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

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U.S. Department of Energy

National Energy Technology Laboratory

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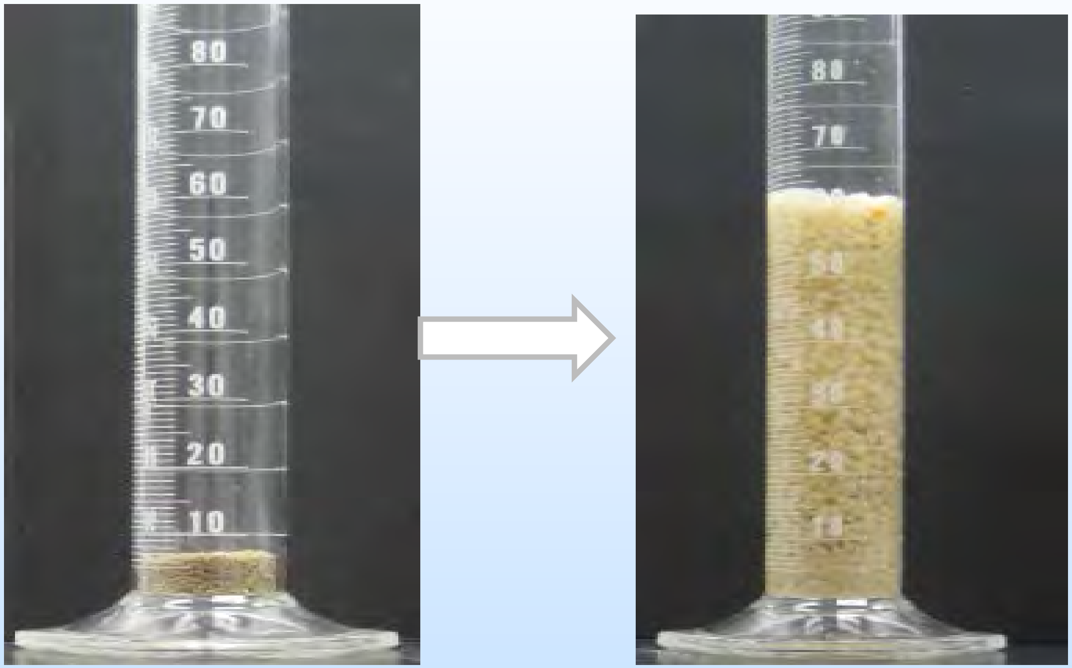
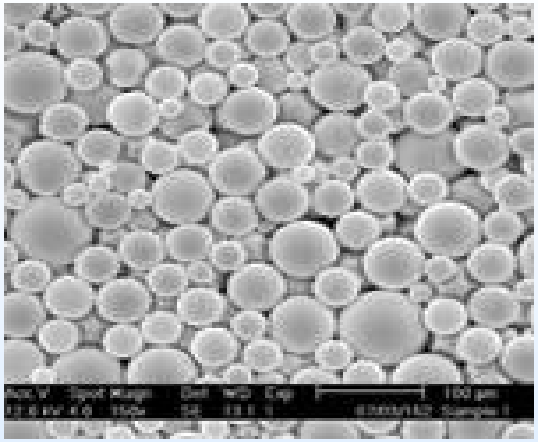
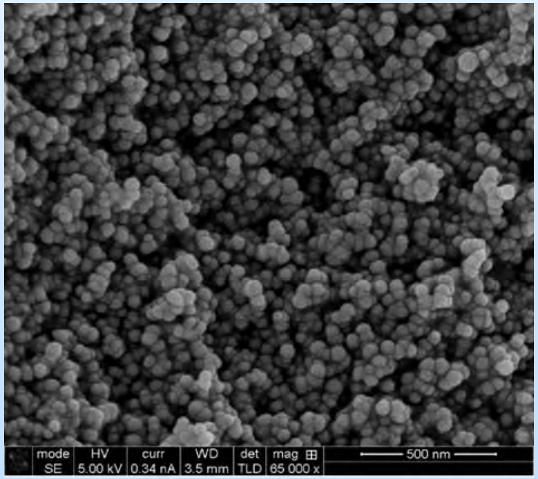
Preformed Particle Gel (PPG)



(a) Before swelling (b) After swelling





Cross-linked polymer powder, Super Absorbent Polymer

Size ranging from nano-meter to millimeter

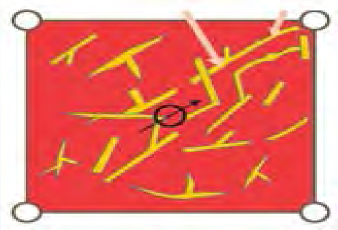
Presentation Outline

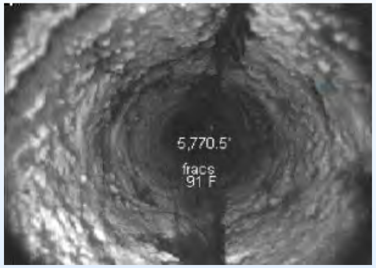
- **Technical Status**
  - ➢ Mm-size Particle Gels for Super-K Channels
  - ➢ Micro-/Nano-gels for Matrix Conformance Problems
  - ➢ Nanogel transport, plugging and EOR mechanisms
- **Lessons Learned**
- **Accomplishments to Date**
- **Synergy Opportunities**
- **Project Summary**
- **Acknowledgement**
- **Appendix**

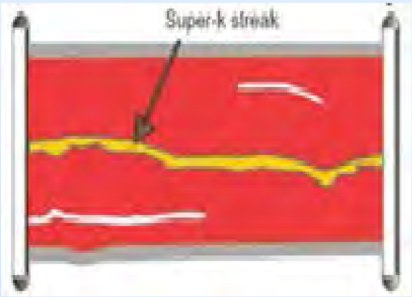
Mm-size Particle Gels for Super-K Channels

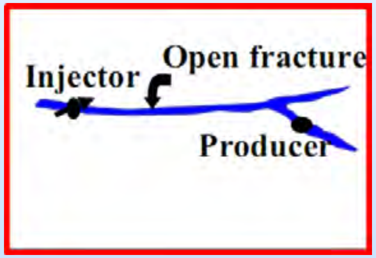
Target Conformance Problems

Targets: Super-K Channels









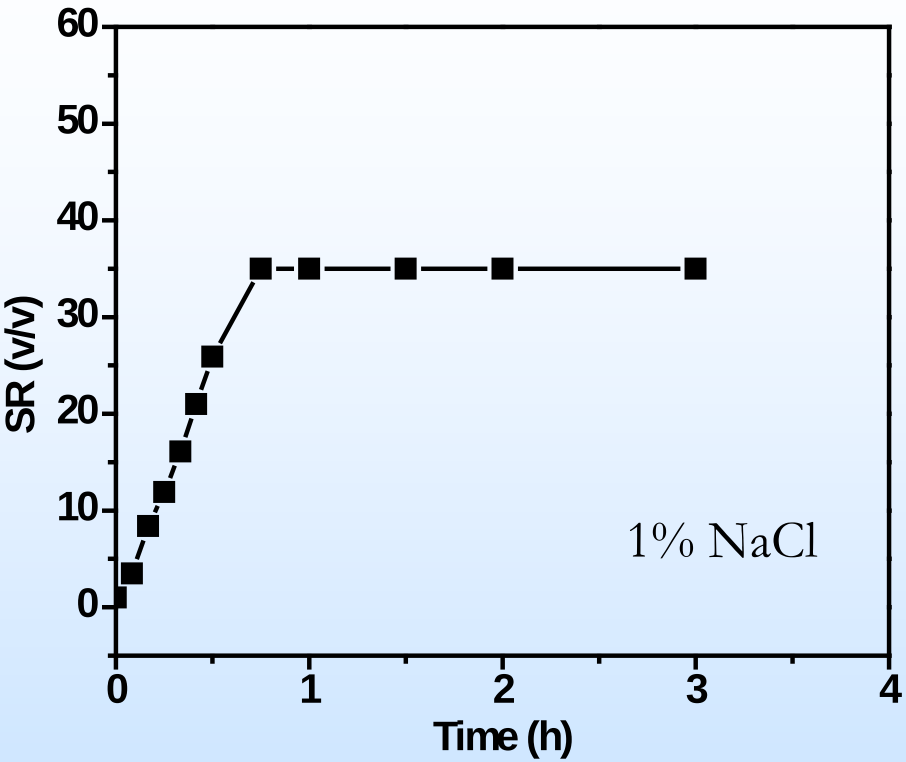
Our Solutions

(a) Before swelling (b) After swelling

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

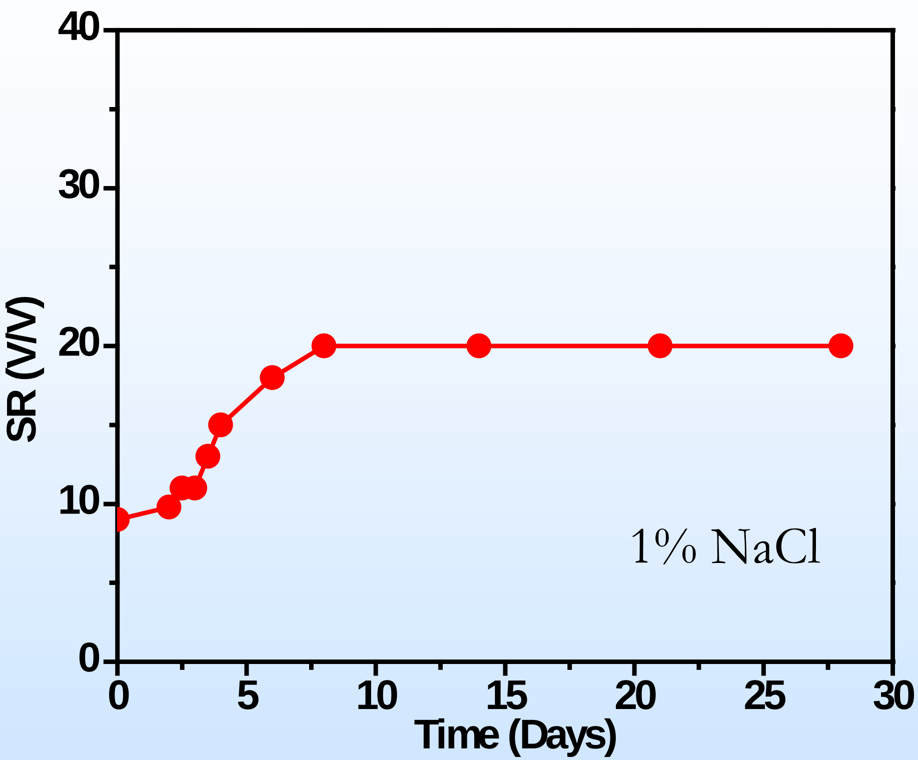
Product 1: Swelling Rate Controlled to Days

Traditional PPGs



Fast swelling within one hour

New monomer addition to traditional PPGs



Delayed swelling to days

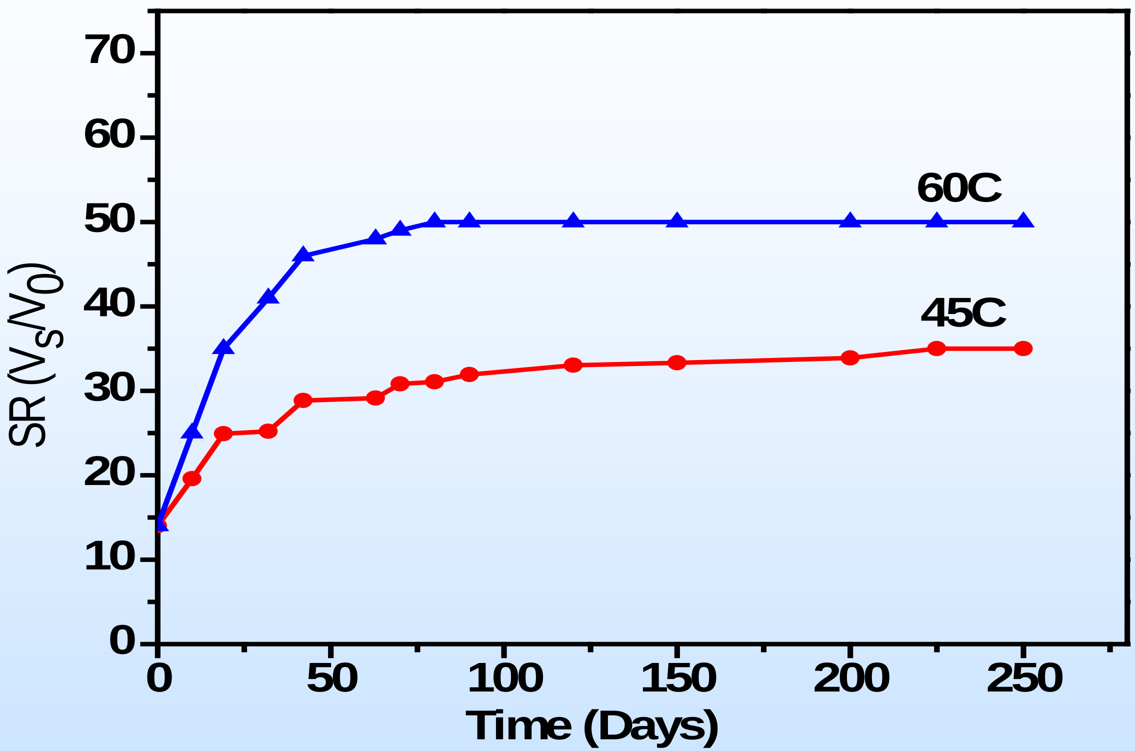
The new product overcome some problems of traditional PPGs

- 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

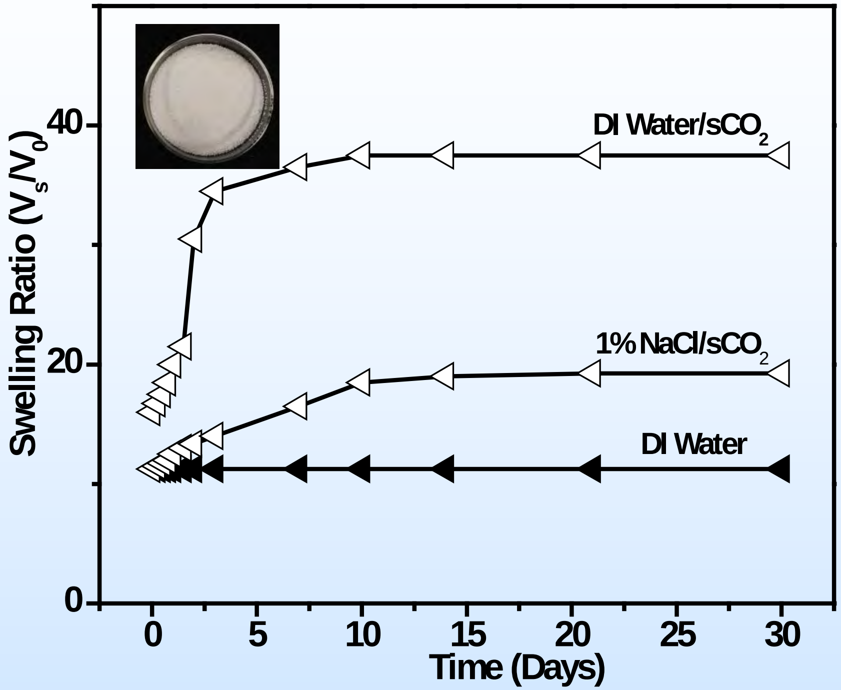


Swelling kinetics and Temperature effect (1% NaCl)

