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Enze Zhou

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BREAKER EVALUATION AND FORMATION DAMAGE REMEDIATION OF RE-CROSSLINKABLE PREFORMED PARTICLE GEL (RPPG)

by

ENZE ZHOU

A THESIS

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Approved by:

Dr. Baojun Bai, Advisor
Dr. Mingzhen Wei
Dr. Shari Dunn-Norman

ABSTRACT

Re-crosslinkable preformed particle gel (RPPG) is a newly developed preformed particle gel for improving sweep efficiency and oil recovery by blocking or reducing the conductivity of fractures and fracture-like channels or conduits. However, RPPG has the potential to plug the facilities or damage the formation if a treatment is not properly conducted.

This work presents the performance of selected oxidizing breakers on the degradation of RPPG. The influence of a few factors on the degradation process was investigated, including breaker type, breaker concentration, temperature, gel concentration, gel aging time, and gel size. Results indicate that breaker type, concentration, and temperature have the most significant effects on RPPG degradation. $Na_2S_2O_8$ activated by NaOH provided the best degradation performance on RPPG compared with other breakers. RPPG degradation degree increased with breaker concentration and temperature. More generally, lowering the RPPG concentration can result in a better degradation degree. Moreover, the aging time of RPPG had negligible effect on the degradation of RPPG.

Besides the static evaluations of RPPG degradation, several core flooding tests were carried out to analyze the RPPG damage remediation by breakers. The results show that breakers could result in the restoration of the cores' permeability. The lower RPPG injection pressure resulted in a better permeability restoration, and low permeability cores can also result in a better permeability restoration compared higher permeability cores.

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NOMENCLATURE

Symbol	Description
W_a	Weight of RPPG samples after degraded
W_i	Initial weight of RPPG samples
W_R	Weights of dry RPPG particles
W_t	Total weight of RPPG samples
K_i	Initial permeability of cores
K_{aR}	Permeability of cores after RPPG injection
K_{ad}	Permeability of cores after RPPG degradation

1. INTRODUCTION

Conformance is a measure of the uniformity of the front of the driving fluid injected during a flooding operation. The major reason that causes conformance problems is heterogeneity of a reservoir, which may be caused by the development of fractures or fracture-like channels. The existence of fractures or fracture-like channels would lead to excessive water production problem which is the major reason of lower oil production and higher cost for wastewater treatment. Gel treatment has been introduced to be widely used for correcting reservoir heterogeneity problems, which has been proven to be an efficiency and inexpensive method to improve sweep efficient by plugging the high permeability zones. Besides the benefits of gel treatments, the application of this technology can also lead to some potential problems such as plugging the facilities and the formation damage if a treatment is not properly designed and executed.

Using chemical breakers is a main method to cleanup gel and polymer. Commonly used breakers usually include oxidizer and enzyme. Oxidizers react non-specifically with any oxidizable material, which includes hydrocarbons, tubular goods, formation components, and other organic additives [1]. Enzymes are non-toxic and can be readily broken down and absorbed back into the environment and are, therefore regarded as environmentally friendly.

Re-crosslinkable preformed particle gel (RPPG) is a new kind of preformed particle gel (PPG) that can be used to efficiently plug or reduce the permeability of opening fractures. The difference between RPPG and conventional PPG is that RPPG can re-crosslink to form a rubber-like bulky material in the large opening features after placement to significantly enhance the plugging efficiency [2].

There are kinds of literature about the degradation of gel and polymers, however, no study is conducted on the breaker of RPPG. It has the potential to plug the facilities and damage formation if a treatment is not properly designed. Thus, finding out a specific breaker for RPPG cleanup is very important for the application of RPPG.

In this study, NaClO, $Ca(ClO)_2$, $Na_2S_2O_8$ activated by high temperature and NaOH have been selected as breakers. Groups of bottle tests have been conducted to analyze the degradation performance of RPPG. How factors like breaker concentration, temperature, gel concentration, and gel aging time influenced the degradation degree of gels have also been studied. Moreover, the damage remediation of RPPG treatment has been investigated by performing core flooding experiments.

2. LITERATURE REVIEW

This section introduces background information for the research. The first subsection provides information about gel treatment which includes gel treatment purposes, gel types, and the potential problems that residual gel may cause. The following subsection focuses on the gel degradation background including the mechanisms of gel degradation, factors which affect degradation, and the methods to determine the gel degradation performance.

2.1. GEL TREATMENT INTRODUCTION

Heterogeneity is one of the major reasons that cause conformance problems and unfavorable oil recovery. Reservoir heterogeneity might result in the development of high-permeability streaks and fracture. And high-permeability streaks and fracture will cause the formation of water channeling which will result in low oil recovery and excessive water production. Excessive water production from a hydrocarbon reservoir is the most common challenge during the production of oil and gas. The significant amount of excessive produced water results in corrosion and scales, an increased load on fluid handling facilities, more environmental concerns, and shorted economic life of wells.

2.1.1. Gel Treatment Purposes. There are many methods used to reduce excessive water production. Chemical conformance/water-control technologies is one of the methods which are widely used for correcting reservoir heterogeneity problems. Gel treatment is one of the widely used chemical treatment technologies that has been proved to be an efficient and economical method to block or reduce the conductivity of high permeability channels, thus resulting in the improvement of sweep efficiency.

2.1.2. General Types of Gels. Gel systems usually consist of water-soluble polymers or monomers, cross linkers, and other auxiliary reagents. The types of gel being applied can be divided into conventional in-situ polymer gels (immature gels); preformed gels (mature gels); and foamed gels as Figure 2.1 shown [3].

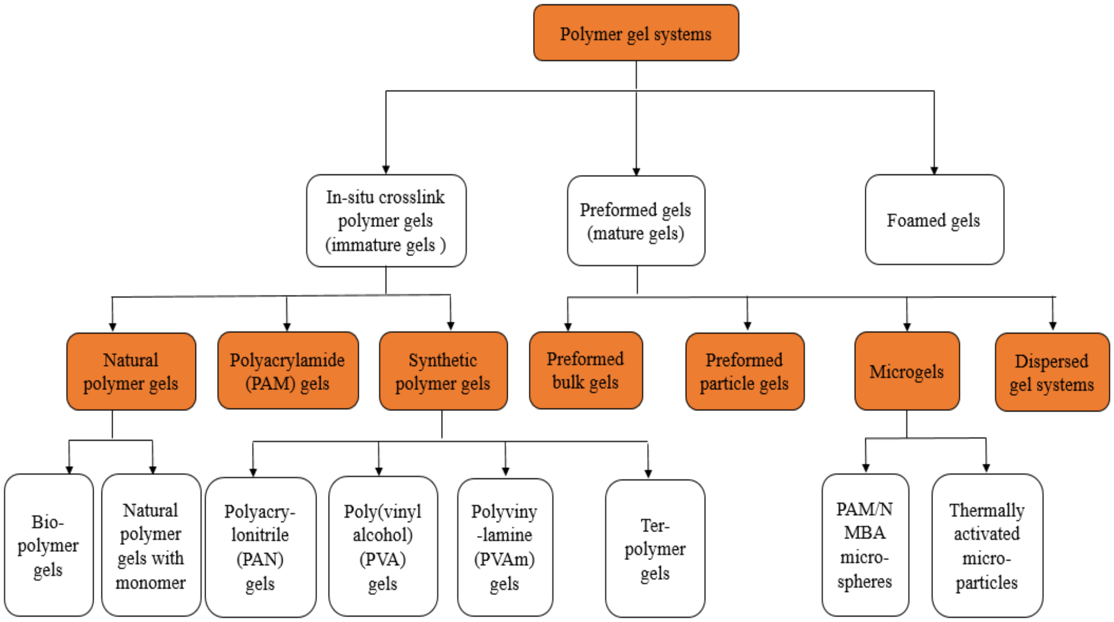
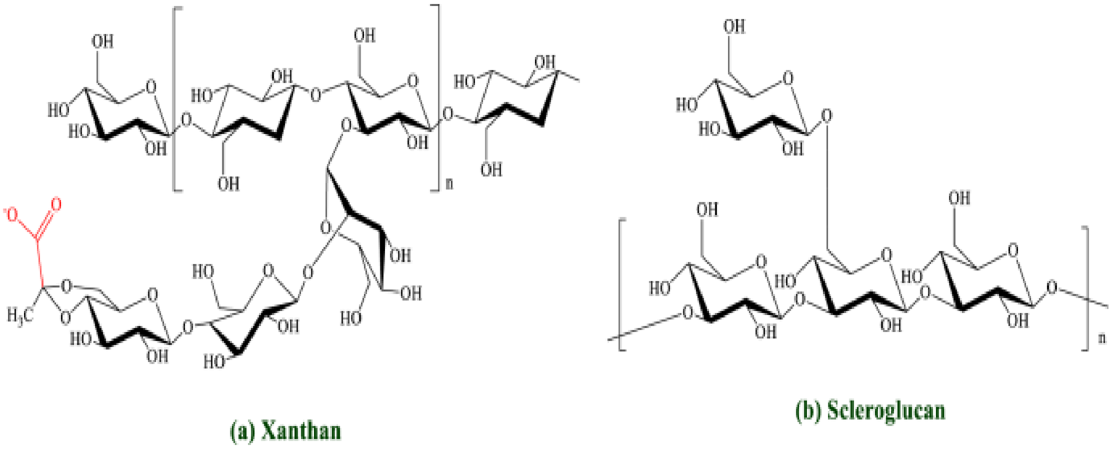


Figure 2.1. Classifications of polymer gel systems [3]

2.1.2.1. In-situ crosslink polymer gels. In-situ crosslink polymer gels are the most commonly used gel system for conformance control. There are two major factors need to be considered for conventional in-situ polymer gels: thermal stability, gels should stay in the structure for a long period; and gelation time, gels need to suit the oilfield applications. Normally, in-situ crosslink polymer gels can be divided into natural polymers, polyacrylamide (PAM) gels, and synthetic polymer gels [3].

Natural polymers. Natural polymers include guar gum, lignin, tannin, and so on. These polymers can be cross-linked by inorganic cross linker systems like aluminum (Al^{3+}), chromium (Cr^{3+}) and zirconium (Zr^{4+}) or organic cross linker systems such as aldehydes and polyethylene-mines. Natural polymer gels can be divided into biopolymer gels and natural polymers with monomer.

Biopolymer gels are formed by crosslinking the biopolymers with organic or inorganic crosslinking agents. Polymer self-induced gels are a kind of biopolymer gel system which involves the injection of the polymer into the treated reservoir volume in the form of an alkaline high-pH solution. The pH of the polymer solution is reduced by spontaneous or induced means since the polymer is emplaced in the reservoir rock. The polymer solution spontaneously forms a gel as the pH of the solution decreases [4]. The most commonly used biopolymer gels are xanthan gum and (nonionic) scleroglucan polysaccharide, their chemical structures are shown in Figure 2.2.



(a) Xanthan

(b) Scleroglucan

Figure 2.2. Chemical structures of (a) xanthan gum and (b) scleroglucan polysaccharide [3]

Polyacrylamide (PAM) gels. Polyacrylamide (PAM) gels can provide better gel strength and viscosity compared with polymer, this kind of gels is mainly used for plugging the high permeability fractures. The structures of PAM are shown in Figure 2.3. Varies types polyacrylamide (PAM) gels have been developed to meet the purpose of conformance control, the most widely used PAM are Cr(III)-carboxylate/acrylamide-polymer (CC/AP) gels and aluminum cross-linked gels.

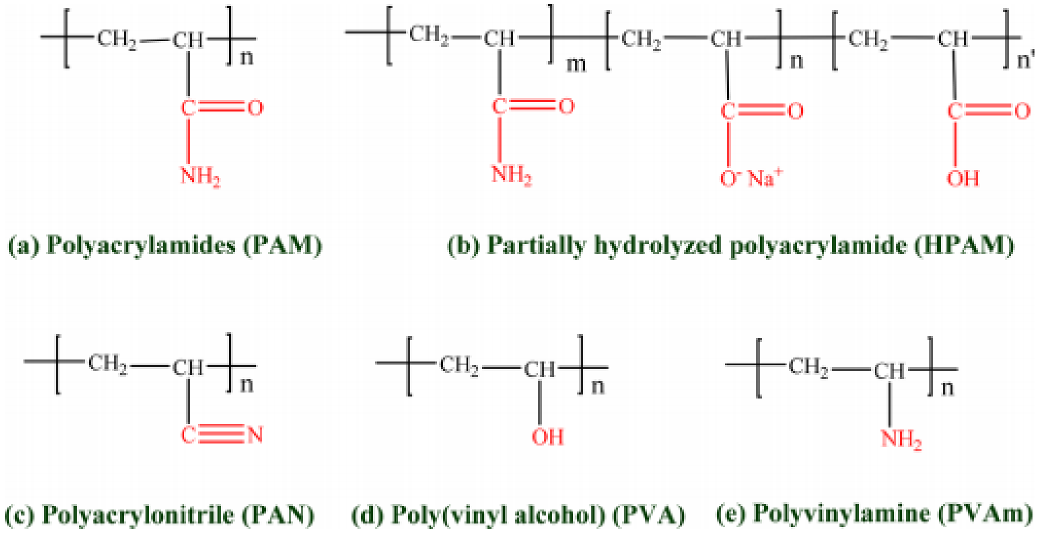


Figure 2.3. Chemical structures of different polymer [3]

CC / AP gels are water-based gels which are widely and successfully applied in the oil field for conformance control. The chromium triacetate compound is typically the preferred Cr(III)-carboxylate cross linker used in conjunction with the gel technique [5]. Over 1400 CC/AP gel treatments, which have been applied for conformance control in order to deal the conformance and fluid-shutoff problems in a wide range, have been performed worldwide [6]. This kind of gels can be applied to a broad pH and temperature range and the crosslinking agents are relatively nontoxic. Also, CC/AP gels have a wide range of gel strength and gelation time.

Aluminum cross-linked gels are aluminum citrated gels which conducted in the sequential-injection mode, involving the repeated sequential injection of aqueous slugs containing, the polymers and the aluminum citrated crosslinking agents. When adding aluminum to a HAPM solution, metal ions will react with carboxyl group [7]. Recently, aluminum citrate-acrylamide-polymer gels formulated with low concentrations (200 to 1200 ppm) of polymer and known as colloidal dispersion gels (CDG) have been widely used as large-volume treatments applied through injection wells to “matrix rock” for improvement of water-flood sweep efficiency [8]. CDGs of acrylamide polymer cross-linked with aluminum citrate are not easily injected and can propagate through normal permeability matrix rocks [9]. Aluminum crosslinking of polymer of CDGs normally occur within several hours and aluminum-citrate CDGs do not viscosity water compared with gel’s polymer without the addition of crosslinking chemical [10].

Organically cross-linked gels are another kind of PAM gels. The purpose of gel cross-linked with an organic cross linker is to using benign organic chemical crosslinking agents which would impart carbon-carbon-bond chemical crosslinks between the gel polymer molecules. The introduction of organic cross linker will result in strong and stable polymer gels. The majority of organically cross-linked polymer-gel technologies developed are based on phenol-formaldehyde chemistries. Attempts have been made to identify and use less toxic and environmentally friendly phenol and formaldehyde derivatives as cross linkers [11].

Synthetic polymer gels. Synthetic polymer gels can be classified into polyacrylonitrile (PAN), poly(vinyl alcohol) (PVA), polyvinylamine (PVAm), and copolymers based on acrylamide (AM) monomers. The structures of those polymers are shown in Figure 2.3.

Polyacrylonitrile (PAN) systems are stable when the temperature up to 150ºC, while, the cross-linking reactions have a more severe effect on pH, which may greatly reduce the range of water management applications. Poly(vinyl alcohol) (PVA), a commercial polymer derived from polyvinyl acetate can be cross-linked by large concentrations of phenol to produce a thermally stable polymer gel [12]. PVAs are not widely used due to its thermal stability problem and the tendency to adsorb on the surface of matrix which may cause problems with the ability of the gel to propagate in the formation.

2.1.2.2. Preformed gels. Preformed gels are formed at the surface, then dried and crushed into small particles to be injected into the reservoir. Preformed gels are designed to overcome some inherent drawbacks such as the change of gelant composition during placement, gelation uncertainly, and uncontrollability [13] [14] [15]. Preformed gels can be classified into 4 types: preformed bulk gels, preformed particle gels (PPG), micro-gels, and dispersed particle gels (DPGs).

Preformed bulk gels. Preformed bulk gels are the gels that re-crosslink in the surface facility before injection. This kind of gels is mainly used for opening fractures, fractures-like channels, or conduits. Due to the high viscosity, pre-formed bulk gels are inhibited from passing through the pore throat and cannot propagate through porous media, which means that potential oil zones are not damaged [3].

Preformed particle gels. Preformed particle gels (PPGs) are dried, crushed and solid particles with the desired size. Particle gels have been applied as a conformance-control treatment to deal with the conformance problems result from reservoir heterogeneity. PPGs are prepared by mixing AM, a cross-linker (e.g., MBA), an initiator (e.g., peroxydisulfate), and other additives [13]. PPGs are slightly sensitive to physical-chemical conditions such as pH, salinity, multivalent ions, H_2S, temperature, and shear rate [7]. PPGs have advantages such as controllable gel strength and size, environment-friendly, stable with the existing of almost all reservoir minerals and water salinities, and only one component during injection. Thus, PPGs have been used to deal with the excessive water production problems or reduce polymer production problems in more than 2000 wells in China [17] [18].

Micro-gels. Micro-gels are developed to deal with the contradiction between injection depth and in-depth plugging efficiency of PPGs which also known as macro-gels. This problem will increase the risk of failing for profile improvement. The difference in the gels' structure between micro-gels and macro-gels is shown in Figure 2.4.

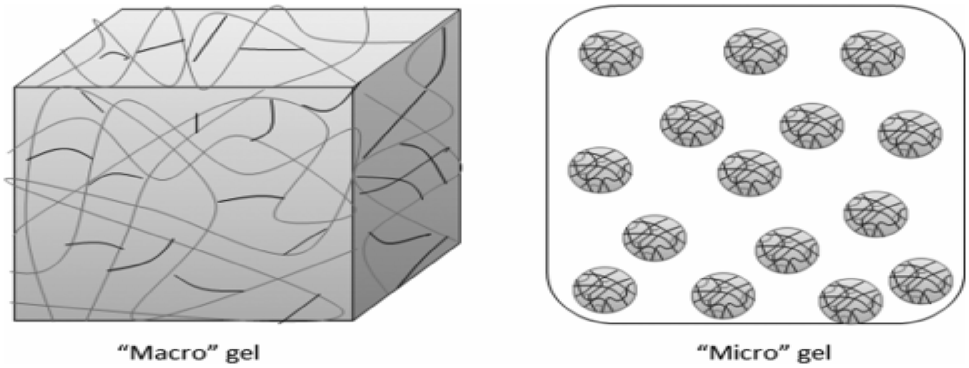


Figure 2.4. Illustration of the structural difference between macro-gels and micro-gels [15]

Micro-gels can be divided into two types: PAM/MBA microspheres and thermally activated micro-particles (Bright Water). These two technologies provide in-depth profile improvement applications in high permeability areas that are responsible for capturing most of the injected water, resulting in poor reservoir cleaning efficiency [3]. Thus, the application of micro-gels can block the high permeability layers and direct water into less-swept or un-swept areas to recover more oil [14].

Dispersed particle gels (DPGs). Dispersed particle gels (DPGs) are prepared by a conventional in-situ polymer gel systems using a colloid mill having a high shear rate on the surface equipment. The mechanism of the DPGs composed is shown in Figure 2.5. Experiments show that DPGs can block the high permeability areas significantly at 80ºC. In addition, the DPG particles will be deformed by the displacement force to propagate through the pore throat, which contributes to the performance of the in-depth profile modification [16].

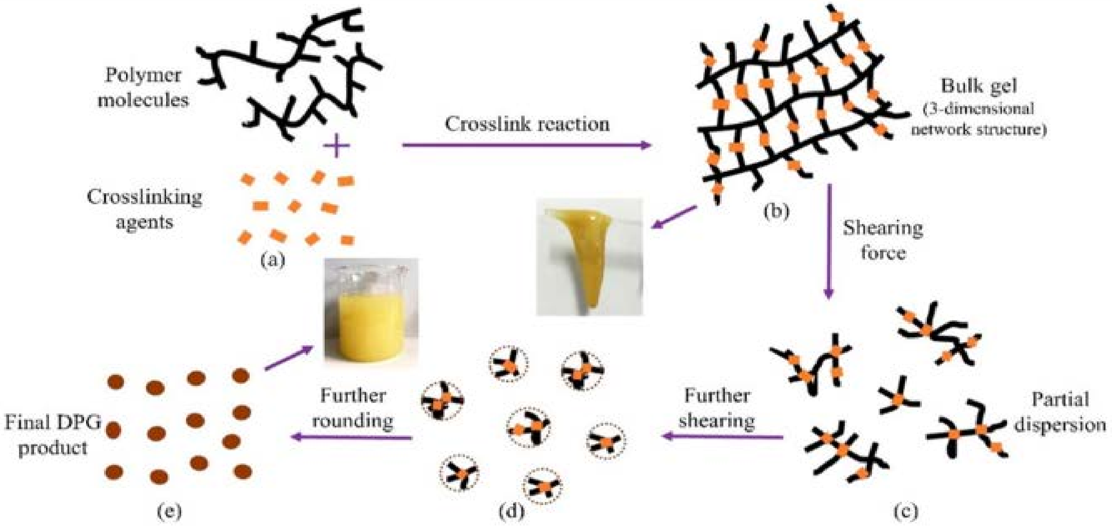


Figure 2.5. Proposed formation mechanism of the DPGs composed of nonionic HPAM and the phenol−formaldehyde cross-linking system [16]

2.1.2.3. Foamed gels. Foamed gels are used to block the high permeability areas in the reservoirs. The lamella of the foam systems is the major difference between conventional foams and foamed foams. For common bulk foams, the lamella is only stabilized by surfactants because surfactants reduce interfacial tension; however, for foam gels, the lamella is stabilized by a more viscous gelants during and after gelation [3]. The application of this new technology can reduce the treatment costs significantly due to its lower gelant concentration compared with conventional gel treatment.

