MATHEMATICAL MODELING AND NUMERICAL SIMULATION OF GELATION BEHAVIOR OF POLYMER GEL SYSTEM FOR PERMEABILITY MODIFICATION IN HIGH-TEMPERATURE RESERVOIR

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DECLARATION

I declare that the thesis entitled **"Mathematical Modeling And Numerical Simulation of Gelation Behavior of Polymer Gel System for Permeability Modification in High-Temperature Reservoir",** has been prepared by me under the guidance of **Dr. D. K. Gupta,** Professor of Department of Petroleum Engineering & Earth Sciences, University of Petroleum and Energy Studies, Dehradun, **Dr. S. K. Nanda,** Professor of Department of Petroleum Engineering & Earth Sciences, University of Petroleum and Energy Studies, Dehradun **& Dr. B. P. Kathel,** Ex-ONGCian, Dehradun. No parts of this thesis has formed the basis for the award of any degree or fellowship previously.

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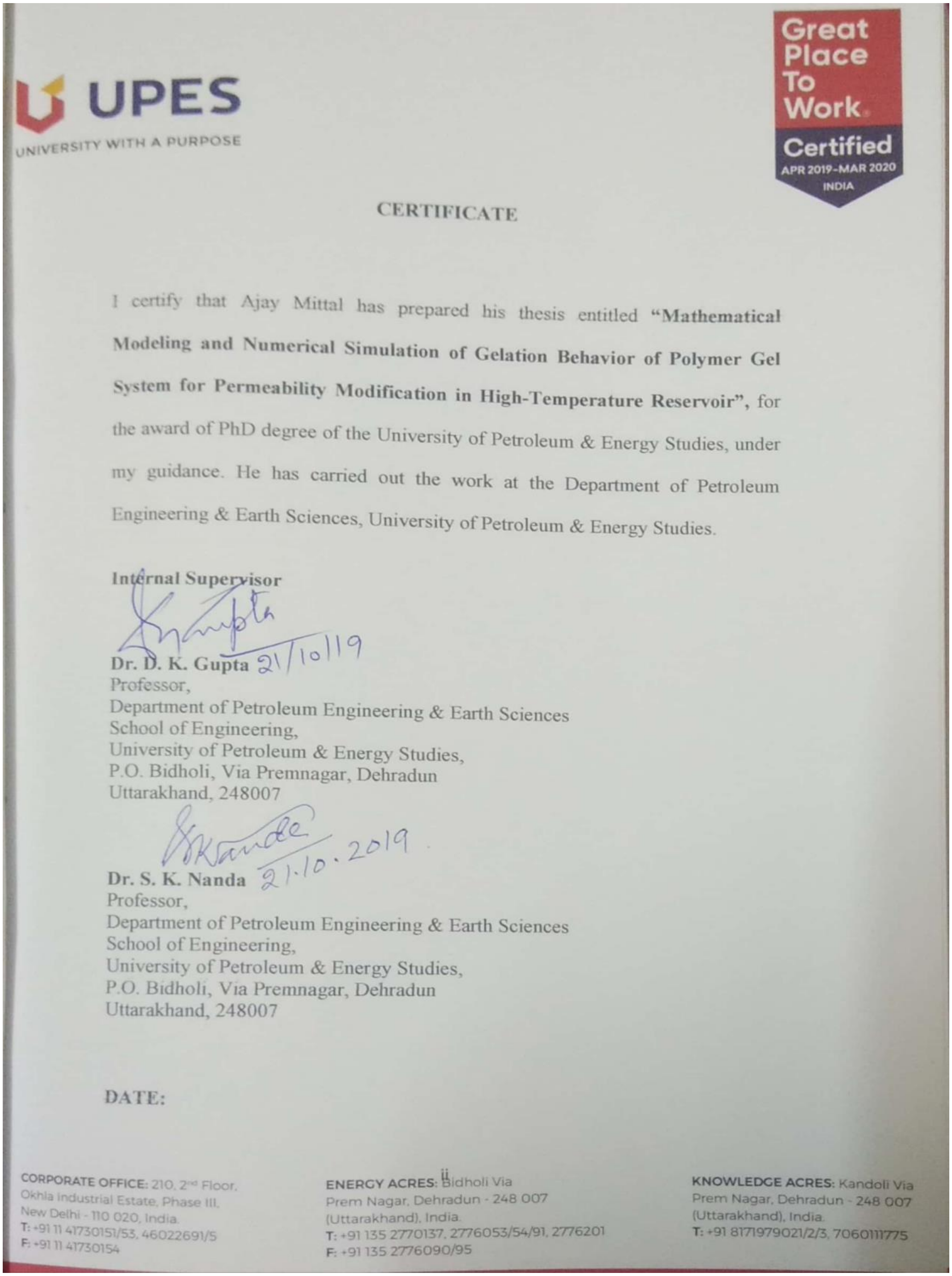

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ABSTRACT

Polymer systems are used for profile modification. Profile modification refers to selectively reducing the permeability of high permeability zones and leading to an improvement in process efficiency. Different polymer systems used for oil recovery have limited applicability at high temperature and high salinity environment. Phenol-formaldehyde gel system found to be stable at high temperature environment. This gel system undergoes gel formulation without the need of metallic or non-metallic cross-linker. The phenol-formaldehyde gel system increases the viscosity of the displacing fluid at desired temperature in the porous media and may be used as a good means of homogeneity.

The existing work therefore, involves the formulation of the phenol-formaldehyde gel system and its laboratory evaluation under different conditions. The experiments are carried out under the following study:

Bulk Gelation Study

The study helps in understanding the gelation behaviour of the phenol-formaldehyde gel system. Bottle test used in bulk gelation study helped in identification and trend analysis of gelation data.

In-Situ Gelation Study

In-Situ gelation study helps in evaluating the effectiveness of the phenol-formaldehyde gel system in porous media.

The results of bottle test studies have indicated that there exists lack of quantitative understanding in between the component of polymer gel and the critical variables and therefore mathematical model has been developed in order to have the

quantitative understanding of the gelation behaviour of phenol-formaldehyde gel system.

CHAPTER 1:

It introduces polymer gels and their features with reference to recovery of oil. This chapter also provides insight into the Gel Characterisation, which involves bulk gelation study and parameters that determines the effectiveness of polymer gels. Reservoir's critical parameter reviewed for screening of polymer gel system.

CHAPTER 2:

Reviews the different natural and synthetic gel systems used in Oil Industry for profile modification and water shutoff jobs. All the gels have the features of increasing the viscosity of the displacing fluid, with respect to time, as a mean of homogeneity. Theoretical and empirical models have been reviewed for the gelation time and critical parameters.

CHAPTER 3:

The chapter highlights the various discussions about the experiments and procedure followed for doing bulk and in-situ gelation study. Phenol-formaldehyde solutions was bottle tested at varying condition of temperature (85, 90, 105, 115 and 130^{0}C), concentration of phenol (2.00, 2.25, 2.50 & 2.75 %) and initial pH (9.5, 10, 10.5, and 11), at constant salinity (3.2 %), by keeping the F/P molar ratio as 3.5, for measuring gelation time and its stability. The gelation behaviour of phenol-formaldehyde gel system in porous media has also been carried out to find the effectiveness of the gel system and computation of porosity, permeability and residual resistance factor is done.

CHAPTER 4:

This chapter summarizes the results evaluated through different experimental studies. Bulk gelation and in-situ gelation study have been conducted for formation and propagation of gel system in porous media. Bulk gelation study helps in determination of gelation time while in-situ gelation study evaluates the effectiveness of the gel system for permeability or profile modification. In bulk gelation study, effect of phenol concentration, temperature, and initial pH of the polymer solution, on the gelation time have been investigated. In-Situ gelation study was carried out on sandstone pack to establish and investigate effectiveness of gel system developed through bulk gelation study. The study emphasize that the phenol-formaldehyde solution formed strong and stable gel and showed its applicability for high temperature and high salinity environment.

CHAPTER 5:

Attempt has been made to describe the reaction mechanism of phenol-formaldehyde polymer system. Mathematical model has been developed in order to have the quantitative understanding of the gelation behaviour of phenol-formaldehyde gel system. The models developed by researchers follow mainly Arrhenius type models as per the literature review. The Arrhenius type models relates the gelation time with only one variable i.e. temperature. The models developed earlier indicate that the reaction temperature is having profound effect on the gelation mechanism; however, the impact of polymer concentration on the gelation time was not considered. Therefore, there is a need to develop the mathematical model that can relate the gelation time with temperature and concentration of reactants. Mathematical model has been developed using power law and Arrhenius equation, which can predict the gelation time of the phenol-formaldehyde gel system at the varying condition of temperature, phenol-formaldehyde concentration. The chapter also provides the steps involved in the simulation study of the mathematical model developed for predicting the gelation behaviour of phenol-formaldehyde gel system.

CHAPTER 6:

This chapter highlights the conclusion of the research work conducted and recommendation for future work.

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ABBREVIATIONS

Δp	Pressure drop across pack, atmosphere
μ	Viscosity, centipoise
a	Reaction order with respect to phenol
A	Cross-sectional area of pack, cm^2
b	Reaction order with respect to formaldehyde
B, C, D, D’	Constants based on empirical correlation
$b_{0,}$ $b_{1,}$ $b_{2,}$ $b_{2,}$	Empirical coefficients
C_F	Formaldehyde concentration, mole/litre
C_{FO}	Initial concentration of formaldehyde, mole/litre
C_P	Phenol concentration, mole/litre
C_{Po}	Base polymer concentration, gm/litre
C_{PO}	Initial concentration of phenol, mole/litre
C_x	Cross-linker concentration, gm/litre
e	Initial concentration of silica, mole/litre
E_a	Activation energy, kJ/mole
K	Permeability, md
k, k’	Rate constant, mole/litre/time
L	Length of pack, cm
M	Time constant, seconds
n	Total reaction order
Ø	Porosity of pack

Q	Flow rate, ml/hr
R	Universal gas constant, kJ/mole/K
S	Salinity, wt. %
T	Reaction temperature, kelvin
t	Gelation time, seconds
x	Stoichiometric coefficient of phenol
y	Stoichiometric coefficient of formaldehyde
S_{NaCl}	Concentration of NaCl, moles
S_{KCl}	Concentration of KCl, moles
z	Conversion of silica, mole/litre
z/e	Fractional conversion of silica
$\frac{-\mathrm{d}C_P}{\mathrm{d}t}$	Change in concentration of phenol per unit time, mole/litre/time

NOMENCLATURE

CTP	Cyamopsis Tetragonoloba Plant
EOR	Enhanced Oil Recovery
H_2SO_4	Sulphuric Acid
HCL	Hydrochloric Acid
HEC	Hydroxyl Ethyl Cellulose
HPAM	Partially Hydrolysed Polyacrylamide
HPC	Hydroxyl Propyl Cellulose
KCl	Potassium Chloride
MR	Molar Ratio
NaCl	Sodium Chloride
NaoH	Sodium Hydroxide
C NMR	C Nuclear Magnetic Resonance Spectroscopy
P/F	Phenol to Formaldehyde Ratio
PAM	Polyacrylamide
PDVSA	Petróleos de Venezuela
PEI	Polyethyl-Eneimine
RRF	Residual Resistance Factor
SDS	Sodium Dodecyl Sulfate
SMRF	Sulfomethylated Resorcinol Formaldehyde

CHAPTER 1: INTRODUCTION

Primary and secondary oil recovery together produce on an average about 1/3 of the original oil in place [1]. A major reason for low oil recovery in water flooding and other displacement type EOR methods is poor efficiency due to reservoir heterogeneity [2]. The process efficiency in heterogeneous reservoir having multiple zones can be improved significantly by using polymer gel systems for profile modification [3]–[7]. Profile modification is a process of reducing the permeability of the high permeable zones by placement of polymer gels. The displacement fluid, subsequent to the placement of polymer gels, passes through the low permeability zones and leading to an improvement in process efficiency [8]–[13]. Polymer gels gained significance importance due to their low cost, deeper penetration, ease of operation, ability to reduce permeability of high permeability zones [14].

During water flooding or displacement processes, sweep efficiency in oil-bearing reservoirs, having high permeability zones, improved by injecting polymer gel system in injection wells, which has viscosity close to water. The objective of polymer gel treatment is to plug the high permeability zones and allowing displacement of oil through the low permeability zones.

The polymer gel system, which found many applications in petroleum industry, shows different characteristic at varied temperature, the concentration of the polymer and cross-linker, salinity of mixing water and pH of the fluid system [9], [15], [16]. One of the important characteristics of the gel system is the gelation time, which is detrimental in the overall success of the enhanced oil recovery process. Temperature has profound effect on the rheological properties of polymeric gels [15], [17]. These gels have the additional advantage of giving much stronger recovery.

1.1 FEATURES OF POLYMER GELS

- Low viscosity gels, which develops their strength in due course of time within the reservoir as a means of homogeneity.
- Gels are stable up to the shear rate of 0.1 - 10 sec^{-1} and possesses characteristics with higher injectivity [18], [19].
- Thermal stability of the gel is also ensured up to the temperature of 130-150^{0}C [20], [21].
- Gels formed are suitable for different type of reservoir, sandstone, limestone and carbonates [3], [16].
- Initiation of gels starts at an average temperature of 70^{0}C-80^{0}C which is considered to be most suitable for hydrocarbon reservoirs.

1.2 SCREENING CRITERION OF POLYMER FLOODING

In homogenous reservoir, the recovery of oil remains almost same in water flooding and polymer flooding. In polymer flooding, the recovery of oil happens at a much-accelerated rate and makes the process economical in comparison to water flooding. Mobility ratio determines the areal sweep efficiency of any displacement process, lesser the mobility ratio higher the sweep efficiency. The mobility ratio decreases due to increased viscosity of the displacing water. In homogenous reservoir, the recovery of oil remains same irrespective of number of times pore volume is flooded with polymer.

The mobility ratio does not remains constant during flooding and therefore concept of relative permeability came into existence to understand the two-phase flow. In heterogeneous reservoir, water flooding gives poor sweep efficiency. Water moves through the high permeable zones and leave behind the immobile oil in low permeable zones and thus recovery of less oil. Polymer flooding plug these high permeability zones, allowing the recovery of immobile oil and thus recovery of more oil [22]. Pilot study done by PDVSA’s in Lagomar field in Venezuela showed positive result, the reservoir in a Lagomar field is highly heterogeneous and high water cut forced the closure of production wells [23].

The recovery of oil by polymer flooding depends on the viscosity of polymer solution. The polymer solution should attain a minimum viscosity for onset of recovery of oil. It is difficult to approximate the minimum viscosity of the polymer solution, earlier research suggest that the viscosity of the polymer solution should roughly be equal to the viscosity of the reservoir oil. The viscosity of the polymer solution depends on many factors like temperature of the reservoir, concentration of polymer, salinity of the crude oil and the associated water. The viscosity is also dependent on the shear rate, the shear rate in-turns depends on the flow geometry and velocity of flow. Higher the shear rate and the velocity of flow, more time it takes the polymer solution to attain minimum viscosity for recovery of oil. Low permeable zones offer higher shear rate compared to high permeable zones. Polymer gels exhibits non-Newtonian behaviour and show pseudo-plastic or shear thinning response in porous media. Residual resistance factor, which is the ratio of the permeability of brine water before and after polymer flooding is used to understand the flow characteristics during polymer flooding.

Enhanced oil recovery processes are used either for low oil recovery reservoirs or for where water cut is high or it is not economical to produce oil from the reservoir. Depending on the scenario, specific EOR process need to be selected. In order to differentiate whether polymer flooding is suitable for the reservoir, reservoir parameters are to be examined. The most critical parameters that helps in deciding the suitability of the polymer flooding are type of reservoir rock, geometry of the reservoir, depth of the reservoir, temperature of the reservoir, properties of the crude oil, salt content of the reservoir.

1.2.1 GEOMETRY OF THE RESERVOIR

Screening of the reservoir geometry, the most important parameter, to be examined before selecting a reservoir as a candidate for polymer flooding. Polymer flooding is most suited for big reservoir where flooding pattern can be changed during the course of the life of the reservoir. Gas cap reservoir are not suitable for polymer flooding due to uncontrolled flow of fluid in the reservoir. Reservoir with bottom-water zone makes the polymer flooding difficult due to unregulated flow of chemicals in the reservoir. Reservoir with large aquifers requires additional treatment for maintaining the higher-pressure gradient requirements for polymer flooding.

1.2.2 RESERVOIR ROCK

In general, reservoir rock is characterise by its mineralogy, porosity and permeability. Permeability and its variation is quite critical in the success of any polymer flooding process. Polymer flooding is most beneficial in cases of high vertical permeability variation. High vertical permeability variation lead to early breakthrough of water and recovery of less oil. Polymer flooding is most preferable for cases where permeability is in the range of 0.5μm^2 to 1μm^2 [24]. The injectability of the polymer solution, into the reservoir, is also dependent on permeability.

1.2.3 SALT CONTENT OF THE RESERVOIR

The salt content of the oil and/or the associated water is the important parameter in selection of a polymer solution for flooding. The polymer solution should be salt resistant in high salinity environment where disposal of the produced brine solution is not possible or availability of fresh water is limited. The alternative to it is to precondition the reservoir by pre-flushing the reservoir with fresh water to decrease the salt content. However, pre-flushing of the reservoir is also dependent on the mineralogy of the reservoir rock.

1.2.4 DEPTH OF THE RESERVOIR

The injection of the polymer solution should always be less than the reservoir fracture pressure. The injection pressure required for polymer flooding is comparatively higher when compared with water flooding. Shallow reservoir cannot sustain high injection pressure due to which polymer flooding is not preferable except for unconsolidated shallow reservoir, which does not exhibit fracture pressure. Screening of the reservoir depth should be done while selecting reservoir as a candidate for polymer flooding.

1.2.5 TEMPERATURE OF THE RESERVOIR

Reservoir depth impact the temperature of the reservoir. Temperature of the reservoir becomes quite critical for selecting a particular solution for flooding. Screening of a polymer solution depends on the temperature of the reservoir. The viscosity of the polymer solution decreases with increase in temperature. Low temperature either does not help the polymer solution to effectively improve the oil recovery. The polymer solution should be characterise in the laboratory for its stability at the reservoir temperature.

1.2.6 PROPERTIES OF THE CRUDE OIL

The most critical properties of the crude oil that helps in deciding a particular EOR process is its viscosity. The crude oil viscosity in turns effect the mobility of the crude oil. Viscosity in range of 5 to 50 mPa.s [24] is advantageous for polymer flooding. Mobility ratio less than 1, considered favourable for polymer flooding. Mobility ratio is the ratio of the mobility of polymer solution to the mobility of the crude oil. Mobility in turns is the ratio of permeability to viscosity. High oil viscosity is preferable for effective polymer flooding. Low oil viscosity leads to small recovery of oil except for cases where permeability variation is high.

1.2.7 SELECTION OF POLYMER SYSTEM

Once the reservoir parameters screened for selecting the reservoir as a candidate for polymer flooding, the next step is the selection of the polymer system for flooding purpose to improve recovery of oil. Different polymer system used for oil recovery are discussed, in details, in the next section. The selection of a polymer system requires characterisation of the polymer system in a laboratory. Study of the rheological, flow properties and stability of the polymer system is done, for its effectiveness, in the laboratory setup.

1.3 GEL CHARACTERISATION

Gel characterisation involves the bulk gelation study, the homogenous solution of polymer solution tested for its technological and economic success. Once a reservoir selected as a candidate for polymer flooding, the next step is the evaluation of a polymer system in terms of gel strength, gel stability, flow characteristics, in a simulated reservoir conditions in the laboratory. The polymer gel system shows different characteristic at varied temperature, the concentration of the polymer and cross-linker, salinity of mixing water and pH of the fluid system. The most important characteristics of the gel system is the gelation time, which is detrimental in the overall success of the enhanced oil recovery process. The gelation time is dependent on many factors like temperature, salinity, pH of the oil and the associated water, shear rate. In bulk gelation study, the effect of these parameters on the gelation time investigated for further evaluation and their effectiveness in the reservoir.

1.3.1 GELATION TIME AND GEL STRENGTH

Gelation time and gel strength were measured through visual inspection in a bottle test and is the most commonly used method. Gel mixture in a glass bottles, placed in hot air ovens, set at desired temperatures to observe gelation time and gel strength. Bottle testing is a simple and inexpensive method to test large number of samples quickly when compared to rheological methods, over a wide range of temperatures, pH, salinity and concentration. The findings and trends of gelation time using visual gelation time need to be substantiated using rheological methods. Earlier research suggest that the gelation time using rheological methods is shorter than the bottle test method [25]–[27]. The gelation time defined by visual method is the earliest time when the gel solution did not fall, due to force of gravity, on inversion of the bottle [3], [10], [13], [15], [25]–[40]. It is a well-known fact that the gelation time, which depends on the type, concentration and molecular weight of the polymer, cross-linker concentration, degree of hydrolysis of the polymer solution at elevated temperature, pH of the polymer solution, salinity and temperature, requires investigation in the laboratory.