Product 2 is good for in-depth fluid diversion

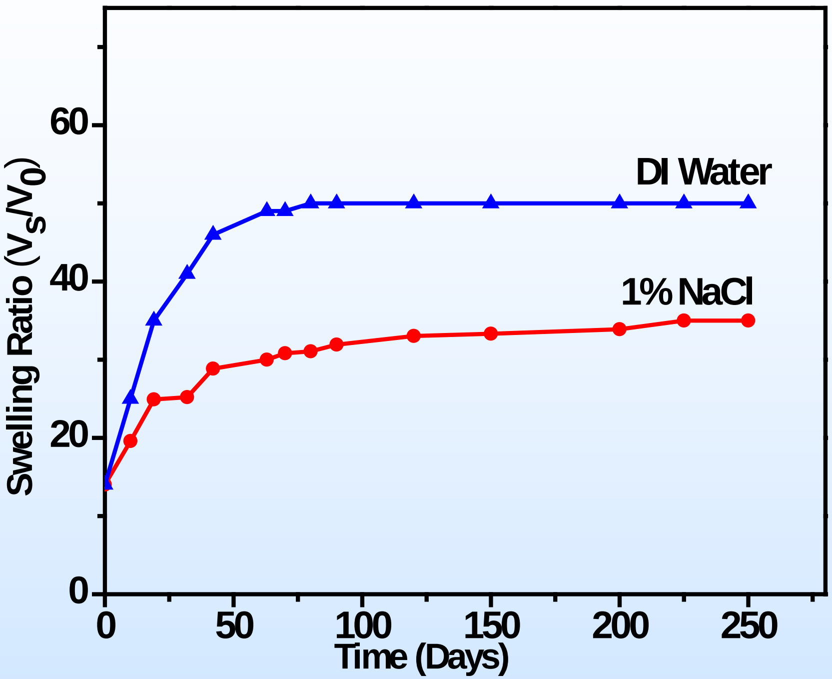
Meet the requirement: development of swelling rate controllable PPG

Product 3: CO_2 Triggered Swelling Delayed Particle Gel



particle size 1-2 mm; 45 °C

Delayed swelling to weeks



particle size 1-2 mm; 45 °C

Delayed swelling to months

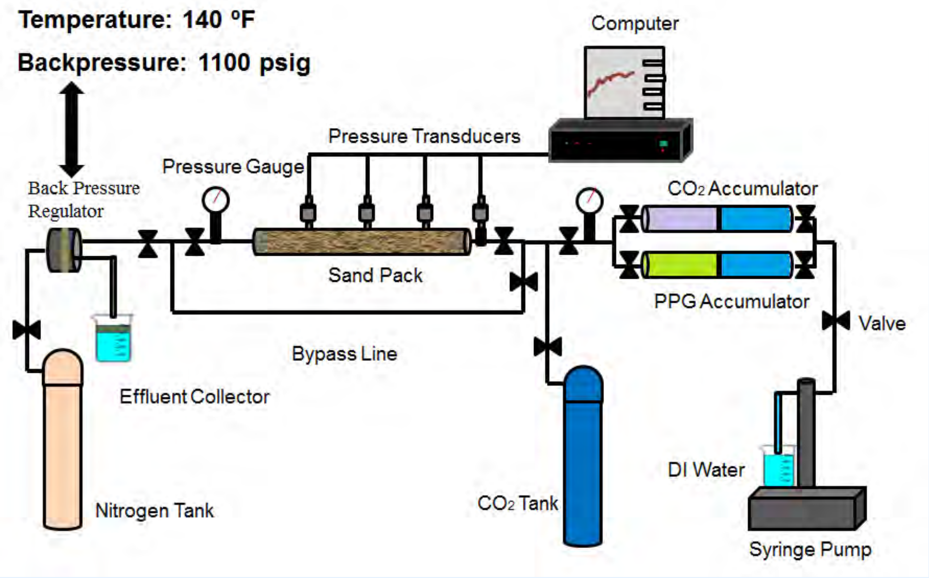
In absence of CO_2, size of the gel would not increase

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

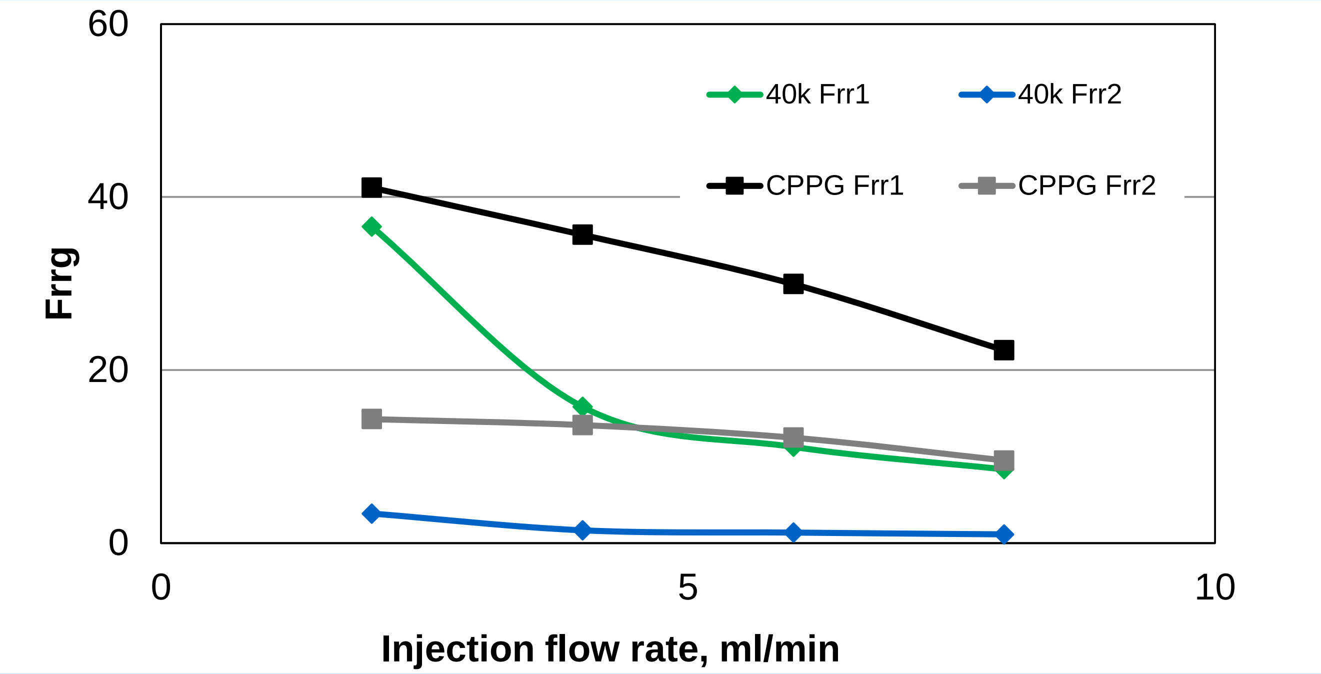
Product good for in-depth reservoir deployment

Meet the requirement: development of swelling rate controllable PPG

Mm-sized CPPG (Product 1) Plugging Efficiency to CO_2



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



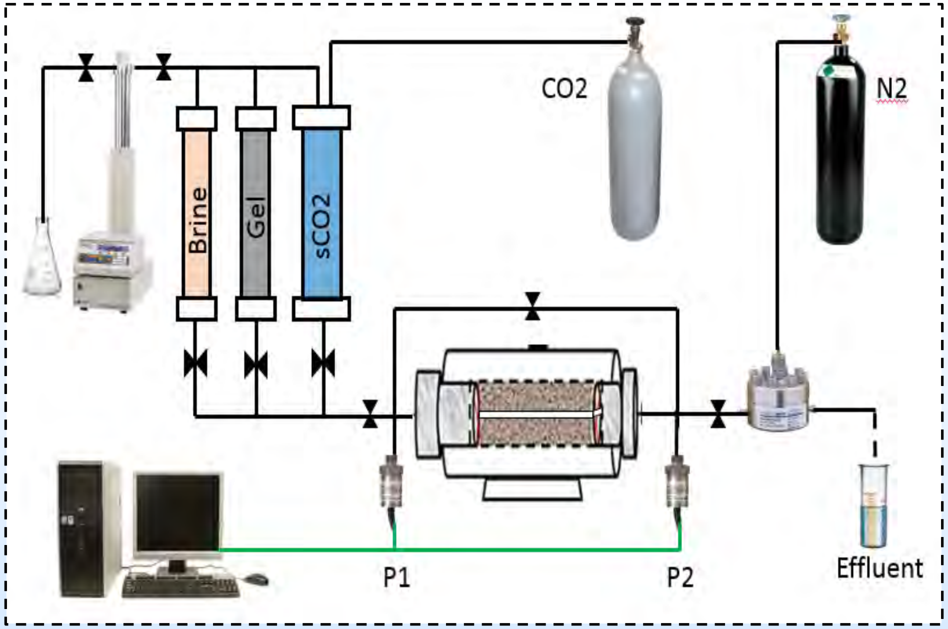
K=~23 Darcy
1 wt% NaCl

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

Mm-sized CPPG (Product 3) Plugging Efficiency to CO_2

Procedures

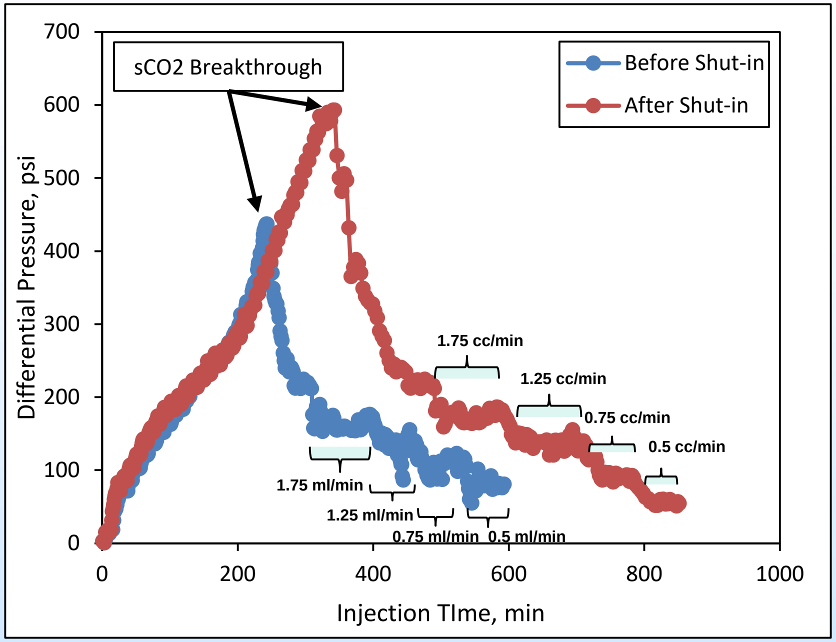
1. Select cores (permeability 50md) and frac.
2. Place fully swollen gel particles into fracture until pressure increases to 1000 psi.
3. Inject sCO2 to test breakthrough pressure. Measure stable pressure at different flow rates.
4. Inject 2 PV brine. Shut in the core holder. Keep core holder temperature at 60 °C.
5. Test sCO2 breakthrough pressure. Measure stable pressure at different flow rates.
6. Analyze data.



CO2 flooding experiment setup.

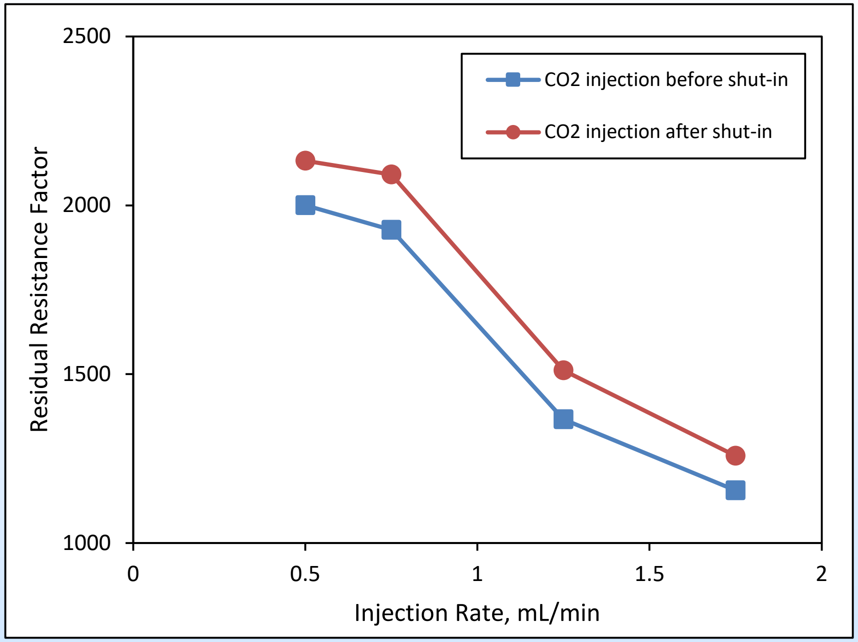
Matrix Permeability	Around 50 md
Stone Type	Sandstone
Fracture Width	0.5 mm
Gel Particle Size	100-125 Micron
Brine Used	1wt.% NaCl

Core Flooding Experiment: Supercritical CO_2



Pressure difference throughout the core.

Shut in for 3 days

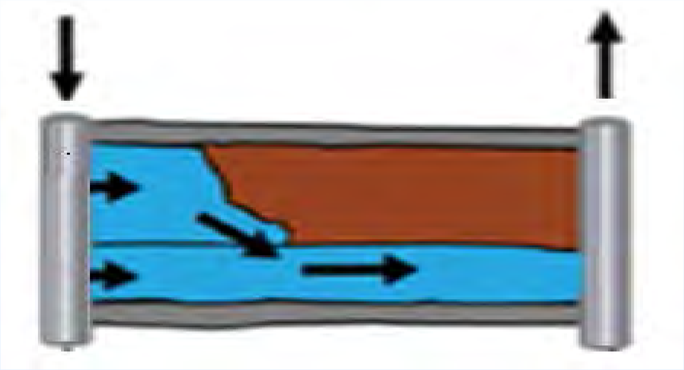


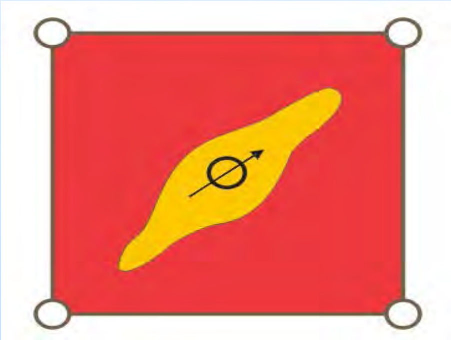
SCO_2 Frr at different injection rates, before and after shut-in.

- "Self-healing" behavior: Supercritical CO_2 reached breakthrough at 617 psi in first CO_2 flood. **After shut-in, another breakthrough at 437 psi was detected.**
- CO_2 residual resistance factors increased after shut-in.

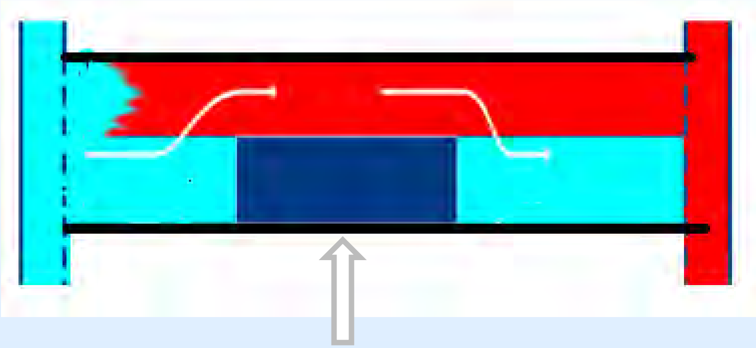
CO_2 Resistant Micro-/Nano-gels for Matrix Conformance Problems

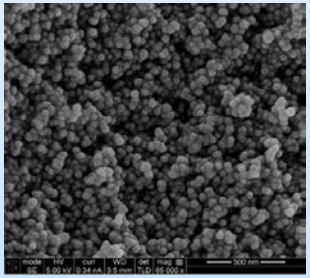
Targets-Matrix Problem





Solution

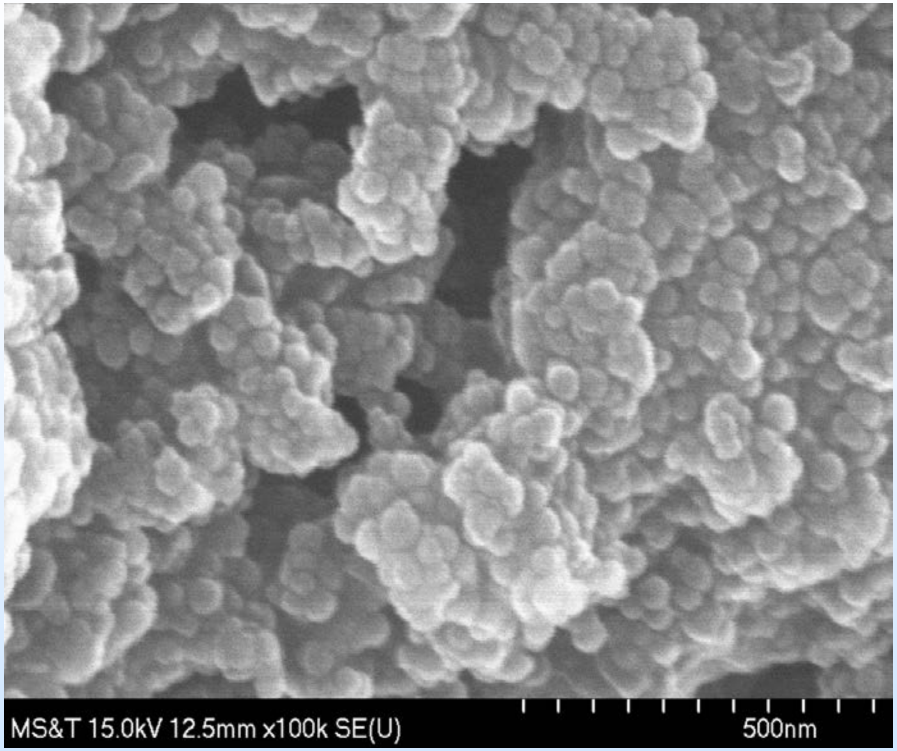




Achievement: Synthesized a series of swelling-delayed CO_2 responsible nano-particle gels that can transport into the in-depth of a reservoir.