2.1.3. Potential Problems of Gel Treatment. The applications of gels treatments can solve the conformance problem and improve oil recovery. However, after the gel treatment, the residue gels need to be cleanup as soon as possible, otherwise, those residue gels can cause some negative effects on the production. First, the residue gels may plug the facilities such as injection pumps and pipelines which may lead to a significantly increase of pressure in the injection facilities. Second, in some cases, the complete gel injection may have negative effects on the production, the oil recovery decreases instead of increasing, the major reason causes this phenomenon is the fracture conductivity or the near fracture reservoir permeability reducing and the increasing of fracture choke skin and fracture skin [17]. Moreover, the residue gels may result in the damage of the formation. The formation damage degree is controlled by the gel properties and rock permeability interactions [18]. Thus, it is necessary to find the methods to remove the residue gel after gels treatments.

2.2. GEL DEGRADATION

The most commonly used method for removing gels is using breakers to degrade the gels. Varies types of breakers have been found to clean up the remaining gels.

2.2.1. General Types of Breakers and Its Mechanism. Oxidizer and enzyme are two most widely used breakers around both laboratory and industry. Moreover, there are some other materials which also can degrade the residue gels, such as acid and metal ions. Different breakers, using at different concentration and temperature will result in different degradation degree.

2.2.1.1. Oxidizer. Oxidative breakers are widely applied in fracturing applications. Oxidizers react non-specifically with any oxidizable materials, such as hydrocarbons, tubes, formation components, and other organic additives [1]. The process by which the oxidant works is the release of free radicals that act on the oxidizable bonds or sites which are susceptible. Free radicals are charged ions with unpaired electrons and are highly reactive because of the natural tendency to form electron pair bonds, and can generate free radicals by stabilizing the thermal or catalytic activation of oxidizing species [19]. Figure 2.6 and Figure 2.7 below show the structure of re-crosslinkable particle gels (RPPG) before and after degradation.

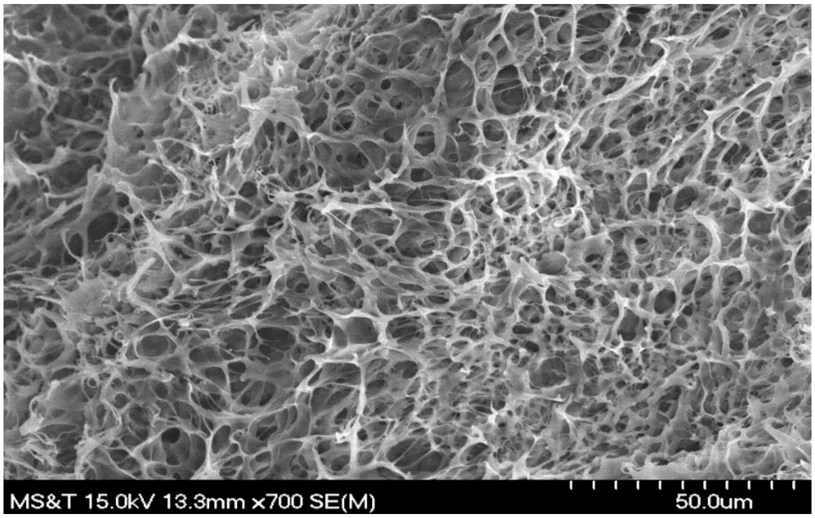


Figure 2.6. Structure of RPPG before degradation

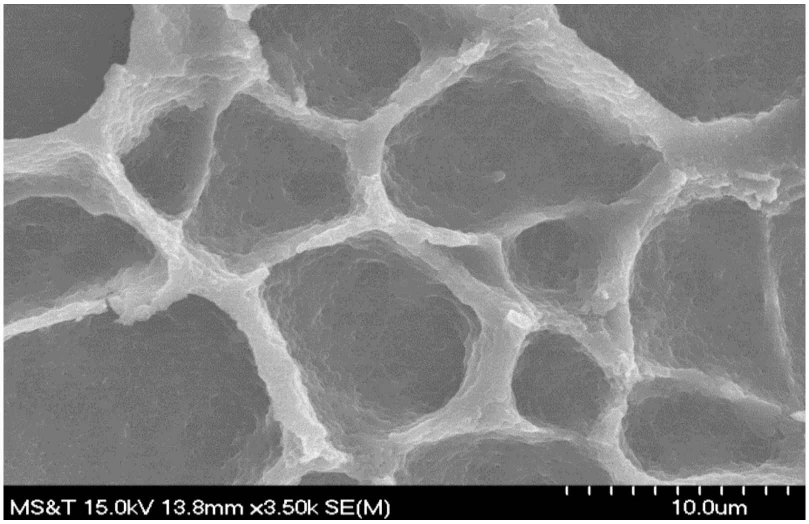


Figure 2.7. Structure of RPPG after degradation

Reactions involving free radicals are often very rapid. Usually, the oxidizing breaker was used for the intermediate temperature around 50°C to 120°C. The viscosity of the gel and the molecular weight of the polymer would reduce significantly after reacting with oxidizers to allow rapid cleanup of the formation [20].

Persulfate salts are the most common oxidative breakers used in fracturing fluids. And the most commonly used persulfate salt is ammonium peroxydisulfate (APS) due to its higher solubility in water than other persulfate salts. ASP is widely used in the fracture fluid treatment, it can degrade several types of gels including guar gum and hydroxyl-propyl guar (HPG). When temperature is below 125°F, persulfates must be activated by the addition of catalysts. When persulfates are catalytically activated, one of the free radicals is consumed by the catalysis [21]. Persulfate catalysts include tertiary amines, ethyl acetoacetate, and reactive metal ions such as iron in the ferric (Fe^{+3}) state [19]. Free radical breakers have the potential to generate free radicals on polymer molecules and produce chain reactions, thereby increasing the efficiency of the breaker [22]. With the increase of temperature, APS radical generation occurs more rapidly. When the temperature is above 125ºC, APS can degrade the gel by itself.

Another oxidizer breaker has been used is hydrogen peroxide (H_2O_2). This kind of breaker is mainly used to degrade hydrolyzed polyacrylamide (HPAM), it can greatly improve the HPAM degradation especially at high temperature [23]. The main causes of HPAM degradation are the strong reduction-oxidation of hydroquinone and generation of H_2O_2. However, during the degradation, it will produce oxygen which is very dangerous for oil production and may result in explosion. Thus, this kind of breaker is rarely used at current production.

Besides persulfate salts and hydrogen peroxide, there are also some other oxidizer breakers being used, such as sodium hypochlorite and calcium hypochlorite. For sodium hypochlorite and calcium hypochlorite, the hypochlorite ions are the major reason that causes the degradation of gel. While the application of NaClO will cause many safety issues. First, NaClO is not stable and it will decompose and produce oxygen when contact with acids, sunlight, certain metals, and poisonous and corrosive gases, the decomposition of NaClO will lead the damage of the reservoirs. Second, the oxygen produced by the decomposition of NaClO may mix up with some gas in the reservoirs and cause explosion. Finally, it is not combustible but is a strong oxidation which will enhance the combustion of other substances. Besides the safety issues, it is very hard to separate the chloride from the crude oil. Base on those reasons, the application of NaClO as a breaker in the oil and gas production will not generate the results as expected due to the narrow range of application, cost, and safety issues of those breakers.

2.2.1.2. Enzyme. Enzymes are large, highly specialized proteins produced by organisms that consist of long-chain amino acids joined together by peptide bonds. [19]Enzymes can be regarded as environmentally friendly because they are non-toxic and can be readily broken down and absorbed back into the environment. Conventional enzymes used in the oil industry are non-specific enzyme substrate by randomly mixing hydrolyze the base polymer or cause irreversible and/or competitive inhibition [24]. Several kinds of enzymes have been developed to address the cellulose-based, guar-based, and starch-based polymer. Identification and optimization of the ability of each specific polymer-specific system to hydrolyze specific bonds within the target polymer chain [1].

Enzymes have the ability to accelerate chemical reactions as catalysts. The catalytic activity does not change the enzyme’s structure during the start of the reaction, so the enzyme can trigger another enzyme [19]. The mechanism of enzymes’ degradation is shown below in Figure 2.8. The reaction of the enzymes begin with the "lock and bond" principle, which means that in order to react with the substrate, the particular enzyme must have a three-dimensional configuration and an active site that is specifically complementary to the substrate site which it is to react, otherwise, if the shape of the enzyme is not completely complementary to the shape of the substrate, similar to the key of the assembly lock, the reaction will not proceed [25]. Therefore, enzymes that react with those specific substrate sites that they can align and match are very limited. All enzymes can perform their specific reaction without being changed in the process, which allows one enzyme strand to break many polymer molecules in succession. This makes them much more attractive than oxidizers as a breaker system, as oxidizers break one linkage site and are exhausted.

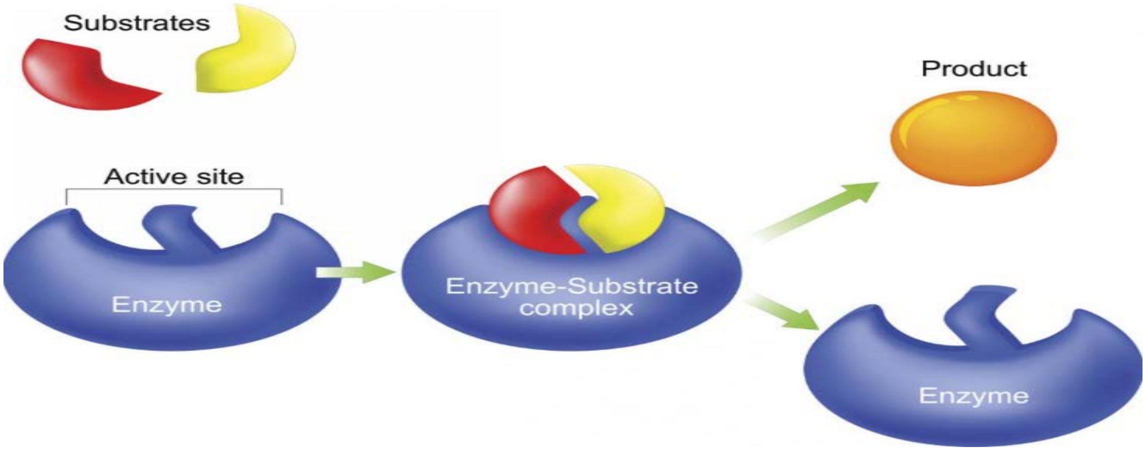


Figure 2.8. Enzymes degradation mechanism

2.2.1.3. Other materials. Besides oxidizers and enzymes, there are still some other materials which can result in the degradation of gels, including acids and irons. The reaction mechanism of those materials is not same with the chemical breakers, however, all of them can degrade the gels. Hydrochloric acid (HCl) is the most often used acid as a breaker. When HCl is combined with gel treatment, it shows promising results as an effective technique for removing gel cakes formed in low permeability areas [26]. Moreover, the existing iron can also degrade the gels. By compared the conditions of polymer in glass and steel bottle, the results showed that the polymers were not degraded when stored in glass bottles and were severely degraded when stored in stainless steel bottles, indicating that the main chemical degradation in this case was oxidation in the presence of iron [27].

2.2.2. Factors Affect Gel Degradation. There are several factors involved in the degradation of these polymers which could potentially affect the amount of residue remaining from polymer: breaker type, breaker concentration, and break temperature [28], those factors have the most significant effect on degradation.

Besides those factors, concentration of gels, pH of the solutions, and the amount of ions in the solutions can also affect the degradation degree of gels [23]. In addition, the fracture mechanism plays an important role in determining the performance of degradation of the gels [28]. Even for the same gel samples, the degradation results will be different at different conditions. Thus, it is very necessary to analyze those factors' effect on the degradation degree of gels.

2.2.2.1. Gel type and concentration. Different kinds of gels have been developed for varies of conditions, and same breaker degrades different gels may lead to totally different results. For example, using APS with same concentration to degrade HPG and guar gel, the rate of degradation of HPG was faster than guar gel, and the residue of HPG was less [20]. While different kinds of gels would have different amount of residue after degradation, the amount of residue mainly depends on the insoluble materials in the gels. Thus, before the cleanup of residue gels, the selection of breakers needs to be considered carefully. For the effect of gel concentration, lowering the polymer concentration leads to a decrease in polymers residue during gel degradation, but the insoluble polymer residue from the broken polymer still causes clogging and reduces formation productivity [29]. As the polymer loading increases, the amount of residue increases [20].

2.2.2.2. Breaker types and concentration. The breaker types used to degrade gels are very important. Since each type of breaker operates under different mechanism to degrade the polymer, each breaker produces a series of different factors that affect the amount of residue [28]. There are mainly two types of breakers, oxidizers and enzymes. Ammonium peroxydisulfate (APS) is one of the most commonly used oxidizers. And the most widely used enzyme is linkage specific enzymes (LSE). Enzyme breakers were observed to provide more efficient molecular weight reduction than oxidative breakers. Studies have shown that enzyme breakers continue to catalyze the molecular weight reduction of polymers for at least eight weeks [19]. However, their temperature and pH limitations have made them undesirable for reliable gels degradation in some field applications [30]. Thus, based on the different conditions of different reservoirs, different types of breakers can be selected to address the purpose of degradation. Moreover, different breakers break the gel in different way results in various breaking time. The time required to degrade the gels was found to be a function of the types of breaker and the initial concentration, and in addition, the amount of residue was related to these factors [22].

The increasing of breaker concentration will short the time for degradation and increase the degradation degree. However, the high concentration of breakers is needed to reduce the damage to the pack [31]. Also the cost of breakers for gels cleanup is another factor need to be considered. Before the applications, several tests need to be done to determine the concentration that can meet both degradation performance as expected and lowest cost.

2.2.2.3. Temperature. Temperature is one of the most important factors which affect the degradation performance of gels. While different kinds of breakers have different application temperature ranges, when the temperature above the highest application temperature, the breakers may decompose which will reduce the degradation effect [21]. With a higher temperature, even do not add breakers, the viscosity of gel will decrease which is similar to gel degradation. The reason is that the reaction kinetics of the temperature-activated cross-linking agent (for example, a delayed titanate system) accelerates at an elevated temperature, so the reaction kinetics become a major factor in controlling the structure and viscosity of the gel [32]. For example, as temperature increased from 150ºF to 175ºF, the kinetics of HPG crosslinking reaction accelerated, causing the initial viscosity to increase, while when the temperature raised to 200ºF, the viscosity decreased [31]. Temperature can also shorten the time required for degrading gels to expected degradation performance, and the use of polymer aggregate dispersants can reduce pore blockage at high temperatures, resulting in retained permeability up to 150% more than separate breakers [33].

However, it does not mean that the higher the temperature, the better the degradation degree. Different breakers have different temperature application ranges, if the temperature is above the range, then the degradation degree will decrease. Especially for enzymes, when the temperature is 75ºF, enzymes have a better degradation performance compared with oxidizer breakers, while when the temperature increase to 175ºF, enzyme breakers are observed to be ineffective for molecular weight reduction [1]. Furthermore, for the application of oxidizers, there are still temperature limitations existed. If the temperature is too high, the breakers may decompose and lose the ability to degrade gels. Thus, the temperature of the reservoirs can control what kinds of breakers used. Different kinds of oxidizers have different application temperature ranges. Ammonium persulfate (APS) is found to provide the greatest degradation effect over the range of 125ºF to 225ºF, magnesium peroxide have better degradation effect than sodium bromate between 200ºF to 240ºF, while sodium bromate is more effective from 250ºF [21].

2.2.2.4. Amount of ions and pH of the solutions. Besides the gel types and concentration, breaker types and concentration, and temperature, the amount of ions and pH values of the solutions can also affect the degradation processes of gels. Thus, the amount of ions and the pH value need to be considered before applying the breakers.

For the influence of ions, the degradation performance of the gels is significantly affected by the type of ions in the produced water, and decreases in the order of $Al^{3+}>Mg^{2+}>Ca^{2+}>Na^{+}$ with same ion concentration [23]. The salinity of ions with higher electron charge have great effect on gels degradation. For example, by using Al^{3+}, HPAM can degrade to 90% because of the agglomeration reaction between Al^{3+} and the gel molecules, the equilibrium of the attraction between the gel molecules was broken, and the molecular chain broke [23]. Thus, the amount of the ions in the formation of water also need to be considered before gel cleanup.

For the effect of pH values, pH can affect the degradation process, specifically for enzymes. The application environments for enzymes are usually recommended for slightly acidic [34]. When the value of pH is 3 to 5, enzymes are most active and have the highest reaction rate, when the value is 8, the reaction rate decreases, with the value of pH increasing to 10, enzymes are inactive but still can degrade gels when pH decreased, while when pH increases to 12, enzymes denature and cannot degrade gels anymore [30]. Therefore, it is vital to control the value of pH when using enzymes as breakers.

2.2.3. Properties to Evaluate Gel Degradation. After the degradation treatments being applied, the degradation performance of the gels needed to be evaluated. There are several properties can be used to evaluate the degradation performance, including viscosity and concentration of gels, and the residue weights of gels. However, the degradation of gels does not mean the fluid return because after degradation there are lots of residues left to damage the permeability of cores [35].

Thus, after using those properties to ensure the degradation of gels, the evaluations also need to analyze the molecule weights and sizes and used core flooding test to measure the permeability of cores to make sure the cleanup of gels is successful.

2.2.3.1. Viscosity and concentration of gels. Viscosity of the solution is the most commonly used property to evaluate the degradation performance of gels. By using viscometer to measure the viscosity before and after gels degradation, it is very easy to determine the degradation performance of gels. Cross linker reaction kinetics and flow conditions control the viscosity of gels [32]. Thus, the degradation will cause the reducing of viscosity.

Moreover, the degradation performance can be evaluated by the measuring of gels concentrations in the solution. This can be achieved by using the test VIS 722 Spectrophotometer with a wavelength accuracy of 2 nm [23]. During degradation, the concentration of gels reduced. The degradation performance can be determined by calculating the ratio of the concentration changed to the initial concentration. However, the reducing of viscosity or gel concentration did not mean reducing of molecule weight and size [25], may still cause the damage of permeability.

2.2.3.2. Residue weights of gels. The measurement of the residue is called residue-after break (RBA) test, the purpose of the RBA test is to measure the residue of the gels and the amount of unbroken gel after the gel was broken [21].

The weight of the residue was measured and compared with the initial weight to calculate the degradation degree. It should be noted that this method has errors and the results are not very accuracy [33]. The errors may be caused by the measurement errors and the volatile particles in the gels.

2.2.3.3. Molecule weights and size of residue gels. The molecule weights of gels after degradation can be determined by using an Ultra-Filtration Molecular Weight cutoff technique [24]. The measurements are helpful to further evaluate the degradation performance of gels and the damage restorations. The molecule weights decrease during degradation, and different types of breakers result in different molecular weights reducing. For example, enzymes will result in lower molecular weights compared with APS when using to degrade guar-gum [1].

The molecule size of the broken gels is another property used to determine the degradation degree. The size of the molecules can be measured by using size exclusion chromatography (SEC). SEC is a high pressure liquid chromatographic technique which distinguishes the molecules based on size [35]. Because the reducing of viscosity does not mean the pack damage will not happen [35], SEC is very helpful to evaluate the permeability damage restoration.

2.2.3.4. Core flooding test. Core-flooding-tests is the most direct method to evaluate the permeability damage and restore conditions of gels treatments. Core flooding tests measure the permeability of cores before and after gels being degraded. The core flooding tests can also be used to evaluate the degradation performance of a kind of breaker [36]. The restoration of the permeability can show the degradation degree of gels significantly. While if the matrix of the core is degraded by the application of breakers also needs to be determined before applying a kind of breaker for gels cleanup.

Overall, to have a better evaluation of gels degradation and formation damage conditions, several methods need to be applied. Viscosity and concentration of gels measurements are the most widely used methods to evaluate the gel degradation. While the reduction of viscosity and concentration sometimes do not mean the damage of formation will not occur, thus, the application of SEC and the measurement of molecule weights are very useful and helpful to determine the damage conditions. Besides these methods, RBA tests can also be used to evaluate the degradation degree of gels. In the end, the core-flooding-tests are introduced to measure the permeability to have a direct evaluation of the damage of formations.

