

POLYACRYLAMIDE/ POLYETHYLENEIMINE-BOTTOM FLY ASH
POLYMER GEL FOR WATER SHUT-OFF IN OIL WELLS

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POLYMER GEL FOR WATER SHUT-OFF IN OIL WELLS

by

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LIST OF ABBREVIATIONS

PAM	Polyacrylamide
PEI	Polyethyleneimine
FA	Fly Ash
WSO	Water Shut-Off
CFA	Coal Fly Ash
PNIPAM	Poly (<i>N</i> -isopropylacrylamide)

POLIAKRILAMID/POLIETILENIMINA-ABU TERBANG DASAR GEL POLIMER SEBAGAI AGEN PENGHADANG AIR DALAM WILAH MINYAK

ABSTRAK

Polyacrylamide (PAM) (1.7-3.6pb%) sebagai polimer dan polietileneimina (PEI)(0.18-0.62pb%) sebagai penyambung silang digunakan dalam kajian ini. Siasatan dijalankan termasuk prestasi gel polimer tulen berdasarkan formulasi yang berbeza, penambahbaikan prestasi gel polimer menggunakan zarah mikro pepejal bukan organik (0.3-0.92pb%) iaitu abu terbang dasar dan abu terbang pendidih di dalam gel polimer tulen yang dipilih, serta kajian prestasi gel polimer yang dioptimumkan pada suhu tinggi melebihi 90 °C. Dalam kajian ini, prestasi gel polimer biasanya diukur dari segi masa gelasi. Untuk kajian gel polimer tulen, kajian ini melibatkan manipulasi kepekatan PAM dan kepekatan PEI di mana kedua-dua eksperimen dijalankan pada 90 °C. Telah didapati bahawa, dengan peningkatan kepekatan PAM atau PEI, masa gelasi cenderung menurun. Gel polimer 2.8pb% PAM dengan 0.37pb% PEI dipilih untuk pengoptimuman selanjutnya. Berdasarkan dua abu terbang berbeza yang digunakan pada 90°C, abu terbang dasar mempamerkan gel polimer yang lebih baik dari segi masa gelasi. Masa gelasi optimum diperolehi apabila 0.3pb% abu terbang digunakan ke dalam matriks gel polimer tulen. Ketiga, untuk kajian gel polimer optimum pada suhu tinggi iaitu 105 °C dan 120 °C, didapati bahawa masa gelasi cenderung berkurangan dengan peningkatan suhu. Walau bagaimanapun, pada 120 °C, gel polimer cenderung mengalami pengurangan isipadu yang menunjukkan gel polimer yang dibentuk adalah terhad untuk berfungsi di bawah 120 °C. Selain itu, pengesahan mengenai kebolehtelapan gel yang optimum terhadap minyak dan air garam juga telah dijalankan untuk memastikan kejayaan ejen penghadang air itu sendiri. Keputusan menunjukkan bahawa tiada penembusan sama ada minyak atau air garam ke dalam matriks gel polimer dan ini menunjukkan ejen penutup air yang dikaji berjaya.

POLYACRYLAMIDE/ POLYETHYLENEIMINE-BOTTOM FLY ASH POLYMER GEL FOR WATER SHUT-OFF IN OIL WELLS

ABSTRACT

Polyacrylamide (PAM) (1.7-3.6wt%) as the polymer and polyethyleneimine (PEI)(0.18-0.62wt%) as the cross-linker were applied in this study. Investigation conducted includes on the performance of the pure polymer gel based on different formulations, performance optimization by incorporation of inorganic solid micro particles (0.3-0.92wt%) which were the Bottom Fly Ash and the Boiler Fly Ash into the selected pure polymer gel matrix, and the behaviour of the optimized polymer gel at elevated temperatures beyond 90°C. In this study, the performance of polymer gel were mainly measured in terms of the gelation time. For the pure polymer gel formulation, the study involves the manipulation of PAM concentration and PEI concentration where both experiment was conducted at 90°C. It was found that, with the increase of either PAM or PEI concentration, the gelation time of polymer gel tend to decrease. 2.8wt% PAM with 0.37wt% PEI polymer gel was chosen for further optimization. Based on the two different fly ash incorporated at 90°C, Bottom Fly Ash exhibits a better performing polymer gel in terms of the gelation time. The optimum gelation time were obtained when 0.3wt% were incorporated into the pure polymer gel matrix. Thirdly, for the optimum polymer gel study at elevated temperatures which were 105°C and 120°C, it was found that the gelation time tend to decrease with the increase of temperature. However, at 120°C, the polymer gel tend experience volume reduction which shows this respective formulated polymer gel are limited to function below 120°C. Besides that, verification on the optimized gel permeability towards oil and brine water also were conducted to ensure the success of the water shut-off agent itself. Results shows that no penetration of either oil or brine water into the polymer matrix and this represents the water shut-off agent formulated is a success.

CHAPTER ONE: INTRODUCTION

1.1 Water Production

In the production of oil from the well bores, the common problem that being faced is the excessive water production which is the high water to oil ratio. This situation undesirably lead to productivity decline and causing an increment of investment in the operating costs. Thus, this situation resulted in shut-in of wells since production is no longer economical due to costs of lifting, separation, handling including disposal of large amounts of produced water. The high water production may also lead to environmental concerns, high incline corrosion rates and scale formation which as mentioned will tend to decrease the economic life of a well (Simjou et al., 2007). There are various reasons behind the unwanted water production in the oil wells and the common one would because of water intrusion. There are high possibilities for other reasons to contribute along to this matter. Each challenge requires a different approach to obtain the optimum solution. It is highly necessary to identify the challenge faced properly before coming up with a solution in order to achieve a high success rate when treating water-production problems.

1.2 Water Shut Off

There are ways of solution for this challenging case and one of them would be the water shut-off (WSO) method. Water shut-off methods can be classified in two different types which are mechanical methods and chemical methods respectively.

The mechanical methods described as a method of providing a seal in the near-wellbore openings by applying packers. Drilling horizontal, multi-lateral wells, placing a linear to block water production and down hole separation equipment such as hydro cyclones also examples of mechanical method in water shut-off which are often uneconomical and expensive (Simjou et al., 2007).

