Development of Swelling-Rate-Controllable Particle Gels to Enhance CO_2 Flooding Sweep and Storage Efficiency

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National Energy Technology Laboratory

Mastering the Subsurface Through Technology Innovation, Partnerships and Collaboration:
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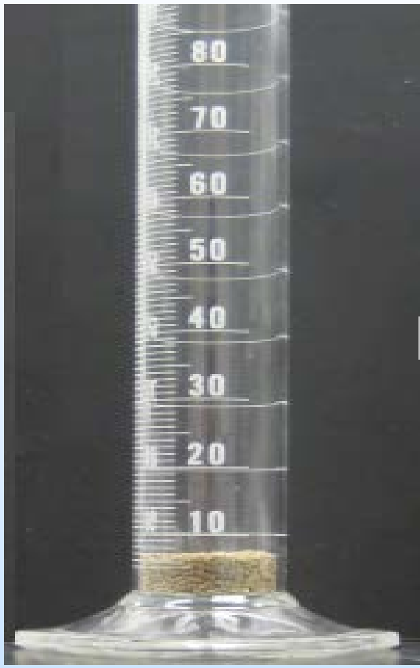
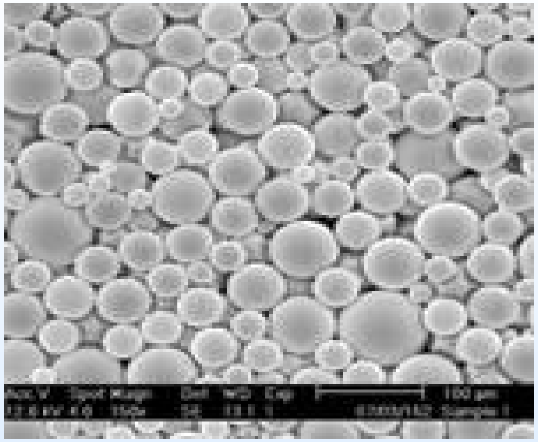
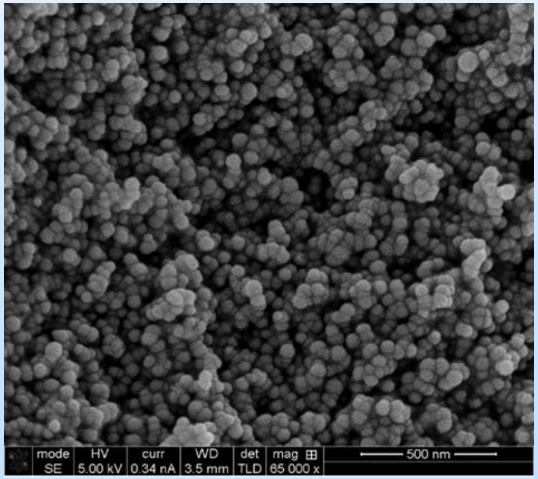
Preformed Particle Gel (PPG)



(a) Before swelling

(b) After swelling





Cross-linked polymer powder, Super Absorbent Polymer

Size ranging from nano-meter to millimeter

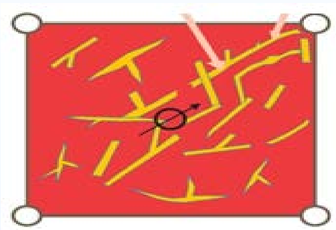
Presentation Outline

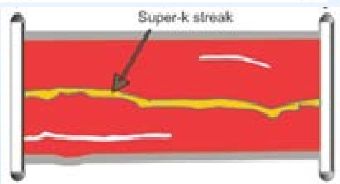
- **Technical Status**
  - Brief Review on 1st year Results
  - Second year results
    - ✓mm-sized Particle Gels and CO_2/Water/Oil Flow by Core Flooding Tests
    - ✓CO_2 Resistant Swelling Rate Controllabe Nano-gels
- **Accomplishments to Date**
- **Lessons Learned**
- **Project Summary**
- **Appendix**

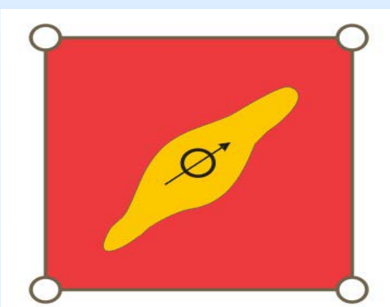
Brief Review of 1st Year Results

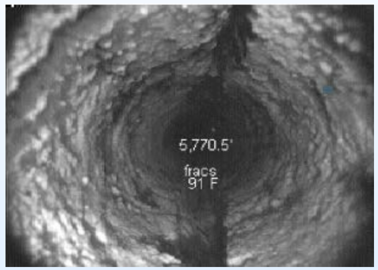
Target Conformance Problems (first year)

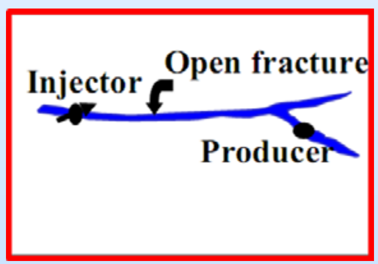
Targets: Super-K Channels



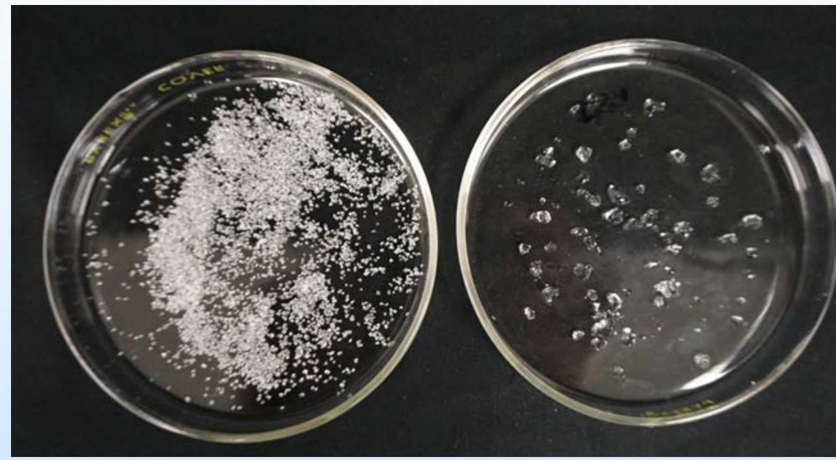








Our Solutions



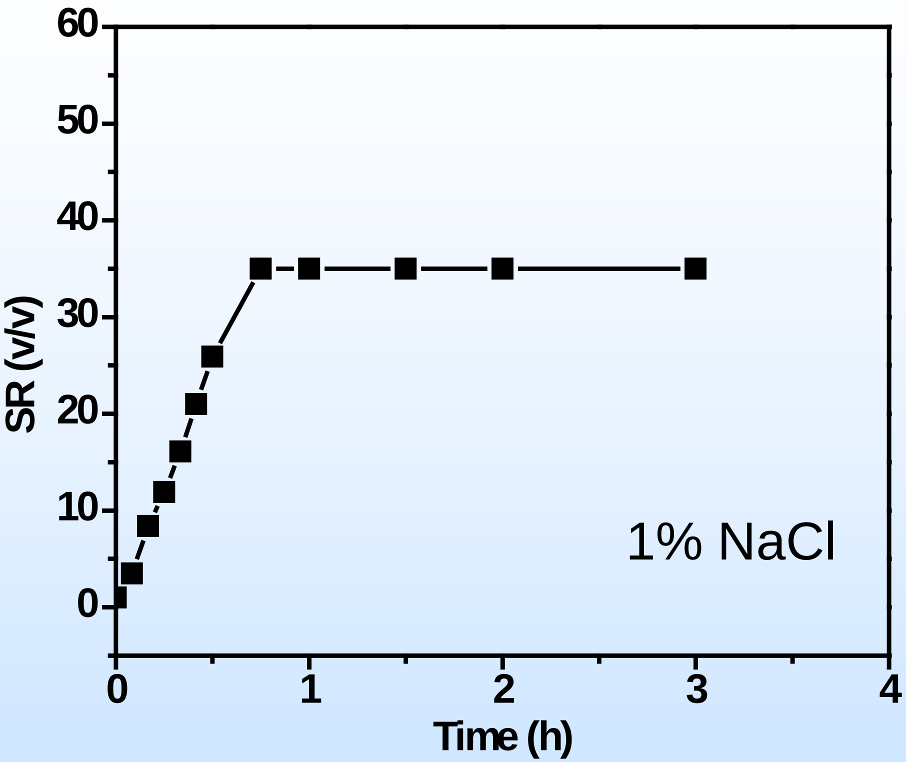
(a) Before swelling (b) After swelling

Achievement 1: Synthesized mm-sized swelling delayed CO_2 resistant PPGs (10 um- mm)

Achievement 2: Identified where mm-sized particle can be used and developed criteria for passing through pore throats and open fractures.

