

Development of Swelling-Rate-Controllable Particle Gels to Enhance CO₂ Flooding Sweep and Storage Efficiency

Project No. DE-FE0024558

Baojun Bai

Missouri University of Science and Technology

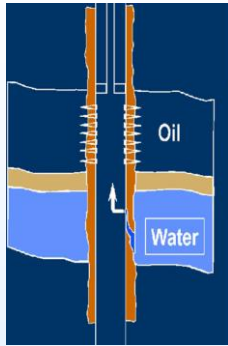
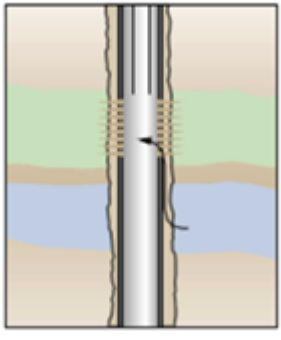
U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Transforming Technology through Integration and Collaboration
August 16-18, 2016

Presentation Outline

- Reservoir Conformance Problems
- Benefit to the Program
- Project Overview: Goals and Objectives
- Accomplishments to Date
 - Swelling Rate Controllable PPGs synthesis
 - Transport behavior of PPG in Porous Media
- Synergy Opportunities
- Summary
- Appendix

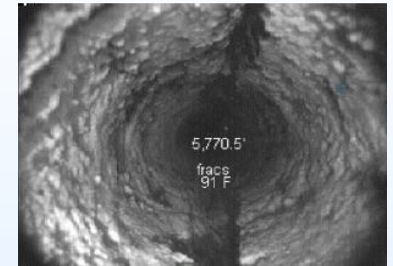
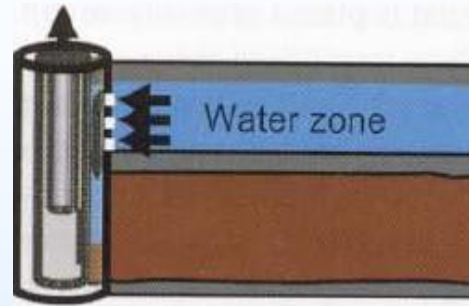
Conformance Problems---Sweep and Storage Efficiency

Wellbore Problems-Integrity



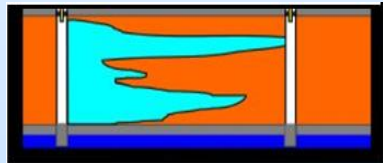
Flow behind casing Casing/tubing leak

Near Wellbore Problems

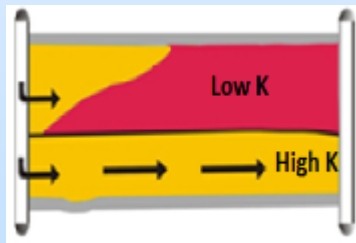


Fractures in AICU 63 Wellbore (Smith, 2006)

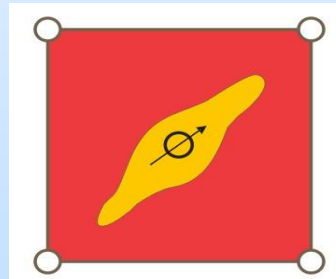
Far Wellbore Problems



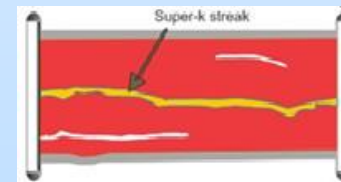
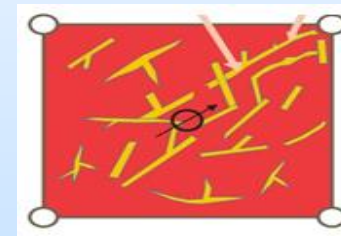
Viscous Fingering and Overriding



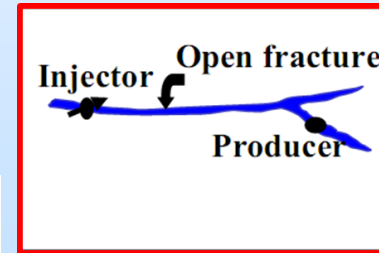
Reservoir strata with crossflow



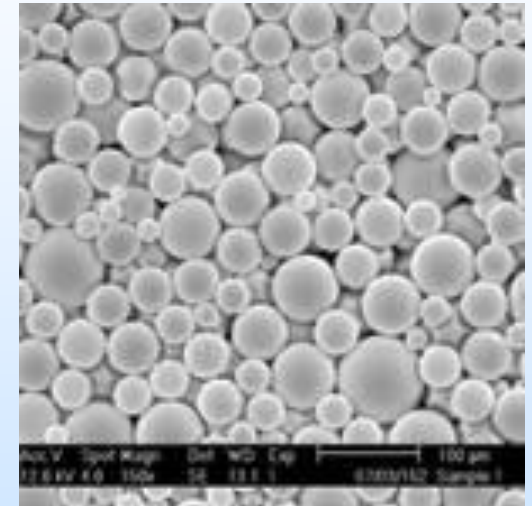
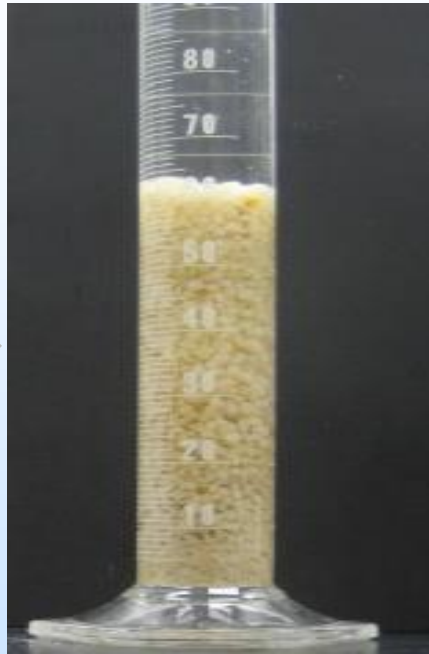
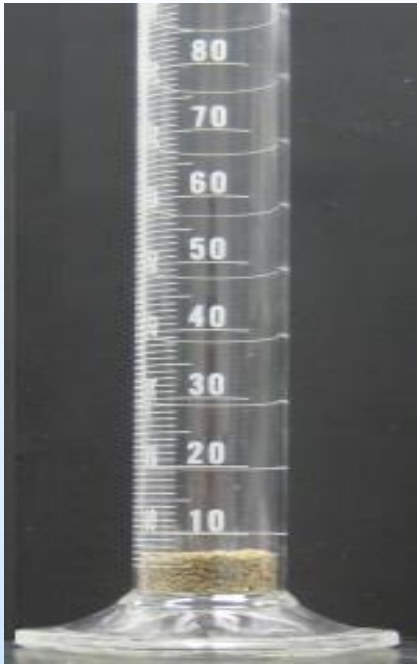
Lateral Permeability streaks



Fracture and Solution channels



Preformed Particle Gel (PPG)



(a) Before swelling

(b) After swelling

Cross-linked polymer powder, Super Absorbent Polymer

Size ranging from nano-meter to millimeter

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 CO₂ 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 CO₂ sweep efficiency and thus improve CO₂ storage in mature oilfields.
- **Project Objectives:**
 - To synthesize a series of environmental-friendly and swelling-rate-controllable particle gels for CO₂ conformance control.
 - To understand the transport behavior and mechanisms of the particle gels in different high permeable features.
 - To understand the plugging mechanisms of particle gels for different types of reservoir conformance problems.

Project Overview:

Goals and Objectives (2)

- Relevance to Program Goals
 - Novel materials will improve CO₂ storage efficiency while ensuring containment effectiveness.
- Success criteria
 - Swelling Rate of particle gels
 - Thermo-stability of particle gels in CO₂
 - Plugging Efficiency of particle gels
 - Successful delivery of particle gels into target locations
 - Costs

Research Schedule

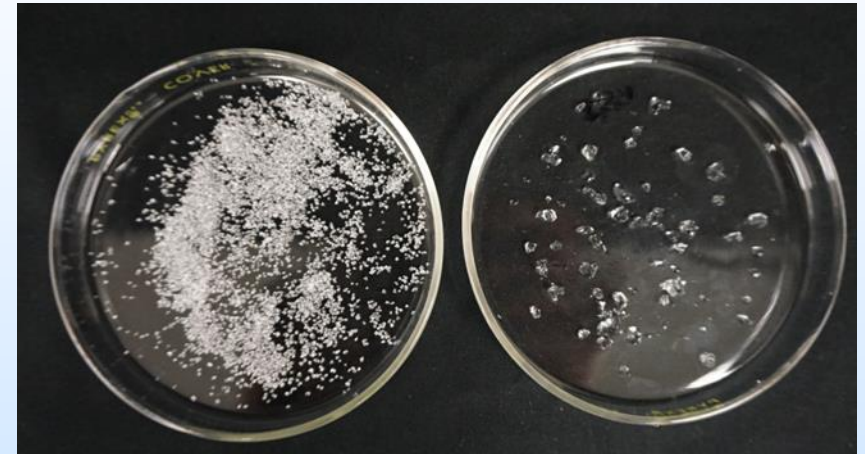
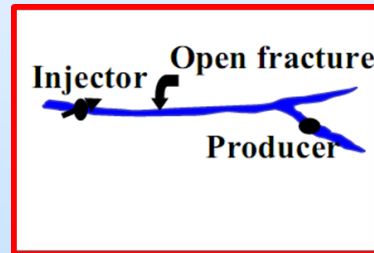
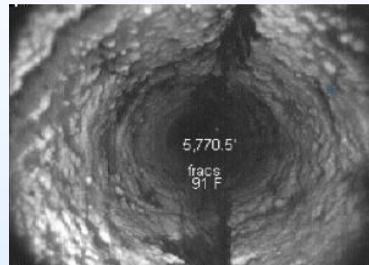
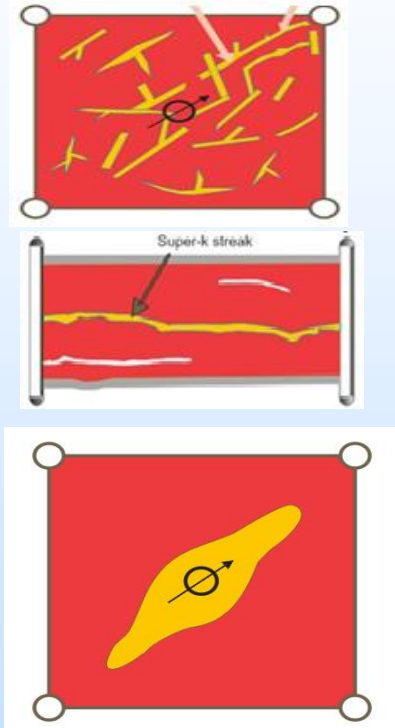
Technical Tasks	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.0 Project management and planning and reporting												
2.0 Synthesis and characterization of particle gels												
2.1 Synthesis and characterization of micro- to millimeter-sized particle gels												
2.2 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 CO₂ 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												
Project Report	QR	QR	QR	QR	QR	QR	QR	QR	QR	QR	QR	FR

Accomplishments to Date

Target Conformance Problems (first year)

