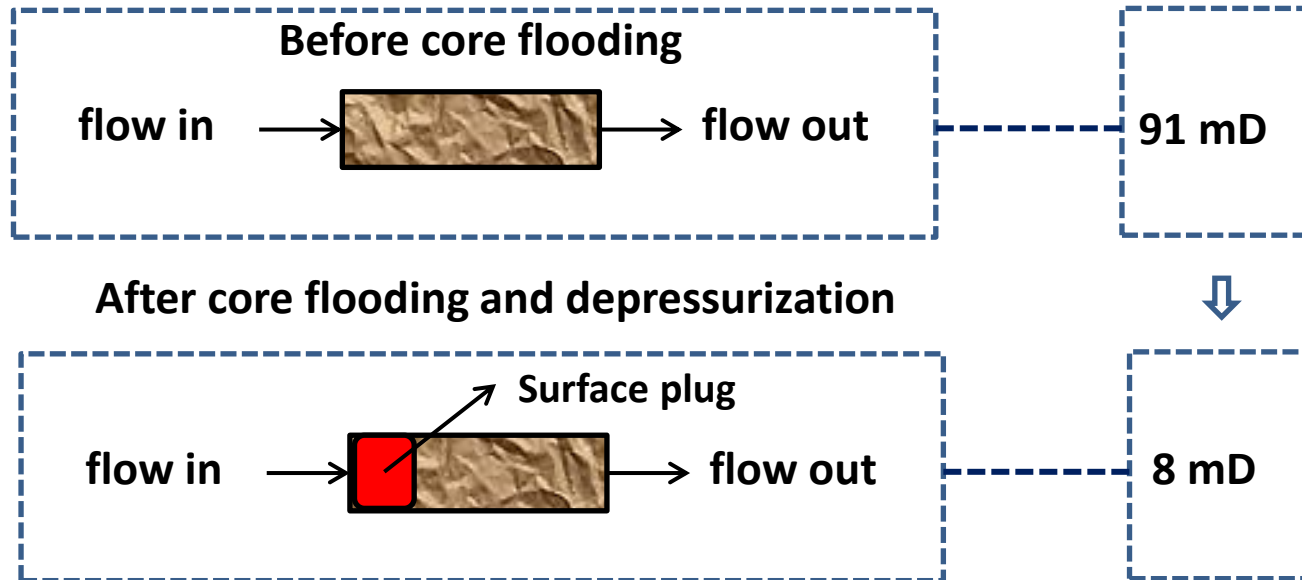
Depressurization



- Depressurization from 1500 psi to 800 psi and then to 200 psi (at 20 °C), we saw a sudden increase of pressure drop (from 20 psi to 60 psi)
- Does the pressure drop indicate core plug?



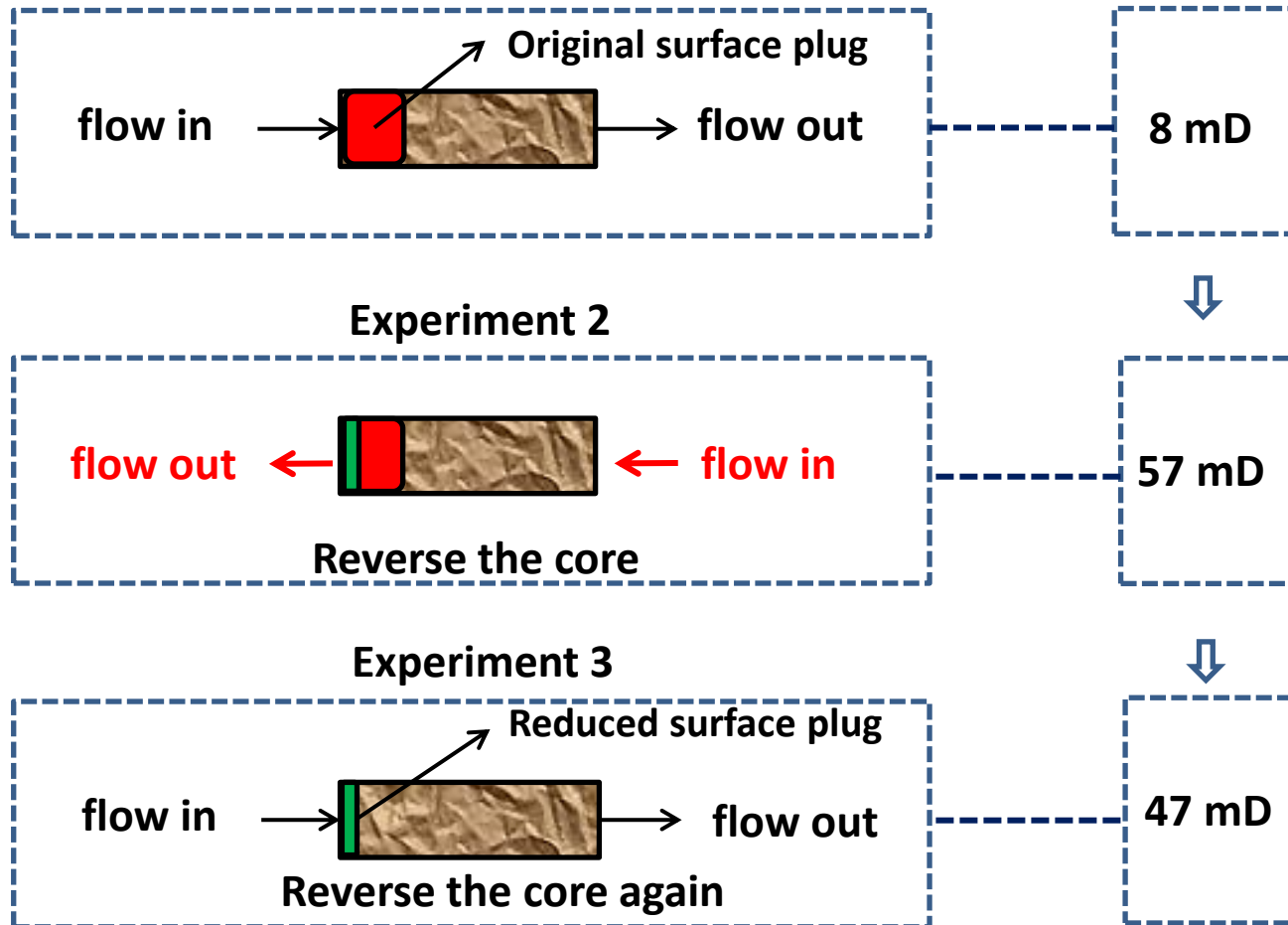
Assumption: Plug of Core



- Permeability decreased from **91 mD** to **8 mD**
- Core was plugged



Confirm Plug of Core

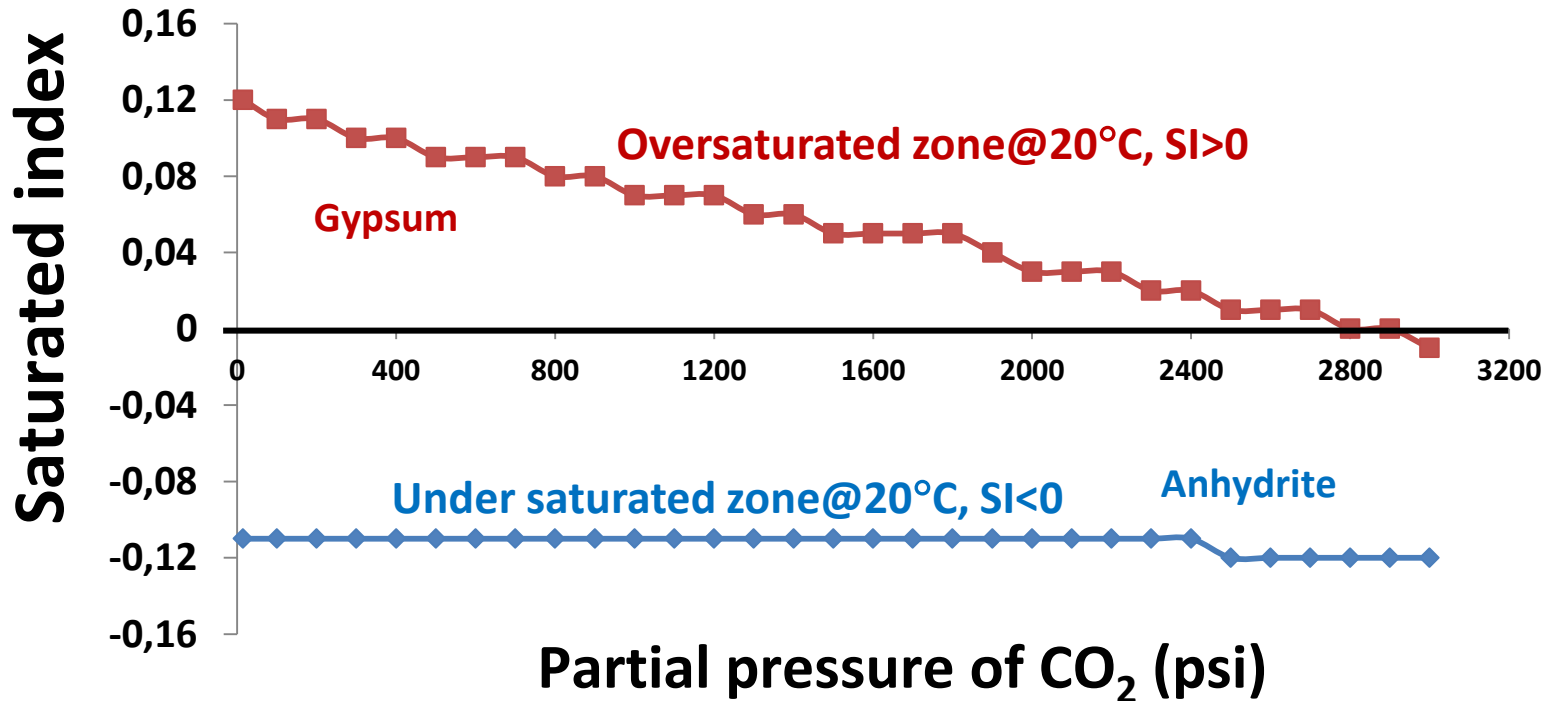


- Plug has been **partially flushed away** which can be reflected from the **permeability change**