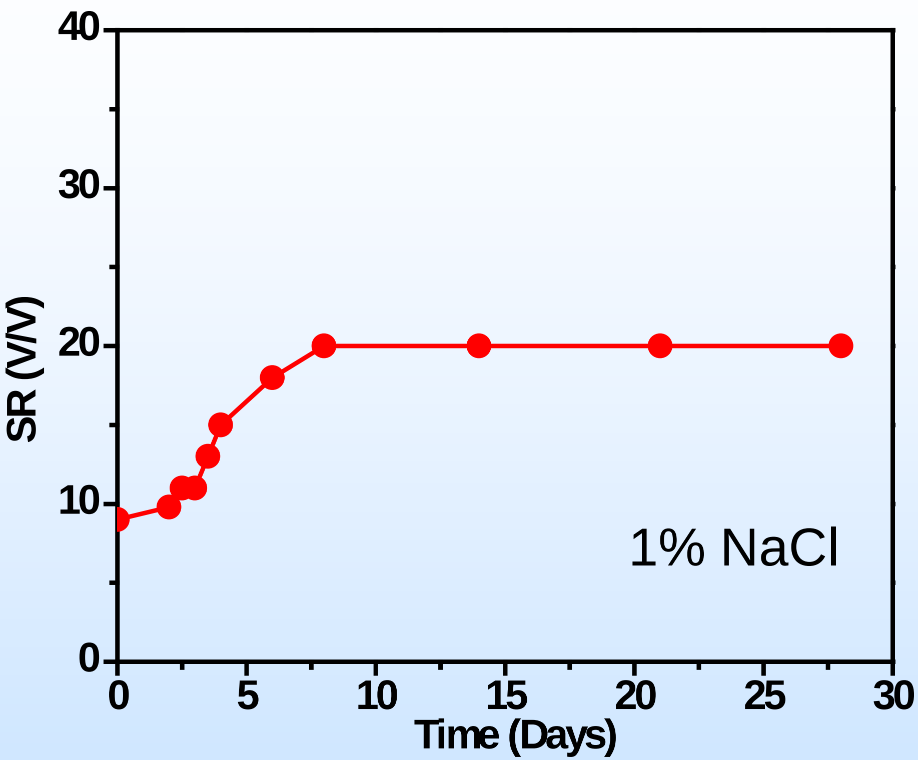
Product 1: Swelling Rate Controlled to Days

Traditional PPGs



Fast swelling within one hour

New monomer addition to traditional PPGs



Delayed swelling to days

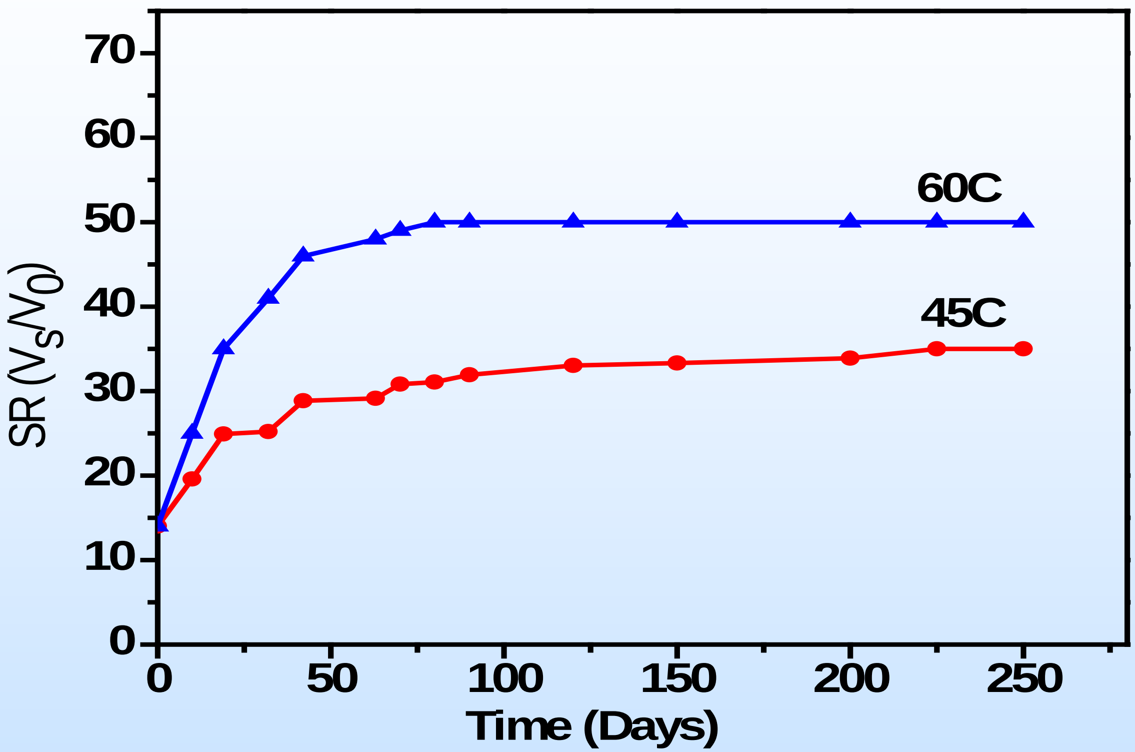
The new product overcome some problems of traditional PPGs

- Fast swelling rate, leading to injectivity issue
- Unable to travel long distance, only for near well-bore treatment

Meet the requirement: development of swelling rate controllable PPG

Product 2: Swelling Rate Controlled to Months

2nd crosslinker addition to traditional PPGs

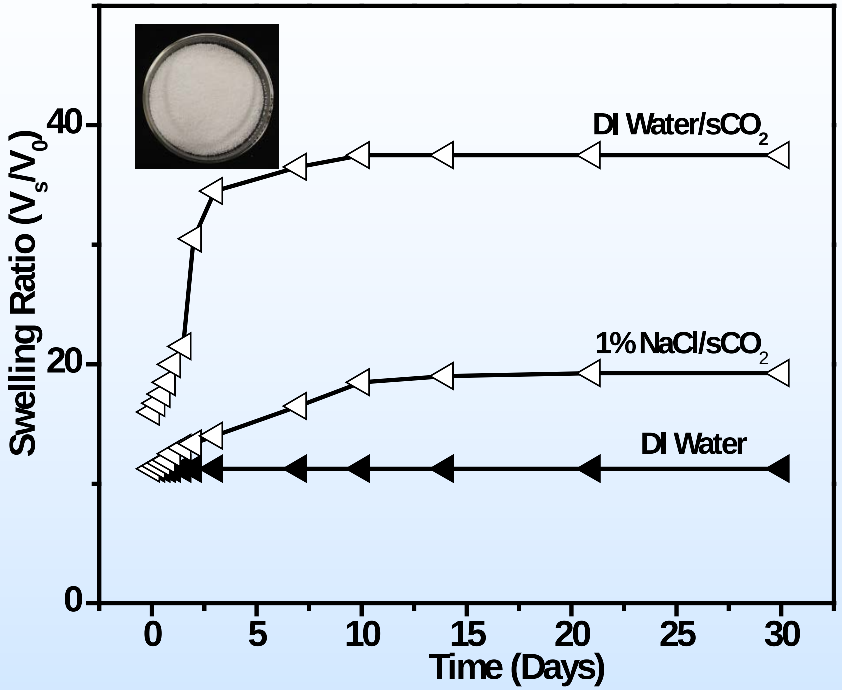


Swelling kinetics and Temperature effect (1% NaCl)

Product 2 is good for in-depth fluid diversion

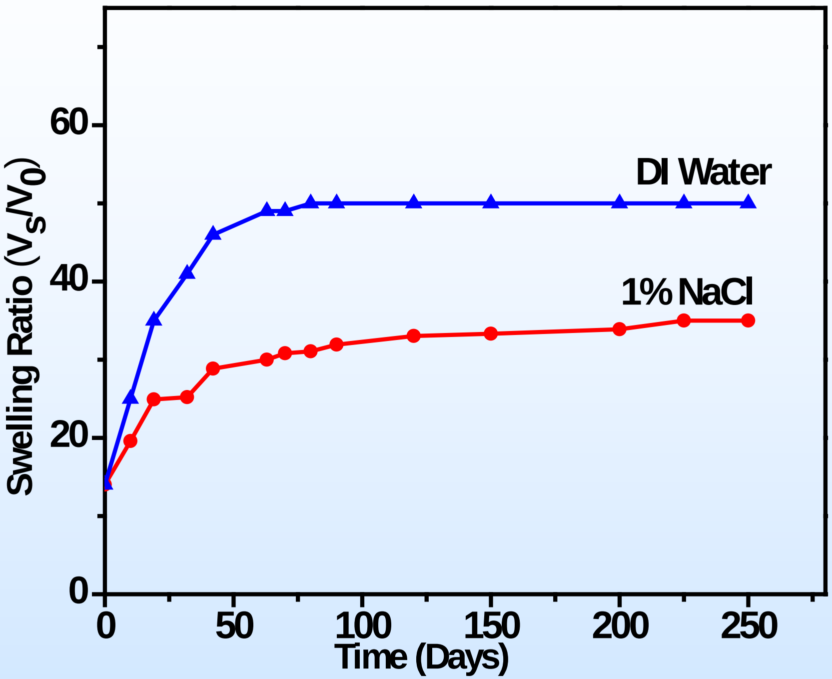
Meet the requirement: development of swelling rate controllable PPG