Targets: Super-K Channels

Our Solutions

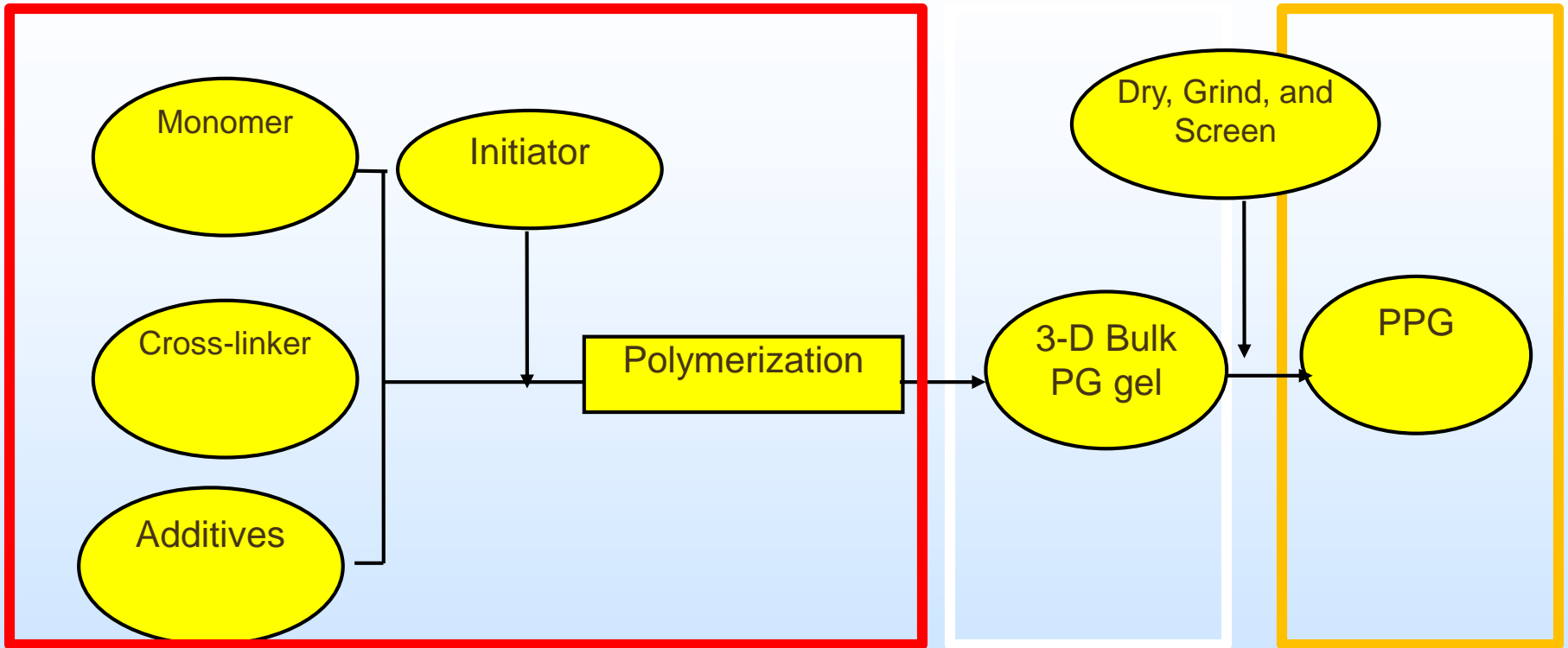


(a) Before swelling (b) After swelling

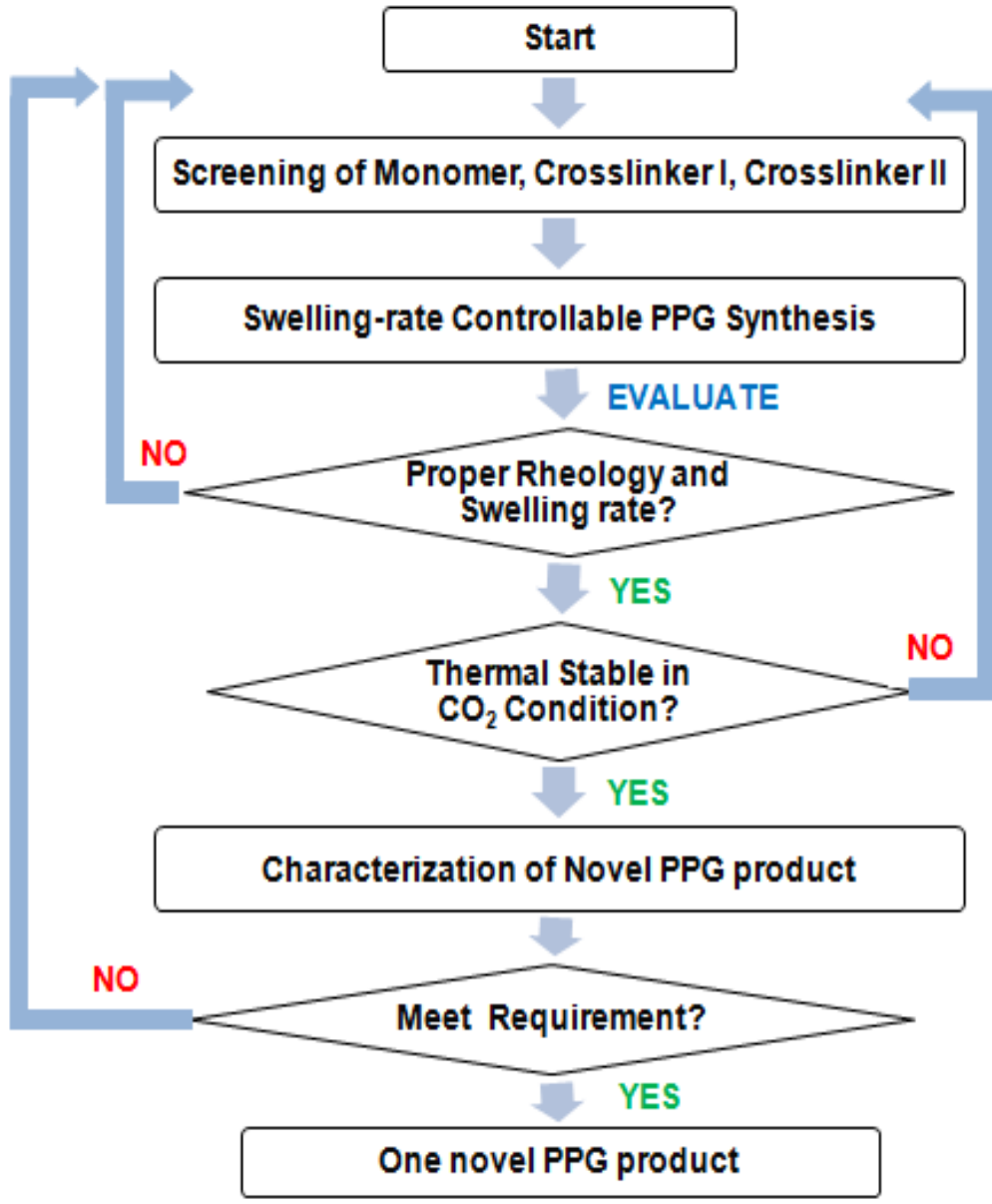
Achievement 1: Synthesized mm-sized swelling delayed CO₂ resistant PPGs (10 um- mm)

Achievement 2: Identified where mm-sized particle can be used and developed criteria for passing through pore throats and open fractures. 9

Achievement 1: Synthesized Millimeter-sized swelling delayed CO₂ resistant PPGs



Particle Gels Formulation and Optimization Procedure



Synthesized Products

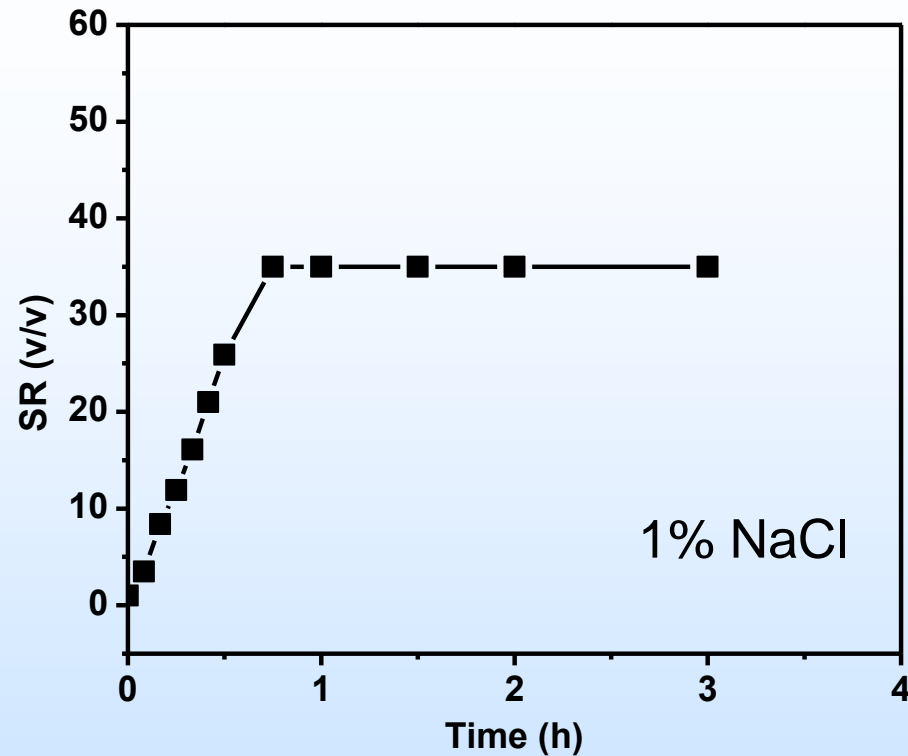
Product 1: Swelling Rate Controlled to hours/Days

Product 2: Swelling Rate Controlled to Months

Product 3: Acid sensitive monomer based PPG

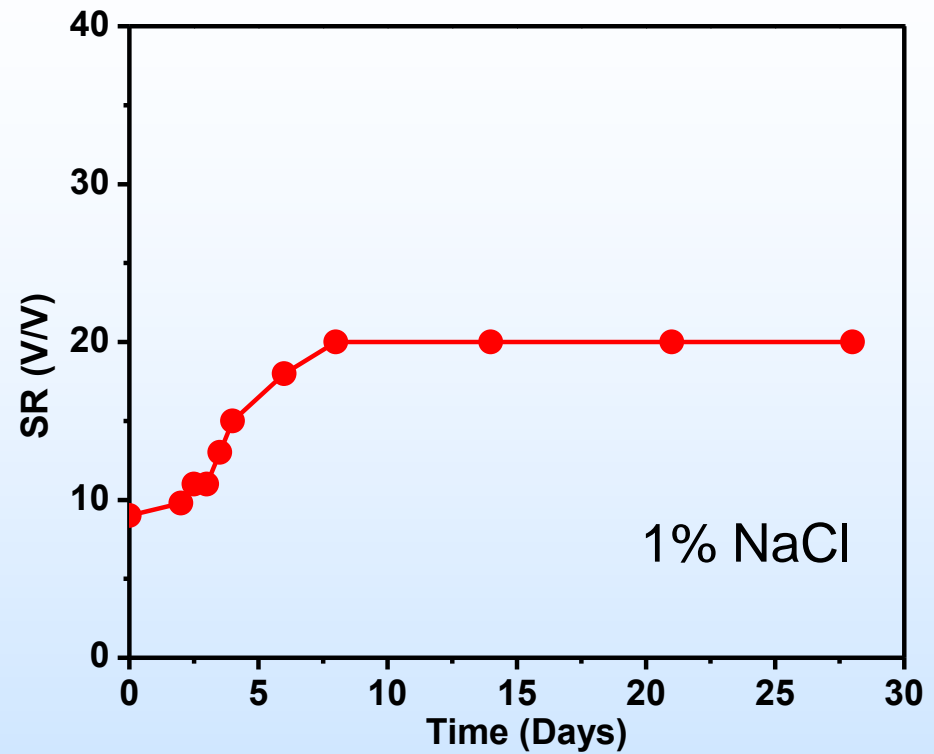
Product 1: Swelling Rate Controlled to Days