3. EXPERIMENTS MATERIALS & PROCEDURES

3.1. EXPERIMENTS MATERIALS

Re-crosslinkable particle preformed gel. RPPG was provided by Daqing Xinwantong Technology Developing Co., Ltd. RPPG is a dry white, granular particle, consisting of a cross-linked polyacrylamide and polyacrylic acid copolymer. This sample needed to be swollen and re-crosslink in brine before used.

Conventional PPG. Conventional PPG is a dry lucid, granular particle which contained 45% AM, 0.06% MBA, and 0.1% APS. The synthesis happened at the oven which temperature was 40ºC and dry at room temperature (25ºC). This kind of sample needed to be swollen in brine water for 4 days before evaluation.

Conventional PPG with clay. Conventional PPG with clay is a dry gray, granular particle contained 45% AM, 0.06% MBA, 0.1% APS, and 1% clay. The synthesis temperature was 65ºC and after synthesis the samples were dried at room temperature (25ºC) for 2 weeks.

Breakers. The breakers used to analyze the degradation degree of gel were sodium hypochlorite (NaClO), calcium hypochlorite ($Ca(ClO)_2$), sodium persulfate ($Na_2S_2O_8$) activated by high temperature and sodium hydrate (NaOH). NaClO is unstable and easy to decompose, thus, a pale greenish-yellow solid sodium hypochlorite pentahydrate ($NaClO \cdot 5H_2O$) received from TCI America which is not explosive and is stable if kept refrigerated was used in our study. $Ca(ClO)_2$ which is a white solid was purchased from Fisher Scientific. $Na_2S_2O_8$ which is a white solid and easy to dissolve in water was provided by Alfa Aesar. And NaOH used in the experiments was supplied by Alfa Aesar.

Brine. A 1% NaCl solution was used to swell the gel samples before the evaluation of their degradation degree and damage remediation. During the measurement of core permeability and gel injection, a 1% NaCl solution has also been used.

Cores. Berea Sandstone cores which brine permeability was 15 md, 120±10 md, 150±10 md, and 250 md were used to measure the damage remediation. All the cores used for experiments were 3.0-cm length and 2.5-cm diameter.

3.2. EXPERIMENTS SETUP & PROCEDURES

The static evaluation of RPPG was designed to analyze how the degradation degree of RPPG change with different breaker types, breaker concentration, temperature, gel concentration, gel aging time and RPPG particle size.

Moreover, several core flooding tests have been done as a dynamic evaluation to study the damage remediation of RPPG degradation, and how injection pressure and core permeability influence the restoration of permeability.

3.2.1. Static Evaluation.

For the static evaluation to test the degradation degree of gels, the environment of degradation such as temperature has been controlled. The weights of samples were measured at certain time. The degradation degree was determined by the ration of sample’s residue weight to its original weight.

Experimental Procedures. The samples were mixed with brine at design gel concentration, shook the bottle until gels absorbed all free water and formed uniform gel slurry. Then, aged the samples for several days at room temperature (depend on the gel type, for RPPG, the aging time was 2 days, while for conventional PPG with/without clay was 4 days). The steps of measuring the degradation degree of gels are summarized as follows:

1) Prepared breaker solution as designed, breakers were dissolved in distilled water and shook until all the breakers dissolved.
2) Then, mixed the samples with 50g breaker solution in the glass bottles which were in either room temperature conditions or ovens with design temperatures.
3) Measured gel weight according to a designed schedule. For measuring weight, the gel was taken out using tweezers and free water was removed by tissue.
4) Summarize the weight change and inspect gel appearance change.

3.2.2. Dynamic Evaluation. For the dynamic evaluation part which used core flooding test to analyze the damage remediation of cores after gel treatment and gel degradation. Figure 3.1 shows the experimental setup for core flooding tests. The models were used to analyze if the breakers used in static evaluation can restore the permeability of cores. In addition, the tests can be used to study the effect of injection pressures cores' permeability on permeability restoration. The models used in the experiments are shown in Table 3.1.

Experimental Procedures. Before the injection of RPPG, RPPG samples were prepared by swelling in brine (1% NaCl) and the ratio of RPPG weight to water weight was 1:16. Moreover, the permeability of each cores was been measured before RPPG injection. The procedures of analysis the damage remediation were summarized as follows:

1) Injected swollen gel to the un-fractured core plugs until the pressure reached the design pressures. After the pressures reaching the design pressures, kept RPPG in the core holder for 2 days to allow RPPG re-crosslinked.
2) After 2 days, measured permeability of cores with gel filter cake or without gel filter cake. Then, took the core out from core holder with care.
3) The following step was to soak the cores in 50mL certain breaker solutions (8% NaClO, 5% $Na_2S_2O_8$ at 80℃ and 5% $Na_2S_2O_8$ & 10% NaOH) for 2 days. Gently shook the cores before taking them out.
4) Finally, injected brine at a low flow rate (1 mL/min) for 5 hours and then measured the core permeability. The restored permeability percentage was calculated by the permeability of cores after RPPG degradation divided by their original permeability.

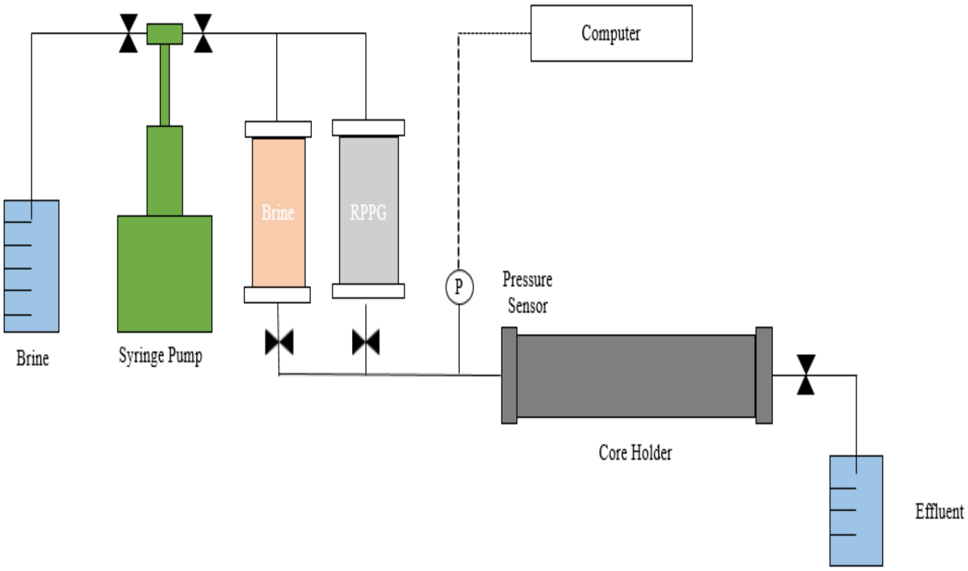


Figure 3.1. Core flooding experiments setup

Table 3.1. Core flooding models used in experiments

Experiment Number #	Core permeability (md)	Injection pressure (psi)	Gel Cake	Breaker Type	Breaker Concentration
1	127.3	200	Kept	NaClO	8%
2	118.3	200	Kept	$Na_2S_2O_8$ @65ºC	5%
3	120	200	Kept	$Na_2S_2O_8$ + NaOH	5% +10%
4	112.6	200	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%
5	117.2	200	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%
6	124.8	200	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%
7	145.1	200	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%
8	164.3	600	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%
9	158.4	1000	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%
10	16	600	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%
11	254.2	600	Peeled	$Na_2S_2O_8$ + NaOH	5% +10%

4. EXPERIMENTS RESULTS

Re-crosslinkable preformed particle gel (RPPG) is a new kind of preformed particle gel which is used to efficiently control the conformance for opening fractures, fractures-like channels, or conduits which exist in many mature oilfields. However, how to remove the RPPG plug in injection facilities and clean the RPPG damage to formation is still a problem need to be solved. Our study mainly focuses on the degradation performance evaluation of RPPG and the damage remediation of RPPG treatments.

4.1. DEGRADATION DEGREE EVALUATIONS

Breaker concentration, RPPG concentration, temperature, and aging time & particle size of RPPG have been analyzed in this part. Moreover, different types of breakers' degradation effect and PPGs' degradation performance have been compared.

4.1.1. Breaker Concentration Effect on Its Performance. There are four different types of breakers being used to test the degradation effect, which are NaClO, $Ca(ClO)_2$, $Na_2S_2O_8$ activated by temperature and NaOH. The performances of breaker degrading RPPG were determined by the value of weight remaining percentage (WRP), which is defined as,

$$RPPG\ WRP = \frac{W_a}{W_i} \times 100\% \tag{1}$$

where W_a is the weight of RPPG after a certain immersing time, and W_i is the original weight of RPPG. Though all the breakers tested have the ability to degrade the RPPG, different concentrations can influence the degradation effect of the breakers a lot. During the application of the breakers in the industry, low breakers' concentration is more economically feasible, however, the degradation effect may not as well as the higher breakers' concentration. Thus, the analysis of the breakers' concentration is very important, the results of this part can provide a reference for the application of the 4 kinds of breakers for the degradation of RPPG.

The tests shown in Figure 4.1 were conducted to investigate the effect of hypochlorite breakers concentration on their breaking performance at room temperature. For the effect of NaClO concentration, all the samples of RPPG have the same gel concentration of 1:20, 2 days as aging time, and add the NaClO with the concentration from 2% to 12% at room temperature. The original weight of each sample was 10g, and the weight of the solution adding to the samples was 50g.

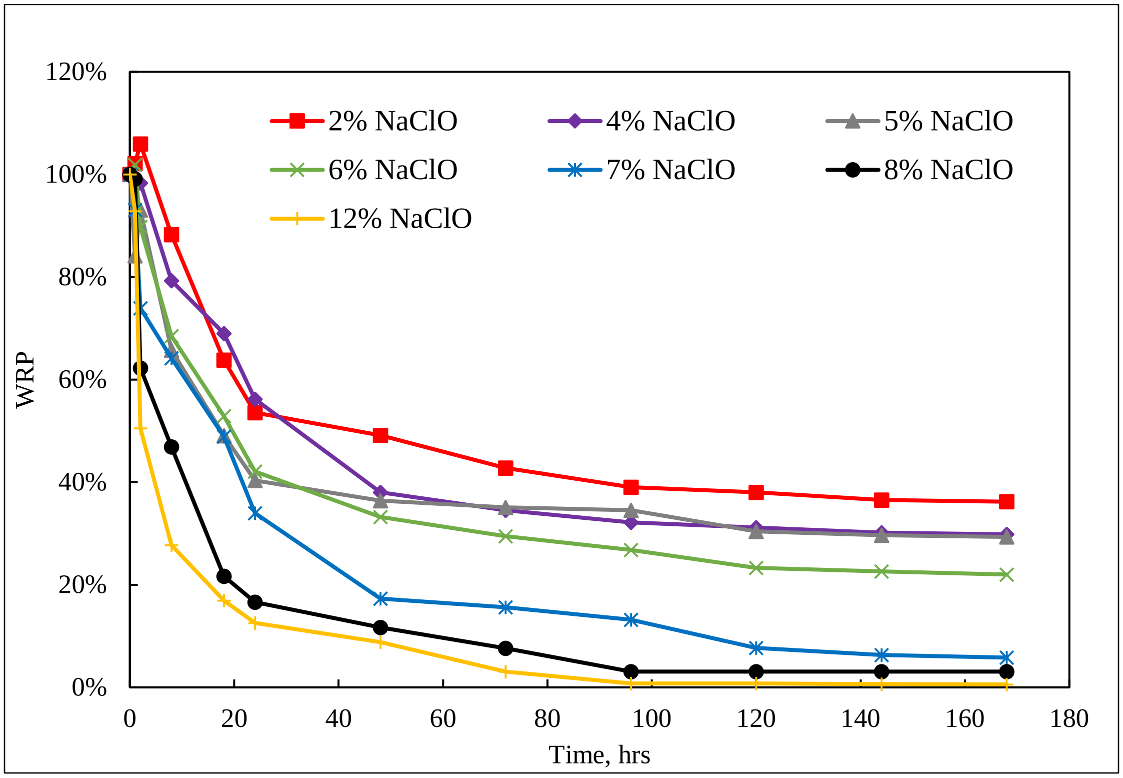


Figure 4.1. NaClO concentration effect for RPPG degrading (Room Temperature)

When the breaker concentration of NaClO was 2%, the decrease of WRP evidently slowed down after 24 hours and stabilized after around the 96 hours. The remaining weight of RPPG after 168 hours was 36% of RPPG's original weight, and a shrunken bulky residue was left in the solution. The stable WRP decreased with the increment of NaClO concentration. When the NaClO solution concentration was over 8%, the WRP was less than 5% after 96 hours, which was a favorable residue weight percentage for the breaking process.

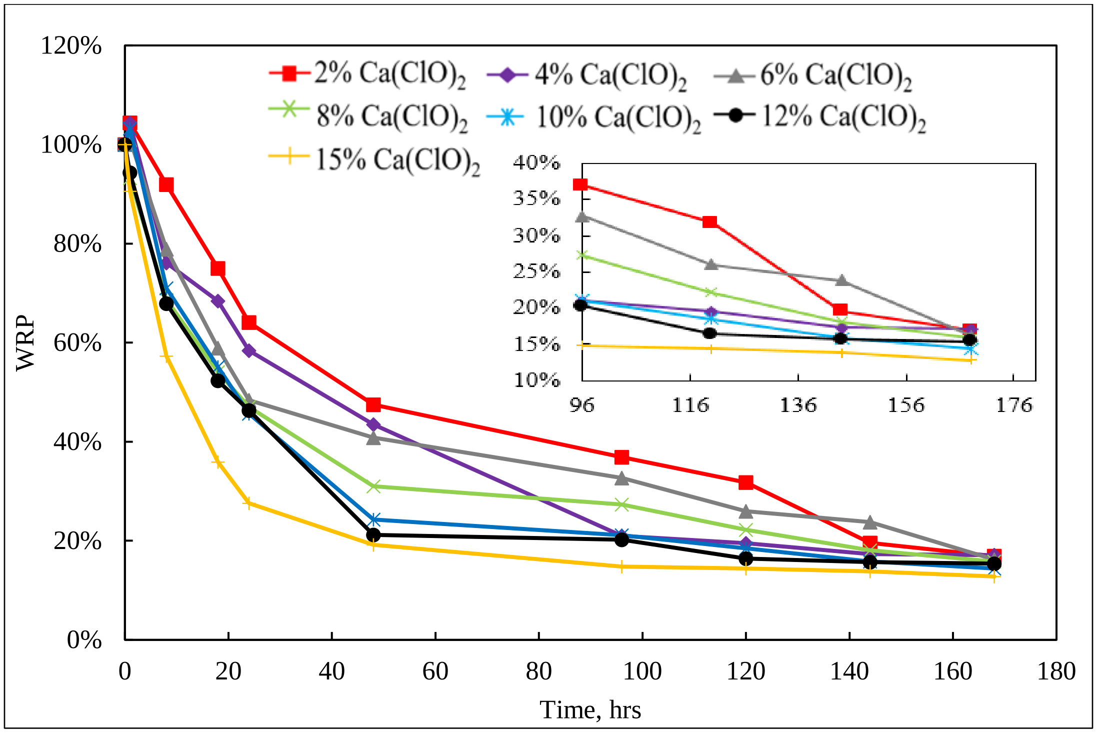


Figure 4.2. Ca(ClO)$_2$ concentration effect for RPPG degrading (Room Temperature)

To analysis the breaker concentration effect of Ca(ClO)$_2$, seven samples each contained 10g RPPG which gel concentration was 1:20, and the aging time was 2 days. The concentration of Ca(ClO)$_2$ ranged from 2% to 15% and the solution weight added to the samples was 50g. The degradation of RPPG happened under room temperature. Figure 4.2 shows the RPPG degradation degree with different concentration of $Ca(ClO)_2$.

According to Figure 4.2, the concentration of $Ca(ClO)_2$ had the similar effect on its breaking performance compared with NaClO. The WRP decreased faster when $Ca(ClO)_2$ had a higher concentration especially in the first 18 hours. Then the curves started to become flat and stabilized after 144 hours.

The results clearly indicate that the higher the concentration of $Ca(ClO)_2$ was, the better the degradation performance would be. The residual weight of RPPG reduced from 17% to 12% of its original weight. Thus, the increase of the $Ca(ClO)_2$ concentration did not have a significant increase of the degradation degree. Based on the results, the best concentration of $Ca(ClO)_2$ to degrade RPPG is 6%.

Samples were set up to analyze the concentration effect of $Na_2S_2O_8$, there were 5 samples with 10g RPPG with 1:20 gel concentration and 2-day aging time, the solution used to degrade the sample was 50g, and the concentration of $Na_2S_2O_8$ changed from 2% to 10%. The degradation temperature was set as 65ºC due to the high temperature required for $Na_2S_2O_8$ to degrade RPPG.

Figure 4.3 below shows the $Na_2S_2O_8$ concentration effect on RPPG degradation. The breaking process was faster when $Na_2S_2O_8$ had a higher concentration, especially in the first 24 hours. Then the curves started to stabilize after 48 hours. The stable WRP decreased with the increase of breaker concentration. At 65ºC, the degradation degree of RPPG increased with the increasing of $Na_2S_2O_8$ concentration. When the concentration of breaker raised from 2% to 10%, the weight of the residue reduced from 20% to 4% of its original weight. So, the best concentration of $Na_2S_2O_8$ should be 8%.

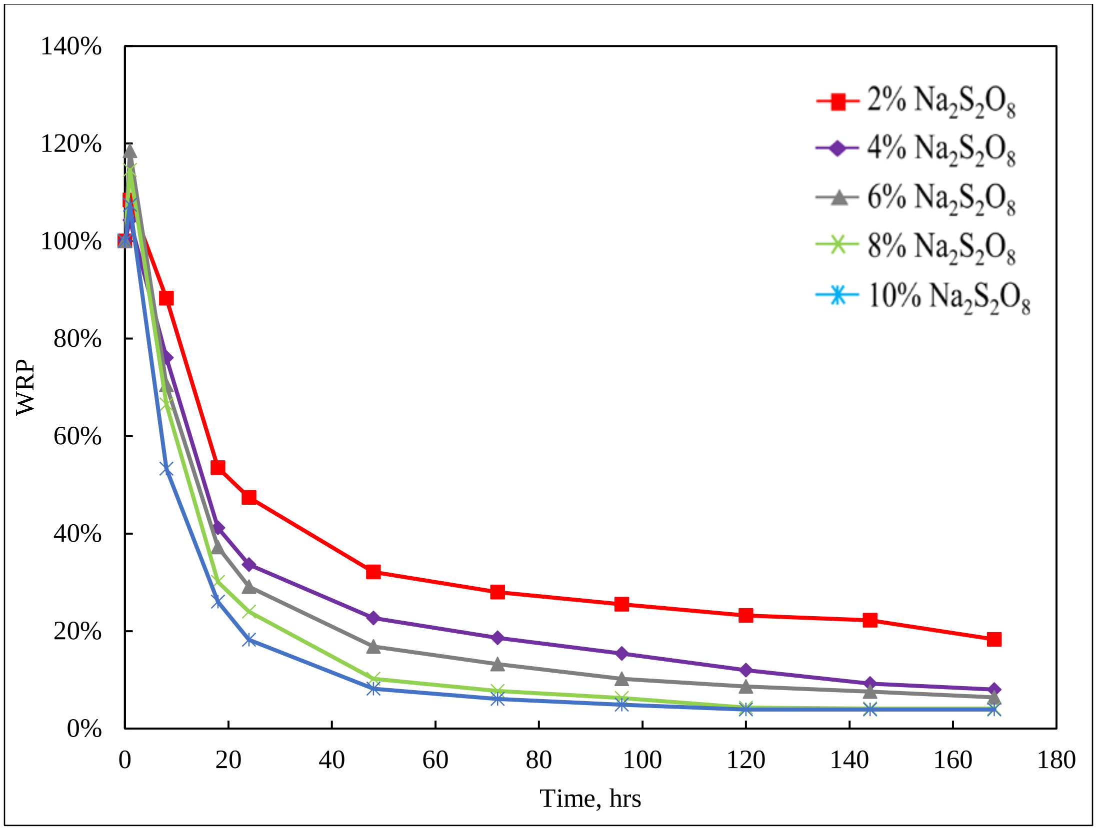


Figure 4.3. $Na_2S_2O_8$ concentration effect for RPPG degrading (65°C)

In order to overcome the temperature limitation of $Na_2S_2O_8$, NaOH was used as an activator to let the degradation of RPPG happen at room temperature. By the review of previous papers, when the concentration of NaOH is 2 times the concentration of $Na_2S_2O_8$, the degradation effect is best. And our experiments also proved this relationship. 4 samples all contain 50g breaker solutions with 6% $Na_2S_2O_8$ and the concentration of NaOH range from 6% to 12%.

Figure 4.4 shows that 12% NaOH has the best degradation effect compared with others which proved that the concentration of NaOH should be 2 times the concentration of $Na_2S_2O_8$ to meet the best degradation performance.

