



بسم الله الرحمن الرحيم

Sudan University of Science & Technology
College of Petroleum Engineering & Technology
Department of Petroleum Engineering



**Research Submitted to College of Petroleum Engineering &
Technology in Partial Fulfillment of the Requirements for the
Degree of B.Sc. in Petroleum Engineering.**

**Primarily Evaluation of STLK – 4 Natural Polymers for
Potential use in Chemical Shut-off**

تقييم اولي لصمغ STLK-4 الطبيعي للاستخدام في الايقاف الكيميائي

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October 2020

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**This project is accepted by College of Petroleum Engineering and
Technology to Department of Petroleum Engineering.**

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Date: / / 2020

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

الإستهلال

سورة الفاتحة (الجزء ١) صفحة (١)

سُورَةُ الْفَاتِحَةِ

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ ١
الْحَمْدُ لِلَّهِ رَبِّ الْعَالَمِينَ ٢
الرَّحْمَنِ الرَّحِيمِ ٣ مَلِكِ يَوْمِ الدِّينِ ٤
إِيَّاكَ نَعْبُدُ وَإِيَّاكَ نَسْتَعِينُ ٥ أَهْدِنَا
الصِّرَاطَ الْمُسْتَقِيمَ ٦ صِرَاطَ الَّذِينَ أَنْعَمْتَ
عَلَيْهِمْ غَيْرِ الْمَغْضُوبِ عَلَيْهِمْ
وَلَا الضَّالِّينَ ٧

Dedication

We would like to donate this unpretentious effort to

Our Parents;

Who have endless presence and for the never ending love and
encouragement

Our brothers and sisters;

Who sustained us in our life and still

Our teachers;

Who lighted candle in our ways and provided us with light of knowledge

Finally; our best friends;

Our Classmates

Researchers...

Acknowledgements

Thanking to Allah before and after...

First and foremost; the greatest thanking to **our teachers** for their continuous support... and for their great efforts, they were the best guide and ad monitor...

Special thanks to Eng. **Ali Mamoun** and **Gisma Alshawani** for their assistance, providing technical support whenever we needed...

Finally; thanking to our colleagues and workers at College of Petroleum Engineering & Technology for their cooperation...

ABSTRACT

Chemical Water shut-off appears as an effective tool for blocking unwanted water zones; the techniques require chemical placement or injection into the reservoir to treat fluids in the target zone. Many types of chemicals were presented in the market includes Inorganic gels, Polymer gels, Biopolymers and Viscous flooding. Polymer is a chain of molecules made up of many repeating units. It has Linear, Branched, or Cross- linked Structure. The synthetic polymers cannot completely meet the requirements under high temperature or high salinity they also non-environmentally friendly and have poor shear resistance.

Although Natural Polymers are abundant in Sudan; recently, no detailed study has been performed for our indigenous natural polymers for potential use in chemical shut off. Through this study, a new discovered natural polymer named as STLK – 4 have been primarily evaluated for potential use in chemical shut off.

Moisture content, critical concentration and insoluble materials were first evaluated according to SY/T 6376 (2008). Aqueous solution was then evaluated under different temperature and shear rate for fluid concentration of 0.5, 1.0, 1.5, and 2.0% using Cannon and Fan 6 speed combined with KINEXUS rheometers.

Moisture content was found to be 11.56%, which is acceptable, according to SY/T 6376 (2008). While the insoluble materials was found to be 19% for fluid concentration of 2%, and was classified in the third category of the category of SY/T 5764. Critical concentration was estimated as 1%.

Aqueous solution presented a Non-Newtonian pseudo plastic (shear thinning) behavior; the viscosity decreased with shearing with power law relationship. The fluid has slight thermal degradation, and a very low biodegradation was observed in

low concentrations; while increment was achieved in viscosity after 24 hr, which indicates fully polymer hydration, occur with time.

Key word:

Synthetic Polymer, Natural Polymer, Fluid Concentrations, Thermal Degradation, Biodegradation.

التجريد

الانتاج الفائض للمياه يشكل معضلة كبيرة لانتاج النفط بالاضافة الى ما يتعلق به من توابع اقتصادية وبيئية، ويعزى هذا الى عدم تجانسية المكن.

تم استخدام الاصماغ البوليمرية بنجاح لتحسين كفاءة الازاحة وتخفيف انتاج المياه، (بسبب تعقيدات المكن، درجة حرارة المكن، نسبة الملوحة، مدى الحامضية او القاعدية، التكوين الصخري والنفاذية) و لكن اختيار هذه البوليمرات ما زال يواجه تحديا.

في اطار هذا البحث تم تضمين عديد من المركبات الكيماييه المستخدمة في الصناعات النفطية، خصائصها و صفاتها بالاضافة الى محاسنها و عيوبها

الصناعة النفطية دائما تتطلع الى تحديثات في العناصر والمواد و بالرغم من توفر الاصماغ الطبيعيه في السودان الا انه لا توجد دراسات تفصيليه للصبغ تحت الدراسة كماده كيميائيه تستخدم لايقاف المياه , تم دراسته صبغ مكتشف حديثا و يشار اليه 4 - STLK و تقييم خصائصه المبدئيه للاستخدام في ايقاف المياه الفائضه تم حساب نسبه الرطوبه للصبغ ب 11.56% و التركيز الحرج للمحلول ب 1% و وجد ان المائع يسلك سلوك غير نيوتوني حيث تنخفض لزوجته مع زياده اجهاد القص

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Nomenclature

WSO: Water Shut-Off

ACP: Annular Chemical Packer

WOR: Water Oil Ratio

DGS: Delayed Gelation System

AM: acrylamide

PAM: Polyacrylamides Gels

DH: degree of hydrolysis

PHPA: Partially Hydrolyzed Polyacrylamide

PVAP: polyvinyl alcohol copolymer

PFP: Phenol formaldehyde polymer

RPM: Relative Permeability Modifier

HEC: hydroxyethyl cellulose

OCP: Organically Cross-linked Polymer

PEI: poly ethylene imine

CT: coiled tubing

PV: Plastic Viscosity

AV: Apparent Viscosity

YP: Yield Point

cP: Centi Poise

θ_{600} : is the dial reading at 600 rpm

θ_{300} : is the dial reading at 300 rpm

θ_{200} : is the dial reading at 200 rpm

θ_{100} : is the dial reading at 100 rpm

θ_6 : is the dial reading at 6 rpm

θ_3 : is the dial reading at 3 rpm

rpm: Revolution per Minute

n: Flow behavior Index

k: Consistency Index

Chapter 1

General Introduction

Produced water (also called brine), is the water extracted from the subsurface associated with oil and gas. It may include water from the reservoir, water been injected into the formation and any chemicals added during the production treatment process (Glossary, 2013).

Excessive water production is one of the most serious problems for oil or gas fields, especially for mature reservoirs. Water production affects the economic life of reservoirs and ultimate recovery. It brings up operating expenses, such as pumping costs, water/oil separation costs, and equipment costs. Every year more than \$40 billion spent dealing with unwanted water (Bailey et al., 2000,). The excessive water production also causes wellbore corrosion, scale, and sand-production problems. Due to the chemical complexity of produced water, it requires seriously environmentally friendly concern when disposing the produced water. This likewise increases the disposal costs. Therefore, coming up with a proper and economical way to shut off or lower the excess water has become one of the most significant tasks for petroleum engineers.

The mechanism and the volume of the water produced into a wellbore mainly depends on petro-physical properties, pressure and temperature conditions of the reservoir, geometry and conditions of the aquifers, trajectory and location of the drilled wells within reservoir structure, type of completion and stimulation methods.

The flow of water to the wellbore can occur through two types of paths. In the first type, the water usually flows to the wellbore through a separate path from that of the hydrocarbons. In this case, reducing water

production increases oil, gas production rates, and improves recovery efficiency. This type of water production should be the primary candidate for water control treatments. The second type of water production is water that co-produced with oil usually later in the life of a water flood. However, controlling water production will result in corresponding reduction in oil production.

In fact, water is present in every oil field and is the most abundant fluid in the field; no operator wants to produce water, however, the classification of produced water indicates that some waters are better than others; hence, when it comes to producing oil, a key issue is the distinction between good (or acceptable), and bad (or excess) water. Sweep water is the water comes from either an injection well or an active aquifer that is controlling to the sweeping of oil from the reservoir. The management of this water is a vital part of reservoir management and can be a determining factor in well productivity and the ultimate reserves.

On the other hand, good water is the water that produced into the well bore at a rate below the economic limit of water /oil ratio (WOR). It is an inevitable consequence of water flow through the reservoir and it cannot be shut off without losing reservoir. Good water production occurs when the flow of oil and water commingled through the formation matrix the fractional water flow dictated by the natural mixing behavior that gradually increases the WOR.

This water should be removed as early as possible to minimize its associated costs, ideally with a down-hole separator. These devices, coupled with electrical submersible pumps, allow up to 50% of the water to be separated and injected down hole to avoid lifting and surface-separation costs as presented through Fig 1. Another type of produced water is known as bad water, It can be defined as water that is

produced into the well bore and produces no oil or insufficient oil to pay for the cost of handling the water-water that is produced above the WOR economic limit.

Numerous technologies developed to control unwanted water production, but the nature of the water production have to be known in order to design an effective treatment. Each water problem type has solution options that range from the simple and relatively inexpensive mechanical and chemical solutions, to the more complex and expensive reworked completion solutions (Bailey et al., 2000).

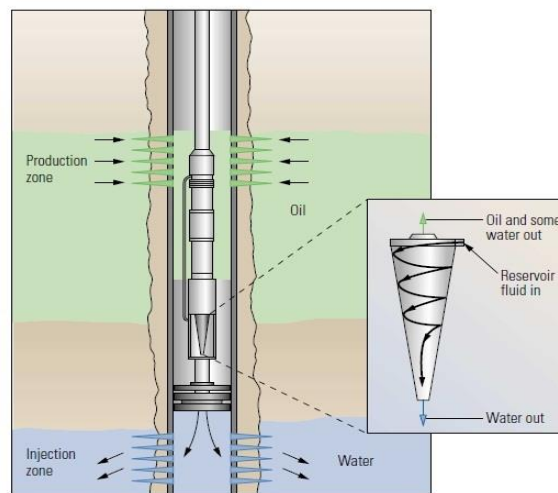


Fig. 1.1 Down hole Separator (Bailey et al., 2000)

Water production is one of the major technical, environmental, and economical problems associated with oil and gas production. In addition, it can limit the productive life of the oil and gas wells and the production of large amount of water results in

1. The need for more complex water–oil separation.
2. Rapid corrosion treatment of well equipment.
3. Rapid decline in hydrocarbon recovery.

Numerous technologies developed to control unwanted water production. In order to design an effective solution, the nature of the water

production must be known. The flow of water to the wellbore can occur through two types of paths. In the first type, the water usually flows to the wellbore through a separate path from that of the hydrocarbons. In this case, reducing water production increases oil, gas production rates, and improves recovery efficiency. This type of water production should be the primary candidate for water control treatments. The second type of water production is water that co-produced with oil usually later in the life of a water flood. However, controlling water production will result in corresponding reduction in oil production.

1.1 Sources of undesired water

Bailey et al., 2000 discuss the source of undesired water that related to mechanical and completion failure and reservoir problem as follows:

1.1.1 Casing, tubing or packer leaks

Leaks through casing, tubing or packers allow water from non-oil productive zones to enter the production string. Detection of problems and application of solutions are highly dependent on the well configuration (Fig 1.2).

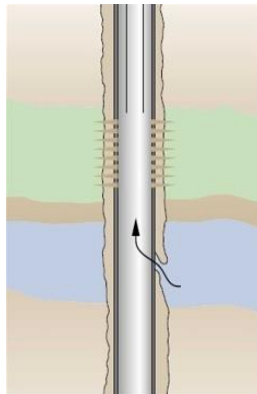


Fig 1.2 Casing, tubing or packer leaks (Bailey et al., 2000)

1.1.2 Channel flow behind casing

Failed primary cementing can connect water-bearing zones to the pay zone. These channels allow water to flow behind casing in the annulus. A secondary cause is the creation of a ‘void’ behind the casing as sand is produced (Fig 1.3).

