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EVALUATION OF PREFORMED PARTICLE GEL AS A DIVERTING AGENT FOR
ACIDIZING

by

BO WEI

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN PETROLEUM ENGINEERING

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Approved by

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ABSTRACT

Preformed particle gels (PPGs) have been developed and successfully used to improve conformance in heterogeneous reservoirs. However, no research has been reported to show their potential diverting applications in acidizing because of their unknown performance in this process. This work targets on evaluating the potential of PPGs to be used as diverting agents and factors influencing the diverting performance.

The swelling properties of three types of PPGs (PPG #1, #2, and #3) were first studied in brine and acid, including the swelling kinetics and equilibrium, PPG strength, and deswelling performance. Effects of different brine concentration, acid concentration, and temperature were also conducted. Then, coreflooding experiments were carried out to investigate their plugging, acid diversion, and permeability recovery performance in carbonate rocks. Effects of PPGs injection volume and particle size were finally investigated.

PPG #1 and #2 can swell up to about 10 times and maintain stable in acid for about one day before deswelling. Moreover, PPG #2 even swells a little more in acid at first several hours at 45°C. PPG #3's swelling ratio ranges from 20 to 65, which is sensitive to the brine concentration and it reaches deswelling equilibrium after 20 minutes in acid. The gel strength of PPG #2 is the highest and it can be degraded in brine at 80 °C in five days. Coreflooding results show that these three PPGs have different diversion ability and can be used as diverting agents to enhance the acid stimulation. Larger injection volume and large particles are favorable by using PPGs as diverting agents in acidizing. The properties evaluation and coreflooding experiments show that PPG #2 can be the best candidate as a diverting agent.

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NOMENCLATURE

Symbol	Description
k	Permeability
h	Production layer thickness
G'	Storage modulus
V _i	Initial volume before swelling
V _t	Swelling volume at the time of t
SR	Swelling ratio
RO	Reverse osmosis

1. INTRODUCTION

1.1 BACKGROUND

Acid stimulation is a commonly used production enhancement technique dating as far back as 1932 when the hydrochloric (HCl) acid was first used to stimulate oil wells in carbonate reservoirs. However, one major problem limiting their application is that the acid is hard to be diverted into a desired treatment zone due to the high heterogeneity in reservoirs, which causes the low acidizing and production efficiency. Moreover, this problem is even more serious in carbonate reservoirs.

The complex heterogeneity in carbonate reservoirs often shows high permeability contrast caused by fractures, streaks, conduits and super-K zone in the formation. In acid stimulation, it can expedite the acid entering these highly permeable un-desired zones, which may cause the temporary or permanent formation damage that leads to extremely high water cut. In addition, the low permeability zones containing large remaining oil are not swept, which results in unexpected exploitation and low oil recovery. As a result, in the production of an oil field, the problem from heterogeneity increases the recovery and production difficulty [1].

In view of the formation damage and low oil recovery resulting from the acid uneven distribution in complex heterogeneous reservoirs, the diversion technique is employed. The diversion in acid stimulation is to injected diverting agents into the formation to temporarily plug the non-target zone, diverting the main stimulation treatment fluid to react with the less permeable or damage zone in the target formation. The diverting agent can be degraded in formation or removed by production fluid during flowing back.

Diverting agents have been developed since 1936 when oil-soluble calcium soap was proposed as the first diverting agent for the acidizing. Until now, four kinds of diverting agents are mainly used in the oilfield, which are: polymer gels, foams, viscoelastic surfactant and solid particulates. The polymer gels appeared during the 1960s to 1970s when the chemical polymer was greatly developed. Foams were developed as diverting agents in 1980s because of their easy degradation and no damage to the formation. The latest one was the viscoelastic surfactant diverters developed in the 21st century, which is now further studied and applied due to its non-damaging and rapid viscosity-development characteristics. Particulate diverters have been used as diverting agent early since the diversion was proposed in 1936. A large number of removable material can be used as particulate diverters for acid diversion. Preformed particle gel (PPG), a kind of particle gels, has the potential to be one of particulate diverters for acid diversion.

Preformed particle gel (PPG) has been used in the gel treatment for the conformance control. The mechanism of the gel treatment is to reduce water flow through channels, fractures, and conduit and then divert the flooding fluids toward the low permeable formation with more remained hydrocarbon, which is quite similar to the diversion way in acid stimulation. In addition, PPGs have some advantages compared to other gels like the in-situ gel: the particle size and gel strength of PPGs can be controlled according to the formation condition; PPGs can enter the large channels like fractures in the formation, which reduces the gel penetration into the low permeability matrix; PPGs can be easily prepared with water due to the single component; some PPGs are stable and strong so that they can withstand acid for a long time and then deswell or degrade with

time. As a consequence, the gel treatment based on PPGs could be used for diversion in acidizing.

1.2. OBJECTIVES

The objective of this research is to evaluate the performance of PPGs used as diverting agents during the acidizing process. The specific objectives of this research are shown as following:

1. Select a best diverting agent candidate from three evaluated PPGs.
2. Evaluate the basic properties of three kinds of PPGs used for acid diversion.

The experiments measured the swelling kinetics, swelling equilibrium, and gel strength during PPGs' swelling process in different concentration brines. The gel performance in acid was measured in the deswelling process to study effects of PPGs' differences, acid concentration, and temperature on deswelling.

3. Investigate the diverting performance of three kinds of PPGs in carbonate rocks acidizing by using coreflooding experiments.
4. Use coreflooding tests to show effects of PPG injection volume and particle size on PPG injectivity and acid diversion.

2. LITERATURE REVIEW

2.1. ACID STIMULATION

Acid stimulation is widely used in well completions, well workover and intervention, EOR (enhance oil recovery), and shale gas production periods. Its objective is to restore or enhance the productivity of a well or reservoir. There are two acid stimulation methods: acid fracturing treatments and matrix acidizing treatments [2]. Both of them are used to remove or bypass any damage or impairment from around the wellbore, or to create conductive fractures, emanating from the wellbore, which enhances the formation's production ability [3].

2.1.1. Acid Fracturing. In most cases, the cause of low productivity is poor reservoir permeability, but this problem can be diminished by using a kind of acid stimulation technique known as acid fracturing. Acid fracturing is primarily used to stimulate a carbonate reservoir especially using hydrochloride (HCl) acid.

In acid fracturing, the acid is used as a pad before the acid is injected down the wellbore at rates greater than that the formation permeability (kh) can accept. It exceeds the compressive earth stresses and tensile rock strength. At this pressure, the rock breaks and creates the new flow path propagating to the wellbore for the production [4].

Figure 2.1 shows a kind of acid fracturing treatment in a carbonate reservoir. Its objective is to etch the open faces of induced fractures using an HCl treatment. The acid is pumped to the fracture to etch it. When the treatment is complete and the fracture closed, the etched surfaces provide high-conductivity flow paths from the reservoir to the wellbore.

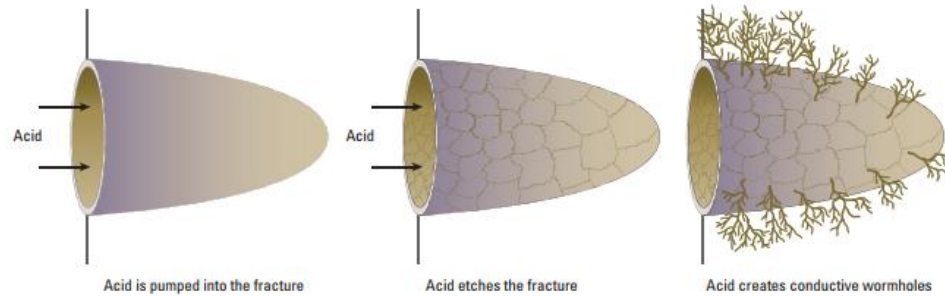


Figure 2.1. Schematic diagram of the acid fracturing treatment [5]

2.1.2. Matrix Acidizing. Matrix acidizing is an essential damage-removing well stimulation technique in which the acid is injected into the formation to dissolve near-wellbore minerals, such as the calcite, dolomite, and siderite, to remove formation damage. Hence, matrix acidizing treatments are usually performed in wells with the low production rate, in which the more recovery and reservoir permeability will be improved. The most commonly used acid is hydrochloric acid (HCl) which is primarily to dissolve carbonate rock and a mixture of hydrochloric/ hydrofluoric acid (HCl/HF) for attacking silica minerals. It is performed below the reservoir rock failure pressure and primarily designed to recover the original permeability of the reservoir following damage to the near-wellbore area [6].

The distinction between fracturing and matrix acidizing is the injection pressure. Matrix acidizing treatments are performed by injecting appropriate acids into the near-wellbore region of the formation at rates low enough to avoid fracturing [7].

2.2. DIVERSION

Both in acid fracturing and matrix acidizing, to ensure the acid entering all perforations and all zones is effectively acidized, a diversion is needed. Diversion is a

kind of technique to distribute the treatment fluid uniformly across the treatment zone. If there is no diversion in stimulation, the least permeable layer will receive inadequate treatment. By using some means of diversion, the stimulation is concentrated on the areas that need the most treatment. In an effective diversion, the treatment should be temporary, so that when the treatment is complete, the full productivity of the well can be recovered. Two ways of diversion are chemical diversion and mechanical diversion [8]. The following subsections illustrate these methods briefly.

2.2.1. Mechanical Diversion. Mechanical diversion uses mechanical devices such as packers, ball sealers, straddle-packer assemblies, and coil tubing to divert reservoir treatments to the target zone. It is also sometimes called external diversion. Ball sealers and solid-particle diverting agents are incorporated into the treatment fluid to form a temporary plug in the perforations accepting the most fluid flow, thereby diverting the remaining treatment fluid to the less permeable zones as Figure 2.2 (a) shows. Packers and straddle-packer assemblies function by performing several short treatments over a longer interval to help ensure an even treatment over the entire zone as shown in Figure 2.2 (b) [9].

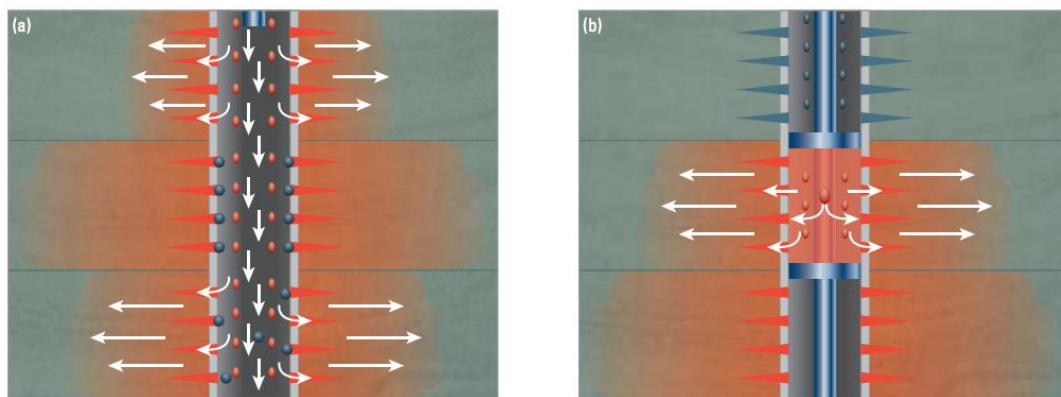


Figure 2.2. Mechanical diversion (a) Ball sealer and solid-particle diverting agent for perforation (b) the packer distributes the fluid [6]

However, mechanical diversion techniques are thought to be expensive and time-consuming. For example, setting packer is a multiple-stage treatment that is complete in operation [10]. Besides, some mechanical diversion is neither applicable nor effective in the openhole, from which there are always operation difficulties and the potential to cause permanent plugging if overtreated [11].

2.2.2. Chemical Diversion. Chemical diversion uses chemical agents to achieve diversion during matrix stimulation. These chemicals are called chemical diverters. They function by creating a temporary blocking effect and can be safely cleaned up afterwards. As a result, it is always called temporary plugging agent. A chemical diverting agent can distribute the acid throughout the zones with low permeability in the well or formation as Figure 2.3 shows [12].

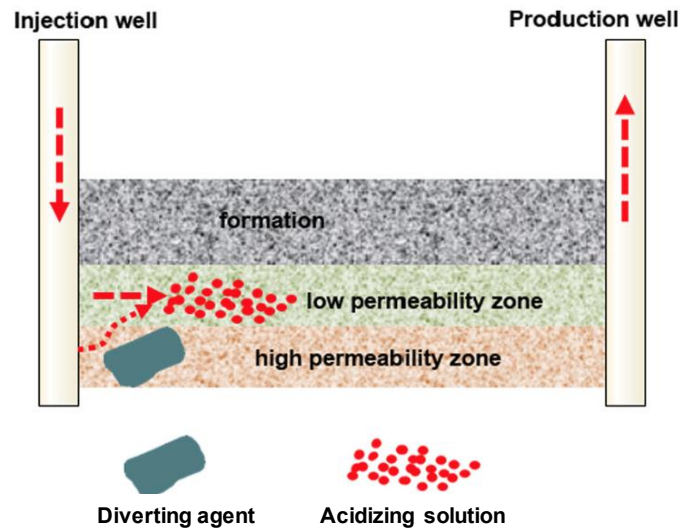


Figure 2.3. Diverting agent mechanism in acidizing [13]

The fundamental difference between a chemical and a mechanical diversion is that a chemical diverting agent achieves diversion by increasing flow resistance inside

the created channels and perforations, whereas a mechanical diversion process controls the fluid entry point at the wellbore. Hence chemical diverting agents can be considered as internal diverting agents as opposed to the external mechanical diversion. Nasr-El-Din et al. [14] review the diverting agent application history and provide the design for the acidizing job in carbonate reservoirs.

In oilfield exploitation, diverting agents can be used in drilling, well completion, cement, acid stimulation, and so on. It can both protect the untreated formation and divert the treatment to the target formation. There are two ways how diverting agents work. The first way, the diverting agents promote to form the filter cake in un-target zone. The pressure drop through this filter cake increases the fluid resistance, diverting the treatment fluids into the target zones. The second way, the diverting agents are added to increase the viscosity of the injection fluid for diversion. When pump these increased viscosity injected fluid, the flow resistance increases in high-permeability regions, which diverts the following fluid to the low permeability target zone.

Either the formed filter cake or the viscous fluid can be safely cleaned up after treatment, enabling enhanced productivity throughout the treated intervals. As a result, diverting agents are frequently used in the acidizing stage to stimulate the reservoir in both matrix acidizing and fracturing treatments.

