2011

Experimental study of the interaction between surfactants and preformed particle gels

Farag Awadh Muhammed

Department:

Recommended Citation

Muhammed, Farag Awadh, "Experimental study of the interaction between surfactants and preformed particle gels" (2011). *Masters Theses*. 7136.
https://scholarsmine.mst.edu/masters_theses/7136

EXPERIMENTAL STUDY OF THE INTERACTION BETWEEN SURFACTANTS AND PREFORMED PARTICLE GELS

by

FARAG AWADH MUHAMMED

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 of

MASTER OF SCIENCE IN PETROLEUM ENGINEERING

2011

Approved by:

Baojun Bai, Advisor
Ralph Flori
Shari Dunn-Norman
Runar Nygaard

ABSTRACT

Gel and surfactant treatment are two principle methods to reduce water production and enhance oil recovery (EOR). However, either method by itself has limitations that can be avoided by combining the two. Gel treatment can improve sweep efficiency but has little effect on micro-displacement efficiency. Surfactants are mainly used to improve displacement efficiency but have little effect on sweep efficiency. This research sought to investigate whether the combination of gel and surfactant treatments can be used to significantly enhance oil recovery while reducing water production for extremely heterogeneous mature reservoirs.

A newer trend in gel treatments is preformed particle gels (PPG) which can overcome some distinct drawbacks inherent in in-situ gelation systems. Therefore, this thesis investigated the interaction between surfactants and PPGs. Two PPGs- negatively charged hydrogel (PPG1) and nanoclay gels (PPG2), and six surfactants- two cationic, two anionic, and two neutral, were used in this study.

Results showed that the swelling of both PPGs in surfactants solutions could increase the concentration of anionic and neutral surfactants in their free aqueous phase but decrease cationic surfactant concentrations. Rheoscope measurement showed that surfactants could significantly reduce the strength of PPG1 but had slightly effect on PPG2; which was consistent with the injection pressure measurement results from the experiments of PPG extrusion through fractured models.

This novel method to combine of PPG and surfactants in one process will provide a practical method to improve both sweep efficiency and displacement efficiency and thus the overall recovery of an oilfield could be significantly improved.

ACKNOWLEDGEMENTS

I would like to thank Dr. Baojun Bai and Dr. Tingji Tang for their guidance. They have always been supportive and helpful throughout my research work. Dr. Bai in particular pushed me hard and always led by example.

I would like to acknowledge the Department of Geological Science and Engineering and its faculty for their work to develop and improve the petroleum engineering program, and for making me feel at home in Rolla.

I would like to thank the Libyan Ministry of Education and Scientific Research for their financial support. Without it, I would not have been able to attend graduate school.

I would also like to thank all the graduate students with whom I have worked for their assistance and for the many suggestions that they offered.

Not least, I would like to thank my sister Arej for her love, support, and encouragement during the past three years. Finally, I would like to thank my parents, Awadh and Ghallia, for their love and blessings.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

1. INTRODUCTION

Chemical enhanced oil recovery, especially gel treatment, is a crucial process to shut off or reduce excess water production while at the same time increasing the hydrocarbon production rate in mature oil and gas fields. However, gel treatment techniques still face some challenges, including high injection rate due to gel friction. The goal of this research is to establish an approach to improve gel treatment by combining a surfactant with PPG.

Water production is a serious problem in mature oil and gas fields. By some estimates, it represents the largest single waste stream in the United States. Much of this water is injected during secondary recovery processes. The injected water tends to pass through highly permeable, low-resistance channels and fractures, rather than sweeping oil into adjacent low-permeability areas. To mitigate this problem, scientists and engineers have introduced gels as a plugging agent. A gel plugs fractures and thus restricts water from following these paths, directing it instead into low-permeability areas. Gel is used to reduce channeling in gas flooding reservoirs (Seright et al. 1995).

Preformed particle gels (PPGs) are an interesting and relatively new type of gel, the polymer and crosslinker of which are formed at a surface facility before injection into a reservoir. PPGs have been used comprehensively in Chinese oilfields since 1995 (Bai et al. 2007; Wu et al. 2010); they have also been successfully introduced in some oilfields in the United States and Canada (Thomas et al. 2002). One type of PPGs is hydrogel, or aquagel which is approximately 99% water; it is widely used in gel treatment because it has exceptional physical properties such as high water affinity and high thermal and mechanical stability. Another type of PPGs is nanoclay gel particles, they are nanostructure polymers mixed with nano-size clay particles (commonly bentonite). They have unique properties due to their small size and high surface area per unit volume. Nanoparticles have the ability to withstand harsh borehole and reservoir conditions, which improves the ability of gels to travel through microchannels.

Application of gel treatment still presents some challenges. Among these challenges is their injectivity, which depends mostly on two factors, gel friction and injection rate. At any given injection rate, the lower the injection pressure, the lower the operations cost (Wu et al. 2010). Costs can be further reduced by adding surfactant to the gel. A surfactant is a good means to reduce the friction of the gel because it plays a critical role in tribology. The addition of surfactants to hydrogel particles influences the frictional behavior of gels. In addition, surfactants can play a significant role in altering the wettability of rocks near the fracture faces, thus increasing oil production. The friction of gels on a solid surface or on other gels has been extensively studied over the last decade, and numerous papers, especially by Gong's group, have addressed this issue.

This research presents extensive study of surfactant influence on the PPG friction. This study was based on a set of laboratory experiments of gel swollen ratio, surfactant concentration, gel dynamic moduli and gel transportation though fracture model. This study focused on the ability of surfactant to reduce the friction among gel particles and between gel particles and the solid surfaces. This mechanism is happening because of the surfactant molecules adsorption onto the gel particles.

1.1 OBJECTIVE OF THESIS

This thesis is a study of interaction between surfactant and PPG. Its objective is to investigate and establish methods to combine gel with surfactants; it is believed that this combination will improve sweep efficiency in both macro and micro scales of a reservoir. The macro scale will be directly affected by the reduction of PPG friction and ultimately optimize PPG treatments to reduce water production. The micro scale will be affected by the process of surfactant imbibitions and the reduction of the interfacial tension. This has direct economic benefits, including increased oil production and lower costs for water separation and handling.

This thesis addresses two types PPGs: hydrogels and nanoclay particles. The goal is to reduce dynamic moduli of PPG by introducing surfactant to the particles so it works as lubricant between particles and surface and particles to particles. The transportation behavior of PPG through fracture model, simulating PPG propagation through high permeability fractures and channels in a reservoir. Efforts have been made to study the PPG behavior during extrusion through the fracture because it is similar to extrusion through fracture models made of sandstone cores. The objective of this second part of the study is to quantify PPG extrusion through fracure and identify the impact of surfactant on the PPG injectivity.

2. REVIEW OF LITERATURE

This section provides background on one of the major challenges facing the petroleum industry; excessive water production in mature oilfields. It explains the industry approach to solving this problem and defines important terms necessary for understanding conformance control. In particular, it focuses on gel treatment and its applications as an enhanced oil recovery (EOR) technology. The chapter also defines important concept related to this research, including preformed particle gels (PPG), nanoclay particles gels, surfactants and surfactant critical micelle concentration (CMC). It briefly explains swelling ratio and the rheology of the cross-linking polymer gels and reviews the effect of surfactant on gel strength, in terms of its dynamic moduli (storage modulus, G' and loss modulus, G"). Finally, gel transportation through porous media and fracture is reviewed.

2.1 BACKGROUND

2.1.1. Enhanced Oil Recovery Potentials. Since the 1970s research have studied surfactants and gels for EOR, seeking to understand the role of surfactant structure on low interfacial tension, and the role of gel as a plugging agent to reduce excess water production.

Rising world oil prices have redirected the interest of oil companies around the globe toward improving the availability of recoverable reserves and protecting EOR technology. EOR projects once considered economically risky now seem practical (Anderson et al. 2006). High prices have also compelled companies to increase their production rates.

Fewer new wells are being drilled (Annual DOE Report, 2008, 2009), and fewer large oil reservoirs are presumed to be available. Drilling expenses have increased dramatically, and fewer companies are capable of making investments in such technologies as deeper wells that are necessary to reach target zones. These and other factors have made EOR much more attractive in the United States, Canada, and other countries.

Secondary production in many fields is reaching its economic limit, and the focus is shifting to asset development. Tertiary methods have been shown to work (Adams et al.1987; Chang et al. 2006; Jayanti et al. 2002; Bai et al. 2007), and in many reservoirs worldwide a large portion of the original oil in place (OOIP) remains. The potential for EOR worldwide therefore is very high. In recent years, numerous advancements have made these technologies not only more practical, but also economically feasible.

2.1.2. Excess Water Problems. A serious problem in oil-producing reservoirs is water production. On average in the United States, more than seven barrels of water are produced for each barrel of oil. Worldwide, the average is three barrels of water for each barrel of oil. The annual cost of disposing of this water is estimated to be $5-10 billion in the United States and around $40 billion worldwide (Seright et al. 2000). As with most things in nature, fluids follow through the paths of least resistance. In reservoirs, such paths are often determined by the heterogeneous nature of the rock. According to the Department of Energy (DOE), produced water is defined as the water brought up from the hydrocarbon bearing strata during extraction of oil or gas. It can include formation water, injection water, condensed water, and trace amounts of treatment chemicals.

Produced water is the highest volume waste generated in association with oil and gas production operations. This waste stream is characterized as a high volume and low toxicity. Over its life span a typical oil field is likely to produce at least as much water as oil. In gas fields, the volumes of produced water are significantly lower.

Diagnosis and management of water production problems have been objectives of the oil industry almost since its inception because produced water has a major impact on the profitability of an oilfield project. Producing one barrel of water requires as much or more energy as producing the same volume of oil (Eoff et al. 2006). Moreover, water production causes major problems such as sand production, reduced oil production, and tubular corrosion.

Remedies have been elusive. The oil industry has seen many attempts to manage water production. Historically, it has used the most convenient or least expensive methods such as reperforation and cement plugs. Today, some strategies have been implemented to restrict water from entering the well bore. These involve mechanical blocking devices or chemicals that shut off water-bearing channels or fracture within the formation and prevent water from making its way to the well.

2.1.3. Methods to Reduce Water Production. Seright (2000) summarized the causes of excess water production (see Table 2.1); each of these problems requires a different approach, therefore, a successful treatment of water production problems depends on correct identification of the nature of the problem. Many different materials and methods can be used to assess excess water production problems. Generally, these methods can be categorized as either mechanical or chemical (see Table 2.2), and each works only for certain types of problems.

Operators have used various mechanical and well construction techniques to block water from entering wells. Seright et al. (2000) offer several examples; including straddle packers, bridge plugs, tubing patches, well bore sand plugs, infill drilling, pattern flow control, and horizontal wells. These techniques have been used for many years, but they do not work well in all applications. Seright recommended that mechanical approaches be used to block casing leaks, flow behind the pipe without flow restrictions, and unfractured wells with barriers to cross flow. However, those approaches may not be effective in solving other types of water production problems.

Another approach of particular interest here is to shut off water production by chemical injection while allowing continued oil production. The chemicals are introduced deep in the formation where they are unlikely to affect the underground water and will thus have a net beneficial impact.

2.1.3 Gel Treatment. When gels set up in the cracks, they block most water movement to the well while still allowing oil to flow to the well. Many different types of gels can be used, depending on the specific type of water flow to be targeted. Thomas et al. (2000), Mack et al. (2003), Seright et al. (2001), and Green et al. (2001) discuss the key factors to be considered when designing and conducting a gel treatment. Among the most important considerations are component ingredients, gel properties, and treatment processes.

Gel's main composition is often polyacrylamide polymers and microbial products; and lignosulfonate have also been applied. They may use metal ion or organic crosslinking agent, and the fluid with which they are mixed may be either fresh or produced water.

Gel properties may vary over several stages during the course of gel treatment, for example, both the concentration and the molecular weight of polymer may vary. Viscosity too, may vary; it affects the size of cracks or fractures that can be penetrated at a given pressure. It also permits injection of the material as a premixed gel or as gelant. The degree of crosslinking might change throughout a treatment. Density is also a significant factor, if the gel is too dense, it can sink too far into the water layer and lose its effectiveness. Finally, setup time, which determines how far into the crack or fractures gel, will penetrate.

In the United States, most of the polymer gel treatments are performed in wells producing water from fractured carbonate or dolomitic formations that operate under a natural water drive.

Reynolds et al. (2002) and Mack et al. (2003) suggest the following criteria for selected candidate wells for gel treatment:

- near the end of their economic life,
- significant remaining mobile oil in place,
- high water oil ratio,
- high producing fluid level,
- declining oil and flat water production,
- wells associated with active natural water drive, and
- high permeability contrast between oil and water saturated rocks.

Literatures reported many successful gel treatments. Seright et al. (2001) evaluated 274 gel treatments conducted in naturally fractured carbonate formations. The median water-to-oil ratio (WOR) was 82 before the treatment, 7 shortly after the treatment, and 20 a year or two after treatment. Oil production increased following treatment and remained above pretreatment levels for 1 to 2 years. Thomas et al. (2000) reported that an initial investment of $231,000 for gel treatments resulted in incremental profits of $1.7-2.3 million over a two-year period.

Green et al. (2001) described a series of gel treatments at four Kansas wells. Each treatment cost $14,000 to $18,000 per well, including polymer and well servicing costs. Following treatment, total oil production increased by about 30 barrels per day (bpd), and water production dropped by about 1,000 bpd. Lifting costs associated with the lower fluid volume decreased by about $300/month/well. With less stress on the lifting equipment, well servicing costs also decreased by about $2,400/year/well. Since mid-2000, a total of about 37,500 bbl of oil have been economically recovered, representing about $1.60 per incremental bbl to date, and several years of production is still anticipated. The gel polymer treatments extended the economic life of the wells by at least seven years.

The examples above demonstrate chemical treatments, especially gel treatment, as an effective and profitable technique. However, some challenges remain; one is the injectivity of the particle gels or the resistance of the gel to squeezing into the matrix during injection. This drawback might be managed by placing the gel particles in a surfactant brine solution.

Wu (2010) reported that when the particle gel and surfactant solution are injected into a reservoir, the filtered solution can be squeezed into the matrix during the injection. As a result, the gel particles enter and remain in the fracture and in the large porous media while the surfactant solutions enter the small pores where most hydrocarbon oil is trapped by capillary force. Thus, the surfactant solution reduces interfacial tension at the oil/brine interface and changes the wettability of the rock surface in the formation.

2.2 BASIC TERMS

2.2.1 Conformance Control.

Daniel et al. (1995) defined conformance control as any technique that brings a production well closer to perfectly conforming condition; in other words, it refers to any technique that somehow encourages the drive mechanism to mobilize rather than avoid those hard-to-move pockets of unswept oil and gas.

Although, the goal of conformance control is to improve macroscopic sweep efficiency, most EOR techniques strive to improve microscopic displacement efficiency using a variety of surfactants and other chemicals to release hydrocarbon stuck to the rock surface. Conformance control is also less expensive than most EOR techniques because the treatments are better targeted and logistically far smaller.

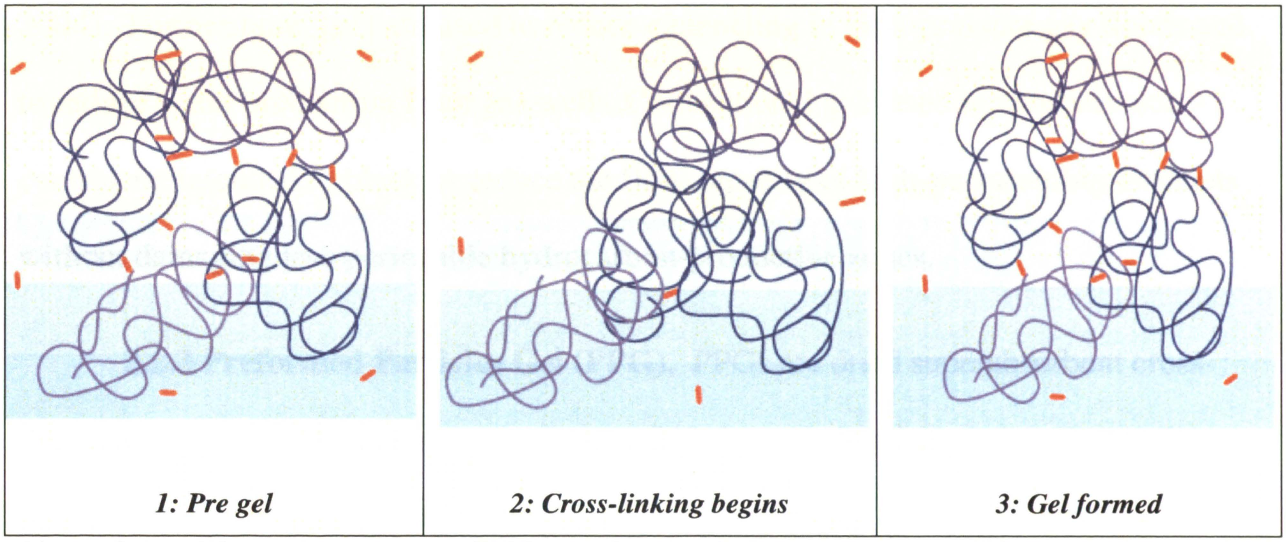
Conformance control also refers to the redistribution of waterdrive so that water sweeps the reservoir evenly, often dramatically reducing water cut. For many mature reservoirs, treatment and disposal of produced water dominate production costs; therefore less water means lower costs.

Conformance control includes any technique designed to reduce water production and redistribute waterdrive, either near the wellbore or deep in the reservoir. Near the wellbore, these techniques include unsophisticated expedients such as setting a bridge plug to isolate part of a well, dumping sand or cement in a well to shut off the bottom perforations, and cement squeezing to correct channeling and fill near-well fractures. Deep in the reservoir, water diversion depends on chemical treatment. Gel treatment is one of the most successful and least expensive techniques used in the oil industry. If the gel is placed correctly in the target zone, it can reduce water production more efficiently with a much smaller volume than straight injection of polymer (Seright et al. 2001).

2.2.2 In Situ Gel. Gels are three-dimensional cross-linked polymers composed of a polymer, a cross-linker and other additives; this liquid formulation is called a gelant. Within a certain range of temperature and pH, the gelant can cross-link to form a gel. Figure 2.1 illustrates the phenomenon of gel formation. Each cross-linking molecule begins attaching itself to two polymer molecules, chemically linking them together. The result is a three-dimensional tangle of interconnected polymer molecules that behave like a fluid, but can eventually constitute a rigid immobile gel. Gel compositions used for conformance control usually contain more than 90% water and frequently more than 99% water. There are two main types of gels:

- In situ gel: A gelant is injected into a formation; where a gel forms under reservoir conditions.
- Preformed particles gel (PPG): A gel is formed in surface facilities; then injected into the reservoirs.

In its pure state the polymer seems to preclude any crosslinking through ionic bonding. However, when subjected to elevated temperature, some of the amide groups convert to carboxylate groups. Each of these carries a negative charge. The proportion of an amide group that converts to carboxylate is called the degree of hydrolysis (DH), and it typically varies from 0% to 60%. Efficient cross-linkers are trivalent metal ions such as aluminum, Al^{3+}, and chromium, Cr^{3+}. These can be packaged either as simple inorganic ions in solution or within soluble chemical complexes.



1: Pre gel

2: Cross-linking begins

3: Gel formed

Figure 2.1 Gel formations as cross-linking molecules (orange) connected polymer molecules (purple).

[Source: Daniel Borling. April (1994). "Pushing out the oil with conformance control". Oilfield Review Magazine].