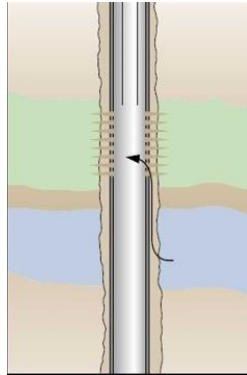


Fig 1.3 Flow behind casing (Bailey et al., 2000)

1.1.3 Moving oil-Water Contact

A uniform oil-water contact moving up into a perforated zone in a well during normal water-driven production can lead to unwanted water production. This happens wherever there is very low vertical permeability (Fig 1.4).

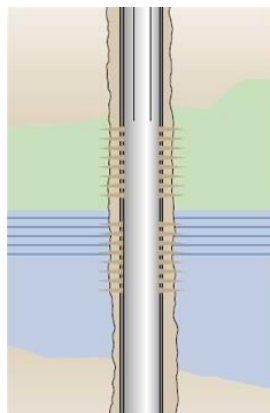


Fig 1.4 Moving oil-water contact (Bailey et al., 2000)

1.1.4 Watered-out layer without cross-flow

A common problem with multilayer production occurs when a high-permeability zone with a flow barrier (such as a shale bed) above and below is watered out. In this case, the water source may be from an active aquifer or a water flood injection well. The watered-out layer typically has the highest permeability (Fig 1.5).

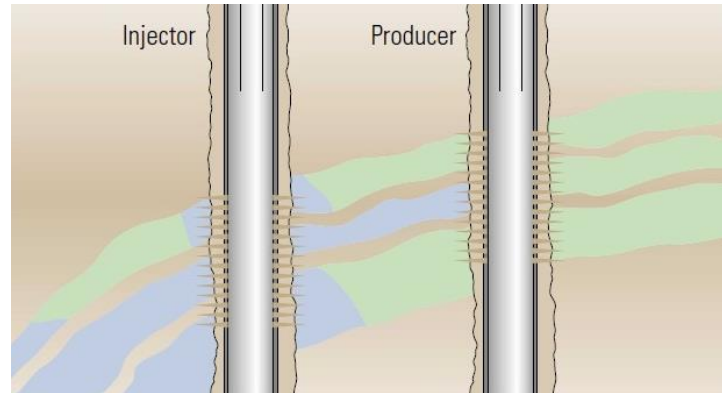


Fig 1.5 Watered-out layer without crossflow (Bailey et al., 2000).

1.1.5 Fractures or faults from a water layer

Water can be produced from fractures or faults that intersect a deeper water zone (Fig 1.6).

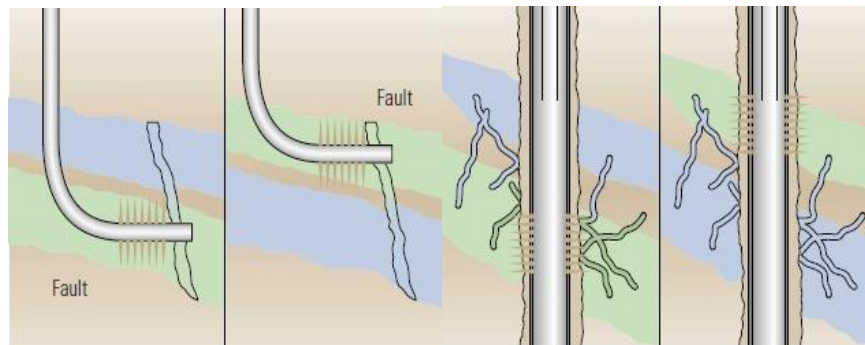


Fig 1.6 Fractures or faults from a water layer (vertical & horizontal well) (Bailey et al., 2000).

1.1.6 Coning (Cusping)

Coning occurs in a vertical well when there is an OWC near perforations in a formation with a relatively high vertical permeability.

The maximum rate at which oil can be produced without producing water through a cone, called the critical coning rate, is often too low to be economic. In horizontal wells, this problem may be referred to as duning or cusping (Fig 1.7).

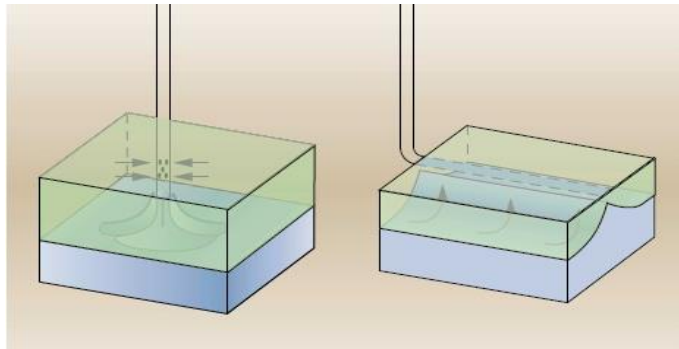


Fig1.7 Coning or Cusping (Bailey et al., 2000).

1.1.7 Gravity-Segregated Layer

In a thick reservoir layer with good vertical permeability, gravity segregation (sometimes called water under-run) can result in unwanted water entry into a producing well. The water, either from an aquifer or water flood slumps downward in the permeable formation and sweeps only the lower part of the reservoir. An unfavorable oil-water mobility ratio can make the problem worse (Fig 1.8).

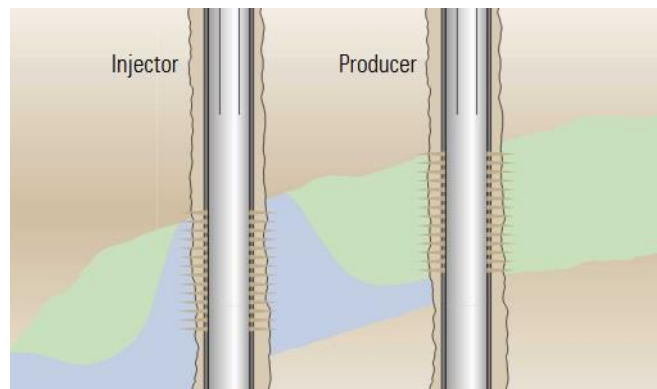


Fig1.8 Gravity-segregated layer (Bailey et al., 2000).

1.1.8 Watered-out Layer with Cross-Flow

Water cross-flow can occur in high-permeability layers that are not isolated by impermeable barriers. Water production through a highly permeable layer with cross flow is similar to the problem of a watered-out layer without cross flow, but differs in that there is no barrier to stop cross-flow in the reservoir (Fig 1.9).

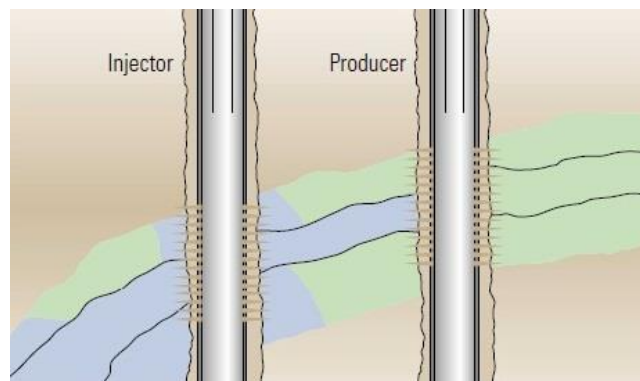


Fig 1.9 Watered-out layer with cross-flow (Bailey et al., 2000).

1.2 Water shut-off Techniques

Water shut-off is defined as any operation that hinders water to reach and enter the production wells. Each water problem type has solution options that range from the simple and relatively inexpensive mechanical and chemical solutions, to the more complex and expensive reworked completion solutions (Bailey et al., 2000).

1.2.1 Mechanical Solutions

In many near wellbore problems, such as casing leaks, flow behind casing, rising bottom water and watered-out layers without cross-flow, mechanical or inflatable plugs are often the solution of choice.

A) Expandable Packers (Posi-Set):

Expandable packers have inflatable elements, which are designed to expand in wellbore and provide isolation. After inflating, the volume of the inflatable elements will increase until fully occupy the gap to provide isolation (Fig 1.10).

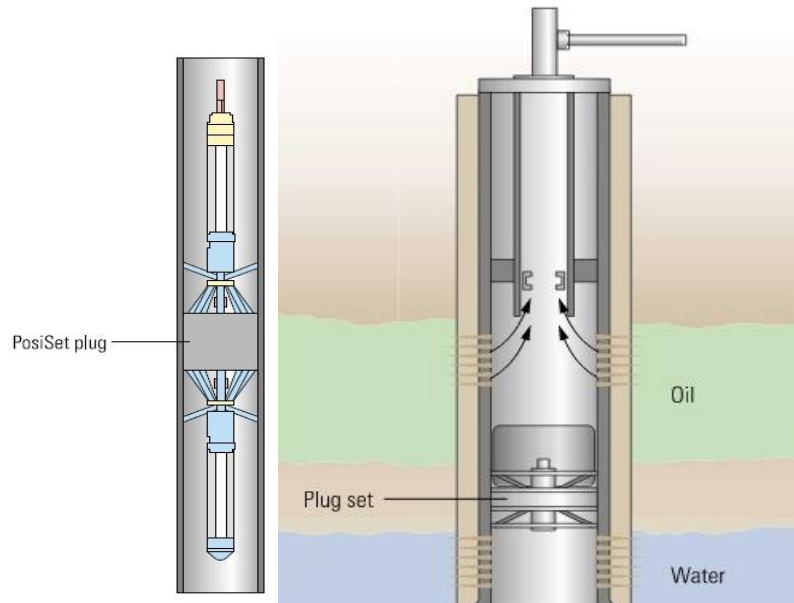


Fig 1.10 Expandable Pack -Posi-SET (Bailey et al., 2000)

B) Patch-Flex sleeve

When the wellbore must be kept open to levels deeper than the point of water entry, a through-tubing patch may be the answer. For example, a new coiled tubing- or wireline deployed, inside-casing patch called the Patch-Flex sleeve has been used successfully in many applications worldwide (Fig 1.11).

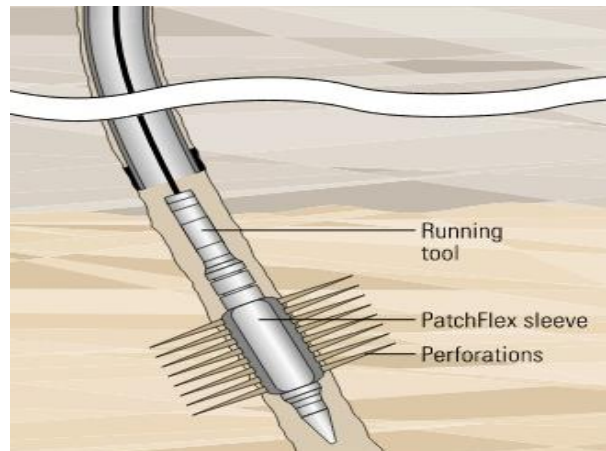


Fig 1.11 PatchFlex Sleeve (Bailey et al., 2000)

1.2.2 Completion Solutions

Alternative completions, such as multilateral wells, sidetracks, coiled tubing isolation and dual completions, can solve difficult water problems such as rising OWCs, coning, incomplete areal sweep and gravity segregation. For example, coproducing water is a preferred strategy for coning in high value wells. It involves perforating the water leg and using dual completions.

1.2.3 Chemical Water shut-off (Chemical Solutions)

Chemical Water shut-off defined as any chemical solution can be performed or injected into the reservoir or near well bore that lead to better conformance in the reservoir as well as blocking unwanted water production zones to be able to close the path of least resistance in front of water by reducing their permeability (A. H. Kabir, 2001).

Conformance is the application of processes to boreholes and near wellbore regions for reducing water production and enhancing oil/gas recovery (Steven H et al., 1999).

Chemical treatments require accurate fluid placement. Coiled tubing with inflatable packers can help place most treatment fluids in the target zone without risk to oil zones. Advantages of chemicals includes:

1. Sealing Matrix and Small Fissures.
2. Selective Reduction of Unwanted Phase Flow.
3. Subsequent Deeper Zone Perforating.
4. Reservoir Conformance.

A) Squeeze (Crete) Cement

Its low fluid loss and capability to penetrate , ideal for remedial treatment of tubing leaks caused by flow behind pipe. Once set, this cement shows high compressive strength, low permeability and high resistance to chemical attack. Often used with common cement for shutting off perforations when the problem is watered-out layers, or rising bottom water, Other applications include sealing gravel packs, casing leaks or channels behind casing.

B) Rigid Gels

Rigid gels are highly effective for near wellbore shutoff of excess water. Unlike cement, gels squeezed into the target formation to give complete shutoff of that zone or to reach shale barriers. They can be bullheaded into the formation to treat specific water problems such as flow behind casing and watered-out layers without cross flow, or selectively placed in the water zone using coiled tubing and a packer.