2.3. DIVERTING AGENT MECHANISM FOR ACIDIZING IN CARBONATE RESERVOIRS

Almost two-thirds of remaining oil reserves in the world are contained in carbonate reservoirs [5], but carbonate reservoirs are always extremely heterogeneous

compared to other reservoirs. They tend to be with complicated porosity, large permeability variations, barriers, and irregular flow paths.

Across the industry, geologists, petrophysicists, and reservoir engineers are seeking to improve their understanding of carbonate formations and reservoir behavior. The accepted experience has shown that even small improvements in stimulation methods can yield dramatic production results in carbonate reservoirs [5]. Therefore, some companies such as Schlumberger and CNPC have done a lot of research on diversion in stimulation. Matrix acidizing with diverting agents is a good method to improve the production profile. The goal of diversion in acidizing is to stimulate the reservoir uniformly to remove the formation damage and reduce the heterogeneity of the reservoir.

2.3.1. The Acid Dissolution Mechanism. Matrix acidizing is the method that acid is injected into the near wellbore formation at the pressure below the rock failure pressure, which dissolves the carbonate minerals. These dissolved patterns are known as wormholes. The acid dissolving mechanism in carbonate reservoir is shown in Table 2.1.

Table 2.1. Major Carbonate reservoir minerals reactions with HCl acid

Rock Type	Reaction Equation
Calcite	$2\text{HCl} + \text{CaCO}_3 = \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$
Dolomite	$4\text{HCl} + \text{CaMg}(\text{CO}_3)_2 = \text{CaCl}_2 + \text{MgCl}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$
Siderite	$2\text{HCl} + \text{FeCO}_3 = \text{FeCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$

The conventional hydrochloride (HCl) acid can dissolve dolomite, limestone and carbonate rocks, which can remove the CaCO_3 and Fe_2O_3 precipitate pollutions near the wellbore to improve permeability of the reservoir. Therefore, it is always used as stimulation fluid, fracturing fluid, and even breaker solution for the plugging gels because

of these reactions. Their reaction outcomes are CaCl_2 and MgCl_2 that can be dissolved in the acid solution and water without forming the precipitates. The produced CO_2 is also favorable for remained acid flow back. In addition, the HCl acid is cheap and has high dissolving capability, which makes it a good candidate for the near-wellbore formation acidizing [6]. Figure 2.4 shows the wormholes dissolved by the HCl acid in the limestone.

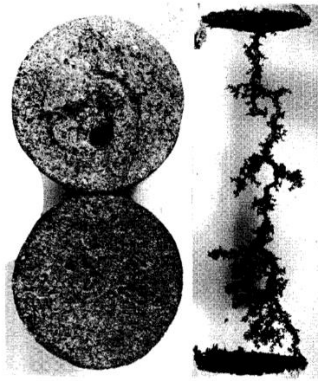


Figure 2.4. Wormholes created by acid dissolution of limestone [6]

In carbonate reservoirs, the acid treatment provides opportunities to remove damage in the vicinity of the wellbore and to improve the near-wellbore permeability by creating large flow channels [15]. But it is quite difficult to predict the acidizing treatment. Though the chemical reaction is easy, the physics is quite more complex. In carbonate formations, the surface reaction rate is quite high, therefore, the mass transfer often limits the overall reaction rate, resulting in serious nonuniform dissolution patterns. Usually, a few of the large channels called wormholes are created, which diameter is between 2 mm and 5 mm [16]. The structure of the wormholes complicatedly depend on

the flow geometry, reaction kinetics, injection rate, and mass transfer rates [17]. The created wormholes by acid penetration are not deep enough because of the high reaction rate, especially when the injection rate is low [18].

2.3.2. Plugging and Diversion Mechanism. In conventional acid stimulation, the treatment cannot satisfy the uniform stimulation and stimulate the low permeability zone because of the differential of rock property, pressure and damage in each layer. The high permeability zone is always overstimulated, in which most of the acid is consumed, but the low permeability zone with high oil saturation is not stimulated. This phenomenon occurs especially in multi-stage acidizing. This increases the heterogeneity of the reservoirs and further increases water cut and worsens production.

In acid treatment, it is expected that the acid enters the formation with low permeability and high oil saturation and stimulates the reservoir uniformly to get the best production results. Diverting agents function to ensure the acidizing solution enter into target zones (low permeability zones) instead of non-target zones (high permeability zones) that should be plugged [19]. Therefore, a diverting agent should be injected into the formation before or during the acidizing treatment. After the treatment, the plugging diverting agents are gradually degraded with time in a variety of ways, and the plugged permeability of non-target zone is recovered. Accordingly, the pollution and damage near wellbore formation are stimulated, and the permeability is improved.

The ideal diverting agent for acidizing should follow these criteria:

1. The material must be effective in reducing fluid loss to thief zones, including existing fractures and very high permeability layers in the formation to be pressure treated.

2. The material must have enough strength to bridge under the treating pressure.
3. The material must be insoluble or slowly soluble in the treating fluids so that the particles retain sufficient size to be effective after they reach the formation zone.
4. The material must be completely soluble in the produced oil or condensate liquid so that it can be removed readily; it must not cause formation damage [20].

2.4. TYPES OF CHEMICAL DIVERTING AGENT

In the last fifty years, materials ranging from mothballs and oyster shells to the modern polymer resins have been used all over the world. Each material has its own disadvantages that cannot fit for the complex formation conditions.

The following sections list four types of diverting agents recently being used all over the world.

2.4.1. Polymer Gel. The polymer gel has been used previously in the gel treatment to block zones and divert the flooding fluid to formation with high oil saturation to improve the oil recovery [21] [22]. Thus, the polymer gels were added into the acid to increase the viscosity of the acid solution to improve the acidizing. It can reduce the acid penetration rate in the existing wormholes so that the following acid will be diverted to contact the target zone where wormholes are not formed. In general, the acid fluid always contains three specific components. The first component is a gelling agent also called common polymer solution, which gives the acid system 20 to 30 cp [37] at the bottomhole conditions. The gelling agents are typically from the polyacrylamide family, phenolaldehyde and amnion acid polymer. The second component is the crosslinker, typically zircon, iron, and aluminum salt. The last component is the common

breaking agent that is usually low-solubility or delayed-release source of fluoride, APS (ammonium persulfate) [23] and hydrazine hydrochloride. Each component's function is often related to the pH change. When the diverting agent is injected with the acid, the acid reacts with carbonate and the pH value of the solution increases. When the pH value increases to a certain boundary, the crosslinker is activated and crosslinks the molecular chains to form the viscous gels, which can divert acid because of its high injection resistance. After the acidizing, the breaker will attack the polymer molecular chains and break the gel network structure due to the pH value recovery, and thereby reduces the gel strength and viscosity of the diverting agent. Finally, the structure of the diverting agent will be totally degraded with time.

Polymer Gel Diverter (PGD) system has been used in the field for many injection wells. It is composed of primary and secondary gelling agents, a pH buffer, and a breaking agent. The overall injection was more than 40% and the skin factor reduced from +1 to -2.5 [24].

Another polymer-based associative polymer technology (APT) has been applied in the field. Several stages of APT and acid were used to divert the treatment fluid to lower permeability zones. The oil recovery improved by 34% and water cut decreased from 21% to 17% [23]. The laboratory test showed that the diverter can divert acid from a water-saturated zone to an oil-saturated zone in carbonate reservoirs [25].

The in-situ-gelled acid [26][27][28] is widely used and studied as a diverting agent during acidizing in highly heterogeneous carbonate reservoirs. The main acid used in this system is hydrochloride (HCl) system. Sometimes, organic acid (acetic, citric or formic acid) is added into HCl system to reduce the strength of acid to increase the HCl

penetration and reduce the load of the corrosion inhibitors. The agent is injected with the acid system. In low pH ranges, gelation occurs because of the working crosslinker. After the acidizing, the crosslinker will be in passivation with pH value increasing, and the breaker activates and breaks the molecule chains, which recovers the permeability of non-target zones.

The plugging and diverting efficiency of polymer gel diverters are high enough, but there are some disadvantages. First, it is hard to distinguish water zones and oil zones. Then, there are always polymer diverters left after the treatment, which negates the stimulation by damaging the matrix, especially when the treatment fluid is designed incorrectly. Some methods were proposed to clean the remaining polymer gels, but the results are not good enough. The temperature also limits the development of the polymer gel diverting agents.

2.4.2. Viscoelastic Surfactant-based Diverting Agent. Viscoelastic surfactant-based diverting agents (VES) have been developed fast in recent years. They have been successfully used in the industry for well stimulation applications.

A surfactant molecule is composed of a hydrophobic tail and a hydrophilic head. Its properties are different because of size of the hydrophilic head, length and structure of hydrophobic tail, charges of the surface, temperature and ion strength. The surfactant monomer forms aggregation structures to increase the apparent viscosity and elastic properties of the treating fluid [29].

According to the differences in the surfactant aggregation structure, the viscoelastic surfactant-based diverting agents can be divided into two categories, as called micelles and vesicles. Both of the structures can generate the adequate viscosity

through the interaction of surfactant molecules, which depends on the surfactant solution [30]. In addition, the VES fluid is very sensitive to the shear stress. It has high viscosity at low shear rate; therefore, it exhibits the low friction pressure when pumped, which makes it ideal fluid for acidizing diversion.

When the acid enters the formation, it reacts with the carbonate rock, producing CaCl_2 and MgCl_2 , as well as the pH increase. The ions force the surfactant molecules to form rod-like micelles, which increases the viscosity and elasticity of the solution. The following acid solution is diverted to stimulate a new zone. After the treatment, the gel breaks when hydrocarbons contact the fluid during the production and the permeability is restored.

Chang et al. [31] studied a type of VES that has the prolong viscosity buildup without having to break back until the production begins. Compared with other polymer gel diverting agents, this VES has the continuous diversion function that can solve the openhole acidizing problems without damaging the formation. The system does not contain solid particles, from which the bridge blocking will not happen.

Alleman et al. [30] described a VES diverting agent, which vesicle structure is formed easily by adding a kind of material, polyQuat. It reduces the concentration of surfactant required and improves the stability. The acid strength, an internal breaker, and temperature can ensure the VES fluids broken during or after the treatment. The coreflooding tests show that there is no damage for the treated core in the experiment.

Taylor et al. [32] proposed a type of VES diverting agent that has a thermal stable property. When the acid is being consumed, the viscosity increases quickly, and this

viscous structure can withstand high temperature (149 °C). The coreflooding tests suggest that it is effective in both high and low permeability cores.

2.4.3. Foam. Foam has been used as a diverting agent since the 1960s [33]. It was found that foams could stay stable in water but easily broke in oil. Recently, people use this property to separate the water zone and oil zone to get the most favorable acidizing results. The acidizing solution foam is made in acid, gas, and surfactant, which is generated by injecting surfactant solution into porous media followed with gas, or by co-mingled injection of gas and a surfactant solution [34]. The foam enters the high permeability zone with a waterflooding first, which forms the stable emulsion and generates the resistance. As additional foam is generated, the resistance increases until the pressure required for further flow exceeds the pressure required to divert to other formation zone [35]. Finally, the foam dissolves in the oil and the acid is released from the foam to the formation to acidize.

The foam has some advantages as a diverting agent, such as no solid material damage to the zone, the low solution loss, high plugging and diverting efficiency, and ease of operation and clean. Best of all, the foam is a two-phase system that has more resistance than the single phase fluid to divert the treatment fluid into the porous media. However, the main problem is, also related to the two-phase condition, the low strength and thermal stability. In high permeability and high temperature, the foam is not so effective in diverting acid [36].

2.4.4. Particulate Diverter. The particulate diverter is common used in carbonate reservoirs for acid stimulation. When fluid containing the particulate material is injected, it creates a low permeability particle pack in the zones of the highest permeability and the

lowest stress (at the surface of the high permeability formation, within the perforation tunnels and on the perforations). The pressure drop from the buildup particle pack causes the flow resistance increase and diverts the treatment fluid to other parts of the interval.

Many particulate diverting agents have been used commercially, such as cellophane flakes, naphthalenes, crushed limestone, sodium tetraborate, oyster shells, gilsonite, paraformaldehyde, perlite, oil-soluble resins, rock salt, benzoic acid, phthalic anhydride, polylactic acid (PLA) and polyimides [37]. Recently in 21st century, the solid organic acid - lactic acid flakes- has been used as a good particulate diverting agent. The material is hydrolyzed to release acid under the reservoir temperature during the treatment. But the material reaction needs a large amount of water to ensure the full conversion of the solids into acid. Otherwise, the solids will remain and the formation will be damaged.

Though the particulate diverters can break down in water or hydrocarbon after the stimulation, their removal requires exposure to the flowing stream when the well is put back on production. Otherwise, severe formation damage will occur to negate the stimulation results [14].

2.5. PREFORMED PARTICLE GEL

Prefomed particle gel (PPG) is a new kind of matured particle gels that are widely used for conformance control. What makes it different from the in-situ gel is that it is crosslinked and formed at surface facilities instead of at reservoir conditions.

Therefore, the gelation time and gel properties can be controlled.

Using preformed particle gel can overcome some disadvantages associated with in-situ gel systems [38]:

1. Shearing from the pump, wellbore and porous media, the adsorption and chromatography of chemical compositions, and the dilution of formation water strongly affect crosslinking reactions.

2. The possible damage in the low permeability oil zone.

Millimeter-size PPG developed by Petro China and Missouri S&T is an improved super absorbent polymer (SAP). It can absorb more than a hundred times its weight in liquid and stay stable under high pressure [39]. Figure 2.5 shows a PPG sample before and after swelling. A PPG's particle size is adjustable from a scale of micrometers to millimeters, depending on the features of the target zones. Most PPGs are sensitive to brine concentrations. They can be adjusted to control the particle size. Therefore, this property permits the use of all salt types and concentrations. When compared to in-situ polymer gels, millimeter PPGs could resist temperature up to 120 °C [40].