For the chemical method of water shut-off (WSO), this method already being extensively applied since the last decade. Chemical water shut-off demonstrates better plugging which is one of them is in term of able to penetrate into matrix or small fissures where the mechanical packers cannot reach to shut-off the excess water in some cases (Sun and Bai, 2017). Generally, chemical method widely demonstrated by the utilization of gelling systems where usually consisting of a water soluble polymer and a crosslinking agent (Simjoo et al., 2009, Augustine et al., 2004). The polymer gel system can be divided into various type of category but the most of that which being used are based on water soluble polymer such as polyacrylamides along with one or more cross-linking agent which after a given time and temperature turn from low viscosity liquid into strong gel with high viscosity. Additives maybe added to modify the property of the respective gel.

Ideally, polymer gels are profitably used to improved oil recovery. The main aim of the polymer gel system is to achieve injection into the oil wells with decreasing relative permeability of water without any change in the oil permeability curve, although there might be some effect from water saturation on oil permeability (Zaitoun et al., 2007, Simjou et al., 2007). This theory is more related to the water control strategy. The difference between water control and water shut-off (WSO) method is that in water control, it focuses in lowering water relative permeability while maintaining the oil permeability unaffected through disproportionate permeability (Zaitoun and Kohler, 1988) while in water shut-off, it is more likely to prevent permanently the participation of highly water content area into the production bore.

Appropriate selection and design of the gel formulations such as type of polymer, type of cross-linker and their concentrations should be based on the operational and reservoir requirements (Mattey et al., 2017). The properties of an ideal chemical system for the water shut-off includes tolerance to high salinity and hardness, compatibility with any mixed water,

thermal stability, low viscosity, ability to penetrate the deep formation, insensitivity to shear rate and pumping capability (Lei et al., 2010) .

It is very significant to make sure that gelation time, stability and gel strength at the best performance to avoid early gelation and at the same time to assure the appropriate placement in the reservoir (Mattey et al., 2017, Whittington et al., 1994). In the water shut-off process, it is also very important to identify the source of water inflow for choosing the correct technique. However, the problem solving would be even more complicated if multiple mechanism of water invasion are simultaneously active in the well.

1.3 Problem Statement

The successfulness and favourable result of the water shut-off method chosen are really dependent on the situation of excess-water-production problem. Thus, it is very crucial to carry out effective identification of challenge faced before attempting a water shut-off method. For this study, the water shut-off method will be fully rely on the chemical method which utilizes the polymer gel along with respective cross-linker. For the polymer gel system, there are various element that contributes to its performance. Temperature plays an important role in demonstrating a well performing gel system. One of the concern when designing the polymer gel would be its resistance and reliability towards the thermal energy which is performs at its best when operating at the given temperature. The strength of the gel and the gelation time tend to change with respect to change in temperature and it may be weak because of the degradation of the polymer gel due to overheat experienced by the polymer itself. So, it is important to recognize the desired properties needed in order for the gel system to able withstand the temperature where it is applied especially at an elevated temperature which may reach 120 °C.

In addition, recognition of contribution of each component in the polymer gel which are usually the polymer and its cross-linker towards its strength and gelation time is very

significant. The selected polymer for this investigation would be the polyacrylamide. Polyacrylamide (PAM) being preferred for its low cost and high selectivity. Polyethyleneimine (PEI) is the cross-linker utilized and this is because of its beneficial characteristics which is less toxic and possesses better solubility in water. Besides their chemical properties, their contribution are mainly being controlled by manipulating their concentration. Thus, effect of each polymer and cross-linker on the gel properties should be identified properly before injecting the gel to the desired reservoir.

1.4 Research Objective

- I. To investigate the gelation time of the pure polymer gel based on different formulation of polyacrylamide (PAM) and its cross-linker, polyethyleneimine (PEI).
- II. To identify the performance of the polymer gel in terms of gelation time based on incorporation of different type inorganic solid micro particles into the matrix of selected pure polymer gel formulation determined earlier.
- III. To evaluate the performance in terms of gelation time of the selected polymer gel incorporated with performing inorganic solid micro-particles at elevated temperatures.
- IV. To verify the performance in terms of permeability of the optimum PAM/PEI-Fly Ash polymer gel obtained with oil and water permeability test.

1.5 Scope Of Study

This study mainly focus on the effect of elevated temperature and concentration of each polymer which the polyacrylamide (PAM) and its cross-linker, the polyethyleneimine (PEI) towards the gelation time of the gel polymer. Generally, to obtain an effective process of injection and hardening of the polymer gel, it must be ensured that the gelation time and the capability of the gel polymer to withstand the reservoir conditions are at optimum performance. For example, if the gel polymer are in a viscous condition during the injection process, thus it will require more power to pump than a low viscosity one.

To optimize the performance of the polymer gel, introducing the utilization of inorganic micro or nanoparticles into the polymer matrix can enhance the thermal stability by functioning as a superior insulator and mass transport barrier to the volatile materials generated during decomposition. Furthermore, the coefficient of thermal expansion (CTE), as the criterion for the dimensional stability of materials do decrease with the incorporation of micro or nano-sized inorganic particles (Vasakh, 2016). In this study, it has been proposed that the inorganic solid particle which been investigated is the fly ash. There are two types of fly ash investigated in this study which were Bottom Fly Ash and Boiler Fly Ash. Both are wastes that been collected from the palm oil processing.

Due to demand of the water shut-off application using the gelling system at higher temperature which is about at 120°C, thus this study will be investigated on the utilization of PAM/PEI polymer incorporated with the solid micro-particle which is the fly ash to achieve best performance of the polymer gel at an elevated temperature of 120 °C.

CHAPTER TWO: LITERATURE REVIEW

1.1 Water Production

Nowadays, oil companies facing the challenge with the production of an average of three barrels of water for each barrel of oil from their depleting reservoirs. From the world statistics, more than \$40 billion every year is spent on the handling and management of the unwanted water (El-Karsani et al., 2015). The involvement of water affects every stage of the oilfield life which starts with the exploration stage, through the development, production and lastly to abandonment. At the gas and oil wells, the water tend to be produced either during initial completion or after they have been producing some time.