Swelling Rate Controllable Nano-gels

Nano-gel in powder form



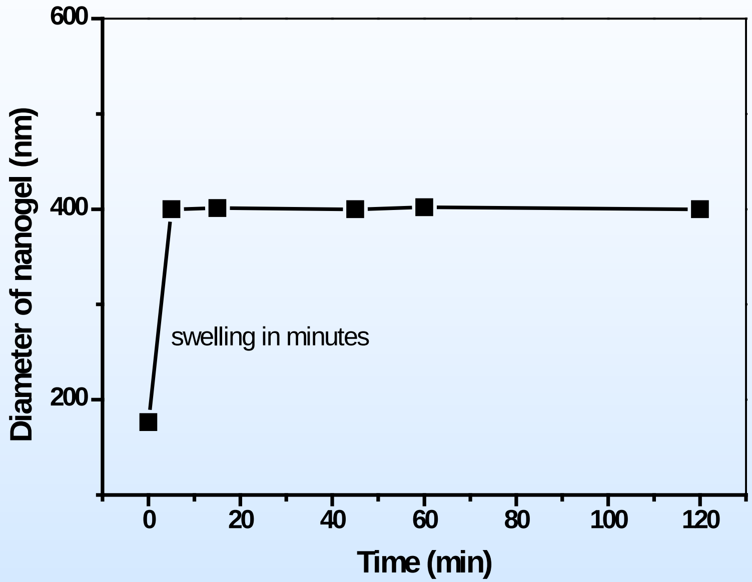
SEM images

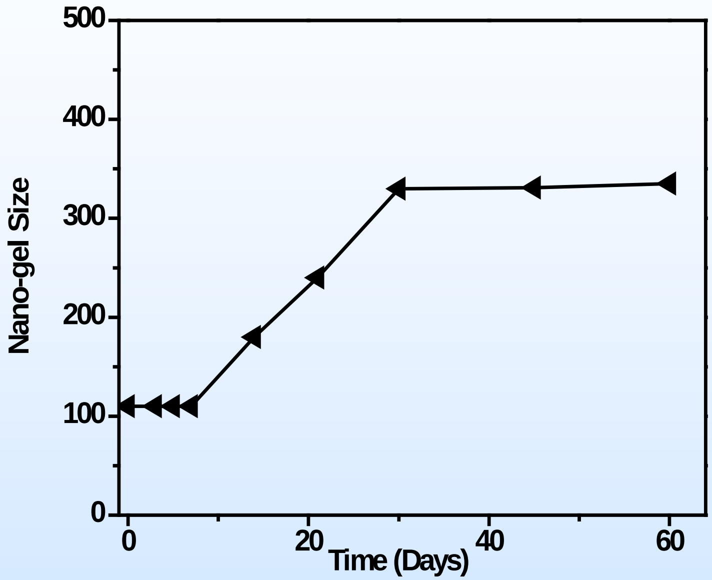
Tunable sizes: in the range of nano to microns

Swelling Rate Controllable Nano-gel

Traditional HPAM nano-gels

Product 1: CO_2 triggered Swelling





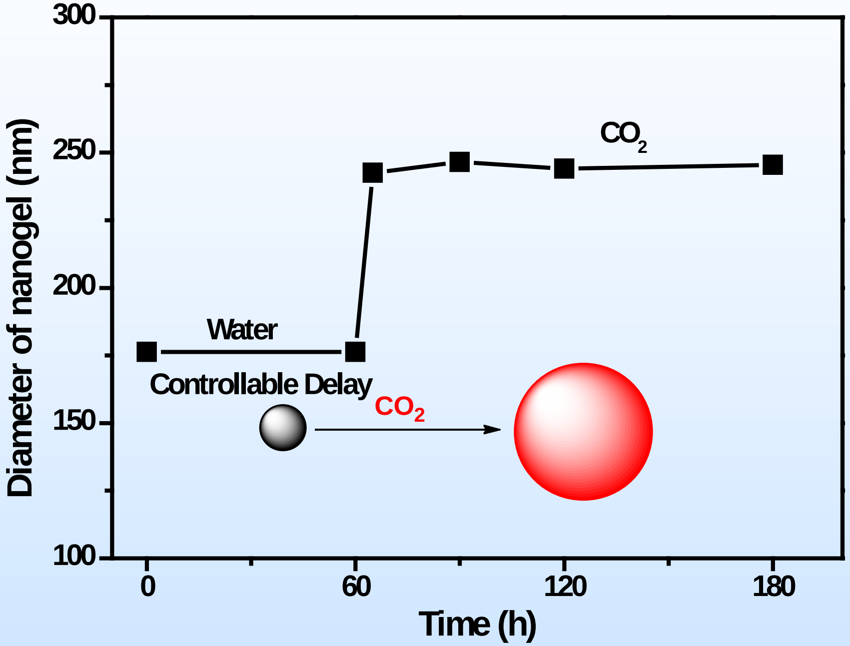
Fast swelling in minutes

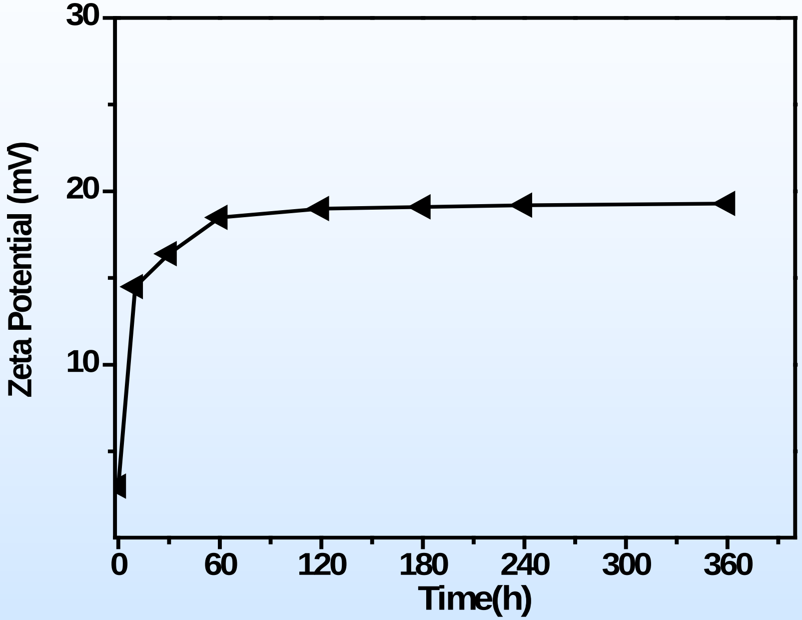
Delayed swelling to weeks

- 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 micro/nano-gels



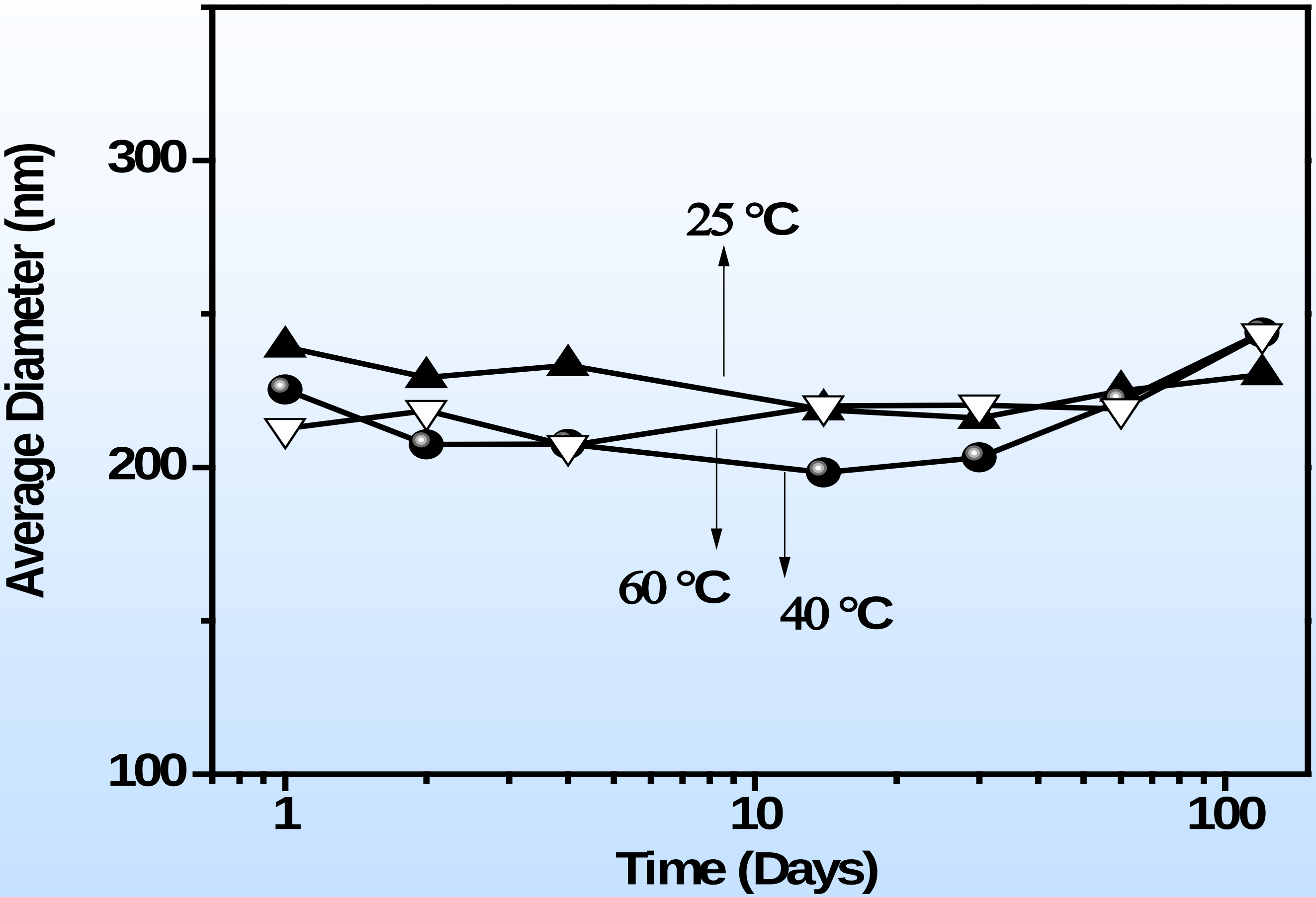


In the presence of CO_2

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.

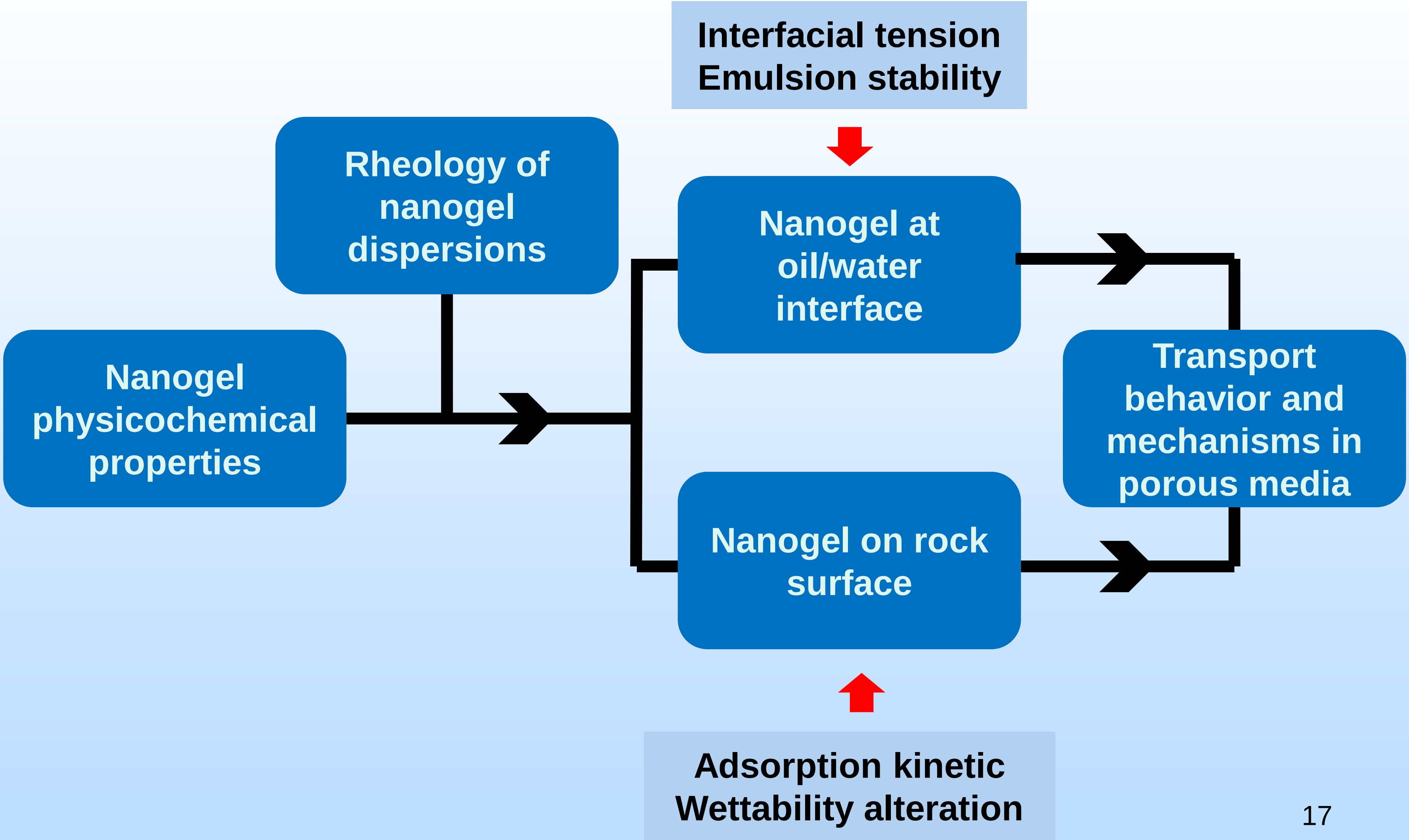
Meet the requirement: development of swelling rate controllable nano-gels

Nano-gel Thermal Stability



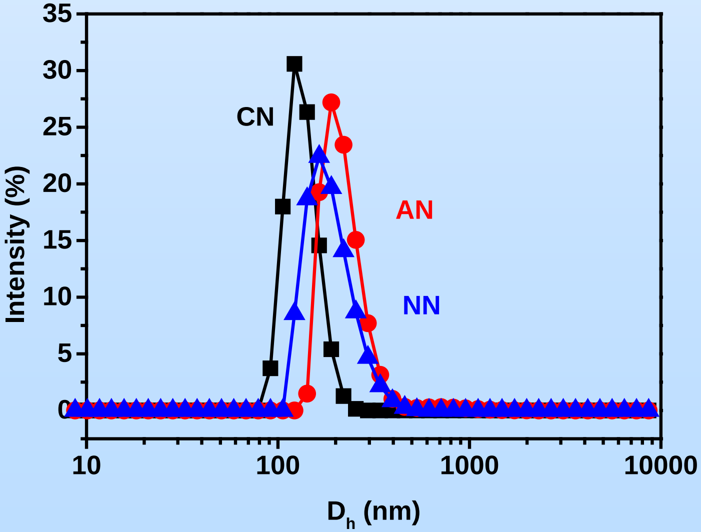
CO_2 resistant Nano-gels had better stability than HPAM-type of nanogels at different temperatures.