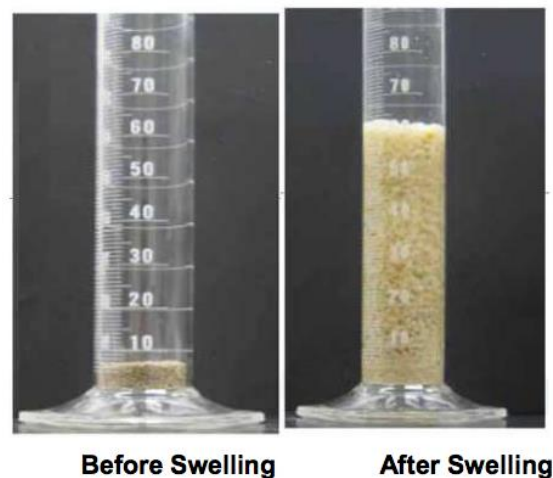


Figure 2.5. Commercial preformed particle gels before and after swelling [41]

Since the application in 1999 by SINOPEC, millimeter-size PPG have been widely applied in around 10,000 wells in China [41]. Because of their applications in conformance control, they should have been used to develop the diversion property in acid stimulation, especially in formations with large channels, fractures, and wormholes.

The following experiments are to evaluate the PPG as a diverting agent in acidizing, and select the best candidate PPG for acid diversion.

3. BASIC PERFORMANCE OF PPGS

3.1 EXPERIMENTAL MATERIAL AND SETUP

Three types of specially designed superabsorbent polymer gel were used as PPGs in this research as shown in Figure 3.1. PPG #1 particles were yellow with particle size around 10-20 mesh. Dry particles of PPG #2 were white with particle size around 20-40 mesh. PPG #3's particles were white, which particle size was 0.45-1mm.

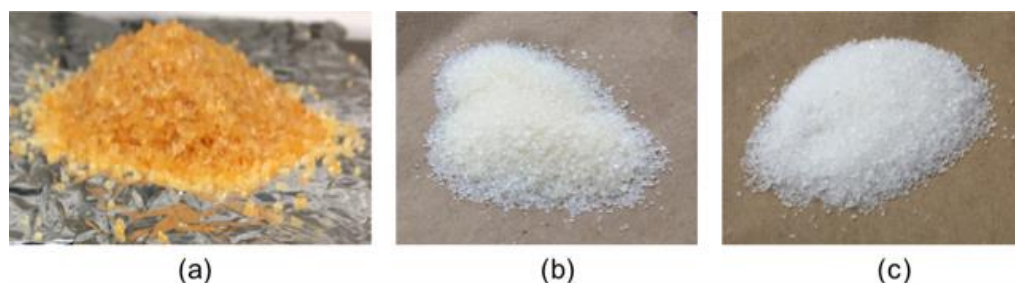


Figure 3.1. Images of dry PPGs a) PPG #1 Particle Size:0.85-2mm (10-20 mesh); b) PPG #2 Particle Size:0.45- 0.9mm (20-40 mesh); c) PPG #3 Particle Size: 0.45- 1mm (20-40)

Four concentration (0.05, 0.25, 1, and 10 wt %) of sodium chloride (NaCl) solution was used to evaluate the swelling performance of PPGs. Figure 3.2 shows the swelled PPGs in 1% brine in two hours.

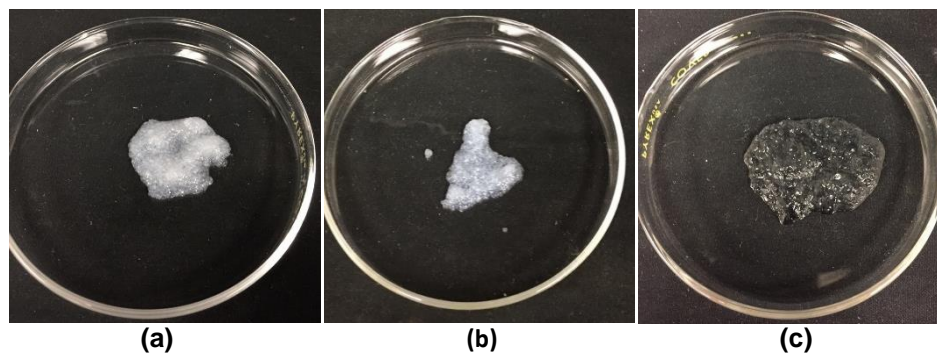


Figure 3.2. Images of PPGs particles swelled in 1% brine: a) PPG #1 (the color changed from yellow to white); b) PPG #2 c) PPG #3

Hydrochloric (HCl) acid (36.5%) from Fisher Scientific was diluted with reverse osmosis water to obtain acid concentration from 1% to 10%.

An oven (Model No.3511FS, Fisher Scientific) was used to evaluate the effect of temperatures that were 45, 60 and 80 °C, respectively.

A rheometer (Haake Mars, Thermo Scientific) was used to measure the storage moduli (G') for gel swelled in brine at room temperature (around 25 °C) as shown in Figure 3.3. The sensor used for measurements was P35 Ti L, with a gap of 1.0 mm between the sensor and the plate.



Figure 3.3. The image of the HAAKE MARS III Rheometer

3.2. EXPERIMENT PROCEDURE

3.2.1. Swelling Evaluation. In general, the swelling ratio can be defined as the ability of gel particles to absorb the aqueous solution in which they are immersed in. There are two methods: the first is measuring by weight ratio, and the other is measuring by volume. In the deswelling process, it was hard to measure the swelling ratio in acid by

the weight method, so that the volume ratio method was used. The swelling ratio is calculated by using Equation (1):

$$\text{Swelling ratio (SR)} = V_t / V_i \quad (1)$$

where V_i is the initial volume of the dry gel particles and V_t is the volume of the swelled particles at the time of t .

Basically, the swelling capacity of most PPGs is associated with the brine concentration. During the test, four tubes each was prepared with 0.5 ml of the same type of dry PPG particles. Then, 40 ml of four different concentration (0.05, 0.25, 1.0 and 10.0 wt. % NaCl) brines were placed separately in four tubes for enough hours at room temperature to evaluate the swelling capacity of the PPGs. Volume value was recorded every 2 to 4 minutes for the first 20 minutes. Then, every 10 minutes, the volume data was updated. Finally, the swelled PPG volume was read to calculate the final swelling ratio by the volume method.

3.2.2. Gel Strength Measurement. Primarily, measuring the gel strength of PPG is to use the dynamic oscillatory rheometer to measure the elastic or storage modulus (G'), which represents the PPG's elastic energy. In this study, the HAAKE MAR III rheometer was used to measure the rheological properties of PPGs as shown in Figure 3.3.

The swelled PPG sample was filtered out from brines in tubes by using a filter screen. Samples were placed between the plate and the sensor of the rheometer. A 1.0 mm gap between the sensor and the plate was used. The oscillation time sweep curve model was selected, which represented the elastic modulus logarithmically in pascal (Pa)

as a function of time in seconds. The frequency was set at 1.00 Hz and G' reading for each measurement was taken every 10 seconds for 120 seconds.

3.2.3. Deswelling Performance. Most PPGs have some different performance when they contact acid. Hydrochloride acid (HCl) is often used to remove damage caused by gel injection. In order to achieve high acidizing efficiency in field applications, a high concentration (10-20 % weight) of HCl acid is frequently chosen for acid stimulation in carbonate reservoirs. As a result, 10% HCl (pH <0) was mainly used in the lab experiments. In addition, 4% (pH =0) and 1% (pH >0) HCl acid were also tested in the experiments.

Water was removed from the tube, leaving the swelled PPG particles. Then, 10% hydrochloride acid (HCl) with different concentration (0.05%, 0.25%, 1% and 10%) brines was poured into tubes to saturate the PPG samples. The concentration of H⁺ in acid solution should be large enough during the PPG degradation period. Tube samples were placed in a 45 °C oven for one week to measure the deswelling process. If the particle cannot shrink in one week, it means that the gel cannot deswell in acid during a short time. The PPG volume was measured to get the swelling ratio. When the PPG did not change for a long time or was totally degraded, the measurement was stopped and the final remained volume was recorded.

3.3. RESULTS AND ANALYSIS

3.3.1. PPG Swelling. It is reported that different PPGs have different swelling processes and swelling ratios [41]. Figure 3.4 shows these three PPG swelled conditions in different concentration brines at room temperature for two hours.

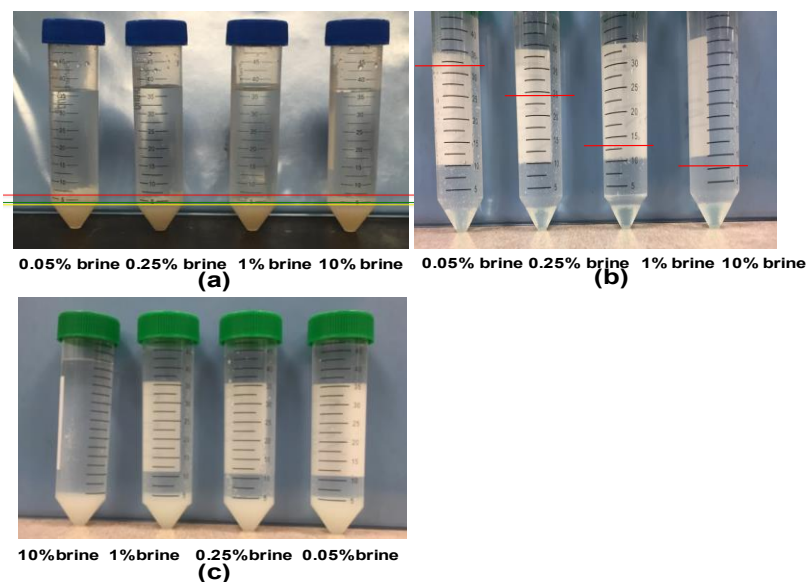


Figure 3.4. Images of PPGs swelled condition in different brine concentrations in two hours (a) PPG#1;(b) PPG#2; (c) PPG#3

3.3.1.1. Effect of brine concentration. Figure 3.5, 3.6, and 3.7 show the swelling process of these PPGs at room temperature. Different brine curves had the similar increasing trend where the brine concentration only changed the swelling ratio. In general, PPG swelling ratio is associated with brine salinity. Increasing the salinity of the aqueous solution will lead to a decrease in the swelling ratio, because the negatively charged group will be balanced by the cations and will restrict further water absorption in high salinity water [41]. This phenomenon was more obvious for PPG #3 in Figure 3.7.

3.3.1.2. Effect of PPG types. Figure 3.5 shows swelling kinetics of PPG #1, which swelling ratio increased so fast at the first 10 min. Then, the pressure increase rate slowed down until the volume of the swelled PPG reached its maximum swelled volume in about 100 min. In Figure 3.6, the swelling ratio of PPG #2 increased remarkably at first 20 minutes, which reached nearly 8 times that was almost same as the maximum swelled volume. Then, the further swelling was not obvious, in which it only swelled the

other 1 time in another 80 minutes. It only took PPG #3 less than 40 minutes to reach the maximum swelling ratio as shown in Figure 3.7.

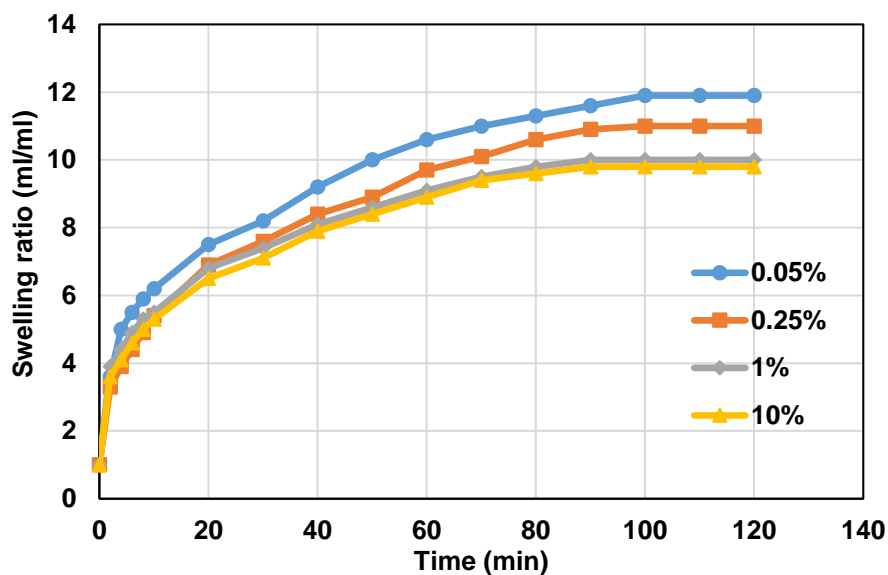


Figure 3.5. The swelling process of PPG #1 in different concentration brines

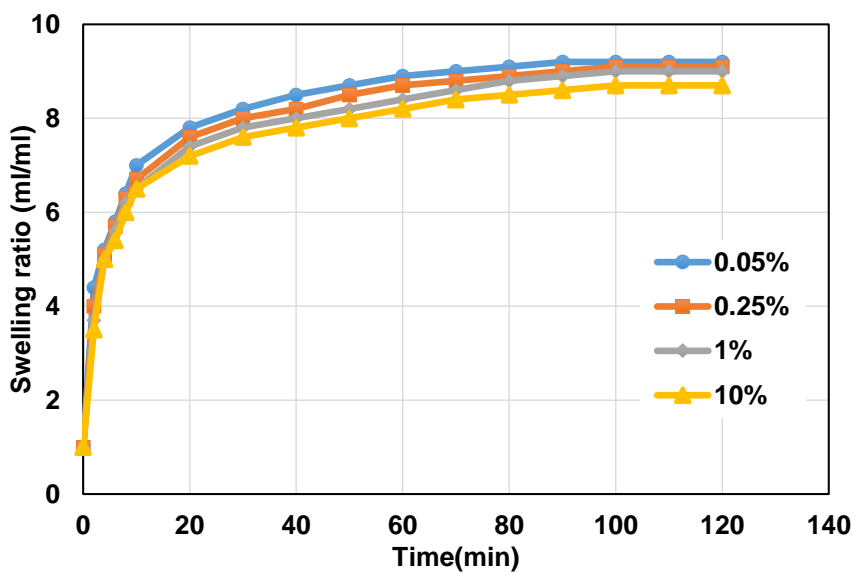


Figure 3.6. The swelling process of PPG #2 in different concentration brines

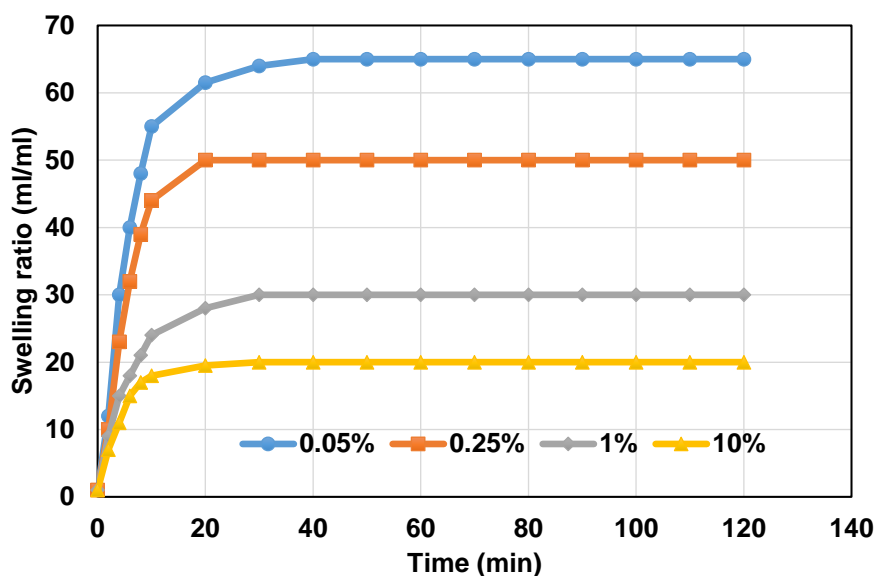


Figure 3.7. The swelling process of PPG #3 in different concentration brines

Results from Figures 3.5 to 3.7 show that PPG #1 and #2 were not sensitive to the brine concentration while PPG #3 was. The swelling ratios and speed of these three PPGs were also different: PPG #3 can swell up to 65 times of its original volume when using 0.05% NaCl solution in 20 minutes, but PPG# 1 and #2 only reach around 10 times. PPG #2 swelled so fast that it almost finished swelling in 20 minutes. This great different swelling performance might be related to the structure differences.

