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Preformed Particle Gel For Conformance Control

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Preformed Particle Gel for Conformance Control
REPSEA Project: 07123-2

Progress Report April 2009

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Missouri University of Science and Technology

First Semiannual Report / Year 1 October 2008 – March 2009

1.0. EXECUTIVE SUMMARY

This report summarizes the work for the first 6-month period of this 2-year project. The ultimate purpose of the project is to establish methods to optimize particle gel treatments to increase oil recovery and reduce water production by improving waterflood sweep efficiency. The project has four research tasks. The first task is to identify where particle gels can be effective and how to best use them by reviewing field application data. The second task is to quantify particle gel propagation for different PPG products during extrusion through open fractures and fracture-like channels and the results will thereby guide selection of the best particle gels for fracture and channels with different widths. The third task is laboratory flow tests to evaluate novel processes that might have significant potential to improve gel particle treatment efficiency. The fourth task is to develop well size-distributed commercial preformed gel particles. The research results of the project are updated and summarized in this semi-annual report with five chapters.

Chapter 1 is a review of the current status of gel treatments and the significance of preformed particle gel treatments to small producers.

Chapter 2 is a summary of the field applications of preformed particle gel (PPG) treatments for conformance control in various reservoir conditions, including reservoirs with high temperature, high salinity, thick heterogeneous zones, severe sand production, polymer flooding and CO_2 flooding. Detailed information is described about an application of PPG treatment for in-depth fluid diversion in four injection wells in a sandstone reservoir with thick net zones. Theoretical models were used to discuss why a large amount of large particles can be injected into the reservoir.

Chapter 3 reports the experiment models that we designed to test the swollen particle strength and to study the transport mechanism of swollen particle through fracture or fracture-like channels and the experimental results from screen models that are used to test the strength of the swollen particle gel and study the effect of injection rate on the injectivity of particle gel. Experiential results from screen model tests indicate the particle injectivity mainly depends on the swelling capacity and the open hole size of a screen. Increasing particle sizes and injection rates can not significantly increase the injection pressure. This is in a good agreement with the real-time injection pressure and injection rate change which were observed during practical particle gel treatments. These gel particle injection behaviors are completely different from conventional particles in that they are elastic and deformable during extrusion.

Chapter 4 reports our research results about the compatibility of particle gels and surfactants**.** The objective of this research is to test if the combined technology of PPG treatments and surfactant injection can significantly improve the gel particle treatment efficiency and thus improve overall oil recovery. Results show (1) surfactants have negligible effect on PPG swelling ratio, (2) surfactant concentration in free water or brine (the water is not absorbed into particles) increases 42% after swelling of gel particles with nonionic surfactants.

Chapter 5 reports the research progress of the Task 7 “Customized PPG Products” of the PPG project. The swelling capacity of two commercial PPG products (PPG-8A, 100-200 mesh, PPG-8B, 40-65 mesh) and two new, customized experimental samples (PPG-8A and PPG-8B) were evaluated as a function of salt type and concentration. Results indicate that PPG swelling capacity is significantly higher in sodium chloride brine than in the same concentration calcium chloride brine and the swelling capacity increases with the salt concentration. One performance feature of the PPG-8B product is that it exhibits gradual swelling, taking as much as 5 days to swell to its maximum extent at room temperature. Compared to the PPG-8 product series, the PPG-1 and PPG-2 are more tolerant of higher temperatures and have greater swelling capacity.

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Chapter 1. Technical Status Assessment

I. Current State of the Technology

A. Summary of Background of Industry/Sector

One out of every six barrels of crude oil produced in the United States comes from stripper wells. These wells produce oil and gas at the low rates of less than 10 barrels per day of oil or 60,000 cubic feet per day of natural gas, and represent typical operations for many of the small producers in the U.S. About 80 percent of the total number of U.S. oil wells is now classified as marginal wells. Tapping into additional oil and gas supplies within the nation's stripper wells for smaller producers can be an important contribution to U.S. energy security. Water production is a major problem for most small producers. Higher levels of water production result in increased levels of corrosion and scale, increased load on fluid-handling facilities, increased environmental concerns, and eventually well shut-in (with associated workover costs). Consequently, producing zones are often abandoned in an attempt to avoid water contact, even when the intervals still retain large volumes of recoverable hydrocarbons. Controlling water production has been one major objective of the oil industry. Gel treatment is one of the most cost-effective methods to control water production.

B. Technologies/Tools Being Used

i. Technology/Tool 1: In-situ Gelation System for Gel Treatments

***a. Description*:** An in-situ gelling system is usually composed of polymer, crosslinker and some other additives. Polymer is usually HPAM, and crosslinkers can be the compounds of Cr^{3+}, Cr^{6+}, or Al^{3+}, or resin. Additives are used to adjust gelation time, control gel strength and thermo-stability. The mixture of polymer and crosslinker called gelant is injected at a high water cut production well into a target formation and reacts in the formation (mainly via temperature effect) to form gel and thus fully or partially seal the formation where gel is placed. Therefore the gelation process occurs in reservoir conditions. Typical in-situ gels included bulk gel (BG) and colloid dispersion gel (CDG).

b. Benefits and Inadequacies of this tool or technology: In-situ crosslinked polymer gels are traditionally mostly applied for conformance control treatments because they have the advantages of controllable gelation time, adjustable strength, and good injectivity. However, there are distinct drawbacks inherent in in-situ gelation systems, such as uncontrolled gelation

times and variations in gelation due to shear degradation, and gelant compositional changes induced by contact with reservoir minerals and fluids. In addition, in-situ gelation systems behave as a polymer solution before gelation. According to polymer flooding mechanisms, polymer solution will more enter the zones unswept by water during water flooding. Once gelant forms gel in unswept zones, it will seriously damage the potential oil production zones.

ii. Technology/Tool 2: Preformed Particle Gels

a. Description: Preformed gel is formed at surface facilities before injection, and then gel is injected into reservoirs. For this technology the gel treatment occurs in injection well. So no gelation occurs in reservoirs. The current available preformed particle gels include mm-size preformed particle gel – PPG (Coste 2000, Bai 2008), microgels (Chauveteau 2000, Zaitoun 2007), and swelling micron-sized polymers (Bright Water®, Pritchett 2003, Frampton, 2004). Field applications of some gels resulted in very positive results (Pritchett 2003, Bai 2008, Liu 2006, Zaitoun 2007, Cheung 2007, Abbasy, 2008, Pyziak et al., 2007, Larkin and Creel, 2008). Their major differences are their sizes and swelling times.

b. Benefits and Inadequacies of this tool or technology. Preformed particle gels have become a newer trend because they can overcome some distinct drawbacks inherent in in-situ gelation system such as lack of gelation time control, uncertainness of gelling due to shear degradation, chromatographic fractionation or change of gelant compositions, and dilution by formation water. The preformed particle gels (PPG) that is the focus in this study have the following unique advantages over traditional in-situ gel, including: (1) PPG are strength- and size-controlled, environmentally-friendly, and they are stable in the presence of almost all reservoirs minerals and formation water salinity; (2) PPG can preferentially enter into fractures or fracture-feature channels while minimizing gel penetration into low permeable hydrocarbon zones/matrix. Gel particles with the appropriate size and properties should transport through fractures or fracture-feature channels, but they should not penetrate into conventional rock or sand; (3) PPG has only one component during injection. Thus, it is a simpler process, and does not require many of the injection facilities and instruments that often are needed to dissolve and mix polymer and crosslinker for conventional in-situ gels, and (4) PPG can be prepared with produced water without influencing gel stability. In contrast, traditional in-situ gels are often very sensitive to salinity, multivalent cations, and H_2S in the produced water. This not only can save fresh water but it also can protect our environment.

However, the PPG injectivity is still questionable to many reservoir engineers because its size is usually much larger than the pore sizes of conventional cores from reservoirs. PPG treatments have been successfully used for more than 2,000 wells by China (Bai, 2007, Liu, 2006), Halliburton (Abbasy, 2008) and Occidental oil company (Pyziak et al., 2007) and Kinder-Morgan (Larkin and Creel, 2008), but its mechanisms to control conformance and its applied conditions are still not clear. Also due to its large size, it definitely can not be used in the reservoirs without super-high permeability channels or fractures.

II. Development Strategies

A. Justification for new research or technology

Unless special efforts are made during gel placement (e.g., zone isolation), theoretical studies and field applications demonstrate that gel treatments are most likely to be successful when treating fractures or fracture-like features that cause channeling in reservoirs. Seright et al, (2003) have studied the propagation of preformed bulk gels through open fractures since 1992. They have also performed extensive core flooding experiments and successfully developed a series of theories and methods to characterize the propagation of preformed bulk gels through porous media. However, although the preliminary studies of particle gel propagation through porous media were performed by the product inventors, all core flooding tests used porous media without channels. The smallest gel particles, such as microgels, collodial dispersion gels, and micron-sized swelling polymers, were marketed only for treatment of matrix problems. However, we are interested in whether these particles gels might have applicability to fractures and fracture-like channels. The ultimate purpose of the project is to provide the fundamental information to select particle gels for mitigating water production and extending field life.

B. Problems Addressed in this Research Project

Our work features the following innovations.

- The transport of particle gels through fractures and channels will be first tested using screens and core flooding experiments. These experiments will give a design basis for fractured or channeled reservoir gel treatments.

- The analysis of connecting laboratory and field data by modern soft-computing methodologies will result in models to optimize particle treatments in fractured reservoirs.
- Three novel methods will be tested to improve gel treatments, including addition of second crosslinker, inclusion of surfactant, exploration of gravity segregation to aid gel placement.

III. Future

A. Barriers imposed by current state of technology

1. Optimized methods to design PPG treatments.
2. Application conditions of successful PPG treatment
3. Mechanisms of PPG transport through porous media

B. Impact on U.S. Domestic Gas Supply

One out of every six barrels of crude oil produced in the United States comes from stripper wells. Excess water production which, when accompanied by low oil production, results in wells becoming unprofitable to operate and leads to early well abandonment and unrecoverable oil. PPG treatments can reverse this trend of decreasing oil production and increasing WOR, based on reported field success elsewhere. Results from field application of PPG can provide an increase of as much as several times the previous oil production for several months, even a couple of years, and reduce the WOR by more than a factor of 2. These treatments typically have ranged from injection of PPG of 2,000 – 30,000 lb of product as a suspension of fine particles. Chemical efficiencies have been very good – as low as 1 bbl incremental oil per pound of PPG chemical. Because the cost of PPG may be $2 - $4/lb, this becomes very attractive economically with current high oil prices. The DOE has estimated that the EOR target for the U.S. to be about 377 billion bbl of oil. Simple technologies like PPG injection are well suited to address the vast reserves of light oil left after mature waterfloods. If this process could just unlock 1% of this oil bypassed by waterflooding, this would represent a potential of 3.7 billion bbl of increased domestic reserves.

C. Likely Environmental Impacts

A significant improvement may be achieved by the successful application of PPG in terms of reduced requirements for fresher water sources and reduced volumes of produced water. Specifically, by PPG creating selective plugging of water thief zones, then there is reduced significantly the volume of salt water produced. The general theme of lower volumes of water associated with hydrocarbon production is a key goal of several U.S. agencies, such as RPSEA, DOE, and EPA. Excess water production is a dominant reason for the abandonment or the low economics of stripper wells. Production of salt water has also resulted in serious environment issues. If the oilfield waters are classified as a hazardous waste, they would contribute over 98% of the waste produced in this country. Even if only a 1% reduction in water production is achieved, between $50 million and $100 million could be saved annually and a substantial positive environmental impact could be realized.

Another advantage of the PPG technology is that it is an effective plugging agent that may used in virtually any source of make-up water. Other waterflood conformance agents in some cases demand relatively fresh water as a make-up. This means the PPG technology can used almost any produced water as make-up, and so there is no demand to dispose the produced water.

D. Path to Application

The path of taking the key information gained from this study to the beneficial application to the small producer as an end user has two different approaches:

First (Fast) Path for Technology Deployment --

Missouri S&T provides already useful insights of field application early in the life of the project, based on their review of a number of prior case histories. BJ Services (and other service providers after these results are published) may take advantage of the general observations and field experience of others almost immediately when designing PPG jobs for small producers in the U.S.

The field data review is also expected to include insights with regards to the type and characteristics of PPG products that seem to have a preferred track record of success elsewhere. This guidance will allow ChemEOR as a product provider to bias their product line towards the specific types and sizes of PPG particles that have been shown to be successful.

Second (Longer-Term) Technology Deployment --

The detailed laboratory studies will be reported later in the life of the project. These results by themselves will offer immediately additional insights with regards to the selection of an optimal PPG product to have a desired effect on a target reservoir. The coupling of these results with prior field experience will solidify criteria for proper PPG product selection. Even longer term, laboratory evaluation of the proposed novel ideas to improve the PPG technology should yield promising results that can be implemented as new products and processes after some additional follow on study.

IV. Deliverables

(1) Monthly status reports using the template provided by RPSEA
(2) A final report on the results of the defined efforts.
(3) MST will build and maintain a web site with information about the project and updates as appropriate
(4) MST will present at least two papers in SPE meetings and submit at least one paper to referred journal.
(5) MST will provide other deliverables as outlined in the following task table.

Table 1-2. Deliverables from Research status reports and final report

Task	Descriptions
Task 1.	Project Management Plan
Task 2.	Technology Status Assessment
Task 3.	Technology Transfer
Task 4.	Theoretical Analysis of Field Applications and Database Building for Parameter Optimization.
4a	Collect PPG field application data.
4b	Build Database and analyze field applications using developed theories.
4c	Identify the best model for candidate selection and well performance prediction.
Task 5.	Core flooding Experiments for Particle Gel Transport through Fractures and Fracture-like Channels.
5a	Screen gel particles for different width of fractures and fracture-like channels.
5b	Study the effect of injection parameters on gel placement.
5c	Update the model from Task 4 using the new experimental results/models.
Task 6.	Novel Methods to Improve Particle Gel Treatments.
6a	Secondary crosslinking reactions to increase gel resistance to washout
6b	Combination PPG and surfactants treatments.
6c	Exploitation of gravity segregation between gel particle and brine to control gel placement in vertical fractures.
Task 7.	Customized PPG Products
7a	Synthesize first novel PPG products that in product line – verify reproducibility
7b	Make a series of PPG products of varying sizes and compositions
7c	Perform laboratory experiments to detail physical properties

V. References (relevant and used in the assessment report)

1. Abbasy, I. et al. "Laboratory Evaluation of Water Swellable Materials for Fracture Shutoff," paper SPE 111494 presented at 2008 SPE North Africa Technical Conference and Exhibition in Marrakech, Morcco, 12-14 March 2008.

2. Bai, et al, "Case Study on Preformed Particle Gel for In-Depth Fluid Diversion, paper SPE 113997 presented at SPE/DOE at the 2008 SPE/DOE 16th Symposium on IOR held in Tulsa, OK, U.S.A., April 20–23.

3. Bai, B., et al, "Conformance Control by Preformed Particle Gel: Factors Affecting its Properties and Applications," *SPE Reservoir Evaluation and Engineering*, Aug 2007, 415-421.

4. Bai, B., et al, "Preformed Particle Gel for Conformance Control: Transport Mechanism through Porous Media," *SPE Reservoir Evaluation and Engineering*, April 2007, 176-184.

5. Chauveteau, G., et al.: "New Size-Controlled Microgels for Oil Production," paper SPE 64988 presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houston, Feb 13-16.

6. Cheung, S.,et al.: "A Swelling Polymer for In-depth Profile Modification: Update on Field Applications," presented at SPE Applied Technology Workshop of "Chemical Methods of Reducing Water Production," San Antonia, Texas, USA, March 4-6, 2007.

7. Coste, J.-P., at al.: "In-Depth Fluid Diversion by Pre-Gelled Particles. Laboratory Study and Pilot Testing," paper SPE 59362 presented at 2000 SPE/DOE Improved Oil Recovery Symposium, 3-5 April, Tulsa, O.K.

8. Frampton, et al.: "Development of a Novel Waterflood Conformance Control System", paper SPE 89391 presented at the 2004 SPE/DOE 14th Symposium on IOR held in Tulsa, OK, U.S.A., April 17–21.

9. Larkin, R. and Creel P., "Methodologies and Solutions to Remediate Inter-well Communication Problems on the SACROC CO2 EOR Project-A case study", paper SPE 113305 presented at 2008 SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, 19-23 Aprill 2008.

10. Liu, Y.Z. et al.: "Application and Development of Chemical-Based Conformance Control Treatments in China Oil Fields," Paper SPE 99641 presented at the 2006 SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA, April 22-26.

11. Pritchett, J., et al.: "Field Application of a New In-Depth Waterflood Conformance Improvement Tool," paper SPE 84897 presented at 2003 International Improved Oil Recovery Conference in Asia Pacific, 20-21 October, Kuala Lumpur, Malaysia.

12. Pyziak, D., et al.: "Update On Anton Irish Conformance Efforts," paper presented at 6th International Conference on Production Optimization-Reservoir Conformance-Profile Control-Water and Gas Shutoff, Houston, TX, 6-7 Nov, 2007.

13. Seright, R.S.: Washout of Cr (III)-Acetate-HPAM Gels from Fractures," paper SPE 80200 presented at the 2003 SPE international Symposium on Oilfield Chemistry, Houston Feb 5-7.

14. Zaitoun, A., et al.:“Using Microgels to Shutoff Water in Gas Storage Wells,” paper SPE106042 presented at 2007 SPE International Symposium on Oilfield Chemistry, Houston, TX, USA, 28 Feb - 2 March.

Chapter 2. Field Application and Data Analysis of Preformed Particle Gel for Conformance Control

Summary

This chapter reports the research progress for the task 4 about field application results. The chapter reviews field applications of preformed particle gel (PPG) treatments for conformance control in various reservoir conditions, including reservoirs with high temperature high salinity, thick heterogeneous zones, severe sand production, polymer flooding and with CO_2 flooding. Detailed information is described about an application of PPG treatment for in-depth fluid diversion in four injection wells in a sandstone reservoir with thick net zones. The selected four injectors have 46 connected producers with average water cut of 95.4% before treatment. The chapter reports the detailed information for the four well treatments, including well candidate selection criteria, PPG treatment optimization, real-time monitoring result during PPG injection and reservoir performance after treatment. In addition, Theoretical models were used to discuss why a large amount of large particles can be injected into the reservoir.

Overview of PPG Treatment Technology and Field Applications

What is PPG?

PPG (mm-sized preformed particle gel) is an improved super adsorbent polymers (SAPs). SAPs are a unique group of materials that can absorb over a hundred times their weight in liquids and do not easily release the absorbed fluids under pressure. Superabsorbent polymers are primarily used as an absorbent for water and aqueous solutions for diapers, adult incontinence products, feminine hygiene products and the agriculture industry. However, the traditional SAPs in the markets do not meet the requirements for conformance control due to their fast swelling time, low strength and instability at high temperature. A series of new SAPs called preformed particle gels (PPGs) have developed for the conformance control purposes (Li, 1997, Bai, 2004, 2007). PPG properties are summarized as follows.

- PPG sizes are adjustable: μm-cm.
- Swelling ratio in formation water: 30~200 times original size.

- Salt resistance: all kinds of formation salts and concentrations are acceptable.
- Thermal stability: more than 1 year below 110 ºC.
- Strength: adjustable, high strength product available.
- Swelling rate: slightly controlled.

Why to Select PPG Treatments

Lab results showed that crosslinking system formed dispersed gels not bulk gel in porous media at flowing condition. Our lab tests have showed gelants will form dispersed gels rather than bulk gels in the porous media without open fractures at flowing condition, shown in Fig.2-1. Therefore, gel treatments in porous media are particle gel treatments.

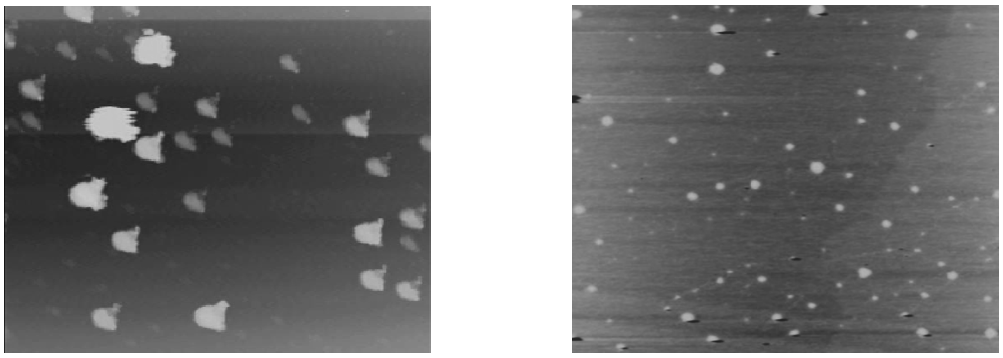


Fig.2-1. Dispersed gel particles from porous media.

Preformed particle gels overcome some distinct disadvantages inherent in traditional in-situ gels. Particle gels have great potential due to their unique advantages over traditional in-situ gels, including:

1. Preformed particle gels are synthesized prior to formation contact, thus overcoming distinct drawbacks inherent in in-situ gelation systems, such as uncontrolled gelation times and variations in gelation due to shear degradation, and gelant compositional changes induced by contact with reservoir minerals and fluids.
2. Preformed particle gels are strength- and size-controlled, environmentally-friendly, and their stability is not sensitive to reservoirs minerals and formation water salinity.
3. These gels usually have one component during injection. Thus, it does not require many of the injection facilities and instruments that often are needed to dissolve and mix polymer and crosslinker for conventional in-situ gels. The simple injection operation processes and surface facilities can significantly reduce operation and labor costs.

PPG has unique properties compared to other preformed particle gels. PPGs are mm-sized gel particles, they cannot be injected in conventional porous media without fractures or void but they can effectively plug fractures or high permeability streaks/channels in mature oilfields which cannot be successfully implemented by nanosized particle gel-Bright Water® (Pritchett 2003, Frampton 2004) or microsized preformed particle gels-microgels (Chauveteau 2001, 2003, Rousseau 2005, Zaitoun 2007). In addition, the PPG has the following advantages:

1. PPG can preferentially enter into fractures or fracture-feature channels while minimizing gel penetration into low permeable hydrocarbon zones/matrix. PPG has adjustable sizes, from a few hundred micrometers to a few centimeters. Gel particles with the appropriate size and properties should transport through fractures or fracture-feature channels, but they should not penetrate into conventional rock or sand. However, in-situ gels behavior begin as a polymer solution when they are injected as gelants. The minimized gel penetration in low permeable areas will also result in significant reductions in the required gel volumes because fracture or fractured-like channels usually comprise less than 10% of the reservoir volume (Tang, 2005). According to polymer flooding mechanisms, more gelants will sweep into un-swept low permeability oil zones than water. Once the gelants crosslink in these oil zones, not only they will waste polymer but they will also block these zones, which will cause serious damage in these potential productive oil zones.
2. PPG suspension can be prepared with produced water without influencing gel stability. This can not only save fresh water but it can also protect our environment. In contrast, traditional gels and nanosized particle gel Bright Water® are very sensitive to salinity, multivalent cations, and H_2S in the produced water.
3. The adjustable size and strength of PPG particles make them suitable to use "Trial and Error" method for better conformance control results. Real-time monitoring data can be used to adjust previous design for better gel treatment results. The success of gel treatments depends on reservoir problem identification, appropriate candidate selection, gel selection, parameter design, and gel placement. However, The reservoir is a black box, and it is not completely understood. The "Trial and Error" provides an effective method to better treat the reservoir.

Field experience has demonstrated mm-sized particle gels are feasible for mature water flooded reservoirs

Fractures or high permeability streaks/channels widely exist in mature water-flooded reservoirs. Field tests and the successful injection of particle-type conformance control agents in China have demonstrated that reservoir pore structures and physical parameters have been significantly changed by long term waterflooding. The existence of induced fractures or high permeability streaks/channels is evidenced by the following field experiences:

Interwell tracer test. Many reservoirs have no initial fracture(s), but tracer tests show in many cases it only took less than 15 days even a few days or hours for the tracers to move from an injector to its adjacent producers with a distance of around 100-300 meters. Tracer test data interpretation using simulation software shows that the permeabilities of these channels or streaks are usually around a few hundred to tens of thousand Darcy and their volumes are only 1 to 10% of the reservoir volume but they adsorb about 80-90% of injected water (Tang, 2005).

Gel treatments. Large volume of gel treatments (more than 5,000 m^3) using in-situ gelation systems were performed on hundreds of wells in China's oilfields in 1990s. Their gelation times were usually only a few hours to less than one day but all gelants were successfully injected even though the injections continue to 15 days even a few months. In addition, many treatments did not increase water injection pressure enough as expected after treatment.

*Particle injections***.** Many kinds of particles, such as montmorillonite clay, fly ash, are quite often applied to control conformance in China in 1990s. Many wells can be successfully injected with a few thousands of cubic meters of the particle-type conformance control agents without any injection problems, which also indicated the formations had extremely large voids or fractures than we expected.

Based on above field practices, mm-sized PPG treatment was proposed to control conformance (Li, 1997, Coste, 2000, Bai, 2004, 2007). Field applications have demonstrated the mm-sized gel particles have no significant injectivity problem in most mature reservoirs.

Application Cases of Preformed Particle Gel for Conformance Control in Different Reservoir Conditions

Application case in a reservoir with high salinity and high temperature

This was the first PPG treatment in Zhongyuan oilfield, SINOPEC. This case includes two

adjacent injection wells, W51-75 and P-72, in Pucheng reservoir of the oilfield. Three production wells are connected with the two injectors. It is a sandstone reservoir with an average permeability of 121 md without fractures. The formation temperature is 107 ºC and the total salinity of the formation water is 15×10^4 mg/l. The reservoir has been developed by water flooding since 1979. The two wells were not hydraulically fractured. The two wells were treated using PPG in 1999 due to the following reasons:

- Each of the two wells has high water injectivity. The injectivity index of W51-75 is 20 m^3/(MPa·d) with threshold pressures (which is defined as the minimum injection pressure that water can be injected) of 9.2 MPa, and the injectivity index of P-72 is 18 m^3/(MPa·d) with threshold pressure of 8.5 MPa;
- Connected production wells had a high average water cut of more than 85%;
- Water injection profile results showed that the wells had an extreme vertical heterogeneity;
- Tracer test results showed that the wells had an extreme severe areal heterogeneity and channel between injectors and producers (tracer breakthrough in two days).

The injected PPG volume of each well was optimized by systematically considering injectivity, water injection profile and tracer test results. 4,300 m^3 PPG suspension prepared by 13,000 kg dry PPG was injected into W51-75 and 2,500 m^3 PPG suspensions prepared by 7,500 kg dry PPG was injected into P-72. PPG concentration is 3,000 mg/L. Produced water was used to prepare the PPG suspensions. PPG size ranges from 0.8 to 2.0 mm with a median diameter of 1.5 mm.

The injection rate was determined by the injectivity index of each well. The highest injection pressure was limited to 80% of the fracturing pressure of the formation. An alternate injection method of water (treated produced water) and PPG suspension was applied: PPG suspension injection was done during the daytime and water injection was done at night.

After the PPG treatment, injection wells and their corresponding production had the following response.

(1) Injection pressure was increased: the water injection pressure of P-72 increased from 19.5 MPa to 24 MPa and W51-75 from 16 MPa to 19 MPa. The injection pressure after treatment kept going higher than that before treatment for more than two years, which indicates PPG is stable for more than one year at the formation conditions.

(2) Vertical injection profile was modified. The improvement of the vertical profile was confirmed by a profile test survey before and after the PPG treatment shown in Figure 2-1. In this figure, each layer represents a separate layer and there is an impermeable barrier between layers (assuming no vertical fracture). As shown in this figure, only two layers took water before treatment, but another two layers began to accept water after the treatment. Of course, it should be noted that the injection well profile results sometimes are not instructive when channels or fractures exist near the wellbore due to the limited depth of investigation limited by this measurement method or the extension of a vertical fracture. In this case, if the channel or fracture just exists in one layer, the comparison results are meaningful because some new layers were affected after the treatment. However, the results are meaningless if the fracture or channel penetrates most layers of the well. Because the detection of fracture penetration is difficult, it cannot be proven whether the channels or fractures penetrate most layers or just one layer.

(3) Water cut of corresponding producers was decreased and daily oil production rate was increased. Figure 2-3 presents a typical production curve of well W51-172, which connects with both W51 and P72. The water cut was decreased from about 80% to about 70% and daily oil production was increased from 40 t/d to 60 t/d.

The two well PPG treatments resulted in a total 3,239 t of oil increase or 158 t of incremental oil per 1,000 kg PPG.