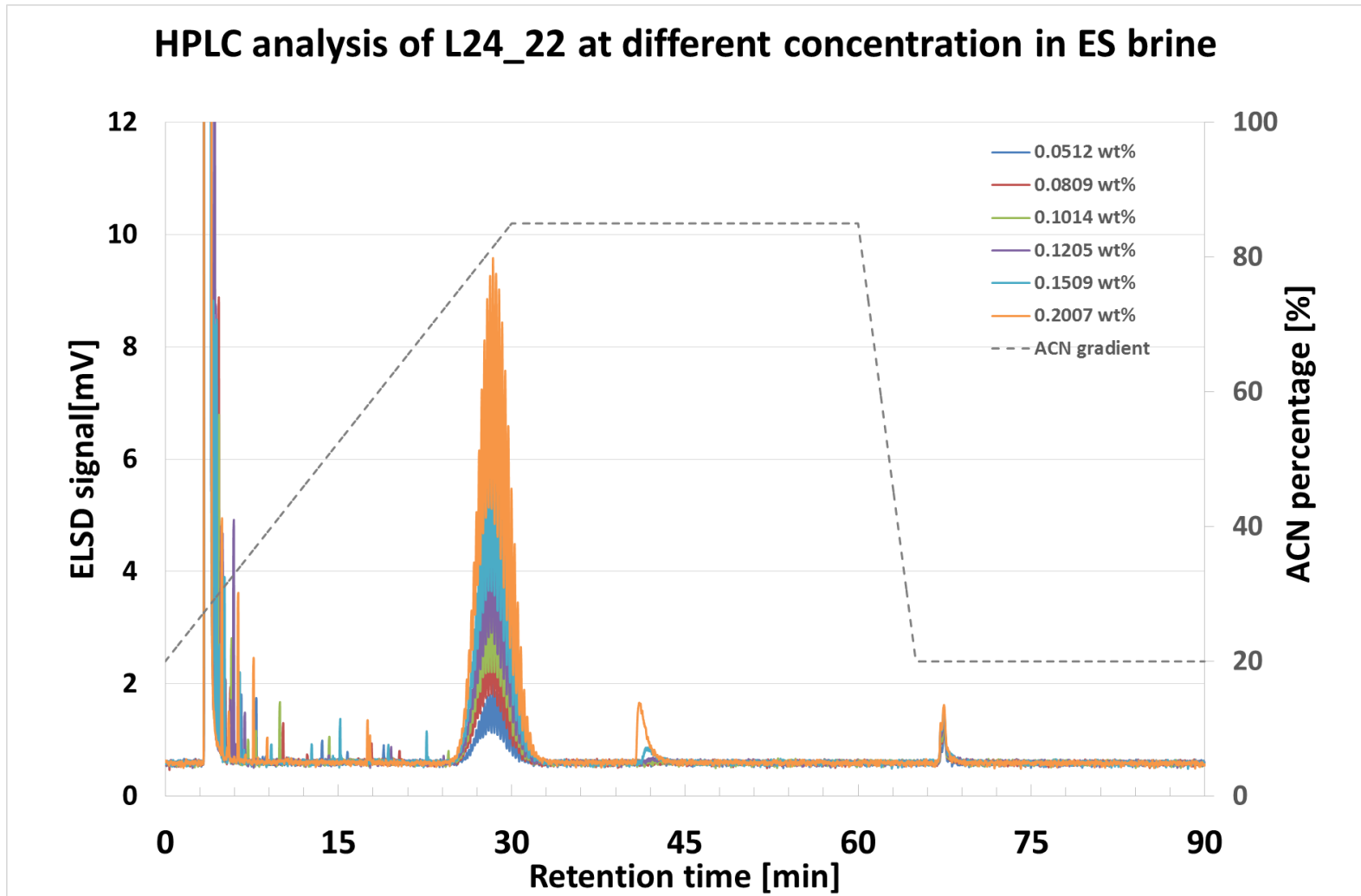
Interpretation of Core Plug

- Saturated Index* of anhydrite and gypsum was simulated by PHREEQC Software
- Negative Saturated index(SI) means under saturated and **positive SI means oversaturated**



- **Anhydrite** is **under saturated** from 14.7 psi to 3000 psi
- **Gypsum** is **over saturated** from 14.7 psi to 2800 psi, which indicates that **depressurization** is **favorable** for **gypsum formation**

*Lopez-Salinas, Jose Luis, George J. Hirasaki, and Clarence A. Miller. *SPE141420*

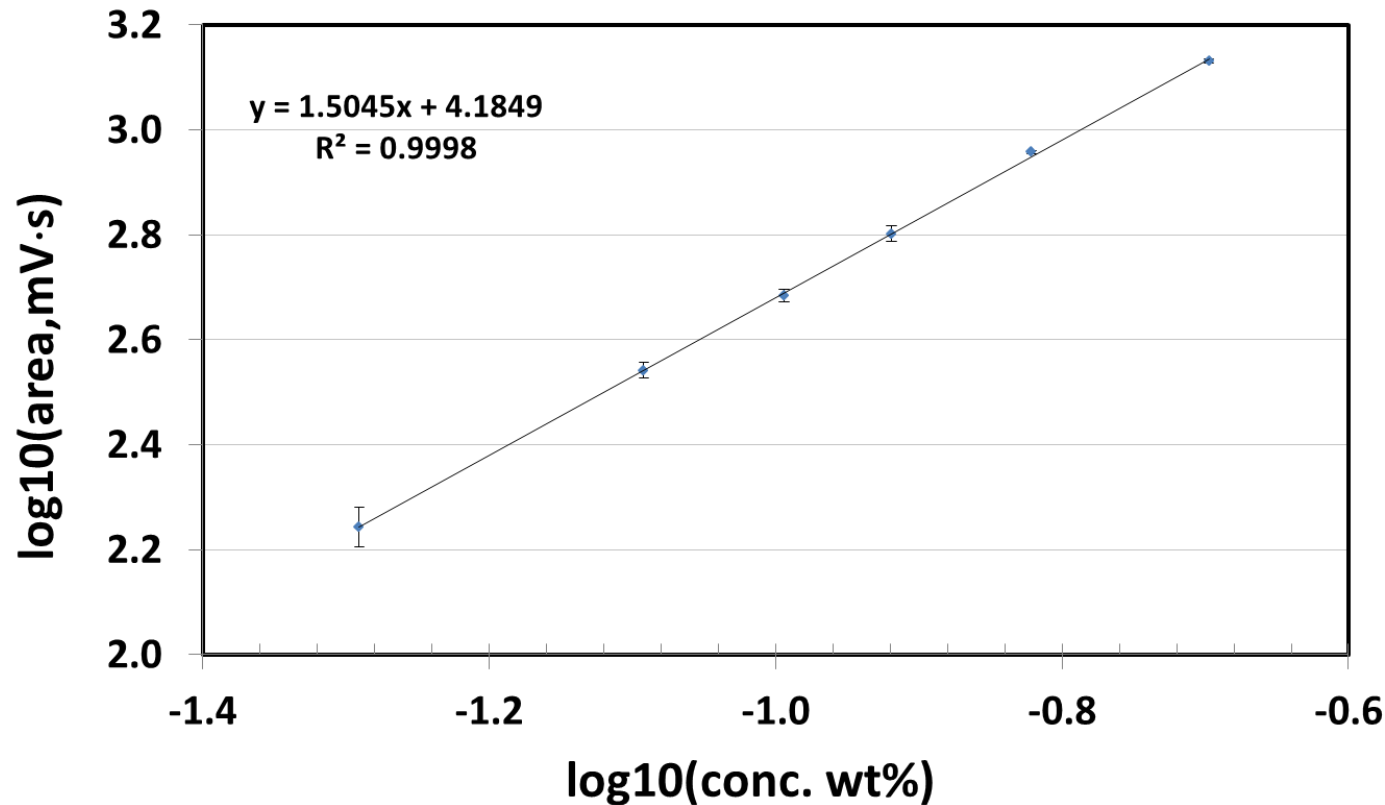


- The peaks with different heights correspond to different surfactant concentrations



Power Law Calibration Curve

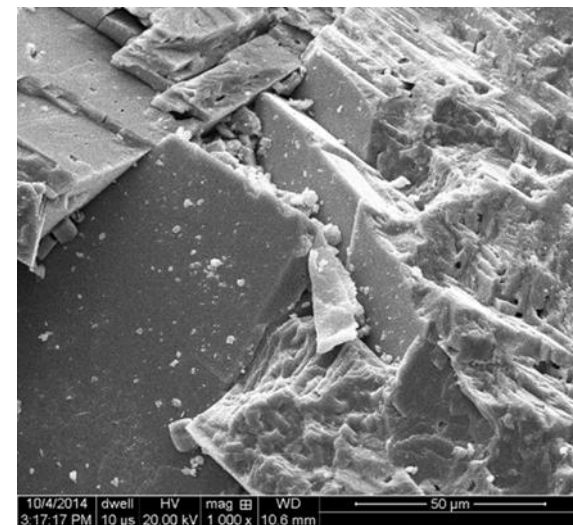
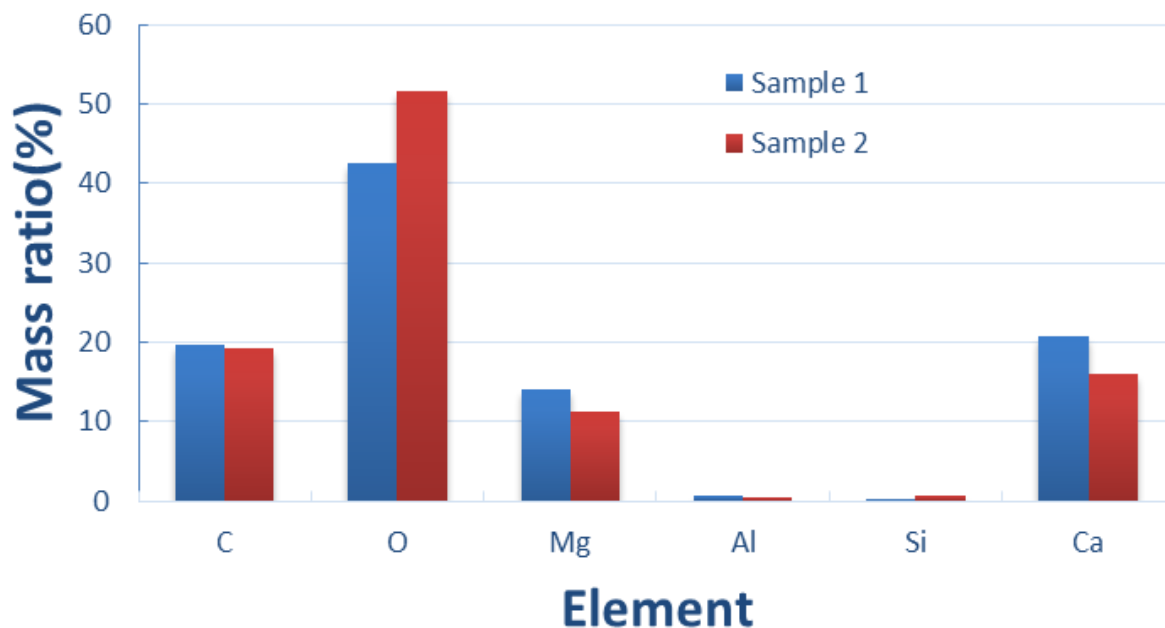
Calibration Curve for L24_22 in ES brine
(log₁₀_log₁₀ scale)



- Calibration curve could be used for determine surfactant concentration in adsorption test