C) Annular Chemical Packer (ACP)

The Annular Chemical Packer (ACP) achieves zonal isolation using coiled tubing-deployed packers or bridge plugs The objective of the ACP is to achieve

full circumferential coverage over a relatively small length while leaving the liner free of material that might obstruct fluid flow or tool passage through the section. A low-viscosity, cement-based fluid is pumped through coiled tubing and a straddle-packer assembly and placed through the small slots in the pipe. Once placed, the fluid immediately develops high gel strength to prevent slumping and ensures complete annular filling and isolation.

ACP technology involves placement of a cement-based fluid into the annular space between an un-cemented slotted liner and the formation. The fluid conveyed to the treatment zone using coiled tubing and injected between inflatable packer assemblies to fill the annulus over a selected interval. It is designed to set in this position forming a permanent, impermeable high-strength plug, fully isolating the volume of the annulus (Fig 1.12).

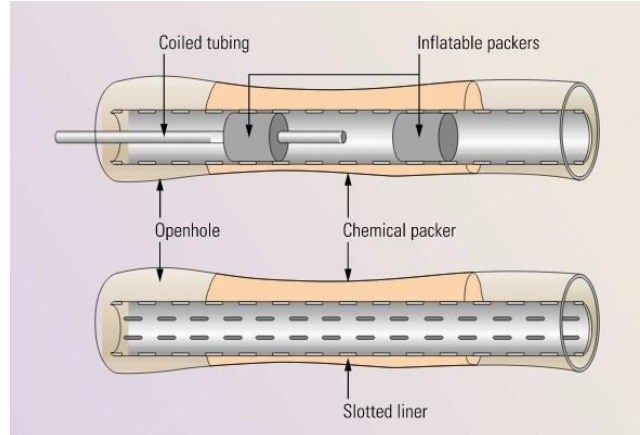


Fig 1.12 ACP technology (Bailey et al., 2000).

Problem Statement:

Chemical Water shut-off appears as an effective tool for blocking unwanted water zones and close the path of least resistance in front of water; it is require chemical placement or injection into the reservoir to treat fluids in the target zone. Many types of chemicals were presented in the literature includes Inorganic gels, Resins, Polymer gels Un-gelled Polymers, Biopolymers and Viscous flooding. Although those chemicals has different advantages, some disadvantages appear and limited the success or effectiveness of their uses; hence, oil industry is always looking for new material and agents; and therefore, the current study is primarily evaluates a new discovered natural polymer (Named as STLK – 4) with respect to chemical shut off and present the general properties of the polymer.

Research Objectives:

The main Objectives of this study is to evaluate primarily a new discovered natural polymer (Named as STLK – 4) with respect to chemical shut off; this includes the following:

1. To measure the Moisture Content of the polymer.
2. To measure the Insoluble Materials of the polymer solution.
3. To estimate the Critical Concentration for crosslinking the polymer solution.
4. To measure the fluid viscosity at different concentrations.
5. To study the effect of salinity in fluid viscosity at different concentrations.
6. To study the effect of temperature in fluid viscosity at different concentrations.
7. To study the effect of shear rate in fluid viscosity at different concentrations.

Chapter 2

Theoretical Background and Literature Review

According to A. H. Kabir, 2001 chemical options can be classified either by the type of chemicals used or by their functionality.

Chemical Options Classification by Type includes inorganic gels, Resins / Elastomers, Monomer systems, Polymer gels, Ungelled Polymers / Viscous Systems, Biopolymers and viscous flooding (with Polymers, optionally foamed). While Chemical options Classification by functionality includes: Sealants (temporary or long lasting), Relative permeability modifiers (liquid), Weak sealant relative permeability modifiers, and Mobility control or flow diverting chemical flooding systems (viscous/ foam flooding, selective plugging)

Petroleum engineer should have an average chemistry background to understanding these chemicals a level that enables him to choose and apply a proper option to the problem at hand.

2.1 Chemical Type for Chemical Shutoff

2.1.1 Inorganic Gels

Inorganic gels discovered in the 1920s and have been used for plugging lost circulation, zone squeezing and consolidating weak formations.

Inorganic gel systems use simple inorganic chemicals, which are water-thin. This water (thin) gelling systems can be injected easily into the matrix rock. Most of them internally activated. They either use an activator, hardening agent or a catalyst for gelation. These additives respond to temperature and initiate the gelation process. The advantages of this type includes that they are water-thin and has deep penetrating, they has temperature resistant (some up to 275°F, some products even

up to 325°F). They are relatively cheap compared to plastics and organic gels. While the disadvantages are, they are very rapid gelation time. React in acidic or basic environments. Also, and will lose gel structure upon contact with divalent ions (Chan et al., 1994).

Inorganic gels have low physical strength in general. Also they are subject to large amounts of syneresis (Hutchins et al., 1998).

i) Sodium Silicates.

Sodium silicate is a commonly used inorganic gel. It reacts with many chemicals to form a “sol” or gel-like mass that is strong enough to prevent water flow through the formation.

A simple system for use in sandstone formations is prepared by slowly adding a sodium silicate solution to a 15% HCl acid solution and then pumped into the well (A. H. Kabir, 2001). This solution solidifies in a few hours, depending on the temperature. Higher bottom-hole temperatures will cause it to solidify more rapidly. This formula works in sandstones with bottom-hole temperatures ranging from 60°F to 200°F. Note Reactants other than acids can be used with sodium silicate for limestone formations or higher temperature applications. Sodium silicate is low cost allows economical treatment of 5 to 10 ft radially around wellbore.; and It invades small formation pore, also it is Stable at high temperatures.

Through all this the Sodium silicate reactive with numerous common ions; and is not have a lot of strength after curing. It is also don't offer much resistance to flow in fractures and fully reacted sodium silicate has a low, but significant solubility in flowing water.

ii) Externally Catalyzed Silicates

Designed to control subsurface brine in production/injection wells in the area near the wellbore (O. Jaripatke et al. 2010). They react with brine to form a stiff gel

in formation pores wherever they contact brine. If formation water is fresh, a calcium chloride solution or seawater injected just ahead of the polymer with a small fresh-water spacer. In addition to the advantages and disadvantages of the silicate systems discussed above, externally catalyzed systems have some extra disadvantages such as depth of matrix invasion is limited and there is lack of control over gelation time.

iii) Non-Silicate Inorganic Gels

Used to overcome the problem associated with rapid gelation of sodium silicate, the use of aluminum has been tried. An example is Dowell's Delayed Gelation System (DGS). It comprises partially hydrolyzed aluminum chloride that precipitates to a gel when an activator responds to temperature and raises the system pH above a certain value. This system is quite tolerant to subsurface environments except that it can be destabilized by divalent anions like sulfates and carbonates, SO_4^{2-} and CO_3^{2-} . In addition, it has many advantages such as Gelation time can be controlled at up to 300°F, insensitive to the salinity of the mix water and multivalent cations, water thin and solid free while pumping-in, Acid removable when formed freshly, internally activated, and reduce permeability by more than 97%. While in the other hand, it can be destabilized by divalent anions like sulfates and carbonates, SO_4^{2-} and CO_3^{2-} . In addition, its stability decreases over time and permeability blocking not 100% (A. H. Kabir, 2001).

2.1.2 Resins / Elastomers

Thermosetting resins and elastomers have sufficient physical strength to seal fractures, channels and perforations. The same types of thermosetting resins used for sand consolidation, but in less concentrated form.

Resins & Elastomers has the following advantages:

- 1) Block fluid movement in pores, fractures and perforations.
- 2) Inert to all common down hole conditions and fluids
- 3) Provide complete, long-term sealing of passages, if properly placed.

While the disadvantages of Resins & Elastomers are

- 1) Relatively expensive.
- 2) Zonal isolation is required for a selective treatment.
- 3) Sensitive to water, surfactants, caustic and acid contamination before curing.
- 4) Hazardous chemicals.

Amongst resins, phenolic, epoxy and furfuryl alcohol resins are used.

i) Phenolic

Is a thermosetting resin. Stable at room temperature. Catalyst, added before pumping, causes liquid plastic to react at bottom-hole temperature. Once phenolic has fully reacted, it is strong and inert, only a strong caustic will attack it.

ii) Epoxy

Epoxy resins are superior among all thermosetting resins in terms of their mechanical, thermal and adhesion properties before and after curing (Khawlah et al., 2019). Epoxy is a product of the reaction between epichlorohydrin and bisphenol A and a common hardener is diethylenetriamine. Epoxy resin normally diluted with a reactive solvent such as EGMBE (ethyleneglycolmonobutyl ether), better known in the oil field as mutual solvent.

iii) Furfuryl Alcohol

Furfuryl alcohol used as a reactive solvent with phenolic and furan resins. This mixture polymerizes to a thermoset, but weak, brittle plastic in the presence of acid, also it can explosive at high temperatures and atmospheric pressures and is difficult to control in a well. A controlled catalyst system using trichlorotoluene and pyridine

with furfuryl alcohol allows safe, controlled treatments. It has higher thermal stability than phenolic and epoxy and it's relatively inexpensive which mean a large quantity injection is possible.

2.1.3 Monomer Based Systems

Various monomer (acrylamide, acrylate etc) based systems can be used for WGSO applications. These materials placed as low viscosity (water-like) solutions that polymerize after placement to form gels with low or high shear strengths depending on the product and application.

Because of their low viscosity, theoretically, they are good for deep matrix placement. However, in reality, gelation control is an issue. Polymerization is a free-radical initiation process that occurs very rapidly once initiated.

i) Acrylamide.

Some earlier applications used acrylamide (AM) monomer system. Premature gelation prevented by adding a retarder (such as potassium ferricyanide). However, since AM is a neurotoxin and a suspected carcinogen, it's use as a WGSO chemical has ceased.

ii) Acrylate based systems

Halliburton's Permaseal is an acrylate based, temperature activated monomer system. Uses an azo compound that undergoes thermal degradation to form a free radical, which initiates the in-situ polymerization of the monomer. The use of temperature to delay the formation of the free radical has resolved the problem of premature polymerization. Its advantages includes that: it is water soluble non-reactive towards formation fluids, contains no heavy metal cross-linkers, stable in temperatures up to 275/300°F, water-thin fluid with controllable gel times up to at least 200°F, and the resulting gel is quite strong and has permeability reduction of

up to 99.7%. The disadvantages are that it is expensive, and lower concentration systems are slightly water-soluble and have lower gel strength.

iii) Organically Cross-linked Monomer System

Halliburton's k-Trol is an in-situ polymerized and organically cross-linked treatment system, which are resistant to low pH and high salinity environment. k-Trol uses a low viscosity acrylamide monomer on the surface that are injected into a well and made to polymerize in the formation. It contains organic cross-linker, which forms a non-ionic cross-linked polymer once gelled. After polymerization occurs, polymer solution viscosity may vary from 10,000 to a million centipoise.

Organically Cross-linked Monomer System is water-thin, therefore deep matrix penetration possible, and quite resistant to low pH environment. On the other hand, it has contamination prone, rapid gelation likely, quite costly system, only low temperature applications reported.

2.1.4 Polymer Gels

Among the chemical methods, polymer gels have widest application because of their economic price, good propagation and absence of facility moderation requirements. Treatments with polymer gels are generally used for permeability modification treatments (Elchin et al., 2019).

Polymers are macromolecules, made up of repeating units joined. Polymer gel systems start as a flowing mixture of two components (high molecular weight polymer and another chemical called a cross-linker). The cross-linking molecules start attaching themselves to two polymer molecules chemically linking them together. The result is a three dimensional tangle of interconnected polymer molecules that ceases behaving like a fluid and can eventually constitute a rigid, immobile gel. The polymer may be naturally occurring or manufactured synthetically. The cross-linker may be metal ions or metallic complexes that bond

ionically or by chelation to the polymer, or organic molecules that bond covalently. The most important and promising polymer gel systems used in the oil industry can be classified as - Polyacrylamides (synthetic), Co-polymers (synthetic) and Biopolymers. Examples of metallic cross-linker: Al^{3+} , Cr^{6+} , Cr^{3+} , zirconium, titanium, boron etc. Examples of organic cross-linkers: Phenolics: phenol, hydroquinone, resorcinol, phenyl acetate, salicyl alcohol, furfuryl alcohol etc. Aldehydes: formaldehyde, paraformaldehyde, hexamethylene tetramine (HMTA) etc.

i) Polyacrylamides Gels (PAM)

PAM in its pure state is electrically neutral (non-ionic), seeming to preclude any cross-linking through ionic bonding. However, when mixed with a little alkaline solution, such as sodium hydroxide, or when subjected to elevated temperature, some of the amide groups convert to carboxylate groups.