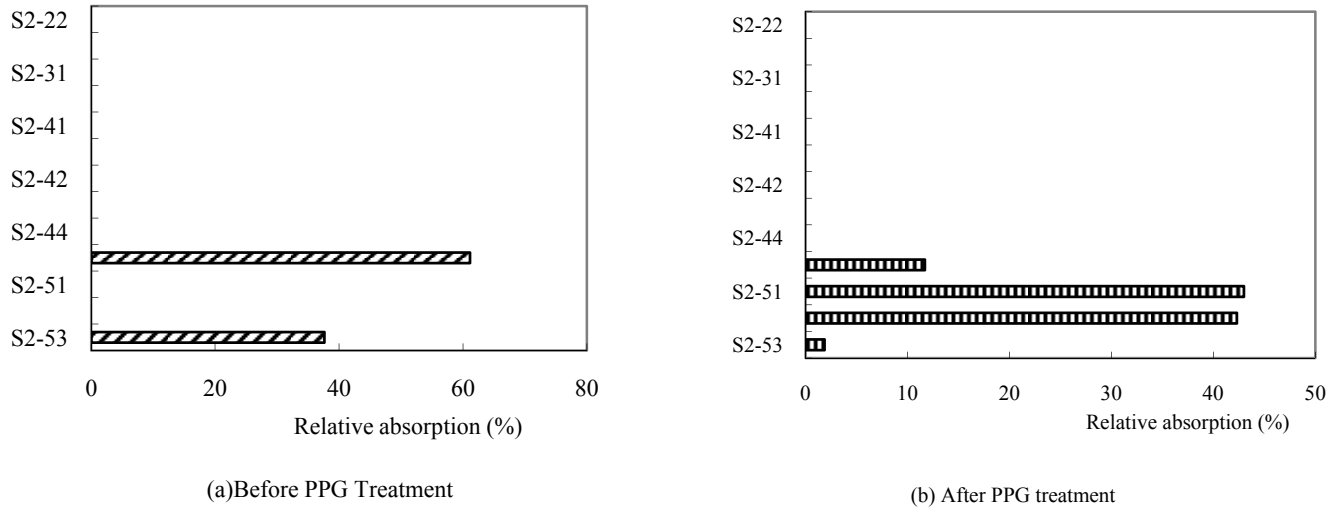


Figure 2-2. Injection profile comparison of well M11-23 before and after PPG treatment.

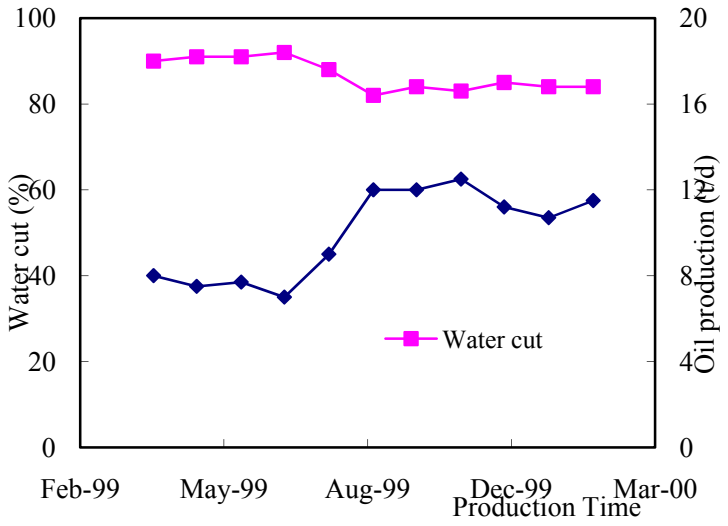


Fig. 2-3. Production curve before and after PPG treatment.

Table 2-1. PPG Injection in Pucheng Oilfield

Well	Treated Time	Total Volume (m^3)	Concentration (mg/L)
W51-75	July 17-Sept 20, 1999	4,323	3,000
P72	July 17-Sept 20, 1999	2,503	3,000

Application case in a sandstone reservoir with thick layers

This is the example of first PPG treatment in Daqing oilfield, PetroChina. The selected injection well is Xing-7-24 in Xingbei oilfield. The reservoir formation is characterized by thick oil layers with severe vertical heterogeneity. Formation temeperature is about 45°C and salinity is about 4,500 mg/L. The perforated depth is from 890 to 1051.4 m. Net pay of the well is 24.5 m. The initial permeability is from several md to more than 1200 md. The well was changed from a producer to a water injection well in November 1992, and the cumulative water injection volume had been 763758 m^3 until Aug, 2000. Four adjacent producers were confirmed to be connected with the injection well with a total of more than 700 m^3/d of liquid and average water cut of more than 90%. Profile tests showed that about 85% injected water directly passed through high permeability parts of the oil zones, which occupied less than 1/5 of the total thickness. Inter-well potential measurements demonstrated that the well group had severe areal heterogeity, shown as Fig. 2-4. PPG treatment was performed in August 2000. The produced water was used

to prepare PPG suspension. As we know, for normal in-situ polymer gelling system, it usually takes some time to prepare polymer and crosslinker before it is injected. But PPG is completely different, and it can be easily dispersed into water. Figure 2-5 shows the flow scheme of PPG mixing and injection system. This system is simple, and so it can reduce some operation and labor costs.

Table 2-2 shows the injection scheme of PPG suspension. A total of 3,100 m^3 PPG suspension was injected into the well. For the first stage, 100 m^3 of 5 mm PPG suspension was injected into the well at a higher flow rate of 25 m^3/h and a higher concentration of 1%. The objective of the first stage is to inject PPG at higher pressure so that PPG suspension can start all open layers. Because PPG cannot penetrate into low permeability zone with permeability below 1,000 md, PPG will form face plugging at the low permeability zone that can prevent the following PPG from entering and damaging these zones. For the second and third stage, an alternating injection method of PPG suspension and water was used: 10 h of PPG suspension injection followed by 14 h of water injection. The difference between the 2nd and 3rd stage is their particle sizes. In fact, we initially designed them in same size, but the injection pressure increase did not achieve our expectation, and so we changed particle size from 1.5 mm to 3 mm. For the fourth stage, 5 mm PPG was continually injected so that the final injection pressure can achieve expected results. Figure 2-6 shows the monitoring injection pressure result during PPG injection while not including water injection periods. As we saw, the injection pressure oscillates, which is caused by the alternating injection of PPG suspension and water. When PPG suspension was injected, the injection pressure gradually increased, but when changed to water injection, the pressure decreased, which indicated injection water could displace part of the PPG away from wellbore.

The injection wells and their corresponding producers showed the following results after the treatment.

(1) Injection pressure increased from an initial 5.0 MPa to 11.6 MPa.

(2) Potential test results showed that the areal heterogeneity was effectively controlled.

(3) About 2,400 t of incremental oil was obtained with a 8% water cut decrease.

(4) The useful life of PPG is more than 6 months.

The above results show that the PPG treatment is positive. In this case, 15.5 t of 1.5~5 mm particles were injected into the wells, but no injectivity problem was encountered. According to

the theoretical particle size of PPG propagation through porous media, the reservoir should have a channel with thousands of Darcy. Of course, there are two other possibilities for this case. The first possibility is that the particles may be broken into small pieces when they were injected or transported through porous media. But for this possibility, no matter how small pieces the particles were broken into, the particles still are a gel and it is very difficult to transport through normal porous media without having a fracture or channel. Another possibility is that there exists a "cave" which is often caused by sand-production near wellbore. For Daqing oilfield, sand-production is not severe, so it has only a low probability that caves exists near wellbore. From the injection history, it can be inferred that the reservoir has some fracture or channel. Otherwise, it is improbable that such a large volume of PPG could be injected. Of course, it cannot be proven that fractures or channels exist nor how far they might extend from the injection well.

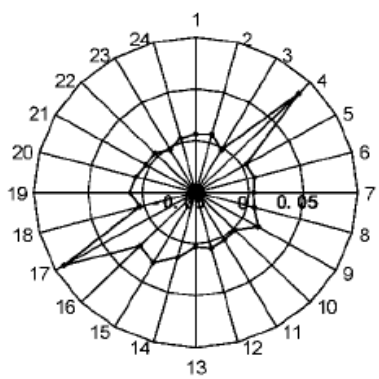


Fig. 2-4—Areal heterogeneity of well group.

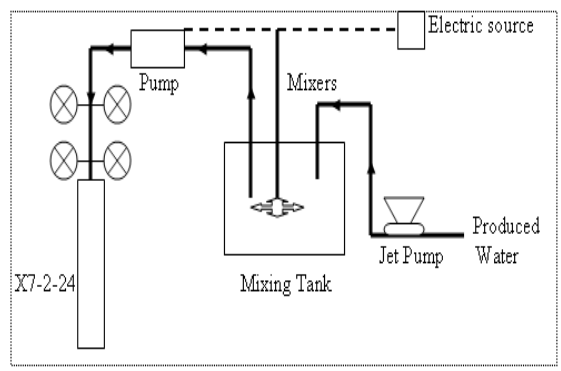


Fig. 2-5—Flow chart of PPG Injection

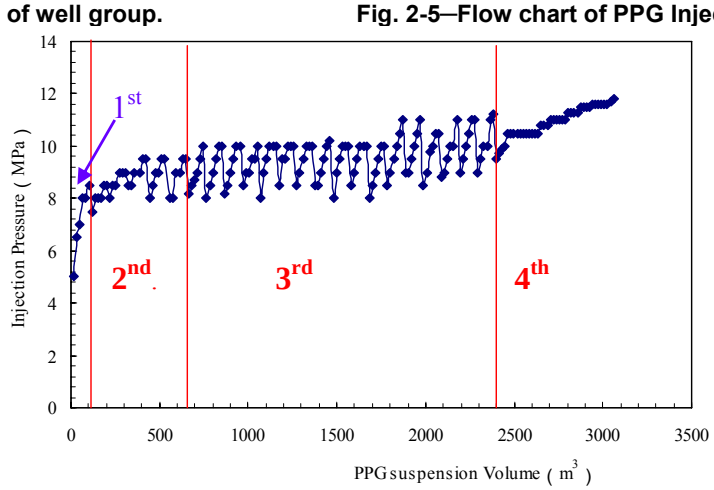


Fig. 2-6—Pressure change during PPG suspension injection.

Table 2-2. PPG Injection in Daqing Oilfield

Stage	PPG Size (mm)	PPG weight (kg)	Volume (m^3)	Concentration (mg/L)	Injection rate (m^3/d)
1	5.0	1,000	100	1.0	25
2	1.5	3,000	600	0.5	14-16
3	3.0	8,500	1,700	0.5	14-16
4	5.0	3,000	600	0.5	14-16
Total		15,500	3,100		

Application in the Reservoir with Severe Sand Production

Two injection wells were selected for PPG treatments in Shengli oilfield, SINOPEC in 1999. Both selected wells (Bin 24-4 and Bin 24-17) are in the block 255 of Shangdian reservoir, which is a sandstone faulted-block reservoir with severe sand production. The oil producing layers in the block are named as S_3 and S_4. The average thickness of layer S_3 is 4.6 meter with a high permeability of 2-6 D and an average porosity of 31%. The crude oil viscosity in the layer ranges from 57 to 148 mPa.s. The average thickness of S_4 layer is 1.6 meter with a low permeability of 0.04 to 0.5 D and an average porosity of about 25%. The oil viscosity in the S_4 layer is high to 7,731 mPa.s (with an average value of 721 mPa.s)

The selection of PPG treatment was selected based on the following considerations:

- The reservoir is mainly composed of loose sands and sand production has resulted in voids or the channels with super-high permeability in the water-flooded areas.
- PPG particles are soft and deformable and could move into in-depth of the formation with channels with super-high permeability to redistribute the fluid flow there.
- The high salinity of the reservoir is not favorable for other gel treatments.
- The PPG injection process is simple compared to in-situ gel treatments.
- The treatment cost is low due to the little requirement of workover.

The reasons for choosing wells Bin 24-4 and 24-17 were:

- High contrast in the vertical fluid distribution (see the injection before treatment in Figures 2-7 and 2-8).
- Most of the offset producers had a water cut of above 90%.
- Both wells were previously unsuccessfully treated with other water control techniques.

The information for the two injection wells are shown on Table 2-3. Table 2-4 provides information for the offset producers of well Bin 24-4 and Table 2-5 for the the offset producers of well Bin 24-17.

The equipment designed for PPG injection is shown on Figure 2-9. The particles and water were mixed prior to injection in a standard tank and then were injected into the formation through the tubing string. Table 2-6 shows the designed injection parameters for the two well treatments.

Figure 2-10 shows the monitored real time pressure response during PPG injection. The pressure curve in both tests can be divided in two parts: In the first part the injection pressure increase steadily indicating the buildup of resistance to flow, the second part is almost a plateau which can be attributed to the in-depth propagation of the gel particles.

Treatment results

The profile surveys for the two injection wells indicated significant change of the vertical fluid distribution for the well Bin 24-4 (Fig. 2-7). After treatment, one of the two initial water entering interval was almost shutoff and the water was redistributed toward the six remaining open intervals. For well Bin 24-17 (Fig. 2-8) the distribution of the fluid was much more homogeneous than that before treatment. The sweep in the low permeability (S_4) layer was improved in both treatments.

For wells Bin 24-4 and bin 24-17, respectively, three and two offset wells responded favorably to the job. The average water-cut decreased and a total of 2,278 t of incremental oil was produced within 8 months following the treatment. Table 2-7 gives the data for the responding producing wells.

Table 2-3. Parameters of treated two injection wells

Well	Depth (m)	Injecting since	Total injection interval (m)	Number of injection layers
Bin 24-4	1465	12/05/90	14.6	7
Bin 24-17	1532	3/1193	15.9	5

Table 2-4. Offset production wells of Bin24-4

Producer	Produced fluids (t/d)	Produced oil (t/d)	Water-cut (%)
B24-1	193.0	10.3	94.7
B24-3	67.7	2.3	95.8
B24-10	130.0	7.0	94.6
B24-2	53.2	8.4	84.3
B24-5	24.4	3.7	84.8

Table 2-5. Offset production wells for Bin-17

Producer	Produced fluids (t/d)	Produced oil (t/d)	Water-cut (%)
B24-9	29.7	2.8	90.4
B259	37.9	2.8	92.7
B24-15	72.1	6.2	91.4
B24-14	15.1	4.1	76.1

Table 2-6. Designed parameters for both treatments

Well	Particle size (mesh)	Particle concentration (%weight)	Injection pressure (MPa)	Treatment duration (min)
Bin 24-4	20-40	5~10	13	320
Bin 24-17	20-40	5~10	10	350

Table 2-7. Production results 8 months after PPG treatments

Producer Well	Produced fluids(t)	Produced oil (t)	Water-cut (%)	Total incremental oil (t)
B24-3	45.4	2.5	94.4	731
B24-10	167	10.3	93.8	728
B24-9	30.4	3.3	89.2	210
B24-15	107	11.2	89.6	1138
B24-14	8.6	3.9	54	62
Total	358.4	31.2		2278

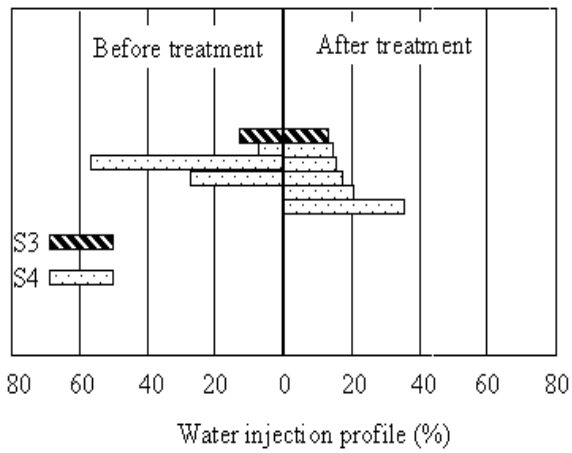


Figure 2-7. Water Injection Profile of Well Bin-24

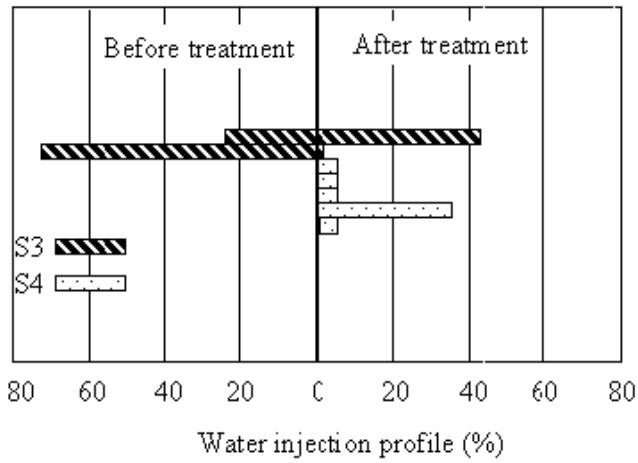
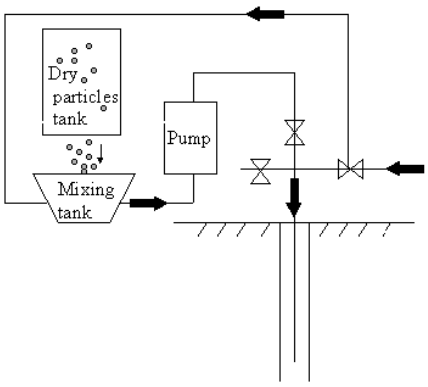


Figure 2-8. Water injection profile of Well Bin24-17.



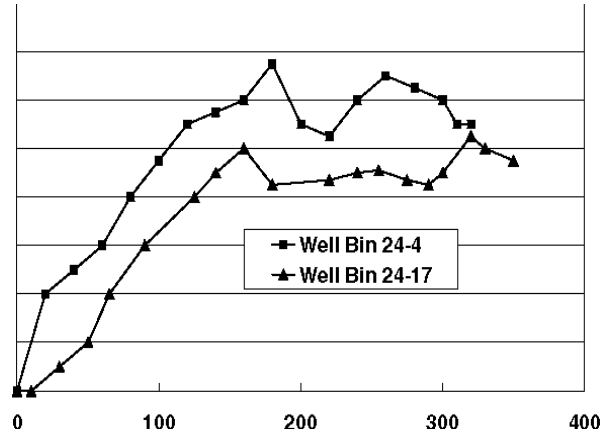


Fig. 2-9. Schematic of Surface Facility for PPG injection. **Fig. 2-10. Real-time pressure results for PPG injection.**

Application in Polymer Flooding Areas

Four injection wells in polymer flooding areas were treated using PPG to control conformance in LMD reservoir, Daqing oilfield, PetroChina. Totally 18,400 m^3 of PPG suspension (99 tons of dry particles) were injected into the four injection wells. The treatment results were very successful as indicated by the following:

The injection pressure for each well significantly increased after treatment. The average water injection pressure after treatment increased 0.6 MPa comparing to the injection pressure before treatment at same injection rates, shown as Table 2-8.

Table 2-8. Comparison of Injection pressure comparion before and after PPG treatment

Well No	PPG Suspension Volume (m^3)	Dry PPG Weight (t)	Before treatment		After treatment	
			Injection rate (m^3/d)	Injection pressure (MPa)	Injection rate (m^3/d)	Injection Pressure (MPa)
4-P163	4400	23	200	11.0	200	11.9
6- P 173	4800	28	150	12.5	150	12.9
5- P 162	4600	24	200	12.4	200	13.1
8- P 122	4600	24	130	14.6	130	14.9

Injection profiles were greatly improved. The well 6-P173 started to inject polymer in Feb 1999 and a total of $31.57\times10^4 m^3$ of 1000 ppm polymer solution was injected before PPG treatment. The polymer injection pressure was 13.2 MPa at the injection rate of 200 m^3/d. The relative polymer absorbent rate of Layer PI2 changed from 96.49% to 52.67% due to the treatment and the reduced absorbent rate contributed to other layers.

The pressure drop rate during pressure drawdown test became slow

Figure 2-11 compared the drawdown test results of well 4-P163 before and after treatment. The pressure drop decreased very quickly before treatment, which indicates there might be fracture or fracture-like channels responsible for the fast pressure drop. The pressure drop rate changes slowly after treatment, indicating that the channels have been effectively plugged.

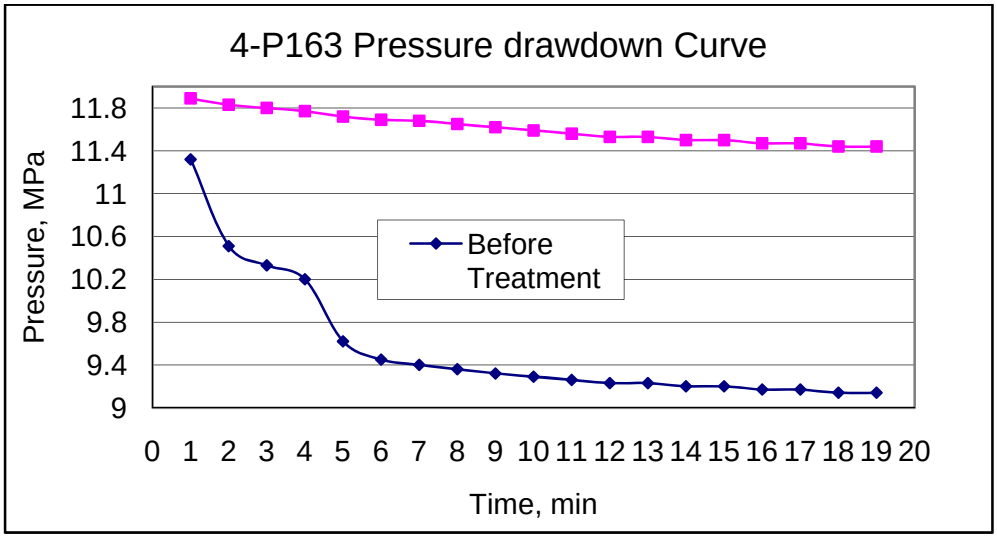


Figure 2-11. Well 4-P163 Pressure drawdown comparison before and after treatment.

The oil production rates of connected wells were increased and the water production rates were decreased after PPG treatment. Figure 2-11 compares the oil production rates, water cut of connected 11 production wells before and after PPG treatments. The average oil increased 3.8 t and water cut reduced 2.8% and produced polymer concentration reduced 33 mg/L due to the PPG treatments.

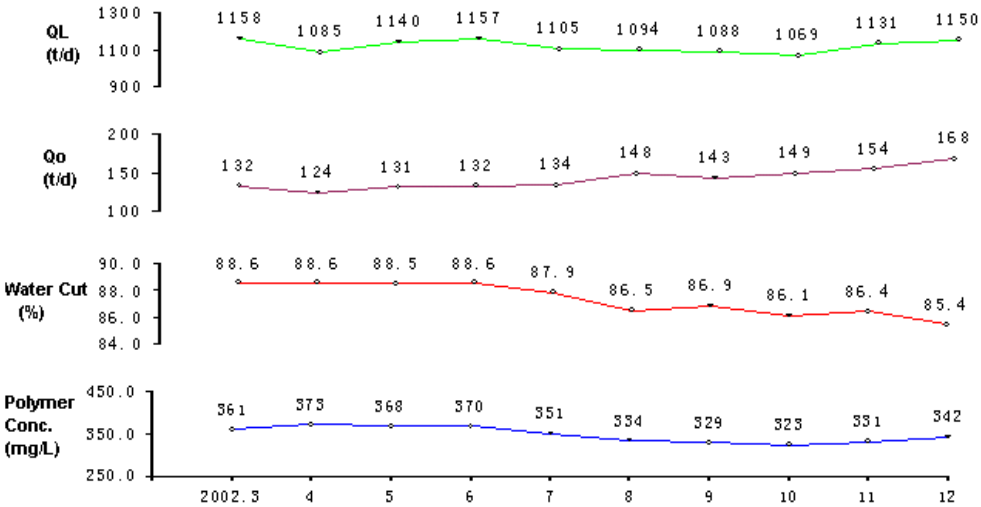


Figure 2-12. Production curves of the production wells connected to the four treated wells.

Remediate Unwanted Communication in a CO_2 Flooding Reservoir.

Larkin et al (2008, Paper SPE 113305) described a case study of conformance problems aggravated by apparent direct communication channels between injector and offset producer(s) in certain pattens of SACROC unit CO_2 EOR project in Scurry County an, Texas and their practice of controlling the confornmce by the injection of swelling gel particles---crystal polymer, CP.

Reservoir Characterization: SACROC Unit within the Kelly-Synder field is located outside the city of Snyder in Scurry County, TX. It was discovered in November 1948, and a water flood started in 1954 and CO_2 flood in 1972. To date, the field has 1956 well bores and 815 active in its 50,000 acres (approx.) with average depth 6,700 ft with average net pay thickness 260' (up to 800'), average Porosity 7.6%, and average permeability 19.4 md. The Unit's reef formation is characterized as highly heterogeneous and short circuit or unwanted communication paths have resulted in serious sweeping problems and operational problems caused by excessive production of CO_2.

Particle Gel Treatment. Superabsorbent Polymers (SAP) was injected in multiple wells to remediate their short circuits and reduce CO_2 production. The properties of injected particle polymers are listed as follow:

- 100% Cross-linked, synthetic (sodium acrylate based)
- Links created from identical acrylic acid monomers neutralized with caustic acid
- Swell 300 to 800 x (various solutions)
- Swelling time relative to size, smaller creates more surface area and faster swelling; general range 30 minutes to 3 hours
- Solutions: fresh water (use caution), produced oil, diesel, brines, produced water (salinity), sodium silicate solutions
- Multiple size grades – solid material
    - Sizes: ground 300-400 mesh, 0.5 mm, 1 mm, 2 mm, 4 mm, and 14 mm diameter
- Does not absorb on rock (wettability unaffected)
- Environmentally friendly
- Acid resistant
- Confined to fractures
- Resistant to degradation by CO2, bacteria and temperature below 275 F.

Treatments Results. The particles with size up to 4 mm were successfully injected into all selected wells. The injection profiles were improved and gas production was reduced with the increase of oil

production. The field application results showed that the particle treatment is a cost-effective profile modification option for CO_2 Flooding oilfields. More detailed information can be found in pages 8-10 of paper SPE 113305.

Plug Void Conduit in Anton Irish Field (Pyziak and Smith, 2006, Updated …and Smith, 2006, SPE 103044)

Reservoir Description. The Anton Irish field, a carbonate reservoir located in West Texas was discovered in 1945. The field was then utilized for a produced gas pressure maintenance project in 1950 and converted to a waterflood in 1969. CO2 Flooding began in 1997 and currently accounts for approximately 85% of the unit production. The rapid breakthrough of injection fluids (CO2 or Water) leads to excessive cycling of the injection fluid through conduits rather than sweeping the reservoir matrix. The downhole video inspection of the wellbore (injection #63) indicated that the well have a larger fracture similar to image in Figure 2-13.

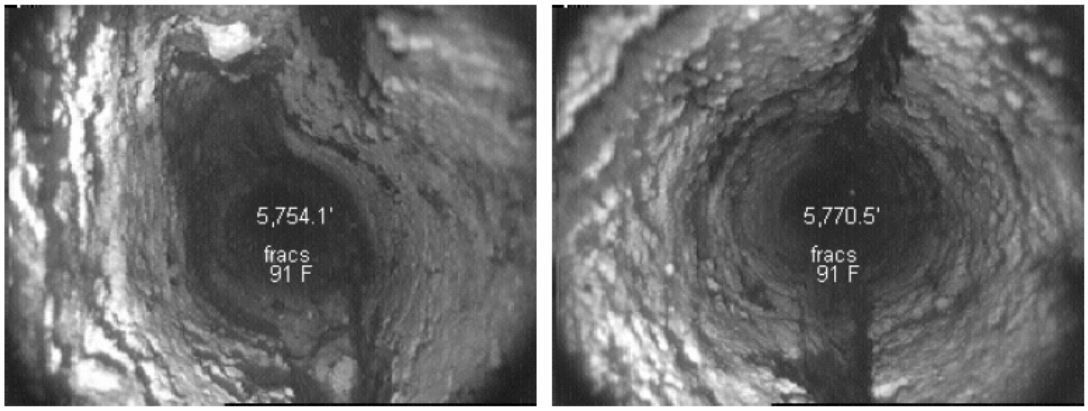


Figure 2-13. Fractures in AICU 63 Wellbore (Courtesy, Pyziak and Smith, 2006)

Particle gel treatment. To fill the void conduit in the well, a swelling polycrystalline material (similar with PPG) where they have seen some benefit of using the product in smaller features. They injected 30,000 lbs of the swelling polycrystals at a mixed ratio of 0.25 lbs/gal which was carried by a 9.5 lbs/gal brine. The swelling ratio of the particle gel in the brine is around 35. It was estimated the the product would occupy a void volume of appropriately 3,000 bbls when they were fully swelling. The pumping flow rate is 4-5 BPM. The injection continues for more than 10 hrs and Figure 2-14 showed the real-time pressure change during the particle injection. It can be seen a steady flow was seen, which possibly indicate the void or conduit feature were filling.