Gels display the characteristic of both solids and liquids. Like solids, they deform with stress and recover their initial shape after removal of stress. Like liquids, they can support fluid convection and diffusion of solutes that are smaller than the mesh size of their network. Gels are wet and soft and look like a solid material, but they are capable of undergoing large deformation.

Gel treatments are among aggressive conformance control techniques. The main advantages of gels over other methods (such as mechanical plugs) is their flexibility for pumping without a work-over rig, the high control of setting time, deeper penetration into the formation, ease of cleaning, and easy of removal from the wellbore by water recirculation (Thomas and Wood 2000).

The main purpose of gel treatment is to block the strongest flow channels from the well, thus forcing subsequent fluid flow into tighter zones (Taabbodi and Asghari

2004). Furthermore, gels are used to reduce channeling in high-pressure gas floods and to reduce water production from gas wells. Conventional gels used in conformance control are intended to block or reduce the flow capacity of high-permeability channels without damaging less-permeable hydrocarbon-productive zones.

2.2.3 Preformed Particles Gel (PPG). PPGs are dried superabsorbent cross-linked polymer powders that can swell up to 200 times their original size (Bai et al. 2007). These particles are prepared by combining monomers, controlled monomers, stable cross-linkers, initiators, and other agents in aqueous solution.

This study focuses on the superabsorbent polymer hydrogels, which can absorb water or saline solution in amounts 10-1000 times, their own weight (Buchholz and Graham 1998). Thus they are ideal candidates for use in water shut-off applications.

The difference between PPGs and in situ gels is that in the later the mixture of cross-linkers and polymer (gelant) is injected into the target formation where they react and form a gel. PPGs on the other hand, are formed in surface facility before injection into the reservoir. PPGs lack some drawbacks inherent in an in situ gel system, such as lack of gelation time control, uncertainty of gelling due to shear degradation, and dilution of formation water (Coste 2000, Chauveteau 2003, and Bai 2007).

Today PPGs are commercially available in many sizes (Bai et al. 2007). They are available as micro gels (Chauveteau 2003; Rousseau 2005; and Zaitoum 2007), pH-sensitive cross-linked polymers (Al-Anazi et al. 2002, Huh et al. 2005), and swelling submicron-sized polymers (e.g. Bright water® (Pritchett et al. 2003, Frampton et al. 2004).

2.2.4 Nanoclay Gels. Nanotechnology is not new, but its application in the oil industry, including in EOR is in its infancy. Nanoclay is defined as clay that can be modified to make the clay complexes compatible with organic monomers and polymers. Polymeric nanocomposites are among the most exciting and promising materials discovered recently (Shahid et al. 2008). If nanoclay is dispersed on a nanoscopic level, its addition can enhance a number of physical properties of a gel. Common clays are naturally occurring minerals and thus subject to natural variation in their formation. The purity of clay can affect the final nanocomposite properties. Clay consists mostly of alumina silicates, which have a sheet-like (layered) structure; it consists of silica SiO_4 tetrahedron bonded to alumina AlO_6 octahedron in various ways.

Natural clays are most commonly formed by the in situ alteration of volcanic ash. Another less common origin is the hydrothermal alteration of volcanic rocks. Silica is the dominant constituent of clays, with alumina being essential as well.

Figure 2.2 shows typical structure of clay, the silica tetrahedral and alumina octahedral sheets. The silica tetrahedral sheet consists of SiO_4 groups linked together to form a hexagonal network of the repeating units of composition Si_4O_{10}.

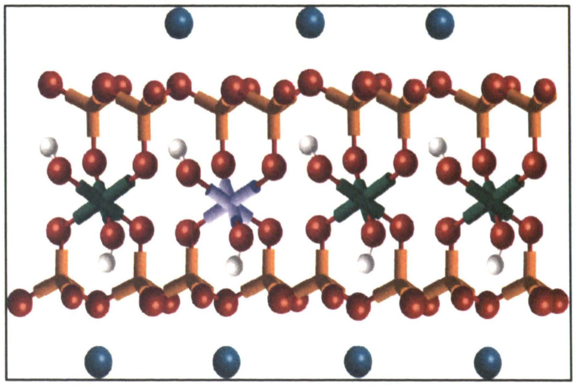


Figure 2.2 Clay Structure

The alumina sheet consists of two planes of close packed oxygen or hydroxyls between which octahedrally coordinated aluminum atoms are imbedded in such a position that they are equidistant from six oxygen or hydroxyls. The two tetrahedral sheets sandwich the octahedral, sharing their apex oxygen with the latter. These three sheets form one clay layer. In this study bentonite was used as the clay mineral; this bentonite has been added to the synthesized performed particles gel

Nanoclay gels are polymers mixed with nano-sized clay particles; they have unique properties due to their small size and high surface area per unit volume. Nanoparticles withstand harsh borehole and reservoir conditions, improve transport through micro-channels, and promote heat transfer efficiency (Bob Briell et al. 2004).

In the early 1990s, Kleinfeld and Ferguson synthesized laponite-PDDA, which was perhaps the first nanoclay polymer multilayer. Since then, various types of nanoclay polymer multilayers have been developed. Many such multilayers used exfoliated montmorillonite (MMT), in which isomorphous substitution gives surfaces a net negative charged, permitting electrostatic assembly. Furthermore, the high aspect ratio of exfoliated MMT ~1 nm thick and 100-1000 nm wide provides a planar surface for the deposition and growth of oppositely charged units. Recently, this class of nanoclay polymer multilayer has attracted great attention.

Nanoclay gels hold promise for application in the oil and gas industry. Current researches address viscosity enhancement, fluid loss control, and emulsion stabilization for EOR applications (Zhang et al. 2010). However, much remains unknown about these gels and why they differ from their larger counterparts.

2.2.5 Surfactant. Surfactants or surface active agents are polar compounds, consisting of an amphiphilic molecule with a hydrophilic part (the head) and a hydrophobic part (the tail). Their dual nature produces a strong affinity for interfaces between immiscible fluids such as oil and water. Surfactants lower the surface tension of a liquid, allowing easier spreading and lowering of the interfacial tension between two liquids (especially water and oil), or between a liquid and a solid. They reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface.

Surfactants help recover oil from a reservoir by the following mechanism: When a surfactant is injected, it disperses into oil and water and lowers the interfacial tension, thereby increasing the capillary number. As a result, more of the otherwise immobile oil becomes mobile. At the same time, an oil-in-water emulsion may form, blocking larger pores. This condition often improves the effective mobility ratio. The injected surfactant continues to mobilize oil and bank up until the surfactant is diluted or otherwise lost due to adsorption by the rock and until it is no longer available to lower the interfacial tension and mobilize oil. At that point, the process degenerates into a water flood.

Surfactants are widely used in the oil industry because of their remarkable ability to influence the properties of surfaces and interfaces. However, they are used mainly in EOR applications to reduce oil-water interfacial tension (IFT) until the capillary number is high enough to mobilize all the residual oil. Typically, surfactants are applied to a reservoir in the form of foam flooding, Alkali Surfactant Polymer Flooding (ASP), Alkali Surfactant Flooding (AS), emulsion, and most recently, as a wettability alteration technique.

Surfactants have been studied for use in EOR for over 45 years. Early work focused on the injection of microemulsions containing high concentrations of surfactant, cosolvent, and oil (Gogarty et al. 1968). While technically successful, this approach was not economically viable due to the high chemical costs and low oil prices at the time. Later work has focused on reducing the amount of chemical required and emphasized low concentration aqueous surfactant solutions with added polymer for mobility control. Austad and Milter (2000) provide an overview of surfactant flooding developments up to 2000 cases, including the development of EOR surfactants. They did not review alkali surfactant polymer flooding even though that has been a major issue since about 1984 (Nelson et al. 1984).

Surfactants are generally classified into four types according to their ionization products:

i. Anionic: The surface-active portion of the molecule bears a negative charge. Such surfactants are dissociated in water into an amphiphilic anion, and a cation. In general, an alkali metal (Na^+, K^+) or a quaternary ammonium, are the most commonly used surfactants.

ii. Cationic: The surface-active portion bears a positive charge. They are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. These surfactants are generally more expensive than anionics because of the high-pressure hydrogenation reaction to be carried out during their synthesis.

iii. Nonionic: The surface-active portion bears no apparent ionic charge (Neutral). They do not ionize in aqueous solution because their hydrophilic group is of a nondissociable type.

iv. Amphoteric (or) zwitterionic: Both positive and negative charges may be present in the surface-active portion. This type of surfactant has no application in the oil industry because of its high toxicity.

When the surfactant concentration in a solution is kept below its critical micelle concentration (CMC), the surfactant solution will be composed of monomers. At concentrations above CMC, surfactant micelles are formed, and the monomer concentration remains relatively constant with increasing surfactant concentration. At low concentrations, the hydrophobic tail group of the surfactant is close or parallel to the surface, and the hydrophilic head group is oriented toward water. As the surfactant adsorption increases, the surfactant molecules become more perpendicular to the surface until the CMC is reached. This difference in the orientations of the surfactant molecules changes the surface from oil-wet at low concentrations to water-wet at CMC and higher concentrations.

2.3 SWELLING RATIO OF PPG

In basic terms, swelling ratio (SR) is the ability of gel particles to absorb the aqueous solution in which they are immersed. It can be measured by a weight method, which depends on knowledge of the initial where weight of the dried particles (m_o) and on the weight of the hydrogels at the point of equilibrium (m_t):

$$Sw = \frac{m_t - m_o}{m_o} \tag{2.1}$$

The swelling of particle gel is influenced by the composition of the polymer (i.e., by the synthetic conditions), including the additive polymeric networks and the nature of the swelling media.

2.4 DYNAMIC RHEOLOGY OF PARTICLE GELS

The basic concept of rheology is that gels are viscoelastic, meaning their properties are intermediate between those of elastic solids and viscous liquids (Liu and Seright 2001). Application of shear stress causes an elastic solid to deform by strain.

Elastic deformation occurs, however when shear stress is applied to viscous liquids; instead, the fluid flows.

The study of dynamic rheology focuses on the elastic modulus or storage modulus (G'), and the viscous modulus or loss modulus (G''), of gels. The storage modulus represents the elastic contribution to the response; the loss modulus represents the viscous contribution. The elastic modulus is defined by

$$G' = \frac{'\tau_o}{\gamma_o} \tag{2.2}$$

where: $'\tau_o$ = maximum component of elastic stress, in psi, and γ_o = maximum strain applied, expressed as a percentage.

Similarly, the viscous modulus is defined as

$$G'' = \frac{''\tau_o}{\gamma_o} \tag{2.3}$$

where: $''\tau_o$ = maximum component of viscous stress, in psi, and γ_o = maximum strain applied, expressed as a percentage.

The phase angle or loss angle, δ, which represents the relationship between storage and loss moduli is described by

$$tan\delta = \frac{G'}{G''} \tag{2.4}$$

The moduli are measured by placing samples between transparent plate and a sensor. The samples are placed under oscillating shear stress, and the reaction force is measured. It has been reported that the elastic modulus of a gel is always greater than the viscous modulus; therefore, a gel is more an elastic solid materials than a viscous liquid.

Kakadjian (1999) presented a method of dynamic rheological characterization to quantitatively evaluate the strength of a polymeric gel system. This method permits study of the general consistency of the gel, the elastic behavior of the gel (G'), the viscous component of the gel (G''), and the relationship between the two moduli (Tanδ). The group's research showed that the behavior of the elastic and loss component was dependent not only on the gelling time and final consistency, but also on the frequency. This behavior can influence the changes in the residual resistance factor at various flow rates. This work established dynamic rheological characterization as an effective tool to determine quantitatively the gel strength of gelling systems.

2.5 SURFACTANT EFFECT ON HYDROGEL FRICTION

Little is known of the surface properties of hydrogels, although this topic has been the interest of a large spectrum of researchers outside the petroleum industry for decades, this branch of science is called *tribology*. The term *tribology* refers to the science and engineering of interacting surfaces in relative motion. It includes the study and application of the principles of friction, lubrication, and wear. Wu et al. (2010) reported that surfactants play critical roles in a gel's tribology. The addition of surfactants to hydrogel particles influences the frictional behavior of gels. The friction of hydrogels on solid surface or on gels has been extensively studied during the last decade, especially by Gong's group, and many papers address this issue.

Amonton's law states that the frictional force F between two solids is proportional to the load W forcing them together, (i.e., $F = \mu W$). According to this law, the coefficient μ, known as the frictional coefficient, depends neither on the sliding velocity nor on the apparent contact area of the two surfaces, but only on the moving materials. However, the frictional relations of gels cannot simply be represented by Amonton's law (Osada et al. 1998). When a gel slides against a solid surface (i.e., formation rock), the frictional force of the gel is slightly dependent on the load *W*, but strongly dependent on the sliding velocity. That is, the surfactant can play a significant role in reducing the friction of gel.

Gong et al. (2002) found that the frictional behaviors of hydrogels do not conform to Amonton’s law, which well describes the friction of solids. He proposed a repulsion-adsorption mechanism to describe the friction of hydrogels on a smooth substrate. If the interfacial interaction between a hydrogel and a solid surface is repulsive, then friction is due to lubrication of the hydrated water layer of the polymer network at the interface.

Philippova et al. (1996) reported that absorption of anionic surfactant is governed primarily by hydrophobic interactions. Due to conditions of electroneutrality, anionic surfactants penetrate the gel together with corresponding co-ions. Therefore, the uptake of cationic surfactant ions results in gel shrinkage, whereas the uptake of anionic surfactants induces gel swelling. In the anionic gel/anionic surfactant system, a significant interaction is observed only for the most hydrophobic gels when hydrophobic interactions overcome the electrostatic repulsion between similarly charged groups.

Osada et al. (2007) reported that the driving force of surfactant diffusion into the gel is the concentration gradient of the surfactant. The binding of surfactant with the polymer network sustains a high concentration gradient that facilitates the subsequent surfactant diffusion. Wu et al. (2010) reported that the injectivity of particle gels can be greatly improved by proper screening of the surfactant.

2.6 GEL TRANSPORTATION THROUGH FRACTURED RESERVOIR

In 1984, in the laboratories of Marathon Oil Company, researchers first established a new polymer-gel system to block high-permeability channels within reservoir and to improve oil recovery. Over 28 years the company performed 29 treatments with the new system in nine of its fields in Wyoming's Big Horn basin (Borling et al. 1994).

Gels have often been used to reduce fluid channeling in reservoirs (Seright et al. 1995). The main objective of these gel treatments is to reduce water flow considerably through high-permeability channels or fractures without damaging the production zones. Theoretical studies demonstrate that gel treatments are most likely to be successful when treating fractures that cause channeling in reservoirs (Seright et al. 1988; Liang et al. 1993). These gel treatments depend heavily on the ability of the gels to extrude through the fractures (Seright et al. 1994, 1999). To optimize treatment design, it is important to understand the behavior of these gels when they extrude through the fractures and high-permeability zones.

Seright et al. (1994, 1997, 2001, and 2004) have extensively investigated the extrusion of bulk gels through fractures and tubes. They have studied the effect of fracture conductivity, tube diameter and gel injection rate on this extrusion behavior. They have also studied gel properties during placement in the fracture. They report that performed gels exhibit water loss and higher pressure gradients during placement, effects that determine their distance of propagation along a fracture or into a fracture system. Furthermore, in wide fractures, gravity segregation can be a problem because the gel mixture tends to settle downward.

Seright et al. (2004) noted that the pressure gradients required to extrude gels through fractures are greater than those required for gelant flow. Depending on conditions, the effective viscosities of formed gels in fractures are typically 10^3 to 10^6 times greater than those for gelants. However, useful gels do not show progressive plugging during extrusion through fractures. A minimum pressure gradient is required to extrude a given gel through a fracture. Once this minimum pressure gradient is exceeded, the gel begins propagating through that fracture.

Pressure gradient during gel extrusion is insensitive to flow rate; therefore the proper blend of surfactant and the gel could play a key role in reducing the pressure gradient of gel injectivity, and thus reduce the cost of gel treatment. Seright also found that only a small fraction of the gel in a fracture is displaced when brine (or oil) is injected after gel placement.

Bai et al. (2007a, 2007b) studied swollen particle gel transportation through porous media using sand pack and micro-models. Seright et Al. (1999) studied the use of gel treatment to reduce natural fractures in a reservoir; they reported that gel treatment has the highest potential when the fracture conductivity R is greater than 10. Zhang et al. (2010) studied the propagation of particle gel during extrusion through a transparent fracture, and they reported that particle gel injection pressure increases with brine concentration and injection flow rates, but decreases as the fracture widens during injection.

Table 2.1 Appropriate treatment for excess water problems

Category A: Conventional treatment	
	Casing leaks without flow restrictions
	Flow behind pipe without flow restriction
	Unfractured wells (injector or producer) with effective barriers to cross-flow
Category B: Gelant treatment	
	Casing leaks with flow restrictions
	Flow behind pipe with flow restriction
	Two-dimensional coning through a hydraulic fracture from an aquifer
	Natural fracture system allowing channeling between wells
Category C: PPG treatments	
	Faults or fractures crossing a deviated or horizontal well
	Single fracture causing channeling between wells
	Natural fracture system allowing channeling between well
Category D: Difficult problems, where gel treatments should not be used.	
	Three-dimensional coning
	Cusping
	Channeling through strata (no fracture), with crossflow

Table 2.2 Water shutoff materials and methods

Chemical and physical plugging agents	**Mechanical and well techniques**
Cement, sand, calcium, carbonate	Packers, bridges plugs, patches
Gels, resins	Well abandonment, infill drilling
Foams, emulsions, particulates, precipitates, microorganisms	Pattern flow control
Polymer/mobility-control floods	Horizontal wells

3. INTERACTION BETWEEN SURFACTANTS AND HYDROGELS

This section describes an experimental study of the interaction between surfactants and hydrogels, analyzing the feasibility of surfactants use and its benefits to the oil industry. Specifically, it describes the swelling tests performed on hydrogel particles and the measurement of surfactant concentration in terms of its effect on the hydrogels. The chapter also describes measurements of the change in dynamic moduli of hydrogel particles and explains an experiment on hydrogel transportation through a fracture model.

3.1 INTRODUCTION

To date, the interaction between surfactants and hydrogel particles has been studied systematically only by Wu et al. (2010). However, Wu's work did not address core flooding, and it focused mainly on structure-property relationship between the uncharged hydrogel particles and surfactant molecules or micelles. The present work builds on his study, investigating more extensively the influence of various surfactant molecules, or micelles, on the swelling behavior of negatively charged hydrogel particles. This section addresses the influence of surfactants in aqueous solution on the dynamic moduli of water-swollen gel in 1.00 wt% NaCl. The work measured gel friction in terms of storage modulus, G', and loss modulus, G'', under various conditions of stress, gap, oscillation frequency; temperature remained consistent for all surfactants. After the gels reached equilibrium, surfactant concentration measured to determine whether surfactant was adsorbed to gel particles.

The gel used in this study was synthesized from an acrylamide monomer; MBAA was used as a crosslinker and potassium persulfate as an initiator. Three different PPG mesh sizes were used: 100/120, 70/80, and 30/40, corresponding to 150-120, 212 -180, and 600- 425μm, respectively. This study used two nonionic, two anionic, and two cationic surfactants (See Table 3.1).

This work relied on a transparent linear fracture model and investigated the propagation of hydrogels through it (See Figure 3.1). Optimal design of hydrogel treatments depends on knowledge of the behavior of swollen hydrogel particles when they extrude through fractures or channels. This portion of the project studied the impact of surfactants on hydrogel particle injection pressure.