Product 3: CO_2 Triggered Swelling Delayed Particle Gel



particle size 1-2 mm; 45 ℃

Delayed swelling to weeks



particle size 1-2 mm; 45 ℃

Delayed swelling to months

In absence of CO_2, size of the gel would not increase

Upon CO_2 flooding, the gel would increase to 4 times of its initial volume

Product good for in-depth reservoir deployment

Meet the requirement: development of swelling rate controllable PPG

Research Efforts for the 2nd year

1st year achievements (1st year)---Solve Fractures or Fracture-like problems

- Swelling controllable CPPGs were synthesized and swelling rate can be controlled from hours to months.
- New mm-sized PPGs showed excellent CO_2 resistance.
- The criteria of the particle gels passing through pore throats and open fractures were developed

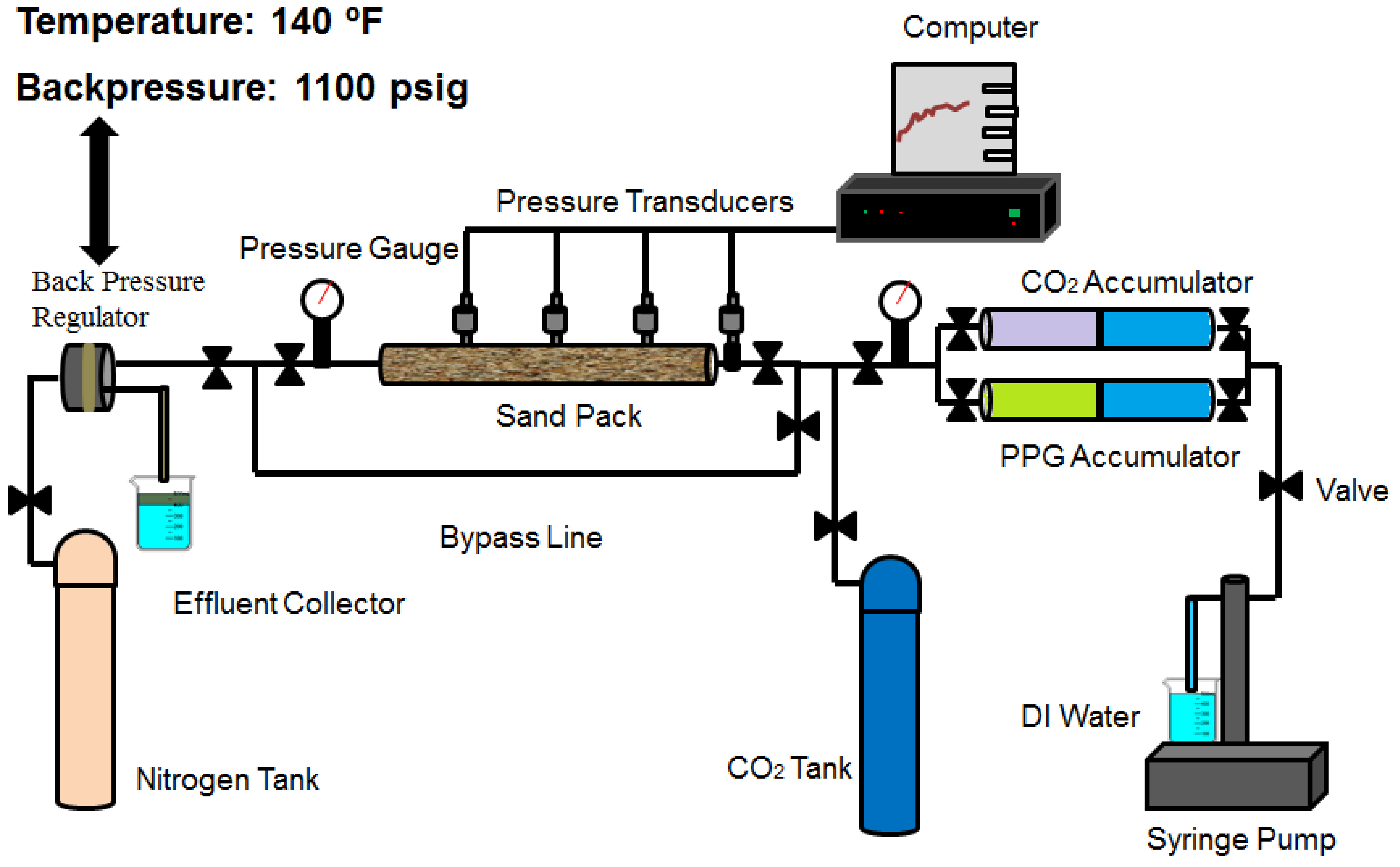
2nd Year Efforts---Solve matrix conformance problems

- Core flooding experiments using mm-sized CPPGs to test CO_2 plugging efficiency
- Nano-gel synthesis under CO_2 conditions and evaluation

