AN EXPERIMENTAL STUDY OF SILICATE-POLYMER GEL SYSTEMS TO SEAL SHALLOW WATER FLOW AND LOST CIRCULATION ZONES IN TOP HOLE DRILLING

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AN EXPERIMENTAL STUDY OF SILICATE-POLYMER GEL SYSTEMS TO SEAL SHALLOW WATER FLOW AND LOST CIRCULATION ZONES IN TOP HOLE DRILLING

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

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Shallow water flow and lost circulation are frequently encountered problems during drilling top holes of oil, gas or geothermal wells. Plenty of methods have been applied to overcome these problems. Placement of silicate based gel systems is one of the oldest methods to seal such undesired zones.

For this study, sodium-silicate based gel system is investigated experimentally. This gel system is deliberately delayed multi-component system mixed as a uniform liquid at the surface but desired to form strong gel where it is placed in the well. The experimentally analyzed system is composed of distilled water, sodium-silicate solution, polymer solution, lost circulation materials, weighting agent and organic initiator. In this study, effect of these components on gel time, gel quality and gel strength at room temperature is investigated as a function of their concentration.

To be able to compare gelation time of different compositions, gel time tests were performed by following the developed method in this study. Observation codes were defined to be able to compare the gel qualities of different compositions. For gel time and quality tests, sodium-silicate concentrations from 3.5% to 15% were studied and the concentrations between 7.5% and 10% were found as optimum. Gel time is getting higher as silicate-initiator ratio (SIR) increases for these optimum concentrations. It was also determined that, addition of polymers reduces the gel time and increases the elasticity of the resulting gels.

Long term gelation process was investigated by monitoring turbidity (NTU) of the mixtures and plotting NTU versus time curves. Viscosity development curves obtained from rotational viscometer at various constant shear rates indicated reduced gelation times with increasing shear rate. Furthermore, by using modified High-Pressure, High-Temperature filter press cell, it was determined that, addition of lost circulation materials increases the extrusion pressure.

Key words: *Drilling, gel, silicate, lost circulation, water flow.*

ÖZ

YÜZEY SONDAJLARI SIRASINDA KARŞILAŞILAN SU GİRİŞİ VE ÇAMUR KAÇAĞI ZONLARININ KAPATILMASI İÇİN SİLİKAT-POLİMER JEL SİSTEMİ DENEYSEL ÇALIŞMASI

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Kuyuya su girişi ve çamur kaçağı petrol, doğal gaz ve jeotermal kuyu sondajlarının yüzey kısımlarında sıklıkla karşılaşılan problemlerdir. Bu problemlerin üstesinden gelmek için çok sayıda yöntem uygulanmış olup bu yöntemlerin en eskilerinden biri de silikat bazlı jel uygulamalarıdır.

Bu deneysel çalışmada, sodyum-silikat bazlı jel sistemi incelenmiştir. Bu jel sistemi, jelleşme zamanı kontrol edilebilen, kuyuya basılmadan önce akışkan, kuyuda bırakıldığı yerde belli bir zaman sonrasında güçlü bir jel yapısı oluşturan karışımdır. Deneysel olarak incelenen bu karışımın içeriğinde damıtık su, sodyum-silikat çözeltisi, polimerler, kaçak kapama malzemeleri, yoğunluk artırıcı malzeme ve aktive edici organik malzeme vardır. Bu çalışmada, adı geçen ürünlerin jelleşme zamanına, jel kalitesine ve jel basınç dayanımına etkisi konsantrasyonlarına bağlı olarak incelenmiştir.

Farklı kompozisyonların jelleşme zamanını karşılaştırabilmek için, jelleşme zamanı, bu çalışmada geliştirilen yöntemle belirlenmiştir. Buna ek olarak gözlem kodları tanımlanmış ve değişik kompozisyonların jel kalitelerinin karşılaştırılması sağlanmıştır. Jelleşme zamanı ve jel kalitesi testlerinde %3.5 ile %15 arasında değişen sodium-silikat konsantrasyonları kullanılmış ve optimum konsantrasyon aralığının %7.5 ile %10 arası olduğu belirlenmiştir. Bu konsantrasyon aralığında Silikat – Aktive Edici oranı artarken jelleşme zamanının yükseldiği belirlenmiştir. Ayrıca polimer ilavesinin jel zamanını düşürdüğü ve daha elastik jellerin oluşmasını sağladığı anlaşılmıştır.

Uzun sureli jelleşme analizi ise turbidite (NTU)-Zaman grafikleriyle yapılmıştır. Ayrıca, döner viskometre kullanılarak elde edilen grafiklerle artan kayma hızlarının jel zamanını kısalttığı belirlenmiştir. Modifiye edilmiş yüksek sıcaklık yüksek basınç filtrasyon cihazı kullanılarak ise darçıkım testleri yapılmış ve kaçak kapama malzemelerinin ilavesinin ekstrüzyon basıncını artırdığı belirlenmiştir.

Anahtar kelimeler: *Sondaj, jel, silikat, kaçak, su girişi.*

To the memory of my grandfather

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NOMENCLATURE

API	American Petroleum Institute
BA	Barite Amount
BHA	Bottom Hole Assembly
CONC	Concentration
DH	Degree of Hydrolysis
DWA	Distilled Water Amount
EOR	Enhanced Oil Recovery
HEC	Hydroxyethyl Cellulose
HPHT	High Pressure High Temperatue
IA	Initiator Amount
LCM	Lost Circulation Material
MW	Molecular Weight
NTU	Nephelometric Turbidity Units
NPT	Non-Productive Time
OBS. CODE	Observation Code
OCP	Originally Cross-linked Polymer
PA	Polymer-A
PB	Polymer-B
PAM	Polyacrylamide
PHPA	Partially hydrolyzed polyacrylamide
RPM	Revolution per minute
PAA	Polymer-A Amount
PAC	Polyanionic Cellulose
PASA	Polymer-A Solution Amount
SIR	Silicate Initiator Ratio
SS	Sodium-Silicate
SSA	Sodium-Silicate Amount
SSSA	Sodium-Silicate Solution Amount
TMA	Total Mixture Amount
TSPF	Total Solid Polymer Fraction
TSSSF	Total Solid Sodium-Silicate Fraction

CHAPTER 1

INTRODUCTION

There are some drilling problems which are recognized since the beginning of the drilling operations. Among these problems, water flow into the well and lost circulation are still open for better and/or cheaper solutions.

Water flow into the well is one of the main problems encountered while drilling top holes of onshore and offshore wells. Water can flow into the well while drilling of over-pressurized sands or unconsolidated sediments which are mainly found in shallow zones of the offshore wells. This flow can cause serious problems by carrying portions of the water producing sand inside. Furthermore, in the presence of water, the well cannot be drilled by air or foam and it is difficult get a good cement job around casing.

Lost circulation is another common problem in the drilling environment. It occurs when hydrostatic pressure of fluid column in the wellbore is higher than the formation pressure and is defined as the loss of drilling fluid into the formation. Lost circulation is usually accompanied by wellbore stability problems which can results in pipe stuck and even the loss of hole.

The drilling problems mentioned above may be solved by conventional cementing operations. However, the one of the aim of this study is to develop an alternative way to cementing. Gel applications have several advantages over cementing. First of all, the application of the developed gel system at the field does not require any special equipment while the pumping unit, batch mixer, cement silos and cementing team is required for a cementing job. Additionally, cement slurries can only be pumped through open-ended pipes due to its high solids content. Gels however, can be pumped through the bottom hole assembly (BHA) which is already being inside the hole. This means, at least two trips are necessary for cementing operation before drilling starts again. This is sometimes not a practical and economical solution especially for offshore drilling operations for which the time is the most expensive material. Furthermore, cement drilling takes much more time than washing out the gel in the hole. Besides loosing time on drilling cement, bit life is also reduced due to hard cement drilling (Burns et al., 2008).

On the other hand, there are some obvious advantages of cementing over gel applications. Firstly, the cured cement is much stronger than the gel. Secondly, cementing is also a long term solution when compared to gel applications. Thirdly, it is sure that, the problem solved by gel applications can also be solved by cementing while the vice versa is not correct for all cases.

Several types of gel systems have been widely used in the petroleum industry for different purposes including water shut-off, gas shut-off, plugging lost circulation zones, consolidation of loose formations, casing repairs, relative permeability modification/disproportionate permeability reduction and conformance control. Kabir (2001) listed the five common chemical sealing systems as: (1) resin and elastomers, (2) monomer systems, (3) polymer gels, (4) biopolymers and (5) inorganic gels. In this study inorganic gel with sodium-silicate is selected and investigated experimentally.

The developed environmentally friendly gel system is a mixture of several materials having a low to moderate viscosity and adjustable wide range of density. The system is liquid when mixed initially and forms a rigid gel after a given period of time. Gel mixtures mainly composed of distilled water, sodium-silicate and organic initiator. The gels formed by using only these materials are brittle with controllable gel times. Initiator is the material that forms gel in the presence of sodium-silicate solution after sufficient time passes. Two different types of polymers were also added to the system to improve the elasticity of the resulting gel and to provide sufficient viscosity to keep the lost circulation materials and weighting agent in suspension. Lost circulation materials and weighting agent are added to the system to improve the plugging ability of the gels and to adjust the density. All of the materials in the proposed system are environmentally friendly and selected concerning their availability at the rigsite.

The proposed viscosity and density controlled silicate-polymer gel system is serving alternative way to cementing for solving aforementioned drilling problems. The use of the polymers together with LCMs and weighting agent may increase the effectiveness and area of application of the silicate based gel systems.

CHAPTER 2

LITERATURE REVIEW

The drilling problems mentioned here are the shallow water flow and the lost circulation. There are several studies for treatment of these problems in the literature. In this chapter the previous works concerning chemical gels for plugging these problematic zones are reviewed.

2.1 Resins and Elastomers

Kabir (2001) listed the common resin types for the water shut-off applications as phenolic, epoxy and furfuryl alcohol resins. Phenolic and epoxy are thermosetting resins while furfuryl alcohol forms thermosetting mixtures with phenolic and furan resins.

Slurries prepared with phenolic are pumped to the well after adding catalyst. Bottom hole temperature and pumping time must be known to prevent early polymerization. It forms a strong and inert plugging material after complete reaction. Its strength can be further increased by adding sand or silica flour which requires another additive, gammaaminopropyltriethoxysilane.

Epoxy is more expensive than others but has greater strength. To be able to polymerize epoxy into a hard, inert plastic, it is required to add a hardener before pumping down. Common hardener is diethylenetriamine which is a product of the reaction between epichlorohydrin and bis-phenol A.

Furfuryl alcohol is different than the above mentioned resins due to the fact that, it is not polimerizable resin by itself. It develops weak and brittle plastic after forming polimerizable mixture with phenolic and furan resins and in the presence of acid. The hard-to-come-by of all mentioned additives for resin/elastomer systems and their high costs make resin type gels non-convenient for drilling problems.

2.2 Monomer Based Systems

Kabir (2001) and Dalrymple et al. (1992) described the mechanism of gelation of monomer based systems that, they are pumped as a low viscosity and form gel after polymerization or cross-linking of monomers. When monomers become polymer, its viscosity increases drastically. Since the polymerization is free-radical initiated process, free gelation is likely to occur once initiated.

Eoff et al. (2001) mentioned about the mechanisms in their study. As free radicals are generated, they react with the monomer to form the beginning of the growing chain. However, the dissolved oxygen reacts with the chain and terminate the growth. Radicals produced after the consumption of all oxygen cause polymer formation and rapid gelation. Contaminants commonly present in oilfields have a potential to provide free radicals to initiate the reaction.

Kabir (2001) listed the three types of monomer gel systems as acrylate based, acrylamide based and in-situ organically cross-linked systems. Some earlier treatments used acrylamide as a monomer type. The use of acrylamide has been terminated due to the fact that, it is neurotoxin and carcinogen.

Woods et al. (1986) presented the results of their applications of the monomer based gel system which is formed in-situ by organic cross-linker. Their aim was to plug the channels and high permeability streaks. They applied this monomer based system after the short-term success due to acidic environment by CO_2 of the chromium/anionic polymer system. They found monomer based system as economically successful with payout occurring in 1½ month and are stable in low pH, CO_2 environment.

Dalyrmple et al. (1994) presents a more ecologically friendly system which avoids use of metal crosslinkers. They listed the conformance problems that might be solved by monomer based systems as coning in production wells, high permeability streaks, interwell channeling and injection out of zone. They used acrylate monomer diluted with tap water containing KCl. The described system has an initial viscosity similar to that of fresh water. The system is also need an activator which undergoes thermal degradation to form a free radical. The use of temperature dependent activator resolved the premature gelation problem. They controlled the gel times with the selected azo initiator ranging from 1 hour to 20 hours at temperatures from 70 to 150 ºF. The gel strength of the system is controlled directly by monomer concentration.

Eoff et al. (2001) used same type of gel system for formation consolidation and plug shallow water flow zones. They used hydroperoxide and azo initiator polymerizing solutions of 2-hydroxiethyl acrylate monomer in aqueous solutions of synthetic seawater, sodium chloride (NaCl), calcium chloride ($CaCl_2$), calcium bromide ($CaBr_2$) and zinc bromide ($ZnBr_2$) with densities from 8.6 to 17.5 lbm/gal. This density adjustment is the main advantage of their system when high hydrostatic pressure is required.

Kabir (2001) also listed the advantages and disadvantages of acrylate based and in-situ cross-linked monomer systems. While the advantages of the acrylate based systems are being inert towards formation fluids, being soluble in water, getting gelation without heavy metal cross-linkers, activation by temperature, its stability up to the temperature of 275/300 ºF, being very thin like water while pumping, forming strong gel and claiming permeability reduction up to 99.7% the only disadvantage of the system is its high cost. The advantages for in-situ organically cross-linked system are being water-thin initially, being resistant to low pH environment, forming rigid gel for complete plugging. The disadvantages are, being indefensible to contaminants, being likely to be gelled rapidly and being expensive.

Due to the unavailability of the materials at the rigsite together with the high cost of the system we decided not to use monomer based gel systems for solving drilling problems. Additionally, for our gel design we decided to avoid using metal cross-linkers due to environmental concerns. However, the use of salts to increase gel slurry density for better placement of the gel in the wellbore tends us to use weighting agent in our gel design. Again due to ecological concerns, we decided to replace chloride based weighting agents with an inert material (barite).

2.3 Polymer Gels

Polymer gels are first applied for water shut-off in the 1970s and many organic polymer gel systems have been developed since that time. Polymer gels are flowing mixture of high molecular weight polymer and a cross-linker. Cross-linker, as it appears from its name, links the polymer molecules to form rigid, immobile gel.

Olsen (1986) presented a case history for the polymer gel application for a well in Wyoming without declaring the polymer type. In their study a polymer gel system included polymer chemical, dichromate and reducing agent. The purpose of the reducing agent was to reduce the valance of dichromate ion so that dichromate would cause the polymer to gel.

Kabir (2001) classified the cross-linking agents as metallic (Al^{3+}, Cr^{6+}, Cr^{3+}, zirconium, titanium, boron etc.) and organic (Phenolics: phenol, hydroquione, resorcinol, phenyl acetate, salicyl alcohol, furfuryl alcohol etc. Aldehydes: formaldehyde, panaformaldehyde, hexamethylene tetramine etc.).

On the following pages, organic polymer gel systems were investigated in three groups. These groups are polyacrylamides (syntethic), co-polymers (syntethic) and biopolymers.

2.3.1 Polyacrylamide (PAM) Gels

PAM gels are formed by the cross-linking of polyacrylamide solutions. PAM is non-ionic polymer and is not subject to cross-linking if its original form is kept. However, they become cross-linkable after some of its amide groups convert to negatively charged carboxylate groups.

Kabir (2001) described this process as follows: conversion occurs when PAM mixed with little alkaline solution or when subjected to elevated temperature. The proportion of amide groups that convert to carboxylate by hydroxyl ions is called the degree of hydrolysis (DH) then the resultant polymer is called partially hydrolyzed polyacrylamide (PHPA).

PAM gels generally applied by using metallic cross-linkers. There are three types of metallic cross-linkers have been used to crosslink polyacrylamides: Al^{3+}, Cr^{6+}, Cr^{3+}

2.3.1.1 PHPA + Al^{3+}

The use of Aluminum as a cross-linker was first introduced by Needham et al. (1974). They have tested their process in the laboratory and proposed a treatment procedure with sequence of three slugs, the first and third being polymer solutions while the second being a solution of a selected multivalent cation. They found the use of aluminum citrate with PHPA produces residual resistance factors about six times larger than the use of only polymer in Repetto sandstone cores.

Ghazali and Willhite (1985) called these sequence processes as “combination process”. They thought permeability reduction is caused by the formation of a layered polymer/aluminum ion network during the injection sequence. They describes the mechanism by three steps: (1) Polymer adsorbed from the first polymer treatment forms the base layer for buildup of the structure, (2) the network is developed when aluminum ions attached to the adsorbed polymer layer, (3) a second polymer layer forms through interaction between retained aluminum ions and the second polymer solution as it flows by.

Mack and Smith (1994) described an aluminum citrate system as “In-Depth Colloidal Dispersion Gels”. They reached some important conclusions as (1) polymer to aluminum ratios between 20:1 and 100:1 gave best results, (2) high molecular weight and high degree of hydrolysis was preferred, (3) gel strength is reduced in saline water, fresh water is preferred, (4) gel strength decreases by increasing shear rate, (5) polymer concentrations should be between 100 and 200 ppm.

According to Kabir (2001) Al^{3+} cross-linker is rarely used anymore because the crosslinking reaction cannot be controlled or delayed.

2.3.1.2 PHPA + Cr^{6+}

Since the reaction took place in two steps, Cr^{6+} as a cross-linker was obviously a better choice when compared to Al^{3+}. First step is to reduce Cr^{6+} to Cr^{3+} by mixing reducing agent and Cr^{6+}. Second is to crosslink polymer by Cr^{3+}. This two steps increases the required time for gelation which is necessary for field applications. However, the gelation time is found still not enough. Also the Cr^{6+} system is sensitive to H_2S, and Cr^{6+} is recognized as toxic and carcinogenic substance. All of these caused to search for more convenient PHPA gel system.

2.3.1.3 PHPA + Cr^{3+} + Acetate

Sydansk (1988) reported laboratory evaluation of his patented PHPA-chromium acetate system (U. S. Patent 4,683,949). He preferred to use acetate as carboxylate anion. Gels are mixed by adding single aqueous cross-linking agent solution to the aqueous polymer solution. In this system chromium acetate (metal-carboxylate complex) is used instead single Cr^{3+}. Since Cr^{3+} is attracted to both the acetate ligand in the complex and carboxylate groups on the PHPA polymer, cross-linking process becomes slower yielding more controllable gelation time.