3.3.2. Gel Strength. PPG strength is an essential parameter for designing gels for the treatment. The swelled samples in the last section were selected to measure their gel strength (G') by using the rheometer.

3.3.2.1. Effect of brine concentration. Results from Figure 3.8 and Table 3.1 show that similar with the swelling ratio, the gel strength was also related to the brine concentration. For each gel, the higher the brine concentration, the higher the gel

strength. The reason might be that PPGs swelling in high salinity brine had the smaller particle size and higher gel strength with stronger polymer network bond [42].

Table 3.1. PPG strength in different concentration brines

Brine concentration	Gel strength G' (Pa)		
	PPG #1	PPG #2	PPG #3
0.05%	1660	3650	900
0.25%	1730	4070	920
1%	1810	4150	1060
10%	1840	4250	1100

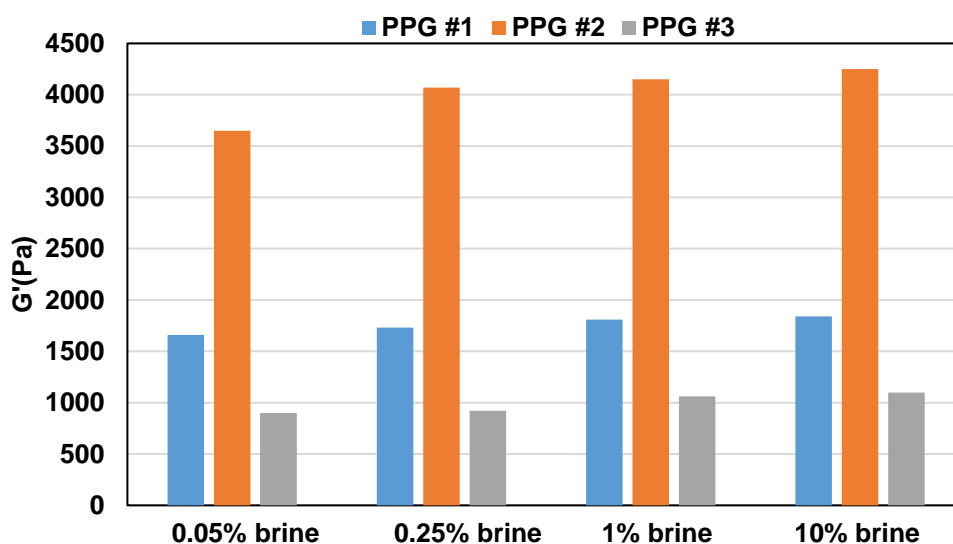


Figure 3.8. Gel strength comparison in different brine concentration

3.3.2.2. Effect of PPG types. PPG #2 had very high gel storage modulus up to 4000 Pa which was a very strong gel. The stronger gel had better blocking performance [38], so that PPG #2 might be preferred in the gel treatment. PPG #3 was the weakest PPG among these three gels which storage modulus was only around 900 Pa, but it was also stronger compared to the common in-situ gel. From Figure 3.8, it is clear that these

three PPGs had different gel strength, and the strength of PPG #2 was quite larger than the other two gels.

3.3.3. PPG Deswelling. Most PPG particles will deswell when they contact with the acid. Some PPGs have acid resistance ability so that they can be used as diverting agents in acidizing. The following sections describe a measurement of different kinds of PPGs deswelling process in different concentration acid and temperature.

3.3.3.1. Effect of PPG types. Three PPGs were saturated in 10% HCl solution with different brine concentration and the deswelling performance was shown in Figure 3.9 to Figure 3.11. PPG #1 could stay stable for about one day before deswelling. But the high salinity (10% NaCl) reduced the stable time of PPG #1 in acid. It reached the deswelling equilibrium in about 70 hours in 10% HCl acid. PPG #2 even swelled a little more for the first six hours at 45 °C and kept stable for more than one days, which might be the good diverting agent in acidizing. In addition, PPG #2 deswelled quickly after the long stable condition. PPG #3 shrank immediately when it contacted the acid, which deswelling equilibrium time was less than 20 minutes. However, when the deswelling reached the equilibrium, the final volume of the remained undegraded PPG #3 was same even though they swelled in different concentration brines. More details about PPG #3's deswelling volume in acid after swelled in different concentration brines are shown in Table 3.2. PPG #3 that swelled in higher concentration brine shrank less in acid as shown in Table 3.2, which might be used to overcome its quick deswelling problem.

Remained un-degraded PPGs are shown in Figure 3.12. Though three PPGs deswelled in acid, PPG #1 and PPG #2 had a little residue at 45 °C as shown in Figure 3.12 (a) (b). Their residues were also different from their swelled condition compared to

Figure 3.2. However, the residues of PPG#3 had nearly the same gel format as the condition before deswelling.

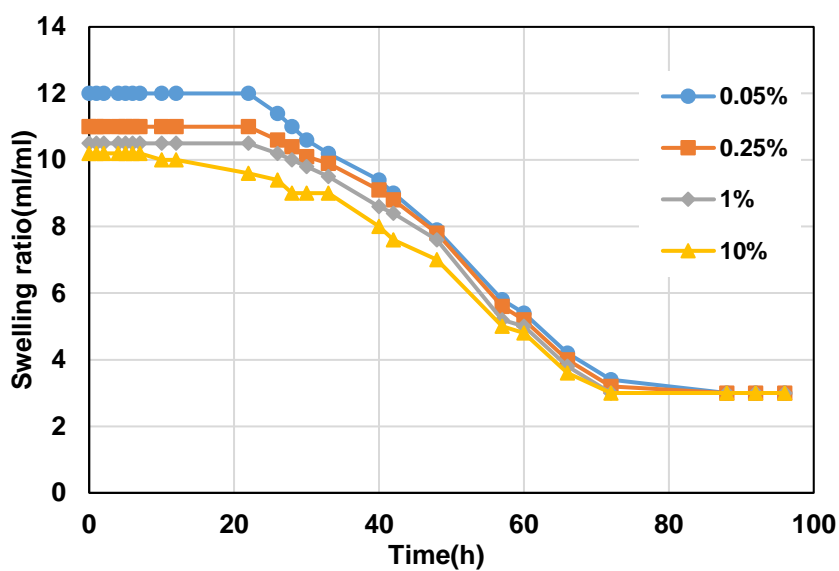


Figure 3.9. The deswelling process of PPG #1 in 10% HCl acid with different concentration brines

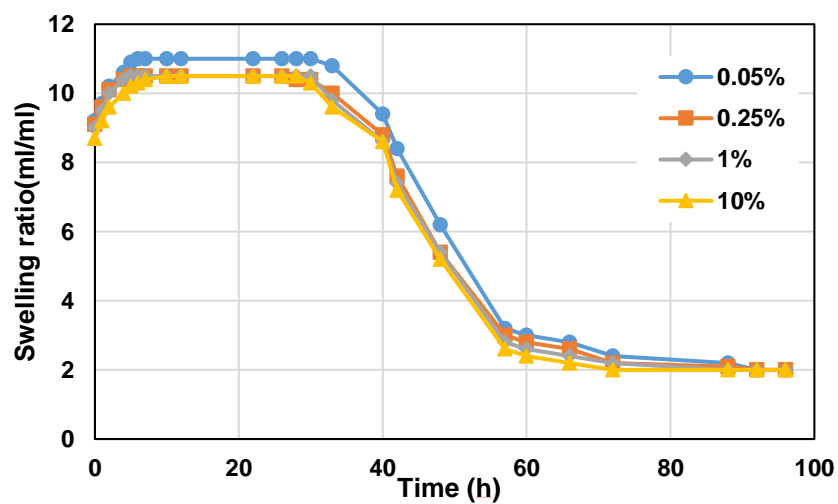


Figure 3.10. The deswelling process of PPG #2 in 10% HCl acid with different concentration brines

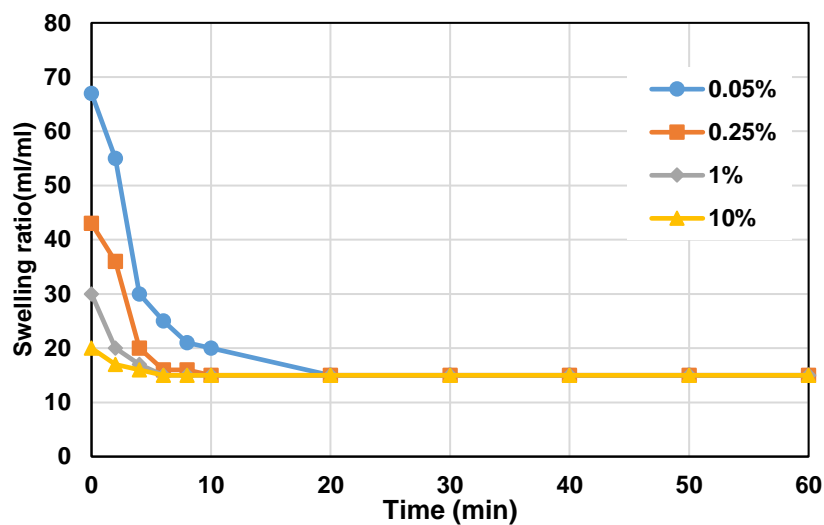


Figure 3.11. The deswelling process of PPG #3 in 10% HCl acid with different concentration brines

Table 3.2. Swelling ratio change of PPG #3 in 10% HCl acid after swelling in brine concentration ranging from 2% to 10% in two days

Brine concentration	Swelling ratio after swelling (ml/ml)	Equilibrium swelling ratio after deswelling (ml/ml)	Shrank volume ratio in deswelling (ml/ml)
2%	27	15	12
4%	24	15	9
6%	22	15	7
8%	21	15	6
10%	20	15	5

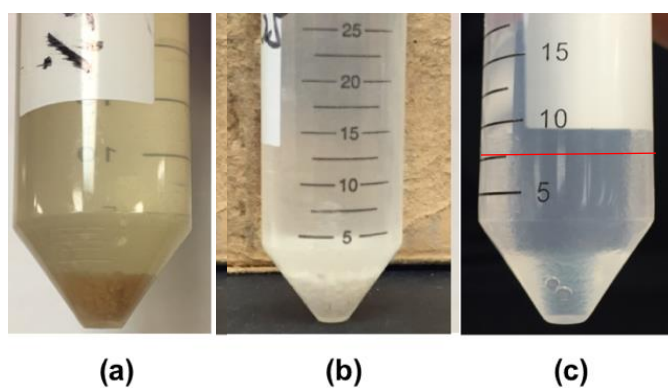


Figure 3.12. Images of remained underswelled volume at 45 °C for six days, respectively (a) PPG #1; (b) PPG #2; (c) PPG #3

3.3.3.2. Effect of acid concentration. Compared to 10% HCl acid, the deswelling kinetics and equilibrium of each kind of PPG in 1% and 4% concentration acid had some difference. Table 3.3 shows the clear comparison about the effect of acid concentration on the deswelling of these three PPGs.

In Table 3.3, increasing the acid concentration (from 4% to 10%) would slightly reduce the PPG deswelling start and deswelling equilibrium time, but increasing the acid concentration cannot reduce the remained undegraded swelling ratio of PPG#1 and #2. As a result, PPG #1 and #2 cannot shrink in the weak acid (1% HCl acid), whereas PPG #3 could in this low concentration but with larger remained un-degraded gel. The explanation might be that 4% and 10% of HCl acid were so strong that a screening effect of the counter ions shielded the charge of the cations and prevented an efficient repulsion and the concomitant release of ions sharply reduced the internal osmotic pressure, which made the gel deswelled [38]. However, PPG saturated in very low concentration of acid (1% HCl) would have the larger separation between molecules with large space containing water [43], accordingly, the remained gel volume was large and deswelling equilibrium time was long.

Table 3.3. Effect of acid concentration on deswelling after swelling in 1% brine (45 °C)

PPG number		#1	#2	#3
Deswelling start time (h)	1% HCl (pH >0)	-	-	0
	4% HCl (pH =0)	26	48	0
	10% HCl (pH <0)	22	32	0
Deswelling equilibrium time (h)	1% HCl (pH >0)	-	-	1/6
	4% HCl (pH =0)	81	90	1/5
	10% HCl (pH <0)	72	85	1/6
Remained gel SR (ml/ml)	1% HCl (pH >0)	-	-	25
	4% HCl (pH =0)	3	2	15
	10% HCl (pH <0)	3	2	15

3.3.3.3. Effect of temperature. Another two temperatures (60 °C and 80 °C) were used to evaluate the effect of temperature on PPGs deswelling performance, which was shown in Table 3.4.