During the extraction of oil from the reservoir, water from the underlying aquifer are tend to be mixed and produced along with the oil. Actually, the water production contributes in removal of oil from the natural water drive reservoirs or during the waterfloods in progress which shows a satisfying benefit to a good production rates and enhanced recovery of hydrocarbons (Sparlin and Hagen, 1984). As in Figure 2.1, the cycle of water flowing starts through the reservoir, then into production tubing, later to surface processing facilities and lastly extracted through water treatment for disposal or injected for maintaining reservoir pressure which can be referred to Figure 1 (Bailey et al., 2000)

The water production can be classified into three distinctive difference which would be sweep, 'good' or 'bad water'. Sweep water origins either from an injection well or an active aquifer. It favours the sweeping of oil from the reservoir. The handling of this water is the crucial step of the reservoir management which is possible to be a determining factor in the well productivity and the ultimate reserves (Kuchuk et al., 1999)

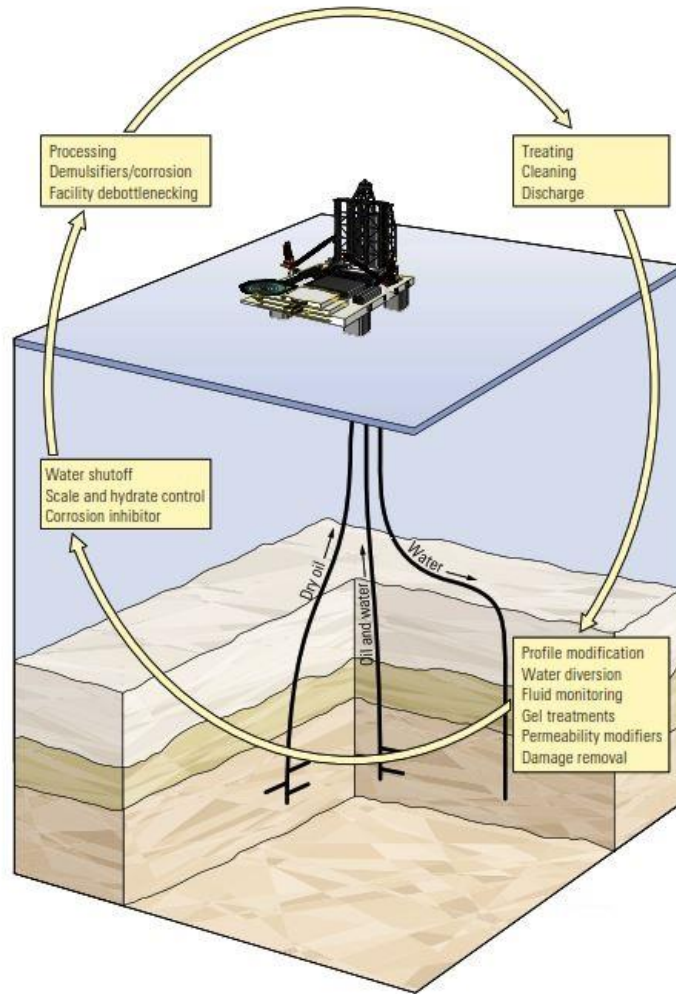


Figure 2.1 Water Cycle in Oil Well (Bailey et al., 2000)

‘Good’ or acceptable water are produced into the wellbore at the rate of under the water/oil ratio. As oil are extracted from the producing well, water begins to push through the formation into the well and this leads to production of oil together with water (Dawson and Van Le, 1995). In order to minimize the water handling cost, this water should be removed at the early stage such as by downhole separator. Water management helps in maximizing the production. On the contrary, ‘bad’ or excess water is opposite to the ‘good’ water which means the water produced is above the water/oil ratio. This can be represented with the situation such as insufficient oil to pay for the cost of handling the water (Bailey et al., 2000).

The excess water production tend to influent the produced fluid head which by increasing it and later causes an extra backpressure on the formation. This situation will eventually result in reduction in well's natural flow capability. Along with decrease of oil production, it also increases operating cost of water management (Sparlin and Hagen, 1984). The source of the water production may be a channel behind the casing which is the consequence of poor cementation, leakages of casing, coning, and water breakthrough (Mattey et al., 2017). Water produced from the mature oil fields may contain mercury, arsenic including other salts and causes impact on the environment if not disposed properly (Hibbeler and Rae, 2005). Besides environmental problem, the excess water also do causes corrosion of wellbore, scale, and sand production problems (Sun and Bai, 2017). Thus, optimum technique are required to reduce or total prevention to block the water source.

2.2 Water Shut-Off

There are various approach that can be applied in order to mitigate the excess water production challenge. Water shut-off are among the most preferable solution in order to reduce or totally prevent the production of water along with the oil production. Referring to Figure 2.2, as most wells matures, the water/oil ratio increases with production (A) and this is because the increasing amount of water by time. Thus, this resulted in unprofitable situation where the cost of handling the water approaches the value of oil being produced and the water/oil ratio (B). The initiative of water control or water shut-off methodology reduces the well's water production (C) and allows continuation of economic oil production. The solution by water control or water shut-off eventually result in profitable and increased economic recovery in the well (D) (Bailey et al., 2000).

