Engineered Nano Materials for Subsurface Multiphase Flow

Center for Frontiers of Subsurface Energy Security

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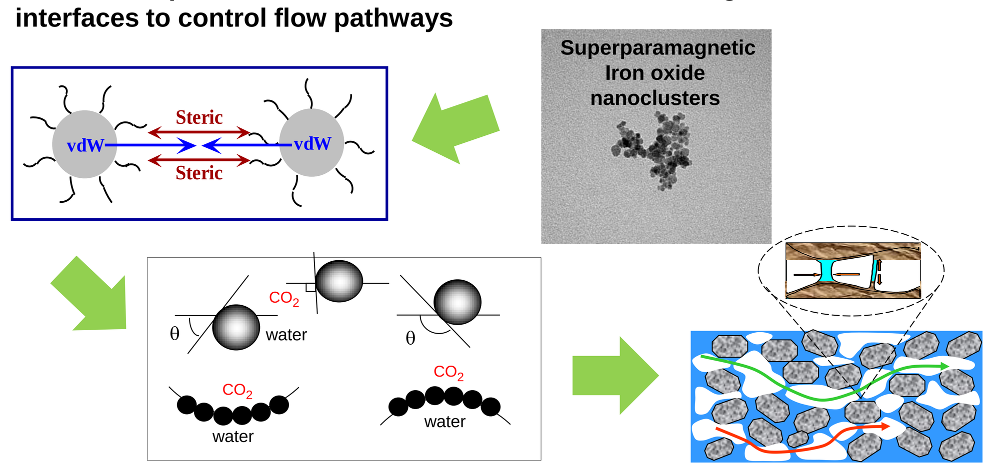
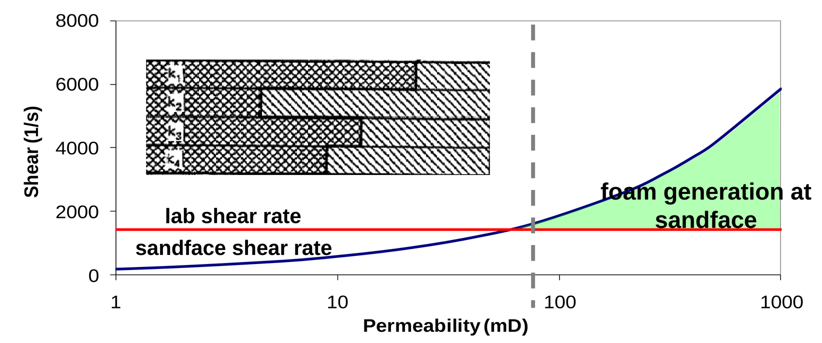
Objectives

- Minimize adsorption on minerals
- High magnetization for iron oxide
- Graphene oxide substrates particles
- Steric/electrosteric stabilization
- Control adsorption at oil-water and water-CO2 interfaces
- Particle surface coating with polymers and surfactants
- Smart nanoparticles for controlled foam formation at targeted interfaces to control flow pathways



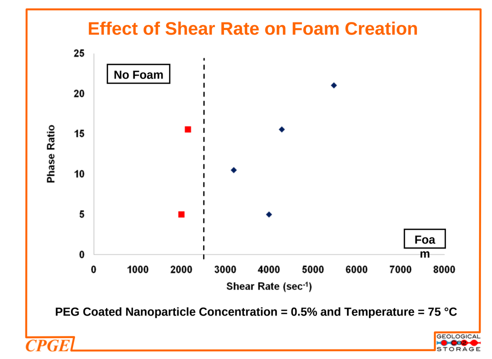
C/W emulsions for CO_2 sequestration Smart nanoparticles to block zones with preferential flow of CO_2

- **Storage efficiency**
  - Can we mitigate movement of CO_2 along high permeability paths?