1.3.2 GEL STABILITY

Gel stability of any polymer solution needs reviewing in terms of thermal stability or phase stability. Thermal stability of the polymer solution is its ability to resist degradation at extreme temperature. Phase stability is to resist syneresis that results in lowering of gel volume due to removal of water with time. The shrinkage in gel volume may takes place due to low concentration of polymer solution [28], [41]. Combination of factors like temperature, salt content, and polymer concentration leads to syneresis. In syneresis, a strong bond formed in between the molecules of the polymer solution, gel volume shrinks which leads to removal of water. Bryant et al. confirmed that the hydrolysis of polymer gel can occurs at high temperature and high concentration of cross-linker and therefore polymer gels, which resist syneresis at high temperature, are desirable. Bryant et al contradicted and achieved residual resistance factor greater than 100 during in-situ gelation study for polymer gels, which showed syneresis up to 95 % during bulk gelation study. This could be attributed due to preferential shrinkage of polymer gels at the starting of pores or due to the fact that syneresis of gel is much slower during flooding when compared with bulk gelation study [42].

1.4 EFFECTIVENESS OF GEL IN POROUS MEDIA

In order to evaluate the effectiveness of the polymer gel in porous media, flooding experiments or in-situ gelation study need to be conducted in the laboratory set up [16], [43], [44]. Sample core holder need to be prepared of the desired porosity.

Residual resistance factor calculated which provides the effectiveness of the polymer gel, pre and post gelation permeability helps to do so.

1.4.1 POROSITY

It is the fraction of rock volume/ (pack volume) or bulk volume occupied by pore space. The volume is estimated by measuring the inner diameter and length of the core holder used. Pore volume is found by volume of brine used during the preparation of pack in the core holder.

Porosity (Ø) is calculated by using the expression

$$Porosity = \frac{Pore\ Volume}{Bulk\ Volume} \tag{1.1}$$

1.4.2 PERMEABILITY

It is the ability of the porous media to conduct a fluid through it. Darcy's law helps in calculating the permeability for laminar and linear flow of non-compressible fluids through homogenous porous media under steady state conditions. Darcy's law for above case is given by the following equation

$$Q = \frac{KA\Delta P}{\mu L} \tag{1.2}$$

1.4.3 RESIDUAL RESISTANCE FACTOR (RRF)

Residual resistance factor is defined as ratio of brine permeability before gel injection to the brine permeability after gel injection. Residual resistance factor is a good measure of indicating the reduction in brine permeability after gelation. Residual resistance effect helps in controlling of water fingering caused due to reservoir heterogeneity and mobility contrast. Decreased permeability is indicated by increased residual resistance factor.

$$\text{Residual Resistance Factor (RRF)} = \frac{\text{Brine Permeability before Gel Injection}}{\text{Brine Permeability after Gel Injection}} \tag{1.3}$$

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

Literature review of the polymer gel systems is done which are used for profile modification and water shutoff jobs. The first section reviews the different natural and synthetic gel systems used in Oil Industry for profile modification and water shutoff jobs and the second section reviews the theoretical and empirical models for the gelation time and critical parameters.

2.2 POLYMER GEL SYSTEMS

Permeability modification or profile modification are done using mechanical or chemical methods. Mechanical methods such as perforated holes and/or liners have demonstrated success in the past but are quite capital intensive and possesses operational difficulties. Chemical methods have been widely used as remedial measures for profile modification and water shut-off jobs [4], [45]. Polymer based water shut off gels and profile modification technology successfully adopted in China for sandstone and limestone reservoirs [46]. Polymer gels was successfully tested in the laboratory for heterogeneous carbonate reservoirs to shut off water zones and improve profile modification [36]. Polymers used for EOR are either natural polymer or synthetic polymer or a combination of natural polymer with cross-linking agent. Natural polymer occurs in nature and are easily extractable. Natural polymers are often water-soluble. Polysaccharides polymers, like cellulose based and xanthan gum, are the most widely used polymers for EOR.

2.2.1 CELLULOSE BASED GEL SYSTEM

Cellulose is a long chain of glucose molecules. In glucose molecule, the smallest unit in the chain, there are three positions where addition reaction can take place.

The three positions are of one CH_2OH group where addition reaction took place, without compromising with the stability of the cellulose ring. Methyl, ethyl, propyl or carboxyl group added to obtained required hydroxyl cellulose. Hydroxyl propyl cellulose (HPC) prepared by mixing propylene oxide with cellulose. It is a water soluble, non-ionic polymer. Hydroxyl propyl cellulose successfully evaluated for oil field application but its use is rather limited due to its high cost. The other disadvantage is requirement of large quantity of HPC for marginal permeability reduction. Hydroxyl propyl cellulose based conventional gel formulated by using suitable cross-linkers like titanium, zirconium etc. The solubility of HPC is very good; it is soluble even in cold water. However, the problem arises when the temperature of the solution raised above 40-45° C, the polymer starts precipitating from solution in the presence of brine. This instability issue with Hydroxyl propyl cellulose overcame by addition of ionic surfactant. Stable gel formed when sodium dodecyl sulfate (SDS), as a surfactant, mixed with HPC. The HPC/SDS gel could able to reduce brine permeability by 95% [34], [47], [48]

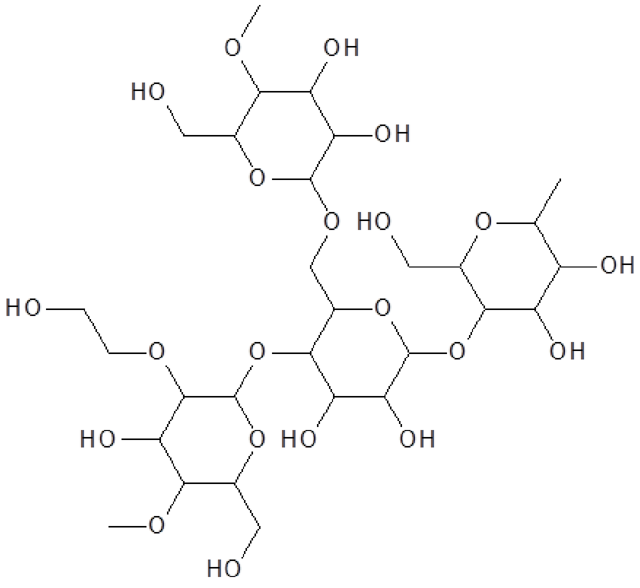
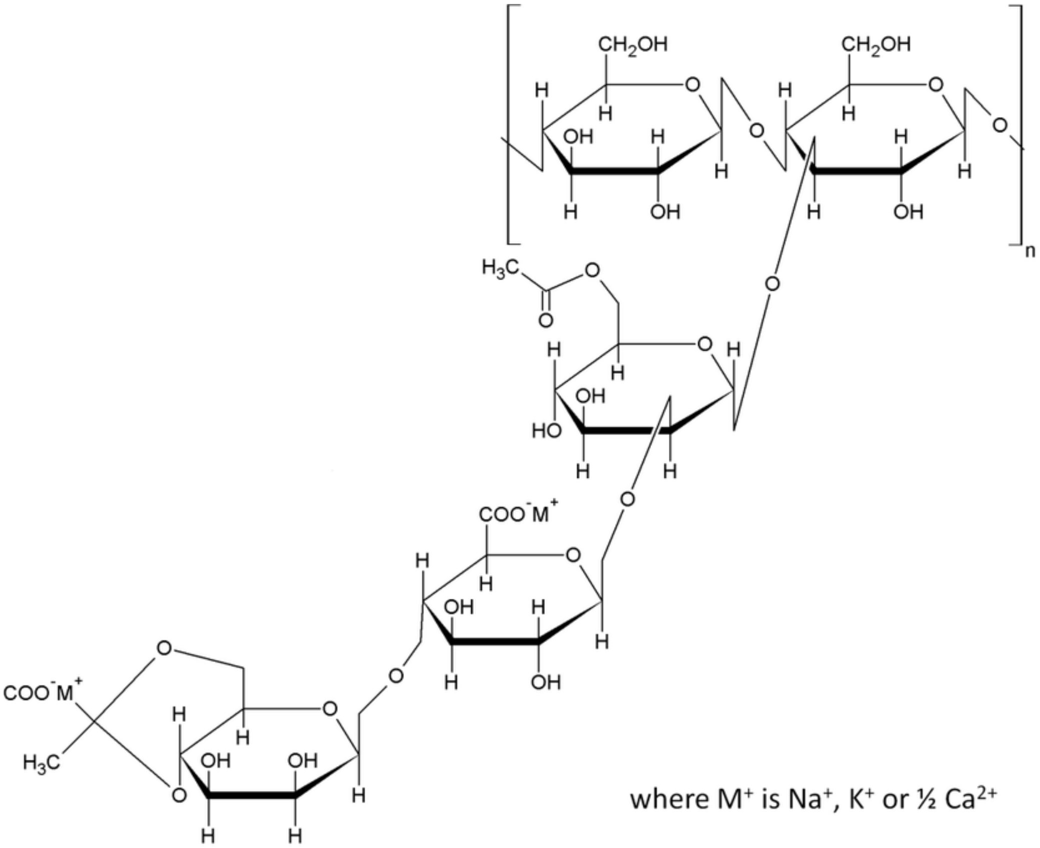


Figure 2.1: Structure of Hydroxyl Ethyl Cellulose (HEC)

2.2.2 XANTHAN GUM

Xanthan is a polysaccharide produced by bacterial fermentation and is similar to cellulose. The most commonly used bacteria for production of xanthan is Xanthomonas campestris [49], [50]. The molecular structure of xanthan gum contains one glucuronic acid unit, two mannose units and two glucose units in the ratio 2-2-2.8. The presence of carboxylate group make this polymer ionic in nature.



where M^+ is Na^+, K^+ or ½ Ca^{2+}

Figure 2.2: Structure of Xanthan Gum

2.2.3 SILICA GEL SYSTEM

Silica based gel systems employs silicates and proven effective under a wide range of temperature, pressure and brine concentration for permeability modification jobs. Silicates are hydrophilic in nature and hence the tendency to be effective for high water zones. . Due to relatively low viscosity, the polymer solution enters into the water channels without displacing the oil, prior to gelation. This helps in minimizing the formation damage. Hurd [51] examined various general theories in relation to formation of silica gel, proves that silica gel follows fibrillar theory or micellar theory or sponge theory. Fibrillar theory postulates that both solid and liquid are in continuous phase, with liquid is stored in the fibrous structure formed by solid.

2.2.3.1 Acidic Silica Gel

The acidic silica gel system is the oldest techniques. These gels found to have low initial viscosity of 1 to 2 cP and have good thermal stability in temperature ranging from 60 to 200^0F, with low to moderate cost. Acidic silicates gels once formed are stiff and rigid in nature. The concentration of silicate kept from 3-15% (by weight). The solution kept acidic in nature by maintaining the pH in between 4-6. The acids commonly used are HCI and H_2SO_4 [52].

2.2.3.2 Alkaline Silica Gel

Alkaline silica gels are softer and weaker in nature as compared to acidic silica gel due to different gelation mechanism. The major difference with acidic gel systems is that, pH maintained alkaline by adding less acid or weak acid like ammonium sulphate. The gel formation achieved faster by making the solution neutral. The gel will not formed having solution pH above 11 [52].

2.2.4 POLYACRYLAMIDES

Acrylamide based copolymers and homo-polymers are most widely used polymers for enhanced oil recovery. Polyacrylamide (PAM) is the most important polymer used for profile modification as well as for mobility control. Polyacrylamide is a water-soluble polymer and made by the polymerization of acrylamide as a monomer. The degree of the hydrolysis is an important parameter, which determines the properties of polyacrylamides in aqueous solutions. Higher the degree of hydrolysis stronger the sensitivity towards salts content in the reservoir fluid. Degree of hydrolysis of commercial polyacrylamides used for enhanced oil recovery is in the range from 25-30 %. Ionic version of polyacrylamide as partially hydrolysed polyacrylamide (HPAM) is the most widely used polymer due to its ability to attain high viscosity at low temperature. Polyacrylamides are sensitive to thermal, shear degradation and therefore limit its applicability for in-depth profile modification. To overcome with the problem associated with polyacrylamides, modified polyacrylamide developed, wherein polyacrylamide cross-linked with metallic (Cr (III), Fe (III), Al (III), and Zr (IV)) [53] or organic cross-linker to resist thermal and shear degradation at higher temperature. A pilot test on modified acrylamide was done in china on Shuanghe reservoir of Henan oil field [54]. The polymer flooding resulted significant increase in oil production. It was concluded that permeability modification is an important parameter in improving the sweep efficiency of heterogeneous reservoir.

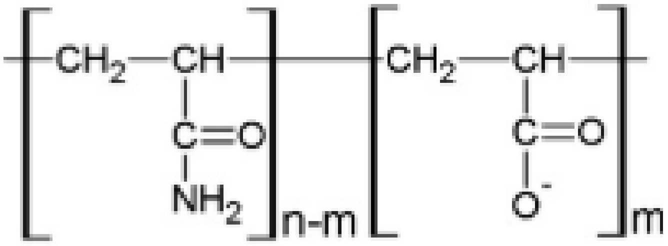


Figure 2.3: Structure of Partially Hydrolyzed Polyacrylamide (HPAM)

2.2.5 ACRYLAMIDE-POLYMER/CHROMIUM (III)-CARBOXYLATE GEL SYSTEM

Sanders, Chambers and Lane et al. [55] has developed acrylamide-polymer/chromium (III)-carboxylate gel system by cross-linking acrylamide polymer with Cr (III) cross-linker. Gel formed was stable up to temperature from 55^0F to 255^0F and pH range from 4 to 12.5 [27]. The gel formed is inexpensive and relatively non-toxic when compared with Cr (VI) gel system [32]. Sydansk [28], [29] confirms the applicability of this system for high salinity reservoirs. Sydansk [28], [29] proposed that the inter-molecular cross-linking in these gels is obtained through Cr (III) and complex with two carboxylate functional groups on two different acrylamide polymer molecules. It has been suggested in several research papers that acrylamide polymer / Cr (III) gels are inherently not stable at elevated temperature (> 170^{0}F). It is attractive to develop PAM / Cr (III) - carboxylate gel that is stable at high temperature. Tackett et al. [56] used chromium (III) acetate to understand the chemistry in between acrylamide and Cr (III) and polymer carboxylate group. X-ray diffraction study conducted confirms the existence of already reported cyclic structure of Cr (III) acetate.

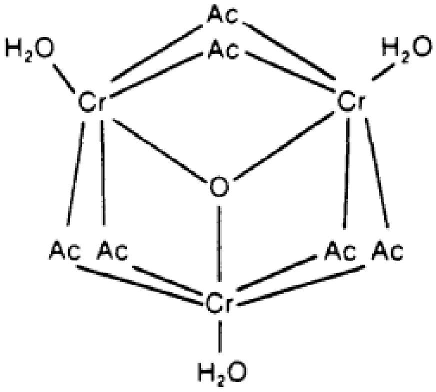


Figure 2.4: Structure of Chromium Acetate confirmed by Tackett et al.[56]

2.2.6 POLYACRYLAMIDE/CHROMIUM (VI)/THIOUREA GEL SYSTEM

Maccool, Green, PauI Willhite et al. investigated polyacrylamide/chromium (VI)/Thiourea gel system under flow conditions in sand packs and identified that in situ gelation occurred over a short length of sand pack [57]. However, previous research in polyacrylamide/chromium (VI)/Thiourea gel system showed that gel solution is constrained by slower pumping rate imposed by the viscosity. Thiourea used as a reducing agent, converts chromium (VI) to chromium (III). The gel formed by the combination of polyacrylamide/chromium (III) is stable but the bonding in between polyacrylamide and chromium (III) takes place at a controlled increase in pH of the gel solution which is difficult to achieve in in-situ gelation and hence the need of the system where in-situ gelation can be controlled. The certain amount of chromium (VI) consumes during the gelation reaction, irrespective of the initial concentration of the chromium (VI), indicating the rate controlling step [58]. Nanda et al. suggest the characterisation of gels is important in judging the effectiveness of polymer gels used for water control [59].

2.2.7 GUAR GUM

Guar Gum, derived from the seed of Cyamopsis Tetragonoloba plant, is a natural polymer and have wide spread applications across various industries like food, pharmaceutical, textile, paper and oil industry. Guar Gum, termed as galactomannan, is a branched copolymer of mannose units and galactose units and is either directly used or by making use of its derivatives. Guar Gum, due to its non-ionic nature is water-soluble. Guar Gum easily hydrated in many types of water-soluble chloride, highly compatible with potassium chloride. It is stable below 85^{0}C and starts degrading above this temperature [49], [58], [60]

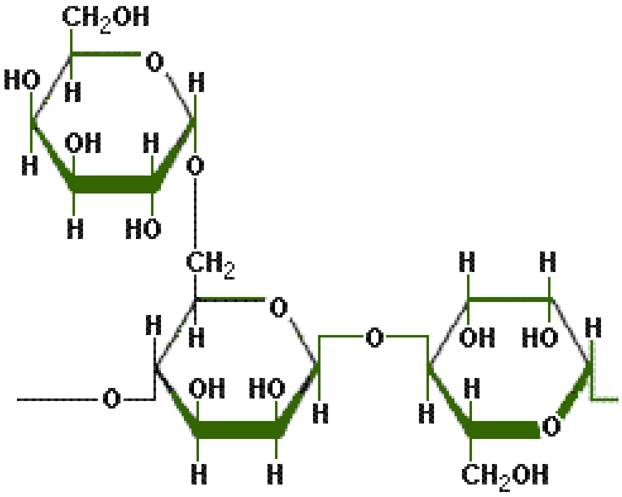


Figure 2.5: Structure of Gaur Gum

2.2.8 XANTHAN-CHROMIUM (III) SYSTEM

The natural xanthan biopolymer cross-linked with metallic cross-linker chromium system, documented well in the literature for profile modification [8], [9], [20], [28], [61]–[67]. Chang et al. observed that xanthan/Cr (III) gels showed temperature resistance up to 194^0F [9]. The xanthan biopolymer solution showed different characteristics when compared with synthetic polymer, the viscosity of the biopolymer solution decreases with increase in shear rate or flow velocity and exhibits the behaviour of pseudo-plastics [61], [64]. The high shear rate rupture the bonding between the cross-links rather than polymer structure [66].

2.2.9 RESORCINOL/PHENOL-FORMALDEHYDE/PARTIALLY HYDROLYZED POLYACRYLAMIDE (HPAM) GEL SYSTEM

Jia et. al. [31] investigated the performance of Resorcinol/Phenol-Formaldehyde/HPAM gel system. In the study, resorcinol and phenol-formaldehyde used as a primary and secondary cross-linker respectively, showed promising result for water shutoff in fractured reservoirs. Secondary cross-linker helps in stabilising the weak gel formed by the first cross-linker. The gelation reaction with metallic cross-linkers is less stable due to ionic bonding in comparison when organic cross-linkers are used. The gelation reaction with organic cross-linkers are more stable due to covalent bonding. Investigation on gelation mechanism using two cross-linkers is scare; this study is unique in itself and showed promising result.

2.2.10 RESORCINOL/FORMALDEHYDE SYSTEM

Resorcinol reacts with formaldehyde in the presence of alkali to form three dimensional gel structure through condensation polymerization. Initially the rate of reaction of resorcinol-formaldehyde gel system is very slow and rate of reaction suddenly increases at the final stage and strong gel forms. Seright et al and Martin et al [16] evaluated the gelation reaction and the effectiveness of the polymer gel system at varying pH and at 41^0C. Gelation results indicated that the gelation reaction is sensitive to pH, strong gel formed at pH = 9, with a short gelation time of 4 hours. Core flood experiments conducted showed the effectiveness of the polymer gel system as the gel occupied 87% to 99% of the pore volume.

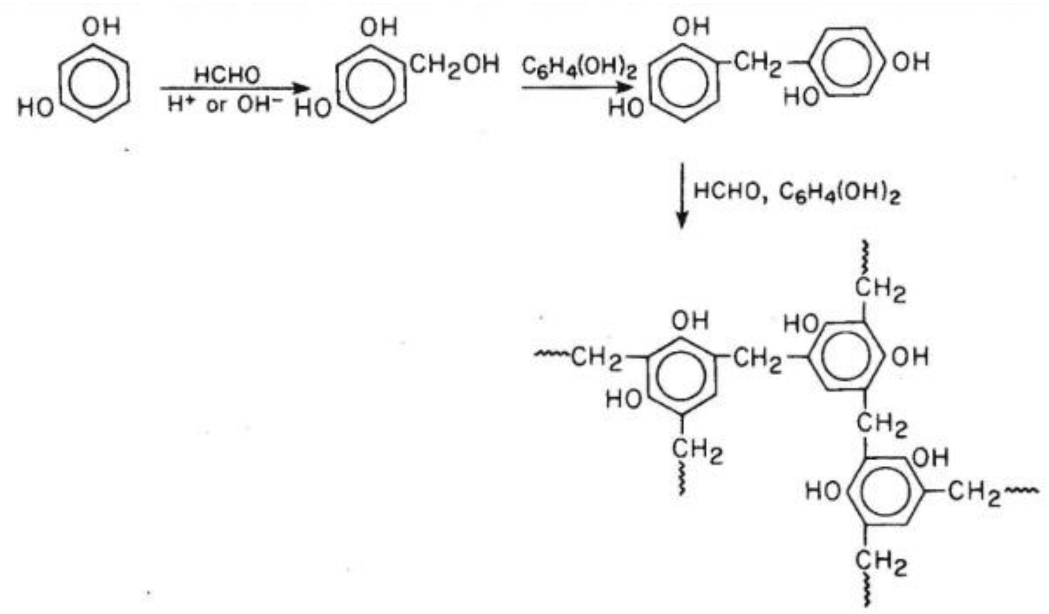


Figure 2.6: Reaction between Resorcinol and Formaldehyde [16]

Zhuang et al. and Pandey et al. [25], [68] modified the resorcinol formaldehyde system by sulfomethylation of the resorcinol to form sulfomethylated resorcinol-formaldehyde (SMRF) system. SMRF system evaluated showed strong and stable gel formed at temperature between 77 and 126^{0}F and in the pH range of 5 to 8. The SMRF system polymerises in-situ in the presence of strong buffer when brine injected in the core flood.

