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

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 CO\textsubscript{2} storage to enhance efficiency of pore volume
Electromagnetic imaging with superparamagnetic nanoparticles may be used to image flow of CO\textsubscript{2} 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 Ca\textsuperscript{2+} ions.
Covalent grafting of Poly(AMPS-co-acrylic acid) to iron oxide via amidation reaction

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Citrate IONPs</th>
<th>TEOS IONPs Tetraethoxysilane</th>
<th>APTES IONPs Aminopropyltriethoxysilane</th>
<th>Poly(AMPS-co-AA) IONPs in brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrodynamic Diameter (nm)</td>
<td>19-26(90)</td>
<td>22-26(78)</td>
<td>50-59(79)</td>
<td>54-79(74)</td>
</tr>
<tr>
<td></td>
<td>67-77(10)</td>
<td>76-90(22)</td>
<td>132-166(21)</td>
<td>159-190(26)</td>
</tr>
<tr>
<td>Zeta Potential at pH 5 (mV)</td>
<td>-34.5 - 6</td>
<td>28.6 - 3</td>
<td>-53.6 - 1</td>
<td></td>
</tr>
<tr>
<td>Organic content (wt. %)</td>
<td>8 - 1.0</td>
<td>19.5 - 1.0</td>
<td>47.9 - 4.5</td>
<td></td>
</tr>
<tr>
<td>Amine content (μmol/mg IO)</td>
<td>---</td>
<td>3.6 - 0.5</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>
### Stability in API brine and transport in Ottawa sandpack

<table>
<thead>
<tr>
<th>Hydrodynamic Diameter (nm), (Cumulative, %V)</th>
<th>0 days</th>
<th>30 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI</td>
<td>API</td>
<td>DI</td>
</tr>
<tr>
<td>153-177</td>
<td>(54)</td>
<td>34.5-48.6</td>
</tr>
<tr>
<td>410-453</td>
<td>(46)</td>
<td>140-185</td>
</tr>
</tbody>
</table>

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

Low retention (3 μg/g) indicates weak interactions of particles with crushed Ottawa sandstone.

(With Kurt Pennell, Tufts University)

Isopar-L is a paraffin oil.

API brine: 8 wt% NaCl  
2 wt% CaCl2
Retention of magnetite particles in consolidated Berea sandstone

-100 fold higher retention of 433 μg/g because of adsorption on stronger binding sites and lower permeability: for example, clays including effect of Ca²⁺ bridging of anionic sites
-Retention improved by blocking reactive sites with hydroxyethylcellulose-10. (252 μg/g)
-Recently, we have lowered the retention to 50 μg/g with block copolymer stabilizers

with Kurt Pennell at Tufts University

4 pore volumes injected
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.