3.2 EXPERIMENTAL

Materials: Monomer acrylamide (98.5%) and cross-linker methylene-bis-acrylamide (MBAA, 97%) were purchased from Alfa Aesar Company (Ward Hill, MA) and used without further purification. Ammonium sulfite was used as initiator for polymer gel synthesis. Cationic surfactants, *n*-dodecylpyridinium chloride (98%), (1-hexadecyl) pyridinium bromide monohydrate (98%), and anionic surfactant, sodium 4-n-octyl benzene sulfonate were also purchased from Alfa Aesar (Ward Hill, MA) and used without further purification. Sodium dodecylbenzene sulfonic acid was purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. Other commercial surfactants were requested from their manufacturers, Igepal® CO-530 from Rhodia, Inc. (Bristol, PA), Tergitol® NP-10 from Dow Chemical (Midland, MI), NaCl (99.8%) was purchased from Fisher Scientific Inc. Water used in all experiments was distilled

Measurement Devices: A UVmini-1240V, UV-Vis spectroscope from Shimadzu (See Figure 3.1.b) was used to measure the change in surfactant concentration. A rheometer (a HAAKE RheoScope from Thermo Scientific, shown in Figure 3.1.b) was used to measure the storage and loss moduli of swollen particle gels. A transparent fractured model (See Figure 3.3) was constructed to evaluate hydrogel injectivity with and without the presence of a surfactant.

3.3 SYNTHESIS OF PREFORMED PARTICLE HYDROGELS

150 g of acrylamide were added to 498.7 g of distilled water. The solution was purged with nitrogen gas for 40 minutes and stirred until the entire solid was dissolved. 0.650 g of methylene-bis-acrylamide (MBAA) was added to the solution for complete dissolution upon stirring. 0.650 g of $(NH_4)_2S_2O_8$ was then added with stirring to the solution prepared above. The mixture solution was placed in an oven at 60 °C for 14 hours for the complete polymerization after 20 grams of Na_2CO_3 were added. A strong bulk gel was formed and then hydrolyzed at 80 °C for another 8 hrs to form the negatively charged carboxylate anions in the network due to the presence of Na_2CO_3. Very strong ammonia gas was generated during this hydrolysis process. Then the hydrolyzed hydrogel was cut into small pieces. The formed hydrogel was then purified by soaking in large amount of distilled water for one week and followed by drying at 60 °C for 4 days to yield 665.83 g of a slightly yellow gel. The yellow color may be due to oxidation of acrylamide during the drying process. The dried gel solids were crushed into small particle powder in a blender machine (Black & Decker). PPGs with the particle size between 100~120 mesh (150μm~120μm) were selected through the standard testing sieves (Fisher Scientific Company).

3.4 SWELLING RATIO MEASUREMENTS

Test tubes (15 ml) were used to measure the swelling ratio of the hydrogel particles. First, 0.1 g of 100/120-mesh dry hydrogel particles was added to 14.9 g of 1.00

wt % NaCl (brine). The test tube was then robustly shaken, and the sample was left overnight on a shaking device to ensure that all hydrogel particles were totally swollen and had reached equilibrium. Six samples were prepared using various surfactants as the swollen media, and the hydrogels were swollen following the same procedures described above for 100/120 mesh particles.

All seven samples were left for several days until they reached equilibrium. The hydrogel swelling ratio was then measured using the weight method; that is, the dry hydrogel particles weighed 0.1 g, and the particles were weighed again after they reached swelling equilibrium to determine the difference which is the swelling ratio.

During the weighing process, some of the swollen hydrogels had to be separated from the solution in which they were floating. To ensure that all hydrogels settled at the bottom of the test tube, the samples were placed in a centrifuge, which was set to 3500 RPM, for 15 minutes. After several days, the hydrogel swelling ratio, *SW*, was measured using the weight method:

$$Sw = \frac{m_t - m_o}{m_o} \tag{3.1}$$

where m_t represents hydrogel weight after x time, and m_o represents the original weight of the dry hydrogels. The procedure was then repeated for each PPG particle size.

3.5 SURFACTANT CONCENTRATION MEASUREMENTS AFTER HYDROGEL REACHED SWELLING EQUILIBRIUM

Three samples of each surfactant were tested. First, 0.1 g of dry hydrogel was poured in 14.9 g of a surfactant solution in a 15-ml test tube. The initial surfactant concentration was relatively low (200 ppm) to ensure accuracy and avoid waste of high-cost surfactant. After the hydrogel particles reached equilibrium (approximately 7 days), the equilibrium solution of NaCl and surfactant was measured at the top of the test tube. The UV-Vis spectrum was scanned from 1100 nm to 190 nm to identify the wavelength at which it reached the maximum of the spectrum (λmax). The equilibrium concentration of each surfactant was measured based on the sample's absorbance at λmax. Figure 3.1.a shows a typical UV/Vis spectrophotometer. The equilibrium concentration of each surfactant was measured through its absorbance equilibrium (ABS equilibrium).

The same procedures were applied to each hydrogel particle size. The ABS equilibrium of each surfactant was measured. Figure 3.4 plots the results for a sample. The graph shows a linear relationship between the initial ABS and various surfactant concentrations. To measure the change in surfactant concentration, the intercept of the ABS value of each surfactant was measured from the line to the horizontal axis.

3.6 MEASUREMENT OF PARTICLE GEL DYNAMIC MODULI

A rheology measurement device was used to measure the storage and loss moduli of the swollen hydrogels. Several pretests were run to establish the required linear viscoelastic range.

Data were gathered using a HAAKE Rheo (job manager software) from Thermo Fisher Scientific Company. The oscillation time sweep curve model was selected for these measurements, it represents the storage and loss moduli logarithmically in Pascal (Pa) as a function of time in seconds. The frequency was set at 1.00 Hz, and a controlled stress (CS) mode was selected because the stress value selected had to be in the linear viscoelastic range. The stress applied to the hydrogel was 1.0 Pa to ensure that gel strain and stress had a linear relationship during measurement. A PP35 Ti Po LO2 016 sensor was used, and a gap of 0.2 mm was left between the sensor and the plate holding the hydrogels sample; the temperature was set to 25.0 °C. For each sample, storage and loss moduli readings were taken every 30 seconds for 5 minutes.

Use of a plate rheometer to measure dynamic moduli (storage and loss moduli) relies on measurement of the torque exerted on the swollen PPGs. The PPG sample is placed on the horizontal glass plate, and another metal sensor plate is placed on top of it. Typically, the top sensor plate is rotated, and the torque exerted on it is measured. However, the movement of this plate is resisted by the frictional force, which is proportional to the frictional coefficient and the stress applied on it. The relationship among torque, stress, and frictional coefficient is calculated using

$$T = r \times F, \tag{3.2}$$

$$F = \mu \times N, \tag{3.3}$$

and

$$T = r \times F = r \times (\mu \times N) \tag{3.4}$$

where T is the torque exerted on the sample, r is the length of the lever arm related here to the geometry of the rheometer sensor, and the same for all gel samples measured, F is the frictional force, which is the product of the frictional coefficient μ between two surfaces and the force N applied on the surfaces. This experiment used a model of controlled stress to take measurements. Therefore, the torque exerted on the sample was directly proportional to the frictional force between the hydrogel particles and the plate surfaces. Furthermore, for a given cap of 0.2 mm between the plate and sensor, the dynamic moduli (storage and loss modulus) were directly proportional to the frictional force coefficient between the particle gel and the plate surfaces.

Figure 3.9 shows a simple mechanism, of friction reduction by a surfactant between the particle gels and the surface of the stainless steel sensor plate and the glass plate. As shown in Figure 3.9.a without the addition of a surfactant to the brine in which the particle gel is swollen, the stainless steel sensor plate presses the particle gel and rotates on it in a constant stress mode when the dynamic modulus is measured. Tables 3.6, 3.7, and 3.8 show the dynamic moduli of hydrogel particles for various sizes.

3.7 HYDROGEL TRANSPORTATION THROUGH TRANSPARENT FRACTURED MODEL

A linear fracture model clarified the influence of the surfactant on the flow of hydrogel particles. The goal was to analyze the injection pressure of the hydrogel through a fracture and determine whether the surfactant would affect this injection pressure. Seright et al. (1994) reported that gel treatment depends heavily on the ability of the gel particles to extrude through fractures and channels. Analysis of the propagation of the hydrogel particles through fractures and the dependence of this process on the friction pressure of the hydrogel is one of the main goals of this study. The surfactant was expected to reduce the friction pressure of the hydrogels and thus ultimately reduce the injection pressure of hydrogel particle.

3.7.1 Materials. Hydrogels: This work used particles with a mesh size of 30/40 mesh (212- 180μm). Two sets of swollen hydrogel particles were prepared for each size, the first in a 1.00 wt. % NaCl (brine) solution, and the second in a surfactant solution

Brine: The brine used in this experiment was prepared in the laboratory; it was a 1.00 wt% concentration NaCl with distilled water.

Surfactant: A nonionic surfactant (Igepal® CO-530) was used because this type has the most stable and significant effect on hydrogel strength; It is also inexpensive and easily available.

3.7.2 Experimental Setup. The experimental apparatus comprised a syringe pump, two 600-ml accumulators with piston, and one fracture model. An Isco pump was used to inject PPG and brine. The transparent linear model was constructed of two acrylic plates with a rubber O-ring between them. Bolts, nuts, and shims were used to fix the two plates and control fracture width. On one side of the plate, a hole functioned as an inlet for the injection of PPG and brine; on the other side, a second hole provided an outlet to discharge PPG and brine. A pressure gauge was connected at the inlet to record the injection pressure. The model was transparent so that the PPG and brine movement would be clearly visible. Dye was mixed with the brine to make its propagation visible through the PPG. The model was 51 cm long and 6.1 cm high. The fracture width used in this experiment was 1.5 mm. The inside diameter of each tube leading into the fracture was about 0.635 cm, and the length was 10.16 cm. Figure 3.2 is a schematic of the experimental setup.

3.7.3 Procedures. Hydrogel particles swollen in surfactant solution (Igepal® CO 530) were extruded into the model using the Isco pump through the 600-ml accumulator. Six flow rates were used: 5, 7.5, 10, 12.5, 15, 17.5, 20, and 15 ml/min. The flow rates were tested in sequence from lowest to highest to determine the corresponding stabilized pressure during hydrogel injection. Once the hydrogels was in place, brine was injected among the particles packed in the fractured model to test the efficiency of using hydrogel to plug brine. The brine injection rates were the same as those used during hydrogel injection. The pressure data were recorded to analyze the pressure change over time and the relationship of this change to the injection rate.

The same procedures were applied to a hydrogel swollen in brine solution (1.00 wt% NaCl) to compare hydrogel extrusion pressure before and after the use of a surfactant. Tables 3.7 and 3.8 show the results of the extrusion of hydrogel through the model.

3.8 RESULTS AND DISCUSSION

3.8.1 Swelling Ratio. The hydrogels were left for several nights until they reached equilibrium; the swelling ratio was then measured using the weighting method. The results summaries in Table 3.2) show no significant change in the swelling ratio for the 1.00 wt % Nacl and any of the six surfactant solutions. The swelling ratios ranged from 24% to 42% in all cases due to the low concentration of surfactant (200 ppm). These swelling ratios were a result of the negative charge of the polycrylamide hydrogels; they were much larger than those of the neutral polyacrylamides hydrogels

For a single type of swelling med(~23%) by Wu (2010).ia, the swelling ratio increased slightly as a function of the hydrogel particle size (see Figure 3.3) because the final equilibrium volume after centrifuge was used to calculate the swelling ratio since these larger hydrogel particles had a larger packing volume, even after centrifuging.

For the same particle size (i.e., 100/120 mesh), the swelling ratio values in surfactant solution were lower than those in 1.00 wt% NaCl solution becuase the charge screening effect from the negatively charged surfactant or the neutralization effect from the positively charged surfactant. In both cases, the effective charges along the hydrolyzed polyacrylamide chains were reduced, leading to a smaller swelling ratio. The small swelling ratio in the neutrally changed surfactant might be due to the hydrogen bonding interaction between the surfactant and the polyacrylamides.

3.8.2 Change in Surfactant Concentration. The initial concentration of all surfactants used in this experiment was 200 ppm. Once the hydrogel particles were fully swollen, the equilibrium concentration of the surfactant in the top excess solution was measured by UV-Vis spectrophotometer.

Tables 3.3-3.5 show that the concentrations of positively changed surfactants (1-hexadecyl pyridinium bromide and n-dodecyl pyridinium chloride) decreased. However, when the negatively charged surfactants or neutral surfactants were used for testing, surfactant concentrations increased.

Because the hydrolyzed polyacrylamide hydrogels were negatively charged, they showed strong electrostatic attraction to the positively charged surfactant molecules, or micelles. This attraction caused them to be absorbed into the swollen hydrogel particles although it is not certain whether surfactants are molecularly dispersed in the solution or, if the surfactants form micelles, they are adsorbed onto the particle surface.

Accordingly, the surfactant concentration in the excess solution decreased. The much larger concentration drop (27%-70%) from 1-hexadecyl pyridinium bromide was a result of its micelle formation (large surfactant aggregates) in solution, the surfactant was more efficiently adsorbed onto the surface of the swollen hydrogel particles. The n-dodecyl pyridinium chloride did not form micelles in surfactant because it was below the CMC. However, it could be molecularly diffused into the swollen hydrogel particles, slightly decreasing the concentration (5%-10%).

Tables 3.3-3.5 show a dramatic concentration increase (15%-40%) with the use of negatively charged and neutral surfactants. Generally, the increase in the surfactant concentration was attributable to the micelles formed in the solution, which were a much larger than the opening of the gel network. When the dry gel particles came into contact with the surfactant aqueous solution and the particles absorbed water and swelled, other single surfactant molecules and ions diffused into the network structure because of their small size and concentration gradient. However, surfactant micelles could not pass through the network to be absorbed to the swollen gel network because they were much larger. Instead, they became attached onto the surfaces of the gel particles. Only unassociated single surfactant molecules could pass through the opening and diffuse into the gel network. By the time the swelling reached equilibrium, the gel had adsorbed water, and fewer surfactant molecules could reach the gel network. As a result, the concentration of surfactant remaining in the excess solution increased.

More specifically, the electrostatic repulsion between the negatively charged surfactants (i.e., sodium 4-*n*-octyl benzene sulfonate and dodecylbenzene sulfonic acid sodium salt) and the hydrolyzed polyacrylamide hydrogels impeded the penetration of surfactant molecules or micelles (but not the water molecules) into the swollen hydrogel particles; therefore, the surfactant concentration in the excess solution increased. In addition, the smaller hydrogel particles (100/120 mesh, see Table 3.3) gave rise to much greater concentration increase (approximatly 40%-48%)than that obseved in relatively large hydrogel particles (approximatly 15% -20% for 70/80 and 30/40 mesh; see Table 3.4 and 3.5, respectively). This increase may be a result of the greater surface area of the smaller particles since the same initial weight of dry gels resulted in a higher surface charge density, thus leading to more repulsion of the negatively charged surfactants.

The neutral surfactants, Igepal CO-530 and Tergitol NP-10, both with very low CMC, formed micelles at their initial concentration of 200 ppm. The micelles were likely larger than the average pore size of the swollen hydrogel particles; therefore, only water molecules could be diffused into the network of hydrogel partciles. As a result, the surfactant concentration increased moderatly since there was no strong secondary electrostatic interaction involved.

3.8.3 Surfactant Effect on Dynamic Moduli of Hydrogel Particles. Dynamic moduli tests were run on the 15-ml samples of swollen hydrogel particles used in the surfactant concentration experiments. Rheology measurements were taken to determine the storage, G', and the loss, G", moduli of the swollen hydrogels in surfactant solution. A sample with 1.00 wt% NaCl was used to perform a blank test.

Table 3.6 shows the effect of various surfactants on storage and loss moduli and the relationship between these two moduli for 100/120 hydrogel particles and compares it with these factors for 1 wt% NaCl. The introduction of surfactants into the swelling media dramatically decreased the swollen gel strength. For example, in the blank test (1.00 wt% NaCl), the storage and loss moduli of the particle gel were 331 Pa and 30 Pa, respectively. However, when Igepal CO-530 was used in the swelling solution, the storage and loss moduli dramatically decreased to between 174 Pa and 19 Pa, corresponding to significant reductions of 47% to 37%.

The neutral surfactant, Tergitol NP-10, also showed significant decreases of 37% and 28% in the storage and loss moduli, respectively. When the negatively charged surfactant sodium salt dodecylbenzene sulfonic acid was used, the storage and loss moduli decreased moderately to between 224 Pa and 20 Pa, corresponding to reduction of

32% and 31%. Another negatively charged surfactant (Sodium salt, dodecylbenzene sulfonic acid) showed a similar effect, decreasing the storage and loss moduli by 27% and 36%, respectively. Use of the positively charged surfactant ((1-hexyldecyl) pyridinium bromide) dramatically decreased the storage and loss moduli by 29% and 17%, respectively. Addition of n-dodecylpyridinium chloride, however, decreased the storage and loss moduli slightly by about 7% to 10%. This minimal decrease may have occurred because micelles did not form with the use of this surfactant.

The dramatic decrease in storage and loss moduli may be attributable to the reduction in friction between the swollen hydrogel particles and the measuring plates (discussed in greater details below). Further, Table 3.6 indicates that the relationship between the storage and loss moduli changed very little by about 0.1 indicating no phase change occured as a result mixing surfactants with gel particles.

Similar trends in storage and loss moduli were observed for 70/80 and 30/40 mesh, as shown in Tables 3.7 and 3.8; they decreased significantly with a neutral surfactant, moderately with a positively charged surfactant, and only slightly with a negatively charged surfactant. The smallest reduction occurred with the use of n-dodecylpyridinium chloride. However, these larger particles had a much smaller value of the relationship between storage and loss about 0.02-0.04, indicating that larger hydrogel particles are more elastic than smaller particles since they are subject to greater compression deformation in the gap between the sensor and the plates.

The original dried particle size ranged between 0.125 and 0.150 mm. Based on a volume swelling ratio of 40, the swollen particle size was between 0.427 and 0.513 mm in diameter. The gap between the sensor plate and the bottom glass plate was 0.2 mm wide much smaller than the particle size. Therefore, the swollen gel particles experienced significant deformation during measurement, and substantial friction between their surfaces. The sensor plate and glass plate were dominated by sliding or translational motion, as in the case of bulk hydrogel on the solid surfaces. However, as shown in Figure 3.9.b, when a surfactant was added, most of its molecules aggregated to form micelles, which were much larger than the opening of the gel network and were adsorbed onto the swollen particle gel surface. These micelles acted like small, flexible balls between the gel particle surface and the plates, much like a lubricant. Thus, the friction behaviors between these surfaces were dominated by the rolling motion of the micelles, dramatically reducing the frictional coefficient between the particle gel surface and the plates.

Consequently, the motion resistance of the sensor and the torque exerted on the instrument during measurement also decreased dramatically. As a result, the dynamic moduli of the hydrogel particles were lower than of particles measured without the addition of surfactant.

3.8.4 Hydrogels Transporation through Transparent Fractured Model. The hydrogel particles swollen in surfactant solution (Igepal® CO-530) were extruded. No injection pressure was recorded until the hydrogel particles began propagating through the transparent model. The pressure then increased incrementally as flow rate increased. Figure 3.6 shows the pressure change during hydrogel propagation through the transparent model; the pressure increased incrementally with flow rate. That of hydrogels swollen in 1.00 wt% NaCl was more than double that of hydrogels swollen in surfactant solution. These results demonstrated that even a low concentration of surfactant can reduce the injection pressure of hydrogels, proving the strog influence of surfactants on hydrogel friction.