Transport and EOR Mechanisms of Nanogels



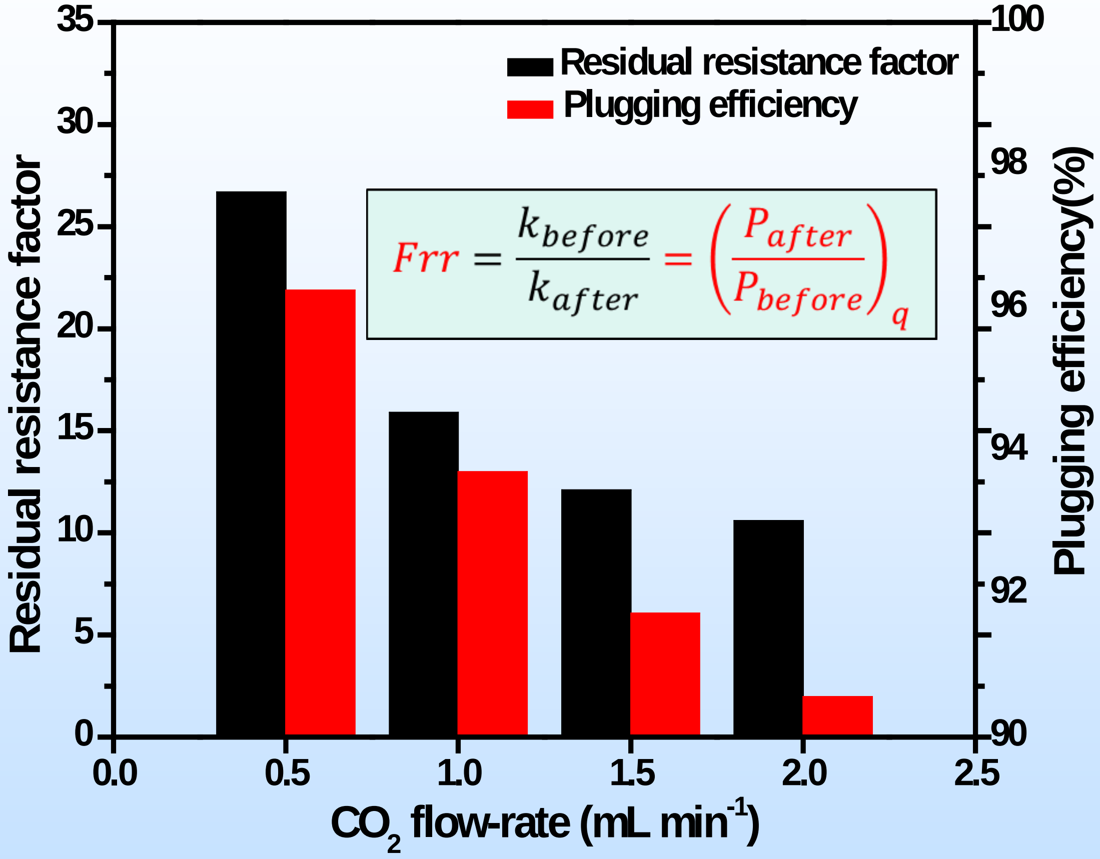
Physicochemical Properties of Nanogels

Property	Nonionic nanogel (NN)	Anionic nanogel (AN)	Cationic nanogel (CN)
Charge	Neutral	Negative	Positive
Zeta potential (mV)	-1.76	-35.90	34.75
Original diameter (nm）	59.00	88.12	65.83
Swollen diameter (nm)	220.14	241.62	151.14
Polydispersity index (PDI)	0.236	0.268	0.482
Swelling ratio	51.92	20.61	12.10
pH (1000 ppm in DI water)	7.8	7.0	4.9



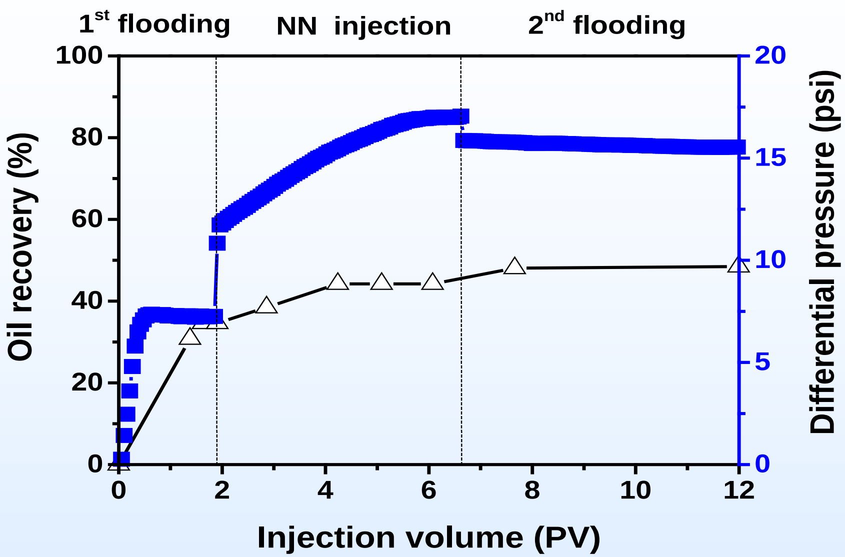
Nanogels with same size distribution and different charges were synthesized and used for following characterizations and evaluations.

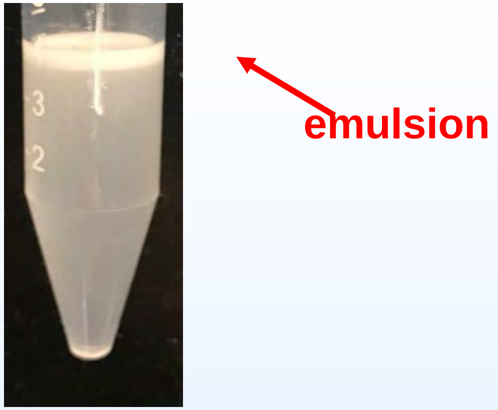
Nano-gel Plugging Efficiency to Matrix



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

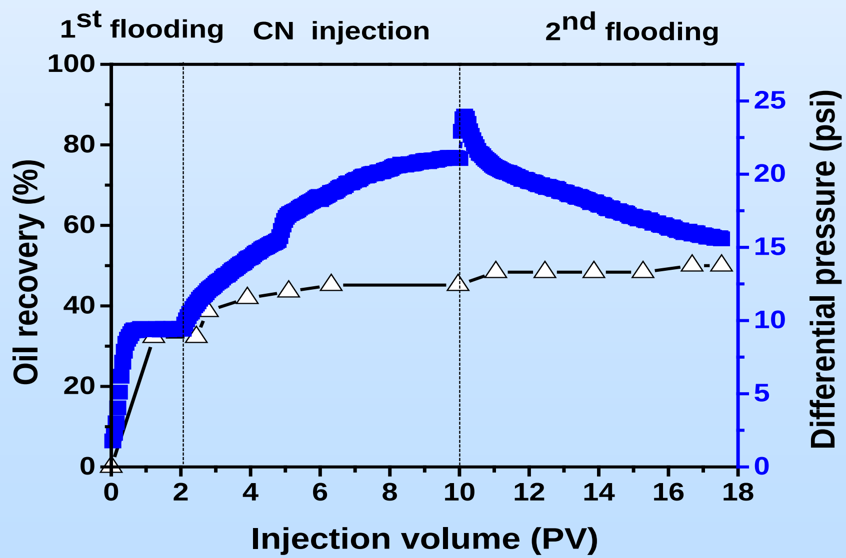
Oil Recovery Improvement by Nanogel Injection

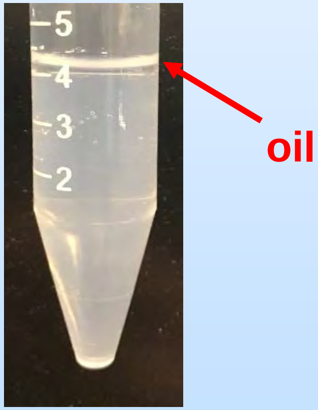




Nanogel injection

Nanogel for emulsification



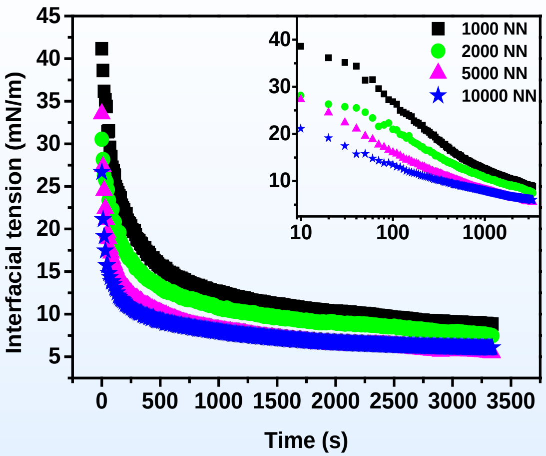


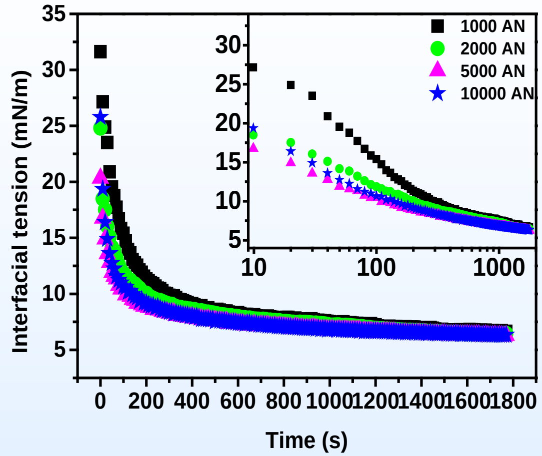
2nd flooding

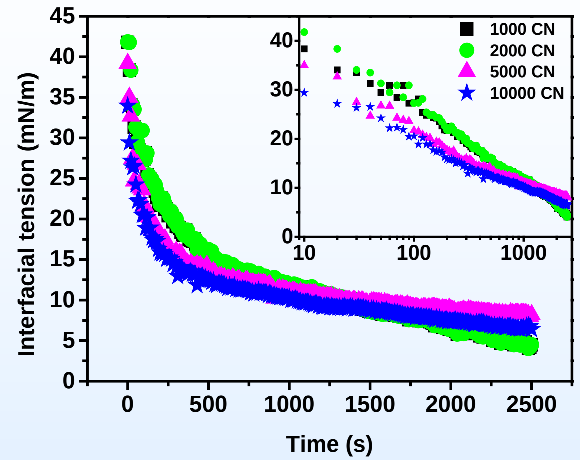
Nanogel for water diversion

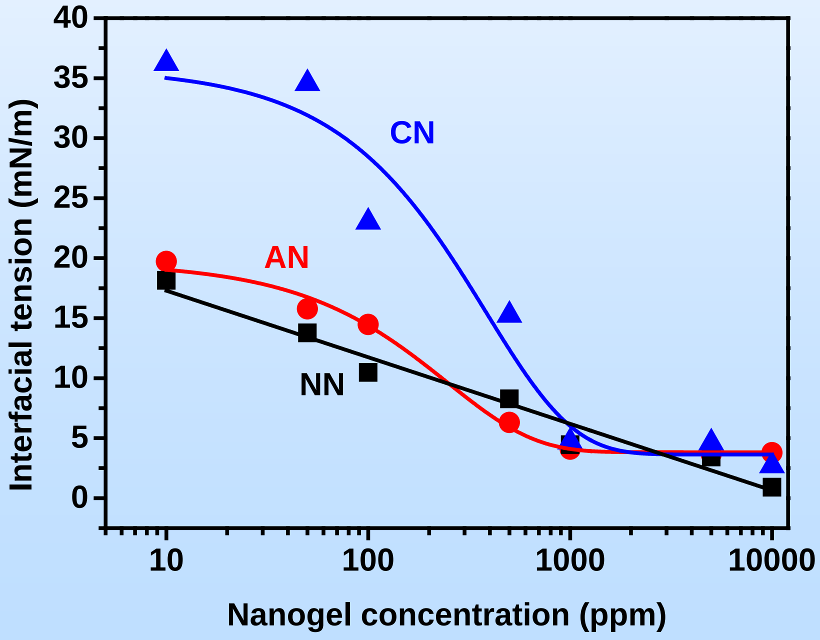
Rock core: Berea sandstone (negative charged), Φ: 20.5%, K: 87 mD

EOR Mechanism 1: Nanogels for Interfacial Tension Reduction







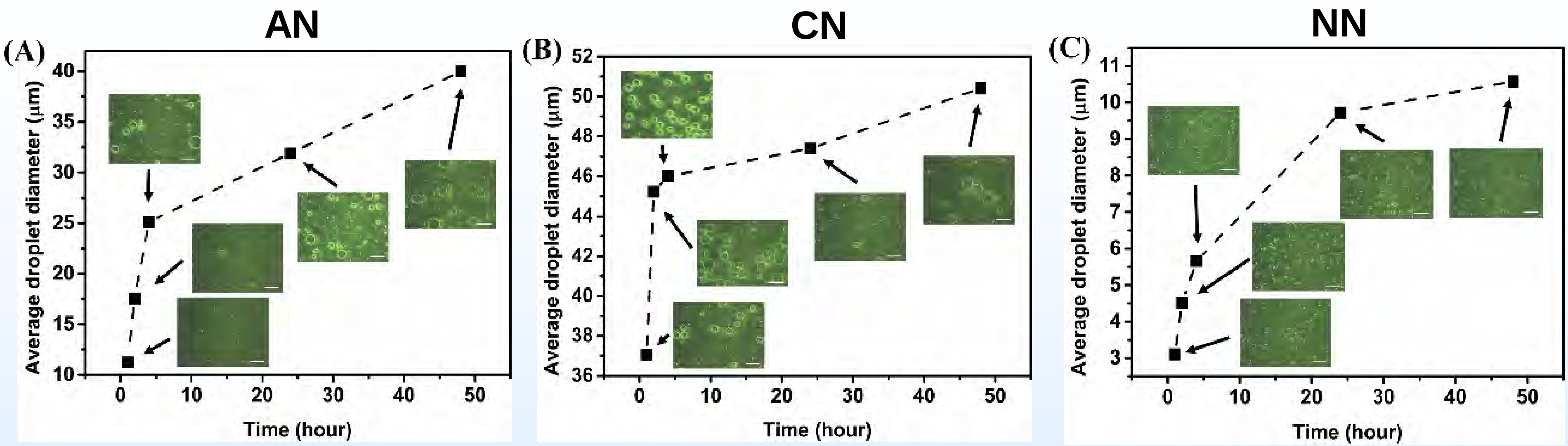


Nanogels can rapidly reduce the oil/water interfacial tension.