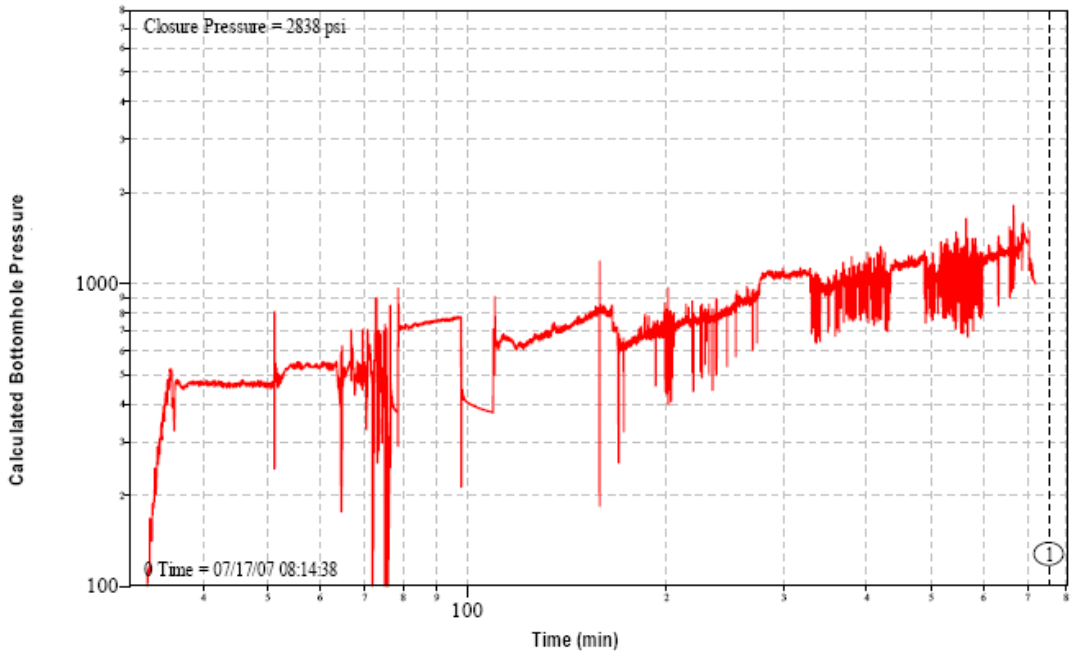


Figure 2-14. Real time pressure monitoring resuits during particle gel injection for the well AICU63.

Results. After initial completion of the treatment and 36 hours of shut-in, the well could not be injected. The well was cleaned out with coil tubing and the injectivity was shown in Figure 2-15.

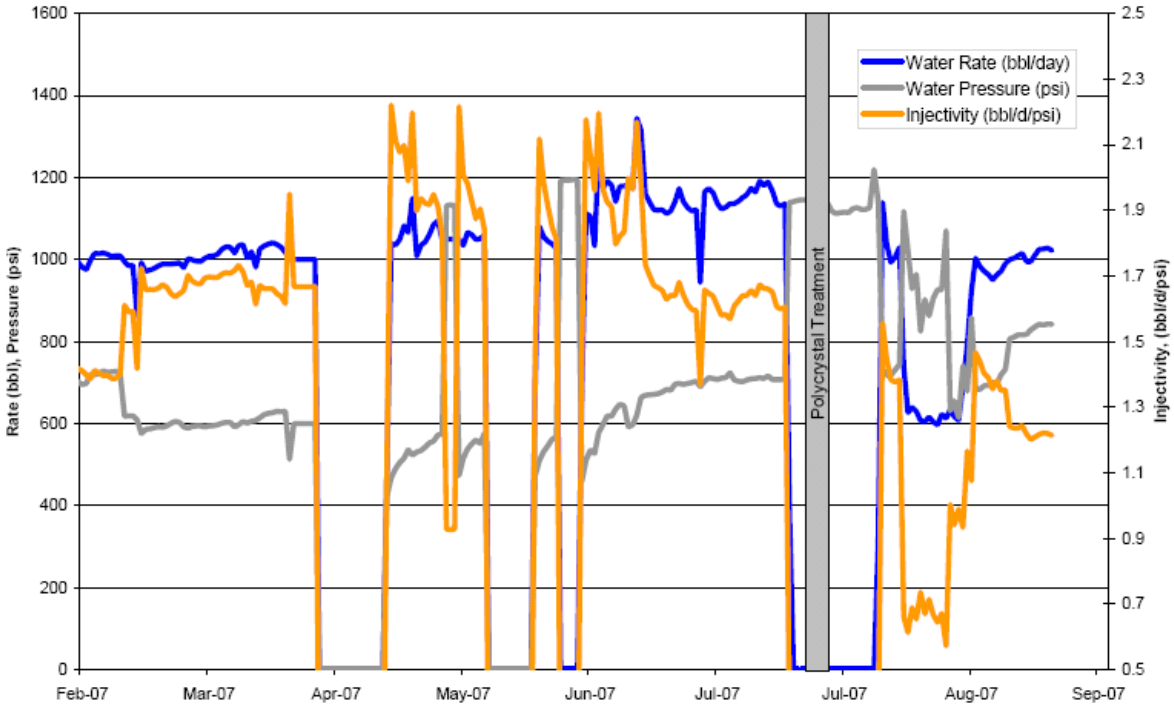


Figure 2-15. The injectivity of AICU 63.

Case Study on Large volume of PPG treatments in Daqing

The selected pilot is in one block of Lamadian reservoir in Daqing oilfield shown in Fig. 2-15.

Their production intervals are PI_4 to GI_{4+5}. Each individual zone is relatively thick and their inner-layer heterogeneity is very serious. The oil-bearing area is 2.43 km^2. The initial-oil-in-place is 594 $\times 10^4$ t. The block was produced for more than 30 years and the average water cut was 95.4% before gel treatments. The reservoir temperature is around 40 ºC and its formation water salinity is around 4,000 mg/l.

Criteria to Well Candidate Selection

The selection of a good candidate is based on the comprehensive understanding on the reservoir geology, wellbore and near wellbore conditions, reservoir surveillance results, and static and dynamic reservoir information. The well candidate selection criteria were set as follows for the large volume of PPG treatments in Daqing:

- The well must be located in the main sand body of the fluvial depositional reservoir with thick oil pay zone and good connectivity with adjacent producers.
- The well must have strong injectivity; the water injection pressure and starting pressure are lower than their average of the whole block.
- The connected producers have relatively high average water cut compared to other well groups.
- Vertical or areal heterogeneity is very serious, and the inner-layer permeability contrast is large, and both injection profile and the production profiles of connected production wells are extremely not homogenous.
- The degree of water-flooded region is very different; there exist middle, low and none flushed zones.

Four injection wells, 7-1827, 7-1927, 8-1827 and 9-1927, were selected based on these criteria and comprehensive geological and engineering understanding on the block. Large volume PPG treatments were carried out from the year of 2003 to 2004 and the target zone was PII. The distance of each injection and its connected edge producer is 300 m. There are 46 production wells connected to these four treated wells. Twenty-three of them are only produced from PII and the other 23 are commingled production from the interval PII and other intervals. Table 2-9 shows the basic parameters for the selected four wells. In the table, the maximum permeability refers to the permeability of the most permeable portion of that specified intervals from well logging. The starting pressure refers to the minimum wellhead pressure that water starts to enter the formation. That is, the water cannot enter the formation if the injection pressure is smaller than the starting pressure. PI is the pressure index which is from the pressure drawdown test for a period of 90 minutes after an injection well is shut down. The PI(90) is calculated from the equation:

$$PI\ (t) = \frac{\int_0^T p(t)dt}{T} \qquad (2\text{-}1)$$

Where

PI (t)---Pressure Index, MPa

P(t)---Pressure at the time t after a well is shut in, MPa.

t---shut in time, min, usually t is set as 90 minutes.

PPG Selection

The selection of PPG mainly considers its compatibility with produced water, swelling ratio, strength after swollen in the injection water and particle size (Bai, 2001, Liu, 2004). Six samples were evaluated for best PPG candidate for the pilot. Results show all PPGs have good compacity with produced water in the pilot and they are thermally stable at reservoir temperature for more than 2 years. Table 2-10 shows the evaluation results for PPG size, swelling ratio, pressure resistance, and breakthrough pressure. All particle dispersions were prepared by produced water from the pilot. The PPG size was seived by screens with proper mesh sizes. The swelling ratio is the gel mass ratio after and before swelling. The pressure resistance is defined as the minimum pressure that the swollen particle resists before breaking into smaller particles. The breakthrough pressure is defined as the minimum water injection pressure that water can be injected after PPG is placed in the cores and the data in the table is measured using the cores with permeabilities of 3-3.5 μm^2 by the injection of 1,000 mg/l of 250 mesh PPG particles (61 μm). The WT product was selected for the pilot because it had relatively high swelling ratio and enough strength.

PPG Treatment Design

Design of Injection Parameters

Reservoir simulation was run to optimize PPG dispersion volume in terms of the input-output ratio. It is assumed that the PPG dispersion only enter those fully flushed areas with residual oil while not low- and none-flushed areas. After the gel placement, the permeability of those areas that are placed by PPG is equal to the permeability of low permeability zone. This assumption is based on the gel property of which gel can reduce permeability to same level (Bai, 1997). The equation to calculate input-output ratio is as follow:

$$R = \frac{e_3 Q_p + e_4 + e_5 + e_6}{e_1 \Delta Q_o + e_2 \Delta Q_w} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2\text{-}2)$$

Where

e_1 ---oil price, \$/t;

e_2 ---produced water treatment cost, \$/m^3;

e_3 ---PPG price, \$/t;

e_4 ---operation cost for PPG injection, \$;

e_5---well service cost due to PPG treatment, \$;

e_6 ---well testing costs, \$;

Q_p---dry PPG particle cost, \$/t;

ΔQ_o---incremental oil, t;

ΔQ_w---decreased oil, t;

R---input-output ratio.

The designed concentration was based on previous successful field experience and laboratory coreflooding testing results. Coreflooding tests showed that low concentration PPG particles had less relatively stable injection pressure and could easier move into in-depth of a reservoir than high concentration PPG particles (Bai, 2001). Field application also demonstrated that low concentration large volume of PPG injection is a key to a successful PPG treatment. Before the first successful application of PPG treatment in Zhongyuan (Bai, 2007), PPG was used in a number of wells but was not very successful. Comparing to those successful treatments, the main difference was that those unsuccessful treatments used high concentration or small amount of PPG. High concentration PPG injection may result in a vigorously vibrating bottom hole pressure, which may cause new hydraulically fractures near wellbore. Most successful applications in China were used PPG suspension with concentration below 5,000 mg/l. The designed concentration was given in a range for each well and the actual concentration was planned to adjust according to real-time injection pressure reponse during PPG injection. To make the front PPG slug move into in-depth, PPG injection was designed to start from small size particle and would be adjusted according to the real-time observed pressure during PPG injection. Low injection rate, similar to previous water injection rate, was designed to reduce PPG damage on low-permeability oil zone. The pilot is close to polymer flooding area and it is easy to get polymer solution, so 200 mg/L polymer was used to better suspend and carry PPG particles. Table 2-11 shows the optimized PPG dispersion volume, PPG weight and other designed injection parameters for each treated well.

Practical Field Injection Parameters

The total 132 tons of PPG with a cumulative suspension volume of 56,268 m^3 was injected. Comparing with the design, six more tons of PPG was injected with additional volume of 3,939 m^3.

Table 2-12 compares the design and practical results. The main reason to increase PPG amount was that the pressure did not increase as expected for wells 7-1937 and 7-1827. The volume of PPG suspension was increased because the well 9-1827 was difficult to inject using designed concentration of 2,000-3,000 mg/l. So the PPG concentration was reduced to prevent the PPG injection pressure from fracturing the reservoir. The volume was increased 2,922 m^3 after its PPG concentration decreased. Mutiple slugs were injected for each well. Tables 2-13 to 2-16 summarize the PPG suspension volume, particle size, swollen PPG volume, and PPG weight for each slug of each well. The swollen particle volume refers to the total particle volume after swelling, which is calculated using the swelling ratio of 70 and dry PPG density of 1.8 g/cm^3.

Real-time Monitoring of PPG Injection

The wells 7-1937 and 7-1827 started to inject at September 5, 2003 and ended at Jan 10 and Jan 31, separately. The Wells 8-1827 and 9-1827 started to inject PPG at September 26, 2003 and ended at Feb 3, 2004, respectively. The real-time pressure was monitored for each well during PPG injection. Particle sizes and PPG concentrations were adjusted according to real-time pressure change. Figures 2-16 to 2-19 show the pressure history, particle sizes and PPG suspension volume for four wells seperately. As shown in each figure, the injection pressure did not increase very fast and very much during PPG injections. No injectivity problem existed in these wells even though they were claimed no fractures in these wells. In addition, there is no particle production from connected adjacent producers during PPG injection.

Reservoir Performance during and after PPG injection

Two methods were used to evaluate the reservoir performance during and after PPG treatment. One method is to measure injection profile, which reflects the plugging effect of PPG on different zones near wellbore. Another method is to perform welltest, including starting pressure, injection pressure at the same injection flow rate as that before treatment, and pressure drawdown test for pressure index PI(90). These parameters reflect the PPG plugging in the in-depth of the reservoir. The pressure gauge was set at the depth of 500 m below the wellhead when drawdown pressure was measured.

Well test results. The pressure drawdown test was performed when 30% of accumulative PPG suspension was injected for each well. As shown in the Table 2-17, the PI(90)s were increased 7.43, 0.93, and 0.42 MPa for wells 7-1937, 8-1827 and 9-1827, respectively. The injection pressure of well 7-1827 was increased 1.2 MPa but the PI(90) did not change. After finishing PPG treatment, the pressure drawdown test was performed again for each well. Table 2-18 compared the PI(90) and injection pressure before and after treatments. The PI(90)s and injection pressure were significantly increased for

each well. Figures 2-20 to 2-23 show the pressure drawdown test curves before, during and after gel treatments for each treated well.

Water injection profiles. The water injection profile was measured for each well when 30% of accumulative PPG suspension was injected and after gel treatments. The well 7-1827 not measured during PPG injection because a block in the wellbore prevented the measurement. Figures 2-24 to 2-27 show the history of injection profiles for each well. Table 2-19 summarizes the injection profile change before and after treatments. All injection profiles were significantly improved after treatments.

Production Performance

The treatments resulted in increased oil production and decreased water cut. Table 12 showed the results of 26 comparable wells which connected to treated wells and had no other well services and operations. After treatments, the oil production rate increased 34.8 t/d and water cut reduced 0.94% for the 26 wells at the condition without considering production decline. Figure 2-28 shows 24 well production curves before, during and after PPG treatment. Before the PPG treatment, oil rate graduately decreased and water cut increased. Immediately after PPG start to be injected, the oil decline trend was decreased and the oil rate increased after PPG treatment. The cumulative incremental oil is about 15,000 tons until March 2005, which means 113 tons oil increase per ton of PPG injection. The output-input ratio can be calculated as follow:

PPG costs: $132 \text{ tons} \times (1.46 \times 10^4) \text{ RMB/ton} = 192.72 \times 10^4 \text{ RMB}$

PPG injection costs: $4 \text{ wells} \times (18 \times 10^4) \text{ RMB/well} = 72 \times 10^4 \text{ RMB}$

Injection profile measurement: $8 \text{ times} \times (1.1 \times 10^4) \text{ RMB/time} = 9.9 \times 10^4 \text{ RMB}$

Pressure drawdown test: $12 \text{ times} \times (0.8 \times 10^4) \text{ RMB/time} = 9.6 \times 10^4 \text{ RMB}$

Total input: 284.22×10^4 RMB

Oil price: 2,100 RMB/ton (~40 $/bbl)

Output from oil sales: $15{,}000 \text{ tons} \times (0.21 \times 10^4) \text{ RMB/ton} = 3150 \times 10^4 \text{ RMB}$

Output-Input ratio: 11.08

Discussion

Seright (Seright, 1994) suggested to use the following simple injectivity calculation to establish the nature of a channeling problem.

$$\frac{q}{p_e - p_{wf}} = \frac{\sum kh}{141.2\,\mu \ln \frac{r_e}{r_w}} \qquad (2\text{-}3)$$

Where q --- Injection rate, bbl/d

p_e --- Reservoir pressure, psi

p_{wf} --- Bottom hole flowing pressure, psi

h --- Perforated net pay practicle thickness that absorb water, ft;

k --- Average permeability of perforated net pay, md;

r_e --- Drainage radius, ft;

r_w --- Wellbore radius, ft;

If the injectivity calculated by the right side of eq. 3 is substantially less than the actual q/Δp, then a fracture or formation part is probably present. When calculation is made using above equation, the formation pressure p_e and bottom hole flowing pressure p_{wf} have to be used. In practical, it is not easy to obtain accurate data for p_e and p_{wf}, so modified equation can be used to avoid the use of p_e and p_{wf}. The equation is as follow:

$$\frac{q_1 - q_2}{p_{wh1} - p_{wh2}} = \frac{\sum kh}{141.2\,\mu \ln \frac{r_e}{r_w}} \qquad \textbf{(2-4)}$$

Where

p_{wh1}---wellhead pressure at flow rate q_1,

p_{wh2}---wellhead pressure at flow rate q_2,

The value of (q_1, p_{wh1}) and (q_2, p_{wh2}) can be obtained from step-rate injectivity test. Similar to Seright's criteria, if the calculation from the right side of Eq. 4 is substantially less than the actual $(q_1-q_2)/(p_{wh1}-p_{wh2})$, the a fracture or formation part is probably present. Actually the $(q_1-q_2)/(p_{wh1}-p_{wh2})$ is the slope of the q - p_{wh} plot from step rate tests.

Figures 2-29 to 2-32 show the step rate test results and fitting equation for each layer of each treated well. Table 13 shows the calculation results using eq. 4 and the step test fitting equation. The drainage radius was 492 ft and the wellbore radius used 0.328 ft and water viscosity was 0.6 cp. The height "h" was calculated by net pay thickness times the percentage of net pay thickness that absorbed main water shown in Table 1. The $(q_1-q_2)/(p_{wh1}-p_{wh2})$ was multiplied by water absorbed percentage of main water absorbing zones shown in Table 1 for the left side of the equation. Comparing the last two columns in the Table, it is shown that the left one is smaller than the right one. Therefore, the simple calculation does indicate the existence of fractures in these wells.

Although the above calculation does not show the existence of obvious fractures in these wells, coreflooding tests uniquely demonstrate the porous media should have super-K channel with permeability of more than 50 Darcy if mm-size particles, 0.06-0.9 mm, can be injected into the porous

media without significant injection pressure increase (Bai, 2001). If we assume there are fractures in each well. The fracture volume can be calculated by the following equations.

For vertical fracture:

$$V = 2 \cdot h_f \cdot w_f \cdot L_f \quad \text{.....(2-5)}$$

Where: V --- fracture volume, m^3

h_f--- fracture height, m

w_f--- fracture width, m

L_f--- fracutre length, m.

For horizontal fracture:

$$V = \pi L_f^{\ 2} \cdot w_f \quad \text{.....(2-6)}$$

If we assume the fracture is vertical fracture in the area, and the fracture width is 5 mm (usually 3-8 mm) and the fracture length is equal to well distance of 300 m, the height of fracture is 10 m (7.5-11 m for the four treated wells) the calculated fracture volume is 30 m^3.

If we assume the fracture is horizontal in the area, and L_f=300, w_f = 5 mm, the fractured volume is 1413 m^3.

Comparing the fracture volume to the swollen particle volume shown in Tables 5-9, it indicates horizontal fractures are more possible for the reservoir. In fact, the reservoir depth is around 1,000 m and many people in Daqing have claimed the hydraulically fracture should be horizontal for this area.

Conclusions

1. Preformed gels overcome some distinct drawbacks inherent in in-situ gelation systems. Millimeter-sized preformed particle gel (PPG) is unique due to its advantages over other particle gels.
2. PPG has been successfully injected into the reservoir with and without initial fractures and no significant injectivity problem was found.
3. PPG has been successfully treated the reservoirs with different conditions, including the reservoir with high salinity high temperature, reservoir with high temperature high salinity, reservoir with thick heterogeneous zones, reservoir with severe sand production, reservoir with polymer flooding and reservoirs with CO_2 flooding.
4. Large volume PPG treatments were presented in details. The results showed that

- There is no injectivity problem for large volume of mm-size PPG treatment for most wells in mature oilfields. All four wells in the case were successfully injected more than 10,000 m^3 of PPG suspension without abrupt pressure increase.
- Real-time PPG injection pressure response can be used to adjust PPG particle size concentration to better fit reservoir. Real-time monitoring data can be used to adjust previous design for better gel treatment results.
- PPG treatment is a cost-effective method to control conformance. The four treatments successfully resulted in improved oil production and reduced water production and better injection profile.
- Simple calculation does not indicate the existence of fracture in these wells, but core flooding test did indicate there should exist super-high permeability channels otherwise such large amount of PPG cannot be steadily injected into these wells.
- The vertical and horizontal fracture volume calculations indicate it is more probable to have horizontal fractures than vertical fractures if there exist fractures in these wells.

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Table 2-9. Basic parameters of four treated wells before PPG injection

Well Name	Objective Zones	Gross Thickness (m)	Net pay thickness (m)	k_{max} (μm^2)	Starting pressure (MPa)	Wellhead Injection Pressure (MPa)	Injection Rate (m^3/d)	Main water-absorbing zones		PI (90) (MPa)
								Thickness (%)	Water Asborbed (%)	
7-1827	PII 1-6	7.4	6.7	0.50	4.5	10.0	58	14.49	81.97	10.80
	PII 5-9	5.2	4.3	0.36	5.0	10.0	60	17.78	89.29	10.80
7-1937	PII 1-9u	10.8	10.5	0.46	1.0	11.5	56	28.57	56.96	6.95
	PII 1-9d				1.5	11.5	47			6.95
8-1827	PII 4-7	7.6	7.4	0.28	6.0	11.2	79	27.78	78.21	10.31
	PII 7-9	1.6	1.6	0.22	5.7	11.2	43	46.00	79.51	10.31
9-1827	PII 1-6	8.0	7.5	0.24	8.5	10.7	63	45.45	74.07	11.58

Table 2-10. Evaluation results for six samples

No.	Product Name	Particle Size (mm)	Swelling Ratio		Pressure Resistance (MPa)	Breakthrough Pressure (MPa/m)	Notes
			Intial (t =10 min)	Final			
1	GS	3-5	5	117	/	4.1	Very weak
2	GS	2-3	15	153	/		
3	WT	3-5	10	83	1.2	10.7	
4	WT	2-3	22	90	0.8		
5	SAP	3-5	3	17	2.3	17.9	
6	SAP	2-3	5	31	1.9		

Table 2-11. Designed injection parameters for four well PPG treatments

Well Name	Water Injection Rate before treatment (m^3/d)	PPG Injection rate (m^3/d)	Dry PPG (kg)	Particle size (mm)	PPG Suspension Volume (m^3)	Concentration (mg/l)	Maximu Pressure limitation (MPa)
7-1937	116	130	32,000	0.06 - 2.00	13,445	2,000-3,000	12.5
7-1827	108	128	41,000	0.16 –2.00	17,135	2,000-3,000	13.0
8-1827	121	133	32,000	0.06 – 0.90	13,214	2,000-3,000	14.0
9-1827	83	138	21,000	0.06 – 0.90	8,536	2,000-3,000	14.0

Table 2-12. Comparison of designed and practical injection parameters

Well Name	Duration of PPG treatment	Practical injection time (D)	Design			Practical Injection			Difference	
			Dry PPG (t)	PPG Suspension Volume (m^3)	PPG concentration (mg/l)	Dry PPG Weight (t)	PPG Suspension Volume (m^3)	PPG Concentration (mg/l)	Dry PPG weight (t)	PPG Suspension Volume (m^3)
7-1937	2003.9.5-2004.1.10	119	32	13,445	2,000 ~ 3,000	35	13,528	2,587	3	83
7-1827	2003.9.5-2004.1.31	124	41	17,135	2,000 ~ 3,000	43	17,625	2,440	2	490
8-1827	2003.9.25-2004.2.3	97	32	13,214	2,000 ~ 3,000	32	13,658	2,343	0	444
9-1827	2003.9.25-2004.2.3	108	21	8,536	2,000 ~ 3,000	22	11,458	1,920	1	2,922
Total			126	52,330		132	56,269	2,346	6	3,939

Table 2-13. Practical PPG injection parameters for Well 7-1827

Start Injection Date	09/05/2003	End date		01/31/2004	
Practical Injection Duration	148 Days	Injection rate (m^3/d)		128	
Dried PPG Weight (t)	43	PPG concentration (mg/l)		2,240	
Initial injection pressure	5.6 MPa	Maximum Injection Pressure (MPa)		8.6	
Slugs					
	1st slug	2nd slug	3rd slug	4th slug	Total
Particle size (mm)	0.16-0.45	0.45-0.90	0.90-2.0	2.0-3.0	0.16-3.0
Dry particle weight (kg)	6,000	25,350	11,300	350	43,000
Swollen particle volume (m^3)	233	986	439	31	1,689
PPG Suspension volume (m^3)	2,261	10,162	3,678	1524	17,625
Notes	Around 200 ppm polymer solution was used as a carrier fluid				

Table 2-14. Practical PPG injection parameters for Well 7-1937

Start Injection Date	09/05/2003	End date			01/10/2004	
Practical Injection Duration	124 Days	Injection rate (m^3/d)			130	
Dried PPG Weight (t)	35	PPG concentration (mg/l)			2,587	
Initial injection pressure	4.9 MPa	Maximum Injection Pressure (MPa)			.8.2	
Slugs						
	1st slug	2nd slug	3rd slug	4th slug	5th slug	Total
Particle size (mm)	0.06-0.16	0.16-0.45	0.45-0.90	0.90-2.0	2.0-3.0	0.06-3.0
Dry particle weight (kg)	2,312	2,925	16,252	7,473	6,038	35,000
Swollen particle volume (m^3)	90	114	632	291	235	1,362
PPG Suspension volume (m^3)	909	1,420	6,877	2,381	1,941	13,528
Notes	Around 200 ppm polymer solution was used as a carrier fluid					

Table 2-15. Practical PPG injection parameters for Well 8-1827

Start Injection Date	09/22/2003	End date		02/03/2004
Practical Injection Duration	134 Days	Injection rate (m^3/d)		138
Dry PPG Weight (t)	32	PPG concentration (mg/l)		2,343
Initial injection pressure	9.0 MPa	Maximum Injection Pressure (MPa)		11.60
Slugs				
	1st slug	2nd slug	3rd slug	Total
Particle size (mm)	0.06-0.16	0.16-0.45	0.45-0.9	0.06-0.90
Dry particle weight (kg)	19,450	7,850	6,700	34,000
Swollen particle volume (m^3)	756	305	261	1,322
PPG Suspension volume (m^3)	9,447	2,434	1,777	13,528
Notes	Around 200 ppm polymer solution was used as a carrier fluid			

Table 2-16. Practical PPG injection parameters for Well 9-1827

Start Injection Date	09/25/2003	End date		02/03/2004
Practical Injection Duration	131 Days	Injection rate (m^3/d)		138
Dry PPG Weight (t)	22	PPG concentration (mg/l)		1,920
Initial injection pressure	7.6 MPa	Maximum Injection Pressure (MPa)		11.02
Slugs				
	1st slug	2nd slug	3rd slug	Total
Particle size (mm)	0.06-0.16	0.16-0.45	0.45-0.90	0.06-0.90
Dry particle weight (kg)	10,290	5,710	6,000	22,000
Swollen particle volume (m^3)	400	222	233	855
PPG Suspension volume (m^3)	7,586	1,977	1,895	11,458
Notes	Around 200 ppm polymer solution was used as a carrier fluid			

Table 2-17. Pressure test result when 30% PPG was injected

Well Name	Starting Injection Date	Before PPG Injection			After 30% PPG Injection			Difference	
		PI (90)		Injection Pressure (MPa)	PI (90)		Injection Pressure (MPa)	PI(90) (MPa)	Injection Pressure (MPa)
		Measured Date	PI(90) (MPa)		Measured Date	PI(90) (MPa)			
7-1937	9/5/2003	6/11/2003	6.95	5.0	10/21/2003	14.38	7.2	7.43	2.2
7-1827	9/5/2003	8/12/2003	9.12	5.7	10/27/2003	9.13	7.2	0.01	1.3
8-1827	9/24/2003	6/30/2003	10.98	8.8	10/22/2003	11.91	10.7	0.93	1.9
9-1827	9/25/2003	6/30/2003	11.12	6.5	10/16/2003	11.54	9.9	0.42	3.4

Table 2-18. Pressure test result after PPG treatment

Well Name	Before PPG Injection		After PPG Treatment		Difference	
	PI (90) (MPa)	Injection Pressure (MPa)	PI (90) (MPa)	Injection Pressure (MPa)	PI (90) (MPa)	Injection Pressure (MPa)
7-1937	6.95	5.0	10.49	8.2	3.54	3.2
7-1827	9.12	5.7	11.58	8.4	2.46	2.7
8-1827	10.98	8.8	13.72	11.5	2.74	2.7
9-1827	11.12	6.5	13.71	10.6	2.59	4.1

Table 2-19. Water injection profile comparision before and after PPG treatment

Well Name	Target Zone	Water Intake interval	Before Treatment		After Treatment		Difference	
			Percentage to intake water (%)	Water Intake (m^3/d)	Percentage to intake water (%)	Water Intake (m^3/d)	Percentage to intake water (%)	Water Intake (m^3/d)
7-1937	$P_{II_{1-9\underline{U}}}$	Low*	26	7	61	69	35	62
		High*	74	20	39	45	-35	25
	$P_{II_{1-10L}}$	Low	25	16	100	45	75	29
		High	75	49	0	0	-75	-49
7-1827	$P_{II_{1-6}}$	Low	18	11	63.6	35	45.6	24
		High	82	50	31.1	55.3	-50.9	5.3
	$P_{II_{5-9}}$	Low	25	14	100	123	75	109
		High	75	42	0	0	-75	-42
8-1827	$P_{II_{4-9}}$	Low	28	24	88	84	60	60
		High	72	60	12	11	-60	-49
	$P_{II_{7-9}}$	High	100	60	100	35	0	-25
9-1827	$P_{II_{1-6}}$	High	47	45	28	17	-19	-28
		Low	8	8	15	9	7	1
		High	29	28	0	0	-29	-28
		Low	16	15	57	34	41	19

Note: Low refers to the interval with low water intake capacity, and High refers to the interval with high water intake capacity.