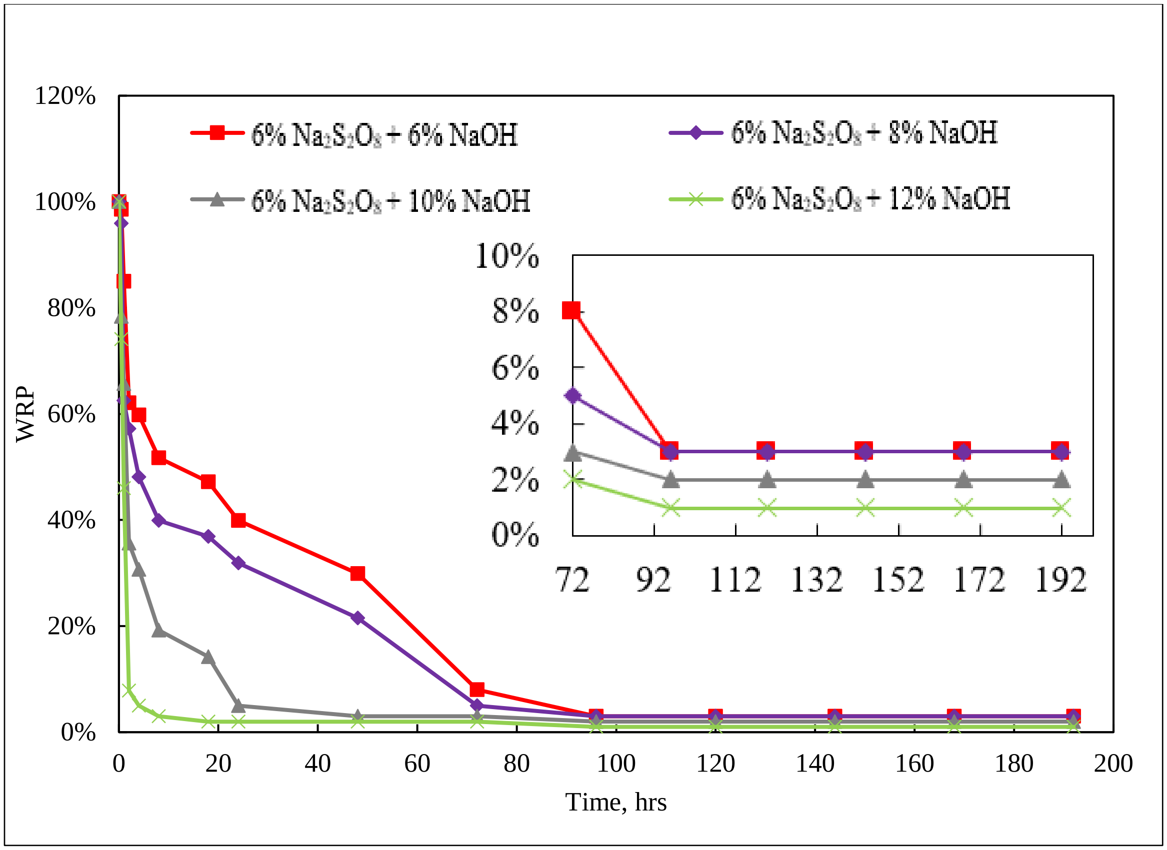


Figure 4.4. NaOH concentration effect on $Na_2S_2O_8$ degrading RPPG (Room Temperature)

Eight samples were used to analyze the concentration effect of this combination, each sample contained 10g RPPG which the gel concentration was 1:20 and the aging time was 2 days. The solution added to the samples was 50g. And the concentration of $Na_2S_2O_8$ changed from 0.25% to 6%, for each sample, the concentration of NaOH was 2 times the breaker concentration.

Figure 4.5 below shows the concentration effect of this combination to RPPG degradation. In the figure, breaker solution with a higher $Na_2S_2O_8$ concentration decreased the WRP faster. Then the WRP values became fixed in all the curves and were below 5%. All curves kept a significantly high slope until the WRP decreased to 5%.

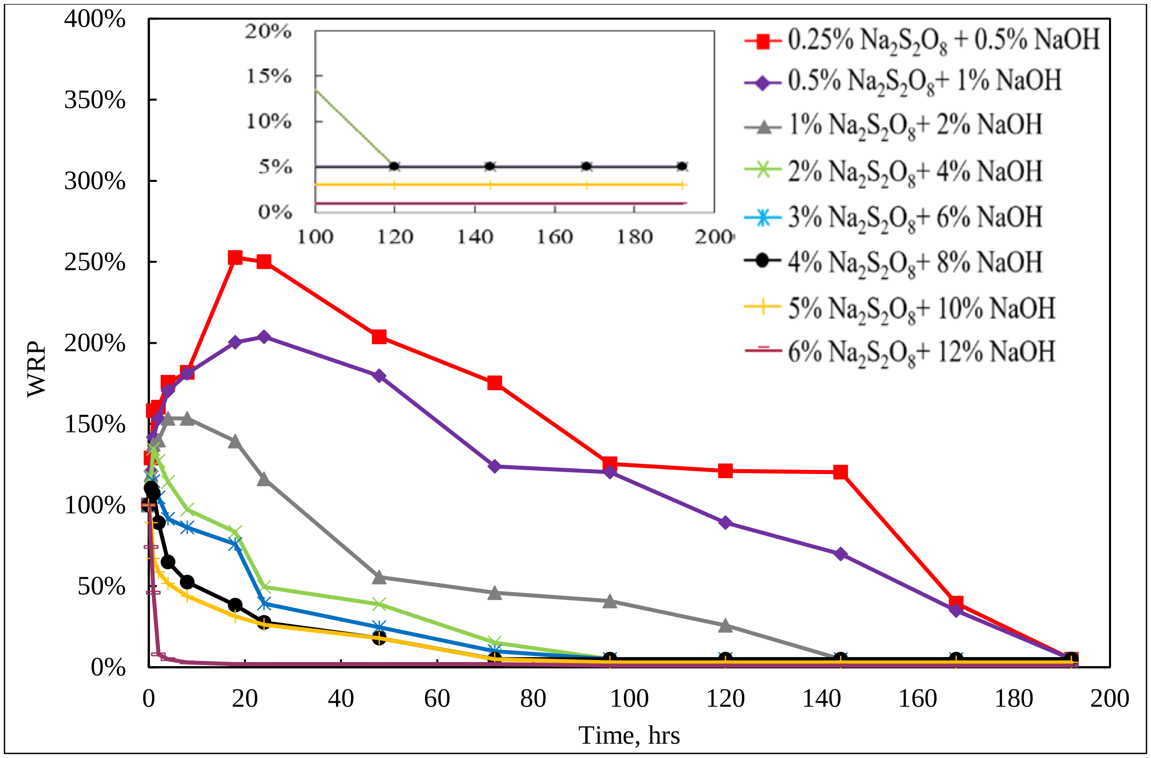


Figure 4.5. NaOH and $Na_2S_2O_8$ concentration effect for RPPG degrading (Room Temperature)

By analyzing the results, it is easy to figure out that the combination of $Na_2S_2O_8$ and NaOH has a great degradation effect on RPPG. Even the concentration of breaker reduced to 0.25%, RPPG can be degraded to less than 5% of its original weight. With the increasing of breaker concentration, RPPG degradation degree had a little increase, while the time needed to reduce RPPG weight to less than 5% of its original weight was reduced significantly. So from the results, the best concentration is 0.25% $Na_2S_2O_8$ and 1% NaOH if not consider the degradation time.

4.1.2. RPPG Concentration Effect on Breaker Performance. RPPG that leads to plugging issue in injection facilities or fractures usually have various concentrations.

The major cause is that RPPG may be partially swollen before injection in order to gain a higher gel strength (elastic modulus).

Another cause is that the gel accumulates and dehydrates during the injection or propagation, thus increases its concentration. Conventional preformed gel will swell to its maximum swelling capacity with sufficient solvent. However, the partially swollen RPPG can only increase its swelling ratio slightly after re-crosslinking. Therefore, the initial RPPG concentration is an important factor for the breaking process.

Normally, the higher the RPPG concentration, the lower gel degradation degree will be. To analysis the concentration of RPPG's effect on RPPG degradation, samples were prepared with the gel concentration as 1:5, 1:10, 1:20, and 1:30 (fully swollen).Gel concentration is defined as the ratio of dry RPPG particle weights to the total weight of RPPG samples,

$$RPPG\ Gel\ Concentration = \frac{W_R}{W_t} \tag{2}$$

where W_R is the weight of dry RPPG particles, and W_t is the weight of total RPPG samples. NaClO, $Ca(ClO)_2$, and $Na_2S_2O_8$ activate by high temperature and NaOH have been tested and the results have been summarized.

To analysis NaClO effect on different RPPG concentrations, 50g solution with 8% NaClO was adding to the samples containing different concentrations RPPG at room temperature. The results in Figure 4.6 indicate that when the concentration was 1:5, it was very hard for NaClO to degrade the samples, the weights of the samples increased first and then kept as their original weights even for a week after adding breakers.

When used 8% NaClO in the solutions to reduce weights of gels, for the higher RPPG concentrations, 1:5 and 1:10, the WRP increased in the first 2 hours due to the additional swelling of re-crosslinked RPPG. Then the WRP decreased in the following hours, where the breaking of NaClO became more dominate than the swelling. The degradation degree of RPPG increased with the decreasing of RPPG concentration. When the concentration was 1:30, at this condition, RPPG was fully swollen, 8% NaClO in the solution can reduce weight of gels to less than 1% of their original weight.

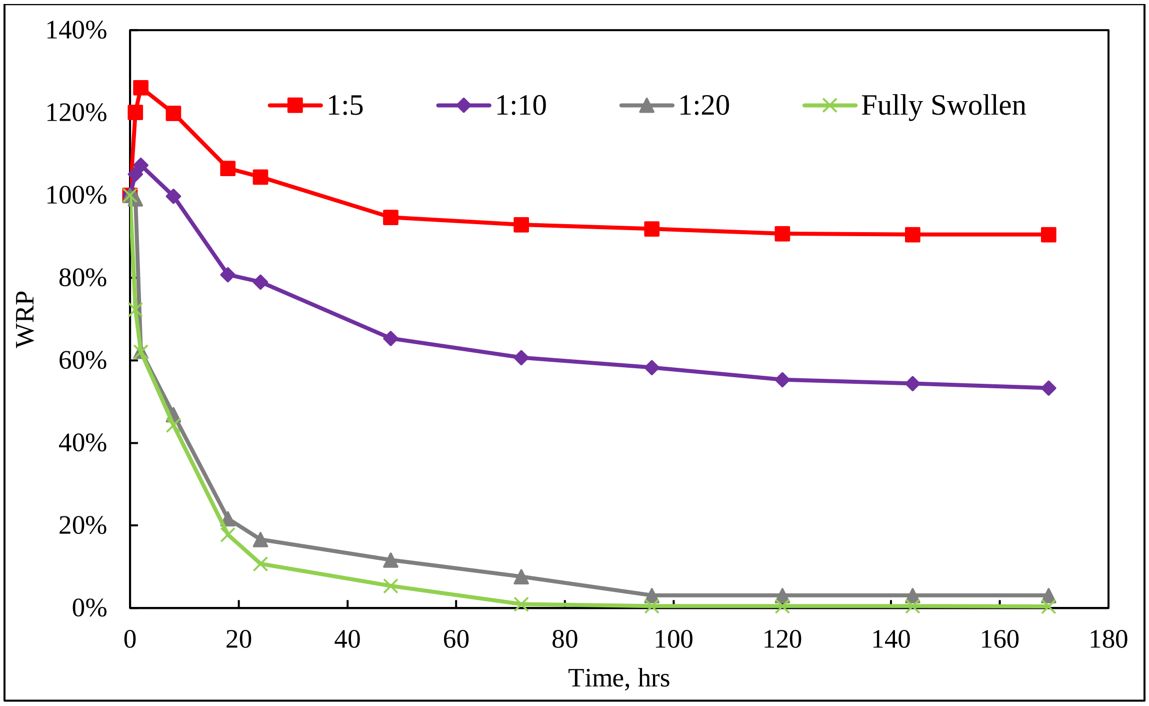


Figure 4.6. Gel concentration effect for NaClO degrading RPPG (Room Temperature)

The effect of $Ca(ClO)_2$ on different RPPG concentration has also been tested, solutions contained 10% $Ca(ClO)_2$ have been added into RPPG with different concentrations at room temperature. For this kind of breaker, when the gel concentration was 1:5, the breaker can first reduce the weight of RPPG while after 2 days, the RPPG samples swelled again and reach to about 2 times their original weights after adding breaker for one week. For the higher RPPG concentrations, 1:5, the WRP increased due to the additional swelling of re-crosslinked RPPG, and the final value of WRP is twice of the initial. For lower RPPG concentration, the WRP decreased where the breaking of NaClO became more dominate than the swelling.

Figure 4.7 shows the same trend with other breakers, the lower the RPPG concentration is, the better degradation degree will be. When RPPG concentration was 1:30 (fully swollen), the residue of the samples will reduce to 5% of their original weights by $Ca(ClO)_2$.

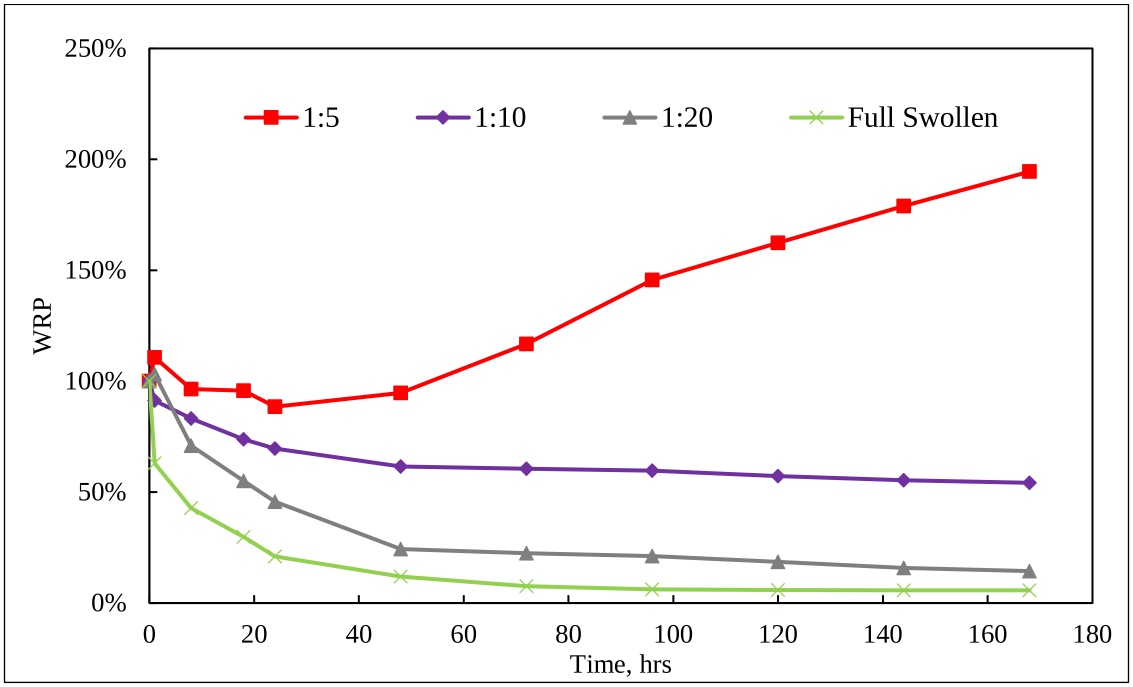


Figure 4.7. Gel concentration effect for $Ca(ClO)_2$ degrading RPPG (Room Temperature)

To study the effect of $Na_2S_2O_8$ activate by high temperature on different concentrations of RPPG, four samples with different RPPG concentrations have been prepared, and each sample was degraded by 50g solutions with 6% $Na_2S_2O_8$ at 65°C**.** Figure 4.8 indicates that 6% $Na_2S_2O_8$ at 65°C can degrade all kinds of RPPG with different gel concentrations, the WRP increased in the first 2 hours due to the additional swelling of re-crosslinked RPPG, then the WRP decreased in the following hours. The results still prove the conclusion that the higher the gel concentration, the less the degradation degree of the samples will be. When the gel was fully swollen, the residue weight was less than 4%. When the gel concentration was 1:5, this kind of breaker can reduce the samples' weight to about 25% of their original weights.

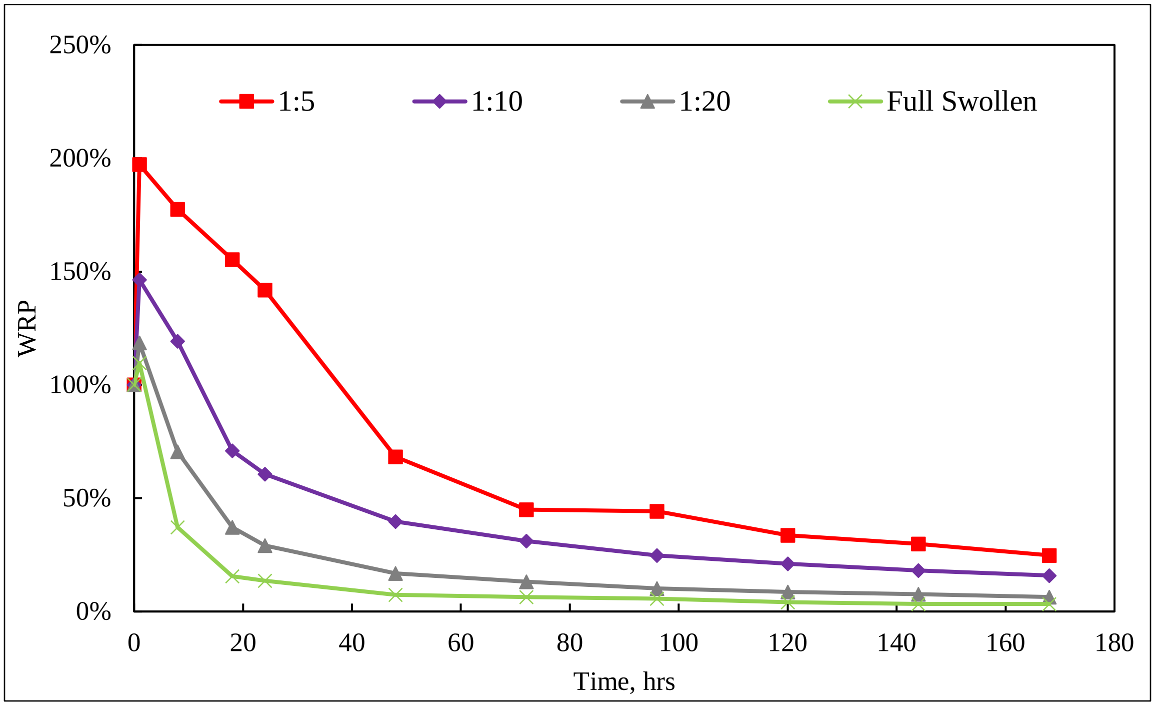


Figure 4.8. Gel concentration effect for $Na_2S_2O_8$ (6%) degrading RPPG (65°C)

The effect of $Na_2S_2O_8$ activate by NaOH on different concentrations of RPPG was studied by using four samples with different RPPG concentrations degraded by 50g solutions with 6% $Na_2S_2O_8$ and 12% NaOH. Figure 4.9 shows the degradation degree of different gel concentration RPPG with 6% $Na_2S_2O_8$ activated by 12% NaOH. For high RPPG gel concentration, the value of WRP increased in the first 24 hours due to the swollen of RPPG samples, after that, the breaking of NaClO became more dominate than the swelling. It is clear that higher RPPG concentration need linger time to be totally degraded. The results indicate that $Na_2S_2O_8$ activated by NaOH can totally degrade RPPG samples even the gel concentration was 1:5. It took 7 days for this kind of breaker to totally degrade RPPG samples with 1:5 gel concentration. And for RPPG samples which gel concentration was 1:30, gel samples were totally degraded in 4 hours.

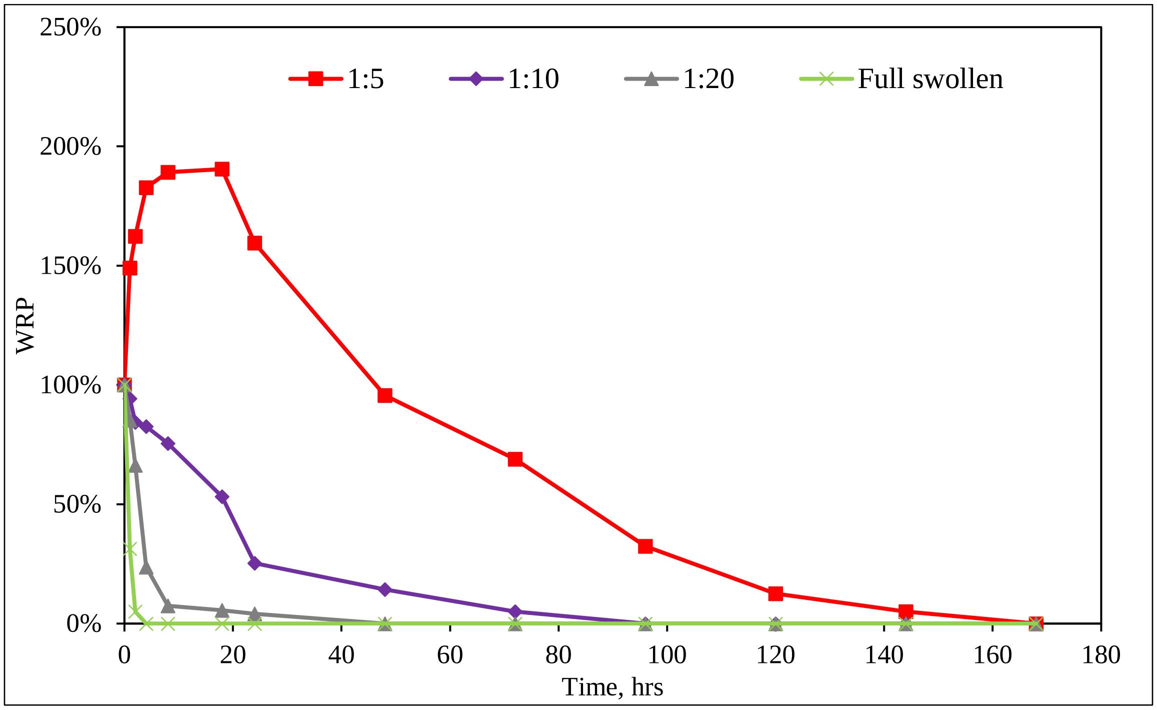


Figure 4.9. Gel concentration effect for $Na_2S_2O_8$ (6%) activated by 12% NaOH degrading RPPG (Room Temperature)

4.1.3. Temperature Effect on Breaker Performance. Different temperatures can have a significant influence on the degradation degree of RPPG, by the increasing of temperatures, the rates of reactions increased. While different reservoirs have different temperatures, thus, it is very important to know how the RPPG degradation degree change with temperatures. Different samples contained 10g RPPG which gel concentration was 1:20 have been tested with different types of breakers at different temperatures.