In 1990 Sydansk reported laboratory testing of this chromium gel technology. The laboratory studies reviewed show the dependence of gelation rate and gel strength on (1) the concentration, molecular weight; (2) polymer-to-Cr(III) ratio; (3) temperature; (4) polymer solution pH; and (5) salinity. He performed bottle test to get semi-quantitative measurement of gelation rate and gel strength. He developed and used gel strength code to characterize the bottle test data. He presented bottle-test gel strength codes as (A) no detectable gel formed; (B) highly flowing gel; (C) flowing gel; (D) moderately flowing gel (E) barely flowing gel; (F) highly deformable nonflowing gel (G) moderately deformable nonflowing gel (H) slightly deformable nonflowing gel (I) rigid gel (J) ringing rigid gel. In 1993 Sydansk introduced high temperature version of the system (up to 260 ºF). Before this system none of the polymer gel based technologies had been reported to promote persistent total shut-off over a broad temperature range.

Sydansk (1993) solve the high temperature stability problem by using ultra-low hydrolysis Polyacrylamide. The polyacrylamide used in these Cr(III)-carboxylate gels is characterized as having low molecular weight and low hydrolysis. While 500,000 to 2,000,000 MW PA and 0.5 to 3.0 mole% hydrolysis level is used for low and intermediate temperature applications, 100,000 to 500,000 MW PA and <0.1 mole% hydrolysis level is preferred for high temperature (exceeding about 220 ºF) applications. These gels remain phase stable, rigid and clear at 255 ºF for 2 ½ years of testing.

Lockhart (1994) is also found that, the dependence of gelation time on pH is much less sensitive for the chromium acetate than that found for inorganic Cr^{3+}. According to Sydansk, this gel technology is applicable to a broad spectrum of conformance problems due to its varying structure ranging from flowing to rigid rubbery and its highly predictable gelation time. These gels are also effective plugging agents and can be formulated to possess impressive gel strengths. Another important result of his study is that, the gels are chemically degradable by contacting with sodium hypochlorite and hydrogen peroxide. Being relatively non-toxic Cr^{3+} is more preferable when compared to Cr^{6+}.

Sanders et al. (1994) choose the same system to plug unwanted gas influx in the Prudhoe Bay Field, Alaska. They used PHPA/Chromium/Acetate gel because of several advantages of the system. First of all, this system is insensitive to formation fluids and stable over a wide range of pH with controllable crosslinking time. Secondly, the system is stable under the bottom hole static temperature of up to 220 ºF. Finally, system can be easily cleaned out from the wellbore with coiled tubing using water through a jet nozzle while it provides sufficient strength in formation matrix to withstand high drawdown pressure (>1500 psi). On the other hand, the disadvantages of the gel squeeze are, its potential to damage the production interval and being weak against high positive differential pressure of hydraulic fracturing. They also presented their gel formulation and placement procedure. They recommended cooling the wellbore before pumping the gel since the gel system used in their work crosslinks in less than 15 minutes at Prudhoe bottomhole temperatures. Another important conclusion was that, the gel was not successful to treat the large hole in casing and leaks with large voids behind pipe successfully.

2.3.2 Co-Polymer Gels

Co-polymer gels are found as a solution for thermal stability problem of the PHPA gels. When DH of the polymer increases the association of Ca^{2+} with carboxylate groups in PHPA is also increases. As previously mentioned, DH is increasing with increasing temperature. 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.

Bjornson et al. (1993) introduced the gelling systems which are suitable for treatment of water shutoff in high temperature reservoirs. Acrylamide gels initially produce good gels above the temperature of 167 ºF, however, hydrolysis of the amide groups followed by additional crosslinking with the divalent cations present in the brine causes substantial synerisis. Synerisis is free water which is expelled from the gel. This is caused by internal pressure due to continued crosslinking after the initial gel set-up. They used other monomers for copolymerization of acrylamide to protect the gel against excessive thermal hydrolysis. The gels produced by the reaction of these acrylamide containing polymers with phenol and formaldehyde in a brine such as sea water have survived over 9 months of aging at 300 ºF (149 ºC), and over 2 ½ years of aging at 235 ºF (113 ºC).

Hardy et al. (1999) used the organically cross-linked polymer (OCP) system which is based on a co-polymer of acrylamide and t-butyl acrylate (PA*t*BA). The cross-linker for the system is polyethylene imine (PEI). OCP system relies on the polymer for cross-linking delay, while the other cross-link systems rely on the chemistry of cross-linker.

2.3.3 Bio-Polymer Gels

Like PAM gels, biopolymers are also be cross-linked for gel applications. The advantages of biopolymer gels are being relatively insensitive to divalent ions and higher temperature resistance. The disadvantage is that, they are susceptible to microbial attack.

Bailey et al. (2000) evaluated the use of biocatalysts to trigger the delayed gelling reaction of a gelant which is glucon biopolymer. They used two bacterial strains as the initiator for gelation. These strains both grew anaerobically and each has distinct effect on the gelation time. They tested the effectiveness of the system by injecting into sand-packed columns, glass bead-packed columns and Barea sandstone cores then triggering by the biocatalysts. It was concluded that, this environmentally friendly system decreased brine permeability and blocked flow through permeable zones.

Kabir (2001) listed the common bio-polymer used for gel applicatios as xanthan, polysaccharide (nonionic scleroglucan), lignosulfonates cross-linked with Cr^{3+}, Na carboxymethyl cellolose, guar derivatives, Hydroxyethylcellulose (HEC) and polyanionic cellulose (PAC).

Although the monomer or polymer based gel treatments are seems suitable to solve drilling problems, we have decided not to work on these systems. The reason is that, they mainly use metallic cross-linkers which are mostly not acceptable due to environmental concerns. Additionally, the systems are commonly used in Turkey for EOR applications and not a new concept in our country. However, silicate based inorganic gels have not found any application in Turkey. One of the main responsibilities of this study is to develop a system which is new in Turkey and increase the diversity of the gel applications. Although the developed system is to solve drilling problems, it may find some applications for EOR operations as well.

2.4 Inorganic Gels

Mills (1922) introduced the first inorganic gels to the industry for the application to solve water production problems.

The first silicate gels providing positively-controlled setting times was introduced to the industry by Stewart and Eilers (1967). They conducted extrusion pressure test using standard taper one foot long by two inches at one end and ¼ inch at the other hand. According to test results, very high (>3200 psi) extrusion pressure is reached after the addition of solids into gel mixture. The same mixture without solids has an extrusion pressure of 140 psi. Use of additives to change strength characteristics of the set gel makes these gels applicable to all types of formations and well conditions. They applied gel treatments both for production and injection wells. They recommend to shut-in the well until the gel reaches its maximum strength. Usually six times the gel time is necessary for the gel to reach its final strength.

Koch and McLaughlin (1970) presented the results of their inorganic gel applications for fifty six wells in USA. They stated after these field applications that, inorganic gels are very useful when proper placement technique is applied. They also recommend the usage of inert solids if fractures and vugs are subject to be shut-off and shut-in time as at least three or four times the expected gel time.

Rensvold et al. (1975) suggested and applied the portland cement as tail-in material which is to be pumped just after the gel to prevent it from erosion by the moving fluid in the well. Although the tail-in material can be prepared by adding an inert filler to the sealing material, they recommend Portland cement. When cement slurry and sodium-silicate contact each other, both will increase in viscosity and stop any further movement into or out of the formation. This synergistic effect is also praised by Dalrymple et al (1992) together with serving knowledge about properly displacement of the slurry.

Herring and Milloway (1984) developed non-rig gas shut-off technique using coiled tubing and sodium-silicate gel. They presented also very successful two case histories which are in the Prudhoe Bay Field, Alaska. They placed the sodium-silicate gel across the gas production zone which is isolated from oil producing zone by temporary bridging agent. After the treatment they removed the remaining gel in the hole by coiled tubing jetting.

Krumrine and Boyce (1985) describes the silicate gelation mechanism with three simultaneous processes: (1) condensation of monomer and dimer silicate species to form higher order oligomers, (2) intermolecular condensation of silanol groups within polymers leading to ring closure and eventual partical formation, (3) aggregation of individual particles to form chains and microgels.

Jurinak and Summers (1991) presented their extensive laboratory and field studies about colloidal silica gel. They used colloidal silica instead of sodium or potassium silicate due to fact that, the gelation of colloidal silica is less sensitive to salinity and pH variations, providing more reliable control of gel time. They stated that, the gelation of colloid silica is caused by particle collision, bonding and aggregation into long chain networks. While particle collision is promoted by pH reduction, adding cation to the solution, increasing particle concentrations or by increasing temperature, particle bonding probably results from formation of siloxane (Si-O-Si) bonds at points of interparticle contact. Bonding is also catalyzed by hydroxide ion. Gelation occurs when particle aggregation ultimately forms a uniform 3D network of long bead-like strings of silica particles. Gel time in inversely proportional to number of silica particles in the solution and temperature and the gel time follow a simple first-order Arrhenius temperature dependence. They controlled the gel time by initial adjustment of silica solution pH (by neutralizing with HCl) and salinity (by addition of food grade NaCl brine to the solution) at application temperatures below 180 ºF. They used triggering agent to achieve required gel time delays at temperatures above 180 ºF.

They found that, at least three times the initial gel time is required for the gel plug to reach 50% of its final pressure-gradient stability. The ultimate gel strength was reached after curing about 20 times the initial gel time. Another important result is that, the pressure gradient stability of silica gel in competent core plugs is much more than in artificially fractured core plugs. They have also stated that, silica solution injectivity one-half that of water in Barea cores and 1/10 in clay-laden field cores. However, this injectivity is an order of magnitude better than that of common high molecular weight polymer gel solutions injected into similar rock.

Dalrymple et al. (1992) have strengthen this by stating that, the gel resists extrusion even after 2000 psi applied pressure when the gel is formed using 1 in. diameter, 3 in. long pack of 100 mesh sand. However, same gel has less than 15 psi compressive strength in its neat form. They classified the silicate gel systems into internally catalyzed and externally catalyzed. Internally catalyzed silicate system (ICSS) is pumped as low viscosity single liquid and forms gel in-situ after a predetermined time is passed. Externally catalyzed silicate system (ECSS), on the other hand, is two fluids and two stage silicate system. In the procedure of their application, brine and silicate solution are pumped sequentially and contacts with each other in the formation to form gel structure. They advised the advantage of the system as selectively blocking water production without greatly affecting oil production.

Shelley and Sciullo (1995) used silicate based gel system for a different purpose. They presented their four successful and one unsuccessful applications for the wells in Eastern, Kentucky. They plugged the zone of initial producing zones to deepen the well for recompleting in another formation. It is needed to plug permeable zone of the initial completion since the produced fluids compromise the efficiency of air drilling operations while deepening the well. They decided to use an externally catalyzed silicate system to replace the cement squeeze because of several reasons. The particles of cement may be too large to penetrate the matrix permeability of a fluid zone resulting in cement particles filtering out on the formation face where they form a shallow seal. Several cement squeezes may be required to plug the zone because of shallow seal. Additionally, premature dehydration of cement can lead to stuck drill pipe and tubing while silicate gel is not subject to dehydration. They used flush of Calcium Chloride in their treatments to catalyze the silicates. The silicate immediately forms an insoluble gel when it contacts the calcium chloride at the point of application. Fresh water was pumped as spacer between calcium chloride and silicate solution to prevent premature gelation. Since no WOC required the second treatment can be applied immediately. Also the pipe can be pulled through the set gel. Multiple treatments can be done in a short time with minimum downtime between treatments.

Bauer et al. (2005) presented their experimental study on sodium-silicate gels. They used sodium-silicate and encapsulated activator which forms silicate hydrate plugs when exposed the high temperature. They investigated the chemistry and mechanical survivability of the materials at geothermal conditions (80 °C – 300 °C). They decided to use sodium-silicate system due to the fact that the material is environmentally acceptable and relatively low cost. Additionally, the mixed slurry is readily pumpable and has controllable gel time with hydrothermal stability for 8 weeks at geothermal conditions.

Burns et al. (2008) introduced a new sodium-silicate – polymer – initiator (SPI) gel system which uses sodium-silicate, various polymers and organic initiator. The system is environmentally friendly and no heavy metal is used. The tested polymers are PHPA, polyacrylates, co-polymer of AMPS and acrylamide, carboxymethylcellulose, HEC and xanthan gum. The test results show that, the impact of polymer is to make the gels elastic. Only CMC polymer produced brittle gel with severe syneresis. They have also compared the polyacrylamide gels cross-linked with chromium and sodium-silicate polymer gels in terms of extrusion pressure. They found that sodium-silicate polymer gel system 2.5-3 times more resistant to extrusion than cross-linked polyacrylamide gels.

After a wide range of gel chemistries was screened, the research focused on the sodium-silicate based systems due to the following reasons:

- The selected system should be environmentally friendly. Sodium-silicate based systems are the most environmentally friendly systems among the sealing type chemical systems.

- The selected system should be economical. SS based systems are economical systems due to its relatively cheap components.

- The components of the system should be available at the rigsite. The most of the materials in our design are the common materials used to mix water based drilling fluids. This is also an advantage for the rig personnel who already know how to use these additives and the necessary personnel protecting equipment.

CHAPTER 3

STATEMENT OF THE PROBLEM

The goal of this study is to develop an efficient and cost effective silicate based polymer gel composition for treating the lost circulation and shallow water flow problems. In this study, new additives are also investigated to improve the sealing ability of silicate based gels.

This study is furthermore aims to encourage the drilling industry in Turkey to use the developed viscosity and density controlled silicate-polymer gel system for solving the aforementioned drilling problems.

CHAPTER 4

EXPERIMENTAL SET-UP AND PROCEDURE

This chapter presents all the equipment and additives in addition to experimental procedures utilized in this study which is performed using the facilities of Central Laboratory of Karkim Drilling Fluids Co.

4.1 Equipment & Additives

Before giving detailed experimental procedures, it is beneficial to mention about the equipment and additives used in this study.

4.1.1 Equipment

In this study, the following equipment are used.

4.1.1.1 Magnetic Stirrer

Magnetic stirrer is a device that employs a rotating magnetic field to cause a stirring bar in liquid to spin quickly to provide stirring. BARNSTEAD THERMOLYNE magnetic stirrer with a model number of SPA1020B (Fig.4.1) is used for mixing gel slurries or preparing polymer solutions. This model has a speed range from 100 to 1,200 rpm.

Figure 4.1 BARNSTEAD THERMOLYNE SPA1020 magnetic stirrer.

4.1.1.2 Beakers

Beaker is a container used for stirring, mixing and heating liquids. FANN 600 ml glass beaker and LAMTEK 100 ml glass beaker (Fig. 4.2) is used for gel slurry and polymer solution preparation. The length and the inside diameter of the beakers used in this study are given at the Table 4.1.

Table 4.1 Dimensions of the beakers used for the experiments.

	Inside Dia, mm	*Length, mm*
100 ml Beaker	45	70
600 ml Beaker	90	120

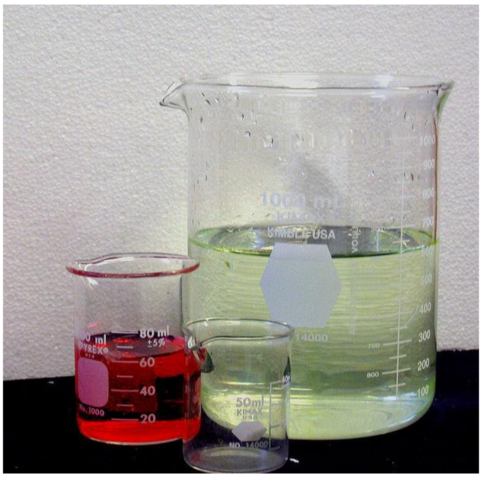

Figure 4.2 Glass beakers of several sizes.

4.1.1.3 Stirring Bars

Stirring bar (Fig. 4.3) is a small teflon-covered magnet used to stir a liquid mixture or solution. FANN stirring bars with lengths of 2.5-cm and 5-cm are used for mixing the polymer solution and gel slurries in this study. The bar with a length of 2.5-cm is used to mix slurries in the 100 ml Beaker while the one with 5-cm is used to mix polymer solutions in 600 ml Beaker.

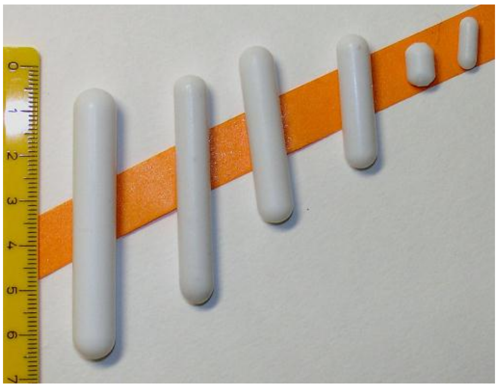

Figure 4.3 Stirring bars with several sizes.

4.1.1.4 pH Meter

A pH meter is an electronic instrument used for measuring the hydrogen ion concentration of a liquid. pH readings are obtained by the pH meter consisting of glass electrode connected to an electronic meter. The pH probe measures pH as the activity of the hydrogen cations. Small voltage produced by the probe converted to pH units by the instrument. The hydrogen concentration (pH) of the mixtures is determined by OAKTON digital pH/Ion meter (Fig. 4.4). It measures the entire pH scale from 0.00 to 14.00 with an accuracy of ±0.01.

Figure 4.4 OAKTON digital pH/Ion meter.

4.1.1.5 Turbidimeter

HF SCIENTIFIC DRT 15-CE Nephelometer type turbidimeter is used to determine the turbidity level of the gel mixtures (Fig. 4.5). Turbidity is caused by fine particles suspended in the mixture. These fine particles cause light to scatter rather than traveling in a straight line. The turbidity level is a measure of the amount of light scattered 90° by the suspended particles. The Turbidimeter converts these measurements to a readings in Nephelometric Turbidity Units (NTU).

Figure 4.5 HF SCIENTIFIC's DRT 15-CE type turbidimeter.

4.1.1.6 Viscometer

FANN 35SA Couette coaxial cylinder rotational viscometers (Fig 4.6) is used to determine shear stress values of the gel slurry at constant shear rate. The instrument is equipped with R1 Rotor Sleeve, B1 Bob, F1 Torsion Spring, and a stainless steel sample cup for testing according to American Petroleum Institute Specification RP 13B. Shear stress is read directly from a calibrated scale. Plastic viscosity and yield point of a fluid can be determined by making two subtractions from the observed data when the instrument is used with the R1-B1 combination and the standard F1 torsion spring.

