Welcome!
The webinar will begin promptly at Noon (CST).

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What you can’t see can actually help you: Nanoparticle applications in the subsurface

Hugh Daigle
Chun Huh
Host: David DiCarlo
Nanoparticles for subsurface engineering themes

• Conceptual focus: *Engineered nanoparticles combined with one or more fluid phases to provide new capabilities or performance*

• Old problems, new tricks
  – *Introduction of other industries’ extensive nanotechnology developments to upstream oil industry*
  – *Environmental focus on utilizing nanoparticles that can be re-used, in place of chemicals*

• Synergy from sustained focus on practical applications

VISION
*Through the NSE, UT CPGE will be the leading academic entity for collaborative invention and development of applications of nanoparticles to oil and gas exploration and production*
Nanoparticles research in CPGE

• 9 projects currently in progress, with participation of 8 faculty members, 3 post-docs, and 7 graduate students

Research focus areas
• Nanoparticle-stabilized foams and emulsions
  • Enhanced oil recovery
  • Conformance control
  • Alternative fracturing fluids
• Well construction
  • Nanoparticles as cement additives to increase compressive & shear bond strength
• Superparamagnetic nanoparticles
  • Reservoir imaging and sensing
  • Focused heating
  • Removal of dispersants and ions from produced water
What are nanoparticles?

International Union of Pure and Applied Chemistry (IUPAC) definition:
A particle of any shape with diameter < 100 nm

Iron oxide nanoparticles
(Suteewong et al. 2010)

Silica nanoparticles
(Nanocomposix)

The use of iron oxide and silica minimizes environmental hazards
Basic Requirements for Nanoparticles

• (1) Long-term dispersion stability in reservoir fluids
(2) Able to transport long distance in the reservoir
(3) Able to attach preferentially at target sites

• NP surface coating should not desorb in reservoir brine; coating needs to be covalently bonded to NP surface, or wrap around NP as a non-detachable polymeric film

• Reservoir brine salinity and pH are important design parameters for optimum surface coating

Oleic acid coating
PEG-based surfactant

Mondini et al., 2013
Synthesis & Surface Coating

Iron-oxide paramagnetic NP clusters

• Synthesis
  – Co-precipitation of iron-chloride salts in alkaline media → Fe₃O₄

• Surface coating
  ✓ The requirements for stability and transportability can be accomplished with optimization of generally hydrophilic coating

  ✓ To achieve the targeted delivery, polymers with 2-3 ligands are usually needed

  (Ligand for attachment to NP surface; hydrophilic ligand; hydrophobic ligand)
Nanoparticle-stabilized emulsions

- Van der Waals forces between nanoparticles stabilize the emulsion droplet interface.
- The wettability of the nanoparticle surface determines the type of emulsion:
  - Hydrophilic nanoparticle: oil-in-water
  - Hydrophobic nanoparticle: water-in-oil

Contact Angle for Oil-Water Interface in Relation to Emulsion Structure
(Dickson et al. 2004)
How do emulsions help with oil recovery?

Schematic of Mechanism of Residual Oil Recovery
Emulsion examples

- Oil-in-water nanoparticle stabilized emulsions are highly shear thinning power-law fluids where higher shear rates form more stable emulsions due to smaller droplet diameters.
- Emulsion used 69% by volume light mineral oil as the organic phase and had a particle diameter of 24 microns.

![Emulsion Droplet Size Dependent on Shear Rate (Gabel et al. 2014)](image1)

![Emulsion Rheology for Various Internal Phases](image2)
Natural gas liquids in emulsions

- NGLs ("wet" natural gas) contain a mixture of gaseous hydrocarbons: ethane, propane, butane, isobutane and pentanes+

- NGLs are produced in gas plants and refineries and are known as the "by-products" of the oil and gas industry

- NGL production has increased significantly in recent years: 1.7 MMBD in 2005 to 2.5 MMBD in 2012 with a projected 3 MMBD by 2025 (Energy Information Administration)