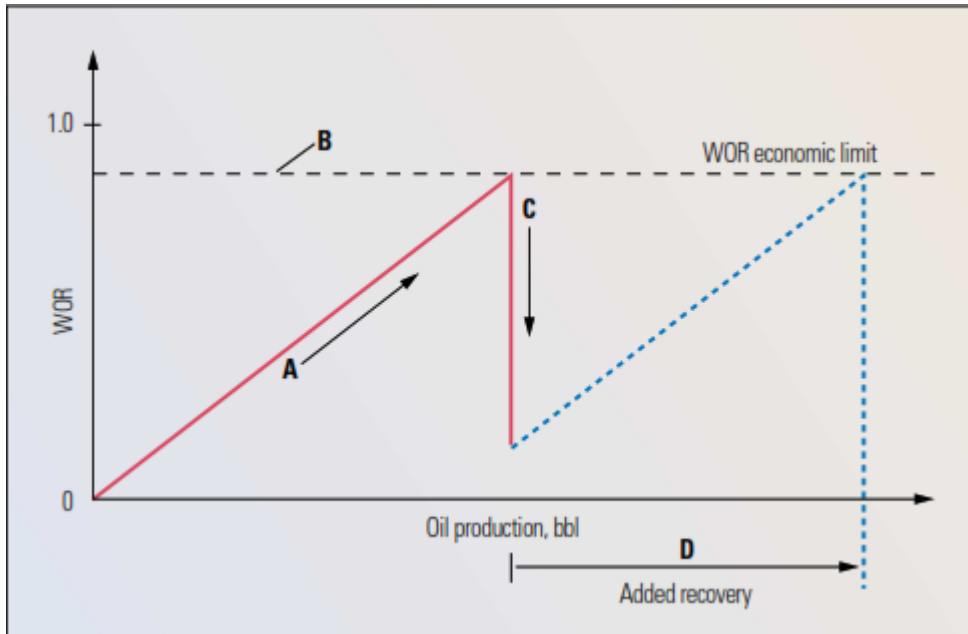


Figure 2.2 : Relation between water/oil ratio, recovery and oil production (Bailey et al., 2000)

Generally, the water shut-off treatment are classified into mechanical method and chemical method. The application of either method do highly depends on the challenge faced. Thus, detailed identification of excess water production problems are really significant which need to be taken into account.

2.2.1 Mechanical Method

Mechanical method is among the simplest alternative that can be applied and it is achieved by using packers to block the water excess zone. As been mentioned, packers can be applied for the water blocking. They can be classified into expandable and non-expandable packers. The expandable packers possesses inflatable elements which are designed in purpose to expand in wellbore and provide isolation. Generally, most of the expandable packers are retrievable and there are also times they are combined with cement plug to provide a better and permanent sealing in open holes. On the other hand, non-expandable packers are also practiced for the water shut-off. Commonly, cement packer as the non-expandable packer are applied in vertical wells. It is not effectively functioned in horizontal wells since it happens to cause

uncompleted sealing in annulus due to the gravity effect. Furthermore, there are various types of cement applicable for the water shut-off which are foamed cement, expanding cement, highly-thixotropic cement, and fibre-reinforced neutral-density cement. All of those varieties possess their own pros and cons. For example, foamed cement features higher mud displacement in a small annulus than conventional cement and the structure of foamed cement favours prevention of development of gas or water channels (Sun and Bai, 2017).

2.2.2 Chemical Method

Water shut-off by chemical method is more practical and reduces the cost of operation. Among the chemical methods available, water shut-off by the application of polymer gels are more preferable to be used. Contrary to cement plugs, chemicals including polymer gels can be penetrated deep into the formation. The mechanism of the polymer gel is such that they form a precipitate that functions as a physical barrier that prevents the flow of water for a long period of time (Nasr-El-Din and Taylor, 2005). Polymer gels have the possibilities of lowering water relative permeability while maintaining the oil permeability unaffected through disproportionate permeability (Zaitoun and Kohler, 1988). In addition, the polymer gel is highly capable of complete water blocking from the highly water zone (Seright et al., 2001). There are some factors that are responsible in determining the success of a chemical system which includes candidate selection, identification of source water, proper choice of chemical system and placement of the chemicals into the target zone (Nasr-El-Din and Taylor, 2005).

Respective to the chemical method, they can be divided into several main categories. First is the polymer gel. For the gelling polymer, water soluble polymers are applied together with a suitable cross-linker to reduce the water production in the field (Jousset et al., 1990, Sydansk and Southwell, 2000). Secondly is phenol-formaldehyde resins. This method has been used for high temperature application (Nagra et al., 1986, Seright and Martin, 1993).

However, utilization of these chemicals are not very environmentally friendly (Nasr-El-Din and Taylor, 2005). Thirdly is chemical precipitation. This method comprises of mechanism as such some inorganic compounds of transition metals possible to be directly or indirectly transformed into gel-like precipitate by in-situ hydrolysis which later immobilized by in-situ flocculation or spontaneous ageing (Lakatos et al., 1996). Lastly is inorganic silica gels. The silica gels can be classified as colloidal silica gels and sodium silicate gels. The mechanism of each silica gels are such particles form a 3-D network in colloidal silica while for sodium silicate, silica particles form in solution and later will tend to create a 3-D network. However, in colloidal silica, the particles actually reduces injection activity into low permeability zones and this requires higher silica concentration and thus more expensive while the drawback of the sodium silicate silica gel is that they are a weaker gel (Iler et al., 1979 , Jurinak and Summers, 1991).

2.3 Polymer Gel

Nowadays, the polymer gel treatment is among the most useful chemical alternative to reduce the unwanted water production. The reason of why gelling system which is the polymer gels being preferable to be utilized is because of their low cost, ease of pumping and ability to penetrate deeper into the reservoir (Mattey et al., 2017). In addition, plugging due to gel polymers are possible to be removed unlike the physical cement plugging from the mechanical method. Plugging of physical cement may leads to permanent plug in the porous media and thus the residual oil cannot be produced from the treated region by cementing method after reduction of excess water production (Simjoo et al., 2009).

The polymer gel treatment can applied to contribute as an improved oil recovery (IOR) method in the injection and production wells. In the injection well, the polymer gel or the gelant is placed into a high permeability fractures and this namely a profile modification control or

conformance control where the injected water being diverted to un-swept zones which helps in improving the distribution of injected fluids into a heterogeneous reservoir. Meanwhile, the polymer gel works in the production wells as such the gelant being injected into the fractures or high permeability zones that causes massive production of water which eventually reduce the oil production (Moradi-Araghi, 2000, Perez et al., 2001). Polymer gel consists of a water soluble polymer and a crosslinking agent and forms gelant solution when they dissolve in water. After some time, the gelant tend to transform into a semisolid mass and able to function as flow diverting or blocking agent (Sydansk, 1988, Vossoughi, 2000). Figure 2.3 below represents the illustration of the polymer gel placing at the desired area as the water shut-off agent.