Figure 3.7 compares the displacement pressure of the hydrogel particles swollen in 1.00 wt% NaCl and that of particles swollen in a surfactant solution. In both cases, the pressure increased gradually, although the hydrogels swollen in 1.00 wt % NaCl showed slightly higher resistance to displacement. This comparison demonstrates that hydrogels swollen in surfactant had a lower injection pressure than those swollen in brine solution; however, they were still highly resistant to displacement by 1.00 wt % NaCl.

Figure 3.8 shows the hydrogel particle front propagation. There was no significant difference in particle front shape between the hydrogel in 1.00 wt % NaCl and that in surfactant. Figure 3.9 shows the dyed brine path through the hydrogels; again, there was little difference between the two hydrogels.

These experiments on hydrogel particle transportation proved that surfactant can reduce the friction of hydrogels and thus their injection pressure. Comparison of the injection pressure of hydrogel particles swollen in 1.00 wt % NaCl with those swollen in surfactant solution (Igepal® CO-530) demonstrates that the surfactant reacted with the hydrogel particle, reducing friction with the plate surface by almost half. Selection of an appropriate surfactant is critical for success. On the other hand, the second stage of the experiment, in which the hydrogel particles were displaced by brine, shows a slight difference in displacement pressure between hydrogels swollen in 1.00 wt % NaCl solution and those swollen in a solution of Igepal® CO-530. This difference is a strong indication that surfactant does not affect hydrogels resistance to displacement.

3.9 SUMMARY

The experiments described here tested surfactant influence on hydrogel particles, focusing on swelling ratio, change in surfactant concentration, and the dynamic moduli of the hydrogels. The transportation of hydrogel particles through a linear fractured model was also studied. These experiments demonstrate that, due to their low concentration (200 ppm) surfactants have only a sight effect on hydrogel swelling ratio. Particle size has a moderate influence on the swelling ratio of hydrogel particles; the larger the particle size, the greater the swelling ratio.

This study has shown that surfactants have a significant influence on hydrogel decreasing their dynamic moduli and reducing friction. It has also clarified the nature of surfactant concentration, showing how it can be changed by the process of adsorption onto hydrogel particles. Finally, this study has proved that surfactants can reduce hydrogel particle friction without reducing the resistance of the particles to displacement.

Table 3.1 Physical properties of surfactants used

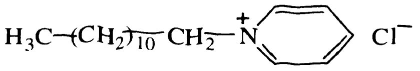
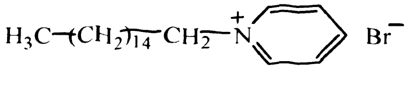
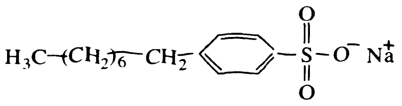
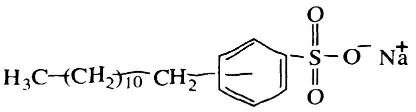
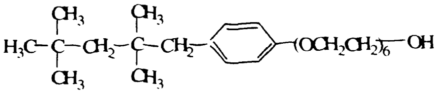
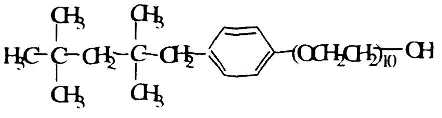
Surfactant	**Charge**	**Molecular Structure**
n-Dodecylpyridinium chloride	cationic	
(1-Hexadecyl)pyridinium bromide	cationic	
Sodium 4-*n*-octyl benzene sulfonate	anionic	
Sodium salt, dodecylbenzene sulfonic acid	anionic	
Igepal® CO-530 Nonylphenoxypoly(ethyleneoxy) alcohol	nonionic	
Tergitol® NP-10 Nonylphenol ethoxylated alcohol	nonionic	

Table 3.2 Hydrogel particle swelling ratio

	100/120 mesh size		**70/80** mesh size		**30/40** mesh size	
	Equilibrium Volume after Using Centrifuge (gram)	Swelling Ratio at Equilibrium (%)	Equilibrium Volume after Using Centrifuge (gram)	Swelling Ratio at Equilibrium (%)	Equilibrium Volume after Using Centrifuge (gram)	Swelling Ratio at Equilibrium (%)
1wt% Nacl	3.3	32	4	39	4.45	43.5
n-dodecyl pyridinium chloride	3	29	3.8	37	4.2	41
(1-hexadecyl)pyridinium bromide	3.1	30	3.8	37	4	39
sodium 4 n-octyl benzene sulfonate	2.8	27	3.9	38	4.2	41
sodium salt,dodecylbenzene sulfonic acid	2.5	24	4.1	40	4	39
Igepal ® CO-530	2.6	25	4	39	4.2	41
Tergitol ® NP-10	2.8	27	3.9	38	4.1	40

(Initial hydrogel weight = 0.1 gram.)

Table 3.3 Measurement of surfactant concentration change after gel swelling (100/120 mesh)

Initial Surfactant Concentration: 200 ppm			Concentration at Swelling Equilibrium		
Surfactant	λ_{max} (nm)	Initial ABS	Equilibrium ABS	Concentration at Equilibrium (ppm)	Concentration Change (%)
n-dodecylpyridinium chloride	259	2.557	2.416	190	-5.0%
(1-hexadecyl)pyridinium bromide	259	1.989	1.465	145	-27.5%
sodium 4-*n*-octyl benzene sulfonate	260	0.28	0.377	280	40.0%
sodium salt, dodecylbenzene sulfonic acid	260	0.277	0.415	295	47.5%
Igepal® CO-530	273	0.745	0.903	242	21.0%
Tergitol® NP-10	273	0.472	0.556	239	19.5%

Table 3.4 Measurement of surfactant concentration change after gel swelling (70/80 mesh)

Initial Surfactant Concentration: 200 ppm			Concentration at Swelling Equilibrium		
Surfactant	λ_{max} (nm)	Initial ABS	Equilibrium ABS	Concentration at Equilibrium (ppm)	Concentration Change (%)
n-dodecylpyridinium chloride	259	2.557	2.311	179	-10.5%
(1-hexadecyl)pyridinium bromide	259	1.989	0.717	70	-65%
sodium 4-*n*-octyl benzene sulfonate	260	0.28	0.361	269	15.5%
sodium salt, dodecylbenzene sulfonic acid	260	0.277	0.381	271	14.5%
Igepal® CO-530	273	0.745	0.913	246	27%
Tergitol® NP-10	273	0.472	0.565	240	30%

Table 3.5 Measurement of surfactant concentration change after gel swelling (30/40 mesh)

Initial Surfactant Concentration: 200 ppm			Concentration at Swelling Equilibrium		
Surfactant	λ_{max} (nm)	Initial ABS	Equilibrium ABS	Concentration at Equilibrium (ppm)	Concentration Change (%)
n-dodecylpyridinium chloride	259	2.557	2.371	181	-9.5%
(1-hexadecyl)pyridinium bromide	259	1.989	0.61	61	-69.5%
sodium 4-*n*-octyl benzene sulfonate	260	0.28	0.354	262	19%
sodium salt, dodecylbenzene sulfonic acid	260	0.277	0.376	259	20.5%
Igepal® CO-530	273	0.745	0.967	262	19%
Tergitol® NP-10	273	0.472	0.57	241	29.5%

Table 3.6 Storage modulus G' and loss modulus G" for 100/120 mesh gel particles

Surfactant (200 ppm)	G' (Pa)	(%) Change	G" (Pa)	(%) Change	Tan δ
1 wt% NaCl	330.75	0	29.60	0	0.0894
n-dodecylpyridinium chloride	308.25	- 6.80	26.57	-10.23	0.0861
(1-hexadecyl)pyridinium bromide	236	-28.60	24.5 0	-17.22	0.1038
sodium 4-*n*-octyl benzene sulfonate	245.75	-25.69	19.07	-35.57	0.0775
sodium salt, dodecylbenzene sulfonic acid	224.25	-32.19	20.47	-30.84	0.0913
Igepal® CO-530	173.75	-47.46	18.75	-36.65	0.1079
Tergitol® NP-10	207	-37.41	21.40	-27.70	0.1033

Table 3.7 Storage modulus G' and loss modulus G" for 70/80 mesh gel particles

Surfactant (200 ppm)	G' (Pa)	(%) Change	G" (Pa)	(%) Change	Tan δ
1 wt% NaCl	721.25	0	25.1	0	0.0348
n-dodecylpyridinium chloride	689.5	-4.40	22.9	-8.76	0.0332
(1-hexadecyl)pyridinium bromide	621.75	-13.79	21.87	-12.86	0.0351
sodium 4-*n*-octyl benzene sulfonate	436.25	-39.51	18.86	-24.86	0.0432
sodium salt, dodecylbenzene sulfonic acid	516.66	-28.36	20.87	-16.85	0.0404
Igepal® CO-530	575.75	-20.17	23.82	-5.10	0.0414
Tergitol® NP-10	570.54	-20.89	22.45	-10.55	0.0393

Table 3.8 Storage modulus G' and loss modulus G" for 30/40 mesh gel particles

Surfactant (200 ppm)	G' (Pa)	(%) Change	G" (Pa)	(%) Change	Tan δ
1 wt% NaCl	1503	0	49.7	0	0.0331
n-dodecylpyridinium chloride	1485	-1.19	46.7	-6.04	0.0314
(1-hexadecyl)pyridinium bromide	1457.5	-3.03	39.72	-19.78	0.0247
sodium 4-*n*-octyl benzene sulfonate	1327.5	-11.6	32.87	-33.86	0.0246
sodium salt, dodecylbenzene sulfonic acid	1210	-19.5	29.8	-40.04	0.0246
Igepal® CO-530	931	-38.05	27.47	-44.72	0.0295
Tergitol® NP-10	1042.5	-30.64	32.4	-34.88	0.0310

Figure 3.1 Spectroscopy UVmini-1240V

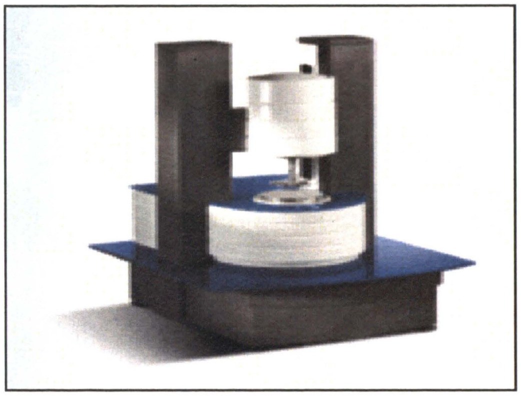


Figure 3.2 Rheometer, HAAKE RheoScope

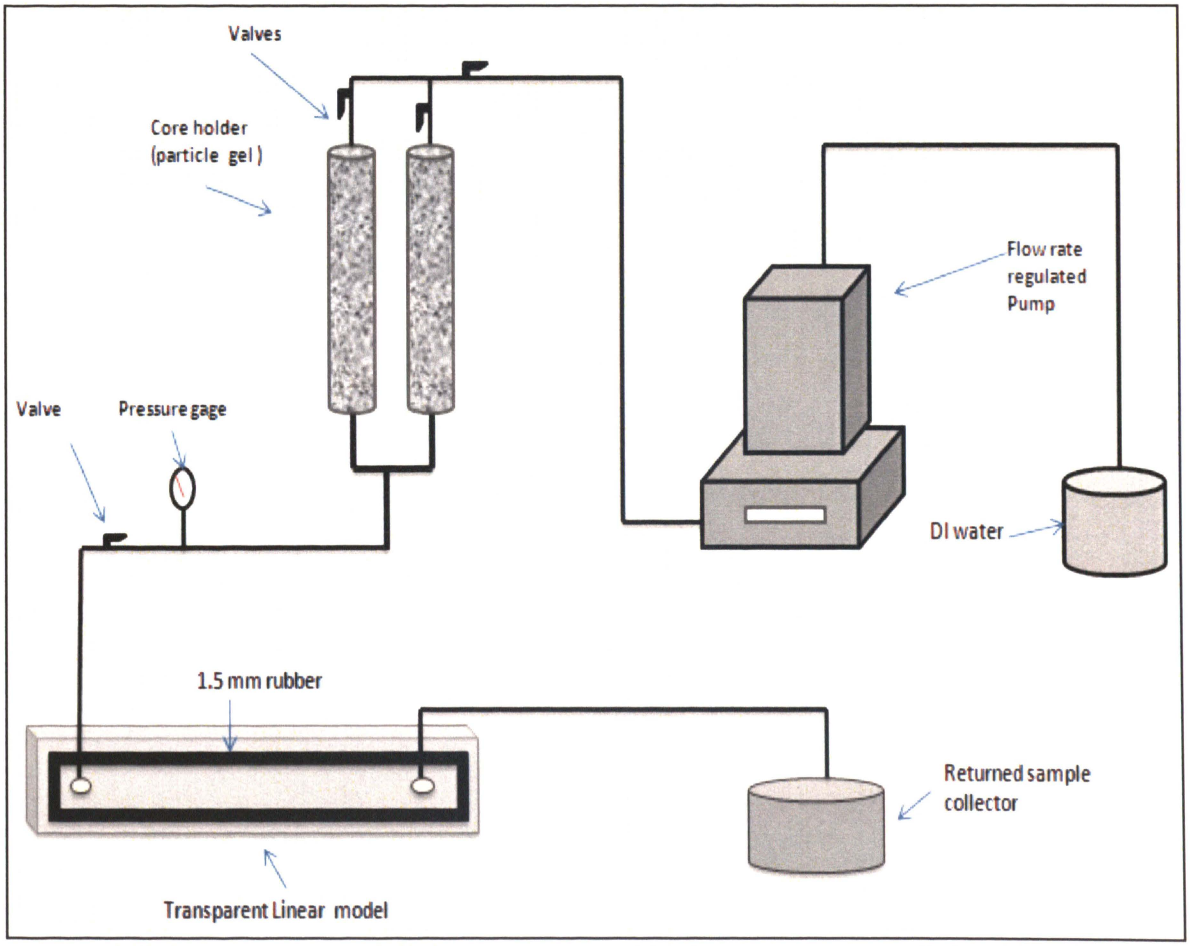


Figure 3.3 Experimental apparatus

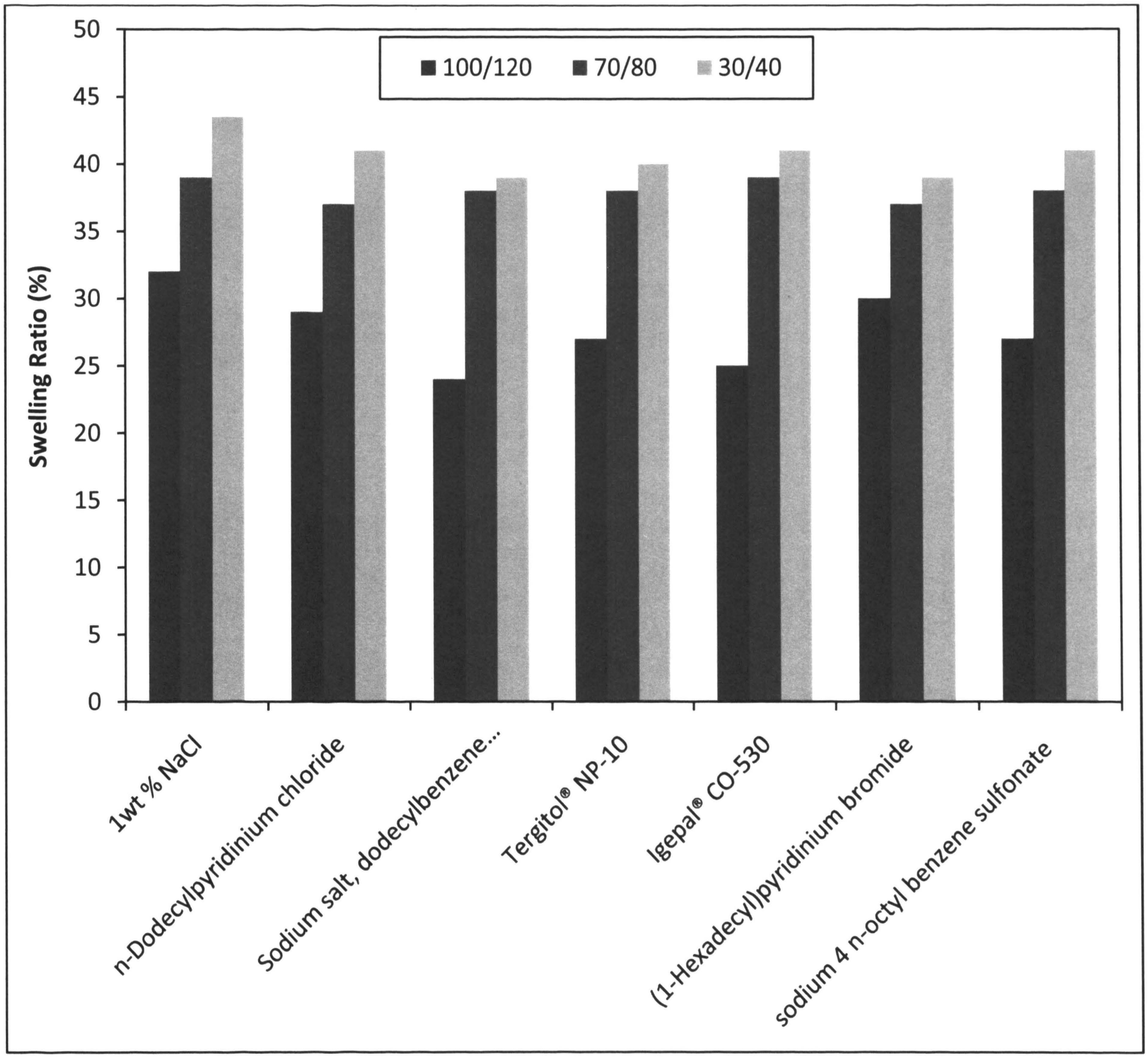


Figure 3.4 Swelling ratios of hydrogel particles in various solutions

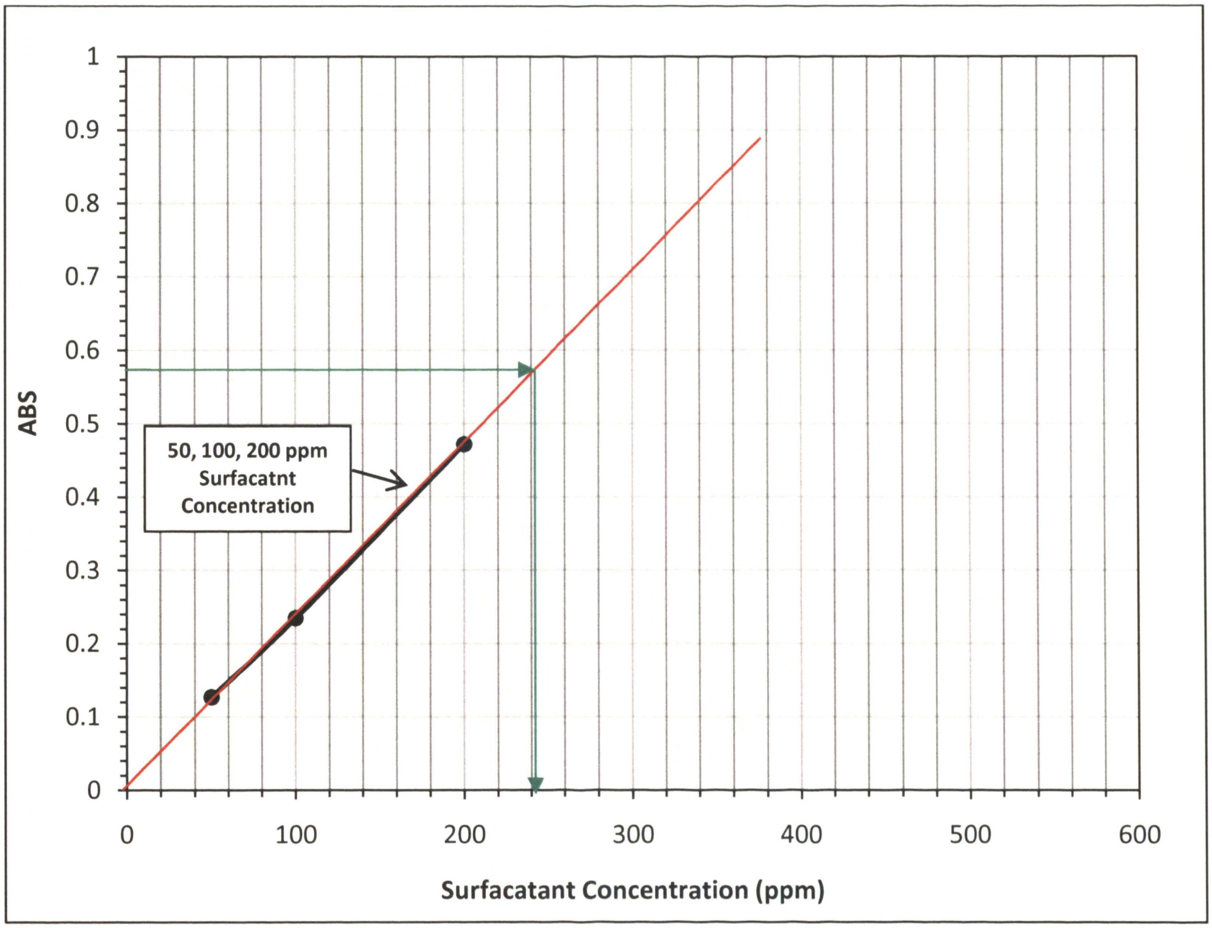


Figure 3.5 Sample of surfactant concentration measurement (Tergitol® NP-10)