2.2.11 PHENOL/FORMALDEHYDE/POLYACRYLAMIDE SYSTEM

Gel formed by cross-linking of Phenol-formaldehyde and different grade of polyacrylamide, tested for their injectivity in porous media. The flooding experiment conducted suggests that the filtration play a prominent role in injectivity of the polymer solution. The rate of injetivity loss by filtration depend on the age of the gelants. Filtration starts well before the initiation of gelation and bulk gelation time can be a good estimate of pumping time [15].

Lockhart et al. [69] evaluated the applicability of Phenol /Formaldehyde/ Polyacrylamide system cross-linked polymer gel for high-temperature. Gel formed in the temperature range from 60^{0}C to 140^{0}C by varying the polymer composition and pH of the solution. The gel performance and injectivity of the polymer solution is independent of the lithology of the porous media. The issue of solubility of the phenol in oil is overcame by injecting a slug of phenol prior injecting polymer solution.

2.3 MODELS OF POLYMER GEL SYSTEMS

2.3.1 ARRHENIUS MODEL

The reaction rate of a chemical reaction is related to the temperature by the Arrhenius equation. Arrhenius equation indicates the effect of temperature on reaction rates, which in turns provides information about reaction mechanism. The Arrhenius equation is given below:

$$k = M * exp\left(\frac{-E_a}{RT}\right) \tag{2.1}$$

Alternatively,

$$\ln k = \ln M - \frac{E_a}{R} * \frac{1}{T} \tag{2.2}$$

or

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \tag{2.3}$$

where, M is the kinetic parameter and is different for different reaction and is related to the frequency of collisions between the reacting molecules, E_a is the activation energy for the particular reaction and represents the minimum amount of energy required to convert reactants into products in a chemical reaction, R is the universal gas constant and T is the absolute temperature of the reaction.

The above equation yields a straight line if graph is plotted in between the logarithm of the rate constant against the reciprocal of the absolute temperature. The above equation is applicable for most of the reactions.

2.3.2 HURD AND LETTERON MODEL

Hurd and Letteron [70] developed correlation for gelation time as a function of temperature for silicic acid gels. The model used the Arrhenius-type equation to find the activation energy of the chemical reaction. Hurd and Letteron used silica acid gels to study the effect of temperature on the gelation time. Hurd and Letteron made simple assumptions and developed empirical correlation similar to Arrhenius equation, which relates gelation time and temperature. The empirical correlation was validated with the experimental data and it was found that the graphs, for different concentration of silica, were linear when plotted between the logarithm of the gelation time and the absolute temperature. Assumptions considered by Hurd and Letteron in analyzing the results:

- Reaction follows the law of an ordinary chemical reaction
- Arrhenius equation may be applicable to the experimental data
- Irrespective of initial concentration of silica (e), the proportion of silica remains same that has reacted at the gelation point, at all temperatures.

Hurd and Letteron considered the nth order rate law for the gelation reaction of silica acid gel

$$\frac{dx}{dt} = k(e - z)^n \tag{2.4}$$

on integration,

$$\int_0^t \frac{dx}{(e-z)^n} = \int_0^e kdt \tag{2.5}$$

on integration,

$$t = \frac{1}{k(n-1)} * \left[\frac{1}{(e-z)^{n-1}} - \frac{1}{(e)^{n-1}}\right] \tag{2.6}$$

or

$$t = \frac{1}{k(n-1)e^{n-1}} * \left[\frac{1}{\left(1-\frac{z}{e}\right)^{n-1}} - 1\right] \tag{2.7}$$

or

$$t = \frac{D}{ke^{n-1}} \tag{2.8}$$

where,

$$D = \frac{1}{(n-1)} * \left[\frac{1}{\left(1-\frac{z}{e}\right)^{n-1}} - 1\right] \tag{2.9}$$

The gelation time is given by equation (2.8) for any fractional conversion of e and the constant D depends on the fraction $\frac{z}{e}$ and n.

Rewriting equation (2.8)

$$\ln t = \ln D - \ln k - (n-1) * \ln e \tag{2.10}$$

From Arrhenius equation (2.1)

$$\frac{d \ln k}{d\frac{1}{T}} = -\frac{E_a}{R} \tag{2.11}$$

From equation (2.10) and (2.11)

$$\ln t = +\frac{E_a}{RT} - (n-1) * \ln e + D' \tag{2.12}$$

Differentiating equation (2.12) with respect to 1/T, considering ‘e’ and ‘z/e’ as constant

$$E_a = R * \frac{d \ln t}{d\left(\frac{1}{T}\right)} \tag{2.13}$$

The above equation suggests that the plot of the logarithmic of gelation time with reciprocal of absolute temperature follows linear relationship; the slope of the curve gives the activation energy for the gelation reaction. The activation energy calculated for gelation reaction was 16.94 kcal, which is in the order of the heat of activation for many chemical reactions.

2.3.3 JORDAN et al. MODEL

Jordan et al. [8] studied the effect of temperature on gelation time for Polyacrylamide/Chromium (III) System and verified the model developed by Hurd and Letteron. Jordan et al confirms the applicability of Arrhenius-type equation for many chemical reactions. The experimental data generated validates the gelation time model developed by Hurd and Letteron. The graph plotted in between the gelation time vs. the reciprocal of the absolute temperature for the gelation reaction found to be linear at varying temperatures. The activation energy correlated using Arrhenius type equation found to vary slightly for the varying concentration of base polymer and polymer system used, showing the Arrhenius equation applicability for many chemical reactions.

2.3.4 BROSETA et al. MODEL

Broseta et al [71] studied the gelation behavior of Polyacrylamide/Chromium (III) acetate (MARASEAL^{TM}) system as a function of temperature, base polymer concentration, cross-linker concentration, brine salinity and degree of hydrolysis. It was experimentally verified that temperature is the parameter that strongly affects the gelation besides other parameters, the gelation time dependence on temperature follows Arrhenius type equation. Broseta et al. studied the effect of temperature, cross-linker concentration, polymer concentration on the gelation time of the Polyacrylamide/Chromium (III) acetate polymer system.

Effect of Temperature

The experimental data generated followed the Arrhenius type equation, which relates gelation time and temperature. The average activation energy calculated for gelation reaction was around 115 KJ/mol, which is again in the order of the heat of activation for many chemical reactions.

Effect of Cross-linker Concentration

Gelation time correlated, by keeping the polymer concentration constant, to study the effect of cross-linker concentration on the gelation time. The gelation time followed the inverse power law as follows:

$$t = \frac{B}{C_x^{0.4}} \tag{2.14}$$

where B is constant and based on empirical correlation.

Effect of Polymer Concentration

Gelation time correlated, by keeping the cross-linker concentration constant and varying the base polymer concentration and temperature, to study the effect of polymer concentration on the gelation time. The gelation time followed the inverse power law as follows:

$$t = \frac{C}{C_{Po}^{1.4}} \tag{2.15}$$

where C is constant and based on empirical correlation.

The above three correlations are combined to obtained the combined effect on the gelation time.

$$t = 7 * 10^{-14} * \exp\left(\frac{14100}{T}\right) * C_x^{-O.4} * C_{Po}^{-1.4} \tag{2.16}$$

where gelation time (t) is in seconds, Temperature (T) is in Kelvin, Cross-linker concentration (C_x) and base polymer concentration (C_{Po}) is in g/L.

2.3.5 REDDY et al. MODEL

Reddy et al. [72] developed correlations for gelation time as a function of salinity of the mixing water for NaCl and KCl. The research finding suggest that, the low concentration of NaCl and KCl have similar effect on gelation time. However, at higher concentration, the gelation time for NaCl follows polynomial relationship while for KCl gelation time varies linearly.

The gelation time for NaCl represented by the following equation

$$t = 6155.7 * S_{NaCl}^2 + 40.936 * S_{NaCl} + 0.5 \tag{2.17}$$

where gelation time (t) is in hours and concentration of NaCl (S_{NaCl}) is in moles

The gelation time for KCl represented by the following equation

$$t = 167.91 * S_{KCl} + 0.4167 \tag{2.18}$$

where gelation time (t) is in hours and concentration of KCl (S_{KCl}) is in moles

2.3.6 AL-MUNTASHERI et al. MODEL

Al-Muntasheri et al [21] investigated the PAM/PEI polymer system at temperature up to 140^0C and pressure up to 435 psi and studied the effects of polymer concentration, cross-linker concentration, salinity, temperature, initial pH and the initial degree of hydrolysis of the polymer system on the gelation time. The stability of the PAM gels cross-linked with PEI was confirmed at 130^0C. In-situ gelation study was conducted at a temperature of 90^0C and observed 100 % reduction in permeability. C NMR has been used to study the gelation with variation in structure of polymer. The study mentioned the importance of thermal stable polymer to form thermal stable gel.

Effect of Temperature on Gelation Time

The experimental data generated followed the Arrhenius type equation and further substantiate its applicability for many chemical reactions. The gelation time was correlated to the temperature by the following equation:

$$t = M * exp\left(\frac{E_a}{RT}\right) \tag{2.19}$$

where gelation time (t) is in seconds, time constant (M) in seconds, temperature (T) is in Kelvin, activation energy (E_a) is in kJ/mole and universal gas constant (R) is in kJ/mole-K. The activation energy of the gel PAM/PEI gel system was calculated as 71.3 kJ/mole. Al-Muntasheri plotted the gelation time data vs temperature first in distilled water than in 10,000 ppm NaCl solution by keeping other parameters constant. In distilled water, the gelation time was correlated to the temperature by the following correlation:

$$t = 2 * 10^{-10} * exp\left(8.57 * \frac{1000}{T}\right) \tag{2.20}$$

where gelation time (t) is in hours and temperature (T) is in Kelvin. In NaCl solution, the gelation time was correlated to the temperature by the following correlation:

$$t = 3 * 10^{-12} * exp\left(10.58 * \frac{1000}{T}\right) \tag{2.21}$$

where gelation time (t) is in hours and temperature (T) is in Kelvin

Effect of Polymer Concentration

Effect of polymer concentration on the gelation time was recorded by varying the polymer concentration and keeping other system parameters constant. It was found that the plot of gelation time vs polymer concentration followed Arrhenius type equation. The gelation time was correlated to the temperature by the following equation:

$$t = 4.08 * C_{po}^{-1.26} \tag{2.22}$$

where gelation time (t) in hours and base polymer concentration (C_{po}) is in wt. %

Effect of Cross-linker Concentration

Effect of cross-linker concentration was investigated by varying the cross-linker concentration and keeping other system parameters constant. The gelation time was plotted vs cross-linker concentration to get the reaction order; the graph plotted followed liner relationship in between the gelation time and cross-linker concentration. The gelation time was correlated to the temperature by the following equation:

$$t = 0.12 * C_{x}^{-0.91} \tag{2.23}$$

Where gelation time (t) is in hours and cross-linker concentration (C_x) is in wt. %

2.3.7 MARCO SA et al. MODEL

Marco SA et al. [73] studied the effect of temperature, water salinity and cross-linker concentration on the gelation time, the polymer system comprised of acrylamide/acrylate copolymer cross-linked with polyamine. The factorial design approach was used to develop the correlation and to understand how the interaction between these three parameters affects the gelation time of polymer system. The results showed that the temperature had the highest impact while water salinity showed the lowest impact. The interaction between the water salinity and the cross-linker concentration showed neutral impact on the gelation time. The predictive correlation developed for gelation time is given below:

$$t = 38.4333 - \frac{13}{75} * T + \frac{19}{30} * S - \frac{67}{30} * C_x + \frac{1}{100} * T * C_x - \frac{1}{300} * T * S \qquad (2.24)$$

Where gelation time (t) is in hours, Temperature (T) is in ^{0}F, salinity (S) is in % and cross-linker concentration (C_x) is in wt. %

2.4 CONCLUSIONS

Polymer systems reviewed for profile modification show their applicability for profile modification but the polymer systems, which are applicable at high temperature environment, are limited and therefore the investigation of polymer gel system at high temperature is needed which may be used for profile modification. In this research study, Phenol-formaldehyde gel system is taken up for investigation for profile modification.

The mathematical model consisting of polymer and cross-linker concentration as well as temperature is necessary for the designing of the profile modification and water-shut off jobs. Research done earlier only focused on relating gelation time with temperature, very few models relates gelation time with temperature and the concentration of polymer and cross-linker. The empirical models developed by researchers followed Arrhenius equation. The Arrhenius type equation supports the linear relationship between temperature and the gelation time.

CHAPTER 3: EXPERIMENT AND PROCEDURE

3.1 INTRODUCTION

The chapter highlights the various discussions about the experiments and procedure followed for doing bulk and in-situ gelation study. In bulk gelation study, experimental investigation of the Phenol-formaldehyde solutions has been investigated using bottle test method, at various conditions, for measuring gelation time and its stability. In in-situ gelation study, effectiveness of the gel system, in porous media, has been investigated.

3.2 BULK GELATION STUDY

Preparing gel mixture and placing it in glass bottles or acrylic bottles carried out bulk gelation studies. These bottles were closed with caps and placed in hot air ovens set at desired temperatures. 20 ml glass bottles with plastic caps were used for studies below 100^0C. Pressure may be build up in the closed bottles after temperatures rises above 100^0C and glass bottle may burst. Typical acrylic bottle with stainless steel cap was specially designed and fabricated for studies above 100^0C. The acrylic transparent plastic material from which bottle is made allows visibility for gel inspection from outside and has capacity to hold high pressure. The stainless steel cap allows conduction of heat to raise the temperature of gel when it is placed in hot air oven.

3.2.1 MATERIALS

Merck standard reagent-grade phenol and formaldehyde (35 % aqueous solution) were used for preparation of solution. Merck Sodium hydroxide (1 N) solution was used for adjustment of pH. The solutions were prepared with distilled water.

3.2.2 PREPARATION OF GEL MIXTURE

Phenol-formaldehyde solutions have been prepared in beaker by keeping the F/P molar ratio as 3.5. The phenol with varying concentration were measured and dissolved in distilled water. Sodium chloride (3.2 %) was then added to the solution and mixed properly using stirrer. Now formaldehyde was added to the solution keeping the formaldehyde to phenol mole ratio as 3.5. Initial pH of the solution was maintained by addition of sodium hydroxide (1 N). These solutions were then transferred to small glass bottles (20 ml) and kept in an oven at different temperature (85, 90, 105, 115 and 130^0C). Viscosity of the solutions and gelation time were measured at different time intervals.

3.2.3 GELATION TIME AND VISCOSITY MEASUREMENT

Solutions of the gel system prepared and kept in an oven at different temperatures (85, 90, 105, 115 and 130^0C) in small bottles (20 ml). The gel mixtures in bottles were manually monitored to check gel formation at different times. The earliest time when the gel solution did not fall on inversion of bottle was recorded as the gelation time. Viscosity of gels were also measured using rotational spindle Brookfield viscometer (Model DV-I +). All the viscosity measurements were done at shear rate of 0.3 rpm.

3.2.4 pH MONITORING OF GEL

Gel pH was measured and monitored using a Systronics make MK-Vi pH meter. It has combined glass electrode. It requires initial calibration with standard solutions of known pH i.e. with 4.0, 7.0 and 9.2. Calibrations need to be done every time before monitoring and displays digitally pH of gel solution on immersion of the electrode.

3.2.5 GEL STABILITY

Stability of gels have been investigated by keeping the gels for 2 months in an oven after their formation. Gels were found to be intact and stable.

3.3 IN-SITU GELATION STUDY

3.3.1 EXPERIMENTAL SETUP

The experimental set-up consists of a stainless steel core holder in which core/rock powder packed. There are two outlets on the body of the core holder apart from inlet and outlet and all these four points on core holder, connected to pressure transducers and pressure recording system for recording pressure at these points during flow studies. The core holder kept in a hot air oven while the temperature maintained at 85^0C. Syringe pump of ISCO make (model 500 D), which maintained high pressure, used for injecting fluids in the core holder. The injection fluid was stored in the buffer cylinder of acrylic pipe; paraffin-oil kept in the pump cylinder, used for displacing injection fluid in the core holder. The injection rate controlled using controller provided with the pressure pump, the inlet pressure displayed on the controller panel helps in calculation of the total pressure, which in turns used to calculate the permeability of the sandstone pack.

3.3.2 POROUS MEDIA

Porous media was prepared with sand stone sand. It was carefully packed in the cylindrical core holder of inner diameter 3.0 cm and length 30.5 cm. To ensure uniformity in packing, core powder was added in small amounts at a time in to the core holder with known volume of brine. This wet packing method was followed in order to avoid creation of any kind of fracture or channel in the core pack. Core powder was added into the tube (followed by brine) in stages and the complete core holder was packed up to the top. Volume of brine solution consumed in packing and saturation was noted as pore volume for determining porosity.

3.3.3 BRINE INJECTION

Initially brine solution was prepared by using sodium chloride (3.2 wt. %) in distilled water. It was then injected in the sand pack through the core holder at a certain flow rate to determine its permeability. Brine solution was injected in the core pack until stabilize injection pressure reading was obtained. Permeability was calculated using the Darcy's law.

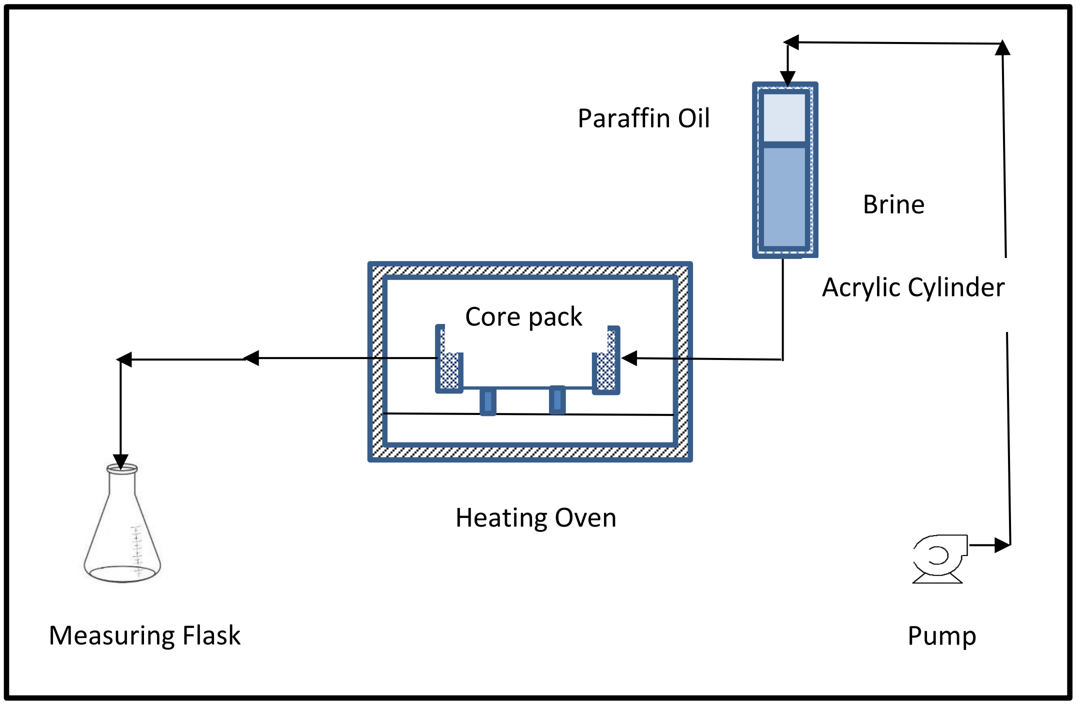


Figure 3.1: Schematic Diagram of a Core-Flooding Setup

3.3.4 GEL MIXTURE INJECTION

Initially, brine solution of 3.2 % NaCI concentration was prepared. It was filled in the buffer cylinder of acrylic pipe and injected in the pack at different rates using the pump. Subsequently, 3 or 4 pore volumes of freshly prepared gel solution were injected through the pack. After gel injection, pump was stopped and inlet and outlet valves of core holder were close. The temperature was maintained at 85^0C.