- Motivation: Incorporate NGLs as the organic phase for oil-in-water emulsions
Residual oil recovery in corefloods

- Boise sandstone
- Core 1” diameter, 12” length
- ISCO syringe pumps used to inject oil and brine
- Accumulator used to inject emulsion
- Differential transducers to measure pressure drop

Experimental Set-Up for Injection of Oil-in-Water Emulsion through a Boise Sandstone Core at Residual Oil Saturation
90-100% recovery of mineral oil with pentane-in-water emulsion (1:1 mixture of 2 wt% Nyacol DP9711 silica nanoparticle dispersion + 0.5 wt% IGEPAL CO-70 surfactant)

Recovered Residual Light Mineral Oil

Emulsion Present in Effluent: Yes

Boise Core – Mineral Oil-in-Water Emulsion Injection

<table>
<thead>
<tr>
<th>k (D)</th>
<th>φ</th>
<th>PV (ml)</th>
<th>Flow Rate (mL/min)</th>
<th>Velocity (ft/day)</th>
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<tbody>
<tr>
<td>4.21</td>
<td>0.28</td>
<td>46.2</td>
<td>4</td>
<td>37.29</td>
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</tbody>
</table>

 Slug Size: Continuous Injection
 Residual Oil: Light mineral oil
 Total Residual Oil Present: 8.5 ml
 Total Residual Oil Recovered: 8.5 ml
 Emulsion Present in Effluent: Yes

<table>
<thead>
<tr>
<th>Viscosity Difference</th>
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</thead>
<tbody>
<tr>
<td>Pentane</td>
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<tr>
<td>Light Mineral Oil</td>
</tr>
<tr>
<td>Scenario</td>
</tr>
<tr>
<td>--------------------------------------------------------</td>
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<tr>
<td>Continuous Injection 4mL/min</td>
</tr>
<tr>
<td>Continuous Injection 1mL/min</td>
</tr>
<tr>
<td>0.50 PV Emulsion Slug 4mL/min</td>
</tr>
<tr>
<td>0.50 PV Emulsion Slug 1mL/min</td>
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<tr>
<td>Continuous Emulsion w/ Surfactant 4mL/min</td>
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Nanoparticle-stabilized CO$_2$ foams

Role of surfactant
- Reduces interfacial tension
- Increase adsorption of polymers/NPs to C/W interface
Nanoparticle-stabilized CO$_2$ foam for conformance control

How do we get good conformance control in a heterogeneous formation like this?
Simulation results

• Co-injection: no foam vs. foam
CO$_2$ foam as an alternative fracturing fluid

Development of nanoparticle-stabilized foams for reduced water usage in hydraulic fracturing

New materials and techniques give tunable foams which are initially high viscosity to carry proppant then low viscosity to help oil production. The foams reduce water usage by over 90%.
Why are nanoparticle foams stable?

NPs irreversibly adsorb at water-gas interface (with molar adsorption energy of ~ 100 kT)

Silica NPs (~0.1-1 wt%)

+ -SiOH / Surfactant / Polymer

Jamming of NPs stabilizes gas bubbles

NP stabilized foams have dense texture and show no visible coarsening within ~24 hours
Fracture cleanup / water saturation

Water
Vis. Fracpad
Foam 70%
High Vis.
Foam 70%
Low Vis.
Foam 90%
High Vis.
Foam 90%
Low Vis.
Gas productivity from the reservoir after 4000 days of production

Gas production rate

Cumulative gas production
Zonal Isolation - Motivation

Incompatibility of cement and shale could lead to an increased risk in:

- gas migration
- inter-layer communication
- well control hazard
- sustained casing pressure
3-day compressive strength test

- 70° F and atmospheric pressure
- Average based on 3 samples

NP promotes cement hydration by acting as nucleation sites
3-day shear bond strength test

- 70°F and atmospheric pressure
- Average based on 3 samples

<table>
<thead>
<tr>
<th>Shear Bond Strength (psi)</th>
<th>Class A</th>
<th>Class C</th>
<th>Class H</th>
<th>ZrO₂ Class H</th>
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</thead>
<tbody>
<tr>
<td></td>
<td><img src="image" alt="Bar Chart" /></td>
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</tbody>
</table>