For temperature effect on NaClO degrading RPPG, 4 samples have been measured with 8% NaClO at room temperature, 40ºC, 65ºC, and 80ºC. Figure 4.10 shows that with the increasing of temperatures, the degradation degree of RPPG will increase and the speed of degradation will slightly increase.

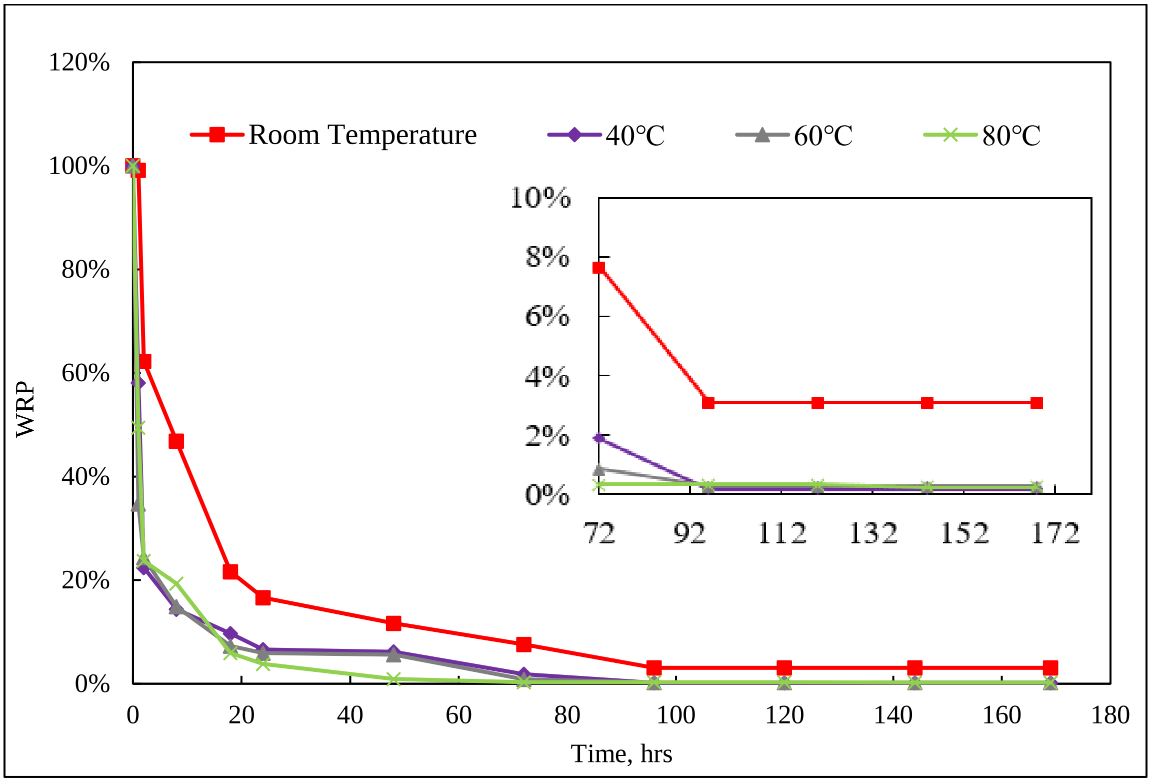


Figure 4.10. Temperature effect for NaClO (8%) degrading RPPG

The reason causes this phenomena is that hypochlorite decompose faster at higher temperature which weakens its oxidizing power at the same time, although the temperature can usually accelerate reaction. The value of WRP reduced significantly faster in the first 24 hours with the increase of temperature, then WRPs stabilized in a range from 0 to 3%.

To analyze the temperature effect when the breaker was $Ca(ClO)_2$, 4 samples contained 10g RPPG with 1:20 gel concentration have been tested by adding 10% $Ca(ClO)_2$ at different temperature.

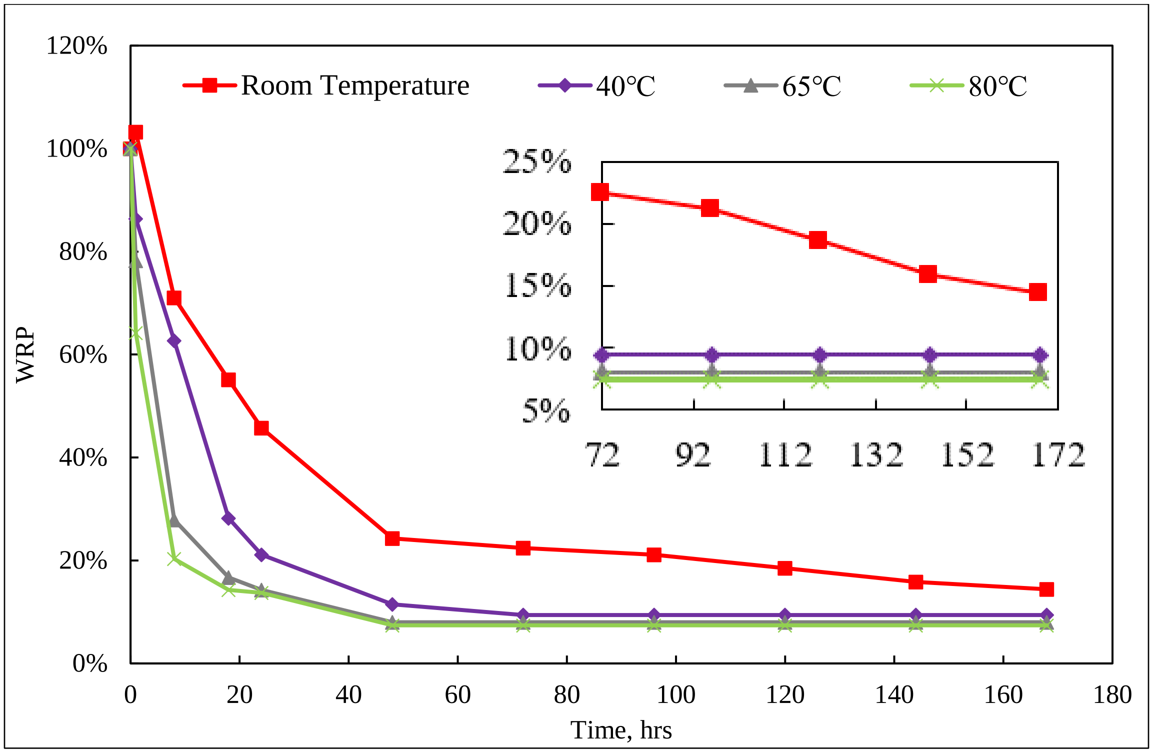


Figure 4.11. Temperature effect for $Ca(ClO)_2$ (10%) degrading RPPG

Figure 4.11 indicates that with the increase of temperature, the degradation effect of $Ca(ClO)_2$ will increase, and the time for breaker to degrade the RPPG to favorable degradation degree will become short. When the temperature was 80ºC, the weight of residue was less than 5% of its original weight. While at room temperature, the residue was about 15% of its original weight. Thus, temperature has a significant influence on the $Ca(ClO)_2$ degradation of RPPG.

For the temperature effect when the breaker is $Na_2S_2O_8$, still 4 samples with the same weight and gel concentration have been tested. All samples were added by 6% $Na_2S_2O_8$ at different temperatures. Figure 4.12 shows that at room temperature, the breaking process was significantly accelerated when the temperature increased from room temperature to 80°C. It is known that the persulfate reaction rate with organic matter is considerably low at a low temperature. However, the reaction becomes faster and efficient when the system temperature increases.

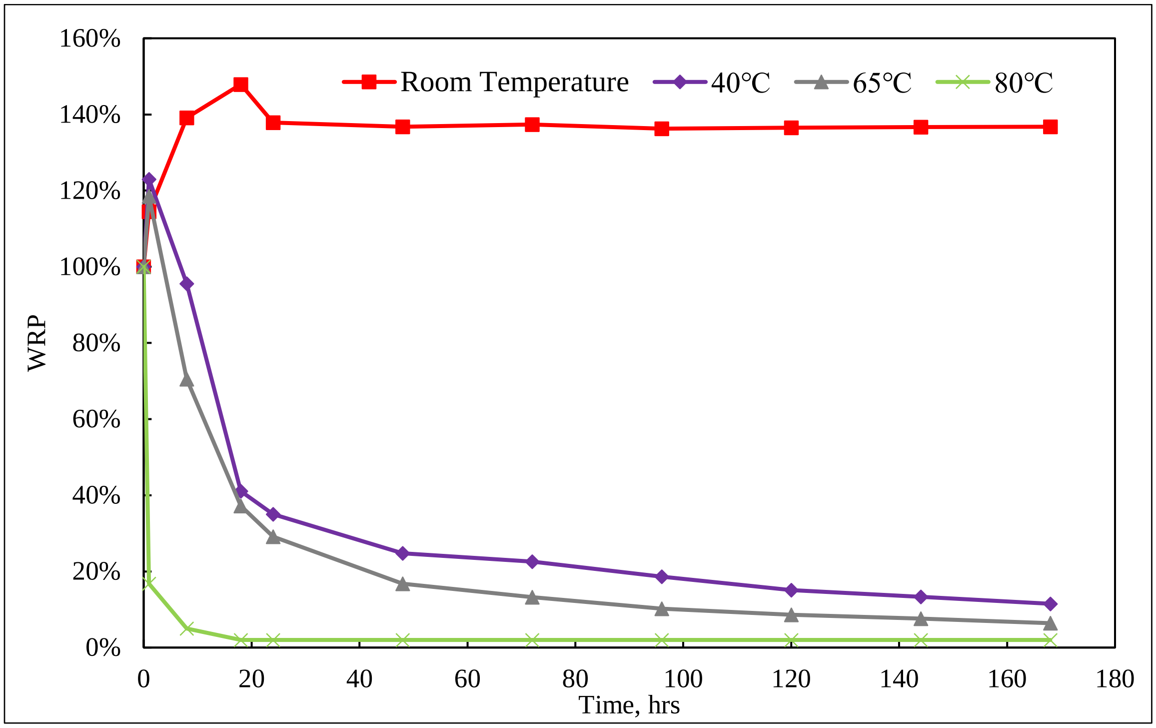


Figure 4.12. Temperature effect for $Na_2S_2O_8$ (6%) degrading RPPG

Persulfate can be activated by high temperature (higher than 50°C) and generated the high-oxidizing-power sulfate radicals (SO_4^-). The curve representing room temperature in Figure 4.12 increased in first 24 hours because of the swelling of RPPG. Then it slightly decreased in the following 72 hours and the WRP stabilized at approximately 137%. When the temperature was higher, the final WRP was 12% at 40 °C, 6% at 65 °C, and 2% at 80 °C. It is believed that the higher temperature both activated the $Na_2S_2O_8$ and improved the reaction rate, thus it significantly accelerated the breaking process.

The temperature effect of $Na_2S_2O_8$ activate by NaOH has also been studied. 6% $Na_2S_2O_8$ and 12% NaOH were added to 10g RPPG at different temperatures.

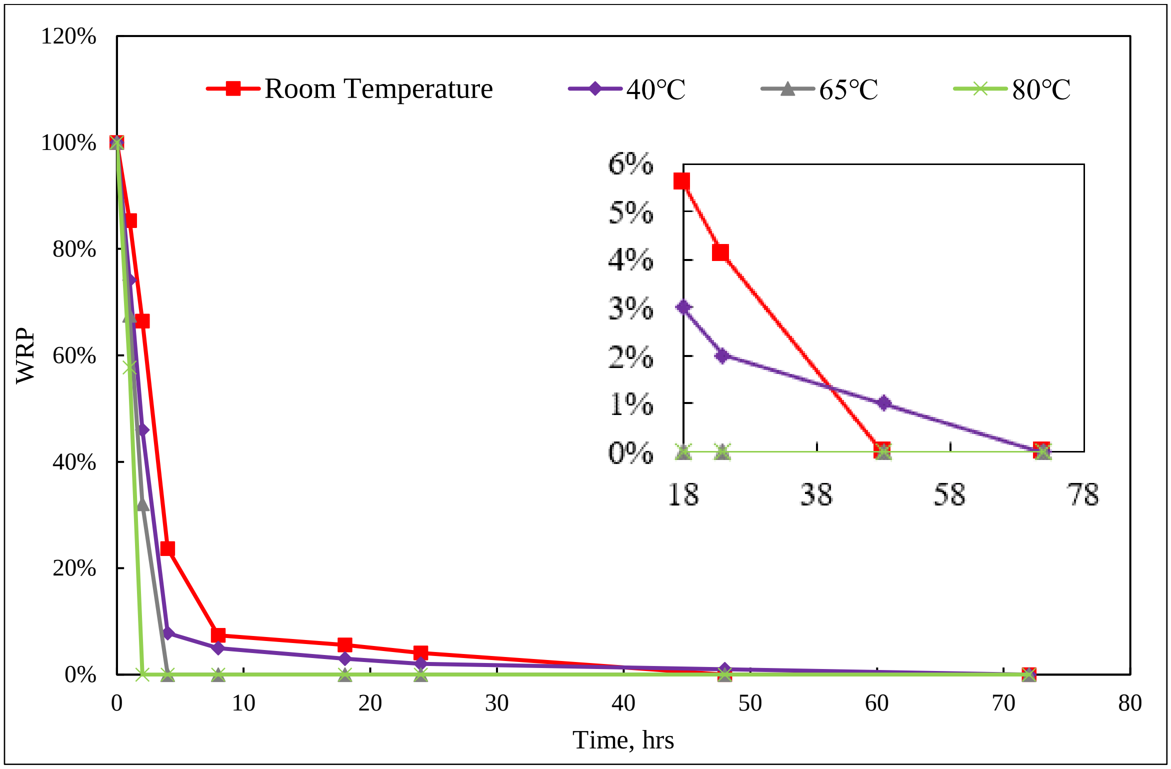


Figure 4.13. Temperature effect for $Na_2S_2O_8$ (6%) activate by NaOH (12%) degrading RPPG

The results in Figure 4.13 show that with the increase of temperature, the time for this kind of breaker to degrade RPPG is much shorter, the higher the temperature, the shorter the time will be. The stable WRPs were 7% and 3% at 23 °C and 80 °C, respectively. Though the Na2S2O8 activated only by NaOH was considerably effective, the higher temperature further improved the rate of breaking.

4.1.4. Aging Time & RPPG Particle Size Effect. The difference in the aging time will cause different properties of the gel. With the increase of aging time, the strength of the gel will increase which make it harder to be degraded. To analyze the effect of aging time, several samples were prepared with aging time of 2, 6, 8, and 14 days. The breaker added in the samples was NaClO which concentration was 8%.

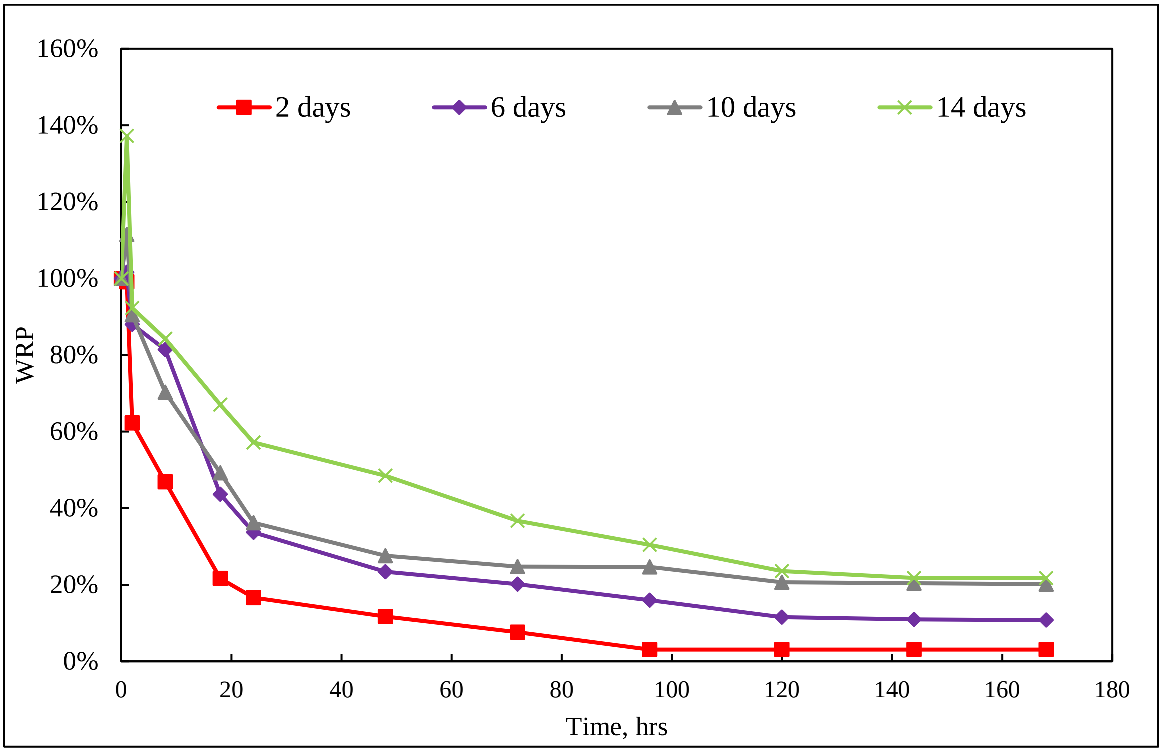


Figure 4.14. Aging time effect for NaClO (8%) degrading RPPG

Figure 4.14 shows clearly that the increase of aging time will prevent the degradation of RPPG and expand the time needed for RPPG to be degraded. For the sample which aging time was 14 days, WRP was about 22%, which was 7 times the WRP for the sample which aging time was 2 days.

The effect of RPPG particle size on RPPG degradation has also been studied. The breaker used was 8% NaClO. And the particle sizes of RPPG were less than 0.5, 0.5~1, 1~2, and 2~4. The temperature was controlled as room temperature. Figure.4.15 shows the degradation degree of RPPG with different particle sizes. The results clearly indicate that RPPG particle size has tiny effect on RPPG degradation. Because after swollen and re0crosslinked, no matter how the particle size was, a homogeneous bulk gel was formed.

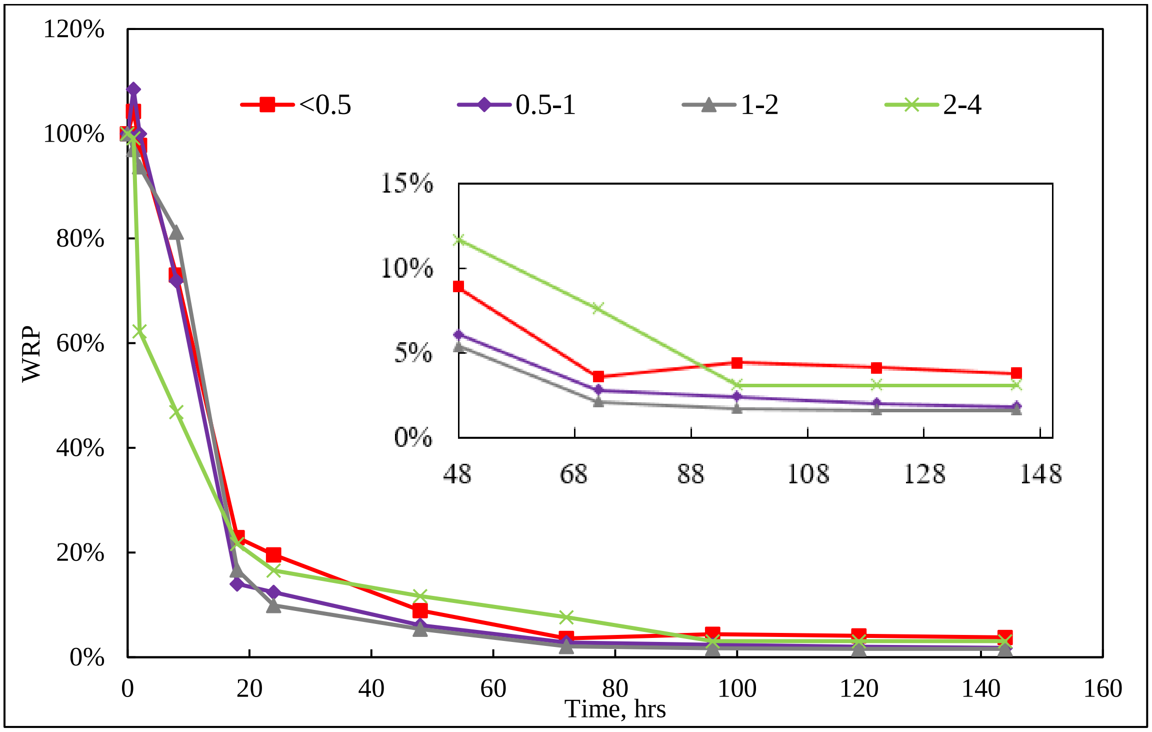


Figure 4.15. RPPG particle size effect on NaClO (8%) degrading RPPG

4.1.5. Screening of Breakers. There were mainly 4 types of breakers being used to degrade RPPG, including NaClO, $Ca(ClO)_2$, and $Na_2S_2O_8$ activated by temperature or NaOH. All of those breakers can degrade the RPPG and reduce the weight of the RPPG to less than 20% of its original weight. Different breaker used will lead to different results for the conditions of the degraded RPPG.