Traditional PPGs



Fast swelling within one hour

New monomer addition to traditional PPGs



Delayed swelling to days

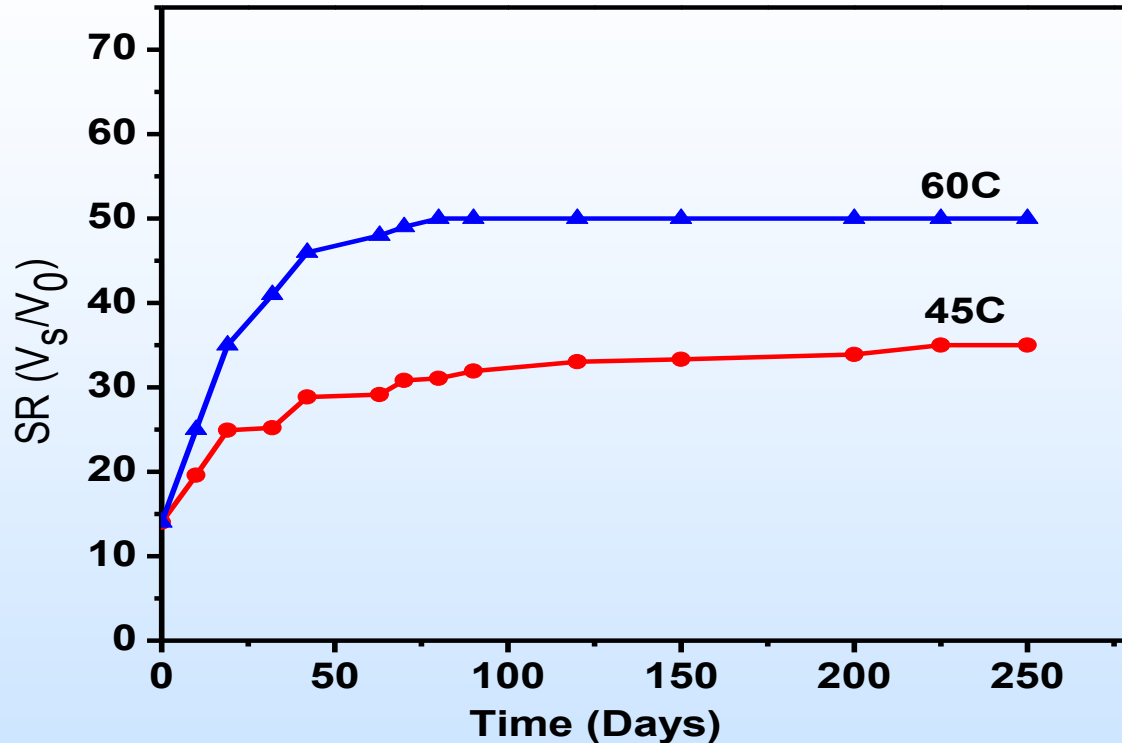
The new product overcome some problems of traditional PPGs

- 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

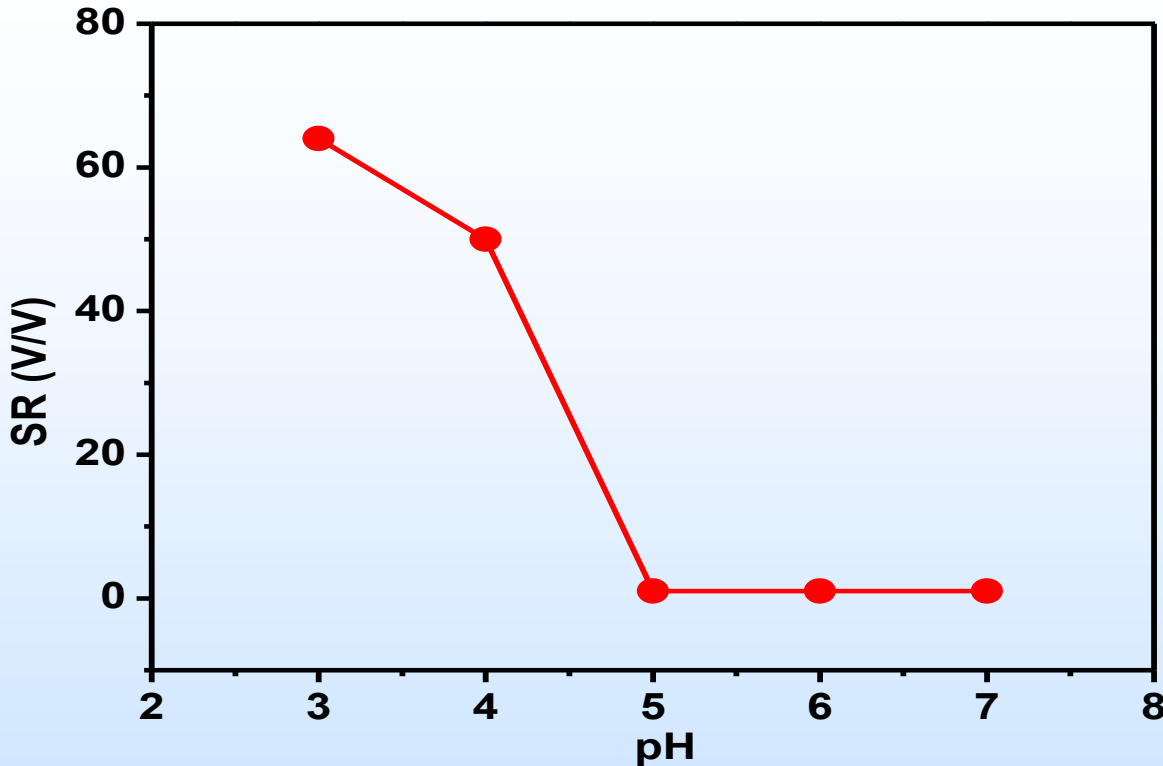


Swelling kinetics and Temperature effect (1% NaCl)

Product 2 is good for in-depth fluid diversion

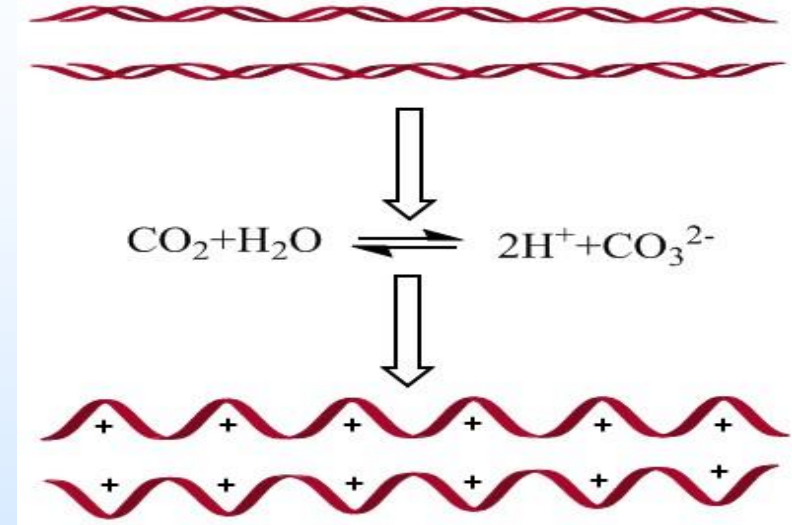
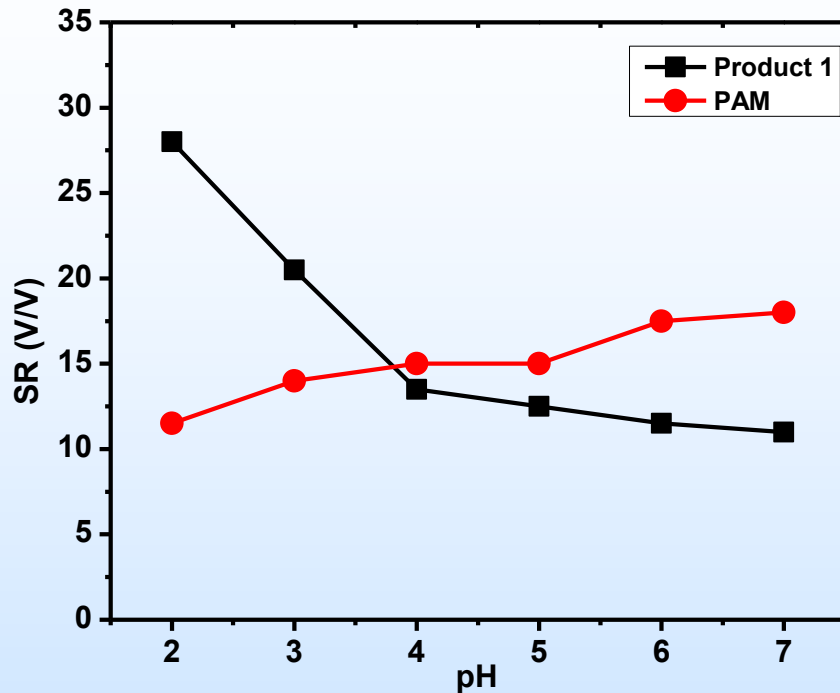
Meet the requirement: development of swelling rate controllable PPG

Product 3: Acid sensitive monomer based PPG



- Controlled swelling, excellent for CO₂ conformance control;
- Increased SR under CO₂ conditions;
- Highly stable; cost-effective to generate nano to mm-sized particles