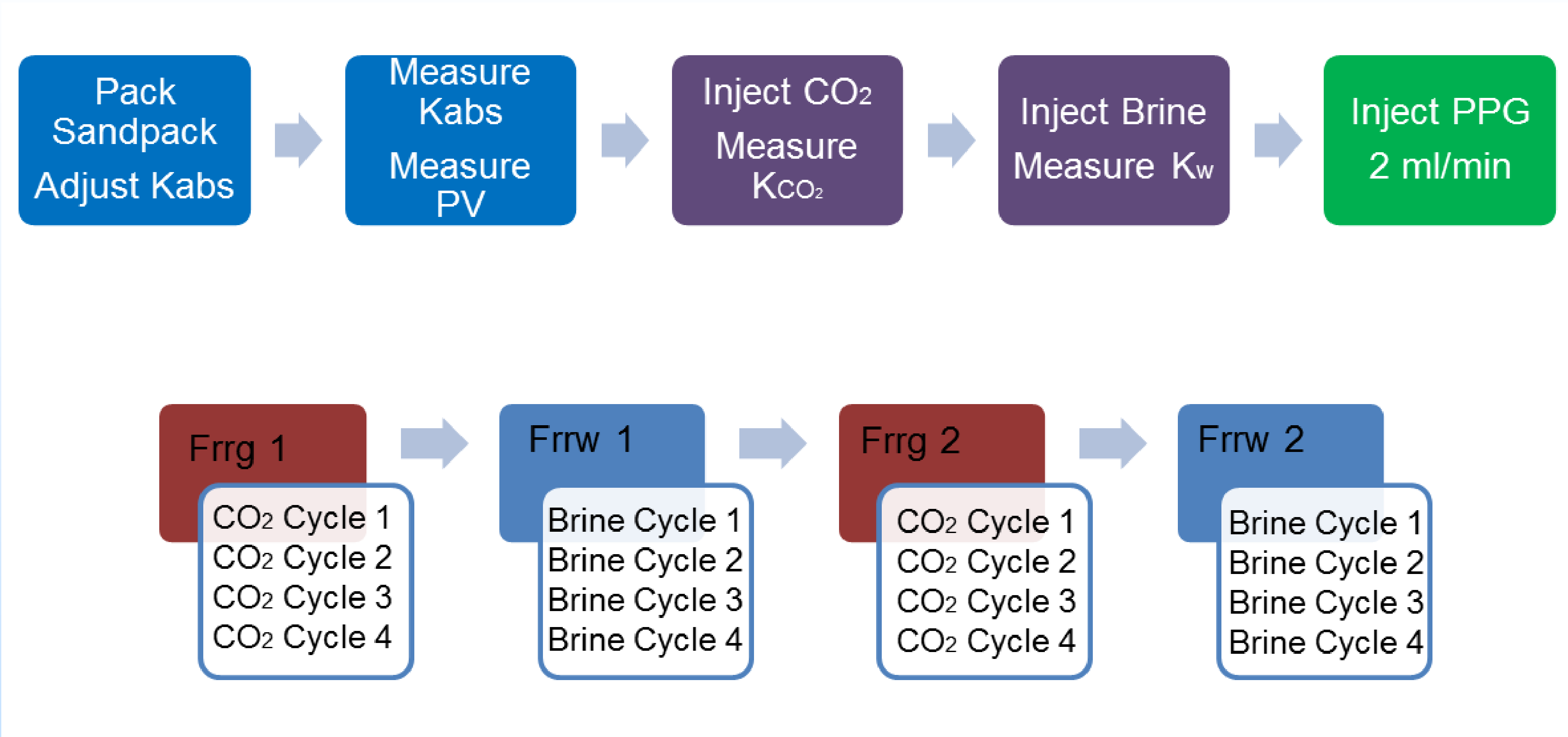
Core Flooding Experiments

Temperature: 140 °F

Backpressure: 1100 psig



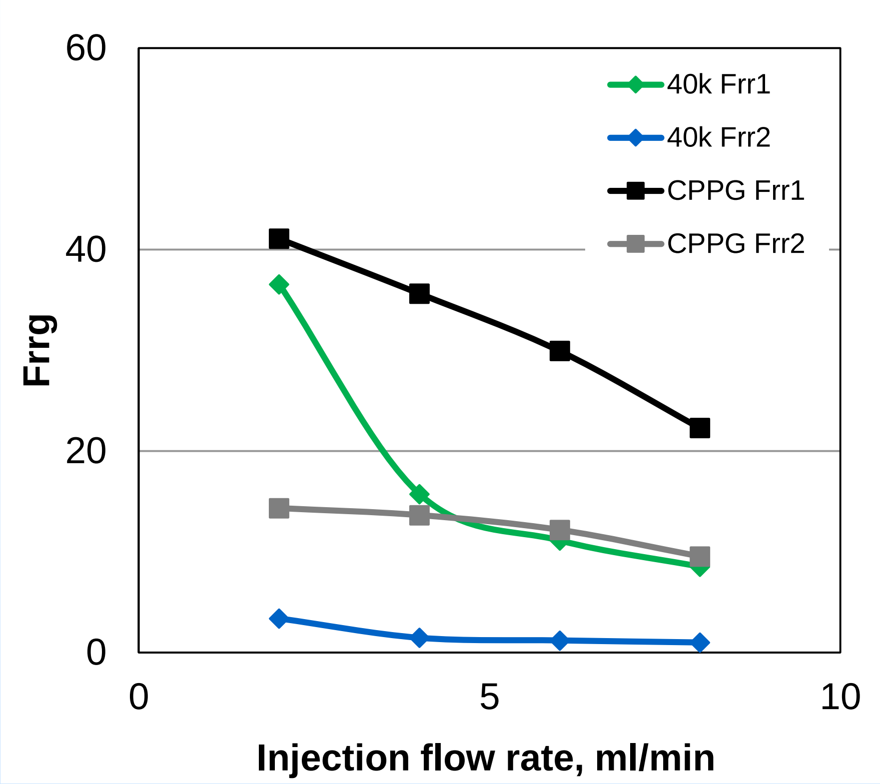
Experiment Steps

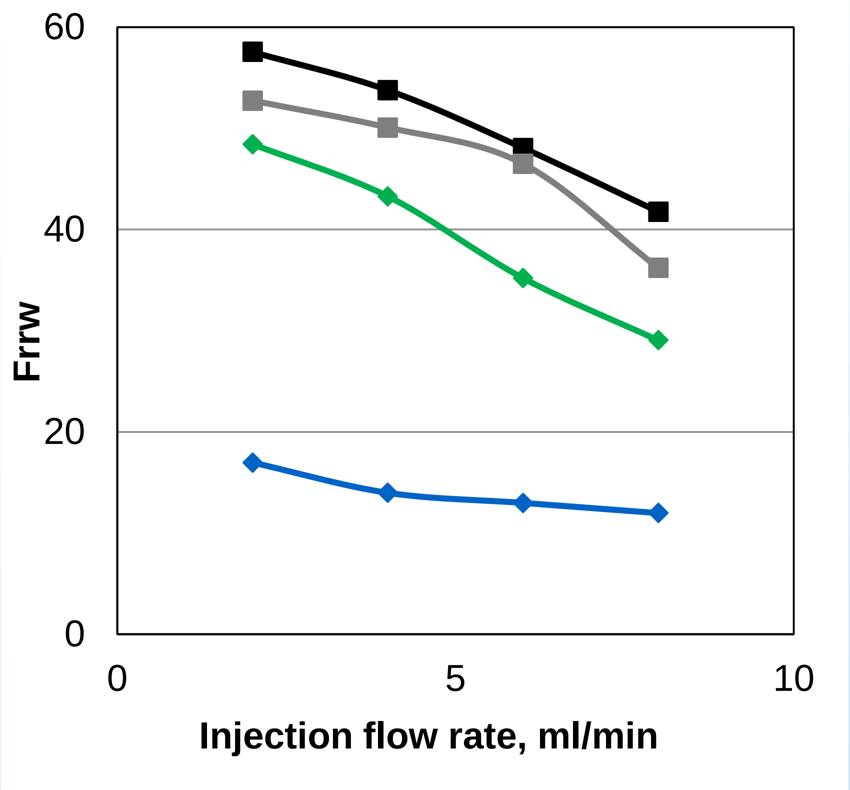


$$Frr = \frac{k_{before}}{k_{after}} = \left(\frac{P_{after}}{P_{before}}\right)_q$$

CPPG Plugging Efficiency to CO_2 and Water

$$Frr = \frac{k_{before}}{k_{after}} = \left(\frac{P_{after}}{P_{before}}\right)_q$$

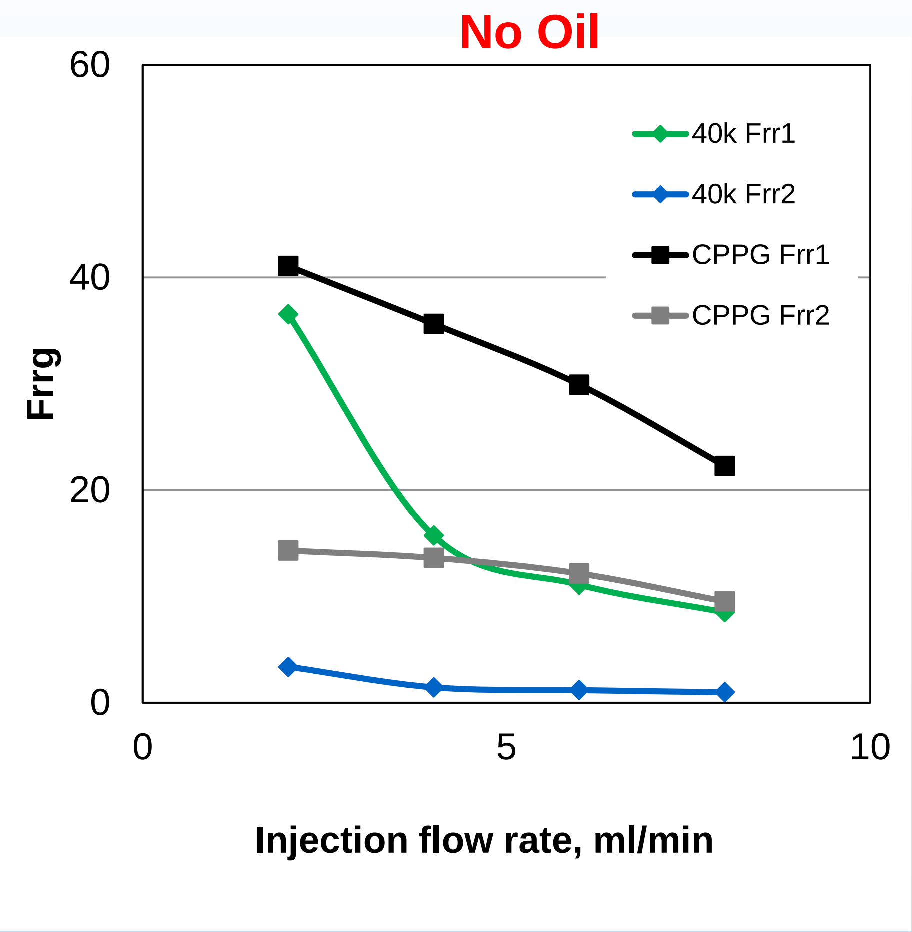


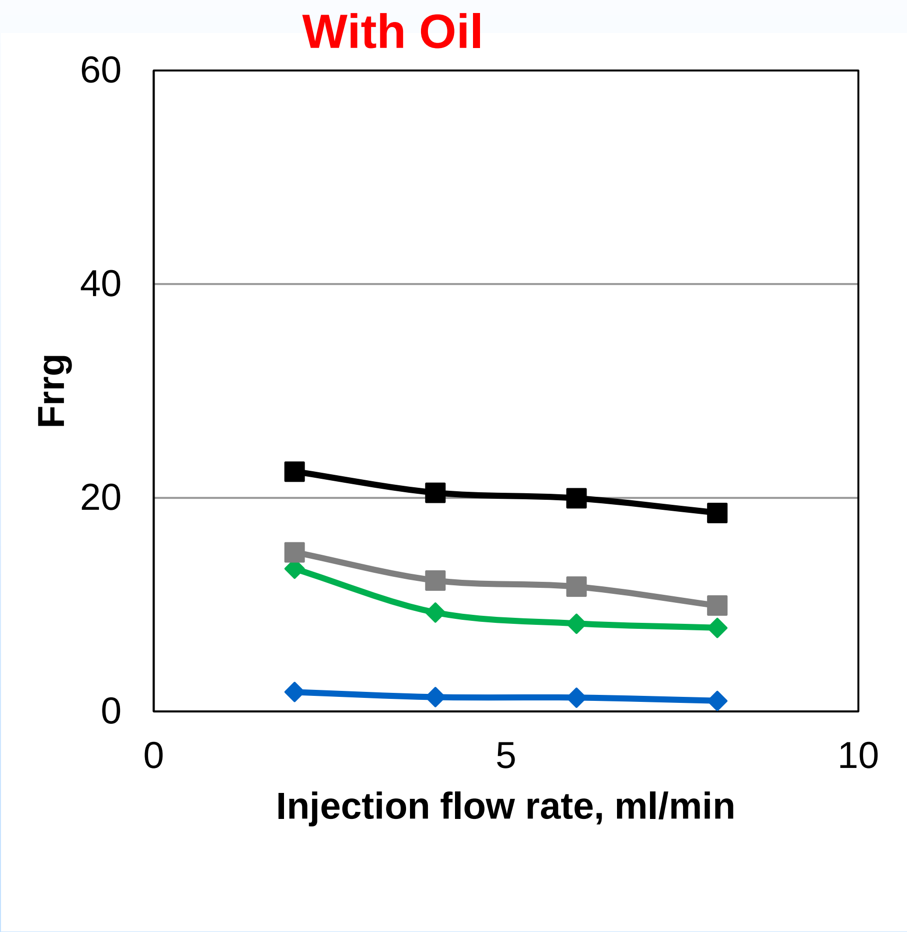


Sandpack permeability ~23 Darcy, brine conc: 1 wt% NaCl

Compare to 40K, CPPG has much better plugging efficiency to CO_2.