Each of these carries a negative charge. The proportion of amide groups that convert to carboxylate is called the degree of hydrolysis (DH) and typically varies from 0 to 60%. In this form, the polymer called partially hydrolyzed polyacrylamide, PHPAM and with its negatively charged carboxylate groups becomes susceptible to ionic cross-linking. Cross-linking of a polyacrylamide solution provides better physical properties (viscosity / gel strength) to facilitate physical plugging of pores or fissures.

(A. H. Kabir, 2001) reported types of cross-linkers used in PAM gel technology as metallic and organic. Metallic cross-linker can be packaged either as simple inorganic ions in solution or within soluble chemical complexes in which the trivalent ion is associated with small inorganic or organic groups called ligands. Aluminum, Al^{3+} is rarely used anymore because the cross-linking reaction can't be

controlled or delayed. Chromium, Cr^{6+} is a better choice since the reaction took place in two steps. In the first step Cr^{6+} is reduced to Cr^{3+} which gives some delay (to allow matrix penetration) before Cr^{3+} does the cross-linking. The Cr^{6+} system is sensitive to H_2S , and recognized as toxic and carcinogenic substance. Chromium, Cr^{3+} , was packaged as a metal-carboxylate complex, chromium acetate. The acetate group has a structure very similar to the carboxylate groups on PHPA polymer. Thus, the Cr^{3+} ion is attracted to both the acetate ligand within the complex and the carboxylate groups on the PHPA polymer.

This slows the cross-linking process and ultimately gives some control over gelation time. Resulted in gel product claimed to be insensitive to pH from about 2 to 12.5, relatively insensitive to ions in formation fluids and untroubled also by H_2S and CO_2 (Ref. 2). It can be formulated to give a wide range of gel strengths and gel times at temperatures up to 255°F [124°C]. Use of organic cross-linkers in place of metal ions provides gels for high temperature / high salinity environment, with more flexibility in gel setting time (delayed gelation).

ii) Co-polymers

PHPAM, before and after gelling may be affected by divalent cations such as Ca^{2+} , which are relatively ubiquitous in formation waters. Ca^{2+} ions associate with the carboxylate groups in PHPA, causing free polymer to precipitate. This becomes more of a problem as the degree of hydrolysis of the polymer increases. Biopolymers like polysaccharide gels are also susceptible to break down due to thermal, hydrolytic, and especially, oxidative degradation. To obtain a thermally stable gel requires the use of a stable parent polymer. One solution is to use synthetic polymers in which some amide groups are replaced by a more inert chemistry that cannot hydrolyze to carboxylate and therefore remain vulnerable to wandering divalent

cations. It was found that co-polymerization of acrylamide with other monomers can provide protection against excess thermal hydrolysis. Copolymer made from polyvinyl alcohol copolymer (PVAP) and phenol formaldehyde polymer (PFP) has been used successfully in some high temperature (320°F), high salinity reservoirs for matrix conformance control. The resulting gel is quite rigid, claimed to have RPM property.

2.1.5 Ungelled Polymers

Their main function is to reduce water or gas permeability more than the oil permeability. Therefore, they are called Relative Permeability Modifiers (RPM). It has been demonstrated experimentally that simple linear polymers like polyacrylamide, polysaccharide (a non-ionic biopolymer) can adsorb on rock surfaces and can cause disproportionate permeability modification. In fact, it was also reported that this disproportionate permeability reduction happens to both to oil wet and water wet rocks and many linear polymers have this RPM property.

The advantages is that it is unaffected by multivalent cations, oxygen and acids and can be used in reservoir temperatures up to 275/300°F.

The disadvantages includes that they always reduce oil permeability as well, they are not currently sufficiently reliable to bull-head into unfractured wells, and PAM can be used in temperatures up to 165°F only and in reservoirs with low salinity

2.1.6 Bio-polymers

Biopolymers are also used in WGSO applications. They also can be cross-linked in the same way as PAMs. They are relatively insensitive to divalent ions. In addition, they are more temperature resistant compared to PAMs. However, they are susceptible to microbial attack. Bio-polymers used for conformance controls are mainly of the following types: polysaccharide (nonionic scleroglucan), xanthan, lignosulfonates cross-linked with Cr^{3+}

Scleroglucan is a non-ionic high molecular weight polysaccharide. It's has temperature, salinity resistant and appears to have better thermal stability than anionic synthetic polymer (A. H. Kabir, 2001). Consist of formaldehyde, as a biocide in the scleroglucan formulation appears to cause a reaction that increases scleroglucan's thermal stability. Its molecules are more rigid and rod-like (stronger gel) and shows superior shear stability. Both scleroglucan and xanthan Gum known to form physical networks (gel) above a critical concentration C_{gp} , "gel point" concentration. However, biopolymer gels are of limited strength and therefore considered not suitable for fracture treatment.

2.1.7 Viscous Flooding

Excessive water production sometimes caused by premature water breakthrough during water flooding. Reservoir heterogeneity and unfavorable mobility ratio are the main causes for poor sweep efficiency. If high permeability streaks and fractures are present between injector-producer pairs, the problem is best addressed by polymer treatment at the injector well.

Cross-linked polymers have been used successfully in many such cases. Sometimes foamed gel is also used.

i) Polymer Flooding.

The objective of viscous flooding is to improve sweep efficiency by means of improving mobility ratio, M . The only polymer to be used commonly for polymer flooding is PHPAM. Other polymers and co-polymers that were considered include xanthan, PAM, copolymers of acrylic acid and acrylamide, copolymers of AM and 2-acrylamide-2methyl propane sulfonate (AM/AMPS), hydroxyethyl cellulose (HEC).

ii) Foam Flooding

Gas/liquid foams offer an alternative to polymers for providing mobility control in chemical floods and have been both proposed and field-tested for steam-floods. Its primary targets have been matrix (unfractured) reservoirs. Their ability to generate and regenerate foams within many fractures is limited; therefore, foam flooding was not used in fractured reservoirs.

iii) Foamed Polymer Flooding.

If the reservoir is heterogeneous/fractured, foamed polymer flooding can achieve conformance improvement (by plugging and diverting fluid flow away from fracture/high permeability thief zone). Polymer addition to the aqueous phase of conventional foams results in foams of enhanced viscosity and stability. It found that foamed acrylamide-polymers promote exceptionally high effective viscosities and were much more stable.

2.2 Parameter affecting on Chemical shut-off

To study the effect of reservoir conditions and parameters on chemical shut-off processes it's critical to know that these effects depends on chemical we use and it change with the change of chemicals. Organic cross-linked polymer have been used to study these effects on shut-off processes.

2.2.1 Effect of Temperature on the Gelation Time

Temperature is a key factor in water shutoff treatments, as it strongly affects the gelation time. G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008 examined the effect of temperature on organic cross-linked polymer OCP (viscosity evolution as a function of time for gelling solutions) as shown in Fig 2.1. Note that the viscosity of the gelling solution remained constant during an induction period. At the end of the induction period, the viscosity gradually increased, indicating the onset of gelation.

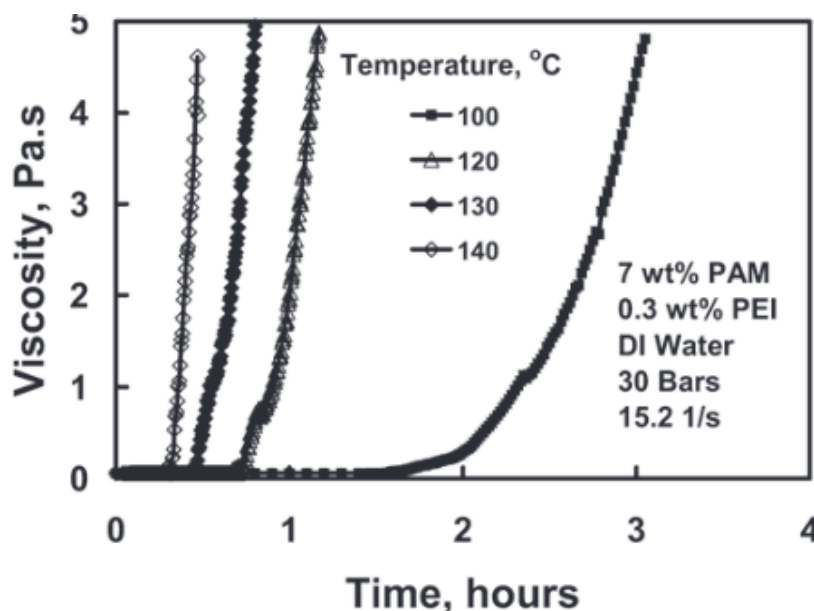


Fig. 2.1 Viscosity of OCP (G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008)

It is clear that gelation time decreased with increasing temperature. (Marfo et al., 2016) explain this by increased hydrolysis of the base polymer at higher temperatures that increased the rate of crosslinking, resulting in decreased the gelation time. An important fact from the data in Fig 2.1 is the short gelation time of this system at high temperatures. This makes the deployment of this system in high temperature reservoirs a difficult task. One way to address this problem is to cool down the near wellbore area by the injection of a suitable preflush this technique successfully applied in various fields worldwide.

2.2.2 Effect of NaCl

G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008 prepared OCP treatments in brines containing various concentrations of salts to examine the effect of sodium ions on the gelation time, NaCl salt was used. Solutions containing 7 wt% PAM and 0.3 wt% PEI. Then, NaCl was added to these solutions such that the Na concentration was 30,000 and 50,000 mg/l. The viscosity evolution of these two solutions and with a salt-free solution is shown in Fig 2.2

The gelation time with zero salt content is 0.67 hour. With the addition of 30,000 and 50,000 mg/l of NaCl, the gelation time increased to 4.4 and 6.8 hours, respectively. This increases the induction period and hence gives longer gelation times. This result also suggests that NaCl can be used as a retardation agent for the crosslinking reaction. This retarder can be used when deploying this PAM/PEI system in high temperature reservoirs to give longer gelation times.

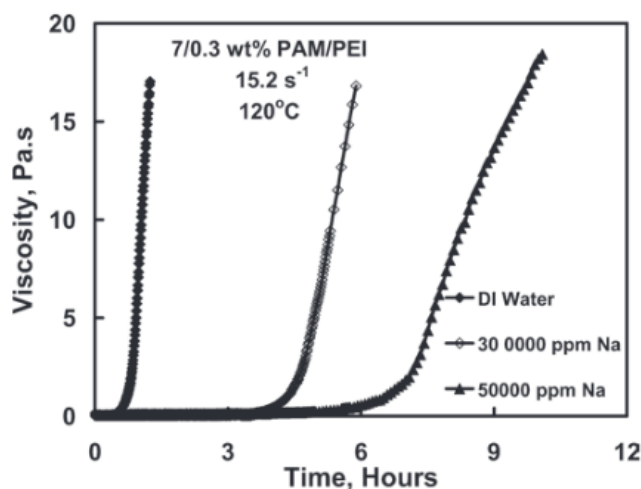


Fig 2.2 Effect of Na content on the viscosity at 120°C (248°F) (G. Al-Muntasheri, and H. Nasr-El-Din 2008)

Marfo et al., 2016 explain this phenomenon as attributed to the effect of brine on the hydrolysis of polymer. Brine is known to cause shrinkage of polymer hydration thereby reducing the crosslinking sites available for reaction leading to slow reaction rate, and thus the elongation in the gelation time.

2.2.3 Effect of the Initial Degree of Hydrolysis

Acrylamide-based polymers are known to hydrolyze under alkaline conditions producing carboxylate groups and ammonia. The degree of hydrolysis of PHPA is defined as the molar concentration ratio of the carboxylate groups to the total number of the amide and carboxylate groups on the PHPA chains. G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008 carried experiments with three samples of

PHPA with degree of hydrolysis of these samples was determined to be 0, 4.7 and 7.2 mol%. Fig 2.3 Shows that with PAM (zero degree of hydrolysis) the gelation time was nearly 2 hours. Then, it decreased to 0.55 hour upon crosslinking with a PHPA with an initial degree of hydrolysis of 4.7 mol%. A similar trend was observed with 7.2 mol% initial degree of hydrolysis. Therefore, increasing the degree of hydrolysis of the PHPA reduced the gelation time.