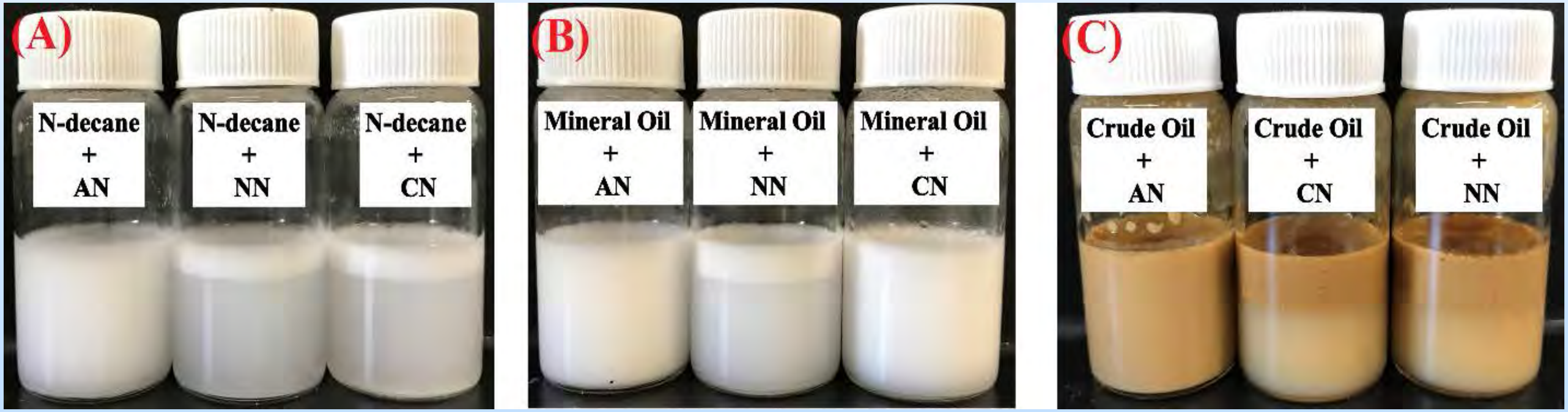
The equilibrium interfacial tension is related to the nanogel concentration.

The equilibrium interfacial tension becomes constant when nanogel concentration above 1000 ppm .

EOR Mechanism 2: Oil-in-Water Emulsion Stabilization

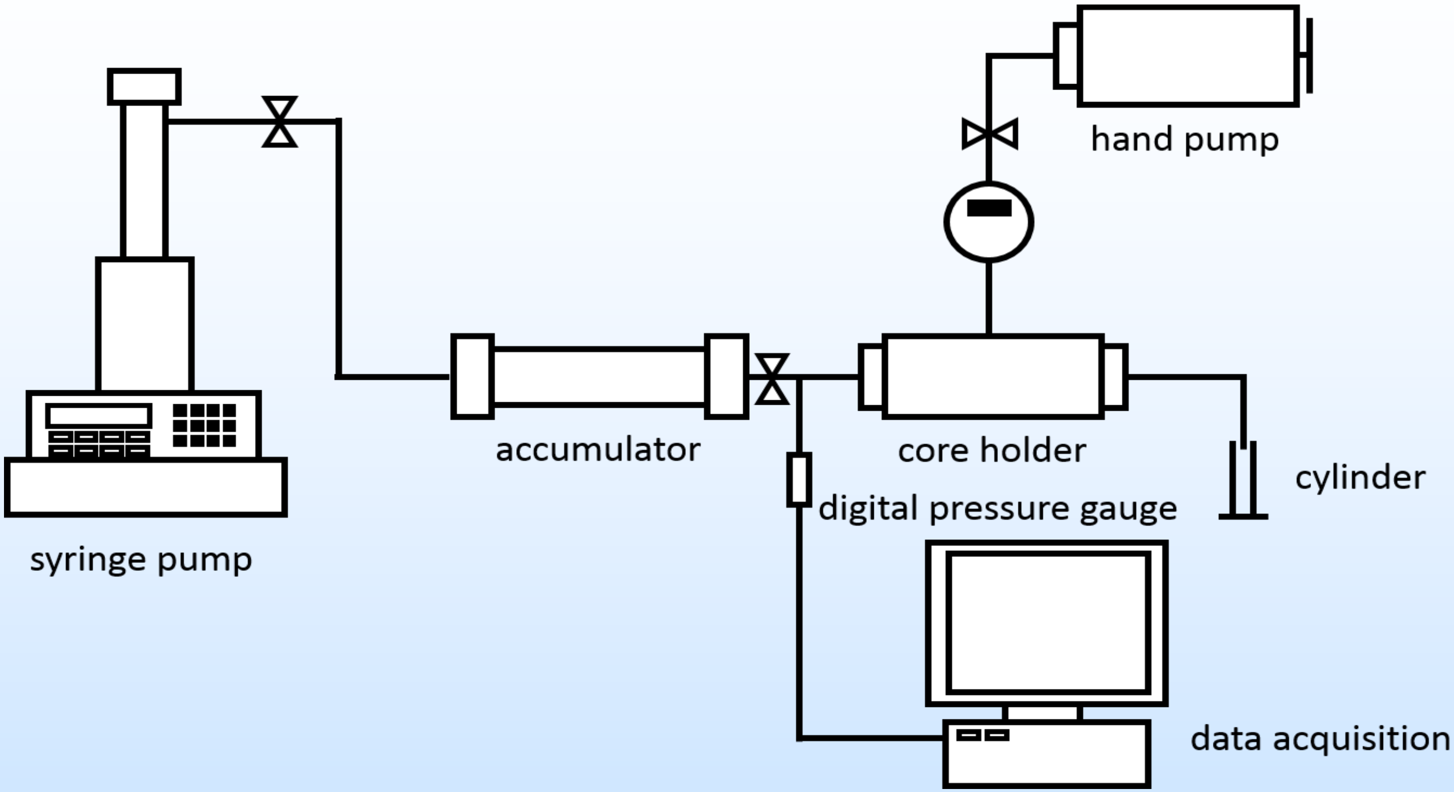


O/w emulsions was prepared with decane and nanogel dispersion (1% NaCl) at 25 °C



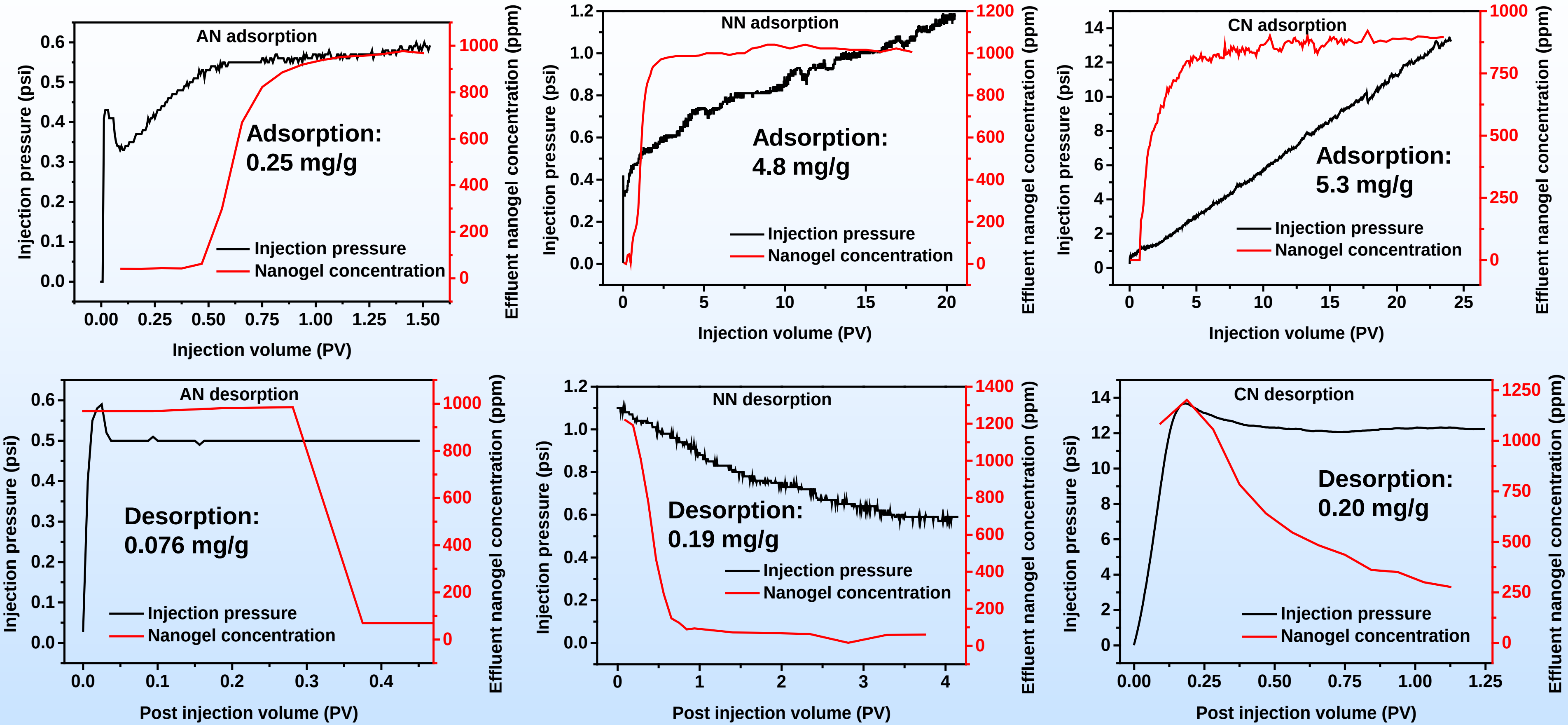
Nanogels can stabilize oil-in-water emulsion for more than 6 months.
The diameter of emulsified oil drops is from several to tens of microns.

Dynamic Adsorption and Desorption Tests



Nanogel concentration measurement

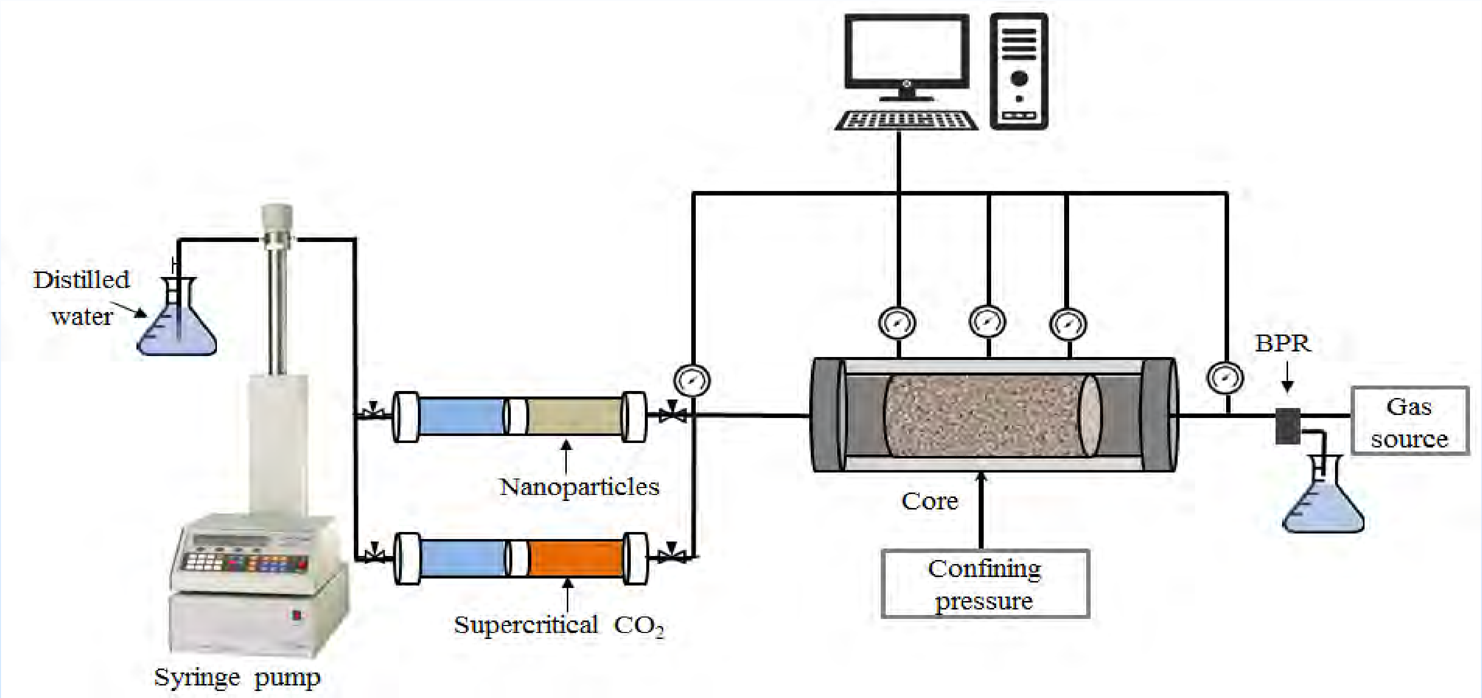
Dynamic Adsorption/Desorption of Nanogel



Rock core: Berea sandstone (negative charged), Φ: 20.5%, K: 266.7mD

Nanogels are able to increase the injection pressure in sandstone saturated with water. Desorption process is depending on the electro-attraction between nanogel and rock.

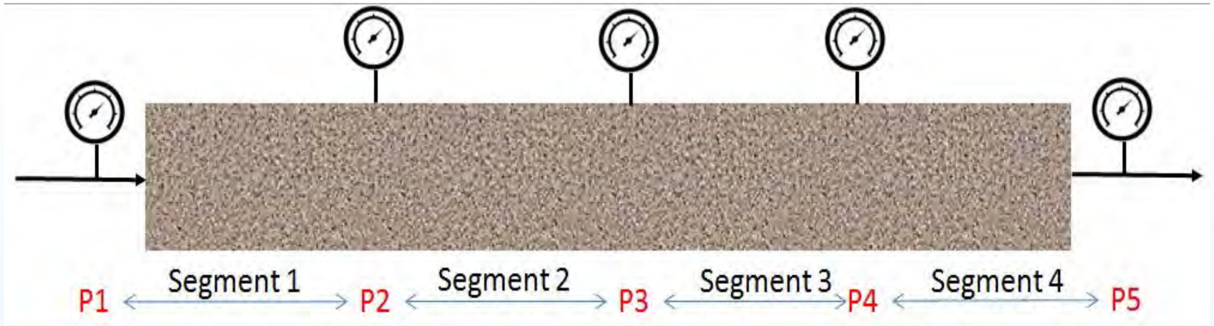
Delivery of Nano-gel in Sandstone



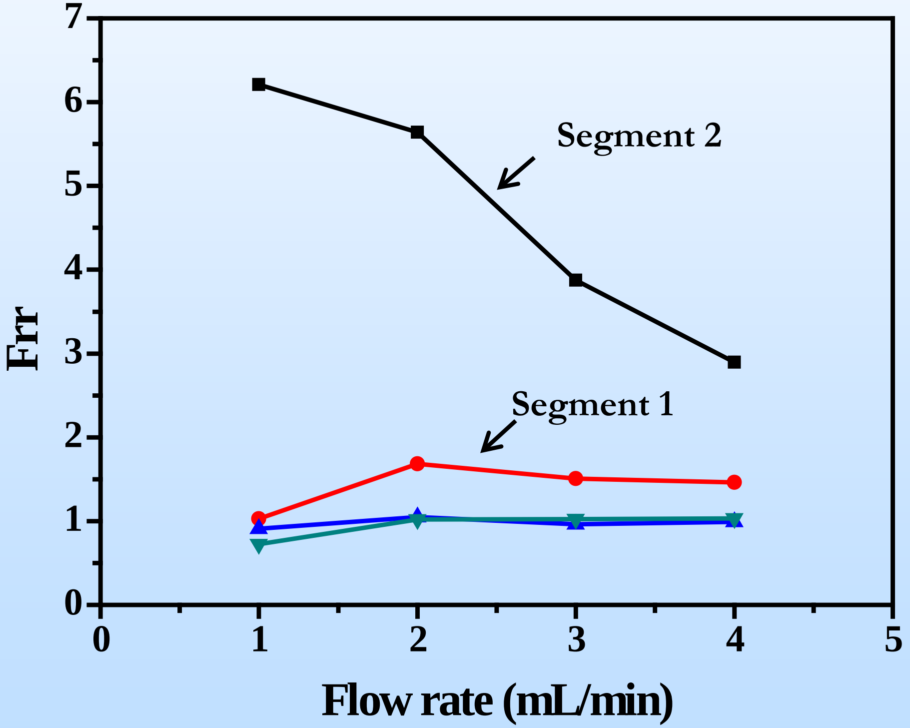
Core information

#	Diameter (mm)	Length (mm)	PV (cc)	Permeability (md)
1	37.9	284	61.67	98

Permeability Reduction in Different Segments



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



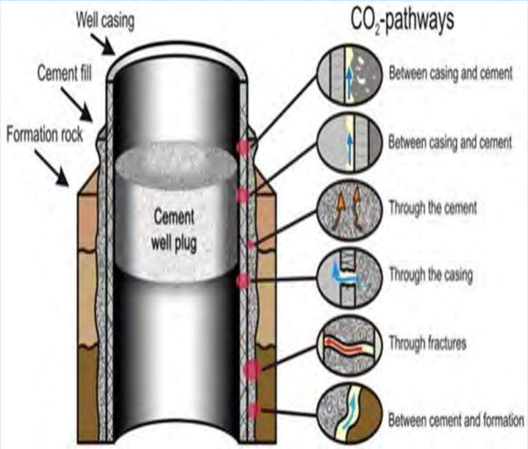
- Nano-gel can be delivered into the far wellbore area
- After CO_2 stimulation, nano-gel provides a sufficient plugging to segment 2 and no penetration to segments 3 and 4

Accomplishments to Date

- Published 11 journal papers, one conference paper, and two presentations.
- Synthesized nano- to millimeter-sized swelling-rate controllable CPPGs for different conformance problems.
- Evaluated the effect of water salinity, pH and temperature on CPPG and nanogel behavior.
- The plugging efficiency of mm-sized CPPG to super-K channels is more than 90%.
- Nanogel synthesized under $scCO_2$ conditions have narrower distribution than those synthesized by emulsion methods.
- Nanogel can transport through Berea sandstone, improve oil recovery by increasing both micro- and macro- displacement efficiency.
- Nanogel can be placed in the far wellbore and provide efficient plugging under $scCO_2$ condition

Synergy Opportunities

- Industry Interest for **mm-sized CPPG product scale-up and field pilot test.**
  - Currently our industry collaborators Conoco-Phillips (CP), Occidental (OXY), and Daqing Wantong are interested in the products for pilot tests.
- CO_2 Storage Partnership Projects
  - The new products can be used to solve early breakthrough or excess CO_2 production problems for CO_2 EOR storage projects.
- Swelling-rate controllable **nano-particles for wellbore leakage** control from minor cracks that cement can not penetrate.