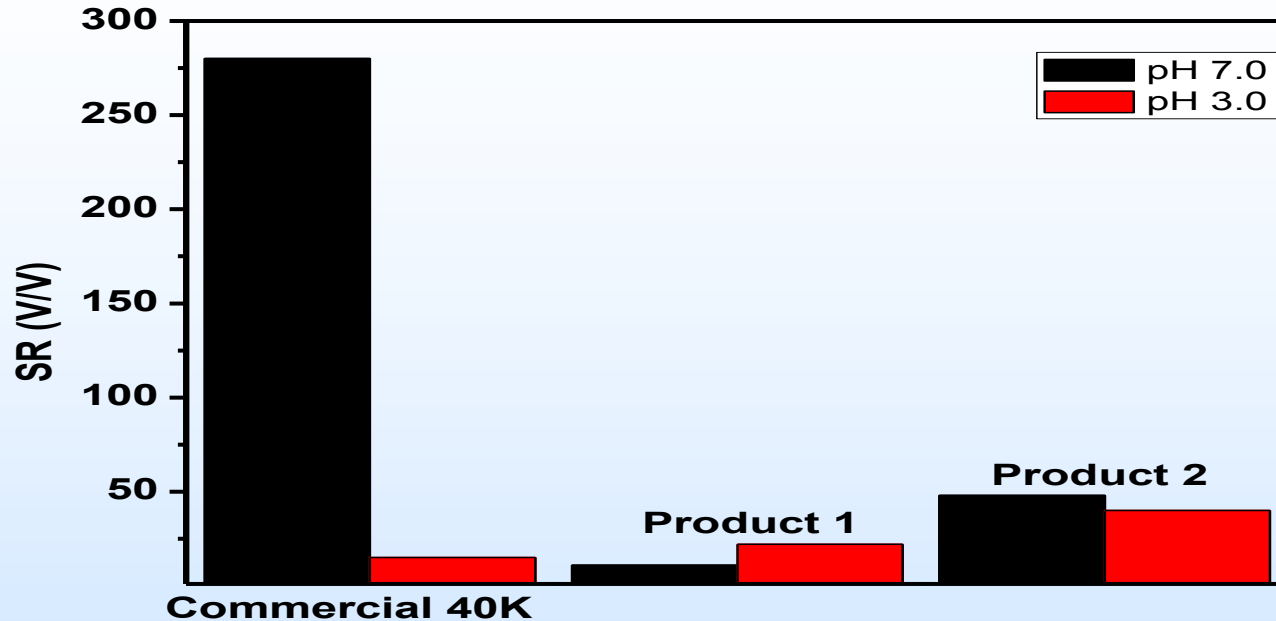
Product 1 Size Increases under CO₂ Condition



- Lower SR at pH of 7.0
- Higher SR under acidic condition

Meet the requirement: development of CO₂ resistant PPG

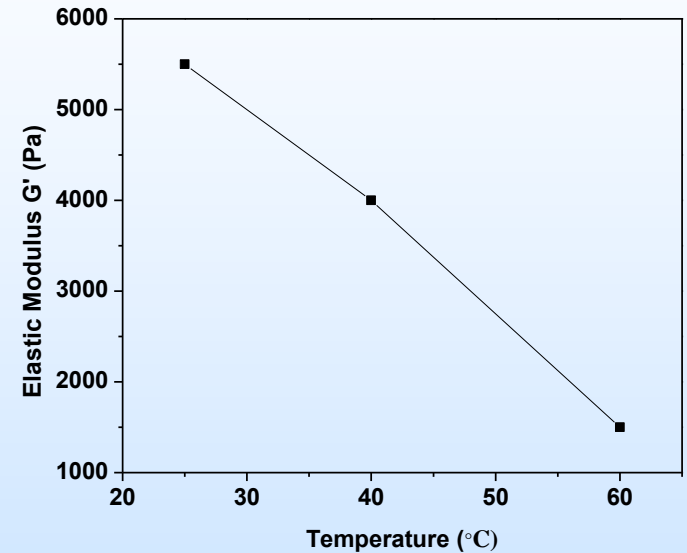
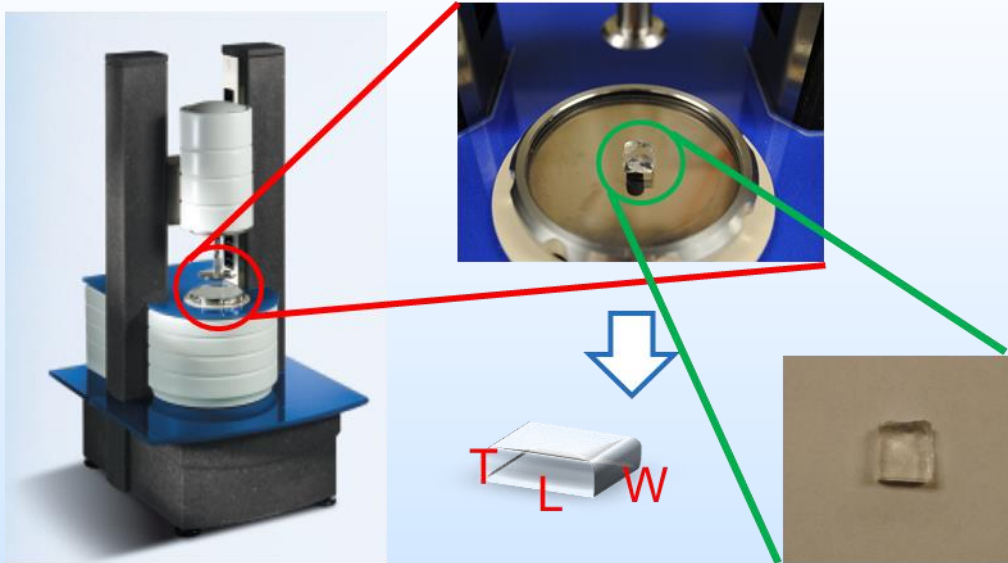
CO₂ Resistant Product 1 and Product 2



- Commercial PPG SR significantly decreased in acid condition.
- Our product 1 SR increased to ~ **200%**;
- Product 2 maintained its SR in neutral conditions ~ **85%**

Meet the requirement: development of CO₂ resistant PPG

Gel Strength Evaluation Methods and Examples

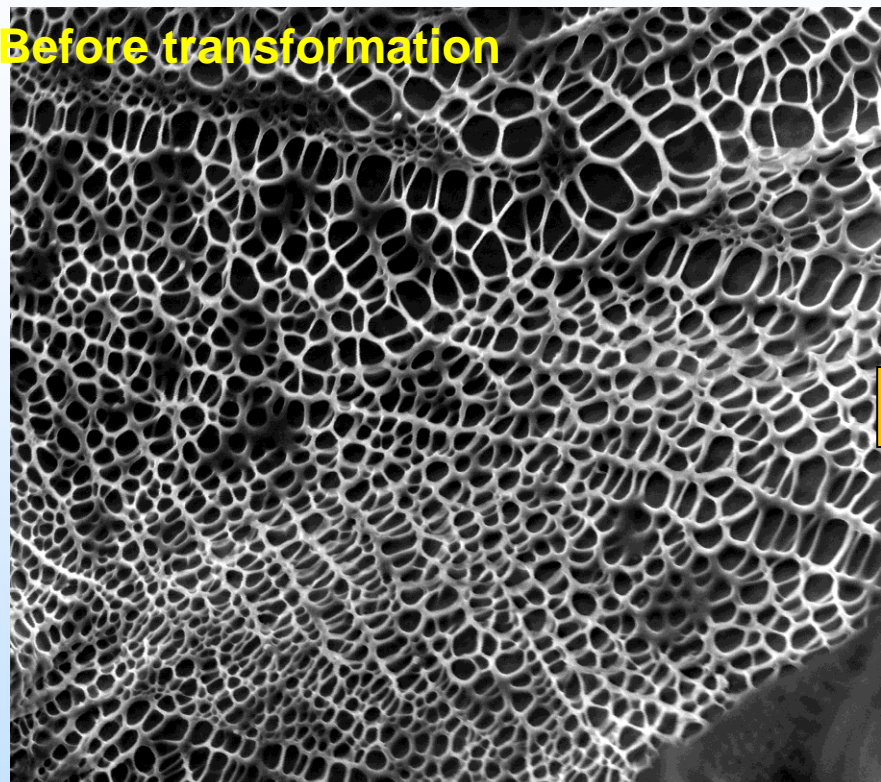


Gel strength after swelling is high enough to meet plugging requirements

Particle Property Characterization after Transformation

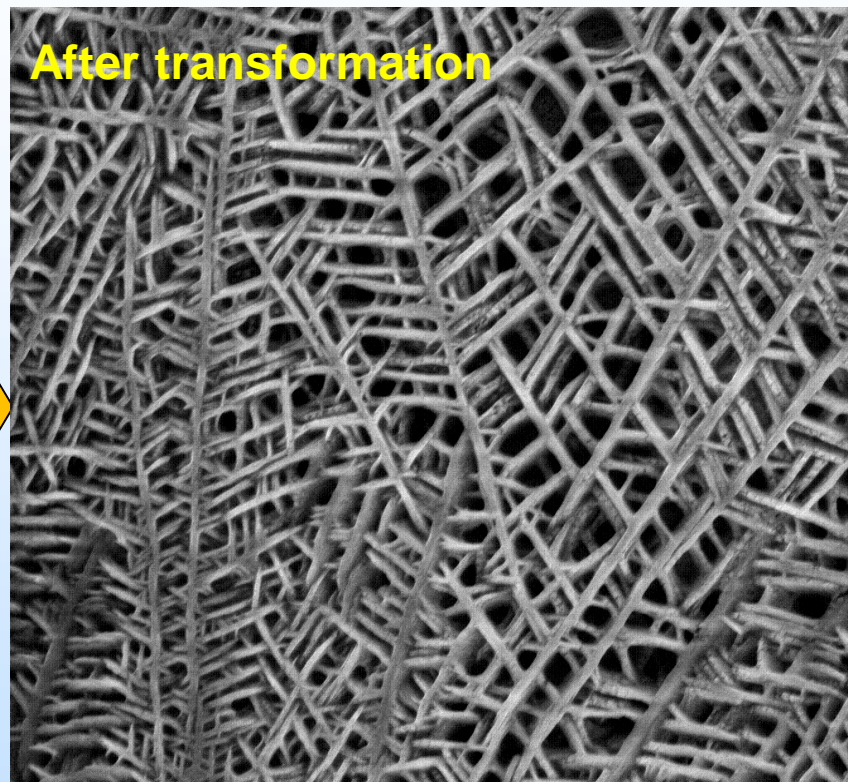
Particle Gel Structure Change by ESEM

Before transformation



HV	mag	HFW	WD	pressure	temp	humidity	10 μm
7.00 kV	5 000 x	59.7 μm	8.1 mm	2.00 Torr	18.5 °C	12.5 %	DCPG50-10000 swollen-vacu

After transformation



HV	mag	HFW	WD	pressure	temp	humidity	10 μm
7.00 kV	5 000 x	59.7 μm	8.0 mm	2.50 Torr	20.0 °C	14.3 %	100222002

(a) particle gel honeycomb network structure by removing surface water before transformation.

(b) Very Loose network structure after Type I particle gels' transformation.