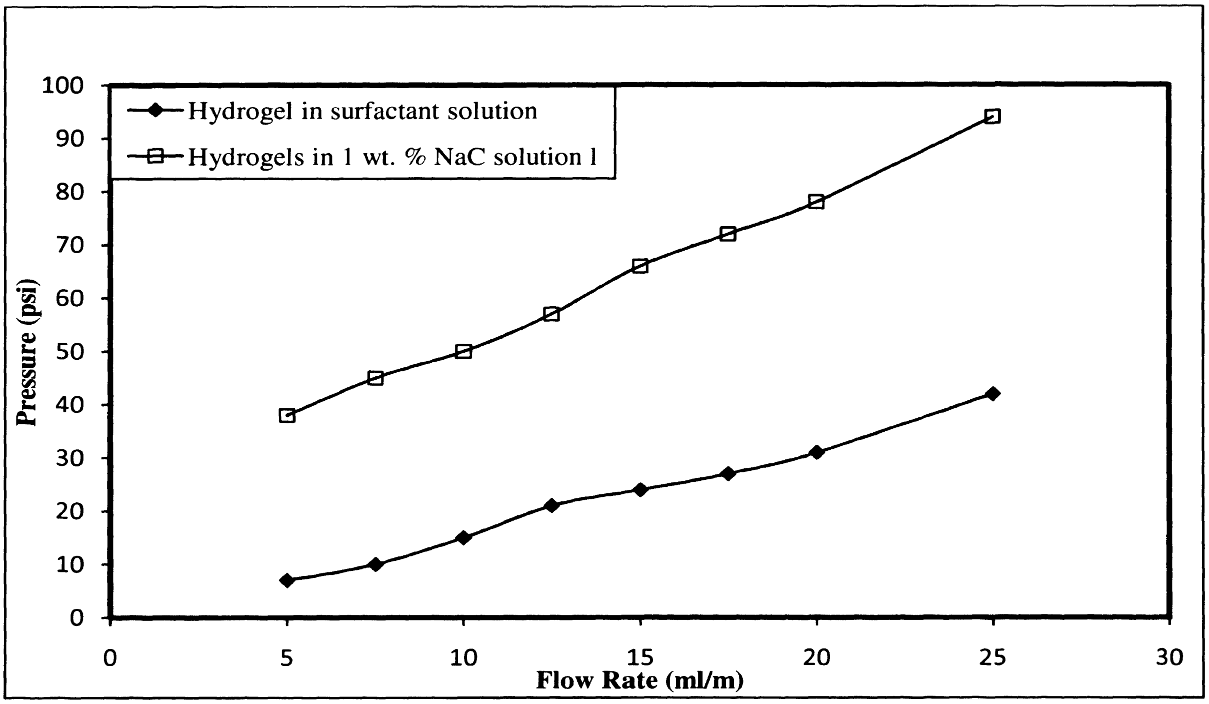


Figure 3.6 Injection pressure changes with flow rate of injected hydrogel particles

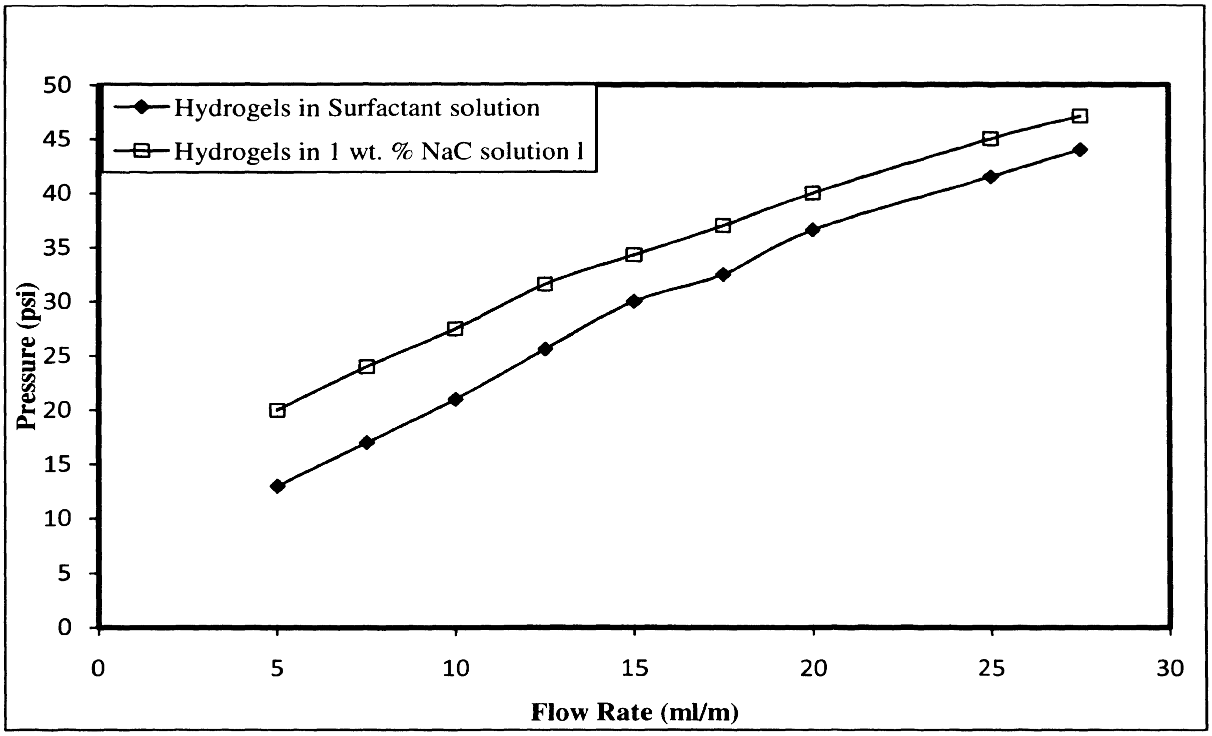


Figure 3.7 Displacement pressure of hydrogel with injection of 1 wt% NaCl

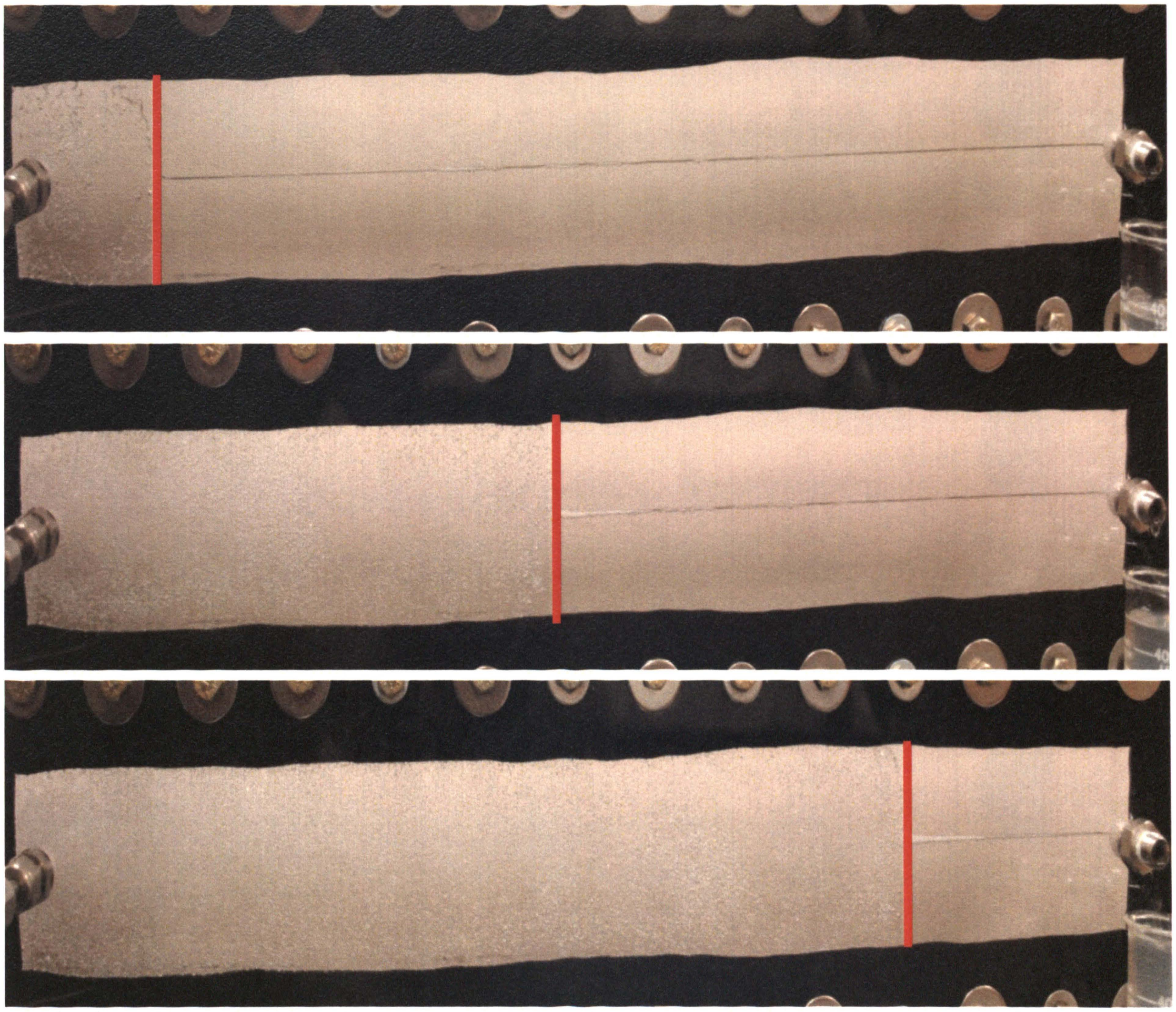


Figure 3.8 Hydrogel propagation through fractured model

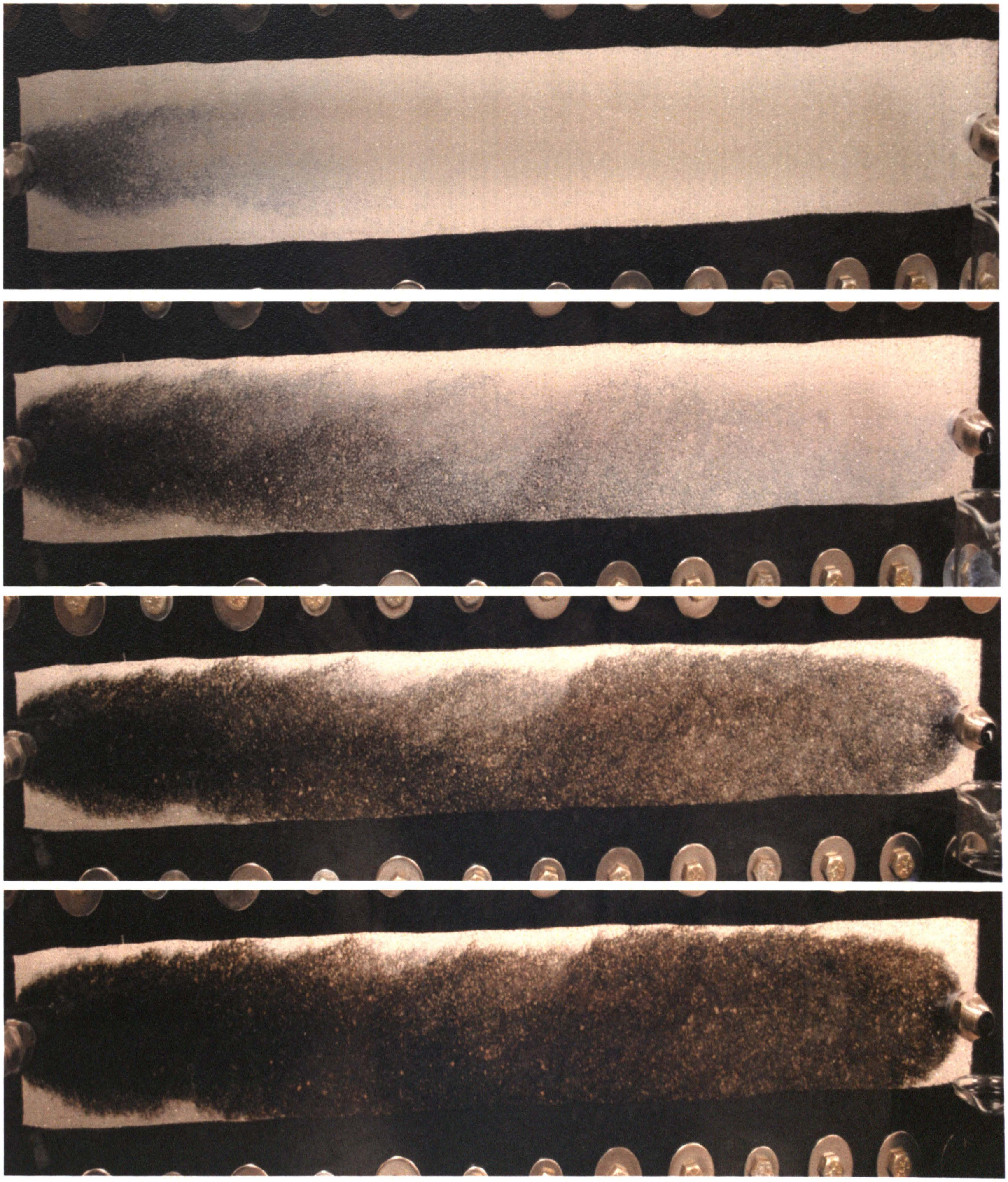


Figure 3.9 Displacement of hydrogel from model using dyed brine

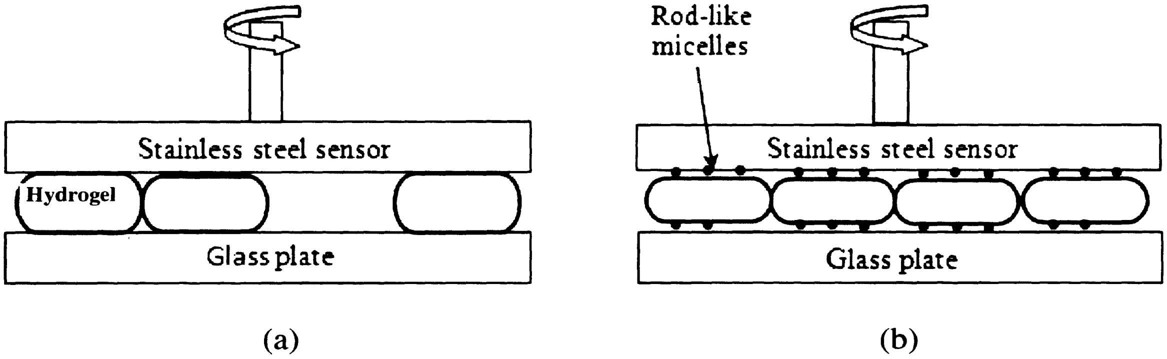


Figure 3.10 Schematic of mechanism to reduce friction between particle gel surfaces and stainless steel sensor and glass plate.

(a) Without of surfactant and (b) With addition of surfactant to brine

4. INTERACTION BETWEEN SURFACTANTS AND NANOCLAY GELS

Most PPGs that have been applied in oilfields contain clay composite because clay as a nano-composite can not only increase the gel strength but it can also reduce the cost of chemicals. This section studied the interaction between surfactants and a clay gel in order to see whether we can combine surfactant and gel treatment in one process to significantly improve oil recovery. A nanoclay composite polymer gel was synthesized, and six surfactants were selected, including two cationic, two anionic and two nonionic surfactants for the experiments. It has been found that all surfactants had negligible influence on the particle swelling ratio. The equilibrium concentration of surfactants depends on its type. A transparent fracture linear model was used to understand the propagation of the swollen nanoclay gel particles through fracture. Test results showed that the surfactant Igepal® CO-530 can reduce gel injection pressure, which is consistent with the rheology measurement results.

4.1 INTRODUCTION

Nanoclays have not been studied as a potential conformance control technique, and previous studies have not addressed the interaction between surfactants and nanoclay gel particles. A combination of the two could solve many problems facing gel treatments technology. Further, nanoclay particles enhance gel strength so that the gel can better plug any fracture or channel.

This section reports an experimental study of the interaction between nanoclays gel and surfactant. To understand the effect of various types of surfactants on this nanoclay gel, the storage modulus (G') and loss modulus (G'') has been measured. Once the gels reached equilibrium, surfactant concentration was measured to determine whether the surfactant had been adsorbed or absorbed to the gel particles.

Three different PPG mesh sizes was used, 100/120, 70/80, and 30/40, corresponds to 150-120, 212-180, and 600-425μm respectively. This study use two nonionic, two anionic, and two cationic surfactants, which were described in chapter 3 above (see Table 3.1).

A transparent fracture linear model was used to understand the propagation of the swollen nanoclay gel particles through fracture. An understanding of the behavior of the swollen particles as they are extruded through fractures or channels is crucial to gel treatment design.

