Preformed Particle Gel for Conformance Control: Factors Affecting Its Properties and Applications

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Summary
Preformed particle gel (PPG) is a particled superabsorbent crossklinking polymer that can swell up to 200 times its original size in brine. The use of PPG as a fluid-diverting agent to control conformance is a novel process designed to overcome some distinct drawbacks inherent in in-situ gelation systems. This paper introduces the effect of gelant compositions and reservoir environments on the two properties of PPG: swollen gel strength and swelling capacity. Results have shown that PPG properties are influenced by gelant compositions, temperature, brine salinity, and pH below 6. Temperature increases PPG swelling capacity but decreases its swollen gel strength. Salinity decreases PPG swelling capacity but increases its swollen gel strength. PPG is thermostable at an elevated temperature of 120°C if a special additive agent is added into its gelant as a composition. PPG is strength- and size-controlled, environmentally friendly, and not sensitive to reservoir minerals and formation water salinity.

Two field applications are introduced to illustrate the criteria of well candidate selection and the design and operation process of PPG treatments. Field applications show that PPG treatment is a cost-effective method to correct permeability heterogeneity for the reservoirs with fractures or channels, both of which are widely found in mature waterflooded oil fields.

Introduction
Most oil fields in China are found in continental sedimentary basins. They are characterized by complex geologic conditions and high permeability contrast inside reservoirs. To maintain or increase the driving force, these oil fields were developed by waterflooding. However, serious vertical and lateral formation heterogeneity has resulted in the rapid water-cut increase of production wells. Moreover, sand production and rock mineral dissolution due to water injection have made reservoirs much more heterogeneous. Many interwell tracer tests have shown that channels or fractures widely exist in most oil fields, whether they have fractures or not during their early development stage. Another demonstration of worsening heterogeneity comes from the clay gel treatments for conformance control in China oil fields. Many injection wells have successfully injected tens or hundreds of tons of clay. If we calculate the permeability from Darcy law according to the “1⁄9-1⁄3” rule (Maroudas 1966; Pautz et al. 1989), which gives the relationship of particle penetration depth into porous media to the ratio of pore-throat diameter and particle size, the formation permeability should be more than 1,000 darcies (Bai 2001). Moreover, early polymer breakthroughs in the Daqing, Nanyan, and Shengli oil fields have further demonstrated that channels or fractures are common in most oil fields (Bai 2001). Severe reservoir heterogeneity has become one of the most urgent problems that reservoir engineers have to solve.

To control water cut and improve the oil recovery of oil fields, many technologies, such as polymer flooding, surfactant flooding, foam flooding, and so on, have been widely applied in China in past decades (Wang et al. 2003; Yang et al. 1988, 2003; Song et al. 1995). One of the most popular methods is to inject gels to reduce the flow capacity of channels or fractures and divert the following fluid (normally, water) to unswept oil zones (Bai et al. 1999; Seright et al. 2001). Before the 1990s, gel treatments focused on correcting permeability heterogeneity near the wellbore (normally 5 to 10 m). However, in-depth gel treatments have become more important within the last 10 years because the crossflow in a heterogeneous thick zone has become a significant factor influencing the oil recovery of mature oil fields; in addition, many wells have been treated multiple times using gels, resulting in no more oil remaining near a wellbore (Liu 1995).

Recently, several authors have recommended using preformed gel to control conformance in mature oil fields (Seright et al. 2001; Seright 2000; Chauvetteau et al. 2000, 2001; Feng et al. 2003; Li et al. 1999; Coste et al. 2000; Bai et al. 2007) because it can overcome some distinct drawbacks inherent in in-situ gelation systems, such as difficulty of gelation time control, potential damage of low-permeability hydrocarbon zones, and the uncertain nature of gelling caused by the shear in surface facilities and porous media.

Seright et al. (2001) and Seright (2000) studied some properties of preformed bulk gel through fractures and stated that preformed gel had better placement than in-situ gel and could effectively reduce gel damage on low-permeability unswept oil zones. Chauvetteau et al. (2000, 2001) synthesized preformed microgels that were crosslinked under shear. Feng et al. (2003) demonstrated that the microgels could be injected easily into porous media without any sign of plugging and showed that these microgels could be good candidates for water-shutoff and profile-control operations.

On the basis of the reservoir status of the China oil fields discussed above, a new idea using PPG to control conformance was proposed by Li et al. (1999) in China. Coste et al. (2000) and Bai et al. (2007) analyzed some properties of PPG and PPG propagation mechanisms through porous media.