Table 2-20. Performance comparsion of 26 connected production wells without other operations

Well type	Number of Producers	Before PPG treatments			After PPG treatment (Aug 2004)			Difference		
		Liquid (t)	Oil (t)	Water cut (%)	Liquid (t)	Oil (t)	Water cut (%)	Liquid (t)	Oil (t)	Water cut (%)
Wells only produced from PII	11	604	26	95.7	563	32.8	94.2	-41	6.8	-1.52
Commingle Wells	15	3717	161	95.7	3644	189	94.8	-73	28	-0.86
Total	26	4321	187	95.7	4207	221.8	94.7	-114	34.8	-0.94

Table 2-21. Determination of potential fractures

Well Name	Layer	k (md)	h (ft)	$(q_1-q_2)/(p_{wh1}-p_{wh2})$ (bbl/psi)	$(q_1-q_2)/(p_{wh1}-p_{wh2})\times f_q$ (bbl/psi)	$kh/(141.2\mu ln(r_e/r_w)$ (bbl/psi)
7-1827	P_{II1-5}	500	3.18	0.617	0.457	2.60
	P_{II5-9}	360	2.51	0.504	0.450	0.87
7--1937	$P_{III1-10}$	460	9.84	0.278	0.158	4.38
8-1827	P_{II4-9}	280	6.74	0.257	0.201	3.05
	P_{II7-9}	220	2.41	0.621	0.494	0.86
9-1827	P_{III1-6}	240	11.18	0.392	0.290	2.60

Note: f_q is the percentage absorbed water of main water-absorbing zones shown in Table 1.

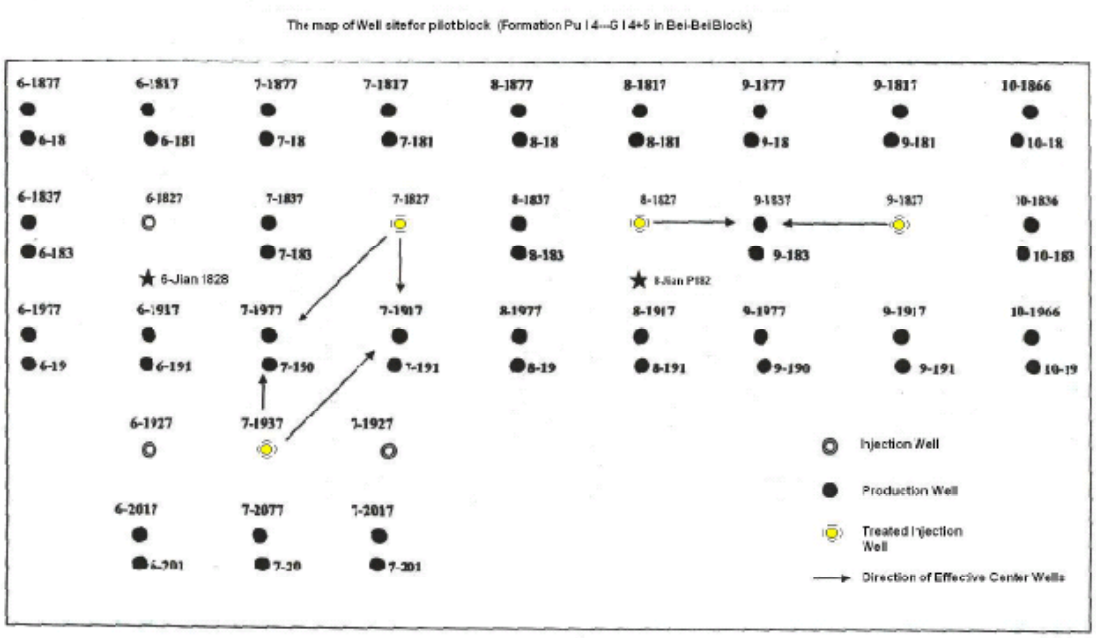


Fig.2-15. Well location map for the pilot.

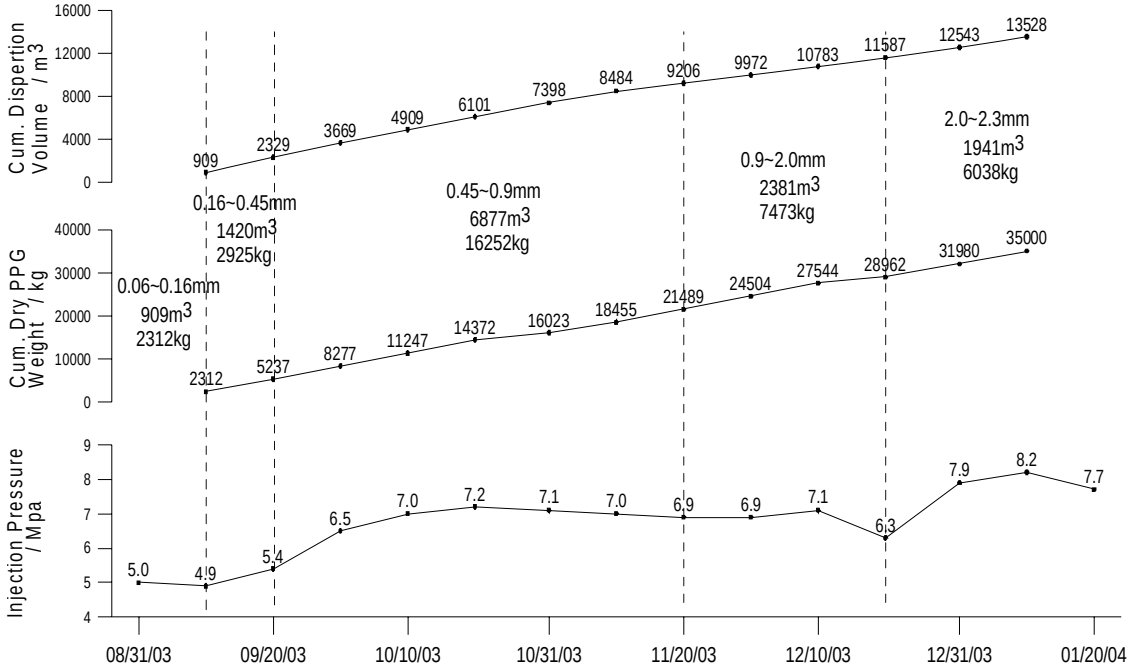


Fig.2-16. PPG Injection Curve for Well 7-1937

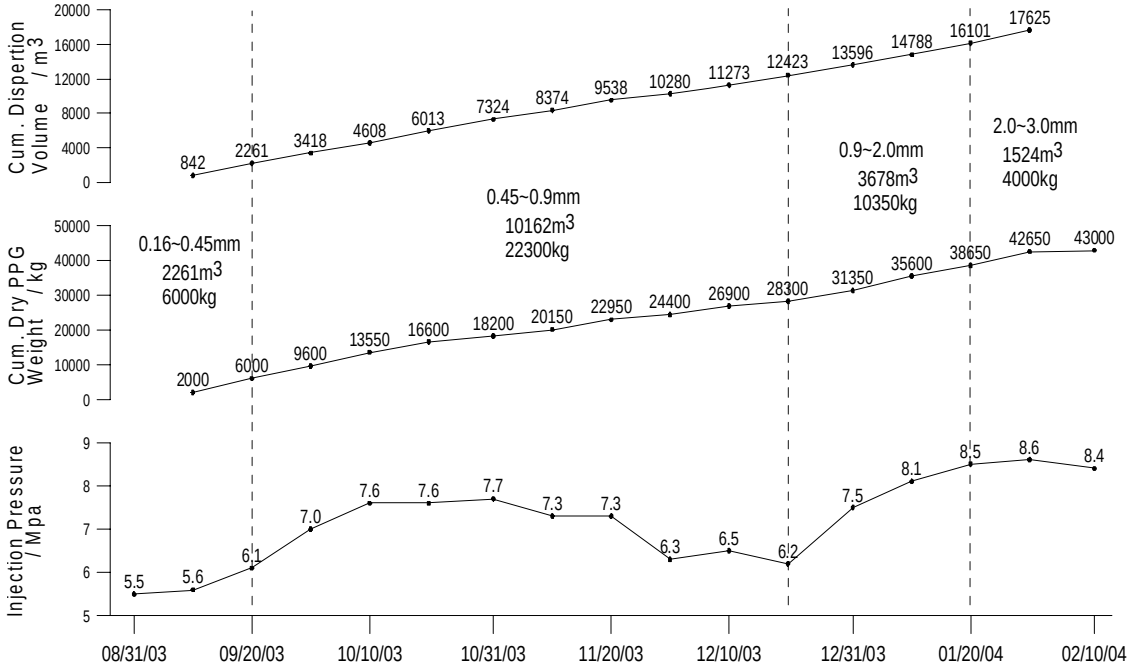


Fig.2-17. PPG Injection Curve for Well 7-1827

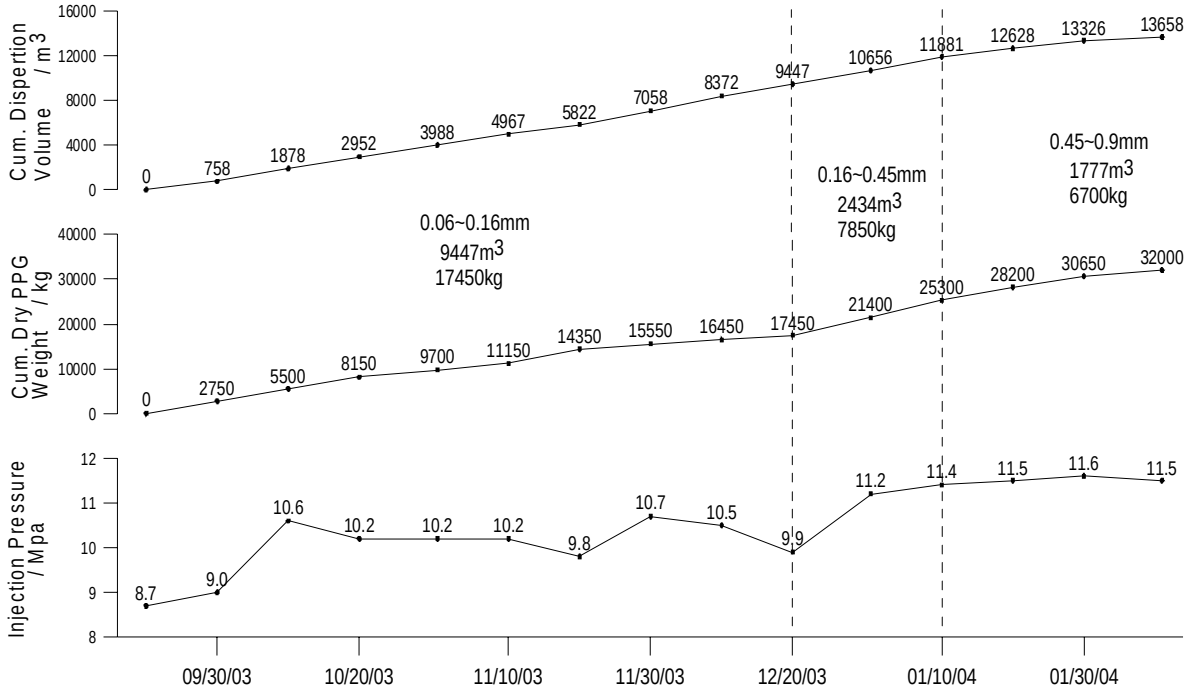


Fig.2-18. PPG injection curve for Well 8-1827

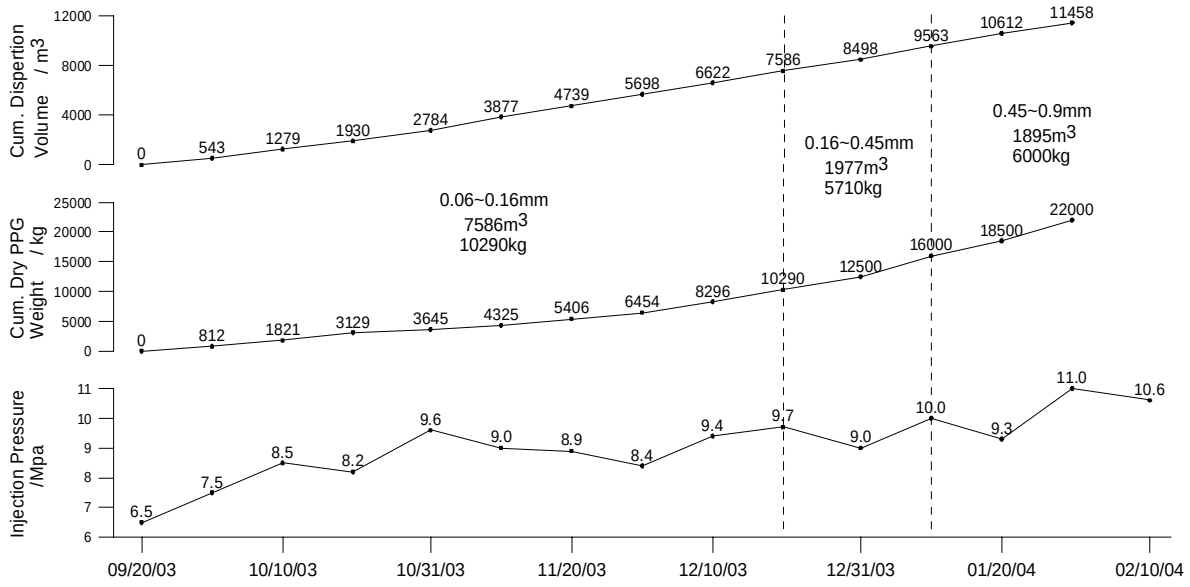


Fig.2-19. PPG Injection Curve for Well 9-1827.

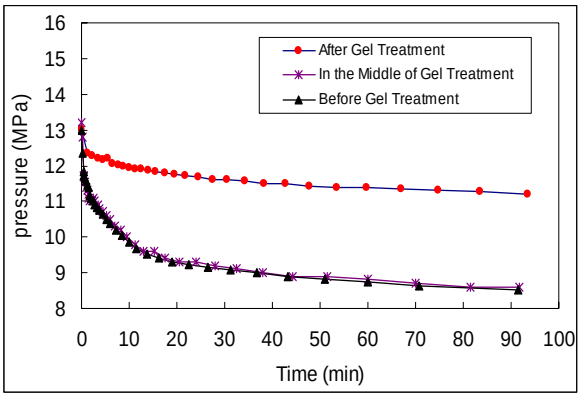


Fig. 2-20. Pressure drawdown test curve for well 7-1827

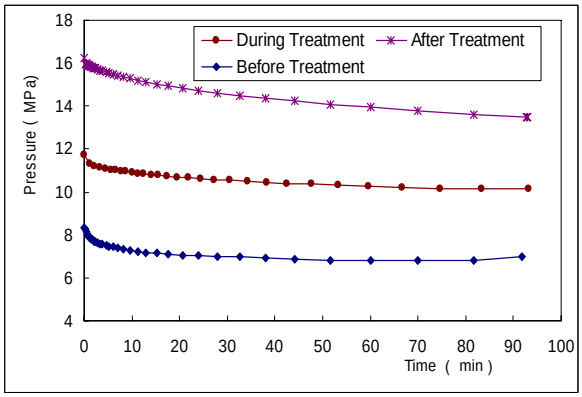


Fig. 2-21. Pressure drawdown test curve for well 7-1937

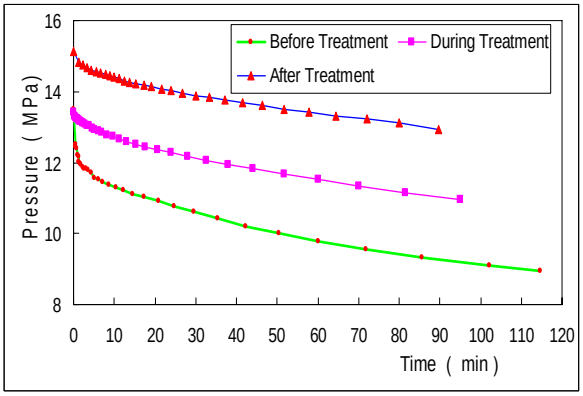


Fig. 2-22. Pressure drawdown test curve for well 8-1827.

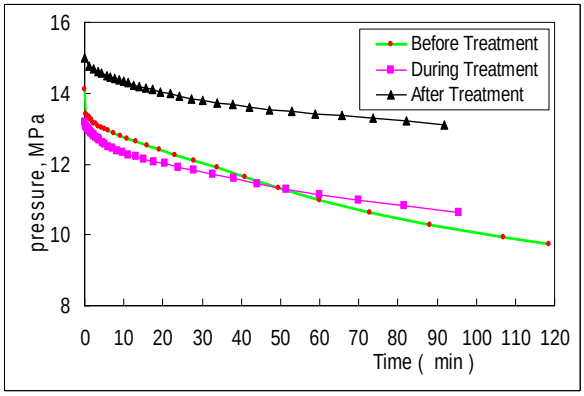


Fig. 2-23. Pressure drawdown test curve for well 9-1827.

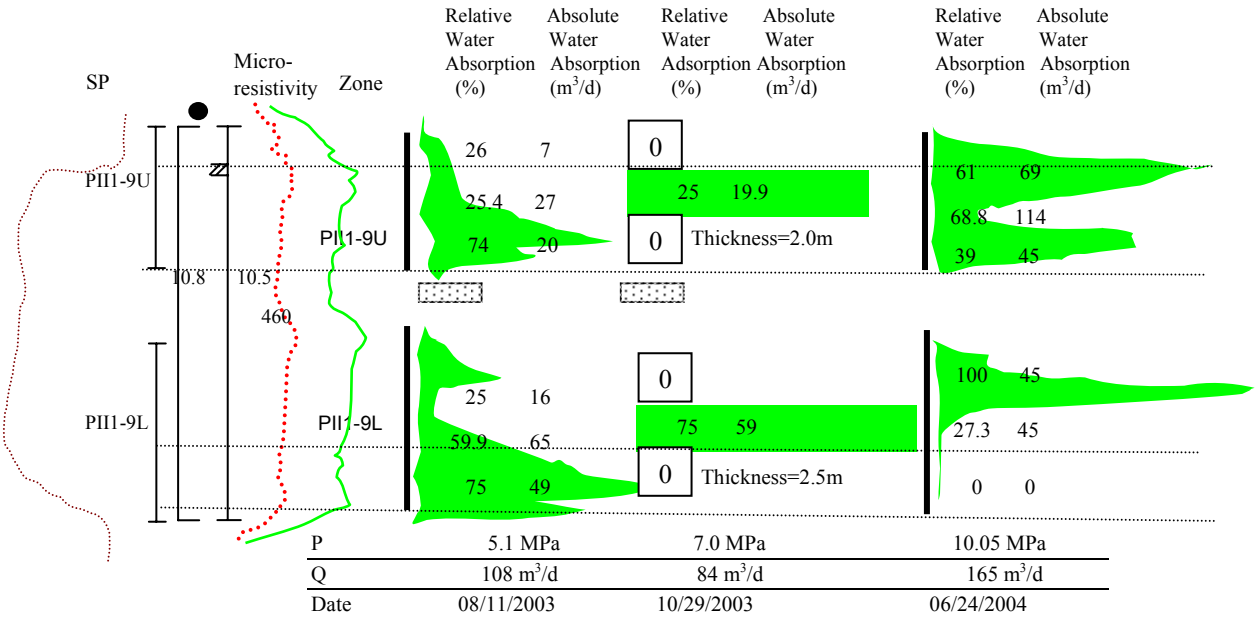
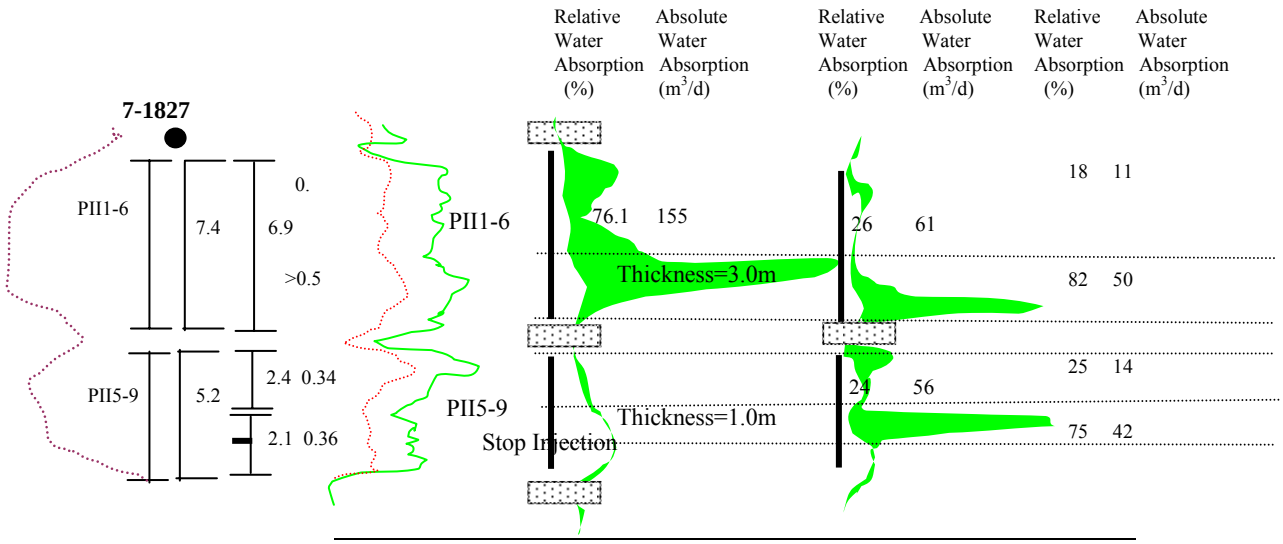
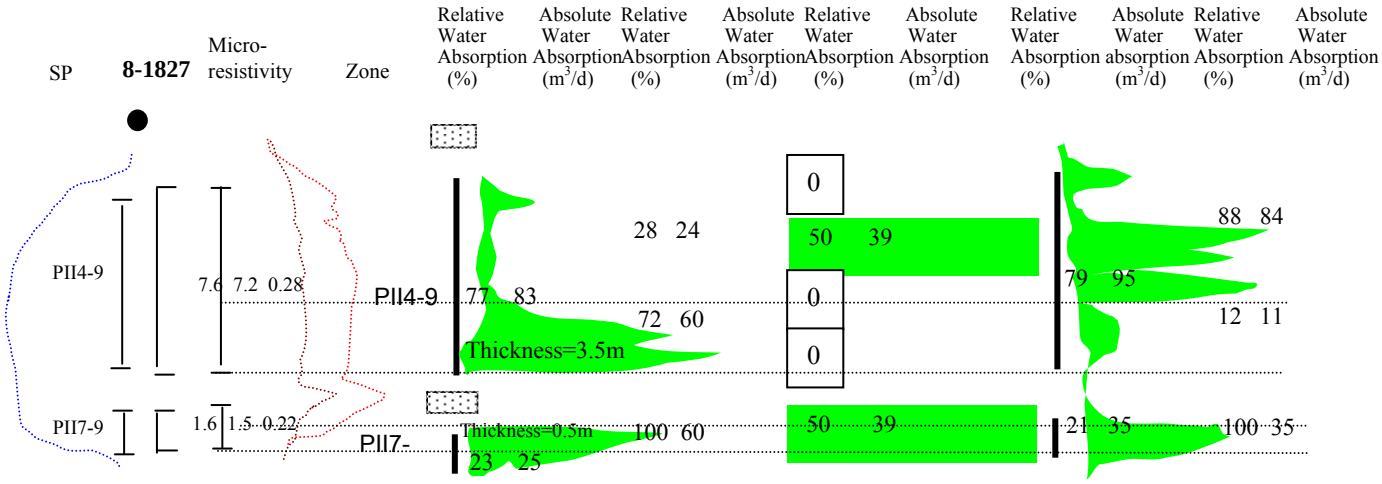


Fig.2-24. Well 7-1937 Water Injection Profile (Sept. 5th, 2003~Jan. 10th, 2004)



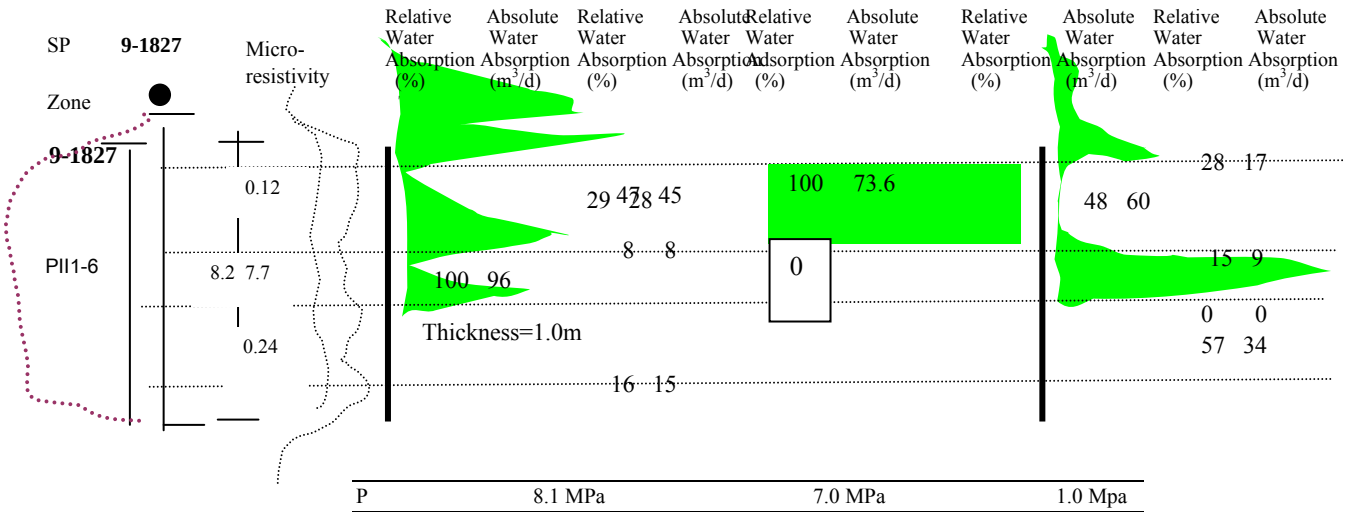
P	8.2 MPa	12.6 MPa	11.6MPa
Q	108 m^3/d	84 m^3/d	165 m^3/d
Date	01/18/2004	12/2/2004	09/3/2004

Fig. 2-25. Well 7-1827 Water Injection Profile (Sept. 5th, 2003~Jan. 31st, 2004)



P	11.3 MPa	7.0 MPa	120 MPa
Q	108 m^3/d	84 m^3/d	84 m^3/d
Date	07/1/2003	10/30/2003	02/13/2004

Fig. 2-26. Well 8-1827 Water Injection Profile (Sept. 5th, 2003~Jan. 31st, 2004)