Nordbotten, et al. 2011

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 nanogel can transport through common porous media and form efficient plugging in far wellbore zone under $scCO_2$ condition.

Next Steps:

- Run coreflooding test to further understand nanogel transport and blocking mechanisms.
- Test whether swelling-rate-controllable nanogel can be used for leakage control.
- Write the final project report

Acknowledgement

- US Department of Energy
- Industry: Conoco-Philips, Occidental Petroleum Corporation
- Project Manager: Kylee Rice
- Graduate students

Appendix

- Benefit to the Program
- Project Overview
- Organization Chart
- Gantt Chart
- Bibliography

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:

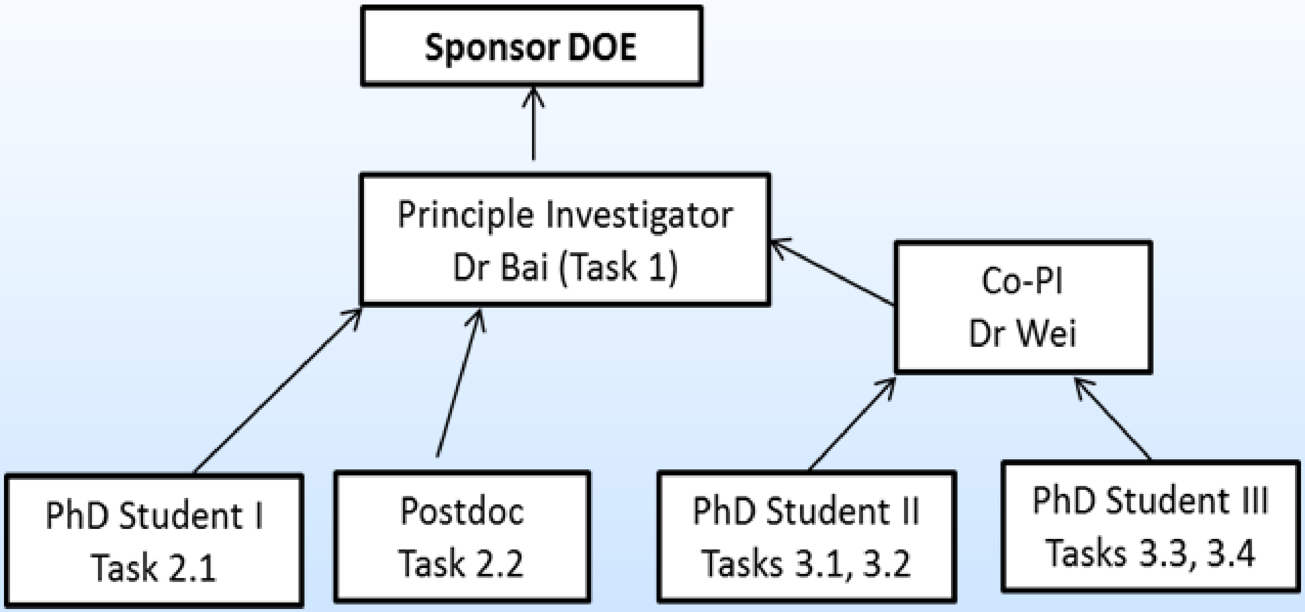
Goals and Objectives (1)

- **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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- Ms. Xindi Sun
- Mr. Yifu Long
- Mr. Jiaming Geng

PI: Baojun Bai
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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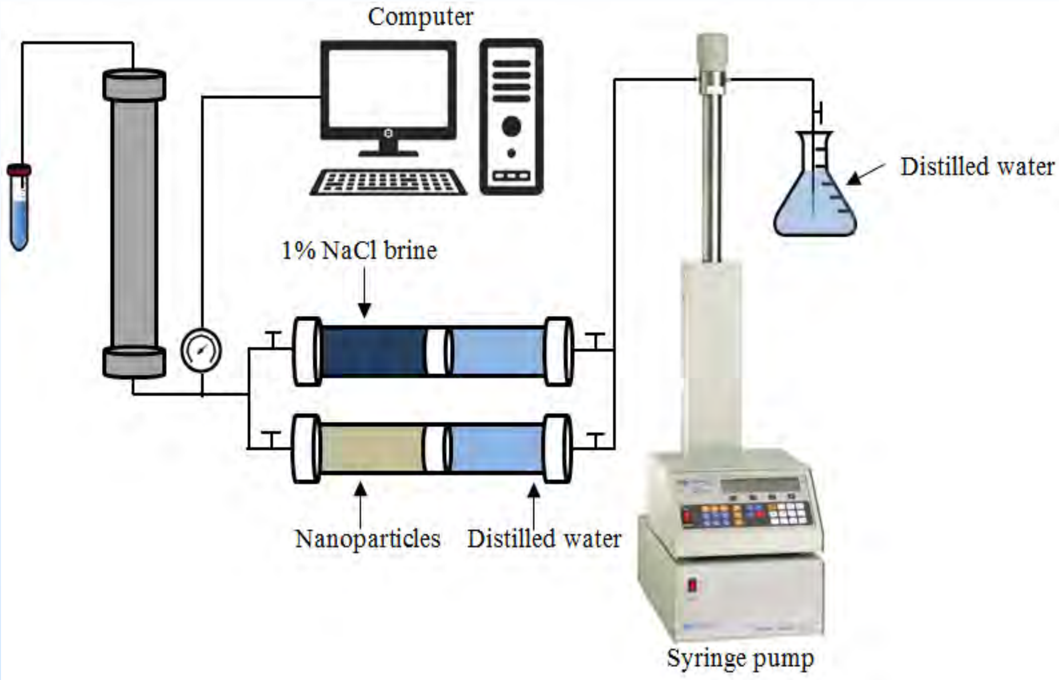
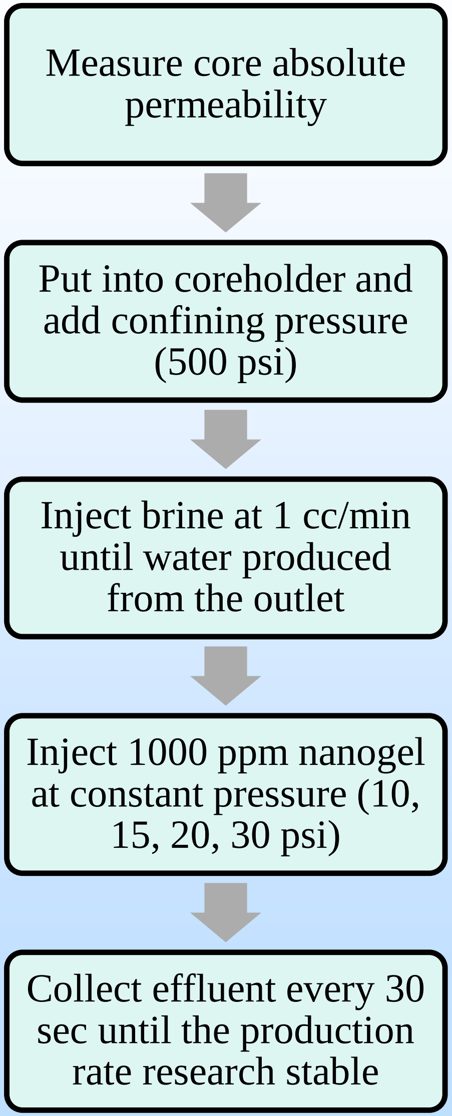
Filtration Test of Nanogel (Product 1)



Experimental apparatus design

Core information

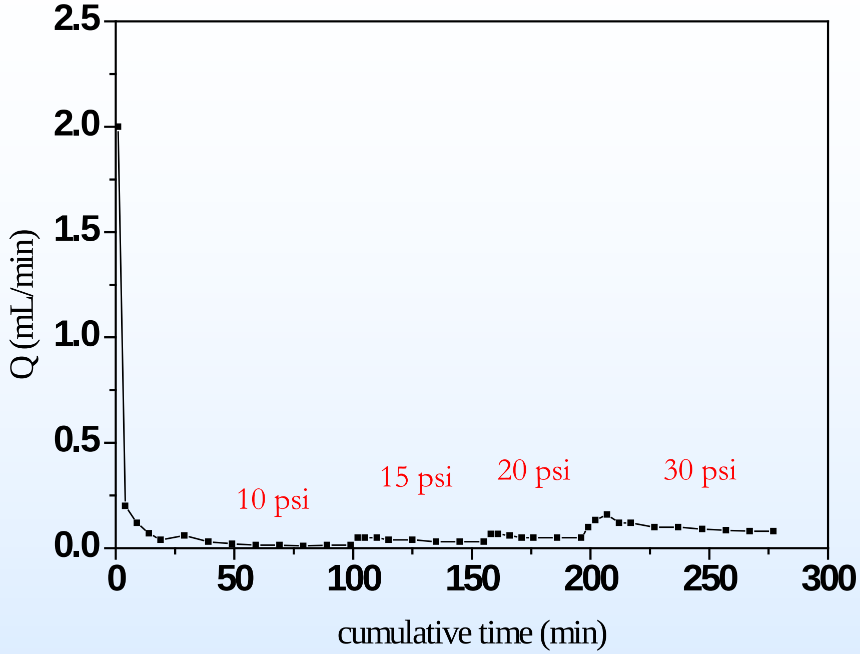
Core #	Length (cm)	Diameter (cm)	Pore volume (mL)	Porosity (%)	Permeability (md)
D6	1.079	2.51	1.02	19.15	36
B1	1.073	2.50	1.05	19.84	84