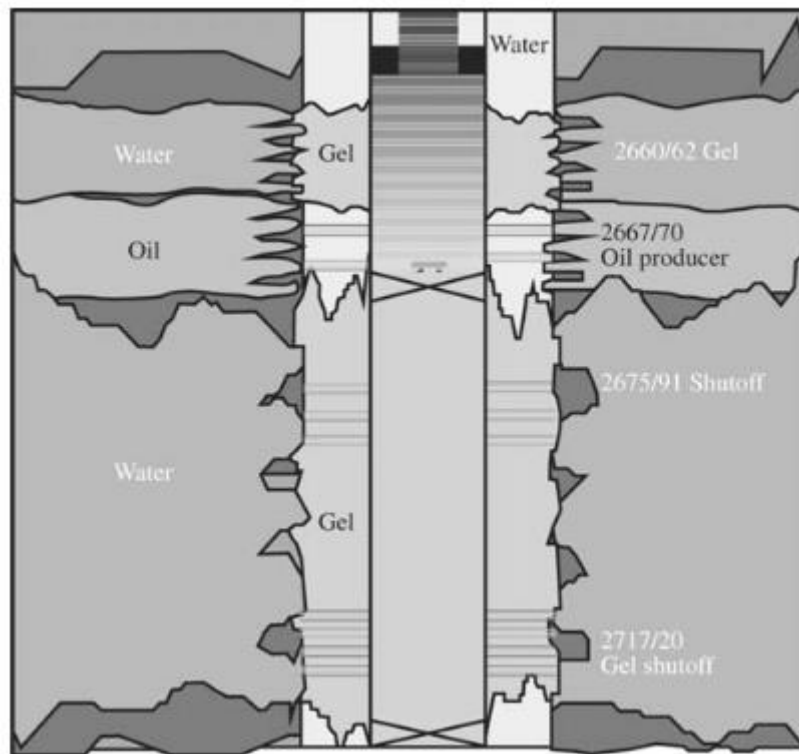


Figure 2.3 : Illustration of water blocking using polymer gel (Perez et al., 2001)

Generally, polymers in the industry are categorised into two main classes which are synthetic polymer and biopolymer. Synthetic polymers are usually mixed with their suitable cross-linkers to be applied in a high temperature and acidity. The gels that origin from this group are relatively low cost since the major constituent in this system is the water. Examples of synthetic polymer includes polyacrylamide (PAM). For biopolymers, they can be cross-linked as well. Biopolymers includes xanthan, polysaccharide and guar derivatives. They are insensitive toward divalent ions and additionally they have a high thermal resistance when been compared to the synthetic polymers. However, they are known to be sensitive towards microbial attacks, expensive and are found to be having difficulty in controlling the water production (Kabir, 2001, Sengupta et al., 2012, Sydansk, 1988)

Cross-linkers enables the polymer chains to be joined together and forming three-dimensional structure of the gel when they are added together with the polymer. This makes the gel to possesses more power and better rheological property (Simjou et al., 2007). The cross-linkers are commonly divided into two categories which are metallic and organic cross-linkers. Example of metal cross-linkers includes boron, titanium, aluminium, chromium (III) and chromium (VI) while polyethyleneimine (PEI), phenyl acetate, phenol, formaldehyde and hydroquinone are example of organic cross-linkers (Kabir, 2001, Al-Muntasheri et al., 2007).

Cross-link such as chromium (III) and chromium (VI) have been widely used in this respective industry. Nevertheless, there are some drawbacks especially referring to the application of chromium (VI). Chromium (VI) are not really preferred due to its carcinogenic and toxic properties besides tend to have difficulty in controlling the gelling time (Kabir, 2001). The application of aluminium cross-linker is recommended more when it comes to its naturalness but it is also less preferable due to its less controllability on the cross-link itself.

The organic cross-linkers offers cross-links in application that runs at an elevated temperature. The cross-link mechanism are such links a covalent bond with the organic polymer and this covalent bonding is the major contributor to the gel sustainability at elevated temperatures (Moradi-Araghi, 2000).

2.4 Polyacrylamide (PAM) / Polyethyleneimine (PEI)

High molecular weight of water soluble polymers such as polyacrylamide (PAM) are enormously applied as thickening agents in the oilfield. They are able to be injected into the near-wellbore zone of a reservoir or to be applied in well treatments or even deeper into the formation (Zaitoun and Kohler, 1988). As been stated, the polymer that is most widely utilized in this application are polyacrylamide (PAM) where they possesses a certain percentage which is commonly less than 30 % of acrylate functions. PAM comes in either as powders or emulsions and they are also relatively cheap. Moreover, they possesses high viscosifying power especially in soft water with additional giving high values of permeability reduction towards brine (Zaltoun et al., 1991) .PAM polymer gel systems are also well known for its contribution in most of the success treatment in near wellbore matrix and fractures at low to moderately high temperature reservoirs (Kabir, 2001). Table 2.1 shows the comparison between different polymers that possible to be applied in this water shut off method with their advantages and disadvantages respectively.

Table 2.1 Comparison between different polymers (Bedaiwi et al., 2009)

Types	Advantages	Disadvantages
Polyacrylamide (PAM)	<ul style="list-style-type: none"> • High injectivity performance • High yield in normal water 	<ul style="list-style-type: none"> • Shear sensitivity • Sensitive towards O₂.
Biopolysaccharides (Xanthan)	<ul style="list-style-type: none"> • High yield in salt water • Shear stable performance • Good thermal stability 	<ul style="list-style-type: none"> • Difficulties in injection • Sensitive towards bacteria • Sensitive towards O₂. • Expensive
Hydroxyethyl cellulose	<ul style="list-style-type: none"> • Resistance to salt • Good solubility 	<ul style="list-style-type: none"> • Low temperature resistance • Lack of structure viscosity. • Sensitive towards pH.

Although biopolymers such as xanthan or hydroxyethyl cellulose demonstrates good characteristics such as good thermal resistance and insensitive towards divalent ions, they are not really preferable due to having difficulty in controlling the water production besides being sensitive towards microbial attacks and expensive (Kabir, 2001, Sengupta et al., 2012, Sydansk, 1988). Thus, synthetic polymers which are the PAM are chosen for this study since it is capable to be applied in high temperatures and acidity when being applied together with suitable cross-linker. Cross-linking of the polyacrylamide solution gives better physical properties such as in terms of its viscosity and the gel strength (Kabir, 2001). Figure 2.4 below represents the molecular structure of the polyacrylamide.