3.3.5 POST GELATION BRINE INJECTION

After keeping the core holder closed for about 36 hrs. or more after gel injection to ensure gel formation in pack. Brine injection through pack was started. The inlet pressure of pack was continuously recorded through pressure recording system and pump panel. Many pore volumes of brine were injected through the pack to observe stability of the gel. Pressure drop across pack was recorded. Post gelation permeability and residual resistance factor at different stages of brine injection were calculated.

3.3.6 COMPUTATION OF RESULTS

Porosity

It is the fraction of rock volume/ (pack volume) or bulk volume occupied by pore space. The volume is estimated by measuring the inner diameter and length of the core holder used. Pore volume is found by volume of brine used during the preparation of pack in the core holder.

Porosity (Ø) is calculated by using the expression

$$Porosity = \frac{Pore\ Volume}{Bulk\ Volume} \tag{3.1}$$

Permeability

It is the ability of the porous media to conduct a fluid through it. Darcy's law helps in calculating the permeability for laminar and linear flow of non-compressible fluids through homogenous porous media under steady state conditions. Darcy's law for above case is given by the following equation

$$Q = \frac{KA\Delta P}{\mu L} \tag{3.2}$$

Residual Resistance Factor (RRF)

Residual resistance factor is defined as ratio of brine permeability before gel injection to the brine permeability after gel injection. Residual resistance factor is a good measure of indicating the reduction in brine permeability after gelation.

Residual resistance effect helps in controlling of water fingering caused due to reservoir heterogeneity and mobility contrast.

$$\text{Residual Resistance Factor (RRF)} = \frac{\text{Brine Permeability before Gel Injection}}{\text{Brine Permeability after Gel Injection}} \qquad (3.3)$$

Decreased permeability is indicated by increased residual resistance factor. The decrease in reservoir permeability depends on the type of reservoir; reduction in permeability for sandstone reservoir is significantly higher than the carbonate cores.

3.4 CONCLUSIONS

The chapter highlights the various discussions about the experiments and procedure followed for doing bulk and in-situ gelation study. Phenol-formaldehyde solutions was bottle tested at varying condition of temperature (85, 90, 105, 115 and 130^{0}C), concentration of phenol (2.00, 2.25, 2.50 & 2.75 %) and initial pH (9.5, 10, 10.5, and 11), at constant salinity (3.2 %), by keeping the F/P molar ratio as 3.5, for measuring gelation time and its stability. The gelation behaviour of phenol-formaldehyde gel system in porous media have also been carried out to find the effectiveness of the gel system and computation of porosity, permeability and residual resistance factor done.

CHAPTER 4: EXPERIMENTAL RESULT AND DISCUSSION

4.1 INTRODUCTION

This chapter summarizes the results evaluated through different experimental studies. Bulk gelation and in-situ gelation study have been conducted for formation and propagation of gel system in porous media. Bulk gelation study helps in determination of gelation time while in-situ gelation study evaluate the effectiveness of the gel system for permeability or profile modification. In bulk gelation study, effect of phenol concentration, temperature, and initial pH of the polymer solution, on the gelation time have been investigated. In-Situ gelation study was carried out on sandstone pack to establish and investigate effectiveness of gel system developed through bulk gelation study. The study emphasis that the phenol-formaldehyde solution formed strong and stable gel and showed its applicability for high temperature and high salinity environment.

4.2 BULK GELATION STUDY

4.2.1 EFFECT OF PHENOL CONCENTRATION ON GELATION TIME

Gel mixture of 3.5 MR, 3.2% NaCl with varying pH (9.5, 10, 10.5, and 11), with different phenol concentration (1, 2, 2.25, 2.5 & 2.75 %) were prepared, and was kept at 85, 90, 105, 115 & 130^{0}C. At 1%, loose gel formed, this concentration was excluded from detailed studies. Detailed gel formation study have been conducted using phenol concentration from 2.00 to 2.75%. It is observed that the gelation time decreases with increase in concentration of phenol, the decrease in gelation time is due to the availability of more formaldehyde molecules for the condensation reaction to take place. The results are plotted in figure 4.1 to figure 4.5.

Table 4-1: Phenol Concentration vs Gelation Time at 85⁰C at different pH

Phenol, % wt	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
2.00	18	22	38	62
2.25	15	19	35	50
2.50	13	17	33	48
2.75	9	13	26	42

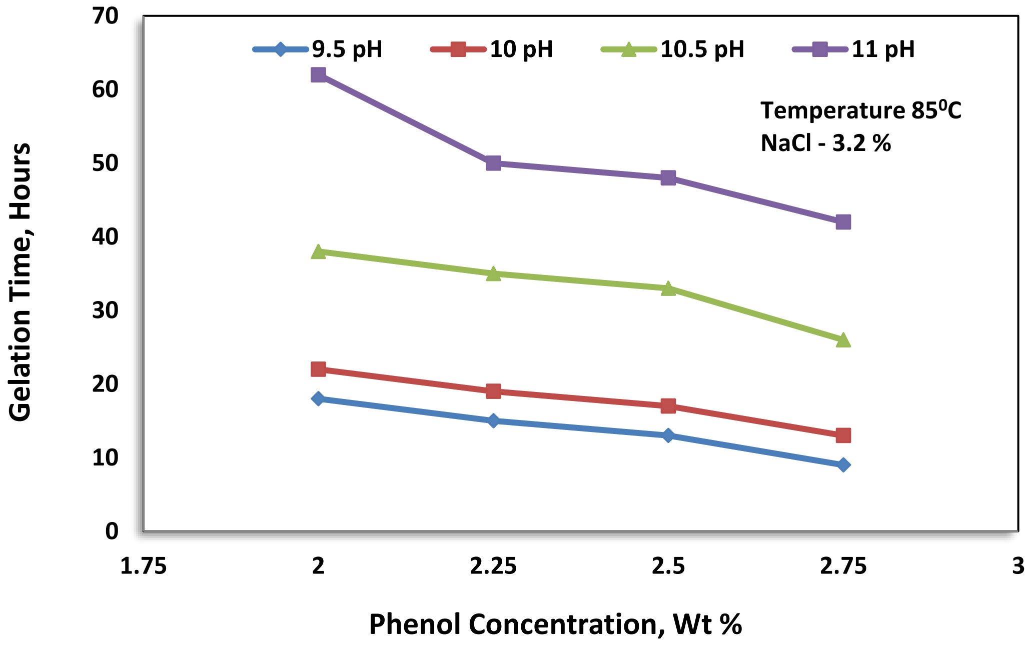


Figure 4.1: Phenol Concentration vs Gelation Time at 85⁰C at different pH

Table 4-2: Phenol Concentration vs Gelation Time at 90^{0}C at different pH

Phenol, % wt	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
2.00	15	18	30	50
2.25	11	14	28	45
2.50	10	13	24	42
2.75	8	10	19	34

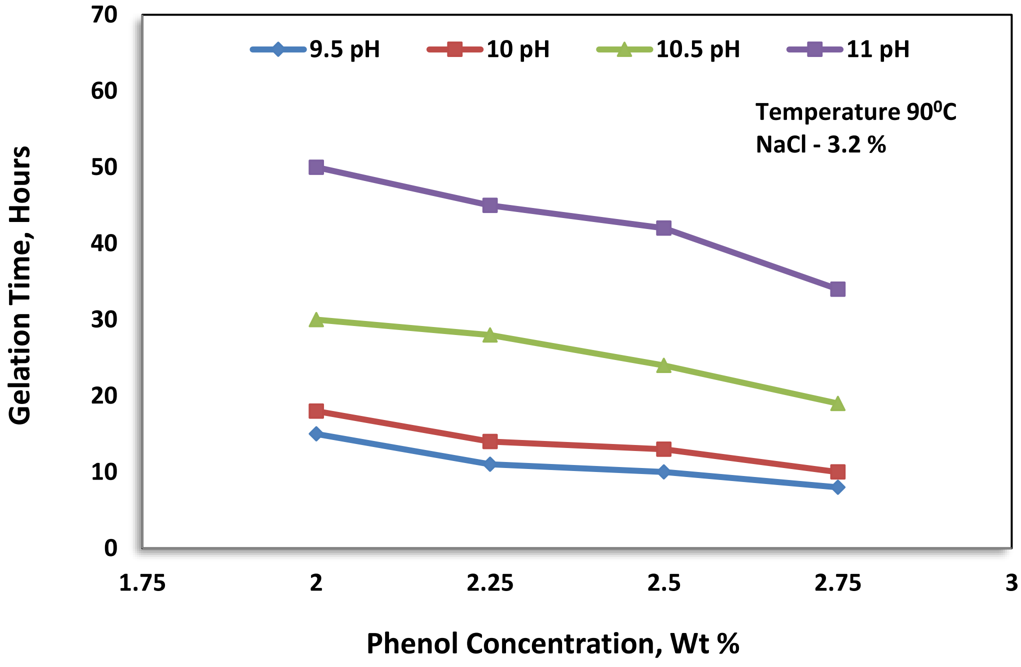


Figure 4.2: Phenol Concentration vs Gelation Time at 90^{0}C at different pH

Table 4-3: Phenol Concentration vs Gelation Time at 105^{0}C at different pH

Phenol, % wt	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
2.00	10	15	23	45
2.25	10	12	23	34
2.50	5	9	18	30
2.75	5	7	14	26

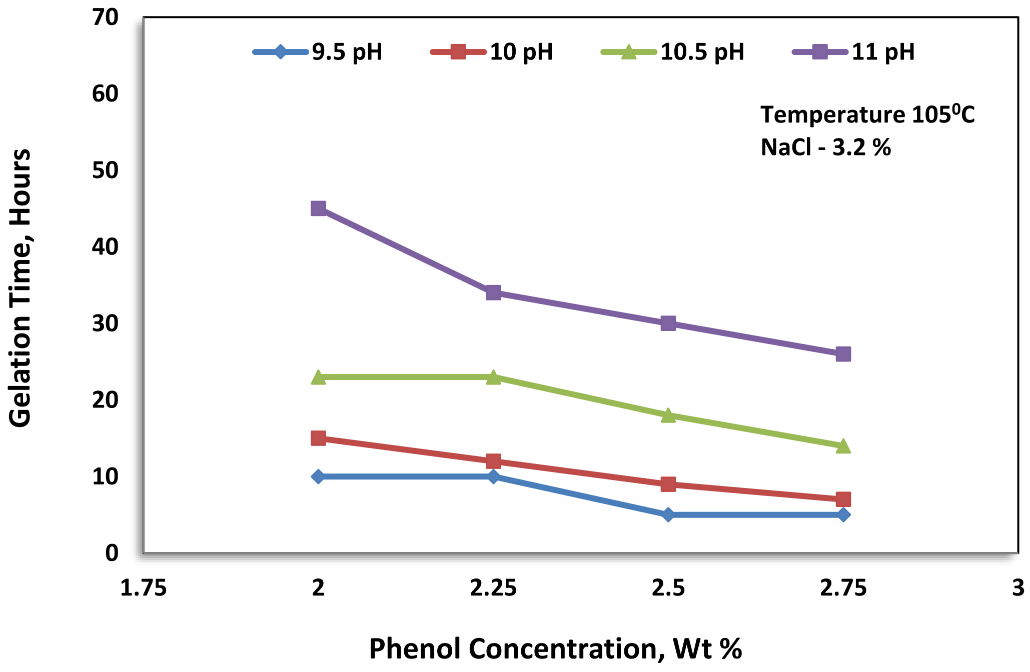


Figure 4.3: Phenol Concentration vs Gelation Time at 105^{0}C at different pH

Table 4-4: Phenol Concentration vs Gelation Time at 115^{0}C at different pH

Phenol, % wt	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
2.00	5	11	15	15
2.25	5	9	11	13
2.50	3	5	9	12
2.75	2.5	4	7	10

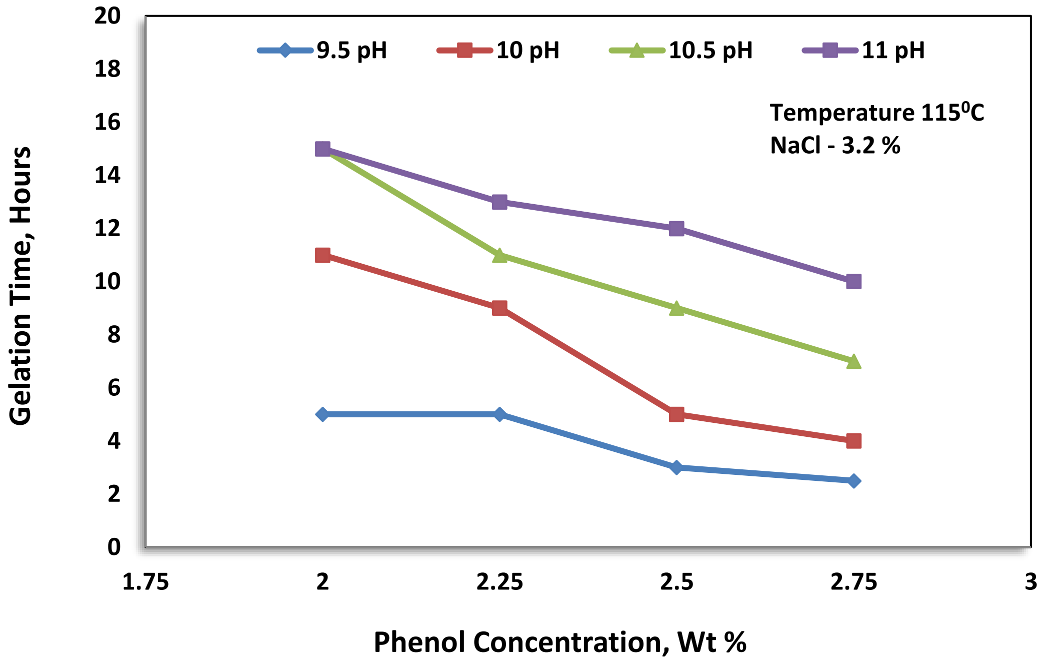


Figure 4.4: Phenol Concentration vs Gelation Time at 115^{0}C at different pH

Table 4-5: Phenol Concentration vs Gelation Time at 130^{0}C at different pH

Phenol, % wt	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
2.00	4	5	5	6
2.25	4	4.5	5	5
2.50	3	4	4.5	4.5
2.75	3	3	4	4

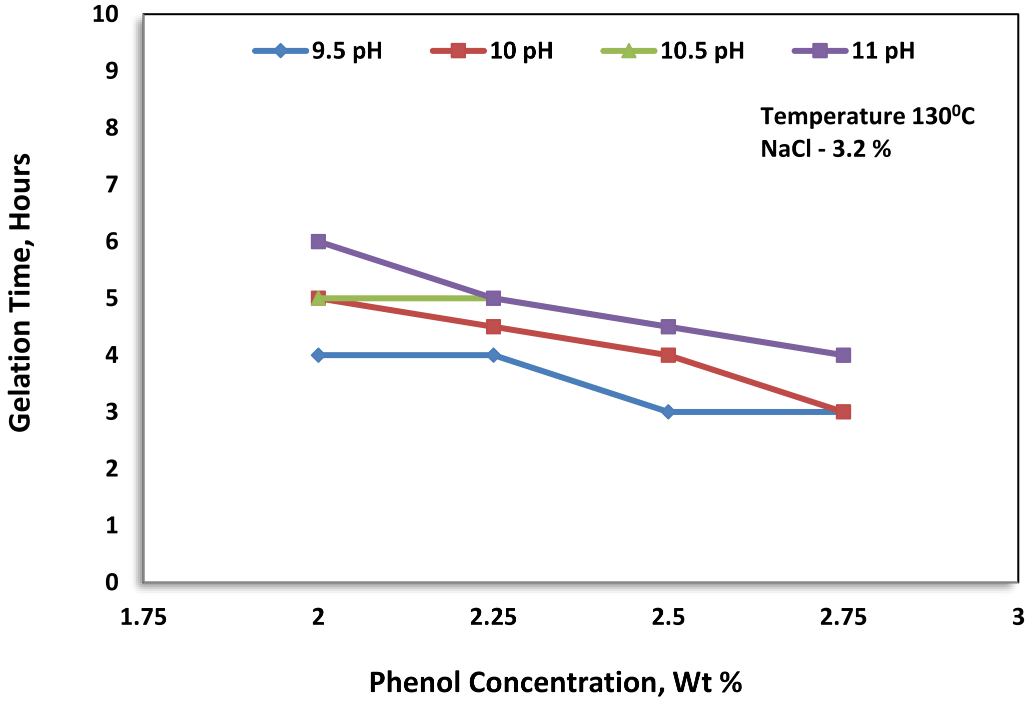


Figure 4.5: Phenol Concentration vs Gelation Time at 130^{0}C at different pH

4.2.2 EFFECT OF TEMPERATURE ON GELATION TIME

The gel mixtures were kept at temperatures 85, 90, 105, 115 and 130^{0}C. It is observed that the gelation time decreases with increase in temperature. As the rate of reaction increases at higher temperatures, the ability of the system to form a rigid gel at higher temperatures is found to be favorable and at lower temperatures the rate of reaction is found to less so, the time taken by the system to form a gel is more. The results are plotted in figure 4.6 to figure 4.9.

Table 4-6: Temperature vs Gelation Time of 2.00 % Phenol-Formaldehyde Gel at different pH

Temperature,^{0}C	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
85	18	22	38	62
90	15	18	30	50
105	10	15	23	45
115	5	11	15	15
130	4	5	5	6

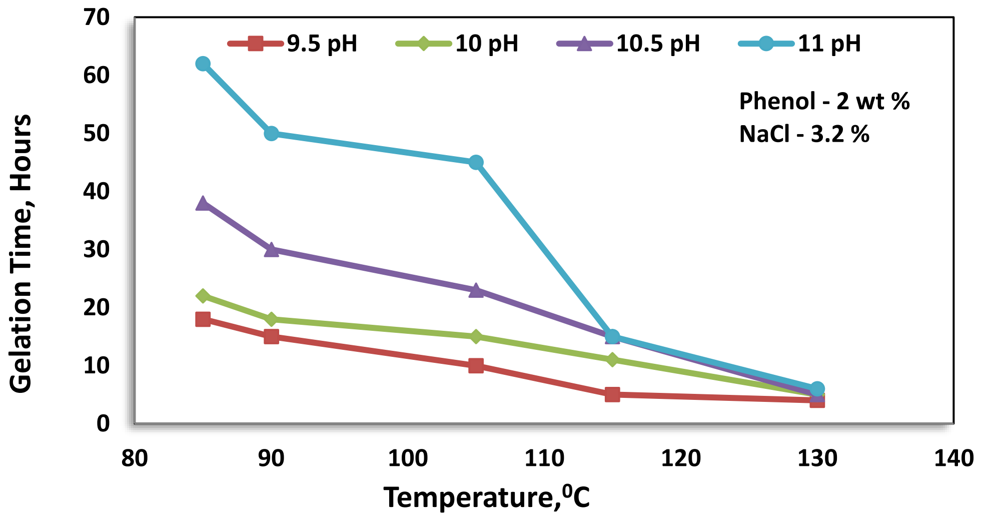


Figure 4.6: Temperature vs Gelation Time of 2.00 % Phenol-Formaldehyde Gel at different pH

Table 4-7: Temperature vs Gelation Time of 2.25 % Phenol-Formaldehyde Gel at different pH

Temperature,^{0}C	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
85	15	19	35	50
90	11	14	28	45
105	10	12	23	34
115	5	9	11	13
130	4	4.5	5	5

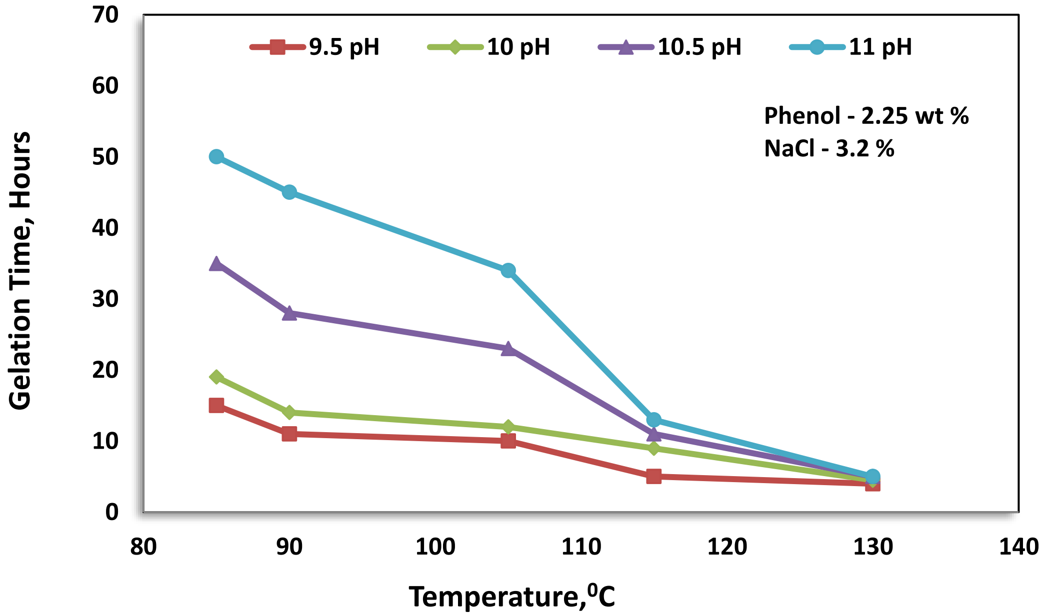


Figure 4.7: Temperature vs Gelation Time of 2.25 % Phenol-Formaldehyde Gel at different pH