4.2 MATERIALS

Monomer acrylamide (98.5%) and cross-linker methylene-bis-acrylamide (MBAA, 97+%) were purchased from Alfa Aesar Company (Ward Hill, MA) and used without further purification. Ammonium sulfite was used as initiator for polymer gel synthesis. Cationic surfactants, *n*-dodecylpyridinium chloride (98%), (1-hexadecyl) pyridinium bromide monohydrate (98%), and anionic surfactant, sodium 4-*n*-octyl benzene sulfonate were also purchased from Alfa Aesar (Ward Hill, MA) and used without further purification. Sodium dodecylbenzene sulfonic acid was purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. Other commercial surfactants were requested from their manufacturers, Igepal® CO-530 from Rhodia, Inc. (Bristol, PA), Tergitol® NP-10 from Dow Chemical (Midland, MI), NaCl (99.8%) was purchased from Fisher Scientific Inc. Water used in all experiments was distilled

Measurement devices: A UVmini-1240V UV-Vis spectrophotometer from Shimadzu (See figure 3.2) was used to measure surfactant concentration. The rheometer, a HAAKE RheoScope from Thermo Scientific (See figure 3.2), was used to measure the storage and loss moduli of swollen particle gels. A transparent fractured model (See figure 3.3) was constructed to evaluate the injectivity of the nanoclay gel particles with and without the presence of a surfactant.

4.3 SYNTHESIS OF NANOCLAY GELS PARTICLES

150 g of acrylamide were added to 498.7 g of distilled water with the bentonite concentration at 10%. The solution was purged with nitrogen gas for 40 minutes and stirred until the entire solid was dissolved. 0.650 g of methylene-bis-acrylamide (MBAA) was added to the solution for complete dissolution upon stirring. 0.650 g of $(NH_4)_2S_2O_8$ was then added with stirring to the solution prepared above. The mixture solution was placed in an oven at 60 °C for 14 hours for the complete polymerization after 20 grams of Na_2CO_3 were added. A strong bulk gel was formed and then hydrolyzed at 80 °C for another 8 hrs to form the negatively charged carboxylate anions in the network due to the presence of Na_2CO_3. Very strong ammonia gas was generated during this hydrolysis process. Then the hydrolyzed hydrogel was cut into small pieces. The formed hydrogel was then purified by soaking in large amount of distilled water for one week and followed by drying at 60 °C for 4 days to yield 695.64 g of dry gel. The dried gel solids were crushed into small particle powder in a blender machine (Black & Decker). PPGs with the particle size between 100~120 mesh ($150\mu m \sim 120\mu m$) were selected through the standard testing sieves (Fisher Scientific Company).

4.4 SWELLING RATIO MEASUREMENTS

Test tubes (15 ml) were used to measure the swelling ratio of the nanoclay gel particles. First, 0.1 g 100/120 mesh nanoclay gel particles were added to 14.9 g 1.00 wt% NaCl brine in a test tube. The test tube was then robustly shaken, and the sample was left overnight on a shaking device to ensure that all the nanoclay gel particles were well mixed with the clay gel particles. Six samples were prepared using various surfactants as the swollen media, and the nanoclay gel particles were swollen following the same procedures mentioned above.

All seven samples were left for several days until they reached equilibrium. The swelling ratio of the nanoclay gel particles was then measured using the weight method, that is, 0.1 g dry nanoclay gel particles was weighed, and the particles were weighed again after they reached swelling equilibrium. The gel particles were perfectly separated from the swelling media; there was no need to use a centrifuge.

The swelling ratio, *SW*, of the particles was measured using the weight method:

$$Sw = \frac{m_t - m_o}{m_o} \tag{4.1}$$

where m_t represents the weight of the gel particles after x time, and m_o represents the original weight of the dry gel particles. The procedure was then repeated for each particle size. Table 4.1 shows the swelling ratio for each particles size.

4.5 SURFACTANT CONCENTRATION AFTER NANOCLAY GELS REACHED SWELLING EQUILIBRIUM

Six surfactants were used for the experiment. Three samples of each surfactant were tested. First, 0.1 g dry nanoclay gel particles was poured into a 15-ml test tube containing 14.9 g a surfactant solution. The initial surfactant concentration was relatively low (200 ppm) to ensure accuracy. After the nanoclay gel particles reached equilibrium (approximately 7 days), the equilibrium solution of NaCl and surfactant was measured at the top of the test tube. The UV-Vis spectrum was scanned from 1100 to 190 nm to identify the wavelength at which it reached maximum spectrum (λmax). The equilibrium concentration of each surfactant was measured based on the sample's absorbance at λmax. Figure 3.1 shows the picture a typical UV/Vis spectrophotometer that was used in the experiment. The equilibrium concentration for each surfactant was measured through its absorbance equilibrium (ABS equilibrium).

The same procedures were applied to each particle size. The ABS of each surfactant solution after equilibrated was measured. Figure 4.1 shows a standard curve of ABS as a function of surfactant concentration. This equation fitting the linear relationship between concentration and ABS was used to calculate the surfactant concentration of each equilibrated solution.

4.6 MEASUREMENT OF DYNAMIC MODULI OF NANOCLAY GELS

A rheology measurement device HAAKE rheometer was used to measure the storage and loss moduli of the swollen nanoclay gel particles. Data were gathered using a HAAKE Rheo (job manager software) from Thermo Fisher Scientific Company. This experiment relied on the oscillation time sweep curve model, which represents the storage and loss moduli logarithmically in Pascal (Pa) as a function of time in seconds. The frequency was set at 1 Hz, and a controlled stress (CS) mode was selected because the stress value had to be in the linear viscoelastic range. The stress applied to the particles was 1 Pa to ensure that gel strain and stress had a linear relationship during measurement. A PP35 Ti Po LO2 016 sensor was used, and a gap of 0.2 mm was left between the sensor and the plate that held the sample. The temperature was set to 25 °C. For each sample, storage and loss moduli readings were taken every 30 seconds for 5 minutes. Tables 4.5, 4.6, and 4.7 show the dynamic modulus results for particles of various sizes.

4.7 NANOCLAY GELS TRANSPORTATION THROUGH TRANSPARENT LINEAR MODEL

A linear fracture model was constructed to demonstrate the influence of the surfactant on the gel particle injection pressure. This work used particles with a mesh size of 30 to 40 (212- 180μm) nanoclay gel. Two sets of swollen gels were prepared for each size, the first in a 1.00 wt% NaCl (brine) solution and the second in a surfactant solution. The nonionic surfactant Igepal® CO-530 was used because this type has the most stable and noticeable effect on nanoclay gel strength. It is also inexpensive and easily available.

4.7.2 Experimental Setup. The experimental apparatus comprised a syringe pump, two 600-ml capacity accumulators with piston, and one fracture model. An Isco pump was used to inject PPG and brine. The transparent linear model was constructed of two acrylic plates with a rubber O-ring between them. Bolts, nuts, and shims were used to fix the two plates and control the fracture width. On one side of the plate, a hole functioned as an inlet for the injection of PPG and brine; on the other side, a second hole provided an outlet to discharge PPG and brine. A pressure gage was connected at the inlet to record the injection pressure. The model was transparent so that the PPG and brine movement would be clearly visible. Dye was mixed with the brine to make its propagation visible through the nanoclay gel. The model was 51 cm long and 6.1 cm high. The fracture width used in this experiment was 1.5 mm. The inside diameter of each tube leading into the fracture was about 0.635 cm, and the length was 10.16 cm. Figure 3.2 shows the experimental setup.

4.7.3 Procedures. Nanoclay gel particles swollen in surfactant solution (Igepal® CO 530) were extruded into the model using the Isco pump through the 600-ml accumulator. Six flow rates were used: 5, 7.5, 10, 12.5, 15, 17.5, 20, and 15 ml/min. The flow rates were tested in sequence from lowest to highest to determine the corresponding stabilized pressure during nanoclay gel injection. Once the nanoclay gel was in place, brine was injected among the particles packed in the fractured model to test the efficiency of using nanoclay gels to plug brine. The brine injection rates were the same as those used during nanoclay gel injection. The pressure data were recorded to analyze the pressure change over time and the relationship of this change to the injection rate.

The same procedures were applied to a nanoclay gel swollen in brine solution (1.00 wt% NaCl) to compare gel extrusion pressure before and after the use of a surfactant. Figures 4.3 and 4.4 show the results of the extrusion of nanoclay gel through the model.

4.8 RESULTS AND DISCUSSION

4.8.1 Swelling Ratio. The nanoclay gel particles were left for 4 days until they reached equilibrium; the swelling ratio was then measured using the weighting method. The results (see Table 4.1) show no significant change in the swelling ratio for the 1.00 wt% NaCl and the six surfactant solutions. The swelling ratios ranged from 44% to 54% in all cases due to the low concentration of surfactants (200 ppm). These swelling ratios of the nanoclay gels used in this experiment were much larger than those from the negatively charged polyacrylamides hydrogels (24% to 42%) used in the previous section. The fact that these swelling ratios are higher than those for hydrogels may be due to the presence of nanoclay particles that can swell more water. Figure 4.2 indicates a slight decrease in the swelling ratio as a function of particle size, perhaps due to the nanocomposition of the gel particles and their greater ability to swell.

For 100/120 mesh particles the swelling ratio values in surfactant solution were less than those in 1.00 wt% NaCl solution because of the charge screening effect greeted by the negatively charged surfactant or the neutralization effect created by the positively charged surfactant. In both cases, the effective charges along the hydrolyzed polyacrylamide chains were reduced, leading to a smaller swelling ratio. The small swelling ratio in the neutrally changed surfactant may have been due to the hydrogen bonding interaction between the surfactant and the polyacrylamides.

4.8.2 Change in Surfactant Concentration. The initial concentration for all surfactants used in this experiment was 200 ppm. Once the nanoclay gel particles were totally swollen, the equilibrium concentration of surfactant solution in the top excess solution was measured by UV-Vis spectrophotometer.

Tables 4.2-4.4 show that the surfactant concentrations dramatically decreased for the positively changed surfactants (n-dodecyl Pyridinium chloride and (1-hexadecyl) pyridinium bromide) to 62 and 17 ppm, respectively. This decrease is attributable to the favorable electrostatic attraction between the clay/hydrogel and the surfactant which might result in the surfactants being adsorbed on the surface of clay gel particles or being absorbed into the pore network of the clay gel particles The measurement results for the anionic surfactants, sodium 4 n-octyl benzene sulfonate and sodium salt, dodecylbenzene sulfonic acid, show a dramatic increase in the surfactant concentration, to 321 and 322 ppm, respectively, about 47% greater than the original surfactant concentration. This increase was due to the electrostatic repulsion between the clays/hydrogel and the surfactant, which might result in the surfactants being adsorbed on the surface of clay gel particles or being absorbed into the pore network of the clay gel particles. The measurement results for the anionic surfactants, sodium 4 n-octyl benzene sulfonate and sodium salt, dodecylbenzene sulfonic acid, show a dramatic increase in the surfactant concentration, to 321 and 322 ppm, respectively, about 47% greater than the original surfactant concentration. This increase was due to the electrostatic repulsion between the clays/hydrogel and the surfactant; this repulsion hampered the penetration of the surfactant into the nanocomposites. In this case, the surfactant remained in solution.

The concentrations of the neutral surfactants, Igepal® CO-530 and Tergitol® NP-10, decreased to 74 and 81 ppm, respectively, due to the adsorption of micelles formed at the surface of the nanocomposites. However this decrease was not as dramatic as that observed for the cationic surfactants.

Tables 4.3 and 4.4 list the surfactant concentration changes for 70/80 and 30/40 mesh particles; the two showed approximately the same trend. The reason for the increase in surfactant concentration was that micelles formed in the solution, and these were a much larger than the opening of the gel network. When the dry particles came into contact with the surfactant aqueous solution, they adsorbed water first. Other molecules and ions then diffused into the network structure because of the concentration gradient and small particle size. However, surfactant micelles could not travel through the gel network to get inside the gels because they were two large. Only unassociated single surfactant molecules could pass through the opening and diffuse into the network. Once swelling reached equilibrium, the gels had adsorbed a substantial amount of water, and few surfactant molecules could enter the network. As a result, a high concentration of surfactant remained in the excess solution.

This work assumed that the interaction between the nanoclay gel particles and the cationic surfactant would decrease the surfactant concentration. Indeed, as substantial decrease was observed for the two cationic surfactants due to the attraction between the positive ions of the surfactants and the negative ions of the gel particles. However, repulsion between the two anionic surfactants and the gel particles resulted in a dramatic increase in surfactant concentrations. The nonionic surfactants had the same reaction to the gel particles as the cationic surfactants; their concentrations decreased dramatically.

4.8.3 Effect of Surfactants on Dynamic Moduli of Nanoclay Gels Particles. Dynamic moduli tests were run on the 15-ml samples of swollen nanoclay gel particles used in the surfactant concentration experiments. Rheology measurements were taken to determine the storage, G', and the loss, G", moduli of the particles in surfactant solution. A sample with 1.00 wt% NaCl was used to perform blank test.

Table 4.5 shows the effect of the surfactants on storage and loss moduli for the 100/120 mesh particles. The surfactant influence was minimal despite expectations that the storage and loss moduli of the gels in cationic and nonionic surfactants would be significant because the huge decrease in surfactant concentration. Instead, however, these values decreased slightly in comparison to the blank test with 1 wt% NaCl. The storage and loss moduli decreased by 10% and 22% respectively for the two cationic surfactants, and by 17% and 28% for the neutral surfactants. On the other hand, there was no significant change in the dynamic moduli with the anionic surfactant, which decreased by as much as 6% or increased by up to 9%. These results echoed those for the surfactant concentration measurements which showed no penetration of surfactants into the nanocomposites.

Table 4.6 lists the storage and loss moduli results for the 70/80 mesh nanoclay gel particles in surfactant solutions. It shows higher values than those obtained for 100/120 particles because of the gap (0.2 mm) between the sensor and the glass plate. The storage modulus of particles swollen in cationic and neutral surfactants decreased from 7.7% to 14% compared to the readings for the blank test at 809.5 Pa. On the other hand, the anionic surfactants caused a negligible change in the storage modlus, as expected based on the surfactant concentration results.

Table 4.7 presents dynamic modulus measurements for 30/40 mesh nanoclay gel particles. It shows a trend similar to that for 70/80 mesh. These results were not encouraging, but they leave room for hope that nanoclay gel particles can work as a plugging agent if they are associated with the proper surfactant.

Overall, the dynamic moduli of the nanoclay gel particles were affected slightly by the presence of surfactants in the swelling media. This slight decrease in the storage modulus is attributable to surfactant reaction with the particles. For example, compared to the blank test (1.00 wt% NaCl), the dynamic moduli of the 100/120 gels decreased by 10% and 22% for the cationic surfactants and by 17% and 28% for the neutral surfactants.

4.8.4 Nanoclay Gel Particles Transporation through Transperent Linear Model. When nanoclay gel particles swollen in a solution of Igepal® CO-530 were extruded, no injection pressure was recorded until the particles began to propagate through the transparent model. The pressure then increased as the flow rate increased. Figure 4.3 shows the pressure change during particles propagation through the model. The pressure increased with the flow rate. The injection pressure of particles swollen in 1.00 wt% NaCl was slightly higher than that of particles swollen in surfactant solution.

Figure 4.4 compares the brine injection pressures in nanoclay gel particles swollen in 1.00 wt% NaCl and those swollen in a surfactant solution. In both cases, the pressure increased gradually with flow rate. The nanoclay gels in 1.00 wt% NaCl had a slightly higher resistance to flow; however, when the flow rate reached 10 ml/min, the pressure rapidly declined to zero. This sudden break in pressure occurred when the brine formed a huge channel through the packed nanoclay gel particles (see Figure 4.6). Although the particles swollen in 1.0 wt% NaCl had slightly higher resistance to displacement, the pressure in both cases dropped at the same flow rate of 10 ml/min, indicating that the particles have little resistance to brine displacement. This low level of resistance may be due to the hard ball-like nature of the particles, which prevents them from being squeezed together to form an impermeable wall against the flooded brine. No such resistance was observed for elastic particles could be squeezed and packed firmly to form a strong plug against displacement.

Figure 4.5 shows the front propagation of the particles; there was no significant difference in the front shape of particles swollen in brine and those swollen in surfactant.

Figure 4.6 shows the dyed brine passing through the particles with a huge channel formed by brine displacement through the packed gels.

Comparison of the injection pressure of the nanoclay gel particles swollen in 1 wt% NaCl with that for particles swollen in surfactant solution (Igepal® CO-530) demonstrates that the surfactant reacted with the particles and reduced their friction with the plate surfaces by approximately 9%. Selecting of the proper surfactant proved critical to the success of this process.

4.9 SUMMARY

This section has described a systematic study of surfactant influence on nanoclay gel in terms of swelling ratio, surfactant concentration change, and dynamic moduli. It also described an experiment on particle transportation through a linear fractured model. The surfactants had no significant influence on the particle swelling ratio. The size of the particles had only a slight effect on swelling ratio, so that larger particles had a higher swelling ratio. This distinction is to be expected since larger particles can absorb more water.

The nanoclay gel particle transportation experiment showed that surfactant can reduce the friction of gel particles and thus reduce gel injection pressure. However, Figure 4.3 shows only a slight reduction in injection pressure.

Overall, this study demonstrates that surfactant has only a slight influence on dynamic moduli of nanoclay gel particles. It has clarified the nature of surfactant concentration and showed how it can be changed by the adsorption of surfactant onto nanoclay gel particle surfaces. Finally, this study has proved that surfactants can reduce nanoclay gel particles friction without reducing their resistance to displacement.

Table 4.1 Nanoclay Gel Particle Swelling Ratio

	100/120 mesh size		**70/80** mesh size		**30/40** mesh size	
	Equilibrium Volume after Using Centrifuge (gram)	Swelling Ratio at Equilibrium (%)	Equilibrium Volume after Using Centrifuge (gram)	Swelling Ratio at Equilibrium (%)	Equilibrium Volume after Using Centrifuge (gram)	Swelling Ratio at Equilibrium (%)
1wt% Nacl	5.5	54	5	49	4.6	45
n-Dodecyl Pyridinium chloride	5.0	49	4.9	48	4.8	47
(1-Hexadecyl)pyridinium bromide	4.8	47	4.7	46.5	4.7	46
Sodium 4 n-octyl benzene sulfonate	5.2	51	5.1	50	4.9	48
Sodium salt,dodecylbenzene sulfonic acid	5.2	51	5.1	50	5.0	49
Igepal® CO-530	4.8	47	4.7	46	4.5	44
Tergitol® NP-10	4.9	48	4.7	46.5	4.7	46

(Initial nanoclay gel weight=0.1 gram.)