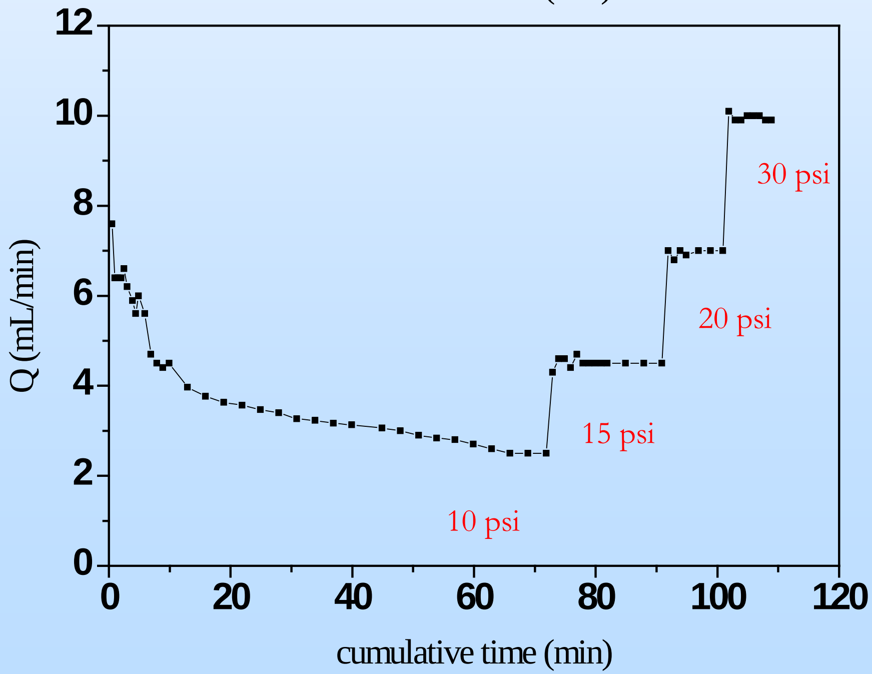
Experimental procedures

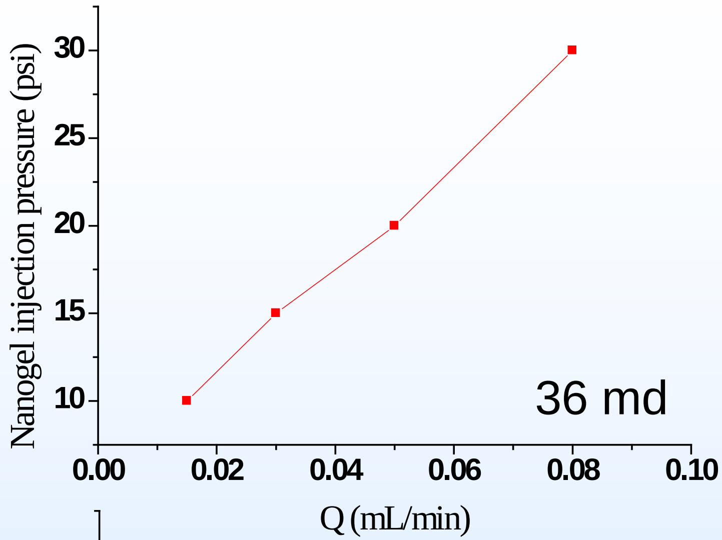
Filtration Test Results

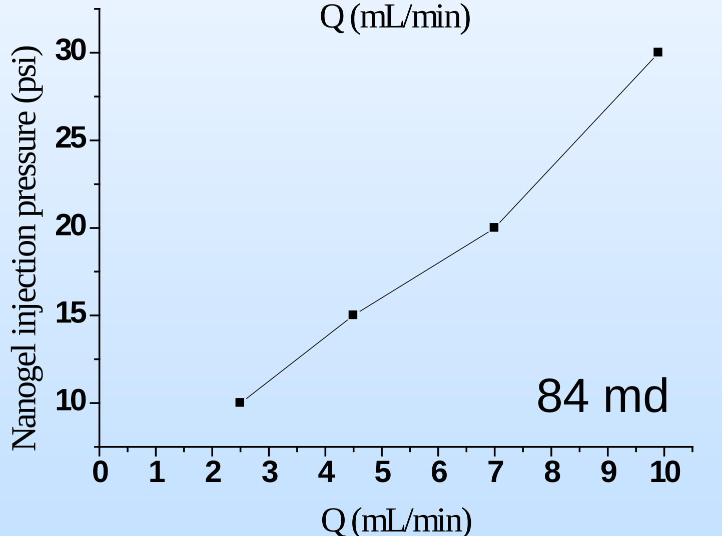
36 md



84 md

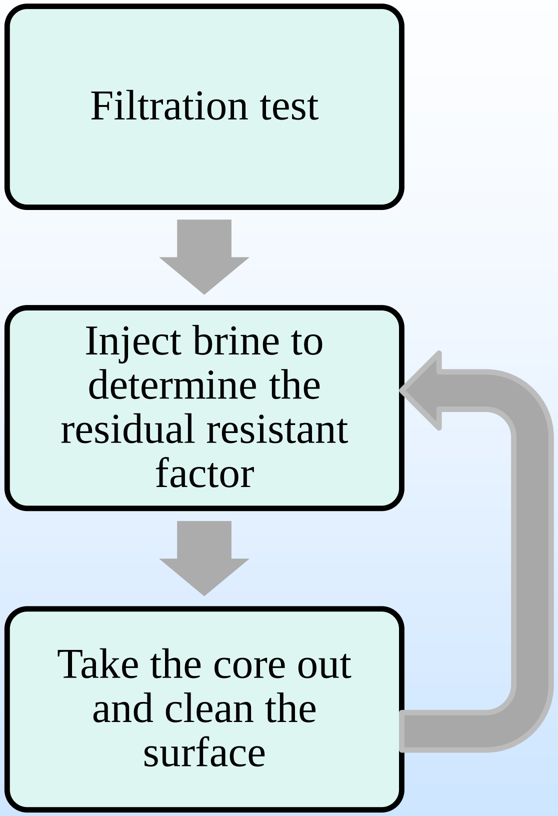


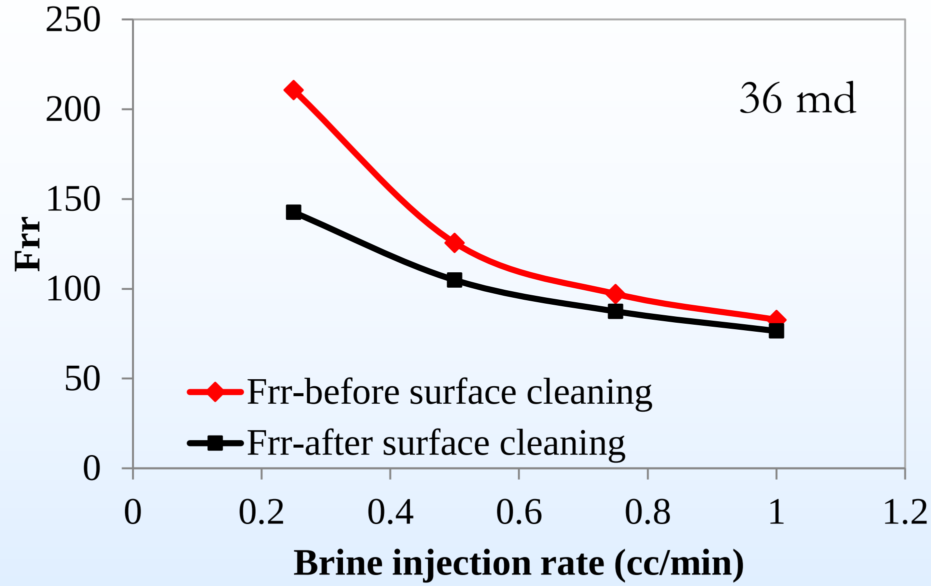


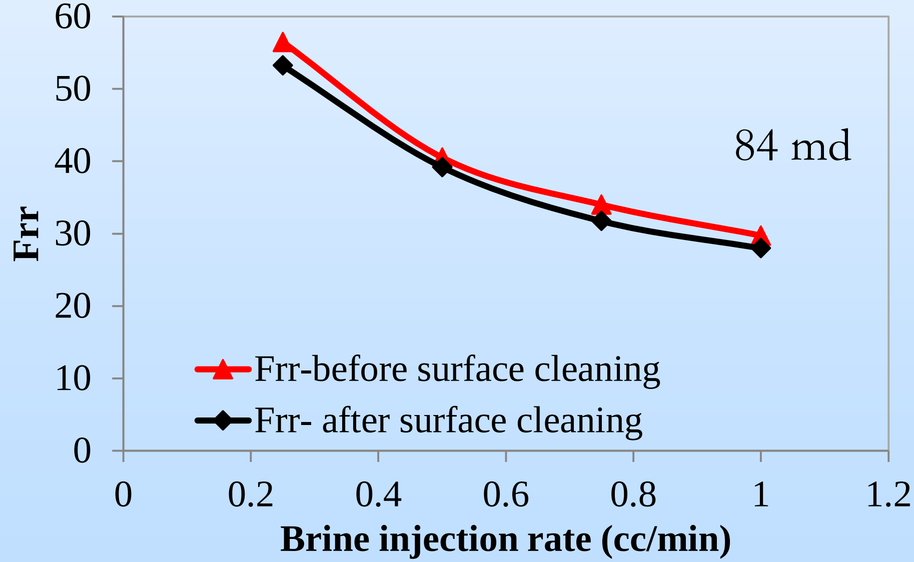


The rapid production rate reduction and low production rate indicate that the nanogel cannot flow through the rock with permeability lower than 36 md

Residual Resistant Factor

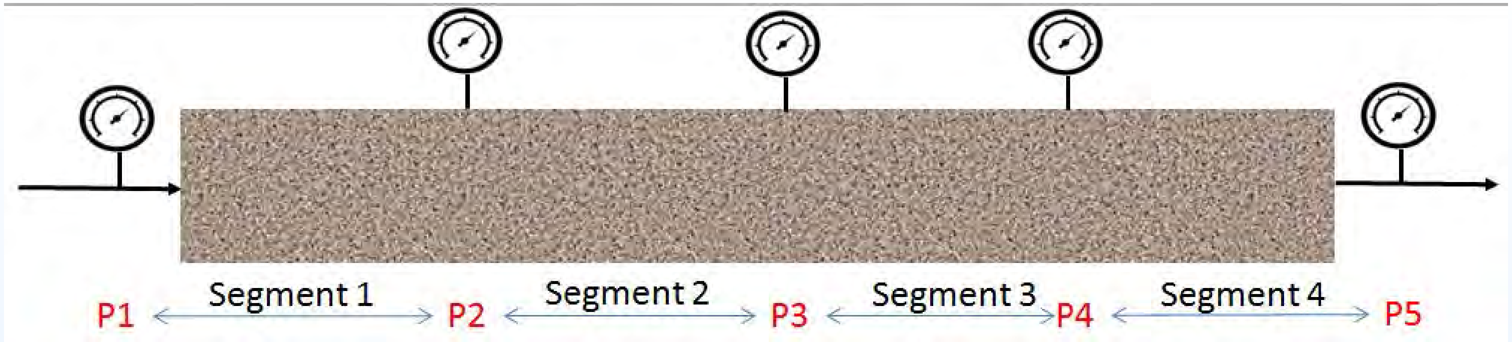


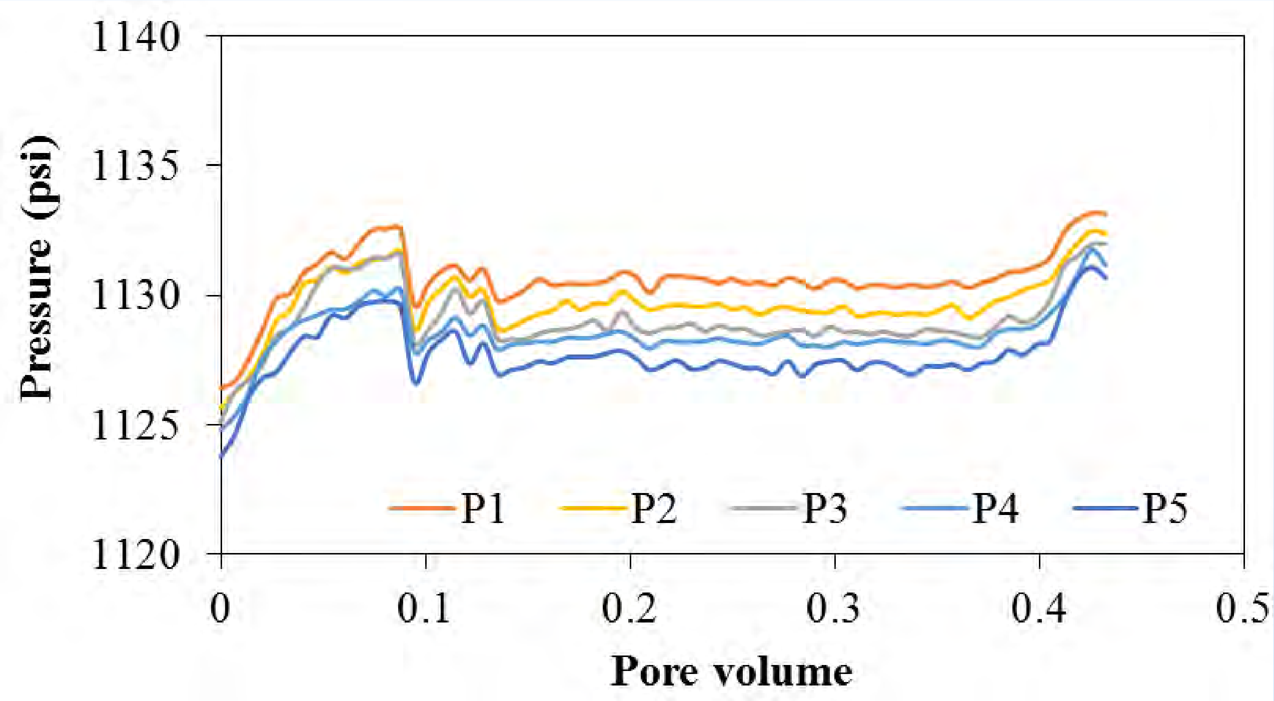




- **Nanogel forms external and internal cake near the inlet in the rock with permeability lower than 36 md**
- **Nanogel can penetrate through the sandstone rock with permeability higher than 80 md**

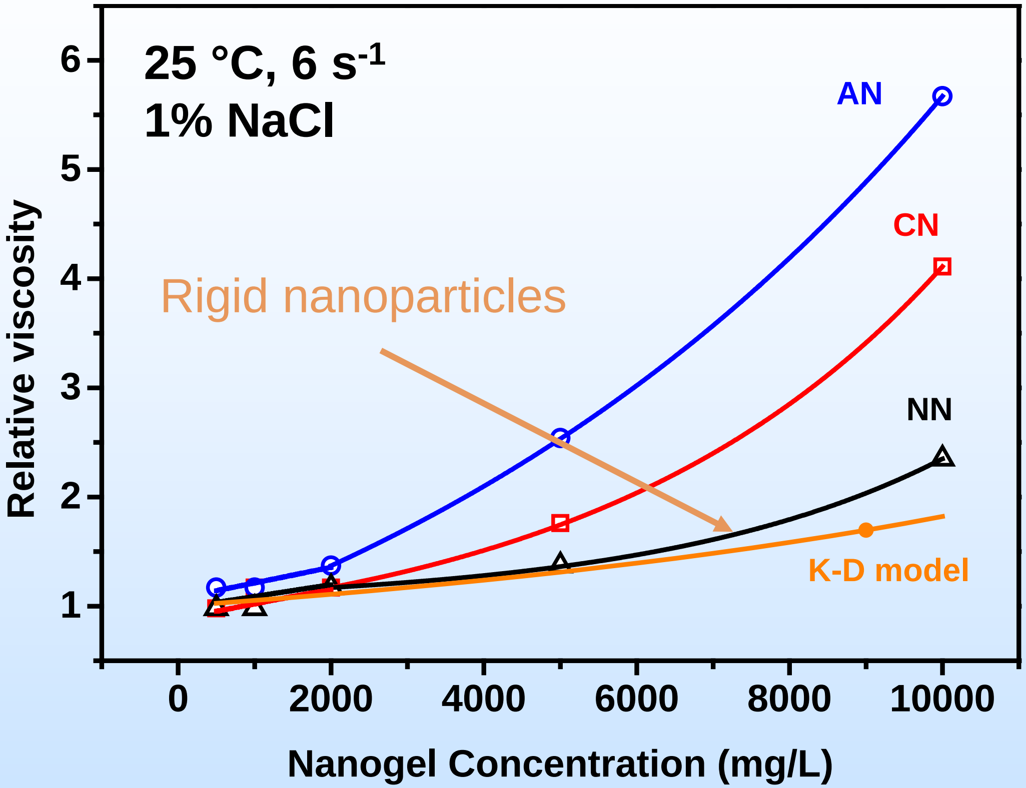
Nanogel Injection





- No pressure buildup at P1 and P2 during the nanogel injection
- Nanogel can penetrate into the in-depth without forming surface plugging

Rheology of Nanogel Dispersions



$$\eta_{rel} = \frac{\eta}{\eta_s}$$

η: viscosity

η_s: solvent viscosity

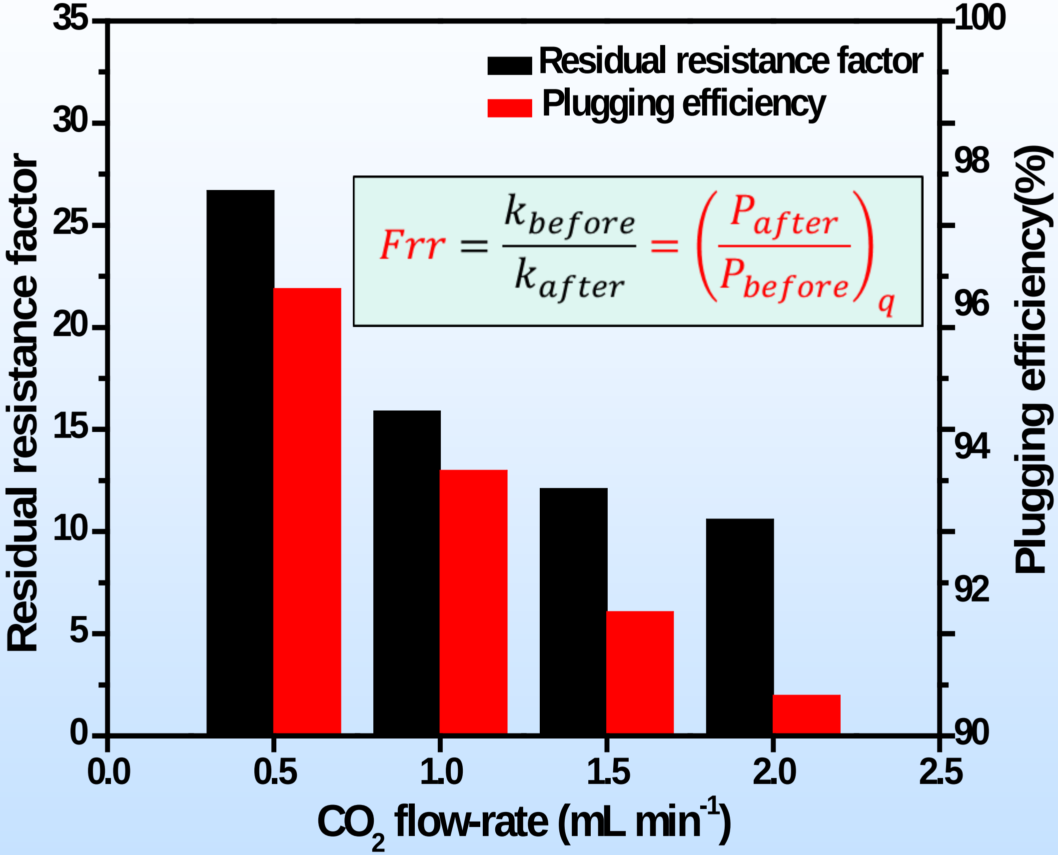
Krieger-Dougherty model:

$$\eta_{\mathrm{rel}} = \left(1 - \frac{\phi}{\phi_{\max}}\right)^{-[\eta]\phi_{\max}}$$

The nanogel dispersions have a concentration-related rheology.