Effect of Residual Oil on PPG Plugging Efficiency



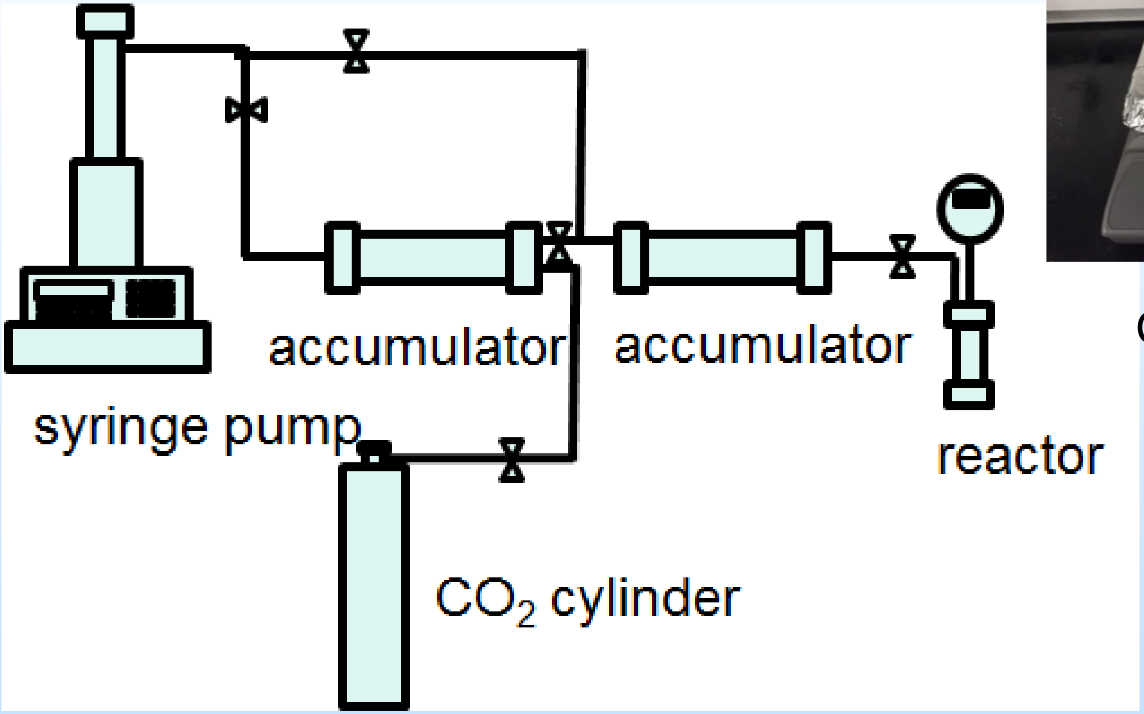


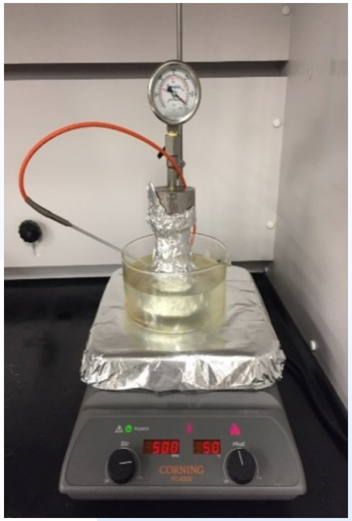
The presence of residual oil had less impact on the new gel's performance compared to traditional PPG 40K.