Figure 4.6 FANN 35SA type rotational viscometer.

4.1.1.7 Mud Balance

The FANN Model 140 Mud Balance (Fig 4.7) is used to determine the density of gel samples. The mud balance is constructed with beam which is graduated into four scales: pounds per gallon (ppg), specific gravity, pounds per cubic foot, and pounds per square inch per 1,000 feet of depth. It has a measuring range of 6-24 ppg.

Figure 4.7 FANN Model 140 mud balance.

4.1.1.8 Precise Balance

PRECISA XT 2200C precision balance (Fig. 4.8) is used to weigh all of the additives used in the experiments. The balance has a capacity of 2,200 g and readability of 0.01 g.

Figure 4.8 PRECISA XT 2200C precision balance.

4.1.1.9 HPHT Filter Press

FANN Filter Press HPHT 175 ML (Fig. 4.9) is used for the pressure extrusion experiments in this study. The High Pressure-High Temperature (HPHT) Filter Presses are used for testing the filtration properties of drilling fluids, cement slurries, and fracturing fluids. High-pressure high-temperature filter presses provide means of evaluating the filtration properties of drilling fluids at high pressures and temperatures. The cells have a filtering area of 3.5 in.^{2} (22.58cm^2). In this study, the equipment is modified to be used for pressure extrusion experiments. The modification details are given at the following pages.

Figure 4.9 FANN Filter Press HPHT 175 ml.

The equipment can be operated at pressures up to 900 psi (6205 kPa) with the CO_2 pressuring unit (Fig. 4.10). Maximum operating temperature is 350°F. Since this study is performed at room temperature, heating feature of the filter press is not used.

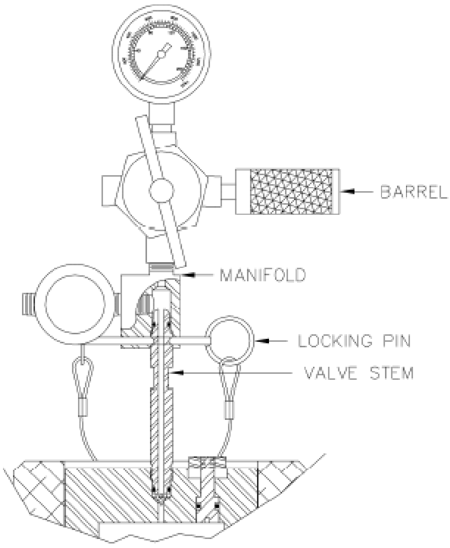

Figure 4.10 CO_2 pressure unit.

Since the opening of the original cap is too big for extrusion tests, another cap is designed and manufactured by using 313 steel. The hole is opened on the cap with a diameter of 1 mm (Fig. 4.11 and Fig. 4.12).

Additionally; a piston is designed and manufactured to prevent fingering effect of Carbon Dioxide gas through the gel. The piston (Fig. 4.13) is made up of teflon and placed between the gel and CO_2 pressure unit. The pressure is applied on the piston to distribute the pressure on the gel evenly and therefore, to prevent fingering effect of gas. The piston has greased o-ring around to provide seal between piston and the inside wall of the cell. The outside of the piston is also lubricated by grease for easier movement inside the cell. A removal tool for the piston is also designed to remove the piston from inside of the cell.

Figure 4.11 HPHT filtration cell and modified lower cap.

Figure 4.12 Modified lower cap.

Figure 4.13 Piston and removal tool.

4.1.2 Additives

In this study eight different additives provided by Karkim Drilling Fluids Co., are used to prepare gel slurries.

4.1.2.1 Distilled Water

Distilled water is obtained by boiling and condensing of the water. Many of impurities in tap water are removed through distillation. Distilled water is used for the study to eliminate the effects of impurities on gel time or gel quality.

4.1.2.2 Sodium-Silicate (SS)

The liquid sodium-silicate, $Na_2O{\cdot}n(SiO_2)$, used in this study has a specific gravity of 1.39 (Fig. 4.14). Solids fraction in the solution is totally 36.81% by weight which composed of 28.09% SiO_2 and 8.72% Na_2O.

Where n identifies the molecular ratio (i.e. the number of SiO_2 molecules relative to one Na_2O molecule) and is 3.22 for the product used here.

$$[SiO_2 / Na_2O] = 3.22$$

Figure 4.14 Liquid Sodium-silicate.

4.1.2.4 Polymer-A (PA)

Polymer-A is an anionic linear synthetic co-polymer (Fig. 4.15).

Figure 4.15 Polymer-A.

4.1.2.5 Polymer-B (PB)

Polymer-B is a slightly anionic biopolymer (Fig. 4.16).

Figure 4.16 Polymer-B.

4.1.2.6 Cellulosic Fibers

In this study, two types of micronized cellulosic fibers, fine grade (KAR-SEAL F) and medium grade (KAR-SEAL M), are used (Fig. 4.17). The particle size distributions of these two products are given in Table 4.2.

Table 4.2 Particle size distribution for KAR-SEAL F & KAR-SEAL M

Particle size	*KAR-SEAL F*	*KAR-SEAL M*
Greater than 425 μm	1.05 %	2.55 %
Between 250 μm & 425 μm	8.35 %	32.80 %
Between 180 μm & 250 μm	9.95 %	25.55 %
Between 150 μm & 180 μm	22.65 %	16.55 %
Between 125 μm & 150 μm	23.05 %	7.35 %
Between 75 μm & 125 μm	20.30 %	9.20 %
Between 45 μm & 75 μm	8.45 %	3.30 %
Smaller than 45 μm	6.20 %	2.70 %

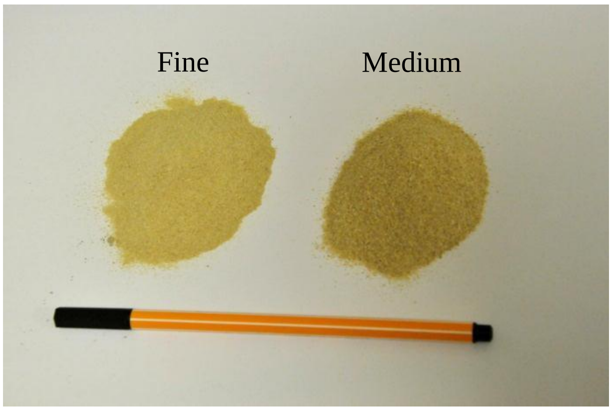

Figure 4.17 Fine and medium grade cellulosic fibers.

4.1.2.7 Barite

American Petroleum Institute (API) test calibration barite (Fig. 4.18) is used for this study. The properties of the barite are given in the Table 4.3.

Figure 4.18 API test calibration barite.

Table 4.3 API test calibration barite properties.

Property	*Range*
Density, g/cm^3	4.23 ± 0.02
Residue greater than 75 micrometers wt. percent	1.62 ± 0.75
Particles less than 6 µm in eqv. spherical dia., wt. percent	22 ± 2.7
Water soluble alkaline earth metals as Ca^{++}, mg/kg	60 ± 15

4.1.2.8 Initiator

A weak organic acid, citric acid (Fig. 4.19) is used to initiate the gelation process. Monohydrate citric acid ($C_6H_8O_7 * H_2O$) is used in this study and having a molar mass of 210.14 g/mol.

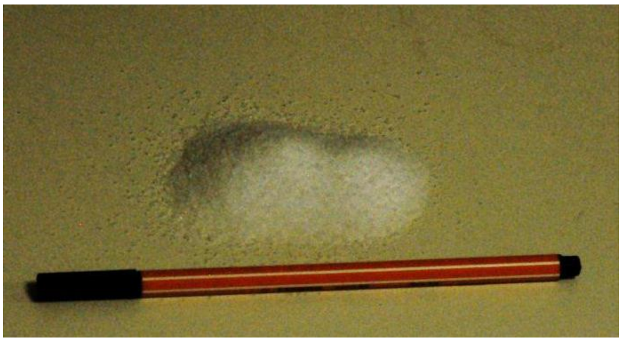

Figure 4.19 Citric acid - Initiator.

4.2 Experimental Procedure

Seven different experiments are conducted to determine gel time, gel quality, pH, turbidity, viscosity, extrusion pressure and density.

4.2.1 Gel Time Determination

For this study, gel time is defined as "the time elapsed between the addition of initiator to the gel mixture (total weight is 100 g) and vortex closure of the mixture while the stirring bar (2.5 cm) turns with maximum rpm (12,000) in the 100 cc beaker on the BARNSTEAD THERMOLYNE SPA120 type magnetic stirrer".

Gel times of the slurries are determined by following the procedure:

1. Prepare the polymer solution as described below:

   Polymer solutions are prepared by adding 2.0 g of dry polymer granules to the vortex shoulder of 498 cc water in beaker (600 cc capacity) which is on the magnetic stirrer. First slowest rpm is used to prevent the water flowing over beaker. While the mixture is getting thicker speed is continuously increased. Each polymer solution contains one type polymer (Polymer-A or Polymer-B) with a concentration of 0.4% by weight. Solutions were stirred for at least 6 hours at room conditions before adding to gel mixture. If there is no polymer solution in the formulation, skip this step.

2. Put the 100 ml glass beaker on the digital balance.
3. Zero the balance.
4. Add required amount of distilled water. Adjust the exact amount by 10 ml syringe.
5. Zero the balance.
6. Add required amount of polymer solution by using 60 ml syringe (If there is no polymer solution in the formulation, skip this step).
7. Zero the balance.
8. Add required amount of SS by using 60 ml syringe.
9. Weigh the required amount of LCM or barite. (If there is no LCM and barite in the formulation, skip this step)
10. Weigh the required amount of initiator.
11. Put the beaker on the magnetic stirrer and start to stir.
12. Add LCM or barite to the mixture in one minute (If there is no LCM and barite in the formulation, skip this step).
13. Add initiator to the mixture in 30 seconds and start chronometer.
14. Check the temperature of the mixture, it should be 23.0 ± 2.0 ºC.
15. Check the gelation frequently by putting the beaker on stirrer and stir with minimum rpm (to prevent overflow) then increase the rotation speed. When the vortex closes at the maximum rpm, read the chronometer and record the time as “gel time” in seconds (Fig. 4.20).

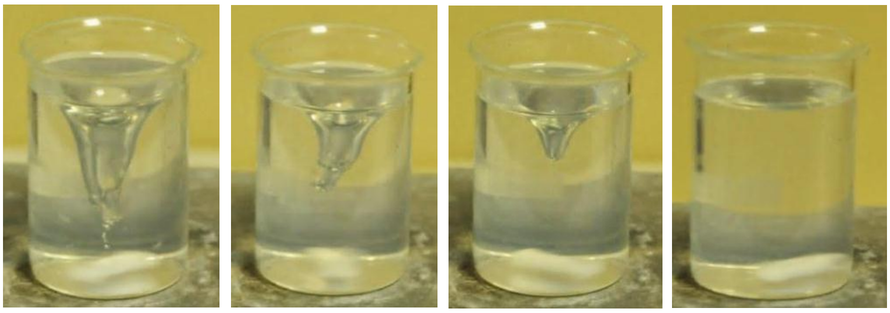

Figure 4.20 Vortex closure with time while gelation occurs.

Gel time tests allowed us to determine the effect of each additive on gel time. Since this study is only for the problems encountered top hole sections, mixtures having gel time between one hour (3,600 s) and four hours (14,400 s) are thought as good candidates for field applications when considering only the gel time. Gel time tests are repeatable for most of the slurries. The limit for the repeatability is accepted as ±10% of the gel time.

4.2.2 Gel Quality Determination

Gel quality is another important parameter while selecting gel compositions for specific operations. Gel quality is evaluated with observation codes which were defined in this study to be able to compare the gels' qualities after four times the gel time. The observation codes and their descriptions are given in the Table 4.4.

Table 4.4 Observation codes and descriptions.

OBSERVATION CODE	*DESCRIPTION*
1	SOFT
2	SOFT ELASTIC
3	MODERATE ELASTIC
4	HARD ELASTIC
5	MODERATE BRITTLE
6	HARD BRITTLE

Some of the gel pictures and given observation codes are presented with the following six figures (Fig 4.21 – Fig. 4.26). Observation codes are given to gels by comparing the gels with these six figures. When considering only the gel quality, gels with the observation codes of 1 and 2 can be eliminated for field applications due to their lack of resistance to pressure.

Figure 4.21 Observation Code: 1 – Soft.

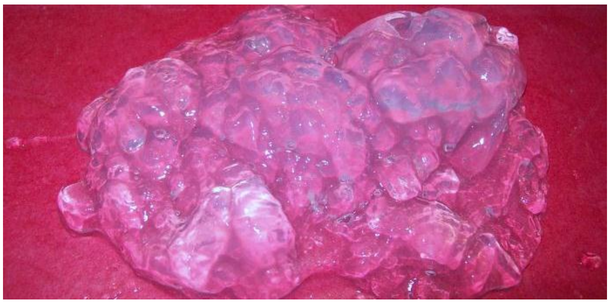

Figure 4.22 Observation Code: 2 – Soft Elastic.

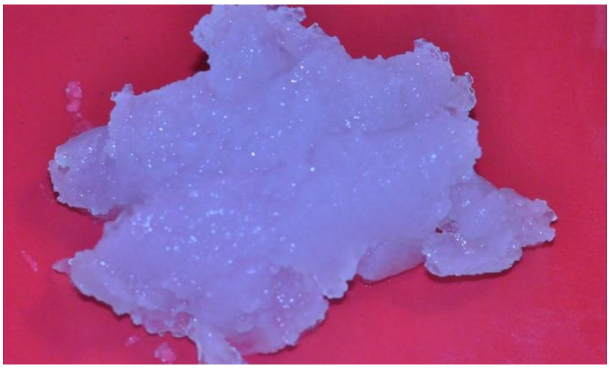

Figure 4.23 Observation Code: 3 – Moderate Elastic.

Figure 4.24 Observation Code: 4 – Hard Elastic.

Figure 4.25 Observation Code: 5 – Moderate Brittle.

Figure 4.26 Observation Code: 6 – Hard Brittle.

4.2.3 Hydrogen Ion Concentration

pH values of the slurries are determined by following the procedure below:

1. Repeat steps from 1 to 13 of the gel time determination test.
2. Immerse the pH meter electrode into the mixture.

3. Record the pH value when the pH display becomes constant.

4.2.4 Turbidity

NTU values are obtained by following the procedure below:

1. Repeat steps from 1 to 13 of the gel time determination test.
2. Pour the mixture to turbidimeter cup in 1 minute after stirring.
3. Adjust the range for the turbidity via the switch on the device.
4. Start to record NTU value (data gathering frequency depends on gelation)
5. Record the data until it reaches plateau on the NTU versus Time Curve.

4.2.5 Rheological Measurements

Viscosity tests of the slurries are performed by following the procedure below:

1. Repeat steps from 1 to 13 of the gel time determination using 600 ml beaker instead of 100 ml.
2. Pour the mixture to the viscometer cup.
3. Adjust the rotation speed as required (6,100,200 or 300 rpm)
4. Start to record readings (data gathering frequency depends on gel time)
5. Record the data until it reaches plateau or fluctuation starts to occur on the viscosity versus Time Curve.

4.2.6 Pressure Extrusion Test

Extrusion pressures of the slurries are determined by following the procedure below:

1. Screw the top cap to the filtration cell body.
2. Place the teflon piston (already greased) inside the cell and move towards the top cap.
3. Repeat steps from 1 to 13 of the gel time determination test.
4. Pour the mixture to the cell.
5. Screw the bottom cap.
6. Place the small needle like metal into the hole of the bottom cap to prevent slurry flow through the hole.

7. Upside down the cell and wait four times the gel time.
8. Gradually increase the pressure from the top.
9. Record the pressure which initiates extrusion.

4.2.7 Density Determination

Densities of the slurries are determined by following the procedure below:

1. Repeat steps from 1 to 13 of the gel time determination using 600 ml beaker instead of 100 ml.
2. Remove the lid and completely fill the mud balance cup with the slurry.
3. Replace the lid rotate slowly until firmly seated.
4. Wash the slurry from outside of the cup and dry it.
5. Place the balance arm on the base and move the rider to catch the balance between two sides.
6. Record the density as ppg at the edge of the rider closest to the cup.

CHAPTER 5

RESULTS AND DISCUSSION

In this chapter, experimental results and observations are given in details. These include gel time and gel quality, pH, density, long term gel formation time, shear effect and gel strength as a function of additives used in silicate based gels studied here. All experiments are performed at room temperature considering low wellbore temperature in top hole drilling.

The concentration of each component in the mixture is “percent by weight” at the following pages. Therefore, the term “by weight” is not used at the subsequent pages to avoid unnecessary duplication.

5.1. Effect of Sodium Silicate and Initiator on Gel Time and Gel Quality

Gel time and gel quality tests were first performed by changing sodium silicate (SS) concentrations in the order of 3.5%, 5%, 7.5%, 10%, 12.5% and 15% while Silicate/Initiator Ratio (SIR) was changed between 0.5 and 7.0.

SIR is the ratio of the concentration of the sodium silicate to the concentration of the Initiator in the mixture. As high initiator is added SIR becomes smaller (The sample calculation is given in details in Appendix-A). The sodium silicate concentration was kept constant for each curve, and SIRs were adjusted by changing the initiator amount. The initiator concentration can be calculated when the sodium silicate amount and SIR are known. For instance, gel mixture containing 15% constant sodium silicate with SIR of 3.0 and 5.0 includes 5% and 3% initiator respectively.

5.1.1 Gel Time

As shown in Figure 5.1. at low sodium silicate concentrations, 3.5% and 5%, gel time first tends to decrease with increasing SIR or decreasing initiator amount. There is a threshold value of SIR after which gel time curve follows an increasing trend with SIR. This limiting value of SIR is directly proportional with sodium silicate concentration. It becomes smaller as sodium silicate concentration is reduced.

However, at relatively high sodium silicate concentrations (7.5% to 15%) gel time continuously increases with increasing SIR. This characteristic behavior of gel time curves can be explained by change in pH with addition of initiator.

The pH of silicate solutions is a function of the molecular ratio, but is always high; pH decreases with increasing ratio Na_2O/SiO_2, i.e. when the silicate becomes more siliceous it also becomes less alkaline. As shown in Table 5.1, increasing sodium silicate ($Na_2O/SiO_2=3.22$) concentration makes the solution more alkaline.