Table 4.2 Change in Surfactant Concentration after Gel Swelling (100/120 mesh)

Initial Surfactant Concentration: 200 ppm			At Equilibrium of Swelling		
Surfactant	λ_{max} (nm)	Initial ABS	Equilibrium ABS	Concentration at Equilibrium ppm	%Change Concentration
n-dodecylpyridinium chloride	259	2.557	0.688	62	-59.0%
(1-dexadecyl)pyridinium bromide	259	1.989	0.194	17	-91.5%
dodium 4-*n*-octyl benzene sulfonate	260	0.28	0.421	321	60.5%
dodium salt, dodecylbenzene sulfonic acid	260	0.277	0.455	322	91%
Igepal® CO-530	273	0.745	0.289	74	-63%
Tergitol® NP-10	273	0.472	0.192	81	-59.5%

Table 4.3 Change in Surfactant Concentration after Gel swelling (70/80 mesh)

Initial Surfactant Concentration: 200 ppm			At Equilibrium of Swelling		
Surfactant	λ_{max} (nm)	Initial ABS	Equilibrium ABS	Concentration at Equilibrium ppm	%Change Concentration
n-dodecylpyridinium chloride	259	2.557	0.648	59	-70.5%
(1-hexadecyl)pyridinium bromide	259	1.989	0.197	18	-91%
sodium 4-*n*-octyl benzene sulfonate	260	0.28	0.422	321	60.5%
sodium salt, dodecylbenzene sulfonic acid	260	0.277	0.457	323	16%
Igepal® CO-530	273	0.745	0.191	49	-75.5%
Tergitol® NP-10	273	0.472	0.188	79	-60.5%

Table 4.4 Change in Surfactant Concentration after Gel swelling (30/40 mesh)

Surfactant Initial Concentration: 200 ppm			At Equilibrium of Swelling		
Surfactant	λ_{max} (nm)	Initial ABS	Equilibrium ABS	Concentration at Equilibrium ppm	%Change Concentration
n-dodecylpyridinium chloride	259	2.557	0.649	59	-70.5%
(1-hexadecyl)pyridinium bromide	259	1.989	0.288	25	-87.5%
sodium 4-*n*-octyl benzene sulfonate	260	0.28	0.434	329	64.5%
sodium salt, dodecylbenzene sulfonic acid	260	0.277	0.45	320	60%
Igepal® CO-530	273	0.745	0.29	74	-63%
Tergitol® NP-10	273	0.472	0.213	90	-55%

Table 4.5 Storage and loss moduli 100/120 mesh nanoclay gel particles

Surfactant (200 ppm)	G' (Pa)	% Change	G" (Pa)	% Change	Tan δ
1 wt% NaCl	560.75	0	39.175	0	0.0698
n-dodecylpyridinium chloride	436.75	-22.11	22.375	-42.88	0.0440
(1-hexadecyl)pyridinium bromide	501	- 10.65	32.175	-17.86	0.0642
sodium 4-*n*-octyl benzene sulfonate	527.5	- 5.92	30.65	-21.76	0.0581
sodium salt, dodecylbenzene sulfonic acid	507.75	- 9.45	37.3	-4.78	0.0854
Igepal® CO-530	402.25	-28.26	18.5	-52.77	0.0459
Tergitol® NP-10	463.5	-17.34	38.5	-1.72	0.0830

Table 4.6 Storage and loss moduli 70/80 mesh nanoclay gel particles

Surfactant (200 ppm)	G' (Pa)	% Change	G" (Pa)	% Change	Tan δ
1 wt% NaCl	809.5	0	33.425	0	0.0412
n-dodecylpyridinium chloride	695.5	-14.08	25.55	-23.56	0.0334
(1-hexadecyl)pyridinium bromide	728.5	-10	32.2	-3.66	0.0407
sodium 4-*n*-octyl benzene sulfonate	764	-5.62	33	-1.27	0.0474
sodium salt, dodecylbenzene sulfonic acid	789.5	-2.47	32.075	-4.03	0.0440
Igepal® CO-530	731.5	-9.63	33.05	-1.12	0.0451
Tergitol® NP-10	747	-7.72	28.1	-15.93	0.0376

Table 4.7 Storage and loss moduli 70/80 mesh nanoclay gel particles

Surfactant (200 ppm)	G' (Pa)	%Change	G" (Pa)	% Change	Tan δ
1 wt% NaCl	885.25	0	35.1	0	0.0396
n-dodecylpyridinium chloride	766.25	-13.44	30.375	-13.47	0.0383
(1-hexadecyl)pyridinium bromide	786.5	-11.16	29.475	-16.02	0.0360
sodium 4-*n*-octyl benzene sulfonate	817	-7.71	25.9	-26.21	0.0329
sodium salt, dodecylbenzene sulfonic acid	793	-10.42	26.375	-24.85	0.0344
Igepal® CO-530	740.75	-16.32	28.775	-18.01	0.0388
Tergitol® NP-10	773.75	-12.59	31.425	-10.47	0.0406

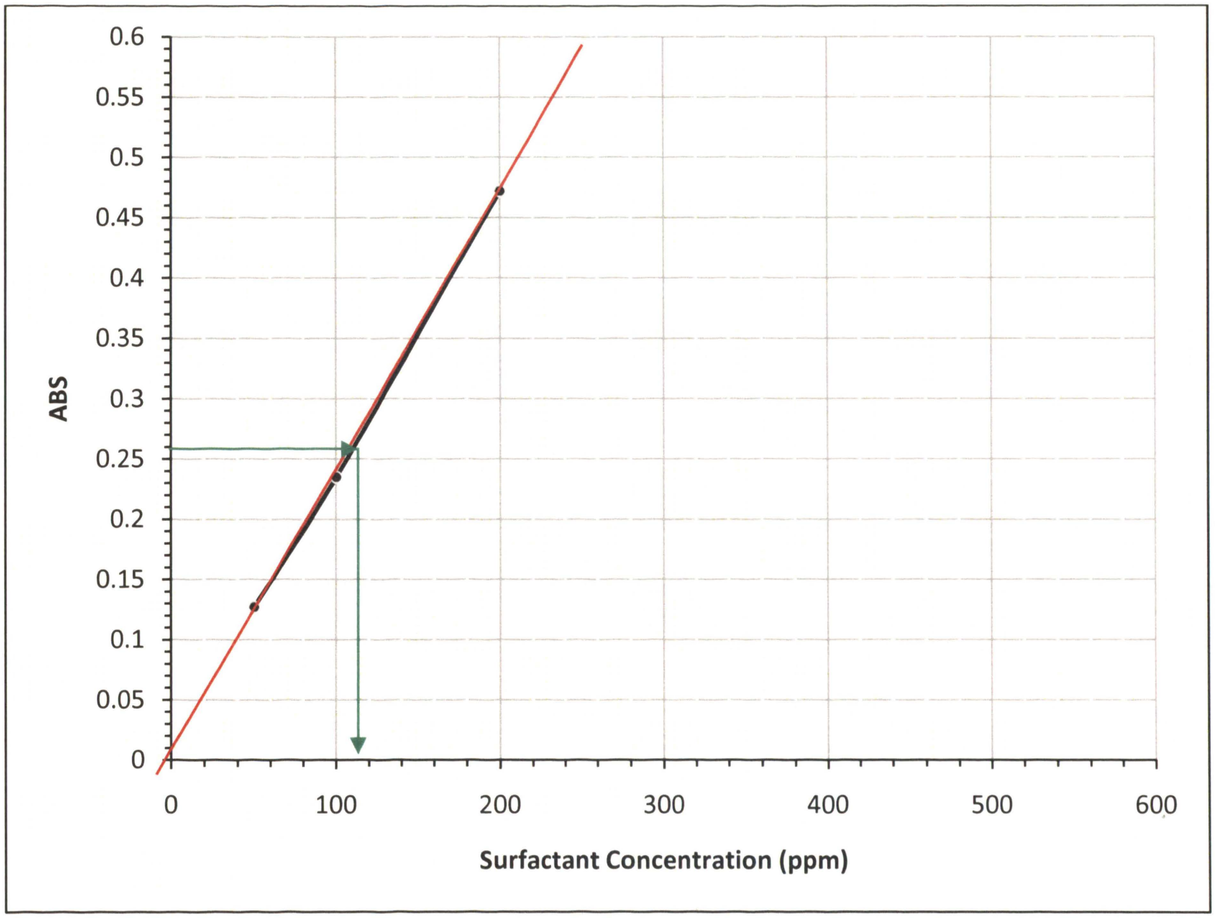


Figure 4.1 Sample surfactant concentration measurement (Tergitol® NP-10)

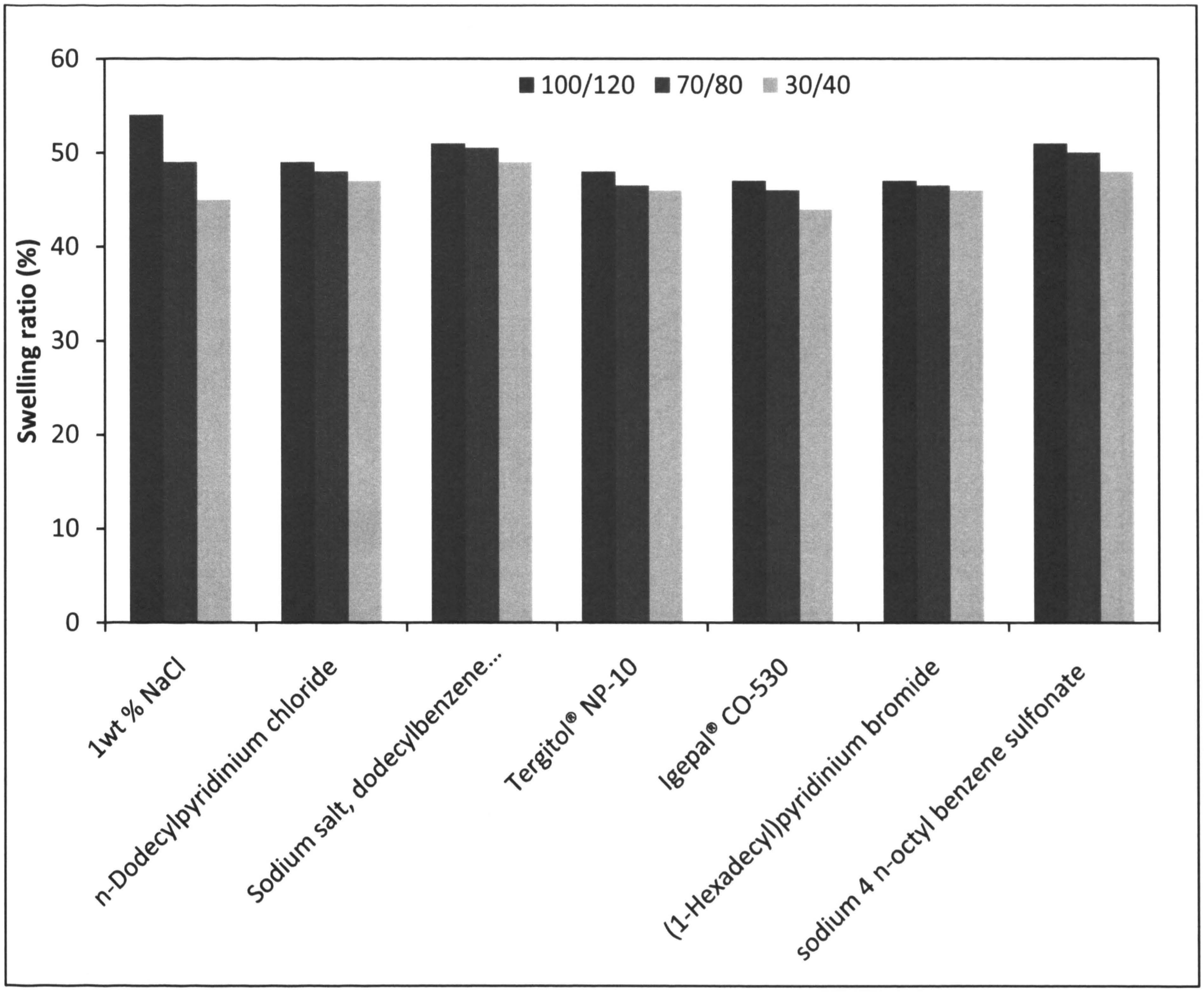


Figure 4.2 Swelling ratio of nanoclay gel particles in various swelling media

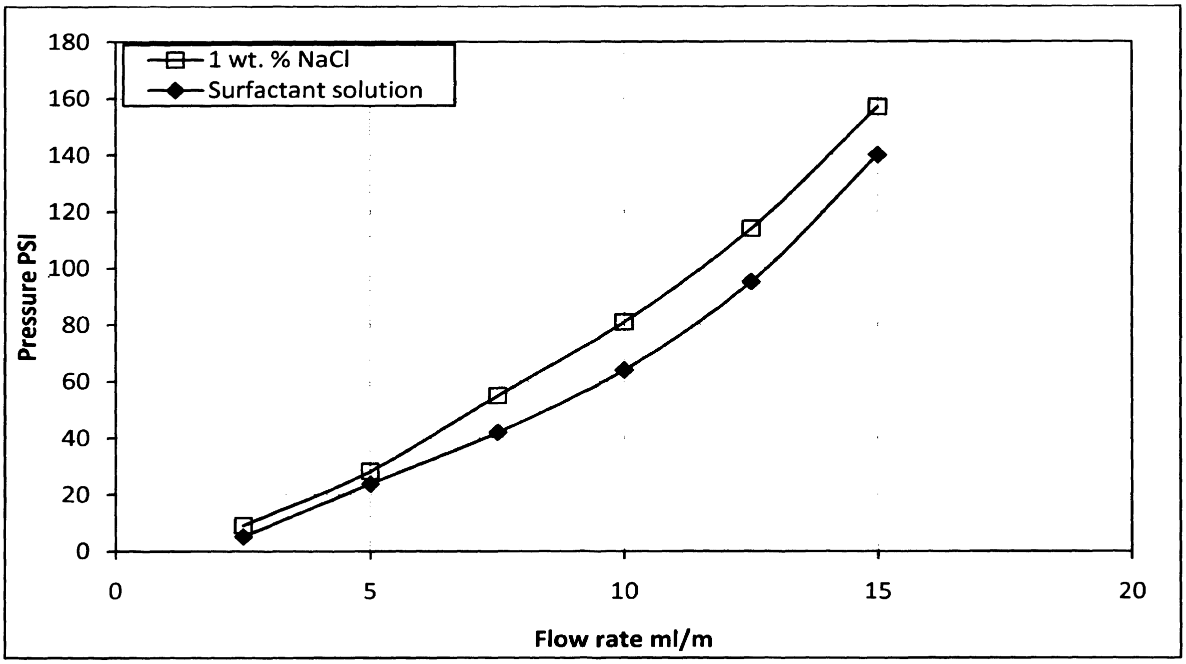


Figure 4.3 Change in injection pressure with flow rate of injected nanoclay gel particles