For the degradation effect of NaClO at the room temperature, by adding 8% of this kind of breaker to RPPG which original weight was 10g, after 3 days, the weight of RPPG finally reduced to less than 5% of its original weight. After 72 hours, the residue was a few pieces of white, thin but rigid flakes as Figure 4.16 shown. And the liquid part became whiter and cloudier than in the beginning.

Figure 4.16. Residue of RPPG after degrading by NaClO (8%) (Room temperature)

For the degradation effect of $Ca(ClO)_2$, the weight of the sample reduced to less than 20% of the its original weight by adding 8% $Ca(ClO)_2$ at room temperature for 3 days. During the degradation, there would be a compact white cover on the surface of the sample which prevented the RPPG inside to be degraded. It is observed that the RPPG remained inside the white cover was still relatively hydrated when the cover open was cut open, thus the degradation effect was not as well as other kinds of breakers. After degraded for 3 days, the sample also became whitish and hard pieces, while there was some white cover on the surface of the residue. The condition of the RPPG after degraded by $Ca(ClO)_2$ is shown in Figure 4.17.

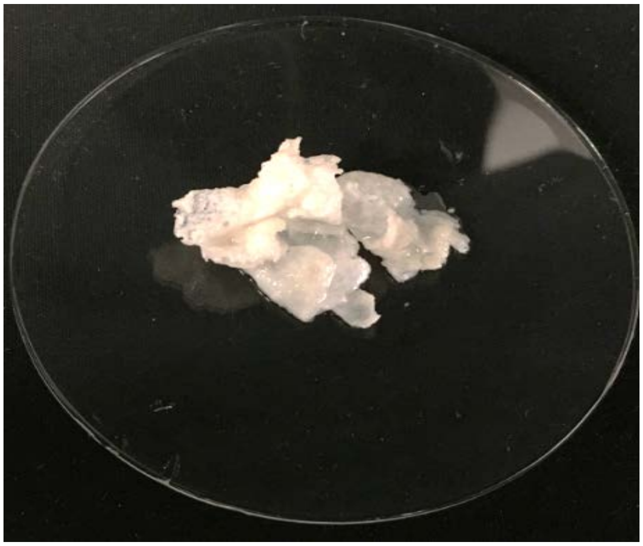


Figure 4.17. Residue of RPPG after degrading by $Ca(ClO)_2$ (10%) (Room temperature)

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) technologies were used to analyze the composition of the white cover. Figure 4.18 and Figure 4.19 provides the results of SEM and EDS test. The EDS result provides the elements information of the white cover, where the Ca, Cl, C, and O had larger portions compared with other elements. It is believed that the white cover was mainly composed of $CaCO_3$.

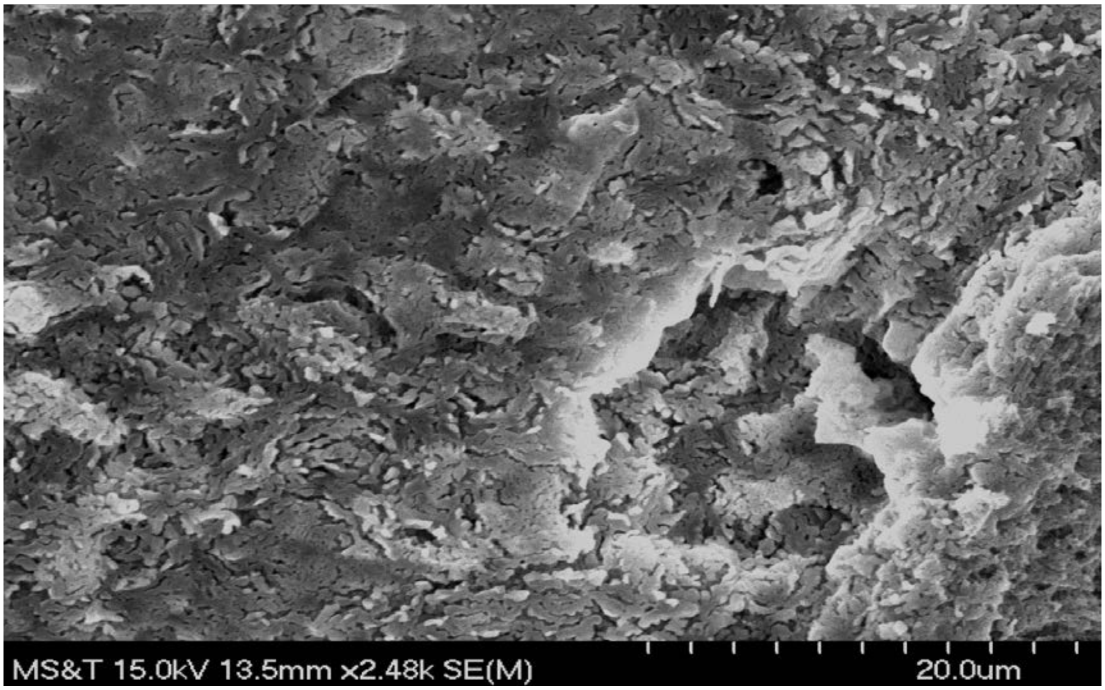


Figure 4.18. SEM image

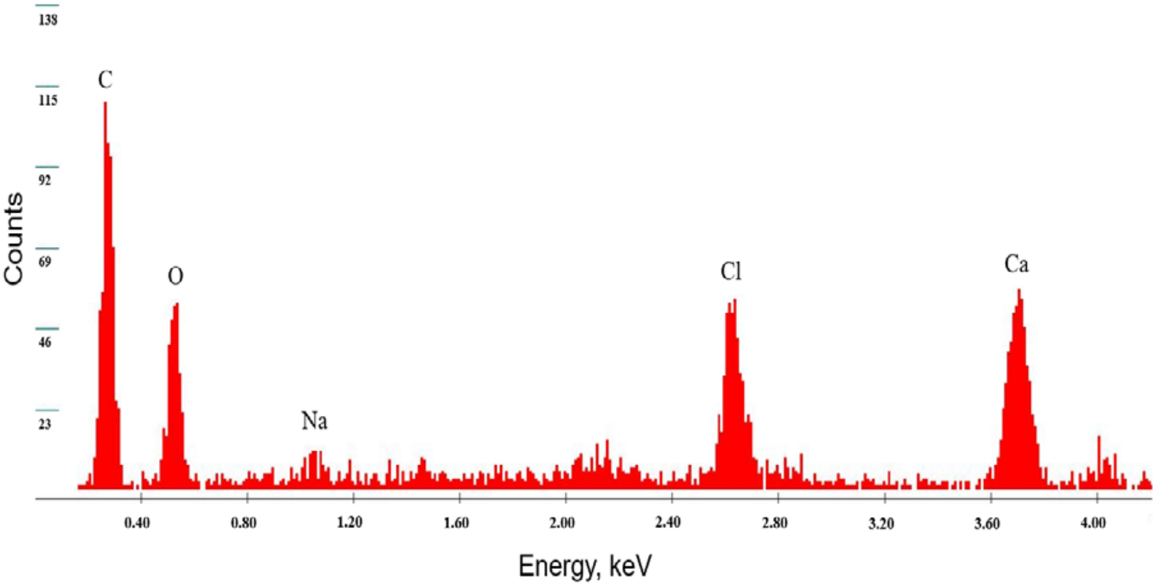


Figure 4.19. EDS analysis

For the degradation performance of $Na_2S_2O_8$ as breaker to degrade RPPG, 8% of $Na_2S_2O_8$ was added to 10g RPPG at room temperature, while the weight of the sample did not change. From literature review, this kind of breaker can only work at the temperature range of 49ºC to 93ºC. Thus the test was reformed by increasing the temperature to 65ºC, finally the weight of the sample decreased to less than 10% of its original weight. After degraded, the RPPG became small, fragile and yellow pieces like Figure 4.20 shown below. The residue is much softer compared with the residue degraded by other kinds of breakers.

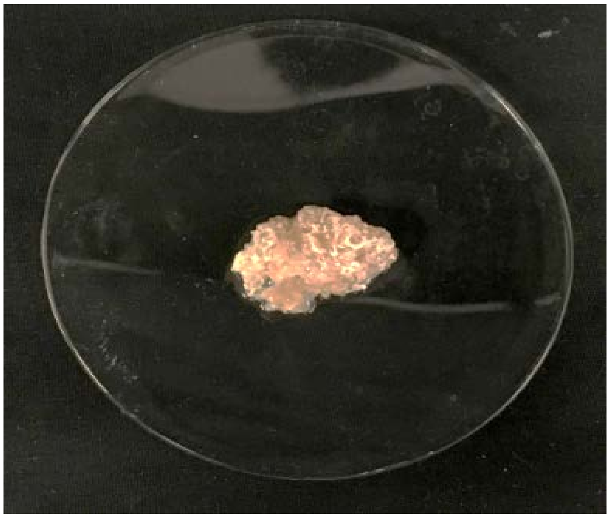


Figure 4.20. Residue of RPPG after degrading by $Na_2S_2O_8$ (8%) (65^{0}C)

It has also been found that by the introduction of activator, $Na_2S_2O_8$ can degrade the RPPG at room temperature. NaOH was chosen as an activator. By adding 6% $Na_2S_2O_8$ with 12% NaOH at room temperature, the weight of RPPG decreased to less than 5% in 8 hours which was much shorter compared with other kinds of breakers. RPPG residue was some extremely fine precipitation that could not be picked up from the bottle, and the solution system became cloudy as shown in Figure 4.21.

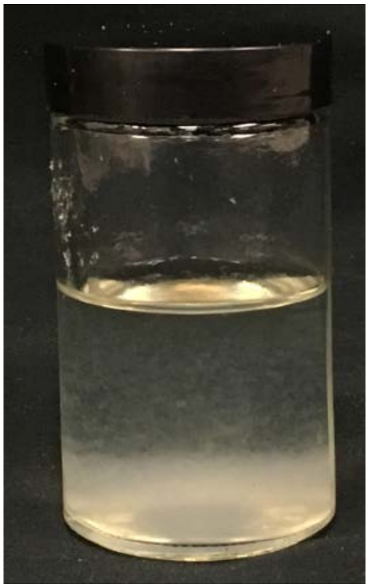


Figure 4.21. Residue of RPPG after degrading by $Na_2S_2O_8$ (6%) activated by NaOH (12%) (Room temperature)

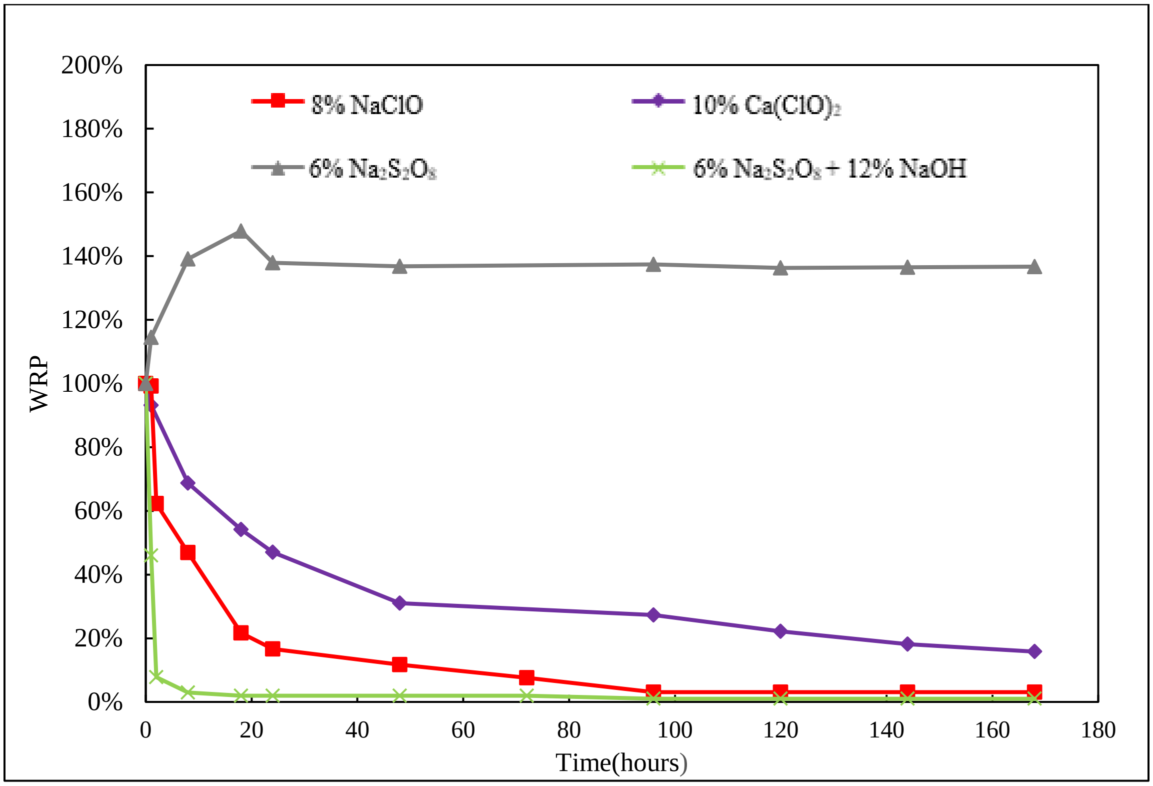


Figure 4.22. Degradation degree of different breakers (Room Temperature)

Since what happened to RPPG after adding different types of breakers have already been known, the degradation performances of those 4 kinds of breakers have also been compared at room temperature. 4 different kinds of breakers were added to RPPG which gel concentration was 1:20 and aging time was 2 days. The concentration for $Na_2S_2O_8$ and NaOH is 6% and 12%, other breakers have the same concentration of 8%.

When the temperature was room temperature, the application of $Na_2S_2O_8$ and NaOH had the best degradation effect compared with others. Except $Na_2S_2O_8$, all the other breakers can reduce the weight of RPPG samples to less than 20% of their original weights. The results for the degradation effect of 4 kinds of breakers is shown in Figure 4.22.

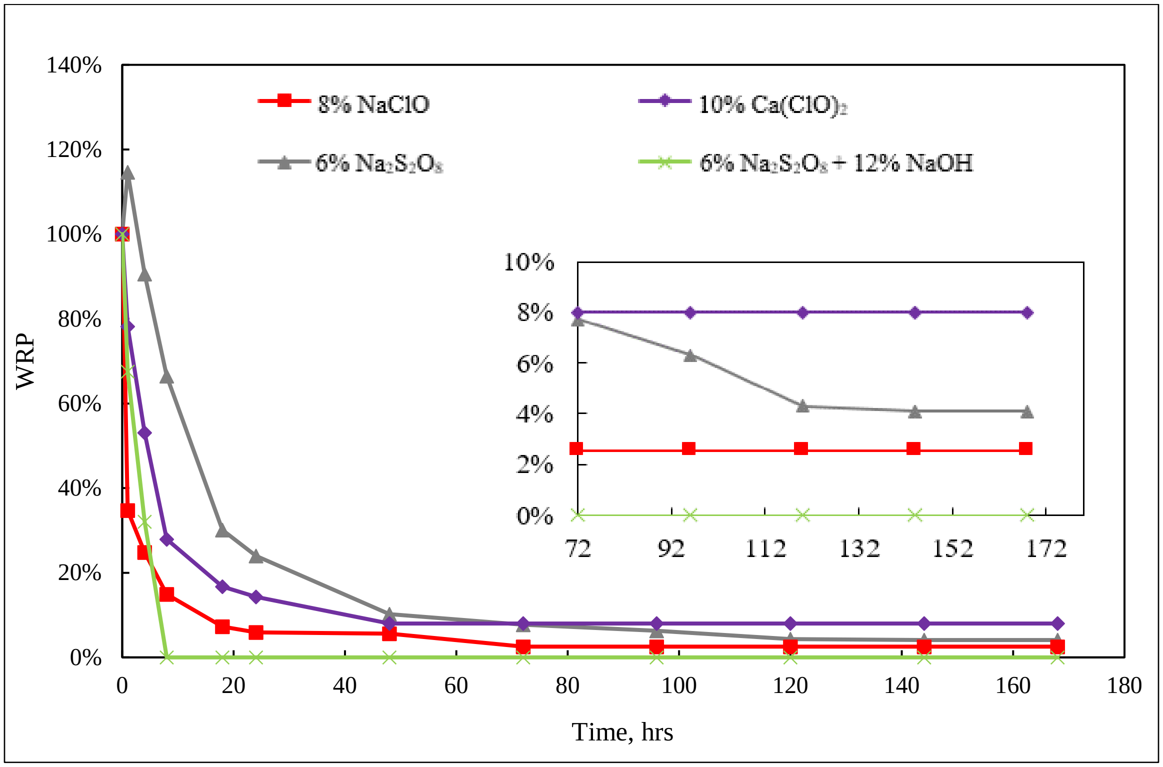


Figure 4.23. Degradation degree of different breakers (65^0C)

Additionally, the degradation effects when the temperature raised to 65ºC have also been analyzed. At this temperature, $Na_2S_2O_8$ has been activated by high temperature and had the ability to degrade RPPG. Thus, all of the breakers can degrade RPPG at this temperature. The concentrations of breakers were same with the test at room temperature. Figure 4.23 shows that $Na_2S_2O_8$ activated by NaOH still had the best degradation effect, and with the increase of temperature, all breakers will have a better degradation performance compared with their effects at room temperature.

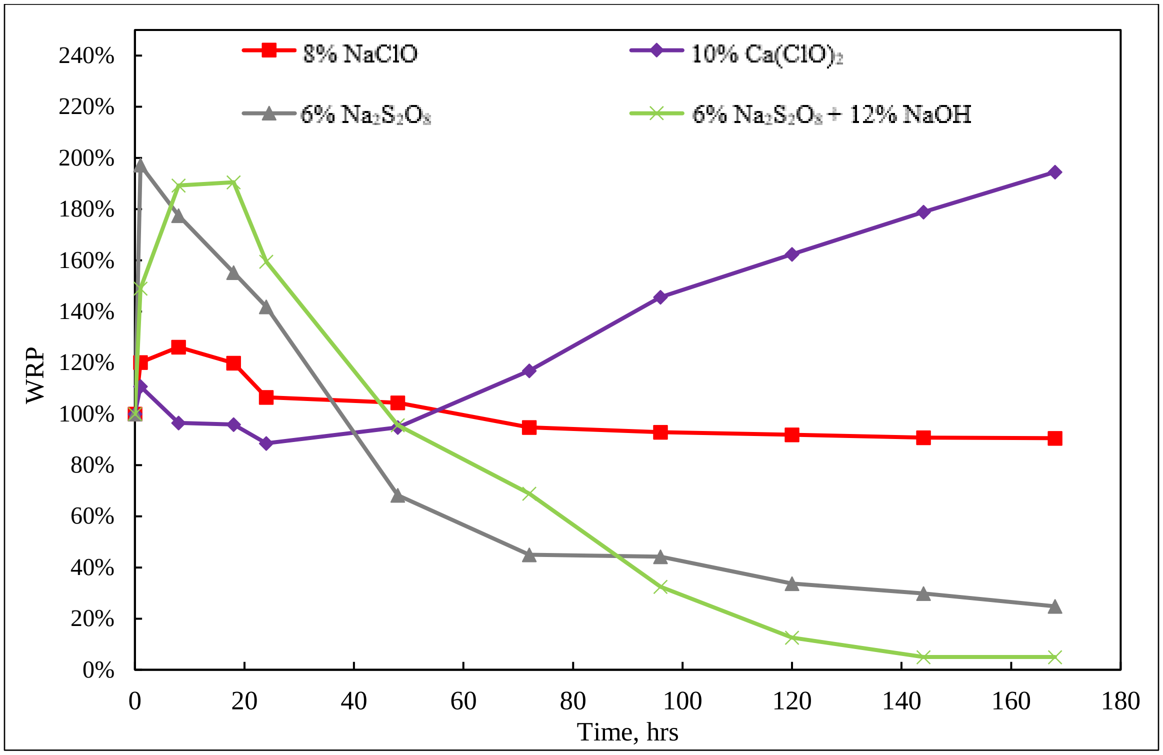


Figure 4.24. Degradation degree of different breakers on 1:5 RPPG

The degradation effects of different kinds of breakers on RPPG which gel concentration was 1:5 have also been compared. From Figure 4.24, all the breakers can degrade RPPG which gel concentration was 1:5, while for $Ca(ClO)_2$, the sample's weight reduced first because degradation and then increased due to re-swollen. For other types of breaker, the weight of RPPG increased first as a result of re-swollen, then decreased because of degradation effect of breakers. By comparing those results, 6% $Na_2S_2O_8$ active 12% NaOH had the least residue weights.