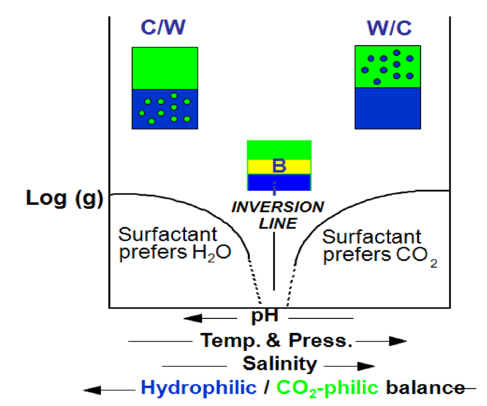


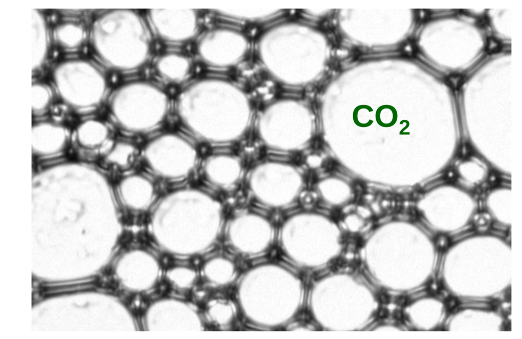
- **Reactive barriers**
  - Would CO_2 leaking through nanoparticle-laden brine create foam?
- **Passive barriers**
  - Can we inject a stable foam at the top of a structure after it is filled with CO_2?

C/W emulsions for CO_2 sequestration Smart nanoparticles to block zones with preferential flow of CO_2



- Viscous Fingering
- Channeling of CO_2 through high permeable regions
- Gravity over-ride (low CO_2 r)
- CO2-in-water foam- 10 micron





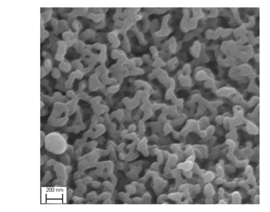
1 vol.% HC surf. in water, 94% CO_2 40°C, 3300 psia, 0.1 to 100 cP

Dhanuka, V. et al. J. Coll. Int. Sci. (06)

Summary

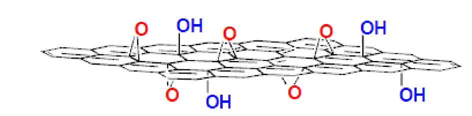
Adsorption of Iron oxide nanoparticles on mesoporous silica and sandstone and the fluid interfaces

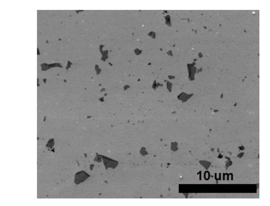
- Nanoparticle synthesis and surface coating
- Interfacial activities between oil and water
- Stability with high salinities



Design Graphene Oxide (GO) platelets for activity at oil-water (o/w) interface

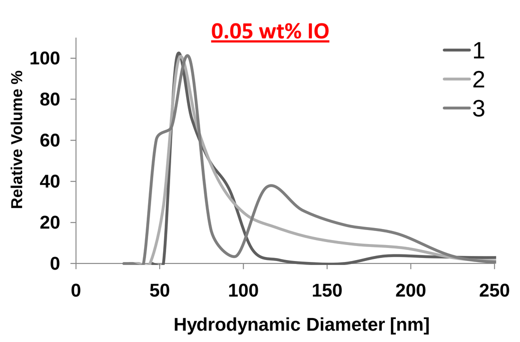
- Long-term emulsion stability due to kinetically trapped particles at the interface
- Stability of aqueous dispersions and emulsions with high salinities



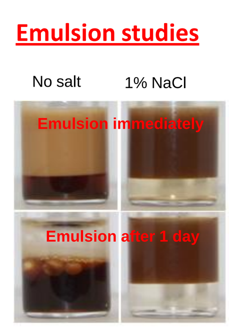


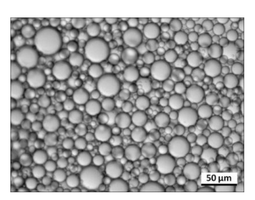
Iron-Oxide Nanoclusters with Cross-Linked PAA

- Anionic polymer: PAA (5100 g/mol)
- Cross-linker: hexane diamine $H_2N\text{-}(CH_2)_6\text{-}NH_2$ $R_1\text{-}N{=}C{=}N\text{-}R_2$
- Catalyst: 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide



Nanocluster Size Distribution by DLS

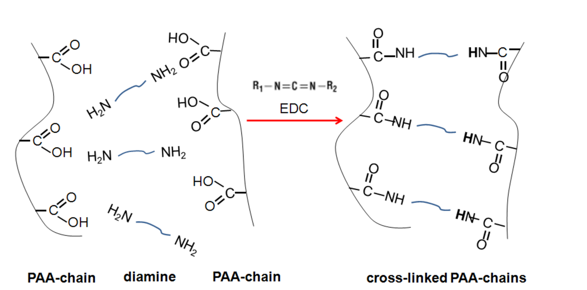




- Formation of gel film around particle prevents PAA desorption
- Cross-linked PAA coating improves interfacial activity (clear aq phase) and salt tolerance

Crosslinking with hexanediamine to bond adsorbed PAA coating on nanoparticle surface

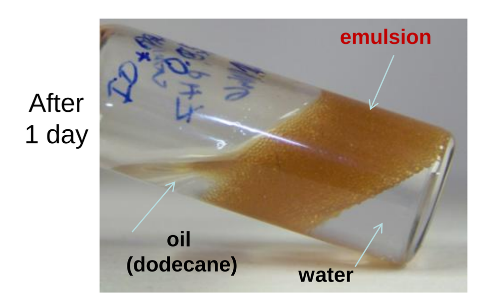
Scheme of Crosslinking



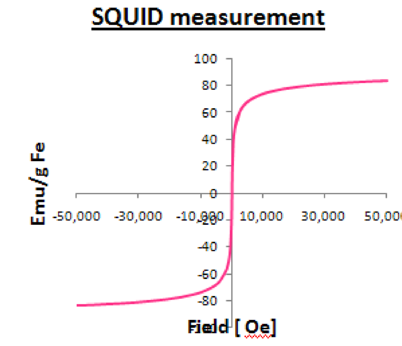
Desorption Study by TGA

Ratio [COOH:NH2]	pH	Salt [wt %]	TGA initial	TGA after washing [14000 rpm, 20 min]
No crosslinking (0.2 wt%)	8	0	14.3 wt%	6.3 wt%
		1		7.8 wt%
4:1 (0.2 wt%)	7			
		1	8.8	9.6 wt%

Emulsion Study :Ratio (COOH : Amine= 4:1 1% salt)

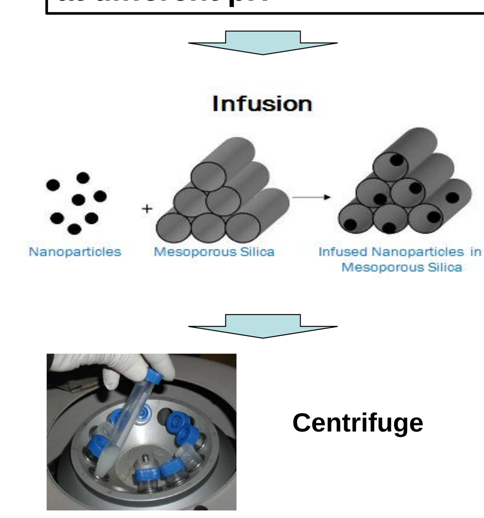


SQUID measurement



Nanoparticle Adsorption in Model Mesoporous Materials and Crushed Minerals

Prepare the citrate-coated Fe_3O_4 nanoparticle solutions at different pH



UV-Vis Spectrophotometer

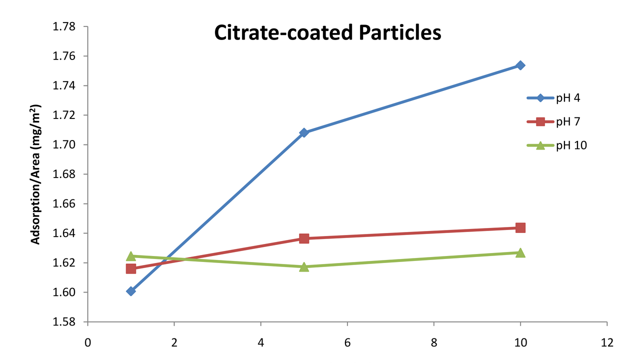
Adsorb nanoparticles into mesoporous silica particles