Table 4-8: Temperature vs Gelation Time of 2.50 % Phenol-Formaldehyde Gel at different pH

Temperature,^{0}C	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
85	13	17	33	48
90	10	13	24	42
105	5	9	18	30
115	3	5	9	12
130	3	4	4.5	4.5

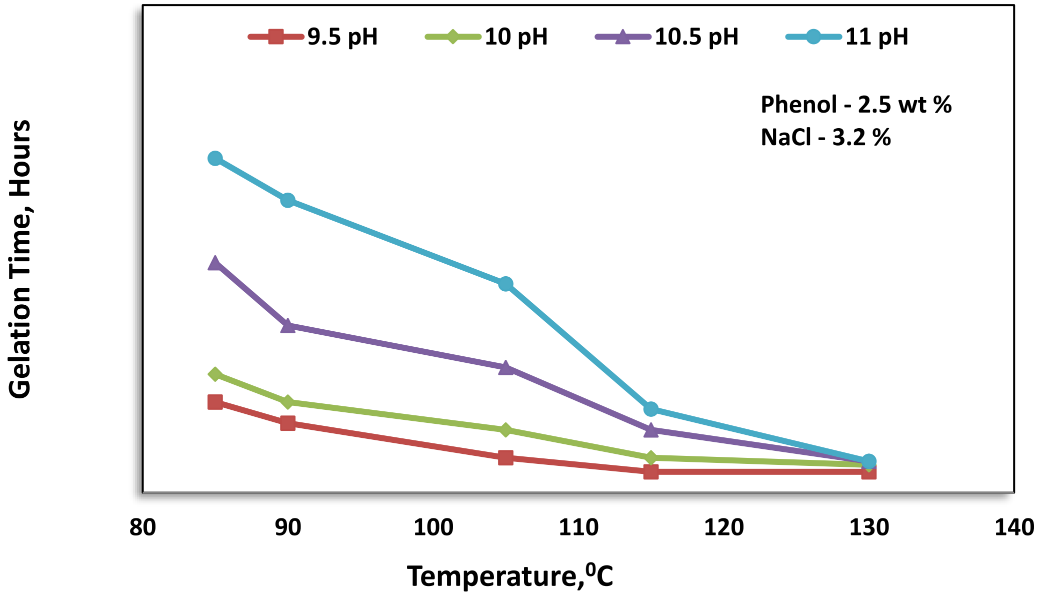


Figure 4.8: Temperature vs Gelation Time of 2.50 % Phenol-Formaldehyde Gel at different pH

Table 4-9: Temperature vs Gelation Time of 2.75 % Phenol-Formaldehyde Gel at different pH

Temperature,^{0}C	**Gelation Time, Hours**			
	pH = 9.5	**pH = 10**	**pH = 10.5**	**pH = 11**
85	9	13	26	42
90	8	10	19	34
105	5	7	14	26
115	2.5	4	7	10
130	3	3	4	4

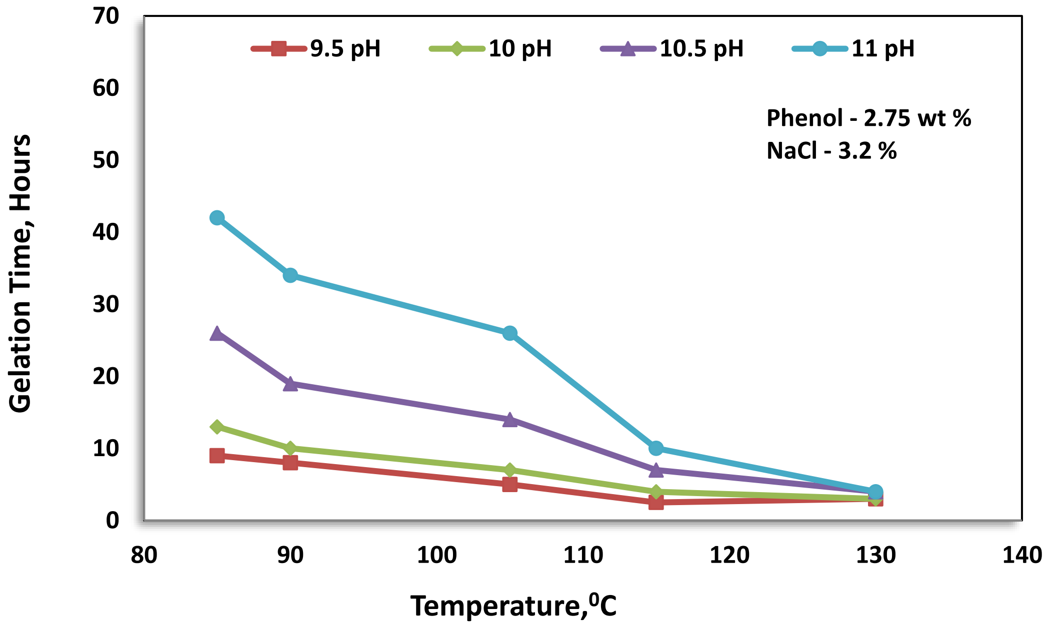


Figure 4.9: Temperature vs Gelation Time of 2.75 % Phenol-Formaldehyde Gel at different pH

4.2.3 EFFECT OF INITIAL pH OF POLYMER SOLUTION ON GELATION TIME

The initial pH of the gel solution was kept at 9.5, 10, 10.5 and 11. It is observed that the gelation time increases with increase in initial pH of the gel solution. As no gel formation took place at 9 pH. Although gel formed sometimes at 11.5 pH, but gel formation was uncertain at this pH. The results are plotted in figure 4.10 to 4.13.

Table 4-10: Initial pH vs Gelation Time of 2.00 % Phenol-Formaldehyde Gel at different Temperature

Initial pH	**Gelation Time, Hours**				
	T = 85^{0}C	**T = 90^{0}C**	**T = 105^{0}C**	**T = 115^{0}C**	**T = 130^{0}C**
9.5	18	15	10	5	4
10	22	18	15	11	5
10.5	38	30	23	15	5
11	62	50	45	15	6

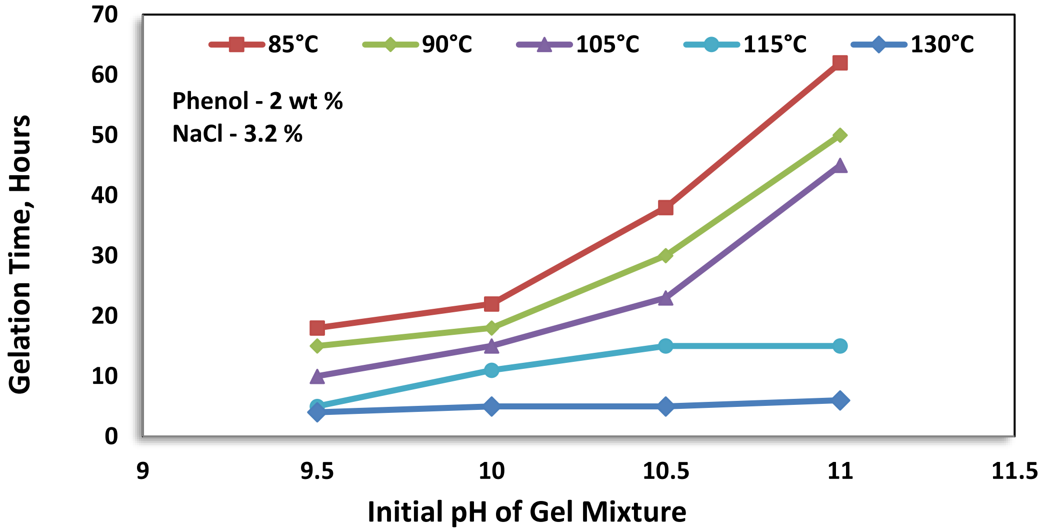


Figure 4.10: Initial pH vs Gelation Time of 2.00 % Phenol-Formaldehyde Gel at different Temperature

Table 4-11: Initial pH vs Gelation Time of 2.25 % Phenol-Formaldehyde Gel at different Temperature

Initial pH	**Gelation Time, Hours**				
	T = 85^{0}C	**T = 90^{0}C**	**T = 105^{0}C**	**T = 115^{0}C**	**T = 130^{0}C**
9.5	15	11	10	5	4
10	19	14	12	9	4.5
10.5	35	28	23	11	5
11	50	45	34	13	5

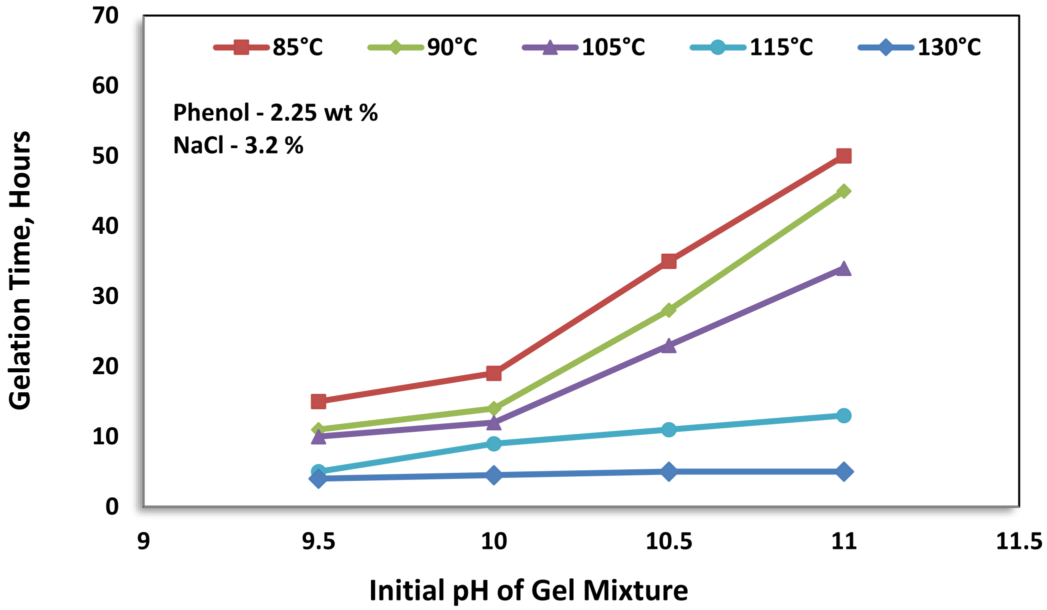


Figure 4.11: Initial pH vs Gelation Time Of 2.25 % Phenol-Formaldehyde Gel at different Temperature

Table 4-12: Initial pH vs Gelation Time of 2.50 % Phenol-Formaldehyde Gel at different Temperature

Initial pH	**Gelation Time, Hours**				
	T = 85^{0}C	**T = 90^{0}C**	**T = 105^{0}C**	**T = 115^{0}C**	**T = 130^{0}C**
9.5	13	10	5	3	3
10	17	13	9	5	4
10.5	33	24	18	9	4.5
11	48	42	30	12	4.5

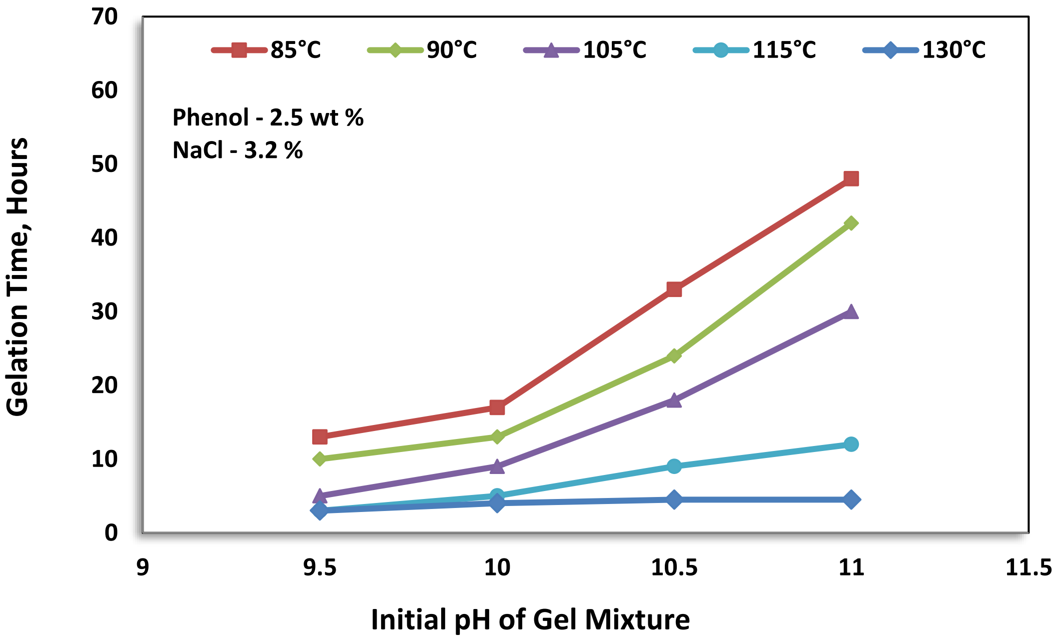


Figure 4.12: Initial pH vs Gelation Time of 2.50 % Phenol-Formaldehyde Gel at different Temperature

Table 4-13: Initial pH vs Gelation Time of 2.75 % Phenol-Formaldehyde Gel at different Temperature

Initial pH	**Gelation Time, Hours**				
	T = 85^{0}C	**T = 90^{0}C**	**T = 105^{0}C**	**T = 115^{0}C**	**T = 130^{0}C**
9.5	9	8	5	2.5	3
10	13	10	7	4	3
10.5	26	19	14	7	4
11	42	34	26	10	4

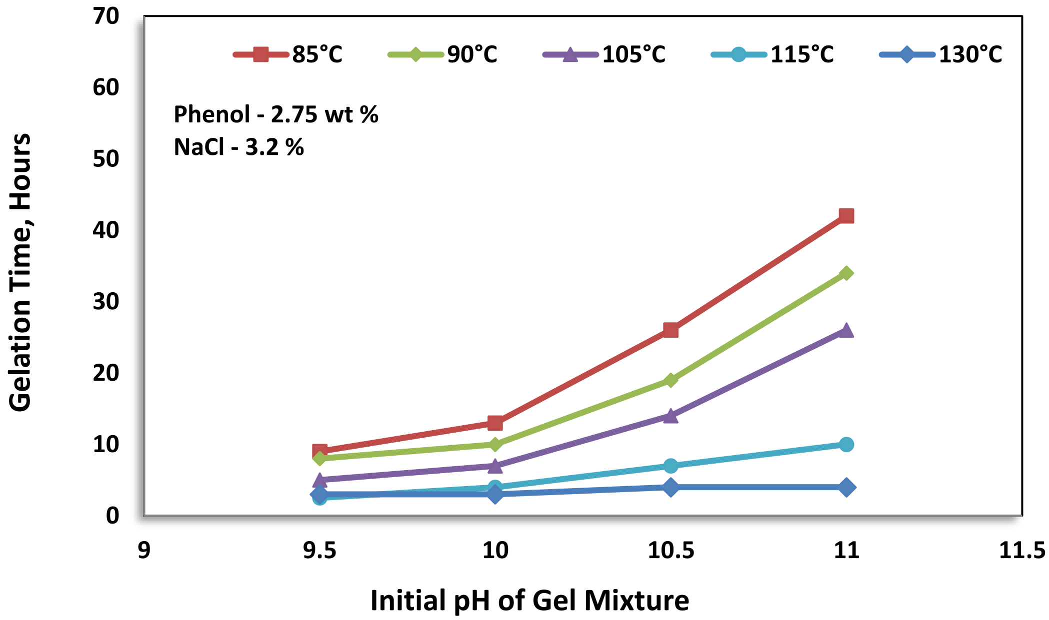


Figure 4.13: Initial pH vs Gelation Time of 2.75 % Phenol-Formaldehyde Gel at different Temperature

4.2.4 VISCOSITY MEASUREMENT OF POLYMER GEL

The increase in viscosity with time is measured at shear rate of 0.3 rpm of 2.00 and 2.25 % phenol in phenol formaldehyde gel system at 85^{0}C and salinity at 3.2 %. The initial pH of the gel solution is maintained as 10. It is observed that the initial viscosity of nearly 1.03 was grown up to 422 for 2.0 % phenol formaldehyde gel and 1.12 cP was grown up to 458 cP for 2.25 % phenol formaldehyde gel. The initial increase in viscosity is found to be slow and it increases rapidly during final gelation period. The reason for the increase in viscosity is due to condensation of more phenolic molecules as the reaction proceeds. The results are plotted in figure 4.14 and 4.15.

Table 4-14: Viscosity vs Gelation Time of Phenol-Formaldehyde Gel at Phenol 2 %, NaCl 3.2 %, Initial pH 10, Temperature 85^{0}C, F/P Mole ratio 3.5

Gelation Time, Hours	Apparent Viscosity, Centipoise
0	1.03
4	1.08
8	1.28
12	218
16	315
22	422

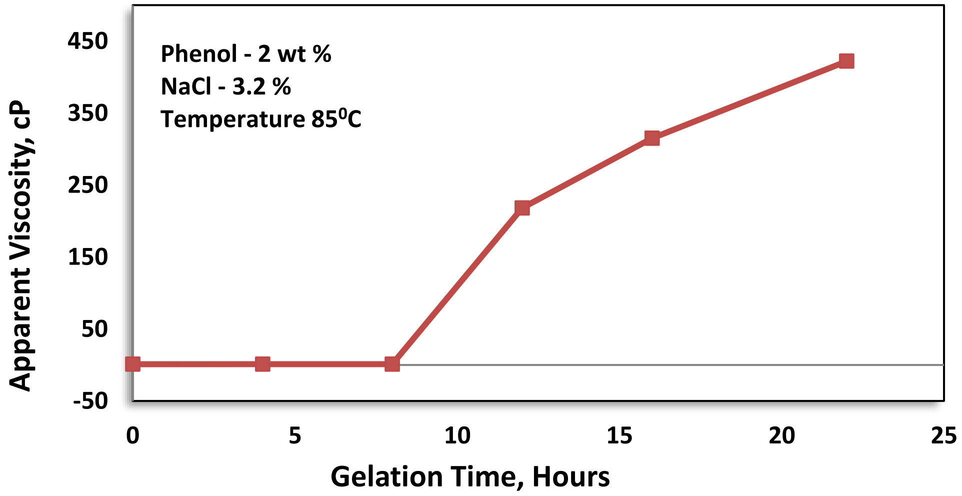


Figure 4.14: Viscosity vs Gelation Time of Phenol-Formaldehyde Gel at Phenol 2.00 %, NaCl 3.2 %, Initial pH 10, Temperature 85^{0}C, F/P Mole Ratio 3.5

Table 4-15: Viscosity vs Gelation Time of Phenol-Formaldehyde Gel at Phenol 2.25 %, NaCl 3.2%, Initial pH 10, Temperature 85^{0}C, F/P Mole Ratio 3.5

Gelation Time, Hours	Apparent Viscosity, Centipoise
0	1.12
4	1.15
8	1.28
12	254
16	378
19	458

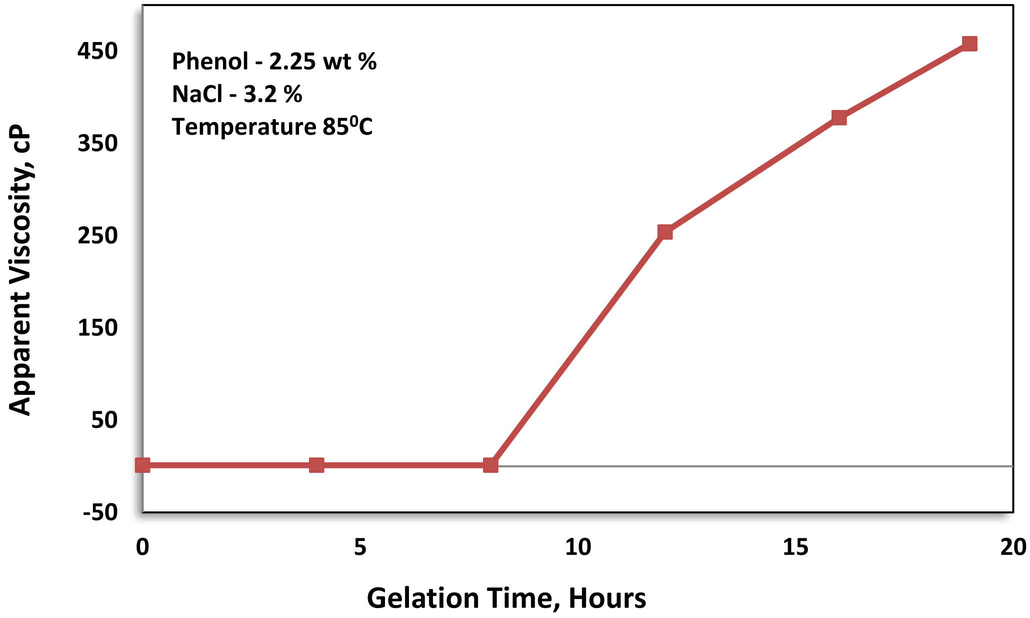


Figure 4.15: Viscosity vs Gelation Time of Phenol-Formaldehyde Gel at Phenol 2.25 %, NaCl 3.2 %, Initial pH 10, Temperature 85^{0}C, F/P Mole Ratio 3.5

4.3 IN-SITU GELATION STUDY

In-Situ gelation study was carried out on sandstone pack to establish and investigate effectiveness of gel system developed through bulk gelation study. Phenol-formaldehyde gel system with 2.25% phenol concentration was used for in-situ gelation studies. Formaldehyde to phenol ratio mole ratio of 3.5 was used to prepare gels for the pack. The study was conducted at 85^0C. In this study pack were prepared from sandstone to observe effectiveness of gel in sandstone reservoir.