Thus, consider the influence of breaker concentration, RPPG concentration, and temperature, NaClO and $Na_2S_2O_8$ activated by NaOH are better breakers compared with others. While for NaClO, the concentration of breaker cannot be too low which cost is more expensive than the application of $Na_2S_2O_8$ activated by NaOH which concentration can be reduced to 0.25% for $Na_2S_2O_8$ and 0.5% for NaOH.

Moreover, the application of NaClO will cause many safety issues. Besides the safety issues, it is very hard to separate the chloride from the crude oil. Base on those reasons, the application of NaClO as a breaker in the oil and gas production will not generate the results as expected. Thus, for the degradation of RPPG, the best breaker is $Na_2S_2O_8$ activated by NaOH due to its stable, great degradation performance, and economical.

4.1.6. Degradation Degree of Different Gels. In addition, the degradation effects of breakers on different kinds of gels have also been studied. In this part, the degradation degree of conventional preformed particle gels with/without clay and RPPG have been compared. The degradation results for conventional PPGs with/without clay at room temperature are shown below in Figure 4.25 and Figure 4.26.

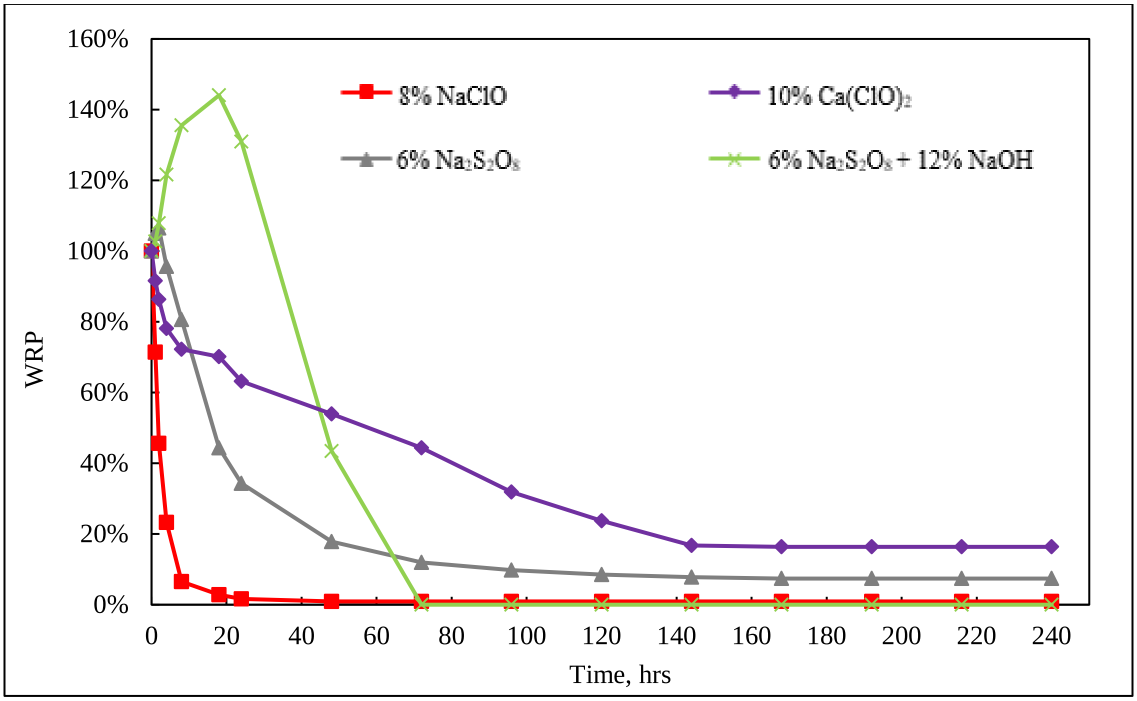


Figure 4.25. Different breakers’ degradation performance on conventional PPG with clay (Room Temperature)

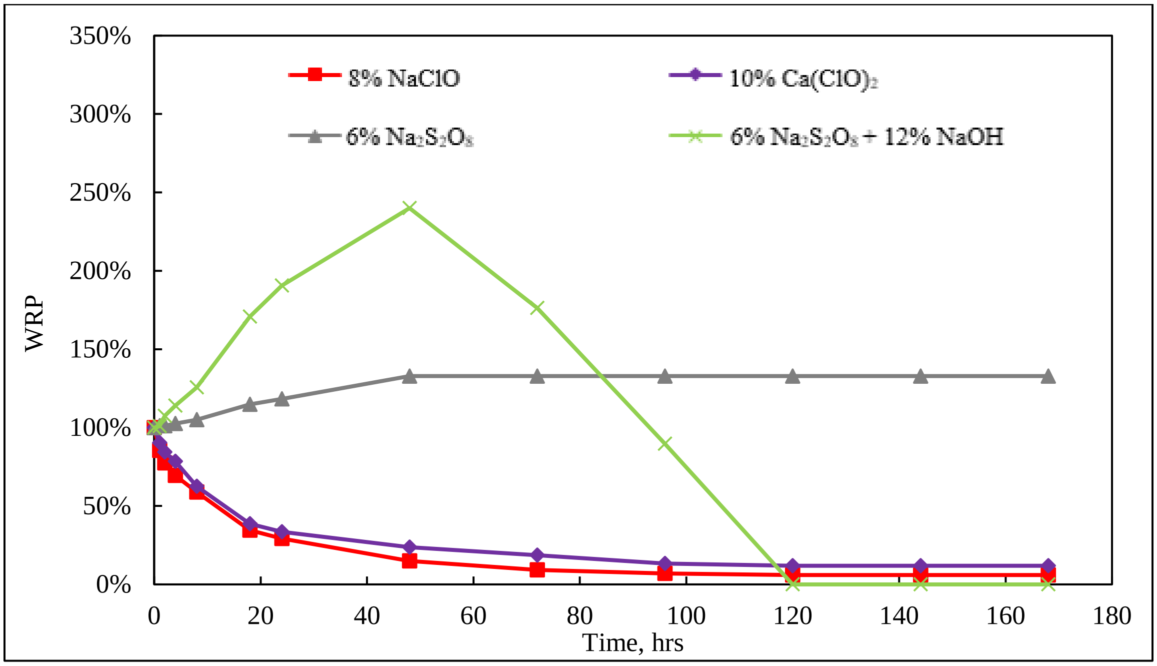


Figure 4.26. Different breakers’ degradation performance on conventional PPG without clay (Room Temperature)

The results clearly indicate that $Na_2S_2O_8$ activated by NaOH has the best degradation effect on those gels. Though NaClO can provide great degradation effect at room temperature, the safety issues of this breaker limit its applications. From Figure 4.25 and Figure 4.26, when the temperature is room temperature, PPG with clay can be totally degraded in 3 days by using 6% Na2S2O8 activated by 12% NaOH as breaker. And for the degradation of PPG without clay, it needs 5 days to totally degrade gels with 4% $Na_2S_2O_8$ activated by 8% NaOH.

Figure 4.27 and Figure 4.28 below show the degradation degree of those 3 different kinds of PPG when temperature is 65°C. When the temperature raised, $Na_2S_2O_8$ can degrade those PPG by itself. While $Na_2S_2O_8$ activated by NaOH still had the best degradation performance on PPG with clay compared with other breakers.

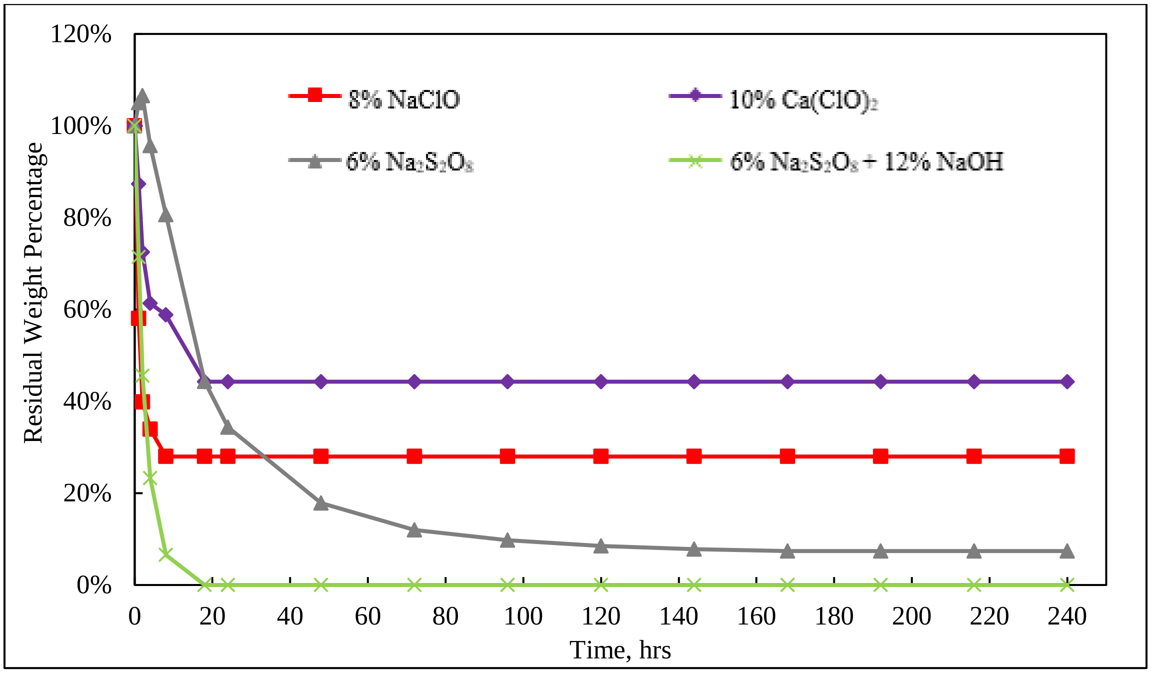


Figure 4.27. Different breakers’ degradation performance on conventional PPG with clay (65°C)

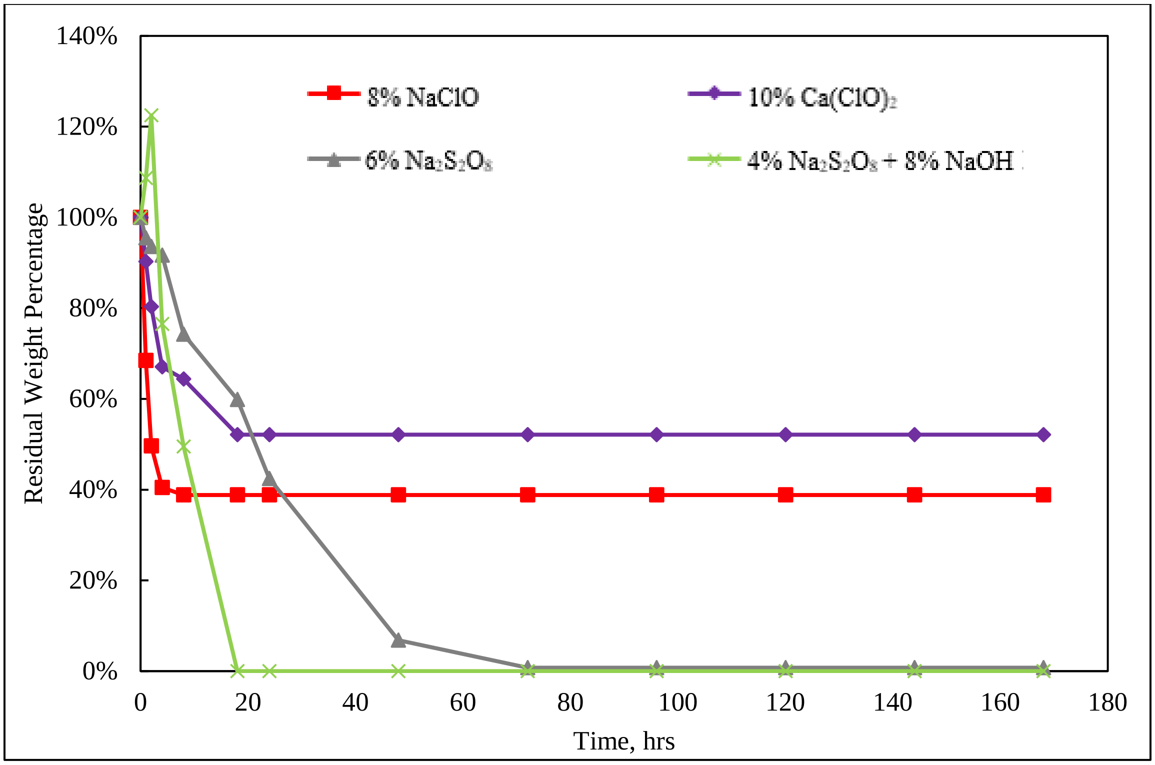


Figure 4.28. Different breakers' degradation performance on conventional PPG without clay (65°C)

By using 6% $Na_2S_2O_8$ activated by 12% NaOH, PPG with clay can be totally degraded in 18 hours. When the gel samples were PPG without clay, $Na_2S_2O_8$ activated by NaOH or high temperature can provide the best degradation performance. Both of them can totally degrade the gels.

Moreover, the degradation degree for those 3 kinds of gels under same breaker concentration (2% $Na_2S_2O_8$ activated by 4% NaOH) have been compared, the results are shown in Figure 4.29. It is clearly to figure out that $Na_2S_2O_8$ activated by NaOH can totally degrade all those 3 kinds of gels at this breaker concentration. And the results also indicate that RPPG need less time to be totally degraded than the other two kinds of gels.

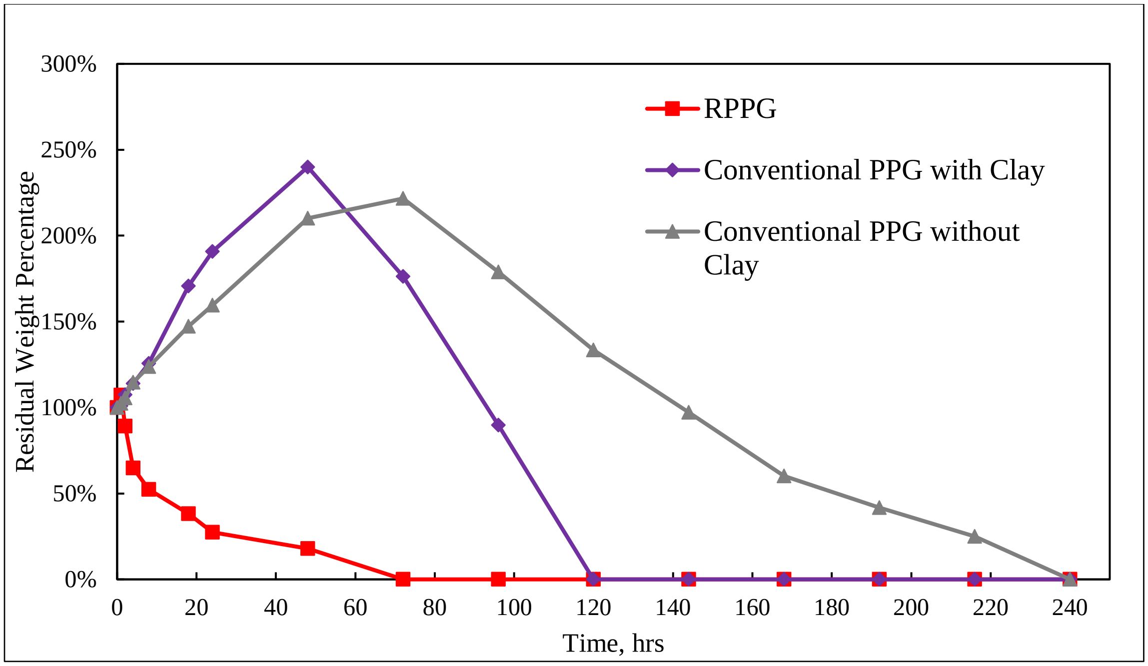


Figure 4.29. Degradation degree of different types PPG by $Na_2S_2O_8$ (2%) activated by NaOH (4%) (Room Temperature)

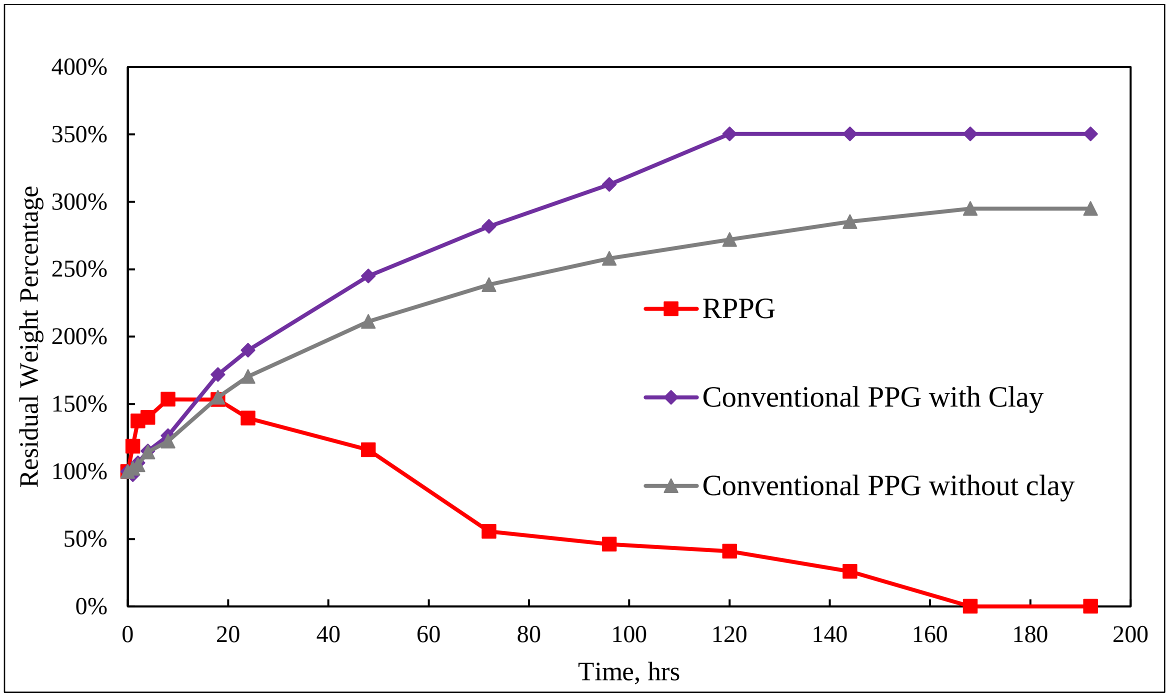


Figure 4.30. Degradation degree of different types PPG by $Na_2S_2O_8$ (1%) activated by NaOH (2%) (Room Temperature)

When the concentration of $Na_2S_2O_8$ decreased to 1%, the remaining weight percentage of different kinds of gels are shown in Figure 4.30. The results indicate that conventional PPG with/without clay cannot be braked by 1% $Na_2S_2O_8$ activated by 2% NaOH, while RPPG still can be totally degraded at this breaker concentration.

Therefore, $Na_2S_2O_8$ activated by NaOH is more suitable for RPPG degradation. For RPPG degradation, a lower $Na_2S_2O_8$ proportion is also effective for removing the plug of re-crosslinked RPPG when the breaking time requirement is not restrict, RPPG samples can be degraded even the concentration of $Na_2S_2O_8$ was 0.25%. While for conventional PPG with/without clay, the gel samples can be degraded only when the concentration of $Na_2S_2O_8$ was higher than 4%.

4.2. DAMAGE REMEDIATION EVALUATIONS

Formation damage is referring to the impairment of the permeability of the formation, is caused by physical-chemical, chemical, biological, hydrodynamic, and thermal interactions of porous formation, particles, and fluid and mechanical deformation of formation under stress and shear. The application of RPPG will cause formation damage for the reservoir. Thus, understanding the damage remediation of different kinds of breakers is very important. Several core flooding tests have been set to analyze the damage remediation. The results of core flooding test will have a more clear indication about the application of different kinds of breakers. In this part, the effect of different types of breaker has been analyzed, injection pressure and permeability of core effects on formation permeability restoration have also been studied. Figure 4.31 shows the core before and after soaking in the breaker solution.

Before RPPG degradation Before RPPG degradation After RPPG degradation

Figure 4.31. Core before RPPG degradation and after RPPG degradation

4.2.1. Breaker Effect on Damage Remediation. For the effect of different kinds of breakers, the breakers selected were 8% NaClO, 5% at $Na_2S_2O_8$ 80ºC and 5 % $Na_2S_2O_8$ activated by 10% NaOH.