P	8.1 MPa	7.0 MPa	1.0 Mpa
Q	108 m^3/d	80 m^3/d	125 m^3/d
Date	07/1/2003	10/29/2003	06/25/2004

Fig.2-27. Well 9-1827 Water Injection Profile (Sept. 25th, 2003~Feb. 3rd, 2004)

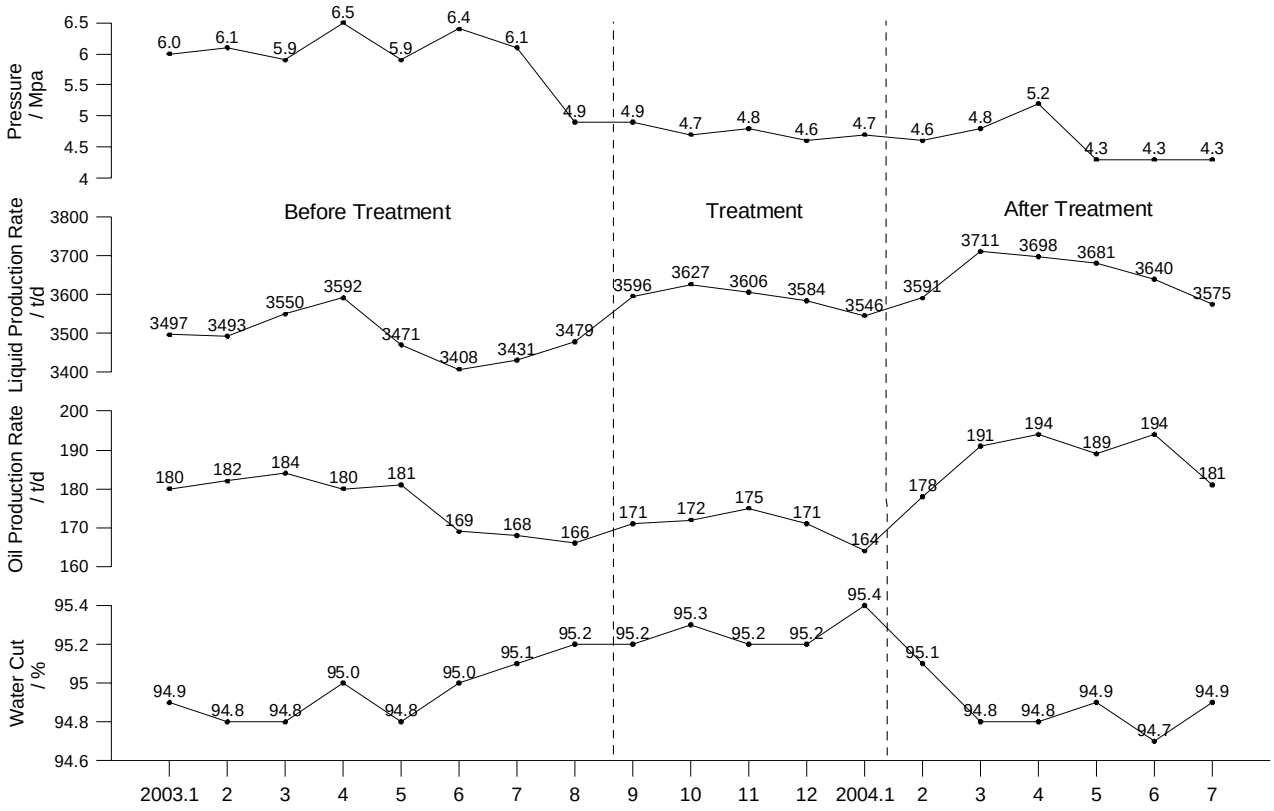


Fig. 2-28. Production curve for 24 connected curves

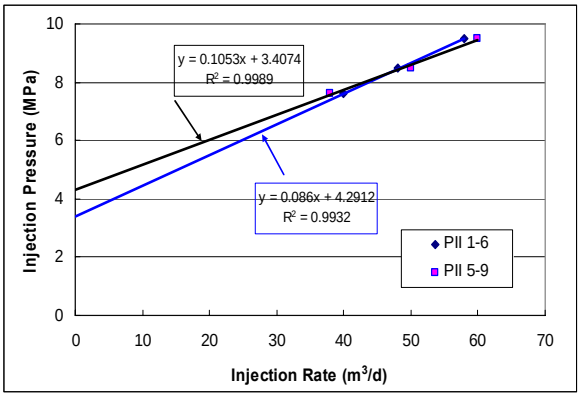


Fig. 2-29. Step test results from well 7-1827.

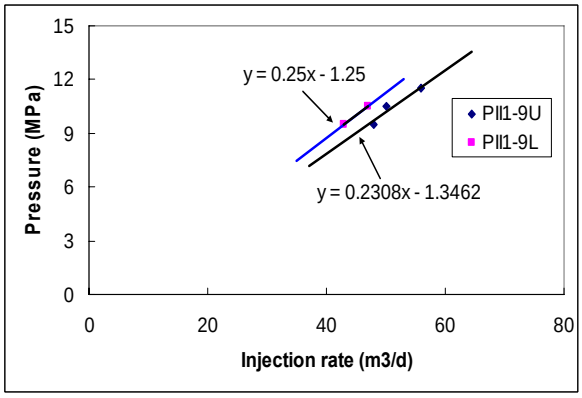


Fig. 2-30. Step test results from well 7-1937.

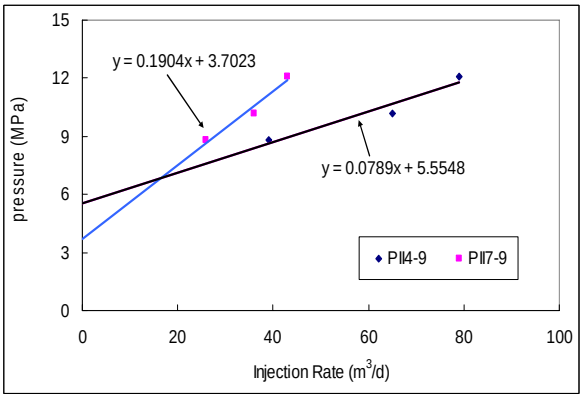


Fig. 2-31. Step test results from well 8-1827.

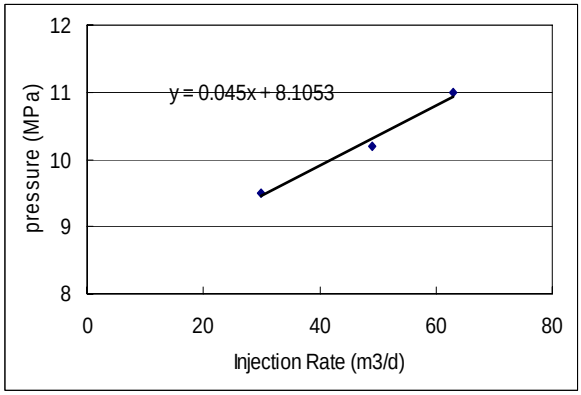


Fig. 2-32. Step test results from well 9-1827.

Chapter 3. Particle Gel Transport through Fractures and Fracture-like Channels

Summary

The chapter reports the research progresss for the Task 5 “Particle Gel Transport through Fractures and Fracture-like Channels” of the PPG project. The objective of the task is to quantify particle gel propagation and dehydration during extrusion through fractures and fracture-like channels and identify the best particle gels for different formation. The results will thereby guide the best particle gels for different width fracture and channels. This task was planned to be fulfilled through experiments using screens and cores with fractures and channels. New theoretical models were planned to be developed based on the experimental data and will be used to update the models of the first task for better design of particle gel treatments and prediction of well performance. During the first semi-annual period, the MST team designed and set up the instruments to test the gel strength and the injectivity of preformed particle gel through fracture-like channels. These designed instruments included a screen model, glass-bead packed model, 2-D transparent open fracture model and pseudo 3-D open fracture model. A series of experiments have been implemented to test the strength of the particle gel and the effect of injection rate on the injectivity of particle gel through screen models. Experiental results from screen model test show the particle injectivity mainly depends on the swelling capacity and the open hole size of screen. And increasing particle sizes and injection rates can not significantly increase the injection pressure, which is very consistent with the real-time injection pressure and injection rate change that were observed during practical particle gel treatments. These gel particle injection behaviors are completely different from conventional particles in that they are elastic and deformable during extrusion.

Four Models Designed for PPG Transport through Fracture and Fracture-like Channels

Model 1. Fracture-like Model—Glass Bead Packed Model

The fracture-like model (glassbead packed model) is a long acrylic tube to which end plates are attached by two flanges using steel rods and nuts (Figures 3-1a and 3-1b). The top flange has

one hole that is connected to an Isco pump through tubing and fitting. The bottom flange has multiple holes which allow PPG particles flow through without the addition of extra pressure. A piston with a hole plugged by a bolt is inserted into the acylic tube to prevent the direct contact of injected fluids and PPG particles. The pressure due to the pumped water push the piston which will press the swollen PPG to enter the glass bead packed porous media in the lower part of the tube. A screen will be placed between the porous media and bottom flange to avoid glass bead plugging the holes on the bottom flange. Because the bolt on the piston is easy to remove, once the PPG injection is finished, the bolt is removed, and the brine with designed salt concentration is pumped into the porous media filled with PPG to determine the residual resistance factor. This model can work well under 1,000 psi. The model is used to study PPG transport through fracture-like channels.

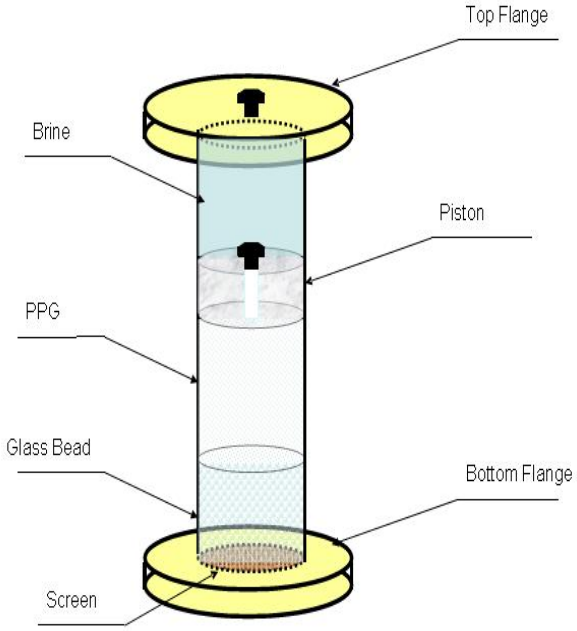


Fig. 3-1a. Details of Fracture-like Model

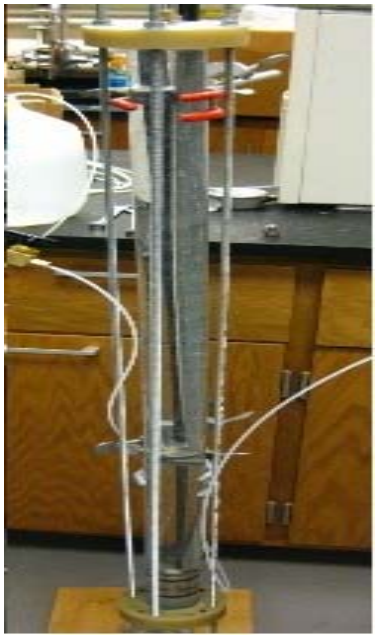


Fig 3-1b. Picture of Fracture-like Model

Model 2--Screen Model

The model is exactly the same as the glass-bead packed model except that there is no glass bead packed section and no bolt in the piston, as shown in Figure 3-2. The model is used to test if the simplified method can be used to test swollen PPG strength and to test the effect of

injection rate and the concentration of brine that is used to prepare swollen gel on the PPG injectivity. Different open hole size of screens represent different permeable formation.

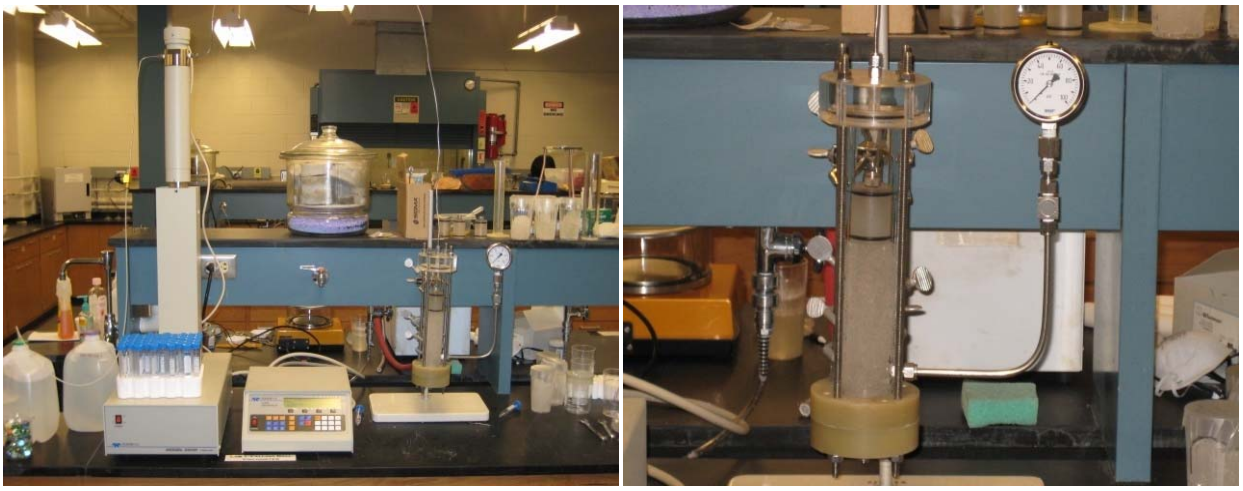


Figure 3-2. Picture of screen model.

Model 3--Transparent Open Fracture Model

A 2-D transparent model Miner P2 (Figures 3-3a, and 3-2b) constitutes two parallel acrylic plates, between which there is a rubber O-ring. Bolts, nuts, and shims are used to fix the two parallel acrylic plates and control the fracture width. On one side of the plate, there is a hole as inlet for the injection of fluids and PPG; and on the other side of plate, there is another hole as the outlet to discharge fluids and PPG. In addition, there are three extra holes on a plate as pressure taps, which connect to the pressure transducers. The model will be used to study the particle strength and size effect on the injectivity and visually observe particle movement in a fracture.

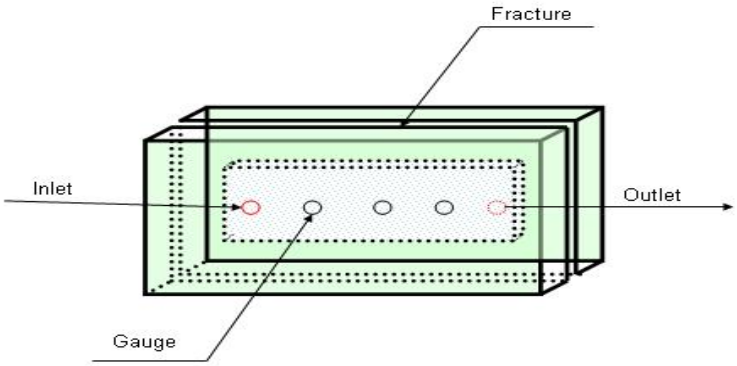


Fig. 3-3a. Details of 2-D Transparent Open Fracture Model Miner P2

Fig. 3-3b. Picture of 2-D Transparent Open Fracture Model Miner P2

Model 4-Pseudo 3-D Open Fracture

The apparatus for our experiments is the same as open fracture model designed by Dr Seright. The core (Figure 3-4a) is prepared from Berea sandstone, fractured lengthways, and cast in epoxy using standard method proposed by New Mexico Petroleum Recovery Research Center. Both the height and width of the cores are 1.5 in. (3.81 cm). The height of the fracture is also 1.5 in. (3.81 cm), and the orientation of the fracture vertical during the experiments. The effective average fracture width will be set at a constant value according to the experiment design. Three equally spaced internal taps are positioned to measure pressures down the length of the fracture, and another three equally spaced internal taps also are included to test pressures along the length of the porous rock. These sets of taps divided the core into four sections of equal length. One additional internal pressure tap is positioned to measure pressure in the matrix just after the inlet sand face. A special fitting (Fig. 3-4b) is joined to the core outlet to separate the effluent from the fracture and that from the porous rock. Before injecting the particle gel, the core is brine saturated and characterized using tracer studies and flow measurements (Seright 1999).

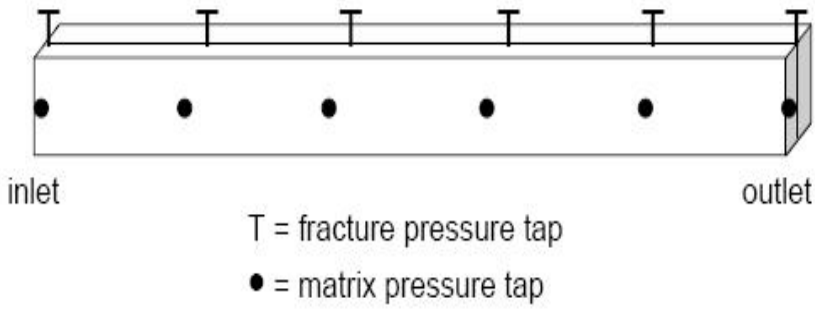


Fig. 3-4a. Illustration of the fractured core (Seright 1999).

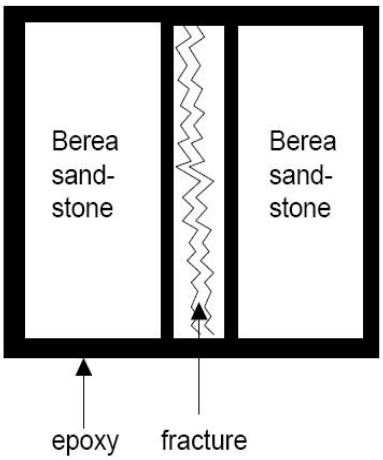


Fig. 3-4b. Core outlet configuration to separate fracture effluent from porous-rock effluent (Seright 1999).

Preformed Particle Gel Used for Experiments

A commercial super absorbent polymer (SAP) was selected as preformed particle gels for our experiments. The main components of the PPG is potassium salt of crosslinked polyacrylic acid/polyacrylamide copolymer. Before swelling, the PPG is dry white granular powder. In aqueous solutions, the PPG could absorb a large amount of water due to hydrogen bond with water molecule. The concentration of sodium chloride will have effect on the water adsorbent capacity. In deionized and distilled water, SAP may absorb 500 times its weight (from 30-60 times its own volume), but when put into a 0.9% saline solution, the absorbency drops to maybe 50 times its weight. Figures 3-5 and 3-6 show the PPG before and after swelling. The presence of valent

cations in the solution will impede the polymers ability to bond with the water molecule (SAP). Some typical characteristics of PPG used are listed in Table 3-1, and the size distribution of PPG was determined by a sieving test and listed in Table 3-2.

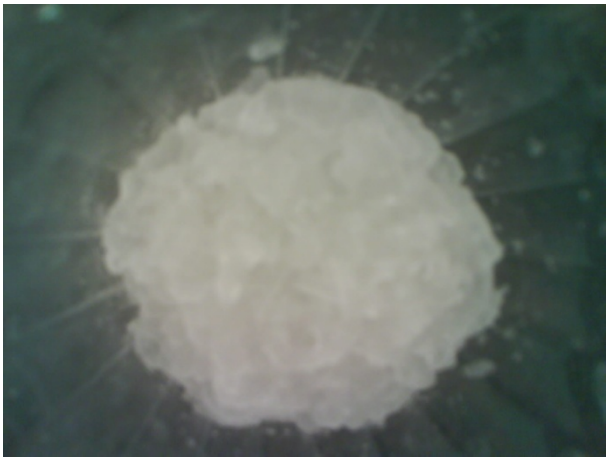


Fig. 3-5. Dry powdered PPG **Fig.3-6. Swollen PPG**

Table 3-1 Typical Characteristics of Preformed Particle Gels

Properties	Value
Absorption Deionized Water (g/g)	>200
Apparent Bulk Density (g/l)	540
Moisture Content (%)	5
pH Value	5.5-6.0 (+/- 0.5; 1% gel in 0.9% NaCl)

Table 3-2. Size Distribution of Preformed Particle Gel

Sieves (Mesh)	Size (microns)	Content (percent)
20	>830	12.01
40	380~830	75.32
60	250~380	12.46
80	180~250	0.20
100	150~180	0.01
120	120~150	0
>120	<120	0

Experimental Results and Analysis

PPG Swelling Kinectics and Effect of Sodium Choloride Concentration on Swelling Capacity.

The swelling ratio which is defined as the ratio of the PPG particle volume after and before swelling is evaluated as a function of salt concentration. Figure 3-7 shows the PPG swelling ratio change with time at different sodium chloride concentrations. The PPG particles swell very fast and the maxium swelling ratio can be reached within 60 mintues for each sample. The final PPG swelling ratio depends on the salt concentration. The higher the salt concentration is, the smaller swelling ratio is, as shown in Figure 3-8. The relationship of swelling ratio and salt concentration can be well fitted using a power equation with a R^2 of 0.96:

$$R = 65.535 \times C^{-0.296}$$

Where R is swelling ratio and C is sodium choloride concentration in percentage.

Figure 3-9 shows the fitting results of PPG swelling ratio as a function of time using pseudo-second order kinetic model. The PPG swelling kinetic data can be well fitted by the model, and thus the PPG swelling kinectic follows the pseudo-second model. The fitting equations are listed in Table 3-3.

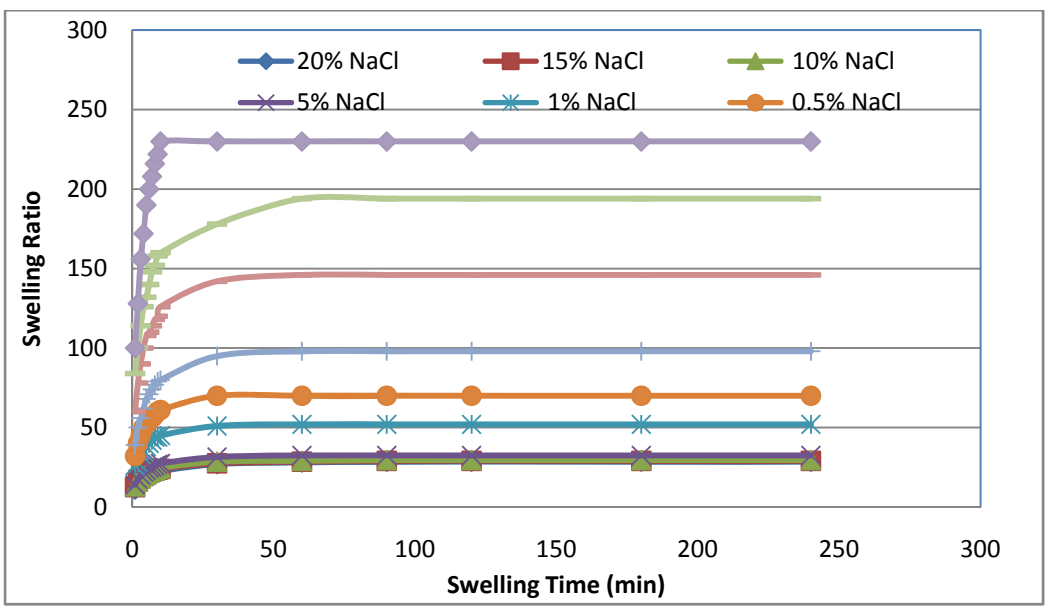


Figure 3-7. The swelling ratio of SAP-40K as a function of time and NaCl concentration.

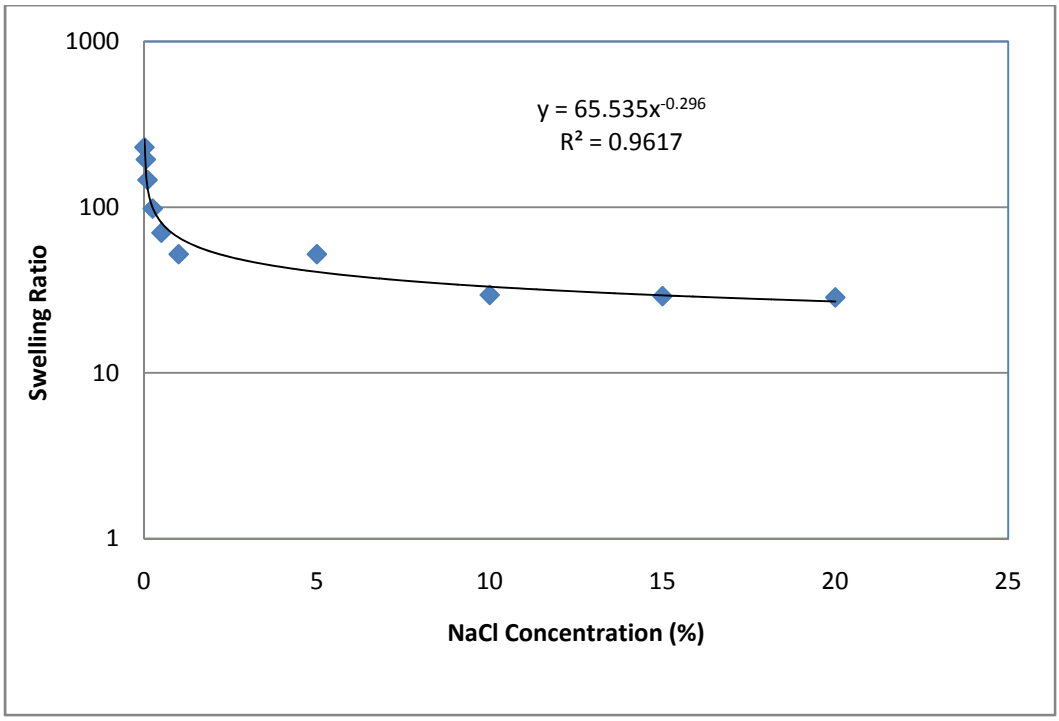


Figure 3-8. Effect of NaCl concentration on the final swelling ratio.

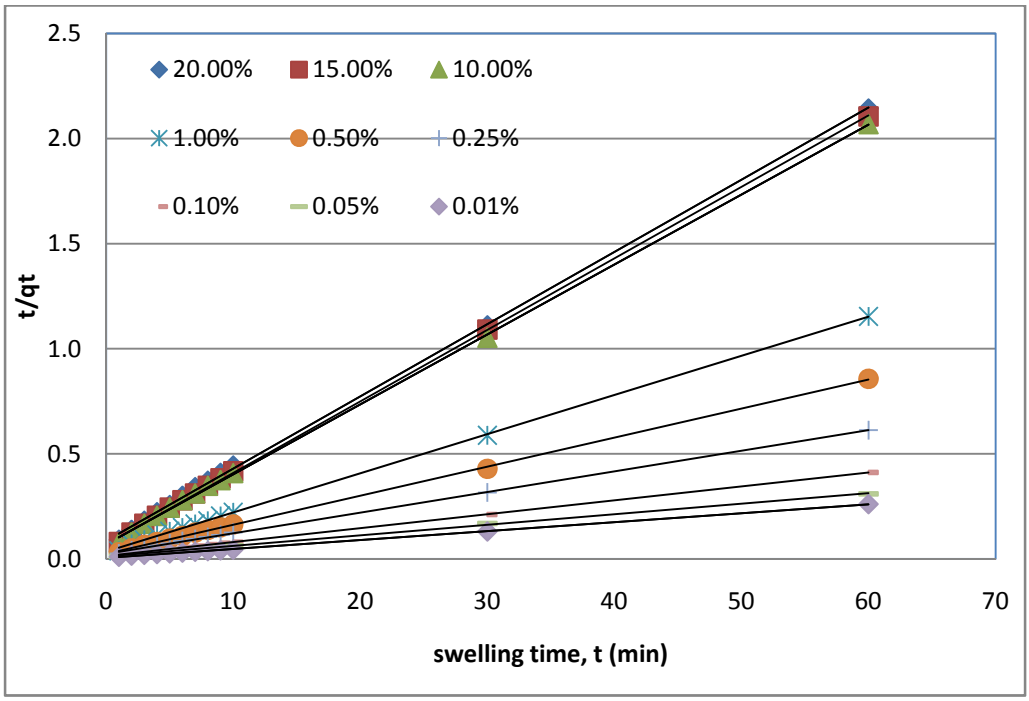


Figure 3-9. The fitting result of SAP-40 K swelling kinetics using pseudo-second kinetic model

Table 3-3. The fitting equations of PPG Swelling Kinetics

Brine Conc.(%)	Fitting Equations	R^2
20	y = 0.0344x + 0.0856	0.9994
15	y = 0.034x + 0.0683	0.9997
10	y = 0.0333x + 0.0695	0.9996
1	y = 0.0186x + 0.0342	0.9997
0.5	y = 0.0138x + 0.0243	0.9996
0.25	y = 0.0098x + 0.0237	0.9996
0.1	y = 0.0066x + 0.0134	0.9998
0.05	y = 0.005x + 0.0117	0.999
0.01	y = 0.0042x + 0.0046	0.9993

Screen Test Results

Twelve experiments were performed to study the effect of injection flow rate, the brine concentration that used to prepare swellon PPG, and the opening hole size of screen on the PPG injection pressure using screen models (Figure 3-2). Figures 3-10 to 3-12 show the 12 tested results from three screen models with different mesh screens. Table 3-4 shows the parameters of the screens that were used.