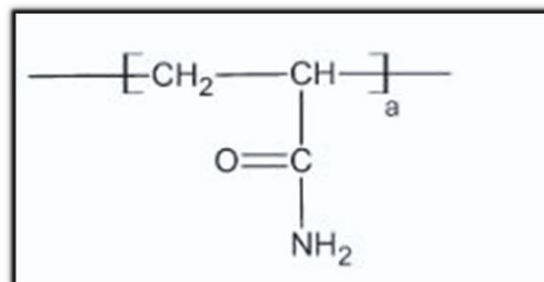


Figure 2.4 : Molecular structure of Polyacrylamide(Al-Muntasheri et al., 2006)

Previous studies have shown that PAM can be utilized with being cross-linked by chromium(III) for water shut-off systems (Hutchins and Parris ,1998 , Sydansk, 1993, Fulleylove et al., 1996). The reaction of cross-linking for this respective mechanism involves the complexation of Cr(III) oligomers with the carboxylate groups on the polymer chains. Due to the chemical bond between Cr(III) and the pendant carboxylate groups, it is possible for the formation of insoluble chromium species at high pH levels. Furthermore, other challenges such as thermal instability, fluctuating gelation times, and gel instability are also related to this respective mechanism (Bartosek et al.,1994, Sydansk, 1995)

Besides, there are also been introduced utilization of organic cross-linkers in obtaining gels that are stable at elevated temperature (121°C) which are cross-linking the polyacrylamide with the organic cross-linkers, phenol/formaldehyde. Polymer gels with organic cross-linkers are found to be thermally stable and provides longer gelation time at elevated temperatures in comparison with utilization of inorganic cross-linkers. It has been reported that the system of polyacrylamide-phenol/formaldehyde has been implemented for 13.3 years approximately (Moradi-Araghi, 2000, Moradi-Araghi, 1993). Nevertheless, the toxicity caused by the cross-linkers of the respective system has restricted its broad use in the field application.

Stable polymer gels are required to be implemented at an elevated temperature system. As been stated, applying organic cross-linkers contributes in achieving thermally stable polymer gel and this is due to the covalent bonding that holds the polymer and the cross-linkers together. Polyethyleneimine (PEI), an organic cross-linker which is less toxic and possesses better solubility in water being an alternative to the phenol/formaldehyde system was found to be capable in forming stable polymer gels with polyacrylamide-based copolymers. Report shows that PEI as the cross-linker with the copolymer polyacrylamide tert-butyl acrylate (PAtBA) have produced a stable gel at high temperatures (Morgan et al., 1998). Figure 2.5 below shows the molecular structure for the polyethyleneimine.



Figure 2.5 Molecular structure of PEI (Jayakumar and Lane, 2013)

Report shows that PEI are capable in forming aqueous gels with simple PAM at room temperature (Allison and Purkapple, 1988). From the success findings, this work will focus on the research on formulating a stable polymer gel at elevated temperature based on utilization of the polymer PAM and PEI as the cross-linker with the incorporation of solid inorganic micro-particle, fly ash as the filler. The mechanism of the cross-linking between PAM and PEI involves the nucleophilic substitution where the imine nitrogen in PEI will tend to replace the amide group at the carbonyl carbon of PAM which are demonstrated in Figure 2.6 below. The gelation time and the strength of the gel which conducted using the bottle test method were mainly based on the Sydnask code. The description of the Sydnask code are as in Table 2.2 below.

Table 2.2 Gel strength code based on Sydnask (Sydnask, 1993)

Gel strength code	Gel description
A	No detectable gel formed: The gel appears to have the same viscosity as the original polymer solution
B	Highly flowing gel: The gel appears to be only slightly more viscous than the initial polymer solution
C	Flowing gel: Most of the gel flows to the bottle cap by gravity upon inversion
D	Moderately flowing gel: Only a small portion (5-10%) of the gel does not flow to the bottle by gravity upon inversion (usually characterized as a tonguing gel)
E	Barely flowing gel: The gel can barely flow to the bottle cap and/or a significant portion (>15%) of the gel does not flow by gravity upon inversion
F	Highly deformable non flowing gel: The gel does not flow to the bottle cap by gravity upon inversion
G	Moderately deformable non flowing gel: The gel deforms about half way down the bottle by gravity upon inversion.
H	Slightly deformable non flowing gel: Only the gel surface slightly deforms by gravity upon inversion.
I	Rigid gel: There is no gel surface deformation by gravity upon inversion