4.3.1 POST GELATION PERMEABILITY AND RESIDUAL RESISTANCE FACTOR

Sandstone pack porosity was found to be 26.90 % with initial permeability of 32.77 md (before gel mixture injection). Initial permeability of 32.77 md is brought down to 2.226 md after gel placement in core pack. The decrease in permeability of the core pack is due to the adsorption of polymer molecules on the rock matrix. Fig 4.16 shows the post gelation permeability at different brine volume injected after in-situ gelation and Fig 4.17 shows the residual resistance factor at different brine volumes injected after in-situ gelation.

The residual resistance factor of 12.498 is observed at 1.159 pore volume of brine injected and increased up to 14.721 at 25.390 pore volume of brine injected.

Table 4-16: In-Situ Gelation Study in Sandstone Pack - Post Gelation Brine Injection

S.No.	Rate (ml./hr)	Brine Volume Injected, Pore Volume, ml.	Post Gelation Permeability, md	Residual Resistance Factor (RRF)
1.	20	0.01	5.13	6.380
2.		0.286	3.10	10.571
3.		0.92	2.809	11.666
4.		0.793	2.682	12.218
5.		1.159	2.622	12.498
6.		2.857	2.622	12.498
7.		3.460	2.622	12.498
8.	30	3.889	3.540	9.257
9.		4.603	3.218	10.183
10.		5.518	2.950	11.108
11.		6.032	2.082	15.739
12.		6.349	2.082	15.739
13.		9.524	2.082	15.739
14.	40	10.952	2.622	12.498
15.		15.079	2.484	13.192
16.		15.555	2.408	13.608
17.		19.286	2.316	14.149
18.		21.031	2.226	14.721
19.		22.381	2.226	14.721
20.		25.390	2.226	14.721

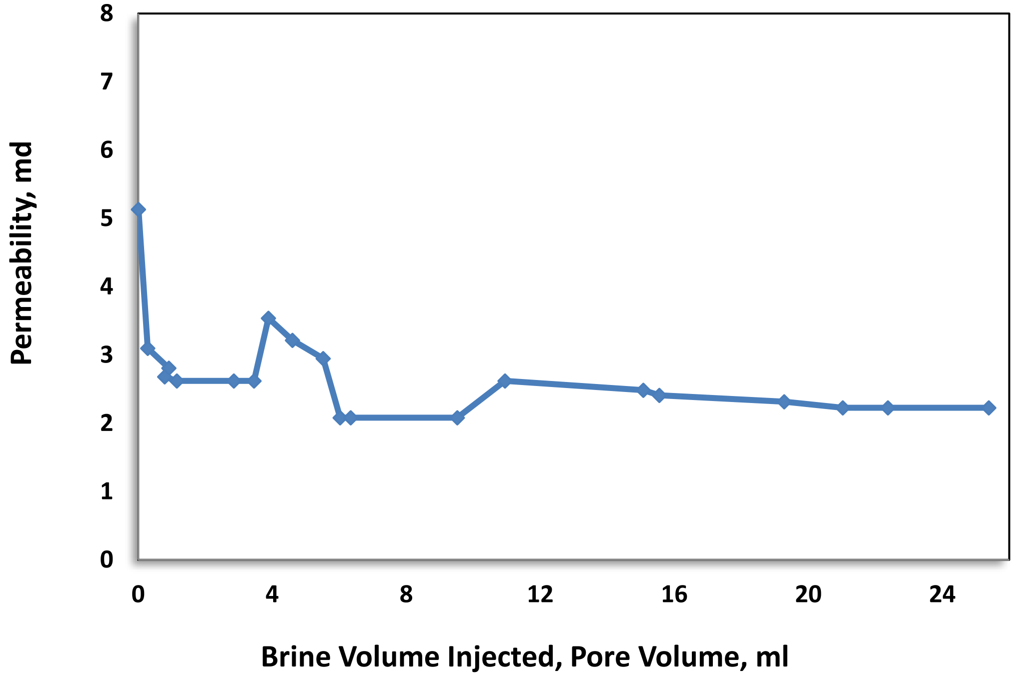


Figure 4.16: Permeability vs Brine Volume Injected

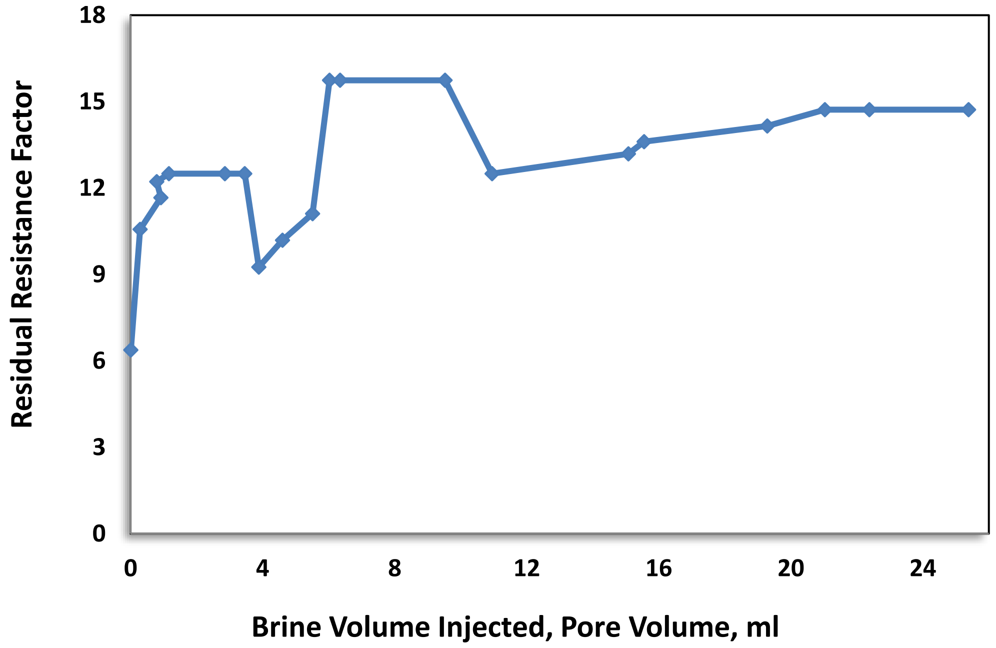


Figure 4.17: Residual Resistance Factor vs Brine Volume Injected

4.4 CONCLUSIONS

This chapter summarizes the results evaluated through different experimental studies. The study emphasis that the phenol-formaldehyde solution formed strong and stable gel and showed its applicability for high temperature and high salinity environment. Phenol formaldehyde system forms a strong gel at the temperature ranging from 85 to 130^0C with phenol concentration ranging from 2.00 to 2.75 % in the pH range of 9.5 to 11.0. Thermal stability of the gel is observed experimentally up to the temperature of 130^0C. Initial gelation has been observed at an average temperature for hydrocarbon reservoirs. Gelation time increases with increase in initial pH of the polymer solution however, it decreases with increase in temperature and phenol concentration at a particular temperature. Viscosity growth is low at initial stage and increases in the later stage. Phenol-Formaldehyde gel system have not indicated any gel syneresis at higher temperature (130^0C) for a period of two months indicating their stability. Phenol-Formaldehyde gel system gives excellent permeability reduction as indicated by Residual Resistance Factor (RRF) values determined experimentally during in-situ gelation studies.

CHAPTER 5: MATHEMATICAL MODELING AND SIMULATION STUDY OF PHENOL-FORMALDEHYDE GEL SYSTEM

5.1 INTRODUCTION

Attempt has been made to describe the reaction mechanism of phenol-formaldehyde polymer system. Mathematical model has been developed in order to have the quantitative understanding of the gelation behaviour of phenol-formaldehyde gel system. The models developed by researchers follows mainly Arrhenius type models as per the literature review. The Arrhenius type models relates the gelation time with only one variable i.e. temperature. The models developed earlier indicates that the reaction temperature is having profound effect on the gelation mechanism; however, the impact of polymer concentration on the gelation time was not considered. Therefore, there is a need to develop the mathematical model that can relate the gelation time with temperature and concentration of reactants. Mathematical model has been developed using power law and Arrhenius equation, which can predict the gelation time of the phenol-formaldehyde gel system at the varying condition of temperature, phenol-formaldehyde concentration. The chapter also provides the steps involved in the simulation study of the mathematical model developed for predicting the gelation behaviour of phenol-formaldehyde gel system.

5.2 GEL STRUCTURE: REACTION MECHANISM OF PHENOL-FORMALDEHYDE GEL SYSTEM

Reaction mechanism of phenol and formaldehyde is quite complex due to the formation of many intermediate products. Phenol-formaldehyde gel formulation depends on the type of catalyst and the mole ratio of the reactants. The reaction can be acid or base catalysed leading to formation of different product. There are two possible courses of reactions between phenol and formaldehyde leading to three dimensional structure gels through polymerization [74] [69] [75]. In case of excess formaldehyde and base catalyst, the initial product formed is resole, which finally leads to formation of network structure. In case of excess phenol and acid catalyst, the initial product formed is novalac. The formation of either resole or novalac is evident by an increase in viscosity.

Luo and Lu et al. [76] suggest that the theoretical molar ratio required in between formaldehyde to phenol (F/P) , to form resole, is in between 1.0 and 3.0 and polymerisation reaction of phenol-formaldehyde in base catalyst takes place in three stages: addition, condensation and curing. In the first step, formaldehyde combine with phenol to form isomers of methyolphenols. In the second step, isomers of methyolphenols condenses to form a low molecular weight prepolymer resole. In the third and final step, the prepolymer on curing converts to a high molecular weight cross-linked polymer.

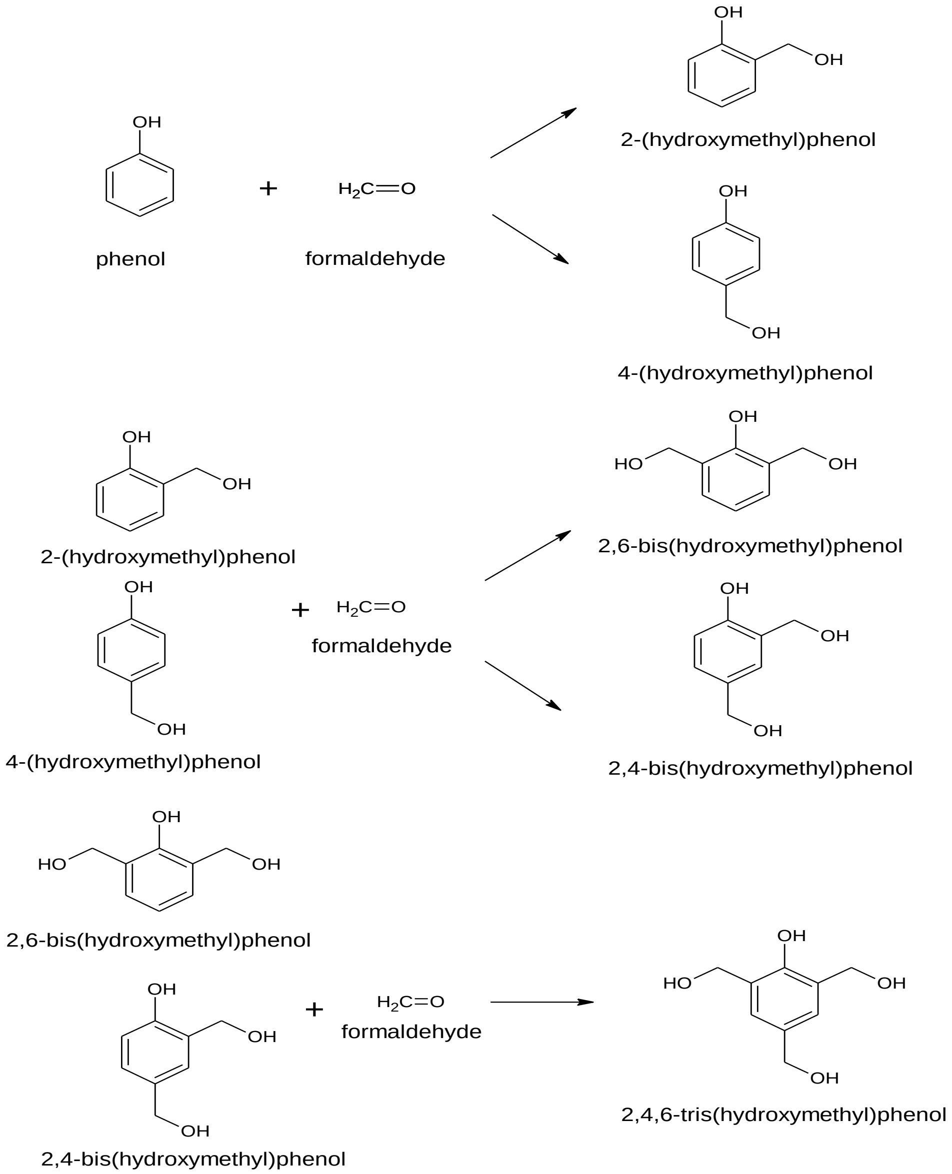
Luo et al. [77] suggest that the theoretical molar ratio required in between formaldehyde to phenol (F/P), to form novalac, is in between 0.7 and 0.9 and polymerisation reaction of phenol-formaldehyde in acid catalyst takes place in three stages: addition, condensation and curing. In the first step, formaldehyde combine with phenol to form isomers of methyolphenols. In the second step, isomers of methyolphenols condenses to form dihydroxydiphenyl methane. In the third and final step, on heating, condensed to form liner structure novalac.

5.2.1 GEL STRUCTURE: THROUGH RESOLE FORMATION

Resoles [78] are the product of the reaction between phenol and excess formaldehyde in the presence of base. When phenol treated with excess formaldehyde in the presence of alkali, the extent of cross-linking is low due to low concentration of phenol used. Due to this, the gel is comparatively soft and not as hard as Bakelite. The general chemistry of phenol-formaldehyde gel formation happens in three steps: addition, condensation and heating.

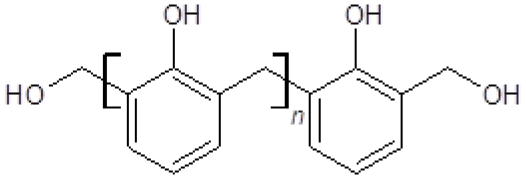
5.2.1.1 ADDITION REACTION

In the first step, phenol and formaldehyde added to form methylol derivatives. The different methylol derivates formed are 2-hydroxymethyl phenol, 4-hydroxymethyl phenol, 2,6-bis hydroxymethyl phenol, 2,4-bis hydroxymethyl phenol, 2,4,6-tris hydroxymethyl phenol



5.2.1.2 CONDENSATION REACTION

In the second step, methylol derivatives and phenol condensed to form prepolymer resole. The prepolymers are low molecular polymer with less number of monomeric units.



5.2.1.3 CURING REACTION

In the third step, the prepolymer is cured on heating to form a high molecular weight cross-linked polymer [75]

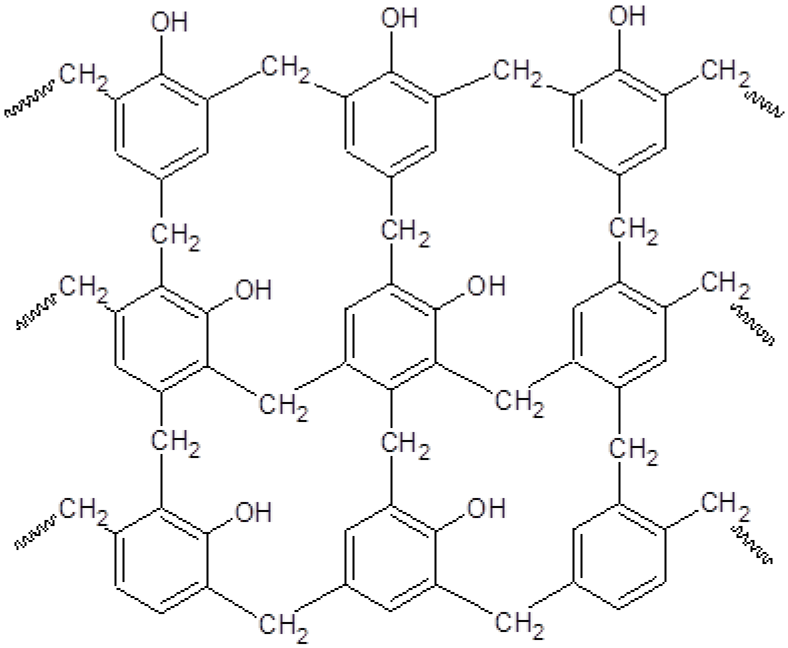


Figure 5.1: Phenol-Formaldehyde Gel Structure

5.3 MATHEMATICAL MODEL AND GOVERNING EQUATIONS

Let the reaction in between phenol and formaldehyde to form gel structure, follows the below chemical reaction:

$$\mathbf{xA + yB \longrightarrow \text{Gel Structure}}$$

In the above chemical reaction, phenol and formaldehyde are represented by "A" and "B" respectively while the stoichiometric coefficient of phenol and formaldehyde are represented by "x" and "y" respectively.

The ***Power Law***, which relates the rate of chemical reaction with the concentration of reactants, is mentioned below for the above chemical reaction

$$-r_P = \frac{-dC_P}{dt} = k\, C_P^a\, C_F^b \tag{5.1}$$

Where, C_P and C_F are the concentration of phenol and formaldehyde respectively, "a" and "b" are the reaction order with respect to phenol and formaldehyde respectively and k is the reaction rate.

If the reactants are present in their stoichiometric ratios, they will remain same throughout the reaction and therefore, the following relation relates the concentration of phenol and formaldehyde

$$\frac{C_F}{C_P} = \frac{y}{x} \tag{5.2}$$

or

$$C_P = \frac{y}{x}\, C_F \tag{5.3}$$

Combining, Equating 5.2 and Equating 5.3, we have

$$-r_P = \frac{-dC_P}{dt} = k\, C_P^a \left(\frac{y}{x}\, C_P\right)^b = k\left(\frac{y}{x}\right)^b C_P^{a+b} \tag{5.4}$$

or

$$-r_P = k' C_P^n \tag{5.5}$$

On integration from initial concentration of phenol (C_{A0}) to final concentration of phenol (C_A)

$$t = \frac{1}{k'} \frac{1}{n-1} \left(\frac{1}{C_P^{n-1}} - \frac{1}{C_{P0}^{n-1}} \right) \tag{5.6}$$

Replacing the value of n and k', the equation becomes

$$t = \frac{1}{k} \frac{1}{(a+b-1)} \left(\frac{C_P}{C_P^a \, C_F^b} - \frac{C_{P0}}{C_{P0}^a \, C_{F0}^b} \right) \tag{5.7}$$

According to ***Arrhenius Equation.***, the rate constant (k) relates with temperature by the following equation

$$k = M * exp \left(\frac{-E_a}{RT} \right) \tag{5.8}$$

Where gelation time (t) is in seconds, time constant (M) in seconds, temperature (T) is in Kelvin, activation energy (E_a) is in kJ/mole and universal gas constant (R) is in kJ/mole/K.

The equation (5.7) and (5.8) are combined to get the combined effect on the gelation time

$$t \quad = \frac{1}{M} \frac{1}{(a+b-1)} \left(\frac{C_P}{C_P^a \, C_F^b} - \frac{C_{P0}}{C_{P0}^a \, C_{F0}^b} \right) * exp \left(\frac{E_a}{RT} \right) \tag{5.9}$$

Taking log on both sides and introducing coefficients,

$$\ln t = b_0 + b_1 \ln C_P + b_2 \ln C_F + \frac{b_3}{T} \tag{5.10}$$

Again, taking antilog on both sides

$$t = C_P^{b_1} + C_F^{b_2} + exp\left(b_0 + \frac{b_3}{T}\right) \tag{5.11}$$

The above equation is a mathematical model of the gelation behavior of the phenol-formaldehyde based on the gelation time and concentration of reactants. The value of the constant depends on the concentration of the phenol, formaldehyde and the temperature at a particular pH.