Table 3.4. Effect of temperature on PPG deswelling in 10% HCl acid

PPG number		#1	#2	#3
Deswelling start time (h)	45°C	22	32	0
	60°C	5	7	0
	80°C	0.5	1.5	0
Deswelling equilibrium time (h)	45°C	72	85	0.5
	60°C	18	22	0.4
	80°C	2	5	22
Remained gel SR (ml/ml)	45°C	3	2	15
	60°C	3	2	15
	80°C	3	2	0

The temperature significantly affected the PPG deswelling process, especially the deswelling start time and equilibrium deswelling time, as shown in Table 3.4. For PPG #1 and #2, when the temperature increased, stable time reduced and the sooner the deswelling reached the equilibrium, but the remained un-degraded gel volumes were constant. However, for PPG #3, the particles can be totally degraded, only if the temperature was 80°C, though the time used was prolonged. Thus, there is a limit on how much increased temperature can affect residue degradation.

PPG #2 was used to test the deswelling performance in low concentration (1%) acid and 1% brine environment at 80°C, which was similar to real formation condition after acidizing. The experiment's results were shown in Table 3.5.

When the gel was saturated in 1% HCl at 45°C, the gel could not deswell in one week. However, high temperature (80 °C) accelerated the gel's deswelling in less than

one day. Another phenomenon was that PPG #2 could fully degrade in 1% brine at 80°C, though it took a long time (118 h).

Table 3.5. PPG #2 deswelling performance in 1% HCl and 1% NaCl brine at 80°C

1% HCl at 80°C	Start deswelling time (h)	6.5
	Deswelling equilibrium time (h)	19.5
	Remained gel SR (ml/ml)	2
1% brine at 80°C	Start de-swelling time (h)	31
	Deswelling equilibrium time (h)	118
	Remained gel (ml/ml)	0

In conclusion, both the acid and the temperature are factors influencing the PPG #2 deswelling performance. The acid could accelerate the deswelling kinetics and high temperature brine can fully degrade the PPG #2.

3.4. SUMMARY

According to these tests for all three kinds of PPGs, the results can be drawn:

1. These three PPGs had lower swelling ratio when swelled in higher concentration brine, which was more obvious for PPG #3. The lower swelling ratio was corresponding to the higher gel strength.

2. PPG #2 was the best diverting agent among these three PPGs for the following reasons:

(a) It had the longest stable time (more than 1 day) before deswelling when saturated in 10% HCl acid, and it could swell a little more in acid at 45 °C.

(b) Its gel strength was the strongest compared to the other two gels.

(c) The gel deswelled fast after the long stable period. In addition, it could deswell in high temperature even with low acid concentration, which was very similar to the real

stimulation conditions after the acidizing. It could also be fully degraded in brine at high temperature.

3. PPG #1 could also maintain stable in 10% HCl acid for one day and then deswelled. PPG #3 shrank immediately when contacted with the acid, but it can be totally degraded in acid at 80 °C. The deswelled volume in acid reduced by increasing the concentration of brines before deswelling.

4. The high temperature and acid concentration would promote the deswelling in acid of all three PPGs.

4. EVALUATION OF PPGS AS A DIVERTING AGENT IN ACIDIZING

4.1. EXPERIMENTAL MATERIAL AND SETUP

PPG. Three types of PPGs described in Section 3.1 were used.

Core samples. Indianan limestones were used in all experiments, which are carbonate rocks. Indiana limestone, also called Bedford limestone, is a rock primarily composed of calcium carbonate which ratio is around 97%. The absolute permeability of these rocks was varying from 20-150md. All core samples were with the diameter of 2 inches and length of around 5 inches.

Brine. NaCl solutions with the concentrations ranging from 1% to 8% were used.

Acid. HCl from Fisher Scientific was diluted with RO water to obtain 4% and 10% HCl acid solution.

The schematic experiment setup is depicted in Figure 4.1, and the actual setup is illustrated in Figure 4.2. The Hassler core holder can hold a core with a diameter of 2 inches and a length between 4 and 5 inches. The syringe pump was used to inject brine and gel through magnetic stirring vessel accumulator into the Hassler core holder. The volume of this accumulator is 1000 ml and its operation impeller speed is 1400 r/min. The impeller was placed at the bottom of the accumulator so that the PPGs remained dispersed in brine when they were injected into the model. There is a piston inside the accumulator, which can be pushed to inject the gel into the core by water. The injection sensor was connected to the inlet of core holder to collect the injection pressure data. P_0 was the confining pressure which was at least 300 psi larger than injection pressure (P). It can ensure that the injected fluid flows through the core sample instead of the gap

between core and holder. The heating jacket was attached to the outside of the core holder to heat it up. The effluent was collected at the outlet of the core holder by tubes.

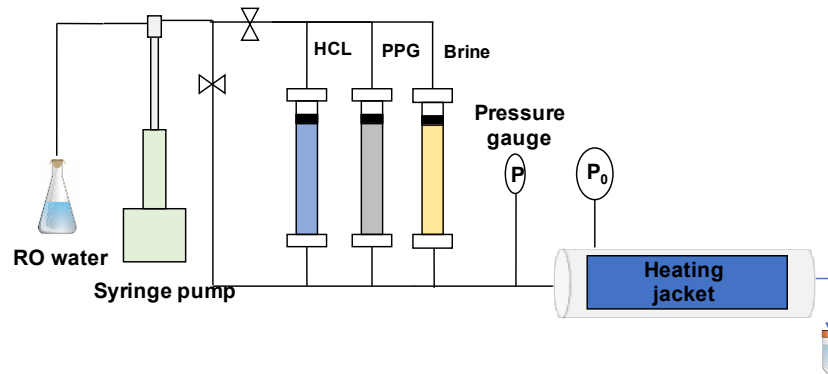


Figure 4.1. Schematic diagram setup of basic core flooding experiments

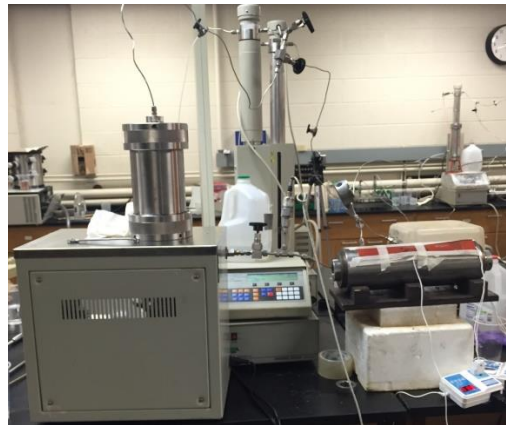


Figure 4.2. The image of the experiment setup

4.2. EXPERIMENT PROCEDURE

Core sample preparation. The cylinder core sample was drilled from the carbonate rock block and put into the 105°C oven for at least 24 hours until no water inside. The weight of the dry core was measured. Then the sample was put in a vacuum tube to pump out the air inside for more than 6 hours. Afterwards, the core was saturated in 1% NaCl

solution for 12 hours. The weight of saturated wet core sample was measured. The weight difference between the dry and wet sample represented brine weight inside the core sample. The porosity of the core sample was calculated by using brine density.

Permeability measurement. 1% NaCl brine was injected into the core sample using four different velocities. Pump flow rates and corresponding velocities used in experiments are summarized in Table 4.1. The core permeability can be calculated by using Darcy's law using the injection pressure data. All core samples in one series of experiments had the same matrix permeability.

Table 4.1. Injection velocities and their corresponding pump rate conversions

Pump flow rate (ml/min)	1	2	3	4	8	10	12
Velocity in real case (feet/day)	2.4	4.8	7.2	9.6	19.2	24	28.8

Channel (wormhole) Creation. The small cylindrical channel in the middle of the core was drilled. The channel was partially opened, which was with the diameter of $5/32$ inch (0.4 cm) and depth of 2.15 inch (5.5 cm) as displayed in Figure 4.3.

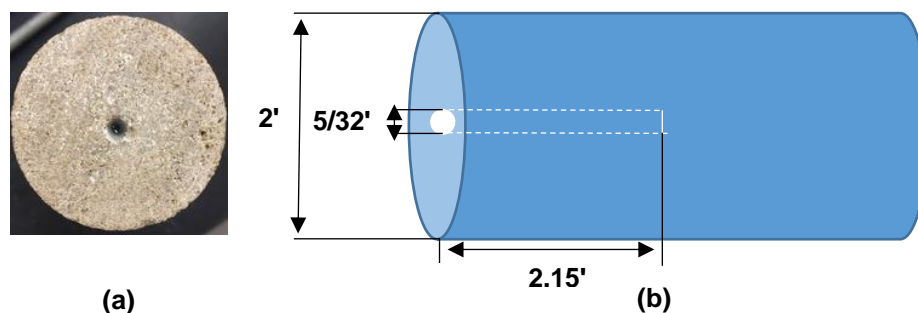


Figure 4.3. The core used in the experiment (a) the image of the core with channel (b) the schematic diagram of the core

Permeability measurement of the core with the channel. The brine was injected into the core in the direction that was from the side without the hole to the side with the hole. The permeability was calculated again.

PPG injection. The magnetic stirring vessel was used to inject PPGs at the temperature of 45°C. Different brine concentrations were used because of the PPG properties differences. PPG particles were injected with brine at a constant flow rate of 2 ml/min. The injection pressure, outflow pore volume (PV) from the outlet, and the injection time was measured. Injected PV was defined as the ratio of the volume of effluent fluids to the original pore volume of the core.

Acid injection. HCl acid was injected to the core sample at the temperature of 45°C by using a transparent accumulator that can withstand HCl acid at favorable flow rates.

Deswelling. The core sample was sealed and put into an oven for two days.

Permeability Measurement after the acid treatment. 1% brine was injected in the direction opposite of acid injection with a high flow rate (12ml/min) for half an hour to remove the remained PPG. Then four different flow rates were used to measure the permeability of the core sample.

4.3. RESULTS AND ANALYSIS

4.3.1. Effect of PPG on Acid Diversion. Table 4.2 gives the basic properties of these three types of PPGs evaluated in Section 3. For PPG #3, it shrank a lot when contacted with acid as shown in Table 3.2. Therefore, the high concentration (8%) brine was used to reduce the deswelling volume in acid, which only shrank 28% after saturated

in 10% acid in two hours. The other two gels swelled in 1% brine before injection. Table 4.3 shows that each PPG was injected into the core sample with the similar permeability at the same injection rate. Additional, a blank control experiment without PPGs injection was conducted.

Table 4.2. PPGs characteristics contrast

PPG type	PPG saturated brine concentration	Particle size (mesh)	Swelling ratio	Shrinking volume ratio in acid within 2 hours	PPG strength (Pa)
#1	1%	30-40	10	0	1780
#2	1%	70-100	9	-0.11	4150
#3	8%	100-120	20	0.28	1040

Table 4.3. Experiments performance

Experiment No.	#1 (blank)	#2	#3	#4
Permeability (md)	14	24	21	18
Porosity (%)	16.4	17.0	16.4	16.8
PPG type	-	#1	#2	#3
Pressure at the end of PPG injection (psi)	-	800	800	800
10% HCl used (ml)	240	240	240	240
PPG (wt%)	-	0.5	0.5	0.5
PPG injection rate (ml/min)	-	2	2	2
Acid injection rate (ml/min)	2	2	2	2
Depth of channel	5.5	5.5	5.5	5.5

Figure 4.4 displays the relationship between the gel injection pressure and the injection time with the injection velocity of 2 ml/min (4.8 feet/day). Three experiments results show the similar pressure increasing trend in gel injection period. The pressure went up slowly at the beginning of injection and then the increase accelerated. Finally, the pressure increased linearly indicating the plugging effect.

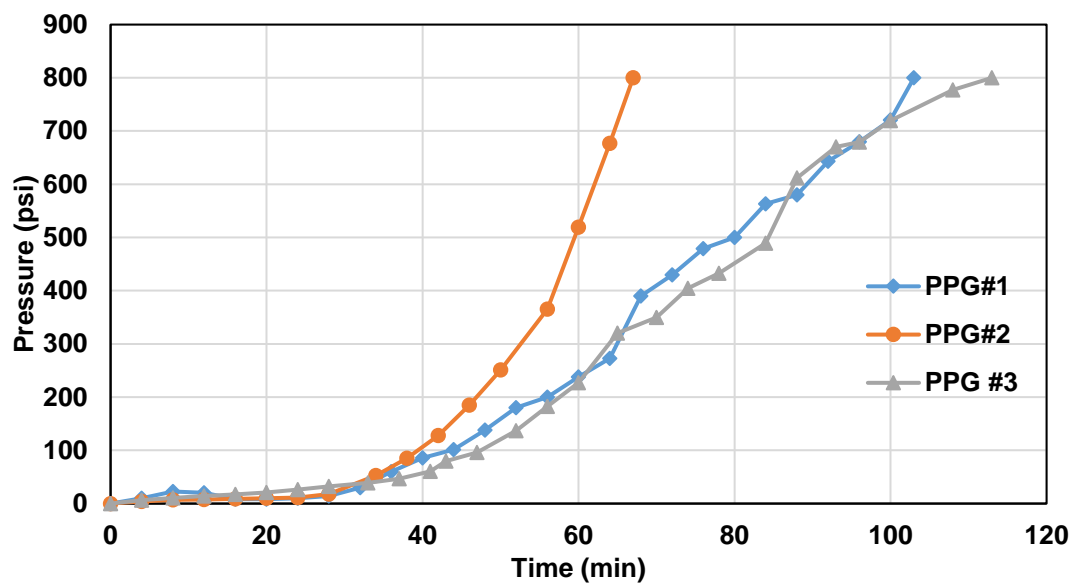


Figure 4.4. Pressure change with time of PPG injection in Experiment #2, #3 and #4

At the beginning of PPG injection, a few particles cannot resist the flowing fluid, and consequently, the pressure was low at first. As more and more gels were injected, PPGs started to form the low permeability gel cake inside of the channel and then at the surface of the core. The pressure expressed a non-linear increase in this period. When the channel was filled or plugged by PPGs, chasing particles cannot enter the channel and turned to aggregate the entrance of the channel to have a face plugging. The near linear increasing injection pressure after the accelerated pressure growth might be due to this face plugging. The face plugging formed gel cake at the surface of the rock further blocked the brine and gel going through the core. Figure 4.5 shows gel cakes formed in front of cores by three different PPGs.