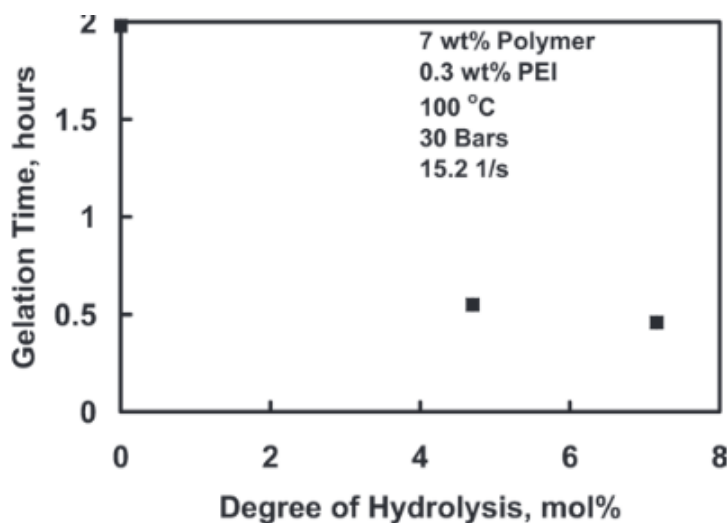


Fig 2.3 Effect of the Initial Hydrolysis on the Gelation Time (G. Al-Muntasheri, and H. Nasr-El-Din 2008)

2.2.4 Effect of Initial pH

In order to examine the effect of the initial pH value on the gelation time (G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008) prepared gelling solutions with different initial pH values and their viscosity monitored as a function of time

The initial pH of these solutions was adjusted to 3.5, 7 and 9.8 by adding a few drops of 20 wt% HCl. Fig 2.4 Shows the gelation time data as a function of initial pH value. The gelation time is longest with an initial pH value of 7. Then, it decreases for the two acidic cases (initial pH values of 3 and 5). Similarly, at an initial pH value of 9.8, the gelation time decreases and becomes less than the case with a pH of 7.

This data can be explained by the difference in hydrolysis rate of the amide groups of the PAM at different pH conditions. The hydrolysis reaches a minimum value at an initial pH value of 7 compared to the other cases. Hence, the longest gelation time is noticed (3 hours). On the other hand, the hydrolysis rate increases with the pH increasing/decreasing from the value of 7. Therefore, the gelation time decreases with the acidic cases (pH of 3 and 5) and with the alkaline case (pH of 9.8).

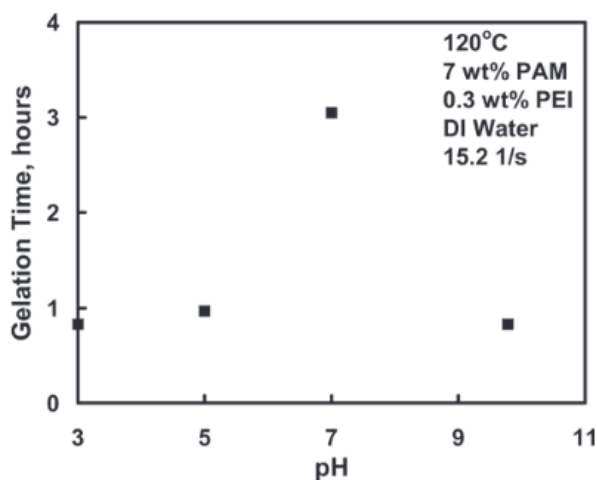


Fig 2.4 Effect of the pH on the gelation time. (G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008)

2.2.5 Effect of Polymer Concentration

G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008 reported the effect of Polymer Concentration on gelation time by preparing three gelling solutions in distilled water with PAM concentrations of 5, 7, and 9 wt%. These solutions contained the same concentration of PEI (0.3 wt%). The gelation time data were found to be 0.53, 0.37, and 0.25 hour for the solutions with 5, 7, and 9 wt% of PAM, respectively.

These data suggest that at low temperature reservoirs, shorter shut-in times can be obtained by using higher polymer loadings. Similarly, the gelation time can be increased at high temperature applications by using lower polymer loadings. However, lower polymer concentrations may lead to weak gels. Therefore, it is

important to examine the gel strength as a function of composition prior to field application in high temperature reservoirs. In addition, when deeper placements are required in matrix reservoirs, the gelant viscosity should be minimized. This might be compromised when high polymer loadings are used.

2.2.6 Effect of the Cross-linker Concentration

G.A. Al-Muntasheri and H.A. Nasr-El-Din 2008 evaluated the effect of PEI cross-linker Concentration on the gelation time.

Fig 2.5 shows the effect of PEI on the gelation time at 266 °F for samples with 7 wt% PAM prepared in distilled water. The PEI concentrations were 0.3, 0.6, 0.9, and 1.2 wt%. Data show that the gelation time decreases with increasing the concentration of the PEI cross-linker.

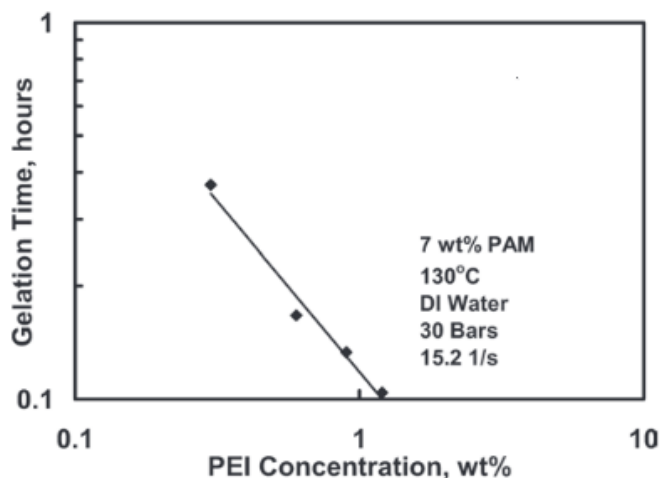


Fig 2.5 The effect of PEI on the gelation time at 266 °F (G.A. Al-Muntasheri, and H.A. Nasr-El-Din 2008)

Based on these results, the gelation time can be adjusted by varying the concentration of PEI. However, high concentrations of the cross-linker can result in gel syneresis, which noted at temperatures of (266 °F). These samples with syneresis contained 5 and 7 wt% of PAM cross-linked with 4 wt% PEI prepared in

distilled water. Syneresis is undesirable, especially when treating naturally fractured reservoirs.

2.3 Applications of Chemical shut-off Treatments

As stated by Vasquez et al. (2005), an offshore well having water-coning problems treated successfully with the OCP system. The results showed the superior capabilities of the OCP system caused by deeper penetration inside the matrix of the formation. The Organically Cross-linked Polymer (OCP) system consist of copolymer of acrylamide and t-butyl acrylate (PAAtBA). The organic cross-linker is a material based on polyethyleneimine (PEI). In-situ gelation takes place through a process activated by the well temperature, plugging pore spaces and channels, thereby limiting undesired water flow.

The OCP system is insensitive to formation fluids, lithology, and/or heavy metals. Another advantage of the OCP system is the predictable viscosity profile (Fig 2.6) that can be used to improve diversion over long treatment intervals.

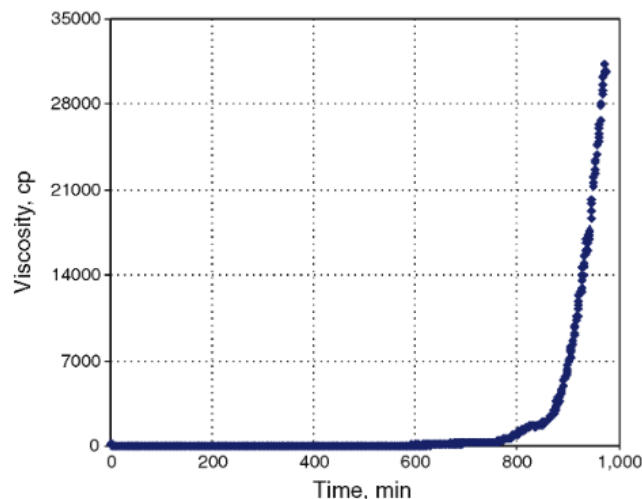


Fig 2.6 Typical gelation-time curve for the OCP system: viscosity versus time J. Vasquez et al., 2010

It was determined that Well A had excessive water production as a consequence of the combination of water coning and the high-permeability streaks present because of the naturally highly fractured reservoir. It was a standard practice by the operator to abandon (isolate) an interval once the water-oil contact reached the perforations and perforate the same formation a few feet higher up. There were only a few feet left to produce in this interval because the producing layer was almost completely invaded by the coning of water.

The OCP system used in combination with a tail-in of standard cement to shut off 98 ft of perforations. The theoretical size of the OCP treatment designed based on 10 ft of radial penetration into the formation. A 315-bbl treatment was injected at 2 bbl/min. The use of cement as a tail-in is not a standard practice for an OCP application; it used on the customer's request. Water production for this well decreased substantially following the polymer treatment and the perforation of the new interval (36 ft of perforations). After perforating the new zone, the customer decided to stimulate the well with an aggressive acid treatment of 190 bbl. Even after the acid job, water cut decreased from 31.7 to 3.7%, as illustrated in Fig 2.7. After one year, this well was still producing at low water cut after the OCP treatment.

An offset Well B producing from the same formation and having similar water-coning problems treated with a standard squeeze-cementing job. As Fig 2.8 illustrates, water cut before the treatment was approximately 22% and eventually had increased to 55.4% after the treatment. Because the squeeze-cementing job did not provide a barrier deep inside the matrix of the formation, the attempt to reduce water production was unsuccessful. Well B abandoned seven months after the squeeze cement job because of excessive water production.

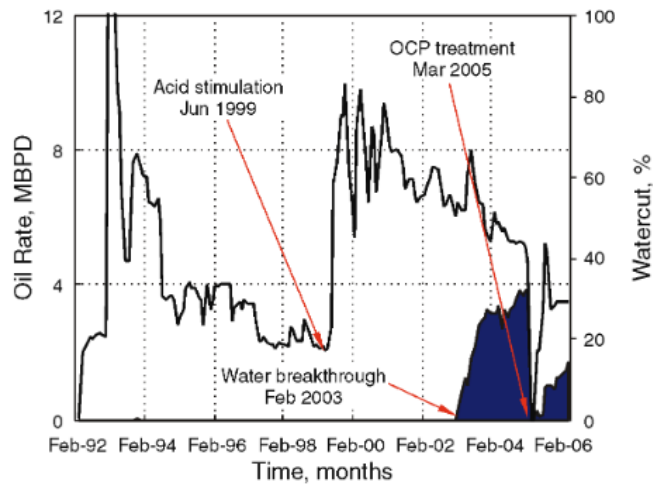


Fig 2.7 Production history of Well A before and after the OCP system treatment. J. Vasquez et al., 2010

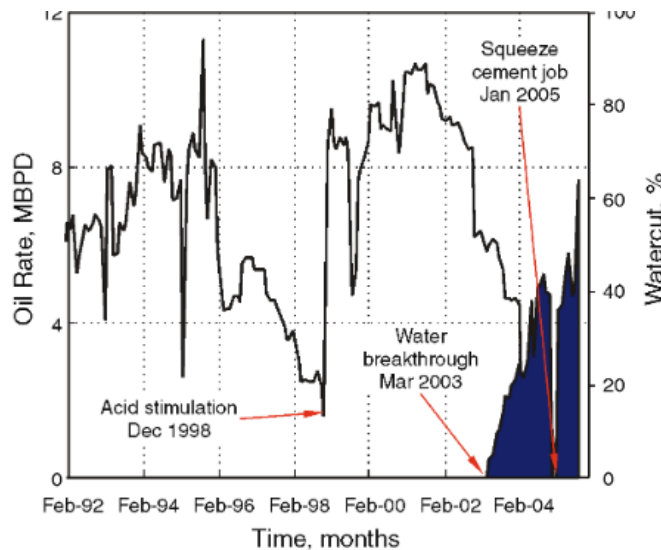


Fig 2.8 Production history of Well B before and after the cement-squeeze job. J. Vasquez et al., 2010

Another application of water shut off is the example presented by Mercado et al. (2010), field in reference is a naturally fractured reservoir formed by limestone and dolomites with permeability that varies from 10 to 120 mD. Matrix porosities vary from 2 to 8%. The reservoir is located at depths of (15,090 to 21,000 ft). The reservoir holds a volatile oil deposit of 38° API, with an initial pressure of 10,056 psi, and a bubble pressure of 3,726 psi.