5.4 SIMULATION STUDY OF POLYMER GEL SYSTEM

The mathematical model of polymer gel system have three independent variables, one dependent variables and four constants (b_0, b_1, b_2 and b_3). The three independent variables are C_P (concentration of phenol in moles/litre), C_F (concentration of formaldehyde in moles/litre) and T (temperature in kelvin); one dependent variable is t (gelation time in seconds); four constants (b_0, b_1, b_2 and b_3). The section provides the steps involved in the simulation study of the mathematical model developed for predicting the gelation behaviour of phenol-formaldehyde gel system.

5.4.1 STEPS INVOLVED IN THE SIMULATION STUDY OF THE MATHEMATICAL MODEL

The model developed is a non-linear regression model, in order to solve the mathematical model four equations, as there are four constants, generated by utilizing the experimental data. The equations are solved using the software MATLAB with four constants estimated utilizing the fsolve optimization tool. The gelation time was calculated by varying the different parameters (C_P, $C_{F,}$ and T) and utilizing the optimized value of four constants (b_0, b_1, b_2 and b_3). Finally, the calculated values of gelation time compared with the experimental data, energy of activation of the reaction between phenol-formaldehyde compared with the literature for verification of the mathematical model. The optimized value of the four constants estimated are $b_0 = 0.349$, $b_1 = 4.016$, $b_2 = -6.531$ and $b_3 = 5326.69$ and the activation energy estimated comes out to be 10.58 Kcal/mole which is matching with literature.

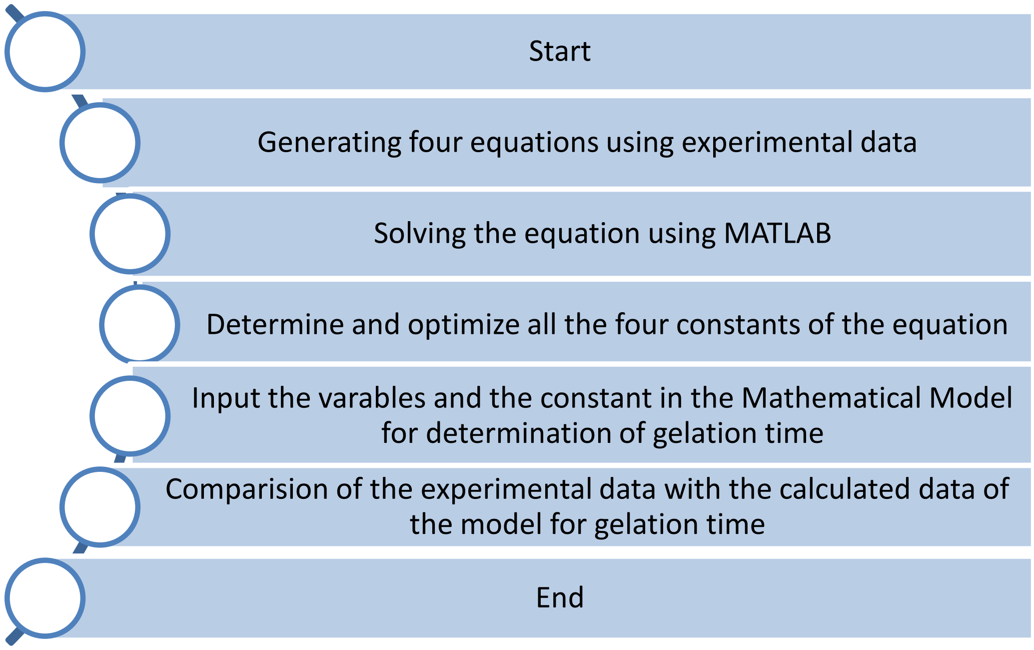


Figure 5.2: Flow Diagram of the Simulation Study of the Mathematical Model of Polymer System

The equation below is a gelation model for phenol-formaldehyde polymer system, the value of the constant depends on the concentration of the phenol, formaldehyde and the temperature at a particular pH.

$$\ln t = b_0 + b_1 \ln C_P + b_2 \ln C_F + \frac{b_3}{T}$$

Where t is the gelation time in sec, C_P is the concentration of phenol in mole/litre, C_F is the concentration of formaldehyde in mole/litre and T is the temperature in kelvin.

The four equations generated using experimental data keeping pH (= 9.5) constant, mentioned below:

At phenol concentration (C_p = 0.2 moles/litre), formaldehyde concentration (C_F = 0.7 moles/litre) and temperature = 358 K, the experimental gelation time is 64800 second, the above equation is written as:

$$\ln 64800 = b_0 + b_1 \ln 0.2 + b_2 \ln 0.7 + \frac{b_3}{358} \tag{5.12}$$

At phenol concentration (C_p = 0.2 moles/litre), formaldehyde concentration (C_F = 0.7 moles/litre) and temperature = 363 K, the experimental gelation time is 39600 second, the above equation is written as:

$$\ln 39600 = b_0 + b_1 \ln 0.2 + b_2 \ln 0.7 + \frac{b_3}{363} \tag{5.13}$$

At phenol concentration (C_p = 0.2 moles/litre), formaldehyde concentration (C_F = 0.7 moles/litre) and temperature = 378 K, the experimental gelation time is 18000 second, the above equation is written as:

$$\ln 18000 = b_0 + b_1 \ln 0.2 + b_2 \ln 0.7 + \frac{b_3}{378} \tag{5.14}$$

At phenol concentration (C_p = 0.2 moles/litre), formaldehyde concentration (C_F = 0.7 moles/litre) and temperature = 388 K, the experimental gelation time is 9000 second, the above equation is written as:

$$\ln 9000 = b_0 + b_1 \ln 0.2 + b_2 \ln 0.7 + \frac{b_3}{388} \tag{5.15}$$

Equation 42, 43, 44 and 45 are solved using fsolve in matlab and the optimized value of the constant b_0 = 0.349, b_1 = 4.016, b_2 = -6.531 and b_3 = 5326.69 are estimated. The gelation time of phenol-formaldehyde polymer gel system with varying concentration of phenol, concentration of formaldehyde and Temperature at constant pH (=9.5) was calculated and compared with the experimental values.

Table 5-1: Experimental vs Theoretical Gelation Time

Phenol (Mole/Litre)	**Formaldehyde (Mole/Litre)**	**Temperature (^{0}C)**	**Experimental Gelation time (Hours)**	**Theoretical Gelation Time (Hours)**
0.2	0.700	85	18	18
0.2	0.700	90	15	15
0.2	0.700	105	10	8
0.2	0.700	115	5	6
0.2	0.700	130	4	3
0.225	0.788	85	15	14
0.225	0.788	90	11	11
0.225	0.788	105	10	6
0.225	0.788	115	5	4
0.225	0.788	130	4	4
0.25	0.875	85	13	10
0.25	0.875	90	10	8
0.25	0.875	105	5	5
0.25	0.875	115	3	3
0.25	0.875	130	3	3
0.275	0.963	85	9	8
0.275	0.963	90	8	7
0.275	0.963	105	5	4
0.275	0.963	115	2.5	3
0.275	0.963	130	3	3

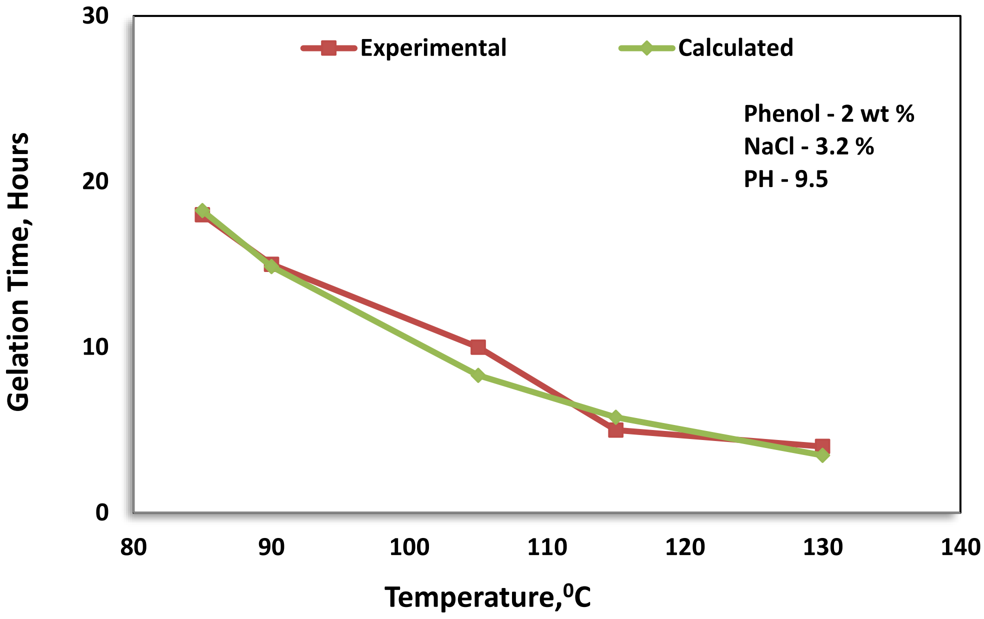


Figure 5.3: Experimental vs Theoretical Gelation Time of 2.00 % Phenol-Formaldehyde Gel

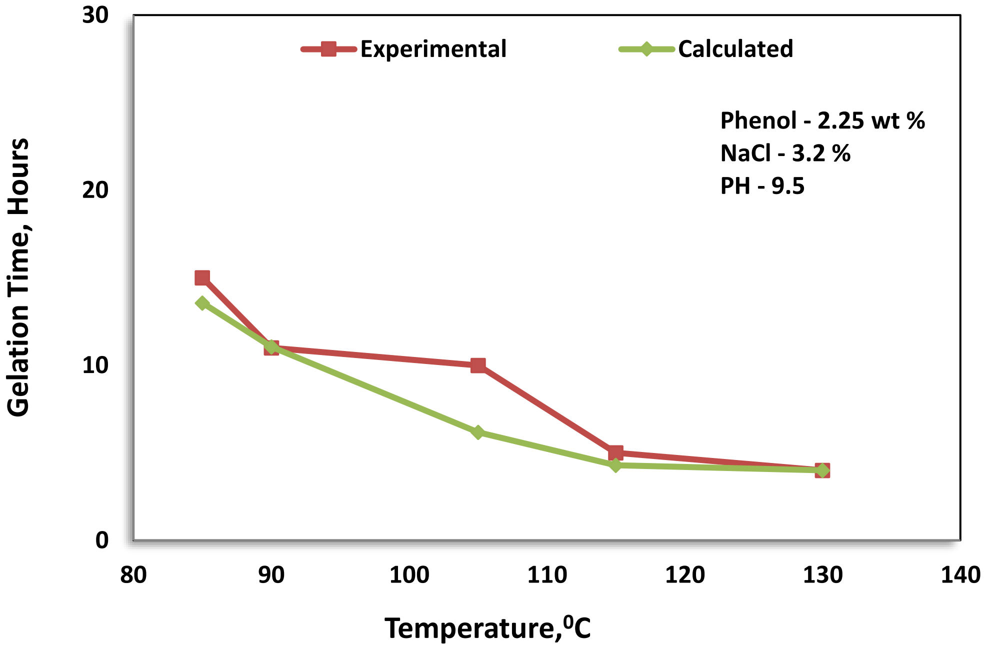


Figure 5.4: Experimental vs Theoretical Gelation Time of 2.25 % Phenol-Formaldehyde Gel

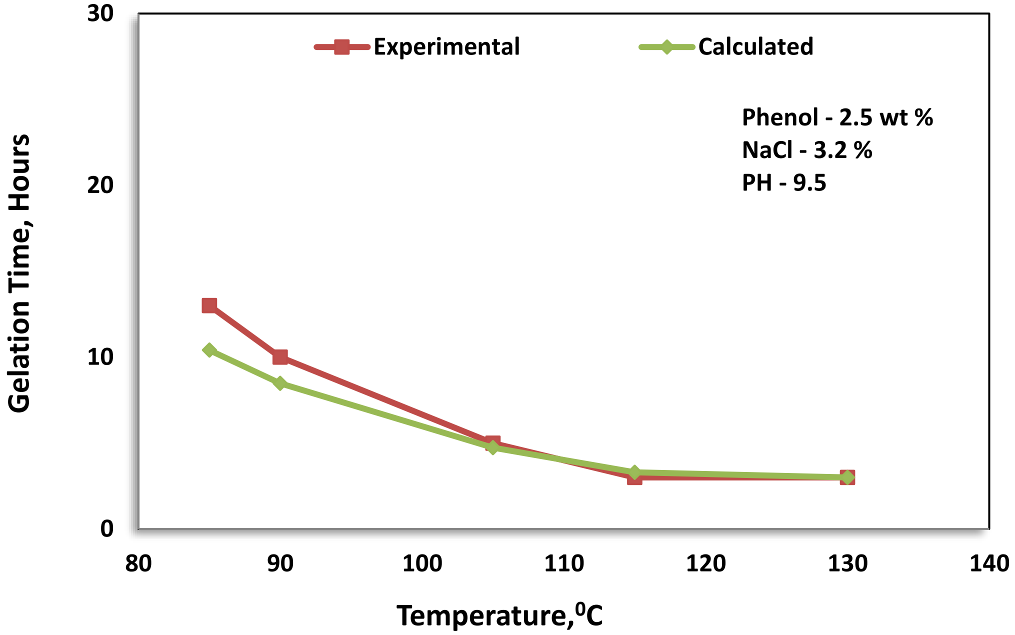


Figure 5.5: Experimental vs Theoretical Gelation Time of 2.5 % Phenol-Formaldehyde Gel

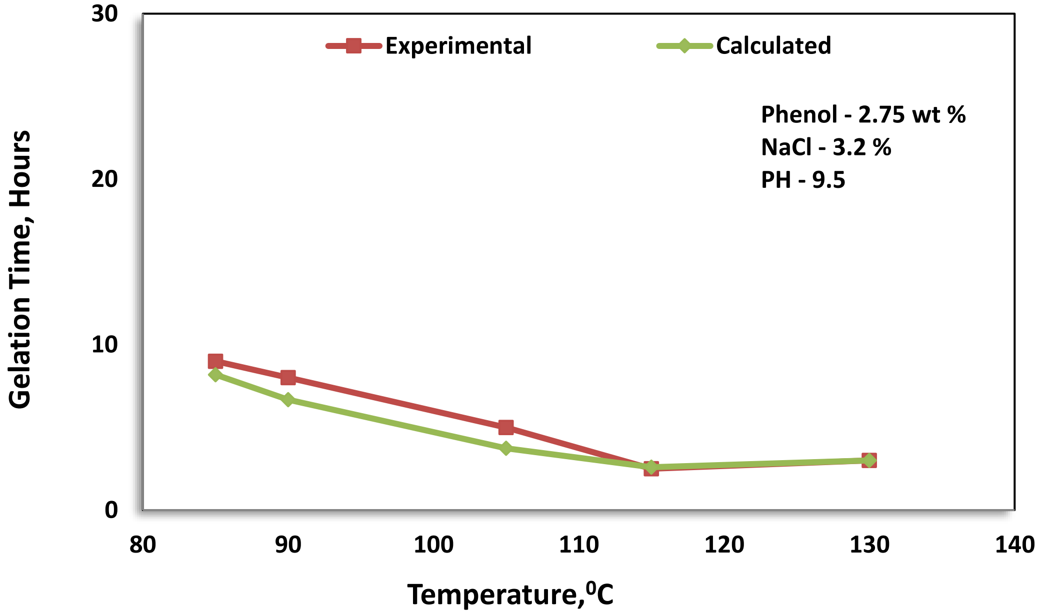


Figure 5.6: Experimental vs Theoretical Gelation Time of 2.75 % Phenol-Formaldehyde Gel

5.5 CONCLUSIONS

- The proposed mathematical model of the gelation behavior of the phenol-formaldehyde based on the gelation time and concentration of reactants as per the following equation

$$t = C_A^{b_1} * C_B^{b_2} * exp\left(b_0 + \frac{b_4}{T}\right)$$

- The value of constantsb_0,b_1, b_2 and b_4 as per simulation are found to be 0.349, 4.016 , -6.531 and 5326.09.

- The final mathematical model of the gelation behavior of the phenol-formaldehyde polymer system based on the gelation time and concentration of reactants as per the following equation

$$t = C_A^{4.0} * C_B^{-6.5} * exp\left(0.35 + \frac{5326}{T}\right)$$

CHAPTER 6: CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORK

6.1 CONCLUSIONS

- Phenol formaldehyde system forms a strong gel at the temperature ranging from 85 to 130°C with phenol concentration ranging from 2.00 to 2.75 % in the pH range of 9.5 to 11.0.
- Thermal stability of the gel is observed experimentally up to the temperature of 130^0C
- Initial gelation has been observed at an average temperature for hydrocarbon reservoirs.
- Gelation time increases with increase in initial pH of the polymer solution however, it decreases with increase in temperature and phenol concentration at a particular temperature.
- Viscosity growth is low at initial stage and increases in the later stage.
- Phenol-Formaldehyde gel system have not indicated any gel syneresis at higher temperature (130^0C) for a period of two months indicating their stability.
- Phenol-Formaldehyde gel system gives excellent permeability reduction as indicated by Residual Resistance Factor (RRF) values determined experimentally during in-situ gelation studies.
- The proposed mathematical model of the gelation behavior of the phenol-formaldehyde based on the gelation time and concentration of reactants as per the following equation

$$t = C_A^{b_1} * C_B^{b_2} * exp\left(b_0 + \frac{b_4}{T}\right)$$

- The value of constantsb_0,b_1, b_2 and b_4 as per simulation are found to be 0.349, 4.016 , -6.531 and 5326.09.

- The final mathematical model of the gelation behavior of the phenol-formaldehyde polymer system based on the gelation time and concentration of reactants as per the following equation

$$t = C_A^{4.0} * C_B^{-6.5} * exp\left(0.35 + \frac{5326}{T}\right)$$

6.2 RECOMMENDATIONS FOR FUTURE WORK

This section is not the outcome of the current research work but the propagation of the futuristic research work with the following recommendations:

- Production of oil from a well with a water cut above the economic limit impacts the profitability and therefore well has to be abandoned which ultimately leads to loss of reserves. In countries having high water cut and oil scarcity, the current research provides boost to oil/gas industry.
- Presence of alternate energy is still at a nascent stage, we have no option but to maximize capacity under the hardest conditions like geological unconformities and complex reservoir conditions. In view of this, the existing wells have to be recovered for profile modification, which has a solid capacity of producing as per the literature survey an additional 15 %, with the average Brent Crude Oil price of $71.34 per barrel and average production of world oil at 84 MMbpd, in 2018. This will fetch a net gain of approx. US $ 0.3 trillion per year, if the recommendation of this research or any other research work is taken into consideration, conveys the lead value of this research work. With the passage of time, research in this direction takes place in leaps and bounds because of oil energy constraints/demands/production.
- Applicable for countries where the source of alternate energy have not acquired the state of independence or self-sufficient.
- The knowledge of gelation, as per the literature survey, has indicated that the gelation process kinetics and its simulation study can be further taken up for their broader utilization in Petroleum Industry.

REFERENCES

[1] A. H. Alagorni, Z. Bin Yaacob, and A. H. Nour, “An Overview of Oil Production Stages: Enhanced Oil Recovery Techniques and Nitrogen Injection,” *Int. J. Environ. Sci. Dev.*, vol. 6, no. 9, pp. 693–701, 2015.

[2] S. Q. Tunio, A. H. Tunio, N. A. Ghirano, and Z. M. El Adawy, “Comparison of Different Enhanced Oil Recovery Techniques for Better Oil Productivity,” *Int. J. Appl. Sci. Technol.*, vol. 1, no. 5, pp. 143–153, 2011.

[3] J. Wang, A. J. Alshehri, A. M. AlSofi, and A. M. AlBoqmi, “A Laboratory Study of In-Depth Gel Treatment to Improve Oil Recovery,” *SPE Kingdom Saudi Arab. Annu. Tech. Symp. Exhib.*, pp. 24–27, 2017.

[4] M. Boothe, A. Kim, and K. Thornton, “Injection and Production Profile Modification for Enhanced Oil Recovery: Mechanical or Chemical Methods?,” *Proc. 2013 SPE Enhanc. Oil Recover. Conf.*, 2013.

[5] R. S. Seright and J. Liang, “A Survey of Field Applications of Gel Treatments for Water Shutoff,” *Proc. SPE Lat. Am. Pet. Eng. Conf.*, pp. 221–231, 1994.

[6] R. C. Fielding Jr, D. H. Gibbons, and F. P. Legrand, “In-Depth Drive Fluid Diversion Using an Evolution of Colloidal Dispersion Gels and New Bulk Gels: An Operational Case History of North Rainbow Ranch Unit,” *SPE/DOE Improv. Oil Recover. Symp.*, pp. 433–444, 1994.

[7] P. Albonico, M. Bartosek, A. Malandrino, S. Bryant, and T. P. Lockhart, “Studies on Phenol-Formaldehyde Crosslinked Polymer Gels in Bulk and in Porous Media,” in *SPE International Symposium on Oilfield Chemistry*, 1995.