Element composition of silurian dolomite

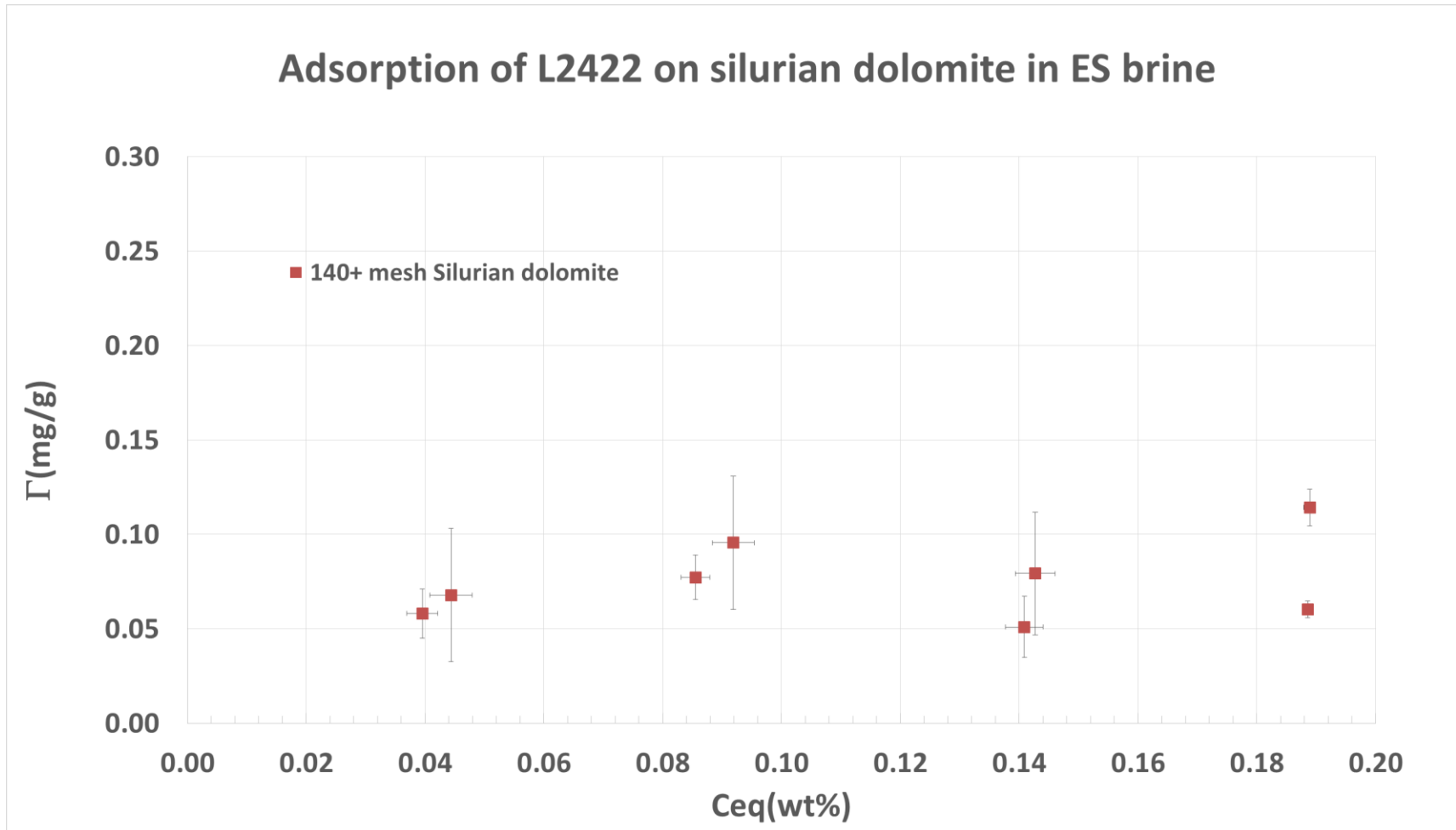


SEM of Silurian dolomite

- The Silurian dolomite are mainly consist of Ca, Mg; little amount of Al, Si
- BET surface area is **0.95 m²/g**



Adsorption on Silurian Dolomite Powder



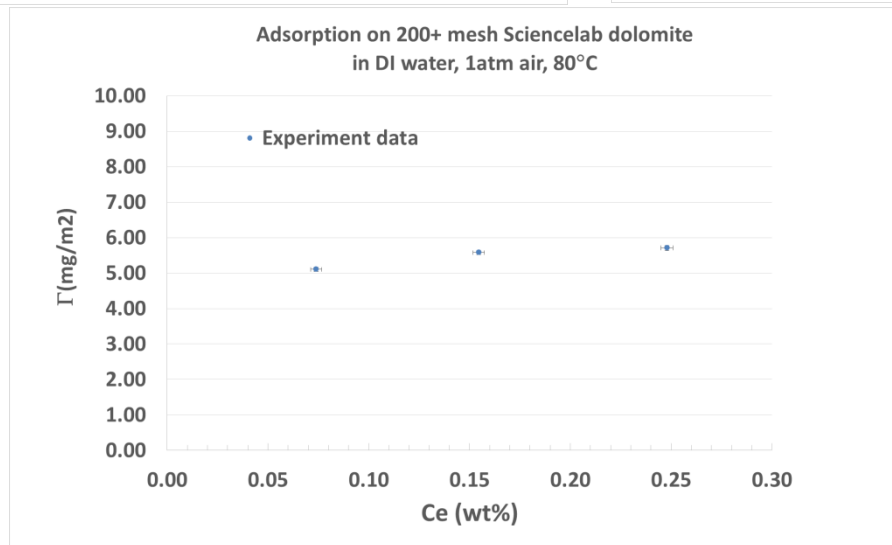
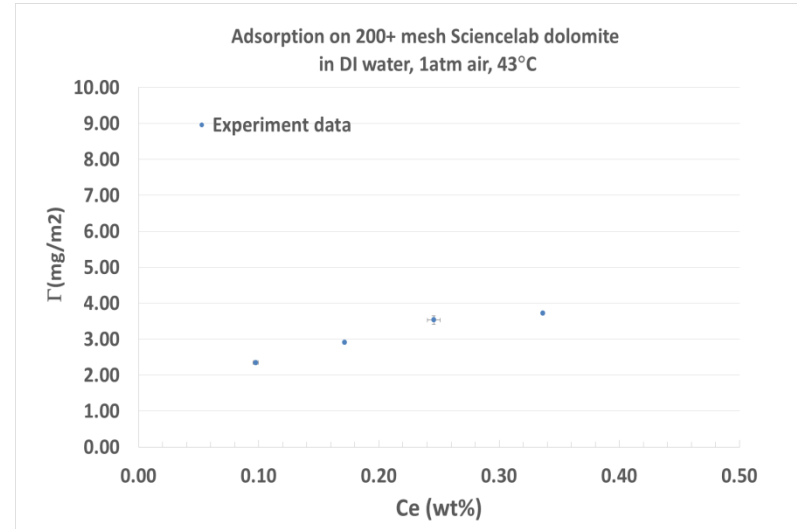
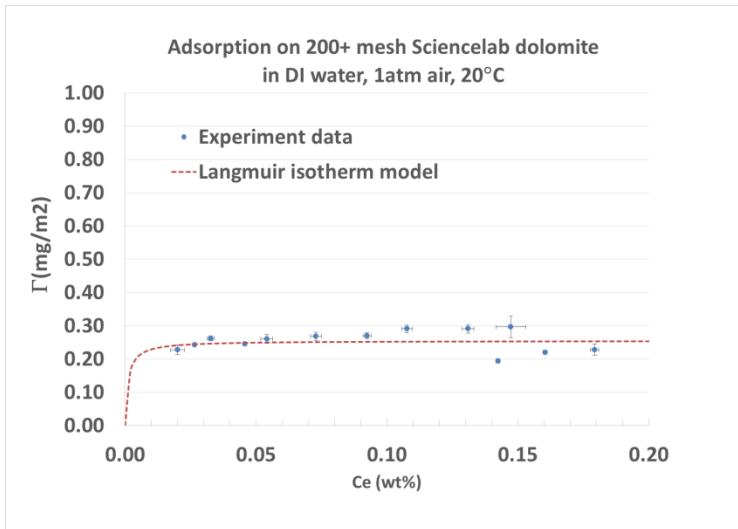
- The equilibrium adsorption amount of L2422 on Silurian dolomite is ~ 0.08 mg/g



- **Everything seems good till now, foam could be generated at reservoir conditions with 23 cp apparent viscosity and adsorption on Silurian dolomite is so low which is about 0.08mg/g [0.08mg/m²] rock.**
- **How about adsorption at higher temperatures?**