Table 3-4. Parameters of screens used for experiements

Screen Type	Wire Diameter (Decimal Inch)	Mesh Per Linear Inch	Width Opening (Decimal Inch)
Small (0.0026)	0.0026”	150 * 150	0.0041”
Medium (0.007)	0.007”	80 * 80	0.0060
Big (0.013)	0.013”	40 * 40	0.0120”

Effect of flow rate on injection pressure

All three figures uniquely indicate that the injection pressure increases with the injection flow rate but its increased trend is not as much as that of the injection rate. The pressure does not change very much with the flow rate, expecially at higher flow rates. The trend is consistent with the findings of practical PPG injection in oilfields for which injection pressure does not significantly increase with the increase of injection pumping rate.

The relationship of injection rate and injection pressure was fitted using a power rheology model and they are fitted very well as shown in Figures 3-13 to 3-15, which indicate the swelling

particle gel is a shear-thinning material that follows power law rheology equation. The fitting equation can be used to predict the injection pressure at different flow rate.

Effect of salt concentration on injection pressure

Four swollen PPG samples were prepared using four different sodium choloride brines with concentrations of 0.05, 0.25, 1.0 and 10%. The PPG swelling ratios are significantly different in the four brines as shown in Figure 3-8. All three Figures (Figs. 3-10 to 3-12) indicate the injection pressure increases with the increase of brine concentration. The trend was not predicted before our experiments because the swollen particle size is larger at low brine concentration than that in high brine concentration and thus it was hypothesized that the injection pressure for the sample prepared with low salinity brine is higher than that prepared with high salinity brine. These experimental results told us the softness or deformability of swollen particle is more dominant to PPG injectivity than the particle sizes. The swollen particle is softer or more deformable in low salinity brine than that in high salinity brine and thus its injectivity is higher.

Effect of open hole sizes of screen.

Comparing the pressure in Figures 3-10 to 3-12, it is obvious that the injection pressure is significantly affected by the open hole size of screen we used. The greater the open hole size, the lower the injection pressure is.

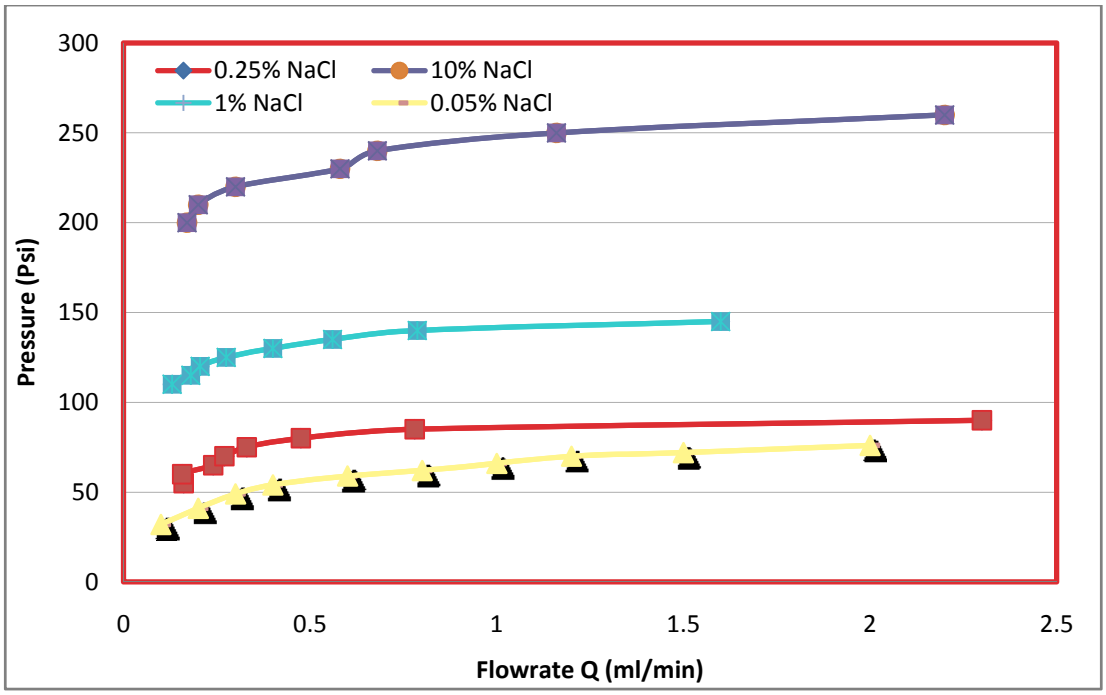


Figure 3-10. Injection pressure as a function of flow rate and brine concentration (150 mesh screen)

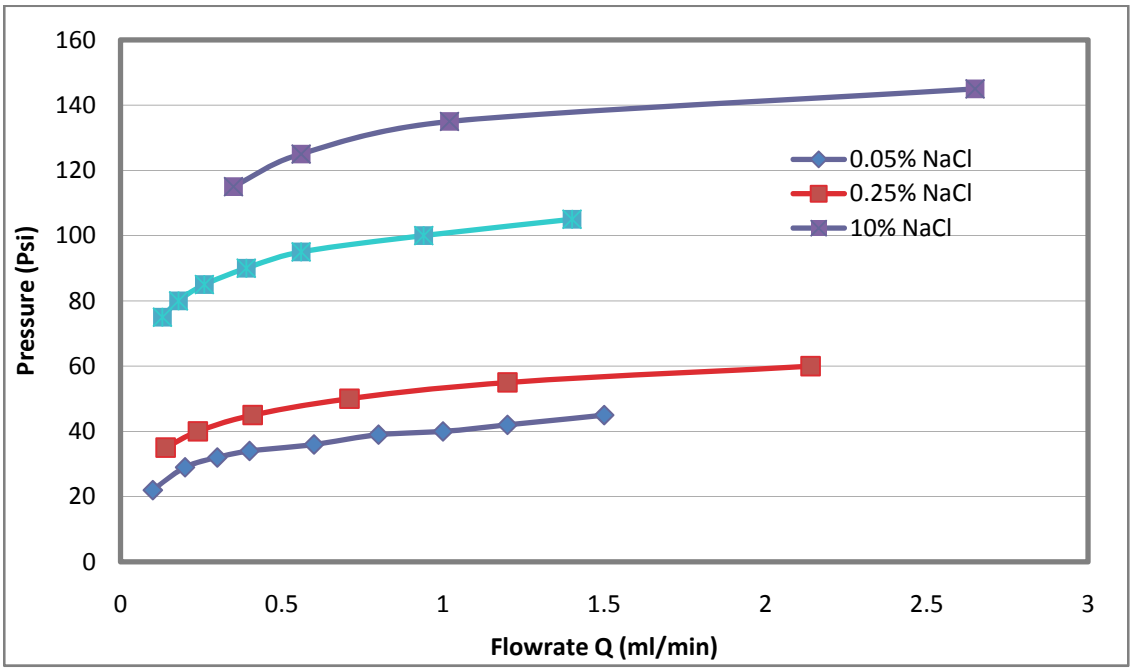


Figure 3-11. Injection pressure as a function of flow rate and brine concentration (80 mesh screen)

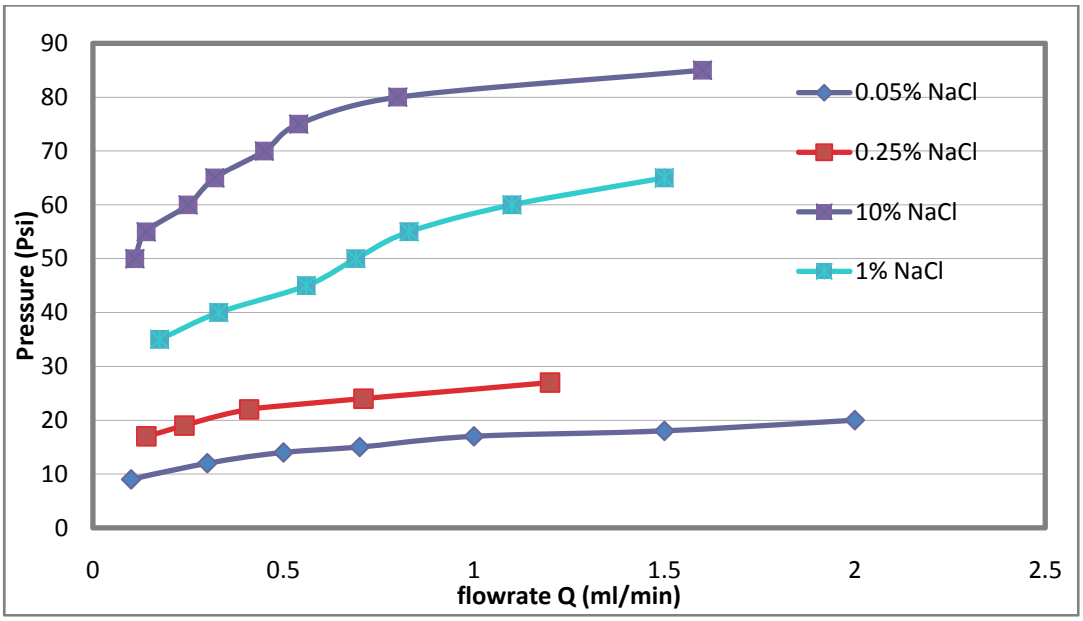


Figure 3-12. Injection pressure as a function of flow rate and brine concentration (40 mesh screen)

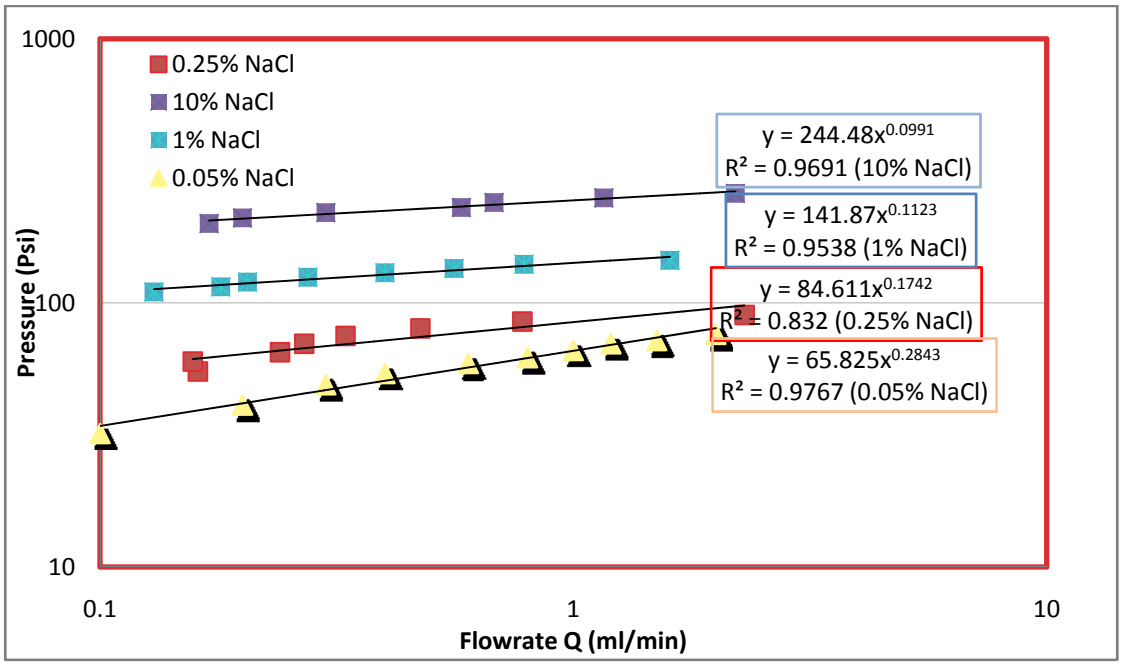


Figure 3-13. The fitting result of Injection pressure as a function of flow rate using power rheology equation (150 mesh screen)

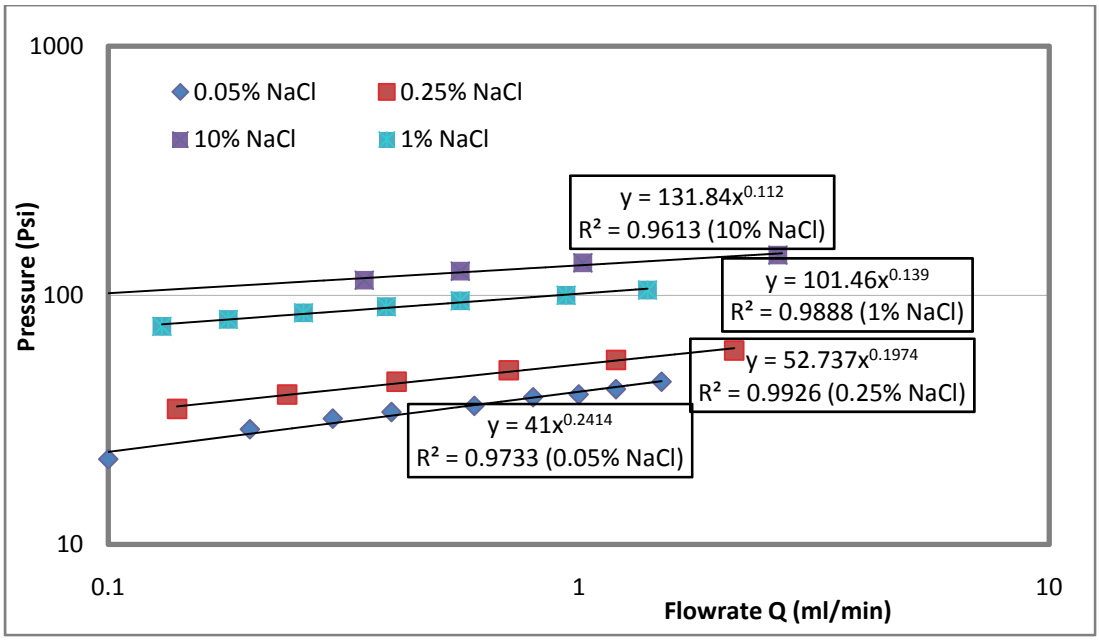


Figure 3-14. The fitting result of Injection pressure as a function of flow rate using power rheology equation (80 mesh screen)

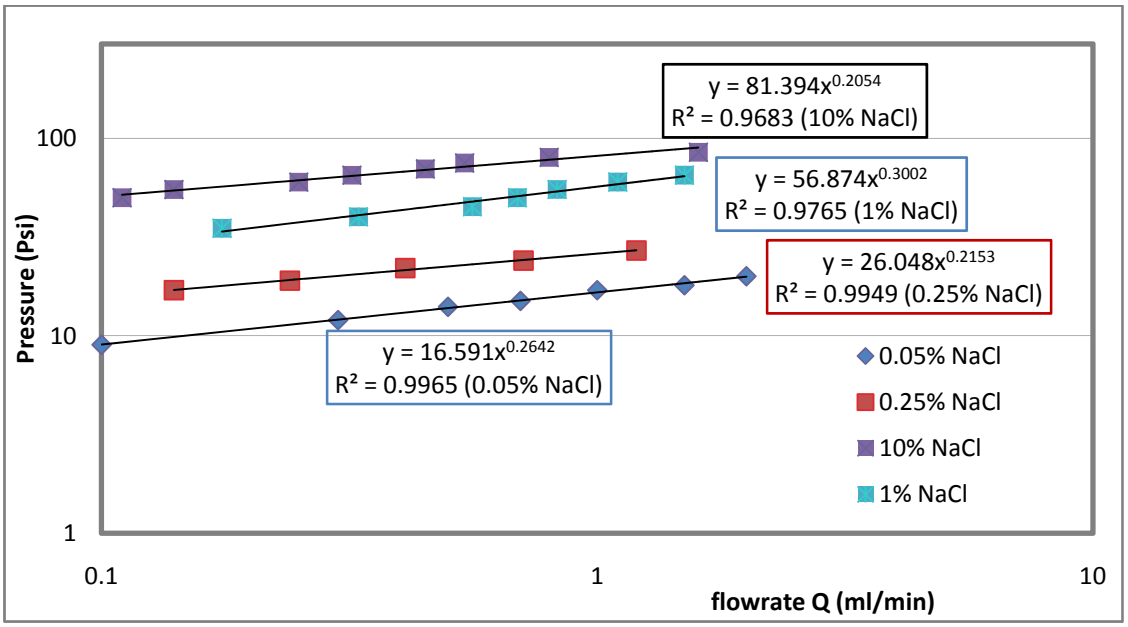


Figure 3-15. The fitting result of Injection pressure as a function of flow rate using power rheology equation (40 mesh screen)

Summary

1. Four experimental models were designed to evaluate PPG transport through fracture and fracture-like models.
2. PPG swelling ratio depends on salt concentration of brine, and they can be fitted well using a power equation.
3. The kinetics of PPG swelling follows a pseudo-second order kinetics model.
4. Swollen PPG is a shear-thinning material that follows a power law rheology equation.
5. Increasing injection rate does not significantly increase PPG injection pressure, which is consistent with the findings of pratitical PPG injection.
6. The injectivity of PPG prepared by low brine concentration is higher than that prepared by high brine concentration even though the former particle size is larger, indicating the deformability is a controlling factor for PPG injectivity.

References

Seright, R.S., et al., " Mechanism for Gel Propagation Through Fractures, paper SPE 55628 presented at the the 1999 SPE Rocky Mountain Regional Meeting held in Gillette, Wyoming, 15–18 May 1999.

Seright, R. S., Webpage http://baervan.nmt.edu/randy/home.html, New Mexico Petroleum Recovery Research Center.

Chapter 4. Compatibility of Particle Gels and Surfactants

Introduction

Task 6 of the project is to improve particle gel treatments. Some novel processes will be tested to determine if they can improve gel particle treatment efficiency. One method incorporates gel particles with surfactant, so that the filtrate that is squeezed into the matrix during gel injection alters the wettability of rock near the fracture faces. By reducing interfacial tension between hydrocarbon and water, it is expected that the squeezed surfactant will not decrease concentration significantly due to the adsorption onto the swelled gel particle. The concentration is very important to lower the capillary pressure and reduce the capillary end effect, which is a dominant factor responsible for low hydrocarbon recovery from reservoirs with low permeability and tight-gas reservoirs. On the other hand, the particle gel strength and viscosity will not decrease too much.

Experiments

4.1 Preparation of Gel Particle

4.1.1 Synthesis of Polymer Gel

Recipe of Methelene Bisacrylamide (ppm)

Component	#1	#2	#3	
AM	30 wt.%	30 wt.%	30 wt.%	
Methelene Bisacrylamide (ppm)	100	500	1000	
Initiator $(NH_4)_2SO_3$ (ppm)	1000	1000	1000	

4.1.2 Procedures to Synthesize the Polymer Gel:

1) Use a 3000 mL beaker to weigh out 500 grams of distilled water
2) Weigh out 150 grams of acrylamide (Alfa Aesar, 98%), then add it the distilled water.
3) Use a magnetic stirring bar to stir the solution at 270 RPM to the solid sample completely dissolved in the water.

4) Use a small piece of weighing paper to weigh out 0.325 grams of methylene bisacrylamide (cross-linker, white powder), add it above solution and continue stirring to ensure the cross-linker dissolved completely.
5) Use a small piece of weighing paper to weigh out 0.650 grams $(NH_4)_2SO_3$ and add it to the solution and continue stirring the solution at 270 RPM for 4 hours.
6) Transfer the solution from beaker to a 1000 mL jar, take the magnetic stir bar out of the solution. Put a cap on the jar.
7) Move the jar containing the polymer solution into an oven with 60 °C temperature and leave it in the oven for 14 hours.
8) After heating in the oven at 60 °C overnight, the polymer solution turns to a strong bulk gel. Take the gel out of the jar and cut it to small pieces.

4.1.3 Drying the Particle Gel

1) Put the small pieces of the gel into two 1000 mL beakers, then dry the gel in an oven with air circulation at 60 °C.
2) After drying for 4 days, weigh the dry solids of polymer gel, 168.390 grams. Some solids turn to slightly yellow. This may be due to oxidation of acrylamide.

4.1.4 Grinding and Sieving

1) Put the dry gel solids in blender machine (Black & Decker), the solids were ground to small particles and powder.
2) Set a series of Standard Testing Sieves (Fisher Scientific Company), No. 40, No.70, No. 100, No.120 and receiver from the top to the bottom on the platform of Test Sieve Shaker (Ro-Tap® Model E, W.S. Tyler, Ohio, USA).
3) Put the small particles and powder into the No. 40 of the series sieve, then put a cover on the top sieve. After everything is ready, turn on power of the shaker to sieve the gel particles.
4) Collect the sample with particle size between 100-120 mesh for next experiments. Put the particles with larger size (<100 mesh) back to the blender to repeat above procedures to get more particles between 100 and 120 mesh.

4.2 Swelling Test

To study compatibility of particle gel and surfactant, the synthesized and sieved particle sample was mixed with surfactants in 1.0 wt.% NaCl solution. The surfactants investigated are listed in Table 1. There are three categories: nonionic, anionic and cationic surfactants. The stock solution were prepared as 2000 ppm based on 100% pure with 1.0 wt.% NaCl as synthetic brine. Then the stock solutions were diluted to 200 ppm with 1.0 wt.% NaCl aqueous solution.

Weigh out 0.300 grams of 100-120 mesh gel particle to a 15 mL test tube, then add 14.700 grams of 200 ppm surfactant solution. Shake the test tubes vigorously for 2 minutes, then place the tubes on a shaker to shake overnight to ensure adsorption of surfactant on the particle reach equilibrium. Then leave the tubes in a rack for two weeks to ensure the particle swelling reaches equilibrium. The gel volume at swelling equilibrium was measured to determine the swelling ratio and the results are listed in Table 3.

4.3 Surfactant Concentration Measurement

To study effect of particle swelling on the surfactant concentration, some surfactants with an absorbance peak in the range of UV wavelength were selected for this purpose. The initial concentration for all surfactants investigated is the same, 200 ppm. After the adsorption and swelling reaches equilibrium, concentration of the surfactants was analyzed using a UV/VIS Spectrophotometer (Shimadzu). UV absorbance (ABS) peak, initial ABS, equilibrium ABS, equilibrium concentration and concentration change due to the gel particle swelling are listed in Table 2.

4.4 Viscosity Measurement

The effect of surfactant on particle gel strength is one of the most important issues concerning its applications in oilfield. Because the particle gel is an elastic gel rather than a fluid, the elastic modulus measurement is more straightforward meurement to this purpose. However, the particles we used have the same particle size and the swelling ratios for all surfactants investigated are almost the same, therefore, viscosity of swelled gel under this circumstance may be used as estimation of the gel strength. Viscosity of particle gels with different surfactants was measured at 25 °C and relatively low RPM using a viscometer (Brookfield, DV-II+ pros.). The lower RPM was used in order to prevent the gel from shear degradation. The results are listed in Table 3.

4.5 Measurement of NaCl Concentration after Swelling

It is recognized that performance of polymer gel and surfactants depend on brine salinity in reservoirs. Because of high swelling ratio, gel particles absorb brine solution like super absorbent polymers. So one question will be raised is whether the brine concentration changes or not after the particle swelling? If it does, does it increase or decrease? In this experiment, to measure concentration of NaCl after particle swelling, an exact amount of 5 grams of NaCl solution after swelling equilibrium was weighed to a clean and pre-weighed test tube, excess 0.500 M $AgNO_3$ aqueous solution (about 2 mL) was add to the NaCl solution to precipitate all chlorine ions (Cl^-). The white precipitate of AgCl was separated using a centrifuge. Carefully pour out the separated liquid without agitation of the solid on the bottom. Then add 12 mL of distilled water to the test tube to wash off any $AgNO_3$ residue. Repeat these procedures three times to ensure all $AgNO_3$ has been washed off completely. Dry the white precipitate in the test tube in an oven at 80 °C for about 2 hours, then cool it to room temperature. Weigh total mass of the test tube and AgCl solids and calculate the mass of AgCl solids, then covert it to NaCl mass to calculate NaCl concentration in the equilibrium solution. To ensure accuracy of this experiment, a test with standard NaCl solution (1.00 wt.) was carried out at the same time. The data and results for the two experiments are listed in Table 4.

Results and Discussion

Swelling ratio: The results of particle swelling ratio in different surfactant solutions with 1.00 % NaCl are listed in Table 3. The ratios are in the range between 22 and 25. Considering the experimental error, there is no significant difference for the different surfactants. Because surfactants investigated in this experiment include nonionic, cationic and anionic surfactant, based on the results, one may conclude that surfactants have no significant effect on swelling ratio. By comparing the swelling ratio of the particle gel in distilled water, 1.00 wt.% NaCl and in 200 ppm surfactant solutions, one may further conclude that NaCl and surfactants have no significant effect on the swelling ratio. This observation consists with the conclusion that particle gel has excellent tolerance with brine salinity.

Effect of surfactant on particle viscosity: As mentioned in the experimental section, due to the particles we used have the same particle size and the swelling ratios for all surfactants

investigated are almost the same, therefore, viscosity of swelled gel under this circumstance may be used as estimation of the gel strength. First in Table 3, it can be found that without addition of any surfactants, viscosity of the gels in distilled water and 1.00 wt. % NaCl are very close to each other; taking the experimental error into consideration, their viscosities are the same. Therefore, one can conclude that NaCl in 1.00 wt.% has negligible effect on polymer gel viscosity and may be also the elastic strength, and no effect on the swelling ratio. For 28 surfactant used in this test, a general trend of their effects on the gel viscosity can be found that all surfactants reduce the viscosity, particularly at low RPM. Further, nonionic surfactants show more significant effect on the viscosity reduction than anionic and cationic surfactants. The reason for viscosity reduction of the particle gel by surfactants may be due to the reduction of interfacial tension at the interfacial surface between the gel soft solid surface and the aqueous solution, and therefore to reduce the resistance between the soft gel particles. Similarly, the reason why nonionic surfactants have more significant effect on reduction of the gel viscosity is probably the nonionic surfactants can reduce the interfacial tension at the interface between the soft gel surface and brine solution much lower than the ionic surfactants can do. On the other hand, nonionic surfactants have a much lower critical micelle concentration (CMC) than ionic surfactants in general, 200 ppm concentration for nonionic surfactants is about or above their CMC, but for ionic surfactants it is much lower than their CMC. It is recognized that the association of surfactant micelles and water soluble polymers has significant effect on rheological properties of the polymers. But the relationship among the surfactant CMC, structures of polymer hydrophobic and hydrophilic groups and electrolyte in the aqueous solution is complicated. At current stage of this project, it is difficult to discuss this topic.

Concentration change of NaCl: The initial concentration of NaCl solution is 1.00wt.%, after particle swelling, the equilibrium concentration has been analyzed to be 1.01 wt.%. The difference is only 0.01 wt.% can be due to the experimental error. Accuracy of the experimental results can be evaluated by analysis results of the standard NaCl aqueous solution. The expected NaCl for the analyzed solution is 0.0501 grams. The actual mass of NaCl solids obtained by the precipitation procedure is 0.0502 grams. The relative experimental error is only 0.2%. Based on the analytical results and the experimental error, one can conclude that the swelling of the particle gel and absorbance of aqueous solution by the particle has no effect on the concentration of NaCl in residual solution.

Concentration change for surfactants: The initial concentration for all surfactants used in this experiment is 200 ppm. At the beginning of the experiments, 14.70 grams of surfactant solution was added to test tube with 0.3000 grams of gel particle. At the equilibrium of swelling, there is about 5.5 grams of solution on the top of the gel. This equilibrium solution contains NaCl, surfactant and polymer dissolved from the particle gel that makes contributions to UV absorbance, or called background absorbance. The equilibrium concentrations for the surfactants investigated and the change of concentration are listed in Table 4.