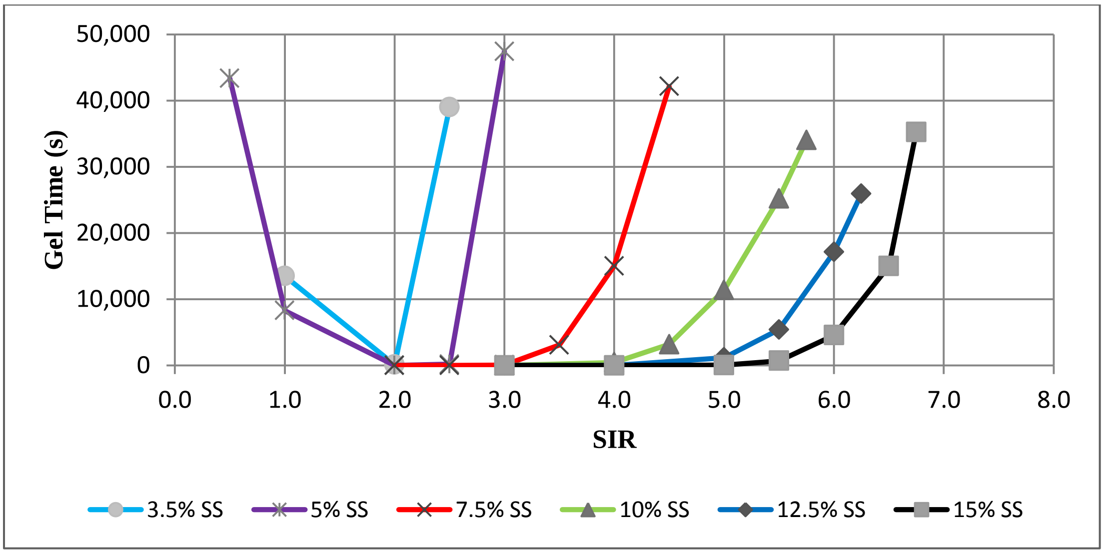

Figure 5.1 Gel time vs. SIR as a function of sodium silicate concentration.

Table 5.1 pH of sodium silicate solutions with $Na_2O/SiO_2=3.22$.

SS Conc.%	*pH*
3.5	11.3
5.0	11.3
7.5	11.5
10.0	11.6
12.5	11.7
15.0	11.9

When pH is lowered artificially by the addition of citric acid in relatively high concentration silicate solutions, the anionic silicate oligomers will polymerize and gel. A particular minimum buffered alkalinity is required for the polymerization of silicate oligomers. Burns et al. (2008) described the mechanism of gelation as follows: When sodium silicate is acidified with the initiator to a pH of less than or around 11, sodium silicate is converted partially to silicic acid. Silicic acid is a weak acid at these alkaline pH values. Silicic acid remains hydrated and forms a three-dimensional network in trapping the solvent water instead of precipitating and making silica, SiO_2. This network is a gel since both phases are continuous. A slight lowering of the pH causes drastic changes in gel time as easily seen from Figure 5.1 and Tables 5.2 to 5.7. Therefore, gel times are difficult to control, and lumping from local acid concentrations during large scale mixing frequently occurs. Gelation is most rapid at neutral pH.

Table 5.2 Gel times and observation codes for gels with 3.5% SS.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
1.0	13,500	4.8	1
2.0	110	7.4	6
2.5	39,000	9.7	1

Table 5.3 Gel times and observation codes for gels with 5% SS.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
0.5	43,320	4.0	1
1.0	8,280	4.8	3
2.0	30	7.0	6
2.5	180	9.0	6
3.0	47,400	10.3	1

Table 5.4 Gel times and observation codes for gels with 7.5% SS.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
2.0	2	-	6
2.5	5	-	6
3.0	57	10.9	6
3.5	3,075	11.0	5
4.0	15,000	11.1	5
4.5	42,120	11.1	5
5.0	87,600	11.2	1

Table 5.5 Gel times and observation codes for gels with 10% SS.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	7	11.0	6
4.0	447	11.1	6
4.5	3,180	11.2	6
5.0	11,400	11.2	5
5.5	25,200	11.4	5

Table 5.6 Gel times and observation codes for gels with 12.5% sodium silicate.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	2	10.7	6
4.0	15	10.8	6
5.0	1,185	10.9	6
5.5	5,400	11.2	5
6.0	17,100	11.3	5

Table 5.7 Gel times and observation codes for gels with 15% SS.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	1	11.0	6
4.0	8	11.1	6
5.0	52	11.3	6
5.5	691	11.3	6
6.0	4,560	11.5	6
6.5	15,000	11.6	4

At relatively low silicate concentrations, i.e. 3.5% and 5%, when sodium silicate is acidified by the addition of initiator (SIR≤1.0) to a pH of less than 7 high gel times are also measured (Fig. 5.1 and Tables 5.1 and 5.2). In of using 3.5% and 5% sodium silicate, gel times are much more sensitive to the initiator amount making the field application much more impractical. For instance, for the mixtures with 5% SS the gel times of the mixtures with SIR of 2.5 and 3.0 are 180 s and 47,400 s respectively.

While treating the shallow water flow and lost circulation zones gel time should be properly adjusted to prevent gelation during pumping but leading to immediate solidification of sodium silicate within the pore throat of the rock matrix with sufficient penetration. Therefore, gel time should be greater than total time required for mixing the gel at surface and pumping it to the target zone.

5.1.2 Gel Quality

Silicate gel quality is determined by sodium silicate concentration and sodium silicate/initiator ratio. The gel quality decreases when the gelation is delayed extensively as apparently seen from Tables 5.1 to 5.7. Hard and brittle gels are generated with high sodium silicate concentration at low sodium silicate/initiator ratio (Fig. 5.2).

Since 3.5% and 5% sodium silicate gels exhibit unstable pH dependent gelation behavior and weak gel structures, they are not recommended for field applications.

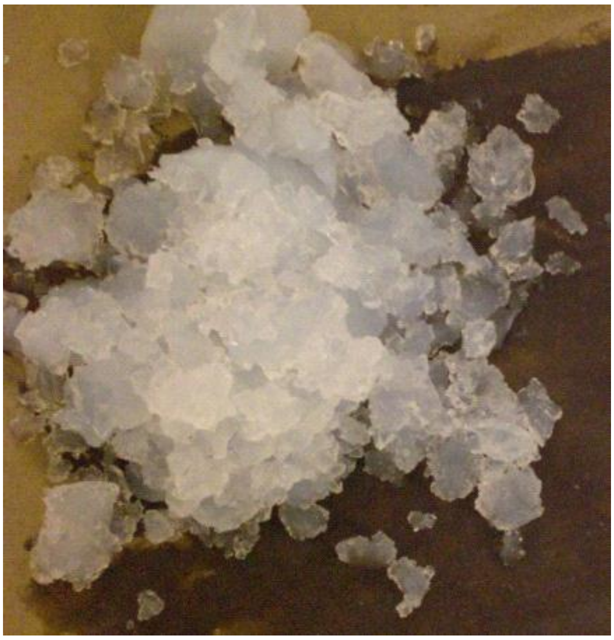

Figure 5.2 Hard and brittle sodium silicate gel.

5.2. Effect of Polymers A and B on Gel Time and Gel Quality

Two different types of polymers, Polymer-A (polyacrylamide) and Polymer-B (biopolymer) are studied here to investigate their effects on gel time and gel quality. Tests are performed on gels with relatively high sodium silicate (>5%) and 3.5% and 5% sodium silicate gels are not included due to the reasoning given in Section 5.1.2.

5.2.1 Gel Time

Polymer-A and B were added to the mixtures with the sequence of 0.05%, 0.10% and 0.15%. From Figures 5.3 to 5.6, it is obvious that polymer addition regardless of polymer type lowers the gel time compared to that of polymer free silicate gels with 7.5% and 10% SS. Consequently they behave like accelerator. On the other hand, this reduction in gel time with polymer addition becomes more pronounced at high values of SIR (low initiator concentration). Furthermore, gel time reductions are not significantly sensitive to type of the polymer.

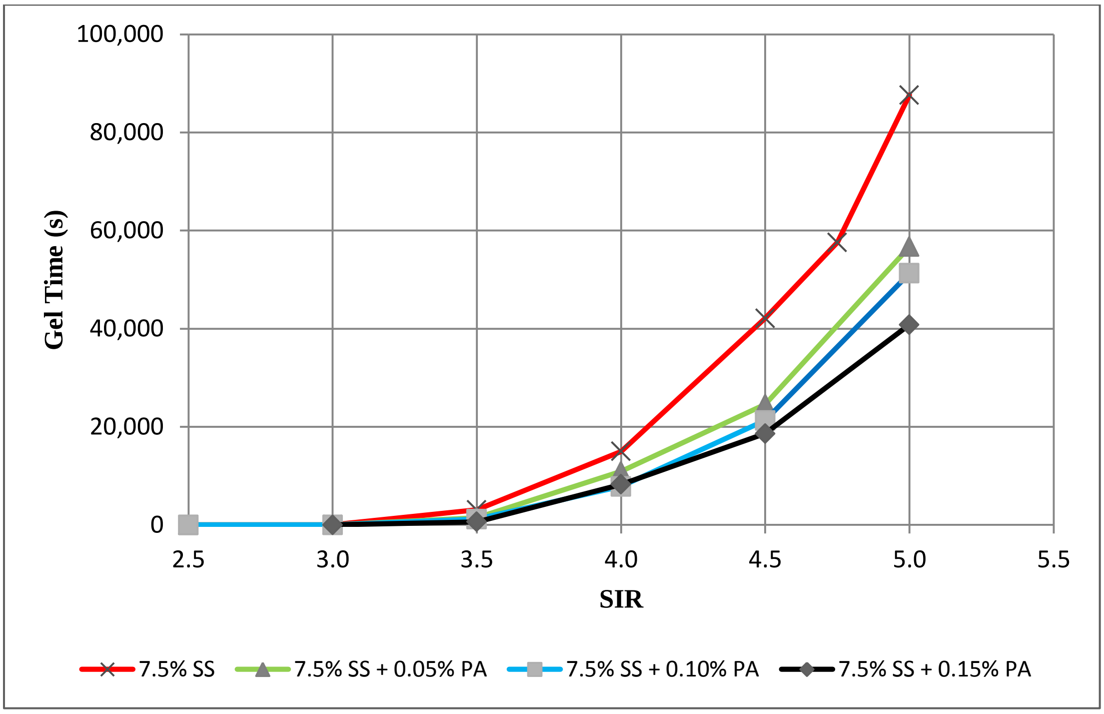

Figure 5.3 Gel time vs. SIR as a function of Polymer-A concentration for 7.5% SS.

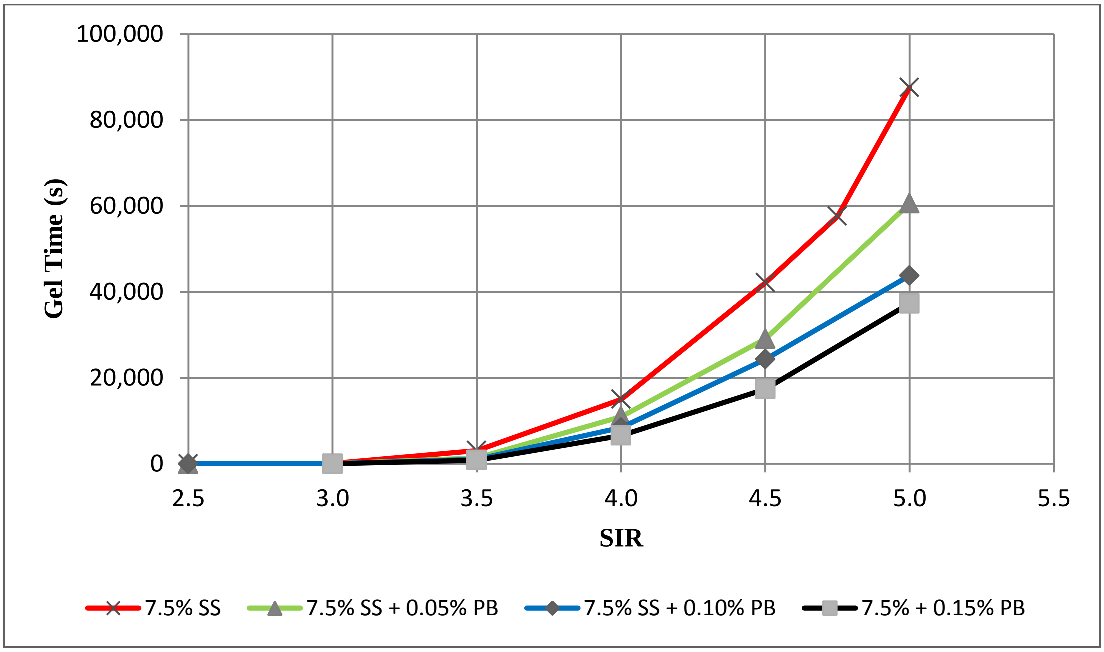

Figure 5.4 Gel time vs. SIR as a function of Polymer-B concentration for 7.5% SS.

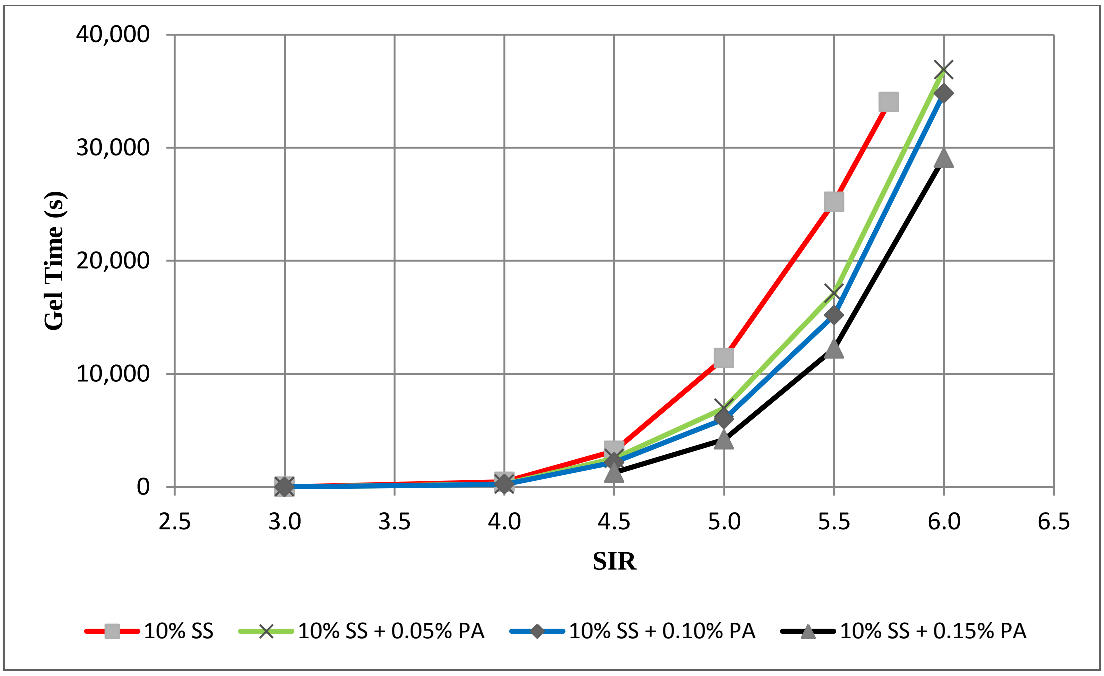

Figure 5.5 Gel time vs. SIR as a function of Polymer-A concentration for 10% SS.

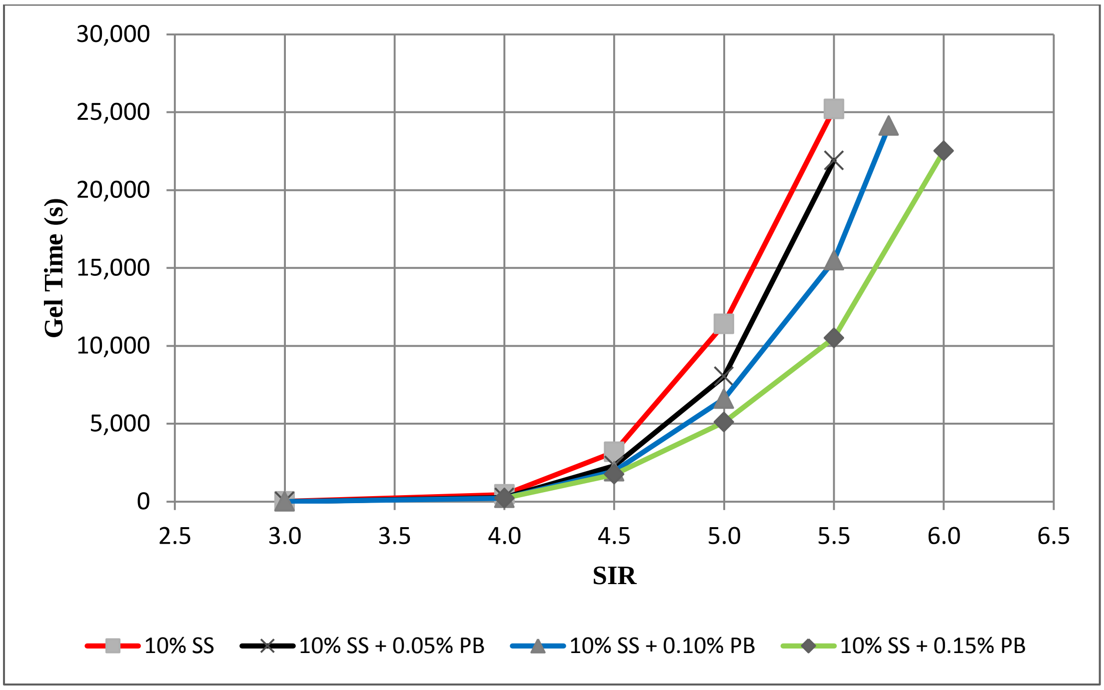

Figure 5.6 Gel time vs. SIR as a function of Polymer-B concentration for 10% SS.

Figure 5.7 Hard particles formed after addition of initiator (12.5% SS + 0.15% PA).

While studying effect of 0.15% Polymer-A on 12.5% sodium silicate solution, small, white and very hard solid particles formed after the addition of initiator (Fig. 5.7). Since gel time measurements for this composition were unreliable and unrepeatable due to formation of these particles its gel time curve is not included in Figure 8. However, no hard particles formed at lower Polymer-A concentrations and at any concentration of Polymer-B. Figures 5.8 and 5.9 indicate that gel time behavior of these gels is very similar to those observed in polymerized 7.5% and 10% sodium silicate gels.