In this paper, the effects of gel compositions and reservoir conditions on PPG properties were systematically studied by evaluating swollen PPG strength and PPG swelling capacity. Two of the earliest field application cases were introduced to show how to screen candidate wells and how to operate the injection procedures.

Preparation of Preformed Particle Gel
Preformed particle gel is a kind of xerogel that can swell by absorbing water. It can swell to many times its original size in brine. Limited swelling occurs when the molecules remain bound in a network, while unlimited swelling causes the xerogel to dissolve.

The processes synthesizing the xerogel are as follows:
1. Prepare an aqueous solution containing acrylamide, crosslinker, initiator, and other additives according to a given recipe.
2. Make the solution crosslink to form bulk gel under a certain temperature.
3. Cut the bulk gel into small pieces and dry them at the temperature of 70°C.  
4. Mechanically grind the dried gel pieces into smaller particles with sizes in micrometer or millimeter scale, depending on field application requirements.

August 2007 SPE Reservoir Evaluation & Engineering
Fig. 1—Morphology of PPG before and after swelling.

Fig. 2—Synthesis of preformed gel.

Fig. 3—Effect of monomer concentration on PPG strength and swelling capacity.

(a) Before swelling  (b) After swelling

**Results and Discussion**

**Effect of Gelant Compositions on PPG Properties.** *Acrylamide Concentration.* Fig. 3 presents the effect of monomer concentration on the swelling capacity and strength of preformed gel (400 mg/L crosslinker +3,000 mg/L initiator). The monomer concentration does not significantly influence the PPG swelling capacity.

The gel strength increases with the increase in monomer concentration and approaches a stable value at monomer concentrations above 15 wt%. It is suggested that the gel strength is a function of both monomer concentration and crosslinker concentration. At an optimized ratio of monomer and crosslinker (375:1 weight ratio), the composite gel has the highest strength and elastic modulus.

**Crosslinker Concentration.** The crosslinker has a multifunctional group that can build a complex network with –CONH– bridges and form a 3D network structure during the polymerization process. The crosslinker concentration is critical for the structure and properties of the gel. Fig. 4 shows the relationship of PPG strength and swelling capacity vs. crosslinker concentration. The increase of gel strength with increased crosslinker concentration is mainly caused by the increase in network density. The swelling capacity in water is mainly attributed to the hydrophilic group in the polymer molecule. Thus, the number of hydrophilic groups and the cage size of the 3D crosslinked gel have a significant effect on swelling capacity. With an increase in crosslinker concentration, more hydrophilic groups will take part in the gelation reaction, resulting in lower hydrophilicity. At the same time, because of steric hindrance, the swelling capacity will be reduced somewhat when the crosslinker concentration is too high. The variation of yield stress with different crosslinker concentrations shows the same trend in Fig. 5. It indicates that the optimized crosslinker concentration ranges from 300 to 400 mg/L.

**Initiator Concentration.** The initiators used to start the polymerization are chemical entities (peroxide compounds), which will produce free radicals during their dissociation at proper conditions. To accelerate the reaction, a catalyst was used to increase the dissociation rate at low temperature. It was observed that the polymerization reaction was retarded by the presence of clay addi-
It is assumed that the clay particles consume some of the free radicals. Normally, some more initiator is necessary for the polymerization reaction when clay is present. Fig. 6 gives the gelation time vs. initiator concentration. More free radicals can be generated at higher initiator concentration. The unsaturated monomer, which is readily susceptible to free radicals, will form long chain polymers.

**NH₄Cl.** The NH₄Cl is used to adjust the pH of the synthesis solution, which will affect the hydrolysis of the –CONH₂ group. Fig. 7 shows the influence of NH₄Cl on the PPG properties at a composition of 15% monomer +400 mg/L crosslinker +3,000 mg/L. The addition of NH₄Cl can decrease the pH of the reaction solution. Thus, the more hydrophilic group –COOH in the gel matrix can be produced at suitable hydrolysis conditions. The hydrolysis is used to control swelling capacity.

**Bentonite Clay.** The layered bentonite clay is used as a reinforcement of the composite PPG. The reinforcement of polymer gel with clay by forming an intercalated composite has been actively studied for approximately 30 years (Theng 1979). In this work, in-situ polymerization is used in the synthesis of the polyacrylamide/clay composite gel. X-ray and transmission electron microscopy investigations have indicated that bentonite clay has a layered structure with an interlayer distance of approximately 1.0 nm (Vogt et al. 2002). The surface property, the trace impurity, and the geometry of clay particles play an important role in the synthesis of composite material (Laus et al. 1998).