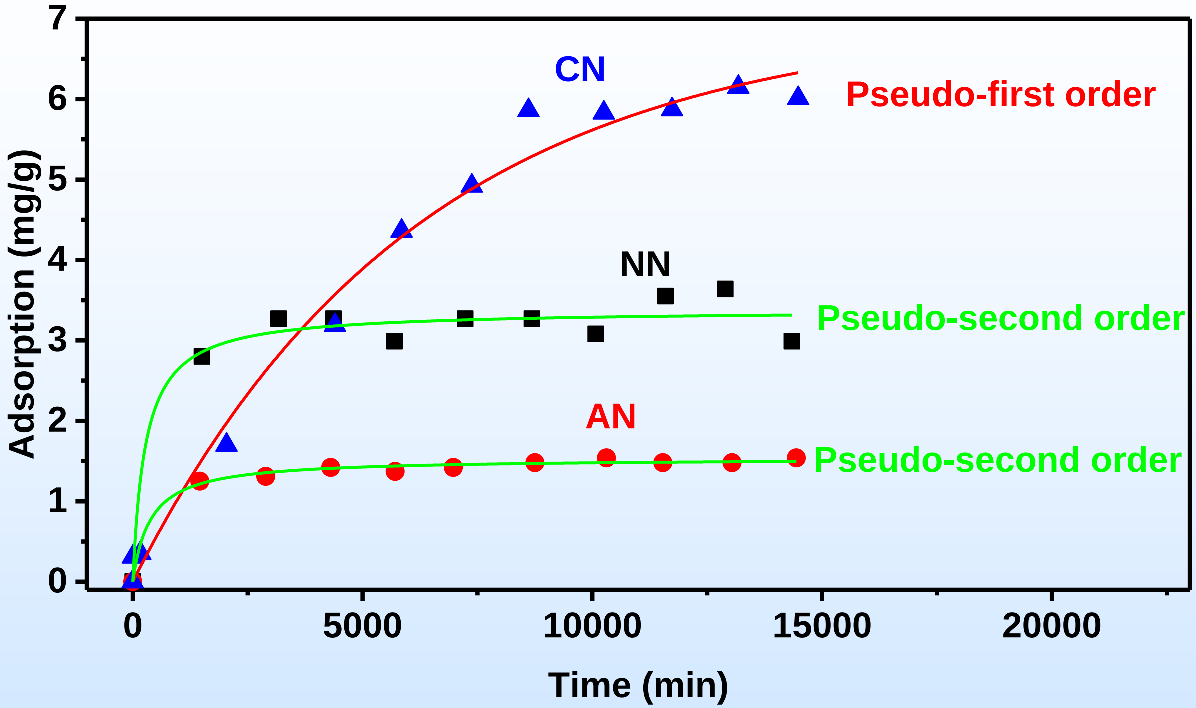
The interparticle reactions increase the viscosity of dispersions with high nanogel concentrations.

Initial Study of Nano-gel Plugging Efficiency to Matrix

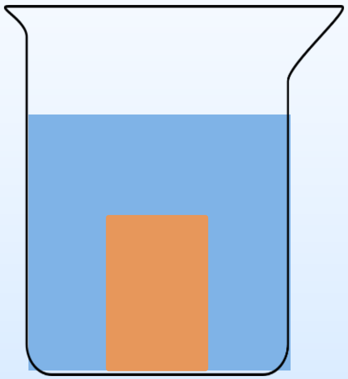


The plugging efficiency of the nano-gel to CO_2 is more than 90%.

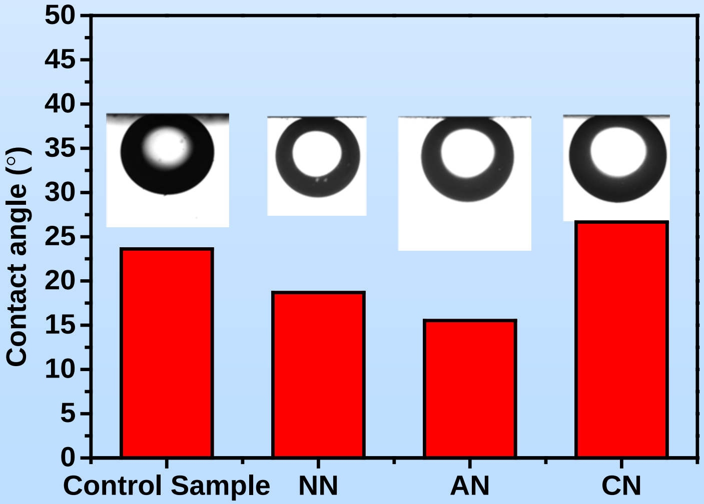
Nanogel for Rock Surface Wettability Alteration



Φ=20.50%
K=87.21mD



Immerse core in nanogel dispersion



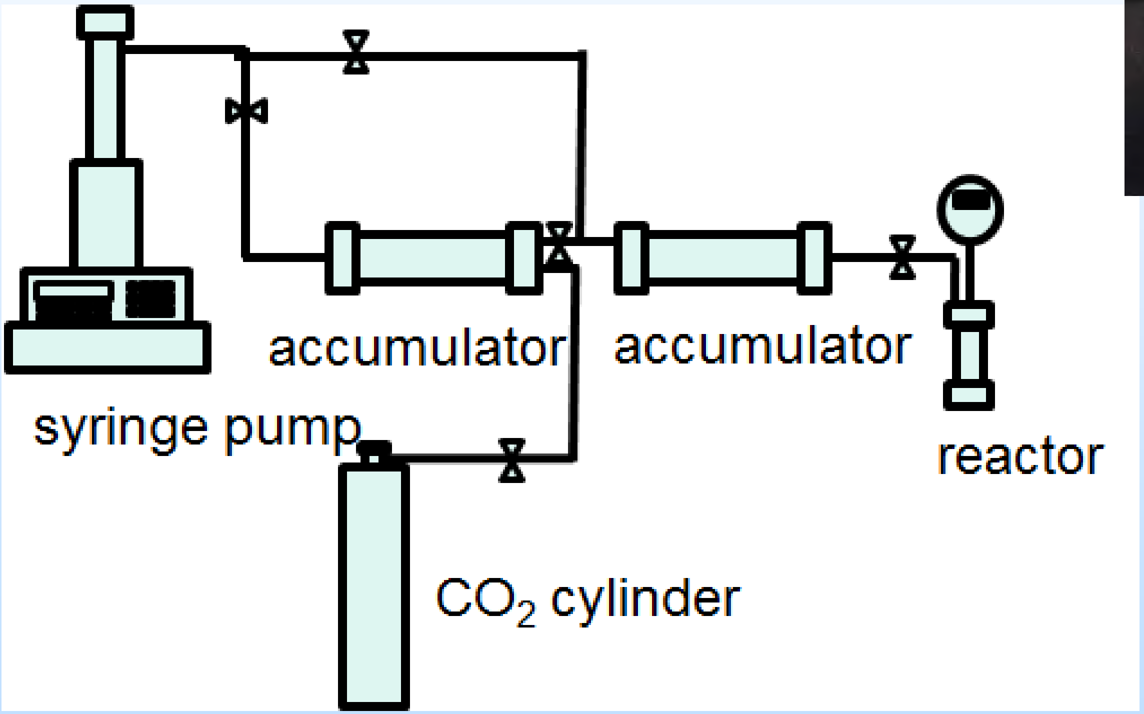
The adsorption of nanogel on rock surface is controlled by electrostatic interactions.

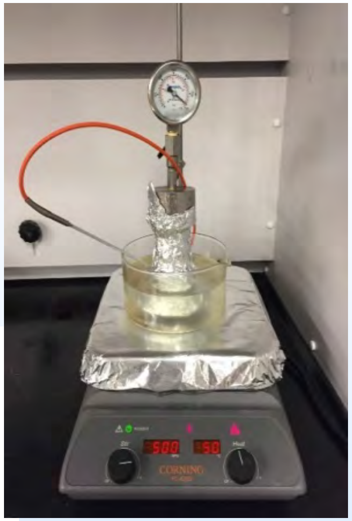
Nanogels with proper hydrophilicities can alter rock surface to more water-wet.

Nano-gel Synthesis and Evaluation

Reactor system

CO_2 delivery pump

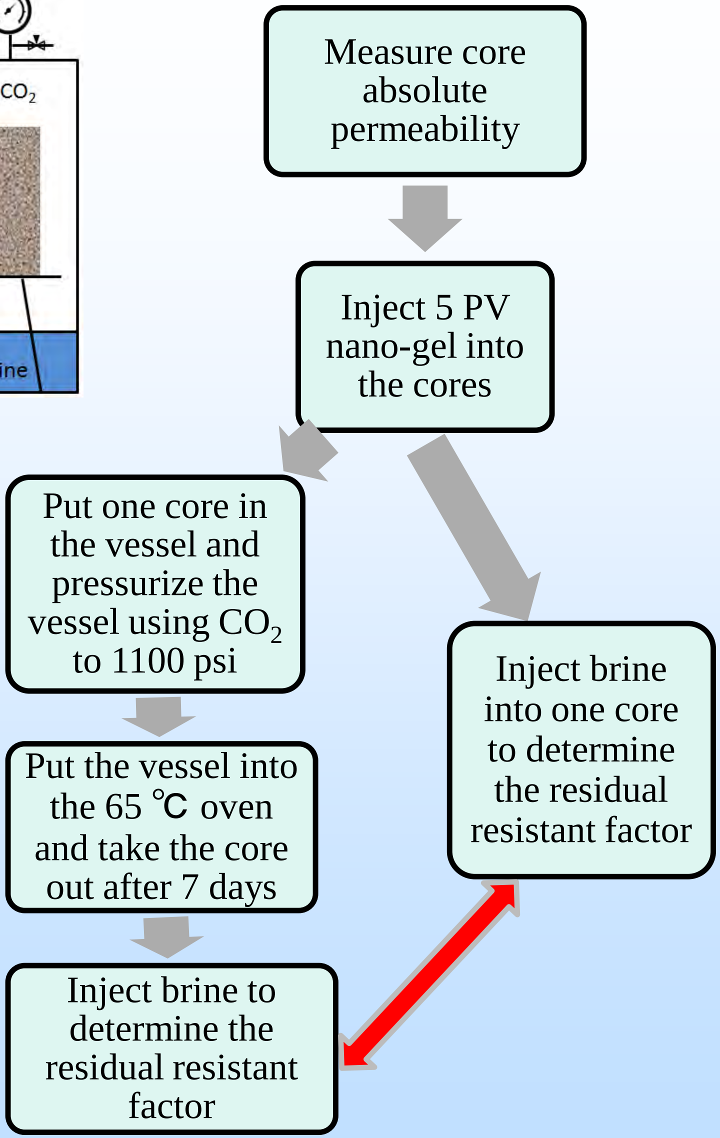


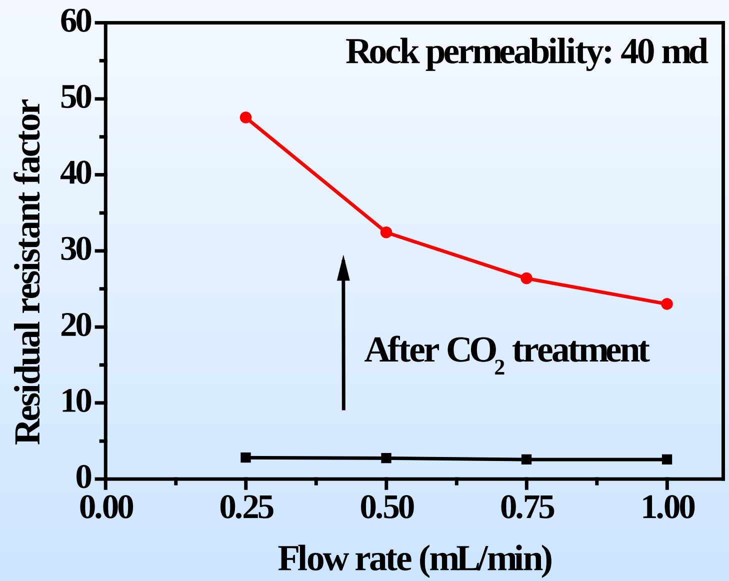


CO_2 reactor

Synthesis under supercritical CO_2

Nano-gel Plugging Efficiency after CO_2 stimulation

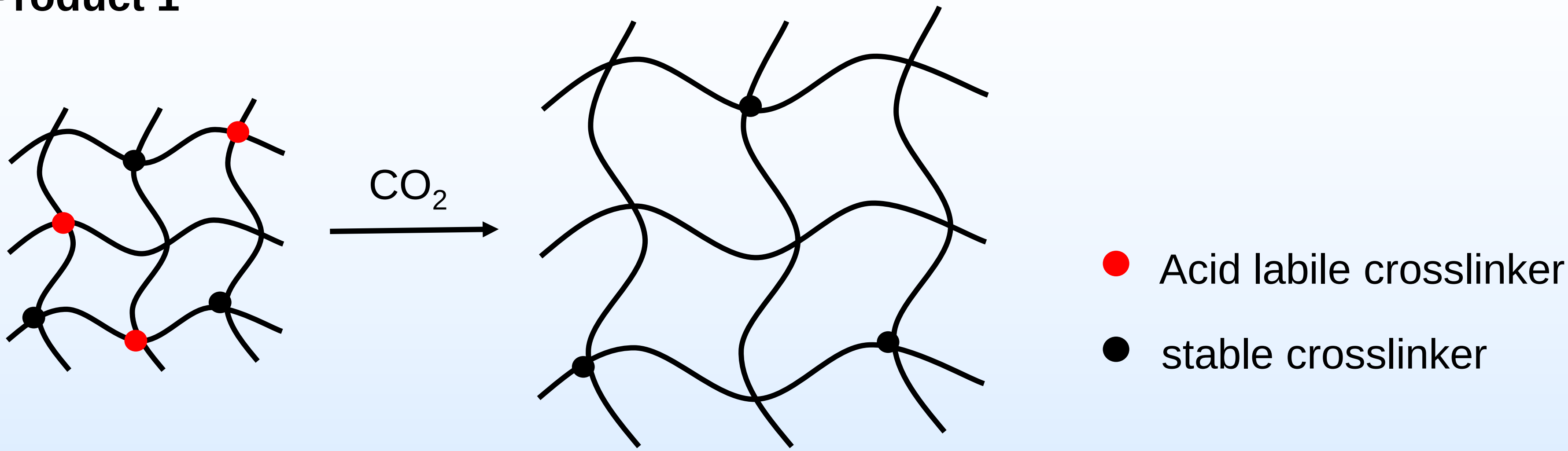




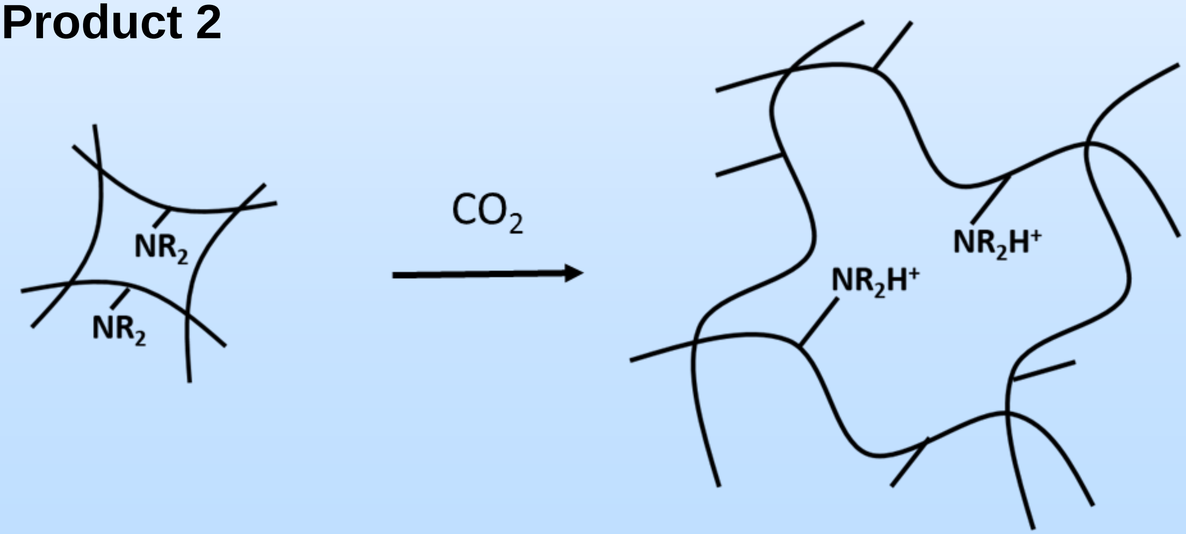
- The plugging efficiency improved after CO_2 stimulation in 40 md cores
- There exists matching ratio between particle size and rock permeability for efficient plugging

Size Increase under CO_2 Condition

Product 1



Product 2



Meet the requirement: development of CO_2 resistant nano-gels