In Table 4, it can be found that the equilibrium concentrations increase after gel swelling. For the three commercial nonionic surfactants, Tergitol NP-10, Igepal CO-530 and Triton X-405, their equilibrium concentrations increased to 283, 282 and 259 ppm, respectively, from the initial concentration of 200 ppm. For the cationic and anionic surfactants, their equilibrium increased, too. The increase percentage of the concentration for the ionic surfactants is in the range of 5% to 23.5%. However, considering the ± 5% experimental error of absorbance measurement, the equilibrium concentrations for n-dodecylpyridinium chloride hydrate and benzalkonium chloride remained unchanged. Basically, benzalkonium chloride is not a surfactants, but an organic salt. Although the surfactant concentrations increased after gel particle swelling to a different extent, the aqueous solutions remaining on the top of the swelling gel is only 5.5 grams compared to their initial amount of 14.7 gram, indicating some of the surfactant was still lost due to the absorbance of their solutions. The reason for this increase of equilibrium concentration is unknown at this time, and may be due to the repulsive interaction between the surfactants and the gel particle surface, which shows high hydrophilicity.

Conclusions:

1) Surfactants reduce viscosity of particle gel. Nonionic surfactants show more significant effect.
2) Surfactant concentration increases after swelling of gel particles. Nonionic surfactants show greater increase. But the surfactants still lose some material into the particle gel.
3) Concentration of NaCl remains unchanged after the swelling of particle gel.

Table 1. Surfactants Used for Compatibility Test with Gel Particle

Surfactant Name	Company	Chemical Description	HLB
Neodol® 1-5	SHELL	Linear C11 primary alcohol with 5 moles of ethylene oxide(EO)	11.2
Neodol® 1-7	SHELL	Linear C11 primary alcohol with 7 moles of ethylene oxide(EO)	12.8
Neodol® 1-9	SHELL	Linear C11 primary alcohol with 9 moles of ethylene oxide(EO)	13.9
Neodol® 25-7	SHELL	Linear C12-C15 primary alcohol with 7 moles of EO	12.3
Neodol® 25-9	SHELL	Linear C12-C15 primary alcohol with 9 moles of EO	13.1
Tomadol® 25-7	Air Products	Linear C12-C15 primary alcohol with 7 moles of EO	12.3
Tomadol® 25-9	Air Products	Linear C12-C15 primary alcohol with 9 moles of EO	13.1
Tomadol® 25-12	Air Products	Linear C12-C15 primary alcohol with 12 moles of EO	14.4
Tomadol® 45-7	Air Products	Linear C14-C15 primary alcohol with 7 moles of EO	11.6
Tomadol® 45-13	Air Products	Linear C14-C15 primary alcohol with 13 moles of EO	14.4
Tergitol® 15-S-3	DOW	C12-14 secondary alcohol ethoxylate with 3 moles of EO	8.3
Tergitol® 15-S-9	DOW	C12-14 secondary alcohol ethoxylate with 9 moles of EO	13.3
Tergitol® 15-S-12	DOW	C12-14 secondary alcohol ethoxylate with 12 moles of EO	14.7
Tergitol® 15-S-20	DOW	C12-14 secondary alcohol ethoxylate with 20 moles of EO	15.7
Tergitol® NP-10	DOW	Ethoxylated nonylphenol with 10 moles of EO	13.2
Igepal® CO-530	Rhodia, Inc.	Ethoxylated nonylphenol with 5 moles of EO	10.8
Triton® X-405	Sigma	Ethoxylated octylphenol with 40 moles of EO	17.6
Calamide® CW100	PILOT	Modified coconut diethanolamide	
Calamide® CWT	PILOT	Modified coconut amidesoap superamide	
Calamide® F	PILOT	Vegetable oil diethanolamide	
Calsoft® LAS-99	PILOT	Benzensulfonic acid, C10-C16 alkyl derivitives	Acid
Calimulse® EM-99	PILOT	Benzensulfonic acid, C10-C16 alkyl derivitives	Acid
Calimulse® PRS	PILOT	Benzensulfonic acid, dodecyl branched	Acid
Pluronic® 25 R-2	BASF	Block copolymers of propylene, ethylene oxides	
Pluronic® L-62	BASF	Block copolymers of propylene, ethylene oxides	7.0
Polystep® B-1	Stepan	Ammonium nonylphenol ethoxylate sulfate, 4 EO	Anionic
Polystep® B-19	Stepan	Sodium lauryl ether sulfate, 30 EO	Anionic
Stepanol® WA-100	Stepan	Sodium lauryl sulfate (S.D.S.)	Anionic
ARQUAD® T-50	Akzo Nobel	Tallowalkyltrimethyl ammonium chlorides	21.0
Ethomeen® C/12	Akzo Nobel	Bis(2-hydroxyethyl)cocoalkylamines	12.2
Ethomeen® S/12	Akzo Nobel	Bis(2-hydroxyethyl)soyaalkylamines	10.0
Aerosol® MA-80	CYTEC	Sodium dihexyl sulfosuccinate, isopropanol and water	Anionic
Alfoterra® 23	Sasol	Branched alcohol propoxylate sulfate with 3 moles of PO	Anionic
Alfoterra® 48	Sasol	Branched alcohol propoxylate sulfate with 8 moles of PO	Anionic
Calfax® 16L-35	PILOT	Sodium n-hexa-decyl diphenyl oxide disulfonate	Anionic
Calsoft® L-40	PILOT	Sodium dodecyl-benzene sulfonate	Anionic
Dowfax® 2A1	DOW	Sodium dodecyl diphenyloxide disulfonate	Anionic
Tomadol® 600	Air Products	C10-C16 ethoxylated alcohol	10.6
Tomadol® 901	Air Products	C9-C11, C10-C16 ethoxylated alcohols	12.1
Tomadol® 91-6	Air Products	C9-C11 ethoxylated alcohol	14.3
Tomadol® 91-8	Air Products	C9-C11 ethoxylated alcohol	15.2

Table 2. Measurement of UV Absorbance Before and After Gel Swelling

Initial Concentration: 200 ppm					April 18, 2009		
Surfactant	**λmax(nm)**	**Initial ABS**	**Equili. ABS**	**Bkground ABS**	**Net ABS**	**Ceq.(ppm)**	**ppm Change**
Tergitol® NP-10	275	0.429	0.834	0.226	0.608	283	41.5%
Igepal® CO-530	276	0.806	1.354	0.217	1.137	282	41.0%
Triton® X-405	274	0.136	0.405	0.229	0.176	259	29.5%
C16 PRDIUM	259	2.106	2.690	0.258	2.432	231	15.5%
C12 PRDIUM	257	2.451	2.590	0.264	2.326	190	-5.0%
BENZALK	261	0.179	0.441	0.254	0.187	209	4.5%
C12BENSULNIC	260	0.227	0.518	0.256	0.262	231	15.5%
C8BENSUL	260	0.232	0.503	0.256	0.247	213	6.5%
Calsoft® LAS-99	260	0.229	0.539	0.256	0.283	247	23.5%
Calimulse® EM-99	260	0.244	0.545	0.256	0.289	237	18.5%
Calimulse® PRS	260	0.202	0.481	0.256	0.225	223	11.5%
Calfax® 16L-35	215	3.768	3.768	3.291	0.477	XXX	XXX
Calsoft® L-40	260	0.237	0.542	0.255	0.287	242	21.0%
Dowfax® 2A1	224	3.757	3.757	2.979	0.778	XXX	XXX

C12 PRDIUM: n-dodecylpyridinium chloride hydrate

C16 PRDIUM: (1-hexadecyl)pyridinium bromide monohydrate

BENZALK: benzalkonium chloride

C12BENSULNIC: sodium dodecyl benzensulfonic acid

C8BENSUL: sodium 4-n-octyl benzene sulfonate

Table 3. Viscosity (cP) of Particle Gel at 25 °C in Various Surfactants and at Different RPM

(0.30 g particle 100~120 mesh and 14.70 g surfactant solution, 200 ppm in 1.00 wt% NaCl)

Surfactant	Swelling ratio	0.5 RPM	1.0 RPM	2.0 RPM	4.0 RPM	5.0 RPM
Distilled Water only	22.4	1630.0	1026.0	808.3	560.9	503.3
1.00 wt.% only	22.4	1590.0	986.8	689.9	485.9	438.5
Aerosol® MA-80	22.6	1440.0	941.8	695.9	580.4	529.1
Calamide® CWT	24.7	1404.0	842.8	644.9	511.4	453.5
Triton® X-405	23.3	1338.0	875.8	667.4	526.4	469.1
Ethomeen® C/12	23.0	1290.0	941.8	745.3	525.6	472.7
Alfoterra® 23	22.6	1254.0	836.8	647.9	524.9	491.3
Neodol® 1-5	22.1	1236.0	725.8	490.4	367.4	344.9
Neodol® 25-7	22.5	1188.0	764.8	530.9	443.2	421.7
Tergitol® 15-S-20	22.8	1182.0	746.8	529.4	411.7	367.7
Neodol® 25-9	23.0	1176.0	794.8	547.4	413.9	382.7
ARQUAD® T-50	22.0	1164.0	689.9	532.4	446.9	400.7
Alfoterra® 48	22.6	1104.0	707.8	514.4	434.9	406.1
Tomadol® 45-13	22.6	1044.0	809.8	608.9	458.9	432.5
Tergitol® 15-S-9	23.1	1038.0	668.9	473.9	397.4	373.1
Tergitol® NP-10	22.6	1026.0	740.8	595.4	506.9	476.9
Tomadol® 25-12	22.6	1020.0	632.9	457.4	383.9	347.9
Tomadol® 91-8	22.8	983.8	698.9	569.9	489.6	461.9
Tergitol® 15-S-3	22.7	929.8	659.9	484.4	348.7	320.9
Tomadol® 45-7	23.6	905.8	572.9	403.4	322.4	295.7
Tomadol® 91-6	23.2	893.8	632.9	520.4	463.4	446.3
Tomadol® 600	23.0	881.8	596.9	436.4	349.4	326.9
Calamide® F	23.4	875.8	554.9	397.4	325.4	294.5
Neodol® 1-9	23.3	863.8	524.9	407.9	341.2	312.5
Igepal® CO-530	23.3	833.8	569.9	455.9	368.9	331.7
Ethomeen® S/12	24.9	833.8	467.9	359.9	278.9	254.9
Tomadol® 901	23.0	821.8	599.9	470.9	425.2	394.1
Neodol® 1-7	22.5	809.8	506.9	332.9	292.4	277.1
Tergitol® 15-S-12	23.1	761.8	473.9	376.4	336.7	316.7
Calamide® CW-100	23.1	617.9	365.9	320.9	260.9	239.9

Table 4. Change of Concentration of NaCl Due to Gel Particle Swelling

Test Procedure	Std. 1.00 wt.% NaCl solution		Equili. NaCl solution
Empty Test Tube	13.9754 g		13.9021 g
NaCl Solution	5.0100 g		5.0081 g
NaCl Expected	0.0501 g		To be measured
Total weight after drying	14.0986 g		14.0259
Mass of AgCl (MW: 143.5)	0.1232 g		0.1238 g
Mass of NaCl (MW: 58.5)	0.0502 g		0.0505 g
Expt. Error	**0.2%**	**Equili. Conc.**	**1.01 wt.%**

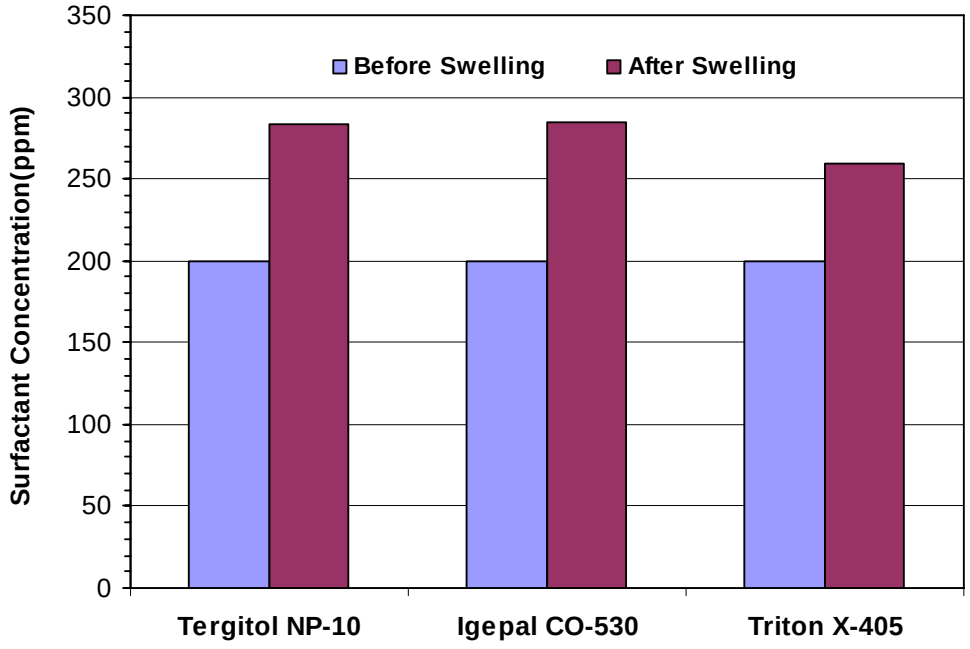


Figure 1. Concentration change for nonionic surfactants

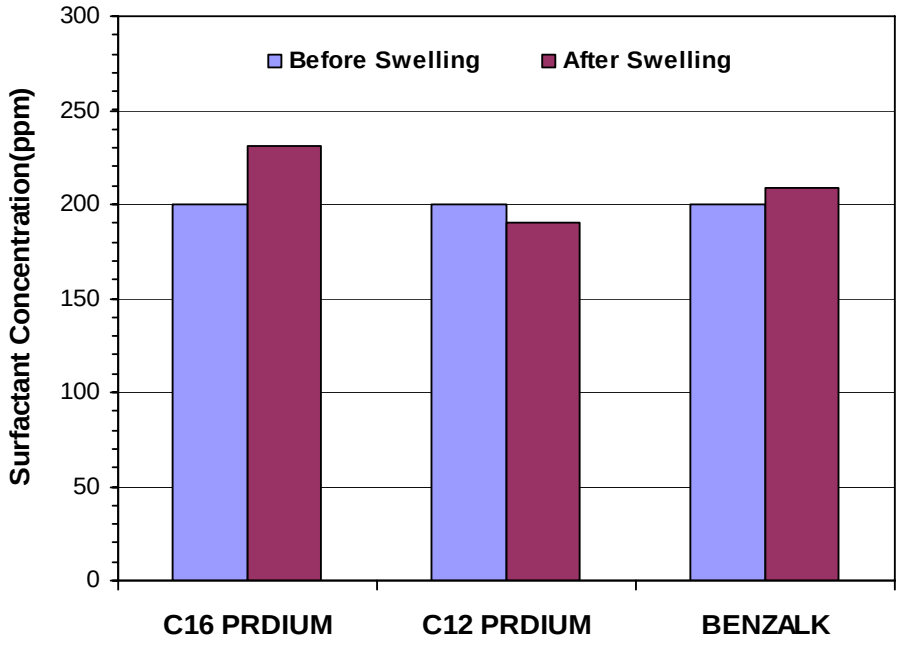


Figure 2. Concentration change for cationic surfactants

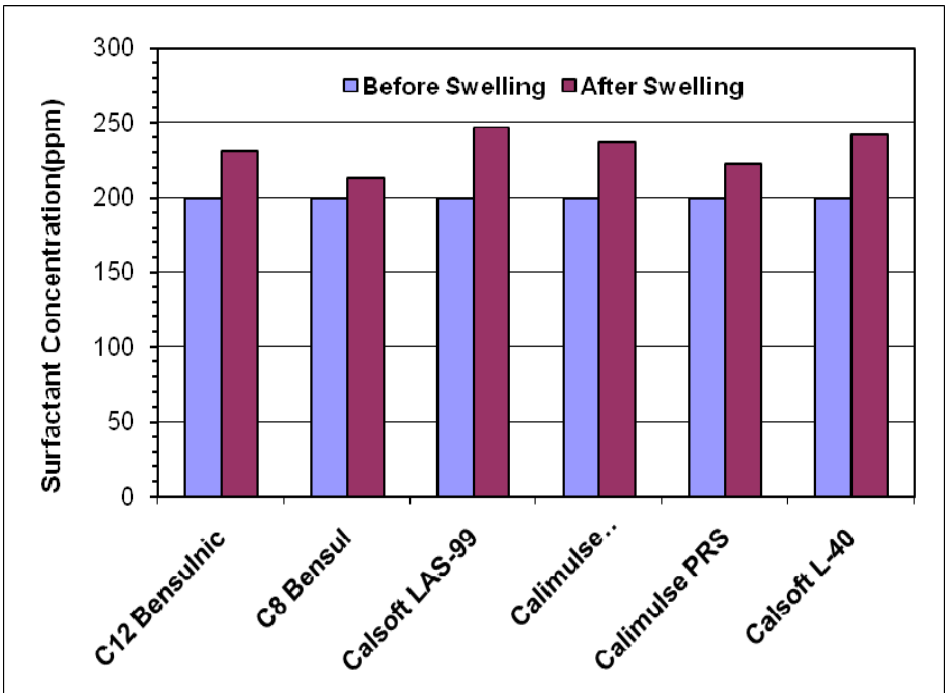


Figure 3. Concentration change for anionic surfactants

Chapter 5. Development and Characterization of PPG Products

SUMMARY

The chapter reports the research progress for the Task 7 “Customized PPG Products” of the PPG project. The task is to provide a series of customized, well-characterized laboratory scale PPG products that cover a wide range of size and chemical characteristics So far, in the first six-months of the project ChemEOR has provided samples of commercial PPG products (PPG-1 and PPG-2, and also a product available from BASF) as well as new, customized experimental samples (PPG-8A and PPG-8B).

After making several experimental trial samples, two custom synthesized PPG samples were sent to Missouri University of Science and Technology (MS&T). These products are the same chemical composition, but ground to two different size particles (PPG-8A, 100-200 mesh, PPG-8B, 40-65 mesh). The PPG-8B product has been characterized by swelling tests in several different combinations of sodium and calcium chloride brines and temperatures.

The results indicate that the swelling amount is significantly higher in a sodium chloride than calcium chloride brine. Also the swelling amount is decidedly less in more saline brine. One performance feature of the PPG-8B product is that it exhibits gradual swelling, taking as much as 5 days to swell to its maximum extent at room temperature. This product seems not to be tolerant at a temperature above 75 C.

Also detailed swelling data are given for the PPG-1 and PPG-2 commercial products. Compared to the PPG-8 product series, the PPG-1 and PPG-2 are more tolerant of higher temperatures and have greater swelling capacity. However the PPG-1 and PPG-2 show quick swelling and may swell less in the presence of high calcium concentration.

EXPERIMENTAL TEST PROCEDURES

Synthesis of PPG

There was an intensive effort to generate some new PPG products during this reporting period. Nearly 10 different PPG experimental samples were prepared during this reporting

period. After being prepared and an initial evaluation of swelling characteristics, one of these (PPG-8 series) was deemed to be sufficiently interesting to be sent on the MS&T.

A general description of the synthesis procedure is given below: In a 2 l beaker in a water bath, add the raw materials sufficient to make 500 grams of final product. The mixture is stirred and purged with pure nitrogen for 30 min at room temperature. Next there is added some initiator while maintaining continuous stirring at 300 rpm. First the mixture is polymerized at room temperature for 30 min to avoid is sudden polymerization. Then the temperature of the water bath is increased to 75 ˚C. The reaction usually is exothermic and produces gel in relatively short time (approximately 20-30 min). The reaction is kept for 3-4 hours at the constant temperature of 75 ˚C to achieve complete polymerization.

After the reaction, the gel formed is dried for 1-2 hours at 50 ˚C oven, cut it into less than 3 mm pieces, then dried again up to complete dryness. These pieces are crushed into smaller particles and dried again at 50 ˚C. Final grinding is performed and the resulting PPG powder is graded with a series of sieves.

Swelling Tests

The purpose of these tests is to assess the tendency of the created PPG particles to swell. Important properties include the rate and extent of the particle swelling, and how this occurs as a function of brine composition and temperature. Such information is needed to aid in the selection of the PPG product best suited for a specific field application.

Materials:

50 ml plastic centrifuge tubes

PPG powder sample

Procedure

1. Add 50 ml of test brine to a centrifuge tube.
2. Weigh out PPG powder
3. Sprinkle gently the PPG powder into the centrifuge tube.
4. Add PPG carefully to avoid creating large lumps of particles.
5. Add remaining PPG slowly.
6. After all of the PPG powder is added, read the interface boundary between the brine portion at the bottom containing the PPG and the brine on top.
7. Read the interface position after a day at room temperature, and after heating for one day

at 50 and 75 ˚C.

8. The degree of swelling is reported as the ratio of the volume (ml) of brine occupied by the PPG powder to the grams of PPG sample added.

RESULTS AND DISCUSSION

Expanded Swelling Data for PPG-1 and PPG-2

Tables 1 and 2 summarize the run conditions and the swelling noted for the several salinity and temperature conditions. These data include a comparison to previous duplicate runs, see also Figures 1 -12. Data are present as normal and also on a log scale for the salinity.

Table 1. Summary Swelling Data for PPG-1

UPDATED -- SUMMARY OF PPG-1 SWELLING DATA

Temp. (C.)	Salinity	Interface (ml)	Sample (gr)	Swelling - ml/gr	Previous Swelling - ml/gr
25	0.1% NaCl	19	0.05	380	300
	0.3% NaCl	17.5	0.1	175	
	1% NaCl	21	0.2	105	130
	3% NaCl	15	0.2	75	
	10 % NaCl	11.5	0.2	57.5	62.5
	0.01% CaCl.2H2O	50	0.1	500	
	0.03% CaCl.2H2O	40	0.1	400	
	0.1% CaCl.2H2O	21	0.2	105	60
	0.3% CaCl.2H2O	16.5	0.2	82.5	
	1% CaCl.2H2O	6.5	0.2	32.5	25
50	0.1% NaCl	18.5	0.05	370	290
	0.3% NaCl	18.5	0.1	185	
	1% NaCl	23	0.2	115	155
	3% NaCl	15.5	0.2	77.5	
	10 % NaCl	11	0.2	55	60
	0.01% CaCl.2H2O	47	0.1	470	
	0.03% CaCl.2H2O	37	0.1	370	
	0.1% CaCl.2H2O	18	0.2	90	55
	0.3% CaCl.2H2O	7	0.2	35	
	1% CaCl.2H2O	4.5	0.2	22.5	25
75	0.1% NaCl	18	0.05	360	400
	0.3% NaCl	19	0.1	190	
	1% NaCl	25	0.2	125	150
	3% NaCl	15.5	0.2	77.5	
	10 % NaCl	11	0.2	55	60
	0.01% CaCl.2H2O	45	0.1	450	
	0.03% CaCl.2H2O	35	0.1	350	
	0.1% CaCl.2H2O	15	0.2	75	40
	0.3% CaCl.2H2O	7.5	0.2	37.5	
	1% CaCl.2H2O	3	0.2	15	15

Table 2. Summary Swelling Data for PPG-2

UPDATED -- SUMMARY OF PPG-2 SWELLING DATA

Temp (C.)	Salinity	Interface (ml)	Sample (gr)	Swelling - ml/gr	Previous Swelling - ml/gr
25	0.1% NaCl	18	0.05	360	300
	0.3% NaCl	22	0.1	220	
	1% NaCl	26	0.2	130	100
	3% NaCl	16.5	0.2	82.5	
	10 % NaCl	14	0.2	70	60
	0.01% CaCl.2H2O	48	0.1	480	
	0.03% CaCl.2H2O	39	0.1	390	
	0.1% CaCl.2H2O	38	0.2	190	120
	0.3% CaCl.2H2O	16	0.2	80	
	1% CaCl.2H2O	3.5	0.2	17.5	36
50	0.1% NaCl	20	0.05	400	80
	0.3% NaCl	28	0.1	280	
	1% NaCl	26	0.2	130	100
	3% NaCl	16	0.2	80	
	10 % NaCl	15	0.2	75	57.5
	0.01% CaCl.2H2O	30	0.1	300	
	0.03% CaCl.2H2O	25	0.1	250	
	0.1% CaCl.2H2O	33	0.2	165	112
	0.3% CaCl.2H2O	9	0.2	45	
	1% CaCl.2H2O	3	0.2	15	50
75	0.1% NaCl	23	0.05	460	80
	0.3% NaCl	35	0.1	350	
	1% NaCl	26.5	0.2	132.5	100
	3% NaCl	16	0.2	80	
	10 % NaCl	15	0.2	75	57.5
	0.01% CaCl.2H2O	15	0.1	150	
	0.03% CaCl.2H2O	13	0.1	130	
	0.1% CaCl.2H2O	30	0.2	150	112
	0.3% CaCl.2H2O	6	0.2	30	
	1% CaCl.2H2O	2.5	0.2	12.5	50

These results show the salinity is the most important factor to determine the degree of swelling. The sodium chloride samples had more swelling than the calcium chloride samples at the same added salt concentration. In addition, increasing the salinity depressed the degree of particle swelling.

Other parameters had little effect on the swelling results. The particle size distribution has minimal effect, with perhaps the PPG-1 having slightly more swelling. The temperature has only a small impact on the particle swelling in the range of 25 – 75 ˚C.

Swelling Data for PPG- 8B

Table 3 summarizes the swelling data of PPG-8B. There swelling data indicate that for the PPG-8 Series of samples:

- There is a delay in the swelling of the particles, with a noticeable increased expansion after 5 days aging at 25 ˚C versus only one day.
- The subsequent aging for one day at 50 ˚C shows little change for the NaCl case. For the CaCl2.2H2O case, there is some contraction of the particles at 50 ˚C.
- The rapid shrinkage at 75 ˚C suggests this product may not be suitable for high temperature applications.

Table 3. Summary Swelling Data for PPG-8B

PPG-8B Swelling Behavior

Salinity	Sample (gr)	1 Day -- 25 C Interface (ml)	3 Day -- 25 C Interface (ml)	4 Day -- 25 C Interface (ml)	5 Day -- 25 C Interface (ml)	6 Day -- 50 C Interface (ml)	7 Day -- 75 C Interface (ml)
0.1% NaCl	0.05	5	5.5	6.5	6.5	6	N/A
0.3% NaCl	0.1	6	6.5	8.5	8.5	7.5	2
1% NaCl	0.2	8.5	9	12.5	12	12	2
3% NaCl	0.2	7.5	8	10.5	10.5	10.5	2
10 % NaCl	0.2	7.5	8	11	11	10.5	3
0.01% CaCl.2H2O	0.1	5	8	7.5	7.5	5	N/A
0.03% CaCl.2H2O	0.1	5.5	6	10	9.5	6	2
0.1% CaCl.2H2O	0.2	7	7	9	8.5	5.5	3
0.3% CaCl.2H2O	0.2	7	7	8	8	7	2
1% CaCl.2H2O	0.2	7.5	8	10	9	10	2

Salinity	Sample (gr)	1 Day -- 25 C Swelling - ml/gr	3 Day -- 25 C Swelling - ml/gr	4 Day -- 25 C Swelling - ml/gr	5 Day -- 25 C Swelling - ml/gr	6 Day -- 50 C Swelling - ml/gr	7 Day -- 75 C Swelling - ml/gr
0.1% NaCl	0.05	100	110	130	130	120	N/A
0.3% NaCl	0.1	60	65	85	85	75	20
1% NaCl	0.2	42.5	45	62.5	60	60	10
3% NaCl	0.2	37.5	40	52.5	52.5	52.5	10
10 % NaCl	0.2	37.5	40	55	55	52.5	15
0.01% CaCl.2H2O	0.1	50	80	75	75	50	N/A
0.03% CaCl.2H2O	0.1	55	60	100	95	60	20
0.1% CaCl.2H2O	0.2	35	35	45	42.5	27.5	15
0.3% CaCl.2H2O	0.2	35	35	40	40	35	10
1% CaCl.2H2O	0.2	37.5	40	50	45	50	10

Table 4. Comparison of Swelling Behavior for Different PPG Samples

COMPARISON OF SWELLING BEHAVIOR AMONG SAMPLES

Temperature	Salinity	PPG-1 (1 Day) Swelling - ml/gr	PPG-2 (1-Day) Swelling - ml/gr	PPG-8B (5-Day) Swelling - ml/gr
25 C	0.1% NaCl	380	360	130
	0.3% NaCl	175	220	85
	1% NaCl	105	130	60
	3% NaCl	75	82.5	52.5
	10 % NaCl	57.5	70	55
	0.01% CaCl.2H2O	500	480	75
	0.03% CaCl.2H2O	400	390	95
	0.1% CaCl.2H2O	105	190	42.5
	0.3% CaCl.2H2O	82.5	80	40
	1% CaCl.2H2O	32.5	17.5	45

Temperature	Salinity	PGG-1 Swelling - ml/gr	PPG-2 Swelling - ml/gr	PPG-8B Swelling - ml/gr
50 C	0.1% NaCl	370	400	120
(1 day aging)	0.3% NaCl	185	280	75
	1% NaCl	115	130	60
	3% NaCl	77.5	80	52.5
	10 % NaCl	55	75	52.5
	0.01% CaCl.2H2O	470	300	50
	0.03% CaCl.2H2O	370	250	60
	0.1% CaCl.2H2O	90	165	27.5
	0.3% CaCl.2H2O	35	45	35
	1% CaCl.2H2O	22.5	15	50

Temperature	Salinity	PGG-1 Swelling - ml/gr	PPG-2 Swelling - ml/gr	PPG-8B Swelling - ml/gr
75 C	0.1% NaCl	360	460	N/A
(1 day aging)	0.3% NaCl	190	350	20
	1% NaCl	125	132.5	10
	3% NaCl	77.5	80	10
	10 % NaCl	55	75	15
	0.01% CaCl.2H2O	450	150	N/A
	0.03% CaCl.2H2O	350	130	20
	0.1% CaCl.2H2O	75	150	15
	0.3% CaCl.2H2O	37.5	30	10
	1% CaCl.2H2O	15	12.5	10

SAP - Super Absorbing Polymer

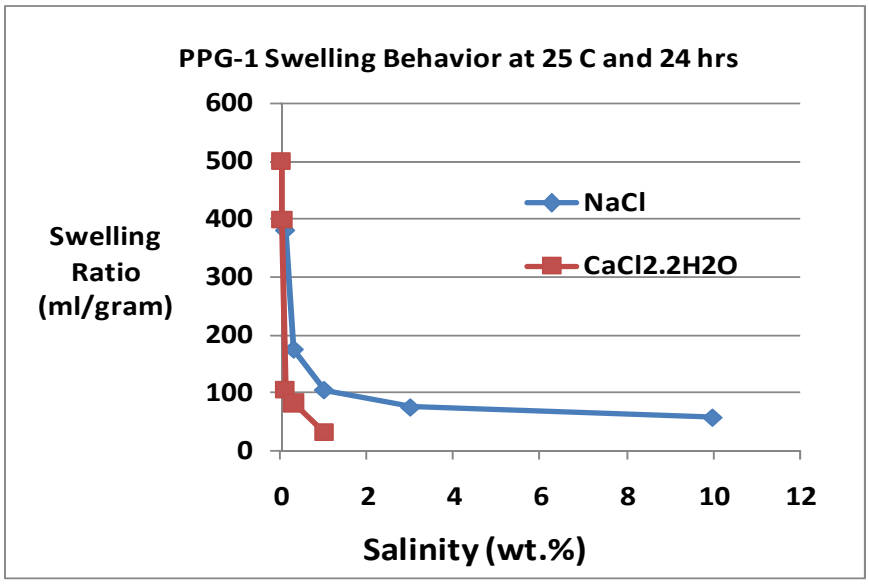
We have identified a household commercial product that may be useful for the intended oil field application. BASF markets in the U.S. polycarbonate gels; they name this series of products Luquasorb. They refer to these as SAP -- Super Absorbing Polymers. For example, these products may be used to retain water for agricultural uses.