Designed Visualized Cells using for Pressure Effect and Thermo-stability Tests



Experimental description

- Testing pressure: 900, 1200, 1500 psi
- Temperature: 60 °C
- PPG prepared in 1% NaCl
- Testing time: 48 hours

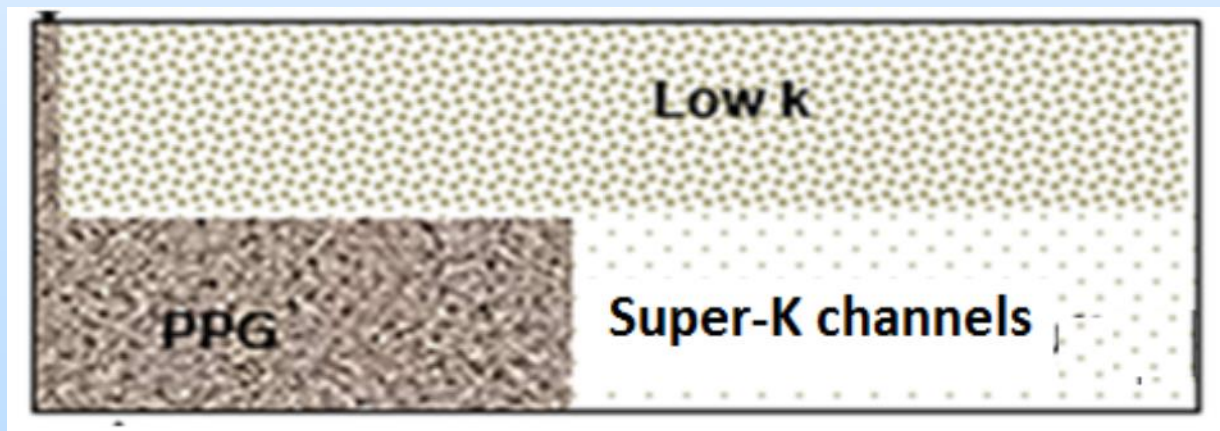
Results

Vessel pressure (psi)	Dehydration ratio (%)	
	Traditional Gel	New PPG 3
900	32.98	0
1200	34.00	
1500	42.78	

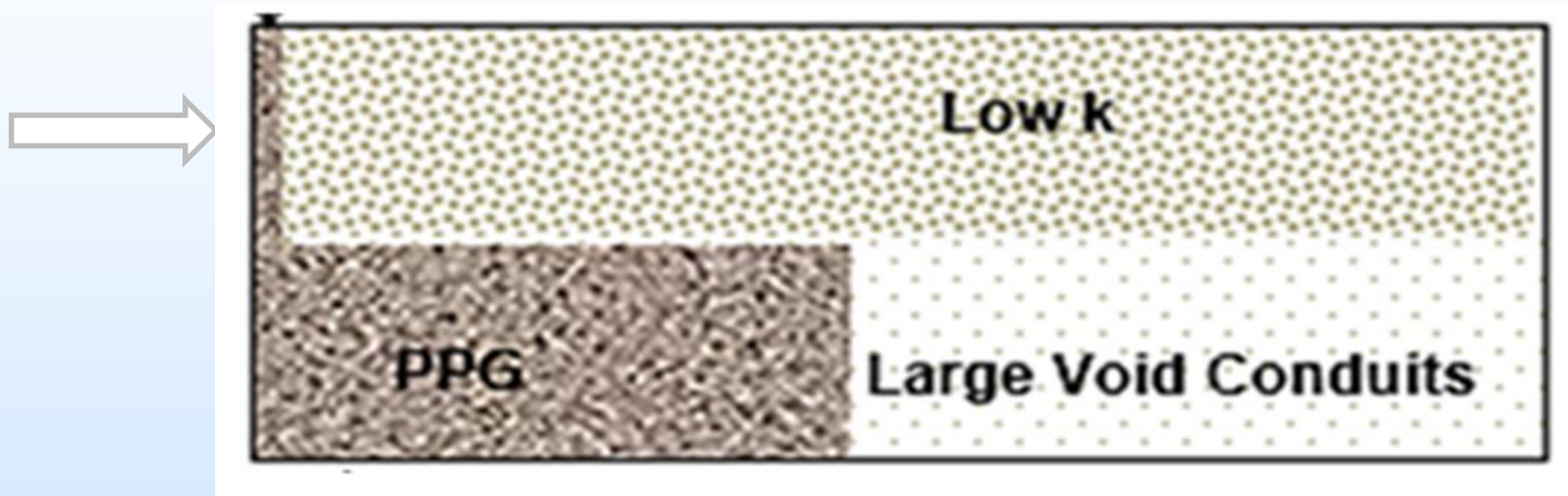
- Novel PPGs had good thermal stability under CO₂ conditions

Accomplishments to Date

- **Achievement 2:** Identified where mm-sized particle can be used and developed criteria for passing through pore throats and open fractures
- ↓
- Mm-size is a selective penetration material that can only transport through fractures and fracture like-conduits and can effectively minimize low permeability damage

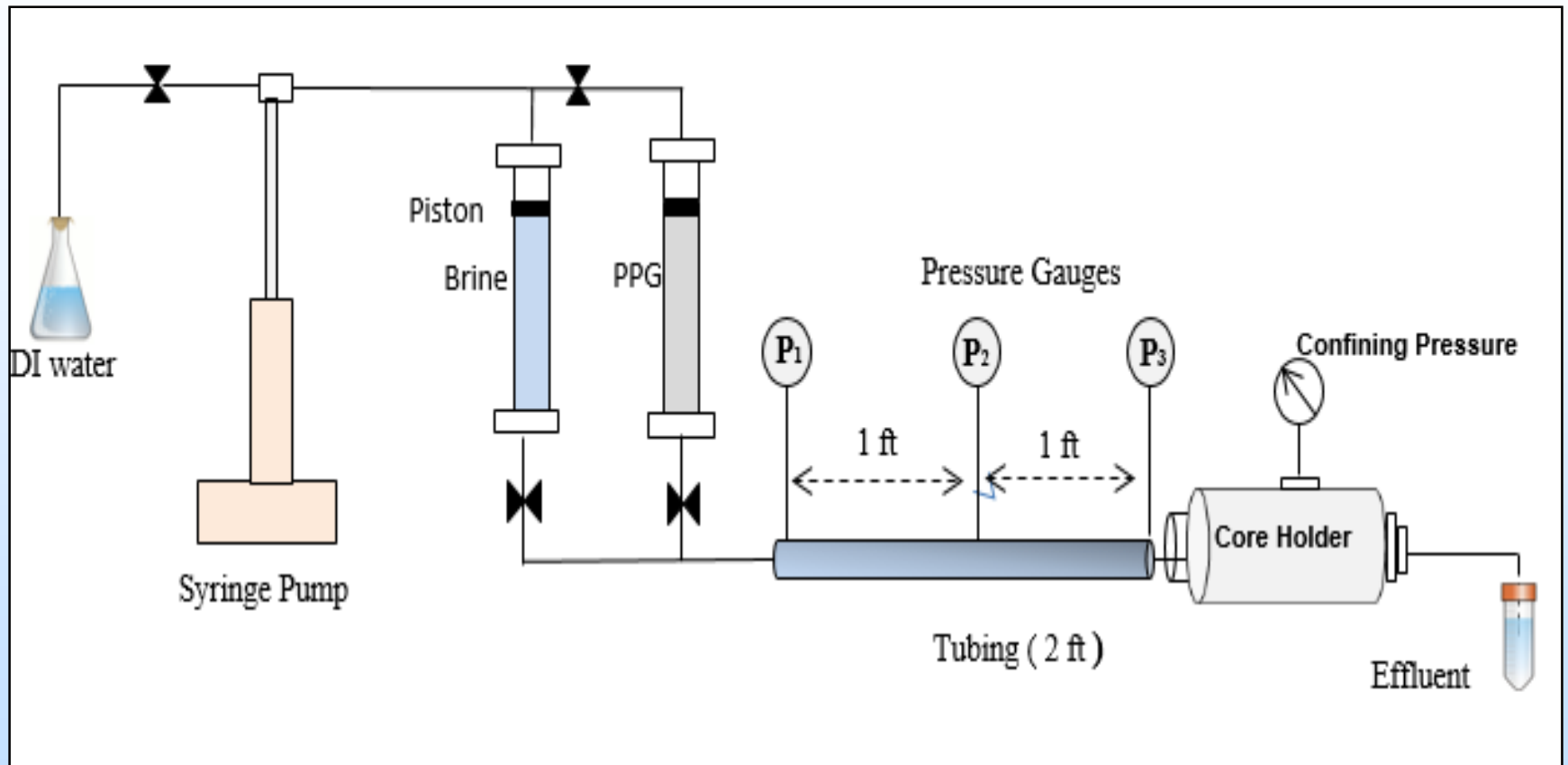


PPGs Effect on Un-swept Zones

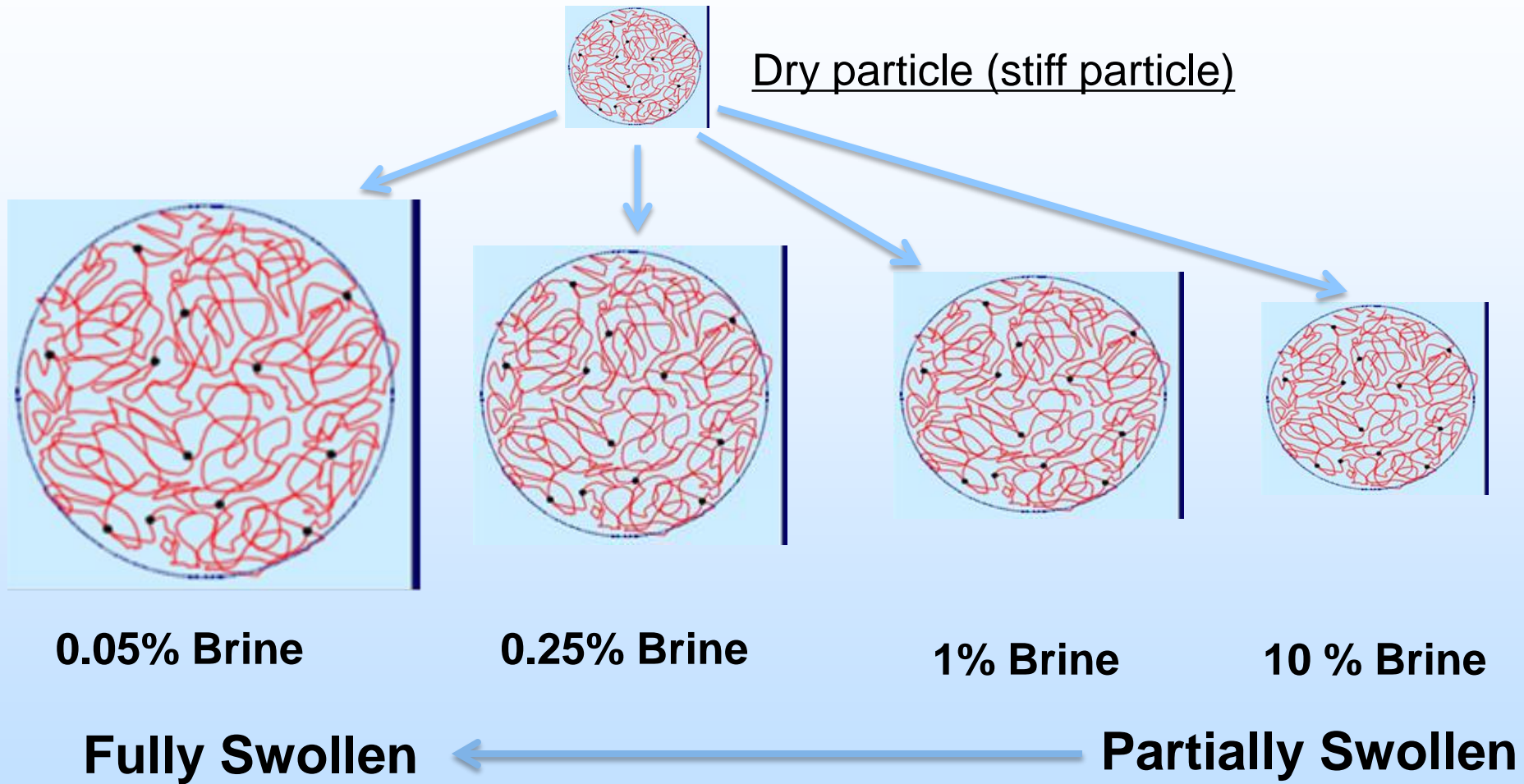


Experimental purpose: Understand whether mm-sized PPGs can propagate through milli-darcy rocks and find ways to reduce PPG damage on un-swept oil-rich zones