Centrifuge at 6000 rpm to remove silica

Determine adsorption by difference between initial and final iron oxide concentrations in the dispersions

Meso-Silica: 90-130 μm (diameter), 250 nm (disordered pore)
Specific area of Meso-silica : 15.3 m^2/g (BET)

Citrate-coated Iron Oxide Nanoparticles in Mesoporous Silica

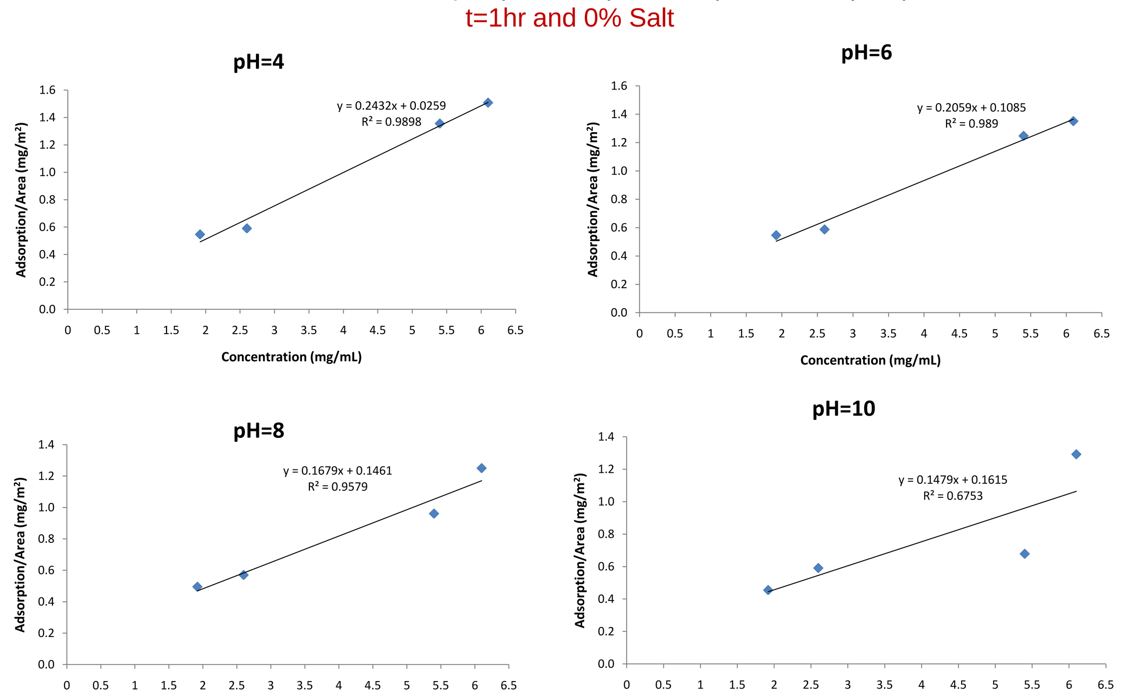


- pH 7-10 individual particles diffuse rapidly- equil < 1 hr
- pH 4 less electrostatic rep. of nps. aggregates diffuse more slowly
- greater adsorption (smaller electrostatic rep. with wall)
- Monolayer: 56.5 mg/m^2

Iron Oxide NPs(Cit-coated): ~5 nm, 0.27 wt % (conc.), 2 ml dispersion, 0.1 g silica
Meso-Silica: 90-130 μm (diameter), 250 nm (disordered pore)
Specific area of Meso-silica : 15.3 m^2/g (BET)

Adsorption of Citrate Coated IO

Iron Oxide NPs: ~5 nm
Meso-Silica: 30-50 μm (diameter), 50 nm (disordered pore)
t=1hr and 0% Salt