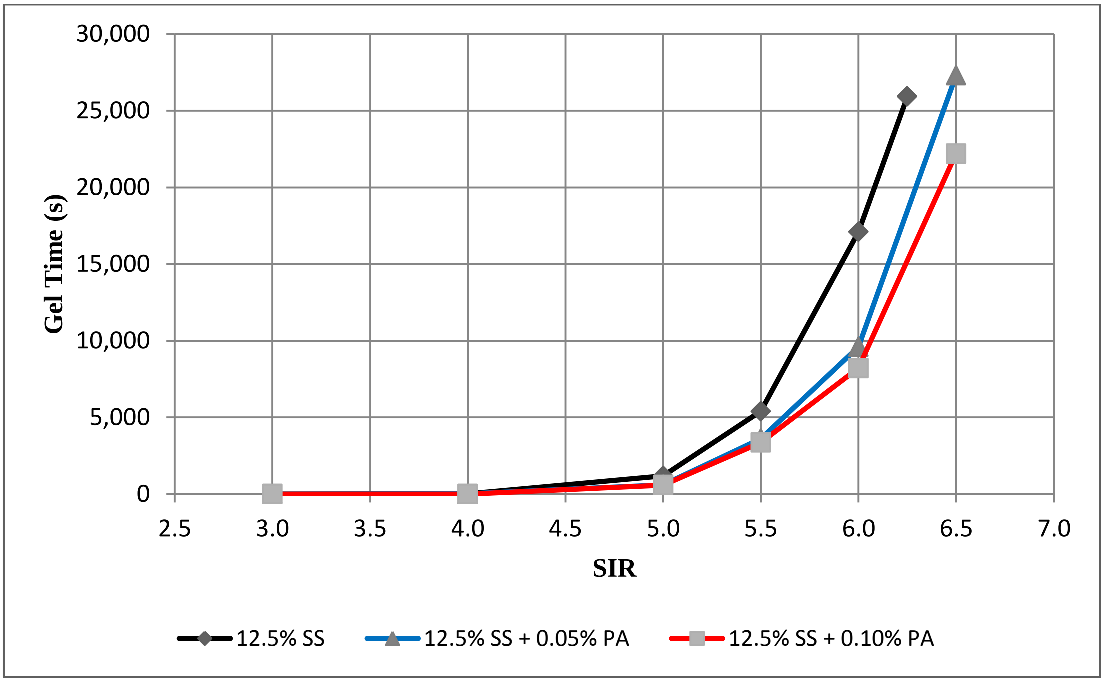

Figure 5.8 Gel time vs. SIR as a function of Polymer-A concentration for 12.5% SS.

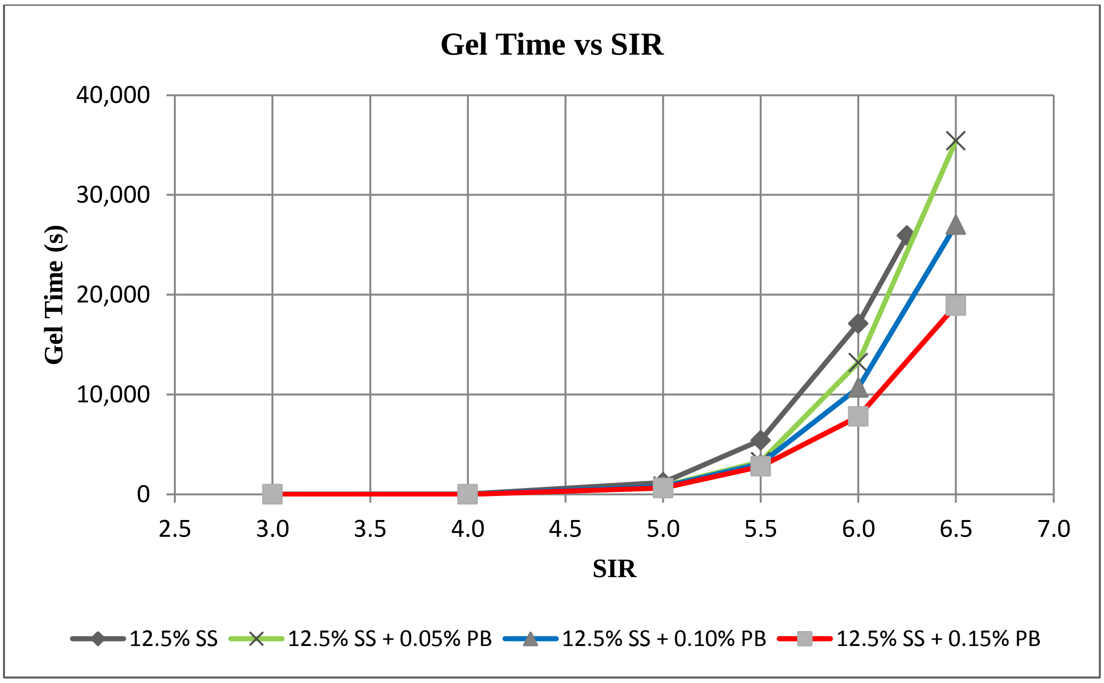

Figure 5.9 Gel time vs. SIR as a function of Polymer-B concentration for 12.5% SS.

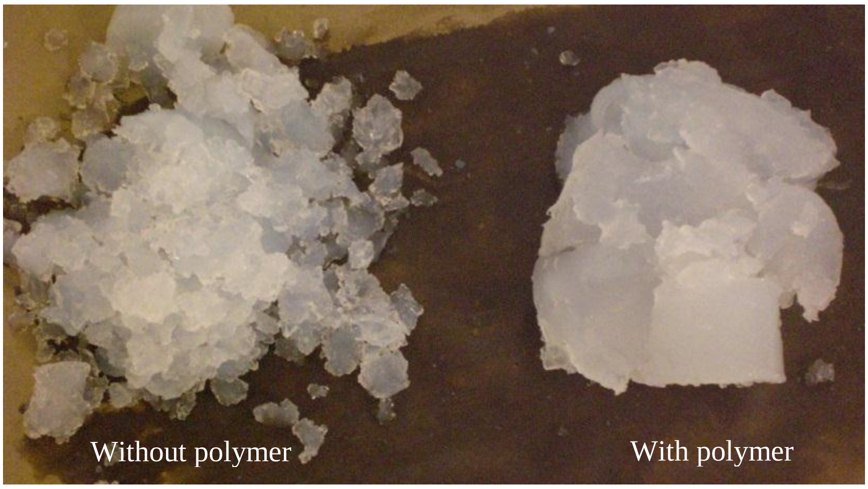

Figure 5.10 Effect of polymers on gel quality.

5.2.2 Gel Quality

Delayed sodium silicate gels formed with organic initiator (citric acid) are brittle lacking elasticity. This characteristic undesirable brittleness of sodium silicate gels can be corrected by adding partially hydrolyzed polyacrylamide type polymer to sodium silicate solutions before commencing gelation with the initiator (Burns et al. 2008). This system is named the Silica Polymer Initiator (SPI) gel.

In this study, two different types of polymers such as Polymer-A (polyacrylamide) and Polymer-B (biopolymer) are used in concentrations of 0.05%, 0.10% and 0.15% to investigate their effect on gel quality.

As seen from Tables 5.8 to 5.26 addition of both Polymer-A and Polymer-B improves gel quality and makes gel more elastic (Fig. 5.10). In general a transition occurs from hard brittle gel to soft gel with increasing silicate/initiator ratio at a constant polymer concentration. Moderate elastic and hard elastic gels develop at intermediate values of SIR. Polymer-A makes the gel more elastic compared to Polymer-B.

Table 5.8 Gel times and observation codes for gels with 7.5% SS + 0.05% PA.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
2.0	1	-	6
2.5	5	-	6
3.0	35	10.5	4
3.5	1,470	10.7	4
4.0	10,920	11.0	4
4.5	24,600	11.2	3
5.0	56,700	11.2	2

Table 5.9 Gel times and observation codes for gels with 7.5% SS + 0.1% PA.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
2.0	1	-	6
2.5	5	-	6
3.0	27	10.8	4
3.5	1,195	10.8	4
4.0	7,860	11.0	3
4.5	21,300	11.1	2
5.0	51,300	11.1	2

Table 5.10 Gel times and observation codes for gels with 7.5% SS + 0.15% PA.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	15	10.2	6
3.5	630	10.4	4
4.0	8,280	10.9	4
4.5	18,600	10.9	3
5.0	40,800	11.0	2

Table 5.11 Gel times and observation codes for gels with 7.5% SS + 0.05% PB.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
2.0	1	-	6
2.5	4	-	6
3.0	36	10.4	6
3.5	1,335	10.9	6
4.0	10,980	10.9	4
4.5	29,100	10.9	3
5.0	60,600	11.1	1

Table 5.12 Gel times and observation codes for gels with 7.5% SS + 0.10% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
2.0	1	-	6
2.5	4	-	6
3.0	32	10.4	6
3.5	1,050	10.8	6
4.0	8,400	11.0	4
4.5	24,300	11.0	3
5.0	43,800	11.2	1

Table 5.13 Gel times and observation codes for gels with 7.5% SS + 0.15% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	17	10.6	6
3.5	850	10.8	4
4.0	6,600	10.8	4
4.5	17,400	11.0	3

Table 5.14 Gel times and observation codes for gels with 10% SS + 0.05% PA

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	5	-	6
4.0	252	11.0	4
4.5	2,520	11.1	4
5.0	6,960	11.3	3
5.5	17,100	11.4	3
6.0	36,900	11.5	2

Table 5.15 Gel times and observation codes for gels with 10% SS + 0.1% PA

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	0	-	6
4.0	242	11.0	4
4.5	2,175	11.2	3
5.0	6,000	11.2	3
5.5	15,180	11.5	3
6.0	34,800	11.4	2

Table 5.16 Gel times and observation codes for gels with 10% SS + 0.15% PA

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
4.5	1,270	11.0	4
5.0	4,200	11.0	4
5.5	12,240	11.1	3
6.0	29,100	11.1	1

Table 5.17 Gel times and observation codes for gels with 10% SS + 0.05% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	1	-	6
4.0	251	11.3	4
4.5	2,300	11.3	4
5.0	8,040	11.3	3
5.5	21,900	11.4	3
6.0	42,000	11.5	2
7.0	178,200	11.6	1

Table 5.18 Gel times and observation codes for gels with 10% SS + 0.1% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	1	-	6
4.0	222	11.4	4
4.5	1,940	11.4	3
5.0	6,600	11.5	3
5.5	15,480	11.6	2

Table 5.19 Gel times and observation codes for gels with 10% SS + 0.15% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
4.0	210	10.7	4
4.5	1,745	10.8	4
5.0	5,100	11.0	4
5.5	10,500	11.0	3
6.0	22,500	11.1	1

Table 5.20 Gel times and observation codes for gels with 12.5% SS + 0.05% PA

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	2	-	6
4.0	9	10.9	6
5.0	603	11.1	6
5.5	3,610	11.4	4
6.0	9,600	11.6	3
6.5	27,300	11.6	1
7.0	118,800	11.7	1

Table 5.21 Gel times and observation codes for gels with 12.5% SS + 0.1% PA

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
4.0	5	10.6	6
5.0	585	10.8	6
5.5	3,360	11.3	4
6.0	8,220	11.6	3
6.5	22,200	11.6	2
7.0	99,000	11.7	1

Table 5.22 Gel times and observation codes for gels with 12.5% SS + 0.05% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
5.0	814	10.9	6
5.5	3,250	11.2	4
6.0	13,200	11.4	1
6.5	35,400	11.5	1

Table 5.23 Gel times and observation codes for gels with 12.5% SS + 0.1% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	4	-	6
4.0	11	10.8	6
5.0	760	10.9	6
5.5	3,063	11.2	4
6.0	10,680	11.4	1
6.5	27,000	11.5	1
7.0	87,600	11.5	1

Table 5.24 Gel times and observation codes for gels with 12.5% SS + 0.15% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	3	10.6	6
4.0	8	10.8	6
5.0	634	10.9	6
5.5	2,790	11.3	4
6.0	7,800	11.4	3
6.5	18,900	11.5	1
7.0	63,900	11.5	1

Table 5.25 Gel times and observation codes for gels with 15% SS + 0.05% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	1	11.1	6
4.0	4	11.1	6
5.0	34	11.3	6
5.5	435	11.4	6
6.0	3,130	11.4	3
6.5	14,040	11.5	1

Table 5.26 Gel times and observation codes for gels with 15% SS + 0.1% PB

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.0	1	10.2	6
4.0	2	10.2	6
5.0	28	10.3	5
5.5	477	10.6	3
6.0	3,210	11.3	3
6.5	9,720	11.4	1

As discussed in Section 5.2.1, small, white and very hard solid particles developed after the addition of initiator to the 15% silicate gel containing Polymer-A. However, these particles formed only in 15% silicate gel with 0.15% Polymer-B and not observed at lower concentrations of Polymer-B. Similar particles also formed in only 12.5% silicate solution containing 0.15% Polymer-A. The rest of polymerized 12.5% silicate solutions were free of solids particles.

Since the gel times cannot be controlled due to formation of solid particles, these compositions are not recommended for field applications. It should also be noted that, these very hard particles in the slurry can cause stuck in the some equipment at the rig site such as mud hoppers, hopper centrifuges, mud pump filters and even nozzles downhole.

5.3. Effect of LCM and Barite on Gel Time and Gel Quality

The silicate gels containing 7.5% and 10% are chosen here to evaluate the effect of LCM and barite on the gel time because of the following reasons:

1. The gels containing 3.5% and 5% sodium silicate exhibit an unstable and pH dependent gelation behavior and weak gel structures. Also small changes in initiator concentration affect the gel time more severely. This is also an unwanted feature especially for field usage of the gels since the field conditions

sometimes prevent the adjust concentrations precisely. Furthermore, the gels produced by using 3.5% or 5% sodium silicate are very soft to achieve an effective seal. Consequently, they are not recommended for field applications.

2. Formation of solid particles in high sodium silicate gels (≥12.5% SS) containing Polymer-A and polymer-B makes these compositions impractical for field applications due to the risk of stuck pipe and other related problems. Additionally, the cost of the gels with high sodium silicate concentration will be apparently higher.

5.3.1 Effect of LCM on Gel Time and Gel Quality

Fine and medium grade cellulosic fibers are used as lost circulation materials to improve the plugging ability of the gels. Sodium silicate gels without polymers cannot provide sufficient gel strength to keep the fibers in suspension. Therefore, it is decided to use Polymer-B (biopolymer) together with LCMs due to its superior suspending ability.

It is observed that, the mixtures with 0.05% Polymer-B cannot provide sufficient suspension for LCMs. According to our laboratory observations no settlement occurs when minimum 0.10% Polymer-B is added to the gel. This polymer concentration also allows the use of more LCM in silicate gels when compared to those containing higher polymer concentration.

Fibers were added with a concentration of 1%, 2%, 3% and 4%. It should also be noted that, there is an upper limit for fiber concentration changing with the gel composition. Upper limit for amount of LCM to be added to the gel decreases as polymer concentration increases. In this study the upper limit for cellulosic fiber concentration is determined experimentally as 4% for the gels with 10% sodium silicate and 0.10% Polymer-B.

5.3.1.1 Gel Time

A 10% Sodium Silicate + 0.10% Polymer-B gel with a SIR of 5.5 is selected as a base fluid to determine the effect of fine and medium cellulosic fibers (KAR-SEAL F and KAR-SEALM) on the gel time. From Figures 5.11 and 5.12, it is apparently seen that, as fiber concentration increases, gel time rapidly decreases.

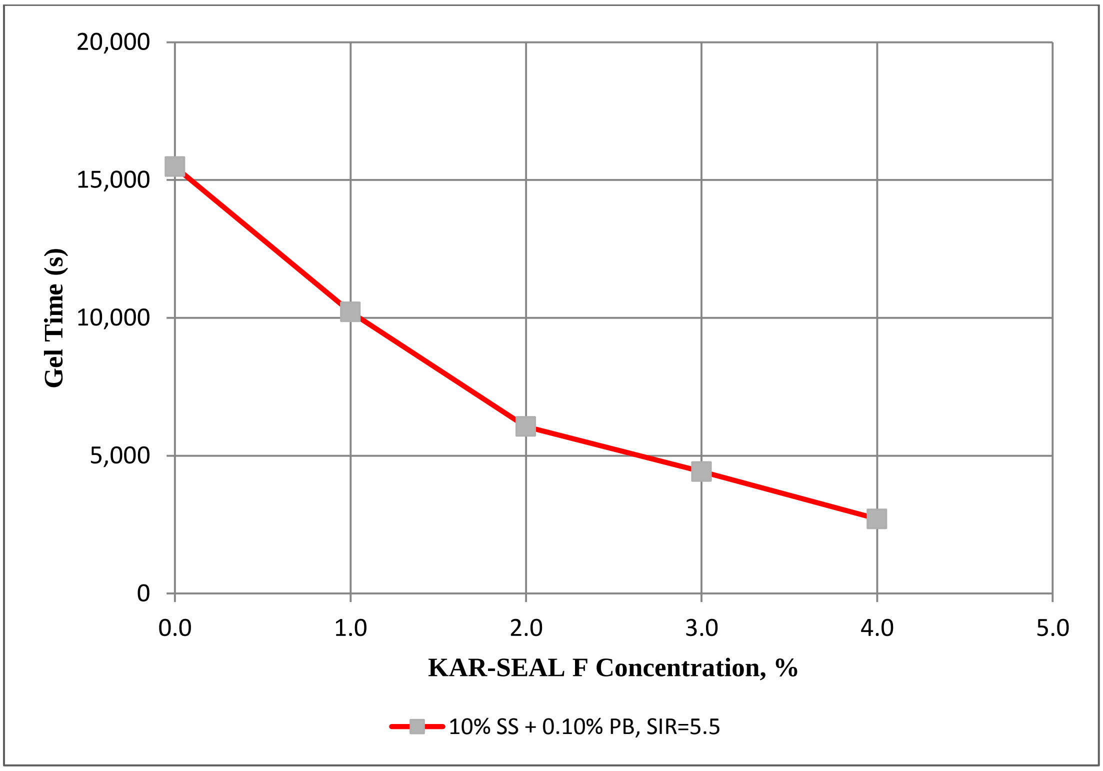

Figure 5.11 The effect of KAR-SEAL F on the gel time**.**

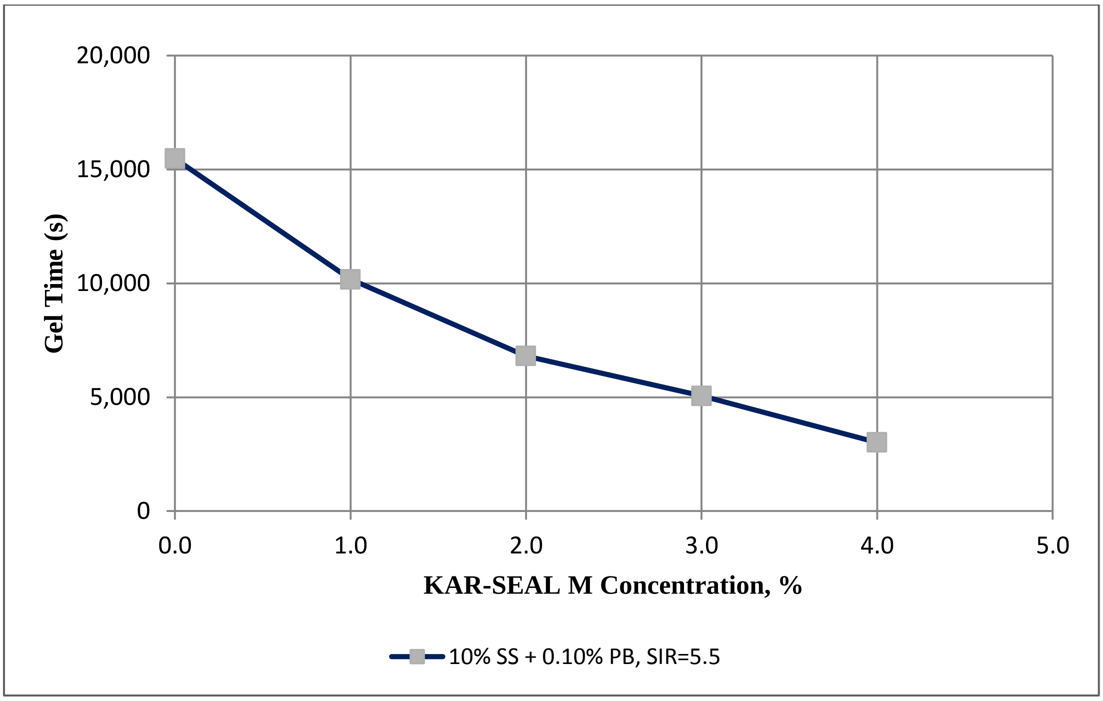

Figure 5.12 The effect of KAR-SEAL M on the gel time**.**

Changes in the gel time at various values of SIR for polymerized silicate gels including 2% KAR-SEAL F and 2% KAR-SEAL M are shown in Figure 5.13. It was again observed that, KAR-SEAL F and KAR-SEAL M addition causes severe reduction of gel time and measured gel times are nearly equal for both type of cellulosic fibers.