- **Cement**
- **Core**
Useful properties of paramagnetic nanoparticles (PMNPs)

- By applying magnetic field gradient, NPs can be forced to move in desired direction
- Under applied high-frequency magnetic oscillation, NPs generate intense, localized heat
- Under applied field, NP ensemble generates magnetic induction field
- Can be designed to attach to desired interfaces, for stable emulsion generation or for targeted delivery
Paramagnetic nanoparticles for improved oil production

Magnetic & paramagnetic NPs are employed for various applications in other industries

- **Enhanced Magnetic Imaging** → **Contrast agents**
  *Injection of NP dispersion to generate magnetic induction field in the reservoir for their detection*

- **Hyperthermia** → **Nano-paint**
  *Intense localized heating to prevent hydrate/wax deposition*

- **Drug Delivery** → **Catalyst/sensor delivery**
  *Delivery of upgrading catalyst or tracer to oil being mobilized*

- **Magnetic Separation** → **Water management**
  *Removal of oil or water droplets from produced fluids*
Use of paramagnetic nanoparticles for oil recovery applications

• PMNPs for reservoir imaging and sensing
  
  -- As contrast agents for enhanced reservoir imaging

• Focused heating using PMNPs

• Removal of dispersants and ions
PMNPs for enhanced reservoir imaging

- Suitably surface-coated superparamagnetic nanoparticles adsorb preferentially at oil/water interfaces

- Applying magnetic field oscillation, make oil/water menisci oscillate, and measure the o/w interface displacement to quantify the PMNP’s magnetization response

- Inject aqueous dispersion of such PMNPs into reservoir
  -- *Post-flush leaves only adsorbed particles*

- Apply magnetic field oscillation at a well, to generate magnetic “hallow” from the injected PMNP bank
  -- *Measurement of magnetic field perturbation at a receiver well*
  -- *From the Maxwell equations inversion, deduce location of PMNP ensemble*
Quantification of PMNP’s magnetization response
from O/W interface displacement measurement
using optical coherence tomography

- Operation Frequency – 2 to 100 Hz
- Depth resolution – 10~15 µm
- Imaging Depth – 2mm
Interface displacement measurement

Water (iron oxide nanoparticles CNR 5wt%) + Air

time-varying magnetic field (frequency 2Hz, amplitude 1100mV).
Water surface displacement: 101nm

Axi-symmetric COMSOL simulation of magnetic field strength inside pore amplified by presence of ferrofluid
Enhancement of crosswell EM tomography

PMNP dispersion as reservoir imaging contrast agents

- Detection of induced field generated by superPMNPs

\[ B = \mu_o (1 + \chi_{\text{eff}}) H \]

- Spatial and temporal distributions of NP ensemble in the reservoir are estimated from inversion of the Maxwell equation solution

- Potential for improved imaging of hydraulic fracture propagation

- Useful when the injection fluid does not provide the salinity contrast
Use of paramagnetic nanoparticles for oil recovery applications

• PMNPs for reservoir imaging and sensing

• Focused heating using PMNPs
  -- “Nano-paint” for thin heated layer generation inside the hydrocarbon transport pipeline
  -- Thin heated layer generation at reservoir pore walls

• Removal of dispersants and ions
PMNP heating E&P applications

- High-frequency paramagnetic NP heating is analogous to microwave heating: Rapid magnetic spin in single-domain NPs generates intense heat, due to Neel’s relaxation.

- Because “hyperthermia” is highly localized and controllable, it is used to kill cancer cells, by delivering and attaching the NPs with engineered surface coating, to the cells, and applying magnetic oscillation.

“Nano-paint”
- Prevent hydrate/wax deposition at inner surface of production facilities.