With the same injection rate, pressure increase rates of PPGs #1 and #3 were slower than PPG #2, which might be caused by their lower gel strength. Gel cakes formed by weaker gels often had a higher permeability than did strong gel [45].

Therefore, the weaker gel needed more time to form the same compact and permeability gel cake with a smaller slope of pressure increase in Figure 4.4. Therefore, PPG #2 was more favorable to form the strong gel cake because of the less volume of gel usage for acid diversion.

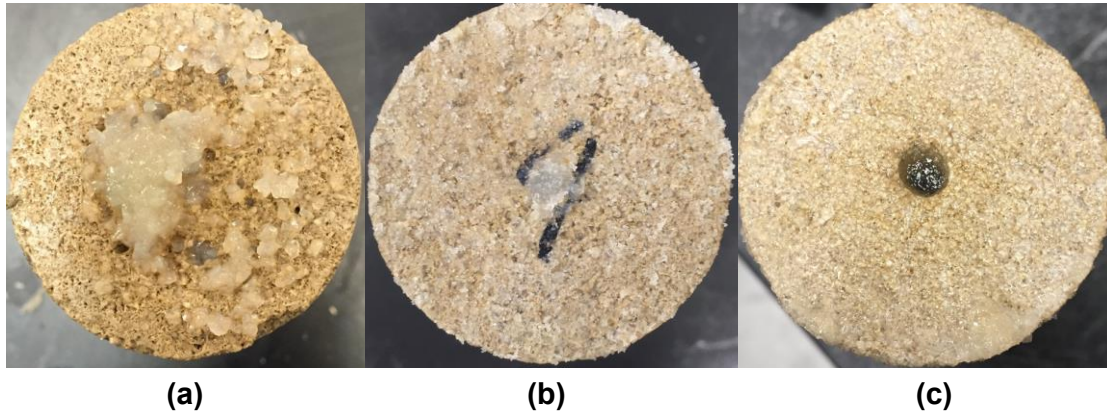


Figure 4.5. The image of gel cakes (a) PPG #1 cake (b) PPG #2 cake (c) PPG #3 cake

Pressure changes of different PPGs in the acidizing process are presented in Figure 4.6. The pressure of Experiment #1 (blank control experiment) increased slower than any other experiments in which PPGs were used as the acid diverting agents. Since no gels blocked the inlet, the acid had no significant resistance entering the channel and reacted with the carbonate. At first, as more and more acid reacted with minerals, the produced CO_2 increased and resulted in the pressure growth. The reaction mainly occurred inside the channel, which made the channel larger and longer. Therefore, the longer and larger channel indicated the permeability increase consistent with injection pressure reduction.

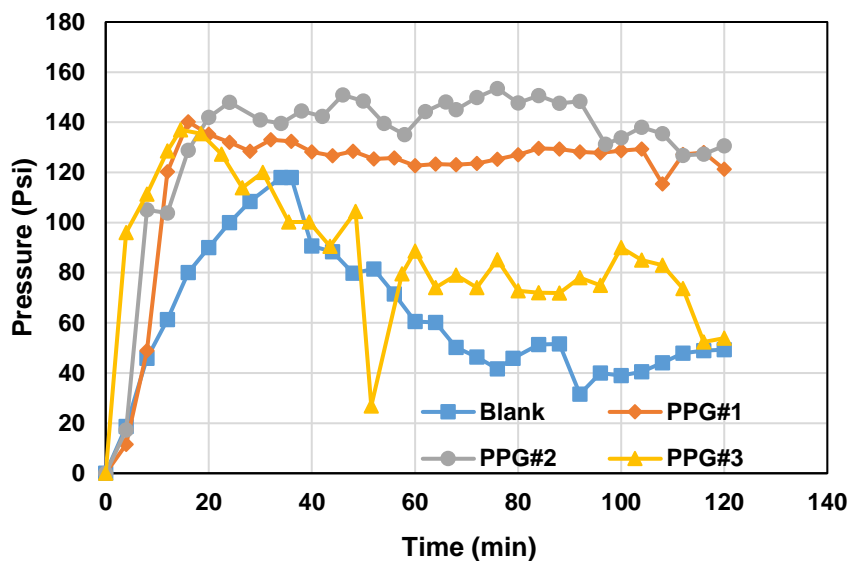


Figure 4.6. Acid injection profile when different PPGs block

With the gel blocking the inlet in Experiment #2 to #4, the acid was resisted and the injection pressure went up quickly. The acid was diverted, which had a large acid coverage area as shown in Figure 4.7. The acid broke through the gel cake ahead of the core and reacted with the rock, in which the injection pressure should reduce. However, accompanying with the gel block, a large amount of produced CO_2 from the reaction between the acid and CaCO_3 would increase the injection pressure. The low permeability of the core sample also led to high injection pressure when CO_2 was produced and flowed through it, which offset the pressure reduction. Therefore, the pressure drop after the peak was not obvious as shown in Figure 4.6, instead, the pressure of PPG #1 and PPG #2 were stable after the increasing. This happened probably because that they did not deswell in acidizing and could plug the channel for diversion. The permeability enhancement (wormholing) and plugging (diversion) net effect were equal [44]. However, PPG #3 cannot effectively plug the channel in acidizing, which might be caused by its quick shrink when contacted with acid. Therefore, its injection pressure

reduce was evident as shown in Figure 4.6, which indicated that the effect of acid enhancing the permeability by etching the channels was larger than the effect of plugging and diversion.



Figure 4.7. The image of the acid diversion coverage (20 min after injecting acid)

Figure 4.8 and Table 4.4 summarize the acidizing results. While injecting acid to the core without the channel and gel, the acid flowed straightly in the middle of the core as shown in Figure 4.8 (a₁). If there was a channel in the middle, the acid would enter the middle channel to increase the conductivity as displayed in Figure 4.8 (a₂). The acid was not diverted to cover a large area of the core in both of these conditions, and no other new channels were created in the acidizing.

Table 4.4. Acidizing results detail

Experiment No.	The diverting depth (cm)	New channel depth (cm)	Permeability after the acid treatment (md)	Permeability recovery
#1 (Blank control)	-	-	136	-
#2	1.2	4.1	33	1.375
#3	1.8	4.3	25	1.19
#4	2.4	3.2	61.7	3.42

When the channel was plugged by gels before acidizing, the acid was diverted to cover a large area of rock surface as clearly shown in Figure 4.8 (b)(c). In addition, the gel inside the channel also diverted the acid to create the new long channel at the depth of 1.2 cm in Figure 4.8 (b) and 1.8 cm in Figure 4.8 (c). Though PPG #3 was injected before acidizing, it did not have a large acid coverage area as shown in Figure 4.8 (d). Nevertheless, the gel cake inside the channel and the remained PPG #3 after deswelling still had a little diverting ability. They diverted the acid at the depth of 2.4 cm of the channel, but the new channel was small and short.

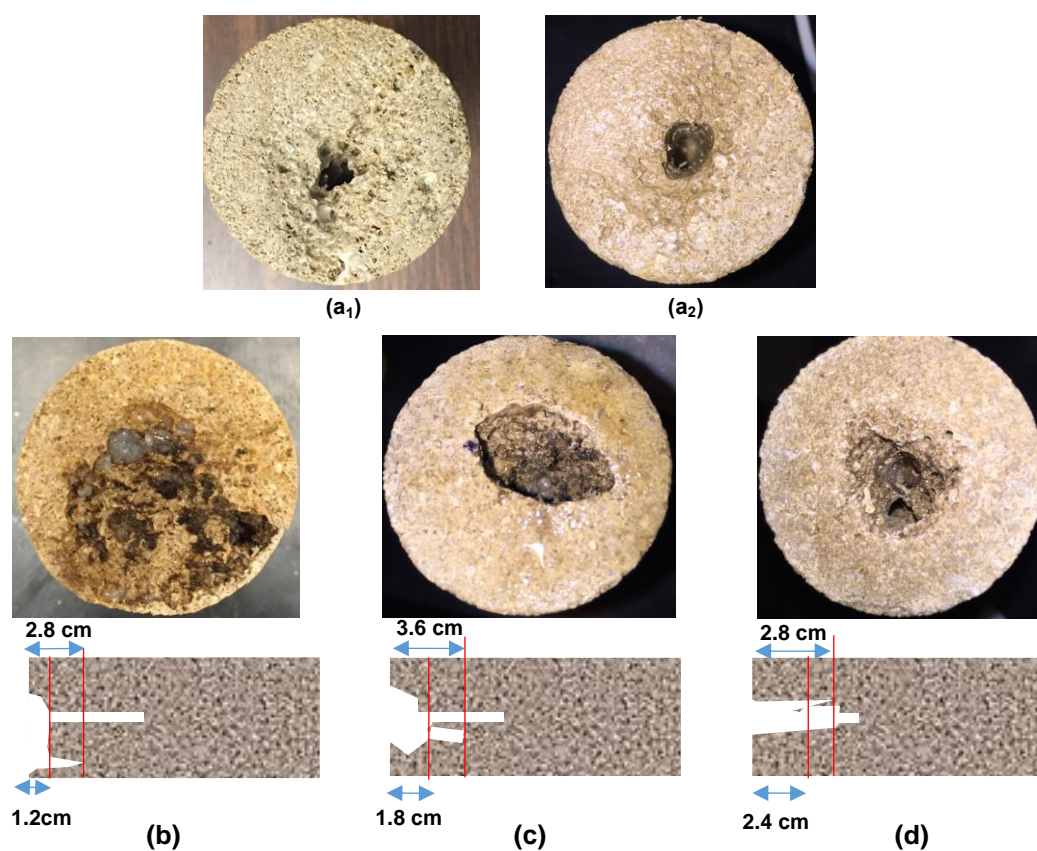


Figure 4.8. Images of effects of PPGs on acid diversion: (a₁) the core without channel etched by acid; (a₂) blank control group (the core with the channel and without gel). The diverting results and their schematic diagram: (b) PPG #1 (c) PPG #2 (d) PPG #3

There were some PPGs still plugging in the channel after the acidizing, especially in Experiment #2 and #3. Figure 4.9 shows the remained PPGs that cannot be degraded or removed from the core. The shape of PPG #1 changed a little and twisted together to form a roll. PPG #2 particles had no particle shape and form a viscous solution after the treatment. PPG #3 shrank a lot that most of the remained particles were removed by the flow back.

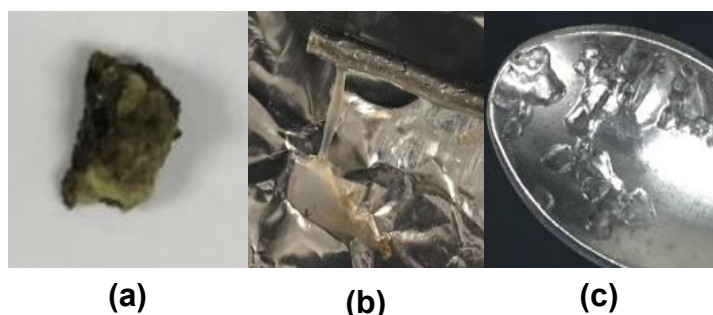


Figure 4.9. Images of remained PPGs from the core after experiments (a) PPG#1; (b) PPG#2; (c) PPG#3

From Table 4.4, because of the gel treatment in Experiment #2, #3, and #4, the permeability did not increase so much compared to that of the blank experiment. In Experiments #2 and #3, because of the gel diverting ability, some gels inside of the channel did not contact or contacted with a little acid so that they did not deswell and still blocked the old channel. The acid diversion and remained gel plugging offset the permeability enhancement. However, PPG #3, shrinking quickly in acid, cannot fully block the acid from entering the channel of which the conductivity was increased. Therefore, its permeability was higher than Experiment #2 and #3. In views of these, as diverting agents, PPG #1 and #2 were better than PPG #3.

4.3.2. Effect of PPG Injection Volume on Acid Diversion. The brine and equipment setup used in this section were same as previous works. PPG #2 was the only PPG used in these experiments. Cores were still Indiana limestone, but with higher permeability. 10% HCl acid was diluted to 4% by adding the RO water. 0.8, 1.0 and 1.4 PV of PPGs were injected into the cores to investigate effects of injection volume on acid diversion. Experiments performance were summarized in Table 4.5

Table 4.5. Experiments performance

Experiment No.	#5	#6	#7
Permeability (md)	158.2	145.5	150.4
Porosity (%)	14.4	14.2	15.1
Pore volume (ml)	29.2	28.8	30.6
Pore volume injected (ml/ml)	0.8	1.0	1.4
Pressure at the end of PPG injection (psi)	93.6	827.5	1683
4% HCl used (ml)	250	250	250
PPG and acid injection rate (ml/min)	2	2	2
Dry PPG size (mesh)	60-120	60-120	60-120
PPG (wt%)	2	2	2
Length of Channel (cm)	5.7	5.7	5.7

Three curves are almost overlapped because of the same injection rate, particle size, and PPG concentration as shown in Figure 4.10. The only differences are the PPG injection volume and the pressures at the end of PPG injection. The injection pressure of 0.8 PV of PPG injected only increased to 93.6 psi. But, injection pressures of 1.0 and 1.4 PV of PPG reached the point that the pressure increased linearly which were 827.5 and 1683 psi, respectively. The injection pressure increased with the more amount of PPG injected. The higher injection pressure meant the thicker and less permeable gel cake was formed.