The commercial bentonite clay was separated by a standard sedimentation process, and the clay that was less than 2.0 μm in size was used as an additive to enhance the strength of the composite polymer/clay gel. It was shown that dramatic changes were obtained in the mechanical and physical properties of polymer clay gel formed by in-situ polymerization. The influence of clay addition on the strength and swelling capacity is given in Fig. 8. The swelling capacity decreases initially with the addition of clay and approaches a stabilized value at the clay concentration of approximately 5.0 wt%. This can be explained by the fact that the bentonite clay has a negatively charged surface in which the hydrolyzed polyacrylamide can bond onto the surface due to the colomic force. Thus, the density of the hydrophilic functional group will decrease when clay is introduced into the matrix. The swelling capacity will decrease with the addition of clay. However, the physical property of composite gel is significantly improved. Tensile strength (σ) and elastic modulus (G') were measured with a rheology meter (RS150, Haake). Eqs. 2 and 3 are used to define G' and σ.

\[
G' = \frac{\tau_0}{\gamma_0} \cos \delta, \quad \text{.................................} \quad (2)
\]

\[
\sigma = E \cdot \varepsilon, \quad \text{.................................} \quad (3)
\]

where σ = stress, \( \varepsilon \) = strain, \( \delta \) = phase angle, and \( E \) = Young's modulus.

It is suggested that the reinforcement properties of polymer clay composite gel are attributed mainly to hybrid effects of interfacial properties and restricted mobility of the polymer chains. Shi et al. (1996) studied the interfacial effects on the influence of nanocomposite strength based on the assumption that the polymers are binding directly on the surface of clay particles. The restricted mobility of the reinforcement mechanism was described and studied by Kojima et al. (1993), who suggested that the constrained
mobility of polymer chains had an energy-dissipation effect under shearing.

**Thermal Stability Agent (SA).** To improve the thermal stability of PPG, 0.2% SA was added during gel synthesis. The thermal stability is defined as the time period in which PPG retains 80% of its original strength in our experiments at a given temperature. Results have demonstrated that PPG without SA can keep 80% of its original strength for 1 year at 90°C when the PPG suspension is prepared with 0 to 30,000 mg/L NaCl solution. PPG can be stable for more than 1 year at the temperature of 120°C when the additive SA is added as a gelant composition.

**Effect of Environmental Factors on PPG Swelling Capacity.**

**Temperature.** At higher temperatures, more amino groups (–CONH₂) will change to an acidic carboxylic group (–COOH) by hydrolysis. **Fig. 9** shows PPG swelling capacity at different temperatures and indicates that the swelling capacity increases with the increase in temperature. The significant swelling capacity increase occurs at the temperature of 60°C or higher.

**Salinity.** **Fig. 10** shows the influence of salinity on the property of PPG. The main effect of salinity is the swelling capacity; at low concentration, the swelling capacity decreases with the increase in salt concentration. The swelling capacity decreases from 120 to approximately 50 g/g when the NaCl concentration increases from 0 (pure water) to 5,000 mg/L. These phenomena can be attributed to the state electric repulsive force and charge balance. The swelling process at different salt concentrations is illustrated in **Fig. 11**.

At low salt concentration, the electric repulsive forces will separate the molecules in gel and create more space for water coming in. However, when the gel is swollen in high-salinity water, the negatively charged group will be balanced by the cations and will restrict further water absorption.

**pH.** The pH effect on the swelling property is given in **Fig. 12**. In acidic conditions, the swelling capacity increases with an increase of pH and approaches a stabilized value at pH = 6.0. In basic conditions, the effect of pH on swelling capacity is undetectable. The pH influence can be attributed to the release of proton ions in an acidic condition, which shields the electric repulsive force of charged groups.

**Applications**

**Field Application Cases.** PPG has been applied successfully to correct in-depth reservoir permeability heterogeneity in most mature oil fields in China, such as Daqing, Zhongyuan, Liaohai, Shengli, Tuha, Dagang, and Jidong. These oil fields cover extremely serious conditions. For example, Zhongyuan oil field is characterized by high salinity and high temperature, Dagang has characteristics of severe channel and high temperature, and Tuha is a naturally fractured reservoir. As of 2007, approximately 2,000 wells in Chinese oil fields had been treated with PPG (Liu 2006). The amount of dried PPG for each treatment ranges from 3,000 to 40,000 kg. All wells were injected successfully without injectivity problems. Two of the earliest field applications are given in this paper to show how to design and operate PPG treatments.