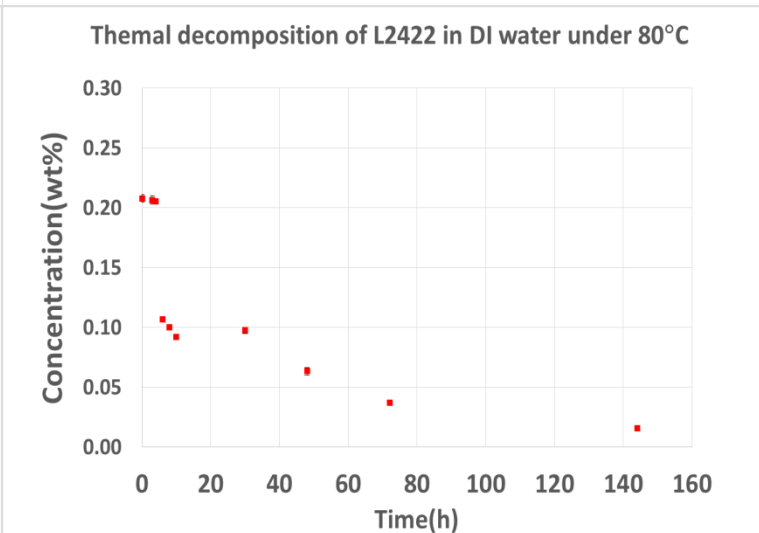
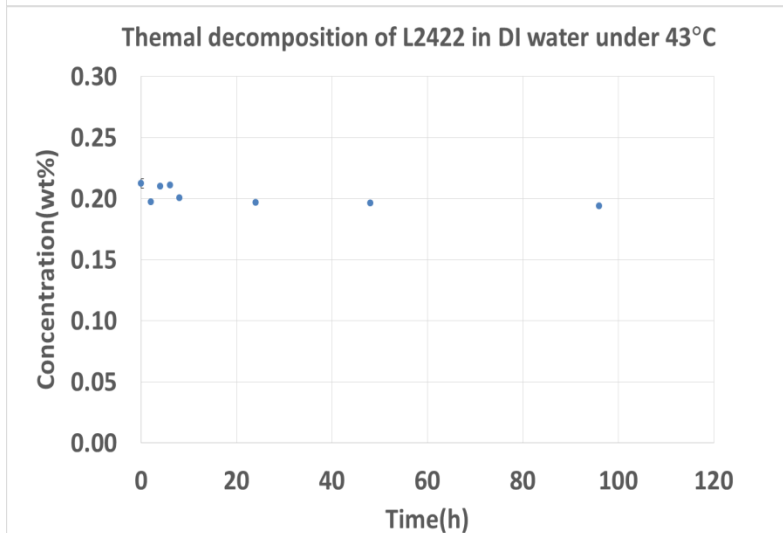
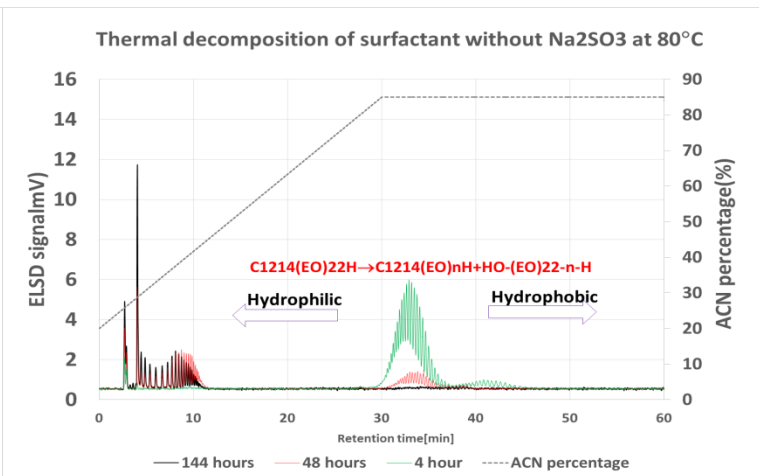
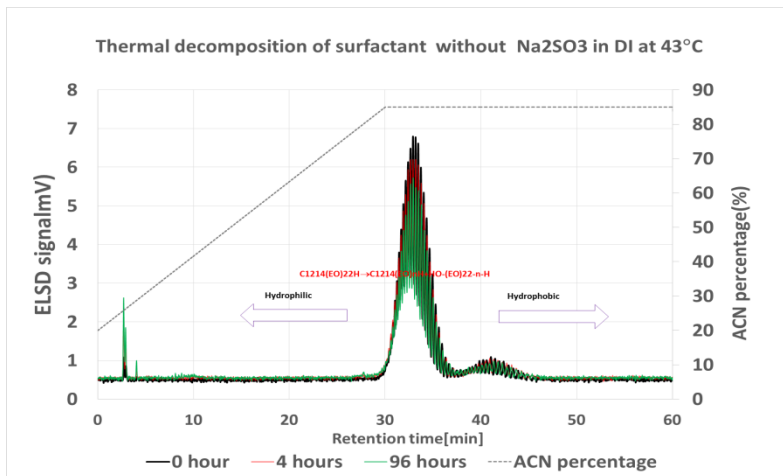
Adsorption without Na₂SO₃



Why is so high adsorption at high Temperature? (on Sciencelab dolomite)



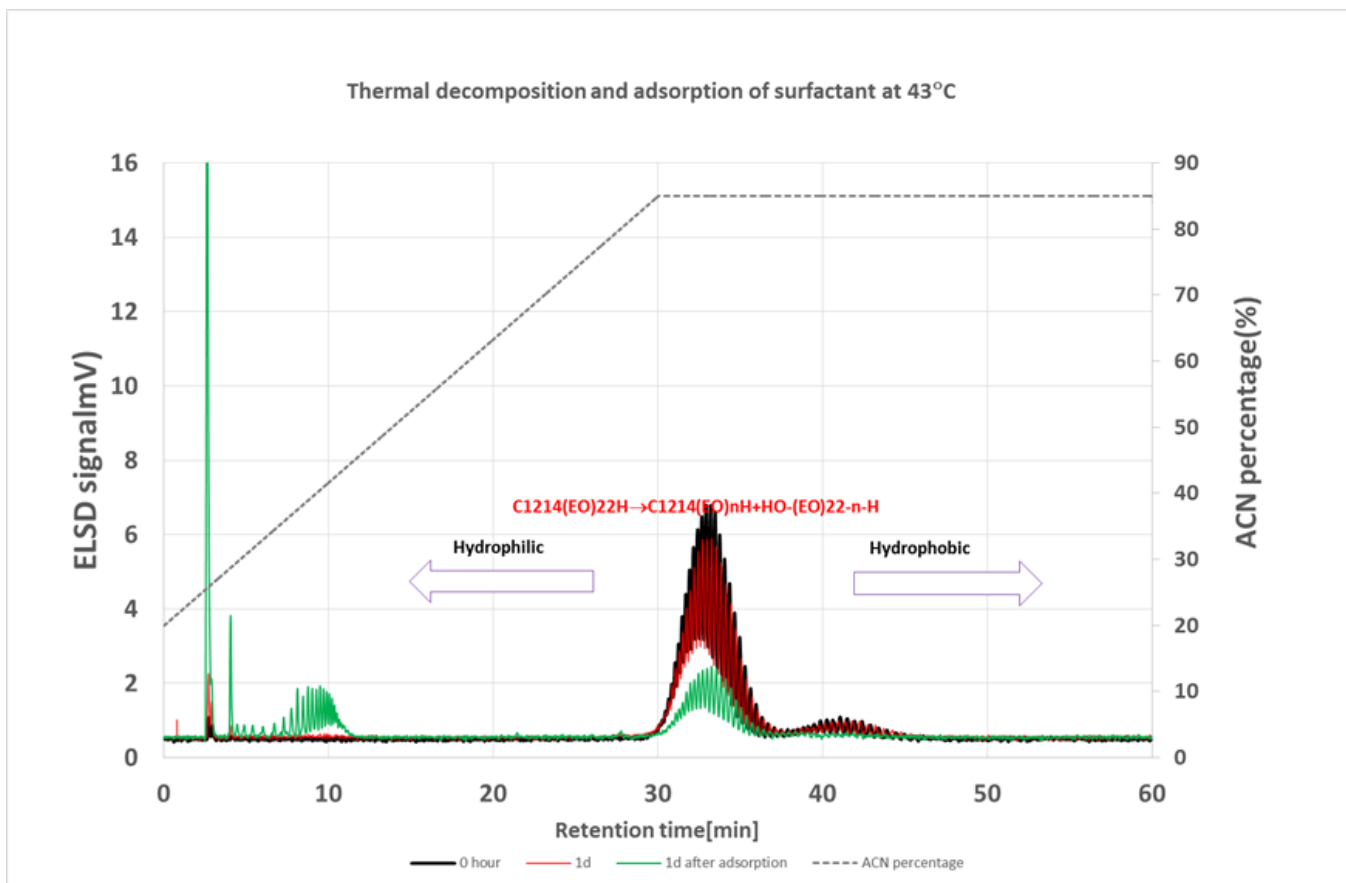
Effect of temperature



- Thermal decomposition is **severe at 80°C but not at 43°C**



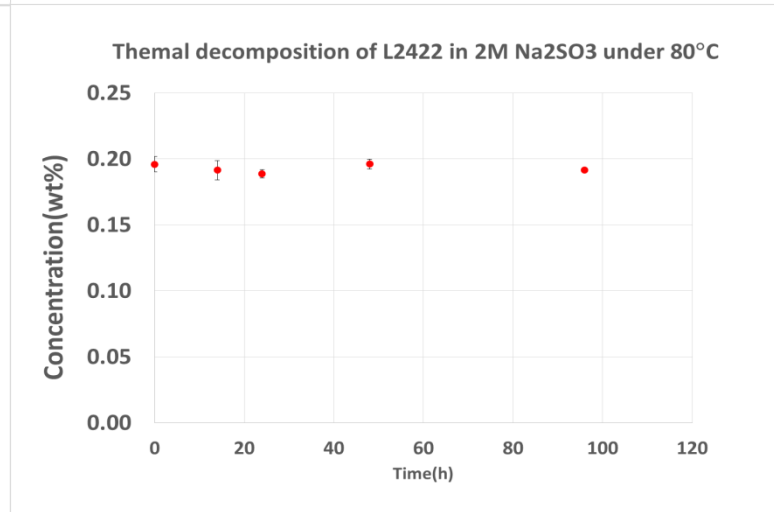
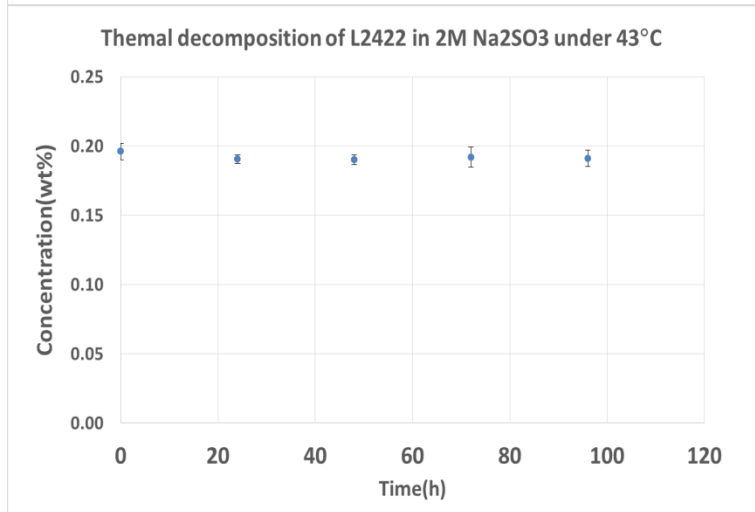
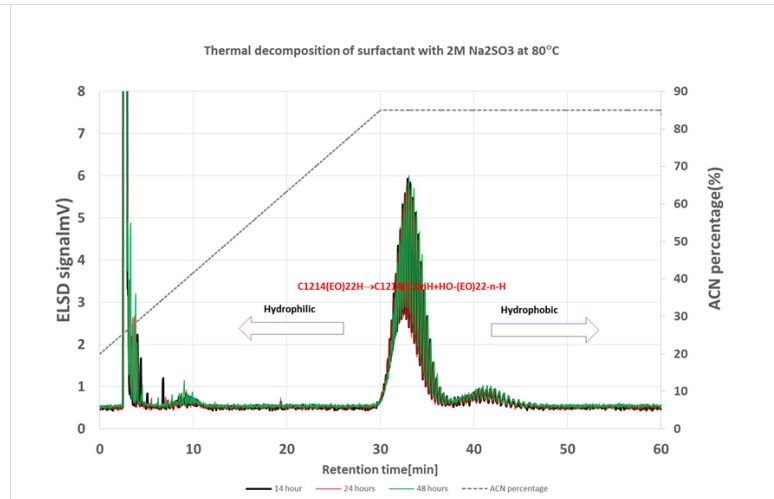
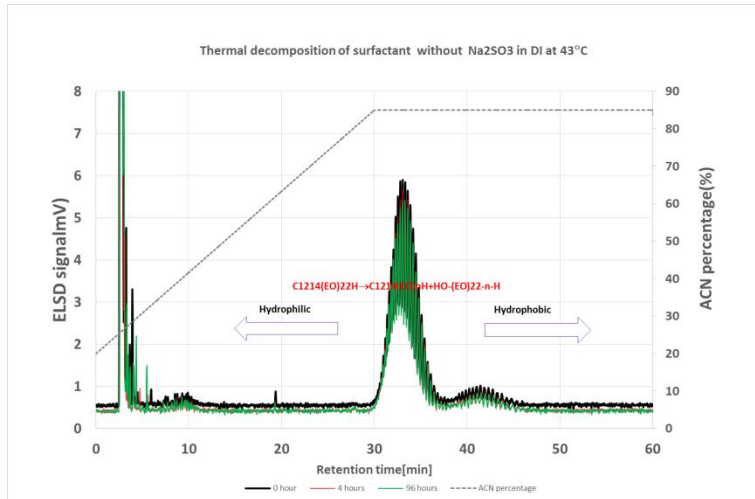
Thermal decomposition



