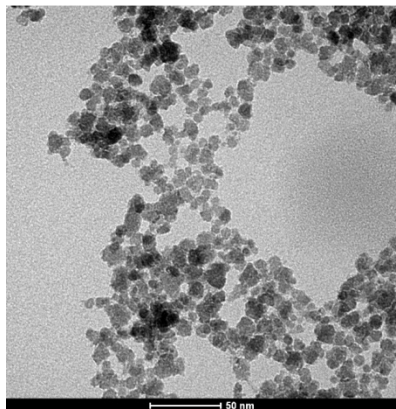
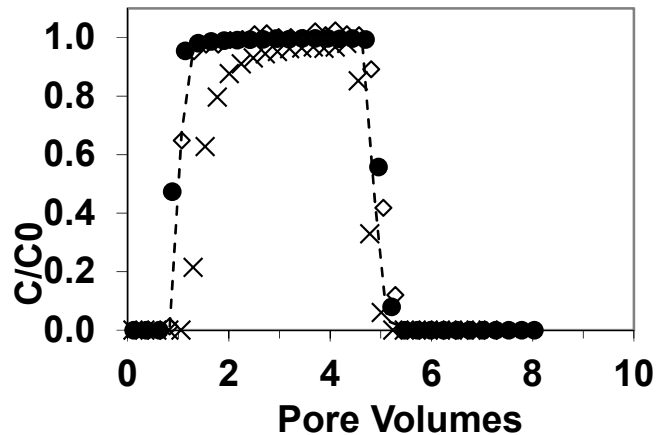


High Temperature Stability and Low Adsorption of Magnetite Particles Grafted with Sulfonated Copolymers on Berea Sandstone in High Salinity Brine



Colloids and Surfaces A:
Physicochemical and Engr. Aspects

Work was performed at University of Texas at Austin

Scientific Achievement

Random copolymers have been covalently grafted to superparamagnetic magnetite to provide electrosteric stabilization and low retention in flow through porous media in high salinity brine.

Significance and Impact

Colloidally stable and mobile nanoparticles in porous media are of interest in foams for mobility control in CO₂ storage to enhance efficiency of pore volume

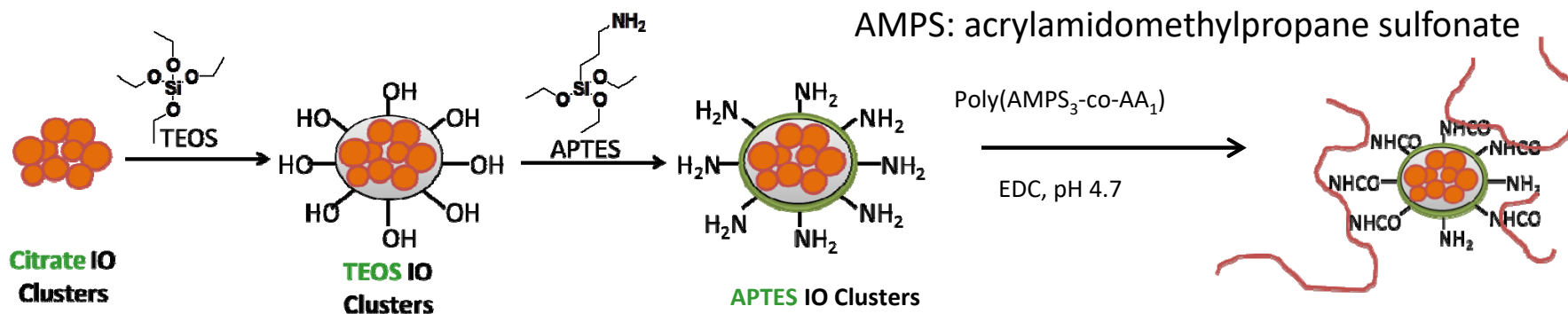
Electromagnetic imaging with superparamagnetic nanoparticles may be used to image flow of CO₂ foams towards understanding leaks

Research Details

Synthetic techniques have been developed to graft copolymers via amidation reactions on nanoparticles to achieve electrosteric stabilization at high salinity.

Random copolymers have been identified with sulfonate groups that produce low retention on sandstone given weak binding of Ca²⁺ ions.