CO_2 Resistant Nano-gel Synthesis and Evaluation

Reactor system

CO_2 delivery pump



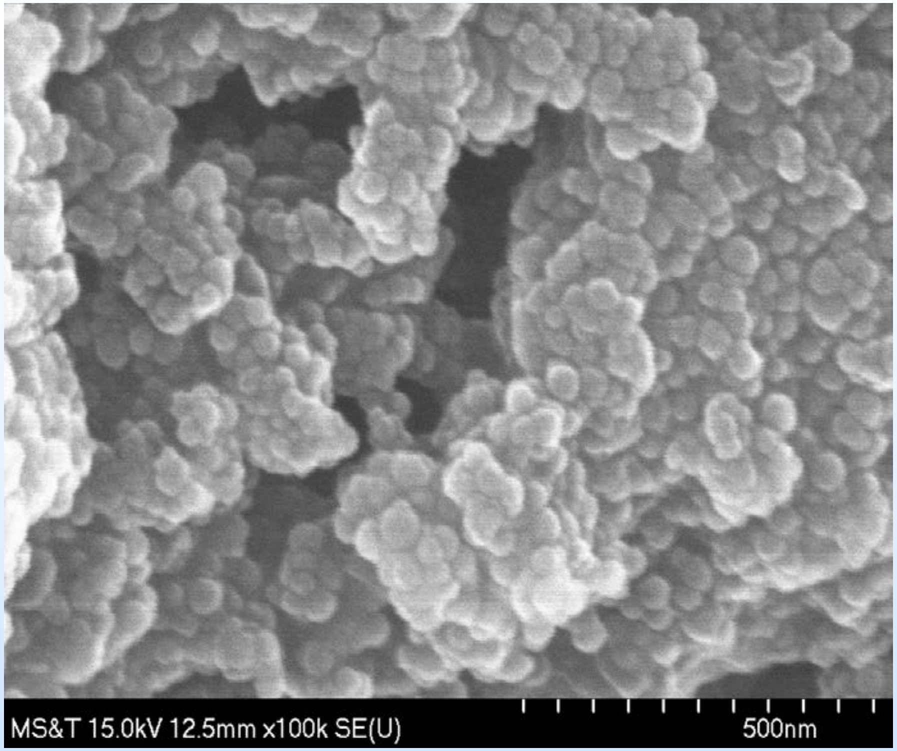


CO_2 reactor

Synthesis under supercritical CO_2

Swelling Rate Controllable Nano-gels

Nano-gel in powder form

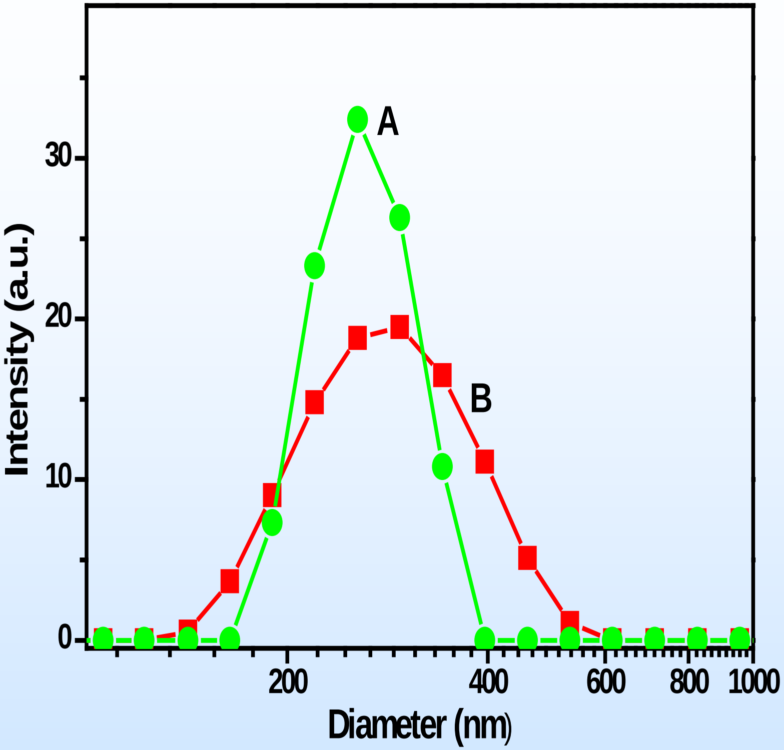


SEM images

Tunable sizes: in the range of nano to microns

Product prepared under sCO_2

Nano-gels after polymerization

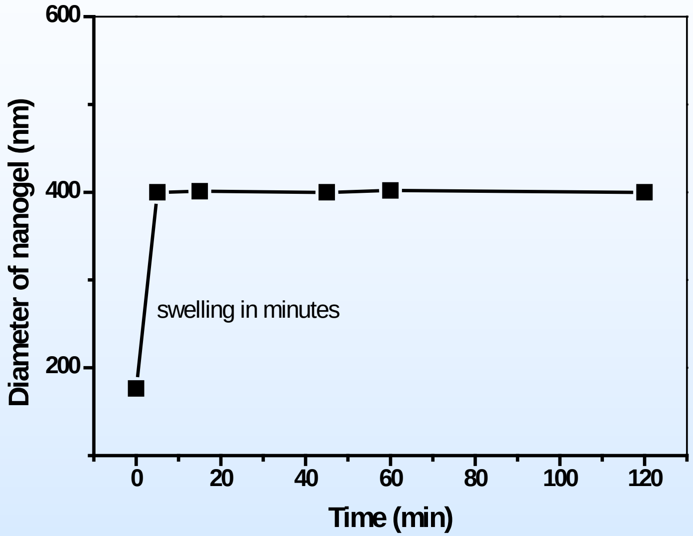


A: CO_2 B: emulsion

The size distribution of Nano-gels synthesized under sCO_2 is narrower than those from conventional emulsion polymerization

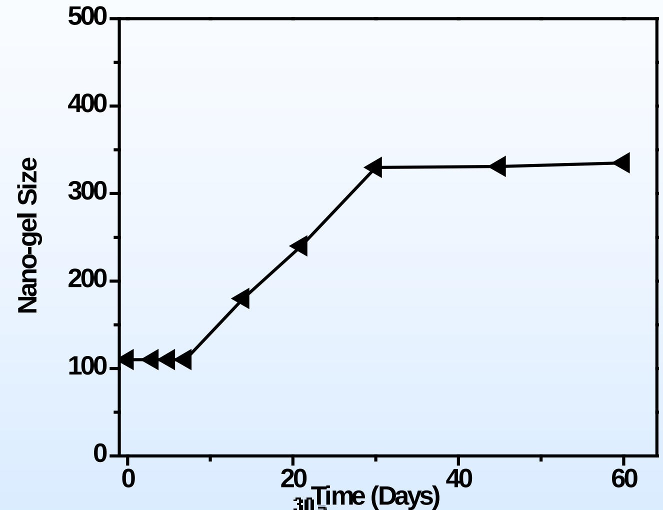
Swelling Rate Controllable Nano-gel

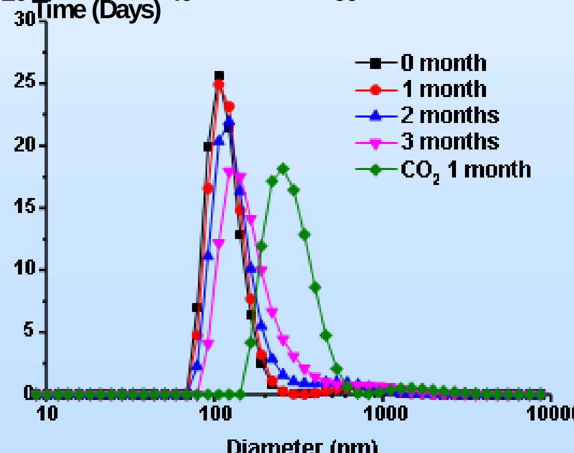
Traditional HPAM nano-gels



Fast swelling in minutes

Product 1: CO_2 triggered Swelling





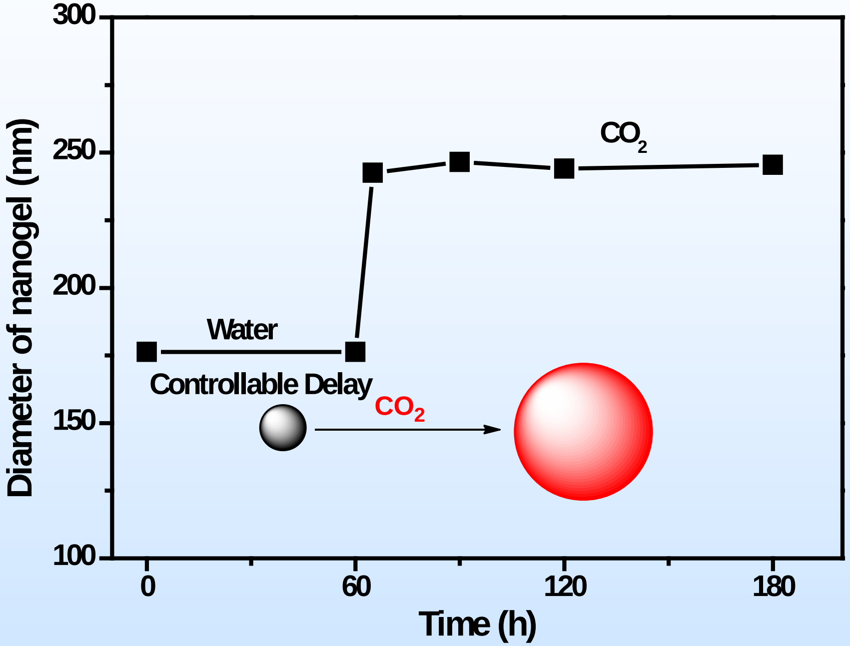
Delayed swelling to weeks

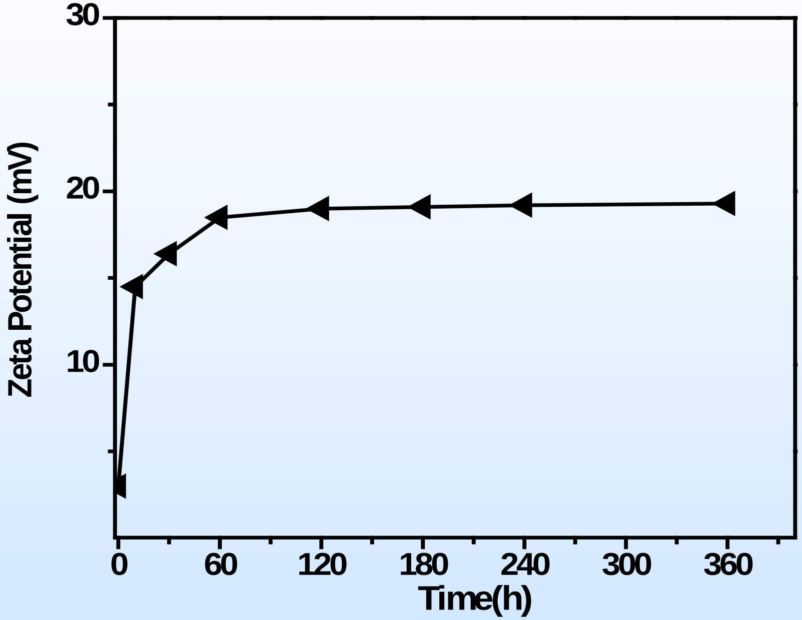
Traditional HPAM nano-gels had fast swelling rate within minutes

Product 1 swelling delayed to weeks

CO_2 Responsive Nano-gel with Swelling Rate Control

Product 2: CO_2 responsive monomer used for nano-gels





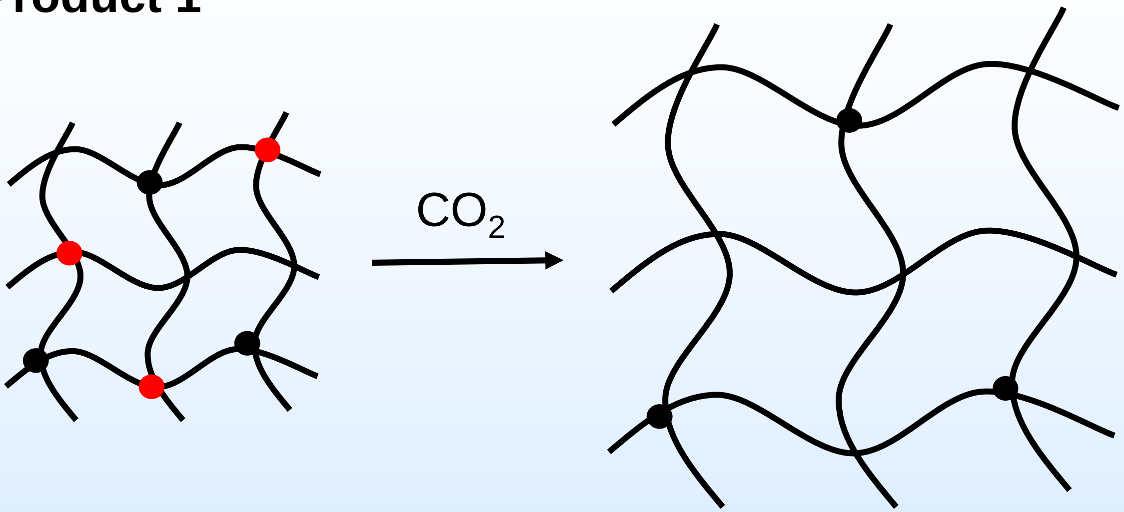
in the presence of CO_2

Swelling could be delayed in a controllable fashion: water flooding for nano-gel delivery and CO_2 flow induced the increase of nano-gel size.