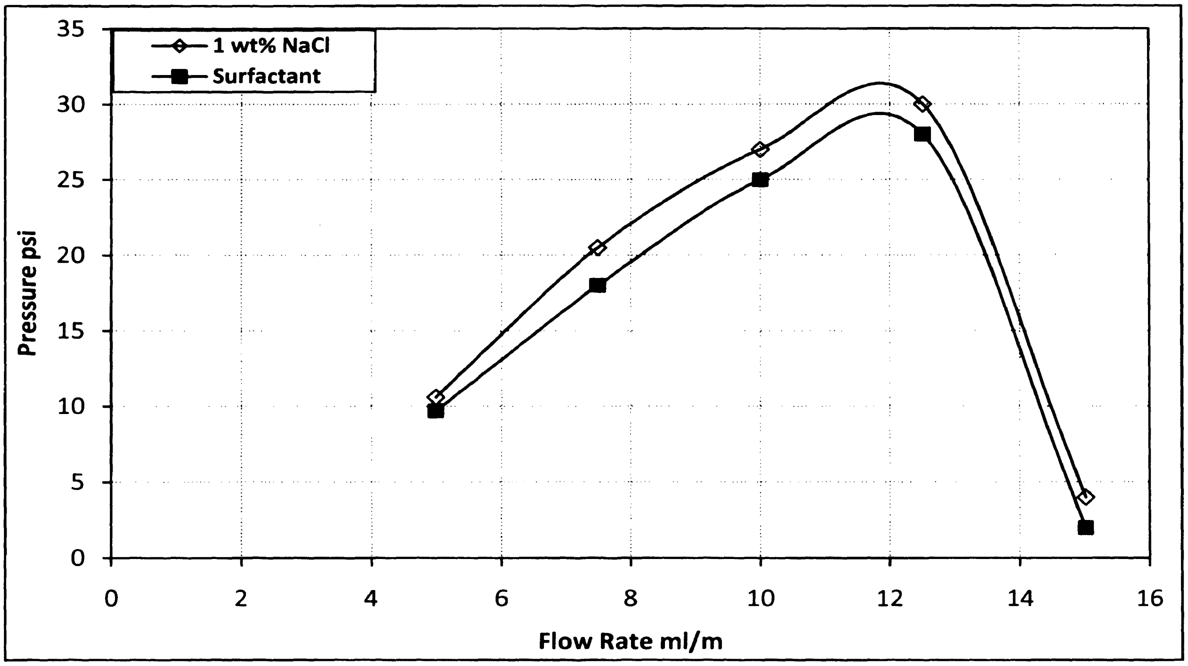


Figure 4.4 Displacement pressure of nanoclay gels with injection of 1 wt % NaCl

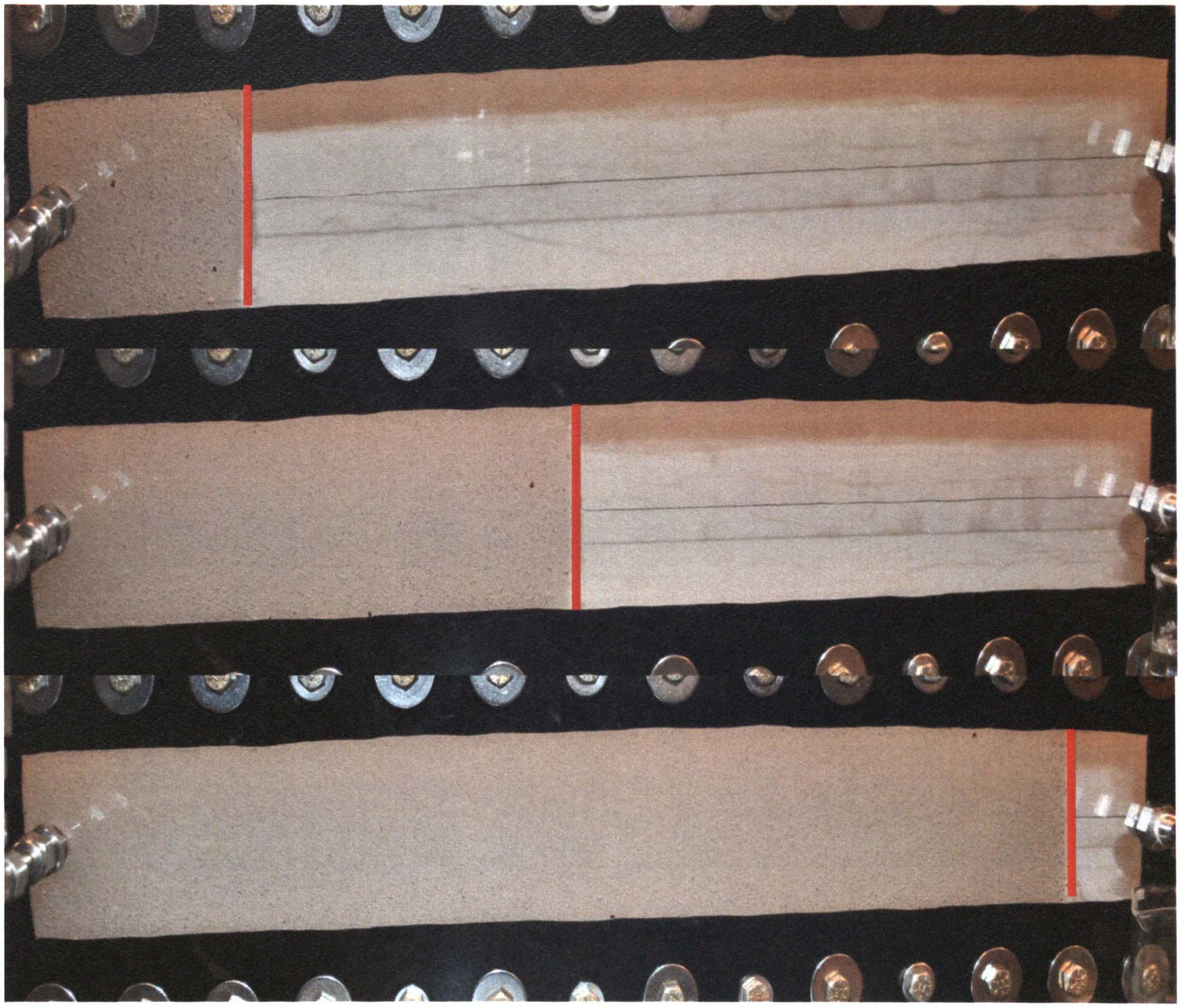


Figure 4.5 Nanoclay gel propagation through fractured model

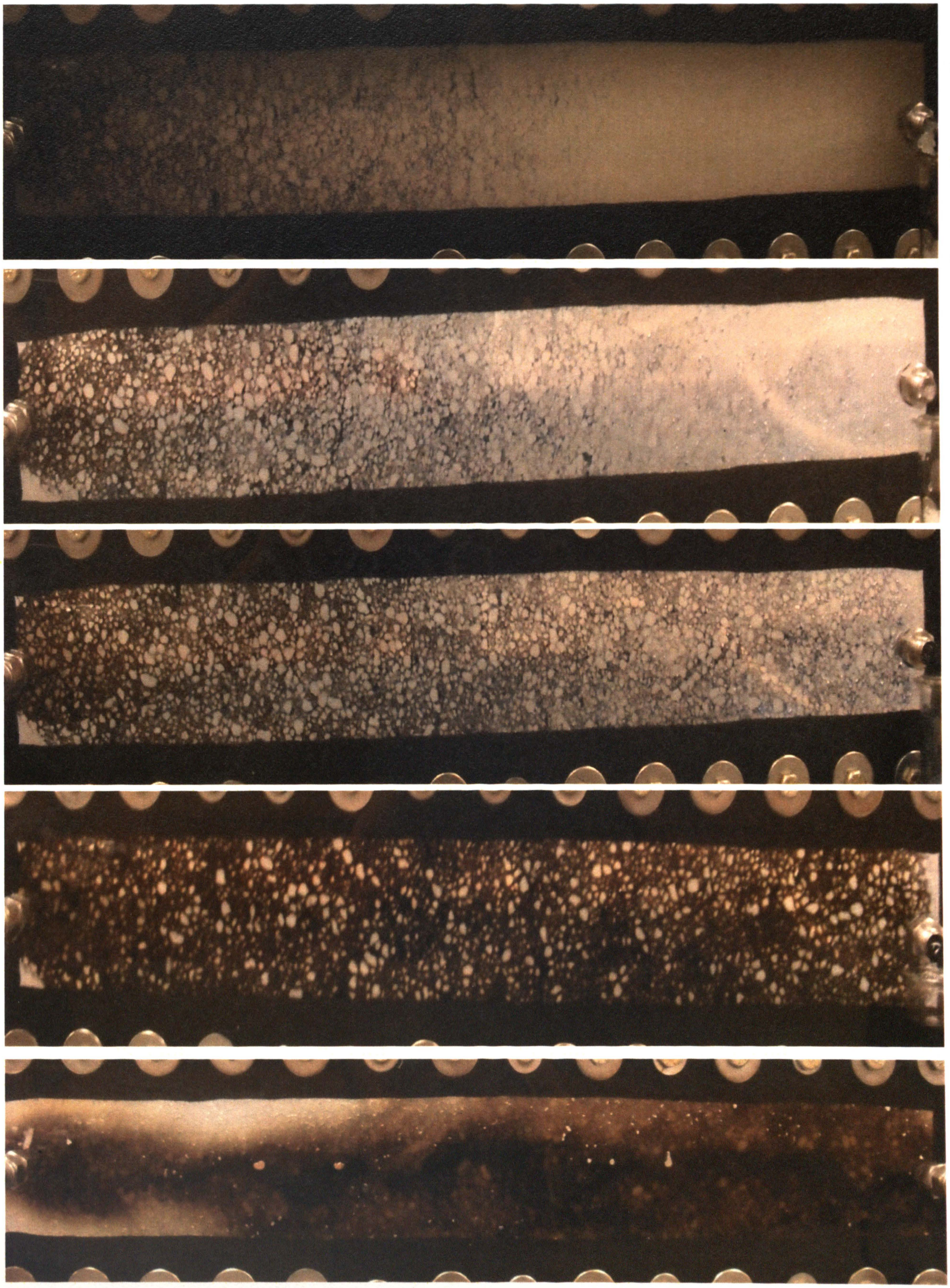


Figure 4.6 Displacement of nanoclay gels from model using dyed brine

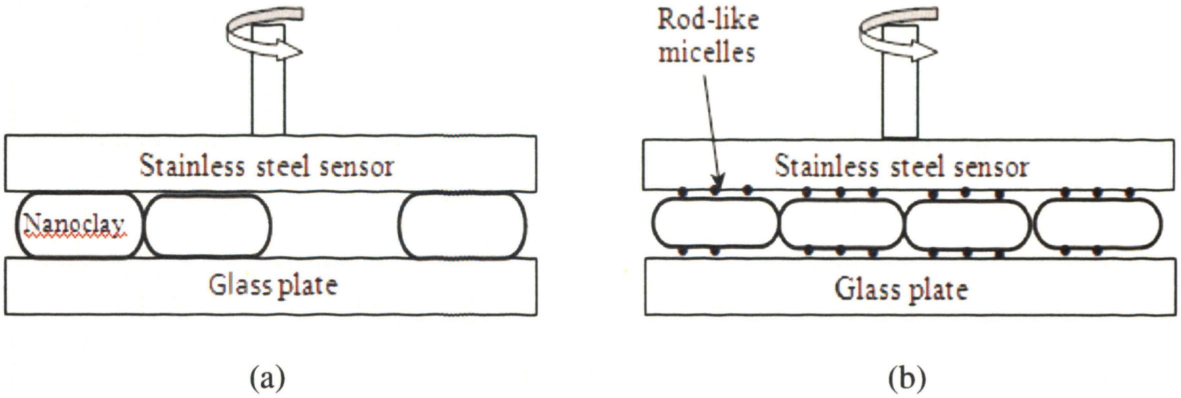


Figure 4.7 Schematic illustration of the mechanism for friction reduction between the surfaces of particle gels, stainless steel sensor and glass plate.

(a) Without addition of surfactant; (b) With addition of surfactant to NaCl brine for the particle gel swelling.

5. CONCLUSIONS, LESSONS LEARNED, AND RECOMMENDATIONS

These section summaries the conclusions drawn from two major experiments described in chapters 3 and 4. It also discusses lessons learned during the course of this research. The chapter will conclude with final thoughts on future work in this area.

5. CONCLUSIONS, LESSONS LEARNED, AND RECOMMENDATIONS

These section summaries the conclusions drawn from two major experiments described in chapters 3 and 4. It also discusses lessons learned during the course of this research. The chapter will conclude with final thoughts on future work in this area.

5.1 CONCLUSIONS

This research supports the following conclusions on the interaction between surfactant and hydrogels and interaction between surfactant and nanoclay gel particles

5.1.1 Interaction between Surfactants and Hydrogels.

- The swelling ratio of the hydrogels was not significantly affected by the surfactant or by the particle size of the hydrogels.
- Surfactant concentration decreased in the cationic surfactants, n-dodecyl pyridinium chloride and (1-hexadecyl) pyridinium bromide.
- The concentrations of the anionic and nonionic surfactants increased after the hydrogel particles swelled in the surfactant solution.
- Hydrogel dynamic moduli can be substantially reduced because the surfactant micelles are adsorbed onto the particle gel surface. These micelles change the friction among the particles and between the particles surfaces and the solid surfaces from sliding or translational motion to rolling motion.
- Surfactants have an enormous influence on hydrogel injectivity; they reduced injection pressure by half compared to hydrogels in a brine solution. The resistance of packed hydrogels to brine was not much affected, which is a good sign that surfactants do not reduce hydrogel resistivity to displacement.

- The injection pressure of hydrogel particles can be significantly reduced by the using proper surfactants.
- Associating surfactant with PPG can be used in oilfields to reduce water production, improve oil recovery, and ultimately reduce the cost of particle gel injection.

5.1.2 Interaction between Surfactants and Nanoclay Gel Particles.

- The swelling ratio of the nanoclay gel particles was not significantly affected by the use of a surfactant or by the size of the gel particles.
- Surfactant concentrations decreased in cationic and nonionic surfactants due to the favorable electrostatic attraction between the clay/hydrogel and surfactant.
- The concentrations of the anionic surfactants increased due to the electrostatic repulsion between the clays/hydrogel and the surfactant. This repulsion inhibited surfactant penetration into the nanocomposites.
- The dynamic moduli of nanoclay gel were affected slightly by the presence of surfactants in the swelling media. However, the storage modulus decreased because surfactants reacted with the particles.
- The surfactants had no significant influence on nanoclay gel injectivity. Meanwhile, the resistance of packed hydrogels to displacement was very limited in both solutions.
- The injectivity of nanocaly gel was higher that the injectivity of hydrogel because clay increased the PPG strength and thus increase injection pressure. However, nanoclay gel had poor resistance to displacement.

5.2 LESSONS LEARNED

This research yielded much information, not just in this area of study, but also in areas related to critical thinking and implementation of ideas. A summary of the lessons learned during this study follow.

- To ensure reliable readings gel particles should be given enough time to reach equilibrium before their swelling ratio is measured. This time may vary from 4 to 8 days.
- Measurement devices must be calibrated before each measurement to ensure accurate results.
- Working in a laboratory could be dangerous work, it is required handling toxic or hazardous chemicals; therefore, precautions and proper apparatus are important.
- Research scheduling is important; a clear schedule must be established at the outset.

5.3 RECOMMENDATIONS

- Different concentrations of surfactants (e.g., 500 ppm or even 1,000 ppm) should be used in future study.
- A radial fracture model should be constructed to understand the extrusion of PPG through fractures.
- Systematic study of the percentage of bentonite in the hydrogel particles would help to understand the interaction between clay gel and surfactants.

BIBLIOGRAPHY

1. A. Abdelhady. (August 2007). "Study of Tertiary oil recovery by surfactant/polymer flooding." www.egyptoil.gas.com.

2. A. Amamath. 1999. "Enhanced Oil Recovery Scoping Study." EPRI Chemicals.

3. A. C. Jackson, (2006). "Experimental study of the benefits of sodium carbonate on surfactants for enhanced oil recovery". University of Texas at Austin.

4. A. H. Kabir. (October 2001). "Chemical water & gas shutoff technology- An overview." SPE Asia Pacific improved oil recovery conference. Kuala Lumpur, Malaysia, 8-9.

5. B. Bai. (2007a). "Preformed Particle Gel for Conformance Control: Factors Affecting its Properties and Applications." SPE Reservoir Evaluation and Engineering 10 (4): 415-421. SPE-89389-PA.

6. B.Bai. (2007b). "Preformed Particle Gel for Conformance Control: Transport Mechanism through Porous Media." SPE Reservoir Evaluation and Engineering 10 (2): 176-184. SPE-89468-PA. Doi: 10.2118/89468-PA.

7. B.Bai. (2008). "Case study on preformed particle gel for in-depth fluid diversion." SPE.DOE improved oil recovery symposium, Tulsa, Oklahoma. USA. 19-23.

8. Bailey. 2000 "Water Control," Oilfield Review.

9. Bob Briall. "Nanoclays-Counting on Consistency."Southern Clay Products, Inc.

10. Catarina G., Paula P., Miguel G. (February 2010). "Self-Assembled Hydrogel Nanoparticles for Drug Delivery Applications." Materials Journal, ISSN 1996-1944.

11. Daniel Borling. (April 1994). "Pushing out the oil with conformance control." Oilfield Review Magazine.

12. David B. Levitt. (Decemer 2006). "Experimental evaluation of high performance EOR surfactants for a dolomite oil reservoir." University of Texas at Austin.

13. Crude oil price: Refiner average domestic crude oil acquisition cost (April 2009). http://tonto.eia.doe.gov/dnav/pet/hist_xls/R1200_3m.xls.

14. F. B. Thomas, D. B. Bennion, R. D. Wood, "Gel Treatment application to reduce water-oil ratio in producing oil wells."

15. Frank F.J. lin George J. Dome Petroleum Ltd Laboratory Evaluation of Crosslinked Polymer and Alkaline/Polymer Flood.

16. F. Wassmuth. (April 2004). "Water shut-off in gas wells: proper gel placement is the key to success." SPE/DOE 15th symposium on improved oil recovery, Tulsa, Oklahoma.U.S.A, 17-21.

17. Glen A. Anderson. (2006). "Simulation of Chemical, Floods Enhanced Oil Recovery Processes Including the Effects of Reservoir Wettability." University of Texas at Austin.

18. G. Lei. (April 2010). "New gel aggregates for water shut-off treatments." SPE improved oil recovery symposium, Tulsa, Oklahoma, USA 24-28.

19. G.P. Hild, R.K. Wackowski (April 1998), "Polymer-gel treatment at rangely weber sand unit." SPE/DOE improved oil recovery symposium, Tulsa Oklahoma, 19-22.

20. G.P. Karmakar, C. Chakraborty. (March 2006). "Improved oil recovery using polymeric gelant: A review." Indian Journal of Chemical Technology, vol.13, pp.162-167.

21. Hao Zhang. (2010). "Preformed Particle Gel Transport through Open Fractures and its Effect on Water Flow." SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 24–28 April 2010.

22. H. Azizi1, J. Morshedian1, M. Barikani1, M. H. Wagner (November, 2010). "Effect of layered silicate nanoclay on the properties of silane crosslinked linear low-density polyethylene (LLDPE)." eXPRESS Polymer Letters Vol.4, No.4 (2010) 252–262.

23. Helena Bysell. (November 2009). "Effect of Hydrophobicity on the interaction between antimicrobial pertides and poly (acrylic acid) microgels." American chemical society.

24. Henry S. Ashbaugh, (November 1999). "Interaction of cationic/nonionic surfactant mixtures with an anionic hydrogel: Absorption equilibrium and thermodynamic." American CHemical Society. 10.1021/la9910778.

25. Hongmin, Y.; Baoquan, Y.; Guorui, X.; Jiexiang, W.; Shao, R.R.; .Weimin, L.; Liang, X.; Haitao, G. (April 2008). "Air Foam Injection for IOR: From Laboratory to Field Implementation in ZhongYuan Oilfield China." (SPE-113913). SPE/DOE Symposium on Improved Oil Recovery, Tulsa, OK, USA, 20–23.

26. J.A. Veil. (January 2004). "A white paper describing produced water from production of crude oil, natural gas, and coal bed methane." U.S. Department of Energy.

27. J.A. Veil. (November 2008). "Water issues associated with heavy oil production." U.S. Department of Energy, National Energy Technology Laboratory.

28. Jean-Louis Salager. (2002). "Surfactants Types and Uses." Laboratory of formulation, Interfaces Rheology and Processes Universidad De Los Andes.

29. J.J. Taber. (August 1997). "EOR screening criteria revisited-part 1: Introduction to screening criteria and enhanced recovery field projects." SPE reservoir engineering.

30. Jian Ping Gong (2006). "Friction and lubrication of hydrogels-its richness and complexity." The royal society of chemistry.

31. L. Taabbodi. (June 2004). "Application of in-depth gel placement for water and carbon dioxide conformance control in carbonate porous media." Canadian international petroleum conference.

32. L. S. Eoff. (February 2006). "Worldwide field application of a polymeric gel system for conformance applications." SPE international symposium and exhibition on formation damage control. Lafayette, LA, 15-17.

33. Lisa Sumi (October 2005). "Produced water from oil and gas production." People's oil and gas summit, Farmington, New Mexico. U.S.A.

34. N. Hain, (July 2004), "Critical aggregation concentration in mixed solutions of anionic polylectrolytes and cationic surfactants." American Chemical Society, 10.1021/la0489918.

35. O.E. Philippova. (December 1995). "Interaction of hydrophobically modified poly (acrylic acid) hydrogels with ionic surfactants." American Chemical Society.

36. Ramanan Krishnamoorti. (November 2006). "Extracting the benefits of nanotechnology for oil industry." Journal of petroleum technology.

37. Per Hansson, Bengt Jonsson. (January 2000 "Determination of micellar aggregation numbers indilute surfactant systems with the fluorencence quenching method." American Chemical Society. 10.1021/jp992444r CCC.
38. Sergey A. Dergunov, Irina Nama, Meruert K. Doldina. (February 2004). "Swelling behavior of chitosan–polyHEA hydrogels in anionic surfactant solutions and their thermo-sensitivity." Colloids and Surfaces A: Physicochem. Eng. Aspects 238.

39. Seright, R.S. (2001). "Gel Propagation through Fractures." SPE Production & Facilities 16 (4): 225-231. SPE-74602-PA. doi: 10.2118/74602-PA.

40. Seright, R.S. (1999). "Gel Treatments for Reducing Channeling in Naturally Fractured Reservoirs." SPE Production & Facilities 14 (4): 269-276. SPE-59095-PA.

41. Seright, R.S. (April 1988). "Placement of Gels to Modify Injection Profiles." Paper SPE 17332 presented at SPE Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, and 16-21.

42. Seright, R.S. and Liang, J-T. (April 1994). "A Survey of Field Applications of Gel Treatments for Water Shutoff." Paper SPE 26991 presented at SPE Latin America/Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina. 27-29.

43. Seright, R.S; Martin, F.D. (February 1993). "Impact of Gelation pH, Rock Permeability, and Lithology on the Performance of a Monomer-Based Gel," SPERE 8(1), Feb 1993, 43-50.

44. Subhash C. Ayirala (December 2002). "Surfactant-Induced Relative Permeability Modifications for Oil Recovery Enhancement." Louisiana State University.

45. Subodh Singh and Ramadan Ahmed. (September 2010)."Vital role of nanopolymers in drilling and stimulations fluid applications." SPE ATCE, Florence, Italy, 19-22.

46. Tiantian Z., Andrew D., Steven L., Chun Hun. (April 2010). "Nanoparticle-Stabilized Emulsion for Applications in Enhanced Oil Recovery." SPE Improved Oil Recovery Symposium, Tulsa OK. USA.

47. Vladimir A. Eduardo M. (2010). "Enhanced Oil Recovery: An Update Review." Energies Journal.

48. William A. Goddard III, Yongchun Tang. (September 2004). "Lower cost methods for improved oil recovery (IOR) via surfactant flooding." California Institute of Technology.

49. Y. Osada and J.-P. Gong, (1998). "Soft and wet materials: Polymer gels." Advanced. Materials 10, 827.

50. Y. M. Mohan. (July 2006). "Poly (N-isopropylacrylamide-co-sodium adrylate) hydrogels: Interactions with surfactants." Www.interscience.wiley.com. DOI 10.1002/app.25448.

51. Y. Misawa. (2008). "Hydrogels based on surfactant-free lonene polymers with N, N#-(p-phenylene) dibenzamide linkages." American Chemical Society.

52. Y. Wu. (2010). "Experimental study of interaction between surfactant and particle hydrogels."

VITA

Farag A. Muhammed was born in Alabrag, Libya on May 12, 1981. He received his B.S. degree in Petroleum Engineering from Altahadi University in Libya in June 2004. He has three years of oilfield experience mostly as a petroleum engineer. His interest and passion for the field of Petroleum Engineering encouraged him to pursue a graduate degree in Petroleum Engineering. He joined Dr. Bai's lab group as a graduate student in August 2009 and started working towards his Master's degree in Petroleum Engineering at Missouri University of Science and Technology. He served as a research assistant for two semesters and as a teaching assistant for one semester in the Well Logging class. Farag actively participated in SPE events organized by the Petroleum Engineering department. In Spring 2011, he received his Master's degree in Petroleum Engineering from Missouri S&T.