Hypothetical heating scheme for pipeline flow.
Experimental apparatus and materials

“Off the shelf” 10 kW high frequency induction heater
  - Frequency range: 400 – 1000 kHz
  - H-field amplitude: 430 – 5000 A/m
  - 1, 2, 3 turn coils

Magnetite (Fe₃O₄) nanoparticles (Ferrotec)
  - Core diameter~12.1±3.0 nm
  - Hydrophilic and hydrophobic coatings

Specific absorption rate of fluid (SAR, W/g) used to quantify experimental NP heating

\[ SAR_{static} = \frac{c_p \Delta T}{\Delta t w_{Fe_3O_4}} \]

\( c_p \) = specific heat capacity of fluid [J g⁻¹ K⁻¹], 
\( T \) = temp. [K], 
\( t \) = time [s], 
\( w \) = wt % Fe₃O₄
Static SAR behavior as a function of magnetic field strength

"Nano-paint"

Magnetic NP for intense localized heating

Hydrophobic nanoparticles embedded in commercial epoxy resin: “Nanopaint” enables the particles to be locally applied where heating is desired

Magnetite (Fe₃O₄) nanoparticles
- Core diameter ~12.1±0.3 nm
- Hydrophilic and hydrophobic coatings

In addition to the utilization for nano-paint, application of hyperthermia for heavy oil heating will be investigated.
Use of paramagnetic nanoparticles for oil recovery applications

- PMNPs for reservoir imaging and sensing
- Focused heating using PMNPs
- Removal of dispersants and ions
  - Removal of oil droplets from produced water
  - Removal of multi-valent ions from injection water
Schematics of the process for oil droplet separation and recycling of MNPs

**Oil droplet separation**

1. **Mix** (1:1 vol)
2. **Collect**
3. **Separate**
4. **Wash oil droplet attached MNPs to desorb oil droplets**
5. **Magnet**
6. **Re-disperse and reuse**

**MNPs regeneration**

- **Separated clean water**
- **Re-disperse and reuse**
Separation of oil droplets by MNP attachment and magnetic force application

**Attachment of MNP on oil droplet**

- **Buoyancy force** ($F_b$)
- **Drag force** ($F_d$)
- **Magnetic force**

Where,
- $V_p$ = volume of particle
- $\chi_p$ and $\chi_f$ = volume magnetic susceptibility of particle and fluid
- $B$ = external magnetic field
Images of 0.25 wt.% of TAN 2.9 oil droplet separation in different MNP concentrations

Fe = 1500 mg/L
Fe = 750 mg/L
Fe = 600 mg/L
Fe = 500 mg/L
Fe = 300 mg/L
Fe = 130 mg/L

MNPs were stuck on a wall that were not collected by a magnet.
Oil droplet removals using regenerated A-MNP

0.25 wt.% oil content: 13000 mg/L of Fe

- **TAN 2.9**
  - Virgin: 99.9%
  - 1st regen.: 99.9%
  - 2nd regen.: 99.9%

- **TAN 4.5**
  - Virgin: 99.9%
  - 1st regen.: 99.9%
  - 2nd regen.: 99.9%
Schematic of the multivalent cation removal

**Cation removal**

- **Fe$_3$O$_4$**
  - Mix and adsorb
  - Magnetic field

**Fe$_3$O$_4$ regeneration**

- Softened water
  - Re-suspend Fe$_3$O$_4$
  - Magnetic field

**Fe$_3$O$_4$ re-use**
Conclusions

- Adaptation of the huge advances made by other industries on the nanotechnology applications is rapidly gaining momentum in the upstream oil industry, with potential of huge business impacts.

- Nanoparticles with a special surface coating tailored to achieve certain desired functionalities (targeted delivery, sensing, “intelligent” mobility control, *etc.*) have great potential for various reservoir applications.

- Nanoparticle-stabilized emulsions and foams show good promise as conformance- and mobility-control agents for EOR; and as “intelligent” additives for drilling fluids and completions cement.

- Paramagnetic nanoparticles have unique properties that could be utilized for many E&P applications: (1) intense localized heating; (2) controllable movement; (3) magnetic pressure generation; and (4) induction field generation for sensing.
Thank you!

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