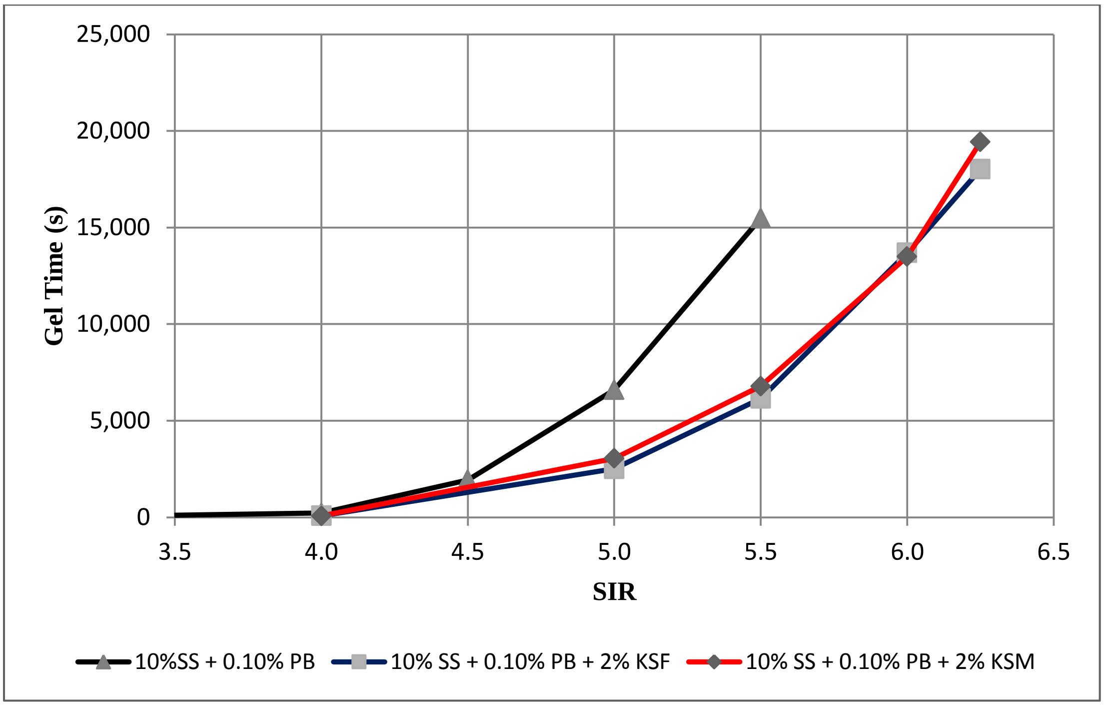

Figure 5.13 The effect of KAR-SEAL F and KAR-SEAL M on the gel time**.**

5.3.1.2 Gel Quality

KAR-SEAL F and KAR-SEAL M addition also affect the gel quality. Addition of these fibers makes the gels more rigid and brittle. Figure 5.14 shows one of the gel including 3% KAR-SEAL F. Tables 5.27 to 5.30 it is obvious that fibers increases gel strength with more compact structure.

Figure 5.14 Sodium silicate gel containing 3% KAR-SEAL F.

Table 5.27 Effect of KAR-SEAL F on gel time and gel quality, 10% SS + 0.1% PB, SIR=5.5

KAR-SEAL F Conc. %	*GEL TIME, s*	*pH*	*OBS. CODE*
0	15,480	11.6	2
1.0	10,211	11.7	5
2.0	6,053	11.7	5
3.0	4,421	11.8	6
4.0	2,706	11.7	6

Table 5.28 Effect of KAR-SEAL M on gel time and gel quality for 10% SS + 0.1% PB, SIR=5.5

KAR-SEAL M Conc. %	*GEL TIME, s*	*pH*	*OBS. CODE*
0	15,480	11.6	2
1.0	10,178	11.7	5
2.0	6,812	11.7	5
3.0	5,058	11.8	6
4.0	3,013	11.8	6

Table 5.29 Gel time and gel quality for 10% SS + 0.10% PB + 2% KAR-SEAL F.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
4.0	80	10.2	6
5.0	2,508	10.4	6
5.5	6,150	10.5	5
6.0	13,693	10.7	5
6.25	18,019	10.9	3

Table 5.30 Gel time and gel quality for 10% SS + 0.10% PB + 2% KAR-SEAL M.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
4.0	75	10.1	6
5.0	3,052	10.4	6
5.5	6,790	10.6	5
6.0	13,493	10.7	5
6.25	19,427	10.9	3

5.3.2 Effect of Barite on Gel Time and Gel Quality

The effect of Barite on gel time is also important for field applications. For some situations, it is necessary to place gel mixture across the zone of interest while the drilling mud being inside the wellbore. It is required to equalize the density of gel slurry to the mud density to keep the gel mixture in place.

API grade barite was used as weighting agent to increase the density of the slurries. Mixtures without polymer cannot provide sufficient carrying capacity to keep the barite in suspension. Due to higher suspending ability of Polymer-B, the mixtures including Polymer-B are selected for barite addition.

Rheology tests were performed at the temperature of 75 °F by changing Polymer-B concentration for the base gel having composition of 10% Sodium silicate + 10% Barite with SIR=6.0. According to the test results, at least 0.30% Polymer-B concentration is required to prevent barite settlement (Table 5.31). However, it is observed that, there is no settlement occurred with 0.15% Polymer-B in the 100 cc beaker, most probably due to the attractive forces between barite particles in that geometry. However, this does not mean that there will be no settlement for field applications.

It is strongly recommended to make rheological analysis before using barite for each particular field application. It should also be noted that, there is an upper limit for barite concentration changing with the gel slurry composition. As polymer concentration increases the upper limit for barite amount decreases. However, the upper limit for barite concentration is also depends on the mixing ability at the rig equipment. In this study magnetic stirrer is used to mix all of the slurries and the upper limit for barite concentration is determined as 10% for the mixtures having 0.35% Polymer-B and 20% for the mixtures having 0.15% Polymer-B.

Table 5.31 The effect of polymer concentration on the rheological of the base gel composition: 10% SS + 10% barite and SIR=6.0.

Visc. Speed (rpm)	*Rheological Properties, Fann degree*				
	0.15% PB	0.20% PB	0.25% PB	0.30% PB	0.35% PB
θ_{600}	15	18	24	32	48
θ_{300}	8	10	15	21	36
θ_{200}	6	7	11	16	27
θ_{100}	4	4	7	10	19
θ_{6}	1	1	2	2	6
θ_{3}	1	1	1	1	5
PV, cp	7	8	9	11	12
YP, lb/100 ft^2	1	2	6	10	24

Since gel time tests with barite were performed to determine the effect of barite on gel time, it was decided to use 0.15% Polymer-B although there is a settlement risk for field applications. Densities of various gel compositions are given in Table 5.32.

Table 5.32 Densities of several gel composition.

Gel Composition	*Density, ppg*
10% SS + 0.15% PB, SIR=4.5	9.0
10% SS + 0.15% PB + 5% Barite, SIR=4.5	9.5
10% SS + 0.15% PB + 10% Barite, SIR=4.5	9.9
10% SS + 0.15% PB + 15% Barite, SIR=4.5	10.4
10% SS + 0.15% PB + 20% Barite, SIR=4.5	10.9
7.5% SS + 0.15% PB, SIR=5.5	8.9
7.5% SS + 0.15% PB + 5% Barite, SIR=5.5	9.25
7.5% SS + 0.15% PB + 10% Barite, SIR=5.5	9.65
7.5% SS + 0.15% PB + 15% Barite, SIR=5.5	10.1
7.5% SS + 0.15% PB + 20% Barite, SIR=5.5	10.6

5.3.2.1 Gel Time

Barite was added with concentrations of 5%, 10%, 15% and 20%. To be able to determine the effect of barite concentration on gel time 10% SS + 0.15% PB with SIR of 5.5 is selected as a base composition. It is observed that, as barite concentration increases gel time decreases significantly (Fig. 5.15).

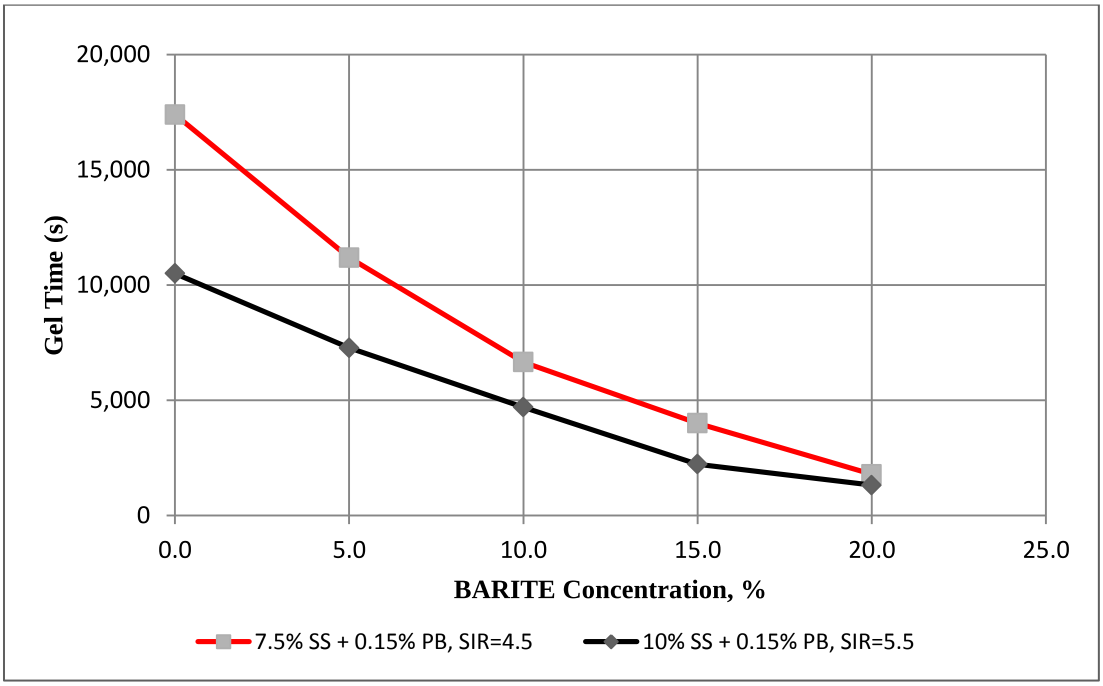

Figure 5.15 The effect of Barite concentration on the gel time**.**

To prove the effect of barite on gel time, it was decided to compare gel times of the slurries with and without barite. With this purpose, gel time tests are performed keeping the concentrations of barite constant and changing the SIR as for the screening tests. It is obvious that, mixtures including barite have lower gel times when compared with the ones without barite (Fig. 5.16 and Fig. 5.17).

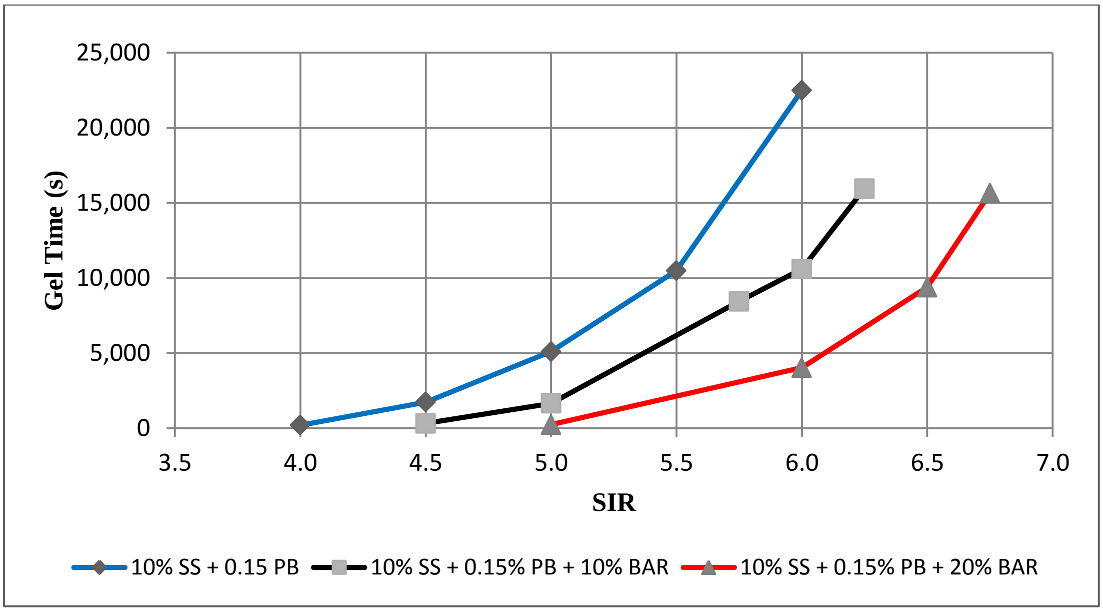

Figure 5.16 The effect of barite concentration on the gel time for the gel with 10% SS + 0.15% PB.

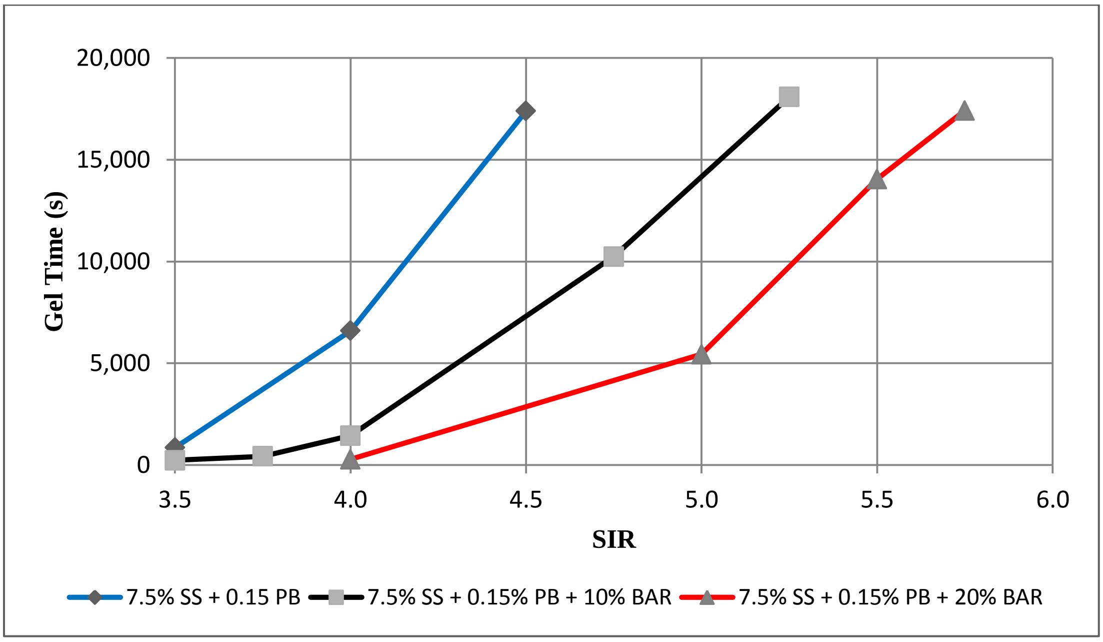

Figure 5.17 The effect of barite concentration on the gel time for the gel with 7.5% SS + 0.15% PB**.**

5.3.2.2 Gel Quality

From Tables 5.33 and 5.34, it is apparently seen that barite addition makes the gels more brittle. Tables 5.35 to 5.38 indicate the weighted gels become more elastic as SIR gets higher values.

Table 5.33 Effect of barite on gel time and gel quality for 7.5% SS + 0.15% PB, SIR=4.5.

BARITE Conc. %	*GEL TIME, s*	*pH*	*OBS. CODE*
0	17,400	11.0	3
5.0	11,192	11.6	3
10.0	6,654	11.6	3
15.0	4,002	11.6	3
20.0	1,792	11.6	5

Table 5.34 Effect of barite on gel time and gel quality for 10% SS+0.15% PB, SIR=5.5.