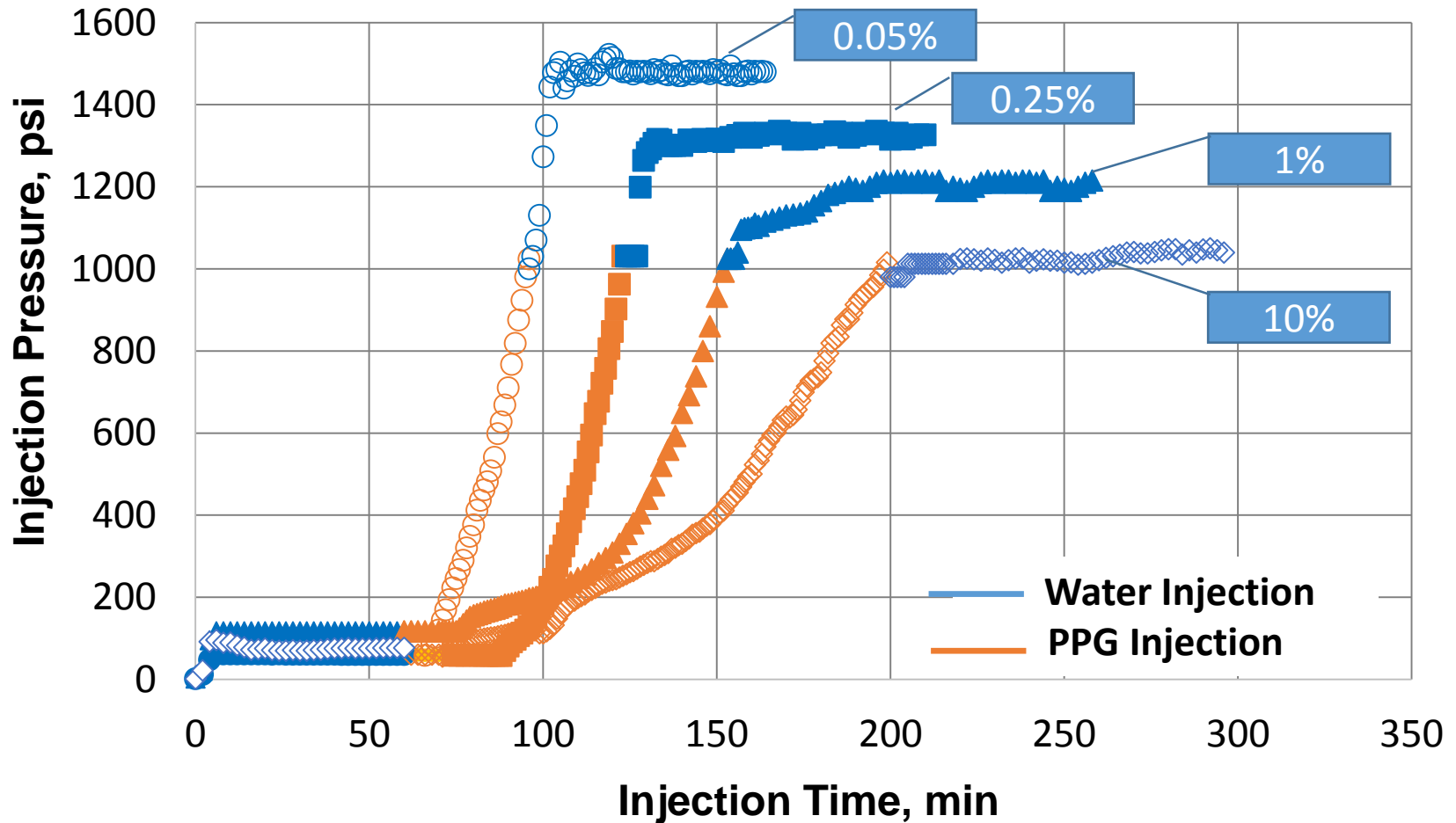
Experiment Set-up



PPGs used for experiments



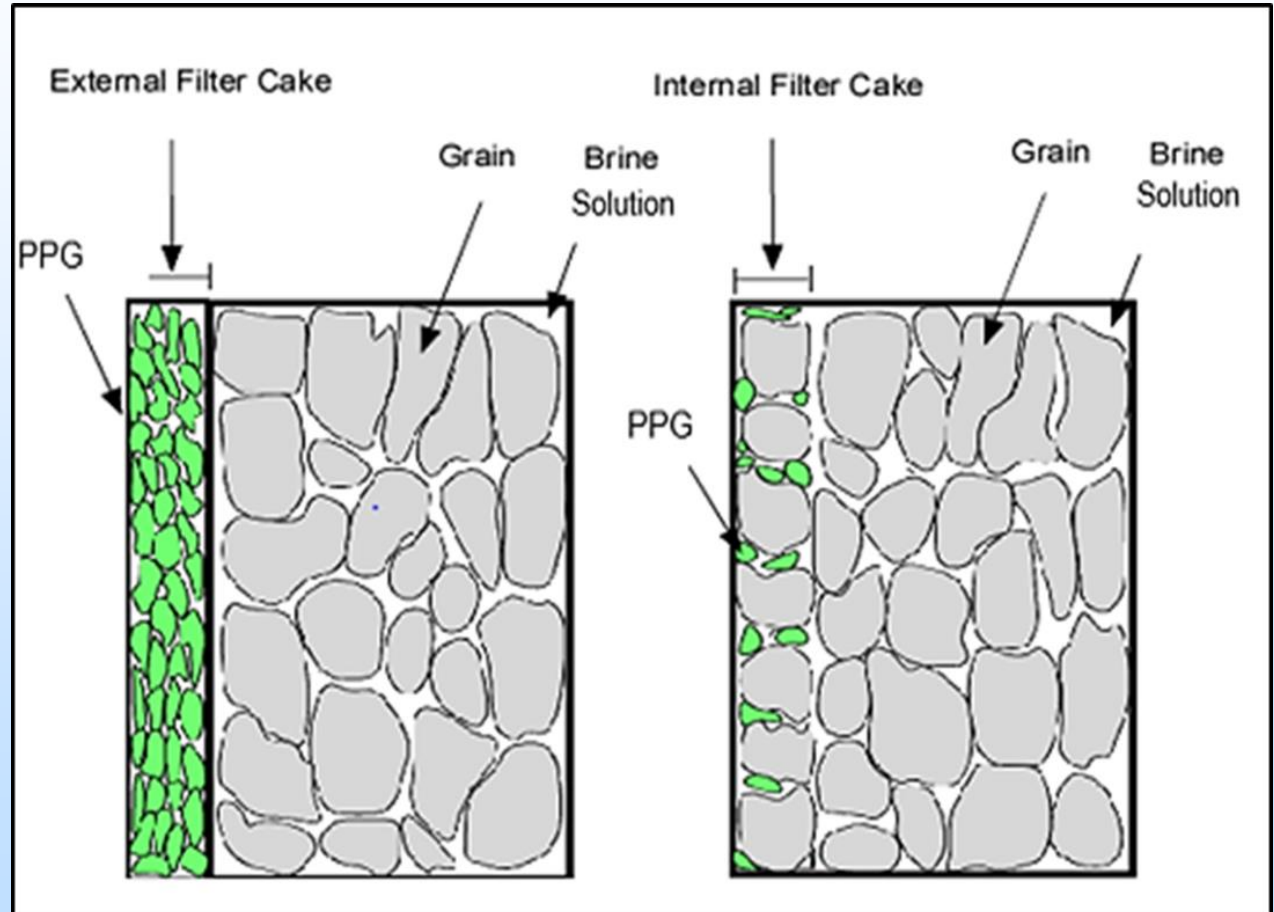
Effect of NaCl concentration (PPG strength)



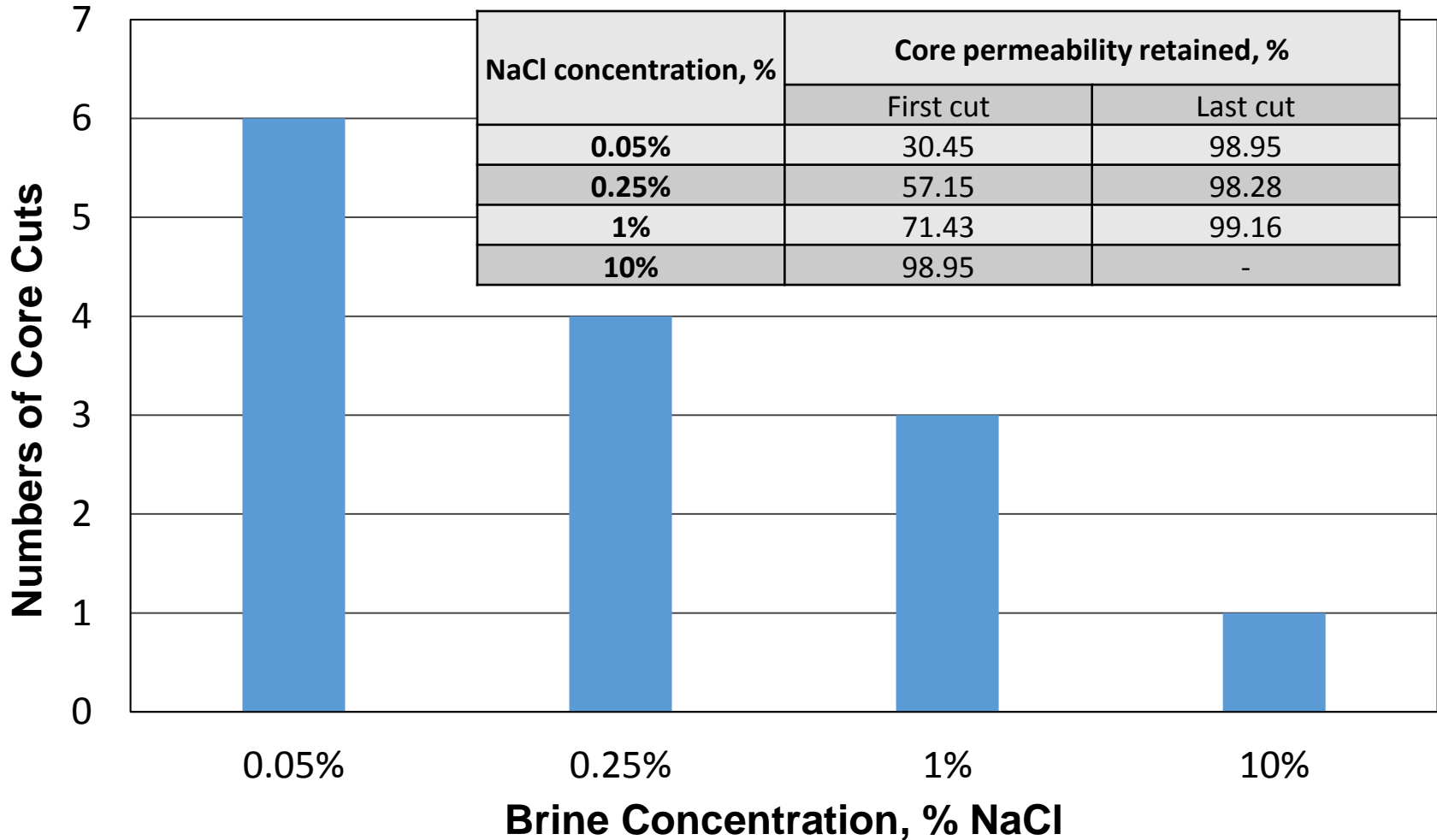
NaCl Conc.: 0.05%, 0.25%, 1%, 10%
PPG size: 20-30 mesh
Injection flow rate: 3 ml/min

PPG Conc.---5000 pm
Core permeability: < 10 md
PPG placement pressure: 1000 psi

How deep will PPG transport into the rock?