Covalent grafting of Poly(AMPS-co-acrylic acid) to iron oxide via amidation reaction



Property	Citrate IONPs	TEOS IONPs Tetraethoxy-silane	APTES IONPs Aminopropyl-triethoxysilane	Poly(AMPS-co-AA) IONPs in brine
Hydrodynamic Diameter (nm)	19-26(90)	22-26(78)	50-59(79)	54-79(74)
	67-77(10)	76-90(22)	132-166(21)	159-190(26)
Zeta Potential at pH 5 (mV)		-34.5 - 6	28.6 - 3	-53.6 - 1
Organic content (wt. %)		8 - 1.0	19.5 - 1.0	47.9 - 4.5
Amine content (μmol/mg IO)		---	3.6 - 0.5	---

Hydrodynamic diameter, zeta potential and organic content after each step used to monitor the coating reactions.

Abbreviations: EDC: ethyl carbodiimide catalyst IO NPs: iron oxide nanoparticles

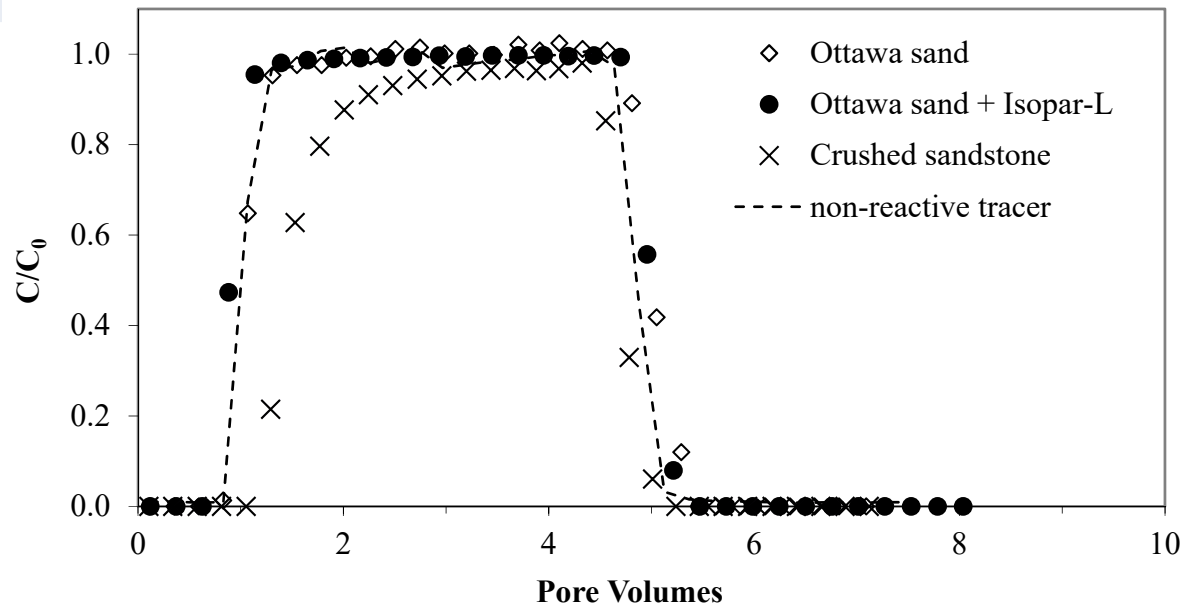
Stability in API brine and transport in Ottawa sandpack

Electrosteric stabilization from poly(AMPS) copolymer in API brine at 120 C based on DLS hydrodynamic diameter

Low retention (3 $\mu\text{g/g}$) indicates weak interactions of particles with crushed Ottawa sandstone

(with Kurt Pennell Tufts University)