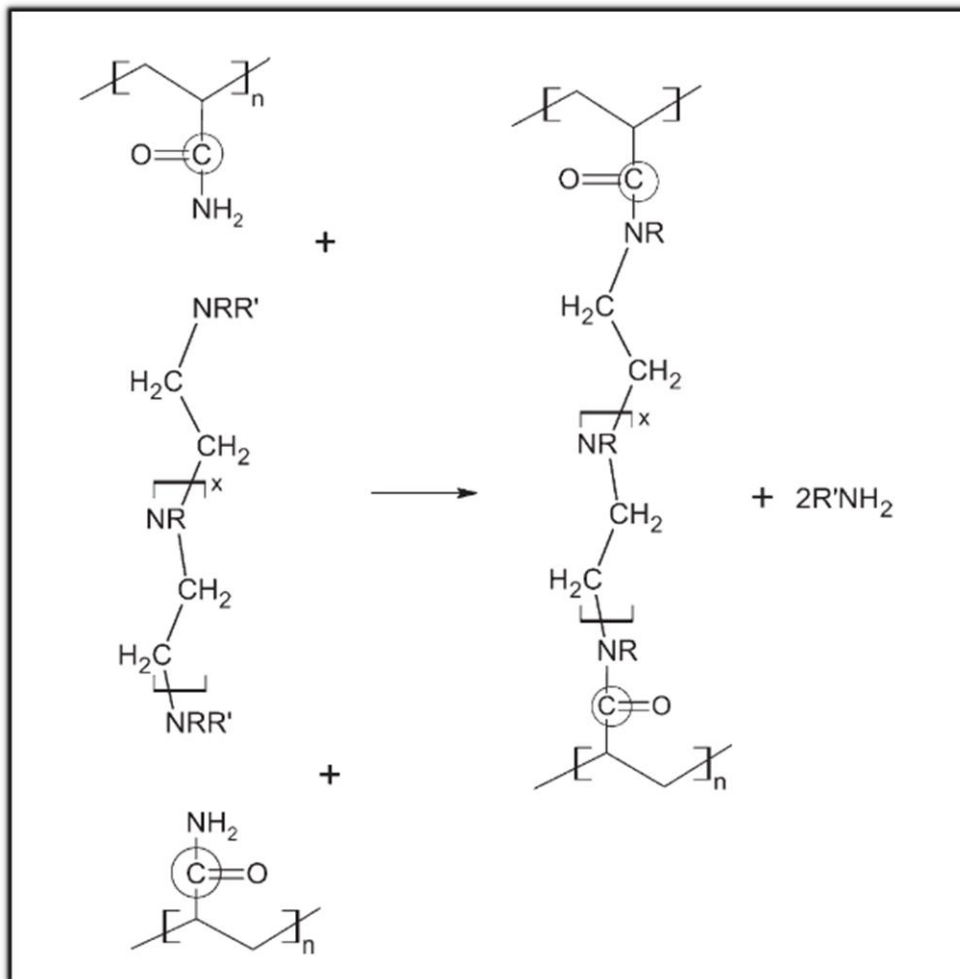


Figure 2.6 Transamidation of Amide group (Reddy et al., 2003)

2.5 Solid Inorganic Particle

Recently, outstanding features have been demonstrated by the polymer gel with incorporation of solid particle into the polymer gel matrix (Zhang et al., 2009). The solid which acts as the fillers in the matrix of the polymer gel tend to improve and enhance the mechanical properties and the swelling ability of the polymer gel itself (Xia et al., 2003, Zhou et al., 2003). Report have shown that, for example, poly (*N*-isopropylacrylamide) (PNIPAM) gel which is sensitive towards temperature possesses volume phase transition at 34°C (Hirotzu et al., 1987, Li and Tanaka, 1992). In addition, the mechanical strength of PNIPAM increases with the

concentration of the cross-linker added. However, the increase in concentration of the cross-linker may cause shifting of the volume transition temperature and also tend to face reduction in swelling capability (Lu et al., 2000). Thus, incorporation of inorganic solid particle which was clay into the gel system helped in improving and enhancing the performance and mechanical properties of the gel itself (Starodoubtsev et al., 2002, Lvov et al., 1996).

Report have shown that formulation of polymer gel of PAM/PEI-Coal Fly Ash (CFA) have been done for it to be tested at temperatures from 80°C to 95°C (Adewunmi et al., 2015). The rheological measurement from the study viewed that the performance in terms of strength of PAM/PEI composite gels with the Coal Fly Ash as the filler was significantly rigid and stronger than that of the pure gel of PAM/PEI. This is because, the presence of CFA promotes the interfacial interaction by the well-dispersed CFA contents itself in the PAM/PEI gel matrix.

As been stated, the solid particle that being utilized in this study is the Bottom Fly Ash and Boiler Fly Ash which believed to possess similar characteristics as the Coal Fly Ash. Both Boiler and Bottom Fly Ash are readily available, in abundance amount, cheap and especially tend to contribute in gelation mechanism and strength. The better performing fly ash among the two which were tested are investigated at elevated temperature for the gel performance and strength.

2.6 Effect of Temperature

Most of the compound that were designed for the water production control in the oil wells tend to be unstable especially at increased temperature due to degradation (Dawson and Van Le, 1995). Temperature plays a dominant role in preventing the production of water or to be accurate, the gelation time and strength. The molecular mobility or the formation of new construction increases with the temperature. In addition, the rate of accessibility of the cross-linker to the polymer tend to become longer which results in faster gelation.

To discuss the relation between the temperature and the gel strength, for instance, report shows that hydrolysed polyacrylamide (PHPA) is affected by hydrolysis at higher temperature. Water tends to move out of the gel structure due to the increase of hydrolysis at increased temperature. This causes the gel strength to decrease.

Thus, this study also involved the investigation of the behaviour and performance based on selected optimum formulation of the PAM/PEI-Fly Ash determined at 90°C and at elevated temperatures which are 105°C and 120°C.

CHAPTER THREE: MATERIALS AND METHOD

For this section, it should be concerned that the gelation process to be carried out qualitatively over an extensive range of polymer, cross-linker and the micro-particles, fly ash weight percent for the measurement of the gelation rate including its thermal stability as a function of time. A synthetic polymer, polyacrylamide (PAM) and its organic cross-linker, polyethyleneimine (PEI) will be utilized for the gelant that will be investigated in this study. For each set of experiment, observation of gelation time was based on the Sydnask code as in Table 2.2 (page17) which assigned together with the bottle testing method.

3.1 Materials

Table 3.1 Materials involved in the experiment

Material	Properties	Function
Polyacrylamide, PAM	MW =250000-500000, pH=4, powder form	As the polymer for the gel formulation
Polyethyleneimine, PEI	MW= 70000, pH=12, liquid with 50wt% concentration	As the cross-linker for the gel formulation
Sodium chloride, NaCl	Powder form	Brine water preparation
Bottom Fly Ash	Powder form	Inorganic solid particle
Boiler Fly Ash	Powder form	Inorganic solid particle

The polyacrylamide (PAM) with molecular weight of 250000-500000, pH=4 were received in powder form which later being utilized without further treatment based on weight percent desired. Polyethyleneimine (PEI) with molecular weight of 70000, pH =12 were obtain in solution with 50wt% of concentration. All gelling solutions were prepared using brine water containing 20000 ppm (2wt%) of NaCl as a synthetic seawater for better accuracy of application. Each set of experiment starts with 75ml (75g) of brine water before mixing with PAM,PEI and the fly ash.