BARITE Conc. %	*GEL TIME, s*	*pH*	*OBS. CODE*
0	10,500	11.0	3
5.0	7,272	11.6	3
10.0	4,700	11.6	3
15.0	2,230	11.4	5
20.0	1,320	11.4	5

Table 5.35 Effect of barite on gel time and gel quality for 7.5% SS + 0.15% PB + 10% Barite.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
3.50	230	11.7	6
3.75	430	11.7	5
4.00	1,443	11.7	5
4.75	10,241	11.7	3
5.25	18,088	11.7	3

Table 5.36 Effect of barite on gel time and gel quality for 7.5% SS + 0.15% PB + 20% Barite.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
4.0	278	11.4	6
5.0	5,444	11.4	5
5.5	14,054	11.6	5
5.75	17,416	11.6	3

Table 5.37 Effect of barite on gel time and gel quality for 10% SS + 0.15% PB + 10% Barite.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
4.5	320	11.7	6
5.0	1,653	11.7	5
5.75	8,453	11.7	5
6.0	10,603	11.7	3
6.25	15,958	11.8	3

Table 5.38 Effect of barite on gel time and gel quality for 10% SS + 0.15% PB + 20% Barite.

SIR	*GEL TIME, s*	*pH*	*OBS. CODE*
5.0	245	11.6	6
6.0	4,033	11.6	5
6.5	9,393	11.6	5
6.75	15,645	11.6	3

5.4 Prediction of Long Term Gelation Process

For this study, gel time is defined as vortex closure on the magnetic stirrer. However, gelation continues after the vortex closure. Turbidity test was utilized here to investigate the gelation after gel time. Turbidity tests were performed on some selected slurries to investigate the gelation after gel time and to determine the time required to finish all gelation process.

The appearance of the mixtures having only distilled water, sodium silicate, polymer solution and the initiator is transparent like the water when first mixed. They become cloudy as gelation occurs. This gelation process in the slurries causes turbidity (NTU value) to increase. Figure 5.18 shows the difference between low turbidity and high turbidity liquids. NTU readings are given in Appendix-B.

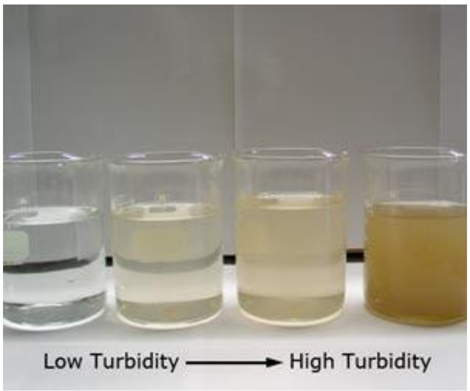

Figure 5.18 The difference between low turbidity and high turbidity liquids.

Figure 5.19 shows the effect of time on turbidity for the gel mixtures for 10% Sodium silicate with different SIR. It can be seen from Figure 5.19 that, NTU values are increasing as gelation continues. NTU value of the mixtures increases and reaches a plateau showing the end of the long term gelation. As gel time decreases, NTU values increases more rapidly as expected.

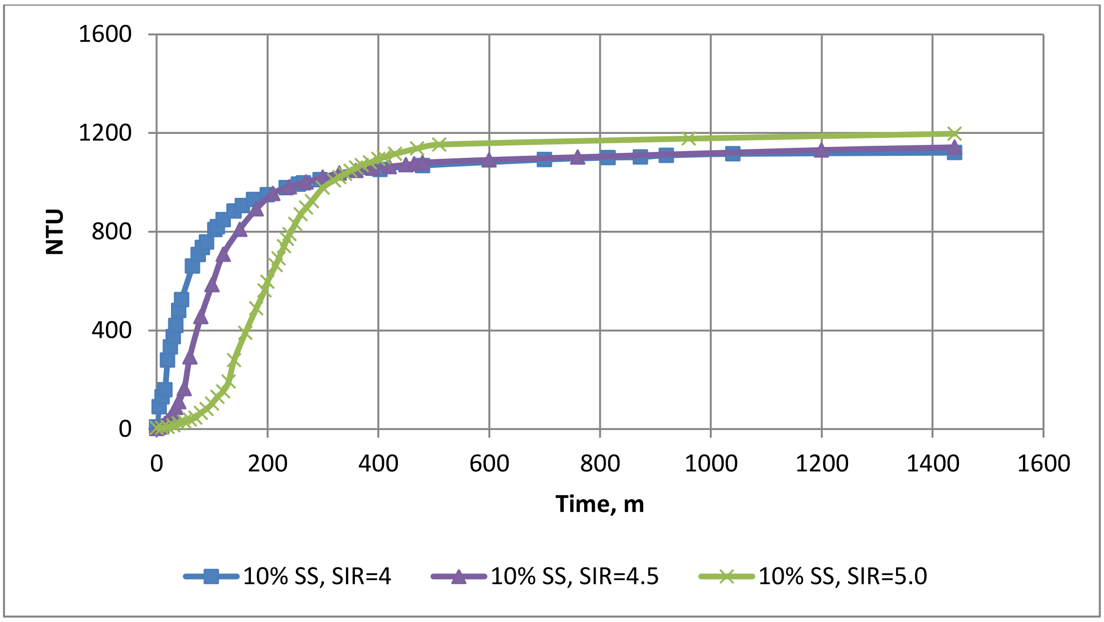

Figure 5.19 Gel turbidity as a function of time for 10%SS with various SIRs.

Figure 5.20 shows the effect of time on turbidity for the gel mixtures 1) 7.5% SS, SIR=4.0, 2) 7.5% SS, SIR=3.5. As gel time increases NTU values increases more rapidly as expected.

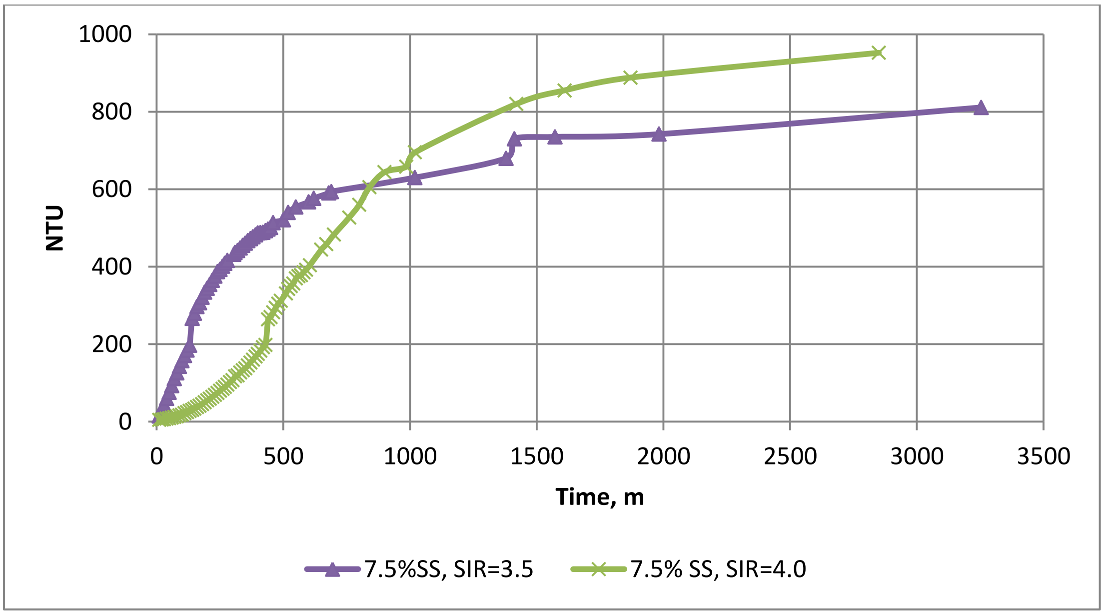

Figure 5.20 Gel turbidity as a function of time for 7.5% SS with various SIRs.

It is apparently seen from Figures 5.19 and 5.20 that gelation process after the vortex closure continues and requires long time to complete the gelation (Table 5.39). This long term gelation process is prolonged for relatively low sodium silicate gels.

Turbidity tests are thought very useful to determine the end of the gelation. The starting time of the next operation can be decided by this knowledge at the rigsite.

Table 5.39 Comparison of gel time and plateau time.

Gel compositions	*Gel Time, s*	*Time required to reach plateau (approximately), s*
7.5% SS, SIR=3.5	3,075	40,800
7.5% SS, SIR=4.0	15,000	96,600
10% SS, SIR=4.0	447	10,500
10% SS, SIR=4.5	3,180	16,800
10% SS, SIR=5.0	11,400	28,200

5.5 Effect of Shear on Gelation

Rheological measurements are performed to detect the effect of shearing on the gelation process. Fann 35 SA viscometer is used at 6 rpm, 200 rpm, 100 rpm and 6 rpm for these experiments. Viscometer readings are given in Appendix C. Fann readings are increasing as gelation occurs at constant shear rate. Three different mixtures with compositions of 1) 7.5% SS, SIR= 4.0 2) 7.5% SS + 0.15% PA, SIR= 4.0 and 3) 7.5% SS + 0.15% PB, SIR= 4.0 were tested to determine the effect of shearing on gelation. It is obvious that gelation occurs earlier at higher shear rates.

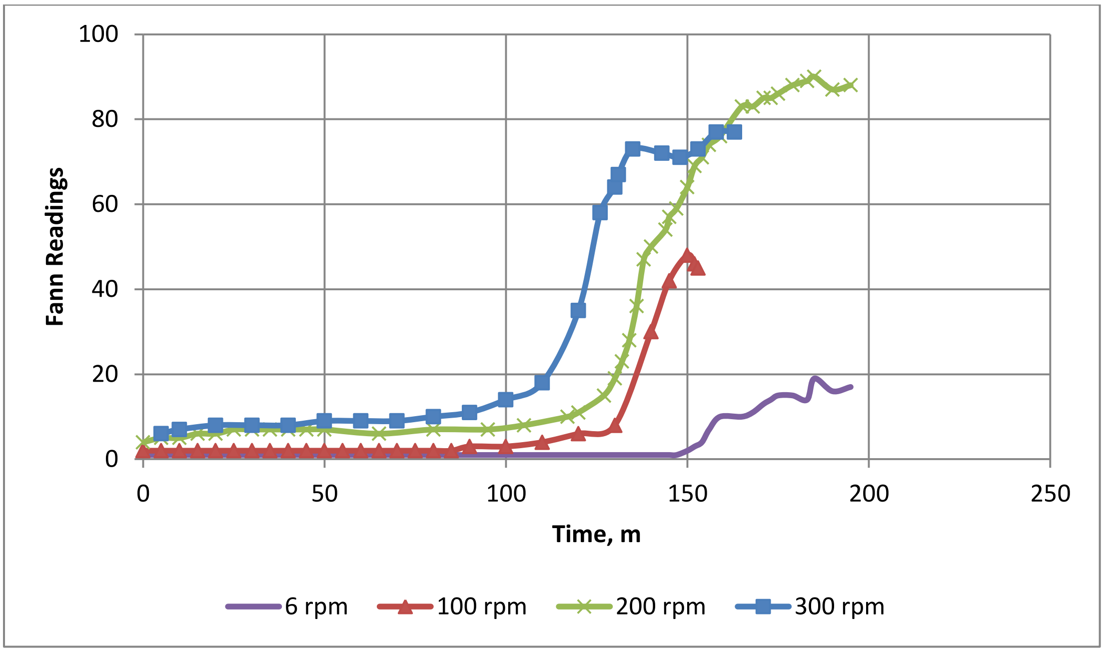

Figure 5.21 The effect shear on gel time for the gel composition: 7.5% SS, SIR=3.5.

It can be seen from Figures 5.21 to 5.23 that, gel time is dependent on the shear rate. When the gels are subjected to high shear rate, thicken faster. Since the gel is subjected to high shear rate while pumping down the drillstring, shear history plays important role for determining gel time and gel quality.

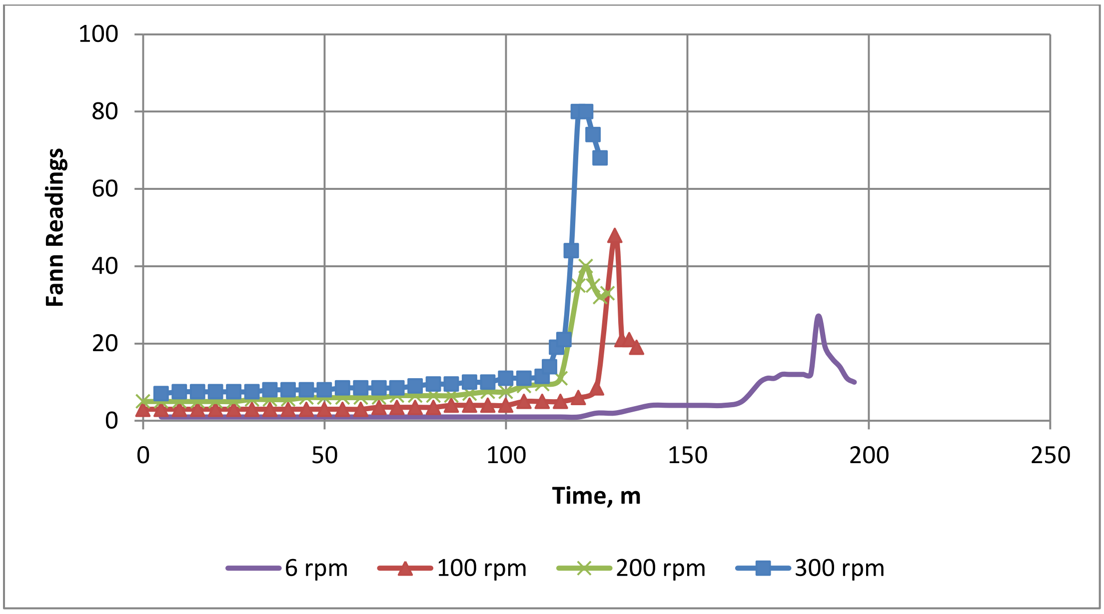

Figure 5.22 The effect shear on gel time for the gel composition: 7.5% SS + 0.15% PA, SIR=4.0.

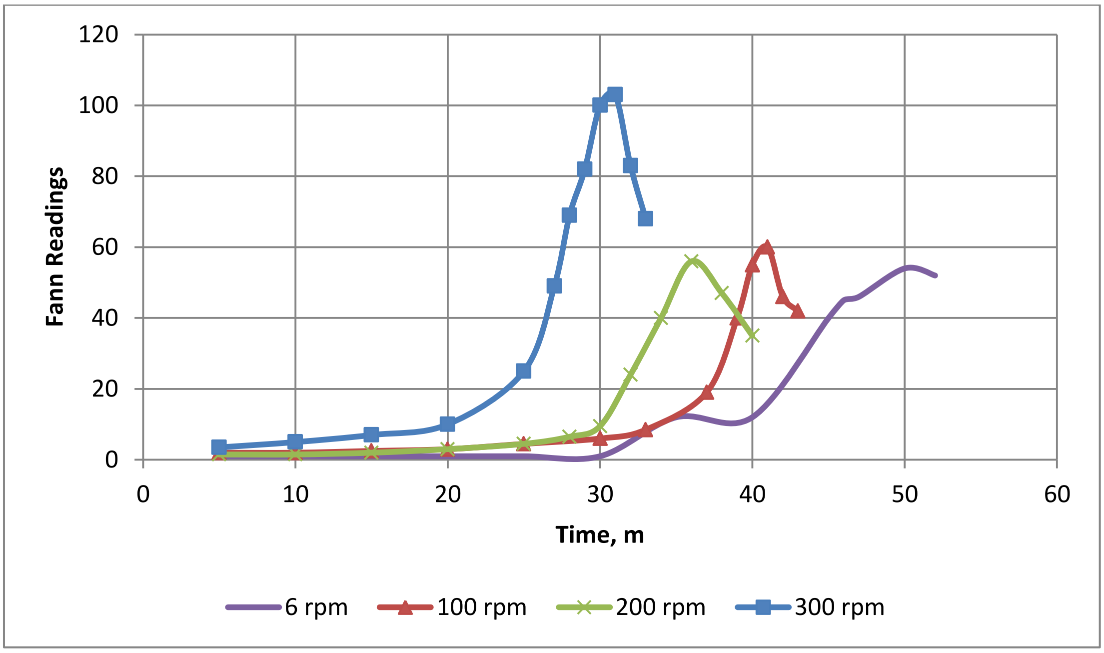

Figure 5.23 The effect shear on gel time for the gel composition: 7.5% SS + 0.15% PB, SIR=4.0.

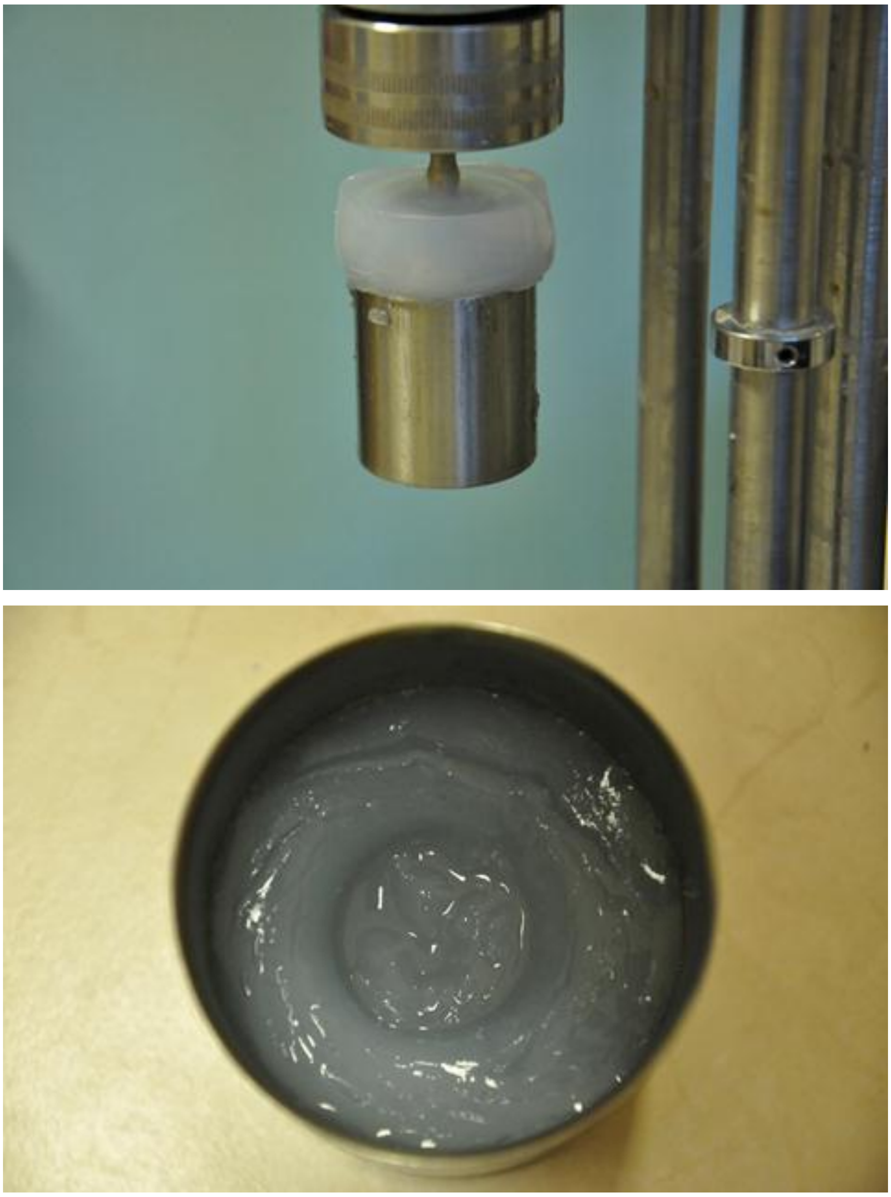

Figure 5.24 Appearance of gel in the viscometer after the completion of gelation.