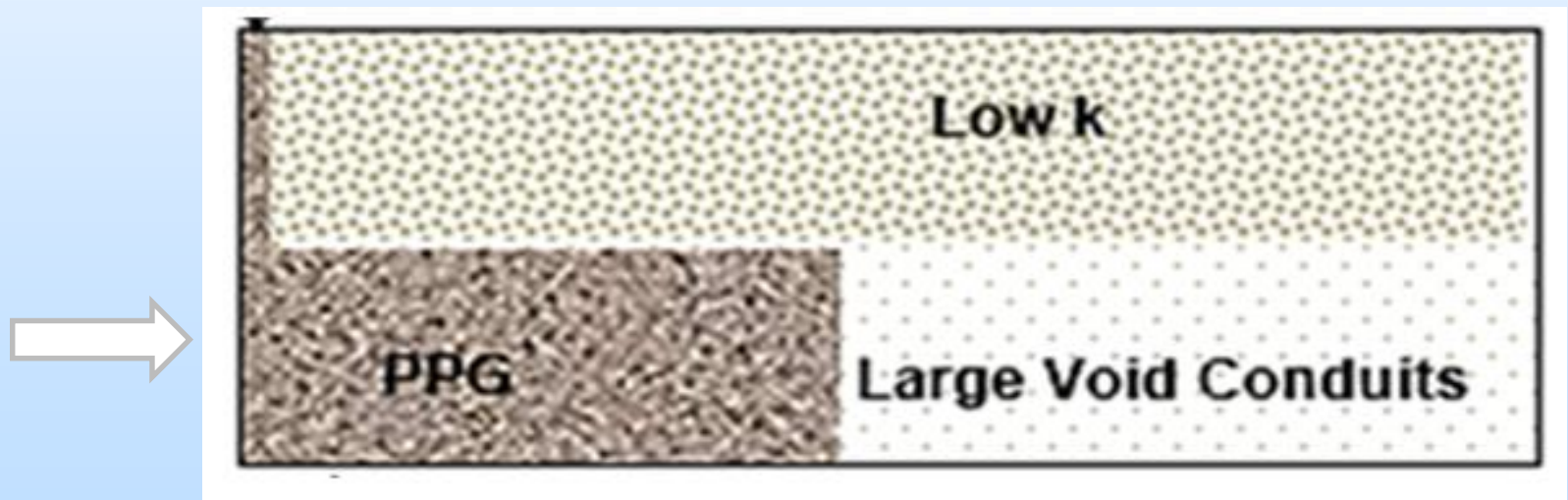
Gel strength (Brine concentration) effect on PPG penetration depth



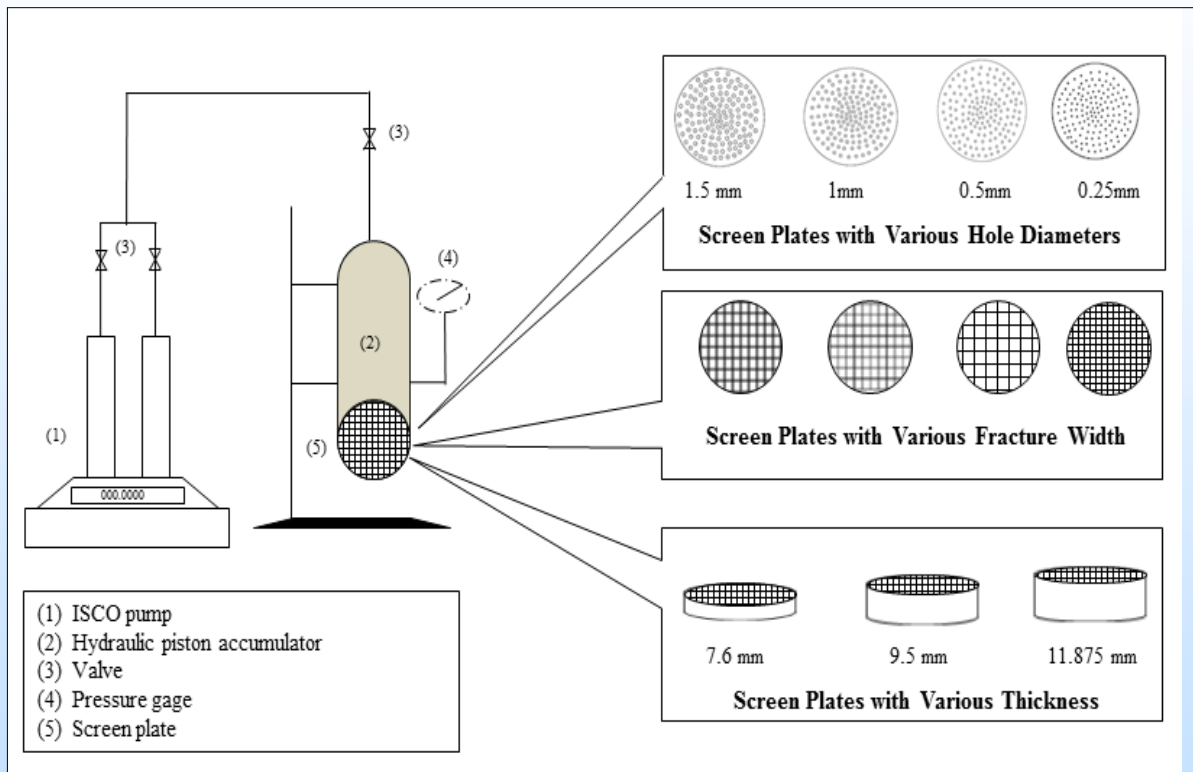
Each cut is 3 mm

PPG Extrusion Through Fracture or Fracture-like Channels

Conduits are large openings that naturally exist or are aggravated by mineral dissolution, sand production or a high injection pressure during a flooding process.

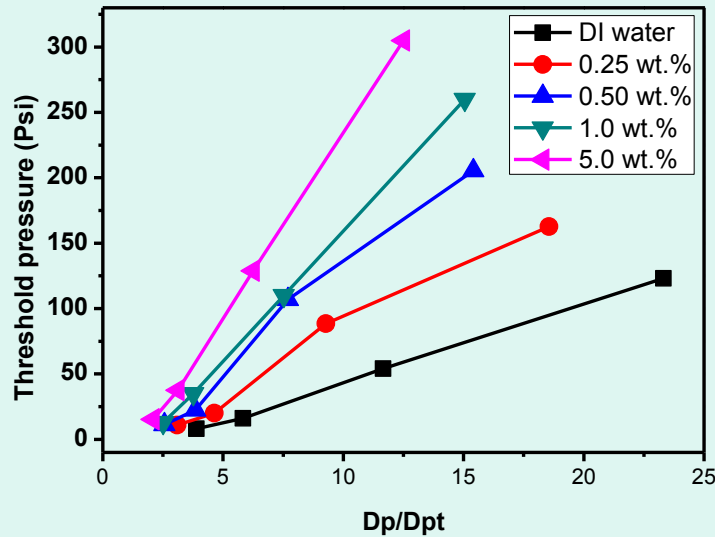


Schematics of Apparatus for Transport Behavior Evaluation

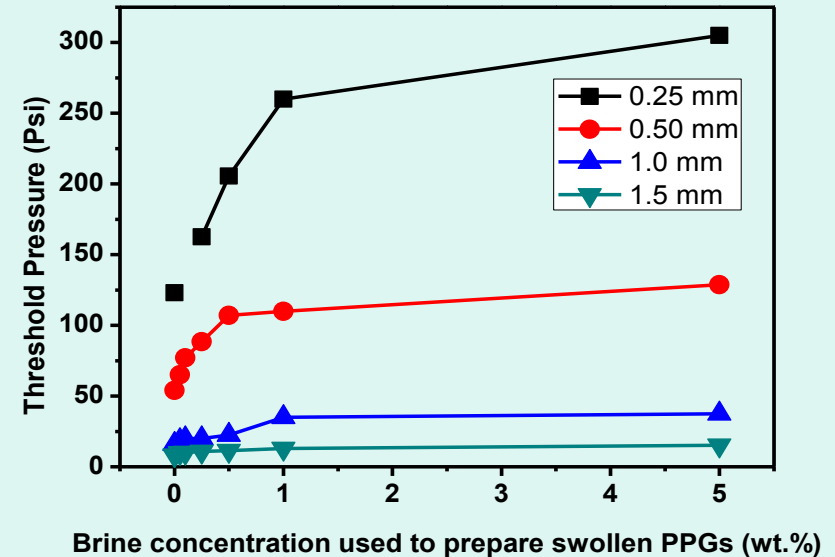


Schematics of apparatus for transport behavior evaluation

Screen Model with Various Hole Diameters

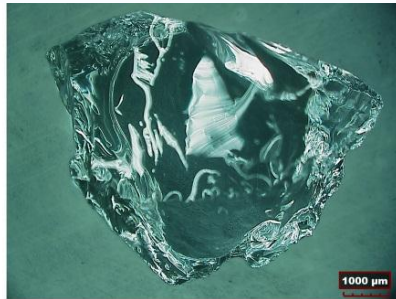


Effect of the ratio of swollen PPG size to hole size on threshold pressure

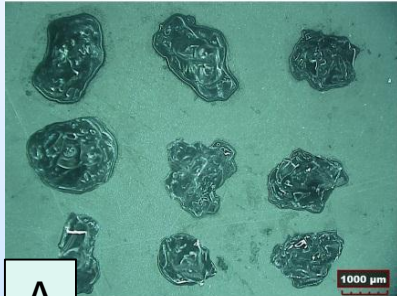


Effect of swelling degree on the threshold pressure of PPGs using four different screen plate hole sizes

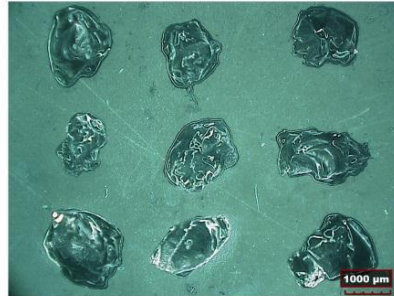
Screen Model with Various Fracture width



(a)



(b)



(c)