**Case 1.** This was the first PPG treatment in Zhongyuan oil field, SINOPEC. This case includes two adjacent injection wells, W51-75 and P-72, in Pucheng oil field. Three production wells are connected with the two injectors. It is a sandstone reservoir with an average permeability of 121 md without natural fractures. The formation temperature is 107°C, and the total salinity of the formation water is 15×10⁴ mg/L. The reservoir has been developed by waterflooding since 1979. The two wells were not hydraulically fractured. The two wells were treated with PPG in 1999 for the following reasons:

- Each of the two wells has high water injectivity. The injectivity index of Well W51-75 is 20 m³/(MPa·d), with a threshold pressure (defined as the minimum injection pressure at which wa-
The injectivity index of Well P-72 is 18 m³/(MPa·d), with a 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 extremely vertical heterogeneity. Tracer-test results showed that the wells had an extremely severe areal heterogeneity and channel between injectors and producers (tracer breakthrough in 2 days).

The injection pressure was increased: The water injection pressure of Well P-72 increased from 19.5 to 24 MPa, and the water-injection pressure of Well W51-75 increased from 16 to 19 MPa. The injection pressure after treatment kept going higher than that before treatment for more than 2 years, which indicates that PPG is stable for more than 1 year at the formation conditions.

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

- The injection water cut of the corresponding producers was decreased, and the daily oil-production rate was increased. Fig. 14 presents a typical production curve for Well W51-172, which connects with both W51 and P72. The water cut was decreased from approximately 80% to approximately 70%, and daily oil production was increased from 40 to 60 t/d.

The two well PPG treatments resulted in a total oil increase of 3239 tons, or 158 tons of incremental oil per 1000 kg PPG. The benefit investment ratio is more than 3.

**Case 2.** This is the first PPG treatment in Daqing, PetroChina. The selected injection well is Xing-7-24 in Xingbei oil field. The reservoir formation is characterized by thick oil layers with severe vertical heterogeneity. Formation temperature is approximately 45°C, and salinity is approximately 4,500 mg/L. The perforated depth is from 890 to 1,051.4 m. Net pay of the well is 24.5 m. The initial permeability is from several millidarcies to 1,200 md. The well was changed from a producer to a water-injection well in November 1992, and the cumulative water-injection volume had
been 763,758 m³ until August 2000. Four adjacent producers were
confirmed to be connected with the injection well, with a total of
more than 700 m³/d of liquid and average water cut of more than
90%. Profile tests showed that approximately 85% of the injected
water passed directly through the high-permeability parts of the oil
zones, which occupied less than one-fifth of the total thickness.
Interwell potential measurements demonstrated that the well group
had severe areal heterogeneity, as shown in Fig. 15. PPG treatment
was performed in August 2000. The produced water was used to
prepare PPG suspension. As we know, for a normal in-situ poly-
ermer-gelling system, it usually takes some time to prepare polymer
crosslinker before it is injected. But PPG is completely dif-
f erent, so it can reduce some operation and labor costs.

Table 2 shows the injection scheme of PPG suspension. A total of
3,100 m³ PPG suspension was injected into the well. For the
first stage, 100 m³ of 5-mm PPG suspension was injected into the
well at a high flow rate of 25 m³/h and a high concentration of 1%.
The reason that we injected the large PPG particle at the high flow
rate and concentration is that we expected that PPG particles could
form face plugging in all open zones in which permeability is
below 1,000 md, and in this way, only super-high-permeability zones or streaks without damaging the zones with a
large amount of remaining oil. For the second and third stages, an
alternated injection method of PPG suspension and water was
used: 10 hours of PPG suspension injection followed by 14 hours
of water injection. The difference between the second and third
stages is their particle sizes. In fact, we initially designed them to
be the same size, but the injection-pressure increase did not reach
our expectations, so we changed the particle size from 1.5 to 3 mm.
For the fourth stage, 5-mm PPG was continually injected so that
the final injection pressure can achieve expected results.

The above results show that the PPG treatment is positive. In
this case, 15.5 tons of 1.5- to 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 (Bai et al. 2007), the reservoir should have a channel with
thousands of darcies. Of course, there may be two other possibili-
ties for this case. The first possibility is that the particles may have
been broken into small pieces when they were injected or trans-
ported through porous media. But for this possibility, no matter
how small those pieces, the particles are still a gel, which is very
difficult to transport through normal porous media without having
a fracture or channel. Another possibility is that there exists a
low-permeability zone or streak without damaging the zones with a
large amount of remaining oil. For Daqing oil field, sand produc-
tion is not severe, so the existence of cave is impossible near the wellbore. From the gel-injection
practices, it can be inferred that the reservoir has some fractures or
channels. Otherwise, it is improbable that such a large volume of
PG could be injected. Of course, it has not been proved whether
fractures or channels exist. Moreover, no effective methods have
been used to demonstrate how far the possible fractures or chan-
nels might extend from the injection well.