[8] D. S. Jordan, D. W. Green, R. E. Terry, and G. P. Willhite, “The Effect of Temperature on Gelation Time for Polyacrylamide/Chromium (III) Systems,” *SPE Int. Symp. Oilf. Chem.*, pp. 463–471, 1982.

[9] P. W. Chang, I. M. Goldman, and K. J. Stingley, “Laboratory Studies and Field Evaluation of a New Gelant for High-Temperature Profile Modification,” *Proc. SPE Annu. Tech. Conf. Exhib.*, 1985.

[10] H. A. Ghazali and W. G. P, “Permeability Modification Using Aluminum Citrate/Polymer Treatments: Mechanisms of Permeability Reduction in Sandpacks,” *Soc. Pet. Eng.*, pp. 367–373, 1985.

[11] R. E. Terry, C. Huang, D. W. Green, M. J. Michnick, and G. P. Willhite, “Correlation of Gelation Times for Polymer Solutions Used as Sweep Improvement Agents,” 1981.

[12] R. B. Needham, C. B. Threlkeld, and J. W. Call, “Control of Water Mobility Using Polymers and Multivalent Cations,” *Soc. Pet. Eng.*, 1974.

[13] H. N. M. Abedi Lenji, M. Vafaie Seftia, M. Baghban Salehi, A. Mousavi Moghadam, “Gelation Time of Hexamethylenetetramine Polymer Gels Used in Water Shutoff Treatment,” *J. Pet. Sci. Technol.*, vol. 2, no. 2, pp. 3–11, 2012.

[14] H. T. Kwak, J. Wang, A. M. Alsofi, and S. Aramco, “Close Monitoring of Gel Based Conformance Control by NMR Techniques,” pp. 6–9, 2017.

[15] S. L. Bryant, G. P. Borghi, M. Bartosek, and T. P. Lockhart, “Experimental Investigation on the Injectivity of Phenol-Formaldehyde/Polymer Gels,” *SPE J.*, vol. 3, no. 4, pp. 373–381, 1998.

[16] R. S. Seright and F. D. Martin, “Impact of Gelation pH, Rock Permeability, and Lithology on the Performance of a Monomer-Based Gel,” *SPE Reserv. Eng.*, vol. 8, no. 1, pp. 43–50, 1993.

[17] D. Dalrymple, J. T. Tarkington, and J. Hallock, “A Gelation System for Conformance Technology,” *Soc. Pet. Eng.*, pp. 397–404, 1994.

[18] R. R. Jennings, J. H. Rogers, and T. J. West, “Factors Influencing Mobility Control by Polymer Solutions,” *J. Pet. Technol.*, vol. 23, no. 3, pp. 391–401, 1971.

[19] R. R. Gleasure, “An Experimental Study of Non-Newtonian Polymer Rheology Effects on Oil Recovery and Injectivity,” *SPE Reserv. Eng.*, vol. 5, pp. 481–486, 1990.

[20] D. Zhu, J. Hou, Q. Wei, Y. Chen, and K. Peng, “Development of a High-Temperature Resistant Polymer Gel System for Conformance Control

in Jidong Oilfield," *SPE/IATMI Asia Pacific Oil Gas Conf. Exhib.*, 2017.

[21] G. A. Al-Muntasheri, H. A. Nasr-El-Din, and P. L. J. Zitha, "Gelation Kinetics and Performance Evaluation of an Organically Crosslinked Gel at High Temperature and Pressure," *SPE J.*, vol. 13, no. 3, pp. 337–345, 2008.

[22] S. Ma, M. Dong, Z. Li, and E. Shirif, "Evaluation of the Effectiveness of Chemical Flooding Using Heterogeneous Sandpack Flood Test," *J. Pet. Sci. Eng.*, vol. 55, no. 3–4, pp. 294–300, 2007.

[23] C. Romero *et al.*, "Non-Selective Placement of a Polymer Gel Treatment To Improve Water Injection Profile and Sweep Efficiency in the Lagomar Field, Venezuela," *Spe Oilf. Chem. Int. Symp. Proc.*, 2003.

[24] S. Navigation and N. S. Route, "Screening Procedures," pp. 10–23.

[25] Y. Zhuang, U. Zhengzhou, S. N. Pandey, and C. S. Mccool, "Permeability Modification With Sulfomethylated Resorcinol-Formaldehyde Gel System," *Soc. Pet. Eng.*, pp. 18–21, 2000.

[26] H. W. Alhashim, J. Wang, A. M. AlSofi, and Z. F. Kaidar, "Gelation Time Optimization of an Organically Crosslinked Polyacrylamide Gel System for In-Depth Fluid Diversion Applications," in *SPE EOR Conference at Oil and Gas West Asia*, 2018.

[27] R. D. Sydansk, "A New Conformance-Improvement-Treatment Chromium(III) Gel Technology," in *SPE Enhanced Oil Recovery Symposium*, 1988.

[28] L. Romero-zeron, F. Manalo, and A. Kantzas, "Characterization of Crosslinked Gel Kinetics and Gel Strength Using NMR," *Soc. Pet. Eng.*, 2004.

[29] R. D. Sydansk and M. O. Company, "Acrylamide-Polymer/ Chromium (III) - Carboxylate Gels for Near Wellbore Matrix Treatments," *Soc. Pet. Eng.*, vol. 1, no. 1, pp. 146–152, 1993.

[30] Al-Muntasheri, L. Sierra, F. O. Garzon, J. D. Lynn, and G. Izquierdo, "Water Shut-off With Polymer Gels in a High Temperature Horizontal Gas Well: A Success Story," *SPE Improv. Oil Recover. Symp. held Tulsa, USA,*

no. 2007, pp. 1–24, 2010.

[31] H. Jia, W. F. Pu, J. Z. Zhao, and R. Liao, "Experimental Investigation of the Novel Phenol-Formaldehyde Cross-Linking HPAM Gel System: Based on the Secondary Cross-Linking Method of Organic Cross-Linkers and and its Gelation Performance Study after Flowing through Porous Media," *Energy and Fuels*, vol. 25, no. 2, pp. 727–736, 2011.

[32] C. De Rooij, R. S. Thompson, V. Garny, A. Lecloux, and D. Van Wijk, "Dichloromethane marine risk assessment with special reference to the osparcom region: North Sea," *Environmental Monitoring and Assessment*, vol. 97, no. 1–3. pp. 3–22, 2004.

[33] H. Jia and Q. Ren, "Evidence of the Gelation Acceleration Mechanism of HPAM Gel With Ammonium Salt at Ultralow Temperature by SEM Study," *SPE Prod. Oper.*, pp. 238–246, 2016.

[34] L. E. Whittington and D. G. Naae, "Conformance control gels-Formation by contact with brine," vol. 7, pp. 45–51, 1992.

[35] H. He, Y. Wang, X. Sun, P. Zhang, and D. Li, "Development and evaluation of organic/inorganic combined gel for conformance control in high temperature and high salinity reservoirs," *J. Pet. Explor. Prod. Technol.*, vol. 5, no. 2, pp. 211–217, 2015.

[36] M. Al-Anazi and S. Al-Mutairi, "Laboratory Evaluation of Organic Water Shut-off Gelling System for Carbonate Formations," *SPE Eur. Form. Damage Conf.*, 2011.

[37] S. M. Vargas-Vasquez, L. B. Romero-Zerón, R. MacGregor, and S. Gopalakrishnan, "Monitoring the Cross-Linking of a HPAm/Cr(III) Acetate Polymer Gel Using HNMR, UV Spectrophotometry, Bottle Testing, and Rheology," *Int. J. Polym. Anal. Charact.*, vol. 12, no. 5, pp. 339–357, 2007.

[38] D. M. Dolan, T. P. Corp, J. L. Thiele, G. P. Willhite, and U. Kansas, "Effects of pH and Shear on the Gelation of a Xanthan-Cr(III) System," 1998.

[39] B. Sengupta, V. P. Sharma, and G. Udayabhanu, "IPTC 14381 Development and Performance of an Eco-Friendly Cross-Linked Polymer System for

Water Shut-Off Technique," 2012.

[40] A. Mittal and D. K. Gupta, "Experimental Investigation of Gelation Behaviour of Polymer Gel System for Profile Modification," *ISST J. Appl. Chem.*, vol. 8, no. 2, pp. 30–34, 2017.

[41] J. R. Gales *et al.*, "Equilibrium Swelling and Syneresis Properties of Xanthan Gum/Cr(III) Gels," *SPE Adv. Technol. Ser.*, 1994.

[42] M. Unomah *et al.*, "Performance of Conformance Gels Under Harsh Conditions," in *SPE Improved Oil Recovery Conference*, 2018.

[43] R. S. Seright, "SPE-18502-PA-Effect of Rheology on Gel Placement," *SPE Reserv. Eng.*, vol. 6, no. 02, pp. 212–218, 1991.

[44] R. S. Seright, "MS-Impact of Permeability and Lithology on Gel Performance," *SPE/DOE Enhanc. Oil Recover. Symp.*, pp. 347–357, 1992.

[45] P. Dore Fernandes, M. G. F. Silva, and P. Bedrikovetsky, "A New IOR Technology To Homogenize Horizontal Well Injectivity/Productivity Profile," *SPE/DOE Symp. Improv. Oil Recover.*, 2006.

[46] X. E. Liu, "Development and Application of the Water Control and Profile Modification Technology in China Oil Fields," *Soc. Pet. Eng.*, pp. 181–207, 1995.

[47] M. T. Szabo, "An Evaluation of Water-Soluble Polymers For Secondary Oil Recovery. Part 2.," *J Pet Technol*, vol. 31, no. 05, pp. 553–570, 1979.

[48] S. Abbas, A. W. Sanders, and J. C. Donovan, "Applicability of Hydroxyethylcellulose Polymers for Chemical EOR," *SPE Enhanc. Oil Recover. Conf.*, pp. 2–4, 2013.

[49] S. G.- Barr, D. Dtd, D. Aliouche, and M. Bouguerra, "Characterisation and Rheological Study of Xanthan Polymer for Enhanced Oil Recovery (EOR) Application," *Soc. Pet. Eng.*, pp. 1–16, 2015.

[50] D. A. Z. Wever, F. Picchioni, and A. A. Broekhuis, "Polymers for enhanced oil recovery: A paradigm for structure-property relationship in aqueous solution," *Prog. Polym. Sci.*, vol. 36, no. 11, pp. 1558–1628, 2011.

[51] C. B. Hurd, "Theories for the mechanism of the setting of silicic acid gels,"

Chem. Rev., vol. 22, no. 3, pp. 403–422, 1938.

[52] P. H. Krumrine and S. D. Boyce, “Profile Modification and Water Control With Silica Gel-Based Systems,” *Proc. SPE Oilf. Geotherm. Chem. Symp.*, 1985.

[53] A. A. Al-Assi, G. P. Willhite, D. W. Green, and C. S. McCool, “Formation and Propagation of Gel Aggregates Using Partially Hydrolyzed Polyacrylamide and Aluminum Citrate,” *SPE J.*, vol. 14, no. 03, pp. 450–461, 2009.

[54] C. Tielong, S. Zhengyu, Y. Fan, H. Changzhong, Q. Ling, and T. Jinxing, “A Pilot Test of Polymer Flooding in an Elevated-Temperature Reservoir,” *Soc. Pet. Eng.*, no. 24–29, 1998.

[55] G. S. Sanders, M. J. Chambers, and R. H. Lane, “Successful Gas Shutoff With Polymer Gel Using Temperature Modeling and Selective Placement in the Prudhoe Bay Field c,” *Soc. Pet. Eng.*, pp. 381–396, 1994.

[56] J. E. Tackett, “Characterization of chromium (III) acetate in aqueous solution,” *Appl. Spectrosc.*, vol. 43, no. 3, pp. 490–499, 1989.

[57] D. W. Green and G. P. Willhite, “Permeability Reduction Mechanisms Involved in In-Situ Gelation,” pp. 77–83, 1991.

[58] J. J. Meister and C. T. Li, “Complex Copolymers for Mobility Control, Water Purification, and Surface Activity,” *Proc; Acs Symp Ser*, no. 396, 1989.

[59] S. K. Nanda, R. Kumar, K. L. Sindhwani, and K. L. Goyal, “SPE 16253 - Characterization of Polyacrylamine-Cr +6 Gels Used for Reducing Water/Oil Ratio,” *Soc. Pet. Eng.*, 1987.

[60] G. Bocchinfuso *et al.*, “Guar Gum and Scleroglucan Interactions with Borax: Experimental and Theoretical Studies of an Unexpected Similarity,” *J. Phys. Chem. B*, vol. 114, no. 41, pp. 13059–13068, 2010.

[61] R. Seright, T. Fan, K. Wavrik, and R. Balaban, “New Insights Into Polymer Rheology in Porous Media,” *SPE J.*, vol. 16, no. 1, pp. 1–11, 2011.

[62] T. Khamees, R. E. Flori, and M. Wei, “Simulation Study of In-Depth Gel

Treatment in Heterogeneous Reservoirs with Sensitivity Analyses," *Soc. Pet. Eng.*, pp. 1–23, 2017.

[63] Fjelde Ingebret. and S. Arne., "Scleroglucan Gels for Profile Modifications in High-Temperature Reservoirs," *SPE Adv. Technol. Ser.*, vol. 3, no. 1, 1995.

[64] T. K. Khamees and R. E. Flori, "Modeling the Combined Effects of Water Salinity and Polymer Rheology on the Performance of Polymer Flooding and In-Depth Gel Treatment," *SPE West. Reg. Meet.*, 2018.

[65] A. Stavland, B. A. Kvanvik, and A. Lohne, "Simulation Model for Predicting Placement of Gels," *SPE 69th Annu. Tech. Conf. Exhib.*, pp. 387–402, 1994.

[66] J. Kolnes, R. U. Centre, A. Stavland, and S. Thorsen, "The Effect of Temperature on the Gelation Time of Xanthan/Cr(III) Systems," 1991.

[67] F. J. Garver, M. M. Sharma, and G. A. Pope, "The Competition for Chromium Between Xanthan Biopolymer and Resident Clays in Sandstones," *Soc. Pet. Eng.*, pp. 61–65, 1989.

[68] Y. Zhuang, S. Pandey, C. McCool, and G. Willhite, "Permeability Modification With Sulfomethylated Resorcinol-Formaldehyde Gel System," *SPE Reservoir Evaluation & Engineering*, vol. 3, no. 5. 2000.

[69] S. L. Bryant, M. Bartosek, and T. P. Lockhart, "Laboratory Evaluation of Phenol-Formaldehyde/Polymer Gelants for High-Temperature Applications," *J. Pet. Sci. Eng.*, pp. 197–209, 1997.

[70] H. A. L. C. B. Hurd, "Studies on Silicic Acid Gels," *J. Phys. Chem.*, vol. 36, no. 2, pp. 604–615, 1932.

[71] D. Broseta, O. Marquer, N. Blin, and A. Zaitoun, "Rheological Screening of Low-Molecular-Weight Polyacrylamide/Chromium(III) Acetate Water Shutoff Gels," *SPE/DOE Improv. Oil Recover. Symp.*, no. 3, 2000.

[72] B. R. R. Reddy, F. Crespo, and L. S. Eoff, "Water Shutoff at Ultralow Temperatures Using Organically Crosslinked Polymer Gels," *SPE Improv. Oil Recover. Symp.*, pp. 1–10, 2013.

[73] M. S. Appah D and J. OF, “Modelling Gelation Time of Organically Cross-linked Water-shutoff Systems for Oil Wells,” *J. Pet. Environ. Biotechnol.*, vol. 7, no. 2, 2016.

[74] T. P. Bryant, S.L., Borghi, G.P., Bartosek, M., Lockhart, “Experimental Investigation on the Injectivity of Phenol-Formaldehyde/Polymer Gelants,” *Society of Petroleum Engineers*. pp. 335–343, 1997.

[75] R. Banerjee, K. Patil, and K. C. Khilar, “Studies on Phenol-Formaldehyde Gel Formation at a High Temperature and at Different pH,” *Can. J. Chem. Eng.*, vol. 84, pp. 328–337, 2006.

[76] K. Luo, “The Critical Runaway Condition and Stability Criterion in the Phenol-Formaldehyde Reaction,” *Elsevier*, vol. 13, pp. 91–108, 2000.

[77] K. T. Lu, K. M. Luo, S. H. Lin, S. H. Su, and K. H. Hu, “The Acid-Catalyzed Phenol-Formaldehyde Reaction Critical Runaway Conditions and Stability Criterion,” *Inst. Chem. Eng.*, vol. 82, pp. 37–47, 2004.

[78] F. W. Billmeyer, *Textbook of Polymer Science*. 1984.

APPENDIX A-1: RESEARCH PUBLICATION BASED ON THIS THESIS WORK

1. Ajay Mittal, D.K. Gupta, 2018. Review of Gelation Time Models of Polymer Systems Used for Profile Modification and Water-Shut off Jobs. Journal For Advanced Research In Applied Sciences, Volume 5, Issue 2, Feb/2018 (ISSN NO: 2394-8442)
2. Ajay Mittal, D.K. Gupta, 2018. Experimental Investigation of Gelation Behaviour of Polymer Gel System for Profile Modification. ISST Journal of Applied Chemistry, Vol. 8 No. 2, (July - December 2017), p.p. 30-34 (ISSN 0976-7355)

APPENDIX A-2: RESUME OF THE AUTHOR

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EXPERIENCE

- Industry Fellow, Department of Chemical Engineering, School of Engineering, University of Petroleum & Energy Studies, Dehradun, India, (Oct 2017 - till date)
- Practice Head, Upstream O&G, Global Data Research Centre, Hyderabad, India, (Mar 2013 - Sep 2017)
- Project Manager, Upstream O&G, Hyderabad, India, (Feb 2010 - Feb 2013)
- Associate Project Manager, Upstream O&G, Hyderabad, India, (Feb 2008 - Jan 2010)
- Senior Analyst, Upstream O&G, Hyderabad, India, (Jan 2007 - Jan 2008)
- Senior Lecturer, Petroleum Engineering, Dehradun, India, (Aug 2003 - Dec 2006)

PROFESSIONAL QUALIFICATION

- M.Tech. (Petroleum Engineering) from Indian School of Mines, Dhanbad, India with Cumulative GPA of 4.34 out of 5.00

- B.Tech. (Chemical Engineering) from Sant Longowal Institute of Engineering & Technology, Punjab Technical University, Jalandhar, India with 70.86%

INDUSTRIAL TRAINING

- Training at Ankleshwar Project, Oil & Natural Gas Corporation (ONGC), Ankleshwar, Gujarat, India
- Training at Hazira Gas Processing Complex, Oil & Natural Gas Corporation (ONGC), Surat, Gujarat, India
- Training at Refining Complex, Indian Oil Corporation Limited (IOCL), Panipat, Haryana, India

INDUSTRIAL PROJECTS

- Creation and Integration of Shape Files
- Exploration Service, Wells Service, Oil & Gas Fields Service
- Oil & Gas Discoveries Service
- Un-conventional Gas Service, Oil Sands Service
- Company Analytics & Benchmarking Service
- Market Profile Service, Information on World's Top Upstream Project
- Developed upstream capital expenditure, operating expenditure benchmarks for comparing costs around the world, and using them for asset valuation.
- Developed decline curve analysis model for forecasting future production and remaining reserves at a field level.
- Developed benchmarking, analytical reports, business insights at industry and country level.

RESEARCH PUBLICATIONS

- Ajay Mittal, D.K. Gupta, 2018. Review of Gelation Time Models of Polymer Systems Used for Profile Modification and Water-Shut off Jobs. Journal For

Advanced Research In Applied Sciences, Volume 5, Issue 2, Feb/2018 (ISSN NO: 2394-8442)

- Ajay Mittal, D.K. Gupta, 2018. Experimental Investigation of Gelation Behaviour of Polymer Gel System for Profile Modification. ISST Journal of Applied Chemistry, Vol. 8 No. 2, (July - December 2017), p.p. 30-34 (ISSN 0976-7355)

WORKSHOPS/SHORT TERM COURSES/TRAINING PROGRAMS

- Attended seven day workshop on Project Management by Ten Step Proficiency, Hyderabad, India
- Attended two day workshop on Modern Practices in Petroleum Exploration by Institute of Drilling Technology at ONGC, Dehradun, India
- Attended two day workshop on IOR/EOR Technologies by Norwegian International programme for Petroleum Management and Administration (PETRAD) at New Delhi, India
- Attended five day workshop on executive development program by Dale Carnegie’s at University of Petroleum & Energy Studies, Dehradun, India

AWARDS & RECOGNITION

- UK Sales Excellence Award, 2012, Project Manager - Managing Director of Global Data Asia gave this prestigious award, to recognize and honour an individual for outstanding contribution for supporting sale services, which enhance customer value.
- GD Asia MD Operational Excellence Award, 2011, Project Manager - Managing Director of Global Data Asia gave this prestigious award, for outstanding performances that have made significant contribution to the company's strategic plan and have provided consistent support to the department's objectives.

COMPUTER PROFICIENCY

Software	:	Black Oil Simulator, MATLAB
Operating System	:	Window, MS DOS
Programming Languages	:	Visual Basic, C

PERSONAL DETAILS

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(Ajay Mittal)