A

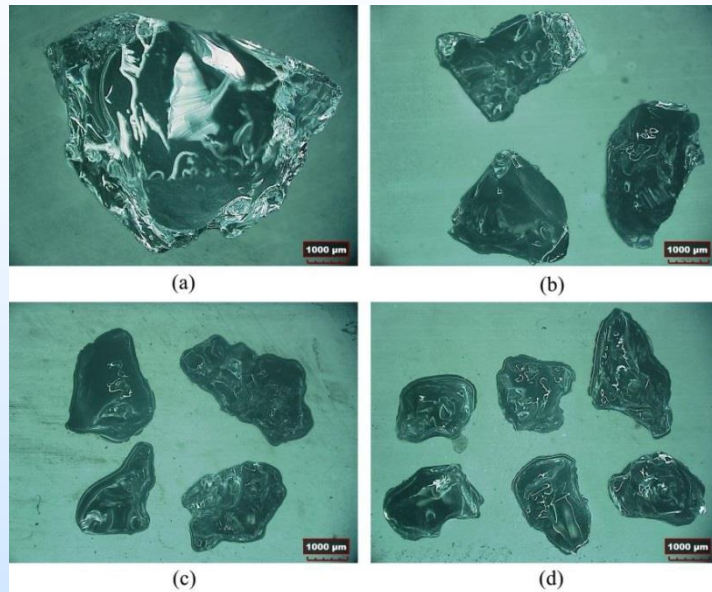
A. Comparison between initial and extruded DI water PPG. (a) Initial (b) extruded through 1.0 mm hole screen plate (c) extruded through 1.5 mm hole screen plate

B. Extrusion pattern for particle gel transport through open hole plates

	Initial Equivalent Diameter (mm)	Extruded through hole size (mm)	Equivalent Diameter After Extrusion (mm)	Particle Evaluation Index	Extrusion Pattern
DI water PPG	5.828	1.5	1.808	0.310	Broken and Pass
		1.0	1.663	0.284	Broken and Pass
		0.5	-	-	Broken, Dehydration and Pass
		0.25	-	-	Broken, Dehydration and Pass
0.25 wt. % NaCl PPG	4.640	1.5	3.362	0.725	Broken and Pass
		1.0	1.847	0.398	Broken and Pass
		0.5	-	-	Broken, Dehydration and Pass
		0.25	-	-	Broken, Dehydration and Pass
1.0 wt. % NaCl PPG	3.764	1.5	3.002	0.798	Broken and Pass
		1.0	1.939	0.515	Broken and Pass
		0.5	-	-	Broken, Dehydration and Pass
		0.25	-	-	Broken, Dehydration and Pass
5.0 wt. % NaCl PPG	3.126	1.5	3.093	0.989	Pass
		1.0	2.047	0.655	Broken and Pass
		0.5	-	-	Broken, Dehydration and Pass
		0.25	-	-	Broken, Dehydration and Pass

B

Fracture Models with Various Fracture Width



	Initial Equivalent Diameter (mm)	Extruded through Fracture size (mm)	Equivalent Diameter After Extrusion (mm)	Particle Evaluation Index	Extrusion Pattern
DI water PPG	5.828	0.25	1.917	0.329	Broken and Pass
		0.50	2.534	0.661	Broken and Pass
		1.0	4.294	0.822	Broken and Pass
0.25 wt. % NaCl PPG	4.640	0.25	3.069	0.661	Broken and Pass
		0.50	3.099	0.668	Broken and Pass
		1.0	3.934	0.848	Broken and Pass
1.0 wt. % NaCl PPG	3.764	0.25	3.093	0.822	Broken and Pass
		0.50	3.62	0.962	Pass
		1.0	3.731	0.991	Pass
5.0 wt.% NaCl PPG	3.126	0.25	2.732	0.874	Broken and Pass
		0.50	3.108	0.994	Pass
		1.0	3.118	0.997	Pass

A. Comparison between initial and extruded DI water PPG. (a) Initial (b) extruded through 1.0 mm fracture (c) extruded through 0.5 mm fracture and (d) 0.25 mm fracture

Extrusion pattern for particle gel transport through open fracture plate model

Synergy Opportunities

- **Partnership Projects**

- Novel monitoring techniques could be used to better identify conformance problems, which is necessary to optimize a conformance control design.
- The success of the project will provide a cost-effective method to solve early breakthrough or excess CO₂ production problems for those CO₂ storage demonstration projects and their deployment.

- **Leakage Mitigation projects**

- Combination will solve both reservoir and wellbore problems

- **EOR Projects---**Conformance control is always necessary, especially for those in mature oilfields³²

Summary

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

- Swelling controllable PPGs were synthesized and swelling rate can be controlled from hours to months.
- Our PPGs showed excellent CO₂ resistance compared to commercial PPG.
- The criteria of the particle gels passing through pore throats and open fractures were developed as a function of particle size to hole size, gel strength, swelling ratio and plate thickness.

Next Year Plan---Solve matrix conformance problems

- Nano-gel synthesis under CO₂ conditions.
- CO₂ Flooding Tests based on our PPGs

Acknowledgement

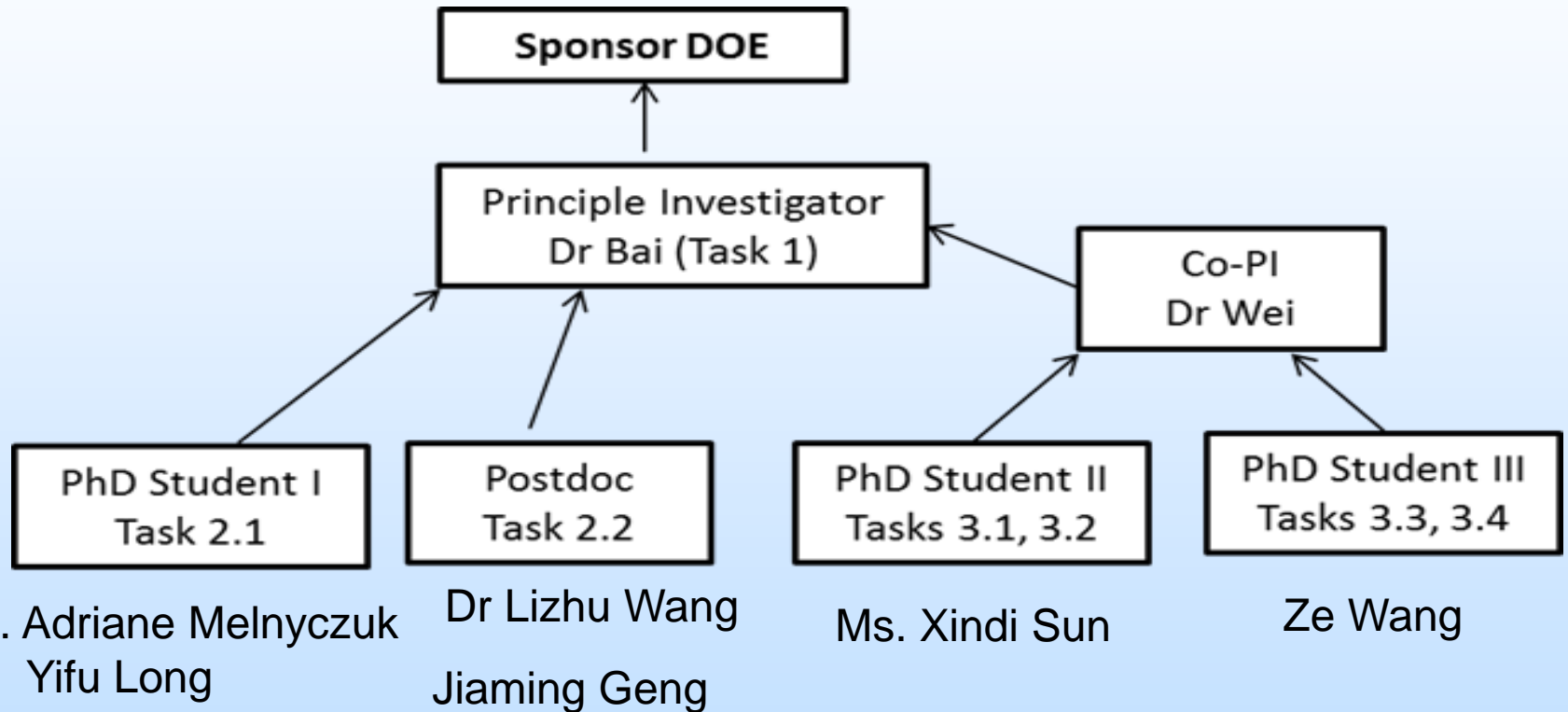


U.S. DEPARTMENT OF
ENERGY



- Mr. David Smith in ConocoPhillips
- Mr. Andrew Johns in Occidental Petroleum Corporation
- Missouri S&T Research group members

Organization Chart



PI: Baojun Bai
Co-PI: Mingzhen Wei

Technician: Ninu Maria
Senior Investigator

Gantt Chart

Technical Tasks	Year 1				Year 2				Year 3			
	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 CO₂ 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												
Project Report	QR	QR	QR	QR	QR	QR	QR	QR	QR	QR	QR	FR

Milestones

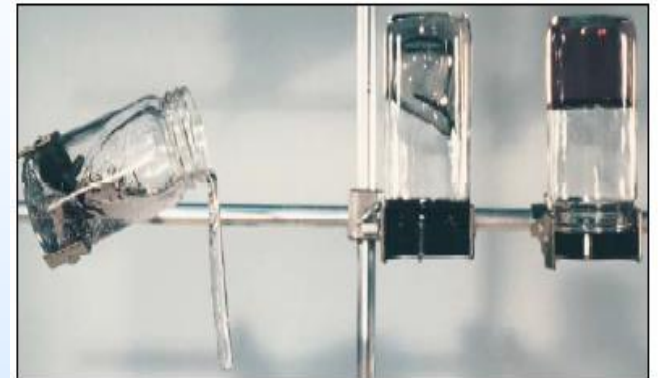
Task/ Subtask	Milestone Title	Planned Completion Date	Verification method
1.0	Project Management Plan		PMP file
1.0	Kickoff Meeting	08/18/15	Presentation file
2.1	Synthesize large size (10 μm -mm) swelling delayed particle and complete characterizations	09/30/16	Summary report or presentation file
2.2	Synthesize nano- and micro-sized swelling delayed particle and complete characterizations	09/30/17	Summary report or presentation file
3.1	Develop criteria for particle passing through pore throats and fractures	09/30/16	Presentation file
3.2	Understand the effect of particle gel on water/oil/CO ₂ flow	09/30/17	Summary report or presentation file
3.3	Understand nano-particle transport mechanisms through porous media	09/30/18	Summary report presentation file
3.4	Develop mathematical models to characterize particle flow behavior	09/30/18	Summary report or presentation file
Papers	Publish at least 3 peer-reviewed papers	09/30/18	Accepted or published papers
Presentations	Make at least 4 presentations in conferences	09/30/18	Presentation files
Final Report		09/30/18	Report

Bibliography

- Imqam, A., Bai, B., Wei, M., Elue, H., & Muhammed, F. A. (2016, August 1). Use of Hydrochloric Acid To Remove Filter-Cake Damage From Preformed Particle Gel During Conformance-Control Treatments. Society of Petroleum Engineers. doi:10.2118/172352-PA
- Imqam, A., Aldalfag, A., Bai, B., Evaluation of Preformed Particle Gels Penetration into Matrix for a Conformance Control Treatment in Partially Open Conduits, paper SPE 181545 accepted for presentation at the SPE Annual Technical Conference and Exhibition held in Dubai, UAE, 26–28 September 2016.

Gels Used for Conformance Control

- In-situ gel systems: Gelant is injected into formation and gel is formed under reservoir conditions after placement. Gelation occurs in the reservoir.



Tonguing (Flowing) Intermediate Rigid

- Preformed gel systems: Gel is formed in surface facilities before injection, and then gel is injected into reservoirs. No gelation occurs in reservoir.