Mercado et al. (2010) presented that the reservoir is under depleted conditions with an actual reservoir pressure of 3,130 psi and an average bottom-hole temperature of 307°F. The recovery mechanism is a water drive, and the depth of the original oil-water contact was located at 21,077 ft. The current oil-water contact varies along the field and influenced by the extensive net of natural fractures and faults.

Well C is a vertical, cased-hole well drilled to (18,100 ft) and completed in an open-hole section of (1,070 ft) of carbonate formation. The bottom-hole temperature for this formation was 300°F. Well C was initially acid-stimulated to improve oil production; however, a water cut of almost 90% observed after this stimulation treatment. The customer then decided to attempt to decrease water production by pumping the OCP system followed by a small tail-in of foamed cement. This operation carried out with coiled tubing (CT) in three stages, alternating the OCP system and the foamed cement.

The three OCP/foamed-cement stages performed focused on sealing off a net of natural fractures present at the bottom of the open-hole section. After the third stage was complete, the well shut in overnight to allow the systems to fully crosslink. Following the treatment, the remaining exposed open-hole section was acid-stimulated and the well put back in production. Fig 2.9 illustrates the results of the treatment that decreased the water cut from 90.0 to 0.2%, even two years after the OCP treatment performed.

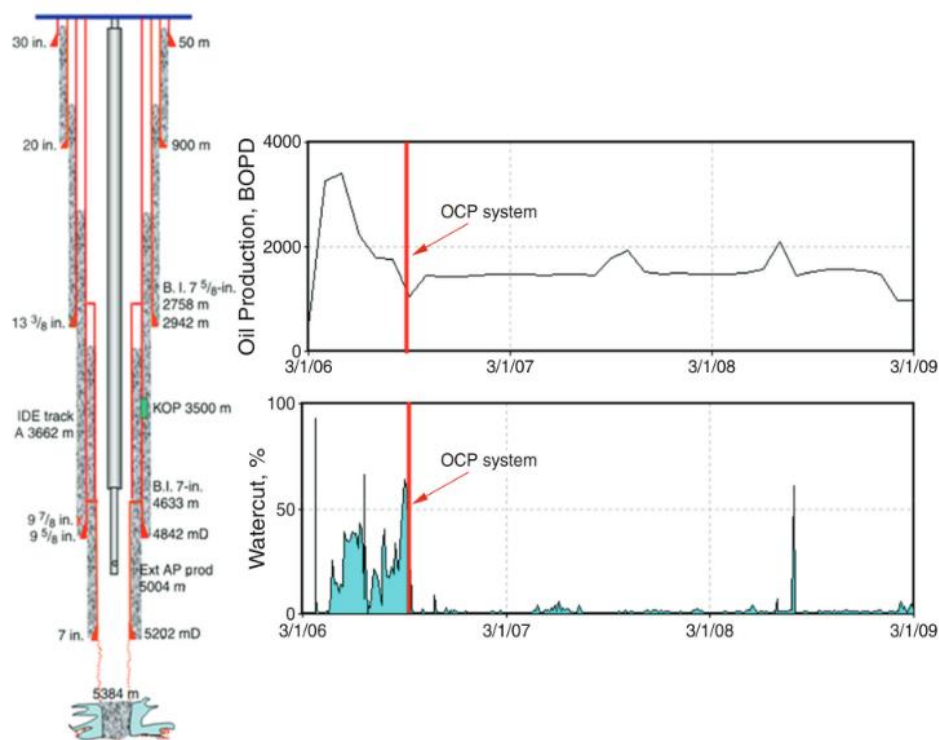


Fig 2.9 Well C water-cut and Production History J. Vasquez et al., 2010

Sharma et al.(2013) presented that a well in the south Ghawar area was treated with water shut-off chemical but the result was not satisfied. reported the well was completed as a single lateral openhole with 360.3 m of reservoir contact. Before the treatment, the well-produced wellbore fluid with 60% water cut. The water entry zone detected at bottom interval. The well de-signed to treat water production zone using cement plugs and organic crosslinked polymer. One inflatable cement ring (ICR) was set at 2636.5 m, and squeezed 23.85 m³ of OCP below ICR. The second one was set at 2617.9 m and a cement plug injected between the two ICRs. The production data showed that after water shutoff treatment, the water cut was almost the same as before. Water shutoff chemical might partly enter the producing interval and almost completely plugged the wellbore.

SUN X. and Baojun B. (2017) presented that chemical materials also can be used not only as plugging agents but also temperature zonal isolation packers. Mechanical methods are always used to do near wellbore or wellbore treatment, while chemical methods can deal with matrix problems or where need maximum penetration in fracture networks. Mechanical methods cost more than chemical methods and the depth correction is always a challenge. They explained that water shutoff methods related to the completion types. Both mechanical and chemical methods can be applied to horizontal wells completed as open hole or cased hole. From the current field applications, water shutoff in slotted liner and sand screen completion wells can only be carried out by chemical methods, while mechanical methods can be used to create temporary isolation. SUN X. and Baojun B. (2017) stated also the chemicals should be selected based on the size of the hole or slots on the liners.

Azza et al.(2016) assessed pilot water shut off in high water production wells in Sudan; in which regular chemical water shut off was applied in high water cut wells is a routine in the wells improvement. Comparing recorded production of oil and water after injection. Pre-test calculation shows injected amount is around 38 m³ into the lower part which is closed to OWC. HE-04 Injectivity Test was successful and meeting the requirement. The authors presented that designed quantity of chemical injected successfully, by monitoring water, noticeable reduction observed during the operation. This attempt may have been completely fail to reduce water production for long term. In addition, they showed that one of the issues associated with the reservoir's diagnosis is the information inaccuracy regarding permeability.

Chapter 3

Methodology and Measurements Procedures

This chapter contains detailed description of the chemicals used in experiments (name and function of each material), as well as detailed description of the experiments used to measure and estimate the polymer properties, which includes measurement principles, devices used, the tests carried out on each concentration and how the testing processes achieved.

Laboratory tests were used to characterize and evaluate the polymer solution; the property that is determined is the apparent viscosity of the fluid as a function of shear rate, temperature, and time. A series of standard laboratory tests were performed to address and evaluate the basic properties of the polymer and the performance of the fluid; all the measurements were performed according to standard procedures defined by the Chinese Standard for Petroleum Industry SY/T

3.1 Materials and Samples Preparation

The polymer was obtained as dry plugs and milled to obtain powder to make it easy to dissolve in the water. 2 % solution of Gum Arabic was prepared, and then diluted to the concentrations of 0.5%, 1.0% and 1.5 according to SY/T 5764 procedures. The solution was prepared using Elecircular Mixer Fig 3.1, which mainly consists of electric motor connected with a fan to stir the components.



Fig 3.1 Elecircular Mixer

Distilled water was prepared to remove impurities from the tap water to prepare the polymer aqueous solution in addition Sodium Chloride NaCl, Magnesium Chloride MgCl₂ have been obtained from College of Petroleum

3. 2 Polymer's Moisture Content Measurement

Moisture Content of the powder was measured by heating of 5.00g of the gum powder in the oven following these steps

1. 5 g from of the powder was prepared using sensitive scale Fig 3.2 (an ADAM PGW153e)
2. The sample Placed in the oven at 105 °C for 1 hour then placed it in the desiccator Fig 3.3 for protecting them from water vapor in the air until the sample temperature reached room temperature.
3. The sample weighed using the above-described sensitive scale.
4. The steps 2 to 4 were repeated until constant weight was obtained.
5. Moisture Content was then calculated using the following equation:

$$W = \frac{w_1 - w_2}{w_1} * 100 \quad \text{----- (3.1)}$$



Fig 3.2 Sensitive Scale



Fig 3.3 Desiccator

3.6.2 Critical Concentration

The critical concentration is the minimum concentration at which intermolecular cross-linking is possible (Elham et al., 2016). The value of critical concentration C^* is determined by measuring the solution viscosity as a function of concentration. The viscosities of the obtained solutions were measured using cannon viscometer using the following steps

1. Cannon viscometer (Fig 3.4) was filled with appropriate quantity of known concentration aqueous solution; then placed in the viscometer into the holder, and inserted it into the constant temperature water bath.
2. The sample was kept for approximately 10 minutes in water bath to reach the desired temperature.
3. Remove the rubber and allow the solution to travel upwards, measuring the efflux time for the solution to pass from the first black line to the second one.
4. Calculate the kinematic viscosity of the sample by multiplying the efflux time in seconds by the viscometer constant (C).

$$\mu(cp) = v(cSt) * \rho \quad \text{-----} (3.2)$$

5. The results were plotted as the log of specific viscosity (μsp) versus the log of polymer concentration.
6. The point in which the resulted curve change its direction represent the critical concentration as presented in Fig 3.5



Fig 3.4 Canon viscometer

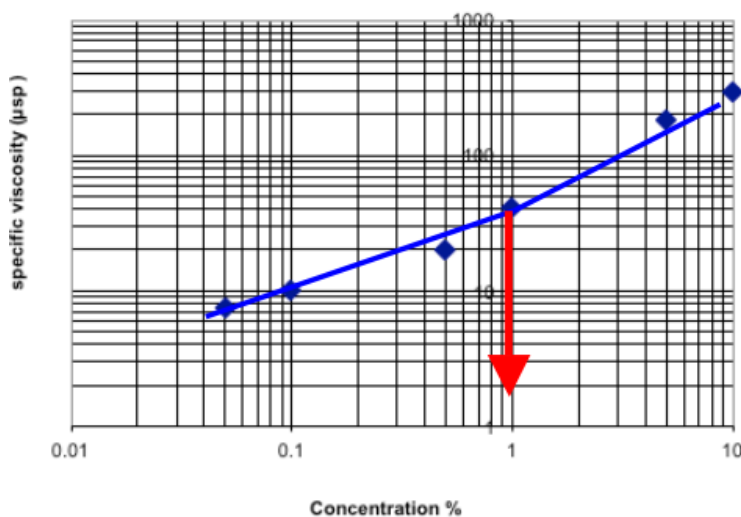


Fig 3.5 Minimum Concentration for Cross-linking the Polymer (After Elham el al., 2016)

3.4 Insoluble Components Measurement

The gum solutions of different concentrations were tested to estimate the insoluble components according to SY/T 5764, General Technical Specifications of Natural Plant Gum.

First 50.20g of the solutions placed in a centrifuge tube then centrifuged at the speed of 3000r/min for 30min.

The upper clear solution in tube was dumped out; 50ml distilled water was added and stirred with a glass rod; the mixture was centrifuged again at the speed of 3000r/min for 20 min and the top solution in tube was also dumped out.

The tube placed in temperature of 105 °C to dry the residual mixture totally. Finally, the sold residual resulting from the mixture was weighted, and then the insoluble components were calculated as follows:

$$\eta = \frac{m_3 - m_2}{0.20X(1 - W)} \times 100\% \quad \text{-----} \quad (3.4)$$

Where:

η The Insoluble Components expressed as a percentage

m_2 The weight of centrifuge tubes, (g)

m_3 The total weight of the centrifuge tube and the liquid with the insoluble components, (g)

W The moisture content in the powder, expressed as a percentage

The test was repeated for 2 times for same liquid and the average was taken as the Insoluble Components.

3.5 Rheological Properties Test Procedure

The Fann viscometer (6- speed viscometer) Fig 3.6 has been used to measure rheological properties of polymer solution. In order to measure Plastic Viscosity (PV) and Yield Point (YP) the following steps were followed:

1. The viscometer cup approximately 2/3 filled with polymer sample, then placed on viscometer and raised the cup until rotary sleeve immersed to scribe lie on sleeve. Started rotating until the viscometer achieved a constant value then the value was recoded. The steps were repeated for the different speed 600, 300, 200, 100, 6, and 3 rpm.

2. Calculate the Apparent Viscosity (AV), Plastic Viscosity (PV) and Yield Point (YP) by using the following equations

$$AV = \theta_{600}/2 \quad \text{----- (3.3 -a)}$$

$$PV = \theta_{600} - \theta_{300} \quad \text{----- (3.3 -b)}$$

$$YP = \theta_{300} - PV \quad \text{----- (3.3 -c)}$$

Where θ_{600} and θ_{300} are the readings at 600 and 300 rpm from the 6 speed viscometer, respectively.