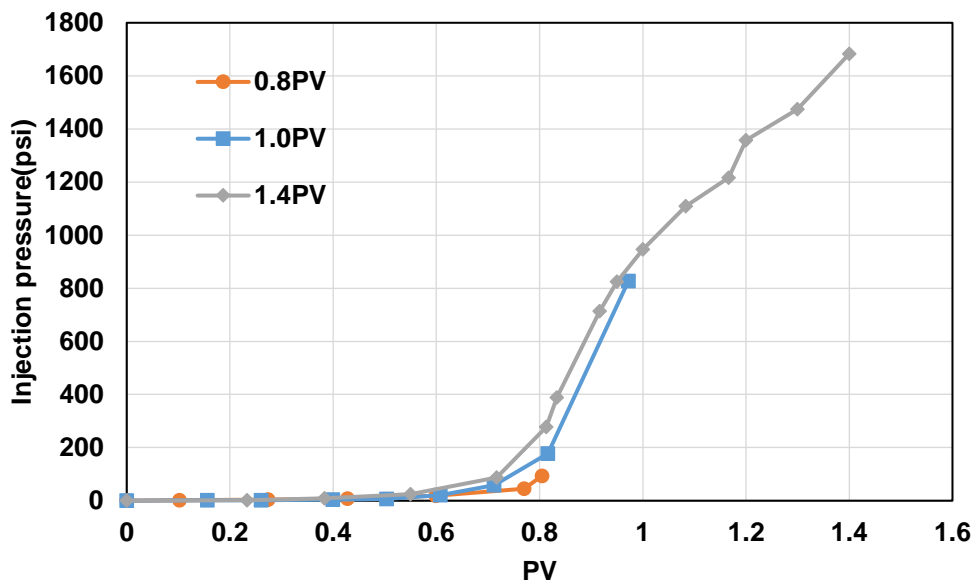


Figure 4.10. The pressure change by using different volume of PPG injection

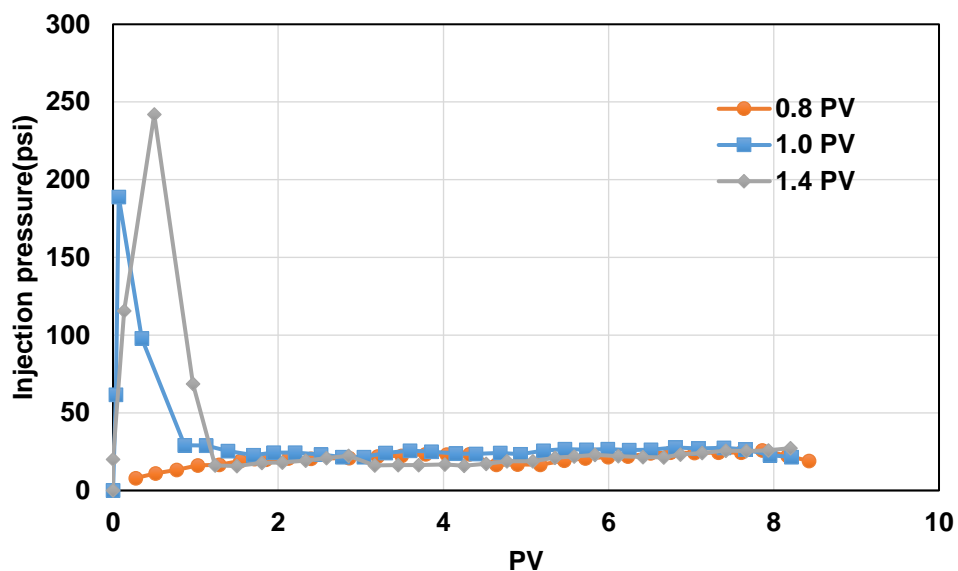


Figure 4.11. Pressure change in acidizing after different volume of PPG injection

Injection pressure differences among three experiments in the acidizing period are shown in Figure 4.11. The experiment with more PV of PPG injection also had higher pressure peak at the beginning of the acid injection. The higher peak pressure meant the

higher resistance, which was the evidence of the acid diversion. However, 0.8 PV of PPG injection did not have the pressure peak during acid injection period. The reason might be that 0.8 PV of the PPG was not enough to form the strong compact gel cake to resist the acid injection.

After the peak, the gel cake was broken by acid with the pressure reduction, which was like the sequences occurred when brine was injected through PPGs as reported in Imaqm's paper [38]. The inter-channels among particles appeared and the acid went through them to react with the carbonate.

Diversion results are shown in Table 4.6 and Figure 4.12, which displays different diversion abilities. New wormholes were created in all three experiments, which meant the diversion happened. However, the result using fewer PPGs (0.8 PV) was different from Experiments #6 and #7 using a large volume of PPGs. Experiment #5 only had small and shallow new channels with the large acid coverage area, which meant a bit external diversion. The reason is probably that the gel cake only formed at the top of the channel. The condition can be explained referring to Bai's paper (2011) [46] that the PPGs propagated like a piston along the channel, so that 0.8 PV of PPG only formed a loose gel cake in a little depth of the channel and concentrated at the channel surface. Therefore, the diversion only took place at the surface indicating that no large new channel was formed as shown in Figure 4.12 (a).

New large and deep channels etched by acid in Experiment #6 and #7 indicated that most of the acid was diverted. A large amount of PPGs could form strong gel cake both at the surface of the core and inside the channel to divert acid. The acid was diverted to cover a large area and then mainly went through the new path instead of straightly

entering the old channel, which was preferred in acidizing diversion. Furthermore, there was also large parts of the old channel protected by PPGs. The diversion depth (1.4 cm) of the Experiment #7 showed the earlier diversion which meant the better acid diverting efficiency when compared to the Experiment #6 (1.6 cm).

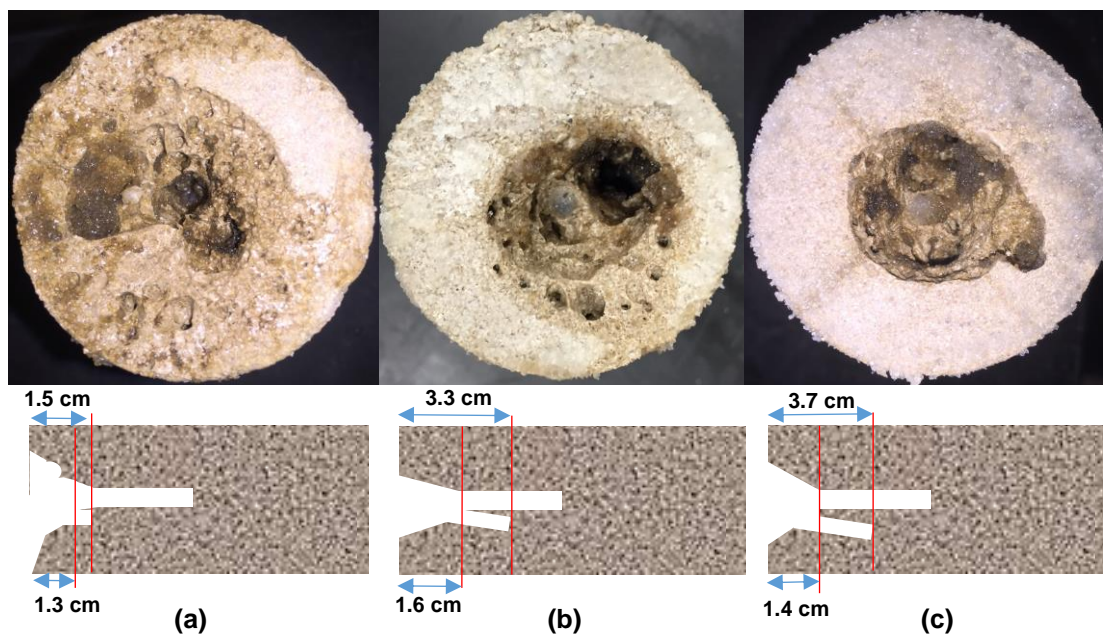


Figure 4.12. Images of the effect of PPG injection pore volume (PV) on final acidizing performance and the corresponding schematic diagrams (a) 0.8 PV (b) 1.0 PV (c) 1.4 PV

Table 4.6. Acidizing results detail by using different volume of PPG injection

Experiment No.	#5	#6	#7
The diverting depth (cm)	1.3	1.6	1.4
New wormhole diameter (cm)	0.5	0.8	1.2
New wormhole depth (cm)	1.5	3.3	3.7
Permeability after acidizing (md)	104.4	76.0	78.1
Permeability recovery	0.66	0.52	0.51

If the diversion is to cover a large area of the core like external diversion in mechanical diversion, the small volume of the gel can be used for diversion. If the

acidizing is going to divert acid to create new channels and protect the original channel to have both external and internal diversions, the strong gel cake is better by injecting large volume of gels.



Figure 4.13. The image of remained PPG #2 after the experiment

As summarized in Table 4.6, the final permeability reduced with more PPG volume injected. The reason might be that the gel in channels and pores was partially degraded by acid. These remained gels, as shown in Figure 4.13, were inevitably left especially inside pore throat to reduce the permeability of the core. Large volume of PPGs injection along with higher injection pressure increased gel particles' penetration into the pore throat [45], which cannot be degraded or removed after the treatment. The acidizing to increase permeability cannot overcome the permeability reduction from the remained PPGs plugging. As a result, the overall permeability reduced. Experiment #5 had higher final permeability and recovery than Experiment #6 and #7 because of its less volume of PPGs injection with smaller injection pressure.

4.3.3. Effect of Particle Sizes on Acid Diversion. Indiana limestones and PPG #2 which particle size ranging from 60 to 120 mesh were used in this series of experiments. The experimental setup and procedure were same as before, but the core

holder was placed vertically to remove the effect of gravity in acid injection period.

Except for this, the gel injection pressure (200 psi) was kept unchanged before the acid injection. The basic information is shown in Table 4.7.

Table 4.7. Experiments performance

Experiment No.	#8	#9	#10
Permeability (md)	32.5	28.3	35.0
Porosity (%)	15.5	15.9	15.6
Pore volume (ml)	37.6	39.4	39.8
Core length (cm)	12.0	12.2	12.6
Pressure at the end of PPG injection (psi)	200	200	200
PPG (wt%)	0.5	0.5	0.5
Channel depth (cm)	5.5	5.5	5.5
Dry PPG size (mesh)	60-70	100-120	60-120

All experiments controlled the same injection pressure after the PPG injection.

There were three ranges of PPG sizes tested: large particles in 60-70 mesh in Experiment #8; small particles (100-120 mesh) in Experiment #9; 60-120 mesh including both large and small particles in Experiment #10. Figure 4.14 shows the PPG injection pressure change with PV from the outlet.

The pressure increased faster if there were large particles injected as two curves (60-70 mesh, 60-120 mesh) shown in Figure 4.14. For Experiment #8 using 60-70 mesh PPGs, the pressure started to increase after only 0.5 PV injected. It was significantly quicker than about 2 PV in Experiment #9 with small particles. This was because that the large particle could bridge the channel and increased the resistance [47], so that the injection pressure went up sooner. However, in the pressure accelerate increasing period, the injection volume of the larger particles was prolonged to nearly 0.75 PV (from 0.4 PV to 1.15 PV) which was a large ratio of its overall injection volume compared to 0.44 PV

(from 1.93 PV to 2.37 PV) of small particles. It might be explained that large particles had the lower gel pack permeability than did small particles [38], which needed more to form the same permeable gel cake. Nonetheless, large particles still took less volume to form the same permeable gel cake, for it was difficult for large particles to penetrate into pores of the core. Therefore, they only formed external gel cakes in the channel and at the core surface. Except for the external gel cake, fine particles could form the internal gel cake by gel penetration to pore throat [45], which increased the gel injection PV.

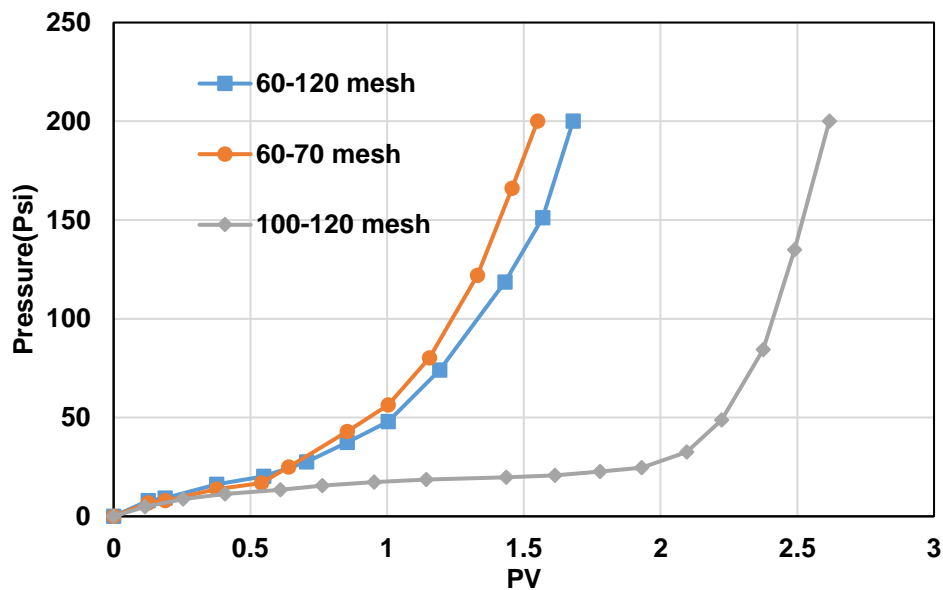


Figure 4.14. Pressure change by using different particle sizes of PPG injection

Experiments #8 and #10 had the similar PPGs injection pressure curves. In fact, large particles in the Experiment #10 could also bridge the channel [47], which reduced the injection volume of PPG. Small particles only filled the space among large particles to increase the formed gel cake resistance. For this reason, the injection profile of Experiment #10 was more like the experiment using large particles.

Figure 4.15 shows the pressure change in acidizing with different sizes of PPGs as diverting agents. These three curves had the pressure sharply increase which showed the diversion from the gel cake formed ahead of the core. Definitely, that small PPGs formed gel cake was more compact and had the higher injection pressure peak (443.5 psi) with the higher flow resistance. The similar high peak pressure occurred in Experiment #10 with 60-120 mesh PPGs owing to its both large and small particles formed gel cake. Large particles formed gel cake had more and larger inter-channels resulting in the lower peak pressure. The following stable pressure after the peak in these three curves showed that the effect of increasing permeability by acid wormholing was equal to the effect of plugging of diversion.