- Thermal Decomposition is also severe at 43°C, if surfactant contacts with dolomite as pH increase from pH=6.2 to pH~9.0



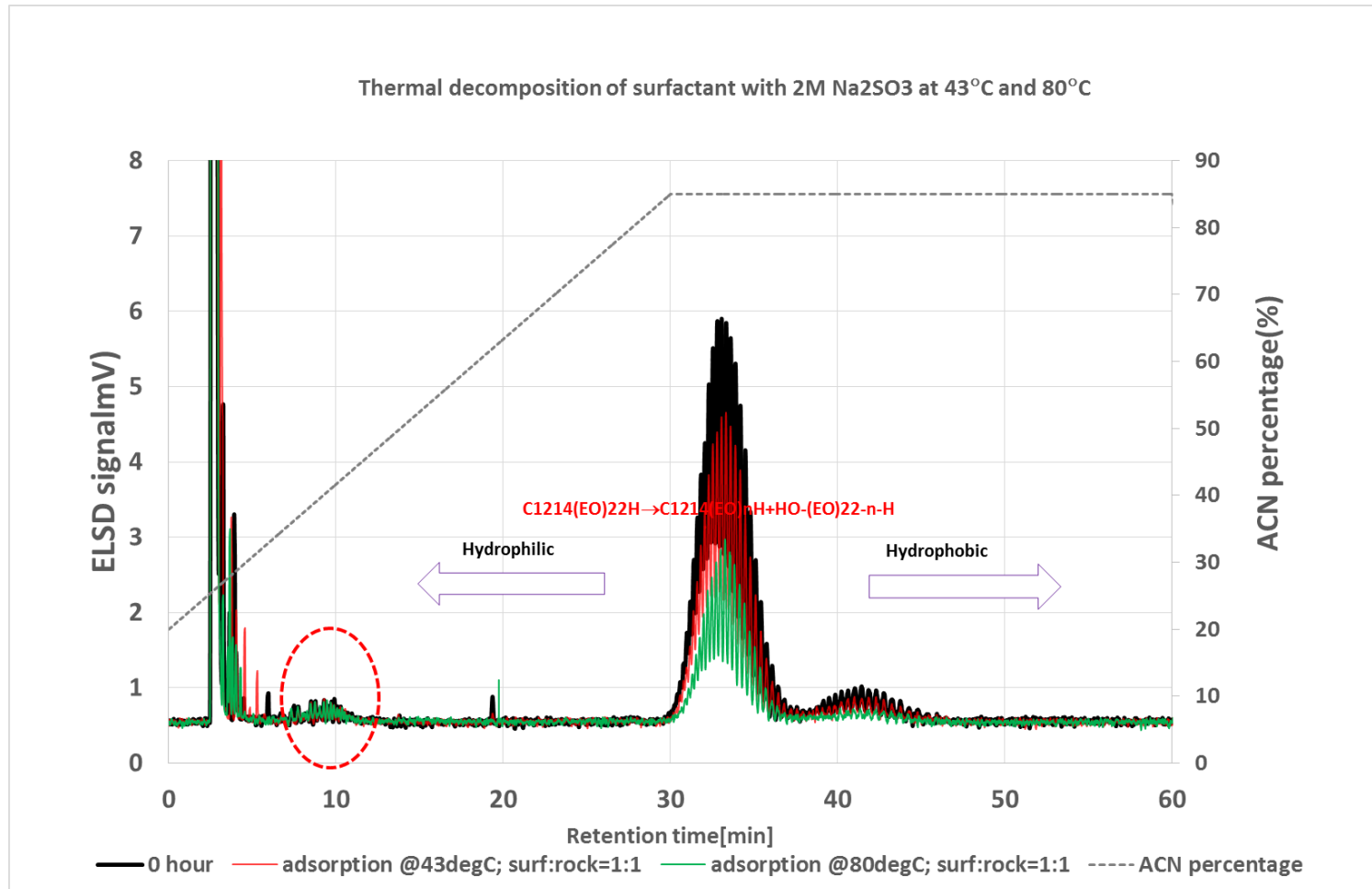
Effect of temperature with 2M Na₂SO₃



- No decomposition was found when 2M Na₂SO₃ was introduced at 43°C and 80°C



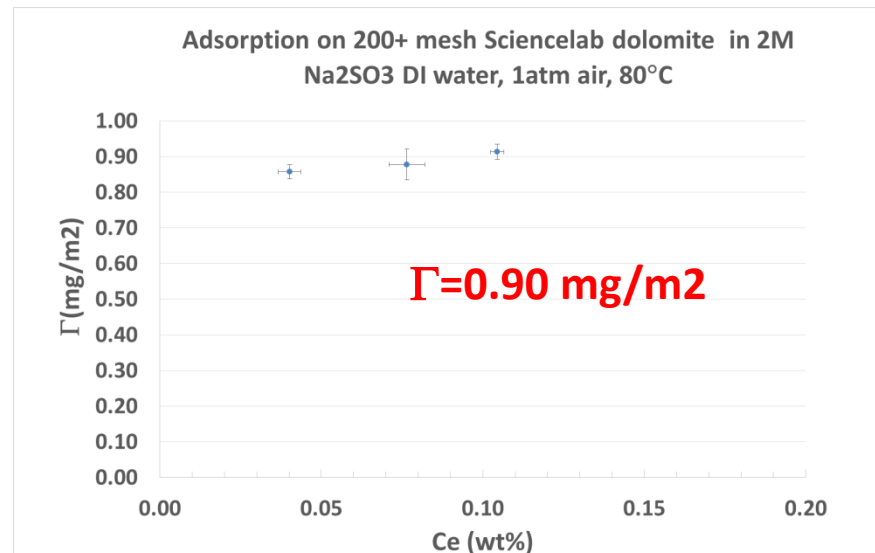
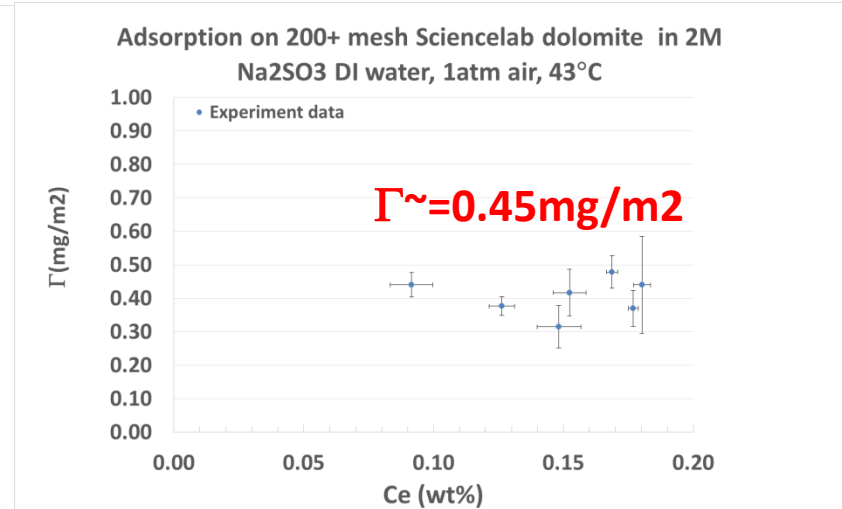
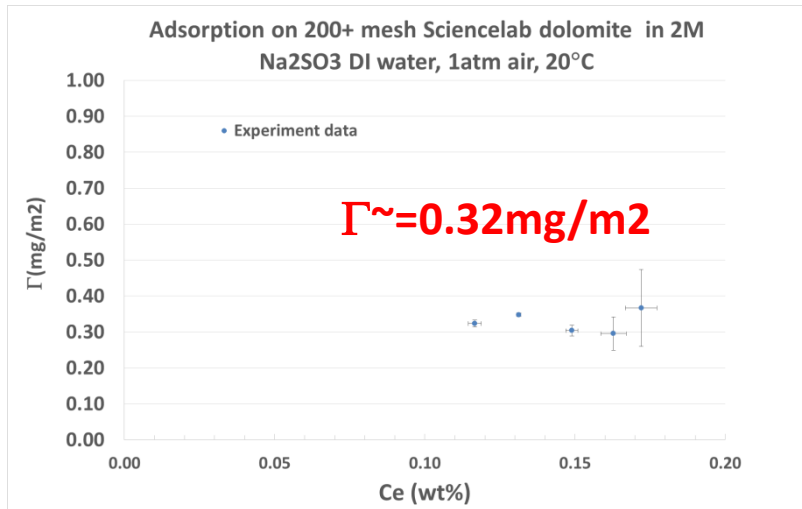
Adsorption (with 2M Na₂SO₃)



- For adsorption at 43°C and 80°C, the decomposition product of **alcohol was not observed** which indicate that **decomposition was inhibited with 2M Na₂SO₃**



Adsorption (with 2M Na₂SO₃)



**Adsorption
increases with
temperature
increase,
 $\Gamma < 1 \text{ mg/m}^2$**



Conclusions

- Using 1wt% L24_22 nonionic surfactant, Foam with apparent viscosity of **23 cp** can be generated in Silurian dolomite core (**80%** foam quality, **4 ft/day** injection rate, **110°F(43.3°C)**, pressure of **2600psi**, reservoir brine)
- **Gypsum** can **precipitate** during **depressurization** at 20°C which was observed by experiment and simulation results from PHREEQC
- **Adsorption on Silurian dolomite is as low as 0.08 mg/g**



Conclusions

- L2422 gets thermal **decomposition at high temperature** in the presence of oxygen
- **Adsorption** of L2422 on Sciencelab dolomite **increases with temperature** at reducing environment (2M Na₂SO₃), $\Gamma < 1 \text{ mg/m}^2$ for temperature range investigated [20°C~43°C~80°C]