Fig 3.6 6-Speed Viscometer

3.6 Shear Rheology and performance evaluation

KINEXUS rotational viscometer (Fig 3.7) was used to estimate the fluid viscosity at shear rate of 20 S^{-1} following SY/T 5107 (1995) procedures, SY/T 5107 includes continuous heating of the fluid under shear rate of 10 S^{-1} with heating rate of $4 \text{ }^\circ\text{C} / \text{minutes}$; fluid viscosity was recorded under different concentrations at different temperature (20 to $70 \text{ }^\circ\text{C}$). The fluid was heated to $70 \text{ }^\circ\text{C}$ and the shear rate was set at 20 sec^{-1} .

The shear rate and shear viscosity were plotted in Cartesian paper to estimate the fluid behavior under different shear rate.

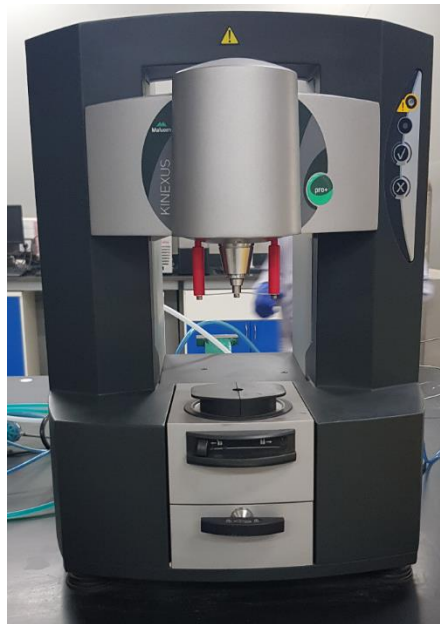


Fig 3.7 KINEXUS Rotational Viscometer

Chapter 4

Results and Discussion

This chapter contains the result of each experiment that conducted in order to evaluate the properties of polymer that required to design an affective gel formulation combatable with Reservoir condition and to achieve the greatest possible effectiveness in water shut-off process.

4.1 Powder Polymer Properties

The polymer has a fine dust appearance, a pink- grey colour and slightly acetic flavour and smell. It is water-soluble however, its solubility is very slow, it is observed that the polymer like to swell resulting in increment in total volume compared with dry mass. Note that a viscose gel was immediately observed while stirring.

4.1.1 Moisture Content

Moisture content represent the percentage of humidity within the powder, of course as long as age of sample increase moisture content decrease therefor it`s also represent the age of the sample.

As presented previously moisture was tested for 5g of the powder and it found to be 11.56%. This result according to the international requirement is acceptable, as the maximum Moisture content should not exceed 15% according to SY/T 6376 (2008).

4.1.2 Critical Concentration

Using the previous described procedures, the minimum concentration required to make crosslinking of polymer. The value of critical concentration of gum is determined by measuring the solution viscosity as a function of concentration (the minimum value of concentration that cause the viscosity curve changes).

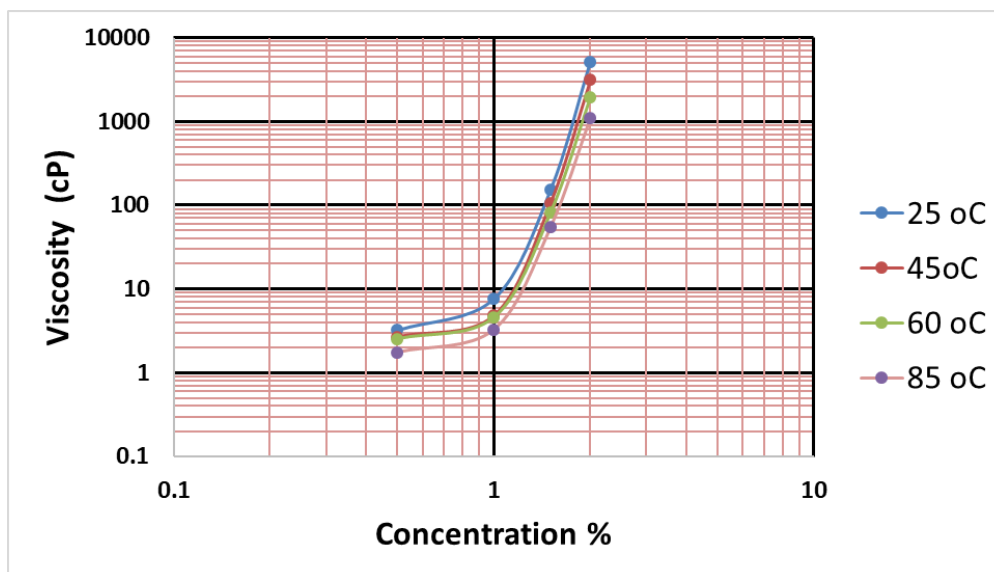


Fig 4.1 Critical Concentration at Different Temperature

Fig 4.1 illustrate that Fluid viscosity increases as the polymer concentration increase at any shear rate. From the figure, it is clearly that critical concentration was found to be 1% for all concentration that present that no crosslinking can be obtained in concentration less than 1%.

4.1.3 Insoluble Materials

One of the most important measures required to use gum in the process of treating the problem of excessive water is to determine the degree of its impurity. Impurity reflects the performance of the polymer in the formation and the effectiveness of the process.

Amount of insoluble components (impurity) give an indication about residual material that form inside the formation as a consequences of fluid flow through porous medium and amount of induced permeability reduction.

The insoluble components was found to be 19% for fluid concentration of 2%, all the other concentrations has insoluble components of less than 19%. Unfortunately, According to SY/T 5764 this value is accepted as the standard is that the insoluble components have to be less than or equal to 20.0 however the polymer classified in the third category (not Good) of the category presented by

SY/T 5764. This behaviour is due to that the polymer like to swell more than dissolve in water.

4.2 Aqueous Solutions Rheological Properties

Rheological Properties control fluid behaviour inside pipes and during pumping through pours medium. Viscosity is the most elementary property dealt with in rheology (Sandvold, 2012). For some fluids the viscosity can be expressed through a coefficient, but for most fluids it is more a factor dependent on other properties. These properties can be, but not limited to, temperature, pressure, shear rate, on how the fluid has been treated before,

4.2.1 Effect of polymer Concentration

The effect of Gum Concentration was studied for concentrations of 0.5, 1.0, 1.5, and 2.0 %. The fluid apparent viscosity was measured at room temperature with Fann 6 speed viscometer; experiments show for the given fluid viscosity is in rise increasing as the polymer concentration increase at any temperature and shear rate (Fig 4.2).

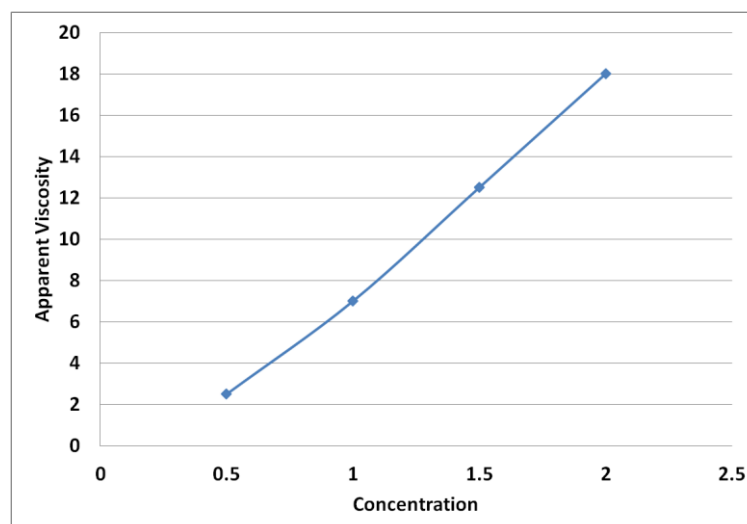


Fig 4.2 Gum viscosity at different concentration

4.2.2 Effect of Shear Rate

The shear rate along with rheological behaviour of the fluid govern viscosity behaviour in pipes and formations for that the fluid was tested to address it's

viscosity response for shear rate change. A plot of shear stress versus shear strain rate was performed to address the type and the fluid behaviour.

A Newtonian fluid is the one in which viscosity is independent of the shear rate (linear plot of shear stress versus shear strain rate). While the fluids in which shear stress is not directly proportional to deformation rate are non-Newtonian flow (the shear stress/strain rate relation is not linear) through which viscosity changes with shear rate. Apparent viscosity always defined by the relationship between shear stress and shear rate. Typically, if the viscosity drops at high shear rates; the phenomenon is known as shear thinning (Pseudoplastic). On the other hand, fluids increase their viscosity exponentially when the shear force is increased, are known as shear thickening (Dilatant)

KINEXUS rheometers measured data were used to represent the fluid type Fig 4.3. Fluid viscosity with concentration of 0.5 and 1.5 % at shear rate between (0 to 20 S⁻¹) and constant temperature of 70 °C were studied the figure presented that the polymer solution exhibit a shear thinning behaviour as it's viscosity decrease as result of shear rate increase. The figure typically presented a pseudo plastic material. They show a decrease in viscosity with increasing shear rate. However, the decrement become very slight at shear rate greater than 10 S⁻¹.

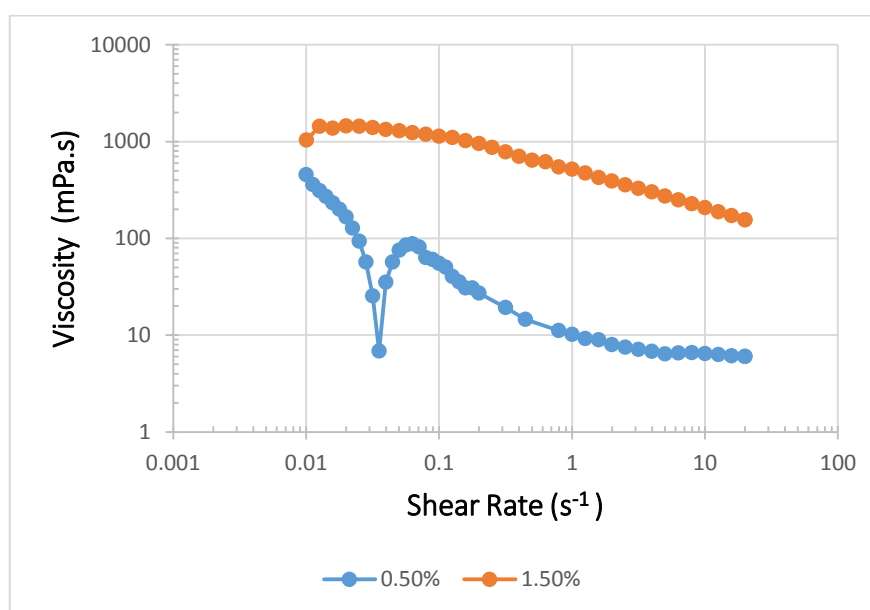


Fig 4.3 Viscosity under Different Shear Rate at Temperature of 70 °C (Different Cocentration)

The sudden drop in 0.5% concentration curve (V shape) was explained as normal behaviour when no time is given to the gum solution to build structure (homogenous) as the shear rate increase.

From the figure, it is also appear that measured data can be described by the power law relationship as can be presented in figure. The power law relationship was presented through Fig 4.4 using Fann 6 speed viscometer Flow behaviour index (n) was found between (0.43 and 0.737) for different concentrations while consistency (k) varies from (0.31 to 41.2) in units of dyne per second per square centimetre.