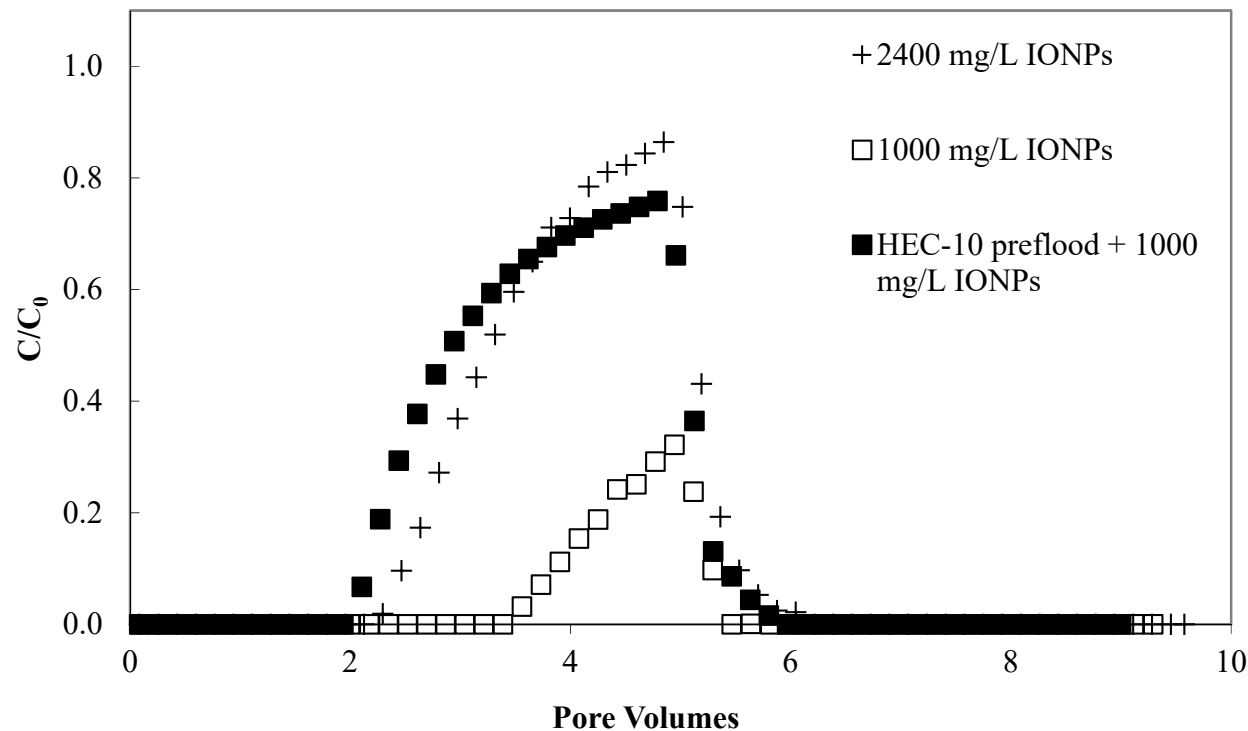
Hydrodynamic Diameter(nm), (Cumulative, %V)			
0 days		30 days	
DI	API	DI	API
153-177 (54)	34.5-48.6 (58)	61-70 (48)	65-97 (74)
410-453 (46)	140-185 (42)	235 (52)	200-267 (26)



Isopar-L is a paraffin oil

API brine: 8 wt% NaCl
2 wt. % CaCl2

Retention of magnetite particles in consolidated Berea sandstone



with Kurt Pennell at
Tufts University

4 pore volumes injected

- 100 fold higher retention of 433 $\mu\text{g/g}$ because of adsorption on stronger binding sites and lower permeability: for example, clays including effect of Ca^{2+} bridging of anionic sites
- Retention improved by blocking reactive sites with hydroxyethylcellulose-10. (252 $\mu\text{g/g}$)
- Recently, we have lowered the retention to 50 $\mu\text{g/g}$ with block copolymer stabilizers



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Conclusions

- **Covalent attachment of random copolymer poly(AMPS-r-AA) provides electrosteric stabilization to 120 C in API brine**
- **Weak Ca^{2+} bridging interactions of AMPS groups with Si-O⁻ surface leads to small retention**
- **Hydroxyethylcellulose adsorbs on more reactive sites and decreases retention by ~ 2 fold**
- **In more recent work we have further reduced retention by reducing Ca^{2+} bridging**
 - End capping of the carboxylate sites on the acrylic acid monomers
 - Keeping acrylic acid sites away from the surface with block copolymers rather than random copolymers