3.2 Methodology

3.2.1 Overall Experiment Flowchart

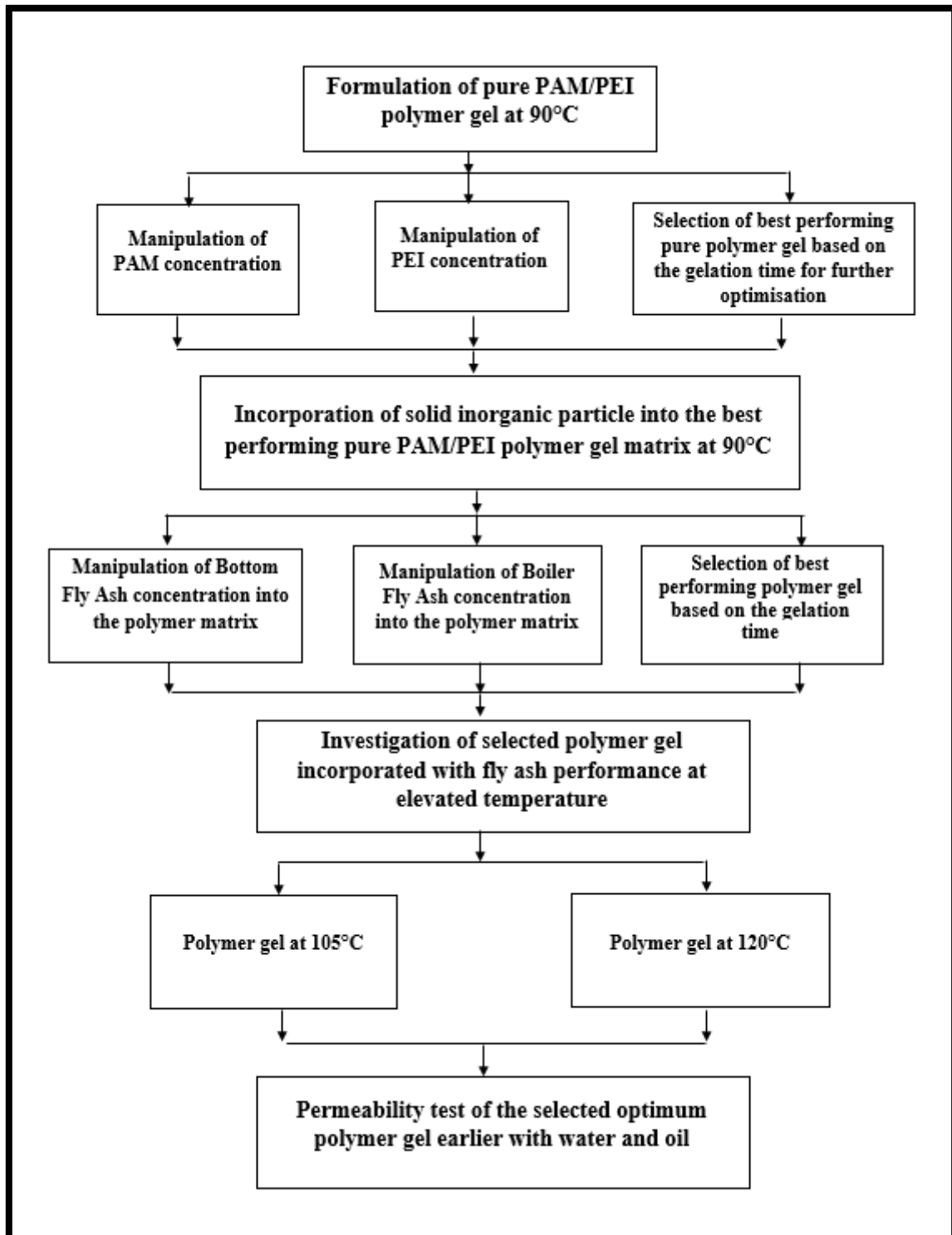


Figure 3.1 Overall Experimental Flowchart

Figure 3.1 above represents the overall view of experiment that being conducted for the research study. The first experiment is on investigating the gelation time based on the pure polymer gel which consists of the polymer polyacrylamide (PAM) and its cross-linker polyethyleneimine (PEI). The study is on different formulation of the pure polymer gel itself where involves different weight percent of each PAM and PEI present in the gel formulation. From this experiment, the performing gel formulation were determined based on desired gelation time obtained at 90°C.

Secondly, the desired formulation obtained in the earlier experiment were applied for further enhancement of the gel with the incorporation of solid micro-particles. This experiment were carried out by investigating the better performing gel with desired gelation time based on two type of fly ash which were Boiler Fly Ash and Bottom Fly Ash that was obtained as a waste from the palm oil company. Better performing gel based on each type of fly ash incorporated into the different formulation were determined at 90°C.

Thirdly, the experiment were pursued to investigate the performance of the selected formulation of polymer gel incorporated with the fly ash determined earlier at elevated temperature which is beyond 90°C. The temperature that investigated were 105°C and 120°C. This experiment is to study the thermal stability of the optimum formulation of polymer gel obtained from previous experiment.

The last step is the permeability test of the polymer gel obtained after the optimum temperature determination. The permeability test was to investigate the behaviour in terms of permeability of the polymer gel itself towards the brine water and the oil. It is desired for the gel to have less permeability towards water and an unaffected permeability for the oil to pass through.

3.2.2 Gelation Time For The Formulation Of Pure PAM/PEI Polymer Gel.

This experiment involves the study of obtaining the formulation of the pure polymer gel that performs at desired gelation time and gel strength based on different formulation proposed which by manipulating the weight percent of PAM and PEI. The calculation of the weight percent of each PAM and PEI in the polymer gel are as follows :

$$\text{PAM (wt\%)} = \frac{b}{a+b+c+d}$$

$$\text{PEI (wt\%)} = \frac{c}{a+b+c+d}$$

where;

a = mass of brine water (75g)

b = mass of PAM powder, g

c = mass of PEI solution, g

d = mass of fly ash incorporated, (0 g for pure gel)

Each set of experiment were started with 75ml (75g) of brine water by pouring it into a beaker. Then, the desired weight percent of each PAM and PEI proposed for the formulation were referred to determine the mass of each PAM and PEI required to be added into the brine water. The mass required for each PAM and PEI were determined by using back calculation of above formula. The mass of PEI obtained from the calculation were converted into volume by using its density value, 1.08 g/ml. Meanwhile, the mass for fly ash for this experiment were kept to 0 g since this experiment studies on pure gel formulation.

Each set of experiment was conducted at two different condition which is under room temperature and the desired temperature 90°C. This is in purpose for observation and comparison of the gel performance at both condition. Table 3.1 below represents the weight percent of each PAM and PEI investigated for the formulation of pure polymer gel at 90°C.