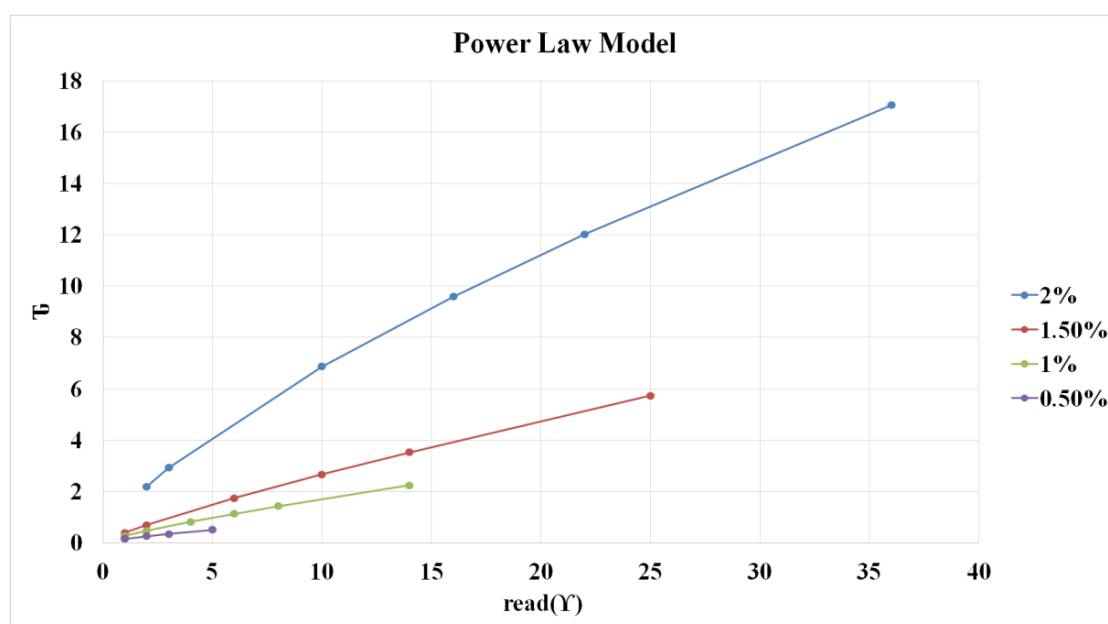


Fig 4.4 Power-Law Model

The shear-thinning viscosity behaviour of these polymer solutions is favourable because the shear rate experienced by the polymer in the vast majority of the reservoir is usually quite low (approximately 1 to 5 s^{-1})

During flooding, deleteriously high- flow shear rates can exist in surface-injection equipment (valves, orifices, pumps, and tubing), at downhole constrictions (tubing orifices, perforations, or screens), and at the formation face of the injection well. This fact need to be considered in other study to insure the behaviour in high shear rate (100 s^{-1}).

4.2.3 Effect of Temperature

The effect of temperature on fluid viscosity under constant shear rate represents the thermal stability of the polymer. Measurements were conducted for two concentrations (samples of 0.5 and 1.5 %) at constant shear rate of 20 S^{-1} the result was presented through Fig 4.5-a (represent the data measured with the rheometers) and Fig 4.5-b (data measured with Cannon viscometer)

The Figures presented that any increase in temperature resulting in a corresponding slight and smooth decreases in viscosity.

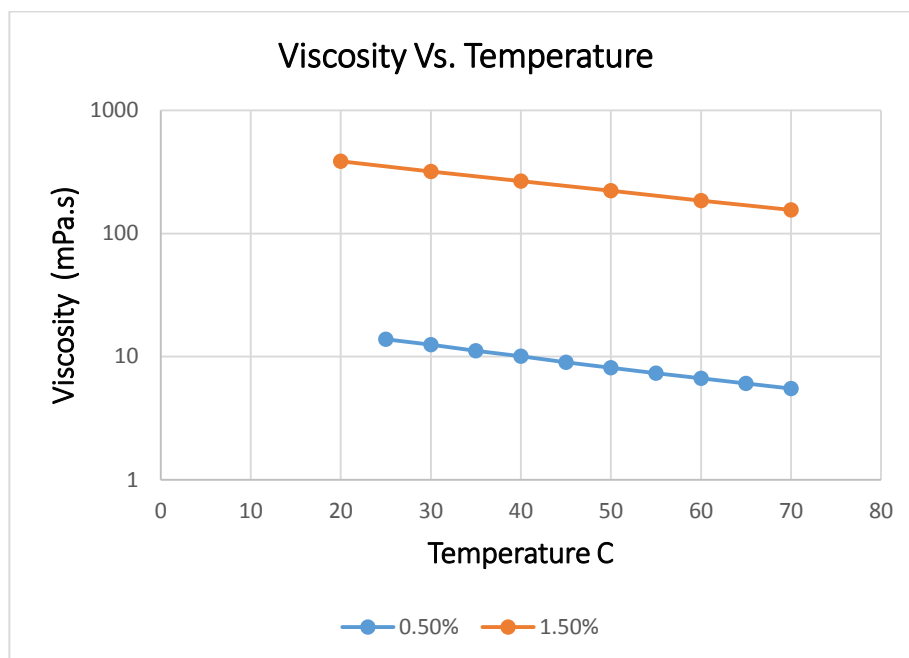


Fig 4.5-a Viscosity Vs. Temperature at Constant shear rate of 20 S^{-1}

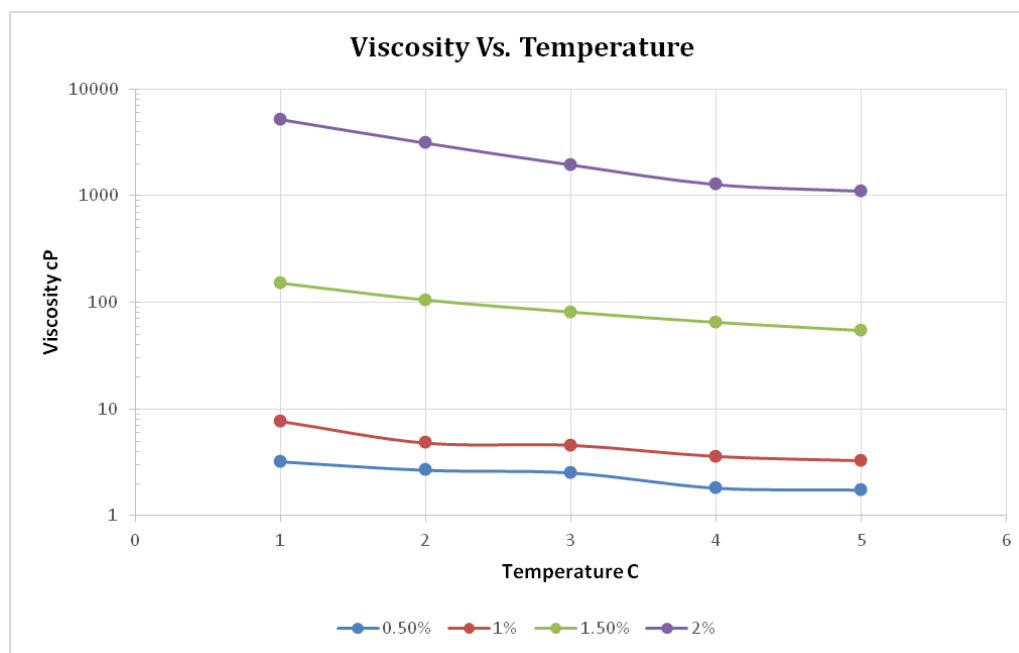


Fig 4.5-b Viscosity Vs. Temperature Cannon viscometer

4.2.4 Biodegradation (Bacterial Degradation)

Fig 4.6 presented the apparent viscosity measured with Fann 6 speed viscometer after 24 hr compared with the result obtained immediately after preparing the solution. Slight degradation observed up to concentration of 1.5 (low concentration), when the concentration reached 1.5 no degradation was observed with time; oppositely an increment was achieved in viscosity after 24 hr which indicates that fully polymer hydration occur with time. It was also observed that the viscosity increment after 24 hr is a function of the solution concentration.

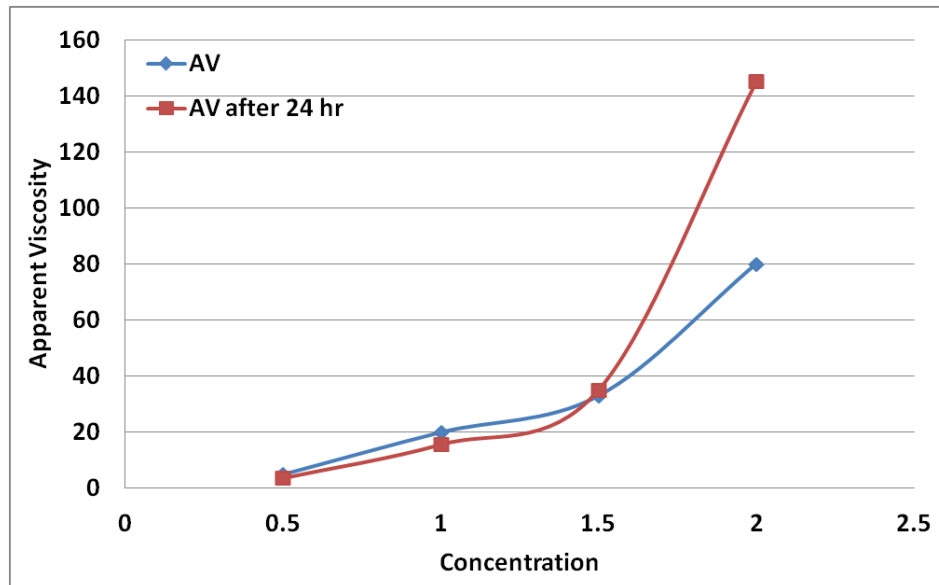


Fig 4.6 Fluid Apparent Viscosity and Biodegradation Effect

4.2.5 Effect of Salinity:

The effect of Salinity in fluid viscosity was studied using 1% NaCl. The result was presented in Fig 4.7. It is observed that the effect of Salinity is high and prime can decrease the viscosity exponentially.

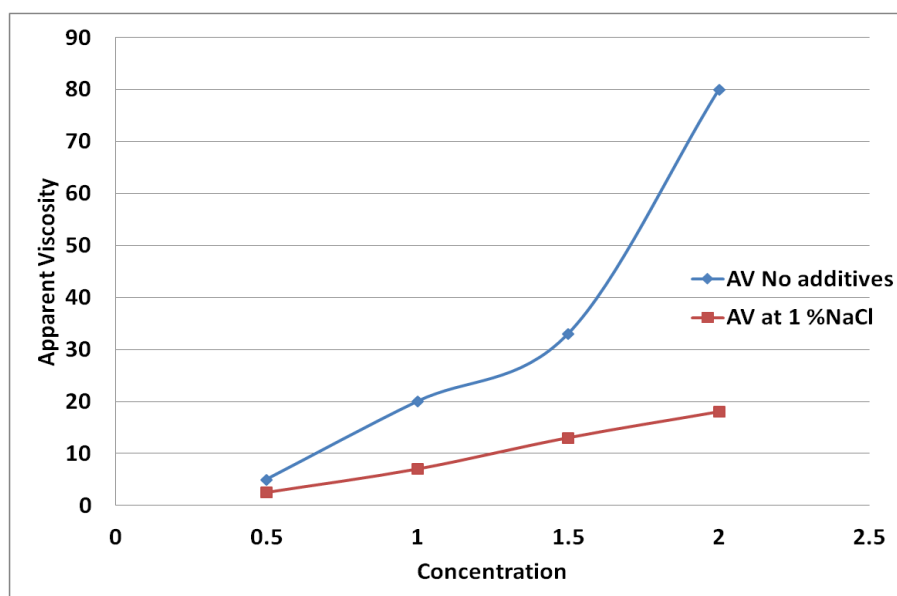


Fig 4.7 Effect of Salinity in Fluid Apparent Viscosity

Chapter 5

Conclusions and Recommendations

Conclusions

Excess water production has always been a major issue in many oil fields worldwide and it is not only negatively affects the oil production rate but also entails costly and time-consuming water management operations from remedial actions in oil well and oil field to the environmental considerations for waste water disposal.

Each problem type has solution options that range from the simple and relatively inexpensive mechanical and chemical solutions, to the more complex and expensive reworked completion solutions. In order to design an effective solution, the nature of the water production must be known.

In this study STLK-4 gum was been evaluated as gelling agent for chemical water shut-off application, from the outcomes of the research, the following conclusions can be made

1. The gum has an average moisture content of 11.56%.
2. The insoluble components was found to be 19% as the maximum value for fluid concentration of 2%
3. It produce solutions in very low concentration, however the critical concentration was found to be 1wt% of solution.
4. In solution form viscosity increase with concentration and reach 5000 cPs in 2% concentration.
5. The gum solutions exhibit a non-Newtonian shear thinning behaviour as it's viscosity decrease as result of shear strain increase.

6. Viscosity of the gum solution decrease in a corresponding to temperature increase, however a value of 150 mPa can be obtained at temperature up to 70 °C for concentration of 1.5%.

Limitations

1. Bacteria affection for more than 24 hrs have not been studied.
2. Salinity had only been studied for brine contain 1% NaCl.
3. Effect of high shear rate had not been studied.
4. The additives that can be used with gum for water shut-off had not been studied.

Recommendation

It is recommended for next researchers to conduct studies focusing on above limitations.

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