Lessons From Applications. Some experiences learned from field
applications are summarized as follows.

Criteria of Well Selection.
- Reservoir temperature below 120°C
- Reservoir with channels or fractures
- High injectivity and low pressure index (PI) (Qiao and
  Li 2000)
- High water cut and high production rate of connected
  producers
- Well group with low oil recovery (preferred)
- Salinity not limited
Before a well is determined to inject PPG, some tests and measurements are strongly recommended; these include water tracer tests, well tests, injection profiles, and so on.

PPG Injection Process.
1. A simple method can be used to inject PPG, as shown in Fig. 16.
2. Produced water can be used to prepare PPG suspension.
3. A small amount of high-concentration, large-size PPG is recommended to be injected first at a high pressure so that PPG can form gel cake on the surfaces of low-permeability zones, which aids in preventing the following injected PPG from penetrating into the low-permeability unswept oil zones.
4. It is suggested that an alternated method of PPG suspension and water be used to conduct PPG treatments.
5. Low-concentration, low-flow-rate PPG suspension injection is recommended so that particles have enough time to move into the reservoir. High-concentration, high-flow-rate PPG injection may cause a large pressure pulse near the wellbore, which may cause the formation to be fractured.
6. Real-time injection pressure should be monitored so that we can adjust some of our initially designed schemes, including PPG size and strength, according to the monitored pressure result. The adjustment is necessary because the reservoir is a black box, and we cannot completely understand it when we make the initial design. This is another advantage of PPG over traditional in-situ gelling systems.
7. It is suggested that 0.5 m³ or less of gel breaker be injected into the well to soak the wellbore and dissolve some gel cake on the low-permeability zones. Then, the well should be washed out before water injection.

Treatment Results. Successful PPG treatment is often accompanied by an injection-pressure increase, an oil-rate increase, and a water-cut decrease, but injection pressure may not be an evaluation criterion because the injection pressure may not increase if PPG moves in-depth into the reservoir.

Knowing New Reservoirs. PPG has been injected in many mature oil fields, and most reservoirs have no fracture at the beginning of their development. But no injectivity problem has been encountered until now for all cases, which indicates that channels exist widely in mature waterflooded oil fields because PPG cannot be injected into those normal porous media without a fracture or channel. It is suggested that we should reconsider the mature reservoirs that may be completely different from their original conditions. Waterflooding has resulted in these reservoirs changing significantly (Seright 1988). Knowing the updated reservoirs is very important for improved-oil-recovery technology applications.

Limitation for PPG Application. PPG can be used to control conformance for the reservoirs with small fractures or high-permeability channels. It should be noted that PPG cannot be injected into normal porous media without fractures or channels. In addition, the PPG cannot singly be applied in the reservoirs with very severe open channels or super-high-permeability open fractures because PPG will be flushed out from the producers.

Conclusions
1. Polymer/clay composite preformed gel (i.e., PPG) is successfully synthesized at laboratory and commercialized scale.
2. PPG is strength- and size-controlled, environmentally friendly, not sensitive to reservoir minerals and formation-water salinity, and stable over a long period of time.
3. PPG, synthesized in a surface facility, can overcome some distinct drawbacks inherent in in-situ gelation systems, such as lack of gelation time, uncertainty of gelling caused by shear, degradation, chromatographic separation of gelation components, and dilution by formation water.
4. PPG can be carried into wells by produced water, which can save fresh water and protect the environment.
5. Operation process and surface-injection facilities are simple, which can reduce operation and labor costs.
6. Proper well-selection and well-injection procedures are critically important for successful PPG treatments.
7. Field application results demonstrate that PPG can effectively improve reservoir conformance.
8. Knowing our updated reservoirs is a key to improving PPG applications in more locations.

Nomenclature
- $A$ = PPG swelling capacity, dimensionless
- $M_s$ = dry PPG mass, g
- $M_l$ = swollen PPG mass, g
- $\sigma$ = stress, Pa
- $\epsilon$ = strain, dimensionless
- $\delta$ = phase angle, degree
- $E$ = Young’s modulus, Pa

Acknowledgments
Financial support for this work is gratefully acknowledged from the China Ministry of Science and Technology (the National High Technology Research and Development Programs of China-863 Program), PetroChina Company, China National Petroleum Corporation (CNPC), China National Offshore Oil Corporation (CNOOC), China Petroleum and Chemical Corporation (SINOPEC), and Daqing Oil Company. We also thank Randy Seright and Reid Grigg (New Mexico Petroleum Recovery Research Center) and Patrick Schuler (California Institute of Technology) for their valuable suggestions.

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*Conversion factor is exact.

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