Acknowledgement

RICE[®]
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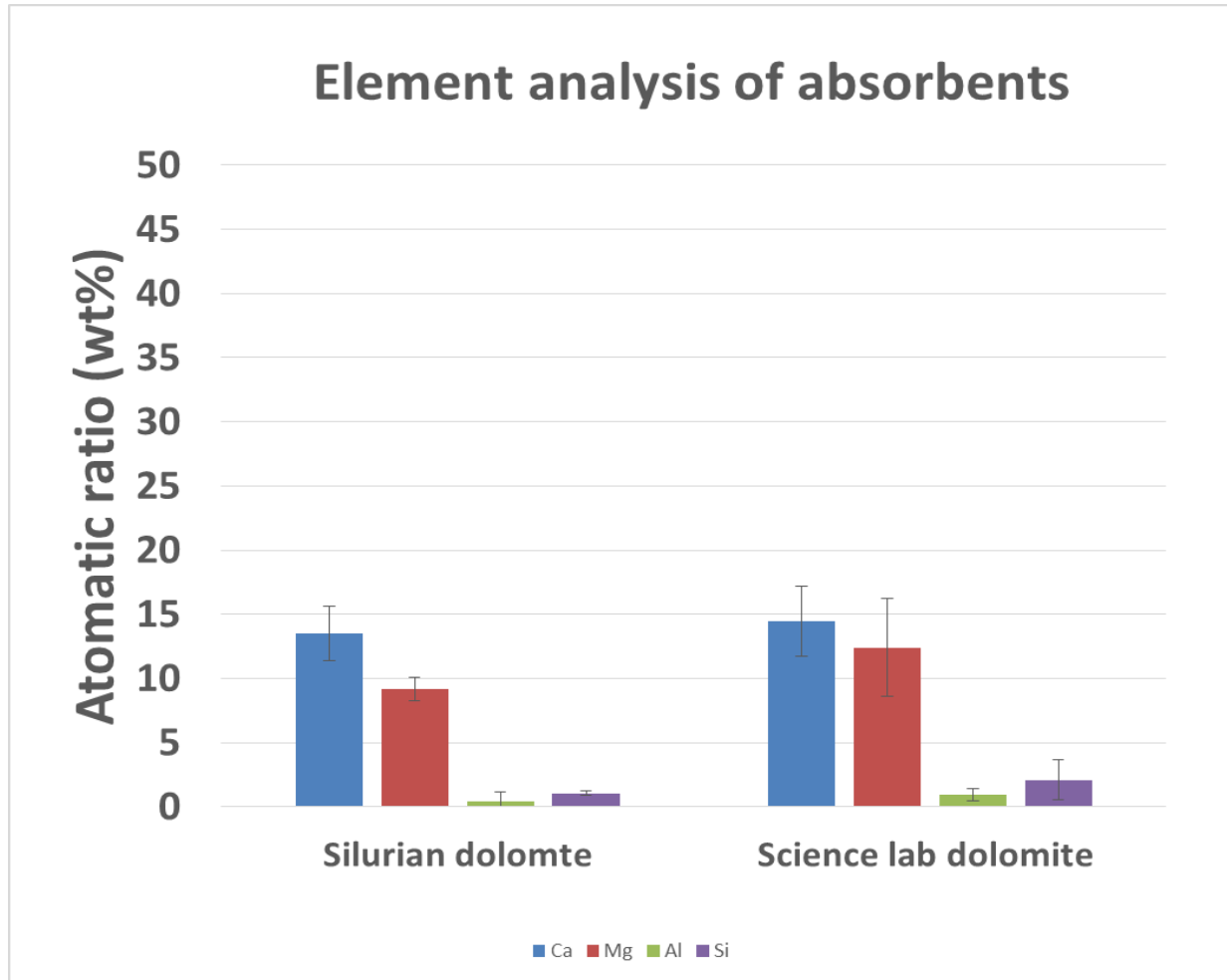
**This work was financially supported by
Department of Energy(DOE) and Rice
consortium for processes in porous media**



Thank you!
Any questions?



Element analysis of dolomite



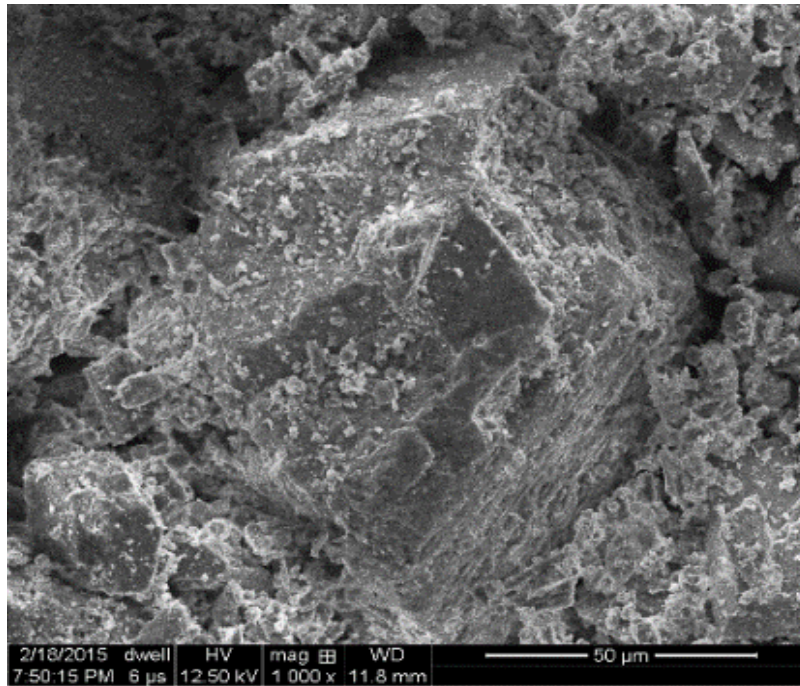


Two dolomite

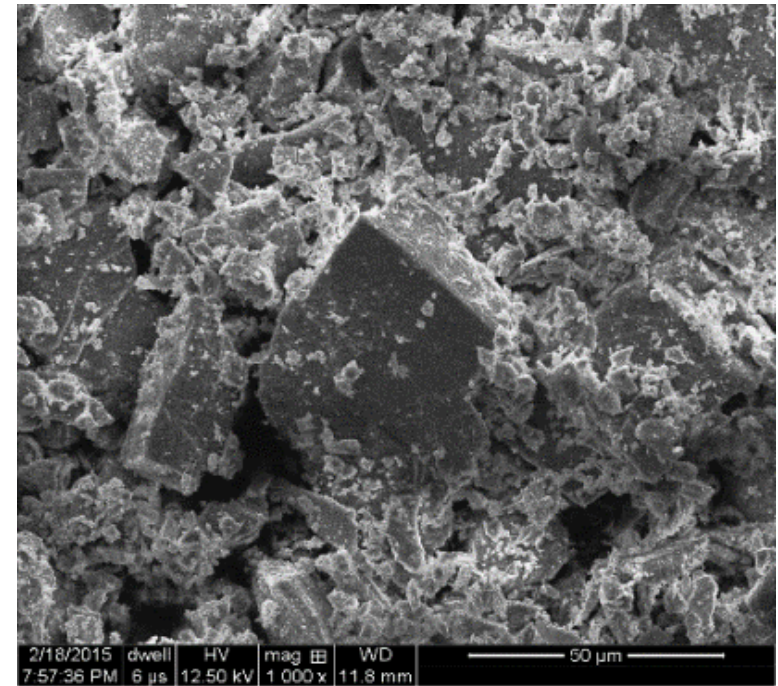
absorbent	Diameter	BET surface area(m ² /g)	Source
Silurian Dolomite	≤105 μm	0.95	Kocurek Industries, silurian dolomite, Ohio, USA
Sciencelab Dolomite	≤74 μm	0.89	Science lab.com, Inc.(Catalog #SLD4477),USA



SEM of two dolomite



Silurian dolomite



Sciencelab dolomite



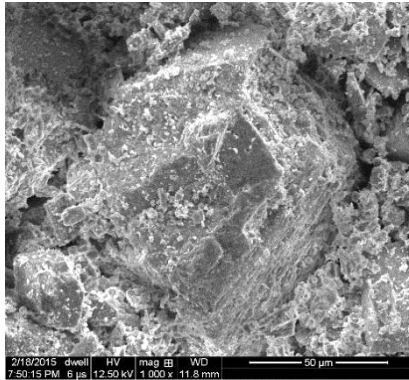
BET surface area of all absorbents

Absorbent	Diameter	BET surface area(m ² /g)	Source
Silurian Dolomite	≤105 μm	0.95	Kocurek Industries, silurian dolomite, Ohio, USA
Sciencelab Dolomite	≤74 μm	0.89	Science lab.com, Inc.(Catalog #SLD4477),USA
Calcite	5 μm	1.65	Alfa Aesar(catalog#11403),USA
silica	≤ 10 μm	1.16	U.S.silica Company, Pacific, MO, USA
Kaolin	0.1-4 μm	26.61	Sigma-Aldrich(Catalog#K7375),USA

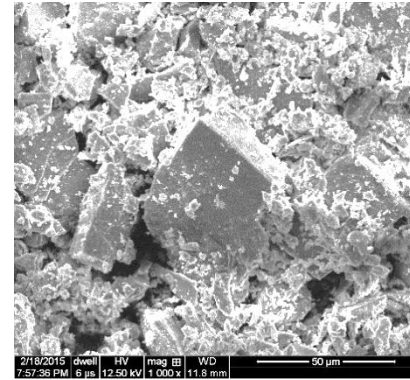


SEM Characterization of Adsorbent

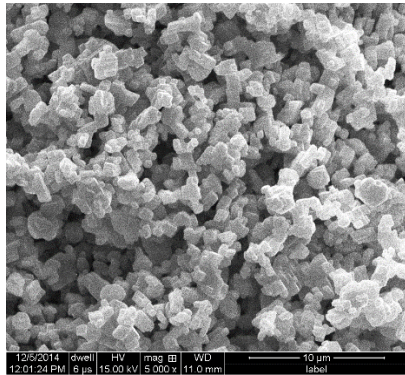
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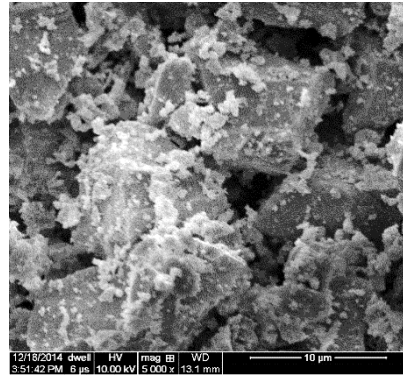
Silurian dolomite