Meet the requirement: development of swelling rate controllable nano-gels

Size Increase under CO_2 Condition

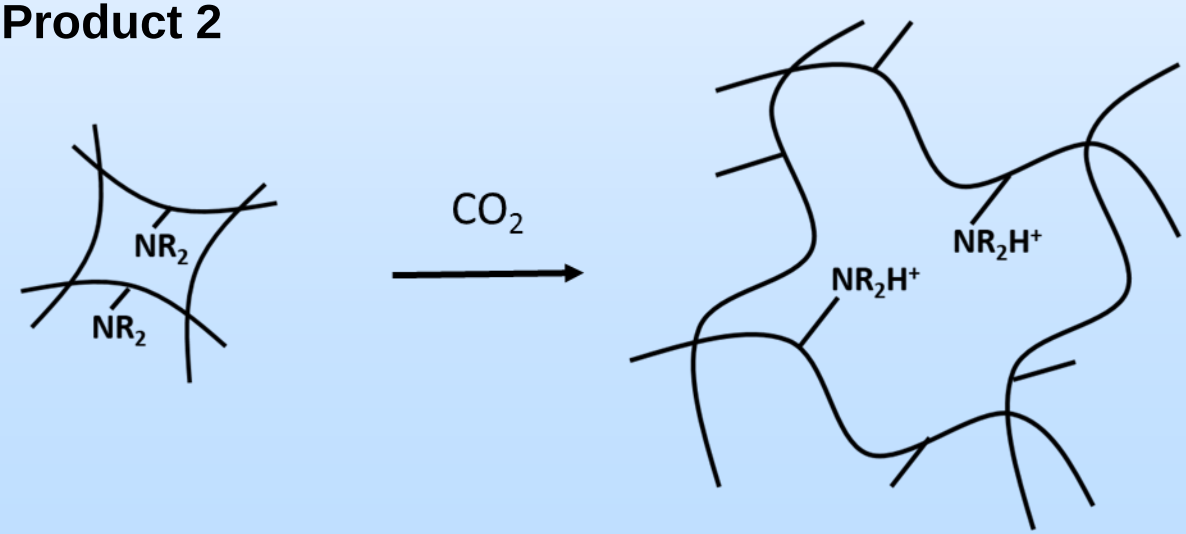
Product 1



Acid labile crosslinker

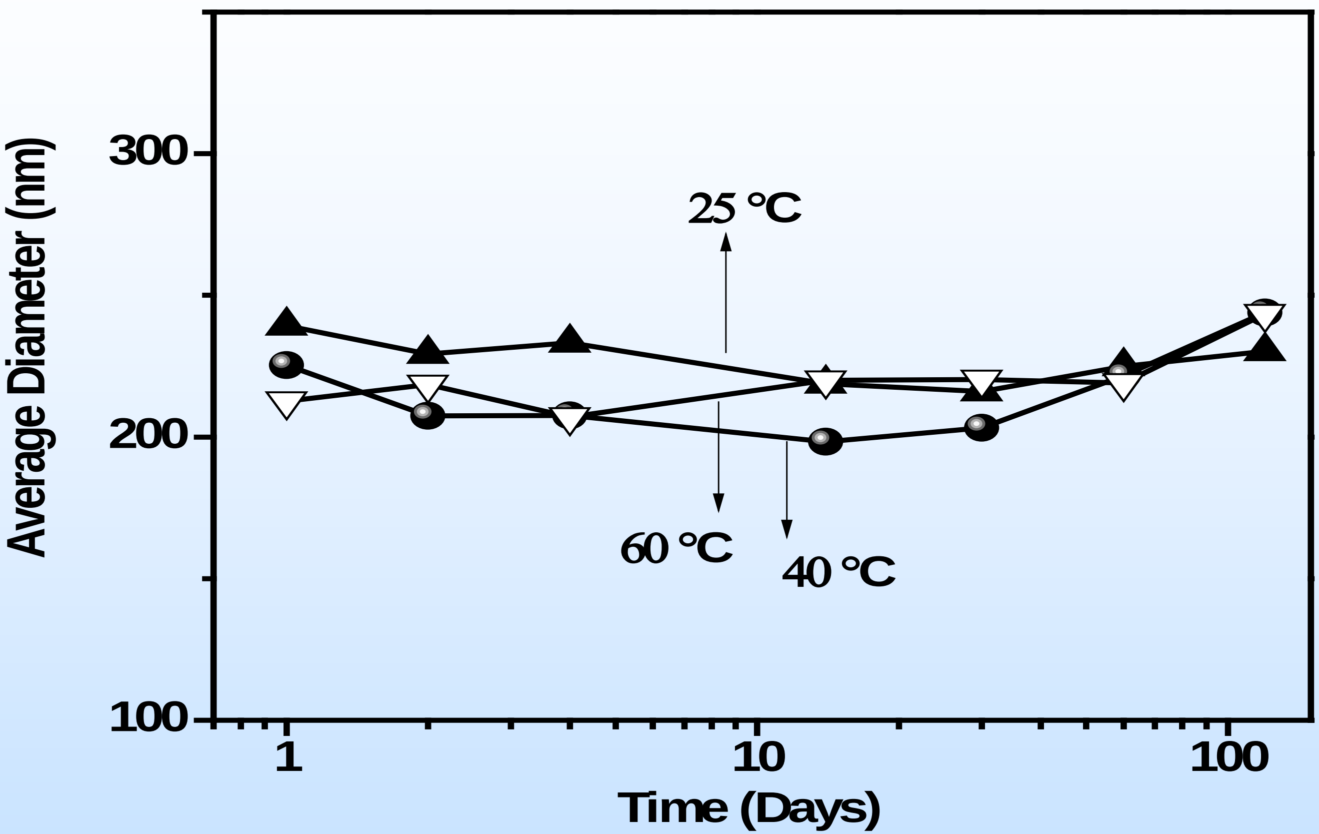
stable crosslinker

Product 2



Meet the requirement: development of CO_2 resistant nano-gels

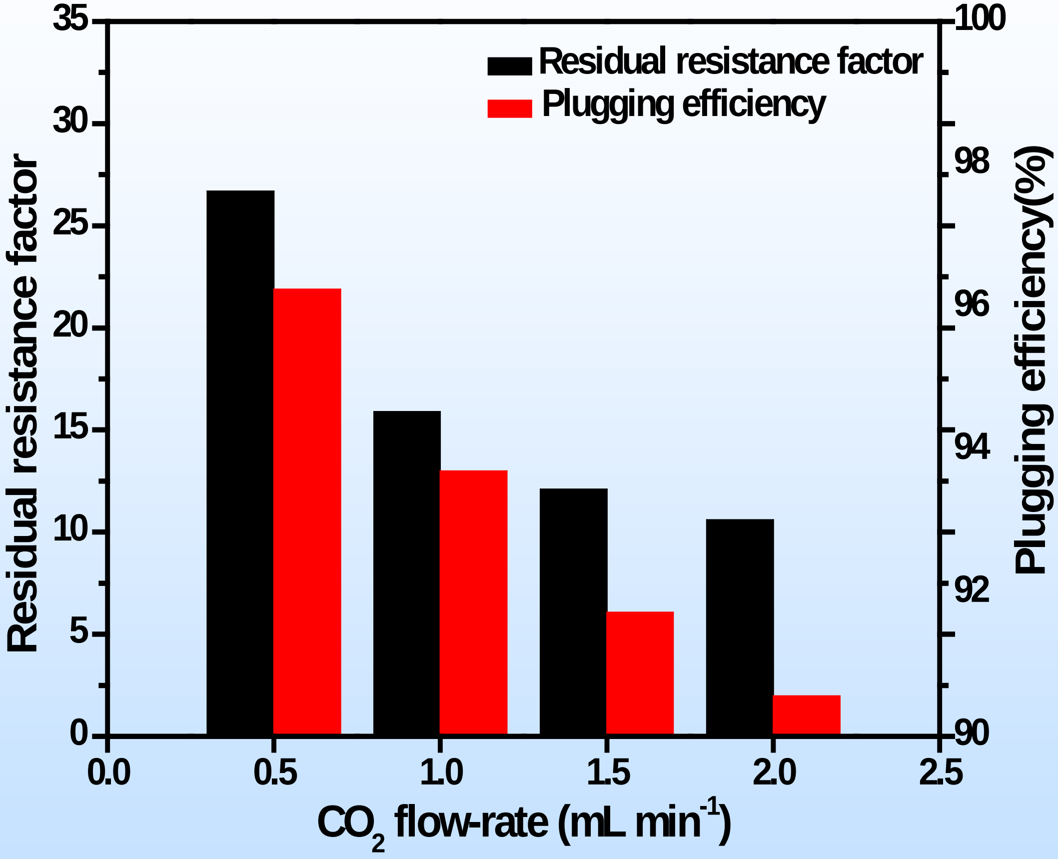
Nano-gel Thermal Stability



Monitoring for long-term stability

CO2 resistant Nano-gels had better stability than HPAM-type of nanogels at different temperatures

Initial Study of Nano-gel Plugging Efficiency to Matrix



The plugging efficiency of the nano-gel to CO_2 is more than 90%.