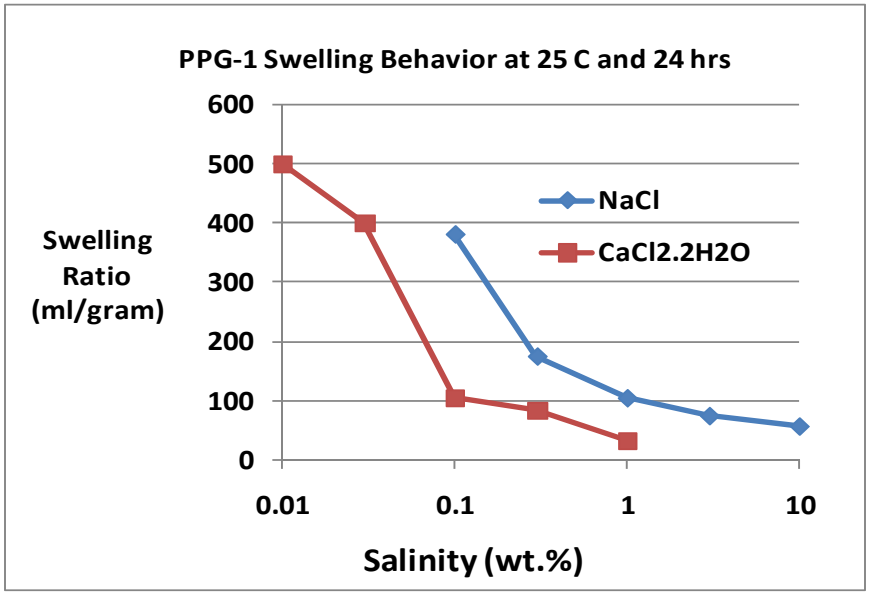
We have obtained samples of the BASF products and have forwarded to MS&T for their consideration.

FUTURE WORK

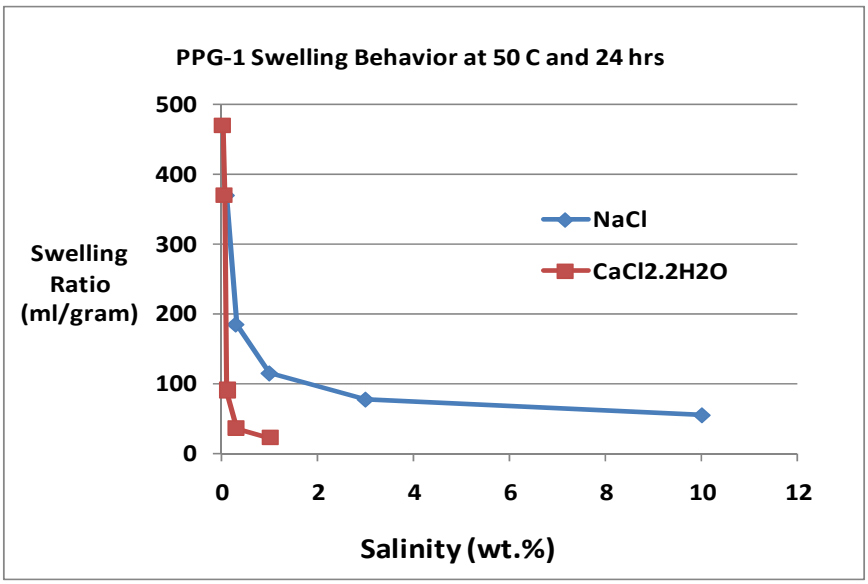
Synthesis of laboratory scale samples of additional PPG candidate products are in progress. The strategy is to alter the chemistry and particle size distribution of these samples; the expectation is in that way the different samples will display different physical characteristics (focus on swelling behavior).

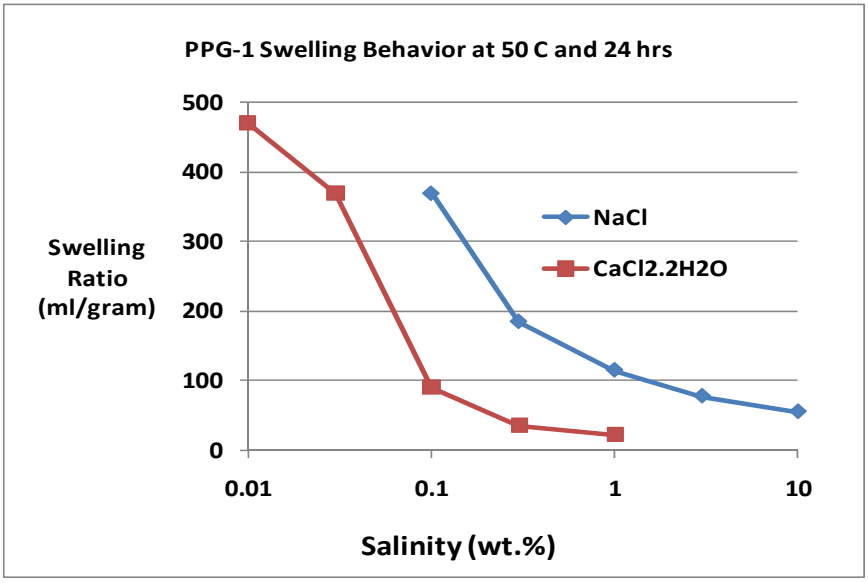
We will continue to characterize the swelling behavior of new commercial products (e.g. SAP) and experimental samples as available.



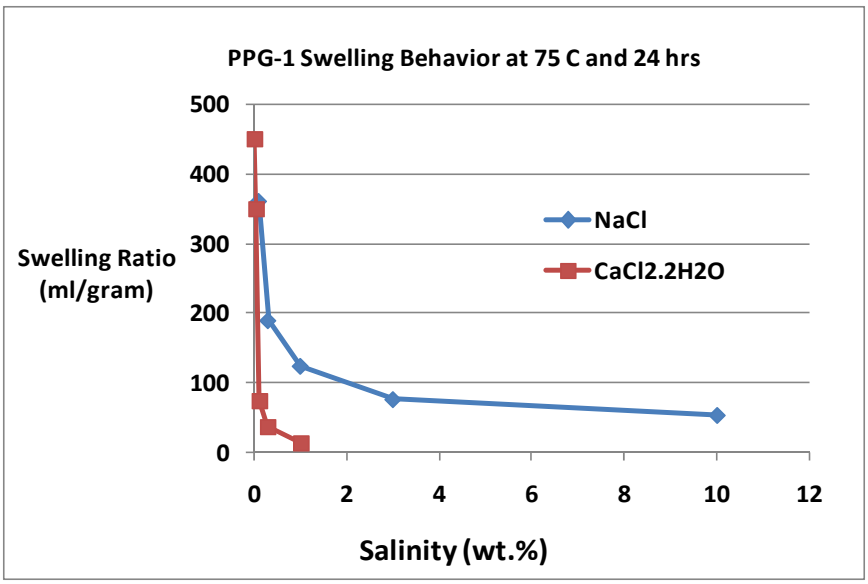


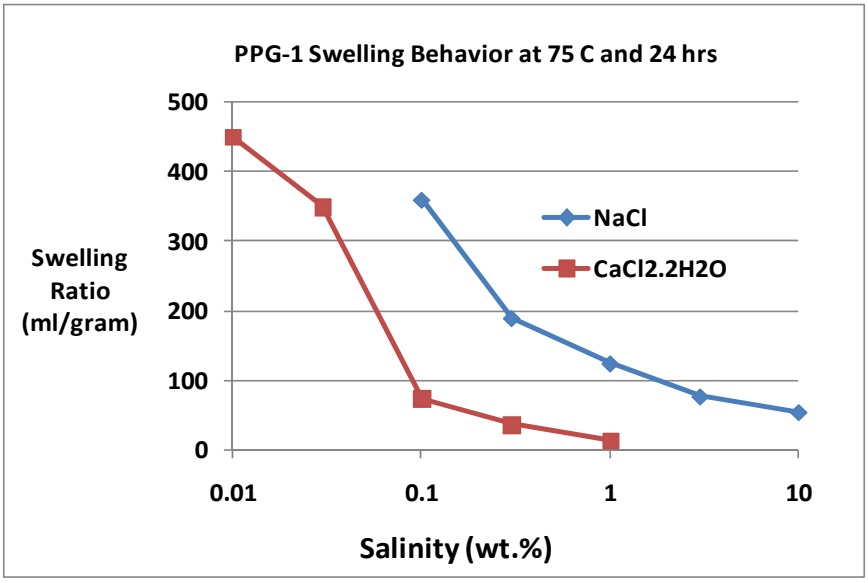
Figures 1 – 2. Swelling data for sample PPG-1 at 25 ˚C.



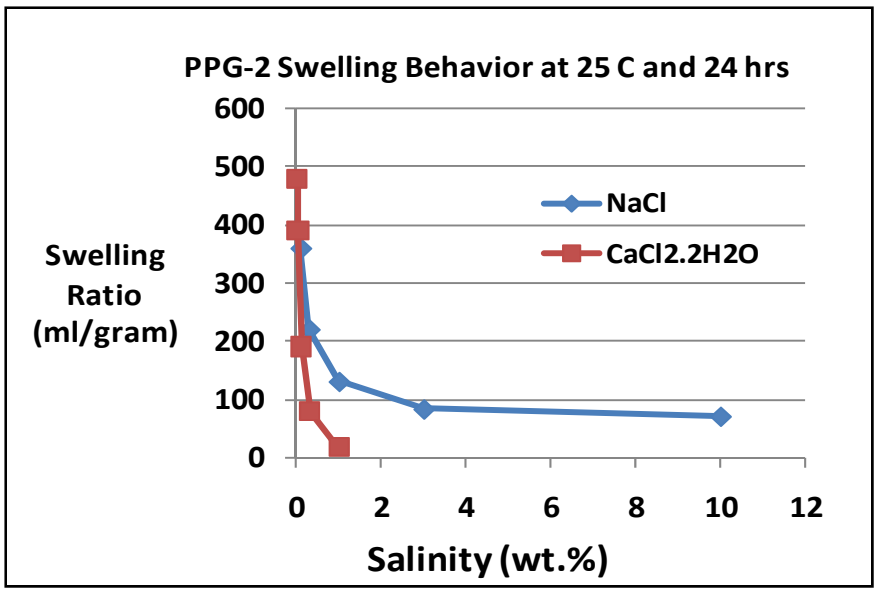


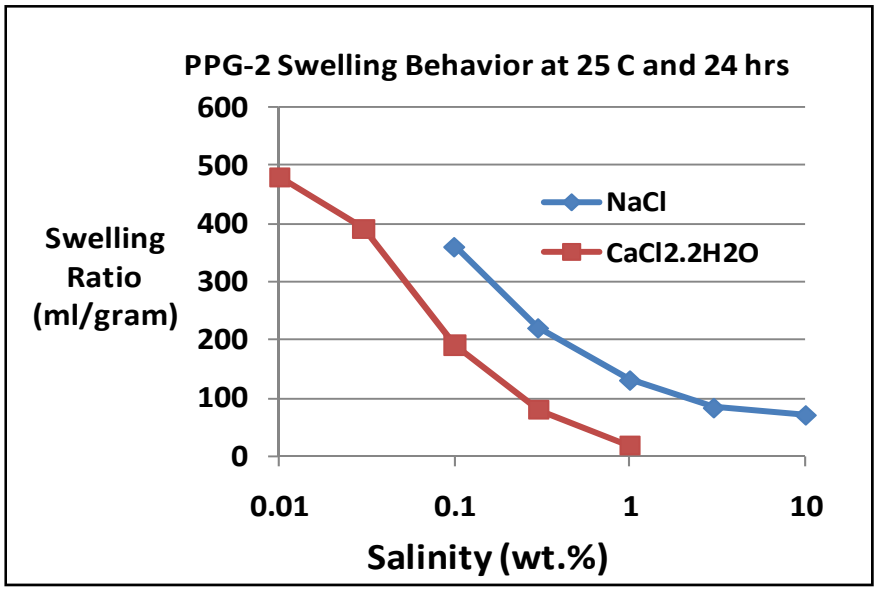
Figures 3 – 4. Swelling data for sample PPG-1 at 50 ˚C.



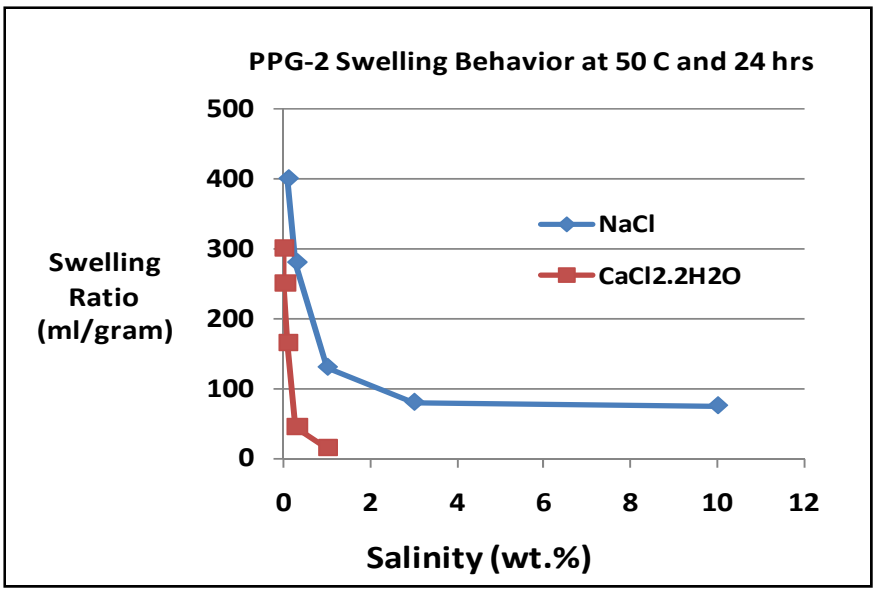


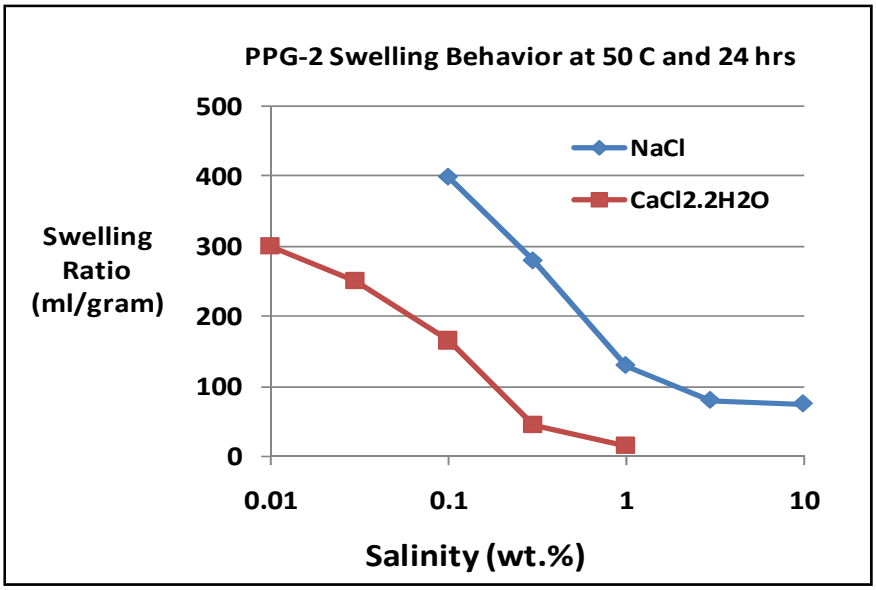
Figures 5 – 6. Swelling data for sample PPG-1 at 75 ˚C.



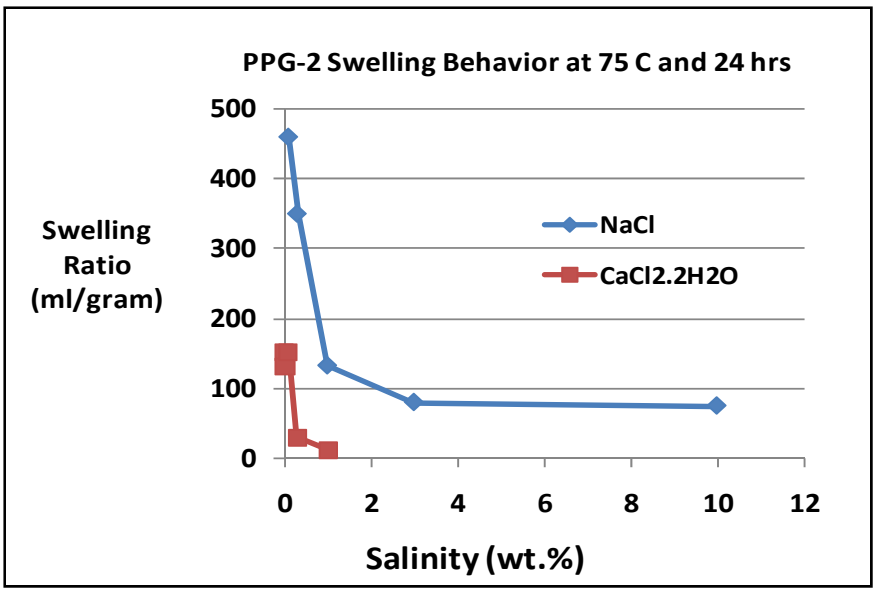


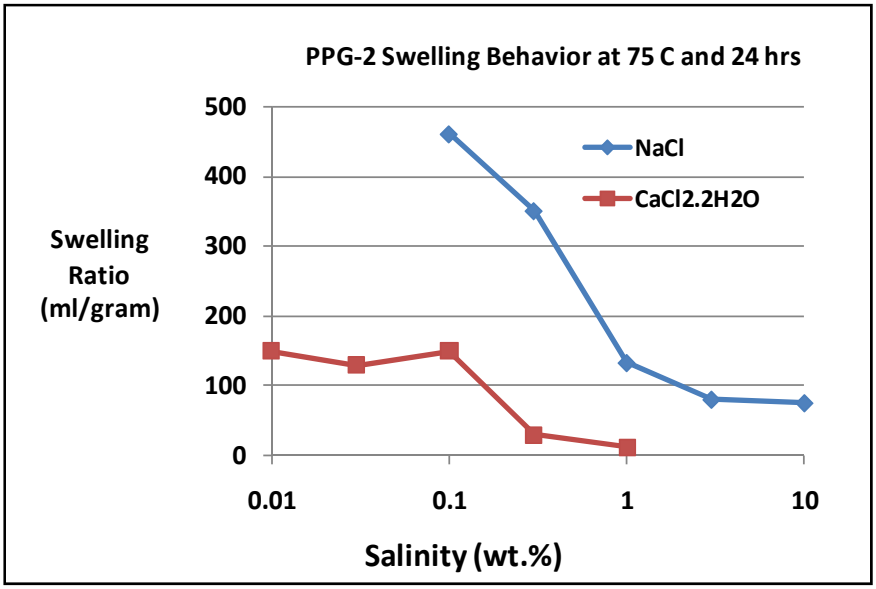
Figures 7 – 8. Swelling data for sample PPG-2 at 25 ˚C.



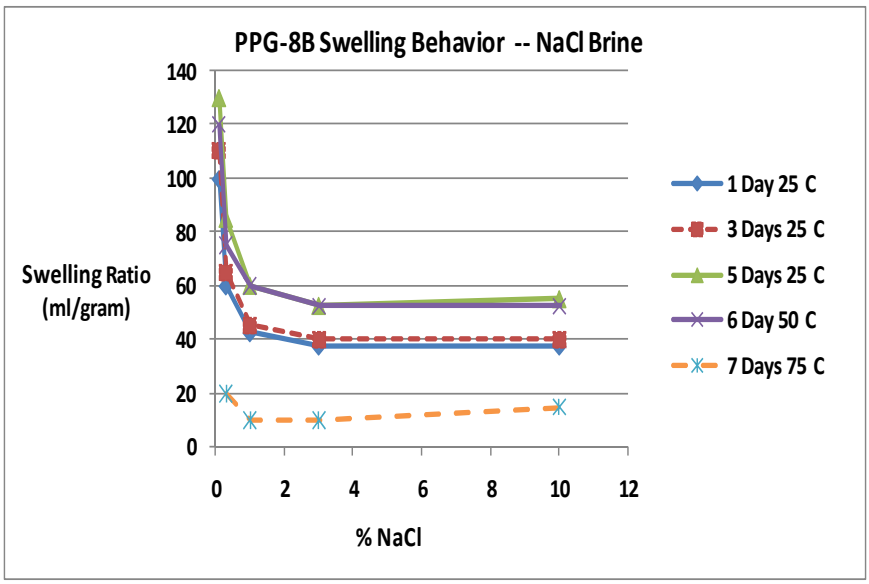


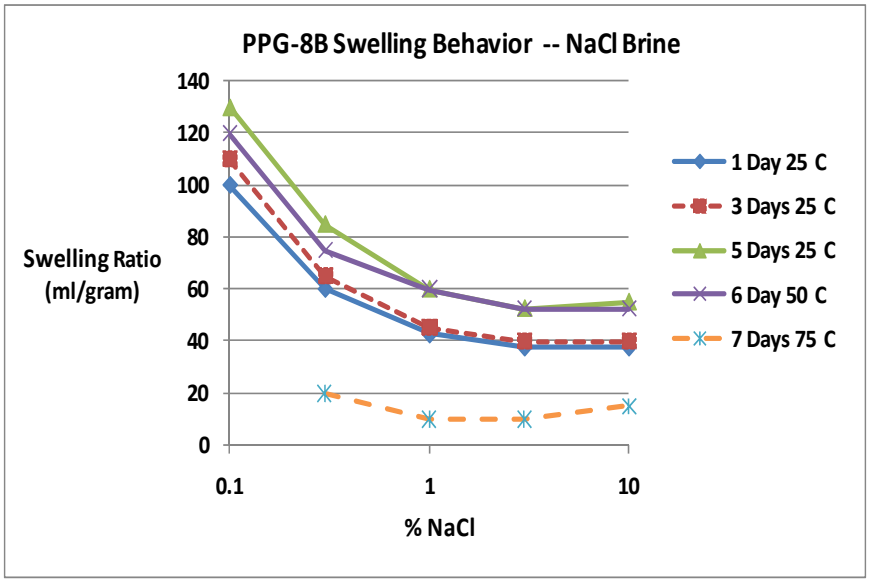
Figures 9 – 10. Swelling data for sample PPG-2 at 50 ˚C.



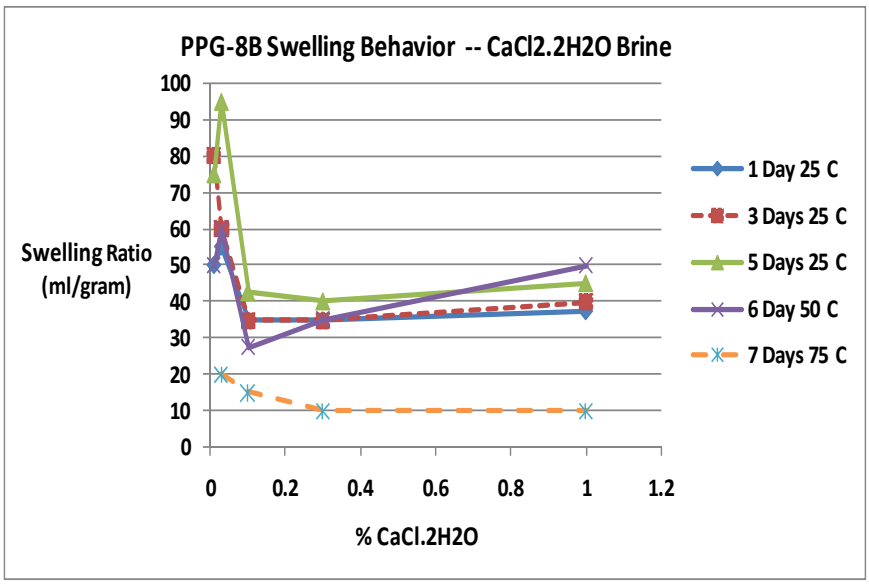


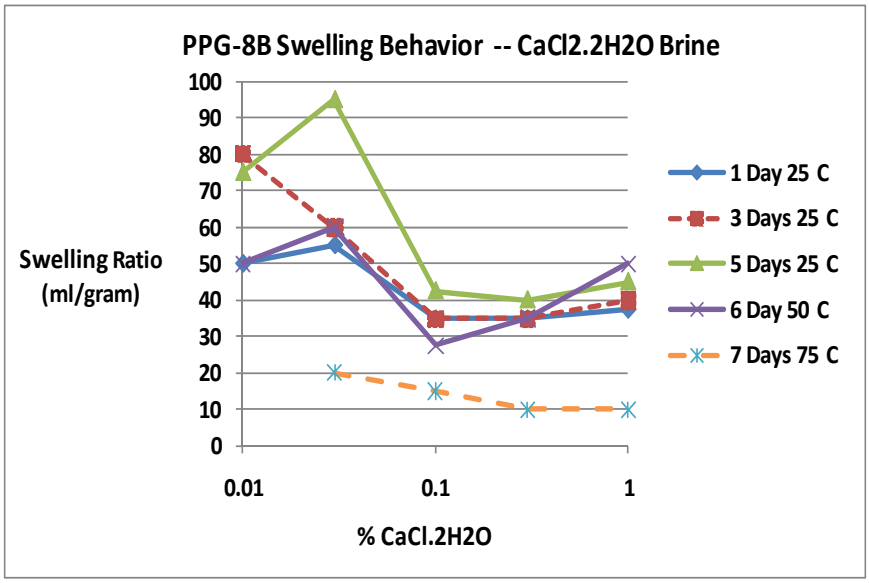
Figures 11 – 12. Swelling data for sample PPG-2 at 75 ˚C.





Figures 13 – 14. Swelling data for sample PPG-8B in NaCl Brine





Figures 13 – 14. Swelling data for sample PPG-8B in $CaCl_2$ Brine