The injection pressure for all cores was 200 psi and the gel concentration was 1:16. The weight of the breaker solution was 50g. After soaking in the solutions for 2 days, the permeability of the cores were measured and compared with their original permeability. Damage remediation was evaluated by damage percentage and restoration percentage which are defined as,

$$Damage\ Percentage = \frac{K_i - K_{aR}}{K_i} \times 100\% \tag{3}$$

$$Restoration\ Percentage = \frac{K_{ad}}{K_i} \times 100\% \tag{4}$$

where K_i is the initial permeability of cores, K_{aR} is the permeability after RPPG injection, and K_{ad} is the permeability after RPPG being degraded.

From Figure 4.31, it is clear that after RPPG being degraded, the gel cakes formed during RPPG injection on the surface of cores have been removed. The results of permeability in Figure 4.32 indicate that all the breakers used have the ability to restore the permeability of the damaged cores by degrading RPPG.

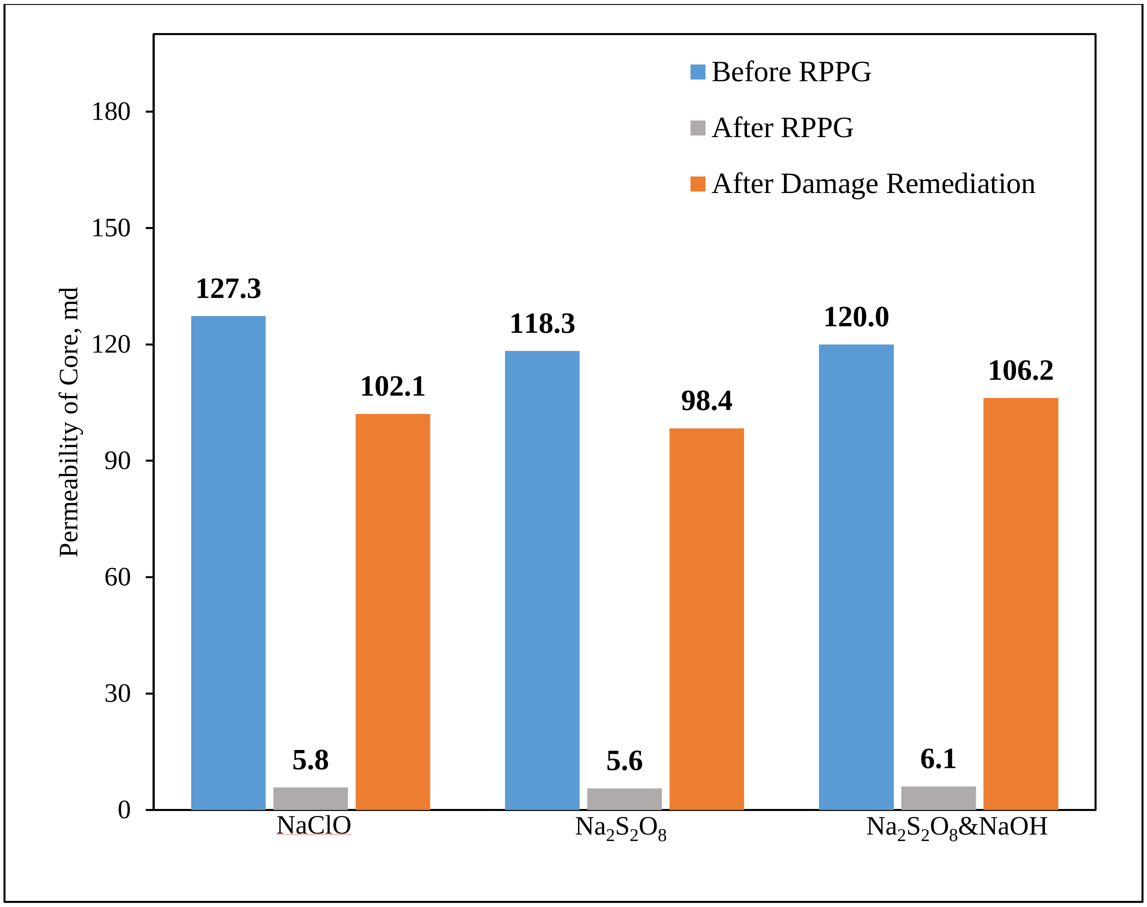


Figure 4.32. Damage remediation with gel cake after soaking in different breakers

And Table 4.1 shows the damage percentage and restoration percentage of cores. It is clearly that the injection of RPPG would result in a significant reduce of cores' permeability. Among the breakers been tested, 5% $Na_2S_2O_8$ activated by 10% NaOH had the highest permeability restoration percentage. By soaking the core in the solution which contained 5% $Na_2S_2O_8$ and 10% NaOH, the core can restore to 81.6% of its original permeability.

Table 4.1. Restored permeability percentage with different breakers (With gel cake)

Gel Breaker	Damage Percentage	Restoration Percentage
8%NaClO	95.4%	75.6%
5%Na2S2O8 @80 ℃	95.3%	78.4%
5%Na2S2O8+10% NaOH	93.1%	81.6%

After the RPPG injection, lots of the RPPG remained on the surfaces of the cores and formed gel cake which had a significant reeducation on the cores' permeability. So different kinds of breakers' degradation performances when the gel cake was removed have also been tested. The setup of experiments was same as the testes for cores with gel cake.

Figure 4.33 and Table 4.2 show that without gel cake, all the breakers have a better degradation performance on the restore of the permeability. And the values of restoration percentage were higher than cores with gel cake which meant that gel cake had more significant influence on cores' damage. While 5% $Na_2S_2O_8$ activated by 10% NaOH still has the best degradation performance.

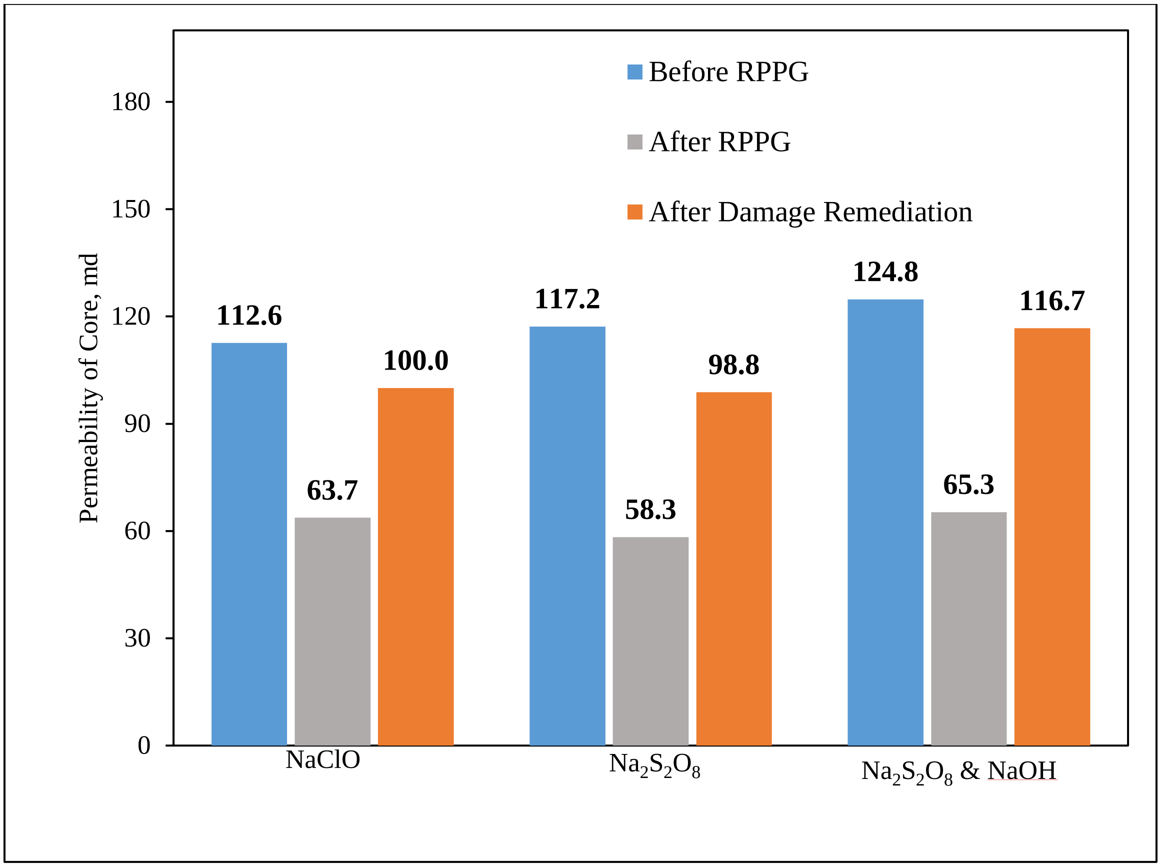


Figure 4.33. Damage remediation without gel cake after soaking in different breakers

Table 4.2. Restored permeability percentage with different breakers (Without gel cake)

Gel Breaker	Damage Percentage	Restoration Percentage
8%NaClO	43.4%	88.8%
5% $Na_2S_2O_8$ @80 ℃	50.3%	84.3%
5%$Na_2S_2O_8$+10% NaOH	47.7%	93.5%

4.2.2. Injection Pressure Effect on Damage Remediation. To analyze the effect of different injection pressures, 3 core flooding tests have been used to determine the effect. RPPG which gel concentration was 1:16 was injected into the core with different pressures: 200psi, 600psi, and 1000psi. Then the cores were soaking in the breaker solutions contained 1% $Na_2S_2O_8$ and 2% NaOH for 2 days. In this part of experiments, the permeability of cores was measured with gel cake.

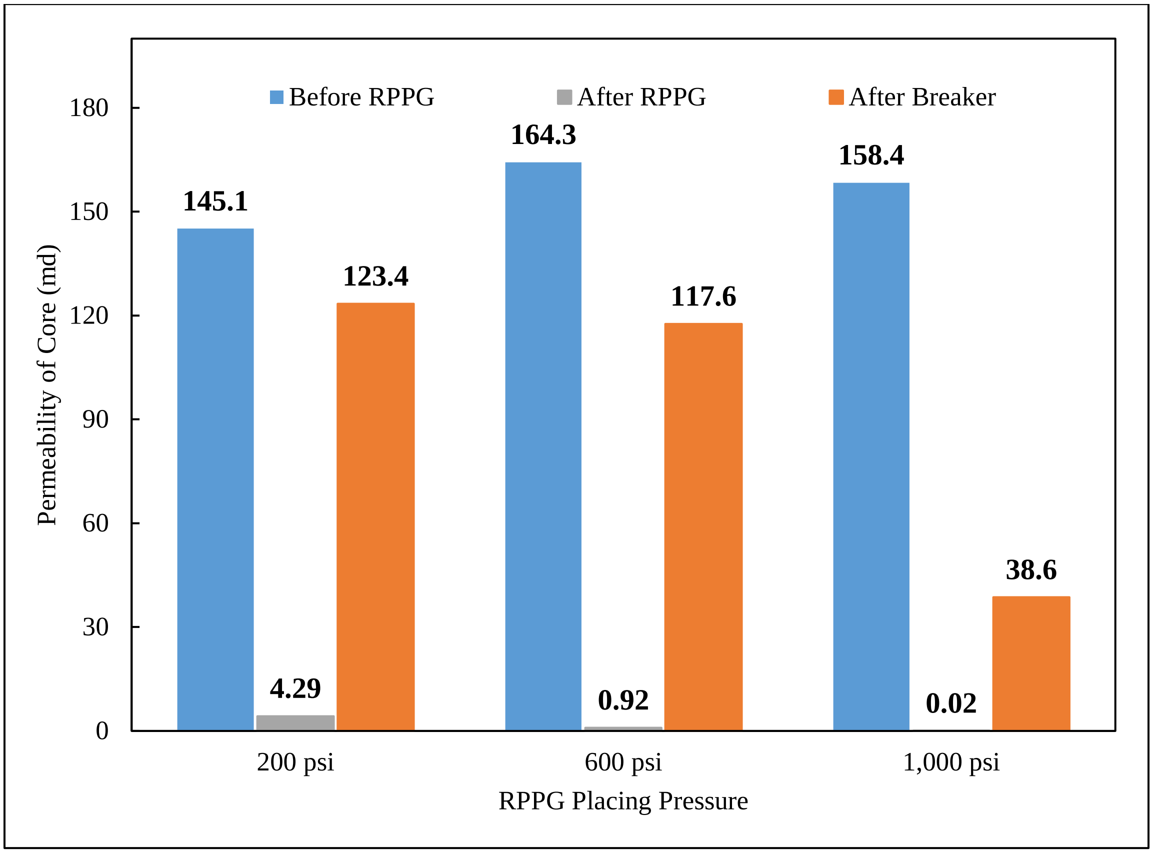


Figure 4.34. Damage remediation in different injection pressures

Figure 4.34 and Table 4.3 show the change on the permeability of cores. From the results, it is clear that with the increasing of injection pressures, the restoration percentage will reduce significantly. When the injection pressure is 1000psi, the restoration percentage is only about 25%. While the increasing of placing pressure has slight effect on core damage percentage.

Thus, when the injection pressure is too high, it is very hard for breaker to degrade RPPG. The reason is that with higher injection pressure, more RPPG were injected into the cores' pores where was very hard for breaker solution to get in and degrade gels. From the results, the degradation performance of gel inside cores is not as good as gel cake on the cores' surfaces.

Table 4.3. Restored permeability percentage with different placing pressures

RPPG Placing Pressure	Damage Percentage	Restoration Percentage
200 psi	97.0%	85.0%
600 psi	99.4%	71.6%
1000 ps	~100.0%	24.4%

4.2.3. Core Permeability Effect on Damage Remediation. Finally, the effect of cores' permeability has also been studied. 3 different cores which permeability was 16md, 164md, and 254md have been tested. Injected RPPG which gel concentration was 1:16 until the pressures reached 600 psi, then soaked in the solutions with 1% $Na_2S_2O_8$ and 2% NaOH for 2 days.

The results in Figure 4.35 and Table 4.4 indicate that the less the permeability of the core, the better the restoration degree will be. Permeability of cores has slightly effect on damage percentage, for all the cores tested, the value of damage percentage can reach to about 100%. However, for restoration percentage of permeability, higher permeability will result in lower restoration percentage.

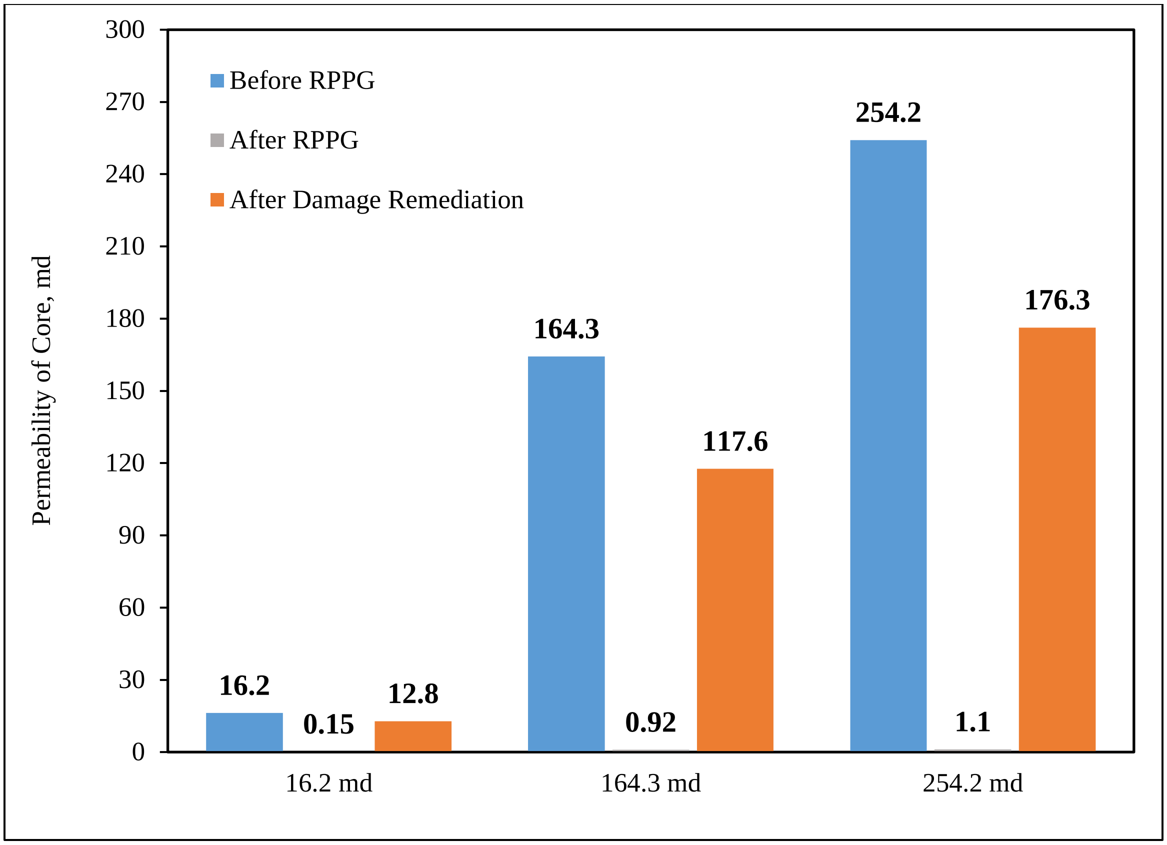


Figure 4.35. Damage remediation of different permeability cores

The reason is that more particle gels will be injected into the cores with higher permeability which is more difficult for breaker solutions to degrade. While even if the permeability of the core is about 254md, breaker can restore the permeability to about 70% of its original value.

Table 4.4. Restored permeability percentage of different permeability cores

Core Permeability	Damage Percentage	Restoration Percentage
16 md	99.1%	79.0%
164 md	99.4%	71.6%
254 md	99.6%	69.4%

5. CONCLUSIONS

In this study, the oxidizing breakers have been evaluated for degrading the re-crosslinked RPPG. Several factors, including breaker type, breaker concentration, temperature, gel concentration, gel aging time, and gel particle size, and their effects on RPPG degradation have been discussed. The damage remediation of cores has also been studied. Following conclusions have been drawn based on the studies.

- $Na_2S_2O_8$ activated by NaOH is the best breaker candidate for RPPG compared with other tested breakers, benefiting its wider practical range in breaker concentration and gel concentration.
- Based on the results, NaClO can provide favorable degradation performance on RPPG. However, the safety issues need to be considered that it may decompose and produce oxygen which can enhance the combustion of other substances. In addition, it is very hard to separate from crude oil.
- It is found that the concentration proportion of NaOH to $Na_2S_2O_8$ influenced the degradation process. The degradation rate and completeness were higher, when NaOH had a higher concentration proportion to $Na_2S_2O_8$.
- Ca(ClO)2 is an ineffective breaker candidate for re-crosslinked RPPG. During the degradation process, a layer of compact cover was generated on the surface of RPPG samples, which significantly decelerated the breaking process. Moreover, it did not break the RPPG to a low remaining weight

percentage when being applied at low concentrations or to high-concentration RPPG.

- Among the factors that influenced degradation process, the increase of breaker concentration and temperature led to the increase of degradation rate and completeness.
- RPPG with a higher gel concentration are more difficult to degrade. The increase of RPPG concentration significantly extended the time required to break the gel.
- The increase of RPPG aging time slightly increased the residue weight percentage after breaking.
- By comparing the degradation performance of three different types of PPG, $Na_2S_2O_8$ activated by NaOH was more suitable for RPPG degradation. For conventional PPG with/without clay, the gel samples can be degraded until the concentration of $Na_2S_2O_8$ was 2%. While RPPG can be totally degraded even the $Na_2S_2O_8$ concentration as low as 0.25%.
- Same breaker will provide different degradation performance on different PPGs. Thus, for the cleanup of different kinds of PPGs, several types of breakers need to be tested in order to find a specific breakers which can provide a favorable degradation performance.
- According to the results of damage remediation, NaClO, $Na_2S_2O_8$ at 80℃ and $Na_2S_2O_8$ activated by NaOH can restore the permeability of cores. Among those 3 breakers, $Na_2S_2O_8$ activated by NaOH had the highest restoration percentage under similar conditions.

- The injection pressure and permeability of cores have a considerable influence on the restoration percentage. The permeability restoration percentage was higher when the RPPG was injected at a lower pressure. In addition, the decrease of core permeability improved the permeability restoration percentage.

6. RECOMMENDATION

Besides the factors analyzed in this study, there are many other factors which can also affect RPPG degradation, such as pH value and salinity of the solution. By analyzing those factors, it will help to have a more comprehensive understanding of RPPG degradation. In addition, RPPG in the cores was removed by soaking the cores in the solutions which contained breaker; besides this method, injecting the breaker solutions into the cores is recommended to figure out whether the injection of breaker solutions can improve the restoration percentage or not.

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VITA

Enze Zhou received a Bachelor of Science degree in petroleum engineering from Missouri University of Science and Technology in May 2017. He began his master's degree in the Department of Geosciences and Geological and Petroleum Engineering at Missouri University of Science and Technology and joined Dr. Baojun Bai's research group in August, 2017. He received a Master of Science in Petroleum Engineering from Missouri University of Science and Technology in May 2019.