Unreliable readings from the viscometer were obtained near the completion of the gelation as shown in Figures 5.21 to 5.23. Since Fann viscometer is designed to measure viscous behavior of fluids, after the formation of elastic gel structure it cannot predict their viscoelastic behavior (Fig. 5.24).

5.6 Effect of LCM and Barite on Extrusion Pressure of Gels

Gels developed to solve drilling problems must withstand a differential pressure which will be applied from formation to the well or well to the formation. Pressure extrusion tests were performed on some selected slurries to be able to determine the required pressure to initiate the extrusion. HPHT filtration test cell was modified to perform this test. Piston was designed and fitted with an o-ring located inside the cell. The piston is driven by the applied pressure at the upper end of the cell and pushes the gel through 1 mm hole opened at the bottom cap of the cell.

The gel compositions of 7.5% and 10% sodium silicate with different SIR values are selected as base mixtures to compare the gels in terms of extrusion pressure. Results of pressure extrusion test performed on the base gels are given in Table 5.40. As seen from this table, both sodium silicate concentration and SIR do not have any effect on extrusion pressure.

The effect of polymer, KAR-SEAL F and KAR-SEAL M on extrusion pressure was also tested. While polymer did not change the required pressure to initiate extrusion, KAR-SEAL F and KAR-SEAL M addition obviously increased the extrusion pressure. However, some of the gels including LCM required more than 750 psi extrusion pressure (Table 5.41). It is probably due to bridging in the hole on the bottom cap of the test cell.

Table 5.40 Extrusion pressures of the sodium silicate gels.

Gel compositions	*Pressure to initiate extrusion, psi*
7.5% SS, SIR=3.0	25-30
7.5% SS, SIR=3.5	20-25
7.5% SS, SIR=4.0	20-25
10% SS, SIR=4.0	25-30
10% SS, SIR=4.5	20-25

Table 5.41 Extrusion pressures of the gels containing Polymer-B and LCM.

Gel compositions	*Pressure to initiate extrusion, psi*
10% SS, SIR=4.5	20-25
10% SS, 0.10% PB, SIR=4.5	20-25
10% SS + 0.10% PB + 1% KAR-SEAL F, SIR=4.5	80-100
10% SS + 0.10% PB + 2% KAR-SEAL F, SIR=4.5	50-60
10% SS + 0.10% PB + 3% KAR-SEAL F, SIR=4.5	>750
10% SS + 0.10% PB + 1% KAR-SEAL M, SIR=4.5	50-60
10% SS + 0.10% PB + 2% KAR-SEAL M, SIR=4.5	>750
10% SS + 0.10% PB + 3% KAR-SEAL M, SIR=4.5	50-60

Table 5.42 Extrusion pressures of the polymerized gels containing barite.

Gel compositions	*Pressure to initiate extrusion, psi*
10% SS + 0.15% PB + 5% Barite, SIR=5.5	25-30
10% SS + 0.15% PB + 15% Barite, SIR=5.5	25-30

Table 5.42 indicates that barite addition to 10% SS + 0.15% PB gel with SIR=5.5 does not change required pressure to initiate extrusion.

Sodium-Silicate concentrations between 7.5% and 10% together with the addition of polymers having concentrations between 0.05% and 0.15% yield elastic and firm gels to be applied for field applications. Since LCM addition increases the extrusion pressure, concentrations between 1% and 4% can also be recommended for LCM usage. Polymer-B having at least 0.15% concentration should be selected for the addition of LCM or Barite. Although it depends on the concentrations of each additive, barite can be added to the slurries up to 20%.

CHAPTER 6

CONCLUSIONS

An experimental study is carried out here about gel treatments for solving some particular drilling problems. Sodium-silicate and the initiator are the main materials for the gel slurries. For additional purposes, some other materials are used: polymers, cellulosic fibers and barite. Gel time experiments were performed for screening purposes. Turbidity, viscosity and pressure extrusion experiments were carried out on some selected slurries. In this chapter all of the findings are listed.

- Controllable gel time is the most important property of the gels for the field applications. Gel times of the gel slurry compositions designed in this study is controllable and depends on the concentrations of each additive.

- Gel quality is another important feature to be concerned for field application. Qualities of the gels after four times the gel time are compared with each other by the introduced observation codes.

- In this study six different concentrations of sodium silicate are investigated (3.5%, 5%, 7.5%, 10%, 12.5%, and 15%). Sodium silicate concentrations of 12.5% and 15% are eliminated for following the gel time and gel quality tests due to formation of very hard solids after addition of initiator to the mixtures containing polymer.

- Gel time depends on the pH for slurries having 3.5% and 5.0% SS. When the slurry becomes acidic, gel time increases with increasing initiator amount. Additionally the gel times of the slurries mixed with 5% and 3.5% SS are very sensitive to initiator amount making the gels impractical for field applications. Therefore, sodium silicate concentrations between 7.5% and 10% are recommended for field applications.

- Increase in sodium silicate concentration causes decrease in gel time and stronger gels. In general, the gels with more gel time are softer than the ones with lower gel time. Among two gels having same gel time, the one with higher sodium silicate is harder than other.

- Increase in initiator amount in the slurry decreases gel time for the mixtures including 7.5%, 10%, 12.5% and 15% SS. On the other hand, the effect of initiator on gel time depends on pH of the slurries including 3.5% and 5% SS.

- Polymer-A and Polymer-B addition reduce the gel time significantly. PA reduces gel time more when compared with PB.

- Addition of polymers also makes the gels more elastic and firmer. For the addition of LCM or weighting material, Polymer-B is selected due to its higher suspending ability coming from its natural structure.

- NTU value is increasing as gelation occurs and reaches a plateau when the gelation is close to finish. Ones the gel is placed in the hole, it is required to wait until the complete gelation. Turbidity test at the rigsite will be a very good indication for the starting time of next operation.

- When the gels are subjected to high shear rate, thicken faster. Therefore, shear history plays important role for determining gel time and gel quality.

- KAR-SEAL F and KAR-SEAL M were used as LCM to increase the plugging ability of the gels. Pressure extrusion tests showed that LCM addition increases the pressure required to initiate extrusion. Addition of these cellulosic fibers reduces gel time significantly. They also make the gels firmer and stronger.

- It is shown that extrusion pressure of the gels is not function of concentrations of sodium silicate, polymer and barite and SIR values.

- The proposed gels are not only environmentally friendly but also less corrosive to tubular goods due to their pH values which are above 10. The pH values of the gels remain same during the gelation most probably due to buffering effect of sodium-silicate.

CHAPTER 7

RECOMMENDATIONS

- All of the experiments in this study were performed at the room temperature due to the fact that the study is only to develop gel mixtures for top hole sections. However, it is well-known that, temperature has significant effect on gel time and gel quality. The effect of temperature should be studied to increase the area of application.

- Gel strength is an important parameter to be able to compare the gel compositions. Especially the effect of introducing solids to the system on gel strength should be quantitatively investigated. Gel strength experiments may be performed by using cement gel strength analyzer.

- In this study only barite is used as a weighting agent. Other materials such as calcium carbonate or hematite may be helpful for some specific applications. Furthermore, optimum polymer type and concentration should be studied for weighting material addition.

- Permeability plugging experiments can be performed for better determination of the plugging ability of the gels. This experiment will also help to determine the type of the LCM should be used for particular field operation.

- The use of monovalent salts may be investigated for density adjustment. However, the environmental regulations should be concerned before using salts.

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APPENDIX A

SAMPLE CALCULATION

All concentrations for the materials in the gel composition are “per cent by weight” in this study. In this Appendix, the amounts of each additive in “gram” are calculated according to given total mixture weight, percentages of each additive and silicate/initiator ratio (SIR).

Given:

Total Mixture Amount (TMA) = 100 g
Sodium-silicate (SSA) = 10%
Polymer-A Amount (PAA) = 0.15%
Barite Amount (BA) = 5%
Silicate-Initiator Ratio (SIR) = 4

Calculation of the amounts of sodium-silicate solution, polymer solution, barite, initiator and distilled water in the gel slurry:

1 - Sodium-silicate solution amount in the mixture (SSSA), g:

First it is required to calculate solid sodium-silicate amount in the mixture, then to calculate solution amount required.

Solid sodium-silicate amount in the mixture, g:

$$
\begin{aligned}
SSA, g &= TMA\ (g)\ x\ SSA\ (\%) \div\ 100 \\
&= 100\ x\ 10\ \div\ 100 \\
&= 10
\end{aligned}
$$

Since sodium-silicate is provided as solution with water it is required to calculate required amount of solution providing 10 g of solid sodium-silicate. Sodium-silicate solution used in this study includes 36.81% total solid sodium-silicate fraction (TSSSF).

Sodium-silicate solution amount in the mixture (SSSA), g:

$$
\begin{aligned}
SSSA, g &= SSA\ (g) \div TSSSF\ (\%)\ \times 100 \\
&= 10 \div 36.81 \times 100 \\
&= 27.17\ g\ sodium - silicate\ solution\ is\ required\ in\ the\ gel\ mixture.
\end{aligned}
$$

2 – Polymer-A solution amount in the mixture (PASA), g:

First it is required to calculate dry polymer-A amount in the mixture, then to calculate polymer solution amount required.

Solid Polymer-A amount in the mixture, g:

$$
\begin{aligned}
PAA, g &= TMA\ (g)\ x\ PAA\ (\%) \div\ 100 \\
&= 100\ x\ 0.15\ \div\ 100 \\
&= 0.15
\end{aligned}
$$

Since polymers are hydrated for at least 6 hours before adding to the gel mixture, it is required to calculate required amount of solution providing 0.15 g of solid polymer-A. Polymer solutions used in this study prepared with 0.4% total solid polymer fraction (TSPF).

Polymer-A solution amount in the mixture (PASA), g:

$$PASA, g = PAA\ (g) \div TSPF\ (\%)\ \times 100$$

$$= 0.15 \div 0.4 \times 100$$
$$= 37.5\ g\ polymer - A\ solution\ is\ required\ in\ the\ gel\ mixture.$$

3 – Barite amount in the mixture (BA), g:

Barite amount in the mixture (BA), g:

$$BA, g = TMA\ (g)\ x\ BA\ (\%) \div\ 100$$
$$= 100\ x\ 5\ \div\ 100$$
$$= 5$$

4 – Initiator amount in the mixture (BA), g:

Initiator amount in the mixture (IA), g:

$$IA, g = SSA\ (g) \div SIR$$
$$= 10 \div 4$$
$$= 2.5\ g\ Initiator\ is\ required\ in\ the\ gel\ mixture.$$

5 – Distilled Water amount in the mixture (DWA), g:

Distilled water amount in the mixture (DWA), g:

$$DWA, g = TMA\ - (SSSA + PASA + BA + IA)$$
$$= 100 - (27.17\ + 37.5 + 5 + 2.5)$$
$$= 27.83\ g\ distilled\ water\ is\ required\ in\ the\ gel\ mixture.$$

APPENDIX B

TURBIDITY READINGS

Table B.1 7.5% SS, SIR=3.5.

Time, m	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*
10	15	160	297	320	442	500	521
20	30	170	307	330	448	520	540
30	44	180	321	340	455	550	554
40	60	190	334	350	461	600	567
50	76	200	344	360	467	620	576
60	92.9	210	354	370	472	680	590
70	111.6	220	365	380	477	690	594
80	126.2	230	376	390	482	1020	630
90	142.7	240	387	400	487	1380	680
100	158	250	393	410	488	1412	730
110	171.1	260	401	420	489	1572	735
120	184.9	270	409	430	493	1983	742
130	197.3	280	416	440	497	3255	811
140	267	305	432	450	501		
150	280	310	437	460	514		

Table B.2 7.5% SS, SIR=4.0.

Time, m	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*
10	4.7	190	50	370	153	560	376
20	5.4	200	55	380	160	570	378
30	6.4	210	59	390	168	580	386
40	7.95	220	64.3	400	175	590	392
50	9.27	230	69.6	410	183	605	404
60	11	240	73.9	420	192	650	444
70	12.2	250	80.3	430	198	670	458
80	14.2	260	85	440	264	700	483
90	16.5	270	90	450	270	760	527
100	18.3	280	96	460	282	800	560
110	22.3	290	102	470	294	840	605
120	24.8	300	107	480	305	900	644
130	27.6	310	117	490	312	985	658
140	30.8	320	120	510	331	1020	695
150	34	330	127	520	343	1420	820
160	37.8	340	133	530	350	1610	855
170	41.2	350	138	540	357	1870	888
180	45.7	360	145	550	370	2850	952

Table B.3 10% SS, SIR=4.0

Time, m	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*
0	8	40	480	120	848	403	1052
5	90	45	525	140	884	480	1068
10	130	65	660	155	905	700	1092
15	159	75	707	175	930	815	1100
20	280	83	736	200	950	873	1102
25	332	90	758	234	978	920	1109
30	374	105	808	256	992	1040	1115
35	420	110	820	295	1011	1440	1120

Table B.4 10% SS, SIR=4.5

Time, m	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*
0	2	40	110.9	210	955	450	1071
5	7.8	50	163.9	240	982	465	1075
10	13.42	60	293	270	1001	480	1080
15	22.8	80	456	300	1021	600	1091
20	33.7	100	585	330	1037	760	1102
25	48	120	708	360	1048	1200	1131
30	65.8	150	810	390	1057	1440	1142
35	87.8	180	892	420	1064	450	1071

Table B.5 10% SS, SIR=5.5.

Time, m	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*	*Time, m*	*NTU*
0	4.2	110	131.1	235	770	360	1059
10	5.4	120	153	240	790	370	1070
20	8.67	130	193	250	831	385	1080
30	15	140	280	260	871	400	1094
40	23	160	390	270	897	410	1101
50	31	180	490	280	924	430	1115
60	38	195	562	300	978	470	1137
70	46	200	597	320	1008	510	1153
80	66	215	665	330	1021	960	1177
90	81.4	220	691	340	1034		
100	103.2	230	741	350	1047		

APPENDIX C

RHEOLOGICAL MEASUREMENTS

Table C.1 7.5% SS + 0.15% PB, SIR= 4.0 (6 RPM Readings)

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
0	1	65	1	140	1	171	13
5	1	80	1	144	1	173	14
10	1	95	1	145	1	175	15
15	1	105	1	147	1	179	15
20	1	117	1	150	2	183	14
25	1	120	1	152	3	185	19
30	1	127	1	154	4	190	16
35	1	130	1	156	7	195	17
40	1	132	1	159	10		
45	1	134	1	165	10		
50	1	136	1	168	11		

Table C.2 7.5% SS + 0.15% PB, SIR= 4.0 (100 RPM Readings).

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
0	2	35	2	70	2	120	6
5	2	40	2	75	2	130	8
10	2	45	2	80	2	140	30
15	2	50	2	85	2	145	42
20	2	55	2	90	3	150	48
25	2	60	2	100	3	152	46
30	2	65	2	110	4	153	45

Table C.3 7.5% SS + 0.15% PB, SIR= 4.0 (200 RPM Readings).

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
0	4	65	6	138	47	168	83
5	5	80	7	140	50	171	85
10	5	95	7	144	54	173	85
15	6	105	8	145	57	175	86
20	6	117	10	147	59	179	88
25	7	120	11	150	64	183	89
30	7	127	15	152	69	185	90
35	7	130	19	154	71	190	87
40	7	132	23	156	74	195	88
45	7	134	28	159	76		
50	7	136	36	165	83		

Table C.4 7.5% SS + 0.15% PB, SIR= 4.0 (300 RPM Readings).

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
5	6	60	9	120	35	148	71
10	7	70	9	126	58	153	73
20	8	80	10	130	64	158	77
30	8	90	11	131	67	163	77
40	8	100	14	135	73		
50	9	110	18	143	72		

Table C.5 7.5% SS + 0.15% PA, SIR= 4.0 (6 RPM Readings).

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
5	1	65	1	125	2	176	12
10	1	70	1	130	2	178	12
15	1	75	1	135	3	180	12
20	1	80	1	140	4	182	12
25	1	85	1	145	4	184	12
30	1	90	1	150	4	186	27
35	1	95	1	155	4	188	19
40	1	100	1	160	4	190	16
45	1	105	1	165	5	192	14
50	1	110	1	170	10	194	11
55	1	115	1	172	11	196	10
60	1	120	1	174	11		

Table C.6 7.5% SS + 0.15% PA, SIR= 4.0 (100 RPM Readings).

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
0	3	40	3	80	3.5	120	6
5	3	45	3	85	4	125	8.5
10	3	50	3	90	4	130	48
15	3	55	3	95	4	132	21
20	3	60	3	100	4	134	21
25	3	65	3.5	105	5	136	19
30	3	70	3.5	110	5		
35	3	75	3.5	115	5		

Table C.7 7.5% SS + 0.15% PA, SIR= 4.0 (200 RPM Readings).

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
0	5	40	5.5	80	6.5	120	35
5	5	45	6	85	6.5	122	40
10	5	50	6	90	7	124	35
15	5	55	6	95	7.5	126	32
20	5	60	6	100	7.5	128	33
25	5	65	6	105	9		
30	5.5	70	6.5	110	9.5		
35	5.5	75	6.5	115	11		

Table C.8 7.5% SS + 0.15% PA, SIR= 4.0 (300 RPM Readings).

Time, m	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*	*Time, m*	*Readings*
5	7	45	8	85	9.5	116	21
10	7.5	50	8	90	10	118	44
15	7.5	55	8.5	95	10	120	80
20	7.5	60	8.5	100	11	122	80
25	7.5	65	8.5	105	11	124	74
30	7.5	70	8.5	110	11.5	126	68
35	8	75	9	112	14	116	21
40	8	80	9.5	114	19	118	44