- linear increase of adsorption with particle concentration

Citrate coated iron oxide in small pore mesoporous silica: Summary

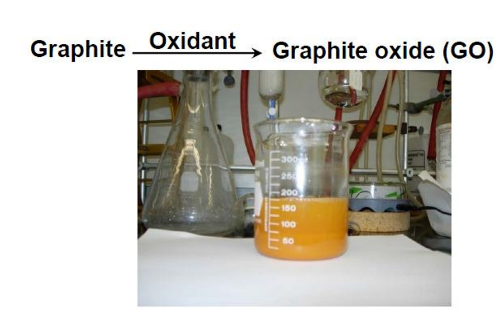
pH	% Salt	Mass IO adsorbed / surface area (mg/m^2)
4	0%	1.00
	3%	1.01
6	0%	0.93
	3%	0.95
8	0%	0.82
	3%	0.77
10	0%	0.75
	3%	0.79

- Citrate coating: zeta pot. -50 to -40 mV
- Small effect of pH on zeta potential and adsorption
- Rapid equilibration in less than 10 min.
- Linear increase of adsorption with particle concentration
- Monolayer: 56.5 mg/m^2 Adsorption 4.8% monolayer
- Iron Oxide NPs: 5-8 nm, Meso-Silica: 30-50 μm (diameter), 50 nm (disordered pore)

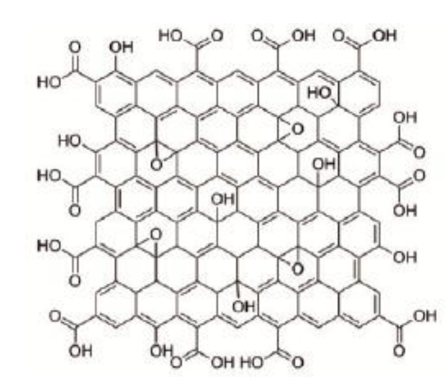
Graphene Oxide Platelets at Interface

Graphene Oxide

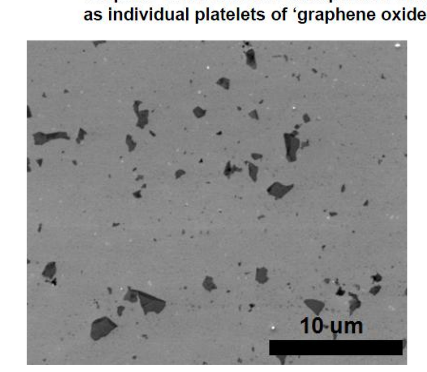
- Amphiphile with hydrophilic edges and a more hydrophobic basal plane
- excellent colloidal stability in water
- ability to adsorb on interfaces and lower the surface or interfacial tension



Graphite oxide exfoliated/suspended in water as individual platelets of 'graphene oxide'

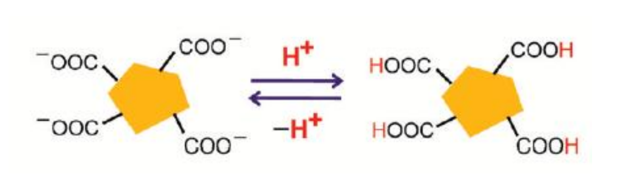


2-Dimensional Image



SEM image of Graphene Oxide sheet

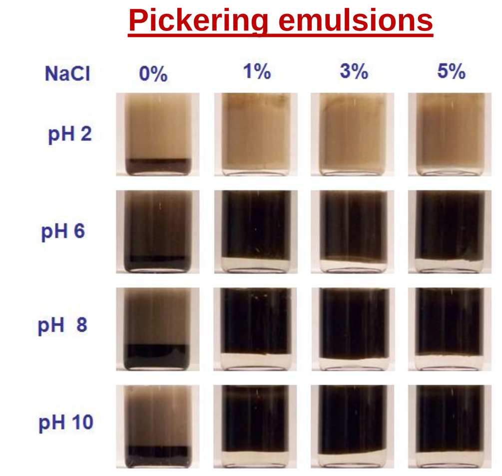
Graphene Oxide Platelets at Interface



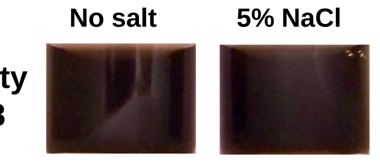
Kim, et al JACS, 2010

- GO is stable with higher concentration of NaCl
- Total volume of mass at interface is negligible
- At pH 2, GO becomes more protonated, less charged, and more hydrophobic, preferring the oil-water interface

Pickering emulsions



Salinity pH 8



pH 8