Accomplishments to Date

- Published three journal papers and one manuscript is under review.
- Synthesized nano- to millimeter-sized swelling-rate controllable CPPGs for different conformance problems.
- Evaluated the effect of water salinity, pH and temperature on CPPG behavior.
- The plugging efficiency of mm-sized CPPG to super-K channels is more than 90%.
- Nano-gels synthesized under sCO_2 conditions have narrower distribution than those synthesized by emulsion methods.
- Nano-particle gels can transport through Berea sandstone.

Lessons Learned

- Traditional polymer gels cannot successfully block sCO_2 flow especially for WAG process.
- Tuning experimental parameters can avoid the use of expensive fluorosurfactant for the synthesis of nano-gels under supercritical CO_2.
- The generation of swelling rate delayed nano-gels was the most challenge in the project. But we have finished the functionality of the nano-gels by introducing state of-the-art technology in polymer chemistry community.

Synergy Opportunities

- **Industry Interest**
  - Our JIP members Conoco-Phillips, Occidental and Daqing Wantong are interested in manufacturing and piloting the mm-sized CO_2 resistant particle gels (CPPG).
- **CO_2 Storage Partnership Projects**
  - Novel monitoring techniques could be used to better identify conformance problems, which is necessary to optimize a conformance control design.
  - The new products can be used to solve early breakthrough or excess CO_2 production problems for CO_2 EOR storage projects.
- **Leakage Mitigation projects**
- Combination will solve both reservoir and wellbore problems

Project Summary

Key findings:

- The swelling-rate controllable CPPGs have been successfully synthesized. Their sizes are adjustable from nano to millimeter.
- The swelling rate of CPPG can be controlled from a few hours to up to a few months.
- The synthesized particle gels is thermo-stable in sCO_2.
- Mm-sized CPPG can effectively reduce CO_2 permeability in super-K channels and their plugging efficiency is over 90%.
- The nano-particle gels can transport through common porous media.

Next Steps:

- Further evaluation of nano-gel performance under CO_2 conditions for conformance control.
- Build mathematical model based on experimental results.

Acknowledgement

- Project manager Kylee Rice in NETL
- Mr. David Smith in ConocoPhillips
- Mr. Andrew Johns in Occidental Petroleum Corporation
- Missouri S&T Research group members

Appendix

– Deliverables
– Decision points
– Risk Analysis
– Benefit to the Program
– Project Overview
– Organization Chart
– Gantt Chart
– Bibliography

Deliverables

- Project Management Plan
- Project Fact Sheet
- Data Submitted to NETL-EDX. Will include:1) various datasets and files as appropriate, 2) metadata, 3) software/tools, and 4) articles developed as part of this project.
- The periodic, topical, and final reports

Decision Points

Phases	Success Criteria
Phase 1 (06/15/15 – 09/30/17)	1. The synthesized particle gels should be thermo-stable in supercritical CO_2 for more than 6 months. 2. The swelling rate of synthesized particle gels can be controlled from a few hours to up to a few months. 3. The nano-particle gels can transport through common porous media. 4. The new particle gels can reduce CO_2 permeability in fractures, fracture-like channels and high permeability rocks and their plugging efficiency should be high than 90%.
Phase 2 (10/01/17– 09/30/18)	1. The transport mechanisms of nanoparticle through porous media can be understood. 2. New mechanistic models will be obtained through lab data analysis.

Risk Analysis

- Technical risks-Low risk
  - Particle gel thermo-stability under CO_2 conditions
  - Delivery of nano-particle into the in-depth of a reservoir
- Environmental, health, or safety issues:
  - Control residual monomer amount in final products
- Resources and management issues
  - University support structure and PI experience in project management

Benefit to the Program

- Program goals being addressed
  - Develop technologies to improve reservoir storage efficiency while ensuring containment effectiveness.
- Project benefits statement
  - The research project is to develop novel environmental friendly swelling-rate-controllable particle gels to improve CO_2 sweep and storage efficiency. The new materials will overcome some distinct drawbacks inherent in the in-situ gels that are traditionally used for conformance control. The technology, when successfully demonstrated, will provide a novel cost-effective technology to the Carbon Storage Program's effort of improving reservoir storage efficiency while ensuring containment effectiveness.

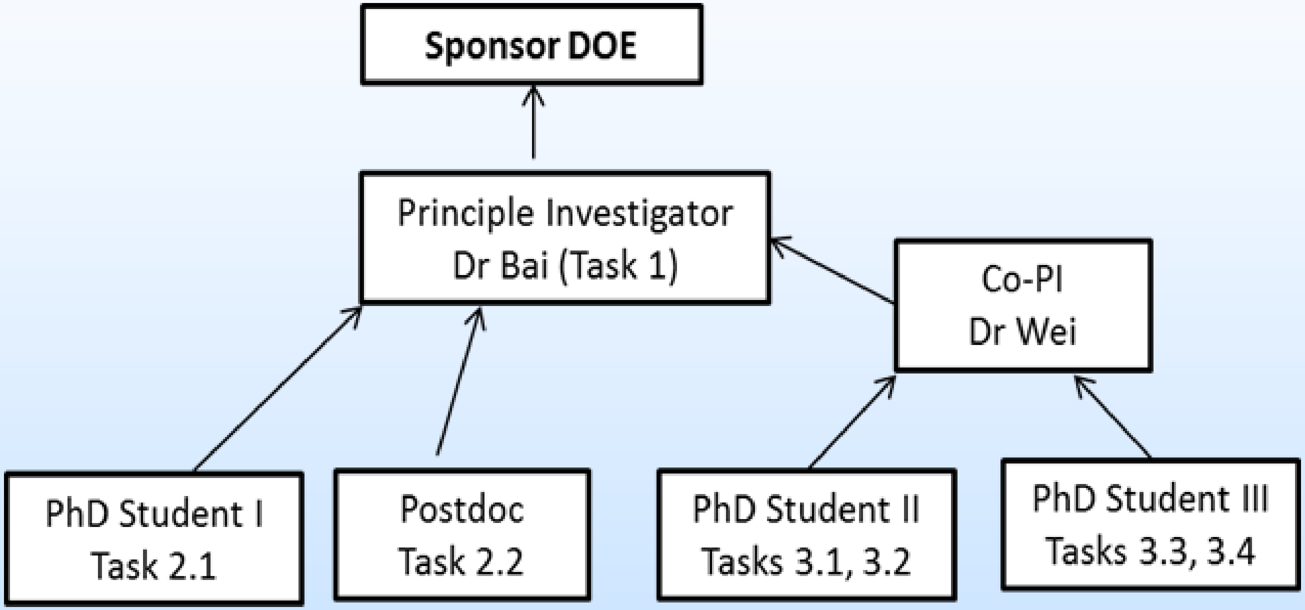
Project Overview:
Goals and Objectives (1)

- **Overall Goal**: to develop a novel **particle-based gel** technology that can be used to enhance CO_2 sweep efficiency and thus improve CO_2 storage in mature oilfields.
- **Project Objectives:**
  - Synthesize swelling rate controllable CO_2-based polymer network nano-particles at supercritical CO_2.
  - To understand the correlation of particle gels and CO_2/water/oil flow by core flooding tests.
  - To understand the plugging mechanisms of particle gels for different types of reservoir problems.

Project Overview: Goals and Objectives (2)

- Relevance to Program Goals
  - Novel materials will improve CO_2 storage efficiency while ensuring containment effectiveness.
- Success criteria
  - Swelling rate controllable particle gels in nano-size
  - Resistance to supercritical CO_2
  - Plugging efficiency of CO_2 resistant particle gels
  - Successful delivery of nano-gels into target locations
  - Understand the relationship of CO_2/water/oil by core-flooding tests in the presence of particle gels.

Organization Chart



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Co-PI: Mingzhen Wei

Gantt Chart

Technical Tasks	2016				2017				2018			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.0 Project management and planning and reporting												
2.0 Synthesis and characterization of particle gels												
2.1 Synthesis and characterization of micro- to millimeter-sized particle gels												
2.2 Synthesis and characterization of CO_2-based polymer network nano-particle gels at supercritical CO_2 fluids												
3.0 transport behavior of millimeter-sized particle gel through fractures or fracture-like channels and their plugging efficiency to supercritical CO_2 fluids												
3.1 develop criteria for particles passing through pore throats and open fractures												
3.2 conduct core-flooding tests to understand the effect of particle gels on CO_2/water/oil flow												
3.3 deliver nano-particle gels for in-depth placement												
3.4 develop the mathematical models												

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