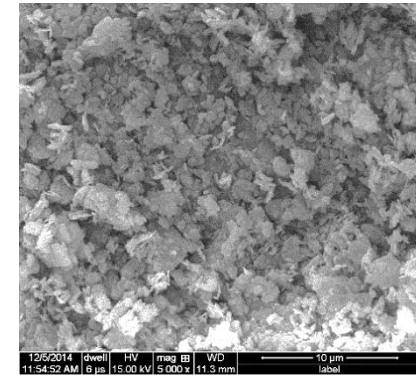
Sciencelab dolomite



Calcite



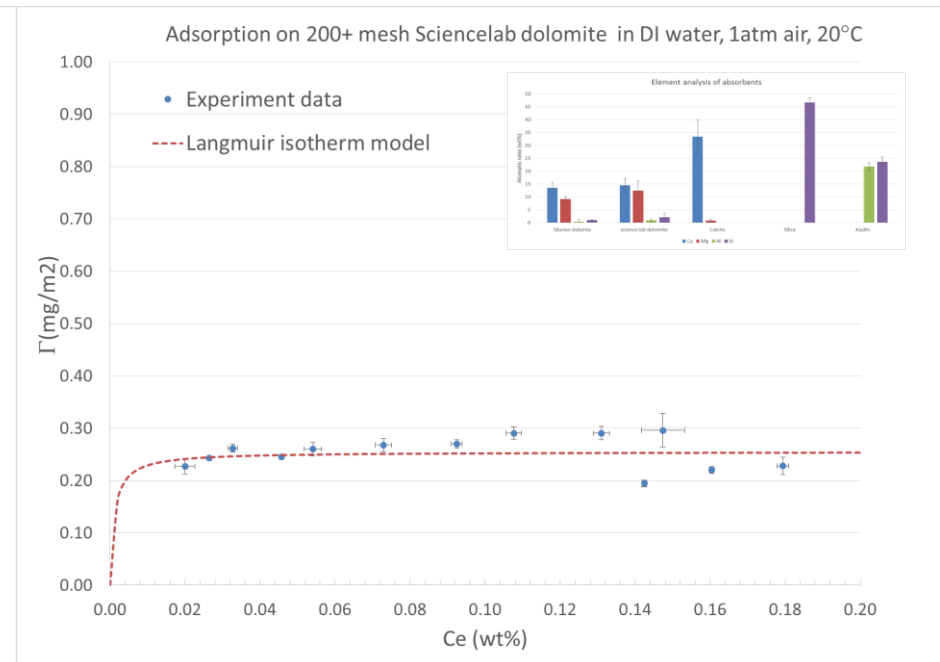
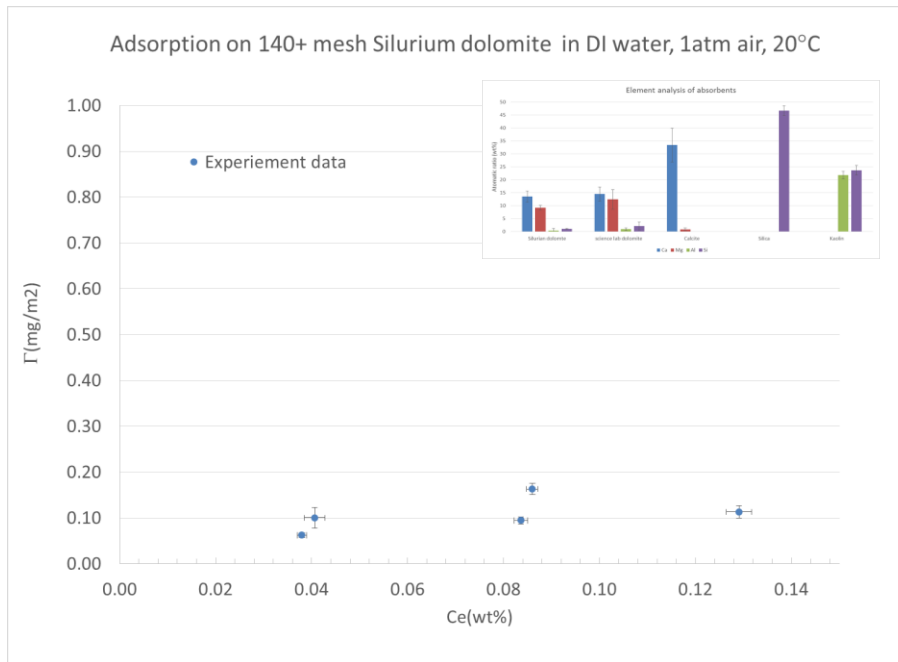
Silica



Kaolin



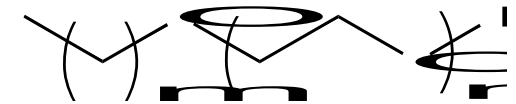
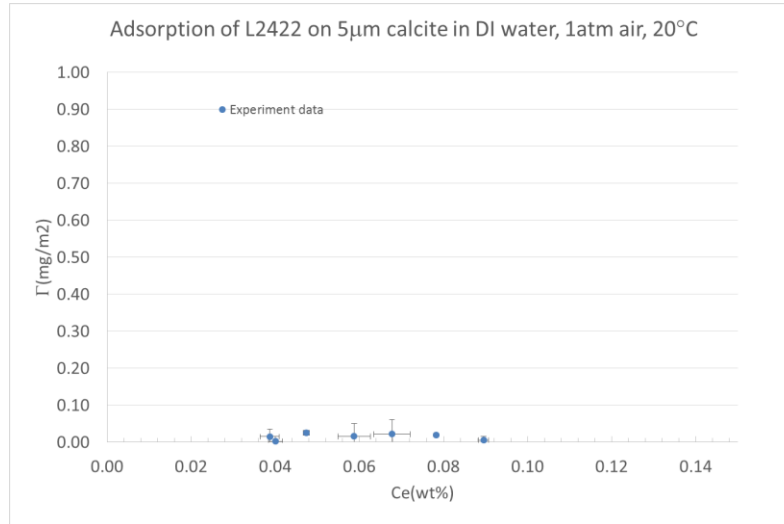
Effect of different dolomite



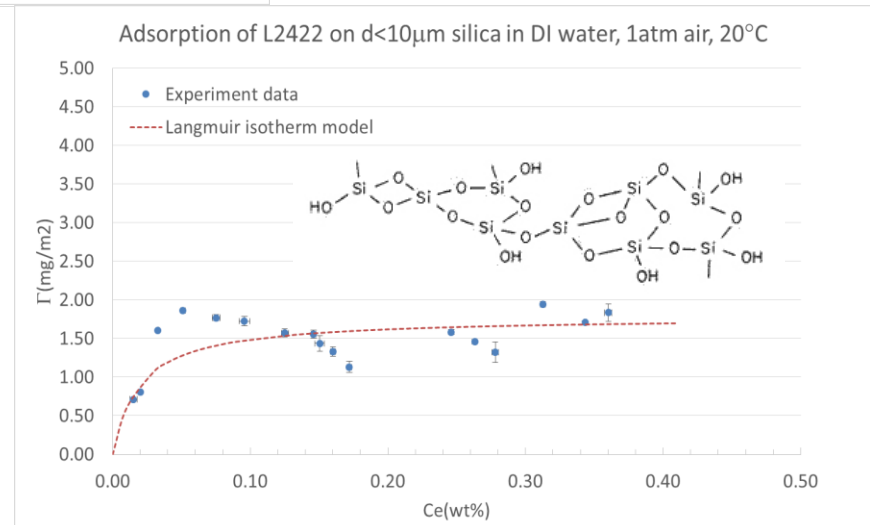
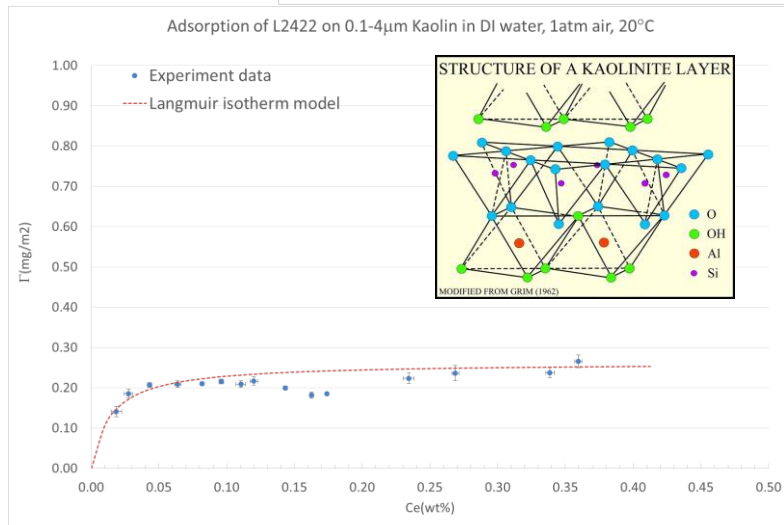
- The equilibrium adsorption amount of L2422 on Silurian dolomite is 0.12 mg/m² and 0.28 mg/m² for sciencelab dolomite
- The difference may be caused by the different amount of silica and clay on dolomite surfaces



Effect of impurities in Carbonate materials



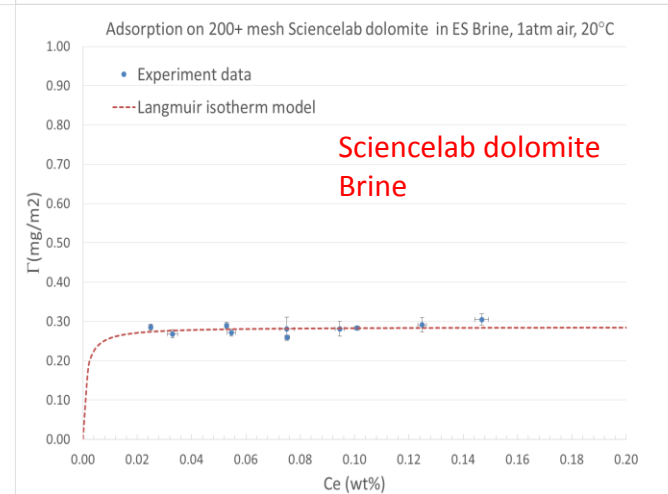
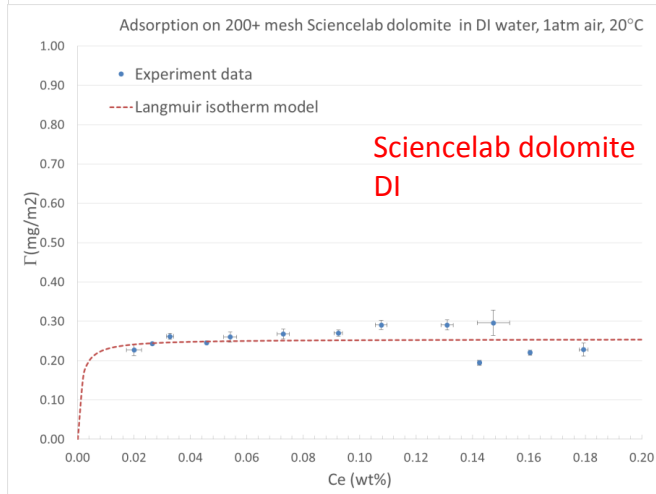
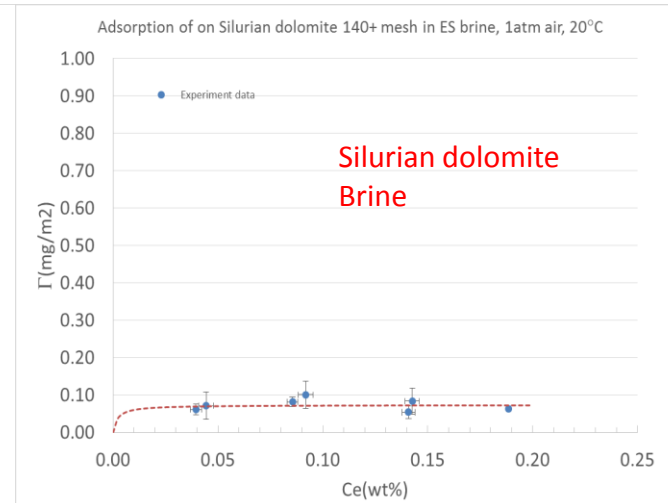
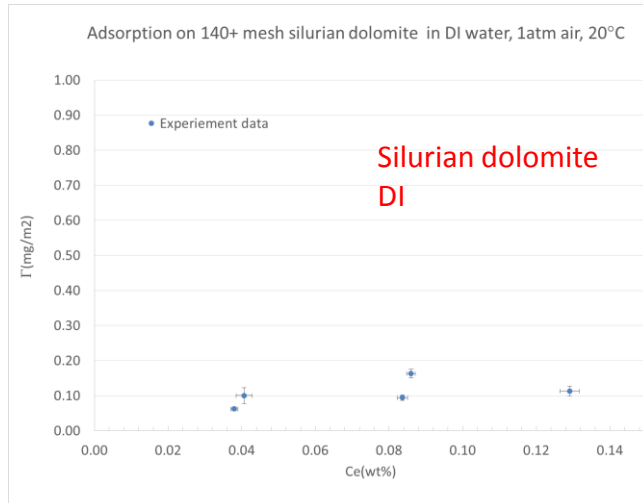
Hydroxyl group