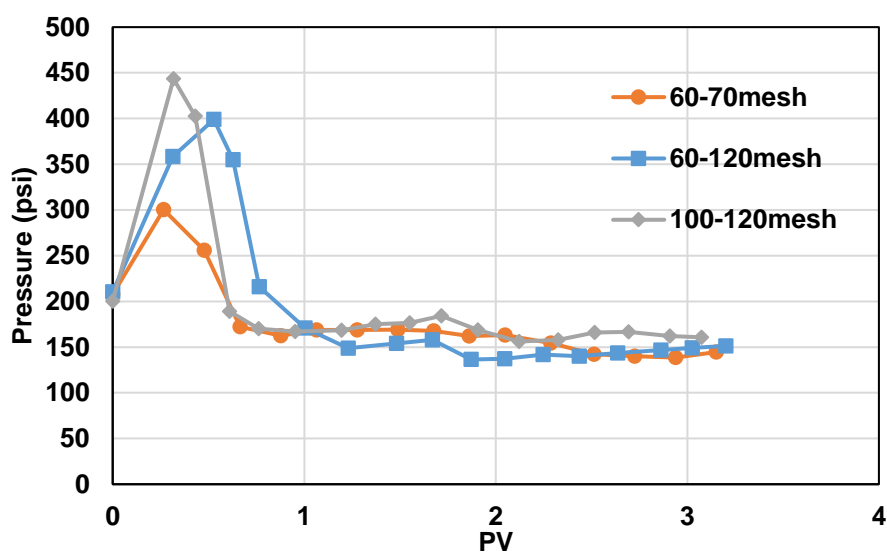


Figure 4.15. The effect of particle sizes on acid injection after gel injection

Figures 4.16, 4.17, 4.18 and Table 4.8 show diversion results of these experiments. Three experiments had good diversions that could be seen from schematic diagrams in these figures. The acid was diverted to cover a large area instead of only

entering the original channel. The original channel blocked by gels was protected, especially in some depth of the core. In addition, created large new channels indicated that the diversion happened.

Table 4.8. Acidizing results detail

Experiment No.	#8	#9	#10
The diverting depth (cm)	0.8	1.4	1.8
New wormhole diameter (cm)	1.2	0.8	0.7
New wormhole depth (cm)	4.2	3.8	5.0
Permeability after acidizing (md)	28.0	16.3	23.1
Permeability recovery	0.86	0.58	0.65

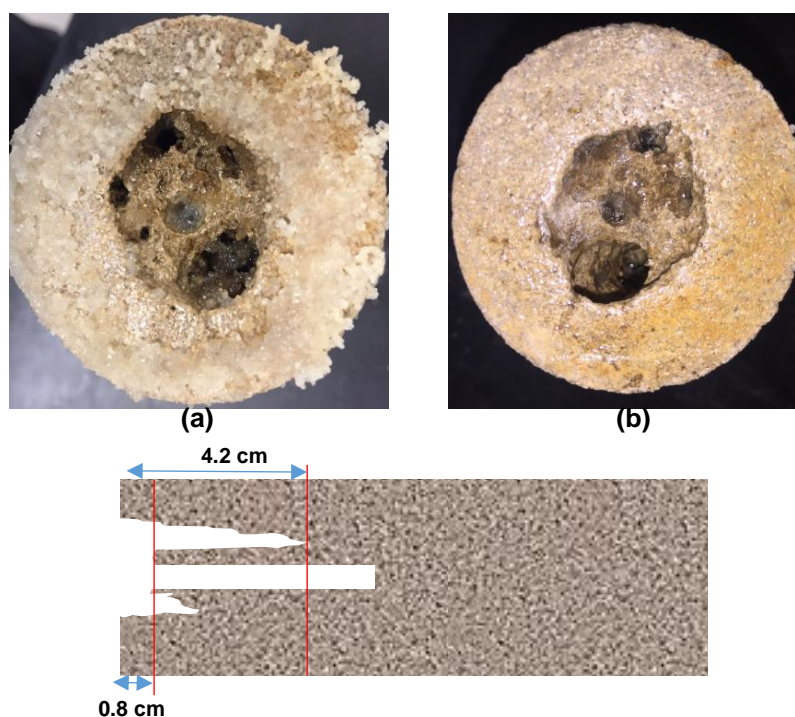


Figure 4.16. Images of 60-70 mesh diverting PPG on final acidizing performance and corresponding schematic diagram (a) after acid treatment (b) after 2nd permeability measurement

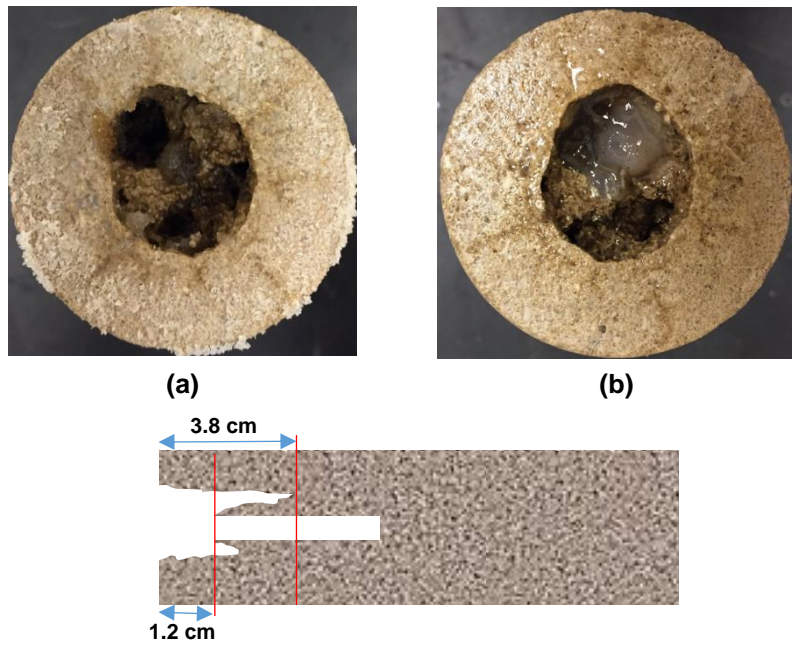


Figure 4.17. Images of 100-120 mesh diverting PPG on final acidizing performance and the corresponding schematic diagram (a) after acid treatment (b) after 2nd permeability measurement

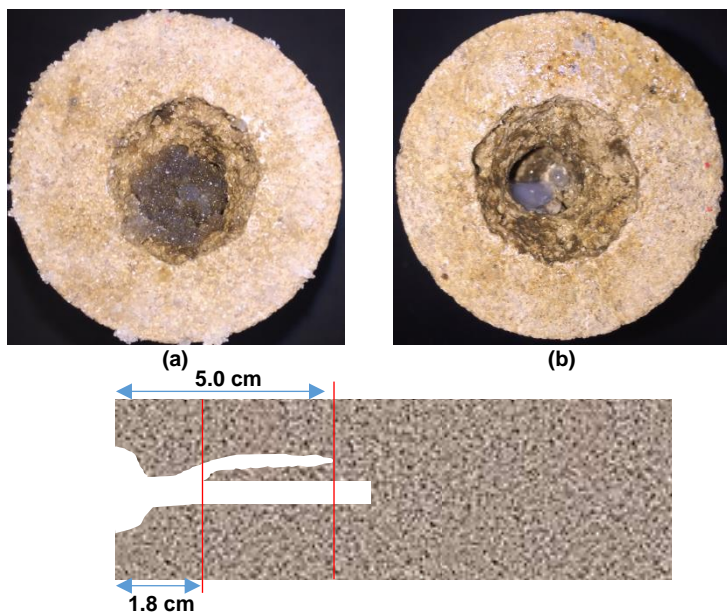


Figure 4.18. Images of 60-120 mesh diverting PPG on final acidizing performance and the corresponding schematic diagram (a) after acid treatment (b) after 2nd permeability measurement

Experiment #8 using large particles had the best result among these three experiments with the diversion near the surface at 0.8 cm depth and the largest (1.2 cm) and long (4.2 cm) new channel etched by diverted acid, which showed the higher acid diversion efficiency. Small particles diverted acid at about 1.4 cm depth of the channel as well as the smaller (0.8 cm) and shorter (3.8 cm) new wormhole that was deeper than large particles. The experiment with both large and small particles had deep diversion at 1.8 cm depth of the core. But a large amount of acid was diverted to create the longer (5 cm) channel which also showed the high diversion efficiency.

The diverting results indicated that large PPG particles could divert the acid near the core surface, and small particles took action for diversion in some depth. From another study like Gomma et al [47], the similar conclusions were drawn. Large particles could bridge the channel at the top part of the channel, which had the diversion close to the core surface. Small particles cannot bridge the channel, which only diverted acid in some depth of the channel.

Except for the diversion, the permeability recovery of the Experiment #8 was the highest among these three experiments, which was a good property as a diverting agent. Though the acidizing could increase the core permeability and remove some PPGs (comparing (a) with (b) in Figure 4.16-4.18), the acid was diverted so that the plugged PPGs inside the channel and pore throat might not contact the acid, so that the overall permeability reduced. However, large particles were more difficult to be penetrated into the pore throat at the same injection pressure. As a result, its plugging damage was the least, which resulted in the highest permeability recovery.

4.3.4. The Diversion Mechanism of PPGs in Acidizing. According to all these coreflooding experiments, the diversion process mechanism in these experiments can be drawn in Figure 4.19.

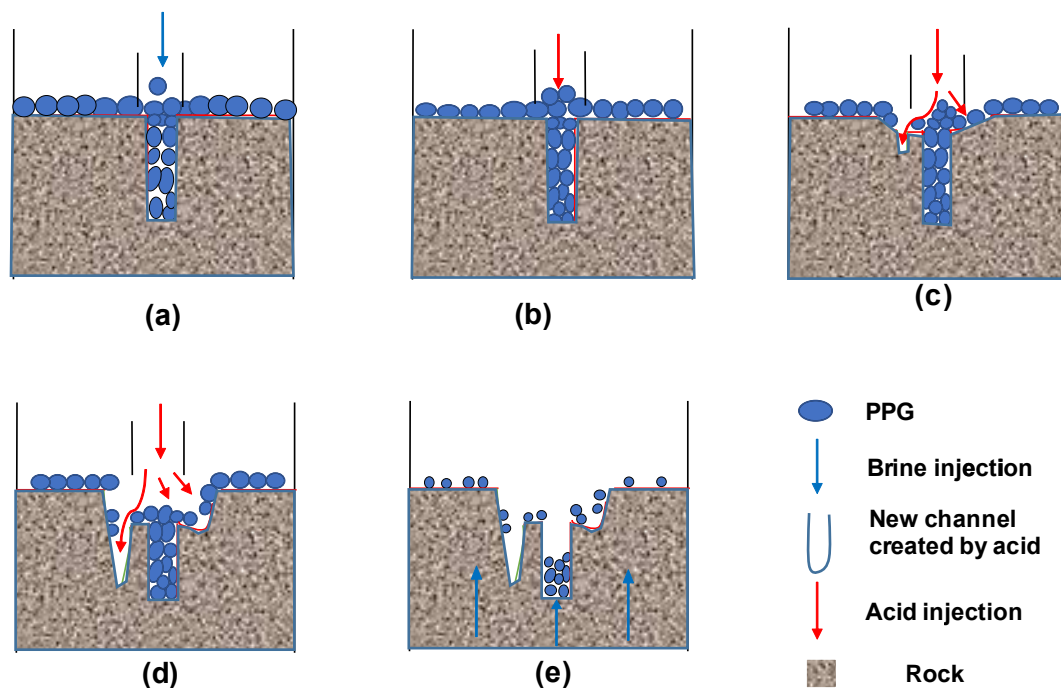


Figure 4.19. The schematic of PPGs diversion performance sequences in acidizing

The sequences of the experiment from PPGs injection to acidizing are as follows:

(a) after PPGs are injected into the channel, gel cakes are formed inside of channel and at the surface of the core; (b) at the beginning of acid injection, PPG particles are compressed by moving closer to each other and the gel cake becomes more compact. In this period, the injection pressure increases significantly because PPGs block the acid injection; (c) as the acid injection continues, there are inter-channels formed among PPGs in the surface gel cake, which diverts the acid to cover more area in the matrix. The gel cake inside channel can divert the acid to etch new area along the old channel. As a

result, there are a large area coverage and new channels created by diverted acid erosion; (d) as more acid enters, the middle part of the core is etched and the surface pit structure appears obviously. Some parts of the old channel are also etched, but the new channel becomes deeper and larger showing the most acid flow path; (e) a few days after the acidizing, particles deswell and then be removed by waterflooding from the production direction.

4.4. SUMMARY

1. PPGs #1, #2, and #3 could divert acid in different degree. PPG #3 was the least suitable diverting agent due to its quick deswelling property. PPG #1 and #2 were suitable as diverting PPGs but PPG #2 was better because of its less volume usage.

2. The more volume of PPGs injected would result in more compact gel cake. It could divert most of the acid flow to new paths deep in the core. Less PPGs injection only formed loose gel cake near the surface, which diverted little acid at core surface.

3. The selected PPG samples cannot be fully degraded and removed after acidizing. There were some gels remained in porous media and channels, which reduced the overall permeability of the core.

4. Large particles could bridge the channel reducing the injection time compared to smaller ones. Large particles were also favorable as diverting agents in acidizing due to its higher diversion efficiency and permeability recovery.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

Three types of PPGs were measured and evaluated in this study in terms of swelling kinetics and equilibrium, gel strength and deswelling aspects. Coreflooding tests were used to examine diversion ability of these gels for acidizing. PPG #2 was used to test several factors on the diversion in acidizing.

From measuring the swelling kinetics and equilibrium, following results can be concluded from the study:

1. Higher brine concentration would result in less swelling ratio and higher gel strength. PPG #1 and #2 were not so sensitive to the brine concentration, while PPG #3 was.
2. The swelling ratios of PPGs #1 and #2 were unchanged for at least one day in 10% HCl acid. PPG #3 deswelled fast in acid within 20 minutes. PPG #2 had longer stable time, higher gel strength and also swelled a little more in acid at 45°C.
3. PPG #3 deswelled less in acid if it was saturated in high concentration brine first.
4. All three PPGs cannot be totally degraded in acid at 45°C, but PPG #3 could at 80 °C. Furthermore, PPG #2 can be completely degraded in 1% brine at 80 °C in about five days.
5. Higher concentration acid and higher temperature would promote the deswelling of these three PPGs.

Core flooding experiments results showed:

1. All three PPGs had the diverting ability, but the result of PPG #3 was not favorable because of its quick deswelling property reducing the diverting efficiency. PPG #2 was the best candidate diverting agent among these three PPGs.
2. All three PPGs cannot be fully degraded and removed after acidizing in coreflooding tests.
3. A large injection volume of PPG could form the compact strong gel cake, which had both external and internal diversion. A small injection volume of PPG formed weak gel cake only had the external diversion at the surface of the core.
4. Large particles had better results, which was favorable as diverting agents compared to small particles in both diversion and permeability recovery aspects.

5.2. RECOMMENDATIONS

In coreflooding experiments, a lot of CO₂ was produced from the experiment. This gas flow inside the core holder might affect the pressure change and the acid diversion. The backpressure is recommended to be used in the future work to keep CO₂ in solution.

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