- The equilibrium adsorption amount of L2422 on silica is **1.8 mg/m²** and **0.26mg/2** for Kaolin clay, which was caused by hydrogen bond formed; Below **0.05 mg/m²** for calcite



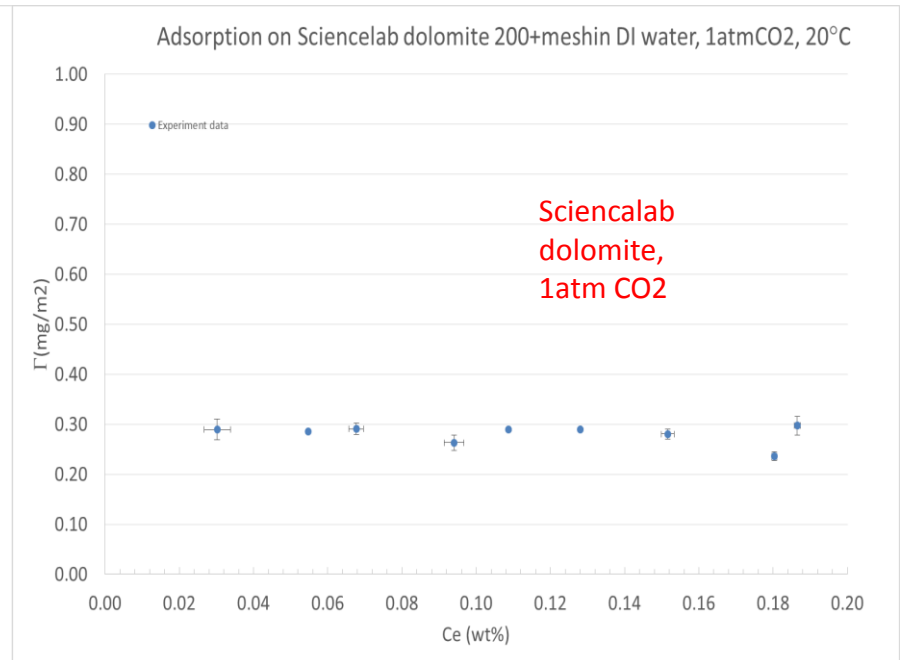
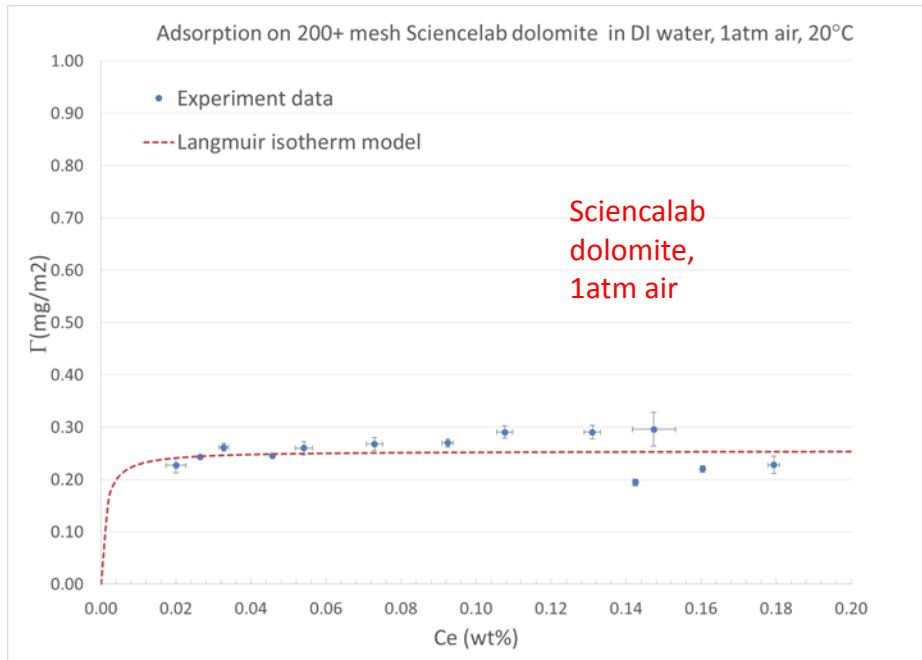
Effect of brine



- The adsorption of L2422 decreased from 0.12mg/m² to 0.09mg/m² for Silurian dolomite in the presence of ES brine
- The equilibrium plateau of adsorption amount of L2422 on sciencelab dolomite in ES brine is around 0.28mg/m² which is almost the same as that in DI water environment



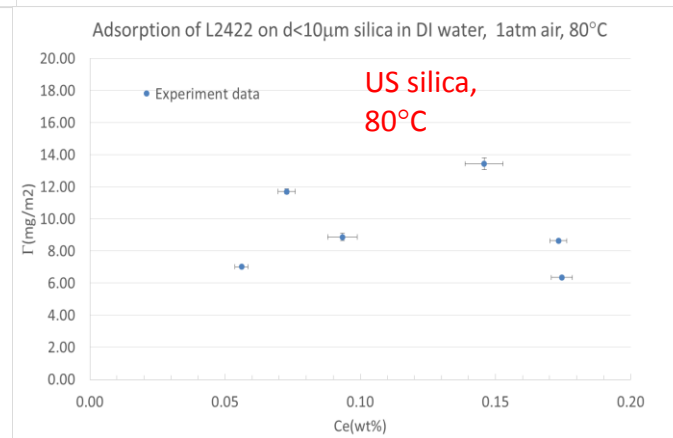
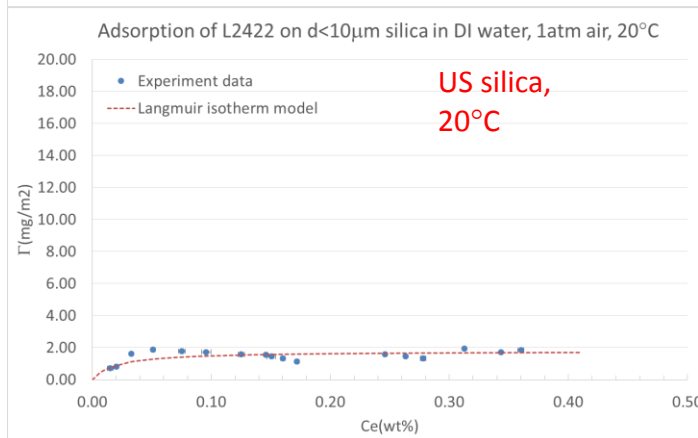
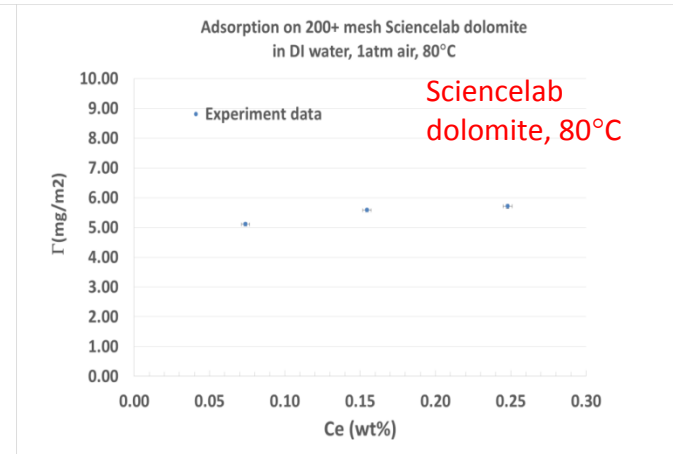
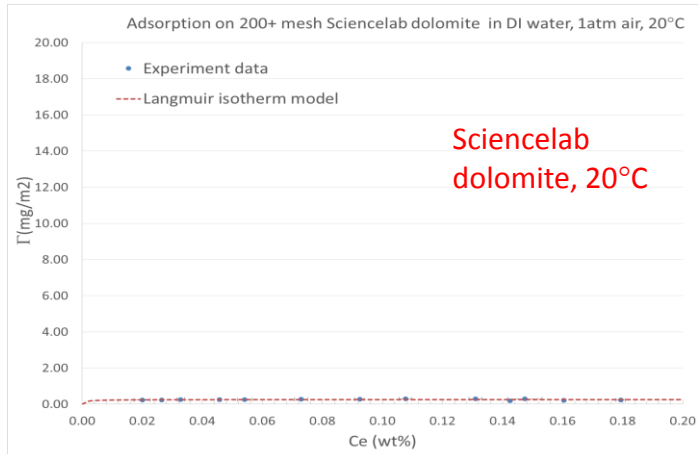
Effect of CO₂



- The adsorption of L2422 was almost the same under the 1atm air and 1atm CO₂, both at room temperature



Effect of Temperature



- The adsorption at 80°C are much higher than that under 20°C on calcite and silica
- Degradation beside of adsorption?



Decomposition



$m=11\sim 13;$
 $n=22$

The thermal decomposition of L2422 under high temperature in oxidization environment